THERMODYNAMICS OF SYSTEMS CONTAINING FLEXIBLE-CHAIN POLYMERS



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Scientific edition by Professor Sergei Ya. Frenkel Translated by Sergei L. Shmakov and Dmitri N. Tychinin

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1999

ELSEVIER Amsterdam - Lausanne - New York - Oxford - Shannon - Singapore - Tokyo

ELSEVIER SCIENCE B.V. Sara Burgerhartstraat 25 P.O. Box 211, 1000 AE Amsterdam, The Netherlands

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First edition 1999

Library of Congress Cataloging-in-Publication Data

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Klenin, Vitaly J.
Thermodynamics of systems containing flexible-chain polymers /
Vitaly J. Klenin : [scientific edition by Sergei Ya. Frenkel :
translated by Sergei L. Shmakov and Dmitri N. Tychinin]. -- ist ed.
p. cm.
Includes bibliographical references and index.
ISBN 0-444-82373-5
1. Polymers--Thermal properties. 2. Thermodynamics. I. Title.
00381.9.T54K57 1999
547'.70456--dc21 99-20359
ISBN. 0-444-82373-5
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⊗ The paper used in this publication meets the requirements of ANSI/NISO Z39 48-1992 (Permanence of Paper). Printed in The Netherlands

Foreword

There are very few serious monographs on polymer thermodynamics. The problems of this science are mainly considered in the courses or monographs on the physical chemistry of polymers, the statistical physics of molecular chains (conformational and configurational statistics), in books dealing with the principles of scaling, intramolecular phase or cooperative transformations, and, finally, in mini-monographs (I would refer them to the category of manuals) treating direct applications of thermodynamics to various chemical and physical polymer technologies. Books dealing with either rough applications or new high technologies are most abundant, but it is difficult to find in them even a trace of thermodynamics—in the proper sense of the word.

Special books on the thermodynamics of polymers or, at least, on the thermodynamics of polymer solutions, at least, have not been widely scattered around the scientific world. In contrast, there is a great number of large reviews or original papers on this subject in the international or Russian scientific journals. Many of them are of a general character but the principle itself of writing problematic or review papers prevents a relatively complete consideration of any branch of science on the whole.

Therefore a possible question of the "why another book again?" type concerning the publication of V.J.Klenin's monograph should not arise.

It would be wrong to consider it a textbook, although students, post-graduate students and fairly ripen researchers are recommended to study macromolecular science by it.

There was no such monograph before, and one must thank the author for its appearance.

Another question may be raised: whether it did not appear too late? At present the school of I.Prigogine (and his followers and proselytes) almost entirely predominated in the thermodynamics, physical and chemical kinetics and non-linear dynamics in general.

The answer to his question is quite definite: the author has not been too late publishing this monograph. It is not possible to "jump" into the modern non-equilibrium dynamics and several more narrow and specialized sciences and theories developed from it (the theory of dissipative structures, synergetics, the theory of catastrophes, fractal "geometry" and dynamics, etc.) on the basis of "nothing". It would be the well-known attempt to jump over the precipice in two jumps. However, the founders of classical statistical thermodynamics, Boltzmann and Gibbs, doubtless firmly occupy the pedestal built for them by History. Any further path begins from their works.

Moreover, the algorithms of classical thermodynamics can be easily transformed into those of Prigogine's one(however, the latter can already be considered to be classical also but with a new shade of meaning).

To start with, it is sufficient to replace the terms "stable" ("equilibrium"), "metastable", and "unstable" by the terms "stationary", "metastationary", and "non-stationary". Thus, with the aid of such a primitive glossary, a complete analogy in description of linear and non-linear phenomena may be attained including even the methods of description and the criteria of first- and second-order (in Landau's sense) phase transitions.

However, this is not the only analogy. There are many situations in which Gibbs' and Prigogine's thermodynamics are related to each other just as Newton's and Einstein's physics.

In many of these situations the New thermodynamics requires such minute corrections

(in the sense of corrections of the same type as the famous root $\sqrt{1 - (v/c)^2}$) that they may be neglected. The author of the present book bears this in mind and restricts himself essentially just to such situations that can become sufficiently complicate on the classical statistical-thermodynamic level. Nevertheless, the introduction of thermokinetic corrections or properly termed Prigogine's corrections into the conventional thermodynamic equations changes the situation even to the first approximation and makes it possible to pass from non-realistic to realistic equations, interpretations, and, if necessary, predictions.

After the first approximation it is not difficult to pass to the second one and thus still to jump over the precipice dividing the two thermodynamics in two jumps!

Another question may also be raised: wy did the author limit himself to systems with flexible-chain polymers ?

In many publications my colleagues and myself have attempted to give quite an unequivocal answer to this question. The "polymer state" may be considered to be a peculiar form of condensation of molecules, and the transition into this state may be regarded as a special fundamental phase transition¹ on the background of which "usual" phase transitions take place. This concept may be proven and developed just for flexible-chain polymers capable of the manifestation of rubber-like elasticity, i.e. of reversible 1000-fold and greater deformations which involve forces of the entropy nature.

In this case it is easy to make a transition to rigid-chain or cross-linked (3D) polymers without introducing any fundamentally new factors into the equations for flexible-chain systems.

For example, chain rigidity may be regarded as due to an increase in internal energy or enthalpy. The results of this concept become clear if an example which I have repeatedly reported is used.

If the melting or dissolution temperature of the polymer system is expressed not by the conventional equation

$$T^{\bullet} = \frac{\Delta H}{\Delta S},$$

but by a ratio of binomials in which subscripts "1" and "2" at the entropy and enthalpy terms refer to conformational and configurational contributions

$$T^* = \frac{\Delta H_1 + \Delta H_2}{\Delta S_1 + \Delta S_2},$$

it becomes clear that upon melting or dissolution of flexible-chain polymers when great changes in both entropies occur, it is possible to increase markedly T^* by simple superposition of external restrictions (e.g., tensile stress which in this case is equivalent to pressure in conventional van der Waals systems). This *trick* may be used in reverse transitions in technology or for the production or transformation of energy. In contrast, in rigid-chain polymers the changes in both entropies are slight (a rod can be only a rod, hence, $\Delta S_1 \rightarrow 0$) and all the "load" is applied to the enthalpy terms.

Moreover, under the conditions of the same uniaxial stretching, the Poisson coefficient that reduces ΔS_2 to zero and increases ΔH_2 , predominates. This can also be directly

¹Here I refer to my mini-tractat "Polymers: problems, prospects, and prognoses" in: "Physics today and tomorrow" (in Russian) Leningrad, "Nauka Press" 1973, p. 176-270

used in technology in the preparation of superfibers from rigid-chain polymers, llowever, in this case the process occurs quite differently from that for flexible-chain polymers.

This is also related to a more fundamental factor: flexible-chain polymers are usually soluble and fusible, whereas rigid-chain ones are thermally stable and often neither dissolve nor melt. This property involves considerable technological difficulties, although in many cases modern high technologies require the application of just rigid-chain polymers.

This postulate may be reinforced as follows: rigid-chain or super-oriented flexible-chain polymers lose to a considerable extent their specific "polymer nature" which combines the possibility of the coexistence of three phase and aggregate states depending on the method of treatment. In many respects they cannot be distinguished from simple solid bodies (it is in this form that L.P.Myasnikova has expressed this principle which is of great importance for polymer physics)².

In contrast, in flexible-chain polymers virtually any superpositions of phase, aggregate and relaxation (glass, rubber, and viscous fluid) states are possible. Hence, the phase equilibria are extremely varied and complex, and phase diagrams are unusual (the author characterizes the states of the system according to Gibbs' configurative points) and the morphological kinetics of phase transformations are also unusual.

Again, this situation, as well as the author's didactics itself, may lead to some miscomprehension of his main aims which became apparently too trended forward essentials of polymers materials science and, consequently, applications. However, in the same Preface V.J.Klenin points several times that the book is planned as a *foundation* of polymers materials science, and one can attain just nothing if the fundamentals (pure science) are omitted.

The epigraph from Münster (Λ .Münster, Chemical Thermodynamics) restarts wholly the logistics and didactic order in the book.

And this book just substantiates this consequence. It deals with the methodology rather than with the methods. This methodology is very logical but often this logic is not sufficiently apparent, and the author confidently leads the reader along the labyrinths of imaginary and real difficulties (that may result from the fact that the readers are not accustomed to the specific form of physical thinking) to indisputable and rigorously demonstrable truths.

In this sense the book might be called "Introduction to the thermodynamics of polymers" but it should be borne in mind that the term "Introduction to..." has two meanings in the scientific literature.

One on them is primitive. The reader is provided with a certain primary information so that he can subsequently begin to study the more special literature.

In the German scientific literature the term "Introduction" or "Einführung" has a much deeper meaning. It need not be followed by a "Handbuch" or "Manual". The "Einführung" gives an almost complete summary of facts, theories, and general principles that should be used by the researcher in his own work and developed not only on the "low" technical level but also on the high fundamental level. Of course, I do not mean to neglect the practice (as was already hinted), which would be silly, but only should

²See in "Oriented Polymer Materials", S.Fakirov editor, Hüthig and Wepf Verlag, Heidelberg-Oxford, 1996, chapter 2 (by V.A.Marikhin and L.P.Myasnikova: Structural basis of high strength and high modulus polymers)

like to emphasize once more that technical applications should naturally follow from pure (fundamental) science.

This is the kind of "Introduction" that V.J.Klenin's book represents. It cannot be ruled out that it will be the last monograph on the *classical* thermodynamics of polymers.

However, it already contains the break through to neoclassicism and, in general, to the "neoclassical" future.

For example, the new principles and approaches based on the hypothesis of similarity (scaling, Chapter 4) are excellently described. After reading this chapter, one should again come back to Chapter 2 dealing with fluctuations.

Scaling for polymers is based just on the fact that fluctuations of segment concentration of a flexible macromolecule are of the same order of magnitude as segment concentration itself. Hence, we notice at once a similarity to magnetics or some other systems in which giant fluctuations appear as these systems approach the second-order transition point (or rather the critical point which term is presently preferred since the 2-nd order transitions are continuous³).

This similarity makes it possible to calculate almost automatically the so-called critical indices, i.e. in this case the exponents relating the chain dimensions and the parameters that are derived from them to the degree of polymerization in various temperatureconcentration ranges. In this similarity scheme, the Flory θ temperature plays the role of a tricritical point.

However, in many cases, after obtaining these critical indices it is better to ignore scaling and carry out further analysis by classical methods. One should only remember that the methods and technical usages should be changed on passing to a region with other critical indices.

In contrast to most authors of monographs dealing with polymer science where thermodynamics is considered only "to a certain extent", V.J.Klenin's in considering the general principles, methods, formalisms, amd methodology profoundly analyzes the related problems of molecular physics, colloidal chemistry, and optics of polymers and describes the procedure for some types of polymer technology.

Moreover, in all cases the author analyzes the phase diagrams or the coexistence ones and according to the movement of the configurative point in these diagrams, characterizes the trajectory (according to Prigogine), i.e. the evolution of multicomponent systems.

In particular, he analyzes complex phase equilibria in which "amorphous" and "crystallike" phase separations coexist. The kinetics of these processes are profoundly affected by the position of the configurative point and its trajectories. If this is not understood, any well-developed technology may become "antitechnology".

The tremendous importance of renormalization group transformations, in particular, in very fine applications, becomes quite comprehensible literally today. I shall give myself liberty to advance just one example. Presently new separation and purification principles are developed starting with more or less conventional column high selectivity chromatography, but aiming to a somewhat chimerical "membrane chromatography" (chimerical since the main spatial dimension of chromatographs, the length of the column is "lost"). A whole group of particular methods turns to be exclusively effective in biotechnologies,

³Concerning this terminology see R.M.White and T.H.Geballe "Long range order in solids" (New York, 1979)

ecology, biomedical applications, pharmacology, and even biological modelling. However, the methods are supported only by truncated and somewhat vulgar kinetic half-theories.

In my opinion, the correct theory must be based on the dimensionality renormalization group transformation (see Chapter 5), with a gradual loss of the "main" dimensionality.

Much attention is devoted to scattering, in particular, to colloidal light scattering. A number of scientific and practical problems is solved in this connection but the main of them is related to the so-called ill-defined systems: colloidal particles of uncertain shape, dimensions, composition, and degree of swelling. It should be noted that the works of V.J.Klenin and his co-workers in this field are widely recognized in the international level. In fact, in Chapters 2, 3, and 6 a fundamental direction in the physics and colloid chemistry of polymers is established. In this case the author successfully avoids the shadow of Hödel's theorem of insufficiency and gives rigorous methods of single and double regularization of incorrect inverse problems of different degrees of complexity with different scientific and applications to purely technological problems in which the superposition of continuously generated colloidal particles in solution or melt may lead to process failure).

However, it is not this foreword to the book that should be read but the book itself. I have written this foreword to make the faint-hearted avoid its reading. Hope, nevertheless, that there will be very few of them.

Professor S. Ya. Frenkel, Head of the Department of Anisotropic Polymer Systems of the Institute of Macromolecular Compounds, Russian Academy of Sciences. St. Petersbourg, March 1998 The mathematics of thermodynamics is, in fact, extremely simple, apart from a few special cases, and consists mainly of the methods of partial differentiation and of ordinary differential equations of simple form. The conceptual aspect of thermodynamics is, in contrast, extraordinary abstract and it is here that the real difficulties arise. It has long been customary to try to avoid these difficulties by means of spurious analogies. It has, however, become clear that this method makes a deeper understanding leading to mastery of the subject more difficult. The characteristic properties of this field must be accepted and, on the one hand, basic concepts must be developed from concrete experience while, on the other, the mathematical structure must be analyzed. These consideration determine the way in which this book is written.

A. Münster. Chemical Thermodynamics⁴

Preface

Modern materials science is mainly based on three sections of physical chemistry, namely, the thermodynamics of multicomponent multiphase systems, the kinetics of phase transitions, and morphology. The location of the configurative point on the state diagram, the trajectory and velocity of its transfer determine the type of phase separation and the mechanism of kinetics, which, in turn, determines the morphology of the system, and, finally, the performance of materials and articles.

The interrelation of these concepts is sketched on the flyleaf.

The advances and achievements of low-molecular materials science are well known: creation of an abundance of general-purpose materials from metal alloys, glasses, liquid crystals. Every possible mixtures, composites, and solutions are employed in various fields of up-to-date high technologies.

By contrast, polymer materials science still is in its early days. In the collection "Physics today and tomorrow", S.Frenkel contrasts nuclear energetics with polymer materials science: the theoretical principles of nuclear physics were developed before their introduction to practice, while polymer technology started for before science *per se* and still uses widely trial-and-error methods.

However, the scientific background of polymer materials science lags behind not only nuclear energetics but also its low-molecular counterpart. To make clear why it is so, let us compare the thermodynamics-kinetics-morphology triad for low- and high-molecular compounds (see the schematic on the flyleaf).

The exploitation and structural study of metals and glasses (low-molecular compounds) are performed in deep overcooling and quenching, which causes no time changes in the structure of systems. To say nothing of performance, this provides convenient conditions for in-depth investigations. Mixtures of low-molecular compounds feature a variety of phases, which leads to rather sophisticated state diagrams. However, due to their sharp morphological distinction, the phases can be completely analyzed by means of a set of sensitive and information-bearing instrumental methods, such as X-ray analysis, electronography, differential thermal analysis, etc. This enabled rich information of the

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structure-property type to accumulate and effective methods for controlling the perforinance of materials and articles to emerge. On the other hand, the high molecular mass and the chain structure of macromolecules, polymolecularity (multicomponent composition of even an individual polymer), the drastic difference in molecular sizes in mixtures with low-molecular compounds find their reflection in thermodynamics (state diagrams).

At the same time, there are great analogies between the thermodynamics (state diagrams) of low- and high-molecular compounds (see the flyleaf). Perhaps, they are systems with network polymers which are specific for the polymer world. Nevertheless, it is they that are associated with the establishment and development of polymer materials science: production of rubber, fibrons, plastics, contact lenses, food, etc.

The largest distinctions between systems with low- and high-molecular compounds are observed, of course, in the kinetics of phase separation and, as a consequence, in the morphology of polymer systems. Due to significant kinetic hindrances, the process of phase separation in polymer mixtures, even in the presence of low-molecular compounds, is retarded already at the early stages, i.e. on the colloidal-disperse level of particles (structures) of the new phase. Therefore, despite of the distinguishing nature of phase separation (eg., liquid-liquid or liquid-crystal), the system remains heterogeneous for a long period of time, showing no distinctive features of the equilibrium state morphology.

The question mark on the scheme shows this circumstance.

The configurative point during operation and study is not located in the range of great overcooling but is located near (or even inside) the region of phase separation, which causes time changes in morphology — this is sometimes called "aging", "ripening", "structure formation", etc.

Polymer systems are often used under conditions of a hydrodynamic field, changing significantly the thermodynamics (state diagram) of the system. The hydrodynamic field strongly influences the thermodynamics and kinetics of phase separation just in the case of polymer systems, as the structure (conformation) of macromolecules change noticeably under the action of a mechanic field. Because of their chain structure, crystallizing polymers cannot form perfect crystal structures and show almost no variety of modifications. In many cases there is no solidus on the state diagram of a crystallizing polymer+LMWL system.

On the other hand, it is kinetic retardation which makes amorphous polymers not to reach, as a rule, the thermodynamically equilibrium structureless state, and ordered areas of various order and length are observed in polymer samples. Because of this, systems, remote from each other along the thermodynamic-morphological scale (crystals and liquids), may prove to differ insignificantly in their actual morphology which is experimentally recorded by conventional methods. Such uncertainty in morphological forms, and the kinetic retardation of phase conversions on the colloidal level of dispersity, give rise to principal difficulties in the phase analysis of polymer systems, and conventional methods may well turn out insensitive and/or non-specific.

These are the circumstances which obviously explain the fact that systematic studies of phase equilibria in polymer systems began since the late 30ies only (Schulz, 1936, 1937ab, 1939ab; Papkov et al., 1937ab; Rogovin et al., 1937; Kargin et al., 1939; Schulz and Jirgensons, 1940).

In spite of the fundamental difficulties in the phase analysis of polymer systems, progress

in polymer materials science should only be expected on the way of developing the classical thermodynamics-kinetics-morphology triad. Polymer systems therefore require novel approaches and experimental methods to make possible phase analysis at the early stages of phase separation, i.e. on the colloidal-disperse level of the system's organization.

In this respect, well suited is the turbidity spectrum method, letting one determine the concentration of the disperse phase (the degree of phase conversion) and the particle sizes on very simple and available apparatus (colorimeters and spectrophotometers of any kind).

The mentioned approach, in combination with other methods, permitted the identification of the nature of phase separation and the development of state diagrams for a number of practically-important systems: poly(vinyl alcohol) + water, polydimethoxyethylene+water, poly(m-phenylenisophthalamide) + dimethylacetamide, <math>polyamidoimide + dimethylfornamide, etc. In the poly(ethylene oxide)+water system, a new morphological form of crystallites in the polymer-dilute concentration range was revealed. Describing this approach in the framework of general problems constitutes an object of this book.

When authors want to give their reasons for writing, "gaps" are often spoken of. The present case makes it reasonable to speak of "yawning gulfs". Neither this book, nor one or two dozens of others on the same topic will drive polymer materials science to the host of books and monographs devoted to the materials science and phase conversions of low-molecular compounds.

In the current polymer literature, common discussions of the structure (in general) of a polymer in a solvent (in general as well) with no specific state diagram, configuration point, or its trajectory still make up a large proportion. To speak more specific is rather difficult, the more so if the state diagram of a given system is unknown or disputable.

Cite the following fact to illustrate the difficulties in the phase analysis of polymer systems. For the poly(vinyl alcohol)+water system, some researchers propose a state diagram of amorphous phase separation with an upper critical solution temperature, others — amorphous separation with a lower critical solution temperature about 100° C; there are some who think that there is no region of amorphous separation below 150° - instead, they observe liquid-crystal phase separation. Such are the discrepancies on the **basic** question of thermodynamics!

In any case, at this point discussing the structure and properties of a polymer-containing system with no, even hypothetical, state diagram proposed makes no sense. As an example, take a popular, among polymer researchers, topic of association in polymer solutions (see the section with this title in Tager's (1978) book).

There is a considerable body of literature describing the association (aggregation) phenomenon in specific systems and under specific conditions. Actually, this material concerns the morphological aspect only. None of the authors has put a question as to the **thermodynamic stimulus** of association as correlated with a certain configurative point on a certain state diagram.

Restricting oneself with morphology gives no clue to the control over the structure of a system and leads, sooner or later, to internal contradictions in the description of the system's properties. For example, the mentioned section contains a phrase that, by its briefness and clarity, sounds like a law: "The degree of association increases with increasing concentration of solution and the molecular mass of a polymer" (this can often be met, in various words, in the literature). However, the same page states that "as the binodal or liquidus curve is approached, the degree of association always increases". But the configurative point can also approach the binodal along an isotherm with decreasing polymer concentration, what's then? Another example from the same source: "Association is a reversible process, and, in contrast to aggregates, associates are statistical fluctuational formations, that are formed and destroyed reversibly". The reader so has left aggregates and approached, to indistinguishability, concentration fluctuations, not saying of what aggregates in their essence are. If association is regarded identical to concentration fluctuations, why a new, confusing term? Otherwise, what is association? What is the thermodynamic stimulus for it? And how can the following fact fit in with the picture of increasing degree of association with increasing concentration: the macromolecule sizes were experimentally established to decrease as the concentration increases?

By now, sufficient information on the dynamics of macromolecules in solution has been accumulated by means of dynamic light scattering, this method being sensitive to the internal modes of a macromolecule's motion and to the process of its reptation among similar molecules in solution or in the condensed state. At the same time, there is a lack of unambiguous evidence for "association modes" or the lifetime of associates in the voluminous literature on dynamic light scattering from polymer solutions.

If one accepts that aggregates (associates) are particles of a new phase upon phase separation, then almost all the enormous material on association in systems without specific interactions is explained naturally, of course, with the exception of "formed and destroyed". In addition, this means that phase particles (aggregates, associates) are formed not with furthermore approaching the binodal or liquidus curve, but at intersecting one of these curves.

In the nearest proximity around the binodal, there appear critical phenomena with their characteristically high level of correlated fluctuations of the order parameter (density for a substance or component concentration for a mixture). By virtue of the universality principle, the properties of such fluctuations are similar for both a one-component liquidvapour system, a solution of low-molecular compounds, and a polymer solution. The critical phenomena in these systems are discussed in this book in detail. The question as to the absence of any pretransition phenomena near the liquidus is discussed as well.

In the case of an unknown state diagram of a polymer + low-molecular-weight liquid (P+LMWL), studying the properties of aggregates (phase particles) arising under various circumstances can serve to identify the phase separation type with determining the phase separation boundary (phase analysis) — this was mentioned above (the turbidity spectrum method). In particular, Chapter 6 will discuss the poly(ethylene oxide) + water system, where the turbidity spectrum method revealed a most interesting situation, when, under the same conditions (at the same configurative point), particles of one type (crystalline) dissolve while those of another type (amorphous) appear.

The closest to this book are, definitely, S.P.Papkov's (1971, 1972, 1974, 1981) monographs⁵. As the author designed, his books take "an intermediate place between pure theoretical monographs ... and narrow-technical manuals on polymer solution processing" (Papkov, 1971).

⁵in Russian

Following this nomenclature, my book belongs to the first kind. I advocate consideration of the whole problem by parts in the thermodynamics-kinetics-morphology sequence. To start this consideration, the thermodynamics of the systems confined in the dashed frame on the flyleaf schematic is dealt with in this book. Therefore, systems with rigid-chain polymers, polyelectrolytes, and copolymers are not covered.

At this stage of development of polymer materials science, deeper detalization with an adequate language is required. "Any natural science contains as much truth as much mathematics it involves" (*Kant*). This proposition must obviously be emphasized for the scientific principles of polymer materials science because of the very stable, persistent traditions and opinions of "spurious analogies" (Münster, 1969).

These traditions have, of course, objective reasons (too!).

The thermodynamic and related properties of compounds and materials are known to be rigorously and consistently described in terms of statistical physics with its wellelaborated ideology. A model letting the partition function to be written is proposed for a given system, then the standard formulae calculate the thermodynamic functions and associated quantities measurable in experiment. Provided that the theoretical and experimental values agree well, the model is regarded adequate, as is the approach (model, etc.), which opens up possibilities to control the structure of substances and materials.

However, this rigorous approach faces serious mathematical difficulties even for an ensemble of simple molecules (inert gases) — one can make sure that this is so if one looks through "Physics of simple liquids" (Temperley et al., eds., 1968) or Croxton's "Liquid state physics — a statistical mechanical introduction" (1974). For the reader's convenience, sections 1.7–1.8 give some quotations from Croxton.

This circumstance is the reason for refusing this methodology when more complicated (in particular, polymer) systems are dealt with. Just here a treacherous danger waylays us. While partition functions and formulae restrict in a way our imagination, their rejection in the case of more complicated systems provokes one to sink into fantastical voluntarism with no limitations towards complication or simplification. To say more, it is simplification that is obviously preferred and expressed in rejection of mathematical language in favour of pure belles-lettres.

Indeed, being enthusiastic about "the freedom from formulae", one may "talk away" whatever he likes, including such things which cannot be proved or disproved.

To enhance the descriptive capabilities, plenty of neologisms are introduced, with various prefixes like "quasi-", "pseudo-", and even "crypto-" (!), etc.

As a result of such belles-letters, the macromolecular world appears ingenuous and simple, where almost numbered groups of macromolecules interact with each other according to the "energetic" principle like "advantageous — disadvantageous" while completely ignoring the entropic factor which, indeed, is difficult to be interpreted purely verbally.

Another typical example of imposed simplicity is that systems of obviously different degrees of simplicity (cg., the binary P+LMWL system and the complicated quaternary system: ternary charged-groups polymer+water+salt+organic solvent) are described with an equal degree of conviction (authentity), using the same language, with no reservation as to the hierarchy of complexity.

Lest false analogies arise between the said simplicity and that spoken of by Ya.Frenkel⁶, the principal difference between these two "simplicities" must be pointed out. Frenkel demanded simplicity just within the framework of a certain model of a system, as distinct from unrestricted simplicity (vulgar structure-speaking).

The present monograph offers the reader a scenario for the thermodynamics of polymer systems, which is different from traditional presentations of the problem. The specific features of the approach follow just from how the material is distributed among the chapters and sections.

In Chapter 1 are presented all the basic terms and definitions needed for the subsequent description of both low-molecular and polymer systems, thereby serving as an always-at-hand manual.

The conditions of the stable one-phase state of multicomponent systems are also determined in Chapter 1. Loss of such stability leads to phase separation. Specially considered is the critical state of a system, where the one-phase state is close to the threshold of violation of the stability condition.

The one-phase state of a binary system is stable at constant temperature and pressure if and only if $(\partial \mu_1/\partial x_2)_{P,T} < 0$ (there are some equivalent quantities such as $(\partial \mu_1/\partial x_1)_{P,T} > 0$, etc.). The reverse inequality satisfied, the stability is lost while the corresponding equalities define the stability boundary (the spinodal).

The quantity $(\partial \mu_1/\partial x_2)_{P,T}$ (and the corresponding ones) in the one-phase region is associated with the level of order parameter fluctuations, the order parameter being the density of a substance (a one-component system) or the concentration of a component (two-and more-component systems). Near the stability boundary, the level of order parameter fluctuations rises, and the system's properties largely depend on the correlation of these fluctuations.

To help the reader to apprehend the principle of universality (discussed at length throughout the book), in Chapter 1 are compared the state equations as virial expansions for ideal and real gases on the one hand, and for ideal and real (regular) solutions on the other. Section 1.5 gives a classification of phase transitions, and introduces into consideration critical indices, which bear a great reason load. That is why a detailed deduction of the critical indices for relatively simple systems (a magnet and real gas-liquid) is given in the mean field approximation. Precisely these systems start detailed development of the mean field methodology, which gets its logical completion in the Landau phenomenological theory (section 1.6) and is applied to describe the properties of polymer systems in Chapter 3.

The Landau formalism possesses a universal meaning and is applicable to a wide range of problems. The chief restriction of this version of the mean field theory is in the lack of proper account for the correlation of order parameter fluctuations, which particularly affect the system's properties near the critical point. In the same paragraph, the concept of the tricritical point is introduced, which seems reasonable in connection with the great popularity of this term in polymer theory since de Gennes showed the θ point in the P+LMWL system to be an analogue of the tricritical point in the field theory formalism.

Certainly, statistical physical methods are successfully applied in the theory of polymer

⁶ "The description of a system should be simple like a cartoon"

systems, and in section 1.7 are given the relevant formulae needed in what follows.

Finally, section 1.8 briefly reports a more rigorous state equation of real gas as a virial expansion with elements of the diagrammatic technique involved, this technique finding wider application later. The intermolecular interactions in real gas are emphasized to be of a common nature with the interactions of chain-far segments in a macromolecular coil.

Chapter 2 treats in detail light (radiation) scattering and diffusion, as the experimentally observed quantities (scattering intensity I and diffusion coefficient D) depend immediately on the derivative $(\partial \mu_1 / \partial x_2)_{P,T}$ (or the equivalent quantities). This derivative stands in the denominator and nominator in the formulae for I and D, respectively, and $I \to \infty$, $D \to 0$ near the stability boundary, which characterises a whole set of phenomena, named critical (eg., critical opalescence).

As the diffusion coefficient is not a purely thermodynamic quantity, but also specifies the transport (kinetic) properties of a system, this leads to a most important phenomenon in the critical region, namely, critical retardation, discussed in the literature more seldom than critical opalescence.

In their relation to critical retardation, the dynamics of order parameter fluctuations in the critical region and the theoretical principles of the dynamic (inelastic) light scattering to characterize fluctuation dynamics are fully considered. Detailed discussion is given for the key sections of classical light scattering, beginning with a dipole's scattering.

Only systems of low-molecular compounds are treated in Chapter 2. They serve the objects of exercising in vocabulary and approaches before passing to high-molecular compounds in Chapter 3, to avoid terms with "quasi-" and "pseudo-".

Such a sequence and completeness of problem presentation (first on the level of lowmolecular stuff) seem important and necessary, since the specific character of polymer systems is often overestimated, especially in belles-letters writings. This often causes an unjustified rejection of the universal terminology in favour of neologisms. On the other hand, such arrangement of the material enables the true peculiarities of polymer systems to be seen obviously and specifically.

The detailed consideration of critical phenomena in this chapter will play its role not only in discussing really critical phenomena in polymer systems in the traditional way (where the specific character of polymer systems is minimal), but also in describing critical phenomena in the new treatment, because a formally-structural analogy between the behaviour of molecular coils in a good solvent (far away from traditional critical phenomena!) with critical phenomena in other systems has been found: in both cases, the level of order parameter fluctuations is comparable with the value of the order parameter itself (the concentration of segments in the case of a macromolecule).

At the end of Chapter 2 is given a version of the general mean-field theory to account for the correlations of order parameter fluctuations. The hypothesis of similarity (scaling) and the hypothesis of universality are considered. Table 2.5 contains a summary of physical systems whose properties are successfully studied by means of the field theory methods, including the conformations of a macromolecule coil in a good solvent.

Finally, section 2.6 represents the Lagrangian formalism of general field theory, following Amit (1978). This formalism was developed in the quantum field theory and has recently come into use in polymer theory.

Chapter 3, the chief one in the book, is devoted to the Flory-Huggins theory, its

premises, main consequences, and applications. The theory of corresponding states is also discussed (section 3.8). The main attention is paid to phase separation processes of the liquid-liquid type and accompanying phenomena and methods such as fractionation, critical opalescence, etc.

There are ample books in the literature considering in detail the thermodynamics of polymer solutions, i.e. the state of the P+LMWL system above the θ point (for systems with an upper critical solution temperature) (see the bibliography). With the exception of Flory (1953) and Tompa (1956), the other authors either did not deal with phase separation or mentioned it only in its relation to fractionation. A need has, therefore, arisen to look into the questions of liquid-liquid phase separation (including multiphase separation) as carefully as possible, the more so that many applications of these problems can be introduced into the technology of polymer materials.

Much attention is given to the experimental methods for determining the phase separation boundary, the critical point, the spinodal, and the interaction parameter.

In Chapter 4, the problems of polymer science are brought into line with other systems, well-studied by means of the rigorous methods of statistical physics. Such an interrelation has proved possible due to the principle of universality, whose capabilities are most clearly seen in predicting the properties of polymer systems with such prototypes, which would seem rather far from polymers, as magnets.

The chapter begins with de Gennes' pioneering work where he presents the results of his comparison of the conformational problem of a macromolecule in a good solvent (the trajectory of self-avoiding linked-segment walking on a lattice \cdots see Figure 1.23) with the problem of the correlated fluctuations of the order parameter (magnetization) near the critical point of a magnet. Both have appeared to be similar but one element, loops, which are absent in the problems of segment walking. The contribution of these loops is proportional to the n — dimension of the order parameter. Be n formally accepted as zero, the magnetic problem becomes a polymer one.

Later, the version with n = 0 for macromolecular conformations was proved analytically by several French researchers from Saclay (Daoud et al., 1975) and expounded in de Gennes' (1979) book. Here Emery's version is presented.

The next serious step toward the application of the universality principle to polymer theory was done by des Cloizeaux, who found a glossary between the parameters of the magnet state equation in a magnetic field and those of the P+LMWL system within a wide polymer concentration range (section 4.2). As the main instrument to realize this glossary for building the P+LMWL state diagram, the scaling approach was taken (section 4.3). In this version, the scaling regularities, examined and proved on magnets, were extended to the polymer system. Such an approach, by analogy in the framework of the universality principle, led to experiment-consistent qualitative dependences, i.e. to correct exponents in the power functions of the characteristic values, but gave no preexponential factor, i.e. the amplitude of a characteristic quantity.

Then, such an approach was named simple (naive, intuitive) scaling. One of de Gennes' remarkable books (1979) is devoted to it, where some fundamental questions of phase separation are discussed as well. The scaling approach, even in the mean field approximation framework, led to a more adequate-to-experiment results concerning critical opalescence in comparison with Debye's early consideration (cf. paragraph 3.3.1.2 and section 4.4).

The scaling ideas have also proved to be useful to interpret dynamic quantities, such as diffusion, viscosity, etc. (section 4.5).

Chapter 5 deserves a special comment, being composed of some abridged and adapted papers devoted to the most up-to-date and rigorous methods in polymer theory, which are based on the Lagrangian formalism of general field theory, and employes several versions of renormalization group transformations, originally developed to describe critical phenomena in general-type systems. Being the developer of the renormalization group transformation method, Kenneth Wilson won the 1982 Nobel prize for physics.

In the critical region, the structure of any system is very complicated. Correspondingly, the Hamiltonian describing it is complex, too, and involves many degrees of freedom. K.Wilson compares this situation with some pattern of a complex structure under a microscope with a focused objective lens. Now, if one slightly drives the lens out of focus, the pattern becomes vague: its fine details become invisible while the big ones are blurred. Such unfocusing corresponds to some transformation of the Hamiltonian $H_1 = \tau(H_0)$. Applying this transformation once again will allow access to a more generalized pattern with its Hamiltonian $H_2 = \tau(H_1)$, and so on. One can find such a transformation τ , that the Hamiltonian would reach a certain fixed point H^* , where $H^* = \tau(H^*)$. Here, it proves to be rather simple to permit the researcher to apply all the procedures needed to simulate experimentally measured quantities.

The chief feature is that the experimentally measured quantities become actually insensitive to the fine elements of the structure; instead, they perceive just the scaled-enlarged pattern of the system's structure. Such a bridge between the theoretico-mathematical procedure of scaling the Hamiltonian (the renormalization group transformation) and an experimentally measured quantity offers considerable scope for studies on substances in their critical state.

All this ideology of renormalization group transformations has proved to be suitable and very effective for the rigorous description of the conformational properties of macromolecules.

Edwards' continuous chain with its corresponding Hamiltonian H_0 is obviously the most suitable, in every respect, model of a polymer chain. However, this model involves plenty of fine details of the conformational structure, which actually have no influence on the experimentally measured quantities, eg. the mean-square end-to-end distance. The theoreticians (Freed, des Cloizeaux, Oono, Ohta, Duplantier, Schäffer, et el.) have found such renormalization group procedures of the source Hamiltonian H_0 to drive it to the fixed point Hamiltonian H^* , which allow access, by the conventional methods of statistical physics, to characteristic quantities close to their experimental values.

In the course of the renormalization group transformation, the structural elements are getting larger step by step, but, even at the fixed point, the Hamiltonian provides for the correlations of order parameter fluctuations, and this approach proves to be more rigorous in comparison with the mean field approximation.

The success of renormalization group transformations for describing conformational changes means a great leading idea for whole polymer science. Indeed, the conformationdependent experimental quantities perceive this conformation in scaled, enlarged form, and are insensitive to fine details, eg., the structure of one or few monomer units. Therefore, to explain the conformation-dependent quantities adequately, scaling transformations (even of a qualitative nature) should be sought for; one should not try to find explanations at the level of fine details (a monomer unit, etc.).

Certainly, some scaling transformations were also in other theories and approaches, which were in good agreement with experiment. For example, Kuhn's segment includes various short-range details (the interactions between the closest neighbours). The size of a blob characterizes, on the average, the specific character of long-range interactions (the interactions between distant segments) in a macromolecule, in a good solvent and at a given concentration.

The idea of step-by-step scaling transformations serves as the basis for the scaling (phenomenological) approach, which leads to power functions for the characteristic quantities and to the property of uniformity of the system's thermodynamic potentials.

However, only in renormalization group methods did the ideas of step-by-step scaling transformations find their rigorous analytical and beautiful realization. One of such procedures was put forward by de Gennes and described in his book.

Chapter 6 occupies the most modest place. This is due to the fact that an enormous literature has accumulated on liquid-crystal phase separation, including Wunderlich's (1973, 1976, 1980) fundamental monographs. Nevertheless, the matter of this chapter, in its relation to the others, must play a positive role in any research on identification of the nature of phase separation in polymer systems. This chapter also reports the results of application of the turbidity spectrum method to phase analysis of some systems with a crystallizing polymers: poly(vinyl alcohol) + water and <math>poly(ethylene oxide) + water, whose treatment by well-established methods did not yield comprehensive information.

Each chapter ends with a summary to briefly describe its content, the main conclusions, and some additional comments.

Due to the huge number of formulae, they are numbered by sections. Within each section, a formula is referenced only by its number. When a formula is referred to from any other section, its number is preceded by the dashed section number. If a reference concerns several formulae from one section, the section number is omitted starting with the second formula. For example, in subsection 3.1.1, I refer to some formulae from sections 1.2 and 1.3 as $(1.2 \ 52, \ 53), (1.3-19, -20)$. To cite a continuous row of formulae, the following denomination is accepted: $(5.1 \ 248...250)$.

Some of the figures in this book have been made with GNUPLOT, Version 3.5 (Copyright © 1986-93 Thomas Williams, Colin Kelley), the others were scanned from their originals in ink into pcx-files and then processed by the emTeX device driver. A small program (Copyright © 1998) by Sergei Shmakov, my secretary and a reader at my chair, enables TeX's formulae to be inserted into pcx-pictures. The text has been written with $PTeX 2_{\varepsilon}$ using an original Elsevier style file espect1.sty.

Acknowledgements

I would like to express my deep gratitude to the scientific editor of the book Professor Sergei Ya. Frenkel who had been patronized the work of the Saratov research team since the very beginning of its formation, whose advices were invaluable for us. At the final stage of making-up the manuscript, tragic news of his death came from Saint-Petersburg.

My cordial appreciation to Dr Sergei L. Shmakov, a reader at my chair, who kindly agreed to act as my secretary in this business, translated the text into English, typeset it, with its numerous formulae and figures, using MIFX and GNUPLOT. Special thanks to Mr Dmitry N. Tychinin who has read carefully the text and made many suggestions on how to improve the English. At last, I most highly appreciate the help of Drs Huub Manten-Werker, her readiness to answer my questions, and her patience in awaiting the manuscript, whose sending to the printer's was delayed because of my underestimation of the amount of work.

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Chapter 1

Stability and Phase Separation

1.1. Stability conditions of the one-phase multicomponent system

1.1.1. Main thermodynamic relationships

Let us consider an open thermodynamic system consisting of ν components, i.e. containing particles of ν kinds. The first and second principles of thermodynamics written together for a quasi-static process in such a system represent the **Gibbs fundamental** equation in its energetic expression:

$$dU = T \, dS - P \, dV + \sum_{i=1}^{\nu} \mu_i \, dn_i, \tag{1}$$

U being the internal energy of the system, S the entropy, V the volume, T temperature, P pressure, μ_i and n_i the chemical potential and number of moles of the *i*th component, respectively.

This equation can be written in the entropy expression as well:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \sum_{i=1}^{\nu} \frac{\mu_i}{T}dn_i.$$
 (2)

and, in the integral form,

$$S = S(U, V, n_1, \dots, n_{\nu}), \quad U = U(S, V, n_1, \dots, n_{\nu}).$$
(3)

As the internal energy U is a state function of the system, Equation 1 is a total differential:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_j} dV + \sum_{i=1}^{\nu} \left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_j \neq i} dn_i,$$

from which

$$\left(\frac{\partial U}{\partial S}\right)_{V,n_1} = T; \qquad \left(\frac{\partial U}{\partial V}\right)_{S,n_1} = -P; \qquad \left(\frac{\partial U}{\partial n_1}\right)_{V,S,n_j \neq 1} = \mu, \tag{4}$$

follows and the corresponding mixed derivatives are equal to each other (Maxwell's relationships). Eg.

$$\frac{\partial^2 U}{\partial S \,\partial V} = \frac{\partial^2 U}{\partial V \,\partial S}, \qquad \text{i.e.} \qquad \left(\frac{\partial T}{\partial V}\right)_{S,n_1} = -\left(\frac{\partial P}{\partial S}\right)_{V,n_1}. \tag{5}$$

The variables in the right-hand side of Equation 1 under the sign of differentiation (i.e. S, V, n_t) are called **thermodynamic coordinates**. Let us denote them by a common letter $Y_l, l = 1, ..., \nu + 2$ to write the following formulae compactly. By virtue of their additivity, the thermodynamic coordinates are extensive parameters.

The parameters defined as

$$X_{l} = \left(\frac{\partial U}{\partial Y_{l}}\right)_{Y_{j \neq l}} \tag{6}$$

are called **thermodynamic forces**. As follows from Equation 1, they are T, (-P), and μ_i . They have the same values over all any equilibrium system, so they are **intensive parameters**. The values Y_i and X_i related by Equation 6 are called conjugate parameters. With these designations Equation 1 takes the form

With these designations Equation 1 takes the form

$$dU = \sum_{l=1}^{r} X_l \, dY_l, \quad r = \nu + 2. \tag{7}$$

The internal energy U is a first-power homogeneous function. According to Euler's theorem for such functions it follows from Equations 1 and 6 that

$$U = TS - PV + \sum_{i=1}^{\nu} \mu_i n_i \quad \text{or} \quad U = \sum_{l=1}^{r} X_l Y_l,$$
(8)

and its differentiation yields

$$dU = T \, dS + S \, dT - P \, dV - V \, dP + \sum_{i=1}^{\nu} \mu_i \, dn_i + \sum_{i=1}^{\nu} n_i \, d\mu_i. \tag{9}$$

Comparison of Equations 9 and 1 leads to the Gibbs-Durgham equation:

$$S dT - V dP + \sum_{i=1}^{\nu} n_i d\mu_i = 0.$$
 (10)

If an intensive parameter is represented as a function of extensive ones, the corresponding equation

$$X_l = X_l(Y_1, \dots, Y_r), \quad l = 1, \dots, r$$
 (11)

is referred to as a state equation (Kluge and Neugebauer, 1976; Sposito, 1981; Zhukovsky, 1983). It can be obtained from Equation 3 by substituting the corresponding specific symbols $U = U(S, V, n_1, \ldots, n_{\nu})$, therefore the latter is called the state equation as well. From the internal energy

$$U = U(Y_1, \dots, Y_r), \tag{12}$$

where the variables Y are arranged according to a certain order, the **thermodynamic** potentials can be found by means of the Legendre transformation (Münster, 1969):

$$\psi_k = U - \sum_{l=1}^k X_l Y_l, \quad k < r.$$
(13)

Differentiating Equation 13 taking into account Equation 7 leads to

$$d\psi_k = -\sum_{l=1}^k Y_l \, dX_l + \sum_{j=k+1}^r X_j \, dY_j.$$
(14)

Substituting Equation 8 into Equation 13, one obtains

$$\psi_k = \sum_{j=k+1}^r X_j Y_j,\tag{15}$$

whence it follows that ψ_k 's are first-power homogeneous functions of the extensive variables. With k < r all the thermodynamic potentials are **characteristic functions**, since they completely characterize the system. Eg. from Equation 14 it follows that

$$\frac{\partial \psi_k}{\partial X_l} = -Y_l, \quad l = 1, \dots, k \tag{16}$$

and

$$\frac{\partial \psi_k}{\partial Y_j} = X_j, \quad j = k+1, \dots, r.$$
(17)

The Gibbs thermodynamic potential

$$G = G(T, P, n_1, \dots, n_\nu) \tag{18}$$

is defined by Equation 13 as

$$G = U - TS + PV, \quad \text{where} \quad k = 2. \tag{19}$$

According to Equation 14

$$dG = -S \, dT + V \, dP + \sum_{i=1}^{\nu} \mu_i \, dn_i, \tag{20}$$

with the partial derivatives (see Equations 16 and 17)

$$\left(\frac{\partial G}{\partial T}\right)_{P,n_1} = -S, \quad \text{i.e.} \quad S = S(T, P, n_1),$$
(21)

$$\left(\frac{\partial G}{\partial P}\right)_{T,n_1} = V, \quad \text{i.e.} \quad V = V(T, P, n_1), \tag{22}$$

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \mu_i, \quad \text{i.e.} \quad \mu_i = \mu_i(T,P,n_{\{i\}}), \tag{23}$$

where $n_{\{i\}}$ points to the dependence on all the n_i , $i = 1, ..., \nu$.

The Helmholtz thermodynamic potential

$$F = F(T, V, n_1, \dots, n_{\nu}), \quad i = 1, \dots, \nu$$
(24)

is also defined by Equation 13 but when k = 1:

$$F = U - TS. \tag{25}$$

According to Equation 14

$$dF = -S \, dT - P \, dV + \sum_{i=1}^{\nu} \mu_i \, dn_i \tag{26}$$

with the partial derivatives (see Equations 16 and 17)

$$\left(\frac{\partial F}{\partial T}\right)_{V,n_1} = -S, \quad \text{i.e.} \quad S = S(T, V, n_1), \tag{27}$$

$$\left(\frac{\partial F}{\partial V}\right)_{T,n_1} = -P, \quad \text{i.e.} \quad P = P(T, V, n_i), \tag{28}$$

$$\left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_j\neq i} = \mu_i, \quad \text{i.e.} \quad \mu_i = \mu_i(T,V,n_{\{i\}}). \tag{29}$$

Equations 19, 21-25, 27-29 are also called equations of state. Those of them which involve two mechanical parameters (P, V) and a thermal parameter (T or S) are referred to as **mechanical state equations**. The equations that involve two thermal parameters and one mechanical parameter are called **thermal state equations**.

The enthalpy is defined as

$$H = U + PV. \tag{30}$$

Taking into account Equation 19, we have

$$G = H - TS, \tag{31}$$

or (see Equation 21)

$$G = H + T \left(\frac{\partial G}{\partial T}\right)_{P,n_i}.$$
(32)

Hence,

$$H = -T^2 \left(\frac{\partial [G/T]}{\partial T}\right)_{P,n_1} = \left(\frac{\partial [G/T]}{\partial [1/T]}\right)_{P,n_1}.$$
(33)

This is one of the **Gibbs-Helmholtz equations** which relate the thermodynamic potentials.

Define the mean molar quantity of any extensive parameter Z as

$$\bar{Z} = \frac{Z}{n}, \quad \text{where} \quad n = \sum_{i=1}^{\nu} n_i.$$
(34)

In the following discussion we will sometimes call it just a **molar** quantity. Let Z be a function of T. P, n_1, \ldots, n_{ν} ; then the partial molar quantity \overline{Z}_i of the *i*th component is determined as

$$\bar{Z}_{i} = \left(\frac{\partial Z}{\partial n_{i}}\right)_{T,P,n_{J\neq i}}.$$
(35)

Since

$$dZ = \left(\frac{\partial Z}{\partial T}\right)_{P,n_{i}} dT + \left(\frac{\partial Z}{\partial P}\right)_{T,n_{i}} dP + \sum_{i=1}^{\nu} \left(\frac{\partial Z}{\partial n_{i}}\right)_{T,P,n_{j\neq i}} dn_{i}, \tag{36}$$

and Z is a first-power homogeneous function of each n_i , then, according to Euler's theorem and in view of Equation 35 with P = const, T = const,

$$Z = \sum_{i=1}^{\nu} Z_i n_i.$$
(37)

Differentiating Equation 37 and comparing it with Equation 36, one obtains

$$\sum_{i=1}^{\nu} n_i \, d\bar{Z}_i - \left(\frac{\partial Z}{\partial T}\right)_{P,n_i} dT - \left(\frac{\partial Z}{\partial P}\right)_{T,n_i} dP = 0. \tag{38}$$

Equation 38 is called a generalized Gibbs-Durgham equation.

Define the mole fraction (concentration) of the *i*th component in the system as

$$x_i = \frac{n_i}{n} \tag{39}$$

(note that

$$\sum_{i=1}^{\nu} x_i = 1). \tag{40}$$

As independent variables, we now use $(x_1, \ldots, x_{\nu-1}, n)$, not (n_1, \ldots, n_{ν}) . In view of Z being independent on n when dP = 0, dT = 0, we have

$$d\bar{Z} = \sum_{i=1}^{\nu-1} \left(\frac{\partial \ddot{Z}}{\partial x_i}\right)_{T,P,x_{k\neq i}} dx_i$$
(41)

(the subscript 'k' is supposed not to be equal to ν). Dividing both sides of Equation 36 by n, for dP = 0, dT = 0, dn = 0, and in view of Equation 39, one has

$$dZ = \sum_{i=1}^{\nu} \left(\frac{\partial Z}{\partial n_i} \right)_{T, P, n_j \neq i} dx_i$$

and (see Equations 35 and 40)

$$dZ = \sum_{i=1}^{\nu-1} (\bar{Z}_i - \bar{Z}_\nu) \, dx_i.$$
(42)

Comparison of Equations 41 and 42 indicates that

$$\left(\frac{\partial \bar{Z}}{\partial x_i}\right)_{T,P,x_{k\neq i}} = Z_i - \bar{Z}_\nu, \quad i = 1, \dots, \nu - 1.$$
(43)

Dividing both sides of Equation 37 by n:

$$\ddot{Z} = \sum_{i=1}^{\nu} \bar{Z}_i x_i \tag{44}$$

and substituting \bar{Z}_i from Equation 43, one obtains

$$Z = \sum_{i=1}^{\nu-1} \left(\frac{\partial \bar{Z}}{\partial x_i} \right)_{T, P, x_k \neq i} x_i + \sum_{i=1}^{\nu-1} \bar{Z}_{\nu} x_i + \bar{Z}_{\nu} x_{\nu}.$$

Hence, in view of Equation 40, it follows that

$$\bar{Z}_{\nu} = \bar{Z} - \sum_{i=1}^{\nu-1} x_i \left(\frac{\partial \bar{Z}}{\partial x_i}\right)_{T, P, x_{k \neq i}}$$

$$\tag{45}$$

(if the ν th component is not the last onc, the summation must be taken over all the components but ν).

In the important specific case of $\nu = 2$ (a binary system)

$$\bar{Z}_2 = \bar{Z} - x_1 \frac{\partial \ddot{Z}}{\partial x_1},\tag{46}$$

$$\bar{Z}_1 = \dot{Z} - x_2 \frac{\partial \dot{Z}}{\partial x_2}.$$
(47)

The tangent line equation to the plot $Z = \overline{Z}(x_2)$ at a certain point x_2° has the form

$$\dot{Z}(x_2) = \left(\frac{\partial \bar{Z}}{\partial x_2}\right)_{x_2 = x_2^{\circ}} (x_2 - x_2^{\circ}) + \bar{Z}(x_2^{\circ}).$$

$$\tag{48}$$

It follows from Equations 46-48 that this tangent line cuts off intervals on the ordinate axes $x_2 = 0$ ($x_1 = 1$) and $x_2 = 1$ ($x_1 = 0$), that are numerically equal to \bar{Z}_1 and \bar{Z}_2 , respectively, for a given mixture composition (Figure 1.1).

The mean molar quantities are convenient due to their independence on n, so they are unambiguously defined by $(\nu + 1)$ parameters $(T, P, x_1, \ldots, x_{\nu-1})$ only, and not by $(\nu + 2)$ parameters $(T, P, n_1, \ldots, n_{\nu})$. From here on, when speaking of the mean molar quantities we will consider the mole fractions of the first $(\nu-1)$ components as independent variables.



Figure 1.1. Determination of \bar{Z}_t by the tangent line method

The theory of solutions uses the quantities of mixing

$$\Delta Z_m = Z - \sum_{i=1}^{\nu} Z_{0i} = Z - \sum_{i=1}^{\nu} n_i Z_{0i} = \sum_{i=1}^{\nu} n_i Z_i - \sum_{i=1}^{\nu} n_i Z_{0i}, \qquad (49)$$

where Z is an extensive parameter of the mixture, Z_{0i} is the corresponding parameter of the *i*th component in its individual state under the same external conditions. For the **mean molar quantities** of mixing, Equation 49 can be rewritten as

$$\Delta \bar{Z}_m = Z - \sum_{i=1}^{\nu} x_i \bar{Z}_{0i} = \sum_{i=1}^{\nu} x_i (\bar{Z}_i - \bar{Z}_{0i}).$$
(50)

According to Equations 50 and 23, for the mean molar Gibbs potential of mixing, the following equation holds:

$$\Delta \bar{G}_m = \sum_{i=1}^{\nu} x_i (\mu_i - \mu_{0i}) = \sum_{i=1}^{\nu} x_i \Delta \mu_i.$$
(51)

All the relationships derived above for Z are valid for ΔZ_m as well.

In an external field with an intensity \mathcal{A} , the Gibbs fundamental equation takes the form

$$dU = T \, dS - P \, dV + \sum_{n=1}^{\nu} \mu_n \, dn_n + \mathcal{A} \, da, \tag{52}$$

a being the thermodynamic coordinate conjugate to the field.

In particular, for a system placed in a magnetic field,

$$dU = T \, dS - P \, dV + \sum_{i=1}^{\nu} \mu_i \, dn_i + H \, dM, \tag{53}$$

where H is the magnetic field strength, M is magnetizability.

Then, according to Equation 1.1.1 13,

$$G = U - TS + PV - HM, (54)$$

and

$$dG = -S \, dT + V \, dP - M \, dH + \sum_{i=1}^{\nu} \mu_i \, dn_i, \qquad (55)$$

and, correspondingly,

$$\left(\frac{\partial G}{\partial H}\right)_{T,P,n_{t}} = -M.$$
(56)

For the Helmholtz potential,

$$F = U - TS - HM, (57)$$

$$dF = -S \, dT - P \, dV - M \, dH + \sum_{i=1}^{\nu} \mu_i \, dn_i, \tag{58}$$

and, correspondingly,

$$\left(\frac{\partial F}{\partial H}\right)_{T,V,n_i} = -M. \tag{59}$$

1.1.2. Stability conditions

We will consider phase separation as a process caused by loss of stability in a one-phase multicomponent system. First of all, it is necessary to discuss the stability conditions of the one-phase state.

Speaking of stability, one should keep in mind the stable equilibrium with the environment (the thermostat). By the thermostat we understand a large embracing thermodynamic system, the intensive properties of which remain constant on a change in the system parameters. in the embraced system.

Any isolated system spontaneously attains a state that undergoes no further changes. Such a state is called equilibrium. In the case of equilibrium, the thermodynamic parameters of a system are time-independent unless some perturbation occurs.

By stability we mean the system property of returning to the equilibrium state after a short-time perturbation.

In usual courses of thermodynamics it is shown that **spontaneous processes** are characterized by the Carnot-Clausius inequality

$$dS > \frac{dQ}{T},\tag{1}$$

where dS is the change in the entropy of the system, dQ is the quantity of heat put into the system at the temperature T for an infinitely small part of the whole process. The equality

$$dS = \frac{dQ}{T} \tag{2}$$

applies to reversible equilibrium processes.

Relationship 1 reflects a universal principle of entropy increase in systems seeking an equilibrium. Consequently, the equilibrium itself is characterized by a maximum of entropy.

Replacing dQ by its expression from the first principle of thermodynamics

$$dQ = dU + P \, dV - \sum^{\nu} \mu_{\star} \, dn_{\star},\tag{3}$$

one obtains for a spontaneous process

$$T \, dS - dU - P \, dV + \sum^{\nu} \mu_i \, dn_i > 0. \tag{4}$$

If, for a certain state of the system, no dS, dU, dV, and dn_i are available so that Equation 4 could be realized, it means that the given state is **stable**. Thus, the stability condition is expressed as

$$T\,\delta S - \delta U - P\,\delta V + \sum_{i=1}^{\nu} \mu_i\,\delta n_i \le 0,\tag{5}$$

with δ to denote infinitely small, but otherwise arbitrary increments (virtual motions).

As a result of perturbation, the thermodynamic parameters can also undergo finite increments. Eg. if after perturbation the entropy takes the value S, its increment is

 $\Delta S = S - S_0,\tag{6}$

 S_0 being the value in the equilibrium state.

It should be emphasized that perturbation may not necessarily be of an external character, since molecular fluctuations may lead to small spontaneous deviations of the system parameters from their mean values (Prigogine and Defay, 1954).

We now turn to consider the specific conditions of the existence of a system.

For an isolated system $(U = const, V = const, n_1 = const)$, Equation 5 gives the condition for stability toward infinitely small perturbations:

 $(\delta S)_{U,V,n_1} < 0. \tag{7}$

The system is stable toward any finite perturbations if the inequality

 $(\Delta S)_{U,V,n_{\star}} < 0 \tag{8}$

holds, i.e. any such perturbation would lead to a decrease in entropy.

The corresponding conditions for a system with $(S = const, V = const, n_i = const)$ are as follows:

 $(\delta U)_{S,V,n} > 0, \tag{9}$

$$(\Delta U)_{S,V,n_{\star}} > 0. \tag{10}$$

There may be situations when Equations 7 and 9 are realized while Equations 8 and 10 are not realized, i.e. the system is stable toward infinitely small perturbations while being unstable toward finite ones (a local maximum of entropy or a minimum of internal energy with at least one additional extremum). In such cases it is generally agreed to speak of a metastable equilibrium (metastable state) of the system. Conditions 8 and 10 define a stable equilibrium. When simultaneously breaking conditions 7 10, the system proves to be absolutely unstable.

In a similar way one can define the stability conditions for the thermodynamic potentials G, F, and H. They are summarized in Table 1.1.

The equality sign denotes the equilibrium state of the system (lack of perturbation).

Assume that the state, which the system has transformed into as a result of a perturbation, obeys Equation 1.1.1-3. In view of this, the increment of internal energy in
Table 1.1

Conditions	for	stability	of a	one-phase	multicomponent	system	\mathbf{to}	finite	per-
turbations									

Conditions for existence	Stability to finite	Extremum
of the system	perturbations	of function
U, V, n_i	$\Delta S \le 0$	max S
S, V, n_i	$\Delta U \ge 0$	$\min U$
T, P, n_i	$\Delta G \geq 0$	$\min G$
T, V, n	$\Delta F \geq 0$	$\min F$
S, P, n_i	$\Delta H \geq 0$	$\min H$

Equation 5 is expressed as changes of the thermodynamic coordinates δY , i.e. δS , δV , and δn_i .

We will also assume that after the perturbation the internal energy increment is sufficiently small and permits one to retain two terms in the Taylor series expansion. Multiplying Equation 5 by (-1) and inverting the inequality, we have

$$\frac{\delta U}{\left(\frac{\partial U}{\partial S}\right)_{V,n_{i}}\delta S + \left(\frac{\partial U}{\partial V}\right)_{S,n_{i}}\delta V + \sum_{i=1}^{\nu} \left(\frac{\partial U}{\partial n_{i}}\right)_{V,S,n_{j\neq i}}\delta n_{i} + \frac{1}{2}\delta^{2}U + \cdots$$

$$- T\delta S + P\delta V - \sum_{i=1}^{\nu} \mu_{i}\delta n_{i} \ge 0.$$
(11)

Based on Equations1.1.1-4 the first and last summands can be reduced, and the condition of stability toward infinitely small perturbations is, therefore, brought to

$$\delta^2 U \ge 0. \tag{12}$$

 $\delta^2 U$ can be presented in two equivalent forms: first,

$$\delta^2 U = \sum_{l,k=1}^r \frac{\partial^2 U}{\partial Y_l \partial Y_k} \, \delta Y_l \, \delta Y_k; \tag{13}$$

and second,

$$\delta^2 U = \sum_{l=1}^r \delta X_l \, \delta Y_l = \delta T \, \delta S - \delta P \, \delta V + \sum_{i=1}^\nu \delta \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j \neq i} \delta n_i. \tag{14}$$

The latter expression is derived by differentiating Equation 1.1.1–7 while keeping in mind that the second differential of the independent variable is equal to zero $(d^2Y_l = 0)$. Equalities 13 and 14 are readily obtainable from each other with

$$\delta X_l = \sum_k \frac{\partial X_l}{\partial Y_k} \delta Y_k = \sum_k \frac{\partial}{\partial Y_k} \left(\frac{\partial U}{\partial Y_l} \right) \delta Y_k.$$
(15)

From the Gibbs fundamental equation in its entropy form, one can similarly derive the condition of stability to infinitely small perturbations:

 $\delta^2 S \le 0. \tag{16}$

Inequality 12 means that the quadratic form 13 is positively defined (Madelung, 1957; Korn and Korn, 1968). For such a form to be positive, all the main minors of its coefficient matrix $[a_{lk}]$ must be positive, that is

$$a_{lk} = \frac{\partial^2 U}{\partial Y_l \, \partial Y_k},\tag{17}$$

i.e.

$$\left|\begin{array}{ccc}
a_{11} > 0; & a_{22} > 0; & \dots & a_{rr} > 0 \\
\left|\begin{array}{ccc}
a_{11} & a_{12} \\
a_{21} & a_{22}
\end{array}\right| > 0; & \left|\begin{array}{ccc}
a_{22} & a_{23} \\
a_{32} & a_{33}
\end{array}\right| > 0; & \dots \\
& \dots & \dots & \dots & \dots \\
& \det[a_{lk}] > 0.
\end{array}\right\}$$
(18)

The first of conditions 18 is the positiveness of all the diagonal terms of the coefficient matrix. Consequently,

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,n_t} = \left(\frac{\partial T}{\partial S}\right)_{V,n_t} = \frac{T}{c_V} > 0,$$
(19)

where

$$c_{V} = \frac{\partial Q}{\partial T} = T \left(\frac{\partial S}{\partial T} \right)_{V,n_{i}}$$
(20)

is the heat capacity at V = const (the condition of thermal stability),

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_{S,n_1} = -\left(\frac{\partial P}{\partial V}\right)_{S,n_1} > 0 \quad \text{or} \quad \left(\frac{\partial P}{\partial V}\right)_{S,n_1} < 0; \tag{21}$$

or, having introduced an isoentropic compressibility

$$\chi_s = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{S,n_1},\tag{22}$$

$$\chi_{s} > 0 \tag{23}$$

(the condition of **mechanical stability**);

$$\left(\frac{\partial^2 U}{\partial n_i^2}\right)_{S,V,n_j \neq i} = \left(\frac{\partial \mu_i}{\partial n_i}\right)_{S,V,n_j \neq i} > 0$$
(24)

(the condition of diffusional stability).

The next condition of stability is the positiveness of the second-order minor:

$$\begin{vmatrix} \frac{\partial^2 U}{\partial S^2} & \frac{\partial^2 U}{\partial V \partial S} \\ \frac{\partial^2 U}{\partial S \partial V} & \frac{\partial^2 U}{\partial V^2} \end{vmatrix} > 0$$
(25)

or

$$\frac{\partial^2 U}{\partial S^2} \cdot \frac{\partial^2 U}{\partial V^2} - \left(\frac{\partial^2 U}{\partial S \,\partial V}\right)^2 = -\frac{T}{c_V} \left(\frac{\partial P}{\partial V}\right)_S > 0$$

Let us write the stability conditions in terms of the thermodynamic potentials ψ_k (Gibbs, 1928; Münster, 1969). By analogy with Equation 14, Equation 1.1.1-14 can be written as

$$\delta^2 \psi_k = -\sum_{l=1}^k \delta Y_l \, \delta X_l + \sum_{j=k+1}^r \delta X_j \, \delta Y_j. \tag{26}$$

In view of Equations 1.1.1 16 and 1.1.1-17, note that

$$\left[\delta^{2}\psi_{k}(Y_{k+1},\ldots,Y_{r})\right]_{X_{l}} = \sum_{j=k+1}^{r} \delta X_{j} \,\delta Y_{j}, \quad l = 1,\ldots,k;$$
(27)

$$\left[\delta^{2}\psi_{k}(X_{1}, X_{2}, \dots, X_{k})\right]_{Y_{j}} = -\sum_{i=1}^{k} \delta Y_{i} \,\delta X_{i}, \quad j = k+1, \dots r.$$
⁽²⁸⁾

From the stability condition (Equations 12 and 14) one has

$$\delta^{2}U = \sum_{l=1}^{r} \delta X_{l} \, \delta Y_{l} = \sum_{l=1}^{k} \delta Y_{l} \, \delta X_{l} + \sum_{j=k+1}^{r} \delta X_{j} \, \delta Y_{j} > 0.$$
(29)

In view of Equations 27 and 28 it follows from Equation 29 that

$$\left[\delta^2 \psi_k(Y_j)\right]_{X_i} - \left[\delta^2 \psi_k(X_i)\right]_{Y_j} > 0.$$
(30)

In the general case, this inequality holds if and only if the former quadratic form is positively-defined, and the latter one is negatively-defined, i.e.

$$\left[\delta^2 \psi_k(X_1, X_2, \dots, X_k)\right]_{Y_j} < 0, \tag{31}$$

$$\left[\delta^2 \psi_k(Y_{k+1}, \dots, Y_r)\right]_{X_l} > 0, \tag{32}$$

which is equivalent to

$$\left| \frac{\partial^2 \psi_k}{\partial X_l \partial X_S} \right| \begin{cases} < 0, & \text{for the odd-order main minors,} \\ > 0, & \text{for the even-order main minors,} \end{cases}$$
(33)

$$\left. \frac{\partial^2 \psi_k}{\partial Y_j \, \partial Y_t} \right| > 0 \qquad \text{for all the main minors.}$$
(34)

The above considerations also hold good for the mean molar quantities defined by $(\nu + 1)$ -independent parameters only (see subsection 1.1.1).

For the mean molar Gibbs potential, conditions 33 reduce to

$$\begin{vmatrix} \frac{\partial^2 G}{\partial T^2} & -\frac{\partial^2 G}{\partial P \, \partial T} \\ -\frac{\partial^2 \hat{G}}{\partial T \, \partial P} & \frac{\partial^2 \hat{G}}{\partial P^2} \end{vmatrix} > 0, \tag{35}$$

$$\frac{\partial^2 \bar{G}}{\partial T^2} < 0, \tag{36}$$

$$\frac{\partial^2 \bar{G}}{\partial P^2} < 0. \tag{37}$$

Only two of these three conditions are independent.

In view of Equation 1.1.1-21 and the determination of the heat capacity at constant pressure according to

$$c_P = T \left(\frac{\partial S}{\partial T}\right)_P,\tag{38}$$

inequality 36 leads to

$$\frac{c_P}{T} > 0. \tag{39}$$

From inequality 37 and Equation 1.1.1-22, it follows that

 $\chi_{T} > 0, \tag{40}$

where

$$\chi_{\tau} = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{T} \tag{41}$$

is the isothermal compressibility. Inequality 35 allows us to derive

$$\frac{\partial^2 \bar{G}}{\partial T^2} \cdot \frac{\partial^2 \bar{G}}{\partial P^2} - \left(\frac{\partial^2 \bar{G}}{\partial T \partial P}\right)^2 = \frac{\chi_T c_P}{T} > 0.$$
(42)

Further analysis of inequalities 39, 40, and 42 (Münster, 1969; Stanley, 1971) yields other important results:

$$c_P > c_V \tag{43}$$

and

$$\chi_{\tau} > \chi_{s}. \tag{44}$$

For the mean molar Gibbs potential, conditions 34 reduce to

$$\left|\frac{\partial^2 \bar{G}}{\partial x_i \, \partial x_j}\right| > 0 \tag{45}$$

for all the main minors $i, j = 1, \ldots, \nu - 1$.

In the case of a binary system, from Equation 45 it follows that

$$\left(\frac{\partial^2 \bar{G}}{\partial x_1^2}\right)_{T,P} > 0 \tag{46}$$

and

$$\left(\frac{\partial^2 \bar{G}}{\partial x_2^2}\right)_{T,P} > 0. \tag{47}$$

For a binary system, Equation 1.1.1-43 yields

$$\frac{\partial G}{\partial x_2} = \mu_2 - \mu_1,\tag{48}$$

and from the Gibbs-Durgham equation (Equation 1.1.1-10) at T = const and P = const it follows that

$$x_1\frac{\partial\mu_1}{\partial x_2} + x_2\frac{\partial\mu_2}{\partial x_2} = 0. \tag{49}$$

Differentiating Equation 48 leads to

$$\frac{\partial^2 G}{\partial x_2^2} = \frac{\partial \mu_2}{\partial x_2} - \frac{\partial \mu_1}{\partial x_2}.$$
(50)

Making a replacement of $\partial \mu_2 / \partial x_2$ or $\partial \mu_1 / \partial x_2$ in Equation 50 using Equation 49, we obtain

$$\frac{\partial^2 G}{\partial x_2^2} = \frac{1}{x_1} \cdot \frac{\partial \mu_2}{\partial x_2} \tag{51}$$

and

$$\frac{\partial^2 G}{\partial x_2^2} = -\frac{1}{x_2} \cdot \frac{\partial \mu_1}{\partial x_2}.$$
(52)

Then, condition 47, according to Equations 51 and 52, reduces to

$$\left[\left(\frac{\partial\mu_2}{\partial x_2}\right)_{P,T} > 0\right]$$
(53)

and

$$\left(\frac{\partial\mu_1}{\partial x_2}\right)_{P,T} < 0 \tag{54}$$

14

Analogous transformations of Equation 46 lead to the conditions

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{P,T} > 0 \tag{55}$$

 and

$$\left(\frac{\partial \mu_2}{\partial x_1}\right)_{P,T} < 0 \tag{56}$$

Inequalities 54 and 56 follow from to each other on the basis of the reciprocity relationship

$$\frac{\partial \mu_i}{\partial x_j} = \frac{\partial \mu_j}{\partial x_i},\tag{57}$$

which is one of Maxwell's relationships (cf. Equation 1.1.1-5).

Prigogine and Defay (1954) have shown the validity of Equations 46 or 47 to cause the validity of Equations 39 and 40, hence, the diffusional stability condition (any of Equations 46, 47, 53-56) is a **necessary and sufficient stability condition** of the one-phase state of multicomponent systems (including the metastable state).

1.1.3. Ideal binary system

The state equation of an ideal gas is the well-known Clapeyron-Clausius equation

$$PV = nRT.$$
 (1)

For a one-component system under isothermal conditions and without any phase transition, Equation 1.1.1-20 reduces to

$$dG = V \, dP. \tag{2}$$

Substitution of V from Equation 1 into Equation 2 and integration of the latter from a certain initial state to the current state lead to

$$G = G_0(T) + nRT \ln \frac{P}{P_0},\tag{3}$$

where the subscript '0' denotes the state accepted as initial. Dividing both sides of Equation 3 by n we obtain

$$\mu = \mu_0(T) + RT \ln \frac{P}{P_0}.$$
(4)

A mixture is referred to as **ideal** if its components behave as if they were in their individual states. Eg. a gas mixture can be described by

$$\mu_{t} = \mu_{0t} + RT \ln \frac{P_{t}}{P_{0t}} \tag{5}$$

for each *i*th component.

From the Dalton law

$$x_{t} = \frac{P_{t}}{P},\tag{6}$$

where P is the total pressure in the mixture, x_1 is the mole fraction of the *i*th component, Equation 5 can be rewritten as

$$\mu_{t} = \mu_{0t}^{O} + RT \ln x_{t}, \tag{7}$$

where

$$\mu_{0i}^{\Theta} = \mu_{0i}(T) + RT \ln \frac{P}{P_{0i}}.$$
(8)

For condensed matter, Equation 7 (for each component) can be thought of as a definition of an ideal mixture. Having represented it as

$$\mu_{i,id} = \mu_{0i}^{O} + RT \ln \frac{n_i}{n_1 + n_2},\tag{9}$$

one can easily see that if $i \neq j$, then

$$\frac{\partial \mu_{i,id}}{\partial n_j} = -\frac{RT}{n} < 0 \quad \text{and} \quad \frac{\partial \mu_{i,id}}{\partial x_j} = -RT < 0$$
 (10)

(cf. Equations 1.1.2-54,-56). If i = j, then

$$\frac{\partial \mu_{i,id}}{\partial n_i} = RT\left(\frac{1}{n_i} - \frac{1}{n}\right) > 0 \tag{11}$$

(cf. Equations 1.1.2-53, 55). According to Equations 1.1.1-44, -35, -23,

$$\dot{G} = \mu_1 x_1 + \mu_2 x_2 \tag{12}$$

and

$$\left(\frac{\partial^2 \bar{G}_{\rm id}}{\partial x_2^2}\right) = \frac{RT}{x_1 x_2} > 0 \tag{13}$$

(cf. Equation 1.1.2-47). The inequality

$$\Delta \bar{G}_{\rm m} < 0. \tag{14}$$

is a necessary condition for the existence of a solution.

Equations 7 and 1.1.1-51 together yield

$$\Delta \hat{G}_{\mathbf{m},\mathrm{id}} = RT \sum_{i} x_i \ln x_i < 0 \tag{15}$$

for an ideal mixture. Consequently, condition 14 is valid over the whole range of mixture concentrations. We note in passing that the following relationships are also realized for an ideal mixture

$$\Delta \bar{H}_{m,id} = -T^2 \frac{\partial (\Delta G_{m,id}/T)}{\partial T} = 0, \qquad (16)$$

$$\Delta \bar{V}_{m,id} = \frac{\partial \Delta \bar{G}_{m,id}}{\partial P} = 0 \tag{17}$$

(see Equations 1.1.1–22,-30,-33). When P = const

$$\Delta \tilde{H}_{\rm m} = \Delta \tilde{U}_{\rm m} + P \Delta \tilde{V}_{\rm m},\tag{18}$$

whence, according to Equations 16 and 17, it follows that

$$\Delta \bar{U}_{\mathbf{m},\mathbf{id}} = 0,\tag{19}$$

which means a lack of difference in the interactions between molecules of one component and of different components in an ideal mixture. For the molar entropy of mixing

$$\Delta \bar{S}_{m,id} = -\frac{\partial \Delta G_{m,id}}{\partial T} = -R(x_1 \ln x_1 + x_2 \ln x_2)$$
(20)

(see Equations 15 and 1.1.1-21).

One can easily see that the one-phase solution stability conditions (Equations 1.1.2-46,-47,-53...56) are valid for the corresponding quantities of mixing as well, since

$$\frac{\partial^2 \hat{G}}{\partial x_2^2} = \frac{\partial^2 \Delta \hat{G}_{\rm m}}{\partial x_2^2}$$

(see Equation 1.1.1-51).

The stability conditions are well illustrated in Figure 1.2. Indeed, μ_1 and $\Delta \mu_1$ are decreasing functions of x_2

$$\frac{\partial \mu_1}{\partial x_2} < 0 \quad \text{and} \quad \frac{\partial \Delta \mu_1}{\partial x_2} < 0,$$
(21)

and μ_2 and $\Delta \mu_2$ are increasing functions of x_2 . The condition

$$\frac{\partial^2 \bar{G}}{\partial x_2^2} > 0 \qquad \left(\frac{\partial^2 \Delta \bar{G}_{\rm m}}{\partial x_2^2} > 0\right)$$

defines convexity of the $\bar{G}(x_2)$ and $\Delta \bar{G}_m(x_2)$ functions by definition (Stanley, 1971).

The formalism of ideal mixtures proves to be very helpful, since **real mixtures** are often characterized by the degree of deviation of their properties from the corresponding ideal properties.

If one writes the chemical potential μ_i for a real substance in form 5, the value corresponding to P_i is called **fugacity** f_i , and

$$\mu_{i} = \mu_{0i} + RT \ln \frac{f_{i}}{f_{0i}},\tag{22}$$

where f_{0i} is the standard-state fugacity and the ratio

$$\frac{f_i}{f_{0i}} = a_i \tag{23}$$



Figure 1.2. Composition dependences of chemical potentials μ_1/RT , mean molar Gibbs potential \bar{G}/RT , chemical potentials of mixing $\Delta \mu_1/RT$, and mean molar Gibbs potential of mixing $\Delta \bar{G}_m/RT$ for an ideal binary system with $\mu_{01}/RT = 1$ and $\mu_{02}/RT = 1.2$

defines the activity of the *i*th component. The activity coefficient is introduced according to

$$\gamma_1 = \frac{a_1}{x_1} \tag{24}$$

and

$$\mu_i = \mu_{0i} + RT \ln a_i \tag{25}$$

$$= \mu_{0t} + RT \ln x_t + RT \ln \gamma_t \tag{26}$$

$$=\mu_{i,id} + RT \ln \gamma_i. \tag{27}$$

The excess quantities of the *i*th component are introduced according to

$$Z_{i,ex} = Z_i - Z_{i,id}.$$
(28)

Eg.

$$\mu_{i,ex} = \mu_i - \mu_{i,id} - RT \ln \gamma_i. \tag{29}$$

Therefore, the activity coefficient γ_i directly characterizes the degree of the deviation of the system's properties from those of the ideal system.

1.2. Conditions for equilibrium and stability of the multiphase multicomponent system

1.2.1. General conditions for equilibrium and stability

Let us consider a closed system containing ν components and γ phases¹. The phases are assumed to be in internal equilibrium and to be open with respect to each other, i.e. the entropy, volume, and mole fractions are variables for each phase.

Write the fundamental equation (Equation 1.1.1-1) for each phase:

$$\delta U_{\alpha} = T_{\alpha} \, \delta S_{\alpha} - P_{\alpha} \, \delta V_{\alpha} + \sum_{\nu=1}^{\nu} \mu_{\nu \alpha} \, \delta n_{\nu \alpha}, \quad \alpha = I, \dots, \gamma.$$
⁽¹⁾

As the internal energy of the system is a state function, under the conditions

$$\sum_{\alpha=1}^{\prime} \delta S_{\alpha} = 0, \tag{2}$$

$$\sum_{\alpha=1}^{\gamma} \delta V_{\alpha} = 0, \tag{3}$$

$$\sum_{\alpha=1}^{\gamma} \delta n_{i\alpha} = 0 \quad (i = 1, \dots, \nu), \tag{4}$$

the equality

$$\sum_{\alpha=1}^{\gamma} \delta U_{\alpha} = 0 \tag{5}$$

holds and should formally be considered as the extremum condition of U in the Lagrange problem with additional relations 2-4, which is solved, by tradition, using the Lagrange multiplier method (Rusanov, 1960, 1967; Semenchenko, 1960b; Storonkin, 1967, 1969; Münster, 1969; Kluge and Neugebauer, 1976). Multiply Equation 2 by an indeterminate but constant multiplier λ_1 , Equation 3 by $(-\lambda_2)$, and Equations 4 by λ_3 ,'s. The equations so obtained are subtracted from Equation 5. Taking Equation 1 into account, we have

$$\sum_{\alpha} (T_{\alpha} - \lambda_1) \delta S_{\alpha} - \sum_{\alpha} (P_{\alpha} - \lambda_2) \delta V_{\alpha} + \sum_{i=1}^{\nu} \sum_{\alpha=I}^{\gamma} (\mu_{i\alpha} - \lambda_{3i}) \delta n_{i\alpha} = 0,$$
(6)

from which

$$\underbrace{T_{\alpha} = \lambda_1, \quad P_{\alpha} = \lambda_2, \quad \text{and} \quad \mu_{i\alpha} = \lambda_{3_i}}_{\alpha = I_{i} \dots, \gamma} \tag{7}$$

follow and, consequently,

¹Hereinafter, phase numbers are denoted by Roman digits and Greek letters

These equalities are the equilibrium conditions for a multiphase multicomponent system.

Such a system is **stable as a whole**, i.e. it is in the state of a stable or metastable equilibrium, if the stability conditions hold for each coexisting phase (see Equation 1.1.2 18) (Gibbs, 1928; Rusanov, 1960, 1967)

$$\det \left| \frac{\partial^2 U_{\alpha}}{\partial Y_{l\alpha} \partial Y_{j\alpha}} \right| > 0 \qquad (\alpha = 1, \dots, \gamma; \quad l, j = 1, \dots, \nu + 2), \tag{9}$$

with all the main minors, or

$$\det \left| \frac{\partial X_{l\alpha}}{\partial Y_{j\alpha}} \right| > 0. \tag{10}$$

The above relationships have been derived without regard for the effects of surface phenomena. The equilibrium conditions of a multiphase (e.g. two-phase) system with allowance made for the interface (the subscript Ω) take the form

$$T_{I} = T_{II} = T_{\Omega},$$

$$\mu_{iI} = \mu_{iII} = \mu_{i\Omega} \quad (i = 1, 2).$$
(11)

The mechanical equilibrium conditions depend on the degree of the interface curvature. E.g. a flat surface implies that

$$P_I = P_{II} = P_{\Omega},\tag{12}$$

and for an interface with the curvature $c = 1/r_1 + 1/r_2$

$$P_I - P_{II} = \sigma c = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2} \right);$$
 (13)

and for a sphere interface with the radius r

$$P_I - P_{II} = \frac{2\sigma}{r},\tag{14}$$

where σ is the interface tension coefficient. Thus, the condition for the interface stability should be taken into account when surface phenomena begin to play a significant role.

1.2.2. Membrane equilibrium. Osmotic pressure

Consider an isolated system with ν components and γ phases, with all the phases separated from each other with a solid semipermeable² membrane. The volume of each phase is therefore fixed. Due to the membrane impermeability to the $(\nu - s)$ components, variations in the $(\nu - s)$ mole fractions are equal to zero.

By analogy with the formulae given in subsection 1.2.1, we write

$$\sum_{\alpha=I}^{\gamma} \delta U_{\alpha} = 0 \tag{15}$$

²i.e. permeable to molecules of s components only $(s < \nu)$

under the conditions

$$\sum_{\alpha=I}^{\gamma} \delta S_{\alpha} = 0, \tag{16}$$

$$\delta V_{\alpha} = 0 \quad (\alpha = I, \dots, \gamma), \tag{17}$$

$$\left. \begin{array}{c} \sum_{\alpha=I}^{\gamma} \delta n_{i\alpha} = 0 \quad (i=1,\ldots,s); \\ \delta n_{j\alpha} = 0 \quad (j=s+1,\ldots,\nu; \quad \alpha=I,\ldots,\gamma). \end{array} \right\}$$
(18)

By means of Lagrange's multipliers (see subsection 1.2.1), the equilibrium conditions can be obtained:

$$T_I = T_{II} = \dots = T_{\gamma},\tag{19}$$

$$\mu_{iI} = \mu_{iII} = \dots = \mu_{i\gamma} \quad (i = 1, \dots, s).$$
(20)

The presence of the solid semipermeable membrane leads to the possibility for the coexisting phases to be under different pressures. Certainly, the equality of the chemical potentials holds only for those s components which the membrane is permeable to.

Osmotic equilibrium is a most important special case of membrane equilibrium. Let γ be 2: one phase (I) is the solvent (component 1) and the other (II) is the solution of component 2 in 1 (mixture 1 + 2). The membrane is impermeable to the molecules of solute 2.

According to the stability condition (Equation 1.1.2–55),

$$\left(\frac{\partial\mu_1}{\partial x_1}\right)_{T,P} > 0. \tag{21}$$

Assume the pressures in both the phases to be equal at the initial moment $(P_I = P_{II} \text{ at } t = 0)$; then the chemical potential of component 1 in solution (say, with $x_1 = x_1^* < 1$, see Figure 1.3) μ_{1II} is less than that in the individual state μ_{01} (with $x_1 = 1$, i.e. in phase I), $\mu_{1II} < \mu_{1I} = \mu_{01}$, which indicates no equilibrium between phases II and I (see Equation 20). For the solvent (Equation 1.1.1-22),

$$\left(\frac{\partial\mu_1}{\partial P}\right)_T = \bar{V}_1 > 0, \tag{22}$$

where \bar{V}_1 is the molar volume of the solvent. It follows that the chemical potential depression of component 1 due to the presence of component 2 can be compensated by a pressure increase in phase II (P_{II}). Indeed, experience shows that P_{II} increases owing to the transport of solvent molecules from phase I to phase II through the membrane. The related concentration changes can, however, be neglected. Therefore, in equilibrium (see Equation 20)

$$\left. \begin{array}{c} T_{I} = T_{II} = T \\ \mu_{1I}(T, P_{I}) = \mu_{1II}(T, P_{II}, x_{1}) \end{array} \right\}$$
(23)



Figure 1.3. Towards the definition of osmotic pressure in solutions

The excessive pressure

$$\pi = P_{II} - P_I$$

is called the osmotic pressure. On the basis of Equations 23 and in view of Equation 22, one can write for $x_1 = x_1^*$

$$\mu_{01}(P_I) = \mu_1(P_I, x_1^*) + \int_{P_I}^{P_{II}} \bar{V}_1 \, dP.$$
(24)

Assuming V_1 to be constant over the pressure range P_I and P_{II} , we obtain

$$\mu_{01}(P_I) - \mu_1(P_I, x_1^*) = \tilde{V}_1(P_{II} - P_I).$$
(25)

If we introduce the chemical potential of mixing of the first component according to

$$\Delta \mu_1 = \mu_1(P_I, x_1^*) - \mu_{01}(P_I), \tag{26}$$

then from Equations 25 and 26 it follows that

$$\Delta \mu_1 = -\bar{V}_1(P_{II} - P_I)$$
 and $\pi = -\frac{\Delta \mu_1}{\bar{V}_1}$

or, for sufficiently dilute solutions $(\bar{V}_1 \simeq \bar{V}_{01})$,

$$\pi \cong -\frac{\Delta \mu_1}{\bar{V}_{01}}.\tag{27}$$

An ideal dilute solution allows one to combine Equations 1.1.3-9 and 27

$$\pi \simeq -\frac{RT}{V_{01}} \ln x_1 = -\frac{RT}{V_{01}} \ln(1 - x_2) \simeq \frac{RT}{\bar{V}_{01}} x_2 \cong \frac{RT}{V} \cdot \frac{m_2}{M_2} = \frac{RTc_2}{M_2},$$
(28)

where m_2 , c_2 , M_2 are the mass, concentration (g/cm³), and molecular mass (g/mol) of the second component, respectively.

For the reduced osmotic pressure π/RTc_2 , the state equation of an ideal dilute solution (Equation 28) shows no concentration dependence

$$\frac{\pi}{RTc_2} = \frac{1}{M_2}.$$
(29)

This equation is used to determine the molecular mass M_2 using the method of osmotic pressure.

From this point on we will omit the subscript '2' in state equation 29.

1.2.3. Phase rule

We continue to consider the system containing ν components and γ phases (Gibbs, 1928; Münster, 1969). It is supposed to be in equilibrium, so conditions 8 hold, and in the case of infinitely small variations of T, P, μ , the equalities

$$dT_{\alpha} = dT; \quad dP_{\alpha} = dP; \quad d\mu_{\alpha} = d\mu, \tag{30}$$

are realized for all γ phases and ν components. Write the Gibbs-Durgham equation 1.1.1– 10 for each phase for the mean molar extensive quantities using Equation 30

$$\bar{S}_{\alpha} dT - \bar{V}_{\alpha} dP + \sum_{i=1}^{\nu} x_{i\alpha}, d\mu_i = 0 \quad (\alpha = I, \dots, \gamma).$$
(31)

This expression can be regarded as a system of γ equations with respect to the $(\nu + 2)$ unknowns dT, dP, and $d\mu_i$. Hence, the number of independent variations in temperature, pressure, and chemical potentials (provided the phase number is kept) is

$$f = \nu + 2 - \gamma. \tag{32}$$

This equation is called Gibbs' phase rule. It defines the number of thermodynamic degrees of freedom f, i.e. the number of variables T, P, μ_i which can arbitrarily be varied without breaking the equilibrium among γ phases. When f = 0, the equilibrium is referred to as non-variant, with f = 1 it is monovariant, when f = 2 it is bivariant, and with $f \ge 3$ it is polyvariant.

1.2.4. Critical phase

One-component systems

The state equation of a one-component system (Equations 1.1.1-11,-28) written as

$$f(P,V,T) = 0 \tag{33}$$

specifies a surface in 3D space P, V, T that represents a state diagram of the system (see Figure 1.20). Every point on this surface corresponds to an equilibrium state and is called a **configurative point**.

To present the surface more clearly, its projections on the planes P = 0, V = 0, and T = 0 are considered. They are called state diagrams as well (Kirillin et al., 1983).

Let us consider a one-component system which obeys the van der Waals equation for one mole of substance

$$\left(P + \frac{a}{V^2}\right)(\bar{V} - b) = RT,\tag{34}$$

where R is the gas constant.

The constants a and b allow for the repulsion and attraction molecular forces. The simplest way to take the repulsion forces into account is to introduce an effective volume of molecules v_m . Then, we specify the molecule-available volume that can be correlated with V_{id} from Equation 1.1.3-2

$$V_{\rm id} \simeq (V - V_{\rm ex}) \quad \text{or} \quad V_{\rm id} \simeq (\bar{V} - b),$$
(35)

where $b = \bar{V}_{ex}$ is the excluded volume.

The existence of attraction forces among the molecules leads to a certain decrease in the real gas pressure on the vessel walls ($P < P_{id}$). Assuming that the attraction forces cause a decrease both in the number of molecule collisions with the walls and in the collision momentum as well, and that each of these effects is proportional to the gas density ($\sim N_A/\bar{V}$), we obtain

$$P \simeq P_{\rm id} - \frac{a}{V^2}.\tag{36}$$

Substitution of P_{id} and \bar{V}_{id} from Equations 36 and 35 into

$$P_{id}V_{id} = RT$$

leads to the van der Waals equation

$$\left(P+\frac{a}{\bar{V}^2}\right)(\bar{V}-b)=RT.$$

In the case of a model for the interacting molecular solid spheres of a radius r_0 , no **two** molecules can approach each other at a distance less than their diameter. Hence, the excluded volume is determined as

$$\beta_{ex} = \frac{4}{3}\pi (2r_0)^3 = \frac{32\pi}{3}r_0^3,$$

and per molecule

$$\beta_{ex}' = \frac{\beta_{ex}}{2} = \frac{16\pi}{3} r_0^3 = 4v_m, \tag{37}$$

and per mole

$$b = 4N_A v_m. \tag{38}$$

Let us analyze Equation 34 using a state diagram on the coordinates P vs \bar{V} (see Figures 1.4 and, also, 1.20, 1.21).



Figure 1.4. State diagram of the van der Waals one-component system: sp, bi, C denote the spinodal, binodal, and critical point, respectively

The boundary of the stability of the one-phase state to infinitely small perturbations is called the **spinodal**. Because the region of mechanical stability is defined by Equation 1.1.2-37 (see also Equations 1.1.2-38...41, 1.1.122)

$$\left(\frac{\partial P}{\partial V}\right)_T < 0,$$

the spinodal is given by the equation

$$\left(\frac{\partial P}{\partial \bar{V}}\right)_T = 0 \tag{39}$$

and corresponds to the locus of the isotherms extrema on the state diagram (curve BB'CC'C) in Figure 1.4.

Every configurative point inside the spinodal implies the violation of the mechanical stability conditions for the one-phase state, and this region of the state diagram is characterized as **absolutely unstable** to the one-phase existence. As a result, the system is divided into two phases, their existence conditions for one-component systems (Equation 8) being

$$T_l = T_{gas}, \quad P_l = P_{gas}, \quad \mu_l = \mu_{gas}.$$
 (40)

Let us find two configurative points on diagram 1.4, one for the liquid phase and the other for the gas one, for which conditions 40 (Kubo, 1968) hold. The first two equalities 40 mean that both the points must belong to a common isotherm (eg. $T_1 = const$) and be located on the line parallel to the abscissa axis. Let AD be one of such lines. Then the third condition 40 is expressed in the following form

$$\int_{ABO} \left(\frac{\partial \mu}{\partial P}\right)_T dP = -\int_{OCD} \left(\frac{\partial \mu}{\partial P}\right)_T dP.$$
(41)

Taking Equation 1.1.1-23 into account, Equation 41 can be written as

$$\int_{ABO} \dot{V} dP = -\int_{OCD} \bar{V} dP.$$
(42)

It follows that the condition $\mu_l = \mu_{gas}$ implies the equality between the areas bounded by the isotherm's branches and line AD:

$$Area of ABO = Area of OCD, \tag{43}$$

which is known as Maxwell's rule. A and D are, therefore, the points on the state diagram, for which conditions 40 are realized, and their abscissae determine the values of the molar volumes of the liquid and gas phases in equilibrium at the temperature T_1 and under the pressure P_1 . The set of such pairs of points corresponding to the phases the system is divided into at different temperatures is called the **binodal** (or the **boundary curve**, the curve AA'CD'D in Figure 1.4), and the lines, which connect the points on each pair, are called the **tie lines**, or **nodes**.

Outside the binodal dome the equilibrium conditions (Equation 1.1.2-37) are fulfilled, and the system exists in its one-phase state: the liquid phase is to the left of the left-hand branch and the gas one is to the right of the right-hand one. Continuous liquid \rightleftharpoons gas transition is possible outside the binodal curve with $T > T_c$. Between the binodal and spinodal is the region of the **metastable state**, where the one-phase system is stable with respect to infinitely small density fluctuations and unstable with respect to finite ones.

The system evolution upon transfer of the configurative point from outside the binodal to inside its dome is considered in a special division of phase transition science, namely, phase transition kinetics. The mechanism of evolution will essentially depend on where the configurative point is: in the metastable or in the absolutely unstable region of the state diagram (even under the same pressure when the final two-phase states will be equal).

As can be seen from Figure 1.4, the values of the molar volumes of the two phases approach each other on an increase in pressure. The configurative point, where they will be equal, is called the **critical point**.

It follows that the critical point is a point of the isotherm inflection (the tangent line is horizontal), i.e. is given by the system of equations

$$\left(\frac{\partial P}{\partial V}\right)_T = 0,\tag{44}$$

$$\left(\frac{\partial^2 P}{\partial \tilde{V}^2}\right)_T = 0. \tag{45}$$

There is a region of absolutely unstable states between two coexisting phases situated as closely to the critical point as one likes. Thus, the critical point must belong to both the spinodal and binodal, it is the point of their being tangent.

A more general approach will give the following form of the spinodal equation for a one-component system (see Equation 1.1.2-12)

 $d^2 U = 0, (46)$

with S and V taken as independent variables.

Contrary to Equation 1.1.2-12, δ is replaced here by d, since variations of U can not be arbitrary due to the conditions of the temperature constancy imposed.

Equation 46 is equivalent to

$$\mathbf{D} = \begin{vmatrix} \frac{\partial^2 U}{\partial \bar{S}^2} & \frac{\partial^2 U}{\partial \bar{S} \partial \bar{V}} \\ \frac{\partial^2 U}{\partial \bar{V} \partial \bar{S}} & \frac{\partial^2 U}{\partial \bar{V}^2} \end{vmatrix} = 0$$
(47)

(see Equations 1.1.2-13,-23), which defines the first equation for the critical point.

Now we have to find the second equation. As Figure 1.4 suggests, the isotherm passing through the critical point nowhere enters the absolutely unstable region, i.e. provides the validity of

 $d^2U \ge 0$ and $\mathbf{D} \ge 0$.

It follows from Equation 47 that with an additional relation T = const there is a conditional minimum of D in the critical point, i.e.

$$\begin{cases} dT = \frac{\partial T}{\partial \bar{S}} d\bar{S} + \frac{\partial T}{\partial \bar{V}} d\bar{V} = 0 \\ d\mathbf{D} = \frac{\partial \mathbf{D}}{\partial \bar{S}} d\bar{S} + \frac{\partial \mathbf{D}}{\partial \bar{V}} d\bar{V} = 0 \end{cases}$$
(48)

The condition of solvability for this system with respect to $d\bar{S}$ and $d\hat{V}$ (with allowance made for $T = \partial \bar{U} / \partial \bar{S}$) is:

$$\mathbf{D}' = \begin{vmatrix} \frac{\partial^2 U}{\partial \bar{S}^2} & \frac{\partial^2 U}{\partial \bar{S} \partial \bar{V}} \\ \frac{\partial \mathbf{D}}{\partial \bar{S}} & \frac{\partial \mathbf{D}}{\partial \bar{V}} \end{vmatrix} = 0.$$
(49)

This is the second equation for the critical point.

In principle, Equations 47 and 49 reduce to Equations 44 and 45, but the proof is clumsy (Münster, 1969).

The isoentropic spinodal corresponds to the condition

$$\left(\frac{\partial P}{\partial V}\right)_{S} = 0 \tag{50}$$

(see Equation 1.1.2-21) and appears behind the **isothermal spinodal** (Equation 44), toward the region of absolutely unstable state on the state diagram (Skripov and Koverda, 1984).

Multicomponent systems

In the general case, two coexisting phases in a ν -component system may prove to be identical at certain values of the intensive parameters and, therefore, constitute one, **critical** phase.

As the mean molar thermodynamic potentials of a ν -component system are functions of the $(\nu+1)$ variables, it is necessary to have at least $(\nu+1)$ parameters to describe the state of such a system. Correspondingly, the state diagram is found to be $(\nu+1)$ -dimensional.

The tie lines are defined as the lines in the two-phase region ($\gamma = 2$) on which the system intensive parameters are constant. It follows from Equation 8 that tie lines connect the binodal points corresponding to the coexisting phases. It should be noted that any tie line is unambiguously defined by ν intensive parameters, according to the phase rule (Equation 32).

The equation for the critical phase of a multicomponent system can be derived in the same way which has led to Equations 47 and 49 for $\nu = 1$.

The spinodal equation, as Equation 1.1.2-12 shows, has the form

$$\mathbf{D} = \begin{vmatrix} \frac{\partial^2 \bar{U}}{\partial \bar{S}^2} & \frac{\partial^2 \bar{U}}{\partial \bar{S} \partial \bar{V}} & \cdots & \frac{\partial^2 \bar{U}}{\partial \bar{S} \partial \bar{x}_{\nu-1}} \\ \frac{\partial^2 U}{\partial \bar{V} \partial S} & \frac{\partial^2 \bar{U}}{\partial \bar{V}^2} & \cdots & \frac{\partial^2 \bar{U}}{\partial \bar{V} \partial x_{\nu-1}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 \bar{U}}{\partial x_{\nu-1} \partial \bar{S}} & \frac{\partial^2 \bar{U}}{\partial x_{\nu-1} \partial \bar{V}} & \cdots & \frac{\partial^2 U}{\partial x_{\nu-1}^2} \end{vmatrix} = 0.$$
(51)

Further, let us draw a curve through every point of the critical phase, which holds ν (of the ($\nu + 1$) intensive parameters) values constant ³

$$\frac{\partial \vec{U}}{\partial \vec{S}}, \quad \frac{\partial \vec{U}}{\partial \vec{V}}, \quad \frac{\partial \vec{U}}{\partial x_1}, \quad \dots, \quad \frac{\partial \vec{U}}{\partial x_{\nu-1}}.$$
(52)

None of such curves can find its way into the absolutely unstable region, since specifying ν intensive parameters defines the tie line unambiguously (here, this tie line degenerates into

³The choice of these ν values is arbitrary and in no case affects the final result

a point in the critical phase). Consequently, the **D** value has a conditional minimum on each curve $\mathbf{D} \ge 0$ where the curve intersects the critical phase, according to Equation 51.

For definiteness, assume ν first values to be chosen for Equation 52. Then, it follows from the above reasoning that under the condition

$$\begin{cases} d\left(\frac{\partial\bar{U}}{\partial\bar{S}}\right) = \frac{\partial^{2}\bar{U}}{\partial\bar{S}^{2}}dS + \frac{\partial^{2}\bar{U}}{\partial\bar{S}\partial\bar{V}}dV + \dots + \frac{\partial^{2}\bar{U}}{\partial\bar{S}\partial\bar{x}_{\nu-1}}dx_{\nu-1} = 0\\ d\left(\frac{\partial\bar{U}}{\partial\bar{V}}\right) = \frac{\partial^{2}\bar{U}}{\partial\bar{V}\partial\bar{S}}dS + \frac{\partial^{2}\bar{U}}{\partial\bar{V}^{2}}dV + \dots + \frac{\partial^{2}\bar{U}}{\partial\bar{V}\partial\bar{x}_{\nu-1}}dx_{\nu-1} = 0\\ \dots \\ d\left(\frac{\partial\bar{U}}{\partial\bar{x}_{\nu-2}}\right) = \frac{\partial^{2}\bar{U}}{\partial\bar{x}_{\nu-2}\partial\bar{S}}d\bar{S} + \frac{\partial^{2}\bar{U}}{\partial\bar{x}_{\nu-2}\partial\bar{V}}d\bar{V} + \dots + \frac{\partial^{2}\bar{U}}{\partial\bar{x}_{\nu-2}\partial\bar{x}_{\nu-1}}dx_{\nu-1} = 0 \end{cases}$$
(53)

the equation

$$d\mathbf{D} = \frac{\partial \mathbf{D}}{\partial \bar{S}} \, d\bar{S} + \frac{\partial \mathbf{D}}{\partial \bar{V}} \, d\bar{V} + \dots + \frac{\partial \mathbf{D}}{\partial x_{\nu-1}} \, dx_{\nu-1} = 0 \tag{54}$$

holds for the critical phase.

The linear homogeneous system of equations 53 and 54 has a non-trivial solution if and only if its determinant is equal to zero

$$\mathbf{D}' = \mathbf{0}.\tag{55}$$

This is the second equation for the critical phase. Note that D' (Equation 55) is distinguished from the determinant D (Equation 51) only by the last row which is replaced by

$$\frac{\partial \mathbf{D}}{\partial S} = \frac{\partial \mathbf{D}}{\partial V} = \cdots = \frac{\partial \mathbf{D}}{\partial x_{\nu-1}}.$$
 (56)

If any other ν parameters (not the first ν ones) had been chosen out of the ($\nu + 1$) ones in Equation 52, the determinant **D'** would have differed from **D** in that the row corresponding to the remaining parameter would have been replaced by row 56.

One can derive the critical phase equation in a much simpler form in many specific cases using Equations 1.1.2-30...34 as the stability conditions rather than Equation 1.1.2-12. The subsequent line of argument should remain unchanged. The molar Helmholtz potential \overline{F} is convenient to use for a one-component system with Equations 1.1.2-31 and 1.1.2-32 to express the thermal and mechanical stability conditions, respectively. As the second inequality is stronger, one can confine oneself with it. In this case, the determinant \mathbf{D}_F degenerates into one term

$$\mathbf{D}_F = \frac{\partial^2 \bar{F}}{\partial \bar{V}^2} = -\left(\frac{\partial P}{\partial \bar{V}}\right)_T,\tag{57}$$

and D' will be $D'_F = -(\partial^2 P/\partial V^2)_T$. The critical point equations 44 and 45 follow immediately.

For a multicomponent system containing condensed phases only, it is only the diffusional stability condition (Equation 1.1.2-45) that matters as the strongest one (Münster, 1969; Glansdorff and Prigogine, 1971), so \mathbf{D} is

$$\mathbf{D}_{G} = \begin{vmatrix} \frac{\partial^{2}\bar{G}}{\partial x_{1}^{2}} & \cdots & \frac{\partial^{2}\bar{G}}{\partial x_{1} \partial x_{\nu-1}} \\ \vdots & \ddots & \vdots \\ \frac{\partial^{2}\bar{G}}{\partial x_{\nu-1} \partial x_{1}} & \cdots & \frac{\partial^{2}\bar{G}}{\partial x_{\nu-1}^{2}} \end{vmatrix},$$
(58)

and a determinant that differs from D_G by any row replaced by

$$\frac{\partial \mathbf{D}_G}{\partial x_1} \quad \frac{\partial \mathbf{D}_G}{\partial x_2} \quad \cdots \quad \frac{\partial \mathbf{D}_G}{\partial x_{\nu-1}} \tag{59}$$

can be accepted as \mathbf{D}'_{G} . Then the critical phase equations have the form

$$\mathbf{D}_{\boldsymbol{G}} = 0 \qquad (\text{spinodal equation}) \tag{60}$$

and

$$\mathbf{D}_G' = \mathbf{0}.\tag{61}$$

1.2.5. Law of the corresponding states. Virial expansion

From Equations 34, 44, and 45, the following expressions emerge for the critical parameters of a one-component system

$$P_c = \frac{a}{27b^2},\tag{62}$$

$$\tilde{V}_c = 3b,$$
 (63)

and

$$RT_c = \frac{8a}{27b}.$$
(64)

Thus,

$$Z_c = \frac{P_c \bar{V}_c}{RT_c} = \frac{a}{27b^2} \, 3b \, \frac{27b}{8a} = \frac{3}{8} = 0.375.$$
(65)

Real liquids possess Z_c somewhat less than 0.375 (Stanley, 1971) and significantly less than Z_{id} for ideal gas (Equation 1.1.3-1)

$$Z_{\rm id} = \frac{P\tilde{V}}{RT} = 1. \tag{66}$$

If both sides of Equation 34 are multiplied by 27b/a, and then a and b are eliminated using Equations 62-64, one obtains the state equation in reduced quantities

$$\left(\tilde{P} + \frac{3}{\tilde{V}^2}\right)(3\tilde{V} - 1) = 8\tilde{T},\tag{67}$$

(where $\tilde{P} \equiv P/P_c$, $\tilde{V} \equiv V/V_c$, $\tilde{T} \equiv T/T_c$). It appears that Equation 67 holds good for many substances. Substances with equal reduced parameters \tilde{V} , \tilde{P} , and \tilde{T} are considered to be in corresponding states, and Equation 67 is called the law of corresponding states.

Generally speaking, many one-component state equations have been proposed (Read et al., 1977), but the van der Waals equation 34 and the virial expansion equation

$$\frac{P\bar{V}}{RT} = 1 + B_2 \frac{1}{\bar{V}} + B_3 \frac{1}{\bar{V}^2} + \cdots$$
(68)

 $(B_2 \text{ and } B_3 \text{ being the second and third virial coefficients, respectively, and so on) are most often used.$

The second virial coefficient B_2 reflects pair interactions among the molecules during their collisions, the third one B_3 characterizes ternary interactions.

Let us confine ourselves to two terms of expansion 68

$$\frac{P\dot{V}}{RT} = 1 + B_2 \frac{1}{\bar{V}}.$$
(69)

In contrast to the van der Waals equation, only one quantity, B_2 , is responsible here for the interactions among molecules. It is desirable to compare it with a and b from Equation 34.

Remove the brackets in Equation 34. Let a and b be sufficiently small to neglect the term ab/\bar{V}^2 and to replace P in (-Pb) by bRT/\bar{V} according to the ideal gas equation. After some algebra we have

$$\frac{P\bar{V}}{RT} = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\bar{V}}.$$
(70)

So,

$$B_2 \cong b - \frac{a}{RT},\tag{71}$$

i.e. B_2 is proportional to the excluded volume and varies with temperature. At the Boyle temperature T_B , there occurs compensation of repulsion and attraction forces ($b = a/RT_B$) and $B_2 = 0$, which makes the isotherm degenerate into that one of ideal gas

$$P\bar{V} = RT_B \tag{72}$$

(see Figure 1.4). When $T \gg T_B$ the second term in Equation 71 (attraction forces) can be neglected, and interaction forces can only be treated as repulsion forces only (excluded volume).

1.3. Phase separation of regular mixtures

1.3.1. Liquid-liquid separation

A mixture is called **regular** if, though intermolecular forces are taken into account in the enthalpy part of G, the interaction is assumed not to be so strong as to affect the

chaotical motion of molecules in the mixture, i.e. no account of this interaction in the entropy part is needed

$$\Delta G_m = \Delta H_m - T \,\Delta S_{m,\text{id}}.\tag{1}$$

Let us calculate $\Delta \overline{H}_m$ for the lattice model of binary initures in the zero approximation (Prigogine and Defay, 1954; Kubo, 1968; Glansdorff and Prigogine, 1971; Andreyev et al., 1974), where molecules of the liquid are presumed to be in the cells of a rigid lattice with the coordination number ν . Every cell contains either a molecule of component 1 or that of component 2. Only molecules in neighbouring cells (*i*th and *j*th) interact, with the energy $\varepsilon_{ij} < 0$ (i, j = 1, 2 are the numbers of components). Thus, short-range repulsion forces are taken into account by a finite volume of the cells while van der Waals attraction forces are allowed for by the energy ε_{ij} .

With m to denote the total number of cells, mx_1 is the number of the *i*th molecules. Each of them has νx_2 of its *j*th neighbours (on the average). The total system energy is the sum of all the pair interactions

$$U = \frac{1}{2} \sum_{i,j=1,2} m x_i \nu x_j \varepsilon_{ij} = \frac{m\nu}{2} \left(x_1^2 \varepsilon_{11} + 2x_1 x_2 \varepsilon_{12} + x_2^2 \varepsilon_{22} \right).$$
(2)

When each component is in its individual state, every ith molecule is surrounded only by molecules of the ith type, and the total energy is

$$U_{0} = \frac{1}{2} \sum_{i=1,2} m x_{i} \nu \varepsilon_{ii} = \frac{m \nu}{2} (x_{1} \varepsilon_{11} + x_{2} \varepsilon_{22}).$$
(3)

As the lattice is rigid,

$$\Delta V_m = 0$$
 and $\Delta H_m = \Delta U_m$.

Subtracting Equation 3 from Equation 2 and performing simple transformations for the enthalpy of mixing, we get

$$\Delta H_m = m\nu x_2(1-x_2)\Delta\varepsilon,$$

where

$$\Delta \varepsilon = \varepsilon_{12} - \frac{\varepsilon_{11} + \varepsilon_{22}}{2} \tag{4}$$

defines the energy of mixing per contact. On a per-niole basis $(n = m/N_A = 1, N_A \text{ being the Avogadro number})$

$$\Delta \tilde{H}_m = N_A \nu x_2 (1 - x_2) \Delta \varepsilon. \tag{5}$$

Substitution of Equations 5 and 1.1.3-20 into Equation 1 yields

$$\Delta \bar{G}_m = N_A \nu x_2 (1 - x_2) \Delta \varepsilon + RT(x_1 \ln x_1 + x_2 \ln x_2).$$
(6)

If
$$\left|\frac{\varepsilon_{11}+\varepsilon_{22}}{2}\right| > |\varepsilon_{12}|$$
, then $\Delta \varepsilon > 0$, $\Delta H_m > 0$ (7)

(endothermic mixing).

If
$$\left|\frac{\varepsilon_{11}+\varepsilon_{22}}{2}\right| < |\varepsilon_{12}|$$
, then $\Delta \varepsilon < 0$, $\Delta H_m < 0$ (8)

(exothermic mixing).

When $\Delta H_m = 0$, the mixing is called athermic (ideal solution).

The assumption of the molecules being distributed chaotically is valid if only $\Delta \varepsilon \ll kT$. Having denoted

$$\alpha = N_A \nu \Delta \varepsilon, \tag{9}$$

we can write

$$\Delta \bar{G}_m = RT(x_1 \ln x_1 + x_2 \ln x_2) + \alpha x_1 x_2 \tag{10}$$

and

$$\Delta G_m = RT(n_1 \ln x_1 + n_2 \ln x_2) + \alpha n x_1 x_2. \tag{11}$$

Now we introduce excess quantities of mixing according to Equation 1.1.3-28:

$$\Delta \bar{G}_{m} = \Delta \bar{G}_{m,id} + \Delta \bar{G}_{m,ex} \tag{12}$$

(see Equation 1.1.3-15),

$$\Delta \bar{G}_{m,ex} = \alpha x_1 x_2 = \Delta H_m. \tag{13}$$

It follows from Equations 11 and 1.1.1-23 that

$$\Delta \mu_1 = RT \ln(1 - x_2) + \alpha x_2^2, \tag{14}$$

$$\Delta \mu_2 = RT \ln x_2 + \alpha (1 - x_2)^2. \tag{15}$$

Differentiating expression 14 leads to

$$\frac{\partial \Delta \mu_1}{\partial x_2} = -\frac{RT}{1 - x_2} + 2\alpha x_2,\tag{16}$$

and the solution stability condition (Equation 1.1.2-54, see also Equation 1.1.3-21) reduces to

$$\frac{2\alpha}{RT} < \frac{1}{x_2(1-x_2)},\tag{17}$$

and for the spinodal one has

$$\frac{2\alpha}{RT} = \frac{1}{x_{2,sp}(1 - x_{2,sp})}.$$
(18)

In the case of a two-component system ($\nu = 2$), the determinants D_G (Equation 1.2-58) and D'_G (see Equations 1.2-58,-59) degenerate to

$$\frac{\partial^2 G}{\partial x_1^2}$$
 or $\frac{\partial^2 \Delta G_m}{\partial x_1^2}$ (19)

1.3.1. Liquid-liquid separation

and

$$\frac{\partial^3 \Delta \tilde{G}_m}{\partial x_1^3}.$$
(20)

Within the limits of the regular solution model (Equation 10) the critical phase equations 1.2-60,-61 (here concerning only the critical point) look as

$$\frac{2\alpha}{RT_c} = \frac{1}{x_{2,c}(1-x_{2,c})} \quad \text{and} \quad \frac{2\alpha}{RT_c} = \frac{1}{(1-x_{2,c})^2},$$
(21)

whence

$$x_{2,c} = 0.5,$$
 (22)

and

$$\Gamma_c = \frac{\alpha}{2R}.$$
(23)

When $T > T_c$, the stability condition (Equation 17) is fulfilled at any x_2 . When $T < T_c$, the solution is stable only within the ranges $x_2 < x_{2spl}$ and $x_2 > x_{2spll}$, where x_{2spl} and x_{2spll} are the roots of the quadratic equation 18

$$x_{2spI} = \frac{1}{2} - \sqrt{\frac{\alpha - 2RT}{4\alpha}},\tag{24}$$

$$x_{2spII} = \frac{1}{2} + \sqrt{\frac{\alpha - 2RT}{4\alpha}}.$$
(25)

Correspondingly, when $T < T_c$, the function $\Delta \bar{G}_m = x_1 \Delta \mu_1 + x_2 \Delta \mu_2$ is convex within the ranges $x_2 < x_{2spl}$ and $x_2 > x_{2spll} (\partial^2 \Delta \bar{G}_m / \partial x_2^2 > 0)$ and concave over $x_{2spl} < x_2 < x_{2spll} (\partial^2 \Delta \bar{G}_m / \partial x_2^2 < 0)$ (see Figure 1.5b).

The set of x_{2spI} and x_{2spII} at different T is the spinodal (sp in Figure 1.5c). The binodal is defined using the conditions

$$\Delta \mu_{1I} = \Delta \mu_{1II},\tag{26}$$

$$\Delta \mu_{2I} = \Delta \mu_{2II} \tag{27}$$

(see Equation 1.2-8).

We can rewrite the equality condition of the chemical potentials, taking Equations 14 and 15 into account

$$RT\ln(1 - x_{2I}) + \alpha x_{2I}^2 = RT\ln(1 - x_{2II}) + \alpha x_{2II}^2,$$
(28)

$$RT \ln x_{2I} + \alpha (1 - x_{2I})^2 = RT \ln x_{2II} + \alpha (1 - x_{2II})^2.$$
⁽²⁹⁾

As the ΔG_m vs x_2 plot is symmetrical about the axis $x_2 = x_{2c} = 0.5$,

$$x_{2I} = 1 - x_{2II},\tag{30}$$



Figure 1.5. Concentration dependence of the chemical potential of mixing $\Delta \mu_1/RT$ (a), the molar Gibbs potential of mixing $\Delta \bar{G}_m/RT$ (b) for regular mixtures with α/RT (the digits at the curves) = 3, $2\frac{1}{2}$, 2, 1 (endothermic mixtures), 0 (ideal mixture), -1 (exothermic mixture). μ_1 stands for $\partial \Delta \mu_i/\partial x_j$. State diagram (c): bi—binodal, sp—spinodal, C—critical point. $\alpha/RTc = 2$ at $T = T_c$

and Equations 28 and 29 are equivalent. Substituting x_{21} from Equation 30 into Equation 28, we obtain

$$\ln \frac{x_{2II}}{1 - x_{2II}} = \frac{\alpha}{RT} (2x_{2II} - 1). \tag{31}$$

With a new variable

$$y = 2x_{2II} - 1, (32)$$

it looks as

$$\ln\frac{1+y}{1-y} = \frac{\alpha}{RT}y,\tag{33}$$

which is simply solved numerically (or graphically, see Figure 1.6). Eg. at $\alpha/RT = 3$,



Figure 1.6. Schematic solution of Equation 1.3-33 for $\alpha/RT = 2.5$ and 3, $y = 2x_{211} - 1$

y = 0.86 and $x_{2II} = 0.93$ (Figure 1.5).

The value of x_{21} is calculated using Equation 30. The functions so obtained $T(x_{21})$ and $T(x_{211})$ at $x_{21} \leq 0.5$ and $x_{211} > 0.5$, respectively, form the left-hand and right-hand branches of the binodal (see Figure 1.5c). According to Equations 1.1.1-46,-47 and

conditions 26 and 27, the tangent lines to the curve $\Delta G_m(x_2)$ coincide at the points x_{21} and x_{211} , cutting off the same intercepts on the ordinate axes:

$$\Delta\mu_{1I}(x_{2I}) = \Delta\mu_{1II}(x_{2II}) \tag{34}$$

at the left and

$$\Delta\mu_{2I}(x_{2I}) = \Delta\mu_{2II}(x_{2II}) \tag{35}$$

at the right (see Figure 1.5b for $\alpha/RT = 3$). The values x_{2spI} and x_{2spII} correspond to the inflection points of the curve $\Delta \bar{G}_m(x_2)$:

$$\frac{\partial^2 \Delta \bar{G}_m}{\partial x_2^2} = 0.$$

Figure 1.5a shows that $\partial \Delta \mu_i / \partial x_i > 0$ and $\partial \Delta \mu_i / \partial x_j < 0$ over the stability range and that it is vice versa within the absolutely unstable range.

The x_2 dependence of $\Delta \mu_1$ (provided that there exists a region of liquid-liquid phase separation) has as characteristic a shape as the *P* vs \bar{V} dependence for a one-component system within the two-phase region (cf. Figures 1.5 and 1.4), which reveals a general character of any {thermodynamic force}—{thermodynamic coordinate} dependence in a two-phase equilibrium.

The state diagram (Figure 1.5c) indicates the stability of a one-phase solution **outside** the binodal and the absolute unstability of any solution **inside** the spinodal. There is a region of metastable state between the binodal and spinodal.

When the critical point is a maximum on the binodal (and also on the spinodal), as in Figure 1.5c, it is called **upper critical solution temperature** (UCST). In the case of systems, where phase separation occurs on an increase in temperature, the critical point corresponds to a binodal (and spinodal) minimum and is referred to as **lower critical solution temperature** (LCST).

Within the framework of the model under consideration, at $T > T_c$ the reduced osmotic pressure (see Equations 1.2–17 and 14) is expressed as

$$\frac{\pi}{RTc_2} \cong \frac{1}{M_2} + \frac{\alpha \bar{V}_{01}}{RTM_2^2} c_2 + \cdots .$$
(36)

Therefore, in the virial expansion of osmotic pressure

$$\frac{\pi}{RTc_2} = \mathcal{A}_1 + \mathcal{A}_2c_2 + \mathcal{A}_3c_2^2 + \cdots, \qquad (37)$$

for the second virial coefficient we obtain

$$\mathcal{A}_2 = \frac{\alpha}{RT} \cdot \frac{V_{01}}{M_2^2}.$$
(38)

If π/RTc_2 vs c_2 is plotted, both the molecular mass M_2 (from the intercept on the y-axis at $c_2 \to 0$) and the interaction constant α (from the slope) can be determined.

When there is no interaction, $\alpha = 0$ ($\Delta H_m = 0$), $\Delta G_{m,ex} = 0$ (see Equations 12 and 13) and Equation 36 reduces to the state equation for an ideal solution (Equation 1.2-29).

It seems to be relevant to consider the analogy between the values which characterize the properties of real solutions and gases.

Let us confine ourselves to the first two terms in Equation 37 and transform it, with the aid of Equation 36, to the form

$$\frac{\pi M_2}{RTc_2} = 1 + \mathcal{A}_2 M_2^2 \frac{c_2}{M_2},\tag{39}$$

where M_2/c_2 is the volume containing one mole of the solute (component 2). It follows that it is like the molar volume \bar{V} in the state equation for real gases (Equation 1.2-70). Certainly, π corresponds to P.¹ Then, correlation between Equations 1.2-70,-71 and Equation 39, in view of Equations 1.2-37,-38, leads to

$$\mathcal{A}_2 M_2^2 \sim B_2 \sim b \sim \frac{\beta_{ex} N_A}{2}$$

(see Equations 1.2-37, -38) and

$$\mathcal{A}_2 \sim \frac{\beta_{ex} N_A}{2M_2^2}.\tag{40}$$

We will now look more closely at the $T < T_c$ situation (Becker, 1938; Andreyev et al., 1974). Figure 1.7 presents a typical isotherm $\overline{G}(x_2)$ with the characteristic points of the binodal and spinodal marked as *biI*, *biII* and *spI*, *spII*.

Suppose that the configurative point has been moved from outside the binodal into the region between the binodal (x_{2I}) and spinodal (x_{2spI}) with the concentration $x_2 = x_{2,0}$ (the point D). The system is composed of n_1 moles of component 1 and of n_2 moles of component 2, so that $n_1 + n_2 = n$ and $x_{2,0} = n_2/n$. Further, assume that a fluctuation of composition spontaneously occurred in a certain local region and the concentration of component 2 became x'_2 there (Figure 1.7 and 1.8). Then, this concentration in the rest of the system is x''_2 . In terms of mole numbers, there are n' moles in the local region $(n' = n'_1 + n'_2; n'_2 = x'_2n')$ and n''_2 moles in the rest of the system $(n''_2 = (n - n')x''_2)$. As a result of such a fluctuation, the Gibbs potential varies by

$$\Delta G = G_2 - G_1.$$

If this value is positive, then the solution is stable (Table 1.1), but if it is negative, the solution is unstable and phase separation will occur. According to the accepted model,

$$\Delta G = G_2 - G_1 = n'\bar{G}(x_2') + (n - n')\bar{G}(x_2'') - n\bar{G}(x_{2,0}).$$
(41)

The total number of moles in the system remains constant,

$$n_2 = nx_{2,0} = n_2'' + n_2' = (n - n')x_2'' + n'x_2'.$$
(42)

Adding and subtracting $n'x_{2,0}$ to/from the right-hand side and some additional manipulations yield

$$x_{2,0} - x_2'' = \frac{n'(x_2' - x_{2,0})}{n - n'}.$$
(43)

¹However, this analogy is not complete



Figure 1.7. An isotherm of the average Gibbs molar potential for a two-component mixture at $T < T_c$



Figure 1.8. Schematic sketch of the appearance of a concentration fluctuation in solution As x_2'' is close to $x_{2,0}$, $\bar{G}(x_2'')$ can be expanded into a Taylor series near $x_{2,0}$ to the terms of 1st-order infinitesimal:

$$\bar{G}(x_2'') \cong \tilde{G}(x_{2,0}) + \left(\frac{\partial \bar{G}}{\partial x_2}\right)_0 (x_2'' - x_{2,0}) + \cdots$$

$$\tag{44}$$

This expression is substituted into Equation 41, and by simple transformations we get

$$\Delta G = n' \left[\bar{G}(x'_2) - \bar{G}(x_{2,0}) \right] + (n - n') \left(\frac{\partial \bar{G}}{\partial x_2} \right)_0 (x''_2 - x_{2,0}), \tag{45}$$

and, in view of Equation 43,

$$\Delta G = n' \left[\bar{G}(x'_2) - \bar{G}(x_{2,0}) \right] - n' \left(\frac{\partial \bar{G}}{\partial x_2} \right)_0 (x'_2 - x_{2,0}).$$
(46)

Figure 1.7 demonstrates that

$$BC = CD\left(\frac{\partial \bar{G}}{\partial x_2}\right)_0 = (x'_2 - x_{2,0})\left(\frac{\partial \bar{G}}{\partial x_2}\right)_0,\tag{47}$$

$$AC = \tilde{G}(x_2) - \bar{G}(x_{2,0}) \quad \text{and} \quad \Delta \bar{G} = \Delta G/n' = AC - BC = AB.$$
(48)

 $\Delta \bar{G} > 0$ when AC > BC, i.e. AB is **under** the curve $\bar{G}(x_2)$, and the solution is stable. As Figure 1.7 shows, this condition is met up to $x'_2 = x^*_2$ (where the tangent line to $\bar{G}(x_2)$) at $x_2 = x_{2,0}$ meets the curve $\bar{G}(x_2)$). If, however, $x'_2 > x^*_2$ in the fluctuation region (eg. $x'_2 = \tilde{x}_2$), then A'B' is situated **above** the curve $\bar{G}(x_2)$, |B'C'| > |A'C'| (Figure 1.7), and $\Delta \bar{G} < 0$ (Figure 1.9a), and a loss of the solution stability will occur. As illustrated in



Figure 1.9. ΔG variation as a result of a concentration fluctuation (a) in the metastable region, (b) in the unstable region

Figure 1.7, the line segment AB is always under the curve $\bar{G}(x_2)$ to a certain x_2^* at any $x_{2,0}$ concentration within the ranges $x_{2I} < x_2 < x_{2spI}$ and $x_{2spII} < x_2 < x_{2II}$. These ranges imply the solution stability to fluctuations less than $(x_2^* - x_{2,0})$ (more exactly, $(x_{2m}^* - x_{2,0})$, see Figure 1.9a) and the instability to fluctuations larger than the mentioned value. It is this property that is characteristic of the metastable state.

Let us discuss the case of as small fluctuations as those which permit $G(x'_2)$ to be represented as a Taylor series expansion near $x_{2,0}$ to the terms of 2nd-order infinitesimal

$$\bar{G}(x_2') \cong G(x_{2,0}) + \left(\frac{\partial \bar{G}}{\partial x_2}\right)_0 (x_2' - x_{2,0}) + \frac{1}{2} \left(\frac{\partial^2 \bar{G}}{\partial x_2^2}\right)_0 (x_2' - x_{2,0})^2 + \cdots$$
(49)

and

$$\bar{G}(x'_{2}) - \bar{G}(x_{2,0}) - \left(\frac{\partial \bar{G}}{\partial x_{2}}\right)_{0} (x'_{2} - x_{2,0}) \cong \frac{1}{2} \left(\frac{\partial^{2} \bar{G}}{\partial x_{2}^{2}}\right)_{0} (x'_{2} - x_{2,0})^{2}.$$
(50)

From Equation 46, in view of Equation 50, it follows that

$$\Delta \bar{G} \cong \frac{1}{2} \left(\frac{\partial^2 \dot{G}}{\partial x_2^2} \right)_0 (x_2' - x_{2,0})^2.$$
(51)

Thus, the sign of $\Delta \bar{G}$ is defined by that of $(\partial^2 \bar{G}/\partial x_2^2)_0$. When the curve $\bar{G}(x_2)$ is concave (i.e. $(\partial^2 \bar{G}/\partial x_2^2) < 0$ within $x_{2spI} < x_2 < x_{2spII}$), then $\Delta \bar{G} < 0$, which means the condition of solution instability even to small fluctuations (see Figure 1.9b). In the metastable and, later on, stable regions, $(\partial^2 \bar{G}/\partial x_2^2) > 0$ and $\Delta \bar{G} > 0$ (the curve $\bar{G}(x_2)$ is convex).

In the metastable region, the solution is stable to small fluctuations and unstable to large ones, as noted above.

Within $0 < x_2 < x_{2I}$ and $x_{2II} < x_2 < 1$, the solution is stable to any fluctuations; the tangent line to $\bar{G}(x_2)$ at any point never meets the curve, and the line segment AB is always under $\bar{G}(x_2)$ (see Figure 1.7), i.e. $\Delta \bar{G} > 0$ at any x_2 (Figure 1.10).



Figure 1.10. $\Delta \bar{G}$ variation as a result of a concentration fluctuation in solution (the stable region)

The above considerations are a relatively rough scheme of the initiation of new-phase particles. In particular, the change of the particle entropy owing to their Brownian motion is not taken into account. In view of this change one can conclude that a certain (and high) concentration of overcritical (with the peak value $x'_2 > x_{2,m}$, see Figure 1.9a) centres of the new phase is necessary for the phase transition to start.

More realistic models for the initiation and growth of new-phase particles are considered in the literature on phase transition kinetics.

The condition

$$\Delta \tilde{G}_m < 0 \tag{52}$$

is often adduced as the condition for component dissolution. However, in order to obtain a one-phase solution, condition 52 is necessary, but not sufficient. The necessary and sufficient condition for a one-phase solution to be obtained is represented by two inequalities:

$$\Delta G_m < 0 \quad \text{and} \quad \frac{\partial^2 \Delta \ddot{G}_m}{\partial x_2^2} > 0,$$
(53)

while the concentration range must lie outside the binodal $0 < x_2 < x_{2I}$ or $x_{2II} < x_2 < 1$. Figure 1.5 illustrates this statement (see the function $\Delta \bar{G}_m/RT$ at $\alpha/RT = 2.5$). Other models of liquid-liquid mixtures can be found elsewhere (Read et al., 1977).

1.3.2. Liquid-crystal separation

Only one simple case of the binary system (A + B) with eutectic crystallization and no region of the mixed crystal existence (Daniels and Alberty, 1975) will be considered here as an example of liquid-crystal phase separation (see Figure 1.11). This kind of phase separation is of special importance for polymer systems as most typical.

The wide variety of the state diagrams of crystal and mixed (semicrystalline) equilibria for low-molecular compounds have been fully considered in the literature (Kogan, 1968; Shpil'rain and Kassel'man, 1977; Vol and Kagan, 1979).

Attention should be paid to the fact that, according to Figure 1.11, crystallization proceeds under conditions of solution thermodynamic stability to liquid-liquid separation: the criteria $\Delta \bar{G}_m < 0$ and $\partial^2 \Delta \bar{G}_m / \partial x_2^2 > 0$ are realized over the whole range of temperatures and concentrations.

The thermodynamic stimulus for crystallization (liquid-crystal phase separation) is the equality of the chemical potentials of each component in the crystal phase $\bar{G}_{0i,cr}$ and in the solution $\bar{G}_{i,s}$ at a certain temperature T_i and concentration x_{il} :

$$\bar{G}_{0i,cr}(T_l) = \bar{G}_{i,s}(T_l, x_{il}).$$
(54)

The locus of configurative points on the state diagram in the temperature-concentration coordinates which meet condition 54 defines a **liquidus** curve, Figure 1.11a.

If the configurative point is at an infinitely small distance from the liquidus curve toward the solution existence region, condition 54 is not satisfied while the solution is obviously stable to amorphous separation. Thus, the closeness of the liquidus manifests itself in no case (cf. Figures 1.11b and c).

The absence of specific precrystallization phenomena in a one-component liquid is the subject of a number of papers (Skripov and Baydakov, 1972; Skripov, 1975).



Figure 1.11. State diagram of the binary mixture A + B with a liquid-crystal phase separation region of the eutectic type in the ab sence of a mixed crystal region. The dashed line denotes the liquid-liquid phase separation region (a). Composition dependence of the average molar Gibbs potential (b- $\tilde{G}_{0i,cr}, \ \bar{G}_{0i,l}$ denote the ſ). molar Gibbs potential of the ith component in its individual crystal and liquid states; $G_{i,s}(x_B)$ stands for the partial molar Gibbs potential of the *i*th component in solution with the concentration x_B (Daniels and Alberty, 1975) [F.Daniels and R.A.Alberty. Physical Chemistry. Copyright © 1975 by Wiley. Reprinted by permission of John Wiley & Sons, Inc.]

1.4. Stability and fluctuations

We will consider fluctuations in a system as such its states in which the fundamental Gibbs equation 1.1.1-3 remains valid, but the equilibrium with the environment (thermostat) is disturbed. According to the Boltzman equation, the total entropy both of the system S and of the thermostat S^* is

$$S + S^* = k \ln W,\tag{1}$$

where W is the statistical weight of the system and the thermostat as a whole, i.e. the number of their microstates. From Equation 1 it follows that

$$W = \exp\left(\frac{S+S^*}{k}\right). \tag{2}$$

According to Einstein (1910), we write the probability of a fluctuation of the system Ω as

$$\Omega \sim \exp\frac{\Delta S + \Delta S^*}{k},\tag{3}$$

with ΔS and ΔS^* to denote the entropy deviations of the system and of the thermostat, respectively, from their equilibrium values.

As we presume fluctuations to be small, it permits us to keep only the second-order infinitesimal terms in the variational series expansion of ΔS (see Equation 1.1.1-2)

$$\Delta S = \frac{1}{T} \,\delta U + \frac{P}{T} \,\delta V - \sum_{i=1}^{\nu} \frac{\mu_i}{T} \,\delta n_i + \frac{1}{2} \delta^2 S + \cdots , \qquad (4)$$

where

$$\delta^2 S = \delta \left(\frac{1}{T}\right) \, \delta U + \delta \left(\frac{P}{T}\right) \, \delta V - \sum_{i=1}^{\nu} \delta \left(\frac{\mu_i}{T}\right) \, \delta n_i. \tag{5}$$

The thermostat being much larger than the system, the fluctuations in the latter in no case affect the thermostat intensive parameters and

$$\Delta S^* = \frac{1}{T} \,\delta U^* + \frac{P}{T} \,\delta V^* - \sum_{i=1}^{\nu} \frac{\mu_i}{T} \,\delta n_i^*. \tag{6}$$

The use of the equalities $\delta U^* = -\delta U$, $\delta V^* = -\delta V$, $\delta n_i^* = -\delta n_i$ $(i = 1, ..., \nu)$ reduces the first-order terms on substituting Equations 4 and 6 into Equation 3 and we get

$$\Omega \sim \exp \frac{\delta^2 S}{2k}.\tag{7}$$

It is obvious that the greater the deviation of the system from its equilibrium state, the less is the probability of such fluctuations, given equilibrium is stable. From Equation 7, it means that

$$\delta^2 S < 0 \tag{8}$$
is in full accordance with Equation 1.1.2-16. Hence it follows that one can obtain the same results which were deduced in Subsection 1.1.2 on the basis of Equation 1.1.2-12; in particular,

$$\frac{c_p}{T} > 0 \tag{9}$$

(the thermal stability condition, Equation 1.1.2 39),

$$\chi_{\tau} > 0 \quad \text{or} \quad \left(\frac{\partial V}{\partial P}\right)_{T} < 0 \tag{10}$$

(the mechanical stability condition, Equation 1.1.2-40),

$$\left(\frac{\partial^2 \hat{G}}{\partial x_2^2}\right)_{T,P} > 0 \tag{11}$$

(the diffusional stability condition, Equation 1.1.2-47),

$$\left(\frac{\partial\mu_2}{\partial x_2}\right)_{T,P} > 0 \tag{12}$$

(see Equation 1.1.2-53),

$$\left(\frac{\partial \mu_1}{\partial x_2}\right)_{T,P} < 0 \tag{13}$$

(see Equation 1.1.2 54).

Let X be the difference between any fluctuating thermodynamic parameter and its mean (equilibrium) value. Eg. $X = T - \langle T \rangle$, whence $\langle X \rangle = 0$. The probability of X taking a value within [X, X + dX] is expressed by Equation 7, but the arbitrary second-order variation $\delta^2 S$ has to be replaced by a second-order derivative of S with respect to X, which transforms Equation 7 into

$$\Omega(X) dX = C \exp\left(-\frac{\alpha X^2}{2}\right) dX,$$
(14)

where

$$\alpha = -\frac{1}{k} \left(\frac{\partial^2 S}{\partial X^2} \right)_{X=0} > 0.$$
(15)

The normalization condition

$$\int_{-\infty}^{\infty} \Omega(X) \, dX = 1$$

gives us

$$C = \left(\frac{\alpha}{2\pi}\right)^{1/2} \tag{16}$$

1.4. Stability and fluctuations

and, therefore,

$$\Omega(X) dX = \left(\frac{\alpha}{2\pi}\right)^{1/2} \exp\left(-\frac{\alpha X^2}{2}\right) dX,$$
(17)

which is the well-known Gaussian distribution.

One can calculate the mean-square fluctuation value using the conventional method:

$$\langle X^2 \rangle = \left(\frac{\alpha}{2\pi}\right)^{1/2} \int_{-\infty}^{\infty} X^2 \exp\left(-\frac{\alpha X^2}{2}\right) dX = \frac{1}{\alpha}$$
 (18)

and rewrite Equation 17 as

$$\Omega(X) dX = \left(2\pi \left\langle X^2 \right\rangle\right)^{-1/2} \exp\left(-\frac{\alpha X^2}{2 \left\langle X^2 \right\rangle}\right) dX.$$
(19)

Let us calculate the fluctuation probabilities for some specific thermodynamic quantities (Landau and Lifshitz, 1964; Münster, 1969; Anselm, 1973; Kluge and Neugebauer, 1976). Eg. for the isothermal volume fluctuation $X = \Delta V = V - \langle V \rangle$, dX = dV, since $d\langle V \rangle = 0$. It follows from Equation 1.1.1-2 that

$$\left(\frac{\partial S}{\partial V}\right)_{T,n_1} = \frac{P}{T} \quad \text{and} \quad \left(\frac{\partial^2 S}{\partial V^2}\right)_{T,n_1} = \frac{1}{T} \left(\frac{\partial P}{\partial V}\right)_{T,n_1}.$$
(20)

Then

$$\Omega(V) \, dV = \Omega_0 \exp\left[\left(\frac{\partial P}{\partial V}\right)_{T,n_t} \frac{(\Delta V)^2}{2kT}\right] \, dV. \tag{21}$$

The relationship obtained defines the probability that the system has a volume within [V, V + dV], where V differs from its equilibrium value $\langle V \rangle$ by ΔV .

Equation 21 can be applied to any part of the system (a subsystem) if only this part contains a large enough number of molecules to provide the validity of the Gibbs fundamental equation. In this case, the other part of the system relates to the thermostat.

Formula 21 readily illustrates the mechanical stability condition (Equation 10): the system is in stable equilibrium if volume fluctuations are small and decrease substantially with increasing ΔV . This is realized when the exponent in Equation 21 is negative. As $(\Delta V)^2$, k, T are always positive, then

$$\left(\frac{\partial P}{\partial V}\right)_{T,n_{1}} < 0, \tag{22}$$

which is identical to the thermodynamic condition of mechanical stability (Equation 10). Combining Equations 17, 18, and 20, we can write

$$\left\langle (\Delta V)^2 \right\rangle = -kT \left(\frac{\partial V}{\partial P} \right)_{T,n_t}.$$
(23)

Represent it as

$$\left\langle \left(\Delta \frac{V}{N}\right)^2 \right\rangle = -\frac{kT}{N^2} \left(\frac{\partial V}{\partial P}\right)_T,\tag{24}$$

where N is the number of molecules in the system.

In the case of constancy of the volume which fluctuations occur in (Landau and Lifshitz, 1968), it follows that

$$\Delta \frac{V}{N} = V \Delta \frac{1}{N} = -\frac{V}{N^2} \Delta N \tag{25}$$

and

$$\left\langle (\Delta N)^2 \right\rangle = -\frac{kTN^2}{V^2} \left(\frac{\partial V}{\partial P}\right)_T.$$
(26)

For an ideal gas

$$PV = nRT = \frac{N}{N_A} N_A kT = NkT$$
⁽²⁷⁾

and

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{NkT}{P^2} = -\frac{V^2}{NkT}.$$
(28)

Substituting Equation 28 into Equation 26 yields

$$\left\langle (\Delta N)^2 \right\rangle = N. \tag{29}$$

Now we are able to write an expression for the mean-square fluctuations of the second component mole fraction x_2 in a binary solution at T, P, n = const (see Equations 15 and 18):

$$\left\langle (\Delta x_2)^2 \right\rangle = -k \left/ \left(\frac{\partial^2 S}{\partial x_2^2} \right)_{T,P,n} \right.$$
 (30)

From Equations 1.1.1-2 and 1.1.1-43, it follows that

$$\frac{\partial S}{\partial x_2} = n \frac{\partial \tilde{S}}{\partial x_2} = n(\bar{S}_2 - \bar{S}_1) = \frac{n}{T}(\mu_1 - \mu_2).$$
(31)

The second derivative of S, in view of Equation 1.1.2-50, is expressed as

$$\frac{\partial^2 S}{\partial x_2^2} = \frac{n}{T} \left(\frac{\partial \mu_1}{x_2} - \frac{\partial \mu_2}{x_2} \right) = -\frac{n}{T} \left(\frac{\partial^2 \bar{G}}{\partial x_2^2} \right)_{T,P}.$$
(32)

Finally, from Equation 30, using Equations 1.1.2-51,-52, we get

$$\left\langle (\Delta x_2)^2 \right\rangle = -\frac{kT}{n\left(\frac{\partial^2 \bar{G}}{\partial x_2^2}\right)_{T,P}} = \frac{kT}{\frac{n}{x_1}\left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P}} = -\frac{kT}{\frac{n}{x_2}\left(\frac{\partial \mu_1}{\partial x_2}\right)_{T,P}}.$$
(33)

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The equation obtained should be followed by inequalities 11-13 (which are identical to the diffusional stability conditions from Subsection 1.1.2) to allow the solution stability condition (the decrease in the probability of composition fluctuations as the system deviates from equilibrium) to be true.

The entropy being an extensive quantity, the probability of fluctuation of a given magnitude rises sharply when the system size diminishes.

In a more general way, the problem of stability and fluctuations is expressed on the basis of the concepts of nonequilibrium thermodynamics (Glansdorff and Prigogine, 1971; Nicolis and Prigogine, 1977; Prigogine, 1978). In accordance with this, the entropy differential in Equation 1.1.2 1 is expressed as the sum of two summands

$$dS = d_e S + d_1 S, \tag{34}$$

where $d_e S$ is the entropy flux caused by energy and matter exchange with the environment $(d_e S = dQ/T)$, and $d_i S$ is the entropy production within the system due to irreversible processes such as diffusion, thermal conduction, chemical reactions, etc.

From the second law of thermodynamics, we have

$$d_c S = 0 \quad \text{and} \quad dS = d_1 S \ge 0 \tag{35}$$

for an isolated system. Letting dt be the time to produce the entropy d_iS , we can obtain the entropy production per unit time:

$$P = \frac{d_i S}{dt} \ge 0. \tag{36}$$

When expanding the entropy expression into a Taylor series, keeping the second-order infinitesimal terms, and differentiating with respect to t, it can be proved (Glansdorff and Prigogine, 1971) that

$$\frac{1}{2}\frac{\partial}{\partial t}(\delta^2 S)_0 = P \ge 0 \tag{37}$$

holds near equilibrium (the subscript '0').

While inequality 35 is the evolution criterion for systems near equilibrium, the reverse inequality, together with Equation 37, can be regarded as a generalized stability condition:

$$(\delta^2 S)_0 \le 0,\tag{38}$$

$$\frac{\partial}{\partial t} (\delta^2 S)_0 \ge 0. \tag{39}$$

On the basis of Equations 7, 38, and 39, a statement is formulated for stable systems: the more the system deviation due to spontaneous fluctuations of any thermodynamic parameter is away of equilibrium, the less such deviation is probable (see Equation 7) and the fluctuations, that have caused this deviation, will decrease (resolve) with time (Figure 12).



Figure 1.12. Fluctuation disappearance with time in the solution stability region (Prigogine, 1978)

1.5. Loss of stability and phase transitions (phase separation)

1.5.1. Types of phase transition

Under certain conditions the phase composition of a system may change as a result of loss of stability. Such a process of the system structure being reorganized is called **phase transition**, or, if the number of phases increases, **phase separation**.

There are different kinds of phase transitions (Figures 1.13-1.15). As an example, let us consider the diagram state of a binary system with liquid-liquid phase separation (Figure 1.13). Along the line $A_1 \rightarrow A_2$ the system can be driven to the metastable region where the initial phase will be remaining for a certain induction period τ : the system is "waiting" for overcritical fluctuations which the initial state is instable to. During this period, the initial phase retains all its specific properties, namely, the thermodynamic potentials and its derivatives.

There is another way, namely, $B_1 \rightarrow B_2$ (through the critical point) for the configurative point, with no induction period: the system immediately finds itself to be in the region of absolute instability. The final state (stable equilibrium) is the same in both the cases, two phases with their concentrations x_{2I} and x_{2II} and different volumes (due to the difference in the initial concentrations) exist.

In the former case, the transition is termed first-order phase transition (via the metastable state) whereas in the latter case it is called continuous transition.

Here are more rigorous definitions: if the first partial derivatives of the thermodynamic potentials G and F with respect to their natural variables have breaks during transition, it is called a **first-order phase transition**. If the mentioned derivatives remain continuous but some higher ones have their breaks (in particular, become infinite), we speak of **high**-



Figure 1.13. State diagram of a binary system with liquid-liquid amorphous separation: a presents the binodal (solid curve) and spinodal (dashed curve). The temperature dependences of the correlation length of the concentration fluctuation ξ_k (at $T > T_c$) and of the order parameter Δx_2 (at $T < T_c$) are described by power functions; b shows the average molar Gibbs potential at $T = T_1$ (bi, sp are points on the binodal and spinodal, respectively)

Figure 1.14. State diagram of a magnetic: a presents the projection of the surface f(H, M, T) = 0 on the plane H = 0; b is the dependence of the Helmholtz potential F(M, T) - F(0, T) on the order parameter (magnetization) M in zero field (H = 0). The temperature dependences of the correlation length of the fluctuations of the order parameter ξ_M (at $T > T_c$) and of the order parameter M (at $T < T_c$) are described by power functions



Figure 1.15. State diagram of a gas-liquid system: the projection of the surface $f(P, \varrho, T) = 0$ on the plane P = 0. Temperature dependences of the correlation length of fluctuations of density ξ_{ϱ} $(T > T_c)$ and of an order parameter analogue $\Delta \varrho = \varrho_l - \varrho_g$ $(T < T_c)$ are described by power functions

order phase transitions, or continuous transitions, see Figure 1.16 (Brout, 1965; Fisher, 1965, 1967; Stanley, 1971; Bruce and Cowley, 1981).

1.5.2. Order parameter

In order to describe such phenomena quantitatively, an additional system parameter varying with phase transitions should be introduced. As these transitions are usually accompanied by **changes in symmetry** (from the structural point of view), the so-called **order parameter** Q is used to characterize these changes (Landau and Lifshitz, 1964; Brout, 1965; Patashinski and Pokrovski, 1979). Eg. in case of a ferromagnetic in a zero field (H = 0) the spontaneous magnetization serves as the order parameter (see Figure 1.14) (Equation 1.1.1-56)

$$M = -\left(\frac{\partial G}{\partial H}\right)_{T,H\to 0},\tag{1}$$



Figure 1.16. Variations in the thermodynamic potentials and their derivatives during phase transitions

where H is the magnetic field strength.

There are several cases (liquid-liquid, Figure 1.13; liquid-gas, Figure 1.15) with, strictly speaking, no changes in symmetry. Here we can formally choose the difference between the component concentrations in the coexisting phases $\Delta x_2 = x_{2II} - x_{2I}$ or the density difference between the liquid and gas phases $\Delta \varrho = \varrho_I - \varrho_g$ as order parameter (Brout, 1965). Being equal to zero on one side of phase transition (see Figures 1.13-1.15: $\Delta x_2 = 0$, M = 0, and $\Delta \varrho = 0$ when $T > T_c$) is a usual requirement to the order parameter.

The dependences of G and F on the order parameter are characteristic of phase transition of both kinds, and are often used to identify the type of transition.



In Figures 1.17 and 1.18 (Umanski and Skakov, 1978; Sonin, 1983), you can see a

Figure 1.17. Dependence of the Gibbs molar potential G on the order parameter Q during first-order phase transition (Umanski and Skakov, 1978)

sketch of G = G(Q) for the hypothetical transition β -phase $\rightarrow \alpha$ -phase of both kinds. In Figure 1.17, the Gibbs potential originates from its value for the initial phase β at any temperature. It is presumed that $T_1 > T_2 > \ldots T_6$.

Let us discuss the dependence G = G(Q) (Figure 1.17). At T_1 and T_2 , the β -phase is thermodynamically stable, i.e. it is stable with respect to order parameter fluctuations of any magnitude. At $T_3 = T_{11}$, the Gibbs potentials of both the phases are the same (cf. Figure 1.16a), but there is a certain potential barrier for the transition $\beta \rightarrow \alpha$, and the metastable state of β is very probable, to recover from which a sufficient concentration of large enough fluctuation regions of the α -phase is necessary.

Small fluctuations occur quite frequently (see section 1.4), but formation of new-phase particles is associated with an input of energy to form the interface: in case of small (undercritical) particles (a large enough surface area/volume ratio), this input is not compensated by energy decrease during the phase transition. Such is the nature of the potential barrier (cf. Figure 1.9a). So, the β -phase is stable to small fluctuations of the



Figure 1.18. Dependence of the Gibbs molar potential \overline{G} on the order parameter Q during continuous phase transition (Umanski and Skakov, 1978)

order parameter.

It is important that with first-order phase transitions the thermodynamic potentials of **both** the phases are **defined** on both the sides of transition (see Figure 1.16ad), with the potential of one phase having a lower value (the equilibrium state) and that of the other phase having a higher value (the metastable state).

In the metastable region, the potentials G and F of the initial phase "invade the foreign territory" (see the dashed lines in Figure 1.16ad) and have no singularities at the transition (equilibrium) point itself. Their values on the "foreign field" correspond to the natural interpolation from their "own field".

During first-order phase transitions, the configurative point moves (with a certain rate, either following a certain time program or at once) to a new position where the parameter

T or P (see Figure 1.16ad) takes on a value differing from that of equilibrium $(T_{t1} \text{ or } P_{t1})$. The differences $(T_{t1} - T)$ or $(T - T_{t1})$, $(P_{t1} - P)$ or $(P - P_{t1})$ define the degree of overcooling/overheating overstretching/overshrinking, respectively.

In the case of conditionally-instantaneous shift of the configurative point to its new position, the thermodynamic potential takes on a value characteristic for the old phase and keeps it (more exactly, does not take on the equilibrium value) for a certain period called an induction period τ .

The duration of τ depends, in particular, on how distant from T_{t1} the configurative point is, i.e. on the degree of overheating $(T - T_{t1})$ or overcooling $(T_{t1} - T)$. Problems associated with the induction period are discussed in the literature on phase transformation kinetics.

The real delay in potential change causes a delay in the appearance of a new phase, called **hysteresis**, which is a most important criterion of first-order transitions.

It should be noted that the system's response always lags behind the external effects or condition changes that are not necessarily related to phase transitions. These delays are defined with **relaxation time**. As a rule, the more gradually external conditions vary, the less is the relaxation time. However, some first-order phase transitions show no decrease in the delays mentioned while slowing up the external condition change. It is in such cases that hysteresis and hysteresis phenomena are spoken of. Therefore, the manifestation of hysteresis is characteristic of first-order transitions (Brout, 1965; White and Geballe, 1979).

At $T_5 = T$ (Figure 1.17), there is no potential barrier and the β -phase is absolutely unstable. When $T \leq T_5$, the so-called barrierless (not going through nuclei) transition occurs (cf. Figure 1.10).

The presence of two minima of G (or F) as functions of the order parameter is the main distinguishing feature of first-order phase transitions.

Different details, of course, depend on a specific system. Currently, the question is discussed as to whether barrierless transition is possible during crystallization.

In view of the factors determining the behaviour of enormous ensembles of molecules, namely, intermolecular interactions and thermal motion, one can expect first-order phase transitions to be universal in one-component systems. In such cases, the isotherm enclosing three states of aggregation, has to have the form as in Figure 1.19. Four points corresponding to the thermodynamic stability boundary $\partial P/\partial \bar{V} = 0$: A, B, C, D are marked on this isotherm. However, no critical point of the liquid-crystal transition has been discovered in spite of numerous attempts.

Geometrical analysis of the state equation surfaces of liquid-vapour and crystal-liquid equilibria (Equation 1.2-33, Figures 1.20 and 1.21), analysis of experimental data and computer simulation results lead to the conclusion¹ of that there is no spinodal of the liquid \rightarrow crystal phase transition while the spinodal of crystal \rightarrow liquid transition does exist (Skripov, 1975; Skripov and Koverda, 1984). Consequently, the liquid crystallization occurs only through the formation of critical nuclei (through the metastable state) and no barrierless transition is possible.

At the same time, Roytburd (1975) discusses the reality of the barrierless transition during martensite-type crystallization (see also: Umanski and Skakov, 1978).

¹This conclusion seems questionable for stretchable melts and polymeric solutions. Editor's note



Figure 1.19. An isotherm of a one-component system with four boundaries of thermodynamic stability (Skripov, 1975)

In the case of the continuous transition $\beta \leftrightarrow \alpha$ (Figure 1.18), the temperature of absolute instability and that of phase transition T_{teon} are the same. The presence of only one minimum of G (or F) as a function of the order parameter at any temperature near the transition point is a specific feature of continuous phase transitions. Therefore, the thermodynamic potentials of each phase are not defined on the other side (on eutering the "foreign field") in principle; therefore, there are no phase equilibria and metastable states. The appearance of system properties characteristic for the new phase takes place all over the bulk simultaneously and no special input of energy to form the interface is required. The continuous transition is prepared in the initial phase with T approaching T_{teon} by the scale growth of correlation of fluctuations of thermodynamic quantities and the order parameter that show specific properties of the new phase.

There are real singularities of G and F in the continuous transition point—their second derivatives with respect to the corresponding variables undergo a first-order break (a finite step) or a second order one $(\rightarrow \infty)$, that makes any interpolation to the "foreign field" meaningless.



Figure 1.20. Surface defined by Equation 1.2-34 to characterize the gas and liquid states of a one-component system in the coordinates $P \ V-T$ (a). Surface defined by Equation 1.2-33 for the crystal and liquid states (b). ACD is the binodal of liquid-vapour phase equilibria; BCC is the spinodal of liquid-vapour phase transition; *Ee* and *Ff* are fragments of the binodal of the crystal-liquid phase equilibria; Kj is the spinodal of the crystal-liquid phase transition; *GAD* is the straight line of three-phase (vapour-liquidcrystal) equilibrium at the triple point (Skripov and Koverda, 1984)

1.5.3. Critical indices

It is interesting that the main thermodynamic functions can be approximated near the transition point as power functions

$$f(\varepsilon) \sim \varepsilon^{\lambda}$$
 and $f(\varepsilon) \sim (-\varepsilon)^{\lambda'}$, (2)

where

$$\varepsilon \equiv \frac{T - T_c}{T_c},\tag{3}$$



Figure 1.21. State diagram of a one-component system in the coordinates P-V: ACD is the binodal of liquid-vapour phase equilibria, Ee and Ff are portions of the binodal of crystal-liquid phase equilibria, GL and DM are portions of the binodal of crystal-vapour phase equilibria (no corresponding surface defined by Equation 1.2-33 is shown in Figure 1.20), BCC is the spinodal of the liquid-vapour phase transition, Kj is the spinodal of the crystal-liquid phase transition, GAD is the straight line of three-phase (vapour-liquid-crystal) equilibrium at the triple point (Kirilin et al., 1983; Skripov and Koverda, 1984)

 T_c being the phase transition temperature or the critical temperature. The dimensionless parameter ε characterizes the temperature distance of the system from the phase transition or critical temperature. The indices λ and λ' are called **critical indices** and vary within 0.3...0.5 in most cases.

More generally,

$$f(\varepsilon) = B_0 \varepsilon^{\lambda} (1 + B \varepsilon^x + \cdots), \tag{4}$$

 B_0 and B being constants, and x > 0. Therefore,

$$\lambda \equiv \lim_{\varepsilon \to 0} \frac{\ln f(\varepsilon)}{\ln \varepsilon}.$$
(5)

The interest in critical indices is caused by their easiness of experimental determination from the plot $\ln f(\varepsilon)$ vs $\ln \varepsilon$. On the other hand, the modern theories of phase transitions

allow the determination of relationships among different critical indices that makes it possible to describe a system near its points of phase transitions more fully (White and Geballe, 1979).

Table 1.2 comprises some critical indices of a number of functions for three systems. The behaviour of $c_V = f(T)$ on both sides from the phase transition point (with the critical indices α and α') is shown in Figures 1.16c,h. The isothermal compressibility χ_{τ} behaves similarly. While approaching the critical point, $\varepsilon \to 0$ (in the general case, while approaching the spinodal), $(\partial P/\partial V)_T \to 0$ (see Figure 1.4). Therefore, from Equation 1.1.2-41, $\chi_{\tau} \to \infty$, which is represented by the formulae in Table 1.2 (the critical indices γ' and γ correspond to the sides $T < T_c$ and $T > T_c$, respectively).

In the region $T > T_c$, the order parameter is equal to zero only on the average, but its local value differs from zero owing to the fluctuations. The characteristic magnitude of such fluctuations (the correlation length ξ) obeys Equations 2-4 with the critical indices ν and ν' as well (see Table 1.2).

When approaching the critical points in a binary system (generally, approaching the spinodal), $\partial \mu_2 / \partial x_2 \to 0$. From Equation 1.4-33, the mean square concentration fluctuation $\langle (\Delta x_2) \rangle^2 \to \infty$. In terms of the order parameter, it means $\xi_k \to \infty$ in accordance with $\xi_k \sim \varepsilon^{-\nu}$ and $\xi_k \sim (-\varepsilon)^{-\nu'}$.

Noticeable growth of fluctuations, while the configurative point approaches T_c , affects many properties of the system. This set of phenomena is referred to as **critical phenomena** with **critical opalescence** (significant rise of scattered light (or other radiation) intensity) as their part.

Critical opalescence will be discussed in detail later in this book (see subsections 2.3.5, 2.4.2, and 3.3.1). Preliminarily it should be noted that the stability parameter $(\partial P/\partial V)_T$ or $(\partial \mu_2/\partial x_2)_{T,P}$ enters into the <u>denominator</u> of the formula for the scattered light intensity I, which causes $I \to \infty$ in the critical point, where $\varepsilon \to 0$.

I also obeys Equations 2-4 with a corresponding critical index (see Table 1.2). On the other hand, the stability parameter enters into the <u>nominator</u> of the formula for the diffusion coefficient D, and $D \rightarrow 0$ when $\epsilon \rightarrow 0$. This also leads to a number of interesting phenomena (see Subsections 2.3.3, 2.4.3, and 3.6.2.7).

1.5.4. Static similarity (scaling) hypothesis

In the theory of phase transitions, the so-called hypothesis of static similarity, or scaling hypothesis, has become very popular (Patashinski and Pokrovski, 1964, 1975; Brout, 1965; Fisher, 1965; Widom, 1965; Kadanoff, 1966; Stanley, 1971; de Gennes, 1979; White and Geballe, 1979). This hypothesis is based on the fact that near the points of continuous phase transition the correlation length of thermodynamic quantity fluctuations gets so large, and gains such importance for the system properties, that the specific features of short-range intermolecular interactions no longer play their significant role. The scaling hypothesis has proved to be very fruitful because it emphasizes the common character (universality) of continuous phase transitions regardless of the features of specific systems. It enables one to extend some regularities of continuous transitions (critical phenomena) from the systems where they are well-known (cg. ferromagnetics) to other systems: the formulae to describe critical phenomena in different systems are mathematically identical and need replacing some symbols by others only with the aid of

Table 1.2. Some critical indices for three systems



 χ_T denotes magnetizability for ferromagnetics and osmotic compressibility for binary liquids

1.5.4. Static similarity (scaling) hypothesis

a special glossary.

Eg. the thermodynamic equations for the one-component system liquid-gas are transferred to those for a ferromagnetic by means of

$$V \to M, \quad (-P) \to H.$$
 (6)

Equation 1.1.1.5 becomes

$$\left(\frac{\partial T}{\partial M}\right)_{S} = \left(\frac{\partial H}{\partial S}\right)_{M} \tag{7}$$

and so on. Table 1.2 and comparison of Figures 1.13-15 are also significant in this respect.

The scaling ideas have turned out to be very helpful not only with respect to the critical phenomena but also for a wide range of problems in the physical chemistry of polymers (de Gennes, 1979) (for details, see Chapter 4).

The similarity hypothesis (with a ferromagnetic as an example) states that the Gibbs potential G is a generalized homogeneous function of ε and H, i.e. there are two similarity **parameters** a_{ε} and a_{H} , for which

$$G(\lambda^{a_{\epsilon}}\varepsilon;\lambda^{a_{H}}H) = \lambda G(\varepsilon,H)$$
(8)

holds for any λ value. As has been specially proved (Stanley, 1981), if Equation 8 holds good, then all the thermodynamic potentials are generalized homogeneous functions.

There are certain relationships between the critical indices and the similarity parameters that are deduced from common thermodynamic or statistical postulates and from the homogeneity property of the thermodynamic potentials. Therefore, they are valid for any specific system.

Thus, if experiment or a model theory allows us to determine the values of any two critical indices, then all the others can be found using these relationships, and the system will turn to be fully characterized.

Here are some relationships given by the similarity hypothesis:

$$\alpha = \alpha'; \quad \gamma = \gamma'; \quad \alpha + 2\beta + \gamma = 2; \tag{9}$$

$$\alpha = 2 - \nu d, \tag{10}$$

where d is the space dimensionality. One can judge how a theoretical model fits the real situation by comparison between the theoretical and experimental values of the critical indices.

1.5.5. Critical index calculation by the van der Waals equation

Let us apply the van der Waals equation 1.2-34 to calculate the critical indices (Stanley, 1971). It is reasonable to rewrite Equation 1.2-67, introducing new variables

$$p \equiv \tilde{P} - 1 \equiv \frac{P - P_c}{P_c},\tag{11}$$

$$v \equiv \tilde{V} - 1 \equiv \frac{V - V_c}{V_c},\tag{12}$$

$$\varepsilon \equiv \tilde{T} - 1 \equiv \frac{T - T_c}{T_c},\tag{13}$$

and

$$\left[(1+p) + 3(1+v)^{-2} \right] [3(1+v) - 1] = 8(1+\varepsilon).$$
⁽¹⁴⁾

Multiplying both the sides by $(1 + v)^2$ and reducing the similar terms yield

$$2p\left(1+\frac{7}{2}v+4v^2+\frac{3}{2}v^3\right) = -3v^3+8\varepsilon(1+2v+v^2).$$
(15)

Consider the behaviour of the temperature dependence of isothermal compressibility χ_T (Equation 1.1.2-41) while the configurative point approaches T_c from the side of lower temperatures $T \to T_c^-$ along the critical isochore (v = 0).

By Equations 1.1.2-41, 11, and 12,

$$(-V_c \chi_T)^{-1} = \left(\frac{\partial P}{\partial V}\right)_T = \frac{P_c}{V_c} \left(\frac{\partial p}{\partial v}\right)_T,$$
(16)

with the right-hand derivative to be determined using Equation 15 at v = 0. Then

$$(-V_c\chi_{\tau})^{-1} = \frac{P_c}{V_c}(-6\varepsilon),\tag{17}$$

i.e. $\chi_{\tau} \sim (-\varepsilon)^{-\gamma'}$, where $\gamma' = 1$ (for $\varepsilon < 0$, see Table 1.2).

What is the value of β (Table 1.2) (Rumer and Ryvkin, 1980)?

Let us restrict ourselves by following the approximation of Equation 15:

$$p = 4\varepsilon - 6\varepsilon v - \frac{3}{2}v^3, \tag{18}$$

which is valid for both the gas (g) and liquid (l) phases when $T < T_c$:

$$p = 4\varepsilon - 6\varepsilon v_g - \frac{3}{2}v_g^3,\tag{19}$$

$$p = 4\varepsilon - 6\varepsilon v_l - \frac{3}{2}v_l^3.$$
⁽²⁰⁾

The equality between the ABO and OCD areas (Equation 1.2 43 and Figure 1.4) can be written as

$$\int_{\bar{V}_l}^{V_g} P' \, d\bar{V} = P(\bar{V}_g - \bar{V}_l),\tag{21}$$

where P' is the current pressure on the isotherm, and P is the constant pressure of liquid and gas in equilibrium (eg. P_1 at $T = T_1$ or P_2 at $T = T_2$ in Figure 1.4). This equation is satisfied for the reduced variables as well:

$$\int_{v_l}^{v_g} p' \, dv = p(v_g - v_l). \tag{22}$$

Now we should substitute p' from Equation 18 into Equation 22, integrate, and reduce both the sides by $(v_g - v_l)$. All this yields

$$4\varepsilon - 3\varepsilon(v_g + v_l) - \frac{3}{8}(v_g + v_l)(v_g^2 + v_l^2) = p,$$
(23)

or, for p, if one substitutes expressions 19 and 20 into Equation 23, one gets

$$4\varepsilon - 3\varepsilon(v_g + v_l) - \frac{3}{8}(v_g + v_l)(v_g^2 + v_l^2) = 4\varepsilon - 6\varepsilon v_g - \frac{3}{2}v_g^3,$$
(24)

$$4\varepsilon - 3\varepsilon(v_g + v_l) - \frac{3}{8}(v_g + v_l)(v_g^2 + v_l^2) = 4\varepsilon - 6\varepsilon v_l - \frac{3}{2}v_l^3.$$
 (25)

Combination of Equations 24 and 25 yields

$$(v_g + v_l)(v_g - v_l)^2 = 0 (26)$$

and

$$v_g = -v_l. \tag{27}$$

The latter equation is useful after subtracting Equation 19 from Equation 20:

$$v_g = -v_l \simeq 2\sqrt{\varepsilon}.\tag{28}$$

Thus,

$$\varrho_l - \varrho_g \sim v_g - v_l = 4\sqrt{\varepsilon},\tag{29}$$

i.e.

$$\beta = \frac{1}{2}.\tag{30}$$

The next point is the temperature dependence of c_V (Equation 1.1.2-20) on the critical isochore v = 0 near the critical point.

Letting T and \overline{V} be independent variables (see Equation 1.1.1 27), we can write

$$d\bar{S} = \left(\frac{\partial\bar{S}}{\partial T}\right)_{\bar{V}} dT + \left(\frac{\partial\bar{S}}{\partial\bar{V}}\right)_{T} dV.$$
(31)

Using Equations 1.1.1-27, 28 (cf. Equation 1.1.1 5)

$$\left(\frac{\partial \bar{S}}{\partial V}\right)_{T} = \left(\frac{\partial P}{\partial T}\right)_{\vec{V}}$$
(32)

and definition 1.1.2-20, we get

$$d\bar{S} = \frac{c_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV.$$
(33)

In order to calculate the derivative $(\partial P/\partial T)_{\tilde{V}}$, P has to be deduced from the van der Waals equation 1.2-34

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \tag{34}$$

and

$$dS = \frac{c_V}{T} dT + \left(\frac{R}{V-b}\right) d\bar{V}.$$
(35)

The two expressions obtained are substituted into Equation 1.1.1-1

$$dU = T \, dS - P \, d\bar{V} = c_V \, dT + \frac{a}{\bar{V}^2} \, d\bar{V} \tag{36}$$

and

$$U = \int c_V \, dT - \frac{a}{\bar{V}} = U_{\rm id} - \frac{a}{\bar{V}}.\tag{37}$$

From the first law $dU = dQ - P d\bar{V}$ and Equation 1.1.2 20, it follows that

$$c_{\mathbf{V}} = \left(\frac{\partial U}{\partial T}\right)_{\mathbf{V}}.\tag{38}$$

In the case of $T > T_c$, Equations 37 and 38 give

$$c_{V} = c_{V, \mathsf{id}}.\tag{39}$$

In the two-phase region $(T < T_c)$, in view of Equation 37,

$$U = xU_g + (1 - x)U_l = U_{\rm id} - \frac{xa}{\bar{V}_g} - \frac{(1 - x)a}{\bar{V}_l},\tag{40}$$

where x is the volume fraction of the gas phase. For the total volume,

$$\bar{V}_0 = x\bar{V}_q + (1-x)\bar{V}_l \tag{41}$$

and

$$x = \frac{V_0 - \bar{V}_l}{V_g - \bar{V}_l},$$
(42)

whence

$$\frac{x}{1-x} = \frac{V_0 - V_l}{V_g - \bar{V}_0}.$$
(43)

If we take \bar{V}_0 as \bar{V}_c , then (cf. Equations 12 and 27)

$$\frac{x_c}{1 - x_c} = \frac{V_c - \bar{V}_l}{\bar{V}_g - \bar{V}_c} = -\frac{v_l}{v_g} = 1$$
(44)

and

$$x_c = \frac{1}{2}.\tag{45}$$

Substituting $x_c = 1/2$ into Equation 40, we have

$$U = U_{\rm id} - \frac{a}{2\bar{V}_c} \left(\frac{1}{1+v} + \frac{1}{1-v} \right) = U_{\rm id} - \frac{a}{\bar{V}_c} \cdot \frac{1}{1-v^2}.$$
(46)

For heat capacity, in view of Equation 13, we get

$$c_V = c_{\rm id} - \frac{2a}{V_c T_c} \cdot \frac{v}{(1-v^2)^2} \cdot \frac{dv}{d\varepsilon}.$$
(47)

Taking Equation 28 into consideration (as well as V_c and T_c from Equations 1.2-63,-64), we finally obtain

$$c_V = c_{\rm id} - \frac{9R}{2(1-4\varepsilon)^2} \approx c_{\rm id} - \frac{9}{2}R.$$
(48)

Thus, the heat capacity c_V undergoes a finite step at the critical region

$$c_V|_{T=T_c} = c_V(T_c + 0) - c_V(T_c - 0) \approx \frac{9}{2}R,$$
(49)

and the corresponding critical index is

$$\alpha' = 0 \tag{50}$$

(see Table 1.2).

We conclude that if a one-component substance obeys the van der Waals equation, its set of critical indices ($\gamma' = 1$, $\beta = 1/2$, and $\alpha' = 0$) satisfies Equation 9.

1.5.6. Magnetic behaviour near the critical point

Let us consider a gas of molecules with a constant magnetic moment $\vec{\mu}$, which is placed into a homogeneous magnetic field of strength \vec{H} (Rumer and Ryvkin, 1977).

The first approximation implies that there is no interaction between the molecules. The potential energy of a molecule is

$$U(\theta) = -\vec{\mu}\vec{H},\tag{51}$$

where θ is the angle between the directions of the magnetic moment $\vec{\mu}$ and of the field \vec{H} . Assuming the space distribution of the molecules to be continuous (the classic system), we apply the Boltzman formula for the relative fraction of molecules with a given energy

$$\frac{dN}{N} = \frac{\exp\left(-\frac{U(\theta)}{RT}\right) d\Omega}{\int \exp\left(-\frac{U(\theta)}{RT}\right) d\Omega},\tag{52}$$

with $d\Omega = \sin \theta \, d\theta \, d\varphi$ to denote the element of solid angle. Its integration, with respect to φ , gives us the θ distribution

$$\frac{dN(\theta)}{N} = \frac{\exp\left(\frac{\mu H}{kT}\cos\theta\right)\sin\theta\,d\theta}{\int\limits_{0}^{\pi}\exp\left(\frac{\mu H}{kT}\cos\theta\right)\sin\theta\,d\theta}.$$
(53)

The denominator can be calculated analytically:

$$Z(T) = \int_{0}^{\pi} \exp\left(\frac{\mu H \cos\theta}{kT}\right) \sin\theta \, d\theta = \frac{2\sinh\left(\frac{\mu H}{kT}\right)}{\left(\frac{\mu H}{kT}\right)}.$$
(54)

The mean projection of the magnetic moment onto the field direction is

$$\overline{\mu \cos \theta} = \mu \int \cos \theta \frac{dN(\theta)}{N}$$
(55)

$$=\mu \frac{\int\limits_{0}^{\pi} \exp(\mu H \cos\theta/kT) \cos\theta \sin\theta \,d\theta}{\int\limits_{0}^{\pi} \exp(\mu H \cos\theta/kT) \sin\theta \,d\theta} = \mu \left[\coth\left(\frac{\mu H}{kT}\right) - \frac{kT}{\mu H} \right].$$

Introducing the Langevin function $L(x) = \coth x - 1/x$, we get the magnetization

$$M = N\mu\overline{\cos\theta} = N\mu L\left(\frac{\mu H}{kT}\right) = M_0 L\left(\frac{\mu H}{kT}\right),\tag{56}$$

 $M_0 = N\mu$ being the maximal value of magnetization that is reached at $H \to \infty$ or $T \to 0$. The ratio of the magnetic energy to the mean heat motion energy $x = \mu H/kT$ has the meaning of the orientation (reorder) parameter.

The magnetization of ferromagnetics reaches its saturation in relatively weak fields, and there is spontaneous magnetization even without external field. This indicates that the orientation of magnetic moments is basically caused by the **internal** orienting field (related to the interactions among magnetic moments) rather than by the external field.

Under the Weiss hypothesis, the internal field is proportional to the existing magnetization

$$H_{int} = \gamma M, \tag{57}$$

 γ being the Weiss dimensionless factor. Hypothesis 57 provides that the internal (molecular) field appears only in a previously magnetized medium with a certain preferable direction for magnetic momenta.

In view of Equation 57, the external field H in Equation 56 has to be replaced by an **effective** one

$$H_{ef} = H + H_{int} = H + \gamma M. \tag{58}$$

Then

$$\frac{M}{M_0} = L\left(\frac{\mu(H+\gamma M)}{kT}\right) = L(x),\tag{59}$$

where

$$x = \mu \frac{H + \gamma M}{kT}.$$
(60)

Resolving Equation 60 with respect to M and dividing both the sides by M_0 , we get

$$\frac{M}{M_0} = \frac{kT}{\gamma M_0 \mu} x - \frac{H}{\gamma M_0}.$$
(61)

which, together with Equation 59, forms an equation set with a clear graphic interpretation (Figure 1.22).



Figure 1.22. Graphical solution of the set of equations 1.5-59,-61. The Langevin curve y = L(x) and line 1: $y = xkT/\gamma M_0\mu - H/\gamma M_0$ (61); line 2: $y = xkT/\gamma M_0\mu$, and line 3: y = x/3

One can see that in the external field $(H \neq 0)$, the Langevin curve (Equation 59) and straight line 1 (Equation 61) always intersect, and a certain magnetization $M \neq 0$ exists at any temperature.

With no field, H = 0, the straight line 2

$$\frac{M}{M_0} = \frac{kT}{\gamma M_0 \mu} x \tag{62}$$

goes through the origin of coordinates and, for the intersection point C to exist, it is necessary that the slope of line 2 should be less than that of the tangent line to the Langevin curve at x = 0.

At small x values, the Langevin function is represented as

$$L(x) \simeq \frac{x}{3} - \frac{x^3}{45} + \cdots$$

whence L'(0) = 1/3. Hence, spontaneous magnetization is possible if only

$$\frac{kT}{\gamma M_0 \mu} < \frac{1}{3},\tag{63}$$

from which the existence of

$$T_c = \frac{\gamma M_0 \mu}{3k} \tag{64}$$

follows. Any substance behaves as a ferromagnetic below this point (denoted by the term **Curie temperature**) and as a paramagnetic above it (see Figure 1.14).

1.5.7. Problem of the magnetic on the Ising lattice within the Bragg-Williams approximation

In order to determine the critical parameters of a magnetic, the functional dependence of any thermodynamic potential should be deduced. Let us take advantage of the Ising lattice model which has turned out to be universal for many systems (see Figure 1.23). The Euclidean dimensionality of the lattice can be any—from 1 to ∞ . Its sites are assigned



Figure 1.23. Ising's lattice for modelling of different systems. The system parameter can take one of two possible values at every site: the particle spin is directed up or down in a magnetic (a), there is a particle or there is no particle in a liquid-vapour system (b), a particle of component 1 or 2 is present in a binary system (c), site-to-site walk of connected particles in the model of a macromolecule (d)

with one of two alternative properties.

The Bragg-Williams approximation is often used together with the Ising lattice (Ansclm, 1973; Rumer and Ryvkin, 1980). Let some particles with two possible opposite spins $s = \pm 1/2$ and the magnetic moment μ be placed at the lattice sites (Figure 1.23a), the coordination number being equal to ν . Let N_+ and N_- denote the number of particles with the magnetic moment along and opposite the field: $N_+ + N_- = N$. We introduce a **long-range order** parameter Q according to

$$Q = \frac{N_{+} - N_{-}}{N} = \frac{M}{M_{0}},\tag{65}$$

so that

$$\frac{N_+}{N} = \frac{1}{2}(1+Q), \qquad \frac{N_-}{N} = \frac{1}{2}(1-Q). \tag{66}$$

These relationships hold true in case of one spin being independent of its neighbours (the absence of short-range spin correlations). In fact, if a site contains a particle with a spin with a given direction, it will be more probable for any of its neighbours to have a spin with the same direction. This provides a lower interaction energy. The situation with an antiferromagnetic is the converse of the above.

In this case, correlation, or near order, is spoken of. The Bragg-Williams approximation allows for long range only, that is why Q in Equation 65 is called a long-range parameter.

Further, only the nearest neighbouring particles are assumed to interact. Let $-\varepsilon$ be the interaction energy for the same spin-directed neighbouring particles, and ε be that for spin-antidirected ones with ε being positive. Thus, the orientation part of the internal energy, including the energy of moments μ in the magnetic field, is expressed as

$$U = (N_{+-} - N_{++} - N_{--})\varepsilon - (N_{+} - N_{-})\mu H,$$
(67)

 N_{++} , N_{--} , N_{+-} being the numbers of neighbouring pairs with spins directed along the field, opposite it, and to different sides, respectively.

To calculate N_{++} , we have to exhaust all N_+ particles bearing in mind that the average number of the same-directed moments is $\nu N_+/N$, ignoring correlation. Every pair being allowed for twice, the result must be divided by 2. Calculation of N_{--} and N_{+-} is similar. In view of Fourtier 66

In view of Equation 66,

$$N_{++} = N_{+} \frac{\nu}{2} \cdot \frac{N_{+}}{N} = \frac{\nu N}{8} (1+Q)^{2}, \quad N_{--} = \frac{\nu N}{8} (1-Q)^{2}, \quad N_{+-} = \frac{\nu N}{4} (1-Q^{2})$$
(68)

and, on substituting Equation 60 into Equation 67,

$$U(Q) = -\frac{\nu N\varepsilon}{2}Q^2 - N\mu HQ.$$
⁽⁶⁹⁾

The Boltzmann formula gives us the entropy for a system of N particles, the N_+ and N_- of which are indistinguishable from each other:

$$S = k \ln \frac{N!}{N_+! N_-!}$$
(70)

and, with due account of the Stirling formula $\ln N! \simeq N \ln N - N$,

$$S = k(N \ln N - N_{+} \ln N_{+} - N_{-} \ln N_{-}).$$
(71)

Expressing N_+ and N_- in terms of Q from Equation 66, we find

$$S = -\frac{kN}{2} \left[(1+Q) \ln \frac{1-Q}{2} + (1-Q) \ln \frac{1-Q}{2} \right]$$
(72)

and the Helmholtz potential

$$F = U - TS = -\frac{N\nu\varepsilon}{2}Q^2 - N\mu HQ + \frac{kTN}{2}\left[(1+Q)\ln\frac{1+Q}{2} + (1-Q)\ln\frac{1-Q}{2}\right].$$
(73)

In equilibrium

$$\left(\frac{\partial F}{\partial Q}\right)_T = 0 \quad \text{and} \quad -N\left(\nu\varepsilon Q + \mu H - \frac{kT}{2}\ln\frac{1+Q}{1-Q}\right) = 0. \tag{74}$$

This equation can be written as (Lyusternik et al., 1963; Bronstein and Semendyaev, 1979)

$$\operatorname{arctanh} Q = \frac{\mu II + \nu \varepsilon Q}{kT}$$

$$Q = \operatorname{tanh} \left(\frac{\mu II + \nu \varepsilon Q}{kT}\right) = \operatorname{tanh} x.$$
(75)

As 'tanh' behaves like the Langevin function, Equations 75 and 59 are equivalent.

Comparison of Equations 59, 60, and 75 allows us to express the Weiss phenomenological factor in terms of molecular parameters:

$$\gamma = \frac{\nu\varepsilon}{M_0\mu} = \frac{\nu\varepsilon}{N\mu^2}.$$
(76)

The equation set 75 and

$$Q = \frac{kT}{\nu\varepsilon}x - \frac{\mu H}{\nu\varepsilon}$$
(77)

should be solved numerically or graphically (Figure 1.22) like the version with the Langevin function.

In contrast to L, 'tanh' has a unit initial slope, since, at small argument values,

$$\tanh x \simeq x - \frac{1}{3}x^3 + \cdots .$$
⁽⁷⁸⁾

Hence, the critical temperature T_c is determined using the equality between the tangent line (Equation 78) at x = 0 and the slope (Equation 77), i.e.

$$\frac{kT_c}{\nu\varepsilon} = i$$
 and $T_c = \frac{\nu\varepsilon}{k}$. (79)

In the case of $T \to T_c - 0$, the order parameter $Q = M/M_0$ is small in comparison with unity that enables us to expand $\tanh x$ (Equation 78) and to get an expression for the order parameter (Equation 75) without field (H = 0) (see also Equation 79):

$$Q = \frac{T_c}{T}Q - \frac{1}{3}\left(\frac{T_c}{T}Q\right)^3 + \cdots$$
(80)

or

or

$$\frac{T-T_c}{T_c} = -\frac{Q^2}{3} \left(\frac{T_c}{T}\right)^2 \approx -\frac{Q^2}{3},\tag{81}$$

whence $(T_c \approx T)$

$$Q = \left(3\frac{T_c - T}{T_c}\right)^{1/2} - (-3\varepsilon)^{1/2},\tag{82}$$

i.e. $\beta = 1/2$.

There is another form for Equation 75 if we use the formula for tanh(x + y) (Bronstein and Semendyaev, 1979)

$$\tanh(x+y) = \frac{\tanh x + \tanh y}{1 + (\tanh x)(\tanh y)},\tag{83}$$

$$\tanh\left(\frac{\mu H}{kT}\right) = \frac{Q - \tanh(T_c Q/T)}{1 - Q \tanh(T_c Q/T)}.$$
(84)

The arguments of all the tanh's are small near the critical point $(H \rightarrow 0, M \rightarrow 0, T \rightarrow T_c)$, and the approximation (Equation 78) can be accepted. Having two polynomials in Equation 84 divided by each other, and the terms with Q^3 kept, we obtain

$$h \equiv \tanh\left(\frac{\mu H}{kT}\right) = Q\left(1 - \frac{T_c}{T}\right) + Q^3\left[\frac{T_c}{3T^3} + \frac{T_c}{T} - 1\right] + O(Q^5).$$
(85)

Differentiating both the sides with respect to h at $T \approx T_c$ yields

$$1 = \frac{\partial Q}{\partial h} \left[\left(1 - \frac{T_c}{T} \right) + Q^2 \left(\frac{T_c^3}{T^3} \right) + \cdots \right], \tag{86}$$

$$\left(\frac{\partial h}{\partial H}\right)_{T,H\to 0} = \left.\frac{\mu}{kT\cosh^2(\mu H/kT)}\right|_{H\to 0} \to \frac{\mu}{kT},\tag{87}$$

and we are able to substitute them into the expression for magnetizability (by definition)

$$\chi_{_{T,H\to 0}} \left(\frac{\partial M}{\partial H}\right)_{_{T,H\to 0}} = \left(\frac{\partial M}{\partial Q}\right) \left(\frac{\partial Q}{\partial h}\right) \left(\frac{\partial h}{\partial H}\right)_{_{T,H\to 0}},\tag{88}$$

$$\chi_{T,H\to 0} = \frac{M_0\mu}{kT} \left[\left(1 - \frac{T_c}{T} \right) + Q^2 \left(\frac{T_c}{T} \right)^3 \right]^{-1}$$
(89)

at $T \rightarrow T_c + 0$ Q = 0 and

$$\chi_{T,H\to 0} = \frac{M_0\mu}{kT} \varepsilon^{-1} \tag{90}$$

and $\gamma = 1$.

With $T \to T_c - 0$ Equation 82 can be accepted for Q and, in view of $T_c \approx T$,

$$\chi_{T,H\to 0} = \frac{M_0\mu}{kT} (\varepsilon - 3\varepsilon)^{-1} = -\frac{M_0\mu}{2kT} \varepsilon^{-1}$$
(91)

and $\gamma' = 1$ as well.

One can see that $\gamma = \gamma' = 1$, but the magnetizability in the ferromagnetic region $(\varepsilon < 0)$ is twice as high as that in the paramagnetic one given $|\varepsilon|$ is the same.

Without the field (H = 0), the expression for internal energy (Equation 69) reduces to

$$U(Q) = -\frac{\nu N \varepsilon}{2} Q^2 = -\frac{N k T_c}{2} Q^2.$$
 (92)

Hence,

$$c_{H\to 0} = \frac{\partial U}{\partial T} = \frac{\partial U}{\partial Q} \cdot \frac{dQ}{dT} = -NkT_c Q \frac{dQ}{dT} = -NkQ \frac{dQ}{d\varepsilon}.$$
(93)

It follows from Equation 93 that, when $T \ge T_c$ (where Q = 0),

$$c_{H\to 0} = 0, \tag{94}$$

and when $T < T_c$ (see Equation 82),

$$c_{H\to 0} = \frac{3}{2}kN. \tag{95}$$

Comparison of Equations 94 and 95 shows the heat capacity $c_{H\to 0}$ to undergo a sudden change at the critical point $T = T_c$ (see Figure 1.24, cf. Figure 1.16h)



Figure 1.24. Temperature dependence of the heat capacity of a magnetic in the Weiss-Bragg-Williams approximation

$$\Delta c_{H\to 0} = c_{H\to 0} (T_c + 0) - c_{H\to 0} (T_c - 0) = -\frac{3}{2} k N,$$
(96)

and $\alpha = \alpha' = 0$. Therefore, this phase transition at $T = T_c$ is continuous.

Such a character of this phase transition also follows from the continuity of entropy at Q = 0, since, for small Q, Equation 72 implies that

$$S(Q) = -kN(Q^2 - \ln 2).$$

1.5.8. Mean field approximation

We conclude that the critical indices of a one-component substance, satisfying the van der Waals equation and those of a magnetic within the Weiss-Bragg-Williams approximation are identical. This is associated with the similarity in the premises, the main of which consists in the replacement of the mutual interactions between all the particles by that one of a given particle with the **mean (molecular, self-consistent**) field generated by the other particles, the latter being assumed not to interact.

Indeed, while solving the problem of a magnetic, we substituted the corrected (selfconsistent) field (Equation 59) into Equation 56 for non-interacting particles. When we were deducing the van der Waals equation heuristically (section 1.2), we recalculated the values (pressure and volume) "corrected" for the overall interactions to $P_{\rm id}$ and $V_{\rm id}$ and substituted them into the equation for the ideal gas

$$\underbrace{\left(P + \frac{a}{\bar{V}^2}\right)}_{P_{\text{id}}}\underbrace{(\bar{V} - b)}_{V_{\text{id}}} = RT.$$
(97)

The self-consistency of the field resides in the fact that the field caused by such "noninteracting" particles matches the mean field of the interacting ones. The mean field approximation is equivalent to the action range being infinite for every particle in the system (Stanley, 1971; Wilson, 1979). Indeed, the rigorous solution of the problem for the one-component substance "liquid-gas" using statistical methods for the model of interacting hard spheres with the potential

$$U = U_{\rm rep} + U_{\rm att},$$

where the repulsion potential $U_{\text{rep}} \to \infty$ when $r = r_0$ (r_0 is the sphere radius) and the attraction one $U_{\text{att}} = -const \sim -1/N$ when $r > r_0$ (i.e. with an infinite range of action) leads to the van der Waals equation (Stanley, 1971).

1.6. Landau's phenomenological theory

1.6.1. State equations. Phase transitions

Landau (1935, 1937ab; Landau and Lifshitz, 1964) postulated that any thermodynamic potential per unit volume can be expanded into a series with respect to the order parameter Q in the vicinity of the critical point (T_c) :

$$G(T,P) = G_0(T,P) + \frac{a}{2}Q^2 + \frac{c}{2}Q^3 + \frac{b}{4}Q^4 + \cdots,$$
(1)

where a, b, c are functions of pressure and temperature.

In most cases of structural phase transitions, there exists a more symmetrical (high-temperature) phase when $T > T_c$. The appearance of the order parameter Q when $T < T_c$ is associated with the appearance of a less symmetrical phase. The high-temperature phase is often identified with the disordered one, and the low-temperature phase with the ordered one.

Let Q be a scalar quantity. More generally, it is a tensor (as for liquid crystals).

The conditions of phase stability with respect to the order parameter are

$$\frac{\partial G}{\partial Q} = 0 \tag{2}$$

and

$$\frac{\partial^2 G}{\partial Q^2} > 0 \tag{3}$$

(the former condition causes the absence of the linear term in Equation 1).

First, let us discuss a simpler case when G is an even function of Q with a minimum at $T = T_c$ (see Figure 1.14), which is provided by the odd-power coefficients being equal to zero (c = 0, ...). Condition 3 then reduces to

$$a + 3bQ^2 > 0. \tag{4}$$

With $T > T_c$, Q = 0; therefore

$$a > 0.$$
 (5)

Assuming b > 0, for a non-zero Q to appear when $T < T_c$ it is necessary that a < 0. It follows that at $T = T_c$ a = 0 and the temperature dependence of a is linear

$$a = \alpha (T - T_c). \tag{6}$$

Thus,

$$G(P,T,Q) = G_0(P,T) + \frac{\alpha}{2}(T-T_c)Q^2 + \frac{b}{4}Q^4.$$
(7)

Further, we neglect the temperature dependence of b, as it is much weaker than that of Q, and, what is more, b is multiplied by Q to the 4th power. Condition 2 gives us the equilibrium value Q_0 :

$$Q_0 = \left[\frac{\alpha}{b}(T_c - T)\right]^{1/2},\tag{8}$$

and the following critical index value emerges:

$$\beta = \frac{1}{2}.\tag{9}$$

Substitution of Equation 3 into Equation 8 yields

$$G = \begin{cases} G_0 - \frac{\alpha^2}{2b} (T_c - T)^2 & \text{when } T < T_c, \\ G_0 & \text{when } T > T_c, \end{cases}$$
(10)

and the heat capacity can also be deduced

$$c_P = -T \frac{\partial^2 G}{\partial T^2} = \begin{cases} c_{0P} + T \alpha^2 / b & \text{at } T < T_c, \\ c_{0P} & \text{at } T > T_c. \end{cases}$$
(11)

Hence, the heat capacity at $T = T_c$ undergoes an abrupt change $\Delta c_P = c_P - c_{0P} = T\alpha^2/b$ and the critical indices are $\alpha = \alpha' = 0$.

Let us compute the magnetizability χ_r . As $G \simeq F$ for condensed systems (Prigogine and Defay, 1954), on the basis of Equations 1.1.1-28 and 1.5-6 we can write

$$\frac{\partial F}{\partial M} = H. \tag{12}$$

From $\chi_T = (\partial M/\partial H)_{T,H\to 0}$ we extract $\chi_T^{-1} = \partial^2 F/\partial M^2$, or, more generally,

$$\chi_{\tau}^{-1} = \frac{\partial^2 F}{\partial Q^2} \approx \frac{\partial^2 G}{\partial Q^2}.$$
(13)

The second derivative of G with respect to Q should be taken using Equation 7 and the Q value from Equation 8. All this yields

$$\chi_T = \frac{1}{2\alpha(T_c - T)} \tag{14}$$

for $T < T_c$.

At Q = 0 and when $T > T_c$,

$$\chi_{\tau} = \frac{1}{\alpha(T_c - T)},\tag{15}$$

i.e. $\gamma = \gamma' = 1$ and the factor before $(-\varepsilon)^{\gamma'}$ in the ferromagnetic area is twice as large as that in the paramagnetic area provided that a magnetic is involved.

The agreement between the critical indices in both Landau's theory and the mean field approximation attests to the equivalence of the two approaches.

We continue analyzing Equation 1 with the cubic term $(c \neq 0)$ (Izyumov and Syromyutnikov, 1984)

$$G(P,T,Q) = G_0(P,T) + \frac{a}{2}Q^2 + \frac{c}{2}Q^3 + \frac{b}{4}Q^4.$$
(16)

Condition 2 leads to the state equation

$$Q_0\left(a + \frac{3}{2}cQ_0 + bQ_0^2\right) = 0 \tag{17}$$

which has a zero solution $(Q_0 = 0)$ and two non-zero ones

$$Q_{0\pm} = -\frac{3c}{4b} \pm \sqrt{\left(\frac{3c}{4b}\right)^2 - \frac{a}{b}}.$$
(18)

The roots of Equation 18 are real numbers if the discriminant is positive, i.e.

$$a \le \frac{9c^2}{16b}.\tag{19}$$

The dependences $\Delta G = G - G_0$ plotted against the order parameter Q are shown in Figure 1.25.



Figure 1.25. Increment of the thermodynamic potential $\Delta G = G - G_0$ as a function of the order parameter (Equation 1.6-16)

For definiteness, assume b > 0, c < 0. The values Q_{0-} and Q_{0+} correspond to the ΔG minimum and maximum, respectively.

When $a > 9c^2/16b$ and $T > T^{**}$ (Figure 1.25), there are no real roots of Equation 18, ΔG has a minimum at $Q_0 = 0$, i.e. it is the disordered (high-temperature) phase that is the only stable one. At $T = T_{t1}$, the system possesses two similar minima $\Delta G = 0$ which implies a first order transition. The temperature T_{t1} and the corresponding order parameter Q_{t1} can be found from Equation 17 and the condition of the thermodynamic potential (Equation 16) being equal in both phases, i.e. $\Delta G = G - G_0 = 0$:

$$Q_{t1}^2 + \frac{3c}{2b}Q_{t1} + \frac{a}{b} = 0, (20)$$

$$Q_{11}^2 + \frac{2c}{b}Q_{11} + \frac{2a}{b} = 0.$$
(21)

Subtracted from each other, they give

$$Q_{t1} = -\frac{2a}{c} \tag{22}$$

which can be substituted into Equation 21:

$$\frac{2a}{c^2} = \frac{1}{b}.\tag{23}$$

Equations 22 and 23 yield

$$Q_{I1} = -\frac{c}{b}.$$
 (24)

Assume the linear dependence for a of the Equation 6 type

$$a = \alpha (T - T^*) \tag{25}$$

which, in view of Equation 23, leads to

$$T_{t1} = T^* + \frac{c^2}{2b\alpha}.$$
 (26)

When $T_{t1} < T < T^{**}$ (see Figure 1.25), ΔG has two minima, namely, a deeper one at $Q_0 = 0$ (the disordered phase) and a more shallow one at $Q_0 \neq 0$ (the ordered phase). It follows that the ordered phase may be in the metastable state. The boundary value of a (Equation 19) enables us to calculate T^{**} :

$$T^{**} = T^* + \frac{9c^2}{16b\alpha} \tag{27}$$

and, together with Equation 18, leads to

$$Q_0^{**} = -\frac{3c}{4b}.$$
 (28)

At $T = T^*$ a = 0 and Equation 20 has two roots: $Q_0 = 0$ (an inflection point of ΔG) and $Q_0^* = -3c/2b$ (a minimum of ΔG), see Figure 1.25.

Within $T^* < T < T_{t1}$, the minimum of ΔG , corresponding to $Q_0 = 0$, is more shallow than when $Q_0 \neq 0$, i.e. the disordered (symmetrical) phase is in the metastable state and the ordered (asymmetric) one is in the stable state. When $T \leq T^*$, the former phase is absolutely instable.

Phase transition hysteresis takes place within $T^* < T < T^{**}$ (see Figures 1.25 and 26), this range depends on the G expansion coefficients (Equation 27)

$$T^{**} - T^* = \frac{9c^2}{16b\alpha}.$$
 (29)

In view of Equations 18, 29, and 25, the temperature dependence of Q_0 can be expressed as

$$Q_0 = -\frac{3c}{4b} \left[1 + \left(1 - \frac{T - T^*}{T^{**} - T^*} \right)^{1/2} \right]$$
(30)

or (with due account of Equations 29 and 26),

$$Q_0 = -\frac{3c}{4b} \left\{ 1 + \left[1 - \frac{8(T - T^*)}{9(T_{t1} - T^*)} \right]^{1/2} \right\}.$$
(31)

Thus, the presence of the cubic term in the G expansion accounts for the presence of a first-order phase transition in the system.



Figure 1.26. Temperature dependence of the order parameter (Equation 1.6 30) for a system with the potential G (Equation 1.6 16)



Figure 1.27. Temperature dependence of the order parameter for continuous (a), first-order continuous-like (b), and first-order phase transitions (c)

At small c values (with the cubic term of the G expansion), the temperature range of hysteresis is narrow, and the order parameter value Q_{t1} is small, in accordance with Equations 29 and 24. Such transitions are referred to as first-order continuous-like transitions (Figure 1.27).

Let us consider a variant of the G expansion (Equation 1) with even powers of Q up to Q^6 (Landau, 1937a; Strukov and Levanyuk, 1983)

$$G(P,T,Q) = G_0(P,T) + \frac{a}{2}Q^2 + \frac{b}{4}Q^4 + \frac{d}{6}Q^6 = G_0(P,T) + \frac{\alpha}{2}(T-T^*)Q^2 + \frac{b}{4}Q^4 + \frac{d}{6}Q^6.$$
(32)

For definiteness, assume $\alpha > 0$, d > 0, and b < 0.

Equation 2 gives

$$Q_0 \left[\alpha (T - T^*) + bQ_0^2 + dQ_0^4 \right] = 0 \tag{33}$$

and, in the low temperature (asymmetric) phase,

$$Q_{0}^{2} = -\frac{b}{2d} \pm \sqrt{\left(\frac{b}{2d}\right)^{2} - \frac{\alpha(T - T^{*})}{d}}$$

$$= -\frac{b}{2d} \left\{ 1 \mp \left[1 - \frac{4\alpha(T - T^{*})d}{b^{2}}\right]^{1/2} \right\}.$$
(34)

All the five roots of Equation 33 arc real in a certain temperature range (Figure 1.28). This range is bounded above by the temperature T^{**} that is defined using the condition



Figure 1.28. Dependence of the thermodynamic potential increment $\Delta G = G - G_0$ on the order parameter (Equation 1.6-32)

of the radicand in Equation 34 being equal to zero:

$$T^{**} - T^* = \frac{b^2}{4\alpha d}.$$
 (35)

If the system is in the symmetrical phase, the dependence G(Q), when $T > T^{**}$, has the only minimum at $Q_0 = 0$. At $T = T^{**}$, there appear points of inflection on the dependence $\Delta G = f(Q)$, and on further cooling $(T < T^{**})$, extrema appear (Figure 1.28). The ΔG minima at Q_{03} and Q_{04} correspond to the metastable asymmetric phase. The system is capable to keep its initial (more symmetrical) phase until the minimum at $Q_0 = 0$ disappears (this will happen when $T = T^*$). Then, the symmetrical phase will prove to be absolutely unstable, and the system will abruptly change to a state with



Figure 1.29. Temperature dependence of the order parameter Q_0 (the positive branch of Equation 1.6-34) for systems with the potential G (Equation 1.6-32)

 $Q_0^2(T^*) = -b/d$ (Figure 1.29). On the other hand, on heating the system can remain in the its asymmetric phase up to T^{**} , at which $Q_0^2 = -b/2d$.

The difference $T^{**} - T^*$ (Equation 35) defines the maximum possible temperature hysteresis of first-order phase transition (Figures 1.28 and 29).

1.6.2. Tricritical point

In a general way, the coefficients of the Landau equation are functions of pressure. When pressure is varying, b may decrease in magnitude, and the temperature hysteresis diminishes according to Equation 35 and disappears at b = 0.

On the state diagram P vs T, the line corresponding to a = 0 may intersect the line b = 0. The point of intersection defined by

$$\begin{cases} a(P,T) = 0, \\ b(P,T) = 0, \end{cases}$$
(36)

is a special one, the so-called tricritical point (Figure 1.30) (Landau, 1935; Griffiths, 1970). On the line a = 0 when b < 0 a first-order phase transition takes place (the last discussed version of the Landau equation) and approaches the continuous transition as pressure increases, reaching it when a = 0 and b > 0.

Consequently, the lines of first-order and continuous phase transitions abut on with each other at the **tricritical** point (P_{tc}, T_{tc}) , which, therefore, defines it.

The tricritical point and its vicinity have their own peculiarities in comparison with the common-type critical point. If the configurative point approaches the tricritical point along the line b = 0, Equation 33 gives

$$\alpha(T - T^*) + dQ_0^4 = 0 \tag{37}$$


Figure 1.30. State diagram of systems with G from Equation 1.6-32, d > 0. Line I of first-order transition with a = 0, b < 0 turns to line II of continuous transition with a = 0, b > 0 at the tricritical point (tc)

and

$$Q_0 = \pm \left[-\alpha (T - T^*)/d \right]^{1/4}, \tag{38}$$

i.e. $\beta_t = 1/4$.

Substituting Equation 38 into Equation 32 allows us to obtain

$$c_{P} = -T \left(\frac{\partial^{2} G}{\partial T^{2}} \right)_{P} = \begin{cases} c_{0P} + \frac{\alpha^{3/2} T}{2d^{1/2}} (T - T^{*})^{-1/2} & \text{when } T < T^{*}, \\ c_{0P} & \text{when } T > T^{*}, \end{cases}$$
(39)

and $\alpha'_{l} = 1/2$.

Thus, the critical indices in the tricritical region do significantly differ from those in the common critical one.

Using a ferroelectric as an example, let us discuss some properties of the tricritical point (in particular, the etymology of the term) (Izyumov and Syromyatnikov, 1984). Figures 1.31 and 1.32 show that the first-order phase transition is accompanied by



Figure 1.31. Isotherms: electric field (*E*) against ferroelectric polarization \mathcal{P}_s for $\mathcal{T} = T_c$, $T_2 < T < T_c$ (Strukov and Levanyuk, 1983)

Figure 1.32. State diagram of a ferroelectric in the coordinates $E \mathcal{P}_s$ -T under constant pressure (Strukov and Levanyuk, 1983)

the spontaneous reversing of the polarization sign \mathcal{P}_s in the absence of the electric field (E = 0) and when $T < T_c$. As temperature increases, the step of \mathcal{P}_s decreases and at $T = T_c$ the transition becomes continuous. Figure 1.32 illustrates the ferroelectric behaviour under constant pressure P = const. T_c varies with P, and this dependence is shown in Figure 1.33.



Figure 1.33. State diagram of a ferroelectric in the coordinates P-E T with a line of continuous phase transitions (Strukov and Levanyuk, 1983)

Provided a first-order phase transition occurs at a certain temperature T_{t1} in the absence of the field in a ferroelectric (see Figure 1.34), then setting up the field (say, E_2) causes the transition temperature $T_{t1,2}$ to rise and the order parameter change \mathcal{P}_s to decrease, so that at a certain field intensity $E_3 = E_c$, the phase transition turns continuous with the corresponding T_c (Figure 1.34). Figure 1.35 comprises the lines of continuous transitions for two field directions (T_c , $+E_c$) and (T_c , $-E_c$) together with those in the absence of



Figure 1.34. Temperature dependence of spontaneous polarization in the absence of the field $(E_1 = 0)$ and of polarization in the electric field $E_2 < E_3 = E_c$ (Strukov and Levanyuk, 1983)



Figure 1.35. Phase diagram of a ferroelectric with the tricritical point P_{tc} , T_{tc} as the point of intersection of three lines of continuous phase transition (T_c, P_c) , $(T_c, + E_c)$, and $(T_c, - E_c)$. First-order phase transitions proceed in the dashed area (Strukov and Levanyuk, 1983)

the field (T_c, P_c) (Figure 1.33).

These three lines of continuous transitions intersect at a point which Griffiths (1970) has called the tricritical point. The dashed area in Figure 1.35 corresponds to first-order transitions, i.e. they abut on with continuous transitions at the tricritical point.

Mixtures reveal their interesting features in connection with the tricritical point (Landau, 1935, 1937a).

It was shown above that a system with its potential like

$$G(P,T,Q,x) = G_0(P,T,x) + AQ^2 + BQ^4$$
(40)

has a tricritical point on the state diagram, but in case of mixtures, the coefficients A and B depend not only on P and T but on the mixture composition x as well.

Owing to the homogeneity of G, we can write for a two-component mixture

$$G = n_2 f(n_1/n_2).$$
 (41)

Then, the chemical potentials are

$$\mu_2 = \frac{\partial G}{\partial n_2} = f - x \frac{\partial f}{\partial x} \quad \text{and} \quad \mu_1 = \frac{\partial G}{\partial n_1} = \frac{\partial f}{\partial x},$$
(42)

where $x = n_1/n_2$. Given that x and x_0 are the concentrations and G and G_0 are the

potentials of the two coexisting phases, the equilibrium conditions have the form

$$\frac{\partial G_0}{\partial x_0} = \frac{\partial G}{\partial x},\tag{43}$$

$$G_0(x_0) - x_0 \frac{\partial G_0}{\partial x_0} = G(x) - x \frac{\partial G}{\partial x}$$
(44)

with the potential being equal to G_0 in a more symmetrical phase (where Q = 0) and taking the form 40 in a less symmetrical one.

The tricritical point must satisfy the condition $x = x_0$.

Let us consider the vicinity of the tricritical point with $x \approx x_0$. Substituting G from Equation 40 into Equation 43 and restricting ourselves to the terms with their powers not larger than 2, we have

$$\frac{\partial G_0}{\partial x_0} = \frac{\partial G_0}{\partial x} + \frac{\partial A}{\partial x}Q^2. \tag{45}$$

Expand $\partial G_0/\partial x$ by its Taylor series expansion (two terms only)

$$\frac{\partial G_0}{\partial x} = \frac{\partial G_0}{\partial x_0} + \frac{\partial^2 G_0}{\partial x_0^2} (x - x_0) + \cdots .$$
(46)

It follows from Equations 45 and 46 that

$$-\frac{\partial^2 G_0}{\partial x_0^2}(x-x_0) = \frac{\partial A}{\partial x}Q^2.$$
(47)

Assuming

$$\frac{\partial G_0}{\partial x} \approx \frac{\partial G_0}{\partial x_0} \tag{48}$$

in Equation 44 with a similar accuracy, we get

$$G = G_0(x_0) + \frac{\partial G_0}{\partial x_0}(x - x_0),$$
(49)

and, with due account of Equation 40,

$$AQ^{2} + BQ^{4} = G_{0}(x_{0}) - G_{0}(x) + \frac{\partial G_{0}}{\partial x_{0}}(x - x_{0}).$$
(50)

The three-term Taylor series expansion for $G_0(x)$ will be

$$G_0(x) = G_0(x_0) + \frac{\partial G_0}{\partial x_0}(x - x_0) + \frac{1}{2}\frac{\partial^2 G_0}{\partial x_0^2}(x - x_0)^2 + \cdots$$
(51)

and, on substituting into Equation 50, we obtain

$$AQ^{2} + BQ^{4} = -\frac{(x - x_{0})^{2}}{2} \cdot \frac{\partial^{2}G_{0}}{\partial x_{0}^{2}}.$$
(52)

Equations 47 and 52 yield

$$AQ^2 + BQ^4 = \frac{x - x_0}{2} \cdot \frac{\partial A}{\partial x}Q^2$$
(53)

ог

$$A + BQ^2 = \frac{x - x_0}{2} \cdot \frac{\partial A}{\partial x}.$$
(54)

We now derive the equilibrium value of the order parameter from Equation 40 with due account of Equation 2

$$Q_0^2 = -\frac{A}{2B},$$
(55)

and another form of Equation 54 emerges:

$$A = (x - x_0) \frac{\partial A}{\partial x}.$$
(56)

On substituting Q_0^2 from Equation 55 and $(x - x_0)$ from Equation 56 into Equation 47, the following result emerges:

$$B = \frac{\left(\frac{\partial A}{\partial x}\right)^2}{2\frac{\partial^2 G_0}{\partial x_0^2}}.$$
(57)

If a two-component solution is stable in the vicinity of its tricritical point (Equation 1.3-53), then

$$\frac{\partial^2 G_0}{\partial x_0^2} > 0 \tag{58}$$

and

$$B > 0 \tag{59}$$

(not equal to zero) at the tricritical point.

Neglecting the Q^4 term and in view of Equation 55, we transform Equation 40 into

$$G = G_0 - \frac{A^2}{2B} \tag{60}$$

and obtain the heat capacity

$$c_P = -T\frac{\partial^2 G}{\partial T^2} = c_{0P} + \frac{T}{B} \cdot \frac{\partial^2 A}{\partial T^2}.$$
(61)

While analyzing the Landau equation of the form (1) or (40), its coefficients are presumed to have no analytical singularities; therefore, the heat capacity has a finite value at the tricritical point (according to Equation 61) rather than diverges as for the common critical point.



Figure 1.36. State diagram of a mixture with the tricritical point O: T and x denote the temperature and concentration of component 1, respectively (Landau, 1937a)

According to Equation 56,

$$A(x_0) = 0, (62)$$

in the vicinity of the tricritical point, i.e. the line of the first-order phase transitions of a more symmetrical phase satisfies the same equation that the line of its continuous transitions, and the state diagram can be represented in Figure 1.36, where O denotes the tricritical point.

The line 1 O corresponds to the continuous transitions between the more symmetrical (I) and the less symmetrical (II) phases, and line 3-O/2 characterizes first-order transitions and bounds the phases I-II separation area.

The mixture ³He +⁴ He has been found to have its state diagram like that shown in Figure 1.36 with $T_{tc} = 0.87$ K and $x_{tc} = 0.67$ (the mole fractions of ³He) (Alvesalo et al., 1969; Griffiths, 1970). In particular, the characteristic kink on the coexisting curve (Figure 1.37) has been confirmed. However, some disparities do exist, namely, the tangent line to the continuous phase transition curve does not coincide with that of first-order ones at the tricritical point. Landau's theory predicts an abrupt change for the heat capacity



Figure 1.37. State diagram (a pattern) of the mixture ${}^{3}\text{He} + {}^{4}\text{He}$ near its tricritical point: *D* is the curve of two liquid phase coexistence, λ is the line of continuous phase transitions (Griffiths, 1970) [Reprinted with permission from: R.B.Griffiths. Phys. Rev. Lett. 24 (1970) 715-717. Copyright © 1970 by the American Physical Society]

of the mixture c_P (as a function of T) at the tricritical point $x = x_{tc}$ (Equation 61), but experiment has revealed this change to be very small (Alvesalo et al., 1969).

Griffiths (1970) has proposed a scaling form for the free energy near the tricritical point, which eliminates the disagreement between theory and experiment. First, he built a state diagram of the given mixture in the coordinates $T-g-\zeta$, where $g = \mu_3 - \mu_4$ is the intensive parameter conjugate to the concentration x ($x = -\partial F/\partial g$), μ_3 and μ_4 are the chemical potentials of ³He and ⁴He, respectively. The quantity ζ is conjugate to the order parameter which, in this case, is the wavefunction amplitude of the hyperfluid phase $\psi = -\partial F/\partial \zeta$.

Note that ζ is a measure of a certain field inaccessible for experiment.

On this state diagram (Figure 1.38), the line of continuous λ -type transitions $(T > T_{tc})$ bounds the region A on the plane $\zeta = 0$. In case of $T < T_{tc}$, this area is bounded by the line of first-order phase transitions D. The order parameter ψ , being unambiguous by magnitude in the configurative points in this region, may be positive or negative,



Figure 1.38. State diagram (pattern) of the mixture ${}^{3}He + {}^{4}He$ in the space $T g - \zeta$. Only the plane $\zeta = 0$ is available for experiment (Griffiths, 1970) [Reprinted with permission from: Copyright © 1970 by the American Physical Society]

according to whether the plane $\zeta \to 0$ is approached from one side, or from the other one.

The surfaces B and B', located symmetrically in the region $\zeta > 0$ and $\zeta < 0$, characterize the regions of first-order phase transitions, bounded by the lines of the critical points (the dashed curves in Figure 1.38). Thus, two curves of critical points and their continuous phase transitions curve counterpart intersect at the tricritical point (Griffiths, 1970, 1973).

The λ curve is proposed to be the continuation of the curve D on the T-g (not T-x !) plane (see Figure 1.37), both the curves represented by the dependence

$$g_1(T) = g_{tc} - A(T - T_{tc}).$$
(63)

Further, assume the free energy per mole to have the form

$$f(T,g) = f_0(T,g) + f_s(T,g),$$
(64)

with $f_{\varsigma}(T,g)$ to include all the singularity of f(T,g). The function f(T,g) must satisfy

$$x = -\frac{\partial f}{\partial g} \tag{65}$$

and

$$s = -\frac{\partial f}{\partial T},\tag{66}$$

s being the entropy per mixture mole.

 f_{λ} should be chosen so that $f_{\lambda} = 0$ along $g_1(T)$ and its first partial derivatives on the λ line (not on D) are equal to zero. Introduce new variables

$$\tau = T - T_{tc} \tag{67}$$

and

$$\varphi(g,T) = g - g_1(T) \tag{68}$$

and a scaling form of f_{ς}

$$f_{\varsigma}/\varphi^{\mu+1} = h(\tau/\varphi^{\mu}) \tag{69}$$

for $\varphi > 0$, where h(z) is a properly chosen function with $-\infty < z < \infty$. For $\varphi < 0$, f_c has a similar form (Equation 69), with φ replaced by $|\varphi|$ and, in the general case, h(z) and μ chosen differently (but the index μ must fall within the range 0...1, cg. 1/2 as a first approximation).

Provided that h(z) is chosen properly, Equations 69 and 64 give a coexistence curve on the plane T vs x that resembles the experimental one (Figure 1.37). Analysis (Griffiths, 1970) has shown further agreement between theory and experiment near the tricritical point.

1.6.3. Crossover

Riedel (1972) has investigated the thermodynamic properties in the tricritical point vicinity for the general case of multicomponent systems in terms of pairwise conjugate thermodynamic parameters S and T; the ordered density of the order parameter Q and the ordering field ζ ; the disordered density n and the corresponding field g:

$$S = -\frac{\partial F}{\partial T}; \qquad Q = -\frac{\partial F}{\partial \zeta}; \qquad n = -\frac{\partial F}{\partial g}.$$
 (70)

In the case of the mixture ${}^{3}He + {}^{4}He$, Q corresponds to the wavefunction amplitude of the hyperfluid component ψ , n to the concentration of ${}^{3}He(x)$, and $g = \mu_{3} - \mu_{4}$ with ζ being beyond experiment in this case.

A hypothesis has been put forward: the asymptotic behaviour of the thermodynamic functions in the tricritical region is defined by competitive influence of the continuous transition region, on the one hand, and of the first-order transition region, on the other hand. This competition appears as the existence of the tricritical region bounded by a **crossover** (Figure 1.39).



Figure 1.39. State diagram (a pattern) near the tricritical point in the plane $\zeta = 0$. The curves $T_c(g)/T_{tc}$ and $T_1(g)/T_{tc}$ are the curves of continuous and first-order transitions, respectively. The Roman digits mark the area of first-order transitions (I), the area of continuous transitions (11), and the tricritical area (III) separated by the dashed lines of the crossover (Riedel, 1972) [Reprinted with permission from: E.K.Riedel. Phys. Rev. Lett. 28 (1972) 675-678. Copyright (c) 1972 by the American Physical Society)

In the literature, different ways are proposed for introducing auxiliary coordinate axes in order to build power functions with critical and, correspondingly, tricritical indices (Riedel, 1972; Griffiths, 1973) and to take advantage of scaling constructions.

As an example, Figure 1.39 presents "scaling axes of fields" μ_1 and μ_2 built along both the tangent and normal lines to the transition lines at the tricritical point. As the system ${}^{3}He + {}^{4}He$ possesses the continuous transition lines in the tricritical point neighbourhood with a quite sharp slope for scaling fields one assume

$$\mu_1 = \delta g = (g - g_{tc})/g_{tc}$$
 and $\mu_2 = \delta T = (T - T_{tc})/T_{tc}$. (71)

With a scale-invariant metrics of scaling fields μ_2 is measured in units of μ_2^{1/φ_t} , φ_t being a new (tri)critical index.

On the scaling field coordinates the tricritical point is defined by $\mu_{1,t} = \mu_{2,t} = 0$ and the continuous transition curve by

$$\mu_{1,c} = r_c \mu_{2,c}^{1/\varphi_t} \tag{72}$$

with a certain constant r_c . A similar relationship satisfies for the first-order transition curve as well. The geometrical distance from the configurative point (μ_1, μ_2) to the continuous transition curve $d_c(\mu_1, \mu_2)$ and to the tricritical point $d_t(\mu_1, \mu_2)$ are uniform functions of their arguments. Competition between scaling with respect to the continuous transition curve and to the tricritical point leads to a crossover condition

$$d_c \approx d_t$$
 (73)

or

ŀ

$$\mu_{1,cr} \sim \mu_{2,cr}^{1/\varphi_t},$$
(74)

that is why φ_t is called the **crossover index**.

The crossover curves are shown on Figure 1.39 by the dashed ones to separate the tricritical region (III), the continuous transition region (II), and the first-order transition one (I).

Below are scaling constructions with some thermodynamic functions (c, Q, $\partial Q/\partial \zeta$, etc.) as B and the corresponding tricritical indices (α_t , β_t , γ_t , etc.) as α_t :

$$B(\mu_1 l; \mu_2 l^{\varphi_1}) = l^{-\alpha_t} B(\mu_1, \mu_2), \tag{75}$$

given $\mu_1, \mu_2^{1/\varphi_l} \ll 1$. For the scaling parameter $l = \mu_2^{-1/\varphi_l}$ we get

$$B(\mu_1,\mu_2) = \mu_2^{-a_t/\varphi_t} W(\mu_1/\mu_2^{1/\varphi_t}).$$
(76)

This relationship holds for any configurative point trajectories near the tricritical point (W is an adjusted function).

Comparison with the results of model calculations (Blume et al., 1971) yields the crossover index at the tricritical point $\varphi_t \approx 1/2$. Just this value is used to describe the properties of polymer systems (section 4.3).

Much attention is paid to the mean field theories in the two last subsections. It should be emphasized that the mean field approximation describes many characteristic features of phase transitions, but serious disagreements with experimental data (in particular, in the critical indices values) exist.

The mean field theories are restricted by their irrealistic premises assuming the range of intermolecular forces to be infinite and neglecting the correlations among thermodynamic function (in particular, the order parameter's) fluctuations in the vicinity of T_c .

According to the thermodynamic function (Equation 1.4-33), fluctuations of the concentration of one component in solution $\langle (\Delta x_2)^2 \rangle \to \infty$ when $T \to T_c$. However, as experiment and more rigorous theories prove, the increase of both the scale and amplitude of new phase region fluctuations in the matrix of the initial phase leads to their correlations that essentially affect the behaviour of thermodynamic quantities.

With some approximation the correlations of the order parameter's fluctuations can be accounted for not leaving the mean field approach, by an additional expansion of the thermodynamic potential G (Equation 1) with new terms of a special form (section 2.5), however, methods of statistics are able to describe correlations more rigorously and consistently.

The correlation functions for thermodynamic quantities' fluctuations will be specially analyzed at the end of Chapter 2, after a detailed discussion of the special forms of the correlation functions of density and concentration fluctuations in solutions near the critical point, or rather, near the spinodal curve.

1.7. Elements of statistical physics and phase transitions

As there will be many references to the relationships of statistical physics, it seems relevant to present a brief summary of the most important formulae.

If a system with a discrete set of its possible states $\{s\}$ has a total energy $\mathcal{H}(s)$ in one of them, then the probability of the system being in the state s is expressed by the **Gibbs** canonical distribution

$$P_{s} = \frac{\exp[-\mathcal{H}(s)/kT]\Omega(s)}{\sum_{s} \exp[-\mathcal{H}(s)/kT]\Omega(s)},\tag{1}$$

where the denominator

$$Z = \sum_{s} \exp[-\mathcal{H}(s)/kT]\Omega(s)$$
⁽²⁾

is referred to as a partition function (or statistical sum) and involves all the possible states, $\Omega(s)$ is the degeneracy order, i.e. the number of states with the energy $\mathcal{H}(s)$ (including the state s itself). The **Hamiltonian** \mathcal{H} is the sum of the kinetic and potential energies and, for a system consisting of N particles, has the form

$$\mathcal{H}(\{p,q\}) = K(\{p\}) + U(\{q\}) = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m_i} + \Phi_N(\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N),$$
(3)

where $\vec{p}_i, m_i, \vec{q}_i$ are the momentum, mass, and coordinates of the *i*th particle, Φ_N denotes the interparticle interaction potential.

For systems whose energy varies quasicontinuously (i.e. the distances between energy levels are small in comparison with kT) the probability of the system being in the state with the energy between \mathcal{H} and $\mathcal{H} + d\mathcal{H}$ is expressed as

$$dP = \frac{\exp[-\mathcal{H}(\{p,q\})/kT] d\Omega}{\int \exp[-\mathcal{H}(\{p,q\})/kT] d\Omega},\tag{4}$$

 $d\Omega$ being the number of states corresponding to the energy range $[\mathcal{H}, \mathcal{H} + d\mathcal{H}]$, which is defined by

$$d\Omega = \frac{d\Gamma}{h^r},\tag{5}$$

where $d\Gamma = dp_x dp_y dp_z dx dy dz = d\{p\} d\{q\}$ is a **phase space** element, h^r is the volume of one cell of this space, r is the number of degrees of freedom, h is Planck's constant (for quantum systems). Integration in Equation 4 is taken over all the phase space. The **statistical integral** from Equation 4 (to replace the statistical sum) for a system of Nidentical (indiscernible) particles with three degrees of freedom each has the form

$$Z = \frac{1}{N! h^{3N}} \int \exp\left[-\mathcal{H}(\{p,q\})/kT\right] d\{p\} d\{q\}.$$
 (6)

Due to the structure of the Hamiltonian (3), it can be presented as

$$Z = Z_k Z_u, \tag{7}$$

where Z_u is called a configurative integral

$$Z_u = \frac{1}{N!} \int \exp\left[\frac{\Phi_N(\{q\})}{kT}\right] d\{q\},\tag{8}$$

and Z_k is usually calculated exactly. Eg. for a one-atomic gas,

$$Z = \frac{1}{N! h^{3N}} \int \exp\left[-\mathcal{H}(\{p,q\})/kT\right] \, dx \, dy \, dz \, dp_x \, dp_y \, dp_z$$

and, with due account of Equation 3.

$$Z = \left(\frac{2\pi m kT}{h^2}\right)^{3N/2} Z_u. \tag{9}$$

Thus, the calculation of statistical integral 6 reduces to the computation of the configurative integral, the latter being a very difficult problem, for the solution of which different approximate methods have been developed.

In view of Equation 1, any thermodynamic quantity, which characterizes the state of a system, is expressed in the standard way

$$\langle X \rangle = Z^{-1} \sum_{s} X(s) \exp\left[\frac{-\mathcal{H}(s)}{kT}\right] \Omega(s)$$
 (10)

(cf. with Equation 1.4 18).

Eg. the internal energy is

$$U = \langle \mathcal{H} \rangle = Z^{-1} \sum_{s} \mathcal{H}(s) \exp\left[\frac{-\mathcal{H}(s)}{kT}\right] \Omega(s) = kT^2 \frac{\partial}{\partial T} \ln Z.$$
(11)

On the other hand, the Gibbs-Helmholtz equation gives

$$U = -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T}\right) \tag{12}$$

(cf. Equations 1.1.1-31,-32, 33), which leads to

$$F = -kT\ln Z,\tag{13}$$

the most important relationship of statistical physics.

Hence, the statistical sum (or integral) for the specific system provides its full thermodynamic description.

In particular, in accordance with Equations 1.1.1-28 and 1.1.1-27,

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = kT \left(\frac{\partial \ln Z}{\partial V}\right)_T,\tag{14}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V} = k \left[\ln Z + T \left(\frac{\partial \ln Z}{\partial T}\right)_{V}\right].$$
(15)

To describe open systems (the grand canonical ensemble), a grand statistical sum, a partition function

$$\Xi = Z \sum_{N} \exp\left(\frac{\mu N}{kT}\right) = \sum_{N} \exp\left(\frac{\mu N - F}{kT}\right)$$
(16)

(N being the number of particles, μ the chemical potential per particle) and a **generalized** thermodynamic potential

$$J = F - G, \tag{17}$$

$$J = -kT\ln\Xi \tag{18}$$

are introduced.

On the other hand, the definitions of F and G (cf. Equations 1.1.1-19,-25) yield

$$J = -PV. \tag{19}$$

For a ν -component system we have (cf. Equations 1.1.1-27,-28,-59)

$$\left(\frac{\partial J}{\partial T}\right)_{V,\mu_1,\dots,\mu_\nu} = -S,\tag{20}$$

$$\left(\frac{\partial J}{\partial \mu_{i}}\right)_{T,V,\mu_{j\neq i}} = N, \quad (i = 1, 2, \dots, \nu), \tag{21}$$

$$\left(\frac{\partial J}{\partial V}\right)_{T,\mu_1,\dots,\mu_\nu} = -P, \qquad \left(\frac{\partial J}{\partial H}\right)_{T,P,\mu_1,\dots,\mu_\nu} = -M.$$
(22)

Thus, the calculation of the statistical sum (or integral) (Equations 2, 6, 16) is the basic method of statistical physics. But their direct estimation is an extremely difficult (not to say impracticable) problem. To solve it roughly, either an approximation or replacement of the system by a simpler model are used.

Many models of phase transitions are based on the Ising lattice (Figure 1.23). E.g. in case of a magnetic, every lattice site (the *i*th) contains a molecule with two possible directions of its spin ($\sigma_i = +1, -1$) (Figure 1.23a). Assume the lattice to consist of N sites. Denote the set of all the N spins as $\sigma = \{\sigma_1, \ldots, \sigma_N\}$. Combinatorial analysis indicates that there are 2^N different sets of σ and each of them describes a certain state of the system. The system Hamiltonian

$$\mathcal{H} = \mathcal{H}(\sigma_1, \sigma_2, \dots, \sigma_N) \quad \text{or} \quad \mathcal{H} = \mathcal{H}(\sigma)$$
(23)

comprises two summands

$$\mathcal{H}(\sigma) = \mathcal{H}_0(\sigma) + \mathcal{H}_1(\sigma), \tag{24}$$

where \mathcal{H}_0 reflects the contribution of intermolecular forces, and $\mathcal{H}_1(\sigma)$ is the contribution of the interactions of every spin with an external magnetic field, which is often assumed to be proportional to the magnetic field H:

$$\mathcal{H}_1(\sigma) = -II \sum_{i} \sigma_i,\tag{25}$$

with the sum taken over all the lattice sites. The corresponding statistical sum equals

$$Z(H,T) = \sum_{\sigma} \exp\left\{-\left[\mathcal{H}_{0}(\sigma) - H\sum_{\tau}\sigma_{\tau}\right] / kT\right\}.$$
(26)

It follows from section 1.5 that the thermodynamic potential (and the statistical sum, of course) must have a singularity at the phase transition point, eg. a first- or second-order break of continuity of the first derivatives with respect to the corresponding variables.

For the models describing finite size systems, the statistical sums (Equations 2, 6, 16, 26) are polynomials in their arguments, i.e. analytical functions without singularities (Landau and Lifshitz, 1964; Fisher, 1965; Rumer and Ryvkin, 1977), and no phase transition is possible. The singularity of thermodynamic functions per particle can be expected in the so-called thermodynamic limit $N \rightarrow \infty$ (Landau and Lifshitz, 1964; Fisher, 1967), which is consistent with experimental conditions.

Then, we can write the free energy per lattice site

$$f(H,T) = -kT \lim_{N \to \infty} N^{-1} \ln Z(H,T),$$
(27)

the internal energy per site

$$u(H,T) = -T^2 \frac{\partial}{\partial T} \frac{f(H,T)}{T},$$
(28)

the heat capacity

$$c_H(H,T) = \frac{\partial}{\partial T} u(H,T), \tag{29}$$

and calculate the critical indices α and α' .

The magnetization per lattice site in this model is calculated using Equations 10 and 26

$$M(H,T) = N^{-1} \langle \sigma_1 + \dots + \sigma_N \rangle$$

$$= N^{-1} Z^{-1} \sum_{\sigma} (\sigma_1 + \dots + \sigma_N) \exp \left\{ - \left[\mathcal{H}_0(\sigma) - H \sum_{\tau} \sigma_{\tau} \right] / kT \right\}$$

$$= \frac{\sum_{\sigma} (\sigma_1 + \dots + \sigma_N) \exp \left\{ - \left[\mathcal{H}_0(\sigma) - H \sum_{\tau} \sigma_{i} \right] / kT \right\}}{N \sum_{\sigma} \exp \left\{ - \left[\mathcal{H}_0(\sigma) - H \sum_{\tau} \sigma_{i} \right] / kT \right\}}$$
(30)

and

$$\chi_{II} = \frac{\partial M}{\partial H} = (NkT)^{-1} \left\{ \left\langle M^2 \right\rangle - \left\langle M \right\rangle^2 \right\},\tag{31}$$

where $M = \sum_{i} \sigma_{i}$. The last expression can be rewritten as

$$\chi_{H} = (NkT)^{-1} \left\langle (M - \langle M \rangle)^{2} \right\rangle.$$
(32)

Correlation between spins i and j is described by a correlation function

$$g_{ij} = \langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle . \tag{33}$$

Then

$$\chi_{II} = (NkT)^{-1} \sum_{ij} g_{ij}.$$
(34)

The Hamiltonian $\mathcal{H}_0(\sigma)$ in Equation 24 is a simplest one, and it takes account of the interaction between the nearest neighbours only (Baxter, 1982)

$$\mathcal{H}_0(\sigma) = -J \sum_{(ij)} \sigma_i \sigma_j, \tag{35}$$

the sum taken over all the pairs of the neighbouring sites, J is the coupling constant. When J > 0, the system of similar-directed spins (a ferromagnet) shows the lowest energy.

The statistical sum takes the form

$$Z = \sum_{\sigma} \exp\left[K\sum_{(ij)} \sigma_i \sigma_j + h\sum_{i} \sigma_i\right], \qquad (36)$$

where

$$K = J/kT \tag{37}$$

and

$$h = H/kT, (38)$$

and, for magnetization per site in the thermodynamic limit,

$$M(H,T) = -\frac{\partial}{\partial H}f(H,T) = \frac{\partial}{\partial H}\lim_{N\to\infty} N^{-1}\ln Z(h,K).$$
(39)

Systems with the Hamiltonian 36 are well studied and analyzed. In case of a twodimensional lattice in the absence of the field (H = 0) the problem has been solved exactly by Onsager and it serves as a "tuning fork" to check the results of different approximate methods that are only possible for three dimensions and two dimensions with $H \neq 0$.

The statistical sum of the form 36 is also valid for other systems described by the Ising lattice (Figure 1.23), e.g. for the system gas-liquid (Figure 1.23b). In this case, two alternative situations are predefined by either the presence or absence of a molecule at every site. The interaction between molecules is described by a pair potential $\varphi(r)$ involving the potentials of repulsion and attraction, the former being more distant-dependent than the latter.

Intermolecular interactions are a superposition of the forces of dipole, inductive, and disperse interactions. Such a composition is often approximated with the Lennard-Johns (12,6) potential

$$\varphi(r) = 4\varepsilon \left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6 \right]$$
(40)

(Figure 1.40a).



Figure 1.40. Lennard-Johns' pair potential (a) and a rectangular pit (b)

As when $r \to 0$ repulsion gets infinitely strong, two molecules can never be located at one site. Hence, we can introduce a new variable s_i : $s_i = 0$ for a free site and $s_i = 1$ for an occupied one.

Any space distribution of molecules in a lattice with N sites is defined with a set of numbers $s = \{s_1, \ldots, s_N\}$. The number of molecules in the system is

$$n = s_1 + s_2 + \dots + s_N \tag{41}$$

and the total potential energy is

$$\mathcal{H} = \sum_{(ij)} \varphi_{ij} s_i s_j, \tag{42}$$

the sum taken over all the site pairs, and $\varphi_{ij} = \varphi(r_{ij})$ is the interaction energy for the molecules at the *i*th and *j*th sites.

The grand canonical sum is written as

$$\Xi = \sum_{s} \exp\left[\frac{(n\mu - \mathcal{H})}{kT}\right]$$
(43)

and

$$P = kT \left(\frac{\partial \ln \Xi}{\partial V}\right)_{T,\mu}.$$
(44)

It appears that the main features of the liquid-gas phase transition do not depend significantly on the details of $\varphi(r_{ij})$, and it can be given the simplest form, namely, a potential pit with the depth ε (Figure 1.40b), i.e.

$$\varphi_{ij} = \begin{cases} \infty & \text{when } i \neq j, \\ -\varepsilon & \text{if } i \text{ and } j \text{ are the nearest neighbours,} \\ 0 & \text{otherwise.} \end{cases}$$
(45)

The Hamiltonian of the system takes the form

$$\mathcal{H} = -\varepsilon \sum_{(ij)} s_i s_j, \tag{46}$$

where the sum is taken over the pairs of the nearest neighbours.

To reduce the gas-liquid problem to the previous one of ferromagnet (Baxter, 1982), σ_i and s, should be related by

$$\sigma_1 = 2s_1 - 1. \tag{47}$$

If every site has ν neighbours, there are $n\nu/2$ pairs of the nearest neighbours. With due account of this fact after elimination of $n, \mathcal{H}, s_1, \ldots s_n$ (Equations 50, 43, 46, 47) we get

$$Z = \sum_{\sigma} \exp\left\{ \left[\varepsilon \sum_{(ij)} \sigma_i \sigma_j + (2\mu + \varepsilon \nu) \sum_i \sigma_i + N\left(\frac{\varepsilon \nu}{2} + 2\mu\right) \right] \middle/ 4kT \right\}.$$
 (48)

With the exception of a negligible factor, this sum is the same as the statistical sum of a magnetic (Equations 36-38) with the conversion glossary

$$J = \frac{\varepsilon}{4}, \quad H = \frac{2\mu + \varepsilon\nu}{4}.$$
(49)

Using the corresponding expressions for thermodynamic quantities, one obtains equivalent formulae (Baxter, 1982)

$$\varepsilon = 4J,$$
 (50)

$$\mu = 2H - 2\nu J,\tag{51}$$

$$P = -\frac{1}{2}\nu J + H - f,$$
 (52)

$$\varrho = \frac{1}{2}(1+M),\tag{53}$$

$$\left(\varrho \frac{\partial \varrho}{\partial P}\right)_T = \frac{1}{4}\chi_T.$$
(54)

The discussion on the universal description of phase transitions in different systems is continued in Chapter 2, section 2.5.

1.8. State equation of real gas

The theory of real gas plays a significant role in creating the theory of macromolecules. The so-called long-range interactions between segments in a macromolecule have, as a matter of fact, the same nature that the intermolecular interactions in real gas but are complicated with segments being linked in a chain and the presence of solvent molecules.¹

In this connection it seems to be expedient to present the main points of deducing the state equation of real gas (Croxton, 1974).

First, assume the intermolecular interaction potential Φ_N from Equation 1.7-8 to be a pair additive function:

$$\Phi_N(\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N) = \sum_{i < j}^N \sum_{j < j}^N \varphi(|\vec{q}_i - \vec{q}_j|),$$
(1)

where $\varphi(|\vec{q_i} - \vec{q_j}|)$ is the interaction potential for the *i j* pair of particles. Hence,

$$\exp\left(-\frac{\Phi_N}{kT}\right) = \prod_{i>j}^N \prod_{j=j}^N \exp\left[-\frac{\varphi(r_{ij})}{kT}\right].$$
(2)

Second, introduce a Mayer function

$$f(r_{ij}) = \exp\left[-\frac{\varphi(r_{ij})}{kT}\right] - 1, \tag{3}$$

which turns out to be a short-range one, being nonzero in the range of pair potential and practically vanishing until two or more molecules approach each other quite closely. Besides, the function f_{ij} is bounded and tends to -1 when $r_{ij} \to 0$, since $\varphi(r_{ij})$ gets very large (> 0) due to repulsion forces.

