Chapter 7

Thermodynamics

7.1 Thermodynamics is the study of heat.

7.2 Examples of systems to which thermodynamics can be applied are: a gas in a box of variable volume as in a steam engine ; a liquid which can evaporate to a gas as in a refrigerator; a mixture of chemicals; a magnet; a star; a blackhole.

7.3 The set of all possible states of a thermodynamic system is a manifold M , called the *state space*. The *thermodynamic observables* are functions on this manifold. Examples of thermodynamic observables are: the pressure exerted by the gas on the walls of its container and its volume; the volume of the gas and the liquid and their pressures; the magnetic moment ; the pressure, volume and relative abundances of various chemicals; the size, pressure, and the abundances of different nuclei in a star; the electric charge, angular momentum and mass of the blackhole.

7.4 In all these cases the system has many more degrees of freedom than the dimension of the thermodynamic state space. But it is too difficult to measure all these variables. Thermodynamics is an approximate or average description of the system in terms of a few degrees of freedom which have a macroscopic meaning.

7.5 In the case of a blackhole, the laws of physics (causality) prevents us from making measurements of the interior of the blackhole; the only degrees of freedom of the blackhole that can be measured are its electric charge, angular momentum and mass. Hence a thermodynamic description is not just a matter of conveinence; it is forced upon us.

7.6 When a system changes its thermodynamic state (eg., when a gas expands pushing on a moving piston in a cylinder) it can perform mechanical work.

7.7 Consider two systems which are isolated from the rest of the world but are in contact with each other. Eventually they come into *equilibrium*; i.e, their thermodynamic variables will become independent of time and they will stop exchanging energy. It is found emprically that *there is a thermodynamic observable called* temperature *such that two systems are in equilibrium if and only if they are at the same temperature*. This is called the *zeroth law* of thermodynamics.

7.8 Note that this law does not set a natural scale for temperature. Indeed any monotonic function $t \mapsto \phi(t)$ will give an equally good notion of temperature.

7.9 For example, two containers of ideal gases are in equilibrium if $P_1V_1 = P_2V_2$.

7.10 *The work done by isolated system in changing the state of a system from a state* p_1 *to another* p_2 *is independent of the path taken.* This is the *first law* of thermodynamics.

7.11 What we mean is that the system is isolated from other thermodynamic systems. It may be in contact with and exchange energy with a mechanical system.

7.12 This implies that there is a function $U : M \to R$ called *internal energy* such that the work done in changing from p_1 to p_2 is $U(p_2) - U(p_1)$. This function is defined only upto the addition of a constant.

7.13 When two systems are brought into contact with each other the internal energy of the total system is just the sum of their internal energies. This is not true in mechanics, due to the possibility of interaction between the systems; however such interaction energies are negligible in the thermodynamic approximation.

7.14 When a body is in contact with another, the work W done in changing its state from p_1 to p_2 depends in general on the path taken. The difference $Q = U - W$, is called *heat*.

7.15 If the change to p is infinitesimal, it is described by a vector v at p ; the infinitesimal amount of heat due to this change depends linearly on v . Hence there is a one-form ω , such that the heat emitted during the infinitesimal change v is $\omega(v)$. We will call this the *heat form*.

7.16 In most older textbooks this heat form is called dQ . But this notation is confusing since there is in general no function $Q : M \to R$ such that $\omega = dQ$: *the heat form is in general not an exact differential.*

7.17 Let us digress to establish a *theorem of Caratheodory* . This theorem will be useful in understanding the second law of thermodynamics. It is of intrinsic interest in geometry.

7.18 Given a one-form ω , let us say that a point $q \in M$ is *accesible* from $p \in M$ if there is a curve γ connecting them such that $\omega(\dot{\gamma}) = 0$. Otherwise q is *inaccessible* from p .

7.19 *Given a one-form ω , suppose that every neighborhood U of a point has inaccessible points. Then $\omega \wedge d\omega = 0$; morever, there are functions $T, S : U \to R$ such that $\omega = TdS$ in U .*

7.20 The function T is called an *integrating factor.* T and S are unique upto two constants: $T \mapsto k_1 T, S \mapsto k_1^{-1} S + k_2$, with $k_1 \neq 0$ gives the same ω .

7.21 Proof of Caratheodory's Theorem: The points accessible to p will form either an open set $V \subset U$ or a surface of some higher codimension (inverse function theorem of calculus). At each point p , there is a subspace of codimension one of the tangent space $T_p M$ of vectors transversal to ω : $\omega(X) = 0$. So the accessible points cannot form a surface of codimension greater than one. If there are inaccessible points in every neighborhood they cannot form an open subset either. Thus the points accesible from p must form a surface of codimension one in U . We can divide U into surfaces of points which are mutually accessible. Because they are of codimension one, there is a function S which is constant on these surfaces; i.e., $dS(X) = 0$ whenever $\omega(X) = 0$. Thus there is a never–vanishing function $T : U \to R$ such that $\omega = TdS$. Then $\omega \wedge d\omega = 0$.

7.22 Let us return to thermodunamics. An *adiabatic process* is a curve $\gamma : [a,b] \to M$ such that the heat form is zero on its tangent vectors: $\omega(\dot{\gamma}(t)) = 0$. Thus infinitesimal adiabatic processes are given by vectors X for which $\omega(X) = 0$. Thus two points are connected by an adiabatic process if they are accessible with respect to the heat form.

7.23 The second law of thermodynamics says that *in every neighborhood of a given state, there exist states that cannot be reached by an adiabatic process.*

7.24 From Caratheodory's theorem, this means that (at least locally) the heat form has an integrating factor: $\omega = TdS$. T is called *temperature* and S *entropy*. To justify the name temperature for T , we must prove that two systems are in equilibrium when they have the same value for T .

7.25 The temperature T does not have to be positive; however it cannot vanish so its sign cannot change. There are systems of negative temperature in nature: population inverted atomic systems for example.

7.26 Standard arguments in most thermodynamics books show that this form of the second law is equivalent to the other forms due for example to Kelvin or Carnot. We will not discuss them here.