1.3 Thermodynamics and Statistical Mechanics

The field of thermodynamics is easiest to understand in the context of Newtonian mechanics. Newtonian mechanics describes the effect of forces on objects. Thermodynamics describes the effect of heat transfer on objects. When heat is transferred,the temperature of an object changes.Temperature and heat are also intimately related to energy. A hot gas in a piston has a high pressure and it can do mechanical work by applying a force to a piston. By Newtonian mechanics the work is directly related to a transfer of energy. The laws of Newtonian mechanics are simplest to describe using the abstract concept of a point object with mass but no internal structure. The analogous abstraction for thermodynamic laws are materials that are in equilibrium and (even better) are homogeneous. It turns out that even the description of the equilibrium properties of materials is so rich and varied that this is still a primary focus of active research today.

Statistical mechanics begins as an effort to explain the laws of thermodynamics by considering the microscopic application of Newton's laws. Microscopically, the temperature of a gas is found to be related to the kinetic motion of the gas molecules. Heat transfer is the transfer of Newtonian energy from one object to another. The statistical treatment of the many particles of a material, with a key set of assumptions, reveals that thermodynamic laws are a natural consequence of many microscopic particles interacting with each other. Our studies of complex systems will lead us to discuss the properties of systems composed of many interacting parts. The concepts and tools of statistical mechanics will play an important role in these studies, as will the laws of thermodynamics that emerge from them. Thermodynamics also begins to teach us how to think about systems interacting with each other.

1.3.1 *Thermodynamics*

Thermodynamics describes macroscopic pieces of material in equilibrium in terms of macroscopic parameters. Thermodynamics was developed as a result of experience/experiment and,like Newton's laws,is to be understood as a set of self-consistent definitions and equations. As with Newtonian mechanics, where in its simplest form objects are point particles and friction is ignored,the discussion assumes an idealization that is directly experienced only in special circumstances. However, the fundamental laws, once understood,can be widely applied. The central quantities that are to be defined and related are the energy U, temperature T, entropy S, pressure P, the mass (which we write as the number of particles) N, and volume V. For magnets,the quantities should include the magnetization M, and the magnetic field H. Other macroscopic quantities that are relevant may be added as necessary within the framework developed by thermodynamics.Like Newtonian mechanics,a key aspect of thermodynamics is to understand how systems can be acted upon or can act upon each other. In addition to the quantities that describe the state of a system, there are two quantities that describe actions that may be made on a system to change its state: work and heat transfer.

The equations that relate the macroscopic quantities are known as the zeroth, first and second laws of thermodynamics. Much of the difficulty in understanding thermodynamics arises from the way the entropy appears as an essential but counterintuitive quantity. It is more easily understood in the context of a statistical treatment included below. A second source of difficulty is that even a seemingly simple material system, such as a piece of metal in a room, is actually quite complicated thermodynamically. Under usual circumstances the metal is not in equilibrium but is emitting a vapor of its own atoms. A thermodynamic treatment of the metal requires consideration not only of the metal but also the vapor and even the air that applies a pressure upon the metal. It is therefore generally simplest to consider the thermodynamics of a gas confined in a closed (and inert) chamber as a model thermodynamic system. We will discuss this example in detail in Question 1.3.1. The translational motion of the whole system, treated by Newtonian mechanics, is ignored.

We begin by defining the concept of equilibrium. A system left in isolation for a long enough time achieves a macroscopic state that does not vary in time. The system in an unchanging state is said to be in equilibrium. Thermodynamics also relies upon a particular type of equilibrium known as thermal equilibrium. Two systems can be brought together in such a way that they interact only by transferring heat from one to the other. The systems are said to be in thermal contact. An example would be two gases separated by a fixed but thermally conducting wall. After a long enough time the system composed of the combination of the two original systems will be in equilibrium. We say that the two systems are in thermal equilibrium with each other. We can generalize the definition of thermal equilibrium to include systems that are not in contact. We say that any two systems are in thermal equilibrium with each other if they do not change their (macroscopic) state when they are brought into thermal contact. Thermal equilibrium does not imply that the system is homogeneous, for example, the two gases may be at different pressures.

The zeroth law of thermodynamics states that if two systems are in thermal equilibrium with a third they are in thermal equilibrium with each other. This is not obvious without experience with macroscopic objects. The zeroth law implies that the interaction that occurs during thermal contact is not specific to the materials, it is in some sense weak, and it matters not how many or how big are the systems that are in contact. It enables us to define the temperature T as a quantity which is the same for all systems in thermal equilibrium. A more specific definition of the temperature must wait till the second law of thermodynamics. We also define the concept of a thermal reservoir as a very large system such that any system that we are interested in, when brought into contact with the thermal reservoir, will change its state by transferring heat to or from the reservoir until it is in equilibrium with the reservoir, but the transfer of heat will not affect the temperature of the reservoir.