Using Equation 3, we rewrite the statistical sum (Equations 1.7-7, 9, -8)

$$Z = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \int \cdots \int \prod_{i=j} \prod_{j=1}^{N} (1+f_{ij}) d1 \dots dN,$$
(4)

¹See Eskin's papers which are, however, questionable. Editor's note

where $f \cdots f d1 \dots dN$ denotes integration over all the positions of molecules $1, \dots, N$. Taylor series expansion gives

$$\prod_{n \ge i > j \ge 1} (1 + f_{ij}) = 1 + \sum_{i} \sum_{j} f_{ij} + \sum_{i} \sum_{j} \sum_{k} \sum_{l} f_{ij} f_{kl} + \cdots$$

$$+ \sum_{i} \sum_{j} \sum_{k} \sum_{l} f_{ij} f_{kl} \cdots f_{mn} \cdots + \cdots$$
(5)

with the common term being the sum over all the connected products of the same order n.

The terms of the series can be rearranged and represented through irreducible diagrams of the following form:

and so on.

Each irreducible diagram is defined by a graph where each point (molecule) is connected with, at least, two other points by an f bond. An exceptional case of two interacting molecules is introduced to make the pattern complete as the smallest irreducible diagram. To clarify the last term, we present two diagrams

which are not irreducible, for the former can be decomposed into two two-particle ones and the latter into a three-particle and a two-particle one with a break in each initial diagram.

The number of topologically different diagrams for every *n*-particle subset increases with n sharply. Eg. there exist 3 four-particle, 10 five-particle, and 56 six-particle irreducible diagrams.

Each diagram in a given subset has its weight depending on the frequency of its appearance in the series (Equation 5).

Combinatorial algebra required to build up the general expression of Equation 5 is very sophisticated.

In order to allow for topologically indiscernible permutations of n molecules, the nparticle subset has to be divided by n!. Indeed, any cyclic permutation of the corners in the three-particle subset

produces' no topologically discernible diagrams.

Thus, the system's statistical sum can be written in the form of cluster (group) expansion

$$Z = \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \int \cdots \int \left\{1 + \frac{N!}{2!(N-2)!} \circ - \circ + \frac{N!}{3!(N-3)!}\right\} ds$$
(7)

1.8. State equation of real gas

$$+ \frac{N!}{4!(N-4)!} \left[3 \underbrace{3}_{-} + 6 \underbrace{3}_{-} + \underbrace{3}_{-} \underbrace{3}_{-} + \underbrace{3}_{-} \underbrace{3}_{-} + \underbrace{3}_{-} \underbrace{3}$$

The coefficients for different subsets

$$\frac{N!}{(N-2)!}$$
, $\frac{N!}{(N-3)!}$, $\frac{N!}{(N-4)!}$

mean the number of ways to build up every n-particle diagram in a N-molecule system. Integration of Equation 7 yields

$$Z = \left(\frac{2\pi m kT}{h^2}\right)^{3N/2} \left\{ V^N + \frac{N}{2!} (N-1) V^{N-1} \bullet \bullet \right.$$

$$\left. + \frac{N}{3!} (N-1) (N-2) V^{N-2} \bullet + \cdots \right\},$$
(8)

where the **cluster integrals** are defined as follows:

$$\underbrace{\bullet}_{1} \equiv \int \circ - \circ d\vec{2} = \int f_{12} d\vec{2} = \int \left\{ \exp\left[-\frac{\varphi(1,2)}{kT}\right] - 1 \right\} d\vec{2}, \tag{9}$$

$$\bigwedge_{1=2}^{3} \equiv \int \bigotimes_{1=2}^{N} d\vec{2} \, d\vec{3} = \iint f_{12} f_{23} f_{31} \, d\vec{2} \, d\vec{3}, \tag{10}$$

$$\prod_{1=2}^{4} \equiv \int \sum_{1=2}^{3} d\vec{2} \, d\vec{3} \, d\vec{4} = \iiint f_{12} f_{13} f_{14} f_{23} f_{34} \, d\vec{2} \, d\vec{3} \, d\vec{4}.$$
 (11)

Then

$$\ln Z = N \ln V + \ln \left\{ 1 + \frac{N(N-1)}{2! V} + \frac{N(N-1)(N-2)}{3! V^2} + \cdots \right\}$$
(12)
+ $\frac{3N}{2} \ln \left(\frac{2\pi m k T}{h^2} \right).$

The state equation is defined as usual (see Equation 1.7-14)

$$P = kT \left(\frac{\partial \ln Z}{\partial V}\right)_T.$$
(13)

As N is a big number, N^2 can be written instead of N(N-1). Besides, $\ln(1+x) \approx x$ when $x \ll 1$.

From Equations 12 and 13, it follows that

$$P = \frac{NkT}{V} - \frac{N^{2}kT}{2! V^{2}} \longrightarrow -\frac{2N^{3}kT}{3! V^{3}} \bigtriangleup - \cdots$$

$$= \frac{NkT}{V} \left\{ 1 - \frac{N}{V} \frac{1}{2!} \longrightarrow -\frac{N^{2}}{V^{2}} \frac{1}{3!} \bigstar - \cdots \right\},$$
(14)

which is a virial (force, from the Latin vires=forces) expansion:

$$P = \frac{NkT}{V} \left\{ 1 + \frac{N}{V} B_2(T) + \frac{N^2}{V^2} B_3(T) + \cdots \right\},$$
(15)

where

$$B_2(T) = -\frac{1}{2!} \bullet \bullet,$$
$$B_3(T) = -\frac{1}{3!} \bullet \bullet$$

are virial coefficients.

By comparing Equations 14 and 15, we get the cluster (group) expansion for P:

$$\frac{P}{\rho kT} = 1 - \sum_{l=2} \frac{l-1}{l} \beta_l \rho^{l-1},$$
(16)

where $\rho = N/V$ and

$$\beta_l = \frac{1}{(l-1)!} \int \cdots \int \left(\sum \prod f_{ij}\right)_\beta d\vec{2} \cdots d\vec{l},\tag{17}$$

the sum of the products f_{ij} is taken over the irreducible diagrams, and

$$B_l = -\frac{l-1}{l}\beta_l.$$

The second and next terms in the virial expansion have a clear physical meaning, pointing to a simultaneous interaction of 2, 3,... molecules. This, however, is not to say that the groups are stable. In fact, they constantly appear and disappear as a result of collisions. The virial expansion describes the situation on the average, for a long period of time.

The probability of n-particle collisions increases with gas density, and the gas properties diverge from those of ideal gas more and more.

It is the second virial coefficient $B_2(T)$ that is most significant in studying the properties of molecules. Different considerations of interactions between the molecules lead to the expression

$$B_2(T) = \frac{1}{2} \int_0^\infty \left\{ \exp\left[\frac{\varphi(r)}{kT} - 1\right] \right\} d\vec{r},$$
(18)

and it follows that the exponential function is close to 1 at high temperatures and $B_2(T) \rightarrow \beta'_{ex}$ (the molecule excluded volume).

At low temperatures, conversely, $B_2(T) \rightarrow -\infty$ since $\varphi(r) < 0$ while the molecules collide.

One can conclude from the above that some temperature must exist at which $B_2(T) = 0$ (a Boyle temperature), and the gas behaves as an ideal one due to compensation of the repulsion and attraction components in the interaction potential.



Figure 1.41. Temperature dependence of the second, third, fourth, and fifth virial coefficients for the Lennard-Johns' (12,6) potential (Rowlinson, 1971) [Reprinted from: J.S.Rowlinson Physics of Simple Liquids. Copyright © 1971, with kind permission from Elsevier NL, Science · --Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands]

The temperature dependence of several first virial coefficients is calculated for the Lennard-Johns (12,6) model potential (Equation 1.7-40). Figure 1.41 contains reduced virial coefficients B_j/b^{j-1} (where b is the excluded volume of hard spheres, see Equation 1.2-38) as functions of the reduced energy $\lg(kT/\varepsilon)$ (ε is the minimum on the potential curve, Figure 1.40a).

These theoretical dependences are in good agreement with the experimental data for simple molecules (Croxton, 1974).

Chapter summary

1. The definitions of the main thermodynamic values are given, as well as the stability criteria for one- and multiphase states of a multicomponent system.

2. The thermodynamic potentials, being a system's state functions of the corresponding (natural) parameters, are of special importance in the system state description, their partial derivatives being the parameters of the system as well. The equalities between the second mixed derivatives are a property of the state functions and lead to relationships between the system parameters (the Gibbs-Helmholtz equations). Hence, once any thermodynamic potential (usually, the Gibbs or the Helmholtz one) has been evaluated, by means of either simulation or experiment, this means the complete characterization of the thermodynamic properties of the system.

3. The topological properties of both the binodal and spinodal as second-order curves in the plane $\{T, x_2\}$ (P = const) for a two-component system, and of both the binodal and spinodal surfaces in the ν -dimensional space $\{T, x_1, \ldots, x_{\nu-1}\}$ $(P = const, \sum_{i=1}^{\nu} x_i = 1)$ for the ν -component system are discussed. The common point of the binodal and spinodal at their joint maximum (or minimum) is the **critical point** of a binary system.

The common line of the binodal and spinodal surfaces defines the critical state for a ν -component system.

4. The structural (morphological) state of a solution is characterized by fluctuations of the concentration of each component. With the two-component system, it is convenient to use the mole fraction of the second component x_2 .

A spontaneous change in concentration by the value $\Delta x_2 = x_2 - \bar{x}_2$ occurs as a result of chaotical thermal motion of molecules within a local space of the extent Δl for each direction. The level of concentration fluctuations is characterized by the **mean scale** $\overline{\Delta l}$ and the mean square amplitude $(\overline{\Delta x_2})^2$. If the spontaneously arisen concentration fluctuations of any scale and amplitude inevitably tend to disappear, this means the solution is **absolutely stable**. It shows such a property if its configurative point is anywhere **except** the binodal dome.

In the case of two-phase equilibrium, any configurative point inside the binodal curve corresponds to two phases (two solutions) in **equilibrium**, their concentrations x_{2I} and x_{2II} determined by the abscissae of the intersection points of the isotherm T = const (the line parallel with the x-axis) and the binodal curve. With the configurative point moving from the one-phase region under the binodal dome, the way for approaching the equilibrium state essentially depends on whether the configurative point is inside the spinodal or between it and the binodal.

In the first case, the solution will loose its stability practically at once: the existing concentration fluctuations of any (even of the smallest) scale and amplitude grow in amplitude and further turn to the fragments (elements) of a new phase. The fragments of a new phase then coalesce or grow, the bigger ones at the expense of the smaller ones (according to Ostwald), depending on the mechanism of secondary growth. The initial period of such evolution mechanism is referred to as the **spinodal separation**. This process culminates in establishing the phase equilibrium.

In the second case, the solution is stable with respect to relatively small concentration fluctuations (by scale and amplitude, according to the model considered in this chapter), but unstable with respect to large ones.

Since large fluctuations arise much more rarely than small ones, before they have arisen, the system corresponds to the **initial state** of solution which is called the **metastable** state (originates from the Greek $\mu c \tau \alpha$, i.e. near, by). The time the system has been in this state is defined by the **induction period** τ , its value depending on the relative position of the configurative point with respect to the binodal and spinodal, as well as on the properties of the specific system.

As the concentration of a certain component in a local region increases, it must decrease in the nearest neighbourhood. A gradient of concentration arises between this layer, depleted of the component, and the matrix of the system, which causes the process of diffusional transport of the component from the matrix to the nearest neighbourhood of the particle being formed. Thus, the conveyance of substance takes place for further growth of the particle. Such a mechanism for growth of new phase particles is called **nucleation**, or **diffusion controlled growth**.

At the second stage of the process, either the particles are being united (coalesced, coagulated) or big particles are growing at the expense of the small ones (Ostwald's ripening) until the two-phase equilibrium is established.

1. Chapter summary

Phase transitions through the metastable state are characteristic of first-order phase transitions.

Phase transitions in the absence of the metastable state of the original phase are classified as **continuous transitions**.

In these cases, the development of high-level (by scale and amplitude) fluctuations of the order parameter (the latter being related to the new phase structure) during the configurative point approach to the transition temperature (the **critical temperature** T_c , in a particular case) is the "preparation" of the system to the transition. That is why in the two-component system the configurative point, approaching the critical point, is accompanied by the enhancement of the concentration fluctuations.

In section 1.5 are given the traditional definitions for the kinds of phase transitions through the special points (the continuity breaks) of the thermodynamic potential derivatives with respect to the variables, which are characteristic for them.

The functional dependence of the thermodynamic potentials of the order parameter is specific for each type of phase transitions, which is widely used for the identification of the type of the phase transition.

The phase transitions, resulting in an increase in the number of phases in a system, should also be classified as the phase separations.

5. Near the temperature of the phase transition of the continuous type T_c (the critical temperature), the thermodynamic functions characterizing the system properties (in the first place, the functions of the system's response to changes in the external conditions, such as heat capacity, susceptibility, correlation length of the order parameter fluctua tions ξ , phase separation region amplitude $(x_{211} - x_{21})$ can be approximated with power functions $c_V \sim \varepsilon^{-\alpha}$, $\chi \sim \varepsilon^{-\gamma}$, $\xi \sim \varepsilon^{-\nu}$, $(x_{211} - x_{21}) \sim \varepsilon^{-\beta}$, where $\varepsilon = (T - T_c)/T_c$, and α , γ , ν , β are the critical indices.

In the following chapters (especially in Chapter 5), it will be noted that the possibility of approximating the thermodynamic functions as power ones is connected with the scaling invariance of systems.

The corresponding theoretical approaches lead to analytical expressions for the critical indices and to explicit relationships between them.

The closeness of the experimental values of the critical indices and the theoretical ones shows the quality of a certain version of the theory.

6. In Landau's phenomenological theory of the mean field the thermodynamic potential G (or F) is considered as a series in terms of the order parameter Q. The series coefficients, generally, depend on temperature and pressure. Depending on the presence of the series term with a certain power n (Q^n), on the coefficients values, and on the relationships between them, the thermodynamic potential assumes a functional dependence being characteristic for the first-order transitions, transitions of the continuous type or for the first-order ones of the near-continuous type.

The given approach has a universal meaning, and any researcher is to find the expression of the series coefficients via the molecular parameters of a certain system. It depends on the coefficient values and on the relationships between them, the lines of the first-order transitions or of the continuous-type ones can be observed in the coordinates P vs T.

At the configurative point where the first-order transition line turns to the continuoustype transition line, the system has special properties. This point is referred to as the tricritical one. There may be another version, where three lines of the continuous-type transitions are converged in the tricritical point.

There is a tricritical region on the state diagram T vs g (g is an intensive value (field), see Equation 1.6-70) near the tricritical point, it has boundary lines of **crossover** with the region of the first order transitions, on the one hand, and with the region of the continuous-type transitions, on the other hand.

In the tricritical region, the power functions approximating the thermodynamic functions have characteristic tricritical indices differing from the critical ones.

The restrictions of the given version of the mean field theory are due to neglecting the correlation between fluctuations of the thermodynamic functions, especially of the order parameter, these fluctuations contributing essentially to the system properties in the critical region.

In terms of microspace, the restrictions of the mean field theories are due to an irrealistic premise of the intermolecular interactions range being infinite.

7. The main formulae of statistical physics are given: the expressions of the thermodynamic functions via the partition function having been taken over all the possible states of the system with Hamiltonian $\mathcal{H}(s)$ representing the sum of the kinetic energy of the system and the potential one.

Hence, having written the partition function for a certain system, one achieves its complete thermodynamic description.

The models of many physical systems are based on a lattice (see Figure 1.23). With the models of finite-size systems the partition function is expressed in terms of polynomials in its arguments, i.e. in terms of non-singularity functions.

That is why no phase transition can occur in a finite system. The singularity of the thermodynamic functions per particle, which is the condition of phase transitions, should be expected in the so-called thermodynamic limit $N \to \infty$, corresponding to the experimental conditions.

Applying the universal lattice model enables one to describe the thermodynamic properties of different physical systems, using the same mathematical expressions and the glossary of variables (eg. Equations 1.7-49...53).

8. The forces of intermolecular interactions are the superposition of the dipole, induction, and disperse interaction forces. They can be expressed as a united function of interactions, such as the sum of two power functions Equation 1.7-39 (the Lennard-Johns potential), the potential pit, etc.

The state equation of real gas in its virial expansion is a series in terms of the gas density powers (N/V) with the virial coefficients proportional to the cluster integrals (Equations 1.8-9...12).

Chapter 2

Fluctuations, Light Scattering and Diffusion

2.1. Light scattering in matter. Main concepts and definitions

An ideally homogeneous medium does not scatter light on the average. Every local space element in such a medium has another one in any direction, which provides the ray path length difference of both the scattered waves to be equal to a halfwave length $\lambda/2$. So, interference extinguishes both the scattered waves.

Hence, light scattering, in principle, can be observed in an inhomogeneous medium only. The causes and character of heterogeneities may be various: an ensemble of particles of one phase in another phase (colloidal, disperse, heterogeneous systems), density fluctuations in gases (vapours) and liquids, concentration fluctuations in multicomponent one-phase systems (solutions).

2.1.1. Rayleigh scattering

Dielectric particles, whose size is much less than the wavelength λ , are the simplest kind of heterogeneities concerning their interaction with light.

Let us consider a case when homogeneous isotropic particles with the **dielectric con**stant ϵ_2 (or with the **refractive index**, or the **index of refraction**, $\mu_2 = \sqrt{\epsilon_2}$) are dispersed in a medium with $\epsilon_1 = \mu_1^2$.

Assume that every particle scatters light irrespective of others and that an incident wave has the same effect on all the particles in the system. Due to its smallness, all the electrons of a particle are in the incident wave's field of equal strength at any moment, and all the set of charges can be regarded as an **induced dipole** \vec{p} proportional to the field strength \vec{E} of the incident wave:

$$\vec{p} = \alpha_p \vec{E},\tag{1}$$

where α_p is called **particle polarizability**. This oscillating dipole, with the frequency matching that of the incident wave ω , is an **elementary dipole**, i.e. a source of secondary (scattered) waves.

Place the particle to the origin of the coordinate system xyz. We will observe scattered light in the plane yOx (plane of scattering). The angle between the incident wave direction and the scattered wave direction will be referred to as a scattering angle ϑ (Figures 2.1–2.5).



Figure 2.1. On the definition of a scattering space V; **R** is a receiver of scattered light; $d\Omega$ is a solid angle element; V_{lum} is a luminous space; **K** is a vessel with scattered medium, **D** are diaphragms



Figure 2.2. Schematic illustration of scattering of horizontally polarized light



Figure 2.3. Radiation diagram in the case of horizontally polarized incident light



Figure 2.4. Schematic illustration of scattering of vertically polarized incident light

Figure 2.5. Radiation diagram in the case of vertically polarized incident light

Let the particle be illuminated by linearly polarized light from negative x values with its plane of polarization matching the plane of scattering (horizontally polarized light) with the electric field strength vector

$$E_y = E_{0y} \cos \delta_x \equiv E_{0y} \cos(\omega t - k_0 x), \tag{2}$$

where E_{0y} and δ_x are the **amplitude** and **phase** of the incident wave, $k_0 = 2\pi/\lambda_0$ is its wave number, λ_0 is the wavelength in vacuum, $\omega = 2\pi\nu = 2\pi/T$ (ν and T are the frequency and period of oscillations).

This expression is often written as a complex quantity

$$\tilde{E}_y = \hat{E}_{0y} \exp(i\delta_x),\tag{3}$$

 \tilde{E}_{0y} being a complex number in the general case.

The electric field strength vector of the scattered light at long distances from the oscillating dipole (in the wave zone) is given by (Rayleigh, 1881; Volkenshtein, 1951; Fabelinski, 1965; Kerker, 1969; Sivukhin, 1980)

$$\vec{E}_{s} = \frac{1}{c^{2/3}} [\vec{l} [\vec{l} \, \vec{p}]]_{t-l/v},\tag{4}$$

where \vec{l} is the radius vector from the particle to the point of observation. The subscript points to the fact that the values of \vec{p} and its derivatives with respect to time are taken

at an earlier instant of time t' = t - l/v since any scattered wave propagates with the velocity v; c is the velocity of light in vacuum.

In the case of a sinusoidal incident wave (Equation 2 or 3), the dipole oscillates as

$$\vec{p} = \vec{p}_0 \exp(i\omega t) \quad (x = 0),$$

with the electric field strength vector of the scattered wave

$$\vec{E}_{s} = -\frac{k_{0}^{2}}{l^{3}} \left[\vec{l} \left[\vec{l} \, \vec{p}_{0} \right] \right] \exp(i(\omega t - kl)), \tag{5}$$

which, in the case of horizontally polarized incident light, leads to

$$E_{s|l} = -\frac{k_0^2}{l} E_{0y} \alpha_p \cos \vartheta \cos(\omega t - kl) = -E_{s,0|l} \cos(\omega t - kl)$$
(6)

or

$$E_{s|l} = -E_{s,0|l} \exp(i(\omega t - kl)),$$

where $k = 2\pi/\lambda$, λ is the wavelength in the medium: $\lambda = \lambda_0/\mu_1 = \lambda_0/\sqrt{\epsilon_1}$. In the chosen coordinate system, the angle ϑ is complementary to the angle β between the dipole \vec{p}_0 and \vec{l} , so $\sin \beta = \cos \vartheta$.

Experiment measures the **intensity of light**, i.e. the radiation energy per unit area per unit time. According to the expression for the Poynting vector, the intensity is proportional to the squared amplitude of the electric field strength vector. As the proportionality coefficient is the same for both the incident and scattered beam, then

$$I_{0y} = AE_{0y}^2 \quad \text{and} \quad i_{||} = AE_{s,0||}^2$$
(7)

or, in the complex form (see Equation 3),

$$I_{0y} = A \hat{E}_{0y} E_{0y}^{*}, \tag{8}$$

with E^*_{0y} to denote the quantity complex conjugate to \hat{E}_{0y} .

Equations 6 and 7 allow us to write the scattered light intensity for one scattering particle and horizontally polarized incident light with the intensity I_{0y} :

$$i_{||} = \frac{k_0^4}{l^2} I_{0y} \alpha_p^2 \cos^2 \vartheta.$$

The receiver measures the intensity I_{\parallel} of light scattered on all the particles inside a scattering space V, which is cut by the receiver's solid angle from the luminous space V_{lum} (Garrabos et al., 1978), see Figure 2.1

$$I_{||} = Ni_{||} = N_2 Vi_{||} = I_{0y} \frac{k_0^4 N_2 V}{l^2} \alpha_p^2 \cos^2 \vartheta = I_{0y} \frac{16\pi^4 \alpha_p^2}{\lambda_0^4 l^2} N_2 V \cos^2 \vartheta,$$
(9)

 N_2 being the number of particles per unit volume.

Define a radiation diagram, or polar diagram of the scattered light intensity, as the locus of the vector ends, where the vectors originate from the scattering space centre and have their lengths equal to the scattered light intensity in this direction. In the case of horizontally polarized incident light, the radiation diagram is shown in Figure 2.3 (Equation 9).

In the case of vertically polarized incident light with its plane of polarization perpendicular to the plane of scattering (Figure 2.4), Equation 5 takes the form

$$E_{s\perp} = -\frac{k_0^2}{l} E_{0z} \alpha_p \cos(\omega t - kl) = E_{s,0\perp} \cos(\omega t - kl), \qquad (10)$$

with

$$E_{s,0\perp} = -\frac{k_0^2}{l} E_{0z} \alpha_{\mathfrak{p}},\tag{11}$$

and, further, by analogy with Equation 9,

$$I_{\perp} = I_{0z} \frac{16\pi^4}{\lambda_0^4 l^2} \alpha_p^2 N_2 V.$$
⁽¹²⁾

Figure 2.5 presents the radiation diagram. The angle between the dipole \vec{p}_0 and \vec{l} is $\beta = 90^\circ$ at any scattering angle.

A beam of unpolarized (natural) light with the intensity I_0 can be represented as a superposition of two linearly polarized beams, namely, a horizontally polarized one with $I_{0y} = I_0/2$ and a vertically polarized one with $I_{0z} = I_0/2$. Then, the scattered light intensity I_y will be the sum of Equations 9 and 12

$$I_{\vartheta} = I_{\perp} + I_{\parallel} = I_0 \frac{8\pi^4}{\lambda_0^4 l^2} \alpha_p^2 N_2 V (1 + \cos^2 \vartheta)$$
(13)

with its radiation diagram shown in Figure 2.6.



Figure 2.6. Radiation diagram in the case of unpolarized incident light

Electrostatics gives us the polarizability of spherical particles (Sivukhin, 1980, 1983)

$$\alpha_p = \frac{3(\epsilon_2 - \epsilon_1)\epsilon_1}{4\pi(\epsilon_2 + 2\epsilon_1)}v_p,$$

where v_{p} is the particle volume. Then,

$$l_{\vartheta} = I_0 \frac{9\pi^2 v_p^2}{\lambda^4 l^2} \left(\frac{\mu_2^2 - \mu_1^2}{\mu_2^2 + 2\mu_1^2}\right)^2 N_2 V \frac{1 + \cos^2 \vartheta}{2}.$$
 (14)

Since Equation 14 determines the power of light energy per unit area, a solid angle unit receives

$$\frac{\text{light energy}}{\text{for s from }\Delta\Omega} = \frac{\text{light energy }l^2}{\text{for s from }\Delta\sigma} = I_{\vartheta}l^2.$$
(15)

The distinctive features of Rayleigh scattering are: $I_{\vartheta} \sim \lambda^{-4}$; the radiation diagram being symmetrical with respect to $\vartheta = 90^{\circ}$ (the **asymmetry ratio** $z = I_{45^{\circ}}/I_{135^{\circ}} = 1$); scattered light being vertically polarized at $\vartheta = 90^{\circ}$ and partially polarized in the range $0 < \vartheta < 180^{\circ}$ with a **depolarization coefficient**

$$\Delta_{\vartheta} = \frac{I_{\parallel}}{I_{\perp}} = \cos^2 \vartheta. \tag{16}$$

The scattered light techniques determine either **Rayleigh's ratio** R_{ϑ} (with nephelometers) (Fabelinski, 1965; Eskin, 1973) or **turbidity** τ (with colorimeters and spectrophotometers). The former quantity

$$R_{\vartheta} = \frac{I_{\vartheta}l^2}{I_0V}, \, \mathrm{cm}^{-1} \tag{17}$$

means the intensity of light scattered at angle ϑ from a unit scattering space at a unit distance from the scattering space centre per unit intensity of the incident beam.

According to Equations 15 and 17, the Rayleigh ratio means the light energy power scattered at an angle ϑ by a unit space of the scattering medium into a unit solid angle per unit intensity of the incident beam.

It follows from Equation 13 for Rayleigh's particles that

$$R_{\vartheta} = \frac{8\pi^4}{\lambda_0^4} \alpha_p^2 N_2 (1 + \cos^2 \vartheta), \tag{18}$$

$$R_{90} = \frac{8\pi^4}{\lambda_0^4} \alpha_p^2 N_2,\tag{19}$$

$$R_{\vartheta} = R_{90}(1 + \cos^2 \vartheta), \tag{20}$$

$$R_{90} = \frac{9\pi^2}{2\lambda^4} \left(\frac{\mu_2^2 - \mu_1^2}{\mu_2^2 + 2\mu_1^2}\right)^2 v_p^2 N_2.$$
⁽²¹⁾

In spectrophotometers, a parallel light beam (with the cross-section S) traverses a rectangular cell of length l_0 . At a certain distance x from the cell's face, the intensity I_x in an elementary layer dx decreases owing to scattering (or absorption) by dI. Then, for optically non-interacting particles and in the absence of multiple scattering,

$$-\frac{dI}{I_x} \sim dx, \qquad \text{i.e.} \qquad -\frac{dI}{I_x} = \tau \, dx.$$
 (22)

The factor τ is called **turbidity**, or scattering index. For absorption,

$$-\frac{dI}{I_x} = \mathcal{R} \, dx,\tag{23}$$

æ is an absorption index. And, in the case of both scattering and absorption,

$$-\frac{dI}{I_x} = (\tau + \infty) \, dx = C \, dx, \tag{24}$$

C is an attenuation index, or extinction coefficient (van de Hulst, 1957).

Integration of Equations 22-23 with respect to I_x (from I_0 to I) and with respect to x (from 0 to l_0) results in Buger's equations

$$I = I_0 \exp(-\tau I_0),$$
(25)

$$I = I_0 \exp(-\omega I_0), \tag{26}$$

and

$$I = I_0 \exp(-Cl_0),\tag{27}$$

where I is the outlet light intensity, whereas I_0 is the inlet one. It follows that

$$\tau \quad (\text{or} \quad \mathcal{X}, \text{or} \quad C) = \frac{D \ln 10}{l_0}, \tag{28}$$

where $D = \lg(I_0/I)$ is called **optical density**, which is measured immediately with spectrophotometers and colorimeters.

On multiplying both the nominator and denominator by S, Equation 22 gives the physical meaning of turbidity τ :

$$\tau = -\frac{dIS}{I_x S \, dx} = -\frac{dIS}{I_x \, dV}, \, \mathrm{cm}^{-1}, \tag{29}$$

and

$$au = -S \, dI$$
 at $I_x = 1 \, \frac{\mathrm{erg}}{\mathrm{s} \cdot \mathrm{cm}^2}$ and $dV = 1 \, \mathrm{cm}^3$. (30)

You see that τ characterizes the decrement of light energy for 1s from the passing beam due to all-directions scattering on particles in a 1 cm³ volume. Thus, the turbidity τ means the energy of light scattered by a unit space for a unit time per unit intensity of the incident beam.

The definitions of R_{ϑ} and τ provide their relationship:

$$\tau = \int_{\substack{\text{over the whole}\\\text{solid angle}}} \int_{R_{ij}} R_{ij} \, d\Omega, \tag{31}$$

where $d\Omega$ is a solid angle element. For Rayleigh's particles,

$$\tau = R_{90} \int\limits_{\varphi} \int\limits_{\vartheta} (1 + \cos^2 \vartheta) \frac{d\sigma}{l^2} = R_{90} \int\limits_{0}^{2\pi} d\varphi \int\limits_{0}^{\pi} d\vartheta (1 + \cos^2 \vartheta) \sin \vartheta = \frac{16\pi}{3} R_{90}.$$
(32)

In view of Equation 19,

$$\tau = \frac{128\pi^5}{3\lambda_0^4} \alpha_p^2 N_2,\tag{33}$$

and of Equation 21,

$$\tau = \frac{24\pi^3}{\lambda^4} v_p^2 \left(\frac{\mu_2^2 - \mu_1^2}{\mu_2^2 + 2\mu_1^2}\right)^2 N_2 \tag{34}$$

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$$\tau = \frac{24\pi^3}{\lambda^4} v_p^2 \left(\frac{m^2 - 1}{m^2 + 2}\right)^2 N_2,\tag{35}$$

where $m = \mu_2/\mu_1$ is the relative refractive index.

Introduce a relative particle size α . For spherical particles, α is the ratio of the particle perimeter to the wavelength

$$\alpha = \frac{2\pi r}{\lambda} = \frac{2\pi r \mu_1}{\lambda_0}.$$
(36)

The ratio

$$\frac{\tau}{N_2} = R(\alpha, m), \, \mathrm{cm}^2 \tag{37}$$

defines an **optical cross-section** of a particle, i.e. the area, which contains as much energy of the incident beam per unit time as scattered by a particle:

$$I_0 R(\alpha, m) = R(\alpha, m), \operatorname{erg/s} \quad \operatorname{at} \quad I_0 = 1 \operatorname{erg/s} \cdot \operatorname{cm}^2,$$
(38)

i.e. $R(\alpha, m)$ is numerically equal to the light energy (per unit time) scattered by the particle on a unit incident beam intensity basis.

A scattering coefficient, or efficiency factor is defined as the ratio of the optical and geometrical cross-sections

$$K(\alpha,m) = \frac{R(\alpha,m)}{\pi r^2}.$$
(39)

It indicates how effectively the optical cross-section (the optical screen) withdraws (and scatters) the energy of light beam (and scatters it) in comparison with a geometrical screen

$$K(\alpha,m) = \frac{R(\alpha,m)I_0, \quad \text{erg/s}}{\pi r^2 I_0, \quad \text{erg/s}}.$$
(40)

Equations 36 and 39 yield

$$\tau = N_2 K(\alpha, m) \pi r^2. \tag{41}$$

In view of Equation 37, τ is referred to as a **full optical cross-section** (in the atmosphere optics literature), and Rayleigh's ratio R_{δ} is a **differential optical cross-section**

$$rac{d au}{d\Omega} = R_{artheta}$$

(see Equation 31).

2.1.2. Rayleigh-Debye scattering

For many particles of polymer and biological origin

$$|m-1| \ll 1 \tag{42}$$

and

$$2kr|m-1| = \rho \ll 1 \tag{43}$$

hold, where r is the characteristic size of a particle (the radius for spheres), ρ is a **phase** shift after the wave has traversed along the diameter of a particle. Inequality 42 is often called a condition of optically "soft" particles. Both the inequalities serve as the premise of Rayleigh-Debye's approximation, whose importance is in its applicability to particles of any shape with sizes commensurable with the wavelength (Rayleigh, 1914; Kerker, 1969). The particle is divided into space elements dv_p to satisfy Rayleigh's condition. Due to Inequality 43, the field inside every particle differs from that one outside neither by phase nor by amplitude, and every space element dv_p is an elementary emitter with the dipole moment

$$d\vec{p} = d\alpha_p \,\vec{E}.\tag{44}$$

It is known from electrostatics that the **polarization vector** $\vec{\mathcal{P}}$ is related to \vec{E} by means of

$$\vec{\mathcal{P}} = \frac{\epsilon - 1}{4\pi} \vec{E}$$

Then, the polarization vector difference in a particle and in the dispersion medium is expressed as

$$\Delta \vec{\mathcal{P}} = \frac{\Delta \epsilon}{4\pi} \vec{E},$$

where $\Delta \epsilon = \epsilon_2 - \epsilon_1$.

As the polarization vector reflects the polarization of a unit space of the dielectric, then

$$\frac{d\vec{p}}{dv_p} = \frac{\Delta\epsilon}{4\pi}\vec{E}.$$
(45)

Substitution of $d\vec{p}$ from Equation 44 gives

$$d\alpha_p = \frac{\Delta\epsilon}{4\pi} dv_p = \frac{\epsilon_2 - \epsilon_1}{4\pi} dv_p. \tag{46}$$

With allowance for Inequality 42, it can be rewritten as

$$d\alpha_{p} = \frac{\mu_{2}^{2} - \mu_{1}^{2}}{4\pi} dv_{p} = \frac{\mu_{1}^{2}(m^{2} - 1)}{4\pi} dv_{p} = \frac{\mu_{1}^{2}(m - 1)(m + 1)}{4\pi} dv_{p} \simeq \frac{(m - 1)\mu_{1}^{2}}{2\pi} dv_{p}.$$
 (47)

The field of the light scattered by a particle at the point of observation is the sum of the fields of all the elementary scatters with due account of their **phase shift** (see Equation 3).



Figure 2.7. Schematic illustration of interference of light scattered by two space elements (O and A) of a particle, \vec{n}_0 and \vec{n}_s are unit vectors at the directions of incident and scattered beams

Fix a point O inside the particle, which belongs to a certain space element (Figure 2.7).

The phase shift of the beams scattered by this space element and by any other one (A) is expressed as

$$\delta = k(\vec{\rho}\,\vec{n}_s - \vec{\rho}\,\vec{n}_0) = k\vec{\rho}(\vec{n}_s - \vec{n}_0) = \vec{q}\,\vec{\rho},\tag{48}$$

 $\vec{\rho}$ being the radius vector connecting the space elements, \vec{n}_0 and \vec{n}_s unit vectors at the directions of incident and scattered beams;

$$\vec{q} = k(\vec{n}_s - \vec{n}_0) \tag{49}$$

is a scattering wavevector.

Figure 2.7 shows that $|\vec{n}_s - \vec{n}_0| = 2\sin(\vartheta/2)$, where ϑ is the scattering angle. Hence,

$$|\vec{q}| = \frac{4\pi}{\lambda} \sin \frac{\vartheta}{2}.$$
(50)

If a particle is in the field of vertically polarized incident light, then, according to Equation 11,

$$E_{s,0\perp} = \int_{\substack{\text{over the} \\ \text{whole particle}}} dE_{s,0\perp} = \frac{k_0^2 E_{0z}}{l} \int d\alpha_p \, \exp(i\delta) = \frac{k_0^2 E_{0z}}{l} \int_{v_p} \frac{\partial \alpha_p}{\partial v_p} \exp(i\delta) \, dv_p. \quad (51)$$

From Equation 46,

$$\frac{\partial \alpha_p}{\partial v_p} = \frac{\epsilon_2 - \epsilon_1}{4\pi} \tag{52}$$

and

$$E_{s,0\perp} = \frac{k_0^2 E_{0z}}{l} \cdot \frac{\epsilon_2 - \epsilon_1}{4\pi} \int_{v_p} \exp(i\delta) \, dv_p.$$
⁽⁵³⁾

For a homogeneous particle

$$\frac{\partial \alpha_p}{\partial v_p} = \frac{\alpha_p}{v_p} = \frac{\epsilon_2 - \epsilon_1}{4\pi},\tag{54}$$

$$E_{s,0\perp} = \frac{k_0^2 E_{0s} \alpha_p}{l v_p} \int_{v_p} \exp(i\delta) \, dv_p \tag{55}$$

ог

$$E_{s,0\perp} = \frac{k_0^2 E_{0z}}{l} \alpha_p \mathcal{F}(\vartheta, D/\lambda), \tag{56}$$

where (see Equation 48)

$$\mathcal{F}(\vartheta, D/\lambda) = \frac{1}{v_p} \int_{v_p} \exp(i\delta) \, dv_p = \frac{1}{v_p} \int_{v_p} \exp(i(\vec{q}\vec{\rho})) \, dv_p, \tag{57}$$

D is the characteristic size of the particle, D/λ is its relative size.

Comparison of Equations 56 and 11 allows one to conclude that interference of the beams scattered on a large homogeneous particle results in multiplying the scattered light intensity by an interference function $\mathcal{F}(\vartheta, D/\lambda)$ (van de Hulst, 1957).

In the case of unpolarized incident light, the scattered light intensity is (see Equation 13)

$$I_{\vartheta} = I_0 \frac{k_0^4 \alpha_p^2}{l^2} N_2 V |\mathcal{F}(\vartheta, D/\lambda)|^2 \frac{1 + \cos^2 \vartheta}{2}.$$
(58)

For homogeneous particles, Equations 46, 47, and 54 give

$$\alpha_p \cong \frac{\epsilon_2 - \epsilon_1}{4\pi} v_p \tag{59}$$

and

$$\alpha_p \cong \frac{(m-1)\mu_1^2}{2\pi} v_p. \tag{60}$$

Then,

$$I_{\vartheta} = I_0 \frac{k_0^4 (\epsilon_2 - \epsilon_1)^2 v_p^2}{16\pi^2 l^2} N_2 V |\mathcal{F}(\vartheta, D/\lambda)|^2 \frac{1 + \cos^2 \vartheta}{2}$$
(61)

and

$$I_{\vartheta} = l_0 \frac{k_0^4 (m-1)^2 v_p^2 \mu_1^4}{4\pi^2 l^2} N_2 V |\mathcal{F}(\vartheta, D/\lambda)|^2 \frac{1+\cos^2 \vartheta}{2} =$$

$$= l_0 \frac{4\pi^2 (m-1)^2 v_p^2}{N_2 V} N_2 V |\mathcal{F}(\vartheta, D/\lambda)|^2 \frac{1+\cos^2 \vartheta}{2}.$$
(62)

$$= I_0 \frac{4\pi^2 (m-1)^2 v_p^2}{\lambda^4 l^2} N_2 V |\mathcal{F}(\vartheta, D/\lambda)|^2 \frac{1+\cos^2 \theta}{2}$$

The function

$$|\mathcal{F}(\vartheta, D/\lambda)|^2 \equiv P(\vartheta, D/\lambda) \tag{63}$$


Figure 2.8. Radiation pattern in the case of vertically polarized incident light for Rayleigh's (1) and Rayleigh-Debye's particles (2)

is called a form factor, or Debye's function.

At the angle $\vartheta = 0$, there is no phase shift among any space elements of the particle dv_p (see Figure 2.7), and such a particle scatters light in this direction as Rayleigh's. It follows from Equation 61 that

$$\frac{1+\cos^2\vartheta}{2}P(\vartheta,D/\lambda) = \frac{I_\vartheta}{I_{\vartheta=0}} = \frac{R_\vartheta}{R_{\vartheta=0}} \le 1,$$
(64)

which is a basis for the experimental measurement of the Debye function (Figure 2.8).

Calculations of the Debye function $P(\vartheta, D/\lambda)$ are well presented in the literature for particles of various shapes: spheres (van de Hulst, 1957), chaotically arranged pivots (Doty and Steiner, 1950; van de Hulst, 1957), thin disks (Debye, 1947; Debye and Anacker, 1951; Becher, 1959), ellipsoids of revolution (Guinier and Fournet, 1955; Beattie and Tisinger, 1969), three-axis ellipsoids (Finnigan and Jacobs, 1971), finite size cylinders (van de Hulst, 1957).

Calculations and calibrations of the asymmetry ratio

$$z = \frac{I_{45}}{I_{135}} = \frac{P(45^{\circ}, D/\lambda)}{P(135^{\circ}, D/\lambda)} = f(D/\lambda)$$
(65)

are widely used to determine macromolecule sizes of various conformations (coils, pivots, spheres) and the correction factor

$$P^{-1}(90^{\circ}, D/\lambda) = f(D/\lambda) \tag{66}$$

to determine the polymer molecular mass by Debye's method (Debye, 1947; Doty and Steiner, 1950; Flory, 1953; Tompa, 1956; van de Hulst, 1957; Tsvetkov et al., 1964; Bresler and Yerusalimski, 1965; Morawetz, 1965; Kerker, 1969; Lipatov et al., 1971; Eskin, 1973; Rafikov et al., 1978), where D is the diameter of spheres, or the length of pivots, or the mean square end-to-end distance of coils. Eg. for spheres

$$P(\vartheta, D/\lambda) = \frac{9}{u^6} (\sin u - u \cos u)^2, \quad u = kD \sin \frac{\vartheta}{2}, \tag{67}$$

and for coils

$$P(\vartheta, D/\lambda) = \frac{2}{x^2}(e^{-x} + x - 1), \quad x = \frac{q^2 D^2}{6}.$$

Integration of Equation 31 in view of Equations 63, 67, 17, 37, and 39 leads to the efficiency factor (van de Hulst, 1957) (Figure 2.9)



Figure 2.9. Efficiency factor $K(\alpha, m)$ in Rayleigh-Debye's approximation (the upper curves of each couple) and from Mie's rigorous theory (the lower curves) (Mie, 1908; Klenin et al., 1977a)

$$K(\alpha, m) = |m - 1|^2 \varphi(\alpha), \tag{68}$$

where

$$\varphi(\alpha) = \frac{5}{2} + 2\alpha^2 - \frac{\sin 4\alpha}{4\alpha} - \frac{7}{16\alpha^2}(1 - \cos 4\alpha) + \left(\frac{1}{2\alpha^2} - 2\right)\left\{\gamma + \ln 4\alpha - \operatorname{Ci}(4\alpha)\right\},$$

 $\gamma \approx 0.577$ is Euler's constant, Ci denotes the integral cosine

$$\operatorname{Ci}(x) = -\int\limits_{x}^{\infty} \frac{\cos u}{u} du.$$

For inhomogeneous particles, the scattered field is expressed as

$$E_{s,0\perp} = \frac{k_0^2 E_{0z}}{l} \int_{v_p} \frac{\partial \alpha_p}{\partial v_p} \exp(i\delta) \, dv_p = \frac{k_0^2 E_{0z}}{l} \alpha_p \mathcal{F}(\vartheta, D/\lambda), \tag{69}$$

where

$$\alpha_p \mathcal{F}(\vartheta, D/\lambda) = \int_{v_p} \frac{\partial \alpha_p}{\partial v_p} \exp(i\delta) \, dv_p.$$
(70)

If the particles possess a spherically symmetrical distribution of optical properties with $\partial \alpha_p / \partial v_p = \alpha'_p(r)$, then the interference function takes the form

$$\alpha_{p}\mathcal{F}(\vartheta, D/\lambda) = \int_{0}^{\infty} \alpha_{p}'(r) \exp(i\vec{q}\vec{\rho}) \, dv_{p} = \int_{0}^{2\pi} d\varphi \int_{0}^{\pi} d\vartheta \int_{0}^{\infty} dr \, \alpha_{p}'(r) \exp(iqr\cos\vartheta) \sin\vartheta r^{2} \quad (71)$$
$$= \int_{0}^{\infty} \alpha_{p}'(r) \frac{\sin qr}{qr} 4\pi r^{2} \, dr.$$

Eg., for the Gaussian distribution of polarizability (van de Hulst, 1957)

$$lpha_p' = rac{dlpha_p}{dr} = lpha_0 \exp\left(-(r/a)^2
ight),$$

where α_0 and a are constants, $\alpha_p = \pi^{3/2} a^3 \alpha_0$ and

$$\mathcal{F}(\vartheta, a) = \exp\left[-\left(ka\sinrac{\vartheta}{2}
ight)^2
ight],$$

and the intensity of unpolarized light scattering is

$$I_{\vartheta} = I_0 \frac{k_0^4 \alpha_p^2}{l^2} V N_2 \exp\left[-2\left(ka\sin\frac{\vartheta}{2}\right)^2\right] \frac{1+\cos^2\vartheta}{2}.$$
(72)

Light scattering on chaotical structure heterogeneities is of great importance, these features are described by a correlation function (Debye et al., 1949, 1957; Kerker, 1969).

Let us consider a body, whose structure is characterized by fluctuations of the dielectric constant (permittivity) ϵ . Assume it to be represented as ($\epsilon + \Delta \epsilon$) at every point, where ϵ is the average (macroscopic) value of the dielectric constant (Figure 2.10).

Eg., at points A and B with the coordinates \vec{r} and \vec{r} : $\epsilon_A = \epsilon + \Delta \epsilon(\vec{r})$ and $\epsilon_B = \epsilon + \Delta \epsilon(\vec{r}')$. Pay attention to $\overline{\Delta \epsilon(\vec{r}')} \Delta \epsilon(\vec{r'})$, where averaging is performed while moving the



Figure 2.10. Instantaneous local fluctuations of the dielectric constant for a longer (1) and a shorter (2) correlation length

fixed straight line segment $AB = \vec{r} - \vec{r'} = \vec{\rho}$ over the whole body. It is clear that at $\vec{\rho} = 0$ $\Delta \epsilon(\vec{r}) \Delta \epsilon(\vec{r'}) = \Delta \epsilon(\vec{r}) \Delta \epsilon(\vec{r'}) = \Delta \epsilon^2$. When $\vec{\rho}$ is large, $\Delta \epsilon(\vec{r})$ and $\Delta \epsilon(\vec{r'})$ do not correlate and $\Delta \epsilon(\vec{r'}) \Delta \epsilon(\vec{r'}) = 0$.

The correlation between $\Delta \epsilon(\vec{r})$ and $\Delta \epsilon(\vec{r'})$ is described with the help of a correlation function $h(\vec{\rho})$ defined as

$$\overline{\Delta\epsilon}(\vec{r})\,\Delta\epsilon(\vec{r'}) = h(\vec{\rho})(\overline{\Delta\epsilon})^2 \tag{73}$$

(Figure 2.11).

By analogy with Equation 51 and in view of Equation 46 one can write

$$E_{s,0\perp} = \int_{\substack{\text{over all the}\\scattering space}} dE_{s,0\perp} = \frac{k_0^2 E_{0z}}{l} \int d\alpha_p \, \exp(i\delta) = \frac{k_0^2}{l} \cdot \frac{E_{0z}}{4\pi} \int \Delta\epsilon(\vec{r}) \exp(i\vec{q}\vec{r}) \, d\vec{r}, (74)$$



Figure 2.11. Correlation function corresponding to averaged structure 1 (Figure 2.10, curve 1) and structure 2 (Figure 2.10, curve 2)

where $d\vec{r} = dv_p$. With allowance for Equation 8, for the intensity of vertically polarized light we have

$$I_{\perp} = I_{0z} \frac{k_0^4}{16\pi^2 l^2} \int \Delta\epsilon(\vec{r}) \exp(i\vec{q}\vec{r}) d\vec{r} \int \Delta\epsilon(\vec{r}') \exp(i\vec{q}\vec{r}') d\vec{r}'$$
(75)
$$= I_{0z} \frac{k_0^4}{16\pi^2 l^2} \int d\vec{r} \int \Delta\epsilon(\vec{r}) \Delta\epsilon(\vec{r}') \exp(iq(\vec{r} - \vec{r}')) d\vec{r}'$$
$$= I_{0z} \frac{k_0^4 V}{16\pi^2 l^2} \int_{\nu} d\vec{\rho} h(\vec{\rho}) \overline{(\Delta\epsilon)^2} \exp(i\vec{q}\vec{\rho})$$
$$= I_{0z} \frac{k_0^2 V \overline{(\Delta\epsilon)^2}}{16\pi^2 l^2} \int_{\nu} d\vec{\rho} h(\vec{\rho}) \exp(i\vec{q}\vec{\rho}),$$

where integration is performed over the inhomogeneous (correlation) area for $h(\rho) = 0$ outside it (see Figure 2.11).

For statistical heterogeneities, $h(\rho)$ can be assumed spherically symmetrical, then

$$I_{\perp} = I_{0x} \frac{k_0^4 V \overline{(\Delta \epsilon)^2}}{16\pi^2 l^2} \int_0^\infty h(\rho) \frac{\sin q\rho}{q\rho} 4\pi \rho^2 \, d\rho \tag{76}$$

with the integral called a correlation volume

$$w_{\epsilon} = \int_{0}^{\infty} h(\rho) \frac{\sin q\rho}{q\rho} 4\pi \rho^2 \, d\rho.$$
(77)

Then (see Equation 17),

$$R_{\perp} = \frac{k_0^4 (\overline{\Delta \epsilon})^2 w_{\epsilon}}{16\pi^2} \tag{78}$$

or

$$R_{\perp} = \frac{\pi^2 \overline{(\Delta\epsilon)^2} w_{\epsilon}}{\lambda_0^4} \tag{79}$$

and (cf. Equations 12 and 13)

$$R_{\vartheta} = \frac{\pi^2 \overline{(\Delta \epsilon)^2} w_{\epsilon}}{\lambda_0^4} \cdot \frac{1 + \cos^2 \vartheta}{2}.$$
(80)

The intensity of scattering on chaotical heterogeneities is defined by the product $(\Delta \epsilon)^2 w_{\epsilon}$, i.e. small-amplitude fluctuations, related by a large correlation region, scatter as intensively as the large-amplitude ones related by a small correlation region. Besides, the correlation volume w_{ϵ} (Equation 77) depends on the scattering angle, diminishing as the angle ϑ increases. If the correlation region $0 < h(\rho) < 1$ is commensurable with λ , there occurs deformation of the radiation diagram (see Figure 2.8).

Analysis of light scattering by means of the correlation function is fully equivalent to the case of scattering on spheres provided that the correlation function is approximated by

$$h(\rho) = 1 - \frac{3}{4} \left(\frac{\rho}{r}\right) + \frac{1}{16} \left(\frac{\rho}{r}\right)^3,$$
(81)

where r is the radius of the sphere.

The condition $|m-1| \approx 0$ is always valid for X-rays, and their scattering obeys Rayleigh-Debye's approximation. In particular, for a spherically symmetrical body (eg. an atom) the function

$$\mathbf{F}(q) = \int_{0}^{\infty} \zeta(\rho) \frac{\sin q\rho}{q\rho} 4\pi \rho^2 \, d\rho \tag{82}$$

characterizes the atom's ability to scatter, and is referred to as an **atomic amplitude** (van de Hulst, 1957; Skryshevski, 1980) (cf. Equation 71), $\zeta(\rho)$ is the electronic density.

In a more general case (Vainshtein, 1963), the atomic amplitude has the form

$$\mathbf{F}(\vec{s}) = \int \zeta(\vec{\rho}) \exp\left(2\pi i (\vec{s}\vec{\rho})\right) d\vec{\rho}$$
(83)

(cf. Equations 70 and 75), where

$$2\pi\vec{s} = \vec{q} \tag{84}$$

(cf. Equation 57).

In its mathematical form, Equation 83 is a Fourier integral. The function $\mathbf{F}(\vec{s})$ is defined in the space of the vector \vec{s} , the so-called **inverse space** with the dimension $[s] = \mathrm{cm}^{-1}$, whereas the function $\zeta(\vec{\rho})$ describes the object's structure in real space. The Fourier integral has the property of inversibility, i.e. once $\mathbf{F}(\vec{s})$ is given, $\zeta(\vec{\rho})$ can be reconstructed by means of the inverse Fourier transform (Madelung, 1957; Korn and Korn, 1968):

$$\zeta(\vec{\rho}) = \frac{1}{(2\pi)^3} \int \mathbf{F}(\vec{s}) \exp\left(-2\pi i (\vec{s}\vec{\rho})\right) \, d\vec{s}. \tag{85}$$

The functions $\zeta(\vec{\rho})$ and $\mathbf{F}(\vec{s})$ form a reciprocal pair of Fourier transforms, and Equations 83 and 85 are considered as the main expressions in solving the chief task of diffraction techniques: to determine the object's structure $\zeta(\vec{\rho})$ from the observed (measured) diffraction pattern $\mathbf{F}(\vec{s})$. In the operational notation

$$\mathbf{F}(\vec{s}) = \mathbf{F}[\zeta(\vec{\rho})] \tag{86}$$

is the direct scattering problem, and

$$\zeta(\vec{\rho}) = \mathbf{F}^{-1}[\mathbf{F}(\vec{s})] \tag{87}$$

is the inverse scattering problem.

The Fourier transform method determines the correlation function (Equations 73 and 76) from the scattering data (Stein, 1978). The function $\mathbf{F}(\vec{s})$ is called a Fourier transform of the structure of scattering elements (particles).

Note that the Fourier transform has a few equivalent forms (Ditkin and Prudnikov, 1961; Korn and Korn, 1968).

The Fourier transform $\mathbf{F}(\vec{s})$ is a function of the structure of the scattering elements if and only if Rayleigh-Debye's conditions (see Equations 57, 64, 71, 76, 77, 83) hold, i.e. the structure characteristic elements are commensurable with the wavelength. For X-rays, this corresponds to the size of atoms and the crystal lattice parameters, the short-range coordinates order in liquids. In this connection, X-ray analysis has gained acceptance for exploring the atomic and atom-crystal structure of substances. The sizes of structural formations during phase separation correspond to the wavelength of visible light, and the light scattering technique is informative for studying phase separation processes.

As the scattering intensity depends on the phase shift δ of the beams scattered on structural elements (see Equations 70 and 75) and δ , in turn, is defined by the wavelength and the scattering angle (see Equations 48-50), then, varying these two experimental factors, one can probe the structural elements of different scales in the object.

Four Debye functions exist for anisotropic particles: P_{\perp}^{\perp} , P_{\perp}^{\parallel} , $P_{\parallel}^{\parallel}$, and $P_{\parallel}^{\parallel \prime}$ (Kerker, 1969; Eskin, 1973), where the subscript and superscript denote the polarization of the incident beam and the receiver's orientation. If distribution is chaotical, $P_{\perp}^{\parallel} = P_{\parallel}^{\perp}$, and only three Debye functions are independent.

In Rayleigh-Debye's approximation, light scattering has been studied on

- anisotropic spheres (spherolites) (Stein and Rhodes, 1960; Stein et al., 1966; Kotov and Novikov, 1967);
- ellipsoides (Finkelstein and Savko, 1972; Kotov et al., 1976; Lopatin and Sidko, 1988);
- disordered or oriented thin pivots (van de Hulst, 1957; Rhodes and Stein, 1969; Masaniko et al., 1971);
- anisotropic cylinders (Horn and Benoit, 1953; van Aartsen, 1970; Hayashi and Kawai, 1972);
- anisotropic disks (van de Hulst, 1957; Picot et al., 1968; Samuels, 1971).

Stein (1966), Volkov and Baranov (1968) provide reviews of light scattering on anisotropic particles.

In the general case, light scattering in matter is caused not only by density fluctuations but also by anisotropy fluctuations and fluctuations of the optical axis orientation of anisotropic areas. Such fluctuations arise as a result of mutual orientation of anisotropic molecules, or of their aggregates, or owing to the internal stresses in solid matter. In this case, the polarizability of scattering elements is represented by a polarizability tensor and two correlation functions (density correlation and orientation correlation) are introduced (Goldstein and Michalik, 1955; van Aartsen, 1972).

2.1.3. Van de Hulst approximation

Having taken

$$|m-1| \ll 1 \qquad (|m-1| \approx 0) \tag{88}$$

and

$$\alpha = \frac{2\pi r \mu_1}{\lambda} \gg 1, \tag{89}$$

van de Hulst (1957) has applied Huygens and Babine's classical principles to the problem of light scattering and derived a most important and rather simple expression for the efficiency factor:

$$K(\rho) = 2 - 4 \frac{\sin \rho}{\rho} + 4 \frac{1 - \cos \rho}{\rho^2}$$
(90)

(Figure 2.12) where

$$\rho = 2\alpha(m-1) = 4\pi r(m-1)\mu_1/\lambda \tag{91}$$

is the phase shift (see Equation 43).

Van de Hulst's approximation is applicable to quite big particles and, what is more, to nonspherical and heterogeneous particles (Tvorogov, 1965; Khlebtsov, 1980) and to absorbing particles (van de Hulst, 1957; Tvorogov, 1965; Bryant and Latimer, 1969; Sukhachyova and Tvorogov, 1973).

Equation 90 has turned out to be valid not only for small |m-1| (which was its premise) but for m significantly deviated from 1 (van de Hulst, 1957; Kerker, 1969; Shifrin, 1971) (see Figure 2.12). This confirms the similarity criterion (Shifrin, 1951), which states that the features of light scattering are determined mainly by the value of phase shift ρ .

By some estimates (Shifrin, 1951; van de Hulst, 1957; Heller, 1963; Kerker and Farone, 1963; Moore et al., 1968; Kerker, 1969), the results of the soft particle approximation are qualitatively true within, at least, $0.8 \le m \le 1.5$ if $\alpha \gg 1$; when $m \le 1.15$ they are valid quantitatively with a slight error. Hence, Rayleigh-Debye and van de Hulst's approximations are very fruitful in studying the heterogeneous structures of polymer and biological origin.



Figure 2.12. Efficiency factors $K(\rho)$ and $K(\alpha, m)$ as functions of $\rho = 2\alpha(m-1)$ according to van de Hulst's formula (Equation 2.1-90) (curve 1) and to Mie's theory for m = 1.05 (2), 1.07 (3), 1.10 (4), 1.15 (5), 1.20 (6) (Mie, 1908)

2.1.4. Rigorous theory of scattering on spherical particles (Mie theory)

Love (1899), Mie (1908), and Debye (1909) obtained a solution of the problem of electromagnetic radiation scattering on a homogeneous particle of any size with any relative refractive index m (including complex refractive index in the case of absorbing particles) in terms of Maxwell's equations. By tradition, it is referred to as Mie's theory which is expounded and discussed in a number of monographs (Shifrin, 1951, 1971; van de Hulst, 1957; Born and Wolf, 1968; Deirmendjan, 1969; Ivanov, 1969; Kerker, 1969; Zuyev, 1970; Bohren and Huffman, 1983).

Tables of computed characteristic functions of scattering on dielectric, absorbing, and polydisperse particles have been compiled (van de Hulst, 1957; Shifrin and Zelmanovich,

1966, 1968; Zelmanovich and Shifrin, 1968, 1971; Deirmendjan, 1969; Ivanov, 1969; Kerker, 1969; Prishivalko and Naumenko, 1972; Prishivalko, 1973ab; Shifrin and Salganik, 1973; Klenin et al., 1977a; Bohren and Huffman, 1983; Shifrin, 1983). See Figures 2.9, 2.12, and 2.13 for examples.



Figure 2.13. Efficiency factor $K(\alpha, m)$ against α by Mie's theory for m = 1.1 (1), 1.2 (2), and 1.3 (3) (Mie, 1908)

Rosenberg (1972) has extended the theory to heterogeneous (including nonconcentric) particles. Lopatin and Sid'ko (1988) have computed the efficiency factor for two- and three-layer spheres.

2.1.5. Turbidity spectrum method for the characterization of ill-defined disperse systems

The turbidity spectrum method is used for a wide range of problems in the physical chemistry of polymers and colloids, biophysics, and biochemistry, including the study of phase separation in polymer systems.

The main premises of this technique are given in the monograph (Klenin et al., 1977a) with calibrations of all the characteristic functions for monodisperse, spherical particles within wide ranges of α and m computed with the use of Mie's theory. Since then, new results have been obtained concerning the problem of phase separation in polymer systems.

Within a restricted wavelength range $\Delta\lambda$, the spectral dependence of turbidity is expressed by Ångström's (1929) equation (van de Hulst, 1957; Heller et al., 1962; Kerker, 1969)

$$\tau = A\lambda^{-n},\tag{92}$$

where the wavelength exponent n is a function of α and m (or ρ).

In the log-log scale,

$$\ln \tau = \ln A - n \ln \lambda, \tag{93}$$

whence the exponent can be extracted from a turbidity spectrum $\tau(\lambda)$ as the slope of

$$\ln \tau \ vs \ \ln \lambda \tag{94}$$

or, as the derivative,

$$n = -\frac{\partial \ln \tau}{\partial \ln \lambda}.$$
(95)

Neglecting the dispersion of the refractive index of both the dispersed phase and disperse medium (see Equations 41, 38, 91) (Slutsker and Marikhin, 1961),

$$n = -\frac{\partial \ln K(\alpha, m)}{\partial \ln \lambda} = \frac{\alpha}{K(\alpha, m)} \cdot \frac{\partial K(\alpha, m)}{\partial \alpha} = \frac{\rho}{K(\rho)} \cdot \frac{\partial K(\rho)}{\partial \rho}.$$
(96)

Heller et al. (1962), Klenin et al. (1977a) have tabulated n from Mic's theory in wide ranges of α and m (Figure 2.14).

According to Equations 68 and 96, in Rayleigh-Debye's approximation (Khlebtsov and Shchyogolev, 1977a; Khlebtsov et al., 1977)

$$n(\alpha) = \{z^2/4 - 2 + \cos z - 6\sin z/z + 22(1 - \cos z)/z^2 + 16 [\operatorname{Ci}(z) - \ln z - \gamma]/z^2\}/\varphi(\alpha),$$
(97)

where $z = 4\alpha$, and the other notation is the same as in Equation 68 and in Figure 2.21 (curve 1).

One can see that the exponent varies from 2 to 4 and does not depend on m (cf. the results of Mie's theory within this range of n in Figure 2.14).

Considering the fact that there is no concentration dependence of n, the turbidity spectrum method provides the most correct determination of particle sizes within $2 \le n \le 4$, which corresponds to the radius of particles $0.02 - 0.03 \dots 0.2 - 0.3 \mu m$ (often encountered in real systems).

In van de Hulst's approximation, Equations 90 and 96 are followed by (Shchyogolev and Klenin, 1971b; Klenin et al., 1977a)

$$n(\rho) = \frac{4\sin\rho/\rho - 2\cos\rho + 4(\cos\rho - 1)/\rho^2}{1 - 2\sin\rho/\rho + 2(1 - \cos\rho)/\rho^2} = \frac{4(1 - \cos\rho)}{K(\rho)} \quad 2$$
(98)

(Figure 2.19, curve 3 which is compared with $\bar{n}(\bar{\rho})$ for polydisperse systems (see further)). When n < 2, this gives ρ and, involving Equation 91, either ρ at a known m, or m at

a known (determined independently) r can be calculated (Klenin et al., 1976b).

From known α and m, the numerical concentration of particles can be estimated by (Ileller and Pangonis, 1957; Klenin and Uglanova, 1969; Klenin and Shchyogolev, 1971a; Klenin et al., 1977a) (see Equation 41)

$$N_2 = \frac{4\pi\tau}{(\lambda')^2 K(\alpha, m)\alpha^2}, \, \mathrm{cm}^{-3}, \tag{99}$$



Figure 2.14. *n* against α for monodisperse spherical particles from Mic's theory: m = 1.03 (1), 1.06 (2), 1.08 (3), 1.12 (4), 1.18 (5), and 1.24 (6) (Heller et al., 1962; Klenin et al., 1977a)

where $\lambda' = \lambda_m / \mu_1$ (here λ' is expressed in cm), $\lambda_m = (\lambda_1 \lambda_2)^{1/2} (\lambda_1 \text{ and } \lambda_2 \text{ are the bound$ arises of the straight line plot 94) or the wavelength at which the derivative (Equation 95) $is taken, <math>\tau$ is the turbidity at λ_m .

Plots are used to estimate the efficiency factor $K(\alpha, m)$ (eg. Figures 2.9, 2.12, 2.13), its accurate tabulation is made in (Klenin et al., 1977a) for wide ranges of α and m.

With ρ and $K(\rho)$ (Equation 90), the number of particles per 1 cm³ is expressed as

$$N_2 = 50.4 \frac{\tau (m-1)^2}{(\lambda')^2 K(\rho) \rho^2}, \, \text{cm}^{-3}.$$
(100)

The mass-volume concentration of the dispersed phase \tilde{M} (g/dl) is equal to the product $N_2 \cdot 100$ by the mass of a particle which, in the general case, contains the low-molecular component (the dispersion medium)

$$\tilde{M} = 100 \varrho_2 \frac{m-1}{m_k - 1} \cdot \frac{4}{3} \pi r^3 N_2$$

or (see Equation 41)

$$\tilde{M} = Sv\tau, \mathbf{g}/\mathrm{dl} \tag{101}$$

where

$$S = \frac{10.61 \rho_2 \lambda'}{m_k - 1}, \, \text{g/100 cm}^2, \tag{102}$$

 ϱ_2 is the polymer density (g/cm³), $m_k = \mu_{2k}/\mu_1$, μ_{2k} is the polymer refractive index in the condensed state, τ is the turbidity at λ' .

A structural factor v is defined (Klenin and Shchyogolev, 1971a) as

$$v = \frac{2\alpha(m-1)}{K(\alpha,m)} = \frac{2n(m-1)}{\partial K(\alpha,m)/\partial \alpha}$$
(103)

or

$$v = \frac{\rho}{K(\rho)} = \frac{n}{\partial K(\rho)/\partial \rho}$$
(104)

(see also Equation 96).

Klenin et al. (1977a) report some analogues of the characteristic functions K, \bar{n} , and \bar{v} for polydisperse systems.

The characteristic functions of a monodisperse particle system are of complex oscillating nature. However, real systems are always polydisperse, and intuition prompts to adapt the characteristic functions of monodisperse systems to polydisperse ones by smoothing the oscillations. This has been done using simple symmetry.

Comparison of such a technique of smoothing with the results of direct computation of the characteristic functions for some model polydisperse systems is made (Klenin et al., 1977a; Ramazanov et al., 1983a) with the gamma size distribution

$$f(r) = \frac{\beta^{\mu+1}}{\Gamma(\mu+1)} r^{\mu} \exp(-\beta r)$$
(105)

as an example, where μ and β

$$\mu = \left(\frac{2.48r_m}{\Delta r}\right)^2 \tag{106}$$

and

$$\beta = \left(\frac{2.48}{\Delta r}\right)^2 r_m,\tag{107}$$

 Δr and r_m are the halfwidth and mode of distribution, respectively. Other uniformal distributions, for which Δr and r_m can be estimated, can be approximated with the gamma distribution.

Figures 2.15-2.18 show a small difference between the results of analytical (Ramazanov et al., 1983a) and simple geometrical smoothing and the results of direct computation of the functions for the model distribution in a wide range of polydispersity. The subscript μ denotes the gamma distribution: $\mu \to \infty$ and $\mu = 0$ are the limiting cases of a monodisperse system and an utmost polydisperse system (see Equations 106 and 107).

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Figure 2.15. *n* and \bar{n}_{μ} against α and α_{μ} at m = 1.01 for monodisperse particles (dashed line) (Klenin et al., 1977a) using the approximate formulae from (Ramazanov et al., 1983a) (1), for polydisperse gamma-distributed particles with $\mu = 10$ (2) and $\mu = 35$ (3) in Rayleigh-Debye's approximation

Klenin et al. (1977a), Ramazanov et al. (1983a) have established that the characteristic functions of polydisperse systems fit the smoothed functions of monodisperse systems in the best way if the λ average value of particle size is used (Shchyogolev and Klenin, 1971a; Klenin et al., 1977a)

$$\dot{r}_{\lambda} = \left(\int_{0}^{\infty} r^{n+2} f(r) \, dr \, \middle/ \int_{0}^{\infty} r^{3} f(r) \, dr \right)^{1/(n-1)}.$$
(108)

The radius \bar{r}_{λ} corresponds to the relative size

$$\alpha_{\lambda} = 2\pi r_{\lambda} \mu_1 / \lambda_m \tag{109}$$

and

$$\rho_{\lambda} = 2\dot{\alpha}_{\lambda}(m-1) = 4\pi \bar{r}_{\lambda}(m-1)\mu_1/\lambda_m. \tag{110}$$

This is illustrated in Figure 2.19, which shows that the dependence n_{μ} vs ρ_{λ} is close to $n = n(\rho)$ for a monodisperse system in contrast to the dependence n_{μ} vs ρ_{2} , where

$$\bar{\rho}_2 = \frac{4\pi \bar{r}_2(m-1)\mu_1}{\lambda_m}$$
(111)



Figure 2.16. n and \bar{n}_{μ} against α and $\bar{\alpha}_{\mu}$ at m = 1.33 for monodisperse particles (dashed line) (Klenin et al., 1977a), using the approximate formulae from (Ramazanov et al., 1983a) (1), for polydisperse gamma-distributed particles with $\mu = 10$ (2)

and

$$\bar{r}_2 = \left(\int_0^\infty r^2 f(r) \, dr\right)^{1/2}.$$
(112)

We consider the approximation of the characteristic functions by smooth analytical functions as a necessary prerequisite for computing the system parameters.

The chief task of the turbidity spectrum method is to characterize ill-defined dispersoids. This makes it necessary to reveal how robust different versions of the reverse problem arc.

Any physical method of exploring the structure of a substance implies the object under investigation is probed by some exposure \mathcal{L} (eg. a ray of light).



Figure 2.17. v and v_{μ} against n and \bar{n}_{μ} by the approximate formulae (Ramazanov et al., 1983a) (1, 1), for polydisperse gamma-distributed particles with $\mu = 10$ (2, 2) and for monodisperse particles (Klenin et al., 1977a) with m = 1.01 (1'-3) and m = 1.33 (1-3)

Suppose the structure of our object is defined by a set of parameters $\{S_i\}$. The receiver measures a response function $\{M_i\}$.

Then, obtaining the functional dependence $\{M_j\}$ with respect to $\{S_i\}$

$$\{M_i\} = f\{S_i\} \quad \text{at a known } \mathcal{L} \tag{113}$$

with a known \mathcal{L} is called a direct problem whereas establishing the dependence

$$\{S_i\} = f\{M_j\} \quad \text{at a known } \mathcal{L} \tag{114}$$

with a known \mathcal{L} as well is called a **reverse problem** (cf. Equations 86 and 87).



Figure 2.18. Dependence of the structural factor v on n for monodisperse particles (Klenin et al., 1977a) (dashed lines) and using the approximate formulae (Ramazanov et al., 1983a) (solid lines) for m = 1.05 (1), 1.15 (2), and 1.30 (3)

The reverse problem may prove to be **incorrect** when calculation of $\{S_i\}$ in accordance with Equation 114 is rather sensitive to M_j variations due to the natural errors in measurements or post-measurement calculations. Incorrectness may often arise from a rather wide problem statement, which involves physically meaningless solutions; moreover, the functions in Equation 114 may be ambiguous owing to the M_j sensitivity to different parameters from $\{S_i\}$.

Making the solution unambiguous by means of additional conditions and restrictions is referred to as **regularization of the reverse problem** and, so, of the investigative method on the whole.

Smoothing of the oscillating functions (geometrical or analytical, in comparison with the results of the direct problem for model systems with polydisperse, anisodiametric, structurally heterogeneous particles, etc.) serves as the aim of regularization of the reverse problem of the turbidity spectrum method. We refuse a priori to characterize the system fully (to determine the full distribution curve, particle shape, details of the particle internal structure, etc.) in order to get information on the averaged (integral) properties, such as the mean size of particles, the numerical and mass-volume concentration of the dispersed phase, etc. which, as experiment suggests, is quite sufficient to solve a number of problems: scientific, technological, and those of maintenance. If one takes account of the great simplicity of the experimental technique, abundance of the required equipment



Figure 2.19. *n* and n_{μ} against ρ and $\bar{\rho}_{\lambda}$ for gamma-distributed particles: $\mu = 0$ (1), 5 (2), and ∞ (monodisperse particles) (3). Dependence \bar{n}_{μ} on $\bar{\rho}_2 = 4\pi \bar{r}^2 (m-1)\mu_1/\lambda_m$, where \bar{r}^2 is the mean square radius (dashed line). Van de Hulst's approximation (Klenin et al., 1977a; Shchyogolev, 1983)

(colorimeters and spectrophotometers of any kind), there being no alternative methods in many applications, the outlook for application and further development of the turbidity spectrum method can be estimated as rather high.

Stability-of-solution analysis has been performed, in particular, with respect to the possible deviation of particles from the spherical form.

The direct and reverse problems of the turbidity spectrum method for systems of anisodiametric particles were solved by simulation in Rayleigh-Debye's $(2 < \bar{n}_p < 4)$ and van de Hulst's $(n_p < 2)$ approximations (Khlebtsov and Shchyogolev, 1977ab; Khlebtsov et al., 1977, 1978abc; Shchyogolev et al., 1977; Khlebtsov, 1980; Shchyogolev, 1983).

The shapes of an clongated ellipsoid of revolution (the axes ratio p > 1) and of an oblate one (p < 1) with wide ranges of size and anisodiametry degree were chosen as model.

The efficiency factor of anisodiametric particles is defined as (Khlebtsov and Shchyogolev, 1977a)

$$\bar{K}_{p}(\alpha,m) = \frac{\bar{R}(\alpha,m,p)}{\pi r^{2}}$$
(115)

(cf. Equation 39), where $\tilde{R}(\alpha, m, p)$ is the optical section averaged over all the possible



Figure 2.20. Schematic of exploring the structure of substance with the action \mathcal{L} : $\{S_i\}$ is a set of parameters to characterize the structure of substance; $\{M_j\}$ is a set of parameters of the object's response to the action \mathcal{L} , i.e. the measured quantities in the physical experiment

particle orientations, p is the axes ratio (the anisodiametric factor), r is the radius of an equivalent sphere, whose volume is equal to that of an anisodiametric particle, i.e.

$$r = \left(\frac{3v_p}{4\pi}\right) \tag{116}$$

and

$$\alpha = \frac{2\pi r}{\lambda'}, \qquad \rho = 2\alpha(m-1). \tag{117}$$

The other characteristic functions of anisodiametric particles are calculated through the efficiency factor (Equation 115) similarly to Equations 99–105.

In Rayleigh-Debye's approximation, it is worthwhile representing the structural factor as

$$\bar{v}_p = \frac{2v_1}{m-1} \tag{118}$$

and writing the results of the direct problem as the dependence $v_1 = f(\alpha)$ with the parameter p.

Figures 2.21-2.25 report some of the obtained results showing that random arrangement of the anisodiametric particles smooths oscillations of the characteristic functions as well.

A more rigorous stability-of-solution analysis with respect to anisodiametry has been carried out by Shchyogolev et al. (1977a) as follows.

A specific model of a system with anisodiametric particles with the parameters $\{S_i\}$ was taken, the response functions $\{M_j\}$ (turbidity τ , exponent *n*, structural factor v_p , etc.) were computed from the general solution of the direct problem (Equation 113). The algorithm of solving the reverse problem was constructed in two ways:

- using adequate response functions (this operation is, of course, conventional, since the "outlet" parameters are predetermined $\{S_i\}$),
- using smoothed universal functions of those for spherical particles (the obtained parameters $\{S'_i\}$ will differ from those given $\{S_i\}$).



Figure 2.21. α against *n* for spherical particles (1) and against \bar{n}_p for elongated ellipsoids of revolution (averaging over all the orientations) with the axes ratio p = 2 (2), 4 (3), 6 (4), and 10 (5). $\alpha = 2\pi r/\lambda'$, *r* is the equivalent sphere radius $(3v_p/4\pi)^{1/3}$, v_p is the volume of an ellipsoid. Rayleigh-Debye's approximation (Khlebtsov and Shchyogolev, 1977a)



2.22. Figure The α -dependence of = $\bar{v}_{p}(m - 1)/2$ v_1 spherical particles for (1) and for elongated ellipsoids with p = 4(2), 10 (3), and 20 (4). Rayleigh-Debye's approximation (Khlebtsov and Shchyogolev, 1977a)

 \bar{n}_p, n



Figure 2.23. Dependence of *n* for spherical particles (1) and \bar{n}_p for elongated ellipsoids of revolution (averaging over all the orientations) with the axes ratio p = 2 (2), 4 (3), 6 (4), and 10 (5) on the equivalent parameter *p* (see caption to Figure 2.21). Van de Hulst's approximation (Khlebtsov and Shchyogolev, 1977b)



Figure 2.24. Dependence of the structural factor v for spherical particles (1) and \bar{v}_p for elongated ellipsoids of revolution (averaging over all the orientations) with the axes ratio p = 2 (2), 4 (3), 6 (4), and 10 (5) on the exponent \bar{n} . Van de Hulst's approximation (Khlebtsov and Shchyogolev, 1977b)

Figure 2.25. The α - and ρ -dependence of n for spherical particles (1, 1) and n_p for oblate ellipsoids of revolution (averaging over all the orientations) with the axes ratio p = 1/2 (2, 2), 1/4 (3, 3), 1/6 (4), and 1/10 (4,5). Rayleigh-Debye's (1-4) and van de Hulst's approximations (1'-5') (Khlebtsov and Shchyogolev, 1978)

The ratio

$$\delta S_i = \frac{S_i - S_i'}{S_i'} \tag{119}$$

was accepted as a measure of deviation to judge the stability of the solution, i.e. the structural parameters are compared, that are calculated by two branches of the algorithm with the same response function M_1 .

To give an example, Figure 2.26 (above) presents the results of determining the particle size through the exponent

$$\delta r = \left(\frac{\rho}{\rho'} - 1\right) 100, \,\%,\tag{120}$$

where ρ' is the root of

$$n(\rho') = \bar{n}_p(\rho),\tag{121}$$



Figure 2.26. The \bar{n}_p -dependence of δr_n , $\delta \dot{M}$, and δN_2 (%) for elongated ellipsoids of revolution with the axes ratio p = 2 (1), 3 (2), 4 (3), 6 (4), 10 (5), and 15 (6). Van de Hulst's approximations (Shchyogolev et al., 1977a)

and $n(\rho')$ and $\bar{n}_p(\rho)$ are the wavelength exponent of spherical particles and that of elongated ellipsoids of revolution with the given parameters (see Figure 2.23).

Figure 2.26 with the obtained results allows one to conclude that neglecting the anisodiametry of particles of any shape factor within $p \leq 3$ will lead to errors with different signs but not exceeding 30% in magnitude (at least, within $0.5 \leq \bar{n} \leq 2$).

The results of calculating $\delta \tilde{M}$ (Figure 2.26) show that for $-0.2 \leq \bar{n} \leq 1.6$ the neglect of non-spherical shape leads to a systematic underestimation of \tilde{M} but not more than by 10...20% for particles with no restrictions to form factor. When $\bar{n} > 1.7$ and $\rho \leq 4...5$, the mentioned error does not exceed 30%. Thus, the determination of the mass-volume concentration from turbidity spectrum has quite a high stability-of-solution of the inverse problem with respect to anisodiametry of particles when n < 2.

Neglect of the anisodiametry of particles (for systems with $0 \le \overline{n} \le 2$) at any form factors ($\rho \le 3$) leads to errors in N_2 of different signs but not exceeding 30...40% in magnitude.

When the form factor is known from a side experiment, δr , δM , and δN_2 can serve as correction factors for experimental results.

This technique has been applied to estimate stability-of-solution of the inverse problem in the case of oblate ellipsoids of revolution (Khlebtsov et al., 1978ab), to the influence of particle and medium substance dispersion (Ramazanov and Shchyogolev, 1979), to the experimental error of τ (Khlebtsov et al., 1978b).

Previously (Klenin et al., 1977a) the stability-of-solution of the inverse problem with respect to polydispersity was shown.

Sedlàček and Jokl (1979) state the stability-of-solution of the inverse problem with respect to dispersion of m in the near-infrared region.

The exponent n exhibits sufficient stability to secondary light scattering (Klenin et al., 1973g) as well as to the structural non-uniformity of particles (Kutuzov and Klenin, 1983). The latter authors have simulated structural non-uniformity using particles consisting of a core and a coating (coated spheres). Solutions of the direct problem of the turbidity spectrum method within wide ranges of the core and coating size have been obtained. The results are applicable for characterizing systems that emerge during **microcapsuling** (Solodovnik, 1980) and are used in industry, medicine, and pharmacology. We note in passing that in many cases microcapsuling is based on phase separation in polymer-containing systems.

Within 2 < n < 4 the exponent is stable to the aperture angle of a spectrophotometer (Dolinnyi, 1978).

A turbidity spectrum in a wide wavelength range (~ $0.2...0.25 \mu$ m) enables one to reconstruct the full distribution curve f(r) (Shifrin and Raskin, 1961; Shifrin and Perelman, 1963abcd, 1964, 1966; Shifrin et al., 1966, 1979; Biryukov, 1970; Shifrin, 1971; Khayrullina and Shumilina, 1973).

Sereda and Shtarkman (1974) has determined f(r) from spectroturbidimetry, involving statistical regularization (Turchin et al., 1970).

As opposed to the turbidity spectrum method, determination of the scattered light intensity at one or two angles does not provide correct information for the ill-defined systems due to the high sensitivity of the radiation diagram to the shape of particles, their polydispersity, and other fine structural features, not to mention multiple scattering. Such sensitivity makes it difficult to regularize the reverse problem.

If a full radiation diagram is measured, statistical regularization reconstructs the size distribution function of spherical particles (Shifrin et al., 1972; Shifrin and Gashko, 1974; Gashko and Shifrin, 1976).

The characteristic functions in the turbidity spectrum method show rather different stability to different parameters in two ranges: 2 < n < 4 and n < 2. Analysis of these dependences allows us to give some recommendations on determining different system parameters of the ill-defined systems. A certain parameter should be determined in a range where the function exhibits the maximal sensitivity to it.

The range 2 < n < 4

Here, n is practically insensitive to m, so a measured spectrum $\tau(\lambda)$ does immediately give the average particle radius \bar{r}_{λ} by the smoothed calibrations $n(\alpha, m)$ vs α (Heller et al., 1962; Klenin et al., 1977a; Ramazanov et al., 1983a) or through $n = n(\alpha)$ in Rayleigh-Debye's approximation (Equation 97) (Khlebtsov and Shchyogolev, 1977a) (Figure 2.27, version 1).

If the relative refractive index m is known from the tabulated data or a side experiment, α and m allow one to find the corresponding $K(\alpha, m)$ through the tables or figures (Heller and Pangonis, 1957; Klenin et al., 1977a) (see Figure 2.13) and to calculate N_2 (Heller et al., 1962) from Equation 99.

When m is known, the particle size can be determined not only within 2 < n < 4, but over all the range of $n(\alpha, m)$ (Figure 2.27, version 2).

In the case of ill-defined systems with a quite rough estimation of m, the lower n, the larger the error in \bar{r}_{λ} ; but antibathy of n vs \bar{r}_{λ} is kept over all the range of n, which is sufficient for qualitative (semiquantitative) evaluation of the average particle size as a function of the parameter of any external action.

The described technique has been applied to many objects of different nature. Let me provide a brief summary of these papers. Studied were:

- liquid-liquid phase separation in the system polymer+low-molecular-weight liquid (P+LMWL) (see subsection 3.6.2.5) (Vainerman et al., 1973; Klenin et al., 1974f, 1979b; Prozorov et al., 1976; Uskov et al., 1976; Klenin, 1977, 1982; Timofeyeva et al., 1977); liquid-crystal phase separation (see sections 6.2 and 6.4) (Klenin et al., 1966, 1973bc, 1974b; Klenina et al., 1970, 1972; Kolnibolotchuk et al., 1974a; Peppas, 1975; Yefimtseva et al., 1975a; Blinas et al., 1976; Uskov et al., 1976; Klenin, 1977a, 1982; Klimanova et al., 1977; Pavlova et al., 1977); and liquid-liquid crystal phase separation (Prozorov et al., 1979; Smirnova et al., 1980);
- structural-physical conversions of particles of insoluble fractions (supramolecular and microgel particles ---SMP and MGP) in solutions of cellulose derivatives under different physicochemical effects (variations of temperature, solvent nature, polymer and third-component concentrations) (Klenin, 1965a, 1966, 1977; Klenin and Klenina. 1966bc, 1977; Klenin and Kolnibolotchuk, 1966a; Klenin et al., 1971, 1973d; Klenin and Denisova, 1975, 1977; Gadzhiev et al., 1981; Smirnova and lovleva, 1986), including some technological processes (Klenin et al., 1973e; Smirnova and lovleva, 1986);
- dependences of the physicochemical characteristics and performance of polymer articles on the parameters of MGP (Klenin et al., 1972a, 1973d; Usmanov et al., 1973; Kharitonov et al., 1977) and phase particles (Alekseyeva et al., 1970; Klenin et al., 1975a, 1976a; Smirnova and Iovleva, 1986) in technological solutions;
- phase separation and conversion in systems polymer 1+polymer 2+low-molecularweight liquid (Wajnerman et al., 1972; Yefimova et al., 1975ab; Klykova et al., 1980), including the so-called coacervate systems (Gladilin et al., 1972), polymer complexes (Nurgasheva et al., 1976; Samsonov et al., 1978; Klenina and Fein, 1981;



Figure 2.27. Flow-chart of characterization of the ill-defined disperse systems by the turbidity spectrum method within 2 < n < 4. The circle and oval enclose the source (measured) quantities, the box contains the derived quantities

Izumrudov et al., 1983) and their parameters' influence on the flocculating properties (Tarasenko et al., 1980) and the ability to reduce hydrodynamic resistance in turbulent streams (Uskov and Uskova, 1983);

- phase separation and conversion in systems polymer 1+polymer 2 (Vershinin et al., 1982; Volkov et al., 1982; Roginskaya et al., 1983; Trostyanskaya et al., 1984), including interpenetrating polymer networks (Klenin et al., 1977b) and in systems with modifying additives of low-molecular-weight, oligomeric, and high-molecular-weight substances (Gavrilov et al., 1982ab; Vershinin et al., 1982);
- phase separation and conversion in the course of polymerization (Nesterov et al., 1970; Myshko et al., 1973; Roshchupkin et al., 1977; Sova and Pelzbauer, 1978; Korshunova et al., 1979; Brestkin et al., 1980; Koton et al., 1981);
- emulsion polymerization (Zhukov et al., 1977) and latices (Klenin et al., 1972b; Sokoletski et al., 1983);
- microheterogeneous structure of technical rubbers and its influence on product performance (Vorobiov et al., 1977; Afanasiev et al., 1979);
- microstructure of polymer gels (Sedlàček, 1967ab);
- structure formation in polymer solutions of different nature (Lipatov et al., 1974; Mayorova et al., 1976; Veselovski et al., 1977) and its influence on polymer adsorption from solution onto a solid substrate (Lipatov and Sergeyeva, 1972; Lipatov et al., 1972, 1974; Lipatov, 1980);
- dispersions of surfactants (Mustafin et al., 1980), proteins (Izmaylova and Rebinder, 1974; Pankratova et al., 1974; Dolinnyi, 1978), DNA (Akhrem et al., 1979; Blagoy et al., 1981), synaptosomes amd mitochondria (Korolyov et al., 1981), liposomes (Bezrukova and Rozenberg, 1981), viruses (Bezrukova et al., 1983; Yefimov et al., 1987), bacteria (Koga and Fujita, 1961; Klenin, 1965b, 1974; Fikhman, 1967; Fikhman and Petukhov, 1967; Petukhov and Fikhman, 1967; Klenin et al., 1970; Dmitrieva et al., 1973, 1974ab; Panasenko et al., 1973) and particles of artificial blood plasma (Kuznetsova and Bezrukova, 1982).

Independent determination of the relative refractive index of particles m may cause difficulties; hence, other ways of determination are of interest, including those based on light scattering.

One of such methods is a variation of the immersion method, whereby turbidity is measured as a function of the refractive index of the dispersion medium. When the refractive indices of particles and the medium match, $\tau = 0$. If particles are heterogeneous, only a minimum of τ is observed.

Sometimes, it is sufficient to measure τ at varying μ_1 in a restricted range: extrapolation of the straight line $\tau^{1/n}$ vs μ_1 to $\tau^{1/n} \rightarrow 0$ leads to μ_2 (Koga and Fujita, 1961; Fikhman, 1967; Fikhman and Petukhov, 1967; Dmitrieva et al., 1973) (see Figure 2.27, version 3).

If the volume concentration of particles of the dispersed phase is known, a turbidity spectrum provides simultaneous estimation of α and m (Shchyogolev and Klenin, 1971a)

(see Figure 2.27, version 4). At a known \tilde{M} , Equation 101 gives v, which strongly depends on m within 2 < n < 4 (see Figure 2.18). The tables from (Klenin et al., 1977a) or smoothed curves from (Ramazanov et al., 1983a) are used to plot v vs m at an experimentally determined n, and this plot gives m for the experimentally estimated v, and, further, $K(\alpha, m)$ and N_2 are calculated (see Figure 2.27, version 5).

For strongly anisodiametric particles, the exponent n and \dot{M} enable one to determine the form factor p (Khlebtsov et al., 1978c) (see Figure 2.27, version 6).

The range n < 2

Here it is the structural factor v (and, hence, the mass-volume concentration of particles \tilde{M}) that shows high stability to m, polydispersity, and anisodiametry (see Figures 2.18, 2.19, 2.23, 2.24, 2.26). Thus, for systems with particles with $\bar{r}_{\lambda} \geq 0.3 \dots 0.5 \,\mu$ m the degree of phase transformation $x = \tilde{M}/c$ can be estimated most reliably (Figure 2.28, version 1). Moreover, at a known m, \bar{r}_{λ} , and N_2 are calculated as follows: the universal calibration $n = n(\rho)$ (Equation 98) (Shchyogolev and Klenin, 1971b) (Figure 2.19, curve 3) gives ρ , Equation 91 gives \bar{r}_{λ} , Equation 90 gives $K(\rho)$ (see Figure 2.12), and, finally, Equation 100 yields N_2 (see Figure 2.28, version 2).

Such technique is employed for characterization of phase separation in STT of polymer solutions (see subsection 3.2.3) (Klenin and Uglanova, 1969; Klenin and Shchyogolev, 1971a, 1973, 1979; Klenin et al., 1974d, 1975b, 1983a; Shchyogolev and Klenin, 1974, 1980; Ramazanov et al., 1982, 1983b; Vyakhirev et al., 1983).

Determination of the parameters of particles allows one to judge the mechanism of new phase particle formation in the course of STT of polymer solutions (Klenin and Shchyogolev, 1972; Klenin et al., 1973f, 1974d; Shchyogolev and Klenin, 1973; Shchyogolev et al., 1977b). In particular, Shchyogolev et al. (1977b) showed that polymer particles are formed which contain no low-molecular-weight component.

This technique is also applicable to characterization of the colloid-disperse phase of insoluble polymer complexes (Klenina and Fein, 1981) and of antigen-antibody complexes (Klenin et al., 1974g, 1979a), and the process of phase conversion in liquid crystals (Klenin and Kolchanov, 1975), formation of turbulent curls in liquid crystals in electric fields (Sidorov and Nedranets, 1978).

During complex formation among miscellaneous macromolecules, separate groups of molecular chains interact, which may lead to appearance of loops and hookings, and a particle of the insoluble complex may contain an immobilized low-molecular-weight component.

If an independent method is employed to determine the mean particle size \bar{r}_{λ} (eg. using light microscopy or dynamic light scattering), n gives ρ , and Equation 91 gives the relative refractive index m of "soft" particles; further, N_2 is calculated as in the previous readings (Klenin et al., 1976b) (Figure 2.28, version 3).

If the numerical concentration N_2 is estimated in a side experiment (eg. in Gorjaev's chamber or in a flow ultrainicroscope), version 4 (see Figure 2.28) shows the order of the full characterization of the disperse system.

Dolinnyi (1983) presents nomograms for determination of α and m from the exponent n at two aperture angles of the receiver, 0° and 4° (see Figure 2.28, version 5).



Figure 2.28. Flow-chart of characterization of the ill-defined disperse systems by the turbidity spectrum method within n < 2

A method of scattering spectra is proposed to characterize very dilute disperse systems (Klenin et al., 1978; Khlebtsov et al., 1990) (Figure 2.29).

$$\begin{array}{c} \hline R_{\vartheta}(\lambda) \longrightarrow n_{\vartheta} \longrightarrow \alpha \longrightarrow r_{\lambda} \\ \\ H_{\vartheta} \longrightarrow c^{*}, g/dl \\ \uparrow & \uparrow \\ \hline R_{\vartheta}(\lambda) \longrightarrow n_{\vartheta} \longrightarrow \alpha & m \\ \downarrow & \downarrow \\ G_{\vartheta} \longrightarrow N_{2} \end{array}$$

Figure 2.29. Flow-chart of characterization of the ill-defined disperse systems using a scattering spectrum in Rayleigh-Debye's approximation (Klenin et al., 1978)

Khlebtsov et al. (1991) have theoretically and experimentally studied the dispersion effect of the refractive indices of particles and dispersion medium in the turbidity spectrum method. A new approach is put forward to estimate the optical dispersion of the components of a colloidal system and to consider it when the system's parameters are determined from the wavelength exponent. The method has been verified on PS lattices with the particle diameter from 80 to 800 nm. The elaborated version of the turbidity spectrum method can be used as a metrological test for particle sizes, not inferior to electron microscopy in accuracy.

Numerical calculations by Mie's theory for model gamma distribution of particles and experiments with bimodal latex suspensions have shown (Khlebtsov and Mel'nikov, 1992) the mean particle size determined by the turbidity spectrum method from n(r) calibrations for monodisperse particles to correspond to the relationship

$$\overline{r_n} = \left[\left(\overline{r^{n+4}} \right) / \left(\overline{r^{n+2}} \right) \right]^{1/2}$$

with the minimal error.

The combination of electro-optical, spectrophotometric, and spectroturbidimetric measurements (Khlebtsov et al., 1991, 1992) enables one to build the adsorption isotherm of a polymer on the particles of a dilute suspension and to find a correlation of its characteristic fragments with the parameters of the electro-optical effect. A relation between the adsorption and electro-optical properties of polymeric cellulose suspensions, and their kinetic stability has been estimated.

In (Shchyogolev and Khlebtsov, 1992; Shchyogolev et al., 1993) are reported reviews of the modern applications of the turbidity spectrum method to study biological disperse systems. The effects of polydispersity in some specific versions of reverse problems are analyzed, and the optimal types of averaged particle sizes are pointed to. New kinds of reverse problems related to the analysis of particle aggregation are considered. Examples of experimental determination of complexing biopolymeric systems are given.

The direct and reverse problems of the spectroturbidimetry of ordered disperse systems are discussed by Khlebtsov et al. (1994), Shchyogolev et al. (1994). Recording the attenuation spectra of disordered, oriented, and relaxing disperse systems, one can obtain information on the mean values of such parameters as volume, shape, and refractive index of particles, their concentration and specific surface, the electrical surface polarizability in one experiment.

Khlebtsov (1993ab), Khlebtsov and Mel'nikov (1993ab) have started a new research direction, namely, the spectroturbidimetry of fractal clusters. The integral functions defining the spectral properties of nonabsorbing fractal clusters have been studied.

In summary, the up-to-date development of the turbidity spectrum method provides rather full characterization of the ill-defined disperse systems.

2.2. Light scattering in gases and vapours

Fluctuations in density (or those in the number of molecules) cause light scattering in gases and liquids. Space elements v should be regarded as scattering centres. Every element must be rather small for the condition of Rayleigh's particles to be satisfied $(v^{1/3} \ll \lambda)$ because light scattering in gases and liquids shows all the features of Rayleigh's scattering ($I_{\vartheta} \sim \lambda^{-4}$, z = 1).

On the other hand, this element must contain a sufficiently large number of molecules to behave as a subsystem, with all the laws of thermodynamics to be applicable to it.

Due to Brownian motion, the space element v contains different numbers of molecules at different instants of time.

So, we conditionally divide the whole scattering space V into N^* equal elements of a volume v each.

As a homogeneous medium does not scatter light, the scattering is due to the difference between the actual number of molecules N in the space v and its mean value: $\Delta N = N - \bar{N}$. Then, the amplitude of a wave scattered by the space v in the case of horizontally polarized incident beam is (see Equation 2.1-6)

$$\Delta E_{s,0\parallel} = \frac{k_0^2}{l} E_{0y} \alpha \cos \vartheta \cdot \Delta N, \tag{1}$$

where α is the polarizability of molecules. The intensity of light scattered on the space element (on the average) is expressed as (see Equation 2.1-9)

$$i_{\parallel \nu} = A \overline{\Delta E_{s,0\parallel}^2} = I_{0y} \frac{k_0^4}{l^2} \alpha^2 \cos^2 \vartheta \cdot \overline{(\Delta N)^2}.$$
 (2)

For an ideal gas (see Equation 1.4-29)

$$\overline{(\Delta N)^2} = N = N_v v, \tag{3}$$

 N_v being the number of molecules per unit volume. Considering fluctuations in the number of molecules in different elements of space v independent, we get for the intensity of scattering on all the scattered space V

$$I_{\parallel} = i_{\parallel v} N^*, \tag{4}$$

where $N^{-} = V/v$ is the number of space elements. And, according to Equations 2-4,

$$I_{\parallel} = I_{0y} \frac{k_0^4}{l^2} \alpha^2 N_v V \cos^2 \vartheta.$$
⁽⁵⁾

This formula agrees with Equation 2.1–9.

Naturally, the formulae for the intensity in the cases of vertically polarized and unpolarized incident light also agree. Hence,

$$I_{\vartheta} = I_0 \frac{8\pi^4}{\lambda_0^4 l^2} \alpha^2 N_{\nu} V (1 + \cos^2 \vartheta).$$
(6)

This formula is valid for isotropic molecules with the scalar polarizability α . For a system of anisotropic molecules, the scattered light intensity comprises two summands, an isotropic one and an anisotropic ones (Vuks, 1977),

$$I_{\vartheta} = I_{\vartheta,\imath s} + I_{\vartheta,an}$$

$$= I_0 \frac{8\pi^4}{\lambda_0^4 l^2} N_{\nu} V \left[\alpha^2 (1 + \cos^2 \vartheta) \right] + I_0 \frac{8\pi^4}{\lambda_0^4 l^2} N_{\nu} V \left[\gamma^2 \left(\frac{13}{45} + \frac{\cos^2 \vartheta}{45} \right) \right],$$

$$(7)$$

where α is the mean polarizability

$$\alpha = \frac{\alpha_1 + \alpha_2 + \alpha_3}{3},\tag{8}$$

 γ is the optical anisotropy

$$\gamma^{2} = \frac{(\alpha_{1} - \alpha_{2})^{2} + (\alpha_{1} - \alpha_{3})^{2} + (\alpha_{2} - \alpha_{3})^{2}}{2},$$
(9)

 α_1 , α_2 , α_3 are the polarizability values along the coordinate axes where the molecule is placed, i.e. the main values of the polarizability tensor. If we introduce a **depolarization** factor for vertically polarized incident light (Vuks, 1977)

$$\Delta_{\perp 90} = \frac{I_{\perp 90}^{\parallel}}{I_{\perp 90}^{\perp}},\tag{10}$$

then

$$\Delta_{\perp 90} = \frac{\frac{3}{45}\gamma^2}{\alpha^2 + \frac{4}{45}\gamma^2} = \frac{3\gamma^2}{45\alpha^2 + 4\gamma^2},\tag{11}$$

and the depolarization factor takes the form

$$\Delta_{90} = \frac{\frac{6}{45}\gamma^2}{\alpha^2 + \frac{7}{45}\gamma^2} = \frac{6\gamma^2}{45\alpha^2 + 7\gamma^2}$$
(12)

according to Equation 2.1-16. Equations 11 and 12 give

~

$$\gamma^2 = 45\alpha^2 \frac{\Delta_{90}}{6 - 7\Delta_{90}} \tag{13}$$

2.2. Light scattering in gases and vapours

and

$$\gamma^2 = 45\alpha^2 \frac{\Delta_{190}}{3 - 4\Delta_{190}}.$$
 (14)

Substitution of Equation 13 into Equation 7 at $\vartheta = 90^{\circ}$ leads to

$$I_{90} = I_0 \frac{8\pi^4 N_v V \alpha^2}{\lambda_0^4 l^2} \cdot \frac{6 + 6\Delta_{90}}{6 - 7\Delta_{90}}.$$
(15)

The quantity $\frac{6+6\Delta_{90}}{6-7\Delta_{90}}$ is called Cabannes' factor: it is equal to 1 for isotropic molecules and exceeds 1 for anisotropic molecules.

It follows from Equation 7 that

$$R_{90} = \frac{8\pi^4}{\lambda_0^4} N_v (\alpha^2 + \frac{13}{45}\gamma^2) \tag{16}$$

with

$$R_{90is} = \frac{8\pi^4}{\lambda_0^4} N_\nu \alpha^2 \tag{17}$$

(cf. Equation 2.1-19) and

$$R_{90an} = \frac{8\pi^4}{\lambda_0^4} N_\nu \frac{13}{45} \gamma^2.$$
(18)

In view of Equation 15,

$$R_{90} = \frac{8\pi^4}{\lambda_0^4} N_\nu \alpha^2 \frac{6 + 6\Delta_{90}}{6 - 7\Delta_{90}},\tag{19}$$

and, according to Equation 17,

$$R_{90} = R_{90is} \frac{6 + 6\Delta_{90}}{6 - 7\Delta_{90}}.$$
(20)

Integration of Equation 7 over all the solid angle (Equation 2.1-31) gives

$$\tau = \frac{128\pi^5}{3\lambda_0^4} N_\nu (\alpha^2 + \frac{2}{9}\gamma^2)$$
(21)

with

$$\tau_{13} = \frac{128\pi^5}{3\lambda_0^4} N_\nu \alpha^2 \tag{22}$$

(cf. Equation 2.1-33) and

$$\tau_{an} = \frac{128\pi^5}{3\lambda_0^4} N_\nu \frac{2}{9} \gamma^2 = \frac{256\pi^5}{27\lambda_0^4} N_\nu \gamma^2.$$
(23)

If one substitutes γ^2 from Equation 13 into Equation 21, then

$$\tau = \frac{128\pi^5 N_{\nu} \alpha^2}{3\lambda_0^4} \cdot \frac{6+3\Delta_{90}}{6-7\Delta_{90}}.$$
(24)

Together with Equation 19, it yields for the general case

$$\tau = \frac{16\pi}{3} R_{90} \frac{1+0.5\Delta_{90}}{1+\Delta_{90}}.$$
(25)

Relationships 22–25 hold true for one component liquids and solutions as well. Mcasuring Δ_{90} and $\Delta_{\perp 90}$ is the experimental basis of determining such important molecular parameters as the polarizability α and anisotropy γ using Equations 13 and 14 (Volkenstein, 1951; Fabelinski, 1965; Kerker, 1969; Vuks, 1977).

2.3. Light scattering in one-component liquids

2.3.1. Light scattering in liquids with isotropic molecules

Density fluctuations in liquids are accompanied by fluctuations in the polarizability α (the dielectric constant ϵ , the refractive index μ) in the space element v. Due to these fluctuations, space elements of v seem to be quasiparticles with the dielectric constant ϵ' (the polarizability α' and the refractive index μ'), which differ from the average macroscopic values: $\Delta \epsilon = \epsilon' - \epsilon$, $\Delta \alpha = \alpha' - \alpha$, $\Delta \mu = \mu' - \mu$. These quasiparticles are chaotically distributed in a matrix with the dielectric constant $\epsilon = \bar{\epsilon}(=\mu^2)$ and their numerical concentration is $N_v = 1/v$. On the basis of Equation 2.1-33 (Kerker, 1969), we can write

$$\tau = \frac{128\pi^5}{3\lambda_0^4} \cdot \frac{\overline{(\Delta\alpha)^2}}{v} \tag{1}$$

and (see Equations 2.1-19, 20)

$$R_{90} = \frac{8\pi^4}{\lambda_0^4} \cdot \frac{\overline{(\Delta\alpha)^2}}{v},\tag{2}$$

$$R_{\vartheta} = \frac{8\pi^4}{\lambda_0^4} \cdot \frac{(\Delta\alpha)^2}{v} (1 + \cos^2 \vartheta).$$
(3)

According to Equation 2.1-46,

$$\Delta \alpha \cong \frac{v}{4\pi} \Delta \epsilon \tag{4}$$

and

$$\tau = \frac{8\pi^3}{3\lambda_0^4} \overline{(\Delta\epsilon)^2} v.$$
 (5)

In view of

$$\Delta \epsilon = {\mu'}^2 - \mu^2 \approx (\mu' - \mu)(\mu' + \mu) \approx 2\mu \,\Delta\mu,\tag{6}$$

$$\overline{(\Delta\epsilon)^2} = 4\mu^2 \,\overline{(\Delta\mu)^2}, \qquad \tau = \frac{32\pi^3\mu^2 \,\overline{(\Delta\mu)^2}}{3\lambda_0^4} v. \tag{7}$$

If the state equation of the liquid is known (Equation 1.2-33), then only two quantities remain as independent thermodynamic parameters. It follows that $\Delta \epsilon$ can be expressed through fluctuations in two quantities, namely, V (or ρ) and T or P and T (the former pair is used more often):

$$\Delta \epsilon = \left(\frac{\partial \epsilon}{\partial \varrho}\right)_T \Delta \varrho + \left(\frac{\partial \epsilon}{\partial T}\right)_{\varrho} \Delta T.$$
(8)

Detailed analysis (Fabelinski, 1965; Kerker, 1969; Vuks, 1977) shows the second summand to be negligible in comparison with the first one, and

$$\tau = \frac{8\pi^3 v}{3\lambda_0^4} \left(\frac{\partial \epsilon}{\partial \varrho}\right)_T^2 \overline{(\Delta \varrho)^2}.$$
(9)

As $\overline{(\Delta v)^2} = -kT(\partial v/\partial P)_T$ (Equation 1.4-23) and $\varrho = m/v$, then $\Delta \varrho = -\varrho \, \Delta v/v$ and

$$\overline{(\Delta\varrho)^2} = -kT \left(\frac{\partial v}{v \,\partial P}\right)_T \frac{\varrho^2}{v} = kT \chi_T \frac{\varrho^2}{v},\tag{10}$$

where

$$\chi_{T} = -\left(\frac{\partial v}{v \, \partial P}\right)_{T} = \frac{1}{\varrho} \cdot \frac{\partial \varrho}{\partial P}$$

is the isothermal compressibility (Equation 1.1.2-44). In view of Equation 10,

$$\tau = \frac{8\pi^3}{3\lambda_0^4} \left(\varrho \frac{\partial \epsilon}{\partial \varrho}\right)_T^2 k T \chi_T,\tag{11}$$

$$R_{90} = \frac{3\tau}{16\pi} = \frac{\pi^2}{2\lambda_0^4} \left(\rho \frac{\partial \epsilon}{\partial \rho} \right)_T^2 k T \chi_\tau, \tag{12}$$

and

$$R_{\vartheta} = \frac{\pi^2}{2\lambda_0^4} \left(\varrho \frac{\partial \epsilon}{\partial \varrho} \right)_T^2 k T \chi_T (1 + \cos^2 \vartheta). \tag{13}$$

These three expressions are referred to as Einstein's equations (Einstein, 1910; Fabelinski, 1965; Kerker, 1969; Vuks, 1977). Their comparison with experiment has turned out to be difficult owing to the complexity of representation of $[\varrho(\partial \epsilon/\partial \varrho)]_T$ as experimental quantities. This question still raises debate (Shakhparonov, 1963, 1970; Fabelinski, 1965; Kerker, 1969; Vuks, 1970, 1977; Ioffe, 1983).

2.3.2. Light scattering in liquids with anisotropic molecules

When considering the anisotropic component of scattered light in gases (Equation 2.2-7), molecules are presumed to be oriented every which way with an equal probability. As there exists a short-range order in liquids, the situation is much more complicated.

However, as the evidence suggests, Equations 2.2-19, 24,-25 are applicable to liquids with a sufficient accuracy. So, the anisotropic component R_{90an} can be calculated from the measured τ or R_{90} and the depolarization factor Δ_{90} .

Assuming the random distribution of molecules in liquids (Vuks, 1977),

$$R_{90an} = \frac{8\pi^4}{\lambda_0^4} \frac{13}{45} N_v \left(\frac{\mu^2 + 2}{3}\right)^2 \gamma^2.$$
(14)

It differs from R_{90an} for gases (Equation 2.2–18) by the internal field factor $[(\mu^2 + 2)/3]^2$ only.

Analysis of the experimental results suggests that R_{90an} appears close to its calculated value (Equation 14) for many liquids. The deviations observed can reasonably be explained by the existence of the short-range order.

If an integral correlation parameter of molecular orientation \mathcal{J} (Anselm, 1947) is introduced within the first coordination sphere

$$\mathcal{J} = \sum^{z} \left(\overline{\cos^2 \vartheta} - \frac{1}{3} \right), \tag{15}$$

where $\overline{\cos^2 \vartheta}$ is the mean statistical value of $\cos^2 \vartheta$ for molecular orientations, z is the number of molecules in the first coordination sphere, ϑ is the angle between the predominant direction and the molecular axis, then

$$R_{90an} = \frac{8\pi^4}{\lambda_0^4} \cdot \frac{13}{45} N_{\nu} \left(\frac{\mu^2 + 2}{3}\right)^2 \gamma_{ef}^2, \tag{16}$$

where

$$\gamma_{ef}^2 = \gamma^2 \left(1 + \frac{3}{2} \mathcal{J} \right).$$

In the absence of an orientational order, $\overline{\cos^2 \vartheta} = 1/3$ and $\mathcal{J} = 0$. Generally, $0 < \overline{\cos^2 \vartheta} < 1$ when $\overline{\cos^2 \vartheta} < 1/3$, $\mathcal{J} < 0$ and vice versa. In the former case, the anisotropic component of scattering (and, hence, γ_{ef}^2) is less, and in the latter case it is more than that in the absence of an orientational interaction (γ^2).

Vuks (1977) reports γ_{ef}^2 and γ^2 for 27 liquids. The values of the optical anisotropy of isolated molecules γ^2 have been determined from Δ_{90} in vapours or solutions and, rarely, using Kerr's effect.

With rare exception, the deviations of γ_{ef}^2 from γ^2 fall within 30%, i.e. they are not too high. Many liquids show deviations not exceeding 6% (the accuracy of measurement). As one can expect, the maximal deviations take place for high-symmetrical molecules of flat (benzene, pyridine, mesitylene) or elongated (*p*-xylene, chlorobenzene, bromobenzene) shape. The orientational order in such liquids is similar to the crystal structure (Frenkel, 1955). Eg. for benzene $\gamma_{ef}^2/\gamma^2 > 1$ and for *p*-dichlorobenzene $\gamma_{ef}^2/\gamma^2 < 1$. X-ray analysis of these two crystals reveals that the planes of molecules in a benzene crystal are arranged at an angle close to 90° (whereas in liquid benzene $\cos^2 \vartheta < 1/3$, $\mathcal{J} < 0$) and the long axes of *p*-dichlorobenzene molecules are mainly parallel (whereas in liquid *p*-dichlorobenzene $\cos^2 \vartheta > 1/3$ and $\mathcal{J} > 0$).

As temperature rises, the short-range order is destroyed and γ_{ef}^2 approaches γ^2 . Propanol, o-xylene, toluene and other liquids do not exhibit any order in the distribution of the nearest molecular orientations.

These data on the short-range order in liquids are in excellent agreement with the views of the structure of liquids developed by Bernal and his followers (Bernal, 1961, 1965; Bernal and King, 1971; Skripov and Koverda, 1984).

2.3.3. Dynamics of density fluctuations. Inelastic light scattering

The study of inelastic light scattering (the spectral dependence of scattered light) has led to a concept of two kinds of density fluctuations, namely, an adiabatic one and an isobaric one (Landau and Placzek, 1934; Gross, 1940, 1946; Fabelinski, 1965; Kerker, 1969; Vuks, 1977).

Adiabatic fluctuations are related to pressure fluctuations, which can be thought of as Debye's thermoelastic waves (from the theory of heat capacity), propagating in liquid along different directions with the velocity of sound. Brillouin (1922) has proposed considering a beam scattered at angle ϑ as reflected from the front of elastic fluctuation waves of a certain orientation with the reflection angle $\varphi = \vartheta/2$ (Figure 2.30) (Brillouin,



Figure 2.30. Schematic of light scattering on Debye's thermoelastic waves or on fluctuation waves of concentration

1922; Mandelshtam, 1926; Fabelinski, 1965; Kerker, 1969; Vuks, 1977). Then, Bragg's relation for the first diffraction maximum (the second one is negligible due to the blurred
character of the elastic wave front) is

$$2\Lambda\sin\varphi = 2\Lambda\sin\frac{\vartheta}{2} = \lambda. \tag{17}$$

With allowance for Equation 2.1 50,

$$\Lambda = \frac{2\pi}{q},\tag{18}$$

where Λ is the elastic wavelength, λ is the wavelength in the liquid. As any fluctuation profile can be represented as a 3D (spatial) Fourier series, condition 17 corresponds to the s (or q) component of the Fourier transform.

An elastic wave propagates with the velocity \mathcal{V} , and Doppler's shift in frequency must occur. Of all possible directions of elastic waves, only two meet condition 17; those which propagate along two opposite directions with the velocities $+\mathcal{V}$ and $-\mathcal{V}$, so the spectrum of scattered light is split into Mandelshtam-Brillouin's doublet (Fabelinski, 1965; Kerker, 1969; Vuks, 1977)

$$\omega = \omega_s - \omega_0 = \pm \mathcal{V}q,\tag{19}$$

where ω_0 and ω_s are the frequencies of the incident and scattered wave, respectively.

Isobaric density fluctuations are due to the entropy fluctuations, i.e. fluctuations in Frenkel's "holes" in the structure of a liquid (Frenkel, 1955). They lead to the density fluctuations which do not depend on pressure fluctuations. Their evolution proceeds quite slowly and causes a much lower frequency shift on scattering. These fluctuations are related to the central component of scattered light called Rayleigh's component.

To consider the spectral dependence of scattered light in liquids more rigorously, we require introducing an idea of a time correlation function (Berne and Pecora, 1976).

Suppose a certain quantity $A(\tau)$ to fluctuate with time (Figure 2.31a) near its mean value

$$\langle A \rangle = \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} A(\tau) \, d\tau.$$
⁽²⁰⁾

At two different instants, τ and $\tau+t$, A has, in general, different values $A(\tau+t) \neq A(\tau)$, but if t is small in comparison with the characteristic period of fluctuations of A, $A(\tau+t)$ will be close to $A(\tau)$. As t increases, one can expect more difference between $A(\tau+t)$ and $A(\tau)$. This, therefore, attests to the correlation between $A(\tau+t)$ and $A(\tau)$ at small t as well as of the absence of any correlation at large t. An **autocorrelation function** of A (a **time correlation function**) serves as the measure of this correlation. It is defined as

$$\langle A(0)A(t)\rangle = \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} A(\tau)A(\tau+t) d\tau.$$
⁽²¹⁾

It follows that $\langle A(0)A(t)\rangle = \langle A^2\rangle$ is the maximal value of this function. As when $t \to \infty$, $A(\tau)$ and $A(\tau + t)$ become fully uncorrelated, then

$$\lim_{t \to \infty} \langle A(0)A(t) \rangle = \langle A(0) \rangle \langle A(t) \rangle = \langle A \rangle^2.$$
(22)



Figure 2.31. Time dependence of a fluctuating quantity A(a) and the time correlation functions $\langle A(0)A(\tau)\rangle(b)$. $t = \tau_{r,A}$ is the time of correlation of A, or the relaxation time of A

So, the time correlation function of a nonperiodic quantity A diminishes with time from $\langle A^2 \rangle$ to $\langle A \rangle^2$ (Figure 2.31b). In many applications, the autocorrelation function decays exponentially and

$$\langle A(0)A(t)\rangle = \langle A\rangle^2 + \left\{ \left\langle A^2 \right\rangle - \left\langle A \right\rangle^2 \right\} \exp\left(-\frac{t}{\tau_{r,A}}\right),\tag{23}$$

where $\tau_{r,A}$ is the **relaxation time**, or the time of correlation of A.

If a deviation of an instantaneous value $A(\tau)$ from the mean one is thought of as a fluctuation of A

$$\delta A(\tau) \equiv A(\tau) - \langle A \rangle, \qquad (24)$$

then

$$\langle \delta A(0) \, \delta A(t) \rangle = \left\langle \delta A^2 \right\rangle \exp\left(-\frac{t}{\tau_{r,A}}\right).$$
 (25)

Consider the time correlation function $\langle A^*(0)A(t)\rangle$, where A^* is the complex conjugate to A. Define a spectral density (or an energy spectrum) $I_A(\omega)$ of $\langle A^*(0)A(t)\rangle$ as

$$I_A(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \left\langle A^*(0)A(t) \right\rangle \, dt.$$
(26)

Thus, the time correlation function is the Fourier transform of the spectral density

$$\langle A^*(0)A(t)\rangle = \int_{-\infty}^{\infty} e^{+i\omega t} I_A(\omega) \, d\omega.$$
⁽²⁷⁾

If A is chosen as E_s (the electric field of the scattered wave), then

$$I_E(\omega_s) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega_s t} \left\langle E_s^*(0) E_s(t) \right\rangle \, dt. \tag{28}$$

Consider light scattering in liquid with due account of the time dependence of the fluctuations in dielectric constants $\epsilon(\vec{r}, t) = \epsilon + \delta \epsilon(\vec{r}, t)$.

In the general case, the scattered wave field, allowing for possible phase shift, has the form (see Equations 2.1-5,-51)

$$E_{s} = -\frac{k_{0}^{2}}{l^{3}} \left[\vec{l} \left[\vec{l} \, \vec{p}_{0} \right] \right] c^{i\delta} c^{i(\omega_{0}t - kl)},$$

where ω_0 denotes the incident wave frequency.

Here \vec{p}_0 is replaced by the dipole momentum increment of a space element (see Equations 2.1-44,-45) and

$$dp_0 = E_{0z} \frac{\delta \alpha}{\delta v} dv = E_{0z} \frac{\delta \epsilon}{4\pi} dv.$$

For simplicity, assume incident light vertically polarized. Then, the scattered wave field is expressed as (cf. Equations 2.1-51, 53)

$$E_{s,\perp}(t) = -\frac{E_{0z}k_0^2}{4\pi l} \exp i(\omega_0 t - kl) \int_V \delta\epsilon(\vec{r}, t) e^{i\delta} dv$$
⁽²⁹⁾

with integration over all the scattering space V.

The integral is the space Fourier transform for the fluctuations of the dielectric constants, i.e. (cf. Equation 2.1-83)

$$\delta\epsilon(\vec{q},t) = \int_{V} \delta\epsilon(\vec{r},t) e^{i\delta} dv$$

and

$$E_{s,\perp}(q,t) = -\frac{E_{0z}k_0^2}{4\pi l} \exp i(\omega_0 t - kl) \,\delta\epsilon(\vec{q},t).$$

Now, write the time correlation function of $E_{s,\perp}(q,t)$:

$$\left\langle E^*_{s,\perp}(q,0)E_{s,\perp}(q,t)\right\rangle = \frac{L_{0z}^2k_0^4}{16\pi^2l^2} \left\langle \delta\epsilon^*(\vec{q},0)\,\delta\epsilon(\vec{q},t)\right\rangle \exp i\omega_0 t. \tag{30}$$

On substituting Equation 30 into Equation 28, we get in an expression for the spectral density

$$I_{E\perp}(\omega) = \frac{E_{0z}^2 k_0^4}{16\pi^2 l^2} \cdot \frac{1}{2\pi} \int_{-\infty}^{\infty} \left\langle \delta \epsilon^*(\vec{q}, 0) \, \delta \epsilon(\vec{q}, t) \right\rangle \exp i(\omega_0 - \omega_s) t \, dt, \tag{31}$$

which up to the constant matches the scattered light intensity $I_{\perp}(\omega)$ measured experimentally (cf. Equation 2.1-75).

This formula shows a frequency change $\omega = \omega_s - \omega_0$ as a result of scattering, which is due to the time dependence $\delta\epsilon(\vec{q}, t)$ whereas scattering on stationary ("frozen") fluctuations leads to no frequency change (see subsection 2.3.1).

If the characteristic time of $\delta \epsilon(\vec{q}, t)$ change is less than or equal to 10^{-10} s, the corresponding frequency change is measured by means of a **filter technique** (prism spectrophotometers, diffraction lattices). If changes of $\delta \epsilon(\vec{q}, t)$ last $10^{-10} \dots 10^{-6}$ s, then Fabry-Perot's interferometers are used. For the fluctuation fall time within $10^{-6} \dots 1$ s, a method of optical mixing has been developed (Forrester, 1961; Cummins et al., 1964; Ford and Benedek, 1965; Cummins and Swinney, 1970; Cummins and Pike, 1974; Dubnishev and Rinkevichyus, 1982).

In the **heterodyne** method (Forrester et al., 1947; Gorelik, 1947; Cummins et al., 1964; Berne and Pecora, 1976) the time correlation function

$$\mathbf{I}_1(t) \equiv \left\langle E_s^*(0) E_s(t) \right\rangle,\tag{32}$$

which is also called a heterodyne correlation function is measured.

In the **homodyne** method (Forrester et al., 1955; Ford and Benedek, 1965; Berne and Pecora, 1976) a **homodyne correlation function**

$$\mathbf{I}_{2}(t) \equiv \left\langle |E_{s}(0)|^{2} |E_{s}(t)|^{2} \right\rangle = \left\langle I(0)I(t) \right\rangle \tag{33}$$

is measured, which is obtained at the output of the block called an **autocorrelator** (a **photon correlator**).

In the case of heterodyning, scattered light of the frequency ω_s is mixed with a part of incident light of the frequency ω_0 in the detector. This provides strong amplification of signals as it happens in a heterodyne receiver of radio signals. Subsequent transformation of this low-frequency signal results in the heterodyne correlation function (Equation 32).

In the case of homodyning, only light scattered by the system reaches the receiver. Let A, denote the number of scattered light photons that have reached the photocathode during the time interval $\Delta \tau$ (see Figure 2.31a). The correlator provides measuring photocurrent during two fixed time intervals $\Delta \tau$ separated by $i \Delta \tau$ (i = 1, 2, ..., n). The two values of the photocurrent, proportional to the scattered light intensity, are multiplied, and this signal goes to the corresponding *i*th channel of the correlator's microprocessor memory. This procedure is repeated many times (eg. $N \sim 10^5$) for every time interval, the signal is cumulated and averaged in each channel. As a result, a value $\langle I(0)I(t) \rangle = I_2(t)$ appears on the correlator's output as a function of the *i*th memory channel or of the time interval $t = i \Delta \tau$ according to Equations 21 and 33 (see Figure 2.31b). In this connection, this method is often referred to as a **photon correlation spectroscopy** of scattered light (or an **self-beat method**).

A special block called a **spectrum analyzer** converts Equations 32 and 33 to their Fourier transforms, the spectral density (Equation 28) and a **spectral power**

$$P(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \langle I(0)I(t) \rangle dt.$$
(34)

In most cases, when the spectral dependence of scattered light reflects Gaussian stationary random process of the object structure changing, information obtained by means of both the techniques is the same and Equations 32 and 33 are related by Siegert's relationship

$$\mathbf{I}_{2}(t) = |\mathbf{I}_{1}(0)|^{2} + |\mathbf{I}_{1}(t)|^{2}.$$
(35)

Light scattering brings detailed information on the dielectric constant's fluctuations if and only if their scale and the wavelength of light are of the same order of magnitude (i.e. ~ 1000 Å or more).

Fluctuations of such extent involve collective motion of a great number of molecules and therefore can be described by the laws of macroscopic physics, namely, thermodynamics and hydrodynamics. Thus, small parts of the system where fluctuations of the macroscopic values manifest themselves in the properties of scattered light (the Fourier transform) contain rather many molecules that enables one to speak of **local values** of such macroscopic terms as entropy, enthalpy, and pressure. Every point \vec{r} corresponding to a small space element in liquid at an instant t can be ascribed some values of entropy density $s(\vec{r},t)$, of molecule number density $\rho(\vec{r},t)$, of energy $e(\vec{r},t)$, of pressure $P(\vec{r},t)$, and of the dielectric constant $\epsilon(\vec{r},t)$.

Local equilibrium is spoken of when the local values of thermodynamic and optical properties relate to each other as if the substance were in the state of general thermodynamic equilibrium. This principle of local equilibrium underlies hydrodynamics (Landau and Lifshitz, 1988) and unequilibrium thermodynamics (Glansdorff and Prigogine, 1971).

The dielectric constant ϵ of a one-component liquid in the state of complete equilibrium is a function of density ρ and temperature T: $\epsilon = \epsilon(\rho, T)$ (see Equation 8) (a dielectric state equation). It is clear that there occur small fluctuations of local density and temperature at the local level, so

$$\rho(\vec{r},t) = \rho + \delta\rho(\vec{r},t) \quad \text{and} \quad T(\vec{r},t) = T + \delta T(\vec{r},t).$$

According to the principle of local equilibrium,

$$\epsilon(\vec{r},t) = \epsilon(\rho + \delta\rho(\vec{r},t); T + \delta T(\vec{r},t)).$$
(36)

As these fluctuations are expected to be rather small, they can be represented as two terms of the Taylor series. If

$$\delta\epsilon(\vec{r},t) = \epsilon(\vec{r},t) - \epsilon(\rho,T),$$

then

$$\delta\epsilon(\vec{r},t) = \left(\frac{\partial\epsilon}{\partial\rho}\right)_T \delta\rho(\vec{r},t) + \left(\frac{\partial\epsilon}{\partial T}\right)_\rho \delta T(\vec{r},t). \tag{37}$$

As $(\partial \epsilon / \partial T)_{\rho} \ll (\partial \epsilon / \partial \rho)_T$, the second term can be neglected in many cases. Then in view of Equations 29-31 and 37, we get

$$I_{\perp}(\vec{q},\omega) = B\left(\frac{\partial\epsilon}{\partial\rho}\right)_{T}^{2} S_{\rho\rho}(\vec{q},\omega), \tag{38}$$

where

$$S_{\rho\rho}(\vec{q},\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-i(\omega_0 - \omega_s)t) \left\langle \delta\rho^*(\vec{q},0)\delta\rho(\vec{q},t) \right\rangle dt$$
(39)

is called a dynamic form factor (cf. Equation 2.1-61),

$$B = \frac{k_0^4 I_{0z}}{16\pi^2 l^2}.$$

Hence, $S_{\rho\rho}(\vec{q},\omega)$ is the spectral density of the autocorrelation function of density fluctuations $\delta\rho(\vec{q},t)$, $\omega = \omega_s - \omega_0$. The integral intensity over all the frequency range is expressed as

$$I_{\perp}(\vec{q}) = \int_{-\infty}^{\infty} I_{\perp}(\vec{q},\omega) \, d\omega = B\left(\frac{\partial\epsilon}{\partial\rho}\right)_{T}^{2} \frac{1}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp(-i\omega t) \left\langle \delta\rho^{*}(\vec{q},0)\delta\rho(\vec{q},t) \right\rangle \, dt \, d\omega(40)$$
$$= B\left(\frac{\partial\epsilon}{\partial\rho}\right)_{T}^{2} \int_{-\infty}^{\infty} \delta(t) \left\langle \delta\rho^{*}(\vec{q},0)\delta\rho(\vec{q},t) \right\rangle \, dt = B\left(\frac{\partial\epsilon}{\partial\rho}\right)_{T}^{2} S(\vec{q}),$$

where

$$S(\vec{q}) = \left\langle |\delta\rho(\vec{q})|^2 \right\rangle = \frac{I_{\perp}(\vec{q})}{I_{\perp}(q=0)} \tag{41}$$

is a structural factor (cf. Equation 2.1-64) which is the mean square value of the \bar{q} th Fourier component of density fluctuations $\delta \rho(\vec{q})$.

In Equation 40

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(-i\omega t)\,d\omega=\delta(t)$$

on the basis of the integral representation of the δ function (Berne and Pecora, 1976; Vladimirov, 1979).

The scale of the scattered light sensitivity to structure is of the order $q^{-1} \sim 1000$ Å of magnitude and turns to be sufficiently larger than the range of molecular interactions in liquid (far from the spinodal), and there is no q-dependence in Equation 41

$$\lim_{q \to 0} \delta \rho(\vec{q}) = \lim_{q \to 0} \int_{V} e^{i\vec{q}\cdot\vec{r}} \delta \rho(\vec{r}) \, d\vec{r} = \int_{V} \delta \rho(\vec{r}) \, d\vec{r} = \delta N, \tag{42}$$

where δN is a fluctuation of the number of molecules in the scattering space.

In view of Equation 1.4-26,

$$l_{\perp} = \frac{l_0 k_0^4}{16\pi^2 l^2} \left(\frac{\partial \epsilon}{\partial \rho}\right)_T^2 V \rho^2 k T \chi_{\tau},\tag{43}$$

that matches Einstein's formula (Equation 13). As the liquid density enters into both the nominator and denominator of Equation 43, its form does not depend on density units.

To derive an explicit form of the spectral dependence $I(\vec{q}, \omega)$ (Equation 38), information on the correlation of density fluctuations in two different points at different instants of time is required. If the distance between these points and the wavelength is of the same order of magnitude, fluctuations must correlate in time, i.e. the density fluctuation at the first point at t = 0 may propagate or spread to the second point for time t. In this connection, the time correlation function can be derived in terms of the hydrodynamic equations and Onsager's principle.

Having taken advantage of thermodynamics of irreversible processes, Onsager (1931ab) proposed a principle (Crossignani et al., 1975; Berne and Pecora, 1976), which claims spontaneous fluctuations of $A(\vec{r}, l)$ to disappear with time according to the same relaxational equations describing macroscopic relaxation processes (Onsager's regression hypothesis). The relaxational equations are valid only for time periods during which a great number of molecular collisions happen and only for distances much longer than the intramolecular ones. Experiments on inelastic light scattering provide the validity of this condition.

For the density A of a quantity A (eg. mass, energy), the conservation equations in the differential form hold

$$\frac{\partial A}{\partial t} + \nabla \vec{\mathcal{J}}_A = 0, \tag{44}$$

where \mathcal{J}_A is the flux density of A. Onsager states the applicability of this equation to equilibrium systems with spontaneous thermal fluctuations, as well as to the systems disturbed from the equilibrium condition. In the former case

$$A(\vec{r},t) = \langle A \rangle + \delta A(\vec{r},t); \quad \vec{\mathcal{J}}_A(\vec{r},t) = \left\langle \vec{\mathcal{J}}_A \right\rangle + \delta \vec{\mathcal{J}}_A(\vec{r},t), \tag{45}$$

where $\langle A \rangle$ and $\langle \vec{\mathcal{J}}_A \rangle$ are the equilibrium values, δA , $\delta \vec{\mathcal{J}}_A$ are fluctuations. At equilibrium $\langle \vec{\mathcal{J}}_A \rangle = 0$ and $\langle A \rangle$ does not depend on (\vec{r}, t) , so Equations 44 and 45 yield

$$\frac{\partial}{\partial t}\delta A(\vec{r},t) = -\nabla \delta \vec{\mathcal{J}}_A(\vec{r},t).$$
(46)

Its space Fourier transform gives

$$\frac{\partial}{\partial t}\delta A(\vec{q},t) = i\vec{q}\,\delta\vec{\mathcal{J}}_A(\vec{q},t) \quad \text{or} \quad \delta\dot{A}(\vec{q},t) = i\vec{q}\,\delta\vec{\mathcal{J}}_A. \tag{47}$$

The time correlation function (see Equation 25) written for this solution has the form (Pike, 1974; Berne and Pecora, 1976)

$$S_{AA}(\vec{q},t) = \left\langle \delta A^{\star}(\vec{q},0) \delta A(\vec{q},t) \right\rangle = \left\langle |\delta A(\vec{q})|^2 \right\rangle e^{-\Gamma(q)t} \cos \omega(q) t, \tag{48}$$

where $\delta A(\vec{q}, t)$ is the *q*th Fourier component of the fluctuation $\delta A(\vec{r}, t)$.

The correlation function (Equation 48) corresponds to the spectral density (see Equation 26), which represents a superposition of Lorentzians, i.e. of curves like $y = a/\pi(x^2 + a^2)$:

$$S_{AA}(\vec{q},\omega) = \frac{1}{\pi} S_{AA}(\vec{q}) \left\{ \frac{\Gamma(q)}{\left[\omega - \omega(q)\right]^2 + \Gamma^2(q)} + \frac{\Gamma(q)}{\left[\omega + \omega(q)\right]^2 + \Gamma^2(q)} \right\},\tag{49}$$



Figure 2.32. Spectral density $S_{AA}(\vec{q},\omega)$ (a) and its dependence on the wave vector q (b)

where $S_{AA}(\vec{q}) \equiv \langle |\delta A(\vec{q})|^2 \rangle$ is the mean square value of the fluctuation $\delta A(\vec{q},t)$, $\Gamma(q)$ is the halfwidth (at the halfheight $S_{AA}(\vec{q},\omega)_{\max}/2$), $\omega(q)$ is the shift of the spectral band (Figure 2.32).

In most applications

$$\Gamma(q) = \gamma q^2, \tag{50}$$

$$\omega(q) = \mathcal{V}q,\tag{51}$$

where γ is an attenuation coefficient and \mathcal{V} is the rate of fluctuation propagation. Usually, γ is the sum of the transport coefficients (in particular, the diffusion coefficient D).

Measurement of the width and shift of the bands as functions of q allows one to determine γ and \mathcal{V} and, therefore, to obtain important information of the collective modes of the molecular motion and other transport properties of molecules in the system.

 $\Gamma^{-1}(q)$ can be regarded as the lifetime of fluctuations $\tau_r(q)$ (see Equations 23 and 48).

It follows from Equation 47 that when $q \to 0$, the rate of changes of $\delta A(\vec{q}, t)$ approaches zero. This means that the density fluctuations of the conservative variable proves to live infinitely long when $q \to 0$ ($\vartheta \to 0$ or $\lambda \to \infty$), i.e. $\tau_r(q) \to \infty$.

Fluctuations responding to the above properties are called a hydrodynamic mode, and the way of their description is called a hydrodynamic approximation. The inequality

$$q \ll \xi^{-1},\tag{52}$$

(ξ being the radius of interactions among the molecules or, in a more general case, the correlation radius of density fluctuations in liquid) serves as the condition of applicability of the hydrodynamic approximation.

Near the critical point (near the spinodal), where $\xi \to \infty$ ($\xi^{-1} \to 0$), the condition of the hydrodynamic approximation (Equation 52) fails to satisfy.

With due account of the q vs λ , ϑ dependence and according to Equation 2.1-50, the range of applicability of the hydrodynamic approximation can be varied through λ and ϑ .

The density autocorrelation function $\langle \delta \rho^-(\vec{q}, 0) \delta \rho(\vec{q}, t) \rangle$ for simple liquids is calculated by hydrodynamic methods (Mountain, 1966; Stanley, 1971; Cummins and Pike, 1974; Lallemand, 1974; Crossignani et al., 1975; Berne and Pecora, 1976; Flygare, 1978). The properties of such liquids are described by the following set of the dynamic variables $\rho(\vec{r}, t), T(\vec{r}, t), \vec{V}(\vec{r}, t)$.

Of these five variables, only three do influence light scattering along a given direction \vec{q} (say, z) since the two transversal components $\vec{\mathcal{V}}$ (\mathcal{V}_x and \mathcal{V}_y) do not comply with Bragg's relation (Equation 17) (see Figure 2.30).

Detailed analysis of the problem of light scattering in a one-atomic liquid (Mountain, 1966; Stanley, 1971; Crossignani et al., 1975; Berne and Pecora, 1976; Flygare, 1978) leads to the dynamic form factor

$$S_{\rho\rho}(\vec{q},\omega) = \frac{\mathcal{V}\rho^2 kT \chi_T}{\pi} \left\{ \left(1 - \frac{1}{\gamma} \right) \left[\frac{2D_T q^2}{\omega^2 + (D_T q^2)^2} \right] + \frac{1}{\gamma} \left(\frac{\Gamma q^2}{\left[\omega - \omega(q) \right]^2 + \left[\Gamma q^2 \right]^2} + \frac{\Gamma q^2}{\left[\omega + \omega(q) \right]^2 + \left[\Gamma q^2 \right]^2} \right) + \frac{b(q)}{\gamma} \left(\frac{\omega + \omega(q)}{\left[\omega + \omega(q) \right]^2 + \left[\Gamma q^2 \right]^2} - \frac{\omega - \omega(q)}{\left[\omega - \omega(q) \right]^2 + \left[\Gamma q^2 \right]^2} \right) \right\},$$
(53)

where $\gamma \equiv c_P/c_V = \chi_T/\chi_S$; c_P and c_V are the specific heat capacities under constant pressure and volume, respectively, $D_T \equiv \lambda/m\rho c_P$ is the thermal diffusion coefficient (or "temperature conductivity"), m is the mass of a molecule, ρ is the number of molecules per unit volume, λ is the thermal conductivity from Fourier's law

$$\vec{Q} = -\lambda \,\nabla T,\tag{54}$$

 \vec{Q} being the diffusive part of the energy flux,

$$b(q) \equiv q \frac{3\Gamma - D_V}{\gamma \mathcal{V}}, \qquad D_V \equiv \frac{\eta_V + \frac{4}{3}\eta_S}{m\rho}$$
(55)

is the longitudinal kinetic viscosity, η_S and η_V are the coefficients of shear and bulk viscosity, respectively,

$$\Gamma \equiv \frac{1}{2} \left[(\gamma - 1)D_T + D_V \right]$$
(56)

is the attenuation coefficient of hypersound waves. With the exception of the two last terms in Equation 53, which can hardly be observed, the scattered spectrum (Equation 53) is the sum of three Lorentzians (see Figure 2.32). The first term defines the central Rayleigh band with the incident light frequency ω_0 and the halfwidth

$$\Delta\omega(q) - D_T q^2 = \frac{\lambda}{m\rho c_P} q^2. \tag{57}$$

The next two terms define Mandelshtam-Brillouin's doublet with the frequency shift $\pm \omega(q) = \pm \mathcal{V}q$ and the halfwidth

$$\Delta\omega_{\rm MB}(q) = \Gamma q^2 \tag{58}$$

(see Figure 2.32). The last two terms in Equation 53 give a non-Lorentzian correction, which shifts slightly Mandelshtam-Brillouin's peaks toward the centre and makes them asymmetric (however, the full spectrum remains symmetrical about ω_0). They are usually very small.

Mandelshtam-Brillouin's spectrum of **molecular** liquids is more complex. The internal molecular degrees of freedom, in general, are related to translational motion of molecules, which leads to additional relaxational mechanisms of density fluctuations.

Experiment (Lastovka and Benedek, 1966; Stanley, 1971; Flygare, 1978) has shown good agreement with the hydrodynamic approximation predictions far from the critical region. In particular, for toluene, plotting $\Delta \omega(q)$ vs q^2 leads to a straight line originating from the zero point according to Equation 57.

Besides the triplet, a wider spectrum (due to the anisotropy fluctuations) is observed in liquids (Pike, 1974; Berne and Pecora, 1976; Vuks, 1977). Its halfwidth gives the anisotropy relaxation time $\tau_{r,an}$ which is of 10^{-12} s order of magnitude. This time is sensitive to molecular associations, eg. to H-bond formation (Vuks, 1977).

2.3.4. Density fluctuations and molecular association

Molecular association in liquids restrains the development of density fluctuations and, therefore, lowers the scattered light intensity (Vuks, 1968; Eisenberg and Kauzmann, 1969; Shakhparonov, 1976). Water is a glowing example, showing the least effect of light scattering among all liquids (1/15 to benzene). Alcohols slightly scatter light as well, though 2-3 times as heavily as does water.

The study of the liquid structure by means of light scattering reveals water to be a very homogeneous liquid. It approaches a crystal by its structural homogeneity that, by the way, contradicts the so-called bistructural models of water (Vuks, 1968, 1977).

2.3.5. Critical opalescence

As the configurative point approaches the spinodal (see Figure 1.4), $(\partial V/\partial P)_T \to \infty$ and $\chi_T \to \infty$ whence, by Einstein's equations 11-13, $I_{\vartheta} \to \infty$ or $\tau \to \infty$, which has no physical meaning.

Such an unreal result is due to the assumed independence of fluctuations in space elements v while deriving Equations 11-13. However, on approaching the spinodal, density fluctuations interact (correlate). As a result, the increment of the scattered light intensity turns out to be lower than that predicted by Einstein's formula; moreover, Rayleigh's scattering law ($\tau \sim \lambda^{-4}$ and z = 1) breaks down. This suggests that the heterogeneous areas have sizes commensurable to the wavelength λ .

Indeed, the increase in the scattering intensity, when the configurative point approaches the spinodal, is accompanied by a deformation of the polar diagram of the scattered intensity (z > 1) and a decrease in the wavelength exponent (Equation 2.1-92) to $n \approx 2$.

These phenomena occurring near the spinodal are called critical **opalescence**. The spinodal can be approached most closely in the region of the critical point (see Figure 1.4).

The correlation among density fluctuations is described by special functions of structural element distribution, or by correlation functions.

Suppose N identical structural elements (eg. atoms) to occupy a volume V. Choose a coordinate system arbitrarily inside the body and draw vectors $\vec{r_1}$ and $\vec{r_2}$ to fix the space elements dV_1 and dV_2 , which are distant at $|\vec{r_{12}}|$. In the case of chaotically distributed atoms, the probability for atom 1 to be in the space element dV_1 and for atom 2 to be in the space element dV_2 simultaneously is equal to the product

$$d\mathcal{P}(\vec{r_1}, \vec{r_2}) = \frac{dV_1}{V} \frac{dV_2}{V}.$$
(59)

However, if there is a correlation between the atom locations,

$$d\mathcal{P}(\vec{r_1}, \vec{r_2}) = g(\vec{r_1}, \vec{r_2}) \frac{dV_1}{V} \frac{dV_2}{V},\tag{60}$$

where $g(\vec{r_1}, \vec{r_2})$ is the correlation function.

For isotropic liquids, g depends on r_{12} only, so

$$g(\vec{r}_1, \vec{r}_2) = g(|\vec{r}_1 - \vec{r}_2|) = g(|\vec{r}_{12}|) = g(r).$$
(61)

If the origin of the coordinates is placed at atom 1, then the probability of atom 2 being in the spherical layer $4\pi r^2 dr$ is equal to

$$d\mathcal{P}(r) = g(r)\frac{4\pi r^2 dr}{V}$$
(62)

with a normalization

$$\frac{1}{V} \int_{0}^{\infty} g(r) 4\pi r^2 \, dr = 1.$$
(63)

g(r) is called a radial distribution function of atoms, or molecules; it defines the probability of an atom being at a distance r from a fixed atom to r + dr (Figure 2.33).



Figure 2.33. Schematic of the radial distribution function, proportional to the probability of any atom being found at a certain distance from a fixed atom (Ziman, 1979) [J.M.Ziman *Models of Disorder*. Copyright © 1979 by Cambridge University Press]

As repulsion forces prevent interpenetration of atoms, g(r) = 0 within $0 \le r < d$ (d is the atom diameter) and $r \to \infty$ when $g(r) \to 1$ (no correlation).

If a spherical layer contains dN atoms, their numerical density is

$$\rho(r) = \frac{dN}{4\pi r^2 dr} \tag{64}$$

and

$$dN = \rho(r)4\pi r^2 \, dr. \tag{65}$$

Integration yields the number of atoms in a volume V except for the one fixed at the origin of the coordinates

$$\int_{0}^{\infty} \rho(r) 4\pi r^{2} dr = N - 1, \tag{66}$$

where N = const. If N fluctuates about its mean value $\langle N \rangle$, then

$$\int_{0}^{\infty} \rho(r) 4\pi r^{2} dr = \frac{\langle N^{2} \rangle}{\langle N \rangle} - 1.$$
(67)

According to Equations 62 and 65,

$$d\mathcal{P}(r) = \frac{dN}{N} = g(r)\frac{4\pi r^2 \, dr}{V} = \frac{\rho(r)4\pi r^2 \, dr}{N},\tag{68}$$

whence

$$g(r) = \frac{V}{N}\rho(r) = \frac{\rho(r)}{\bar{\rho}},\tag{69}$$

 $\bar{\rho}$ being the mean number of atoms per unit volume.

Consider a system of N identical atoms interacting through central forces (Skryshevsky, 1980). Choose a set of n atoms (n = 1, 2, ..., N - 1) inside it. The probability of these atoms being placed in space units $dV_1, dV_2, ..., dV_n$ near the ends of the vectors $\vec{r_1}, \vec{r_2}, ..., \vec{r_n}$ from a fixed atom when the others (N - n) are placed arbitrarily is represented by

$$d\mathcal{P}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) = \mathcal{F}_n(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) \frac{dV_1 \, dV_2, \dots, dV_n}{V^n},\tag{70}$$

where $\mathcal{F}_n(\vec{r_1}, \vec{r_2}, \ldots, \vec{r_n})$ are the radial distribution functions normalized so that

$$\frac{1}{V^n} \int \cdots \int \mathcal{F}_n(\vec{r_1}, \vec{r_2}, \dots, \vec{r_n}) \, dV_1 \, dV_2, \dots, dV_n = 1.$$
(71)

A unary function $\mathcal{F}_1(\vec{r}_1)$ is the simplest radial distribution function

$$d\mathcal{P}(\vec{r_1}) = \mathcal{F}_1(\vec{r_1}) \frac{dV_1}{V} \tag{72}$$

to define the probability of existence of an atom in a space element dV_1 at a distance $\vec{r_1}$ from the origin of the coordinates, when the others (N-1) are placed arbitrarily. If two atoms interact with each other, the probability of their existence at a definite distance is defined by

$$d\mathcal{P}(\vec{r}_1, \vec{r}_2) = \mathcal{F}_2(\vec{r}_1, \vec{r}_2) \frac{dV_1 \, dV_2}{V^2},\tag{73}$$

where $\mathcal{F}_2(\vec{r}_1, \vec{r}_2)$ is a binary (pair) distribution function.

For isotropic systems

$$\mathcal{F}_2(\vec{r}_1, \vec{r}_2) = \mathcal{F}_2(|\vec{r}_1 - \vec{r}_2|) = \mathcal{F}_2(r_{12}). \tag{74}$$

Comparison between Equation 73 and Equation 60 reveals that

$$\mathcal{F}_2(r_{12}) \equiv g(r_{12}). \tag{75}$$

In liquids, as the distance between two molecules increases, their correlation weakens, so

$$\mathcal{F}_2(|\vec{r}_1 - \vec{r}_2|) - \mathcal{F}_1(\vec{r}_1) \cdot \mathcal{F}_1(\vec{r}_2) \to 0 \quad \text{when} \quad |\vec{r}_1 - \vec{r}_2| \to \infty.$$

$$\tag{76}$$

The distance, at which this difference varies from zero, defines the range of correlation.

In the case of a simultaneous interaction among three atoms, the probability of their existence in space elements dV_1 , dV_2 , dV_3 at distances $\vec{r_1}$, $\vec{r_2}$, $\vec{r_3}$ is defined by a **ternary distribution function** $\mathcal{F}_3(\vec{r_1}, \vec{r_2}, \vec{r_3})$:

$$d\mathcal{P}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \mathcal{F}_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) \frac{dV_1 \, dV_2 \, dV_3}{V^3}.$$
(77)

Distribution functions of different order are related by

$$\mathcal{F}_{n}(\vec{r}_{1},\vec{r}_{2},\ldots,\vec{r}_{n}) = \frac{1}{V} \int \mathcal{F}_{n+1}(\vec{r}_{1},\vec{r}_{2},\ldots,\vec{r}_{n+1}) \, dV_{n+1}.$$
(78)

In particular,

$$\mathcal{F}_{1}(\vec{r}_{1}) = \frac{1}{V} \int \mathcal{F}_{2}(\vec{r}_{1}, \vec{r}_{2}) \, dV_{2}; \quad \mathcal{F}_{2}(\vec{r}_{1}, \vec{r}_{2}) = \frac{1}{V} \int \mathcal{F}_{3}(\vec{r}_{1}, \vec{r}_{2}, \vec{r}_{3}) \, dV_{3}. \tag{79}$$

The binary distribution function has assumed a particular significance in the theories of liquids. The methods of statistical physics allow one to express the main thermodynamic functions through the binary function, namely, the internal energy

$$U = \frac{3}{2}NkT + \frac{1}{2}N\rho \int_{0}^{\infty} \varphi(r)g(r)4\pi r^{2} dr,$$
(80)

the state equation

$$PV = NkT + \frac{1}{6}N\rho \int_{0}^{\infty} r \frac{d\varphi(r)}{dr} g(r) 4\pi r^2 dr, \qquad (81)$$

the isothermal compressibility

$$\chi_{\tau} = \frac{1}{\rho kT} + \frac{1}{kT} \int_{0}^{\infty} [g(r) - 1] 4\pi r^{2} dr.$$
(82)

Here $\varphi(r)$ is the intermolecular potential of a pair interaction (see Figure 1.40).

The binary distribution function g(r) is related to the intermolecular potential of the pair interaction $\varphi(r)$ via an integro-differential equation, which comprises an unknown function $\mathcal{F}_3(\vec{r_1}, \vec{r_2}, \vec{r_3})$, which is the main difficulty in determining $g(\vec{r_1}, \vec{r_2})$.

Various approaches and approximations have been proposed, aiming to solve this problem within the framework of statistical physics (Temperley et al., 1968; Croxton, 1974; Skryshevski, 1980; Smirnova, 1982).

As an example, Figure 2.34 presents g(r) for Lennard-Johnes' intermolecular potential and for the rigid sphere model (Stanley, 1971). Hence, the theory of liquids replaces calculation of the statistical sum and the configurative integral by consideration of the probability of configuration groups of 2, 3, and more particles. Therefore, computation of the correlation functions leads to the description of all the thermodynamic functions (Croxton, 1974).

To describe the substance behaviour at the critical point, a pair correlation function

$$h(r_{12}) = g(r_{12}) - 1 \tag{83}$$

and a direct correlation function C(r) are often introduced according to Ornstein-Zernike's equation

$$h(r_{12}) = C(r_{12}) + \rho \int h(r_{13})C(r_{23}) \, dV. \tag{84}$$

If $C(r_{ij})$ are known or derived from any simplifying ideas, then this equation is solved by means of iterations. $h(r_{12})$ is written as

$$h(r_{12}) = C(r_{12}) + \rho \int C(r_{13})C(r_{23}) \, dV_3 + \rho^2 \int \int C(r_{13})C(r_{34})C(r_{42}) \, dV_3 \, dV_4 + \cdots (85)$$



Figure 2.34. Interconnection between the radial distribution function g(r) and the pair interaction potential $\varphi(r)$ for the model of rigid spheres with $\varphi(r) \rightarrow$ ∞ when $r < r_0$ and $\varphi(r) = 0$ when $r > r_0$ (a) and for Lennard-Johnes' potential with $\varphi(r) =$ $\varphi_0\{(r_0/r)^{12}-2(r_0/r)^6\}$ (b) (Stanley, 1971) [H.E.Stanley Introduction to Phase Transitions and Critical Phenomena. Copyright (c) 1971 by permission of Oxford University Press]

where the first summand describes the immediate (direct) correlations between the positions of structural elements (atoms, molecules, etc.) 1 and 2. The second one is due not to direct correlations, but to the correlations of structural elements 1 and 2 via a third element placed at the point \vec{r}_{13} . The third summand defines such correlations through two intermediate elements, at the points \vec{r}_{13} and \vec{r}_{34} . When the distribution is random, $h(r_{12}) = C(r_{12})$.

Hence, to describe the internal structure of even simple one-atom liquids (liquidified inert gases) is a complex and approximate to some degree matter. More sophisticated relationships arise in the case of molecular liquids and their mixtures. At the same time, the methods of statistical physics show a basic possibility to describe the internal structure of a liquid and its association with the equilibrium properties.

Let us define a relation between the correlation functions of the internal structure of a liquid and the phenomenon of light scattering (Skryshevsky, 1980). The total amplitude of the waves scattered by a given configuration of structural elements, each approximated by a Rayleigh particle, in the case of vertically polarized light is expressed by (Equations 2.1-51,-48,-49)

$$E_{s,0\perp} = E' \sum_{j=1}^{N} \mathcal{F}_j \exp\left[\frac{2\pi i}{\lambda} (\vec{r}_j (\vec{n}_s - \vec{n}_0))\right], \qquad (87)$$

where E' is a constant.

For the scattered light intensity (see Equation 2.1-8),

$$I = I' \sum_{j=1}^{N} \mathcal{F}_j \exp\left[\frac{2\pi i}{\lambda} (\vec{r}_j (\vec{n}_s - \vec{n}_0))\right] \times \sum_{k=1}^{N} \mathcal{F}_k \exp\left[\frac{2\pi i}{\lambda} (\vec{r}_k (\vec{n}_s - \vec{n}_0))\right]$$
(88)

$$= I' \sum_{j=1}^{N} \sum_{k=1}^{N} \mathcal{F}_{j} \mathcal{F}_{k} \exp\left[\frac{2\pi i}{\lambda} (\vec{r}_{j} - \vec{r}_{k})(\vec{n}_{s} - \vec{n}_{0})\right].$$

Among N^2 terms of this double sum there exist N terms with j = k and, hence, the exponent is equal to 1. This means that

$$I = I' \mathcal{F}^2 \left[N + \sum_{j \neq k}^N \sum_{k=1}^N \exp\left[\frac{2\pi i}{\lambda} (\vec{r_j} - \vec{r_k})(\vec{n_s} - \vec{n_0}))\right] \right].$$
(89)

This formula defines the intensity of light scattered from the configuration of the structural elements at some instant of time.

For comparison with experimental data I, Equation 89 needs to be averaged over all the possible locations of the structural elements. The results of this averaging depend on whether or not the vector $\vec{r}_{jk} = \vec{r}_j - \vec{r}_k$ is constant in magnitude. The case of $\vec{r}_{jk} = const$ means a rigid molecule, whereas the other relates to the case of time changing in the location of the structural elements.

Away from the spinodal, the size of the density fluctuation distance is commensurable with the atom size, and the structural heterogeneity of a liquid can be probed by Xrays and neutron radiation. Near the critical region, the scale of density fluctuation is commensurable with the wavelength of light, and the light scattering methods becomes informative.

Calculation of sum 89 is performed by the radial distribution function g(r) related to the probability of the presence of atom (molecule) j in a space element dV_j and of atom k in dV_k :

$$d\mathcal{P}(r_{jk}) = g(r_{jk})\frac{dV_j}{V}\frac{dV_k}{V},\tag{90}$$

where V is the scattering space, r_{jk} is the atom-to-atom distance.

Therefore, each summand in the double sum 89 must be multiplied by $d\mathcal{P}(r_{jk})$ and integrated over the space elements dV_j and dV_k :

$$I = I' \mathcal{F}^2 \left[N + \sum_{j \neq k}^{N} \int \int \exp\left[\frac{2\pi i}{\lambda} (\vec{r}_j - \vec{r}_k) (\vec{n}_s - \vec{n}_0) g(r_{jk}) \frac{dV_j \, dV_k}{V^2} \right] \right].$$
(91)

As $g(r_{jk}) \rightarrow 1$ with increasing r_{jk} , it is reasonable to represent $g(r_{jk})$ as

$$g(r_{jk}) = [g(r_{jk}) - 1] + 1.$$
(92)

Assuming all the N(N-1) terms of the double sum to be equal, and neglecting 1 in comparison with N, we write:

$$I = I' \mathcal{F}^2 \left\{ 1 + N \int \int \exp\left[\frac{2\pi i}{\lambda} (\vec{r}_j - \vec{r}_k) (\vec{n}_s - \vec{n}_0)\right] [g(r_{jk}) - 1] \frac{dV_j \, dV_k}{V^2} + N \int \int \exp\left[\frac{2\pi i}{\lambda} (\vec{r}_j - \vec{r}_k) (\vec{n}_s - \vec{n}_0)\right] \frac{dV_j \, dV_k}{V^2} \right\}$$
(93)

or

$$= I'N\mathcal{F}^{2}(1+NX_{1}+NX_{2}), \tag{94}$$

where

I

$$X_{1} = \int \int \exp\left[\frac{2\pi i}{\lambda}(\vec{r}_{j} - \vec{r}_{k})(\vec{n}_{s} - \vec{n}_{0})\right] \left[g(r_{jk}) - 1\right] \frac{dV_{j} \, dV_{k}}{V^{2}}$$
(95)

and

$$X_{2} = \frac{1}{V^{2}} \int \int \exp\left[\frac{2\pi i}{\lambda} (\vec{r}_{j} - \vec{r}_{k})(\vec{n}_{s} - \vec{n}_{0})\right] dV_{j} dV_{k}.$$
 (96)

In Equation 95, integration with respect to V_j is extended over all the scattering space given as a sphere with a radius L. The volume V_k depends on the mutual arrangement of atoms. Due to the spherical symmetry of $g(r_{jk})$ and to the fact that $g(r_{jk}) \rightarrow 1$ when $r_{jk} > r_k$, the space V_k is assumed as a sphere with a radius r_k defining the range of the correlated area. If a given atom is supposed to be anywhere within the scattering space with an equal probability, then

$$\frac{1}{V}\int dV_{J} = 1. \tag{97}$$

The centre of atom j is placed at the origin of coordinates. The location of atom k with respect to atom j can be expressed in the spherical coordinates. Giving due consideration for the spherical symmetry of the structure and the wave vector (Equation 2.1-48), we write

$$X_{1} = \frac{1}{V} \int_{0}^{2\pi} d\varphi \int_{0}^{r_{k}} r^{2} \left[g(r) - 1 \right] dr \int_{0}^{\pi} \exp(iqr\cos\vartheta) \sin\vartheta \,d\vartheta \tag{98}$$
$$= \frac{1}{V} \int_{0}^{r_{k}} 4\pi r^{2} \left[g(r) - 1 \right] \frac{\sin qr}{qr} \,dr$$

(cf. Equation 2.1-76). The double integral in Equation 96 is also calculated on the assumption of the spherical form of the scattering space with radius L. The integrand is the product of two multipliers, of which one is related to atom j and the other to atom k, and each integration is extended over all the scattering space:

$$X_{2} = \left\{ \int \exp\left[\frac{2\pi i}{\lambda} (\vec{r}(\vec{n}_{s} - \vec{n}_{0}))\right] \frac{dV}{V} \right\}^{2}$$

$$= \left[\frac{1}{V} \int_{0}^{2\pi} d\varphi \int_{0}^{L} r^{2} dr \int_{0}^{\pi} \exp(iqr\cos\vartheta) \sin\vartheta d\vartheta \right]^{2}$$

$$= \frac{1}{V} \cdot \frac{4}{3} \pi L^{3} \left[\frac{3(\sin qL - qL\cos qL)}{(qL)^{3}}\right]^{2}.$$
(99)

Substituting X_1 from Equation 98, and X_2 from Equation 99 to Equation 94, we get

$$I(q) = I'N\mathcal{F}^{2} \left\{ 1 + \frac{N}{V} \int_{0}^{r_{k}} 4\pi r^{2} \left[g(r) - 1 \right] \frac{\sin qr}{qr} dr + \frac{N}{V} \cdot \frac{4}{3}\pi L^{3} \left[\frac{3(\sin qL - qL\cos qL)}{(qL)^{3}} \right]^{2} \right\}.$$
(100)

As g(r) = 1 when $r \gg r_k$, the limits of integration can be extended to infinity. With due account of Equation 69, we have ∞

$$I(q) = I'N\mathcal{F}^{2} \left\{ 1 + \int_{0}^{\infty} 4\pi r^{2} \left[\rho(r) - \bar{\rho} \right] \frac{\sin qr}{qr} dr + \frac{4}{3}\pi L^{3} \bar{\rho} \left[\frac{3(\sin qL - qL\cos qL)}{(qL)^{3}} \right]^{2} \right\}.$$
(101)

The first summand defines the intensity of scattering by separate atoms with no interference among them, and the second one the scattering with allowance for interference caused by the near order in the atom location (correlation of density fluctuations). The third term represents the scattering intensity at very small angles and depends on the shape and size of the sample with no dependence on its internal structure.

Indeed, the maximum value of the function $\varphi(qL) = 3(\sin qL - qL\cos qL)/(qL)^3$ is about 1 when $qL \to 0$. With increasing qL, $\varphi(qL)$ undergoes hardly decaying oscillations about its zero value defined by $qL = \tan qL$, i.e. at $qL \approx 4.49$, 7.74. When qL > 4.49, $\varphi(qL) \ll 1$. It follows from q = 4.49/L that for samples of $\sim 0.1~0.2$ cm, $q \approx 4.5 \cdot 10^{-7} \text{ Å}^{-1}$. Low-angle scattering in this case is practically unresolvable with modern equipment. This may appear when density fluctuations, colloidal particles or macromolecules are of order 1000 Å. Neglecting the component of low-angle scattering (see Equations 100, 83, 69), we have the following equivalent formulae

$$I(q) = I'N\mathcal{F}^{2}\left\{1 + \rho \int_{0}^{\infty} 4\pi r^{2} \left[g(r) - 1\right] \frac{\sin qr}{qr} dr\right\}$$
(102)

$$= I'N\mathcal{F}^2\left\{1 + \ddot{\rho}\int_0^\infty 4\pi r^2 h(r)\frac{\sin qr}{qr}dr\right\}$$
(103)

$$= I'N\mathcal{F}^{2}\left\{1 + \int_{0}^{\infty} 4\pi r^{2} \left[\rho(r) - \bar{\rho}\right] \frac{\sin qr}{qr} dr\right\}.$$
 (104)

Denoting $I'N\mathcal{F}^2I_{\Theta}$, and including the normalization condition (Equations 66 and 67) at $q \to 0$,

$$\frac{I(q)}{I_{\ominus}} = 1 + \int_{0}^{\infty} 4\pi r^{2} \left[\rho(r) - \bar{\rho}\right] \frac{\sin qr}{qr} dr = 1 + \int_{0}^{\infty} 4\pi r^{2} \left[\rho(r) - \bar{\rho}\right] dr$$
(105)

$$=1+\frac{\langle N^2\rangle-\langle N\rangle}{\langle N\rangle}-\langle N\rangle=\frac{\langle N^2\rangle-\langle N\rangle^2}{\langle N\rangle}.$$

The methods of statistical physics (see, for example, Stanley, 1971) prove that

$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \bar{\rho} k T \chi_{\tau}, \tag{106}$$

where χ_{τ} is the isothermal compressibility (Equation 1.1.2-41):

$$\chi_{\tau} = -\left(\frac{\partial V}{V \,\partial P}\right) = \frac{\partial \rho}{\rho \,\partial P}$$

Then (see Equations 103, 104, and 105),

$$\frac{I(q)}{I_{\Theta}} = 1 + \bar{\rho} \int_{0}^{\infty} 4\pi r^{2} h(r) \frac{\sin qr}{qr} dr = kT \bar{\rho} \chi_{\tau} \approx 1 + S(q) \bar{\rho}, \qquad (107)$$

where S(q) is the structural factor (see Equations 2.1-64, -76...80, 82, 2.3-41).

Thus, the light scattering intensity is immediately related to fluctuations in the number of particles in the system (Equation 105) and the isothermal compressibility (Equation 107). If the radial function of density distribution is permitted to be spherically asymmetrical, the equation

$$\mathbf{I}(q) = \frac{I(q)}{I_{\odot}} = 1 + \bar{\rho} \int_{0}^{\infty} h(r) \exp\left(-i(\vec{q}\,\vec{r})\right) d\vec{r}$$
(108)

holds in a more general case.

Define the experimental scattering function as

$$i(q) = \mathbf{I}(q) - 1 \tag{109}$$

(Rushbrook, 1968), then

$$\dot{i}(q) = \rho \dot{h}(q), \tag{110}$$

where $\tilde{h}(q)$ is the 3D Fourier transform of h(r) (see Equation 2.1-83)

$$\tilde{h}(q) = \int h(r) \exp\left(-i(\vec{q}\,\vec{r})\right) d\vec{r} \tag{111}$$

or (for a spherically symmetrical function h(r))

$$q\tilde{h}(q) = 4\pi \int_{0}^{\infty} rh(r) \sin qr \, dr.$$
(112)

The inverse Fourier transformation gives

$$h(r) = \frac{1}{(2\pi)^3} \int \tilde{h}(q) \exp(i(\vec{q}\,\vec{r})) \, d\vec{q}.$$
(113)

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or (for a spherically symmetrical h(q))

$$h(r) = \frac{1}{(2\pi)^2} \int_0^\infty q \tilde{h}(q) \frac{\sin qr}{r} \, dq.$$
(114)

Then (see Equations 83 and 110)

$$g(r) = 1 + \frac{1}{2\pi^2 \bar{\rho}} \int_0^\infty i(q) \frac{\sin qr}{r} q \, dq,$$
(115)

that enables one to determine experimentally the radial distribution function g(r) using the radiation diagram i(q).

Applying the Fourier transformation (Equation 84) and the convolution theorem, we obtain

$$\check{h}(q) = \tilde{C}(q) + \rho \tilde{C}(q) \check{h}(q) \tag{116}$$

ог

$$(1+\rho\tilde{h}(q))(1-\rho\tilde{C}(q)) = 1.$$
(117)

Near the critical point $\chi_{\tau} \to \infty$, therefore, it follows from Equation 107 that

$$h(q) \to \infty \quad \text{at} \quad q \to 0,$$
 (118)

however, according to Equation 117, $\tilde{C}(q)$ is finite and

$$\tilde{C}(q) \to \frac{1}{\rho_c} \quad \text{at} \quad q \to 0.$$
 (119)

Thus, Ornstein-Zernike's equation 84 introduces the direct correlation function C(r) which is short-range in the critical region. On the other hand, the form of $\tilde{C}(q)$ given by other relationships of statistical physics, or by a simpler approximation, enables one to obtain the functional dependence of the pair correlation function h(r).

Ornstein and Zernike (1914, 1918; Stanley, 1971; Kociński and Wojtezak, 1978) have supposed $\tilde{C}(q)$ to be an even spherically-symmetrical analytical function of q in the vicinity q = 0 for any temperature (including T_c), i.e.

$$\rho \tilde{C}(q) = 4\pi \rho \int_{0}^{\infty} r C(r) \frac{\sin qr}{q} dr \cong \rho \tilde{C}(0) - R^2 q^2 + \cdots$$
(120)

(if only two terms in the expansion $\sin x/x \approx 1 - x^2/3! + \cdots$ are left),

$$R^{2} = \frac{1}{6}\rho \int r^{2}C(r) \, d\vec{r}.$$
(121)

In view of Equations 108-110, 117, and 120, we can write

$$\mathbf{I}^{-1}(q) = 1 - \rho \tilde{C}(0) + R^2 q^2 + \cdots .$$
(122)

It also follows from Equations 116 and 120 for small q that

$$\tilde{h}(q) = \tilde{C}(q) + \tilde{h}(q) \left[\rho \tilde{C}(0) - R^2 q^2 \right].$$
(123)

Fourier transformation of Equation 123 leads to

$$h(r)\left[1 - \rho \tilde{C}(0)\right] = C(r) + R^2 \nabla^2 h(r),$$
(124)

 $\tilde{h}(q)q^2 = -\nabla^2 \tilde{h}(q).$

From Equations 107 and 117, we have for $q \rightarrow 0$:

$$1 - \rho \tilde{C}(0) = \frac{1}{kT\bar{\rho}\chi_T} = \frac{1}{kT} \left(\frac{\partial P}{\partial \rho}\right)_T.$$
(125)

If the short-range direct correlation function C(r) in Equation 124 is neglected in comparison with the pair correlation function h(r), then Equation 124 reduces to a differential equation

$$\Delta h(r) - \frac{1 - \rho \tilde{C}(0)}{R^2} h(r) = 0$$
(126)

or

$$\Delta h(r) - \xi_{\rho}^{-2} h(r) = 0, \tag{127}$$

where

$$\xi_{\rho}^{-2} = \frac{1 - \rho \tilde{C}(0)}{R^2} = \frac{\left(\frac{\partial P}{\partial \rho}\right)_T}{kTR^2} = \frac{1}{kT\bar{\rho}\chi_T R^2}$$
(128)

(in terms of Equation 125).

The solution of Equation 127 has the following form (at large r):

$$h(r) = \frac{A}{\xi_{\rho}^{2} r} \exp\left(-r/\xi_{\rho}\right),$$
(129)

where A is the constant, ξ_{ρ} characterizes the efficiency of the correlation fall with distance and is called a **long-range correlation distance**.

A is defined from the normalization condition (here from the condition that the formula for the scattered light intensity at a finite ξ_{ρ} in the limiting case $\xi_{\rho} \to 0$ must reduce to Einstein's formula 13).

According to Equation 2.1-73, h(r) can be considered as a correlation function of the dielectric constant: the conversion factor for $\Delta \rho \rightarrow \Delta \epsilon$ appears in both the sides of Equation 2.1-73 and cancels out.

If the correlation function of the dielectric constant h(r) (Equation 2.1-73) is defined, we obtain Equation 2.1–80 for R_{ϑ} (see also Table 2.4) with Equation 2.1-77. Replacing $(\Delta \epsilon)^2$ as we did for Equations 9 and 10, we get

$$R_{\vartheta} = \frac{\pi^2}{2\lambda_0^4} \left[\varrho \left(\frac{\partial \epsilon}{\partial \varrho} \right)_T \right]^2 \frac{k T \chi_T}{v} \omega_\epsilon (1 + \cos^2 \vartheta).$$
(130)

According to Equation 2.1-77, ω_{ϵ} is the Fourier transform of h(r), i.e. $\omega_{\epsilon} = \tilde{h}(q)$ in this section's notation. In terms of Equation 129,

$$\omega_{e} = \tilde{h}(q) = \frac{4\pi A}{\xi_{\varrho}^{2} q} \int_{0}^{\infty} \exp\left(-r/\xi_{\varrho}\right) \sin qr \, dr = \frac{4\pi A}{1 + \xi_{\varrho}^{2} q^{2}}.$$
(131)

Comparison between Equations 131 and 130 yields the normalization constant

$$A = \frac{v}{4\pi},\tag{132}$$

and, finally, we get

$$R_{\vartheta} = \frac{\pi^2}{2\lambda_0^4} \left[\varrho \left(\frac{\partial \epsilon}{\partial \varrho} \right)_T \right]^2 \frac{kT \chi_T (1 + \cos^2 \vartheta)}{1 + \xi_\varrho^2 q^2}.$$
 (133)

This equation defines the main properties of light scattered by liquid in a wide region of the state diagram. Away from the spinodal $\xi_{\varrho} \rightarrow 0$ and Equation 133 reduces to Finstein's equation 13. As the spinodal is approached, the correlation of density fluctuations ξ_{ϱ} increases, and Equation 133 predicts a deformation of the radiation diagram and a fall in the wavelength exponent n from 4 to 2: Rayleigh's scattering gradually passes to Rayleigh-Debye's scattering, the intensity of scattering increases due to χ_T rise.

According to Equation 133 at low angles $(q \rightarrow 0)$, light scattering is also described by Einstein's formula. Elementary transformations of Equation 133 lead to

$$R_{\vartheta}^{-1} = R_{\vartheta=0}^{-1} (1 + \xi_{\varrho}^2 q^2) = R_{\vartheta=0}^{-1} \left[1 + \xi_{\varrho}^2 \frac{16\pi^2}{\lambda^2} \sin^2 \frac{\vartheta}{2} \right].$$
(134)

Hence, from the slope of R_{ϑ}^{-1} vs q^2 or R_{ϑ}^{-1} vs $\sin^2 \vartheta/2$, one can determine the long-range correlation distance ξ_{ϱ} (Stanley, 1971; Skripov, 1972; Vuks, 1977).

Debye (1959) has applied another approach to describe critical opalescence, which has turned out to be reasonable both for multicomponent and for one-component systems.

The space distribution of density fluctuations is expressed by a Fourier transform, whose qth component is a sinusoid with a wavelength Λ :

$$\Delta \varrho = \eta = \eta_0(q) \sin \frac{2\pi}{\Lambda} x,\tag{135}$$

x being the propagation direction of a fluctuation hypersound wave, which, according to Brillouin's formalism of light scattering (see Figure 2.30) makes an angle of $\varphi = \vartheta/2$ with the direction of incident light (the vector k_0).

The scattered light intensity is presumed to be equal to the squared amplitude of this qth wave (see Equation 9), i.e. Equation 1.4-18 which is calculated with the densityfluctuations-related Helmholtz potential increment as a distribution function

$$I_{\vartheta} \sim \overline{\Delta \varrho_0^2} \sim \overline{\eta_0^2(q)} = \frac{\int\limits_0^\infty \eta_0^2 \exp\left(-\frac{\Delta F}{kT}\right) d\eta_0}{\int\limits_0^\infty \exp\left(-\frac{\Delta F}{kT}\right) d\eta_0}.$$
(136)

If fluctuations are small, the expansion of ΔF into a Taylor series can be confined to two terms, the first of which corresponds to the first derivative of F and is equal to zero, since the system is in equilibrium (see Table 1.1). Then, Equation 136 reduces to Einstein's equation 13.

As the critical region is approached, fluctuations become correlated (and no more Gaussian, cf. Equation 1.4–17), so the subsequent terms in the ΔF expansion have to be taken into account. Special analysis (Zeldovich and Todes, 1940; Cahn and Hilliard, 1958; Cahn, 1959; Debye, 1959; Landau and Lifshitz, 1964) led to the next term in the ΔF scries being proportional to the squared density gradient (one-component system), or to the squared concentration gradient (binary system). Introduction of an additional term is caused by the appearance of surface energy in a system with strongly developed fluctuations (like a microheterogeneous structure). Debye (1959) indicates it was Rocard (1933) who first pointed to the importance of the effect of fluctuation gradient with light scattering near the critical point. Since then, this idea has been used repeatedly.

For a one-component system, Debye (1960) has derived

$$R_{\vartheta} = \frac{\pi^2 (1 + \cos^2 \vartheta) \left[\varrho \left(\frac{\partial \epsilon}{\partial \varrho} \right)_T \right]^2 k T \chi_T}{2\lambda_0^2 \left\{ 1 + \frac{8\pi^2}{3} \frac{l^2}{\lambda^2} \left[\frac{\sin^2(\vartheta/2)}{\tilde{T} - 1} \right] \right\}},\tag{137}$$

where $\tilde{T} = T/T_c$ is the reduced temperature.

The parameter l is defined as the range of molecular interaction

$$l^{2} = \frac{\int r^{2} \varepsilon(r) \, dv}{\int \varepsilon(r) \, dv},\tag{138}$$

where $\varepsilon(r)$ is the potential energy of interaction, and the space integral is calculated from the "contact" point to infinity. The quantity l is also called **Debye's length**. Debye (1963) has shown the full equivalence of Equations 137 and 133 for a system with the van der Waals state equation and the conversion rules

$$6\xi_{\varrho}^{2} = L_{\varrho}^{2}, \tag{139}$$

and

$$L_{\varrho}^{2} = \frac{l^{2}}{\tilde{T} - 1} \tag{140}$$

has the meaning of a correlation length and is defined as

$$L_{e}^{2} = \frac{\int h(r)r^{2} d\vec{r}}{\int h(r) d\vec{r}},$$
(141)

$$\xi_{\varrho}^2 = \frac{kT\varrho}{6m} \chi_T l^2,$$

 ρ being the density of the substance, m the mass of a molecule.

When $T \to T_c$, $\xi_{\ell} \to \infty$ by the power law (see Table 1.2)

$$\xi_{\boldsymbol{\varrho}} \sim \begin{cases} \exp\left(-\nu\right), & (\varepsilon > 0)\\ (-\varepsilon)^{-\nu'}, & (\varepsilon < 0). \end{cases}$$
(142)

According to Equation 128,

$$\xi_{\ell} \sim \chi_T^{1/2}.\tag{143}$$

As $\chi_{T} \sim \exp(-\gamma)$, then

$$\nu = \frac{1}{2}\gamma\tag{144}$$

and

$$\nu' = \frac{1}{2}\gamma'.\tag{145}$$

The mean field theories give

$$\gamma = \gamma' = rac{1}{2}$$

Hence

$$\nu = \nu' = \frac{1}{2}.$$
 (146)

On the basis of Equation 133,

$$R_{\vartheta} \sim q^{-2}.\tag{147}$$

Equation 147 applies to many systems, but the dependence $R_{\theta}^{-1} \sim q^2$ shows concavity at $T \to T_c$ in some cases (Stanley, 1971). More rigorous analysis (Fisher, 1964; Stanley, 1971) has led to a modification of Ornstein-Zernike's approximation

$$R_{\vartheta} \sim q^{-2+\eta}.\tag{148}$$

Its Fourier transform is

$$h(r) \sim r^{-(d-2+\eta)},$$
 (149)

where d is the space dimension. The exponent η is also classified among the critical indices (Stanley, 1971) though it does not reflect the temperature dependence of R_{ϑ} .

For d-dimensional space, Equation 82 allows us to write

$$\chi_{\tau} \sim \int_{0}^{\infty} h(r) r^{d-1} \, dr, \tag{150}$$

and, in view of Equation 149 (Baxter, 1982),

$$\chi_{\tau} \sim \int r^{1-\eta} dr \sim \int \xi_{\varrho}^{1-\eta} d\xi_{\varrho} \sim \xi_{\varrho}^{2-\eta}, \tag{151}$$

and (see Equations 144 and 142)

$$\exp\left(-\gamma\right) \sim \exp\left(-\nu(2-\eta)\right),\tag{152}$$

so

$$\gamma = \nu(2 - \eta). \tag{153}$$

Analysis based on Ising's 3D model (Fisher, 1967) yields

$$\gamma = \frac{5}{4} \pm 0.003, \quad \nu = \frac{9}{14} \pm 0.0025, \quad \eta = \frac{1}{18} \pm 0.008.$$
 (154)

Chu (1970) has established experimentally that $\gamma \ge 1.2$ and $\nu \ge 0.6$ for one- and two-component systems.

It follows from Equation 57 that measuring the halfwidth of the central band on the dynamic light scattering spectrum defines the λ/c_P ratio. In view of Equations 1.1.2-19, 43, $c_P \to \infty$ on the spinodal and $\Delta \omega(q) \to 0$.

Benedek (1969) reports Zaxman's data as processed by Lastovka to determine $D_T = \lambda/c_{P}m\rho$ of SF_6 on the characteristic lines of the state diagram $P-\rho$ (Figure 2.35).



Figure 2.35. A family of curves on the state diagram $P-\rho$ near the critical point, along which the inelastic scattering bandwidth for SF₆ was measured (Benedek, 1969). *1* is the critical isochore, 2 is noncritical isochores, 3 is the critical isotherm, 4 is the spinodal, 5 is the binodal. P_c and ρ_c are the critical pressure and density, respectively

The following results have been obtained: along the critical isochore $(T \ge T_c)$

$$D_T = (1.26 \pm 0.04) 10^{-2} \left(\frac{T - T_c}{T_c}\right)^{1.26 \pm 0.02} \text{ cm}^2/\text{s}, \tag{155}$$

along the coexistence curve (binodal) $(T \leq T_c)$

$$D_T = (1.79 \pm 0.01) 10^{-3} \left(\frac{T - T_c}{T_c}\right)^{0.632 \pm 0.002} \text{ cm}^2/\text{s}$$
(156)

on the side of vapour,

$$D_T = (1.75 \pm 0.02) 10^{-3} \left(\frac{T - T_c}{T_c}\right)^{0.635 \pm 0.003} \text{ cm}^2/\text{s}$$
(157)

on the side of liquid.

Along the critical isotherm as a function of density

$$D_T = 1.65 \cdot 10^{-3} \left(\frac{\varrho - \varrho_c}{\varrho_c}\right)^{2.4 \pm 0.01} \text{ cm}^2/\text{s.}$$
(158)

Such data are of great importance for comparison with the critical indices from different models and theories (see section 1.5).

By extrapolation $\Delta \omega \rightarrow 0$ on the non-critical isochores (see Figure 2.35), the spinodal temperatures corresponding to

$$\frac{|\varrho - \varrho_c|}{\varrho_c} = 0.315 \left[\frac{T_c - T_{sp}}{T_c} \right]^{0.58 \pm 0.1},\tag{159}$$

were obtained, this equation being similar to the spinodal equation in the van der Waals approximation

$$\frac{|\varrho - \varrho_c|}{\varrho_c} = \frac{2}{\sqrt{3}} \left[\frac{T_c - T_{sp}}{T_c} \right]^{0.5}.$$
(160)

Analysis of experimental data (Kadanoff et al., 1967; Pokrovski, 1968; Stanley, 1971; Skripov, 1972; Anisimov, 1974) shows the critical indices to be universal for the majority of liquids within the limits of experimental error. Near the critical point, as should be expected, a deviation of experimental data from the predictions of hydrodynamic approximation is observed. Other approaches are being developed for this vicinity.

Near the critical point, an increase in the scattered light intensity (critical opalescence) is observed. The Rayleigh (non-frequency-shifted) line chiefly contributes to this increase, its intensity being proportional to $c_P - c_V$ (see Equation 53) and exceeding that of Mandelshtam-Brillouin's (MB) components (proportional to c_V/c_P , see Equation 53) by several orders of magnitude (Swinney, 1978).

Moreover, as the critical point is approached, the shift of the Mandelshtam-Brillouin components $\pm \omega(q) \rightarrow 0$, because the velocity of sound

$$\mathcal{V} = \left(\frac{c_P}{\varrho c_V \chi_T}\right)^{1/2} \sim c_V^{-1/2} \sim \exp\left(\alpha/2\right).$$
(161)

At the same time, the width of the Mandelshtam-Brillouin components rises due to a sharp increase in the bulk viscosity η_V (see Equations 58, 55, 56).

The width of the Rayleigh central band in a one-component liquid (see Equations 53, 57) or in a solution (see section 2.4) does actually correspond to the decay rate of fluctuations in the order parameter, and can be expressed in the general form as

$$\Gamma = \frac{\mathcal{L}}{X}q^2,\tag{162}$$

where \mathcal{L} is the Onsager kinetic factor (thermal conductivity for a one-component liquid and diffusion coefficient for a solution, see section 2.4), X is the generalized susceptibility which diverges in the critical point, causing $\Gamma \rightarrow 0$ which is reflected in a critical retardation of the order parameter relaxation.

Indeed, as the configurative point approaches the critical one, more and more time is required for the equilibrium state to establish in the system (see further the conclusion to subsection 2.4.3).

The order parameter relaxation near the critical point is quantitatively described by the mode-mode coupling theory (Kawasaki, 1966, 1970ab; Kadanoff and Swift, 1968; Kawasaki and Lo, 1972; Lo and Kawasaki, 1972; Swinney, 1974; Anisimov, 1987).

Near the critical point, the different modes of motion corresponding to heat flux

$$S_T = \frac{\lambda}{m\varrho c_P} q^2,\tag{163}$$

viscous flux

$$S_{\eta} = \frac{\eta_s}{m\varrho} q^2, \tag{164}$$

sound

$$S_S = \pm i \mathcal{V} q \tag{165}$$

interact with each other, which leads to a complex pattern of molecular dynamics in liquid. According to the mode-mode coupling theory,

$$\Gamma_q = \frac{kT}{6\pi \eta^* \tilde{\xi}^3} K_0(q\tilde{\xi}),\tag{166}$$

where $\tilde{\xi}$ is the correlation length of fluctuations in the order parameter in dynamic phenomena, η^* is the so-called high-frequency shear viscosity

$$K_0(x) = \frac{3}{4} \left[1 + x^2 + (x^3 - x^{-1}) \arctan x \right],$$
(167)

where $x = q\tilde{\xi}$.

The viscosity η^* is related to the macroscopic shear viscosity η through (Kawasaki and Lo, 1972)

$$\eta(T) = \frac{K(q\bar{\xi})}{K_0(q\bar{\xi})} \eta^*,\tag{168}$$

where $K(x)/K_0(x)$ is a function varying from 1.06 within 0.1 < x < 1 to ~ 1.2 at $x \sim 10$. Correspondingly, for the decay rate of fluctuations in the order parameter,

$$\Gamma_q = \frac{kT}{6\pi\eta\tilde{\xi}^3}K(q\tilde{\xi}),\tag{169}$$

where $K(q\tilde{\xi})$ is Kawasaki's modified function (Kawasaki, 1970a; Kawasaki and Lo, 1972).

Near the critical point, the characteristic correlation length of fluctuations in the order parameter $\tilde{\xi}$ is related to the characteristic lifetime (relaxational time) of the critical fluctuations

$$\tilde{\tau} = \frac{\tilde{\xi}^2}{\lambda},\tag{170}$$

where the thermal conductivity λ obeys

$$\lambda = \frac{kT}{6\pi\tilde{\eta}\tilde{\xi}}.$$
(171)

This formula is similar to the relation between the diffusion coefficient of a "drop" with the size $\tilde{\xi}$ in a liquid with the viscosity $\tilde{\eta}$. Correspondingly, for $\tilde{\tau}$

$$\tilde{r} = \frac{6\pi\tilde{\eta}\xi^3}{kT} \tag{172}$$

is valid.

Thus, the dynamic scaling invariance holds in the critical region (see Equations 169, 172)

$$\frac{\tilde{r}}{r_q} = K(q\tilde{\xi}),\tag{173}$$

where $K(q\tilde{\xi})$ is a universal function, $\tau_q = \Gamma_q^{-1}$.

2.4. Concentration fluctuations, light scattering and diffusion in solutions

2.4.1. Light scattering. Mean statistical fluctuations

A new kind of fluctuations (concentration fluctuations) appear in solutions, so the full intensity of scattered light has three terms:

$$I = I_{den} + I_k + I_{an},\tag{1}$$

due to the fluctuations in density I_{den} , in concentration I_k , and in orientation (anisotropy) I_{an} . As I_{an} is incalculable in the general case, anisotropic scattering is taken into account phenomenologically through Cabannes' factor to be determined experimentally (Equations 2.2-19, 20,-24,-25)

$$R_{90} = (R_{den,90} + R_{k,90}) \frac{6 + 6\Delta_{90}}{6 - 7\Delta_{90}} = R_{is,90} \frac{6 + 6\Delta_{90}}{6 - 7\Delta_{90}}$$
(2)

 \mathbf{and}

$$\tau = (\tau_{den} + \tau_k) \frac{1 + 0.5\Delta_{90}}{1 + \Delta_{90}}.$$
(3)

In the case of scattering on concentration fluctuations,

$$\overline{(\Delta\epsilon)^2} = \left(\frac{\partial\epsilon}{\partial x_2}\right)_{T,P}^2 \overline{(\Delta x_2)^2} \tag{4}$$

Then (see Equation 2.3–5)

$$\tau_k = \frac{8\pi^3}{3\lambda_0^4} \left(\frac{\partial c}{\partial x_2}\right)_{T,P}^2 v \overline{(\Delta x_2)^2} \tag{5}$$

and (see Equations 2.3-3,-4, 4)

$$R_{k,\vartheta} = \frac{\pi^2}{2\lambda_0^4} \left(\frac{\partial\epsilon}{\partial x_2}\right)_{T,P}^2 \overline{\upsilon(\Delta x_2)^2} (1 + \cos^2\vartheta),$$

where x_2 is the mole fraction of the second component. Similar expressions can be written for the first component as well. According to Equation 1.4-33,

$$\overline{(\Delta x_2)^2} = \frac{kT}{\tilde{n} \left(\frac{\partial^2 \bar{G}}{\partial x_2^2}\right)_{T,P}} = \frac{kT}{\frac{\tilde{n}}{x_1} \left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P}} = -\frac{kT}{\frac{\tilde{n}}{x_2} \left(\frac{\partial \mu_1}{\partial x_2}\right)_{T,P}},\tag{6}$$

where μ_i is the chemical potential of the mixture components, \tilde{n} is the overall number of moles of two components in the volume v. Substituting the first expression into Equation 5, we get

$$R_{k,90} = \frac{\pi^2}{2\lambda_0^4} \left(\frac{\partial\epsilon}{\partial x_2}\right)_{T,P}^2 kT \left(\frac{\partial^2 \bar{G}}{\partial x_2^2}\right)_{T,P}^{-1} v_{12},\tag{7}$$

where $v_{12} = v/\tilde{n}$ is the molar volume of solution. Doing the same with the second expression in Equation 6, we obtain for $\vartheta = 90^{\circ}$

$$R_{k,90} = \frac{\pi^2}{2\lambda_0^4} \left(\frac{\partial\epsilon}{\partial x_2}\right)_{T,P}^2 kT x_1 \left(\frac{\partial\mu_2}{\partial x_2}\right)_{T,P}^{-1} v_{12}.$$
(8)

It follows from the last two equations that away from the spinodal, $R_{k,90}$ is small and increases as the configurative point approaches the spinodal. Lisnyanski (1961, 1966), Lisnyanski and Vuks (1962, 1964, 1969), Vuks (1977) have proposed to characterize the level of concentration fluctuations by a concentration fluctuation function f:

$$\frac{1}{f} = \frac{x_1 x_2}{RT} \left(\frac{\partial^2 \bar{G}}{\partial x_2^2} \right)_{T,P}.$$
(9)

f = 1 for ideal solutions (Equation 1.1.3-13), f > 1 for solutions with a positive deviation from ideality, and f < 1 for solutions with a negative deviation from ideality. Then, with allowance for Equations 7 and 9, we can write

$$R_{k,90} = \frac{\pi^2}{2\lambda_0^4 N_A} \left(\frac{\partial \epsilon}{\partial x_2}\right)_{T,P}^2 x_1 x_2 v_{12} f.$$
(10)

Comparison of Equations 7, 8, 10 with experimental values of $R_{k,90}$ also causes great difficulties to express $(\partial \epsilon / \partial x_2)_{T,P}$ via experimentally measured values (cf. subsection 2.3.1) (Fabelinski, 1965; Kerker, 1969; Vuks, 1977). Vuks (1977) has proposed a formula firmly confirmed by light scattering data together with other independent methods:

$$R_{k,90} = \frac{\pi^2}{\lambda_0^4 N_A} \left(n \frac{\partial n}{\partial x_2} \right)^2 \left[\frac{9n^2}{(2n^2 + 1)(n^2 + 2)} \right]^2 x_1 x_2 v_{12} f, \tag{11}$$

where n is the refractive index of the solution and $\partial n/\partial x_2$ is its increment. An example of the concentration dependence of f and $R_{k,90}$, $R_{den,90}$ of a binary solution is shown in Figure 2.36.

If the last expression from Equation 6 is substituted to Equation 5, we obtain

$$R_{k,90} = -\frac{\pi^2}{2\lambda_0^4} \left(\frac{\partial \epsilon}{\partial x_2}\right)_{T,P}^2 \frac{kTx_2\bar{V}_1}{\frac{\partial \mu_1}{\partial x_2}},$$

assuming $v/\tilde{n} \cong \bar{V}_1$.

In view of Equation 1.2-27 and the relationships

$$\epsilon = \mu^2; \quad \frac{\partial \epsilon}{\partial x_2} = \frac{\partial n^2}{\partial x_2} = 2n \frac{\partial n}{\partial x_2}; \quad \left(\frac{\partial \epsilon}{\partial x_2}\right)^2 = 2n^2 \left(\frac{\partial n}{\partial x_2}\right)^2,$$

we get

$$R_{k,90} = \frac{2\pi^2 n^2}{\lambda_0^4 N_A} \left(\frac{\partial n}{\partial x_2}\right)^2 \frac{x_2}{\frac{\partial}{\partial x_2} \left(\frac{\pi}{RT}\right)}.$$

The last formula is valid for concentration expressed in any units, as the conversion factor reduces, so

$$R_{k,90} = \frac{2\pi^2 n^2}{\lambda_0^4 N_A} \left(\frac{\partial n}{\partial c}\right)^2 \frac{c}{\frac{\partial}{\partial c} \left(\frac{\pi}{RT}\right)}.$$

Accepting $n \approx n_1$, we derive the traditional formula for Rayleigh's ratio for polymer solutions of moderate molecular weights, which is applied to determine the molecular weights of polymers

$$R_{k,90} = \frac{2\pi^2 n_1^2}{\lambda_0^4 N_A} \left(\frac{\partial n}{\partial c}\right)^2 \frac{c}{\frac{\partial}{\partial c} \left(\frac{\pi}{RT}\right)}$$



Figure 2.36. Concentration dependence of the concentration fluctuation function f at $T = 20^{\circ}$ C (1), of Rayleigh's ratio $R_{is,90}$ (2), of the component $R_{is,90}$ due to the density fluctuations $R_{is,90,den}$ (3), of the diffusion coefficient D (4) in the system CCl₄ + C₂H₅OH. Ethanol mole fractions are laid off as abscissa. f and $R_{is,90}$ are taken from (Vuks, 1977, pp. 164-165), D is from (Hammond and Stokes, 1956) [Reprinted with permission from: B.R.Hammond, R.H.Stokes. Trans. Faraday Soc. 52 (1956) 781-786. Copyright © 1956 by the Royal Society of Chemistry]. Curves 2 and 3 are calculated by Equations 2.4-8 and 2.3-12 for individual liquids and their mixtures using volume fractions: $R_{is,90,den} = v_1 R_{is,90,den1} + v_2 R_{is,90,den2}$. The circles on curve 2 relate to the experimental values of $R_{is,90}$ with the anisotropic component excluded by Equation 2.4-2, $\lambda = 546.1$ nm. The temperatures of the measurement of the scattered light intensity and diffusion are 20 and 25°C, respectively

2.4.2. Critical opalescence

As the spinodal is approached, the applicability of Equations 7, 8, 10, 11 disappear $(R_{k,90} \rightarrow \infty \text{ on the spinodal})$ due to the correlation of concentration fluctuations, so in this vicinity the formalism of correlation functions has to be employed to describe critical opalescence.

In the case of solutions, the following parameters of interaction are introduced (Debye,

2.4.2. Critical opalescence

1959):

$$l_{ij}^{2} = \frac{\int r^{2} \varepsilon_{ij}(r) \, dv}{\int \varepsilon_{ij}(r) \, dv} = \frac{\int r^{2} \varepsilon_{ij}(r) \, dv}{W_{ij}},\tag{12}$$

where $\varepsilon_{ij}(r)$ is the potential energy of interaction between two individual molecules of the *i*th and *j*th kind. The integration extends over the space with volume element dv from the value of r at "the moment of contact" to $r = \infty$. Then, a **mean range of molecular interactions between two molecules** (an analogue of Equation 2.3-138), or Debye's length l is expressed as (Debye, 1959; Chu, 1970)

$$l^{2} = \frac{l_{11}^{2} \frac{W_{11}}{w_{1}^{2}} + l_{22}^{2} \frac{W_{22}}{w_{2}^{2}} - 2l_{12}^{2} \frac{W_{12}}{w_{1}\omega_{2}}}{\frac{W_{11}}{w_{1}^{2}} + \frac{W_{22}}{w_{2}^{2}} - 2\frac{W_{12}}{w_{1}w_{2}}},$$
(13)

where w_i is the volume of a molecule of the *i*th component. W_{ij}/w_iw_j is called the **cohe**sion energy density (CED). Hence, Debye's length *l* can be expressed via Gildebrand's solubility parameters (Rowlinson, 1969) δ_{ij} :

$$\delta_{ij}^2 = \frac{W_{ij}}{w_i w_j}.\tag{14}$$

Relationship 14 is an approximation, valid for regular solutions and van der Waals' interaction forces, in particular, for the rigid sphere model ($\varepsilon \to \infty$ when r < d) with the attraction potential

$$\varepsilon(r) = -\varepsilon_0 \left(\frac{d}{r}\right)^6,\tag{15}$$

d being the sphere diameter.

In the case of variously-sized spheres, a contact diameter σ_{ij} is introduced (Chu, 1970). Then, according to Equations 12 and 15,

$$l_{ij}^{2} = \frac{\int_{\sigma_{ij}}^{\infty} -\varepsilon_{0} \left(\frac{\sigma_{ij}}{r}\right)^{6} r^{2} dv}{\int_{\sigma_{ij}}^{\infty} -\varepsilon_{0} \left(\frac{\sigma_{ij}}{r}\right)^{6} dv} = 3\sigma_{ij}^{2}.$$
(16)

In view of Equation 13, we get

$$l^{2} = 3 \frac{\delta_{11}^{2} \sigma_{11}^{2} + \delta_{22}^{2} \sigma_{22}^{2} - 2\delta_{12}^{2} \sigma_{12}^{2}}{(\delta_{11} - \delta_{22})^{2}},$$
(17)

where $\delta_{11}\delta_{22} = \delta_{12}^2$ is accepted.

Debye (1959) has introduced the symbols # and Ω as

$$= \frac{1}{6} \left(\frac{W_{11}}{\omega_1^2} l_{11}^2 + \frac{W_{22}}{\omega_2^2} l_{22}^2 - 2 \frac{W_{12}}{\omega_1 \omega_2} l_{12}^2 \right)$$
(18)

and

$$\Omega = \frac{W_{11}}{\omega_1^2} + \frac{W_{22}}{\omega_2^2} - 2\frac{W_{12}}{\omega_1\omega_2}.$$
(19)

Then for Debye's length the following relationship is valid:

$$l^2 = \frac{6 \#}{\Omega}.$$
(20)

Debye has considered the effect of light scattering by two-component solutions within a wide area of the state diagram, using the formalism of Brillouin's scattering (see subsection 2.3.5) with the gradient term entering into the energy term of the Helmholtz potential only (the entropy term corresponds to random distribution of molecules, i.e. the model of regular solution). This led to the following result:

$$R_{k,\vartheta} = \frac{2\pi^2 n_1^2 \left(\frac{\partial n}{\partial \mathbf{c}}\right)^2 \mathbf{c}}{\lambda_0^4 N_A \left[\frac{\partial}{\partial \mathbf{c}} \left(\frac{\pi}{RT}\right) + \frac{\mathbf{c} \not\models}{\varrho^2 RT} \frac{16\pi^2}{\lambda^2} \sin^2 \frac{\vartheta}{2}\right]} (1 + \cos^2 \vartheta), \tag{21}$$

where π (in the denominator) is osmotic pressure, n_1 is the solvent refractive index, **c** and ρ are the concentration (g/cm³) and density of the second component, respectively. With an **optical constant**

$$\mathcal{K} = \frac{2\pi^2 n_1^2}{\lambda_0^4 N_A} \left(\frac{\partial n}{\partial \mathbf{c}}\right)^2 \tag{22}$$

Equation 21 takes the form

$$\frac{\mathcal{K}\mathbf{c}}{R_{k,\vartheta}}(1+\cos^2\vartheta) = \frac{\partial}{\partial\mathbf{c}}\left(\frac{\pi}{RT}\right) + \frac{\mathbf{c} \not\models}{\varrho^2 RT} \frac{16\pi^2}{\lambda^2} \sin^2\frac{\vartheta}{2}.$$
(23)

Away from the spinodal, the second summand in the right-hand side is small in comparison with the first one, and

$$\frac{\mathcal{K}\mathbf{c}}{R_{k,\vartheta}}(1+\cos^2\vartheta) \approx \frac{\partial}{\partial \mathbf{c}} \left(\frac{\pi}{RT}\right)$$
(24)

reduces to Debye-Einstein's equation (Debye, 1947) to determine the molecular mass of the solute (the second component) M

$$\frac{\mathcal{K}\mathbf{c}}{R_{k,90}} = \frac{1}{M} + 2\mathcal{A}_2\mathbf{c} + \cdots .$$
⁽²⁵⁾

Used here is the virial two-term expansion of osmotic pressure

$$\frac{\pi}{RT} = \frac{\mathbf{c}}{M} + \mathcal{A}_2 \mathbf{c}^2 + \cdots, \qquad (26)$$

where \mathcal{A}_2 is the second virial coefficient.

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Relationship 25 also follows immediately from Equation 5. If one substitutes the last expression from Equation 6 to Equation 5 and considers Equation 1.2-27, $v/\tilde{n} \simeq \bar{V}_{01}$ and

$$\varepsilon = n^2;$$
 $\left(\frac{\partial \varepsilon}{\partial x_2}\right)^2 = 4n^2 \left(\frac{\partial n}{\partial x}\right)^2,$

then he gets

$$R_{k,90} = \frac{2\pi^2 n^2}{\lambda_0^4 N_A} \left(\frac{\partial n}{\partial x_2}\right)^2 \frac{x_2}{\frac{\partial}{\partial x_2} \left(\frac{\pi}{RT}\right)}.$$

This formula is valid for polymer concentrations expressed in any unit, as the conversion factor reduces. If $n^2 \approx n_1^2$ in the denominator, then, in view of Equations 22 and 26, Equation 25 will result.

Equation 25 has gained acceptance to determine the molecular weights of macromolecules with moderate sizes to satisfy the condition of Rayleigh's scattering (Doty and Steiner, 1950; Flory, 1953; Stacey, 1956; Tompa, 1956; Tanford, 1961; Tsvetkov et al., 1964; Morawetz, 1965; Kerker, 1969; Eskin, 1973; Rafikov et al., 1978).

Near the spinodal, the second term in the right-hand side of Equation 53 predominates, since on the spinodal (Equations 1.2–52, 1.3–19) $\partial \Delta \mu_1 / \partial x_2 = 0$, therefore, $\partial \Delta \mu_1 / \partial \mathbf{c} = 0$, and, according to Equation 1.2–27,

$$\frac{\partial \pi}{\partial \mathbf{c}} = 0. \tag{27}$$

Owing to the second term in the right-hand side of Equation 23, $R_{k,\vartheta}$ is finite on the spinodal, but when $\vartheta \to 0$ this term also tends to zero, whence

$$R_{k,\vartheta\to 0} \to \infty \quad (R_{k,\vartheta\to 0}^{-1} \to 0) \quad \text{on the spinodal},$$
 (28)

which was used by Chu et al. (1969) to determine the spinodal location (Figures 2.38 2.39).

The measurements of the scattered light intensity were carried out in the stability region of a one-phase solution. The validity of such an extrapolation, which passes through a part of the stability area, and through all of the metastable area, seems rather problematic, and Chu et al. (1969) call the obtained curve a pseudospinodal (see Figures 2.37-2.39), as do the curve obtained from extrapolation $D \rightarrow 0$, where D is measured using the narrowing of the central band of scattering $\Delta \omega$ (see subsection 2.4.4).

The experimental values of $R_{k,\vartheta=0}^{-1}$ (or $I_{k,\vartheta=0}^{-1}$) in the region of critical opalescence also obey the experimental law like Equation 1.5-1,-5. Eg. Figure 2.38 shows

$$I_{k,\vartheta=0}^{-1} \sim \left(\frac{T - T_{sp,sc}}{T_{bi}}\right) \quad \text{with} \quad \gamma = 1.26,$$
(29)

where $T_{sp,sc}$ is the spinodal temperature determined from light scattering $(I_{k,\vartheta=0}^{-1} \to 0)$ (see Equation 2.38), T_{bi} is the binodal temperature.

In the region of critical opalescence, the parameters of the fluctuation correlation (the long-range correlation distance ξ_k , the radius of intermolecular interaction forces, i.e.



Figure 2.37. System isobutylic acid+water. Isotherms $I_{k,\vartheta=0}^{-1}$ and D at the critical temperature $T_c = 26.086^{\circ}$ C as a function of the mole fraction of isobutylic acid (Chu et al., 1969) [B.Chu, F.J.Schoenes, M.E.Fisher. Phys. Rev. 185 (1969) 219-226. Copyright © 1969 by the American Physical Society]

Debye's length l, the correlation length L_k) are determined as in the case of a onecomponent system (see subsection 2.3.5).

Eg. in the system perfluoromethylcyclohexane+ CCl_4 near the critical point

$$L_k \sim \varepsilon^{-\nu}, \quad \nu = 0.540 \pm 0.013$$
 (30)

(Chu ct al., 1972).

According to Equation 23, critical opalescence begins near the curve of loss of stability, i.e. near the spinodal. In this connection, it seems relevant to recall that during the solution-crystal phase separation, the system has no pretransition phenomena like critical opalescence (see subsection 1.3.2), and the scattered light intensity starts to increase only after the intersection of the configurative point by the liquidus curve, owing to the emergence of particles of a new phase (colloidal scattering).



Figure 2.38. System isobutylic acid+water. Reciprocal intensity of scattered light $I_{k,\vartheta=0}^{-1}$ extrapolated to $\vartheta \to 0$ with respect to $T - T_{bi}$ for 0.0906 mole fraction of isobutylic acid (Chu et al., 1969). Dependence $D = \lim_{q \to 0} (\Delta \omega/q^2)$ vs $T - T_{bi}$ for isobutylic acid concentrations 0.0906 (1), 0.14 (2), 0.114 (3) mole fractions [B.Chu, F.J.Schoenes, M.E.Fisher. Phys. Rev. **185** (1969) 219–226. Copyright © 1969 by the American Physical Society]

2.4.3. Diffusion

The diffusion coefficient D_i is another experimentally measured quantity sensitive to the level of the concentration fluctuations in solution. It is derived from the first (phenomenological) Fick law

$$\vec{j}_{D_i} = -D_i \nabla \mathbf{c}_i,\tag{31}$$

where j_{D_i} is the flux density of the *i*th component in the mixture $(g/cm^2 s)$, c_i is the concentration of the *i*th diffusing component (g/cm^3) . If a concentration gradient exists only along the direction x, then

$$\vec{D}_{D_{i}} = -D_{i}\frac{d\mathbf{c}_{i}}{dx}\vec{x}_{0},\tag{32}$$

 \vec{x}_0 being a unit vector.


Figure 2.39. System isobutylic acid+water. Coexistence curve (binodal) (1) and pseudospinodal (2) from light scattering studies, $I_{k,\vartheta=0}^{-1} \rightarrow 0$ (circles) and diffusion $D = \Delta \omega/q^2$ (triangles) (Chu et al., 1969) [B.Chu, F.J.Schoenes, M.E.Fisher. Phys. Rev. **185** (1969) 219-226. Copyright © 1969 by the American Physical Society]

The flux density is defined as the amount of substance (in grams, moles, or any other units) diffusing through a unit surface normal to the flux direction per unit time. Concentration is expressed in the corresponding units.

On the other hand, due to one of the basic principles of nonequilibrium thermodynamics, the diffusional flux density of components 1 and 2 in a binary mixture (solution) is written as (Rehage et al., 1970; Bazarov, 1976; Gurov, 1978)

$$\vec{j}_{D_1} = -\mathcal{L}_{11} \left(\frac{\partial \mu_1^*}{\partial x} \right) \vec{x}_0 - \mathcal{L}_{12} \left(\frac{\partial \mu_2^*}{\partial x} \right) \vec{x}_0, \tag{33}$$

$$\vec{j}_{D_2} = -\mathcal{L}_{21} \left(\frac{\partial \mu_1^*}{\partial x} \right) \vec{x}_0 - \mathcal{L}_{22} \left(\frac{\partial \mu_2^*}{\partial x} \right) \vec{x}_0, \tag{34}$$

where μ_i^* is the chemical potential of the *i*th component per molecule, \mathcal{L}_{ik} stands for Onsager's phenomenological coefficients. $-\partial \mu_i^* / \partial x$ has the meaning of a motive force.

It follows from Equations 33-34 and Gibbs-Durgham's equations 1.1.2-49 written as

$$\mathbf{c}_{1}\left(\frac{\partial\mu_{1}^{*}}{\partial x}\right) + \mathbf{c}_{2}\left(\frac{\partial\mu_{2}^{*}}{\partial x}\right) = 0 \tag{35}$$

(here x is the coordinate), that

$$\vec{j}_{D_1} = -\mathcal{L}_1 \mathbf{c}_1 \left(\frac{\partial \mu_1^*}{\partial x} \right) \vec{x}_0, \qquad \mathcal{L}_1 = \frac{\mathcal{L}_{11}}{\mathbf{c}_1} - \frac{\mathcal{L}_{12}}{\mathbf{c}_2}, \tag{36}$$

$$\vec{j}_{D_2} = -\mathcal{L}_2 \mathbf{c}_2 \left(\frac{\partial \mu_2^*}{\partial x}\right) \vec{x}_0, \qquad \mathcal{L}_2 = \frac{\mathcal{L}_{22}}{\mathbf{c}_2} - \frac{\mathcal{L}_{21}}{\mathbf{c}_1}. \tag{37}$$

For the flux density, the phenomenological relationships

$$\vec{j}_{D_1} = \mathbf{c}_1 \bar{v}_1 \vec{x}_0, \quad \vec{j}_{D_2} = \mathbf{c}_2 \bar{v}_2 \vec{x}_0$$
(38)

hold, where v_i is the mean velocity of particles (molecules). Comparison between Equations 36 and 38 leads to

$$\mathcal{L}_1 = \frac{\bar{v}_1}{-\frac{\partial \mu_1^*}{\partial x}} = u_1, \quad \mathcal{L}_2 = \frac{\bar{v}_2}{-\frac{\partial \mu_2^*}{\partial x}} = u_2. \tag{39}$$

The mean velocity/motive force ratio defines a mobility u_i . Therefore,

$$\vec{j}_{\mathcal{D}1} = -u_1 \mathbf{c}_1 \left(\frac{\partial \mu_1^*}{\partial x}\right) \vec{x}_0 = -u_1 \mathbf{c}_1 \left(\frac{\partial \mu_1^*}{\partial \mathbf{c}_1}\right) \left(\frac{d\mathbf{c}_1}{dx}\right) \vec{x}_0; \qquad (40)$$
$$\vec{j}_{\mathcal{D}2} = -u_2 \mathbf{c}_2 \left(\frac{\partial \mu_2^*}{\partial \mathbf{c}_2}\right) \left(\frac{d\mathbf{c}_2}{dx}\right) \vec{x}_0.$$

It results from comparison of Equations 32 and 40 that

$$D_1 = u_1 \mathbf{c}_1 \left(\frac{\partial \mu_1^*}{\partial \mathbf{c}_1} \right); \quad D_2 = u_2 \mathbf{c}_2 \left(\frac{\partial \mu_2^*}{\partial \mathbf{c}_2} \right). \tag{41}$$

In the course of a diffusional experiment, the concentrations of the diffusing components vary in a restricted physical space (a diffusional cell), which leads to changes in the density and volume in parts of the diffusional cell with respect to a immovable coordinate system. That is why choosing a location of the reference plane of the section, through which passes a unit of the substance amount, is not a simple matter, and the coordinate system for flux density is fixed in different ways (Erdey-Gruz, 1974; Read et al., 1977; Malkin and Chalykh, 1979), which leads to different diffusion coefficients, according to Equation 31.

In the case of binary systems, the coordinate system (the reference plane of the diffusional flux) is often chosen so that the diffusion coefficients of both the components could be equal:

$$D_1 = D_2 = D.$$

D is often called an interdiffusion coefficient (Erdey-Gruz, 1974). Then,

$$D = u_1 \mathbf{c}_1 \frac{\partial \mu_1^*}{\partial \mathbf{c}_1} = u_2 \mathbf{c}_2 \frac{\partial \mu_2^*}{\partial \mathbf{c}_2}.$$
(42)

Thus, the interdiffusion coefficient (to be called in what follows just a diffusion coefficient) depends on the hydrodynamic factor u_i and the thermodynamic factor $\mathbf{c}_i(\partial \mu_i^*/\partial \mathbf{c}_i)$.

The quantity $f_i = 1/u_i$ is often referred to as friction coefficient, then

$$D = \frac{\mathbf{c}_i}{f_i} \frac{\partial \mu_i^*}{\partial \mathbf{c}_i}.$$
(43)

This notation is valid for concentrations expressed in any units. With mole fractions, in view of Equation 1.1.3-7 and $\mu_i^* = \mu_i/N_A$, Equation 43 gives Einstein's equation

$$D_{id} = \frac{kT}{f_i} \tag{44}$$

for ideal solutions.

The positiveness of the diffusion coefficient (D > 0) in the solution stability area (including the metastable region) is an important corollary of Equation 43 (cf. Equations 1.1.2-53,-55 with 43). In an absolutely unstable region

$$D < 0 \tag{45}$$

and

$$D = 0 \tag{46}$$

on the spinodal.

When studying diffusion in the solution stability region, in many cases the relationship (Lisnyanski and Vuks, 1964, 1969; Read et al., 1977)

$$D = D_{id} \frac{1}{f} = D_{id} \frac{x_1 x_2}{RT} \left(\frac{\partial^2 \bar{G}}{\partial x_2^2} \right)_{T,P}$$
(47)

applies, where $D_{id} = x_1 D_1^* + x_2 D_2^*$; D_{id} is the diffusion coefficient in an ideal solution, D_i^* is an **self-diffusion coefficient** of molecules of the *i*th component in its individual state: $D_{id} \rightarrow D_i^*$ when $x_i \rightarrow 1$; f is the function of the concentration fluctuations (Equation 9).

Hence, the function f relates both to diffusion and to light scattering (see Figure 2.36). In this case, f is calculated from vapour pressure at $T = 20^{\circ}$ C (Vuks, 1977).

The maximal value f_{max} corresponds to the critical concentration of the mixture. The magnitudes of f_{max} enable one to judge how distant from T_c the isotherm is, since, at T_c , $f_{\text{max}} \to \infty$.

According to Equation 47, the critical concentration corresponds to the minimum D_{\min} .

The concentration at the maximum of Rayleigh's ratio, $R_{is,90,\max}$, slightly differs from the critical one owing to the influence of the concentration dependence of other optical quantities of the mixture (Equation 10).

The study of the concentration dependence f is a very informative and sensitive method for analyzing the molecular interactions in binary systems (Vuks, 1974). This dependence is obtained experimentally from light scattering data in solution or diffusion. Then, using $f = f(x_2)$, one can calculate the most important thermodynamic quantities of the system.

For instance, systematic studies on light scattering in the systems toluene+an alcohol (Vuks, 1974) have shown f_{\max} to increase in the line methanol—ethanol—propanol—butanol—decanol, with x_{2c} shifting towards higher alcohol concentrations. These data, in comparison with similar ones for other systems, have led to important conclusions about the structure and character of the intermolecular interactions.

The same approach was successfully applied to study Il-bonds and more common association phenomena in solutions (Vuks, 1974).

In agreement with Equation 46, experimental studies on diffusion in the critical region of the system phenol+water (Krichevski et al., 1954; Krichevski and Khazanova, 1960) have indeed shown a negligibly small value of D at the critical point (Figure 2.40, see also Figures 2.37-2.39).

An infinitely small value of the diffusion coefficient $D \rightarrow 0$ at the critical point (and, generally, on the spinodal) leads to infinitely slow substance transport even at great



Figure 2.40. Dependence of the diffusion coefficient in the system phenol+water on the phenol concentration (wt %) at 67°C. C denotes the critical point (Krichevski and Khazanova, 1960)

concentration gradients (see Equation 31). This explains a significant difficulty in driving experimentally the configurative point to the nearest vicinity of the critical point. In the view of Semenchenko (1960), to reach the critical point is a principally unsolvable experimental problem.

There is another corollary of $D \rightarrow 0$ near the spinodal: an infinitely low rate of dispersal of the fluctuations arisen spontaneously. According to Onsager's criterion (see subsection 2.3.3), these fluctuations turn out to be long-living regions of heterophase fluctuations which can be regarded as colloidal particles, and the system itself as a quasicolloidal one (microheterogeneous) (J. Frenkel, 1938; Skripov, 1960).

2.4.4. Dynamics of the concentration fluctuations. Scattered light spectrum

Alpert et al. (1965) were the first to measure the width of Rayleigh's band in the binary system aniline+cyclohexane at the critical concentration. They found that the band contracts as the configurative point approaches the critical temperature T_c . A direct proportionality of $\Delta \omega$ vs q^2 was also found.

Debye (1965) was the first to explain these experimental data. According to Onsager's (1931ab) principle, concentration fluctuations in solutions $\delta \mathbf{c}(\vec{r}, t)$ must obey an equation, which is applicable to macroscopic diffusion, i.e. (in this case) to Fick's second law (Berne and Pecora, 1976; Marshall, 1978)

$$\frac{\partial[\delta \mathbf{c}(\vec{r},t)]}{\partial t} = D\nabla^2 \delta \mathbf{c}(\vec{r},t)$$
(48)

(Equation 48 is obtained by substitution of Equation 31 into Equation 2.3-46, D is the diffusion coefficient of the second component).

Fourier transform of Equation 48 results in

$$\frac{\partial}{\partial t} [\delta \mathbf{c}(\vec{q}, t)] = -q^2 D \,\delta \mathbf{c}(\vec{q}, t),\tag{49}$$

where $\delta \mathbf{c}(\vec{q}, t)$ is the spatial Fourier transform of the concentration fluctuations (cf. Equation 2.3 47). The solution is

$$\delta \mathbf{c}(\vec{q},t) = \delta \mathbf{c}(\vec{q},0) \exp\left[-Dq^2 t\right],\tag{50}$$

where $\delta \mathbf{c}(\vec{q}, 0)$ is the initial fluctuation of the \vec{q} th component of the Fourier transform of the concentration fluctuations (see Figure 2.30). Multiplying by the complex conjugate $\delta \mathbf{c}^{*}(\vec{q}, 0)$ with subsequent averaging (see Equations 2.3-21,-25,-48) yields the temporal correlation function

$$\left\langle \delta \mathbf{c}(\vec{q},t) \delta \mathbf{c}^{*}(\vec{q},0) \right\rangle = \left\langle |\delta \mathbf{c}(\vec{q})|^{2} \right\rangle \exp(-Dq^{2}t), \tag{51}$$

where $\langle |\delta \mathbf{c}(\tilde{q})|^2 \rangle$ is the mean square concentration fluctuation, which is derived from the statistical-thermodynamic theory of fluctuations (see Equation 1.4 33).

The Fourier transform of this temporal correlation function (Oberhettinger, 1973) is the spectral density accurate up to the constant (see Equation 2.3-26) and represents the Lorentzian

$$S_{cc}(\vec{q},\omega) = \pi^{-1} \left\langle \left| \delta \mathbf{c}(\vec{q}) \right|^2 \right\rangle \frac{Dq^2}{\omega^2 + (Dq^2)^2}$$
(52)

with its halfwidth (see Equation 2.3-49)

$$\Delta \omega = Dq^2, \tag{53}$$

which explains Alpert's results: with approaching the critical point, $D \to 0$, $\Delta \omega \to 0$, and $\Delta \omega \sim q^2$.

However, a more rigorous solution of this problem should account for six conservative variables in a binary system, namely, energy, kinetic momentum (three components), the concentration of the solution, and the total density of the liquid. In the general case, it should be taken into account that the solute flux \vec{j} involves the diffusional and heat fluxes

$$\vec{j} = \vec{j}_D + m\rho \mathbf{c}\vec{v},\tag{54}$$

where ρ is the numerical concentration of molecules, **c** is the solute/solvent masses ratio, m is the mass of the solute molecule, \vec{v} is the local velocity, \vec{j}_D is the mass diffusional flux.

Experiments show the dielectric constant to be a function of P, T, and c:

$$\epsilon = \epsilon(P, T, \mathbf{c}). \tag{55}$$

Be the problem simplified by considering the pressure as constant and non-fluctuating, then

$$\delta\epsilon(\vec{q},t) = \left(\frac{\partial\epsilon}{\partial\mathbf{c}}\right)_{P,T} \delta\mathbf{c}(\vec{q},t) + \left(\frac{\partial\epsilon}{\partial T}\right)_{P,\mathbf{c}} \delta\mathcal{T}(\vec{q},t).$$
(56)

The scattered light intensity is proportional to the Fourier transform of

$$\langle \delta \epsilon^*(\vec{q}, 0) \delta \epsilon(\vec{q}, t) \rangle \tag{57}$$

$$=\left\langle \left[\left(\frac{\partial \epsilon}{\partial T}\right)_{P,\mathbf{c}} \delta T^{*}(\vec{q},0) + \left(\frac{\partial \epsilon}{\partial \mathbf{c}}\right)_{P,T} \delta \mathbf{c}^{*}(\vec{q},0) \right] \left[\left(\frac{\partial \epsilon}{\partial T}\right)_{P,\mathbf{c}} \delta T(\vec{q},t) + \left(\frac{\partial \epsilon}{\partial \mathbf{c}}\right)_{P,T} \delta \mathbf{c}(\vec{q},t) \right] \right\rangle$$

(see Equations 2.3–30,–31).

This is a linear superposition (in the linearized approximation) of the temporal autocorrelation and **cross-correlation functions** $\langle \delta \mathbf{c}^*(\vec{q}, 0) \delta \mathbf{c}(\vec{q}, t) \rangle$, $\langle \delta \mathbf{c}^*(\vec{q}, 0) \delta T(\vec{q}, t) \rangle$ etc., which are obtained (Berne and Pecora, 1976) after the hydrodynamic and conservative equations (Equation 54 being one of them) have been solved jointly.

On substituting these correlation functions into Equation 57 with subsequent Fourier transformation, an expression for the dynamic form factor is deduced (Berne and Pecora, 1976):

$$\begin{split} \pi S_{\epsilon\epsilon}(\vec{q},\omega) &= \left(\frac{\partial\epsilon}{\partial \mathbf{c}}\right)_{P,T}^{2} \left[kT\left(\frac{\partial \mathbf{c}}{\partial \mu}\right)_{P,T}\right] \frac{1}{s_{+}-s_{-}} \left[\frac{(s_{-}+Dq^{2})s_{+}}{\omega^{2}+s_{+}^{2}} - \frac{(s_{+}+Dq^{2})s_{-}}{\omega^{2}+s_{-}^{2}}\right] (58) \\ &+ 2\left(\frac{\partial\epsilon}{\partial \mathbf{c}}\right)_{P,T} \left(\frac{\partial\epsilon}{\partial T}\right)_{P,\mathbf{c}} \frac{kT}{c_{P}} \cdot \frac{K_{T}Dq^{2}}{s_{+}-s_{-}} \left(\frac{s_{+}}{\omega^{2}+s_{+}^{2}} - \frac{s_{-}}{\omega^{2}+s_{-}^{2}}\right) \\ &+ \left(\frac{\partial\epsilon}{\partial T}\right)_{\mathbf{c},P} \frac{kT^{2}}{c_{P}} \cdot \frac{1}{s_{+}-s_{-}} \left[\frac{(s_{-}+Dq^{2})s_{+}}{\omega^{2}+s_{+}^{2}} - \frac{(s_{+}+Dq^{2})s_{-}}{\omega^{2}+s_{-}^{2}}\right], \end{split}$$

where

$$s_{\pm} = -\frac{1}{2}(D_T + \Delta)q^2 + \frac{1}{2}\left[(D_T + \Delta)^2 - 4D_T D\right]^{1/2} q^2, \tag{59}$$

$$\Delta = D \left[1 + \frac{K_T^2}{c_P T} \left(\frac{\partial \mu}{\partial \mathbf{c}} \right)_{P,T} \right],\tag{60}$$

 $K_T = D_T/D$ is a thermal diffusion ratio, μ is the chemical potential of the mixture per unit mass:

$$\mu = \frac{\mu_1}{m_1} - \frac{\mu_2}{m_2}$$

 m_i being the masses of molecules in the mixture (cf. Equation 1.1.2-48).

The spectrum (Equation 58) is a superposition of Lorentzian bands

$$\frac{s_+}{\omega^2 + s_+^2}$$
 and $\frac{s_-}{\omega^2 + s_-^2}$ (61)

with their weights depending on many parameters. The complexity of this spectrum arises from the relation between diffusion and heat flux. We are dealing with the central band of the triplet: Equation 58 lacks Mandelshtam-Brillouin's doublet caused by regard for the pressure fluctuations while Equation 58 was derived without it.

The central Rayleigh's band of the solution spectra can be simplified only under certain circumstances. In the limit of small concentrations, $\mathbf{c} \to 0 \lim_{c \to 0} K_T = 0$ and

$$s_+ \cong -Dq^2, \quad s_- \cong -D_T q^2, \tag{62}$$

i.e. the spectrum is a superposition of two Lorentzians, one of which is due to the molecular diffusion, while the other is due to the thermal diffusion only:

$$\pi S_{\epsilon\epsilon}(\vec{q},\omega) = \tag{63}$$

$$= \left(\frac{\partial\epsilon}{\partial\mathbf{c}}\right)_{P,T}^2 kT \left(\frac{\partial\mathbf{c}}{\partial\mu}\right)_{P,T} \left[\frac{Dq^2}{\omega^2 + (Dq^2)^2}\right] + \left(\frac{\partial\epsilon}{\partial T}\right)_{\mathbf{c},P}^2 \frac{kT^2}{\mathbf{c}_P} \left[\frac{D_Tq^2}{\omega^2 + (D_Tq^2)^2}\right].$$

Hence, in the limit of low concentrations, heat flux and molecular diffusion are not related, and D_T and D can be determined separately. Usually, ε is a weak function of temperature and only the diffusional band predominates in Equation 63.

In solutions, $D_T \gg D$ often holds, then

$$s_+ \simeq -Dq^2, \quad s_- \simeq -D_T q^2, \tag{64}$$

and the spectrum also reduces to a superposition of two Lorentzians, due to the molecular and thermal diffusion, respectively. The diffusional component of the spectrum manifests itself as a very intensive sharp peak of width Dq^2 located at the top of a wider band of width D_Tq^2 due to heat flux. For the majority of suspensions (including biological objects, such as viruses, cells, etc.) $D \sim 10^{-6}$ cm²/s or lower, so $D_T \gg D$ is satisfied. In this case, the sharp central component

$$\pi S_{\epsilon\epsilon}(\vec{q},\omega) \simeq \left(\frac{\partial\epsilon}{\partial \mathbf{c}}\right)_{P,T}^2 kT \left(\frac{\partial \mathbf{c}}{\partial \mu}\right)_{P,T} \left[\frac{Dq^2}{\omega^2 + (Dq^2)^2}\right]$$
(65)

strongly resembles the spectrum (Equation 52) derived from simpler premises.

Certainly, there are also pressure fluctuations in real binary mixtures. Complete analysis in the limit of small q leads to

$$S_{\epsilon\epsilon}(\vec{q},\omega) = S_{\epsilon\epsilon}^{c}(\vec{q},\omega) + S_{\epsilon\epsilon}^{d}(\vec{q},\omega), \tag{66}$$

where $S_{\epsilon\epsilon}^{\mathbf{c}}$ is the central component defined by Equation 58, $S_{\epsilon\epsilon}^{d}$ is the spectrum corresponding to Mandelshtam-Brillouin's doublet

$$S^{d}_{\epsilon\epsilon}(\vec{q},\omega) = \frac{1}{\pi} \left(\frac{\partial\epsilon}{\partial\rho}\right)^{2}_{c,T} \frac{kT\rho}{\chi_{s}} \left[\frac{\Gamma q^{2}}{\left[\omega_{0}+\omega(q)\right]^{2}+(\Gamma q^{2})^{2}} + \frac{\Gamma q^{2}}{\left[\omega_{0}-\omega(q)\right]^{2}+(\Gamma q^{2})^{2}}\right],$$

where $\omega(q) = \mathcal{V}q$, \mathcal{V} is the adiabatic velocity of sound, χ_s is isoentropic compressibility, Γ is the attenuation factor of the sound wave

$$\Gamma = \frac{1}{2} \left[D_T(\gamma - 1) + \frac{\eta_\nu + \eta_S/3}{m\rho} + \frac{D\mathcal{V}^2}{m^2\rho^2} \left(\frac{\partial \mathbf{c}}{\partial \mu} \right)_{P,\mathbf{c}} B^2 \right],\tag{67}$$

where $\gamma = c_P/c_V$ and

$$B = \left[\left(\frac{\partial \rho}{\partial \mathbf{c}} \right)_{P,T} + \frac{K_T}{c_P} \left(\frac{\partial \rho}{\partial T} \right)_{P,\mathbf{c}} \left(\frac{\partial \mu}{\partial \mathbf{c}} \right)_{P,T} \right].$$
(68)

The quantity Γ from Equation 67 differs from that in Equation 2.3-56 owing to the appearance of a contribution of diffusion and to the mutual influence of diffusion and heat flux. Equation 66 does not comprise negligible non-Lorentzian terms like those in Equation 2.3-3.

Thus, the scattered light spectrum of the binary solutions consists of four components. Two MB peaks are located at $\pm \omega(q)$ from the centre with width Γq^2 . The central component comprises a superposition of two Lorentzians, with their parameters depending on many factors.

Currently, the inelastic light scattering technique has been applied to determine the diffusion coefficient D in different parts of the state diagram of a binary system, using the simplified formula 52 mainly.

Provided that special equipment is available, a merit of this technique is in the short duration of measurements (from several minutes to an hour). No underlayering procedure is required, with its requirements of long and thorough thermostating and high skills of the operator.

This advantage of the inelastic scattering technique seemed most promising for measuring D near the spinodal and critical point, where equilibrium is reached very slowly due to $D \rightarrow 0$. The first applications were devoted to measuring D near the spinodal on one-component (Ford and Benedek, 1965) and binary systems (Alpert et al., 1965; Chu, 1967; Cummins and Pike, 1974) through $\Delta \omega vs q^2$ (Equations 2.3-57 and 53). Such values of D were used to plot a "pseudospinodal" with $D \rightarrow 0$ extrapolation (see Figures 2.38 and 2.39) (Chu et al., 1972; Tscharnuter et al., 1972) (cf. Figure 2.35).

By virtue of Equation 31, the diffusion coefficient is classified with the parameters characterizing a system in nonequilibrium, i.e. with the dynamic parameters of the system. The behaviour of such parameters near the spinodal and critical point is called **dynamic critical phenomena**. To describe them, an approach in the fashion of the similarity hypothesis has proved to be very fruitful, this hypothesis in its application to the dynamic parameters being called a **dynamic similarity hypothesis** (Stanley, 1971).

Eg. the experimental data of D near the spinodal (see Figure 2.38) obeys the exponent law

$$D_{q \to 0} = const \left(\frac{T - T_{sp,D}}{T_{bi}}\right)^{\gamma}$$
(69)

with $\gamma = 0.67$ (curves 1, 2) and $\gamma = 0.68$ (curve 3), and $T_{sp,D}$ being the spinodal temperature determined from diffusion $D \to 0$, T_{bi} is the binodal temperature.

The same critical index, which defines osmotic compressibility in Table 1.2 ($\chi_T \sim \varepsilon^{-\nu}$, where $\chi_T = -1/x_2(\partial x_2/\partial \pi)_T$), enters into Equation 69.

According to Equations 47, 1.1.2-52, 1.2-27,

$$D \sim x_1 x_2 \frac{\partial^2 G}{\partial x_2^2} = -x_1 \frac{\partial \mu_1}{\partial x_2} \sim +x_1 \frac{\partial \pi}{\partial x_2} \sim x_1 \left(\frac{\partial x_2}{\partial \pi}\right)^{-1}$$

However, near the spinodal, the approach based on Onsager's hypothesis and on the solution of the hydrodynamic equations loses its validity. With allowance for the long-range correlation distance of the concentration fluctuations ξ_k , the validity condition of

Onsager's hypothesis (Halperin and Hohenberg, 1967) is

$$\lambda \gg \xi_k \quad \text{or} \quad q\xi_k \ll 1. \tag{70}$$

The regions on the state diagram, where these conditions are satisfied, are called **hydrodynamic** (and the condition itself is referred to as a hydrodynamic mode). In the critical region and near the spinodal

$$q\xi_k \gg 1, \tag{71}$$

and Onsager's principle is not obviously satisfied (Figure 2.41) along with formulae like Equations 2.3-57 and 53.



Figure 2.41. Schematic of the mutual location of the hydrodynamic and critical regions: *I* is the low-temperature hydrodynamic area $(q|\xi| \ll 1)$, 2 is the critical area $(q|\xi| \gg 1)$, 3 is the high-temperature hydrodynamic area $(q|\xi| \ll 1)$. *q* of neutrons exceeds that of light by 3 orders of magnitude (IIalperin and Hohenberg, 1967) [B.J.Halperin, P.C.Hohenberg. Phys. Rev. Lett. **19** (1967) 700-703. Copyright © 1967 by the American Physical Society]

For the dynamic critical phenomena, Debye's phenomenological approach, developed for mean-statistical critical phenomena (see subsection 2.3.5), has turned out to be helpful. Introducing a gradient term into ΔF has led (Fixman, 1966; Chu et al., 1972; Tscharnuter et al., 1972) to

$$\Delta \omega = Dq^2 (1 + B\tilde{\xi}_k^2 q^2). \tag{72}$$

Hence, the plot $\Delta \omega/q^2 vs q^2$ is a straight line cutting off a segment equal to D on the ordinate axis and with the slope proportional to $\tilde{\xi}_k^2$, $\tilde{\xi}_k$ being a **dynamic correlation** range of the concentration fluctuations (Figure 2.42).

A formula of the type 72 is valid for a one-component system as well, where ξ_{ρ} is the dynamic correlation range of the density fluctuations.

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Figure 2.42. System fluoromethylcyclohexane+ CCl_4 . Plot $\Delta \omega/q^2 vs q^2$ at $T - T_c = 0.30^{\circ}$ C (1) and 0.10°C (2) (Cluu et al., 1972)[B.Chu, D.Thiel, W.Tscharnuter, D.V.Fenby. J. de Phys. **33** (1972) Cl-111-Cl-120. Copyright © 1972 by EDP Sciences]

The hypothesis of dynamic similarity also yields a similar relationship (Halperin and Hohenberg, 1967; Stanley, 1971).

For two-component systems, the mode-mode coupling theory in the critical region leads to expressions like those given at the end of subsection 2.3.5.

In the case of solutions, λ is replaced by the diffusion coefficient

$$D = \frac{kT}{6\pi\tilde{\eta}\tilde{\xi}}.$$
(73)

The mode-mode coupling theory predicts the universality of the dimensionless width of the central (diffusional) spectrum line

$$\Gamma^* = \frac{6\pi\tilde{\eta}}{kT} \frac{\Gamma_q}{q^3},\tag{74}$$

since Γ^* is expressed through the universal function $K(q\xi)$:

$$\Gamma^* = \frac{K(q\dot{\xi})}{(q\ddot{\xi})^3}.$$
(75)

Indeed, this theoretical curve fits well into the experimental Γ^* (from Equation 74) measured by means of dynamic light scattering for solutions (Swinney, 1974; Anisimov, 1987), as well as for pure liquid (subsection 2.3.5).

We conclude that the scattering of electromagnetic radiation serves as a powerful tool in exploring the structure of a substance.

The effect of light scattering is characterized by several quantities: I_{ϑ} , R_{ϑ} , τ , etc., which can be expressed through different parameters of the system: the dielectric constant ϵ , the polarizability α , the refractive index μ . Moreover, the polarization of incident light beam may be of different character.

Mismatches in formulae (especially, in numerical coefficients), while using different parameters are often met in the light scattering literature. Neglect of the conversion factors among ε , α , and μ may cause more serious misunderstanding. Eg. Equations 2.1-76,-80 etc. with correlation functions are often applied without any changes for $(\Delta \varepsilon)^2$, $(\Delta \alpha)^2$, $(\Delta \mu)^2$, which leads to the breakdown of dimensions.

In conclusion, we present summary tables of the most important formulae of light scattering in Rayleigh's and Rayleigh-Debye's (Rayleigh-Debye-Hans') approximations as a supplement to the topic "Light scattering" (Tables 2.1-2.4).

2.5. Correlation of the order parameter fluctuations in the critical region. Hypothesis of similarity. Hypothesis of universality

In many cases, experiment does not fit with the predictions of the mean field theory, especially in the nearest vicinity of the critical point. Naturally, it is owing to the simplifying premises on the basis of mean field approximations.

