CHAPTER 3

EQUILIBRIUM

3.1 Introduction

In this chapter, we introduce the important idea of *equilibrium*, and some new properties which tell us about equilibrium. We discuss how to measure two of these properties (pressure and temperature), and conclude with some observations about thermodynamic equilibrium states of matter.

3.2 Equilibrium

It's a universal observation that any real system, if left alone for enough time, reaches a state where the macroscopic properties stop changing. If a ball is dropped onto the floor, it will bounce for a while but eventually it will sit motionless. If a drop of dye is placed in a glass of water, the dye will slowly diffuses away until the dye concentration is the same everywhere in the glass, after which no further change is observed. If a fluid is stirred and then left alone, the motion will eventually cease, due to viscosity. We call the motionless, unchanging state a physical system approaches at long times the *equilibrium state*.

The word equilibrium is defined as "a state of balance between opposing forces or actions."¹ When a physical system is in an equilibrium state, every part of it is in balance (equilibrium) with every other part. There is no net transfer of matter or energy between any two parts of the system. The balance is dynamic, since molecules may leave one region and enter another (in a liquid or gas), but the same number must be going the opposite direction, since otherwise there would be a net transfer of molecules.

Some idealized systems studied in introductory physics courses do not approach equilibrium states. Perfectly elastic balls keep bouncing forever, objects sliding across frictionless tables don't slow down, and a mass hanging from a frictionless spring will oscillate forever. But the motion of every *real* object is subject to non-zero friction or drag forces. No matter how small these forces are, they will eventually cause the object to stop moving and come into equilibrium.

¹Webster's New Collegiate Dictionary



Figure 3.1: Diffusion of a drop of dye in water.

A general characteristic of equilibrium states is that they are much simpler to describe than non-equilibrium states. For example, to describe the state shortly after a drop of dye has been introduced into a glass of water requires specifying the concentration $C(\mathbf{x})$ throughout the glass. Once equilibrium has been achieved, it is only necessary to know how much dye was added to fully specify the state.

The dye/water example illustrates another characteristic of equilibrium states: they depend only on "intrinsic" factors (the amount of dye in this case), not one the time history of the non-equilibrium states which preceded it. In general, the characteristics of systems in equilibrium states depend on intrinsic factors such as the volume available to the system, the energy and mass it contains, and its chemical composition. They do not depend on the time-history of how the state was prepared. Any substance which has properties which depend on past processing history is not in an equilibrium state. For example, the properties of glass depend on the *rate* it is cooled from the molten state. Therefore, glass is not an equilibrium state.

Thermodynamics deals primarily with the properties of matter in the simpleto-describe equilibrium states. To describe matter in non-equilibrium states, we would have to supplement thermodynamics with results from the theories of fluid mechanics, diffusion, heat conduction, electromagnetics, or other areas of physics beyond the scope of thermodynamics. The nature of these states and how they evolve with time is the subject of courses in these other fields.

Although the restriction to equilibrium states seems drastic, it's really not so bad. In many processes, a system begins and ends in an equilibrium state, even if it passes through non-equilibrium states during the process (for example, rapid exansion of a gas). Since the First Law only requires evaluation of $\Delta U = U_f - U_i$, in many cases we only need to evaluate properties (e.g. U) in equilibrium states.

We can define several different types of equilibrium, depending on what type



Figure 3.2: Mechanical equilibrium: the piston moves until $P_A = P_B$.

of "force or action" is in balance within a system. For every type of equilibrium, we would like to define some property which can be used to determine if two parts of a system are in equilibrium. In the following sections, various types of equilibrium, and the properties associated with each type, will be discussed.

3.2.1 Mechanical Equilibrium

Suppose a cylinder is divided in two parts (A and B) by a piston, which can move back and forth (Fig. 3.2). The piston is initially locked rigidly in place and some gas is added to each side of the cylinder. The piston is now unlocked, and oscillates back and forth a while. Eventually, friction or viscous forces damp out the piston motion, and it will stop, though perhaps not at its initial position. Once it has stopped, we say A and B are in *mechanical equilibrium* with each other.