Quite basic to the formulation and assumptions of thermodynamics is that the macroscopic state of an isolated system in equilibrium is completely defined by a specification of three parameters: energy, mass and volume (U,N,V). For magnets we must add the magnetization M; we will leave this case for later. The confinement of the system to a volume V is understood to result from some form of containment. The state of a system can be characterized by the force per unit area—the pressure P—exerted by the system on the container or by the container on the system, which are the same. Since in equilibrium a system is uniquely described by the three quantities (U,N,V), these determine all the other quantities, such as the pressure P and temperature T. Strictly speaking, temperature and pressure are only defined for a system in equilibrium, while the quantities (U,N,V) have meaning both in and out of equilibrium.

It is assumed that for a homogeneous material, changing the size of the system by adding more material in equilibrium at the same pressure and temperature changes the mass, number of particles N, volume V and energy U, in direct proportion to each other. Equivalently, it is assumed that cutting the system into smaller parts results in each subpart retaining the same properties in proportion to each other (see Figs.1.3.1 and 1.3.2). This means that these quantities are additive for different parts of a system whether isolated or in thermal contact or full equilibrium:

$$\begin{aligned} N &= \sum_{\alpha} N^{\alpha} \\ V &= \sum_{\alpha} V^{\alpha} \\ U &= \sum_{\alpha} U^{\alpha} \end{aligned} \tag{1.3.1}$$

where α indexes the parts of the system. This would not be true if the parts of the system were strongly interacting in such a way that the energy depended on the relative location of the parts. Properties such as (U,N,V) that are proportional to the size of the system are called extensive quantities. Intensive quantities are properties that do not change with the size of the system at a given pressure and temperature. The ratio of two extensive quantities is an intensive quantity. Examples are the particle density N/V and the energy density U/V. The assumption of the existence of extensive and intensive quantities is also far from trivial, and corresponds to the intuition that for a macroscopic object,the local properties of the system do not depend on the size of the system. Thus a material may be cut into two parts, or a small part may be separated from a large part, without affecting its local properties.

The simplest thermodynamic systems are homogeneous ones,like a gas in an inert container. However we can also use Eq.(1.3.1) for an inhomogeneous system. For example,a sealed container with water inside will reach a state where both water and vapor are in equilibrium with each other. The use of intensive quantities and the proportionality of extensive quantities to each other applies only within a single phase—a single homogeneous part of the system, either water or vapor. However, the additivity of extensive quantities in Eq. (1.3.1) still applies to the whole system. A homogeneous as well as a heterogeneous system may contain different chemical species. In this case the quantity N is replaced by the number of each chemical species N_i and the first line of Eq.(1.3.1) may be replaced by a similar equation for each species.

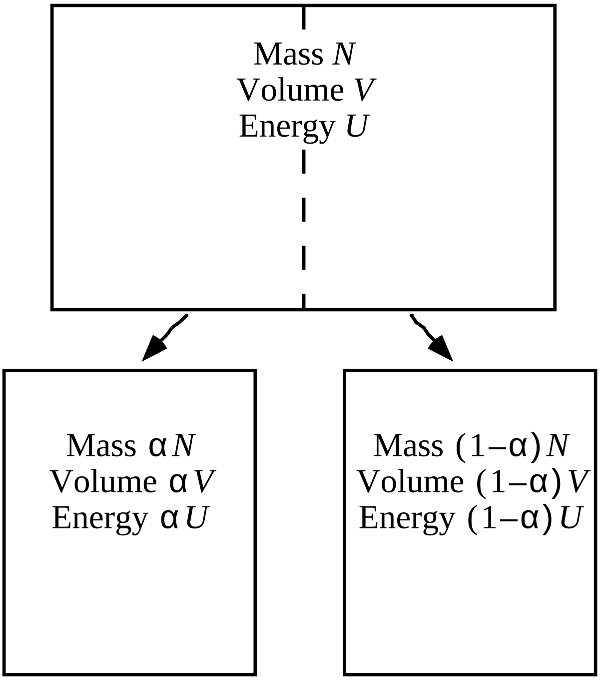


Figure 1.3.1 Thermodynamics considers macroscopic materials. A basic assumption is that cutting a system into two parts will not affect the local properties of the material and that the energy U, mass (or number of particles) N and the volume V will be divided in the same proportion. The process of separation is assumed to leave the materials under the same conditions of pressure and temperature. ▮

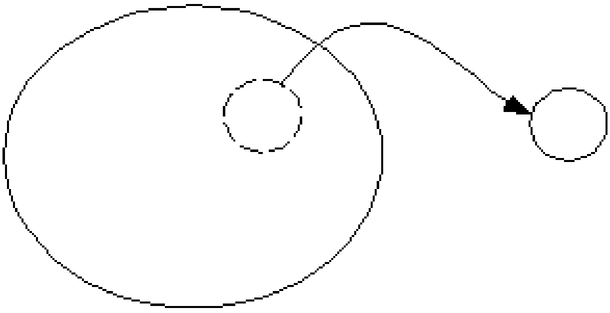


Figure 1.3.2 The assumption that the local properties of a system are unaffected by subdivision applies also to the case where a small part of a much larger system is removed. The local properties, both of the small system and of the large system are assumed to remain unchanged. Even though the small system is much smaller than the original system, the small system is understood to be a macroscopic piece of material. Thus it retains the same local properties it had as part of the larger system. ▮

The first law of thermodynamics describes how the energy of a system may change. The energy of an isolated system is conserved. There are two macroscopic processes that can change the energy of a system when the number of particles is fixed.