The nearest neighbourhood of T_c is characterized by significant fluctuations in the order parameter Q. This follows already from the form of G (Equation 1.6-1) near the critical point (see Figures 1.14, 1.25, and 1.28). When $T > T_c$, the potential has a minimum at $Q_0 = 0$, and when $T < T_c$ it has a maximum; therefore, near $T \approx T_c G$ becomes a very weak function of Q. Significant variations of Q do not cause noticeable changes in the thermodynamic potential, which causes significant fluctuations in the order parameter Q(see Equation 1.4-33).

As the amplitude and scale of Q fluctuations increase, their correlation arises, which is in no way represented by an equation of the type 1.6-1. Moreover, correlated, extended and long-living fluctuations of Q lead to a spatially inhomogeneous distribution of $Q(\vec{r})$ in the range $T < T_c$, which also is not taken into account in Equation 1.6-1.

As the first approximation, the above phenomena can be allowed for by supplementing Equation 1.6-1 with new terms with different-order derivatives of $Q(\vec{r})$. The simplest potential is written as

$$G = G_0 + \frac{1}{2} \int \left\{ aQ^2(\vec{r}) + \frac{1}{2} bQ^4(\vec{r}) + \delta \cdot \left[\nabla Q(\vec{r})\right]^2 - 2h(\vec{r})Q(\vec{r}) \right\} d^3r, \tag{1}$$

a, b, δ being functions of pressure and temperature, $h(\vec{r})$ a inhomogeneous external field. Here G is a functional, whose minimum is given by Euler's variational equation

$$\frac{\delta G}{\delta Q(\vec{r})} = aQ(\vec{r}) + bQ^3(\vec{r}) - \delta \cdot \Delta Q(\vec{r}) - h(\vec{r}) = 0.$$
⁽²⁾

Then, assume $Q(\vec{r})$ to differ slightly from the equilibrium value Q_0 with no gradient term taken into consideration (see Equation 1.6-8), so

$$Q(\vec{r}) = Q_0 + Q_1(\vec{r}).$$
(3)

Hence, the equation for $Q_1(\vec{r})$ in the first approximation in the absence of field $h(\vec{r})$ has the form (Patashinski and Pokrovski, 1975)

$$\Delta Q_1(\vec{r}) - \frac{a + 3bQ_0^2}{\delta} Q_1(\vec{r}) = 0 \tag{4}$$

Hypotheses of similarity and universality

2.5.

Table 2.1. Light scattering formulae in colloidal solutions of small isotropic spherical particles <u>Rayleigh's scattering</u>

The conditions are: $|m-1| \ll 1$, $\alpha \ll 1$, where $\alpha = 2\pi r/\lambda = 2\pi r\mu_1/\lambda_0$ is the relative size, $\mu = \mu_2/\mu_1$ is the relative refractive indices of the disperse phase and dispersion medium, respectively, λ and λ_0 are the wavelengths in the medium and vacuum, respectively, r, v_p , and α_p are the radius, volume, and polarizability of a particle, respectively, N_2 is the number of particles per volume unit, ϵ_1 and ϵ_2 are the permittivities of the disperse phase and dispersion medium, respectively, ϑ is the scattering angle, $\epsilon = \mu^2$, $\alpha_p = \frac{(\epsilon_2 - \epsilon_1)\epsilon_1}{\epsilon_1 + 2\epsilon_2}r^3 = \mu_1^2 \left(\frac{\mu_2^2 - \mu_1^2}{\mu_2^2 + 2\mu_1^2}\right)r^3 = \frac{3}{4\pi} \cdot \frac{(\mu_2^2 + \mu_1^2)\mu_1^2}{\mu_2^2 + 2\mu_1^2}v_p$.

Parameter	Characteristic functions				
	au, cm ⁻¹	$R_{90}, { m cm^{-1}}$	$R_{\vartheta}, \mathrm{cm}^{-1}$	$R_{90,\perp},~{ m cm^{-1}}$	
Polarizability, α , cm ³	$\frac{128\pi^5}{3\lambda_0^4}\alpha_p^2N_2$	$\frac{8\pi^4}{\lambda_0^4}\alpha_p^2 N_2$	$\frac{8\pi^4}{\lambda_0^4}\alpha_p^2 N_2(1+\cos^2\vartheta)$	$\frac{16\pi^4}{\lambda_0^4}\alpha_p^2N_2$	
Permittivity, ϵ	$\frac{24\pi^3}{\lambda^4} v_p^2 \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1}\right)^2 N_2$	$\frac{9\pi^2}{2\lambda^4} v_p^2 \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1}\right)^2 N_2$	$\frac{9\pi^2}{2\lambda^4} v_p^2 \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1}\right)^2 N_2(1 + \cos^2\vartheta)$	$\frac{9\pi^2}{\lambda^4} v_p^2 \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1}\right)^2 N_2$	
Refractive in- dex, μ	$\frac{24\pi^3}{\lambda^4} v_p^2 \left(\frac{\mu_2^2 - \mu_1^2}{\mu_2^2 + 2\mu_1^2}\right)^2 N_2$	$\frac{9\pi^2}{2\lambda^4} v_p^2 \left(\frac{\mu_2^2 - \mu_1^2}{\mu_2^2 + 2\mu_1^2}\right)^2 N_2$	$\frac{9\pi^2}{2\lambda^4} v_p^2 \left(\frac{\mu_2^2 - \mu_1^2}{\mu_2^2 + 2\mu_1^2}\right)^2 N_2(1 + \cos^2\vartheta)$	$\frac{9\pi^2}{\lambda^4} v_p^2 \left(\frac{\mu_2^2 - \mu_1^2}{\mu_2^2 + 2\mu_1^2}\right)^2 N_2$	

Table 2.2. Light scattering formulae in colloidal solutions with optically "soft" particles Rayleigh-Debye's approximation

The conditions are: $|m-1| \ll 1$, $\rho \ll 1$, α is any, where $\rho = 2\alpha |m-1| = 4\pi r \mu_1 |m-1|/\lambda_0$ is the phase shift, $P(\vartheta, \lambda, D)$ is Debye's function; D is the characteristic size of nonuniform particles. $\alpha_p = \frac{\epsilon_2 - \epsilon_1}{4\pi} v_p$; $\alpha_p = \frac{(m-1)\mu_1^2}{2\pi} v_p$; $P(\vartheta, \lambda, D) = \frac{1}{2\pi} v_p$ $\frac{1}{v_p^2}\left|\int\limits_{v_p}e^{i\delta}\,dv_p\right|^2.$ 2.5.

Parameter	Characteristic functions			
	R ₉₀ , cm ⁻¹	$R_{\vartheta}, \mathrm{cm}^{-1}$	$R_{90,\perp}, { m cm^{-1}}$	
Polarizability, α , cm ³	$\frac{8\pi^4}{\lambda_0^4}\alpha_p^2 N_2 P(90^\circ, \lambda, D)$	$\frac{8\pi^4}{\lambda_0^4}\alpha_p^2 N_2 P(\vartheta,\lambda,D)(1+\cos^2\vartheta)$	$\frac{16\pi^4}{\lambda_0^4}\alpha_p^2 N_2 P(90^\circ, \lambda, D)$	
Permittivity, ϵ	$\frac{\pi^2}{2\lambda_0^4} \left(\epsilon_2 - \epsilon_1\right)^2 v_p^2 N_2 P(\lambda, D)$	$\frac{\pi^2}{2\lambda_0^4} \left(\epsilon_2 - \epsilon_1\right)^2 v_p^2 N_2 P(\vartheta, \lambda, D) (1 + \cos^2 \vartheta)$	$\frac{\pi^2}{\lambda_0^4} \left(\epsilon_2 - \epsilon_1\right)^2 v_p^2 N_2 P(\lambda, D)$	
Refractive in- dex, μ	$\frac{2\pi^2}{\lambda^4}(m-1)^2 v_p^2 N_2 P(\lambda, D)$	$\frac{2\pi^2}{\lambda^4}(m-1)^2 v_p^2 N_2 P(\vartheta,\lambda,D)(1+\cos^2\vartheta)$	$\frac{4\pi^2}{\lambda^4}(m-1)^2 v_p^2 N_2 P(\lambda,D)$	

Table 2.3. Light scattering formulae in liquids with isotropic molecules and their solutions Rayleigh's scattering

$v\ll \lambda$

v is a space unit where permittivity ϵ' , polarizability α' , and refraction index μ' differ from the corresponding average macroscopic values ϵ , α and μ by

 $\Delta \epsilon = \epsilon' - \epsilon; \qquad \Delta \alpha = \alpha' - \alpha; \qquad \Delta \mu = \mu' - \mu.$ The conversion formulae are: $\Delta \alpha \cong v \Delta \epsilon / 4\pi; \quad \Delta \epsilon = \epsilon' - \epsilon = {\mu'}^2 - \mu^2 = (\mu' - \mu)(\mu' + \mu) \approx 2\mu \Delta \mu$ In the case of solutions, the mean square fluctuation of every parameter is replaced like

$$\overline{\left(\Delta\alpha\right)}^2 = \left(\frac{\partial\alpha}{\partial c}\right)^2 \overline{\left(\Delta c\right)}^2,$$

c being the solution concentration.

Parameter	Characteristic functions			
	au, cm ⁻¹	$R_{90}, { m cm^{-1}}$	$R_{\vartheta}, \mathrm{cm}^{-1}$	$R_{90,\perp}, { m cm^{-1}}$
Polarizability, α , cm ³	$\frac{128\pi^5}{3\lambda_0^4}\overline{\frac{\left(\Delta\alpha\right)^2}{v}}$	$\frac{8\pi^4}{\lambda_0^4} \frac{\overline{(\Delta\alpha)^2}}{v}$	$\frac{8\pi^4}{\lambda_0^4} \overline{\frac{(\Delta\alpha)^2}{v}} (1 + \cos^2\vartheta)$	$\frac{16\pi^4}{\lambda_0^4} \frac{\overline{(\Delta\alpha)^2}}{v}$
Permittivity, ¢	$\frac{8\pi^3}{3\lambda_0^4}\overline{\left(\Delta\epsilon\right)^2}v$	$\frac{\pi^2}{2\lambda_0^4}\overline{\left(\Delta\epsilon\right)^2}v$	$\frac{\pi^2}{2\lambda_0^4}\overline{(\Delta\epsilon)^2}v(1+\cos^2\vartheta)$	$\frac{\pi^2}{\lambda^4}\overline{\left(\Delta\epsilon\right)^2}v$
Refractive in- dex, μ	$\frac{32\pi^3}{3\lambda_0^4}\mu^2\overline{(\Delta\mu)^2}v$	$\frac{2\pi^2}{2\lambda_0^4}\mu^2 \overline{\left(\Delta\mu\right)^2}v$	$\frac{2\pi^2}{2\lambda_0^4}\mu^2\overline{(\Delta\mu)^2}v(1+\cos^2\vartheta)$	$\frac{4\pi^2}{\lambda_0^4}\mu^2\overline{(\Delta\mu)^2}v$

Table 2.4. Light scattering formulae in liquids at critical opalescence and in solids with density fluctuations Rayleigh-Debye's approximation

The definitions of the correlation functions of parameter fluctuations are:

$$\overline{(\Delta\epsilon(\vec{r})\cdot\Delta\epsilon(\vec{r'}))} = h(\rho)\overline{(\Delta\epsilon)^2}; \qquad \overline{(\Delta\alpha(\vec{r})\cdot\Delta\alpha(\vec{r'}))} = \gamma(\rho)\overline{(\Delta\alpha)^2}; \qquad \overline{(\Delta\mu(\vec{r})\cdot\Delta\mu(\vec{r'}))} = n(\rho)\overline{(\Delta\mu)^2}$$

The equivalent volumes on condition that the inhomogeneity areas are spherically symmetric:

$$\omega_{\epsilon} = \int_{0}^{\infty} h(\rho) \frac{\sin q\rho}{q\rho} 4\pi \rho^{2} d\rho, \qquad w_{\alpha} = \int_{0}^{\infty} \gamma(\rho) \frac{\sin q\rho}{q\rho} 4\pi \rho^{2} d\rho, \qquad w_{\mu} = \int_{0}^{\infty} n(r) \frac{\sin q\rho}{q\rho} 4\pi \rho^{2} d\rho,$$
$$q = \frac{4\pi}{\lambda} \sin \frac{\vartheta}{2}$$

Parameter	Characteristic functions			
	τ , cm ⁻¹	R_{90}, cm^{-1}	$R_{\vartheta}, \mathrm{cm}^{-1}$	$R_{90,L}, \mathrm{cm}^{-1}$
Polarizability, α, cm ³	$\frac{128\pi^5}{3\lambda_0^4} \frac{\overline{(\Delta\alpha)^2}}{w_\alpha}$	$\frac{8\pi^4}{\lambda_0^4} \frac{\overline{(\Delta\alpha)^2}}{w_\alpha}$	$\frac{8\pi^4}{\lambda_0^4} \frac{\overline{(\Delta\alpha)^2}}{w_\alpha} (1 + \cos^2 \vartheta)$	$\frac{16\pi^4}{\lambda_0^4} \frac{\overline{\left(\Delta\alpha\right)^2}}{w_\alpha}$
Permittivity, ε	$\frac{8\pi^3}{3\lambda_0^4}\overline{\left(\Delta\epsilon\right)^2}w_\epsilon$	$\frac{\pi^2}{2\lambda_0^4}\overline{(\Delta\epsilon)^2}w_\epsilon$	$\frac{\pi^2}{2\lambda_0^4}\overline{\left(\Delta\epsilon\right)^2}w_\epsilon(1+\cos^2\vartheta)$	$\frac{\pi^2}{\lambda^4}\overline{\left(\Delta\epsilon\right)^2}w_\epsilon$
Refractive in- dex, μ	$\frac{32\pi^3}{3\lambda_0^4}\mu^2\overline{(\Delta\mu)^2}\omega_\mu$	$\frac{2\pi^2}{2\lambda_0^4}\mu^2 \overline{\left(\Delta\mu\right)^2}\omega_\mu$	$\frac{2\pi^2}{2\lambda_0^4}\mu^2 \overline{(\Delta\mu)^2}\omega_\mu (1+\cos^2\vartheta)$	$\frac{4\pi^2}{\lambda_0^4}\mu^2\overline{\left(\Delta\mu\right)^2}\omega_\mu$

(it results from substitution of Equation 3 into Equation 2 with allowance for Equation 2 for Q_0 and keeping only the first-order derivative term $Q_1(\vec{r})$ in $[Q_0 + Q_1(\vec{r})]^3$).

If we denote

$$\xi^{-2} = \frac{a + 3bQ_0^2}{\delta},\tag{5}$$

then

$$\Delta Q_1(\vec{r}) - \xi^{-2} Q_1(\vec{r}) = 0 \tag{6}$$

with its solution (for spherically symmetrical $Q_1(r)$ and long r)

$$Q_1(r) = \frac{A}{\xi^2 r} e^{-r/\xi},\tag{7}$$

where ξ is the long-range correlation distance.

If the correlation function of dielectric constant (permittivity) h(r) is taken as the order parameter, Equation 7 is similar to Equation 2.3 129. It reveals Landau's mean field theory with a gradient term equivalent to Ornstein-Zernike's approximation (section 2.3).

In turn, Debye's consideration of critical opalescence is equivalent to these approaches, since the method was the same in essence: to supplement the functional dependence of the thermodynamic potential with a gradient term, by density or by concentration for one-component liquids and solutions, respectively, i.e. by the order parameter Q.

Analysis of the most significantly varying parameter of the mean square value of the order parameter's fluctuations $(\overline{\Delta Q})_T^2$ in terms of Equation 1 has led Ginzburg (1960) to an applicability criterion of the mean field theory:

$$(\overline{\Delta Q})_T^2 \ll Q_0^2. \tag{8}$$

Estimations (Ginzburg, 1960; Strukov and Levanyuk, 1983) yield

$$\overline{(\Delta Q)_T^2} \sim \frac{k'T}{8\pi\delta} \sqrt{\frac{a}{\delta}}$$
⁽⁹⁾

and

$$Q_0^2 = \frac{a}{b} = \frac{\alpha(T_c - T)}{b},$$
(1.6-8)

whence

$$\frac{kT}{8\pi\delta}\sqrt{\frac{lpha(T_c-T)}{\delta}}\ll \frac{lpha(T_c-T)}{b},$$

and, with $T_c \approx T$ allowed for,

$$\varepsilon = \frac{T - T_c}{T_c} \gg \frac{k^2 T_c b^2}{64\pi^2 \alpha \delta^3} = \text{Gi},$$
(10)

where Gi is Ginzburg's dimensionless parameter.

With due account of the expression for a heat capacity jump at T_c (Equation 1.6-11)

$$\Delta c = \frac{\alpha^2}{b} T \approx \frac{\alpha^2}{b} T_c,\tag{11}$$

this parameter is expressed as

$$\operatorname{Gi} = \frac{k^2 \alpha^3 T_c^3}{64\pi^2 (\Delta c)^2 \delta^3} \tag{12}$$

as well. Besides, in the range $T > T_c$, $Q_0 = 0$ and the long-range correlation distance, according to Equation 5, is

$$\xi = \sqrt{\frac{\delta}{a}} = \sqrt{\frac{\delta}{\alpha(T - T_c)}},\tag{13}$$

i.e. the critical index in

$$\xi \sim |\varepsilon|^{-\nu} \tag{14}$$

is equal to 1/2, which also agrees with the value of ν in Ornstein-Zernike's approximation (Equation 2.3-146).

Away from T_c , where

$$\varepsilon = \frac{T - T_c}{T_c} \approx 1 \tag{15}$$

with $a = \alpha(T - T_c)$ (Equation 1.6-6) and Equation 13,

Gi =
$$\frac{k^2}{64\pi^2\xi^6(\Delta c)^2} \ll 1.$$
 (16)

Hence, **away** from the critical point (see Equation 15), the applicability range of Landau's approximation extends with increasing the long-range correlation distance. Increasing ξ away from T_c is equivalent to an admission of a longer range of particle interactions in the system, which is the premise of applicability of the mean field theories (see section 1.5).

Ginzburg's parameter is derived from the coefficients of the potential G, using the substance properties. Eg. corresponding estimations for superconductors give Gi ~ 10^{-14} (Ginzburg, 1960; Patashinski and Pokrovski, 1975), it means the inapplicability region of the mean field theory is not yet accessible experimentally, and the behaviour of superconductors and some ferroelectrics is well described by the mean field theory.

Eg. experiment discloses a simple jump of heat capacity at T_c .

To carry out similar analysis in d-dimension space, Equation 1 in the absence of the field should be written as

$$G = G_0 + \frac{1}{2} \int d^d r \left[aQ^2 + \frac{1}{2}bQ^4 + \delta \cdot (\nabla Q)^2 \right]$$
(17)

(Ma shang-keng, 1976). Then, for heat capacity,

$$c \sim \xi^{-d+2/\nu} \sim (T - T_c)^{-(2-\nu d)} \sim (T - T_c)^{-\alpha}$$
 (18)

and

$$\alpha = 2 - \nu d \tag{19}$$

(see Equation 1.5–10). $\nu = 1/2$, as before, and

$$c \sim (T - T_c)^{(d-4)/2}$$
 (20)

which means that heat capacity does not diverge when d > 4, i.e. the system obeys the regularities of the mean field theory. This conclusion also follows from Ginzburg's number

$$Gi = \left[\frac{k}{\pi (2\xi)^d \Delta c}\right]^{\frac{2}{4-d}}.$$
(21)

Kadanoff's transformation (Kadanoff, 1966; Kadanoff et al., 1967) has gained acceptance in the modern theories of critical phenomena.

The area of strong correlation among the structural elements (say, spins on a ferromagnet) is arbitrarily divided into blocks with a size $L \ll \xi$. In each block, the spins are added according to a certain rule (eg. in Figure 2.43a, each block of 9 spins in the initial lattice is replaced by one spin with its direction given by the sum of 9 spins).

Suppose there is a *d*-dimension spin lattice with constant *a* (White and Geballe, 1979). Write its Hamiltonian following the pattern of Equations 1.7-24,-25,-35:

$$\mathcal{H} = -\mathcal{J}\sum_{ij} s_i s_j - H \sum_i s_i.$$
⁽²²⁾

Divide the spin lattice into square blocks with side L (cf. Figure 2.43a). The total spin of the block I is

$$S_I' = \sum_{i \in I} s_i. \tag{23}$$

Further, the block spin S'_I needs scaling so that the new block "spin" could take only two values, ± 1 :

$$S_I' = ZS_I. \tag{24}$$

In the case of a complete spin correlation in a block

$$Z = L^d \tag{25}$$

(see Figure 2.43). As the spin block lattice is constructed like the initial one, its Hamiltonian has the same form as Equation 22:

$$\mathcal{H}_{L} = -\mathcal{J}_{L} \sum_{I,J} S_{I} S_{J} - H_{L} \sum_{I} S_{I}, \qquad (26)$$

where \mathcal{J}_L is a new coupling constant, $H_L = ZH$.

By virtue of the fact that the spin (Equation 22) and block (Equation 26) Hamiltonians are of the same type, the thermodynamic potential per spin will have the same functional form in both cases with conversion factor L^d :

$$g(\varepsilon_L, H_L) = L^d g(\varepsilon, H). \tag{27}$$



Figure 2.43. Kadanoff's transformation in a magnetic: a is the initial lattice and formation of blocks; b is replacement of the spin blocks by single spins using the rule of simple addition of spins; c is adjusting the scale of the spin block lattice (Wilson, 1979)

On the basis of the analogy between \mathcal{H} and \mathcal{H}_L , ε_L and ε are presumed to be proportional in the critical region ($\varepsilon \to 0$). Increasing the block size L is equivalent to effective moving away from the critical point, since the more extended correlation range ξ trans-

forms into a less extended one. So, one can expect ε_L to be a function of L, say, L^x , where x is a positive number. Hence, we get

$$\varepsilon_L = L^r \varepsilon. \tag{28}$$

In view of the partial correlation of the spins in a block, consider that

$$Z = L^y. (29)$$

Then Equation 27 rearranges to

$$g(L^{x}\varepsilon, L^{y}H) = L^{a}g(\varepsilon, H),$$
(30)

i.e. we have arrived at the condition of generalized uniformity of $g(\varepsilon, H)$, underlying the similarity hypothesis (see section 1.5).

Indeed, λ can be chosen as L^d , then $L = \lambda^{1/d}$, $\lambda^{x/d} = \lambda^{a_t}$, and $\lambda^{y/d} = \lambda^{a_H}$, i.e. $x/d = a_{\varepsilon}$, $y/d = a_H$ in accordance with the notation in Equation 1.5-8.

Differentiate Equation 30 with respect to H (cf. Equation 1.5-1):

$$L^{\mathbf{y}}M(L^{\mathbf{x}}\varepsilon, L^{\mathbf{y}}H) = L^{\mathbf{d}}M(\varepsilon, H).$$
(31)

As this relationship should not depend on the choice of scaling at $L \ll \xi$, assume

$$L = \left(-\frac{1}{\varepsilon}\right)^{1/x}.$$

Then, in the limit $H \rightarrow 0$, Equation 31 takes the form

$$\left(-\frac{1}{\varepsilon}\right)^{\frac{y-d}{x}} M(-1,0) = M(\varepsilon,0)$$

$$(-\varepsilon)^{(d-y)/x} M(-1,0) = M(\varepsilon,0),$$
(32)

when $\varepsilon \to -0$,

$$M(\varepsilon, 0) \sim (-\varepsilon)^{\beta}$$

and

$$\frac{d-y}{x} = \beta. \tag{33}$$

Other critical indices are defined through x and y in a similar way. Eg.

$$x = \frac{1}{\nu} = \frac{d}{2} - \alpha \tag{34}$$

and so on.

Thus, the existence of correlated areas of the structural elements with long extension ξ serves as a physical background of the similarity hypothesis, so blocks of the structural element of a length $L \ll \xi$ can be chosen.

The main properties of a system such as compressibility χ_{τ} and heat capacity c are related to the correlation length of the order parameter (eg. Equations 2.3-80...82,-150), which results in a relation among the critical indices to define the meaning of the similarity hypothesis.

Near the critical point, the system's properties are mainly influenced by the correlation range ξ , while the character of interaction between the structural elements plays no significant part. Therein lies the universality of the critical phenomena for different physical systems, the specific character of which is in the nature of interaction among the nearest structural elements.

The idea of universality goes back to the law of corresponding states, by which all liquids and gases have the same state equations accurate up to the renormalization of length and energy scales.

The universality principle has been further developed into a method of renormalization group (Wilson and Kogut, 1974; Wilson, 1979).

Suppose the initial system to comprise structural elements at the nodal points of a lattice with constant a. Admit that blocks of structural elements $L_1 = 2a$, $L_2 = 4a$ and so on, where $L_1 \ll \xi$, $L_2 \ll \xi$ can be considered as new effective structural elements.

The initial system is characterized by a Hamiltonian \mathcal{H}_0 with its interaction range $L_0 \approx a$, this range for \mathcal{H}_1 is of the order $L_1 \approx 2a$ of magnitude, $\mathcal{H}_2 \sim L_2 \approx 4a$, and so on. The effect of such a transformation (Figure 2.43) is in neglecting all the fluctuations in the arrangement of the structural elements, whose scale is less than the block size. This can be imagined as looking at the initial lattice through a non-focusing lens (Wilson, 1979), when small details are invisible, and big ones are fuzzy and vague.

The sequence \mathcal{H}_0 , \mathcal{H}_1 , \mathcal{H}_2 ...reflects subsequent roughening of the pattern. Every Hamiltonian has its own coupling constant \mathcal{J}_l . The success of those manipulations depends on the possibility to discover a certain regularity in the coupling constants, when every subsequent \mathcal{J}_l is deduced from the previous \mathcal{J}_{l-1} . Then, \mathcal{H}_1 is derived from the initial Hamiltonian \mathcal{H}_0 , \mathcal{H}_2 from \mathcal{H}_1 , eg. up to \mathcal{H}_n for which

$$2^n L_0 \sim \xi. \tag{35}$$

Hence, the technique of renormalization group reduces the problem of a huge number of degrees of freedom (in the initial Hamiltonian) to a problem of relatively small degrees of freedom, which is soluble by means of specific tools of statistical physics.

The chain of Hamiltonian transformations is represented as

The same operation of transformation τ is applied at different stages of iteration. It is to apply n times, so that $2^n L_0 \approx \xi$.

 τ should be such that the sequence of \mathcal{H}_l converges to a fixed point for which

$$\tau(\mathcal{H}^*) = \mathcal{H}^*. \tag{37}$$

There exist several transformations τ for any initial Hamiltonian \mathcal{H}_0 , which lead, generally speaking, to different fixed points \mathcal{H}_A^* , \mathcal{H}_B^* , or \mathcal{H}_C^* , each of them characterizing a certain type of cooperative interaction.

Universality, i.e. independence on the initial \mathcal{H}_0 , exists only for a given type of cooperative interaction.

When calculations by means of renormalization group method are made, the space dimensionality d and the order parameter dimensions (the number of components) n play an important role.

Eg. for a ferromagnet with n = 1, spins can be placed only along one direction. If they are on a film surface, d = 2; if in bulk material, d = 3. n = 2 in the so-called XY model of a ferromagnet. If the magnetic momentum vector can be oriented along any direction in space, then n = 3 (Heisenberg's model) (Table 2.5).

For a system with a scalar order parameter (density, concentration difference), n = 1.

A special universality class has been found by de Gennes for a random walk of connected structural elements over a 3D lattice (n = 0, d = 3). This class took on great significance for modelling of the macromolecular behaviour in solution (to be considered in detail in Chapters 4 and 5).

Calculations by renormalization group method have shown that different physical systems with the same d and n values have the same values of critical indices (see Table 2.5) and a common state equation in the scaling form (Stanley et al., 1980).

d and n in the equations of the renormalization group method take arbitrary continuous values though only natural d's and n's have physical meaning.

Figure 2.44 presents a line of common values of the critical indices β and γ on the plane *n* against *d*. Dashed is the area of constant values of these quantities, which agree with the values from the mean field approximation. Hence, in multidimensional space $d \ge 4$, the critical indices also take values characteristic of the mean field approximation, so $d^* = 4$ acquires the meaning of the critical dimension (see also Equations 20 and 21) (Riedel and Wegner, 1972b).

This is associated with an increase in the number of the nearest neighbours of a structural element with d, and the interaction sphere (i.e. the character of interaction) begins to respond to the mean field theory assumption of an extended range of structural element interactions to a greater degree.

Calculations by the renormalization group method in the tricritical point vicinity (Larkin and Khmel'nitski, 1969; Riedel and Wegner, 1972) have led to values of the tricritical indices, coinciding with those in the mean field approximation for 3D space $d^* = 3$.

2.6. Lagrangian formalism of the field theory

The recent, most significant achievements in studying the structure of polymer systems are based on applying the field theory formalism. This section contains the definitions and brief characterization of the main quantities and terms of the field theory in the Lagrangian form. Hereinafter, we follow Amit (1978).

In classical mechanics, a Lagrangian L is defined as the difference between the kinetic

Universality class		Theoretical model	Physical system	Order parameter
	n = 1	Ising's model on a	adsorption films	surface concentra-
		plane		tion
d = 2	n = 2	XY-model on a	4He films	superfluid phase
		plane		wavefunction am-
				plitude
	n = 3	Heisenberg's model		magnetization
		on a plane		
d > 2	$n = \infty$	"spherical" model	none	
	n = 0	random self-	polymer chain con-	monomeric unit
		avoiding walk	formation	density
		model		
[uniaxial ferromag-	magnetization
			net	
			liquid near its criti-	liquid-vapour den-
1			cal point	sity difference
d = 3	n = 1	Ising's model in 3D	liquid mixture near	component concen-
		space	its critical point	tration difference
((alloys near the-	component concen-
			ir order-disorder	tration difference
			transition	
		· · · · · · · · · · · · · · · · · · ·	stratified ferromag-	magnetization
	ļ		net	_
	n = 2	XY-model in 3D	4He near the super-	superfluid pha-
		space	fluid transition	se wavefunction
				amplitude
1	n = 3	Heiscnberg's model	isotropic ferromag-	magnetization
		in 3D space	net	
	n = -2		none	
$d \leq 4$	n = 32	quantum chromo-	quarks confined in	
-		dynamics	protons, neutrons,	
			etc.	

Table 2.5. Universality classes of some physical systems (Wilson, 1979)

and potential energies of a particle

$$L = T - V = \frac{m}{2} \left(\frac{dx}{dt}\right)^2 - V(x) = \frac{m}{2} (\dot{x})^2 - V(x), \tag{1}$$

m being the mass of the particle.

An **action** \mathcal{A} is defined by

$$\mathcal{A} = \int_{t_1}^{t_2} L(x, \dot{x}) \, dt. \tag{2}$$

The particle's motion from the point $x(t_1)$ to the point $x(t_2)$ may, in principle, occur along one of an infinite number of trajectories. In reality the particle moves along the tra-



Figure 2.44. Critical indices β and γ as parameters of plotting: the order parameter dimension nvs the space dimension d, calculated by the renormalization group technique (Wilson, 1979). Data of M.Fisher as cited by Wilson

jectory, which satisfies the **principle of the least action**, i.e. the true motion trajectory implies the minimum of \mathcal{A} (Goldstein, 1950; Ryder, 1985).

On transfer to a field, x should be replaced by the order parameter or just the field $\Phi(x)$.

Mass m preserves its meaning in the field theory, since a classical scalar field after its quantization is interpreted as a particle with mass m.

Thus, the action in d-dimensional space in the field theory is written as

$$\mathcal{A} = \int L \, dt = \int \mathcal{L} \, d^{d+1} x, \tag{3}$$

where $L = \int \mathcal{L}(\Phi, \nabla \Phi) d^d x$ is called a Lagrangian, and \mathcal{L} is a Lagrangian density.

All the most important properties of the field can be described if the Lagrangian density is approximated by a polynomial in $\Phi(x)$ of the most common type plus a gradient term $(\nabla \Phi)^2$ (cf. Equation 2.5-1).

If there is symmetry about a certain direction,

$$\Phi = -\Phi, \tag{4}$$

then the polynomial includes only its even powers:

$$\mathcal{L}[\Phi(x)] = A_0(\nabla\Phi)^2 + A_1\Phi^2(x) + A_2\Phi^4(x) + h\Phi(x),$$
(5)

where h is an external field, or a source.

The probability of existence of any field distribution is

$$W \{\Phi\} = \exp\left\{-\int dx \mathcal{L} \left[\Phi(x)\right]\right\}.$$
(6)

If the system has an *n*-component order parameter, then

$$\Phi = [\Phi_1(x), \dots, \Phi_n(x)].$$
⁽⁷⁾

In the case of

$$\Phi_i = -\Phi_i \tag{8}$$

being invariant, there is one quadratic invariant

$$\sum_{i=1}^{n} \Phi_i^2 = \vec{\Phi}^2 \tag{9}$$

and two quaternary ones

$$\left(\vec{\Phi}^2\right)^2$$
 and $\sum_{i=1}^n \Phi_i^4$, (10)

which leads to

$$\mathcal{L}\left[\vec{\Phi}(x)\right] = A_0(\nabla\vec{\Phi})^2 + A_1\vec{\Phi}^2(x) + A_2\left[\vec{\Phi}^2(x)\right]^2 + A_3\sum_i \Phi_i^4(x),\tag{11}$$

where

$$(\nabla \vec{\Phi})^2 = \sum_{i=1}^n (\nabla \Phi_i)^2.$$
(12)

The parameters A_0, A_1, \ldots , whose set specifics a certain vector \vec{A} , are arbitrary and play no significant role in the theory applications.

So, the distribution probability can be written as

$$W\left\{\vec{\Phi},\vec{A}\right\} = \exp\left\{-\int dx \mathcal{L}\left[\vec{\Phi},\vec{A}\right]\right\}.$$
(13)

The source, or external field, is included into the Lagrangian in the form

$$-\vec{h}(x)\vec{\Phi}(x) = -\sum_{i=1}^{n} h_i(x)\Phi_i(x).$$
(14)

If $W\left\{\vec{\Phi},\vec{h}\right\}$ defines the distribution probability in functional space, then the functional

$$Z\left\{\vec{h}\right\} = \int D\vec{\Phi} \cdot W\left\{\vec{\Phi}, \vec{h}\right\}$$
(15)

is the statistical integral, where

$$D\vec{\Phi} = \prod_{i=1}^{n} d\Phi_i.$$
⁽¹⁶⁾

The majority of systems have translational invariancy, and the Fourier transform

$$\Phi(x) = \frac{1}{\sqrt{V}} \sum \Phi_k \exp(-ikx)$$
⁽¹⁷⁾

is often justified, with an imposed restriction $|\vec{k}| \leq 1/a$, where a is a quantity commensurable with the cell linear sizes in Ising's lattice, V is the system volume.

If $\Phi(x)$ describes a real field then

$$\Phi_{\vec{k}} = \Phi^*_{-\vec{k}} \tag{18}$$

and

$$D\Phi = \prod d^2 \Phi_{\vec{k}} \quad \text{with} \quad \vec{k} > 0; \quad |\vec{k}| < a^{-1}.$$
(19)

With allowance for Equations 13 and 15, the mean value of any quantity is expressed by

$$X = \frac{\int D\vec{\Phi} \cdot X\left\{\vec{\Phi}, \vec{h}\right\} W\left\{\vec{\Phi}, \vec{h}\right\}}{Z\left\{\vec{h}\right\}}.$$
(20)

In particular, for the mean value of $\Phi_i(x)$,

$$\langle \Phi_i(x) \rangle = Z^{-1} \frac{\delta Z\left\{\vec{h}\right\}}{\delta h_i(x)},\tag{21}$$

and for the correlation function

$$G_{ij}^{(2)}(\vec{x} - \vec{y}) = \langle \Phi_i(\vec{x})\Phi_j(\vec{y}) \rangle = Z^{-1} \left. \frac{\delta^2 Z}{\delta h_i(\vec{x}) \,\delta h_j(\vec{y})} \right|_{\vec{h}=0}$$
(22)

or, in a more general case,

$$G_{i_1...i_n}^{(n)}(\vec{x}_1,...,\vec{x}_n) = Z^{-1} \left. \frac{\delta^n Z}{\delta h_{i_1}(\vec{x}_1) \cdots \delta h_{i_n}(\vec{x}_n)} \right|_{\vec{h}=0}$$
(23)

In view of Equation 23, the Taylor series expansion of $Z\{h\}$ can be represented as

$$\frac{Z\{h\}}{Z\{0\}} = 1 + \sum_{N=1}^{\infty} \frac{1}{N!} \sum_{i_1 \dots i_N} \int dx_1 \cdots dx_N h_{i_1}(x_1) \cdots h_{i_N}(x_N) G_{i_1 \dots i_N}^{(N)}(x_1, \dots, x_N).$$
(24)

The functions G are called **Green's functions**, and Z is a generating functional for these functions.

2.6.1. Free field

The magnet system on Ising's lattice (see section 1.7) is translated into the notation of the Lagrangian form of the field theory (Amit, 1978). As a result, an expression in the Fourier transform for the Lagrangian is obtained

$$\int dx \,\mathcal{L}_{0} = \frac{1}{2} \sum_{\vec{k}} (k^{2} + \mu^{2}) \Phi(\vec{k}) \Phi(-\vec{k}), \tag{25}$$

 \vec{k} being the wavenumber,

$$\mu^{2} = \frac{1}{\rho^{2}} \cdot \frac{T - T_{c}}{T_{c}},\tag{26}$$

where $\rho \approx a$ is the lattice constant.

So, the square of the "free mass" μ^2 is proportional to temperature in the field theory notation.

In the coordinate representation (cf. Equation 17), on replacing summation by integration, the Lagrangian takes the form

$$\int dx \,\mathcal{L}_0 = \frac{1}{2} \int dx \left[(\nabla \Phi)^2 + \mu^2 \Phi^2 \right]. \tag{27}$$

Thus, the Lagrangian with a quadratic polynomial term describes non-interacting (free) field that is marked by the subscript '0' at \mathcal{L} . Recall that this magnet model (see section 1.7) takes into account the interaction among the nearest spins only.

The correlation function (Green's function) in the k representation (momentum space) is defined as (see Equations 20, 13, and 25)

$$G_0(\vec{k}) = \left\langle \Phi(\vec{k})\Phi(-\vec{k}) \right\rangle_0 = \frac{\int D\Phi\Phi(\vec{k})\Phi(-\vec{k})\exp\left[-\sum_k \frac{1}{2}(k^2 + \mu^2)\Phi(\vec{k})\Phi(-\vec{k})\right]}{\int D\Phi\exp\left(-\int dx \,\mathcal{L}_0\right)}$$
(28)

and is the Fourier transform of the correlation function in the coordinate space

$$G_0(\vec{r}) = \langle \Phi(\vec{r}) \Phi(0) \rangle_0 = \frac{1}{V} \sum_{\vec{k}} \exp(-i\vec{k}\vec{r}) G_0(\vec{k}), \tag{29}$$

which passes into an integral in d-dimension space when $V \to \infty$:

$$G_0(\vec{r}) = \int \frac{dk}{(2\pi)^d} \exp(-i\vec{k}\vec{r}) G_0(\vec{k})$$
(30)

(the factor $(2\pi)^d$ is explained in Equation 79).

To get $G_0(\vec{k})$ through the generating functional (see Equation 23), to the free Lagrangian density \mathcal{L}_0 should be added an addend with the source

$$\sum_{\vec{k}} \Phi(\vec{k})h(-\vec{k}). \tag{31}$$

Then

$$G_0(\vec{k}) = \frac{1}{Z^0 \{h\}} \cdot \frac{\partial^2 Z^0 \{h\}}{\partial h(\vec{k}) \partial h(-\vec{k})} \bigg|_{h=0}$$
(32)

and

$$Z^{0} \{h\} = \int D\Phi \exp\left\{-\sum_{k} \left[\frac{1}{2}(k^{2} + \mu^{2})\Phi(\vec{k})\Phi(-\vec{k}) + \Phi(\vec{k})h(-\vec{k})\right]\right\},$$
(33)

which, after the replacement (shift) of the variable

$$\Phi(\vec{k}) \to \Phi(\vec{k}) - (k^2 + \mu^2)^{-1} h(\vec{k})$$
(34)

acquires the form

$$Z^{0} \{h\} = \left[\int D\Phi \exp\left\{ -\frac{1}{2} \sum_{k} \Phi(\vec{k}) (k^{2} + \mu^{2}) \Phi(-\vec{k}) \right\} \right]$$

$$\times \exp\left\{ \frac{1}{2} \sum_{k} h(\vec{k}) (k^{2} + \mu^{2})^{-1} h(-\vec{k}) \right\}.$$
(35)

To derive $G_0(k)$ according to Equation 32, this integral needs no calculation, since it will be cancelled with the same integral in Equation 32's denominator.

Hence, Equation 32 gives

$$G_0(\vec{k}) = (k^2 + \mu^2)^{-1}.$$
(36)

The correlation function in Equation 1.7-33 can be written as

$$g(r_i - r_j) = \langle (\sigma_i - \langle \sigma_i \rangle) (\sigma_j - \langle \sigma_j \rangle) \rangle = G_{ij}^{(2)}(r_i - r_j)$$
(37)

and, in view of Equations 1.7-34 and 29, the susceptibility is expressed through Green's function

$$\chi = G_0(k=0), \tag{38}$$

and, in view of Equation 36,

$$\chi = \mu^{-2},\tag{39}$$

i.e. Green's function $G_0(k=0)$ diverges at $\mu \to 0$ with $\gamma = 1$ (see Equation 26). If the correlation length ξ is defined as

$$\xi^{2} = \frac{\int r^{2} G(r) \, dr}{\int G(r) \, dr} \tag{40}$$

(cf. Equation 2.3-141), then it is expressed through G(k):

$$\xi^{2} = - \left. \frac{\frac{\partial^{2}}{\partial k^{2}} G(k)}{G(k)} \right|_{k=0}$$
(41)

(to verify this, substitute $G(k) = \int G(r) \exp(ikr) dr$ into Equation 41). On substituting Equation 36 into Equation 41, we get $\xi^2 = 2\mu^{-2}$ and $\nu = 1/2$.

In the case of a free field, the Lagrangian (Equation 27) is a quadratic function of $\Phi(\vec{x})$, and the probability distribution for the field Φ (Equation 6) is Gaussian; all the fields $\Phi_{\vec{k}}$ are statistically independent (Patashinski and Pokrovski, 1975).

It follows that if $\vec{k} + \vec{k'} \neq 0$, then **correlators** of the type $\langle \Phi_{\vec{k}} \Phi_{\vec{k'}} \rangle$ are decomposed into a product of the means $\langle \Phi_{\vec{k}} \rangle = 0$, so $\langle \Phi_{\vec{k}} \Phi_{\vec{k'}} \rangle = 0$. Hence,

$$G_0(\vec{k}) = \left\langle \Phi_{\vec{k}} \Phi_{\vec{k}'} \right\rangle = \frac{\delta_{\vec{k}, -\vec{k}'}}{k^2 + \mu^2},\tag{42}$$

where Kronecker's symbol

$$\delta_{\vec{k},-\vec{k}'} = \begin{cases} 1 & \text{at } \vec{k} = \vec{k}', \\ 0 & \text{at } \vec{k} \neq \vec{k}' \end{cases}$$
(43)

Due to the statistical independence of the fields $\Phi_{\vec{k}}$, the correlator

$$G_{\vec{k}_1,\vec{k}_2,\dots,\vec{k}_n}^{(n)} = \left\langle \Phi_{\vec{k}_1} \Phi_{\vec{k}_2} \dots \Phi_{\vec{k}_n} \right\rangle \tag{44}$$

is decomposed into a product of means for different independent values of \vec{k} . That is why $G_{\vec{k}_1,\vec{k}_2,\ldots,\vec{k}_n}^{(n)} = 0$ if even one value \vec{k}_i $(i = 1, 2, \ldots, n)$ lacks the pair value $\vec{k}_{i'}$ so that $\vec{k}_i + \vec{k}_{i'} = 0$.

In particular, it is always the case for odd values n = 2m + 1.

In view of this property, the *n*-order correlator (Equation 44) is equal to the sum of terms, each of which represents a result of different pair combinations. This is the meaning of Wick's theorem for \vec{k} space. If the fields to be grouped are denoted by a connecting line, then, for example,

$$\left\langle \Phi_{\vec{k}_1} \Phi_{\vec{k}_2} \Phi_{\vec{k}_3} \Phi_{\vec{k}_4} \right\rangle = \overbrace{\Phi_{\vec{k}_1} \Phi_{\vec{k}_2}}^{\text{comp}} \overbrace{\Phi_{\vec{k}_3} \Phi_{\vec{k}_4}}^{\text{comp}} + \overbrace{\Phi_{\vec{k}_1} \Phi_{\vec{k}_2} \Phi_{\vec{k}_3}}^{\text{comp}} \Phi_{\vec{k}_4}^{\text{comp}} \right\rangle$$
(45)

$$\widetilde{\Phi_{\vec{k}_1} \Phi_{\vec{k}_2} \Phi_{\vec{k}_3}} \Phi_{\vec{k}_4} = \delta_{\vec{k}_1, -\vec{k}_2} \delta_{\vec{k}_3, -\vec{k}_4} \left\langle |\Phi_{\vec{k}_1}|^2 \right\rangle \left\langle |\Phi_{\vec{k}_3}|^2 \right\rangle + \cdots$$

Wick's theorem also holds for coordinate space and a 2m-point correlator

$$G^{(2m)}(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_{2m}) = \sum_{\vec{k}_1, \vec{k}_2 \dots \vec{k}_{2m}} \exp\left[i(\vec{k}_1 \vec{x}_1 + \vec{k}_2 \vec{x}_2 + \dots + \vec{k}_{2m} \vec{x}_{2m})\right]$$
(46)

$$\times \left\langle \Phi_{\vec{k}_1} \Phi_{\vec{k}_2} \cdots \Phi_{\vec{k}_{2m}} \right\rangle$$

is the sum of the products of pairs of all the possible means. Eg.

$$G^{(4)}(\vec{x}_{1}, \vec{x}_{2}, \vec{x}_{3}, \vec{x}_{4}) = \langle \Phi(\vec{x}_{1}) \Phi(\vec{x}_{2}) \Phi(\vec{x}_{3}) \Phi(\vec{x}_{4}) \rangle = \langle \Phi(\vec{x}_{1}) \Phi(\vec{x}_{2}) \rangle \langle \Phi(\vec{x}_{3}) \Phi(\vec{x}_{4}) \rangle$$

$$+ \langle \Phi(\vec{x}_{1}) \Phi(\vec{x}_{4}) \rangle \langle \Phi(\vec{x}_{2}) \Phi(\vec{x}_{3}) \rangle + \langle \Phi(\vec{x}_{1}) \Phi(\vec{x}_{3}) \rangle \langle \Phi(\vec{x}_{2}) \Phi(\vec{x}_{4}) \rangle$$

$$= G(\vec{x}_{1} - \vec{x}_{2}) G(\vec{x}_{3} - \vec{x}_{4}) + G(\vec{x}_{1} - \vec{x}_{4}) G(\vec{x}_{2} - \vec{x}_{3}) + G(\vec{x}_{1} - \vec{x}_{3}) G(\vec{x}_{2} - \vec{x}_{4}).$$
(47)

The number of different pairs of groups depends, of course, on the symmetry character of the system's structural elements.

The correlator $G(\vec{x} - \vec{x}')$ tends to infinity at $\vec{x} \to \vec{x}'$ (see Equation 30). Hence, the 2*m*-point correlators $G^{(2m)}(x_1, x_2, \ldots, x_{2m})$ also tend to infinity when several points merge into one (Patashinski and Pokrovski, 1979).

2.6.2. Interacting fields

The terms of the polynomial, approximating the Lagrangian density above the second order \mathcal{L}_{int} , describe the behaviour of the interacting fields

$$\mathcal{L} = \mathcal{L}_0 + \mathcal{L}_{int}. \tag{48}$$

For such fields with source \mathcal{J} , the statistical integral has the following general form (Popov, 1976; Amit, 1978; Ryder, 1985)

$$Z\{J\} = \frac{\exp\left\{-\int dx \,\mathcal{L}_{int}\left(\frac{\delta}{\delta J(x)}\right)\right\} Z_0\{J\}}{\mathcal{N}},\tag{49}$$

where

$$Z_0 \{J\} = \exp\left\{\frac{1}{2}\int dx \, dy \, J(x)G_0(x-y)J(y)\right\},$$

$$\mathcal{N} = \exp\left\{-\int dx \,\mathcal{L}_{int}\left(rac{\delta}{\delta J}
ight)
ight\} \exp\left\{rac{1}{2}\int dx \,dy \,J(x)G_0(x-y)J(y)
ight\}\Big|_{J=0}$$

As the argument of \mathcal{L}_{int} , the operator $(\delta/\delta J)$ stands instead of the field Φ . The normalization factor \mathcal{N} is defined by

$$Z\{J=0\} = 1. (50)$$

Green's functions are defined at different points of the field (\mathcal{N}) using the number of fields $J(x_i)$ as functional derivatives Z with respect to J:

$$G^{(N)}(x_1, x_2, \dots, x_N) = \left. \frac{\delta^N Z\left\{J\right\}}{\delta J(x_1) \cdots \delta J(x_N)} \right|_{J=0},\tag{51}$$

where the generating functional $Z\{J\}$ has the structure of Equation 49.

Green's functions are of great importance in field theory: through them are expressed many experimentally measured quantities, therefore in what follows their properties will be considered in detail.

To take an example, discuss the derivation of Green's function of the Φ^4 theory. The Lagrangian of the interaction has the form

$$\mathcal{L}_{int} = \frac{\lambda}{4!} \Phi^4, \tag{52}$$

where λ is an interaction parameter.

The generating functional $Z\{J\}$ is considered only as an expansion in terms of λ , i.e. as a series of perturbation theory:

$$Z\left\{J\right\} = \mathcal{N}^{-1} \sum_{0}^{\infty} \frac{1}{n!} \left(-\frac{\lambda}{4!}\right)^n \int dx_1 \cdots dx_n \left[\frac{\delta}{\delta J(x_1)}\right]^4 \left[\frac{\delta}{\delta J(x_2)}\right]^4 \cdots \left[\frac{\delta}{\delta J(x_n)}\right]^4 Z_0\left\{J\right\}. (53)$$

In the zeroth order of λ^0 , the generating functional for free field $Z_0\{J\}$ is obtained. In the first order of λ , we have for the nominator of $Z\{J\}$

$$\left[1-\frac{\lambda}{4!}\int\left(\frac{\delta}{\delta J(x')}\right)^4 dx' + O(\lambda^2)\right]\exp\left[\frac{1}{2}\int J(x)G_0(x-y)J(y)\,dx\,dy\right]$$

and

$$\begin{split} \frac{\delta}{\delta J(x')} \exp\left[\frac{1}{2} \int J(x)G_0(x-y)J(y) \, dx \, dy\right] \\ &= \int G_0(x'-x)J(x) \, dx \cdot \exp\left[\frac{1}{2} \int J(x)G_0(x-y)J(y) \, dx \, dy\right]; \\ \left[\frac{\delta}{\delta J(x')}\right]^2 &= \left\{G_0(0) + \left[G_0(x'-x)J(x) \, dx\right]^2\right\} \exp\left[\frac{1}{2} \int J(x)G_0(x-y)J(y) \, dx \, dy\right]; \\ \left[\frac{\delta}{\delta J(x')}\right]^3 &= \left\{3G_0 \int G_0(x'-x)J(x) \, dx \right. \\ &+ \left[\int G_0(x'-x)J(x) \, dx\right]^3\right\} \exp\left[\frac{1}{2} \int J(x)G_0(x-y)J(y) \, dx, dy\right]; \\ \left[\frac{\delta}{\delta J(x')}\right]^4 &= \left\{3\left[G_0(0)\right]^2 + 6G_0(0) \left[\int G_0(x'-x)J(x) \, dx\right]^2\right\} \end{split}$$

$$+\left[\int G_0(x'-x)J(x)\,dx\right]^4\bigg\}\exp\left[\frac{1}{2}\int J(x)G_0(x-y)J(y)\,dx\,dy\right].$$

This expression is worthwhile representing as Feynman's diagram. The external coordinates and every interaction are marked by points on graphs. A line between the points x and y is the symbol of the function $G_0(x-y)$. So, the function $G_0(0)$ is represented by a closed circle. The last derivative can be written in terms of Feynman's diagram as

$$\left\{3\bigotimes_{x'}+6\bigotimes_{x'}+\underset{x'}{\hookrightarrow}\right\}\exp\left[\frac{1}{2}\int J(x)G_0(x-y)J(y)\,dx\,dy\right].$$

The form of the third diagram is determined by the factor Φ^4 in \mathcal{L}_{int} . The factors 3, 6, and 1 follow from the symmetry character of the system. The first term is obtained as a result of connecting two line pairs of the third term in all the possible ways (namely, three). The second term is obtained by connecting any two lines of the third term, there are six such ways. These numerical factors are called **symmetry factors**. The first term with two closed loops is referred to as a **vacuum graph** since it has no external lines. The term with one closed loop has two external lines (two factors J), while the last one has four such lines (four factors J).

Thus, the generating functional (Equation 53) in this approximation is written as

$$Z\{J\} = \frac{\left[1 - \frac{\lambda}{4!}\int (-3\bigcirc +6\bigcirc +\infty) \, dx'\right] \exp\left[\frac{1}{2}\int J(x_1)G_0(x_1 - x_2)J(x_2) \, dx_1 \, dx_2\right]}{1 - \frac{\lambda}{4!}\int (-3\bigcirc) \, dx'}$$

As the denominator is defined at J = 0, there are no J-containing terms whose graphs have twigs.

On dividing the nominator by the denominator, we get

$$\mathcal{Z}\left\{J\right\} = \left[1 - \frac{\lambda}{4!} \int (6 \underline{O} + \infty) \, dx'\right] \exp\left[\frac{1}{2} \int J(x_1) G_0(x_1 - x_2) J(x_2) \, dx_1 \, dx_2\right].$$
(53a)

It is an important circumstance that the expression of $Z\{J\}$ lacks the vacuum diagram. This is the case in all orders of perturbation theory, which is a common property of all normalized generating functionals.

1. Now derive the two-point Green function in the Φ^4 theory (Amit, 1978; Ryder, 1985).

According to Equation 51,

$$G^{(2)}(x_1, x_2) = \left. \frac{\delta^2 Z\left\{J\right\}}{\delta J(x_1) \,\delta J(x_2)} \right|_{J=0}.$$
(51a)

Equation 53a shows that the contribution of the functional's first term to Green's function is equal to $G_0(x_1 - x_2)$, which corresponds to a free propagator in field theory. The four-twig term comprises four factors J and, hence, does not contribute to the two-point function defined by two derivatives with respect to J. After differentiation, factors with J remain, which are cancelled on substitution of J = 0. The term with a loop and two twigs is equal to

$$\frac{\lambda}{4}G_0(0)\int dx_1\,dx_2\,dx'\,G_0(x'-x_1)J(x_1)G_0(x'-x_2)J(x_2)\exp\left(\frac{1}{2}\int JG_0J\right)$$

and double differentiation yields

$$\frac{\delta}{\delta J(x_1)}(\cdots) = -\frac{\lambda}{4}G_0(0)2\int dx_2 \, dx' \, G_0(x'-x_1)G_0(x'-x_2)J(x_2)\exp\left(\frac{1}{2}\int JG_0J\right);$$

$$\frac{\delta}{\delta J(x_2)}\frac{\delta}{\delta J(x_1)}(\cdots) = -\frac{\lambda}{2}G_0(0)\int dx' \, G_0(x'-x_1)G_0(x'-x_2)\exp\left(\frac{1}{2}\int JG_0J\right).$$

Hence, Green's two-point function in the first approximation by λ is

$$G^{(2)}(x_1,x_2) = G_0(x_1-x_2) - \frac{\lambda}{2}G_0(0)\int dx' G_0(x'-x_1)G_0(x'-x_2) + O(\lambda^2).$$

In field theory, this function describes the rise of a particle at a certain point x_1 in space at an instant of time τ_1 , its motion to a point x_2 , and disappearance at this point at an instant τ_2 .

It is reasonable to derive Green's function by means of the diagrammatic technique in terms of Wick's theorem.

Applying Equation 51 in view of the specific character of the generating functional expression reduces to the calculation of several derivatives of the Gaussian form. It is clear that a derivative of the characteristic exponent eliminates the term with J. Hence, if a term is not equal to zero on substitution of J = 0, the next derivative must cancel this multiplier. Therefore, if the free part of the generating functional $Z_0 \{J\}$ is treated by a number of differentiations with further J = 0 to be substituted, then the derivative-containing terms must be paired, and what is more, in all the possible ways. For every pair, the factor $G_0(x - y)$ must appear, where x and y are the coordinates of the fields J in the pair.

The result of this procedure with an odd number of derivatives of Z_0 at J = 0 will be equal to zero. This is a manifestation (and the proof) of Wick's theorem.

For Green's two-point function in the zeroth order of λ , we have

$$G_0^{(2)}(x_1, x_2) = \frac{\delta}{\delta J(x_1)} \cdot \frac{\delta}{\delta J(x_2)} \int dx' \exp\left\{\frac{1}{2} dx \, dy \, J(x) G_0(x-y) J(y)\right\} \Big|_{J=0} = G_0(x-y),$$

and, in view of Equations 30 and 41,

$$G_0(x_1 - x_2) = \int \frac{dp}{(2\pi)^d} \cdot \frac{\exp[ip(x_1 - x_2)]}{p^2 + \mu^2}.$$
(54)

In this order $\mathcal{N} = 1$.

In the first order

$$G_{1}^{(2)} = -\frac{\lambda}{4!} \frac{\delta}{\delta J(x_{1})} \frac{\delta}{\delta J(x_{2})} \int dx' \left[\frac{\delta}{\delta J(x')} \right]^{4} \exp\left\{ \frac{1}{2} \int dx \, dy \, J(x) G_{0}(x-y) J(y) \right\} \bigg|_{J=0} (55)$$

+ $\mathcal{N}_{1} G_{0}(x_{1}-x_{2}),$

where \mathcal{N}_1 is the first-order term of the normalization factor.

According to Wick's theorem, the six derivatives in the right-hand side of Equation 55 must be paired. This can be done in the following way:

a) $J(x_1)$ is paired with $J(x_2)$, and the four J's in the interaction are paired among themselves;

b) $J(x_1)$ and $J(x_2)$ are paired with J's in the interaction.

The version a has three combinations to group for J with the result

$$-\frac{\lambda}{8}G_0(x_1-x_2)\int dx' G_0(x'-x')G_0(x'-x').$$
(56)

The version b includes 12 combinations: $J(x_1)$ and $J(x_2)$ with four fields J of the interaction. So, this point gives the contribution

$$-\frac{\lambda}{2}\int dx' G_0(x_1-x')G_0(x'-x_2)G_0(x'-x').$$
(57)

Equation 56 is of the same form as the second term in Equation 55, namely, $G_0(x_1-x_2)$ is multiplied by an expression independent on x_1 and x_2 . These two terms cancel in accordance with the theorem on the vacuum parts.

In diagram form, Equations 56 and 57 are depicted by the graphs a and b in Figure 2.45.



Figure 2.45. First-order graphs of $G_1^{(2)}$ [Figures 2.45-2.61 are reprinted from: D.J.Amit Field Theory, the Renormalization Group, and Critical Phenomena. Copyright © 1984 by World Scientific Publishing Co Pte Ltd]

An algebraic expression not depending on the external coordinates corresponds to the vacuum graph. All the graphs corresponding to the terms in N, have this structure.

The graphs (Figure 2.45) enable one to reconstruct the algebraic expressions, using the following rules.

1) Every non-external point is given a factor $\left(-\frac{\lambda}{4!}\right)$.

2) Every line between x and y has its own $G_0(x-y)$.

This expression can be integrated with respect to all the non-external coordinates. The result must be multiplied by two factors: the first one originates from the factorial 1/n! in Equation 53, the second one reflects the internal symmetry of the structure and is represented by the number of ways of pairing of the same type as in the given graph. In the case considered, these factors are equal to 3 (the graph *a*) and 12 (the graph *b*).

In the second order, Green's functions have the form

$$G_{2}^{(2)} = \frac{1}{2!} \left(-\frac{\lambda}{4!} \right)^{2} \int dx_{1}' \, dx_{2}' \, \frac{\delta}{\delta J(x_{1})} \cdot \frac{\delta}{\delta J(x_{2})} \left[\frac{\delta}{\delta J(x_{1}')} \right]^{4} \left[\frac{\delta}{\delta J(x_{2}')} \right]^{4}$$
(58)

$$\times \exp \left\{ \frac{1}{2} \int dx \, dy \, J(x) G_{0}(x-y) J(y) \right\} \Big|_{J=0} + \mathcal{N}_{1} G_{1}^{(2)} + \mathcal{N}_{2} G_{0}^{(2)}.$$

Pairing is carried out by three categories:

1) x_1 and x_2 are paired;

2) x_1 and x_2 are paired with either x'_1 or x'_2 ;

3) x_1 is paired with x'_1 and x_2 is with x'_2 (or vice versa), x'_1 is with x'_2 .

The first category comprises three expressions (Figure 2.46).



Figure 2.46. Second-order graphs of $G_2^{(2)}$, which cancel with $N_2 G_0^{(2)}$

(a)
$$\frac{1}{2!}9\left(\frac{\lambda}{4!}\right)^2 G_0(x_1-x_2) \int dx_1' G_0^2(x_1'-x_1') \int dx_2' G_0^2(x_2'-x_2'),$$
 (59)

(b)
$$\frac{1}{2!}72\left(\frac{\lambda}{4!}\right)^2 G_0(x_1-x_2)\int dx_1'\,dx_2'\,G_0(x_1'-x_1')G_0^2(x_1'-x_2')G_0(x_2'-x_2'),$$
 (60)

(c)
$$\frac{1}{2!} 24 \left(\frac{\lambda}{4!}\right)^2 G_0(x_1 - x_2) \int dx_1' \, dx_2' \, G_0^4(x_1' - x_2').$$
 (61)

All of these involve vacuum terms, and finally cancel out.

There is one expression in the second category

$$\frac{1}{2!}36 \times 2\left(\frac{\lambda}{4!}\right)^2 \int dx_1' G_0(x_1 - x_1') G_0(x_1' - x_1') G_0(x_1' - x_2) \int dx_2' G_0^2(x_2' - x_2'), \quad (62)$$

which is represented by a graph in Figure 2.47

$$\bigcirc$$
 1 $1'$ 2 \bigcirc $2'$

Figure 2.47. Second-order graphs of $G_2^{(2)}$, which cancel out with $N_1 G_1^{(2)}$

It also contains a vacuum graph, and therefore cancels out. All the expressions of the third category remain (Figure 2.48).

(a)
$$\frac{1}{2!} 144 \times 2\left(\frac{\lambda}{4!}\right)^2 \int dx_1' \, dx_2' \, G_0(x_1 - x_1') G_0(x_1' - x_2) G_0^2(x_1' - x_2') G_0(x_2' - x_2'), (63)$$

(b)
$$\frac{1}{2!}96 \times 2\left(\frac{\lambda}{4!}\right)^2 \int dx_1' \, dx_2' \, G_0(x_1 - x_1') G_0^3(x_1' - x_2') G_0(x_2' - x_2),$$
 (64)



Figure 2.48. Second-order graphs of $G_2^{(2)}$ without the vacuum component

(c)
$$\frac{1}{2!} 144 \times 2\left(\frac{\lambda}{4!}\right)^2 \int dx_1' \, dx_2' \, G_0(x_1 - x_1') G_0(x_1' - x_1') G_0(x_1' - x_2') G_0(x_2' - x_2') (65)$$
$$\times G_0(x_2' - x_2).$$

Factor 2 is introduced into Equations 62-65, which accounts for the permutations of the interaction points.

It should be noted that the remaining expressions correspond to connected graphs involving one element, or graphs plotted with one pencil motion. With respect to algebraic expressions this means that all the coordinates are connected by integration.

2. Consider the graphs appearing in Green's four-point function of the Φ^4 theory. In the zeroth order,

$$G_{0}^{(4)}(x_{1}, x_{2}, x_{3}, x_{4}) = \frac{\delta}{\delta J(x_{1})} \cdots \frac{\delta}{\delta J(x_{4})} \exp\left\{\frac{1}{2}\int dx \, dy \, J(x)G_{0}(x - y)J(y)\right\}\Big|_{J=0} (66)$$

$$= G_{0}(x_{1} - x_{2})G_{0}(x_{3} - x_{4}) + G_{0}(x_{1} - x_{3})G_{0}(x_{2} - x_{4}) + G_{0}(x_{1} - x_{4})G_{0}(x_{2} - x_{3}).$$

$$1 - \frac{2}{3} - \frac{3}{4} \cdot 2 - \frac{3}{4} \cdot 2 - \frac{3}{4} \cdot 2 - \frac{3}{3} \cdot$$

-4²

3

Figure 2.49. Zeroth order of $G_0^{(4)}$

3

Figure 2.49 shows that all the graphs are not connected in this case, and do not contain vacuum terms.

In the first order, there are three possible expressions with a changed notation $x_i \rightarrow i$ (Figure 2.50).



Figure 2.50. First-order graphs of $G_1^{(4)}$
(a)
$$-\left(\frac{\lambda}{4!}\right) 24 \int G_0(1-1')G_0(2-1')G_0(3-1')G_0(4-1')d1',$$
 (67)

(b)
$$-\left(\frac{\lambda}{4!}\right) \left[12 \int G_0(1-1')G_0(1'-1')G_0(1'-2) d1'\right] G_3(3-4) + 5 \text{ permutations}, (6)$$

(c)
$$-\left(\frac{\lambda}{4!}\right) 3\left[\int d1' G_0^2(1'-1')\right] G_0(1-2)G_0(3-4) + 2 \text{ permutations.}$$
(69)

The graphs in Figure 2.50abc are connected, disconnected, and disconnected with a vacuum term (which cancels out upon normalization), respectively.

Now we are able to formulate the general rules of graph building in the scalar field theory for the interacting Lagrangian of the general form

$$\mathcal{L}_{int} = \sum_{r} \frac{\lambda_r}{r!} \Phi^r.$$
(70)

All the possible graphs in the series expansion of Green's functions $G^{(N)}(x_1, x_2, \ldots, x_N)$ are built as follows.

Rule 1. A graph must comprise N external points $1, \ldots, N$ and n_r interaction vertices of type r, where r is the power at Φ^r (Equation 70), n is the expansion degree of Green's function. Every interaction vertex is a point with its coordinate from which r lines originate. All these lines must be connected either with each other or with the external points. To eliminate vacuum terms, every interaction line is necessarily connected with an external point either immediately or indirectly.



Figure 2.51. An example of building the graph $G_2^{(6)}$ in the Φ^4 , Φ^3 theory (Amit, 1978)

Figure 2.51 (left) shows the constituents for building the graph $G_2^{(6)}$ in the Φ^4 , Φ^3 theory.

To calculate the numerical value of the perturbation series term corresponding to a given graph, rule 2 should be applied.

Rule 2. Every internal point of type r corresponds to the factor $(-\lambda_r/r!)$. To every line corresponds G_0 (the end-to-end coordinate difference). The factor $1/n_r!$ (where n_r is the number of r-type points) and a symmetry factor to show the number of ways to connect

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the lines according to Rule 1 for building a graph of the same topological structure should be provided. Integration must be carried out over all the internal coordinates.

These rules are rigorously proved in the special literature.

Let us adduce two examples (Amit, 1978).



Figure 2.52. Constituents and graph $G_3^{(3)}$ in the Φ^3 theory (Amit, 1978)

1. Figure 2.52 shows the graph $G_3^{(3)}$ in the Φ^3 theory, to which corresponds the expression

$$-\left(\frac{\lambda_3}{3!}\right)^3 \int G_0(1-1')G_0(2-2')G_0(3-3')G_0(1'-2')G_0(2'-3')G_0(3'-1')\,d1'\,d2'\,d3'(71)$$

$$\times \frac{1}{3!} \times \text{symmetry factor.}$$

Calculate the symmetry factor. There are 3 vertices and 3 external points (see the left side of Figure 2.52). The first external point can be connected to the vertices in 9 ways. To preserve the same graph topology, the second external point can be connected to the other vertices in 6 ways and, finally, the third one in 3 ways.

A situation shown in Figure 2.52 has appeared. The vertex connected to point 1 can be connected with one of the two lines to the remaining vertices 2 and 3. The other line 1 must be connected to one of the two lines of the remaining vertex. Therefore, the symmetry factor is $9 \times 6 \times 3 \times 2 \times 2 \times 2 = (3!)^4$, and the final numerical factor in Equation 71 is equal to 1.

2. Discuss the graph $G^{(2)}$ in the Φ^4 , Φ^3 theory shown in Figure 2.53.

To this graph corresponds the equation

$$\left(-\frac{\lambda_3}{3!}\right)^2 \left(-\frac{\lambda_4}{4!}\right) \int G_0(1-1')G_0(2-2')G_0(1'-3')G_0(1'-2')G_0^2(2'-3')\,d1'\,d2'\,d3'(72)$$

 $\times \frac{1}{2!\,1!} \times \text{symmetry factor.}$

There are 6×4 versions of connection of the external points. After realization of one of them (see Figure 2.53b), one of the three remaining lines 2' can be connected to one of the two remaining ones 1'. One of the three lines 3' is connected to 1'. At last, the two



Figure 2.53. Graph $G^{(2)}$ in the Φ^4 , Φ^3 theory (c); a are its constituents, b are its constituents after connecting the external points (Amit, 1978)

remaining lines 2' and 3' can be combined in two ways. Hence, the symmetry factor is $6 \times 4 \times 3 \times 2 \times 3 \times 2 = (3!)^2 (4!)$ and the numerical factor in Equation 72 is equal to 1/2.

Indeed, the factor 1/r! in Equation 70 is chosen so that if the graph has no symmetry allowing line exchange in the graph representation, then the numerical factor is equal to 1. The loop between 2' and 3' provides with the symmetry which leads to the factor 1/2.

As the Lagrangian is translation inversion, the key expressions of the theory are simplified as a result of the Fourier transformation. The translation invariance of Green's function is confirmed by the dependence of $G^{(N)}$ on (N-1) coordinate differences only, not on all the N coordinates. This can be verified by a simple checking.

For a scalar field with a source $J(\vec{x})$, the generating functional of the free field in the k-representation (in momentum space) has the form (cf. Equation 33)

$$Z^{0}\{J\} = \int D\Phi \exp\left\{-\sum_{k} \left[\frac{1}{2}\Phi(k)(k^{2}+\mu^{2})\Phi(-k) - J(k)\Phi(-k)\right]\right\},$$
(73)

where

$$\Phi(\vec{x}) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} \exp(-i\vec{k}\vec{x})\Phi(\vec{k})$$
(74)

and

$$J(\vec{x}) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} \exp(-i\vec{k}\vec{x}) J(\vec{k}).$$
(75)

Just in the same way, any term of the Lagrangian can be expressed via $\Phi(\vec{k})$. For the polynomial form of the Lagrangian

$$\mathcal{L}_r = \int \Phi^r(x) \, dx. \tag{76}$$

Substitute Equation 74 into Equation 76:

$$\mathcal{L}_{r} \left\{ \Phi \right\} = V^{-r/2} \sum_{\vec{k}_{1}...\vec{k}_{r}} \Phi(\vec{k}_{1}) \cdots \Phi(\vec{k}_{r}) \int dx \exp\left(-i\sum_{i} \vec{k}_{i}\right) \vec{x}$$

$$= V^{-r/2+1} \delta^{K} \left(\sum_{i} \vec{k}_{i}\right) \sum_{\vec{k}_{1}...\vec{k}_{r}} \Phi(\vec{k}_{1}) \cdots \Phi(\vec{k}_{r}),$$

$$(77)$$

where Kronecker's function

$$\int \exp(-ikx) \, dx = V \delta^K(\vec{k}) \tag{78}$$

is used for a finite volume V and discrete values of \vec{k}_i .

If $V \to \infty$, then k becomes a continuous quantity and

$$V\delta^{K}(\vec{k}) \Rightarrow (2\pi)^{d}\delta(\vec{k}) \tag{79}$$

with Dirac's δ function. It follows form its Fourier transform

$$\delta(\vec{k}) = \frac{1}{(2\pi)^d} \int e^{-ikx} d^d x \tag{80}$$

that Equation 79 holds at both k = 0 and $k \neq 0$. In this limit $\sum_{\vec{k}} f(\vec{k}) \rightarrow V/(2\pi)^d \int d\vec{k} f(\vec{k})$ and the interaction Lagrangian takes the form (see Equation 70)

$$\int \mathcal{L}_{int}(\Phi) \, dx = \sum_{r} \frac{\lambda_r}{r!} V^{-r/2+1} \sum_{\vec{k}_1 \dots \vec{k}_r} \Phi(\vec{k}_1) \cdots \Phi(\vec{k}_r) \delta\left(\sum_{i=1}^r \vec{k}_i\right). \tag{81}$$

By its structure, Equation 81 corresponds to a field with many components \vec{k}_i and the coefficient tensor

$$\mathcal{F}(\vec{k}_1,\ldots,\vec{k}_r) = V^{-r/2+1}\delta\left(\sum_{i=1}^r \vec{k}_i\right).$$
(82)

Green's function is written as in Equation 74:

$$G^{(N)}(x_1, x_2, \dots, x_N) = V^{-N/2} \sum_{\vec{k}_1 \dots \vec{k}_N} \exp\left[-i(k_1 x_1 + \dots + k_N x_N)\right] G^{(N)}(k_1, \dots, k_N), \quad (83)$$

where

$$G^{(N)}(k_1,\ldots,k_N) = \langle \Phi(k_1)\ldots\Phi(k_N) \rangle.$$
(84)

According to the common rule (see Equation 20),

$$\langle \Phi(k_1)\dots\Phi(k_N)\rangle = \mathcal{N}^{-1}\int D\Phi\cdot\Phi(k_1)\cdots\Phi(k_N)\exp\left[-\int\mathcal{L}(\Phi)\,dx\right],$$
 (85)

which immediately gives (cf. Equation 23)

$$G^{(N)}(k_1,\ldots,k_N) = V^{N/2} \left. \frac{\delta^N Z \left\{ J \right\}}{\delta J \langle -k_1 \rangle \cdots \delta J \langle -k_N \rangle} \right|_{J=0},\tag{86}$$

where

$$Z \{J\} = \mathcal{N}^{-1} \exp\left\{-\sum_{r} \frac{\lambda_{r}}{r!} \sum_{k_{1} \dots k_{r}} \delta\left(\sum k_{r}\right) \frac{\delta}{\delta J(-k_{1})} \cdots \frac{\delta}{\delta J(-k_{r})}\right\}$$

$$\times \exp\left\{\frac{1}{2} \sum_{k} J(k) G_{0}(k) J(-k)\right\}$$
(87)

with

$$G_0(k) = (k^2 + \mu^2)^{-1}.$$
(88)

In the expressions for Green's functions, a volume-containing factor always appears due to Equations 74 and 75. In what follows we will omit this factor, since it can be restored by dimension analysis at any time.

The translation invariance of $G^{(N)}(x_i)$ manifests itself with a shift of \vec{x}_i by \vec{a} : $\vec{x}_i + \vec{a}$. Applying Equation 83 we get

$$G^{(N)}(\vec{x}_i) \rightarrow \sum_{k_1,\dots,k_N} \exp(-i\vec{a}\sum \vec{k}_i) \exp(-i\sum \vec{k}_i \vec{x}_i) G^{(N)}(\vec{k}_i).$$

Thus, if $G^{(N)}(\vec{x}_i)$ must not change by translation by \vec{a} , we must have

$$G^{(N)}(\vec{k}_i) = \bar{G}^{(N)}(\vec{k}_i)\delta\left(\sum \vec{k}_i\right)$$

whence an important property of momentum conservation follows.

In the following, special denomination of the vector quantities will be sometimes omitted when there is no ambiguity.

The quantities k_i in $G^{(N)}$ (Equation 86) are called **external momenta**. The fields J related to these must be paired with other derivatives related to the external points or the derivatives in \mathcal{L}_{int} . In the expansion of Equation 86 by powers of λ_r only paired products must remain. Pairing must combine k and -k due to Z^0 being a diagonal matrix in the k-space. The factor \mathcal{N} will cancel with the vacuum components of the function expansion.

Consider the second-order term in the expansion $G^{(4)}(k_1, \ldots, k_4)$ with $\mathcal{L}_{int} = (\lambda/4!)\Phi^4$ (Amit, 1978)

$$G_{2}^{(4)}(k_{1},\ldots,k_{4}) = \frac{1}{2!} \frac{\delta}{\delta J(-k_{1})} \cdots \frac{\delta}{\delta J(-k_{4})} \left[\frac{\lambda}{4!} \sum_{q_{1}\ldots q_{4}} \delta\left(\sum q_{i}\right) \frac{\delta}{\delta J(-q_{1})} \cdots \frac{\delta}{\delta J(-q_{4})} \right]$$
(89)

$$\times \left[\frac{\lambda}{4!} \sum_{p_{1}\ldots p_{4}} \delta\left(\sum p_{i}\right) \frac{\delta}{\delta J(-p_{1})} \cdots \frac{\delta}{\delta J(-p_{4})} \right] \exp\left\{ \frac{1}{2} \sum_{k} J(k) G_{0}(k) J(-k) \right\} \Big|_{J=0}$$

(there are no vacuum terms).

Extract a special term in the expansion, where two external derivatives are paired with the derivatives of another vertex. The two remaining derivatives in each vertex are paired (see Figure 2.54a).

There are three different versions of pairing the external derivatives. Select 1 and 2 for connection to the same vertex. The other combinations correspond to the number of the external index permutations.

There are 8 pairing versions for k_1 , three for k_2 , four for k_3 , and three for k_4 . Lastly, the two remaining derivatives at each vertex can be combined in two ways.

As a result, we obtain a factor 1/2.

After the counterpairs $q_1 = -k_1$, $q_2 = -k_2$, $p_1 = -k_3$, $p_2 = -k_4$ and $q_3 = -p_3$, $q_4 = -p_4$ are chosen, the expression reduces to

$$\frac{\lambda^2}{2}G_0(k_1)G_0(k_2)G_0(k_3)G_0(k_4)\sum_{p_3,p_4}\delta(k_1+k_2+p_3+p_4)\delta(-k_3-k_4+p_3+p_4)G_0(p_3)G_0(p_4).$$
(90)



Figure 2.54. Graphs $G_2^{(4)}$ in momentum space

After summation over p_4 :

$$\frac{\lambda^2}{2}G_0(k_1)\dots G_0(k_4)\sum_p G_0(p)G_0(k_1+k_2-p)\delta\left(\sum k_i\right).$$
(91)

Moreover, there are two permutations, where $k_1 + k_2$ are replaced by $k_1 + k_3$ or $k_1 + k_4$. Equation 90 corresponds to the graph in Figure 2.54a. The lines marked k_i give the function $G_0(k_i)$. For every vertex, which k_i reaches, a factor $\left(-\frac{\lambda}{4!}\right)\delta\left(\sum k_i\right)$ is provided for.

Summation (integration) must be performed over all the internal momenta. The graph in Figure 2.54b corresponds to Equation 91. Again, $G_0(k_i)$ corresponds to every line. There are no δ functions but the common $\delta(\sum k_i)$. The arrows mark the direction of the momentum input to output from the vertex. The internal momenta are eliminated due to the total momentum for each vertex being equal to zero. Thus, the rules of graph building in the k presentation are formulated as follows.

Rule 3. The graph constituents are N external points, from each of which a line denoted by k_i (i = 1, ..., N) originates. The other constituents are n_r vertices of type r, consisting of n (the order of the function expansion term) points, from which r lines originate, denoted by $q_1^{(i)}, \ldots, q_r^{(i)}$ (i marks a given vertex of interaction). All the lines must be pairwise connected and the sum of the paired indices is equal to zero. One needs not build graphs with vacuum terms.

Rule 4 for the calculation of expressions. For each internal point of type r, a factor

$$-\left(rac{\lambda_r}{r!}
ight)\delta\left(\sum q_i
ight)$$

is provided, where q_i is the momenta of the lines originating from the point. Each line is denoted by \vec{q} and implies $G_0(\vec{q})$. The numerical factor is calculated in the same way as above (see Rule 2).

The summation must be performed over all the internal momenta. In practice, summation is carried out over as many internal momenta as there are vertices, since every vertex has a δ function.

As one δ function which conserves the total momentum always remains, (n-1) internal sums can be eliminated, where n is the number of vertices.

There exist such important properties of graphs as their one-particle reducibility (1PR) and, correspondingly, one-particle irreducibility (1PI).

Consider 1PR with the graph $G_8^{(4)}$ of the Φ^3 theory as an example (Figure 2.55), to



Figure 2.55. Graph $G_8^{(4)}$ in the Φ^3 theory (Amit, 1978)

which corresponds the algebraic expression

$$G_{8}^{(4)} = G_{0}(k_{1})G_{0}(k_{2}) \left[\int dq_{1} G_{0}(q_{1})G_{0}(k_{1}+q_{1})G_{0}(k_{2}-q_{1}) \right]$$

$$\times G_{0}(k_{1}+k_{2}) \left[\int dq_{2} G_{0}(q_{2})G_{0}(k_{3}-q_{2})G_{0}(q_{2}-k_{1}-k_{2}-k_{3}) \right]$$

$$\times G_{0}(k_{1}+k_{2}+k_{3})G_{0}(k_{3}) \left[\int dq_{3} G_{0}(q_{3})G_{0}(k_{3}-q_{3}) \right] G_{0}(k_{3}),$$
(92)

where the numerical factor and δ function are not given.

There is no integration over the momenta connecting the separate parts, and only $G_0(k)$ and the functions $\Gamma_3^{(2)}$ and $\Gamma_2^{(2)}$ should be known to deduce the dependence of $G_8^{(4)}$ on k_1 , k_2 , and k_3 . Their graphs are shown in Figure 2.56:



Figure 2.56. Graphs $\Gamma_3^{(3)}$ and $\Gamma_2^{(2)}$ (Amit, 1978)

$$G_8^{(4)}(k_1, k_2, k_3) = G_0(k_1)G_0(k_2) \left[\Gamma_3^{(3)}(k_1, k_2) \right] G_0(k_1 + k_2) \left[\Gamma_3^{(3)}(k_4, k_3) \right]$$
(93)

$$\times G_0(k_1 + k_2 + k_3)G_0(k_3) \left| \Gamma_2^{(2)}(k_3) \right| G_0(k_3).$$

The definitions of $\Gamma_3^{(3)}$ and $\Gamma_2^{(2)}$ result from comparison of Equation 93 and 92. Once a graph can be divided into two ones by breaking an internal line, the momentum of this broken line is fixed by means of the momentum of an external line connected to one of the disconnected ends. It follows from the fact that the momentum remains for every vertex, so the momentum outgoing along an external line is equal to the sum of the pulses ingoing along the external lines of the same graph.

This property of graphs due to the absence of integration over one-line-connected variables is called a one-particle reduction (1PR). In the contrary version, a graph is called one-particle irreducible (1PI).

Green's connected functions and the vertex functions play an important role in field theory.

Green's connected function G_c , with connected graphs to correspond to it, exhibits interesting and important properties.

If $\mathbb{Z}\left\{J\right\}$ is the generating functional of Green's function, i.e.

$$G^{(N)}(k_1,\ldots,k_N) = \left. \frac{\delta^N Z\left\{J\right\}}{\delta J(-k_1)\cdots\delta J(-k_N)} \right|_{J=0},\tag{94}$$

then it can be written as a Taylor series with Green's functions instead of derivatives $Z\{J\}$

$$Z(J) = 1 + \sum_{N=1}^{\infty} \frac{1}{N!} \sum_{k_1,\dots,k_N} G^{(N)}(k_1,\dots,k_N) J(-k_1) \cdots J(-k_N).$$
(95)

It is specially proved in the field theory that if $F\{J\}$ is the generating functional of Green's connected functions

$$F\{J\} = 1 + \sum_{N=1}^{\infty} \frac{1}{N!} \sum_{k_1,\dots,k_N} G_c^{(N)}(k_1,\dots,k_N) J(-k_1) \cdots J(-k_N),$$
(96)

then

$$Z\left\{J\right\} = e^{F\left\{J\right\}} \tag{97}$$

is realized.

Thus, according to Equation 96,

$$G_{c}^{(N)}(k_{1},\ldots,k_{N}) = \left. \frac{\delta^{N}F\{J\}}{\delta J(-k_{1})\cdots\delta J(-k_{N})} \right|_{J=0}.$$
(98)

In terms of statistical physics, $Z\{J\}$ is the statistical integral, $F\{J\}$ is the free energy (with a negative sign).

Applying Equations 97 and 98, Green's function can be compared with Green's connected functions

$$G_c^{(1)}(k_1) = \langle \Phi(k_1) \rangle = G^{(1)}(k_1),$$

$$\begin{split} G_c^{(2)}(k_1, k_2) &= \langle \Phi(k_1) \Phi(k_2) \rangle - \langle \Phi(k_1) \rangle \langle \Phi(k_2) \rangle \\ &= G^{(2)}(k_1, k_2) - G^{(1)}(k_1) G^{(1)}(k_2). \\ G_c^{(3)}(k_1, k_2, k_3) &= \langle \Phi(k_1) \Phi(k_2) \Phi(k_3) \rangle - \langle \Phi(k_1) \Phi(k_2) \rangle \langle \Phi(k_3) \rangle \\ &- \langle \Phi(k_1) \rangle \langle \Phi(k_2) \Phi(k_3) \rangle - \langle \Phi(k_2) \rangle \langle \Phi(k_1) \Phi(k_3) \rangle + 2 \langle \Phi(k_1) \rangle \langle \Phi(k_2) \rangle \langle \Phi(k_3) \rangle \\ &= G^{(3)}(k_1, k_2, k_3) - G^{(1)}(k_3) G^{(2)}(k_2, k_1) - G^{(1)}(k_1) G^{(2)}(k_2, k_3) - \\ &- G^{(1)}(k_2) G^{(2)}(k_1, k_3) + 2 G^{(1)}(k_1) G^{(1)}(k_2) G^{(1)}(k_3). \end{split}$$

The functions in the right-hand sides are the cumulants of the statistical distribution of the system fields. In their turn, Green's functions are expressed via Green's connected ones by means of

$$\begin{aligned} G^{(1)}(k_1) &= G^{(1)}_c(k_1), \\ G^{(2)}(k_1, k_2) &= G^{(2)}_c(k_1, k_2) + G^{(1)}_c(k_1)G^{(1)}_c(k_2), \\ G^{(3)}(k_1, k_2, k_3) &= G^{(3)}_c(k_1, k_2, k_3) + G^{(1)}_c(k_1)G^{(2)}_c(k_2, k_3) + G^{(1)}_c(k_2)G^{(2)}_c(k_1, k_3) \\ &+ G^{(1)}_c(k_3)G^{(2)}_c(k_1, k_2) + G^{(1)}_c(k_1)G^{(1)}_c(k_2)G^{(1)}_c(k_3), \end{aligned}$$

etc.

Therefore, using the known Green connected functions, one is able to build a complete Green function.

It follows from the above equations that if two coordinates of a line are distant from each other, Green's connected functions tend to zero.

There are connected and disconnected graphs in every order of Green's function expansion.

Eg. Figure 2.57 (top) presents disconnected graphs of Green's four-point function up to the second order of the Φ^4 theory, below are the connected graphs.

Figure 2.58 presents Green's two-point connected functions up to the third order. The sum of all the terms of this series is called a **total** (or **dressed**) propagator and is denoted by (Ryder, 1985)



Consider a diagram in the second order (λ)



The corresponding expression can be represented as the product





Figure 2.57. Connected and disconnected graphs of $G^{(4)}$ (Amit, 1978)



Figure 2.58. Graph of the Green connected function $G_c^{(2)}$ up to the third order (Ryder, 1985) [Reprinted with permission from: L.H.Ryder *Quantum field theory*. Copyright © 1985 by Cambridge University Press]

The first and last multipliers of this product are external propagators common to diagrams. The field theory (Ryder, 1985) introduces **truncated** diagrams obtained from the total ones by multiplying the external propagators by the reciprocal values of the propagators. This procedure is marked with dashed lines as

As a result of this operation, the second diagram of the λ^2 order takes the form

and the third one the form

The diagrams of all orders are subjected to this procedure.

Of the second-order diagrams, only Equation 99 contains the propagator in the centre and turns to be one-particle reducible: it can be divided into two diagrams by cutting one internal line. The other diagrams of λ^2 lack this property and are classified with the one-particle irreducible diagrams. The sum of 1PI diagrams is denoted by

$$= \sum_{k} (k) = (100)$$

$$= \sum_{k} (k) = k + \sum_{k} (k) +$$

Hence, the total propagator (Figure 2.58) can be written as

$$G_{c}^{(2)}(k) = G_{0}(k) + G_{0}(k) \sum_{k} G_{0}(k)$$

$$+ G_{0}(k) \sum_{k} G_{0}(k) \sum_{k} G_{0}(k) + \cdots$$

$$= G_{0} \left(1 + \sum_{k} G_{0} + \sum_{k} G_{0} \cdot \sum_{k} G_{0} + \cdots \right)$$

$$= G_{0} \left(1 - \sum_{k} G_{0} \right)^{-1} = \left[G_{0}^{-1}(k) - \sum_{k} (k) \right]^{-1} = \frac{1}{k^{2} + \mu^{2} - \sum_{k} (k)},$$
(101)

with allowance for Equation 2.6-88.

Equation 101 is written in the accepted notation

$$---\bigcirc --- = ---- + --- \bigcirc --- + \cdots .$$

If physical mass μ_{Φ} is defined as a pole of the propagator

$$G_c^{(2)}(k) = \frac{1}{k^2 + \mu_{\Phi}^2},\tag{102}$$

then comparison of Equations 101 and 102 leads to

$$\mu_{\Phi} = \mu^2 - \sum(k), \tag{103}$$

i.e. $\sum(k)$ is a correction to be added to the mass of the bare propagator to obtain the physical mass of a wave-particle in terms of field theory.

Equation 101 gives

$$\left[G_{c}^{(2)}(k)\right]^{-1} = G_{0}^{-1}(k) - \sum(k) = \Gamma^{(2)}(k), \qquad (104)$$

which defines a second-order vertex function $\Gamma^{(2)}(k)$, which contains only 1Pl diagrams but the reciprocal bare propagator.

In the general case, a vertex function is Green's reciprocal connected function in the matrix sense.

The vertex functions play an important role in the field theory.

The momentum subscript and designation of a field component in coordinate space play similar roles in the theory, if the free part of the Lagrangian is a diagonal matrix in both spaces. Then, the same subscript can be applied in either case

$$\langle \Phi(i) \rangle \equiv \langle \Phi_{\alpha_i}(k_i) \rangle \equiv \bar{\Phi}(i) = \frac{\delta F \{J\}}{\delta J \{i\}}.$$
(105)

Define a functional I' $\{\bar{\Phi}\}$ through Legendre's transformation

$$\Gamma\left\{\Phi\right\} + F\left\{J\right\} = \sum_{i} \dot{\Phi}_{i}(i)J(i).$$
(106)

After functional differentiation,

$$\frac{\delta\Gamma\left\{\bar{\Phi}\right\}}{\delta\bar{\Phi}(i)} = -\sum_{i} \frac{\delta F\left\{J\right\}}{\delta J(j)} \frac{\delta J(j)}{\delta\bar{\Phi}(i)} + \sum_{j} \bar{\Phi}(j) \frac{\delta J(j)}{\delta\bar{\Phi}(i)} + \sum_{j} J(j) \delta(i,j),$$

and, with due account of Equation 105,

$$\frac{\delta\Gamma\left\{\bar{\Phi}\right\}}{\delta\bar{\Phi}} = -\sum_{i}\bar{\Phi}(j)\frac{\delta J(j)}{\delta\bar{\Phi}(i)} + \sum_{j}\bar{\Phi}(j)\frac{\delta J(j)}{\delta\bar{\Phi}(i)} + \sum_{j}J(j)\delta(i,j) = J(i).$$
(107)

Legendre's transformation (Equation 106) and the derivatives in Equations 105 and 107 possess some interesting properties. In the area of the state diagram, where symmetry breaks down spontaneously, and a spontaneous field (the order parameter) arises without any external source (external field), i.e.

$$\Phi_i \{J\} = \frac{\delta F\{J\}}{\delta J(i)} \xrightarrow[J \to 0]{} v(i) \neq 0,$$
(108)

according to Equation 107,

$$\frac{\delta \Gamma\left\{\bar{\Phi}\right\}}{\delta\bar{\Phi}(i)}\bigg|_{\Phi(i)=\nu(i)} = 0.$$
(109)

Hence, $\Gamma\left\{\bar{\Phi}\right\}$ has an extremum at $\bar{\Phi}(i) = v(i)$. Differentiate $\bar{\Phi}(i)$ in Equation 105 with respect to $\bar{\Phi}(j)$ once again:

$$\delta(i,j) = \frac{\delta^2 F\{J\}}{\delta J(i)\,\delta\bar{\Phi}(j)} = \sum_k \frac{\delta^2 F\{J\}}{\delta J(i)\,\delta J(k)} \cdot \frac{\delta J(k)}{\delta\bar{\Phi}(j)}.$$
(110)

The last derivative is obtained by differentiating Equation 107, and the equation takes the form

$$\sum_{k} \frac{\delta^2 F}{\delta J(i) \,\delta J(k)} \cdot \frac{\delta^2 \Gamma}{\delta \bar{\Phi}(k) \,\delta \bar{\Phi}(j)} = \delta_{ij}.$$
(111)

When $J \rightarrow 0$, then (see Equation 98)

$$\frac{\delta^2 F}{\delta J(i) \,\delta J(k)} \to G_c^{(2)}(i,k). \tag{112}$$

Thus, the two-point vertex function $\Gamma^{(2)}(k,j)$ defined by

$$\frac{\delta^2 \Gamma\left\{\bar{\Phi}\right\}}{\delta\bar{\Phi}(k)\,\delta\bar{\Phi}(j)}\bigg|_{J=0} = \Gamma^{(2)}(k,j) \tag{113}$$

in view of Equation 111 is the inverse function of Green's two-point connected function in the matrix sense.

An N-point vertex function is defined by

$$\Gamma^{(N)}(1,\ldots,N) \equiv \left. \frac{\delta^N \Gamma\left\{\bar{\Phi}\right\}}{\delta\bar{\Phi}(1)\cdots\delta\bar{\Phi}(N)} \right|_{J=0}$$
(114)

It follows from Equation 114 that $\Gamma\left\{\bar{\Phi}\right\}$ is the generating functional for the vertex function, i.e. the latter can be applied for expansion of $\Gamma\left\{\bar{\Phi}\right\}$ into a Taylor series by analogy with Equations 95 and 96.

But earlier (Equations 94 and 98) the derivatives were taken at J = 0, and expansion was carried out in terms of J. In the case of $\Gamma \{\Phi\}$, the derivatives are taken at J = 0 as well, but the expansion is performed in terms of Φ .

When $\bar{\Phi} = v \neq 0$ at J = 0,

$$\Gamma\left\{\bar{\Phi}\right\} = \sum_{N=1}^{\infty} \frac{1}{N!} \sum_{i_1,\dots,i_N} \int dx_1 \dots dx_N \, \Gamma_{i_1,\dots,i_N}^{(N)}(x_1,\dots,x_N;v)$$

$$\times \left[\bar{\Phi}_{i_1}(x_1) - v_{i_1}\right] \cdots \left[\bar{\Phi}_{i_N}(x_N) - v_{i_N}\right],$$
(115)

where

$$v_i = \lim_{J \to 0} \bar{\Phi}_i. \tag{116}$$

If the source disappears, then the summation of Equation 115 starts from N = 2, as for J = 0

$$\Gamma^{(1)} = \frac{\delta \Gamma}{\delta \bar{\Phi}} = J = 0. \tag{117}$$

In the region of the state diagram, where the system's symmetry remains, $v_i = 0$ and

$$\Gamma\left\{\bar{\Phi}\right\} = \sum_{N=1} \frac{1}{N!} \sum_{i_1,\dots,i_N} \int dx_1 \cdots dx_N \,\Gamma^{(N)}_{i_1,\dots,i_N} \bar{\Phi}_{i_1}(x_1) \cdots \bar{\Phi}_{i_N}(x_N). \tag{118}$$

The question of symmetry breakdown is solved by means of

$$\frac{\delta\Gamma\left\{\bar{\Phi}\right\}}{\delta\bar{\Phi}} = 0,\tag{119}$$

the solutions of which are defined when $\overline{\Phi} \neq 0$.

As

$$\frac{\delta^2 \Gamma}{\delta \bar{\Phi}(1) \, \delta \bar{\Phi}(2)} = \left[G_c^{(2)} \right]^{-1} \tag{120}$$

and

$$G_c^{(2)}(1,2) = \langle (\Phi(1) - v_1)(\Phi(2) - v_2) \rangle$$
(121)

which is a positive semi-definite matrix, then the extremum of $\Gamma \left\{ \tilde{\Phi} \right\}$ (Equation 119) is a minimum. Another useful function is Γ for a uniform distribution $\tilde{\Phi} = \Phi$.

If the field distribution is uniform $(\bar{\Phi} = \Phi)$, then

$$\Gamma \{\Phi\} = \sum_{N=2}^{\infty} \frac{1}{N!} \sum_{i_1, \dots, i_N} \left[\int dx_1 \cdots dx_N \, \Gamma_{i_1, \dots, i_N}^{(N)}(x_1, \dots, x_N) \right] \Phi_{i_1} \cdots \Phi_{i_N}.$$
(122)

The Fourier transform of $\Gamma^{(N)}$ in the limit of an infinite volume

$$\Gamma^{(N)}(x_1, \dots, x_N) = \int \frac{dk_1}{(2\pi)^d} \cdots \frac{dk_N}{(2\pi)^d} \Gamma^{(N)}(k_1, \dots, k_N) \exp\left\{-i\sum k_i x_i\right\}.$$
 (123)

It follows from translational invariance that

$$\Gamma^{(N)}(k_1,\ldots,k_N) = (2\pi)^d \delta\left(\sum k_i\right) \overline{\Gamma}^{(N)}(k_1,\ldots,k_N)$$
(124)

and Equation 122 can be written as

$$\Gamma \{\Phi\} = \sum_{N=1}^{\infty} \frac{1}{N!} \sum_{i_1, \dots, i_N} \dot{\Gamma}_{i_1, \dots, i_N}^{(N)}(0, \dots, 0) \Phi_{i_1} \cdots \Phi_{i_N}(2\pi)^d \delta(0)$$
(125)
$$\equiv (2\pi)^d \delta(0) U(\Phi).$$

The emergence of $(2\pi)^d \delta(0)$ simply means that the quantity $\Gamma \{\Phi\}$ is proportional to the system's volume. The quantity $U(\Phi)$ is called a **potential**, or an effective potential. The condition of symmetry breakdown of a system (continuous phase transition) results from $U(\Phi)$'s minimum for $\Phi \neq 0$.

The source J can be identified with an external physical field. If this field is assumed to be uniform, the mean value of Φ is calculated from

$$\frac{\partial U(\Phi)}{\partial \Phi_i} = J_i. \tag{126}$$

Equation 125 enables us to deduce

$$J_{i} = \sum_{N=1}^{\infty} \frac{1}{N!} \sum_{i_{1},\dots,i_{N}} \bar{\Gamma}_{i_{1},\dots,i_{N}}^{(N+1)}(0,\dots,0) \Phi_{i_{1}} \cdots \Phi_{i_{N}}$$
(127)

which is the state equation of the system.

Hence, the vertex function determines the free energy and the state equation of a system.

Discuss the main *n*th-order graph in perturbation theory, which is related to the vertex function with E external points and I internal lines. Integration should be performed in the k-space over each internal line but with the momentum of each vertex to be conserved. As one δ function must remain for the conservation of the total momentum, only (n-1) δ functions of the remaining ones turn out to be effective, and the integration number (or the number of integrations) in momentum space is

$$L = I - (n - 1) = I - n + 1.$$
(128)

In this connection, the approximate approaches and theories, where expressions are written up to a certain integration number in the k space, are called **loop approximations**.

Landau-Ginzburg's approximation with the free energy

$$U(\Phi) = \frac{1}{2}\mu^2 \Phi^2 + \frac{\lambda}{4!} \Phi^4$$
(129)

results in the zero loop approximation. In the one-loop approximation,

$$U(\Phi) = \frac{1}{2}\mu^2 \Phi^2 + \frac{\lambda}{4!} \Phi^4 + \frac{1}{2} \int dq \,\ln(q^2 + \mu^2 + \lambda \frac{\Phi^2}{2}). \tag{130}$$

Depending on the space dimensionality, the integrals in one- (and so on) loop approximation may diverge at small q (an infrared divergence), as well as at large q (a ultraviolet divergence).

Methods of revealing and classifying divergences are related to a **regularization** procedure. The ways of eliminating divergences constitute the context of **renormalization** methods (eg. Wilson's renormalization group approach).

A dimensional regularization is one of the methods of regularization, based on the idea to use the space dimensionality d as a continuous variable. Application of the method begins with calculating the integrals at d < 2 to yield forms that are subsequently extrapolated to any d (Kholodenko and Freed, 1983).

Vertex and Green's functions involving combined operators are used in polymer theory (see section 5.5).

First, let us discuss these functions as applied to magnetics and general-type systems (Amit, 1978).

If, for example, the correlation between energy density and magnetization at different points inside a magnetic needs to be determined, the means of the type

$$G_{i_1,\dots,i_N,j_1,\dots,j_{\mathcal{L}}}^{(N,\mathcal{L})}(x_1,\dots,x_N,y_1,\dots,y_{\mathcal{L}})$$
(131)

.....

$$= \left(\frac{1}{2}\right)^{\mathcal{L}} \left\langle \Phi_{i_1}(x_1) \Phi_{i_2}(x_2) \cdots \Phi_{i_N}(x_N) \Phi_{j_1}^2(y_1) \cdots \Phi_{j_{\mathcal{L}}}^2 \right\rangle(y_{\mathcal{L}})$$

should be considered. These correlation functions allow generalization by means of introducing a new source

$$-\frac{1}{2}\sum_{j}t_{j}(y)\Phi_{j}^{2}(y) \tag{132}$$

into the Lagrangian (apart from Equation 14). Then

$$G_{i_{1},\dots,i_{N},j_{1},\dots,j_{L}}^{(N,\mathcal{L})}(x_{1},\dots,x_{N},y_{1},\dots,y_{L})$$

$$= Z^{-1} \left. \frac{\delta^{N+\mathcal{L}}Z}{\delta h_{i_{1}}(x_{1})\cdots\delta h_{i_{N}}(x_{N})\delta t_{j_{1}}(y_{1})\cdots\delta t_{j_{L}}(j_{L})} \right|_{h=t=0}.$$
(133)

The combined operators of the Φ^2 type acquire special and independent meaning when fluctuations of the thermodynamic quantities play a significant part in the system's properties.

The function $G^{(N,\mathcal{L})}$ can be also deduced from the function $\left(\frac{1}{2}\right)^{\mathcal{L}} G^{(N+2\mathcal{L})}$ by means of pairwise combination of the last $2\mathcal{L}$ points and consideration of the points in the pairs as identical.

Away from the critical point, the equality

$$G^{(N,\mathcal{L})}(x_1, \dots, x_N, y_1, \dots, y_{\mathcal{L}})$$

$$= \left(\frac{1}{2}\right)^{\mathcal{L}} G^{(N+2\mathcal{L})}(x_1, \dots, x_N, y_1, y_1, y_2, y_2, \dots, y_{\mathcal{L}}, y_{\mathcal{L}})$$
(134)

holds.

Eq. the function $G^{(4)}(x_1, \ldots, x_4)$, calculated in the first order with respect to the interaction constant (Equations 66-69), can be employed to derive the function $G^{(2,1)}(x_1, x_2, y)$, assuming $x_3 = x_4 = y$ with subsequent multiplication of the result by 1/2:

$$G^{(2,1)}(x_1, x_2, y) = \frac{1}{2}G_0(x_1 - x_2)G_0(y - y) +$$
(135a)

$$+G_0(x_1-y)G_0(x_2-y)$$
 (b)

$$-\frac{\lambda}{2}\int dx' G_0(x_1-x')G_0(x_2-x') \left[G_0(y-x')\right]^2$$
(c)

$$-\frac{\lambda}{4}\int dx' G_0(x_1 - x')G_0(x' - x')G_0(x' - x_2)G_0(y - y) \tag{d}$$

$$-\frac{\lambda}{2}\int dx' G_0(x_1-x')G_0(x'-x')G_0(x'-y)G_0(y-x_2)$$
(c)

$$-\frac{\lambda}{2}\int dx' G_0(x_2 - x')G_0(x' - x')G_0(x' - y)G_0(x_1 - y) \tag{f}$$

$$-\frac{\lambda}{4}\int dx' \left[G_0(y-x')\right]^2 G_0(x'-x')G_0(x_1-x_2) \tag{g}$$

$$-\frac{\lambda}{16}\int dx' \left[G_0(x'-x')\right]^2 G_0(x_1-x_2)G_0(y-y) \tag{h}$$

$$-\frac{\lambda}{8}\int dx' \left[G_0(x'-x')\right]^2 G_0(x_1-y)G_0(x_2-y)$$
(i)

Different permutations in Equations 66-69 are presented here explicitly, since some of them prove to be identical after $x_3 = x_4 = y$.



Figure 2.59. Graphs $G^{(2,1)}$ in the first order of the interaction constant (Amit, 1978)

The graphs, corresponding to the 9 summands (Equations 135a...), are shown in Figure 2.59. Two external points, merging into one, are denoted by a point with a wave line. The point y plays the same role as the interaction vertex (having, as in this case, two twigs) except that no integration is performed.

The choice of the factor 1/2! in the definition of the combined operator Φ^2 implies that the graph symmetry factor follows immediately from considering the point y as a vertex; therefore, the symmetry factor can be determined from the graph topology (see Figure 2.59 and the factors in the summands of Equation 135).

This property turns out to be common.

If the Φ^2 inclusions are generated by the term

$$\frac{1}{2!}t(x)\Phi^2(x),$$
 (136)

it can be included into the interaction Lagrangian density \mathcal{L}_{int} . Then, the expression for $Z\{J\}$ (Equation 53) is generalized:

$$Z \{J,t\} = \mathcal{N}^{-1} \sum_{n=0}^{\infty} \sum_{l=0}^{\infty} \frac{1}{n! \, l!} \left(-\frac{\lambda}{4!}\right)^n \int dx_1 \cdots dx_n \left(\frac{1}{2!}\right)^l \int dy_1 \cdots dy_l \qquad (137)$$
$$\times t(y_1) \cdots t(y_l) \left[\frac{\delta}{\delta J(x_1)}\right]^4 \cdots \left[\frac{\delta}{\delta J(x_n)}\right]^4 \left[\frac{\delta}{\delta J(y_1)}\right]^2 \cdots \left[\frac{\delta}{\delta J(y_l)}\right]^2 Z^{\circ} \{J\}.$$

Applying the operation in Equation 133 to $G^{(N,\mathcal{L})}$, we find that \mathcal{L} derivatives with respect to $t(y_1)$ at t = 0 choose one term of all of the sum over l, namely, the term with

2.6.2. Interacting fields

 $l = \mathcal{L}$, and exclude integration with respect to y. \mathcal{N} does not depend on J and t, and, therefore, will not depend on the derivatives.

Then $G^{(N,\mathcal{L})}$ can be written in the form

$$G^{(N,\mathcal{L})}(x_1,\ldots,x_N,y_1,\ldots,y_{\mathcal{L}}) = \mathcal{N}^{-1} \frac{\delta}{\delta J(x_1)} \cdots \frac{\delta}{\delta J(x_N)} \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{\lambda}{4!}\right)^n$$
(138)

$$\times \int dz_1 \cdots dz_n \left[\frac{\delta}{\delta J(z_1)}\right]^4 \cdots \left[\frac{\delta}{\delta J(z_n)}\right]^4 \left(\frac{1}{2}\right)^{\mathcal{L}} \left[\frac{\delta}{\delta J(y_1)}\right]^2 \cdots \left[\frac{\delta}{\delta J(y_{\mathcal{L}})}\right]^2 Z^{\circ} \{J\} \bigg|_{J=0}.$$

Hence, the *n*th-order terms in the perturbation expansion of $G^{(N,\mathcal{L})}$ are calculated in the same way as the *n*th-order terms of $G^{(N)}$ with ordinary interaction vertices and the first-order ones in \mathcal{L} vertices with two different twigs, whose integration is not performed over. In other words, there is no $(\mathcal{L}!)^{-1}$ multiplied by the expression corresponding to the graph.



The second-order graph of $G^{(2,2)}(x_1, x_2, y_1, y_2)$ shown in Figure 2.60 is derived by multiplying by $(-\lambda/4!)$ for each Φ^4 vertex, by 1/2 for each Φ^2 inclusion, by 1/2! by virtue of the second λ order (not due to two Φ^2 inclusions). Then, the number of ways to build this specific graph is calculated.

The symmetry factor 1/2 is caused by the graph symmetry about replacing its lower part by two lines. The final expression is

$$\frac{\lambda^2}{2} \int dx_1' \, dx_2 \, G_0(x_1 - x_1') G_0^2(x_1' - x_2') G_0(x_1' - y_1)$$

$$\times G_0(y_1 - y_2) G_0(y_2 - x_2') G_0(x_2' - x_2).$$
(139)

Cancellation of the vacuum graphs happens just as before, since N has not been altered. It follows that only h and i of the graphs in Figure 2.59 are cancelled.

The effect of merging of two coordinates into $G^{(N+2)}$ to build $G^{(N,1)}$ is really illustrated in the momentum representation.

The Fourier transform of $G^{(N,1)}$ is defined by

$$G^{(N,1)}(x_1,\ldots,x_N,y) = \sum_{k_1,p} G^{(N,1)}(k_1,\ldots,k_N,p) \exp\left[-i(k_ix_i+py)\right].$$
(140)

By analogy with Equations 83 and 84,

$$G^{(N,1)}(k_1,\ldots,k_N,p) = \frac{1}{2} \left\langle \Phi(k_1)\cdots\Phi(k_N)\Phi^2(p) \right\rangle, \qquad (141)$$

where $\Phi^2(p)$ is derived from

$$[\Phi(x)]^2 = \sum_{p} \exp(-ipx)\Phi^2(p).$$
(142)

If the left-hand side of Equation 142 is subjected to the Fourier transformation with respect to $\Phi(x)$, then

$$\Phi^{2}(\vec{p}) = \sum_{k} \Phi(\vec{k}) \Phi(\vec{p} - \vec{k}).$$
(143)

Hence,

$$G^{(N,1)}(k_1,\ldots,k_N,p) = \frac{1}{2} \sum_k G^{(N+2)}(k_1,\ldots,k_N,k,p-k).$$
(144)

The combined operator $\Phi^2(x)$ implies summation over two momenta of (N + 2) momentum variables in $G^{(N+2)}$ with their sum being fixed. These relationships provide one of the ways to calculate $G^{(N,1)}$ from $G^{(N+2)}$ in the momentum space.

Another way consists in considering Φ^2 as vertex inclusions. Then $G^{(N,\mathcal{L})}(k_1,\ldots,k_N,p_1,\ldots,p_{\mathcal{L}})$ in the *n*th order of ordinary interactions is the first-order in \mathcal{L} ϕ^2 -interactions, i.e. there is no $(\mathcal{L}!)^{-1}$. Moreover, though all the interactions have the form

$$\frac{\lambda_r}{r!} \sum_{\vec{k}_i} \Phi(\vec{k}_1) \cdots \Phi(\vec{k}_r) \delta\left(\sum \vec{k}_i\right), \tag{145}$$

 Φ^2 has the form:

$$\Phi^{2}(p) = \frac{1}{2!} \sum_{\vec{k}_{1}, \vec{k}_{2}} \Phi(\vec{k}_{1}) \Phi(\vec{k}_{2}) \delta(\vec{k}_{1} + \vec{k}_{2} - \vec{p}).$$
(146)

Therefore, to calculate the graph $G^{(N,\mathcal{L})}$, the rules of $G^{(N)}$ calculation are applicable just in the same sequence by the ordinary interactions, and in the first order by \mathcal{L} interactions like Equation 146.

There must be a δ function at Φ^2 interaction vertices to make the sum of two ingoing momenta to be equal to \vec{p} .



Figure 2.61. Second-order graphs $G^{(2,2)}(k_1, k_2, p_1, p_2)$ in momentum space (Amit, 1978)

In the momentum space, the graph in Figure 2.60 takes the form shown in Figure 2.61. The graph in Figure 2.61a has five internal momenta. In Figure 2.61b, the momentum of

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 δ functions is taken into account. As a result of the conservation of the total momentum, we have $k_1 - k_2 + p_1 + p_2 = 0$.

The expression corresponding to the graph in Figure 2.61b has the form

$$\frac{\lambda^{2}}{2} \frac{1}{k_{1}^{2} + \mu^{2}} \frac{1}{k_{2}^{2} + \mu^{2}}$$

$$\times \int \frac{1}{(q_{1}^{2} + \mu^{2})(q_{2}^{2} + \mu^{2})[(k_{1} + q_{1} - q_{2})^{2} + \mu^{2}][(q_{2} - p_{1})^{2} + \mu^{2}][(q_{2} + p_{1} + p_{2})^{2} + \mu^{2}]}$$

$$\times (2\pi)^{d} \delta(k_{1} - k_{2} + p_{1} + p_{2}) \frac{dq_{1}}{(2\pi)^{d}} \frac{dq_{2}}{(2\pi)^{d}}.$$

$$(147)$$

2.6.3. Tricritical state

Section 1.6 has described the tricritical state of a thermodynamic system whose potential expansion coefficients in terms of even powers of the order parameter are functions of temperature and pressure.

In a more general case, for determination of the properties of the tricritical state, a Hamiltonian with even powers of the order parameter and coefficients depending, except temperature and pressure, on the nonorienting field g (see section 1.6) and the tricritical interaction parameter (see further) is considered (Riedel and Wegner, 1972).

The behaviour of such systems has been studied using the renormalization group method. In particular, the tricritical indices have been estimated. Eg. for 3D space (d=3)

$$\beta_t - \frac{1}{4}; \quad \gamma_t = 1; \quad \eta_t = 0; \quad \alpha_t = \frac{1}{2}; \quad \varphi_t = \frac{1}{2},$$
 (148)

i.e. they agree with their values in the mean field approximation (cf. section 1.6). Therefore, the boundary value of space dimensionality (beginning with which the mean field relationships become valid in the tricritical region) is $d^* = 3$, in contrast to the critical phenomena during continuous transitions, where $d^* = 4$ (see section 2.5, Figure 2.44). The examples considered in section 1.6 relate to symmetrical tricritical points where the positive and negative values of the order parameter are equivalent due to the even powers in the potential expansion series.

Asymmetric tricritical points are observed in mixtures of several components (Griffiths, 1974), and will be considered in detail later using polymer systems as examples (section 3.10).

So, symmetrical tricritical points are observed in systems with the Hamiltonian (in 3D space)

$$\frac{\mathcal{H}}{kT} = \int d^3x \left[\frac{1}{2} \sum_i \left\{ r_0 s_i^2(x) + \left[\nabla s_i(x) \right]^2 \right\} + \frac{u_4}{4!} \left(\sum_i s_i^2(x) \right)^2 + \frac{u_6}{6!} \left(\sum_i s_i^2(x) \right)^3 \right], (149)$$

where s_i is the *n*th-component spin $(-\infty < s_i < \infty)$ (Stephen et al., 1975).

The parameters r_0 , u_4 , and u_6 depend on the thermodynamic fields in the system. Using the mixture ${}^3He + {}^4He$ as an example, these are temperature T and the chemical potential difference $\mu_{34} = \mu_3 - \mu_4$. The field ζ is conjugate to the order parameter (see section 1.6).

Near the tricritical point, it is more reasonable to measure the thermodynamic quantities as functions of their distance from the tricritical point in a specially chosen coordinate system of scaling fields, which provides the validity of the scaling relationships for thermodynamic quantities (see section 1.6).



 $\mu_{34} = \mu_3 - \mu_4$

Figure 2.62. Lines of first order (1) and continuous (11) transitions, which converge in the tricritical point, with the mixture ³He + ⁴He. μ_3 and μ_4 are the chemical potentials of the components, Q and μ are the axes of the scaling fields (Stephen et al., 1975) [M.J.Stephen, E.Abrahams. Phys. Rev. B 12 (1975) 256-262. Copyright © 1975 by the American Physical Society]

Here Q and μ are chosen as the coordinate axes of scaling fields (Figure 2.62). They are drawn from the tricritical point perpendicularly and tangentially to the continuous critical point curve (Riedel, 1972).

In the first approximation of perturbation theory, the new variables are related to the system parameters by (Stephen et al., 1975)

$$\mu = r_0 + \frac{n+2}{6} u_4 \mathcal{F}_1(0) + \frac{(n+2)(n+4)}{5!} u_6 \mathcal{F}_1^2(0), \tag{150}$$

$$Q = u_4 + \frac{1}{10}(n+4)u_6\mathcal{F}_1(0), \tag{151}$$

where

$$\mathcal{F}_1(r) = \frac{1}{(2\pi)^3} \int d^3k \, G(k, r) \tag{152}$$

with Green's function

$$G(k,r) = (k^2 + r)^{-1},$$
(153)

and r is the reciprocal susceptibility (see Equations 36 and 39).

$$\mu = 0, \quad Q = 0, \quad \text{and} \quad \zeta = 0$$
 (154)

corresponds to the tricritical point in the new coordinates.

Stephen et al. (1975) have employed the diagrammatic technique to build the theory of the tricritical region provided that

$$u_6 < 1 \quad \text{and} \quad Q^2/r < 1.$$
 (155)

The results have been obtained in terms of the vertex functions $\Gamma^{(2)}(r)$, $\Gamma^{(4)}(r)$, and $\Gamma^{(6)}(r)$:

$$\Gamma^{(2)}(r) = \mu - \frac{5}{6} \cdot \frac{n+2}{6-n} \cdot \frac{Q^2}{u_6} \left[\mathcal{L}^{1-2p}(r) - 1 \right], \tag{156}$$

$$\Gamma^{(4)}(r) = \frac{Q}{\mathcal{L}^p(r)},\tag{157}$$

$$\Gamma^{(6)}(r) = \frac{u_6}{\mathcal{L}(r)},\tag{158}$$

where

$$\mathcal{L}(r) = 1 - \frac{3n + 22}{480\pi^2} u_6 \ln r, \tag{159}$$

$$p = \frac{2(n+4)}{3n+22}.$$
(160)

The vertex functions and the order parameter M are used to express, eg., the reciprocal susceptibility

$$r = \Gamma^{(2)}(r) + \frac{1}{2}\Gamma^{(4)}(r)M^2 + \left(\frac{1}{4!}\right)\Gamma^{(6)}(r)M^4$$
(161)

and the state equation

$$\zeta = \Gamma^{(2)}(r)M + \frac{1}{3!}\Gamma^{(4)}(r)M^3 + \frac{1}{5!}\Gamma^{(6)}(r)M^5.$$
(162)

Equations 154, 156, and 157 are followed by the conditions of the tricritical state, expressed through the vertex functions

$$\Gamma^{(2)}(r) = 0$$
 and $\Gamma^{(4)}(r) = 0.$ (163)

These results are applied to build the theory of tricritical region in polymer systems (see section 5.5).

Chapter summary

1. Light scattering by a dipole in a plane is considered. Colloidal scattering is discussed using the Rayleigh-Debye approximation, which holds for optically-soft any-form particles comparable with the wavelength.

The Rayleigh-Debye approximation is of great significance for exploring substance with a statistically-heterogeneous (continuous) structure described with the correlation functions formalism. In this case, the scattering intensity is proportional to the correlation volume (w) representing the Fourier image of the correlation function for the order parameter (such as: the density of one-component substance, the component concentration in mixture).

The premises and main results of the van de Hulst approximation are given and used (as well as the rigorous Mie theory) in the turbidity spectrum method applied for the characterization of ill-defined disperse systems.

In particular, the ensemble of a new phase during phase separation proceeding in a multi-component system belongs to such systems. In this case, the turbidity spectrum method provides the determination of the mass-volume new-phase particle concentration, as well as the degree of phase transition; this can be used to construct the molecular-mass polymer distribution function (the method of spectroturbidimetric titration for polymer solutions—subsection 3.2.3) and for a phase analysis (identification) of the phase separation type in polymer systems (paragraph 3.6.2.5, sections 6.2 and 6.4).

The determination of particle sizes in the process of phase separation gives information about the mechanism of phase separation kinetics.

The schemes and tables of various applications of the turbidity spectrum method are given, and the fields of its practical applications are briefly listed.

A master table is presented containing the formulae of colloidal scattering for the characteristic quantities τ , R_{90} , R_{θ} , and $R_{90\perp}$ in terms of polarizability α , permittivity ϵ and refractive index μ of the components in the Rayleigh and Rayleigh-Debye approximations is given.

2. Light scattering in one-component liquids (including the region of critical opalescence) is of great importance in solving a number of problems discussed in this book.

A radial function of molecule distribution and interparticle distribution functions are included into consideration.

The pair distribution function, in terms of which all the thermodynamic functions of liquid are expressed, is of particular significance in the liquid state theories.

To describe the liquid behaviour in the critical region, the pair correlation function h(r) and the direct correlation function C(r) are introduced.

The correlation of density fluctuations in the critical region is determined by the longrange correlation distance ξ_{ρ} (Equation 2.3 129) characterizing the efficiency of the correlation falls of density fluctuations with distance.

Light scattering in liquids within the critical region is described with the Rayleigh-Debye approximation including the correlation functions formalism.

The intensity of light scattering is proportional to the correlation volume w_{ϵ} corresponding to the Fourier transformant h(r), i.e. $w_{\epsilon} = \tilde{h}(q)$.

2. Chapter summary

To such a formalism of light scattering in the critical region leads Debye's consideration based on adding to the free energy function a term containing the square of the density gradient and taking into account the correlation of density fluctuations in the critical region as the first approximation.

3. The opinion on the symbathy of the scattered light intensity and the molecular association can often be found in the literature. Meanwhile, there can be just the other way about. The low value of the intensity of light scattered in water being the most structured (associated) liquid is an example.

The matter is the association suppresses the development of density fluctuations, which causes a low compression and a low turbidity value.

A similar effect can be observed in polymer systems as well. For instance, the intensity of scattered light is an extremal function of the polymer concentration in solution (section 3.3.1.1.1).

At high polymer concentrations, the solution turns very transparent (up to the condensed state of the polymer) due to suppressing concentration fluctuations by the increas ing viscosity.

In gels, cross-links withstand concentration fluctuations and classic gels are characterized by high transparency.

Of course, if cross-links are caused by crystallites, the gel structure becomes heterogeneous, which is accompanied by high turbidity of such gels (section 3.5.5).

Dynamic light scattering in one-component liquid is the beginning of the consideration of this phenomenon as well as of the investigative method.

4. In a two-component system, both light scattering and diffusion depend directly upon the value of $\partial \mu_1/\partial x_2$ (or an equivalent one) which, in turn, determines the thermodynamic stability of the one-phase system state and the level of concentration fluctuations (cf. formulae 1.1.2-53, 1.4-35, and 2.4-8,-9,-43). Due to this, near the mixture critical concentration x_{2c} at the isotherm of the state diagram there are both a maximum of the scattered light intensity and a minimum of the diffusion coefficient $D(x_2)$ (see Fig-

ures 2.36 and 2.37). As the configurative point approaches the spinodal, $\left(\frac{\partial \mu_1}{\partial x_2}\right)_{T,P} \to 0$,

the scattered light intensity increases and the diffusion coefficient D decreases.

In the nearest vicinity of the spinodal, concentration fluctuations become correlated, and it is necessary to pass from Rayleigh-Einstein's scattering to Rayleigh-Debye's approximation for the correct description of light scattering.

In the spinodal vicinity $D \rightarrow 0$, and according to the Fick first law, it must cause an infinitely slow diffusional stream (the so-called critical retardation). This leads to principal difficulties in the approach of the configurative point to the spinodal. According to Onsager's hypothesis, the evolution of the order parameter fluctuations in the critical region obeys macroscopic regularities. In that case, the effect of critical retardation shows itself in a low rate of the resolution of spontaneously appeared concentration fluctuations, and the solution morphology in the critical region can be compared with a colloidal system, with long-living heterophase concentration fluctuations being particles (quasi-particles) of the disperse phase.

5. The relation between the scattering of radiation and diffusion manifests itself directly in the dynamics of concentration fluctuations as well; as a result, the diffusion coefficient,

as well as other transport (hydrodynamic) solution characteristics, can be obtained from the spectrum of scattered light. However, some difficulties in interpreting experimental data near the spinodal due to the increase of the correlation range of concentration fluctuations arise in the methodology of inelastic light scattering. It causes the failure of Onsager's principle being the basis for the theory of dynamic light scattering in the hydrodynamic approximation. That is why a theory of dynamic light scattering in the approximation of mode-mode coupling has been developed for the nearest vicinity of the spinodal.

6. The influence of the order parameter fluctuations on the system's properties is taken into account to a first degree within the general mean field theory by means of adding a gradient term to the expansion of the thermodynamic potential in terms of the order parameter.

In this approximation, the correlations of the order parameter fluctuations are described with the exponential correlation function within long-range correlations ξ . The level of the order parameter fluctuations allowing the mean field approximation is determined by the Ginzburg parameter.

The given mean field approximation enables one to relate ξ to the coefficients of both the square and gradient terms in the expansion of the potential (Equation 2.5–13).

On the basis of this relation, the deduction of the state equation for polymer systems, taking into account the fluctuations in the component concentration in the mean field approximation has been done (Equation 3.7-36).

7. The existence of large correlated regions of the order parameter ξ in the critical region affects mainly the system's properties, so the specific features of the short-range intermolecular interactions no longer play a significant role.

This serves as a physical basis for the scaling hypothesis regarding the critical indices to be related to each other, so only the values of any two ones are necessary for the determination of them all.

It follows from the same that the property of homogeneity of the system's thermodynamic potentials holds.

The existence of large-distance fluctuations of the order parameter in the critical region leads also to the universality hypothesis, according to which the properties of thermodynamic functions of different physical systems are given by the space dimensionality d and the order parameter dimensionality n. The systems with equal d and n form a class of universality with the same critical indices.

The model of self-avoiding walks of segments on a 3D lattice, which is equivalent to a polymer chain conformation in a good solvent, is a special class of universality with d = 3 and n = 0.

Section 2.6 gives the Lagrangian formalism of field theory. The properties of the correlation function of the order parameter G (Green's function) are treated in detail, since many experimentally determined values are expressed in terms of this function.

The diagrammatic technique is successfully used to calculate Green's functions. The rules for drawing graphs, as well as many examples of the correspondence between algebraic expressions and graphs representing different contributions into Green's function values, are given.

The properties of the connected Green function are specially discussed. The latter can

2. Chapter summary

be represented with a connected graph.

For the majority of physical systems, the Lagrangian is invariant to any space translation. In this case, all the equations of the theory can be simplified by means of Fourier's transformation, i.e. by considering the characteristic values in the momentum space. The rules for drawing graphs of the characteristic values in the momentum space are given.

The property of the graph one-particle reducibility allowing to simplify significantly the corresponding algebraic expressions is considered.

The properties of vertex functions playing an important role in field theory (the free energy and the state equation of a system can be obtained with their help) are discussed in detail.

Vertex functions and Green's ones, including combined operators are considered. They are of great significance for the description of the phase transitions of the continuous type.

The attributes of the symmetrical tricritical point in the common-type system described by the Hamiltonian (2.6-149) are given.

The expressions for the susceptibility and the state equations of a system in terms of the vertex functions $\Gamma^{(2)}$, $\Gamma^{(4)}$, and $\Gamma^{(6)}$ in the tricritical region are given. The equalities $\Gamma^{(2)} = \Gamma^{(4)} = 0$ serve as a condition of the tricritical state.

Chapter 3

Polymer+low-molecular-liquid system. Mean field approaches. Liquid-liquid phase separation

3.1. Binary systems

3.1.1. State equations

The ideas of regular mixtures find application in the description of the properties of the system polymer+low-molecular-weight liquid (P+LMWL).

Flory-Huggins' theory (Flory, 1941, 1942, 1945; Huggins, 1941, 1942abc, 1958; Tompa, 1956; Volkenshtein, 1959; Casassa, 1976, 1977) is based on a model of a rigid lattice of m cells, whose volume w_1 is commensurable to that of the LMWL molecule. The lattice with the coordination number ν contains m_2 macromolecules and m_1 LMWL molecules. Each macromolecule is composed of z fragments (segments), each occupying one cell of the lattice:

$$z = \frac{w_2}{w_1} = \frac{w_2 N_A}{w_1 N_A} = \frac{\bar{V}_{02}}{\bar{V}_{01}} = \frac{v_2 M_2}{\bar{V}_{01}},\tag{1}$$

 V_{0i} being the molar volume of the components, \bar{v}_2 the specific partial volume of polymer, M_2 its molecular weight (hereinafter $M_2 = M$), w_2 the volume of a macromolecule. Then, the volume fractions of the components are expressed as

$$v_1 = \frac{m_1}{m_1 + zm_2} = \frac{n_1}{n_1 + zn_2},\tag{2}$$

$$v_2 = \frac{zm_2}{m_1 + zm_2} = \frac{zn_2}{n_1 + zn_2},\tag{3}$$

where $n_i = m_i/N_A$ are the numbers of moles.

According to the general principles of statistical thermodynamics, ΔS_m , ΔH_m and

$$\Delta G_m = \Delta H_m - T \,\Delta S_m \tag{4}$$

are derived in terms of this model. In view of Equation 1.1.1 49,

$$\Delta S_m = S - n_1 \tilde{S}_{01} - n_2 \bar{S}_{02} = n_1 \bar{S}_1 + n_2 S_2 - n_1 \bar{S}_{01} - n_2 \bar{S}_{02}.$$
(5)

The entropy S of the mixture, using Boltzmann's formula

$$S = k \ln \Omega, \tag{6}$$

is expressed via the number of ways to realize the state system Ω , i.e. the number of ways to arrange the structural elements on the lattice.

In this approximation, the lattice contains m_2 macromolecules, while the other cells are occupied with m_1 LMWL molecules.

In order to calculate Ω , determine the number β_{i+1} of possible arrangements of the (i + 1)th macromolecule given the *i* previous ones are prearranged, and the fraction of occupied cells zi/m is assumed equal over the whole lattice as well as in its certain local place (the mean field approximation). This situation is valid for moderate (middle) polymer concentrations and, certainly, is not the case in dilute solutions.

In the case of **flexible** chains, no restrictions are imposed on the placement of all the z chain fragments, i.e. every next fragment can occupy any neighbouring cell but one occupied by the previous fragment.



Figure 3.1. A pattern of the (i + 1)th macromolecule being placed on the lattice

Thus, (m-zi) cells are accessible, on the average, for the first fragment of the (i + 1)th macromolecule. The second fragment, due to its being linked with the first one, can occupy, generally speaking, ν neighbouring cells but the part of them occupied by fragments of the i previously arranged macromolecules, so the number of accessible cells is

$$\Omega_{(i+1)2} = \nu - \nu_{oc}.$$

It is presumed that

$$\frac{\nu_{oc}}{\nu} = \frac{zi}{m},\tag{7}$$

then

$$\Omega_{(i+1)2} = \nu \left(1 - \frac{zi}{m} \right). \tag{8}$$

The number of accessible cells for the third and subsequent fragments is

$$\Omega_{(i+1)3} = (\nu - 1) \left(1 - \frac{zi}{m} \right), \tag{9}$$

as one cell is occupied by the previous fragment.

For simultaneous arrangement of, say, four fragments,

$$\beta_{(i+1)4} = (m-zi)\nu(\nu-1)^2 \left(1-\frac{zi}{m}\right)^3,\tag{10}$$

and of all z ones,

$$\beta_{i+1} = (m-zi)\nu(\nu-1)^{z-2} \left(1-\frac{zi}{m}\right)^{z-1},\tag{11}$$

or, assuming $\nu \approx \nu - 1$,

$$\beta_{i+1} = \frac{(m-zi)^{z}(\nu-1)^{z-1}}{m^{z-1}}.$$
(12)

In the case of large m, z, and i, the relationship

$$(m-zi)^{z} \approx \frac{(m-zi)!}{[m-z(i+1)]!}$$
 (13)

applies with good accuracy; one can verify it, taking specific examples. Then,

$$\beta_{i+1} \cong \frac{(m-zi)! \, (\nu-1)^{z-1}}{[m-z(i+1)]! \, m^{z-1}}.$$
(14)

When m_2 macromolecules are arranged simultaneously,

$$\Omega = \frac{\prod_{i=0}^{m_2-1} \beta_{i+1}}{m_2!},$$
(15)

where possible identical conformations of m_2 macromolecules are excluded. Substituting Equation 14 to Equation 15, we get

$$\Omega = \frac{m!(\nu-1)^{z-1}(m-z)!(\nu-1)^{z-1}\cdots[m-z(m_2-1)]!(\nu-1)^{z-1}}{m_2!(m-z)!m^{z-1}(m-2z)!m^{z-1}\cdots[m-z(m_2-1)]!m^{z-1}(m-zm_2)!m^{z-1}}$$
$$= \frac{(m_1+zm_2)!}{m_1!m_2!} \left(\frac{\nu-1}{m_1+zm_2}\right)^{m_2(z-1)}$$
(16)

With Stirling's formula applied to Equation 6, in view of Equation 16, and transferring to moles, we obtain

$$S = -Rn_1 \ln \frac{n_1}{n_1 + zn_2} - Rn_2 \ln \frac{n_2}{n_1 + zn_2} + Rn_2(z-1) \ln \frac{\nu - 1}{e}.$$
 (17)

By virtue of m_1 LMWL molecules being indiscernible in the lattice of m_1 cells,

$$S_{01} = k \ln \frac{m_1!}{m_1!} = 0, \tag{18}$$

while

$$n_2 \bar{S}_{02} = (n_1 \hat{S}_1 + n_2 \tilde{S}_2) |_{n_1 = 0} = S|_{n_1 = 0}, \qquad (19)$$

which reflects the entropy of polymer disorientation from complete order (an ideal crystal) to chaotical disorder (the amorphous state). Equations 5, 17–19, including Equations 2 and 3, yield

$$\Delta S_{m,comb} = -R(n_1 \ln v_1 + n_2 \ln v_2). \tag{20}$$

The mean molar combinatorial entropy of mixing (Equation 1.1.1-50) per mole of lattice cells $n = n_1 + zn_2$ is expressed as

$$\Delta \hat{S}_{m,comb} = -R(v_1 \ln v_1 + \frac{v_2}{z} \ln v_2).$$
(21)

If we pass onto mole fractions,

$$x_1 = \frac{n_1}{n_1 + n_2} = \frac{zv_1}{zv_1 + v_2}; \qquad x_2 = \frac{n_2}{n_1 + n_2} = \frac{v_2}{zv_1 + v_2}$$
(22)

and

$$v_1 = \frac{x_1}{x_1 + zx_2}; \qquad v_2 = \frac{zx_2}{x_1 + zx_2},$$
(23)

we can make sure that the entropy of mixing $\Delta \bar{S}_{m,comb}$ (Equation 21) is larger than that of an ideal mixture $\Delta \bar{S}_{m,id}$ (Equation 1.1.3-20) (Kubo, 1968) ($\Delta S_{m,comb} = \Delta \bar{S}_{m,id}$ at z = 1). This is a peculiar feature of mixing of flexible macromolecules in comparison with that of the rigid ones of the same molecular weight.

Of course, the entropy of mixing of m_1 LMWL molecules with the same number zm_2 of disconnected fragments (i.e. with zm_2 molecules of a LMW substance) will be larger.

Note that the restrictions of the above deduction are also caused by the fact that the links among the fragments of the previously placed i macromolecules were in no way accounted for, though these links were certainly taken into account when placing the (i + 1)th macromolecule (Equations 8-10).

According to the general idea of the model of regular solutions (subsection 1.3.1), it is assumed that $\Delta H_m \neq 0$ in Equation 4 and the combinatorial entropy of mixing $\Delta S_{m,comb}$, whose derivation neglects the influence of energy interactions on the character of arrangement of the mixture's structural elements, acts as the entropy of mixing.

The excess functions of mixing are usually defined by Equation 1.1.3-28, though other versions are known (Shakhparonov, 1956). In particular, it is reasonable to define excess functions of mixing for polymer solutions by

$$\Delta Z_m = \Delta Z_{m,comb} + \Delta Z_{m,ex},\tag{24}$$

with $\Delta S_{m,ex} = 0$ in the model of a regular solution. If the calculation of ΔH_m in Flory-Huggins' theory is carried out by means of the pair interaction model (see subsection 1.3.1 and section 1.5), then the contacts 1-2 and 2-2 are understood as a contact between a LMWL molecule and a fragment of a macromolecule, and a contact between two fragments of macromolecules, respectively,

$$\Delta H_m = P_{12} \,\Delta \varepsilon,\tag{25}$$

where P_{12} is the number of contacts between LMWL molecules with macromolecule fragments, $\Delta \varepsilon$ is the difference between the energies of interaction of the structural elements (the energy of mixing) per contact (Equation 1.3-4). As well as in subsection 1.3.1, $\Delta H_m = \Delta E_m$ owing to $\Delta V_m = 0$ (the model of a rigid lattice).

In the arrangement pattern (Figure 3.1), every non-end macromolecule fragment contacts $(\nu - 2)$ LMWL molecules, and the whole of the macromolecule possesses $z(\nu - 2)$ mixed contacts and 2 end ones. For m_2 macromolecules, the number of contacts is $m_2[(\nu - 2)z + 2]$.

Only a part of these contacts are realized due to the prearrangement of the *i* macromolecules. The efficiency factor of the mixed contact number is assumed to be equal to v_1 , so

$$P_{12} = m_2 [(\nu - 2)z + 2]v_1 \approx m_2 \nu z v_1.$$
⁽²⁶⁾

Substituting zm_2 from

$$\frac{zm_2}{m_1} = \frac{v_2}{v_1}$$

to Equation 26, we get

$$P_{12} \simeq \nu v_2 m_1. \tag{27}$$

Introduce a dimensionless interaction parameter (Flory-Huggins' parameter) χ as the interaction energy per LMWL molecule expressed in kT units

$$\chi = \frac{\nu \,\Delta\varepsilon}{kT},\tag{28}$$

i.e. χ characterizes the variation of the interaction energy as a result of an arbitrary transfer of a LMWL molecule from the medium of LMWL into the surrounding of polymer fragments after their disconnection (see Figure 3.1). After such a procedure, ν bonds with ε_{11} and ν bonds with ε_{22} are broken and ν bonds with ε_{12} appear.

Substituting Equation 27 to Equation 25, and with due account of Equation 28, we obtain

$$\Delta H_m = RT n_1 v_2 \chi,\tag{29}$$

and, per mole of the lattice's cells,

_

$$\Delta H_m = RT v_1 v_2 \chi. \tag{30}$$

With allowance for Equations 20 and 29, the Gibbs potential of mixing can be written as

$$\Delta G_m = RT(n_1 \ln v_1 + n_2 \ln v_2 + \chi n_1 v_2) \tag{31}$$

and (see Equations 30 and 21)

$$\Delta \tilde{G}_m = RT(v_1 \ln v_1 + \frac{v_2}{z} \ln v_2 + \chi v_1 v_2).$$
(32)

Comparison of Equations 28 and 1.3-9 leads to

$$\chi = \frac{\alpha}{RT} \tag{33}$$

(see section 1.3 to refresh α).

Thus, on replacement of the volume fractions by the mole ones, Equation 32 exhibits a deep analogy with Equation 1.3-10.

The first versions of the theory considered only endothermic mixing and $\chi \ge 0$, i.e. the energy of mixed contacts ε_{12} is less than the sum of the energies of homogeneous contacts ε_{ij} by magnitude (cf. Equation 1.3-7). The choice of this condition seems completely natural in the methodology of regular mixtures where the non-combinatorial entropy of mixing is neglected (to simplify calculations). By virtue of $\chi \ge 0$, the third term in Equations 31 and 32 is positive, while the first and second ones are always negative. It follows that χ determines the thermodynamic **quality** (affinity) of the solvent: the less χ , the more negative the Gibbs potential of mixing ΔG_m is and the more preferable is mixing (see Equation 1.1.3-14).

As z increases, the second negative term in Equation 32 diminishes in magnitude, leading to the same decrease of the negative potential of mixing. This explains the wellknown fact: the higher the molecular weight of a polymer, the worse its solubility.

Flory-Huggins' interaction parameter χ proves to be semiempirical (in particular, due to ν being indetermined). On the other hand, this circumstance enables χ to be generalized with the model of regular solutions to be replaced by a more realistic model of **strictly regular solutions** with $\Delta S_{ex} \neq 0$ or with a non-zero uncombinatorial contribution to the entropy of mixing (cf. Equation 24)

$$\Delta S_{\text{uncomb}} \neq 0. \tag{34}$$

Such a transfer to the model of strictly regular solutions can be made by giving the quantity $\Delta \epsilon$ in Equation 28 the meaning of an additional increment of the Gibbs potential

$$\Delta \varepsilon \to \Delta g = \Delta h - T \,\Delta s_{uncomb},\tag{35}$$

where Δs_{uncomb} is given the sense of a non-combinatorial component of the overall entropy change (the zero approximation of strictly regular solutions) (Tompa, 1956), Δh is the enthalpy change.

In the general case, χ should be, of course, a function of the polymer concentration and molecular weight (more rigorously, a function of the molecular-weight distribution). The concentration dependence of χ can be represented, generally, by means of an expansion series in terms of v_2

$$\chi = \chi_1 + \chi_2 v_2 + \chi_3 v_2^2 + \cdots .$$
(36)

Then, no concentration dependence $(\chi = \chi_1)$ can be accepted as the first approximation of Flory-Huggins' theory. The second one must be related to an explicit concentration dependence of χ with the coefficients χ_1, χ_2, χ_3 etc. to be determined (see subsection 3.6.2 for details).

The third approximation accounts for the dependence of χ on the polymer molecular weight (see subsection 3.6.3 for details).

So, at $\chi = \chi_1 = const$ and including Equations 35 and 28, we get

$$\chi_1 = \frac{\nu \Delta h}{kT} - \frac{\nu \Delta s_{uncomb}}{k}.$$
(37)

Introduce two interaction parameters, namely, the enthalpy parameter

$$\kappa_1 = \frac{\nu \,\Delta h}{kT} \tag{38}$$

and the entropy parameter

$$\psi_1 = \frac{1}{2} + \frac{\nu \,\Delta s_{uncomb}}{k},\tag{39}$$

then

$$\chi_{1} = \kappa_{1} - \psi_{1} + \frac{1}{2}.$$
(40)

Their ratio defines the Flory temperature θ

$$\frac{\kappa_1}{\psi_1} = \frac{\theta}{T}.\tag{41}$$

Therefore, transfer to the model of strictly regular solutions leads to the addition of the second summand to the expression for χ in comparison with Equation 33

$$\chi = \chi_1 = \frac{\alpha}{RT} + \beta. \tag{42}$$

It follows from Equation 37, with allowance for Equation 38, that

$$\frac{\partial \chi_1}{\partial T} = -\frac{\nu \,\Delta h}{kT^2} = -\frac{\kappa_1}{T}, \qquad \text{and} \qquad \kappa_1 = -T\left(\frac{\partial \chi_1}{\partial T}\right),\tag{43}$$

and (see Equation 39)

$$\frac{\partial(\chi_1 T)}{\partial T} = \frac{1}{2} - \psi_1. \tag{44}$$

In the symbols of Equation 42,

$$\kappa_1 = \frac{\alpha}{RT},\tag{45}$$

$$\psi_1 = \frac{1}{2} - \beta. \tag{46}$$

The expressions of the Gibbs potential of mixing, like Equations 31 and 32 with χ comprising two summands, $\chi_s + \chi_H$, are derived immediately within the framework of the methodology of strictly regular solutions, see Equations 4.65 and 4.80 in (Tompa, 1956). In the zero approximation

$$\chi = \chi_s + \chi_H \tag{47}$$

with

$$\lim_{\nu_2 \to 0} \chi_H = \kappa_1, \tag{48}$$

$$\lim_{\nu_2 \to 0} \chi_s = \frac{1}{2} - \psi_1. \tag{49}$$

At $\chi = \chi_{1}$, it follows from Equation 31 that

$$\Delta \mu_1 = \frac{\partial \Delta G_m}{\partial n_1} = RT \left[\ln(1 - v_2) + \left(1 - \frac{1}{z}\right) v_2 + \chi_1 v_2^2 \right],\tag{50}$$

$$\Delta \mu_2 = \frac{\partial \Delta G_m}{\partial n_2} = RT \left[\ln v_2 - (z-1)(1-v_2) + \chi_1 z (1-v_2)^2 \right].$$
(51)

In comparison with the plots of the concentration dependences of $\Delta \mu_1$ and $\Delta \mu_2$ (Figure 1.5), the functions $\Delta \mu_1(v_2)$ and $\Delta \mu_2(v_2)$ (Figures 3.2 and 3.3) show a strong asymmetry caused by a drastic difference in the molecular sizes of the components. If we confine ourselves to small v_2 in Equation 50 (so that $\ln(1-v_2) \approx -v_2 - v_2^2/2 - \cdots$) and let $z \to \infty$, then it follows from Equations 1.2-27, 1.3-37, 1, 2.4-26 and 50 that

$$\mathcal{A}_{2} = \frac{\dot{v}_{2}^{2}}{\bar{V}_{01}} \left(\frac{1}{2} - \chi_{1} \right)$$
(52)

or (see Equation 40)

$$\mathcal{A}_2 = \frac{\bar{\mathbf{v}}_2^2}{V_{01}} \psi_1 \left(1 - \frac{\kappa_1}{\psi_1} \right) \tag{53}$$

or (see Equation 41)

$$\mathcal{A}_2 = \frac{\bar{\mathbf{v}}_2^2}{\bar{V}_{01}} \psi_1 \left(1 - \frac{\theta}{T} \right). \tag{54}$$

Certainly, the second virial coefficient A_2 also determines the solvent thermodynamic quality, being related (in this approximation) to χ_1 by Equation 52 and to other parameters by Equations 53 and 54, which is shown in Figure 3.4.

At $T = \theta$, $A_2 = 0$ (see Equation 54) and, according to Equations 52 and 53,

$$\chi_1 = \frac{1}{2}, \quad \kappa_1 = \psi_1 \tag{55}$$

(see Figure 3.4).

At $T = \theta$, a polymer solution is sometimes called ideal as $A_2 = 0$ (cf. Equations 1.2-29 and 1.3-38).

In contrast to the ideal mixtures of LMW substances, here $A_2 = 0$ is not a consequence of the solution being **athermal**. As $\Delta \bar{S}_{m,comb} > \Delta S_{m,id}$, for $\Delta \bar{G}_m = \Delta \bar{G}_{m,id}$ (where $\Delta \bar{G}_m$ and $\Delta \bar{G}_{m,id}$ are defined by Equations 32 and 1.1.3–15, respectively) to be valid, the large combinatorial entropy of mixing must be compensated for by a negative contribution of the enthalpy of mixing (see Equation 55).

To emphasize this circumstance, polymer solutions at $T = \theta$ are sometimes called **pseudoideal**, or just solutions in the **theta solvent**.

Unlike Equations 52-54, experimental data show a power dependence of \mathcal{A}_2 on molecular weight: $\mathcal{A}_2 \sim M^{-i}$.

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Figure 3.2. Chemical potential of mixing of LMW component (a) and that of polymer (b) in RT units against the volume fraction of polymer v_2 , z = 1,000 (the values of χ_1 are specified near the curves) (Tompa, 1956) [H.Tompa Polymer Solutions. Copyright © 1956 by Academic Press]

That there is no M dependence of A_2 in Equations 52-54 is due to the fact that the segments of i macromolecules are regarded as disconnected when the number of ways to place the (i + 1)th one is being determined.


Figure 3.3. Chemical potential of mixing of LMW component $\Delta \mu_1$ in its mixture with polymer (z = 1,000) against the volume fraction of polymer (the values of χ_1 are specified near the curves) (Tompa, 1956) [H.Tompa *Polymer Solutions*. Copyright © 1956 by Academic Press]

There is an alternative approach to evaluate χ_1 . Extract it from Equation 50:

$$\chi_1 = \frac{\Delta \mu_1}{v_2^2 RT} - \frac{1}{v_2^2} \left[\ln(1 - v_2) + \left(1 - \frac{1}{z}\right) v_2 \right].$$
(56)

On the other hand,

$$\Delta \mu_1 = \Delta \mu_{1\text{comb}} + \Delta \mu_{1\text{ex}}.$$
(57)

According to Equation 50,

$$\Delta \mu_{1\text{comb}} = \Delta \mu_1 \Big|_{\chi_1 = 0} = RT \left[\ln(1 - v_2) + \left(1 - \frac{1}{z} \right) v_2 \right].$$

Having divided both the sides of Equation 57 by $v_2^2 RT$ and rearranged the terms, we get

$$\frac{\Delta\mu_{1ex}}{v_2^2 RT} = \frac{\Delta\mu_1}{v_2^2 RT} - \frac{1}{v_2^2} \left[\ln(1-v_2) + \left(1-\frac{1}{z}\right)v_2 \right].$$
(58)

Comparison between Equations 56 and 58 leads to

$$\chi_1 = \frac{\Delta \mu_{1ex}}{v_2^2 RT},\tag{59}$$

which can be regarded as the definition of χ_1 in the first approximation of the model of strictly regular solutions. The zero approximation (Shakhparonov, 1956, p. 327) follows from Equations 58 and 59 provided that $v_2 \rightarrow 0$ and $z \rightarrow \infty$, so that

$$\ln(1-v_2) \approx -v_2 - \frac{v_2^2}{2} - \cdots,$$



Figure 3.4. Thermodynamic and structural parameters in the P+LMWL system with an UCST $\,$

$$\chi_1 \cong \frac{\Delta \mu_1}{v_2^2 RT} + \frac{1}{2}.$$
(60)

If $\Delta \mu_1$ is represented as

$$\Delta \mu_1 = \Delta \bar{h}_1 - T \,\Delta \bar{s}_1 \tag{61}$$

and

$$\kappa_1 = \frac{\Delta h_1}{v_2^2 RT},\tag{62}$$

$$\psi_1 = \frac{\Delta \bar{s}_1}{v_2^2 R},\tag{63}$$

are defined, then Equation 60 yields

$$\chi_1 = \kappa_1 - \psi_1 + \frac{1}{2} \tag{64}$$

in accordance with Equation 40.

If we substitute Equation 64 to Equation 60 and take Equation 41 into account, then

$$\Delta \mu_1 = v_2^2 R T(\kappa_1 - \psi_1), \tag{65}$$

$$\Delta \mu_1 = -v_2^2 RT \psi_1 \left(1 - \frac{\theta}{T} \right). \tag{66}$$

In view of Equation 54,

$$\Delta \mu_1 = -\frac{\mathcal{A}_2 \bar{V}_{01}}{\bar{v}_2^2} v_2^2 RT.$$
(67)

Huggins (1942a) has shown that in Equation 47, $\chi_s \cong 1/\nu$. Typical experimental values of χ_s fall inside 0.3...0.4 in excellent agreement with the theory (Blanks and Prausnitz, 1964; Rebenfeld et al., 1976).

For the enthalpy component, Huggins (1942a) obtained

$$\chi_{\mu} \simeq \frac{V_{01}}{RT} (\delta_P - \delta_1)^2, \tag{68}$$

where δ_P , δ_1 are Hildebrand's solubility parameters of the polymer and solvent which have the same meaning as in the theory of regular solutions of LMW components by Hildebrand and Scott (1950). This theory gives for the enthalpy of component mixing (Shakhparonov, 1963: Read et al., 1977)

$$\Delta H_m = V \left[\left(\frac{W_1}{\bar{V}_{01}} \right)^{1/2} - \left(\frac{W_2}{\bar{V}_{02}} \right)^{1/2} \right]^2 \upsilon_1 \upsilon_2, \tag{69}$$

where W_i is the energy of liquid vapourization per mole and V is the total volume of mixing. The **cohesion energy density** (CED) W_i/\bar{V}_{0i} is determined by the set of intermolecular forces in liquid, and the quantity

$$\delta_i = \left(\frac{W_i}{V_{0i}}\right)^{1/2} \tag{70}$$

is called Hildebrand's solubility parameter (cf. Equation 2.4-14).

There appears a solubility parameter δ_1 of a LMWL in Equation 68, corresponding to Equation 70. The solubility parameter of polymer δ_P is calculated by means of Small's (1953) group contribution or measured by the density of a dilute solution, by equilibrium swelling (van Krevelen, 1972; Barton, 1975), and by turbidimetric titration (Suh and Clarke, 1967, 1968; Elias, 1977). See also: Lipatov et al. (1971), Tager et al. (1976b), Yakovlev et al. (1984).

Askadski et al. (1977) have proposed a procedure to calculate the CED of LMWL and polymers in terms of the molecule packing coefficients. These values match those calculated by means of Small's method in the case of simple non-polar liquids and are closer to the experimental ones for more complex (polar and with II-bonds) liquids.

Thus, assuming Equation 68 for χ_{μ} and the mean experimental value for χ_{s} , we obtain

$$\chi_1 = \chi_s + \chi_H = 0.34 + \frac{\bar{V}_{01}}{RT} (\delta_P - \delta_1)^2.$$
(71)

Initially, the solubility parameter δ was applied to liquids with intermolecular interactions of the dispersion type. Then, δ has been represented by a three-component parameter caused by dispersion δ_d and polar interactions δ_p , and the ability to form H-bonds δ_h (Crowley et al., 1966, 1967; Barton, 1975; Rebenfeld et al., 1976; Blanks, 1977)

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2}.$$

It follows from Equation 71 that the best solubility (compatibility) is shown by components with close solubility parameters.

Tager and Kolmakova (1980) report the details and a discussion of the solubility parameters of polymers.

Let us emphasize once again that state equation 31 does not suit dilute solutions where macromolecules are separated by long spaces on the lattice (see Figure 3.1) filled with LMWL molecules, which excludes Equations 7 and 26 while deriving Equation 31.

That is why the state equation of the P+LMWL system in the range of small concentrations turns out to be that of a macromolecular coil, which is a system (subsystem) of inany structural elements.

Ilence, to an individual molecular coil are applicable the relationships of statistical thermodynamics and statistical physics, on the basis of which the state equation of a molecular coil is written down. To solve this problem, a model of the system (subsystem) is required. One model (lattice's, more exactly, cell's) was used at the beginning of this section.

Let us consider other models. One of them (Freed, 1972) assumes a chain to comprise (n + 1) units (monomers), linked to each other consecutively and enumerated $0, 1, \ldots n$.

The locations of the units are defined by a set of coordinates $\{\vec{r}_k\}$ with respect to a certain arbitrarily-chosen origin of coordinates. If no external force is applied and space is isotropic, $\vec{r}_0 \equiv 0$ can be chosen as a coordinate origin. Then, the potential energy of the chain is written as

$$u(\{\vec{r}_k\}) = \sum_{j=1}^{n} u_j(\vec{r}_{j-1}, \vec{r}_j) + \varphi(\{\vec{r}_k\}).$$
(72)

Here u_j reflects the chains being sequentially linked, and φ involves all the other interactions. All the statistical properties of the chain are defined by the distribution

$$G(\{\vec{r}_k\}) = \exp\left[-u(\{\vec{r}_k\})/kT\right].$$
(73)

The partition function is calculated as

$$\mathcal{Z} = \int d\{\vec{r}_k\} \exp\left[-u(\{\vec{r}_k\})\right] \equiv \int d\{\vec{r}_k\} G(\{\vec{r}_k\}),$$
(74)

where $d\{\vec{r}_k\} = \prod_{k=1}^n d\vec{r}_k$, when $\vec{r}_0 \equiv 0$. The normalized distribution function of chain conformations is defined in the standard way

$$P(\{\vec{r}_k\}) = \mathcal{Z}^{-1} G(\{\vec{r}_k\}).$$
(75)

As usual, $P(\{\vec{r}_k\}) d\{\vec{r}_k\}$ is the probability of such a conformation, when the chains are placed between $\{\vec{r}_k\}$ and $\{\vec{r}_k + d\vec{r}_k\}$ (all $k \neq 0$).

The main property of a polymer chain is, indeed, sequential binding of the segments, and **bond vectors** arc often introduced (Yamakawa, 1971)

$$\vec{R}_{j} = \vec{r}_{j} - \vec{r}_{j-1}.$$
(76)

The character of linking is, therefore, expressed via the probabilities of bonds

$$\tau(\vec{R}_j) = \exp\left[-u_j(\vec{R}_j)/kT\right],\tag{77}$$

where $u_i(\vec{R}_i) \equiv u_i(\vec{r}_i, \vec{r}_{i-1})$. The zero energy level is chosen so that the normalization

$$\int d\vec{R}_j \,\tau(\vec{R}_j) = 1 \tag{78}$$

is realized, and $\tau_j(\vec{R}_j)$ is the probability of the *j*th bond being of length \vec{R}_j . Then, $G(\{\vec{r}_k\})$ from Equation 73 takes the form

$$G(\{\vec{r}_k\}) = \prod_{j=1}^{n} \tau_j(\vec{R}_j) \exp\left[-\varphi(\{\vec{R}_k\})/kT\right].$$
(79)

As usually happens in statistical physics, this equation contains more information than is really required. Experimentally measured quantities result from these distributions by means of integration over all the set of bond vectors (Equation 79) or over all the set of chain locations (Equation 73).

Consider the end-to-end vector \vec{h} distribution function

$$G(\vec{h},n) = \int G(\{\vec{R}_k\}) \delta(\vec{r}_n - \vec{h}) \, d\{\vec{R}_k\}, \tag{80}$$

which (without regard for normalization) is the probability of the last chain $\vec{r_n}$ hitting the point \vec{h} .

Allowing for Equation 76, we have

$$\vec{r}_n = \sum_{j=1}^n \vec{R}_j,\tag{81}$$

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where the end-to-end vector $\vec{h} = \vec{r_n}$ is represented as the sum of bond vectors, then

$$G(\vec{h},n) = \int G(\{\vec{R}_k\}) \delta\left(\sum_{j=1}^n \vec{R}_j - \vec{h}\right) d\{\vec{R}_k\},$$
(82)

and the partition function is

$$\mathcal{Z} = \int d\vec{h} \, G(\vec{h}, n), \tag{83}$$

and the end-to-end vector probability distribution is

$$P(\vec{h},n) = \mathcal{Z}^{-1}G(\vec{h},n).$$
(84)

The δ function in Equations 80 and 82 selects, of all the possible conformations, only those for which

$$\vec{r}_n = \vec{h} = \sum_{j=1}^n \vec{R}_j$$
 (85)

satisfies.

$$\int d\vec{h} P(\vec{h}, n) = 1 \tag{86}$$

serves as the condition of $P(\vec{h}, n)$ normalization.

If all the bonds are accepted as identical, then $au_j(ec{R}_j)= au(ec{R}_j)$ for every j and

$$G(\{\vec{R}_k\}) = \exp\left[-\varphi(\{\vec{R}_k\})/kT\right] \prod_{j=1}^n \tau(\vec{R}_j).$$
(87)

Let us consider the simplest case with $\varphi = 0$ (an unperturbed chain): it follows from Equations 78 and 83 that

$$\mathcal{Z} \equiv 1$$
 (88)

and

$$P(\vec{h}, n) = G(\vec{h}, n) = \int d\{\vec{R}_k\} \left[\prod_{j=1}^n \tau(\vec{R}_j) \right] \delta\left(\sum_{j=1}^n \vec{R}_j - \vec{h} \right).$$
(89)

Such a chain is also called a chain of random (free) walk, since Equation 89 matches the distribution calculation of random walk probability of a structural element in space with n jumps (steps) from one position to another with the length of each jump (step) defined by the probability distribution $\tau(\vec{R}_j)$ (Flory, 1953; Yamakawa, 1971). Hence, Equation 89 relates the statistics of polymer chains to the problems of random walk and diffusion. As the diffusion equation is mathematically similar to Schrödinger's one, the common ideology and common mathematical solutions unite the conformational tasks of a polymer chain, the state of quantum-mechanical systems, and the field theory. Supposing no bond-bond interaction (no short-range interactions), all the bonds are of the same length l, and

$$\tau(\vec{R}_j) = \frac{1}{4\pi l^2} \delta(|\vec{R}_j| - l), \tag{90}$$

and $P(\vec{h}, n)$ concerns random walk with *n* equal steps of length *l*. Equation 89, therefore, can be solved for $\tau(\vec{R}_j)$ (Equation 90) by means of Markov's method (Yamakawa, 1971) as follows.

Introduction of the Fourier representation of the δ function

$$\delta\left(\sum_{j=1}^{n} \vec{R}_{j} - \vec{h}\right) = \int \frac{d^{3}k}{(2\pi)^{3}} \exp\left[i\left(\sum_{j=1}^{n} \vec{R}_{j} - \vec{h}\right) \cdot \vec{k}\right]$$
(91)

into Equation 89 yields the product of n identical functions

$$P(\vec{h},n) = \int \frac{d^3k}{(2\pi)^3} \exp(-i\vec{k}\vec{h}) \left[\int d\vec{R}_j \tau(\vec{R}_j) \exp(i\vec{R}_j\vec{k}) \right]^n$$
(92)

$$\equiv \int \frac{d^3k}{(2\pi)^3} \exp(-i\vec{k}\vec{h}) \mathcal{K}(\vec{k},n), \tag{93}$$

where

$$\mathcal{K}(\vec{k},n) = \int d\vec{h} P(\vec{h},n) \exp(i\vec{k}\vec{h})$$
(94)

is the characteristic function of the distribution $P(\vec{h}, n)$ which, in the case of Equation 90, is calculated exactly:

$$\mathcal{K}(\vec{k},n) = \left[\frac{\sin kl}{kl}\right]^n,\tag{95}$$

where $k = |\vec{k}|$. But $P(\vec{h}, n)$ can be derived from Equation 93 as a series only.

From probability theory, it is known that the moments of any quantity by the distribution $P(\vec{h}, n)$ are deduced immediately from the characteristic function; here, from $\mathcal{K}(\vec{k}, n)$ (Equation 94).

Eg. the pth end-to-end distance moment

$$\langle h^{p} \rangle = \int d\vec{h} P(\vec{h}, n) \vec{h}^{p} \tag{96}$$

is proportional to the coefficient of \vec{k}^p in the power series $\mathcal{K}(\vec{k},n)$ in terms of \vec{k} .

It results that $\langle \vec{h}^p \rangle = 0$, if p is odd and, for instance,

$$\left\langle h^2 \right\rangle = nl^2 = Ll,\tag{97}$$

where L = nl is the contour length of a polymer chain.

In the case of a sufficiently long polymer chain, $P(\vec{h}, n)$ is determined by means of the central limit theorem $n \to \infty$.

If n is large, then $\mathcal{K}(\vec{k}, n)$ (Equation 95) has a sharp peak about $\vec{k} = 0$. Such behaviour of the characteristic function should be expected at any other choice of $\tau(\vec{R}_j)$. Then, from Equation 92, we have for long enough polymer chains

$$\lim_{n \to \text{large}} P(\vec{h}, n) = P_a(\vec{h}) =$$

$$\lim_{n \to \text{large}} \int \frac{d^3k}{(2\pi)^3} \exp(-i\vec{k}\vec{h}) \exp\left(n \ln\left\{\int d\vec{R}_j \,\tau(\vec{R}_j) \left[1 + i\vec{k}\vec{R}_j - \frac{1}{2}(\vec{k}\vec{R}_j)^2 + \cdots\right]\right\}\right).$$
(98)

Here the power series expansion reflects the expectation of the Fourier transform of $\tau(\vec{R}_j)$ having a sharp peak about $\vec{k} = 0$. By virtue of the spherical symmetry of $\tau(\vec{R}_j)$ in Equation 98, the term linear with respect to \vec{k} vanishes. If we define l as

$$\frac{1}{3}\delta_{\alpha\beta}l^2 = \int d\vec{R}_j \,\tau(\vec{R}_j)R_j^{\alpha}R_j^{\beta} \tag{99}$$

and expand the ln in Equation 98 into a series up to order k^2 , then we get

$$P_{a}(\vec{h}) = \int \frac{d^{3}k}{(2\pi)^{3}} \exp(-i\vec{k}\vec{h}) \exp\left(-\frac{nl^{2}k^{2}}{6}\right)$$
$$= \left(\frac{3}{(2\pi nl^{2})}\right)^{3/2} \exp\left[-\frac{3(h_{x}^{2} + h_{y}^{2} + h_{z}^{2})}{2nl^{2}}\right].$$
(100)

It is characteristic that $P_a(\vec{h})$ is rather small but not equal to zero for $\vec{h} > nl$, while Equations 90 and 92 equal zero for any length greater than the overall length of the chain.

In a more general case of n and \dot{h} being varied, the distribution with $\tau(\dot{R_j})$ has a more sophisticated expression (according to Equation 90) (Yamakawa, 1971). In this connection, it seems reasonable to have such an approximation of $\tau(\vec{R_j})$ that would lead to the chief properties of the chain (Equations 97 and 100) with simpler mathematical operations. The Gaussian function

$$\tau(\vec{R}_j) = \left(\frac{3}{2\pi l^2}\right)^{3/2} \exp\left(-\frac{3\vec{R}_j^2}{2l^2}\right) \tag{101}$$

has turned out to be such a function $\tau(\vec{R}_j)$ to satisfy Equations 97 and 100 for any *n* (one can verify it by substituting Equation 101 into Equation 92).

In the general case, there is an interaction between \vec{R}_j and, say, \vec{R}_{j-s} , \vec{R}_{j-s-1} , \vec{R}_{j+s} for $s \ll n$ due to the hindered rotation of the monomeric units about each other (short range effects, chain skeleton effect).

In this case, a model has proved to be reasonable, which implies substitution of the real polymer chain by an equivalent random-walk one comprising N segments of the length $A = \Delta s$ to be chosen from

$$NA = L \tag{102}$$

and

$$NA^2 = \left\langle h_\theta^2 \right\rangle. \tag{103}$$

In other words, a segment includes as many monomeric units of the real chain as is needed for the spatial orientation of each chain not to depend on the orientation of the previous and next ones as a result of micro-Brownian thermal motion.

The quantity A depends on the correlation among the neighbouring monomeric units, caused by the character of motion about valent boulds and other short-range effects. So, A is defined by the **rigidity** of a polymer chain. Then the probability density of distribution of N linked non-interacting (bodyless) segments of length A is expected by the Gaussian random-walk function (Equation 100)

$$P(\vec{h}) = P(h_x, h_y, h_z) = \left(\frac{2}{3}\pi N A^2\right)^{-3/2} \exp\left(-\frac{h_x^2 + h_y^2 + h_z^2}{\frac{2}{3}N A^2}\right),$$
(104)

where $\vec{h} = h_x \vec{i} + h_y \vec{j} + h_z \vec{k}$ is the end-to-end distance.

If one end of the chain is fixed, the probability of the end-to-end distance being within $[\vec{h}, \vec{h} + d\vec{h}]$ (i.e. the other end finding itself within the space element with the coordinates $h_x, h_x + dh_x; h_y, h_y + dh_y; h_z, h_z + dh_z$) is expressed as

$$P_{\vec{h},\vec{h}+d\vec{h}} = \left(\frac{2}{3}\pi NA^2\right)^{-3/2} \exp\left(-\frac{h_x^2 + h_y^2 + h_z^2}{\frac{2}{3}NA^2}\right) \, dh_x \, dh_y \, dh_z.$$

The probability of the end-to-end distance being within [h, h+dh] despite of its spatial orientation is

$$P_{h,h+dh} = \left(\frac{2}{3}\pi NA^2\right)^{-3/2} \exp\left(-\frac{h_x^2 + h_y^2 + h_z^2}{\frac{2}{3}NA^2}\right) 4\pi h^2 dh$$
(105)
= $P(h_x, h_y, h_z) 4\pi h^2 dh = \tilde{P}(h) dh,$

and the second moment of the distribution function gives the mean-square end-to-end distance

$$\left\langle h_{\theta}^{2} \right\rangle = \int_{0}^{\infty} h^{2} \tilde{P}(h) \, dh = N A^{2}. \tag{106}$$

The subscript ' θ ' denotes the lack of long-range effects (unperturbed state). In fact, distant (along the chain) segments (monomeric units), having come together as a result of micro-Brownian motion, interact with a common-type potential $\varphi(r)$ the examples of which are shown in Figures 1.40 and 2.34.

Sometimes, the repulsion component $\varphi_{rep} > 0$ in $\varphi(r)$ predominates, and the chain sizes increase in comparison with the unperturbed state, and $\langle h^2 \rangle > \langle h_{\theta}^2 \rangle$.

If the attraction component $\varphi_{attr}(r) < 0$ predominates, then $\langle h^2 \rangle < \langle h_{\theta}^2 \rangle$, and the coil contracts (collapses) in comparison with its unperturbed state.

A Gaussian chain divided into subchains with the Gaussian distribution function is a modification of this model.

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While modelling, the chain is represented as a result of random walk over the nodes of Ising's lattice with edge A (an equivalent of the unperturbed chain with its distribution function (Equation 104) (see Figure 1.23d). The quantity A, as in the previous case, involves short-range effects while the long-range ones are taken into account by imposing special conditions of walk, in particular, the condition of self-avoiding.

In some cases, a model of pearl necklace is used where N beads are threaded on a bodyless thread with the distance between the neighbouring beads determined by the Gaussian distribution function of the type 105. Long-range effects are taken into account by an interaction potential among the beads.

It has proved to be important that the properties of macromolecules and polymer systems on the whole are practically independent of the model of the molecular chain. Every separate problem allows the researcher to apply the most convenient (for computation) model (Khokhlov, 1985).

Write the state equation for an ideal (without long-range effects) molecular chain whose internal energy is equal to zero, i.e. (see Equation 1.1.1-25)

$$F = -TS.$$

Applying Boltzmann's formula (Equation 1.4-1) for the entropy of a molecular coil, and in view of Equations 104 and 106, we write

$$S(\vec{h}) = const - \frac{3k \langle h^2 \rangle}{2NA^2} = const - \frac{3k \langle h^2 \rangle}{2 \langle h_{\theta}^2 \rangle}$$
(107)

and

$$F(\vec{h}) = const + \frac{3kT \langle h^2 \rangle}{2NA^2} = const + \frac{3kT \langle h^2 \rangle}{2 \langle h_{\theta}^2 \rangle}.$$
(108)

If the chain ends are stretched by action of force \vec{f} , then the equilibrium in the system is achieved with a compensating elastic force f_{el} of entropy nature: while stretching the chain (increasing \vec{h}), its entropy diminishes as the set of conformations to realize the coil state with a given distance \vec{h} is depleted. So, $\vec{f} + \vec{f}_{el} = 0$ and

$$\vec{f}_{el} = -\frac{dF(\vec{h})}{d\vec{h}} = -\frac{3kT}{NA^2}\vec{h} = -\frac{3kT}{\langle h_\theta^2 \rangle}\vec{h}.$$
(109)

This formula is of key importance in explaining the phenomena of high-elastic deformation of polymer materials.

In his theory of polymer dilute solutions, Flory (1945, 1949c, 1953) (Orofino and Flory, 1957; Flory and Fisk, 1966) (see also: Morawetz, 1965; Tanford, 1961; Tsvetkov et al., 1964: Bresler and Yerusalimski, 1965; Yamakawa, 1971; Casassa, 1976, 1977; Rafikov et al., 1978) modelled a macromolecule with a cloud of disconnected segments distributed about the centre of mass by the Gaussian law (Equation 104). The equivalent sphere is subdivided into elementary spherical layers for which the Gibbs potential (Equation 31) $\Delta G_{m,i}$ is realized.

In a thermodynamically good solvent ($0 < \chi_1 < 0.5$), where the repulsion component of the interaction potential $\varphi_{rep}(r)$ among distant segments predominates, the chain size increases so that

$$\left\langle h^2 \right\rangle^{1/2} = \alpha \left\langle h_\theta^2 \right\rangle^{1/2},$$
(110)

where $\langle h_{\theta}^2 \rangle^{1/2}$ is the root-mean-square end-to-end distance in the unperturbed state, i.e. in the theta solvent where the effective long-range forces (with allowance for the polymer-solvent interaction) are mutually compensated, α is an expansion factor.

A coil is being swollen owing to the Gibbs potential of mixing summarized over all the sphere layers $\sum_i \Delta G_{m,i}$. Increasing $\langle h^2 \rangle^{1/2}$ leads to a decrease in entropy which causes a returning force with the potential $\Delta G_{cl}(\alpha)$. To calculate ΔG_{cl} , we should assume that the Gaussian character of segment distribution remains while the coil is heing expanded.

Hence, the overall change of the Gibbs potential involves two summands

$$\Delta G(\alpha) = \sum_{i} \Delta G_{m,i}(\alpha) + \Delta G_{el}(\alpha). \tag{111}$$

The condition of the thermodynamic equilibrium

$$\frac{\partial \Delta G(\alpha)}{\partial \alpha} = 0 \tag{112}$$

leads (Flory, 1953; Tompa, 1956) to Flory's equation

$$\alpha^5 - \alpha^3 = 2C_M \psi_1 \left(1 - \frac{\theta}{T} \right) M^{1/2}, \tag{113}$$

where

$$C_{M} = \frac{27 v_{2}^{2}}{2^{5/2} \pi^{3/2} N_{A} V_{01}} \left(\frac{M}{\langle h_{\theta}^{2} \rangle}\right)^{3/2}$$
(114)

(a factor with a certain dimension to adjust both sides of Equation 113 to a common dimension) which is also written as

$$\alpha^5 - \alpha^3 = 2.6z,\tag{115}$$

where

$$z = \frac{4}{3^{3/2}} C_M \psi_1 \left(1 - \frac{\theta}{T} \right) M^{1/2}$$
(116)

is the excluded volume parameter.

Flory's derivation of Equation 115 is rather cumbersome. Many years later, the state equation of a molecular coil in the mean field approximation came to be derived in a much simpler manner (de Gennes, 1979; Khokhlov, 1985) in terms of the segment excluded volume β for the range of a very good solvent,

Consider the influence of long-range effects on the chain model (Equation 72), taking segments of length A as units (to allow for short-range effects). Let the pair potential

$$\varphi_{ij} = \varphi(\vec{r}_i - \vec{r}_j) \tag{117}$$

act among all the pairs of segments, which is justified at a low segment density. As the chain is in solution, Equation 117 involves all the effects of polymer segment interactions with LMWL molecules.

Equation 117 is often approximated by a short-range repulsion potential that is mathematically expressed with the space δ function (Staverman, 1962; Yamakawa, 1971; Freed, 1972)

$$\exp\left[-\varphi(\vec{r}_{ij})/kT\right] = \exp\left[-\beta\delta(\vec{r}_{ij})\right] = 1 - \beta\delta(\vec{r}_{ij}),\tag{118}$$

where

$$\beta = \int d\vec{r}_{ij} \left\{ 1 - \exp\left[-\varphi(\vec{r}_{ij})/kT\right] \right\}$$
(119)

 $(-\beta$ is the binary cluster integral, Equation 1.8-9). For a spherically symmetrical potential $\varphi(r)$.

$$\beta = 4\pi \int_{0}^{\infty} [1 - \exp(-\varphi(r)/kT)] r^2 dr.$$
(120)

The quantity β is a so-called excluded volume of a segment, i.e. that which is excluded for all the other segments due to their repulsion. Then, the mean-square end-to-end distance is expressed as (see Equation 87)

$$\left\langle h^2 \right\rangle = \int d\vec{r}_i \, P(\vec{r}_i)(\vec{r}_{ij})^2, \tag{121}$$

$$P(\vec{r}_{j}) = G(\vec{r}_{i}) / \int G(\vec{r}_{i}) \, d\vec{r}_{i}, \tag{122}$$

$$G(\vec{r}_i) = \int \exp\left[-\beta \sum_{i < j} \delta(\vec{r}_{ij})\right] \prod_{k=1}^N \tau(\vec{R}_k) \, d(\vec{R}_k) / d\vec{h}, \qquad (123)$$

where the symbol $\prod d(\vec{R}_k)/d\vec{h}$ points to integration over all the values of \vec{R}_k provided that (see Equation 85) $\vec{h} = \sum_k \vec{R}_k$ remains constant.

For further calculations, probability distribution functions of segment free walk are introduced (Zimm et al., 1953; Fixman, 1955; Kurata and Yamakawa, 1958; Kurata, 1961; Staverman, 1962)

$$P_0(\vec{r}_{ij},\dots,\vec{r}_{st},\vec{h}) = \int \prod_{k=1}^N \tau(\vec{R}_k) \, d\vec{R}_k / d\vec{r}_{ij} \cdots d\vec{r}_{st} \cdot d\vec{h},$$
(124)

$$P_0(O_{ij},\ldots,O_{st},\vec{h}) = \int \delta(\vec{r}_{ij})\cdots\delta(\vec{r}_{st})P_0(\vec{r}_{ij},\ldots,\vec{r}_{st},\vec{h})\,d\vec{r}_{ij}\cdots d\vec{r}_{st}.$$
(125)

The latter function is the probability that the mentioned segment pairs contact each other, and the Nth segment is in a space unit at the distance \vec{h} from the zero segment. Applying Equations 124 and 125, Equation 123 can be expanded in a power series of β (the series of perturbation theory)

$$G(\vec{r}_i) = P_0(\vec{r}) \left[1 - \beta \sum_{i < j} P_0(O_{ij}/\vec{h}) + \beta^2 \sum_{i < j} \sum_{k=1} P_0(O_{ij}, O_{kl}/\vec{h}) - \cdots \right],$$
(126)

where

$$P_0(O_{ij},\ldots,\vec{h}) = \frac{P_0(O_{ij},\ldots,\vec{h})}{P_0(\vec{h})}.$$
(127)

Substituting Equation 126 into Equations 122 and 121, we get

$$\langle h^2 \rangle = \int \vec{r^2} P_0(\vec{r}) \, d\vec{r}$$

$$+ \beta \sum_{i < j} \vec{r^2} \left[P_0(\vec{r}) P_0(O_{ij}) - P_0(O_{ij}, \vec{h}) \right] \, d\vec{r} + \cdots$$

$$(128)$$

and on performing calculations within the framework of perturbation theory,

$$\left\langle h^2 \right\rangle = N A^2 \alpha_h^2 = \left\langle h_\theta^2 \right\rangle \alpha_h^2, \tag{129}$$

where

$$\alpha_h^2 = 1 + \frac{4}{3}z - 2.08z^2 + \cdots$$
(130)

and

$$z = \left(\frac{3}{2\pi}\right)^{3/2} \beta A^{-3} N^{1/2}.$$
(131)

Similar calculations carried out for the radius of gyration of a coil

$$R^{2} = \frac{1}{N^{2}} \sum_{i < j} \left(\vec{R}_{ij} \right)^{2}, \tag{132}$$

in the first order of perturbation theory have led to

$$\alpha_R^5 - \alpha_R^3 = \frac{134}{105}z\tag{133}$$

while those in the second order (Yamakawa et al., 1966; Chikahisa, 1970) have yielded

$$\alpha_R^2 = 1 + 1.276z - 2.082z^2 + \cdots, \tag{134}$$

where $\alpha_R = R/R_{\theta}$.

Chikahisa (1970) has introduced a diagrammatic calculation technique for the excluded volume effects of polymer chains like multi-particle systems in statistical physics of real gas and ionic solutions.

 α_h and α_R somewhat differ due to a slight anisodiametry of coil expanding.

Thus, in higher orders of the theory, results are derived as a series in z (Equations 116 and 131), which must be rather small to confine the series to two or three terms and, generally speaking, for the series to converge.

However, z is proportional to a large quantity, $M^{1/2}$, and can be small if only $M^{1/2}$ is compensated for by another multiplier $(1 - \theta/T) = (T - \theta)/T$, which must, therefore, be much less than 1:

$$\frac{T-\theta}{T} \ll 1.$$

This is the main restriction¹ of perturbation theory which is valid in the close vicinity of the θ temperature only.

On the other hand, the potential in Equations 118-120 has no attraction component, so it is valid only for a solution in a very good solvent, i.e. far from the θ point (cf. B_2 of real gas molecules at high temperatures, the last paragraph of subsection 1.2.4). This is a manifestation of the inconsistency of the formalism of this approach.

In accordance with the general mean field theory, the parameter z acts as Ginzburg's parameter Gi $\approx z$ (Nyström and Roots, 1982).

Special analysis shows β to depend slightly on a specific form of $\varphi(r)$, so a model of potential barrier can be accepted

$$\varphi = \begin{cases} 0 & \text{at } r > A, \\ kT - k\theta & \text{at } r < A \end{cases}$$
(135)

with the barrier value being so low as to permit one to confine oneself with only two terms in the Taylor series of $\exp(-\varphi/kT)$. It follows from Equation 120 that

$$\beta \cong A^3 \frac{T - \theta}{T} = \beta_0 \left(1 - \frac{\theta}{T} \right) = \beta_0 \tau \tag{136}$$

or (see Equations 40 and 41)

$$\beta \cong \beta_0 \left(1 - \frac{\kappa_1}{\psi_1} \right) = \beta_0 \psi_1^{-1} \left(\frac{1}{2} - \chi_1 \right) = \beta_0' \left(\frac{1}{2} - \chi_1 \right), \tag{137}$$

where

$$\beta_0 = A^3 \tag{138}$$

is the segment excluded volume at $T \to \infty$ or at $\theta \to 0$, i.e. in an athermal solvent (see Equation 41) — the thermodynamically best one, $\tau = (T - \theta)/T$ is reduced temperature.

In a good solvent, the interaction energy is the segment repulsion energy proportional to the number of segment pairs, i.e. to the squared local density of segments in a coil

$$U \simeq \frac{kT\beta}{2} \sum_{ij} \rho_{ij}^2 \to \frac{kT\beta}{2} \int \rho^2(r) \, d\vec{r}.$$
(139)

As F = U - TS, then (see Equation 108)

$$\frac{F}{kT} = \frac{3R^2}{2R_{\theta}^2} + \frac{\beta}{2} \int \rho^2(r) \, d^3r.$$
(140)

In the mean field approximation, the local density of segments in a coil is constant

$$\rho(r) = const \sim \frac{N}{R^3} \quad \text{and} \quad \frac{F}{kT} = \frac{3R^2}{2R_{\theta}^2} + \frac{\beta N^2}{2R^3}.$$
(141)

The equilibrium value of R is determined from the condition $\partial F/\partial R = 0$:

$$R^{5} = \frac{\beta}{2} R_{\theta}^{2} N^{2} = \frac{\beta}{2} N^{3} A^{2}, \qquad (142)$$

 1 In general, perturbation theories have too many restrictions and presently come out of fashion. Editor's note

i.e. (see Equation 136)

$$R \cong N^{3/5} A^{2/5} \beta^{1/5} \cong N^{3/5} \tau^{1/5} A.$$

This equation coincides with Flory's one (Equations 115, 116) in the limit of large coil sizes. In Flory's approximation, coil expansion is regarded isotropic with no differences between α_R and α_h (α is written without any subscript). Flory's equation has been confirmed by numerous experimental data.

Chapters 4 and 5 will explicitly consider the significant role of the order parameter (the segment density in a coil) fluctuations in the system P+LMWL, so the mean field approximation, strictly speaking, is not correct for describing the behaviour of this system.

The success of Flory's formula is due to the mutual compensation of the effects not taken into account. In effect, the entropy component in Equation 111 or 141 is overestimated owing to the Gaussian statistics applied. The energy component is also overestimated by a close value due to the neglect of the correlation of segment density fluctuations in a coil.

In d-dimensional space, Equation 141 takes the form (de Gennes, 1979)

$$\frac{F}{kT} \cong \frac{R^2 d}{2NA^2} + \frac{\beta}{2} \cdot \frac{N^2}{R^4}.$$
(143)

F is minimal when

$$R^{d+2} \simeq \beta A^2 N^3 \quad \text{and} \quad R \sim N^{\nu},\tag{144}$$

where

$$\nu = \frac{3}{d+2},\tag{145}$$

whence it follows that, in d = 4 space, chains become ideal at $\nu = 1/2$ (cf. Figure 2.44). If z in d-dimensional space is written as

$$z \sim \beta N^{(4-d)/2},$$

then for d > 4 and $N \to \infty$, z tends to zero and so are the interaction terms in Equation 143. Hence, the chain turns out to be ideal in any $d \ge 4$ -dimensional space.

The methods of statistical physics (Flory, 1945, 1949c; Orofino and Flory, 1957; Kurata and Yamakawa, 1958; Tanford, 1961; Staverman, 1962; Tsvetkov et al., 1964; Bresler and Yerusalimski, 1965; Morawetz, 1965; Flory and Fisk, 1966; Yamakawa, 1971; Casassa, 1976, 1977; Rafikov et al., 1978) applied to the problem of collisions among the segments of two coils lead to the following expression for \mathcal{A}_2

$$\mathcal{A}_{2} = \frac{N_{A}\beta}{2M_{s}^{2}}h(z) = \frac{\bar{v}_{2}^{2}}{\bar{V}_{01}}\psi_{1}\left(1 - \frac{\theta}{T}\right)h(z) =$$
(146)

$$=\frac{\mathbf{v}_{2}^{2}}{V_{01}}\left(\frac{1}{2}-\chi_{1}\right)h(z)=\mathcal{A}_{2}^{L}h(z),\tag{147}$$

where M_s is the molecular weight of a segment, β is its excluded volume.

The expression

$$\mathcal{A}_2^L = \frac{N_A \beta}{2M_s^2} \tag{148}$$

(see Equation 146) has the meaning of the second virial coefficient of a "disconnected" segment solution (cf. Equation 1.3-40) with h(z) defining the correction for their bonds and being a sophisticated function of z (Equation 116).

For a Gaussian coil,

$$\left\langle h_{\theta}^{2} \right\rangle = 6 \left\langle R_{\theta}^{2} \right\rangle \tag{149}$$

holds (Volkenshtein, 1959; Tsvetkov et al., 1964; Flory, 1969; Yamakawa, 1971). It follows from Equations 114, 116, 146, and 149 that

$$z = \frac{\beta M^{1/2}}{(4\pi \langle R_{\theta}^2 \rangle / M)^{3/2} M_s^2}$$
(150)

$$=\frac{\beta N^2}{\left(4\pi\right)^{3/2} \left\langle R_0^2 \right\rangle^{3/2}}.$$
(151)

The nominator of the last line is the effective excluded volume of the whole coil v_{ex} due to intercollisions of N segments while the denominator is proportional to the coil volume in the unperturbed state v_{θ} , so

$$z \sim \frac{v_{ex}}{v_{\theta}},\tag{152}$$

which determines the physical meaning of the parameter z (Birshtein et al., 1975).

Including Equation 106, Equation 150 is transformed into

$$z = \left(\frac{3}{2\pi}\right)^{3/2} \frac{\beta N^{1/2}}{A^3}.$$
(153)

The theory of dilute solutions is often referred to as the **two-parameter theory**. This is due to the fact that the main quantities characterizing coil conformations are expressed through the three chief parameters N, A and β combined into **two** expressions, namely, NA^2 and $z \sim \beta N^{1/2}/A^3$ (see Equations 106, 153, 110, 113, 114, 146, 147). The function h(z) can be expanded into a Taylor series with respect to z (Albrecht, 1957; Stockmayer, 1960; Kurata et al., 1964; Yamakawa, 1971 Casassa, 1976, 1977), but this series turns out to be hardly convergent; near the θ point

$$h(z) = 1 - Bz + Cz^2 - \cdots .$$
(154)

For a linear chain, B = 2.865, C = 9.201 (Yamakawa, 1971; Casassa, 1976, 1977).

Yamakawa (1971) reports closed expressions for h(z) as well.

Analysis (Schulz et al., 1960, 1963, 1966; Lechner and Schulz, 1973) shows that no mean field theory explains the experimental data; however, near the θ point, the best results are obviously given by Orofino-Flory's (1957) theory and, in the case of good (athermal)

solvents, Casassa's (1959, 1976, 1977) (see also: Casassa and Markovitz, 1958) theory is the best choice with

$$h(z) = \frac{1 - \exp(-5.68z/\alpha_R^3)}{5.68z/\alpha_R^3}$$
(155)

and

$$\alpha_R^5 - \alpha_R^3 = 2.04z, \tag{156}$$

where α_R is defined by

$$\langle R \rangle = \alpha_R \langle R_\theta \rangle. \tag{157}$$

Combination of Equations 146 and 151 gives

$$zh(z) = \frac{\mathcal{A}_2 M^{1/2}}{\left(\pi \left\langle R_{\theta}^2 \right\rangle / M \right)^{3/2} 4N_A}.$$
(158)

Thus, the product zh(z) is determined experimentally. Then the theoretical dependence h(z) vs zh(z) (Figure 3.5) enables us to determine h(z) and, according to Equations 155 and 156, α_R and z.



Figure 3.5. Plot of h(z)vszh(z) for Casassa's function (Casassa, 1959; Lechner and Schulz, 1973) [Reprinted from Europ. Polym. J. 9 (1973) 723-733. Copyright © 1973 with kind permission of Elsevier Science -- NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands]

Different theoretical approaches are compared by the form of the function $\psi(\alpha_R)$ (Ya-makawa, 1971; Eskin, 1973; Rafikov et al., 1978) (see Figure 5.19).

$$\psi(\alpha_R) = \frac{zh(z)}{\alpha_R^3} = \frac{\mathcal{A}_2 M^{1/2}}{\left(\pi \left< R^2 \right> / M \right)^{3/2} 4N_A}.$$
(159)

The right-hand side means $\psi(\alpha_R)$ is evaluated experimentally with subsequent derivation of $\psi(\alpha_R)$. The experimental $\langle R \rangle$ and α_R found, according to Equation 157, yields the unperturbed coil size $\langle R_{\theta} \rangle$ which can be compared with independent experimental data or calculations of the thermodynamic rigidity of a chain (Equation 106).

Hence, in a good solvent $(T > \theta$ for systems with UCST), the repulsion component predominates in the potential $\varphi(r)$ (Figures 1.40a, 2.34b), the segment excluded volume $\beta > \beta_0$ (Equation 136), which leads to an increase in the molecular coil size in dilute solutions (see Equations 157, 113, 153, 115).

However, with increasing polymer concentration, effective repulsion of segments of different macromolecules should result in a decrease in the molecular coil sizes. This does qualitatively follow from Equations 113 and 114. An increase in polymer concentration for a labelled (eg. deuterated) macromolecule can be regarded as effective increase in the solvent molecular volume, which leads to a decrease in C_M in Equation 114 and, therefore, to a decrease in α in Equation 113². In the limit $v_1 \rightarrow 0$, the labelled macromolecule finds itself to be among similar ones (in the thermodynamic and morphological sense). In view of Equations 113 and 114, $\bar{V}_{ef} \rightarrow 0$, $C_M \rightarrow 0$ and $\alpha \rightarrow 1$.

Hence, a macromolecular coil takes its unperturbed size $\langle R_{\theta} \rangle$ in the amorphous condensed state of polymer.

More rigorous considerations lead to (Eizner, 1961; Yamakawa, 1971)

$$\alpha_h(\mathbf{c}) = \alpha_h \left[1 - \left(\frac{N_A N^2 \beta}{M} \right) \left(0.1138 \frac{z}{\alpha_H^3} + \cdots \right) \mathbf{c} + \cdots \right], \tag{160}$$

$$\alpha_R(\mathbf{c}) = \alpha_R \left[1 - \left(\frac{N_A N^2 \beta}{M} \right) \left(0.1025 \frac{z}{\alpha_R^3} + \cdots \right) \mathbf{c} + \cdots \right], \tag{161}$$

$$\alpha_{R}(\mathbf{c}) = \alpha_{R} \exp\left\{-0.0397 \frac{N_{A} N^{2} \beta}{M} \left[1 - h_{0} \left(\frac{z}{\alpha_{R}^{3}}\right)\right] \mathbf{c}\right\},\tag{162}$$

where $\alpha_R = \alpha_R(0)$, $\alpha_h = \alpha_h(0)$, i.e. at c = 0, $h_0(z/\alpha_R^3)$ is the function from Equation 155.

Contraction of macromolecules with increasing polymer concentration has been confirmed by neutron scattering in polystyrene solutions in the good solvent CCl_4 (Figure 3.6).

The contrast required for neutron scattering was provided by deuterating some of the macromolecules (for comparison: light scattering, Chapter 2, requires an increment in refractive index for contrast).

Baranov et al. (1986, 1987) have proposed a way of measuring the limiting viscosity number at a finite polymer concentration $[\eta]_c$ and shown that, as the polymer concentration in a good solvent (polystyrene in bromoform, 25°C) increases, $[\eta]_c$ gradually diminishes to the value of $[\eta]_{\theta}$ in the theta solvent (polystyrene in decaline, 25°C).

Let us discuss another model of a polymer chain, which has assumed an importance in developing the theory of polymer solutions based on the field theory formalism (Freed, 1972).

²This may not be the case. Eg., neutron scattering allows one to observe segregation of D- and H-polyethylenes up to superlattices appear. Editor's note



Figure 3.6. Concentration dependence of the radius of gyration of polystyrene macromolecules in CCl_4 as given by neutron scattering. A part of polystyrene macromolecules was deuterated to provide contrast. The values c along the abscissa axis relate to the overall concentration of both protonated and deuterated polystyrene macromolecules (Daoud et al., 1975) [Reprinted with permission from: M.Daoud et al. Macromolecules 8 (1975) 804-818. Copyright © 1975 American Chemical Society]

An equivalent Gaussian chain, obeying Equations 102 and 103, is subdivided into m Gaussian segments of length Δs each, so that

$$m\,\Delta s \equiv L \tag{163}$$

with the bond probability distribution

$$\tau(\vec{R}_{j}) = \tau(\vec{r}_{j} - \vec{r}_{j-1}) = \left(\frac{3}{2\pi A \Delta s}\right)^{3/2} \exp\left(-\frac{3\vec{R}_{j}^{2}}{2A \Delta s}\right)$$
(164)

(Freed, 1972).

On substituting Equations 163 and 164 into Equation 92, one can see that

$$P(\vec{R};m) = \left(\frac{3}{2\pi \left\langle \vec{R}^2 \right\rangle_m}\right)^{3/2} \exp\left(-\frac{3\vec{R}^2}{2\left\langle \vec{R}^2 \right\rangle_m}\right),\tag{165}$$

where

$$\left\langle \vec{R}^2 \right\rangle_m = \int d\vec{R} \, P(\vec{R}, m) \vec{R}^2. \tag{166}$$

Including the normalization of $\tau(\vec{R}_j)$ (Equation 78), and assuming $\varphi = 0$ in Equation 79, we obtain for the probability distribution function of all the chain conformations

$$P(\{\vec{r}_k\}) = \prod_{j=1}^{m} \left\{ \left(\frac{3}{2\pi A\Delta S}\right)^{3/2} \exp\left[-\frac{3(\vec{r}_j - \vec{r}_{j-1})^2}{2A\Delta s}\right] \right\}$$
(167)

$$= \mathcal{N} \exp\left[-\sum_{j=1}^{m} \frac{3(\vec{r}_{j} - \vec{r}_{j-1})^{2}}{2A\Delta s}\right],$$
(168)

where

$$\mathcal{N} = \left(\frac{3}{2\pi A\Delta s}\right)^{3m/2} \tag{169}$$

is the normalization factor from

$$\int d\{\vec{r}_k\} P(\{r_k\}) \equiv 1.$$
(170)

As the distribution (Equation 168) gives the probability of a specific chain conformation with $\vec{r_0} \equiv 0, \vec{r_1}, \ldots, \vec{r_m}$, this conformation $\{\vec{r_k}\}$ can be assumed as a discrete representation of the continuous curve $\vec{r}(s)$, so that

$$\vec{r}_j = \vec{r}(j\Delta s) \equiv \vec{r}(s_j) \tag{171}$$

defines the position of the *j*th segment with respect to the origin $(s_0 = 0)$ for which $\vec{r}_0 = 0$ is presumed in the absence of external fields.

Then, in the limits

$$\Delta s \to 0, \qquad m \to \infty, \qquad m \Delta s = L \tag{172}$$

a model of continuous equivalent random-walk chain (CERWC) results, and the exponent in Equation 168 is written as

$$\lim_{C \in RWC} \sum_{j=1}^{m} \frac{3}{2A} \left[\frac{\vec{r}(s_j) - \vec{r}(s_j - \Delta s)}{\Delta s} \right]^2 \Delta s \equiv \lim_{C \in RWC} \sum_{j=1}^{m} \frac{3}{2A} \left[\frac{\partial \vec{r}(s)}{\partial s} \Big|_{s=s_j} \right]^2 \Delta s \quad (173)$$
$$\equiv \int_{0}^{L} ds \left[\frac{\partial \vec{r}(s)}{\partial s} \right]^2 \frac{3}{2A} = \frac{3}{2A} \int_{0}^{L} ds \left[\dot{\vec{r}}(s) \right]^2.$$

In this limit.

$$P(\{\vec{r}_k\}) \prod_{j=1}^m d\vec{r}_j \to P[\vec{r}(s)] \ d\vec{r}(s)$$
(174)

is the probability that the chain conformation is represented by a continuous curve located between $\vec{r}(s)$ and $\vec{r}(s) + d\vec{r}(s)$.

The normalization factor is often included into the differential and is denoted as

$$\mathcal{N}\,d\vec{r}(s)\equiv D\vec{r}(s).\tag{175}$$

Thus,

$$P[\vec{r}(s)] \, d\vec{r}(s) \equiv D[\vec{r}(s)] \exp\left\{-\frac{3}{2A} \int_{0}^{L} [\dot{\vec{r}}(s)]^2 \, ds\right\}$$
(176)

is the probability of the chain conformation $\vec{r}(s)$ (Wiener's measure).

By virtue of Equation 172,

$$\lim \mathcal{N} \to (\infty)^{\infty}. \tag{177}$$

Mathematically, Wiener's measure is not defined; however, its introduction has proven to be reasonable and very fruitful physically (cf. Dirac's δ function) (Freed, 1972).

In the continuous limit, it follows from Equation 170 that

$$\int_{\vec{r}(0)=0} P[\vec{r}(s)] \, d\vec{r}(s) = 1 = \int_{\vec{r}(0)=0} D[\vec{r}(s)] \exp\left\{-\frac{3}{2A} \int_{0}^{L} [\vec{r}(s)]^2 \, ds\right\},\tag{178}$$

where integration is taken over all the continuous curves $\vec{r}(s)$, $0 \le s \le L$ with $\vec{r}(0) \equiv 0$. Hence, the probability that the chain should have some conformation is equal to 1, and the "infinite" normalization (Equations 175 and 177) must lead to this value.

The second integral in Equation 178 is classified with functional integrals, which have taken on great significance in field theory and are finding applications in polymer theory.

Consider the case of a polymer chain being subject to external field, cg. in gravitational one or in a field appearing due to polymer-solvent or polymer-polymer interactions.

If we denote $W(\vec{r})$ the potential energy per unit chain length, then the distribution function of thermal motion for a discrete chain will be

$$G(\{\vec{r}_k\}) d\{\vec{r}_k\}$$
(179)
= $\mathcal{N} d\{\vec{r}_k\} \exp\left[-\frac{3}{2A\Delta s} \sum_{j=1}^m (\vec{r}_j - \vec{r}_{j-1})^2 - \frac{\Delta s}{kT} \sum_{j=1}^m W\left(\frac{\vec{r}_j + \vec{r}_{j-1}}{2}\right)\right],$

where the centre of force application is assumed to be at the centre of each bond (at $\Delta s \rightarrow 0$, this approximation becomes exact). That there is an external force means that space is no longer isotropic. Let us presume that

$$r_0 \equiv \vec{R}',\tag{180}$$

$$d\{\vec{r}_k\} = \prod_{j=1}^m d\vec{r}_j.$$
(181)

The partition function results from Equation 179 through

$$\mathcal{Z} = \int d\vec{r}_0 \int d\{\vec{r}_k\} G(\{\vec{r}_k\}) \tag{182}$$

and the probability distribution is

$$P(\{\vec{r}_k\}) = \mathcal{Z}^{-1}G(\{\vec{r}_k\}).$$
(183)

Assuming

$$\mathcal{V} \equiv \frac{W}{kT},\tag{184}$$

we obtain in the limit of a continuous chain

$$\frac{1}{kT}\sum_{j=1}^{m} W\left(\frac{\vec{r}_j + \vec{r}_{j-1}}{2}\right) \Delta s \to \int_0^L ds \,\mathcal{V}[\vec{r}(s)],\tag{185}$$

$$G[\vec{r}(s)] \, d\vec{r}(s) = D[\vec{r}(s)] \exp\left(-\int_{0}^{L} ds \, \left\{\frac{3}{2A} \dot{\vec{r}}^{2}(s) + \mathcal{V}[\vec{r}(s)]\right\}\right). \tag{186}$$

As noted above, $G[\vec{r}(s)]$ contains all the information related to the conformational statistics of a polymer chain.

To obtain expressions for experimentally measured quantities, a more restricted number of distributions will suffice.

Among the simplest distributions, there is the distribution of the vector between the chain ends $G(\vec{h}, \vec{R}'; L)$ which is obtained by selection of those chains from Equation 179 for which $\vec{r}_0 = \vec{R}'$ and $\vec{r}_m = \vec{h}$, i.e.

$$G(\vec{h}, \vec{R}'; L) \equiv \int d\vec{r}_0 \int d\{\vec{r}_k\} \delta(\vec{r}_0 - \vec{R}') \delta(\vec{r}_m - \vec{h}) G(\{\vec{r}_k\}),$$
(187)

and, in the continuous limit,

$$G(\vec{h}, \vec{R}'; L) = \int d\vec{r}(s) \int d\vec{r}_0 \delta[\vec{r}_0 - \vec{R}'] \delta(\vec{r}(L) - \vec{h}) G[\vec{r}(s)].$$
(188)

In the explicit form,

$$G(\vec{h}, \vec{R}'; L) = \int_{\vec{r}(0)=\vec{R}'}^{\vec{r}(L)=\vec{h}} D[\vec{r}(s)] \exp\left\{-\int_{0}^{L} ds \left(\frac{3}{2A}\vec{r}^{2}(s) + \mathcal{V}[\vec{r}(s)]\right)\right\}$$
(189)
$$= \lim_{CERWC} \int d\vec{r}_{0} \,\delta(\vec{r}_{0} - \vec{R}') \int d\{\vec{r}_{k}\} \,\delta(\vec{r}_{m} - \vec{h})\mathcal{N}$$
$$\times \exp\left\{-\frac{3}{2A\Delta s} \sum_{j=1}^{m} [\vec{r}_{j} - \vec{r}_{j-1}]^{2} - \Delta s \sum_{j=1}^{m} \mathcal{V}\left[\frac{\vec{r}_{j} + \vec{r}_{j-1}}{2}\right]\right\},$$

which provides a definition for the functional integral for $G(\vec{h}, \vec{R}'; L)$ as a limit of the iterative one. This functional integral is also called Wiener's integral.

The function $G(\vec{h}, \vec{R}'; L)$ from Equation 189 satisfies the diffusion equation for a particle in the external field potential $\mathcal{V}(\vec{h})$ (Gelfand and Yaglom, 1956; Freed, 1972)

$$\left[\frac{\partial}{\partial L} - \frac{A}{6}\nabla_{\vec{h}}^2 + \mathcal{V}(\vec{h})\right]G(\vec{h}, \vec{R}'; L) = 0, \quad L \neq 0$$
(190)

with the boundary condition

$$\lim_{L \to 0} G(\vec{h}, \vec{R}'; L) = \delta(\vec{h} - \vec{R}'), \tag{191}$$

i.e. $G(\vec{h}, \vec{R'}; L)$ is Green's function in the diffusion problem.

In Equation 190, the contour length is an analogue of time. Free walking or Brownian motion is regarded as a diffusion process for quite long periods of time with the "diffusion constant" defined as the mean squared displacement along the chain per unit time.

Applying Equation 164, one can obtain

$$D_{\alpha\beta}_{\alpha,\beta=x,y,z} = \frac{1}{\Delta s} \left\langle \vec{R}^{\alpha} \vec{R}^{\beta} \right\rangle_{\Delta s} = \frac{1}{\Delta s} \int d\vec{R}_{j} \vec{R}_{j}^{\alpha} \vec{R}_{j}^{\beta} \tau(\vec{R}_{j}) = \frac{A}{6} \delta_{\alpha\beta}.$$
(192)

We now discuss the excluded volume problem in terms of the CERWC model when a chain comprises N segments of length A each. The repulsion potential

$$W_{ij} = \varphi(\vec{r}_i - \vec{r}_j) \tag{193}$$

acts among all the pairs of segments at short distances.

As the polymer chain is in solution, here φ is the mean field potential including polymersolvent interactions. Its short-range character is mathematically expressed through the δ function of the "pseudopotential"

$$\frac{\varphi(\vec{r}_i - \vec{r}_j)}{2kT} = \beta \delta(\vec{r}_i - \vec{r}_j), \tag{194}$$

 β having the meaning of the segment excluded volume (see Equations 118 and 119)

$$\beta \to \int d^3r \left\{ 1 - \exp\left[-\frac{\varphi(r)}{kT}\right] \right\}.$$
(195)

Consider the distribution function (Equations 73 and 79)

$$G\left(\{\vec{r}_k\}\right) = \left[\prod_{j=1}^m P(\vec{r}_j - \vec{r}_{j-1}; \Delta s_j)\right] \exp\left[-\frac{1}{2kT} \sum_{i \neq j} \varphi(\vec{r}_i - \vec{r}_j)\right],\tag{196}$$

where, for the sake of generality, Δs_j is assumed to be of different length.

The bond probability is expressed through the Gaussian function (see Equation 101)

$$P(\vec{r}_j - \vec{r}_{j-1}; \Delta s_j) = \left(\frac{3}{2\pi A \Delta s_j}\right)^{3/2} \exp\left[-\frac{3(\vec{r}_j - \vec{r}_{j-1})^2}{2A \Delta s_j}\right].$$
(197)

In the continuous limit

$$\lim_{\text{CERWC}} \equiv \lim_{m \to \infty} \sum_{\substack{j=1 \\ \max \Delta s_j \to 0}}^{m} \Delta s_j = L,$$
(198)

and it is reasonable to represent the interaction as the interaction energy of two segments per unit squared length

$$\frac{\varphi_{ij}}{A^2}.$$
(199)

Then the energy of the interaction between two chain fragments Δs_i and Δs_i will be

$$\frac{\varphi_{ij}\Delta s_i\Delta s_j}{A^2}.$$
(200)

Hence, for a discrete chain (the subscript g'), the end-to-end distribution function is

$$G_{g}(\vec{h};L) = \int d\vec{r}_{0} \left[\prod_{j=1}^{m} \int d\vec{r}_{j} P(\vec{r}_{j} - \vec{r}_{j-1};\Delta s_{j}) \delta(\vec{r}_{0}) \delta[\vec{h} - \vec{r}_{m}] \right]$$

$$\times \exp\left(-\frac{1}{2} \sum_{ij} \mathcal{V}_{ij} \Delta s_{i} \Delta s_{j} \right),$$
(201)

where

$$\mathcal{V}_{ij} = (1 - \delta_{ij}) \frac{\varphi_{ij}}{kTA^2}.$$
(202)

Then the distribution function for the end-to-end vector is

$$P_{g}(\vec{h};L) = \mathcal{Z}_{g}^{-1}(L)G_{g}(\vec{h};L)$$
(203)

with the partition function

$$\mathcal{Z}_g(L) = \int d\vec{h} \, G_g(\vec{h}; L). \tag{204}$$

On passing to the continuous limit,

$$G(\vec{h}0;L0) = \int_{\vec{r}(0)=0}^{\vec{r}(L)=\vec{h}} D[\vec{r}(s)] \exp\left\{-\frac{3}{2A} \int_{0}^{L} ds \, \vec{r}^{2}(s) - \frac{1}{2} \int_{0}^{L} ds \int_{0}^{L} ds' \, \mathcal{V}[\vec{r}(s) - \vec{r}(s')]\right\}. \quad (205)$$

The interrelation between Wiener's integral (Equation 189) and the diffusion equation (Equation 190) presupposes the existence of a differential equation for $G(\vec{h}0, L0)$ (Gelfand and Yaglom, 1956). Special analysis (Freed, 1972) shows that the function from Equation 205 can be represented only by a hierarchy of integro-differential equations. For this purpose, Green's three-point function

$$G_{3}(\vec{h}\vec{R}'0;LL'0) = \int_{\vec{r}(0)=0}^{\vec{r}(L)=\vec{h}} D\left[\vec{r}(s)\right] \delta\left[\vec{r}(L') - \vec{R}'\right]$$

$$\times \exp\left\{-\frac{3}{2A} \int_{0}^{L} ds \, \vec{r}''(s) - \frac{1}{2} \int_{0}^{L} ds \int_{0}^{L} ds' \, \mathcal{V}\left[\vec{r}(s) - \vec{r}(s')\right]\right\}$$
(206)

is defined, which selects chains having their segments at the points 00, $\vec{R'}L'$, and $\vec{h}L$ out of a large set of chains with the contour length L. The corresponding probability is

$$P(\vec{R}'L'|\vec{h}L) = \frac{G_3(\vec{h}\vec{R}'0;LL'0)}{G(\vec{h}0;L0)}.$$
(207)

If no fixing of the chain ends in space is required, then the probability of the presence of the segment at $(\vec{R'}, L')$ at any end-to-end vector will be

$$P(\vec{R}'L'|L) = \frac{\int d\vec{h} \, G_3(\vec{h} \, \vec{R}'0; LL'0)}{\int d\vec{h} \, G(\vec{h}0; L0)}$$
(208)

and the hierarchy begins with

$$\left[\frac{\partial}{\partial L} - \frac{A}{6}\nabla_{\vec{h}}^{2}\right]G(\vec{h}0;L0) + \int d\vec{R}' \,\mathcal{V}(\vec{h} - \vec{R}')\int_{0}^{L} ds \,G_{3}(\vec{h}\vec{R}'0;Ls0)$$

$$= \delta(\vec{h})\delta(L).$$
(209)

Then follows a similar equation for G_3 , involving the four-point function G_4 , etc. For a continuous chain, the hierarchy is endless while for a discrete one it finishes at $G_n \equiv G(\{\vec{r}_k\})$ (Equation 79).

The assumption that there exists an appropriate self-consistent field implies break-down of the space isotropy in some way. Such anisotropy is introduced either by a statement that the initial point preserves its position $\vec{r}(0) \equiv 0$ or by additional fixing of the second end of the chain at $\vec{r}(L) \equiv \vec{h}$. In the first case, the field is spherically symmetrical about the origin of coordinate. In the second case, $(\vec{r}(0) \equiv 0 \text{ and } \vec{r}(L) \equiv \vec{h} \text{ are fixed})$, the field has the symmetry $D_{\infty h}$ with respect to these two points (focuses).

In addition to break-down of the space isotropy, introduction of the self-consistent field implies the approximation of Markov's processes for an actually non-Markov one described by Equation 209. Hence, if V_{SCF} is the self-consistent field, then Markov's approximation of Equation 205 is contained in

$$G_{\rm SCF}(\vec{h}0; L0[\vec{h}L]) = \int_{\vec{r}(0)=0}^{\vec{r}(L)-\vec{h}} D[\vec{r}(s)] \exp\left\{-\frac{3}{2A}\int_{0}^{L} ds \, \vec{r}^{2}(s) - \int_{0}^{L} ds \, \mathcal{V}_{\rm SCF}[\vec{r}(s)]\right\}$$
(210)
$$= \lim_{\rm CERWC} \int d\vec{r}_{0} \left\{\prod_{j=1}^{m} \int d\vec{r}_{j} \, P(\vec{r}_{j} - \vec{r}_{j-1}; \Delta s_{j}) \exp\left(-\mathcal{V}_{j}\Delta s_{j}\right)\right\} \delta(\vec{r}_{0}) \delta(\vec{r}_{n} - \vec{h}),$$

where $[\vec{h}L]$ means that \vec{h} and L are fixed, $[\mathcal{V}_0(0) \equiv 0]$. This equation shows that G_{SCF} obeys the differential equation

$$\left[\frac{\partial}{\partial s} - \frac{A}{6}\nabla_{\vec{R}'}^2 + \mathcal{V}_{\rm SCF}(\vec{R}'[\vec{h}L])\right] G_{\rm SCF}(\vec{R}'\vec{R}'';ss'[\vec{h}L]) = \delta(\vec{R}' - \vec{R}'') \times \delta(s-s'), \quad (211)$$

where \mathcal{V}_{SCF} is a certain functional of G_{SCF} .

Thus, this equation is closed. Its defining G_{SCF} as Green's function of the diffusion equation points to the fact that it describes Markov's process in an external field (Gelfand and Yaglom, 1956).

To get Markov's approximation for G_3 , the number of the chains going from 00 to $\vec{R}'s$ is multiplied by that of the chains going from $\vec{R}'s$ to $\vec{h}L$, or

$$G_{3\,\text{SCF}}(\vec{h}\vec{R}0;Ls0[\vec{h}L]) = G_{\text{SCF}}(\vec{h}\vec{R}';Ls[\vec{h}L])G_{\text{SCF}}(\vec{R}'0;Ls0[\vec{h}L]).$$
(212)

Introduction of Green's function of the self-consistent field including an intermediate point along the chain (in addition to the end points of the chain) is the cost to be paid for using Markov's approximation.

Closure of the self-consistent field equation requires a motion equation for the main propagator $G_{\text{SCF}}(\vec{R}'\vec{R}''; ss'[\vec{h}L])$. It is specially proven (Freed, 1972) that if \mathcal{V}_{SCF} is chosen to give the best approximation for direct calculating $\langle h^2 \rangle$ by

$$\left\langle h^2 \right\rangle_L = \frac{\int d\vec{h} \, \vec{h}^2 G(\vec{h}0; L0)}{\int d\vec{h} \, G(\vec{h}0; L0)},$$
(213)

then Equation 211 with

$$\mathcal{V}_{\rm SCF}(\vec{R}'[\vec{h}L]) = \int d\vec{r} \int_{0}^{L} ds \, \mathcal{V}(\vec{R}' - \vec{r}) G_{\rm SCF}(\vec{h}\vec{r}; Ls[\vec{h}L]) \times \frac{G_{\rm SCF}(\vec{r}0; s0[\vec{h}L])}{G_{\rm SCF}(\vec{h}0; L0[\vec{h}L])}$$
(214)
$$\equiv \int d\vec{r} \int_{0}^{L} ds \, \mathcal{V}(\vec{R}' - \vec{r}) P_{\rm SCF}(\vec{r}; s|\vec{h}L)$$

should be used as a motion equation.

This problem is mathematically similar to the problem of electron motion in the mean (self-consistent) field of the other electrons in a multiatomic molecules (Edwards, 1965, 1966, 1967; Freed, 1972), its solution is

$$G(h0; L0) = \mathcal{N}(L) \exp\left\{-27\left\{h - \left(\frac{5}{3}\right)^{3/5} \left(\frac{\beta}{3\pi A}\right)^{1/5} L^{3/5}\right\} \frac{1}{20LA}\right\},\tag{215}$$

$$\left\langle h^2 \right\rangle^{1/2} = \left(\frac{5}{3}\right)^{3/5} \left(\frac{\beta}{3\pi A}\right)^{1/5} L^{3/5},$$
 (216)

which matches, in essence, Flory's results (Equation 113)

Now let us discuss the morphological features of polymer solutions within a wide concentration range. To this end, a pair correlation function of segment density $g(\vec{r})$ is introduced (de Gennes, 1979; Khokhlov, 1985): a certain chain segment is placed at the origin of coordinates and the numerical density of all the other segments at distance \vec{r} is determined with subsequent averaging of the results over all the possible ways of choosing the first (fixed) segment.

In view of Equations 104 and 149,

$$g_{\rm id}(\vec{r}) = \frac{3}{\pi A^2 \vec{r}}.$$
 (217)

In a rough approximation (see Equation 106)

$$g_{\rm id}(r) \sim \frac{N}{r^3} \sim \frac{r^2}{A^2 r^3} \sim \frac{1}{A^2 r}.$$
 (218)

Morphologically, a **dilute** solution is spoken of when molecular coils do not overlap.

In a semidilute solution, the coils overlap, but the segment density is small in comparison with that in the condensed state. If we denote the overlap density as

$$c = \frac{N}{V},\tag{219}$$

then the overlap (mutual touch) boundary corresponds to the equality of the segment densities in solution and inside a coil

$$c^* \sim \frac{N}{\left(\overline{R^2}\right)^{3/2}}.$$
(220)

Hence, at

$$c < c^* \tag{221}$$

the solution is dilute, at

$$c^* < c \ll c_\rho \tag{222}$$

it is semidilute (where c_{ρ} is the segment density in the condensed state). In the range

$$c \le c_{\rho} \tag{223}$$

the solution is regarded as concentrated .

In the range of dilute solutions, the density of non-interacting segments inside a coil with reference to the fixed segment decreases according to Equations 217 and 218 (Figure 3.7, curve 1).



Figure 3.7. Pair correlation function of segments g(r) in dilute solutions (a single chain) in ideal (1) and good (2) solvent, and in semidilute solutions (3) (de Gennes, 1979) [Reprinted from Pierre-Gilles de Gennes *Scaling Concepts in Polymer Physics*. Copyright © 1979 by Cornell University. Used by permission of the publisher, Cornell University Press]

In a good solvent (see Equation 142),

$$g(r) \sim \frac{N}{r^3} \sim \frac{r^{5/3}}{A^{2/3}r^3} \sim \frac{1}{A^{2/3}r^{4/3}},$$
 (224)

i.e. the segment concentration measured from a fixed point inside the coil diminishes with distance somewhat stronger (Figure 3.7, curve 2).

As the polymer concentration increases, at small $(r < \xi)$ distances, the distribution (Equation 224) characteristic of a good solvent remains. But at large $(r > \xi)$ distances, the distribution of chain fragments of length ξ becomes Gaussian (Equation 218) (as in the θ solvent) due to the repulsion of the segments of other macromolecules.

The distance ξ is called a screening length (originally introduced by Edwards, 1966).

In dilute solutions, no compensation of the segment excluded volume by other macromolecules takes place, so the coil size R determines the upper boundary of ξ . As the polymer concentration rises, ξ may, in principle, diminish to the linear sizes of the segment excluded volume

$$\beta^{1/3} < \xi < \left(\overline{R^2}\right)^{1/2}.\tag{225}$$

We remind that when $T \to \theta$, the excluded volume $\beta \to 0$.

In terms of segment density (Equation 224), the screening length ξ in semidilute solutions is equivalent to the distance from a certain fixed segment, where the local segment concentration $c_0(\xi)$ becomes equal to the mean c over all the solution.

At distances $r \leq \xi$, chain fragments (alias called **blobs**) behave as if the molecular chain were isolated, i.e. a blob "keeps its memory" of the structure of an isolated coil in a good solvent. If a blob comprises g segments, then (see Equation 142)

$$\xi \sim g^{3/5}$$
. (226)

At distances $r > \xi$, the "memory" of the structure of an isolated coil in a good solvent (semidilute solution) gets lost, and the blobs form already a chain of non-interacting elements, so

$$\overline{h^2}(c) = \frac{N}{g}\xi^2,\tag{227}$$

where N/g is the number of blobs in a macromolecule (cf. Equation 103) (Figure 3.8).

In semidilute solutions with $c > c^*$, the screening length ξ does not depend on the number of segments in a macromolecule and corresponds (on the average) to the distance between the contacts of non-neighbouring segments (see Figure 3.8).

The length ξ is called screening due to the sufficient analogy with Debye-Hückel's screening length (interaction between a charged surface and ions in solution in the problem of a double electrical layer).

In the approximation of ideal chains being in the mean field of the potential $\varphi(\vec{r})$ owing to the presence of other chains (Edwards, 1966; de Gennes, 1979), the segment concentration near the point $\vec{r'}$ given $\varphi(\vec{r'})$ is small falls according to

$$c \exp\left[-\frac{\varphi(\vec{r}')}{kT}\right] \approx c - \frac{c\varphi(\vec{r}')}{kT},\tag{228}$$

and the correlation function $g(\vec{r})$ differs from $g_{\rm id}(\vec{r})$ by

$$g(\vec{r}) - Cg_{\rm id}(\vec{r}) = -\int g_{\rm id}(\vec{r} - \vec{r}') \frac{c\varphi(\vec{r}') \, d\vec{r}'}{kT},\tag{229}$$



Figure 3.8. Schematic of the structure of a polymer semidilute solution (de Gennes, 1979) [Reprinted from Pierre-Gilles de Gennes Scaling Concepts in Polymer Physics. Copyright © 1979 by Cornell University. Used by permission of the publisher, Cornell University Press]

where C is a normalization constant differing from that $g(\vec{r})$. In terms of generalized functions (see, eg. Vladimirov, 1967, 1979),

$$\Delta\left(\frac{1}{\vec{r}}\right) = -4\pi\delta(\vec{r}). \tag{230}$$

In view of Equations 230 and 217, applying Laplace's operator to both the sides of Equation 229 gives

$$\nabla^2 g(\vec{r}) = \frac{12rc\varphi(\vec{r})}{A^2kT} - \frac{12}{A^2}\delta(\vec{r})C.$$
(231)

Here we have used the property of the $\delta(\vec{r})$ function:

$$\int \delta(\vec{r} - \vec{r}')\varphi(\vec{r}') d\vec{r}' = \varphi(\vec{r}).$$

Further, the potential $\varphi(\vec{r})$ is assumed to be proportional to the local concentration $g(\vec{r})$, and the excluded volume β , i.e.

$$\varphi(\vec{r}) = kT\beta g(\vec{r}). \tag{232}$$

Therein lies the self-consistent field procedure.

Substitution of Equation 239 into Equation 231 leads to an equation of the Debye-Hückel type in the problem of a double electrical layer

$$\nabla^2 g(\vec{r}) = \xi^{-2} g(\vec{r}) - \frac{12}{A^2} \delta(\vec{r}) C, \qquad (233)$$

where

$$\xi^{-2} = \frac{12c\beta}{A^2}.$$
 (234)

Of all the solutions of Equation 233, only that must be selected which reduces to an unperturbed function g_{id} at small distances, since, in this case, the situation due to one chain always predominates, and Edwards' (1966) approximation (de Gennes, 1979) presumes every chain to be ideal (see Equation 217), i.e.

$$g(\vec{r}) = \frac{3C}{\pi A^2 r} \exp\left(-\frac{r}{\xi}\right)$$
(235)

with C to be determined from

$$g(\xi) = c. \tag{236}$$

Finally, we have

$$g(\vec{r}) = \frac{\varepsilon\xi e}{r} \exp\left(-\frac{r}{\xi}\right)$$
(237)

(Figure 3.7, curve 3).

Its Fourier transform (de Gennes, 1979) (cf. Equations 2.3-129,-131...133)

$$g(\vec{q}) \sim \frac{c\xi}{q^2 + \xi^{-2}}$$
 (238)

is proportional to the scattered light intensity with an appropriate λ range (see Chapter 2 for details).

By means of light scattering, the screening length ξ can be defined with Equation 238. According to Equation 234, $\xi\sqrt{c}$ must be constant, which has been observed in experiments on light and neutron scattering in polystyrcne solutions in cyclohexane (Cotton et al., 1972). There are two plateaux on the curve $\xi\sqrt{s}$ vs c. According to Equation 234, the data at high or low concentrations correspond to the excluded volume of a segment or of the whole macromolecule v_{ex} , respectively. Further details about the properties of ξ will be considered in Chapter 4.

3.1.2. Conditions of liquid-liquid phase separation

Figures 3.2 and 3.3 show that when $\chi_1 > 0.5$

$$\frac{\partial \Delta \mu_1}{\partial v_2} > 0; \qquad \frac{\partial \Delta \mu_2}{\partial v_2} < 0$$

hold within a certain concentration range v_2 , which points to the existence of a region of absolute instability.

One can easily make sure of the identity of the spinodal conditions (Equations 1.2 60, 1.3 19) and the critical point conditions (Equations 1.2 60, 61, 1.3 19, 20) when concentrations are expressed in different units.

The spinodal equation in the P+LMWL system results from state equation 50 and $\partial \Delta \mu_1 / \partial n_1 = 0$ (Figure 3.9)

$$\chi_1 = \frac{1}{2(1-v_2)} + \frac{1}{2zv_2}.$$
(239)



Figure 3.9. State diagram of the binary system P+LMWL from Flory-Huggins' lattice model. Plot χ_1 vs v_2 (solid lined are binodals, dotted lines are spinodals, and the digits at the curves are the values of z) (Tompa, 1956) [H.Tompa *Polymer Solutions*. Copyright © 1956 by Academic Press]

For the critical point, in addition,

$$\frac{\partial^2 \Delta \mu_1}{\partial n_1^2} = 0$$

must be satisfied

$$\chi_{1e} = \frac{1}{2(1 - v_{2e})^2}.$$
(240)

It can be obtained from Equations 239 and 240 by solving the quadratic equation with respect to v_{2c} that

$$v_{2c} = \frac{1}{1 + \sqrt{z}}.$$
(241)

In the limit $z \to \infty$, $v_{2c} \to 0$, and, in view of Equation 240, $\chi_{1c} \to 1/2$.

In the other limiting case z = 1, $v_{2c} \rightarrow 1/2$ in accordance with Equation 1.3-22 (x_2 replaced by v_2) and $\chi_{1c} = 2$. In view of Equation 33, $\chi_{1c} = \alpha/RT_c = 2$ in accordance with Equation 1.3-23 as well.

Excluding v_{2c} from Equations 240 and 241, we have

$$\chi_{1\epsilon} = \frac{1}{2z} + \frac{1}{z^{1/2}} + \frac{1}{2}.$$
(242)

Taking Equations 40 and 41 into account,

$$\chi_{1e} = \kappa_{1e} - \psi_1 + \frac{1}{2} \tag{243}$$

and

$$\frac{\kappa_{1c}}{\psi_1} = \frac{\theta}{T_c}.$$
(244)

Substitution of Equation 243 into Equations 244 and 242 yields

$$\frac{1}{T_c} = \frac{1}{\theta} + \frac{1}{\psi_1 \theta} \left(\frac{1}{2z} + \frac{1}{\sqrt{z}} \right)$$
(245)

or (see Equation 1)

$$\frac{1}{T_c} = \frac{1}{\theta} \left[1 + \frac{1}{\psi_1} \left(\frac{\bar{V}_{01}}{\bar{v}_2} \right)^{1/2} M^{-1/2} + \frac{\bar{V}_{01}}{2\psi_1 \bar{v}_2} M^{-1} \right].$$
(246)

Hence, the plot

$$\frac{1}{T_c} vs \frac{1}{2z} + \frac{1}{\sqrt{z}}$$

or

$$\frac{1}{T_c} vs \frac{1}{2M} + \frac{1}{\sqrt{M}}$$

is a straight line whose parameters give $1/\theta$ and ψ_1 (Shultz and Flory, 1952). Then, it follows from Equation 244 that

$$\kappa_{1c} = \frac{\theta \psi_1}{T_c} \tag{247}$$

or, for any other temperature,

$$\kappa_1 = \frac{\theta \psi_1}{T},\tag{248}$$

and (see Equations 40 and 41)

$$\chi_1 = \frac{1}{2} - \psi_1 \left(1 - \frac{\theta}{T} \right). \tag{249}$$

So, we are able to convert the χ_1 axis (see Figure 3.9) into a temperature one which is necessary to a comparison between the theoretical spinodals (Equation 239) and binodals (further) and the experimental ones.

Equation 245 implies that Flory's temperature θ is the critical one T_c for $z \to \infty$ (Shultz and Flory, 1952).

The plot of Equation 245 is valid, strictly speaking, only when $\psi_1 = const$ (see Figure 3.4), but Equations 245 and 246 have turned out to be low sensitive to a number of details of the P+LMWL lattice model. More rigorous consideration involving the third virial coefficient \mathcal{A}_3 (Stockmayer, 1960) leads to

$$\frac{1}{\mathcal{T}_c} = \frac{1}{\theta} \left[1 + \frac{1}{\psi_1} \left(\frac{\dot{V}_{01}}{\mathbf{v}_2^2} \right) \left(\frac{3\mathcal{A}_3^\circ}{M} \right)^{1/2} \right],\tag{250}$$

 \mathcal{A}_3° being the third virial coefficient at the θ point (cf. Figure 1.41).

The parameters θ , χ_1 , ψ_1 , and κ_1 can be also estimated from the temperature dependence of \mathcal{A}_2 . The θ temperature results immediately from the plot of \mathcal{A}_2 vs T at $\mathcal{A}_2 = 0$ (see Figure 3.4) (Shultz et al., 1960, 1963, 1966; Eskin, 1973), and ψ_1 (Equation 53 or 146) is obtained from

$$\left(\frac{\partial \mathcal{A}_2}{\partial (1/T)}\right)_{T=\theta} = -\frac{\bar{\mathbf{v}}_2^2}{\bar{V}_{01}}\psi_1\theta \tag{251}$$

(when $T \to \theta$, $h(z) \to 1$).

As experiment shows, the θ values determined from Equations 246 and 250 are in excellent agreement while ψ_1 from the same equations differ noticeably. Eg. for the systems polyisobutylene+diisobutylketone and polystyrene+cyclohexane, according to Equation 246, $\psi_1 = 0.65$ and 1.06, respectively, while those calculated from Equation 25 are of the order of 0.1 (Shultz and Flory, 1952). This discrepancy reveals the limitations of the lattice model (Flory, 1953).

Application of the binodal conditions (Equations 1.3-26 and 1.3-27) for liquid-liquid two-phase separation $\Delta \mu_{1I} = \Delta \mu_{1II}$, $\Delta \mu_{2I} = \Delta \mu_{2II}$ to the P+LMWL system with state equations 50 and 51 leads to

$$v_{2II} = v_{2I} \exp(z\sigma), \tag{252}$$

where

$$\sigma = 2\chi_1(v_{2II} - v_{2I}) + \ln \frac{v_{1II}}{v_{1I}}.$$
(253)

As $\sigma > 0$ and z is large, Equation 252 shows great asymmetry of the binodal curves (see Figure 3.9).

Flory (1944, 1953) has proposed the following method for binodal calculations at small v_{2I} and v_{2II} .

If we exclude χ_1 from Equations 1.3–23 and 1.3–27 with allowance for Equations 50 and 51, then

$$\left[1 - \frac{(\gamma+1)v_{2I}}{2}\right]\ln\frac{1 - \gamma v_{2I}}{1 - v_{2I}} + \left[\left(1 - \frac{1}{z}\right)(\gamma-1) + \frac{1}{2z}(\gamma+1)\ln\gamma\right]v_{2I} = 0$$
(254)

will result, where $\gamma = v_{2II}/v_{2I}$. Now the logarithmic terms should be expanded into their Taylor series with keeping the terms with v_{2I}^3 , and several summands are approximated by

$$\frac{1}{6} \left[1 - (\gamma + 1) v_{2I} \right]^{-1}$$

and

$$v_{2I} \simeq \frac{-(\gamma+1)h + [(\gamma+1)^2h^2 + 4(\gamma-1)^3h]^{1/2}}{2(\gamma-1)^3},$$
(255)

where

$$h = \frac{12}{z} \left[\frac{1}{2} (\gamma + 1) \ln \gamma - (\gamma - 1) \right].$$

Solving Equations 1.3-26 and 1.3-27 together with Equations 50 and 51 with respect to χ_1 yields

$$\chi_{1} = \frac{(\gamma - 1)(1 - z^{-1}) + (\ln \gamma)/v_{2I}z}{2(\gamma - 1) - v_{2I}(\gamma^{2} - 1)}.$$
(256)

Binodals are calculated as follows: γ is chosen arbitrarily. For a given z and chosen γ , v_{2I} is calculated according to Equation 255 and $v_{2II} = \gamma v_{2I}$. Then, Equation 256 enables χ , to be calculated. Conversion to the T scale is performed by means of Equation 249.

Figure 3.9 presents examples of binodals and spinodals.

Shultz and Flory (1952) have compared theory and experiment for the polystyrenc+cyclohexane system and revealed qualitative agreement in the locations of phase separation regions, but the theoretical region of incompatibility proved to be more narrow; this was explained by the authors by the imperfection of the theory. On the other hand, this discrepancy may be caused by polymolecularity of polymer fractions (Koningsveld, 1968; 1970a; Koningsveld and Staverman, 1966, 1967ab, 1968abcde; Rehage and Koningsveld, 1968; Gordon et al., 1969; Koningsveld et al., 1970ab, 1974a; Koningsveld and Kleintjens, 1971) (see below).

In the general case, expansion of the logarithmic terms into a Taylor series with respect to v_{21} powers brings Equation 254 to the form (Klenin and Shchyogolev, 1979)

$$\frac{h}{12} + \sum_{k=3}^{\infty} A_k v_{2I}^{k-1} = 0,$$
(257)

where

$$A_{k} = -\sum_{l=1}^{k-2} l C_{k}^{l+2} (\gamma - 1)^{l+2} / 2k(k-1),$$

 C_k^{l+2} are the binomial coefficients. This equation is solved by successive approximations with Equation 255 accepted as the first approximation.

For a given χ_1 , the points v_{2sp1} and v_{2sp11} on the spinodal are obtained by solving the quadratic (with respect to v_{2sp}) equation 239.

In particular, near the critical point, the solution of Equation 239 is (Klenin and Shchyogolev, 1979)

$$v_{2spl}, v_{2spll} = \frac{z^{-1} + \Delta \chi_1 + z^{-1/2} \mp \sqrt{\Delta \chi_1 (\Delta \chi_1 + 2z^{-1/2})}}{2\chi_1},$$
(258)

where $\Delta \chi_1 = \chi_1 - \chi_{1c}$, and χ_{1c} is determined by Equation 242. The minus sign before the radical relates to v_{2spI} , and the plus sign relates to v_{2spII} .

Maron and Nakajima (1966) plotted binodals using the $\Delta \mu_1(v_2)$ and $\Delta \mu_2(v_2)$ dependences. By the trial and error method, they found such values of v_{2I} and v_{2II} as to satisfy $\Delta \mu_{1I} = \Delta \mu_{1II}$ and $\Delta \mu_{2I} = \Delta \mu_{2II}$.

Van Emmerik and Smolders (1973a) calculated $\Delta \bar{G}_m/RT$ and plotted $\Delta \bar{G}_m/RT$ vs w, w being the weight fraction of a polymer. The two points of the straight line's tangency to the isotherm corresponded to the binodal concentrations (w_I and w_{II}) for a given T (see Figures 1.7 and 1.13b). Budtov (1983, 1985b, 1986) has proposed an analytical approximation for the binodal and spinodal near the critical point with the interaction parameter χ_i replaced by the parameter E

$$E = 2\chi_1 - 1,$$
 (259)

which is larger than zero for a non-solvent and a poor solvent at a finite molecular mass and is less than zero for a good solvent. E = 0 and E = -1 in the case of the θ solvent and an athermal one, respectively.

At the critical point,

$$v_{2c} = \frac{1}{\sqrt{z+1}} \sim \frac{1}{\sqrt{z}}, \qquad E_c = \frac{2\sqrt{z+1}}{z} \approx \frac{1}{\sqrt{z}}.$$
 (260)

Near it,

$$E = E_c(1+\delta),\tag{261}$$

$$\delta = \frac{2\chi'_{H}}{T_{c}E_{c}} \left(1 - \frac{T}{T_{c}}\right),\tag{262}$$

where

$$\chi_1 = \chi_s + \frac{\chi'_H}{T}.$$
(263)

Substitution of Equations 259 and 261 to spinodal equation 239 leads to expressions for the left-hand v_{2spl} and right-hand v_{2spll} branches of the spinodal

$$v_{2spI} = v_{2c} e^{-\sqrt{2\delta}}; \quad v_{2spII} = v_{2c} e^{\sqrt{2\delta}} \quad \text{at } 0 < \delta < 1,$$
 (264)

$$v_{2spl} = \frac{E_c}{4(1+\delta)}; \quad v_{2spll} = \frac{E}{1+E} \quad \text{at } \delta > 1.$$
 (265)

To calculate the binodal,

$$\Delta v_{2I} = v_{2spI} - v_{2I} \quad \text{and} \quad \Delta v_{2II} = v_{2spII} - v_{2II} \tag{266}$$

are accepted with

$$\Delta v_{21} \ll v_{2c} \quad \text{and} \quad \Delta v_{211} \ll v_{2c}. \tag{267}$$

The Taylor series expansion of $\Delta \mu_1$ and $\Delta \mu_2$ near v_{2spl} and v_{2spll} , in view of Equations 259 and 261, followed by approximation of the first terms by an analytical function, gives

$$v_{2I} = v_{2c} e^{-1.817\sqrt{2\delta}}$$
 and $v_{2II} = v_{2c} e^{1.817\sqrt{2\delta}}$. (268)

Determine the critical indices β (for the binodal) and β_{sp} (for the spinodal) according to the above approximations of Flory-Huggins' theory.