If the piston is stationary, the force must be the same on both sides. Therefore, $P_A = P_B$ if A and B are in mechanical equilibrium. Pressure is seen to be the property which tells us if two adjacent parts of a system are in mechanical equilibrium with one another.

3.2.2 Thermal Equilibrium

Consider now two systems connected by a rigid wall which can conduct heat (Fig. 3.3). (We say they are in "thermal contact.") When they are placed in thermal contact, energy may transfer through the wall as heat, but eventually no *net* energy transfer will occur. When this condition is reached, the two systems are in *thermal equilibrium*.

What property tells us if two systems are in thermal equilibrium? It's clearly



Figure 3.3: Thermal equilibrium: heat flows until $T_A = T_B$.

not the energy, since the two systems may have very different compositions and sizes, and so will have different energies even at thermal equilibrium.

We introduce a new property, specifically for the purpose of determining if systems are in thermal equilibrium. We make the following postulate.

Postulate: There exists a scalar property called *temperature* with the following characteristic: two systems placed in thermal contact will be in thermal equilibrium if and only if they have the same value of temperature.

The so-called zeroth law of thermodynamics is the postulate that if A is in thermal equilibrium with B, and B is with C, then A is with C. The zeroth law is equivalent to the postulate that the temperature property exists.

3.2.3 Diffusive Equilibrium

If a dye drop is added to a glass of water, we know that at equilibrium the dye will diffuse throughout the glass. This type of equilibrium is known as *diffusive equilibrium*. We would like to define some property of the water/dye system we could calculate for various regions in the water, to test if they are in diffusive equilibrium.

We might consider using the dye concentration as this property. But this is not a good choice in general, since there are some situations where the concentration is not equal everywhere, even though the system is in diffusive equilibrium. These situations arise if more than one phase is present or if external conservative forces act on the system. For example, in a gasous mixture of heavy and light species in a very tall column, the heavy ones will be preferentially concentrated near the bottom of the column, and the light ones near the top.

We would like a property that can handle even these cases. Not knowing what else to do, let us postulate that such a property exists:

Postulate: There exists a scalar property called *chemical potential* with the following characteristic: two parts of a system will be in diffusive equilibrium if and only if they have the same value of chemical potential.

The chemical potential is given the symbol μ . In situations where multiple chemical species are present, we need to test for diffusive equilibrium for each one, so each will require its own chemical potential. We will show later that μ for a particular species depends on its concentration² and on temperature and pressure. If the system has macroscopic potential energy (e.g. due to gravity), the chemical potential will also depend on the local value of the potential energy. We'll see in Chapter 6 how to calculate the chemical potential.

3.2.4 Phase Equilibrium

If a substance is placed in a sealed container, under some conditions it segregates into separate regions with distinct properties (for example, solid and liquid, or liquid and vapor). We call each region with homogeneous properties a *phase*. When the amount of each phase is constant, the substance is in *phase equilibrium*.

What property tells us when systems are in phase equilibrium? Again it's the chemical potential. Phase equilibrium is similar to diffusive equilibrium, since molecules are moving between the phases, but at equilibrium the rate they move is the same for both directions. For example, in a mixture of ice and liquid water, the rate at which H_2O molecules from the liquid stick onto the solid ice equals the rate molecules detach from the ice and enter the liquid.

The chemical potential of any given phase of a pure substance is some function of T and P. For example, for water there exist two functions $\mu_{ice}(T, P)$ and $\mu_{liquid}(T, P)$. The condition $\mu_{ice}(T_m, P) = \mu_{liquid}(T_m, P)$ determines the temperature where the two phases can co-exist (the melting temperature T_m) for a given P.

 $^{^2\}mathrm{In}$ some cases, it depends on the concentration of other species too.