The first is work, in the sense of applying a force over a distance, such as driving a piston that compresses a gas. The second is heat transfer. This may be written as:

$$dU = q + w \tag{1.3.2}$$

where q is the heat transfer into the system, w is the work done on the system and U is the internal energy of the system. The differential d signifies the incremental change in the quantity U as a result of the incremental process of heat transfer and work. The work performed on a gas (or other system) is the force times the distance applied Fdx, where we write F as the magnitude of the force and dx as an incremental distance. Since the force is the pressure times the area $F = PA$, the work is equal to the pressure times the volume change or:

$$w = -PAdx = -PdV \tag{1.3.3}$$

The negative sign arises because positive work on the system, increasing the system's energy, occurs when the volume change is negative. Pressure is defined to be positive.

If two systems act upon each other, then the energy transferred consists of both the work and heat transfer. Each of these are separately equal in magnitude and opposite in sign:

$$\begin{gathered} dU_1 = q_{21} + w_{21} \\ dU_2 = q_{12} + w_{12} \\ q_{12} = -q_{21} \\ w_{12} = -w_{21} \end{gathered} \tag{1.3.4}$$

where q_{21} is the heat transfer from system 2 to system 1, and w_{21} is the work performed by system 2 on system 1. q_{12} and w_{12} are similarly defined. The last line of Eq. (1.3.4) follows from Newton's third law. The other equations follow from setting $dU = 0$ (Eq. (1.3.2)) for the total system, composed of both of the systems acting upon each other.

The second law of thermodynamics given in the following few paragraphs describes a few key aspects of the relationship of the equilibrium state with nonequilibrium states. The statement of the second law is essentially a definition and description of properties of the entropy. Entropy enables us to describe the process of approach to equilibrium. In the natural course of events, any system in isolation will change its state toward equilibrium. A system which is not in equilibrium must therefore undergo an irreversible process leading to equilibrium. The process is irreversible because the reverse process would take us away from equilibrium, which is impossible for a macroscopic system. Reversible change can occur if the state of a system in equilibrium is changed by transfer of heat or by work in such a way (slowly) that it always remains in equilibrium.

For every macroscopic state of a system (not necessarily in equilibrium) there exists a quantity S called the entropy of the system. The change in S is positive for any natural process (change toward equilibrium) of an isolated system

$$dS \geq 0 \tag{1.3.5}$$

For an isolated system, equality holds only in equilibrium when no change occurs. The converse is also true—any possible change that increases S is a natural process. Therefore, for an isolated system S achieves its maximum value for the equilibrium state.

The second property of the entropy describes how it is affected by the processes of work and heat transfer during reversible processes. The entropy is affected only by heat transfer and not by work. If we only perform work and do not transfer heat the entropy is constant. Such processes where $q = 0$ are called adiabatic processes. For adiabatic processes $dS = 0$.

The third property of the entropy is that it is extensive:

$$S = \sum_{\alpha} S^{\alpha} \tag{1.3.6}$$

Since in equilibrium the state of the system is defined by the macroscopic quantities (U,N,V), S is a function of them—$S = S(U,N,V)$—in equilibrium. The fourth property of the entropy is that if we keep the size of the system constant by fixing both the number of particles N and the volume V, then the change in entropy S with increasing energy U is always positive:

$$\left(\frac{\partial S}{\partial U}\right)_{N,V} > 0 \tag{1.3.7}$$

where the subscripts denote the (values of the) constant quantities. Because of this we can also invert the function $S = S(U,N,V)$ to obtain the energy U in terms of S, N and V: $U = U(S,N,V)$.

Finally, we mention that the zero of the entropy is arbitrary in classical treatments. The zero of entropy does attain significance in statistical treatments that include quantum effects.

Having described the properties of the entropy for a single system, we can now reconsider the problem of two interacting systems. Since the entropy describes the process of equilibration, we consider the process by which two systems equilibrate thermally. According to the zeroth law, when the two systems are in equilibrium they are at the same temperature. The two systems are assumed to be isolated from any other influence,so that together they form an isolated system with energy U_t and entropy S_t. Each of the subsystems is itself in equilibrium, but they are at different temperatures initially, and therefore heat is transferred to achieve equilibrium. The heat transfer is assumed to be performed in a reversible fashion—slowly. The two subsystems are also assumed to have a fixed number of particles N_1,N_2 and volume V_1,V_2. No work is done, only heat is transferred. The energies of the two systems U_1 and U_2 and entropies S_1 and S_2 are not fixed.