According to Equation 258,

$$v_{2spII} - v_{2spI} = \frac{\sqrt{\Delta\chi_1(\Delta\chi_1 + 2z^{-1/2})}}{\chi_1}.$$
(269)

Neglecting $\left(\Delta\chi_{1}\right)^{2}$ in the nominator,

$$v_{2spll} - v_{2spl} \approx \sqrt{\frac{2}{\chi_1}} \left(\frac{\Delta\chi_1}{\chi_1}\right)^{1/2} z^{-1/4}.$$
 (270)

Setting the approximation $\chi_i \sim 1/T$, it follows that

$$v_{2spII} - v_{2spI} \sim \left(\frac{T_c - T}{T_c}\right)^{\beta_{sp}} z^{-1/4} = (-\varepsilon)^{\beta_{sp}} z^{-1/4}, \tag{271}$$

where $\beta_{sp} = 1/2$, which is in agreement with the mean field approximation.

Equations 264 and 268 yield the law of $\beta = 1/2$ and $\beta_{sp} = 1/2$:

$$v_{2spII} - v_{2spI} = v_{2c} \left[1 + \sqrt{2\delta} + \dots - \left(1 - \sqrt{2\delta} + \dots \right) \right] \approx 2\sqrt{2} v_{2c} \sqrt{\delta}.$$
(272)

With due account of Equations 262 and 260, we get

$$v_{2spII} - v_{2spI} \approx A(-\varepsilon)^{1/2} z^{-1/4}.$$
 (273)

Similarly, it follows from Equations 268, 260, and 262 that

$$v_{2II} - v_{2I} = 1.817A(-\varepsilon)^{1/2} z^{-1/4}, \tag{274}$$

i.e. near the critical point, the **binodal amplitude** (Equation 274) exceeds the **spinodal amplitude** (Equation 273) by 1.817.

Sanchez (1984) has performed analysis of the binodal and spinodal amplitudes, using Flory-Huggins's theory in the fashion of Landau's phenomenological theory.

The Gibbs potential is written as

$$G = G(T_c, \Phi_c) + G_{\Phi} \Delta \Phi + G_T \Delta T + G_{\Phi T} \Delta \Phi \Delta T$$

$$+ \frac{1}{2} G_{TT} (\Delta T)^2 + \frac{1}{2} G_{\Phi \Phi T} \Delta T (\Delta \Phi)^2 + \frac{1}{4!} G_{\Phi \Phi \Phi \Phi} (\Delta \Phi)^4,$$
(275)

where Φ is the volume fraction of a polymer, $\Delta T = T - T_c$, $\Delta \Phi = \Phi - \Phi_c$. The superscripts denotes the derivative with respect to the corresponding variables at the critical point.

According to Equations 1.2-60,-61, and 1.3-19,-20, $G_{\Phi\Phi} = G_{\Phi\Phi\Phi} = 0$.

For the binodal (Equations 1.3 26.-27),

$$\left(\frac{\partial G}{\partial \Phi}\right)_{\Phi=\Phi_I} = \left(\frac{\partial G}{\partial \Phi}\right)_{\Phi=\Phi_{II}} \tag{276}$$

According to Landau's theory, the binodal is symmetrical about Φ_c near the critical point, and

$$\Phi_{II} - \Phi_c = \Delta \Phi_{bi} = \Phi_c - \Phi_I, \tag{277}$$
and, together with Equation 276,

$$G_{\Phi\Phi T}\Delta T + \frac{1}{6}G_{\Phi\Phi\Phi\Phi} \left(\Delta\Phi_{bi}\right)^2 = 0 \tag{278}$$

ог

$$\Delta \Phi_{bi} = \pm \left(\frac{6S_{\Phi\Phi}\Delta T}{G_{\Phi\Phi\Phi\Phi}}\right)^{1/2},\tag{279}$$

where

$$-G_{\Phi\Phi T} = S_{\Phi\Phi} = \left(\frac{\partial^2 S}{\partial \Phi^2}\right)_{T_c, \Phi_c},$$

S is the entropy.

For systems with an UCST, $\Delta T < 0$ and $S_{\Phi\Phi} < 0$ while for systems with a LCST $\Delta T > 0$ and $S_{\Phi\Phi} > 0$ (Prigogine and Defay, 1954), so $S_{\Phi\Phi}\Delta T$ is always positive.

As the function $G = G(\Phi)$ has a shallow minimum on the critical isotherm at $\Phi = \Phi_c$, $G_{\Phi\Phi\Phi\Phi} > 0$. Hence, according to Equation 279, $\Delta \Phi_{bi}$ is always real for systems with either UCST or LCST.

With the new notation, the Gibbs potential takes the form (cf. Equation 31)

$$G = G_0 + kT \left[(1 - \Phi) \ln(1 - \Phi) + \frac{\Phi}{z} \ln \Phi + \Phi (1 - \Phi) \chi_1 \right].$$
(280)

The spinodal equation is (cf. Equation 239)

$$\left(\frac{\partial^2 G}{\partial \Phi^2}\right)_T = \left\{ (1-\Phi)^{-1} + (z\Phi)^{-1} - 2\chi_1 \right\} kT = 0.$$
(281)

At the critical point, $G_{\Phi\Phi\Phi} = 0$ and (cf. Equation 241)

$$\Phi_c = \frac{1}{1+z^{1/2}}.$$
(282)

With the approximation $2\chi_1 = \theta/T$ and

$$2\chi_{1e} = \frac{\theta}{T_c} \qquad \left(\psi_1 = \frac{1}{2}\right) \tag{283}$$

(cf. Equations 248, 243, and 249) and substituting Equation 282 to Equation 281, we get

$$2\chi_{1c} = \left(1 + z^{-1/2}\right)^2 = \frac{\theta}{T_c}.$$
(284)

Equation 280 yields

$$G_{\Phi\Phi T} = -S_{\Phi\Phi} = k \left(1 + z^{-1/2}\right)^2 = \frac{k\theta}{T_c}$$
(285)

and

$$G_{\Phi\Phi\Phi\Phi} = 2z^{1/2} \left(1 + z^{-1/2} \right)^4 k\theta.$$
(286)

Substitution of these equations to Equation 279 leads to

$$\Delta \Phi_{bi} = \pm \left[\frac{3(T_c - T)}{T_c z^{1/2}} \right]^{1/2} \frac{T_c}{\theta},$$
(287)

i.e.

$$\Delta \Phi_{bi} \sim (-\varepsilon)^{\beta} z^{-1/4}, \tag{288}$$

where $\beta = 1/2$.

Having denoted

$$\Phi_{spII} - \Phi_c = \Delta \Phi_{sp} = \Phi_c - \Phi_{spI}, \tag{289}$$

we obtain from the spinodal condition $\partial^2 G/\partial \Phi^2 = 0$ and Equation 275

$$\Delta \Phi_{sp} = \pm \left(\frac{2S_{\Phi\Phi}\Delta T}{G_{\Phi\Phi\Phi\Phi}}\right)^{1/2}.$$
(290)

It is characteristic that the relationship

$$\frac{\Delta\Phi_{bi}}{\Delta\Phi_{sp}} = \sqrt{3} \approx 1.73 \tag{291}$$

matches that for the binary low-molecular mixture (Cook and Hilliard, 1965) and for liquid-vapour transitions (a so-called "square root of three" rule) (cf. Equations 273 and 274) (Landau and Lifshitz, 1964).

A simulation on the 3D Ising's lattice (Gaunt and Baker, 1970) has shown the spinodal to be located closer to the binodal

$$\frac{\Delta \Phi_{bt}}{\Delta \Phi_{sp}} = 1.18, \tag{292}$$

In any case, estimations of the relative position of the binodal and spinodal may be helpful from different viewpoints since the spinodal is calculated in a much simpler way than the binodal.

Either Equations 290, 291, 287 or Equations 280, 290 give, in Flory-Huggins-Sanchez' approximation,

$$(\Delta \Phi_{sp})^2 = \frac{(\Delta \Phi_{bi})^2}{3} = \frac{\Delta T T_c}{z^{1/2} \theta^2} , \qquad (293)$$
$$\Delta \Phi_{sp} \simeq \frac{1}{\theta} (-\varepsilon)^{\beta_{sp}} z^{-1/4}, \quad \beta_{sp} = \frac{1}{2}.$$

The location of the binodals and spinodals in polymer systems will be discussed in section 4.3.

In the above considerations, only binary interactions of macromolecule(s) segments were taken into account in the state equations. The measure of the intramolecular pair interactions is the segment excluded volume β (the binary cluster integral, Equation 120).

The measure of the intermolecular pair interactions is the second virial coefficient A_2 in the virial expansion of osmotic pressure (see Equations 1.3-37, 52-54, 146-148).

Now, let us take into account ternary interactions which are reflected in the third virial coefficient A_3 , i.e. the coefficient with the cubic term of the virial series expansion of π (de Gennes, 1979; Perzynski et al., 1987).

In conformity to the real gas theory, the third virial coefficient (see Equation 1.2-68) is proportional to the triple cluster integral (see Equations $1.8 \cdot 15, -14, \cdot 10$).

According to what has been said, when π is expressed through $\Delta \mu_1$ (Equation 1.2-27), $\ln(1-v_2)$ in Equation 50 should be approximated by a three-term series expansion

$$\ln(1-v_2) \approx -v_2 - \frac{v_2^2}{2} - \frac{v_2^3}{3} - \cdots$$

Then

$$\frac{\Delta\mu_1}{RT} = -\left[\frac{v_2}{z} + \left(\frac{1}{2} - \chi_1\right)v_2^2 + \frac{v_2^3}{3}\right]$$
(294)

and

$$\frac{\pi}{RT} = -\frac{\Delta\mu_1}{\bar{V}_{01}} \approx \frac{v_2}{z\bar{V}_{01}} + \frac{1}{\bar{V}_{01}} \left(\frac{1}{2} - \chi_1\right) v_2^2 + \frac{v_2^3}{3\bar{V}_{01}}.$$
(295)

If we expand π with respect to c (g/cm³), then

$$\frac{\pi}{RT} = \frac{\mathbf{c}\bar{\mathbf{v}}_2}{z\bar{V}_{01}} + \frac{\bar{\mathbf{v}}_2^2}{\bar{V}_{01}} \left(\frac{1}{2} - \chi_1\right) \mathbf{c}^2 + \frac{\bar{\mathbf{v}}_2^3}{3\bar{V}_{01}} \mathbf{c}^3$$
(296)

or (see Equations 1, 52)

$$\frac{\pi}{RT\mathbf{c}} = \frac{1}{M} + \mathcal{A}_2\mathbf{c} + \mathcal{A}_3\mathbf{c}^2 + \cdots$$
(297)

where

$$\begin{aligned} \mathcal{A}_2 &= \frac{\bar{v}_2^2}{\bar{V}_{01}} \left(\frac{1}{2} - \chi_1 \right), \\ \mathcal{A}_3 &= \frac{\bar{v}_2^3}{3\bar{V}_{01}}. \end{aligned}$$

In what follows, we will perform virial expansion in terms of the number of polymer fragments per unit volume (Perzynski et al., 1987)

$$\psi = \frac{v_2 N_A}{\tilde{V}_{01}},\tag{298}$$

i.e.

$$\frac{\pi}{kT} = \frac{\psi}{z} + \frac{V_{01}}{N_A} \left(\frac{1}{2} - \chi_1\right) \psi^2 + \frac{\dot{V}_{01}^2}{3N_A^2} \psi^3.$$
(299)

Introduce the second virial coefficient of the last expansion series as

$$\mathbf{v} = \frac{V_{01}}{N_A} (1 - 2\chi_1) \tag{300}$$

and the third one \mathbf{w} by means of

$$\frac{\pi}{kT} = \frac{\psi}{z} + \frac{1}{2}\mathbf{v}\psi^2 + \frac{1}{3}\mathbf{w}\psi^3,$$
(301)

generalizing

$$\frac{\tilde{V}_{01}^2}{N_A^2} \to \mathbf{w} \tag{302}$$

to a function responsible for the specific features of ternary interactions.

Accepting the expansion series of $\ln(1-v_2)$ with three terms, we write for the potential (Equation 32)

$$\frac{\Delta G_m}{RT} \cong \frac{v_2}{z} \ln v_2 + (\chi_1 - 1)v_2 + \left(\frac{1}{2} - \chi_1\right)v_2^2 + \frac{v_2^3}{6}$$
(303)

and, using concentration ψ (Equation 298),

$$\frac{\Delta \tilde{G}_m}{RT} = \frac{V_{01}}{N_A z} \psi \ln \frac{\bar{V}_{01}}{N_A} \psi + \frac{V_{01}}{N_A} (\chi_1 - 1) \psi + \frac{\bar{V}_{01}^2}{N_A^2} \left(\frac{1}{2} - \chi_1\right) \psi^2 + \frac{V_{01}^3}{6N_A^3} \psi^3 \tag{304}$$

ог

$$\frac{\Delta G'_m}{kT} = \frac{\psi}{z} \ln \frac{\psi \bar{V}_{01}}{N_A} + (\chi_1 - 1)\psi + \frac{\mathbf{v}}{2}\psi^2 + \frac{\mathbf{w}}{6}\psi^3, \tag{305}$$

where $\Delta G'_m = \Delta G'_m / V_{01}$ is the Gibbs potential of mixing per unit lattice volume.

Let us derive a binodal equation for the P+LMWL system with due account of the ternary interactions.

One condition of the two-phase equilibrium $\Delta \mu_{1I} = \Delta \mu_{1II}$ is given by the equality of the osmotic pressure in both the phases (see Equations 295 and 301). To obtain the second condition, $\Delta \mu_{2I} = \Delta \mu_{2II}$, we differentiate Equation 305 with respect to the second component concentration ψ

$$\frac{\Delta\mu_2'}{kT} = \frac{1}{kT} \frac{\partial\Delta G_m'}{\partial\psi} = \frac{1}{z} \ln \frac{\psi V_{01}}{N_A} + \frac{N_A}{zV_{01}} + \chi_1 - 1 + \mathbf{v}\psi + \frac{\mathbf{w}}{2}\psi^2.$$
(306)

According to $\Delta \mu'_{2I} = \Delta \mu'_{2II}$, write

$$\frac{1}{z}\ln\frac{\psi_{I}V_{01}}{N_{A}} + \mathbf{v}\psi_{I} + \frac{\mathbf{w}}{2}\psi_{I}^{2} = \frac{1}{z}\ln\frac{\psi_{II}V_{01}}{N_{A}} + \mathbf{v}\psi_{II} + \frac{\mathbf{w}}{2}\psi_{II}^{2}$$
(307)

and, assuming $\psi_I \ll 1$, neglect the second and third terms in the left-hand side

$$\frac{1}{z}\ln\frac{\psi_{I}}{\psi_{II}}\approx\mathbf{v}\psi_{II}+\frac{\mathbf{w}}{2}\psi_{II}^{2}.$$
(308)

According to Equation 301, write

$$\frac{\psi_I}{z} + \frac{\mathbf{v}}{2}\psi_I^2 + \frac{\mathbf{w}}{3}\psi_I^3 = \frac{\psi_{II}}{z} + \frac{\mathbf{v}}{2}\psi_{II}^2 + \frac{\mathbf{w}}{3}\psi_{II}^3.$$
(309)

In a rough approximation, presume $\psi_I \rightarrow 0$ and $\psi_{II}/z \rightarrow 0$, whence

$$-\frac{\mathbf{v}}{2}\psi_{II}^{2} = \frac{\mathbf{w}}{3}\psi_{II}^{3} \quad \text{and} \quad \psi_{II} = -\frac{3\mathbf{v}}{2\mathbf{w}}.$$
 (310)

Substituting it to Equation 308, we get for the binodal

$$\frac{1}{z}\ln\frac{\psi_I}{\psi_{II}} = -\frac{3\mathbf{v}^2}{8\mathbf{w}} \qquad \text{or} \qquad \frac{1}{z}\ln\frac{\upsilon_{2I}}{\upsilon_{2II}} = -\frac{3}{8}\frac{\mathbf{v}^2}{\mathbf{w}}.$$
(311)

From the critical point condition,

$$\frac{\partial \Delta \mu'_2}{\partial \psi} = 0$$
 and $\frac{\partial^2 \Delta \mu'_2}{\partial \psi^2} = 0.$ (312)

From Equations 306 and 312 we get

$$\mathbf{w} = \frac{1}{z\psi_c^2}$$
 and $\psi_c = \frac{1}{\sqrt{z\mathbf{w}}}$ (313)

and

$$v_c = -2\sqrt{\frac{\mathbf{w}}{z}}.\tag{314}$$

Approximate the second virial coefficient (cf. Equations 146 and 136)

$$\mathbf{v} = \beta \tau, \tag{315}$$

where

$$\tau = \frac{T - \theta}{T}.$$
(316)

Equations 314 and 315 also yield

$$\tau_c = -\frac{2}{\beta} \sqrt{\frac{\mathbf{w}}{z}} \tag{317}$$

and

$$\mathbf{w} = \frac{\beta^2 \tau_c^2 z}{4}.\tag{318}$$

 \mathbf{w} is considered to be temperature-independent in this approximation.

Combining Equations 313, 315, and 318, we get for the binodal

$$\ln\frac{\psi_I}{\psi_{II}} = -\frac{3}{2} \left(\frac{\tau}{\tau_c}\right)^2 \tag{319}$$

or (see Equations 310 and 311),

$$\ln\left[\psi_I\left(-\frac{2\mathbf{w}}{3\mathbf{v}}\right)\right] = -\frac{3\mathbf{v}^2}{8\mathbf{w}}.$$
(320)

Correlation between this binodal and experimental data (Perzynski et al., 1987) will be followed in section 5.5 where the results of polymer theories based on the ideas of the general field theory are considered.

Introduction of ternary interactions is of principal significance for a **shift effect** of the θ point. By definition, this point implies that the second virial coefficient is equal to zero. If Equation 301 is represented as

$$\frac{\pi}{kT\psi} = \frac{1}{z} + \left(\frac{\mathbf{v}}{2} + \frac{\mathbf{w}\psi}{3}\right)\psi\tag{321}$$

and the expression in the parentheses is defined as an effective second virial coefficient $\tilde{\mathbf{v}}$, then this quantity vanishes at the true Flory point $\tilde{\theta}$ (dc Gennes, 1979)

$$\tilde{\mathbf{v}} = \frac{1}{2}\mathbf{v} + \frac{1}{3}\mathbf{w}\psi = 0$$
 and $\mathbf{v} = -\frac{2}{3}\mathbf{w}\psi.$ (322)

This means, at the true θ point, the attraction-repulsion compensation takes place not only at the level of two-particle interactions, but two-particle attraction is compensated for by three-particle repulsion.

At the intramolecular level, the shift of the θ point must be observed with a rather large w and provided that the segment concentration in a coil is quite high, which depends on coil topology. Eg. three-particle interactions are most probable in branching (star-like) macromolecules with other conditions being equal.

The fine compensation effect at the θ point will be discussed in more detail in section 5.5 in connection with renormalization group approaches in polymer theory.

As to the measurable properties of polymer systems, three-particle interactions are not fully described in the literature and, as a rule, are not explicitly taken into account while interpreting results in the mean field approximation.

3.2. Polynary systems

3.2.1. State equations

For real systems containing ν components of a polymolecular polymer and a LMWL (Flory, 1944, 1953, 1970; Scott and Magat, 1945; Stockmayer, 1949; Tompa, 1956; Koningsveld and Staverman, 1966, 1967ab, 1968abcde; Koningsveld, 1968, 1970a, 1975; Rehage and Koningsveld, 1968; Gordon et al., 1969; Koningsveld et al., 1970ab, 1974ab; Koningsveld and Kleintjens, 1971; Kennedy et al., 1972, 1975; Kleintjens et al., 1976ab; Vink, 1976), a natural generalization of the Gibbs potential of mixing $\Delta \bar{G}_m$ (Equation 3.1–32) takes the form

$$\Delta G_m = RT \left(\varphi_0 \ln \varphi_0 + \sum_{i=1}^{\nu} \varphi_i p_i^{-1} \ln \varphi_i + \chi \varphi_0 \varphi \right), \tag{1}$$

where φ_0 is the volume fraction of LMWL, φ_i and p_i are the volume fraction and relative chain length of the *i*th polymer homologue, $\varphi = \sum_{i=1}^{\nu} \varphi_i$ is the overall volume fraction of a polymer.

While passing on to polynary systems, we have to change our notation. If the subscript '1' remains to denote LMWL, the polymer homologues should be denoted by '2' etc. which is inconvenient. On the other hand, the components of binary systems are most naturally denoted by the subscripts '1' and '2'. To emphasize the difference between the binary and the polynary systems, it is reasonable to change the notation of volume fractions (v_i and φ_i , respectively).

In what follows, we will replace χ by g.

For a polynary (ν + 1)-component system, the spinodal equation is expressed (Stockmayer, 1949; Flory, 1953; Prigogine and Defay, 1954; Tompa, 1956; Koningsveld, 1968, 1970b; Koningsveld and Staverman, 1968b; Kennedy et al., 1975; Vink, 1976) as (see Equations 1.2 58...61)

$$\mathbf{D}_{G} \equiv \left| \frac{\partial^{2} \Delta G_{m}}{\partial \varphi_{i} \partial \varphi_{j}} \right| = 0, \qquad i, j = 0, 1, \dots \nu,$$
⁽²⁾

and the critical state (see Equations 1.2-60, 61) is defined by this equation and

$$\mathbf{D}_G' = 0, \tag{3}$$

where \mathbf{D}'_{G} is the determinant of $(\nu + 1)$ columns and rows, \mathbf{D}'_{G} is that resulted from replacement of one row or column on \mathbf{D}_{G} by $\partial \mathbf{D}_{G}/\partial \varphi_{j}$ (Equation 1.2-59).

Equation 2 defines a spinodal surface in $(\nu + 1)$ -dimensional space based on the ν dimensional composition polyhedron (providing for the material balance condition, Equation 1.1.1-40) plus the temperature axis, P = const. Equations 2 and 3 define a ν dimensional critical surface.

It follows from Equation 1 (cf. Equations 3.1-50 and 51)

$$\frac{\mu_0}{RT} = \ln(1-\varphi) + \left(1-p_n^{-1}\right)\varphi + \chi_1\varphi^2,\tag{4}$$

$$\frac{\Delta\mu_i}{RT} = \ln\varphi_i + 1 - \frac{p_i\varphi}{p_n} - p_i(1-\varphi) + \chi_1 p_i(1-\varphi)^2,$$
(5)

where p_n is the number average relative chain length

$$p_n = \frac{\sum n_i p_i}{\sum n_i} = \frac{\sum \varphi_i}{\sum \frac{\varphi_i}{p_i}},\tag{6}$$

$$\varphi_i = \frac{n_i p_i}{n_S}, \qquad n_S = n_0 + \sum n_i p_i, \qquad p_i = \frac{V_{0i}}{\bar{V}_0} = \frac{V_p M_i}{\bar{V}_0},$$
(7)

 $\varphi_0 = n_0/n_S$, n_0 being the number of LMWL moles, n_S the number of moles of the lattice cells, \bar{V}_{0i} the molar volume of the *i*th polymer homologue, \bar{V}_0 the molar volume of LMWL, \bar{v}_p the specific partial volume of a polymer in solution (in a polymary mixture).

The condition of two-phase coexistence in equilibrium (Equation 1.2-8) at T = constand P = const

$$\Delta \mu_{iI} = \Delta \mu_{iII}, \quad i = 0, 1, \dots \nu, \tag{8}$$

supplemented by the material balance expression gives equations to define a ν -dimensional binodal surface (Flory, 1944, 1953; Tompa, 1956; Koningsveld and Staverman, 1967a, 1968a; Huggins and Okamoto, 1967).

According to Equations 1 and 2, the spinodal equation (Stockmayer, 1949; Koningsveld, 1975) is

$$2\chi_1 = (\varphi p_w)^{-1} + (1 - \varphi)^{-1}, \tag{9}$$

and the critical concentration (combine Equations 1, 2, and 3) is

$$\varphi_c = \frac{1}{1 + p_w^{1/2} / (p_z/p_w)^{1/2}} = \left(1 + p_w p_z^{-1/2}\right)^{-1},\tag{10}$$

where p_w and p_z are the weight- and z-average chain lengths, respectively.

Its substitution to Equation 3 leads to

$$2\chi_{1c} \coloneqq \left(1 + p_w^{-1/2}\right)^2 + \frac{\left(p_z^{1/2} - p_w^{1/2}\right)^2}{p_w p_z^{1/2}}.$$
(11)

Flory (1944, 1953) has used Equation 8 to obtain an interphase separation coefficient $K(p_i)$

$$K(p_i) = \frac{\varphi_{iII}}{\varphi_{iI}} = \exp(\sigma p_i), \tag{12}$$

where

$$\sigma = 2\chi_1(\varphi_{II} - \varphi_I) + \ln \frac{1 - \varphi_{II}}{1 - \varphi_I}.$$
(13)

The volume fraction of the *i*th fraction's macromolecules in phase II with respect to the overall content of this phase is expressed as

$$f_{iII} = \frac{\varphi_{iII}V_{II}}{\varphi_{iI}V_{I} + \varphi_{iII}V_{II}},$$

or. including Equation 12,

$$f_{iII} = \frac{1}{1 + r \exp(-\sigma p_i)},$$
(14)

where

$$r = \frac{V_I}{V_{II}},\tag{15}$$

 V_I and V_{II} are the volumes of polymer-depleted phase I and of polymer-enriched phase II, respectively.

When a polymer with different p_i is settled step-by-step, eg. during accumulating fractionation (Cantow, 1967; Koningsveld and Staverman, 1968de; Koningsveld, 1970a), its fraction transferred to the precipitated phase (II)

$$x = \sum_{i=1}^{n} f_{iII} \tag{16}$$

is called a degree of phase transformation/separation of this polymolecular polymer.

If the initial polymer is characterized by a continuous differential MWD function with respect to weight f(p), the similar function of the precipitated phase $f_{II}(p)$ is expressed (Huggins and Okamoto, 1967; Koningsveld and Staverman, 1967b; Kamide, 1977) (cf. Equation 14) as

$$f_{II}(p) = \frac{f(p)}{1 + r \exp(-\sigma p)} = f(p)\Omega,$$
(17)

where

$$\Omega(r,\sigma,p) = \frac{1}{1+r\exp(-\sigma p)},\tag{18}$$

$$x = \int_{0}^{\infty} f_{II}(p) \, dp = \int_{0}^{\infty} \frac{f(p) \, dp}{1 + r \exp(-\sigma p)},\tag{19}$$

i.e. $f_{II}(p)$ is normalized on the basis of x. The difference $f(p) - f_{II}(p) = f_I(p)$ represents the (1 - x)-normalized distribution function $f_I(p)$ in phase I.

Thus, Equation 8 reduces (by Flory) to two equations

$$\frac{1}{\varphi_I} \left[1 - \frac{\varphi_I(\beta+1)}{2} \right] \ln \frac{1 - \varphi_I \beta}{1 - \varphi_I} + \beta - 1 + \frac{\sigma(\beta+1)}{2} - \delta = 0, \tag{20}$$

$$x = \int_{0}^{\infty} \frac{f(p) dp}{1 + r \exp(-\sigma p)},\tag{21}$$

where

$$\beta = \frac{\varphi_{II}}{\varphi_I} = \frac{x(r,\sigma)r}{1 - x(r,\sigma)},\tag{22}$$

$$\delta = \frac{\beta}{p_{n,II}} - \frac{1}{p_{n,I}},\tag{23}$$

$$p_{n,I} = \frac{1 - x(r,\sigma)}{\int\limits_{0}^{\infty} f_{I}(p)p^{-1} dp} = \frac{1 - x(r,\sigma)}{\int\limits_{0}^{\infty} \frac{f(p) dp}{[1 + r^{-1}\exp(\sigma p)] p}};$$
(24)

$$p_{n,II} = \frac{x(r,\sigma)}{\int_{0}^{\infty} f_{II}(p)p^{-1} dp} = \frac{x(r,\sigma)}{\int_{0}^{\infty} \frac{f(p) dp}{p[1 + r \exp(\sigma p)] p}};$$

 $p_{n,I}$ and $p_{n,II}$ are the number average lengths of macromolecules in phases I and II. The material balance condition reduces to

$$\varphi_I = [1 - x(r, \sigma)] \varphi(1 + r^{-1}).$$
(25)

 $\varphi_{II} = x(r+1)\varphi.$

Equations 20 and 21 can be used, in principle, to determine any pair of the four main quantities of phase separation, namely, σ , r, x, and φ . First, we arbitrarily choose values of r and σ ; second, we calculate other quantities using Equations 21–24. Third, we employ Equation 20 to calculate φ_I and, through β , φ_{II} . Flory (1944) expands the logarithmic functions in Equation 20 into a series with several terms with subsequent approximation by a closed function. A quadratic (with respect to φ_{II}) equation results.

Equation 21 lets one calculate x, Equation 25 gives φ

$$\varphi = \frac{\varphi_I/\beta}{x(1+r)}.$$
(26)

Using Equation 13,

$$\chi_1 = \frac{\sigma + \varphi_I(\beta - 1 - \delta)}{\varphi_I(\beta - 1)[2 - \varphi_I(\beta + 1)]}$$
(27)

is calculated. This ends the calculation of all the characteristic quantities from the chosen pair r and σ .

A number of practically important problems, in particular, plotting a quasibinary section of a polynary system (see further) requires a way of determining the characteristic quantities of phase separation from a given overall polymer concentration that Flory's method is unable to provide.

Koningsveld and Staverman (1968a) have worked out a computer algorithm to search for such values of r and σ which make Equations 20 and 21 valid for given values of φ and x (Koningsveld, 1968, 1970b).

A more effective procedure for computing the characteristic values of phase separation in terms of Equations 20 and 21 at given φ and x has been proposed by Shchyogolev (1983).

At a sufficiently low polymer concentration

$$\varphi_I \ll \varphi_{II} < 1 \tag{28}$$

is valid, and φ_I in Equation 8 in negligible. If, in addition, p_n^{-1} is neglected in Equation 4, then Equation 20 is drastically simplified (Scott, 1945)

$$\ln(1 - \varphi_{II}) + \chi_1 \varphi_{II}^2 + \varphi_{II} = 0.$$
⁽²⁹⁾

So is for the expression for σ

$$\sigma = 2\chi_1\varphi_{II} + \ln(1-\varphi_{II}) \approx 2\chi_1\varphi_{II} - \varphi_{II} - \frac{\varphi_{II}^2}{2} - \cdots$$
(30)

and, in view of Equation 29,

$$\sigma = 2\chi_1 \varphi_{II} - \chi_1 \varphi_{II}^2 - \varphi_{II}. \tag{31}$$

By definition,

$$\varphi = \frac{\mathbf{v}_p}{V_I + V_{II}}$$
 and $\varphi_{II} = \frac{x\mathbf{v}_p}{V_{II}}$, (32)

 v_p being the polymer volume in the system.

Substituting V_{II} from Equation 32 to Equation 15, we get (Sayre, 1953)

$$r = \frac{\varphi_{II}V_I}{xv_p}.$$
(33)

It follows from the first of Equations 32 and Equation 15 that

$$\frac{\mathbf{v}_{p}}{V_{I}} = \frac{\varphi(V_{I} + V_{II})}{V_{I}} = \varphi(1 + r^{-1}).$$
(34)

Substitution of Equation 34 to Equation 33 yields

$$r = \frac{\varphi_{II}}{x\varphi(1+r^{-1})} \tag{35}$$

and, when $r \gg 1$,

$$r = \frac{\varphi_{II}}{x\varphi},\tag{36}$$

and also (see Equations 17 and 19)

$$f_{II}(p) = \frac{f(p)}{1 + \frac{\varphi_{II}}{x\varphi} \exp(-\sigma p)},\tag{37}$$

$$x = \int_{0}^{\infty} \frac{f(p) dp}{1 + \frac{\varphi_{II}}{x\varphi} \exp(-\sigma p)}.$$
(38)

To grasp the features of phase separation in polynary systems (a polymolecular polymer+LMWL), the ternary system LMWL+2 polymer homologues $O + P_1 + P_2$ can be taken as a model one (Rehage et al., 1965; Koningsveld and Staverman, 1967a; Koningsveld, 1968, 1970b; Vink, 1976). According to Equations 2, 3, and 8, the spinodal and binodal surfaces are surfaces in 3D space inside a prism with its basis being the composition triangle OP_1P_2 and its edges being the temperature axes (Figure 3.10). The binodal $(DBCAEC_0C_4C)$ and spinodal $(KCLC_0C_4C)$ surfaces have a common curve of critical points (C_0C_4C) .

At a constant temperature (eg. $T = T_4$), the state diagram is represented by the section of the prism by the plane $T = T_4$ (Figure 3.11). The curve $D_4C_4E_4$ defines the binodal as the locus of points corresponding to the composition of two equilibrium phases.

The straight lines $a\varphi_1$, bc, dl, eg, $\varphi_4 f$ are tie lines, C_4 is the critical point. The binodal $D_4C_4E_4$ separates the regions of the one-phase and two-phase states of the system and so is the **boundary of a phase separation region**, or, for brevity, a **phase boundary** (Cahn and Charles, 1965).

While the configurative point moves along the line OX (see Figures 3.10 and 3.11), the $(P_1 + P_2)/\text{LMWL}$ ratio varies, i.e. the volume concentration of the polymer varies with a constant P_1/P_2 ratio. So, the location of the straight line OX on the composition triangle models the MWD of the polymer. In multi-dimensional composition space, the point X

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Figure 3.10. State diagram of the ternary system $O + P_1 + P_2$ where Ois LMWL, P_1 and P_2 are polymer homologues with different chain lengths. DBCAE is the section of the binodal surface by the plane T = const; KCL is the section of the spinodal surface: $BC_{4}A$ is a quasibinary section; C_0C_4C is the critical point curve (Koningsveld, 1968, 1970b) [Reprinted from Advances in Colloid and Interface Science 2 (1968) 151-215. Copyright @ 1968 with kind permission of Elsevier Sci-NL, Sara Burgerhartence straat 25, 1055 KV Amsterdam, The Netherlands]

defines the MWD of the polymer, and the point on the line OX defines the total polymer concentration φ .

The curve of intersection of the plane TOX with the binodal surface is a **quasibinary** section (see Figure 3.10), also called a **cloud-point curve** (CPC) according to a way of its experimental determination when a solution (a system with an UCST) is being cooled and then temperature of its turning cloudy is fixed by means of a colorimeter or nephelometer, as well as visually.

Emphasis should be placed on the obvious imperfection of this method which is not capable of recording **precisely** the phase separation region boundary T_{Φ} .

On the one hand, there is a critical opalescence region in front of the liquid-liquid separation region, the former being extended by temperature (see paragraph 3.3.1.2) and having a high turbidity level. So, one may well erroneously take the temperature within the critical opalescence region as T_{Φ} . The distance along the temperature axis from such a temperature to the phase boundary depends on the experimental conditions and on the way of recording turbidity visually (the volume and shape of the vessel, the background colour, the skills and mood of the experimenter, etc.) or instrumental (the volume and shape of the vessel, the minimum discernible signal of instruments, etc.).



Figure 3.11. State diagram of the ternary system $O + P_1 + P_2$ at the temperature $T = T_4$ (see Figure 3.10). O is LMWL, P_1 and P_2 are polymer-homologues, $D_4C_4E_4$ and $K_4C_4L_4$ are the binodal and spinodal sections, respectively, C_4 is the critical point. The axis OX defines variation of the total polymer concentration with a constant component ratio $P_1/P_2 = X$ (a quasibinary system). At the total polymer concentration $\varphi_1, \varphi_2, \varphi_3, \varphi_c$, and φ_4 , the system is divided into two phases with the component concentrations represented by the points on the state diagram: φ_1 and a; c and b; l and d; g and e; f and φ_4 with the polymer concentrations φ_1 and $\varphi_{1II}; \varphi_{2I}$ and $\varphi_{2II}; \varphi_{3I}$ and $\varphi_{3II}; \varphi_{cI}$ and $\varphi_{cII}; \varphi_{4I}$ and φ_4 . For $\varphi_2: r = b\varphi_2/\varphi_2c$ (the lever rule); for $\varphi_1, r = \infty$ ($r^{-1} = 0$); for $\varphi_4, r = 0$. The sections OX_{2II} and $OX_{2I}; OX_{3II}$ and OX_{3I} represent the redistribution of the homologues P_1 and P_2 in both the phases (the fractionation effect) (Koningsveld, 1968, 1970b) (Reprinted from Advances in Colloid and Interface Science 2 (1968) 151-215. Copyright © 1968 with kind permission of Elsevier Science — NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands]

On the other hand, the system may be overcooled (oversaturated) due to the long induction period of formation of the new phase particles and/or the absence of heterogeneous nuclei (if the solution was carefully cleared prior to cooling). Indeed, according to the majority of patterns of formation of the new phase particles, the induction period on the binodal seems to be infinitely long. In this case, the system will remain transparent (the metastable state) till a certain overcooling level is reached. Moreover, the effect of critical retardation may complicate the situation. These questions are of principal significance and will be discussed in detail later though they are related in full measure to phase separation kinetics.

Tompa (1956) has called the highest (in case of UCST) or lowest (in the case of LCST) temperature T_{pt} at which phase separation may occur (the maximum or minimum of the phase boundary) a **precipitation threshold**.

Thus, by the CPC, the phase boundary on a quasibinary section of a polynary system is really meant.

The location of the phase coexistence curves on a quasibinary section of a polynary system depends on the total polymer concentration (Figures 3.11–3.13).



Figure 3.12. Schematic of the quasibinary section of a ternary (multicomponent) system, T_{pt} is the temperature of the precipitation threshold; CPC is the cloud-point curve (the phase boundary). I stands for the phase coexistence curves at the total polymer concentration: $\varphi_1, \varphi_2, \varphi_3, \varphi_c$, and φ_4 . SL is the shadow line. The concentrations of the coexisting phases at the temperature $T = T_4$ are marked (Koningsveld, 1968, 1970b) [Reprinted from Advances in Colloid and Interface Science 2 (1968) 151–215. Copyright © 1968 with kind permission of Elsevier Science — NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands]

At $\varphi < \varphi_c$, the left-hand branch of the coexistence curve goes inside the area bounded by the CPC and ends on the CPC at the concentration equal to the initial polymer concentration. The right-hand branch of the coexistence curve goes outside the CPC region and ends at the point corresponding to the temperature of the end of the lefthand branch of the coexistence curve. The set of the endpoints of the coexistence curve's right-hand branch forms a shadow line (SL).



Figure 3.13. Phase diagram of the system polystyrene+cyclohexane. Polystyrene: $M_n = 210,000$, $M_w = 346,000$, $M_z = 550,000$. CPC is the cloud-point curve. SL is the shadow line. C is the critical point. The coexistence curves have been obtained for the polymer concentrations (wt %) 2 (1), 6 (2), 10(3), 15 (4), and 20 (5) (Rehage et al., 1965) [Reprinted with permission from: G.Rehage, D.Möller, O.Ernst. Die Makromolckular Chemie **88** (1965) S. 232-255. Copyright © 1965 by Hüthig & Wept Publishers, Zug, Switzerland]

Such a location of the characteristic curves of a quasibinary system follows from consideration of the schemes (see Figures 3.11 and 3.12) and experimental data of Rehage et al. (1965) (see Figure 3.13) recorded while the configurative point was moved from $\varphi = 0$ (the point O) along the line OX (see Figure 3.11). The entry point (to the phase separation region) φ_1 corresponds to the second equilibrium phase (the point a) with the polymer concentration φ_{1II} , which is greater than the concentration φ_4 corresponding to the exit from the phase separation region at $T = T_4$ (see Figure 3.12). At any configurative point on the tie line $a\varphi_1$, the system is separated into two phases with their compositions given by the points a and φ_1 . The concentration φ_2 corresponds to the configurative point on the tie line cb. The system is separated into phases with φ_{2I} (on the left-hand branch of the coexistence curve) and φ_{2II} (on the right-hand one).

On a further increase in temperature, the phase separation region contracts. On the left-hand branch (see Figure 3.12), φ_{2I} approaches φ_2 and at $\varphi_{2I} = \varphi_2$ all the polymer is in the "left-hand" phase alone (the end of the left-hand branch of the coexistence curve). As temperature increases, the polymer concentration in the second ("right-hand") phase decreases, and the right-hand branch of the coexistence curve ends at the temperature where $\varphi_{2I} = \varphi_2$. Therefore, the end of the right-hand branch of the coexistence curve can be treated as the point on the state diagram with an infinitesimal amount of the second phase in equilibrium with the first ("left-hand") one, which contains all the polymer

 $\varphi_{2I} = \varphi_2$. The set of these points where the right-hand branch of the coexistence curve breaks defines the shadow line. Correspondingly, the phase boundary temperature T_{Φ} (the cloud temperature) can be defined as the temperature at which an infinitesimal amount of the second ("right-hand") phase coexists with the polymer solution of the given concentration. The concentration of this infinitesimal amount is defined as the intersection point of the line $T = T_{\Phi}$ with the SL (see Figure 3.12).

One can observe that at $\varphi > \varphi_c$ (eg. $\varphi = \varphi_4$ in Figures 3.11 and 3.12), the right-hand branch of the coexistence curve, going outside the CPC-bounded region, ends on the CPC at $\varphi_{4II} = \varphi_4$. At this temperature, the left-hand branch ends at the point φ_{4I} i.e. on the shadow line, which now (at $\varphi > \varphi_c$) goes inside the CPC-bounded region.

Koningsveld-Staverman's methods of computing the basic quantities of phase separation are capable of determining the location of the characteristic curves of a quasibinary section for some model MWD functions.

Eg. Koningsveld and Staverman (1968abc) have calculated a number of phase separation functions for a chosen polymer concentration φ and a number of large r (if $\varphi < \varphi_c$) or small r (if $\varphi > \varphi_c$). The calculated values of χ_1 (at $\varphi = const$) were extrapolated to $r^{-1} = 0$ or r = 0, respectively. Repeating this procedure for different φ yields the dependences χ_1 vs φ . Further passing from χ_1 to T_{Φ} leads to the CPC (Table 3.1)

Table 3.1 Values of some parameters on the phase separation boundary

Concentration region	Values
$\varphi < \varphi_c$	$r = \infty; r^{-1} = 0; x = 0$
$arphi > arphi_c$	r = 0; x = 1
$\varphi = \varphi_I$	$M_{nI} = M_n; \ M_{wI} = M_w$
$\varphi = \varphi_{II}$	$M_{nII} = M_n; \ M_{wII} = M_w$

When $\varphi < \varphi_c$, the plot φ_{II} vs r^{-1} at a given φ gives a point on the SL on extrapolating to $r^{-1} = 0$. In the case of $\varphi > \varphi_c$, φ_I should be plotted against r and extrapolated to r = 0.

As the choice of r depends on whether φ is larger or smaller than φ_c , the critical conditions must be known beforehand.

In strictly binary systems, the precipitation threshold matches the critical temperature and the CPC matches the binodal (the phase coexistence curve) (Francis, 1963). The CPC location on a quasibinary section of a polynary system depends on the MWD function and the thermodynamic properties through $\chi = \chi(T, \varphi, \text{MWD})$.

Equations 2, 3, and 8 serve, in principle, as the basis for calculating the CPC location on a quasibinary section of the ν -dimensional binodal surface at a given form of the dependence $\chi = \chi(T, \varphi, \text{MWD})$ (or $g = g(T, \varphi, \text{MWD})$ in Koningsveld-Staverman's notation). However, such calculations are extremely laborious even using modern computers. Koningsveld and Staverman applied their own method of calculating the CPC and spinodals for systems with the logarithmically normal and exponential MWD functions. Shchyogolev (1983) plotted the characteristic curves of phase separation for the differential MWD function of the gamma function type.



Figure 3.14. Simulated CPC of the P+LMWL system where the polymer has the same p_w with different polymolecularity (*sp* is the spinodal, circles are the critical points, w_{10} , w_{14} present hypothetical mixtures of two polymers with the exponential MWD) (Koningsveld, 1968) [Reprinted from Advances in Colloid and Interface Science 2 (1968) 151-215. Copyright © 1968 with kind permission of Elsevier Science NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands]

Figure 3.14 shows simulated phase boundaries for P+LMWL mixtures where the polymers comprises two fractions with the exponential MWD functions taken in such a proportion that the resulted MWD functions have different widths but the same p_w .

According to Equation 9, these systems must have the same spinodal while φ_c increases with the p_z/p_w ratio (Equation 10).

Some other computational procedures for systems with a polymolecular polymer are presented in (Baysal and Stockmayer, 1967, Šolc, 1974; Shishov and Frenkel, 1979).

The series of papers by Koningsveld et al. (Koningsveld and Staverman, 1966, 1967ab, 1968abcde; Koningsveld, 1968, 1970a, 1975; Rehage and Koningsveld, 1968; Gordon et al., 1969; Koningsveld et al., 1970ab, 1974ab; Koningsveld and Kleintjens, 1971; Kennedy et al., 1972; Kleintjens et al., 1976ab) has provided the basis for modification of Flory-Huggins' traditional theory, and has fostered the new level of its development (see below).

3.2.2. Fractionation

Equations 13-19 serve as the a basis of polymer fractionation. The character of macromolecule length distribution p in phase II is described by the function Ω (see Equations 17-19 and Figure 3.15).

Fractionation is called **ideal** when all macromolecules of length p above a certain fixed value p_t are in the precipitate phase (see the dashed area of f(p) in Figure 3.16). Ideal fractionation is depicted by line 4 in Figure 3.15. A problem how much the results of real and ideal fractionations differ is often solved in preparative and analytical fractionation.

The conditions of real fractionation approach the ideal ones as the character of Ω approaches line 4 in Figure 3.15.

In real fractionation, the function Ω has an inflection point at

$$p_t = \frac{\ln r}{\sigma},\tag{39}$$

where

$$\Omega = 0.5. \tag{40}$$



Figure 3.15. Function $\Omega(r, \sigma, p)$ (Equation 3.2-18) vs p for r = 10 (1), 100 (2), 1000 (3). The values of σ are adjusted so that each curve should have an inflection point at equal p values. For comparison, line 4 (ideal fractionation) is drawn (Huggins and Okamoto, 1967) [Polymer Fractionation Ed. M.J.R.Cantow. Chapter 1. Copyright © 1967 by Academic Press]

The derivative at this point

$$\varepsilon_t = \frac{d\Omega}{d\ln p} = \frac{\ln r}{4} \tag{41}$$

is accepted as a measure of the width of distribution of the macromolecule length in a fraction or a **resolution degree** of fractionation.

The function Ω approaches line 4 as r and σ increase (see Figure 3.15). The polymer concentration in phase II increases with σ (see Figure 13) due to a decrease in the volume of this phase V_{II} (i.e. due to an increase in r).

Hence, the conditions of r and σ increases are compatible. Large values of σ correspond to increasing χ_1 (Figure 3.17). σ or the concentration ratio $\varphi_{iII}/\varphi_{iI}$ (Equation 12) rises as the total polymer concentration decreases. Qualitatively, this follows from Figure 3.11. When the configurative point moves along the line OX at low polymer concentrations, the utmost difference in phase volumes and in the P_1/P_2 ratio in both the phases (the fractionation effect) is observed (cf. the sections OX_{2II} and OX_{2I} , OX_{3II} and OX_{3I} in Figure 3.11). So, fractionation is recommended to be carried out at low concentrations far from the critical one (Flory, 1953).

Huggins and Okamoto (1967) have theoretically studied the efficiency of fractionation at some simplifications, namely, the initial polymer comprises two discrete fractions, phase II is removed at every fractionation stage; χ_1 is the same for both the phases.

Koningsveld and Staverman (1968de), Koningsveld (1970a) have simulated analytical and preparative fractionation with the exponential and logarithmically normal MWD functions as examples, and they have shown that polymer fractionation by conventional methods (precipitation or extraction) is a very laborious and inaccurate procedure of



Figure 3.16. Differential MMD function of the initial polymer f(p) and in the precipitate phase at ideal $(f_{II,id})$ and real fractionation (f_{II})



Figure 3.17. σ vs χ_1 as $M \to \infty$ according to Equation 3.2-13 (Scott, 1945, 1949a) [Reprinted with permission from: R.L.Scott. J. Chem. Phys. **13** (1945) 178–187. Copyright © 1945 American Institute of Physics]

determining the MWD of the initial polymer sample. Extraction has some advantage with respect to efficiency.

As an alternative approach, Koningsveld (1970a) proposes a way to develop methods using critical phenomena in the P+LMWL system (see subsection 3.3.1).

The fractionation problems within the framework of the second approximation of Flory-Huggins' theory (see subsection 3.6.1) are reviewed by Kamide (1977).

3.2.3. Spectroturbidimetric titration of polymer solutions as a method for analytical fractionation

Accumulating fractionation is one of the ways of polymer fractionation, where addition of a new portion of the precipitant is followed by determination of the total amount of the precipitate without removal of the precipitated fractions (Battista, 1967). As a matter of fact, the degree of phase conversion is determined at different stages of fractionation.

Turbidimetric titration (TT) of polymer solutions refers to a version of accumulating fractionation (Morey and Tamblyn, 1945; Claesson, 1955; Shatenshtein et al., 1964; Urwin, 1972; Elias, 1977) which implies "optical weighing" of the polymer converted into a colloidal-disperse insoluhle state in the process of either step-hy-step addition of a precipitant (precipitating titration) or varying temperature (temperature titration). The amount of polymer in the colloidal state (the degree of phase conversion x) is judged from the effect of light scattering (measurement of the optical density (turbidity) or scattering intensity at a certain angle).

TT is attractive owing to a number of its advantages: simplicity of equipment, low time expenses, high productivity. Very dilute solutions are used to provide high efficiency of fractionation. Besides, small amounts of the sample are enough for analysis, which is of special importance for polymers of biological origin and while searching for new polymers.

Thus, the ideas of the method are simple and attractive, but their realization is not as simple as that.

Application of TT to evaluate MWD means to correctly solve two reverse problems. The first, **optical** problem consists in calculating a **precipitation curve** $x = x(\gamma)$ from the measured properties of scattered light; the second, **thermodynamic** problem must provide a means of converting this curve $x = x(\gamma)$ into the corresponding MWD function $(\gamma \text{ is the volume fraction of precipitant in the system}).$

Within the framework of traditional TT, these reverse problems are solved (explicitly or implicitly) inadequately, especially the optical one.

The main premise of traditional TT is the proportionality between precipitate concentration \tilde{M} and turbidity τ

$$\dot{M} = A\tau. \tag{42}$$

However, Equations 2.1-41,-101 imply that this simple formula holds true only if the particle size and relative refractive index are not subject to change. This necessary condition is often violated. Introduction of corrections for these changes is not helpful, and the way of this introduction is not always correct.

Theory and practice show even 1% of the precipitated polymer may cause a "typical precipitation curve $\tau = \tau(\gamma)$ " which falls outside any reasonable limits, and shows high values of turbidity and other details imitating MWD.

Hence, another, maybe more significant, disadvantage of traditional TT follows, namely, a lack of an objective criterion of completion, i.e. x = 100%. To think x = 100% is achieved when $\tau = \tau(\gamma)$ reaches its limiting value is a gross error, which is discussed in detail elsewhere (Klenin and Shchyogolev, 1973; Shchyogolev and Klenin, 1974).

Spectroturbidimetric titration (STT) of polymer solutions improves the situation. It is a version of TT which enables one to solve correctly both the reverse problems at the cost of a slight complication of the experimental technique and the calculational procedure. STT implies measuring turbidity at several wavelengths (not at one), i.e. recording a turbidity spectrum.

Then, the solution of the first reverse problem is given by Equation 2.1-101 with consideration of the possible changes in particle size and relative refractive index in the course of titration.

The M/c (where c is the initial solution concentration, g/dl) immediately defines the degree of phase conversion

$$\frac{\tilde{M}}{c} = x. \tag{43}$$

It follows from Equation 2.1-101 and Figure 2.18 that the proportionality between M and τ (Equation 42) really takes place in the case of sufficiently big particles (n < 1.5) which accounts for the success of the traditional TT in some cases (Ilisekus, 1967; Urwin, 1972; Elias, 1977). The researchers obviously succeeded in maintaining Equation 42 by a merely empirical way. However, STT has an advantage even in this case (n < 1.5) as n needs being estimated to ensure that it does not exceed 1.5 and Equation 42 is valid. Moreover, it is the absolute value of \tilde{M} (given by STT only) that is required to calculate the conversion degree x (Equation 43).

The chief thing is that an objective and rigorous criterion of titration completion appears at

$$x = 100\%$$
 (44)

which enables $x = x(\gamma)$ to be quantitatively determined.

Strictly speaking, only on achieving x = 100%, one may proceed to solve the second reverse problem, i.e. restoring the MWD function from the **complete** precipitation curve $x = x(\gamma)$.

The practice of STT application to a number of systems (Klenin and Shchyogolev, 1971a, 1972, 1973, 1979; Klenin et al., 1973f, 1974de, 1975b; Shchyogolev and Klenin, 1973, 1974) has shown that the condition of Equation 44 can be met though it is a difficult task.

Partial precipitation is caused by a number of reasons with two being of most importance (of thermodynamic and colloidal-optical nature).

First, consider the thermodynamic one.

By definition, the volume fractionation of a polymer in the system is

$$\varphi = \frac{\mathbf{v}_{p,II}}{V_I + V_{II}} + \frac{\mathbf{v}_{p,I}}{V_I + V_{II}},\tag{45}$$

where $v_{p,I} v_{p,II}$ are the volumes of the polymer in phases I and II, respectively.

The volume concentration of the polymer in phase II referred to the volume of the whole system $V = V_I + V_{II}$ is

$$\varphi_{II}^{*} = \frac{v_{p,II}}{V_{I} + V_{II}}.$$
(46)

Its substitution into Equation 45, followed by dividing both the nominator and denominator of the second summand by V_I in view of Equation 15 leads to

$$\varphi = \varphi_{II}^* + \varphi_I (1 + r^{-1})^{-1}. \tag{47}$$

For dilute systems, which STT deals with, $r \gg 1$, so it follows from Equation 43 that

$$\varphi_{II}^* \cong \varphi - \varphi_I. \tag{48}$$

Naturally, it holds true for concentrations expressed in other units, eg. in g/dl

$$\mathbf{c}_{II}^* \cong \mathbf{c} - \mathbf{c}_I. \tag{49}$$

Using the notation accepted in the turbidity spectrum method and STT,

$$\mathbf{c}_{II}^* = \tilde{M},\tag{50}$$

$$x = \frac{\dot{M}}{c} = \frac{\mathbf{c}_{II}^*}{c} = 1 - \frac{\mathbf{c}_I}{c},\tag{51}$$

or

$$x = 1 - \frac{\varphi_I}{\varphi}.\tag{52}$$

Precipitation titration requires consideration of a decrease in c due to the added precipitant by means of

$$x = \frac{\tilde{M}}{\mathbf{c}} = \frac{\tilde{M}}{\mathbf{c}_0(1-\gamma)} = 1 - \frac{\mathbf{c}_I}{\mathbf{c}_0(1-\gamma)},\tag{53}$$

where \mathbf{c}_0 is the initial solution concentration.

According to Equation 49, on the T - c (temperature STT) or $\gamma - c$ (precipitation STT) state diagram of the binary system monomolecular polymer+LMWL, the precipitated polymer concentration \mathbf{c}_{II}^* is given by the segment of the line parallel to the abscissa axis between the current configurative point and the left-hand branch of the binodal \mathbf{c}_I (Figure 3.18).

At the first stage of determining the MWD of a polymolecular polymer, it is reasonable to analyze the values of \mathbf{c}_{II}^* (or x) using the $T - \mathbf{c}$ or $T - \gamma$ state diagrams of binary systems.

In the case of dilute solutions, the polymer concentration c_I corresponding to the lefthand branch of the binodal is often called a **solubility** of the polymer (Giesekus, 1967: Elias, 1977), which is determined with the use of "cloud points".

An empirical equation

$$\beta = -\left(A_{\theta} + AM^{-a}\right)\ln \mathbf{c}_{I} + BM^{-a} + B_{\theta},\tag{54}$$

where A_{θ} , A, B, B_{θ} , a are constants, has been proposed for a great number of systems (Giesekus, 1967; Elias, 1977). In the case of temperature STT, $\beta = 1/T_{\Phi}$, $B_{\theta} = 1/\theta$ and $\beta = T_{\Phi}$, $B_{\theta} = \theta$ for systems with UCST and LCST, respectively.

In the case of precipitation titration, $\beta = \gamma$, $B_{\theta} = \gamma_{\theta}$, and after a = 0.5, $A_{\theta} = 0$ (Giesekus, 1967; Elias, 1977) which reduces Equation 54 to

$$\gamma = -\frac{A}{\sqrt{M}}\ln \mathbf{c}_I + \frac{B}{\sqrt{M}} + \gamma_0 \tag{55}$$

or

$$\gamma = -a \ln \mathbf{c}_I + b, \tag{56}$$



Figure 3.18. State diagram (the left-hand branches of the binodal) of the systems $P\alpha MS$ +cyclohexane+octanol (solid lines 1 4) and $P\alpha MS$ +dioxane+octanol (dashed lines 1'-4') for $M \cdot 10^{-3}$: 5 (1, 1'), 10 (2, 2'), 100 (3, 3'). Lines 4 and 4' are related to the θ composition. Lines marked with "tr" show the trajectories of the configurative point during precipitation turbidimetric titration of solutions with the initial concentration $\mathbf{c}_0 = 5 \cdot 10^{-3}$ and $8 \cdot 10^{-3}$ g/dl (Ramazanov et al., 1982)

where

$$a = \frac{A}{\sqrt{M}},\tag{57}$$

$$b = \frac{B}{\sqrt{M}} + \gamma_{\theta}.$$
(58)

From Equation 55 follows an equation for c_I

$$\mathbf{c}_{I} = \exp\left\{\frac{B - (\gamma - \gamma_{\theta})\sqrt{M}}{A}\right\}, \,\mathrm{g/dl},\tag{59}$$

while the degree of phase conversion is given by Equations 53 and 59

$$x = 1 - \frac{\exp\left\{\left[B - (\gamma - \gamma_{\theta})\sqrt{M}\right]/A\right\}}{\mathbf{c}_0(1 - \gamma)}.$$
(60)

Figure 3.18 presents the state diagrams (the left-hand branches of the binodals) of two systems, $P\alpha MS$ +cyclohexane+octanol and $P\alpha MS$ +dioxane+octanol, approximated by Equation 55. The details of fitting are given below. Trajectories of the configurative point during precipitation TT of $P\alpha MS$ solutions with two initial concentrations are shown on the diagram.

According to Equations 49 and 50, the segment KL defines the concentration of the precipitated polymer \mathbf{c}_{II}^* at $\gamma = 0.25$ and the initial concentration $\mathbf{c}_0 = 5 \cdot 10^{-3}$ g/dl, the segment KM is equal to \mathbf{c}_{II}^* for $\mathbf{c}_0 = 8 \cdot 10^{-3}$ g/dl. A comparison of these data shows the role of the polymer initial concentration for the experimentally obtainable maximal degree of phase conversion at STT.

Figure 3.18 also illustrates the dependence of this degree on the polymer molecular mass. Eg. the STT trajectories do not intersect the binodals with M = 5,000 and 10,000 (the system with dioxane) and the binodal with M = 5,000 (the one with cyclohexane). Therefore, monomolecular P α MS with such MW (and less) is not precipitated under these titration conditions ($c_{II}^* = 0$).

In the first approximation, no precipitation of the fractions within this MW range could be expected in a polymolecular polymer sample. Comparison of the segments NR and SDindicates that the increase in the precipitated content from 0.75 to 0.85 results in partial dissolution of the previously precipitated polymer in the system $P\alpha MS$ +cyclohexane+octanol due to the decrease in the total polymer concentration. The effect of repeat dissolution is specific for precipitation TT and is not observed in temperature titration.

Thus, during precipitation STT, the concentration of the precipitated polymer \mathbf{c}_{II}^* (and, hence, the degree of phase conversion, Equation 51) as a function of γ goes through a maximum (Figure 3.19).

The maximal value x_{max} is derived from the extremum condition applied to Equation 60

$$x_{\max} = 1 - \frac{\sqrt{M}}{Ac_0} \exp\left\{\frac{A + B - (1 - \gamma_\theta)\sqrt{M}}{A}\right\}.$$
(61)

The x_{max} vs $-\lg c$ and MW dependence is shown in Figure 3.20 (Ramazanov et al., 1982) which indicates the range of MW and c where complete precipitation of the polymer $(x_{\text{max}} = 100\%)$ can be expected.

At temperature STT (eg. a system with a UCST), its trajectories are lines parallel to the ordinate axis. In this case, the fractionation of the precipitated polymer rises with the initial solution concentration and the polymer MW (Figure 3.21).

Figures 3.18 and 3.20 clarify the role of the peculiar features of thermodynamic interactions among the components in the P+LMWL1+LMWL2 system.

Consider these interactions in Scott's (1949a) approximation of common liquid where the contributions of separate component pairs to the entropy of mixing are assumed to be additive. If, in addition, the molar volumes of two liquids are assumed to be equal, an expression of the Equation 4 type for the chemical potential of mixing of a LMWL (a binary system) with the polymer will result with

$$\chi_{1} = \chi_{13}(1-\gamma) + \chi_{23}\gamma - \chi_{12}\gamma(1-\gamma) = \chi_{12}\gamma^{2} + (\chi_{23} - \chi_{13} - \chi_{12})\gamma + \chi_{13},$$
(62)

where χ_{i_1} are the parameters of component pair interactions: χ_{12} (LMWL1+LMWL2), χ_{13} (P+LMWL1), χ_{23} (P+LMWL2).



Figure 3.19. Solubility curves (the left-hand branches of the spinodal) c_1 given by Equation 3.2-59 (1, 6-8), trajectories of a model TT (9, 10) with precipitation curves (2-5) for a system with the parameters: $\gamma_{\infty} = 0.1$, A = 21.72, B = 70, $M \cdot 10^{-3} = 12$ (1), 40 (2-4, 6), 200 (5), 1,000 (7), $\rightarrow \infty$ (8) at $c_0 \cdot 10^4 = 5$ (2, 10), 10 (3, 5, 9), 30 (4) g/dl (Klenin and Shchyogolev, 1979)



For the two-phase state of the system P+LMWL1+LMWL2, this approximation presumes that the liquid composition in both the phases is the same, and the interaction parameter χ_1 is unambiguously defined by Equation 62 to be solved with respect to γ

$$\gamma = \frac{\chi_{13} + \chi_{12} - \chi_{23} + \sqrt{(\chi_{13} + \chi_{12} - \chi_{23})^2 + 4\chi_{12}(\chi_1 - \chi_{13})}}{2\chi_{12}}.$$
(63)

At least, for mixtures with $\chi_{13} \leq 0.5$, the value γ_{θ} corresponding to the θ conditions is derived by means of substituting $\chi_1 = 0.5$ into Equation 63, whence the precipitation



Figure 3.21. State diagram χ_1 vs $\lg v_2$ of the binary system P+LMWL given Flory-Huggins' by theory for p = 19.8(1), 59 (2), 100 (3),200 (4), 1,000 (5),107,000 (6). The lines dashed are spinodals. The line "tr" is the trajectory of the configurative point at temperature TT (Klenin and Shchyogolev, 1979)

range $\gamma_{\theta} < \gamma < 1$ is obtained.

Using Equation 63, the γ axis (Figures 3.18 and 3.19) can be converted to the χ_1 coordinate (Figure 3.22). The relation between χ_1 and temperature is defined by Equation 3.1–33 or 3.1–42 (see also subsection 3.1.1). At temperature STT, the experimentally obtainable temperature restricts the possibility of raising χ_1 . In Figure 3.21, $\chi_{1,\text{max}} = 0.75$ is accepted.

The examples of the $\chi_1(\gamma)$ dependence at certain χ_{ij} (Figure 3.23) are in good accordance with known experimental facts: lack of solubility in an exothermic mixture $(\chi_{12} < 0)$ of two solvents, or, vice versa, solubility in an endothermic $(\chi_{12} > 0)$ mixture of non-solvents (curve 2) (Bekturov, 1975).

A smooth dependence $\chi_1 = \chi_1(\gamma)$ of the curve 3 type should be admitted as optimal for STT. The condition of increasing function is $\chi'_1 = 2\gamma\chi_{12} + \chi_{23} - \chi_{13} - \chi_{12} > 0$ or $(2\gamma - 1)\chi_{12} + \chi_{23} > \chi_{13}$.

The parameters of the pair interaction for any system LMWL1+LMWL2+P can be determined experimentally (see subsection 3.6.2) or estimated using

$$\chi_{ij} = \chi_s + \frac{\tilde{V}_{0i}}{RT} (\delta_j - \delta_i)^2, \tag{64}$$

 χ_s being the entropy component (see Equation 3.1–71).

In particular, χ_{12} can be determined from scattering data for a solution of two LMWL (Abdel-Azim and Huglin, 1984).



Figure 3.22. Theoretical curves of polymer precipitation during temperature ($\chi_{1m} = 0.75$) (1-3) and precipitation STT ($\chi_{13} = 0.48$, $\chi_{23} = 0.75$, $\chi_{12} = 0.1$) (4, 5), p = 150 (1, 2), 200 (3 5), $c_0 \cdot 10^3 = 1.0$ (1, 3), 2.9 (4), 8.7 (5), and 10.0 (2) g/dl (Klenin and Shchyogolev, 1979)

Equation 2.4-8 enables $(\partial \Delta \mu_2 / \partial x_2)_{T,P}$ and $(\partial \Delta \mu_1 / \partial x_2)_{T,P}$ to be determined at different concentrations x_2 (see also Equations 2.4-11, 9,-6). Graphical or numerical integration yields $\Delta \mu_1$ and $\Delta \mu_2$ (see paragraph 3.6.2.4), whose combination gives (see Equation 1.1.1-51)

$$\Delta G_m = x_1 \Delta \mu_1 + x_2 \Delta \mu_2. \tag{65}$$

In view of Equation 1.1.3-15, calculate $\Delta \hat{G}_{m,ex}$ (Equation 1.1.3-28)

$$\Delta \bar{G}_{m,ex} = \Delta \bar{G}_m - \Delta \bar{G}_{m,id} = \Delta \bar{G}_m - RT(x_1 \ln x_1 + x_2 \ln x_2).$$
(66)

Comparison of Equations 1.3-13 and 3.1-33 results in

$$\chi_{12} = \frac{\Delta G_{\mathrm{m,ex}}}{x_1 x_2 R T}.$$
(67)

For example, depending on the tetraline molar fraction, the interaction parameter χ_{12} of the mixture tetraline (1)+cyclohexane (2) thus obtained has the form

$$\chi_{12} = 0.526 - 0.377x_1 + 0.0935x_1^2 \tag{68}$$

(Abdel-Azim and Huglin, 1984).

Hence, determination or estimation of χ_{i} , with subsequent plotting $\chi_{i} = \chi_{i}(\gamma)$ (Equation 62) can serve as a preliminary criterion of selection of liquids for STT.

Let us try to substantiate the solubility equation 55 in terms of Flory-Huggins' theory for binary systems. It is reasonable to consider just binary systems as Equation 55 is obtained on polymer fractions.



Dependence of the general interaction parameter χ_1 in the system Figure 3.23. P+LMWL1+LMWL2 on the volume fractionation γ of LMWL2 at different interaction parameters of the binary systems P+LMWL1 (χ_{13}), LMWL1+LMWL2 (χ_{12}), LMWL2+P (χ_{23}) , viz, 0.2:-2:0.4 (1), 0.6:2:1 (2), 0.5:0.55:1.05 (3), 0.5:1:1 (4), 0.5:2:0.6 (5), 0.5:-2:0.6 (6). The $\gamma_{\theta 1}$ and $\gamma_{\theta 2}$: θ compositions apply to curve 2 (Ramazanov et al., 1982)

First of all, Equation 3.1-256 implies that in a certain concentration range, the dependence χ_1 vs $\lg v_{2I}$ is approximated by lines (see Figure 3.21), the extrapolation of which to the ordinate axis $\lg v_{2I} \to 0$ gives the values χ^{\ominus}_1 linear relative to $z^{-1/2}$

$$\chi_1^{\ominus} = 0.5 + \frac{0.55}{\sqrt{z}}.$$
(69)

Talamini and Vidotto (1967), Napper (1969) analyzed the dependences $\chi_1 = f(\lg v_{2II})$

and $\chi_1^{\ominus} = f(z)$ using Equation 3.1 256. Plotting χ_1 vs $\lg v_{2I}$ within $v_{2I} \sim 5 \cdot 10^{-3} \dots 5 \cdot 10^{-1}$ for large z (say, z > 700) yields straight lines, which cut off the axis $\lg v_{2I} = 0$ the value $\chi^{O} = 0.5$.

Talamini and Vidotto (1967) first wrote Equation 3.1-256 in the form

$$\chi_1 = D - E \frac{1}{z},\tag{70}$$

where

$$D = \frac{1}{2 - v_{2II} - v_{2I}},\tag{71}$$

$$E = \frac{1}{2 - v_{2II} - v_{2I}} \left[1 - \frac{\ln \frac{v_{2II}}{v_{2I}}}{v_{2II} - v_{2I}} \right].$$
(72)

Had it not been for the dependence of D and E on MW, at $v_2 = const$, Equation 70 would have described a straight line χ_1 vs 1/z.

However, numerical calculations using Equations 71–72 (Talamini and Vidotto, 1967) lead to

$$D = 0.5 + \frac{K}{z^{0.6}},\tag{73}$$

$$E = K' z^{0.4}, (74)$$

where K and K' are constants, and Equation 70 is transformed to

$$\chi_1 = 0.5 + \frac{K - K'}{z^{0.6}}.\tag{75}$$

If γ is small and/or $\chi_{_{12}}$ is also small, we have instead of Equation 62

$$\chi_1 \cong \tilde{\chi}\gamma + \chi_{13},\tag{76}$$

where

 $\tilde{\chi} = \chi_{_{23}} - \chi_{_{13}} - \chi_{_{12}},$

which, with due account of Equation 75, gives

$$\gamma = \frac{0.5 + \chi_{13}}{\tilde{\chi}} + \frac{K - K'}{\tilde{\chi}z^{0.6}}.$$
(77)

At the θ point, $\chi_{_1}$ = 0.5 and, according to Equations 76 and 75,

$$\gamma_{\theta} = \frac{0.5 - \chi_{13}}{\tilde{\chi}},\tag{78}$$

$$\gamma = \gamma_{\theta} + \frac{K - K'}{\tilde{\chi}z^{0.6}}.$$
(79)

It follows from Equations 3.1-40,-41 that

$$\chi_1 = 0.5 - \psi_1 \left(1 - \frac{\theta}{T} \right), \tag{80}$$

whose combination with Equation 75 leads to

$$\frac{1}{T_{\Phi}} = \frac{1}{\theta} \left(1 + \frac{K - K'}{\psi_1 z^{0.6}} \right), \tag{81}$$

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where T_{Φ} is the temperature of the phase boundary.

If the difference in power of z (0.5 and 0.6) is neglected, Equation 79 matches Equation 55 with

$$B - A \ln \mathbf{c}_I \approx \frac{K}{\tilde{\chi}} - \frac{K'}{\tilde{\chi}}.$$
(82)

Elias (1959, 1977) has proposed an equation of the Equation 56 type

$$\gamma = -a \ln \mathbf{c}_I + \gamma_\theta \tag{83}$$

or

$$\gamma = -a' \ln v_{2I} + \gamma_{\theta} \tag{84}$$

to determine the θ composition at a given temperature using cloud points. Extrapolation of the line $\gamma vs - \ln c_I$ to $-\ln c_I \rightarrow 0$ yields the value γ_{θ} .

As follows from the above analysis (cf. Equations 55 and 79), such a way of determining the θ composition is possible provided that Equation 76 holds (small γ and/or χ_{12}), and M is high in order that

$$\frac{B}{\sqrt{M}} \to 0$$

in Equation 55 or

$$\frac{K}{\tilde{\chi}z^{0.6}} \to 0$$

in Equation 79.

The temperature equivalent of this approach (Cornet and van Ballegooijen, 1966) is based on

$$\frac{1}{T_{\Phi}} = \frac{1}{\theta} + K \ln v_{2I},\tag{85}$$

where K is the constant for a specific M (cf. Equations 81 and 82) with

$$\frac{B}{\sqrt{M}} \to 0$$
 or $\frac{K}{\tilde{\chi}z^{0.6}} \to 0.$

to be satisfied.

As opposed to Shultz-Flory's plot (Equation 3.1-246) with T_c (i.e. phase boundary at the critical temperature) for several polymer fractions, the plot

$$\frac{1}{T_{\Phi}} vs \ln v_{2I}$$

is performed using cloud points (the phase boundary temperature T_{Φ}) for solutions with different concentrations of the polymer of **one** fraction.

In the general case, the expression $\gamma = f(\ln \varphi_I)$ can be obtained by combining Equations 62, 31, and 12; this, however, produces an awkward formula which, however, can apply to the specific system.

It follows from the previous analysis that more complete polymer precipitation at STT can be promoted by raising the initial concentration, increasing the M of the polymer, and by selection of LML, in particular, to provide $\chi'_{1} > 0$, etc.

Subsection 3.2.2 discussed the increase of fractionation efficiency on the polymer concentration decrease. In fact, this efficiency ε_t is an extremum-containing function of polymer concentration, which follows from analysis of fractionation with a two-fraction polymer sample as a model (Huggins and Okamoto, 1967), but the region where ϵ_t falls as **c** rises lies at very low concentrations not used in most fractionation methods, and this effect was neglected.

STT employs a concentration range corresponding to the descending branch of $\varepsilon_t = f(\mathbf{c})$ and the higher concentration, the more the degree of phase conversion. However, raising the concentration is bounded by optical interference of particles of the precipitated polymer (secondary or multiple scattering), which decreases turbidity after a certain maximum (Klenin et al., 1975b; Klenin and Shchyogolev, 1979; Shchyogolev and Klenin, 1980).

The effect of low-angle scattering leads to a decrease in the turbidity being measured when some of the scattered light is received by the colorimeter's detector due to the finite aperture value. The bigger particles and relative refractive index, the more pronounced is this effect.

We note in passing that the possibility of secondary or low-angle scattering is not considered in traditional TT at all.

Underestimation of turbidity due to the secondary scattering, naturally, results in an underestimation of the calculated concentration of the precipitated polymer (Equation 2.1-101)

$$\tilde{M}' < \tilde{M}.$$
(86)

Studies made on a number of systems LML1+LML2+P and latices (Klenin and Shchyogolev, 1979; Shchyogolev and Klenin, 1980) have shown \tilde{M}'_{max}/c to decrease as the concentration of particles increases, and to be independent of the nature of a given system.

The low concentration boundary of secondary scattering \mathbf{c}_t^* is defined by the instrument's geometry and the cell length.

For the FET turbidimeter with a standard 45 mm cell, the threshold concentration $c_{l,FET} = 10^{-3}$ g/dl. At another cell length (given the instrument's geometry remains the same)

$$\frac{\mathbf{c}_{t}^{*}}{\mathbf{c}_{t,\text{FET}}^{*}} = \frac{l_{0,\text{FET}}}{l_{0}} \tag{87}$$

or

$$\mathbf{c}_t^* = \frac{4.5 \cdot 10^{-3}}{l_0}, \, \mathrm{g/dl}$$

and, with respect to the initial solution concentration,

$$\mathbf{c}_{t_0} = \frac{4.5 \cdot 10^{-3}}{(1-\gamma)l_0}, \, \text{g/dl}.$$
(88)

STT in the system $P\alpha MS$ +cyclohexane+octanol with the standard FET cell has resulted in (Ramazanov et al., 1982)

$$\frac{M'_{\text{max}}}{\mathbf{c}}, \,\% = \frac{\mathbf{c}_{\text{max}}^*}{\mathbf{c}} = -70 \,\text{lg}\,\mathbf{c}^* - 110, \tag{89}$$

where c^* is the actual concentration of the precipitated polymer with allowance for dilution (Figure 3.24, curve 1).



Figure 3.24. STT optimization diagram of P α MS solutions. Curves 1-3 and 1'-3 are the dependences of the maximal fraction of the precipitated polymer $\mathbf{c}_{IImax}^{*}/\mathbf{c}$ on lg \mathbf{c}^{*} (\mathbf{c}^{*} is the actual polymer concentration, g/dl, in the systems cyclohexane+octanol [1 3] and dioxane+octanol [1'-3]). $M \cdot 10^{-3} = 5$ (1, 1'), 10 (2, 2'), 15 (3, 3'). Curves I-III represent the measured maximal fraction of precipitated polymer $\mathbf{c}_{max}^{*}/\mathbf{c}$ on $-\log \mathbf{c}^{*}$ during the optical interaction among particles. The length of the cell is $l_0 = 4.5$ (I), 2.9 (II), 0.45 cm (III), the empty circles are experimental data for $l_0 = 4.5$ cm, the solid ones for $l_0 = 2.9$ cm (Ramazanov et al., 1982)

Joint consideration of Equations 89 and 88 reveals that changes of l_0 displace the straight line given by Equation 89 parallel to the abscissa axis $(-\lg c^*)$ (Figure 3.24, lines II and III).

Optical distortions (Klenin and Shchyogolev, 1979; Shchyogolev and Klenin, 1980) were interpreted as an effect of secondary (multiple) scattering. Special analysis (Khlebtsov, 1984) has shown such effects to be obviously caused by a large receiver aperture of serial instruments. This effect needs further investigations.

Search for the conditions of the maximal x_{max} is called an **optimization** of STT.

It is worthwhile analyzing the factors which influence x_{max} on an optimization diagram (Klenin and Shchyogolev, 1979), an example of which is given in Figure 3.24.

The position of the left-hand (thermodynamic) branch of the diagram is defined by the solution concentration, polymer M and the interaction parameters χ_{ij} . The position of the right-hand (optical) one is defined by the instrument's geometry and cell length. The system is considered as optimized if there exists a initial solution concentration range between these two branches where $x_{max} = 100\%$.



Figure 3.25. Precipitation curves of PaMS with octanol $(M_w \cdot 10^{-3} = 11, M_n \cdot 10^{-3} = 9.6)$ from dioxane (1, 2) and cyclohexane (3 5) solutions. The initial concentrations $c_0 = 0.010$ (1, 4), 0.015 (2, 3, 5) g/dl, the cell length $l_0 = 2.9$ (1, 4, 5) and 4.5 cm (2, 3) (Ramazanov et al., 1982)

An example of experimental realization of the diagram in Figure 3.24 is presented in Figure 3.25. One can understand the role of the initial concentration c_0 , cell length l_0 and thermodynamic features of the solvent and precipitant in obtaining a suitable precipitation curve at STT of P α MS solutions (Ramazanov et al., 1982).

Comparison of curves 1 and 4 shows that, with other conditions being equal, the amount of precipitated polymer in the system $P\alpha MS$ +cyclohexane+octanol exceeds 2.6-fold that one in the system $P\alpha MS$ +dioxane+octanol. Comparison of curves 1 and 2 ($P\alpha MS$ +dioxane+octanol) and curves 4 and 5 ($P\alpha MS$ +cyclohexane+octanol) reveals the effect of a rise in the precipitation degree with polymer concentration. Comparison of curves 3 and 5 provides an example of elimination of the optical distortions by means of shortening the cell length.

Figure 3.26 gives complete precipitation curves of a sample of $P\alpha MS$ ($M_w \cdot 10^{-3} = 80$, $M_n \cdot 10^{-3} = 70$) with octanol from cyclohexane (1) and dioxane (2) solutions. Here, precipitation from cyclohexane solutions is more preferable as the precipitation interval $\Delta\gamma$ in this system is almost twice wider, which causes better resolution of MWD details.

Upon obtaining the complete precipitation curve, one can proceed to fulfil the second reverse problem, i.e. to convert this curve to the corresponding MWD function. Here, Equation 55 plays an important role, and we should pay attention to determining the constants of this equation. To this end, titration of several narrow fractions of the polymer with different M in the chosen system LML1+LML2+P must be performed at several solution concentrations. An example of titration of one polymer fraction is given in Figure 3.27.

The literature contains different recommendations as to how to choose a pair of γ and \mathbf{c}_{l} to plot data using Equation 56: γ_{0} and $\mathbf{c}_{l} = \mathbf{c}(1 - \gamma_{0})$; γ and $\mathbf{c}_{l} = \mathbf{c}(1 - \gamma_{1/2})/2$;



Figure 3.26. Precipitation curves for the systems $P\alpha MS$ ($M_n = 7 \cdot 10^4$)+cyclohexane (1) ($c_0 = 0.0038$ g/dl, the cell length $l_0 = 2.9$ cm) and $P\alpha MS$ +dioxane (2) ($c_0 = 0.0060$ g/dl, $l_0 = 1.8$ cm) with octanol as the precipitant (Ramazanov et al., 1982)

 γ' and $\mathbf{c}(1-\gamma')$, where γ_0 and γ correspond to the beginning and the middle point of polymer precipitation, respectively, and γ' is the intersection point of the straight line approximating the linear segment of the precipitation curve with the γ axis. We choose the second version with the reasons to follow.

The titration data of one fraction are used to plot a straight line in the γ vs $(-\ln c_I)$ coordinates (Figure 3.28). The slope and the segment on the ordinate axis at $\ln c_I = 0$ give a and b, respectively. This procedure is repeated for each fraction to determine a set of a and b. Then, constructions like those shown in Figure 3.29 enable one to determine the constants A, B, and γ_{θ} (see Equations 57, 58, 55).

It should be noted that the reproducibility of the precipitation curves $x = x(\gamma)$ is always better than that of the turbidity curves. The latter have a particularly poor reproducibility in parallel experiments at slower addition of the precipitant, which is used to eliminate relaxational phenomena and to reach a complete thermodynamic equilibrium



Figure 3.27. Precipitation curves of a P α MS sample with $M_n = 19.6 \cdot 10^3$ from its cyclohexane solution with octanol as a precipitant. The concentrations are $c_0 = 0.033$ (1), 0.012 (2), and 0.005 g/dl (3) (Ramazanov et al., 1982)

(Klenin and Shchyogolev, 1971a; Klenin et al., 1973f, 1974d).

The irreducibility of the turbidity curve, the sizes and numerical concentration of particles is obviously caused by titration being performed in the metastable area of the state diagram as the spinodals are far from the TT trajectory (see Figure 3.21). This explains the high sensitivity of the system structure to slight changes in titration conditions which are often uncontrollable in the traditional experimental technique.

The better reproducibility of the precipitation curves $x = x(\gamma)$ is related to the \mathbf{c}_{II}^* calculational algorithm being sensitive to uncontrollable changes in titration conditions and more stable to variations of anisodiametry and polydispersity at n < 2 (see subsection 2.1.5).

The algorithm of \mathbf{c}_{II}^* calculation is also of little sensitivity to the relative refractive index of particles in the range n < 1; therefore, it seems reasonable to develop ways for controlling the particle size at STT (an additional way of STT optimization).

The data on particle sizes $\bar{r}_{\lambda} = \bar{r}_{\lambda}(\gamma)$ obtained in the course of TT allow one to elucidate the mechanism of appearance and growth of colloidal particles, which is of importance for



Figure 3.28. Estimation of the constants *a* and *b* in Equation 3.2-56. P α MS samples with $M_n \cdot 10^{-3} = 3310$ (1), 98 (2), 54 (3), 42 (4), and 19.5 (5) in the cyclohexane+octanol mixture (Ramazanov et al., 1983b)

STT optimization as well as from the viewpoint of general problems of colloidal chemistry. Some data on this subject have been reported in (Klenin and Shchyogolev, 1972, 1973; Klenin et al., 1973f, 1974d; Shchyogolev and Klenin, 1973; Shchyogolev et al., 1977b) but further investigations of colloidal particle genesis are of current concern.

Papers on STT place emphasis on the fact that the value of the wave exponent $n \approx 2$ remains during quite a long period of titration of different systems. This is most likely due to the configurative point crossing the critical opalescence region in the course of titration with the value n = 2 being characteristic for it (see subsections 2.3.5, 2.4.2, and 3.3.1).

In this region of the state diagram, there appears the effect of critical retardation of relaxational processes due to the small values of the diffusion coefficient D.

Thus, the velocity of motion of the configurative point during titration proves to be rather high, and the critical concentration fluctuations with $n \approx 2$ are so frozen by critical retardation that, while crossing the binodal, they change, as a matter of fact, to colloidal particles with the same sizes corresponding to $n \approx 2$ (Lebedeva et al., 1991).

Critical retardation is obviously the cause of a relative stability of emulsion at the "bin-


De-Figure 3.29. termination of the constants A and B in Equation 3.2-55 (scc also Equations 3.256...-58using the data of Figure 3.28(Ramazanov \mathbf{ct} al.,

odal top" in the systems paraffin+8-hydroxyquinoline and tricosane+8-hydroxyquinoline (Kochanova et al., 1973ab).

Recently, the importance of allowing for the dispersion of the refractive indices of the disperse phase and dispersion medium has been shown for a number of systems for precise determination of the concentration of disperse phase particles and the particle size over a small size range (3 < n < 4) (Khlebtsov et al., 1991).

We now turn to consideration of the way of converting the precipitation curve $x = x(\gamma)$ into the corresponding MWD function.

The traditional TT version uses Morey-Tamblyn's (1945) and Claesson's (1955) approaches based on the principle of independent precipitation of fractions which is, of course, a rather rough approximation.

On the basis of approximating the fundamental Equations 13 and 19, some conversion procedures have been developed to take the interaction among polymer fractions into account (Rayner, 1969; Peaker and Rayner, 1970; Ramazanov et al., 1983b, 1984; Shehyogolev, 1983; Shehyogolev et al., 1985, 1987).

According to Equation 12,

$$\varphi_{II} \exp(-\sigma p) = \varphi_I. \tag{90}$$

Substitution of Equation 90 into Equation 38, valid for polymer-diluted systems, yields

$$x = \int_{0}^{\infty} \frac{f(p) \, dp}{1 + \frac{\varphi_{\mathrm{I}}}{x\varphi}}.\tag{91}$$

The approximation in Equations 38 and 91 consists in replacement of the polymolecular polymer solubility φ_I in Equation 91 by the monomolecular polymer one v_{2I} (Scott, 1945;

Shchyogolev, 1983; Shchyogolev et al., 1983, 1985) which can be determined experimentally (see Figures 3.27-3.29) (Equation 59) or calculated using Equations 3.1-252...256. Hence,

$$x = \int_{0}^{\infty} \frac{f(p) dp}{1 + \frac{v_{21}}{x\varphi}}$$
(92)

and (see Equation 37)

$$f_{II}(p) = \frac{f(p)}{1 + \frac{v_{2I}}{x\varphi}}.$$
(93)

The expediency of approximation 91 by Equation 92 has been confirmed by simulations (Shchyogolev, 1983; Shchyogolev et al., 1985) with precipitation curves of a polymolecular polymer $x = x(\chi_1)$ to be plotted and $f_{II}(p)$ to be determined at different x.

If the condition

$$\frac{f_{II}(p_t)}{f(p_t)} = \frac{1}{2}$$
(94)

(Rayner, 1969; Shchyogolev, 1983; Shchyogolev et al., 1985) is accepted, then real fractionation (curve ABD in Figure 3.16) can be approximated by the ideal one (p_tCD) since the areas are roughly equal $(DCp_t = DBA \text{ or } DCB \approx ABp_t)$ (see Figure 3.16). This means the nonprecipitated part of the polymer (CBD) in real fractionation is compensated for the overprecipitated (with respect to ideal fractionation's predictions) one (ABp_t) . The value p_t corresponds to the inflection point of the function $\Omega(p)$ (Equation 18) (see Figure 3.15).

The possibility of fixing 50% precipitation of a fraction during its titration to determine the constants in the solubility equation (see above) serves as the experimental basis of Equation 94.

With Equation 93 involved, Equation 94 takes the form

$$v_{2I} = x\varphi \tag{95}$$

or, in g/dl and with due account of dilution with a solvent,

$$\mathbf{c}_I = x \mathbf{c}_0 (1 - \gamma). \tag{96}$$

Substituting the expression for c_I (Equation 59) in Equation 96 and solving Equation 96 with respect to M, we get

$$M = \left[\frac{B - A \ln x \mathbf{c}_0 (1 - \gamma)}{\gamma - \gamma_{\theta}}\right]^2.$$
(97)

For ideal fractionation (see subsection 3.2.2)

$$x = \int_{M_t}^{\infty} f(M) \, dM = 1 - \int_{0}^{M_t} f(M) \, dM \equiv 1 - W(M_t) \tag{98}$$

is valid, where $W(M_t)$ is the integral MWD function, M_t is the current value of the polymer M.

Equations 97 and 98 provide the basis for conversion of the precipitation curve $x = x(\gamma)$ into the integral MWD function W(M).

The abscissa axis γ of the precipitation curve $x = x(\gamma)$ is subdivided into ranges (fractions) with fixed γ_i values. x_i is found for each γ_i and, according to Equation 98,

$$W_i = 1 - x_i \tag{99}$$

is determined.

The value of W_i is used to calculate M_i from Equation 97 for the given x_i and γ_i . The constants of Equation 55 (A, B, γ_{θ}) have been determined beforehand, \mathbf{c}_0 is the initial solution concentration (g/dl).



Figure 3.30. Precipitation curves of a P α MS sample with octanol from its cyclohexane solution ($c_0 = 0.0038$ g/dl, $l_0 = 4.5$ cm) (1) and the restored integral MWD function (2) (Ramazanov et al., 1983b)

An example of the conversion is presented in Figure 3.30 for the $P\alpha MS$ +cyclohexane+octanol system (Ramazanov et al., 1983b).

To verify approximation 92, precipitation curves $x = x(\chi_1)$ obtained by simulation (Equations 20, 21 for the γ function as f(p)) were used as "experimental" ones (Shchyogolev, 1983; Shchyogolev et al., 1985). The solubility v_{2I} as a function of p and χ_1 was calculated by Equation 3.1-256.

Figure 3.31 shows integral MWD functions obtained by conversion of a simulated model curve $x = x(\chi_1)$ using approximation 92 and Equations 97 and 98 in comparison with the "true" MWD functions introduced into calculations of $x = x(\chi_1)$. Good agreement



Figure 3.31. Integral MWD functions restored from the results of a simulative STT at $\varphi = 10^{-5}$ for polymolecular polymers with $p_{w} = 1,000$ (1-3) and 5,000 (4) with $p_{w}/p_{n} = 1.05$ (1), 1.25 (2), 2.0 (3), and 5 (4) in comparison with the "true" MWD functions (dashed lines) (Shchyogolev, 1983)

between these MWD functions attests to the expediency of approximation 92 in the problem of restoring MWD functions from STT data.

Khlebtsov (1984) has proposed a more rigorous procedure of its restoring. He replaced the function I(M) complementary to W(M)

$$I(M) = 1 - W(M) \tag{100}$$

by an iterative form I_n in which the first iteration is represented by

$$I_1(M) = x(\gamma(M)). \tag{101}$$

Equations 100 and 101 coincide with Equation 99 above and the second iteration is

$$I_{2}(M) = 2x + \mathbf{c}_{II}^{*} \int_{0}^{\infty} \frac{x(\gamma'(M')) \frac{\partial \mathbf{c}_{I}(\gamma',M')}{\partial M'} dM'}{\left[\mathbf{c}_{II}^{*} + \mathbf{c}_{I}(\gamma',M')\right]^{2}} - , \qquad (102)$$

where x in the integral is taken at the point γ' corresponding to M' by Equation 96.

The series I_n converges rather quickly, so there is often no need for a third iteration.

Thus, STT as an analytical method for restoring the MWD function of polymers is promising.

A solubility equation of a polymolecular polymer φ_1 has been proposed based on approximation 93 (Shchyogolev, 1983; Shchyogolev et al., 1983, 1985), which serves as an alternative to the principle of independent fraction precipitation.

By definition, the differential MWD function in phase I is

$$f_I(M) \, dM = \varphi_I \, dM. \tag{103}$$

On the other hand, in view of Equation 93 with p to be replaced by M, we get

$$f_{I}(M) = f(M) - f_{II}(M) = \frac{f(M)v_{2I}(M)}{x\varphi + v_{2I}(M)}.$$
(104)

It follows from the last two equations that

$$\varphi_I(M) \, dM = \frac{f(M) v_{2I}(M) \, dM}{x\varphi + v_{2I}(M)}.$$
(105)

With mixtures of two polymer homologues ($w_i = 0.5$) with LML (P_1+P_2+LML) ($p_w = 1,000, \varphi = 10^{-3}, p_w/p_n$ to vary) as an example, mathematical analysis (Shchyogolev, 1983) has shown a substantial fall in the component P_2 solubility (the smaller p) in the ternary P_1+P_2+LML mixture as compared with the binary P_2+LML one, which is in agreement with a more rigorous (but a more bulky as well) theoretical analysis and experiment (Cornet, 1968).

3.3. Composition fluctuations, light scattering and diffusion

3.3.1. Mean-statistical fluctuations Region of solution stability

Light scattering

Debye and Bucche (1950) have employed Einstein's (1910) expression for the turbidity of a two-component solution to calculate the turbidity of a monomolecular polymer solution over the whole concentration range (c in g/cm^3) (see Equations 2.1-32, 2.4-7,-24)

$$\tau' = \tau_0 + IIRT \frac{\bar{V}_{01} \mathbf{c}}{\frac{\partial(\pi \bar{V}_{01})}{\partial \mathbf{c}}},\tag{1}$$

 τ_0 being the turbidity induced by density fluctuations (the solvent turbidity) while the second summand is due to the concentration fluctuations

$$II = \frac{32\pi^3 n^2}{3\lambda_0^4 N_A} \left(\frac{\partial n}{\partial \mathbf{c}}\right)^2,\tag{2}$$

where n is the refractive index of the solution (cf. Equations 2.4-22,-24, 2.1-32). Using the expressions for $\Delta \mu_1$ (Equation 3.1 50) and for osmotic pressure (Equation 1.2-27), we obtain an expression for the concentration-fluctuation-caused turbidity

$$\tau = \tau' - \tau_0 = \frac{\frac{HM\varrho_2}{z}}{\frac{1 + (z - 1)v_2}{zv_2(1 - v_2)} - 2\chi_1},$$
(3)

where ρ_2 is the polymer density.

The maximum τ_{max} corresponds to

$$v_{2\max} = \frac{1}{1+z^{1/2}},\tag{4}$$



Figure 3.32. Turbidity of a polymer solution. z = 100, $\chi_1 = 0.45$ (1); z = 100, $\chi_1 = 0$ (2); z = 1, $\chi_1 = 0.45$ (3). The vertical dashed lines mark the position of $v_{2\text{max}} = v_{2c}$ (Debye and Bueche, 1950) [Reprinted with permission from: P.Debye, A.M.Bueche. J. Chem. Phys. 18 (1950) 1423–1425. Copyright © 1950 American Institute of Physics]

i.e. to the critical concentration v_{2c} (Equation 3.1-241). The absolute value of τ depends on χ_1 and z according to Equation 3 (Figure 3.32).

Here χ_1 has the same value as the function of concentration fluctuations 1/f (Equations 2.4 9...11) of LMW solutions (cf. Figures 2.36 and 3.32). Debye and Bueche (1950) proposed to use v_{2c} for molecular weight determination by Equation 4, but this suggestion has not found practical use.

Experimental data, in general, confirm Equation 3, but there are relatively few papers on this subject (Tager et al., 1964b, 1968; Andreyeva et al., 1970; Hyde, 1972).

The functional dependence of turbidity in polymer systems is also based on Einstein's equation (Equations 2.4-24, 2.1-32; Table 2.3), but calculation of the mean square fluctuation of refractive index $(\Delta n)^2$ in

$$\tau = \frac{32\pi^3 n^2}{3\lambda_0^4} v \overline{(\Delta n)^2} \tag{5}$$

or that of dielectric constant $\overline{(\Delta \epsilon)^2}$ in

$$\tau = \frac{8\pi^3}{3\lambda_0^4} v(\Delta\epsilon)^2 \tag{6}$$

(cf. Table 2.3) is a more difficult task.

Here we denote the refractive index of solution by the letter n as μ_i means the chemical potential of the *i*th component in solution.

Calculation of $(\overline{\Delta n})^2$ (Gross, 1940; Brinkman and Hermans, 1949; Stockmayer, 1950) and $(\overline{\Delta \epsilon})^2$ (Kirkwood and Goldberg, 1950) is performed using statistical physics methods, most often using Gibbs' grand canonical ensemble. Eg. if N_i is the number of moles of the *i*th component, then (Brinkman and Hermans, 1949)

$$\overline{(\Delta n)^2} = \overline{\left(\sum_i n_i \Delta N_i\right)^2}$$

$$= \frac{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \left(\sum_i n_i \Delta N_i\right)^2 \exp\left(-\frac{\Delta F}{kT}\right) \prod_i d(\Delta N_i)}{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \exp\left(-\frac{\Delta F}{kT}\right) \prod_i d(\Delta N_i)},$$
(7)

where $\Delta F = \sum_{i} \sum_{j} F_{ij} \Delta N_i \Delta N_j, n_i = \left(\frac{\partial n}{\partial N_i}\right)_{V,T}, F_{ij} = \left(\frac{\partial^2 F}{\partial n_i \partial n_j}\right)_{V,T}$

Zernike (reported in: Brinkman and Hermans, 1949) was the first to calculate $(\overline{\Delta n})^2$ for a polymer system. Since then, this question has been addressed in a number of papers (Brinkman and Hermans, 1949; Kirkwood and Goldberg, 1950; Stockmayer, 1950; Casassa and Eisenberg, 1960; Vrij and Overbeek, 1962; Scholte, 1970b, 1971; Nagasawa and Takahashi, 1972; Vrij and van den Esker, 1972; Vrij, 1974, 1978; Yerukhimovich, 1979), in particular, to build the theory of light scattering from polyelectrolyte solutions in aqueous solutions of LMW electrolytes (Casassa and Eisenberg, 1960; Stigter, 1960; Vrij and Overbeek, 1962; Nagasawa and Takahashi, 1972).

In the general case of a $(\nu + 1)$ -component system $(i = 0, 1, \dots, \nu)$ (Stockmayer, 1950)

$$\tau = \frac{H'v\sum_{i=0}^{\nu}\sum_{j=0}^{\nu}\psi_i\psi_j A_{ij}}{|a_{ij}|},$$
(8)

where $|a_{ij}|$ is a determinant with its elements

$$a_{ij} = \left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,P,N_{i\neq j}};\tag{9}$$

 $A_{ij} = \frac{\partial |a_{ij}|}{\partial a_{ij}}$ is the cofactor of a_{ij} , resulting from deletion of the *i*th row and the *j*th column

$$\psi_{i} = \left(\frac{\partial n}{\partial N_{i}}\right)_{T,P,N_{j\neq i}}, \quad H' = \frac{32\pi^{3}n^{2}kT}{3\lambda_{0}^{4}}$$

 $A_{ij}/|a_{ij}|$ is identical to the inverse matrix **A** (Korn and Korn, 1968)

$$\mathbf{A}^{-1} \equiv |a_{ij}|^{-1} \equiv \frac{A_{ij}}{|a_{ij}|}.$$

It is seen from comparison of Equation 9 and Equation 3.2-2 that the spinodal condition coincides with the determinant $|a_{ij}|$ being equal to zero. Thus, according to Equation 8, $\tau \to \infty$ on the spinodal, which attests to the unsuitability of Equation 8 near the spinodal as $(\Delta n)^2$ was calculated in the absence of the correlation of composition fluctuation in elementary volumes v. The expression, valid near the spinodal as well, will be given below (Equation 35).

An expression for Rayleigh's ratio for polymolecular polymer solution results from Equation 8 (see the conversion formulae in Table 2.3) (Scholte, 1970b, 1971)

$$R_{\vartheta} = \frac{4\pi^2 n^2}{\lambda_0^4} \left(\frac{\partial n}{\partial w}\right)^2 v \frac{\sum \sum A_{ij}}{|a_{ij}|} \cdot \frac{1 + \cos^2 \vartheta}{2}$$
(10)

with $a_{ij} = \frac{\partial^2 \Delta G_m}{\partial w_i \partial w_j}$, where ΔG_m is the increment of the Gibbs potential of mixing in the volume v, w_i is polymer concentration in weight fractions. This formula neglects intramolecular interference, i.e. valid for moderate molecular weights only. Otherwise, extrapolation $\vartheta \to 0$ (Figure 2.8) is required to eliminate this effect.

Equation 8 can be represented in the form traditional for light scattering methods

$$\frac{Hw}{\tau} = \frac{1}{M_w} + 2\mathcal{A}_2 w,$$

where

$$\mathcal{A}_{\mathbf{z}} = \sum_{\mathbf{i}} \sum_{j} \mathcal{A}_{2,i,j} \cdot \frac{M_{\mathbf{i}} M_{j}}{M_{w}^{2}} w_{\mathbf{i}} w_{j},$$

w is the total polymer concentration.

Hence, the value of the second virial coefficient depends on the degree and character of polymer polymolecularity.

Experiments with toluene solutions of P α MS showed a stronger dependence of \mathcal{A}_2 on M and MWD than that predicted by the above formula (Elias et al., 1975).

In the case of high molecular weights, when the effect of intermolecular interference manifests itself, polymolecularity leads to a deformation of the radiation diagram

$$\check{P}(\vartheta) = \frac{\int\limits_{0}^{\infty} q_{w}(M)MP(\vartheta, M) \, dM}{\int\limits_{0}^{\infty} q_{w}(M)M \, dM},$$

where $q_w(M)$ is the differential MWD function.

This formula enables the z-average macromolecular sizes to be determined from the radiation diagram (Zimm, 1948; Stacey, 1956; Tanford, 1961; Tsyian Zhen-yuan, 1962; Rafikov et al., 1963, 1978; Shatenshtein et al., 1964; Tsvetkov et al., 1964; Bresler and Yerusalimski, 1965; Morawetz, 1965; Kerker, 1969; Huglin, 1972; Eskin, 1973).

An expression for Rayleigh's ratio R_0 with due account of polymolecularity, intra- and intermolecular interference, the spinodal proximity, and appropriate dependence of the interaction parameter χ has been derived by Vrij (1974, 1978) and will be discussed later.

Diffusion

As the diffusion coefficient depends on the hydrodynamic and thermodynamic factors (Equation 2.4-43), its behaviour in a wide concentration range significantly differs for solutions in a good or poor solvent.

The mobility of macromolecules monotonically diminishes as the concentration rises. Far from the liquid-liquid phase separation region (in a good solvent), $d\mu_2/dv_2$ monotonically increases with the polymer concentration v_2 (see Figure 3.2c, the curves for $\chi_1 = 0.25$); hence, the concentration dependence $D = D(v_2)$ (or $D = D(c_2)$) goes through a maximum at moderate concentrations (Figure 3.33).



Figure 3.33. Concentration dependence of the diffusion coefficient D in the polystyrene+ethylbenzene system at 20 (1), 30 (2), 40 (3), 50 (4), and 60°C (5). x_2^* is the segment mole fraction of polymer, i.e. $x_2^* = zn_2/(n_1 + n_2)$, where n_1 and n_2 are the number of moles of the solvent and polymer, respectively, z is the degree of polymerization (Rehage et al., 1970) [G.Rehage, O.Ernst, J.Fuhrmann. Disc. Faraday Soc. 49 (1970) 208-221. Copyright © 1970 by the Royal Society of Chemistry]

Indeed, combination of Equation 2.4-43 (with a replacement $\mu_i^* = \mu_i/N_A$) and the Gibbs-Durgham one (Equation 1.1.2 49) leads to

$$D = \frac{\mathbf{c}_2}{N_A f_2} \frac{\partial \mu_2}{\partial \mathbf{c}_2} = \frac{x_2}{N_A f_2} \frac{\partial \mu_2}{\partial x_2} = -\frac{x_1}{N_A f_2} \frac{\partial \mu_1}{\partial x_2}.$$
 (11)

As the molecular weight of the polymer $M_2 \gg M_1$, then

$$x_{2} = \frac{\frac{m_{2}}{M_{2}}}{\frac{m_{1}}{M_{1}} + \frac{m_{2}}{M_{2}}} \approx \frac{m_{2}M_{1}}{m_{1}M_{2}}$$

If we multiple both the nominator and denominator of the last fraction by the solvent density ϱ_1 , we get the molar volume of the solvent $M_1\varrho_1 = V_1$ and the solvent volume

 $m_1\varrho_1 = V_1$, which is approximately equal to the volume of the solvent for dilute solutions $V_1 \cong V$, and

$$x_2 \cong \frac{m_2 M_1 \varrho_1}{m_1 M_2 \varrho_1} \approx \frac{m_2 V_1}{M_2 V} = \frac{\mathbf{c}_2 V_1}{M_2}$$

Whence

$$dx_2 = \frac{V_1}{M_2} d\mathbf{c}_2,$$

$$D = -\frac{x_1 M_2}{N_2 f_2 V_1} \frac{\partial \mu_1}{\partial \mathbf{c}_2}.$$

Differentiating Equation 1.2–27 with respect to c_2 , we have

$$\frac{\partial \pi}{\partial \mathbf{c}_2} = -\frac{1}{V_1} \frac{\partial \mu_1}{\partial \mathbf{c}_2}.$$

Then

$$D = \frac{x_1 M_2}{N_A f_2} \frac{\partial \pi}{\partial \mathbf{c}_2}.$$
(12)

The concentration dependence of the friction coefficient of macromolecules f_2 is approximated by

$$f_2 = f_{02}(1 + B\mathbf{c}_2 + \cdots) \tag{13}$$

(Tsvetkov et al., 1964).

It is often assumed that $x_1 \approx v_1 = 1 - v_2 = 1 - \mathbf{c}_2 \overline{V}_2$ as well.

If only two terms in the virial expansion of π are left (Equation 1.3-37), then

$$D = \frac{M_2 RT}{N_A f_2} (1 - \mathbf{c}_2 \bar{\mathbf{v}}_2) \left(\frac{1}{M_2} + 2\mathcal{A}_2 \mathbf{c}_2\right)$$

$$= \frac{kT(1 - \mathbf{c}_2 \bar{\mathbf{v}}_2)}{f_{02}(1 + B\mathbf{c}_2)} (1 + 2\mathcal{A}_2 \mathbf{c}_2 M_2).$$
(14)

As we see, the product of the ascending and descending functions of \mathbf{c}_2 , $D = f(\mathbf{c}_2)$ must have an extremum (see Figure 3.33).

As the phase separation region gets nearer, $\partial \mu_2 / \partial v_2$ decreases (see Figure 3.2c, the curves for $\chi_1 = 0.5$), therefore, in a polymer solution in a poor solvent $D = D(\mathbf{c}_2)$ passes through a minimum corresponding to the critical concentration (Figure 3.34). Since the mobility of macromolecules inevitably diminishes with rising concentration (Equation 13), this factor must overcompensate for the thermodynamic one at high concentrations: as a result, the curves $D = D(\mathbf{c}_2)$ (see Figure 3.34) should be expected to have a maximum at high concentrations \mathbf{c}_2 (Rehage et al., 1970).

New ideas on the mechanism of the diffusion mobility of macromolecules in solution and in the condensed state have been put forward within the framework of the scaling approach (see section 4.5 (de Gennes, 1968, 1976a, 1979; Gotlib et al., 1986)).

Dynamic light scattering provides new capabilities of experimental studies of the mobility of macromolecules at different levels of relaxation times (see subsection 3.3.2).



Figure 3.34. Concentration dependence of the diffusion coefficient D in the polystyrene+cyclohexane system at 28 (1), 30 (2), 40°C (3) (a) and the state diagram of this system (b) (Rehage et al., 1970) [Reprinted with permission from: G.Rehage, O.Ernst, J.Fuhrmann. Disc. Faraday Soc. 49 (1970) 208-221. Copyright © 1970 by the Royal Society of Chemistry]

Critical opalescence

The relationships given in subsection 2.4.3 for critical opalescence of solutions hold good for polymer solutions as well with a modification of the quantities # and Ω as w_2 should be the volume of a monomeric unit and the potential energy functions $\varepsilon_{ij}(r)$ concern interactions among the monomeric units and LMWL molecules. When z monomeric units are Gaussianly distributed about their centre of gravity (Debye, 1959),

$$\Psi = \frac{a^2}{2} \left(\frac{W_{22}}{w_2^2} - \frac{W_{12}}{w_1 w_2} \right) = \frac{a^2}{2} (\delta_{22} - \delta_{12}), \tag{15}$$

where a is the distribution mode. It follows from Equation 3.1-149 that

$$a^{2} = \frac{2}{3}\overline{R^{2}} = \frac{\overline{h^{2}}}{9}.$$
 (16)

Equations 2.4 18...20, 15, 16 give the Debye length l (Equation 2.4 20) (Debye et al., 1960b; Eskin, 1973) as

$$l^2 = \frac{\delta_{11}}{\Delta_1 + \Delta_2} l_{11}^2 + \frac{2\Delta_2}{\Delta_1 + \Delta_2} \overline{R^2},\tag{17}$$

where $\Delta_1 = \delta_{11} - \delta_{12}, \ \Delta_2 = \delta_{22} - \delta_{12}.$

The corresponding estimations (Debye et al., 1960ab) lead to

$$l_{11}^2 \ll \overline{R^2}$$
 and $\frac{2\Delta_2}{\Delta_1 + \Delta_2} \approx 1$, (18)

whence it follows that

$$l^2 \approx \overline{R^2}.$$
(19)

For solutions of macromolecules, whose size is commensurable with λ , internal interference contributes to the scattering asymmetry as well. Then (Debye et al., 1962b)

$$I_{\vartheta} = I_0 \frac{4\pi^2 V \left[\frac{\mathbf{c}}{\mu} \cdot \frac{\partial \mu}{\partial \mathbf{c}}\right]^2 \left[1 - \frac{4\pi^2}{3} \overline{R^2} s^2\right]}{l^2 \lambda^4 \mathbf{c} \left[\frac{\partial}{\partial \mathbf{c}} \left(\frac{\pi}{RT}\right)\right]} \cdot \frac{1 + \cos^2 \vartheta}{2}.$$
(20)

Here μ is the refractive index, $s = \frac{2}{\lambda} \sin \frac{\vartheta}{2}$ (see Equations 2.1–50,-84) or according to (Vrij and van den Esker, 1972)

$$\frac{\mathcal{K}\mathbf{c}(1+\cos^2\vartheta)}{R_{k,\vartheta}} = \frac{\partial}{\partial\mathbf{c}}\left(\frac{\pi}{RT}\right) \left[1 + \frac{16\pi^2\overline{R^2}}{3\lambda^2}\sin^2\frac{\vartheta}{2}\right].$$
(21)

As the critical point is approached $T \to T_c$ at $\varphi = \varphi_c$ (or $\mathbf{c} = \mathbf{c}_c$), it follows from Equation 20 that (Debye et al., 1962b)

$$I_{\vartheta}^{-1} = D\frac{T_c}{T} \left[\frac{\Delta T}{T_c} + \left(\frac{8\pi^2 l^2}{3\lambda^2} + \frac{\Delta T}{T_c} \cdot \frac{16\pi^2}{3} \cdot \frac{\overline{R^2}}{\lambda^2} \right) \sin^2 \frac{\vartheta}{2} \right],$$
(22)

where D is a quantity depending on the system P+LMWL and including instrumental corrections; $\Delta T = T - T_c$.

Debye et al. (1962b) have suggested representing Equation 22 as

$$I_{\vartheta}^{-1} = A + B \sin^2 \frac{\vartheta}{2}.$$
 (23)

The plot I_{ϑ}^{-1} vs $\sin^2(\vartheta/2)$ constructed from the indicatrix I_{ϑ} at different temperatures T (or ΔT) enables T_c , $\overline{R^2}$, and l^2 to be determined simultaneously from the B/A or A/B ratios. The critical temperature T_c is found by extrapolation

$$\frac{A}{B} = f(T) \to 0. \tag{24}$$

If we introduce a function

$$s = \frac{B}{A} \Delta T, \tag{25}$$

then, according to Equation 22,

$$s = \frac{8\pi^2}{3} \cdot \frac{l^2}{\lambda^2} T_c + \frac{16\pi^2}{3} \cdot \frac{\overline{R^2}}{\lambda^2} \Delta T, \tag{26}$$

whence it follows that in the s vs ΔT plot, the initial ordinate s_0 and the slope define l^2 and $\overline{R^2}$, respectively

$$l^2 = \frac{3\lambda^2 s_0}{8\pi^2 T_c},\tag{27}$$

$$\overline{R^2} = \frac{3\lambda^2}{16\pi^2} \cdot \frac{s - s_0}{\Delta T}.$$
(28)

As $\overline{R^2} \sim M$ for Gaussian chains, according to Equation 19,

$$l^2 \sim M.$$
 (29)

Analysis of Equations 20 22 shows that critical opalescence in polymer solutions is observed over a wider temperature range than in solutions of LMW compounds. For a given, sufficiently high, and reliably fixed asymmetry $I_{0^\circ}/I_{180^\circ} = 2$ at $\lambda = 3,000$ Å and $T_c = 300$ grad, Equation 22 gives for the polymers of the vinyl row (Eskin, 1973)

Polymerization	$(\bar{R}^2)^{1/2},$	$T-T_{c}$,
degree (p)	Å	grad
5620	187	30
540	58	3
56	9	0.3

These estimations show the asymmetry of the critical opalescence for polymers with $p \sim 1,000$ is observed over a range of several degrees while ΔT is about $10^{-2} \dots 10^{-3}$ K in solutions of LMW components for $I_{0^{\circ}}/I_{180^{\circ}} = 2$. On the other hand, such a wide extension of the critical opalescence of polymer solutions along the temperature scale significantly hinders identification of the binodal (the boundary of the phase separation region) in contrast to LMW mixtures, where the scattered light intensity rises so sharply (by the temperature scale) that the way of recording this effect turns out to play no significant part.

Studies of the macromolecular structure in the precritical region (Debye et al, 1960ab, 1962ab; Eskin and Magarik, 1960; Skazka et al., 1960; Skazka and Nikitin, 1963; Eskin and Nesterov, 1965ab, 1966ab, 1967ab; Eskin and Serdyuk, 1969; Eskin, 1973) have shown Equation 29 to fail sometimes. The proportionality $l^2 \sim M$ was fixed in the polymethylsiloxane+tetraline (Eskin and Nesterov, 1965b), poly- β -vinylnaphthalene (P- β -VN)+toluene+decaline, P- β -VN+benzyl alcohol, P- β -VN+phenylethyl alcohol (Eskin and Nesterov, 1965a, 1967b; Eskin, 1973) systems. In the poly- β -naphthylmethacrylate (P- β -NM)+toluene, P- β -NM+totraline, P- β -NM+phenylethyl alcohol, P- β -NM+benzyl alcohol (Eskin and Nesterov, 1966a), polybutylmethacrylate+isopropanol (Eskin and Nesterov, 1967; Eskin, 1973), polystyrene+cyclohexane (Debye et al., 1962b) systems, the l^2 vs M dependence is weaker.

In contrast to Equation 19, l turns out to be significantly smaller than $(\overline{R^2})^{1/2}$ (Debye et al., 1962b; Eskin and Nesterov, 1966a; Eskin, 1973).

Measurements in the precritical region and calculations from Equation 26 have shown a significant decrease in coil size in comparison with the sizes of the coils at the θ temperature and infinite dilution ($\mathbf{c} \rightarrow 0$) (Debye et al., 1960b, 1962ab; Eskin and Nesterov, 1966ab, 1967a; Eskin, 1973).

This circumstance caused a discussion. Attention was paid to the way of determining the critical concentration from the asymmetry maximum $I_{45^o}/I_{135^o} = f(\varphi_2)$ at $T > T_c$ (Debye et al., 1960b, 1962b). Several researchers (Rehage et al., 1965; Rehage and Koningsveld, 1968; Koningsveld, 1970b; Borchard and Rehage, 1971) has shown that the

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asymmetry maximum is observed at a concentration lower than the critical one determined independently (eg. using the volume-to-volume ratio at phase equilibrium). Vrij and van den Esker (1972), Vrij (1974), as well as the abovementioned authors, relate the maximum of light scattering asymmetry to the precipitation threshold concentration φ_{pt} (the spinodal's maximum, see Figure 3.35). The actual polymolecularity of polymer



Figure 3.35. Spinodal calculated from Equation 3.3-44, $p_w = 10^4$. The straight line corresponds to the scattering asymmetry maximum $z = R_{k,45}/R_{k,135}$ and connects the spinodal's maximum with the θ point (Vrij and van den Esker, 1972) [Reprinted with permission from: A.Vrij, M.W.J. van den Esker. J. Chem. Soc. Faraday Trans. 68 (1972) 513-525. Copyright © 1972 by the Royal Society of Chemistry]

fractions shifts the location of φ_c to the right along the boundary of the phase separation region (see Equation 3.2–10, Figures 3.12-3.14). As this location is dependent on the M_z to- M_w ratio (Equation 3.2–10), this shift may be observed at a rather small ratio M_w/M_n as well. Indeed, Rehage et al. (1965), Rehage and Koningsveld (1968) have reported on a 2.4-fold difference between φ_c and φ_{pt} in the polystyrene+cyclohexane system though $M_w/M_n = 1.07$ only (but $M_z/M_w = 1.4$!). Besides, even at small M_w/M_n and M_z/M_w , the difference between φ_c and φ_{pt} increases due to the strong dependence of the interaction parameter χ on polymer concentration (see the remark in the proof in Chu's (1970) review).

As the method for determining the θ temperature and thermodynamic parameters from T_c of polymer solutions has gained acceptance (Shultz-Flory's method, see Equation 3.1 246), the question naturally arises as to the degree of correctness of the determined parameters in the case of replacing T_c by T_{pt} , since it was T_{pt} and φ_{pt} that were measured in most cases, i.e. the location of the intensity maximum of light scattering in the region of critical opalescence. Meanwhile, Flory-Shultz' construction (Shultz and Flory, 1952, 1953ab) is valid, strictly speaking, only for binary systems where $T_c = T_{pt}$ and $\varphi_c = \varphi_{pt}$.

Even if T_{pt} and φ_{pt} are measured on traditionally good polymer fractions $(M_w/M_n \leq 1.05...1.1)$, artifacts might appear owing to a high sensitivity of T_{pt} and φ_{pt} to the MWD momenta, which are usually not fixed. That is why Koningsveld and Staverman's (1968c) analysis of applicability of Equation 3.1 246 to quasibinary systems is of importance. It involves the following temperature dependence of interaction parameter

$$\chi_1 = g_{0,1} + \frac{g_{0,2}}{T}.$$
(30)

Then, for the critical value,

$$\chi_{1,c} = g_{0,1} + \frac{g_{0,2}}{T_c}.$$
(31)

Substitution of Equation 31 to Equation 3.1-242 leads to

$$T_c^{-1} = \frac{0.5 - g_{0,1}}{g_{0,2}} + \frac{p^{-1/2} + 0.5p^{-1}}{g_{0,2}}$$
(32)

٥r

$$T_c^{-1} = \theta^{-1} + \frac{p^{-1/2} + \frac{1}{2}p^{-1}}{g_{0,2}}$$
(33)

(cf. Equation 3.1 246). From the ordinate and slope of the line

 $T_c^{-1} vs \left(p^{-1/2} + 0.5 p^{-1} \right),$

 θ , $g_{0,1}$, and $g_{0,2}$ or θ , ψ_1 , κ_1 can be determined (see subsection 3.1.1, Equations 3.1-42...46).

On the other hand, Shultz (1953) has derived a relationship between T_{pi} and the MWD parameters for the exponential MWD functions

$$T_{pt}^{-1} = \frac{(0.5 - g_{0,1})}{g_{0,2}} + \frac{Q p_w^{-1/2} + 0.5 p_w^{-1}}{g_{0,2}},$$
(34)

where $Q = 1 - 0.25 (1 - 0.184q^{-7/6}) q^{-2}$, q = b/(b-1), $b = p_w/p_n$. If b = 1, it reduces to Equation 32.

As seen from Equation 34, if T_{pt} stands instead of T_c , the θ value found by extrapolation $p \to \infty$ on the construction

$$T_{p'}^{-1}$$
 vs $\left(p^{-1/2} + 0.5p^{-1}\right)$

will be correct if only p_w is used and there is no difference in the Q factor of the polymer samples (i.e. all the samples possess the experimental MWDs of the same width).

Figure 3.36 shows a very slight difference in slope and the complete coincidence of θ for model samples with different b's. Yet, in the case of the exponential MWD, the CPC and binodals with $p = p_w$ do not differ significantly, and it was important to verify the correctness of Shultz-Flory's construction for other MWD kind as well (Koningsveld and Staverman, 1968c).



Figure 3.36. Determination of the θ temperature in the polystyrene+cyclohexane system using Shultz-Flory's method with b = 1, Q = 1 (a binary mixture, $T_{pt} = T_c$) (1); b =1.5 (2), and b = 2 (3) for an exponential MWD (Koningsveld and Staverman, 1968c) [R.Koningsveld, A.J.Staverman, J. Polym. Sci. A-2 6 (1968) 349 366. Copyright © 1968 by Wilcy. Reprinted by permission of John Wiley & Sons, Inc.]

Figure 3.37 presents Shultz-Flory's simulations for the exponential and logarithmically normal MWDs of different width. All the lines are extrapolated to $\chi_1 = 0.5$ for $p_w \to \infty$, i.e. the value $\chi_1 = 0.5$ results if the fractions are equal in width of the same distribution. When b < 1.25, even the kind of distribution (of the two considered) does not matter. Whether a difference is observed in the MWD kinds of the fractions (samples) can be, to a certain extent, judged by the CPC shape, and the relative locations of the CPCs must not show irregularities. An intersection, for example, would directly point to a difference in the MWD kinds. In this case, the Shultz-Flory's construction remains linear, but the ordinate intercept **does not** define the θ temperature.

Koningsveld and Staverman (1968c) have also calculated the ratios φ_c/φ_{pt} and $\chi_{1,c}/\chi_{1,pt}$ as functions of $b = p_w/p_n$ (Figure 3.38). The $\chi_{1,c}/\chi_{1,pt}$ ratios corresponds to T_{pt}/T_c . It follows from these data that polymolecularity shifts the precipitation threshold along the concentration axis stronger than along the temperature axis with this shift substantially depending on the kind of MWD function, especially, at b > 1.25. We note in passing that this effect may provide a way of determining b with a better accuracy than do the traditional methods.

The presented analysis shows that the significant difference in φ_c calculated by Flory (Equation 3.1-241) and experimentally obtained (φ_{pt} , in fact), revealed in papers on critical opalescence (Eskin, 1973, page 307, table 7.2), may be attributed to the difference between p_z and p_u (Vrij and van den Esker, 1972). This effect of the difference between theoretical and experimental φ_c 's also depends on the possible concentration



dependence of the order parameter (see subsection 3.6.1), which requires special analysis. The corresponding estimations for the polystyrene+cyclohexanc system are given in subsection 3.6.1.

Eskin and Nesterov (1966b, 1967b), Eskin (1973) have proposed a method to study the energy of polymer molecular cohesion based on critical opalescence in the P+LMWL system, in particular, on a careful study of the dependence $l^2 = f(\overline{R^2})$ (Equation 17). The obtained quantities of the molar cohesion energy of a number of polymers are in good agreement with the data yielded by other methods (Eskin, 1973, table 7.3).

Since then, attempts have been made to improve and modify Debye's (1959) theory of critical opalescence. Vrij and van den Esker (1972) have accounted for the influence of local concentration gradients on the entropy term of the free energy F in their consideration of light scattering from moderately-concentrated polymer solutions in terms of Silberberg's (1952) model (recall that Debye allowed for their influence on the entropy term only). To calculate the scattering intensity I_{ϑ} , they used the Fourier transformation of the concentration fluctuations and Brillouin (1922)-Debye's (1959) formalism

$$\frac{\mathcal{K}\mathbf{c}(1+\cos^2\vartheta)}{R_{k,\vartheta}} = \frac{\partial}{\partial \mathbf{c}}\left(\frac{\pi}{RT}\right) + \frac{16\pi^2\overline{R^2}}{3\lambda^2}M^{-1}\sin^2\frac{\vartheta}{2},\tag{35}$$

with $\overline{R^2}$ relating to the macromolecular size at a given concentration c.



Figure 3.38. φ_c/φ_{pt} and $\chi_{1,c}/\chi_{1,pt}$ as functions of the parameter $b = M_w/M_n$ calculated for the exponential (1, 2) and logarithmically normal (3, 4) MWD functions for $M_w = 131,700$ (1, 3) and 26,340 (2, 4) (Koningsveld and Staverman, 1968c) [R.Koningsveld, A.J.Staverman, J. Polym. Sci. A 2 6 (1968) 349-366. Copyright © 1968 by Wiley. Reprinted by permission of John Wiley & Sons, Inc.]

This equation, in the general case, significantly differs from Debye's one (Equation 21), but at $\mathbf{c} \to 0$ both reduce to

$$\mathcal{K}\mathbf{c}(1+\cos^2\vartheta)R_{k,\theta}^{-1} = M^{-1}\left[1 + \frac{16\pi^2 \overline{R_0^2}}{3\lambda^2}\sin^2\frac{\vartheta}{2}\right],\tag{36}$$

where $\overline{R_0^2}$ is the mean square radius of gyration of the macromolecules at $\mathbf{c} = 0$, and the expression in the square brackets is equal to $P^{-1}(\vartheta)$ for coils at low scattering angles ϑ .

For finite concentrations of solutions, Equation 35 leads to

$$\mathcal{K}\mathbf{c}(1+\cos^2\vartheta)R_{k,\theta}^{-1} = M^{-1}\left[1+\frac{16\pi^2\overline{R^2}}{3\lambda^2}\sin^2\frac{\vartheta}{2}\right] + 2\mathcal{A}_2\mathbf{c}.$$
(37)

If $\overline{\mathbb{R}^2}$ does not change with concentration **c**, it reduces to Debye-Zimm's equation (Zimm, 1948).

On the spinodal, $\frac{\partial}{\partial \mathbf{c}} \left(\frac{\pi}{RT} \right) = 0$, and the scattering is defined by the second term in the right-hand side (Equation 35) with its strong dependence on ϑ (critical opalescence). Taking just the same form of the enthalpy summand in the Gibbs potential as did Debye

$$h(\varphi) = \frac{\Omega}{2kT}\varphi(1-\varphi) \tag{38}$$

(where Ω is a constant with $\chi_1 = \Omega/2kT$, cf. Equations 3.1 30 and 3.1 33), Vrij and van den Esker (1972) arrive at an equation for the square Debye length

$$l^2 = 2\overline{R^2} \frac{T}{T_c} \varphi_c \tag{39}$$

or, in view of Equation 3.1 241,

$$l^{2} = 2\overline{R^{2}}\frac{T}{T_{c}}\left(1+p^{1/2}\right)^{-1}.$$
(40)

Thus, according to these authors, l^2 turns out to be $p^{1/2}/2$ times less than that given by Debye's theory, which shows better agreement with experimental data. Moreover, according to Equation 40,

$$l^2 \sim M^{1/2}$$
. (41)

Results in agreement with this equation have been obtained for a number of systems. In particular, for the polybutylmethacrylate+benzene+heptane system, Equation 41 works well (Eskin, 1973) while for the polystyrene+cyclohexane system (Debye et al., 1960ab, 1962ab; Chu, 1970)

$$l^2 = 0.91 M_n^{0.57}.$$
(42)

Relationship 41 follows from the scaling approach as well (de Gennes, 1968) (see section 4.4).

For a polymolecular system, Vrij and van den Esker (1972) have derived

$$\frac{2\pi^2}{\lambda^4\mu^2} \left(\frac{\partial\mu}{\partial\varphi}\right)^2 (1+\cos^2\vartheta) R_{k,\vartheta}^{-1} = \left\{ (w_1\varphi_0)^{-1} + (w_{2,w}\varphi)^{-1} + \frac{\partial^2 h}{\partial\varphi^2} \right\} + \frac{16\pi^2 \overline{R_z^2}}{3\lambda^2} w_{2,w}\varphi \sin^2\frac{\vartheta}{2}, (43)$$

 w_i being the volume of the component molecules.

In the accepted model, the spinodal equation has the form

$$(w_1\varphi_0)^{-1} + (w_{2,w}\varphi)^{-1} + \frac{\partial^2 h}{\partial \varphi^2} = 0,$$
(44)

whence the maximum on the spinodal corresponds to the polymer concentration

$$\varphi_{m,sp} = \left(1 + p_w^{1/2}\right)^{-1} \tag{45}$$

with

$$T_{m,sp} = \frac{\Omega w_1}{k} \left(1 + w_{2,w}^{-1/2} \right)^{-2}.$$
(46)

Equation 43 calculates the location of the maximum of the asymmetry coefficient $z = R_{k,45^{\circ}}/R_{k,135^{\circ}}$. At a fixed temperature T, the maximum of z_m corresponds to the expression

$$(1 - \varphi_{m,as})^2 = \frac{kT}{\Omega w_1},\tag{47}$$

where $\varphi_{m,as}$ is the polymer concentration at the maximum of asymmetry (see Figure 3.35).

The asymmetry maximum z_m gets more expressed as T approaches the spinodal; however, one should keep in mind that in polynary systems, the boundary of the phase separation region goes above the spinodal maximum and touches the spinodal on its right-hand branch at the critical point (see Figure 3.14). This means that particles of a new phase may appear in the system when the configurative point approaches the spinodal near its maximal value.

Thus, according to Debye, the critical concentration proves to be the concentration of the maximum z_m which lies on the line connecting the spinodal maximum with the θ temperature on the ordinate axis (see Figure 3.35). In view of this circumstance, Vrij and van der Esker (1972) interpret Debye's construction like

$$CI_{\vartheta}^{-1} = A + B\sin^2\frac{\vartheta}{2} \tag{48}$$

in another way, using

$$\Lambda = (w_1 \varphi_0)^{-1} + (w_{2,w} \varphi_0)^{-1} - \frac{\Omega}{kT},$$
(49)

$$B = \frac{16\pi^2 R_z^2}{3\lambda^2} (w_{2,w}\varphi)^{-1},$$
(50)

where C is an instrumental constant.

The quantity ΔT is given the meaning of the difference between the temperature of experiment and that of the spinodal maximum

$$\Delta T = T - T_{m,sp}.\tag{51}$$

Then (cf. Equation 25),

$$s = \frac{B\Delta T}{A} = \frac{16\pi^2}{3\lambda^2} (1 + p_w^{1/2})^{-1} T_{m,sp} \bar{R}_{z,T_{m,sp}}^2 + \frac{16\pi^2}{3\lambda^2} (1 + p_w^{1/2})^{-1} \frac{d(T\bar{R}_z^2)}{dT} \Delta T.$$
(52)

At $\Delta T = 0$,

$$s_0 = \frac{8\pi^2 l^2}{3\lambda^2} T_{m,sp},$$
(53)

where

$$l^{2} = 2\overline{R_{z}^{2}} \frac{T}{T_{m,sp}} (1 + p_{w}^{1/2})^{-1}.$$
(54)

The slope of the plot $(s - s_0)/T$ yields the quantity

$$\frac{d(T\,\overline{R_z^2})}{dT} \tag{55}$$

which can unlikely be compared with experiment for the moment.

Vrij and van den Esker (1972) used the experimental data of Debye et al. (1960b, 1962b) and determined $\overline{R_z^2}$ at $T = T_{m,sp}$ (at the spinodal maximum) from Equation 54. It turned out that the value

$$(\overline{R_z^2}/M_w)^{1/2} = 3.12 \cdot 10^{-7} \,\mathrm{cm} \cdot \mathrm{mol}^{1/2} \cdot \mathrm{g}^{-1/2} = 3.12 \,\mathrm{nm} \cdot \mathrm{mol}^{1/2} \mathrm{g}^{-1/2}$$

is constant within $0.1 \cdot 10^6 \leq M_w \leq 3 \cdot 10^6$ and even somewhat more than at the θ point at $c \to 0$ (~ 2.8 nm $\cdot mol^{1/2} \cdot g^{-1/2}$) (Notley and Debye, 1955). In their calculations, Vrij and van den Esker accepted the critical concentrations reported by Debye as $\varphi_{m,sp}$. Replacing $(1 + p_w^{1/2})^{-1}$ by $\varphi_{m,sp}$ in Equation 54 according to Equation 45, they calculated $\overline{R_z^2}$ and, then, $(\overline{R_z^2}/M_w)^{1/2} \simeq 2.27 \text{ nm} \cdot mol^{1/2} \cdot g^{-1/2}$.

The disagreement between the values 3.12 and 2.27 points to the fact that Equation 45 is incorrect owing to the neglect of the concentration dependence of the interaction parameter. The chief result of Vrij (1974) is in the fact that near the spinodal maximum, macromolecules have the statistical coil conformation with sizes slightly different from those in the θ state at $c \rightarrow 0$ (at least, for the polystyrene+cyclohexane system). Generally, however, this may not be the case (Vrij and van den Esker, 1972).

With allowance for the concentration dependence of χ (Scholte, 1971) (see subsection 3.6.2), Vrij (1974) derives $(\overline{R_z^2}/M_w)^{1/2} = (2.27 \pm 0.1) \operatorname{nin} \cdot \operatorname{mol}^{1/2} \cdot \mathrm{g}^{-1/2}$ and explains the slightly overestimated value, as compared with the value at the θ temperature and $\mathbf{c} \to 0$, by polymolecularity of Debye's samples. The value $M_z/M_w \approx 1.5$ would eliminate this difference.

Vrij (1974) deduces his basic equation 35 in another way, using the correlation function formalism.

Tager et al. (1976a) have determined the sizes of polystyrene molecules in cyclohexane at the critical concentration near both the UCST ($T_c = 33^{\circ}$ C, $\mathbf{c}_c = 2.05$ g/dl) and LCST ($T_c = 215^{\circ}$ C, $\mathbf{c}_c = 4.3$ g/dl), from Debye's equation 26 ($(\overline{R_c^2})^{1/2} = 130$ Å at 34°C and ($\overline{R_c^2})^{1/2} = 110$ Å at 215°C) and from Vrij and van den Esker's equation (($\overline{R_c^2})^{1/2} = 430$ Å from Equation 35 and ($\overline{R_c^2})^{1/2} = 320$ Å from Equation 52 at 34°C). The R_c sizes estimated from Vrij and van den Esker's theory are close to the unperturbed ones at $\mathbf{c} \to 0$: ($\overline{R_g^2})^{1/2} = 460$ Å.

The correlation of concentration fluctuations in the P+LMWL system (increase in the long-range correlation distance ξ_k) near the phase separation region finds use in other methods for investigation of the structure of solutions, i.e. flow birefringence (Eskin and Magarik, 1960; Frisman and Mao Sui, 1961ab; Budtov, 1985a), viscosity of solutions (Frisman and Mao Sui, 1961ab; Debye et al., 1963; Tager et al., 1964a), scattered light depolarization (Skazka et al., 1960).

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The increase in the long-range correlation distance ξ_k significantly strengthens the effect of shape in birefringence while the segmental anisotropy of macromolecules remains constant up to polymer precipitation (Frisman and Mao Sui, 1961ab). The precritical correlations of the concentration fluctuations does not, however, affect Kerr's effect (electrical birefringence) in polymer solutions (Frisman and Mao Sui, 1961ab).

3.3.2. Brownian motion of macromolecules in solution. Inelastic (dynamic) light scattering

More rigorous consideration of light scattering phenomenon by colloidal or polymer solutions should account for the time effects due to the Brownian motion of their structural elements.

In Rayleigh-Debye's approximation (subsection 2.1.2), the density correlation function (the **dynamic form factor**) $S(\vec{q}, t) = \langle \rho(\vec{q}, t) \cdot \rho^*(\vec{q}, 0) \rangle$ (cf. Equations 2.3–38,-39) acts as form factor (Debye's function) (Equation 2.1-64).

Then.

$$R_{90,\perp}(\vec{q},t) = \frac{16\pi^4}{\lambda_0^4} \alpha_p^2 N_2 S(\vec{q},t)$$
(56)

(see Equation 2.3–30), which is also calculated for variously shaped particles (balls, pivots, Gaussian coils, etc.), in view of the dynamics of their motion. For colloidal particles (viruses, latices), with no account for internal interference,

$$S(\vec{q},t) = S(\vec{q},0)\exp(-Dq^2t)$$
(57)

(cf. Equations 2.3-48 and 2.4–51), and the corresponding energy spectrum of scattering (see Equations 2.3-26,-28)

$$S(\vec{q},\omega) = \pi^{-1} \left[\frac{Dq^2}{\omega^2 + (Dq^2)^2} \right]$$
(58)

(cf. Equation 2.4–52). The diffusion coefficient D defines the mean relaxation time of change in a particle's location,

$$\bar{\tau}_r = (Dq^2)^{-1} \tag{59}$$

(cf. Equations 2.3-23,-48, and 57) and the scattering bandwidth

$$\Delta\omega_q = Dq^2 \tag{60}$$

(cf. Equation 2.4–53). The slope of τ_r^{-1} or $\Delta \omega_q vs q^2 = 4k^2 \sin^2 \frac{\vartheta}{2} = \frac{16\pi^2}{\lambda^2} \sin^2 \frac{\vartheta}{2}$ gives the self-diffusion coefficient of colloidal particles owing to the Brownian motion. From this coefficient, the hydrodynamic radius of particles R_H is determined using Stokes-Einstein's equation 2.4-44

$$D = \frac{kT}{6\pi\eta_0 R_H},\tag{61}$$

where η_0 is the viscosity of the dispersion medium.

In the case of polymer solutions, a macromolecule is modelled (Kargin and Slonimski, 1948, 1949; Gotlib and Volkenstein, 1953; Prince and Rouse, 1953; Zimm, 1956) by (N+1) beads, with the isotropic polarizability α , connected to each other by N segments with the root-mean square length $\langle l^2 \rangle^{1/2}$ (like "springs" which realize the restoring force of entropy nature, which arises when the beads, during their Brownian motion, diverge from each other at a distance different from the statistically most probable one). The distribution of the distances between the beads is accepted Gaussian. Every bead hydrodynamically interacts with the solvent through the friction coefficient ζ and, besides, is subject to the Brownian motion of the solvent molecules.

Consideration of this problem (Kargin and Slonimski, 1948, 1949; Gotlib and Volkenstein, 1953; Prince and Rouse, 1953; Zimm, 1956; Askadski, 1973; Vinogradov and Malkin, 1977; de Gennes, 1979; Koenig, 1979) leads to a pattern of discrete kinds of macromolecular motion (relaxational modes) with a set of relaxational times

$$\tau_k = \frac{\langle l^2 \rangle N^2 \zeta}{3kT\pi^2 k^2},\tag{62}$$

with $k = 1, 2, \ldots, N$ defines each mode.

The first mode can be regarded as a pulsation when a coil alternately stretches and shrinks (de Gennes, 1968).

To calculate $S(\vec{q}, t)$ of a macromolecule, the microscopic density of segments at the point \vec{r} at the instant t is introduced (Gotlib et al., 1986)

$$\rho(\vec{r},t) = \sum_{k} \delta(\vec{r} - \vec{r}_{k}(t)),$$

where $\delta(x)$ is Dirac's δ function, $\vec{r}_k(t)$ is the radius vector of the kth segment at the instant t; summation is performed over all the N segments of the macromolecule.

The Fourier transform $\rho(\vec{r}, t)$ in the momentum space is

$$\rho(\vec{q},t) = \int d\vec{q} \exp(i\vec{q}\vec{r})\rho(\vec{r},t) = \sum_{k} \exp\left[i\vec{q}\vec{r}_{k}(t)\right].$$

Then, the Fourier transform of the density correlation function takes the form

$$S(\vec{q},t) = \langle \rho(\vec{q},t)\rho^{\bullet}(\vec{q},0) \rangle = \left\langle \sum_{j,k} \exp\left\{ i\vec{q} \left[\vec{r}_{j}(t) - \vec{r}_{k}(0) \right] \right\} \right\rangle$$

The angular parentheses '(...)' mean averaging over all the possible conformations of the macromolecule at the instant t and t = 0, i.e. double averaging.

The first averaging is performed with the distribution function

$$\psi\left[rac{ec{C}\left\{ec{r_k(t)}
ight\}}{ec{C}\left\{0
ight\}}
ight]$$
 ,

where $\vec{C}\{\vec{r}_k(t)\}$ is the 3N-dimensional vector describing the macromolecular conformation.

The function $\psi \left[\frac{\vec{C} \{\vec{r}_k(t)\}}{\vec{C} \{0\}} \right]$ is the conditional probability of the transition from the fixed initial conformation $\vec{C} \{0\}$ at t = 0 into the conformation $\vec{C} \{\vec{r}_k(t)\}$ for a period

t, and satisfies Kirkwood-Riseman's diffusional equation $\partial \psi / \partial t = D\psi$ with the initial condition

$$\left.\psi\right|_{t=0} = \delta\left[C - C\left\{0\right\}\right],$$

D being an operator of a special type.

The second averaging is performed over all the possible chain conformations at the initial instant t = 0: $\vec{C} \{\vec{r}_i(0)\}$ with the Gaussian chain model.

In the absence of external forces and hydrodynamic interactions among the beads (Berne and Pecora, 1876),

$$S(\vec{q},t) = \exp\left[-\frac{Dq^2t}{N^2} \sum_{i,j}^{N} \prod_{k=1}^{N} \exp\left\{-\frac{q^2 N^2 \overline{R^2}}{36\pi^2 k^2} \left[\mathcal{Q}_{jk}^2 + \mathcal{Q}_{ik}^2 - 2\mathcal{Q}_{ik} \mathcal{Q}_{jk} \exp\left(-\frac{t}{\tau_k}\right)\right]\right\}\right], \quad (63)$$

where

$$\mathcal{Q}_{ik} = \left(\frac{2}{N}\right)^{1/2} \begin{cases} \cos \pi k \left(i/N - 1/2\right) & \text{for even } k\\ \sin \pi k \left(i/N - 1/2\right) & \text{for odd } k \end{cases},$$

 $\overline{\mathbb{R}^2}$ is the mean square radius of gyration of the macromolecule.

This expression has been derived for so-called long slow wavelength modes with $k \ll N$. On expansion of the exponent in Equation 63 into a series and calculation of the coefficients (Berne and Pecora, 1976), we get

$$S(\vec{q},t) = S_0(u) \exp(-Dq^2 t) + S_2(u) \exp\left[-\left(Dq^2 + \frac{2}{\tau_1}\right)t\right] + \cdots,$$
(64)

where

1

$$u = q^2 \overline{R^2} \tag{65}$$

and

$$S_0(u) = \frac{\pi}{u} \exp\left(-\frac{u}{6}\right) \left[\operatorname{erf} \frac{\sqrt{u}}{2}\right]^2,\tag{66}$$

 $\operatorname{erf} y$ is the error function of y:

$$\operatorname{erf} y = \frac{1}{\sqrt{\pi}} \int_{0}^{y} \exp(-z^{2}) \, dz.$$

The coefficient $S_0(u)$ determines the contribution to a spectrum depending on the translational diffusion coefficient of the coil as a whole only. The coefficient $S_2(u)$ determines the first, most significant summand depending on the intramolecular motion with the mode relaxational time with $k_0 = 1$; S_1 is absent in Equation 6I as $S_1 \ll S_0$, and $S_1 \ll S_2$. Substitution of t = 0 into Equation 64 leads to Debye's function $P(\vartheta, \overline{R^2})$ for Gaussian coils:

$$S(u) = S_0(u) + S_2(u) + \dots = \frac{2}{u^2}(e^{-u} - 1 + u) = P(\vartheta, \overline{R^2})$$



Figure 3.39. Relative integral intensity of light scattered by Gaussian coils as a function of $\sqrt{u} = qR$, S is the total integral intensity, S_0 is the component due to the coil as a whole, S_2 is the first largest component due to internal relaxational time, $S_h = S - (S_0 + S_2)$ (Berne and Pecora, 1976) [B.J.Berne, R.Pecora Dynamic Light Scattering with Application to Chemistry, Biology, and Physics. Copyright © 1976 by Wiley. Reprinted by permission of John Wiley & Sons, Inc.]

Figure 3.39 contains S(u), $S_0(u)$, $S_2(u)$, and $S_h = S - S_0 - S_2$ plotted against u. The quantities $S_i(u)$ are the components of the integral scattering intensity. For small u's, $S \approx S_0$, and the time correlation function is defined by the translational diffusion coefficient only. When $u \ge 3$, the effect of time decay in the fluctuations is substantially dependent on the intramolecular relaxation time.

Thus, at low molecular masses and $q \to 0$ (see Equation 65), the scattering spectrum of polymer solutions is a simple Lorentzian. As molecular mass increases, the intramolecular motion complicates the spectrum. $S(\vec{q}, \omega)$ turns out to be the sum of several Lorentzians.

Dynamic scattering occurs due to the relaxation of the concentration fluctuations of polymer segments with the scale commensurable with q^{-1} (see subsection 2.1.2). So, the relative contribution of the diffusion mobility of the macromolecules and their internal modes of motion depends on the wave vector q.

In this connection, three different modes of dynamic scattering by solutions of macromolecules, for which $R \ll q^{-1}$ and $R \gg q^{-1}, R \approx q^{-1}$, are spoken of.

In the mode

$$Rq \ll 1,$$
 (67)

a macromolecule behaves as a particle with no internal modes of motion: Equations 57 and 58 hold good for the correlation function $S(\vec{q}, t)$ and scattering spectrum $S(\vec{q}, \omega)$.

As q and R increase, the internal modes of motion of a macromolecular coil gain in more and more importance: at

 $Rq \approx 1$ (68)

the diffusional mode is commensurable with the longest wavelength mode with the relaxation time τ_1 (see Equation 64). In the mode

$$Rq \gg 1,$$
 (69)

the subsequent modes of internal mobility get involved according to Equation 63.

See section 4.5 for more information on the influence of bulk effects and hydrodynamic interactions on the mobility modes of macromolecules within the framework of scaling constructions.

To analyze the complex form of experimental $S(\vec{q}, t)$ (the superposition of exponential functions 57) and $S(\vec{q}, \omega)$ (the superposition of Lorentzians 58), special procedures using the **normalized functions of time correlation** have been developed (Jamieson and McDonnell, 1979).

If $|\mathbf{I}_1(0)|^2$ is taken out of the parentheses in the right-hand side of Equation 2.3–35, we get (see Equation 2.3–32)

$$|\mathbf{I}_{2}(0)| = |\mathbf{I}_{1}(0)|^{2} \left(1 + \frac{|\mathbf{I}_{1}(t)|^{2}}{|\mathbf{I}_{1}(0)|^{2}}\right) = |\mathbf{I}_{1}(0)|^{2} \left(1 + |g_{1}(t)|^{2}\right),$$
(70)

where

$$g_1(t) = \frac{\langle E_s^{\scriptscriptstyle \circ}(0)E_s(t)\rangle}{\langle E_s^{\scriptscriptstyle \circ}(0)E_s(0)\rangle} = \frac{S(\vec{q},t)}{S(\vec{q},0)}$$
(71)

is the normalized time correlation function of the electric field of a scattered wave. In view of Equations 2.3-30, 37, 2.4-56, -50, and 57,

$$g_1(t) = \exp(-\Gamma t) = \exp(-Dq^2 t). \tag{72}$$

Including the details of the measuring technique, we finally obtain

$$\mathbf{I}_{2}(q,t) = A\left(1+b|g_{1}(q,t)|^{2}\right),\tag{73}$$

where A is the background photocurrent of a photoelectrical multiplier, b is the spatial coherence factor allowing for the violation of scattered light coherence due to the finite volume of the scattering space (usually $b \approx 1$).

Taking the logarithm of Equation 73, with due account of Equation 72, we derive

$$\ln \left[\mathbf{I}_2(q,t) - A \right] = \ln Ab + 2\ln |g_1(q,t)| = \ln Ab - 2Dq^2t, \tag{74}$$

whence it follows that the plot

$$\ln \left[\mathbf{I}_2(q,t) - A \right]$$
 vs t

is a line with its slope $2Dq^2$ given the polymer is strictly monomolecular.

For an actual polymer system, the expression for $g_1(t)$ (cf. Equation 72) must be written as

$$|g_1(t)| = \int_0^\infty G(\Gamma) e^{-\Gamma t} \, d\Gamma \tag{75}$$

with the normalization

$$\int_{0}^{\infty} G(\Gamma) \, d\Gamma = 1. \tag{76}$$

Here $G(\Gamma)$ is the distribution function to characterize the fall rate of structural reorganizations' fluctuations. Generally, the Laplace inverse transformation (Equation 75) is required to determine $G(\Gamma)$, but the function $|g_1(t)|$ is suitable for this operation if only determined with a high accuracy, not achievable even by the up-to-date methods. Several versions of how to extract information on the properties of the macromolecules from an experimentally measured (see Equation 73) normalization function $g_1(t)$ have been proposed.

In the cumulant method (Koppel, 1972; Pusey, 1974), the function $\ln g_1(t)$ is expanded into its Maclaurin series in powers of t at $t \to 0$ and is written as

$$\ln|g_1(t)| = \sum_{m=1}^{\infty} \mathcal{K}_m(\Gamma) \frac{(-t)^m}{m!},$$
(77)

where $\mathcal{K}_m(\Gamma)$ are the **cumulants** (semiinversions) of order *m* of the vector $\Gamma = (\Gamma_1, \Gamma_2, \ldots, \Gamma_m)$ (Shiryaev, 1984). Such a cumulant characterizes random variables related to the high-order moment.

To get the explicit form of the first-order cumulant, the function $e^{-\Gamma t}$ is written as

$$e^{-\Gamma t} = e^{-\Gamma t} \cdot e^{-(\Gamma - \Gamma)t},\tag{78}$$

where $\bar{\Gamma} = \int_{0}^{\infty} G(\Gamma) \Gamma d\Gamma$ is the first-order **moment** of the vector Γ . Then, it is substituted to Equation 75 and taken the logarithm of:

$$|g_1(t)| = e^{-\tilde{\Gamma}t} \int_0^\infty G(\Gamma) e^{-(\Gamma-\tilde{\Gamma})t} \, d\Gamma,\tag{79}$$

$$\ln|g_1(t)| = -\ddot{\Gamma}t + \ln\int_0^\infty G(\Gamma)e^{-(\Gamma-\Gamma)t}\,d\Gamma.$$
(80)

Expanding this logarithm into a Maclaurin series, we obtain

$$\ln|g_1(t)| = -\Gamma t + \frac{\mu_2}{2!\bar{\Gamma}^2}(\bar{\Gamma}t)^2 - \frac{\mu_3}{3!\bar{\Gamma}^3}(\bar{\Gamma}t)^3 + \frac{(\mu_4 - 3\mu_2^2)}{4!\bar{\Gamma}^4}(\bar{\Gamma}t)^4 + \cdots,$$
(81)

where μ_m are the central moments of the distribution $G(\Gamma)$

$$\mu_m = \int_0^\infty (\Gamma - \bar{\Gamma})^m G(\Gamma) \, d\Gamma. \tag{82}$$

It follows from comparison between Equation 77 and 81 that the cumulants of the first three orders coincide with the central moments, and

$$\mathcal{K}_4 = \mu_4 - 3\mu_2^2, \tag{83}$$

etc.

The first cumulant

$$\mathcal{K}_1 = \bar{\Gamma} = \int_0^\infty \Gamma G(\Gamma) \, d\Gamma \tag{84}$$

defines the average weight diffusion coefficient (in the mode $qR \ll 1$):

$$D = \frac{\Gamma}{q^2} = \frac{\mathcal{K}_1}{q^2}.$$
(85)

The function $G(\Gamma)$ in experiment corresponds to the scattered light intensity (cf. Equations 56, 57, 72, and 75) which, in turn, is proportional to $c_i M_i$ (for the *i*th fraction). Therefore, in the discrete description, Equation 84 can be written as

$$\bar{\Gamma} = \frac{\sum_{i} \Gamma_{i} c_{i} M_{i}}{\sum_{i} c_{i} M_{i}}$$
(86)

and

$$\bar{D}_z = \frac{\sum_i D_i c_i M_i}{\sum_i c_i M_i}$$

is the z-average diffusion coefficient cf. the z-average molecular weight

$$ilde{M}_z = rac{\displaystyle \sum_i c_i M_i^2}{\displaystyle \sum_i c_i M_i}.$$

Experimentally, the first cumulant is determined as the slope of $\ln g_1(t)$ at $t \to 0$ (see Equation 81), i.e.

$$\mathcal{K}_1 = -\left(\frac{d\ln|g_1(t)|}{dt}\right)_{t\to 0}.$$
(87)

The second cumulant \mathcal{K}_2 characterizes the width of distribution (dispersion) $G(\Gamma)$, the third \mathcal{K}_3 and fourth \mathcal{K}_4 ones are responsible for the asymmetry of $G(\Gamma)$ distribution.

With the help of an equation of Mark-Kuhn-Howink's type

$$M=K_D D^{-b},$$

the function $G(\Gamma)$ is converted into the MWD differential function.

The same procedure can be applied to the cumulants or moments $G(\Gamma)$. With Stokes-Einstein's formula, the z-average hydrodynamic radius of the macromolecules is determined from the z-average diffusion coefficient

$$D_z = \frac{kT}{6\pi\eta_0} \left\langle \frac{1}{R_H} \right\rangle_z \tag{88}$$

(cf. Equation 61).

For many kinds of distribution $G(\Gamma)$, the terms of the series (Equation 81) rapidly diminish with an increase in their order, and $\ln g_1(t)$ can be approximated by the first two-four terms.

The complexity (and disadvantage) of such processing of the experimental data is that the order of the polynomial is unknown beforehand while the modern equipment of dynamic scattering is not capable of determining cumulants above the third order with sufficient accuracy.

In the diagrammatic method of approximation (Gulari et al., 1979), $|g_1(t)|$ is represented as

$$|g_1(i\Delta t)| = \sum_{j=1}^{\mathcal{M}} G(\Gamma_j) \int_{\Gamma_j - \Delta\Gamma/2}^{\Gamma_j + \Delta\Gamma/2} \exp\left[-\Gamma(i\Delta t)\right] d\Gamma$$
(89)

with the normalization

$$\sum_{j=1}^{\mathcal{M}} G(\Gamma_j) \Delta \Gamma = 1,$$

where \mathcal{M} is the number of histogram bars, $\Delta l' = (\Gamma_{\max} - \Gamma_{\min})/\mathcal{M}$ is the width of each step, Γ_{\max} and Γ_{\min} are the upper and lower limits of the region where Γ varies, $\Gamma_j = \Gamma_{\min} + (j - 1/2)\Delta\Gamma$, Δt is the delay time, *i* is the channel number of the correlator (see subsection 2.3.3). The output signal takes the form (see Equation 73)

$$\mathbf{I}_2(i\Delta t) \cong \tag{90}$$

$$\cong A + Ab\left(\sum_{j=1}^{\mathcal{M}} a_j\left(-\frac{1}{i\Delta t}\right)\left\{\exp\left[-\left(\Gamma_j + \frac{\Delta\Gamma}{2}\right)i\Delta t\right] - \exp\left[-\left(\Gamma_j - \frac{\Delta\Gamma}{2}\right)i\Delta t\right]\right\}\right)^2,$$

where $a_j = G(\Gamma_j)$. Then, the least squares method minimizes χ^2 with respect to each a_j

$$\frac{\partial}{\partial a_j}\chi^2 = \frac{\partial}{\partial a_j}\sum \left(\frac{1}{\sigma_i^2}\left[\mathbf{I}_{2m}(i\Delta t) - \mathbf{I}_2(i\Delta t)\right]^2\right) = 0,\tag{91}$$

where σ_i is the experimental error of $I_2(i\Delta t)$, I_{2m} and I_2 are the calculated (adjusted) and experimental values, respectively. The values $a_j = G(\Gamma_j)$; Γ_{\max} , Γ_{\min} , and \mathcal{M} are corrected on every cycle until I_{2m} differs from I_2 by a minimal quantity within the calculation accuracy.

The **regularization** methods (Provencher et al., 1978; Braginskaya and Klyubin, 1986; Chu, 1985) are more rigorous and based on the general regularization principles of solving reverse ill-posed problems, elaborated by Tikhonov (see, eg., Tikhonov, 1973; Tikhonov and Arsenin, 1974). Equation 75 is Fredholm's first-kind integral equation typical for the reverse problems of experimental methods for investigation of the structure of a substance:

$$y(t) = \int_{a}^{b} Z(\Gamma) K(\Gamma, t) \, d\Gamma$$
(92)

with the core $K(\Gamma, t) = e^{-\Gamma t}$ and the desired function $Z(\Gamma)$. Determination of $Z(\Gamma)$ by the standard method (the Laplace reverse transformation of Equation 92) is impossible because of the fact that the necessary experimental accuracy in measuring y(t) is unattainable.

In the regularization methods, Equation 92 is replaced by a system of linear algebraic equations

$$\sum_{k=1}^{N} a_{ik} Z(\Gamma_k) = y(t_i), \quad i = 1, 2, \dots, \mathcal{M},$$
(93)

where \mathcal{M} is the number of the correlator's channels, $a_{ik} = \exp(-\Gamma_k t_i)$. Or, in operator form,

$$AZ = y.$$

The only solution of Equation 94 in the classical sense

$$Z = A^{-1}y \tag{95}$$

does not exist as the determinant of the system 93 rapidly diminishes with the matrix A dimension $(A^{-1} \to \infty)$ when the components of the vector $y: (y_1, y_2, \ldots, y_M)$ are defined with a finite degree of accuracy. An approximate solution of system 95 only can be spoken of.

The regularization method consists in finding an approximate solution of system 95 stable to small variations in the components y_1, y_2, \ldots, y_M . As a rule, additional information on the system and special numerical methods are used to this end.

Experiments (Kramer and Frederick, 1972; Huang and Frederick, 1974) on polystyrene solutions within $8.7 \cdot 10^3 < M < 5 \cdot 10^7$ in the θ solvent confirm, in general, the main conclusion of the theory (Berne and Pecora, 1976). Indeed, during simple data processing, when the spectrum shape is assumed to be Lorentzian, for polymer solutions (including proteins) with a moderately high molecular mass to satisfy $qK \ll 1$, a good agreement between D calculated from $\Delta \omega_q$ (Equation 60) and the results of independent experiments has been achieved (Dubin et al., 1967; Cummins and Pike; 1974; Skazka, 1975; Marshall, 1978).

In the systems polystyrene+cyclohexane (Geissler and Hecht, 1976), polystyrene+nbutylacetate (Hecht and Geissler, 1977), PDMS (M = 130,000)+toluene (Patterson, 1981), PIB (M = 35,000)+cyclohexane (Patterson, 1981), an extremum-containing (with a maximum) dependence $D_z(c)$ has been obtained, as with the traditional method of measuring D in polymer solutions in a good solvent (Rehage et al., 1970) (see Figure 3.33).

In agreement with (Rehage et al., 1970) as well (see Figure 3.34), in (Lempert and Wang, 1980, 1981) a minimum on the dependence $D_z = D_z(c)$ at $c_* = 22\%$ was found in polystyrene solutions ($M_w = 20,000, M_w/M_n = 1.8$) in cyclohexane within $0...50^{\circ}$ C by dynamic light scattering. At the same concentration c_* , the scattered light intensity is maximal (cf. Figures 2.36 and 2.37).

In a number of papers (eg. Jamieson et al., 1980; Burchard and Eisele, 1984; Chu, 1985), measurements of $g_1(t)$ in a wide concentration range show two diffusional modes (Figures 3.40 and 3.41). Special analysis proves that these modes are of a diffusional character which do not associate with intramolecular relaxation of the macromolecules.

The diffusion coefficient (curve 3, Figure 3.41) is calculated from the first cumulant \mathcal{K}_1 (Equations 84, 85, 87) at $q \to 0$ (to exclude the contribution of the internal motion modes) and corresponds to the interdiffusion coefficient which follows from the relationships of

(94)



Figure 3.40. Dynamic light scattering by aqueous solutions of polyvinylpyrrolidone with relative concentrations $\mathbf{c/c^*}$ of 0.1 (1), 0.9 (2), 3 (3), 4.5 (4), 5.9 (5), where $\mathbf{c^*}$ is the coil overlap concentration, $\mathbf{c^*} = 1/[\eta] =$ 0.00716 g/cm³. $M_w = 560,000, \vartheta = 90^\circ$ (Burchard and Eisele, 1984) [Reprinted with permission from: W.Burchard, M.Eisele. Pure and Appl. Chem. 56 (1984) 1379-1390. Copyright © 1984 by the American Chemical Society]

Figure 3.41. Concentration dependence of the diffusion coefficient D_z normalized by $D_2^{\circ} = D_z$ at $\mathbf{c} \to 0$ for polyvinylpyrrolidone in aqueous solutions from Figure 3.40's data. Fast (1) and slow (2) modes. Curve 3 is the interdiffusion coefficient from the first cumulant \mathcal{K}_1 at $q \to 0$ (Burchard and Eisele, 1984) [Reprinted with permission from: W.Burchard, M.Eisele. Pure and Appl. Chem. 56 (1984) 1379-1390. Copyright © 1984 by the American Chemical Society]

nonequilibrium thermodynamics (Equations 2.4-41 and 14) (cf. Figure 3.33). This coefficient is also called the **cooperative** diffusion coefficient. At low concentrations, it coincides with the self-diffusion coefficient of the fast mode's macromolecules $D_{x,f}$.

The mechanism of the slow mode is currently the subject of discussion. According to one version, the slow mode diffusion coefficient $D_{z,s}$ (Figure 3.41, curve 2) corresponds to reptation motion of an individual macromolecule between entanglements, which form a certain pipe inside which the macromolecule creeps (de Gennes, 1968, 1971, 1976a, 1979). The number of entanglements increases with concentration, which reduces the reptation mobility of macromolecules (for details see subsection 4.1.3). According to another version, the slow mode is due to some clusters of macromolecules (Burchard and Eisele, 1984; Chu, 1985), whose mechanism of formation still remain enigmatic.

In other papers (Chu and Nose, 1979) the diffusion between the two diffusional modes seems not so significant, and the coil overlap concentration \mathbf{c}_{\bullet} serves as the concentration threshold of their manifestation (Adam and Delsanti, 1977). When $\mathbf{c} < \mathbf{c}_{\bullet}$, the macromolecules behave as independent particles, and the characteristic size of the heterogeneous area is $L \sim R_H$ (the slow mode, Chu and Nose, 1979). When $\mathbf{c} > \mathbf{c}_{\bullet}$, $L \sim \xi$, where ξ is the distance between entanglements in polymer chains (the fast mode).

According to de Gennes (1979), a blob, rather than a macromolecule, is the independent dynamic structural element in semidilute solutions, so the interdiffusion coefficient D_z coincides with the blob self-diffusion coefficient D_{bl} .

If a blob is considered as an non-draining (impermeable) coil of the radius ξ , where ξ is the screening length of the excluded volume (subsection 3.1.1) and hydrodynamic (!) interactions among segments, then

$$D_z \sim D_{bl} = \frac{kT}{6\pi\eta_0\xi(\mathbf{c})}.$$
(96)

The dependence $\xi(\mathbf{c})$ is found from scaling constructions, whence follows the character of the concentration dependence of the diffusion coefficient (see section 4.5).

The properties of crosslinked gels are considered in detail in section 3.5. Here we note the analogy of the dynamic properties of concentration fluctuations in semidilute and concentrated solutions with the screening length ξ and in polymer networks with the same distance ξ between entanglements.

From the equation for polymer network motion to broaden concentration fluctuations of the longitudinal mode with the vector \vec{q} (Candau et al., 1982), one obtain

$$u_q(t) = \exp\left(-\frac{M}{\mathbf{c}f}q^2t\right),\tag{97}$$

where M is the longitudinal modulus, \overline{f} is the friction coefficient of a monomeric unit. c is the density of monomeric units (see section 3.5 for details).

Comparison of Equations 97 and 57 shows that

$$\frac{M}{f} = \frac{M}{cf} = D,$$
(98)

and M/f = M/cf can be regarded as the interdiffusion coefficient in a polymer gel. Further analysis (Candau et al., 1982) leads to the relationship

$$D \simeq \frac{kT}{6\pi\eta_0\xi},\tag{99}$$

where ξ is the distance between entanglements in a gel, which is in full accordance with Equation 96 (see section 4.5, Equation 4.5-22 for detail).

Unlike a crosslinked gel, in semidilute and concentrated solutions, entanglements with the distance ξ arise for a certain characteristic period, which were denoted by de Gennes (1971) as T_r . Then, provided that

$$\Gamma = Dq^2 > T_r^{-1},\tag{100}$$

the solution must exhibit the dynamic properties of a gel, which is what was proved experimentally (Geissler and Hecht, 1976; Hecht and Geissler, 1977).

Tanaka et al. (1973), Munch et al. (1976) have shown that in crosslinked gels, the dynamic scattering spectrum has the Lorentzian form with the relaxation time

$$\tau_r = \Gamma^{-1} = (Dq^2)^{-1},\tag{101}$$

where D obeys Equation 98.

In solutions of epoxy resin based on *bis*-phenol A and glycerol (M = 6,500) in ethylenglycol acetate and in the gel obtained from these compounds by crosslinking by polypropyleneglycol with amino endgroups, the concentration dependence D(c) remains the same up to c = 65% (Patterson, 1981).

Now let us consider some results from experiments on dynamic light scattering, related to the internal mode relaxation of the macromolecular motion.

Within $0 \le qR \le 3$, the two exponents in Equation 64 provide a 96% contribution to the spectrum magnitude $S(q,\omega)$.

Tsunashita et al. (1983a) studied dynamic light scattering by polystyrene solutions in trans-decaline at 25°C for scattering angles ϑ from 10 to 150°C, i.e. within 0.24 $< qR_q < 2.70$, $M_w = 5.5 \cdot 10^6$, $R_g^2 = 5.5 \cdot 10^{-11}$ cm².

The histogram method led to a bimodal character of $g_1(t) \sim S(q, t)$ (Equation 71) at $\vartheta > 30^{\circ}$ C, which can be attributed to the combination with the diffusional mode width $D_z = \overline{\Gamma}_1/q^2$ and the relaxation process $\overline{\Gamma}_z = D_z q^2 + 2/\tau_1$ according to Equation 64.

Such an interpretation is confirmed by the independence of $\overline{\Gamma}_1/q^2$ on q^2 (Figure 3.42, line 1), which enables the purely diffusional mode to be distinguished from the internal



Figure 3.42. Diffusional mode $\Gamma_1 / \sin^2 \vartheta / 2$ (1) and intramolecular relaxation $(\bar{\Gamma}_2 - \bar{\Gamma}_1) = 2/\tau_1$ (2) as functions of $\sin^2 \vartheta / 2$. Polystyrene solution in *trans*-decaline, $T = 25^{\circ}$ C, $c = 2.15 \cdot 10^{-4}$ g/cm² (Tsunashima et al., 1983a)[Reprinted with permission from Macro-molecules 16 (1983) 584-589. Copyright © 1983 American Chemical Society]

motion relaxation of a macromolecule. The difference $\bar{\Gamma}_2 - \bar{\Gamma}_1 = 2/\tau_1$ (Figure 3.42, curve 2) does not depend on ϑ at small ϑ , but when $\vartheta > 90^{\circ}$ C ($q^2 R_g^2 > 5$), it sharply rises, which suggests an increase in the contribution of the subsequent modes of internal mobility. By extrapolation $c \to 0$, values $D_z^{\circ} = 1.84 \cdot 10^{-8} \text{ cm}^2/\text{s}$ and $\tau_1 = 0.908 \cdot 10^{-3} \text{ s}$ were obtained. The experimental value of τ_1 is compared with the theoretical one (Tsunashima et al.,

1983a; Gotlib et al., 1986)

$$\tau_1 = \frac{M[\eta]\eta_0}{BRT},\tag{102}$$

where B is a constant, different for different models of chain motion: B = 0.822 for Rause's free-draining chain, B = 1.184 for a chain with the preliminary averaged Ozeen tensor corresponding to the hydrodynamic interaction among the chain segments, B = 0.574 for a chain, whose hydrodynamic interaction is considered by Ozeen's tensor. Tsunashima et al. (1983a) reported $B = 1.06\pm0.03$, which is in good agreement with the value B = 1.184.

In the mode $Rq \approx 1$, the first cumulant is

$$\mathcal{K}_1 = D_z q^2 (1 + C \bar{R}_g q^2 + \cdots).$$
(103)

The quantity C depends on the topology, rigidity of a molecular chain, and polydispersity, and is a weak function of the solvent quality and the method of allowing for the hydrodynamic interaction.

Analysis of the dependence of C on the details of molecular structure still attracts research attention (Schmidt and Stockmayer, 1984; Stockmayer and Hammouda, 1984).

In the mode $Rq \gg 1$ and $l_q \ll 1$, for the first cumulant

$$\mathcal{K}_1 = b \frac{kT}{\eta_0} q^3 \tag{104}$$

holds, where b depends on the method of allowing for the hydrodynamic interaction in a molecular chain. Eg. the complete calculation of Ozeen's tensor leads to b = 1/16 while in the case of its preliminary averaging, $b = 1/6\pi$. Experimental data show a better fit to the more rough model with preliminary averaging, as in the case of relaxation time τ_1 (Equation 102). Different considerations exist on this subject (Stockmayer and Hammouda, 1984; Gotlib et al., 1986), and the question is still under study (Han and Akcasu, 1981; Tsunashima et al., 1983b; Balabanov et al., 1987).

Inelastic light scattering was applied to study the behaviour of D and other characteristic functions near the spinodal (White et al., 1966; Chu, 1967, 1969, 1970; Lao and Chu, 1975; Chu et al., 1980).

The dynamic properties of macromolecules in the critical opalescence region have been found to share common properties with the binary systems of LMW compounds (Chu et al., 1980).

The restriction of the hydrodynamic approximation in inelastic scattering near the spinodal was spoken of the final remarks to subsection 2.4.4.

It should be specially emphasized that studying dynamic light scattering near the spinodal in one-component liquids and solutions is a rather difficult problem, both theoretically and experimentally; now these problems are being investigated (Swinney, 1974). True, the method of dynamic scattering is not simple in the non-critical region as well, and specifies strict requirements to data processing and comparison with the corresponding theoretical approaches. The body of data concerning of the P+LMWL system from dynamic light scattering is rapidly growing. The report on dynamic scattering by polymers, colloids, and gels (Štėpanek and Koňàk, 1984) contains 502 references to papers published before summer 1983. This stream of investigations must lead to substantially new information on the macromolecular properties in the P+LMWL system.

3.4. Random coil—globule transition

The main properties of a macromolecule in solution are reflected in the model introducing a chain of N Kuhn's segments of length A each. As a result of Brownian motion, segments, far along the chain, may come close with their interaction to be described by a pair potential like that shown in Figures 1.40 or 2.34b. This kind of interaction is often called an **excluded volume** or **long-range** interaction. The quantity A characterizes the hindered rotation of monomeric units around valent bonds (**short-range** interactions) and, therefore, defines the degree of **rigidity** of a molecular chain.

The pair interaction potential models the interaction among the molecules in any substance and is a superposition of van der Waals' (intermolecular) forces of repulsion and attraction of different nature, namely, dipole, inductive, and disperse ones.

The potential like that shown in Figures 1.40 and 2.34b is a premise for the firstkind phase transition to occur in substance (condensation-evaporation, crystallizationmelting).

The peculiarity of a macromolecule as a system containing a huge number of elements N (with a rather adequate extrapolation $N \rightarrow \infty$) is in the structural elements being connected to a chain, which leads to characteristic features of the subsystem (and the system as a whole) but cannot suppress the basic properties due to the attraction and repulsion forces.

For the macromolecule's segments in LMWL medium, the interaction potential property changes (renormalizes) to consider the influence of LMWL molecules.

It follows from the aforesaid that, when $T > \theta$ (for definiteness, take systems with an UCST), the repulsion forces between chain-distant segments predominate over the attraction ones.

For a system of a huge number of LMW component (disconnected segments), such a situation means the existence of vapour with a lower density in comparison with the liquid density.

In the case of linked segments, the coil conformation with a low ($\sim 1\%$) segment density (concentration) in the coil is realized under these conditions.

Extension of this analogy to the temperature range $T < \theta$ leads to a conclusion of inevitable "condensation" of the linked segments to form a "drop" (globule) with its segment density exceeding that in a coil up to the density of the condensed polymer.

When the total concentration of polymer substance in the system is small, the predominance of the attraction forces may cause globulization of a coil (the coil-globule transition), i.e. to the existence of a dispersion of molecular globules (a "molecular latex").

A globule is the state of a polymer macromolecule which has a certain thermodynamically probable space structure, i.e. where density fluctuations are small in comparison with the density itself, and their correlation radius is much less than the size of the whole macromolecule. On the contrary, a coil is the state of a macromolecule with no certain spatial structure. In this state, density fluctuations and density are of the same order of magnitude, and their correlation radius and the macromolecular size are also of the same order of magnitude (Lifshitz et al., 1979) The definition of these two conformations (as two states of the subsystem) through density fluctuations leads to very important consequences to be applied to a development of adequate theoretical approaches (Lifshitz, 1968; Lifshitz et al., 1979). Eg. in the coil range, density (concentration) fluctuations of the segments are of importance for the state of the subsystem (and the system), which is similar to the state of a substance near continuous phase transitions. It is significant that this analogy is realized for macromolecules in a **good** solvent, i.e. **far** from the critical state of the P+LMWL system. In view of this circumstance, development of theories for the P+LMWL systems in a given area of the state diagram is characterized by applying a wide set of ideas and methods of the phase transition theories in systems of different classes (see Chapters 4 and 5). On the other hand, the methods of the mean (self-consistent) field theories are quite effective to describe the globular state.

Stockmayer (1960) was the first to draw attention to the possibility for a coil to globulize, with reference to Langmuir who predicted swinging of hydrocarbon chains in rarefied gas into a densely globule due to the intramolecular attraction forces.

Moreover, Stockmayer has established that Flory's equation 3.1-115

$$\alpha^5 - \alpha^3 = Cz \tag{1}$$

has no real roots at $z < z^* \approx -0.14$ while there are two roots at $z > z^*$, of which the biggest and the smallest correspond to the conformation of a coil and to a substantially shrunk coil (a globule), respectively.

Quantitatively, this problem was approached by Ptitsyn and Eizner (1965), on the basis of virial expansion, and by Eizner (1969), in the mean field approximation with Flory's theory. During motion of the configuration point, the change in the free energy of a coil is

$$\frac{\Delta F}{kT} = \frac{\Delta F_m}{kT} + \frac{\Delta F_{el}}{kT} = \frac{gD}{\alpha^3} + \frac{3}{2}(\alpha^2 - 1) - \ln\alpha^3,$$
(2)

where ΔF is the difference between the free energies at the end and the beginning of the configuration point trajectory, g is a parameter of the chain model (g = 1 for a cloud of segments whose density diminishes from the centre according to the Gaussian distribution, $g \simeq 0.95$ for a sphere uniformly filled with segments),

$$D = \left(\frac{9}{2\pi}\right)^{3/2} \frac{\bar{V}_{2M}}{\bar{V}_1 A^3} \left(\frac{1}{2} - \chi_1\right) N^{1/2},\tag{3}$$

where \tilde{V}_{2M} , V_1 are the partial molar volumes of a monomeric unit and of a LMWL molecule (Figure 3.43). The extremal values of α are found from the condition $\frac{\partial}{\partial \alpha} \frac{\Delta F}{kT} = 0$, that yields Flory's equation in the form

$$\alpha^5 - \alpha^3 = gD. \tag{4}$$

At the θ point (D = 0), this equation has the only root $\alpha = 1$ (Figure 3.43, curve 1). When $T > \theta$ (D > 0), the summand gD/α^3 shifts the minimum to the right (Figure 3.43, curve 2). Within -0.186 < gD < 0, Equation 4 has two roots, with the biggest one corresponding to the minimum of ΔF and the smallest to the maximum of ΔF (Figure 3.43,


Figure 3.43. Dependence of $\Delta F/kT$ (Equation 3.4-2) on α according to Flory-Eizner's theory for gD = 0 (1), 0.4 (2), -0.05 (3), -0.3 (4) (Eizner, 1969)

curve 3). Curve 3 shows the existence of the metastable state of a coil (at α close to 1) and its stable state (at $\alpha \to 0$) responding to the ultimately shrunk coil. When gD < -0.186, the metastable state is absent (Figure 3.43, curve 4). Tending of $\Delta F \to -\infty$ at $\alpha \to 0$ reflects neglect of the volume of segments. On introduction of a finite volume of segments (Eizner, 1969), the character of the curve $\Delta F/kT$ (the existence of two minima, Figure 3.44) shows that the coil-globule transition is that of the first order (cf. section 1.5, Figure 1.17). This transition is more expressed for less flexible chains.

As the concentration rises, the boundaries of the transition temperature range slightly shift towards the poor and good solvent for flexible and rigid chains (with a large segment A), respectively (Eizner, 1972).

At the next step, de Gennes (1975) and Sanchez (1979) have considered ternary interactions in the state equation of a molecular chain and derived an equation (Sanchez, 1979; Chu et al., 1987)

$$\alpha^{5} - \alpha^{3} - \frac{\mathbf{w}}{\alpha^{3} A^{6}} = \frac{3}{2} \frac{\mathbf{v} N^{1/2}}{A^{3}},\tag{5}$$



Figure 3.44. Dependence of $\Delta F/kT$ on α with regard for the volume of segments. $N(\bar{V})_{2M}/V_1 =$ 10^3 , $(V_{2M}/V_1)^{1/2}(\bar{V}_{2M}/A^3) = 0.0614$, $\alpha_{\min} =$ 0.178, $(3/4\pi)(18/5)^{3/2}(V_{2M}^2/\bar{V}_1b)(1/2 - \chi_1)\sqrt{N} =$ -0.1 (1), -0.15 (2), -0.2 (3) (Eizner, 1969)

where \mathbf{v} and \mathbf{w} are the second and third virial coefficients (the binary and ternary cluster integrals), respectively (see the end of section 1.8, and subsection 3.1.1).

For v, approximation 3.1-315 is accepted, so that near the θ temperature, $\mathbf{v} \sim A^3 \tau$. The parameter w is regarded to be temperature-independent.

According to Equation 5, α turns out to be proportional to $(|\tau|N^{1/2})^{-1/3}$ when $\alpha \ll 1$, i.e. $R \sim N^{1/3}$.

Sun et al. (1980), Swislow et al. (1980) have modified Sanchez' (1979) formula and obtained

$$\frac{7}{3} \cdot \frac{\Phi_R}{N} (1 - \alpha_R^2) = -\frac{\Delta G}{2kT} \Phi_R^2 + \ln(1 - \Phi_R) + \Phi_R,$$

where Φ_R is the volume fraction of segments in a macromolecule with a radius of gyration R and the number of segments N, ΔG is the change in the Gibbs potential. Expansion of the logarithmic term into a two-term series with replacing ΔG by $\Delta H - T \Delta S$ leads to

$$\frac{14\Phi_R}{3N}(1-\alpha_R^2) = \sigma\left(\frac{\theta}{T}-1\right)\Phi_R^2 - \frac{2}{3}\Phi_R^3 - \frac{1}{2}\Phi_R^4 - \cdots,$$
(6)

where

$$\theta \equiv \frac{-\Delta H/k}{1 - \Delta S/k} \tag{7}$$

(cf. Equations 3.1 38, 39,-41),

$$\sigma \equiv 1 - \Delta S/k \tag{8}$$

(cf. Equation 3.1-39).

Analysis of Equation 6 shows (Sanchez, 1969) that in the limiting case $N \to \infty$, the coil-globule transition is a continuous one with $T_t = T_c = \theta$. The first derivative of the

order parameter (here Φ_R) with respect to temperature undergoes a second-order break of continuity (tending for ∞). For a finite chain, $T_t < \theta$, and $\partial \Phi_R / \partial T$ has a first-order break.

While trying to observe the coil-globule transition experimentally, researchers faced a difficulty. On the one hand, high molecular mass provides a more significant effect of changes in the macromolecule sizes (Figure 3.45), but the temperature gap between the



Figure 3.45. Dependence of the coil swelling coefficient α_R on T/θ . The theoretical curves are plotted according to Equation 3.4-6 with $\sigma = 4$, $N = 9.06 \cdot 10^{-4} \cdot M_w$, and $M_w = 2.9 \cdot 10^3$ (1), $1.0 \cdot 10^5$ (2), and $2.6 \cdot 10^7$ (3). The experimental values (circles) relate to the polystyrene+cyclohexane system with $M_w = 2.9 \cdot 10^3$ (1) (Nierlich et al., 1978), $M_w = 2.6 \cdot 10^7$ (3) (Sun et al., 1980) [Reprinted with permission from: S.-T.Sun, J.Nishio, G.Swislow, T.Tanaka. J. Chem. Phys. 73 (1980) 5971-5975. Copyright © 1980 American Institute of Physics]

 θ point and the binodal is narrow (see Figures 3.9 and 3.21), where the transition occurs. On the other hand, in solutions of LMW polymers, this range is wider, but the effect of changes in the macromolecular sizes is insignificant.

Moreover, when macromolecules are relatively small, the choice of methods to determine their sizes is quite limited.

Here, the neutron scattering method is of importance. The wavelength of neutron radiation is a few Å, and, even for LMW polymers, the sizes of coils are larger than the wavelength of radiation; moreover, $|m-1| \ll 1$ is satisfied, so Rayleigh-Debye's approximation can be applied, i.e. the standard Debye-Zimm data processing procedure, despite large relative sizes of scattering particles. The first attempts to observe the coil-globule transition were made with this very method on the polystyrene+cyclohexane system (Nierlich, 1978).

Measurements of the temperature dependence of macromolecular sizes of a very highmolecular-weight polystyrene sample ($M_w = 44.4 \cdot 10^6$) in cyclohexane within the range of polymer concentration 0.002...0.02 g/dl by means of classical light scattering (Slagowski et al., 1976) has revealed a significant change in the coil swelling coefficient α , though, as Swislow et al. (1980) think, the above authors observes the initial stage of the coil-globule transition only.

The most convincing experimental demonstration of this transition was made on the systems polystyrene + cyclohexane (Sun et al., 1980; Swislow et al., 1980) ($M_w = 2.6 \cdot 10^7$; $M_w/M_n = 1.3$; $0.03 < c < 3 \mu g/cm^3$) and PAA+water+acetone ($M_w = 5 \dots 6 \cdot 10^6$; $c < 10 \mu g/cm^3$) (Nishio et al., 1979) by means of dynamic light scattering with measuring the diffusion coefficient and hydrodynamic radius of a coil R_H (Equation 3.3-61), and the mean radius of gyration R in the approximation of Gaussian segment distribution in the chain. These results show good agreement of experimental data with the predictions of Sanchez-Tanaka's theory (Sanchez, 1979; Sun et al., 1980) (see Figure 3.45).

A similar agreement was found in the polystyrene+dioctylphthalate system $(M_w = 2 \cdot 10^6; M_w/M_n = 1.3; 1 \cdot 10^{-4} < c < 8 \cdot 10^{-4} \text{ g/cm}^3)$ studied by means of dynamic and elastic light scattering (Štèpanek et al., 1982). The authors emphasize that high viscosity of the solvent hinders the process of macromolecular aggregation and expands the concentration range where the coil-globule transition is observed. In this connection, experiments on the PAA+water+acctone are remarkable (Nishio et al., 1979; Baranovskaya et al., 1982; Klenina and Lebedeva, 1987).

Baranovskaya et al. (1982) have established a sharp (300-fold) decrease in the macromolecule volume (while the molecular mass remains constant) in the branched PAA $(M_w = 30 \cdot 10^6)$ +water+acetone system at the volume fraction of acetone $\gamma = 0.35$ by means of classical light scattering.

These authors, as well as Nishio et al. (1979), do not report the boundary of the liquid-liquid phase separation region and the θ composition in the PAA+water+acetone system. This might possibly be due to the system being "inclined" to oversaturation at high molecular masses, which hinders obtaining the boundary curve of phase separation (Klenina and Lebedeva, 1987).

Special experiments (Klenina and Lebedeva, 1987) have shown a great irreproducibility of cloud points when PAA aqueous solutions are titrated with acetone and the invalidity of the standard solubility equation 3.2-55, which manifested in higher cloud points γ for high-molecular PAA samples than for the low-molecular ones. Solutions of highmolecular fractions could not often be titrated, i.e. remained transparent at a sufficiently high content of acetone $\gamma \rightarrow 1$. However, in hours or days, the systems spontaneously grew turbid. These facts attest to the system being "inclined" to oversaturation owing to some kinetic difficulties in new phase particle formation.

Klenina and Lebedeva (1987) has finally succeeded in finding a method (even two were proposed) of obtaining the equilibrium values of the cloud points in this system. The first method envisages adding acetone in excess amounts, waiting for phase separation, and performing back titration, i.e. turbidity was measured on adding water. The value of γ at which $\tau \to 0$ was accepted as the boundary of the phase separation region. This method gave well-reproducible results. Moreover, such well-reproducible γ were obtained with direct turbidimetric titration as well as with the back one provided that a small amount

of NaCl (5 · 10⁻⁴ < c_s < 2 · 10⁻² M) was added.

Special experiments have established no influence of small amounts of NaCl on the location of the boundary of the phase separation region. The role of NaCl is in elimination of kinetic hindrances and letting new-phase particles form. The mechanism of such an action is not clear as yet, but work in this direction is promising. We note that with an equal volume of the second phase (an equal concentration of the precipitated polymer), the sizes of the new-phase particles have been found to depend on the NaCl concentration, which points to a new way of optimization of STT of polymer solutions (see subsection 3.2.3).

On establishing the boundary of the phase separation region within $10^{-6} < v_{2I} < 10^{-3}$, Klenina and Lebedeva (1987) determined the θ composition of the water+acetone mixture by Elias' method (see Equation 3.2-83): $\gamma_{\theta} = 0.32$, which was confirmed by light scattering ($\mathcal{A}_2 = 0$).

Comparison of the value $\gamma_{\theta} = 0.32$ and the location of the boundary curve of the phase separation region on a quasibinary section (Klenina and Lebedeva, 1987), on the one hand, and the experimental conditions in (Nishio et al., 1979; Baranovskaya et al., 1982), on the other hand, suggests that the coil-globule transition is observed not only when $\gamma > \gamma_{\theta}$, but also when γ exceeds the value γ of the boundary curve, i.e. in the liquid-liquid phase separation region. A similar situation was found for the PAA+water+methanol system (S.Klenin et al., 1983b; Klenina and Lebedeva, 1987) as well.

Recall that the thermodynamically equilibrium coil-globule transition must occur between the θ temperature (the θ composition) and the boundary curve of the phase separation region. Hence, it was observed (Nishio et al., 1979; Baranovskaya et al., 1982) in the metastable region of the liquid-liquid phase transition and with an essential oversaturation with respect to the coil-globule transition. Technically, such a tendency of the system to oversaturation enhances the possibility to observe the coil-globule transition with respect to the concentration scale of polymer and precipitant. This may serve as an explanation why the most significant effects of the coil-globule transition have been found in systems with oversaturation (in a "foreign field", see section 1.5).

The coil-globule transition proceeding under conditions of oversaturation counts in favour of its being close to the first-order transition.

Chu et al. (1987), Park et al. (1987) report the results of a study of the coil-globule transition in the systems polystyrene+cyclohexane, polystyrene+methylacetate, and polystyrene+methylacetate+1% antioxidant by both elastic and dynamic light scattering on a number of polymer samples. It has been established that in the polystyrene+cyclohexan system, the globular mode of molecular chains $(\alpha_R^3 |\tau| M_w^{1/2} = const$) settles within the range $|\tau| M_w^{1/2} > 30$ (up to ~ 50) with $\alpha_R^3 |\tau| M_w^{1/2} \simeq 20$.

The same polymer samples under the same experimental conditions showed no globular mode for the hydrodynamic radius R_H .

Within the range $0 < |\tau| M_w^{1/2} < 10$, the θ mode was revealed with $\alpha_R \sim 1$, so the globular mode must exist within $10 < |\tau| M_w^{1/2} < 30$.

For the systems polystyrene+methylacetate and polystyrene+methylacetate+1% antioxidant, coil globulization was observed near both the UCST (Figure 3.46a) and LCST (Figure 3.46b). The collapsed mode for the radius of gyration R in these systems was observed in a rather extended range of $|\tau| M_w^{1/2}$, while for the hydrodynamic radius R_H , the



Figure 3.46. α vs $|\tau M_w^{1/2}$ for the system polystyrene+methylacetate+1% antioxidant near the UCST ($\theta_{UCST} = 43^{\circ}$ C) (a) and LCST ($\theta_{LCST} = 114^{\circ}$ C) (b) from elastic light scattering data (α_R) (a, curve 1 and b) and dynamic light scattering data (α_H) (a, curve 2). The straight lines have slopes -0.31 ± 0.03 (a) and -0.32 ± 0.02 (b) (Chu et al., 1987)[Reprinted with permission from Macromolecules 20 (1987) 2833–2840. Copyright © 1987 American Chemical Society]

globular state in the polystyrene+methylacetate systems was not observed; in the system polystyrene+methylacetate+1% antioxidant, chains nearly reach the globular mode near the UCST (see Figure 3.46b).

Strictly speaking, the authors have revealed two modes of the globular state, namely, one that is more crumbly and one that is more compact. The second mode is, for some unknown reason, named metastable by the authors, though they drove the configuration point along one direction only, towards the poorer solvent. It would be more reasonable to classify the crumbly globular state with the metastable states, according to the above observations.

Lifshitz (1968) has developed a new formalism of polymer theory, based on the mathematical analogy between the state equation of a molecular coil with Schrödinger's equation of a quantum mechanical particle placed in an external potential field. This analogy was mentioned in section 3.1 when speaking of Edwards' solution of the conformational problem of a molecular coil in a good solvent with the help of the solutions of the diffusion equations for Green's functions in the self-consistent field approximation.

The coil conformation in a good solvent is characterized by a low density of segments, and fluctuations of segment density (as the order parameter of the system) must play a large role. Indeed, in the self-consistent field approximation, Edwards, actually, has arrived at results similar to Flory's approximation (see Equation 3.1-216).

Not so with the globular state of a molecular chain where segment density fluctuations must not play any role. Therefore, the self-consistent field method can be applied in the globular state region on a more solid basis.

Using the Schrödinger stationary equation formalism in the SCF approximation, a number of investigations of the globular state of macromolecules have been carried out

(Lifshitz, 1968; Lifshitz and Grosberg, 1973, 1975; Lifshitz et al., 1978, 1979; Grosberg, 1979, 1980abc; Kuznetsov and Khokhlov, 1981; Grosberg and Khokhlov, 1989).

This problem is considered by Khokhlov (1985) in detail.

In the bulk approximation, i.e. neglecting any surface effects, an expression has been obtained for the numerical concentration of chain units in a globule

$$n_0 = -\frac{B}{2C},\tag{9}$$

where B and C are the second and third virial coefficients in the expansion of the osmotic pressure π of a "disconnected segments" solution

$$\pi = kT\rho(1+\rho B+\rho^2 C+\cdots),\tag{10}$$

where ρ is the number of macromolecules per unit volume.

To correct for segments being linked, the virial coefficients are renormalized so that they should relate to longer chain fragments than A. Khokhlov (1985) calls such fragments "quasimonomers" while "monomers" are chain fragments of length A. Recall that the function h(z) reflects segments being linked in a chain in the classical theories of polymer solutions (see Equation 3.1-146).

Taking

$$\rho = \frac{cN_A}{M} \tag{11}$$

into account and comparing the virial expansions in Equations 1.3-37 and 10, we get a relationship between the virial coefficients in these expansions

$$\mathcal{A}_2 = \frac{N_A}{M^2} B,\tag{12}$$

$$\mathcal{A}_3 = \frac{N_A^2}{M^3}C,\tag{13}$$

i.e. (cf. Equation 1.3 40)

$$B = \frac{\beta}{2},\tag{14}$$

which coincides with the definitions of β and B through the pair interaction potential (see Equation 3.1-120 and formula 5.9 in (Khokhlov, 1985)).

The same approximation gives the difference between the free energies of a globule and an unperturbed coil without excluded-volume effects

$$\Delta F = -\frac{kTNB^2}{4C},\tag{15}$$

where N is the number of units in a macromolecule, and the globule radius is

$$R_{gl} = \left(\frac{3N}{4\pi n_0}\right)^{1/3} = \left[\frac{3NC}{2\pi(-B)}\right]^{1/3}.$$
(16)

It follows from Equation 15 that the condition $\Delta F = 0$ corresponds to the coil-globule transition, i.e. the transition temperature T_t coincides with the θ temperature, where $\mathcal{A}_2 = 0$ and B = 0.

Near the θ temperature, the virial coefficients are approximated as

$$B(T) \cong b\frac{T-\theta}{T} = b\tau, \tag{17}$$

$$C(T) = C(\theta) > 0, \tag{18}$$

where b and $C(\theta)$ are constants.

In view of Equation 17, we obtain from Equation 15

$$\Delta F \sim -\tau^2,\tag{19}$$

i.e. the coil-globule transition turns out to be a continuous one (one minimum of the potential, see section 1.5).

Consideration of the surface effects gives (Khokhlov, 1985)

$$\Delta F = -kT \frac{b^2 \tau^2}{4C} \left[1 - \left(\frac{\tau_t}{|\tau|} \right)^{2/3} \right],\tag{20}$$

where

$$\sigma_t \sim \frac{A^{3/2}C^{1/4}}{bN^{1/2}}.$$
 (21)

Qualitative analysis of Equation 20 does not change the character of phase transition and points to the existence of pretransition swelling phenomena when a macromolecule is in the globular phase, so that at the transition point, the local unit concentration in a globule is already sufficiently low.

More rigorous analysis of simulations based on the globule theory (Grosberg and Kuznetsov, 1984ab) shows the validity of Equation 19 away from the transition point (at $q \leq -200$) while near this point

$$\Delta F \sim -\frac{\tau - \tau_l}{\tau_l},\tag{22}$$

which is characteristic for a first-order phase transition.

Here

$$q = \left(\frac{6^{3/2}N}{C^{1/2}A^3}\right)^{1/2} B,\tag{23}$$

j.e.

$$q \sim \tau \quad \text{and} \quad \tau_t \sim q_t = -10.4 \,.$$

$$\tag{24}$$

The condition of globulization $\Delta F < 0$ is satisfied when

$$-\infty < q < q_t \simeq -10.4 \,. \tag{25}$$

The radial distribution of quasimonomer density in a globule strongly depends on q and varies from a sharp step at $q \to -\infty$ to a fuzzy profile at $q = q_t = -10.4$.

It follows from the theory that the q-dependence of the coil expansion factor $\alpha = \left(\overline{R^2}\right)^{1/2} / \left(\overline{R_{\theta}^2}\right)^{1/2}$ is defined by one parameter only, namely, \sqrt{C}/A^3 , whose decrease is accompanied by a sharp change in the segment density profile. For comparison with experiment, the theory envisages two parameters to be determined from the best fit to the experimental data: \sqrt{C}/A^3 and $(N/M)^{1/2}bA^3$ or $q/\tau M^{1/2}$.



Figure 3.47. Dependence of the macromolecular expansion factor on the relative distance from the θ point $\tau_1 = (T - \theta_1)/\theta_1$ $(\theta_1 = 308.5 \text{ K})$ for polystyrene in cyclohexane (1) (Sun et al., 1980) [Reprinted with permission from: S.-T.Sun, J.Nishio, G.Swislow, T.Tanaka. J. Chem. Phys. 73 (1980) 5971 5975. Copyright © 1980 American Institute of Physics] and $\tau_2 = (T - \theta_2)/\theta_2$ ($\theta_2 =$ 295.1 K) for polystyrene in dioctylphthalate (2) (Stèpanek et al., 1982) [Reprinted with permission from: Macromolecules 15 (1982) 1214. Copyright @ American Chemical Society], and the corresponding theoretical curves with the abscissa q (Grosberg and Kuznetsov, 1984b)

Presented in Figure 3.47 are experimental values of the coil expansion factor of polystyrene macromolecules $(M_w = 2.6 \cdot 10^7)$ in cyclohexane (Sun et al., 1980) and polystyrene $(M_w = 2 \cdot 10^6)$ in dioctylphthalate (Štěpanek et al., 1982). Curves 1 and 2 are drawn for $\sqrt{C}/A^3 \simeq 0.12$; $(N/M)^{1/2}b/A^3 \simeq 0.029$; $(q/\tau M^{1/2} \simeq 0.33)$ (to the polystyrene+cyclohexane system) and for $\sqrt{C}/A^3 \simeq 0.09$; $(N/M)^{1/2}b/A^3 \simeq 0.009$; $(q/\tau M^{1/2} \simeq 0.12)$ (to the polystyrene+dioctylphthalate system). As can be seen, for the chosen values of \sqrt{C}/A^3 , there is good agreement between theory and experiment.

Due to the predominance of the attraction forces among polymer segments at $T < \theta$, of special interest is the question of globule stability (Lifshitz, 1968; Lifshitz et al., 1979) within the framework of the general problem of stability (more precisely, instability) of

colloidal systems (Shchukin et al., 1982).

Globule coagulation leads to a gain in free energy due to a decrease in the globulesolvent interface area ($\sim \sigma R_{gl}^2$), but it is accompanied by a loss in the entropy term of free energy, $\sim kT \ln(n_{gl}/c)$ on a macromolecular basis, where n_{gl}/c is the volume fraction of globules in the system. On this basis, Lifshitz et al. (1979) have obtained the globule stability conditions as

$$kT\ln\frac{n_{\rm gl}}{c} \ge \sigma R_{\rm gl}^2 \tag{26}$$

or, including the temperature dependence of σ and Equations 16 and 17,

$$\left| \ln \frac{cv}{\tau} \right| \ge N^{2/3} \left(\frac{A^3}{v} \right)^{1/3} \tau^{4/3}, \tag{27}$$

where v is the volume of a segment, c is the average concentration of segments in solution.

Similar considerations to establish the stability conditions of general-type colloidal systems have been made by Rebinder (1958), Shchukin and Rebinder (1958), Pertsov et al. (1964), Rebinder and Fux (1973), Shchukin et al. (1982).

In this connection, it seems reasonable to refer once again to the studies on the systems PAA+water+acetone and PAA+water+methanol (Nishio et al., 1979; Baranovskaya et al., 1982; S.Klenin et al., 1983b; Klenina and Lebedeva, 1987).

The possibility itself to study globules under conditions of substantial oversaturation attests to their sufficiently high kinetic stability. The invariance of globule size (lack of aggregation) was observed up to $\gamma \approx 0.75$ (Nishio et al., 1973) ($\gamma_{\Phi} \approx 0.32...0.33$) (Klenina and Lebedeva, 1987).

In the PAA+water+methanol system, single globules were observed at a relatively high polymer concentration ($c \le 0.01 \text{ g/dl}$) (S.Klenin et al., 1983b).

Globule stability is obviously evidenced by a delay in phase separation during acctone titration of aqueous solutions of PAA high-molecular samples ($\mathbf{c} \approx 2...6 \cdot 10^{-3} \text{ g/dl}$) up to $\gamma \approx 0.8...0.9$. However, as mentioned earlier, long storage of precipitant-rich systems makes them more and more turbid, i.e. globule dispersion, as a typical colloidal system. is characterized by kinetic (aggregative) stability **rather** than the thermodynamic one. It should be noted that the stability of dispersion macromolecular globules has not been subjected to special experiments.

The literature reports failure in experimental observation of the coil-globule transition as well. Eg. Bauer and Ullman (1980) measured R_H of polystyrene macromolecules in cyclohexane ($M = 5 \cdot 10^4 \dots 4.4 \cdot 10^7$ with a narrow MWD, within a concentration range 0.150...0.001%) by means of photon correlation spectroscopy (dynamic light scattering). When $T < \theta$, R_H linearly diminishes with lowering temperature, and no coil-globule transition was detected.

In all the above cases, the coil-globule transition proceeds in a very dilute polymer solution below the θ point when attraction predominates with pair contacts of segments, but repulsion remains at ternary contacts: B < 0, C > 0 (Equations 17, 18).

Another kind of globulization must be observed when repulsion predominates with pair contacts (B > 0), and attraction is due to higher-multiple contacts (C < 0) (Grosberg and Panchenko, 1987). Such a situation may occur in rigid-chain polymers (Kuznetsov

and Khokhlov, 1981; Khokhlov and Semyonov, 1985), macromolecules with mesogeneous groups (Grosberg, 1980c), and in heteropolymers.

The structure of globule organization in this case comprises two phase regions, namely, a solid core and fluctuating loop-like fragments forming a so-called **globule trimming** (Lifshitz, 1968; Lifshitz and Grosberg, 1973, 1975; Kuznetsov and Khokhlov, 1981).

The vapour pressure P_r over a liquid drop of a radius r (the system of "disconnected segments") is known to exceed that over a flat surface P_{∞} of the same liquid, which is reflected in Thomson's (Kelvin's) equation

$$\ln \frac{P_r}{P_{\infty}} = \frac{2\sigma \bar{V}}{\bar{R}Tr},\tag{28}$$

where σ is the surface tension coefficient at the liquid-vapour interface, \bar{V} is the molar volume.

A globule with a trimming is an analogue of such a situation in the system of linked segments (in a macromolecule), as longitudinal links do not allow segments to leave the globule (drop) at a long distance.

Grosberg and Panchenko (1987) present a state diagram of a molecular chain where the regions of the existence of coils and globules with different trimmings are marked.

Unlikely the previous calculations of ΔF of the coil-globule transition, where the Gaussian distribution of segments in a macromolecule was assumed (eg. see Equation 2), Birshtein and Pryamitsyn (1987) have applied Fixman's (1962) distribution function valid for the range $R \ll R_{\theta}$

$$W_0(R) \sim \frac{\langle R_{\theta}^2 \rangle^2}{R^5} \exp\left\{-\frac{9}{4} \cdot \frac{\langle R_{\theta}^2 \rangle}{R^2}\right\}.$$
(29)

The increment of the free energy of mixing ΔF_m was approximated by a virial expansion

$$\frac{\Delta F_m}{kT} = \sum_{k=2} \frac{N^k B_k}{k! R^{3(k-1)}},\tag{30}$$

where B_k is the kth virial coefficient of the segment interactions.

If we confine ourselves to two virial coefficients

$$B_2 = b\tau, \tag{31}$$

$$B_3 \equiv c > 0, \tag{32}$$

then for $\tau < 0$, $\alpha < 1$ the authors get

$$\frac{\Delta F}{kT} = \gamma \left[\left(\frac{1}{\alpha^2} - 1 \right) + \ln \alpha^2 \right] + \frac{N^{1/2} b\tau}{2\alpha^3 A^3} + \frac{c}{6A^6} \left(\frac{1}{\alpha^3} - 1 \right)^2, \tag{33}$$

where γ generalizes the numerical factor in the exponent of Equation 29.

Minimization of ΔF with respect to α yields an equation

$$\alpha^{3} - \alpha = \frac{3N^{1/2}b\tau}{2\gamma A^{3}} + \frac{c}{2A^{6}\gamma} \left(\frac{1}{\alpha^{3}} - 1\right).$$
(34)



Figure 3.48. Dependence of the free energy increment ΔF and coil expansion factor α on the parameter $\tau B^* N^{1/2}$, where $B^* = b/A^3 \gamma$ at $C = c/2A^6 \gamma = 1$ (1), 10^{-1} (2), and 10^{-2} (3) (Birshtein and Pryamitsyn, 1987)

The right-hand sides of Equations 33 and 34 are represented in such a form that $\Delta F = 0$ and $\alpha = 1$ at $\tau = 0$.

In Figure 3.48, the dependences $\Delta F = f(\tau)$ (Equation 33) and $\alpha = f(\tau)$ (Equation 34) are plotted for three values of $C = c/2A^6\gamma$. It is seen that the temperature region of significant ΔF and α variations becomes narrower as $N^{1/2}b/A^3$ increases and c/A^6 diminishes.

To analyze the behaviour of α , Birshtein and Pryamitsyn (1987) represent Equation 34 as

$$-\Phi_1(\alpha) = -\Phi_2(B\tau) + \Phi_3(\alpha, C), \tag{35}$$

where

$$B = bN^{1/2}/A^3\gamma, \quad C = c/2A^6\gamma.$$

At $\tau = 0$, $\alpha = 1$, $\Phi_1 = \Phi_2 = \Phi_3 = 0$. At $\tau < 0$, $\alpha < 1$, $\Phi_1, \Phi_2, \Phi_3 > 0$.

The function Φ_1 is associated with the entropy losses of ΔF_{cl} on shrinking the chain; Φ_2 and Φ_2 characterize the two- (attraction) and three-particle (repulsion) interactions among the segments.

As $|\tau|$ increases and α decreases, Φ_2 and Φ_3 infinitely rise while Φ_1 goes through a maximum and then vanishes at $\alpha \to 0$. The possibility to realize two modes with different Φ_1 , Φ_2 , and Φ_3 ratios follows.

At mode I, $|\tau| < |\tau_0|$, $\Phi_1 \cong \Phi_2 \gg \Phi_3$, i.e. chain compression due to the pair interactions is hindered by entropy obstacles to compression. At mode II, $|\tau| > |\tau_0|$, $\Phi_2 \cong \Phi_3 \gg \Phi_1$, i.e. coil compression is hindered by three-particle interactions among the segments. The crossover point τ_0 is defined by the condition $\Phi_1 = \Phi_3$. The characteristic of a globular structure at mode II results from the equality $\Phi_2 = \Phi_3$, i.e.

$$\alpha^3 \cong C \frac{|\tau|^{-1}}{B},\tag{36}$$

$$R = \left(\frac{CN^{3/2}}{B\tau}\right)^{1/3},$$
(37)

$$\frac{\Delta F}{kT} = \frac{\Delta F_m}{kT} \cong -\frac{B}{C}\tau^2.$$
(38)

From the condition $\Phi_1 \simeq \Phi_3$ and Equations 36 and 38, the characteristic quantities of the crossover result:

$$\alpha(\tau_0) \cong C^{3/4} \cong \left(\frac{c}{A^6}\right)^{1/4},\tag{39}$$

$$\tau_0 = -\frac{C^{1/4}}{B} \cong -\frac{A^{3/2}c^{1/4}}{N^{1/2}b},\tag{40}$$

$$\frac{\Delta F(\tau_0)}{kT} = -C^{1/2} \cong -\frac{A^3}{c^{1/2}},\tag{41}$$

$$\Delta \tau = \left(\frac{d\Delta F}{kT \, d\tau}\right)_{\tau=\tau_0}^{-1} \cong C^{3/4} B^{-1} \cong |\tau_0| C^{1/2} \cong |\tau_0| \frac{c^{1/2}}{A^3}.$$
(42)

Thus, these quantities are defined by two combined parameters B and C with $z = B\tau$, where z is the excluded volume parameter from the two-parameter theory. As is seen from Equations 40 and 42, $\tau_0 \sim \Delta \tau \sim B^{-1}$, i.e. as N and b/A^3 increases, the crossover points shifts to the θ point, and the transition becomes more sharp.

The ternary interaction parameter C, which does not manifest itself in the range $\tau > 0$, plays a significant role in the coil-globule transition. It follows from Equations 34 and 35 that at $C \sim 1$, the values of Φ_3 are commensurable with Φ_1 even at $\alpha \sim 1$ ($\alpha(\tau_0) \sim 1$). As C decreases, the limiting contraction degree $1/\alpha$ rises and $\alpha(\tau_0)$ diminishes. As a result, the dependence $\alpha(\tau)$ becomes steeper, the crossover point τ_0 approaches the θ point ($\tau = 0$), and the range $\Delta \tau$ becomes narrower (see Equations 40 and 42). In the case of $C \leq 10^{-3}$, there emerges a narrow region where α jumps on the curves $\alpha = f(B\tau)$ (see Figure 3.48). It is seen from Equation 37 that this jump relates to the nonmonotonic character of Φ_1 .

The contraction effect reaches a maximum in the absence of ternary interactions ($C \rightarrow 0$), diminishes with increase of C, and vanishes at $C > 10^{-3}$.

The largest changes of $\alpha = f(B\tau)$ are observed at $|\tau| < |\tau_0|$, i.e. in mode I.

The results of these considerations agree, in general, with the bulk approximation of Lifshitz-Khokhlov-Grosberg's theory (cf. Equations 37 and 38 with Equations 15 and 16), but there are differences in details. In particular, according to Birshtein-Pryamitsyn's (1987) theory, the coil-globule transition remains continuous to considerably less values of C.

To be compared with experimental data, Equation 34 is written as

$$\frac{\alpha^3 - \alpha}{\alpha^{-3} - 1} = B \frac{\tau}{\alpha^{-3} - 1} + C.$$
(43)

Indeed, if experimental results (Sun et al., 1980; Štèpanek et al., 1982) are plotted in the coordinates

$$\frac{\alpha^3 - \alpha}{\alpha^{-3} - 1} vs \frac{\tau N^{1/2}}{\alpha^{-3} - 1},\tag{44}$$

straight lines appear, whose slope is defined by the parameter $B^* = b/\gamma A^3$ while their intercept at the ordinate axis is by $C = c/2\gamma A^6$.

In the case of the polystyrene+cyclohexane system (Sun et al., 1980), plotting 44 leads to values $B^- \simeq 0.56$, $C \simeq 0.03$ (Birshtein and Pryamitsyn, 1987); in the case of the polystyrene+dioctylphthalate system (Štěpanek et al., 1982), $B^- \simeq 0.15$, $C \simeq 0.008$.

Thus, the value of C in these systems is rather small to provide a sharp coil-globule transition. The value of C for polystyrene in different solvents varies with B^* , so that B^*/C ratio remains approximately invariant.

Within the framework of Birshtein-Pryamitsyn's theory, experimental results correspond to a continuous coil-globule transition at the found values of C, while processing the same experimental data according to the theoretical relationships (Grosberg and Khokhlov, 1984ab) (see Figure 3.47) assumes a jump in the chain sizes.

Data processing on the coil-globule transition within the framework of the existing theories (see also the end of section 5.5) does obviously provide a real way to evaluate ternary interactions in the P+LMWL systems.

Attempts are described in the literature to extend the specific features of the coil-globule transition to a number of problems of polymer material science up to the description how

films are formed from solutions in solvents of different thermodynamic quality, to explain the mechanism of plastification, etc.

According to Matveyev and Askadski (1986), when two globules with trimmings collide, the trimmings overlap to form a "coupled globule". If the size of such a globule is commensurable with those of the source globules, "there emerges an element of supramolecular structure (SMP) of the ellipsoid type".

When the formed SMP interact with each other or with macromolecular globules, new binding globules arise that lead to the formation of supermacromolecules built of the globule macromolecules (Matveyev and Askadski, 1986).

Thus, in their scheme of polymer material formation, the authors discuss a part of the state diagram of amorphous separation, very well apart from the actual situation during film (and other things) formation, and this part is treated as a certain universal key regardless of the state diagram of a specific system. Then the authors "talk a lot of kinetics" of the process of morphological structures getting complex...up to... (see above). In this "verbal portrait" of kinetics, there is no place for such a parameter as "time". What does **kinetics** without **time** mean? In particular, from what it follows that the contact time at the collision of two trimmed globules suffices to form a binding globule, even if the possibility of this act is granted?

Meanwhile, the above discussion of macromolecule globulization under conditions of deep oversaturation implied a relative stability of globules, which enables them to exist days and weeks colliding billions and billions times. Finally, why, "due to the diffusion motion", do the structural elements arrange along the same axis to form "clongated SMPs"? Moreover, fibrillar to justify such an exotic mechanism of structural element formation, the rejection of the classical, elaborated, and justified mechanism of growth (coagulation by Smolukhovski, Ostwald's ripening, in particular, in Lifshitz-Slyozov's modification, etc.) needs a motivation.

Thus, the extension of the specific features of the coil-globule transition to the problems of film formation and plastification seems incorrect.

The most success of the theory of the coil-globule transition should be expected in investigative methods involving very dilute polymer solutions.

Besides, the theory of globular state and the coil-globule transition finds use in understanding the functional properties of protein molecules and in analyzing their role at the early prebiological evolution of living matter (Grosberg and Shakhnovich, 1986).

3.5. Phase equilibrium in the crosslinked polymer + low-molecular-weight liquid system

If, during polymerization, a certain amount of a multifunctional monomer (a crosslinking agent) is added to the system, a **crosslinked** (**network**) polymer appears. Many linear polymers are crosslinked by vulcanization and radiation. Polymer microcrystallites can serve as linking knots as well.

Regardless of the way of obtaining, the system network polymer (NP)+LMWL, where the polymer forms a spatial network-crosslinked structure, will also be called a **gel**.

Such systems play a large role in a diversity of technological processes of polymer production and exploitation (Papkov, 1974). A polymer is often crosslinked to give highelastic properties to the polymer-based article. Sometimes, conversely, spontaneously arisen crosslinkings hinder processing or exploitation of polymer solutions.

Great attention is paid to gelation in preparing foodstuffs. Besides traditional fruit jellies, aspic jelly, fish jelly, and calves' foot jelly, the network polymer structure with a liquid component has been used to create novel food products (protein caviar, artificial meat, etc.) (Tolstoguzov, 1978; Elias, 1987).

Making contact lenses from gels to correct myopia, long sight, and other defects of eye refraction is turning into a special branch of medical industry (Wichterle and Lim, 1960). We note in passing that both the eye crystalline lens and the vitreous body are natural gels. Disturbances in their physiologically normal structure are associated with serious cyc illnesses. The dimness of the crystalline lens (cataract) is due to a process, during which the degree of its heterogeneity increases, which, in turn, is owing to phase separation (microsyneresis, crystallization ?). Contraction of the vitreous body may lead to peeling of the retina (Tanaka et al., 1973).

These examples attest to the importance of studying NP+LMWL systems, in particular, phase separation processes in such systems.

3.5.1. High-elastic properties of gels

Elastic properties, characteristic for an isotropic solid polymer body, are a specific feature of gels. There exist and find practical use anisotropic gels resembling the structure of liquid crystals, but this subsection will discuss isotropic gels only.

Under external forces, a solid body is deformed, i.e. changes its **shape** and/or **volume**. The location of every point of the body is defined by a radius-vector \vec{r} with its components $x_1 = x, x_2 = y, x_3 = z$.

As a result of deformation, the radius vector takes some value \vec{r} , so that

$$\vec{u} = \vec{r}' - \vec{r} \quad \text{or} \quad u_i = x'_i - x_i. \tag{1}$$

The quantity \vec{u} is called a **deformation vector** (or a **shift vector**). The specifying of this vector as a function of x_i defines the body deformation completely. In the general case, deformation is characterized by a **deformation tensor** with its components (in the case of small deformations)

$$u_{ik} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right) \tag{2}$$

(Feynman et al., 1964; Landau and Lifshitz, 1987).

In an undeformed body, the location of its molecules corresponds to the state of its thermal equilibrium. All its parts are in mechanical equilibrium with each other. This means that if a certain space inside the body is selected, the resultant force from the other parts is equal to zero.

Under deformation, the location of molecules changes, and the body leaves the initial equilibrium state. As a result, forces arise trying to return the body to its equilibrium state. These internal forces arising from deformation are called **internal stresses**. If the body is not deformed, there are no internal stresses in it (Landau and Lifshitz, 1987).

Set aside a certain space in the body with a resultant force on it

 $\int \vec{F} \, dV,$

 \vec{F} denoting the force acting on a unit volume.

Each of the three components $\int F_i dV$ of the resultant force (concerning all the internal stresses) can be transformed to a surface integral (Landau and Lifshitz, 1987). It follows from the general field theory that, in this case, the components of F_i must be the divergences of a certain second-rank tensor, i.e.

$$F_i = \frac{\partial \sigma_{ik}}{\partial x_k}.$$
(3)

The tensor σ_{ik} is called a stress tensor.

The component σ_{ik} is the *i*th component of the force acting on a unit surface perpendicular to the x_k axis. Thus, a unit surface, perpendicular to the x axis, is affected by a **normal** (with respect to it) (directed along the x axis) force σ_{xx} and **tangential** (directed along the y and z axes) forces σ_{yx} and σ_{zx} .

At equilibrium, the forces of internal stresses are mutually compensated for in every space element, and $F_i = 0$, i.e.

$$\frac{\partial \sigma_{ik}}{\partial x_k} = 0,\tag{4}$$

which is the equilibrium equation of a deformed body.

For such a body, the Gibbs fundamental equation 1.1.1-1 takes the form

$$dU = T \, dS + \sigma_{ik} \, du_{ik},\tag{5}$$

and, correspondingly (cf. Equations 1.1.1-20 and 1.1.1-26),

$$dF = -S \, dT + \sigma_{ik} \, du_{ik},\tag{6}$$

$$dG = -S \, dT - u_{ik} \, d\sigma_{ik},\tag{7}$$

whence

$$\sigma_{ik} = \left(\frac{\partial U}{\partial u_{ik}}\right)_S = \left(\frac{\partial F}{\partial u_{ik}}\right)_T,\tag{8}$$

$$u_{ik} = -\left(\frac{\partial G}{\partial \sigma_{ik}}\right)_T.$$
(9)

Hereinafter, summation over indices '1', '2', '3' is assumed in the right-hand sides. The free energy of a deformed body is

$$F = F_0 + \frac{\lambda}{2} u_{ii}^2 + \mu u_{ik}^2.$$
(10)

The constants λ and μ are called Lamè's coefficients.

The relative volume variation under deformation is defined by the sum of the diagonal components

$$\Delta V = u_{ii}.\tag{11}$$

Deformations, when the body's volume remains constant and only its shape changes. are called **shear** (Figure 3.49a). Deformations, when the volume rather than the shape, changes are called **uniform compression** (Figure 3.49b). The tensor of such a deformation is expressed through

$$u_{ik} = const \cdot \delta_{ik}. \tag{12}$$

Any deformation can be represented by the sum of deformations of simple shear and uniform compression

$$u_{ik} = \left(u_{ik} - \frac{1}{3}\delta_{ik}u_{ll}\right) + \frac{1}{3}\delta_{ik}u_{ll}.$$
(13)

Then, the first term in the right-hand side gives a simple shear as the sum of its diagonal terms is equal to zero ($\delta_{ii} = 3$) while the second term defines uniform compression.

If the sums of the squared components of the first and second terms in the right-hand side (Equation 13) are chosen as two independent second-power scalars, the free energy is

$$F = \mu \left(u_{ik} - \frac{1}{3} \delta_{ik} u_{ll} \right)^2 + \frac{K}{2} u_{ll}^2, \tag{14}$$

where K and μ are called a **compressional modulus** and a **shear modulus**, respectively.

Comparison between Equations 14 and 8 expresses the stress tensor through the deformation tensor

$$\sigma_{ik} = K u_{ll} \delta_{ik} + 2\mu \left(u_{ik} - \frac{1}{3} \delta_{ik} u_{ll} \right).$$
⁽¹⁵⁾

It follows, in particular. that

$$\sigma_{ii} = 3Ku_{ii}.\tag{16}$$

If u_{ii} from Equation 16 is substituted to Equation 15 and Equation 15 is resolved with respect to u_{ik} , the deformation tensor will be expressed through the stress tensor

$$u_{ik} = \frac{1}{9K} \delta_{ik} \sigma_{ll} + \frac{1}{2\mu} \left(\sigma_{ik} - \frac{1}{3} \delta_{ik} \sigma_{ll} \right).$$
⁽¹⁷⁾



Figure 3.49. Different kinds of a cube's deformation (the edge $L_{0x} = L_{0y} = L_{0z}$): a simple shear (a), a uniform compression (b), a one-side tension (c). A one-side compression of a cylinder (d). To the left – at the initial instant of stress application (t = 0), to the right – at the final state $(t \to \infty)$

Upon uniform compression of a body (Figure 3.49b), the stress tensor is

$$\sigma_{ik} = -P\delta_{ik}.\tag{18}$$

From Equations 18 and 16 we get

$$u_{ii} = -\frac{P}{K}.$$
(19)

As u_{ii} and P are small quantities, this equation can be written in the differential form

$$\frac{1}{K} = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T.$$
(20)

According to Equation 17, the deformation tensor u_{ik} is a linear function of the stress tensor σ_{ik} (Hooke's law).

On simple tension of a body (a pivot), the forces are applied to the pivot's ends and stretch them towards different directions (eg. along the axis z). In this case, $\sigma_{zz} = P$, and it follows from Equation 17 that

$$u_{xx} - u_{yy} = -\frac{1}{3} \left(\frac{1}{2\mu} - \frac{1}{3K} \right) P,$$
(21)

$$u_{zz} = \frac{1}{3} \left(\frac{1}{3K} + \frac{1}{\mu} \right) P.$$
 (22)

The component u_{zz} defines the relative elongation of the pivot along the axis z. The coefficient by P is called a **tension coefficient** while the inverse quantity is referred to as a **tension modulus** (or the **Young modulus**) E

$$u_{zz} = \frac{P}{E},\tag{23}$$

where

$$E = \frac{9K\mu}{3K+\mu}.$$
(24)

The ratio of the lateral compression $(u_{xx} \text{ or } u_{yy})$ to the longitudinal tension is called the **Poisson coefficient**

$$\frac{u_{xx}}{u_{zz}} = -\sigma, \tag{25}$$

with

$$\sigma = \frac{1}{2} \cdot \frac{3K - 2\mu}{3K + \mu}.\tag{26}$$

The relative increase in the pivot's volume upon tension (Landau and Lifshitz, 1987) is

$$u_{ii} = \frac{P}{K},\tag{27}$$

and the free energy is

$$F = \frac{u_{zz}\sigma_{zz}}{2} = \frac{P^2}{2E}.$$
 (28)

The deformation moduli of a body are related to each other by the following equations

$$K = \frac{E}{3(1-2\sigma)},\tag{29}$$

$$\mu = \frac{E}{2(1+\sigma)},\tag{30}$$

$$\lambda = \frac{E\sigma}{(1-2\sigma)(1+\sigma)}.$$
(31)

Gibbs fundamental equation 1.1.1-1 for a pivot upon tension can be written as

$$dU = T \, dS - P \, dV + f \, dL,\tag{32}$$

f being the applied force, L the length of the sample.

Correspondingly,

$$dF = -P \, dV - S \, dT + f \, dL,\tag{33}$$

whence it follows (cf. Equation 1.1.1-27...29) that

$$f = \left(\frac{\partial F}{\partial L}\right)_{T,V} \tag{34}$$

or, as F = U - TS,

$$f = \left(\frac{\partial U}{\partial L}\right)_{T,V} - T\left(\frac{\partial S}{\partial L}\right)_{T,V}$$
(35)

There exist a wide range of materials (metals, minerals, and other LMW compounds) for which the energy component of the force in Equation 35 predominates over the entropy component while for polymers the situation is *vice versa*.

For the model of a network with an equal length of the network chains, the Gaussian character of segment distribution between the crosslinks, and the affinity principle (similarity of geometry changes for a network chain and for the whole sample), the entropy change of the sample under deformation is expressed by (Flory, 1950, 1953; Volkenshtein, 1975; Bartenev and Zelenev, 1983; Khokhlov, 1985)

$$\Delta S_{el} = -\frac{\nu_e R}{2} \left[\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 - \ln(\lambda_1 \lambda_2 \lambda_3) \right], \tag{36}$$

where ν_c is the effective number of network chains (crosslinked units) (moles), λ_i is the **relative deformation** of the sample along the three coordinate axes ($\lambda_i = L_i/L_{0i}$); L_{0i} and L_i are the sample's lengths before and after deformation. The axes are denoted by figures: $x, y, z \rightarrow 1, 2, 3$ (see Figure 3.49). The functionality of a branch point, or

functionality of the crosslinks f, i.e. the number of chains originating from a junction is equal to f = 4 in this case.

From the condition of volume conservation

$$\lambda_1 \lambda_2 \lambda_3 = 1. \tag{37}$$

In the particular case of simple tension along the axis z,

$$\lambda_3 = \lambda, \quad \lambda_1 = \lambda_2 = \lambda^{-1/2},\tag{38}$$

$$\Delta S_{cl} = -\frac{R\nu_c}{2} \left(\lambda^2 + \frac{2}{\lambda} - 3\right). \tag{39}$$

For ideal rubbers and gels

$$\left(\frac{\partial U}{\partial \dot{L}}\right)_{T,V} = 0,\tag{40}$$

and Equation 35 is written as

$$f = -\frac{T}{L_0} \left(\frac{\partial S}{\partial \lambda}\right)_{T,V}.$$
(41)

Applying Equation 39, we have

$$\left(\frac{\partial S}{\partial \lambda}\right)_{T,V} \equiv \left(\frac{\partial \Delta S_{el}}{\partial \lambda}\right)_{T,V} = -R\nu_e \left(\lambda - \frac{1}{\lambda^2}\right). \tag{42}$$

Substituting this into Equation 41 and dividing it by the cross-section of the sample $(V_0/L_0 \text{ or } V/L_0)$, we obtain for stress

$$\tau = \frac{RT\nu_c}{V} \left(\lambda - \frac{1}{\lambda^2}\right). \tag{43}$$

In the case of a simple shear (see Figure 3.49a), $\lambda_1 = \lambda$, $\lambda_2 = 1/\lambda$, $\lambda_3 = 1$, and the entropy change per unit volume is

$$\Delta S_{el,\nu} = -\frac{R\nu_c}{2V} \left(\lambda^2 + \frac{1}{\lambda^2} - 2\right). \tag{44}$$

The simple shear deformation γ (see Figure 3.49a) is equivalent to tension along the axis x(1), $\lambda_1 = \lambda$ and compression along the axis y(2), $\lambda = -1/\lambda$ (Feynman et al., 1964), i.e.

$$\gamma = \lambda - \frac{1}{\lambda},\tag{45}$$

then

$$\Delta S_{el,\nu} = -\frac{R\nu_e}{2V}\gamma^2. \tag{46}$$

For shear stress,

$$\tau_s = -T \frac{\partial \Delta S_{el,\nu}}{\partial \gamma} \tag{47}$$

is valid (Treloar, 1958) and, in view of Equation 46,

$$\tau_s = \frac{RT\nu_c}{V}\gamma. \tag{48}$$

Thus,

$$\tau_s = \mu \gamma, \tag{49}$$

where

$$\mu = \frac{RT\nu_e}{V} \tag{50}$$

is the shear modulus of the network.

For the NP+LMWL system (Flory, 1953) where a network sample with a volume V_0 swells to a volume V, the polymer volume concentration is expressed as $v_2 = V_0/V$. Volume is assumed not to change under deformation, and

$$\lambda_1 \lambda_2 \lambda_3 = \frac{1}{v_2} = const , \qquad (51)$$

 λ_i 's correspond to changes in the sample's sizes at deformation and swelling. Besides, for isotropic swelling,

$$L_{0,sw} = \left(\frac{V}{V_0}\right)^{1/3} L_0,$$
(52)

$$\lambda_1 = \lambda \left(\frac{V}{V_0}\right)^{1/3} = \frac{\lambda}{v_2^{1/3}},\tag{53}$$

and, in view of Equation 51,

$$\lambda_2 = \lambda_3 = (v_2 \lambda_1)^{-1/2} = \frac{1}{\lambda^{1/2} v_2^{1/3}}.$$
(54)

Substitution of the obtained λ_i to Equation 36 yields

$$\Delta S_{el} = -\frac{R\nu_e}{2} \left(\frac{\lambda^2}{v_2^{2/3}} + \frac{2}{\lambda v_2^{2/3}} - 3 + \ln v_2 \right).$$
(55)

Then, Equation 43 with L_0 replaced by $L_{0,sw}$ gives for a gel (Flory, 1953)

$$\tau = \frac{RT\nu_e}{Vv_2^{2/3}} \left(\lambda - \frac{1}{\lambda^2}\right) =$$
(56)

$$=\frac{RT\nu_c}{V_0}v_2^{1/3}\left(\lambda-\frac{1}{\lambda^2}\right).$$
(57)

 $\mathbf{392}$

Experiments confirm, in general, the above relationships for polymer network deformations, which show a significant difference from the elastic behaviour of LMW compound samples (Treloar, 1970). In particular, for polymer networks, Hooke's law is valid for shear only (Equation 49) and fails upon one-axis tension (Equation 43) and under other kinds of deformation.

By virtue of the body's volume being invariant under deformation, Poisson's coefficient (Equation 25) for dry networks $\sigma \approx 0.5$, and (see Equation 30) the Young modulus is

 $E = 3\mu. \tag{58}$

It is remarkable that both tension (Equation 43) and shear (Equation 49) are defined by the same modulus, which can be treated as the universal modulus of polymer network elasticity, proportional to temperature.

The ability of polymer networks for large reversible deformations under a small load is due to a small value of the modulus. For example, for crosslinked rubber, the Young modulus is $E \simeq 0.8 \text{ kG/mm}^2$ while for steel it is $E \simeq 2 \cdot 10^4 \text{ kG/mm}^2$ (Sedov, 1983).

At the same time, the compressional modulus K of polymer networks is of the same order of magnitude than that of water (Treloar, 1970). This is associated with the fact that compressibility is due to the manifestation of intermolecular forces which are not specific for polymers; compressibility is by no means related to the network properties which manifest themselves under deformation.

Thus, polymer networks as well as LMW compounds are classified with practically incompressible matter, and the variations of their volume on tension and other kinds of deformation can be neglected (Treloar, 1970).

When an elastic wave (sound) with a wavelength substantially shorter that the sample's sizes propagates, a **longitudinal modulus** M appears, which may be imagined as the action of tension or compression of a thin flat infinite sample along the other axes (Ferry, 1961) (Figure 3.49d,3). In this case, both the shape and volume of the sample change. The stress/deformation ratio σ/γ gives the longitudinal modulus M related to the compressional and shear modulus by

$$M = K + \frac{4}{3}\mu. \tag{59}$$

For polymer networks, $K \gg \mu$, and M reflects, on the whole, compressibility. Indeed, under deformation of polymer networks, the energy component partially shows itself, some other deviations from the Gaussian network model have also been discussed. These phenomena are discussed in the special literature (Birshtein and Ptitsyn, 1964; Dušek and Prins, 1969).

3.5.2. State equations

If a network polymer is brought into a contact with a LMWL, the Gibbs potential in the system ΔG changes, the variation comprising two parts

$$\Delta G = \Delta G_m + \Delta G_{cl} \tag{60}$$

(cf. Equation 3.1–111).

The first summand is the change of G due to the mixing of LMWL with polymer (see Equation 3.1-31), while the second one ΔG_{el} reflects the change in the network

entropy under molecular branch deformation due to LMWL molecules penetrating into the polymer network as well as due to an applied external stress. Neglecting the energy component,

$$\Delta G_{el} = -T \,\Delta S_{el},\tag{61}$$

and, in view of Equation 36,

$$\Delta G_{el} = \frac{\nu_e RT}{2} \left[\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 - \ln(\lambda_1 \lambda_2 \lambda_3) \right]. \tag{62}$$

This equation holds true for **sparse** networks (with a low concentration of crosslinks). In the absence of the external forces, swelling proceeds isotropically, and

$$\lambda = \lambda_i = \left(\frac{V}{V_0}\right)^{1/3} = v_2^{-1/3}.$$
(63)

In the absence of the external stress, the change of the LMWL's chemical potential in a swollen gel is expressed (Flory, 1953) through

$$\Delta \mu_{1} = \left(\frac{\partial \Delta G_{m}}{\partial n_{1}}\right)_{T,P} + \left(\frac{\partial \Delta G_{m}}{\partial \lambda}\right)_{T,P} \left(\frac{\partial \lambda}{\partial n_{1}}\right)_{T,P}$$

$$= RT \left[\ln(1-v_{2}) + v_{2} + \chi_{1}v_{2}^{2} + \bar{V}_{01}\frac{\nu_{e}}{V_{0}}\left(v_{2}^{1/3} - \frac{v_{2}}{2}\right)\right]$$
(64)

for a tetrafunctional network with f = 4. In a more general case,

$$\Delta \mu_1 = RT \left[\ln(1 - v_2) + v_2 + \chi_1 v_2^2 + \bar{V}_{01} \frac{\nu_e}{V_0} \left(v_2^{1/3} - \frac{2v_2}{f} \right) \right].$$
(65)

The absence of the multiplier $(1 - z^{-1})$ before v_2 in Equations 64 and 65 in comparison with Equation 3.1-50 is owing to the fact that the network polymer should be regarded as a giant macromolecule with $z \to \infty$.

The component concentrations in gel are often expressed in so-called ground mole fractions

$$x_{1}^{*} = \frac{\frac{\overline{M}_{1}}{M_{1}}}{\frac{\overline{m}_{1}}{M_{1}} + \frac{\overline{M}_{2}}{M_{2}}}, \qquad x_{2}^{*} = 1 - x_{1}^{*}, \tag{66}$$

where m_1 and M_1 are the overall mass and molecular weights of the LMWL, m_2 is the weight of the polymer, M_2 is the molar weight of polymer chains between crosslinks. The temperature independence of x_i^* is their advantage. M_2 is often used to express the effective number of chains per unit volume in a dry polymer

$$\frac{\nu_c}{V_0} = \frac{\varrho_2}{M_2}.\tag{67}$$

In this case, with certain detalization of the model,

$$\Delta \mu_1 = RT \left[\ln x_1^* + x_2^* + \chi_1 x_2^{*2} + \frac{1}{z} \left(A \eta x_2^{*1/3} - B x_2^* \right) \right], \tag{68}$$

where z is the number of lattice sites in one polymer branch (see Equation 3.1-1), the structural factor A expresses the network functionality

$$A = 1 - \frac{2}{f}.\tag{69}$$

For the volume factor B, Dušek and Prins (1969), and Rehage (1977) propose values from 0 to 1. The memory factor (Dušek and Prins, 1969) is

$$\eta = \overline{h^2} / \overline{h_{\theta}^2},\tag{70}$$

where $\overline{h^2}$ is the mean square end-to-end distance of network chains (without external load). $\overline{h_{\theta}^2}$ is the mean square distance between the ends of free (not fixed) chains with $M = M_2$ surrounded by similar chains (in the unperturbed θ state).

If crosslinking is performed in a dry polymer (rubber vulcanization, radiation, etc.), then $\eta \approx 1$. Crosslinking of chains in solution is a different thing (Dušek and Prins, 1969).

Introduction of the constants A and B is associated with an uncertainty in the definition of the network structure, and different versions of theory assign them different values.

The state equation of a swollen network is also written as

$$\Delta \mu_1 = RT \left[\ln(1 - q^{-1}) + q^{-1} + \chi_1 q^{-2} + \nu \tilde{V}_{01} \left(A \eta q^{-1/3} - B q^{-1} \right) \right], \tag{71}$$

and the chemical potential of a crosslinked polymer per segment is

$$\frac{\Delta\mu_2}{z} = RT\left\{\chi_1 q^{-2} - q^{-1} + \nu \bar{V}_{01}\left[\eta\left(\frac{q^{2/3}}{2} + q^{-1/3} - \frac{3}{2}\right) + \frac{\ln q^{-1} + q^{-1}}{2}\right]\right\}$$
(72)

(Dušek and Patterson, 1968), where $q = 1/v_2 = V/V_0$ is the volume degree of network swelling, $\nu = \nu_e/V_0$ is the volume concentration of network chains.

The swollen polymer network is in equilibrium with individual LMWL provided that

$$\Delta \mu_1 = \Delta \mu_{1sw} = 0, \quad T, P = const , \tag{73}$$

where the subscript 's' means equilibrium swelling.

Substituting the expression for $\Delta \mu_1$ from Equations 64, 65, 68, or 72 into Equation 73 and solving it with respect to x^*_{1sw} (or v_{1sw}), we obtain a state equation for gel

$$\mathbf{r}_{1,\mu\nu}^{*} = f(T). \tag{74}$$

The plot of this dependence in the T vs x_{1sw}^* (or x_{2sw}^*) coordinates is called a **swelling curve**, which is the state diagram for the NP+LMWL system. Its slope shows the character of the gel behaviour with temperature: swelling or compression. The slope can be determined from rather general considerations (Rehage, 1964a).

Write the condition of gel-LMWL phase equilibrium as

$$d\mu_1 = d\mu_0 \tag{75}$$

(cf. Equation 1.2-30).