3.2.5 Chemical Equilibrium

If multiple chemical species are mixed together, they might chemically react. If they do, the concentration of each reactant will decrease, and the concentrations of the products of the reaction will build up. The products may react with one another, too, "reversing" the reaction and re-forming the reactants. Eventually, the concentrations of all species will settle at values such that the forward reaction rate just balances the reverse one. When this happens, the concentrations will no longer change, and we say the system is in *chemical equilibrium*. As we'll see later, the chemical potential is again the relevant property to determine when a system is in chemical equilibrium, although the analysis is more complicated than for diffusive or phase equilibrium.

3.2.6 Thermodynamic Equilibrium

When all parts of a system are equilibrated in all ways (mechanical, thermal, diffusive, phase, chemical), we say the system is in *thermodynamic equilibrium*. The temperature, pressure, and chemical potential will be the same in all parts of a system in thermodynamic equilibrium, and the concentrations of every chemical species will be constant in time.

3.2.7 Restricted Equilibrium

Sometimes a system is kept from attaining one type of equilibrium, although it is equilibrated in other ways. For example, a rigid, heat-conducting partition dividing a system in two parts will allow thermal, but not mechanical, equilibrium to be attained. In other cases, there is no partition but one type of equilibrium is attained very slowly compared to other types. When a system is equilibrated in some ways but not others, we say it is in *restricted equilibrium*.

For example, a mixture of methane and air at room temperature is not in chemical equilibrium, although it may be in mechanical, thermal, and diffusive equilibrium. The reaction

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{3.1}$$

is running very slowly in the forward direction, while the reverse reaction is hardly occurring due to the very low CO_2 and H_2O concentrations. Therefore, some of the methane is continually being oxidized, but the rate is so small at room temperature to be virtually impossible to detect. If the temperature is increased by adiabatically compressing the mixture or a spark is provided, the mixture may rapidly approach chemical equilibrium (it may burn or explode). Almost always the slow component is some type of chemical, phase, or nuclear equilibrium. Examples of substances approaching true equilibrium very slowly include radioactive elements with very long half-lives, any type of glass, or cold-worked steel. In many cases, the slow process is so slow that it may be neglected entirely – the properties of cold-worked steel do not change *measurably* over any practical timescale.

3.3 Pressure and Its Measurement

3.3.1 Hydrostatics

The pressure at any point in a fluid at rest is the same in all directions. If a fluid is contained in a cylinder and you push on a piston to apply a force in one direction, the fluid transmits the force in all directions, so the pressure at the piston equals the pressure on the cylinder walls.

If no external body forces act on a fluid at rest, then the pressure is the same at every point. But in a fluid sitting in a gravitational field, the pressure will depend on height y, due to the weight of the fluid above y.



A force balance on a vertical column of fluid yields

$$P_1 A = P_2 A + Mg. \tag{3.2}$$

Since $M = \rho A(y_2 - y_1)$ (assuming constant density), we find

$$P_1 - P_2 = \rho g(y_2 - y_1). \tag{3.3}$$

Differentiating with respect to y_1 yields

$$\frac{dP}{dy} = -\rho g \tag{3.4}$$

which is the basic equation of *hydrostatics*, and describes how pressure varies with height in a static fluid. Since Eq. (3.4) is a differential equation, it applies even if the density ρ depends on height y, as would be the case if the fluid is a gas. In this case, Eq. (3.3) would be replaced by

$$P_2 - P_1 = -\int \rho(y)g \, dy.$$
 (3.5)

Example 3.1 A dam of length L holds water to depth H. What is the net horizontal force on the dam if L = 200 m and H = 30 m?