The transfer of heat results in a transfer of energy between the two systems according to Eq. (1.3.4), since the total energy

$$U_t = U_1 + U_2 \tag{1.3.8}$$

is conserved, we have

$$dU_t = dU_1 + dU_2 = 0 \tag{1.3.9}$$

We will consider the processes of equilibration twice. The first time we will identify the equilibrium condition and the second time we will describe the equilibration. At equilibrium the entropy of the whole system is maximized. Variation of the entropy with respect to any internal parameter will give zero at equilibrium. We can consider the change in the entropy of the system as a function of how much of the energy is allocated to the first system:

$$\frac{dS_t}{dU_1} = \frac{dS_1}{dU_1} + \frac{dS_2}{dU_1} = 0 \tag{1.3.10}$$

in equilibrium. Since the total energy is fixed, using Eq. (1.3.9) we have:

$$\frac{dS_t}{dU_1} = \frac{dS_1}{dU_1} - \frac{dS_2}{dU_2} = 0 \tag{1.3.11}$$

or

$$\frac{dS_1}{dU_1} = \frac{dS_2}{dU_2} \tag{1.3.12}$$

in equilibrium. By the definition of the temperature,any function of the derivative of the entropy with respect to energy could be used as the temperature. It is conventional to define the temperature T using:

$$\frac{1}{T} = \left(\frac{dS}{dU}\right)_{N,V} \tag{1.3.13}$$

This definition corresponds to the Kelvin temperature scale. The units of temperature also define the units of the entropy. This definition has the advantage that heat always flows from the system at higher temperature to the system at lower temperature.

To prove this last statement, consider a natural small transfer of heat from one system to the other. The transfer must result in the two systems raising their collective entropy:

$$dS_t = dS_1 + dS_2 \geq 0 \tag{1.3.14}$$

We rewrite the change in entropy of each system in terms of the change in energy. We recall that N and V are fixed for each of the two systems and the entropy is a function only of the three macroscopic parameters (U,N,V). The change in S for each system may be written as:

$$\begin{aligned} dS_1 &= \left(\frac{\partial S}{\partial U}\right)_{N_1,V_1} dU_1 \\ dS_2 &= \left(\frac{\partial S}{\partial U}\right)_{N_2,V_2} dU_2 \end{aligned} \tag{1.3.15}$$

to arrive at:

$$\left(\frac{\partial S}{\partial U}\right)_{N_1,V_1} dU_1 + \left(\frac{\partial S}{\partial U}\right)_{N_2,V_2} dU_2 \geq 0 \tag{1.3.16}$$

or using Eq. (1.3.9) and the definition of the temperature (Eq. (1.3.13)) we have:

$$\left[\left(\frac{1}{T_1}\right) - \left(\frac{1}{T_2}\right)\right] dU_1 \geq 0 \tag{1.3.17}$$

or:

$$(T_2 - T_1)\, dU_1 \geq 0 \tag{1.3.18}$$

This implies that a natural process of heat transfer results in the energy of the first system increasing ($dU_1 > 0$) if the temperature of the second system is greater than the first ($(T_2 - T_1) > 0$), or conversely, ifthe temperature of the second system is less than the temperature of the first.

Using the definition of temperature, we can also rewrite the expression for the change in the energy of a system due to heat transfer or work, Eq.(1.3.2). The new expression is restricted to reversible processes. As in Eq. (1.3.2), N is still fixed. Considering only reversible processes means we consider only equilibrium states of the system, so we can write the energy as a function of the entropy $U = U(S,N,V)$. Since a reversible process changes the entropy and volume while keeping this function valid, we can write the change in energy for a reversible process as

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial S}\right)_{N,V} dS + \left(\frac{\partial U}{\partial V}\right)_{N,S} dV \\ &= TdS + \left(\frac{\partial U}{\partial V}\right)_{N,S} dV \end{aligned} \tag{1.3.19}$$

The first term reflects the effect of a change in entropy and the second reflects the change in volume. The change in entropy is related to heat transfer but not to work. If work is done and no heat is transferred,then the first term is zero. Comparing the second term to Eq. (1.3.2) we find

$$P = -\left(\frac{\partial U}{\partial V}\right)_{N,S} \tag{1.3.20}$$

and the incremental change in energy for a reversible process can be written:

$$dU = TdS - PdV \tag{1.3.21}$$

This relationship enables us to make direct experimental measurements of entropy changes. The work done on a system, in a reversible or irreversible process, changes the energy of the system by a known amount. This energy can then be extracted in a reversible process in the form of heat. When the system returns to its original state, we can quantify the amount of heat transferred as a form of energy. Measured heat transfer can then be related to entropy changes using $q = TdS$.

Our treatment of the fundamentals of thermodynamics was brief and does not contain the many applications necessary for a detailed understanding. The properties of S that we have described are sufficient to provide a systematic treatment of the thermodynamics of macroscopic bodies. However, the entropy is more understandable from a microscopic (statistical) description of matter. In the next section we introduce the statistical treatment that enables contact between a microscopic picture and the macroscopic thermodynamic treatment of matter. We will use it to give microscopic meaning to the entropy and temperature.Once we have developed the microscopic picture we will discuss two applications. The first application, the ideal gas, is discussed in Section 1.3.3. The discussion of the second application,the Ising model of magnetic systems, is postponed to Section 1.6.