In partial derivatives, under P = const, it takes the form

$$\left(\frac{\partial\mu_1}{\partial T}\right)_{x_{1sw}^*,P} dT + \left(\frac{\partial\mu_1}{\partial x_{1sw}^*}\right)_{T,P} dx_{1sw}^* = \left(\frac{\partial\mu_{01}}{\partial T}\right)_P dT$$
(76)

or, in view of Equations 1.1.1-21,-23,-35,

$$-S_{1sw} dT + \left(\frac{\partial \mu_1}{\partial x_{1sw}^*}\right)_{T,P} dx_{1sw}^* = -\bar{S}_{01} dT,$$
(77)

whence

$$\left(\frac{\partial x_{1sw}^*}{\partial T}\right)_P = \frac{\Delta \bar{S}_{1sw}}{\left(\frac{\partial \mu_1}{\partial x_{1sw}^*}\right)_{T,P}},\tag{78}$$

where

$$\Delta \bar{S}_{1sw} = \bar{S}_{1sw} - \bar{S}_{01}. \tag{79}$$

It follows from the equilibrium condition (Equation 73) that

$$\Delta \mu_{1sw} = \Delta \bar{H}_{1sw} - T \,\Delta \bar{S}_{1sw} = 0 \quad \text{and} \quad \Delta \bar{S}_{1sw} = \frac{\Delta H_{1sw}}{T}.$$
(80)

Substituting Equation 80 to Equation 78 yields

$$\left(\frac{\partial x_{1sw}^{*}}{\partial T}\right)_{P} = \frac{\Delta H_{1sw}}{T\left(\frac{\partial \Delta \mu_{1}}{\partial x_{1sw}^{*}}\right)_{T,P}},\tag{81}$$

where $\Delta \bar{H}_{1sw}$ is the dilution enthalpy on saturation:

$$\Delta \bar{H}_{1sw} = \bar{H}_1(x_{1sw}^*) - \bar{H}_{01}, \quad T, P = const ,$$
(82)

 $\bar{H}_1(x^*_{1sw})$ is the partial molar enthalpy of LMWL in saturated gel, \bar{H}_{01} is the molar enthalpy of LMWL.

According to the accepted model, the crosslinks are points in the structural respect, so the NP+LMWL in its swollen state is a single phase. As in the one-phase (stable and metastable) region

$$\left(\frac{\partial \Delta \mu_1}{\partial x_{1sw}}\right)_{T,P} > 0, \tag{83}$$

then the slope of the swelling curve is defined by the sign of $\Delta \bar{H}_{1sw}$. For very good solvents, $\Delta \bar{H}_{1sw} < 0$ (an exothermic mixture), and the gel contracts with rising temperature according to Equation 81 (Figure 3.50). For poor solvents, $\Delta H_{1sw} > 0$ (an endothermic mixture), and increasing temperature leads to an additional gel swelling (Figure 3.51). For an athermic mixture, $\Delta \bar{H}_{1sw} = 0$, and the saturation concentration x_{1sw}^* is temperature independent.



Figure 3.50. Swelling curves of network polystyrene in chlorobenzene ($\chi_1 = 0.441$ at $T = 50^{\circ}$ C). The average polymerization degree of branches is z = 463 (1), 524 (2), 833 (3), 1030 (4), 1170 (5), 2520 (6), 3580 (7) (Rehage, 1964b, 1977) [Reprinted with permission from: G.Rehage. Berichte der Bunsengeselschaft Phys. Chem. 81 (1977) 969 979. Copyright © 1977 by Steinkopft Publishers Damstedt]



Figure 3.51. Swelling curves of network polystyrene in cyclohexane ($\chi_1 = 0.590...0.704$ depending on polymer concentration, $T = 50^{\circ}$ C). The average polymerization degree of branches is z = 191 (1), 437 (2), 667 (3), 855 (4), 1080 (5) (Rehage, 1964b, 1977) [Reprinted with permission from: G.Rehage. Berichte der Bunsengeselschaft Phys. Chem. **81** (1977) 969 979. Copyright © 1977 by Steinkopft Publishers Damstedt]

Experimental results show the sign at $(\partial x_{1sw}^*/\partial T)$ to be really defined by the sign at $\Delta \bar{H}_{1sw}$, i.e. the one-phase system condition (Equation 83) is fulfilled.

If the swelling curve intersects the glass temperature of the P+LMWL system, it shows a bend (Rehage, 1964c, 1977).

If there is a liquid-liquid phase separation region in a certain temperature range (eg. with a UCST), then the swelling curve of the NP+LMWL system on the state diagram goes to the right of the phase separation region (Figure 3.52).

If, for some reason, the density of crosslinks ν increases with time, a part of LMWL molecules transfers from the gel to the pure liquid phase (gel syneresis, plasticizer sweating) (see Figure 3.52).



Figure 3.52. Phase separation region of the system (linear polystyrene)+cyclohexane for a finite molecular mass of polystyrene (1), at $M \rightarrow \infty$ (2), (C are critical points, dashed lines are spinodals). Swelling curves of (network polystyrene)+cyclohexane with an increasing density of crosslinks $\nu_1 < \nu_2 < \nu_3$ (3-5) (Rehage, 1977) [Reprinted with permission from: G.Rehage. Berichte der Bunsengeselschaft Phys. Chem. **81** (1977) 969 979. Copyright © 1977 by Steinkopft Publishers Danistedt]

For equilibrium swelling (saturation) of gel with LMWL, it follows from Equations 73 and 64 that

$$-\ln(1-v_{2s}) - v_{2s} - \chi_1 v_{2s}^2 = V_{01} \frac{\nu_e}{V_0} \left(v_{2s}^{1/3} - \frac{v_{2s}}{2} \right).$$
(84)

In the case of a low degree of crosslinking, when $M_2 \ge 10^5$, in a good solvent $v_{2s}^{1/3} \gg v_{2s}$. By neglecting the term with v_{2s} in the right-hand side and the higher terms of logarithm expansion in the left-hand side, with $q_s = v_{2s}^{-1}$ Equation 84 transforms to the form:

$$q_s^{5/3} \approx \frac{V_0}{V_{01}\nu_e} \left(\frac{1}{2} - \chi_1\right)$$
(85)

(Flory, 1953).

See section 6.2 for how to determine the temperature dependence $\chi_1 = \chi_1(T)$ for the (network PVA)+water system from swelling data.

The further improvement of the theory of NP+LMWL systems (Flory and Tatara, 1975) followed the path of modifying expressions for ΔG_{el} and ΔG_m in Equation 60.

To get a better fit of the theoretical analytical expressions to experimental data on the elasticity problem of real network polymers, Mooney (1940) and Rivlin (1948abcd) have proposed an additional term to the potential ΔG_{el}

$$\Delta G_{cl} = C_1 \left(I_1 - 3 - \ln I_3^{1/2} \right) + \Delta G_{MR} \tag{86}$$

with

$$\Delta G_{MR} = C_2(I_2I_3^{-1} - 3) = C_2(\lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2} - 3), \tag{87}$$

where $C_1 = \nu_e RT/2$ (see Equation 62), C_2 is a parameter depending on the network structure and temperature, I_i are the deformation invariants (Sedov, 1983)

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2,$$

$$I_{2} = \lambda_{2}^{2} \lambda_{3}^{2} + \lambda_{3}^{2} \lambda_{1}^{2} + \lambda_{1}^{2} \lambda_{2}^{2},$$

$$I_{3} = \lambda_{1}^{2} \lambda_{2}^{2} \lambda_{3}^{2}.$$
(88)

Formula 87 is based on no molecular model, it is just an empirical adjusting expression. Further modification following the same path leads to the expression (Flory and Tatara, 1975)

$$\Delta G_{MR} = C_2 \left(I_2 I_3^{-1+m/2} - 3 \right), \tag{89}$$

where m is an adjustable parameter.

Another modification of ΔG_m in Equation 60 is associated with cancellation of the concentration independence of χ_1 .

In the case of a simple single-axis deformation of the sample, the total potential change is written in view of Equation 54 as

$$\Delta G = RT(n_1 \ln v_1 + n_2 \ln v_2 + \chi n_1 v_2) + C_1(\lambda^2 + 2v_2^{-1}\lambda^{-1} - 3)$$

$$+ C_2(v_2^{-m}\lambda^{-2} + 2v_2^{1-m}\lambda - 3) + 2C_3 \ln v_2,$$
(90)

where $C_3 = C_1/2$ (for a tetrafunctional network). Then (Flory and Tatara, 1975)

$$\Delta \mu_1 = \left(\frac{\partial \Delta G}{\partial n_1}\right)_{T,P,L} = \bar{V}_{01} \left(\frac{\partial \Delta G}{\partial V}\right)_{T,P,\lambda} \tag{91}$$

$$= RT\left(\left[\ln(1-v_2)+v_2+\chi v_2^2\right] + B\left\{\left(\lambda^{-1}-\frac{v_2}{2}-\frac{C_2}{C_1}v_2^{2-m}\left[(1-m)\lambda-\frac{m}{2v_2\lambda^2}\right]\right)\right\}\right)$$

where $B = 2C_1 V_{01} / V_0 RT$, $\chi = \bar{\chi} + n_1 v_2^{-1} \partial \bar{\chi} / \partial n_1$.

As a result of experiments on the (network PDMS)+benzene system (Flory and Tatara, 1975), it was established that the adjustable parameter m = 1/2. Then, for swelling in the absence of an external force, including Equations 63 and 73, the equation

$$\frac{B}{4}\frac{C_2}{C_1}v_{2s}^{7/6} - B\left(v_{2s}^{1/3} - \frac{v_{2s}}{2}\right) = \ln(1 - v_{2s}) + v_{2s} + \chi v_{2s}^2$$
(92)

holds good.

The concentration dependence of the interaction parameter χ , obtained from experimental data according to Equation 92, matches that of the (linear PDMS)+benzene system (see subsection 3.6.2, Figure 3.79).

In the NP+LMWL system (a good solvent), the molecular branches are repelled from each other due to the long-range interactions (cf. subsection 3.1.1), but the crosslinks bring them into contact. The situation that arises is similar to the overlap threshold on the dilute/semidilute solution interface provided that the length of the macromolecules in them is equal to that of the gel branch in the same solvent.

Thus, the segment concentration in gel must correspond to that in the coil overlap threshold, $c = c^*$ (see Equations 3.1-22 and 3.1-142),

$$c = k(f)c^{*} = k(f)N^{-4/5}\beta^{-3/5}A^{-6/5},$$
(93)

where c^{-} is the crossover between dilute and semidilute concentrations, k is a first-order factor, depending on the functionality f of a branch point and gel preparation conditions.

Relationship 93 expresses Flory's c^* theorem of gels (Flory, 1953; de Gennes, 1979). This is the very reason why, in gel, the end-to-end distance ξ of a network chain is established equal to the screening length ξ in semidilute solutions of linear macromolecules (cf. section 3.3).

As in the case of a single chain, a good quality of the gel state equations in the mean field approximation (Equations 64, 65, 68, 72, 92) is explained by compensation of the errors corresponding to the neglect of fluctuation correlation of segment concentration in ΔG_m and the Gaussian character of the branch distribution in ΔG_{el} (see Equation 60).

3.5.3. Phase separation in gels

In some particular cases (large values of χ and ν), the $\Delta \mu_1$ vs q^{-1} (or v_2) dependence has two maxima (correspondingly, two minima on $\Delta \mu_2$ vs q^{-1}) (Dušek and Patterson, 1968; Dušek and Prins, 1969).

Such a shape of the curves $\Delta \mu_1$ (and $\Delta \mu_2$) points to the possibility of existence of two phases of a network polymer with different conformations of network chains. In equilibrium, the condition

$$\Delta \mu_{1In} = \Delta \mu_{1IIn},$$

$$\Delta \mu_{2In} = \Delta \mu_{2IIn}, \quad T, P = const$$
(94)

must be satisfied, where the subscripts 'n' denote the network and its different states ('I' and 'II') differing in the network chain conformation.

Little is known on the morphological realization of this separation kind. Most likely, the separation proceeds in small volumes of the system and leads to a great heterogeneity in the gel structure. Such a separation is called **microsyneresis**.

While χ (temperature) continuously changes, conditions 94 give rise to a phase transition, which sharply changes the network chain conformation, which, in turn, leads to a significant decrease (or increase) in the gel volume — a so-called collapse (or overswelling, superswelling) of gels.

Of special interest is the case of $P \neq 0$ (when polymer is placed into a fixed volume accessible to LMWL molecules). Then, the equality between the chemical potentials of LMWL in the network and outside it is due to the LMWL transport into the network, which causes a pressure increase in the gel by

$$\pi = P - P_0,\tag{95}$$

where P_0 is the initial pressure in the gel and the pressure of LMWL in equilibrium with the gel (Surdutovich et al., 1972).

In this case, the situation is similar to a solvent and a solution separated with a semipermeable membrane (see subsection 1.2.2).

Considerations similar to those given in subsection 1.2.2 yield

$$\pi = -\frac{\Delta\mu_1}{\bar{V}_1} \tag{96}$$

and, together with Equation 64 (as an example),

$$\pi = -\frac{RT}{\bar{V}_1} \left[\ln(1 - v_2) + v_2 + \chi_1 v_2^2 + V_{01} \frac{\nu_e}{V_0} \left(v_2^{1/3} - \frac{v_2}{2} \right) \right]$$
(97)

(Tanaka, 1979).

The π/RT vs v_2 dependence, in the general case, has the form shown in Figure 3.53a (Tanaka, 1978, 1979).



Figure 3.53. Dependence of the gel osmotic pressure on v_2 (a) and the state diagram of the NP+LMWL system at $\pi = 0$ (b). ABDIJM is the swelling curve, *IECFJ* is the coexistence curve of two states of gel, *KGCHL* is the curve at which $(\partial \pi / \partial v_2) = 0$ (Tanaka, 1979) [Reprinted from: Polymer 20 (1979) 1404–1412. Copyright © 1979 with kind permission of Elsevier Science – NL, Sara Burgerhartstraat 25. 1055 KV Amsterdam, The Netherlands]

By analogy with the state diagrams of other systems (one-component liquid-vapour, see Figure 1.4: binary systems liquid-liquid, LMW compounds, see Figure 1.5; P+LMWL, see Figures 3.2, 3.3, and 3.9), Figure 3.53b shows the following curves in the T vs v_2 coordinates: the coexistence curve of two gel states IECFJ, the curve at which $(\partial \pi/\partial v_2) = 0$ (KGCIIL) close to the spinodal (see subsection 3.5.4), and the swelling curve IDBA. The curve ABDIJM (see Figure 3.53b) defines the equilibrium isotherm of the NP+LMWL system at $\pi = 0$, i.e. under conditions of free swelling (or contraction) of the polymer network. This curve is a model one, for example, for the experimental swelling-contraction

curve obtained on the network PAA+water+acetone system (Tanaka, 1979) (Figure 3.54, curve 1). It is seen from this figure that an abrupt change in the gel volume is really



Figure 3.54. Swelling curves for the (network PAA)+water+acetone system. Φ/Φ^* is the volume/initial polymer concentration ratio. Conditions for gel synthesis: 5 g of acrylamide and 0.133 g of N, N'methylene-bis-acrylamide were dissolved in 100 ml water, 40 mg of ammonium persulphate acting as the polymerization initiator, 40 μ l tetramethylethylenediamine in 25 ml of gel acting as the reaction regulator. Curve 1: the gel ripened for 30 days; 42% of acetone is contained in the LMWL mixture. Curve 2: the gel ripened for 3 days; the LMWL mixture contains 40% of acetone. The ratios $\Phi/\Phi^* < 1$ and > 1 correspond to swelling and contraction of the source gel, respectively (Tanaka, 1979) [Reprinted from: Polymer 20 (1979) 1404-1412. Copyright (c) 1979 with kind permission of Elsevier Science - NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Nertherlands]

observed at a certain temperature. Such a conformational transition of the gel molecular branches is similar to the coil-globule transition in a dilute solution (see section 3.4).

The internal structure of another gel sample (Figure 3.54, curve 2) does not correspond to the loop π vs v₂ dependence, and its swelling curve shows no break.

At the temperatures and concentrations enclosed by the curve IECFJ (see Figure 3.53b), the coexistence conditions of two gel states with different chain conformations in a closed space are realized. Eg. for $T = T_2$, the value of π is determined by the ordinate of the straight line EF drawn on the isotherm T_2 (see Figure 3.53a) according to Maxwell's rule (Equation 1.2-43).

Thus, in the NP+LMWL system, two important parameters, χ and the crosslinks concentration ν , play a chief role in phase separation: their increase promotes separation (see Equations 64, 65, 68, 72, 92, 97). Therefore phase separation in gels may occur in the presence of that LMWL which is a very good solvent for the corresponding linear polymer.

Moreover, in the course of the initiated phase separation, a local volume reduction

takes place, which leads to an increase in the crosslinks concentration and, further, to changes in the microphase separation process. The final pattern of phase separation will, therefore, depend on the kinetics of the process and the appearing morphology when surface phenomena begin to manifest themselves (Flory, 1960; Dušek, 1967, 1971; Dušek and Patterson, 1968; Dušek and Prins, 1969).



Figure 3.55. Phase separation during crosslinking of linear polymer branches of a very large MW in solution. Flory-Huggins' interaction parameter $\chi_1 = 0.45$, NC is the segment concentration in the network's molecular branches, C is the segment concentration at the crosslinks. 'a' is the configurative point's trajectory in the course of crosslinking; 'b' is the cloud-point curve (the boundary of the phase separation region), 'c' is the phase coexistence curve at different stages of polymer chain crosslinking (a). Phase separation in the process of 3D copolymerization in an inert solvent. The interaction parameter of NP+(monomer+diluent) $\chi_1 = 0.45$, 'a' is the configurative point's trajectory during copolymerization, NC, C, b, c are as in p. a (b) (Dušck, 1971) [Reprinted with permission from: K.Dušek. Chem. zvesti **25** (1971) 184-189. Copyright © 1971 Slovak Academic Press Ltd.]

Shown in Figure 3.55 are the results obtained by Dušek (1971) for some model systems, where phase separation occurs in the process of crosslinking of linear macromolecules with a very large M in solution (Figure 3.55a) and in the process of 3D copolymerization of two monomers with two (NC) and three (C) active centres (Figure 3.55b).

In the first case, crosslinking proceeds at a constant LMWL concentration, i.e. the configurative point moves along the straight line *a* parallel to the NC-C side of the composition triangle. The system remains homogeneous until the configurative point intersects the solid curve *b* (the boundary of the phase separation region), an analogue of the cloud-point curve in the P+LMWL system (cf. Figures 3.11–3.13). The dashed lines *c* are the phase coexistence curve (cf. Figures 3.11–3.13 as well). As the crosslinking progresses, the volume of the network phase and the sizes of branches decrease, which causes a transmission of the point corresponding to the concentrated phase, to the coexistence curves (see the empty circles in Figure 3.55a).

As the individual LMWL is in equilibrium with gel, the tie lines originate from the LMWL corner of the triangle.

Figure 3.55b represents a system comprising, at the initial instant, a monomer and an inert diluent (LMWL) which are thermodynamically equivalent to each other except for the ability for polymerization; so, one parameter $\chi_1 = 0.45$ characterizes the interaction in the NP+(LMWL+monomer) system.

At the initial instant of time, the polymer is absent, and the configurative point starts its motion from the LMWL corner, goes along the curve a, which reflects polymer formation and the increase of the crosslinked segments polymer fraction (C) (Dušck, 1971). As is seen from Figure 3.55b, phase separation proceeds at low degrees of conversion and leads to a heterogeneous gel structure. If, at some polymerization stage, the gel is separated from the LMWL and, further, the LMWL is evaporated from the whole sample volume, a porous material will appear with the porosity character (in particular, the pore sizes) defined by the conditions and duration of phase separation.

Indeed, with copolymerization of styrene with divinylbenzene as an example, Dušek (1971) has attained a good agreement between the turbidity and porosity of dried gel and the theoretical boundary of the phase separation region as functions of divinylbenzene concentration.

Obviously, ν -induced phase separation of gels with microcrystallites as the crosslinks must occur during their storage due to the increasing number of crystallization nuclei.

Mechanical stresses applied to gel samples shift the phase transition region (Dušek and Patterson, 1968; Dušek and Prins, 1969; Khokhlov, 1980ab).

Under conditions of uniaxial tension with a relative deformation λ (Dušek and Patterson, 1968),

$$\Delta \mu_1 = RT \left[\ln(1 - v_2) + v_2 + \chi_1 v_2^2 + \nu \dot{V}_{01} \left(\frac{\eta}{\lambda} - \frac{v_2}{2} \right) \right], \tag{98}$$

and the tangential stress is

$$\tau = \frac{RT\nu_e\eta}{V} \left(\lambda - \frac{1}{\nu_2\lambda^2}\right),\tag{99}$$

where λ is the deformed (swollen)/undeformed (dried) sample length ratio.

Relationships 98 and 94 lead to the state diagram shown in Figure 3.56.

Tension of a sample is equivalent to a decrease in pressure and promotes phase transition (cf. Figure 3.53a) (Dušek and Patterson, 1968; Dušek and Prins, 1969; Khokhlov, 1980a). Compression, on the contrary, corresponds to an increase in pressure and prevents phase transition (Dušek and Patterson, 1968; Dušek and Prins, 1969).

Singularities (first-order continuity breaks) must be observed on the τ vs λ dependences (Dušek and Patterson, 1968; Khokhlov, 1980b).

The influence of stress on the shifting of the collapse-swelling phase transition was observed experimentally (Starodubtsev et al., 1985ab) on polyacrylamide gels in the water+precipitant mixture at constantly changing tension strength (Starodubtsev et al., 1985b) and at a varying mixture composition at a constant compression (Starodubtsev et al., 1985a).

Under compression, the collapse-swelling transition occurs at a lower precipitant content (dioxane and methanol), but these data can hardly be compared with Figure 3.56, as the transition from the volume fraction of precipitant to χ_1 may turn to be difficult



Figure 3.56. State diagram of the NP+LMWL system under conditions of uniaxial tension up to the values of relative deformation η/λ : 0.050 (1), 0.025 (2), 0.02348 (3), 0.02106 (4), 0.01746 (5), 0.0133 (6) (Dušek and Patterson, 1968) [Reprinted with permission from: K.Dušek, D.Patterson, J. Polym. Sci. A 2 6 (1968) 1209 1216. Copyright © 1968]

(see subsection 3.2.3), especially in water-containing (aqueous) systems, where specific interactions may occur.

Britton et al. (1979) have shown that either compression or swelling of gel may occur in the NP+LMWL systems with specific interactions under stress. The specific interactions have been fixed and very carefully analyzed on the basis of the theory with the model of Gaussian network chains with the (network PVA)+water system as an example, upon tension.

3.5.4. Solution-gel transition

To describe the process of 3D polymerization of a polyfunctional monomer in solution, an approach has become popular based on the **percolation** problem.

First, consider bond percolation.

Let every site of Ising's lattice (see Figure 1.23) contain one structural element. There exists a **bond** between the neighbouring structural elements with a probability P_b . The character of bonds may be various: electrical conduction, elastic force, infection transfer. etc. Eg. Figure 3.57 shows a rectangular 16 × 16 lattice with randomly arising bonds with the probability $P_b = 0.2$; 0.4; 0.6, and 0.8 (Stanley et al., 1984).

Sets of linked structural elements are called **clusters** whose mean size ξ increases with P_b (see Figure 3.57).

At a certain value $P_{b,c}$, the upper and lower sides of the lattice are connected by bonded elements. A certain property is said to **percolate** from one side to the other. If the bonds define electrical conduction along them, and a power source is hooked up, the current traverses the lattice. If we expand the lattice itself, then the size of the cluster, through which percolation proceeds, also increases, and this cluster is called an **infinite cluster**. The value $P_{b,c}$ is referred to as the **percolation threshold**. Near it, the cluster size is


Figure 3.57. Bond percolation problem with the probability for bonds to arise between the neighbouring structural elements $P_b = 0.2$ (a), 0.4 (b), 0.6 (c), and 0.8 (d) (Stanley et al., 1980) [Reprinted with permission from: Dynamics of Synergetic Systems: Proc. Int. Symp. on Synergetics, Bullfeld, Germany, September 24 29, 1979 Ed. M.Haken. Copyright © 1980 by Springer-Verlag]

described by

$$\xi = \xi_0 |P_b - P_{b,c}|^{-\nu},\tag{100}$$

where ν is a critical index which coincides, by its physical meaning, with that of the fluctuation correlation length of the order parameter in critical phenomena (see Table 1.2).

At $P_b > P_{b,c}$, in the system modelled by the lattice, a property appears, which was absent at $P_b < P_{b,c}$, eg. electrical conduction. If elastic links between the structural elements are meant as bonds, at $P_b > P_{b,c}$ the system starts to show macroscopic elasticity.

The number of all the bonds in the infinite cluster (and the quantitative expression of the system property) rises as

$$Q = Q_0 |P_b - P_{b,c}|^{-\beta}, \tag{101}$$

where β is a critical index analogous to that of the order parameter in critical phenomena (see Table 1.2).

Table 3.2

Critical index values in the problem of bond percolation (Obukhov, 1985)

Critical	Space	dimens	ionality, d
index	2	3	6
β	5/36	0.45	1
ν	4/3	0.88	1/2

Table 3.2 collects the index values of the problem of bond percolation, calculated for lattices of different space dimensions d (Obukhov, 1985).

Another typical problem of percolation theory is the problem of node percolation. Assume that atoms of two kinds are randomly placed in Ising's lattice (see Figure 1.23c), where the black nodes are occupied by atoms with a permanent magnetic moment while the white ones are occupied by non-magnetic (diluent) atoms.

Obviously, at a high concentration of the magnetic atoms $(x \approx 1)$, they form an infinite cluster. On the contrary, at $x \ll 1$ the clusters of magnetic atoms are composed of small numbers of atoms, and the lattice as a whole possesses no magnetic moment.

At a certain concentration of magnetic atoms $x = x_c$, the cluster becomes infinite, and at $x > x_c$ the lattice acquires a spontaneous magnetization M. Relationships similar to Equations 100 and 101 will hold good for this problem as well

$$\xi = \xi_0' | x - x_c |^{-\nu}, \tag{102}$$

$$Q = Q_0' |x - x_c|^{\beta}.$$
 (103)

The given examples show a close analogy between the approach of percolation theory and the problems of critical phenomena theory.

However, the critical indices of the correlation length ν and of the order parameter β in the percolation problem (equal for both bond and node percolation) take the values characteristic for the mean field approximation: $\beta = 1$ and $\nu = 0.5$ for six-dimensional space $d^* = 6$ (cf. $d^* = 4$ for critical phenomena in Figure 2.44).

The solution-gel transition is modelled by the percolation problem, which combines node and bond percolations.

Let white nodes (molecules of a polyfunctional monomer) and black nodes (solvent molecules) be randomly placed in Ising's lattice (see Figure 1.23c). The bonds between the white nodes appear (polymerization) with a probability P_b depending on temperature and other conditions.

The formation of an infinite cluster from bonded white nodes means the solution (of macromolecules)-gel transition with the appearance of a new macroscopic property (clasticity) as every isolated bond possesses elasticity.

Let the probability of any node being white be the concentration of monomer molecules $P_n = x$, and the probability of a bond between two neighbouring monomers be P_b . Gel is

formed in those configurative points of the state diagram of "bond and node" percolation where the infinite cluster from connected white nodes (polymer molecules) exists.

By definition, $0 \le P_n \le 1$ and $0 \le P_b \le 1$ (Figure 3.58).



Figure 3.58. Problem of bond and node percolation: a model of gel formation during polymerization of a polyfunctional monomer in solution (Stanley et al., 1980; Efros, 1982;) [Reprinted with permission from: Dynamics of Synergetic Systems: Proc. Int. Symp. on Synergetics, Bullfeld, Germany, September 24-29, 1979 Ed. M.Haken. Copyright © by Springer-Verlag]

If $P_b = 1$, the infinite cluster appears at any P_n above the percolation threshold $P_{n,c}$ of the node problem, i.e.

$$P_{n,c} \le P_n \le 1. \tag{104}$$

If $P_n = 1$ (all the nodes are occupied by the monomer molecules),

$$P_{b,c} \le P_b \le 1 \tag{105}$$

must be satisfied for the infinite cluster to appear, where $P_{b,c}$ is the percolation threshold in the bond problem.

The function $P_{n,min} = f(P_b)$ is the boundary curve of the solution-gel transition (see Figure 3.58),

Formally speaking, the reaction of polymerization seems most effective at $T \to \infty$, and on the T vs v_2 state diagram (Figure 3.59), the asymptote $T \to \infty$ corresponds to v_{2n} responding to $P_{n,c}$. At lower $v_2 < v_{2,n}$, the curve Δ of the solution-gel transition has a positive first derivative. The specific shape of the curve Δ depends on the model's details. This curve ends on the binodal curve of the two-phase gel state due to the elasticity forces of the network chains and the interaction between polymer and LMWL (see above). The numerical values of $v_{2,B}^*$ have been determined for different types of lattice. It has also been established that the inequality $v_{2,B}^* < v_{2,c}$ holds true (de Gennes, 1979).

When the configurative point moves at a certain $v_2 = const$ within the range $v_{2,B}^* < v_2 < v_{2,n}$ and temperature decreases, the solution-gel transition proceeds at the point Q with the critical indices from the percolation problem (see Table 3.2).



Figure 3.59. State diagram of the NP+LMWL system. BiG is the binodal curve of phase separation. C is the critical point. Δ is the line of the solutiongel transition. v_{2n} is the polymer concentration corresponding to the node percolation threshold $P_{n,c}$: v_{2H}^* is the concentration at the configurative point where the transition curve Δ meets BiG (de Gennes, 1979)[Reprinted from: Pierre-Gilles de Gennes Scaling Concepts in Polymer Physics. Copyright © 1979 by Cornell University. Used by permission of the publisher, Cornell University Press]

3.5.5. Light scattering in gels

The morphology of gels, which are a framework of macromolecular branches filled with LMWL, leads to specific properties of structural fluctuations causing scattering of light and other kinds of radiation.

The motion equation of gel (as an elastic motion) (Equation 22.1 in Landau and Lifshitz, 1987) comprises an additional term owing to the friction forces arising when liquid moves over the elements of a polymer framework (Tanaka et al., 1973)

$$\varrho\ddot{u}_i = \frac{\partial\sigma_{ik}}{\partial x_k} - f\dot{u}_i. \tag{106}$$

This motion equation of an elastic medium is, in fact, the Newton second law. Its left-hand side is the product of the acceleration of a network unit cube by its mass (ρ is the network density). The right-hand side contains the sum of the forces acting on a unit cube. The first summand of the force corresponds to Equation 3 while the second one represents the friction force and is written like the Stokes formula: $\vec{F}_{fr} = -6\pi R \eta \dot{u}$.

The value f can be determined by measuring the flow rate of a liquid through the polymer network under a given pressure acting on the liquid only¹. In connection with the mentioned morphological peculiarity, four kinds of motion (modes) in structural fluctuations arise in gels in the general case: the network elements may move with $(\uparrow\uparrow)$ or against $(\uparrow\downarrow)$ the liquid as longitudinal or translational (transversal) waves (see Table 3.3).

Special analysis shows the modes in Table 3.3 to have significantly different relaxation periods which enables them to be distinguished.

 $^{^{1}}$ Polyelectrolyte superswelling gels, however, may not give such an opportunity to the experimenter *Editor's note*

Wave	Structural elements			
character	Liquid	Network	Liquid	Network
Longitudinal	I		III	
_	1	Ļ	1	1
Transverse	II		IV	
	1	Ļ	1	1

Table 3.3				
Modes of structural	fluctuations	in gels	(Tanaka,	1973)

The type I modes manifest themselves in inelastic light scattering. In experiments on polyacrylamide gels in water (Tanaka et al., 1973), their relaxation times are $\tau_r \sim 10^{-3}$ s for the fluctuations with a wave vector $|q| = 10^5$ cm⁻¹. The time mode of type III the fluctuations can be estimated using the frequency and relaxation time of sound waves in pure water, which are measured on the basis of the shift and bandwidth of Mandelshtam-Brillouin's spectrum of light scattering (Benedek and Greytak, 1965; Benedek and Fritsch, 1966; Tanaka et al., 1973). For the scattering angle $\vartheta = 90^{\circ}$, the oscillation period is $\sim 10^{-9}$ s and the relaxation time is $\tau_r \sim 10^{-7}$ s. Hence, if the evolution times of the type I fluctuations are considered, the type III modes in liquid are averaged, and the liquid can be regarded as a nonfluctuating medium. The transversal (translational) type II modes have the relaxation time of the same order of magnitude that the type I modes. The translational type IV modes propagate with a frequency $\omega = \sqrt{\mu/\varrho}$, where μ is the shear modulus.

The I and II type modes are of most interest for light scattering (see Figure 2.30).

Substitution of Equation 15 into motion equation 106 transforms it into the vector form

$$\rho \frac{\partial^2 \vec{u}}{\partial t^2} = \mu \Delta \vec{u} + \left(K + \frac{1}{3}\mu\right) \operatorname{grad} \operatorname{div} \vec{u} - f\left(\frac{\partial \vec{u}}{\partial t}\right).$$
(107)

It should now be used to find an expression for the spatial and temporal correlation of the shift vector $\langle u_j(\vec{r},t)u_j^*(\vec{r'},t')\rangle$ and its Fourier transform $\langle u_j(\vec{q},t)u_j^*(\vec{q'},t')\rangle$, where j = x, y, z. These quantities are proportional to the corresponding correlation functions of the dielectric constant of the material (see subsection 2.3.3).

The Fourier transform of the shift vector is introduced as

$$\vec{u}(\vec{q},\omega) = (2\pi)^{-5/2} \int_{-\infty}^{\infty} \vec{u}(\vec{r},t) \exp\left[-i(\vec{q}\cdot\vec{r}+\omega t)\right] d\vec{r} dt.$$
(108)

Due to gel isotropy, the fluctuations must not depend on the direction of the vector \vec{q} . Therefore, one axis (eg., the z axis) can be chosen in the q-space as the direction q:

$$\vec{q} = (0, 0, q).$$
 (109)

Substituting Equation 108 into Equation 109, we find

$$\varrho\omega^2 u_z - if\omega u_z - \varrho c_l^2 q^2 u_z = 0, \tag{110}$$

$$\varrho\omega^2 u_j - if\omega u_j - \varrho c_i^2 q^2 u_j = 0, \tag{111}$$

where j = x, y,

$$c_l = \sqrt{\frac{K + \frac{4}{3}\mu}{\varrho}} = \sqrt{\frac{M}{\varrho}},\tag{112}$$

$$c_t = \sqrt{\frac{\mu}{\varrho}}.$$
(113)

Equations 110 and 111 are the equations of longitudinal and transversal sound waves (respectively) propagating in the gel with velocities c_i and c_i , respectively, M is the longitudinal modulus (see Equation 59).

From this point on, no subscripts are required in Equations 110 and 111 due to their identical form.

Non-trivial solutions of u_j exist provided that

$$\varrho\omega^2 - if\omega - \varrho c^2 q^2 = 0, \tag{114}$$

whence

$$i\omega = -\frac{f}{2\varrho} \left(1 \pm \sqrt{\frac{1 - 4\varrho^2 c^2 q^2}{f^2}} \right) \tag{115}$$

$$= -(\tau_0)^{-1} \left(1 \pm \sqrt{1 - \omega_0^2 \tau_0^2} \right), \tag{116}$$

where

$$\tau_0 = \frac{2\varrho}{f},\tag{117}$$

$$\omega_0 = cq. \tag{118}$$

In the case of $\omega_0 \tau_0 \gg 1$, Equation 116 yields two frequencies

$$i\omega = \pm i\omega_0 - \tau_0^{-1},$$
 (119)

where $\omega_0 = cq$ is the frequency of sound with the wave vector q, τ_0 is the relaxation time due to the friction between the polymer framework and LMWL. More generally, $i\omega$ is a complex number which means a propagating wave. If $i\omega$ is a real number, the wave decays. It follows from Equation 116 that if $\omega_0\tau_0 > 1$ or $\omega_0\tau_0 \leq 1$, then the sound wave propagates or decays, respectively.

Consider the two limiting cases of Equation 107. In the first one, we neglect the summands of elastic deformation, then

 $\varrho\ddot{u} = -f\dot{u}.$

According to Equations 112 and 113, $c \approx 0$, $\omega_0 \approx 0$, and

$$i\omega = -\frac{2}{\tau_0} \equiv \tau_f^{-1},\tag{120}$$

where τ_f is the relaxation time of the fluctuations.

In the other limiting case, we neglect the acceleration term in Equation 107. Then, Equation 114 is written as

 $-if\omega - \varrho c^2 q^2 = 0,$

and, in view of Equation 117, we obtain

$$i\omega = -\frac{\tau_0 \omega_0^2}{2} \equiv \tau_s^{-1}.$$
 (121)

With an approximation

$$u \sim e^{iqz},\tag{122}$$

we have in this case

$$f\frac{\partial u}{\partial t} = G\left(\frac{\partial^2 u}{\partial z^2}\right),\tag{123}$$

where

 $G = K + 4/3\mu = M$ (124)

for a longitudinal wave and

$$G = \mu \tag{125}$$

for a tangential wave.

Equation 123 coincides, by its form, with Fick's second law for diffusion, i.e. the shift diffuses along the z axis with a diffusion constant

$$D = \frac{G}{f} = \begin{cases} M/f & \text{for a longitudinal wave,} \\ \mu/f & \text{for a tangential wave.} \end{cases}$$
(126)

Recall that the diffusion coefficient of macromolecules in solution is

$$D = \frac{kT}{\zeta},\tag{127}$$

where $\zeta = 6\pi\eta_0 \langle R_H \rangle$ (see Equation 3.3-88).

The denominators of Equations 126 and 127 are the same while the nominators differ: the diffusional motion of a macromolecule is caused by collisions with small molecules of the solvent which is directly associated with temperature, and the motion of the polymer network is caused by its elasticity.

Applying the Fourier transformation to Equation 123, we see that the fluctuation of the wave vector q decays with a constant

$$\tau_s^{-1} = \frac{Gq^2}{f}$$
(128)

(cf. Equation 3.3-98).

In the general case, the time correlation of the shift vector has the form

$$\left\langle u_j(\vec{q},t)u_j(\vec{q},0)\right\rangle = \left\langle u_j^2(\vec{q})\right\rangle \left[A_s \exp\left(-\frac{t}{\tau_s}\right) + A_f \exp\left(-\frac{t}{\tau_f}\right)\right],\tag{129}$$

where $A_s + A_f = 1$. Tanaka et al. (1973) prove that $|A_s/A_f| \gg 1$ and

$$\langle u_{z}(\vec{q},t)u_{z}(\vec{q},0)\rangle = \frac{VkT}{(2\pi)^{3}\left(K + \frac{4}{3}\mu\right)q^{2}}\exp\left[-\frac{\left(K + \frac{4}{3}\mu\right)q^{2}t}{f}\right]$$
(130)

and

$$\langle u_j(\vec{q},t)u_j(\vec{q},0)\rangle = \frac{VkT}{(2\pi)^3\mu q^2} \exp\left(-\frac{\mu q^2 t}{f}\right)$$
(131)

hold true for the longitudinal and transversal fluctuations, respectively; j = x, y.

The longitudinal and transversal fluctuations of the shear modulus cause time correlation functions of the electric field, which are measured by the heterodyne method (dynamic scattering of polarized and unpolarized light) (see Equation 2.3-32).

As measurements show (Tanaka et al., 1973), the relaxation time of the density of a PAA network is $\tau = (Dq^2)^{-1}$ with $D \approx 10^{-7}$ cm²/s while that of the thermal diffusion of water is $\tau_T = (D_T q^2)^{-1}$ with $D_T \sim 1.4 \cdot 10^{-3}$ cm²/s, whence it follows that thermal diffusion is faster than polymer network structure relaxation. Consequently, in the time scale characteristic for the fluctuations in polymer network structure, temperature can be regarded constant and the process is isothermal (not adiabatic, as in the case of Mandelshtam-Brillouin's scattering).

Accordingly, the constants K and μ in Equations 130 and 131 have their isothermal values as well.

At a distance l from a luminous gel volume V, the correlation of the electric field vector (the scattering light intensity) has the form

$$I_{\perp} = \langle E_{\perp}(\vec{q}, t) E_{\perp}(\vec{q}, 0) \rangle = I_{0\perp} \frac{k_0^4 \pi}{2l^2} \left(\frac{\partial \epsilon}{\partial \varrho} \right)_T^2 \varrho^2 \frac{VkT}{\left(K + \frac{4}{3}\mu\right)q^2} \exp\left[-\frac{\left(K + \frac{4}{3}\mu\right)q^2t}{f} \right]$$
(132)

4 5

and

$$I_{\perp}^{\parallel} = \left\langle E_{\perp}^{\parallel}(\vec{q},t)E_{\perp}^{\parallel}(\vec{q},0)\right\rangle = I_{0\perp}\frac{k_0^4\pi}{2l^2} \left(\frac{\partial\varepsilon_D}{\partial u_{xy}}\right)_T^2 \varrho^2 \frac{VkT}{\mu q^2} \exp\left[-\frac{\mu q^2 t}{f}\right]$$
(133)

for vertically polarized and depolarized light, respectively, ε_D and ε are the diagonal and off-diagonal elements of the dielectric constant tensor. The quantity $(\partial \varepsilon / \partial \varrho)_T$ can be obtained by measuring the gel refractive index n at its various concentrations ϱ , as $\varepsilon = n^2$. The quantity $(\partial \varepsilon_D / \partial u_{xy})$ can be obtained under shear deformation of gel u_{xy} , by measuring the depolarization of light crossing the gel along the axis z. The depolarized/polarized

light intensity ratio measured in the direct direction is defined as $I_D/I_P - (\epsilon_d/\epsilon)^2$ and, therefore, ϵ_D can be derived as a function of u_{xy} (Tanaka et al., 1973).

Thus, the ratios $(K + 4/3\mu)/f$ and μ/f can, in principle, be obtained from the time correlation of scattered light. The measured integral intensity of scattered light (see Equation 2.3 40) (whose theoretical value is calculated from Equations 132 and 133 at t = 0) gives the quantities $K + 4/3\mu$ and μ (cf. Equations 2.3-39,-40, 43,-48). Hence, all the elasticity parameters of the gel K, μ , and f can be determined by means of the polarized/depolarized scattering technique only.

Tanaka et al. (1973) have compared the elasticity moduli of 5% and 2.5% polyacrylamide gels in water, obtained by measuring the deformation of their cylindrical samples and by means of dynamic light scattering. The time correlations of scattered light were measured on a set of the homodyne spectroscopy of mixing, and the squared correlation function of the field was determined (see Equation 2.3-33).

Thus, the decay constant is

$$\Gamma = \frac{1}{\tau} = 2 \left[\frac{(K+4/3\mu)}{f} \right] q^2 \quad \text{and} \quad \Gamma = \frac{1}{\tau} = \frac{2\mu}{f} q^2 \tag{134}$$

for polarized and depolarized light scattering, respectively.

For cylindrical samples (see Figure 3.49d, 1, 2),

$$E = \frac{\Delta P}{\Delta l/l},\tag{135}$$

$$\sigma = \frac{\Delta d/d}{\Delta l/l}.$$
(136)

Measurements have shown that $\sigma \approx 0$, whence, in view of Equations 29-30,

$$K = \frac{E}{3},\tag{137}$$

$$\mu = \frac{E}{2}.\tag{138}$$

Hence, in this case, the measured Young modulus (Equation 135) enables K and μ to be determined from Equations 137 and 138.

Autocorrelation data were analyzed using the cumulant method (see subsection 3.3.2). See Figure 3.60 as an example. By fitting two cumulants to experimental data, $\bar{\Gamma}/2q^2 = 2.38 \cdot 10^{-7} \text{ cm}^2/\text{s}$ was found. The results obtained are recorded in Table 3.4.

The third row of Table 3.4 reports the value $D_{calc} = 2\mu/f$ calculated from the deformation data (μ) and the liquid rate of flow through gcl (f) (the first two rows).

For further checking of the theory of light scattering in gels, the dependence $\Gamma/2 = (2\mu/f)q^2 vs q^2$ was plotted (Figure 3.61, the experimental points). The dashed line is drawn using independent measurements of μ and f. A very good match between the two approaches (Figure 3.61 and Table 3.4) is seen.

Thus, optical mixing spectroscopy is a powerful tool for exploring gel structure and for experimental determination of the elasticity moduli and hydrodynamic interactions between the polymer network and liquid.



Figure 3.60. Experimental time correlation function for 5% polyacrylamide gel at 25°C and the scattering angle 90°. One channel corresponds to 10 μ s. The line provides the best fit to the experimental values (Tanaka et al., 1973) [Reprinted with permission from: T.Tanaka, L.O.Hocker, G.B.Benedek, J. Chem. Phys. **59** (1973) 5151-5159. Copyright © 1973 American Institute of Physics]

Table 3.4

Experimental data by mechanical methods and optical mixing spectroscopy on poly(acrylic amide) gels (Tanaka, 1973)

Parameters	Polymer concentration, %		
	5	2.5	
f, dyn s/cm ⁴	$(2.2 \pm 0.3) \cdot 10^{11}$	$(3.5 \pm 0.1) \cdot 10^9$	
2μ , dyn/cm ²	$(5.2 \pm 0.3) \cdot 10^4$	$(4.4 \pm 0.9) \cdot 10^2$	
$D_{\text{calc}} = 2\mu/f, \text{ cm}^2/s$	$(2.4 \pm 0.4) \cdot 10^{-7}$	$(1.3 \pm 0.3) \cdot 10^{-7}$	
$D_{\rm exp} = l^2/2q^2$, cm ² /s	$(2.4 \pm 0.1) \cdot 10^{-7}$	$(1.6 \pm 0.1) \cdot 10^{-7}$	

Though μ and f can be measured independently by macroscopic methods, such measurements are laborious and time-consuming. More precise measurements of $2\mu/f$ in optical mixing spectroscopy are carried out in 2 minutes (Tanaka et al., 1973).

On the basis of the definition of the compressional modulus K (Equation 20) and the expression for π (Equation 97), we write (Tanaka et al., 1977)

$$K = v_2 \frac{\partial \pi}{\partial v_2}$$
(139)
$$= v_2 \frac{\partial}{\partial v_2} \left\{ -\frac{RT}{\bar{V}_{01}} \left[\ln(1 - v_2) + v_2 + \left(\beta + \frac{\alpha}{RT}\right) v_2^2 + V_{01} \frac{\nu_c}{V_0} \left(v_2^{1/3} - \frac{v_2}{2} \right) \right] \right\}$$
$$= RT \left[\frac{\nu_e}{V_0} \left(\frac{v_2}{2} - \frac{v_2^{1/3}}{3} \right) + \left(\frac{1}{1 - v_2} - \frac{2\beta}{R} \right) \frac{v_2^2}{\bar{V}_{01}} \right] - \frac{2\alpha}{\bar{V}_{01}} v_2^2,$$

where $\chi_1 = \beta + \alpha/RT$ is accepted (Equation 3.1–42).



Figure 3.61. Dependence of the relaxation rate $\Gamma/2 = (2\mu/f)q^2$ and the time correlation of scattered light in 5% polyacrylamide gel at 25°C of q^2 (circles). The line shows the $(2\mu/f)q^2$ dependence with μ , f measured in independent experiments (mechanics) (Tanaka et al., 1973) [Reprinted with permission from: T.Tanaka, L.O.Hocker, G.B.Benedek, J. Chem. Phys. **59** (1973) 5151 5159. Copyright © 1973 American Institute of Physics]

The absence of the minus in Equation 139 in comparison with Equation 20 is due to an obvious requirement for K to be positive in both cases.

If the expression

$$\mu = \frac{\nu_r RT}{2V_0} \left(v_2 + \frac{v_2^{5/3}}{2} \right) \tag{140}$$

is accepted for the shear modulus of a swollen gel (Flory, 1953; Tanaka et al., 1977), then we can write for the longitudinal modulus (Equation 59)

$$M = K + \frac{4}{3}\mu = a(T - T_{sp}), \tag{141}$$

where

$$a \equiv R \left[\frac{\nu_{\epsilon}}{V_0} \left(\frac{7}{6} v_2 - \frac{1}{3} v_2^{1/3} + \frac{1}{3} v_2^{5/3} \right) + \left(\frac{1}{1 - v_2} - \frac{2\beta}{R} \right) \frac{v_2^2}{V_{01}} \right], \tag{142}$$

$$T_{sp} = \frac{2\alpha v_2^2}{aV_{01}}.$$
(143)

It is seen from Equation 141 that the longitudinal modulus M = 0 at $T = T_{sp}$.

It follows from Equation 132 that at M = 0 $(T = T_{sp})$, the intensity of light scattered on the longitudinal fluctuations of the gel structure $I \to \infty$ while the fluctuation lifetime $\tau_s \to \infty$ (Equations 124, 128), which defines a configurative point on the **spinodal**. This is a difference between the spinodal conditions for gel (M = 0) and for solution (K = 0), i.e. $(\partial \pi / \partial v_2) = 0$ (see Equation 139).



Figure 3.62. Scattered light intensity *I* and $\Gamma/q^2 = (K + 4\mu/3)/f$ for 2.5% polyacrylamide gel (Tanaka et al., 1977) [Reprinted with permission from: T.Tanaka, S.Ishiwata, C.Ishimoto. Phys. Rev. Lett. **38** (1977) 771-774. Copyright © 1977 by the American Physical Society]

If $K \gg \mu$, then $M \sim K$, and the spinodal conditions for gel and solution are close. However, for PAA gels, the closeness $M \sim K$ is not the case (see Equations 137 and 138).

Figure 3.62 contains experimental data for 2.5% polyacrylamide gels (acrylamide+bis-acrylamide+water=37.5:1:1500 wt fractions) at a scattering angle of 90° (Tanaka et al., 1977).

According to Kawasaki (1970a)-Ferrel's (1970) mode-mode coupling theory (see subsections 2.35 and 2.44 as well as: Flory, 1953), the curve Γ/q^2 is expressed as (Tanaka, 1976; Tanaka et al., 1977) (see Equation 2.4-73)

$$\frac{\Gamma}{q^2} = D = \frac{kT}{6\pi\eta_0\xi},\tag{144}$$

where the correlation length of fluctuations near the spinodal has the form

$$\xi = \xi_0 \left(\frac{T}{T - T_{sp}} \right)^{1/2}.$$
(145)

The same expression (Equation 144) holds true for solutions of LMW compounds and polymers near the spinodal as well (Chu and Schoenes, 1968; Berge et al., 1970; Lai and Chen, 1972) (cf. subsection 2.4.4 and section 2.5).

The given relationships relate to light scattering by one-phase gels.

We remark incidentally that the scattered light intensity in gels must be lower than that in solutions with other conditions being equal, as the development of polymer concentration fluctuations is restricted by the presence of crosslinks. So, gels may well be very transparent if, of course, the number of crosslinks does not exceed the threshold of ν -induced microphase separation.

The ν -phenomena of "fluctuation limitations" can explain a decrease in the scattered light intensity after the maximum in the course of 3D polymerization is reached (Volkova et al., 1987).

The approaches of colloidal optics are required for analysis of light scattering on heterogeneous gels. In particular, Rayleigh-Debye's approximation with the correlation function formalism finds application (see subsection 2.1.2) (Gallacher and Betterheim, 1962; Bueche, 1970; Pokrovski et al., 1976; Volkova et al., 1987).

In this approximation, Bueche (1970) has related the correlation function of the dielectric constant ε (Equation 2.1-73) to the fluctuations in the crosslinks density in gel $(\nu - \nu_0)$ and obtained the relationship

$$R_{\vartheta} = \frac{\pi^2}{2} \left(\frac{3}{2\pi n \lambda_0^5 \nu_0 v_2} \right)^{1/2} \left(\frac{\partial v_2}{\partial \nu} \right)_{\nu_0}^2 \frac{(n_p^2 - n_s^2)^2}{\sin^{3/2} \frac{\vartheta}{2}},$$
(146)

where n, n_p, n_s are the refractive indices of gel, polymer, and LMWL, respectively.

Experiments with polystyrene gels in benzene and PMAA gels in methylethylketone (Bueche, 1970) have confirmed the character of the dependences R_{ϑ}^{-1} vs $\sin^{3/2} \frac{\vartheta}{2}$ and R_{ϑ}^{-1} vs $\lambda_{0}^{5/2}$, but the corollary of Equation 146 ($R_{\vartheta} \to \infty$ at $\vartheta \to 0$) was not observed.

The parameters of the anisotropic elements of gel structure were determined from scattering depolarization $R_{0\perp}^{\parallel}$ (Donkersloot et al., 1967; Gouda et al., 1970).

The turbidity spectrum method (see subsection 2.1.5) is worthwhile applying to characterize the heterogeneous structure of gels (Sedlàček, 1967ab; Maslova, 1969; Masimov et al., 1983, 1984).

No object in polymer science gave and still does give rise to so much discussions and disputes as gels (jellies) and the gel state of polymers (Glikman, 1959; Papkov, 1974; Rogovina and Slonimski, 1974; Tager, 1978; Lipatov, 1984). Much stir were produced at the stage of definitions. In this connection, it should be noted that the present paragraph treats gel (jelly) in a sense narrower than Papkov's (1974, p. 12) definition:

Jellies are multicomponent systems comprising a high-molecular substance and LMWL (which predominates) and showing the ability for high-reversible deformation and the inability to flow,

i.e. jellies are considered as "such polymer solutions..., which have lost their fluidity".

This definition gives preference to the morphological properties, chiefly, to the mechanical ones. So, systems with different state equations (correspondingly, with different state diagrams), which are thought to describe one (?!) "gel-like state of polymers", are classified with jellies. The case at hand is the NP+LMWL system with state equations 64, 65, 68, 71, 72 (their state diagram are shown in Figures 3.53 and 3.59) (Ia jellies after Papkov) and the P+LMWL system with state equations 3.1-50,-51 (their state diagrams are shown in Figures 3.2, 3.3, and 3.9) with the configurative point inside the phase separation region and with kinetic features ("systems with incomplete phase separation") (jellies type II after Papkov, in Figures 1.5ab in Papkov, 1974).

We, in the context of section 3.5, give preference to thermodynamics and state equation regardless of the location of the configurative point and specific realization of the system's morphology (through the specific conditions of the phase separation kinetics). Our classification proves to be much more simple and natural. Disputes "about structure" always arise when the traditional approach of physical chemistry (a model of the body structure is designed with subsequent deriving of the relationships to be tested in experiment) is neglected. In the case of a satisfactory agreement between model predictions and experiment, the structure of this specific object is accepted to correspond to the model one. Otherwise, the model must be altered until a satisfactory agreement with experiment is reached.

Attempts to describe the structure and to define exhaustively the name of a system as a "thing in itself" are usually fruitless, and discussions of jellies have shown this once again.

If we stay in the framework of the traditional approach, state equations 64, 65, 68, 71, 72 reflect a specific model of the NP+LMWL system, which leads to the two summands ΔG_m and ΔG_{el} . As experiments agree with these equations, it means the **prescribed** model is close to the actual structure of the body which can, for example, be called **gel** or jelly It is known that, to reach better agreement between the state equations and experimental data, the model of the NP+LMWL system (and the details of the state equations) were changed, but its main points remained: the presence of crosslinks, the entropy term ΔG_{el} .

On the other hand, in different realizations of the P+LMWL state equations, concerning the location of the configurative point and the features of its motion on the state diagram, the system may show different morphological (in particular, mechanical) properties.

In the case of the spinodal separation mechanism, a spatial polymer framework appears in the system, and this system will show the high-clastic properties of a solid polymer body. Unlike the above model NP+LMWL system, this framework is composed not of **molecular network chains** but of much larger constructions, which can hardly be ascribed the entropy term ΔG_{el} .

Upon further motion of the configurative point to outside the phase separation region, the system will return to the structure of true solution.

Moreover, true solutions (both semidilute and concentrated), regarded in the time scale $t < T_r$, "legally" show gel properties in the sense of the appearance of the high-elastic properties.

Special discussion is required for gels where **molecular** network chains are crosslinked due to the local crystallization of fragments of polymer chains (jellies type Ib after Papkov).

In this case, we are dealing with crystallizing polymers only whose mixtures with solvent have the state diagram with a liquidus curve (in the simplest variant) (see section 6.1). On the other hand, the fact of crosslinking must lead to the state equations of gels (Equation 64 etc.). As soon as the state equations of the NP+LMWL system hold true for such systems (see section 6.2 for details), this attests to the independence of the two kinds of phase separation, according to Papkov's concept.

Gels with crystal fragments as crosslinks are, as a rule, **thermoreversible** due to the liquidus curve being intersected while the configurative point moves along the temperature axis.

In contrast to crosslinked gels, thermoreversible gels must possess the elastic modulus which is an extremal function of temperature: far from the melting temperature of crystallites, Equation 50 with $\nu = const$ holds good, while near this temperature, the reduction of the number of crosslinks ν will inevitably overcompensate for the temperature effect.

Discussion about the "one-phase or two-phase character" of gels prove to be absolutely fruitless without a state diagram (typical or, better, specific). Depending on the configurative point position on the state diagram, gels may be two-phase as well as one-phase which was discussed above.

Gels with crystallite crosslinks, naturally, are, in principle, two-phase ones with respect to the liquid-crystal phase separation, though crystallites may be "silent" as crystal bodies (fragments) within the resolving power of a specific analysis method (see section 6.2 for details). As to phase separation within the framework of the NP+LMWL system, this case amounts to the previous one.

3.6. Improvement of Flory-Huggins' lattice theory

3.6.1. Concentration dependence of Flory-Huggins' interaction parameter (the second approximation of the theory)

Flory-Huggins' classical theory has turned out to be improvable by assuming a certain type of the interaction parameter dependence on the concentration and MWD of a polymer.

In the second-approximation theories, the interaction parameter is denoted by the letter g. Then, the state equation has the form

$$\frac{\Delta G_m}{RT} = \varphi_0 \ln \varphi_0 + \sum_i \varphi_i p_i^{-1} \ln \varphi_i + g \varphi_0 \varphi.$$
⁽¹⁾

Most often, g increases with concentration which attests to the contribution to the interaction parameter of not only the closest neighbours in the lattice (cf. Equations 3.1-28 and 1.3-4). In terms of screening length and blobs (see subsection 3.1.1), it is equivalent to a decrease in the blob sizes with increasing concentration.

A general dependence of g on φ and T is derived from simple phenomenological considerations (Koningsveld, 1968). First of all,

$$\Delta \bar{G}_m = \Delta \bar{H}_m - T \,\Delta \bar{S}_m,\tag{2}$$

$$\left(\frac{\partial \Delta \bar{H}_m}{\partial T}\right)_P = \Delta c_P,\tag{3}$$

$$\left(\frac{\partial \Delta \bar{S}_m}{\partial T}\right)_P = \frac{\Delta c_P}{T}.$$
(4)

For most liquids, a linear temperature dependence of Δc_P is observed with the simplest approximation

$$\Delta c_P = (c_{P0} + c_{P1} T \varphi_0 \varphi). \tag{5}$$

Integration of Equations 3 and 4 in view of Equation 5 with subsequent substitution of $\Delta \bar{H}_m$ and $\Delta \bar{S}_m$ into Equation 2 leads to

$$\Delta \dot{G}_m = \left(H_1 + c_{P0}T + \frac{1}{2}c_{P1}T^2 \right) \varphi_0 \varphi - T(S_1 + c_{P0}\ln T + c_{P1}T) \varphi_0 \varphi, \tag{6}$$

where H_1 and S_1 are integration constants.

Then, the next approximation of a rather general form is introduced (Koningsveld, 1968)

$$\frac{\varphi_0 \ln \varphi_0 + \sum_i \varphi_i p_i^{-1} \ln \varphi_i}{\varphi_0 \varphi} = \sum_{k=0}^l P_k \varphi^k, \tag{7}$$

where all the coefficients are functions of MWD. Then, elimination of ΔG_m from Equations 1 and 6 with due account of Equation 7 leads to

$$Rg = c_{P0} - S_1 - R \sum P_k \varphi^k + \frac{H_1}{T} - \frac{1}{2} c_{P1} T - c_{P0} \ln T$$
(8)

or

$$g = \sum g_k \varphi^k. \tag{9}$$

It follows from these two equations that the temperature and concentration dependence of g are separated, and g = g(T) can be represented as the temperature dependence of the first term in Equation 9

$$g_0 = g_{01} + \frac{g_{02}}{T} + g_{03}T + g_{04}\ln T.$$
 (10)

The fourth term is less sensitive to T. The third one has a significant impact if Δc_P is a strong function of temperature, as it happens when the vapour-liquid critical point is approached (see section 3.8).

Often (when $T \ll T_c$), g_{03} and g_{04} either are negligible or compensate for each other: only the two first terms remain in Equation 10.

In a wide temperature range, function 10 provides the existence of UCST and LCST (cf. section 3.8) and explains all the observed kinds of liquid-liquid phase separation regions (see below).

If the concentration dependence $g = g(\varphi)$ is accepted in the absence of the MWD (the second approximation of the theory), then Equation 1, according to Equations 1.1.1–23, 3.1-50,-51, 3.2-4, 5, produces

$$\frac{\Delta\mu_0}{RT} = \ln(1-\varphi) + \left(1-p_n^{-1}\right)\varphi + \left[g - (1-\varphi)\frac{\partial g}{\partial\varphi}\right]\varphi^2,\tag{11}$$

$$\frac{\Delta\mu_i}{RT} = \ln\varphi_i + 1 - \frac{p_i\varphi}{p_n} - p_i(1-\varphi) + \left(g + \varphi\frac{\partial g}{\partial\varphi}\right)p_i(1-\varphi)^2 \tag{12}$$

(Koningsveld and Staverman, 1968b).

If we denote the expression in the brackets in Equation 11 as χ in order to have one form for Equations 11 and 3.2 4, then

$$\chi = g - (1 - \varphi) \frac{\partial g}{\partial \varphi}.$$
(13)

If χ is represented as a series

$$\chi = \sum \chi_k \varphi^k, \tag{14}$$

then Equations 9, 13, 14 yield a relationship among the coefficients of series 9 and 14

$$\chi_{k+1} = (k+1)(g_k - g_{k+1}) \tag{15}$$

(Koningsveld, 1968).

In view of the concentration dependence $g = g(\varphi)$, the conditions of the spinodal and critical state (Equations 3.2-2,-3) lead to the equations of the spinodal

$$\varphi_0^{-1} - 2g + 2(1 - 2\varphi)\frac{\partial g}{\partial \varphi} + \varphi_0 \varphi \frac{\partial^2 g}{\partial \varphi^2} = -\frac{1}{\varphi p_w}$$
(16)

and the critical state

$$\varphi_{0,c}^{-2} - 6\left(\frac{\partial g}{\partial \varphi}\right)_{c} + 3(1 - 2\varphi_{c})\left(\frac{\partial^{2}g}{\partial \varphi^{2}}\right)_{c} + \varphi_{0,c}\varphi_{c}\left(\frac{\partial^{3}g}{\partial \varphi^{3}}\right)_{c} = \frac{p_{z}}{\varphi_{c}^{2}p_{w}^{2}}$$
(17)

(Koningsveld, 1968, 1970b; Koningsveld and Staverman, 1968b; Rehage and Koningsveld, 1968).

If g is a function of temperature only, these equations reduce to Equations 3.2–9,-10. In the case of a linear dependence $g = g(\varphi)$, series 9 contains two summands

$$g = g_0 + g_1 \varphi. \tag{18}$$

Then, according to Equations 16 and 17, the spinodal equation is

$$2g_0 = (p_w\varphi)^{-1} + \varphi_0^{-1} + 2(1 - 3\varphi)g_1, \tag{19}$$

and

$$6g_1 = \varphi_{0,c}^{-2} - \frac{p_z}{\varphi_c^2 p_w^2} \tag{20}$$

holds true for the critical state.

For a quadratic dependence

$$g = g + g_1 \varphi + g_2 \varphi^2, \tag{21}$$

the spinodal equation

$$2g_0 = (1 - \varphi)^{-1} + (\varphi p_w)^{-1} + 2g_1(1 - 3\varphi) + 6g_2(1 - 2\varphi)\varphi$$
(22)

and the critical state equation

$$g_1 - g_2 + 4g_2\varphi_c = \frac{1}{6} \left[(1 - \varphi_c)^{-2} - \frac{p_z}{p_w^2 \varphi_c^2} \right]$$
(23)

are derived from Equations 16, 17.

It follows from Equations 16, 19, 22, and 3.2-9 that the polynary P+LMWL system has the same spinodal for polymers with different MWD but the same p_w , which coincides with the spinodal of the binary P+LMWL system with $p = p_w$ (see Figure 3.14).

The spinodal goes through the critical point, whose position, in turn, depends on p_z and p_w . It follows from Equations 17, 20, 23, and 3.2-11 that the more the p_z/p_w ratio, the stronger φ_c differs from φ_{pt} (the concentration at the spinodal maximum).

Gordon et al. (1969) have found the critical point of the polynary system to be located on the right-hand branch of the spinodal and on the right-hand boundary of the phase separation region for systems with a LCST as well as for systems with a UCST. The critical point is the common point of the spinodal and the boundary of the phase separation region (the cloud-point curve). The spinodal and the CPC has a common tangent line at it.

Equation 23 is a test to define the character of the $g = g(\varphi)$ dependence and the coefficients of series 9 (Koningsveld, 1968). Its right-hand side is denoted by Y:

$$Y = \frac{1}{6} \left[(1 - \varphi_c)^{-2} - \frac{p_z}{p_w^2 \varphi_c^2} \right].$$
(24)

Y is, therefore, a function of the experimentally measured quantities φ_c , p_w , and p_z for a number of polymer samples.

If, now, the dependence

$$Y vs \varphi_c$$
 (25)

is plotted, its shape points to the character of the $g = g(\varphi)$ dependence.

If Y = 0, then it follows from Equation 23 that g does not depend on φ . If Y = const, Equation 23 gives

$$Y = g_1, \tag{26}$$

$$g = g_0 + g_1 \varphi. \tag{27}$$

If Y is a linear function of φ_c , then

$$g = g_0 + g_1 \varphi + g_2 \varphi^2 \tag{28}$$

and the slope and intercept of the straight line

$$Y=g_1-g_2+4g_2arphi_c$$

determine the coefficients g_1 and g_2 .

The coefficient g_0 is determined from spinodal equations 19, 22, and 3.2-9. If the critical points φ_c and T_c are measured for a number of samples, g_0 is calculated for each value of φ_c by Equation 19 or 22 or 3.2-9. The temperature dependence of g_0 results from comparison of g_0 vs T_c or g_0 vs T_c^{-1} , where T_c corresponds to the values φ_c which g_0 's are calculated for.

Additional information is given by the spinodal slope at the critical point (in the T vs φ coordinates). Eq., if Equation 18 holds good and the g_0 comprises the two first terms (Equation 10), then substitution of

$$g_0 = g_{01} + \frac{g_{02}}{T} \tag{29}$$

into Equation 19 and differentiation with respect to φ lead to

$$\left(\frac{dT}{d\varphi}\right)_{c} = T_{c}^{2} \frac{6g_{1} + p_{w}^{-1}\varphi_{c}^{-2} - \varphi_{0c}^{-2}}{2g_{02}},\tag{30}$$



Figure 3.63. Dependence of Y on the polymer critical concentration (in mole fractions $x_2 = 1/(1 + w_0 M_m/w_p)$, where w_0 and w_p are the masses of the solvent and polymer, respectively, M_m is the molecular weight of styrene) (a). Temperature dependence of g_0 (b). Polystyrene+cyclohexane system (Koningsveld, 1970b; Koningsveld et al., 1970b) [Reprinted with permission from: R.Koningsveld. Disc. Faraday Soc. 49 (1970) 144-161. Copyright © 1970 by the Royal Society of Chemistry]

from which g_{02} is determined. With known g_0 and g_{02} , g_{01} is calculated by Equation 29.

This method was applied to the systems polystyrene+cyclohexane, polyethylene+diphenyl ether (Koningsveld and Staverman, 1967b, 1968c; Koningsveld, 1968, 1970b; Rehage and Koningsveld, 1968; Koningsveld et al., 1970b), polystyrene+methylcyclohexane (Dobashi et al., 1980b) (Figures 3.63 and 3.64).

The plot in Figure 3.63 for the polystyrene+cyclohexane system gives a quadratic dependence of g on φ (Equation 21) with $g_1 = 0.2312$ and $g_2 = 0.0750$ (for polymer concentration in mole fractions x_2 , see the caption to Figure 3.33) or $g_1 = 0.2064$ and $g_2 = 0.0518$ (for volume fractions). The $g_0 = g_0(T)$ dependence (Figure 3.63b) can be represented in the form

$$g_0 - g_{00} + \frac{g_{01}}{T} \tag{31}$$

with the coefficients $g_{00} = 0.4961$; $g_{01} = 71.920$ (at x_2), and $g_{00} = 0.4099$, $g_{01} = 90.65$ (at



Figure 3.64. Dependence of Y on φ (a). Temperature dependence of g_0 (b) for the polyethylene+diphenyl ether system (Koningsveld, 1968, 1970b) [Reprinted with permission from: R.Koningsveld. Disc. Faraday Soc. 49 (1970) 144-161. Copyright © 1970 by the Royal Society of Chemistry]

 φ). As a result,

g

$$g(x_2, T) = 0.4961 + \frac{71.92}{T} + 0.2312x_2 + 0.0750x_2^2$$
(32)

οг

$$(\varphi, T) = 0.4099 + \frac{90.65}{T} + 0.2064\varphi + 0.0518\varphi^2$$
(33)

or

$$g(w,T) = 0.6035 + \frac{47.36}{T} + 0.2580w + 0.1012w^2,$$
(34)

where w is the weight fraction of the polymer (Koningsveld et al., 1970b).

Representing the logarithmic term and $g(\varphi, T)$ in Equation 12 as series in φ and truncating the high-order terms, we obtain

$$\frac{\Delta\mu_0}{RT} = -\frac{\varphi}{p_n} - \left[\frac{1}{2} - (g_0 - g_1)\right]\varphi^2 - \left[\frac{1}{3} - 2(g_1 - g_2)\right]\varphi^3 + \cdots$$
(35)

The coefficient attached to φ^2 is proportional to \mathcal{A}_2 (Equations 1.2-27, 1.3-37, 2.4-26), and at $T = \theta$

 $g_0-g_1=\frac{1}{2}.$

For the polystyrene+cyclohexane system, $g_1 = 0.2312$; hence, the θ temperature corresponds to $g_0 = 0.5 + 0.2312 = 0.7312$, and this value of g_0 responds to $\theta = 32.7^{\circ}$ C in Figure 3.63, in excellent agreement with light scattering and sedimentation data ($\theta = 33^{\circ}$ C) (Koningsveld et al., 1970b).

At any other temperature, the relationship $g_0 - g_1 = \chi_1 = \frac{1}{2} - \psi_1 + \kappa_1 = \frac{1}{2} - \psi_1 + \psi_1 \theta / T$ (cf. Equations 15 and 3.1-40, 41) holds (Koningsveld et al., 1970b).

The plot $Y = Y(\varphi)$ for the polyethylene+diethyl ether system (Koningsveld, 1970b) (see Figure 3.64) points to the φ -dependence of g (Y = 0). Extrapolation of g to the value g = 0.5 ($g = g_0$, as $g_1 = 0$) in the g vs T^{-1} construction (see Figure 3.64b) yields $\theta = 161.8^{\circ}$ C which agrees with Chiang's (1965) independent data ($\theta = 161.4^{\circ}$ C).

Using the plot (Figure 3.64b), g = g(T) is expressed as

$$g = -0.6086 + \frac{482.2}{T} \tag{36}$$

(Koningsveld, 1968, 1970b).

Koningsveld and Kleintjens (1971) have proposed a closed expression for $g = g(\varphi, T)$ like

$$g = \alpha + \frac{\beta_0}{1 - \gamma \varphi},$$

$$\beta_0 = \beta_{00} + \frac{\beta_{01}}{T},$$
(37)

which produces good agreement between the theoretical and experimental spinodals for the polystyrene+cyclohexane system with the values of the parameters included in Table 3.5.

Table 3.5

Values of the parameters in Equation 3.6-37

	Fraction		
Parameters	Weight	Volume	Segment mol
α	0.1290	-0.1597	0.0276
βυυ	0.4212	0.4987	0.3899
β_{01}	72.91	111.74	98.55
γ	0.4373	0.2365	0.3365
$ u=2\gamma^{-1}$	4.6	8.5	5.9
0, °C	32.90	32.70	32.85

 ν is the lattice coordination number

The concentration dependence of Flory-Huggins' interaction parameter in the molecular parameters follows from the theoretical development of the lattice model correcting for the change in the system's volume on mixing (Cohen, 1977). In subsection 3.3.1, we mentioned the difference (by 1.5...2 times) between the φ_c calculated after Flory (Equation 3.1-241) and the experimental ones (in fact, φ_{pt}), which was reported in a number of papers. The difference between p_z and p_w is a cause of this (see subsection 3.3.1). Now we are able to quote the corresponding estimations (Koningsveld, 1970b), which involve the concentration dependence $g = g(\varphi)$.

For the polystyrene+cyclohexane system, $\varphi_c(\text{theory})/\varphi_{pt}(\exp.) \approx 2$ (Debye et al., 1960b). If $M_z \approx M_w$ is assumed for the polystyrene samples examined by Debye et al., even in this case the φ_c calculated from Equation 23 exceeds the measured φ_{pt} by 1.35...1.5 times. If $M_z > M_w$, the $\varphi_c(\text{theory})/\varphi_{pt}(\exp.) \approx 2$ ratio can be regarded as real (Koningsveld, 1970b).

Further improvements of Flory-Huggins' theory (the third approximation) were possible after development of experimental methods to determine the phase separation region, the spinodal, the critical point, and Flory-Huggins' interaction parameter.

For this reason, the next section is devoted to these problems.

3.6.2. Development of experimental methods for determining the phase separation region, critical point, spinodal and interaction parameter

Phase-volume ratio method

In most of his papers, Koningsveld (1968, 1970ab, 1975) (including: Koningsveld and Staverman, 1966, 1967ab, 1968abcde; Gordon et al., 1969; Koningsveld et al., 1970ab, 1974ab; Gordon et al., 1969; Koningsveld and Kleintjens, 1971; Kennedy et al., 1972, 1975) determined the critical point by means of the phase-volume ratio method which implies complete phase separation (the appearance of layers) and direct measurement of their volumes.

Theory and experiment (see the papers indicated above and Kleintjens et al., 1976ab) show a strong temperature dependence of the phase-volume ratio r near φ_c . It is demonstrative to plot r against the difference ΔT between the current temperature and the cloud point at different φ/φ_c ratios.

It is seen from Figures 3.65 and 3.66 how an arbitrarily chosen φ relates to φ_c . Measuring r for different φ , φ_c can be determined with a desired accuracy. The experimental technique is simple and includes measuring the height of layers in a sealed glass tube having been thermostated (with an accuracy of 0.1°C) for a required period of time (hours, weeks, and even months). The cloud point at φ_c defines the critical temperature.

The requirement for the phase separation process to cease prior to measurements (which is often not the case in polymer systems) is a restriction of the method. Indeed, only few systems (eg. polystyrene+cyclohexane and polyethylene+diethyl ether) have been studied in detail by the phase-volume ratio method (see the above-mentioned papers).

Long periods of equilibrium establishment can be shortened using an ultracentrifuge at small speeds of rotation (to prevent sedimentation of macromolecules) (Scholte and Koningsveld, 1967; Koningsveld, 1968).

As model calculations and experiment show (Koningsveld and Staverman, 1968b), in the case of some strongly asymmetric MWD functions, the branch $r = r(\Delta T)$ at $\varphi < \varphi_c$ may fall below 1 and, having gone through a minimum, tend to infinity. The curve $r = r(\Delta T)$ responding to $\varphi = \varphi_c$ also goes through a minimum below 1 but with subsequent $(\Delta T \to 0)$ attainment of r = 1. This circumstance requires special care in experimental



Figure 3.65. Phase-volume ratio as a function of the difference ΔT between the current temperature and the cloud point at different polymer concentrations (schematic) (Koningsveld, 1970b) [Reprinted from: R.Koningsveld, L.A.Kleintjens, A.R.Shultz. J. Polym. Sci. A-2 8 (1970) 1261-1278. Copyright © 1970 by Wiley. Reprinted by permission of John Wiley & Sons, Inc.]



Figure 3.66. Experimental phase-volume ratio against the difference ΔT between the current temperature and the cloud point for different polymer concentrations (wt %). $M_n =$ 375,000, $M_w =$ 394,000, $M_z =$ 423,000. Polystyrenc+cyclohexane system, $w_c =$ 0.0695% (Koningsveld, 1970)[Reprinted from: R.Koningsveld, L.A.Kleintjens, A.R.Shultz. J. Polym. Sci. A-2 8 (1970) 1261-1278. Copyright © 1970 by Wiley. Reprinted by permission of John Wiley & Sons, Inc.]

technique and rigour in interpretation of results.

Sole (1970, 1974) has found that the break point on the CPC does not coincide with the critical point for strongly asymmetric MWDs (cg. for logarithmically normal MWDs, w_1 , w_2 , and w_3 in Koningsveld, 1970ab). Such CPC point is not singular but the interaction point of the branches of CPC whose continuation (after this point) defines the mentioned branch. In such cases, the critical point lies on the metastable branch of the CPC and is



called an unstable critical point (Figure 3.67). Sole has called the intersection point

increase of MWD's asymmetry

Figure 3.67. The emergence of the metastable critical point when the asymmetry of MWD gets stronger: 1 is the boundary of the phase separation region (the cloud-point curve); 2 is the spinodal; 1a and 1b are the metastable branches of curve 1 (Koningsveld, 1975) [Reprinted from: R.Koningsveld. Brit. Polym. J. 7 (1975) 435-466. Copyright © 1975 by Wiley. Reprinted by permission of John Wiley & Sons, Inc.]

of the CPC branches a **triple point** (see section 3.10 for details). The coincidence of the triple point with the critical point for logarithmically normal MWDs in Koningsveld's (1970ab) experiments is explained by Šolc by the approximate character of the numerical calculation of the CPC by Koningsveld (1970a)-Staverman's method: it does not account for all the details of phase separation in the case of strongly asymmetric MWDs, and the critical point cannot be determined from the dependence $r = f(\Delta T)$. Šolc's considerations were confirmed experimentally by Koningsveld (1975) (see Figure 3.67).

The necessity to have polymer fractions or samples in large amounts (several hundred grams) is a substantial limitation of the phase-volume ratio method (Koningsveld, 1968).

Refractometry

In some cases, the boundary of the phase separation region (or the configurative point close to it) can be recorded using a kink on the temperature dependence of the refractive index of solution while the configurative point moves along the temperature axis at a constant composition of the system (Rehage, 1963; Tager et al., 1982c).

One should keep in mind that the character of this singularity on $\mu = \mu(T)$ significantly depends on the rate of the configurative point's motion (Rehage, 1963).

In the most favourable variant, when phase separation is completed in reasonable periods, refractometry can be used to determine the polymer concentration in both phases and, therefore, the phase coexistence points at T = const (Dobashi et al., 1980ab) (Figure 4.8).

Thermal effects

For amorphous separation systems with a UCST and LCST, heat effects of mixing (dilution) arc, as a rule, of an endothermic (Prigogine and Defay, 1954; Tager, 1978) and



Figure 3.68. Concentration dependence of the enthalpy of mixing ΔH_m for systems with amorphous separation (Smirnova and Morachevski, 1966)

exothermic character (Figure 3.68) (Prigogine and Defay, 1954; Smirnova and Morachevski, 1966; Tager and Bessonov, 1975ab), respectively. It follows that the measurement of the thermal effects can be used to determine the location of the phase separation region (Kagemoto et al., 1972; Tamura et al., 1972; van Emmerik and Smolders, 1973b; Tsiperman et al., 1974 as well as the above-cited papers).

When the configurative point moves from the one-phase region to the two-phase one and intersects the binodal, a sigma-like signal with its sign opposite to that of the mixing effect appears in the DTA technique. Eg., in the MC+water system (amorphous separation with a LCST) at a heat rate 0.625 grad/min, the beginning of the sigma-like endothermic signal is associated (Kagemoto et al., 1972) with the binodal temperature (the boundary of the phase separation region), which exceeds the cloud temperature by 1.3° in the polymer concentration range 0.016...1.15 vol %.

In a number of cases, analysis of the thermal effects enables one to reveal additional information of the state diagram: the presence of a glass transition curve, the identification of the phase separation regions of both the amorphous and crystalline types in the same system (van Emmerik and Smolders, 1973b). However, the thermal effects of phase separation in polymer systems often turn out to be insignificant for reliable determination of the phase separation region (Papkov, 1981).

Determination of the spinodal and the interaction parameter by light scattering

As far back as in 1968, Koningsveld wrote that the spinodal cannot be studied experimentally. But soon a method to determine the spinodal using light scattering from polymer solutions was proposed (Chu et al., 1969; Scholte, 1970b, 1971, 1972). The method is based on the calculation of the determinant and cofactor in the expression for Rayleigh's ratio R_{ϑ} of a polymolecular polymer solution (Equation 3.3-10) in terms of Flory-Huggins' equation 3.2-1 with volume fractions φ replaced by weight fractions w_0 and w_i

$$\frac{\Delta G_m}{RT} = \left[w_0 \ln w_0 + \sum_i \frac{M_0}{M_i} w_i \ln w_i + \chi_\omega w_0 w \right] \frac{\varrho \,\Delta V}{M_0},\tag{38}$$

where ΔG_m is the Gibbs potential of mixing in $\rho \Delta V$ grams of solution, ρ is the solution's density, w_0 and w_i are the weight fractions of LMWL and polymer components, respectively, w is the weight fraction of the whole polymer ($w = \sum_i w_i$), M_0 and M_i are the molecular weights of LMWL and the *i*th component, respectively, χ_w is the interaction parameter which must differ from χ from Equation 13 due to the different concentration units. It follows that

$$\frac{\Delta\mu_0}{RT} = \ln(1-w) + \left(1 - \frac{M_0}{M_n}\right)w + \left[g - (1-w)\frac{\partial g}{\partial w}\right]w^2,\tag{39}$$

$$\frac{\Delta\mu_i}{RT} = \ln w_i + 1 - \frac{M_i}{M_n}w - \frac{M_i}{M_0}(1-w) + \left[g + w\frac{\partial g}{\partial w}\right]\frac{M_i}{M_0}(1-w)^2 \tag{40}$$

(cf. Equations 11 and 12). As a result, an equation is obtained for Rayleigh's ratio R_{ϑ} (Scholte, 1970ab, 1971; Vrij, 1974)

$$\frac{\mathcal{K}'(1+\cos^2\vartheta)}{R_{k,\vartheta}\varrho} = \frac{1+\mathcal{L}M_ww}{M_ww} + \frac{16\pi^2\bar{R}_z^2}{3\lambda^2} \cdot \frac{\varrho^2\mathbf{v}_1^2}{M_ww}\sin^2\frac{\vartheta}{2},\tag{41}$$

where v_1 is the specific volume of LMWL; \mathcal{K}' differs from the optical constant \mathcal{K} (Equation 2.4-22) by dn/dc replaced by dn/dw

$$\mathcal{L} = \frac{1}{M_0} \left\{ \frac{1}{1-w} + \frac{\partial^2 [w(1-w)g]}{\partial w^2} \right\}$$
(42)

or

$$\mathcal{L} = \frac{1}{M_0} \left\{ \frac{1}{1 - w} - 2\chi_w - w \frac{\partial \chi_w}{\partial w} \right\}$$
(43)

with

$$\chi_{\psi} = g - (1 - w) \frac{\partial g}{\partial w}.$$
(44)

Comparison of the derivative $\partial(\Delta\mu_0)/\partial w$ at $M_n = const$ (see Equation 39) with Equation 41 for $\vartheta = 0$ leads to (Scholte, 1970b, 1971)

$$-\left(\frac{\partial\Delta\mu_0}{\partial w}\right)_{M_n} = RT M_0 \left[\frac{2\mathcal{K}'w}{R_{k,\vartheta=0}\varrho} + \frac{1}{M_n} - \frac{1}{M_w}\right].$$
(45)

This equation is used to determine the derivative $(\partial \Delta \mu_0 / \partial w)_{M_n}$ at several solution concentrations, then $\Delta \mu_0$ is calculated by integration for any (prescribed) values of w.



Figure 3.69. Concentration (wt %) dependence of the interaction parameter χ_w in the polystyrene+cyclohexane system $(M_w = 163,000)$ at $T = 35^{\circ}$ C, 45° C, and 65° C from light scattering (1) (Scholte, 1970b), the critical state (2) (Koningsveld et al., 1970b), and the ultracentrifuge equilibrium (3) (Scholte, 1970b) [Reprinted from: Th.G.Scholte. Europ. Polym. J. 6 (1970) 1063-1074. Copyright © 1970 with kind permission of Elsevier Science – NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands]

Using $\Delta \mu_0$, χ_{ω} is calculated from Equations 39 and 44. The obtained dependence $\chi_{\omega} = f(w)$ for the polystyrene+cyclohexane system is in good agreement with the data by other methods (Figure 3.69). Repetition of this procedure at different temperatures yields the temperature dependence $\chi_{\omega} = f(T)$ (Scholte, 1971).

Differentiation of $\Delta \mu_i$ with respect to w at the same MWD (Equation 40), summation and comparison with Equation 41 at $\vartheta = 0$ lead to a differential equation for the polymer number average chemical potential (Scholte, 1970ab)

$$\left(\frac{\partial(\Delta\mu_n)}{\partial w}\right)_{\text{MWD}} = RTM_n \left[\frac{2\mathcal{K}'(1-w)}{\varrho R_{k,\theta=0}} + \frac{1-w}{w}\left(\frac{1}{M_n} - \frac{1}{M_w}\right)\right].$$
(46)

Integration of Equation 46 provides the calculation of $\Delta \mu_n$. If a quantity

$$A \equiv \varrho \left(\frac{dn}{dw}\right)^{-2} \mathcal{K}' R_{k,\vartheta=0} = \frac{\mathcal{K}'}{(dn/dw)^2} \cdot \frac{M_w w}{1 + \mathcal{L} M_w w}$$
(47)

is introduced, then, in view of Equation 42,

$$A^{-1} = \frac{(dn/dw)^2}{\mathcal{K}'} \frac{1}{M_0} \left(\frac{M_0}{M_w w} + \frac{1}{1-w} - 2\chi_w - w \frac{\partial \chi_w}{\partial w} \right).$$
(48)

The condition $R_{k,\vartheta=0}^{-1} = 0$ means the spinodal (Equation 3.3–10), hence, according to Equation 47, $A^{-1} = 0$ defines the spinodal as well. Then, on the basis of Equation 48, the spinodal condition is expressed by

$$\frac{M_0}{M_w w} + \frac{1}{1-w} - 2\chi_w - w \frac{\partial \chi_w}{\partial w} = 0.$$
(49)

The plot A^{-1} vs 1/T (Figure 3.70) at a given concentration intersects $1/T_{sp}$ on the axis 1/T ($A^{-1} = 0$) while the slope shows the character of the 1/T-dependence of $2\chi_{w} +$



Figure 3.70. Extrapolation A^{-1} = 0 for determination of the spinodal temperature at different w's: 0.0186 0.0407 (2), 0.062 (3), (1),0.08210.1012 (5), 0.1243 (6), (4),0.1496(7). Polystyrene+cyclohexane sys-(Scholte, 1971) [Reprinted tem from: Th.G.Scholte. J. Polym. Sci. A 2 9 (1971) 1553 -1577. Copyright © 1971 by Wiley. Reprinted by permission of John Wilcy & Sons, Inc.]

 $w(\partial \chi_w/\partial w)$. In particular, it is seen from the figure that at any small w, such a dependence manifests itself in a bend of the A^{-1} vs T^{-1} plot and makes the extrapolation $A^{-1} \to 0$ less reliable. Figure 3.71 represents an example of spinodals determined in this way (see also: Andreyeva et al., 1976; Tager et al., 1976a).

The chief condition of applicability of this method is that $R_{\vartheta=0} = f(w,T)$ must be determined in the one-phase region (homogeneity), i.e. outside the phase separation region (Figure 3.72). The stronger w differs from w_c , the wider the temperature range between the boundary of the phase separation region and the spinodal, the extrapolation range gets longer, and the accuracy of T_{sp} determination gets worse. It is for this very reason that Chu et al. (1969) called the corresponding curve a **pseudospinodal**.

To improve the accuracy and reliability of the extrapolation procedure $A^{-1} \sim R_{\partial=0}^{-1} \rightarrow 0$ and to increase the efficiency of the analysis, a special nephelometer was designed and manufactured at the University of Essex (Great Britain) (Gordon et al., 1974, 1975). The method itself was named "**pulse-induced critical scattering**" (PICS) (Derham et al., 1974; Gordon et al., 1974, 1975; Kennedy et al., 1975).

The design of the PICS device provides for the motion of the configurative point to the metastable region for a period, sufficient for establishing heat equilibrium and measuring the scattered light intensity at two angles, $\vartheta = 30^{\circ}$ and $\vartheta = 90^{\circ}$, but less than the induction period of the formation of a new phase's particles.

The device described in (Kennedy et al., 1975) comprises two chambers: one with a maintained temperature known to correspond to the one-phase state while the other with a slowly varying temperature towards the existence of the phase separation region. An optical scheme for recording $R_{\vartheta=30^\circ}$ and $R_{\vartheta=90^\circ}$ with fiber lightguides is mounted



Figure 3.71. Spinodals for the polystyrene+cyclohexane system: $M_w = 520,000 \ (5a), \ 163,000 \ (1a),$ 51,000 (7a) determined by extrapolation $A^{-1} = 0$ (Scholte, 1971) [Reprinted with permission from: Th.G.Scholte. J. Polym. Sci. A-2 9 (1971) 1553-1577. Copyright © 1971] (see Figure 3.70) (1), calculated from one of the approximations $\chi_{w} = \chi_{w}(T, w)$ obtained from light scattering data (Scholte, 1970b)(see Figure 3.69) (2); from the dependence $\chi_{m} =$ $\chi_{w}(T, w)$ obtained from critical state data (Koningsveld et al., 1970b) (3). The critical points have been determined by the phase-volume ratio method (Koningsveld et al., 1970b)

Figure 3.72. Scholte's (1971) method of spinodal determination (1), 2 is the boundary of the phase separation region, 3 is the critical point. The crosses mark the configurative points where the scattered light intensity was measured [Reprinted from: Th.G.Scholte. J. Polym. Sci. A-2 9 (1971) 1553-1577. Copyright © 1971 by Wiley. Reprinted by permission of John Wiley & Sons, Inc.]

in the second chamber. Cells (capillar vessels of 10 μ l) are fixed by clamps set on a whirligig. A special time program transfers the clamp with the cell on the whirligig by a step-by-step motor from the first chamber to the second one with subsequent returning

after establishment of heat equilibrium and measuring $R_{\vartheta=30^{\circ}}$ and $R_{\vartheta=90^{\circ}}$. Thus, the configurative point is, by turn, at a constant temperature far from the phase separation region or at a temperature drifting towards this region. The duration of the cycles can be chosen short enough to make the time of the system being in the metastable region shorter than the induction period (Figure 3.73). This enables the extrapolation gap $I_{30^{\circ}}^{-1} \rightarrow 0$



Figure 3.73. Typical pattern of scattering I_{30° in heating-cooling cycles. The values at the I_{30° maxima correspond to the temperature where the configurative point is recorded. The minimal values of respond to heating $I_{30^{\circ}}$ cycles up to the one-phase state temperature of the polystyrene+cyclohexane system. $M_n = 193,000,$ M_w = 200,000, w = 0.15 wt % (Derham et al., 1974) [Reprinted with permission from: K.W.Derham, J.Goldsbrough, M.Gordon. Pure and Appl. Chem. 38 (1974) 97-116. Copyright @ 1974 by IUPAC]

to be significantly shortened and, hence, improve the accuracy of the T_{sp} determination. Derham et al. (1974) and Kennedy et al. (1975) consider the extrapolation $I_{30^{\circ}}^{-1}$ (instead of $I_{\theta=0}^{-1}$) not to introduce a significant error into the T_{sp} determination. The way of extrapolation is the same as in Chu-Scholte's method.

This nephelometer does not determine the boundary of the phase separation region (the CPC): the temperature T_{Φ} of a sharp fall in I_{ϑ} in a cooling impulse is recorded (see the arrow in Figure 3.73). The authors associate this fall with the beginning of new phase particle formation which causes a sharp deformation of the radiation diagram.

The PICS method is most advantageous when performing a huge number of measurements using a huge number of P+LMWL samples, for which the phase separation region is known on the whole and careful measurements are required to clarify the fine features of this region and spinodals depending on the compositional peculiarities of the polymer (polymolecularity, branching, etc.).

It should be noted that this way of determination of the boundary of the phase separation region (the binodal) is in no case flawless. Generally speaking, nothing evidences that the deformation of the radiation diagram occurs on the binodal, not at any point between the binodal and spinodal or behind the binodal.

The PICS method has, on the whole, confirmed Scholte's (1971) data on the dependence of the spinodal position on the higher average molecular weights M_z , M_{z+1} , etc. (Kennedy et al., 1975), which enables the circle of the problems under study to be expanded to develop the third approximation of lattice theory (dilute solutions, the $\chi = \chi(M)$ dependence, see subsection 3.6.3). The successful development of the theory provides, in turn, the basis for application of the methods, determining the critical quantities, to evaluate the higher average molecular weights, which is of great importance in polymer production and processing technology (Kennedy et al., 1975).

Determination of characteristic curves of the phase separation region by the turbidity spectrum method

The state-of-the-art of the turbidity spectrum method enables the parameters of illdefined disperse systems to be determined (Klenin et al., 1977a).

An ensemble of particles of a new phase in the metastable region is a typical example of such systems, where nothing is known of the structure of the particles but the fact of their existence.

The turbidity spectrum method is capable of determining the particle sizes and weight concentration \tilde{M} of the new phase, i.e. in essence, the degree of phase conversion $x = \tilde{M}/c$, c being the polymer concentration in the system.

This serves as the basis for a technique of plotting the characteristic curves of the phase separation region, namely, its boundary and the spinodal, with the former being determined much more legally than the latter.

The chief point of the approach is that the configurative point is driven into the metastable region and the rate of phase conversion v = dx/dt (or $v_{\tau} = d\tau/dt$, or the degree of phase conversion) is therefore changed. Extrapolation $v \to 0$ (or $v_{\tau} \to 0$, or $x \to 0$) defines the boundary of the phase separation region (Klenin et al., 1974acf; Klenin, 1977, 1982) in accordance with the conditions of Table 3.1. In one variation of the method, temperature at constant concentration is measured. If the turbidity of the system substantially increases in a certain temperature range, the turbidity spectrum is recorded at a few fixed temperatures with measuring the rate of phase conversion v = dx/dt at the initial stage of conversion (or after the induction period). Extrapolation $v(T) \to 0$ defines the boundary of the phase separation region at a given concentration c while $v^{-1}(T) \to 0$ defines the spinodal temperature.

This procedure is performed in a certain range where the concentration dependence of the boundary of the phase separation region in the P+LMWL system is determined. The character of this dependence indicates the type of phase separation: liquid-liquid (UCST or LCST) or liquid-crystal (see Chapter 6). The technique of determining the characteristic curves of the liquid-liquid phase separation region is outlined in Figure 3.74.

Thus, this approach determines the spinodal by a phenomenological kinetic principle $(v \rightarrow \infty)$. How closely this obtained curve (perhaps, a quasispinodal) may fit to the thermodynamic spinodal can be determined only from experience in studying a number of systems. One particular case is dealt with below.

In contrast to the common technique of recording the boundary of the phase separation



Figure 3.74. Schematic of the determination of the boundary of the liquid-liquid phase separation region (1) and the spinodal (2) by the turbidity spectrum method

region by turbidity (see subsections 3.2.1 and 3.3.1) where the critical opalescence phenomenon may be mistaken for phase separation, the measurement of the **rate** of phase separation prevents any possibility of such artifacts.

Among the advantages of the method is the simplicity of experimental technique using common instruments (colorimeters, spectrophotometers of any kind whose measuring cells are equipped with a thermostating unit).

The fact that it is the **integral** properties of scattered light that are measured is of utmost importance as they weakly depend on some anisodiametry of particles (Khlebtsov and Shchyogolev, 1977ab; Khlebtsov et al., 1977, 1978ab; Shchyogolev et al., 1977a), their polydispersity (Ramazanov et al., 1983a), and other fine details of the structure of particles (Ramazanov and Shchyogolev, 1979), which causes a sufficient stability of the solutions of the inverse problems in different variations of the turbidity spectrum method (Khlebtsov et al., 1978b; Ramazanov and Shchyogolev, 1979; Shchyogolev, 1983) (see subsection 2.1.5). Besides, the turbidity spectrum method is effective in a wide concentration range of the P+LMWL system provided that special care is taken against information distortions caused by multiple and low-angle scattering.

This method is most reasonable in venture researches when even preliminary data on the type of phase separation are lacking. It was the case while studying phase separation in the poly-*m*-phenylene isophthalamide (PPhIA)+dimethylacetamide (DMA) (Klenin et al., 1974af, 1976a).



Figure 3.75. Determination of the boundary of the phase separation region (a) and the spinodal (b) by extrapolation of the phase separation rate $v \to 0$ (a) and $v^{-1} \to 0$ ($v \to \infty$) (b) for the poly-*m*-phenylene isophthalamide+dimethylacetamide system (Klenin et al., 1974a). $M_n = 65,000, M_w = 341,000, M_z = 570,000$ (Klenin et al., 1976a). Numbers at curves denote polymer concentration, g/dl

It follows from Figures 3.75 and 3.76 that liquid-liquid phase separation with a LCST



Figure 3.76. Boundary of the phase separation region (1) and the spinodal (2) plotted in accordance with the data of Figure 3.75; the spinodal (3) obtained by Chu-Scholte's method (Klenin et al., 1974a) [V.J.Klenin, L.V.Prozorov, M.Yu.Prozorova, B.I.Zhizdyuk, J. Polym. Sci. Symp. 44 (1974) 131. Copyright © 1974 by Wiley. Reprinted by permission of John Wiley & Sons, Inc.]

proceeds in the PPhIA+DMA system. The absence of the point of tangency between the boundary of the phase separation region and the spinodal is obviously associated with a shift of the critical point towards higher concentrations, as the polymer (a commercial sample) was significantly polymolecular $(M_w/M_n = 5.3, M_z/M_w = 1.67)$ (Klenin et al., 1974a). Advance to the region of higher concentrations was hindered by preparative difficulties. In this system, the spinodal determined by $v \to \infty$ practically coincides with that given by Chu-Scholte's method (see Figure 3.76).

The liquid-liquid phase separation with a LCST in the system PPhIA+DMA was also recorded using measurements of the thermal effects and vapour pressure over polymer solutions (Tsiperman et al., 1974).



Figure 3.77. Cloud-point curve (1), the boundary of the phase separation region by $\hat{M}/\mathbf{c} \rightarrow 0$ (2), and line corresponding to the conversion degree $\tilde{M}/\mathbf{c} = 10\%$ (3) for the poly(dimethoxy ethylene)+water system. $M_{s,D} = 45,000$ (Klenin et al., 1979b)

With the poly(dimethoxy ethylene)+water system as an example (Klenin et al., 1979b) (Figure 3.77), one can see how sharply the CPC determined by the conventional technique (using a certain turbidity threshold which corresponds to the visual effect) may differ from the boundary of the phase separation region recorded in the metastable region by $x = \tilde{M}/\mathbf{c} \rightarrow 0$. The curve corresponding to any finite degree of conversion (say, x = 10%, see Figure 3.77) can be plotted in the same coordinates.

Measuring the complete precipitation curve (with x = 100%) provides the basis for

/ / \

the determination of the integral MWD function (Ramazanov et al., 1983b; Shchyogolev, 1983), which was discussed in subsection 3.2.3.

The turbidity spectrum method was applied to determine the phase separation region in the systems: cellulose triacetate+nitromethane with a UCST (Timofeyeva et al., 1977), polyamidhydrazide+DMA with a LCST (Prozorov et al., 1976), and poly(ethylene oxide)+water with a closed phase separation region (Uskov et al., 1976).

Section 6.3 reports on a series of investigations to clarify the nature of phase separation in the poly(vinyl alcohol)+water by the turbidity spectrum method.

It should be noted that measuring particle sizes using a turbidity spectrum in the course of phase separation gives additional and very important information about fine details of separation. In particular, the character of the time dependence of new-phase particle sizes allows one to judge the mechanism of phase separation, but these questions concern phase separation kinetics which is not the subject of the present book.

Determination of the interaction parameter by equilibrium ultracentrifugation

All the polymer fractions are in equilibrium in the centrifugal force field of an analytical ultracentrifuge when the equation

$$\frac{d\Delta \bar{G}_i}{dr} = 0 \tag{50}$$

is satisfied, and, together with the Gibbs potential of mixing (Equation 38), it leads to the expressions (Rietveld et al., 1972)

$$-\frac{w}{1-w}M_0(1-\bar{\mathbf{v}}_2\varrho_0)\omega^2 r = \left[\left(\frac{\partial(\Delta\mu_0)}{\partial w}\right)_{M_n} + RT\left(\frac{M_0}{M_n} - \frac{M_0}{M_w}\right)\right]\frac{\left(\frac{dn}{dr}\right)_{(w)}}{\left(\frac{dn}{dw}\right)} \tag{51}$$

$$M_0(1 - \dot{\mathbf{v}}_2 \varrho_0) \omega^2 r \tag{52}$$

$$=\left[\left(\frac{\partial(\Delta\mu_n)}{\partial w}\right)_{\rm MWD}-RT\frac{1-w}{w}\left(1-\frac{M_n}{M_w}\right)\right]\frac{\left(\frac{dn}{dr}\right)_{(w)}}{\left(\frac{dn}{dw}\right)},$$

where r is the distance at the rotation axis, ϱ_0 is the solvent density, ω is the angular velocity of rotation, $(dn/dr)_{(w)}$ is the gradient of the refractive index in the ultracentrifuge's cell due to the concentration gradient, and the subscript points to an increment of the refractive index with respect to concentration (dn/dw). The first derivatives of the chemical potential of mixing of solvent (Equation 51) and of the number average chemical potential of mixing of polymer (Equation 52) with respect to the weight fraction of polymer are taken at constant M_n and MWD, respectively. Once an equilibrium is established in the cell at a given angular velocity of rotation, the quantity $(dn/dr)_{(w)}$ can be determined using the optical system in the ultracentrifuge. From Equations 51 and 52, the derivatives

$$\left(rac{\partial(\Delta\mu_0)}{\partial w}
ight)_{M_w} \hspace{1cm} ext{and} \hspace{1cm} \left(rac{\partial(\Delta\mu_n)}{\partial w}
ight)_{ ext{MWD}}$$

are calculated.

The procedure of integration and calculation of the interaction parameter is similar to that described in subsection 3.6.2.

Diffusion and methods defining molecular mobility

The concentration dependence of the diffusion coefficient $D = D(\mathbf{c})$ has a minimum at $\mathbf{c} = \mathbf{c}_c$ on an isotherm near the critical point (see Figures 2.36 and 3.34). On the critical isotherm, $D_{\min} = 0$ (see Figure 2.37).

Thus, the concentration dependence $D = D(\mathbf{c})$ can be used to determine the critical concentration by means of dynamic light scattering (Chu et al., 1969; Lempert and Wang, 1980, 1981) (Figure 2.37) as well as by the routine diffusional methods (Rehage et al., 1970) (Figure 3.34).

An interference method was proposed for determining the binodals and spinodals in mixtures (Chalykh, 1975). Two components are placed into the cell of an interference diffusiomer (Malkin and Chalykh, 1979) (Figure 3.78) with the interface between them to be taken X = 0.

At the initial instant $(t_0 \approx 0)$, the interference pattern corresponds to the pure separated components (the dashed lines in Figure 3.78a) but, further, the process of mixing of the components **only** in the range of their miscibility (outside the binodal curve) takes place, i.e. up to the concentrations corresponding to the points on the binodal at $T = T_1$. Once an equilibrium is established (t_{∞}) , the points, at which the interference band breaks, define the binodal concentrations at T_1 . The interference bands are continuous in the range of complete miscibility of the components (T_3) . Thus, by raising temperature step by step and waiting for the equilibrium of the concentration fields in the cell, one can determine the binodal points. The spinodal position is determined with the aid of a rapid transfer of the configurative point from outside to inside the binodal. The inflection of the interference band at the first stage of the separation process $(t_0 \approx 0)$ corresponds to the absolute instability boundary, i.e. the spinodal (see Figure 3.78c,d).

This method must be most effective for very viscous components (even one of them) to initially form a sharp interface (Malkin and Chalykh, 1979).

Indeed, the method has received acceptance and development for plotting the state diagrams of oligomer-polymer systems (Kotova et al., 1982; Chalykh et al., 1978).

When the system is thermostated in the phase separation region, two layers appear, and the component concentrations in them are determined from the difference between the refractive indices. A set of such measurements near the critical point enables the critical index β to be determined (Balzarini, 1974).

Introduction of a polarizer and analyzer into the optical system of the interferometer provides a possibility to determine the crystal separation region as well as the amorphous separation region, if they lie within the same temperature range (Kulichikhin et al., 1978).

A new modification of the diffraction method has been applied to study phase separation, namely, electron-probe X-ray spectral analysis (Chalykh et al., 1979b; Malkin and Chalykh, 1979; Chalykh and Sapozhnikova, 1981).

The relationship for the interdiffusion coefficient (Equation 2.4-47) can be written as a function of the first derivative of the chemical potential of the *i*th component with respect to the concentration of any component by means of Equations 1.1.2-51, 52.


Figure 3.78. Schematic of the determination of the boundary of the phase separation region and the spinodal by the microinterference method (Chalykh, 1975; Malkin and Chalykh, 1979)

The first derivative of the chemical potential can be calculated either by Equations 11, 12 (in the framework of the second approximation of lattice theory) or according to Equations 3.1-50, 51 (in the framework of the first approximation, where $\chi = \chi_1 = const$) (Chalykh et al., 1979a; Roginskaya et al., 1984).

Development of this approach enables one, in principle, to determine the value of χ_1 (Chalykh et al., 1979a; Roginskaya et al., 1984) or the concentration dependence $g = g(\varphi)$ as it is done in the light scattering method (see subsection 3.6.2) where a number of additional quantities and simplifying assumptions are introduced.

As the configurative point approaches the liquid-liquid phase separation region, the diffusion coefficient decreases (at the spinodal, D = 0) and the diffusional flow of the molecules (rotational and translational) is substantially retarded near the phase separation region. This is accounted for in methods where the measured quantity depends on the

velocity (rotational frequency, mobility) of the molecules or of their parts either directly or through a special mark (probe), connected to a molecule covalently or introduced into the system as an additive. In this connection, recently, the possibility to apply the following methods to the study of mixtures near and in the phase separation region has been investigated:

- EPR (the method of paramagnetic probe), measuring the spectral bandwidth of the EPR radical introduced into the system (Buchachenko et al., 1973; Alexandrova et al., 1977; Dovbiy et al., 1977);
- NMR, measuring the periods of longitudinal (spin-lattice) T_1 and transversal (spin-spin) T_2 nuclear magnetic relaxation (Gotlib et al., 1975ab; Paul and Newman, 1978; Maklakov and Derinovski, 1979);
- NMR with a magnetic field gradient, measuring the spin echo signal amplitude as a function of the impulse gradient parameters (Steiskal and Tanner, 1965; Kärger, 1969; Tanner, 1970; Maklakov et al., 1987);
- dielectric polarization, measuring the relaxation time of dipole polarization (Burshtein and Malinovskaya, 1973, 1976; Burshtein et al., 1978);
- luminescence depolarization, measuring the mobility of a luminescent mark (Anufrieva et al., 1971);
- 1R spectroscopy, measuring the intensity and frequency shift of the absorption band of characteristic groups in the molecules (Lirova et al., 1972; Tager, 1972; Tager et al., 1975; Kuznetsov et al., 1978).

These investigations will obviously be developed in the framework of other methods sensitive to the molecular mobility of mixture components as well as the methods referred to above.

Other methods for determining the interaction parameter Osmotic pressure in solutions

The expression

$$\chi = -\frac{\pi V_{01}}{v_2^2 RT} - \frac{1}{v_2^2} \left[\ln(1 - v_2) + \left(1 - \frac{1}{z} v_2\right) \right]$$
(53)

follows from Equations 1.2–57 and 3.1–56, which enables the interaction parameter χ to be calculated from the measured osmotic pressure of solutions (Figure 3.79). If Equation 53 is solved with respect to π , χ is represented by a series

$$\chi = \chi_1 + \chi_2 v_2 + \chi_3 v_2^2 + \cdots$$
 (54)

with the coefficients $\chi_1 = \chi_{v_2=0}$, $\chi_2 = (\partial \chi / \partial v_2)_{v_2=0}$, etc., the logarithmic term is represented by a two term series, and the concentration c is introduced as

$$v_2 = \mathbf{c} \frac{V_{02}}{M} = \mathbf{v}_2 \mathbf{c},$$



Figure 3.79. Interaction parameter in the (network PDMS)+benzene system at 25°C as a function of the volume concentration v_2 , $M = 1.3 \cdot 10^6$. Different signs denote polymer samples crosslinked under different conditions (Flory and Tatara, 1975). The solid line is from the osmotic pressure data of linear PDMS solutions in benzene (Flory and Shih, 1972) [Reprinted from: P.J.Flory, Y.-J.Tatara. J. Polym. Sci.: Polym. Phys. Ed. 13 (1975) 683-702. Copyright © 1975 by Wiley. Reprinted by permission of John Wiley & Sons, Inc.]

then

$$\frac{\pi}{RTc} = \frac{1}{M} + \frac{\dot{\mathbf{v}}_2^2}{\bar{V}_{01}} \left(\frac{1}{2} - \chi_1\right) \mathbf{c} + \frac{\bar{\mathbf{v}}_2^3}{\bar{V}_{01}} \left(\frac{1}{3} - \chi_2\right) \mathbf{c}^2 + \cdots .$$
(55)

The coefficient attached to c is the second virial coefficient \mathcal{A}_2 , which is determined from the original slope of π/RTc vs c (Equations 2.4-26, 1.3-37) or $\mathcal{K}c/R_{k,90}$ vs c (Equation 2.4-25). The interaction parameter χ_1 (χ at $v_2 = 0$) is calculated using Equation 3.1-52 (see also Equation 55).

Due to the different nature of M averaging, the values of A_2 obtained from osmotic pressure and light scattering differ, but χ_1 proves to be much less sensitive to such differences in M (Orwoll, 1977).

The second virial coefficient A_2 can also be determined from sedimentation equilibrium of polymer solutions (Chu and Munk, 1977; Nefyodov and Lavrenko, 1979).

Vapour pressure of a low-molecular-weight liquid

The chemical potential of mixing of LMWL relates to its vapour pressure by the relationship (Equation 1.1.3-5)

$$\Delta \mu_1 = RT \ln \frac{P_1}{P_{01}},\tag{56}$$

where P_1 and P_{01} are the vapour pressures over solution and individual liquid, respectively, the liquid being accepted as a reference state.

This equation is only valid if the behaviour of LMWL pressure can be approximated by the state equation of ideal gas.

In the general case (see Equation 1.1.3 22),

$$\Delta \mu_i = RT \ln \frac{f_i}{f_{0i}} = RT \ln a_i, \tag{57}$$

where f_i is the fugacity of the *i*th component in the system, f_{0i} is the standard fugacity, i.e. the fugacity of a pure liquid of the *i*th component at the same pressure and temperature (Read et al., 1977), a_i is the activity.

The activity a_1 is determined from the experimentally measured vapour pressure of LMWL using (Baughan et al., 1954; Moore and Shuttleworth, 1963; Medved' et al., 1983)

$$\log a_1 = \log \frac{f_1}{f_{01}} = \log \frac{P_1}{P_{01}} - \frac{(B_{11} - \tilde{V}_{01})P_{01}}{2.303RT} \left(1 - \frac{P_1}{P_{01}}\right),\tag{58}$$

where B_{11} is the second virial coefficient on the virial expansion of vapour pressure P of an individual LMWL by powers of (1/v) (Equation 1.2-68) (eg. see: Kogan, 1968; Read et al., 1977; Smirnova, 1982); the first digit in the subscript denotes the first component while the second one points to the individual state of the component.

It follows from Equations 57 and 3.1-56 that

$$\chi = \left\{ \ln \frac{f_1}{f_{01}(1 - v_2)} - v_2 \left(1 - \frac{1}{z} \right) \right\} \middle/ v_2^2.$$
(59)

Using Equation 59, the parameter χ can be calculated over a wide concentration range. In accordance with Equations 1.1.1–23,-33, the basic thermodynamic parameters are calculated (Moore and Shuttleworth, 1963; Golovin and Lotmintsev, 1981):

$$\Delta \tilde{H}_1 = \frac{\partial (\Delta \mu_1 / T)}{\partial (1/T)},\tag{60}$$

$$\Delta \bar{S}_1 = -\frac{\partial (\Delta \mu_1)}{\partial T}.$$
(61)

If $\Delta \mu_1$ is measured in a certain concentration range, Gibbs-Durgham's equation enables the polymer chemical potential of mixing to be determined by numerical or graphical integration

$$\Delta\mu_2 = -\int \frac{w_1}{w_2} d(\Delta\mu_1),\tag{62}$$

 w_1 and w_2 being the weight fractions of the LMWL and polymer, respectively. Then, from equation

$$\Delta g_m = w_1 \Delta \mu_1 + w_2 \Delta \mu_2, \tag{63}$$

the concentration dependence of the mean specific Gibbs potential of mixing Δg_m is determined or (see Equations 1.1.1-49, -51) (Tager et al., 1972)

$$\Delta G_m = n_1 \Delta \mu_1 + n_2 \Delta \mu_2. \tag{64}$$

One should keep in mind that the thermodynamic parameters calculated from vapourliquid equilibrium should be applied to liquid-liquid equilibrium with great caution, as the parameters of the latter equilibrium are much more sensitive to small variations of activity coefficients (Read et al., 1977).

If there exists a liquid-liquid phase separation region at a given temperature T, then $P_1/P_{01} = const$ in this concentration range, which can be used to determine the binodal concentrations (Golovin et al., 1975; Papkov, 1981).

Equilibrium swelling of a crosslinked polymer

The state equation of the NP+LMWL system (Equation 3.5-97) can be transformed, in view of Equation 3.5-67, to the form

$$\frac{-\frac{\dot{n}}{RT} - \ln(1 - v_2) - v_2}{v_2^{1/3} - v_2/2} = \frac{\varrho_2 \bar{V}_{01}}{M_2} + \chi \frac{v_2^2}{v_2^{1/3} - v_2/2},$$
(65)

from which it follows that if the left-hand side is plotted against $v_2^2/(v_2^{1/3} - v_2/2)$, then a straight line must appear, whose slope is equal to χ and the intercept gives the weight of a molecular branch M_2 (Mula and Chinellato, 1971).

In the case of free swelling of a network polymer, it follows from Equation 3.5-92 that (Flory and Tatara, 1975)

$$\chi = -\left[\ln(1 - v_{2sw}) + v_{2sw}\right]v_{2sw}^{-2} - B\left(v_{2sw}^{1/3} - v_{2sw}/2\right)v_{2sw}^{-2} + \frac{B}{4}\frac{C_2}{C_1}v_{2sw}^{-5/6}.$$
(66)

Figure 3.79 presents the data of χ calculations by Equation 66 for the (network PDMS) + benzene system at 25°C. The concentration dependence $\chi = \chi(v_2)$ practically coincides with the data of osmotic pressure measurements in linear PDMS solution in benzene (Flory and Shih, 1972).

Viscosity of polymer solutions

The limiting viscosity number of a polymer solution obeys Flory's equation

$$[\eta] = \Phi \frac{\left(\overline{h^2}\right)^{3/2}}{M} = \Phi \frac{\alpha_h^3 \left(\overline{h_\theta^2}\right)^{3/2}}{M},\tag{67}$$

where Φ is Flory's parameter, which depends weakly on the thermodynamic quality of the solvent. In the θ solvent,

$$[\eta]_{\theta} = \Phi_{\theta} \frac{\left(\overline{h_{\theta}^2}\right)^{3/2}}{M},\tag{68}$$

where $\Phi_{\theta} = 2.86 \cdot 10^{21} \text{ mol}^{-1}$ is Flory's constant, if $[\eta]_{\theta}$ is in dl/g (Ptitsyn, 1961).

According to the theory of Ptitsyn (1961), Eizner and Ptitsyn (1964), near the θ point,

$$\Phi \cong \Phi_{\theta}(1 - 0.472z + \cdots), \tag{69}$$

while with a certain distance from it

$$\Phi \cong \Phi_{\theta} \left(0.753 + \frac{0.247}{\alpha_{\eta}^3} \right), \tag{70}$$

i.e. Φ diminishes when the thermodynamic quality of the solvent improves from $2.86 \cdot 10^{21}$ to ~ $1.175 \cdot 10^{21}$.

In view of a weak dependence of Φ on the solvent quality, Flory (1969) has proposed $\Phi \simeq 2.6 \cdot 10^{21}$ near the θ point, which agrees with a large body of experimental data.

Comparison between Equations 67 and 68 leads to

$$\alpha_{\eta}^{3} = \frac{\Phi_{\theta}[\eta]}{\Phi[\eta]_{\theta}}.$$
(71)

As the first approximation,

$$\alpha_{\eta}^{3} \cong \frac{[\eta]}{[\eta]_{\theta}}$$

is often accepted.

Flory's equation 67 has another form

$$[\eta] = K_{\theta} M^{1/2} \alpha_{h}^{3}, \tag{72}$$

where $K_{\theta} = \Phi(\overline{h_{\theta}^2}/M)^{3/2}$ is the flexibility parameter of a polymer chain.

The experimentally determined (by Equation 71) swelling coefficient α_{η} is substituted into Equation 3.1 113 and, with account of Equations 3.1-41,-64, χ_1 is calculated.

There are some difficulties concerning different values of the constant C_m (Equation 3.1-114) in different versions of the theory (see subsection 3.1.1) and, strictly speaking, a necessity to estimate Φ/Φ_{θ} according to Equation 70. One might fail to get the θ solvent, or the θ temperature may prove to be rather low, which makes it difficult, or even impossible, to determine $[\eta]_{\theta}$ and to estimate the thermodynamic flexibility of the polymer molecular chains.

The interaction χ_1 and flexibility parameters K_{θ} are determined from $[\eta]$ and M measured on a series of polymer fractions in a good solvent by means of Flory-Fox' (1951) equation. The latter results from substitution of α from Equation 72 into Equation 3.1-113

$$\frac{[\eta]^{2/3}}{M^{1/3}} = K_{\theta}^{2/3} + 2C_M \left(\frac{1}{2} - \chi_1\right) K_{\theta}^{5/3} \frac{M}{[\eta]}.$$
(73)

Hence, the plot $[\eta]^{2/3}/M^{1/3}$ vs $M/[\eta]$ gives a straight line which intersects the value $K_{\theta}^{2/3}$ at the ordinate axis. The slope yields the interaction parameter χ_1 .

A few equations to relate $[\eta]$, M, and K_{θ} , χ_1 , as Equation 73 does, have been proposed in the literature (Rafikov et al., 1978; Rabek, 1980; Tverdokhlebova, 1981). Fixman-Stockmayer's (1963) equation is most often applied:

$$\frac{[\eta]}{M^{1/2}} = K_{\theta} + 0.51 B \Phi_{\theta} M^{1/2},$$

where

$$B = \frac{\bar{\mathbf{v}}_2^2(1-2\chi_1)}{N_A \bar{V}_{01}}.$$

Reverse gas chromatography

A portion of LMWL vapours in a flow of a carrier gas (helium, nitrogen) is passed through a chromatographic column packed with a polymer, directly or as a covering on a solid support. The effect of vapour sorption depends on χ , and in the limit $v_2 \rightarrow 1$ the following expression results (Patterson et al., 1971; Newman and Prausnitz, 1972; Summers et al., 1972; Brawn and Guillet, 1975; Nesterov and Lipatov, 1976; Orwoll, 1977)

$$\chi = \ln \frac{273.2R\bar{V}_{02}}{P_{01}\bar{V}_{01}\bar{V}_g} - \left(1 - \frac{\dot{V}_{01}}{M_2\bar{V}_{02}}\right) - P_{01}\frac{B_{11} - \bar{V}_{01}}{RT},\tag{74}$$

where P_{01} is the vapour pressure of LMWL in the system at T (in K), \mathcal{V}_g is the **retention volume** of the sorbate, B_{11} is the second virial coefficient of LMWL vapours (see Equation 1.2-68).

The reverse gas chromatography method implies control over equilibrium and elimination of a number of instrumental and methodical distortions (eg. the dependence of sorption on the amount of polymer adsorbent, the nature of motionless support for polymer, etc.) (Nesterov and Lipatov, 1976; Tager et al., 1978). The method is capable of determining χ at small amounts of LMWL ($v_2 \rightarrow 1$).

The reverse gas chromatographic method has been applied to determine the dependences of χ on temperature, molecular weight, and concentration for a number of the P+LMWL systems (Nesterov and Lipatov, 1976; Orwoll, 1977; Tager et al., 1978; Tait and Abushihada, 1978; Klein and Jeberien, 1980).

See Chapter 6 for the determination of Flory-Huggins' parameter χ_1 at liquid-crystal phase separation.

3.6.3. Third approximation of Flory-Huggins' theory

The development of experimental methods of determining the spinodal, the interaction parameter χ (or g), and other critical parameters has promoted the appearance of the third approximation of Flory-Huggins' lattice theory where the dependence of the interaction parameter g on the polymer molecular weight (or MWD) and the peculiar features of dilute polymer solutions or of polymer-depleted phase at phase separation are taken into account.

The dependence g = g(M), especially at low M's, was revealed experimentally by means of equilibrium centrifugation (Scholte, 1970b; Rietveld et al., 1972).

The PICS method (Kennedy et al., 1975) (see subsection 3.6.2) indicated a difference in the spinodals for polymer samples with equal p_w but different MWDs (as the second approximation predicts, $g = g(T, \varphi)$ and the spinodals must be invariant with respect to p_w , Equations 19, 22). Moreover, the M dependence of g follows from the relation between g (or χ) and \mathcal{A}_2 (Equation 3.1-51) while the M dependence of \mathcal{A}_2 , in turn, has been established both experimentally and theoretically (Equations 3.1-146,-158) (Yamakawa, 1971; Elias et al., 1975).

In view of $g = g(\varphi, T, M)$, the expressions for the spinodal and critical state (Equations 3.2-2,-3) become more complicated (Koningsveld and Kleintjens, 1971; Kennedy et al., 1972).

Kennedy et al. (1972) have proposed a five-parameter system, which showed good agreement between the theoretical and experimental spinodals $g = g(\varphi, T, M)$:

$$g = \left[\beta_{01} + \beta_{02}T^{-1} + (\beta_{11} + \beta_{12}T^{-1})m_n^{-1}\right](1 - \gamma\varphi)^{-1}$$
(75)

with $\gamma = 0.3408$, $\beta_{01} = 0.1744$, $\beta_{02} = 176.89$, $\beta_{11} = -260.92$, $\beta_{12} = 72.426$.

Reduction of the number of parameters to 4 (with $\gamma = 1/3$) leads to a good fit to experimental data as well $\beta_{01} = 0.2151$, $\beta_{02} = 162.21$, $\beta_{11} = -193.95$, $\beta_{12} = 53.821$.

The features of dilute solutions are considered by representation of g with two summands, of which g_{conc} has the form of the second-approximation function (eg. Equation 37) while the second summand contributes greatly at low concentrations and negligibly at high concentrations.

For binary systems (Koningsveld et al., 1974a)

$$g = g_{\text{conc}} + \left(\frac{1}{2} - \chi_{1}\right) \left[1 - h(z)\right] (1 + \lambda)^{-1} \exp(-\lambda\varphi).$$

$$(76)$$

The quantity $1/\lambda$ corresponds to the polymer volume fraction where the sum of the volumes of all the molecular coils is equal to the volume of the system. λ relates to the rigidity of a molecular chain via a characteristic parameter λ_0

$$\lambda = \lambda_0 p^{1/2},\tag{77}$$

where

$$\lambda_0 = 4\pi a N_A b^3 \frac{V_{01}^{1/2}}{3\dot{v}_2^{3/2}},\tag{78}$$

a is a parameter close to 1 to correct the coil shape if the coil volume is calculated by $v_{coil} = \frac{4\pi}{3} a \left(\overline{R_{\theta}^2}\right)^{3/2},$

$$b = \left(\overline{R_{\theta}^2}\right)^{1/2} M^{-1/2}.$$

For the polystyrene+cyclohexane system, $g_{conc} = g$ from Equation 37 (see also Table 3.3 for the volume fractions), $\bar{v}_2 = 0.925 \text{ cm}^3/\text{g}$, $\dot{V}_{01} = 108 \text{ cm}^3/\text{mol}$, $b^2 = 7.6 \cdot 10^{-18} \text{ cm}^2/\text{g}$, $\lambda_0 = 0.57a$,

$$z = 0.305 \left(\frac{1}{2} - \chi_1\right) p^{-1/2}.$$

In accordance with Equations 37 and 13,

$$\chi_1 = \alpha + \beta_0 (1 - \gamma). \tag{79}$$

Koningsveld et al. (1974a) have analyzed a number of approximations for h(z): Flory-Krigbaum-Orofino's (FKO)

$$h(z) = \frac{1}{5.73z} \ln(1 + 5.73z), \tag{80}$$

Stockmayer's (S)

$$h(z) = \frac{1}{1 + 2.865z},\tag{81}$$

Kurata-Yamakawa's (KY)

$$h(z) = 1 - \frac{(1+3.903z)^{-0.4683}}{1.828z},$$
(82)

Casassa-Markovitz' (KM)

$$h(z) = \frac{1 - \exp(-5.73z)}{5.73z}.$$
(83)

The spinodal equation, according to Equations 3.2-2, 76, 37, looks as

$$(1 - \varphi)^{-1} + (m\varphi)^{-1} = 2\alpha + 2\beta_0(1 - \gamma)(1 - \gamma\varphi)^{-3}$$
(84)

$$+\left[\frac{1}{2}-\alpha-\beta_0(1-\gamma)\right]\left[1-h(z)\right](1+\lambda)^{-1}\left[2+2\lambda-4\lambda\varphi-\lambda^2(1-\varphi)\varphi\right]\exp(-\lambda\varphi).$$



Figure 3.80. The spinodals calculated by Equation 3.6-84 (Koningsveld et al., 1974a) with $\lambda_0 = 1/2, M_w$ are marked at curves. The experimental spinodals are given on the data of Scholte (1971) (1), Derham et al. (1974), Goldsbrough (1972) (2). The critical points are taken from: Scholte, 1971 (3). The spinodals are calculated for different h(z) (see Equations 3.6-80...83) (abbreviations at the curves). The curve conc is calculated for h(z) = 1, i.e. with no respect to the peculiar features of a dilute solution (Koningsveld et al., 1974a) [Reprinted with permission from: Macromolecules 7 (1974) 73-79. Copyright © 1974 American Chemical Society]

The spinodals calculated using this equation and the experimental spinodals are presented in Figure 3.80; it follows that the effect of the dilute solution manifests itself at $M_w < 500,000$.

The application of this approximation, considering the peculiar features of a dilute solution at equilibrium between the dilute and concentrated phases, produces a good fit between theory and experiment.

Generally, the account of the dependence of g on M or MWD is very complicated and poorly known (as the dependence $\mathcal{A}_2 = f(M)$ itself: Elias et al., 1975).

Thus, the temperature dependence of the interaction parameter g (or χ) (Equation 10 which has the form

$$g = g_{01} + \frac{g_{02}}{T} + g_{03}T \tag{85}$$

without the fourth, almost temperature-insensitive parameter) has the main effect on how the phase separation region is located on the state diagram T vs v_2 .

Depending on the signs of the parameters in Equation 85, the phase separation regions may be located in the $T vs v_2$ plane as shown in Figure 3.81.

The diagrams like those shown in Figure 3.81a are exemplified by to the polystyrene+cyclohexane system (Koningsveld, 1968, 1970b; Saeki et al., 1973a); like those shown in Figure 3.81b — by the polystyrene+acetone system (Siow et al., 1972) (see Figure 3.89); like those shown in Figure 3.81c — by the systems: copolymer of vinyl alcohol with vinylacetate (6.8% of AG)+water (Rehage, 1963) and copolymer of vinyl alcohol with ethylene (3.13 mol % of ethylene units)+water (Shibatani and Oyanagi, 1971), poly(ethylene oxide)+water (Malcolm and Rowlinson, 1957; Saeki et al., 1976; Uskov et al., 1976; Kjellander and Florin, 1981) (see Figure 6.9).

A closed phase separation region can be explained by the specific interactions and poses the greatest difficulties in interpretation with respect to molecular parameters.

The dependences of g on concentration and M in the above proposed form, shift, to some degree, the phase separation regions shown in Figure 3.81.

Within the framework of the third approximation, Einaga et al. (1984) put forward a new version of the expression of the interaction parameter g, including the dependences on T, φ , and M. The development of characteristic dependences of the theory is based on measurements of light scattering of polystyrene solutions in cyclohexane, performed up to the nearest proximity of the binodal (below the θ temperature).

Pouchlý (1969) has generalized Flory-Huggins' model to account for specific interactions (H-bonds, etc.) in the ternary system A+B+C susceptible to the formation of complexes of the $A_iB_jC_k$ type.

The third approximation of the theory implies substantial redistribution of the macromolecules of a polymolecular polymer between two phases at equilibrium (Kleintjens et al., 1976b).

Analyzing the advantages of the third approximation, Gordon and Torkington (1980) consider as inconsistent any arguments against using the mean field theory to describe conversions in polymer solutions. In their opinion, this theory predicts the character and the peculiar features of phenomena (an outstanding role of polymolecularity) much better than the modern theories of similarity.

3.7. Polymer mixtures

3.7.1. State equations

The systems polymer 1+polymer 2 and polymer 1+polymer 2+LMWL are increasingly gaining in importance and currency in technological practice to create materials with various properties; therefore, they have been dealt with in many publications, including monographs (van den Esker and Vrij, 1976; Manson and Sperling, 1976; Tager and Sholokhovich, 1976; Tager, 1977; Krause, 1978; Paul and Newman, 1978; Kuleznev, 1980; Onclin et al., 1980; Sperling, 1981).

We will outline only the basic properties of such systems.

The Gibbs potential of mixing per mole of lattice cells (Equation 3.2-1) for a mixture



Figure 3.81. Arrangement of phase separation regions for the temperature dependence of the interaction parameter g (or χ) of the type $g = g_{01} + g_{02}/T + g_{03}T$ at different values of the parameters in this equation (schematic) (Koningsveld, 1975) [Reprinted from: R.Koningsveld. Brit. Polym. J. 7 (1975) 435-458. Copyright © 1975 by Wiley. Reprinted by permission of John Wiley & Sons, Inc.]

of two different polymers is naturally generalized (Koningsveld, 1970b; Koningsveld et al., 1970a)

$$\frac{\Delta G_m}{RT} = \sum_i \varphi_{1i} m_{1i}^{-1} \ln \varphi_{1i} + \sum_j \varphi_{2j} m_{2j}^{-1} \ln \varphi_{2j} + \Gamma(P, T, \varphi_2), \tag{1}$$

where φ_{1i} and φ_{2j} are the volume fractions of the *i*th fraction of polymer 1 and of the *j*th fraction of polymer 2 with the relative chain lengths m_{1i} and m_{2j} expressed through the number of cells occupied by the polymer molecules. The volume fractions of polymers 1 and 2 are expressed as $\varphi_1 = \sum_i \varphi_{1i}$ and $\varphi_2 = \sum_j \varphi_{2j}$, so

$$\varphi_1 + \varphi_2 = 1. \tag{2}$$

In the simplest version of a mixture of two monomolecular polymers with the interaction parameter χ_1 depending on T only, one can write

$$\frac{\Delta \bar{G}_m}{RT} = \frac{\varphi_1}{m_1} \ln \varphi_1 + \frac{\varphi_2}{m_2} \ln \varphi_2 + \chi_1 \varphi_1 \varphi_2.$$
(3)

The spinodal (Equation 3.2-2) and critical point (Equations 3.2-2,-3) conditions lead, in this case, to

$$\frac{\partial^2}{\partial \varphi_1^2} \left(\frac{\Delta G_m}{RT} \right) = \frac{1}{m_1 \varphi_1} + \frac{1}{m_2 (1 - \varphi_1)} - 2\chi_1 = 0, \tag{4}$$

$$\frac{\partial^3}{\partial z^3} \left(\frac{\Delta G_m}{RT} \right) = -\frac{1}{m_1 \varphi_1^2} + \frac{1}{m_2 (1 - z_0)^2} = 0,$$

$$\frac{\varphi_{1c}}{1-\varphi_{1c}} = \left(\frac{m_2}{m_1}\right)^{1/2}$$

$$(5)$$

ог

$$\varphi_{1c} = \frac{m_2^{1/2}}{m_1^{1/2} + m_2^{1/2}}.$$
(6)

If $m_1 = m_2$, then $\varphi_{1c} = 1/2$; if $m_2 > m_1$ then φ_{1c} shifts towards high concentrations of P1. It follows from Equations 6 and 4 that

$$\chi_{1r} = \frac{\left(m_1^{1/2} + m_2^{1/2}\right)^2}{2m_1 m_2},\tag{7}$$

and if $m_1 = m_2 = m$, then

$$\chi_{\mu} = \frac{2}{m},\tag{8}$$

i.e. for a polymer mixture, χ_{1e} is a very small quantity (cf. $\chi_{1e} = \frac{1}{2} + \frac{1}{\sqrt{m}} + \frac{1}{2m}$, Equation 3.1-242, when $m_1 = 1$ and $m_2 = m$).

Equations 8 and 3 imply that, even at small χ_1 , two polymers prove to be **incompatible** (insoluble).

An interesting and important feature of polymer mixtures is that they almost strictly obey the mean field approximation.

De Gennes (1979) demonstrates this in a simple and illustrative way. Suppose $m_1 > m_2$. A chain of polymer 1 has its size $(\overline{h^2})^{1/2} \sim Am_1^{1/2}$ and occupies the volume

$$v_1 \sim A^3 m_1^{3/2}$$
. (9)

A is the step length of Ising's lattice which contains macromolecules (see Figure 1.23d). The short-range interaction is included into Λ , therefore it is equivalent to Kuhn's segment.

Further, a parameter P is introduced, equal to the average number of other chains of the same kind 1 which are within the given coil. Now, if $P \sim 1$, the fluctuation effects must be of much importance, and the mean field theory is incorrect. If $P \gg 1$, these phenomena substantially reduce: as a matter of fact, every chain is subject to the mean field generated by other chains, and the mean field theory is applicable.

The number of P1 chains per unit volume is φ_1/m_1A^3 , and

$$P \sim \frac{\varphi_1}{m_1 A^3} v_1 \simeq \varphi_1 m_1^{1/2}.$$
 (10)

Near the critical point, Equation 6 holds true, and

$$P \sim \frac{(m_2 m_1)^{1/2}}{m_1^{1/2} + m_2^{1/2}}.$$
(11)

In a symmetrical case of large $m_1 = m_2 = m$,

$$P \sim \frac{m^{1/2}}{2}.\tag{12}$$

P proves to be a large quantity and the mean field approximation holds good. If $m_1 \gg m_2$, then

$$P \sim m_2^{1/2}$$
 (13)

and the mean field approximation is valid if only $m_2 \gg 1$. In the case of P+LMWL (where $m_2 = 1$), $P \sim 1$, and the mean field approximation in the neighbourhood of the critical point turns out to be incorrect.

In the framework of the second approximation of theory (the multicomponent version),

$$\Gamma = g(P, T, \varphi_2)\varphi_1\varphi_2,\tag{14}$$

the spinodal equation (Koningsveld et al., 1974b) is

$$-\left(\frac{\partial^2 \Gamma}{\partial \varphi_2^2}\right)_{P,T} = \frac{1}{m_{w1}\varphi_1} + \frac{1}{m_{w2}\varphi_2},\tag{15}$$

and for the critical state

$$-\left(\frac{\partial^{3}\Gamma}{\partial\varphi_{2}^{3}}\right)_{P,T} = \frac{m_{z1}}{m_{w1}^{2}\varphi_{1c}^{2}} - \frac{m_{z2}}{m_{w2}^{2}\varphi_{2c}^{2}}.$$
(16)

If g = g(T, P) and P = const (atmospheric), then

$$-\left(\frac{\partial^2 \Gamma}{\partial \varphi_2^2}\right)_T = 2g = \frac{1}{m_{w1}\varphi_1} + \frac{1}{m_{w2}\varphi_2},\tag{17}$$

and the critical state

$$-\left(\frac{\partial^3 \Gamma}{\partial \varphi_2^3}\right)_{P,T} = \frac{m_{z1}}{m_{w1}^2 \varphi_{1c}^2} - \frac{m_{z2}}{m_{w2}^2 \varphi_{2c}^2} = 0,$$
(18)

$$\varphi_{2c} = \frac{1}{1 + \left(\frac{m_{w2}a_1}{m_{w1}a_2}\right)^{1/2}},\tag{19}$$

where $a_k = m_{zk}/m_{wk}$, k = 1, 2. For $m_{w1} = m_{z1} = 1$, Equation 19 reduces to Equation 3.2 10. Figure 3.82 demonstrates the spinodals and critical points for a few systems calculated from Equations 17 and 19.

Koningsveld et al. (1974b) have developed numerical methods for calculating the boundary of the phase separation region. To provide an example, Figure 3.83 is presented, from which one can see a shift of the boundary of the phase separation region towards higher g, as the average length of P1's with the lower M macromolecule diminishes.

Comparison between Figures 3.83 and 3.84 shows how drastically the location of the phase separation region changes if the interaction parameter depends on concentration, say, linearly

$$g = g_0 + g_1 \varphi_2. \tag{20}$$

An interesting peculiarity of polymer mixtures is bimodality of the phase separation region (Koningsveld et al., 1974b) (Figure 3.85). This figure also shows the effect of the strong shift of the phase separation region at a small variation of the M of one of the polymers (here — polystyrene).

Such bimodality may appear due to the quadratic concentration dependence of g

$$g = g_0 + g_1 \varphi_2 + g_2 \varphi_2^2, \tag{21}$$

as it follows from model calculations of the locations of the phase separation region and the spinodals presented in Figure 3.86. Such shape of CPC suggests a possibility of a three-phase separation (see section 3.10). A strong dependence of the location of the phase separation region in the P1+P2+LMWL system on the M of one of the polymers served as the basis for a way of determining the M of a polymer in its mixture with a standard polymer with a known M (Berek et al., 1967ab, 1969).

Indeed, experiments have proved the validity of the relationship

 $\mathbf{c}_{\mathbf{\Phi}} = AM^{-2/3} + \mathbf{c}_{\infty},$



Figure 3.82. The spinodals of quasibinary sections of the P1+P2 (upper curves) and P+LMWL (lower curves) systems with polymolecular polymers. Dashed and dot-anddash lines correspond to the spinodals of systems with concentrationdependent (according to Equation 3.7-20) g: $g_1 = -0.1$ and +0.1, respectively. The ratios m_1/m_2 and m_{w1}/m_{w2} (figures) are marked at the curves. Empty circles denote the critical points for systems with monomolecular polymers, solid circles denote the critical points of polynary systems with $a_2/a_1 = (m_{z_2}/m_{w_2})/(m_{z_1}/m_{w_1}) =$ 0.5, 0.2, 0.1, 0.05, 0.02, 0.01, 0.001 (clockwise from the empty circle) and 2, 5, 10, 20, 50, 100, 1000 (anticlockwise from the empty circle) (Koningsveld et al., 1970a, 1974b; Koningsveld, 1975) [Reprinted with permission from: R.Koningsveld, H.A.G.Chermin, M.Gordon. Proc. Roy. Soc. London A 319 (1970) 331-349. Copyright © 1970 by the Royal Society of Chemistry]

where \mathbf{c}_{Φ} is the boundary of the phase separation region determined from a sharp growth of turbidity (see subsection 3.2.3), A and \mathbf{c}_{∞} are constants for a given system P1+P2+LMWL, $\bar{M} = (M_1M_2)^{0.5}$ or $\bar{M} = Y_1M_1 + Y_2M_2$, where M_i are the molecular weights of P1 and P2, Y_i is the relative weight fraction of the *i*th polymer component

$$Y_i = \frac{w_i}{1 - w_{\rm LMWL}}$$

where w_i and w_{LMWL} are the weight fractions of the *i*th polymer and LMWL, respectively. Various ways of how the phase separation region may be located are calculated for the

systems P1+P2+LMWL (Scott, 1949b; Tompa, 1956) and observed in practice.

Of special interest are systems where the pairs P1+LMWL and P2+LMWL are mutually soluble in the whole concentration range (Figure 3.87).

A phase separation region may appear even when all the components are pairwise compatible (Figure 3.87c).



Krause (1978) gives an extensive review of experimental results in the phase separation of polymer mixtures.

The phase separation of polymer mixtures exhibits so great a variety of properties in comparison with LMW mixtures that not all the peculiarities of this phase separation have hitherto been amenable to a theoretico-calculational justification.

Certain progress has been made in LCST predictions for polymer mixtures by the theory of corresponding states (see the next paragraph), but this theory fails to explain the bimodality of the boundary of the phase separation region.

The search for new ways and opportunities is continuing in the framework of the third approximation of Flory-Huggins' theory, with due account of fine effects of changes in the molecular coil sizes of one polymer with the concentration of the other polymer in the mixture.

3.7.2. Light scattering. Dynamics of concentration fluctuations in the critical region. Critical indices

1. The fluctuations in the order parameter (component concentrations) in polymer mixtures are expressed so weakly that it is quite correct to consider the thermodynamic



Figure 3.84. Same as in Figure 3.83, but $g = g_0 + g_1\varphi_2$, $g_1 = 0.02$ (Koningsveld et al., 1974b) [Reprinted with permission from: R.Koningsveld, L.A.Kleintjens, H.M.Schoffelens. Pure and Appl. Chem. **39** (1974) 1-32. Copyright © 1974 by IU-PAC]



Figure 3.85. Experimental cloud-point curves for the system polypropylene (PP) $(M_n = 2,700)$ +polystyrene $(M_n$ are indicated at curves); w_{PS} is the weight fraction of polystyrene (Koningsveld et al., 1974b) [Reprinted with permission from: R.Koningsveld, L.A.Kleintjens, H.M.Schoffelens. Pure and Appl. Chem. **39** (1974) 1-32. Copyright © 1974 by IUPAC]

properties of such a system in the mean field approximation.

Using this approximation, de Gennes (1979) obtained a formula for the structural scattering factor in the P1+P2 mixture

$$S^{-1}(q) = \frac{1}{\varphi_1 g_D(m_1, q)} + \frac{1}{\varphi_2 g_D(m_2, q)} - 2\chi_1,$$
(22)



Figure 3.86. Calculated cloudpoint curves and critical points for mixtures of two polymers with m_{w1}/m_{w2} denoted at the curves; $g = g_0 - 0.04\varphi_2 + 0.04\varphi_2^2$ (Koningsveld et al., 1974b) [Reprinted with permission from: R.Koningsveld, L.A.Kleintjens, H.M.Schoffelens. Pure and Appl. Chem. **39** (1974) 1–32. Copyright © 1974 by IUPAC]

where $g_D(m_i, q)$ is Debye's function describing scattering on one chain in the θ solvent

$$g_D(m_i, q) = \frac{2m_i}{x_i} \left(1 - \frac{1 - e^{-x_i}}{x_i} \right),$$

$$x_i = \frac{1}{6} m_i A^2 q^2$$
(23)

(cf. Equation 2.1-67).

The structural factor $S(\vec{q})$ proportional to the scattered light intensity (see, eg., Equation 2.3–107) is the Fourier transform of the correlation function of concentration $S(\vec{r})$ (see Equation 2.1-83)

$$S(\vec{q}) = A^{-3} \int S(\vec{r}) \exp(i\vec{q}\vec{r}) d\vec{r}, \qquad (24)$$

where the factor A^{-3} is introduced for $S(\vec{q})$ to be dimensionless.

By definition, the correlation function of the concentration is (see Equations 1.7-33 and 2.1-73)

$$S_{12}(\vec{r} - \vec{r}') = \langle \varphi_1(\vec{r}) \varphi_2(\vec{r}') \rangle - \langle \varphi_1(\vec{r}) \rangle \langle \varphi_2(\vec{r}') \rangle.$$
⁽²⁵⁾

As $\varphi_1 + \varphi_2 = 1$, then

$$S_{11} = S_{22} = -S_{12} = S(\vec{r}). \tag{26}$$



Location of the Figure 3.87. phase separation region in the system P1+P2+LMWL when the systems P1+LMWL and P2+LMWL (and P1+P2 in the case c) are completely compatible (Scott, 1949b; Tompa, 1956; Koningsveld et P2_{al., 1974b}). Examples: a polystyrene + polypropylene + toluene (Berek ct al., 1967a); b - polystyrene+PIB+toluene(van den Esker and Vrij, 1976); c butyl rubber+EPS rubber+benzene (Koningsveld et al., 1974b); d — polypropylene+polyethylene+diphenyl ether (Koningsveld ct al., 1974b) [Reprinted with permission from: R.Koningsveld, L.A.Kleintjens, H.M.Schoffelens. Pure and Appl. Chem. 39 (1974) 1 32. Copyright © 1974 by IUPAC]

Denote $\varphi_1 = \varphi$, $\varphi_2 = 1 - \varphi$. At q = 0, Debye's function (Equation 23) $g_D(m_i, q = 0) = m_i$ and

$$S_{q=0}^{-1} = \frac{1}{m_1 \varphi} + \frac{1}{m_2 (1-\varphi)} - 2\chi_1 = \frac{1}{RT} \cdot \frac{\partial^2 \Delta G_m}{\partial \varphi^2}$$
(27)

(cf. Equation 4) in accordance with the thermodynamic theorem which relates the structural factor with the thermodynamic quantities of a system (see Equations 2.3–107 and 2.4–7).

In particular, on the spinodal (see Equation 4), all the sides of Equation 27 vanish. At small q's, i.e. given $qR \ll 1$,

$$g_D(m_i, q \to 0) = 1 - \frac{1}{3}q^2 R^2.$$
 (28)

Substituting it to Equation 22, we have

$$S^{-1}(q) = 2\left[\chi_{1,p}(\varphi) - \chi_{1}\right] + \frac{q^{2}A^{2}}{18}\frac{1}{\varphi(1-\varphi)},$$
(29)

where $\chi_{\rm ren}(\varphi)$ satisfies the spinodal equation 4.

If Equation 29 is transformed to the standard form with a correlation length of the concentration fluctuations ξ_k (cf. Equation 2.3-133), then

$$S(q) = \frac{S_{11}(0)}{1 + q^2 \xi_k^2}, \quad qR \ll 1,$$
(30)

where

$$\xi_k = \frac{A}{6} \left\{ \varphi(1-\varphi) \left[\chi_{_{1sp}}(\varphi) - \chi_{_1} \right] \right\}^{-1/2}.$$
(31)

Thus, when the configurative point approaches the spinodal, ξ_k diverges with its singularity being of a reverse quadratic root nature.

In the other limiting case, qR > 1,

$$g_D(m,q) \cong \frac{12}{q^2 A^2} \tag{32}$$

(regardless of m), and $g_D(m,q)$ grows so sharply that $-2\chi_1$ in Equation 22 can be neglected

$$S(q) \cong \frac{12\varphi(1-\varphi)}{q^2 A^2},\tag{33}$$

i.e. the scattering intensity is proportional to Debye's function (Equation 32).

If Equations 30 and 33 are subjected to the inverse Fourier transformation, then

$$S(\vec{r}) = \frac{3}{\pi}\varphi(1-\varphi)\frac{A}{r}, \quad r \ll R,$$
(34)

$$S(\vec{r}) = \frac{9\varphi}{2\pi}(1-\varphi)\frac{A}{r}\exp\left(-\frac{r}{\xi_k}\right), \quad r \gg R.$$
(35)

So, near the spinodal, the correlation function of the concentration fluctuations $S(\vec{r})$ decreases as 1/r (Equation 34) or as the exponent (Equation 35), when $r < \xi_k$ and $r > \xi_k$, respectively.

Budtov (1986) applied Equation 22 to the P+LMWL system, which, strictly speaking, is incorrect because correlations of the concentration fluctuations in this system cannot be neglected (see subsection 3.7.1).

Nevertheless, he obtained a $\xi_k \sim M^{1/2}$ dependence which coincides with the result of de Gennes' (1968) rigorous consideration (see section 4.4).

Equation 31 can be used to determine the gradient term of the P1+P2 system's potential in the general mean field theory (see Equation 2.5–1). According to Equation 2.5–13,

$$\xi_k^2 = \frac{\delta}{a}$$

where a is the coefficient at the quadratic term of the potential's expansion with respect to the order parameter. With allowance for the expansion of the Gibbs potential (Equation 3.1–275) near the spinodal,

$$a = G_{\Phi\Phi T} \Delta T, \quad G_{\Phi\Phi T} = \frac{k\theta}{T_{sp}}, \tag{3.1-285}$$

Following the approximation

$$2\chi_1 = \frac{\theta}{T}, \quad 2\chi_{1,p} = \frac{\theta}{T_{sp}}$$
(3.1-283)

we have

$$G_{\phi\phi T} = 2\chi_{isp}k$$
 and $\Delta T = T - T_{sp} = \frac{\theta(\chi_{isp} - \chi_i)}{2\chi_{isp}\chi_i}$.

At last, including the coefficient 1/2 by the gradient term in Equation 2.5-1, we get

$$\frac{\delta}{2} = \frac{\xi_k^2 a}{2} = \frac{A^2 kT}{36\varphi(1-\varphi)}$$

and for polymer mixtures

$$\frac{\Delta G_m^*}{kT} = \frac{\varphi}{m_1} \ln \varphi + \frac{1-\varphi}{m_2} \ln(1-\varphi) + \chi_1 \varphi (1-\varphi) + \frac{A^2}{36\varphi (1-\varphi)} (\nabla \varphi)^2.$$
(36)

2. Consider the dynamics of the concentration fluctuations near the critical point for a symmetrical version of mixture with $m_1 = m_2 = m$ according to de Gennes (1980). Then, the Gibbs potential of mixing has the form (de Gennes, 1977) (see Equation 36)

$$\frac{\Delta G_m^*}{kT} = m^{-1} \left[\varphi \ln \varphi + (1-\varphi) \ln(1-\varphi) \right] + \chi_1 \varphi (1-\varphi) + \frac{\Lambda^2}{36\varphi (1-\varphi)} (\nabla \varphi)^2.$$

The asterisk marks the deviation from ΔG_m (per mole of lattice sites).

Fluctuation dynamics is characterized by the fall rate of the fluctuation wave amplitude. If a fluctuation perturbation is modelled by the sum of the Fourier transforms, then the relaxation rate of the component $\delta\varphi_q$ with the wave vector q is defined by $1/\tau_q$.

Accepting Onsager's hypothesis of the fluctuation perturbation evolution $\delta \varphi_q$ obeying the macroscopic equations, we write the equation of continuity

$$\frac{\partial(\delta\varphi_q)}{\partial t} + \operatorname{div} \vec{J}_q = 0, \tag{37}$$

where J_q is the local flux of P1 after resolution of the concentration fluctuation.

According to Onsager's theorem from nonequilibrium thermodynamics, the flux is proportional to the gradient of the chemical potential of this component (see Equation 2.4-33)

$$\vec{J}_q = -\mathcal{M}(\nabla\mu_1)_q. \tag{38}$$

If we separate the temperature dependence of M, we obtain

$$\vec{J}_q = \left(-\frac{\Lambda(q)}{kT}\right) (\nabla \mu_1)_q,\tag{39}$$

where $\Lambda(q)$ is Onsager's coefficient. The chemical potential μ_1 is calculated routinely

$$\frac{\mu_1 - \mu_{01}}{kT} = \frac{\partial}{\partial\varphi} \left(\frac{\Delta G^*}{kT}\right) = m^{-1} \ln \frac{\varphi}{1 - \varphi} + \chi_1 (1 - 2\varphi) - \frac{\Lambda^2}{18\varphi(1 - \varphi)} \nabla^2 \varphi.$$
(40)

In the linearized approximation,

$$\varphi(\vec{r},t) = \varphi + \delta\varphi(\vec{r},t) \tag{41}$$

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is accepted.

If it is substituted to Equation 40 and only the terms linear with respect to $\delta \varphi(\vec{r}, t)$ are kept, we obtain

$$\frac{\mu_1(\vec{r},t) - \mu_0}{kT} = \left[\frac{1}{m\varphi(1-\varphi)} - 2\chi_1 + \frac{A^2}{18\varphi(1-\varphi)}\nabla^2\right]\delta\varphi(\vec{r},t).$$
(42)

Then, the gradient of the chemical potential of P1 at the q vector is

$$\frac{(\nabla\mu_1)_q}{kT} = \nabla(\delta\varphi_q) \left[\frac{1}{m\varphi(1-\varphi)} - 2\chi_1 \right] + \frac{A^2}{18\varphi(1-\varphi)} \nabla^3(\delta\varphi_q).$$
(43)

The solution of Equation 37 has the form

$$\delta\varphi_q = (\delta\varphi_{0q})e^{iqr}e^{-t/\tau_q} \tag{44}$$

(cf. Equations 2.3-48 and 2.4–50). Therefore, $\nabla(\delta\varphi_q) = q(\delta\varphi_q)$, and

$$\nabla^2(\delta\varphi_q) = q^2(\delta\varphi_q); \quad \nabla^4(\delta\varphi_q) = q^4(\delta\varphi_q), \tag{45}$$

$$\frac{\partial(\delta\varphi_q)}{\partial t} = -\frac{1}{\tau_q}\delta\varphi_q \quad \text{or} \quad \frac{1}{\tau_q} = -\frac{1}{\delta\varphi_q}\frac{\partial(\delta\varphi_q)}{\partial t}.$$
(46)

Substituting, in turn, Equation 43 into Equation 39, Equation 39 into Equation 37 (in view of Equation 45), and Equation 37 into Equation 46, we get (de Gennes, 1980)

$$\frac{1}{\tau_q} = q^2 \Lambda(q) \left[\frac{1}{m\varphi(1-\varphi)} - 2\chi_1 + \frac{A^2 q^2}{18\varphi(1-\varphi)} \right],\tag{47}$$

and, for $\varphi_c = 1/2$,

$$\frac{1}{\tau_q} = q^2 \Lambda(q) \left(\frac{4}{m} - 2\chi_1 + \frac{2A^2 q^2}{9} \right).$$
(48)

The relation of $\Lambda(q)$ with the diffusion coefficient is found in terms of reptation motion of the macromolecules in the mixed melt P1+P2.

The entanglement points of a polymer chain with the neighbouring chains are represented as obstacles preventing the transversal motion of this macromolecule: it can just diffusionally "reptate" along its longitudinal axis (see Figure 4.2). Such motion resembles a reptilian's creeping in a certain pipe, and is therefore named **reptation**.

If m_e is the number of steps (segments) of length A between the entanglements, then the pipe diameter is about

$$d \sim m_e^{1/2} A,\tag{49}$$

and the pipe length is

$$L \cong \frac{\overline{h^2}}{d} = \frac{mA^2}{m_e^{1/2}A} = mm_e^{1/2}A.$$
 (50)

The chain moves along the pipe with a mobility μ_p inversely proportional to the chain length, i.e.

$$\mu_p = \frac{\mu_1}{m},\tag{51}$$

where μ_1 is the segment mobility, and, according to Einstein's law,

$$D_p \simeq kT\mu_p,\tag{52}$$

as $\mu_p = 1/f$ (the subscript denotes a "pipe"). By another Einstein's law, the squared diffusional displacement is proportional to the product of the diffusion coefficient and time, so, in this case,

$$D_p T_{\rm rep} \simeq L^2, \tag{53}$$

where T_{rep} is the so-called **fundamental relaxation time**, during which the chain has reptated a distance of the order of L along the pipe.

Combining Equations 50-53, we derive

$$T_{\rm rep} = \frac{L^2}{D_p} = \frac{m^2 A^2}{m_e k T \mu_p} = \frac{m^3 A^2}{m_e k T \mu_1} = \frac{m^3}{m_e} \tau_1,$$
(54)

where

$$\tau_1 = A^2 / kT \mu_1 \tag{55}$$

is the microscopic relaxation time.

For $m = m_e$, Equation 54 gives the Rouse relaxation time (Equation 3.3-62)

$$T_R \sim \tau_1 m^2. \tag{56}$$

For any time $T > T_{rep}$, the chain completely forgets the previous pipe and moves over a distance compatible with the coil size $R_{\theta} = m^{1/2}A$. Hence, the translational diffusion coefficient, in view of Equation 54, is

$$D_{\rm rep} \cong \frac{R_{\theta}^2}{T_{\rm rep}} = \frac{m\Lambda^2 m_e}{m^3 \tau_1} = D_1(T) m_e m^{-2}, \tag{57}$$

where

$$D_1(T) = A^2 / \tau_1 \tag{58}$$

is the microscopic diffusion coefficient.

Now, let us find the concentration dependence of Onsager's coefficient.

Assume, first, that there is no interaction between the components. Then, according to Fick's first law (Equation 2.4-31),

$$J_i = -D_i \nabla \varphi_1, \quad i = 1, 2. \tag{59}$$

On the other hand (see Equation 39),

$$J_{i} = -\Lambda_{i} \nabla \left(\frac{\mu_{i}}{kT}\right), \tag{60}$$

and, according to Equation 36,

$$\frac{\mu_i}{kT} = \frac{\partial}{\partial \varphi_i} \left(\frac{\varphi_i}{m} \ln \varphi_i + const \right) = m^{-1} \ln \varphi_i + const .$$
(61)

We now write Equation 60 with allowance for Equation 61:

$$J_i = -\frac{\Lambda_i}{m} \cdot \frac{\nabla \varphi_i}{\varphi_i}.$$
(62)

Comparison between Equations 59 and 62 yields

$$\Lambda_i = m\varphi_i D_i. \tag{63}$$

If we now "turn on" the interaction, then

$$\frac{\mu_1}{kT} = m^{-1} \ln \varphi_1 + \chi_1 \varphi_2, \tag{64}$$

$$\frac{\mu_2}{kT} = m^{-1} \ln \varphi_2 + \chi_1 \varphi_1.$$
(65)

The introduction of the interaction means that the chemical potential in Equation 60 increases by the value of a certain repulsion potential u, which can be estimated as

$$J_{i} = -\Lambda_{i} \nabla \left(\frac{\mu_{i} + u}{kT} \right). \tag{66}$$

At equilibrium,

$$J_i + J_2 = 0, (67)$$

which yields

$$u = \frac{\Lambda_1 \mu_1 + \Lambda_2 \mu_2}{\Lambda_1 + \Lambda_2}.$$
(68)

If now Equation 68 is substituted into Equation 66, then

$$J_1 = -\frac{2\Lambda_1}{kT} \cdot \frac{\Lambda_1 \nabla \mu_1 + \Lambda_2 \nabla \mu_2}{\Lambda_1 + \Lambda_2},\tag{69}$$

$$J_2 = -\frac{2\Lambda_2}{kT} \cdot \frac{\Lambda_1 \nabla \mu_1 + \Lambda_2 \nabla \mu_2}{\Lambda_1 + \Lambda_2}.$$
(70)

It follows from Equation 67, applied with Equations 69 and 70, that

$$\Lambda_1 = -\Lambda_2. \tag{71}$$

In view of this, Equation 69 has the form

$$J_1 = \frac{2\Lambda_1 \Lambda_2}{kT(\Lambda_1 + \Lambda_2)} \nabla(\mu_1 - \mu_2).$$
(72)

Let us denote

$$\Lambda = \frac{2\Lambda_1\Lambda_2}{\Lambda_1 + \Lambda_2} \tag{73}$$

and substitute Λ_i into Equation 73 expressed through the diffusion coefficients (Equation 63). Then, we accept $D_1 = D_2 = D_{rep}$:

$$\Lambda = 2D_{\rm rep} m\varphi(1-\varphi). \tag{74}$$

For small $q \rightarrow 0$, in view of Equation 57,

$$\Lambda(0) = 2D_1 m_e m^{-1} \varphi(1-\varphi). \tag{75}$$

Return to Equation 48. For

$$\varphi = \varphi_c = 1/2, \quad \chi_{1sp} = \chi_{1c} = 2/m, \tag{76}$$

the relaxation rate of the concentration fluctuations in the limit $q \rightarrow 0$ takes the form

$$\frac{1}{\tau_q} = 2q^2 \Lambda(0) \left(\chi_{1\epsilon} - \chi_1 + \frac{A^2 q^2}{9} \right), \tag{77}$$

and the correlation length (Equation 31) is

$$\xi_k = \frac{\Lambda}{3} (\chi_{1c} - \chi)^{-1/2}.$$
(78)

Combining Equations 78 and 77 leads to

$$\frac{1}{\tau_q} = 2q^2 \Lambda(0)(\chi_{1c} - \chi_1)(1 + q^2 \xi_k^2), \tag{79}$$

and, including Equations 74 and 76,

$$\frac{1}{\tau_q} = q^2 D_{\rm rep} m(\chi_{1c} - \chi_1) (1 + q^2 \xi_k^2)$$
(80)

$$=2q^2 D_{\rm rep} \frac{\chi_{\rm 1c} - \chi_{\rm 1}}{\chi_{\rm 1c}} (1 + q^2 \xi_k^2).$$
(81)

When the configurative point approaches T_c , $(\chi_{1c} - \chi_1) \rightarrow 0$ and $\tau_q \rightarrow \infty$.

Relationships 80 and 81 reflect the law of so-called **thermodynamic retardation** near the critical point (van Hove, 1954; de Gennes, 1979, 1980), where concentration fluctuations practically do not disappear and they may be regarded as long-living colloidal particles which was discussed above with other systems as examples.

For $q \neq 0$ and one relaxation time $\tau(q)$ in the mode $T < T_{\text{rep}}$, de Gennes (1980) deduced a relationship

$$\Lambda(q) \sim q^2. \tag{82}$$

However, later on, de Gennes (1981) found the existence of two relaxation times in the mode $T < T_{rep}$ due to the short-amplitude rapid mode and large-amplitude slow mode.

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In view of this circumstance, Pinkus (1981) obtained

$$\Lambda(q) \sim q^{-2}.\tag{83}$$

Further development of this topic was performed by Binder (1983).

3. Binder (1983) obtained expressions for critical indices in the P1+P2 system for the symmetrical case $m_1 = m_2 = m$

$$\Delta \mu_{1I} = \Delta \mu_{2I}, \quad \Delta \mu_{1II} = \Delta \mu_{2II}, \quad \varphi_c = \frac{1}{2}, \tag{84}$$

and, in view of Equation 40, we get

$$\ln \frac{\varphi_I}{1 - \varphi_I} + m\chi_1(1 - 2\varphi_I) = 0, \qquad \ln \frac{\varphi_{II}}{1 - \varphi_{II}} + m\chi_1(1 - 2\varphi_{II}) = 0.$$
(85)

The order parameter Q is defined according to

$$Q_{I,II} = \frac{\varphi_{I,II} - \varphi_c}{\varphi_c},\tag{86}$$

where φ_I and φ_{II} relate to the left-hand and right-hand branches of the binodal, respectively. The order parameter Q varies within the limits

$$-1 \le Q \le +1. \tag{87}$$

Equation 85 can be written (see Equations 1.5-74,-75) as

$$Q_{I,II} = \tanh \frac{m\chi_1 Q_{I,II}}{2}.$$
(88)

Near the critical point, two terms of tanh's (Equation 1.5-78) are enough

$$Q_{I,II} \approx \frac{m\chi_1 Q_{I,II}}{2} - \frac{1}{3} \left(\frac{m\chi_1 Q_{I,II}}{2}\right)^3.$$
(89)

As $\chi_{1c} = 2/m$ (Equation 8), then

$$Q_{I,II} = \pm \left[3 \left(\frac{\chi_1}{\chi_{1c}} - 1 \right) \right]^{1/2} \left(\frac{\chi_{1c}}{\chi_1} \right)^{3/2}.$$
(90)

For a system with a UCST, $\chi_1 \sim 1/T$ and

$$Q_{I,II} \simeq B \left(\frac{T_c - T}{T_c}\right)^{\beta},\tag{91}$$

where $\beta = 1/2$. It follows from Equation 29 that at $q \to 0$ in the one-phase region $(\chi_i < \chi_{ic}, T > T_c)$

$$S(0) = \frac{1}{2\chi_{1c}} \left(1 - \frac{\chi_1}{\chi_{1c}} \right)^{-1},$$
(92)

i.e. (cf. Equation 2.3 107 and Table 1.2)

$$\chi_T \sim S(0) \simeq \Gamma \left(\frac{T - T_c}{T}\right)^{-\gamma} \simeq \Gamma \left(\frac{T - T_c}{T_c}\right)^{-\gamma},\tag{93}$$

where $\gamma = 1$.

At last, from Equation 31 we get

$$\xi_k = \frac{A}{3\chi_{1c}^{1/2}} \left(1 - \frac{\chi_1}{\chi_{1c}} \right)^{-1/2} \cong \xi_{0c} \left(\frac{T - T_c}{T_c} \right)^{-\nu}, \tag{94}$$

where $\nu = 1/2$. Thus, the critical indices have values typical for the mean field theory.

On the basis of Equations 22 and 27, Akcasu and Sanchez (1988) obtained the most general expression for the potential of the P1+P2 system to account for the order parameter's fluctuations $\varphi_i = \varphi_i + \delta \varphi_i$:

$$\frac{F}{kT} = \int d^3r \left[\frac{\ln \varphi_1}{m_1} A_1(\nabla^2) \varphi_1 + \frac{\ln \varphi_2}{m_2} A_2(\nabla^2) \varphi_2 + \varphi_1 \varphi_2 \chi_1 \right], \tag{95}$$

where

$$A_{i}(-q^{2}) = \frac{1}{2} \left[g_{D}^{-1}(q^{2}R_{i}^{2}) + 1 \right]$$

$$= \frac{1}{2} \left[\frac{1}{1 - \frac{1}{3}(qR_{i})^{2}} + 1 \right] \cong 1 + \frac{1}{6}(qR_{i})^{2} + \cdots,$$
(96)

and

$$A_i(\nabla^2) = 1 - \frac{R_i^2}{6} \nabla^2 = 1 - \frac{m_i A_i^2}{36} \nabla^2.$$
(97)

Substituting Equation 97 into Equation 95, we get

$$\frac{F}{kT} = \int d^3r \left\{ \frac{f_{\rm FH}}{kT} - \frac{1}{36} \left(A_1^2 \ln \varphi_1 \nabla^2 \varphi_1 + A_2^2 \ln \varphi_2 \nabla^2 \varphi_2 \right) \right\},\tag{98}$$

where $f_{\rm FH}$ is Flory-Huggins' potential (Equation 3).

If we assume that on the system's boundary $\nabla \varphi = 0$ is met, then

$$\int d^3r \left(\ln \varphi_i \nabla^2 \varphi_i \right) = - \int d^3r \frac{|\nabla \varphi_i|^2}{\varphi_i}.$$
(99)

In view of this, Equation 98 reduces to de Gennes' potential (Equation 36).

With φ_i taken as a non-fluctuating quantity ($\varphi_i = \varphi_i$), Equation 98 reduces to Flory-Huggins' standard potential.

Akcasu and Sanchez (1988) have written potential 95 as a series in the vertex functions $\tilde{\Gamma}_i^{(n)}$ which, in their turn, are expressed via Debye's functions $g_D(q^2 R_i^2)$.

3.7.3. Interpenetrating polymer networks

If, to prepare a NP+LMWL system, a monomer with an initiator and crosslinker is taken as LMWL, then, on 3D polymerization of the second polymer, the system network P1+network P2 appears, so-called **interpenetrating polymer networks** (IPN). If there is no crosslinker, **semiinterpenetrating polymer networks** (SIPN) are formed, i.e. network P1+P2. A great body of publications, including reviews and monographs (Manson and Sperling, 1976; Tomas and Sperling, 1978; Lipatov and Sergeyeva, 1979; Sperling, 1981; Sergeyeva and Lipatov, 1986) are devoted to the problems of such systems.

It follows from sections 3.5 and 3.7 that the conditions of the one-phase state (compatibility) of IPN and SIPN are more restricted in comparison with polymer networks and mixtures. On the other hand, chemical crosslinks hinder phase separation which, therefore, has to be realized on the colloidal level of dispersion. As a rule, microphase separation begins to be observed even at the stage of polymerization and crosslinking of the second polymer.

Superposition of processes of different nature leads to a diverse morphological pattern of polymer materials which, in turn, provides their wide technical applications. The sequential thermodynamic description of such systems presents significant difficulties; one can test this with an example of the PIPN structure model from (Donatelly et al., 1977; Sperling, 1981).

Morphologically, the turbidity spectrum method has great advantages to characterize the microheterogeneous structure of IPN and SIPN (see subsection 2.1.5) (Klenin et al., 1977b).

3.8. Theory of corresponding states

The restrictions of the initial version of Flory-Iluggins' lattice model (P+LMWL mixtures) were obvious from the very beginning and, first and foremost, to the authors themselves. Indeed, the model did not foresee the change in volume on mixing and, as a sequence, the additional variation of the configurative entropy of mixing. χ_1 was considered to have a reciprocal dependence on T which specifies the existence of the UCST only.

Since 1960's, a LCST near the critical vapour-liquid temperature of the LMW component has been revealed experimentally for many P+LMWL systems (Freeman and Rowlinson, 1960; Baker et al., 1962).

To explain the existence of the LCST of such a type, a theory of corresponding states (called the theory of liquid state as well) has received a large development effort by Prigogine et al. (1953), Prigogine (1957), Flory et al. (1964ab), Flory (1965, 1970), Patterson and Delmas (1970), Siow et al. (1972). This approach is based on the theory of r-dimensional liquids developed by the Brussels school (Ilia Prigogine et al.)

The theory involves the molecular properties of liquids (the chain length; the number of molecular degrees of freedom, contributing to heat expansion; the cohesion energy between unlinked segments) and accepts the statement of the law of corresponding sates of there being a universal state equation of liquids and their mixtures in the reduced variables \tilde{T} , \tilde{V} , \tilde{P} . For polymer liquids, Prigogine et al. introduce the concept of internal and external degrees of freedom. The number of external freedom degrees of a spherical macromolecule is 3 for a LMW compound (monomer, or just mer). When spherical molecules are linked into a chain, the number of external freedom degrees reduces, which leads to a decrease in the heat energy providing heat expansion, i.e. to a decrease in the so-called **free volume of liquid**. A polymer molecule is assumed to have 3c external degrees of freedom and q intermolecular contacts with the energy ε^* each. For an ensemble of r independent molecules,

$$3c = 3r.$$
 (1)

On linking monomers (segments, mers) into a chain,

$$3c = 2r + 1; \tag{2}$$

with due account of valent angles, 3c = r + 3, etc. (Patterson and Tager, 1967).

Hence, 3c is the number of external (intermolecular) degrees of freedom per segment (mer) with c < 1 (Eichinger and Flory, 1968a).

Thermal expansion or the free volume of liquid is characterized by the reduced temperature \tilde{T} ; in fact, it is the ratio of the thermal energy of external freedom degrees and the energy of intermolecular contacts \cdot

$$\tilde{T} = \frac{ckT}{q\varepsilon^*} = \frac{T}{T^*},\tag{3}$$

where

$$T^* = \frac{q\varepsilon^*}{ck} \tag{4}$$

is reduced temperature.

The molecular characteristics, which depend on the intermolecular interactions only, are called **configurational**.

The molar configurational quantities under constant and negligible pressure are defined as

$$\frac{V}{V^*} = \tilde{V}(\tilde{T}),\tag{5}$$

$$V^* = N_A r v^*, \tag{6}$$

where v^* is the volume of the densely packed part or solid core of the monomer (mer),

$$\frac{U}{U^{*}} = \tilde{U}(\tilde{T}), \tag{7}$$

$$U^* = N_A q \varepsilon^*, \tag{8}$$

$$\frac{S}{S^{*}} = \tilde{S}(\tilde{T}), \tag{9}$$

$$S^* = N_A ck, \tag{10}$$

$$T^{\star} = \frac{U^{\star}}{S^{\star}} = \frac{q\varepsilon^{\star}}{ck} \tag{11}$$

in accordance with Equation 4. Reduced pressure P^* results from Equations 6 and 8:

$$P^* = \frac{U^*}{V^*} = \frac{q\varepsilon^*}{rv^*}.$$
(12)

In view of Equation 4,

$$P^* = \frac{T^*ck}{rv^*}.$$
(13)

The characteristic reduced quantities V^* , U^* , and S^* are found from the molecular and thermodynamic properties of a pure liquid.

Prigogine et al. (1957) considered a polymer chain consisting of spherical segments. Any segment is a part of the molecule, equal (in length) to the chain diameter measured in either van der Waals' diameters σ or r^* , where r^* is the distance between two unlinked segments at the potential minimum ε^* . Then, they introduced the parameter

$$\rho = \frac{r_{22}^*}{r_{11}^*} - 1 \tag{14}$$

to characterize the difference between the diameters of spherical molecules (two componeuts) or between the diameters of the chain and of a spherical molecule of LMWL.

The state equation in reduced quantities is derived from (see Equation 1.7-14)

$$\tilde{P} = k\tilde{T} \left(\frac{\partial \ln Z(\tilde{T}, \tilde{V})}{\partial \tilde{V}} \right)_{\tilde{T}},$$
(15)

where Z is the partition function for a specific model of liquid (individual one or a mixture).

Prigogine (1957) applied the partition function of Eyring and Hirschfelder (1937) and used Lennard-Johns' potential as the potential energy between two molecules (mers)

$$\varepsilon(r) = \varepsilon^* \varphi\left(\frac{r}{r^*}\right) \tag{16}$$

where

$$\varphi\left(\frac{r}{r^*}\right) = \left(\frac{r^*}{r}\right)^{12} - 2\left(\frac{r^*}{r}\right)^6,\tag{17}$$

or, more generally,

$$\varphi\left(\frac{r}{r^*}\right) = \nu\left(\frac{r^*}{r}\right)^n - \mu\left(\frac{r^*}{r}\right)^m.$$
(18)

In this version of the theory (Prigogine, 1957; Patterson and Delmas, 1970), the reduced energy is

$$\tilde{U} = \frac{-n\tilde{V}^{-m/3} + m\tilde{V}^{-n/3}}{n-m},$$
(19)

and the state equation is

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \left(1 - b\tilde{V}^{-1/3}\right)^{-1} + \frac{mn}{3(m-n)} \left(\tilde{V}^{-n/3} - \tilde{V}^{-m/3}\right),\tag{20}$$

where $b = (m/n)^{1/(n-m)}$ is the packing factor.

Flory et al. (1964ab) applied a partition function of the same form but with van der Waals' interaction potential, which is a specific case of Lennard-Johns' potential at m = 3 and $n \to \infty$. For N molecules of an r-mer, the partition function is

$$Z(\tilde{T}, \tilde{v}) = Z_{\text{comb}} \left(gv^* \right)^{rNc} \left(\tilde{v}^{1/3} - 1 \right)^{3rNc} \exp\left(\frac{rNc}{\tilde{v}\tilde{T}} \right),$$
(21)

where $\tilde{v} = v/v^* = V/V^* = \tilde{V}$, v = V/rN is the volume per segment (mer), V is the total volume of the system, g is the geometrical factor (in Eyring-Hirschfelder's partition function c = 1 while in Equation 21 c < 1).

It results for this model that

$$\tilde{U} = -\tilde{V}^{-1},\tag{22}$$

$$c_P^{-1} = 1 - \frac{2}{3}\tilde{V}^{-1/3} - \frac{2\left(1 - \tilde{V}^{-1/3}\right)}{\tilde{P}\tilde{V}^2 + 1},\tag{23}$$

and the state equation is

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{\tilde{V}^{1/3} - 1} - \frac{1}{\tilde{V}\tilde{T}},$$
(24)

which, at $\tilde{P} = 0$, takes the form

$$\tilde{T} = \left(\tilde{V}^{1/3} - 1\right)\tilde{V}^{-4/3} \tag{25}$$

OF

$$T^* = \frac{T\tilde{V}^{4/3}}{\tilde{V}^{1/3} - 1}.$$
(26)

The characteristic reduced quantities fit Equation 13.

If a thermal expansion coefficient

$$\alpha = V^{-1} \left(\frac{\partial V}{\partial T}\right)_P \tag{27}$$

is introduced, then it follows from Equation 26 that

$$\tilde{V}^{1/3} - 1 = \frac{\alpha T}{3(1 + \alpha T)}.$$
(28)

On differentiating Equation 24 with respect to temperature, one derives

$$P^* = \beta T \tilde{V}^2, \tag{29}$$

where

$$\beta = \left(\frac{\partial P}{\partial T}\right)_{V} \tag{30}$$

is the **thermal pressure coefficient**. By the experimentally determined α , \tilde{V} is obtained from Equation 28 and V^* from Equation 5. For $\tilde{P} = 0$ (P = 0), T^* is determined from Equation 26 and P^* is from Equation 29 (von Tapavicza and Prausnitz, 1975; Casassa, 1976).

Equations 19-29 are regarded valid for each individual component as well as for their mixture.

The reduced thermodynamic functions of mixture (solution) are found with the help of the characteristic reduced quantities, which are determined from the corresponding quantities of the components according to a certain law of mixing (Patterson and Delmas, 1970). Eg.

$$S^* = x_1 S_1^* + x_2 S_2^*, \tag{31}$$

where x_i are the mole fractions of the components. Additivity in this equation reflects the absence of interaction between the external freedom degrees of molecules of both the components. On the other hand,

$$U^* = x_1 U_1^* + x_2 U_2^* - x_1 U_1^* X_2 \nu^2, \tag{32}$$

where

$$\nu^{2} \equiv \frac{\varepsilon_{11}^{*} + \varepsilon_{22}^{*} - 2\varepsilon_{12}^{*}}{\varepsilon_{11}^{*}} + 18\rho^{2}, \tag{33}$$

$$X_2 = \frac{x_2 q^2}{x_1 q_1 + x_2 q^2} \tag{34}$$

is the **surface fraction** of the second component (Prigogine, 1957). Therefore, Equation 32 accounts for a relative weakness of the 1-2 interaction in comparison with the 1-1 and 2-2 ones and a difference between the diameters of the components' molecules (the chain diameter in the case of a polymer chain).

Combining Equations 31, 32, and 11 leads to

$$\tilde{T} = \frac{\psi_1 \tilde{T}_1 + \psi_2 \tilde{T}_2}{1 - \psi_1 X_2 \nu^2},\tag{35}$$

where

$$\psi_{i} = \frac{x_{i}U_{i}^{*}}{x_{1}U_{1}^{*} + x_{2}U_{2}^{*}} = \frac{x_{1}q_{i}\varepsilon_{1}^{*}}{x_{1}q_{1}\varepsilon_{11}^{*} + x_{2}q_{2}\varepsilon_{22}^{*}} = \frac{P_{i}^{*}\Phi_{i}}{P_{1}^{*}\Phi_{1} + P_{2}^{*}\Phi_{2}},$$
(36)

$$\Phi_{i} = \frac{N_{i}V_{i}^{*}}{N_{1}V_{1}^{*} + N_{2}V_{2}^{*}} = \frac{x_{i}V_{i}^{*}}{x_{1}V_{1}^{*} + x_{2}V_{2}^{*}} = \frac{x_{i}r_{i}v_{i}^{*}}{x_{1}r_{1}v_{1}^{*} + x_{2}r_{2}v_{2}^{*}} = \frac{m_{i}v_{sp,i}^{*}}{m_{1}v_{sp,i}^{*} + m_{2}v_{sp,i}^{*}}, \quad (37)$$

 m_i and $v^*_{sp,i}$ are the mass and specific volume of the *i*th component, respectively.

Equations 31-37 are given in Prigogine's notation. In Flory's notation (Eichinger and Flory, 1968a) for mixture,

$$Z = const \cdot Z_{comb} \left(\tilde{v}^{1/3} - 1 \right)^{3\tilde{r}N\tilde{c}} \exp\left(-\frac{E_0}{kT}\right),$$
(38)

where $N = N_1 + N_2$; $\bar{r} = (r_1 N_1 + r_2 N_2)/N$; $\bar{c} = (r_1 N_1 c_1 + r_2 N_2 c_2)/\bar{r}N$. It is assumed that $v_1^* = v_2^* = v^*$, $V_1^* = r_i v^*$, $V_2^*/V_1^* = r_2/r_1$,

$$k \ln Z_{\text{comb}} = \Delta S_{\text{m,comb}} = -k(n_1 \ln \Phi_1 + n_2 \ln \Phi_2)$$
(39)

(see Equation 3.1-20). The surface fraction is

$$\theta_2 = 1 - \theta_1 = \frac{s_2 r_2 N_2}{s_1 r_1 N_1 + s_2 r_2 N_2} = \frac{\Phi_2 s_2}{\Phi_1 s_1 + \Phi_2 s_2},\tag{40}$$

 s_i is the number of molecular contacts per mer, proportional to the cross-section of the *i*th mer (Eichinger and Flory, 1968a).

It follows from Equations 31, 32, 11, 13 that

$$P^* = \Phi_1 P_1^* + \Phi_2 P_2^* - \Phi_1 \theta_2 X_{1,2}, \tag{41}$$

and

$$T^{*} = \frac{\Phi_{1}P_{1}^{*} + \Phi_{2}P_{2}^{*} - \Phi_{1}\theta_{2}X_{1,2}}{\frac{\Phi_{1}P_{1}^{*}}{T_{1}^{*}} + \frac{\Phi_{2}P_{2}^{*}}{T_{2}^{*}}},$$
(42)

where

$$X_{1,2} = \frac{s_1}{2(v^*)^2} \left(\eta_{11} + \eta_{22} - 2\eta_{12}\right).$$
(43)

Equations 40-43 (in Flory's notation) are equivalent to Equations 31-37 (in Prigogine's notation) with the following glossary

$$\eta_{ij} = 2v^* \varepsilon^*_{ij},\tag{44}$$

$$X_2 \equiv \theta_2, \tag{45}$$

$$\nu_2 \equiv \frac{X_{1,2}}{P_1^*},\tag{46}$$

and ψ_i is transformed to Φ_i according to Equation 36.

Partition function 38 enables the chemical potential of the first component to be calculated:

$$\mu_1 = \left(\frac{\partial F}{\partial N_1}\right)_{T, V, N_2} = -kT \left(\frac{\partial \ln Z}{\partial N_1}\right)_{T, V, N_2} \tag{47}$$

and

$$\ln a_1 = \frac{\mu_1 - \mu_{01}}{RT} = \ln(1 - \Phi_2) + \left(1 - \frac{l}{r}\right)\Phi_2 + \frac{\Delta\mu_{1ex}}{RT}$$
(48)

3.8. Theory of corresponding states

with

$$\Delta \mu_{1ex} = P_1^* V_1^* \left\{ 3T_1 \ln \left[\left(\tilde{v}_1^{1/3} - 1 \right) \left(\tilde{v}^{1/3} - 1 \right) \right] + \tilde{v}_1^{-1} - \tilde{v}^{-1} \right\} + \frac{V_1^*}{\tilde{v}} X_{1,2} \theta_2^2.$$
(49)

Expanding into a series and eliminating the third-order terms gives (Eichinger and Flory, 1968a)

$$\Delta \mu_{1ex} \cong \frac{P_1^* V_1^*}{\tilde{v}_1} \left[\frac{A^2 \alpha_1 T}{2} + Y_{1,2} \right] \Phi_2^2 + O(\Phi_2^3), \tag{50}$$

where

$$A = \left(1 - \frac{T_1^*}{T_2^*}\right) \frac{P_2^*}{P_1^*} - \frac{s_2}{s_1} \cdot \frac{X_{1,2}}{P_1^*},$$

$$Y_{1,2} = \left(\frac{s_2}{s_1}\right)^2 \frac{X_{1,2}}{P_1^*}.$$
(51)

It follows from Equation 50 that (see Equation 3.1-59)

$$\chi_{1} \approx \frac{\Delta \mu_{1ex}}{RT\Phi_{2}^{2}} = \frac{P_{1}^{*}V_{1}^{*}}{RT\tilde{V}_{1}} \left[\left(\frac{s_{2}}{s_{1}}\right)^{2} \frac{X_{1,2}}{P_{1}^{*}} + \frac{\alpha_{1}T}{2} \left\{ \frac{P_{2}^{*}}{P_{1}^{*}} \tau - \frac{s_{2}}{s_{1}} \cdot \frac{X_{1,2}}{P_{1}^{*}} \right\}^{2} \right],$$
(52)

where

$$\tau = 1 - \frac{T_1^*}{T_2^*}.$$
(53)

If we neglect the third-order infinitesimal (Siow et al., 1972), then

$$\chi_{1} \simeq \frac{P_{1}^{*} V_{1}^{*}}{RT \tilde{v}_{1}} \left[\left(\frac{s_{2}}{s_{1}} \right)^{2} \frac{X_{1,2}}{P_{1}^{*}} + \frac{\alpha_{1} T}{2} \tau^{2} \right].$$
(54)

For the model used in Flory's theory,

$$-U_1 = \frac{P_1^* V_1^*}{\tilde{v}_1},\tag{55}$$

$$c_{P,1} = \frac{P_1^* V_1^* \alpha_1}{\tilde{v}_1},\tag{56}$$

and Equation 54 is identical to χ_1 from Prigogine-Patterson's version of the theory

$$\chi_1 = -\frac{U_1}{RT}\nu^2 + \frac{c_{P,1}}{2R}\tau^2,$$
(57)

where

$$\nu^2 = \left(\frac{s_2}{s_1}\right)^2 \frac{X_{1,2}}{P_1^*} \approx \frac{X_{1,2}}{P_1^*}.$$
(58)

 U_1 is the configurational (intermolecular) energy of the solvent (the energy of liquid except the energy of the same substance as ideal gas at the same temperature). It is a

negative value equal to the evaporation energy. The parameters ν and τ are temperatureindependent and are related to Prigogine's (1957) molecular parameters ρ from Equation 14 and

$$\delta = \frac{\varepsilon_{22}^*}{\varepsilon_{11}^*} - 1, \tag{59}$$

$$-\lambda = \frac{c_2}{c_1} \frac{q_1}{q^2} - 1 \tag{60}$$

by means of (Saeki et al., 1973b)

$$\tau \simeq \delta + \lambda, \tag{61}$$

$$\nu^2 = \frac{\delta^2}{4} + 9\rho^2. \tag{62}$$

The first term in Equation 57 is similar to the temperature dependence of χ_1 in Flory-Huggins' classical theory and responsible for the appearance of an UCST. The second term in Equation 57 increases with temperature, tending to a very large value $(c_{P,1} \rightarrow \infty$ as the critical vapour-liquid temperature of the first component is approached) (see Equations 1.1.2-19,-43).

Hence, with increasing temperature, the second term will inevitably overcompensate for the first one, and, when χ_1 exceeds 1/2, a LCST will appear for, in principle, any P+LMWL pair.

 $c_1 = P_1^* V_1^* / RT_1^*$ results from Equation 6 and 13. In view of this and Equations 26 and 28, we get from Equation 54

$$\chi_{1} = \frac{c_{1}\nu^{2}}{1 - \tilde{V}_{1}^{-1/3}} + \frac{c_{1}\tau^{2}}{2\left(\frac{4}{3}\tilde{V}_{1}^{-1/3} - 1\right)}.$$
(63)

In the notation of this paragraph, we write Equation 3.1-242 as

$$\chi_{1e} = \frac{1}{2\left(1 + r^{-1/2}\right)^2}.$$
(64)

Then, for the critical state, Equations 63 and 64 yield

$$\frac{c_1\nu^2}{1-\tilde{V}_1^{-1/3}} + \frac{c_1\tau^2}{2\left(\frac{4}{3}\tilde{V}_1^{-1/3} - 1\right)} = \frac{\left(1+r^{-1/2}\right)^2}{2}.$$
(65)

With allowance for Equation 25, Equation 65 predicts the appearance of UCST and LCST in the temperature scale depending on $c_1\nu^2$, $c_1\tau^2$, and the molecular weight of the polymer (Figure 3.88) (Siow et al., 1972). If the system contains polymer homologues, then $\nu = 0$ (Figure 3.88 presents only one root of Equation 64, corresponding to the LCST). If $\nu \neq 0$, then \tilde{T} goes through a point with an infinitely sharp slope with a certain molecular weight. To the left of this point, there exist two roots for T, corresponding to UCST and LCST; to the right there are no roots, i.e. two phase separation regions



Figure 3.88. Dependence of \tilde{T} on $c_1\tau^2/(1+r^{-1/2})^2$ at different values of $c_1\nu^2/(1+r^{-1/2})^2$. $\tilde{l}^2 = 0$ (Siow et al., 1972) [Reprinted with permission from: Macromolecules 5 (1972) 29-34. Copyright © 1972 American Chemical Society]

 $T. ^{\circ}C$



Figure 3.89. State diagram of polystyrene+acctone. The MW of the polymer is: 4,800 (1), 10,300 (2), 19,800 (3) (Siow et al., 1972) [Reprinted with permission from: Macromolecules 5 (1972) 29-34. Copyright © 1972 American Chemical Society]

overlap each other, forming a "sand clock". This has indeed been experimentally revealed for the system polystyrene+acetone and polystyrene+diethyl ether (Siow et al., 1972) (Figure 3.89).

The existence of two roots is provided by low values of τ^2 and ν^2 while there are no roots at a high value of any of these parameters.

Figure 3.88 shows the influence of M on the critical solution temperatures. A decrease in r (the molecular weight) leads to the corresponding decrease in the function's argument, which lowers the UCST and raises the LCST. An increase in r (the molecular weight),
on the contrary, may cause merging of the UCST and LCST (a "sand clock"). In



Figure 3.90. Calculated and experimental dependences of UCST and LCST on $r^{-1/2}$ for the systems CTA+acetone (1) and CDA(2,8)+acetone (2) (Cowie et al., 1971) [Reprinted with permission from: Macromolecules 4 (1971) 57-61. Copyright © 1971 American Chemical Society]

Figure 3.90 are presented the experimental values of UCST and LCST with theoretical values for the systems cellulose 3,0-acetate (CTA) + acetone and cellulose 2,8-acetate (CDA(2,8)) + acetone (Cowie et al., 1971). The authors calculated T_1^* from the thermal expansion coefficient of acetone and from Equations 28 and 26. The figure demonstrates qualitative agreement between theory and experiment, after the axes for the theoretical and experimental curves \tilde{T} are shifted by 169° relative to each other.

To interpret the results of experimental investigations within the theory of corresponding states, one needs to determine experimentally the temperature dependence of heat capacity and density, the thermal coefficients of expansion and pressure of the individual components, and such properties of mixtures as the chemical potentials and enthalpy of mixing (Cowie et al., 1971), i.e. measuring a number of quantities on a specialized, sophisticated, and expensive equipment is required (Blanks, 1977).

For the polystyrene+acetone system, the calculated phase separation region (a "sand clock") proves to be more narrow than the experimental one, and the theoretical critical concentrations at the UCST and LCST are twice as lower as the experimental ones (Siow et al., 1972).

In the systems $P\alpha MS+cyclohexane$, $P\alpha MS+methylcyclohexane$, $P\alpha MS+butyl chlo$ $ride, and <math>P\alpha MS+propylene$ oxide, Cowie and McEwen (1975) also observed a qualitative agreement between the theoretical and experimental curves (UCST and LCST vs $r^{-1/2}$) which, however, was achieved by means of arbitrary changes in a number of parameters. In particular, T_1^* must remain constant, but its variation with T was observed in experiment.

Measurements of χ from vapour pressure and osmotic pressure have shown a concentration dependence $\chi = \chi(\Phi)$ which is in semiquantitative agreement with χ_{theor} calculated using Equation 52 for the systems natural rubber+benzene (Eichinger and Flory, 1968a), polyisobutylene (PIB)+benzene (Eichinger and Flory, 1968b), PIB+cyclohexane (Eichinger and Flory, 1968ac), PIB+n-pentane (Eichinger and Flory, 1968d).

For the systems polystyrene+decaline, polystyrene+benzene, polystyrene+ethylbenzene, polystyrene+cyclohexane, Vshivkov and Komolova (1981) have revealed significant disagreement between the theoretical and experimental spinodals.

McMaster (1973) has found a strong influence of the thermal expansion coefficient α and the thermal pressure coefficient β on the location of the phase separation region in polymer mixtures.

Due to a difference in the state equations of two polymers, a phase separation region with a LCST should be expected in their mixtures, which drastically shifts along the T axis when the differences $(\alpha_1 - \alpha_2)$ and $(\beta_1 - \beta_2)$ increase (Figure 3.91).



Figure 3.91. Dependence of the location of the phase separation region in P1+P2 mixtures on the difference between the thermal expansion coefficients $(\alpha_1 - \alpha_2)$, the thermal pressure coefficients $(\beta_1 - \beta_2)$, and the interaction parameter X_{12} of polymers. $M_1 < M_2$ (McMaster, 1973) [Reprinted with permission from: Macromolecules 6 (1973) 760–773. Copyright © 1973 American Chemical Society]

In polymer mixtures, two phase separation regions with a LCST and UCST may be observed at low values of the interaction parameter X_{12} (Equation 43) (cf. Equation 58 and Figure 3.88). As X_{12} increases, these two phase separation regions merge into a "sand clock" (Figure 3.91).

Hence, to enhance the compatibility region of two polymers, close values of their thermal coefficients α and β and small positive (or negative) values of X_{12} (and small values of MW) are needed. Eg., a large compatibility region of two polymers with their MW $2 \cdot 10^5$ and $X_{12} = 0$ is provided if their α differ by not more than 4%.

A version of the corresponding states theory, which is able to predict some new types of the location of the phase separation regions (Figure 3.92) and has proved to be rather fruitful in predicting the incompatibility region (phase separation) of polymer mixtures, has been elaborated by Lacombe and Sanchez (1976), Sanchez and Lacombe (1976, 1977), Sanchez (1978).

Sugamiya's (1977) version involves the dipole moment of a monomer unit and (or) LMWL molecules.

In summary, the theory of corresponding states has made much progress; however, it is far from harmony with experiment.

3.9. Relaxational thermodynamics

Frenkel and Eliashevich (1971, 1975), Frenkel (1974) have put forward an idea to construct a theory of relaxational thermodynamics (thermokinetics). Its basic principle is



Figure 3.92. State diagrams of liquid-liquid phase separation, predicted by the theory of corresponding states, besides those shown in Figure 3.81 (Lacombe and Sanchez, 1976) [Reprinted with permission from: R.H.Lacombe, J.C.Sanchez. J. Phys. Chem. 80 (1976) 2568-2580. Copyright © 1976 American Chemical Society]

the dependence of the thermodynamic potentials of a system (in particular, the Gibbs potential of mixing or the Helmholtz free energy of mixing) on the velocity of motion of the configurative point

$$\Delta F_m(t) = \int_0^t \frac{\partial \Delta F_m}{\partial T} \frac{\partial T}{\partial t} dt.$$
⁽¹⁾

The question is not about the formalism of irreversible thermodynamics or merely relaxational processes in phase separation kinetics, but, precisely, about the possibility to modify traditional thermodynamic potentials as seen in Equation 1.

According to the thermokinetic principle, the location of the phase separation region must depend on the velocity of the configurative point approaching it.

A multilevel structural organization is characteristic for many polymer systems. If each level is related to a relative minimum of the thermodynamic potential and a dependence of the Equation 1 type accepted, one can understand, qualitatively and semiquantitatively, the morphological variety of polymer systems, i.e. their polymorphism.

The thermokinetic approach ideas have found their place in phase separation kinetics, and, especially, in morphology.

Involving the time dependence $\Delta F_m(t)$ (Equation 1) is close to the thermodynamics of systems with fading memory (Day, 1972) and the TTT type (time-temperaturetransformation) diagram, a so-called "nose" diagram in the spinodal decomposition theory (Huston et al., 1966; Cahn, 1968).

As to the explicit form of Equation 1, nothing definite can be said. Perhaps, such attempts may be exerted by plotting spinodals using Chu-Scholte's method (see subsection 3.6.2) at different velocities of motion of the configurative point in the one-phase region.

3.10. Multiphase separation

In a binary system, equilibrium of three phases takes place when the tangent lines to $\Delta \bar{G}_m = f(v_2)$ at three values of v_2 merge into one straight line (Figure 3.93, $T = T_3$). In



Figure 3.93. Diagram of three-liquid-phase equilibrium at the temperature T_3 in a binary system. The dashed lines in the upper figure are the spinodals. The dashed lines on the isotherms $\Delta \bar{G}_m/RT$ show the metastable equilibrium of phases, the empty circles are critical points (Koningsveld, 1975) [Reprinted from: R.Koningsveld. Brit. Polym. J. 7 (1975) 435-458. Copyright © 1975 by Wiley. Reprinted by permission of John Wiley & Sons, Inc.]

polynary systems, in equilibrium there are as many phases as many times a plane can be tangent to the folding surface $\Delta \hat{G}_m$.

If, under certain conditions, γ phases transform to one phase, such a state of the systems is referred to as the γ -order critical state (or the γ -order critical point) (Kohnstamm, 1926).

According to Gibbs' phase rule (Equation 1.2-32), in a ν -component system with γ phases, f parameters (such as temperature, pressure, component concentrations) may

vary without any change in the number of phases (see subsection 1.2.3)

$$f = \nu + 2 - \gamma. \tag{1}$$

If all the γ phases turn out to be identical, the number of degrees of freedom in the critical state decreases by $(\gamma - 1)$, so

$$f = \nu + 2 - \gamma - (\gamma - 1) = \nu - 2\gamma + 3.$$
⁽²⁾

The number of degrees of freedom f cannot be negative; therefore, for a γ -order critical point to exist, $2\gamma - 3$ components are required at minimum.

Hence, the 2nd-order critical point is realized in a one-component system, the 3rd-order one may be observed in a three-component (ternary) system, the 4th-order one — in a five-component system, and so on.

Griffiths and Widom (1973), Widom (1973), Griffiths (1974) prove that the 3rd-order critical point is a tricritical point in the sense accepted in section 1.6.



Figure 3.94. Three-phase equilibrium $\alpha + \beta + \gamma$ (*a*, dashed area in *e*); finite critical point $\alpha\beta$ (fc $\alpha\beta$) (*b*, *e*); finite critical point $\beta\gamma$ (*c*, *e*); tricritical point (tc) (*d*, *e*); μ_1 is the chemical potential of one of the components (Griffiths, 1974) [Reprinted with permission from: R.B.Griffiths. J. Chem. Phys. 60 (1974) 195-206. Copyright © 1974 American Institute of Physics]

Figure 3.94 demonstrates how two lines of the double critical points $\alpha\beta$ and $\beta\gamma$ can merge into one point, namely, the tricritical point of the asymmetrical type.

As theoretical calculations and experiments show, three-phase equilibrium is observed in the P+LMWL system, when the polymer comprises two polymer homologues with their M differing by more than 10 times, or when the polymolecular sample has a strongly asymmetrical MWD, and in a binary P1+P2 system where the interaction parameter is concentration-dependent. Analysis of this situation can be carried out within Flory-Huggins' theory (Tompa, 1949; Šolc, 1970, 1974, 1977, 1982, 1983; Chermin, 1977; Šolc et al., 1984).

According to the first approximation of the theory, the distribution of polymer substance in phases obeys the exponential function (Equation 3.2-12)

$$\frac{\varphi_{II}}{\varphi_{I}} = \exp(K\sigma p),\tag{3}$$

where

$$\sigma = 2\chi_1(\varphi_{II} - \varphi_I) + \ln \frac{1 - \varphi_{II}}{1 - \varphi_I}, \quad K = \pm 1.$$
(4)

We assume the system to be in the one-phase state and to be subject to phase separation by means of a temperature or composition variation, and the amount of the second phase is infinitely small $(x \rightarrow 0)$, which corresponds to the CPC (see section 3.2). This phase is called a **conjugate (incipient) phase** while the initial phase is called a **principal phase**.

As was mentioned above, the CPC is of great importance in the study of phase separation in polymer systems as one of the few experimental methods for recording phase separation.

We denote the incipient-principal phase ratio as

$$Q = \frac{V_{II}}{V_I} = \frac{1}{r} \tag{5}$$

(cf. Equation 3.2-15). Besides, we accept K = +1 if $\varphi_{II} > \varphi_I$, and K = -1 if $\varphi_{II} < \varphi_I$ in Equation 3.

The material balance condition yields the relationship

$$\varphi_{II} = \frac{\varphi f(p)(Q+1)}{Q + \exp(-K\sigma p)} \tag{6}$$

(cf. Equation 3.2-25), where f(p) is the differential polymerization-degree distribution function (by weight) of the polymer in the initial solution, φ is the polymer concentration in the initial solution.

The CPC corresponds to the $Q \rightarrow 0$ limit of the ratio

$$\lim_{Q \to 0} \frac{\varphi_{II}}{\varphi_{I}}.$$
(7)

As the conjugate phase is present in an infinitesimal amount, $\varphi_i \approx \varphi$ and

$$\lim_{Q \to 0} \frac{\varphi_{II}}{\varphi} = f_{II}(p) = f(p) \exp(K\sigma p).$$
(8)

We now introduce moments μ_k of the normalized MWD function f(p) of the polymer in the initial solution

$$\mu_k = \int_0^\infty p^k f(p) \, dp,\tag{9}$$

and moments ν_k of the non-normalized MWD function $f_{II}(p)$ of the polymer in the conjugate phase

$$\nu_{k} = \int_{0}^{\infty} p^{k} f_{II}(p) \, dp = \int_{0}^{\infty} p^{k} f(p) \exp(K\sigma p) \, dp.$$
(10)

On the basis of Equation 8, any distribution moment ν_k may be expressed through σ and the moments of the distribution function f(p) of the initial polymer

$$\nu_{k} = \int_{0}^{\infty} p^{k} f_{II}(p) \, dp = \int_{0}^{\infty} f(p) \sum_{i=0}^{\infty} \frac{(K\sigma)^{i} p^{k+i}}{i!} dp \tag{11}$$
$$= \mu_{k} + \sum_{i=1}^{\infty} \frac{(K\sigma)^{i} \mu_{k+i}}{i!}.$$

Here, the exponential function is represented by a series.

With Equations 7 and 8, the zeroth moment ν_0 defines the volume concentration ratio of the polymer in the phases

$$\nu_0 = \frac{\varphi_{II}}{\varphi_I}.\tag{12}$$

Differentiating Equation 11 with respect to σ n times, we get

$$\frac{d^n \nu_k}{d\sigma^n} = K^n \nu_{k+n}.$$
(13)

Under the CPC condition, the amount of the conjugate phase II tends to zero; hence, the parameters characterizing the principal phase in Equation 3.2-20 can be replaced by the parameters of the initial solution. With due account of the notation accepted in this section, Equation 3.2-20 takes the form

$$F(\sigma,\varphi) = K\sigma \frac{1+\nu_0}{2} + (\nu_0 - 1) - (\nu_{-1} - \mu_{-1}) + \left(\varphi^{-1} - \frac{1+\nu_0}{2}\right) \ln \frac{1-\varphi\nu_0}{1-\varphi} = 0,(14)$$

and allows the direct calculation of CPC.

For the chosen φ and MWD function specifying the moments μ_k , the root σ of Equation 14 is sought for, ν_0 and ν_{-1} are determined using Equation 11. The interaction parameter χ_1 is then calculated from Equation 4 with allowance for the accepted notation (Equation 12)

$$2\chi_{1}\varphi(\nu_{0}-1) = K\sigma + \ln\frac{1-\varphi}{1-\varphi\nu_{0}}.$$
(15)

Analysis (Solc, 1970, 1974) shows that, provided that f(p) is not strongly asymmetrical, Equation 14 has one non-trivial root σ , which tends to zero when φ approaches its critical value $\varphi_c = (1 + p_w p_z^{-1/2})^{-1}$ (Equation 3.2-10). In this case, the root σ is always positive provided that K = 1 for $\varphi < \varphi_c$ and K = -1

for $\varphi > \varphi_c$.

The trivial root of Equation 14 is $K\sigma = 0$.

In other cases of rather asymmetrical distributions of f(p), Equation 14 may have two or three different non-trivial roots depending on f(p) and φ . Each root corresponds to a conjugate phase which is in equilibrium with the principal phase at the concentration φ and χ , corresponding to Equation 15.

Thus, Equation 14 proves to be valid for multiphase separation as well.

This circumstance has an effect on the behaviour of CPC which undergoes a break (see below).

In a system with an UCST, the CPC corresponds to the χ_1^{-1} vs φ dependence.

As the shadow line (SL) is the curve of coexistence to the CPC (see section 3.2), it is represented by the χ_1^{-1} vs $\varphi \nu_0$ dependence in simulation (see Equation 12).

Equations 11, 13-15, in the limit $\sigma \to 0$ and $\varphi \to \varphi_c$, have yielded (Šolc, 1970, 1974) relationships, including the known one for χ_{1c} (Equation 3.2–11):

$$\chi_{1c} = \frac{1}{2} \left(1 + p_z^{1/2} p_w^{-1} \right) \left(1 + p_z^{-1/2} \right), \tag{16}$$

$$\left(\frac{d\sigma}{d\varphi}\right)_{c} = -4K \frac{p_{\omega} p_{z}^{-1/2} \left(1 + p_{z}^{1/2} p_{\omega}^{-1}\right)^{2}}{3p_{z} + 2p_{z}^{1/2} - p_{z+1}},$$
(17)

$$\left(\frac{d\chi_1}{d\varphi}\right)_c = \frac{1}{2} \left(1 + p_z^{1/2} p_w^{-1}\right)^2 \left(1 - p_w p_z^{-1}\right),\tag{18}$$

$$\left[\frac{d(\varphi\nu_0)}{d\varphi}\right]_c = 1 - 4\left(p_w + p_z^{1/2}\right)\left(3p_z + 2p_z^{1/2} - p_{z+1}\right)^{-1},\tag{19}$$

$$\left(\frac{d^2\chi_1}{d\varphi^2}\right)_c = p_w^{-1} \left(1 + p_w p_z^{-1/2}\right)^3 + \left(1 + p_z^{1/2} p_w^{-1}\right)^3 \left\{1 - \frac{4}{3} \left[\frac{p_w^2 p_z^{-1/2} \left(1 + p_z^{1/2} p_w^{-1}\right)^2}{3p_z + 2p_z^{1/2} - p_{z+1}}\right]\right\}, (20)$$

where the usual average values are applied

$$p_w = \frac{\mu_1}{\mu_0} = \mu_1, \quad p_z = \frac{\mu_2}{\mu_1}, \quad p_{z+1} = \frac{\mu_3}{\mu_2}, \cdots$$
 (21)

It follows from Equation 17 that the positive-by-definition parameter σ will be really positive near $\varphi - \varphi_c$ if only the denominator of Equation 17 S > 0:

$$S \equiv 3p_z + 2p_z^{1/2} - p_{z+1} > 0.$$
⁽²²⁾

The same result follows from comparison of Equations 18 and 20 with the derivatives taken along the spinodal (Equation 3.2-9).

While $(d\chi_{1n}/d\varphi)_c$ fits Equation 18, the second derivative differs from Equation 20

$$\left(\frac{d^2\chi_{1sp}}{d\varphi^2}\right)_c = p_w^{-1} \left(1 + p_w p_z^{-1/2}\right)^3 + \left(1 + p_z^{1/2} p_w^{-1}\right)^3.$$
(23)

Until S > 0,

$$\left(\frac{d^2\chi_{_{1\rm sp}}}{d\varphi^2}\right)_c > \left(\frac{d^2\chi_{_1}}{d\varphi^2}\right)_c,\tag{24}$$

and the spinodal, going through the critical point and being tangent here to the CPC, remains inside the two-phase region. But, as soon as S < 0, the CPC "jumps away" from the spinodal-bounded region (see Figure 3.67). Remaining on the spinodal, the critical point (in the event of S < 0) loses its physical reality, and just at S = 0 the critical point shows a singularity.

Condition 22 is always satisfied for certain types of MWD (eg. like Shultz-Zimm's kind) while it is not the case for other types.

According to Equation 18, the critical point is always observed either at the maximum (a monomolecular polymer) or on the right-hand branch of the CPC (a polymolecular polymer).

By direct testing, one can prove that the derivative from Equation 19 is always negative given condition 22 is satisfied; it follows that the SL and CPC approach the critical point from different sides.

Detailed analysis of the function $F(\sigma, \varphi)$ and of the roots of Equation 14 for different ranges of S was made by Solc (1970). In particular, for $\sigma = 0$

$$\left(\frac{\partial F}{\partial \sigma}\right)_{\varphi} = \left(\frac{\partial^2 F}{\partial \sigma^2}\right)_{\varphi} = 0.$$

At K = +1, the function $F(\sigma)$ at a constant γ and $\sigma \to 0$ is nondecreasing if $\varphi < \varphi_c$ or nonincreasing if $\varphi > \varphi_c$. At $\varphi = \varphi_c$, even the third derivative of $F(\sigma)$ with respect to σ is equal to zero:

$$\left(\frac{\partial^3 F}{\partial \sigma^3}\right)_{\varphi=\varphi_{\epsilon}}=0$$

Eg., in the case of $S \ll 0$, when the MWD is very asymmetrical, the function $F(\sigma,\varphi)$ at $\varphi = \varphi_c$ shows a flat minimum at the origin of coordinate ($\sigma = 0$), and Equation 14 must have two different roots (σ_1 and σ_2) which are called by Solc **noncritical** while the **critical** roots tend to zero at $\varphi \to \varphi_c$.

Correspondingly, the CPC branch is called **critical**, if it corresponds to a critical root, and otherwise **noncritical**.

In the case being discussed, $S \ll 0$; the CPC, therefore, comprises two non-critical branches relating to the roots σ_1 and σ_2 .

The branch going at lower polymer concentrations will be hereinafter referred to as lefthand and the other one as right-hand. They intersect at the triple (or three-phase: Šolc, 1970) point φ_i where

$$\chi_{11} = \chi_{12}.$$
 (25)

As $\sigma_1 \neq \sigma_2$, then

$$\frac{\partial \chi_{11}}{\partial \varphi} \neq \frac{\partial \chi_{12}}{\partial \varphi}$$
 and $\varphi_{II,1} \neq \varphi_{II,2}$.

Hence, at $\varphi - \varphi_i$, the CPC shows a bend while the SL has a break, i.e. the principal phase and two conjugate phases are in equilibrium. This situation is portrayed in Figure 3.95 (Solc, 1974). The complex shape of CPC indicates that only the segments GT



Figure 3.95. Schematic of the CPC location with a three-phase point T. GTBDTF are the CPC's branches, GTF is the stable part, TBDT is the metastable part; G''B'D'F is the SL; G''T'' and T'F' are the stable parts, T''B'D'T' is the metastable part; C is the metastable critical point (Šolc, 1974) [Reprinted from: K.Šolc. J. Polym. Sci.: Polym. Phys. Ed. 12 (1974) 555-562. Copyright © 1974 by Wiley. Reprinted by permission of John Wiley & Sons, Inc.]

and TF are real and have a physical meaning, while DB is in the unstable region. Depending on the MWD details, the critical point may be located either on the metastable branches TB or TD, or on the unstable branch DB. Rarely, the critical point will coincide with the triple point T. In the figure, the critical point C is on the segment TB, being a **metastable critical point**; the SL is denoted by the dashed line.

Subsection 3.6.2 discussed the properties of the neighbourhood of the critical points where at $\Delta T \rightarrow 0$

$$i) \quad r \to \infty, \quad \text{if} \quad \varphi < \varphi_c, \tag{26}$$

$$ii) \quad r \to 0, \quad \text{if} \quad \varphi > \varphi_c, \tag{27}$$

$$iii) \quad r \to 1, \quad \text{if} \quad \varphi = \varphi_c. \tag{28}$$

For the considered type of systems, these rules may not be observed. Let us discuss the behaviour of the limit (Šolc, 1974)

$$r_0 = \lim_{\Delta T \to 0} r. \tag{29}$$

It is seen from Figure 3.95 that only the SL's branch G''B', corresponding to the CPC's branch GB, goes through the critical point. According to the lever rule and considering the relative location of the CPC and SL (see Figure 3.95), Equation 26 holds true if only $\varphi < \varphi_t$. At the triple point, the quantity r_0 is undeterminable in principle, since there exist two different incipient phases, namely, T' and T'', in equilibrium with the original solution of the concentration $\varphi = \varphi_t$. If, however, $\varphi > \varphi_t$, then $r_0 \to 0$ always, and Rules 26 and 28 are not observed. For $\varphi_t < \varphi < \varphi_c$ we have $r_0 = 0$ although the concentration is smaller than the critical one. For $\varphi = \varphi_c$, $r_0 = 0$ as well, and Rule 28 is not fulfilled.

Similarly, at $\varphi_c < \varphi_t$, when the critical point is on the CPC segments *BD* or *DT*, requirements 27 and 28 may fail.

Hence, rules 26-28 are valid for the stable critical point only, i.e. when it is located on the stable branches of the CPC (GT or TF) or on the CPC without a triple point.

This is concerned with the necessity of those cautions while determining critical points by the phase-volume ratio method, which were dealt with in subsection 3.6.2.



Figure 3.96. Surface χ_1 in the ternary system 0+1+2: LMWL+monomer $(p_1 = 1) + P(p_2 = 25)$. φ is a quasibinary section 0-(1+2); $w_2 = \varphi_2/(\varphi_1 + \varphi_2)$ φ_2) (the LMWL concentration is constant). The sections of the χ_1 surface by parallel planes w_2 and φ show the CPC; the dotted line is the critical line in the unstable region; the dashed line is the critical line in the stable region; the circles are the critical points; the dot-and-dash line is the three-phase line (Solc, 1970) [Reprinted with permission from: Macromolecules 3 (1970) 665-673. Copyright © 1970 American Chemical Society]

Figure 3.97. Characteristic curves in the ternary system: LMWL+monomer $(p_1 = 1)+P(p_2 = 25)$. DGHC is the three-phase line; the upper (DFAC) and lower dashed lines (DBEC) are the cusp lines; the stable (thin solid) and metastable (dotted) lines are the critical lines (Šolc, 1982) [Reprinted from: K.Šolc. J. Polym. Sci.: Polym. Phys. Ed. 20 (1982) 1947-1961. Copyright © 1982 by Wiley. Reprinted by permission of John Wiley & Sons, Inc.]

Figures 3.96 and 3.97 present the results of calculation of CPC and other characteristic curves of phase separation in a model ternary system 0+1+2: LMWL+monomer (p_1 =

1)+P($p_2 = 25$) (Šolc, 1970). There is no interaction between components 1 and 2 $\chi_{1(12)} = 0$ while the interactions between 0–1 and 0–2 are the same:

$$\chi_{1(01)} = \chi_{1(02)} = \chi_1. \tag{30}$$

A variation of the total (1+2) concentration with reference to zero is a quasibinary section φ ; at a constant LMWL (component 0) concentration:

$$w_2=rac{arphi_2}{arphi_1+arphi_2}$$

Different planes with a constant w_2 model systems with changing MWD asymmetry (S).

The line of the critical points for individual CPC called a critical line, drops down with decreasing w_2 , goes through a minimum at $w_2 \simeq 9.4 \cdot 10^{-3}$ ($\chi_1 = 2.08$, the point B in Figure 3.97), then grows again to reach a maximum at $w_2 \simeq 4.2 \cdot 10^{-4}$ (the point A) and reaches $\chi_1 = 2$ at $w_2 \to 0$. Both the extrema correspond to S = 0. First, the critical line is located on the χ_1 surface, and the critical points have a real meaning, though there are triple points on the CPC. As w_2 decreases, the critical line approaches the three-phase line, intersects it at $w_2 \simeq 2 \cdot 10^{-2}$ and drops down under the χ_1 surface, losing, hence, its physical stability. At w_2 , corresponding to the critical points after their minimal values, the critical points are located on the extended left-hand CPC branches (see Figures 3.95 and 3.96). On a further decrease of w_2 , the critical point move, under the χ_1 surface, from the continuation of the left-hand CPC branches to that of the right-hand ones and appear on the χ_1 surface at the maximum of the three-phase line (see Figure 3.97).

Each CPC branch, which goes through the three-phase point, has singular points (cusp points) where it abruptly inverses its course, i.e. the derivative $d\sigma/d\varphi$ along the CPC diverges and changes its sign at these points while $d\chi_1/d\varphi$ behaves as usual (the points *B* and *D* in Figure 3.95).

In addition to Equations 14 and 15, the relationship

$$2\chi_1 = (\varphi \nu_1)^{-1} + (1 - \varphi \nu_0)^{-1} = (\varphi_{II} p_{\omega II})^{-1} + (1 - \varphi_{II})^{-1}$$
(31)

must be satisfied at the cusp point.

The cusp lines are entirely under the thermodynamically stable binodal surface (see the points D and B in Figure 3.95) except their end points C and D (see Figure 3.97) where they appear on the binodal surface. Thus, the cusp lines are boundary curves between the metastable and unstable binodal surfaces.

It is seen from Figure 3.97 that the maximum A (minimum B) of the critical line coincides with the maximum (minimum) of the upper (lower) cusp point line. This relation is valid generally. The extremum condition of the cusp point line requires $d\chi_1$ to be equal to zero along the cusp line. Calculations involving Equations 14, 15, and 31 lead to an equation symmetrical with Equation 31

$$2\chi_{1} = (\varphi \mu_{1})^{-1} + (1 - \varphi)^{-1} = (\varphi p_{w})^{-1} + (1 - \varphi)^{-1},$$
(32)

which shows the cusp point at the extremum of the cusp point curve to belong to the spinodal.

One of the possibilities for Equations 31 and 32 to be satisfied simultaneously is in $\varphi \rightarrow \varphi_{II}$ and $p_w \rightarrow p_{wII}$, i.e. the two phases differ by an infinitesimal quantity. This

occurs at the double critical points at the double point of the spinodal. Another possibility is provided when two extrema of the cusp-point lines turn out to be conjugate, i.e. represent two phases in equilibrium. Exactly such a case is shown in Figure 3.97 when the maximum of the lower cusp-point curve $E(w_{2,E} \simeq 7.0 \cdot 10^{-6})$ is in equilibrium with the minimum of the upper cusp-point line $F(w_{2,F} \simeq 3.8 \cdot 10^{-2})$.

At last, the three-phase line, appearing when two binodal surfaces intersect, reflects all the stable three-phase equilibria in the system: the horizontal line χ_1 in Figure 3.97 intersects the three-phase one just three times, i.e. at the points corresponding to three conjugate phases.

The three-phase line merges with the upper and lower cusp-point lines at the points C and D where three-phase equilibrium finishes to exist. These points meet Equations 14, 15, 31 (Solc, 1977), and

$$\frac{\varphi_{II}}{1 - \varphi_{II}} = \frac{p_{zII}^{1/2}}{p_{wII}},\tag{33}$$

i.e. the phases, conjugate at the points C and D, must be critical points, and, hence, the double (extremal) points of the three-phase line as well (the points G and H in Figure 3.97).

Of the three characteristic curves (Figure 3.97), only the three-phase line is thermodynamically stable over its entire length. Recall that the critical line becomes metastable where it is dropped under the stable binodal surface on the segments GB and HA, and becomes unstable between the extrema A and B.

The curves in Figure 3.97 help us to obtain an impression of the evolution of the three-phase equilibrium, say, during cooling of the system, by means of plotting the binodals which appear when the binodal surface is intersected by χ_1 -constant planes with a constantly decreasing temperature level (when the values of χ_1 increase). At the lowest values of χ_1 , the binodals have only one critical point L on the sharply-dropping right-hand stable branch of the critical line (see Figures 3.96 and 3.97).

At χ_{1A} , the double cusp point coinciding with the double critical point (Figure 3.97, the point A), appears inside the initial binodal at w_{2A} . A new binodal then arises from this point. An increase in χ_1 within $\chi_{1A} < \chi_1 < \chi_{1D}$ causes a splitting of the double cusp point into two cusp points with two arcs of the new binodal between them (Figure 3.98a) (cusp--also means the moon's horn as two arcs of the binodal look).

The double critical point also splits into two single ones, namely, the metastable one M (to the left from the point A in Figure 3.97), which moves toward the external arc of the binodal and becomes stable, and the unstable one N, which moves towards the internal arc of the binodal (Figure 3.97, to the right from the point A to the point B).

As χ_1 further increases, the new binodal (now stable) grows and approaches, by its external arc, the initial binodal and, at last, touches it at $\chi_{1D} = \chi_{1H}$ (see Figure 3.97).

The old and new binodals touch each other at the critical point \tilde{M} (H in Figure 3.97), and, at the same time, a new configuration with cusp points, corresponding to the beginning of development of the third phase (Figure 3.98b), forms near the distant point of the initial binodal P (D in Figure 3.97). Two phases with an infinitesimal difference in composition appear at the point M.

 χ_1 , increasing within $\chi_{1H} < \chi_1 < \chi_{1E}$, leads to an advance of the external arc of the new



Figure 3.98. Development of the phase separation region during temperature variations in a ternary system with a three-phase separation region. The solid circles are the critical points, the empty triangles are points defining the composition of three-phase equilibrium (Šolc, 1982) [Reprinted from: K.Šolc. J. Polym. Sci.: Polym. Phys. Ed. 20 (1982) 1947-1961. Copyright © 1982 by Wiley. Reprinted by permission of John Wiley & Sons, Inc.]

binodal over the initial binodal, and the extremal part of the arc becomes stable along with the critical point M. Two bend points of the external contour of the new and old binodals and the bend point of the binodal together with the cusp points near the point P give the composition triangle of the three-phase state of the system (Figure 3.98c).

A unique symmetrical construction of the binodals appears at $\chi_{1E} = \chi_{1F}$ (Figures 3.97 and 3.98d) where two cusp points of two different configurations with cusp points merge at the point F, and, simultaneously, the internal (unstable) branch of the new binodal touches the old one at the point E. This contact point E is not critical. The unstable critical point N is located in the central, most internal branch of the binodals.

When χ_1 appears to be greater than χ_{1E} , the behaviour of the binodals changes as described above but in the reverse order and with roles swopped. Two cusp points diverge from the point E (see Figure 3.97), forming a configuration with cusp points to the left (Figure 3.98e) while the internal arc of the binodal breaks away from the point F(Figure 3.97) with the formation of another new binodal to the right (Figure 3.98c) with the stable critical point L (Figure 3.98c; the solid line in Figure 3.97). At $\chi_{1C} = \chi_{1G}$, the external arc of the new right-hand binodal meets the old one at the critical point L, and the left-hand configuration with the cusp points disappear. At last, at $\chi_1 = \chi_{1B}$, the new binodal contracts down to a point while the critical points N and L merge into one double critical point (the point B in Figure 3.97).

Figure 3.99 shows a number of CPC going through the three-phase region where φ varies; w_2 is a parameter varying from a certain $w_2 > w_{2,D}$ (see Figure 3.97) down to zero.

At $w_2 > w_{2,D}$, the CPC is of a smooth, gradual nature. At $w_2 = w_{2,D}$, a double cusp point is reached (Figure 3.97, the point D), which the CPC h corresponds to (Figure 3.99).



Figure 3.99. CPC for the ternary system 0+1+2: LMWL+monomer $(p_1 = 1)+P(p_1 = 25)$. φ is the concentration of (1+2); $w_2 = \varphi_2/(\varphi_1 + \varphi_2) = 0$ (o), $9 \cdot 10^{-8}$ (a), $1 \cdot 10^{-6}$ (b), $5 \cdot 10^{-5}$ (c), $4 \cdot 10^{-4}$ (d), $2 \cdot 10^{-3}$ (e), $9.4 \cdot 10^{-3}$ (f), $2 \cdot 10^{-2}$ (g), $5 \cdot 10^{-2}$ (h). The empty triangles are the critical points for the curves o, a, b; the solid circles are the critical points for the other curves (Šolc, 1982) [Reprinted from: K.Šolc. J. Polym. Sci.: Polym. Phys. Ed. 20 (1982) 1947-1961. Copyright © 1982 by Wiley. Reprinted by permission of John Wiley & Sons, Inc.]

When $w_2 = w_{2,D}$, the double cusp point splits into two cusp points, and there appears a configuration with two cusp points. The stable critical point is far from the cusp points on the left-hand branch of the CPC (see Figure 3.97) and, apparently, does not play any role.

As w_2 diminishes, the critical point falls (Figure 3.99, line g), turns out to be metastable on passing the three-phase point G (Figure 3.97), and reaches the lower double cusp points at $w_{2,B}$ (see Figure 3.97; Figure 3.99, curve f). Then, it goes up along the CPC's unstable branch (Figure 3.99, curve e), reaching the upper double cusp point at $w_{2,A}$ (Figure 3.99, curve d); then it changes its direction, moves down along the CPC's right-hand branch, and becomes stable when it appears on the binodal surface at the maximum of the threephase line H (Figure 3.97; Figure 3.99, curves c, b). About $w_2 \approx 1 \cdot 10^{-5}$ (between the curves c and b in Figure 3.99), the configuration of the cusp points changes its orientation, and the three-phase point is at lower values of χ_1 . On a decrease in w_2 , the configuration with the cusp points disappears, and the CPC becomes smooth again (Figure 3.99, curve a).

The CPC for the binary system 0+1 ($w_2 = 0$, Figure 3.99, curve o) forms an envelope for the right-hand branches of other CPCs; it means that the LMW fractions of the polymer play a large role in phase equilibria at high polymer concentrations (1+2).

The three-phase behaviour of a model quasiternary system, containing LMWL and two polymolecular homologues, substantially differs from that of true ternary systems (Šolc, 1982). In the second approximation of Flory-Huggins' theory (state equation 3.6-1), the phase equilibrium relationships have the form (Šolc et al., 1984)

$$\ln \frac{\varphi_{0II}}{\varphi_{0I}} + \varphi_{II} - \varphi_I - \left(\frac{\varphi_{II}}{p_{nII}} - \frac{\varphi_I}{p_{nI}}\right) + \varphi_{II}^2 \left[g_{II} - (1 - \varphi_{II})g_{1II}\right] - \varphi_I^2 \left[g_I - (1 - \varphi_I)g_{1I}\right] = 0,(34)$$

$$\ln \left(\frac{\varphi_{III}}{\varphi_{iI}}\right) = \sigma p_i,$$
(35)

where

$$\sigma = \ln \frac{\varphi_{0II}}{\varphi_{0I}} - (g_{II} - g_I) + \varphi_{II}(2g_{II} - \varphi_{0II}g_{1II}) - \varphi_I(2g_I - \varphi_{0I}g_{1I}), \tag{36}$$

and $g_k = \partial^k G / \partial \varphi^k$ is the *k*th derivative in phase I or II.

Accepting the same approximation for the principal (I) and incipient (II) phases (see Equations 7 and 8), Equations 34-35 are transformed into the CPC equations:

$$F_{1}(\sigma,\varphi,T) \equiv \frac{1}{2}\sigma(\nu_{0}+1) + \nu_{0} - 1 - (\nu_{-1}-\mu_{-1}) + \left(\varphi^{-1} - \frac{\nu_{0}+1}{2}\right)\ln\frac{1-\varphi\nu_{0}}{1-\varphi} \quad (37)$$
$$-(g_{II}-g_{I})\left[\varphi\nu_{0} - \frac{1}{2}(\nu_{0}+1)\right] - \frac{1}{2}(\nu_{0}-1)\varphi\left[g_{1II}\nu_{0}(1-\varphi\nu_{0}) + g_{1I}(1-\varphi)\right] = 0$$

and

$$F_{2}(\sigma,\varphi,T) \equiv 2g\varphi(\nu_{0}-1) + \ln\frac{1-\varphi\nu_{0}}{1-\varphi} - \sigma -$$

$$-(g_{11}-g)(1-2\varphi\nu_{0}) - \varphi \left[g_{111}\nu_{0}(1-\varphi\nu_{0}) - g_{11}(1-\varphi)\right] = 0.$$
(38)

If g is φ -independent, $F_1(\sigma, \varphi)$ (Equation 37) is temperature-independent and reduces to Equation 14.

Generally, analysis of Equations 37 and 38 is very laborious, even if computer-aided. Their basic properties are revealed if the interaction parameter is represented by the sum of two summands, temperature-dependent and concentration-dependent

$$g(T,\varphi) \approx g^{T}(T) + g^{\varphi}(\varphi).$$
(39)

At the critical point, the coexisting phases become identical; hence, $\sigma \to 0$, $\nu_k \to \mu_k$, $g_k \to g_{k,11}$, etc.

Near the critical point, the interaction parameter and its derivatives with respect to concentration can be represented as the series

$$g_{k,II} = g_k + \sum_{i=1}^{k} \frac{g_{k+i}\varphi^i(\nu_0 - 1)^i}{i!}, \qquad k = 0, 1, 2, \dots$$
(40)

Then, the functions F_1 and F_2 are also represented as series by Equation 11 and an expansion into series of logarithmic functions. It turns out that, at $\sigma \to 0$, F_1 converges

as σ^3 while F_2 converges as σ , and the trivial roots of Equations 37 and 38 are eliminated by introducing new functions

$$\bar{F}_1 \equiv \frac{F_1}{\sigma^3},\tag{41}$$

$$\bar{F}_2 \equiv \frac{F_2}{\sigma}.\tag{42}$$

Therefore, the critical state is defined by

$$\lim_{\sigma \to 0} \bar{F}_1 = \lim_{\sigma \to 0} \bar{F}_2 = 0.$$
(43)

The multiple critical points correspond to the multiple roots of the phase equilibrium equations related to the critical point of the system.

Because phase equilibrium exists under isothermal conditions, the multiple roots are obtained, in turn, by analysis of the partial derivatives with respect to σ of any of F_1 , F_2 , F_1 , or F_2 at constant T and φ . Eg., the condition

$$\lim_{\sigma \to 0} \dot{F}_1 = 0 \tag{44}$$

along with the spinodal equation corresponds to one nontrivial root (the single critical point).

If

$$\lim_{\sigma \to 0} \left(\frac{\partial F_1}{\partial \sigma} \right)_{T,\varphi} = 0, \tag{45}$$

then the function $\bar{F}_1(\sigma)$ at constant T and φ shows an extremum at $\sigma = 0$ and has a double root (the double critical point).

In the general case, the condition of existence of an *m*-multiple critical point is

$$\lim_{\sigma \to 0} \left(\frac{\partial^n F_1}{\partial \sigma^n} \right)_{T,\varphi} = 0; \quad n = 0, 1, \dots, m-1$$
(46)

and the spinodal condition (Equation 46 at n = -1).

Thus, the *m*-multiple critical point is defined by (m + 1) independent equations 46, including n = -1.

Sole et al. (1984) have analyzed the conditions of existence of multiphase equilibrium and multiple critical points in the system (polymolecular P)+LMWL when a concentrationindependent interaction parameter and in binary systems with a concentration-dependent interaction parameter $g = f(\varphi)$.

Gibbs' phase rule (Equation 1) for the system (polymolecular P)+LMWL requires some modification. First, phase equilibria are considered under constant (atmospheric) pressure, i.e. pressure is fixed and no longer a variable. Second, the degrees of polymerization p_i with i = 1, 2, ..., s-1 and concentrations of components become variables. The number of degrees of freedom for the *m*-multiple critical points is cancelled by (m + 1) conditions of its existence (see Equation 46, including n = -1), so there remains

$$f = 2s - 1 - (m+1) = 2s - 2 - m, \quad s > 1, \quad 1 \le m \le 2s - 3 \tag{47}$$

Table 3.6

Number of degrees of freedom in the critical state of a polynary system with a concentration-independent parameter g

Number of	Number of	Critical point		
components,	independent	Multiplicity	Number of	Degree of freedom, f^{a}
s	variables	m	equations, $m + 1$	
2	3	1	2	<i>p</i> ₁
3	5	1	2	p_1, p_2, w_2
		2	3	p_1, p_2
		3	4	p_1
4	7	1	2	p_1, p_2, p_3, w_2, w_3
		2	3	p_1, p_2, p_3, w_3
		3	4	p_1, p_2, p_3
		4	5	p_1, p_2
		5	6	p_1

^a the most typical combinations; others are also possible

degrees of freedom.

According to Equation 47, Table 3.6 reports the degrees of freedom of 2...4-component systems in the *m*-multiple critical state.

Polymer homologues are arranged in the ascending order of their molecule lengths, $p_1 < p_2 < \cdots < p_{s-1}$. The length is often expressed in relative units $r_j = p_j/p_{j-1}$, $j = 2, 3, \ldots, s-1$ with $r_j > 1$.

For a given number of components, the critical points of a certain multiplicity exist only at a certain combination of r_j , and such critical points can be represented in r-space.

The state of a binary system (at a fixed pressure) is characterized by three variables, T, φ , and p_1 (see Equation 3.1-32) and two equations that define the only critical point: Equation 46 at n = 0 and n = -1 (see also Equation 3.1-50 and $\partial \Delta \mu_1 / \partial n_1 = 0$).

Hence, according to Equation 47, f = 1. Indeed, the location of the critical point is defined by one parameter, eg., by the chain length p_1 (Equation 3.1-241).

Every ternary system has a line of simple critical points, which is defined in the whole concentration range of the polymer homologues P_1 and P_2 . Hence, p_1 , p_2 , and w_2 may vary (see Table 3.6). In ternary systems, where three-phase separation is possible, double critical points with a fixed composition w_2 appear as the extrema of the lines of simple critical points while p_1 and p_2 remain variables. At the triple critical point of a ternary system, a certain p_2/p_1 ratio must be preserved while p_1 remains a variable (see Table 3.6).

The diagram of multiple critical points for ternary and quaternary systems in *r*-space is presented in Figure 3.100.

For a ternary system, the diagram is one-dimensional with a triple critical (tricritical) point which separates the three-phase region from the two-phase ones with double critical points (Figure 3.100a; see also Figures 3.93 and 3.94). The location of the tricritical point $r_{2,tc} \equiv r^*(p_1)$ depends on p_1 , varying from $r^* \simeq 15.645$ for $p_1 = 1$ to $r^* \simeq 9.899$ for $p_1 \to \infty$ (Tompa, 1949; Solc et al., 1984).

For the three-phase state of a quaternary system, there exists an infinite number of



Figure 3.100. Diagram of multiple critical points in r-space $(r_j = p_j/p_{j-1})$: ternary systems (a), quaternary systems (b). Multiple critical points: T \cdots triple, Q_a — quaternary, Q_i pentary. The position of the triple point T and both the lines of the quaternary critical points depends on the value of p_1 (Šolc, 1984) [Reprinted with permission from: Macromolecules 17 (1984) 573-585. Copyright © 1984 American Chemical Society]

double critical points which form a continuous line, and, at least, one triple critical point at a fixed composition w_2 , w_3 .

Quaternary critical points are revealed in systems where r_3 takes a certain value which functionally related to p_1 and p_2 .

At last, the pentary critical point requires fixed relations between r_3 and r_2 ; only p_1 remains variable.

The diagram of the critical points of a quaternary system is shown in Figure 3.100b. The existence condition of a line of double critical points is $p_3/p_1 = r_2r_3 \ge r^*(p_1)$, i.e. a hyperbola in the r_2 and r_3 coordinates (the lower dashed line, Figure 3.100b).

The set of the quaternary critical points Q_a comprises two asymptotic branches which meet at the cusp point – it defines the pentary critical point. These asymptotic branches are boundaries between systems with simple three-phase separation and systems with a more complex behaviour (two different three-phase regions, one of which may be unstable, and four-phase separation).

Figure 3.101 demonstrates the behaviour of CPC in systems with multiphase separation (Šolc et al., 1984). For comparison, a CPC for two-phase separation in the system (polymolecular P)+LMWL is shown in Figure 3.101a (see section 3.2). In systems with three-phase separation, the CPC has the shape discussed above in detail. Two stable branches of CPC intersect at the point P. At its concentration φ_p , the principal phase is in equilibrium with two different incipient (conjugate) phases (Figure 3.95, the points T' and T"), i.e. three-phase separation originates from the point P which, hence, is called a three-phase point on the CPC. Depending on MWD, the critical point may be located on the CPC, including its metastable branches PB and PC, and the unstable segment CB. If the critical point coincides with one of the cusp points C or B, it is referred to as a **heterogeneous double critical point**. The word "heterogeneous" is associated with the fact that on a certain change in the composition of the P+LMWL system, the critical



Figure 3.101. Cloud-point curves during multiphase separation (Šolc et al., 1984) [Reprinted with permission from: Macromolecules 17 (1984) 573-585. Copyright © 1984 American Chemical Society]

point (say, the point B in Figure 3.101b) may turn out to be either a simple unstable critical point (while moving towards the point C) or a simple metastable critical point (while moving towards the point P). Being metastable, the critical point is stable with

respect to separation into two infinitesimally-differing phases.