Solution: Taking the density of water to be constant at $\rho = 10^3 \text{ kg/m}^3$, the pressure distribution on the dam is

$$P(y) = P_0 + \rho g y, \tag{3.6}$$

where P_0 is atmospheric pressure and y is the distance below the surface. The force due to the water is

$$F_w = L \int_0^H P(y) dy = L(P_0 H + \rho g H^2/2).$$
(3.7)

Since the force due to atmospheric pressure on the other side is P_0LH , the net force is

$$F_{net} = \rho g L H^2 / 2 = 8.8 \times 10^8 \text{ N.}$$
 (3.8)

We have neglected the variation in air pressure with height. Since the density of air is about 1.2 kg/m³, for H = 30 m, $\Delta P_{air} = 345$ N/m², which is much less that P_0 , which is about 10⁵ N/m². If H were several km, then ΔP_{air} would have to be considered.

3.3.2 Manometers

A simple arrangement to measure the pressure of a gas is shown in Figure 3.4. Mercury fills a U-shaped tube of constant cross-sectional area, which is closed on the left and can be connected to a system of unknown pressure on the right. The region on the left above the mercury column is evacuated.³ A device like this is known as a *manometer*.

At the height of the gas/mercury interface in the right-hand column, the pressure is the gas pressure P_{gas} . The pressure in the left-hand column at the same height must therefore also equal P_{qas} . From Eq. (3.3), the pressure at

³Actually it is filled with mercury vapor. But mercury has a very low vapor pressure, and exerts negligible force on the liquid.



Figure 3.4: A manometer.

this location is also ρgh . Therefore, the unknown gas pressure is related to the measurable height h by

$$P_{gas} = \rho gh. \tag{3.9}$$

A different type of manometer can be used to measure the pressure difference between two systems. If instead of evacuating the region above the column on the left we attach it to a system with some pressure P_A , and attach the other side to a system with P_B , then

$$P_B - P_A = \rho g h. \tag{3.10}$$

The SI unit for pressure is the *Pascal*, which is simply the name given to 1 N/m². A standard atmosphere (1 atm) is defined to be 1.01325×10^5 Pa, or 0.101325 MPa. Other common units for pressure are the Torr (1/760 atm or 133.32 Pa), the bar (10⁵ Pa), and lbf/in² or psi (1 atm = 14.7 psi).

Usually, pressure is measured with other, more convenient instruments which may be calibrated against mercury manometers. In some pressure gauges, gas at the unknown pressure enters a curved, flexible tube. The tube tends to straighten as the gas pressure increases, which causes a needle on a dial to move. Another type of gauge, known as a *capacitance manometer*, consists of an evacuated disk-shaped cavity, one side of which consists of a thin, flexible membrane. As the membrane deflects due to external pressure, the capacitance of the disk changes. Since capacitance can be determined very accurately by electrical measurements, capacitance manometers are designed to produce an electrical signal (usually a voltage) proportional to pressure.

Sometimes you will hear a pressure described as a "gauge pressure." This is defined as the pressure difference between the actual pressure and the local atmospheric pressure, and is what is directly measured by some types of pressure gauges.

3.4 Temperature and Its Measurement

3.4.1 Thermometers

To measure temperature, we need some system with an easily-measurable property which changes as its temperature changes (a "thermometer"). A simple thermometer can be constructed by filling a glass tube with some fluid which expands when heated. Mercury is again a convenient choice. The tube is marked at the mercury level corresponding to some reference temperature (maybe the freezing point of water), and marked again at another reference temperature (maybe the boiling point).

The interval between the two marks is then divided into an arbitrary number of equal segments, and the mark the mercury rises is used as the measure of temperature. The marks could be assigned numbers, but letters, names, or any other symbols would work too. The Fahrenheit temperature scale assigns the values 32 and 212 to the freezing and boiling points, respectively, of water at a pressure of 1 atm. The Celsius scale (formerly called the centigrade scale) assigns the values 0 and 100.

This procedure defines a practically-useful temperature scale, but has a few shortcomings for accurate work. For example, the freezing and boiling points of water depend on pressure; if you wanted to check the calibration of the thermometer you'd have to know and reproduce the atmospheric pressure when the marks were made. The thermal expansion properties of mercury also depend slightly on pressure. For a temperature reading to be meaningful, you would need to report the pressure at which the measurement was made.