1.3.2 *The macroscopic state from microscopic statistics*

In order to develop a microscopic understanding of the macroscopic properties of matter we must begin by restating the nature of the systems that thermodynamics describes. Even when developing a microscopic picture, the thermodynamic assumptions are relied upon as guides. Macroscopic systems are assumed to have an extremely large number N of individual particles (e.g.,at a scale of 10^{23}) in a volume V. Because the size of these systems is so large,they are typically investigated by considering the limit of $N \rightarrow \infty$ and $V \rightarrow \infty$, while the density $n = N/V$ remains constant. This is called the thermodynamic limit. Various properties of the system are separated into extensive and intensive quantities. Extensive quantities are proportional to the size of the system. Intensive quantities are independent of the size of the system. This reflects the intuition that local properties of a macroscopic object do not depend on the size of the system. As in Figs.1.3.1 and 1.3.2, the system may be cut into two parts, or a small part may be separated from a large part without affecting its local properties.

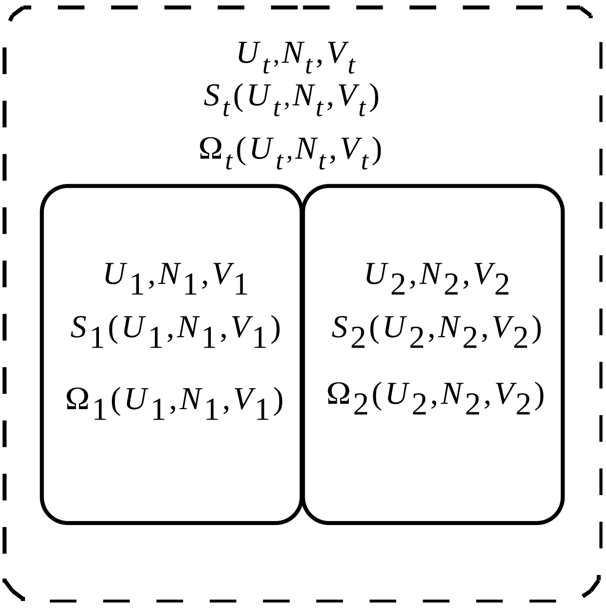
The total energy U of an isolated system in equilibrium, along with the number of particles N and volume V, defines the macroscopic state (macrostate) of an isolated system in equilibrium. Microscopically, the energy of the system E is given in classical mechanics in terms of the complete specification of the individual particle positions, momenta and interaction potentials. Together these define the microscopic state (microstate) of the system. The microstate is defined differently in quantum mechanics but similar considerations apply. When we describe the system microscopically we use the notation E rather than U to describe the energy. The reason for this difference is that macroscopically the energy U has some degree of fuzziness in its definition, though the degree of fuzziness will not enter into our considerations. Moreover, U may also be used to describe the energy of a system that is in thermal equilibrium with another system. However, thinking microscopically, the energy of such a system is not well defined,since thermal contact allows the exchange of energy between the two systems. We should also distinguish between the microscopic and macroscopic concepts of the number of particles and the volume,but since we will not make use of this distinction, we will not do so.

There are many possible microstates that correspond to a particular macrostate of the system specified only by U,N,V. We now make a key assumption of statistical mechanics—that all of the possible microstates of the system occur with equal probability. The number of these microstates $\Omega(U,N,V)$, which by definition depends on the macroscopic parameters, turns out to be central to statistical mechanics and is directly related to the entropy. Thus it determines many of the thermodynamic properties of the system, and can be discussed even though we are not always able to obtain it explicitly.

We consider again the problem of interacting systems. As before, we consider two systems (Fig. 1.3.3) that are in equilibrium separately, with state variables (U_1,N_1,V_1) and (U_2,N_2,V_2). The systems have a number of microstates $\Omega_1(U_1,N_1,V_1)$ and $\Omega_2(U_2,N_2,V_2)$ respectively. It is not necessary that the two systems be formed of the same material or have the same functional form of $\Omega(U,N,V)$, so the function Ω is also labeled by the system index. The two systems interact in a limited way, so that they can exchange only energy. The number of particles and volume of each system remains fixed. Conservation of energy requires that the total energy $U_t = U_1 + U_2$ remains fixed, but energy may be transferred from one system to the other. As before, our objective is to identify when energy transfer stops and equilibrium is reached.

Consider the number of microstates of the whole system Ω_t. This number is a function not only of the total energy of the system but also of how the energy is allocated between the systems. So, we write $\Omega_t(U_1,U_2)$, and we assume that at any time the energy of each of the two systems is well defined. Moreover, the interaction between the two systems is sufficiently weak so that the number of states of each system

Figure 1.3.3 Illustration of a system formed out of two parts. The text discusses this system when energy is transferred from one part to the other. The transfer of energy on a microscopic scale is equivalent to the transfer of heat on a macroscopic scale, since the two systems are not allowed to change their number of particles or their volume. ▮



may be counted independently. Then the total number of microstates is the product of the number of microstates of each of the two systems separately.

$$\Omega_t(U_1,U_2) = \Omega_1(U_1)\Omega_2(U_2) \tag{1.3.22}$$

where we have dropped the arguments N and V, since they are fixed throughout this discussion. When energy is transferred, the number of microstates of each of the two systems is changed. When will the transfer of energy stop? Left on its own, the system will evolve until it reaches the most probable separation of energy. Since any particular state is equally likely, the most probable separation of energy is the separation that gives rise to the greatest possible number of states. When the number of particles is large, the greatest number of states corresponding to a particular energy separation is much larger than the number of states corresponding to any other possible separation. Thus any other possibility is completely negligible. No matter when we look at the system, it will be in a state with the most likely separation of the energy. For a macroscopic system, it is impossible for a spontaneous transfer of energy to occur that moves the system away from equilibrium.