On a substantial and arbitrary shift in composition w_2 , the area *PBC* contracts, and the points *P*, *B*, *C* merge into one point, the three-phase region no longer exists, and the CPC is a smooth curve. Besides, the critical point may be located on the CPC either higher or lower than the merging point *PBC*. Only if the homologue lengths ratio r_2 meets the prescribed value, the critical point coincides with the merging point *PBC*, i.e. joins two cusp points. In the immediate vicinity of such a point, the CPC changes its direction twice (the point *T* in Figure 3.101b). Such a critical point can also be regarded as the merging point of two heterogeneous critical points and characterized as a triple critical (tricritical) point. It is seen that the CPC shows no peculiarities at this point.

The quaternary critical point Q_a emerges as a result of the junction of three double critical points or the junction of three cusp points with the critical point on the CPC (Figure 3.101c). The system may travel to the quaternary critical point through the triple critical point either on the metastable branch of the CPC (the point T_3 in Figure 3.101c) or on its unstable branch (the point T_2 in Figure 3.101c).

Thus, in a four-(and more)-component system, the triple critical point may be located on the metastable or unstable branch of the CPC while its stable branch shows a kink similar to that in Figure 3.101b.

The pentary critical point results from the junction of four double critical points or of two pairs of cusp points with the critical point (Figure 3.101d). Such a point on the CPC is indistinguishable from the tricritical one in a ternary system. In the general case, the *m* multiple critical point gets into the CPC when the critical point merges with the (m-1)-multiple cusp point. The even-multiple critical points are always away from the CPC stable branch while an odd-multiple critical point may well appear on the CPC stable branch.

It follows from the aforesaid that the multiplicity of the critical point cannot be determined from the character of the CPC stable branch. To identify it, the changes in the CPC or the phase state of the system should be followed upon a change in the polymer composition and/or MWD.

The influence of the concentration dependence $g(v_2)$ on three-phase equilibrium, the existence of multiple critical points and associated features were shown by Šolc et al. (1984) using model calculations for binary systems P+LMWL.

In this version, conditions 42 (including n = -1) lead to the equations

$$n = -1: \quad (pv_2)^{-1} + (1 - v_2)^{-1} - 2g + 2(1 - 2v_2)g_1 + v_2(1 - v_2)g_2 = 0; \tag{48}$$

$$n = 0: -(pv_2^2)^{-1} + (1 - v_2)^{-2} - 6g_1 + 3(1 - 2v_2)g_2 + v_2(1 - v_2)g_3 = 0;$$
(49)

$$n = 1: \quad 2(pv_2^3)^{-1} + 2(1-v_2)^{-31} - 12g_2 + 4(1-2v_2)g_3 + v_2(1-v_2)g_4 = 0; \tag{50}$$

$$u = 2: -6(pv_2^4)^{-1} + 6(1 - v_2)^{-4} - 20g_3 + 5(1 - 2v_2)g_4 + v_2(1 - v_2)g_5 = 0, \quad (51)$$

or, in the general case,

1

$$(-1)^{n+1}(n+1)! (pv_2^{n+2})^{-1} + (n+1)! (1-v_2)^{-(n+2)} - (n+2)(n+3)g_{n+1}$$
(52)
+ $(n+3)(1-2v_2)g_{n+2} + v_2(1-v_2)g_{n+3} = 0.$

The concentration dependence $g = g(v_2)$ is represented as usual (cf. Equation 3.6-9) as a series

$$g = \sum_{i=0}^{k} a_i(T) v_2^i.$$
 (53)

Then, for a certain type of functionality (eg., cubic with k = 3), all the highest derivatives g_i with i > 3 in Equations 48-52 disappear. Thus, the system's behaviour is defined by the set of coefficients $a_i(T)$. Their interrelations result in changes in the shape of the CPC, the existence of three-phase separation, appearance or disappearance of multiple critical points, etc.

Systems with the linear dependence g ($g_i = a_i = 0$ for i > 1) do not satisfy Equation 50 and, therefore, comprise only a single critical point with its existence conditions prescribed by Equations 48 and 49.

Systems with the quadratic dependence g may have, at least, a triple critical point. Equation 51 gives the tricritical concentration value

$$v_{2tc} = \left(1 + p^{1/4}\right)^{-1}.$$
(54)

Equations 49 and 50 lead to interrelations between a_{1lc} and a_{2lc} :

$$2a_{2tc} = \frac{\left(1+p^{1/4}\right)^4}{p} = \left(1-v_{2tc}\right)^{-4},\tag{55}$$

$$12a_{1tc} = \frac{\left(1+p^{1/4}\right)^3 \left(3p^{1/4}-5\right)}{p} = 12a_{2tc}(3-8v_{2tc}).$$
(56)

All the variables but one are fixed at the tricritical point. For example, the chosen chain length p defines the tricritical concentration of a polymer according to Equation 54 while the relationships a_{2tc} vs a_{1tc} are defined by Equations 55 and 56. In the limiting cases

$$p = 1:$$
 $v_{2tc} = \frac{1}{2}, \quad a_{1tc} = -\frac{4}{3}, \quad a_{2tc} = \frac{4}{3}, \quad a_{0tc} = \frac{8}{3};$ (57)

$$p \to \infty: \quad v_{2tc} \to 0, \quad a_{1tc} \to -\frac{1}{4}, \quad a_{2tc} \to \frac{1}{12}, \quad a_{0tc} \to \frac{3}{4}.$$
 (58)

As an example, Figure 3.102 reproduces Figure 9 from Solc et al. (1984). The CPC shows three break points which are the points of intersection of the CPC's isolated portions. These points define three-phase equilibrium which exists at a certain temperature. For binary systems, the CPC contains complete information on the phase state of the system, as it coincides with the binodal curve. Moreover, the critical points are here always located at the CPC's maximum, as opposed to a polynary system. The spinodal touches (or intersects) the CPC at its extremal points.

When the coefficients a_1 and a_2 vary, the characteristic curves transform, and, given Equation 57 is satisfied, the system has a CPC with a tricritical point (Figure 3.103).



Figure 3.102. State diagram of a binary system with p = 1, $a_1 = -2.0$, $a_2 = 2.02$. The stable (1) and unstable (2) CPC portions and the spinodal (3). The stable (M, S) and unstable (N) critical points. P'P''P''' denotes three-phase equilibrium. The coexisting phases are marked by the same letters with primes (Šolc et al., 1984) [Reprinted with permission from: Macromolecules 17 (1984) 573-585. Copyright © 1984 American Chemical Society]

Figure 3.103. State diagram of a binary system with a triple critical point: p = 1, $a_{1tr} = -4/3$, $a_{2tr} = 4/3$ (Šolc et al., 1984) [Reprinted with permission from: Macro-molecules 17 (1984) 573-585. Copyright © 1984 American Chemical Society]

Special analysis (Solc et al., 1984) shows that the greater the critical point's multiplicity, the flatter the CPC vertex.

At p > 1, the maximum of the CPC shifts towards lower concentrations.

There is a principally new property of the CPC with the quadratic dependence of g in comparison with g = const or the linear dependence of g, namely, its compositional character (see Figure 3.102).

Detailed analysis (Solc et al., 1984) shows that several points on the CPC may have one value of σ , and this parameter, therefore, turns out to be ambiguous in determining phase equilibrium. In this case, in solving Equation 37, particular attention should be paid to the possibility of existence of several roots.

The CPCs of the type shown in Figure 3.102 have been observed experimentally on polymer mixtures with a narrow MWD (see Figure 3.95). Thus, multiple equilibrium and the existence of multiple critical points are caused by either a substantial MWD asymmetry or a strong concentration dependence of the interaction parameter g, or both.

In conclusion, we note that Solc's classification of critical point multiplicity using the

number of Equation 49's roots also accounts for unstable critical roots while Griffiths-Widom's (Griffiths and Widom, 1973; Widom, 1973; Griffiths, 1974) (see the beginning of the paragraph and Equation 2) relates to stable critical points only, and does not consider even-multiple critical points.

Chapter summary

1. The state equation for the system polymer+low-molecular-weight liquid (P+LMWL) is deduced by the methods of statistical thermodynamics in the mean field approximation (Flory-Huggins' equation).

The interaction parameter $\chi = \chi_1 + \chi_2 v_2 + \chi_3 v_2^2 + \cdots$ (the interaction energy per molecule of the LMWL, in units of kT) is assumed to be the only parameter characterizing the specific features of a system.

The approximation $\chi = \chi_1 = \alpha/RT$ (Equation 3.1-33) leads to a model for the regular solution, for which $\Delta S_{mix,uncomb} = 0$.

A model for the strictly regular solution $(\Delta S_{mix,uncomb} \neq 0)$ requires $\chi = \chi_1 = \beta + \alpha/RT$ (Equation 3.1-42) or $\chi_1 = \kappa_1 - \psi_1 + 1/2$ (Equation 3.1-40) and has four approximations:

Oth: $v_2 \to 0$ and $z \to \infty$;

1st: $\chi_1 = \Delta \mu_{1exc} / v_2^2 RT$, where $\Delta \mu_{1exc}$ is given by (Equation 3.1-58);

2nd: the concentration dependence of χ is to be given (Equation 3.1-36, subsection 3.6.1);

3rd: χ is a function of both the concentration and molecular weight distribution (MWD), subsection 3.6.3.

2. As the combinatorial mixing entropy is usually large, for the condition $\Delta \overline{G}_{mix} = \Delta \overline{G}_{mix,id}$ to be satisfied, the contribution of the mixing enthalpy must be positive. Hence, polymer solutions with $A_2 = 0$ (in the θ solvent) cannot be athermic, in contrast with those of low-molecular-weight compounds. Indeed, for the θ solvent $\chi_1 = 1/2$ and $\kappa_1 = \psi_1$.

3. Different models are proposed for the conformational description of a macromolecule. The model for a continuous equivalent chain proposed by Edwards is of special significance for further applications. Being applied to conformational problems it has led to the formalism of functional (path) integrals, which is well-elaborated in quantum field theory.

The model approximating a polymer chain by N linked segments of length A each is widely used. The value of A is determined by the interactions between the neighbouring monomer units, such as short-range ones (the framework effect, the stiffness of chain). The distribution of N segments in space is well described by the Gaussian function.

4. The state equation for a single polymer chain is given from the Flory theory. In the case of a thermodynamically good solvent (i.e. away from the θ temperature), the interaction potential between chain-distant segments (the long-range, or space interactions) has, as a matter of fact, only the repulsion component. This can be formalized by introducing an excluded volume of a segment β and that of a macromolecule v_{ex} at the intramolecular and intermolecular level, respectively. The existence of the excluded volume explains why the coil linear size is $\alpha (= R/R_{\theta})$ times as large as that in the case of the unperturbed state, α being a function (Equation 3.1-115) of the excluded volume parameter z (Equation 3.1-116). This function is the state equation for a single molecular chain. It may be noted in passing that the second virial coefficient A_2 depends on z as well (Equations 3.1-146,-147).

The functional dependence of R on N, A, and β can be alternatively defined in terms of the general principles of the mean field approximation in three-dimensional (Equation 3.1 142) and d-dimensional (Equation 3.1-144) space.

5. The effective repulsion between segments of different macromolecules causes a decrease in the coil size, as the polymer concentration in solution increases.

Morphologically, solutions can be divided into dilute, semidilute, and concentrated. In semidilute solutions, the segment distribution, which is characteristic for the dilute solution in the given (good) solvent, holds within the distance ξ in a macromolecule. At longer distances $r > \xi$, the distribution of chain units of the size ξ becomes Gaussian (as in the unperturbed state) due to the repulsion from segments of other macromolecules. The distance ξ is referred to as the screening length, and a portion of chain of size ξ is a blob.

In dilute solutions there is no compensation for the excluded volume of segment by other macromolecules, and the coil size R defines the upper limit of ξ . As the polymer concentration increases, ξ diminishes, and at a certain, characteristic concentration it becomes equal to the linear size of the excluded volume of segment.

From this concentration and till the condensed state of the polymer, the coil has the unperturbed size, as in the θ solvent.

6. Both the binodal and spinodal of the Flory-Huggins state equation have an extremely asymmetric form in the coordinates T (or γ) vs v_2 due to the wide difference between the sizes of the component molecules.

The higher the molecular weight of a polymer, the higher T_c , the less v_{2c} , so $v_{2c} \to 0$, $\chi_{1c} \to 1/2$ if $z \to \infty$ $(M \to \infty)$.

In the given approximation, the plot $\frac{1}{T_c} vs\left(\frac{1}{2z}\right) + \frac{1}{\sqrt{z}}$ is a straight line with the slope being proportional to $1/\theta\psi_1$ and cutting off $1/\theta$ at the ordinate axis. The mixing enthalpy parameter κ_1 is calculated according to Equation 3.1-248: $\kappa_1 = \theta\psi_1/T$.

7. Due to the natural polymolecularity of any polymer sample, the system P+LMWL should be regarded as a polynary one, containing $(\nu + 1)$ components provided that the polymer consists of ν polymer homologues. When P = const, the stability boundary of the single-phase system state is a spinodal surface in the $(\nu + 1)$ -dimensional space based on the ν -dimensional polyhedron of composition (with the material balance taken into account) and the temperature axis, the critical state being defined by a ν -dimensional surface.

The conditions of equilibrium in the two-phase state lead to relationships, which require special computational methods to obtain a $(\nu + 1)$ -dimensional binodal surface. The intersections of the plane T vs φ (φ is the concentration of a polymolecular polymer) with the binodal and spinodal surfaces give the boundary of the phase separation region (also called a cloud-point curve (CPC)) and the spinodal curve (spinodal), respectively.

The plot T vs φ (or T_{sp} vs φ) remains in a plane regardless of the number of components,

3. Chapter summary

since in the quasi-binary section T vs φ , the ratio between polymer homologues (ν) remains constant, and the concentration of one component (LMWL) changes with respect to the sum of all the polymer homologues. This situation is more often than not realized on preparing solutions of a polymolecular polymer with different concentrations.

In a polynary system at two-phase equilibrium, there is a curve of coexistence of phases on the T vs φ diagram for each polymer concentration, and it shows a break at high temperatures (if the system has the upper critical solution temperature UCST) and at all the concentrations except one: $\varphi = \varphi_c$.

When $\varphi < \varphi_c$ the left-hand branch of the phase coexistence curve goes under the CPC lefter than φ and finishes on the CPC (a break!) at the point corresponding to the given polymer concentration φ . The right-hand branch goes out of the CPC and finishes at the temperature of the left-hand branch break and at the polymer concentration in the second phase when the amount of this phase is infinitesimal. A set of endpoints of this right-hand branch of the phase coexistence curve (PCC) forms a shadow line (SL).

Thus, the right-hand branch of the PCC finishes on the SL at the temperature of the left-hand branch finishing on the CPC.

When $\varphi > \varphi_c$, the PCC right-hand branch goes more to the right than the CPC and finishes on it at a given concentration φ . The PCC left-hand branch goes between the CPC left-hand branch and the SL left-branch and breaks on the SL at the temperature of the PCC right-hand branch finishing on the CPC right-hand.

When $\varphi = \varphi_c$ the two-phase co-existence curve is uninterrupted and has an extremum (a maximum with UCST) at the critical point.

The CPC shape depends on both the MWD and the concentration dependence of the interaction parameter $g = g(\varphi)$ (the second approximation of the Flory-Huggins theory).

The critical point (T_c, φ_c) is the common point of the spinodal and CPC, at which a common tangent line exists. It is located on the CPC right-hand branch for systems with either UCST or LCST, and the greater the ratio M_z/M_w , the farther is this point away from the CPC maximum (the precipitation threshold) along the concentration scale.

The second approximation of the theory assumes the spinodal position to depend on M_w only. That is why the spinodal is invariant for polymer samples with different MWD but with the same M_w .

If this property is not realized, this attests to the dependence of the interaction parameter on the MWD (the third approximation of the Flory-Huggins theory).

8. Redistribution of the polymer homologues occurs between coexisting phases, with the second (more concentrated with the polymer) phase enriched (and no more!) with homologues with greater molecular weights. This effect is the base for the procedure of fractionation of polymolecular polymers. Different means of fractionation are used. The precipitation method consists in decreasing the temperature stepwise (for systems with UCST) or adding a non-solvent; on achieving equilibrium, the second phase is removed, which is followed by a further decrease in temperature, etc. With the extraction method, either the temperature is increased or a better solvent is added; on achieving equilibrium, the first phase is removed (decanted) that is followed by a further temperature increase, etc.

The theory of fractionation is rather complex. Different computational versions require simplifications, simulations, and computers.

The summative fractionation is a method of fractionation with the determination of the overall polymer precipitate mass in the second phase (without removing the previously precipitated polymer fractions) on adding a due portion of non-solvent (or on decreasing temperature). Thus, the degree of phase transformation x is determined at the stage of summative fractionation.

Spectroturbidimetric titration (STT) of polymer solutions is a version of summative fractionation with "optical weighing" of the polymer in the colloid-disperse state.

It is based on solving two inverse problems, namely, optical and thermodynamic. In the first problem, the mass (concentration) of the precipitated polymer is determined as a function of the precipitant volume part γ , i.e. the precipitation curve $x = x(\gamma)$ is to be obtained. The aim of the second inverse problem is to converse this curve into the MWD function.

9. When the correlations of concentration fluctuations are not taken into account, the theory of light scattering in polynary systems gives an expression for R_{ϑ} with the determinant a_{ij} appearing in the denominator and vanishing on the spinodal. Hence, on the spinodal $R_{\vartheta\to 0} \to \infty$, which is unreal and due to the neglect of the correlations of concentration fluctuations. However, there is a method for determining the spinodal temperature at a given polymer concentration φ by measuring R_{ϑ} in the single-phase region during successive cooling of the solution (system with UCST). Following extrapolation $R_{\vartheta\to 0} \to \infty$ gives the spinodal temperature. Repeating the procedure for a number of concentrations φ yields the spinodal curve.

We remark incidentally that such a problem for low-molecular-weight liquid mixtures presents significant experimental difficulties.

The diffusion coefficient as a function of the concentration φ is an extremal dependence with a minimum at $\varphi = \varphi_c$. The nearer the isotherm to the critical isotherm (where $D_{min} = 0$) the lesser the minimal value of D_{min} .

10. Critical opalescence in polymer solutions is observed in a much wider temperature range than in solutions of low-molecular-weight compounds. This makes it more difficult to identify the binodal curve (the boundary of the region of phase separation or CPC) as distinct from low-molecular-weight solutions. The latter show so sharp a rise in the scattered light intensity in the critical region that the method of recording makes no matter.

The experimental radiation diagram of the critical opalescence and the existing theories allow one to determine the radius of coil gyration $\sqrt{R^2}$, Debye's length of interactions l, the energy of polymer molecular cohesion. What is more, the order of the value $\sqrt{R^2}$ determined by the critical opalescence is much lesser than the lower limits of the macromolecule size, with the latter being determined by the effect of intrinsic interference in dilute solutions away from the critical point.

Both the theoretical and experimental studies have shown the macromolecule sizes near the critical point to be comparable with the size of an unperturbed coil at the θ -state, and $l^2 \simeq \sqrt{M}$.

11. Dynamic light scattering is due to the relaxation of the concentration fluctuations when the scale of segments is comparable with q^{-1} . So, the relative contribution of macromolecule diffusional mobility and their internal modes depend on the wave vector q:

3. Chapter summary

 $Rq \ll 1$: the macromolecule behaves as a particle with motionless segments;

 $Rq \simeq 1$: the macromolecule diffusion mode is comparable with the longest wave mode of segment mobility having the relaxation time τ_1 .

 $Rq \gg 1$: the following modes for the motion of segments are "turned on".

The experimental results concerning dynamic light scattering in polymer solutions indicate the existence of two diffusion modes of a macromolecule. The first mode is concerned with the conventional self-diffusion coefficient of the polymer. To the second one is as cribed the reptation motion of the macromolecule in an imaginary pipe of entanglement points formed from other macromolecules.

The hydrodynamic interactions of segments in a macromolecule is screened by other macromolecules on increasing the polymer concentration in solution. In semidilute and concentrated solutions of the polymer, there occur fluctuation entanglements with the scale ξ and existence time T_r . With $Dq^2 > T_r^{-1}$ the solution behaves as a gel in respect to its dynamic properties.

12. As the configurative point goes down along the temperature scale (a system with UCST) on the state diagram T vs v_2 , the transition coil-globule occurs between the ordinate axis and the left-hand branch of the binodal. The character of this transition depends essentially on the ternary interactions between segments in the coil: in the absence of these interactions, the transition is like that of the first kind, while with the ternary interactions being enhanced it approaches the transition of the continuous type.

13. The system network polymer+LMWL shows properties both of the solid and of high elasticity of entropy nature. The system models proposed lead to state equations which are verified by experimental results. In the single-phase region, the state equation in the coordinates T vs v_2 is expressed by a swelling curve with either positive or negative slope depending on the sign of the mixing enthalpy.

There may exist two phases of a network polymer with different chain conformations at some values of the system parameters (high χ and the concentration of crosslinks ν). Due to the fixed state of the chains, such a phase separation happens in local volumes and causes a significant heterogeneity of the gel structure (microsyneresis).

When χ (temperature, non-solvent concentration) varies continuously, the achievement of the condition of the gel two-phase state leads to a sharp reduction in the gel volume (collapse), which is similar to the transition coil -globule.

The dominant influence ν (in comparison with χ) may lead to the fact that phase separation in gel takes place in the presence of LMWL being a good solvent in solutions of the linear modification of a polymer.

As the parameter ν may change its value during the process of phase separation due to the local reduction of volume, the final pattern of this process depends on its kinetics and is rather difficult for quantitative analysis.

These effects are of special significance in systems with three-dimensional polymerization. This process for polyfunctional polymers in solution may be successfully described in the fashion of percolation problem.

Both static and dynamic light scattering in homogeneous molecular gel are due to the modes of structural fluctuations depending on the gel elasticity moduli.

All the gel moduli can be defined by a combination of the static and dynamic light scattering methods.

The configurative point with the longitudinal modulus M = 0 corresponds to the condition of spinodal scattering $R_{\vartheta \to 0} \to \infty$.

Analysis of the gel literature has shown the effectiveness of the classic approach of physical chemistry, including preliminary introduction of a system model and followed by derivation of a state equation, which is then compared with the experimental results. It is distinct from the truly morphological approach, which inevitably leads to internal contradictions and gives no key to controlling the properties of things and materials based on polymer gels.

14. To verify the theory of phase separation in the system P+LMWL, it was required to improve the methods for determining the characteristic values and phase separation functions, first of all, of the phase separation boundary, the spinodal, the critical point and the Flory-Huggins interaction parameter. The development of experimental methods has lead, in turn, to new modifications of the theory, in particular, to its second and third approximations.

For kinetic difficulties, the phase separation in polymer systems seldom finishes with phase equilibrium. This is the reason why only several systems are known for which the binodals have been traced using the determined polymer concentration in the coexisting phases, and the critical concentration has been evaluated by extrapolating the phase-volume ratio $\tau \rightarrow 1$.

The theory of light scattering in polymolecular polymer solutions enables one to determine the derivative $(\partial(\Delta\mu_0)/\partial w)_{Mn}$ using the Rayleigh ratio $R_{k,\vartheta\to 0}$. Integrating this derivative gives $\Delta\mu_0$ for any given value of w, and $\Delta\mu_0$ is used for the calculation of the Flory-Huggins interaction parameter. Carrying out this procedure for a number of solutions with different concentrations, one can determine the concentration dependence of the interaction parameter. The latter can also be determined using osmotic pressure in solutions, the LMWL vapour pressure over solution, the effect of gel swelling, and the unethod of inverse gas chromatography.

A method is proposed for determining the boundary of the phase separation region by means of extrapolating the new-phase particle-forming rate $v \to 0$. The rate v is calculated using the kinetics of the phase transformation degree x = x(t) obtained by the turbidity spectrum method. Knowing the character of the kinetic dependences of formedphase particle sizes $\bar{r}_{\lambda} = \bar{r}_{\lambda}(t)$, one can judge the mechanism of the phase separation kinetics.

In the third approximation of the mean field theory, the dependence of the interaction parameter on the concentration and M (MWD) of a polymer is taken into account, with the specific features of dilute solutions for systems with low polymer concentrations or with a low-concentrated phase during phase separation.

15. The position of the phase separation region on the state diagram is mainly defined by the temperature dependence of the interaction parameter. Depending on the sign of the coefficients (Equation 3.6-85), this region may be located in the plane $T vs v_2$ in a characteristic way (see Figure 3.81) in accordance with the state diagrams known from experimental works.

16. Mixtures of different polymers obey the mean field approximation almost exactly.

3. Chapter summary

Due to the significant mixing entropy effects, the conditions of the phase separation in the system P1+P2 are observed at a markedly lower value of the interaction parameter χ , in contrast with the system P+LMWL.

Due to the more pronounced dependence of the interaction parameter on both concentration and molecular weight, the phase separation in polymer mixtures is very diverse.

On combining the theory of light scattering with the state equations for polymer mixtures, de Gennes deduced an expression for the correlation length of the concentration fluctuations ξ_k .

Taking into account the relation of ξ_k to the thermodynamic potential expansion coefficients in the general field theory (Equation 2.5-13), one can derive a state equation for a polymer mixture (Equation 3.7-36) with a gradient term, which involves the correlation of concentration fluctuations of the components. Using this state equation, in particular, an analytical expression for the coil relaxation time was obtained, which shows that near the critical point the effect of thermodynamic retardation must occur.

Interpenetrating polymer networks form a special class of polymer systems extremely expanding the field of application of polymer materials.

17. The theory of corresponding states, developed for polymer systems, is in good agreement with experimental results in a number of cases.

The direct relation of experimentally measured values to the molecular parameters of components is an advantage of the theory. Its restrictions are due to the necessity to introduce adjustable parameters.

18. Relaxation thermodynamics (thermokinetics) includes an explicit dependence of the thermodynamic potentials on the rate of motion of the configurative point.

19. A three-phase equilibrium is observed in the system P+LMWL, if the polymer has a very asymmetric MWD, or is represented by two polymer homologues with molecular weights differing more than ten-fold, or there is a square (at least) concentration dependence of the interaction parameter.

In these cases at a certain temperature the CPC has a break (Figure 3.95), where the principal phase is in equilibrium with two different incipient (conjugate) phases (two SL), i.e. a three-phase separation (asymmetric tricritical point) begins (or ends) with this point.

Depending on the MWD features, the critical point may be located on the continuation of one of the two branches of the CPC drawn inside the phase separation region (metastable critical point) or on the line connecting two cusp points with which the continuations of the CPC branches end (unstable critical point).

The features of the three-phase separation are discussed in detail in section 3.10.

Thus, many properties of polymer systems can be sufficiently explained within the framework of the mean field approximation theory.

With polymer mixtures the theory proves to be quite exact due to the low level of concentration fluctuations, which, in turn, is caused by steric difficulties.

Anyhow, the mean field theories can play a dominant role in the development of the scientific basis for technologies for creating polymer materials, beginning with polymer synthesis (Budtov and Konsetov, 1983).

Besides, the mean field theories are very important as models for comparison while

developing more rigorous theories, which are discussed in Chapters 4 and 5.

Chapter 4

Universality Principle. Scaling Ideas. Dynamics of Macromolecules

4.1. Conformational problem of a molecular chain

Wilson (1972) has calculated the values of the critical indices γ and η for a system with the Hamiltonian

$$\frac{\mathcal{H}}{kT} = \int \left\{ \frac{1}{2} r_0 s^2(\vec{x}) + \frac{1}{2} \left[\nabla s(\vec{x}) - \nabla \nabla^2 s(\vec{x}) \right]^2 + u_0 s^4(\vec{x}) \right\} d^d x, \tag{1}$$

where $s(\vec{x})$ is the spin with *n*-components $s_i(\vec{x})$;

$$s^{2}(\vec{x}) = \sum_{i} s_{i}^{2}$$
, and $s^{4}(\vec{x}) = \left(\sum_{i} s_{i}^{2}\right)^{2}$,

 r_0 and u_0 are constants. The term $\nabla \nabla^2 s(\vec{x})$ is included to ensure the convergence of the integrals: it accounts for the elimination of fluctuations with a wavelength $\ll 1$ (the so-called cut-off).

In that paper the correlation functions (the Green functions, the ordered Green functions, etc.) near the critical point were expressed as series in u_0 and ε , where $\varepsilon = 4 - d$. In particular, the Green function $G(\vec{k})$ for $\vec{k} = 0$ was calculated, that corresponds to the permeability χ_T (see Equation 2.6–38), which, in its turn, is proportional to the scattered light intensity (see Equation 2.3–133) for which

$$G(\vec{k}) \sim k^{-2+\eta} \tag{2}$$

holds (the k-dependence of the Equation 2.3–148 type).

The correlation functions were calculated by Wilson using the diagrammatic technique and the renormalization procedure.

As a result, the following expressions were obtained:

$$\gamma = 1 + \frac{n+2}{2(n+8)}\varepsilon + \frac{(n+2)(n^2+22n+52)}{4(n+8)^3}\varepsilon^2 + O(\varepsilon^3),$$
(3)

$$\eta = \frac{n+2}{2(n+8)^2} \varepsilon^2 + \frac{n+2}{2(n+8)^2} \left[\frac{6(3n+14)}{(n+8)^2} - \frac{1}{4} \right] \varepsilon^3 + O(\varepsilon^4).$$
(4)

A problem of random self avoiding walks on a lattice with interactions (with due account for the excluded volume) has been considered by de Gennes (1972) in his pioneering work.

If $\Gamma_N(\vec{h})$ denotes the number of random self-avoiding walk trajectories (with interaction) of N steps (units), connecting the points 0 and \vec{h} , then the Green function in momentum space takes the form

$$G(\varepsilon, \vec{k}) = \sum_{N=0}^{\infty} \sum_{\vec{h}} \Gamma_N(\vec{h}) \exp(i\vec{k}\vec{h}) \exp(-N\varepsilon),$$
(5)

where ε accounts for the interaction between units so that approaching some value of ε_c , the function $G(\varepsilon, \vec{k})$ shows a singularity of the type

$$\lim_{\varepsilon \to \varepsilon_c} G(\varepsilon, \vec{k} = 0) = const \ (\varepsilon - \varepsilon_c)^{-\gamma},\tag{6}$$

i.e. ε can be related to the magnet temperature. It is also expected that at $\varepsilon = \varepsilon_c$

$$G(\varepsilon_c, k) = const \ k^{-2+\eta}. \tag{7}$$

Further, the mean square end-to-end distance $\langle h_N^2 \rangle^{1/2}$ is related to the spin correlation distance ξ in the magnetic problem, where

$$\xi \sim \varepsilon^{-\nu} \sim \varepsilon^{-\gamma/(2-\eta)} \tag{8}$$

(cf. Equations 2.3-142 and 2.3-153). Correlating the two small parameters ε with N^{-1} in these two problems, we obtain

$$\left\langle h_N^2 \right\rangle^{1/2} \sim N^{2\nu} \quad \text{with} \quad \nu = \frac{\gamma}{2-\eta}.$$
 (9)

De Gennes compared the graphs of the Green function in the magnetic problem (Equation 1) (Wilson, 1972) with those of the macromolecule excluded volume problem (Fixman, 1955; Yamakawa et al., 1966). He discovered that they coincide provided that the loops with their contribution being proportional to the number of spin components n are excluded from the "magnetic" graphs. Thus, to reduce the magnetic problem to the polymer one, the equality n = 0 must be formally accepted.

Consequently, the results of the magnetic problem solution (Equations 3 and 4) can be used for the macromolecule excluded volume problem granted n = 0, i.e.

$$\gamma = 1 + \frac{\varepsilon}{8} + \frac{13}{2^8}\varepsilon^2 + O(\varepsilon^3),\tag{10}$$

$$\eta = \frac{\varepsilon^2}{64} \left(1 + \frac{17\varepsilon}{16} \right) + O(\varepsilon^4). \tag{11}$$

For $\varepsilon = 1$ (d = 3) $\gamma = 1.176$, $\eta = 0.032$, and

$$2\nu = \frac{2\gamma}{2-\eta} \approx 1.195,\tag{12}$$

i.c.

$$\left\langle h_N^2 \right\rangle^{1/2} \sim N^{1.195}.$$
 (13)

That the exponent in the last equation is practically the same as Flory's, as stated in Chapter 3, is due to the compensation of the neglected contributions in the state equation for a molecular coil in the mean field approximation.

Later, Emery (1975) found an analytical solution of both the magnetic and polymer problems at n = 0.

The starting point of his consideration is the Hamiltonian of the form

$$\mathcal{H} = \sum_{\alpha}^{n} \sum_{ij}^{N} J_{ij} s_{i\alpha} s_{j\alpha} + \sum_{i}^{N} \left[r \sum_{\alpha}^{n} s_{i\alpha}^{2} + \frac{u}{4} \left(\sum_{\alpha}^{n} s_{i\alpha}^{2} \right)^{2} \right], \tag{14}$$

where J_{ij} is the interaction function involving temperature, N is the number of sites in the lattice. Here is the corresponding partition function:

$$\mathcal{Z}_n = \int_{-\infty}^{\infty} \prod_{i=\alpha}^{N} \prod_{\alpha=\alpha}^{n} ds_{i\alpha} e^{-\mathcal{H}}.$$
(15)

Emery goes on to transform this expression so that an explicit n-dependence should appear, which enables him to deduce Z_n for some special values of n, involving $n \to 0$. This can be achieved by means of an integral representation of the four-order term in the exponent $e^{-\mathcal{H}}$

$$\exp\left[-\frac{u}{4}\left(\sum_{\alpha}^{n}s_{i\alpha}^{2}\right)^{2}\right] = (\pi u)^{-1/2}\int_{-\infty}^{\infty}d\psi_{i}\exp\left(-\frac{\psi_{i}^{2}}{u} + i\psi_{i}\sum_{\alpha}^{n}s_{i\alpha}^{2}\right).$$
(16)

To let this integral converge, we must accept u > 0. The correctness of Equation 16 can be verified by replacing the integration variable by

$$\psi_i = i\left(\frac{1}{2}u\right)\sum_{\alpha}^n s_{i\alpha}^2$$

Substitution of Equations 14 and 16 into Equation 15 and castling ψ_i and $s_{i\sigma}$ yield

$$\mathcal{Z}_n = (\pi u)^{-N/2} \int\limits_{-\infty}^{\infty} \prod_i^N d\psi_i \, \exp\left(-\frac{1}{u} \sum_i^N \psi_i^2 - n\Phi_g[\psi_i]\right),\tag{17}$$

where

$$e^{-n\Phi_g[\psi_i]} = \int_{-\infty}^{\infty} \prod_{i=\alpha}^{N} \prod_{\alpha=\alpha}^{n} ds_{i\alpha} \exp\left[\sum_{\alpha=\alpha}^{n} \left(-\sum_{i,j=\alpha}^{N} J_{ij} s_{i\alpha} s_{j\alpha} + \sum_{i=\alpha}^{N} (r+i\psi_i) s_{i\alpha}^2\right)\right].$$
 (18)

The exponent in the right-hand side is the sum over α , and the integral is split into the product of n- and N-dimensional integrals with all the n integrals being the same (for α is but an index of the integration variable). Hence,

$$e^{-\Phi_{g}[\psi_{i}]} = \int_{-\infty}^{\infty} \prod_{i}^{N} ds_{i} \exp\left(-\sum_{ij}^{N} J_{ij}s_{i}s_{j} + \sum_{i}^{N} (r+i\psi_{i})s_{i}^{2}\right),$$
(19)

i.e. $\Phi_g[\psi_i]$ does not depend on n, and all the n dependence of \mathcal{Z}_n is reflected in Equations 17 and 18.

As the exponent in Equation 19 is a quadratic form in s_i , calculating the integral gives

$$\Phi_{g}[\psi_{i}] = \frac{1}{2} \ln \det(\hat{J} + r + i\hat{\psi}) - \frac{1}{2}N\ln\pi$$

$$= \frac{1}{2} \operatorname{tr} \ln(\hat{J} + r + i\hat{\psi}) - \frac{1}{2}N\ln\pi,$$
(20)

where \hat{J} and $\hat{\psi}$ are matrices with the elements J_{ij} and ψ_{ij} .

The free energy per component in the limit $n \to 0$ is written using Equation 17

$$F_{0} = -\lim_{n \to 0} \frac{1}{n} \ln \mathcal{Z}_{n} = (\pi u)^{-N/2} \int_{-\infty}^{\infty} \prod_{i}^{N} d\psi_{i} \Phi_{g}[\psi_{i}] \exp\left(-\frac{1}{u} \sum_{i}^{N} \psi_{i}^{2}\right).$$
(21)

The correlation function is

$$G_{ij}^{n} = \frac{1}{n} \sum_{\alpha}^{n} \langle s_{i\alpha} s_{j\alpha} \rangle = \frac{1}{n} \cdot \frac{\partial F_{n}}{\partial J_{ij}}.$$
(22)

For n = 0, Equations 20 and 22 give

$$G_{ij}^{\circ} = (\pi u)^{-N/2} \int_{-\infty}^{\infty} \prod_{k}^{N} d\psi_k \exp\left(-\frac{1}{u} \sum_{k}^{N} \psi_k^2\right) \left[\hat{J} + r + i\hat{\psi}\right]^{-1}.$$
 (23)

Emery demonstrates that

$$\left(\hat{J} + r + i\hat{\psi}\right)^{-1} \tag{24}$$

is the lattice walk propagator, i.e. the probability of a spin being in the cell j provided that there is a spin in the cell i.

In field theory, the Laplace transformation of the propagator can be expressed via a functional (continual) integral.

For instance, the Laplace transform of propagator (24) with respect to p = r + 3J is put in the form

$$\left\langle \vec{r}_{j} \left| \exp\left[-l\left(-\frac{|J|a^{2}}{2} \nabla^{2} + i\psi \right) \right] \right| \vec{r}_{i} \right\rangle$$

$$= \mathcal{N} \int_{\vec{R}(t)=\vec{r}_{i}}^{\vec{R}(0)=\vec{r}_{j}} \delta \vec{R} \exp\left\{ \int_{0}^{t} d\tau \left[-\frac{Ja^{2}}{2} \left(\frac{d\vec{R}}{d\tau} \right)^{2} + i\psi \left(\vec{R}(\tau) \right) \right] \right\},$$
(25)

where N is a normalization constant, and the integration is taken over all the space-time trajectories connecting the end points.

In view of Equation 25, the Laplace transform g_{ji}^{o} of the Green function G_{ji}^{o} (Equation 23), on integration with respect to ψ , takes the form

$$g_{ji}^{0} = \mathcal{N} \int_{\vec{R}(0)=\vec{r}_{i}}^{\vec{R}(1)-\vec{r}_{j}} \delta \vec{R} \exp\left[-\int_{0}^{t} d\tau \frac{|J|a^{2}}{2} \left(\frac{d\vec{R}(\tau)}{d\tau}\right)^{2} - \frac{u}{4} \int_{0}^{t} d\tau_{1} d\tau_{2} \,\delta\left(\vec{R}(\tau_{1}) - \vec{R}(\tau_{2})\right)\right]. \tag{26}$$

Equation 26 agrees precisely with the continuous limit probability of finding the polymer chain end at the point $\vec{r_j}$ given the beginning is at the point $\vec{r_i}$ and the chain length is L = t (see Equation 3.1-205).

To provide the complete analogy of Equation 26 with Equation 3.1–205, the interaction potential \mathcal{V} from the latter is assumed as short-range

$$\mathcal{V} = \frac{u}{2} \delta\left(\vec{R}(\tau_1) - \vec{R}(\tau_2)\right),\tag{27}$$

and the lattice parameters are related through the Kuhn segment A using

$$|J|a^2 = \frac{3}{A}.$$
(28)

The properties of systems with a Hamiltonian of the type (14) have been under intensive investigation. The results can be applied to the study of the macromolecule's properties with n = 0 as de Gennes did to evaluate the index ν (Equation 13).

Let us mention Stephen's (1975) results as another example.

As it follows from Equation 5, the Green function $G(\varepsilon, \vec{k})$ is the Laplace transform of $\Gamma(\vec{h})$. Hence, $\Gamma(\vec{h})$ or any quantity proportional to it (the probability $P(\vec{h}, L)$ for a polymer chain with the length L to have the end-to-end distance \vec{h}) can be found by means of the inverse Laplace transformation of the Green function.

Stephen examines the Hamiltonian

$$\frac{\mathcal{H}}{kT} = \int d^d x \, \left[\frac{r_0}{2} \sum_{\alpha=1}^n s_\alpha^2(x) + \frac{1}{2} \sum_{\alpha=1}^n |\nabla s_\alpha(x)|^2 + \frac{u_4}{4!} \left(\sum_{\alpha=1}^n s_\alpha^2(x) \right)^2 + \frac{u_6}{6!} \left(\sum_{\alpha=1}^n s_\alpha^2(x) \right)^3 \right], (29)$$

which differs from that of Emery (Equation 14) by an additional term with u_6 , i.e. Stephen's Hamiltonian (at n = 0) describes a random self-avoiding walk of structural elements (spins) or a polymer chain composed of segments with the length A, taking the excluded volume (pair interactions u_4) and ternary interactions (u_6) into account.

The two-segment interaction potential expressed in dimensionless units is proportional to

$$u_4 A^{4-d}$$
, (30)

where

$$\dot{u}_4 = u_4 + \alpha_d u_6 A^{2-d}, \tag{31}$$

and α_d is a constant. The parameter

$$u_6 \Lambda^{6-2d} \tag{32}$$

corresponds to the three-particle interaction potential of three chain segments. The segment length A is proportional to the diffusion coefficient D (see Equation 3.1–192).

The Green function is defined as

$$G^{(n)}(\vec{h}, r_0) = \frac{1}{n} \sum_{\alpha=1}^n \left\langle s_\alpha(0) s_\alpha(\vec{h}) \right\rangle.$$
(33)
The probability $P(\vec{h}, L)$ is calculated using the inverse Laplace transform of the Green function with respect to r_0 at $n \to 0$:

$$P(\vec{h},L) \sim \frac{1}{2\pi i} \sum_{\sigma-i\infty}^{\sigma+i\infty} dr_0 \, \exp(DLr_0) G^{(0)}(\vec{h},r_0). \tag{34}$$

In the polymer modification of the theory, t (time) corresponds to L (length) and the diffusion coefficient takes the dimension of length (cm²/cm).

The following result was obtained in field theory for the inverse susceptibility of the dimensionality $(4 - \varepsilon)$ at n = 0 up to $O(\varepsilon)$ (Stephen and Abrahams, 1973; Wegner and Riedel, 1973):

$$\chi^{-1} = r = G_0^{-1}(k=0) = r_0 \left[1 + \frac{\dot{u}_4}{6\pi^2 \varepsilon} r_0^{-\varepsilon/2} \right]^{-1/4}.$$
(35)

On substituting Equation 35 into Equation 34 and calculating $\langle h^2 \rangle$ by the standard method (eg. see Equations 3.1 121, 183, 203), Stephen obtained

$$\left\langle h^2 \right\rangle = 8DL \left[1 + \frac{u_4}{6\pi^2 \varepsilon} (DL)^{\varepsilon/2} \right]^{1/4},\tag{36}$$

For a very good solvent with $\bar{u}_4(DL)^{\epsilon/2} > 1$, this equation is followed by

$$\left\langle h^2 \right\rangle \sim L^{2\nu} \quad \text{with} \quad 2\nu = 1 + \frac{\varepsilon}{8}$$
(37)

which is in agreement with de Gennes' result (Equation 13).

If $\tilde{u}_4(DL)^{\epsilon/2} < 1$, then Equation 36 gives a relationship for the segment free walk

$$\langle h^2 \rangle \sim L \sim N.$$
 (38)

For magnetic systems, the configurative point with $\bar{u}_4 \rightarrow 0$ approaches the tricritical point (see Equations 31 and 2.6–163).

This corresponds to the absence of excluded volume (the θ point) in the polymer problem.

At d = 3, the tricritical point theory has to be modified with logarithmic corrections (Riedel and Wegner, 1972; Stephen et al., 1975).

The reciprocal susceptibility of a disordered phase at n = 0 and $u_4 = 0$ has the form

$$G^{-1}(k=0,r_0) = r = r_0 \left(1 + \frac{49}{484 \ln r_0} \right), \tag{39}$$

$$G^{-1}(k, r_0 = 0) = k^2 \left(1 - \frac{1}{1452 \ln k^2} \right).$$
(40)

Using this results (Stephen, 1975)

$$\left\langle h^2 \right\rangle = 6DL \left(1 + \frac{37}{363 \ln DL} \right),\tag{41}$$

which defines the molecular coil size at the θ point with a logarithmic correction for

$$u_6 \ln DL > 1. \tag{42}$$

Otherwise, the second summand in Equation 41 has to be replaced by a constant.

4.2. Lagrangian formalism of polymer theory

In order to study the properties of polymer solutions, des Cloizeaux (1975) writes the action in the absence of the field $\mathcal{A}\{\phi\}$ as

$$\mathcal{A}\{\phi\} = \mathcal{A}_0\{\phi\} + \mathcal{A}_I\{\phi\},\tag{1}$$

where

$$\mathcal{A}_0\{\phi\} = \frac{1}{2} \int d^d x \left\{ \sum_{i,j}^n \left[\frac{\partial}{\partial x_i} \phi^j(\vec{x}) \right]^2 + m_0^2 \sum_j^n \left[\phi^j(\vec{x}) \right]^2 \right\},\tag{2}$$

$$\mathcal{A}_{I}\{\phi\} = \frac{1}{8} \int d^{d}x \int d^{d}y \sum_{j,l=1}^{n} \left[\phi^{j}(\vec{x})\right]^{2} \left[\phi^{l}(\vec{y})\right]^{2} \mathcal{V}(\vec{x}-\vec{y}), \tag{3}$$

where $l, j = 1 \dots n, d$ is the space dimension.

The mean value of a functional $O\{\phi\}$ is defined as

$$\langle O\{\phi\}\rangle = \frac{\int d\omega\{\phi\} O\{\phi\} \exp(-\mathcal{A}\{\phi\})}{\int d\omega\{\phi\} \exp(-\mathcal{A}\{\phi\})},\tag{4}$$

where $d\omega\{\phi\}$ is an integration element of the functional integral.

The Fourier transforms have the form:

~

$$\phi^{j}(\vec{k}) = \int d^{d}x \, \exp(i\vec{k}\vec{x})\phi^{j}(\vec{x}), \tag{5}$$

$$\tilde{\mathcal{V}}(\vec{q}) = (2\pi)^{-d} \int d^d x \, \exp(i\vec{q}\vec{x})\mathcal{V}(\vec{x}). \tag{6}$$

After the mass renormalization in a space with d < 4, the short-range interaction potential is assumed to be

$$\overline{\mathcal{V}}(\vec{q}) = g_0. \tag{7}$$

Therefore, the Lagrangian density takes the form

$$\mathcal{L}(\vec{x}) = \sum_{i,j} \left[\frac{\partial}{\partial x_i} \phi^j(\vec{x}) \right]^2 + m_0^2 \sum_j \left[\phi^j(\vec{x}) \right]^2 + (2\pi)^d g_0 \left[\sum_j \left[\phi^j(\vec{x}) \right]^2 \right]^2.$$
(8)

The Green functions are defined by

$$G_{j_1\dots j_q}^{(q)}(\vec{x}_1\dots\vec{x}_q) = \left\langle \phi^{j_1}(\vec{x}_1)\dots\phi^{j_q}(\vec{x}_q) \right\rangle,\tag{9}$$

$$G_{j_1\dots j_q}^{(q)}(\vec{k}_1\dots\vec{k}_q) = \left\langle \tilde{\phi}^{j_1}(\vec{k}_1)\dots\tilde{\phi}^{j_q}(\vec{k}_q) \right\rangle.$$
(10)

Functions 10 can be expanded into a Taylor series in terms of the interaction parameter. If one employs the following expression for the free propagator

$${}^{0}G_{jj'}(\vec{k},\vec{k'}) = \left\langle \phi^{j}(\vec{k})\phi^{j'}(\vec{k}) \right\rangle_{0} = \delta_{jj'} \frac{\delta(\vec{k}+\vec{k'})}{k^{2}+m_{0}^{2}}$$
(11)

as well as the Wick's theorem (see section 2.6), one can present the Green functions $G_{j_1...j_q}^{(q)}(\vec{k}_1...\vec{k}_q)$ as graphs (see Figure 4.1a) in accordance with the following rules:



Figure 4.1. Graphs of the Green function (a) and of the ordered Green function (b) for Lagrangian 4.2- ϑ ; graphs of polymer theory (c) (des Cloizeaux, 1975) [Reprinted with permission from: Des Cloizeaux, J. de Phys. **36** (1975) 281-291. Copyright © 1975 by EDP Sciences]

- 1. a factor $(k^2 + m_0^2)^{-1}$ is associated with each part of the solid line;
- 2. a factor $\tilde{V}(\vec{q})$ is associated with each dashed line;
- 3. a factor $\delta(\vec{k} + \vec{k'} + \vec{q})$ is given to each vertex (the momentum-conservation rule);
- 4. corresponding symmetry numbers are introduced, and all the free momenta are integrated in the dimension d;
- 5. each solid line corresponds to a well-defined field component j;
- 6. for closed loops, summation over j is taken to yield the number n.

Des Cloizeaux also introduces ordered Green functions $G^{(2\mathcal{M})}(\vec{k}_1 \dots \vec{k}_{2\mathcal{M}})$ as a sum of graph contributions defined as follows. Each graph of the rank \mathcal{P} is composed of \mathcal{P} open lines and several closed loops: each closed loop is connected with, at least, one open line. Each line is marked with the index \mathcal{M} , where $\mathcal{M} = 1, \dots, \mathcal{M}$. The corresponding input momenta are $\vec{k}_{2\mathcal{M}-1}$ and $\vec{k}_{2\mathcal{M}}$. Hence, the indices j do not appear in the definition of $G^{(2\mathcal{M})}(\vec{k}_1 \dots \vec{k}_{2\mathcal{M}})$ (see Figure 4.1b) but the ordered Green function depends on n (a power series n), keeping its sense at any n, in particular, n = 0.

On the other hand, if n is an integer positive number, then the Green functions are expressed as the ordered ones:

$$G_{j_1\dots j_{2\mathcal{M}}}^{(2\mathcal{M})}(\vec{k}_1\dots\vec{k}_{2\mathcal{M}}) = \frac{1}{2^{\mathcal{M}}\mathcal{M}!} \sum_{\mathcal{P}} \left[\delta(j_{\mathcal{P}_1} - j_{\mathcal{P}_2}) \cdots \delta(j_{\mathcal{P}_{\{2\mathcal{M}-1\}}} - j_{\mathcal{P}_{\{2\mathcal{M}\}}}) \right]$$
(12)

$$\times G^{(2\mathcal{M})}(\vec{k}_{\mathcal{P}_1}\ldots\vec{k}_{\mathcal{P}_{2\mathcal{M}}})$$

where $\mathcal{P}_1, \ldots, \mathcal{P}_{(2\mathcal{M})}$ are the numbers obtained by rearrangement of $\mathcal{P}: 1 \ldots 2\mathcal{M}$.

Thus,

$$\frac{1}{(2\mathcal{M})!}G_{1\dots 1}^{(2\mathcal{M})}(0,\dots 0) = \frac{1}{2^{\mathcal{M}}\mathcal{M}!}G^{(2\mathcal{M})}(0,\dots 0).$$
(13)

The generating functional is expressed as the Green functions

$$\mathcal{Z}\{\vec{H}\} = 1 + \sum_{N=1}^{\infty} \frac{1}{N!} \int d^d k_1 \cdots d^d k_N H_{j_1}(-\vec{k}_1) \cdots H_{j_N}(-\vec{k}_N) G^{(N)}_{j_1 \dots j_N}(\vec{k}_1, \dots, \vec{k}_N).$$
(14)

and the ordered Green functions

$$\mathcal{Z}\{\vec{H}\} = 1 + \sum_{\mathcal{M}=1}^{\infty} \frac{1}{2^{\mathcal{M}} \mathcal{M}!} \int d^{d}k_{1} \cdots d^{d}k_{2\mathcal{M}} \left[\vec{H}(-\vec{k}_{1}) \times \vec{H}(-\vec{k}_{2})\right] \cdots$$

$$\times \left[\vec{H}(-\vec{k}_{2\mathcal{M}-1}) \times \vec{H}(-\vec{k}_{2\mathcal{M}})\right] G^{(2\mathcal{M})}(\vec{k}_{1}, \dots, \vec{k}_{2\mathcal{M}}).$$
(15)

The generating functional of the connected Green functions $G_{c,j_1...j_N}^{(N)}(\vec{k_1},...\vec{k_N})$ is the free energy of the system (see subsection 2.6.2)

$$I'\{\vec{II}\} = 1 + \sum_{N=1}^{\infty} \frac{1}{N!} \int d^d k_1 \cdots d^d k_N H_{j_1}(-\vec{k}_1) \cdots H_{j_N}(-\vec{k}_N) G_{c,j_1...j_N}^{(N)}(\vec{k}_1,\ldots,\vec{k}_N), (16)$$

that can be expressed as the connected ordered Green functions in the following way

$$F\{\vec{H}\} = 1 + \sum_{\mathcal{M}=1}^{\infty} \frac{1}{2^{\mathcal{M}}\mathcal{M}!} \int d^{d}k_{1} \cdots d^{d}k_{2\mathcal{M}} \left[\vec{H}(-\vec{k}_{1}) \times \vec{H}(-\vec{k}_{2})\right] \cdots$$

$$\times \left[\vec{H}(-\vec{k}_{2\mathcal{M}-1}) \times \vec{H}(-\vec{k}_{2\mathcal{M}})\right] G_{c}^{(2\mathcal{M})}(\vec{k}_{1}, \dots, \vec{k}_{2\mathcal{M}}).$$

$$(17)$$

The functionals $\mathcal{Z}\{\vec{H}\}$ and $F\{\vec{H}\}$ are related to each other by

$$\mathcal{Z}\{\vec{H}\} = \exp\left[F\{\vec{H}\}\right].$$
(18)

Correspondingly, the generating functional $\Gamma\{\vec{M}\}$ is expressed as the vertex functions:

$$\Gamma\{\vec{M}\} = \sum_{N=1}^{\infty} \frac{1}{N!} \int d^d k_1 \cdots d^d k_N M^{j_1}(-\vec{k}_1) \cdots M^{j_N}(-\vec{k}_N) \delta(\vec{k}_1 + \cdots + \vec{k}_N)$$
(19)

$$\times \Gamma^{(N)}_{j_1 \dots j_N}(\vec{k}_1, \dots, \vec{k}_N).$$

or as the ordered vertex functions

$$\Gamma\{\vec{M}\} = \sum_{\mathcal{M}=1}^{\infty} \frac{1}{2^{\mathcal{M}} \mathcal{M}!} \int d^{d}k_{1} \cdots d^{d}k_{2\mathcal{M}} \left[\vec{M}(-\vec{k}_{1}) \times \vec{M}(-\vec{k}_{2})\right] \cdots$$

$$\times \left[\vec{M}(-\vec{k}_{2\mathcal{M}-1}) \times \vec{M}(-\vec{k}_{2\mathcal{M}})\right] \delta(\vec{k}_{1} + \cdots + \vec{k}_{2\mathcal{M}}) \Gamma^{(2\mathcal{M})}(\vec{k}_{1}, \dots, \vec{k}_{2\mathcal{M}}).$$
(20)

Thus, the vertex functions $\Gamma_{j_1...j_N}^{(N)}(\vec{k}_1,...\vec{k}_N)$ and $\Gamma^{(2\mathcal{M})}(\vec{k}_1,...\vec{k}_{2\mathcal{M}})$ are obtained for N > 2 and $\mathcal{M} > 1$ by cutting off the external lines from the corresponding one-particle

irreducible Green functions (see Section 2.6.2) and reversing the sign. For instance, for $\mathcal{M}=1$

$$G^{(2)}(\vec{k}_1, \vec{k}_2) = \delta(\vec{k}_1 + \vec{k}_2) \left[\Gamma^{(2)}(\vec{k}_1, \vec{k}_2) \right]^{-1}.$$
(21)

The generating functionals $\Gamma\{\vec{M}\}$ and $F\{\vec{H}\}$ are related by the Legendre transformation

$$\Gamma\{\vec{M}\} + F\{\vec{H}\} = \int d^d x \, \vec{M}(\vec{x}) \vec{H}(\vec{x}).$$
(22)

with

$$M^{j}(x) = \frac{\partial F\{\tilde{H}\}}{\partial H^{j}(x)}$$
 and $H^{j}(x) = \frac{\partial \Gamma\{\tilde{M}\}}{\partial M^{j}(x)}$. (23)

External constant field \vec{H}_0 having been introduced, the action is written as

$${}^{H}\mathcal{A}\{\phi\} = \mathcal{A}\{\phi\} - \sum_{j} H_0^j \int d^d x \, \phi^j(\vec{x}).$$
⁽²⁴⁾

The generating functional for the Green function is

$${}^{H}\mathcal{Z}\{\vec{H}\} = \frac{\mathcal{Z}\{\vec{H} + \vec{H}_{0}\}}{\mathcal{Z}\{\vec{H}_{0}\}}.$$
(25)

In order to define the relationship between ${}^{H}F\{\vec{H}\}$ and ${}^{H}\Gamma\{\vec{H}\}$, let us rewrite Equations 22 and 23 with due account of the external field:

$$M^{j}(\vec{x}) + M_{0}^{j} = \frac{\partial F\{\vec{H} + \vec{H}_{0}\}}{\partial H^{j}(\vec{x})},$$
(26)

$$H^{j}(\vec{x}) + H_{0}^{j} = \frac{\partial \Gamma\{\vec{M} + \vec{M}_{0}\}}{\partial M^{j}(\vec{x})}.$$
(27)

$$F\{\vec{H} + \vec{H}_0\} + \Gamma\{\vec{M} + \vec{M}_0\} - \int d^d x \left[\vec{M}(\vec{x}) + \vec{M}_0\right] \left[\vec{H}(\vec{x}) + \vec{H}_0\right] = 0.$$
(28)

We write $F\{\vec{H}_0\}$ and $\Gamma\{\vec{M}_0\}$ in the form

$$F\{\hat{H}_{0}\} = VF(H_{0}),$$
(29)

$$\Gamma\{\vec{M}_0\} = V\Gamma(M_0). \tag{30}$$

 $F\{\vec{H}_0\}$ and $\Gamma\{\vec{M}_0\}$ having their finite limits on an increase in the system's volume $V \to \infty$. Then, it follows from Equations 26-28 that

$$M_0 = \frac{\partial F(H_0)}{\partial H_0},\tag{31}$$

$$H_0 = \frac{\partial \Gamma(H_0)}{\partial M_0},\tag{32}$$

$$F(H_0) + \Gamma(M_0) - M_0 H_0 = 0. \tag{33}$$

Using

$$\vec{M}_0(\vec{k}) = (2\pi)^{d/2} M_0 \delta(\vec{k}), \tag{34}$$

one can write, in accordance with Equation 20,

$$\Gamma(M_0) = \sum_{\mathcal{M}=1}^{\infty} \frac{1}{2^{\mathcal{M}} \mathcal{M}!} \left[M_0(2\pi)^{d/2} \right]^{2\mathcal{M}} \Gamma^{(2\mathcal{M})}(0, \dots 0).$$
(35)

Now Equations 26-28 yield

$${}^{II}F\{\vec{II}\} = F\{\vec{H} + \vec{II}_0\} - F\{\vec{II}_0\} - \int d^d x \, \vec{M}_0 \vec{H}(\vec{x}), \tag{36}$$

$${}^{H}\Gamma\{\vec{M}\} = \Gamma\{\vec{M} + \vec{M}_{0}\} - \Gamma\{\vec{M}_{0}\} - \int d^{d}x \, \vec{H}_{0}\vec{M}(\vec{x}).$$
(37)

If

$$H_0^j = \delta_{ij} H_0 \quad \text{and} \quad M_0^j = \delta_{ij} M_0 \tag{38}$$

are given, then the abovedefined functions in the presence of the field are modified so that

$${}^{II}G_{c,j_1\dots j_N}(\vec{k}_1,\dots\vec{k}_N) = \sum_{N'=0}^{\infty} \frac{1}{N'!} \left[H_0(2\pi)^{d/2} \right] G_{c,j_1\dots j_N,1,\dots 1}^{(N+N')}(\vec{k}_1,\dots\vec{k}_N,0,\dots 0),$$
(39)

$${}^{H}\Gamma_{j_{1}...j_{N}}(\vec{k}_{1},\ldots,\vec{k}_{N}) = \sum_{N'=0}^{\infty} \frac{(-1)^{N'}}{N'!} \left[M_{0}(2\pi)^{d/2} \right] \Gamma_{j_{1}...j_{N},1,\ldots,1}^{(N+N')}(\vec{k}_{1},\ldots,\vec{k}_{N},0,\ldots,0).$$
(40)

The corresponding ordered functions can be defined as well.

As n is an integer positive number, we can define one **longitudinal** (L) and (n-1) transversal (T) functions. Eg, the second-rank vertex function implies

$${}^{II}\Gamma_{jj}^{(2)}(\vec{k},-\vec{k}) = \delta_{j_1}\Gamma_L^{(2)}(\vec{k},-\vec{k}) + (1-\delta_{j_1})\Gamma_T^{(2)}(\vec{k}_1-\vec{k}).$$
(41)

In view of Equation 40, one can get the expression corresponding to Equation 12:

$${}^{H}\Gamma_{T}^{(2)}(\vec{k},-\vec{k}) = \sum_{\mathcal{M}=0}^{\infty} \frac{\left[M_{0}(2\pi)^{d/2}\right]^{\mathcal{M}}}{2^{\mathcal{M}}\mathcal{M}!} \Gamma^{(2\mathcal{M}+2)}(\vec{k},-\vec{k},0,\ldots,0),$$
(42)

$${}^{II}\Gamma_{L}^{(2)}(\vec{k},-\vec{k}) - {}^{II}\Gamma_{T}^{(2)}(\vec{k},-\vec{k}) = \sum_{\mathcal{M}=0}^{\infty} \frac{\left[M_{0}(2\pi)^{d/2}\right]^{\mathcal{M}}}{2^{\mathcal{M}}\mathcal{M}!} 2\mathcal{M}\Gamma^{(2\mathcal{M}+2)}(\vec{k}_{1},0,-\vec{k},0,\ldots,0).$$
(43)

These functions retain their meaning even if n is a non-integer number, or $n \to 0$.

We now go on to discuss a polymer system of \mathcal{M} chains in the volume V. Each chain is marked by its index m, L_m being the length of the *m*th chain. The vector $\vec{r}_m(\lambda_m)$ characterizes the spatial arrangement of the *m*th chain, where λ_m is the length measured along the chain from its beginning to the point with the mark \vec{r}_m ($0 < \lambda_m < L_m$). Following Edwards (1965) (see Equation 3.1-205), des Cloizeaux (1975) writes the Hamiltonian of the cth conformation

$$\mathcal{H}(L_1,\ldots,L_{\mathcal{M}};c)=\mathcal{H}_0(L_1,\ldots,L_{\mathcal{M}};c)+\mathcal{H}_1(L_1,\ldots,L_{\mathcal{M}};c),$$

where

$$\mathcal{H}_0(L_1,\ldots,L_{\mathcal{M}};c) = \sum_{m=1}^{\mathcal{M}} \frac{1}{4l} \int_0^{L_m} d\lambda_m \left[\frac{\partial \vec{r}_m(\lambda_m)}{\partial \lambda_m} \right]^2, \tag{44}$$

$$\mathcal{H}_1(L_1,\ldots,L_{\mathcal{M}};c) = \frac{l^2}{2} \sum_{m=1}^{\mathcal{M}} \sum_{m'=0}^{\mathcal{M}} \int_0^{L_m} d\lambda_m \int_0^{L_{m'}} d\lambda_{m'} \mathcal{V}\left[\vec{r}_m(\lambda_m) - \vec{r}_m(\lambda_{m'})\right].$$

Hamiltonians 44 are dimensionless. The length l can be considered as the length of a unit though a continuous limit is meant in Equation 44.

As it usually is, the mean value of the conformation functional $O\{c\}$ is given by

$$\langle O\{c\}\rangle = \frac{\int d\Omega_{\mathcal{M}} \exp\left[-\mathcal{H}(L_1, \dots, L_{\mathcal{M}}, c)\right] O\{c\}}{\int d\Omega_{\mathcal{M}} \exp\left[-\mathcal{H}_0(L_1, \dots, L_{\mathcal{M}}, c)\right]},\tag{45}$$

where

$$d\Omega_{\mathcal{M}} = \prod_{1}^{\mathcal{M}} d\omega_{m}, \quad d\omega_{m} = \prod_{\lambda=0}^{\lambda=L_{m}} d^{d} r_{m}(\lambda).$$
(46)

Temperature is included into the Hamiltonian definitions.

The main correlation effects in the system can be described using the probabilities of a given chain end conformation. That is why we consider the probability of the *m*th chain ends $r_m(0)$ and $r_m(L_m)$ being fixed at the points r_{2m-1} and r_{2m} , respectively,

$$\mathcal{S}(\vec{r}_1,\ldots,\vec{r}_{2\mathcal{M}};L_1,\ldots,L_{\mathcal{M}}) = \left[Vl^{-d}\right]^{\mathcal{M}} \left\langle \prod_{m=1}^{m=\mathcal{M}} \delta(r_m(0) - r_{2m-1})\delta\left[r_m(L_m) - r_{2m}\right] \right\rangle$$
(47)

and its Fourier transform

$$\tilde{\mathcal{S}}(\vec{r}_1, \dots, \vec{r}_{2\mathcal{M}}; L_1, \dots, L_{\mathcal{M}}) = \left[V(2\pi l)^{-d} \right]^{\mathcal{M}}$$

$$\times \left\langle \exp\left\{ -i \sum_{m=1}^{m=\mathcal{M}} \left[\vec{k}_{2m-1} \vec{r}_m(0) + \vec{k}_{2m} \vec{r}_m(L_m) \right] \right\} \right\rangle.$$
(48)

These quantities can be expanded into a series in terms of interaction which allows one to calculate the functional integrals in the following way. Consider a chain (for instance, $\mathcal{M} = 1$) of the length L with sets of lengths $\lambda_1, \ldots, \lambda_J$ and momenta $\vec{q_1}, \ldots, \vec{q_L}$.

Assuming the chain to be free (interaction-free), define the mean value

$$I\{\vec{q},\lambda\} = \left\langle \exp\left\{-i\left[\vec{k}_0\vec{r}(0) + \vec{k}_1\vec{r}(L) + \sum_{j=1}^{j=J}\vec{q}_j\vec{r}(\lambda_j)\right]\right\}\right\rangle_0$$
(49)

$$= (2\pi)^{d} V^{-1} \delta(\vec{k}_{0} + \vec{k}_{1} + \vec{q}_{1} + \dots + \vec{q}_{J}) \exp\{-l[\lambda_{1}\vec{k}_{0}^{2} + (\lambda_{2} - \lambda_{1})(\vec{k}_{0} + \vec{q}_{1})^{2} + \dots + (\lambda_{J} - \lambda_{J-1})(\vec{k}_{0} + \vec{q}_{1} + \dots + \vec{q}_{L-1})^{2} + (L - \lambda_{J})(\vec{k}_{0} + \vec{q}_{1} + \dots + \vec{q}_{J})^{2}]\}.$$

On the other hand, the interaction potential in $\mathcal{H}_1(L_1, \ldots, L_M)$ is expressed as its Fourier transform

$$\mathcal{V}\left[\vec{r}_{m}(\lambda_{m}) - \vec{r}_{m'}(\lambda_{m'})\right] = \int d^{d}q \,\tilde{\mathcal{V}}(\vec{q}) \exp\left\{-i\vec{q}\left[\vec{r}_{m}(\lambda_{m}) - \vec{r}_{m'}(\lambda_{m'})\right]\right\}.$$
(50)

The successive terms of this expansion can be found with equality 49. Define the ordered Green functions of polymer theory

$$G^{(2\mathcal{M})}(\vec{k}_1, \dots, \vec{k}_{2\mathcal{M}}) = l^{\mathcal{M}(d+2)} \int \frac{dL_1}{l} \cdots \frac{dL_{\mathcal{M}}}{l} \exp\left(-sLl^{-1}\right)$$

$$\times \tilde{\mathcal{S}}(\vec{k}_1, \dots, \vec{k}_{2\mathcal{M}}, L_1, \dots, L_{\mathcal{M}}),$$
(51)

where

$$L = L_1 + L_2 + \dots + L_M, \quad s = m_0^2 l^2.$$

The diagrammatic technique should be employed with the very rules as for the Green functions with the field Lagrangian 8.

Each graph line corresponds to a polymer chain. To provide the calculation of the ordered Green functions, an intermediate expression is introduced:

$$I(\vec{k}_{0},\vec{k}_{1},\vec{q}_{1},\ldots,\vec{q}_{J}) = l^{2} \int_{0}^{\infty} \frac{dL}{l} \exp\left(-sLl^{-1}\right) \int d\lambda_{1}\cdots d\lambda_{J} I\{\vec{q},\lambda\}$$
(52)
$$= (2\pi)^{d}V^{-1}l^{-J}\delta(\vec{k}_{0}+\vec{k}_{1}+\vec{q}_{1}+\cdots+\vec{q}_{J})\frac{1}{sl^{-2}+\vec{k}_{0}^{2}}\cdot\frac{1}{sl^{-2}+(\vec{k}_{0}+\vec{q}_{1})^{2}}\times\cdots$$
$$\times \frac{1}{sl^{-2}+(\vec{k}_{0}+\vec{q}_{1}+\cdots+\vec{q}_{J})^{2}},$$
$$0 < \lambda_{1} < \cdots < \lambda_{J} < L.$$

The only distinction of the polymer theory graphs (Figure 4.1c) from the field theory ones (Figure 4.1ab) is in the absence of loops (in the former case), which means n = 0.

Hence, des Cloizeaux has generalized de Gennes' (1972) and Emery's (1975) result for a single chain to an ensemble of \mathcal{M} macromolecules.

In infinite space, such a quantity as $\tilde{S}(0, \ldots, 0, L_1, \ldots, L_M)$ is infinite as well and so loses its physical meaning. But for a big "case", these quantities can be given a reasonable interpretation, writing (see Equation 2.6-80)

$$\delta(0) = V(2\pi)^{-d}.$$
(53)

It follows from Equations 45 and 48 that the number of conformations $\mathcal{Z}(L_1, \ldots, L_M)$ is defined by

$$\mathcal{Z}(L_1,\ldots,L_{\mathcal{M}}) = \tilde{\mathcal{S}}(0,\ldots,0,L_1,\ldots,L_{\mathcal{M}}).$$
(54)

Des Cloizeaux introduced a grand canonical partition function $\mathcal{Z}(H_0)$ depending on two chemical potentials H_0 and $s = m_0^2 l^2$

$$\mathcal{Z}(H_0) = 1 + \sum_{\mathcal{M}=1}^{\infty} \frac{1}{2^{\mathcal{M}} \mathcal{M}!} \left[H_0 l^{d/2+1} (2\pi)^{d/2} \right]^{2\mathcal{M}} \int_0^\infty \frac{dL_1}{l} \cdots \int \frac{dL_{\mathcal{M}}}{l} \exp\left(-sLl^{-1}\right)$$
(55)
× $\mathcal{Z}(L_1, \dots L_{\mathcal{M}})$

with $L = L_1 + L_2 + \cdots + L_M$.

 $H_0 l^{d/2+1}$ should be thought of as a dimensionless parameter and, hence, H_0 can be interpreted as a magnetic field. The integral $\int l^{-1} dL_p$ corresponds to summation over all the units of chain p, since the number of units is $N_p = l^{-1}L_p$ by definition. In view of Equations 51 and 54, we write

$$\mathcal{Z}(H_0) = 1 + \sum_{\mathcal{M}=0}^{\infty} \frac{1}{2^{\mathcal{M}} \mathcal{M}!} \left[H_0(2\pi)^{d/2} \right]^{2\mathcal{M}} G^{(2\mathcal{M})}(0, \dots, 0).$$
(56)

If we accept

$$H^{j}(x) = H_{0}\delta_{1j}, \quad \vec{H}(\vec{k}) = (2\pi)^{d/2} H_{0}\delta_{1j}\delta(\vec{k}),$$
(57)

for Equation 15 and go over to the limit n = 0, we can write

$$\mathcal{Z}(H_0) = \mathcal{Z}\{\vec{H}_0\}_{n=0},\tag{58}$$

and, in view of Equations 18, 29, 30,

$$\mathcal{Z}(H_0) = \exp[VF(H_0)]. \tag{59}$$

As $F(H_0)$ is the free energy per unit volume, then

$$\frac{\pi}{kT} = F'(H_0). \tag{60}$$

The concentrations of polymer chains c_p and monomer units c are defined from Equation 55, allowing for Equation 59 and using the standard formulae of statistical physics (see Section 1.7)

$$c = \frac{\langle Ll^{-1} \rangle}{V} = -\frac{\partial}{\partial s} F(H_0), \tag{61}$$

$$\frac{2\langle \mathcal{M} \rangle}{V} = \frac{\partial F(H_0)}{\partial \ln H_0} = H_0 \frac{\partial F(H_0)}{\partial H_0},$$

$$c_p = \frac{\langle \mathcal{M} \rangle}{V} = \frac{H_0}{2} \cdot \frac{\partial F(H_0)}{\partial H_0}.$$
(62)

In particular, with no interaction, Equations 11 and 53 yield

$$G_c^{(2)}(0,0) = \frac{V(2\pi)^{-d}}{m_0^2} = \frac{V(2\pi)^{-d}l^2}{s}.$$
(63)

Ilence (cf. Equation 2.6-98),

$$F'(H_0) = \frac{l^2 H_0^2}{2s}.$$
(64)

It follows from Equations 60, 62, 64 that

$$\pi = kT \frac{l^2 H_0^2}{2s} = kT \frac{H_0}{2} \cdot \frac{\partial F(H_0)}{\partial H_0} = kT c_p, \tag{65}$$

and the average value of polymer chains is

$$\mathcal{N} = \frac{c}{c_p} = \frac{1}{s}.\tag{66}$$

If an interaction is present, the vertex functions prove to be more appropriate, and it is reasonable to express all the active quantities as the potential $\Gamma(M_0)$.

Combining Equations 31 and 33, rewrite Equation 60 as

$$\frac{\pi}{kT} = M_0 \frac{\partial \Gamma(M_0)}{\partial M_0} \quad \Gamma(M_0), \tag{67}$$

and the concentrations of chains and units (Equations 62, 61) as

$$c_p = \frac{M_0}{2} \cdot \frac{\partial \Gamma(M_0)}{\partial M_0} = \frac{H_0}{2} \cdot \frac{\partial F(H_0)}{\partial H_0} = \frac{M_0 H_0}{2}$$
(68)

$$c = \frac{\partial \Gamma(M_0)}{\partial s}.$$
(69)

Here, s functions as the temperature ε of a magnetic system, since $s = m_0^2 l^2$ (cf. Equations 2.6-26,-36 and Equation 11) so

$$c = \frac{\partial \Gamma(M_0)}{\partial \varepsilon}.$$
(70)

4.3. State diagram: polymer+low molecular weight liquid

4.3.1. Theory

Equations 4.2-66...69 constitute a glossary between the quantities characterizing the properties of a magnetic and a polymer system (P+LMWL). Using it together with scaling (mainly intuitive at this stage), Daoud and Jannink (1976) have built a state diagram of the system P+LMWL.

In accordance with Equation 4.2-33 and the parity of $\Gamma(M_0, H_0, T)$, we write

$$\Gamma(M_0, H_0, T) = F(M_0, H_0, T) - M_0 H_0.$$
⁽¹⁾

and see that the singularities of the functions Γ and F coincide.

The free energy $F(M_0)$ below T_c has a minimum at

$$M_0 = M_{0M} \sim |\varepsilon|^{\beta}$$

(see Figure 1.14). Thus, if $F(M_0)$ is put in the scaling form

$$F(M_0) = \varepsilon^{2-\alpha} f_F(x), \tag{2}$$

 $x = M_0/|\varepsilon|^{\beta}$ is the argument of $f_F(x)$.

The factor $\varepsilon^{2-\alpha}$ is necessary to obtain a proper singularity for the heat capacity $c_H \sim \varepsilon^{-\alpha}$ (see Table 1.2), since c_H is proportional to the second derivative of $F(M_0)$ with respect to temperature (eg. Equation 1.6-11).

When $\varepsilon > 0$ and M_0 is small we can confine ourselves to one term of the $f_F(x)$ expansion with respect to x. As $F(M_0)$ is an even function (see Figure 1.14),

$$F = F(x)|_{x=0} + const \ \varepsilon^{2-\alpha} \left(\frac{M_0^2}{\varepsilon^{2\beta}}\right). \tag{3}$$

From

$$\chi_{T,H}^{-1} = \frac{\partial^2 F}{\partial M_0^2}$$

(see Equation 1.6-13) it follows that

 $\chi_{\tau,\mu} \sim \varepsilon^{2\beta+\alpha-2}$ and $\varepsilon^{-\gamma} \sim \varepsilon^{2\beta+\alpha-2}$. (4)

and Widom's relationship (Equation 1.5-9) emerges

$$\alpha + 2\beta + \gamma = 2. \tag{5}$$

The scaling expression

$$\Gamma(M_0) \sim \varepsilon^{2-\alpha} f_{\Gamma}\left(\frac{M_0}{|\varepsilon|^{\beta}}\right) \tag{6}$$

holds true for the potential $\Gamma(M_0)$ as well.

The following equation (de Gennes, 1979) applies for the spontaneous magnetization correlation function $\langle \vec{M}_0(0)\vec{M}_0(\vec{r}) \rangle$, i.e. for the mean value of the product of the local magnetization \vec{M}_0 existing at two points separated by a distance \vec{r} :

$$\left\langle \vec{M}_{0}(0)\vec{M}_{0}(\vec{r})\right\rangle \sim \frac{1}{r^{d-2+\eta}}f_{M_{0}}\left(\frac{r}{\xi}\right) \tag{7}$$

(see Figure 4.2, cf. Equation 2.3-149).



Figure 4.2. Spontaneous magnetization correlation function

The dimensionless function $f_{M_0}(x)$ obeys the following conditions:

$$f_{M_0}(0) = 1, f_{M_0}(x) \simeq x^{\eta} \exp(-x), \quad x \gg 1.$$
(8)

Thus, at long distances $(x \to \infty)$ the spontaneous magnetization correlations correspond to Ornstein-Zernike's function (Equations 2.5-7, 2.3-129) (when d = 3). The other limit $(x \to 0)$ corresponds to $T = T_c$ $(\xi \to \infty)$ and the correlation diminishes with distance as $r^{-(d-2+\eta)}$.

Near $T \to T_c$

$$\xi \simeq |\varepsilon|^{-\nu} \tag{9}$$

(see Table 1.2 and Equation 4.1 8).

In the case of the polymer problem, the segment concentration in a coil is an analogue for $\langle \vec{M}_0(0)\vec{M}_0(\vec{r}) \rangle$ (cf. Figures 4.2 and 3.8). In dilute solutions, ξ is associated with the polymer coil size R, and ε with N^{-1} , thus

$$R(N) \sim N^{\nu}. \tag{10}$$

The susceptibility $\chi_{_{T,M_0}}$ is related to the magnetization correlation function as

$$\chi_{_{T,M}} \sim (kT)^{-1} \int \left\langle \vec{M}_0(0) \vec{M}_0(\vec{r}) \right\rangle d\vec{r}$$
 (11)

(see Equation 1.7-34).

In view of Equations 7-9, we write

$$\chi_{TM} \sim \xi^{2-\eta} \tag{12}$$

(see Equations 2.3-150, 151) and

$$\varepsilon^{-\gamma} \sim \varepsilon^{-\nu(2-\eta)},\tag{13}$$

and another useful relationship between the critical indices appears

$$\gamma = \nu(2 - \eta) \tag{14}$$

(see Equation 2.3-153).

Further, from the scaling expression for $I'(M_0)$ (Equation 6) and the glossary (Equations 4.2-68,-70), we obtain

$$c \approx \varepsilon^{1-\alpha} f_c(x) \tag{15}$$

and

$$c_p \approx \varepsilon^{2-\alpha} f_p(x),$$
 (16)

where x is a dimensionless parameter proportional to $M/|\varepsilon|^{\beta}$. Including Kadanoff's equality (Equation 1.5-10; see also Equation 2.5-19)

$$\alpha = 2 - \nu d, \tag{17}$$

Equations 15 and 16 take the form

$$c \approx \varepsilon^{\nu d-1} f_c(x) \tag{18}$$

and

$$c_p \approx \varepsilon^{\nu d} f_P(x). \tag{19}$$

Substituting Equations 18 and 19 into Equation 4.2-66, one obtains

$$\frac{f_{\varepsilon}(x)}{f_{p}(x)} = N\varepsilon, \tag{20}$$

which means x is a function of one variable only:

$$N\varepsilon = y.$$
 (21)

The coil-overlap concentration in the d-dimensional space (Equation 3.1-220) is

$$c^* = \frac{NA^d}{R^d} = N^{1-\nu d}.$$
 (22)

According to Equations 18 and 21, we write

$$\frac{c}{c^*} = (N\varepsilon)^{\nu d-1} f_c(x) = y^{\nu d-1} f_c(x).$$
(23)

Hence, the c/c^* ratio is a function of x (or y). Allowing for relationships 6, 4.2–68, 17, and 19, we have for the osmotic pressure (Equation 4.2–67)

$$\frac{\pi}{kT} = \varepsilon^{\nu d} f_{\pi}(x) = c_p \frac{f_{\pi}(x)}{f_p(x)} = c_p f_d\left(\frac{c}{c^*}\right),\tag{24}$$

where $f_d(c/c^*)$ is a new dimensionless function.

Relationship 24 is the fundamental result by des Cloizcaux, stating the osmotic pressure π of real solution to be expressed by the product of the osmotic pressure of the ideal solution π_{id} and the dimensionless c/c^* ratio.

Now we turn to the state diagram of a magnetic (Figure 4.3). Curve 1 shows magneti-



Figure 4.3. State diagram of a ferromagnetic in a zero field (1) and the isometric line (2) as an analogue of the state diagram of polymer solution (de Gennes, 1979) [Reprinted from: P.J. de Gennes Scaling Concepts in Polymer Physics. Copyright © 1979 by Cornell University Press. Used by permission of Cornell University Press]

zation in the absence of the field $M_0(0, T/T_c)$ which, for the polymer analogue, corresponds to a single molecular chain. As to an ensemble of many chains (i.e. polymer solution), the so-called **isometric line** (curve 2) corresponds to it and brings into agreement M_0 and T/T_c in accordance with Equations 4.2-66 and 20 for a given N.

Let us discuss the isometric line behaviour. It follows from the partition function (Equation 4.2-55) that the variant of extremely dilute solution should correspond to $H_0 \rightarrow 0$, i.e. the statistical weights of two, three, and more chains are small in comparison with that of a single chain. Moreover, the existence of a single chain on a lattice should correspond to the condition $T > T_c$, since the polymer coil size is related to the correlation function of magnetization fluctuations, existing only when $T > T_c$. In case of dilute solutions $c_p \approx 0$, and, hence, $M_0 = 0$ (Equation 4.2-68). The condition $M_0 = 0$, $H_0 \rightarrow 0$, and $T > T_c$ is related to the abscissa axis in Figure 4.3, to the right of the point C. Now it is natural to admit that the isometric line intersects the abscissa axis at such point T/T_c which corresponds to the relative temperature ε that, in turn, corresponds to 1/N, therefore the distance CD on the abscissa axis $\sim 1/N$.

In the other limiting case, namely, high concentrations of polymer solution $c > c^*$, all the thermodynamic properties should not depend on N, which is formalized by $N \to \infty$ and, according to Equations 4.2-67 and 19, $c_p \to 0$. In view of Equation 4.2-68, this corresponds to $H_0 = 0$, but $M_0 \neq 0$, and the isometric line should be close to the coexistence curve $M_0(0, T/T_c)$.

Under conditions of a semidilute solution ξ refers to the blob size and

$$\xi \approx A|\varepsilon|^{-\nu}.\tag{25}$$

The number of segments per blob is g, so

$$\xi \sim g^{\nu} \tag{26}$$

with

$$q = |\varepsilon|^{-1} \tag{27}$$

remaining valid.

Then, the parameter $y = N|\varepsilon|$ is equal to the number of blobs per chain.

The polymer system's behaviour near the θ point corresponds to that of a more general kind in the vicinity of the tricritical point (de Gennes, 1975) (see subsection 4.1.1) where thermodynamic functions are described by scaling fields (see section 1.6).

Here the scaling fields μ_1 and μ_2 have the meaning of the reduced temperature of the magnetic ε and of the polymer system $\tau = (T - \theta)/\theta$, respectively. Then, in the vicinity of the tricritical point, the potential F (Equation 6) is written as (Riedel and Wegner, 1972; Wegner and Riedel, 1973)

$$F(M_0,\varepsilon,\tau) = \varepsilon^{2-\alpha_t} f(\frac{M_0}{|\varepsilon|^{\beta_t}};\frac{\tau}{|\varepsilon|^{\varphi_t}}),$$
(28)

and the crossover line is defined by Equation 1.6-74 (Riedel and Wegner, 1972)

$$\tau_{c\tau} \sim \epsilon^{\varphi_{\tau}},$$
 (29)

where φ_t is the crossover index.

In view of the equivalence $\varepsilon \sim N^{-1}$, for the crossover line we write:

$$\tau_{cr} \sim N^{-\varphi_t}.\tag{30}$$

As for $d = 3 \varphi_t = 1/2$, then

$$\tau_{cr} \approx N^{-1/2}.\tag{31}$$

Figure 4.4 shows a state diagram of the system P+LMWL, based on scaling constructions using the analogy between a ferromagnetic and a polymer system. The following characteristic regions should be marked: region I of a dilute solution which is separated from the tricritical region I' by the crossover line (Equation 31); region 11 of a semidilute solution and region I are separated by the molecular chain overlap line c^* (Equation 22). The line c^{**} is the crossover between the region of the semidilute solution 11 and the tricritical region of the semidilute and concentrated solutions 111.

Thus, the crossover line (Equation 29) separates the tricritical region (I' and III), where

$$\frac{\tau}{\varepsilon^{\varphi_t}} \ll 1,$$
 (32)

from the critical region (I and II) for which the reverse inequality holds good:

$$\frac{\tau}{\varepsilon^{\varphi_1}} \gg 1. \tag{33}$$



Figure 4.4. State diagram of P+LMWL by the scaling theory (Daoud and Jannink, 1976) [Reprinted with permission from: M.Daoud, G.Jannink. Le J. de Phys. 37 (1976) 973 979. Copyright © 1976 by EDP Sciences]

In the tricritical region, where inequality 32 holds, the potential (Equation 28) is written as (Daoud and Jannink, 1976):

$$F(M_0,\varepsilon,\tau) = \varepsilon^{2-\alpha_t} g(M_0/\varepsilon^{\rho_t}), \tag{34}$$

since the dependence on the second parameter of the dimensionless function (Equation 28) can be neglected due to its being small. Then, according to Equations 34 and 4.2–70, for a semidilute solution

$$c = \varepsilon^{1-\alpha_t} \left[(2-\alpha_t)f(x) - \beta_t x \frac{\partial f}{\partial x} \right]$$
(35)

holds, where $x = M_0 / \varepsilon^{\beta_t}$.

In this concentration range the isometric line M_0 and $M_0(0) \sim \varepsilon^{\beta_t}$ almost coincide (see Figure 4.3) so that x becomes constant (x_0) and

$$c = \varepsilon^{1 - \alpha_t} h(x_0) = K \varepsilon^{1 - \alpha_t} \tag{36}$$

or (see Equation 17)

$$\varepsilon \sim c^{1/(1-\alpha_1)} = c^{1/(\nu_1 d-1)}.$$
(37)

For the crossover line (Equation 29) in the semidilute region c^{**} we have

$$c^{**} \sim \tau^{(\nu_t d - 1)/\varphi_t} \approx \tau \tag{38}$$

for d = 3, where $\nu_t = 1/2$, $\varphi_t = 1/2$.

Let us discuss the functional dependence of the osmotic pressure π in the tricritical region. On the basis of Equations 4.2-67 and 34 one can write (Daoud and Jannink, 1976):

$$\frac{\pi}{kT} \cong \varepsilon^{2-\alpha_1} \left[-g(x) + x \frac{\partial g(x)}{\partial x} \right]$$
(39)

or

$$\frac{\pi}{kT}\varepsilon^{\alpha_t-2} = h(x),\tag{40}$$

where $x = M_0 / \varepsilon^{\beta_t}$.

Having excluded x from Equations 35 and 40, we have

$$\frac{\pi}{kT}\varepsilon^{\alpha_t-2} = f(c\varepsilon^{\alpha_t-1}). \tag{41}$$

In the dilute solution region (where $x \to 0$), the function f(x) is approximated as $f(x) \approx x$ and, in view of $\varepsilon \sim 1/N$, it follows from Equation 41 that

$$\pi \sim \frac{c}{N}.\tag{42}$$

Regions I' and III are separated by the coil overlap line (Equation 22), which takes the dependence

$$c_t^* \sim N^{1-\nu_t d} \approx N^{-1/2} \tag{43}$$

for the tricritical region and d = 3.

In the tricritical region of semidilute solution III, combining Equations 37 and 40 including Widom's equality $\alpha - 2 = -\nu d$ (see Equation 2.5–19) yields

$$\frac{\pi}{kT} \sim \varepsilon^{\nu_t d} \sim c^{\nu_t d/(\nu_t d-1)} \sim c^3 \tag{44}$$

for d = 3.

In the critical region, where inequality 33 applies, the potential is patterned after Equation 28 (Daoud and Jannink, 1976):

$$F(M_0,\varepsilon,\tau) = \varepsilon^{2-\alpha_t} \left(\frac{\tau}{\varepsilon^{\varphi_t}}\right)^x g\left(\frac{M_0}{\varepsilon^{\beta_t}} \left(\frac{\varepsilon^{\varphi_t}}{\tau}\right)^y\right).$$
(45)

This comparison allows one to find x and y, and the potential can be written as

$$F(M_0,\varepsilon,\tau) = \varepsilon^{2-\alpha_t} \tau^{(\alpha-\alpha_t)/\varphi_t} g\left(\frac{M_0}{\varepsilon^{\beta}} \tau^{(\beta-\beta_t)/\varphi_t}\right).$$
(46)

Applying analogous considerations to the critical region leads to a relationship

$$\frac{\pi}{kT}\varepsilon^{-\nu d}\tau^{(\nu-\nu_t)d/\varphi_t} = f\left(\frac{c\varepsilon^{1-\nu d}}{\tau^{(\nu_t-\nu)d/\varphi_t}}\right)$$
(47)

or, for d = 3,

$$\frac{\pi}{kT}\varepsilon^{-9/5}\tau^{3/5} = f(c\varepsilon^{-4/5}\tau^{3/5}).$$
(48)

In the coil overlap region the argument of f(x) should be assumed to be equal to 1 (see Equation 24) from which we get

$$c^* \sim \tau^{(\nu_t - \nu)d/\varphi_t} \varepsilon^{\nu d - 1}. \tag{49}$$

In the dilute solution region $\varepsilon \sim 1/N$ and

$$c^* \sim \tau^{-3/5} N^{-4/5}$$
 for $d = 3, \ \nu = 3/5.$ (50)

Further, in this region $f(x) \sim x$, then it follows from Equation 48, with allowance for $\varepsilon \sim 1/N$, that

$$\frac{\pi}{kT} \sim \frac{c}{N}.\tag{51}$$

For semidilute solutions, Equation 4.2–70 with the potential from Equation 46 and the condition that a function analogous to h(x) from Equation 36 proves to be constant, as well yield

$$\varepsilon \sim c^{1/(\nu d-1)} \tau^{(\nu-\nu_t)d/(\nu d-1)\varphi_t}.$$
(52)

In this concentration range, it also follows from Equation 47 that f(x) = const and, in view of Equation 52

$$\pi \sim c^{\nu d/(\nu d-1)} \tau^{\nu d(\nu-\nu_t)d/(\nu d-1)\varphi_1} \tau^{(\nu_t-\nu)d/\varphi_1} = c^{\nu d/(\nu d-1)} \tau^{(\nu-\nu_t)d/(\nu d-1)\varphi_t} \sim c^{9/4} \tau^{3/4}$$
(53)

for d = 3, $\nu = 3/5$.

The difference in powers ($c^{9/4}$ in Equation 53 and c^2 in the Flory-Hugging approximation, see Equations 3.1-66 and 1.2-27) is caused by consideration of the correlation effect of concentration fluctuations in Equation 53.

The scaling dependence of π (Equations 50 and 53) is followed by temperature-concentration dependences of other π -dependent quantities.

According to Equation 2.4-24, the Rayleigh ratio is

$$R_{k,\vartheta \to 0} \sim \mathbf{c} \frac{\partial \mathbf{c}}{\partial \pi},$$

and, in view of Equation 53, we get

$$R_{k,\vartheta\to 0} \approx \mathbf{c}^{-1/4} \tau^{-3/4} \tag{54}$$

for d = 3.

If solutions are subjected to mechanical stress with such frequency that the time of load action would be less than the coupling lifetime (Equation 3.3-100) $t < T_r$ then they are expected to exhibit the properties of gels with the shear modulus μ proportional to temperature and the bulk concentration of molecular chain couplings (contacts) (Equation 3.5-50). According to Daoud et al. (1975), the number of couplings in semidilute solutions $\sim \pi/kT$, and Equation 53 gives a dependence for the shear modulus in a thermodynamically good solvent:

$$\mu \sim T \mathbf{c}^{9/4},\tag{55}$$

and, in the tricritical region (see Equation 44),

$$\mu \sim T \mathbf{c}^3. \tag{56}$$

The general scaling expression (Equation 1.6 76) for the correlation length ξ in the vicinity of the tricritical point leads to

$$\xi(\varepsilon,\tau) \simeq \tau^{-\nu_t/\varphi_t} f\left(\frac{\varepsilon}{\tau^{1/\varphi_t}}\right).$$
(57)

At about the critical point, as usual (Equation 1.5-2),

 $\xi(\varepsilon,\tau) \approx \varepsilon^{-\nu} \xi(1,\tau)$

and, with due account of Equation 57,

$$\xi(\varepsilon,\tau) \approx \omega \varepsilon^{-\nu} \tau^{(\nu-\nu_t)/\varphi_t};\tag{58}$$

at about the tricritical point

$$\xi_t(\varepsilon,\tau) \approx \omega_t \varepsilon^{-\nu_t}.\tag{59}$$

In dilute solutions, where $\varepsilon \sim 1/N$,

 $\xi \sim c^{\nu/(1-\nu d)} \tau^{(\nu-\nu_t)/(1-\nu d)\varphi_t}$

$$\xi \sim N^{\nu} \tau^{(\nu-\nu_i)/\varphi_i} \tag{60}$$

holds for critical region I; for d = 3, $\nu = 3/5$

$$\xi \sim N^{3/5} \tau^{1/5};$$
 (61)

for tricritical region I'

$$\xi_t \sim N^{\nu_t} \sim N^{1/2} \tag{62}$$

for d = 3.

In semidilute solutions for critical region II, where ε obeys Equation 52, we can write

$$\xi \sim c^{-3/4} \tau^{-1/4}$$
 for $d = 3, \nu = 3/5,$ (63)

and for tricritical region III, where ε corresponds to Equation 37,

$$\xi_t \sim c^{\nu_t/(1-\nu_t d)},\tag{64}$$

and for d = 3

$$\xi_t \sim c^{-1}.\tag{65}$$

In dilute solutions, ξ corresponds to the molecular coil size (Equations 9 and 10), so Equation 80 yields

$$\overline{R^2} \sim N^{2\nu} \tau^{2(\nu-\nu_l)/\varphi_l},\tag{66}$$

and for $d = 3, \nu = 3/5$

$$\overline{R^2} \sim N^{6/5} \tau^{2/5} \tag{67}$$

in agreement with Flory's (Equations 3.1-115, 142) and Edwards' (Equation 3.1 216) relationships.

Having taken Equation 66 into consideration, we obtain for the coil overlap concentration

$$c^* \sim \frac{N}{R^d} \sim N^{1-\nu d} \tau^{d(\nu_l - \nu)/\varphi_l},\tag{68}$$

and for d = 3, $\nu = 3/5$

$$c^* \sim N^{-4/5} \tau^{-3/5} \tag{69}$$

(cf. Equations 49 and 50).

For the second virial coefficient A_2 which is proportional to the excluded volume divided by N^2 (see Equation 1.3-40), R^d/N^2 , it follows from Equation 66 that

$$\mathcal{A}_2 \sim N^{\nu d-2} \tau^{d(\nu-\nu_t)/\varphi_t} \tag{70}$$

and for $d = 3, \nu = 3/5$

$$\mathcal{A}_2 \sim N^{-1/5} \tau^{3/5}.$$
(71)

Table 4.1 shows the basic properties of the P+LMWL system in different regions of the state diagram. Besides the dependences discussed, the table gives relationships for $\overline{R^2}$ in regions II and III derived by Daoud et al. (1975) and Daoud and Jannink (1976).

The main feature of the magnetic polymer system glossary (Equations 4.2 66...69) is in the fact that it brings the size of the region of magnetization correlated fluctuations $\langle \vec{M}_0(0)\vec{M}_0(\vec{r}) \rangle$ near the critical temperature T_c (see Figures 4.2 and 4.3) into agreement with the molecular coil size R far from the critical temperature T_c of the P+LMWL system.

The essence is that both these quantities, so different in their physical nature, prove to be highly fluctuating, and just this is the deciding factor in the realization of the universality principle (section 2.5).

In this connection, the designation of regions I and II on the P+LMWL system state diagram (Figure 4.4), as critical and regions I' and III as tricritical, should not be taken in a literal sense: these denominations have been transferred from the language of magnetics where they play their real part. As to polymer systems, they denote regions of the state diagram where the characteristic quantities have different parameter dependences, and Table 4.1

Scaling dependences of the basic quantities characterizing the properties of the P+LMWL system for d = 3 in different regions of the state diagram - Figure 4.4 (Daoud and Jannink, 1976) [Reprinted with permission from: M.Daoud, G.Jannink, J. de Phys. 37 (1976) 973 979. Copyright © 1976 by EDP Sciences]

Region	R^2	Formula in text	$\frac{\pi}{kT}$	Formula in text	ξ2	Formula in text
l'	N	(62)	c/N	(42)	N	(62)
1	$N^{6/5} \tau^{2/5}$	(67)	c/N	(51)	$N^{6/5} \tau^{2/5}$	(61)
п	$Nc^{-1/4}\tau^{1/4}$		c ^{9/4} 73/4	(53)	$e^{-3/2}\tau^{-1/2}$	(63)
ш	N		و م	(44)	c^{-2}	(65)

these regions are separated by crossover lines that are not phase transition lines (as they are defined in section 1.5) but, however, are lines of the changes in the behaviour modes of the characteristic values.

The use of these terms (the critical and tricritical regions) is justified as the dependences elaborated for the true critical and tricritical regions and crossover lines are extended from magnetic and other systems to polymer ones (see section 1.6). This extension proved to be very useful within the framework of the universality principle, in particular, in drawing crossover lines in the single-phase region of the P+LMWL system. They are radically new properties of polymer solutions previously known neither in the Flory-Huggins mean field theory nor in the Edwards theory. As to the true critical phenomena in the P+LMWL system, they do, certainly, obey the universality principle but in a more natural way, without the help of a sophisticated glossary. In this case, the scaling approach leads to no unexpected results. Moreover, the first papers in this direction bave derived their chief results mainly from some heuristical and *a posteriori* considerations.

As an example, let us discuss the scaling relationships for the coil size and location of the phase transition region (a true first-order transition) on the lower half-plane of the state diagram where $\tau < 0$.

In the dilute solution region, there occurs globulization of coils (section 3.4). The homologous relation between the size R and N for globules is defined by the general relationship

$$R^2 \sim N^{2/3}$$
. (72)

On the other hand, the scaling dependence for $\xi \sim R$, valid near the tricritical point, is proposed (de Gennes, 1975; Daoud and Jannink, 1976) to be written as

$$\xi \sim R \sim N^{\nu_i} f(\tau N^{\nu_i}) \sim N^{1/2} (\tau N^{1/2})^r.$$
(73)

These two equations correlate well provided that x = -1/3. Thus, in region IV of the state diagram, the relationship

$$R \sim \left(\frac{N}{\tau}\right)^{1/3} \tag{74}$$

holds.

Further, assume that during a phase transition the morphology of the second, polymerenriched phase presents densely packed globules. The globule contact concentration, in view of Equation 74, is written as

$$c_{\star} \sim \frac{N}{R^3} \sim \tau. \tag{75}$$

Daoud and Jannink (1976) have admitted that the line of Equation 75 separates the tricritical region and the first-order phase transition region (cf. Figure 1.39). The morphology of the first, polymer-diluted phase is an ensemble of collapsed coils, for which Equation 74 is realized.

Further, suppose the bulk effects in tricritical region III, when $\tau < 0$, to cancel each other and, hence,

$$R \sim N^{1/2} \tag{76}$$

and does not depend on τ .

The critical point is the only one where conditions 74 and 76 should be simultaneously realized, i.e.

$$R \sim \left(\frac{N}{\tau_c}\right)^{1/3} \sim N^{1/2},\tag{77}$$

which leads to

$$\tau_c \sim N^{-1/2} \tag{78}$$

and to

$$c_c \sim N^{-1/2}$$
. (79)

The latter dependence is in agreement with the result of the Flory-Huggins theory (see Equation 3.1 241), and Equation 78 corresponds to Equation 3.1 245 up to 1/N.

So, the curve, bounding the phase separation region, has the line of Equation 75 and the ordinate axis (where $\tau < 0$) as its asymptotes and, hence, can be approximated by a hyperbola

$$\tau = -\alpha \left(c + \frac{1}{Nc} \right),\tag{80}$$

where α is a positive constant.

Equation 80 can be rewritten in the form:

$$-\frac{\tau N^{1/2}}{\alpha} = c N^{1/2} + (c N^{1/2})^{-1}$$
(81)

and in a more general scaling form:

$$\tau N^{1/2} = f(cN^{1/2}). \tag{82}$$

The utility of the latter notation is that the boundary of the phase separation region should obey the exponent dependence in accordance with the universality principle (Table 1.2) when Equation 81 does not show this dependence to an acceptable degree and, so, is a rather rough approximation.

The function f in Equation 82 can be obtained, in principle, from experimental data plotted

$$\tau N^{1/2}$$
 vs $f(cN^{1/2})$.

4.3.2. Experimental data

The neutron scattering technique has played a significant role in correlating scaling constructions in wide temperature and concentration ranges (Table 4.1). It enables one to evaluate the parameters of deuterated macromolecules which form a certain, suitable under the given experimental conditions, fraction of usual (protonated) macromolecules.¹ The total polymer concentration may vary in a wide range and is restricted mainly by purification capabilities and other preparative details.

Just as in the case of light scattering (see Equation 2.4-24), the following relationship (Daoud et al., 1975) is valid for neutron scattering

$$\lim_{q \to 0} S(q) \to T \mathbf{c} \frac{\partial \mathbf{c}}{\partial \pi} = T \mathbf{c} \chi_{\tau}, \tag{83}$$

where S(q) is the Fourier transform of the correlation function of concentration fluctuation (cf. Equation 2.1-83)

$$S(q) = \int \left\langle \delta \mathbf{c}(0) \delta \mathbf{c}(\vec{r}) \right\rangle e^{i\vec{q}\vec{r}} d\vec{r}.$$
(84)

Experiments (Benoit and Picot, 1966; Daoud et al., 1975) have shown that

$$\chi_{\tau}^{-1} \sim \mathbf{c}^{\mathbf{y}}, \quad \text{where} \quad y = 1.25 \pm 0.04,$$
(85)

in good agreement with Equation 53 (see also Table 4.1)

The concentration dependence of the coil size (Figure 3.6) corresponds to the scaling construction (Table 4.1) as well

$$\frac{R^2}{M_w} \sim c^{-0.25}.$$
 (86)

Cotton et al. (1976) estimated the radius of gyration of deuterated polystyrene macromolecules in their mixture with protonated polystyrene in cyclohexane (the overall polymer concentration 15 g/dl falls within region II) (Figure 4.5).

As one can see, the temperature dependence of macromolecular sizes obeys the scaling (Table 4.1)

$$\overline{R^2} \sim N c^{-1/4} \tau^{1/4}.$$
(87)

The bend (Figure 4.5) corresponds to the crossover between regions II and III (see Figure 4.4).

The situation with the screening length ξ is much more complex. In defining ξ according to the Debye-Edwards construction (Equation 3.1-238) from light scattering data (Cotton et al., 1972), $\xi\sqrt{\mathbf{c}} = const$ seemed to be valid in two polymer concentration ranges: $\xi \sim R$ in dilute solutions and $\xi \sim \beta$ in semidilute ones, as it follows from the Edwards theory (see Equation 3.1-234).

However, more systematic measurements of ξ in solutions by means of neutron scattering (Daoud et al., 1975) have shown that

$$\boldsymbol{\xi} \sim \mathbf{c}^{0.72},\tag{88}$$

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¹In some special cases (eg. for block-copolymers), this "contrast condition" is even not necessary. Editor's note



Figure 4.5. Double logarithmic curve R_w vs $\theta \tau$ for the system *D*-polystyrene+*H*polystyrene+cyclohexane. The overall polymer concentration is $c = 15 \cdot 10^{-2} \text{ g/cm}^3$. The horizontal line defines R_w in the θ conditions (Cotton et al., 1976) (Reprinted with permission from: J.P.Cotton, M.Nierlich, F.Bone, M.Daoud, B.Farnoux, G.Jannink, R.Dupplesix, C.Picot. J. Chem. Phys. 65 (1976) 1101-1108. Copyright © 1976 American Institute of Physics]

which is very close to the scaling construction (Equation 63).

Specifically, Edwards' results (Equations 3.1-234,-238) hold only within the mean field approximation. Moreover, his calculations assumed the segment density distribution function $g(\vec{r})$ as one of ideal chains in external potential over all the range of r (see Equations 3.1-218,-229) though in practice it is valid only at small distances $r < \xi$.

An appropriate correction (Daoud et al., 1975) has been introduced and led to the form factor

$$S(q) = const \ \frac{\xi^{-2}}{q^2 + \xi^{-2}},\tag{89}$$

i.e. to a Lorentzian with its halfwidth defined by the screening length ξ .

It is Equation 88 that has just resulted from the halfwidth of the Lorentzian (Equation 89) while determining ξ .

Figure 4.6 presents an experimental reduced-coordinates state diagram of Equation 82 for the system polystyrene+cyclohexane (Cotton et al., 1976), which is in excellent agreement with the theoretically predicted one (Figure 4.4).

Ito et al. (1984) measured osmotic pressure by means of a specially designed osmometer (Kuwahara et al., 1968) near the θ point for two systems: polystyrene+cyclohexane and polyisobutylene+benzene; the reduced value $\pi M/cRT$ was found to be a universal function of the c/c^* ratio, c^* being the crossover concentration (of overlapping coils). At high concentrations (0.25 < c, g/cm³ < 0.32) osmotic pressure is proportional to $c^{2.98}$ just as theory predicts (see Equation 44 and Table 4.1).

Stèpanek et al. (1984) applied light scattering to measure the reduced osmotic compressibility (see Equation 83) in the θ region and while going through the crossover (by temperature, $\mathbf{c} = const$) in polystyrene solutions in cyclohexane; they established that in the concentration range $2 \leq \mathbf{c}/\mathbf{c}_{\theta}^{*} < 11$ at $T = \theta$

$$\frac{M}{RT} \left(\frac{\partial \pi}{\partial \mathbf{c}} \right) = 2 \left(\frac{\mathbf{c}}{\mathbf{c}_{\theta}^*} \right)^{1.94} \tag{90}$$



Figure 4.6. State diagram of polystyrene+cyclohexane. The phase separation area is outlined using the data of Shultz and Flory (1952) for $M \cdot 10^{-3} = 43.6$ (1), 89 (2), 250 (3), and 1270 (4). The gyration radius of macromolecules (6) and the screening length (5) have been determined by means of neutron scattering (Cotton et al., 1976) [Reprinted with permission from: J.P.Cotton, M.Nierlich, F.Bone, M.Daoud, B.Farnoux, G.Jannink, R.Dupplesix, C.Picot. J. Chem. Phys. 65 (1976) 1101-1108. Copyright © 1976 American Institute of Physics]

holds (\mathbf{c}_{θ}^{*} is the coil-overlap concentration in the θ solvent – see Equation 43) and fits the theoretical dependence (Equation 44).

According to Equation 53, while passing through the crossover line c^{**} (or τ^{**} in connection with the ordinate axis) (see Figure 4.4)

$$\left(\frac{\partial \pi}{\partial \mathbf{c}}\right) \left/ \left(\frac{\partial \pi}{\partial \mathbf{c}}\right)_{\theta} \simeq \left(\frac{\tau}{\tau^{**}}\right)^{x}$$
(91)

is valid, where x = 0.691 if $\nu = 0.588$ (from calculations).

Within $10 < \tau/\tau^{**} < 33$ experiments have given the dependence

$$\left(\frac{\partial \pi}{\partial \mathbf{c}}\right) \left/ \left(\frac{\partial \pi}{\partial \mathbf{c}}\right)_{\theta} = 1.13 \left(\frac{\theta \tau}{w}\right)^{0.68 \pm 0.08},\tag{92}$$

for the polymer weight fraction $w = 2.57 \cdot 10^{-2}$, $M = 20.6 \cdot 10^{6}$ in good agreement with theory.

The same paper also concerns measurements of the screening length ξ using the scattered light intensity ratio at $\lambda_1 = 6328$ Å and $\lambda_2 = 4880$ Å (see Equation 89)

$$r = \frac{I_1}{I_2} = X \frac{1 + q_2^2 \xi}{1 + q_1^2 \xi},\tag{93}$$

where X = 0.299 was estimated by means of light scattering in benzene. The results obtained for three polymer concentrations w = 2.57, 3.28, 5.26 (wt %) obey the relationship

$$\xi w = (6.73 \pm 1.4) \cdot 10^{-8} \operatorname{cm} \cdot \mathrm{g/g},\tag{94}$$

and agree with the theoretical dependence (Equation 65).

Solutions of polystyrene and its deuterated homologues (deuterated polystyrene) in deuterated toluene have been studied in a wide concentration range using low-angle neutron scattering (King et al., 1985), and the results differ from the intuitive scaling predictions

$$\overline{R^2} \sim \mathbf{c}^{-0.156 \pm 0.012} \tag{95}$$

within 0.03 < c < 1 (cf. Table 4.1 $\overline{R^2} \sim c^{-0.25}$ and Equations 86 and 87) and

$$\xi \sim c^{-0.7} \tag{96}$$

(cf. Equation 63, Table 4.1, and Equation 88).

The authors believe that the intuitive scaling theory does not apply to polymers with low molecular weights (say, M < 110,000).

Huber et al. (1985b) put together the A_2 vs M dependences for polystyrene solutions in toluene at 20 and 25°C (Bantle et al., 1982; Huber et al., 1985a) and revealed that

$$\mathcal{A}_2 \sim M^{-t} \tag{97}$$

with the asymptotic value t = 0.2 for high molecular weights, which is in full agreement with the excluded volume model of the scaling type (Equations 70 and 71).

The lower the molecular weight, the higher t.

Now let us discuss the mechanical properties of semidilute solutions and gels in connection with scaling constructions (Candau et al., 1979, 1982). The elastic properties of semidilute solutions are controlled by two parameters: the screening length ξ corresponding to the mean distance between cross-links (see Subsection 3.1.1) and the cross-link lifetime T_r . Any solution exhibits its elasticity only over intervals shorter than T_r (see Section 3.5). Hence, semidilute solutions can not show mechanical elasticity since mechanical measurements require much more time than T_r . 540

On the other hand, light scattering measures the high-frequency system response characterized by the elastic shear modulus μ proportional to the cross-link number density (de Gennes, 1976a), i.e.

$$\mu \sim \xi^{-3}.\tag{98}$$

In view of Equations 63 65,

$$\mu \sim \mathbf{c}^{2.25} \tag{99}$$

in a good solvent and

$$\mu \sim \mathbf{c}^3 \tag{100}$$

in the θ solvent.

In the case of cross-linked gels having swelled in a good solvent up to equilibrium, T_r is, of course, infinitely long. Hence, both mechanical measurements of compression/tension and light scattering relate to times shorter than T_r . Munch et al. (1977) have shown that the distance between cross-links in gels ξ_l at the equilibrium concentration c_l in the good solvent also obeys its scaling expression

$$\xi_l \sim \mathbf{c}_l^{-0.75}$$
. (101)

So, both the mechanical μ_l and optical μ shear moduli in gels are related to each other and

$$\mu_l \approx \mu \sim \mathbf{c}_l^{2.25}.\tag{102}$$

Strictly speaking, axial compression and light scattering do not measure the same modulus. The kinetics of gel swelling/compression is a very slow process and upon mechanical gel deformation, the liquid does not shift with respect to the network. Axial compression, therefore, takes place under conditions of constant volume, and the Young modulus obeys Equation 3.5 58 $E = 3\mu_l$.

On the other hand, light scattering owes its origin to the longitudinal modulus (Equation 3.5-59) $M = K + 4\mu/3$, which involves changes in the network local concentration.

However, both the multifold compression modulus K and the shear modulus μ are proportional to the cross-link numerical density (de Gennes, 1976a) and scaling behaviour of both the mechanical μ_l and optical μ moduli with respect to polymer concentration must be the same. Indeed, an experiment with polystyrene-benzene networks (Candau et al., 1979) has shown the validity of Equation 102.

At the same time, for polyacrylamide gels in the poor θ solvent (water+methanol, 3:1 by volume)

$$\mu \sim c^{3.07 \pm 0.07} \tag{103}$$

was found (Geissler and Hecht, 1978), which fits Equation 100 excellently.

Thus, the experimental data obtained confirm, on the whole, the theoretical predictions arising from the analogy of magnetics in their critical state and the system P+LMWL through the glossary.

4.3.3. Further developments

An extended description of the macromolecule solution in terms of the magnetic analogy is given by Nikomarov and Obukhov (1981).

It should be noted that the same limiting dependences of characteristic values (see Table 4.1) in the form of scaling relationships are led to by scaling transforms of the expression for

- the partition function Z(L),
- the probability function $P(\vec{h}, L)$,
- the root mean square distance $\langle h^2 \rangle^{1/2}$,

etc. in the model of continuous Gaussian chains with excluded volume (see Equations 3.1– 173, 179, 3.1–201...205) (Kosmas and Freed, 1978). All the results of this theory are obtained without resorting to any analogy with critical phenomena in magnetics and any renormalization technique. Moreover, there is no need to assume the space dimensionality d to be a continuous variable and to get expressions as a series of (4 - d). The main expressions are deduced in more natural discrete space dimensionalities 2, 3, 4, and so on.

For the scattered light intensity, this analysis uses a dependence of the Equation 89 type. Turning to the Edwards-type continuous Gaussian chains will play a part in a further development of polymer theory.

Dayantis (1982) has made an interesting correlation of the above considered theories and approaches (mean field of Flory-Huggins, corresponding states, and scaling) in the phase separation region.

Solving Equation 3.1–239, with respect to v_{2sp} , leads to

$$v_{2sp}^2 + v_{2sp} \left(\frac{1}{2\chi_1} - \frac{1}{2\chi_1 z} - 1 \right) + \frac{1}{2\chi_1 z} = 0.$$
(104)

If we neglect the term 1/2z in Equation 3.1–245, we derive

$$\tau_c = \frac{T_c - \theta}{T_c} \approx -\frac{1}{\psi_1 z^{1/2}}.$$
(105)

The same neglection in Equation 3.1–242 yields

$$\chi_{1c} \approx \frac{1}{2} + \frac{1}{z^{1/2}}.$$
(106)

The two latter equations produce

$$\chi_{1c} = \frac{1}{2} - \tau_c \psi_1 \tag{107}$$

and

$$\chi_{1} = \frac{1}{2} - \tau \psi_{1}. \tag{108}$$

Substituting Equation 108 into Equation 104 gives

$$v_{2sp}^2 - v_{2sp} \frac{1 - 2\psi_1 \tau z}{z - 2\psi_1 \tau z} + \frac{1}{z - 2\psi_1 \tau z} = 0.$$
 (109)

 τ_c in Equation 105 can be assumed to be equal to τ and

$$|\tau\psi_1| \approx z^{-1/2} \tag{110}$$

ог

$$z\tau\psi_1 \approx z^{1/2}.\tag{111}$$

The approximation

$$1 \ll 2\psi_1 \tau z$$
 and $z \gg z^{1/2}$, i.e. $z \gg 2\psi_1 \tau z$, (112)

allows one to simplify Equation 109:

$$v_{2sp}^2 + 2\psi_1 \tau v_{2sp} + \frac{1}{z} = 0, \quad \tau < 0$$
⁽¹¹³⁾

and to convert it into an equation of hyperbola with its axes: the ordinate axis $v_{2sp} = 0$ and the straight line

$$v_{2sp} + 2\psi_1 \tau = 0. \tag{114}$$

If one inserts new variables from the intuitive scaling approach (Equation 82) into Equation 113

$$\Phi' = v_{2sv} z^{1/2}$$
 and $\tau' = \tau z^{1/2}$, (115)

one gets the expression

$$\Phi'^2 + 2\psi_1 \tau' \Phi' + 1 = 0, \qquad \tau' < 0 \tag{116}$$

which is the spinodal equation along the lines of the corresponding state equations. It coincides with the equation predicted by the scaling concept (Equation 81) provided that α is presumed to be

$$\alpha = (2\psi_1)^{-1} \tag{117}$$

and Equation 81 is considered as a spinodal, not binodal as in Daoud and Jannink's (1976) equation.

Equation 81 with Equation 117 for spinodal (!) has a universal meaning for all systems P+LMWL, i.e. satisfies the basic principle of corresponding states. The binodal curve, though not approximated rigorously by hyperbola (in general, by any second-order curve) even when $N \to \infty$, nevertheless, also reduces to a universal curve for all systems P+LMWL in the coordinates

$$\left(\chi_1 - \frac{1}{2}\right) N^{-1/2} vs c N^{1/2}$$
 (118)

in accordance with the principle of corresponding states.

Figure 4.7 sketches the binodal and spinodal positions satisfying the requirements of the Flory-Huggins mean field theory, scaling constructions, and the principle of corresponding states.



T, ⁰C



Figure 4.7. Binodal (7) and spinodal (6) locations as $(\chi, -$ 1/2) vs v₂ and the characteristic curves: the limiting slope of the binodal envelope (1), the spinodal asymptotics (2), the median of the binodal $(v_{2II} + v_{2I})/2$ (3), the locus of critical points (4), the spinodal axis (5), C denotes the critical point (Dayantis, 1982) [Reprinted with permission from Macromolecules 45 (1982) 1107 -1110. Copyright @ 1982 American Chemical Society]

Figure 4.8. Phase separation (binodals) areas in the polystyrene+methylcyclohexane system with the molecular weight of polymer: $M_w \cdot 10^{-4} = 1.02 \ (1), \ 1.61 \ (2), \ 2.02 \ (3),$ 3.49 (4), 4.64 (5), 10.9 (6), 18.1 (7), 71.9 (8) (Dobashi et al., 1980b) [Reprinted with permission from: T.Dobashi, M.Nakata, M.Kaneko. J. Chem. Phys. 72 (1980) 6692-6697. Copyright © 1980 American Institute of Physics]

Careful experimental measurements of the binodal curves in the system polystyrene+methylcyclohexane by Dobashi et al. (1980ab) were of great importance for a further development of the theory of phase separation in polymer systems. The investigators strove for the complete equilibrium of two liquid phases in each experiment and then determined

the polymer concentration by means of refractometry (Figure 4.8).

The data obtained were processed using the Flory-Huggins theory (state equation 3.6-1, the interaction parameter from Equation 3.6-37) in the fashion of Koningsveld's constructions (see subsection 3.6.1).

In this case, the conditions of spinodal and the critical state lead to the following relationships at the critical point (Gordon et al., 1969; Koningsveld and Kleintjens, 1971)

$$\alpha + \frac{\beta_0(1-\gamma)}{(1-\gamma\varphi_c)^3} = \frac{1}{2} \left[(\varphi_c p_w)^{-1} + (1-\varphi_c)^{-1} \right] \equiv X,$$
(119)

$$\frac{\beta_0 \gamma (1-\gamma)}{(1-\gamma \varphi_c)^4} = \frac{1}{6} \left[(1-\varphi_c)^{-2} + \frac{p_z}{p_w^2 \varphi_c^2} \right] \equiv Y$$
(120)

(see Equation 3.6-24). Equations 119 and 120 yield

$$X + \varphi_c Y = \alpha + \frac{Y}{\gamma}.$$
(121)



Figure 4.9. Plot according to Equation 4.3-121 for the polystyrene + methylcyclohexane system using the data of Figure 4.8 (Dobashi et al., 1980b) [Reprinted with permission from: T.Dobashi, M.Nakata, M.Kaneko. J. Chem. Phys. 72 (1980) 6692-6697. Copyright © 1980 American Institute of Physics]

Figure 4.9 shows data according to Equation 121 and some experimental results (see Figure 4.8). $\alpha = -0.1091$ and $\gamma = 0.2481$ were determined. Then β_0 was calculated using Equation 120 for each critical temperature.

The obtained dependence $\beta_0 \text{ us } 1/T$ (Figure 4.10) was approximated by

$$\beta_0 = \beta_{00} + \frac{\beta_{01}}{T} + \beta_{02}T \tag{122}$$

(cf. Equation 3.6-10 and 3.6-37), which leads to a state diagram with two phase separation regions (with UCST and LCST — see Equation 3.6-85 and Figure 3.81).

The least squares method applied to Equation 122 has given $\beta_{00} = 0.5832$, $\beta_{01} = 278.6$, and $\beta_{02} = 1.695 \cdot 10^{-3}$.



Figure 4.10. Temperature dependence of the parameter β_0 from the relationship for the interaction parameter of the Equation (3.6-37) type for the polystyrene+methylcyclohexane system (Dobashi et al., 1980b) [Reprinted with permission from: T.Dobashi, M.Nakata, M.Kaneko. J. Chem. Phys. 72 (1980) 6692-6697. Copyright © 1980 American Institute of Physics]

Therefore, the interaction parameter is expressed as

$$g = -0.1091 + \frac{-0.5832 + 278.6/T + 1.695 \cdot 10^{-3}T}{1 - 0.2481\varphi}$$
(123)

(cf. Equation 3.6-37).

The θ temperatures (T_c at $p \to \infty$) follow from Equations 123 and 3.6-1: $\theta_{\text{UCST}} = 343.4$ and $\theta_{\text{LCST}} = 479$ K, which agree with independent experimental data from the literature. Of great interest is the fact that the existence of θ_{LCST} and the determination of its

value proved to be possible on critical evidence for the UCST.

The general expression for the Gibbs potential as a Taylor series (Equation 3.1-275) and the phase separation conditions (Equation 3.1-276) enable the phase separation region amplitude to be calculated (Dobashi et al., 1980ab)

$$\varphi_{II} - \varphi_I = \left(-12 \frac{G_{12}}{G_{04}}\right)^{1/2} (T_c - T)^{1/2} \tag{124}$$

and its diameter

$$\frac{\varphi_{II} + \varphi_I}{2} - \varphi_c = \left(\frac{G_{13}}{G_{04}} - \frac{3G_{05}G_{12}}{5G_{04}^2}\right)(T_c - T),\tag{125}$$

where

$$G_{12} = \left(\frac{\partial^3 G}{\partial T \partial \varphi^2}\right)_c; \quad G_{13} = \left(\frac{\partial^4 G}{\partial T \partial \varphi^3}\right)_c; \quad G_{04} = \left(\frac{\partial^4 G}{\partial \varphi^4}\right)_c; \quad G_{05} = \left(\frac{\partial^5 G}{\partial \varphi^5}\right)_c.$$

These derivatives are calculated from Equation 3.6-1 and depend on the molecular chain length.

On the other hand, near the critical point both the amplitude and diameter of the phase separation region are expressed by simple scaling relationships

$$\varphi_{II} - \varphi_I = B(-\varepsilon)^\beta \tag{126}$$

and

$$(\varphi_{II} + \varphi_I) - 2\varphi_c = A(-\varepsilon)^{\mu}.$$
(127)

For the system polystyrene+methylcyclohexane (Dobashi et al., 1980ab), the indices β and μ do not depend on molecular weight and have the values $\beta = 0.332 \pm 0.001$ and $\mu = 0.858 \pm 0.005$, that differ from $\beta = 1/2$ (Equation 124) and $\mu = 1$ (Equation 125) as the mean field approximation predicts.



Figure 4.11. Comparison of the coefficients A and B from Equations 4.3–126,-127 with the theoretical coefficients (the mean field approximation, Equations 4.3–124,-125 — dashed lines) for the polystyrene+methylcyclohexane system (Dobashi et al., 1980b) [Reprinted with permission from: T.Dobashi, M.Nakata, M.Kaneko, J. Chem. Phys. 72 (1980) 6692-6697. Copyright © 1980 American Institute of Physics]

Figure 4.11 compares the coefficients B (Equation 126) and A (Equation 127) with those calculated employing the mean field approximation (Equations 124, 125, and 3.6-1). The experimental values of B differ noticeably from the theoretical ones for high molecular weights.

A correlation of the full phase separation region and the theoretical binodals calculated numerically by

$$\mu_{0I} = \mu_{0II}, \quad \mu_{1I} = \mu_{1II} \tag{128}$$

and state equations 3.6-1 for two polystyrene samples are presented in Figure 4.12. The low-molecular sample shows the largest distinctions. For the higher-molecular-weight sample, the agreement between theory and experiment is quite satisfactory in general, but near the critical point, of course, a difference in the phase separation region amplitude manifests itself, which is associated with the difference in the amplitude exponent index β . It was found by Shultz and Flory (1952) and interpreted by Koningsveld et al. as a manifestation of polymolecularity (see subsection 3.6.1).

Close β values have been obtained for some low-molecular weight systems as well: methanol + cyclohexane $\beta = 0.326 \pm 0.003$ at $|\varepsilon| < 0.06$ (Jacobs et al., 1977); aniline+cyclohexane $\beta = 0.328 \pm 0.007$ at $|\varepsilon| < 0.03$ (Balzarini, 1974); isobutyric acid+water $\beta = 0.328 \pm 0.004$ at $|\varepsilon| < 0.06$ (Greer, 1976). These values are in good agreement with β calculated for the Ising model by means of the renormalization group method (Wilson and Kogut, 1974; Baker et al., 1976; Golner and Riedel, 1976; Ma shang-keng, 1976; le Guillou and Zimm-Justin, 1977).



Figure 4.12. Comparison of the experimental and calculated Flory-Huggins (by the theory) the binodals (dashed lines) for polystyrene+methylcyclohexane system for samples with $M_w = 1.61 \cdot 10^4$ (1) and $M_w = 7.99 \cdot 10^5$ (2) (Dobashi et al., 1980b) [Reprinted with permission from: T.Dobashi, M.Nakata, M.Kaneko. J. Chem. Phys. 72 (1980) 6692-6697. Copyright © 1980 American Institute of Physics]

So, both low- and high-molecular weight binary systems belong to the same universality class with respect to phase separation (see Table 2.5).

Asymmetry is a characteristic feature of the binodals (Figure 4.8), which is inconsistent with the principles of universality and corresponding states. However, Sanchez (1985) has established that the data of Figure 4.8 and also from (Dobashi et al., 1980ab) allow one to choose such a parameter of order ψ which provides

$$|\psi - \psi_c| = \psi_0 \left[(-\varepsilon) N^b \right]^{\beta} \tag{129}$$

with a universal β value and a universal symmetrical binodal (Figure 4.13).



Figure 4.13. Universal binodal (Equation 4.3-129) and the data of Dobashi et al. (1980ab) [Reprinted with permission from: T.Dobashi, M.Nakata, M.Kaneko. J. Chem. Phys. 72 (1980) 6692-6697. Copyright © 1980 American Institute of Physics] (Figure 4.8) (Sanchez, 1985) [Reprinted with permission from: I.Sanchez, J. Appl. Phys. 58 (1985) 2871–2874. Copyright © 1985 American Institute of Physics] As a new order parameter, Sanchez proposed

$$\psi = \frac{\varphi}{\varphi + R_c(1 - \varphi)},\tag{130}$$

where R_c is a constant with a vague physical meaning.

Using 10 experimental binodals of the system polystyrene+methylcyclohexane (Dobashi et al., 1980ab) Sanchez has fitted: $\psi_0 = 0.564 \pm 0.004$, $\psi_c = 0.307 \pm 0.001$, $b = 0.313 \pm 0.004$, and $\beta = 0.327 \pm 0.002$. His calculations involved 14 adjustable parameters (10 values of R_c , ψ_0 , ψ_c , b, and β) and 166 experimental binodal points.

The value $\beta = 0.327 \pm 0.002$ is in excellent agreement with the latest calculations using the Ising lattice and the renormalization group method $\beta = 0.3265 \pm 0.0011$ (le Guillou and Zinn-Justin, 1980; Albert, 1982).

If Equation 130 is expanded into a Taylor series near $\varphi = \varphi_c$

$$\psi = \psi_c \left[1 + \frac{R_c \psi_c}{\varphi_c} \left(\frac{\varphi}{\varphi_c} - 1 \right) + \cdots \right], \tag{131}$$

then, for $|\varepsilon| \to 0$ and large N,

$$\psi_{II} - \psi_I \sim \frac{\varphi_{II} - \varphi_I}{\varphi_c} \tag{132}$$

and, in the mean field approximation (see Equation 3.1-288)

$$\psi_{II} - \psi_I \sim \frac{\varphi_{II} - \varphi_I}{\varphi_c} \sim N^{1/4} (-\varepsilon)^{1/2}.$$
(133)

Thus, the index $b\beta = 0.102 \pm 0.002$ obtained in accordance with Equation 129 is much lower than that of the mean field approximation.

For the binodal amplitude index Dobashi et al. (1980ab) give

$$\varphi_{II} - \varphi_I \sim N^{-0.23},$$
 (134)

and Shinozaki et al. (1982a) give for the same system polystyrene+methylcyclohexane

$$\varphi_{II} - \varphi_I \sim N^{-0.34}. \tag{135}$$

Moreover, as reported by Dobashi et al. (1980ab)

$$\varphi_c \sim N^{-0.39} \tag{136}$$

and by Shinozaki et al. (1982a)

$$\varphi_c \sim N^{-0.40\pm0.02}.\tag{137}$$

Sanchez' paper demonstrated the importance of a proper choice of order parameter when experimental values are compared with modern theories.

Critical indices are thought, as a rule, as indices in the power dependences of temperature ε . In the case of polymer systems, of special interest is the power dependence of the factor $|\varepsilon|^x$ on N (Shinozaki and Nose, 1981):

$$\xi = \xi_0 |\varepsilon|^{-\nu} \sim N^n |\varepsilon|^{-\nu} \quad (\varepsilon \gtrless 0), \tag{138}$$

$$\chi = \chi_{o} |\varepsilon|^{-\gamma} \sim N^{g} |\varepsilon|^{-\gamma} \quad (\varepsilon \gtrless 0), \tag{139}$$

$$c = c_0 |\varepsilon|^{-\alpha} \sim N^c |\varepsilon|^{-\alpha} \quad (\varepsilon \gtrless 0), \tag{140}$$

$$\Delta \varphi = \varphi_{II} - \varphi_I = B[\varepsilon]^\beta \sim N^b[\varepsilon]^\beta \quad (\varepsilon < 0),$$
(141)

$$\sigma = \sigma_0 |\varepsilon|^{(d-1)\nu} \sim N^m |\varepsilon|^{(d-1)\nu} \quad (\varepsilon < 0), \tag{142}$$

$$\pi = D(\Delta \varphi)^{\delta} \sim N^{j} (\Delta \varphi)^{\delta} \quad (\varepsilon = 0),$$
(143)

$$\chi(k) = \hat{D}k^{\eta-2} \sim N^k k^{\eta-2} \quad (\varepsilon = 0, \ \pi = 0).$$
(144)

The indices at N also have the meaning of critical ones (Shinozaki and Nose, 1981) and are related to each other by relationships with only two independent indices (cf. section 1.5, Equations 8–10 with section 2.5, Equation 30).

This question is under intense investigation (Shinozaki and Nose, 1981; Shinozaki et al., 1982b).

Shinozaki et al. (1982b) employed sophisticated equipment for measuring the critical indices ν and γ in the system polystyrene+methylcyclohexane by means of light scattering:

$$\frac{R_{\vartheta=0}}{T} \sim \left(\frac{T-T_c}{T_c}\right)^{-\gamma},\tag{145}$$

$$\chi = \frac{1}{\varphi_c} \cdot \frac{\partial \varphi}{\partial \pi} = \frac{R_{\vartheta=0} \lambda^4}{2\pi^2 n_1^2 (\partial n/\partial \varphi)^2 \varphi_c^2 kT}$$
(146)

(cf. Equations 2.4–21...23 at $\vartheta = 0$),

$$\chi = \chi_0 \left(\frac{T - T_c}{T_c}\right)^{-\gamma}.$$
(147)

The correlation length ξ was measured with the aid of Ornstein-Zernike-Debye's plots (cf. Equation 89)

$$\frac{R_{\vartheta=0}}{R_{\vartheta}} = 1 + q^2 \xi^2. \tag{148}$$

The critical index ν was evaluated using the least squares method for the straight line $\ln \xi \ vs \ \ln(\Delta T/T_c)$.

The values of γ obtained in solutions with different (within the range 9000 < M_w < $1.26 \cdot 10^6$) polymer fractions group together around the universal value 1.24 derived by means of the renormalization group method (le Guillou and Zinn-Justin, 1977) as well as obtained in experiments (Kuwahara et al., 1975). The values of ν are also near the universal value $\nu = 0.63$ (le Guillou and Zinn-Justin, 1977).

The exponent in the dependence of ξ_0 (Equation 138) and χ_0 (Equation 139) on N was evaluated at $\ln(\Delta T/T_c) = -5.0$:

$$\xi_{\rm o} \sim N^{0.28 \pm 0.03} \tag{149}$$
and

$$\chi_{0} \sim N^{0.48 \pm 0.03}.$$
 (150)

The value $n = 0.28 \pm 0.03$ is in good agreement with de Gennes' predictions (intuitive scaling in the mean field approximation — see section 4.4) and the data by Vrij and van den Esker (see subsection 3.3.1).

Table 4.2 gives the experimental values of the N indices from (Shinozaki et al., 1982b) in comparison with the predictions of the mean field theory.

Table 4.2

Exponents N in the amplitude factor of the characteristic values (Equations 138-143) (Shinozaki et al., 1982b) [Reprinted with permission from: K.Shinozaki, T.Hamada, T.Nose. J. Chem. Phys. 77 (1982) 4734–4738. Copyright © 1982 American Institute of Physics]

Amplitude factor	Exponent	Experiment		Mean field theory
ξ	n	0.28 ± 0.03	0.285^{a}	0.25
X _o	g	0.48 ± 0.03		0.5
B	ь	-0.34 ± 0.03	-0.23^{b}	-0.25
σ_0	m	-0.44 ± 0.03		-0.25
φ_c	\boldsymbol{x}	-0.40 ± 0.02	-0.39^{h}	-0.5

^a (Chu, 1969); ^b (Dobashi et al., 1980ab)

The differences are apparently caused by the fact that the order parameter fluctuation correlation is not taken into account.

Stepanow (1987) modified the Flory-Huggins state equation in an interesting way, having gotten from it a Hamiltonian of the Landau-Ginzburg-Wilson (LGW) type, with these correlations allowed for automatically.

If we choose

$$\Phi = \frac{\varphi_{spll} - \varphi_{spl}}{2} = \varphi_{spll} - \varphi_c \tag{151}$$

as a fluctuating order parameter, the spinodal equation in the Flory-Huggins approximation can be put as

$$\frac{\partial^2 G}{\partial \Phi^2} = 2(\chi_{1\epsilon} - \chi_1) + N^{1/2} \Phi^2 = 0$$
(152)

(see Equations 3.1-239, -258, -269, -270 and the assumptions accepted there).

Here we assume $z \sim N$, where N is a quantity proportional to the polymerization degree, molecular weight, etc. as accepted in the scaling theories.

If we integrate Equation 152 twice with respect to the fluctuating parameter Φ , we get a Hamiltonian in the fashion of the Landau phenomenological theory (section 2.5)

$$G \sim \mathcal{H}_L = (\chi_{1c} - \chi_1) \Phi^2 + \frac{1}{12} N^{1/2} \Phi^4 + \cdots$$
 (153)

To convert \mathcal{H}_l into the LGW Hamiltonian, a gradient term

$$\frac{A^2}{36\Phi(1-\Phi)}(\nabla_r\Phi)^2\tag{154}$$

should be added (see Equations 2.5-1 and 3.7-36).

Then we replace Φ in the denominator by φ_c and assume $(1 - \varphi_c) \approx 1$; the LGW Hamiltonian

$$\mathcal{H} = \frac{A^2}{36\varphi_c} (\nabla_r \Phi)^2 + (\chi_{1c} - \chi_1) \Phi^2 + \frac{2}{4!} N^{1/2} \Phi^4$$
(155)

emerges.

The replacements

$$M = \frac{\Phi}{\varphi_c^{3/2} N^{1/4}},$$
(156)

$$x = \frac{r N^{1/2} \varphi_c^2 \sqrt{18}}{A} \tag{157}$$

transform Equation 155 into the standard Hamiltonian of field theory (see Equations 2.6 11,-129, 4.1 1)

$$\mathcal{H}_{x} = \mathcal{H}N^{3/2}\varphi_{c}^{6} = \frac{1}{2}(\nabla_{x}M)^{2} + \frac{\mu^{2}}{2}M^{2} + \frac{u_{0}}{4!}M^{4}$$
(158)

with the free mass (Equation 2.6-26)

$$\mu^{2} = \frac{2(\chi_{1c} - \chi_{1})}{N\varphi_{c}^{3}}$$
(159)

and the interaction constant

$$u_0 = 2.$$
 (160)

The correlation length ξ_r related to \mathcal{H}_r (Equation 158) has the scaling expression (see Equations 2.6-39 and 4.3-12)

$$\xi_x \sim \mu^{-\nu}.\tag{161}$$

The correlation lengths ξ_x and ξ_r of systems with the Hamiltonians 158 and 155, respectively, are related to each other by (Stepanow, 1987)

$$\frac{x}{\xi_x} = \frac{r}{\xi_r},\tag{162}$$

from which

$$\xi_r \sim (\chi_{1e} - \chi_1)^{-\nu} N^{\nu - 1/2} \varphi_c^{3\nu - 2}. \tag{163}$$

In the mean field approximation $\nu = 1/2$ and $\varphi_c \sim N^{-1/2}$, and Equation 163 reduces to

$$\xi_r \sim (\chi_{1c} - \chi_1)^{-1/2} N^{1/4}, \tag{164}$$

which agrees with de Gennes' result (see Equation 3.7-31).

The phase separation region corresponding to the Hamiltonian 158 varies in accordance with the scaling rule (Brezin et al., 1973ab)

$$M \sim (-\mu)^{\beta},\tag{165}$$

where $\beta = 0.327$. Equations 151, 156, 159, and 165 give

$$\varphi_{II} - \varphi_c \sim \varphi_{spII} - \varphi_c = \Phi \sim (\chi_1 - \chi_{1c})^{\beta} N^{-\beta + 1/4} \varphi_c^{-3\beta + 3/2}.$$
 (166)

Using the common approximation (Equation 3.1-283)

$$2\chi_1 = \frac{\theta}{T},\tag{167}$$

we replace $\Delta \chi_{c}$ in Equation 166 by ϵ . If the mean field law $\varphi_{c} \sim N^{-1/2}$ holds for φ_{c} , then

$$\varphi_{II} - \varphi_c \sim (-\varepsilon)^{\beta} N^{\beta/2 - 1/2}. \tag{168}$$

If the experimental value (Equation 136) is accepted for scaling φ_c , Equation 166 is followed by

$$\Delta \varphi \sim (-\varepsilon)^{\beta} N^{-0.28} \tag{169}$$

in quite good agreement with experiment (see Equations 134, 135) or

$$\frac{\Delta\varphi}{\varphi_c} \sim (-\varepsilon)^{\beta} N^{0.1} \tag{170}$$

in agreement with the scaling of Sanchez' universal binodal (Equation 129)

$$b\beta = 0.327 \cdot 0.313 \approx 0.102. \tag{171}$$

The scaling law (Equation 170) is valid in the limit $\mu \rightarrow 0$. From the definition of μ (Equation 159) it follows that μ decreases with increasing N at any fixed temperature ε . This means that the region of the realization of scaling (Equation 169) increases with molecular weight. This prediction agrees with Dobashi et al.'s results (1980ab).

The critical region reducing is caused by the dependence of the Hamiltonian gradient term on molecular weight (via φ_c).

Thus, away from the critical point, the experimental data on phase separation satisfy the universal approach of Flory-Huggins' mean field, the principles of corresponding states, and scaling.

Near the critical point, the concentration fluctuation correlations contribute significantly to the system state.

4.4. Critical opalescence

The intensity of light scattered on concentration fluctuations in the critical region is expressed as (see Equation 2.4-24)

$$I(q) = const \, \frac{cT \left(\frac{\partial c}{\partial \pi}\right)_T}{1 + q^2 \xi^2}.$$
(1)

Let us write scaling expressions for $\partial \pi / \partial c$ and ξ .

For low-molecular-weight mixtures, the law of corresponding states is written as

$$\frac{\partial \pi}{\partial \nu} = kT \cdot f(\varepsilon/T, \nu/\nu_c), \tag{2}$$

 ν being the numerical concentration of molecules.

For macromolecules, $\nu = c/N$; T_c is close to θ . The size of macromolecules in the critical region is comparable with their unperturbed sizes (see paragraph 3.3.1.2):

$$\begin{split} R_{\theta} &\approx \left(\frac{N}{6}\right)^{1/2} A; \\ \sigma &\to R_{\theta}; \\ \nu_c &\to R_{\theta}^{-3}; \end{split}$$

 σ being the attractive force range with the potential pit ε (cf. Figure 1.40).

$$c_c \to \frac{N}{R_{\theta}^3} \sim \frac{N}{N^{3/2} A^3} \to N^{-1/2} A^{-3}.$$
 (3)

Segment-segment interactions are described by the excluded volume $\beta(T) \sim A^3(T - \theta)/\theta$.

The effective interaction of a coil segment in the point \vec{r} with another coil with the segment distribution density $c_2(\vec{r})$ is $\beta kT c_2(\vec{r})$ (cf. Equation 3.1-232).

The interaction between two coils ε is of the order

$$\varepsilon' = \varepsilon k \approx N\beta kT c_2 \sim N\beta kT c_c \sim N^{1/2} kT\beta/A^3.$$
⁽⁴⁾

Then

$$\frac{\varepsilon'}{kT} \simeq \varepsilon/T \to x = N^{1/2} \beta/A^3.$$
(5)

In polymer systems, some complication appears, related to the fact that under the critical conditions, in the expansion of π in terms of $c \sim c_c \sim N^{-1/2}$, the third virial coefficient $\mathcal{A}_3(T)$ is significant, since $\beta c_c \sim \mathcal{A}_3 c_c^2 \sim N^{-1}$ (see Equation 3.1-313). This circumstance causes introduction of the second dimensionless parameter $y = \mathcal{A}_3(T)A^{-6}$. Admittedly, the temperature dependence of \mathcal{A}_3 is very weak in the critical region. So,

50,

$$\frac{\partial \pi}{\partial c} = \frac{kT}{N} f\left(x, \frac{c}{c_c}, y\right) = \frac{k\theta}{N} f\left(x, \frac{c}{c_c}, y\right) \tag{6}$$

(cf. Equation 4.3-24). At the critical point $T = T_c$, $c = c_c$, and $x = x_c(y)$. At a temperature a bit higher than T_c $(c = c_c; T = T_c + \Delta T)$:

$$\left(\frac{\partial \pi}{\partial c}\right)_T = \left(\frac{\partial \pi}{\partial c}\right)_{T_c} + \frac{k\theta}{N}\left[f(x,1,y) - f(x_c,1,y)\right] = 0 + \frac{k\theta}{N}\lambda(y)(x-x_c)^{\gamma}.$$
(7)

The common power dependence is accepted for the fluctuation correlation length ξ :

$$\xi = \sigma (x - x_c)^{-\nu}.$$
(8)

Substitution of Equations 7 and 8 into Equation 1 in view of Equations 3 and 5 leads to

$$I^{-1}(q) = \Phi(y) \left(\frac{T - T_c}{T_c}\right)^{\gamma} N^{(\gamma - 1)/2} + \psi(y) \left(\frac{T - T_c}{T_c}\right)^{\gamma - 2\nu} N^{1 - \nu} A^2 q^2.$$
(9)

Having assumed for γ and ν their values as the mean field theory gives: $\gamma = 1$ (Equation 1.5-17) and $\nu = 1/2$ (Equations 2.5-14, 3.7-94) (see Figure 2.44), we have

$$I^{-1}(q) = \Phi(y) \left(\frac{T - T_c}{T_c}\right) + \psi(y) N^{1/2} A^2 q^2.$$
⁽¹⁰⁾

If this equation is compared with Debye's form of Equation 3.3-22:

$$I^{-1}(q) = const \left(\frac{T - T_c}{T_c} + \frac{l^2}{6} q^2 \right),$$
(11)

then

1

$$N^2 \sim N^{1/2}$$
. (12)

In subsection 3.3.1 were discussed experiments in the region of critical opalescence (polymer solutions), their results are rather inconsistent, but some of them (including Debye's et al., 1960b) corroborates Equation 12.

In the same way, employing the principle of corresponding states and scaling plots, de Gennes has obtained Equations 11 and 12 in the mean field approximation. The equations differed essentially from Debye's results (section 3.3.1.2). Debye took a different approach within the framework of the mean field approximation (see the end of section 4.3, Equations 4.3–148 and further).

4.5. Dynamic scaling

The profile of concentration fluctuations of any complexity can be presented as a superposition of sinusoidal waves (the Fourier transform), so we write the local value of concentration for one q-component of the Fourier transform only:

$$c(\vec{r}) = c + \delta c_{\vec{q}}(\vec{r}, t) = c + \delta c_{\vec{q}}(t) e^{iqz},\tag{1}$$

where the axis z is chosen as the direction of perturbation propagation (cf. Equation 3.5–12). The perturbation amplitude $\delta c_{\bar{q}}(t)$ decreases exponentially (cf. Equations 2.3 48, 2.4–51):

$$\delta c_{\vec{q}}(t) = \delta c_{\vec{q}}(0) e^{-t/\tau_{\vec{q}}},\tag{2}$$

where $\tau_{\vec{q}}$ is the relaxation time; so $\tau_{\vec{q}}^{-1}$ is the perturbation relaxation rate.

In the following subsection let us consider those motion modes for which

$$\tau_{\vec{q}} < T_r \tag{3}$$

is satisfied, where T_r is the relaxation time for the complete change of chain conformation (the relaxation time for complete disentanglement of one chain)¹.

¹Evaluation of T_r will be performed later

4.5.1. Motion modes

The properties of a molecular chain concerning its thermal mobility essentially depend on polymer concentration and wave vector of probing radiation q, since the perturbation front wavelength A is related to the wave vector immediately (see Equation 2.3-18):

$$\Lambda = \frac{2\pi}{q}.\tag{4}$$

In other words, radiation with the wave vector q "sees" concentration perturbations with the wavelength Λ only.

If the scale of each molecular chain or of their set is characterized (in the general case) by the screening length ξ , then different regions on the q vs $1/\xi$ diagram (de Gennes, 1976a) correspond to essentially different motion modes of molecular chains or of their fragments (see Figure 4.14).



Figure 4.14. Types of modes in the polymer solution. q is the wave vector, R the gyration radius of a coil. A denotes the macroscopic limit $qR \ll 1$. B denotes the multi-chain region: pseudogel solution behaviour $q\xi < 1$. C denotes the intramolecular modes $q\xi \ll 1$ (dc Gennes, 1976a) [Reprinted with permission from Macromolecules 9 (1976) 587. Copyright © 1976 American Chemical Society]

The regions A and B reflect the mobility of molecular chains taken as a whole (the collective mode) when

$$q\xi < 1, \tag{5}$$

the region C where

$$q\xi > 1 \tag{6}$$

provides every condition for observation of intramolecular modes of chain motion.

In the region of long-wave fluctuations (A) where

$$qR < 1$$
 and $R < \Lambda$ (7)

hold, on the frequencies ω small enough but higher than $1/T_r$:

$$\omega > \frac{1}{T_r},\tag{8}$$

the polymer solution behaves as a gel and should be characterized by the longitudinal modulus M and the friction coefficient f caused by solvent flow through the polymer network (see subsection 3.5.4).

In accordance with Equations 3.5-50,-59, the modulus M is proportional to the numerical concentration of molecular chain cross-links (contacts), the distance between which is of the order of the screening length ξ (see subsection 3.1.1, Figure 3.7). Hence, the number of cross-links per unit volume is $\sim \xi^{-3}$, and

$$M \simeq \frac{kT}{\xi^3}.\tag{9}$$

In view of Equation 4.3 63,

$$M \sim c^{9/4}$$
. (10)

Using the equation of the network motion (see subsection 3.5.4), for the interdiffusion coefficient we get Equation 3.5.126

$$D = \frac{M}{f},\tag{11}$$

where the friction coefficient f is related to the segment friction coefficient ζ by means of

$$f = \zeta c. \tag{12}$$

With due allowance for Equations 10 and 12, Equation 11 yields the concentration dependence of the diffusion coefficient:

$$D \sim c^{5/4}.\tag{13}$$

In the case of d-dimensional space, with Equation 4.3-63:

$$\xi \sim c^{\nu/(1-\nu d)},\tag{14}$$

$$M \sim \xi^{-d} \sim c^{-\nu d/(1-\nu d)} \sim c^{\nu d/(\nu d-1)}$$
(15)

and Equation 12, we have:

$$D \sim c^{[\nu d/(\nu d-1)]-1} \sim c^{1/(\nu d-1)}.$$
(16)

At the crossover point $c = c^*$ (Equation 4.3-68)

$$D \sim c^{*1/(\nu d - 1)} \sim N^{-1}.$$
(17)

Thus, at the crossover point the interdiffusion coefficient D abuts smoothly with the diffusion coefficient for the maximum dilute solution D_0 :

$$D_0 = \frac{kT}{\zeta N}.$$
(18)

Equation 16 allows us to verify one of the main scaling relationships in macromolecule dynamics:

$$D(c) = D_0 f\left(\frac{c}{c^*}\right),\tag{19}$$

where f(x) does not depend on N, and f(0) = 1. Suppose $f(x) = x^m$, then

$$D(c) \sim \frac{1}{N} c^m c^{*-m} = N^{-1+m(\nu d-1)} c^m \sim c^m \sim c^{1/(\nu d-1)},$$
(20)

since $-1 + m(\nu d - 1) = 0$ and $m = 1/(\nu d - 1)$.

We see that Equation 20 agrees with Equation 16, and a scaling plot of the Equation 19 type is justified and appropriate for predicting characteristic dependences in other cases as well.

In the foregoing discussion, the hydrodynamic interaction has not been taken into account; it implies that the *m*th segment of a macromolecule moves in the field of solvent velocities which is perturbed by the motion of the *n*th chain segment (for details see (de Gennes, 1976b, 1979; Gotlib et al., 1986)).

On an increase in the polymer concentration in a solution, the hydrodynamic interaction weakens due to the hydrodynamic perturbation of the *n*th segment being suppressed (screened) by the neighbouring macromolecule segments (Freed and Edwards, 1974; Wang and Zimm, 1974; de Gennes, 1976b).

Thus, hydrodynamic interactions also have their screening length $\tilde{\xi}$ which special analysis (de Gennes, 1976b) has shown to depend on concentration analogously to Equation 14:

$$\tilde{\xi} \sim c^{\nu/(1-\nu d)},\tag{21}$$

i.e. both the static ξ and dynamic $\tilde{\xi}$ screening lengths are identical.

Further analysis (de Gennes, 1976b) leads to a concept of hydrodynamic blobs of the size ξ inside which the hydrodynamic interaction manifests itself, and a set of such blobs becomes independent both of bulk effects (subsection 3.1.1) and of the hydrodynamic interactions. That is the reason the diffusion coefficient D proves to be, in fact, the blob diffusion coefficient D_{bl} :

$$D \sim D_{\rm bl} \sim \frac{kT}{6\pi\eta_0\tilde{\xi}},$$
 (22)

i.e. (see Equation 21)

$$D \sim \tilde{\xi}^{-1} \sim c^{\nu/(\nu d-1)} \sim c^{3/4} \quad \text{for} \quad d = 3.$$
 (23)

If wavelengths A are shorter (the region B), i.e.

$$\xi < \frac{2\pi}{q} < R; \qquad \frac{1}{R} < q < \frac{1}{\xi},\tag{24}$$

many relations of the region A apply: the distance between cross-links in the dynamic mode is of the order of $\xi \approx \tilde{\xi}$.

Let us consider at greater length the case of $\Lambda \sim R$ and $qR \sim 1$, which is important for deriving characteristic dependences by means of scaling plots in the other limiting case $q\xi \gg 1$ (within the region C).

For the Rouse chain model in the absence of excluded volume and hydrodynamic interactions, the relaxation time of the first mode with $k_0 = 1$ (Equation 3.3-62) is

$$\tau_1 = \frac{l^2 N^2 \zeta}{3\pi^2 kT}.\tag{25}$$

In view of $R^2 \sim Nl^2$, we obtain

$$\tau_1 \sim \frac{R^4 \zeta}{l^2 k T} \tag{26}$$

and, correspondingly,

$$\frac{1}{\tau_1} = \Delta \omega_q \sim \frac{l^2 kT}{\zeta R^4} \sim \frac{kT l^2}{\zeta} q^4.$$
⁽²⁷⁾

On the other hand (see, for instance, Equation 3.3 60)

$$\Delta \omega_q = Dq^2 \sim \frac{kTl^2}{\zeta} q^4,$$

from which

$$D \sim \frac{kTl^2}{\zeta} q^2 \sim \frac{kTl^2}{\zeta R^2} \sim \frac{kT}{\zeta N}$$
(28)

(cf. Equation 18).

If now we take excluded volumes into account (de Gennes, 1976a), for the relaxation rate the following expression emerges:

$$\frac{1}{\theta_1} \simeq \frac{kT}{\zeta N R_F^2},\tag{29}$$

i.e. $\theta_1 \sim N^{1+2\nu}$ while for the Rouse chain $\tau_1 \sim N^2$ (see Equation 25).

In view of the hydrodynamic interaction, for the first mode we get the relaxation rate (de Gennes, 1976b):

$$\frac{1}{\theta_1} \simeq \frac{kT}{6\pi\eta_0 R_F^3} = D_0 q^2.$$
(30)

Transfer to chain properties in the region C with $q\xi \gg 1$ is conducted by means of scaling plots. For example, considering the frequency difference in inelastic light scattering, de Gennes (1976b) writes the dependence

$$\Delta\omega_q = \frac{1}{\theta_1} f_S(qR_F) \tag{31}$$

with the limiting values of the dimensionless function $f_S(x)$:

• for $x \ll 1$ $f_S(x) = x^2$ and, in view of Equation 30,

$$\Delta \omega_q = D_0 q^2 \quad \text{and} \quad D_0 = \frac{kT}{6\pi\eta_0 R_F} \tag{32}$$

that is the Einstein-Stokes formula for an isolated coil;

- for $x \sim 1$ $f_S \sim 1$ and Equation 30 applies;
- for $x \gg 1$ an expression independent on the chain molecular weight should be obtained. This condition is satisfied by $f_S \sim x^3$, which yields

$$\Delta\omega_q \simeq \frac{kT}{6\pi\eta_0}q^3\tag{33}$$

for d = 3 and

$$\Delta \omega_q \sim q^d \tag{34}$$

for *d*-dimensional space.

 ν being absent in the exponent attests to the absence of influence of excluded volume on light frequency changes in dynamic scattering in the intramolecular mode.

The crossover between the states of pseudogel $(q\xi < 1)$ and of individual coils $(q\xi > 1)$, i.e. near $q\xi \sim 1$, is also described by the scaling plot

$$\Delta\omega_q = \Delta f_m(q\xi),\tag{35}$$

where the characteristic frequency Δ is

$$\Delta = \frac{kT}{6\pi\eta_0\xi^3} \sim \xi^{-3} \sim c^{2.25},$$
(36)

and the dimensionless function $f_m(x)$ satisfies

- when $x \to 0$ $f_m(x) \to x^2$ in agreement with Equation 22, in view of $\Delta \omega_q = Dq^2$;
- when $x \gg 1$ $f_m(x) \to x^3$ in agreement with Equation 33.

Thus, on the basis of the form of Equation 36, the quantity Δ can be considered as the blob relaxation rate (cf. Equation 30).

4.5.2. Reptation motion of macromolecules

We now turn to discussion of the macromolecule reptation motion model which has already been referred to above.

De Gennes (1979) has emphasized that, depending on the performance of an experiment, two different diffusion coefficients are observed in polymer systems, namely, the selfdiffusion coefficient (D_2) and the interdiffusion one (D), the latter also called by him the cooperative diffusion coefficient (cf. subsections 2.4.3 and 3.2.1).

The interdiffusion coefficient D is measured when polymer is redistributed under a gradient of its concentration. Theoretical consideration of this process is based on the laws of unequilibrium thermodynamics (see subsections 2.4.3 and 3.3.1). If a labelled macromolecule is present among their ensemble (see subsection 3.6.2) its motion is characterized by the self-diffusion coefficient (D_2) . Both those quantities coincide in dilute solutions $D \sim D_2 \sim D_0$, but the coefficient D rises with polymer concentration while D_2 decreases significantly.

It is apparently this circumstance that causes serious difficulties while interpreting data on dynamic light scattering in experiments like those described in subsection 3.6.2.

When $c \to 0$ (where $D \sim D_2 \sim D_0$) the experimenter's main trouble is to eliminate the contribution of intramolecular motion modes by means of extrapolation $q \to 0$. At finite polymer concentrations, measurements of the first cumulant $\mathcal{K}_{1,q\to 0}$ give an average diffusion coefficient (see Equation 3.3-85 and curve 3 in Figure 3.41).

However, sometimes there appear two peaks (eg, see Figure 13 (Kubota et al., 1983)) in the histogram technique or two values of relaxation time in $g_1(t)$ (see Figure 3.40) connected with the fast and slow motion modes. The highest value of the diffusion coefficient increases (curve 1 in Figure 3.41) and the lowest one decreases (curve 2) while raising polymer concentration. It is the latter quantity that is most often associated with the self-diffusion coefficient, its behaviour to be interpreted in terms of the chain reptation motion model by de Gennes (1971, 1976ab, 1979).



Figure 4.15. Chain C_L diffusionally reptates among the chains C_1 , C_2 , C_3 , etc. During little time it can be considered as confined in a pipe of the radius ξ (de Gennes, 1976a) [Reprinted with permission from Macromolecules 9 (1976) 587. Copyright © 1976 American Chemical Society]

Look at Figure 4.15. The fragments of the neighbouring chains C_1-C_5 form a certain pipe, inside which the labelled macromolecule C_L creeps. The diameter of this pipe is comparable with the distance between the chain contact points in the ensemble, i.e. with

 ξ . Every blob has g segments and the size ξ , hence, the labelled chain has N/g non-interacting blobs. So, in terms of dynamic properties, the labelled chain can be regarded Rousian consisting of N/g segments of the length ξ .

The overall length of the elongated pipe is therefore $L_{pipe} = (N/g)\xi$. Let us first presume the pipe to be motionless. In the range

$$\Delta^{-1} < t < T_t \tag{37}$$

the labelled molecule is supposed to have one-dimensional thermal diffusional motion along the pipe with the diffusion coefficient D_{pipe} as the only possible one (T_r is the time of pipe conformational reorganization).

Granted the coefficient D_{pipe} is known, the time T_{rep} for the chain to have crept at the distance equal to the pipe length L_{pipe} can be evaluated. This time is also treated as necessary for a complete reorganization of chain conformation. Then

$$T_{\rm rep} \simeq \frac{L_{\rm pipe}^2}{D_{\rm pipe}} \sim \left(\frac{N\xi}{g}\right)^2 \frac{N\zeta}{kT},$$
(38)

where $D_{\text{pipe}} \approx D_0$ is accepted (see Equation 28 for D_0).

As $\xi \sim g^{\nu}$ and, correspondingly,

$$g = \xi^{-\nu},\tag{39}$$

substitution of Equation 39 into Equation 38 with Equation 21 allowed for, we get

$$T_{\rm rep} \sim N^3 c^{2(1-\nu)/(\nu d-1)},$$
(40)

which for $\nu = 3/5$ means

$$T_{\rm rep} \sim N^3 c. \tag{41}$$

Thus, the time necessary to have the labelled chain unravelled depends on N. Estimation of heat changes in the pipe itself θ_{Γ} (de Gennes, 1976a) leads to

$$\theta_{\Gamma} \sim T_{rep},$$
(42)

so that

$$\frac{1}{T_r} = \frac{1}{T_{rep}} + \frac{1}{\theta_{\Gamma}} \simeq \frac{1}{T_{rep}}.$$
(43)

Now "turn on" hydrodynamic interaction and consider

$$T_r = \theta_1 \varphi\left(\frac{c}{c^*}\right). \tag{44}$$

When $c > c^*$, hydrodynamic interactions are screened, and regarding T_r

$$T_r(N, c \gg c^*) \sim N^3 \quad (c = const)$$
⁽⁴⁵⁾

must be true.

When $c < c^*$, T_r must be comparable with the relaxation time of the first mode of an isolated coil θ_1 (see Equation 30 for d = 3), and in the general case

$$\theta_1 \sim R_F^d \sim N^{\nu d},\tag{46}$$

i.e.

$$T_r(c \ll c^*) \sim N^{\nu d}. \tag{47}$$

Therefore, for the dimensionless function $\varphi(x)$ the following must apply

 $\varphi(0) = 1, \quad \varphi(x \gg 1) = x^m.$

Comparison with Equation 45 yields

$$N^{\nu d} \left(\frac{c}{c^*}\right)^m = c^m N^{\nu d + m(\nu d - 1)} \sim c^m N^3,\tag{48}$$

from which

r

$$n = \frac{3 - \nu d}{\nu d - 1} \quad \text{and} \quad T_r = N^{\nu d} \left(\frac{c}{c^*}\right)^{(3 - \nu d)/(\nu d - 1)}.$$
(49)

For d = 3 and m = 1.5 Equation 44, with due account of Equation 30, produces

$$T_r \simeq \frac{6\pi\eta_0 R_F^3}{kT} \left(\frac{c}{c^*}\right)^{1.5}.$$
 (50)

Hence, the hydrodynamic interaction changes the concentration dependence of T_r from $T_r \sim c$ (see Equation 41) to $T_r \sim c^{1.5}$ (Equation 50).

The functional dependence of the self-diffusion coefficient D_2 is obtained according to

$$D_2 = \frac{R^2(c)}{T_r} \sim N^{-2} c^{-1.75} \quad (d=3), \tag{51}$$

as $R^2 \sim Nc^{-1/4}$ (Table 4.1), $R_F \sim N^{3/5}$ (Equation 4.3-67), $c^* \sim N^{-4/5}$ (Equation 4.3-69). At the θ state where $\nu = 1/2$, it follows from Equations 49, 51, 4.3-68 that

$$D_2 \simeq N^{-2} c^{-3}. \tag{52}$$

This relationship must be satisfied also in case of a good solvent in a concentration range wherein the excluded volume is fully screened by the presence of other chains, i.e. when $c > c^{**}$, where c^{**} is the screening threshold concentration.

Finally, de Gennes (1976b) evaluates the solution viscosity according to

$$\eta \simeq MT_r \simeq \eta_0 \left(\frac{R}{\xi}\right)^3 \left(\frac{c}{c^*}\right)^{1.5} \sim c^{3.75} N^3 \tag{53}$$

(see Equations 9, 50, and 36).

Analysis of the free energy in the continuous Gaussian chain model (see Equation 3.1-189), the complete equation for molecular chain diffusion (cf. Equation 3.1-190), and the diffusion coefficient (cf. Equation 3.1-192) (Adler and Freed, 1979) has led to equations of dynamic scaling that agree with de Gennes' results. Currently there are insufficient experimental data for systematic comparison with the theoretical dependences of the dynamic scaling, but the data already obtained are either in agreement with the theoretical predictions or close to them. For example, by Equation 32

$$D_0 \sim R^{-1} \sim N^{-\nu}$$
. (54)

The dependence

$$D_{z,0} = (3.7 \pm 0.1) \cdot 10^{-4} M^{-0.587 \pm 0.002} \,\mathrm{cm}^2 /\mathrm{s}$$
(55)

has been obtained by the dynamic light scattering method for polystyrene in toluene at 30°C using the first cumulant \mathcal{K}_1 measured (Equation 3.3-85) (McDonnell and Ramanathan, 1984).

Due to the low fraction polymolecularity $\mathcal{K}_3 \approx 0$, and \mathcal{K}_2 was small, but its value was used to estimate the polymolecularity of polystyrene samples $(M_w/M_n \sim 1.05...1.15)$.

The value $\tilde{\nu} = 0.587 \pm 0.002$ in Equation 55 is in good agreement with ν measured in static experiments designed to determine the dependence of the gyration radius of a polystyrene coil in benzene on molecular weight: $\nu = 0.595 \pm 0.005$ (Miyaki et al., 1978) and $\nu = 0.58$ (Fukuda et al., 1974) and also with the theoretically calculated $\nu = 0.588$ (le Guillou and Zinn-Justin, 1977).

Thus, in accordance with the theoretical predictions of the dynamic scaling, the exponent of both dynamic $\tilde{\nu}$ and static ν quantities has the same value.

Wiltzius et al. (1983, 1984) have compared the dynamic ξ and static ξ correlation length within a wide range of polystyrene concentrations in benzene and methylethylketone. $\tilde{\xi}$ was determined using Equation 22, and D measured from the first cumulant $\mathcal{K}_1(q \to 0)$ of dynamic scaling (Equation 3.3-85). ξ was evaluated by

$$S^{-1}(q) \sim \left(\frac{\partial \pi}{\partial \mathbf{c}}\right)_T [1 + q^2 \xi^2 + O(q^4 \xi^4)].$$
(56)

At low concentrations $(c \rightarrow 0)$

$$\xi = R/\sqrt{3},\tag{57}$$

and then decreases as c increases:

$$\xi \sim c^{-z},\tag{58}$$

where $z = 0.70 \pm 0.03$, which agrees well with Equation 4.3-63 (see also Table 4.1) and with the above experimental data: Equation 4.3-88 (Daoud et al., 1975).

In Figure 4.16, ξ and ξ are directly compared (when $c \to 0, \xi \to R_H - cf$. Equation 57). Their ratio does not depend on molecular weight or solvent concentration. The equality $\tilde{\xi} \simeq \xi$ expected from scaling is satisfied in dilute solutions only.

At present, it would be difficult to comment on these features. They may be related to imperfections in theory and experiment, especially if we take into account the way of measuring ξ employing the Debye-Edwards formula (Equation 56), which is not rigorous (see comment to Equation 4.3-89).



Figure 4.16. Dynamic ξ and static ξ correlation length ratio in polystyrene solutions in toluene (transparent signs) and in methylethylketone (black signs) as a function of polymer concentration (Wiltzius et al., 1984) [Reprinted with permission from: P.Wiltzius, H.R.Haller, D.S.Cannell, D.W.Schaefer. Phys. Rev. Lett. 53 (1984) 834-837. Copyright © 1984 by the American Physical Society]

As Schäfer et al. (1980) have established, the exponent $\tilde{\nu}$ from dynamic measurements (Equation 32)

$$R_H \sim M_w^{0.53\pm0.02} \tag{59}$$

somewhat differs from that from the static ones

$$R \sim M_w^{0.58\pm0.01}.$$
 (60)

Difficulties also arise when one tries to comment on the exponent value 3 in Equation 53, that is a little less than the experimental values 3.3...3.4 often given in the literature (de Gennes, 1979).

An experimental work (Adam and Delsanti, 1977) presents different dynamic modes of polystyrene in a good solvent (benzene) as a diagram qR vs c/c^* (see Figure 4.17).

In the dilute solution region $(\mathbf{c}/\mathbf{c}^* < 1)$, a molecular coil serves as a morphological unit of the structure L = R, and in the semidilute region $(\mathbf{c}/\mathbf{c}^* > 1)$ $L = \xi$.

The boundary of the mode change individual coil/internal motion modes is defined by the condition

$$q_{\max}L = 1, \tag{61}$$

so that at $c/c^* < l$

$$q_{\max} = R^{-1} \sim N^{-\nu}.$$
 (62)

When $\mathbf{c} > \mathbf{c}^*$, the screening length ξ decreases in accordance with Equation 4.3 63. If we include $\xi \approx R$ at $\mathbf{c} \simeq \mathbf{c}^*$, then

$$R \sim \mathrm{e}^{*\nu/(1-3\nu)} \tag{63}$$

and

$$\xi \sim R \left(\frac{\mathbf{c}}{\mathbf{c}^*}\right)^{\nu/(1-3\nu)} \tag{64}$$



Figure 4.17. Diagram of the dynamic modes of polymer solution: individual macromolecules (1,1); pseudogel (2), and of the internal modes of molecular chains (3) (Adam and Delsanti, 1977) [Reprinted with permission from Macromolecules 10 (1977) 1229–1237. Copyright © 1977 American Chemical Society]

and when $c/c^* > 1$

$$q_{\max} \simeq R^{-1} \left(\frac{\mathbf{c}}{\mathbf{c}^*}\right)^{0.75} \tag{65}$$

(see the curve $q_{\max}R$ in Figure 4.17).

The elastic properties of the solution manifest themselves when

$$\tau(q) < T_r \qquad \tau(q) = \frac{1}{D_{\Gamma}(\mathbf{c})q^2} < T_r, \tag{66}$$

i.e. when

$$q \ge q_{\max} = \left(\frac{1}{D_{\Gamma}(\mathbf{c})T_r}\right)^{1/2},\tag{67}$$

where $D_{\Gamma}(\mathbf{c}) = M/f$ (see Equation 3.5–126).

Substituting the values of D and T_r from Equations 23 and 51 into Equation 67 and in view of Equation 64, we get

$$q_{\min} \sim \left(\frac{R}{R^3(\mathbf{c/c^*})^{1.5}(\mathbf{c/c^*})^{0.75}}\right)^{1/2} \sim R^{-1}(\mathbf{c/c^*})^{-1.125},$$
 (68)

which predetermines the dashed line in Figure 4.17, and

$$q_{\min}R \simeq (\mathbf{c/c^*})^{-1.125}.$$
 (69)

Thus, region 2 on the diagram (Figure 4.17) corresponds to the pseudogel mode, and region 3 to the internal motion modes where, in particular, Equation 33 is satisfied.

Adam and Delsanti (1977) report a study on polystyrene solutions using dynamic light scattering in different regions of the diagram (Figure 4.17) with the molecular weight, concentration c and scattered light angle g being varied.

Experimental data were used to determine the dynamic indices $\tilde{\nu}$, β , and γ in the power functions of the hydrodynamic radius

$$R_H \sim M^{\tilde{\nu}},\tag{70}$$

the diffusion coefficient

$$D \sim c^{\beta},\tag{71}$$

and the relaxation time

 $\tau^{-1} \sim q^{\gamma}. \tag{72}$

To study a dilute solution at $qR \ll 1$, a homodyne variant of dynamic light scattering with a photon correlation was used (see Equation 2.3-33). The normalized function of time correlation of the effective field of the scattered wave had an exponential profile (see Equation 3.3-72) and the dependence

$$\tau^{-1}(q) \simeq D(c, M)q^2 \tag{73}$$

held.

The diffusion coefficient D(c, M) obeys, in its turn, the relationship

$$D(c, M) = D_0(M)[1 + k_D(M)c],$$
(74)

 $D_0(M)$ being the diffusion coefficient at $c \to 0$, to calculate which a formula

$$D_0(M) = (2.18 \pm 0.32) \cdot 10^{-4} M^{-\tilde{\nu}} \,\mathrm{cm}^2/\mathrm{s} \tag{75}$$

has been proposed, with

$$\tilde{\nu} = 0.55 \pm 0.02.$$
 (76)

For $k_D(M)$, the relationship

$$k_D(M) = M^{0.8} (77)$$

has been found.

So, the homology of the hydrodynamic radius

$$R_H \sim M^{\nu}$$
 with $\tilde{\nu} = 0.55 \pm 0.02$ (78)

differs from that of the geometrical gyration radius

$$R \sim M^{\nu}$$
 (79)

with an experimental value $\nu = 0.6$ from the same paper (Adam and Delsanti, 1977).

In region 2 of the diagram (Figure 4.17) the dynamic structural factor (see Equation 3.3-71) is also of the exponential form with a direct proportionality τ^{-1} vs q^2 .

For the diffusion coefficient, the relationship

$$D_{\Gamma}(c) = (5.63 \pm 0.16) \cdot 10^{-6} c^{-\beta}$$
(80)

has been obtained with $\beta = 0.67 \pm 0.02$, which is different from the theoretical expectations according to Equation 23. However, the most important conclusion that D_{Γ} does not depend on the molecular weight in the pseudogel mode is confirmed experimentally for three samples with $M = 1.27 \cdot 10^6$, $3.8 \cdot 10^6$, and $8.4 \cdot 10^6$.

One blob contains

$$N(\xi) = c\xi^3 \tag{81}$$

segments, or (with allowance for Equation 4.3 63)

$$N(\xi) \sim c^{1/(1-3\nu)}.$$
 (82)

Equations 22 and 80 taken together imply

$$\xi \sim c^{-\beta} \qquad \beta = 0.67 \pm 0.02.$$
 (83)

If one substitute c from Equation 82 into Equation 83

$$c \sim N(\xi)^{1-3\nu},\tag{84}$$

one obtains

$$\tilde{\xi} \sim N(\tilde{\xi})^{(3\nu-1)\beta}.$$
(85)

If the experimental value $\beta = 0.67$ is taken into account, then

$$(3\nu - 1)\beta = 0.536 \pm 0.016 \tag{86}$$

in conformity with $\alpha = 0.55 \pm 0.02$ from Equation 78.

This comparison shows that the dynamic screening length ξ in semidilute solutions and the hydrodynamic radius R_H in dilute ones have the same homology in reference to the contour length.

Finally, at $qR \gg 4$ (region 3 in Figure 4.17) for two high-molecular samples ($M = 24 \cdot 10^6$ and $8.4 \cdot 10^6$) while varying the scattering angle (q) and concentration c, the dependence of the relaxation time of the internal motion mode

$$r^{-1}(q) \sim q^{\gamma} \quad \text{with} \quad \gamma = 2.85 \pm 0.05$$
(87)

and no dependence on molecular weight has been established, which is in agreement with the scaling (Equation 33).

The dynamic mode in the θ solvent proved to be much more complicated in comparison with the dynamic behaviour of macromolecules in a good solvent (Brochard and de Gennes, 1977) due to the fact that in the θ solvent, macromolecules get knottily with a high probability (Vologodsky et al., 1974; K.Klenin, 1988; K.Klenin et al., 1988), which leads to a more complex behaviour in dynamics.

As measurements of the self-diffusion coefficient D_2 is of specific character, interpretation of such measurements causes certain difficulties. Figure 3.41 demonstrates the exponent in the concentration dependence of D_2 to be ~ -1.5 , which is different from -1.75 as in Equation 52; however, this difference seems not to be so significant in view of the essential novelty of the theoretical approach and complexity of experiment.

Maklakov et al. (1987) and Skirda et al. (1988) give a large body of experimental data on measuring the self-diffusion coefficient D_2 of polystyrene, PEO, PDMS, and dextrane in different solvents within wide ranges of molecular weight, polymer volume concentration φ , and temperature using NMR with an impulse gradient of magnetic field. They place emphasis on that the method measures the local mobility of macromolecular chains and carry out an empirical renormalization of $D_2(\varphi)$ using the correlation times $\tau_c(\varphi)$ of segment small-scale motion and the relationship

$$D_2'(\varphi) = D_2(\varphi) \frac{\tau_c(\varphi)}{\tau_0(\varphi)},\tag{88}$$

where $D'_2(\varphi)$ is the self-diffusion coefficient normalized to the local mobility

$$\tau_c(0) = \lim_{\varphi \to 0} \tau_c(\varphi).$$

The values of $\tau_c(\varphi)$ were determined from independent measurements of the nuclear magnetic relaxation times T_1 and \dot{T}_2 . In most cases, the direct proportionality $T_1, T_2 \sim \tau_c^{-1}$ applies.

Further, employing the method of successive approximations, the authors find the universal curve

$$\frac{D_2'(\varphi)}{D_2(0)} = f\left(\frac{\varphi}{\hat{\varphi}}\right),\tag{89}$$

where $D_2(0) = \lim_{\varphi \to 0} D_2(\varphi)$, $\hat{\varphi}$ is a certain threshold concentration depending on molecular weight.

To obtain the molecular dependence $\hat{\varphi}(M)$, the expressions for the chain reptation motion models (Equations 51-53)

$$D_2(M) \sim M^{-2}$$
 (90)

and

$$f\left(\frac{\varphi}{\hat{\varphi}}\right) \sim \left(\frac{\varphi}{\hat{\varphi}}\right)^{-3} \tag{91}$$

are used for large enough concentrations, where the excluded volume is screened. In the θ solutions, $\hat{\varphi}$ is interpreted just as the concentration of coil overlap

$$\hat{\varphi} = \varphi^*(M) \sim M/R^3,\tag{92}$$

but, in case of good solvents, $\hat{\varphi}$ is found from the condition of the function (Equation 89) being universal *a priori* with allowance for Equations 90, 54, and 91:

$$\hat{\varphi}(M) \sim M^{-(2-\tilde{\nu})/3}$$
. (93)

As a result, the plot of the universal function $f(\varphi/\hat{\varphi})$ as

$$\lg \frac{D'_2(\varphi)}{D_2(0)} vs \, \lg \left(\frac{\varphi}{\hat{\varphi}}\right) + const \tag{94}$$

has been obtained on a large body of experimental points concerning different polymers, solvents, and temperatures. The asymptotics of the function at high concentrations corresponds to

$$\left(\frac{\varphi}{\dot{\varphi}}\right)^{-3}.\tag{95}$$

Having noted an uncertainity in the physical meaning of the threshold concentration $\hat{\varphi}$, the authors, nevertheless, propose to treat it as a certain dynamic critical concentration defining changes in the macromolecular dynamic properties subject to φ .

Skirda et al. (1988) draw attention to the absence of any no-matter-how-extended concentration area where $f(\varphi/\hat{\varphi})$ would be approximated by a power function with the exponent -1.75 expected in accordance with the reptation model within $\varphi^* < \varphi < \varphi^{**}$ (see Equation 52). In their opinion, the reason is in employing the **static** characteristics of macromolecules to describe the **dynamic** properties of polymer chains in reptation theory (de Gennes, 1976a, 1979). This is unlikely to be correct. It is a different matter that $\tilde{\nu} = \nu$ appears in a particular case.

Moreover, in deriving Equation 93, it is the results of reptation theory that have been used by the authors, in particular, Equations 90 and 91.

Apparently, to interpret correctly the experimental data of Skirda et al. (1988), no rejection of reptation theory is required but just some modification or updating. The more so that, except Equation 95, the molecular dependence $D_2(M)$ for high molecular weights satisfies the model of reptation motion (see Equation 90).

To clarify the dependence of D_2 on molecular weight, Equation 88 is rewritten as

$$D_2'(\varphi, M) = D_2(0, M) \frac{\tau_c(0)}{\tau_c(\varphi)} f\left(\frac{\varphi}{\hat{\varphi}}\right),$$
(96)

where $f(\varphi/\hat{\varphi})$ is approximated by a power function $(\varphi/\hat{\varphi})^{-\alpha}$ with $\alpha = 3$ over the region of large $\varphi/\hat{\varphi}$ values and $\alpha \to 0$ when $\varphi/\hat{\varphi} \to 0$. In view of Equations 54 and 93, Equation 96 implies

$$D'_2(\varphi, M) \sim M^{-(3\tilde{\nu} + \alpha(2 - \tilde{\nu}))/3}.$$
 (97)

Due to $\hat{\varphi}$ depending on molecular weight, every concentration has its own molecular weight, for which the values of $\varphi/\hat{\varphi}$ fall within the region where $\alpha = 3$. Hence (see Equation 97), $D_2 \sim M^{-2}$.

Indeed, the plot

$$\lg D'_2 + const \ vs \ lg(M_n/M_{KD}) \tag{98}$$

at high molecular weights is a straight line with the slope -2. In Equation 98, M_{KD} is the critical molecular weight corresponding to the intersection of the lines (Equation 98) with the slopes -2 and -1.

Thus, the comprehensive cycle of investigations considered can be interpreted in terms of the reptation motion model for polymer chains. The large scale and systematic character of these investigations must play an important part in the final elucidation of the dynamic properties of polymer systems.

4.5.3. Critical phenomena

Now let us discuss the region of critical phenomena and dynamic scaling.

The most general theory of the dynamic properties in critical phenomena (see subsections 2.3.5 and 2.4.4) leads to scaling plots for polymer systems as well.

According to the modified (Lo and Kawasaki, 1972) theory of connected modes (Kawasaki, 1966, 1970ab; Kadanoff and Swift, 1968; Kawasaki and Lo, 1972; Lo and Kawasaki, 1972; Swinney, 1974; Anisimov, 1987) the equality

$$\frac{H(q\tilde{\xi})}{(q\tilde{\xi})^3} = \frac{6\pi\tilde{\eta}\Gamma_c}{kTq^3},\tag{99}$$

holds, where $H(q\xi)$ is Kawasaki's modified universal function (Lo and Kawasaki, 1972), and the right-hand side is the dimensionless rate of the critical fluctuation fall (see Equation 2.4-74).

The complexity of comparison of Equation 99 with experiment is due to the fact that the dynamic light scattering technique gives the value Γ consisting of Γ_c proper and the background value Γ_b . So, a special means for extracting Γ_c from experimental Γ data is required. To do this, Lao et al. (1975) acted as follows. The scattered light intensity of polystyrene solutions in cyclohexane in the critical region was approximated by

$$\frac{I}{T} = A_0 / \varepsilon (1 + q^2 \tilde{\xi}_0^2 \varepsilon^{-2\nu})^{1-\eta/2}, \tag{100}$$

where A_0 involves λ_0^{-4} , $(\partial n/\partial c)^2$, k, etc.,

$$\tilde{\xi} = \tilde{\xi}_0 e^{-\nu}.$$
(101)

Equation 100 corresponds to the function of the concentration fluctuation correlations²

$$C(r) \sim e^{-r/\xi} / r^{1+\eta}.$$
 (102)

A value $\eta = 0.05$ was chosen for the Fisher index η .

A plot $\lim_{q\to 0} (I/T)^{-1}$ vs ε in the double logarithmic scale yielded a straight line with the slope $\gamma = 1.25 \pm 0.03$.

Since calculation of ξ by Equations 100 and 101 is sensitive to secondary scattering, the straight line

 $\lg \xi$ vs $\lg \varepsilon$

was corrected in accordance with the scaling relationship $\nu = \gamma(2-\eta)$ and $\eta = 0.64 \pm 0.02$ was obtained.

²Other analytical expressions of the correlation function (Zubkov and Romanov, 1988) are applied to describe the critical opalescence in solutions as well

In the formula for the Rayleigh central line width (Equation 2.3-162)

$$\Gamma = \left(\frac{L_q}{X_q}\right)q^2\tag{103}$$

the Onsager coefficient L_q was approximated as

$$L_q = L_b + L_{c,q},\tag{104}$$

and, for the generalized susceptibility,

$$X_q = X_b + X_{c,q},\tag{105}$$

where 'b' denotes the background value in the absence of critical anomalies, and 'c' denotes a value in the critical region.

Further, as $X_q \gg X_b$,

$$\frac{L_q}{X_q} = \frac{L_{c,q}}{X_{c,q}} + \frac{L_b}{X_{c,q}} = \frac{L_{c,q}}{X_{c,q}} + B\varepsilon^{\gamma}(1+q^2\tilde{\xi}^2),$$
(106)

was accepted, where $X_{c,q}$ is given with the Ornstein-Zernike form of the correlation function, B is a constant.

In binary liquid mixtures, the Onsager kinetic coefficient L_q corresponds to the diffusion coefficient D, and the generalized susceptibility is expressed as

$$X_{q} = \left(\frac{\partial c}{\partial \Delta}\right)_{T,P},\tag{107}$$

with Δ to denote the chemical potential difference of two components (see subsection 2.4.3). It follows from Equations 103 and 106 that

$$\frac{6\pi\tilde{\eta}\Gamma_c}{kTq^3} = \frac{6\pi\tilde{\eta}\Gamma}{kTq^3} - \frac{6\pi\tilde{\eta}}{kTq}B\varepsilon^{\gamma}(1+q^2\tilde{\xi}^2).$$
(108)

Figure 4.18 illustrates this dependence with respect to $q\tilde{\xi}$ for polystyrene solutions in cyclohexane (Lao et al., 1975), $B = 7.48 \cdot 10^{-6} \text{ cm}^2/\text{s}$.

The viscosity $\tilde{\eta}$ was measured with a capillary viscosimeter. The correlation radius of the concentration fluctuations was determined from the radiation diagram (Equations 100-102).

Equation 108 corresponds to the theoretical expression of the connected mode theory: $II(q\tilde{\xi})/(q\tilde{\xi})^3$.

Thus, in the critical opalescence region, polymer solutions show the same properties as low-molecular solutions provided that the critical indices are the same as well (cf. data for the low-molecular-weight compounds (Zubkov and Romanov, 1988)).

At $\xi \to \infty$, $D \to 0$ near the spinodal (as for low-molecular-weight solutions -- Equation 2.4 73 and in full accordance with scaling plots — Equation 22), which reflects the law of thermodynamic retardation (cf. Equation 3.7-81).

Some specific features of the system P+LMWL manifest themselves in a scaling expression for ξ like that of de Gennes (1979)

$$\xi = R_{\theta} \left(\frac{\theta - T_c}{T - T_c} \right)^{\nu}, \tag{109}$$



Figure 4.18. Dependence of $6\pi \tilde{\eta} \Gamma_c/kTq^3$ vs q for polystyrene solutions in cyclohexane (see Equation 4.5–108). $M_n = 1.96 \cdot 10^5$, $M_w/M_n < 1.02$ (Lao et al., 1975) [Reprinted with permission from: Q.H.Lao, B.Chu, N.Kuwahara. J. Chem. Phys. 62 (1975) 2039 2044. Copyright © 1975 American Institute of Physics]

where ν is the index close to 2/3, i.e. to the universal value; at $T = \theta$, the formula gives

$$\xi = R_{\theta}, \tag{110}$$

which is in agreement with the data on critical opalescence presented in subsection 3.3.1 and section 4.2.

Chapter summary

1. According to the principle of universality, the system's characteristic properties are defined by two parameters, namely, the space dimension d and the order parameter dimension n.

Systems, having equal d and n values, are included in the same class of universality, with their properties in the critical state being analogous.

The properties of molecular chain conformations or of random self-avoiding walks of linked segments belong to the class of universality with d = 3 and n = 0. It was first established by de Gennes, who brought the parameters of the magnetic problem into agreement with those of the polymer problem:

$$\xi \simeq \sqrt{\langle h^2 \rangle}$$
 and $\varepsilon \simeq N^{-1}$

He has obtained the index value in the function $\langle h_N^2 \rangle \simeq N^{2\nu}$, having put n = 0 into the equation for the critical index of the magnetic correlation length ξ , the latter having been calculated by Wilson with the method of renormalization group transformations for a general-type system with arbitrary values of d and n. We note in passing that de Gennes established the Green function $G(\varepsilon, \vec{k})$ at n = 0 to be a representation of $\Gamma_N(\vec{h})$ in the Laplace transform, where $\Gamma_N(\vec{h})$ is the number of self-avoiding walks of Nsteps connecting the sites 0 and \vec{h} on the lattice. Hence, for a polymer chain with the length L, the probability $P(\vec{h}, L)$ for the end-to-end distance to be \vec{h} can be found by means of the inverse Laplace transform applied to the Green function at n = 0. Knowing the problem solution, in fact, Emery has transformed the partition function Z_n of a more general system with a finite n in such a way as to obtain an explicit relationship between Z_n and n, that opened up the possibility to write $Z_{n=0}$ for n = 0.

The analytical solution of the problem has lead to the fact that at n = 0, the Laplace transform of the Green function G_{ij}^{o} is the probability to find the end of a polymer chain with the length L = t (where t is time in the problem of the general type) in the point \vec{r}_{j} , if the first segment is located at point \vec{r}_{i} . As a matter of fact, it is in agreement with the formulation of the continuous-chain model by Edwards.

These theoretical achievements opened up extraordinarily broad ways for the theoretical study of coil conformations, since statistical physics of general-type systems has been developed very well as applied to different thermodynamic functions.

The results of these investigations can be extended to polymer systems with the simple substitution n = 0 (or the extrapolation $n \to 0$). For example, in such a way Stephen analyzed the coil conformation at the θ point, using the solution for general-type systems at the tricritical point.

It was de Gennes who first pointed to the correspondence between the θ point of the polymer problem and the tricritical state of general-type systems.

2. The establishment of a glossary between the magnetic and polymer characteristic values for a wide range of polymer concentrations in the system P+LMWL (Equations 4.2 67...70) using both the Lagrangian formalism of field theory and the general relationships of statistical physics was the next great achievement of polymer theory.

Using this glossary and the scaling rules established for general-type systems, a group of French scientists (Saclay) advanced a state diagram for the system P+LMWL.

Distinctly from the mean field approximation in the Flory-Huggins theory (see Chapter 3), the lines of crossover (i.e. the lines representing the change of the conformational mode of macromolecules) are readily plotted on this diagram in the single-phase region (solution).

The diagram is in good agreement with experimental results.

The fruitfulness of the principle of universality was shown by Stepanow, who extended Flory-Huggins' thermodynamic potential to the Landau-Ginzburg-Wilson Hamiltonian, which takes into account the correlations of the order parameter fluctuations.

Having been performed over this Hamiltonian, the standard procedures lead to the critical index of the order parameter amplitude, that shows the binodal form near the critical point which is in agreement with experimental results.

3. Application of the principle of corresponding states and scaling considerations for the description of the critical opalescence phenomenon (even within the mean field approximation) led de Gennes to a new relationship between the Debye length l and the molecular weight, which is in better agreement with experimental data than Debye's initial formula.

4. The ideas of scaling have also proved to be correct in studying the dynamic characteristics of macromolecules in solution. In particular, a dynamic state diagram was constructed in the coordinates q vs $1/\xi$ (Figure 4.14). Three modes of dynamic properties can be observed.

In region A, where qR < 1 $(R < \Lambda)$ and frequencies ω are rather low but larger than T_r^{-1} $(T_r$ is the relaxation time for the full change of chain conformation), the solution behaves as a gel and is characterized by the longitudinal modulus M.

In region *B*, where $\xi < 2\pi/q < R$, the individual properties of coil manifest themselves. It turns out that the hydrodynamic interactions have their own screening length $\tilde{\xi}$ matching one for space interactions $\tilde{\xi} \simeq \xi$.

In region C, where $q\xi \gg 1$, the internal modes of polymer chain show themselves.

De Gennes has emphasized that one of the two different diffusion coefficients (of interdiffusion D and of self-diffusion D_2) must be used with the choice depending on the experiment performance.

The former coefficient is measured in experiments with a polymer concentration gradient. The theoretical consideration of the process of substance redistribution is based on the laws of unequilibrium thermodynamics. The latter coefficient characterizes the moves of a single macromolecule (highlighted or labelled) if the experiment allows one to follow it.

De Gennes has proposed and developed a mechanism of reptational motion of a macromolecule in a self-like medium, which is in good agreement with experimental results.

5. The most general theory of dynamic properties in the critical region, namely, the coupled modes theory, leads to scaling plots, that are justified by experimental data.

6. The best agreement between the results of scaling plots and experimental values is found in the case of high-molecular polymer samples, that reflects the premises of the theory: $M \to \infty$.

Chapter 5

Methods for Renormalization Group Transformations

As was repeatedly emphasized, **away** from the phase separation region (i.e. at high temperatures for systems with a UCST), the intersegment interaction in a polymer chain reduces to the existence of segment excluded volume, which manifests itself by swelling (expansion) of polymer coils. These interactions also lead to a correlation of the segment density fluctuations as it occurs in general-type systems near the critical point.

To study the properties of systems **near** the critical point, methods of the renormalization group approach have been developed (see section 2.5); therefore, the development of polymer theory has led to similar methods.

The renormalization group approach features extraction, from a microscopic model of a system, of relationships for experimentally measured, macroscopic, thermodynamic (in the long-wavelength limit) quantities, whose principal property is their independence from any fine details of the microscopic pattern of the system (Oono et al., 1981). If a system (eg. a macromolecular chain) is rather large, then the macroscopic relationships among experimentally observed quantities must be invariant at any coarse graining transformation (eg. Kadanoff's transformation, see: Kadanoff, 1966; Kadanoff et al., 1967, and section 2.5) which fuzzifies the finest details of a macroscopic model. Such an approach leads to a renormalization group transformation of the Wilson type (Wilson, 1972, 1979; Wilson and Kogut, 1974; Oono and Freed, 1981a).

De Gennes (1979) was the first to apply the idea of coarse graining transformations in polymer theory: he grouped chain segments into blobs. Then, this approach was developed by Gabay and Garel (1978) but it could not provide a high accuracy.

Oono, Ohta, and Freed have worked out a renormalization method of configurational space of polymer chains in several versions.

Section 5.1 presents renormalization of the Wilson type following Oono and Freed (1981a), and renormalization by Gell-Mann and Low following Oono et al. (1981). In section 5.1, polymer chain renormalization in the momentum space of Kholodenko and Freed (1983) will be discussed.

5.1. Renormalization of the conformational space of polymer chains

5.1.1. Renormalization of the Wilson type

If a polymer chain model is microscopic, it must reflect the atomic discrete structure of a chain, i.e. there must exist a fundamental scale of length to meet this discreteness. For the model of continuous chains (see subsection 3.1.1), this gives rise to the necessity to cut-off a length a, the minimal length along the chain, within which no integration is taken when the probabilities of different chain conformations are calculated. Such a cut-off is also necessary from a mathematical angle to obtain mathematically well-defined quantities. On the other hand, the introduction of the cut-off immediately leads to the need of the renormalization group approximation, as the value of a relates to the finest details of a model.

Let N denote the number of segments, of length l each, v_2 be the excluded volume parameter, and a be the contour length cut-off.

The mean-square end-to-end distance $\langle h^2 \rangle$ is a function of N, l, and v_2 for a system with the cut-off a.

Simple analysis of dimensions shows that this functional dependence in 3D space has the transformational property

$$\left\langle h^2 \right\rangle = b^2 l^2 f\left(\frac{N}{b^2}, v_2 b l^{-4}, \frac{a}{b^2}\right),\tag{1}$$

b being a positive real number, and f denotes a certain functional relationship with its properties being of interest. The quantity b always exceeds 1 and, in the most important case, $b \sim N^{1/2}$.

Thus, transformational property 1 relates the source system to the cut-off a in a scales stipulated, remains the same:

$$\left\langle h^2 \right\rangle = b^2 l^2 f(\tilde{N}, \tilde{v}_2, a). \tag{2}$$

Given N and \tilde{v}_2 are chosen properly, the function f in Equation 2 will remain the same as in Equation 1.



Figure 5.1. Scaling transformation of a molecular chain: S_s uniformly reduces all the chain \longrightarrow transfer from A to B. Kadanoff's transformation \mathcal{K}_s smooths the fine structural details, bringing the coil to the form C. The statistical form C may be similar to the form A' which is part of the source chain A (Oono and Freed, 1981a) [Reprinted with permission from: Y.Oono, K.F.Freed. J. Chem. Phys. 75 (1981) 993-1008. Copyright © 1981 American Institute of Physics]

The idea of the cut-off preservation is illustrated in Figure 5.1, where the form C follows the fragment A' of the source chain structure A. Therein lies the **fractal principle** of a polymer chain.

Generally, the relationships between N and \tilde{N} , v_2 and \tilde{v}_2 are very sophisticated; however, be N rather large, b can be chosen large enough to obtain a simple asymptotic relationship between the quantities with and without a tilde.

For large \bar{N} and $\tilde{v}_2 > 0$, \tilde{v}_2 turns out to acquire a constant value insensitive to \hat{b} , i.e. \tilde{v}_2 approaches the fixed point v_2^* (see section 2.5) and, besides, $\hat{N} \sim N/b^{1/\nu}$. Then, Equation 2 reduces to

$$\left\langle h^2 \right\rangle = b^2 l^2 f\left(\frac{N}{b^{1/\nu}}, v_2^*, a\right). \tag{3}$$

This is the fundamental scaling law followed by

$$\left\langle h^2 \right\rangle = l^2 N^{2\nu} \hat{f}(v_2^*, a), \tag{4}$$

if $b^{1/\nu} \sim N$ is chosen.

Let us discuss another macroscopic variable Q depending on the set of macroscopic quantities M_1, M_2, \ldots (such as an external force, the diameter of the embracing pipe, etc.) and on the microscopic quantities v_2, a , etc.

Like Equation 3, the introduction of scaling transformation and subsequent enlargement of the structural elements, with the cut-off value to be preserved, lead to a scaling law

$$Q = b^{D} f_{Q} \left(\frac{N}{b^{1/\nu}}, v_{2}^{*}, M_{1}, M_{2}, \dots, a \right),$$
(5)

which for $b \sim N^{\nu}$ reduces to

$$Q = N^{\nu D} \hat{f}_Q(v_2^*, M_1, M_2, \dots, a).$$
(6)

As a and v_2^* are fixed, they can be absorbed in the definition of f_Q .

Equations 4 and 6 can formally be combined to eliminate N:

$$Q = F_Q\left(\left\langle h^2 \right\rangle, M_1, M_2, \ldots\right). \tag{7}$$

This is the relationship between the macroscopic (experimentally measured) variables and the basic equation of de Gennes' (1979) scaling approximation.

Thus, the stage of enlargement of structural elements, corresponding to the Equation $1 \rightarrow Equation 2$ conversion, is due to the necessity of the existence of the cut-off length and to selection of macroscopic relationships insensitive to this cut-off.

In the model of a continuous chain (see subsection 3.1.1), Kadanoff's enlargement of structural elements is provided by integration over the small loops of the contour length.

On developing this concept, Oono and Freed obtained unambiguous correspondence between the renormalization procedure of the conformational space of a polymer chain and the characteristic values in critical phenomena within Wilson-Fisher's theoretical field approach (some differences do, certainly, exist and will be discussed at the end of this subsection).

As an example of application of this procedure, the main terms in the ε expansion of the index ν are calculated using the simplest model of the short-range repulsion potential

(the δ function). This potential quite satisfactorily describes the behaviour of a macromolecular coil in the maximum good solvent but, naturally, cannot be responsible for this behaviour in the θ state.

To discuss the coil properties at the θ point, a more realistic interaction potential was applied, including both repulsion and attraction (Lennard-Johns' potential, Figure 1.40a) and the contribution of three-(and more)-body interactions (the interactions on simultaneous contacts of three and more points along the polymer chain) (Freed, 1972).

In the model of a continuous chain of length N, the microscopic state of the chain is described by the conformation $\vec{c}(\tau)$ ($0 \le \tau \le N$), with $\vec{c}(\tau)$ denoting the spatial location of the point at a dimensionless distance τ from the chain's end (Freed, 1972). Moreover, $\vec{c}(\tau) = (d/l)^{1/2}\vec{r}(\tau)$ is accepted, where l is an analogue of Kuhn's segment. This is introduced to simplify the Hamiltonian of the coil.

All the detailed information concerning the statistical microscopic properties of such a polymer chain with its ends fixed at the points 0 and \vec{h} in *d*-dimensional space is contained in the distribution function

$$G(\vec{h},N) = \int_{\vec{c}(0)=0}^{\vec{c}(N)=\vec{h}} W_a[\vec{c}] \exp\left(\frac{-\mathcal{V}_a[\vec{c}]}{kT}\right),$$
(8)

where $W_a[\vec{c}]$ denotes the statistical weight of the conformation $\vec{c}(\tau)$ when there is no intersegment interaction (the "unperturbed" statistical weight), $\mathcal{V}_a[\vec{c}]$ is the interaction energy of the conformation \vec{c} ; the integral sign denotes summation over all the possible conformations satisfying the conditions $\vec{c}(0) = 0$ and $\vec{c}(N) = \vec{h}$.

If the excluded volume interactions are defined by the mean-force pair potential φ acting between two points on the chain, then $\mathcal{V}_a[\vec{c}]$ is

$$\mathcal{V}_{a}[\vec{c}] = \frac{1}{2} \int_{|\tau-\tau'|>a} d\tau' \,\varphi\left(\vec{c}(\tau) - \vec{c}(\tau')\right). \tag{9}$$

The subscripts by W_a and \mathcal{V}_a mean the explicit dependence of the excluded volume interaction energy on the contour length cut-off, the condition $|\tau - \tau'| > a$ stands for the elimination of the self-interaction inside the same segment.

To explain the renormalization transformation of a polymer chain, the simplest form of pair potential (see Equation 3.1–94) is accepted

$$\varphi(r) = kTv_2\delta(r),\tag{10}$$

where v_2 is the excluded volume parameter.

Thus, the simplest model for the distribution function with excluded volume and with a non-perturbed Gaussian chain is (see Equation 3.1-205)

$$G(\vec{h}, N) = \tag{11}$$

$$= \int_{\vec{c}(0)=0}^{\vec{c}(N)=\vec{h}} D[\vec{c}] \exp\left[-\frac{d}{2l^2} \int_{0}^{N} [\dot{\vec{c}}(\tau)]^2 d\tau - \frac{1}{2} \int_{|\tau_1-\tau_2|>a} d\tau_1 \int_{0} d\tau_2 v_2 \delta\left(\vec{c}(\tau_1)-\vec{c}(\tau_2)\right)\right],$$

where $\vec{c}(\tau) = d\vec{c}(\tau)/d\tau$.

This distribution function comprises many details not reflected in experimentally measured quantities. For example, the form of Equation 4 is not affected by whether the cut-off has the length a or 2a.

Further, let us consider the problem of developing a method for extracting the corresponding macroscopic relationships (quantities) from Equation 11. They result from calculation of mean values on distribution function 11, including integration over τ and $\vec{c}(\tau)$.

The replacement of variables

$$\vec{c}'(\tau') \equiv \frac{\vec{c}(\tau)}{s^{\nu}}, \quad \tau' \equiv \frac{\tau}{s^{(2-\eta)\nu}} \tag{12}$$

transforms Equation 11 to another one, identical in form and with variables l', N', a', v'_2 , and \vec{h}' providing for scaling transformations

$$l'^{2} = \frac{l^{2}}{s^{\eta\nu}}, \quad N' = \frac{N}{s^{(2-\eta)\nu}}, \quad a' = \frac{a}{s^{(2-\eta)\nu}}, \quad v'_{2} = v_{2}s^{(\varepsilon-2\eta)\nu}, \quad \vec{h}' = \frac{\vec{h}}{s^{2\nu}}, \quad (13)$$

s being a certain positive scaling quantity, $\varepsilon = 4 - d$, η , ν are certain real constants. Let us denote the scaling transformation (Equations 12-13) by S_s .

Consider a certain macroscopic quantity Q explicitly depending on N, v_2 , and a:

$$Q = f_Q(N^{-1}, v_2, a).$$
(14)

If the scaling transformation S_s is applied to the quantity Q (a thermodynamic mean value), then an invariant relationship of the form results:

$$Q = s^{\nu D} f_Q \left(\mathcal{S}_s(N^{-1}), \mathcal{S}_s(v_2), \mathcal{S}_s(a) \right), \tag{15}$$

where D is a real constant.

Equation 2 for $\langle h^2 \rangle$ is a specific case of Equation 15. Further, we assume the longwave properties of Q to be invariant in enlarging, the structural elements (Kadanoff's transformation) \mathcal{K}_s . The transformation \mathcal{K}_s is chosen so that to set $\mathcal{K}_s \mathcal{S}_s a$ equal to a, to restore the cut-off of the source chain (see Figure 5.1).

Thus, the condition of long-wave macroscopic detection of Q implies the invariance of Q after the scaling and Kadanoff's transformations of structural elements

$$Q = s^{\nu D} f_Q(\mathcal{K}_s \mathcal{S}_s(N^{-1}), \mathcal{K}_s \mathcal{S}_s(v_2), a).$$
(16)

Define $\mathcal{R}_s \equiv \mathcal{K}_s \mathcal{S}_s$ as a renormalization transformation. Equation 16 then takes the form

$$Q = s^{\nu D} f_Q(\mathcal{R}_s(N^{-1}), \mathcal{R}_s(v_2), a).$$

$$\tag{17}$$

It has to be specially noted that the set of S_s for s real numbers is an Abelian group while that of \mathcal{K}_s for s non-negative numbers is a commutative semigroup. S_s and \mathcal{K}_s commute; therefore, the set of \mathcal{R}_s for s non-negative numbers is also a commutative semigroup called a renormalization transformation group (renormalization group). Discuss $\langle h^2 \rangle$ from which D = 2 as Q (Oono and Freed, 1981a). Renormalization transformation 17 gives

$$\left\langle h^{2} \right\rangle = s^{2\nu} f_{\left\langle h^{2} \right\rangle}(\mathcal{R}_{s}(N^{-1}), \mathcal{R}_{s}(v_{2}), a).$$
 (18)

The renormalization transformation \mathcal{R}_s converts the parameters N^{-1} and v_2 to $\mathcal{R}_s(N^{-1})$ and $\mathcal{R}_s(v_2)$ (Figure 5.2). When s is continuously varying in d(< 4)-dimensional space,



 \mathcal{R}_s converts N^{-1} and v_2 to points which move along the flux line in the (N^{-1}, v_2) plane. U and S are fixed points for \mathcal{R}_s . U is an unstable (fixed) point, as near it the points are transformed by \mathcal{R}_s at distances far away from U. S is a saddle point: the flux lines approach it along one direction but recede from it along the other one. In d(> 4)dimensional space, S and U are interchanged, and $v_2^* = 0$, i.e. there are no excluded volume interactions.

For a sufficiently long chain, very large values of s can be taken so that the point $(\mathcal{R}_s(N^{-1}), \mathcal{R}_s(v_2))$ will be in the region C classified as critical due to its closeness to the saddle point S.

As a result of the transformations, the point will be located in the region C regardless of the initial values of v_2 and N^{-1} , which predetermines the universality of the excluded volume problem: the transformation \mathcal{R}_s converts all the chains into the macroscopically equivalent ones in the region C. Near the fixed point, \mathcal{R}_s can be assumed to be linearized, namely,

$$\mathcal{R}_s(N^{-1}) = s^{\alpha} N^{-1},\tag{19}$$

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 α being a function of ν chosen in Equation 13. In turn, the choice $\alpha = 1$ implies a restriction on ν , so that in the region C, Equation 18 should reduce to

$$\left\langle h^2 \right\rangle = s^{2\nu} f_{\left\langle h^2 \right\rangle}(sN^{-1}, v_2^*, a).$$
 (20)

A further choice of s of the order of N yields an asymptotic law

$$\left\langle h^2 \right\rangle \sim N^{2\nu}.$$
 (21)

The value of ν does not depend on $v_2(>0)$; therein lies the property of universality.

In this case, Kadanoff's transformation \mathcal{K}_s is proceeded as follows.

1. The interactions within a small loop, where the interaction points are at a distance (along the contour length) shorter than a, are included into the redefinition of l^2 and N in the scaled chain.

Therefore, the scaling value $l'^2 N'$, i.e. $s^{-2\nu} l^2 N$ (see Equation 13) is transformed by \mathcal{K}_s to

$$\mathcal{R}_{s}(l^{2}N) \equiv \mathcal{K}_{s}(s^{-2\nu}l^{2}N).$$
⁽²²⁾

As the transformation S_s is carried out first, then, in the scaled system, the interactions can be observed over contour lengths longer than the scaling cut-off $as^{-(2-\eta)\nu}$ (see Equation 13) but shorter than the initial cut-off a.

2. If two pairs of interactions in the scaled system are separated by a contour length shorter than a, these interactions are combined into a new effective binary interaction parameter

$$\mathcal{R}_{s}(v_{2}) \equiv \mathcal{K}_{s}\left(s^{(\epsilon-2\eta)\nu}v_{2}\right) \tag{23}$$

as well as higher-order interactions (Figure 5.3).

The scaling transformation S_s substantially reduces all the chain (see Figure 5.1). This is equivalent to looking at the chain from a longer distance when small details are indiscernible and the neighbouring interactions are seen as one effective interaction (see Figure 5.3).

Partition function 11 can be expanded as a series in powers of v_2 (cf. Equation 3.1-126)

$$G(\vec{h},N) = G_0(\vec{h},N) - v_2 \int_{a \le \tau_0 + a \le \tau_1 \le N} d\tau_0 \int d\tau_0 \int d\tau_0 G_0(\vec{r}_0,\tau_0) G_0(0,\tau_1-\tau_0) G_0(\vec{h}-\vec{r}_0,N-\tau_1) (24)$$

$$+ v_2^2 \int_{\exists a \le \tau_0 + \exists a \le \tau_1 + 2a \le \tau_2 + a \le \tau_3 \le N} d\tau_3 \int d\vec{r}_0 \int d\vec{r}_1 G_0(\vec{r}_0, \tau_0) \Big[G_0(0, \tau_1 - \tau_0) G_0(\vec{r}_1 - \vec{r}_0, \tau_2 - \tau_1) \\ \times G_0(0, \tau_3 - \tau_2) + G_0(\vec{r}_1 - \vec{r}_0, \tau_1 - \tau_0) G_0(0, \tau_2 - \tau_1) G_0(\vec{r}_0 - \vec{r}_1, \tau_3 - \tau_2) \\ + G_0(\vec{r}_1 - \vec{r}_0, \tau_1 - \tau_0) G_0(\vec{r}_0 - \vec{r}_1, \tau_2 - \tau_1) G_0(\vec{r}_1 - \vec{r}_0, \tau_3 - \tau_2) \Big] G_0(\vec{h} - \vec{r}_1, N - \tau_3) \\ + O(v_2^3),$$



Figure 5.3. Reduction of composite two-body transformations v_{2}^{2} to simple two-body ones v_2 . The small loops include the contour lengths less than a (in the scaling units) (Oono and Freed, 1981a) [Reprinted with permission from: Y.Oono, K.F.Freed. J. Chem. Phys. 75 (1981)993 1008. Copyright © 1981 American Institute of Physics]



Figure 5.4. Elements for constructing diagrams (Oono and Freed, 1981a) [Reprinted with permission from: Y.Oono, K.F.Freed. J. Chem. Phys. 75 (1981) 993-1008. Copyright © 1981 American Institute of Physics]

where the unperturbed distribution function in d-dimensional space is

$$G_0(\vec{r},n) = \int_{\vec{c}(0)}^{c(n)} C[\vec{c}] \exp\left[-\frac{d}{2l^2} \int_0^n \left[\dot{\vec{c}}(\tau)\right]^2 d\tau\right] = \left(\frac{d}{2\pi l^2 n}\right)^{d/2} \exp\left(-\frac{d \cdot \vec{r}^2}{2l^2 n}\right).$$
(25)

In terms of diagram elements shown in Figure 5.4, series 24 is written in the diagrammatic form (Figure 5.5).

The interaction points between solid G_0 and dotted v_2 lines are termed interaction vertices and integration is to be performed over all the interaction vertices \vec{r} and τ .



Figure 5.5. Diagrammatic representation of the perturbation series $G(\vec{h}, N)$ (Oono and Freed, 1981a) [Reprinted with permission from: Y.Oono, K.F.Freed. J. Chem. Phys. 75 (1981) 903 1008. Copyright © 1981 American Institute of Physics]

The points, where the straight line G_0 contact the dashed line of interaction v_2 , are called **interaction vertices**. The diagrams shown in Figure 5.5 imply integration over all the interaction vertices \vec{r} and τ .

To represent a renormalization or scaling transformation in the diagrammatic form, the following definitions are introduced.

- **Def. 1** A diagram is called **connected** if each of its part is connected to other parts, at least, by one polymer line or interaction line.
- **Def. 2** A subchain is a part of a polymer chain between some neighbouring interaction points along the chain.
- **Def. 3** An **irreducible** diagram (l-diagram) is the one which cannot be divided into two separate noninteracting pieces by cutting any subchain.
- **Def. 4** A short subchain is the one whose contour length is shorter than a (or any certain prescribed length).
- Def. 5 A locally-interacting irreducible diagram (LI-diagram) is an I-diagram, each subchain of which is short.
- **Def. 6** An effective r-body interacting diagram (an E-r diagram) is a connected diagram which
 - 1. has the properties of an 1-diagram;
 - 2. contains only short subchains;
 - 3. if all the interaction lines are cut, then it is separated into exactly r pieces.
- Def. 7 The successive connection of two diagrams means a connection of two parts of diagrams with only a polymer line.

Kadanoff's transformation means that the coarse-grained unperturbed distribution function G_0 is

 $\tilde{G}_0 = G_0 + \text{LI-diagrams} + \text{successively connected LI-diagrams};$ (26)

the coarse-grained two-body interaction v_2 is

 $\tilde{v}_2 = v_2 + E - 2 \quad \text{diagrams.} \tag{27}$

A coarse-graining procedure also produces "buildup" effective r-body (r > 2) interactions defined by

$$\tilde{v}_r = E - r$$
 diagrams $(r \ge 3)$. (28)

This situation corresponds exactly to Wilson-Fisher's theoretical field ε expansion (Wilson and Kogut, 1974).

Let us discuss the diagrammatic representation of \mathcal{R}_s . The transformation \mathcal{S}_s converts Equation 24 to

$$G(\vec{h}', N'; l') = G_0(\vec{h}', N'; l') - v'_2 \int_{a' \le \tau'_0 + a' \le \tau'_1 \le N'} d\tau'_1 \int d\vec{\tau}'_0 G_0(\vec{\tau}'_0, \tau'_0)$$
(29)

$$\times G_0(0,\tau_1'-\tau_0')G_0(h'-\vec{r}_0',N'-\tau_1')+O(\nu_2'^2)$$

The second term in the right-hand side is divided into two parts, subject to whether the distance between the interacting points along the contour length is less or larger than a:

$$-v_{2}' \left(\int_{\substack{a' \leq \tau_{1}' - \tau_{0}' \leq a \\ a' \leq \tau_{1}' \leq N'}} \int d\tau_{0}' d\tau_{1}' + \int_{a \leq \tau_{0}' + a \leq \tau' \leq N'} d\tau_{0}' d\tau_{1}' \right) \int d\vec{r}_{0}' G_{0}(\vec{r}_{0}', \tau_{0}') G_{0}(0, \tau_{1}' - \tau_{0}')$$

$$\times G_{0}(\vec{h}' - \vec{r}_{0,1}'N' - \tau_{1}').$$
(30)

Due to property 1 of Kadanoff's transformation, the contribution of the first integral must be included into renormalization of N and l. Hence, the renormalized "nonperturbed" distribution function \tilde{G}_0 , in the first order of v_2 , is defined by including the excluded volume interactions on small loops into G_0 :

$$\tilde{G}_{0}(\vec{h}', R(N); R(l)) = G_{0}(\vec{h}', N'; l') - v_{2}' \int_{\substack{a' \leq \tau_{1}' - \tau_{0}' \leq a \\ a' \leq \tau_{1}' \leq N'}} d\tau_{1}' \int d\vec{\tau}_{0}'$$
(31)

$$\times G_0(\vec{r}_0', \tau_0')G_0(0, \tau_1' - \tau_0')G_0(\vec{h}' - \vec{r}_0', N' - \tau_1') + O(v_2'^2).$$

If small loops (short subchains) are represented by a wavy line, then Equation 31 and the higher-order terms can be expressed by means of the diagrams shown in Figure 5.6.

There are two second-order interaction pairs; both can be separated as in Equation 30. These second-order terms (A-C in Figure 5.5) can be classified under 5 categories/classes $(V_>\tilde{G}_0, \tilde{G}_0, V_>^2, V_3, \text{ and } \tilde{V})$ as shown in Figure 5.7. The terms \tilde{G}_0 already comprise all the contributions with integration over all the interactions with two interaction points within short subchains. The second-order contributions of this type are shown in Figure 5.6 and presented in Figure 5.7 as the \tilde{G}_0 terms. The second-order terms $V_>^2$ constitute contributions where all the four interaction points are **a**t a distance (along the contour



Figure 5.6. Diagrammatic representation of the perturbation series of the renormalized unperturbed distribution function \tilde{G}_0 : notched line is \tilde{G}_0 , wavy lines are short subchains (Oono and Freed, 1981a) [Reprinted with permission from: Y.Oono, K.F.Freed. J. Chem. Phys. 75 (1981) 993-1008. Copyright © 1981 American Institute of Physics]



Figure 5.7. Classification of second-order diagrams. The contour length of straight lines \tilde{G}_0 between the interaction vertices is always more than the truncation *a* while, for wavy lines, \tilde{G}_0 is less than the truncation *a* in scaling units (Oono and Freed, 1981a) [Reprinted with permission from: Y.Oono, K.F.Freed. J. Chem. Phys. 75 (1981) 993-1008. Copyright © 1981 American Institute of Physics]

length) longer than a. The second-order terms $V_>\tilde{G}_0$ contain integration over one small loop and are the first-order terms in the perturbation series in the scaled interaction parameter. The V_3 terms denote the contribution of the three-body interactions into the two-body ones upon scaling.

Property 2 of Kadanoff's transformation requires including additional terms \tilde{V} as a part of new scaled interactions. These terms have interaction points from different interaction lines with the contour length less than a. An intuitive explanation of the terms \tilde{V} results from consideration of polymer conformations corresponding to the diagrams shown in Figures 5.8 and 5.9 (see section 2.6). The latter one compares different types of diagrams used in polymer theory and the theoretical field approach. Higher orders are


Figure 5.8. Correspondence between chain conformation in actual space (a) and diagrams (b) (Oono and Freed, 1981a) [Reprinted with permission from: Y.Oono, K.F.Freed. J. Chem. Phys. 75 (1981) 993-1008. Copyright © 1981 American Institute of Physics]

represented similarly.

The renormalized terms of the interaction $\mathcal{R}_s(v_2)$ are obtained from the row of diagrams (see Equation 27), which must have only two interaction points if all the wavy lines contract into a point (Figure 5.10). In this scaling procedure of structural elements \tilde{G}_0 and $\mathcal{R}_s(v_2)$, the new renormalized series of perturbation takes the form

$$G(\vec{h}', N'; l') = \tilde{G}_0(\vec{h}', N'; l')$$
(32)

$$-\int_{a\leq \tau_0'} d\tau_0' \int_{a} d\tau_1' \int_{a} d\vec{r}' \,\mathcal{R}_{\mathfrak{s}}(v_2) \tilde{G}_0(\vec{r}',\tau_0') \tilde{G}_0(0,\tau_1'-\tau_0') \tilde{G}_0(\vec{h}'-\vec{r}',N'-\tau_1') + O(\mathcal{R}_{\mathfrak{s}}(v_2)^2),$$

where $\mathcal{R}_s(v_2)$ collects all the contributions in the scaled interaction row which contains one interaction between any points separated (along the contour length) by a distance longer



Figure 5.9. Bringing different types of diagrams into agreement (Oono and Freed, 1981a) [Reprinted with permission from: Y.Oono, K.F.Freed. J. Chem. Phys. **75** (1981) 993–1008. Copyright © 1981 American Institute of Physics]: Oono and Freed (a), Yamakawa (1971) (b); actual conformations of molecular chains (c); φ^4 field diagrams contributing to the vertex function Γ^4 (d)

Figure 5.10. Diagrammatic series $\mathcal{R}_s(v_2)$. Wavy lines denote summation over all the local conformations of small loops (Oono and Freed, 1981a) [Reprinted with permission from: Y.Oono, K.F.Freed. J. Chem. Phys. 75 (1981) 993-1008. Copyright © 1981 American Institute of Physics]

than a in the scaled system. For example, the four terms in Figure 5.10, beginning with diagram A, originate from the four contributions \tilde{V} in Figure 5.7 (see also Figure 5.9).

Thus, with the aid of the renormalized distribution function G_0 (see Figure 5.6) and the renormalization parameter $\mathcal{R}_s(v_2)$ (see Figure 5.10), the perturbation series (see Figure 5.5) is representable as the diagrams shown in Figure 5.11.



Figure 5.11. Diagrammatic representation of the renormalization perturbation row through the first order in the renormalization interaction (see Figure 5.10): cross-dashed straight line is the unperturbed distribution function (see Figure 5.6), crosses denote the "interaction line" $\mathcal{R}_s(v_2)$ (see Figure 5.10) (Oono and Freed, 1981a) [Reprinted with permission from: Y.Oono, K.F.Freed. J. Chem. Phys. 75 (1981) 993-1008. Copyright © 1981 American Institute of Physics]

Further, Oono and Freed (1981a) derive analytical expressions for $\mathcal{R}_s(N^{-1})$ and $\mathcal{R}_s(v_2)$ in the $\varepsilon = 4 - d$ order. In calculations, the integrals are taken analytically in 4D space (d = 4):

$$\mathcal{R}_{s}(N^{-1}) = s^{2\nu} N^{-1} \left[1 - v_{2} \left(\frac{2}{\pi l^{2}} \right)^{2} 2\nu \ln s + \cdots \right],$$
(33)

$$\mathcal{R}_{s}(v_{2}) = s^{\varepsilon \nu} v_{2} \left[1 - 4v_{2} \left(\frac{2}{\pi l^{2}} \right)^{2} 2\nu \ln s + \cdots \right].$$
(34)

These expressions enable the flux lines in Figure 5.1 to be drawn explicitly. In the ε order, the constant η is equal to zero.

The fixed point of the interaction parameter $v_2^* \neq 0$ must obey

$$\mathcal{R}_s(v_2^*) = v_2^*,\tag{35}$$

which, in view of Equation 34, yields

$$v_2^* = \frac{\pi^2 l^4 \varepsilon}{32},\tag{36}$$

if two expansion terms of $s^{-\epsilon\nu}$ are taken: $a^x = 1 + x \ln a + \cdots$.

From Equation 33, the following expression for the fixed point emerges:

$$(N^*)^{-1} = (N^*)^{-1} s^{2\nu} \left(1 - \frac{1}{4} \varepsilon \nu \ln s + \cdots \right).$$
(37)

As this equality must be satisfied over all the domain of s, the solutions are $(N^*)^{-1} = 0$ or $(N^*)^{-1} = \infty$; the solution $N^* = 0$ is trivial and of no interest.

Linearization of Equation 33 near the fixed point $(N^*)^{-1} = 0$ and reversion of $\ln s$ into an exponent (which is correct in the ε order) lead to

$$\mathcal{R}_{s}(N^{-1}) = s^{2\nu - \epsilon\nu/4} N^{-1}. \tag{38}$$

On the other hand, in accordance with the previously chosen identification of ν (see Equations 19 and 20) in region C (see Figure 5.2), the asymptotic form

$$\mathcal{R}_s(N^{-1}) \simeq s N^{-1} \tag{39}$$

must be satisfied.

Comparing Equations 38 and 39, we get $2\nu - \varepsilon \nu/4 = 1$ and

$$\nu = \frac{1}{2} \left(1 + \frac{\varepsilon}{8} + \cdots \right). \tag{40}$$

Up to this point, our discussion has been confined to the simplest pair potential of the Equation 10 type, which is widely used in traditional theories of polymer chains (see subsection 3.1.1). Of course, when the attraction component becomes significant, such a potential is no longer correct.

If we apply more realistic potentials, especially, solid-core potential functions (see Figure 1.40b), the distribution function G can no longer be expanded into a φ -power series, as it was proved in the theory of real gas (Croxton, 1974). In this case, it is expanded into a Mayer-function series

$$f(\vec{r}) = \exp\left(-\frac{\varphi(\vec{r})}{kT}\right) - 1.$$
(41)

The details are given in (Yamakawa, 1971); here is the leading term of this series

$$G(\vec{h}, N) = G_0(\vec{h}, N) + \int d\tau_0 \int d\tau_1 \int d\vec{R}_0 \int d\vec{R}_1 G_0(\vec{h} - \vec{R}_0, N - \tau_0) f(\vec{R}_0 - \vec{R}_1)$$
(42)
 $\times G_0(\vec{R}_0 - \vec{R}_1, \tau_0 - \tau_1) G_0(\vec{R}_1, \tau_1) + \cdots$

The lowest non-trivial order does not require any change in the diagrammatic representation of the coarse-grained transformation of structural elements. Hence, the above analysis remains valid for this case, if only the dashed lines in the diagrams (Figures 5.6 and 5.10) are considered as f lines. Analysis shows that the scale change

$$f'(\vec{r}') = s^{2(2-\eta)\nu} f(s^{\nu}\vec{r}) \tag{43}$$

keeps the distribution function $G(\vec{h}, N)$ invariant after the transformation S_s .

Discuss an important case of a solid-core potential with Mayer's function

$$f(\vec{r}) = \begin{cases} -1, & |\vec{r}| < \sigma, \\ 0, & |\vec{r}| > \sigma, \end{cases}$$
(44)

where σ is the solid core diameter.

Owing to a formal similarity between series 42 and 24, the diagrammatic representation of \mathcal{K}_s , in the latter case, is identical to the diagrams shown in Figures 5.6 and 5.10 with the dashed lines to be interpreted as (-f).

On executing the calculational ε -order routine, we obtain

$$\mathcal{R}_{s}(N^{-1}) = s^{2\nu} N^{-1} \left(1 - \frac{4\sigma^{4}}{l^{4}} \nu \ln s + \cdots \right), \tag{45}$$

$$[\mathcal{R}_s(\sigma)]^4 = s^{\epsilon\nu} \sigma^4 \left(1 - \frac{16\sigma^4}{l^4} \nu \ln s \right) \quad (\eta = 0).$$

$$\tag{46}$$

Equation 46 provides the fixed point of the solid core diameter σ^* from the condition $\mathcal{R}_s(\sigma^*) = \sigma^*$:

$$\sigma^{\bullet} = \frac{l\varepsilon^{1/4}}{2}.\tag{47}$$

The series of G in f includes diagrams with three-body irreducible integrals. For instance, the diagram in Figure 5.12a is defined by



Figure 5.12. Parametrization of integration variables in a diagram containing an irreducible integral (a); the corresponding conformation in actual space with a three-body interaction (b); diagrammatic representation (c) (Oono and Freed, 1981a) [Reprinted with permission from: Y.Oono, K.F.Freed. J. Chem. Phys. 75 (1981) 993-1008. Copyright © 1981 American Institute of Physics]

$$\begin{split} &\int d\tau_0 \int d\tau_1 \int d\tau_2 \int d\vec{\tau}_0 \int d\vec{r}_1 \int d\vec{r}_2 G_0(\vec{r}_0, \tau_0) G_0(\vec{r}_1 - \vec{r}_0, \tau_1 - \tau_0) G_0(\vec{r}_2 - \vec{r}_1, \tau_2 - \tau_1) (48) \\ &\times G_0(\vec{h} - \vec{r}_2, N - \tau_2) f(\vec{r}_1 - \vec{r}_0) f(\vec{r}_2 - \vec{r}_1) f(\vec{r}_2 - \vec{r}_0) \\ &\cong \int_{2n \le \tau_0 + 2a \le \tau_1 + a \le \tau_2 \le N} d\tau_0 \int d\vec{\tau}_1 \int d\tau_2 \int d\vec{r}_0 G_0(\vec{r}_0, \tau_0) G_0(\vec{h} - \vec{r}_0, N - \tau_2) G_0(0, \tau_1 - \tau_0) \\ &\times G_0(0, \tau_2 - \tau_1) \int d\vec{x} \int d\vec{y} f(\vec{x}) f(\vec{y}) f(\vec{x} - \vec{y}). \end{split}$$

In perturbation theory for simple liquids, an **irreducible cluster integral** (see section 1.8)

$$v_3 = -\int d\vec{x} \int d\vec{y} f(\vec{x}) f(\vec{y}) f(\vec{x} - \vec{y})$$
(49)

is defined, which is always positive for the usual pair potentials.

With due account of conformations of actual chains (Figure 5.12b), the interactions, contributing to Equation 48, is a three-body one with its diagram of the type that shown in Figure 5.12c.

Thus, the next approximation level makes it necessary to take account of the v_3 interactions as well as the v_2 ones. The idea of a coarse-graining procedure of the structural elements remains as in the case considered above. The coarse-grained propagator \tilde{G}_0 in its diagrammatic form is shown in Figure 5.13, and the interaction line is in Figure 5.14.

Figure 5.13. Diagrammatic perturbation series for the scaling propagator \tilde{G}_0 in the presence of three-body interactions (Oono and Freed, 1981a) [Reprinted with permission from: Y.Oono, K.F.Freed, J. Chem. Phys. 75 (1981) 993-1008. Copyright © 1981 American Institute of Physics]

The corresponding expressions are derived by almost the same methods as in the case

Figure 5.14. Diagrammatic representation of the renormalization of v_2 in the presence of the three-body interactions. The wavy line denotes summation over all the possible local conformations of small loops (see Figures 5.6, 5.7, 5.10, etc.) (Oono and Freed, 1981a) [Reprinted with permission from: Y.Oono, K.F.Freed. J. Chem. Phys. 75 (1981) 993-1008. Copyright © 1981 American Institute of Physics]

of the two-body interaction. However, in the case of three-body interactions, the critical space dimension becomes $d_c = 3$. The space dimension d_c is called **critical** if it makes the parameter P limiting (marginal), i.e.

$$S_s P \sim P s^{\circ}. \tag{50}$$

By virtue of $d_c = 3$, the integrals in 3D space are evaluated analytically (Oono and Freed, 1981a)

$$\mathcal{R}_{\mathfrak{s}}(N^{-1}) = s^{2\nu} N^{-1} \left\{ 1 - 3 \left(\frac{3}{2\pi l^2} \right)^{3/2} \left[v_2 + 4 \left(\frac{3}{2\pi l^2} \right) v_3 \right] a^{1/2} s^{\nu} + \cdots \right\},\tag{51}$$

5.1. Renormalization of the conformational space

$$\mathcal{R}_{s}(v_{2}) = s^{(4-d)\nu} \left[v_{2} + 4v_{3} \left(\frac{3}{2\pi l^{2}} \right)^{3/2} + \cdots \right],$$
(52)

$$\mathcal{R}_{s}(v_{3}) = s^{(6-2d)\nu} v_{3}. \tag{53}$$

Near the critical point (or in the region C (see Figure 5.2)), ν is chosen so that $\mathcal{R}_s(N^{-1}) \simeq sN^{-1}$ (see Equation 39, cf. Equations 19, 20, and 39).

For Equation 51 to lead to asymptotic formula 39, the expression in the square brackets in Equation 51 must contain only terms proportional to $(\ln s)^n$, as $\mathcal{R}_s(N^{-1})$ is proportional to s. This implies that the coefficient by s^{ν} in the square brackets should vanish near the fixed point

$$v_2 + 4v_3 \left(\frac{3}{2\pi l^2}\right)^{3/2} = 0.$$
(54)

This condition automatically gives (see Equation 52)

$$\mathcal{R}_s(v_2^*) = 0, \tag{55}$$

i.e. the phenomenological two-body interaction asymptotically vanishes. The simultaneous tending to zero of the interchain interaction, which, in fact, is the second virial coefficient of osmotic pressure, is explained graphically in Figure 5.15. However, as



Figure 5.15. Renormalization of the interchain two-body interactions (cf. Figure 5.14, the second virial coefficient vanishes simultaneously with the renormalized v_2 (Oono and Freed, 1981a)) (Reprinted with permission from: Y.Oono, K.F.Freed. J. Chem. Phys. 75 (1981) 993-1008. Copyright © 1981 American Institute of Physics]

Oono and Freed (1981a) emphasize, Equations 51 and 52 are valid only after a sufficient number of renormalizations has been performed. Hence, v_2 and v_3 are not simple (original) interaction parameters.

In the lowest order of approximation, v_3 is obviously invariant in 3D space, but, in higher orders, Equation 53 contains a term proportional to $(-v_3^2)$, whence an asymptotic tendency $v_3^* \to 0$ follows.

Thus, there exists a temperature, at which a molecular chain **asymptotically** (i.e. on the whole) behaves in 3D space as a unperturbed (free) one, and this temperature can be defined as the θ temperature. Indeed, a joint consideration of Equations 51, 39, and 54 gives $\nu = 1/2$ at the θ temperature in 3D space.

Equation 54 points to the fact that the morphological state of a molecular coil is characterized by a balance among fine interaction effects at the θ temperature. Therefore, the calculation of nonuniversal quantities (such as the mean square end-to-end distance) must not neglect the higher-order terms. But, on performing a sufficient number of transformations \mathcal{R}_s , the renormalized multi-body interactions $\mathcal{R}_s^k(v_r)$ ($r \ge 4$, where v_r is the irreducible integral of r-body interactions) decay very quickly, and $\mathcal{R}_s^k(v_2) < 0$ and $\mathcal{R}_s(v_3) > 0$ turn out to be non-equivalent. As a result, at $k \to \infty$, $\mathcal{R}_s^k(v_2) \to 0$ and $\mathcal{R}_s^k(v_3) \to 0$.

It follows from the foregoing that the local effect of the attraction component manifests itself stronger than the global effect, i.e. the chain contracts on local portions ($v_2 < 0$). Another important circumstance follows. The problem of the θ state of a coil proves to be much more sophisticated than the problem of a self-avoiding walk on a lattice. And what is more, a study of conformations on a restricted chain fragment (eg, by neutron scattering) may lead to non-Gaussian local interactions in the θ point.

Most likely, there exist fine differences between the θ state of a molecular coil and the tricritical state in the Φ^6 Lagrangian theoretical field model (see the end of section 4.1) (Oono and Freed, 1981a).

In the most realistic case, the $r(\geq 3)$ -body irreducible integrals v_r should be included into the above considerations. The scaling transformation v_r upon action of S_s is performed in the same way and yields

$$S_s(v_r) = v_r' = s^{\nu[2r - d(r-1)]} v_r.$$
(56)

Then, with the known Kadanoff transformation $\mathcal{K}_s(v_m)$,

$$\mathcal{R}_s(v_m) = s^{\nu[2m-d(m-1)]} \mathcal{K}_s(v_m). \tag{57}$$

At d = 3, v_m $(m \ge 4)$ are renormalized to a constantly decreasing quantity. When enlarging, v_m (m > r) enters into $\mathcal{K}_s(v_r)$ in just the same way as it happens in the simplest case (see Equation 52 and Figure 5.16).

It is important that the v_4 , v_5 , ... influence such quantities as the θ temperature, the mean square end-to-end distance $\langle h^2 \rangle$, etc. Hence, macroscopic quantities in the θ state are very sophisticated functions of microscopic variables, and, at present, it is almost impossible to derive the microscopic interactions v_r from experimentally observed quantities.

k-tolerant walking (Malakis, 1976), i.e. random walking of structural elements on the lattice's sites with each site being permitted to be visited not more than k times, is an example of the manifestation of multi-body interactions.

Hence, 1-tolerant walking is a self-avoiding walk. For k-tolerant walking, $v_2 = v_3 = \cdots = v_k = 0$; $v_{k+1} > 0$.



Figure 5.16. Transformation of multi(4,5)-body interactions (a) into an effective threebody interaction (b) (small loops have their contour length shorter than the cut-off a in the scaling system) (Oono and Freed, 1981a) [Reprinted with permission from: Y.Oono, K.F.Freed. J. Chem. Phys. **75** (1981) 993-1008. Copyright © 1981 American Institute of Physics]

In the conventional two-parameter theory, $\nu = 0.5$ for $k \ge 2$. However, involving multi-body interactions means $\nu = 0.6$ (a self-avoiding walk) for every k in the limit $N \to \infty$.