If a thermometer were contructed using a different fluid (an alcohol, for example), the freezing and boiling points measured by the two thermometers would agree, but other temperatures would not, since the second fluid expands with temperature in a somewhat different way than mercury does. So when the mercury thermometer reads, say, 50 marks above the freezing-point mark, an alcohol thermometer might read 52 marks. To record a meaningful temperature, you'd have to always record what sort of thermometer was used.

3.4.2 Ideal Gas Temperature Scales

It would be preferable to measure temperature in a way which is completely *independent* of the particular thermometer used. One interesting possibility is to use the fact that *all* gases obey the same equation – the ideal gas law – in

the limit of zero density. (No real gas exactly satisfies the ideal gas law at any finite density – see Chapter 4).

The procedure to construct a substance-independent ideal-gas thermometer is as follows. A low density gas is put in a small, fixed-volume closed container. This serves as the thermometer. A pressure gauge of some sort (maybe a capacitance manometer) is connected to the container to measure its pressure.

Now a *single* reproducible reference state is chosen, and the ideal-gas thermometer is put in thermal contact with it and allowed to come to thermal equilibrium.⁴ The pressure reading P_{ref} is recorded.

To measure an unknown temperature, the ideal-gas thermometer is placed in thermal contact with the system of unknown temperature and allowed to come to thermal equilibrium. The pressure in the gas in the container will change to a new value P (remember the thermometer volume and amount of gas inside are fixed). We will *define* the temperature on the ideal-gas scale by

$$T = T_{ref} \left(\frac{P}{P_{ref}}\right). \tag{3.11}$$

Here T_{ref} is an arbitrary constant, which sets the size of a degree.

An interesting feature about this temperature scale is that only *one* reference state is needed (not two, as with the Celsius or Fahrenheit scales). It is best to pick a reference state which can be precisely reproduced. It will be shown in Chapter 4 that for any pure substance there is a *single* temperature (and pressure) at which solid, liquid, and vapor all co-exist. This point is called the *triple point*. The most common procedure is to take the triple point of water as the reference point.

Then to specify a particular ideal-gas scale, all that is left is is to decide what number we should assign to T_{ref} . It might seem logical to pick a round number (say, 1, 100, 1000, etc.). On the other hand, it might be convenient if the size of a degree was the same as we are accustomed to on the Celsius or Fahrenheit scale.

To find the necessary T_{ref} value to reproduce the degree size of the Celsius scale, the following experimental procedure can be used. Go to the reference temperatures used to establish the Celsius scale (the freezing and boiling points of water at 1 atm), and measure the pressure ratios (P_{fp}/P_{ref}) and (P_{bp}/P_{ref}) with the ideal-gas thermometer. If we want $T_{bp} - T_{fp}$ to be 100 on the ideal-gas

 $^{^{4}}$ We assume that the ideal gas only exchanges a negligibly small amount of energy with the system in coming to thermal equilibrium, so that it doesn't affect the temperature being measured. We can make this assumption as good as we like by simply decreasing the total amount of gas in the thermometer.

scale, then T_{ref} must satisfy

$$T_{ref}\left[\left(\frac{P_{bp}}{P_{ref}}\right) - \left(\frac{P_{fp}}{P_{ref}}\right)\right] = 100.$$
(3.12)

With the measured pressure ratios, the required value for T_{ref} is found to be

$$T_{ref} = 273.16.$$
 (3.13)

The temperature scale defined in this way is known as the Kelvin scale. Since the triple point of water occurs at 0.01 $^{\circ}$ C,

$$T(K) = T(^{\circ}C) + 273.15.$$
 (3.14)

Note that the Kelvin temperature scale has an *absolute* zero, where the pressure in the gas in principle becomes zero. The only freedom we have is in setting the size of a degree, not where the zero point is.