The last paragraph implies that the transfer of energy from one system to the other stops when Ω_t reaches its maximum value. Since $U_t = U_1 + U_2$ we can find the maximum value of the number of microstates using:

$$\begin{gathered}\frac{\partial\Omega_t(U_1,U_t-U_1)}{\partial U_1} = 0 = \frac{\partial\Omega_1(U_1)}{\partial U_1}\Omega_2(U_t-U_1) + \Omega_1(U_1)\frac{\partial\Omega_2(U_t-U_1)}{\partial U_1}\\ 0 = \frac{\partial\Omega_1(U_1)}{\partial U_1}\Omega_2(U_2) - \Omega_1(U_1)\frac{\partial\Omega_2(U_2)}{\partial U_2}\end{gathered} \tag{1.3.23}$$

or

$$\begin{gathered}\frac{1}{\Omega_1(U_1)}\frac{\partial\Omega_1(U_1)}{\partial U_1} = \frac{1}{\Omega_2(U_2)}\frac{\partial\Omega_2(U_2)}{\partial U_2}\\ \frac{\partial\ln\Omega_1(U_1)}{\partial U_1} = \frac{\partial\ln\Omega_2(U_2)}{\partial U_2}\end{gathered} \tag{1.3.24}$$

The equivalence of these quantities is analogous to the equivalence of the temperature of the two systems in equilibrium. Since the derivatives in the last equation are performed at constant N and V, it appears, by analogy to Eq. (1.3.12), that we can identify the entropy as:

$$S = k\ln(\Omega(E,N,V)). \tag{1.3.25}$$

The constant k, known as the Boltzmann constant, is needed to ensure correspondence of the microscopic counting of states with the macroscopic units of the entropy, as defined by the relationship of Eq. (1.3.13), once the units of temperature and energy are defined.

The entropy as defined by Eq.(1.3.25) can be shown to satisfy all of the properties of the thermodynamic entropy in the last section. We have argued that an isolated system evolves its macrostate in such a way that it maximizes the number of microstates that correspond to the macrostate. By Eq. (1.3.25), this is the same as the first property of the entropy in Eq. (1.3.5), the maximization of the entropy in equilibrium.

Interestingly, demonstrating the second property of the entropy, that it does not change during an adiabatic process, requires further formal developments relating entropy to information that will be discussed in Sections 1.7 and 1.8. We will connect the two discussions and thus be able to demonstrate the second property of the entropy in Chapter 8 (Section 8.3.2).

The extensive property of the entropy follows from Eq.(1.3.22). This also means that the number of states at a particular energy grows exponentially with the size of the system. More properly, we can say that experimental observation that the entropy is extensive suggests that the interaction between macroscopic materials, or parts of a single macroscopic material, is such that the microstates of each part of the system may be enumerated independently.

The number of microstates can be shown by simple examples to increase with the energy of the system. This corresponds to Eq.(1.3.7). There are also examples where this can be violated, though this will not enter into our discussions.

We consider next a second example of interacting systems that enables us to evaluate the meaning of a system in equilibrium with a reservoir at a temperature T. We consider a small part of a much larger system (Fig. 1.3.4). No assumption is necessary regarding the size of the small system; it may be either microscopic or macroscopic. Because of the contact of the small system with the large system, its energy is not

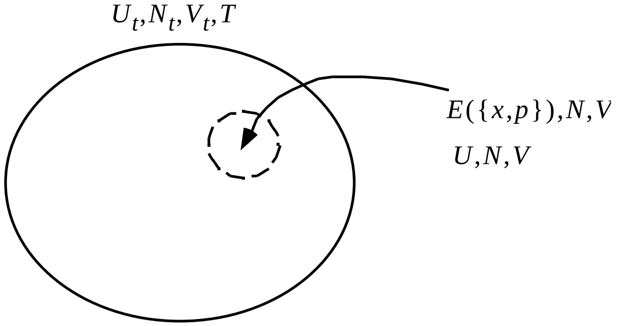


Figure 1.3.4 In order to understand temperature we consider a closed system composed of a large and small system, or equivalently a small system which is part of a much larger system. The larger system serves as a thermal reservoir transferring energy to and from the small system without affecting its own temperature. A microscopic description of this process in terms of a single microscopic state of the small system leads to the Boltzmann probability. An analysis in terms of the macroscopic state of the small system leads to the principle of minimization of the free energy to obtain the equilibrium state of a system at a fixed temperature. This principle replaces the principle of maximization of the entropy, which only applies for a closed system. ∎

always the same. Energy will be transferred back and forth between the small and large systems. The essential assumption is that the contact between the large and small system does not affect any other aspect of the description of the small system. This means that the small system is in some sense independent of the large system, despite the energy transfer. This is true if the small system is itself macroscopic, but it may also be valid for certain microscopic systems. We also assume that the small system and the large system have fixed numbers of particles and volumes.