The renormalization group approximation of conformational space can be performed, in principle, with any desired accuracy, but at present, calculations can be carried out near 4D space only. As a result, theoreticians use expansion in $\varepsilon = 4 - d$. This is obviously a temperature limitation of the method which is of rather general significance (Oono and Freed, 1981a).

Oono-Freed's scaling transformation proves to be a more general procedure than Kadanoff's transformation of spin blocks. Indeed, Kadanoff's original transformation combines block spins from neighbouring spins. Hence, in the lattice problem, the most important (with respect to interaction) nearest spins are spatially neighbouring spins as well (see Figure 2.43). In the polymer excluded volume problem, chain-distant segments may turn out to be close in space and, therefore, interact effectively. Therein lies the difference between Oono-Freed's renormalization and the previous renormalization schemes based on a literal analogy with the concept of spin blocks (the first g segments are combined into the first renormalization unit, the next g segments along the chain are into the second one, etc. until N source segments are converted into N/g renormalized ones, i.e. blobs). This is the very reason why de Gennes' and Gabey-Harel's renormalization group approximations cannot provide a higher accuracy than the first order in ε .

Oono and Freed (1981b) applied the renormalization procedure of conformational space to describe the dynamics of chains. They performed the scaling transformation of the complete diffusion equation with the free energy of a chain system written in terms of the model of a continuous chain. Besides, the static quantities in Equation 13, the friction coefficient of a chain fragment with its size less than a

$$\zeta_{a'}' = \zeta_a s^{(4-z-\eta)\nu} \tag{58}$$

is also subjected to the transformation, where z is a new, specifically dynamic index.

Kadanoff's transformation, besides static properties, provides for including the effect of hydrodynamic interactions between chain points separated by a contour length less than a' into the redefinition of ζ_a .

When renormalizing the functions in the diffusion equation, Oono and Freed (1981b) used the ideas of renormalization schemes for the dynamic properties of substance in the critical region. Analysis of this situation, as well as intuitive scaling (see section 4.5), has led to an equality between the static and dynamic indices

$$\nu = \tilde{\nu}$$
. (59)

The renormalization transformation in the problem of polymer chain conformations in the Kadanoff-Wilson fashion forms, in essence, a semigroup. A version of such transformations based on the true group (also called the renormalization group) was applied by Alkhimov (1991, 1994). This method provides an asymptotical solution of the exact equation for the end-to-end distance probability distribution of a self-avoiding trajectories. The following formula has been obtained for the critical index ν in *d*-dimension space:

$$\nu = \frac{1}{2} + \frac{\varepsilon}{12} + O(\varepsilon^2).$$

Klinskikh (1993) develops a continual model of a macromolecule with excluded volume with the variational principle of the free energy of a molecular chain underlying. As a zeroth approximation, the continual integral of Feynmann's model for polarons in the solid body has been taken. The paper reports calculation of the free energy and the expansion coefficient of a molecular chain and the static and dynamic scattering form factors.

5.1.2. Renormalization with dimensional regularization

Two important consequences follow from the fact of the atomic scale of length a being indistinguishable in experimentally observed quantities (Oono and Freed, 1981a; Oono et al., 1981). First, the macroscopic properties do not depend on the existence of the natural minimum on the molecular scale a, so, they must be well-defined in the limit $a \rightarrow 0$. In the excluded volume problem of a molecular coil, the limit $a \rightarrow 0$ should be regarded as a rejection of the consideration how a segment interacts with itself (the self-excluded volume). Second, there is no natural unit length in macroscopic theory, and such a length L can be chosen arbitrarily regardless of the microscopic natural unit of length a^1 .

Gell-Mann-Low-Oono-Ohta-Freed's renormalization approximation (Oono et al., 1981) provides a method of constructing, in terms of a microscopic model, such macroscopic quantities which are well-defined in the limit $a \rightarrow 0$.

The scaling invariance of microscopic theory to the choice of the macroscopic unit of length L follows, which, together with the renormalization relationships of well-defined macroscopic quantities, leads to scaling laws.

Oono, Ohta, and Freed have developed a renormalization method for conformational space of Gell-Mann and Low's (1954) type for the excluded volume problem. In a number of cases, this approach proves to be more effective than Kadanoff-Wilson's approximation (see subsection 5.1.1); it provides a higher accuracy of the calculation of such quantities as the end-to-end vector distribution function, the scattering function, the conformation of a macromolecule as a function of polymer concentration, etc.

As experimentally observed quantities must be well-defined in the limit $a \to 0$, the series of perturbation theory for macroscopic quantities must be regular at $\varepsilon = 0$. However, the microscopically-calculated (simple) series of perturbation theory are not regular at $\varepsilon = 0$.

The essence of the renormalization with dimensional regularization is in introduction of some relationships between microscopic and macroscopic quantities to reduce (absorb) these singularities and to make macroscopic quantities regular in ε at $\varepsilon = 0$.

Polymer theory classifies the following quantities with macroscopic Q; the degree of polymerization N (the contour chain length), the dimensionless excluded volume parameter per segment u, and the unit length L for the chain scale to produce dimensionless quantities. The experimental results are therefore presented as Q(N, u, L, ...).

On the other hand, microscopic theories originate from a model of the system under study, which involves microscopic parameters. For example, the model of a continuous molecular chain uses the contour chain length N_0 ($N_0 = n_0 l$), the excluded volume parameter v_0 , and the minimal scale length a, which can be identified with the length of a chain segment. The microscopic model of a polymer chain with excluded volume is defined by a bare (i.e. non-renormalized) dimensionless Hamiltonian to be derived from the end-to-end distance distribution function (Equations 3.1–204,-205)

$$G_{B}(N_{0},\vec{h},v_{0},a) = \int_{\vec{r}(0)=0}^{\vec{r}(N_{0})=\vec{h}} D[\vec{r}(s)] \exp\left\{-\mathcal{H}_{a}\left[\vec{r}(s)\right]\right\}.$$
(60)

For the Hamiltonian to be dimensionless in d-dimensional space, the following transformations are carried out: the expression for G_B (Equation 3.1-205) is written in ddimensional space (see Equation 11); the pair potential φ (Equation 3.1-202) is approximated with the δ function (Equations 3.1-194, 195); a simple renaming $s \equiv \tau$, $\Lambda \equiv l$, and a new variable

$$\vec{c}(\tau) = \left(\frac{d}{l}\right)^{1/2} \vec{r}(\tau) \tag{61}$$

¹This circumstance is also reflected in the early versions of Flory-Huggins' theory by an arbitrary choice of segments "to fit the solvent". Editor's comment

are introduced, where $\vec{r}(\tau)$ is the segment coordinates in space.

Then, the dimensionless bare Hamiltonian has the form (Kosmas and Freed, 1978)

$$\frac{\mathcal{H}_{a}(\vec{r})}{kT} = \frac{1}{2} \int_{0}^{N_{0}} [\vec{c}(\tau)]^{2} d\tau + \frac{1}{2} v_{0} \int_{0}^{N_{0}} d\tau \int_{0}^{N_{0}} d\tau' \, \delta\left[\vec{c}(\tau) - \vec{c}(\tau')\right]. \tag{62}$$

Here $\vec{c}(\tau)$ is the conformation of a continuous chain in *d*-dimensional space with the contour variable $\tau \in [0, N_0], \vec{c}(\tau) \equiv d\vec{c}(\tau)/d\tau$;

$$v_0 = \beta l^{-2} \left(\frac{l}{d}\right)^{-d/2},\tag{63}$$

where β has the meaning of excluded volume (see Equations 3.1–195 and 1.8–9).

Then, the theory introduces an arbitrary scale length L which will later play a significant role in renormalization group transformations.

The dimensionality of the model parameters is expressed through L, using the condition of the Hamiltonian 62 being dimensionless

$$[N_0] = L, \quad [\vec{c}] = L^{1/2}, \quad [v_0] = L^{d-2-d/2} = L^{d/2-2} = L^{-\epsilon/2}, \tag{64}$$

where $\varepsilon = 4 - d$.

The macroscopic chain length N is proportional to the microscopic one

 $N = Z_2 N_0. \tag{65}$

The microscopic v_0 and macroscopic v excluded volume parameters are converted into dimensionless quantities by means of

$$u_0 = v_0 L^{\epsilon/2},\tag{66}$$

$$u = v L^{c/2}.$$
(67)

Microscopic theories lead to an expression for $Q_B(N_0, v_0, a)$, which is, generally, not a true macroscopic quantity and contains many microscopic details insignificant in the long-wave macroscopic limit. In particular, this enables the pair interaction potential in the model Hamiltonian to be replaced by the short-range δ function.

The quantity Q_B is related to the corresponding renormalized quantity Q by the renormalization factor Z_B (eg. see Equation 65) $Q = Z_Q Q_B$. These factors Z_Q play a key role in theory, as their analytical form is chosen (defined) from the condition of absorption (climination) of divergences in Q_B . To apply the perturbation method, the microscopic quantity Q_B should be represented as a series in powers of v_0 , i.e.

$$Q_{B} = \sum_{m=0}^{\infty} Q_{m}^{o} v_{0}^{m}.$$
(68)

However, in $d(\neq 4)$ -dimensional space, v_0 is not dimensionless, as it follows from Equation 64. In this case, expansion into a series should be performed in powers of the dimensionless parameter $v_0 N_0^{\varepsilon/2}$. However, in the long-chain limit $N_0 \to \infty$ for $v_0 > 0$ and $\varepsilon > 0$, the parameter $v_0 N_0^{\varepsilon/2}$ turns out to be large. Indeed, the parameter $v_0 N_0^{\varepsilon/2}$ can be associated with the similar dimensionless excluded volume parameter z_d from parametric theory in *d*-dimensional space (Equation 3.1-153)

$$z_d \cong \beta l^{-d} N_0^{\epsilon/2}.$$

To overcome these difficulties, Q_B is expanded into a series near d = 4 ($\varepsilon = 0$) by ε expansion, i.e. is represented as a double series in v_0 and ε

$$Q_B = \sum_{m,n} Q^o_{m,n} v^m_0 \varepsilon^n, \tag{69}$$

where v_0 is the dimensionless (at d = 4) interaction constant, the coefficients $Q_{m,n}^{\alpha}$ are calculated in 4D space; a continuous variation of the space dimension d is assumed.

On elimination of the contributions of segment self-interaction, the coefficients of series 69 do not contain divergencies while $\varepsilon > 0$, even in the limit $a \to 0$. It has been found, however, that at $d_c = 4$ ($\varepsilon = 0$), i.e. at the critical dimension of the excluded volume effect of a polymer chain, Q_m° contains numerous terms with $\ln a$ which diverge at $a \to 0$ even after subtraction of the self-interaction. This means that the coefficients Q_m° $(a \to 0)$ have singularities at $\varepsilon = 0$, and the series of Q_m° in ε ,

$$Q_m^{\circ} = \sum_n Q_{m,n}^{\circ} \varepsilon^n \tag{70}$$

has its principal part, i.e. the terms with a negative power of n. Conversely, if series 70 has its principal part for $a \to 0$, Q_m^o ($\varepsilon = 0$) diverges in the limit $a \to 0$.

The macroscopic relationships for Q are assumed to be expandable into an asymptotic series

$$Q = \sum_{m} Q_m v^m, \tag{71}$$

which, in turn, must be expanded in powers of the dimensionless quantity $vN^{\epsilon/2}$; so, Equation 71 contains the same difficulty as Equation 68. Therefore, a double series in ε and v is introduced

$$Q = \sum_{m,n} Q_{m,n} v^m \varepsilon^n.$$
⁽⁷²⁾

Macroscopic quantities are considered to be well-defined in the limit $a \to 0$ at a certain dimension d. This basic statement of theory presumes Q_m to be regular at $\varepsilon = 0$, i.e.

$$Q_m = \sum_n Q_{m,n} \varepsilon^n \tag{73}$$

has no principal part.

The limiting procedure $a \rightarrow 0$ proves to be very unnatural in the macroscopic context; so it comes as no surprise that there emerge many divergences. However, there must not be divergences in this limit in macroscopic theory, as long-wave properties do not depend on *a* by definition. Therefore, the divergences must be absorbed in the relationships between the microscopic and macroscopic quantities. As the divergences $a \to 0$ are found when the principal parts in the c expansion of Q_m° appear, the very principal parts must be absorbed in the relationships between the microscopic and macroscopic quantities. Therein lies the method of dimensional regularization proposed by t'Hooft and Veltman (1972) in field theory.

To have an example, let us discuss $G(N, \vec{h}, v; L)$ (the macroscopic non-normalized endto-end vector distribution function), where L is an arbitrary scale length (Oono et al., 1981).

The series of perturbation theory (Equation 69) provides the definition for the bare distribution function $G_B(N_0^{-1}, \vec{h}, v_0; a)$ in its expansion in v_0 and ε .

Provided that they are normalized, G and G_B produce the distribution function of \vec{h} , i.e. they must be proportional to each other. The factor of proportionality Z is chosen so that some remaining principal parts in the ε expansion are absorbed. Therefore, Z, Z₂, and the relation v vs v_0 lead to micro-macro relationships, which absorb all the principal parts of the bare perturbation series, if there is a macroscopic distribution function with two macroscopically-controllable parameters, viz., the chain length and the excluded volume of a segment. Thus,

$$G(N^{-1}, \vec{h}, v; L) = \lim_{a \to 0} Z^{-1} G_B(N_0^{-1}, \vec{h}, v_0; a).$$
(74)

In view of Equation 65, we rewrite it as

$$G(N^{-1}, \vec{h}, v; L) = \lim_{a \to 0} Z^{-1} G_H(Z_2 N^{-1}, \vec{h}, v_0; a).$$
(75)

The ability of Z to eliminate the remaining principal part from series 72 should be verified with respect to each power of v.

To calculate Z, Z_2 , and v, and to demonstrate the absence of the principal part in the ε expansion of Equation 73, the series of perturbation theory are employed.

We write the dimensionless interaction constant introduced in Equations 66 and 67

$$u = v L^{\varepsilon/2}, \quad u_0 = v_0 L^{\varepsilon/2}.$$

Multiplying Equation 75 by Z yields

$$ZG(Z_2^{-1}N_0^{-1}, \vec{h}, u; L) = G_B(N_0^{-1}, \vec{h}, u_0; a)$$
(76)

in the limit $a \to 0$. The main property of G_B must be its invariance to the choice of L. Then, it follows from Equation 76 that

$$L \left. \frac{\partial}{\partial L} \right|_{v_0; N_0, \alpha} G_B(N_0^{-1}, \vec{h}, u_0; \alpha) = 0$$
(77)

or

. .

$$L \left. \frac{\partial}{\partial L} \right|_{v_0; N_0, a} ZG(Z_2^{-1} N_0^{-1}, \vec{h}, u; L) = 0$$
(78)

Having noticed that u, Z, and Z_2 depend on L, we rewrite Equation 78 as

$$\left(L\frac{\partial}{\partial L} + L\frac{\partial u}{\partial L}\frac{\partial}{\partial u} + L\frac{\partial \ln Z}{\partial L} - L\frac{\partial \ln Z_2}{\partial L} + \frac{\partial}{\partial t}\right)G(t,\vec{h},u;L) = 0,$$
(79)

where $t \equiv N^{-1}$.

This is a renormalization group equation which involves the principal statement that the macroscopic scale L is chosen arbitrarily and independent of the microscopic scale.

The first point of the renormalization transformation (Amit, 1978) is determined from the condition

$$L \left. \frac{\partial u}{\partial L} \right|_{u=u^*} = 0, \tag{80}$$

where u^* is the fixed point of the interaction constant (see the conclusion in section 2.5). Introducing then

$$A \equiv L \left. \frac{\partial \ln Z}{\partial L} \right|_{u=u^*} \tag{81}$$

and

$$B \equiv L \left. \frac{\partial \ln Z_2}{\partial L} \right|_{u=u^*},\tag{82}$$

we transform Equation 79 into

$$\left(L\frac{\partial}{\partial L} + A - B + \frac{\partial}{\partial t}\right)G(t, \vec{h}, u^*; L) = 0.$$
(83)

The general solution of Equation 83 is

$$G(t, \vec{h}, u^*; L) = L^{-A} F(\vec{h}, Lt^{1/B}),$$
(84)

where F is a function which is unknown but allows being well-defined, A and B are constants to be determined by Equations 81 and 82.

To obtain the scaling relationship for G, Equation 84 should be combined with dimensional analysis of G in the following way. For the model Hamiltonian (Equation 62), G_B is represented as

$$G_B(N_0^{-1}, \vec{h}; v_0; a) = \int_{\vec{c}(0)}^{\vec{c}(N_0)} D[\vec{c}] \exp\left[-\mathcal{H}_a(\vec{c})\right],$$
(85)

where D is the standard measure of a set of conformations (see Equation 3.1-189).

The dimensionality of different variables and parameters follows from Equations 62-64:

$$[N] = L, \quad [G] = L^{-d/2}. \tag{86}$$

Hence, conventional dimensional analysis means that, for any s > 0, G satisfies the relationship $(t \equiv N^{-1})$

$$G(t, \vec{h}, u; L) = s^{-d/2} G(st, s^{-1/2} \vec{h}, u; s^{-1} L).$$
(87)

Assuming $u \rightarrow u^*$ in Equation 87 and including Equation 84, one can write

$$G(t, \vec{h}, u^{*}; L) = s^{-d/2} \left(s^{-1}L \right)^{-A} F(s^{-1/2}\vec{h}, s^{-1}L(st)^{1/B})$$

$$= s^{-d/2+A} L^{-A} F(s^{-1/2}\vec{h}, Lt^{1/B}s^{1/B-1}).$$
(88)

Choosing s so that the condition

$$Lt^{1/B}s^{1/B-1} = 1 (89)$$

is satisfied, let us transform Equation 89 to

$$G(t, \vec{h}, u^*; L) = L^{-B(d/2 - A)/(B - 1)} N^{-(d/2 - A)/(B - 1)} f\left(\frac{\vec{h}}{N^{1/2(1 - B)}}, L^{B/2(B - 1)}\right),$$
(90)

where f is a function which is unknown but permits being well-defined.

The relationships between A and B, and the usual (standard) indices are derived as follows. The mean square end-to-end distance is written as

$$\left\langle h^{2} \right\rangle_{u^{*}} = \frac{\int d\vec{h} \, |\vec{h}|^{2} G(t, \vec{h}, u^{*}; L)}{\int d\vec{h} \, G(t, \vec{h}, u^{*}; L)} \sim N^{1/(1-B)} \cong N^{2\nu}, \tag{91}$$

whence, in view of Equation 82, we obtain

$$B = \frac{2\nu - 1}{2\nu} \cong L \left. \frac{\partial \ln Z_2}{\partial L} \right|_{u=u^*}.$$
(92)

The index γ is introduced similarly to determine the N dependence of the total number of conformations

$$c_N \sim N^{\gamma - 1} \mu^N \sim \int d\vec{h} \, G(\vec{h}, N),\tag{93}$$

where μ is a constant not to be discussed hereinafter.

Substituting Equations 90 and 92 into Equation 93, we obtain

$$A = \frac{\gamma - 1}{2\nu} \equiv L \left. \frac{\partial \ln Z}{\partial L} \right|_{u = u^*}$$
(94)

as a way to determine γ from Z. Substituting Equations 92 and 94 into Equation 90, we obtain a scaling law (for Z = 1)

$$G(N,\vec{h};u^*) = N^{\gamma-\nu d-1} f\left(\frac{\vec{h}}{N^{\nu}}\right).$$
(95)

The distribution function $G(N, \vec{h}, u; L)$ must be finite in u, and the dimensionless quantities Z and Z_2 are defined as series in u, i.e.

$$Z = 1 + \hat{A}u + O(u^2), \tag{96}$$

$$Z_2 = 1 + \hat{B}u + O(u^2), \tag{97}$$

where \hat{A} and \hat{B} are dimensionless quantities to be determined. They can be calculated with the help of Equations 65, 96, and 97 from the expansion series for G_B , which is well-defined in the limit $a \to 0$

$$G_B(N_0, \vec{h}, v_0; 0) = G_0(N_0, \vec{h}) - v_0 \int_0^{N_0} d\tau \int_0^{\tau} d\tau' \int d\vec{r}$$

$$\times G_0(N_0 - \tau, \vec{h} - \vec{r}) G_0(\tau - \tau', 0) G_0(\tau', \vec{r}) + O(v_0^2);$$
(98)

the free $G_0(N_0, \vec{h})$ is presumed to relate to a Gaussian chain

$$G_0(N_0, \vec{h}) = G_B(N_0, \vec{h}, 0; 0) = (2\pi N_0)^{-d/2} \exp\left(-\frac{h^2}{2N_0}\right).$$
(99)

On integration with respect to \vec{r} , the second summand in Equation 98 is written as

$$-v_0 \int_0^{N_0} d\tau \int_0^{\tau} d\tau' G_0 \left[N_0 - (\tau - \tau'); \vec{h} \right] G_0(\tau - \tau', 0).$$
(100)

If we introduce a variable $x = \tau - \tau'$, then Equation 98 is rewritten as

$$G_B(N_0, \vec{h}, v_0; 0) = G_0(N_0, \vec{h}) - u_0 L^{-\epsilon/2} I,$$
(101)

where the order of integration can be changed which yields

$$I = \int_{0}^{N_0} dx \, (N_0 - x) G_0(\vec{h}, N_0 - x) G_0(0, x). \tag{102}$$

This integral, on replacement of the variable $z = x/(N_0 - x)$, is transformed into

$$I = (2\pi)^{-d} N_0^{2-d} e^{-\alpha} G(\alpha), \tag{103}$$

where $\alpha = h^2/2N_0$, and

$$G(\alpha) = \int_{0}^{\infty} dz \, (1+z)^{1-\varepsilon} z^{\varepsilon/2-2} e^{-\alpha z}.$$
(104)

Integration by parts (t'Hooft and Veltman, 1972; Oono et al., 1981) gives

$$G(\alpha) = \frac{2}{2-\varepsilon} \left\{ \left[-(z+1)^{1-\varepsilon} z^{\varepsilon/2-1} e^{-\alpha z} \right] \Big|_{0}^{\infty} + (1-\varepsilon) J(\varepsilon,\alpha) - \alpha K(\varepsilon,\alpha) \right\},$$
(105)

where

$$J(\varepsilon,\alpha) = \int_{0}^{\infty} (z+1)^{-\varepsilon} z^{\varepsilon/2-1} e^{-\alpha z} dz, \qquad (106)$$

$$K(\varepsilon,\alpha) = \int_{0}^{\infty} (z+1)^{1-\varepsilon} z^{\varepsilon/2-1} e^{-\alpha z} dz.$$
(107)

The first summand in Equation 105 is infinite. This divergence arises from segment self-interactions $(z \rightarrow 0)$, so the summand can be just rejected, which means the elimination of segment self-interactions. This operation corresponds to subtraction of mass in field theories (Amit, 1978).

A more standard argument of dimensional regularization is in the following. If d is made rather small (d < 2), then the first term in Equation 105 vanishes. If the expression is then analytically extended to d > 2, we obtain

$$G(\alpha) = \left(1 + \frac{\varepsilon}{2}\right) \left[(1 - \varepsilon)J(\varepsilon, \alpha) - \alpha K(\varepsilon, \alpha)\right].$$
(108)

The integrals J and K can be expanded into a series in ε

$$J(\varepsilon, \alpha) = \frac{2}{\varepsilon} - (\hat{\gamma} + \ln \alpha) + O(\varepsilon), \qquad (109)$$

$$K(\varepsilon, \alpha) = \frac{2}{\varepsilon} + \frac{1}{\alpha} - (\hat{\gamma} + \ln \alpha) + O(\varepsilon), \qquad (110)$$

where $\hat{\gamma} \approx 0.5772$ is Euler's constant.

To calculate ν and γ in the ε order, we need the principal parts of Equations 109 and 110 only. Hence,

$$G(\alpha) = \frac{2}{\varepsilon}(1-\alpha) - 2 - \alpha + (\alpha - 1)(\hat{\gamma} + \ln \alpha) + O(\varepsilon).$$
(111)

On the other hand, using Equations 96 and 97 in Equation 99, a u expansion results (hereinafter, $\alpha = h^2/2N$)

$$G_0(Z_2^{-1}N,\vec{h}) = G_0(N,\vec{h}) \left[1 - \hat{B}u \left(\frac{\varepsilon - 4}{2} + \alpha \right) + \cdots \right], \tag{112}$$

so it follows from Equations 76, 103, and 101 that

$$G(N,\vec{h}) = (1 - \hat{A}u + \cdots)G_0(N,\vec{h})$$

$$\times \left[1 - \hat{B}u\left(\frac{\varepsilon - 4}{2} + \alpha\right) - uL^{-\epsilon/2}\frac{N^{\epsilon/2}}{(2\pi)^{2-\epsilon/2}}G(\alpha)\right].$$
(113)

The quantities \hat{A} and \hat{B} are determined from the condition of lack of the principal part in Equation 113 in the ε expansion, i.e. the term with the *u* power. This just means that all the singularities in microscopic theory must be absorbed by micro-macro relationships. Therefore,

$$\hat{A} - 2\hat{B} + \alpha\hat{B} + \frac{1}{(2\pi)^2} \cdot \frac{2}{\varepsilon} (1 - \alpha) = 0.$$
(114)

This equation defines α , and its solution is

$$\hat{A} = \hat{B} = \frac{1}{2\pi^2 \varepsilon},\tag{115}$$

which drives function 113 to the form

....

$$G(N,\hat{h}) = \left(\frac{1}{2\pi N}\right)^2 e^{-\alpha} \left(1 + \frac{\varepsilon}{2} \ln 2\pi N\right)$$

$$\times \left\{1 + \frac{u}{(2\pi)^2} \left[1 + \alpha + (1 - \alpha)(\hat{\gamma} + \ln \alpha) - (1 - \alpha)\ln\left(\frac{2\pi N}{L}\right)\right]\right\}.$$
(116)

The relationship between u and u_0 follows from another condition.

The distribution function $G^{(2)}(M, \vec{r}, N, \vec{h}, v; L)$ is introduced to fix a point inside the chain M, \vec{r} , in addition to the end-to-end vector

$$G^{(2)}(M, \vec{r}, N, \vec{h}, v; L) = Z_{(2)}^{-1} G_B^{(2)}(Z_2^{-1}M, \vec{r}, Z_2^{-1}N, \vec{h}, v_0; a),$$
(117)

$$G_B^{(2)}(M_0, \vec{r}, N_0, \vec{h}, v_0; a) = \int_{\vec{c}(0)}^{\vec{c}(N_0)} D[\vec{c}]\delta[\vec{c}(M_0) - \vec{r}] \exp[-\mathcal{H}_a(\vec{c})].$$
(118)

If we derive $G_B^{(2)}$ in the same way of perturbation theory as G_B and consider the terms with and without \vec{r} and \vec{h} in the expansion, we obtain three independent conditions to eliminate the principal parts in the ε expansion of the constant and the \vec{r} (or \vec{h})-dependent part, which can be used for calculating $Z_{(2)}$, Z_2 and v.

The calculation of Z, Z_2 , and v can be performed immediately with the help of $G^{(2)}$, but preliminary calculation of G provides a simpler way to determine Z and Z_2 , as simple as the introduction of the dimensional regularization methods.

Analysis of the perturbation series enables the terms to be rearranged as

$$G_B^{(2)}(M_0, \vec{r}, N_0, \vec{h}, v_0; a) = G_B(M_0, \vec{r}, v_0; a) G_B(N_0 - M_0, \vec{h} - \vec{r}, v_0; a)$$
(119)

+ some remaining terms, which involve the terms with their diagrammatic representation (Figure 5.17), and the terms not contributing with respect to v. The diagram b in Figure 5.17 has its analytical expression

$$v_{0}^{2} \int_{0}^{M_{0}} dn_{1} \int_{0}^{N_{0}} dn_{2} \int d\vec{r}_{1} \int d\vec{\rho} \int dx \int^{n_{1}} dx \int^{M_{0}-n_{1}} dy G_{0}(\vec{r}_{1}+\vec{\rho},n_{1})G_{0}(\vec{\rho},x)G_{0}(\vec{\rho},y)$$
(120)

$$\times G_{0}(\vec{r}-\vec{r}_{1}-\vec{\rho},M_{0}-y-n_{1}-x)G_{0}(\vec{r}_{1}-\vec{r},n_{2}-M_{0})G_{0}(\vec{h}-\vec{r}_{1},N_{0}-n_{2}),$$

where x and y denote the integrals of the contour line between the neighbouring interaction vertices, $\vec{\rho}$ is the spatial vector between them, and $\vec{\rho} + \vec{r_1} = \hat{\rho}$.

The principal part of the ε expansion 120 arises from the contributions due to the local interactions arising from small values of x and y. Therefore, to extract the singular part of Equation 120 in the ε order, one could, for example, expand Equation 120 in $\vec{\rho}^2$ and



Figure 5.17. Diagrams for calculation of v_0 in the order v_0^2 : in Oono-Freed's (b, left) and Yamakawa's (b, center) notations, and the pattern of a chain conformation in actual space (b, right) (cf. Figure 5.9). Diagrams b and c are of the second order of v_0 : their singular parts are identical and defined by Equations 5.1-121,-122 (Oono et al., 1981) [Reprinted with permission from: Y.Oono, T.Ohta, K.F.Freed. J. Chem. Phys. 74 (1981) 6458–6466. Copyright © 1981 American Institute of Physics]

x powers. Involvement of higher powers of x, y, or $\vec{\rho}^2$ weakens the singularity of the integrand near x = y = 0. Moreover, the upper limit of integration over x and y does not affect the singularities with respect to ε , so these upper limits can be chosen arbitrarily. Hence, the singular part of Equation 120 has the form

$$v_0^2 I(M_0 \vec{r}, N_0 \vec{h}) \int d\vec{\rho} \int_0^1 dx \int_0^1 dy \, G_0(\vec{\rho}, x) G_0(\vec{\rho}, y), \tag{121}$$

where

$$I(M_0\vec{r}, N_0\vec{h}) = \int_0^{M_0} dn_1 \int_{M_0}^{N_0} dn_2 \int d\vec{r}_1 G_0(\vec{r}_1, n_1)$$
(122)

$$\times G_0(\vec{r}-\vec{r}_1, M_0-n_1)G_0(\vec{r}_1-\vec{r}, n_2-M_0)G_0(\vec{h}-\vec{r}_1, N_0-n_2)$$

Calculations show that the singular parts of the other three second-order diagrams (see Figure 5.17c) coincide with Equation 121.

The remaining terms in Equation 119 can be written in the u_0^2 order up to non-singular terms as

$$I(M_0\vec{r}, N_0\vec{h}) \left[u_0 - 4u_0^2 \int d\vec{\rho} \int_0^1 dx \int_0^1 dy \, G_0(\vec{\rho}, x) G_0(\vec{\rho}, y) \right]$$
(123)

(i.e. the diagrams can be practically eliminated) + the singular terms already absorbed by Z and Z_2 (see Equations 96 and 97).

Let u_0 be expanded as

$$u_0 = u - Du^2 + \cdots \tag{124}$$

We are able to choose D so that the principal part appearing in Equation 123 is absorbed in all the orders with respect to u. The principal part of the integral in Equation 123 is found to be

$$\left[\int d\rho \int_{0}^{1} dx \int_{0}^{1} dy \, G_{0}(\rho, x) G_{0}(\rho, y)\right]_{s} = \frac{1}{(2\pi)^{2}} \cdot \frac{2}{\varepsilon}.$$
(125)

The requirement that there should be no principal part in Equation 123 leads to

$$-Du^{2} - 4u^{2} \left(\frac{1}{2\pi}\right)^{2} \frac{2}{\varepsilon} = 0.$$
(126)

Substituting the solution of this equation with respect to D to Equation 124, we get

$$u_0 = u + \frac{2}{\varepsilon \pi^2} u^2 + O(u^3).$$
(127)

Using the rule of differentiating a composite function

$$\left(\frac{\partial u}{\partial L}\right)_{v_0,a} = \left(\frac{\partial u}{\partial u_0}\right)_{v_0,a} \left(\frac{\partial u_0}{\partial L}\right)_{v_0,a},\tag{128}$$

one can derive

$$L \left. \frac{\partial u}{\partial L} \right|_{v_0, a} = \frac{\varepsilon}{2} \left(\frac{\partial \ln u_0}{\partial u} \right)^{-1} = \frac{1}{2} \left[\varepsilon u - \frac{2}{\pi^2} u^2 + O(u^3) \right].$$
(129)

The non-trivial fixed point, according to Equation 80, is defined as

$$u^* = \frac{\varepsilon \pi^2}{2}.\tag{130}$$

Applying the rule

$$L\left(\frac{\partial}{\partial L}\right)_{u=u^*} = L\left(\frac{\partial u}{\partial L}\right)_{u=u^*} \left(\frac{\partial}{\partial u}\right)_{u=u^*}$$
(131)

to define Equations 81 and 82, and to expand Equations 96, 97, 127, and 130, Oono et al. (1981) have obtained

$$A = \frac{1}{2}\varepsilon u^* \hat{A} = \frac{\varepsilon}{8},\tag{132}$$

$$B = \frac{1}{2}\varepsilon u^{\varepsilon} \hat{B} = \frac{\varepsilon}{8}.$$
(133)

Substitution of Equations 132 and 133 into Equations 92 and 94 leads to the following results in the ε order:

$$\nu = \frac{4}{8 - \varepsilon},\tag{134}$$

$$\gamma = 1 + \frac{\varepsilon}{8 - \varepsilon},\tag{135}$$

which agree well with other independent calculations.

Crossover region of solvent strength

The renormalization method for the conformational space of polymer chains has been applied to calculate the characteristic quantities in the crossover region, i.e. in the intermediate area between the Gaussian behaviour and the limiting case of interaction of segments with excluded volume: a self-avoiding walk (Oono and Freed, 1982).

Basic renormalization group equation 79 is written in a new notation

$$\left(L\frac{\partial}{\partial L} + \beta(u)\frac{\partial}{\partial u} + \gamma_1(u) + \gamma_2(u)N\frac{\partial}{\partial N}\right)G(\vec{h}, N, u; L) = 0,$$
(136)

where

$$\beta(u) \equiv L \left. \frac{\partial u}{\partial L} \right|_{N_0, u_0, u}, \tag{137}$$

$$\gamma_1(u) \equiv L \left. \frac{\partial \ln Z}{\partial L} \right|_{N_0, u_0, a}, \qquad \gamma_2 \equiv L \left. \frac{\partial \ln Z_2}{\partial L} \right|_{N_0, u_0, a}.$$
(138)

Any experimentally observed quantity must obey Equation 136 in the limit $a/L \rightarrow 0$. Previously (see Equations 128, 81, 82, 96, 97, etc.), the following relationships were derived for quantities equivalent to $\beta(u)$, $\gamma_1(u)$, and $\gamma_2(u)$

$$\beta(u) = \pi^{-2}u(u^* - u) + O(u^3, \varepsilon u^2),
\gamma_1(u) = \gamma_2(u) + O(u^2) = (2\pi)^{-2}u + O(u^2),$$
(139)

where the non-trivial fixed point u^* is the solution of the equation $\beta(u^*) = 0$ (see Equation 130)

$$u^* = \frac{1}{2}\varepsilon\pi^2 + O(\varepsilon^2).$$

The main solution of Equations 136 has the form

$$G(\vec{h}, N, u; L) = \exp\left(-\int_{u_1}^{u} \frac{\gamma_1(u)}{\beta(u)} dx\right)$$

$$\times F\left(L \exp\left(-\int_{u_1}^{u} \frac{dx}{\beta(x)}\right), N \exp\left(-\int_{u_1}^{u} \frac{\gamma_2(x)}{\beta(x)} dx\right), \vec{h}\right),$$
(140)

where u_1 is a constant, F is an arbitrary function which, in principle, can be well-defined.

As Equation 136 must be satisfied in the limit $a/L \rightarrow 0$, the solution of Equation 140 must not depend on a. Therefore, u_1 cannot have the meaning of a microscopic quantity, i.e. Equation 136 is satisfied after a sufficient number of renormalization procedures have been performed.

Thus, the renormalized interaction parameter u takes a value between 0 and u^* , where u^* corresponds to the limiting case of the maximum good solvent. Hence, the quantity u_1 must be chosen within this range: for definiteness, it is accepted (Oono and Freed, 1982) that

$$u_1 = \frac{u^*}{2}.\tag{141}$$

Then, a crossover variable is introduced

$$w = \frac{u}{u^* - u},\tag{142}$$

varying from 0 to ∞ .

On introducing u, the solution of Equation 140 is transformed into

$$G(\vec{h}, N, u; L) = \left(\frac{2}{1+w}\right)^{1/4} F\left(Lw^{-2/\epsilon}, N\left(\frac{2}{1+w}\right)^{1/4}, \vec{h}\right).$$
(143)

If we choose

$$s = N \left(\frac{2}{1+w}\right)^{1/4} \tag{144}$$

as the arbitrary parameter s in Equation 87, then combination of Equations 143 and 87 leads to

$$G(\vec{h}, N, u; L) = N^{-2+\epsilon/2} \left(\frac{2}{1+w}\right)^{-1/4+\epsilon/8} \hat{F} \left\{ L N^{-1} \left(\frac{2}{1+w}\right)^{-1/4} w^{-2/\epsilon};$$
(145)
$$\vec{h} N^{-1/2} \left(\frac{2}{1+w}\right)^{-1/8} \right\}.$$

As $w \to 0$, this equation gives the Gaussian limit, where the function G depends only on $\vec{h}N^{-1/2}$, and the other limit of a self-avoiding walk is obtained when $w \to \infty$.

If scaling variables

$$\zeta = \left(\frac{2\pi N}{L}\right)^{\epsilon/2} w(1+w)^{-\epsilon/8},$$
(146)

$$X = \frac{h^2 (1+w)^{1/4}}{2N} \tag{147}$$

are introduced, then Equation 145 is transformed into a new form

$$G(\vec{h}, N, u; L) = N^{-2+\varepsilon/2-\varepsilon\zeta/8(1+\zeta)} L^{\varepsilon\zeta/8(1+\zeta)} F_1(X, \zeta),$$
(148)

where the numerical factors are included into the definition of F_1 .

Equation 146 can be transformed in the ε order

$$(1+w)^{1/4} = \left[1 + \zeta(1+\zeta)^{\varepsilon/8}\right]^{1/4} \left(\frac{2\pi N}{L}\right)^{-\varepsilon\zeta/8(1+\zeta)}.$$
(149)

For G (see Equation 148) to exist in the limit $u \to u^*$, F_1 must depend on one variable only when $w \to \infty$

$$\mathcal{X} = X\zeta^{-(1+\epsilon/8)/4},\tag{150}$$

which is the only combination of X and ζ providing the limit $w \to \infty$.

With the aid of the above definitions, the solution of G from Equation 116, on simplification and elimination of the higher-order terms, takes the form

$$G(\vec{h}, N, u; L) = (2\pi N)^{-2+\epsilon/2-\epsilon\zeta/8(1+\zeta)\epsilon\zeta/8(1+\zeta)} \left[X(1+\zeta)^{-1/4} \right]^{\epsilon\zeta/8(1+\zeta)}$$
(151)
 $\times \exp\left\{ - \left[X(1+\zeta(1+\zeta)^{\epsilon/8})^{-1/4} \right]^{1+\epsilon\zeta/8(1+\zeta)} + (1-\hat{\gamma})\frac{\varepsilon}{8} \cdot \frac{\zeta}{1+\zeta} X(1+\zeta)^{-1/4} + \frac{\varepsilon}{8} \cdot \frac{\zeta}{1+\zeta} (1+\hat{\gamma}) \right\}.$

In the limit $\zeta = 0$, G (see Equation 151) reduces to the Gaussian distribution; in the limit $\zeta \to \infty$, G describes a self-avoiding walk.

With the help of Equation 151, Oono and Freed (1982) have obtained for $\langle h^2 \rangle$

$$\left\langle h^2 \right\rangle = 4N \left(\frac{1+\zeta(1+\zeta)^{\epsilon/8}}{1+w} \right)^{1/4} \left(1 - \frac{\varepsilon}{4} - \frac{\varepsilon}{8} \cdot \frac{\zeta}{1+\zeta} \right), \tag{152}$$

$$\left\langle h^2 \right\rangle = 4N \left(\frac{2\pi N}{L}\right)^{\varepsilon \zeta/8(1+\zeta)} \left(1 - \frac{\varepsilon}{4} - \frac{\varepsilon}{8} \cdot \frac{\zeta}{1+\zeta}\right). \tag{153}$$

On the basis of Equations 152 and 151, the distribution function for $\vec{r} = \vec{h} / \langle h^2 \rangle^{1/2}$ has the form

$$f(\vec{r}) = \left(\frac{2}{\pi}\right)^{2-\varepsilon/2} 2^{\varepsilon\zeta/8(1+\zeta)} \exp\left[\hat{\gamma}\frac{1}{8} \cdot \frac{\zeta\varepsilon}{1+\zeta} - \left(\frac{1}{4} \cdot \frac{\zeta}{1+\zeta} + \frac{1}{2}\right)\varepsilon\right] |r|^{\varepsilon\zeta/4(1+\zeta)}$$
(154)

$$\times \exp\left[-(2r^2)^{1+1/8+\zeta/(1+\zeta)} \left(1 - \frac{\varepsilon}{4} - \frac{\varepsilon\zeta}{8(1+\zeta)}\right) + \frac{\varepsilon}{4} \cdot \frac{\zeta}{1+\zeta} (1-\hat{\gamma})r^2\right]$$



Figure 5.18. Distribution function of segment density f(r) for the normalized end-to-end distance, $\vec{r} = \vec{h}/\langle h^2 \rangle^{1/2}$ (a), and distribution function of segment density versus distance |r|, $4\pi r^2 f(r)$ (b). Numbers at the curves relate to the crossover parameter ζ ($\zeta = 0$ corresponds to a Gaussian chain, $\zeta \to \infty$ corresponds to a self-avoiding walk) (Oono and Freed, 1982) [Reprinted with permission from: Y.Oono, K.F.Freed. J. Phys. A: Math. Gen. 15 (1982) 1931-1950. Institute of Physics Publishing Ltd.]

and is a universal function of the scaling variable ζ (Figure 5.18).

Substitution of Equation 146 into Equation 153 yields the equivalent form

$$\left\langle h^2 \right\rangle = 4N \left(\frac{1 + (2\pi N/L)^{\epsilon/2} w}{1 + w} \right)^{1/4} \left(1 - \frac{\varepsilon}{4} - \frac{\varepsilon}{8} \cdot \frac{\zeta}{1 + \zeta} \right) + O(\varepsilon^2).$$
(155)

For small w, Equation 142 leads to $w \sim u$. If N is sufficiently large, Equation 155 reduces to

$$\left\langle h^2 \right\rangle \simeq d \cdot N \left(\frac{2\pi N}{L}\right)^{\epsilon/8} u^{1/4},$$
(156)

which, in the ε order, serves as an equivalent of the following relationship of mean field theory

$$\left\langle h^2 \right\rangle \sim N^{6/5} u^{2/5}. \tag{157}$$

The coil expansion factor α_h^2

$$\alpha_h^2 = \frac{\langle h^2 \rangle}{\langle h^2 \rangle_{u=0}} \tag{158}$$

has two equivalent forms

$$\alpha_h^2 = \left(\frac{1+\zeta(1+\zeta)^{\varepsilon/8}}{1+w}\right)^{1/4} \left(1-\frac{\varepsilon}{8}\cdot\frac{\zeta}{1+\zeta}\right),\tag{159}$$

$$\alpha_h^2 = \left(\frac{2\pi N}{L}\right)^{\epsilon\zeta/8(1+\zeta)} \left(1 - \frac{\varepsilon}{8} \cdot \frac{\zeta}{1+\zeta}\right),\tag{160}$$

i.e. α_h^2 is not a universal function of one variable, as in the two-parameter theory, where α_h^2 is a universal function of the excluded volume parameter z (see Equation 3.1-130).

If w is small and N is large enough, then introduction of a new parameter \hat{z}

$$\hat{z} = \left(\frac{2\pi N}{L}\right)^{\epsilon/2} w \tag{161}$$

brings Equation 160 to a new form

$$\alpha_h^2 = \left(\frac{1+\hat{z}}{1+w}\right)^{1/4} \left(1 - \frac{\varepsilon}{8} \cdot \frac{\hat{z}}{1+\hat{z}}\right) \simeq (1+\hat{z})^{1/4} \left(1 - \frac{\varepsilon}{8} \cdot \frac{\hat{z}}{1+\hat{z}}\right),\tag{162}$$

which is a universal function of \hat{z} only approximately.

For the mean square radius of gyration of a molecular coil $\langle R^2 \rangle$, this approach leads to

$$\left\langle R^2 \right\rangle = \frac{d}{6} \left(1 - \frac{13}{96} \varepsilon \frac{\zeta}{1+\zeta} \right) \left(\frac{1+\zeta(1+\zeta)^{\varepsilon/8}}{1+w} \right)^{1/4} N + O(\varepsilon^2).$$
(163)

Combination of Equations 163 and 155 gives a universal function for the ratio

$$\frac{\langle R^2 \rangle}{\langle h^2 \rangle} = \frac{1}{6} \left(1 - \frac{\varepsilon}{96} \cdot \frac{\zeta}{1+\zeta} \right) + O(\varepsilon).$$
(164)

At the same time, the expansion factor α_R^2 ,

$$\alpha_R^2 = \frac{\langle R^2 \rangle}{\langle R^2 \rangle_{u=0}} = \left(\frac{1+\zeta(1+\zeta)^{\epsilon/8}}{1+w}\right)^{1/4} \left(1-\frac{13}{96}\cdot\frac{\epsilon\zeta}{1+\zeta}\right),\tag{165}$$

5.1. Renormalization of the conformational space

$$\alpha_R^2 = \left(\frac{2\pi N}{L}\right)^{\epsilon\zeta/8\zeta(1+\zeta)} \left(1 - \frac{13}{96} \cdot \frac{\epsilon\zeta}{1+\zeta}\right),\tag{166}$$

like α_h^2 , is not a universal function of one variable.

Only if w is small and N is large enough, the approximate universal form arises

$$\alpha_R^2 = (1+\hat{z})^{1/4} \left(1 - \frac{13}{96} \varepsilon \frac{\hat{z}}{1+\hat{z}} \right).$$
(167)

In this approximation, Oono and Freed (1982) have obtained for the second virial coefficient

$$\mathcal{A}_{2} = \frac{N_{A}N^{2-\epsilon/2}(1+w)^{-1/2+\epsilon/8}\zeta\pi^{2}\exp\left[-\frac{1}{2}\varepsilon\ln 2\pi + \frac{1}{8}\varepsilon\zeta(1+4\ln 2)/8(1+\zeta)\right]}{4M^{2}\left[1+\zeta(1+\zeta)^{\epsilon/8}\right]^{1/2}}.(168)$$

In the limit of a self-avoiding walk, Equation 168 reduces to

$$\mathcal{A}_{2} = \frac{N_{A}}{4M^{2}} N^{2-\epsilon/4} L^{-\epsilon/4} (4e)^{\epsilon/8} \pi^{-\epsilon/4}$$

$$\sim \frac{N^{2-\epsilon/4}}{M^{2}} = \frac{N^{\nu d}}{M^{2}} \sim N^{\nu d-2},$$
(169)

which matches the scaling expression (Equation 4.3-70).

For the coil interpenetration function ψ (see Equation 3.1–159), Oono and Freed (1982) have obtained

$$\psi = \frac{\varepsilon N \exp\left[-\frac{1}{2}\ln 2 + \frac{\varepsilon\zeta}{8} \cdot \frac{6\ln 2 - 1}{1 + \zeta}\right]}{16M\left[1 + \zeta(1 + \zeta)^{\varepsilon/8}\right]^{1 - \varepsilon/8} \left[\frac{d}{6}\left(1 - \frac{13}{96}\varepsilon\frac{\zeta}{1 + \zeta}\right)\right]^{2 - \varepsilon/2}},\tag{170}$$

i.e. ψ proves to be a universal function of the scaling variable ζ only.

In the limit of self-avoiding segments $\zeta \to \infty$, Equation 170 reduces to

$$\psi^* = \frac{\varepsilon \exp\left(-\frac{\varepsilon}{8} + \frac{\ln 2}{4}\right)}{16\left[\frac{d}{6}\left(1 - \frac{13}{96}\varepsilon\right)\right]^{2-\varepsilon/2}},\tag{171}$$

which at $\varepsilon = 1$ and d = 3 gives $\psi^* = 0.231$.

If w is small and N is large enough, then ζ can be replaced by \hat{z} in Equation 170. Applying Equation 167, we plot a common dependence ψ vs α_R^3 , as accepted in the two-parameter theory (Yamakawa, 1971) (Figure 5.19). It is seen that renormalization group theory corresponds to experimental values better than does the mean field theory. Unlike different versions of the two-parameter theory, the renormalization group approach predicts a constant limiting value ψ^* and needs no adjustable parameters.

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Figure 5.19. Plot ψ vs α_R^3 in the case of the renormalization group approach (RG). For comparison, the same dependence for different versions of the two-parameter theory is taken from (Yamakawa, 1971): Flory (1949b), Flory and Krigbaum (1950) $\psi = [\ln(1 +$ $(2.3z/\alpha_R^3)]/2.3$ with $\alpha_R^5 - \alpha_R^3 =$ 2.6z (I), Stockmayer (1960) $\psi =$ $[\ln(1+5.73z/\alpha_R^3)]/5.73$ with α_R^5 – $\alpha_R^3 = 1.276z$ (II), Kurata et al. (1964), Yamakawa and Tanaka (1967), Yamakawa (1971) ψ = $0.547[1 - (1 + 3.903z/\alpha_R^3)^{-0.4683}]$ with $\alpha_R^2 = 0.541 + 0.46(1 + 0.46)$ $(6z)^{0.46}$ (III). The experimental values are taken from (Norisuye et al., 1968) for polystyrene in trans-decaline at different temperatures (1), polystyrene+pbutylacetate at 25°C (2), and polychloroprene in CCl₄ at 25°C (3) (Freed, 1985) [Reprinted with permission from: K.F.Freed. Acc. Chem. Res. 18 (1985) 38-45. Copyright (c) 1985 American Chemical Society]

Region of the semidilute solution

Ohta and Oono (1982) applied the method of conformational space renormalization to calculate the osmotic pressure of solutions and the sizes of macromolecules in semidilute solutions of polymers.

In order to solve this problem, the authors also used Edwards' (1966) formalism, according to which the influence of the macromolecular surrounding of a given macromolecule is equivalent to the existence of an external stochastic field $\Phi(\vec{R})$, where conformational "diffusion" of the given chain proceeds (see Equation 3.1-205).

The diffusion equation (see Equation 3.1–190) can be written as (Freed, 1972)

$$\left[\frac{\partial}{\partial \mathcal{L}} - \frac{A}{6}\nabla_{\vec{R}}^2 + i\Phi(\vec{R})\right]G(\vec{R}0;\mathcal{L}0[\Phi]) = \delta(\mathcal{L})\delta(\vec{R}),\tag{172}$$

where $\Phi(\vec{R})$ is the stochastic field, and the imaginary unit *i* is included for convenience of mathematical transformations.

The correspondence between Green's function (Equation 3.1-205) and Green's theoret-

ical field function $G([\Phi])$ is reflected in the identity

$$G(\vec{R}0;\mathcal{L}0) \equiv \left\langle G(\vec{R}0;\mathcal{L}0[\Phi]) \right\rangle_{\Phi}, \qquad (173)$$

i.e. G is the mean of $G([\Phi])$ over the Gaussian statistically heterogeneous field $\Phi(\vec{R})$ possessing the following properties:

$$\left\langle \Phi(\vec{R}) \right\rangle_{\Phi} \equiv 0, \tag{174}$$

$$\left\langle \Phi(\vec{R})\Phi(\vec{R}')\right\rangle_{\Phi} = \mathcal{V}(\vec{R}-\vec{R}'). \tag{175}$$

In the case of macromolecules with excluded volume, averaging (Equations 174 and 175) is performed as integration over all the functions $\Phi(\vec{R})$ (Gelfand and Yaglom, 1956; Freed, 1972). To clarify this operation, consider a simple integral

$$v = \frac{\int_{-\infty}^{\infty} x^2 \exp\left(-\frac{v^{-1}x^2}{2}\right) dx}{\int_{-\infty}^{\infty} \exp\left(-\frac{v^{-1}x^2}{2}\right) dx},$$
(176)

which is generalized for many variables as

$$\mathcal{V}_{ij} = \frac{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} x_i x_j \exp\left[-\frac{1}{2} \sum_{k,l} x_k \mathcal{V}_{kl}^{-1} x_l\right] \prod_m dx_m}{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \exp\left[-\frac{1}{2} \sum_{k,l} x_k \mathcal{V}_{kl}^{-1} x_l\right] \prod_m dx_m},$$
(177)

where

$$\sum_{i,j} \mathcal{V}_{ij}^{-1} \mathcal{V}_{jk} = \delta_{ik} \quad \text{or} \quad \mathcal{V} \mathcal{V}^{-1} = 1,$$
(178)

 \mathcal{V}^{-1} is the inverse matrix to \mathcal{V} .

If i, j, \ldots in Equation 177 are associated with the points of field $\vec{R}_i, \vec{R}_j, \ldots$ and $\Phi(\vec{R}_i) = x_i, \ldots$ is accepted, then, on passing to continuous variables in Equation 177, we obtain

$$\mathcal{V}(\vec{R},\vec{R}') = \mathcal{N} \int \Phi(\vec{R}) \Phi(\vec{R}') \exp\left[-\frac{1}{2} \int d\vec{R} \int d\vec{R}' \, \Phi(\vec{R}) \mathcal{V}^{-1}(\vec{R},\vec{R}') \Phi(\vec{R}')\right] \delta\Phi, \quad (179)$$

where

$$\int \mathcal{V}(\vec{R}, \vec{R}') \mathcal{V}^{-1}(\vec{R}', \vec{R}'') \, d\vec{R}' = \delta(\vec{R} - \vec{R}''), \tag{180}$$

$$\mathcal{N}^{-1} = \int \exp\left[-\frac{1}{2} \int d\vec{R}' \int d\vec{R} \,\Phi(\vec{R}) \mathcal{V}^{-1}(\vec{R},\vec{R}') \Phi(\vec{R}')\right] \delta\Phi,\tag{181}$$

$$\delta \Phi \equiv \prod_{\vec{R}} d\Phi(\vec{R}). \tag{182}$$

Equation 179 corresponds to averaging of Equation 175. Moreover,

$$\mathcal{N}\int\Phi(\vec{R})\exp\left[-\frac{1}{2}\int d\vec{R}\int d\vec{R}'\,\Phi(\vec{R})\mathcal{V}^{-1}(\vec{R},\vec{R}')\Phi(\vec{R}')\right]\delta\Phi=0,\tag{183}$$

i.e. Equation 174 is satisfied.

Comparison of Equations 174, 175, 179, and 183 leads to the probability $(P[\Phi]\delta\Phi)$ of the partition function Φ taking a value from $\Phi(\vec{R})$ to $\Phi(\vec{R}) + \delta\Phi$:

$$P[\Phi]\delta\Phi = \mathcal{N}\exp\left[-\frac{1}{2}\int d\vec{R}\int d\vec{R}'\,\Phi(\vec{R})\mathcal{V}^{-1}(\vec{R},\vec{R}')\Phi(\vec{R}')\right]\delta\Phi.$$
(184)

If the mean values (Equations 174 and 175) are represented as functional integrals (see subsection 3.1.1), then function 3.1-205 satisfies the diffusion equations 172 and 173. This follows from the equality

$$\exp\left\{-\frac{1}{2}\int\limits_{0}^{\mathcal{L}}ds\int\limits_{0}^{\mathcal{L}}ds' \mathcal{V}\left[\vec{r}(s)-\vec{r}(s')\right]\right\}$$
(185)

$$\equiv \mathcal{N} \int \delta \Phi \exp\left\{-i \int_{0}^{\mathcal{L}} ds \Phi\left[\vec{r}(s)\right] - \frac{1}{2} \int \int \Phi(\vec{r}) \mathcal{V}^{-1}(\vec{r}-\vec{r}') \Phi(\vec{r}') d\vec{r} d\vec{r}'\right\},\$$

where \mathcal{N} is from Equation 181, \mathcal{V}^{-1} is from Equation 180.

Equality 185 is checked by the replacement

$$\Phi(\vec{r}) = \Phi'(\vec{r}) + i \int_{0}^{\mathcal{L}} ds \, \mathcal{V}(\vec{r} - \vec{r}(s)), \quad \delta \Phi' \equiv \delta \Phi$$
(186)

in the right-hand side of Equation 185 with subsequent replacement of the integration variable Φ' by Φ .

Substituting Equation 185 into Equation 3.1–205 and changing the order of integration over $\delta \Phi$ and $D[\vec{r}(s)]$, Freed obtains

$$G(\vec{R}0;\mathcal{L}0) = \mathcal{N} \int \delta\Phi \exp\left[-\frac{1}{2} \int d\vec{r} \int d\vec{r}' \,\Phi(\vec{r})\mathcal{V}^{-1}(\vec{r}-\vec{r}')\Phi(\vec{r}')\right]$$
(187)

$$\times \int_{\vec{r}(0)=0}^{\vec{r}(s)} D[\vec{r}(s)] \exp\left\{-\int_{0}^{\mathcal{L}} ds \left(\frac{3}{2A}\vec{r}^{2}(s)+i\Phi[\vec{r}(s)]\right)\right\}$$

$$\equiv \int \delta\Phi P[\Phi]G(\vec{R}0;\mathcal{L}0[\Phi]) \equiv \langle G([\Phi]) \rangle_{\Phi} ,$$

where $P[\Phi]$ is defined according to Equation 184.

Thus, Green's function $G([\Phi])$ in Equation 187 is Wiener's integral which implies the fulfillment of diffusion equation 172.

Let a box with a volume Ω contain *n* macromolecules modelled by continuous chains (see subsection 3.1.1) (Ohta and Oono, 1982; Freed, 1983).

The chains have their length distributions: the α fraction has n_{α} chains with length $N_{0,\alpha}$, the set of chains is denoted by $i_{\alpha} = 1, \ldots, n_{\alpha}$. In principle, any distribution function

$$P(N_{0,\alpha}) = \frac{n_{\alpha}}{n} \tag{188}$$

can be introduced into the model.

The dimensionless Hamiltonian of the system with n chains with their excluded volume v_0 is written as (Freed, 1983) (cf. Equation 62)

$$\mathcal{H} = \frac{1}{2} \sum_{\alpha, i_{\alpha}} \int_{0}^{N_{0,\alpha}} |\vec{c}_{i}(\tau_{i})|^{2} d\tau_{i} + \frac{1}{2} v_{0} \sum_{\alpha, i_{\alpha} \atop \beta, i_{\beta}} \int_{0}^{N_{0,\alpha}} d\tau_{i} \int_{0}^{N_{0,\beta}} d\tau_{j} \,\delta\left[\vec{c}_{i}(\tau_{i}) - \vec{c}_{j}(\tau_{j})\right].$$
(189)

The bare (non-renormalized) partition function of the system Z_B is expressed as a functional integral

$$Z_{B} = \left\{ \prod_{\alpha, i_{\alpha}} \int D[\vec{c}_{i}] \right\} \exp\left\{ -\mathcal{H}\left[\vec{c}_{i}(\tau_{i})\right] \right\},$$
(190)

where the integration $\{\vec{c}_i(\tau_i)\}$ is performed over all the volume Ω $(\vec{c}_i(\tau_i) \in \Omega)$, and the chain ends $\{\vec{c}_i(0), \vec{c}_i(N_{0,\alpha})\}$ are also located in the volume Ω . The partition function Z_B is an explicit function of the numerical concentration of macromolecules $c_p = n/\Omega$, v_0 , $\{N_{0,\alpha}\}$ and $a \to 0^+$. Moving on to a variable conformation \vec{c}_i (Equation 61) and considering the whole ensemble of macromolecules, Freed (1983) writes equality 185 as

$$\exp\left\{-\frac{1}{2}\sum_{\substack{i_{\alpha},\alpha\\i_{\beta},\beta}}\int_{0}^{N_{0,\alpha}}d\tau_{i}\int_{0}^{N_{0,\beta}}d\tau_{j} \mathcal{V}[\vec{c}_{i}(\tau_{i})-\vec{c}_{j}(\tau_{j})]\right\}$$
(191)

$$\equiv \int D[\Phi] \exp\left\{\pm i \sum_{\beta,i_{\beta}} \int_{0}^{N_{0,\beta}} d\tau_{j} \Phi[\vec{c}_{j}(\tau_{j})] - \frac{1}{2} \int d^{d}r \int d^{d}r' \Phi(\vec{r}) \mathcal{V}^{-1}(\vec{r}-\vec{r}') \Phi(\vec{r}')\right\},\$$

where

$$D[\Phi] \equiv \delta \Phi \left[\int \delta \Phi \exp \left\{ -\frac{1}{2} \int d^d r \int d^d r' \, \Phi(\vec{r}) \mathcal{V}^{-1}(\vec{r} - \vec{r}') \Phi(\vec{r}') \right\} \right]^{-1}, \tag{192}$$

$$\int d^{d}r' \mathcal{V}(\vec{r} - \vec{r}') \mathcal{V}^{-1}(\vec{r}' - \vec{r}'') = \delta(\vec{r} - \vec{r}'').$$
(193)

For the simplest case, the δ function is employed as the potential $\mathcal{V}(\vec{r})$:

$$\mathcal{V}(\vec{r}) = v_0 \delta(\vec{r}), \qquad \mathcal{V}^{-1}(\vec{r}) = v_0^{-1} \delta(\vec{r}).$$
 (194)

On substitution of Equations 191-193 into Equation 190 with changing the order of integration over Φ and \vec{c}_j , one obtains

$$Z_B = \int D[\Phi(\vec{r})] \left[\prod_{\beta,i_{\beta}} \int D[\vec{c}_j] \right]$$
(195)

$$\times \exp\left\{-\frac{1}{2}\int_{0}^{N_{0,\beta}} d\tau_{j} |\dot{\vec{c}}_{j}(\tau_{j})|^{2} \pm i \int_{0}^{N_{0,\beta}} d\tau_{j} \Phi[\vec{c}(\tau_{j})]\right\} \right] \times \\ \times \exp\left\{-\frac{1}{2}\int d^{d}r \int d^{d}r' \Phi(\vec{r}) \mathcal{V}^{-1}(\vec{r}-\vec{r}') \Phi(\vec{r}')\right\}.$$

According to this formula, the partition function Z_B describes a set of independent (disconnected) polymer chains interacting with the stochastic field $\Phi(\vec{r})$. Therein lies the specific character of consideration of the intermolecular interaction in a semidilute polymer solution according to Edwards' (1966) idea, when one considers **disconnected** macromolecules placed in the stochastic field due to the presence of other macromolecules.

Transformation 191-193 just enable the chains to be separated in the partition function 195, and the diffusion equation 172 specifies a "conformational flux" in a force field, which finally leads to an effective "shrinking" of conformations, i.e. to a decrease in the coil size.

With the conformation variable \vec{c} , the distribution function 187 is written as

$$G(N_0, \Phi) = \int D[\vec{c}] \exp\left\{-\frac{1}{2} \int_0^{N_0} d\tau |\dot{\vec{c}}(\tau)|^2 \pm i \int_0^{N_0} d\tau \, \Phi[\vec{c}(\tau)]\right\}.$$
(196)

In view of Equation 196, the partition function is rewritten as

$$Z_{B} = \int D[\Phi] \exp\left\{-\frac{1}{2} \int d^{d}r \int d^{d}r' \Phi(\vec{r}) \mathcal{V}^{-1}(\vec{r}-\vec{r}') \Phi(\vec{r}')\right\} \prod_{\beta} [G(N_{0,\beta},\Phi)]^{n_{\beta}}$$
(197)

with the last multiplier to be expressed as

$$\prod_{\beta} [G(N_{0,\beta}, \Phi)]^{n_{\beta}} = \exp\left[n \sum_{\beta} \frac{n_{\beta}}{n} \ln G(N_{0,\beta}, \Phi)\right].$$
(198)

Proceeding to the continuous description (continuity) in Equation 198, one can consider the macromolecular length distribution (Equation 188)

$$\prod_{\beta} [G(N_{0,\beta}, \Phi)]^{n_{\beta}} \to \exp\left[n \int_{0}^{\infty} dN_{0} P(N_{0}) \ln G(N_{0}, \Phi)\right]$$
(199)

$$\equiv \exp\left[n\left\langle \ln G(N_0, \Phi)\right\rangle\right]. \tag{200}$$

Introduction of Equation 200 into Equation 197 yields

$$Z_{\mathcal{B}} = \int D[\Phi] \exp\left\{ n \left\langle \ln G(N_0, \Phi) \right\rangle - \frac{1}{2} \int d^d r \int d^d r' \, \Phi(\vec{r}) \mathcal{V}^{-1}(\vec{r} - \vec{r}') \Phi(\vec{r}') \right\}.$$
(201)

With potential 194, the bare partition function of the system takes the form (Ohta and Oono, 1982)

$$Z_{\mathcal{B}} = \int D[\Phi] \prod_{\alpha=1}^{n} G(N_0, \Phi) \exp\left(-\frac{1}{2v_0} \int \Phi^2 d^d r\right).$$
(202)

In the method of renormalization group transformations, the characteristic quantities are calculated as a series in powers of v_0 .

In Equation 202, the measure $v_0^{-1}\Phi^2$ gives the order $v_0^{1/2}$ for $\Phi(\vec{r})$, and the first-order v_0 theory requires expansion up to Φ^2 . To take higher concentrations into account, the quantity $c_p v_0$ is accepted to be near 1 by the order of magnitude.

Distribution function 187, 196 describes random walking of segments in the external potential field $\pm i\Phi$, so $G(N_0, \Phi)$ is written as a series in Φ on expanding the exponent in Equation 196 in $i\Phi$ (Freed, 1972) (cf. Equation 24)

$$G(N_{0}, \Phi) = \int \int d^{d}r_{f} d^{d}r_{i} \Big\{ G_{0}(\vec{r}_{f} - \vec{r}_{i}, N_{0}) \pm i \int_{0}^{N_{0}} d\tau \int d^{d}r \ G_{0}(\vec{r}_{f} - \vec{r}, N_{0} - \tau) \quad (203)$$

$$\times \Phi(\vec{r})G_{0}(\vec{r} - \vec{r}_{i}, \tau) - \int_{0}^{N_{0}} d\tau \int_{0}^{\tau} d\tau' \int d^{d}r \int d^{d}r' \ G_{0}(\vec{r}_{f} - \vec{r}, N_{0} - \tau) \Phi(\vec{r})$$

$$\times G_{0}(\vec{r} - \vec{r}', \tau - \tau') \Phi(\vec{r}')G_{0}(\vec{r}' - \vec{r}_{i}; \tau') + O(\Phi^{3}) \Big\}$$

with an "unperturbed" function (see Equation 3.1-104)

$$G_0(\vec{R},T) = (2\pi T)^{-d/2} \exp\left(-\frac{\vec{R}^2}{2T}\right).$$
(204)

The normalization condition (Equation 3.1-178)

$$\int d^{d}\vec{r} G_{0}(\vec{r} - \vec{r}'; T) \equiv 1$$
(205)

provides a possibility to calculate the integrals over \vec{r}_{f} and \vec{r}_{i} in Equation 203 (Freed, 1983), which leads to

$$G(N_0, \Phi) = \Omega \pm i N_0 \int d^d r \, \Phi(\vec{r}) - \int d^d r \int d^d r' \, \Phi(\vec{r}) S_0(\vec{r} - \vec{r}', N_0) \Phi(\vec{r}') + O(\Phi^3), (206)$$

where

$$S_0(\vec{r} - \vec{r}', N_0) = \int_0^{N_0} d\tau \int_0^{\tau} d\tau' G_0(\vec{r} - \vec{r}', \tau - \tau').$$
(207)

Further expansion of the logarithm of $G(N_0, \Phi)$ yields

$$\ln G(N_0, \Phi) = \ln \Omega \pm i N_0 \Omega^{-1} \int d^d r \, \Phi(\vec{r}) + N_0^2 (2\Omega^2)^{-1} \left[\int d^d r \, \Phi(\vec{r}) \right]^2$$
(208)
$$- \Omega^{-1} \int d^d r \int d^d r' \, \Phi(\vec{r}) S_0(\vec{r} - \vec{r'}, N_0) \Phi(\vec{r'}) + O(\Phi^3).$$

To calculate the functional integrals, the Fourier transformation is applied

$$\Phi(\vec{r}) = \Omega^{-1} \sum_{\vec{q}} \exp(i\vec{q} \cdot \vec{r}) \Phi_{\vec{q}},$$
(209)

$$\mathcal{V}(\vec{r}) = \Omega^{-1} \sum_{\vec{q}} \exp(i\vec{q} \cdot \vec{r}) \mathcal{V}_{\vec{q}}$$
(210)

with due account of

$$\delta \Phi \equiv \prod_{\vec{q}} d\Phi_{\vec{q}} \quad \text{and} \quad \int d^d r \exp(i\vec{q} \cdot \vec{r}) = \Omega \delta_{\vec{q},0}. \tag{211}$$

After spatial integration of Equation 201, in view of Equation 208, Freed (1983) has obtained

$$Z_{B} = \mathcal{N}\left[\prod_{\vec{q}} \int d\Phi_{\vec{q}}\right] \exp\left\{n \ln \Omega \pm in \langle N_{0} \rangle \,\Omega^{-1} \Phi_{0} + \frac{1}{2} \langle N_{0} \rangle^{2} n \Omega^{-2} \Phi_{0}^{2} - \Omega^{-2} n \sum_{\vec{q}} |\Phi_{\vec{q}}|^{2} \langle S_{0}(\vec{q}, N_{0}) \rangle - (2\Omega)^{-1} \sum_{\vec{q}} |\Phi_{\vec{q}}|^{2} \mathcal{V}_{\vec{q}}^{-1} \right\} \left[1 + O(\Phi^{3})\right],$$
(212)

where

$$\mathcal{N}^{-1} = \left[\prod_{\vec{q}} \int d\Phi_{\vec{q}}\right] \exp\left\{-(2\Omega)^{-1} \sum_{\vec{q}} |\Phi_{\vec{q}}|^2 \mathcal{V}_{\vec{q}}^{-1}\right\},\tag{213}$$

$$S_0(\vec{q}, N_0) = 2N_0 q^{-2} + 4q^{-4} \left[\exp\left(-\frac{q^2 N_0}{2}\right) - 1 \right].$$
(214)

The exponent in Equation 212 is interpreted (Ohta and Oono, 1982; Freed, 1983) in terms of Edwards' screening. All the terms with $|\Phi_{\vec{q}}|^2$ are combined into an expression of the type

$$-\Omega^{-1}\sum_{\vec{q}} |\Phi_{\vec{q}}|^2 \mathcal{V}_{eff}^{-1} \langle \vec{q} \rangle.$$
(215)

If only q^{-1} commensurable with the coil size are considered, then Equation 214 can be approximated by

$$S_0(\vec{q}, N_0) \approx 2N_0 q^{-2}.$$
 (216)

Returning from \vec{c} to \vec{r} through Equation 61, we find

$$\mathcal{V}_{eff}(\vec{q}) = \mathcal{V}_{\vec{q}} - \frac{\mathcal{V}_{\vec{q}}}{1 + q^2 \hat{\xi}_B^2},\tag{217}$$

where

$$\hat{\xi}_{B}^{2} = \frac{(d/l)^{d/2-1}}{4c_{p} \gamma_{q} \langle N_{0} \rangle}.$$
(218)

The volume Ω is replaced by $\Omega(d/l)^{d/2}$ by virtue of the variable replacement (Equation 61).

Equation 212 is subdivided into components for each \vec{q} . As $\Phi(\vec{r})$ is the actual field, then

$$\Phi_{\vec{q}} = \Phi_{-\vec{q}}^*, \quad \Phi_{\vec{q}} = R_{\vec{q}} + iI_{\vec{q}}, \quad \Phi_{-\vec{q}} = R_{\vec{q}} - iI_{\vec{q}}, \tag{219}$$

and the integrals with respect to $d\Phi_{\vec{q}}d\Phi_{-\vec{q}}$ can be calculated for a fixed \vec{q} :

$$\int d\Phi_{\vec{q}} \int d\Phi_{-\vec{q}} \exp\left[-\frac{A_{\vec{q}}}{2}|\Phi_{\vec{q}}|^2\right] \equiv \int_{-\infty}^{\infty} dR_{\vec{q}} \int_{-\infty}^{\infty} dI_{\vec{q}} \exp\left[-\frac{A_{\vec{q}}}{2}\left(R_{\vec{q}}^2 + I_{\vec{q}}^2\right)\right] = \frac{2\pi}{A_{\vec{q}}}.$$
 (220)

Thus, for $\vec{q} \neq 0$ there appears a product $(2\pi/A_{\vec{q}})^{1/2}$ for all \vec{q} in the nominator of Equation 212. Evaluating the integrals with respect to $d\Phi_{\vec{q}}$ in an identical manner, extracting $\vec{q} = 0$ separately, one obtains (Freed, 1983)

$$Z_{B} = \exp\left[\frac{n\ln\Omega - \langle N_{0}\rangle^{2} \mathcal{V}_{0} n^{2} (2\Omega)^{-1}}{1 - c_{p} \mathcal{V}_{0} \langle N_{0}^{2} \rangle + 2 \mathcal{V}_{0} c_{p} \langle S_{0}(0, N_{0}) \rangle}\right] \times \prod_{\vec{q} \neq 0} \left\{ \left[\frac{2\pi}{(2\mathcal{V}_{\vec{q}}\Omega)^{-1} + c_{p}\Omega^{-1} \langle S_{0}(\vec{q}, N_{0}) \rangle}\right]^{1/2} \left[\frac{2\pi}{(2\mathcal{V}_{\vec{q}}\Omega)^{-1}}\right]^{-1/2} \right\}.$$
(221)

According to Equation 214,

$$-c_{p}\mathcal{V}_{0}\left\langle N_{0}^{2}\right\rangle + 2\mathcal{V}_{0}c_{p}\left\langle S_{0}(0,N_{0})\right\rangle \equiv 0,$$
(222)

and the infinite product ratio can be replaced by the sum of logarithms. Then

$$Z_{B} = \exp\left\{n\ln\Omega - n^{2}\left\langle N_{0}^{2}\right\rangle \mathcal{V}_{0}(2\Omega)^{-1} - \frac{1}{2}\sum_{\vec{q}\neq 0}\ln[1 + 2n\Omega^{-1} + \mathcal{V}_{\vec{q}}\left\langle S_{0}(\vec{q}, N_{0})\right\rangle] + O(\mathcal{V}_{\vec{q}}^{2})\right\}.$$
(223)

For large Ω , we can proceed to the limit

$$\sum_{\vec{q}} \to \frac{\Omega}{(2\pi)^d} \int d^d q.$$
(224)

On performing this operation, the (bare) free energy of the system is derived from Equation 223:

$$F_{B} = -kT \ln Z_{B} = -kT \Big\{ n \ln \Omega - n^{2} \langle N_{0} \rangle^{2} \mathcal{V}_{0}(2\Omega)^{-1}$$

$$- \frac{\Omega}{2} \int \frac{d^{d}q}{(2\pi)^{d}} \ln \Big[1 + 2n \mathcal{V}_{\vec{q}} \Omega^{-1} \langle S_{0}(\vec{q}, N_{0}) \rangle \Big] + O(\mathcal{V}_{\vec{q}}^{2}) \Big\}.$$
(225)

Correspondingly, for the (bare) osmotic pressure we write

$$\pi_{B} = -\left(\frac{\partial F_{B}}{\partial\Omega}\right)_{n,T} = c_{p}kT \left[1 + \frac{c_{p}\mathcal{V}_{0}\langle N_{0}\rangle^{2}}{2} - (2c_{p})^{-1}(2\pi)^{-d}\int d^{d}q \left\{\ln[1 \qquad (226)\right] + 2c_{p}\mathcal{V}_{\vec{q}}\langle S_{0}(\vec{q}, N_{0})\rangle - 2c_{p}\mathcal{V}_{\vec{q}}\langle S_{0}(\vec{q}, N_{0})\rangle \left[1 + 2c_{p}\mathcal{V}_{\vec{q}}\langle S_{0}(\vec{q}, N_{0})\rangle\right]^{-1} + O(\mathcal{V}_{\vec{q}}^{2})\right\}.$$

In view of Equation 194, for potential 225 we have (Ohta and Oono, 1982)

$$F_{B} = -kT \left\{ n \ln \Omega - \frac{n^{2} \langle N_{0} \rangle^{2} v_{0}}{2\Omega} - \frac{\Omega}{2(2\pi)^{d}} \int d^{d}q \ln \left[1 + \frac{2nv_{0}}{\Omega} \langle S_{0}(\vec{q}, N_{0}) \rangle \right] \right\}.$$
 (227)

Since there is no cut-off in Equation 189, integral 226 converges only when d < 2, so regularization (bringing the expression with d < 2 to the dimension d < 4) is required. After this procedure (Freed, 1983), the following expression results for dimensionless reduced osmotic pressure

$$\tilde{\pi}_{B}(N_{0};c_{p},v_{0}) = \frac{\pi_{B}(N_{0},c_{p},v_{0})}{c_{p}kT} = 1 + \frac{1}{2}X_{0} - v_{0}(4\pi^{2}X_{0})^{-1}$$

$$\times \int_{0}^{\infty} dz \, z^{3} \Big\{ \ln \Big[1 + 2X_{0}g(z^{2}) \Big] - 2X_{0}g(z^{2}) \Big[1 + 2X_{0}g(z^{2}) \Big]^{-1}$$

$$- 2X_{0}^{2}z^{-4}(1-e^{-z}) \Big\} - v_{0}X_{0}(2\pi \langle N_{0} \rangle)^{\varepsilon/2}(2\pi^{2}\varepsilon)^{-1},$$
(228)

where

$$z^2 = \frac{q^2 \langle N_0 \rangle}{2},\tag{229}$$

$$X_{0} = c_{p} \langle N_{0} \rangle^{2} v_{0}, \qquad (230)$$

$$g(z^2) = z^{-2} + z^{-4} \left\langle \exp\left(-z^2 \frac{N_0}{\langle N_0 \rangle}\right) - 1 \right\rangle.$$
(231)

 $\bar{\pi}_B$ (Equation 228) is a function of microscopic quantities, while experimentally measured quantities reflect the system's properties in the enlarged scale of length L. That is why the macroscopic parameters N and v substantially differ from the microscopic ones N_0 and v_0 : the microscopic model (Equation 189) has fine details not reflected in experimental quantities.

Introducing dimensionless quantities $u = vL^{\epsilon/2}$ (Equation 67) and $u_0 = v_0L^{\epsilon/2}$ (Equation 66) leads to the micro-macro relationships $N = Z_2 N_0$ (Equation 65) and

$$u_0 = Z_u u, \tag{232}$$

where Z_2 and Z_u are dimensionless quantities depending on u, the only dimensionless quantity remaining in the limit $a/L \rightarrow 0$.

Analytical expressions $Z_2 = Z_2(u)$ and $Z_u = Z_u(u)$ are chosen so that the perturbation series for the quantity under renormalization in u and $\varepsilon = 4-d$ powers has no singularities at $\varepsilon \to 0^+$.

In particular, for reduced osmotic pressure

$$\pi(N, c_p, u) = \pi_B(Z_2^{-1}N, c_p, Z_u u), \tag{233}$$
where

$$Z_2 = 1 + \frac{u}{2\pi^2\varepsilon} + O(u^2)$$

(see Equations 97 and 115),

$$Z_u = 1 + \frac{2u}{\pi^2 \varepsilon} + O(u^2)$$

(see Equation 127).

The expression for $\bar{\pi}(N, c_p, u)$ is found in the scaling limit

$$u^* = \frac{\varepsilon \pi^2}{2}$$

(see Equation 130).

Finally, we obtain (Ohta and Oono, 1982; Freed, 1983)

$$\bar{\pi}(N, c_p, u^*) = 1 + \frac{1}{2}X - \frac{\varepsilon}{8X} \int_0^\infty dz \, z^3 \Big\{ \ln \Big[1 + 2Xg(z^2) \Big] - 2Xg(z^2) \Big[1 + 2Xg(z^2) \Big]^{-1} - 2X^2 z^{-4} (1 - e^{-z}) \Big\},$$
(234)

where Freed (1983) means that

$$X = 2\varepsilon c_p \left(\frac{\pi}{2}\right)^{d\nu} \langle N \rangle^{d\nu} , \qquad (235)$$

while Ohta and Oono (1982) mean that

$$X = c_p \langle N \rangle^{d\nu} \frac{\pi^2 \varepsilon}{2} \qquad (d\nu = 2 - \frac{\varepsilon}{4} + O(\varepsilon^2)), \tag{236}$$

i.e. X is a quantity proportional to c_p/c_p^* , c_p^* being the coil overlap concentration.

In the same approach, Ohta and Oono (1982) have obtained the concentration dependence of the mean square end-to-end distance

$$\frac{\langle h^2 \rangle}{\langle h^2 \rangle_{c_p=0}} = \exp\left(-\frac{\varepsilon}{8} \int_0^1 dx \,(1-x) x^2 \int_0^\infty dz \, z^5 e^{-xz^2} \frac{2Xg(z^2)}{1+2Xg(z^2)}\right). \tag{237}$$

Approximation of Equation 231 by

$$g(z^2) = (z^2 + 2\mu)^{-1}, (238)$$

where $\mu = \langle N_0 \rangle^2 / \langle N_0^2 \rangle = M_n / M_w$, provides an analytical calculation of Equations 234 and 237 with a good accuracy. Equation 238 becomes exact for $\mu = 1/2$ given P is defined by the exponential distribution.

Calculation of Equations 234 and 237 with the aid of Equation 238 has led (Ohta and Oono, 1982) to

$$\bar{\pi} = \frac{\pi}{c_p kT} = 1 + \frac{1}{2} X \exp\left\{\frac{\varepsilon}{4} \left[\frac{\mu}{X} + \frac{\mu^2}{X^2} \ln \mu + \left(1 - \frac{\mu^2}{X^2}\right) \ln(X + \mu)\right]\right\},\tag{239}$$

$$\frac{\langle h^2 \rangle}{\langle h^2 \rangle_{c_p=0}} = \exp \frac{\varepsilon X}{8} \left\{ \frac{3}{X+\mu} - \left(\frac{3}{2(X+\mu)^2} + \frac{1}{X+\mu} \right) \right\}$$
(240)

×
$$\left[\ln 2(X+\mu) + \hat{\gamma}\right] + e^{2(X+\mu)} \operatorname{Ei}(-2(X+\mu)) \left(1 - \frac{2}{X+\mu} + \frac{3}{2(X+\mu)^2}\right) \right\},$$

where $\hat{\gamma} \approx 0.5772$ is Euler's constant,

$$X = \varepsilon \pi^2 c_p \langle N \rangle^{d\nu} \left(1 + \frac{\frac{1}{2} + \ln 2}{4} \varepsilon \right) / 2,$$

$$d\nu = 2 - \frac{\varepsilon}{4} + O(\varepsilon^2),$$

$$\operatorname{Ei}(-x) = -\int_x^\infty \frac{e^{-t}}{t} dt.$$
(241)

Figure 5.20 shows the dependence of $\pi/(c_pkT)$ vs X in comparison with experimental results obtained using a P α MS solution in toluene at 25°C (Noda et al., 1981). For this comparison, Ohta and Oono (1982) have adjusted a proportionality constant between X and c_p/c_p^* , where c_p^* is the coil overlap concentration. A study was made (Noda et al., 1981) on polymer samples with a narrow MWD. The agreement between the experimental values of π and the curve of a monomolecular polymer is very good except for large values of X, which is explained by the authors by the first order of approximation in this version of theory.

Equation 239 gives $\bar{\pi} \sim X^{1+\epsilon/4}$ at large X while experiment corresponds better to $\sim X^{1/(d\nu-1)}$ with $\nu = 0.585$. The second-order approximation must improve the agreement with experiment. The behaviour of $\bar{\pi} \sim X^{1+\epsilon/4}$ correlates with the results of intuitive scaling (see Equation 4.3-53). The theory (Ohta and Oono, 1982) shows a slight influence of polymolecularity on the osmotic pressure of a polymer solution.

In contrast to this, the plot

$$\frac{\langle h^2 \rangle}{\langle h^2 \rangle_{c_p=0}} vs H, \tag{242}$$

where

.

$$H = \left(\frac{\pi}{c_p kT} - 1\right) \frac{N_A}{M_n^2 \mathcal{A}_2 c_p},$$

exhibits a significant sensitivity to the polymolecularity of the concentration dependence of macromolecular sizes (Figure 5.21).

The renormalization method of conformational space has been further developed by Ohta and Nakanishi (1983), Nakanishi and Ohta (1985), who defined analytical expressions for the structural factor of light scattering and screening length ξ in a semidilute polymer solution

$$\xi^2 = K(X) R_g^2 \left(\frac{\partial \pi}{\partial c_p}\right)^{-1},\tag{243}$$



Figure 5.20. Dependence of π/c_pkT vs c_p/c_p^* . The solid line corresponds to $\mu = 1$ (a monomolecular polymer), the dashed line corresponds to $\mu = 0.01$ (a very wide MWD) (Ohta and Oono, 1982) [Reprinted from: T.Ohta, Y.Oono. Phys. Lett. 89A (1982) 460-464. Copyright © 1982 with kind permission of Elsevier Science NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands]. The symbols relate to experimental results (Noda et al., 1981) for P α MS in tolucne at 25°C with different values of MW

where K(X) and R_g are numerically calculated in (Ohta and Nakanishi, 1983).

Equation 243 has been compared with the experimentally measured screening length (Wiltzius et al., 1983) obtained by light scattering from polystyrene solutions in tolucne (a good solvent) and in methylethylketone (a marginal solvent). The same paper runs a correspondence between the theoretical variable X and the polymer concentration c_p , which arises on expansion of Equation 239 into a series in X

$$X\left[\frac{9}{16} + \frac{\ln\frac{M_w}{M_n}}{8}\right] = \mathcal{A}_2 c_p.$$
(244)

Thus, this formula allows direct comparison between theory and experiment (Figure 5.22) without using any adjustable parameter (as in Figure 5.20). Very good agreement between theory and experiment is evident.

Moreover, Ohta and Oono (1982), using experimental data of light scattering from polystyrene solutions of different fractions $(3 \cdot 10^5 \leq M \leq 2.6 \cdot 10^7)$ in toluenc and methylethylketone (Wiltzius et al., 1983), have plotted a universal dependence of



Figure 5.21. Plot of $\langle h^2 \rangle / \langle h^2 \rangle_{c_p=0}$ vs H as held by the theory (Ohta and Oono, 1982) [Reprinted from: T.Ohta, Y.Oono. Phys. Lett. **89A** (1982) 460 464. Copyright © 1982 with kind permission of Elsevier Science NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands], $\mu = M_n/M_w = 0.1, 0.5, 1$



Figure 5.22. Dependence of $\xi/R_{g,0}$ vs X as held by the theory (Ohta and Oono, 1982) and the experimental data obtained by light scattering of different-MW polystyrene solutions in solvents of different thermodynamic quality (toluene, methylethylketone) (Wiltzius et al., 1983) [Reprinted with permission from: P.Wiltzius, H.R.Haller, D.S.Cannell. Phys. Rev. Lett. **51** (1983) 1183–1186. Copyright © 1983 by the Anmerican Physical Society]

 $(\partial \pi/\partial c_p)$ vs X (Figure 5.23) that checks nicely with the theoretical expression corresponding to Equation 239. The same experimental data $(\partial \pi/\partial c_p)$ vs X (Wiltzius et al., 1983) agree better with the theoretical dependence of the next order of accuracy (Ohta and Oono, 1982)

$$\frac{\partial \pi}{\partial c_p} \sim X^{1/(d\nu-1)} \quad \text{for} \quad X \gg 1.$$
 (245)

A version of theory with explicit account of the chain segment density fluctuations with increasing polymer concentration has been put forward by Muthukumar and Edwards



Figure 5.23. Dependence of $(\partial \pi / \partial c_p)$ vsX according to Equation 5.1-239 (Ohta and Oono, 1982). Different symbols relate to polystyrene samples with different MMs in solvents of different quality (Nakanishi and Ohta, 1985) [Reprinted with permission from: A.Nakanishi, T.Ohta. J. Phys. A: Math. Gen. 18 (1985) 127 139. Institute of Physics Publishing Ltd.]

(1982). The system P+LMWL with a volume V contain n chains of length N_0 with the number of segments N ($N = N_0/l$). The distribution function is accepted in the form

$$P = \exp\left\{-\frac{3}{2l}\sum_{\alpha=1}^{n}\int_{0}^{N_{0}}ds_{\alpha}\left[\frac{\partial\vec{R}_{\alpha}(s_{\alpha})}{\partial s_{\alpha}}\right]^{2} - \frac{g}{2}\sum_{\alpha}\sum_{\beta}\int_{0}^{N_{0}}ds_{\alpha}\int_{0}^{N_{0}}ds_{\beta}\,\delta\left[\vec{R}(s_{\alpha}) - \vec{R}(s_{\beta})\right]\right\},\,(246)$$

where α and β relate to different chains. Then, the free energy of the system is expressed as

$$\exp\left(-\frac{F}{kT}\right) = \int \prod_{\alpha=1}^{n} D\vec{R}_{\alpha} P(\{R_{\alpha}\}), \qquad (247)$$

where integration is performed over all the conformations of all the chains.

Equation 247 considers all the chains. When one of them is separated out, the influence of others is reflected by introducing a field by means of Equation 185

$$\exp\left\{-\frac{1}{2}\sum_{\alpha}\sum_{\beta}\int_{0}^{N_{0}}ds_{\alpha}\int_{0}^{N_{0}}ds_{\beta}\mathcal{V}\left[\vec{R}_{\alpha}(s_{\alpha})-\vec{R}_{\beta}(s_{\beta})\right]\right\}$$
(248)

$$\equiv \mathcal{N} \int D\Phi \exp\left\{-i\sum_{\alpha} \int_{0}^{N_{0}} ds_{\alpha} \Phi[\vec{R}_{\alpha}(s_{\alpha})] - \frac{1}{2} \int d\vec{r} d\vec{r}' \Phi(\vec{r}) \mathcal{V}^{-1}(\vec{r},\vec{r}') \Phi(\vec{r}')\right\},\$$

where

$$\int d\vec{r}' \mathcal{V}(\vec{r}, \vec{r}') \mathcal{V}^{-1}(\vec{r}'', \vec{r}') = \delta(\vec{r} - \vec{r}''), \qquad (249)$$

$$\mathcal{N} = \int D\Phi \exp\left[-\frac{1}{2}\int d\vec{r}d\vec{r}' \,\Phi(\vec{r})\mathcal{V}^{-1}(\vec{r},\vec{r}')\Phi(\vec{r}')\right].$$
(250)

As usual, a short-range potential of the form

$$\mathcal{V}(\vec{r}) = g\delta(\vec{r}) \tag{251}$$

is accepted, and it follows from Equations 246 and 248 that

$$P(\{R_{\alpha}\}) = \frac{\int D\Phi \exp\left\{-\frac{3}{2l}\sum_{\alpha}\int_{0}^{N_{0}} ds_{\alpha} (\vec{R}_{\alpha}')^{2} - i\sum_{\alpha}\int_{0}^{N_{0}} ds_{\alpha} \Phi[\vec{R}(s_{\alpha})] - \frac{1}{2g}\int d\vec{r} \Phi^{2}(\vec{r})\right\}}{\int D\Phi \exp\left[-\frac{1}{2g}\int d\vec{r} \Phi^{2}(\vec{r})\right]} (252)$$
$$= \frac{\int D\Phi[G(\Phi)]^{n} \exp\left(-\frac{1}{2g}\int d\vec{r} \Phi^{2}(\vec{r})\right)}{\int D\Phi \exp\left(-\frac{1}{2g}\int d\vec{r} \Phi^{2}(\vec{r})\right)}.$$

Here $G(\Phi)$ is Green's function describing "diffusion of chain conformations" in the external stochastic field $\Phi(\vec{R})$ (due to the presence of other chains) and satisfying the diffusion equation (see Equations 3.1-190,-211, 172)

$$\left(\frac{\partial}{\partial N_0} - \frac{l}{6}\nabla_{\vec{R}}^2 + i\Phi(\vec{R})\right)G(\vec{R},\vec{R}';N_0[\Phi]) = \delta(N_0)\delta(\vec{R}-\vec{R}'),\tag{253}$$

where \vec{R} and $\vec{R'}$ are the vector end coordinates of a chain with length N_0 .

For a certain marked chain with segment l, the interaction of the segment excluded volume is modified by the presence of other chains and described by a new quantity of interaction Δ . Depending on the nature of Δ , the marked chain is characterized by an altered statistics, either Gaussian or non-Gaussian. Even if the statistics proves to be non-Gaussian, the end-to-end distance vector permits application of the Gaussian distribution function with a new effective segment l_1 , which must be a function of the original segment l and motion of the chain in the stochastic field: the mean square end to-end distance must be $N_0 l_1$.

Further, the theory envisages renormalization of the segment length and interaction with due account of the segment density fluctuations. Thus, the quantities Δ and l_1 are the key functions of theory. Their definition provides a possibility to calculate the free energy of the system. Solving the problem has led to the following results (Muthukumar and Edwards, 1982)

$$\Delta_k = \frac{g}{1 + \frac{1}{k^2 \xi^2}},\tag{254}$$

where k is the wavevector in momentum space. Therefore, the effective interactions decay with the screening length ξ .

In coordinate space,

$$\Delta(\vec{r}) = g \left[\delta(\vec{r}) - \frac{1}{4\pi\xi^2 r} e^{-r/\xi} \right].$$
(255)

Generally, the renormalized quantities ξ and l_1 are related by integral equations. However, in the limit where ξ and l_1 do not depend on wavevectors, their interrelation takes the form of algebraic equations

$$\xi^{-2} = \frac{6gcl}{l_1} \cdot \frac{1 + 27g\xi}{8\pi l_1^2},\tag{256}$$

$$l_1^3\left(\frac{1}{l} - \frac{1}{l_1}\right) = \alpha g\xi,\tag{257}$$

where α is a certain number near 1 in the order of magnitude, $c = N_n/V$ is the segment concentration. In the "critical" limit $(N_0 \to \infty \text{ and } c \to 0)$, the effective segment l_1 and the screening length ξ have the functional dependences

$$l_1 = \left(\frac{9\alpha}{16\pi}\right)^{1/4} g^{1/4} c^{-1/4},\tag{258}$$

$$\xi = \left(\frac{9}{16\pi\alpha^{1/3}}\right)^{3/4} g^{-1/4} l^{-1} c^{-3/4} \tag{259}$$

provided that

$$\left\langle \left[\vec{R}_{\alpha}(N_{\alpha}) - \vec{R}_{\alpha}(0) \right]^2 \right\rangle = N_0 l_1.$$
(260)

Thus, in a good solvent, $\langle h^2 \rangle$ decreases with increasing concentration

$$\left\langle h^2 \right\rangle \sim c^{-1/4}.\tag{261}$$

If we accept the temperature dependence

$$g \sim rac{T- heta}{ heta} \sim au,$$

then Equation 258 agrees with the conclusions of intuitive scaling (see Table 4.1). In the other limit $(c \to \infty)$,

$$l_1 = l + \frac{\alpha g^{1/2}}{6^{1/2} l c^{1/2}},$$

$$\xi = (6gc)^{-1/2}.$$
(262)
(263)

For the free energy F of a polymer solution containing n macromolecules in the volume V, the expression

$$-\frac{F}{kT} = n \ln V - \frac{nF_1(\xi \to \infty)}{kT} + \frac{9}{16\pi} \cdot \frac{gN_0n}{l_1\xi} - \frac{1}{24\pi} \cdot \frac{V}{\xi^3} - gl^2 c^2 V,$$
(264)

where $F_1(\xi \to \infty)$ is the free energy of an infinitely dilute solution, has been obtained.

In the limit $(N_0 \to \infty, c \to 0)$, Equation 264 for osmotic pressure is followed by the dependence

$$\frac{\pi}{kT} = \frac{cl}{N_0} + \frac{40\pi}{243} \left(\frac{16\pi\alpha^3}{9}\right)^{1/4} g^{3/4} l^3 c^{9/4}.$$
(265)

For a very concentrated solution

$$\frac{\pi}{kT} = \frac{cl}{N_0} - \frac{5\sqrt{6}}{32\pi} g^{3/2} c^{3/2} + gl^2 c^2, \tag{266}$$

i.e. $\pi \sim c^2$. Corresponding calculations lead to an estimation of the second virial coefficient

$$4_2 \sim l_1^2 \xi^{-1}.$$
 (267)

As
$$l_1 \sim c^{-1/4}$$
 and $\xi \sim c^{-3/4}$, then
 $\mathcal{A}_2 \sim c^{1/4}$. (268)

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5.2. Renormalization of polymer chain conformations in momentum space

The method of conformational renormalization of a polymer chain in momentum space turns out to be suitable in many respects for calculation of the characteristic quantities in polymer theory. This method is widely applied in the general field theory, and many ideas and methods can be adopted for polymer chains (Kholodenko and Freed, 1983).

The chief significance in this approach is placed upon calculation of the distribution function G_B at a fixed end-to-end vector (Equation 5.1-85) and at an additional fixing of a point inside the chain (Equation 5.1-118). Using the Fourier transform

$$F(\vec{k}) = \int d^d \vec{R} f(\vec{R}) \exp(-i\vec{k} \cdot \vec{R}), \tag{1}$$

$$f(\vec{R}) = \int \frac{d^d \vec{k}}{(2\pi)^d} F(\vec{k}) \exp(i\vec{k} \cdot \vec{R}), \qquad (2)$$

the average end-to-end distance $\left< \vec{h}^{2n} \right>$ is written as

$$\left\langle \vec{h}^{2n} \right\rangle = d^{-n} \frac{\int d^d \vec{h} \, (\vec{h})^{2n} G_B(\vec{h}, N_0; v_0)}{\int d^d \vec{h} \, G_B(\vec{h}, N_0; v_0)} =$$
(3)

$$= d^{-n} \frac{\sum_{i=1}^{d} \left(\frac{\partial^{2}}{\partial k_{i}^{2}}\right)^{n} (-1)^{n} G_{B}(\vec{k}, N_{0}; v_{0})}{G_{B}(0, N_{0}; v_{0})} \bigg|_{\vec{k}=0}, \qquad (4)$$

 $n = 1, 2, \dots$ (cf. Equations 2.6 40, -41).

Here the variable \vec{c} is transformed to \vec{r} by means of

$$\vec{c}(\tau) = \left(\frac{d}{l}\right)^{1/2} \vec{r}(\tau).$$
(5)

In Equations 3 and 4, l is accepted to be 1.

As discussed above, the macroscopic properties of a system (in this case, $\langle \vec{h}^{2n} \rangle$) must not depend on fine-scaled details. When Equation 4 is calculated on the basis of Hamiltonian 5.1-62, divergences arise due to the fine details. To eliminate them, a renormalization procedure is required.

The microscopic distribution function of the end-to-end vector $G(\vec{h}, N; v, L, \varepsilon)$ differs from that calculated using Hamiltonian 5.1-62 G_B by the factor Z (Equation 5.1-75)

$$G(\vec{h}, N; u, L, \varepsilon) = Z^{-1} G_B(\vec{h}, Z_2^{-1} N; v_0).$$
(6)

The arbitrariness of the scale length L leads to the arbitrariness in the numerical values of the final quantities, which remain even on elimination of singularities. This arbitrariness is eliminated by correlation of theory with experimental quantities (Oono and Freed, 1982).

Extending the renormalization method to momentum space (k, s) is accompanied by the representation of G_B through the inverse Laplace transform (cf. Equations 4.1-5 and 4.1-34)

$$G_B(\vec{k}, N_0; v_0) = \frac{1}{2\pi i} \int_c ds' \frac{\exp(s'N_0)}{k^2/2 + s' + \sum(\vec{k}, s')}$$
(7)

$$= \frac{1}{2\pi i} \int_{c} ds' \exp(s' N_0) G_B(\vec{k}, s'; v_0).$$
(8)

The Fourier-Laplace transform G_B for a free Gaussian chain in the chosen units gives

$$G_B = \left(\frac{k^2}{2} + s'\right)^{-1},\tag{9}$$

whence it follows that the "mass operator" from field theory $\sum(\vec{k}, s')$ (cf. Equation 2.6–36) arises from the excluded volume interactions. Substitution of Equation 5.1–65 to Equation 7 yields

$$G_B(\vec{k}, Z_2^{-1}N; v_0) = \frac{1}{2\pi i} \int_c ds' \frac{\exp(Z_2^{-1}Ns')}{k^2/2 + s' + \sum(\vec{k}, s)}$$
(10)

or, with variable substitution $Z_2^{-1}s' = s$,

$$G_{B}(\vec{k}, Z_{2}^{-1}N; v_{0}) = \frac{Z_{2}}{2\pi i} \int_{c} ds \frac{\exp(sN)}{k^{2}/2 + Z_{2}s + \sum(\vec{k}, sZ_{2})}.$$
(11)

If both the sides of this equation are multiplied by Z^{-1} and Equation 6 is taken into account, we get

$$G(\vec{k}, N, u, L, \varepsilon) = Z^{-1}G_B(\vec{k}, N_0; v_0) = \frac{1}{2\pi i} \int_c^{\infty} ds \frac{\exp(sN)}{ZZ_2^{-1}(k^2/2) + Zs + ZZ_2^{-1}\sum(\vec{k}, Z_2s)}.$$
(12)

In view of the bare (Equation 5.1-66) and renormalized (Equation 5.1-67) dimensionless excluded volume, the dimensionless quantities Z and Z_2 can be dependent on u only. The new quantity

$$\tilde{Z} = Z Z_2^{-1} \tag{13}$$

is introduced.

The quantities \tilde{Z} , Z, Z_2 can be represented as series in u:

$$\tilde{Z} = 1 + \sum_{i=1}^{\infty} a_i u^i, \tag{14}$$

$$Z = 1 + \sum_{i=1}^{\infty} b_i u^i,$$
 (15)

$$Z_2 = 1 + \sum_{i=1}^{\infty} d_i u^i.$$
(16)

The mass operator can also be expanded in u_0 powers

$$\sum_{i=1}^{\infty} c_i(\vec{k}, s) u_0^i.$$
(17)

Then, a variable Z_u

$$Z_u = 1 + \sum_{i=1}^{\infty} f_i u^i \tag{18}$$

is defined so that

$$u = u_0 Z_u^{-1}, (19)$$

i.e. u vanishes when $u_0 = 0$.

The renormalized constants eliminate all the singularities in G_B completely by means of defining the coefficients a_i, b_i, \ldots in subsequent orders of perturbation theory.

As opposed to renormalization in coordinate space (see section 5.1), the renormalization in momentum space (\vec{k}, s) is performed more rigorously, using the achievements of field theory. If G from Equation 6 is substituted to Equation 4, then $\langle \vec{h}^{2n} \rangle$ proves to be a function of N, u, L, ε

$$\left\langle \vec{h}^{2n} \right\rangle = F(N; u, L, \varepsilon).$$
 (20)

Dimensional analysis of Equation 5.1-62 for a certain l > 0 gives

$$\left\langle \vec{h}^{2n} \right\rangle = l^n F(\frac{N}{l}; u, \frac{L}{l}, \varepsilon).$$
⁽²¹⁾

For the case l = N, we have

$$\left\langle \vec{h}^{2n} \right\rangle = N^n F(\frac{N}{L}; u, \varepsilon).$$
 (22)

On the other hand, introducing the left-hand and right-hand sides of Equation 6 to Equation 4 by turns, we obtain

$$F(N; u, L, \varepsilon) = F_B(N_0 = Z_2^{-1}N; v_0).$$
⁽²³⁾

Note that the right-hand side of Equation 23 is L-independent. Applying $L(\partial/\partial L)$ to both the sides, we derive a renormalization group equation

$$\left(L\frac{\partial}{\partial L} + \beta(u)\frac{\partial}{\partial u} + \gamma(u)N\frac{\partial}{\partial N}\right)F(N;u,L,\varepsilon) = 0,$$
(24)

where

$$\beta(u) = L \frac{\partial}{\partial L} u, \tag{25}$$

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$$\gamma(u) = L \frac{\partial}{\partial L} \ln Z_2.$$
(26)

With the help of the differentiation rule of a composite function, we write

$$\gamma(u) = \beta(u)\frac{\partial}{\partial u}\ln Z_2 = \beta(u)\frac{1}{Z_2} \cdot \frac{\partial Z_2}{\partial u}.$$
(27)

If, for a certain $u = u^*$, $\beta(u^*) = 0$, then it follows from Equation 24 that

$$\left[\frac{\partial}{\partial L} + \gamma(u^*)N\frac{\partial}{\partial N}\right]F(N;u^*,L,\varepsilon) = 0,$$
(28)

which permits its solution to be in the form

$$F = F\left(\frac{N}{L^{\gamma(u^{*})}}; u, \varepsilon\right).$$
⁽²⁹⁾

Comparison of Equation 29 with Equations 20 and 21 gives

$$F = l^{n} F \left[\frac{N}{L} \left(\frac{l}{L} \right)^{\gamma(u^{*})}; u^{*}, \varepsilon \right].$$
(30)

Let us choose l so that

$$\frac{N}{L} \left(\frac{l}{L}\right)^{\gamma(u^{\bullet})} = 1$$

or

$$l = N^{1/[1-\gamma(u^*)]} L^{-\gamma(u^*)/[1-\gamma(u^*)]}.$$
(31)

If Equation 31 is substituted to Equation 30, we obtain a scaling law

$$F = N^{n/[1-\gamma(n^*)]} L^{-n\gamma(u^*)/[1-\gamma(u^*)]} F(u^*, \varepsilon).$$
(32)

For a fixed L, Equations 32 and 20 lead to

$$\left\langle h^2 \right\rangle_{u^*} \sim N^{2\nu},\tag{33}$$

where

$$2\nu = \frac{1}{1 - \gamma(u^*)}.$$
(34)

Let us follow the regularization and renormalization of the distribution function G_B (Kholodenko and Freed, 1983). The series for G_B (Equation 5.1-85) in v_0 powers contains the terms

$$\exp\left\{-\frac{v_0}{2}\int\limits_0^{N_0} d\tau \int\limits_0^{N_0} d\tau' \,\delta\left[\vec{c}(\tau) - \vec{c}(\tau')\right]\right\} \tag{35}$$

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$$= 1 - \frac{v_0}{2} \int_0^{N_0} d\tau \int_0^{N_0} d\tau' \delta [\vec{c}(\tau) - \vec{c}(\tau')] + \frac{1}{2!} \cdot \frac{v_0^2}{4} \int_0^{N_0} d\tau \int_0^{N_0} d\tau' \int_0^{N_0} d\nu \int_0^{N_0} d\nu' \delta [\vec{c}(\tau) - \vec{c}(\tau')] \delta [\vec{c}(\nu) - \vec{c}(\nu')] + \cdots$$

Substitution of this equation to Equation 5.1-85 yields a series for G_B in the form

$$G_{\mathcal{B}} = G_{\mathcal{B}}^{(0)} + G_{\mathcal{B}}^{(1)} + G_{\mathcal{B}}^{(2)} + G_{\mathcal{B}}^{(3)} + \cdots$$
(36)

The following rules have been formulated for successive calculation of the terms of this series (Freed, 1972; Kholodenko and Freed, 1983).

1. The factor 1/2 before $\int_0^\infty d\tau \int_0^\infty d\tau'$ in Equation 35 cancels due to the two possible sequence orders of τ and τ' along the chain.

2. In this, so-called "temporal" representation, interactions are displayed by a dashed line on the diagram, while the factors G_0 are shown by a solid line (Figure 5.24a). In



Figure 5.24. Diagrams of the perturbation series G_B (the complete G_{B^-} boldface line, G_0 -thin line): the "temporal" representation (a)- dashed lines show the arrangement of the interaction points along the chain and correspond to the contribution of the interaction $-v_0\delta(\vec{r}-\vec{r'})$, the "spatial" representation (b)—an interaction is displayed by an intersection point and reflects the topology of the interaction points of the chain when its parts come together (Kholodenko and Freed, 1983) [Reprinted with permission from: A.L.Kholodenko, K.F.Freed, J. Chem. Phys. **78** (1983) 7390–7411. Copyright © 1983 American Institute of Physics](cf. Figures 5.8 and 5.9)

the *n*th order, there are n! equivalent variants of the arrangement of the interaction lines relative to each other, and this factorial cancels by $(n!)^{-1}$ before the corresponding expansion number G_B (see Equation 35).

3. A "spatial" representation of an expansion diagram G_B (Figure 5.24b) finds use as well. Here, the interaction points reflect the actual coming together of the chains at the instant of their interaction (cf. Figure 5.9 and 5.17). The diagram topology in this representation coincides with the situation in the one-component (φ^4) field theory (see section 2.6) (Amit, 1978), but the combinatorial factors by the expansion terms differ.

Following these rules and using the casual character of the bare propagator, the contribution of the first-order $G_B^{(1)}$ can be written as (cf. Equation 5.1–98)

$$G_B^{(1)} = -v_0 \int d\vec{r} \int_0^{N_0} d\tau \int_0^{\tau} d\tau' G_0(\vec{h} - \vec{r}, N_0 - \tau) G_0(0, \tau - \tau') G_0(\vec{r}, \tau'), \tag{37}$$

where $G_0(\vec{r}, \tau)$ is the free propagator in \vec{r} -and- N_0 space (see Equation 5.1–85 with $v_0 = 0$). The direct Laplace transform is defined by

$$F(s) = \int_{0}^{\infty} dx f(x) \exp(-sx), \qquad (38)$$

and the Laplace transform of a convolution is

$$F(s) = \int_0^\infty dx \ e^{-sx} \int_0^x d\tau \ \varphi(x-\tau) f(\tau) = f(s)\varphi(s).$$
(39)

Using Equations 38 and 39, the $G_B^{(1)}$ from Equation 37 reads

$$G_B^{(1)}(\vec{h},s) = -v_0 \int d\vec{r} \, G(\vec{h}-\vec{r},s) G_0(0,s) G_0(\vec{r},s). \tag{40}$$

Finally, applying the Fourier transform (Equations 1 and 2) to Equation 40, we get

$$G_B^{(1)}(\vec{k},s) = -G_0(\vec{k},s) \sum^{(1)}(\vec{k},s) G_0(\vec{k},s),$$
(41)

where

$$\sum^{(1)}(\vec{k},s) = v_0 \left(\frac{1}{2\pi}\right)^d \int d^d k \frac{1}{k^2/2 + s} \tag{42}$$

and follows from comparison of Equation 40 with series 7 in v_0 powers, i.e. with the series

$$G_{B}(\vec{k},s) = G_{0}(\vec{k},s) - G_{0}(\vec{k},s) \sum_{\vec{k},s} G_{0}(\vec{k},s) + G_{0}(\vec{k},s) \left[\sum_{\vec{k},s} G_{0}(\vec{k},s) \right]^{2} + \cdots,$$
(43)

where \sum denotes a series of the Equation 17 type.

In order to calculate $\sum^{(1)}$, the *d*-dimensional integral (Equation 42) must be evaluated. For $d \ge 2$, this integral formally diverges, unless a cut-off is accepted in Equation 5.1 62.

The d-dimensional regularization is a method for extracting a non-singular contribution and based is on the idea of using d as a continuous variable. The corresponding integrals are calculated for d < 2, and, then, such forms of their representation are sought for which can be analytically extended to any d. In particular, Kholodenko and Freed (1983) used this way to derive the expression

$$\sum^{(1)}(\vec{k},s) = v_0 \frac{\pi^{d/2}}{(2\pi)^d} \cdot \frac{\Gamma(1-d/2)}{\Gamma(1)} (2s)^{d/2-1}.$$
(44)

By virtue of the equivalence between the polymer theory of excluded volume and the one-component φ^4 field theory (except the numerical factor), the arguments of renormalizability in field theory (Amit, 1978) are used in (\vec{k}, s) space of the polymer problem.

Field theory proves that the standard φ^4 theory is renormalizable when d = 4 (Amit, 1978), i.e. a finite number of renormalization constants is required to eliminate all the singularities in the expressions for characteristic functions. In polymer theory, the dimension d = 3 is of importance, and the parameter $\varepsilon = 4 - d$ is used in expansion into series 44. In particular, the ε^0 -order term in Equation 44 has the form

$$\sum_{B}^{(1)}(\vec{k},s) = -\frac{2u'_{0}s}{\varepsilon} + u'_{0}s\left(\ln\frac{sL}{2\pi} - \psi(2)\right),\tag{45}$$

where $u'_0 = u_0/(2\pi)^2$; $\psi(2) = 1 - \hat{\gamma}$; $-\psi(1) = \hat{\gamma}$ is Euler's constant.

From this point on, the prime is omitted, but the multiplier is meant as being included. With the use of Equation 45, the denominator of Equation 12 in the first order of u_0 , in view of Equations 14 and 15, takes the form

$$\tilde{Z}\frac{k^{2}}{2} + Zs + \tilde{Z}Z(\vec{k}, Z_{2}s) = (1 + a_{1}u)\frac{k^{2}}{2} + (1 + b_{1}u)s$$

$$+ (1 + a_{1}u)su_{0}\left[-\frac{2}{\varepsilon} + \ln\frac{sL}{2\pi} - \psi(2)\right].$$
(46)

This relationship must be renormalized, after which no singularities will be present. This is achieved by the proper choice of the constants a_1 and b_1 to cancel the terms with ε^{-1} . Indeed, such terms cancel each other provided that

$$a_1 = 0, \qquad b_1 = \frac{2}{\varepsilon}, \qquad u_0 = u + O(u^2),$$
(47)

which leads to $ZZ_2^{-1} = 1$ or

$$Z_2 = Z. \tag{48}$$

Hence, in the first order of u, the renormalization constants, according to Equations 13 15, take the form

$$Z = 1 + \frac{2}{\varepsilon}u + O(u^2), \tag{49}$$

$$Z_2 = 1 + \frac{2}{\varepsilon}u + O(u^2).$$
⁽⁵⁰⁾

In the second order of u, we have

$$f_1 = \frac{8}{\varepsilon},\tag{51}$$

$$u_0 = u \left(1 + \frac{8}{\varepsilon} u \right), \tag{52}$$

$$Z = 1 + \frac{2u}{\varepsilon} + \frac{10u^2}{\varepsilon^2} - \frac{3u^2}{\varepsilon},\tag{53}$$

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$$\tilde{Z} = Z Z_2^{-1} = 1 - \frac{u^2}{2\varepsilon},\tag{54}$$

$$Z_{2} = 1 + \frac{2u}{\varepsilon} - \frac{5u^{2}}{\varepsilon} + \frac{10u^{2}}{\varepsilon^{2}} + O(u^{3}).$$
(55)

To calculate the higher-order terms, vertex parts and vertex functions (see section 2.6) must be introduced. The same functions are used to calculate the second virial coefficient which characterizes the intermolecular interactions.

If two different chains with the interchain interaction parameter v_{03} differ in their lengths N_{01} and N_{02} and their interaction parameters v_{01} and v_{02} , then, on the basis of Equations 5.1-62, -85, -118, a two-chain distribution function with fixed ends

$$G_B^{(2)}(\vec{R}_1, \vec{R}_1'; \vec{R}_2, \vec{R}_2'; N_{01}, N_{02}; v_{01}, v_{02}, v_{03}) \equiv G_B^{(2)}$$
(56)

is introduced, when the ends of chain 1 are at the points \vec{R}_1 and \vec{R}'_1 while those of chain 2 are at the points \vec{R}_2 and \vec{R}'_2 . As is accepted in the statistical physics of pair distributions, a **connected** two-chain distribution function with fixed ends

$$G_{Bc}^{(2)}(\vec{R}_1, \vec{R}_1'; \vec{R}_2, \vec{R}_2'; N_{01}, N_{02}; \{v_{0i}\})$$

$$= G_B^{(2)} - G_B(\vec{R}_1, \vec{R}_1'; N_{01}, v_{01}) G_B(\vec{R}_2, \vec{R}_2'; N_{02}, v_{02}), \quad i = 1 \dots 3$$
(57)

is defined. Then, the bare (non-renormalized) second virial coefficient in d-dimensional space is expressed as

$$\mathcal{A}_{2B} = \frac{\int d^d \vec{R}_1 \int d^d \vec{R}_2 \int d^d \vec{R}_1' \int d^d \vec{R}_2' G_{Bc}^{(2)}(\vec{R}_1, \vec{R}_1', \vec{R}_2, \vec{R}_2'; N_{01}, N_{02}; \{v_{0i}\})}{\int d^d \vec{R}_1 \int d^d \vec{R}_1' G_B(\vec{R}_1, \vec{R}_1'; N_{01}, v_{01}) \int d^d \vec{R}_2 \int d^d \vec{R}_2' G_B(\vec{R}_2, \vec{R}_2'; N_{02}, v_{02})}.$$
 (58)

In turn, the connected functions are expressed through the vertex ones by means of

$$G_{Bc}^{(2)}(\vec{R}_{1},\vec{R}_{1}',\vec{R}_{2},\vec{R}_{2}';N_{01},N_{02};\{v_{0i}\}) = \int d^{d}\vec{r}_{1} \int d^{d}\vec{r}_{2} \int d^{d}\vec{r}_{1}' \int d^{d}\vec{r}_{2}' \qquad (59)$$

$$\times \int_{0}^{N_{01}} d\tau_{1} \int_{0}^{\tau_{1}} d\tau_{1}' \int_{0}^{N_{02}} d\tau_{2} \int_{0}^{\tau_{2}} d\tau_{2}' G_{B}(\vec{R}_{1}-\vec{r}_{1};N_{01}-\tau_{1})G_{B}(\vec{R}_{2}-\vec{r}_{2};N_{02}-\tau_{2})$$

$$\times G_{B}(\vec{r}_{1}'-\vec{R}_{1}';\tau_{1}')G_{B}(\vec{r}_{2}'-\vec{R}_{2}';\tau_{2}')\Gamma_{B}^{(4)}(\vec{r}_{1},\vec{r}_{1}',\vec{r}_{2},\vec{r}_{2}',\tau_{1}-\tau_{1}';\tau_{2}-\tau_{2}').$$

The functions $G_{Bc}^{(2)}$, \mathcal{A}_{2B} , and $\Gamma_B^{(4)}$ need renormalization. As an example, Figure 5.25 shows diagrams for $G_{Bc}^{(2)}$ up to the third order of the interaction parameter in the "temporal" representation.

Analysis of the singularities in the vertex portions does not practically depend on whether two different chains or two fragments of the same chain are considered. The renormalization procedure is very cumbersome.

Finally, the renormalization of the functions under question yields the value of the second coefficient of series 18 which is needed to calculate the exponent 2ν in Equation 34 and $\langle h^2 \rangle$ in the second order of ε

$$f_2 = \frac{64}{\varepsilon^2} - \frac{21}{\varepsilon}.$$
(60)

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Figure 5.25. Diagrams up to the third order of u for the second virial coefficient (Kholodenko and Freed, 1983) [Reprinted with permission from: A.L.Kholodenko, K.F.Freed, J. Chem. Phys. **78** (1983) 7390 7411. Copyright © 1983 American Institute of Physics]

According to Equations 18 and 19 up to the third order, the authors write

$$u_0 = u \left[1 + f_1 u + f_2 u^2 + O(u^3) \right].$$
(61)

In view of Equation 5.1–66, the $\beta(u)$ in Equation 24 is transformed to

$$\beta(u) = L \frac{\partial}{\partial L} u = L \frac{\partial}{\partial L} u_0 \frac{\partial u}{\partial u_0} = \frac{\varepsilon}{2} \cdot \frac{u_0}{(\partial u_0/\partial u)}.$$
(62)

Substitute Equation 61 to Equation 62:

$$\beta(u) = \frac{\varepsilon}{2} u \left[1 - f_1 u + 2(f_1^2 - f_2) u^2 + O(u^3) \right].$$
(63)

In order for $\beta(u)$ to remain finite with $\varepsilon \to 0$, the terms with ε^{-2} must cancel out, i.e.

$$f_2 = f_1^2. (64)$$

Taking Equations 51 and 60 into account, let us transform Equation 63:

$$\beta(u) = \frac{\varepsilon u}{2} \left[1 - \frac{8}{\varepsilon} u + \frac{42}{\varepsilon} u^2 + O(u^3) \right].$$
(65)

Similarly, up to the second order of u^2 , the Z_2 (see Equation 16) reads

$$Z_2 = 1 + d_1 u + d_2 u^2 + O(u^3).$$
(66)

Applying the composite function differentiation rule to Equation 26 yields

$$\gamma(u) = L \frac{\partial}{\partial L} \ln Z_2 = \beta(u) \frac{1}{Z_2} \cdot \frac{\partial Z_2}{\partial u}.$$
(67)

It follows from Equations 63, 66, and 67 that

$$\gamma(u) = \frac{\varepsilon}{2} \left[d_1 u + u^2 (2d_2 - d_1^2 - d_1 f_1) + O(u^3) \right].$$
(68)

The existence condition for $\gamma(u)$ at $\varepsilon = 0$ leads to the cancellation of the term with ε^{-2} in $2d_2$ with the same terms in $d_1^2 + d_1f_1$. Substitution of d_1 , d_2 (see Equations 16 and 55) and f_1 (see Equation 51) to Equation 68 leads to

$$\gamma(u) = u - \frac{5}{2}u^2 + O(u^3), \tag{69}$$

whence the exponent 2ν , according to Equation 34, results in the form

$$2\nu = [1 - \gamma(u)]^{-1} = 1 - u - \frac{3}{2}u^2 + O(u^3).$$
⁽⁷⁰⁾

The fixed point u^* results from the condition

$$\beta(u^*) = 0. \tag{71}$$

Applying Equation 71 to Equation 65 gives

$$\varepsilon = 8u^* - 42u^{*2}.\tag{72}$$

The solution is found in the form

$$u^{*} = a\varepsilon + b\varepsilon^{2},\tag{73}$$

the substitution of which to Equation 72 yields

$$a = \frac{1}{8}, \qquad b = \frac{21}{4} \left(\frac{1}{8}\right)^2.$$
 (74)

At last, it follows from Equation 70, in view of Equations 73 and 74, that

$$2\nu = 1 + \frac{\varepsilon}{8} + \frac{15}{4} \left(\frac{\varepsilon}{8}\right)^2,\tag{75}$$

which is in agreement with the result in the limit $n \to 0$ in field theory (Amit, 1978).

The quantity $\langle h^2 \rangle$ can be calculated according to Equation 4. As $G(\vec{k}, s)$ depends on $k^2 = |\vec{k}|^2$ only, one can write

$$G(\vec{k},s) = G(k^2,s).$$

Then, in *d*-dimensional space,

$$\sum_{i=1}^{d} \left. \frac{\partial^2}{\partial k_i^2} G(k^2, s) \right|_{k^2 = 0} = 2d \left. \frac{\partial}{\partial k^2} G(k^2, s) \right|_{k^2 = 0}.$$
(76)

A fairly elaborate calculation (Kholodenko and Freed, 1983) leads to

$$\left\langle h^2 \right\rangle = N \left(\frac{2\pi N}{L}\right)^{\epsilon/8 + (15/4)(\epsilon/8)^2} \left[1 - \frac{\varepsilon}{8} + 0.300 \left(\frac{\varepsilon}{8}\right)^2\right],\tag{77}$$

where N is the chain length. The term with ε^2 is about 4% of that with ε .

Of course, besides the limiting value $\langle h^2 \rangle$ (Equation 77) corresponding to $u = u^*$ and $N \to \infty$, the problem of calculation of $\langle h^2 \rangle$ in the crossover region (i.e. in the intermediate range of excluded volume with $0 \leq u \leq u^*$ and with a finite value of N) is of great significance. That is why the technique of conformational renormalization of polymer chains in momentum space has been applied to the dependence u = u(T) with $u(\theta) = 0$ at a fixed $N \neq N^*$, and upon variation of N with a fixed $u \neq u^*$. These two problems prove, indeed, to be interrelated (Kholodenko and Freed, 1983).

In the second order in ε , the crossover parameter is defined as follows (Kholodenko and Freed, 1983; Douglas and Freed, 1984)

$$\zeta_2 = \left(\frac{2\pi N}{L}\right)^{\epsilon/2} \bar{u}(1-\bar{u})^{x_2-1} \exp\left(\frac{11\epsilon^2 \bar{u}}{256}\right) + O(\epsilon^3),\tag{78}$$

where

$$x_2 = -\frac{17\varepsilon}{32} + \frac{\varepsilon^2}{8} + O(\varepsilon^3),\tag{79}$$

$$u = \frac{u}{u^*}.$$
(80)

Douglas and Freed (1984) introduce and discuss several crossover parameters. In particular,

$$\eta = \left(\frac{2\pi N}{L}\right)^{\epsilon/2} \bar{u}(1-\bar{u})^{-1},\tag{81}$$

which relates to ζ_1 (Equation 5.1 146) in the first order of ε

$$\eta = \zeta_1 (1 + \zeta_1)^{\epsilon/8} = \zeta_1 (1 - \bar{u})^{-\epsilon/8}; \tag{82}$$

and to ζ_2 (Equation 78) in the second order of ε

$$\eta = \zeta_2 (1 + \zeta_2)^{-17\varepsilon/32}.$$
(83)

Correspondingly, the mean-square end-to-end distance is expressed through ζ_1 and η

$$\left\langle h^{2}\right\rangle = Nl\left(\frac{2\pi N}{L}\right)^{\epsilon\zeta_{1}/8(1+\zeta_{1})} \left[I - \frac{\epsilon\zeta_{1}}{8(1+\zeta_{1})}\right] + O(\epsilon^{2}), \tag{84}$$

$$\left\langle h^2 \right\rangle = Nl \left(\frac{2\pi N}{L}\right)^{\epsilon\eta/8(1+\eta)} \left[1 - \frac{\epsilon\eta}{8(1+\eta)}\right] + O(\epsilon^2).$$
 (85)

To make a comparison between the results of the renormalization group approach, the two-parameter theory and experiment, Douglas and Freed (1984) introduce a parameter

$$z_{\mathcal{B}} = u_0 \left(\frac{2\pi N_0}{L}\right)^{\epsilon/2} = \left(\frac{d}{2\pi l^2}\right)^{d/2} \beta_0 n_0^{\epsilon/2},\tag{86}$$

where $N_0 = n_0 l$, n_0 is the number of segments. For d = 3, the parameter z_B agrees with the parameter z from the two-parameter theory (Equation 3.1-153).

With the aid of the renormalization parameter z_{RG}

$$z_{RG} = u \left(\frac{2\pi N}{L}\right)^{\epsilon/2} = Z_u^{-1} Z_2^{\epsilon/2} z_B,$$
(87)

one can determine the renormalized quantities β_{RG} , $\langle h^2 \rangle_{aRG}$, and n through

$$z_{RG} = \left(\frac{d}{2\pi l^2}\right)^{d/2} \beta_{RG} n^{1/2},$$
(88)

$$\beta_{RG} = Z_u^{-1} \beta_0, \tag{89}$$

$$N = nl, (90)$$

$$\left\langle h^2 \right\rangle_{oRG} = Z_2 \left\langle h^2 \right\rangle_0. \tag{91}$$

In the second order of ε , Douglas and Freed (1984), Freed (1987) have obtained the following expression for the second virial coefficient

$$\mathcal{A}_2(N, u, L) = \left(\frac{l}{d}\right)^{d/2} \left(\frac{2\pi N}{L}\right)^{d\nu(\eta)} L^{d/2} N_A (2M^2)^{-1} f_{\mathcal{A}_2}(\eta, \varepsilon), \tag{92}$$

where

$$d\nu(\eta) = 2 - \frac{\varepsilon}{2} + \frac{\varepsilon\eta}{4(1+\eta)} + O(\varepsilon^2)$$
(93)

is the effective index in the crossover region, and

$$f_{\mathcal{A}_{2}}(\eta,\varepsilon) = \frac{\varepsilon}{8} \cdot \frac{\eta}{1+\eta} + \left(\frac{\varepsilon}{8}\right)^{2} \left[(4\ln 2 - 1)\left(\frac{\eta}{1+\eta}\right)^{2} + \frac{21}{4} \cdot \frac{\eta}{1+\eta} \right] + O(\varepsilon^{3})$$
(94)

 $(at \eta \to \infty, \varepsilon = 1, f_{\mathcal{A}_2} = f^*_{\mathcal{A}_2} = -0.235).$

The interpenctration function in d-dimensional space is defined as

$$\psi = \frac{2M^2 \mathcal{A}_2(d/3)^{d/2}}{N_A(4\pi)^{d/2} \langle R^2 \rangle^{d/2}},\tag{95}$$

and, for d = 3, reduces to the standard form (Equation 3.1-159) accepted in the twoparameter theory. As $f_{A_2}(\eta, \varepsilon)$ in Equation 94 is defined in the first order of ε only, $\langle R^2 \rangle^{d/2}$ must be substituted into Equation 95 in the first order of ε as well (Douglas and Freed, 1984)

$$\left\langle R^2 \right\rangle^{d/2} = \left(1 - \frac{13}{12} \cdot \frac{\varepsilon}{8} \cdot \frac{\eta}{1+\eta}\right)^{d/2} \left(\frac{d}{6}\right)^{d/2} \left(\frac{2\pi N}{L}\right)^{d\nu(\eta)} \left(\frac{L}{2\pi}\right)^{d/2}.$$
(96)

Substitution of Equations 96 and 92 to Equation 95 gives

$$\psi(\eta,\varepsilon) = \frac{\varepsilon}{8} \cdot \frac{\eta}{1+\eta} + \left(\frac{\varepsilon}{8}\right)^2 \left[\left(4\ln 2 + \frac{7}{6}\right) \left(\frac{\eta}{1+\eta}\right)^2 + \frac{21}{4} \cdot \frac{\eta}{1+\eta} \right] + O(\varepsilon^3), \quad (97)$$

i.e. the interpenetration function is a universal function of η .

In the asymptotic limit of a good solvent,

$$\psi(\eta \to \infty, d=3) = \psi^* = 0.269,$$
(98)

which agrees well with the experimental data (see Figure 5.19).

The dimensionless second virial coefficient in the two-parameter theory (Equation 3.1 147)

$$h_B = \mathcal{A}_{2B} \frac{2M^2}{N_A n_0^2 \beta_0} \tag{99}$$

has its analogue the renormalized expression

$$h(\eta,\varepsilon) = \left(\frac{2\pi N}{L}\right)^{-\alpha(\eta)} f_h(\eta,\varepsilon), \qquad (100)$$

where

$$f_h(\eta,\varepsilon) = 1 + (4\ln 2 - 1)\frac{\varepsilon}{8} \cdot \frac{\eta}{1+\eta} + O(\varepsilon^2), \tag{101}$$

$$\alpha(\eta) = (2 - d\nu)\frac{\eta}{1 + \eta}.$$
(102)

For the whole region of change in the solvent strength, from the θ point to the maximum good solvent Douglas and Freed (1983, 1984), Kholodenko and Freed (1983), Freed (1985) have obtained expressions for $\langle h^2 \rangle$:

$$\left\langle h^2 \right\rangle = \left\langle h^2 \right\rangle_{oRG} \left(1 - \bar{u} + \frac{z_{RG}}{u^*} \right)^{2(2\nu-1)/\varepsilon} \left(1 - \frac{\varepsilon}{8} \lambda \right), \tag{103}$$

where, in the first order,

$$u = \frac{\varepsilon}{8} \cdot \frac{\eta}{1+\eta},\tag{104}$$

$$\frac{2(2\nu-1)}{\varepsilon} = \frac{1}{4},\tag{105}$$

$$\lambda = \frac{\eta}{1+\eta} = \frac{z_{RG}/u^*}{1-\bar{u}+z_{RG}/u^*};$$
(106)

in the second order

$$\left\langle h^2 \right\rangle = \left\langle h^2 \right\rangle_{oRG} \left\{ 1 - \bar{u} + \frac{z_{RG}}{u^*} \left(1 - \bar{u} + \frac{z_{RG}}{u^*} \right)^{-17\epsilon/32} \right\}^{1/4}$$

$$\times \left(1 - \bar{u} + \frac{z_{RG}}{u^*} \right)^{\epsilon/4 - 11\epsilon(1 - \bar{u})/128} \left[1 - \frac{\epsilon}{8}\lambda - 0.2294 \left(\frac{\epsilon}{8}\right)^2 \lambda - 0.0706 \left(\frac{\epsilon}{8}\right)^2 \lambda^2 + \cdots \right].$$

$$(107)$$

Let us discuss three modes of the coil state.

1. Weak interaction mode, where

$$\zeta = \frac{z_B}{\bar{u}^*} \ll 1, \qquad \frac{z_{RG}}{u^*} \ll 1. \tag{108}$$

Equation 103 reduces to

$$\left\langle h^2 \right\rangle \simeq \left\langle h^2 \right\rangle_{oRG} \left(1 + \frac{z_{RG}}{u^*} \right)^{1/4} \left[1 - \varepsilon \frac{z_{RG}/u^*}{8(1 + z_{RG}/u^*)} \right],\tag{109}$$

where $\langle h^2 \rangle_{oRG} = Nl$.

In the lowest limit, this state borders on the θ state of the coil; in the highest one—on $z_B \approx u^*$.

2. Strong interaction mode, where $\zeta \gg 1$ or $z_{RG} \gg 1$.

Equations 103 and 107 reduce to

$$\left\langle h^2 \right\rangle \simeq \left\langle h^2 \right\rangle_{oRG} \left(\frac{z_{RG}}{u^*} \right)^{2(2\nu-1)/\varepsilon} \left(1 - \frac{\varepsilon}{8} \right) + O(\varepsilon^2),$$
 (110)

$$\left\langle h^2 \right\rangle \simeq \left\langle h^2 \right\rangle_{oRG} \left(\frac{z_{RG}}{u^*}\right)^{2(2\nu-1)/\epsilon} \left[1 - \frac{\varepsilon}{8} - 0.3 \left(\frac{\varepsilon}{8}\right)^2 \right] + O(\varepsilon^3),$$
 (111)

respectively.

As $z_{RG} \sim N^{\epsilon/2}$ and $\langle h^2 \rangle_{oRG} \sim N$, then

$$\left\langle h^2 \right\rangle \sim N^{2\nu}.$$
 (112)

3. Crossover mode, where $\zeta \approx 1$.

Here, the complete expression 107 should be applied.

The quantity z_{RG} is not calculated in the theory of renormalization group transformations and is assumed as an empirical parameter, like z_B in the two-parameter theory. To correlate the conclusions of these two approaches, a new parameter is introduced (Douglas and Freed, 1984)

$$\bar{z}_B = \frac{(d-2)(6-d)}{4} z_B, \qquad \bar{z} = \frac{(d-2)(6-d)}{4} z_{RG},$$
(113)

where d is not considered as a continuous variable. The factor in Equation 113 is chosen so that the leading expansion term α_h^2 with respect to \bar{z} should have the same form as in one of the versions of the two-parameter theory (see Equation 3.1-130), viz. $\alpha_h^2 \simeq (4/3)\bar{z}$ for d = 3.

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This adjustment of the two theories concerning one property of the macromolecules shows their differences in other properties. The variable \bar{z} is also convenient for comparison between theory and experiment.

Thus, the characteristic functions of \bar{z} in polymer theory have the following form (Douglas and Freed, 1984)

$$\alpha_h^2 \approx \left(1 + \frac{32}{3}\bar{z}\right)^{1/4} \left(1 - \frac{\lambda_1}{8}\right) \approx 1 + \frac{4}{3}z + O(\bar{z}^2).$$
(114)

Here $(4/3)z_{RG}/u^* = 32\bar{z}/3$ (in the first order in ε), $\bar{z} < 3u^*/4 \approx 0.15$ (in the second order in ε), and $\lambda_1 = \frac{32\bar{z}/3}{1+32\bar{z}/3}$;

$$\alpha_b^2 \approx 1.73 \bar{z}^{0.3672},\tag{115}$$

where $\bar{z} > 3/4$ and $(2/\epsilon)(2\nu - 1) = 1/4 + (15\epsilon/128)|_{d=3} = 0.3672;$

$$\alpha_R^2 \approx \left(1 + \frac{32}{3}\bar{z}\right)^{1/4} \left(1 - \frac{13}{96}\lambda_1\right) \approx 1 + 1.22\bar{z} + O(\bar{z}^2) \quad (\bar{z} \le 0.15, \alpha_R^2 \le 1.2); \quad (116)$$

$$\alpha_R^2 \approx 1.71 \bar{z}^{0.3672} \quad (\bar{z} > \frac{3}{4}, \alpha_R^2 > 2);$$
 (117)

$$h(z) = \frac{2\mathcal{A}_2 M^2}{N_A n^2 \beta_{RG}} \approx \left(1 + \frac{32}{3}\bar{z}\right)^{-1/2} \left[1 + \frac{4\ln 2 - 1}{8}\lambda_1\right] \approx 1 - 2.97z + \cdots \ (z \le 0.15);(118)$$

$$h(\bar{z}) \approx 1.22 \left(\frac{32\bar{z}}{3}\right)^{-1/2} \quad (\bar{z} > \frac{3}{4});$$
 (119)

$$\psi(z) = 2\nu(z) - 1 = \gamma(\bar{z}) - 1 = u(\bar{z}) = \psi^* \lambda_1 \quad (\psi^* = \frac{\varepsilon}{8} \Big|_{d=3} = \frac{1}{8})$$
(120)

(to the first order in ε),

$$\psi(z) = 0.207\lambda_2 + 0.062\lambda_2^2 \quad \left(\lambda_2 = \frac{6.44\bar{z}}{1+6.44z}\right) \tag{121}$$

(to the second order in ε).

The theory of renormalization group transformations of the conformational space of polymer chains contains the phenomenological parameters L and ζ which are not natural, experimentally produced ones. However, the results of theory are approximated, to a large extent, with the variable \bar{z} which is written through experimentally measured quantities as

$$z = AM^{1/2} \left(1 - \frac{\theta}{T} \right), \tag{122}$$

where A is a constant depending on the polymer and solvent; in fact, it is an adjustable parameter.



Figure 5.26. Comparison between the experimental data of Miyaki and Fujita (1981) related to polystyrene in different solvents with the curves from the renormalization group theory (Douglas and Freed, 1984; Freed, 1985) (1) [Reprinted with permission from: K.F.Freed. Acc. Chem. Res. 18 (1985) 38-Copyright © 1985 Amer-45. ican Chemical Society], simulation (Domb and Barrett, 1976) (2), from Flory's theory (Flory, 1953; Yamakawa, 1971) (3), and Yamakawa-Tanaka's theory (Yamakawa, 1971) (4)

In Figure 5.26 is presented the α_R^2 ns \bar{z} dependence as given by the theory of renormalization group transformations (Equations 116 and 117) in comparison with the twoparameter theories and experiment (Freed, 1985).

Note that Freed (1985) has changed the empirical parameter \bar{z} (introduced by Miyaki and Fujita, 1981) by a factor of 0.906 ($\dot{z} = 0.906z$ (M.-F.)). They, in turn, have adjusted this parameter for the best fit to Domb-Barrett's (1976) simulation.

As is seen from Figure 5.26, the results of the theory of renormalization group transformations and simulations agree with the experimental data better than do the twoparameter theories.

It follows from Equations 34, 75, and 77 that

$$\langle h^2 \rangle_{u^*} \sim N^{2\nu} L^{+(2\nu-1)}.$$
 (123)

Comparison of Equation 123 with the experimental data concerning macromolecular sizes in a good solvent (Douglas and Freed, 1983, 1984; Freed, 1985) has shown that

$$L^{-1/2} \sim \left(1 - \frac{\theta}{T}\right),\tag{124}$$

and this relates the theoretical parameter to experiment. According to the model of heat blobs (Akcasu et al., 1981) in a good solvent

$$\alpha_R = 0.930 \left(\frac{n}{n_r}\right)^{0.092},$$
(125)

where nl = N, n_r is the blob size, and, according to Equation 77 (Douglas and Freed, 1983, 1984; Kholodenko and Freed, 1983)

$$\alpha_R = 0.929 \left(\frac{2\pi N}{L}\right)^{0.092}.$$
 (126)

Therefore, L from the renormalization group approach serves as an analogue of the blob size in scaling theories of heat blobs (Akcasu et al., 1981).

5.3. Hydrodynamic properties of macromolecules

When the *i*th element of a chain (a bead, a segment) moves in a liquid (solvent), there arises the friction force

$$\vec{F}_i = \zeta_0(\vec{u}_i - \vec{v}_i^{\mathbf{o}}),\tag{1}$$

where ζ_0 is the friction coefficient of the chain segment, \vec{u}_i is the velocity of this segment, \vec{v}_i^o is the velocity of the element of the liquid at the same point of space, where the *i*th segment is located, in the absence of this segment. The velocity \vec{v}_i^o has two components

$$\vec{v}_i^{\circ} = \vec{v}_i + \vec{v}_i',\tag{2}$$

where \vec{v}_i is the velocity of the liquid element in the absence of the whole macromolecule, \vec{v}'_i is the velocity of the liquid element due to the presence of all the chain segments but the *i*th one. The perturbation \vec{v}'_i is expressed by

$$\vec{v}_i' = \sum_{j \neq i}^N T_{ij} \vec{F}_j,\tag{3}$$

where T_{ij} is Ozeen's tensor characterizing the hydrodynamic interactions of the segments of a molecular chain (Flory, 1953; Tsvetkov et al., 1964; Yamakawa, 1971; Rafikov et al., 1978; Oono and Kohmoto, 1983; Tsvetkov, 1986; Gotlib et al., 1986).

Substituting Equations 2 and 3 to Equation 1, we get

$$\vec{F}_{i} = \zeta_{0}(\vec{u}_{i} - \vec{v}_{i}) - \zeta_{0} \sum_{j \neq i}^{N} T_{ij} \vec{F}_{j}, \tag{4}$$

which is the key equation in Kirkwood-Raizman's approach.

The calculation of the hydrodynamic properties of macromolecules comprises two stages (Oono and Kohmoto, 1983): first, Equation 4 should be solved with respect to \vec{F}_i ; second, one can calculate a characteristic value containing \vec{F}_i as an ensemble average.

The first stage presents significant difficulties, as Ozeen's tensor T_{ij} explicitly depends on the chain conformation, so, \vec{F}_i must be calculated for every possible chain conformation. To get around this difficulty, methods of preliminary averaging (preaveraging) of Ozeen's tensor over the equilibrium distribution functions have been developed

$$\vec{F}_i = \zeta_0(\vec{u}_i - \vec{v}_i) - \zeta_0 \sum_{j \neq i}^N \langle T_{ij} \rangle \vec{F}_j.$$
⁽⁵⁾

The approximate nature of different calculational procedures using preaveraging of Ozeen's tensor is discussed in detail in the special literature (eg. see the aforecited papers).

The method of renormalization group transformations has an advantage of the actual opportunity to calculate the characteristic values without preaveraging of Ozeen's tensor. As a model, a continuous chain with its Hamiltonian of the Equation 5.1-62 type is accepted.

If an external force moves the centre of mass of a macromolecule with a velocity \vec{u} , then the friction coefficient of translation of the macromolecule is defined by

$$f\vec{u} = \int_{0}^{N_{0}} d\tau \left\langle \vec{F}(\tau) \right\rangle, \tag{6}$$

where $\vec{F}(\tau)$ is the friction force per unit length of the model chain at point τ . By virtue of the smallness of \vec{u} , the force averaging can be performed over the equilibrium ensemble (Equation 5.1-62).

For the continuous chain model, Equation 4 becomes

$$\vec{F}(\tau) = \zeta_0 \vec{u} - \zeta_0 \int_{|\tau - \tau'| > a}^{N_0} d\tau' T(\tau, \tau') \vec{F}(\tau'),$$
(7)

where ζ_0 is a bare (model, microscopic) friction coefficient. The hydrodynamic interaction is described by Ozeen's tensor

$$T_{\alpha\beta}(\tau,\tau') = (2\pi)^{-d} \int d^d k \frac{1}{\eta_e k^2} \left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2} \right) \exp\left\{ -i\vec{k} [\vec{c}(\tau) - \vec{c}(\tau')] \right\},\tag{8}$$

where η_c is the effective viscosity of the medium, which may not coincide with that of the solvent η_s ; nevertheless, $\eta_c \approx \eta_s$ is often accepted. From Equations 6 and 7, for the friction coefficient f in the lowest non-trivial order we have

$$f = N_0 \zeta_0 - \zeta_0^2 \int_0^{N_0} d\tau \int_0^{N_0} d\tau' \left\langle \frac{1}{d} \sum_{\alpha} T_{\alpha\alpha}(\tau, \tau') \right\rangle.$$
(9)

Averaging is performed over the equilibrium ensemble with Hamiltonian 5.1-62. In order to calculate ζ_0/η_e in the first order in ε , it will suffice to apply Equation 5.1-62 without the excluded volume interaction term. On averaging with the Gaussian distribution function, Oono and Kohmoto (1983) have obtained

$$f = N_0 \zeta_0 - \frac{N_0 \zeta_0^2}{(2\pi)^2 \eta_e} (2\pi N_0)^{\epsilon/2} \left(\frac{3}{2\epsilon} - \frac{1}{8}\right).$$
(10)

The existence of a singularity here with $\varepsilon = 0$ makes renormalization of f necessary. In addition to the dimensionless parameter of excluded volume $u_0 = v_0 L^{\varepsilon/2}$ (Equation 5.1-66), the dimensionless hydrodynamic parameter

$$\xi_0 = \frac{\zeta_0}{\eta_e} L^{\epsilon/2} \tag{11}$$

is introduced, which characterizes the efficiency of the hydrodynamic interaction. This bare parameter is assumed to be related to the renormalized strength of the hydrodynamic interaction ξ by the relationship

$$\xi_0 = \xi(1 + E_1\xi + E_2u + \cdots), \tag{12}$$

considering the combination of the hydrodynamic and thermodynamic interactions. The singularity in Equation 10 must disappear if f is written in terms of the renormalized parameters N, u, and ξ . This requirement defines a relationship between ξ and ξ_0 .

Recall the interrelation between u and u_0

$$u_0 = u \left[1 + \frac{2}{\pi^2 \varepsilon} u + O(u^2) \right]$$

(see 5.1 127),

$$N = Z_2 N_0$$

(see 5.1-65), where

$$Z_2 = 1 + \frac{1}{2\pi^2 \varepsilon} u + O(u^2)$$

(see 5.1-97,-115).

First, a dimensionless constant of the interaction between ξ_0 and N is introduced into Equation 10

$$\frac{L^{\epsilon/2}}{\eta_c}f = Z_2^{-1}N\xi_0 - \frac{1}{(2\pi)^2}N\xi^2 \left(\frac{2\pi N}{L}\right)^{\epsilon/2} \left(\frac{3}{2\varepsilon} - \frac{1}{8}\right).$$
(13)

The second summand here has a higher order of ξ , and ξ_0 and N_0 in it are just replaced by the renormalized ξ and N, as these hare and renormalized quantities coincide in the lowest order.

From Equations 5.1-97, -115, 12, 13, the coefficients E_1 and E_2 are determined:

$$\xi_0 = \xi \left(1 + \frac{3}{8\pi^2 \varepsilon} \xi + \frac{1}{2\pi^2 \varepsilon} u + \cdots \right). \tag{14}$$

With the renormalized quantities, the friction coefficient is written (Oono and Kohmoto, 1983) as

$$f = N\zeta \left\{ 1 - \frac{\xi}{(2\pi)^2} \left[\frac{3}{4} \ln \left(\frac{2\pi N}{L} \right) - \frac{1}{8} \right] \right\},$$
(15)

where ζ is the renormalized friction coefficient of a chain element

$$\zeta = \eta_e \xi L^{-\varepsilon/2}. \tag{16}$$

To analyze the universal properties of the friction coefficient f, one should write the basic renormalization group equation and choose fixed points. Solving this equation together with dimensional analysis (Oono et al., 1981) (see section 5.2) yields the scaling form of f.

The renormalization group equation for f is derived on the basis of independence of the bare friction coefficient f from the macroscopic scale length L. On the other hand, N, u, and ξ may depend on L. Then,

$$\left(L\frac{\partial}{\partial L} + \beta_{u}\frac{\partial}{\partial u} + \beta_{\xi}\frac{\partial}{\partial\xi} + \gamma N\frac{\partial}{\partial N}\right)f = 0,$$
(17)

where

$$\beta_u = L \left(\frac{\partial u}{\partial L}\right)_{N_0, v_0, \xi_0},\tag{18}$$

$$\beta_{\xi} = L \left(\frac{\partial \xi}{\partial L} \right)_{N_0, \nu_0, \xi_0},\tag{19}$$

$$\gamma = L \left(\frac{\partial \ln Z_2}{\partial L} \right)_{N_0, \nu_0, \xi_0}.$$
(20)

These functions are calculated from Equations 5.1-127, 97, 115, and 14:

$$\beta_u(u) = u\left(\frac{\varepsilon}{2} - \frac{u}{\pi^2}\right) + O(u^3),\tag{21}$$

$$\beta_{\xi}(\xi, u) = \xi \left(\frac{\varepsilon}{2} - \frac{3\xi}{16\pi^2} - \frac{u}{4\pi^2} \right), \qquad (22)$$

$$\gamma(u) = \frac{u}{(2\pi)^2} + O(u^2).$$
(23)

The fixed points $u = u^*$ and $\xi = \xi^*$ are defined from the conditions $\beta_u(u) = 0$ and $\beta_{\xi}(\xi, u) = 0$.

Thus, four points

(A)
$$u^* = 0, \quad \xi^* = 0;$$
 (24)

(B)
$$u^* = \frac{\pi^2}{2}\varepsilon, \quad \xi^* = 0;$$
 (25)

(C)
$$u^* = 0, \quad \xi^* = \frac{8}{3}\pi^2\varepsilon;$$
 (26)

(D)
$$u^* = \frac{\pi^2}{2}\varepsilon, \quad \xi^* = 2\pi^2\varepsilon$$
 (27)

are determined from Equations 21 and 22.

Fixed points A and B are versions of free draining of the chain while C and D relate to a nondraining chain. The fixed points with $u^* = 0$ correspond to the θ state, while $u^* = \pi^2 \varepsilon/2$ correspond to the self-avoiding limit (the maximum good solvent).

At the fixed points, the renormalization group equation 17 reduces to

$$\left(L\frac{\partial}{\partial L} + \gamma^* N \frac{\partial}{\partial N}\right) f = 0, \qquad (28)$$

where

$$\gamma^* = 1 - \frac{1}{2\nu} \tag{29}$$

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(see Equation 5.2-34). Equation 28 restricts the functional form of f by

$$f^* = f(L, N, u^*, \xi^*) = f_1\left(LN^{-1/\gamma^*}, u^*, \xi^*\right).$$
(30)

On the other hand, the scaling properties of f, following from Equations 15 and 16, are expressed in

$$f(SL, SN, u, \xi) = S^{(d/2)-1} f(L, N, u, \xi),$$
(31)

where S is a certain positive number. Combining Equations 30 and 31 leads to

$$f^* = \left[\frac{1}{L} \left(\frac{N}{L}\right)^{-2\nu}\right]^{1-d/2} f_2(u^*, \xi^*).$$
(32)

At the fixed points, the expression for the friction coefficient f (see Equation 15), in view of Equation 32, becomes

$$f^* = \frac{\eta_c}{2\pi} \xi^* \exp\left[\frac{\xi^*}{(2\pi)^{28}}\right] L^{d/2-1} \left(\frac{2\pi N}{L}\right)^{1-\frac{3}{4}\cdot\frac{\xi^*}{(2\pi)^{2}}}$$

$$= \frac{\eta_c}{2\pi} \xi^* \exp\left[\frac{\xi^*}{(2\pi)^{28}}\right] L^{(d/2)-1} \left(\frac{2\pi N}{L}\right)^{(d-2)\nu}.$$
(33)

. .

In the case of a nondraining coil in the self-avoiding limit (point D) $\xi^* = 2\pi^2 \varepsilon$, so

$$f^* = \pi \eta_c \varepsilon \exp\left(\frac{\varepsilon}{16}\right) L^{(d/2)-1} \left(\frac{2\pi N}{L}\right)^{(d-2)\nu}$$
(34)

where

$$\nu = \frac{1}{2} + \frac{\varepsilon}{16} \tag{35}$$

(see Equation 5.2-75).

In another fixed point (C) of a nondraining Gaussian chain, where $\xi^* = 8\pi^2 \varepsilon/3$,

$$f^* = \frac{4}{3}\pi\varepsilon\eta_e \exp\left(\frac{\varepsilon}{12}\right)(2\pi N)^{(d-2)\nu} \qquad (\nu = \frac{1}{2}).$$
(36)

The coefficient of translational diffusion is defined by Einstein's equation

$$D = \frac{kT}{f}.$$
(37)

According to Equations 34 and 36, expressions for D for a nondraining coil in the maximum good solvent (the self-avoiding limit)

$$D^* = \frac{kT}{\pi \eta_e \varepsilon} \exp\left(-\frac{\varepsilon}{16}\right) L^{1-(d/2)} \left(\frac{2\pi N}{L}\right)^{(2-d)\nu} \qquad (\nu = \frac{1}{2} + \frac{\varepsilon}{12})$$
(38)

and for a nondraining Gaussian chain in the θ state

$$D^* = \frac{3kT}{4\pi\varepsilon\eta_e} \exp\left(-\frac{\varepsilon}{12}\right) (2\pi N)^{(2-d)\nu} \qquad (\nu = \frac{1}{2})$$
(39)

are obtained.

Calculations done in the same fashion (Oono and Kohmoto, 1983) have led to the renormalized limiting number of viscosity

$$\frac{M\eta_s}{N_A}[\eta] = \frac{\zeta N^2}{12} \left[1 - \frac{u}{(2\pi)^2} \left(\frac{13}{12} - \ln \frac{2\pi N}{L} \right) - \frac{\xi}{(2\pi)^2} \left(-\frac{7}{6} + \frac{3}{4} \ln \frac{2\pi N}{L} \right) \right].$$
(40)

Special analysis (Oono and Kohmoto, 1983) has shown this function at the fixed points u^* and ξ^* to take the form

$$\frac{M\eta_s}{N_A}[\eta] = \frac{\eta_e \xi^*}{12} L^{-\epsilon/2} N^2 \exp\left[\frac{7\xi^*}{6(2\pi)^2} - \frac{13}{12} \cdot \frac{u^*}{(2\pi)^2}\right] \left(\frac{2\pi N}{L}\right)^{\frac{u^*}{(2\pi)^2} - \frac{3\xi^*}{4(2\pi)^2}} \tag{41}$$

$$= \frac{\eta_c \xi^*}{12(2\pi)^2} \exp\left[\frac{7\xi^*}{6(2\pi)^2} - \frac{13u^*}{12(2\pi)^2}\right] L^{d/2} \left(\frac{2\pi N}{L}\right)^{d\nu}.$$
 (42)

In particular, at the self-avoiding fixed point D for a nondraining chain in the maximum good solvent,

$$\frac{M\eta_s}{N_A}[\eta] = \frac{\eta_c \varepsilon}{24} \exp\left(\frac{43}{96}\varepsilon\right) L^{d/2} \left(\frac{2\pi N}{L}\right)^{d\nu}.$$
(43)

The calculational algorithm of the renormalization group approximation enables $[\eta]$ to be calculated directly (without preaveraging), as well as with the preaveraging of Ozeen's tensor. The ratio of the $[\eta]$'s calculated in these two cases shows the effect of preaveraging

$$\frac{[\eta]_{\text{pre}}}{[\eta]} = \exp\left\{\frac{5}{24} \cdot \frac{\xi^*}{(2\pi)^2}\right\} = 1.11 \text{ (point } D\text{) or } 1.15 \text{ (point } C\text{)}.$$
(44)

Thus, the preaveraging procedure of Ozeen's tensor increases $[\eta]$ by ~10%. Indeed, Miyaki et al. (1980) have found the measured $[\eta]$ in polystyrene solutions in the θ solvent to be by ~10% less than that calculated for a Gaussian coil with Ozeen's tensor having been preaveraged.

The hydrodynamic properties of macromolecules reported above have been calculated in the ε order. The results contain the macroscopic scale length L which, in particular, depends on the chemical structure of a polymer. Of course, L-free expressions possess a universal meaning regardless of this structure. Such expressions can be obtained by combining the characteristic quantities $[\eta]$, f (or D), $\langle R^2 \rangle$, and \mathcal{A}_2 .

In the case of a nondraining coil in the maximum good solvent (the self-avoiding limit), we have

$$\frac{M}{N_A} \cdot \frac{\eta_s}{\eta_e} [\eta] = \frac{\varepsilon}{24} \exp\left(\frac{43}{96}\varepsilon\right) L^{d/2} \left(\frac{2\pi N}{L}\right)^{d\nu},\tag{45}$$

$$\frac{f}{\eta_e} = \pi \varepsilon \exp\left(\frac{\varepsilon}{16}\right) L^{(d/2)-1} \left(\frac{2\pi N}{L}\right)^{(d-2)\nu},\tag{46}$$

$$\frac{\mathcal{A}_2 M^2}{N_A} = \frac{\varepsilon}{16} \exp\left[-\frac{\varepsilon}{8}(1-4\ln 2)\right] L^{d/2} \left(\frac{2\pi N}{L}\right)^{d\nu},\tag{47}$$

$$\left\langle R^2 \right\rangle = \frac{1}{3\pi} \exp\left(-\frac{37}{96}\varepsilon\right) L\left(\frac{2\pi N}{L}\right)^{2\nu};$$
(48)

in the nondraining Gaussian limit

$$\frac{M}{N_A} \cdot \frac{\eta_s}{\eta_e} [\eta]_{\theta} = \frac{\varepsilon}{18} \exp\left(\frac{7}{9}\varepsilon\right) (2\pi N)^{d/2},\tag{49}$$

$$\frac{f_{\theta}}{\eta_e} = \frac{4}{3} \pi \varepsilon \exp\left(\frac{\varepsilon}{12}\right) (2\pi N)^{(d-2)/2},\tag{50}$$

$$\left\langle R_{\theta}^{2} \right\rangle = \frac{2}{3} \exp\left(-\frac{\varepsilon}{4}\right) N.$$
 (51)

In the multipliers of Equations 45-51, all d's are represented as a series in the ε order with subsequent exponentiation. For example, Equation 51 is derived as

$$\left\langle R_{\theta}^{2} \right\rangle = \frac{dN}{6} = 4\left(1 - \frac{\varepsilon}{4}\right) \cdot \frac{N}{6} = \frac{2}{3}N\exp\left(-\frac{\varepsilon}{4}\right).$$
 (52)

In the case of a nondraining coil in the maximum good solvent, the following expressions are obtained. Combination of Equations 45 and 48 leads to

$$U_{\eta R} \equiv \frac{M\eta_{*}[\eta]}{N_{A}\eta_{e} \left\langle R^{2} \right\rangle^{d/2}} \tag{53}$$

with which Flory's parameter Φ (Equation 3.6-67) is related by

$$\Phi = \frac{N_A U_{\eta R}}{6^{3/2}}.$$
 (54)

The universal ratio

$$U_{A\eta} \equiv \frac{\mathcal{A}_2 M \eta_e}{[\eta] \eta_s} \cong \frac{\mathcal{A}_2 M}{[\eta]}$$
(55)

arises from Equations 47 and 45.

Combination of Equations 46 and 48 yields

$$U_{fR} = \frac{(f/\eta_e)^{1/(d-2)}}{\langle R^2 \rangle^{1/2}} = \frac{(kT/D\eta_e)^{1/(d-2)}}{\langle R^2 \rangle^{1/2}}.$$
(56)

In 3D space, the hydrodynamic radius is derived as

$$R_{II} = \frac{f}{6\pi\eta_s}.$$
(57)

Hence, for d = 3,

$$\frac{\langle R^2 \rangle^{1/2}}{R_H} = \frac{6\pi}{U_{fR}},$$
(58)

i.e. Flory's hydrodynamic parameter P is proportional to U_{IR} :

$$P = \frac{U_{fR}}{\sqrt{6}}.$$
(59)

The universal ratio also results from Equations 45 and 46:

$$U_{\eta f} \equiv \frac{\left(\frac{M}{N_A} \cdot \frac{\eta_s}{\eta_e}[\eta]\right)^{(d-2)/d}}{f/\eta_e}.$$
(60)

It corresponds to Flory-Scheraga-Mandelkern's parameter β in 3D space as

$$\beta = \frac{\Phi^{1/3}}{P} = \left(\frac{N_A}{100}\right)^{1/3} U_{\eta f}; \tag{61}$$

and to Tsvetkov-S.Klenin's (1953) parameter as

$$A_0 = \frac{D\eta_s(M[\eta])^{1/3}}{T} \qquad \text{erg/grad mol}^{1/3} \tag{62}$$

through

$$A_0 = U_{\eta f} \left(\frac{N_A}{100}\right)^{1/3} k = \beta k.$$
(63)

It results from Equations 47 and 48 that (Oono, 1983)

$$U_{AR} = \frac{\mathcal{A}_2 M^2}{\langle R^2 \rangle^{3/2} N_A} = \psi 4\pi^{3/2}.$$
 (64)

The given ratios are related to each other as well:

$$U_{A\eta}U_{\eta R} = U_{AR},\tag{65}$$

$$U_{\eta f} U_{fR} = U_{\eta R}^{1/d}.$$
 (66)

Tables 5.1 and 5.2 compare the predictions of Oono-Kohmoto's (1983) theory with experimental results. Theory is seen to agree well with experiment. For the parameters β and A_0 , the experimental accuracy is, of course, insufficient to detect a very small effect (~ 5%) of solvent strength.

The ratio Φ/Φ_{θ} in the first row of Table 5.2 can be written as

$$\frac{\Phi}{\Phi_{\theta}} = \frac{\alpha_{\eta}^3}{\alpha_R^3},\tag{67}$$

where

$$\alpha_{\eta}^{3} = \frac{[\eta]}{[\eta]_{\theta}} \tag{68}$$

(see also Equation 3.6-71).

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Table 5.1

Universal relationships with hydrodynamic quantities (Oono and Kohmoto, 1983) [Reprinted with permission from: Y.Oono, M.Kohmoto. J. Chem. Phys. 78 (1983) 520-528. Copyright © 1983 American Institute of Physics]

Universal ratios (asymp- totic values)		Nondraining coil in the θ	g Gaussian solvent	Nondraining self-avoid- ing coil in the maximum good solvent		
		Oono and Kohmoto's theory $(d = 3, \epsilon = 1)$	Experiment	Oono and Kohmoto's theory $(d = 3, \varepsilon = 1)$	Experiment	
$U_{\eta R} = \frac{M[\eta]}{N_A \langle R^2 \rangle^{3/2}} $	53)	5.768	$\sim 6.22^{a}$ $\sim 6.12^{b}$	4.078	4.5^d 3.5^c $3.4\ldots 3.8$	
$U_{A\eta} = \frac{\mathcal{A}_2 M}{[\eta]} $	55)	0	0	1.196	1.3^{e} $1.2 \dots 1.4^{f}$	
$U_{JR} = \frac{f}{\eta_S \langle R^2 \rangle^{1/2}} $	56)	15.189	$\sim 14.7^{\flat}$ $\sim 17^{\circ}$	12.067	12^g	
$U_{\eta f} = \left(\frac{M[\eta]}{N_A}\right)^{1/3} \eta_s \middle/ f ($	60)	0.1236	0.126^{b} 0.12^{c}	0.1297		

^a polystyrene in cyclohexane (Miyaki et al., 1980),

^b asymptotic estimations using data by Monte-Carlo simulations (Zimm, 1980),

^c Monte-Carlo simulations (de la Torre et al., 1982),

^d poly(D- β -hydroxybutylate) in trifluoroethanol (Miyaki et al., 1977),

^c poly(D,L- β -methyl- β -propiolactone) in tetrahydrofuran (Miyaki et al., 1978),

^J polystyrene in benzene (Miyaki et al., 1978),

^g PMMA in acctone (Ter Meer et al., 1980).

Oono (1983) has applied the method of renormalization group transformations for hydrodynamic quantities in the whole crossover region. In this case, the complete renormalization group equation 17 should be considered, with its general solution of the form

$$f = \tilde{F}\left[Lw^{-2/\varepsilon}, N(1+w)^{-1/4}, (1+w)^{3/4}\frac{1-\hat{z}}{\hat{z}}\right],$$
(69)

where

$$w = \frac{u}{u^* - u},\tag{70}$$

$$\hat{z} = \frac{u^*}{u} \cdot \frac{\xi}{\xi^*},\tag{71}$$

Table 5.2

Traditional universal relationships with hydrodynamic quantities (Oono and Kohmoto, 1983) [Reprinted with permission from: Y.Oono, M.Kohmoto, J. Chem. Phys. 78 (1983) 520-528. Copyright @ 1983 American Institute of Physics]

		Nondraining chain in the θ so	Gaussian olvent	Nondraining self- avoiding chain in the maximal good solvent		
Universal ships (a values)	relation- asymptotic	Oono and Kohmoto's theory $(d = 3, \epsilon = 1)$	Experiment	$\begin{array}{llllllllllllllllllllllllllllllllllll$	Experiment	Theory $\frac{X}{X_{\theta}}$
Flory's constant \$\Phi \cdot 10^{-23}\$	(54)	$\frac{2.36}{\frac{\Phi_{\theta}}{N_{A}}} = 0.3917$	2.55ª 2.51 ^{\$}	$\frac{1.67}{N_A} = 0.277$	$\sim 1.8^{\circ}$ $\sim 1.4^{d}$	0.707
Flory's con- stant P	(59)	6.201	$\sim 6^{b}$ $\sim 7^{e}$	4.926	4.9 ^d	0.794
Flory-Sche- raga-Man- delkern's parameter $\beta \cdot 10^{-6}$	(61)	2.249	2.29 ^b 2.2*	2.36		1.049
Tsvetkov- S.Klenin's parameter A ₀ · 10 ¹⁰	(62) (63)	3.13	$(3.2 \pm 0.2)^3$	3.29	$(3.2 \pm 0.2)^{g}$	1.05
$\frac{\langle \mathcal{H}^2 \rangle^{1/2}}{\langle \mathcal{R}_H \rangle}$	(58)	1.241	1.1567	1.562	1.5557	1.259
Penetration function Ψ	(64)	0	9	0.219	0.22 ^{c,d}	

^a polystyrene in cyclohexane (Miyaki et al., 1980),

^b asymptotic estimations using data by Monte-Carlo simulations (Zimm, 1980),

^c poly(D-\$\beta\$-hydroxybutylate) in trifluoroethanol (Miyaki et al., 1977),

^d poly(D,L-β-methyl-β-propiolactone) in tetrahydrofuran (Miyaki et al., 1978),

¹ PMMA in acetone (Ter Meer et al., 1980),

⁹ 200 P+LMWL systems (more than 2,000 fractions), including 160 systems in the θ solvent (750 fractions) (Tsvetkov, 1986; Tsvetkov et al., 1982).

5.3. Hydrodynamic properties

 u^* and ξ^* are the values at the fixed point D (Equation 27),

The hydrodynamic quantities and their ratios have been calculated as functions of the crossover parameters ζ and δ :

$$\zeta = \left(\frac{2\pi N}{L}\right)^{\epsilon/2} w(1+w)^{-\epsilon/8} \tag{72}$$

(see Equation 5.1-146) and

$$\delta = (1+w)^{3/4} \frac{1-\hat{z}}{\hat{z}}.$$
(73)

However, the δ dependence of the hydrodynamic quantities has proved to be weak, i.e. the draining effect of a molecular chain is negligible.

As in the static case, when $w \to 0$ $(u \to 0)$ and $N \to \infty$, the hydrodynamic quantities become universal functions of one variable (see Equation 5.1-161) (here Oono introduces a new designation $\hat{z} \to Z$):

$$Z = \left(\frac{2\pi N}{L}\right)^{\epsilon/2} w. \tag{74}$$

Bearing in mind the dependence of α_R vs Z (see Equation 5.1-167), Oono has recalculated the hydrodynamic quantities as dependent on α_R (eg, see the dependence $U_{A\eta}$ vs α_R^2 in Figure 5.27).



Figure 5.27. Dependence $U_{A\eta} = \mathcal{A}M/[\eta]$ vs α_R^2 as held by Oono's (1983) theory [Reprinted with permission from: Y.Oono. J. Chem. Phys. **79** (1983) 4629-4642. Copyright © 1983 American Institute of Physics]. Experimental values relate to a solution of polychloroprene in decaline (Kawahara et al., 1968; Norisuye et al., 1968) (1) and poly(paramethylstyrene) in diethylsuccinate (Tanaka et al., 1970) (2)

Despite the accepted assumption $w \to 0$ $(u \to 0)$, the approximate version of theory fits the experimental data well in a wide range of α_R (therefore, of w as well). Oono

(1983) has also calculated and compared the indices ν (static) and $\tilde{\nu}$ (dynamic) in the whole range of Z. In the limiting cases of small and large w(Z), ν and $\tilde{\nu}$ coincide, while they somewhat diverge in the crossover region, and $\tilde{\nu}$ vs Z lies below ν vs Z and with a smaller slope.

5.4. Direct renormalization method

Des Cloizeaux (1981) has offered another approach using the direct renormalization method on the basis of the continuous chain model in continuous d-dimensional Edwards-type space.

Owing to the infinite number of macromolecular conformations, the analytical expressions of theory have different-type divergences at the first stage to be subject to renormalization. In order to study the asymptotic properties of chains with a high molecular weight, three successive renormalization procedures must be performed on the whole.

Unperturbed chains are Brownian chains, i.e. the continuous limit of chains with independent segments. The partition function (the functional integral) of a Brownian chain diverges due to the infinite number of degrees of freedom. To cancel this divergence, the first renormalization procedure is required.

Introduction of interactions gives rise to "ultraviolet" divergences at short distances, which also need renormalization.

Introduction of interactions to very long chains leads to "infrared" divergences requiring the third renormalization procedure of the analytical expressions.

The probability distribution function of a unperturbed (Brownian) chain can be represented as

$$P_0\{r\} = \exp\left\{-\frac{1}{2}\int\limits_0^S ds \left[\frac{d\vec{r}(s)}{ds}\right]^2\right\}.$$
(1)

As the exponent must be dimensionless, the parameter S has the dimension of area $[S] \sim \mathcal{L}^2$, where \mathcal{L} is the chain length.

Using Equation 1, the mean value of the exponent

$$\mathfrak{Z}_{0}(k) = \left\langle e^{i\vec{k}[\vec{r}(S) - \vec{r}(0)]} \right\rangle_{0} \tag{2}$$

is calculated as usual

$$\begin{aligned}
\mathcal{J}_{0}(k) &= \frac{\int d\{r\} P_{0}\{r\} \exp\left\{+i\vec{k}[\vec{r}(S) - \vec{r}(0)]\right\}}{\int d\{r\} P_{0}\{r\}} \\
&= \frac{\int d\{r\} \exp\left\{-\frac{1}{2} \int_{0}^{S} ds \left[\left(\frac{d\vec{r}(s)}{ds}\right)^{2} - 2i\vec{k}\frac{d\vec{r}(s)}{ds}\right]\right\}}{\int d\{r\} \exp\left\{-\frac{1}{2} \int_{0}^{S} ds \left[\left(\frac{d\vec{r}(s)}{ds}\right)^{2}\right]\right\}},
\end{aligned}$$
(3)

as

$$\frac{1}{2}\int_{0}^{S} 2i\vec{k}\frac{d\vec{r}(s)}{ds} = i\vec{k}[\vec{r}(S) - \vec{r}(0)].$$

The expression in the square brackets in the nominator of Equation 3 can be written as

$$\left[\frac{d\vec{r}(s)}{ds}\right]^2 - 2i\vec{k}\frac{d\vec{r}(s)}{ds} = \left[\frac{d\vec{r}(s)}{ds} - i\vec{k}\right]^2 + k^2.$$
(4)

By virtue of the invariability of the Gaussian integrals on a shift of the variables \vec{r} in a complex plane, the Gaussian integrals in both the nominator and denominator of Equation 3 cancel out and only

$$\mathfrak{Z}_0(k) = \exp\left(-\frac{k^2 S}{2}\right) \tag{5}$$

remains. Calculating $\langle (\vec{r}(S) - \vec{r}(0))^2 \rangle_0$ in an identical manner, we get for *d*-dimensional space

$$\langle h_{\theta} \rangle^2 = \left\langle (\vec{r}(S) - \vec{r}(0))^2 \right\rangle_0 = Sd.$$
(6)

Hence, the properties of a Brownian chain depend on one variable S only.

To study the macromolecular properties in a good solvent, the two-body (pair) interactions should be introduced, which in the model of a continuous chain is written as

$$P\{r\} = \exp\left[-\mathcal{H}(S,b)\right] = \exp\left\{-\frac{1}{2}\int_{0}^{S} ds \left[\frac{d\vec{r}(s)}{ds}\right]^{2} - \frac{b}{2}\int_{0}^{S} ds' \int_{0}^{S} ds'' \,\delta(\vec{r}(s') - \vec{r}(s''))\right\}.$$
 (7)

To ensure the convergence of the expressions based on distribution function 7, a cut-off s_0 must be introduced, i.e. it is presumed that $|s'' - s'| > s_0$ in the double integral, where $s_0 \ll S$. Physically, the cut-off prevents consideration of the self-interactions of segments, for which s' = s''.

It follows from form 7 that the parameter b must have its dimension

$$b \sim L^{d-4},\tag{8}$$

whence it is seen that d = 4 plays the role of the critical index in the problem. Then, the dimensionless parameter z

$$z = bS^{2-d/2}(2\pi)^{-d/2} \tag{9}$$

is introduced. Here, the quantities S and b can be related to more common ones

$$S = Nl^2, \tag{10}$$

$$b = vl^{-4},\tag{11}$$
where N is the number of segments with length l and v is the excluded volume. The quantities N, l, and v have the meaning of phenomenological parameters of the system (cf. Equation 3.1-153).

Let us consider a set of N macromolecules of different lengths. Each macromolecule is denoted by the index j with the corresponding area S_j . The chain itself is denoted by the vector $\vec{r}_j(s)$ ($0 < s < S_j$).

The probability distribution function associated with the conformations of the whole set of chains is written as

$$P\{r\} = \exp\left\{-\frac{1}{2}\sum_{j=1}^{N}\int_{0}^{S_{j}} ds \left[\frac{d\vec{r}(s)}{ds}\right]^{2} - \frac{b}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\int_{0}^{S_{i}} ds''\int_{0}^{S_{j}} ds' \,\delta(\vec{r}_{i}(s'') - \vec{r}_{j}(s'))\right\}.$$
 (12)

Here the cut-off $|s'' - s'| > s_0$ is also introduced to the integrals corresponding to the terms with i = j in the double sum.

All the physical quantities of a polymer system can be expressed through the **statistical** integrals with an imposed constraint. The fixing of several p points relating to the given macromolecules may serve as such a constraint. Each of the point, called a correlation point, is denoted by the index q $(1 \le q \le p)$. The point with the index q is assumed to relate to the chain j_q with the area S_q , and the coordinate of the point along the chain is s_q $(0 \le s_q \le S_q)$, its spatial position is characterized by the vector $\vec{r_q}$. The imposed constraint implies that the condition

$$\vec{r}_{jq}(s_q) = \vec{r}_q \tag{13}$$

is satisfied for every q within the range $1 \le q \le p$.

So, the statistical integral with an imposed constraint is designated as

$$+ \mathfrak{Z}_{G}(\vec{r}_{1}, \dots, \vec{r}_{p}; j_{1}, \dots, j_{p}; s_{1}, \dots, s_{p}; S_{1}, \dots, S_{\mathcal{N}}),$$
(14)

where the subscript 'G' denotes the general type of the integral, the plus means the introduced cut-off s_0 . Then, by definition,

$${}^{+}\mathfrak{Z}_{G}(\vec{r}_{1},\ldots,\vec{r}_{p};j_{1},\ldots,j_{p};s_{1},\ldots,s_{p};S_{1},\ldots,S_{\mathcal{N}})$$

$$=\frac{\int d\{r\} P\{r\}\delta(\vec{r}_{j1}(s_{1})-\vec{r}_{1})\cdots\delta(\vec{r}_{jp}(s_{p})-\vec{r}_{p})}{\int d\{r\} P_{0}\{r\}\delta(\vec{r}_{1}(0))\cdots\delta(\vec{r}_{\mathcal{N}}(0))},$$
(15)

and the general statistical integral of the system (with no imposed constraint) has the form

$${}^{+}\mathfrak{Z}_{G}(S_{1},\ldots,S_{N}) = \frac{\int d\{r\} P\{r\}}{\int d\{r\} P_{0}\{r\}\delta(\vec{r}_{1}(0))\cdots\delta(\vec{r}_{N}(0))}.$$
(16)

Thus, the statistical integrals are defined with the help of functional integrals. The denominator in Equations 15 and 16 is a normalizing factor which prevents the divergence of the statistical integrals—this constitutes the first renormalization procedure.

Partition function 7 suffices to study the conformational problems of macromolecules in a good solvent (b > 0) in the limit of long chains.

To analyze the situation in a poor solvent, ternary interactions must be taken into account. Then,

$$P\{r\} = \exp\left\{-\frac{1}{2}\int_{0}^{S} ds \left[\frac{d\vec{r}(s)}{ds}\right]^{2} - \frac{b}{2}\int_{0}^{S} ds'' \int_{0}^{S} ds' \,\delta(\vec{r}(s'') - \vec{r}(s')) \right. \tag{17}$$

$$-\frac{\mathbf{c}}{6}\int_{0}^{S} ds''' \int_{0}^{S} ds'' \int_{0}^{S} ds' \,\delta(\vec{r}(s''') - \vec{r}(s'))\delta(\vec{r}(s'') - \vec{r}(s')) \bigg\},$$

where the coefficient c characterizes the ternary interactions and has the dimension

$$[\mathbf{c}] \sim L^{2d-6},\tag{18}$$

whence it follows that d = 3 serves as the critical value of dimension in this case.

The coefficient c has, as well, the meaning of a phenomenological quantity which depends on the chemical structure of the polymer and solvent in a sophisticated and implicit way.

Results of the studies of polymers with their partition function of the Equation 17 type will be discussed in detail in section 5.5; now, we return to the partition function of the Equation 12 type which can be expanded into a series in powers of b. The interaction term is written as a short-range action through the Fourier transform:

$$b\delta(\vec{r}_i(s'') - \vec{r}_j(s')) = \frac{b}{(2\pi)^d} \int d^d k \exp\left\{i\vec{k}[\vec{r}_i(s'') - \vec{r}_j(s')]\right\}.$$
(19)

Therefore, the expansion of the Fourier transform of the statistical integral contains a number of terms, each being the mean value of the exponent of the $\exp[i\vec{k}\cdot\vec{r}(s)]$ type. The mean value is taken over all the set of Brownian chains and calculated from Equations 2 and 5.

The diagrams, displaying the *n*th-order terms, consist of \mathcal{N} lines (the number of macromolecules) and *n* interaction lines which connect the lines of macromolecules in some way. As an example, shown in Figure 5.28 are five-chain diagrams.



Figure 5.28. Diagram for $+\mathfrak{Z}_G(S_1,\ldots,S_5)$ consisting of two separated connected parts (des Cloizeaux, 1981) [Reprinted with permission from: J. des Cloizeaux, J. de Phys. 42 (1981) 635-652. Copyright © 1981 by EDP Sciences]: the solid lines are macromolecules, the dashed lines are interactions

Of special interest are the contributions of connected diagrams, as all the physical quantities can be expressed through the sums $[^+\mathfrak{Z}_G(\ldots)]_{con}$ of the very contributions. The connected statistical integrals are denoted as

$$+\mathfrak{Z}(S_1,\ldots,S_N) = V^{-1} \left[+\mathfrak{Z}_G(S_1,\ldots,S_N) \right]_{con};$$
⁽²⁰⁾

$$+ \Im(\vec{r}_{1}, \dots, \vec{r}_{p}; j_{1}, \dots, j_{p}; s_{1}, \dots, s_{p}; S_{1}, \dots, S_{\mathcal{N}})$$

$$= V^{-1} \left[+ \Im_{G}(\vec{r}_{1}, \dots, \vec{r}_{p}; j_{1}, \dots, j_{p}; s_{1}, \dots, s_{p}; S_{1}, \dots, S_{\mathcal{N}}) \right]_{con}.$$

$$(21)$$

If the volume of the system V increases, statistical integrals 20 and 21 become independent of V. For further analysis, the dimension of statistical integrals, which follows from Equations 16 and 20,

$$+\mathfrak{Z}(S_1,\ldots,S_N) \sim L^{d\mathcal{N}-d} = L^{d(\mathcal{N}-1)}$$
(22)

is of importance.

The Fourier transform of the connected statistical integrals is defined as

If V becomes infinite, the integral

$$+\bar{\mathfrak{Z}}(\vec{k}_1,\ldots,\vec{k}_p;j_1,\ldots,j_p;s_1,\ldots,s_p;S_1,\ldots,S_N)$$

remains finite and determined provided that

$$\vec{k}_1 + \vec{k}_2 + \dots + \vec{k}_p = 0.$$
⁽²⁴⁾

If the endpoints of the chains are fixed, the notation is simplified: the quantity

 $\tilde{\mathfrak{Z}}(\vec{k}_1,\ldots,\vec{k}_{2N};S_1,\ldots,S_N)$

corresponds to the situation with $p = 2\mathcal{N}$ and

$$(j_1, \ldots, j_{2\mathcal{N}}) = (1, 1; 2, 2; \ldots; \mathcal{N}, \mathcal{N}),$$

 $(s_1, \ldots, s_{2\mathcal{N}}) = (0, S_1; 0, S_2; \ldots; 0, S_{\mathcal{N}}).$

In the long-wave limit,

$${}^{+}\bar{\mathfrak{Z}}(0,0;\ldots;0,0;S_{1},\ldots,S_{N}) = {}^{+}\mathfrak{Z}(S_{1},\ldots,S_{N}).$$
⁽²⁵⁾

The terms of the expansion series of $+\Im(S_1,\ldots,S_N)$ or

$$+3(\vec{k}_1,\ldots,\vec{k}_p;j_1,\ldots,j_p;s_1,\ldots,s_p;S_1,\ldots,S_N)$$
(26)



Figure 5.29. A diagram with correlation points with introduced external vectors $(\vec{k}_1 + \vec{k}_2 + \vec{k}_3 = 0)$ (des Cloizeaux, 1981) [Reprinted with permission from: J. des Cloizeaux, J. de Phys. 42 (1981) 635-652. Copyright © 1981 by EDP Sciences]

in powers of b are connected graphs, as the interaction is denoted by connection lines. These graphs (diagrams) are constructed in all the possible ways and calculated according to the following rules.

1. The diagram consists of \mathcal{N} lines representing \mathcal{N} macromolecules; each line is denoted by the subscript 'j' and has the area S_i (Figures 5.28 and 5.29).

2. The macromolecular lines are connected by interaction lines which end on the macromolecular lines at the interaction points. Actually, the endpoints of the interaction lines coincide in physical space, not in the diagram (cf. Figures 5.8 and 5.9).

3. Correlation points are placed on the macromolecular lines.

4. The interaction points and the correlation points separate the macromolecular lines into segments. Each segment has its area. The sum of these areas of the polymer segments per line j is equal to S_j .

5. Each polymer segment and each interaction line contain a wavevector. **External** wavevectors $(\vec{k}_1, \ldots, \vec{k}_p)$ (see Figure 5.29) are introduced at the correlation points. Each segment at the free end of the polymer line is endowed with a wavevector 0. The flux of the wavevectors is preserved at the interaction points and at the correlation points.

6. The factor (-b) is associated with each interaction line.

7. Each polymer segment with the area s endowed with the wavevector \vec{q} , has its factor $\exp(-sq^2/2)$.

8. The product of all the factors is calculated over each independent internal vector \vec{q} and integration of the type

$$\frac{1}{(2\pi)^d}\int d^d q\ldots$$

is performed. One wavevector is attached to every internal loop.

9. Integration like $\int ds...$ is performed over every independent area s. The limits of integration are defined by the imposed constraints (see rule 4).

10. In integrating, the area of every polymer segment is assumed to be larger than the cut-off area s_0 , to avoid short-range (ultraviolet) divergences.

A cut-off at short distances is necessary for convergence but inconvenient for two reasons: it brings an additional parameter and makes the calculation of diagrams more difficult. The procedure of cutting-off is replaced by renormalization, and the renormalized quantities can be calculated with rule 10 slightly modified. In particular, the cut-off can be eliminated by the second renormalization of the integrals:

$$+ \Im(S_1, \dots, S_N) = \exp\left[(S_1 + \dots + S_N) s_0^{-1} C(z_0) \right] \Im(S_1, \dots, S_N);$$
(27)

$$^{\dagger}\mathfrak{Z}(\ldots,S_{1},\ldots,S_{\mathcal{N}}) = \exp\left[(S_{1}+\cdots+S_{\mathcal{N}})s_{0}^{-1}C(z_{0})\right]\overline{\mathfrak{Z}}(\ldots,S_{1},\ldots,S_{\mathcal{N}}),\tag{28}$$

where

 $z_0 = b s_0^{2-d/2} (2\pi)^{-d/2}.$

If $s_0 \to 0$, $\mathfrak{Z}(S_1, \ldots, S_N)$ and $\overline{\mathfrak{Z}}(\ldots, S_1, \ldots, S_N)$ remain well-defined (while the exponent diverges).

Thus, des Cloizeaux (1981) considers \mathcal{N} polymer connected *n*th-order $(n \geq \mathcal{N} - 1)$ diagrams contributing to $+3(\vec{S}_1, \ldots, S_N)$.

Before integration with respect to the independent wavevectors and the independent areas, the contribution of diagrams constitutes the product b^n as a dimensionless finite multiplier, which is a function of areas and wavevectors. The number of the independent areas is 2n. The number of the loops \mathcal{L} (i.e. the number of the independent wavevectors) is n - N + 1. On integration with respect to \mathcal{L} wavevectors, a homogeneous function $b^n D\{s\}$ of internal areas is obtained:

$$D\{\lambda s\} = \lambda^{-(n-N+1)d/2} D\{s\}.$$
(29)

Integration with respect to the internal independent areas $\{s\}$ may lead to a divergence, if $s_0 \to 0$.

To study this property, the concept of *P*-reducibility should be introduced. A diagram is thought of as *P*-reducible if it can be divided into two separate non-trivial parts by breaking one polymer line. Otherwise, it is considered as *P*-irreducible (Figure 5.30).



If a diagram is P-reducible to parts 1 and 2, one can write

$$D\{s_1 + s_2\} = D_1\{s_1\}D_2\{s_2\}.$$
(30)

The wavevector, related to the polymer segment connecting 1 and 2, depends on the external wavevectors only; hence, the integrals with respect to the wavevectors can be factorized. Then, the short-scale divergences, that exist in parts 1 and 2, are multiplied.

If a diagram is *P*-irreducible, the number of independent "internal" areas appearing in $D\{s\}$ is (2n - N). Therefore, such a diagram primitively diverges at short distances if (see Equation 29)

$$2n - \mathcal{N} \le \frac{d}{2}(n - \mathcal{N} + 1), \qquad \mathcal{L} = n - \mathcal{N} + 1 \ge 0.$$
(31)

This expression can also be written as

$$(n - \mathcal{N} + 1)\left(2 - \frac{d}{2}\right) + \mathcal{N} \le 2.$$
(32)

For d < 4, the product in the left-hand side is positive. This means that there is no primitively divergent diagrams for N > 1.

For $\mathcal{N} = 1$, this conditions degenerates to

$$n\left(2-\frac{d}{2}\right) \le 1. \tag{33}$$

At d < 2, all the diagrams converge at short distances, and there is no need either in cut-off or in renormalization. For $2 \le d < 4$, the degree of convergence (in area units) is [1 - n(2 - d/2)]. In principle, one subtraction suffices to ensure convergence, if a *P*-irreducible diagram contains no *P*-irreducible insertions (Figure 5.31a). In this simple



Figure 5.31. A *P*-irreducible diagram without (a) and with (b) a *P*-irreducible insertion (des Cloizeaux, 1981) [Reprinted with permission from: J. des Cloizeaux, J. de Phys. **42** (1981) 635-652. Copyright © 1981 by EDP Sciences]

case, the diagram diverges but contains no divergent subdiagrams, and subtraction can be performed as follows.

Let the point with its coordinate s_1 at the beginning of the chain be the point of the first interaction on a polymer line, and s_2 is the coordinate of the last interaction point (near the other end of the chain). Assuming s_1 and s_2 to be fixed, one can integrate $D\{s\}$, and this integral is convergent.

Dimensional analysis leads to

$$b^{n} \int_{s_{1}, s_{2} \text{fix}} d\{s\} D\{s\} = Ab^{n} |s_{2} - s_{1}|^{-2 + n(2 - d/2)} +$$
(34)

+ some terms vanishing if $s_0 \rightarrow 0$.

(35)

If $(s_2 - s_1) \to s_0$, then for $\mathcal{N} = 1$ $Ab^n \int_{s_1 + s_0} ds_2 |s_2 - s_1|^{-2 + n(2 - d/2)} = \frac{Ab^n}{1 - n(2 - d/2)} s_0^{-1 + n(2 - d/2)} +$

+ regular terms.

Thus, the integral can be written as the sum of the regular s_0 -independent components and the singular component which is a power function of s_0 . This singular component can be isolated from the regular one and regarded as an "insertion point" (Figure 5.32).

> Figure 5.32. A diagram with four insertion points (des Cloizeaux, 1981) [Reprinted with permission from: J. des Cloizeaux. J. de Phys. **42** (1981) 635-652. Copyright © 1981 by EDP Sciences]

Now let us discuss a diagram containing P-irreducible insertions (Figure 5.31b). Isolate the regular component from the s_0 -containing irregular one in the internal P-irreducible insertions. The process is iterated step by step. Finally, the contributions of the maximal P-irreducible subdiagrams are replaced by their regular parts. On integration (and subtracting the divergent part, if the entire diagram is P-irreducible), one obtains the final contribution of the diagram.

In such a way, the renormalized statistical integral $\mathfrak{Z}(S_1,\ldots,S_N)$ is calculated. The same procedure is applicable to calculation of the statistical integral with an imposed constraint $\bar{\mathfrak{Z}}(\ldots;S_1,\ldots,S_N)$.

Indeed, the s_0 -dependent terms are the same and do not depend on the external wavevectors.

Now let us have a look at how the total non-normalized contributions relate to the renormalized ones. The sum of the divergent contributions of all the primitively divergent *n*th-order diagrams is proportional to $z_0^n s_0^{-1}$ as is seen from Equation 35. The sum of these terms over *n* has the form $C(z_0)^n s_0^{-1}$ and can be regarded as an insertion point (see Figure 5.32). These points may be placed arbitrarily on the polymer lines. Inclusion of *q* points to a polymer line of the area S_i gives the multiplier

$$\frac{1}{q!} (S_j)^q \left(C(z_0) s_0^{-1} \right)^q. \tag{36}$$

Therefore, on introduction of insertion points in all the possible ways on all the polymer lines, the following multiplier emerges:

$$F = \exp\left[\left(\sum_{j=1}^{N} S_j\right) s_0^{-1} C(z_0)\right].$$
(37)



In just the same way, the s_0 -dependent regularized statistical integrals are obtained as the product of statistical integrals renormalized by this multiplier. The results obtained have the form of Equation 27.

To calculate $\mathfrak{Z}(S_1, \ldots, S_N)$ or $\mathfrak{Z}(\vec{k_1}, \ldots, \vec{k_p}; j_1, \ldots, j_p; s_1, \ldots, s_p; S_1, \ldots, S_N)$, rule 10 should be formulated as follows: summing over independent areas, one begins with the calculation of the maximal internal *P*-irreducible components (thus, the *P*-irreducible components are calculated consequently), the integral divergent at short ranges is replaced by its principal part; eg, for a certain n.

$$\int ds \, s^n = \frac{s^{n+1}}{n+1}.$$
(38)

This rule defines the two-parameter model. The renormalized statistical integrals in this model depend on b and the areas S_1, \ldots, S_N of macromolecules only. If all the areas are equal to S, the physical quantities depend on one dimensionless parameter z (Equation 9).

In what follows, the properties of solutions of a monomolecular polymer, i.e. chains with the same area S, will be discussed. However, in principle, this method of des Cloizeaux is applicable to polymolecular polymers as well.

The most important quantities of theory are:

- 1. the one-chain $\mathfrak{Z}(S)$ and two-chain $\mathfrak{Z}(S,S)$ statistical integrals;
- 2. the Fourier transform $\bar{\mathfrak{Z}}(\vec{k}, -\vec{k}; S)$ of the statistical integral with an imposed constraint $\mathfrak{Z}(\vec{r_1}, \vec{r_2}; S)$.

According to Equations 13, 23-26,

$$\overline{\mathfrak{Z}}(\vec{k}, -\vec{k}; S) = \mathfrak{Z}(S) \left\langle \exp\left\{ i\vec{k}[\vec{r}(S) - \vec{r}(0)] \right\} \right\rangle.$$
(39)

In particular, this function defines the mean square end-to-end distance of an isolated chain

$$\left\langle h^2 \right\rangle = \left\langle \left(\vec{r}(S) - \vec{r}(0)\right)^2 \right\rangle = -\frac{2d}{\mathfrak{Z}(S)} \left[\frac{\partial}{\partial k^2} \bar{\mathfrak{Z}}(\vec{k}, -\vec{k}; S) \right]_{k=0}.$$
(40)

On the basis of Equations 4.2–59, -60, -62, the first terms of the c_p -expansion of π have the form

$$\frac{\pi}{kT} = c_p - \frac{c_p^2 \mathfrak{Z}(S,S)}{2[\mathfrak{Z}(S)]^2}.$$
(41)

Des Cloizeaux introduced the concept of a **critical object** as applied to a polymer chain. Suppose the chain comprises N segments with excluded volume. Let us apply the following procedure to this chain: i) increase the number of segments; and ii) vary the segment length scale so that the mean square end-to-end distance remains constant. Multiple repetition of this procedure leads to a **continuous limit**. Thus, we have obtained a statistical chain to be characterized by one quantity of length only, namely, by the mean square end-to-end distance. Continuously increasing the length of such a chain, we proceed to an **infinite** chain whose scale proves to be invariant. By definition, such a chain is a **critical object** (des Cloizeaux, 1981).

The excluded volume interactions are characterized by the parameter z. If z = 0, the chain as a critical object is called a **Brownian chain**. When $z \to \infty$, there appears a new critical object called **Kuhn's chain**. So, this chain is the limit of a chain with interacting segments.

There is a crossover region between these two limiting cases, with a finite value of z. As z increases at a given b (or S), all the physical quantities increase, too; however, one can expect the universal behaviour and fulfillment of scaling relationships in the asymptotic limit. To express these physical quantities, it is worthwhile to employ a new scale.

For an isolated polymer chain with an interaction, the area ^{e}S can be defined by

$$\left\langle h^2 \right\rangle = \left\langle \left[\vec{r}(S) - \vec{r}(0) \right]^2 \right\rangle = {}^\circ Sd,$$
(42)

where

$$\frac{^{*}S}{S} = X_0(z). \tag{43}$$

It is this area that defines the new scale.

With $z \to \infty$, factor $X_0(z)$ becomes infinite. For long polymer chains on a lattice $(S \gg l^2)$, the relationships

$$S \sim Nl^2$$
 (44)

and

$${}^{e}S \sim N^{2\nu}l^2 \tag{45}$$

hold true. Hence,

$$\frac{^{c}S}{S} \sim N^{2\nu-1} \sim S^{2\nu-1}.$$
(46)

On the other hand, for the two-parameter theory with a constant b, according to Equation 9,

$$\varepsilon \sim S^{\varepsilon/2} \qquad (\varepsilon = 4 - d).$$
 (47)

Thus, one can expect the asymptotic behaviour of the function $X_0(z)$:

$$X_0(z) \sim z^{2(2\nu-1)/\varepsilon} \qquad (z \to \infty). \tag{48}$$

At S = const, "S tends to infinity, if $z \to \infty$. This circumstance shows the wisdom of choosing "S as a new scale, and $X_0(z)$ can be regarded as the renormalization factor.

The statistical integrals, corresponding to a polymer chain, and the binary system P+LMWL, are functions of S and z and can be expressed in terms of the new variables ${}^{e}S$ and z. The physical quantities, deduced from the statistical integral, are also expressed through ${}^{e}S$ and z, and at ${}^{e}S = const$ they must reach their finite limit, if $z \to \infty$ (Kuhn's behaviour). However, when ${}^{e}S = const$, the statistical integrals turn out to be infinite, if $z \to \infty$.

For example, discuss $\mathfrak{Z}(S)$. As this quantity is dimensionless, then

$$\mathfrak{Z}(S) = [X_1(z)]^2. \tag{49}$$

On the other hand, the behaviour of the partition function of a discrete chain with N segments on a lattice is expected to follow the form

$$\mathfrak{Z}(N) \sim N^{\gamma-1} \mu^N. \tag{50}$$

This result can be expressed in terms of the two-parameter theory provided that b = constand S is large, namely,

$$\mathfrak{Z}(S) \sim S^{\gamma-1}.\tag{51}$$

The coefficient μ is absorbed on the first and second renormalizations. Due to Equation 47.

$$X_1(z) \sim z^{(\gamma-1)/\varepsilon} \qquad (z \to \infty) \tag{52}$$

can be expected.

Now we are able to define the renormalized statistical integral $\mathfrak{Z}_R(^{c}S)$, which, like $\mathfrak{Z}(S)$, must be dimensionless. By definition, this statistical integral must depend on the physical scale ^{c}S only and, therefore, be a constant; then,

$$\mathfrak{Z}_R(^*S) = 1 \tag{53}$$

can be accepted.

In accordance with Equation 49, we have

$$\mathbf{\mathfrak{Z}}(S) = [X_1(z)]^2 \,\mathbf{\mathfrak{Z}}_R({}^{e}S). \tag{54}$$

Thus, X_1 can be regarded as the second renormalization factor defined by renormalization condition 53. Such a renormalization is applied in field theory for d = 4 to eliminate "ultraviolet" divergences.

In polymer theory, "infrared" divergences are discussed as well: the behaviour of the partition functions is analyzed at d < 4 and $z \to \infty$. In other words, the dimension d proves to be marginal in polymer theory as well as in quantum electrodynamics and Landau-Ginzburg-Wilson's field theory. In particular, this explicitly manifests itself in the definition of z (see Equation 9).

Indeed, the "ultraviolet" marginal divergence can easily be transformed to the "infrared" marginal one, as it follows from the example $(A \gg 1)$

$$\int_{1}^{A} \frac{dx}{x} = \int_{1/A}^{1} \frac{dy}{y}.$$
(55)

Hence, the renormalization technique applied in field theory is suitable in polymer theory as well. The chief idea is in the 'S dependence of the basic quantities at $z \to \infty$. However, these hopes are realized only partially.

For this behaviour of physical quantities, the statistical integrals must be renormalized (once again!), and des Cloizeaux assumes that only few renormalization factors are enough for this. By analogy with field theory, these renormalization factors are associated with the end effects, i.e. with the vertex insertions (see section 2.6).

More precisely, if a statistical integral is associated with the situation where \mathcal{M} polymer segments with their areas $S_1, \ldots, S_{\mathcal{M}}$ are attached to one point, the renormalization



Figure 5.33. Vertex functions (insertions) and the corresponding renormalization factors. The wavevector is attached to the vertex. If the wavevector is equal to zero, the dashed line can be omitted (des Cloizeaux, 1981) [Reprinted with permission from: J. des Cloizeaux. J. de Phys. **42** (1981) 635-652. Copyright © 1981 by EDP Sciences]

factor $X_{\mathcal{M}}(z_1, \ldots, z_{\mathcal{M}})$ must be introduced (Figure 5.33). In particular, such renormalization factors must be introduced to renormalize star-like polymers. Besides, they may be reasonable to study the contacts between the internal points of a polymer chain.

If all the areas S_1, \ldots, S_M of the vertex point's branches have the same order of magnitude $S_1 = n_1 S_1 \ldots S_M = n_M S$ $(n_1, \ldots, n_M$ are finite), more simple renormalization factors $X_M(z)$ can be introduced.

Thus, the statistical integral $\mathfrak{Z}(C)$, corresponding to the ensemble of conformations C, can be renormalized as

$$\mathfrak{Z}(C) = \prod_{i} X_i \mathfrak{Z}_R(C),\tag{56}$$

where the subscript 'i' denotes the external vertices. For instance, the statistical integral $\Im(S_1, \ldots, S_N)$ of \mathcal{N} macromolecules with their area S_i is renormalized by the following procedure:

$$\mathfrak{Z}(S_1,\ldots,S_N)=X_1^2(z_1)\cdots X_1^2(z_N)\mathfrak{Z}_R({}^eS_1,\ldots,{}^eS_N). \tag{57}$$

For $\mathcal{N} = 1$, Equation 57 agrees with Equation 54.

The renormalization factors can be exactly determined in all cases given adequate renormalization conditions are introduced, which the renormalized statistical integrals must obey.

For $X_2(z_1, z_2)$, the condition

$$X_2(z_1, z_2) = 1 (58)$$

can be accepted. If the zero wavevector is introduced into a certain point of the macromolecule, a two-vertex insertion results (Figure 5.34). In the diagram, this point is located on the polymer segment with its area s with its own wavevector q.

When there is no interaction, the factor associated with the segment is

$$\exp\left(-\frac{q^2s}{2}\right).\tag{59}$$



Figure 5.34. A two-vertex insertion in a polymer segment, which connects the interaction points A and B: a segment with its area s without insertion (a) and a segment with a two-vertex insertion $s = s_1 + s_2$ (b) (des Cloizeaux, 1981) [Reprinted with permission from: J. des Cloizeaux, J. de Phys. 42 (1981) 635-652. Copyright © 1981 by EDP Sciences]

The two-vertex insertion divides the segment into two segments with the areas s_1 and s_2 so that $s_1 + s_2 = s$. Then, the factors associated with these segments are

$$\exp\left(-\frac{q^2s_1}{2}\right)\exp\left(-\frac{q^2s_2}{2}\right) = \exp\left(-\frac{q^2s}{2}\right).$$
(60)

Thus, the two-vertex insertion does not change the contribution of the diagram and, therefore, the value of the corresponding statistical integral. This means that $X_2(z_1, z_2)$ must be equal to 1.

By definition,

$$X_{\mathcal{M}} \sim N^{\sigma_{\mathcal{M}}} \tag{61}$$

must be satisfied for large N. Then (see Equations 47 and 44),

$$\sigma_{\mathcal{M}}(z) = \frac{\varepsilon}{2} \cdot \frac{\partial \ln X_{\mathcal{M}}(z)}{\partial \ln z}.$$
(62)

The critical index $\sigma_{\mathcal{M}}$ is defined as the limit

$$\sigma_{\mathcal{M}} = \lim_{z \to \infty} \sigma_{\mathcal{M}}(z). \tag{63}$$

 σ_0 and σ_1 are the most important critical indices. Indeed, it follows from Equations 48 and 52 that

$$\sigma_0 = 2\nu - 1, \tag{64}$$

$$\sigma_1 = \frac{\gamma - 1}{2}.\tag{65}$$

The functional ^{c}S dependence of the renormalized statistical integrals is defined by Equation 23.

The renormalization condition to define $X_1(z)$ is

$$\mathfrak{Z}_{R}(^{c}S) = \mathfrak{l}, \quad X_{\mathfrak{l}}^{2}(z) = \mathfrak{Z}(S),$$
(66)

while that to define $X_0(z)$ is

$$X_0(z) = \frac{{}^{*}S}{S} = -\frac{2}{\mathfrak{Z}(S)} \left[\frac{d}{d(k^2S)} \bar{\mathfrak{Z}}(\vec{k}, -\vec{k}; S) \right]_{k=0}.$$
(67)

On the other hand, dimensional analysis (see Equation 22) shows that the renormalized statistical integral $\mathfrak{Z}_R({}^eS,{}^eS)$ can be written as

$$\mathfrak{Z}_{R}({}^{e}S, {}^{e}S) = -(2\pi)^{d/2} ({}^{e}S)^{d/2}g, \tag{68}$$

where g is a quantity having the meaning of the dimensionless second virial coefficient (see Equation 41). Thus, the first two terms of the virial expansion can be written in the virial form

$$\frac{\pi}{kT} = c_p \left[1 + \frac{1}{2} (2\pi)^{d/2} g c_p ({}^e S)^{d/2} + \cdots \right].$$
(69)

The fundamental idea of renormalization theory is in establishing relationships between physical quantities. For instance, if z = 0, then g = 0, but if $z \to \infty$, g has its finite limit g^* . Besides, for $d \ge 4$, $g^* = 0$. Hence, for small positive quantities $\varepsilon = 4 - d$, g can be expanded into a series in powers of ε . The ε expansion of the critical indices can be obtained identically.

The renormalization strategy is as follows. Beginning with Equations 66 and 67, $X_0(z)$ and $X_1(z)$ as functions of z and the effective critical indices $\sigma_0(z)$ and $\sigma_1(z)$ are calculated by the perturbation method. Using Equation 68, g can be expressed as a series in powers of z, which can be transformed as to express z as a series in powers of g.

Let us discuss the function

$$w(z) = \varepsilon z \frac{dg}{dz}.$$
(70)

As is seen from the plot of g vs $\ln z$, if $z \to \infty$, then $g \to g^*$ and $w(z) \to 0$. If z is expressed as a function of g, then

$$w[g] = w(z). \tag{71}$$

Therefore, g^* is determined from the equation

$$w[g^*] = 0.$$
 (72)

As w[g] is defined as a series in powers of g, we get the expansion of g^* in powers of ε . The effective critical indices can be expressed through g

$$\sigma_0[g] = \sigma_0(z), \quad \sigma_1[g] = \sigma_1(z), \tag{73}$$

and all the terms singular with respect to $1/\varepsilon$ disappear.

Hence, the critical indices are defined by

$$\sigma_0 = \sigma_0[g^*] \quad \text{and} \quad \sigma_1 = \sigma_1[g^*]. \tag{74}$$

These equalities are used to obtain the ε expansion of σ_0 and σ_1 .

In such a way, one can obtain the index which determines the degree of approach to the asymptotic behaviour, i.e. determines the nature of the first corrections to scaling.

Des Cloizeaux defines

$$\sigma_a[g] = -\frac{d\omega[g]}{dg},\tag{75}$$

$$\sigma_a = \sigma_a[g^*]. \tag{76}$$

In comparison with the second-order theory of critical phenomena, he has found that

$$\sigma_{\mathbf{a}} = 2\omega\nu = 2\Delta_1,\tag{77}$$

and calculated the terms of the expansion of $\overline{\mathfrak{Z}}(\vec{k}, -\vec{k}; S)$ and $\mathfrak{Z}(S, S)$ in the second order of z and in the first order of (k^2S) , keeping two leading (with respect to ε) terms in each coefficient. The diagrams contributing to $\mathfrak{Z}(\vec{k}, -\vec{k}; S)$ are shown in Figure 5.35. Let us



Figure 5.35. Zeroth-order, first-order, and second-order diagrams contributing to $\ddot{\mathbf{3}}(\vec{k}, -\vec{k}; S)$, and second-order (with respect to (k^2S)) contributions (des Cloizeaux, 1981) [Reprinted with permission from: J. des Cloizeaux. J. de Phys. 42 (1981) 635–652. Copyright © 1981 by EDP Sciences]

write the result

$$\bar{\mathfrak{Z}}(\vec{k},-\vec{k};S) = 1 + z\frac{1}{\varepsilon}(2+\varepsilon) - z^2\frac{1}{\varepsilon^2}(6+7\varepsilon)$$

$$-\frac{k^2S}{2}\left[1 + z\frac{1}{\varepsilon}(4+0\varepsilon) - z^2\frac{1}{\varepsilon^2}\left(8 + \frac{3}{2}\varepsilon\right)\right].$$
(78)

The diagrams contributing to $\Im(S, S)$ are either 1-reducible (des Cloizeaux, 1980ab), by cutting the interaction line, or 1-irreducible. The 1-reducible diagrams are presented in Figure 5.36. Calculation of the contributions of these diagrams is performed in view of their product form. The 1-irreducible diagrams are depicted in Figure 5.37. By



Figure 5.36. l-reducible diagrams contributing to $\mathfrak{Z}(S,S)$. Their contributions are represented as products and can be obtained from the contribution of the diagrams $\mathfrak{Z}(S) = \mathfrak{Z}(0,0,S)$ (see Figure 5.34). Third-order diagrams are not displayed here (des Cloizeaux, 1981) [Reprinted with permission from: J. des Cloizeaux. J. de Phys. 42 (1981) 635-652. Copyright © 1981 by EDP Sciences]

summation of the contributions of the reducible and irreducible diagrams, des Cloizeaux has obtained

$$\mathfrak{Z}(S,S) = -bS^2 \left[1 + z(1 + 4\ln 2) + z^2 \frac{1}{\varepsilon} (2 - 32\ln 2) \right]$$

$$= -(2\pi)^{d/2} S^{d/2} \left[z + z^2 (1 + 4\ln 2) + z^3 \frac{1}{\varepsilon} (2 - 32\ln 2) \right].$$
(79)

Equations 67 and 78 lead to

$$\frac{{}^{e}S}{S} = \frac{1+z\frac{1}{\varepsilon}(4+0\varepsilon) - z^{2}\frac{1}{\varepsilon^{2}}\left(8+\frac{3}{2}\varepsilon\right)}{1+z\frac{1}{\varepsilon}(2+\varepsilon) - z^{2}\frac{1}{\varepsilon^{2}}(6+7\varepsilon)},$$
(80)

and, therefore,

$$X_0(z) = \frac{{}^{\epsilon}S}{S} = 1 + z\frac{1}{\varepsilon}(2-\varepsilon) + z^2\frac{1}{\varepsilon^2}\left(-6 + \frac{11}{2}\varepsilon\right).$$
(81)

Equations 66 lead to

$$X_1(z) = 1 + z\frac{1}{\varepsilon}\left(1 + \frac{\varepsilon}{2}\right) + z^2\frac{1}{\varepsilon^2}\left(-\frac{7}{2} - 4\varepsilon\right).$$
(82)

It follows from Equation 62 and the results obtained for $X_0(z)$ and $X_1(z)$ that

$$\sigma_0(z) = z \left(1 - \frac{\varepsilon}{2} \right) + z^2 \frac{1}{\varepsilon} \left(-8 + \frac{15}{2} \varepsilon \right), \tag{83}$$

$$\sigma_1(z) = z \left(\frac{1}{2} + \frac{\varepsilon}{4}\right) + z^2 \frac{1}{\varepsilon} \left(-4 - \frac{9}{2}\varepsilon\right).$$
(84)

Now we express g through z. According to Equations 68 and 57,

$$(2\pi)^{-d/2}\mathfrak{Z}_R({}^eS, {}^eS) = -({}^eS)^{d/2}g,\tag{85}$$



Figure 5.37. I-irreducible second-order and third-order diagrams contributing to $\Im(S, S)$ and their algebraic contributions (des Cloizeaux, 1981) [Reprinted with permission from: J. des Cloizeaux, J. de Phys. 42 (1981) 635-652. Copyright © 1981 by EDP Sciences]

$$\mathfrak{Z}_{R}({}^{\epsilon}S, {}^{\epsilon}S) = [X_{1}(z)]^{-4}\mathfrak{Z}(S, S), \tag{86}$$

whence (see Equation 79)

$$g = [X_1(z)]^{-4} {}^{c}S)^{-d/2} \left[-(2\pi)^{-d/2} \Im(S,S) \right]$$

$$= [X_1(z)]^{-4} [X_0(z)]^{-2+\epsilon/2} \left[z + z^2 (1 + 4\ln 2) + z^3 \frac{1}{\epsilon} (2 - 32\ln 2) \right],$$
(87)

and, in view of Equations 81 and 82,

$$g = z + z^{2} \frac{1}{\varepsilon} \left[-8 + \varepsilon (2 + 4 \ln 2) \right] + z^{3} \frac{1}{\varepsilon^{2}} \left[64 + \varepsilon (-15 - 64 \ln 2) \right].$$
(88)

According to Equation 70,

$$w(z) = \varepsilon z + z^{2} [-16 + \varepsilon (4 + 8 \ln 2)] + z^{3} \frac{1}{\varepsilon} [192 + \varepsilon (-45 - 192 \ln 2)].$$
(89)

By inversion of Equation 88, one obtains

$$z = g + \frac{g^2}{\varepsilon} [8 + \varepsilon(-1 - 4\ln 2)] + \frac{g^3}{\varepsilon^2} [64 + \varepsilon(-49 - 64\ln 2)],$$
(90)

whence (see Equations 89 and 90)

$$w[g] = \epsilon g + g^2 [-8 + \epsilon (2 + 4 \ln 2)] + g^3 (34) + \cdots$$
(91)

All the singularities in $1/\epsilon$ are seen to disappear.

Fquations 72 and 91 yield for the first two expansion terms of g^* in terms of ε

$$g^* = \frac{\varepsilon}{8} + \frac{\varepsilon^2}{16} \left(\frac{25}{16} + \ln 2\right) + \cdots .$$
 (92)

In the asymptotic long-chain limit in good solvents, $g = g^*$ should be accepted in virial expansion 69. For d = 3 ($\varepsilon = 1$), it follows from Equation 92 that $g^* = 0.266$. On the basis of Equations 83, 84, and 90, des Cloizeaux obtains

$$\sigma_0[g] = g\left(1 - \frac{\varepsilon}{2}\right) + g^2\left(\frac{3}{2} - 4\ln 2\right),\tag{93}$$

$$\sigma_1[g] = g\left(\frac{1}{2} + \frac{\varepsilon}{4}\right) + g^2\left(-\frac{7}{2} - 2\ln 2\right).$$
(94)

Again, the singularities in powers of $1/\varepsilon$ disappear. The series for $\sigma_a[g]$ is derived from Equations 75 and 91

$$\sigma_a[g] = -\varepsilon + g[16 + \varepsilon(-4 - 8\ln 2)] - g^2(102).$$
(95)

On substituting g for g^* in Equations 93–95 and including Equation 92, des Cloizeaux obtains

$$\sigma_0 = \frac{\varepsilon}{8} + \frac{15}{256}\varepsilon^2 + \cdots, \qquad (96)$$

$$\sigma_1 = \frac{\varepsilon}{16} + \frac{13}{512}\varepsilon^2 + \cdots, \qquad (97)$$

$$\sigma_a = \varepsilon - \frac{17}{32} \varepsilon^2 + \cdots . \tag{98}$$

The values of the common indices γ , ν , and $\Delta_1 = \omega \nu$ result on substituting the above results to Equations 64, 65, and 77

$$\nu = \frac{\sigma_0 + 1}{2} = \frac{1}{2} \left(1 + \frac{\varepsilon}{8} + \frac{15}{256} \varepsilon^2 + \cdots \right), \tag{99}$$

$$\gamma = 2\sigma_1 + 1 = 1 + \frac{\varepsilon}{8} + \frac{13}{256}\varepsilon^2 + \cdots,$$
(100)

$$\Delta_1 = w\nu = \frac{\sigma_a}{2} - \frac{\varepsilon}{2} - \frac{17}{64}\varepsilon^2 + \cdots .$$
(101)

and, at $\varepsilon = 1$ (i.e. d = 3)

$$\nu = 0.592, \quad \gamma = 1.175, \quad \Delta_1 = \omega \nu = 0.234.$$
 (102)

To reveal fine effects in the properties of polymer solutions, des Cloizeaux (1981) calculates the mean square radius of gyration of macromolecules, which is defined through

$$R^{2} = \frac{1}{2} \int_{0}^{1} dx \int_{0}^{1} dy \left\langle \left[\vec{r}(s_{2}) - \vec{r}(s_{1}) \right]^{2} \right\rangle,$$
(103)

where the integrand is expressed through the Fourier transforms of the statistical integrals

$$\frac{\mathbf{\bar{3}}(\vec{k}, -\vec{k}; s_1, s; S)}{\mathbf{\bar{3}}(0, 0; s_1, s; S)} = \left\langle \exp\left\{i\vec{k}[\vec{r}(s_2) - \vec{r}(s_1)]\right\}\right\rangle \simeq 1 - \frac{k^2}{2d} \left\langle [\vec{r}(s_2) - \vec{r}(s_1)]^2 \right\rangle; \quad (104)$$

 $0 < s_1 < s_2 < S; x = s_1/s_2; y = (S - s_1)/S.$

First-order calculations in z have led to the following results:

$$\bar{\mathfrak{Z}}(\vec{k},-\vec{k};s_1,s_2;S) = \exp\left[\frac{-k^2 S(1-x-y)}{2}\right] \left[1 - \frac{z}{(1-d/2)(2-d/2)} - \frac{k^2 S}{2} z I(x,y)\right], (105)$$

where

$$I(x,y) = \frac{1}{(-d/2)(1-d/2)} \left[(1-x-y)^2 + \frac{2(1-x-y)^{3-d/2}}{(2-d/2)(3-d/2)} - 2\frac{(1-x)^{3-d/2} + (1-y)^{3-d/2}}{3-d/2} + 2\frac{y(1-x)^{2-d/2} + x(1-y)^{2-d/2}}{2-d/2} - 2\frac{x^{3-d/2} + y^{3-d/2}}{(2-d/2)(3-d/2)} \right];$$

$$\left\langle [\vec{r}(s_2) - \vec{r}(s_1)]^2 \right\rangle = Sd[1-x-y-I(x,y)].$$
(106)

The diagrams contributing to the statistical integral $\overline{\mathbf{\mathfrak{Z}}}(\vec{k},-\vec{k};s_1,s_2;S)$ are shown in Figure 5.38.

Further, des Cloizeaux (1981) has calculated $\langle R^2 \rangle$ for d-dimensional space:

$$\left\langle R^2 \right\rangle = \frac{Sd}{6} \left[1 + 2 \frac{d^2 - 26d + 136}{(4-d)(6-d)(8-d)(10-d)} z \right]$$
 (107)

and, in the ε expansion,

$$\left\langle R^2 \right\rangle = \frac{Sd}{6} \left[1 + \frac{2}{\varepsilon} \left(1 - \frac{13}{24} \varepsilon \right) z \right]. \tag{108}$$



Figure 5.38. Diagrams contributing to $\bar{\mathfrak{Z}}(\vec{k}, -\vec{k}; s_1, s_2; S)$, in the zeroth and first order in ε (des Cloizeaux, 1981) [Reprinted with permission from: J. des Cloizeaux. J. de Phys. 42 (1981) 635–652. Copyright © 1981 by EDP Sciences]

On the other hand,

$$\frac{\bar{\mathfrak{Z}}(\vec{k},-\vec{k};S)}{\bar{\mathfrak{Z}}(0,0;S)} = 1 - \frac{k^2 S}{2d} \left\langle [\vec{r}(S) - \vec{r}(0)]^2 \right\rangle.$$
(109)

According to Equation 78,

$$\langle h^2 \rangle = \langle [\vec{r}(S) - \vec{r}(0)]^2 \rangle = Sd \left[1 + \frac{2}{\varepsilon} \left(1 - \frac{\varepsilon}{2} \right) z \right].$$
 (110)

So, it results that

$$\frac{\langle R^2 \rangle}{\langle h^2 \rangle} = \frac{1}{6} \left(1 - \frac{z}{12} + \cdots \right). \tag{111}$$

In the first order, $z \simeq g$, i.e.

$$\frac{\langle R^2 \rangle}{\langle h^2 \rangle} = \frac{1}{6} \left(1 - \frac{g}{12} + \cdots \right). \tag{112}$$

In the asymptotic limit, g must be replaced by $g^* \simeq \varepsilon/8$ (see Equation 92). Then, in the first order of ε ,

$$\frac{\langle R^2 \rangle}{\langle h^2 \rangle} = \frac{1}{6} \left(1 - \frac{\varepsilon}{96} + \cdots \right). \tag{113}$$

At finite values of z, the crossover effects are observed. In this connection, of great significance is the z dependence of g, which follows from Equation 70

$$\varepsilon z \frac{dg}{dz} = w[g]. \tag{114}$$

If $z \to 0$, $g \to 0$, and $w[g] \simeq \varepsilon g$. The solution of Equation 114 has been obtained (des Cloizeaux, 1981) in the form

$$\ln z = \ln g + \int_{0}^{g} dg' \left[\frac{\varepsilon}{w[g']} - \frac{1}{g'} \right].$$
(115)

The series w[g] in g is written just as Equation 91, whence

$$w[g^*] = 0$$

follows. This series has an approximate formula,

$$w[g] = \frac{\varepsilon g}{1 + \Lambda g} \left[1 - \frac{g}{g^*} \right], \tag{116}$$

where

$$A = \frac{17}{4} \left[1 + \varepsilon \left(\frac{25}{32} + \frac{1}{2} \ln 2 \right) \right].$$
(117)

In accordance with this and in view of Equations 75 and 76,

$$\sigma_a = \frac{\varepsilon}{1 + Ag^*}.\tag{118}$$

With due account of Equation 116 and 117, we derive from Equation 115:

$$z = g \left(1 - \frac{g}{g^*} \right)^{-\epsilon/\sigma_a}.$$
(119)

Equations 117, 92, and 118 lead to

$$Ag^* = \frac{17}{32}\varepsilon,\tag{120}$$

$$\sigma_a = \frac{\varepsilon}{1 + \frac{17}{32}\varepsilon}.$$
(121)

Equation 121 agrees with Equation 95 and yields $\sigma_a = 32/49 = 0.653$. Substituting $g^* = 0.266$ and $\varepsilon/\sigma_a = 1.531$, des Cloizeaux obtains

$$z = 0.266 \frac{g}{g^*} \left(1 - \frac{g}{g^*} \right)^{-1.531}.$$
 (122)

This relationship defines the function g(z), whose plot is depicted in Figure 5.39. The g dependence of the renormalization factor $X_{\mathcal{M}}(g)$ is defined by Equations 62 and 70

$$z\frac{d}{dz}\ln X_{\mathcal{M}} = \frac{2}{\varepsilon}\sigma_{\mathcal{M}},\tag{123}$$

$$z\frac{dg}{dz} = \frac{w}{\varepsilon}.$$
(124)

They lead to

$$\frac{d}{dy}\ln X_{\mathcal{M}}[g] = 2\frac{\sigma_{\mathcal{M}}[g]}{w[g]}.$$
(125)



Figure 5.39. The z dependence of g proportional to the second virial coefficient (des Cloizeaux, 1981) [Reprinted with permission from: J. des Cloizeaux. J. de Phys. 42 (1981) 635-652. Copyright C 1981 by EDP Sciences]

In the proximity $g = g^*$ (see Equations 72, 75, 76),

$$w[g] = \sigma_a(g^* - g), \tag{126}$$

$$\sigma_{\mathcal{M}}[g^*] = \sigma_{\mathcal{M}},\tag{127}$$

$$\frac{\sigma_{\mathcal{M}}[g]}{w[g]} \simeq \frac{\sigma_{\mathcal{M}}}{(g^* - g)\sigma_a}.$$
(128)

On the other hand, $X_{\mathcal{M}}[0] = 1$. Integration of Equation 125 gives

$$X_{\mathcal{M}}[g] = \left(1 - \frac{g}{g^*}\right)^{2\sigma_{\mathcal{M}}/\sigma_a} \exp\left\{2\int_0^g dg' \left[\frac{\sigma_{\mathcal{M}}[g']}{w[g']} - \frac{\sigma_{\mathcal{M}}}{(g^* - g)\sigma_a}\right]\right\}.$$
 (129)

A reasonable approximation (Equation 129) results when simple expressions for $\sigma_{\nu}[g]$ and w[g] are used.

In the second order, the following relationships have been derived:

$$\sigma_{\mathcal{M}}[g] = a_{\mathcal{M}}g + b_{\mathcal{M}}g^2, \tag{130}$$

$$w[g] = \frac{\varepsilon g}{1+Ag} \left(1 - \frac{g}{g^*} \right), \tag{131}$$

$$\sigma_a = \frac{\varepsilon}{1 + Ag^*}.\tag{132}$$

For the difference in the square brackets in the integrand of Equation 129, it has been obtained (des Cloizeaux, 1981)

$$\frac{\sigma_{\mathcal{M}}[g]}{w[g]} - \frac{\sigma_{\mathcal{M}}}{(g^* - g)\sigma_a} = \left(\frac{a_{\mathcal{M}}}{\varepsilon} - \frac{\sigma_{\mathcal{M}}}{g^*\sigma_a}\right) + \left(\frac{1}{\varepsilon} - \frac{1}{\sigma_a}\right)b_{\mathcal{M}}g,\tag{133}$$

$$X_{\mathcal{M}}(g) = \left(1 - \frac{g}{g^*}\right)^{-2\sigma_{\mathcal{M}}/\sigma_a} \exp\left\{2\left(\frac{a_{\mathcal{M}}}{\varepsilon} - \frac{\sigma_{\mathcal{M}}}{g^*\sigma_a}\right)g + \left(\frac{1}{\varepsilon} - \frac{1}{\sigma_a}\right)b_{\mathcal{M}}g^2\right\}.$$
 (134)

For $\varepsilon = 1$, it follows from Equation 43 that

$$\sigma_0[g] = \frac{g}{2} + \left(\frac{3}{2} - 4\ln 2\right)g^2,\tag{135}$$

and, therefore, $a_0 = 0.5$ and $b_0 = -1.272$.

On the other hand, Equation 96 yields $\sigma_0 = 47/256 = 0.183$. As earlier, $\sigma_a = 0.653$ and $g^* = 0.266$ are assumed. Substituting these values to Equation 134, we have for $\mathcal{M} = 0$:

$$X_0 = \left(1 - \frac{g}{0.266}\right)^{-0.562} \exp(-1.113g + 0.676g^2).$$
(136)

Besides, Equation 122 leads to

$$z = g \left(1 - \frac{g}{0.266} \right)^{-1.531}.$$
(137)

These equations define the function $X_0(z)$.

Dcs Cloizeaux compares his result of the renormalization approximation (R) with Flory's (1949b) equation (F) (see also: Flory and Fox, 1951) in the form

$$X_0^{5/2} - X_0^{3/2} = \frac{3^{3/2}}{2}z \tag{138}$$

and with Domb-Barrett's (1976) phenomenological formula (D)

$$X_0^5 = 1 + \frac{20}{3}z + 4\pi z^2.$$
(139)

All these approximations are presented in Figure 5.40. For small z, according to Equations 136 and 137,

$$[X_0]_R \simeq 1 + z, \tag{140}$$

while

$$[X_0]_F \simeq 1 + \frac{3^{3/2}}{2}z \simeq 1 + 2.6z, \tag{141}$$

$$[X_0]_D \simeq 1 + \frac{4}{3}z. \tag{142}$$

For large z, where

$$X_0 \sim z^{2(2\nu-1)/\varepsilon}$$
 (143)



Figure 5.40. Dependence of $\ln X_0 vs \ln(1+z)$ for different approximations: Flory's (F), Domb-Barrett's (D), des Cloizeaux' (the second-order renormalization) (R). The dashed lines correspond to the asymptotics (des Cloizeaux, 1981) [Reprinted with permission from: J. des Cloizeaux. J. de Phys. 42 (1981) 635-652. Copyright © 1981 by EDP Sciences]

is satisfied, we have

$$\ln[X_0]_R = 0.367 \ln(1+z) + 0.238, \tag{144}$$

$$\ln[X_0]_F = 0.4\ln(1+z) + 0.382, \tag{145}$$

$$\ln[X_0]_D = 0.4\ln(1+z) + 0.506. \tag{146}$$

The curves F and D are of significantly different shapes while the curve R occupies an intermediate position between (F) and (D).

Des Cloizeaux and Duplantier (1985), using the direct renormalization method (Duplantier, 1986a), have calculated the form factor of scattering

$$H(\vec{q}) = \frac{1}{S^2} \int_0^S ds' \int_0^S ds'' \left\langle \exp\left\{i\vec{q}[\vec{r}(s') - \vec{r}(s'')]\right\} \right\rangle.$$
(147)

If X^2 is defined by

$$\left\langle \left[\vec{r}(s) - \vec{r}(0)\right]^2 \right\rangle = d \cdot X^2 \tag{148}$$

(cf. Equation 42), then the function $H(\vec{q})$ can be written as

$$H(\vec{q}) = h\left(\frac{q^2 X^2}{2}\right) = h(x).$$
(149)

The function h(x) for small values of x has been calculated by Schäfer and Witten (1977), and by Witten and Schäfer (1981) using another version of the renormalization group approach

$$h(x) = 1 - \frac{x}{3} \left(1 - \frac{\varepsilon}{96} \right) + \frac{x^2}{12} \left(1 - \frac{19\varepsilon}{240} \right).$$
(150)

For large values $x = q^2 X^2/2 \gg 1$, the chain is assumed to be infinitely long, and Equation 151 is approximated by

$$H(\vec{q}) = \frac{2}{S} \int_{0}^{\infty} ds \left\langle \exp\left\{i\vec{q}[\vec{r}(s) - \vec{r}(0)]\right\} \right\rangle;$$
(151)

h(x), in its scaling form, is

$$h(x) \simeq h_{\infty} x^{-1/2\nu}.\tag{152}$$

In particular, for a Brownian chain,

...

$${}^{o}h(x) = \frac{2}{x^2}(e^{-x} - 1 + x) \tag{153}$$

(Debye's formula),

$$^{\circ}h_{\infty}=2.$$

For large \vec{q} , we write

$$H(\vec{q}) = \frac{2}{S} \int_{0}^{S} ds \frac{\mathbf{3}(\vec{q}, s)}{\mathbf{3}(0, s)},\tag{154}$$

where $\mathfrak{Z}(\vec{q}, s)$ is the statistical integral of the chain, including the vectors \vec{q} and $-\vec{q}$ at two points on the infinite chain, separated by the Brownian area s (see Equation 104). The contributions to the $H(\vec{q})$ expansion in the zeroth and first-order of b correspond to the diagrams shown in Figure 5.41 with the designations

$$z = bS^{2-d/2}(2\pi)^{-d/2}$$

(see Equation 9)

$$y = \frac{q^2 S}{2},\tag{155}$$



Figure 5.41. Diagrams representing the contributions to $H(\vec{q})$ for large \vec{q} : the zeroth (a) and first (b) order of b (des Cloizeaux and Duplantier, 1985) [Reprinted with permission from: J. des Cloizeaux, B.Duplantier. J. de Phys. Lett. 46 (1985) L-457 L-461. Copyright © 1985 by EDP Sciences]

 $t = q^2 s/2$, s' = t's, s'' = t''s, where s, s', s'' are the "areas" of the polymer segments (Figure 5.41).

In the first order of z, des Cloizeaux and Duplantier (1985) have obtained

$$H(\vec{q}) = \frac{2}{y} - \frac{2z}{y^{3-d/2}}(I_b + I_c + I_d + I_e).$$
(156)

Here $I_b - I_e$ are the contributions represented by the diagrams (see Figure 5.41)

$$I_b = \int_0^\infty dt \int_0^t dt' (t-t') \frac{e^{-(t-t')} - e^{-t}}{t'^{d/2}} = \frac{2}{\varepsilon} + 1 - C + \cdots, \qquad (157)$$

$$I_c = I_d = \int_0^\infty dt \int_0^t dt' \int_0^\infty dt'' \frac{\exp\left[-\left(t - \frac{t'^2}{t' + t''}\right)\right] - e^{-t}}{(t' + t'')^{d/2}} = 1 + \cdots,$$
(158)

$$I_e = \int_0^\infty dt \int_0^\infty dt' \int_0^\infty dt'' \frac{\exp\left[-\left(t - \frac{t^2}{t + t' + t''}\right)\right] - e^{-t}}{(t + t' + t'')^{d/2}} = 1 + \cdots,$$
(159)

and

$$H(\vec{q}) = \frac{2}{y} - \frac{2z}{y^{1+\epsilon/2}} \left(\frac{2}{\varepsilon} + 4 - C\right),\tag{160}$$

where $C \approx 0.577$ is Euler's constant.

If we introduce

$$X_0(z) \equiv \frac{X^2}{S} = \frac{x}{y},\tag{161}$$

then, according to Equation 81,

$$X_0(z) \simeq 1 + \frac{z}{\varepsilon} (2 - \varepsilon), \tag{162}$$

$$H(\vec{q}) = \frac{2}{x} + \frac{2z}{x}(C - 5 + \ln x).$$
(163)

In accordance with Equation 88,

$$z = g + \cdots, \tag{164}$$

and, when $z \to \infty$, $g \to g^*$ and (see Equation 92)

$$g \to g^* = \frac{\varepsilon}{8}.\tag{165}$$

Then,

$$H(q) \simeq h(x) = \frac{2}{x} + \frac{\varepsilon}{4x}(c - 5 + \ln x).$$
 (166)

This equation can be also written as

$$h(x) = \frac{2\left[1 - \frac{\varepsilon}{8}(5 - C)\right]}{x^{1 - \epsilon/8}}.$$
(167)

As

$$\nu = \frac{1}{2} \left(1 + \frac{\varepsilon}{8} + \cdots \right)$$

(see Equation 99), comparison between Equations 167 and 152 gives

$$h_{\infty} = 2\left[1 - \frac{\varepsilon}{8}(5 - C) + \cdots\right].$$
(168)

Hence, for $\varepsilon = 1$ (d = 3),

$$h_{\infty} = 0.89.$$
 (169)

Previously (Peterlin, 1955; Ptitsyn, 1957), the expression for the scattering form factor has been a generalization of Debye's formula and, in the notation accepted here, has the form

$$h_A(x) = 2 \int_0^1 dt \, (1-t) e^{-xt^{2\nu}}.$$
(170)

If $\nu = (1 + \varepsilon/8)/2$ is accepted for $0 < x \ll 1$, then

$$h_A(x) = 1 - \frac{x}{3} \left(1 - \frac{5\varepsilon}{48} \right) + \frac{x^2}{12} \left(1 - \frac{7\varepsilon}{48} \right), \tag{171}$$

and, for $x \gg 1$,

$$h_A(x) = \frac{2}{x^{1-\epsilon/8}} \left[1 - \frac{\epsilon}{8} (1-C) \right].$$
(172)

Comparison of Equations 171 and 172 with renormalized Equations 150 and 167 shows a substantial difference. In particular, for $\varepsilon = 1$, Equation 172 gives $h_{\infty} = 1.89$.

The matter is that these papers suggested the same swelling law for the internal parts of a macromolecule and for its ends. According to Equations 150 and 167, the internal swelling is stronger. This circumstance influences the expression for the radius of gyration, which is more sensitive to the internal part of the coil than $\langle h^2 \rangle$. Using Equation 150, des Cloizeaux and Duplantier (1985) obtain

$$R^2 = dX^2 \left(1 - \frac{\varepsilon}{96}\right) \tag{173}$$

while it follows from Equation 171 that

$$R_A^2 = dX^2 \left(1 - \frac{5\varepsilon}{48} \right), \tag{174}$$

which turns out to be smaller due to an underestimation of the contributions of the macromolecule's internal parts. This also explains the lower value $h_{\infty} = 0.89$ in comparison with $h_{\infty} = 1.89$.

Duplantier (1985, 1986c) examines this question more thoroughly.

5.5. Tricritical state. Phase separation region

In a very good solvent, a chain's segments are repelled from each other, which is formalized in the existence of segment excluded volume at the intramolecular level and of polymer coil excluded volume at the intermolecular level. In this case, very long chains obey the universal scaling laws characteristic of the proximity of the critical point in general-type systems.

With decreasing temperature (the solvent strength gets worse), the segment excluded volume decreases, and the segments stop avoiding each other; as a result, the coil conformation becomes near to the Gaussian one at the θ point where the second virial coefficient vanishes. However, the θ point is a compensation point arising as a result of rather strong interactions of both positive (repulsion) and negative (attraction) signs.

De Gennes (1975) was the first to show that the state of long polymer chains near the compensative θ point is similar to the tricritical state of general-type systems in terms of statistical physics (see sections 2.6 and 4.1). By analogy with the tricritical behaviour of general-type systems, the Gaussian behaviour of the molecular chains is expected to be corrected (at d = 3) by different universal logarithmic terms, which may diverge (see subsection 4.1).