To construct an ideal-gas scale with the degree size of the Fahrenheit scale, choose $T_{ref} = 1.8 \times 273.16 = 491.69$. This scale is known as the Rankine temperature scale, and of course has its zero at the same temperature as the Kelvin scale. Since on the Fahrenheit scale the triple point of water is at 32.02 °F,

$$T(\mathbf{R}) = T(^{\circ}\mathbf{F}) + 459.67.$$
 (3.15)

In practice, ideal gas temperature scales have some limitations. First of all, the pressure readings not entirely independent of the gas chosen, since P may be small but it is not zero. To remove this dependence, multiple thermometers would have to be used, each with a different amount of gas inside, and their readings extrapolated down to zero pressure. Also, gases condense at low temperature. Even using helium it is not possible to measure temperatures below 1 K with an ideal gas thermometer. At the other extreme, at temperatures above a few thousand Kelvin, gases dissociate to form plasmas. This puts an upper limit on the useful temperature range. Outside this range, temperature must be defined and measured some other way.

3.4.3 Thermodynamic Temperature

We'll show in Chapter 6 that there is a more fundamental thermodynamic way to define temperature, which is not dependent on the behavior of any particular type of thermometer, not even an ideal gas one. This *thermodynamic temperature* may be defined over the range zero to infinity, and can be measured with good accuracy in various temperature ranges using different physical phenomena. Temperatures as low as 10^{-8} K and higher than 10^{6} K have been measured using techniques which rely on the definition of the thermodynamic temperature.

In the temperature range where ideal-gas thermometers can be used, the thermodynamic temperature is identical to the temperature defined by the ideal gas scale. Both the Kelvin and Rankine scales may be considered to be thermodynamic temperature scales. The Celsius and Fahrenheit scales are not, however, since they have their zero points in the wrong place. They are acceptable to use for temperature differences, but not for absolute (i.e. thermodynamic) temperatures.

3.5 Intensive and Extensive Properties

In Chapter 2, we introduced several thermodynamic properties of macroscopic matter, such as the volume V, the mass M, the total energy E, the internal energy U, the surface area A, the total electric dipole moment $V\mathbf{P}$, and the total magnetic moment $V\mathbf{M}$. These properties are defined both for equilibrium and non-equilibrium states of matter. They are also additive: if we have a system composed of two parts A and B, $M_{A+B} = M_A + M_B$, $E_{A+B} = E_A + E_B$, etc. Thermodynamic properties with these characteristics are called *extensive*.

In this chapter, we have introduced three new properties (T, P, μ) which serve to determine whether or not two systems or parts of a single system are in equilibrium with one another. These properties have a very different character. For a system composed of parts A and B, T_{A+B} is meaningful only if $T_A = T_B$ (thermal equilibrium). Otherwise, there is no *single* temperature of the whole system. If A and B are in thermal equilibrium, then $T_{A+B} = T_A$ (not $2T_A$). Pressure and chemical potential have similar characteristics: they are only defined for systems in equilibrium, and are not additive for systems composed of multiple parts. Properties like this are called *intensive*. All properties in thermodynamics are either extensive or intensive.

The extensive properties depend on how much matter the system contains. If a substance in an equilibrium state with mass M, volume V and internal energy U is divided into n equal parts, each part will have mass M/n, volume V/n, and internal energy U/n. Because the extensive properties are proportional to how much matter is in the system, it is usually more convenient to work with quantities normalized to a unit amount.

One choice is to normalize to a unit mass. The *specific* internal energy is defined to be the internal energy per unit mass:

$$u = \frac{U}{M}.$$
(3.16)

We always use the term "specific" to mean "per unit mass," and use a lower-case letter to denote a specific property. We can also define the specific volume

$$v = \frac{V}{M},\tag{3.17}$$

which is simply the reciprocal of the mass density ρ .