Our objective is to consider the probability that a particular microstate of the small system will be realized. A microstate is identified by all of the microscopic parameters necessary to completely define this state. We use the notation $\{x,p\}$ to denote these coordinates. The probability that this particular state will be realized is given by the fraction of states of the whole system for which the small system attains this state. Because there is only one such state for the small system, the probability that this state will be realized is given by (proportional to) a count of the number of states of the rest of the system. Since the large system is macroscopic, we can count this number by using the macroscopic expression for the number of states of the large system:

$$P(\{x,p\}) \quad \Omega_R(U_t - \mathrm{E}(\{x,p\}), N_t - N, V_t - V) \tag{1.3.26}$$

where $E(\{x,p\}),N,V$ are the energy, number of particles and volume of the microscopic system respectively. $E(\{x,p\})$ is a function of the microscopic parameters $\{x,p\}$. U_t,N_t,V_t are the energy, number of particles and volume of the whole system, including both the small and large systems. Ω_R is the entropy of the large subsystem (reservoir). Since the number of states generally grows faster than linearly as a function of the energy, we use a Taylor expansion of its logarithm (or equivalently a Taylor expansion of the entropy) to find

$$\begin{aligned}
&\ln \Omega_R(U_t - E(\{x,p\}), N_t - N, V_t - V) \\
&\quad = \ln \Omega_R(U_t, N_t - N, V_t - V) + \left(\frac{\partial \ln \Omega_R(U_t, N_t - N, V_t - V)}{\partial E_t}\right)_{N_t,V_t} (-E(\{x,p\})) \\
&\quad = \ln \Omega_R(U_t, N_t - N, V_t - V) + \frac{1}{kT}(-E(\{x,p\}))
\end{aligned} \tag{1.3.27}$$

where we have not expanded in the number of particles and the volume because they are unchanging. We take only the first term in the expansion, because the size of the small system is assumed to be much smaller than the size of the whole system. Exponentiating gives the relative probability of this particular microscopic state.

$$\Omega_R(U_t - E(\{x,p\}), N_t - N, V_t - V) = \Omega_R(U_t, N_t - N, V_t - V) e^{-E(\{x,p\})/kT} \tag{1.3.28}$$

The probability of this particular state must be normalized so that the sum over all states is one. Since we are normalizing the probability anyway, the constant coefficient does not affect the result. This gives us the Boltzmann probability distribution:

$$\begin{aligned} P(\{x,p\}) &= \frac{1}{Z} e^{-E(\{x,p\})/kT} \\ Z &= \sum_{\{x,p\}} e^{-E(\{x,p\})/kT} \end{aligned} \tag{1.3.29}$$

Eq. (1.3.29) is independent of the states of the large system and depends only on the microscopic description of the states of the small system. It is this expression which generally provides the most convenient starting point for a connection between the microscopic description of a system and macroscopic thermodynamics. It identifies the probability that a particular microscopic state will be realized when the system has a well-defined temperature T. In this way it also provides a microscopic meaning to the macroscopic temperature T. It is emphasized that Eq.(1.3.29) describes both microscopic and macroscopic systems in equilibrium at a temperature T.

The probability of occurrence of a particular state should be related to the description of a system in terms of an ensemble. We have found by Eq. (1.3.29) that a system in thermal equilibrium at a temperature T is represented by an ensemble that is formed by taking each of the states in proportion to its Boltzmann probability. This ensemble is known as the canonical ensemble. The canonical ensemble should be contrasted with the assumption that each state has equal probability for isolated systems at a particular energy. The ensemble of fixed energy and equal a priori probability is known as the microcanonical ensemble. The canonical ensemble is both easier to discuss analytically and easier to connect with the physical world. It will be generally assumed in what follows.

We can use the Boltzmann probability and the definition of the canonical ensemble to obtain all of the thermodynamic quantities. The macroscopic energy is given by the average over the microscopic energy using:

$$U = \frac{1}{Z} \sum_{\{x,p\}} E(\{x,p\}) e^{-E(\{x,p\})/kT} \tag{1.3.30}$$

For a macroscopic system,the average value of the energy will always be observed in any specific measurement, despite the Boltzmann probability that allows all energies. This is because the number of states of the system rises rapidly with the energy. This rapid growth and the exponential decrease of the probability with the energy results in a sharp peak in the probability distribution as a function of energy. The sharp peak in the probability distribution means that the probability of any other energy is negligible. This is discussed below in Question 1.3.1.

For an isolated macroscopic system, we were able to identify the equilibrium state from among other states of the system using the principle of the maximization of the entropy. There is a similar procedure for a macroscopic system in contact with a thermal reservoir at a fixed temperature T. The important point to recognize is that when we had a closed system,the energy was fixed. Now, however, the objective becomes to identify the energy at equilibrium. Of course, the energy is given by the average in

Eq.(1.3.30). However, to generalize the concept of maximizing the entropy, it is simplest to reconsider the problem of the system in contact with the reservoir when the small system is also macroscopic.