Let us consider Duplantier's (1980ab, 1982) theory based on the grand canonical ensemble of polymer chains with its chemical potential related to the number of segments and with the fugacity related to the number of chains (des Cloizeaux, 1975) (see section 4.2). This ensemble is identical to the system in the Lagrangian field theory of Landau-Ginzburg-Wilson with n = 0. The tricritical Lagrangian contains the terms of binary $g_0(\varphi^2)^2$ and ternary $w(\varphi^2)^3$ interactions (cf. section 4.1). The first-stage theoretical expressions for physical quantities prove to be divergent, so a renormalization procedure is required to consider the specific features of polymer systems.

$$\left\langle h^2 \right\rangle_{Br} = d \cdot S. \tag{1}$$

For a chain of N non-interacting segments of length l

$$S = Nl^2.$$
⁽²⁾

The conformation of the *m*th continuous chain is described by the vector $\vec{r}_m(s_m)$, where $0 < s_m < S_m$. The set of \mathcal{M} chains is characterized by the conformation $\{\vec{r}\} = \{\vec{r}_1, \ldots, \vec{r}_{\mathcal{M}}\}$.

The Lagrangian formalism represents the set of \mathcal{M} chains as an action (Duplantier, 1980b, 1982)

$$\mathcal{A}\{\vec{r}\} = \sum_{m=1}^{\mathcal{M}} \mathcal{A}_0\{\vec{r}_m\} + \mathcal{A}_{inl}\{\vec{r}\},\tag{3}$$

where

$$\mathcal{A}_0\{\vec{r}_m\} = \frac{1}{2} \int_0^{S_m} ds_m \left(\frac{d\vec{r}_m(s_m)}{ds_m}\right)^2 \tag{4}$$

is the action of free chains,

$$\mathcal{A}_{int}\{\vec{r}\} = \frac{g_0}{4!} \sum_{m,m'=1}^{\mathcal{M}} \int_0^{S_m} ds_m \int_0^{S_{m'}} ds_{m'} \,\delta\left[\vec{r}_m(s_m) - \vec{r}_{m'}(s_{m'})\right]$$

$$+ \frac{w}{6!} \sum_{m,m',m''=1}^{\mathcal{M}} \int_0^{S_m} ds_m \int_0^{S_{m'}} ds'_m \int_0^{S_{m''}} ds_{m''} \,\delta\left[\vec{r}_m(s_m) - \vec{r}_{m'}(s_{m'})\right]$$

$$\times \,\delta\left[\vec{r}_{m'}(s_{m'}) - \vec{r}_{m''}(s_{m''})\right]$$
(5)

is the action of interaction.

The factors 1/4! and 1/6! are chosen by analogy with the corresponding expression in the general field theory (cf. Equation 2.6-149), and this choice is immaterial. The quantities g_0 and w are phenomenological parameters of the binary (g_0) and ternary (w)interactions of the chain segments in the presence of a LMWL. In this consideration, either $g_0 > 0$ (repulsion) or $g_0 < 0$ (attraction) while w > 0 always (repulsion), which is necessary to assume for the system with action 3 to be stable.

For the model of the system (Equations 3.5), the partition function of \mathcal{M} chains is defined by Wiener's functional integral with respect to all the conformations of all the chains

$$\mathfrak{Z}(S_1,\ldots,S_{\mathcal{M}}) = \int d^d \{r\} \exp\left(-\mathcal{A}\{\vec{r}\}\right),\tag{6}$$

and the mean value of the functional $O\{r\}$ with respect to all the conformations $\{r\}$ is

$$\langle O \rangle = \mathfrak{Z}^{-1}(S_1, \dots, S_{\mathcal{M}}) \int d^d \{r\} O\{r\} \exp\left(-\mathcal{A}\{r\}\right).$$
⁽⁷⁾

The integral 3 is infinite for continuous chains due to the infinite number of degrees of freedom; that is why a regularized statistical integral

$$^{+}\mathfrak{Z}(S_{1},\ldots,S_{\mathcal{M}})=V^{\mathcal{M}}\frac{\mathfrak{Z}(S_{1},\ldots,S_{\mathcal{M}})}{\mathfrak{Z}_{0}(S_{1})\cdots\mathfrak{Z}_{0}(S_{\mathcal{M}})}$$
(8)

is introduced (Duplantier, 1982), where 3_0 is the statistical integral of a free chain

$$\mathfrak{Z}_{0}(S) = \int d^{d}\{r\} \exp\left(-\mathcal{A}_{0}\{\vec{r}\}\right),\tag{9}$$

The mean value $\langle O \rangle_0$ is defined as

$$\langle O \rangle_{0} = \mathfrak{Z}_{0}^{-1}(S) \int d^{d}\{r\} O\{r\} \exp\left(-\mathcal{A}_{0}\{\vec{r}\}\right).$$
⁽¹⁰⁾

In particular (see Equations 5.4-2...5),

$$\left\langle \exp\left[i\vec{k}(\vec{r}(S) - \vec{r}(0))\right] \right\rangle_{0} = \exp\left(-\frac{Sk^{2}}{2}\right).$$
(11)

This equation provides the Gaussian correlation function in the Fourier transform for the ends of a free polymer chain.

As all the physically measured quantities are derived from the chain statistical integral with an imposed constraint (see section 5.4), this integral is then introduced (Duplantier, 1982) to express the fixing of the chain ends

$$^{+}\mathfrak{Z}(\vec{x}_{1},\ldots,\vec{x}_{2\mathcal{M}};S_{1},\ldots,S_{\mathcal{M}}) =$$

$$= \int d^{d}\{r\} \prod_{m=1}^{\mathcal{M}} \delta(\vec{x}_{2m-1}-\vec{r}_{m}(0))\delta(\vec{x}_{2m}-\vec{r}_{m}(S_{m}))\exp(-\mathcal{A}\{\vec{r}\})V^{\mathcal{M}} \prod_{m=1}^{\mathcal{M}} \mathfrak{Z}_{0}^{-1}(S_{m}),$$

$$(12)$$

where \vec{x}_{2m-1} and \vec{x}_{2m} are the fixed points of the *m*th chain. The Fourier transform of Equation 12 gives

$$(2\pi)^{d}\delta(\vec{k}_{1} + \dots + \vec{k}_{2\mathcal{M}})^{+}\tilde{\mathfrak{Z}}(\vec{k}_{1}, \dots, \vec{k}_{2\mathcal{M}}; S_{1}, \dots, S_{\mathcal{M}}) =$$

$$= \int d^{d}x_{1} \cdots d^{d}x_{2\mathcal{M}} \exp\left[i\sum_{m=1}^{\mathcal{M}} (\vec{k}_{2m-1}\vec{x}_{2m-1} + \vec{k}_{2m}\vec{x}_{2m})\right]^{+}\mathfrak{Z}(\vec{x}_{1}, \dots, \vec{x}_{2\mathcal{M}}; S_{1}, \dots, S_{\mathcal{M}}).$$
(13)

In particular, for one chain

$${}^{+}\tilde{\mathfrak{Z}}(0,0;S) = \frac{1}{V}{}^{+}\mathfrak{Z}(S), \tag{14}$$

and the mean square end-to-end distance is expressed by Equation 5.4-40

$$\left\langle h^2 \right\rangle = -2d \left. \frac{1}{\tilde{\mathfrak{Z}}(0,0;S)} \cdot \frac{\partial}{\partial (k^2)} {}^{\dagger} \tilde{\mathfrak{Z}}(\vec{k},-\vec{k},S) \right|_{k^2=0}.$$
(15)

Just like des Cloizeaux (1975) (see Equation 4.2-55), Duplantier (1982) introduces the grand canonical partition function of polymer chains

$$Z(h) = 1 + \sum_{\mathcal{M}=1}^{\infty} \frac{h^{2\mathcal{M}}}{2^{2\mathcal{M}}\mathcal{M}!} \prod_{m=1}^{\mathcal{M}} \int_{0}^{\infty} dS_m \exp\left(-\frac{a_0 S_m}{2}\right) * \mathfrak{Z}(S_1, \dots, S_{\mathcal{M}}),$$
(16)

where $h^2/4$ is the fugacity related to the number of \mathcal{M} chains, a_0 is the chemical potential associated with the area of the chains S. Comparison of Equation 16 with des Cloizeaux' formula (see Equation 4.2-55) yields the interrelations

$$h = H_0, \qquad \frac{a_0}{2} = s = m_0^2.$$

In the grand canonical ensemble, the average number of chains $\langle \mathcal{M} \rangle$, the average chain area $\langle S \rangle$, and the osmotic pressure π are determined using the standard formulae (cf. section 1.7 and Equations 4.2-59...62):

$$\langle \mathcal{M} \rangle = \frac{1}{2} h \frac{\partial}{\partial h} \ln Z \langle h \rangle, \tag{17}$$

$$\langle S \rangle = 2 \frac{\partial}{\partial a_0} \ln Z(h), \tag{18}$$

$$\frac{\pi}{kT} = \frac{1}{V} \ln Z(h). \tag{19}$$

The concentration of chains c_p , the concentration of "areas" C, and the average concentration of area per chain S are determined as follows

$$c_p = \langle \mathcal{M} \rangle V^{-1}, \tag{20}$$

$$C = \langle S \rangle V^{-1}, \tag{21}$$

$$S = \frac{\langle S \rangle}{\langle \mathcal{M} \rangle} = \frac{C}{c_p}.$$
(22)

For the model of chains with the segment lengths l,

$$C = cl^2, (23)$$

where c is the concentration of segments.

For the set of \mathcal{M} chains, a symmetrical moment

$$X^2(S_1,\ldots,S_{\mathcal{M}}) = \tag{24}$$

$$\int \prod_{m=1}^{\mathcal{M}} d^d x_{2m-1} d^d x_{2m} \left[\sum_{m=1}^{\mathcal{M}} (\vec{x}_{2m} - \vec{x}_{2m-1})^2 \right] + \Im(\vec{x}_1, \dots, \vec{x}_{2\mathcal{M}}; S_1, \dots, S_{\mathcal{M}})$$

is introduced.

The total square end-to-end distance is defined as

$$\mathcal{X}^{2} = Z^{-1}(h) \sum_{\mathcal{M}=1}^{\infty} \frac{h^{2\mathcal{M}}}{2^{2\mathcal{M}}\mathcal{M}!} \prod_{m=1}^{\mathcal{M}} \int dS_{m} \, e^{-a_{0}S_{m}/2} X^{2}(S_{1}, \dots, S_{\mathcal{M}}), \tag{25}$$

then, the square end-to-end distance of a chain is written in the form

$$\left\langle h^2 \right\rangle = \frac{\chi^2}{\langle \mathcal{M} \rangle},$$
(26)

and can be calculated by the methods of field theory.

The statistical integral of the *n*-component field $\varphi^{j}(x)$ with j = 1, ..., n has the form

$$Z\{\vec{h}\} = \int d^{n}\{\varphi\} \exp\left(-\mathcal{A}\{\varphi\} + \int d^{d}x \sum h^{j}(x)\varphi^{j}(x)\right), \qquad (27)$$

where the action $\mathcal{A}\{\varphi\}$ has Landau-Ginzburg-Wilson's form

$$\mathcal{A}\{\varphi\} = \int d^d x \mathcal{L}\{\varphi\},\tag{28}$$

$$\mathcal{L}\{\varphi\} = \frac{1}{2} \sum_{i,j} \left[\frac{\partial \varphi^{j}(x)}{\partial x_{i}} \right]^{2} + \frac{a_{0}}{2} \sum \left[\varphi^{j}(x) \right]^{2} + \frac{g_{0}}{4!} \sum_{j,l} \left[\varphi^{j}(x) \right]^{2} \left[\varphi^{l}(x) \right]^{2} + \frac{w}{6!} \sum_{j,l,m} \left[\varphi^{j}(x) \right]^{2} \left[\varphi^{l}(x) \right]^{2} \left[\varphi^{m}(x) \right]^{2}.$$

$$(29)$$

Equation 27 is equivalent to Equation 16 for a homogeneous field in the direction j = 1 $h^{j}(x) = \delta_{j1}h$ and in the limit n = 0 as it follows from comparison between the expansion of Green's function (de Gennes, 1972) and direct analysis (Emery, 1975) (see section 4.1).

For polymer chains generated by a spatial-dependent fugacity $h^{j}(x)$, we have

$$Z\{\vec{h}\} = 1 + \sum_{\mathcal{M}=1}^{\infty} \frac{1}{2^{2\mathcal{M}}\mathcal{M}!} \int \prod_{m=1}^{\mathcal{M}} d^{d}x_{2m-1} d^{d}x_{2m} \prod_{m=1}^{\mathcal{M}} \left(\sum_{j} h^{j}(\vec{x}_{2m-1})h^{j}(\vec{x}_{2m})\right)$$
(30)

$$\times \prod_{m=1}^{\mathcal{M}} \int dS_{m} \exp\left(-\frac{a_{0}S_{m}}{2}\right) \, {}^{*}\mathfrak{Z}(\vec{x}_{1},\ldots,\vec{x}_{2\mathcal{M}};S_{1},\ldots,S_{\mathcal{M}}),$$

and for the homogeneous fugacity h $(h^{j}(\vec{x}) = \delta_{j1}h)$

$$Z\{\vec{h}\}\Big|_{\vec{h}=h} = Z\{h\}.$$
(31)

Having defined the Fourier transform as

$$h^{j}(\vec{k}) = (2\pi)^{-d} \int d^{d}x \, h^{j}(\vec{x}) e^{-i\vec{k}\vec{x}}, \tag{32}$$

one can write (cf. Equation 4.2-15)

$$Z\{\vec{h}\} = 1 + \sum_{\mathcal{M}=1}^{\infty} \frac{1}{2^{2\mathcal{M}}\mathcal{M}!} \int \prod_{m=1}^{\mathcal{M}} d^d k_{2m-1} d^d k_{2m} (2\pi)^d \delta(\vec{k}_1 + \dots + \vec{k}_{2\mathcal{M}})$$
(33)

$$\times \prod_{m=1}^{\mathcal{M}} \left[\sum_{j} h^{j}(\vec{k}_{2m-1}) h^{j}(\vec{k}_{2m}) \right] G^{(2\mathcal{M})}(\vec{k}_{1}, \ldots, \vec{k}_{2\mathcal{M}}).$$

Here $G^{(2M)}$ is Green's ordered functions defined in (des Cloizeaux, 1975) (see Equation 4.2–51)

$$G^{(2\mathcal{M})}(\vec{k}_1,\dots,\vec{k}_{2\mathcal{M}}) = \prod_{m=1}^{\mathcal{M}} \int_0^\infty dS_m \, \exp\left(-\frac{a_0 S_m}{2}\right) \,^* \tilde{\mathfrak{Z}}(\vec{k}_1,\dots,\vec{k}_{2\mathcal{M}};S_1,\dots,S_{\mathcal{M}}) \quad (34)$$

provided that $\vec{k}_1 + \cdots + \vec{k}_{2M} = 0$.

Applying the Fourier transform (Equation 13), we calculate the moment X^2 (Equation 24) from

$$X^{2}(S_{1},\ldots,S_{\mathcal{M}}) = -\mathcal{M}V2d \left. \frac{\partial}{\partial(k^{2})}^{\dagger} \tilde{\mathfrak{Z}}(\vec{k},-\vec{k},0,\ldots,0;S_{1},\ldots,S_{\mathcal{M}}) \right|_{k_{2}=0},$$
(35)

where the general translational invariant of the set of chains is used. Then, the \mathcal{X}^2 from Equation 25, in view of Equation 34, is expressed in the following form:

$$\mathcal{X}^2 = -2dVZ^{-1}(h)\frac{\partial}{\partial(k^2)} \left[\sum_{\mathcal{M}=1}^{\infty} \frac{h^{2\mathcal{M}}}{2^{2\mathcal{M}}\mathcal{M}!} G^{(2\mathcal{M})}(\vec{k}, -\vec{k}, 0, \dots, 0)\right]_{k^2=0}.$$
(36)

Green's transverse functions are defined through the generating functional (Equation 33)

$$(2\pi)^{d}\delta(\vec{k}+\vec{k}')G_{T}^{(2)}(\vec{k},-\vec{k};h) = \frac{\partial}{\partial h^{j}(\vec{k})}\frac{\partial}{\partial h^{j}(\vec{k}')}Z\{\vec{h}\}\Big|_{\substack{\vec{k}=h\\j\neq 1}}.$$
(37)

Here the functional derivatives are taken with respect to the component h^j $(j \neq 1)$ perpendicular to the direction j = 1. On differentiation, the field fugacity \vec{h} in the direction j = 1 is assumed to be homogeneous

$$h^{j}(\vec{k}) = \delta(\vec{k})\delta_{j1}h.$$
(38)

It follows from Equations 37 and 33 that

$$G_T^{(2)}(\vec{k}, -\vec{k}; h) = h^{-2} \sum_{\mathcal{M}=1}^{\infty} \frac{h^{2\mathcal{M}}}{2^{2\mathcal{M}}\mathcal{M}!} 2\mathcal{M}G^{(2\mathcal{M})}(\vec{k}, -\vec{k}, 0, \dots, 0),$$
(39)

and for $h \to 0$

$$G_T^{(2)}(\vec{k}, -\vec{k}; h=0) = \frac{1}{2}G^{(2)}(\vec{k}, -\vec{k}).$$
(40)

Equation 37, in view of Equations 33 and 39, also gives

$$G_T^{(2)}(0,0,h) = V^{-1} \frac{1}{h} \cdot \frac{\partial}{\partial h} Z(h).$$
(41)

Thus, with the help of Equations 36, 39, 17, 41, for $\langle h^2 \rangle$ we obtain from Equation 26

$$\left\langle h^2 \right\rangle = -2d \left. \frac{\partial}{\partial (k^2)} \ln G_T^{(2)}(\vec{k}, -\vec{k}, h) \right|_{k^2 = 0},\tag{42}$$

which defines the mean-square end-to-end distance of the polymolecular grand canonical ensemble.

For a single chain, using the Laplace inverse transform $G_T^{(2)}$, including Equations 40 and 34, we get

$${}^{+}\tilde{\mathfrak{Z}}(\vec{k},-\vec{k},S) = \frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} da_0 \, e^{a_0 S/2} G_T^{(2)}(\vec{k},-\vec{k},h=0).$$
(43)

This formula enables $\langle h^2 \rangle$ to be calculated according to Equation 15. Here the integration contour in a complex plane lies on the right-hand side of the integrand's singularities and closes to infinity from the left-hand side.

Functional 30 is a field statistical integral (Equation 27) with the action \mathcal{A} (Equation 29) in the limit n = 0. Then, the free energy (with the sign '-' omitted) has the form

$$F\{\vec{h}\} = \ln Z\{\vec{h}\} \tag{44}$$

(cf. Equation 4.2-18).

The free energy $F\{\vec{h}\}$ is related to the generating functional $\Gamma\{\vec{h}\}$ by Legendre's transform (Equations 4.2-22,-23). Then, functions 17-22 can be expressed through the vertex functions (see Equation 4.2-67...69)

$$c = 2 \frac{\partial \Gamma(f)}{\partial a_0} \Gamma(f), \tag{45}$$

$$c_p = \frac{f}{2} \cdot \frac{\partial \Gamma(f)}{\partial f},\tag{46}$$

$$\frac{\pi}{kT} = f \frac{\partial \Gamma(f)}{\partial f} - \Gamma(f) \tag{47}$$

with allowance for the difference between des Cloizeaux' and Duplantier's notations: $f = M_0$, $a_0 = 2s$, $\vec{h} = \vec{H}$ (see Equations 16 and 4.2-55).

The transverse vertex functions $\Gamma_T^{(2)}$ are defined by Duplantier as

$$(2\pi)^{d}\delta(\vec{k}+\vec{k}')\Gamma_{T}^{(2)}(\vec{k},-\vec{k},f) = \frac{\partial}{\partial f^{j}(\vec{k})}\frac{\partial}{\partial f^{j}(\vec{k}')}\Gamma\{\vec{f}\}\Big|_{\substack{\vec{l}=f\\j\neq 1}},$$
(48)

where $\vec{f}(\vec{k}) = (2\pi)^{-d} \int d^d x \, \exp(-i\vec{k}\vec{x})\vec{f}(\vec{x})$ (cf. Equation 4.2-42).

The transverse vertex functions are similar to Green's transverse functions (Equation 37) and the equation of the Equation 41 type

$$\Gamma_T^{(2)}(0,0,f) = \frac{1}{f} \cdot \frac{\partial}{\partial f} \Gamma(f)$$
(49)

is fulfilled for them.

Considering the interrelation between Green's functions and the vertex functions (Equation 4.2-21), we can write for the mean square end-to-end distance in the polymolecular grand canonical ensemble (Equation 42)

$$\left\langle h^2 \right\rangle = 2d \frac{1}{\Gamma_T^{(2)}(0,0,f)} \left[\frac{\partial}{\partial (k^2)} \Gamma_T^{(2)}(\vec{k},-\vec{k};f) \right]_{k^2=0}.$$
(50)

In view of Equations 43 and 50, Equation 15 is satisfied for one chain

$${}^{*}\tilde{\mathfrak{Z}}(\vec{k},-\vec{k},S) = \frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} da_0 \, e^{a_0 S/2} \left[\Gamma_T^{(2)}(\vec{k},-\vec{k};f=0) \right]^{-1}.$$
(51)

The general-type $2\mathcal{M}$ -order vertex functions are defined in k-space (Duplantier, 1982) by the functional derivatives

$$(2\pi)^{d}\delta(\vec{k}_{1}+\cdots+\vec{k}_{2\mathcal{M}})\Gamma^{(2\mathcal{M})}_{j_{1}\ldots j_{2\mathcal{M}}}(\vec{k}_{1},\ldots,\vec{k}_{2\mathcal{M}}) = \frac{\partial}{\partial f^{j_{1}}(\vec{k}_{1})}\cdots\frac{\partial}{\partial f^{j_{2\mathcal{M}}}(\vec{k}_{2\mathcal{M}})}\Gamma\{\vec{f}\}\Big|_{\vec{f}=0}$$
(52)

i.e. they are the coefficients of the Taylor expansion series of $\Gamma\{\vec{f}\}$ with respect to \vec{f} and have a fundamental meaning for the application of a renormalization procedure.

In the case of a homogeneous field $f_j(\vec{k}) = \delta_{j1}\delta(\vec{k})f$, the generating functional $\Gamma(f)$ has its expansion

$$\Gamma(f) = \sum_{\mathcal{M}=1}^{\infty} \frac{1}{(2\mathcal{M})!} f^{2\mathcal{M}} \Gamma_{1,\dots,1}^{(2\mathcal{M})}(0,\dots,0),$$
(53)

where conversion 2.6 79

$$V = (2\pi)^d \delta(\vec{k} = 0) \tag{54}$$

is used.

In what follows only those vertex functions will be discussed which include a symmetrical set of external moments only, and their dependence on indices is trivial and will not be discussed. These functions are similar and proportional to des Cloizeaux' ordered vertex functions (Equations 4.2-20).

In particular, transverse vertex functions 48 are related to the general-type vertex functions by

$$\Gamma_T^{(2)}(\vec{k}, -\vec{k}; f=0) = \Gamma_{jj}^{(2)}(\vec{k}, -\vec{k}) \equiv \Gamma^{(2)}(\vec{k}, -\vec{k}).$$
(55)

The vertex functions can be expanded as a series in powers of the interaction parameter and represented with the aid of diagrams (Figure 5.42). In polymer theory (n = 0), the second term of the right-hand side is absent.

The diagram calculation rules correspond to the form of action 28 and 29.

1) each solid internal line between two interaction points gives the factor $(q^2 + a_0)^{-1}$, where \vec{q} is the wavevector going along the line;

2) there is an independent moment variable \vec{q} for each closed loop, with respect to which integration should be performed with the measure $d^d q/(2\pi)^d$;



Figure 5.42. Order g_0 diagrams contributing to the vertex function $\Gamma^{(2)}$. To the right is shown separation of the diagram to reveal its explicit dependence on the number of components *n* of the field vector. In polymer theory (n = 0), the second term of the righthand side (a loop) is absent (Duplantier, 1982) [Reprinted with permission from: B.Duplantier. J. de Phys. 43 (1982) 991 1019. Copyright © 1982 by EDP Sciences]

3) the rule of moment conservation is fulfilled for each vertex;

4) each vertex gives the factor $(-g_0)$ or (-w) with the factor (-1) standing before the whole diagram and including, at least, one interaction vertex;

5) "symmetry weights" $\Phi(n)$, depending on the number of components n, are introduced.

"Ultraviolet" divergences appear for infinite values of the integration moments q. For example, in Figure 5.42, the contribution of such integration is proportional to

$$\int d^d q \, (q^2 + a_0)^{-1}. \tag{56}$$

This expression diverges for $d \ge 2$. The renormalization procedure envisages the introduction of a short cut-off range s_0 , where s_0 is a small area, and the propagator

$$G_0(q) = (q^2 + a_0)^{-1}$$

is replaced by the regularized propagator

$$G_{s_0}(q) = (q^2 + a_0)^{-1} \exp\left[-(q^2 + a_0)s_0\right],$$
(57)

which can be rewritten in the form

$$G_{s_0}(q) = \frac{1}{2} \int_{2s_0}^{\infty} ds \, \exp\left(-\frac{a_0 s}{2}\right) + \tilde{\mathfrak{Z}}_0(\vec{q}, -\vec{q}; s).$$
(58)

Hence, G_{s_0} appears as Laplace's specific transform of correlation function 11 for a free polymer segment. G_0 should be replaced by G_{s_0} in Rule 1, and $2s_0$ can be regarded as the minimal area between two interaction points along the continuous chain.

An "infrared" divergence arises if the chain areas S_m become infinite. The problem of "infrared" divergence was first solved in the statistical physics of critical and tricritical phenomena with the help of the regularization procedure based on action in Landau-Ginzburg-Wilson's form (Equations 28 and 29). Substituting Equation 53 to Equations 46 and 47, we obtain for the first expansion terms

$$c_p = \frac{1}{2}\Gamma^{(2)}(0,0)f^2 + \frac{1}{12}\Gamma^{(4)}(0,0,0,0)f^4 + \cdots,$$
(59)

$$\frac{\pi}{kT} = c_p + \frac{1}{6} \frac{\Gamma^{(4)}(0,0,0,0)}{[\Gamma^{(2)}(0,0)]^2} c_p^2 + \cdots,$$
(60)

and for the mean square end-to-end distance (see Equation 50)

$$\left\langle h^2 \right\rangle \sim \left[\Gamma^{(2)}(0,0) \right]^{-1} \frac{\partial}{\partial (k^2)} \Gamma^{(2)}(0,0).$$
 (61)

The θ state is defined by the second virial coefficient being equal to zero for infinitely long chains $(\langle h^2 \rangle \to \infty)$. According to Equations 60 and 61, the set

$$\left. \begin{array}{ccc} \Gamma^{(2)}(0,0) &= & 0, \\ \Gamma^{(4)}(0,0,0,0) &= & 0 \end{array} \right\}$$
(62)

corresponds to this condition and characterizes the tricritical point in field theory (see Equation 2.6-163).

At zero moments, the vertex functions depend on the parameters a_0 , g_0 , w, s_0 . Hence, two conditions 62 implicitly define the tricritical values a_0 , g_0 , i.e.

$$a_{0l}(w, s_0)$$
 and $g_{0l}(w, s_0)$. (63)

With due account of the dimensions of a_{0t} , g_{0t} and the dimensionless character of w, parameters 63 must possess the form

$$a_{0t}(w, s_0) = s_0^{-1} f_1(w), \quad g_{0t}(w, s_0) = s_0^{-1/2} f_2(w).$$
(64)

These functions can be calculated from perturbation theory; at the first order in w (d = 3), the following expressions have been obtained (Duplantier, 1982)

$$f_1(w) = \frac{w}{8} \cdot \frac{n+4}{5} \cdot \frac{n+2}{3} \cdot \frac{1}{2^{2d}\pi^d} \cdot \frac{1}{\left(\frac{d}{2}-1\right)^2} + O(w^2),\tag{65}$$

$$f_2(w) = -\frac{w}{2} \cdot \frac{n+4}{5} \cdot \frac{1}{2^d \pi^{d/2}} \cdot \frac{1}{d/2 - 1} + O(w^2)$$
(66)

The complexity is in the fact that the vertex functions have "ultraviolet" divergences at short distances $(s_0 \rightarrow 0)$. So, a renormalization procedure is required to suppress divergences like the power function $s_0^{-\alpha}$ ($\alpha > 0$).

Renormalization scheme (Duplantier, 1982)

The Lagrangian density has the form

$$\mathcal{L}(\varphi) = \frac{1}{2}(\nabla\varphi) + \frac{a_0}{2}\varphi^2 + \frac{g_0}{4!}(\varphi^2)^2 + \frac{w}{6!}(\varphi^2)^3,$$
(67)

and the condition of the tricritical point is defined by

$$\left. \begin{array}{l} \Gamma^{(2)}(0,0;a_{0t},g_{0t},w,s_0) = 0, \\ \Gamma^{(4)}(0,0,0;a_{0t},g_{0t},w,s_0) = 0, \end{array} \right\}$$
(68)
where s_0 is the ultraviolet cut-off appearing in regularized propagator 57.

Equation 68 must lead to a_{0t} and g_{0t} as functions of w and s_0

$$a_{0t} = a_{0t}(w, s_0), \quad g_{0t} = g_{0t}(w, s_0).$$

As renormalization should be performed precisely in the tricritical point, we will discuss the vertex function $\Gamma^{(L,N,2\mathcal{M})}$ with $2\mathcal{M}$ external points, L insertions of the φ^2 type, and N insertions of the $(\varphi^2)^2$ type, constructed with $w(\varphi^2)^3$ interactions. The diagram $\Gamma^{(L,N,2\mathcal{M})}$ comprises J internal lines and V six-point verteces.

The diagram $\Gamma^{(L,N,2M)}$ comprises J internal lines and V six-point verteces. Counting the vertex-related points yields

$$2J + 2\mathcal{M} = 6V + 2L + 4N.$$
(69)

On the other hand, the number of the conditions of moment conservation is written as

$$N_c = L + N + V - 1. (70)$$

Each integration along an internal lines contributes to the dimension as

$$\int \frac{d^d q}{q^2}.$$

Therefore, the degree of the ultraviolet superficial divergence $\Gamma^{(L,N,2\mathcal{M})}$ is written as

$$\delta = J(d-2) - d \cdot N_c. \tag{71}$$

For d = 3, in view of Equations 69 and 70,

$$\delta = 3 - \mathcal{M} - (2L + N),\tag{72}$$

which leads to a set of divergent vertex functions with $\delta \ge 0$ (the matrix for δ).

 $\mathcal{M} = 0$ 1 2 - 3 (L, N)(0, 0)3 2 1 0 (0, 1)2 1 1 (0,2)1 0 (1,0)1 0 (1, 1)0

For polymer chains, $\mathcal{M} \geq 1$, and the first column plays no role. $\Gamma^{(0,0,2)}$, $\Gamma^{(0,0,4)}$, and $\Gamma^{(0,1,2)}$ are seen to have a positive divergence degree $\delta > 0$.

As it follows from the general field theory, a divergence can be eliminated by subtraction of the counterterms from the mass and interaction vertex. If we define the variations aand g by

$$a \equiv a_0 - a_{0t} + (g_0 - g_{0t})c_t, \tag{73}$$

$$g \equiv g_0 - g_{0t} \tag{74}$$

 $(c_t \text{ is a function determined by order in powers of } w \text{ by a renormalization condition at the tricritical point, it accounts simply for the mass shift due to the <math>(\varphi^2)^2$ insertion, see Figure 5.42), then Lagrangian density 67 reads

$$\mathcal{L}(\varphi) = \frac{1}{2} (\nabla \varphi)^2 + \frac{a_{0t}}{2} \varphi^2 + \frac{g_{0t}}{4!} (\varphi^2)^2 + \frac{w}{6!} (\varphi^2)^3 + \frac{a}{2} \varphi^2 + g \left(\frac{(\varphi^2)^2}{4!} - \frac{c_t}{2} \varphi^2 \right).$$
(75)

Now we define anew the vertex functions $\Gamma^{(L,N,2M)}$ with $L \varphi^2$ -insertions and $N \tilde{\varphi}^4$ -insertions

$$\tilde{\varphi}^4 \equiv \frac{(\varphi^2)^2}{4!} - c_l \frac{\varphi^2}{2}$$

at the tricritical point by means of the functional derivatives

$$\Gamma^{(L,N,2\mathcal{M})} \equiv \left. \frac{\partial^{[L]}}{\partial a^{[L]}} \frac{\partial^{[N]}}{\partial g^{[N]}} \frac{\partial^{[2\mathcal{M}]}}{\partial \varphi^{[2\mathcal{M}]}} \Gamma\{\varphi, a, g\} \right|_{a=0,g=0,\varphi=0},\tag{76}$$

where $\Gamma\{\varphi, q, g\}$ is the generating functional dependent on the spatially varying parameters q(x), g(x), $\varphi(x)$. In this case, the power divergences in $\Gamma^{(0,0,2)}$ and $\Gamma^{(0,0,4)}$ are eliminated under condition 68. The linear divergence of $\Gamma^{(0,1,2)}$ is removed by the proper choice of c_t so that

$$\Gamma^{(0,1,2)}(0,\ldots,0;a_{0t},g_{0t},w,s_0) = 0.$$
⁽⁷⁷⁾

Application of the perturbation theory method leads to the following expression in the first order for d = 3

$$c_t(w, s_0) = s_0^{-1/2} f_3(w), \tag{78}$$

$$f_3(w) = \frac{n+2}{3} \cdot \frac{w}{2} \cdot \frac{1}{2^d \pi^{d/2}} \cdot \frac{1}{d/2 - 1} + \cdots .$$
(79)

The θ point corresponds to

$$q = 0 \quad \text{and} \quad g = 0. \tag{80}$$

Thus, the phenomenological quantity g is identified as the deviation from the θ point and is approximated by

$$g = g_0 - g_{0l} \simeq \alpha s_0^{-1/2} \frac{T - \theta}{\theta},$$
 (81)

where α is a numerical constant.

Expressed through the parameters a and g (instead of a_0 and g_0), all the vertex functions are regular for $s_0 \rightarrow 0$ except the logarithmic divergences which should be handled by the second renormalization series.

In particular, the expansion series of $\Gamma^{(2)}(\vec{k}, -\vec{k})$ can be calculated to the first order in g and w (Duplantier, 1982)

$$\Gamma^{(2)}(\vec{k}, -\vec{k}) \equiv \Gamma^{(2)}_T(\vec{k}, -\vec{k}; f = 0)$$
(82)



Figure 5.43. Diagrams contributing to the vertex function $\Gamma^{(2)}$ in the general case $(n \neq 0)$ (a) and the corresponding diagrams of polymer theory (n = 0) for one chain (b) (Duplantier, 1982) [Reprinted with permission from: B.Duplantier. J. de Phys. 43 (1982) 991-1019. Copyright © 1982 by EDP Sciences]

$$= k^{2} + a - g \frac{n+2}{6} \cdot \frac{a^{-1/2}}{4\pi} + w \frac{(n+2)(n+4)}{15} \cdot \frac{a}{2^{7}\pi^{2}} + \cdots$$

This expression corresponds to diagrams 1-3 in Figure 5.43a. At the next order, a term containing a logarithmic divergence

$$\delta\Gamma^{(2)}(\vec{k},-\vec{k}) = k^2 w^2 \frac{n+2}{15} \cdot \frac{n+4}{5!} \cdot \frac{1}{2^{10}} \cdot \frac{1}{3\pi^4} \ln(as_0)^{-1}$$
(83)

is added.

The six-point vertex function $\Gamma^{(6)}$ is calculated in a similar way (for g = 0 and $\vec{k}_i = 0$)

$$\Gamma^{(6)}(\vec{k}_{i}=0) = w - \frac{10}{2^{5}\pi^{2}} \cdot \frac{1}{3!} \cdot \frac{3n+22}{25} w^{2} \ln(as_{0})^{-1} + O(w^{3}),$$
(84)

to which there correspond the diagrams shown in Figure 5.44.



Figure 5.44. Diagrams contributing to the vertex function $\Gamma^{(6)}$ in the general case $(n \neq 0)$ (a) and the corresponding polymer analogue with n = 0 (b) (Duplantier, 1982) [Reprinted with permission from: B.Duplantier. J. de Phys. 43 (1982) 991–1019. Copyright © 1982 by EDP Sciences]

The series of the vertex function in powers of w and in the loop expansion are seen to diverge in the neighbourhood of the tricritical point a = 0 at d = 3 at the expense of the term including

$$\ln(as_0)^{-1}$$
 $(as_0 \to 0).$ (85)

The dimension d = 3 corresponds to the upper critical dimension, at which logarithmic divergences appear due to the term $w(\varphi^2)^3$ in the Lagrangian (or Hamiltonian).

At d = 3, the limits $a \to 0$ (corresponding to $S \to \infty$) and $s_0 \to 0$ are equivalent. These tricritical divergences, arising from the interaction term $w(\varphi^2)^3$, differ from those related to the excluded volume term $g(\varphi^2)^2$.

The latters are associated with the dimensionless parameter $ga^{-1/2}$ (see Equation 82). This parameter diverges at $a \rightarrow 0$. In the course of renormalization near the tricritical point (Stephen et al., 1975; Stephen, 1980; Duplantier, 1982), only the logarithmic divergence (Equation 85) is considered, as the parameter $ga^{-1/2}$ turns out to be small and irrelevant.

The technical aspect of the tricritical renormalization is very sophisticated and lengthy. Its main stages based on the general field theory are as follows (Duplantier, 1982).

First, the renormalization group equation is derived, which relates the values of the vertex functions for the cut-off s_0 to their values for a larger (in magnitude) and arbitrary cut-off area S. The replacement $s_0 \to S$ can be considered as expansion of the scale of the chain fragments' internal area.

Therefore, there exists the scaling equation (as a dilatation of the internal area scale) both for the generating functional

$$\Gamma\{\vec{f}, a, g, w, s_0\} = \Gamma\{\vec{f}(\mathcal{S}), a(\mathcal{S}), g(\mathcal{S}), w(\mathcal{S}), \mathcal{S}\},\tag{86}$$

and for the vertex functions

$$f^{2\mathcal{M}}\Gamma^{(2\mathcal{M})}\{\vec{k},\ldots,a,g,w,s_0\} = f^{2\mathcal{M}}(\mathcal{S})\Gamma^{(2\mathcal{M})}\{\vec{k},\ldots,a(\mathcal{S}),g(\mathcal{S}),w(\mathcal{S}),\mathcal{S}\},\tag{87}$$

where S is an arbitrary area-dimension parameter replacing s_0 , and $S \ge s_0$. The functions f(S), a(S), g(S), w(S) actually depend on the dimensionless ratio S/s_0 but are written as a(S) etc. for brevity. Determination of the functions constitutes the task of renormalization calculations. The said functions have their boundary conditions

$$a(s_0) = a, \quad g(s_0) = g, \quad w(s_0) = w, \quad f(s_0) = f.$$
 (88)

As Equations 86 and 86 are satisfied only for small values of as_0 as well as a(S)S, the maximal value of S, satisfying Equations 86 and 87, obeys the condition

$$S = const \left| a^{-1}(S) \right|. \tag{89}$$

To calculate the vertex functions, one should first find the right-hand sides of Equations 86 and 87 for the values of S satisfying the maximum condition (Equation 89). Owing to this, the logarithmic divergence in the perturbation series $(\ln(|a(S)|S) = const)$ is eliminated, and this row is therefore valid for the scale parameter S.

Renormalization scheme

At the tricritical point, the Lagrangian density has the form

$$\mathcal{L}_{tc}(\varphi) = \frac{1}{2} (\nabla \varphi)^2 + \frac{a_{0t}}{2} \varphi^2 + \frac{g_{0t}}{4!} (\varphi^2)^2 + \frac{w}{6!} (\varphi^2)^3.$$
(90)

As is usually done in field theory, field renormalization is performed

$$\varphi = Z^{1/2} \varphi_R. \tag{91}$$

The need in this is due to the logarithmic divergence in $\Gamma^{(0,0,2)}$ which appears beyond the superficial divergence of the degree $\delta = 2$, and to the logarithmic divergence $\Gamma^{(0,0,6)}$.

The subsequent renormalization of the vertex functions with insertion of φ^2 and $\tilde{\varphi}^4$, corresponds to the renormalizing Lagrangian in the vicinity of the tricritical point.

The characteristic quantities have the following dimensions

$$[\varphi] = \frac{d}{2} - 1 = \frac{1}{2}, \quad [a] = 2, \quad [g] = 4 - d = 1, \quad [w] = 6 - 2d = 0, \quad [L] = d = 3.(92)$$

Hence, the counter-terms to be added to the tricritical Lagrangian 90 are monomials including the renormalized sources $a_R(x)$ and $g_R(x)$ and the renormalized monomials φ_R^2 , φ_R^4 , so that their dimension could not exceed [L] = 3. This implies that the counterterms have the form

$$c_l Z g_R \varphi_R^2, \quad Z_1 Z a_R \varphi_R^2, \quad Z_2 Z^2 g_R (\varphi_R^2)^2, \quad \zeta (Z_2 g_R)^2 Z \varphi_R^2.$$
 (93)

First of them, $c_t Z g_R \varphi_R^2$, appeared in Lagrangian 75 for renormalization of $\Gamma^{(0,1,2)}$. Total Lagrangian density 75 is written in the renormalized form

$$\mathcal{L}(\varphi) = \mathcal{L}_R(\varphi_R),\tag{94}$$

$$\mathcal{L}_{R}(\varphi_{R}) \equiv \frac{1}{2} Z (\nabla \varphi_{R})^{2} + \frac{a_{0t}}{2} Z (\varphi_{R})^{2} + \frac{g_{0t}}{4!} Z^{2} (\varphi_{R}^{2})^{2} + \frac{w}{6!} Z^{3} (\varphi_{R}^{2})^{3} + \frac{1}{2} a_{R} Z_{1} Z (\varphi_{R})^{2} + g_{R} Z_{2} \left[Z^{2} \frac{(\varphi_{R}^{2})^{2}}{4!} - c_{t} Z \frac{(\varphi_{R})^{2}}{2} \right] + \frac{1}{2} (g_{R} Z_{2})^{2} \zeta Z \frac{(\varphi_{R})^{2}}{2}.$$

Lagrangians 75 and 94 coincide, provided that

$$a = a_R Z + \frac{1}{2} (g_R Z_2)^2 \zeta, \quad g = g_R Z_2 \tag{95}$$

is substituted. The dimensionless renormalization factors Z, Z_1 , Z_2 , ζ are determined from the renormalization conditions.

The renormalized vertex functions with insertions are determined in the following way. Let

$$\Gamma_R\{\varphi_R, a_R, g_R\} = \Gamma\{\varphi, a, g\} \tag{96}$$

be the generating functional corresponding to the renormalized form of Lagrangian density 94. Then the renormalized vertex functions with insertions $\Gamma_R^{(L,N,2\mathcal{M})}$ at the tricritical point are defined as functional derivatives

$$\Gamma_{R}^{(L,N,2\mathcal{M})} \equiv \frac{\partial^{[L]}}{\partial a_{R}^{[L]}} \frac{\partial^{[N]}}{\partial g_{R}^{[N]}} \frac{\partial^{[2\mathcal{M}]}}{\partial \varphi_{R}^{[2\mathcal{M}]}} \Gamma_{R}\{\varphi_{R}, a_{R}, g_{R}\}\Big|_{a_{R}^{=0,g} = 0, \varphi_{R}^{=0,\varphi_{R}^{=$$

The bare (Equation 76) and renormalized (Equation 97) vertex functions are related linearly due to the following definitions

$$\left. \frac{\partial}{\partial (k^2)} \Gamma_R^{(0,0,2)} \right|_{k^2 = \mathcal{M}^2} = 1, \quad (Z);$$

$$\Gamma_{R}^{(0,0,6)}\Big|_{s,p,^{(6)}(\mathcal{M})} \equiv w_{R}, \quad (w_{R});$$

$$\Gamma_{R}^{(1,0,2)}\Big|_{s,p,^{(3)}(\mathcal{M})} = 1, \quad (Z_{1});$$

$$\Gamma_{R}^{(0,1,4)}\Big|_{s,p,^{(5)}(\mathcal{M})} = 1, \quad (Z_{2});$$

$$\Gamma_{R}^{(0,2,2)}\Big|_{s,p,^{(4)}(\mathcal{M})} = 0. \quad (\zeta)$$
(98)

 $s.p.(\mathcal{M})$ is some symmetrical point for the external momentum in the scale \mathcal{M} . The dimensionless renormalization term, determined by each equation, is written between the braces. As these relationships are valid for the tricritical point, and Z, w_R , Z_1 , Z_2 , ζ are dimensionless, these quantities are obtained as functions of the dimensionless parameters w and \mathcal{M}^2s_0 and define, in turn, the renormalized quantities a_R , g_R , φ_R according to Equations 91 and 95.

Renormalization theory implies that the generating functional $\Gamma_R\{\varphi_R, a_R, g_R, w_R, s_0\}$ reaches a finite limit for $\mathcal{M}^2 s_0 \to 0$ when the renormalization conditions (Equation 98) are satisfied, if s_0 varies. Hence, in the limit

$$s_0 \frac{\partial}{\partial s_0} \Gamma_R \{ \varphi_R, a_R, g_R, w_R, s_0 \} = 0 \qquad (\mathcal{M}^2 s_0 \to 0).$$
⁽⁹⁹⁾

On the basis of Equation 96, from Equation 99, we obtain an equation for the generating functional Γ , expressed through the simple parameters φ , a, g, w

$$0 = s_0 \left. \frac{\partial}{\partial s_0} \Gamma_R \right|_R =$$
(100)

$$\equiv \left[s_0 \frac{\partial}{\partial s_0} + s_0 \left. \frac{\partial \varphi}{\partial s_0} \right|_R \frac{\partial}{\partial \varphi} + s_0 \left. \frac{\partial a}{\partial s_0} \right|_R \frac{\partial}{\partial a} + s_0 \left. \frac{\partial g}{\partial s_0} \right|_R \frac{\partial}{\partial g} + s_0 \left. \frac{\partial w}{\partial s_0} \right|_R \frac{\partial}{\partial w} \right] \Gamma(\varphi, a, g, w, s_0).$$

The notation $s_0 \frac{\partial}{\partial s_0}\Big|_R$ stands for differentiating at fixed values of φ_R , a_R , g_R , w_R . Further, the following functions are defined:

$$\begin{split} W(w) &= s_0 \left. \frac{\partial}{\partial s_0} w \right|_{w_R}, \\ \eta(w) &= s_0 \left. \frac{\partial}{\partial s_0} \ln Z \right|_{w_H}, \\ \gamma_1(w) &= s_0 \left. \frac{\partial}{\partial s_0} \ln Z_1 \right|_{w_R}, \\ \gamma_2(w) &= s_0 \left. \frac{\partial}{\partial s_0} \ln Z_2 \right|_{w_R}, \end{split}$$

$$\gamma_{\zeta}(w) = s_0 \left. \frac{\partial}{\partial s_0} \zeta(w) \right|_{w_R},\tag{101}$$

which are regular in the limit $\mathcal{M}^2 s_0 \to 0$ and depend only on w.

On the basis of Equations 91 and 95, we have

$$s_{0} \left. \frac{\partial \varphi}{\partial s_{0}} \right|_{R} = \eta(w)\varphi, \tag{102}$$

$$s_{0} \left. \frac{\partial a}{\partial s_{0}} \right|_{R} = a\gamma_{1}(w) + \frac{g^{2}}{2} \left[\gamma_{\zeta}(w) + \zeta(2\gamma_{2}(w) - \gamma_{1}(w)) \right] \equiv a\gamma_{1}(w) + g^{2}\gamma_{3}(w), \tag{102}$$

$$s_{0} \left. \frac{\partial g}{\partial s_{0}} \right|_{R} = g\gamma_{2}(w).$$

Calculation of functions 101 with the aid of renormalization conditions 98 has led (for $\mathcal{M}^2 s_0 \to 0$) to (Duplantier, 1982)

$$W(w) = -\frac{3n+22}{25} \cdot \frac{1}{3!} \cdot \frac{10}{2^5 \pi^2} w^2 + O(w^3), \tag{103}$$

$$\eta(w) = \frac{1}{2}w^2 \frac{(n+2)(n+4)}{15} \cdot \frac{1}{5!} \cdot \frac{1}{3 \cdot 2^{10}} \cdot \frac{1}{\pi^4} + O(w^3), \tag{104}$$

$$\gamma_1(w) = -\frac{16}{15} \cdot \frac{(n+2)(n+4)}{5!} \cdot \frac{1}{3 \cdot 2^{10}} \cdot \frac{1}{\pi^4} w^2 + O(w^3), \tag{105}$$

$$\gamma_2(w) = -\frac{n+4}{15} \cdot \frac{1}{2^4} \cdot \frac{1}{\pi^2} w + O(w^2), \tag{106}$$

$$\gamma_3(w) = -\frac{n+2}{3} \cdot \frac{1}{3!} \cdot \frac{1}{2^5} \cdot \frac{1}{\pi^2} + O(w).$$
(107)

Substitution of Equations 101 to Equation 100 leads to the linear equation of the renormalization group

$$\left[s_0\frac{\partial}{\partial s_0} + \eta(w)\varphi\frac{\partial}{\partial \varphi} + (108)\right]$$

$$\left(a\gamma_1(w)+g^2\gamma_3(w)\right)\frac{\partial}{\partial a}+\gamma_2(w)g\frac{\partial}{\partial g}+W(w)\frac{\partial}{\partial w}\right]\Gamma(\varphi,a,g,w,s_0)=0.$$

It can be integrated by the method of characteristics. On replacement of $s_0 \rightarrow S$, an equivalent equation arises

$$\mathcal{S}\frac{\partial}{\partial \mathcal{S}}\Gamma(\varphi(\mathcal{S}), a(\mathcal{S}), g(\mathcal{S}), w(\mathcal{S}), \mathcal{S}) = 0,$$
(109)

where the functions $\varphi(\mathcal{S}), a(\mathcal{S}), g(\mathcal{S}), w(\mathcal{S})$ are defined by

$$S\frac{\partial}{\partial S}\varphi(S) = \eta(w(S))\varphi(S), \tag{110}$$

$$\begin{split} & \mathcal{S}\frac{\partial}{\partial \mathcal{S}}a(\mathcal{S}) = a(\mathcal{S})\gamma_1(w(\mathcal{S})) + g^2(\mathcal{S})\gamma_3(w(\mathcal{S})), \\ & \mathcal{S}\frac{\partial}{\partial \mathcal{S}}g(\mathcal{S}) = \gamma_2(w(\mathcal{S}))g(\mathcal{S}), \\ & \mathcal{S}\frac{\partial}{\partial \mathcal{S}}w(\mathcal{S}) = W(w(\mathcal{S})), \end{split}$$

and satisfy the boundary conditions

$$\varphi(s_0) = \varphi, \quad a(s_0) = a, \quad g(s_0) = g, \quad w(s_0) = w.$$
 (111)

Equations 110 can be solved by means of the perturbation method (Equations 103-107) valid for small w(S). Self-consistent calculations show that w(S) logarithmically tends to zero for $S/s_0 \to \infty$.

Integration of Equations 110 yields, for n = 0, the following results (Duplantier, 1982)

$$w(S) = \frac{w}{1 + \frac{11}{240\pi^2} w \ln \frac{S}{s_0}}.$$
(112)

In the tricritical limit $w \ln S/s_0 \gg 1$ we obtain

$$w(S) = \frac{240\pi^2}{11} \left(\ln \frac{S}{s_0} \right)^{-1}.$$
 (113)

Therefore, the effective constant of the ternary interactions is logarithmically small. In this limit, the functions f(S), a(S), g(S) (for n = 0) can be calculated (Duplantier, 1982)

$$f(\mathcal{S}) = K(\mathcal{S})f,\tag{114}$$

$$K(S) = k(w) \left(1 - \frac{1}{\pi^2 1 1.3^2 5.2^7} w(S) + \cdots \right),$$

$$g(S) = g\sigma(w) [w(S)]^p \qquad \left(p = \frac{4}{11} \right),$$
 (115)

$$a(S) = P^{-1}(S)a - \frac{5}{18}g^2(S) [w(S)]^{-1}, \qquad (116)$$

where

$$P(S) = \rho(w) \left(1 - \frac{1}{\pi^2 11.2^2 3^2 5} w(S) + \cdots \right).$$
(117)

The coefficients k(w), $\sigma(w)$, $\rho(w)$ are well-defined positive functions of the original w:

$$k(w) \ge k(0) = 1, \quad \rho(w) \ge \rho(0) = 1, \quad \sigma(w) = w^{-p} \qquad (w \to 0).$$
 (118)

According to Equations 115 and 116,

$$a(S) = P^{-1}(S)a - Q(S)g^2,$$
(119)

where

$$Q(S) = \frac{5}{18}\sigma^2(w) [w(S)]^{2p-1} \qquad \left(2p - 1 = -\frac{3}{11}\right).$$

The critical curve a(S) = 0 serves as the tricritical region boundary, so, in view of Equation 119, the tricritical region corresponds to

$$g^2 Q(\mathcal{S}) \le |a(\mathcal{S})| \tag{120}$$

in agreement with the condition of the tricritical region from the general field theory (Stephen et al., 1975). For S, obeying Equation 89, the right-hand side of Equation 86 can be calculated by expansion in powers of w(S) or of the numbers of loops (see subsection 2.6.2). For instance, Duplantier calculated the vertex function $\Gamma^{(2)}$ using expansions 82, 97, and 114:

$$\Gamma^{(2)}(\vec{k}, -\vec{k}) = \Gamma_T^{(2)}(\vec{k}, -\vec{k}; f = 0;)$$

$$= K^2(S) \left(k^2 + a(S) - \frac{1}{2\pi} g(S) a^{1/2}(S) + \frac{1}{2^4 \pi^2 15} a(S) w(S) + \cdots \right).$$
(121)

Substituting Equation 121 to Equation 51 and, then, to Equation 15, he calculated the mean square end-to-end distance near the tricritical point as an expansion series in powers of g(S) and w(S) in the first order:

$$\left\langle h^2 \right\rangle_{tc} = d \cdot SP(S) \left(1 + \frac{g(S)}{9(2\pi)^{3/2}} [SP(S)]^{1/2} - \frac{w(S)}{60(2\pi)^2} + \cdots \right).$$
 (122)

In the course of calculation of statistical integral 51, the renormalization parameter S is transformed to the Brownian area $S \approx S$ with the same restriction (Equation 89)

$$|a(S)| = const S^{-1}. \tag{123}$$

In view of Equations 115 and 117, one finally obtains

$$\left\langle h^2 \right\rangle_{tc} = d \cdot S \rho(w) \left[1 + \frac{1}{9(2\pi)^{3/2}} \sigma(w) \rho^{1/2}(w) g S^{1/2}[w(S)]^p - \frac{37w(S)}{60 \cdot 33(2\pi)^2} \right],$$
 (124)

where $\rho(w)$, $\sigma(w)$, and w(S) are determined according to Equations 118 and 113.

In Duplantier's approach, g = 0 corresponds to the θ point for an infinitely long chain. For this point, he reports the following expression for a finite chain:

$$\left\langle h_{\theta}^{2} \right\rangle = d \cdot S \rho(w) \left[1 - \frac{37}{3 \cdot 11^{2}} \left(\ln \frac{S}{s_{0}} \right)^{-1} \right] \qquad (\rho(w) > 1).$$
 (125)

This result differs from Stephen's expression (Equation 4.1-41) in the sign of the second (logarithmic) summand and in the function $\rho(w)$.

According to Equation 124, the infinite chain at the θ point appears to be swollen by the three-body interactions, and this swelling is reduced for finite chains by a logarithmic correction.

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By analogy with $S \to \infty$, one can define the effective θ point as a function $\theta(S)$ according to the condition

$$\left\langle h_{\theta}^{2} \right\rangle = d \cdot S \rho(w).$$
 (126)

Then it follows from Equation 124 that

$$g_S \sim \sigma^{-1}(w) \rho^{-1/2}(w) S^{-1/2}[w(S)]^{1-p},$$
 (127)

and the relative deviation from the asymptotic $\theta(\infty)$ point is expressed by the ratio

$$\frac{\theta(S) - \theta(\infty)}{\theta(\infty)} \sim \sigma^{-1}(w) \left(\frac{S}{s_0}\right)^{-1/2} \left(\ln\frac{S}{s_0}\right)^{-7/11}.$$
(128)

These formulae involve asymptotic functions 113 and 115 and are valid for very long chains which meet the condition

$$w\ln\frac{S}{s_0} \gg 1. \tag{129}$$

Now, the boundary of the tricritical region specified by inequality 120 is transformed, with the aid of Equations 116 and 123, to the condition

$$|g| \le Q^{-1/2}(S)S^{-1/2}P^{-1/2}(S).$$
(130)

These boundary, in turn, are converted, according to Equations 119 (for Q(S)) and 117 P(S)), to

$$|g| \le \rho^{-1/2}(w)\sigma^{-1}(w)[w(S)]^{1/2-p}S^{-1/2} \qquad \left(\frac{1}{2} - p = \frac{3}{22}\right).$$
(131)

If the approximation $\sigma(w) = w^{-p}$ for small w and Equation 113 for w(S) are accepted, then we get for the tricritical region

$$|g| \le w^{1/2} \rho^{-1/2}(w) \left(w \ln \frac{S}{s_0} \right)^{-3/22} S^{-1/2}.$$
(132)

The exponent (-3/22) agrees with de Gennes' (1978) result. To discuss the properties of dilute and semidilute solutions, Duplantier employs the loop expansion (see section 2.6) of one-line-irreducible vertex functions.

The general idea behind his approach is the following. There are no tricritical divergences for short chains in solution. Therefore, a simple loop expansion in terms of f, a, g, w, s_0 is enough for the generating functional $\Gamma(f)$. In this procedure, c and c_p are calculated through a and f according to Equations 45 47, and a rule for short chains in solution with weak ternary interactions emerges, which corresponds to the path $1 \rightarrow 2$ on the following scheme:

where $\left\{\frac{\partial}{\partial a_0}, \frac{\partial}{\partial f}\right\}$ denote Equations 45.47 relating to a specific case of field theory with n = 0.

On the other hand, tricritical divergences appear in the expressions of the corresponding field theory in the case of long chains.

Then, scaling equation 86 holds good and renormalization is required, which corresponds to the path $3' \rightarrow 1' \rightarrow 2'$ on the given scheme. In this case, the loop expansion turns out to be regular for scaling theory in the scale S (see Equation 89).

On the path 2', c and c_p are calculated through a and f according to Equations 45-47, which leads to tricritical laws for long chains.

An alternative way of obtaining tricritical laws is in following the path $1 \rightarrow 2 \rightarrow 3$. The path fragment 3 corresponds to involvement of the functions c(S), $c_p(S)$, g(S), w(S) defined below.

In his theory, Duplantier follows the scheme $1 \rightarrow 2 \rightarrow 3$, as, at an intermediate stage of the loop expansion $1 \rightarrow 2$, expressions are obtained for short chains, which can be compared with the previous results, and procedure 3 gives equations for both short and long chains. For the grand potential $\Gamma\{\vec{f}\}$, its one-loop expansion has the form

$$\Gamma\{\vec{f}\} = \int d^d x \,\mathcal{L}(\vec{f}) + \frac{1}{2} \operatorname{tr} \int d^d x \,\ln \mathcal{L}^{(2)}(x,y;\vec{f}) + \cdots, \qquad (133)$$

where $L^{(2)}$ is the operator

$$\mathcal{L}_{ij}^{(2)}(x,y;\vec{f}) = \frac{\partial^2 \mathcal{L}(\vec{f})}{\partial f^i(x) \, \partial f^j(y)}.$$
(134)

The trace in Equation 133 is taken as being with respect to the subscripts 'i' and 'j'. For a uniform field f, the grand potential $\Gamma(f)$ acquires the form

.

$$\Gamma(f) = \mathcal{L}(f) + \frac{1}{2}V^{-1} \operatorname{tr} \int d^{d}x \, \ln \mathcal{L}^{(2)}(x,x;f) + \cdots \,.$$
(135)

Corresponding calculations lead, for d = 3 and n = 0, to

$$\Gamma(f) = \Gamma_0(f) + \Gamma_1(f) + \cdots .$$
(136)

Here $\Gamma_0(f)$ is the zeroth loop order (the mean field approximation)

$$\Gamma_0(f) = \mathcal{L}(f) = \frac{1}{2}af^2 + \frac{1}{4!}gf^4 + \frac{1}{6!}wf^6,$$
(137)

while $\Gamma_1(f)$ is the one-loop order

$$\Gamma_1(f) = -\frac{1}{12\pi} \left[X^{3/2}(f^2) - Y^{3/2}(f^2) \right], \tag{138}$$

where

$$X(f^2) = \frac{\partial^2 \Gamma_0(f)}{\partial f^2} = a + \frac{1}{2}gf^2 + \frac{1}{4!}wf^4,$$
(139)

$$Y(f^2) = \frac{1}{f} \frac{\partial \Gamma_0(f)}{\partial f} = a + \frac{1}{3!} g f^2 + \frac{1}{5!} w f^4.$$
 (140)

The one-loop expansion of the transverse vertex function is calculated according to Equation 49 (Duplantier, 1982)

$$\Gamma_T^{(2)}(0,0;f) = \frac{1}{f} \cdot \frac{\partial}{\partial f} \left[\Gamma_0(f) + \Gamma_1(f) + \cdots \right]$$
(141)
$$= Y(f^2) - \frac{1}{12\pi} \cdot \frac{1}{f} \cdot \frac{\partial}{\partial f} \left[X^{3/2}(f^2) - Y^{3/2}(f^2) \right],$$

$$\frac{\partial \Gamma_T^{(2)}(0,0;f)}{\partial (k^2)} = 1 + \frac{1}{12\pi} f^{-2} \left[X^{1/2}(f^2) - Y^{1/2}(f^2) \right]^2 \left[X^{1/2}(f^2) + Y^{1/2}(f^2) \right]^{-1}.$$
(142)

Finally, one calculates π

$$\pi = f \frac{\partial \Gamma}{\partial f} - \Gamma \tag{143}$$

(see Equation 47) and $\langle h^2 \rangle$

$$\left\langle h^2 \right\rangle = 2d \frac{\partial}{\partial (k^2)} \ln \Gamma_T^{(2)}(0)$$
 (144)

(see Equation 50) with replacement of a and f by c and c_p , following

$$c = 2\frac{\partial \Gamma}{\partial a}$$

(see Equation 45),

$$c_p = \frac{1}{2} f \frac{\partial \Gamma}{\partial f}$$

(see Equation 46) in the one-loop non-renormalized approximation.

 $\frac{\partial}{\partial a_0} = \frac{\partial}{\partial a}$ follows from Equation 73. The corresponding calculations yield (Duplanticr, 1982)

$$\frac{\pi}{kT} = c_p + \frac{g}{24}c + \frac{w}{3\cdot 5!}c^3 - \frac{3}{2} \cdot \frac{1}{12\pi}cX^{1/2}(X' - Y') + \frac{1}{12\pi}(X^{3/2} - Y^{3/2}), \quad (145)$$

$$\left\langle h^2 \right\rangle = \frac{d \cdot c}{c_p} \left\{ 1 + \frac{1}{12\pi c} (X^{1/2} - Y^{1/2}) \left[3 + \frac{(X^{1/2} - Y^{1/2})^2}{X - Y} \right] \right\},$$
 (146)

where

$$X = 2\frac{c_p}{c} + \frac{g}{3}c + \frac{w}{30}c^2, \qquad Y = 2\frac{c_p}{c},$$
(147)

$$X' = \frac{g}{12} + \frac{w}{12}c, \qquad Y' = \frac{g}{6} + \frac{w}{60}c.$$
 (148)

The adduced relationships are valid in the one-loop approximation. In the zeroth order,

$$a = 2\frac{c_p}{c} - \frac{g}{3!}c - \frac{g}{3!}c^2 \tag{149}$$

has been obtained as well.

In this grand canonical formalism, the mean area of the chains is defined as

$$S = \frac{c}{c_p}.$$
(150)

Prior to renormalization, it is necessary to distinguish between two limiting cases of dilute and semidilute solutions of short chains.

Dilute solutions of short chains

Let us assume that $c \to 0$ with a fixed S. Accepting (see Equation 149)

$$a = 2S^{-1} + O(gc; wc^2) \tag{151}$$

and rejecting the higher-order terms in expansions 147 and 148, we get

$$\frac{\pi}{kT} = c_p + \frac{g}{24}c^2 + \frac{w}{3\cdot 5!}c^3 - \frac{wc^2}{20\cdot 12\pi} \left(\frac{2c_p}{c}\right)^{1/2} + c^2 \left(\frac{c_p}{c}\right)^{-1/2} + O(g^2, gwc, w^2c^2), (152)$$

$$\left\langle h^2 \right\rangle = \frac{d \cdot c}{c_p} \left\{ 1 + \frac{1}{24\pi} \left(g + \frac{wc}{10}\right) \left(\frac{2c_p}{c}\right)^{-1/2} + c \left(\frac{c_p}{c}\right)^{-3/2} + O(g^2, gwc, w^2c^2) + \cdots \right\}. (153)$$

The quantity $\langle h^2 \rangle$ in the one-loop approximation in the limit $c \to 0$ is corrected by the term of the two-loop approximation (Duplantier, 1982)

$$\delta \left\langle h^2 \right\rangle = \frac{d \cdot c}{c_p} \left(-\frac{1}{60(2\pi)^2} w \right). \tag{154}$$

Now we are able to compare the expressions for $\langle h^2 \rangle$ obtained for a polymolecular grand ensemble and for a single chain (see Equations 15, 51, 122–125). In the first order of gand w (without renormalization), Equation 122 reads

$$\left\langle h^2 \right\rangle = d \cdot S \left\{ 1 + \frac{1}{9(2\pi)^{3/2}} g S^{1/2} - \frac{1}{60(2\pi)^2} w \right\}.$$
 (155)

Comparison with $\langle h^2 \rangle$ calculated from Equations 153 and 154 at c = 0 shows the S-dependent term $gS^{1/2}$ to have a different coefficient in a grand polymolecular ensemble.

Semidilute solutions

are characterized by

$$S \to \infty, \quad c_p \text{ is fixed}, \quad wc^2 S \gg 1.$$
 (156)

In fact, we are dealing in this case with short fragments between the contact points of the macromolecules.

In this limit, the loop approximation for a grand polymolecular ensemble must give the same results as does the perturbation theory of monomolecular chains.

Provided that Equation 156 holds, the quantity S^{-1} is small in comparison with other quantities of the same dimension (eg. wc^2) and $Y = 2S^{-1} + \cdots \rightarrow 0$ can be accepted.

Then, Equation 149 takes the form

$$a = -\frac{g}{3!}c - \frac{w}{5!}c^2 + O(S^{-1}), \tag{157}$$

while osmotic pressure (see Equation 152) is expressed as

$$\frac{\pi}{kT} = c_p + \frac{g}{24}c^2 + \frac{w}{3\cdot 5!}c^3 + \delta\left(\frac{\pi}{kT}\right),$$
(158)

where

$$\delta\left(\frac{\pi}{kT}\right) = -\frac{c^{3/2}}{12\pi} \left(\frac{g}{6} + \frac{w}{15}c\right) \left(\frac{g}{3} + \frac{wc}{30}\right)^{1/2} + O(wc^2 S^{-1/2}).$$

Under the same conditions for $\langle h^2 \rangle$ (see Equation 146), we have

$$\left\langle h^2 \right\rangle = d \cdot S \left\{ 1 + \frac{1}{3\pi c^{1/2}} \left(\frac{g}{3} + \frac{wc}{30} \right)^{1/2} + O \left[\left(cS^{1/2} \right)^{-1} \right] \right\}.$$
 (159)

This formula generalizes Edwards' (1975) result and coincides with it for w = 0.

Tricritical scaling laws for long chains in solution

Replacement of variables in the expressions for short chains by scaling variables has proved to produce formulae for the description of the tricritical behaviour of long chains. Let us discuss renormalization group equation 86, having rewritten it in the form

$$\Gamma(f, a, g, w, s_0) = \Gamma(f(\mathcal{S}), a(\mathcal{S}), g(\mathcal{S}), w(\mathcal{S}), \mathcal{S}) \equiv \Gamma_{\varphi}.$$
(160)

As is accepted in renormalization group theory,

$$S \left. \frac{d}{dS} \Gamma_{\varphi} \right|_{f,a,g,w,s_0} = 0.$$
(161)

For the time being, S is a free parameter.

We now express π and $\langle h^2 \rangle$ (see Equations 47 and 50) in terms of renormalization scaling theory. By virtue of the recurrence of renormalization (Equation 114), the identity owing to the multiplicative renormalization

$$f\left.\frac{\partial}{\partial f}\right|_{a.g.w,s_0} \equiv f(\mathcal{S})\left.\frac{\partial}{\partial f(\mathcal{S})}\right|_{a(\varphi),g(\varphi),w(\varphi),\varphi}$$
(162)

is valid.

Applying renormalization group equations 86 and 87, it is found for Equations 47 and 50 that

$$\frac{\pi}{kT} = f \frac{\partial}{\partial f} \Gamma - \Gamma = f(\mathcal{S}) \frac{\partial}{\partial f(\mathcal{S})} \Gamma_{\varphi} - \Gamma_{\varphi}, \tag{163}$$

$$\left\langle h^2 \right\rangle = -2d \left. \frac{\partial}{\partial (k^2)} \ln \Gamma_{T,\varphi}^{(2)} \right|_{k^2 = 0},\tag{164}$$

where Γ_{φ} and $\Gamma_{T,\varphi}$ are functions calculated for the scaling parameters f(S), a(S), g(S), w(S), S.

Now, auxiliary scaling variables

$$c_p(\mathcal{S}) \equiv \frac{1}{2} f(\mathcal{S}) \frac{\partial}{\partial f(\mathcal{S})} \Gamma_{\varphi}, \qquad c(\mathcal{S}) \equiv 2 \frac{\partial \Gamma_{\varphi}}{\partial a(\mathcal{S})}$$
 (165)

are defined. The scaling variables $c_p(S)$ and c(S) play just the same role for Γ_{φ} as the variables c_p and c in Equations 45 and 46 do for Γ_{s_0} .

Therefore, the loop expansion of the quantities in Equations 164 and 165 results immediately by replacing c_p , c, g, w, a by $c_p(S)$, c(S), g(S), w(S), a(S) in Equations 145 and 150.

At the final stage, the functions $c_p(S)$ and c(S), should be expressed through the true physical concentrations c_p and c defined in Equations 45 and 46. Using Equations 86 and 162, we get

$$c_{p} = \frac{1}{2} f \frac{\partial \Gamma}{\partial f} = \frac{1}{2} f(\mathcal{S}) \frac{\partial \Gamma_{\varphi}}{\partial f(\mathcal{S})} \equiv c_{p}(\mathcal{S}).$$
(166)

Applying then the operation

$$\frac{\partial}{\partial a} = P^{-1}(\mathcal{S}) \frac{\partial}{\partial a(\mathcal{S})} \tag{167}$$

which follows from Equation 116, we obtain

$$c \equiv 2\frac{\partial\Gamma}{\partial a} = 2P^{-1}(\mathcal{S})\frac{\partial}{\partial a(\mathcal{S})}\Gamma_{\varphi} \equiv P^{-1}(\mathcal{S})c(\mathcal{S}).$$
(168)

So, the rules of obtaining results in the tricritical state are as follows: in the expressions, given in section 5.4 to describe the properties of a polymer, the parameters c_p , c, g, w are replaced by a set of $c_p(S)$, c(S), g(S), w(S) which is

$$c_p, \quad cP(\mathcal{S}), \quad g(\mathcal{S}), \quad w(\mathcal{S}),$$

$$(169)$$

and, also, $a \to a(\mathcal{S})$.

The mean area of the chains, having been determined as c/c_p , is transformed according to Equation 169 into

$$S \to SP(\mathcal{S}).$$
 (170)

This procedure culminates in the determination of the area. S satisfies the basic equation 89, and the result for it depends on the concentration range.

Tricritical state of a dilute solution of long chains

Equation 151 defines the value of the parameter a for a dilute solution of chains, according to Equation 170

$$a(S) = 2[SP(S)]^{-1}.$$
(171)

Then, on the basis of Equation 89, we have

$$S = const \cdot SP(S) \simeq const \cdot SP(S) = const \cdot \rho(w)S.$$
(172)

Here the approximation includes only logarithmic terms. For dilute solutions, S can be replaced by S in the logarithm up to the numerical additive summand

$$\ln\frac{S}{s_0} \cong \ln\frac{S}{s_0}.$$
(173)

Rule 169 then leads to the transformation

$$c, c_p, S, g, w \to cP(S), c_p, SP(S), g(S), w(S).$$

$$(174)$$

All these renormalization procedures are necessary and valid in the asymptotic limit of very long chains, which meet the condition

$$w\ln\frac{S}{s_0} \gg 1,\tag{175}$$

and, in this case (see Equation 113),

$$w(S) = \frac{60(2\pi)^2}{11} \left(\ln \frac{S}{s_0} \right)^{-1},$$
(176)

$$P(S) = \rho(w) \left\{ 1 - \frac{1}{(2\pi)^2 45 \cdot 11} w(S) \right\},\tag{177}$$

$$g(S) = gw^{-p}[w(S)]^{p} \qquad \left(p = \frac{4}{11}\right).$$
(178)

The concentration range, corresponding to the tricritical state of dilute solutions, follows from Equation 151

$$w(S)c^2SP^3(S) \ll 1,$$
 (179)

which is transformed using the expressions for w and P:

$$c^2 \ll \rho^{-3}(w) \left(\ln \frac{S}{s_0} \right) S^{-1}.$$
 (180)

The expression for (h^2) in the tricritical region was obtained above (see Equation 122); now we are able to derive it immediately from Equation 155 with the aid of Rule 174.

Applying Equation 153 with Rule 174 for the concentration-dependent component $\delta \langle h^2 \rangle (c)$, we derive for $P(S) \approx \rho(w)$

$$\delta \left\langle h^2 \right\rangle(c) = \frac{1}{2^{1/2} 240\pi} d \cdot S \rho^{5/2}(w) w(S) c S^{1/2},\tag{181}$$

where d = 3. The numerical coefficient corresponds to a polymolecular system and. of course, differs from that in the formula for equiareal chains.

The virial expansion of the osmotic pressure of a grand ensemble with very long chains results from Equation 152, also transformed by Rule 174

$$\frac{\pi}{kT} = c_p + \left\{ \frac{1}{24}g(S) - \frac{1}{240\pi}w(S) \left[\frac{SP(S)}{2} \right]^{-1/2} \right\} P^2(S)c^2 + \frac{1}{3 \cdot 5!}w(S)P^3(S)c^3.$$
(182)

Using asymptotics 115 and 117, we have for osmotic pressure in the tricritical region

$$\frac{\pi}{kT} = c_p + \left[\frac{\sigma(w)}{24}g[w(S)]^p - \frac{2^{1/2}}{240\pi}w(S)(S\rho(w))^{-1/2}\right]\rho^2(w)c^2 + \frac{1}{3\cdot 5!}w(S)\rho^3(w)c^3,$$
(183)

where w(S) is determined from Equation 176.

The extension of the tricritical domain, where the above relationships hold true, is defined by conditions 131 and 132. This domain is marked as D in Figure 5.45.

Semidilute solutions (long intrachains)

Within this concentration range, the parameter a is formally defined by Equation 157, where the *g*-including term can be neglected.

Rule 169 then leads to

$$a(S) = -\frac{1}{5!}w(S)P^{2}(S)c^{2}.$$
(184)

The area S is defined by Equation 89 and relates to the concentration c (which has the dimension of area^{-1/2}) by

$$\mathcal{S} = const \cdot w^{-1}(\mathcal{S})P^{-2}(\mathcal{S})c^{-2}.$$
(185)

Neglecting the double logarithmic dependence in Equation 185, we can approximate

$$\ln(c^2 s_0)^{-1} = \ln \frac{S}{s_0}.$$
(186)

Here $s_0/S \approx c^2 s_0$ is considered as very small. Then it follows from Equation 113 that

$$w(c^{-2}) = \frac{60}{11} (2\pi)^2 |\ln c^2 s_0|^{-1}.$$
(187)

Transformation of Rule 169 for the tricritical semidilute solutions gives

$$c, c_p, g, w \to c\rho, c_p, g(c^{-2}), w(c^{-2}),$$
 (188)

where

$$P(c^{-2}) \simeq P(\infty) = \rho(w). \tag{189}$$

The theory of the tricritical state is valid where cs_0 is small to meet condition 129. In view of Equation 186,

$$w|\ln c^2 s_0|^{-1} \gg 1. \tag{190}$$



Figure 5.45. The tricritical state region on the state diagram. The solid line is the phase coexistence curve at $S \rightarrow \infty$. Inside it is the dashed line, the binodal for finite S (Duplantier, 1982) [Reprinted with permission from: B.Duplantier. J. de Phys. 43 (1982) 991-1019. Copyright © 1982 by EDP Sciences]

Otherwise, the simple expressions of perturbation theory work (see above).

On the other hand, the semidilute solution domain is bounded by conditions 156, 188, and

$$\rho^3(w)w(c^{-2})c^2S \ge 1. \tag{191}$$

Hence, the semidilute solutions with a high value of the characteristic dimensionless parameter cS have the tricritical properties if and only if the other dimensionless parameter c^2s_0 turns out to be small to satisfy inequality 190.

In this case, the quantities π and $\langle h^2 \rangle$ should be calculated using formal expressions 158 and 159 with due account of Rule 188, which leads to

$$\frac{\pi}{kT} = \frac{1}{3\cdot 5!} w(c^{-2})(c\rho(w))^3 + \frac{1}{24} g(c^{-2})(c\rho(w))^2 + \cdots .$$
(192)

Including $\delta \pi$ from Equations 158 and 115, a more complete expression

$$\frac{\pi}{kT} = \frac{1}{3\cdot 5!} w(c^{-2})(c\rho(w))^3 + \frac{1}{24} g\sigma(w)[w(c^{-2})]^p [c\rho(w)]^2 + \cdots$$
(193)

results, where $w(c^{-2})$ is defined by Equation 187, p = 4/11.

Under the same conditions of the tricritical state,

$$\left\langle h^2 \right\rangle = d \cdot S\rho(w) \left\{ 1 + \frac{1}{3\pi (c\rho(w))^{1/2}} \left[\frac{\sigma(w)}{3} g[w(c^{-1})]^p + \frac{w(c^{-2})}{30} c\rho(w) \right]^{1/2} + \cdots \right\}.$$
 (194)

The sizes of the tricritical region on the state diagram of c vs g for semidilute solutions are also defined by the predominance of the first term in Equation 193 over the second one, i.e.

$$|g| \le \rho(w)\sigma^{-1}(w)[w(c^{-2})]^{1-p}c \qquad \left(1-p=\frac{7}{11}\right).$$
(195)

This agrees with Equation 120 rewritten in view of Equation 184. According to Equations 195 and 187, the tricritical effects predominate over the critical ones due to the excluded volume g in the range (see Figure 5.45)

$$|g| \le w(w|\ln c^2 s_0|)^{-7/11}c.$$
⁽¹⁹⁶⁾

In this formalism, the phase separation region is defined in the limit of infinitely long chains $(S \to \infty)$, i.e. in the semidilute system mode. The left-hand branch of the binodal, in this approximation, coincides with the ordinate axis on the state diagram

$$g < 0, \quad c = 0,$$
 (197)

i.e. $\pi = 0$ on this branch. The right-hand branch is then determined from the condition $\pi = 0$.

Applying Equation 193 for g_e , one obtains for the right-hand branch of the binodal

$$g_c = -\frac{1}{15}\sigma^{-1}(w) \left[w(c^{-2})\right]^{1-p} c\rho(w) \qquad \left(1-p=\frac{7}{11}\right).$$
(198)

For small w (but sufficiently large to obey Equation 190), using Equations 118 and 187 enables one to obtain

$$g_e \simeq -\frac{1}{15} w \left(\frac{11}{60(2\pi)^2} w |\ln c^2 s_0| \right)^{-7/11} \times c.$$
(199)

Thus, the right-hand branch of the binodal for infinitely long chains has a zero slope at the origin of coordinates (see Figure 5.45), which is a characteristic property of the tricritical phenomena.

However, the binodal is located on the border of the domain of validity of the tricritical theory, as it follows from Equation 195.

The question of how the g-related critical effects correspond to the w-related tricritical ones, if they are commensurable, remains open in this approximation.

On the other hand, the state equation for finite chains provides the binodal asymptotics in the semidilute region.

For chains with the area S, the critical concentration in the binary system P+LMWE has the value

$$v_c \approx S^{-1/2}.\tag{200}$$

The binodal curvature near c_c corresponds to the universal critical index for liquid binary systems (not to the tricritical one!).

The tricritical state theory is not applicable in the neighbourhood of the critical concentration c, but only when $c > c_c$.

The theory becomes valid in the limit $S \to \infty$, when the critical point (g_c, c_c) moves towards the tricritical one (0,0).

Then, the binodal curve becomes asymptotic to the tricritical curve (Equation 198). Hence, Lagrange's formalism 0(n) of field theory (with n = 0) shows the tricritical point of the system with infinitely long polymer chains to correspond to the θ point, where there occur hyperfine compensative effects of the pair and ternary interactions. Long chains are established not to be Gaussian near the θ point.

A universal behaviour asymptotically arises from the mean square end-to end distance, and the exponent of the logarithmic component has been calculated in this version of theory.

The renormalization group method has been applied for description of the solution behaviour at finite concentrations. In particular, the mean square end-to-end distance in solution, averaged over the grand canonical ensemble and containing the logarithmic function as well, have been calculated.

The osmotic pressure for a set of monomolecular chains and that averaged over the grand canonical ensemble have also been calculated. The boundary of the tricritical region have been outlined on the state diagram (see Figure 5.45) in the g vs c coordinates, where $g \sim (T - \theta)/\theta$.

An analytical expression for the right-hand branch of the binodal in the limit of infinitely long chains has been also derived.

Since then, the theory of the tricritical phenomena has been developed by the direct renormalization methods (des Cloizeaux, 1981) (see section 5.4) in (Duplantier, 1986bd), by the dimensional regularization in momentum space (see section 5.2) in (Kholodenko and Freed, 1984; Cherayil et al., 1985; Douglas and Freed, 1985).

Duplantier (1987) correlated the results of different approaches in renormalization theory to clear up a number of contradictions described by different authors in the course of development of the tricritical state theory.

He uses the probability distribution function for the state of a system in the notation

$$P\{\vec{r}\} = \exp\left\{-\frac{1}{2}\int_{0}^{S} \left[\frac{d\vec{r}(s)}{ds}\right]^{2} ds - \frac{b}{2}\int_{0}^{S} ds \int_{0}^{S} ds' \,\delta^{d}[\vec{r}(s) - \vec{r}(s')]$$
(201)

$$-\frac{\mathbf{c}}{3!}\int_{0}^{S} ds \int_{0}^{S} ds' \int_{0}^{S} ds'' \,\delta^{d}[\vec{r}(s) - \vec{r}(s')]\delta^{d}[\vec{r}(s') - \vec{r}(s'')]\Big\}.$$

The mean square end-to-end distance is defined as

$$\left\langle h^2 \right\rangle = \left\langle \left| \vec{r}(S) - \vec{r}(0) \right|^2 \right\rangle \tag{202}$$

and calculated by the formula (see Equations 5.4-40 and 15)

$$\left\langle h^2 \right\rangle = -2d \left. \frac{\partial}{\partial (k^2)} \frac{Z(\vec{k}, -\vec{k}, S)}{Z(S)} \right|_{\vec{k}=0}.$$
(203)

Here $Z(\vec{k}, -\vec{k}, S)$ is the generating function,

$$Z(\vec{k}, -\vec{k}, S) = \frac{\int d\{\vec{r}\} P\{\vec{r}\} \exp\left\{i\vec{k}[\vec{r}(S) - \vec{r}(0)]\right\}}{\int d\{\vec{r}\} P_0\{\vec{r}\}},$$
(204)

 $P_0\{\vec{r}\}$ obtained from Equation 201 for b = 0 and $\mathbf{c} = 0$.

The mean square radius of gyration of a coil is defined by (cf. Equation 5.4-103)

$$\left\langle R^2 \right\rangle = \frac{1}{2S^2} \int_0^S ds_1 \int_0^S ds_2 \left\langle |\vec{r}(s_1) - \vec{r}(s_2)|^2 \right\rangle$$
 (205)

and calculated by the formula

$$\left\langle R^2 \right\rangle = -d \left. \frac{\partial}{\partial (k^2)} \frac{Z_G(\vec{k}, -\vec{k}, S)}{Z(S)} \right|_{\vec{k}=0}$$
(206)

with the generating function

$$Z_G(\vec{k}, -\vec{k}, S) = \frac{1}{S^2} \int_0^S ds_1 \int_0^S ds_2 \frac{\int d\{\vec{r}\} P\{\vec{r}\} \exp\left\{+i\vec{k}[\vec{r}(s_1) - \vec{r}(s_2)]\right\}}{\int d\{\vec{r}\} P_0\{\vec{r}\}}$$
(207)

proportional to the structural factor in radiation scattering.

In Equations 203 and 206, Z(S) is the single-chain partition function

$$Z(S) = Z(0,0,S) = Z_G(0,0,S) = \frac{\int d\{\vec{r}\} P\{\vec{r}\}}{\int d\{\vec{r}\} P_0\{\vec{r}\}}.$$
(208)

The diagram $Z(\vec{k}, -\vec{k}, S)$ in the first-order is presented in Figure 5.46. The corresponding contributions are determined according to des Cloizeaux' (1981) rules (see section 5.4) extended to the three-particle interactions

$$Z_{a}(\vec{k}, -\vec{k}, S) = \exp\left(-\frac{k^{2}S}{2}\right), \qquad (209)$$

$$Z_b(\vec{k}, -\vec{k}, S) = -b \int \frac{d^d q}{(2\pi)^d} \int_{s_0}^S ds \, (S-s) e^{-q^2 s/2} e^{-k^2 (S-s)/2}, \tag{210}$$

$$Z_{c}(\vec{k},-\vec{k},S) = -\mathbf{c} \int \frac{d^{d}q}{(2\pi)^{d}} \int \frac{d^{d}q'}{(2\pi)^{d}} \int_{s_{0}}^{S} ds \int_{s_{0}}^{S} ds' \,\theta(S-s-s')(S-s-s')$$
(211)



Figure 5.46. First-order diagrams giving the generating function $Z(\vec{k}, -\vec{k}, S)$ (Duplantier, 1987) [Reprinted with permission from: B.Duplantier. J. Chem. Phys. 86 (1987) 4233-4244. Copyright © 1987 American Institute of Physics]

$$e^{-q^2s/2}e^{-(q')^2s'/2}e^{-k^2(S-s-s')/2}$$

As the values $Z(\vec{k}, -\vec{k}, S)$ at small \vec{k} are needed to calculate $\langle h^2 \rangle$ and $\langle R^2 \rangle$, these functions can be represented by two terms of the k^2 series

$$Z(\vec{k}, -\vec{k}, S) = Z(S) - \frac{k^2}{2}SZ'(S) + \cdots .$$
(212)

The versions of theory to be compared are described in terms of

$$z = (2\pi)^{-d/2} b S^{2-d/2},\tag{213}$$

$$y = (2\pi)^{-d} \mathbf{c} S^{3-d}, \tag{214}$$

$$x_0 = \frac{s_0}{S}.$$
 (215)

This three-parameter model should be regarded in the dimension $d \leq 3$, as at d > 3 the three-particle interaction effects are drastically reduced for long chains. Indeed, for $S \rightarrow \infty$ it follows from Equation 214 that

$$y \rightarrow \begin{cases} \infty & \text{for } d < 3, \\ (2\pi)^{-3}\mathbf{c} & \text{for } d = 3, \\ 0 & \text{for } d > 3. \end{cases}$$
(216)

In view of Equation 215, we discuss either small cut-offs s_0 or long chains $S \to \infty$, i.e.

$$x_0 \to 0. \tag{217}$$

In the version of theory with a cut-off within $2 < d \leq 3$, Duplantier (1987) obtained the following expressions

$$Z(S) = 1 - z \left[-\frac{x_0^{1-d/2}}{1-d/2} + \frac{1}{(1-d/2)(2-d/2)} + \frac{x_0^{2-d/2}}{2-d/2} \right] - y \left[\frac{x_0^{2-d}}{(1-d/2)^2}$$
(218)

$$-\frac{2x_0^{1-d/2}}{(1-d/2)^2(2-d/2)}+b_d-\frac{2x_0^{3-d}}{(1-d/2)(2-d/2)}+O(x_0^{2-d/2})\bigg],$$

where

$$b_d = \frac{1}{1 - d/2} \frac{\Gamma(1 - d/2)\Gamma(2 - d/2)}{\Gamma(4 - d)}, \qquad 2 < d \le 3;$$
(219)

$$Z'(S) = 1 - z \left[-\frac{x_0^{1-d/2}}{1-d/2} + a_d + 2\frac{x_0^{2-d/2}}{2-d/2} - \frac{x_0^{3-d/2}}{3-d/2} \right] - y \left[\frac{x_0^{2-d}}{(1-d/2)^2} \right]$$
(220)

$$-\frac{2}{1-d/2}a_dx_0^{1-d/2}+a_db'_d-\frac{4x_0^{3-d}}{(1-d/2)(2-d/2)}+O(x_0^{2-d/2})\bigg],$$

where

$$a_d = \frac{1}{1 - d/2} + \frac{1}{3 - d/2} - \frac{2}{2 - d/2},$$
(221)

$$b'_{d} = \frac{\Gamma(1 - d/2)\Gamma(4 - d/2)}{\Gamma(5 - d)}, \qquad 2 < d \le 3.$$
(222)

Calculation of Z(S) and Z'(S) in the dimensional regularization method gives for d < 3

$$Z(S)|_{dim.reg.} = 1 - z \frac{1}{(1 - d/2)(2 - d/2)} - yb_d,$$
(223)

$$Z'(S)|_{dim,reg.} = 1 - za_d - ya_d b'_d.$$
(224)

Analytical continuation of these equations to d = 3 leads to

$$Z(S)|_{dim.reg.} = 1 + 4z - 4\pi y \qquad (d = 3),$$
(225)

$$Z'(S)|_{dim.reg.} = 1 + \frac{16}{3}z - 8\pi y \qquad (d=3).$$
(226)

The expansion

$$Z_G(\vec{k}, -\vec{k}, S) = Z(S) - \frac{k^2 S}{2} \cdot \frac{1}{3} Z'_G(S) + \cdots$$
(227)

is also valid for the gyration generating function $Z_G(\vec{k}, -\vec{k}, S)$. Duplantier (1987) provides expressions for $Z'_G(S)$ in the versions of theory with a cut-off and dimensional regularization.

In view of Equations 203, 212, 206, and 222, one can write

$$\left\langle h^2 \right\rangle = d \cdot S \frac{Z'(S)}{Z(S)},\tag{228}$$

$$\left\langle R^2 \right\rangle = \frac{d \cdot S}{6} \cdot \frac{Z'_G(S)}{Z(S)},\tag{229}$$

which gives in the cut-off version

$$\left\langle h^2 \right\rangle = d \cdot S[1 - zg(x_0) - y\mathbf{h}(x_0)]. \tag{230}$$

Here

$$g(x_0) = -\frac{1}{(2-d/2)(3-d/2)} + \frac{x_0^{2-d/2}}{2-d/2} - \frac{x_0^{3-d/2}}{3-d/2},$$
(231)

$$\mathbf{h}(x_0) = 2\frac{x_0^{1-d/2}}{1-d/2}\frac{1}{(2-d/2)(3-d/2)} + a_db'_d - b_d - 2\frac{x_0^{3-d}}{(1-d/2)(2-d/2)} + O(x_0^{2-d/2}); (232)$$

$$\left\langle R^2 \right\rangle = \frac{d \cdot S}{6} [1 - zg_G(x_0) - y\mathbf{h}_G(x_0)],$$
 (233)

where

$$g_G(x_0) = A'_d + \frac{x_0^{2-d/2}}{2-d/2} + O(x_0^{3-d/2});$$
(234)

$$\mathbf{h}_G(x_0) = -2A'_d \frac{x_0^{1-d/2}}{1-d/2} + B'_d - 2\frac{x_0^{3-d}}{(1-d/2)(2-d/2)} + O(x_0^{2-d/2}),$$
(235)

where

$$A'_{d} = \frac{1}{2(4-d/2)(5-d/2)} - \frac{1}{(2-d/2)(3-d/2)},$$
(236)

$$B'_d = B_d - b_d \tag{237}$$

(the expression for B_d is not reported here).

The functions $g(x_0)$ and $g_G(x_0)$ are similar as are $h(x_0)$ and $h_G(x_0)$. They can be written in the general form

$$g(x_0) = A + \frac{x_0^{2-d/2}}{2-d/2} + O(x_0^{3-d/2}),$$
(238)

$$\mathbf{h}(x_0) = -2A \frac{x_0^{1-d/2}}{1-d/2} + B - 2 \frac{x_0^{3-d}}{(1-d/2)(2-d/2)} + O(x_0^{2-d/2}),$$
(239)

where A and B are the dimensionless regularized components of g and h: for $\langle h^2 \rangle$

$$A = -\frac{1}{(2 - d/2)(3 - d/2)}, \quad B = a_d b'_d - b_d$$
(240)

and for $\langle R^2 \rangle$

$$A = A'_d, \quad B = B'_d \tag{241}$$

As the final result of the dimensional regularization procedure, the following expressions are obtained:

$$\langle h^2 \rangle \Big|_{dim,reg.} = d \cdot S \left[1 - z \frac{-1}{(2 - d/2)(3 - d/2)} - y(a_d b'_d - b_d) \right],$$
 (242)

$$\left\langle R^2 \right\rangle \Big|_{dim.reg.} = \frac{d \cdot S}{6} \left[1 - zA'_d - yB'_d \right], \tag{243}$$

Hence, Equations 230-232 (the cut-off version) are seen to be completely equivalent (at $x_0 \rightarrow 0$) to Equations 242 and 243 (the dimensional regularization method).

Extension of the virial expansion (Equation 5.4 41) up to the third term has the form (Duplantier, 1986b)

$$\frac{\pi}{kT} = c_p - \frac{c_p^2}{2} \frac{Z(S,S)}{[Z(S)]^2} - \frac{c_p^3}{3} \left\{ \frac{Z(S,S,S)}{[Z(S)]^3} - 3 \frac{[Z(S,S)]^2}{[Z(S)]^4} \right\} + \cdots$$
(244)

The dimensionless virial coefficients are determined from the expansion

$$\frac{\pi}{kTc_p} - 1 + (2\pi)^{d/2} \frac{g}{2} c_p \left\langle \frac{h^2}{d} \right\rangle^{d/2} + (2\pi)^d \frac{\mathbf{h}}{3} c_p^2 \left\langle \frac{h^2}{d} \right\rangle^d + \cdots, \qquad (245)$$

where g is the dimensionless second virial coefficient

$$g = g(y, z, \varepsilon) = -\left(2\pi \left\langle \frac{h^2}{d} \right\rangle \right)^{-d/2} \frac{Z(S, S, b, c, \varepsilon)}{[Z(S, S, b, c, \varepsilon)]^2}$$
(246)

and h is the dimensionless third virial coefficient

$$\mathbf{h} = \mathbf{h}(y, z, \varepsilon) = -\left(2\pi \left\langle \frac{h^2}{d} \right\rangle\right)^{-d} \left\{ \frac{Z(S, S, S, b, \mathbf{c}, \varepsilon)}{[Z(S, b, \mathbf{c}, \varepsilon)]^3} - 3\frac{[Z(S, S, b, \mathbf{c}, \varepsilon)]^2}{[Z(S, b, \mathbf{c}, \varepsilon)]^4} \right\}$$
(247)
$$= -\left(2\pi \left\langle \frac{h^2}{d} \right\rangle\right)^{-d} \frac{Z(S, S, S, b, \mathbf{c}, \varepsilon)}{[Z(S, b, \mathbf{c}, \varepsilon)]^3} + 3g^2.$$

Figure 5.47 presents the diagram of the two-chain connected distribution function $Z(S, S, b, c, \varepsilon)$ proportional to the second virial coefficient.

In the cut-off version (Duplantier, 1987),

$$Z(S,S) = -bS^2 - 2\mathbf{c}S^{3-d/2}(2\pi)^{-d/2} \left[-\frac{x_0^{1-d/2}}{1-d/2} + \frac{1}{(1+d/2)(2-d/2)} + \frac{x_0^{2-d/2}}{2-d/2} \right]$$
(248)

or, in the notation with z and y,

$$(2\pi S)^{-d/2}Z(S,S) = -z - 2yf(x_0), \tag{249}$$

where

$$f(x_0) = -\frac{x_0^{1-d/2}}{1-d/2} + \frac{1}{(1-d/2)(2-d/2)} + \frac{x_0^{2-d/2}}{2-d/2}.$$
(250)



Figure 5.47. First-order diagram reflecting the contribution to the two-chain connected distribution function Z(S, S) proportional to the second virial coefficient A_2 (Duplantier, 1987) [Reprinted with permission from: B.Duplantier, J. Chem. Phys. 86 (1987) 4233-4244. Copyright © 1987 American Institute of Physics]

The effective theta point $\theta(S)$ of chains with a finite size S is defined by

$$Z(S,S) = 0,$$
 (251)

i.e.

$$z[\theta(S)] = -2yf(x_0). \tag{252}$$

The θ point of infinitely long chains is defined by an asymptotic expression for $f(x_0)$, i.e. $f_{\infty}(x_0)$ in the limit $x_0 = s_0/S \to 0$.

It follows from Equation 250 that

$$f_{\infty}(x_0) = -\frac{x_0^{1-d/2}}{1-d/2},\tag{253}$$

$$z[\theta(\infty)] = -2y f_{\infty}(x_0), \qquad (254)$$

and from Equations 214, 213, and 250 that

$$b[\theta(S)] = -2\mathbf{c}(2\pi)^{-d/2} s_0^{1-d/2} \left[-\frac{1}{1-d/2} + \frac{x_0^{d/2-1}}{(1-d/2)(2-d/2)} + \frac{x_0}{2-d/2} \right], \quad (255)$$

$$b[\theta(\infty)] = -2\mathbf{c}(2\pi)^{-d/2} s_0^{1-d/2} \left(-\frac{1}{1-d/2}\right).$$
(256)

Thus, the pair interaction parameter at the tricritical point $\theta(\infty)$ has a finite value which is exclusively dependent on the cut-off s_0 . Besides, for finite chains

$$b[\theta(S)] = b[\theta(\infty)] - 2\mathbf{c}(2\pi)^{-d/2} \frac{S^{-[d/2-1]}}{(1-d/2)(2-d/2)} + O(S^{-1}).$$
(257)

In particular, at d = 3 this shift corresponds to $S^{-1/2}$ in the mean field approximation and to $S^{-1/2}(\ln S)^{-3/22}$ in the next order of renormalization theory (cf. Equation 128). The distribution function Z(S, S) is also calculated by the dimensional regularization method

$$Z(S,S)|_{dim,reg.} = -bS^2 - \mathbf{c}S^{3-d/2}(2\pi)^{-d/2}\frac{1}{(1-d/2)(2-d/2)}.$$
(258)

It is seen that this equation differs from Equation 248 by the absence of cut-off dependent terms. Further, Duplantier finds expressions for $\langle h^2 \rangle$ and $\langle R^2 \rangle$ near the tricritical point $\theta(\infty)$ by replacement of z by

$$z - z[\theta(\infty)] - 2y f_{\infty}(x_0) \tag{259}$$

in Equations 230 and 233:

$$\left\langle h^2 \right\rangle = d \cdot S \left(1 - \left\{ z - z[\theta(\infty)] \right\} g(x_0) - y \left[\mathbf{h}(x_0) - 2f_\infty(x_0)g(x_0) \right] \right),$$
 (260)

$$\left\langle R^2 \right\rangle = \frac{d \cdot S}{6} \left(1 - \left\{ z - z[\theta(\infty)] \right\} g_G(x_0) - y \left[h_G(x_0) - 2f_\infty(x_0)g(x_0) \right] \right)$$
 (261)

An important result

$$\mathbf{h}(x_0) - 2f_{\infty}(x_0)g(x_0) = B + O(x_0^{2-d/2})$$
(262)

emerges while using general expressions 238 and 239.

Therefore, in the function **h**, both the diverging term of order $x_0^{1-d/2}$ and the "dangerous" regular term of order x_0^{3-d} are subtracted by $f_{\infty}(x_0)$. We see that this is not a coincidence: it is intimately related to the general form of the functions g and **h** (Equations 238 and 239) and it applies to $\langle h^2 \rangle$ and $\langle R^2 \rangle$ (and actually also to all other physical quantities). Having applied Equations 240 and 241 to Equations 238 and 262, Duplantier has found for $\langle h^2 \rangle$ (see Equation 260)

$$\left\langle h^2 \right\rangle = d \cdot S \left(1 - \left\{ z - z [\theta(\infty)] \right\} \left[-\frac{1}{(2 - d/2)(3 - d/2)} + O(x_0^{2 - d/2}) \right]$$

$$- y \left[a_d b'_d - b_d + O(x_0^{2 - d/2}) \right] \right),$$

$$(263)$$

and for $\langle R^2 \rangle$ (see Equation 261)

$$\left\langle R^{2} \right\rangle = \frac{d \cdot S}{6} \left(1 - \left\{ z - z[\theta(\infty)] \right\} \left[A'_{d} + O(x_{0}^{2-d/2}) \right] - y \left[B'_{d} + O(x_{0}^{2-d/2}) \right] \right).$$
(264)

When 2 < d < 4, $x_0^{2-d/2} \rightarrow 0$ for $x_0 \rightarrow 0$. In this limit of the expression from the cut-off version, Equations 263 and 264 fully coincide with Equations 242 and 243 from the dimensional regularization version provided that the quantity z from dimensional regularization is identified as $z - z[\theta(\infty)]$ in the cut-off version.

Thus, the dimensional regularization method provides an effective way of automatic subtraction in all the orders, which was performed in the vicinity of the tricritical point by Duplantier (1986bd).

Correspondingly, the expressions for $\langle h^2 \rangle$ and $\langle R^2 \rangle$ can be obtained for the proximity of the effective $\theta(S)$ point defined by Equations 250 and 252. A trivial replacement $z \rightarrow z - z[\theta(S)] - 2yf(x_0)$ enables one to derive

$$\left\langle h^2 \right\rangle = d \cdot S \left(1 - \left\{ z - z[\theta(S)] \right\} \left[-\frac{1}{(2 - d/2)(3 - d/2)} + O(x_0^{2 - d/2}) \right]$$

$$- y \left[a_d b'_d - b_d + \frac{2}{(3 - d/2)(2 - d/2)^2(1 - d/2)} + O(x_0^{2 - d/2}) \right] \right),$$

$$\left\langle R^2 \right\rangle = \frac{d \cdot S}{6} \left(1 - \left\{ z - z[\theta(S)] \right\} \left[A'_d + O(x_0^{2 - d/2}) \right]$$

$$- y \left[B'_d - 2 \frac{A'_d}{(1 - d/2)(2 - d/2)} + O(x_0^{2 - d/2}) \right] \right).$$

$$(265)$$

In comparison with Equations 263 and 264, these equations differ with respect to the coefficients at the y-containing term due to a shift of the reference point z.

Certainly, the last expressions can be obtained with respect to the finite θ point by means of the direct dimensional renormalization as well when the θ point of linite chains results from the equality Z(S, S) = 0 in the dimensionally regularized expression 258, whence

$$z[\theta(S)]|_{dim.reg.} = -2y \frac{1}{(1-d/2)(2-d/2)}$$
(267)

and corresponds to the finite part of $f(x_0)$ in Equations 250 and 252.

The finite component of $f_{\infty}(x_0)$ (Equation 253) vanishes. Hence,

$$z[\theta(\infty)]_{dim,reg.} = 0 \tag{268}$$

is accordance with the essence of dimensional regularization, i.e. automatic subtraction of $\theta(\infty)$.

Subtraction of $z[\theta(S)]$ (see Equation 267) in Equations 244 and 245 (the dimensional regularization) immediately yields

$$\left\langle h^2 \right\rangle |_{dim,reg.} = d \cdot S \left(1 - \left\{ z - z[\theta(S)] \right\} \left[-\frac{1}{(2 - d/2)(3 - d/2)} \right]$$

$$- y \left[a_d b'_d - b_d + \frac{2}{(3 - d/2)(2 - d/2)^2(1 - d/2)} \right] \right),$$

$$\left\langle R^2 \right\rangle |_{dim,reg.} = \frac{d \cdot S}{6} \left(1 - \left\{ z - z[\theta(S)] \right\} A'_d - y \left[B'_d - 2\frac{A'_d}{(1 - d/2)(2 - d/2)} \right] \right).$$

$$(269)$$

These agree with Equations 265 and 266 at $x_0 = 0$.

Thus, the direct renormalization version produces the same results as does the cut-off version. All the divergent and finite components, which explicitly reduce in the cut-off version, simply do not emerge in the direct renormalization method. These operations are performed automatically during the analytical passing from d < 2 to $2 < d \leq 3$.

In 3D space, the constants in Equations 219, 221, and 220 have their values

$$b_3 = 4\pi, \quad a_3 = -\frac{16}{3}, \quad b'_3 = -\frac{3\pi}{2};$$
 (271)

in Equations 236 and 237

$$A'_3 = -\frac{134}{103}, \quad B'_3 = B_3 - b_3 = \frac{13\pi}{4}.$$
 (272)

Substituting these values to Equations 230-233 (the cut-off version) we get for 3D space

$$\left\langle h^2 \right\rangle = 3S \left\{ 1 + z \left(\frac{4}{3} - 2x_0^{1/2} + \frac{2}{3}x_0^{3/2} \right) + y \left[\frac{16}{3}x_0^{-1/2} - 4\pi - 8 + O(x_0^{1/2}) \right] \right\},$$
 (273)

$$\left\langle R^2 \right\rangle = \frac{S}{2} \left\{ 1 + z \left[\frac{134}{105} - 2x_0^{1/2} + O(x_0^{3/2}) \right] + y \left[\frac{4 \cdot 134}{105} x_0^{-1/2} - \frac{13\pi}{4} - 8 + O(x_0^{1/2}) \right] \right\}.$$
(274)

If z is measured with reference to the tricritical point $z[\theta(\infty)]$, then it follows from Equations 273 and 274 that

$$\left\langle h^2 \right\rangle = 3S \left(1 + \frac{4}{3} \left\{ z - z[\theta(\infty)] \right\} - 4\pi y \right), \tag{275}$$

$$\left\langle R^2 \right\rangle = \frac{S}{2} \left(1 + \frac{134}{105} \left\{ z - z[\theta(\infty)] \right\} - \frac{13}{4} \pi y \right).$$
 (276)

All the terms with x_0^0 cancel, and a result is obtained, fitting closely the direct renormalization version.

If z is measured with reference to the effective θ point, then we get from Equations 265 and 266

$$\langle h^2 \rangle = 3S \left(1 + \{ z - z[\theta(\infty)] \} \left[\frac{4}{3} - 2x_0^{1/2} + O(x_0^{3/2}) \right] \right)$$

$$- y \left[4\pi - \frac{32}{3} + O(x_0^{1/2}) \right] ,$$

$$\langle R^2 \rangle = \frac{S}{2} \left(1 + \{ z - z[\theta(S)] \} \left[\frac{134}{105} - 2x_0^{1/2} + O(x_0^{3/2}) \right] \right)$$

$$+ y \left[-\frac{13\pi}{4} + 8\frac{134}{105} + O(x_0^{1/2}) \right]).$$

$$(277)$$

In connection with consideration of the tricritical effects, the question arises of the conformation of a polymer chain at the tricritical point.

For simplicity, introduce a designation z' for a parameter shift

$$z' = z - z[\theta(\infty)]. \tag{279}$$

Thus, $z' \equiv 0$ for the θ point of infinitely long chains. For S-sized chains, the effective θ point (where $A_2 = 0$) in 3D space is given according to Equation 267

$$z'[\theta(S)] = 8y. \tag{280}$$

Then, the first-order result in the cut-off version at d = 3 and $x_0 \rightarrow 0$, according to Equations 275 and 276, has the form

$$\left\langle h^2 \right\rangle_{tc} = 3S \left(1 + \frac{4}{3}z' - 4\pi y \right), \tag{281}$$

$$\left\langle R^2 \right\rangle_{tc} = \frac{S}{2} \left(1 + \frac{134}{105} z' - \frac{13}{4} \pi y \right).$$
 (282)

Thus, at the θ point of infinite chains (z' = 0), the mean square end-to-end distance is smaller than its Brownian sizes 3S; the square radius of gyration is also less than its Brownian value S/2.

This contraction effect in the first order of y is somewhat weaker for $\langle R^2 \rangle$ than for $\langle h^2 \rangle$. According to the definition, $\langle R^2 \rangle$ (see Equation 205) is more sensitive to the coil state at short distances, where the three-body repulsion interactions are likely to predominate over the two-body attraction interactions, which was pointed out by Khokhlov (1977).

The same conclusion follows for the effective θ point of finite chains (Equation 280) in the first order. Indeed, it follows from Equations 281 and 282 that

$$\left\langle h^2 \right\rangle \Big|_{\theta(S)} = 3S \left[1 + \left(-4\pi + \frac{32}{3} \right) y \right] < 3S, \tag{283}$$

$$\left\langle R^2 \right\rangle \Big|_{\theta(S)} = \frac{S}{2} \left[1 + \left(-\frac{13\pi}{4} + \frac{134}{105} 8 \right) y \right] \simeq \frac{S}{2} (1 - 0.00065y).$$
 (284)

The above results are valid in the first order only. For long chains, the next-order terms turn out to be significant due to the tricritical effects, and the renormalization methods are needed to reveal the chief (logarithmic) divergences in all the orders.

By the cut-off methods of field theory (Duplantier, 1982) (see the beginning of section 5.5) and the direct renormalization (Duplantier, 1986bd) for the continuous chain model (Equation 201), it was obtained that

$$\left\langle h^{2} \right\rangle = 3S \left\{ A_{0}(y) \left(1 - \frac{148}{33} \pi \mathbf{h} \right) + \frac{4}{3} z' \left(\frac{\mathbf{h}}{y} \right)^{4/11} A_{4}(y) \right\},$$
 (285)

$$\left\langle R^2 \right\rangle = \frac{S}{2} \left\{ A_0(y) \left(1 - \frac{493}{33 \cdot 4} \pi \mathbf{h} \right) + \frac{134}{105} z' \left(\frac{\mathbf{h}}{y} \right)^{4/11} A_4(y) \right\},$$
 (286)

where $A_0(y)$ and $A_4(y)$ are regular functions of y:

$$A_0(y) = 1 + \frac{16}{33}\pi y + \cdots, \qquad A_4(0) = 1.$$
 (287)

The parameter h is the renormalized term of the three-body interactions

$$\mathbf{h} = \frac{y}{1 + 44y\pi\ln(S/s_0)}.$$
(288)

For small y, i.e. for extremely weak three-body interactions or short chains, a simple linear approximation results

$$\mathbf{h} = \mathbf{y},\tag{289}$$

and renormalized expressions 285-287 reduce to linear Equations 281-282. Otherwise, i.e. for long chains, the h attains its universal value

$$\mathbf{h} = \frac{1}{44\pi \ln(S/s_0)}.$$
(290)

In the limit of infinitely long chains, $\mathbf{h} \to 0$ and, at the corresponding θ point (z' = 0), Equations 285 and 286 lead to

$$\left\langle h^2 \right\rangle = 3SA_0(y) - 3S\left(1 + \frac{16}{33}\pi y + \cdots\right),$$
(291)

$$\left\langle R^2 \right\rangle = \frac{S}{2} A_0(y), \tag{292}$$

which show residual swelling $A_0(y) > 1$ dependent on fine details of the interaction y. Of course, such residual swelling cannot be fixed experimentally, and it depends on the details of the chosen model.

Nevertheless, of interest is comparison of the residual swelling as given by renormalization theory with the residual contraction $\langle h^2 \rangle$ in the linear approximation of the theory (see Equation 281).

The residual effects of the three-body interactions on $\langle h^2 \rangle$ lead to opposite contributions with respect to the Brownian value $\langle h^2 \rangle_{br} = 3S$, cf. Equations 281 and 291, and they correspond to the short and long chains.

This situation is sketched in Figure 5.48 for a fixed three-body interaction y.

At any temperature different from $\theta(\infty)$, the tricritical effects are associated with the temperature-dependent term $z'(\mathbf{h}/y)^{4/11}$ (see Equations 285 and 286). For long chains, the **h**, in accordance with Equation 290, may turn out to be substantially lower than y, and the tricritical behaviour term $(\mathbf{h}/y)^{4/11}$ can obviously be fixed experimentally (Duplantier et al., 1989).

Data on light scattering from PS solutions ($M_w = 1,260,000$) in cyclohexane (Perzynski, 1984) are interpreted in (Duplantier, 1989).

To compare experimental results with theory, first, the quantities b, c, and h should be determined. The parameter b has been obtained from coil swelling data at a temperature above θ as against the theoretical curve of swelling (des Cloizeaux et al., 1985)

$$b = 2.918 - \frac{896K}{T} \,\mathrm{nm^{-1}}.$$
(293)



Figure 5.48. Schematic of the change in the chain sizes $X_0 = \langle h^2 \rangle / 3S$ and $X = 2 \langle R^2 \rangle / S$ at the tricritical point $\theta(\infty)$ as functions of the parameter $\mathbf{h} = [44\pi \ln(S/s_0)]^{-1}$. $\mathbf{h} = 0$ and $\mathbf{h} = y$ correspond to infinitely long chains and the linear theory (short chains), respectively (Duplantier, 1987) [Reprinted with permission from: B.Duplantier, J. Chem. Phys. 86 (1987) 4233-4244. Copyright © 1987 American Institute of Physics]

This means that b = 0 at $T = \theta = 34^{\circ}$ C in accordance with the definition of θ ($\theta = T_c$ at $S \to \infty$). Then, the dependence $T_c = f(M)$ is determined by Flory-Huggins' theory and the experimental data of Perzynski (1984)

$$\frac{10^3}{T_c} = 3.257 + \frac{47}{\sqrt{M}}.$$
(294)

It follows from comparison of Equations 293 and 294 that

$$b_c = -\frac{42}{\sqrt{M}}.\tag{295}$$

The relation of c with b_c ,

$$\mathbf{c} = \frac{b_c^2 S}{4} \tag{296}$$

(cf. Equation 3.1-314), results from the condition of the critical point

$$rac{\partial \pi}{\partial c_p} = 0 \qquad ext{and} \qquad rac{\partial^2 \pi}{\partial c_p^2} = 0$$

and a rough approximation of the virial expansion

$$\frac{\pi}{kT} = c_p + \frac{1}{2}bS^2c_p^2 + \frac{1}{3}cS^3c_p^3.$$
(297)

Then, $S/s_0 = N$ is accepted, where N is the number of monomers in a coil and s_0 is the area corresponding to the monomer sizes.

Moreover,

$$S = 2 \langle \Lambda \rangle M, \tag{298}$$

where $\langle \Lambda \rangle = 8.3 \cdot 10^{-4} \text{ nm}^2/\text{dalton for PS}$.

According to Equations 213 and 214,

$$z = bS^{1/2}(2\pi)^{-3/2}, \quad y = c(2\pi)^{-3}$$
(299)

and for PS in cyclohexane

$$\mathbf{c} = 0.73, \quad y = 0.0029.$$
 (300)

For the specific sample of PS $M_w = 1.26 \cdot 10^6$, $S = 2090 \text{ nm}^2$, $S/s_0 = M_w/M_0 = 1.21 \cdot 10^4$, According to Equation 290,

$$\mathbf{h} = 7.7 \cdot 10^{-4}.\tag{301}$$

Using z, y, and h, Duplantier et al. (1989) calculated theoretical dependences

$$X_{0,L} = \frac{\langle h^2 \rangle}{3S} = 1 - 4\pi y + \frac{4}{3}z$$
(302)

(the linear approximation of the tricritical effects, see Equation 281);

$$X_{0} = \frac{\langle h^{2} \rangle}{A_{0}(y)3S} = 1 - \frac{148}{33}\pi \mathbf{h} + \frac{4}{3}z \left(\frac{\mathbf{h}}{y}\right)^{4/11}$$
(303)

(the renormalized relationship of theory, see Equation 285).

It is assumed that

$$\frac{A_4(y)}{A_0(y)} \simeq \frac{A_4(0)}{A_0(0)} = 1$$

These theoretical dependences are also compared with the corresponding expression in Flory's approximation with allowance for the ternary interactions (de Gennes, 1975)

$$X_{0,F}^{5/2} - X_{0,F}^{3/2} = \frac{1}{3} 3^{3/2} z + 3^{1/2} 8 y X_{0,F}^{-3/2}$$
(304)

(cf. the formula for pair interactions in the same notation, Equation 5.4-138). The calculated theoretical dependences are presented in Figure 5.49 and compared with experimental values $X = \langle R^2 \rangle / \langle R^2(T_1) \rangle$, where $T_1 = 35^{\circ}$ C is the reference temperature chosen near $\theta = 34^{\circ}$ C.

First, let us discuss the temperature $T_{X_0}(S)$ at which no swelling occurs (X = 1). For infinite chains, this temperature corresponds to Flory's temperature $T_{X_0}(S \to \infty) = \theta = 34^{\circ}$ C.

With a finite MM, Flory's approximation yields $T_{X_0}(S) < \theta$ (see Figure 5.49). In the continuous chain model, $T_{X_0}(S) > \theta$ with a finite S. For the given PS sample, $T_{X_0}(S) - \theta = 1^{\circ}C$ (the linear approximation) and $T_{X_0}(S) - \theta = 0.5^{\circ}C$ (renormalization theory).

The most important results, shown in Figure 5.49, is in agreement between the theoretical curves (involving the tricritical effects) and the experimental values of the related quantity X.

For the theoretical curves, T_1 , at which experiment gives X = 1, is chosen as the reference temperature. After normalization, the line X_0 shifts towards T_1 by 0.5° while $X_{0,L}$ does not shift (0°). The best fit to experiment is achieved when the tricritical effects in the version with renormalization of X_0 are taken into account.



Figure 5.49. Temperature dependence of the swelling factor X_0 as given by the linear approximation of the tricritical effects $X_{0,L}$, by renormalization theory X_0 , and by Flory's approximation $X_{0,F}$: the crosses are the experimental values from light scattering of PS solutions in cyclohexane (Perzynski, 1984); the dashed line is the theoretical curve after a shift of X_0 to the right to obtain $X_0 = X = 1$ at the same temperature ($T_1 = 35^{\circ}$ C) (Duplantier et al., 1989) [Reprinted with permission from: B.Duplantier, G.Jannink, J. des Cloizeaux. Phys. Rev. Lett. **56** (1986) 2080-2083. Copyright © 1986 by the Anmerican Physical Society]

It goes without saying that it is more correct to compare the theoretical dependences deduced for the square radius of gyration with these experimental values. In the linear approximation (see Equation 282)

$$X_L = \frac{\langle R^2 \rangle}{\langle R^2(T_1) \rangle} = 1 + \frac{134}{105}(z - z_1).$$
(305)

For the renormalization version (see Equation 286),

$$X = 1 + \frac{134}{105} \left(\frac{\mathbf{h}}{y}\right)^{4/11} (z - z_1), \tag{306}$$

where z_1 relates to $T_1 = 35^{\circ}$ C (Figure 5.50).

One can note the closeness between 4/3=1.333 (see Equations 302 and 303) and 134/105 = 1.2762 (see Equations 305 and 306).

Thus, the chief results of the papers under consideration is experimental detection of the renormalization of the coefficient z to X (or X_0) by the tricritical factor $(h/y)^{4/11} \simeq 0.62$.

As Duplantier et al. (1989) conclude on the basis of Duplantier's theory discussed above, the validity range of the tricritical state theory (tricritical theory) is near θ

$$|z| \le \mathbf{h}^{1/2} \left(\frac{y}{\mathbf{h}}\right)^{4/11} const \tag{307}$$



Figure 5.50. X values normalized to 1 at $T_1 = 308$ K: the crosses stand for experimental values, the straight lines stand for theory (Duplantier et al., 1986) [Reprinted with permission from: B.Duplantier, G.Jannink, J. des Cloizeaux. Phys. Rev. Lett. 56 (1986) 2080-2083. Copyright © 1986 by the Anmerican Physical Society]

In this case, $|z| \leq 0.045 \cdot const$. The constant in Equation 307 is not known exactly but is assumed to be ~ 1 , i.e. the tricritical range is

$$305 \,\mathrm{K} < T \leq \theta$$
.

Indeed, it is over this range that the best fit of the tricritical theory to experiment is observed $(303 \text{ K} < T \leq \theta)$. It is interesting that 303 K is the temperature of the boundary of the phase separation region for a given PS sample. Below 303 K, a more sharp decrease in the experimental values of coil size is observed, but not so drastic as Flory's approximation predicts.

In agreement with the state diagram (Figure 5.45), Perzynski et al. (1982, 1987) experimentally fixed the θ region. The expansion factor of PS coils in cyclohexane

$$\alpha_H(T) = \left[\frac{\langle R_H(T) \rangle}{\langle R_H(\theta) \rangle}\right]_{c=0},\tag{308}$$

as dependent on $\tau\sqrt{M}$, changes linearly on both the sides of θ in the range $|\tau\sqrt{M}| < 10$.

Using light scattering data (PS solutions in cyclohexane at $T < 35^{\circ}$ C), $\partial \pi / \partial c$ has been found to be proportional to c in the range of dilute solutions (eg. see Equation 3.1–297).

In the θ region, \mathcal{A}_2 does not depend on M_w and is proportional to τ for both $T \geq \theta$ and $T \leq \theta$, given $|\tau| \leq 2 \cdot 10^{-2}$. This agrees with the predictions of the mean field theory, viz. that \mathcal{A}_2 is proportional to the segment excluded volume β (see Equation 3.1-146) or v (see Equation 3.1-52,-300). It follows from the experimental data for \mathcal{A}_2 (Perzynski et al., 1987) that (see Equations 3.1-297, 301)

$$\mathcal{A}_2 = \frac{\mathbf{v}\psi^2}{\mathbf{c}^2 N_A} = 5 \cdot 10^{-3} \tau \text{ cm}^3 \text{mol/g}^2.$$
(309)

In a semidilute solution at the θ temperature, $\partial \pi/\partial c$ is proportional to c^2 (or ψ^2) (see Equations 3.1–297,-301) with the proportionality factor being the three-body interaction M_w -independent parameter (Perzynski, 1984; Perzynski et al., 1987)

$$\frac{\mathbf{w}\psi^3}{\mathbf{c}^3 N_A} = 1.25 \cdot 10^{-3} \,\mathrm{cm}^6 \mathrm{mol/g}^3. \tag{310}$$

From this quantity w, the ternary interaction parameter y (see Equation 299) has a value $\approx 10^{-2}$.

Substitution of the experimental values (Equations 309 and 310) to the formulae of the mean field theory (Equations 3.1–313,-317,-320) leads to

$$\tau_c = -\frac{14}{\sqrt{M_w}},\tag{311}$$

$$c_c = \frac{28}{\sqrt{M_w}} \,\mathrm{g/cm^3},\tag{312}$$

$$\frac{1}{M_w} \ln\left(-\frac{c_I}{6\tau_I}\right) = -7.5 \cdot 10^{-3} \tau_I^2.$$
(313)

Perzynski et al. (1987) also analyze the data of Koningsveld et al. (1970b), Saeki et al. (1973a), Derham et al. (1974), Strazielle and Benoit (1975), Nakata et al. (1978), which are presented in Figure 5.51.

Experimental data (see Figure 5.51a) obey the straight line equation

$$\frac{10^3}{T_c(K)} = 3.256 \left[1 + \frac{14.6 \pm 0.2}{\sqrt{M_w}} \right],\tag{314}$$

in good agreement with theory (Equation 311).

Experimental data (see Figure 5.51b) obey the dependence

$$c_{\rm c} = 6.8 M_w^{-0.38 \pm 0.01} \,{\rm g/cm^3},\tag{315}$$

which differs from the predictions of the mean field theory (Equation 312) (the dashed line in Figure 5.51b).

This difference is explained by a stronger manifestation of the tricritical effects in $c_c = f(M_w)$ than on $T_c = f(M_w)$.

Under Duplantier's (1982) theory, the tricritical corrections correspond to the expressions (Perzynski et al., 1987)

$$\tau_c \sim N^{-1/2} (\ln N)^{-3/2},$$
(316)

$$c_c \sim N^{-1/2} (\ln N)^{1/2}.$$
 (317)

Experimental data (Perzynski et al., 1987) on c_I , $\tau_I(T_{\Phi})$, and M_w do not obey the mean field universal dependence (Equation 313). One should note that Equation 313 was derived from very rough assumptions (see Equations 3.1-306...320).

It follows from experimental data (Perzynski et al., 1987) that the reduced parameter for the binodal is $\varepsilon M_w^{0.31}$, where $\varepsilon = (T_c - T)/T_c$ (Figures 5.52 and 5.53).


Figure 5.51. Dependence of T_c^{-1} vs $M_w^{-1/2}$ for the system PS+cyclohexane on evidence of Koningsveld et al. (1970b), Saeki et al. (1973a), Derham et al. (1974), Strazielle and Benoit (1975), Nakata et al. (1978) (a); dependence of c_c vs M_w (b); the solid line corresponds to Equation 5.5-315, the dashed line corresponds to Equation 5.5-312 (Perzynski et al., 1987) [Reprinted with permission from: R.Perzynski, M.Delsanti, M.Adam. J. de Phys. 48 (1987) 115-124. Copyright © 1987 by EDP Sciences]

5.6. Direct evaluation of the order parameter fluctuations

A more general version of the theory of P+LMWL systems, which expresses the Gibbs potential of mixing with due account of the order parameter's fluctuations (the concentration of polymer segments) has been put forward by Muthukumar (1986) on the basis of Edwards' (1965, 1966) formalism and their mutual paper (1982) (see Equations 5.1-246...268).



Figure 5.52. Dependence $\varepsilon = (T_c - T_{\Phi})/T_c$ vs M_w for $c_I/c_c = 3.2 \cdot 10^{-3}$ in the logarithmic scale for the system PS+cyclohexane. The straight line corresponds to $\varepsilon = 1.1 \cdot M_w^{-(0.32\pm0.04)}$ (Perzynski et al., 1987) [Reprinted with permission from: R.Perzynski, M.Delsanti, M.Adam. J. de Phys. 48 (1987) 115–124. Copyright © 1987 by EDP Sciences]



Figure 5.53. Semilogarithmic dependence of c_I/c_c vs $\in M_w^{0.31}$. Different signs relate to polymer fractions (Perzynski et al., 1987) [Reprinted with permission from: R.Perzynski, M.Delsanti, M.Adam. J. de Phys. **48** (1987) 115–124. Copyright © 1987 by EDP Sciences]

Let us consider a P+LMWL system containing n chains of length L = Nl and N_S molecules of LMWL in the volume V.

In the mean field approximation and in view of the ternary interactions, the Gibbs potential of mixing is written in the form

$$\frac{\Delta G_{\rm FH}}{kT} = \frac{\Phi}{N}\ln\Phi + (1-\Phi)\ln(1-\Phi) + \chi\Phi(1-\Phi) + \left(w - \frac{1}{6}\right)\Phi^3,\tag{1}$$

where Φ is the volume fraction of the polymer (= Nnl^3/V) (cf. Equation 3.1-32, -303).

As the second virial coefficient of the osmotic pressure expansion, the quantity $(1/2 - \chi)$ is accepted here, while the difference between the characteristic parameter of the ternary interactions w and the trivial factor 1/6 acts as the third virial coefficient (see

Equation 3.1-303).

The correction to Equation 1 due to the fluctuations in the order parameter must have the form

$$\frac{\Delta G'}{kT} = -\ln \int D[\vec{R}_{\alpha}] P\left(\left\{\vec{R}_{\alpha}\right\}\right)$$
(2)

(see Equation 5.1-247), where

$$\ln P\left(\left\{\vec{R}_{\alpha}\right\}\right) = -\frac{3}{2l} \sum_{\alpha=1}^{n} \int_{0}^{L} ds_{\alpha} \left(\frac{\partial \vec{R}_{\alpha}(s_{\alpha})}{\partial s_{\alpha}}\right)^{2} - \frac{l}{2} \left(\frac{1}{2} - \chi\right)$$
(3)

$$\times \sum_{\alpha} \sum_{\beta} \int_{0}^{L} ds_{\alpha} \int_{0}^{L} ds_{\beta} \delta \left[\vec{R}_{\alpha}(s_{\alpha}) - \vec{R}_{\beta}(s_{\beta}) \right] - \frac{l^{3}w}{2} \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \int_{0}^{L} ds_{\alpha}$$
$$\times \int_{0}^{L} ds_{\beta} \int_{0}^{L} ds_{\gamma} \delta \left[\vec{R}_{\alpha}(s_{\alpha}) - \vec{R}_{\beta}(s_{\beta}) \right] \delta \left[\vec{R}_{\alpha}(s_{\alpha}) - \vec{R}_{\gamma}(s_{\gamma}) \right]$$

The functional integral $\int D[\vec{R}_{\alpha}]$ in Equation 2 corresponds to the summation over all the chain conformations regardless of how the polymer chains are packed in the volume, which is considered by state equation 1.

The quantity $(1/2 - \chi)l^3$ is an averaged binary cluster integral. Correspondingly, wl^6 is an averaged ternary cluster integral for three segments (cf. Equations 1.8-9, 10 and 3.1-52,-300).

In this approach, both χ and w are considered temperature-dependent. Below the θ temperature, $(1/2 - \chi) < 0$ and w is positive and sufficiently large in magnitude (cf. Figure 1.41, where the temperature dependences of the second and third virial coefficients for real gas are compared).

In this version of theory, Muthukumar suggests the possibility of replacing the ternary contact term in Equation 3 by the effective pair interaction term

$$\sum_{\alpha} \sum_{\beta} \sum_{\gamma} \int_{0}^{L} ds_{\alpha} \int_{0}^{L} ds_{\beta} \int_{0}^{L} ds_{\gamma} \delta \left[\vec{R}_{\alpha}(s_{\alpha}) - \vec{R}_{\gamma}(s_{\gamma}) \right] \delta \left[\vec{R}_{\gamma}(s_{\gamma}) - \vec{R}_{\beta}(s_{\beta}) \right]$$
(4)
$$= \sum_{\alpha\beta\gamma} \int_{0}^{L} ds_{\alpha} \int_{0}^{L} ds_{\beta} \int_{0}^{L} ds_{\gamma} \int \frac{d^{3}k}{(2\pi)^{3}} \int \frac{d^{3}k'}{(2\pi)^{3}} \exp \left[i\vec{k}\vec{R}_{\alpha}(s_{\alpha}) - i\vec{k}'\vec{R}_{\beta}(s_{\beta}) - i(\vec{k} - \vec{k}')\vec{R}_{\gamma}(s_{\gamma}) \right]$$
$$\cong \sum_{\alpha} \sum_{\beta} \int_{0}^{L} ds_{\alpha} \int_{0}^{L} ds_{\beta} \int \frac{d^{3}k}{(2\pi)^{3}} \int \frac{d^{3}k'}{(2\pi)^{3}} \exp \left[i\vec{k}\vec{R}_{\alpha}(s_{\alpha}) - i\vec{k}'\vec{R}_{\beta}(s_{\beta}) \right]$$
$$\times \left\langle \sum_{\gamma} \int_{0}^{L} ds_{\gamma} \exp \left[-i(\vec{k} - \vec{k}')\vec{R}_{\gamma}(s_{\gamma}) \right] \right\rangle$$

$$= \rho l \sum_{\alpha} \sum_{\beta} \int_{0}^{L} ds_{\alpha} \int_{0}^{L} ds_{\beta} \, \delta \left[\vec{R}_{\alpha}(s_{\alpha}) - \vec{R}_{\beta}(s_{\beta}) \right],$$

where $\rho = N_n/V$ is the numerical concentration of segments.

So, the probability partition function can be simplified

$$\ln P\left(\left\{\vec{R}_{\alpha}\right\}\right) = -\frac{3}{2l} \sum_{\alpha=1}^{n} \int_{0}^{L} ds_{\alpha} \left(\frac{\partial \vec{R}_{\alpha}(s_{\alpha})}{\partial s_{\alpha}}\right)^{2} - \frac{lu}{2} \sum_{\alpha} \sum_{\beta} \int_{0}^{L} ds_{\alpha} \int_{0}^{L} ds_{\beta} \qquad (5)$$
$$\times \delta \left[\vec{R}_{\alpha}(s_{\alpha}) - \vec{R}_{\beta}(s_{\beta})\right],$$

where

$$u \equiv 1/2 - \chi + w\Phi. \tag{6}$$

Now, the partition function 5 is subjected to the same analysis as described by Muthukumar and Edwards (1982) (see Equations $5.1\ 246...268$).

The interaction term in Equation 5 describes the pair interaction between any two chains. Mathematically, it can be put into the behaviour of one chain placed in the field due to the presence of other chains (Edwards' formalism see subsection 5.1.2, Equations 5.1-191...195, 252). Then

$$P\left(\left\{\vec{R}\right\}\right) = \tag{7}$$

$$\frac{\int D[\Phi] \exp\left\{-\frac{3}{2l} \sum_{\alpha} \int_{0}^{L} ds_{\alpha} \left(\frac{\partial \vec{R}_{\alpha}(s_{\alpha})}{\partial s_{\alpha}}\right)^{2} - i \sum_{\alpha} \int_{0}^{L} ds_{\alpha} \Phi\left[\vec{R}_{\alpha}(s_{\alpha})\right] - \frac{1}{2ul} \int d\vec{r} \Phi^{2}(\vec{r})\right\}}{\int D[\Phi] \exp\left[-\frac{1}{2ul} \int d\vec{r} \Phi^{2}(\vec{r})\right]} = \int D[\Phi] P\left(\Phi, \left\{\vec{R}_{\alpha}\right\}\right).$$

The second term in the braces represents the interaction of the α th chain with the field while the third term is the field's Lagrangian. The denominator in Equation 7 is the normalizing factor.

This mathematical formalism implies consideration of disconnected chains placed in the field. As now there remains the sum over chains with the subscript α in Equation 7, one can write (see Equation 5.1–252)

$$P\left(\left\{\vec{R}_{\alpha}\right\}\right) = \frac{\int D[\Phi][G(\Phi)]^{n} \exp\left[-\frac{1}{2ul} \int d\vec{r} \,\Phi^{2}(\vec{r})\right]}{\int D[\Phi] \exp\left[-\frac{1}{2ul} \int d\vec{r} \,\Phi^{2}(\vec{r})\right]}$$
(8)
$$= \frac{n! \oint \frac{d\mu}{2\pi i} \exp\left[-(n+1)\ln\mu\right] \int D[\Phi] \exp\left[\mu G(\Phi) - \frac{1}{2ul} \int d\vec{r} \,\Phi^{2}(\vec{r})\right]}{\int D[\Phi] \exp\left[-\frac{1}{2ul} \int d\vec{r} \,\Phi^{2}(\vec{r})\right]},$$

where

$$G(\Phi) \equiv \exp\left\{-\frac{3}{2l}\int_{0}^{L} ds_{\alpha} \left(\frac{\partial \vec{R}_{\alpha}(s_{\alpha})}{\partial s_{\alpha}}\right)^{2} - i\int_{0}^{L} ds_{\alpha} \Phi\left[\vec{R}_{\alpha}(s_{\alpha})\right]\right\}$$
(9)

(cf. Equation 51-187).

The second equality in Equation 8 is obtained by parametrization $[G(\Phi)]^n$ (see section 5.1 and: Muthukumar and Edwards, 1982).

Calculation of the integrals in Equation 8 is obviously impossible in full. Hence, an effective partition function for a chosen chain has to be introduced. Muthukumar chooses such a function \bar{G} in terms of the variational principle.

The function \bar{G} describes the partition function of a chosen chain with a certain pair of its segments which interact through the field due to all the other chains. \bar{G} can, therefore, be written as

$$\bar{G} = \frac{\int D[\Phi]G(\Phi) \exp\left[\mu G(\Phi) - \frac{1}{2ul} \int d\vec{r} \, \Phi^2(\vec{r})\right]}{\int D[\Phi] \exp\left[\mu G(\Phi) - \frac{1}{2ul} \int d\vec{r} \, \Phi^2(\vec{r})\right]} =$$
(10)

$$= \exp\left\{-\frac{3}{2l}\int_{0}^{L} ds \left(\frac{\partial \vec{R}(s)}{\partial s}\right)^{2} - \frac{1}{2}\int_{0}^{L} ds \int_{0}^{L} ds' \Delta \left[\vec{R}(s) - \vec{R}(s')\right]\right\},\tag{11}$$

where Δ is an effective potential to be determined.

If the quantity $\mu \bar{G}$ is added to and subtracted from Equation 8, we get

$$P\left(\left\{\vec{R}_{\alpha}\right\}\right) =$$

$$= n! \oint \frac{d\mu}{2\pi i} \exp\left[-(n+1)\ln\mu + \mu\bar{G}\right] \int D[\Phi] \exp\left[\mu[G(\Phi) - \bar{G}] - \frac{1}{2ul} \int d\vec{r} \, \Phi^{2}(\vec{r})\right]$$

$$= n! \oint \frac{d\mu}{2\pi i} \exp\left[-(n+1)\ln\mu + \mu\bar{G}\right] \int D[\Phi] \exp\left[\mu[G(\Phi) - \bar{G}] - \frac{1}{2ul} \int d\vec{r} \, \Phi^{2}(\vec{r})\right]$$

$$= n! \oint \frac{d\mu}{2\pi i} \exp\left[-(n+1)\ln\mu + \mu\bar{G}\right] \int D[\Phi] \exp\left[\mu[G(\Phi) - \bar{G}] - \frac{1}{2ul} \int d\vec{r} \, \Phi^{2}(\vec{r})\right]$$

$$= n! \oint \frac{d\mu}{2\pi i} \exp\left[-(n+1)\ln\mu + \mu\bar{G}\right] \int D[\Phi] \exp\left[\mu[G(\Phi) - \bar{G}] - \frac{1}{2ul} \int d\vec{r} \, \Phi^{2}(\vec{r})\right]$$

$$= n! \oint \frac{d\mu}{2\pi i} \exp\left[-(n+1)\ln\mu + \mu\bar{G}\right] \int D[\Phi] \exp\left[\mu[G(\Phi) - \bar{G}] - \frac{1}{2ul} \int d\vec{r} \, \Phi^{2}(\vec{r})\right]$$

$$=\frac{n! \varphi \frac{1}{2\pi i} \exp\left[-(n+1)\ln\mu + \mu G\right] \int D[\Psi] \exp\left[\mu[G(\Psi) - G\right] - \frac{1}{2ul} \int d\vec{r} \Psi^{-}(\vec{r})\right]}{\int D[\Psi] \exp\left[-\frac{1}{2ul} \int d\vec{r} \Phi^{2}(\vec{r})\right]}.$$

The term $[G(\Phi)-\bar{G}]$ contains the fluctuations of the partition function about its effective partition function, and $\oint d\mu \exp(\mu \bar{G})$ contributes to the free energy of *n* effective chains.

Equation 11 is the rigorous equation while the approximation arises through the choice of \overline{G} . Redefinition of $\mu G(\Phi)$ through the unknown quantity Π gives

$$\mu G(\Phi) = \mu G(0) - \frac{1}{2ul} \int \frac{d^3k}{(2\pi)^3} \Phi_k \Pi_k \Phi_k,$$
(13)

where Φ_k is the Fourier transform $\Phi(\vec{r})$,

$$\Phi_k = \int d\vec{r} \,\Phi(\vec{r}) \exp(-i\vec{k}\vec{r}). \tag{14}$$

Equations 9 and 10 lead to

$$\ln \bar{G} = -\frac{3}{2l} \int_{0}^{L} ds \left(\frac{\partial \vec{R}(s)}{\partial s}\right)^{2} - \frac{ul}{2} \int_{0}^{L} ds \int_{0}^{L} ds' \int \frac{d^{3}k}{(2\pi)^{3}}$$
(15)

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$$imes (1+\Pi_k)^{-1} \exp\left(i \vec{k} \left[\vec{R}(s) - \vec{R}(s')
ight]
ight).$$

Comparison of Equation 15 with Equation 11 yields

$$\frac{1}{1+\Pi_k} = \Delta_k,\tag{16}$$

where Δ_k is the Fourier transform of the effective interaction $\Delta(\vec{r})$.

Indeed, Δ_k is the mean of Φ_k^2 :

$$\Delta_k = \left\langle \Phi_k^2 \right\rangle \tag{17}$$

taken over the field partition function.

From Equations 10, 13, and 17 we obtain

$$\mu \left[G(\Phi) - \dot{G} \right] = -\frac{1}{2ul} \int \frac{d^3k}{(2\pi)^3} \left(\Phi_k \Pi_k \Phi_k - \Delta_k \Pi_k \right), \tag{18}$$

which brings Equation 12 to

$$P\left(\left\{\vec{R}_{\alpha}\right\}\right) = (G)^{n} \exp\left\{\frac{1}{2} \int \frac{d^{3}k}{(2\pi)^{3}} \left[\frac{\Pi_{k}\Delta_{k}}{ul} - \ln(1 + \Pi_{k})\right]\right\}.$$
(19)

Thus, Δ_k defines the contribution of the fluctuations in segment density to the free energy through Equations 2, 19, and 6.

Calculation of Δ_k

Any two points in space \vec{r} and $\vec{r'}$ correlate in the field through the interaction $\Delta(\vec{r}-\vec{r'})$, and the field Lagrangian can be defined as

$$-\frac{1}{2}\int d\vec{r}\,d\vec{r}'\,\Phi(\vec{r})\Delta^{-1}(\vec{r}-\vec{r}')\Phi(\vec{r}'),\tag{20}$$

where

$$\Delta(\vec{r} - \vec{r}') = \langle \Phi(\vec{r}) \Phi(\vec{r}') \rangle.$$
⁽²¹⁾

Therefore, any pair of segments of the chosen chain interacts via $\Delta \left[\vec{R}(s) - \vec{R}(s')\right]$, where $\vec{R}(s) - \vec{R}(s')$ is the segment-to-segment distance.

So, the statistics of the chosen chain deviates from the Gaussian statistics, depending on the nature of Δ .

Edwards' formalism (1965, 1966) suggests that the chosen chain can be described by the effective Gaussian distribution with the effective segment l_1 :

$$\int D[\vec{R}] \exp\left[-\frac{3}{2} \int_{0}^{L} \frac{ds}{l_{1}} \left(\frac{\partial \vec{R}(s)}{\partial s}\right)^{2}\right].$$
(22)

Generally, l_1 proves to be a very complicated function of Δ and reflects the non-Markov nature of the process. Therefore, one can expect that the effective partition function for the system has the form

$$P\left(\Phi, \left\{\vec{R}_{\alpha}\right\}\right) \sim \exp\left[-\frac{3}{2} \sum_{\alpha} \int_{0}^{L} \frac{ds}{l_{1}} \left(\frac{\partial \vec{R}(s)}{\partial s}\right)^{2} - \frac{1}{2} \int \frac{d^{3}k}{(2\pi)^{3}} \Delta_{k}^{-1} \Phi_{k}^{2}\right] \qquad (23)$$
$$\equiv \exp(-H_{0}).$$

In fact, $P\left(\Phi, \left\{\vec{R}_{\alpha}\right\}\right)$ is defined by Equation 7.

Hence, adding and subtracting H_0 in the exponent $P\left(\Phi, \left\{\vec{R}_{\alpha}\right\}\right)$ to and from Equation 7, one can obtain a form characteristic for perturbation theory using Equation 23 as a bare propagator. From Equation 7 one derives

$$P\left(\Phi,\left\{\vec{R}_{\alpha}\right\}\right) = \exp(-H_0 - H'),\tag{24}$$

where

$$H' = \sum_{\alpha} \int_{0}^{L} ds_{\alpha} \left[\frac{3}{2} \left(\frac{1}{l} - \frac{1}{l_{1}} \right) \left(\frac{\partial \vec{R}_{\alpha}(s_{\alpha})}{\partial s_{\alpha}} \right)^{2} + i \int \frac{d^{3}k}{(2\pi)^{3}} \Phi_{k} \exp(i\vec{k}\vec{R}_{\alpha}(s)) + \frac{1}{2} \int \frac{d^{3}k}{(2\pi)^{3}} \left(\frac{1}{l_{u}} - \Delta_{k}^{-1} \right) \Phi_{k}^{2} \right].$$
(25)

By definition,

$$\Delta_{k} = \left\langle \Phi_{k}^{2} \right\rangle = \frac{\int D[\vec{R}_{\alpha}] D[\Phi] \Phi_{k}^{2} P\left(\Phi, \left\{\vec{R}_{\alpha}\right\}\right)}{\int D[\vec{R}_{\alpha}] D[\Phi] P\left(\Phi, \left\{\vec{R}_{\alpha}\right\}\right)}.$$
(26)

A series in terms of perturbation theory results on expansion of $\exp(-H')$ in Equation 26. The leading term of this perturbation series is Δ_k .

In the limit $k \rightarrow 0$ (i.e. for very large characteristic length scales), calculation (Muthukumar and Edwards, 1982; Muthukumar, 1986) has led to

$$\Delta_k = \frac{\left(\frac{1}{2} - \chi + w\Phi\right) lk^2 \xi^2 l^2}{1 + k^2 \xi^2 l^2}$$
(27)

(cf. Equation 5.1-254).

Thus, the effective interaction has the form of decay (screening), and ξ is the screening length in the units of Kuhn's segment (cf. Equation 5.1–256)

$$\xi^{-2} = \frac{6\left(\frac{1}{2} - \chi + w\Phi\right)\Phi}{\alpha^{2} + \frac{27}{8\pi}\left(\frac{1}{2} - \chi + w\Phi\right)\xi\alpha^{-2}},$$
(28)

where $\alpha \equiv l_1/l$.

This relationship is valid only in the limit of ξ and l_1 not depending on wavevector and for concentrations exceeding the overlap concentration Φ^* .

The quantity l_1 (and, therefore, α) is obtained while calculating the mean square endto-end distance of the chosen chain

$$\left\langle h^{2} \right\rangle = \frac{\int D[\vec{R}_{\alpha}] D[\Phi] \left[\vec{R}(L) - \vec{R}(0) \right]^{2} P\left(\Phi, \left\{ \vec{R}_{\alpha} \right\} \right)}{\int D[\vec{R}_{\alpha}] D[\Phi] P\left(\Phi, \left\{ \vec{R}_{\alpha} \right\} \right)}.$$
(29)

As earlier, a series of perturbation theory is constructed by expanding $\exp(-H')$ in Equation 29. The leading term is Ll_1 , and l_1 is determined when all the other terms of the perturbation theory tend to zero.

The l_1 -defining equation takes the form

$$\alpha^{5} - \alpha^{3} = \frac{2.207\sqrt{6}}{\pi^{3/2}} \left(\frac{1}{2} - \chi + w\Phi \right) N^{1/2} \left[\frac{1}{2} - \frac{6}{\kappa^{2}} + \frac{\sqrt{\pi}}{\kappa} \left(1 + \frac{3}{\kappa^{2}} \right) - \frac{\sqrt{\pi}}{2} \left(1 - \frac{4}{\kappa^{2}} + \frac{6}{\kappa^{4}} \right) \kappa \exp(\kappa^{2}) \operatorname{erfc}(\kappa) \right],$$
(30)

where

$$\kappa^2 = N\alpha^2/6\xi^2,\tag{31}$$

and erfc is an error function.

The numerical prefactor in Equation 30 is chosen so that Flory's modified equation (Yamakawa, 1971) would appear for an infinitely dilute solution ($\kappa = 1$). For semidilute solutions ($\Phi \ge \Phi^*$) with $N \to \infty$, Equation 30 leads to

$$\alpha^{5} - \alpha^{3} = 13.245\xi \frac{1/2 - \chi + w\Phi}{\pi\alpha}.$$
(32)

Substituting Equations 27 and 16 to Equation 19, we get

$$P\left(\left\{\vec{R}_{\alpha}\right\}\right) = (\bar{G})^{n} \exp\left[-(24\pi\xi^{3})^{-1}\right],\tag{33}$$

where ξ is defined by Equations 28 and 32.

The free energy of the effective chain is obtained by maximizing

$$\ln \int D[\vec{R}]G \tag{34}$$

with respect to l_1 . Here \overline{G} is given by Equation 11.

Substitution of Equation 33 to Equation 2 yields

$$\frac{\Delta G'}{kT} = (24\pi\xi^3)^{-1} - \frac{9(1/2 - \chi + w\Phi)\Phi}{16\pi\alpha^2\xi}.$$
(35)

Thus, the total expression for the Gibbs energy of mixing, in view of Equations 1 and 35, has the form

$$\frac{\Delta G_m}{kT} = \frac{\Phi}{N} \ln \Phi + (1 - \Phi) \ln(1 - \Phi) + \chi \Phi (1 - \Phi) + \left(w - \frac{1}{6}\right) \Phi^3$$
(36)

+
$$(24\pi\xi^3)^{-1} - \frac{9}{16\pi} \frac{(1/2 - \chi + w\Phi)\Phi}{\alpha^2\xi}$$

Let us discuss some asymptotic forms and limiting expressions. For $\Phi > \Phi^*$ but still low enough Φ values, the asymptotic formula

$$\xi^{-1} = \frac{16\pi}{9} \alpha^2 \Phi \tag{37}$$

follows from Equation 28.

Under the same conditions, combination of Equations 32 and 37 yields

$$\alpha^8 - \alpha^6 = 0.755 \frac{1/2 - \chi + w\Phi}{\Phi}.$$
(38)

In the case of the absence (w = 0) or insignificance $(w\Phi \ll (1/2 - \chi))$ of the three-body interactions, an asymptotic result for α^2

$$\alpha^2 = 0.932 \left(\frac{1}{2} - \chi\right)^{1/4} \Phi^{-1/4} \tag{39}$$

follows from Equation 38.

Inclusion of Equation 39 to Equation 37 gives

$$\xi^{-1} = 5.206 \left(\frac{1}{2} - \chi\right)^{1/4} \Phi^{3/4}.$$
(40)

Substituting Equations 39 and 40 to Equation 36, we get for w = 0

$$\frac{\Delta G_m}{kT} = \frac{\Phi}{N} \ln \Phi + (1 - \Phi) \ln(1 - \Phi) + \chi \Phi - \frac{1}{2} \Phi^2$$

$$+ 1.872 \left(\frac{1}{2} - \chi\right)^{3/4} \Phi^{9/4}.$$
(41)

From Euler's theorem for the potential of mixing (Equation 1.1.1-37)

 $\Delta G_{\rm m} = \Delta \mu_1 n_1 + \Delta \mu_2 n_2,$

the formula for osmotic pressure (per unit molar volume of the system)

$$\pi = \Phi^2 \frac{\partial}{\partial \Phi} \left(\frac{\Delta G_m}{\Phi} \right) \tag{42}$$

is easily derived.

Using Equation 41, we get from Equation 42

$$\frac{\pi}{kT} = \frac{\Phi}{N} + 2.34\Phi^{9/4}.$$
(43)

Thus, the character of the concentration dependence of such quantities as the mean square end-to-end distance expansion factor (Equation 39), the correlation length (Equation 40), and the osmotic pressure (Equation 43) coincides with the results of familiar scaling laws (see Table 4.1).

Correction of the relevant dependences can be performed according to the total equations 28 and 32. In the case of the predominance of the three-body interactions $w\Phi > (1/2 - \chi)$, Equation 38 shows the concentration independence of α

$$\alpha^8 - \alpha^6 = 0.755w,\tag{44}$$

while Equation 37 holds good for ξ . In particular, the three-body interactions must predominate at the θ point, where $\chi = 1/2$, and ξ is inversely proportional to concentration, in agreement with the scaling approach as well (see Equation 4.3-65 and Table 4.1, region III).

For very concentrated solutions, the same dependence $\xi \sim \Phi^{-1}$ is expected. If only w = 0 and $(1/2 - \chi) > 0$, $\xi \sim \Phi^{-1/2}$ at high concentrations, which is in keeping with the result of the authors' previous paper (see Equation 5.1–263).

Substituting Equations 37 and 44 to Equation 36, we get

$$\frac{\Delta G_m}{kT} = \frac{\Phi}{N} \ln \Phi + (1 - \Phi) \ln(1 - \Phi) + \chi \Phi - \frac{1}{2} \Phi^2 - \frac{1}{6} \Phi^3 + 1.872 w^{3/4} \Phi^3, \tag{45}$$

whence

$$\frac{\pi}{kT} = \frac{\Phi}{N} + 4.68\Phi^3.$$
 (46)

Hence, in a poor solvent with the predominance of the three-body interactions over the two-body ones, $\pi \sim \Phi^3$, which also agrees with the scaling (see Equation 4.3-44 and Table 4.1, region III).

Equations 36, 30, and 32 provide an iterative procedure for ΔG_m , ξ , and α with any combinations of the parameters of the two-body and three-body interactions and with any concentration.

State equation 36 is valid in the phase separation region as well, but due to the interdependence of on ξ and α through Equations 31 and 32, the phase diagram can be calculated only numerically. However, in the case of the predominance of the three-body interactions (that is obviously the case in the phase separation region), results can be obtained analytically. For the spinodal, write

$$\frac{\partial^2 \Delta G_m}{\partial \Phi^2} = kT \left[\frac{1}{1 - \Phi} + \frac{1}{N\Phi} - 1 + (11.23w^{3/4} - 1)\Phi \right] = 0, \tag{47}$$

and for the critical point, besides,

$$\frac{\partial^3 \Delta G_m}{\partial \Phi^3} = kT \left[\frac{1}{(1-\Phi)^2} - \frac{1}{N\Phi^2} + 11.23w^{3/4} - 1 \right] = 0, \tag{48}$$

Hence, for the critical concentration Φ_c , we have

$$\Phi_c^3 - \frac{2}{N}(\Phi_c^2 - 2\Phi_c + 1) = 0, \tag{49}$$

the solution of which yields

$$\Phi_c = \left(\frac{2}{N}\right)^{1/3} + O\left(N^{-2/3}\right),\tag{50}$$

This result differs substantially from the prediction of Flory-Huggins' theory ($\Phi_c \sim N^{-1/2}$).

Let us substitute Equation 50 to Equation 48

$$w_c \simeq 0.068 \Phi_c^{4/3} \tag{51}$$

$$\simeq 0.093 N^{-4/9} \left[1 + O\left(N^{-1/3}\right) \right].$$
(52)

The matter is complicated by the temperature dependence of the third virial coefficient being unknown a priori. If we assume (Yamakawa, 1971; Muthukumar, 1986)

$$w \approx \left(\frac{1}{2} - \chi\right)^2,\tag{53}$$

then, in view of the approximation

$$2\chi_c = \frac{\theta}{T_c},\tag{54}$$

we get

$$w_c = \frac{1}{4} \left(1 - \frac{\theta}{T_c} \right)^2 \equiv (\psi_1 \tau_c)^2, \tag{55}$$

where ψ_1 is Flory's entropic parameter.

Near Φ_c , $\Phi \ll 1$ is satisfied, which can be taken into account when expanding $(1-\Phi)^{-1}$ in Equation 47 into a series. Then, for sufficiently large N, spinodal equation 47 takes the following form

$$\Phi_{\rm sp}^3 + 11.23w^{3/4}\Phi_{\rm sp}^2 + \frac{1}{N} = 0.$$
(56)

With allowance for Equations 53 and 55, and the common approximation for χ

$$2\chi = \frac{\theta}{T},\tag{57}$$

on passing to new variables

$$\Phi'_{\rm sp} = \Phi_{\rm sp} N^{1/3} \qquad \tau' = \tau N^{2/9} \tag{58}$$

in Equation 56, we obtain

$$\Phi_{sp}^{\prime 3} + \psi_1^{3/2} \tau^{\prime 3/2} \Phi_{sp}^{\prime 2} + 12.23 = 0, \tag{59}$$

whose structure corresponds to the principle of corresponding states. Equation 59 differs from the corresponding spinodal equation in Flory-Huggins' approximation (Equation 4.3-113)

$$\Phi_{\rm sp}^{\prime\prime 2} + 2\psi_1 \tau^{\prime\prime} \Phi_{\rm sp}^{\prime\prime} + 1 = 0, \tag{60}$$

where

 $\Phi_{
m sp}^{\prime\prime}=\Phi_{
m sp}N^{1/2}$

and

 $\tau'' = \tau N^{1/2}.$

This difference is due to the account of the fluctuations in segment density in Equation 59.

Naturally, a relationship between the parameters of the two-body and three-body interactions, other than Equation 53, will lead to a different spinodal equation.

Using ΔG_m in the form of Landau's potential (see Equation 3.1-275), we obtain for the amplitude of the phase separation region (see Equation 3.1-278)

$$|\Phi - \Phi_c| = \left[\frac{6(\Delta G_m)_{\Phi \Phi T}(T_c - T)}{(\Delta G_m)_{\Phi \Phi \Phi \Phi}}\right]^{1/2}.$$
(61)

Applying Equation 45 to Equation 61, in view of Equations 48, 50, and 55, yields

$$\Phi - \Phi_c | \sim N^{-2/9} \tag{62}$$

ог

$$\frac{\Phi - \Phi_c}{\Phi_c} \sim N^{1/9}.$$
(63)

The value $1/9 \approx 0.11$ is close to Sanchez' (1985) index $b\beta = 0.102$ (Equations 4.3 129, 132).

The exponent in Equation 63 is also rather close to Dobashi et al.'s (1980ab) experimental values, -0.16 (see Equations 4.3-134, 136) and to Shinozaki et al.'s (1982a), -0.06(see Equations 4.3-135, -137).

The exponent in Equation 50 is close to Kaneko et al.'s experimental results, -0.39 (see Equation 4.3-136). The exponent reported by Shinozaki et al. (1982a), -0.40 (see Equation 4.3-137), is an intermediate between -0.33 (Muthukumar, see Equation 50) and -0.5 (Flory-Huggins).

It should be emphasized that the above exponents from Muthukumar's theory (Equations 50 and 62) relate to the limiting case of the predominance of the three-body interactions with the two-body ones being fully ignored. In the opposite limiting case (the predominance of the two-body interactions and neglect of the three-body ones), the exponents of Muthukumar's characteristic quantities are concordant with Flory-Huggins' approximation. The fluctuation contribution affects the factors at the power function only.

Equations 36, 28, and 30 of Muthukumar's theory enable both the two-body and three body interactions to be accounted for in their different combinations.

Comparison of these equations with the experimental data will allow researchers to study the contribution of the two-body and three-body interactions and the temperature dependence of χ and w for specific systems.

In any case, theoretical results show that the account of the order parameter's fluctuations may well lead to a substantial correction of the characteristic dependences in polymer theory in the mean field approximation.

Chapter summary

1. The renormalization group transformation of the Wilson type for the macromolecular conformational space \mathcal{R}_S is composed of the scaling transformation \mathcal{S}_S and Kadanoff's transformation \mathcal{K}_S :

 $\mathcal{R}_S \equiv \mathcal{K}_S \mathcal{S}_S.$

The scaling transformation S_S essentially reduces all the chain (Figure 5.1) which is equivalent to looking at it from a longer distance, with small loops becoming indistinguishable and short interactions manifesting themselves as one effective interaction (Figure 5.3). Kadanoff's transformation K_S is composed of two operations:

Kadanoff's transformation \mathcal{K}_S is composed of two operations:

- when the interacting points are at a distance along the contour length less than the cutting length a, the interactions within a small loop are included into the redefinition of l^2 and N in the scaled chain.
- if two pairs of interactions in the scaled system are separated by a contour length less than a, then these interactions are combined into a new effective parameter of interaction.

Applying the renormalization group transformation with the interaction potential as a short-range δ function yields analytical expressions for $\mathcal{R}_S(N^{-1})$ (Equation 5.1-33) and $\mathcal{R}_S(v_2)$ (Equation 5.1-34).

From (Equation 5.1-34) and the condition of existence of the fixed point $\mathcal{R}_S(v_2^*) = v_2^*$ an expression for $v_2^* = \pi^2 l^4 \varepsilon/32$ (Equation 5.1-36) follows. $(N^*)^{-1} = 0$ is the fixed point of the transformation $\mathcal{R}_S[(N^*)^{-1}] = (N^*)^{-1}$ near which linearizing $\mathcal{R}_S(N^{-1})$ (Equation 5.1-33) leads to

$$\mathcal{R}_S(N^{-1}) = s^{2\nu - \epsilon\nu/4} N^{-1} \tag{5.1.38}$$

The choice condition of ν (see Equations 5.1-19,-20) gives the asymptotic form $\mathcal{R}_{S}(N^{-1}) = sN^{-1}$ and leads to

$$\nu \cong \frac{1}{2}(1 + \frac{\varepsilon}{8} + \cdots). \tag{5.1-40}$$

2. In the case of a more realistic interaction potential including both attraction and repulsion (a solid core of the diameter σ) the renormalization group transformation has the analytic form $\mathcal{R}_S(N^{-1})$ (Equations 5.1 45, 51); $\mathcal{R}_S(\sigma)$ (Equation 5.1-46); $\mathcal{R}_S(v_2)$ (Equation 5.1-52), and $\mathcal{R}_S(v_3)$ (Equation 5.1-53).

Near the fixed point (within the region C, Figure 5.2) the equations $v_2 = -4v_3(3/2\pi l^2)$ (Equation 5.1-54) and $\mathcal{R}_S(v_2^*) = 0$ hold, i.e. the asymptotic phenomenological two-body interaction vanishes. Therefore, there exists a temperature at which the molecular chain as a whole behaves in 3D space as a unperturbed (free) one, and this temperature can be referred to as the θ temperature.

Equation 5.1-54 indicates that at the θ temperature, the morphological state of a coil is characterized by a balance of fine interaction effects concerned with the two-body attraction interactions being compensated for by the three-body repulsion interactions.

5. Chapter summary

Thus, the problem of the coil θ state proved to be much more sophisticated than the problem of the self-avoiding walks of segments.

3. In polymer theories, the length of a segment (molecular unit) a is the natural unit of the length scale at the molecular level, but experimentally measured quantities Q do not feel this molecular discrepancy. Hence mathematical expressions of the macroscopic quantity Q have to be well-defined in the limit $a \rightarrow 0$. Regarding the problem of the molecular coil excluded volume, this limit should be treated as a rejection with the consideration of the interactions of a segment with itself (self-excluded volume).

On the other hand, there is no natural unit length in the macroscopic description of macromolecule conformations, but it seems reasonable to introduce some unit length L to the macroscopic theory for conversing dimensional units to dimensionless ones. It follows that this unit may be chosen arbitrarily, regardless of the microscopic natural unit length a.

It is the renormalization approximation of the Gell-Mann, Low, Oono, Ohta, and Freed type that gives a method of introduction of such macroscopic values which are well-defined in the limit $a \rightarrow 0$, on the basis of a microscopic model. The following scale invariance of the microscopic theory to the choice of L together with the renormalization relations of well-defined macroscopic values leads to scaling regularities.

As the experimentally observed values must be well-defined in the limit $a \rightarrow 0$, the series of the perturbation theory must be regular at $\varepsilon = 0$ for macroscopic values. It is not, however, the case for the corresponding series obtained from the microscopic model.

The essence of the renormalization method with dimensional regularization is the introduction of relationships between microscopic and macroscopic values, which absorb these singularities, so at $\varepsilon = 0$, the macroscopic quantities turn out to be regular in ε .

In Oono, Ohta, and Freed's version, a continuous chain with the contour length N_0 , excluded volume parameter v_0 , and minimal scale length *a* being equal to a segment is chosen as the model for the macromolecule. On this basis, expressions are written for the partition function of the end-to-end distance (Equation 5.1-60), and a bare dimensionless Hamiltonian (Equation 5.1-62).

The microscopic parameter of the excluded volume v_0 is conversed to a dimensionless parameter u_0 by $u_0 = v_0 L^{\epsilon/2}$. For the macroscopic parameter of the excluded volume $u = v L^{\epsilon/2}$ is accepted.

The microscopic values are related to the macroscopic ones by the relationships

$$N = Z_2 N_0 \tag{5.1 65}$$

and

$$G(N, \vec{h}; v; L) = \lim_{a \to 0} Z^{-1} G_B(N_0, \vec{h}; v_0; a)$$
(5.1 74)

The main property of G_B must be its invariance to the choice of L, and the key equation of the theory follows:

$$L\frac{\partial}{\partial L}\bigg|_{v_0,N_0,a}G_B(N_0^{-1},\vec{h},u_0,a) \equiv 0$$
(5.1 77)

by which it is possible to find Z, Z_2 , and the relationship of v vs v_0 with all the main parts (singularities) of the bare (microscopic) perturbation series being absorbed (excluded).

The relationship between u and u_0 follows from a consideration of the three-point partition function

$$G^{(2)}(M,\vec{r};N,\vec{h};v,L) = Z^{-1}_{(2)}G^{(2)}(Z^{-1}_2M,\vec{r};Z^{-1}_2N,\vec{h};v_0,a).$$

With respect to the coil sizes in the maximum good solvent, the approach has led to the index $\nu = 4/(8 - \varepsilon)$ (Equation 5.1 134) being in good agreement with other exact approaches as well as with experiment for 3D space with $\varepsilon = 1$.

The technique of this version of the renormalization theory enables one to calculate such quantities as: the partition function for the end-to-end vector, the scattering function, the macromolecular conformations in solutions with finite concentrations, etc. more accurately than in the Kadanoff-Wilson approximation. Besides, this approach provides the calculation of the characteristic functions in the crossover region, i.e. in the intermediate region between the Gaussian behaviour of a coil and the limiting case of the interaction between segments with the excluded volume.

4. In order to solve the problem of determining the sizes of macromolecules in solution with a finite polymer concentration, the method of renormalization of the conformational space of polymer chains was applied using Edwards' formalism by which the effect of the surrounding macromolecules is equivalent to the existence of an external stochastic field $\Phi(\vec{R})$ with the so-called conformational "diffusion" of a given chain taking place. The "stream of conformations" in a power field turns out to lead to the effective "concentrating" of conformations which shows itself by the reduction of the coil with the increase in the polymer concentration.

5. To calculate the characteristic quantities of polymer theory, the method of the renormalization of polymer chain conformations in momentum space proved to be reasonable in every respect.

Here, the partition function for the end-to-end distance is represented through Laplace's inverse transform.

The technique of calculations is based on the well-elaborated formalism of the general field theory; therefore all the achievements of the latter can be applied to its polymer version.

6. The method of renormalization of the conformational space is also successfully used for the calculation of hydrodynamic parameters of macromolecules.

The possibility to calculate hydrodynamic quantities (eg, $[\eta]$) both with preaveraging Ozeen's tensor and directly (without any preaveraging) proves to be a serious advantage of the calculational procedure of the renormalization group approximation. This allowed researchers to estimate the error of determination of the hydrodynamic quantities caused by this preaveraging.

Different combinations of the expressions for hydrodynamic quantities with each other and with other characteristic quantities, formed according to the principle of reducing the arbitrary length L, lead to hydrodynamic invariants which tally with the traditional ones up to a constant.

7. A version of the direct renormalization method in the polymer theory was proposed by des Cloizeaux.

5. Chapter summary

The probability partition function for an unperturbed (Brownian) chain is written as

$$P_0\{r\} = \exp\left\{-\frac{1}{2}\int_0^S ds \,\left[\frac{d\vec{r}(s)}{ds}\right]^2\right\},\tag{5.4.1}$$

where s and S have the dimension of area: $[S] \sim \mathcal{L}^2$.

The partition function

$$\mathfrak{Z}_0(k) = e^{-k^2 S/2} \tag{5.4-5}$$

corresponds to this partition function in momentum space.

To describe the macromolecular properties in a good solvent, two-body interactions are introduced. They make the partition function to have the form of Equation 5.4-7, and for an ensemble of N chains—of Equation 5.4-12.

For the functions (Equation 5.4-7, 12)-based expressions to converge, a cut-off implying $|s'' - s'| > s_0$ must be introduced. Physically, this cut-off prevents the account of self-interactions between the segments for which s' = s''.

An important point of the approach is in the possibility to express all the physical (experimentally measured) values of a polymer system through its partition function with an imposed constraint. Fixing some p points, belonging to given macromolecules, may be such a constraint. Such points are referred to as the correlation points.

The diagrams representing the expansion series members of *n*-order partition functions are composed of N lines (one for each macromolecule) and *n* interaction lines connecting the lines of macromolecules in a way.

Hence, the interacting macromolecules are described with the fixed partition function

$$^{+}\mathfrak{Z}(\vec{r_{1}},\ldots,\vec{r_{p}};j_{1},\ldots,j_{p};s_{1},\ldots,s_{p};S_{1},\ldots,S_{\mathcal{N}}), \qquad (5.4-21)$$

where j is the number of the macromolecule, the sign "+" marks the introduction of the cut-off s_0 , and in momentum space are with

$$^{+}\bar{\mathfrak{Z}}(\vec{k}_{1},\ldots,\vec{k}_{p};j_{1},\ldots,j_{p};s_{1},\ldots,s_{p};S_{1},\ldots,S_{\mathcal{N}}),$$
 (5.4 23)

determined together with

$$\vec{k}_1 + \vec{k}_2 + \dots + \vec{k}_p = 0. \tag{5.4-24}$$

Fixing the chains' endpoints is a special case of the imposed constraint. Here, the partition function $\mathfrak{Z}(\vec{k_1},\ldots,\vec{k_{2N}};S_1,\ldots,S_N)$ corresponds to the situation where p=2N and

$$(j_1, \ldots, j_{2N}) = (1, 1; 2, 2; \ldots; \mathcal{N}, \mathcal{N})$$

 $(s_1, \ldots, s_{2N}) = (0, S_1; 0, S_2; \ldots; 0, S_N),$

and in the long-wave limit it corresponds to

$$^{+}\overline{\mathfrak{Z}}(0,0;\ldots;0,0;S_{1},\ldots,S_{\mathcal{N}}) = ^{+}\mathfrak{Z}(S_{1},\ldots,S_{\mathcal{N}}).$$
(5.4-25)

The terms of the expansion series of $+\bar{\mathfrak{J}}(S_1,\ldots,S_N)$ or $+\bar{\mathfrak{J}}(\vec{k_1},\ldots,\vec{k_p};j_1,\ldots,j_p;s_1,\ldots,s_p;S_1,\ldots,S_N)$ in terms of b powers are connected graphs (diagrams), since an interaction is reflected by connection lines. These diagrams are formed by all the means possible and calculated according to the rules given in section 5.4.

The most important quantities of the theory are:

- the partition function of one $\mathfrak{Z}(S)$ and of two chains $\mathfrak{Z}(S,S)$;
- the Fourier transform $\overline{\mathfrak{Z}}(\vec{k}, -\vec{k}, S)$ of the partition function with an imposed constraint $\mathfrak{Z}(\vec{r_1}, \vec{r_2}; S)$.

The mean-square end-to-end distance of an isolated chain

$$\left\langle h^2 \right\rangle = \left\langle \left(\vec{r}(S) - \vec{r}(0)\right)^2 \right\rangle = -\frac{2d}{\mathbf{3}(S)} \left[\frac{\partial}{\partial k^2} \mathbf{\bar{3}}(\vec{k}, -\vec{k}; S) \right]_{k=0}$$
(5.4-40)

and the state equation

$$\frac{\pi}{kT} = c_p - \frac{c_p^2 \mathfrak{Z}(S,S)}{2[\mathfrak{Z}(S)]^2} + \cdots$$
(5.4-41)

are expressed through the mentioned functions

In particular, for the Brownian chain, involving $\mathfrak{Z}_0(k)$ (Equation 5.4-5) according to (Equation 5.4-40) one can obtain

$$\left\langle h_{\theta}^{2} \right\rangle = \left\langle \left(\vec{r}(S) - \vec{r}(0)\right)^{2} \right\rangle_{0} = Sd, \tag{5.4-6}$$

i.e. the properties of the Brownian chain depend on the variable S only.

The space interactions in a chain is characterized by the parameter

$$z = bS^{2-d/2}(2\pi)^{-d/2}.$$
(5.4-9)

Des Cloizeaux introduced the conception of a critical object in reference to a polymer chain. With z = 0 the chain as a critical object is the Brownian chain. With $z \to \infty$ one will obtain a critical object as the limit of the chain with interacting segments (the Kuhnian chain). Between these two limits there is a crossover region with a finite value of z. All the physical quantities at a given b (or S) increase with z; however, in the asymptotic limit the universal behaviour and the correctness of the scaling relationships can be expressed.

For an isolated polymer chain with interactions, the area $^{\circ}S$ is defined as

$$\langle h^2 \rangle = \langle (\vec{r}(S) - \vec{r}(0))^2 \rangle = Sd,$$
 (5.4-42,-67)

where

$$\frac{{}^{e}S}{S} = X_0(z) = -\frac{2}{\mathbf{3}(S)} \left[\frac{d}{d(k^2S)} \bar{\mathbf{3}}(\vec{k}, -\vec{k}; S) \right]_{k=0}.$$
(5.4-43)

With S = const ${}^{e}S \to \infty$, if $z \to \infty$. This shows the advisability of choosing ${}^{e}S$ as a new scale, and $X_0(z)$ may be regarded as a renormalizing multiplier. In the case of $z \to \infty X_0(z) \sim z^{2(2\nu-1)/e}$ (Equation 5.4-48)

5. Chapter summary

The physical quantities, originating from the partition function, are also expressed through ${}^{c}S$ and z, and with ${}^{c}S = const$ they must reach a finite limit, if $z \to \infty$ (the Kuhnian behaviour).

However, for "S = const the partition function proved to be infinite, if $z \to \infty$, so renormalization is required.

As $\mathfrak{Z}(S)$ is dimensionless, we can define

$$\mathfrak{Z}(S) = [X_1(z)]^2. \tag{5.4-49}$$

An appropriate analysis shows that

$$X_1(z) \sim z^{(\gamma-1)/\epsilon}, \qquad z \to \infty.$$
 (5.4–52)

The renormalized partition function $\mathfrak{Z}_R({}^eS)$ must depend on the physical scale eS alone, and, therefore, be a constant. So we can define $\mathfrak{Z}_R({}^eS) = 1$ (Equation 5.4-53).

Hence, $\mathfrak{Z}(S) = [X_1(z)]^2 \mathfrak{Z}_R({}^eS)$ (Equation 5.4-54) and $X_1(z)$ can be regarded as the second renormalizing factor defined by the renormalization condition (Equation 5.4-53). By definition, for large N

$$X_{\mathcal{M}} \sim N^{\sigma_{\mathcal{M}}} \tag{5.4.61}$$

holds. and

$$\sigma_{\mathcal{M}}(z) = \frac{\varepsilon}{2} \cdot \frac{\partial \ln X_{\mathcal{M}}(z)}{\partial \ln z}.$$
(5.4-62)

The critical index $\sigma_{\mathcal{M}}$ is defined as

$$\sigma_{\mathcal{M}} = \lim_{z \to \infty} \sigma_{\mathcal{M}}(z). \tag{5.4-63}$$

 σ_0 and σ_1 are the most important critical indices, for which

$$\sigma_0 = 2\nu - 1, \tag{5.4-64}$$

and

$$\sigma_1 = \frac{\gamma - 1}{2} \tag{5.4-65}$$

hold.

Analysis of dimensions reveals that the renormalized partition function $\mathfrak{Z}_R({}^{e}S, {}^{e}S)$ can be written as

$$\mathfrak{Z}_{R}({}^{e}S, {}^{e}S) = -(2\pi)^{d/2} ({}^{e}S)^{d/2}g, \qquad (5.4\ 68)$$

where g is a quantity having the meaning of the dimensionless second virial coefficient.

The state equation of a polymer solution is written as

$$\frac{\pi}{kT} = c_p \left[1 + \frac{1}{2} (2\pi)^{d/2} g c_p ({}^e S)^{d/2} + \cdots \right].$$
(5.4 69)

According to the fundamental idea of the renormalization theory, g must possess the following properties.

If z = 0, then g = 0, but if $z \to \infty$, then g has a finite limit g^* . Besides, for $d \ge 4$, $g^* = 0$. Hence, with a small positive $\varepsilon = 4 - d$, g can be expanded by its Taylor series expansion in powers of ε . The ε expansion of the critical indices can be obtained in a similar way.

The strategy of renormalization is as follows.

In terms of (Equations 5.4-49, 53,-43, 67) by means of the perturbation method $X_0(z)$ and $X_1(z)$ are calculated as functions of z, which is followed by calculation of the critical indices $\sigma_0(z)$ and $\sigma_1(z)$.

Using (Equation 5.4 68), g can be represented as a series in powers of z. This series can be reversed so that z will be expressed as a series in powers of g. As a result, des Cloizeaux calculated $\Im(\vec{k}, -\vec{k}, S)$ and $\Im(S, S)$ in the second order of z and in the first order of (k^2S) , and, therefore, $X_0(z) = S/S$, $X_1(z)$, $\sigma_0(z)$, $\sigma_1(z)$, g(z), g^* , $\sigma_0(g)$, $\sigma_1(g)$ and, finally,

$$\nu = \frac{\sigma_0 + 1}{2} = \frac{1}{2} \left(1 + \frac{\varepsilon}{8} + \frac{15}{256} \varepsilon^2 + \cdots \right)$$
(5.4-99)

with $\nu \simeq 0.569$ for d = 3 ($\varepsilon = 1$).

To reveal fine phenomena in the properties of polymer solutions, des Cloizeaux calculated the mean square gyration radius of macromolecules by means of (Equation 5.4-103,-104). In particular, it was found that

$$\frac{\langle R^2 \rangle}{\langle h^2 \rangle} = \frac{1}{6} \left(1 - \frac{\varepsilon}{96} + \cdots \right). \tag{5.4-113}$$

With finite values of z, the crossover effect manifests itself. As a result of calculations, an expression for $X_0(z)$ (Equation 5.4–136, 137) was obtained.

This method of renormalization was used to calculate the form factor of light scattering $H(\vec{q})$ (Equation 5.4-147), which differs essentially from that presented in some previous papers accepting the rule of swelling of the macromolecule to be the same for both the internal and the external parts of a macromolecule.

In contradiction to this, the method of direct renormalization predicts the swelling of the internal parts of a macromolecular chain to be more intensive. It affects the expression for the radius of gyration which is more sensitive to the internal part of coil than is $\langle h^2 \rangle$.

8. As temperature decreases (the properties of a solvent get worse), the excluded volume of segments decreases, too, and the coil conformation approaches the Gaussian one at the θ point, where the second virial coefficient is equal to zero. This conformation is realized as a result of the compensation of rather strong interactions of both positive (repulsion) and negative (attraction) signs rather than due to the absence of interaction.

The state of long polymer chains near the compensation θ point is similar to the tricritical state of general-type systems.

A theory of polymer systems near the θ point (by Duplantier) has been worked out with the grand canonical ensemble of polymer chains, the grand canonical partition function being written as

$$\mathcal{Z}(h) = 1 + \sum_{\mathcal{M}=1}^{\infty} \frac{h^{2\mathcal{M}}}{2^{2\mathcal{M}}\mathcal{M}!} \prod_{m=1}^{\mathcal{M}} \int_{0}^{\infty} dS_m \, e^{-a_0 S/2} \, {}^+\mathfrak{Z}(S_1, \dots, S_{\mathcal{M}}), \tag{5.5.16}$$

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where a_0 is the chemical potential related to the chain area S, and $h^2/4$ is the fugacity associated with the number \mathcal{M} of chains.

Through the partition function (Equation 5.5–16) are expressed the numeric concentration of polymer chains c_p , the average total area of chains $\langle S \rangle$ and the osmotic pressure π :

$$c_p = \frac{h}{2V} \cdot \frac{\partial}{\partial h} \ln \mathcal{Z}(h), \qquad (5.5-17,-20)$$

$$\langle S \rangle = \frac{\partial}{\partial a_0} \ln \mathcal{Z}(h),$$
 (5.5.18)

$$\frac{\pi}{kT} = \frac{1}{V} \ln \mathcal{Z}(h), \tag{5.5.19}$$

the symmetrical moment X^2 , the total square end-to-end distance \mathcal{X}^2 , and the square distance between the ends of the same chain $\langle h^2 \rangle$ being expressed by (Equation 5.5 24...26).

Within the Lagrangian formalism, the set of \mathcal{M} chains is represented by an action $\mathcal{A}\{\vec{r}\}$ (Equation 5.5-3...5), to which there corresponds the partition function $\mathcal{Z}\{\vec{h}\}$ of *n*-component field $\phi^j(x), j = 1, ..., n$ (Equation 5.5-27...29) coinciding with $\mathcal{Z}(h)$ (Equation 5.5-16) in the case of a homogeneous field along the direction j = 1 $h^j(x) = \delta_{j1}h$ and in the limit n = 0.

 c, c_p , and π are expressed through vertex functions by means of

$$c = 2\frac{\partial \Gamma(f)}{\partial a_0} \Gamma(f), \tag{5.5 45}$$

$$c_p = \frac{f}{2} \cdot \frac{\partial \Gamma(f)}{\partial f},\tag{5.5-46}$$

$$\frac{\pi}{kT} = f \frac{\partial \Gamma(f)}{\partial f} - \Gamma(f), \qquad (5.5 - 47)$$

where $f = \partial F(h) / \partial h$, F(h) is the free energy of the system.

These quantities can be expressed through the vertex functions in the k-representation as well:

$$c_p = \frac{1}{2}\Gamma^{(2)}(0,0)f^2 + \frac{1}{12}\Gamma^{(4)}(0,0,0,0)f^4 + \cdots$$
(5.5-59)

$$\frac{\pi}{kT} = c_p + \frac{1}{6} \cdot \frac{\Gamma^{(4)}(0,0,0,0)}{\left[\Gamma^{(2)}(0,0)\right]^2} c_p^2 + \cdots$$
(5.5-60)

$$\left\langle h^2 \right\rangle = \left[\Gamma^{(2)}(0,0) \right]^{-1} \frac{\partial}{\partial (k^2)} \Gamma^{(2)}(0,0).$$
 (5.5-61)

If the θ state is defined by the second virial coefficient being equal to zero for infinitely long chains $(\langle h^2 \rangle \to \infty)$, then the condition of the θ state via the vertex functions follows:

$$\Gamma^{(2)}(0,0) = 0, \quad \Gamma^{(4)}(0,0,0,0) = 0,$$
(5.5-62)

which characterizes the tricritical point in the field theory.

At short distances $(s_0 \rightarrow 0)$, the vertex functions have "ultraviolet" divergences, so renormalization is required to suppress the divergences of the power function type $s_0^{-\alpha}$, $\alpha > 0$.

As a result of the renormalization by mass and vertex of two-body interactions (Equation 5.5–73,-74), one can obtain an expansion series $\Gamma^{(2)}(\vec{k},-\vec{k})$ in the first order of g and w (Equation 5.5–82) and the six-point vertex function $\Gamma^{(6)}$ (Equation 5.5–84).

The series of vertex functions diverge in respect of w powers in the neighbourhood of the tricritical point when d = 3 at the expense of the term including

$$\ln(as_0)^{-1}, \quad as_0 \to 0.$$
 (5.5.85)

The dimensionality d = 3 corresponds to the highest critical dimensionality causing the appearance of logarithmic divergences because of the term $w(\varphi^2)^3$ in the Lagrangian. With d = 3 two limits $a \to 0$ (corresponding to $S \to \infty$) and $s_0 \to 0$ are equivalent. These tricritical divergences, appearing from the interaction term $w(\varphi^2)^3$, differ from those relating to the excluded volume term $g(\varphi^2)^2$.

The technical side of tricritical renormalization is very sophisticated and laborious.

As a result, Equation 5.5–124 was derived for a single infinitely long chain at the tricritical point, and Equation 5.5–125 for a finite chain at the θ point. Therefore, an infinitely long chain at the θ point somewhat swells because of the three-body interactions, and for a finite chain a reduction with a logarithmic correction takes place.

9. For finite-concentrated solutions Duplantier considered the versions of dilute and semidilute solutions separately for short and long chains.

The matter is that there is no tricritical divergence for short chains in solution, and for the generating functional $\Gamma(f)$ a simple loop expansion in terms of f, a, g, w, s_0 is sufficient.

For dilute solutions of short chains, characterized by $c \rightarrow 0$ and S being fixed the expression of π (Equation 5.5–152) and of $\langle h^2 \rangle$ (Equation 5.5–153) with a correction term $\delta \langle h^2 \rangle$ (Equation 5.5–154) were obtained.

Semidilute solutions of short chains are characterized by the following conditions:

$$S \to \infty, c_p \text{ is fixed, } wc^2 S >> 1.$$
 (5.5–156)

In fact, in this case we are dealing with short sections between the entanglements of the macromolecules. For π and $\langle h^2 \rangle$, Equations 5.5–158 and 5.5–159 were obtained.

For long chains in the tricritical state of dilute solutions, the renormalization procedure allowed researchers to calculate π (Equation 5.5–183) and w(S) (Equation 5.5–176), and for $\langle h^2 \rangle$, Equation 5.5–122 with a distinct concentration-dependent correction (Equation 5.5–181) was obtained.

For semidilute solutions of long chains in the tricritical state, after the renormalization π has the form (Equation 5.5–193) with $w(c^{-2})$ (Equation 5.5–187) and $\langle h^2 \rangle$ has the form (Equation 5.5–194).

Therefore, the Lagrange formalism O(n) of the field theory (with n = 0) shows the tricritical point of the system of infinitely long polymer chains to correspond to the θ point, at which there occur very fine effects of compensation of two-body and three-body interactions. Near the θ point long chains are not Gaussian.

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10. Within the given formalism, the region of phase separation is defined in the limit of infinitely long chains $(S \to \infty)$ in the semidilute region.

The left-hand branch of the binodal within the accepted approach matches the ordinate axis (g < 0, c = 0), and for the right-hand branch

$$g_e \simeq -\frac{1}{15} w \left(\frac{11}{60(2\pi)^2} w |\ln c^2 s_0| \right)^{-7/11} \cdot c.$$
 (5.5 199)

Therefore, the latter branch has a zero slope at the origin of coordinates for infinitely long chains which is a characteristic feature of the tricritical phenomena.

11. The theory of tricritical phenomena was developed by different methods: the direct renormalization, the dimensional regularization in momentum space, etc. There are some contradictions between different authors which can be explained by certain specific features of different approaches. However, Duplantier performed comparative calculations and an analysis of the tricritical state of polymer systems by different methods (in particular, by the method of dimensional regularization and using a cut-off) and achieved equivalent results.

Therefore, the contradictions appear to be related to the technical side of calculations and are of no consequence.

In connection with the consideration of tricritical effects, the conformation of a polymer chain at the θ point is gaining in importance. In the first order of the interaction parameters at the θ point, there occurs a contraction of the chain in comparison with the unperturbed state of the coil. With sufficiently long chains and an essential contribution of the three-body interactions, a residual swelling of the coil is observed.

The experiments, which seem to report the tricritical effects for the first time, are discussed.

12. Muthukumar proposed the most general version of the theory of systems P+LMWL in which the Gibbs mixing potential is given with due account of fluctuations in the order parameter (the concentration of polymer segments) (Equation 5.6-36). This approach is based on the step-by-step application and the development of the Edwards formalism. A peculiar feature of this approach is the reduction of the three-body interactions to the effective two-body ones.

The Muthukumar theory enables one to account both for two-body and for three-body interactions in any ratio in solutions of any concentration in principle.

Within the region of a good solvent, the three-body interactions can be neglected, and the results of the Muthukumar theory are in agreement with those obtained by the scaling approach.

There may be analogies with the scaling expressions of the characteristic quantities in the region of a poor solvent, too (near the θ temperature), if special significance is attached to three-body interactions in the Muthukumar state equation.

In the case of the account of both two-body and three-body interactions, the region of phase separation has to be defined by means of numerical methods.

With the predominance of three-body interactions, the results can be obtained analytically; they show a significant difference from Flory-Huggins' predictions and are in good agreement with experiment. In another limiting case, the case of the predominance of two-body interactions, the characteristic quantities of the Muthukumar theory tally with Flory-Huggins' approximation. The contribution of the segment concentration fluctuations is only reflected in the factors standing by the power functions.

As the Muthukumar equalities (Equation 5.6-36, 28,-30) enable one to take account of two-body and three-body interactions in different combinations, the comparison of these equations with experimental data will allow one to study the contribution of two-body and three-body interactions as well as the temperature dependence of the parameters of the two-body χ and three-body w interactions for certain systems.

Chapter 6

Liquid(Solution)-Crystal Phase Separation

6.1. Conditions of phase equilibrium

If in the system P+LMWL at some temperature T_1 the chemical potential of mixing of the polymer in solution per mole of monomeric units $\Delta \mu_{2s}$ at some concentration $v_2 = v_2^*$ proves to be equal to the difference of the chemical potentials of polymer in the crystal and amorphous phases $\Delta \mu_{2cr}$, then there will be two phases in equilibrium, namely, polymer solution of the concentration $v_2 = v_2^*$ and polymer crystals (Figure 6.1).

Let us write the condition of the chemical potentials of polymer being equal in solution and in the solid state per mole of monomeric units (because it is the monomeric unit that acts as the structural element in the process of crystallization) (Flory, 1949):

$$\Delta\mu_{2s} = \Delta\mu_{2cr},\tag{1}$$

where $\Delta \mu_{2s} = (\mu_2 - \mu_{02})/p = \Delta \mu_2/p$; $\Delta \mu_{2cr} = \mu_{2cr} - \mu'_{02}$; μ'_{02} is the polymer chemical potential in the amorphous state per mole of monomeric units; $\Delta \mu_2 = \mu_2 - \mu_{02}$ is the chemical potential of mixing of the polymer, and p is polymerization degree which is equal, according to the lattice model, to $\bar{V}_{01}z/V_{02M}$, where \bar{V}_{02M} is the molar volume of a monomeric unit (cf. Equation 3.1.1).

Hence, in the approximation of Equation 3.1-51,

$$\Delta \mu_{2s} = \frac{RTV_{02M}}{\bar{V}_{01}} \left[\frac{\ln v_2}{z} - \left(1 - \frac{1}{z} \right) v_1 + \chi_1 v_1^2 \right],\tag{2}$$

and in the limit $z \to \infty$

$$\Delta \mu_{2s} = \frac{RTV_{02M}}{\bar{V}_{01}} \left[-v_1 + \chi_1 v_1^2 \right], \tag{3}$$

According to the reversibility condition of crystallization-melting processes,

$$\Delta\mu_{2cr} = -\Delta\mu_{2m},\tag{4}$$

and

$$\Delta \mu_{2\mathbf{m}} = \Delta \hat{G}_{2\mathbf{m}} = \Delta \tilde{H}_{2\mathbf{m}} - T \,\Delta \tilde{S}_{2\mathbf{m}}.$$



Figure 6.1. Temperature dependence of $\Delta \mu_{2cr}$ and $\Delta \mu_{2s}$ (a), concentration dependence of ΔG_m for solution (the single-phase state) (b), and the dependence of the melting temperature of polymer crystals on polymer concentration in solution (the liquidus curve) (c) (Schematic)

Fixing temperature at the first-order phase transition of polymer in the condensed state, we replace T by $T_{\rm m}^{\circ}$:

$$\Delta G_{2m} = 0 \quad \text{and} \quad \Delta H_{2m} - T_m^{\circ} \Delta \bar{S}_{2m} = 0, \quad \text{where} \quad T_m^{\circ} = \frac{\Delta \bar{H}_{2m}}{\Delta \bar{S}_{2m}}.$$
 (5)

In solution and at any other temperature T:

$$\Delta \mu_{2m} = \Delta H_{2m} - T \Delta \hat{S}_{2m} = \Delta H_{2m} \left(1 - \frac{T \Delta S_{2m}}{\Delta \bar{H}_{2m}} \right) = \Delta H_{2m} \left(1 - \frac{T}{T_m^o} \right).$$
(6)

Equations 1, 4, and 6 together give

$$\Delta \mu_{2s} = -\Delta \mu_{2m} = -\Delta \bar{H}_{2m} \left(1 - \frac{T}{T_m} \right),$$

and, in view of Equation 2,

$$RT\frac{\bar{V}_{02M}}{\bar{V}_{01}}\left[-v_{1}+\chi_{1}v_{1}^{2}\right] = -\Delta\bar{H}_{2m}\left(1-\frac{T}{T_{m}^{o}}\right) = -\Delta H_{2m}T\left(\frac{1}{T}-\frac{1}{T_{m}^{o}}\right).$$
(7)

Here T denotes the melting temperature $T_{\rm m}$ of polymer crystals in solution with the polymer concentration v_2 , so

$$\frac{RV_{02M}}{\Delta H_{2m}V_{01}} \left[(1 - v_2) - \chi_1 (1 - v_2)^2 \right] = \frac{1}{T_m} - \frac{1}{T_m^{\circ}},$$

or

$$\frac{1}{v_1} \left(\frac{1}{T_m} - \frac{1}{T_m^{\circ}} \right) = \frac{R \dot{V}_{02M}}{\Delta H_{2m} \dot{V}_{01}} - \frac{R \bar{V}_{02M}}{\Delta \bar{H}_{2m} \bar{V}_{01}} \chi_1 v_1.$$
(8)

It means the better the solvent (lower χ_1), the deeper the melting temperature depression of crystallites formed from solution. Plotting

$$\frac{1}{v_1} \left(\frac{1}{T_m} - \frac{1}{T_m^o} \right) vs v_1 \tag{9}$$

one gets a straight line whose intersection and slope enable one to calculate the melting molar enthalpy per monomeric unit ΔH_{2m} and the interaction parameter χ_1 , respectively (Figure 6.2).

In systems P+LMWL high in polymer, crystallites may function as crosslinks, and the amorphous part of polymer with LMWL forms the system "crosslinked polymer+LMWL" with its characteristic features (section 3.5) (Rogers et al., 1959).

The consideration presented (Flory, 1953; Mandelkern, 1964) is valid only if the crystal lattice contains polymer molecules alone and no mixed crystals are formed (no solidus curve on the state diagram). Moreover, in comparison with any mixture of low-molecular-weight compounds (see Figure 1.11) in the system P+LMWL the eutectic temperature is markedly shifted towards the side of high LMWL content and, as a rule, the effect of solvent (LMWL) melting temperature depression is very insignificant (Papkov, 1981).

Such approach is justified for a huge body of systems P+LMWL. However, recently a number of systems have been described where mixed crystals, or crystal solvates, are formed (see Figure 3) (Papkov and Dibrova, 1978; Papkov, 1981; Iovleva and Papkov, 1982).

To provide their formation, steric coincidence and strong interactions between LMWL molecules and separate groups of macromolecules must exist with the packing of them being densest (Papkov, 1981).



Figure 6.2. Liquidus curves of the system P+LMWL in a poor (large χ_1) (1) and good (small χ_1) (2) solvents (a), according to Equation 8 (b) (Schematic)

Papkov (1978, 1981) presented different versions of P+LMWL state diagrams where LMWL crystallization is important. For instance, a water melting temperature depression to -60° C has been observed in the system dextrane+water at a 50% dextrane content (Ioelovich et al., 1975).

In macromolecules with strong intramolecular interactions, a cooperative order-disorder (helix-coil) transition is possible, which is of prime importance for solutions containing proteins and nucleic acids. The formation of a system of intramolecular H-bonds among the groups of the main chain, stabilized by hydrophobic interactions, leads to the helix conformation. As temperature rises, or an active solvent is introduced, intramolecular H-bonds break down, and the helix-coil transition occurs. It is reversible with decreasing temperature or removing the active solvent, respectively.¹

¹In some special cases (eg. a mixed binary solvent with one component very active, and the second one of low activity), an <u>increase</u> of temperature leads to coil-helix transition. *Editor's note*



Figure 6.3. Liquid-crystal phase equilibrium (a) with the formation of a congruently (b) or incongruently (c) melting crystal solvates. T_{m1} and $T_{m,CrS}$ denote the melting temperature of the crystals of the low-molecular-weight component (CrLMWC) and of the crystal solvates (CrS), respectively (Papkov, 1981; Iovleva and Papkov, 1982)

The helix-coil transition has been well studied by now and is described in detail in a number of books and monographs (Birshtein and Ptitsyn, 1964; Mandelkern, 1964; Bresler, 1973; Volkenstein, 1975; Khokhlov, 1985).

Traditional methods for crystal structure investigation used to study liquid-crystal

phase separation are: X-ray analysis (Rabek, 1980b, Chapter 28), electronography (Rabek, 1980b, Chapter 29), thermal analysis (Rabek, 1980b, Chapters 26, 34, 32), electron microscopy (Rabek, 1980b, Chapter 27), densitometry (Rabek, 1980b, Chapter 31).

The method of light scattering on anisotropic structures in the Rayleigh-Debyc approximation (Frenkel et al., 1965; Baranov, 1966; Stein, 1966; Volkov and Baranov, 1968) is being developed.

Investigative techniques and properties of crystal structures are presented in a number of monographs (Geil, 1963; Mandelkern, 1964; Sharples, 1966; Bukhina, 1973; Wunderlich, 1973, 1976, 1980; Rabek, 1980b) and guidebooks (Rabek, 1980b), in a comprehensive fundamental work (Vainshtein, 1979; Vainshtein et al., 1979; Chernov et al., 1980; Shuvalov et al., 1981).

Wunderlich (1973, 1976, 1980) has discussed the questions of the thermodynamics, kinetics, and morphology of polymer crystallization.

Most of the methods for crystal phase investigation are based on the essential structural difference between the amorphous phase and the crystal one, but in the case of polymer systems, these differences may prove to be insufficient for effective implementation of the classic procedures. The matter is that polymer crystals are much less perfect than those of low molecular compounds.

On the other hand, due to relaxation effects the amorphous phase may not show completely structureless morphology.

Besides, the features of relaxation kinetic processes of structure reconstruction in polymer systems lead to significant retardation of phase separation even at the early stages of the process, and the system structure is frozen for quite a long period in its colloidaldisperse state.

The complete conversion of the polymer crystal phase is also impossible for merely thermodynamic reasons (Mandelkern, 1964; Mandelkern and Stack, 1984).

Phase analysis of such colloidal systems is very difficult, and discussions arise not only on details of a given phase diagram but even on the principal kind of phase separation in a specific system (liquid-liquid or liquid-crystal ?).

Despite of the fact that the morphology of the separating systems of two kinds may not differ essentially, the phase identification of the kind of transition is absolutely necessary to control the system structure with the aim of optimizing the technology of making polymer materials and improving their service properties.

6.2. Phase analysis of the system poly(vinyl alcohol) + water

The literature on the character of phase separation in the system PVA+water is characteristic for phase analysis of polymer systems in general. Several researchers (Kormanovskaya, 1967; Kormanovskaya et al., 1968; Tager et al., 1971; Shakhova and Meyerson, 1972) classify this system with those of amorphous separation with an UCST.

For instance, Kormanovskaya (1967) and Kormanovskaya et al. (1968) have proposed a phase diagram of the liquid-liquid type with an UCST at $\sim 80^{\circ}$ C. The left-hand branch of the phase separation region was obtained by extrapolation of the phase separation rate to zero, and the right-hand one was obtained by measuring the swelling degree of the polymer in water. The phase separation kinetics was determined using light scattering intensity at 45°.

Shakhova and Meyerson (1972) have employed the conventional procedure of thermostating at different temperatures with subsequent measuring polymer concentration in the two resulting layers.

The conclusion on improvement of the solvent power of water with rising temperature was made on data for water vapour sorption by PVA by Tager et al. (1971). Such simple observation as polymer dissolution in water during heating only suggests the existence of an amorphous separation region with an UCST.

On the other hand, some researchers (Amaya and Fujishiro, 1953; Dieu, 1954; Matsuo and Inagaki, 1962ab; Sakurada et al., 1965) have obtained experimental data about decrease in the solvent power of water with rising temperature, namely: negative values of κ_1 and ψ_1 calculated from solution viscosity (Dieu, 1954) and crosslinked gels swelling (Sakurada et al., 1965) (cf. Figure 3.81); negative values of dilution heat (Amaya and Fujishiro, 1953) (cf. Figure 3.68); fragmentary data on the decrease in the second virial coefficient \mathcal{A}_2 as temperature rises (Matsuo and Inagaki, 1962ab).

Extrapolation of viscosity (Dicu, 1954; Dmitrieva et al., 1971) has led to the θ temperature at the LCST ~ 100°C.

While analyzing the literature on the properties of PVA aqueous solution, one notices that there exists a quite limited body of data of PVA molecular parameters obtained by means of light scattering. This may be attributed to the presence of particles of the colloidal degree of dispersion (supramolecular particles—SMPs) in PVA aqueous solutions; difficulties arise while trying to remove them (Matsuo and Inagaki, 1962ab; Klenin and Klenina, 1971b). Meanwhile, these particles significantly distort the pattern of light scattering and birefringence flow in solutions (Matsuo and Inagaki, 1962ab; Peter and Noetzel, 1962; Peter and Fasbender, 1964; Klenin and Klenina, 1971) which hinders or even makes it impossible to obtain information on the molecular parameters of the polymer.

Matsuo and Inagaki (1962ab) admitted these particles to be of a paracrystalline nature. Indeed, PVA is a crystallizing polymer (Tadokoro et al., 1957) regardless of molecular chain stereoregularity owing to the "compactness" of OH-groups (Bunn, 1948). However, X-ray analysis of PVA aqueous gels (even with a high polymer content) did not show any reflexes of crystal structure (Rehage, 1963). Baranov et al. (1967) have emphasized the internal diphility of PVA molecular chains in water, which leads to coiled (more coiled than a statistical coil) macromolecular conformations and kinetic difficulties for polymer crystallization in the presence of water.

A cycle of investigations of the SMP thermodynamic nature and phase separation character in the system PVA+water have been performed mainly by the turbidity spectrum method (subsections 2.1.5 and 3.6.2) (Klenin et al., 1966, 1973abc, 1974bc; Klenina et al., 1970, 1972, 1979; Kolnibolotchuk et al., 1970, 1974ab; Klenin and Klenina, 1971b; Kolnibolotchuk, 1975; Klenina, 1977) and led to a conclusion that the nature of SMPs is crystalline and that there is no region of amorphous separation.

The following facts count in favour of this conclusion:

 character of the kinetics of growth of the new phase particles which comprises two stages, namely, fast (exponential after Avraami) and slow (linear) rise; both can be related to the processes of crystallization itself and postcrystallization (Klenin et al., 1974bc; Klenina, 1977) (see Figure 6.4);



Figure 6.4. Kinetics of growth of supramolecular particles in PVA aqueous solutions $(M_{\eta} = 140,000; \Lambda G=0.43\%, c = 5 \text{ wt }\%, T = 20^{\circ}\text{C})$. Different signs mark independent experimental results (Klenin et al., 1974c)

- extremal (with a maximum) temperature dependence of particle growth rate v = v(T) (see Figure 6.5) and what is more, this function has an asymmetric form with a gently sloping low-temperature branch ending on the abscissa axis (v = 0) at the glass transition temperature, T_g , and with a steep high-temperature branch ending on the same axis at the melting temperature T_m (liquidus);
- extremal (with a maximum) concentration dependence of particle growth rate (Figure 6.6) with its left and right branches intersecting the abscissa axis at T_m and T_g , respectively;
- liquidus curve plotted according to the temperature (Figure 6.5) and concentration (Figure 6.6) dependences of the growth rate of the new phase particles Figure 6.7;



- the annealing phenomenon is characteristic for crystallization-melting: within the range of 60 100°C, the polymer dissolves in water and then, at the **dissolution** temperature, particles of a new phase are formed;
- no SMPs are formed when there are outsize acetyl groups breaking the chain regularity (5% and higher) (Budtov et al., 1974, 1978; Kolnibolotchuk et al., 1974ab);
- SMPs melt with raising temperature; the dependence of T_m on the formation temperature is characteristic for crystallization-melting (Klenina et al., 1970, 1972; Klenina, 1977);
- rate of SMP formation (crystallization) rises when a hydrodynamic field is applied (Kolnibolotchuk et al., 1970, 1974ab; Klenin et al., 1973b; Kolnibolotchuk, 1975);
- a significant difference in particle morphology after isothermal and non-isothermal (involving cooling cycles) formation; in the latter case, particles are larger in size and more perfect structurally with the narrower melting temperature range to evidence that (Klenina et al., 1970, 1972; Klenin et al., 1974bc; Klenina, 1977);



Figure 6.7. Liquidus curve of the PVA+water system. The points are calculated using the data of Klenin et al. (1974c), Klenina (1977) (1), and Klenin et al. (1973c) (2); the melting temperature of PVA crystallites (3) is the average value on evidence of Pritchard (1970)

- w, wt %
- high sensitivity of the particle parameters during particle formation to external impacts, even such as the volume and shape of the vessel, rocking or shaking up the vessel, etc. (Klenina et al., 1972);
- dependence of the induction period of formation on SMP initial level parameters, this initial level playing the role of seeds (Klenin and Klenina, 1971b; Klenin et al., 1974bc; Klenina, 1977).

As a rule, after preparing PVA aqueous solutions, they always contain SMPs which are fragments of the most perfect crystallites of the polymer. Due to their presence (it means the initial level of supramolecular organization—SMO) the formation (crystallization) of new SMPs proceeds almost with no induction period. If a solution is somewhat freed of SMPs (by filtration, ultracentrifugation, melting, etc.), the induction period rises up to several days (under static conditions) (Klenin and Klenina, 1971b; Klenin et al., 1974c; Klenina, 1977).

Three structural levels of SMO have been discovered and studied in the system PVA+water (Klenin et al., 1966, 1973abc, 1974bc; Klenina et al., 1970; Kolnibolotchuk et al., 1970; Klenina, 1977).

The first level: SMPs which remain in solution on dissolving the greater part of the polymer under given conditions.

The **second level** is formed during storage of solutions, its degree of evolution depending on temperature, concentration, and the structural features of the polymer.

The SMPs, that have appeared in solution at a high temperature ($\geq 80^{\circ}$ C), are aggregated on cooling into anisodiametric structures which are very sensitive to temperature variations. They define the **third level** of SMO (Klenin et al., 1974bc).

The parameters of the first (initial) SMP level do not depend on polymer concentration when $c \ge 3 \text{ g/dl}$. If $c \le 3 \text{ g/dl}$, the size of SMPs decreases, and, at a certain concentration c_l (0.5...0.8 g/dl in accordance with polymer molecular weight), the particles dissolve. There are no SMPs in solution when $c \le c_l$ (Klenin et al., 1973c, 1974bc).

Preparing solutions with concentrations $c \leq c_l$ allowed us to obtain **molecular** aqueous solutions and to measure the molecular and thermodynamic properties of PVA in water by the Debye-Zimm classical light scattering method (Klenin et al., 1973c, 1974bc).

It should be specially noted that PVA aqueous solutions in the presence of SMPs are not practically amenable to clearing to the molecular degree of disperse. On filtering, SMPs bridge the pores of filters, and the pressure rising leads to hydrodynamic effects and, further, to the emergence of new SMPs and even macrostructures (fibrilles, flakes, etc.). Centrifugation is also of limited use for removing SMPs due to their relatively small sizes (in any case, for the smallest fraction). In the absence of SMPs (as a result of their dissolution or melting), clearing solutions from dust and other particles proves to be effective even with simple filtration through Shott's and membrane filters (Klenin et al., 1973c, 1974c).

On evidence from classical light scattering, PVA aqueous solutions show an interesting feature: an extremal (with a minimum) temperature dependence of the second virial coefficient ($\mathcal{A}_2 = \mathcal{A}_2(T)$) and, correspondingly, a dependence with a maximum for $\chi_1 = \chi_1(T)$ (Figure 6.8).

In essence, such a dependence $\chi_1 = \chi_1(T)$ concerns that shown in Figure 3.81c so as $\chi_1 = \chi_1(T)$ (g = g(T)) (Figure 3.81b) concerns $\chi_1 = \chi_1(T)$ (Figure 3.81a).

In the second case, a slight increase in g_{01} from Equation 3.6-85 will lead to g(T) not intersecting g = 0.5 and to no θ point in the system: the phase separation region looks like a sand-glass (Figure 3.81b). In Figure 3.81c, the constant g_{01} decreases so that g = g(T) does not intersect g = 0.5, and the system has no θ point as well, but, this time, it is owing to the absence of the phase separation region. This is the case with the system PVA+water (Figure 6.8).

The dependence $\chi_1 = \chi_1(T)$ (curve 1, Figure 6.8) was obtained from the experimental one $\mathcal{A}_2 = \mathcal{A}_2(T)$ (Klenin et al., 1974b) according to Equation 3.1-52. In calculating the temperature dependence of the water partial molar volume V_{01} (Eisenberg and Kauzmann, 1969) and of the PVA specific partial volume v_2 (Sakurada et al., 1965) were taken into account.

The values $\chi_1 = \chi_1(T)$ (curve 2, Figure 6.8) were calculated in view of the function h(z). Equation 3.1–158 allowed us to determine zh(z) and, then, h(z) using the plot in Figure 3.5 and χ_1 using Equation 3.1–147 (Klenin, 1985).

The unperturbed coil sizes of PVA were evaluated from $K_{\theta} = 16.2 \cdot 10^{-4} \text{ dl/g}$ (Klenina, 1977) (see Equation 3.6 72) which, in its turn, was found in (Klenina, 1977) from $[\eta]$,



Figure 6.8. Temperdependence ature of the second virial coefficient A_2 in PVA aqueous solutions, $M_w = 85,000$ (Klenin et al., 1974b) curve 1: the χ_1 values calculated according to Equa-3.1 - 52tion and approximated by the formula 0.8033 -= χ_1 57/T - 0.000421T;curve 2: those calculated from \mathcal{A}_2 with a correction for molecular weight with the approximation $\chi_1 = 1.1103 -$ 113/T - 0.00085T(Klenin, 1985); the κ_1 and ψ_1 values calculated from curve 2 with Equation 3.1 43, 3.1 44. T is in K in the equations and in °C on the plot. The χ_1 data are from Sakurada et al. (1965) (3), Ogosawa et al. (1976) (4), Peppas et al. (1976) (5)

[The data gotten from: V.J.Klenin, O.V.Klenina, B.I.Shvartsburd, S.Ya.Frenkel. J. Polym. Sci. Symp. 44 (1974) 131-140. Copyright © 1974 by John Wiley & Sons, Inc.; I.Sakurada, T.Nakajima, I.Shibatani. Makromolek. Chem. 87 (1965) 103-118. Copyright © 1965 Hüthig & Wept Publishers, Zug, Switzerland; K.Ogosawa, T.Nakajima, K.Yamaura, S.Matsurawa. Coll. and Copym. Sci. 254 (1976) 553-558. Coipyright © 1976 Steinkopff Publishers, Darmstadt, FRG; N.A.Peppas, E.W.Merril. J. Polym. Sci.: Polymer Chem. Ed. 14 (1976) 459-464. Copyright © 1976 by John Wiley & Sons, Inc.]

 M_w , and A_2 by means of the Kriegbaum (1958) semiempirical relationship

$$[\eta]_{\theta} = [\eta] - 3 \frac{134}{105} \left(\frac{3}{2\pi}\right)^{3/2} \frac{\Phi_{\theta}}{N_A} \mathcal{A}_2 M_w \simeq 5 \cdot 10^3 \mathcal{A}_2 M_w$$

and

$$[\eta]_{\theta} = K_{\theta} M^{1/2}$$

Klenina (1977) notes that this K_{θ} value is in good agreement with other, independent estimations (eg. see (Matsuo and Inagaki, 1962b)).

The temperature dependences $\kappa_1 = \kappa_1(T)$ and $\psi_1 = \psi_1(T)$ were calculated by Formulae 3.1-43, 3.1-44 from $\chi_1 = \chi_1(T)$ using curve 2. The dependence $\chi_1 = \chi_1(T)$ (curve 2 corrected for h(z)) is approximated by a Koningsveld-type formula 3.6–85 (Klenin, 1985):

$$\chi_1 = 1.1103 - \frac{113}{T} - 0.00085 \, T. \tag{1}$$

Figure 6.8 shows also literature data on the temperature dependence $\chi_1 = \chi_1(T)$ obtained from experiments with the system crosslinked PVA+water (Sakurada et al., 1965; Ogosawa et al., 1976; Peppas and Merrill, 1976). Sakurada et al. (1965) and Peppas and Merrill (1976) have crosslinked the polymer with α - and β -radiation, respectively. Ogosawa et al. (1976) have employed, as crosslinks, polymer crystallites which appeared in PVA aqueous solutions at a concentration 5...10 wt % during 24 hours with temperature fixed within 0-60°C.

Calculation of χ_1 was performed (Sakurada et al., 1965) by Relationship 3.5–84 with $\chi_1 = 0.494$ at $t = 30^{\circ}$ C (the cross-containing box on curve 3, from data on osmotic pressure-- see subsection 3.6.2) accepted as a reference point of χ_1 for preliminary evaluation of ν_c/V_0 . The concentration of an atactic PVA sample with $M_\eta = 136,000$ varied within $v_2 = 0...0.3$, where χ_1 was considered as independent from polymer concentration according to the data on vapour pressure over solutions (Sakurada et al., 1959) (see subsection 3.6.2). Peppas and Merrill (1976) calculated χ_1 within 0-90°C and $v_2 = 0.03...0.12$ by an equation like Equation 3.5-84.

In (Ogosawa et al., 1976), χ_1 was calculated by Formula 3.5-85, and the ratio V_0/ν_c by the Flory (1953) formula for the network modulus μ (Equation 3.5-50). The polymer concentration ($M_\eta = 123,000$, the content of sindiotactic diades 60.9%) varied within 13.6...17.6 wt %.

There is qualitative agreement between curves 1 and 3 in Figure 6.8 in a limited temperature range (the left-hand branch of $\chi_1 = \chi_1(T)$) because of differences in molecular weight of PVA samples and possible differences in other details of molecular structure.

Moreover, $M \to \infty$ should be accepted for any network polymer, but in (Sakurada et al., 1965; Ogosawa et al., 1976; Peppas and Merrill, 1976) no correction for molecular weight (h(z)) was provided.

The extremal dependence $\mathcal{A}_2 = \mathcal{A}_2(T)$ $(\chi_1 = \chi_1(T))$ corresponds to the data of Shibatani and Oyanagi (1976) concerning amorphous separation in the system vinyl alcohol ethylene copolymer (6...13 mol % of ethylene units - E)+water with a closed separation region like that shown in Figure 3.81c.
Interpolation of the dependences $\theta_{UCST} = f(E)$ and $\theta_{LCST} = f(E)$ brings the curves to intersect at the point with $E \simeq 3 \mod \%$ within the range 80–85°C. Hence, the system copolymer+water with $E < 3 \mod \%$ up to the homopolymer (PVA) no longer has the θ point. From these data, the system PVA+water should be expected to show a positive value of A_2 over all the temperature range ($T < 200^{\circ}$ C) with a minimum at about 80-85°C, which has been confirmed experimentally (Figure 6.8).

Besides, the closed phase separation region of the system copolymer+water is extrapolated at $E \rightarrow 0$ to a point $T \approx 80~90^{\circ}$ C and $c \approx 2...3\%$.

Experimental data on the concentration dependence $\chi = \chi(c)$ for the system PVA+water (their summary is given by Peppas and Merrill, 1976) are very conflicting. On these data, the dependence $\chi = \chi(c)$ within c = 3...12 vol % is like the left-hand branch of the extremal curve in the temperature range 10 90°C, but the χ values are quite large.

On the same data, a very strong temperature dependence $\chi = \chi(T)$ was obtained (curve 5 in Figure 6.8).

Therefore, on Shibatani's and Oyanagi's (1971) evidence, as on our own data, the system PVA+water is a degenerated version of systems with a closed amorphous separation region and minimal solution stability (a maximum of χ) at the configurative point $T = 90^{\circ}$ C and $c \approx 2...3$ % for $M \approx 100,000$, i.e. PVA aqueous solutions are thermodynamically stable with respect to amorphous separation when $T < 200^{\circ}$ C and over all the concentration range. This emphasizes once again that the new phase particles formed in the system are of a crystal nature.

An amorphous separation region with a LCST is discovered in the system PVA+water at high (above 200°C) temperatures (Andreyeva, 1969), so more generally, the system is described by a state diagram like that shown in Figure 3.92b with the degenerated closed separation region.

All the published experimental facts find their explanation on the strength of the presented data on the character of phase separation in the system PVA+water, including those serving as the reason to accept the existence of an amorphous separation region with an UCST about 80°C.

The inferences of Kormanovskaya (1967), Kormanovskaya et al. (1968), and Tager et al. (1971) about amorphous separation within 20-80°C and the increase of solvent power of water, based on studying polymer swelling in water and water vapour adsorption, are related to neglecting the dependence of swelling degree and water vapour sorption on the crystallinity degree of a polymer sample (Takizawa et al., 1968).

With a high relative humidity, partial fusion of crystallites (Takizawa et al., 1968) acting as crosslinks occurs even at room temperature, and a long-term treatment of PVA with water vapour will lead to an additional crystallization (Pricst, 1951) (the effect of annealing).

In any case, the degree of crystallinity may vary with keeping PVA in water vapour and may affect sorption significantly. On thermostating PVA with water, its crystallinity degree influences polymer swelling and redistribution among the layers. Restricted PVA swelling in water and the increase in swelling degree with temperature (Kormanovskaya, 1967; Kormanovskaya et al., 1968; Tager et al., 1971; Shakhova and Meyerson, 1972) are related to fusion of a part of crystallites-crosslinks as temperature increases. Thus, the increase in swelling degree is due to the decrease in the number of crosslinks despite the thermodynamic power of water getting worse, i.e. the former effect takes preference over the latter one.

The same feature explains the fact of polymer dissolution at higher temperatures. At room temperature, crystallites keep the polymer from dissolution like fasteners, but its swelling takes place (the maximal value of \mathcal{A}_2). On heating, crystallites melt and let the polymer dissolve though the thermodynamic power of water is getting worse at high temperatures. The most complete fragments of crystallites remain in solution, forming the first level of SMO. On the other hand, vinyl alcohol copolymers with vinyl acctate (10...12 mol % of acetate units) dissolve well at room temperature in the nearest vicinity of the closed region of phase separation due to the absence of crystallites in the copolymer: outsize acetate units are not incorporated into the crystal lattice.

Recall that the experiments, where PVA aqueous gels swelled with a fixed number of crosslinks, showed the thermodynamic power of water getting worse with increasing temperature (Figure 6.8).

The left-hand branch of $\mathcal{A}_2 = \mathcal{A}_2(T)$ confirms the data of Amaya and Fujishiro (1953), Dieu (1954), Matsuo and Inagaki (1962ab), Dmitrieva et al. (1971) on the thermodynamic power of water getting worse with raising temperature, except some extrapolation techniques (Dieu, 1954; Dmitrieva et al., 1971) for the evaluation of θ_{LCST} . The system PVA+water taken as an example demonstrates that great care should be taken in such extrapolations.

In subsequent works (Halboth and Rehage, 1974), the crystal nature of phase separation in the system PVA+water has been confirmed, even using X-ray analysis.

Budtov et al. (1974, 1976ab, 1978), Budtov and Domnicheva (1978) have determined the parameters of supramolecular particles in PVA aqueous solutions by a new technique of flow birefringence, and have come to the conclusion that they are of a crystal nature. This approach (Budtov et al., 1976a, 1978, Budtov and Domnicheva, 1978) undoubtedly deserves attention and consideration of its peculiar features. The matter is that the hydrodynamic field is a factor which will certainly affect phase separation. This is particularly true for crystallization.

On the other hand, the method of flow birefringence, of course, allows one to study how the hydrodynamic field influences the formation of the new phase particles. Besides, difficulties arise in data interpretation using this method. The effect of flow birefringence in a system with colloidal particles, measured by the method traditional for polymers, has several components as in the case of macromolecules: the proper anisotropy of particles, the effects of macro- and microforms (Tsvetkov et al., 1964), and **conservative dichroism**, i.e. the light scattering efficiency factor K of oriented anisodiametric, anisotropic particles differs in different observation planes (Onuki and Doi, 1986; Khlebtsov, 1988ab; Khlebtsov and Melnikov, 1990).

In (Budtov et al., 1976a, 1978; Budtov and Domnicheva, 1978) conservative dichroism is not considered, and it is difficult to expect quantitative agreement with other methods of parameter determination.

It is natural that the method of flow birefringence does not detect particles of the first organization level in PVA aqueous solutions (Budtov et al., 1976b) as they possess almost a spherical form.

This example of the identification of the thermodynamic stimulus of phase separation

in the system PVA+water reveals some difficulties in phase analysis of polymer systems when traditional methods may prove to be low-sensitive due to the colloidal level of the new phase as well as to the structural imperfection of the crystal phase. In such cases, new methods and new approaches are needed, some of them have been already discussed in this section.

Blinas et al. (1976) presented another example of an effective application of the turbidity spectrum method for finding the crystal stimulus of polyamidimide solution in dimethylformamide aging.

Anomalies of molecular light scattering, discovered in polyamidoacid and polyimide solutions in dimethylformamide and dimethylacetamide at concentrations $c > c_l \approx 0.5$ g/dl (Diakonova et al., 1986) are apparently related to the presence of crystallites. The absence of scattering asymmetry ($I_{45^{\circ}}/I_{135^{\circ}} \approx 1.1$) attests to the small sizes of these particles.

The configurative point intersecting the liquidus curve on a decrease in polymer concentration (along the isotherm) leads to crystallite dissolution at $c < c_l$ and the solution shows the typical properties of molecular scattering.

6.3. Mixed types of phase separation

Mixed types of phase separation are observed in polymer systems as well as in lowmolecular ones (Richards, 1946; Malcolm and Rowlinson, 1957; Papkov and Yefimova, 1966; van Emmerik and Smolders, 1971, 1973a; Ogawa and Hoshino, 1971; Papkov, 1972; Saeki et al., 1976; Tager et al., 1976c; Uskov et al., 1976; Kulichikhin et al., 1978; Kjellander and Florin, 1981).

Generally speaking, for a crystallizing polymer, the liquidus curve may be located on the state diagram together with the liquid-liquid phase separation region of any kind from the existing ones (see Figure 3.81 and 3.92).

For some systems, the liquid-liquid and liquid-crystal phase separation regions are separated on the state diagram; this is the case, for instance, with the system poly(ethylene oxide)+water (Malcolm and Rowlinson, 1957; Saeki et al., 1976; Uskov et al., 1976; Kjellander and Florin, 1981) (Figure 6.9).

A mutual overlap of phase separation regions of different thermodynamic nature occurs in a number of systems (Figure 6.10).

Overlapping regions of liquid-liquid (UCST) and liquid-crystal phase separation were discovered for isotactic polypropylene in some solvent+precipitant mixtures (Ogawa and Hoshino, 1971).

Another example of the superposition of phase separation regions of different nature is shown in Figure 6.11 (Koningsveld, 1975).

In particular, there exist three phases in equilibrium in this system at the temperature T_2 : two liquid and one crystal phases while at the temperature T_E two crystal phases and one liquid one are present.

A special classification for the systems P+LMWL has been proposed by Papkov and Yefimova (1966) and Papkov (1971), using the mutual location of phase separation regions of different nature.



Figure 6.9. State diagram of the system PEO+water: liquid-liquid separation-M =5,000 (1), M = 3,000 (2); liquid-crystal separation -M = 5,000 (3), M = 3,000 (4) (Malcolm et al., 1957) [Reprinted with permission from: G.N.Malcolm, J.S.Rowlinson. Trans. Faraday Soc. 7(415) (1957) 921-931. Copyright © 1957 by the Royal Society of Chemistry]

Figure 6.10. State diagram of the system polyethylene+LMWL (nitrobenzene (1), amyl acetate (2), xylene (3)) (Richards, 1946) [Reprinted with permission from: R.B.Richards. Trans. Faraday Soc. 42 (1946) 10-20. Copyright \bigcirc 1946 by the Royal Society of Chemistry].

The identification of mixed types of phase separation in polymer systems causes great difficulties. Important information for phase analysis of a system with a mixed type of phase separation regions can be given by differences in the kinetics of phase separation of different nature.

With due allowance for high rate of liquid-liquid phase separation, Papkov (1971, 1981) develops a concept of mutual independence of phase separation of different nature.



Figure 6.11. Superposition of the liquid-liquid and liquid-crystal phase equilibria in a binary system and the corresponding isotherms $\Delta G_m/RT$. Equilibrium of three phases of different nature: two liquid phases and one crystal one $(T = T_2)$, and two crystal phases and one liquid one $(T = T_c)$ (Koningsveld, 1975) [Reprinted from: R.Koningsveld. Brit. Polym. J. 7 (1975) 435-458. Copyright © 1975 by Wiley. Reprinted by permission of John Wiley & Sons, Inc.]

6.4. Phase analysis of the system poly(ethylene oxide) + water

The following details of phase separation in the system PEO+water indicate how difficult it is to identify phase separation in polymer systems.

By the state diagram (Figure 6.9), one could expect that molecular PEO solution in water can be obtained without great difficulties within $0-90^{\circ}$ C and 0...5 wt %. However, even under the most optimal conditions of PEO dissolution in water, the SMPs remain which parameters depend on the sample dissolved and the way of dissolution. Visually, such solutions are transparent with SMPs being detected by means of the turbidity spectrum method with a photoelectric colorimeter or a spectrophotometer.

Studies have shown SMPs to be of crystalline nature and to be fragments of polymer crystallites, whose structure, in its turn, depends on the ways of synthesis, subsequent treatment, and polymer storage.

The liquidus curve on the state diagram (Figure 6.9) was obtained by using DTA

and, therefore, concerns the main amount of polymer, while the existence of the most perfect crystallites is beyond the capabilities of the method, apparently due to their small content. Meanwhile, these crystallites and their fragments may significantly affect the properties of PEO aqueous solutions. First, their presence in solution causes some methodical difficulties in determining the molecular and thermodynamic parameters of the polymer by means of classical light scattering and other methods sensitive to SMPs. Indeed, such data are lacking essentially in the literature. Second, the presence of SMPs in PEO aqueous solutions may change their performance concerning filling in oil pools with water (in secondary oil production), lowering water hydrodynamic resistance in turbulent flows etc. Third, these crystallites act as crosslinks hindering the polymer dissolution even in the case of rather dilute solutions at usual temperatures. They remain in the solution after the usual macrodissolution of a polymer sample when the solution looks homogeneous.

That is why it is reasonable to introduce another liquidus curve responsible for SMPs in solution along with the "macroliquidus" curve related to the main amount of polymer. Such "microliquidus" curve has been obtained by the turbidity spectrum method while measuring SMP dissolution rate v_d as a function of temperature and PEO concentration (Figure 6.12).





Extrapolation of the dependence $v_d = v_d(T)$ to $v_d = 0$ at a given concentration c gives a limit temperature of SMP dissolution. A set of such temperatures evaluated within a certain concentration range will lead to the "microliquidus" (liquidus-2) (Figure 6.13).

One can see that the liquidus 2 curve is significantly shifted towards small concentrations and high temperatures, which attests to a much more perfect structure of SMPs in comparison with the bulk amount of crystallites.

Practically, the liquidus 2 curve is the line on the state diagram under which SMPs do not dissolve, but no new ones are formed because some are already present in the system. But if the existing SMPs are melted or ultracentrifuged, the new ones will be formed under the liquidus-2 curve. Above it, the SMPs melt over a very wide temperature range, including the amorphous separation range, which is of interest in connection with the superposition of several phase separation regions of different thermodynamic nature. Relaxation times of amorphous phase separation are very small and cannot be measured with traditional methods. On the contrary, those of crystalline particles seem huge (a few days).



Figure 6.13. Liquidus curves in the systems PEO+water (1-4) and PEO+diethyl cebacate (5) obtained by DTA (1, 2, 5) and turbidity spectrum analysis (1). $M_{\eta} = 1 \cdot 10^6$ (1, 1), $4 \cdot 10^4$ (2), $3 \cdot 10^3$ (3), $5 \cdot 10^3$ (4) by Jain and Swinton (1967) (5) [Reprinted from: N.J.Jain, F.L.Swinton. Europ. Polym. J. 3 (1967) 371-378. Copyright © 1967 with kind permission of Elsevier Science — NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands], Malcolui et al. (1957) (3, 4), Klenin et al. (1987) (1, 1', 2). Amorphous phase separation region in the system PEO+water (Klenin et al., 1987). $M_{\eta} = 1 \cdot 10^6$ (a). Curve 1' is scaled up (b)

In view of the character of the state diagram in Figure 6.13b, one can explain the complex dependence of turbidity in the system PEO+water with raising temperature and subsequent cooling (Figure 6.14).

The smooth turbidity fall is related to crystalline melting in a wide temperature range. As the configurative point has intersected the binodal, liquid-liquid phase separation proceeds practically at once, which can be fixed just visually (the system grows very turbid). At the same time, the SMPs as crystalline particles continue to melt. After an insignificant decrease in temperature sufficient to withdraw the configurative point out of the amorphous separation region, the heterogeneous regions of amorphous separation disappear, and the system gets transparent. Incidentally, the SMPs prove to be partially melted and the more so the longer the system has stayed at a high temperature in the amorphous separation region (Figure 6.14).

These combined phase transformations are distorted by PEO macromolecule destruction, and the liquid-liquid phase separation region then shifts towards higher temperatures.

These observations also count in favour of the independence of the amorphous and



Figure 6.14. Temperature dependence of turbidity in the system PEO+water at polymer concentrations 1.0 (1) and 0.1 g/dl (2), $M_{\eta} = 10^{6}$) (Klenin et al., 1988)

crystalline phase separations.

Thus, when the configurative point is above the liquidus-2, the particles, which are fragments of the most perfect crystallites of the source polymer sample, dissolve. Their parameters (sizes, numerical and weight-volume concentrations) depend on the quality of the polymer sample, and, mainly, on the duration of its storage. The matter is that the polymer is usually kept overcooled with respect to the liquidus-1 and crystallizes, which leads to an increase in particle concentration after dissolution of the bulk of the polymer.

Hence, the liquidus-2 characterizes particles formed in a polymer sample in an uncontrollable way: during polymer extraction from solution after synthesis, then, in the course of its drying, storage, etc. owing to the configurative point's motion under the liquidus 1 curve and its staying there during the storage of the air-dried (5-8% of water) polymer sample.

Under the liquidus-2, particles will remain infinitely long, which should be taken into account when PEO aqueous solutions are used in practice, or studied by methods sensitive to the presence of these particles in solution (such as light scattering, flow birefringence, etc.), the more so as the liquidus-2 is in the range of polymer-diluted compositions (2 6 wt %). The liquidus-2 is found to have a more general thermodynamic meaning, as during the motion of the configurative point under its curve, new particles of the crystalline type are formed. However, the system must preliminary be cleaned from particles of the initial supramolecular level by centrifugation or long-term storage at any configurative point to the left of the liquidus 2.

Klenin et al. (1988) drove the configurative point under the liquidus 2 along the isotherm $T \sim 25^{\circ}$ C from left to right, i.e. by means of concentration of the polymer solution.

As the configurative point penetrates deep into the phase separation region (polymer concentration rises), particles of the new phase are formed, their concentration increases, and the particles grow larger (Figure 6.15, curve 1).

For comparison, this figure reports the parameters of particles that remained in the system after dissolution of the greater part of the polymer (c = 2 g/dl) and subsequent dilution (Figure 6.15, curve 2). Curve 3 relates to the parameters of particles that re-



Figure 6.15. Formation of the new phase particles after concentrating PEO aqueous solutions $(M_{\eta} = 3.5 \cdot 10^6)$ (1) in comparison with particle dissolution on diluting the solution with c = 2 g/dl (2) and with the parameters of particles which remain in the system after the greater part has dissolved at a given concentration (3). τ/c is the reduced turbidity at $\lambda = 546$ nm, \bar{r}_{λ} is the mean particle size (Klenin et al., 1988)

mained in the system after the bulk of the polymer had dissolved at a given (fixed) concentration. Clearly, the parameters of particles in the three mentioned versions are in good agreement.

The proximity of the concentration, where $\tau \rightarrow 0$ (the absence of particles within the limits of experimental accuracy), when either dilution (the configurative point moves from right to left) or concentrating (backwards) means the proximity of a fixed liquidus 2 point to its equilibrium value. Thus, two phases coexist within a large area of the state diagram (to the right of the liquidus-2), namely, polymer solution and crystallites (a small fraction—polymer). These crystallites apparently do not affect measurement of intrinsic viscosity but significantly hinder (or even prevent) employing the classical methods of light scattering and flow birefringence.

The existence of these particles may influence the performance of the system used as a thickener, an active agent in filling in oil pools, or for lowering hydrodynamic resistance in turbulent flows.

In the hydrodynamic field, the liquidus-2 curve drifts to the left (by concentration) by three decimal orders (Klenin et al., 1993).

The SMP properties in solutions of crystallizing polymers, which have been discussed in this chapter, can be explained in a rather general context. It follows that a similar morphological crystallite fraction is likely to be characteristic for systems crystallizing polymer+LMWL of a more general type (Klenin et al., 1991).

Chapter summary

1. With the mean field approximation, the better the thermodynamic power of a solvent, the greater the depression of temperature of the crystallites melting in the system crystallizing polymer+LMWL.

2. Traditional methods of the structural analysis of crystalline solids are used to study the structure of polymer crystalline forms.

However, the imperfection of crystalline structure and the colloidal degree of dispersion of the crystalline phase may cause significant difficulties in the identification and study of the properties of this phase.

6. Chapter summary

In this connection, a new approach in the phase analysis of polymers based on the use of the turbidity spectrum method as a structural one in terms of physico-chemical analysis is proposed.

3. Applying this approach to the phase analysis of the system poly(vinyl alcohol) (PVA)+ water has shown supramolecular particles (SMPs) formed in this system in a wide temperature and composition range to be of a crystalline nature.

Three levels of the crystallite organization are reported.

The SMPs which remain in the system on dissolution of the bulk of the polymer belong to the first level.

The second level of the supramolecular organization (SMO) is formed in a wide temperature and composition range and the degree of its morphological perfection depends on the formation conditions.

The SMPs, appearing in the system at high temperatures (> 80°C) after cooling, aggregate into anisodiametric structures of the third SMO level. The structural transition 3rd level \leftrightarrow 2nd one, connected with the SMP aggregation \leftrightarrow deaggregation, proceeds with a small relaxation time which can not be fixed with the common equipment. As the transition 3rd \leftrightarrow 2nd levels of SMO is accompanied with a significant turbidity change, the system PVA+water (in this structural modification) is a sensitive temperature indicator with a small response time.

Due to the anisodiametric shape of SMO third-level particles, the system is expected to show the properties of liquid crystals.

4. Applying other methods, Debyc-Zimm classical light scattering in the first place, has shown the system PVA+water to have no amorphous separation region below 200°C.

The state diagram of the system PVA+water can be represented as a couple of two melting lines (macro- and microliquiduses) with lines χ_1 being parallel to the abscissa axis, that represent extremal dependences along the temperature axis with a minimum near 80°C (for $M \approx 100,000$), if χ_1 is considered not to depend upon the polymer concentration in solution. Otherwise, the concentration dependence of χ will superpose on its temperature one.

As the maximal value χ_{max} does not reach 1/2, the system has no θ point and, hence, has no amorphous separation region.

The state diagram of the system PVA+water presented here explains all its properties known to date.

5. The systems "copolymer of vinyl alcohol with hydrophobic ethylene or acetate units"+water show a closed region of the amorphous separation with the centre at $T \approx 80^{\circ}$ C, $c \approx 2...3\%$ of the polymer. Due to the absence of crystallites, solvates (copolymers of vinyl alcohol with 8...12% of acetic groups) dissolve well in water at room temperature (below the closed binodal).

6. In polymer systems (as well as in low-molecular-weight ones), mixed types of phase separation can be observed, namely, crystalline and amorphous. In principle, for the system crystallizing polymer+LMWL the liquidus curve can be combined with the amorphous separation region of any kind. On the state diagram, the separation regions of both the crystalline and amorphous type can either be separated spatially or superposed to each other.

7. Owing to the significant difference in the phase separation rates, a mutual inde-

8. A complex pattern of phase equilibria (involving crystal solvates) is characteristic for systems crystallizing polymer+LMWL with strong interactions between LMWL molecules and single groups of the polymer.

9. Due to the independence of the phase separation of two types in the system poly(ethylene oxide) (PEO)+water, the phase separation of the amorphous type proceeds at a high rate, while under the same conditions crystallites melt very slowly.

10. Using the systems PVA+water, PEO+water, etc. as model ones, a new morphological form of crystalline particles being in equilibrium with a dilute solution (liquidus-2) has been revealed.

The fraction of these crystallites amounts to a small part of the polymer (less than 0.1%) and can have no effect on the intrinsic viscosity as well as on some other properties of the solution, but essentially breaks the method of classic light scattering and of flow birefringence of solutions of crystallizing polymers.

These particles can also influence the service properties of solution, which are sensitive to the presence of supramolecular particles there.

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