Alternatively, we could choose to normalize to one mole. The *molar* internal energy is defined to be

$$\hat{u} = \frac{U}{N},\tag{3.18}$$

where N is the number of moles, and the molar volume is

$$\hat{v} = \frac{V}{N}.\tag{3.19}$$

We use the hat notation to denote molar properties. Note that both specific and molar properties are intensive (independent of the size of the system), since they are the ratio of 2 extensive properties.

In engineering thermodynamics, it is most common to work with specific properties (per unit mass), since mass is conserved in any process but moles may not be if chemical reactions occur. Also, important engineering quantities like the momentum of a flowing fluid depend on the rate of *mass* flow, not the molar flow rate.

3.6 The Thermodynamic State

We've now introduced a rather long list of material properties $(U, V, M, P, T, \sigma, A, \mathbf{E}, \mathbf{P}, \mathbf{H}, \mathbf{M})$ and we will soon introduce more properties. Fortunately, we usually only need to work with a subset of these which relate to the ways energy can be transferred to or from the substance as work or heat.⁵ For equilibrium states, even the properties in this subset are not all independent. Specifying a small number of them is sufficient to determine all the rest. For example, if the mass, volume, and temperature of an equilibrium sample of water are given, then its pressure, internal energy, and phase are fully determined.

When enough property values for an equilibrium state are specified so that all the other relevant properties of that state can be determined, we say that the *thermodynamic state* is specified. The number of properties which must be given to specify the thermodynamic state is called the number of *degrees of freedom* f of the substance.

⁵For example, we don't usually care about the magnetization of water, since for achievable magnetic fields it is very, very, small, and the possible magnetic work is therefore negligible.

The number of degrees of freedom is also equal to the number of independent ways the equilibrium state can be altered. If there are two independent ways to change the state, two independent properties will be needed to specify the state, etc.

Consider a fixed mass M of some substance for which the only reversible work mode is compression, and which is in an equilibrium state with no macroscopic kinetic or potential energy. The substance is in a cylinder with a piston which can be used to change its volume. The substance may be solid, liquid, or gaseous, or may consist of an equilibrium mixture of phases.

If we add heat dQ and do quasi-static work $dW_{qs} = -PdV$, the First Law for this process is

$$dU = dQ - PdV. (3.20)$$

From this, we see that the two extensive properties U and V may be varied independently. To change U by dU holding V constant, just add heat in the amount dQ = dU. To change V by dV holding U constant, add heat in the amount dQ = +PdV while changing the volume. This is true no matter what the details are of the substance in the container (a single phase, a mixture of phases, etc.)

Suppose U and V are held fixed and we try to vary something else (maybe T or P). Since V is fixed, no compression work can be done. But since U is fixed, no heat can be added either. So there's really no way to change any other properties (T, P, etc.) without changing U or V or both. We conclude that specifying U and V (for given M) fully specifies the thermodynamic state of this substance.

Now consider a substance with two reversible work modes – maybe in addition to being compressible, it has a surface area, and non-negligible surface tension. Then the First Law would become

$$dU = dQ - PdV + \sigma dA. \tag{3.21}$$

Now it *is* possible to hold U and V fixed and vary another property: all we have to do is change the shape at constant volume, changing the surface area. This does some work, but as before we just remove some heat to get U back to the original value ($dQ = -\sigma dA$). So in this case, A can be varied independently of U and V. But there would be no way to hold U, V, and A fixed for this system and vary something else. We conclude that specifying U, V, and A in this case fully specifies the thermodynamic state of the system.

We begin to see a pattern here: The number of degrees of freedom equals the number of reversible work modes, plus one more (to account for heat addition).

If the number of reversible work modes is r, then we have

$$f = r + 1 \tag{3.22}$$

The independently-variable properties which serve to specify the thermodynamic state are U plus the generalized displacements corresponding to each reversible work mode.

It might be objected that in this analysis we have only considered reversible work, and have ignored irreversible work modes. But as we discussed in Chapter 2, the change of state produced by irreversible work can be reproduced by reversible work plus some amount of heat input. For example, electrical work done on a system by current flowing through a resistor is fully equivalent to heat addition, while rapid compression of a gas results in a state which can be reproduced by quasi-static, reversible compression plus heat input. Irreversible work does not represent an *independent* way to alter the state of the system, and therefore does not affect the calculation of the number of degrees of freedom.

3.7 Equations of State

From Eq. (3.22), we see that a substance with only one reversible work mode has 2 degrees of freedom. Such substances are known as *simple substances*. If only compression work can be done, then the substance is a *simple compressible substance* (SCS); if only magnetic work can be done, it is a *simple magnetic substance* (SMS), and so on. Often, a substance may really have more than one reversible work mode, but only one is important. In this case, the substance is often approximated as a simple one, considering only the dominant work mode. For example, we usually may neglect compression work in comparison to magnetic work when dealing with magnetic solids.

For a simple compressible substance, specifying U and V fixes the thermodynamic state for given M. Since U and V are extensive and simply scale with the total mass, the more important parameters are actually u = U/M and v = V/M. Therefore, properties such as temperature and pressure are fixed once u and v are specified: there must exist some single-valued function T(u, v) and some single-valued function P(u, v). We call functions like this which express relationships among properties of substances in equilibrium states equations of state.

The two independent variables in the equation of state don't have to be (u, v). For example, if heat dQ is added to an SCS holding v constant, u increases



Figure 3.5: Inverting T(u, v) to form u(T, v) by reflecting across the dashed u = T line for specified v.

by dQ (the First Law); it is also always observed that the temperature change dT is positive.⁶ That is, $(\partial T(u, v)/\partial u)_v > 0$, which means that T(u, v) is a monotonically increasing function of u for fixed v. Since monotonic function can be inverted, it is possible to form the function u(T, v) (Fig. 3.5).

Therefore, the pair (T, v) are always independently variable. Now substitute u(T, v) into P(u, v) = P(u(T, v), v) resulting in a new function P(T, v). This new function doesn't involve energy, and is called the *mechanical equation of state*. It is also relatively easy to measure, which is why most experimental investigations of equations of state of simple compressible substances focus on measuring P(T, v). We will examine the nature of this function for an SCS in the next chapter.

Note that P(T, v) is a very different function than P(u, v), and the partial derivative $(\partial P/\partial v)$ depends very much on whether it is u or T we're holding constant. For this reason, we always use a subscript in thermodynamics to state what variable is being held constant in a partial derivative: $(\partial P/\partial v)_T$ is a partial derivative of P(T, v), while $(\partial P/\partial v)_u$ is a partial derivative of P(u, v).⁷

We have to be a little careful in choosing which 2 variables to take as the independent ones. Both (u, v) and (T, v) are always independent, but not all pairs of variables are. In particular, P and T are not always independent. If, for example, the substance consists of an equilibrium solid/liquid mixture, then P and T become coupled – T must equal the melting temperature at the pressure P.

Equations of state also may be defined for substances other than simple compressible substances. For a simple magnetic substance, an argument analogous

⁶This observation will be proven to be true in Chapter 6.

⁷This is no different than with any other functions. For example, consider $f(x, y) = x^2 y$. Differentiating with respect to x, $(\partial f/\partial x)_y = 2xy$. Now change variables to (x, z), where z = xy. Then f(x, z) = xz and $(\partial f/\partial x)_z = z = xy$ not 2xy.

to the one above leads to the conclusion that u and \mathbf{M} are always independently variable, and can be used to define the thermodynamic state. Therefore, there must exist equations of state $T(u, \mathbf{M})$ and $\mathbf{H}(u, \mathbf{M})$. Also, $T(u, \mathbf{M})$ can be inverted to form $u(T, \mathbf{M})$, which can then be used to form the equation of state $\mathbf{H}(T, \mathbf{M})$. Like P(T, v), this equation of state can be easily measured. For other simple substances, the procedure is analogous to that outlined here.