Instead of considering the probability of a particular microstate of well-defined energy E, we consider the probability of a macroscopic state of the system with an energy U. In this case, we find the equilibrium state of the system by maximizing the number of states of the whole system, or alternatively of the entropy:

$$\begin{aligned} &\ln\Omega(U,N,V)+\ln\Omega_R(U_t-U,N_t-N,V_t-V) \\ &\quad=S(U,N,V)/k+S_R(U_t-U,N_t-N,V_t-V)/k \\ &\quad=S(U,N,V)/k+S_R(U_t,N_t-N,V_t-V)/k+\frac{1}{kT}(-U) \end{aligned} \tag{1.3.31}$$

To find the equilibrium state, we must maximize this expression for the entropy of the whole system. We can again ignore the constant second term. This leaves us with quantities that are only characterizing the small system we are interested in, and the temperature of the reservoir. Thus we can find the equilibrium state by maximizing the quantity

$$S-U/T \tag{1.3.32}$$

It is conventional to rewrite this and, rather than maximizing the function in Eq. (1.3.32), to minimize the function known as the free energy:

$$F=U-TS \tag{1.3.33}$$

This suggests a simple physical significance of the process of change toward equilibrium. At a fixed temperature, the system seeks to minimize its energy and maximize its entropy at the same time. The relative importance of the entropy compared to the energy is set by the temperature. For high temperature, the entropy becomes more dominant, and the energy rises in order to increase the entropy. At low temperature, the energy becomes more dominant, and the energy is lowered at the expense of the entropy. This is the precise statement of the observation that "everything flows downhill." The energy entropy competition is a balance that is rightly considered as one of the most basic of physical phenomena.

We can obtain a microscopic expression for the free energy by an exercise that begins from a microscopic expression for the entropy:

$$S=k\ln(\Omega)=k\ln\left(\sum_{\{x,p\}}\delta_{E\left(\{x,p\}\right),U}\right) \tag{1.3.34}$$

The summation is over all microscopic states. The delta function is 1 only when $E(\{x,p\})=U$. Thus the sum counts all of the microscopic states with energy U. Strictly speaking, the δ function is assumed to be slightly "fuzzy," so that it gives 1 when $E(\{x,p\})$ differs from U by a small amount on a macroscopic scale, but by a large amount in terms of the differences between energies of microstates. We can then write

$$\begin{aligned} S &= k\ln(\Omega) = k\ln\left(\sum_{\{x,p\}} \delta_{E(\{x,p\}),U}\, e^{-E(\{x,p\})/kT} e^{U/kT}\right) \\ &= \frac{U}{T} + k\ln\left(\sum_{\{x,p\}} \delta_{E(\{x,p\}),U}\, e^{-E(\{x,p\})/kT}\right) \end{aligned} \tag{1.3.35}$$

Let us compare the sum in the logarithm with the expression for Z in Eq.(1.3.29). We will argue that they are the same. This discussion hinges on the rapid increase in the number of states as the energy increases. Because of this rapid growth, the value of Z in Eq.(1.3.29) actually comes from only a narrow region of energy. We know from the expression for the energy average, Eq.(1.3.30), that this narrow region of energy must be at the energy U. This implies that for all intents and purposes the quantity in the brackets of Eq. (1.3.35) is equivalent to Z. This argument leads to the expression:

$$S = \frac{U}{T} + k\ln Z \tag{1.3.36}$$

Comparing with Eq. (1.3.33) we have

$$F = -kT\ln Z \tag{1.3.37}$$

Since the Boltzmann probability is a convenient starting point, this expression for the free energy is often simpler to evaluate than the expression for the entropy, Eq. (1.3.34). A calculation of the free energy using Eq.(1.3.37) provides contact between microscopic models and the macroscopic behavior of thermodynamic systems. The Boltzmann normalization Z, which is directly related to the free energy is also known as the partition function. We can obtain other thermodynamic quantities directly from the free energy. For example, we rewrite the expression for the energy Eq. (1.3.30) as:

$$U = \frac{1}{Z}\sum_{\{x,p\}} E(\{x,p\}) e^{-\beta E(\{x,p\})} = -\frac{\partial \ln(Z)}{\partial \beta} = \frac{\partial \beta F}{\partial \beta} \tag{1.3.38}$$

where we use the notation $\beta = 1/kT$. The entropy can be obtained using this expression for the energy and Eq. (1.3.33) or (1.3.36).

Question 1.3.1 Consider the possibility that the macroscopic energy of a system in contact with a thermal reservoir will deviate from its typical value U. To do this expand the probability distribution of macroscopic energies of a system in contact with a reservoir around this value. How large are the deviations that occur?

Solution 1.3.1 We considered Eq.(1.3.31) in order to optimize the entropy and find the typical value of the energy U. We now consider it again to find the distribution of probabilities of values of the energy around the value U similar to the way we discussed the distribution of microscopic states $\{x, p\}$ in Eq.(1.3.27). To do this we distinguish between the observed value of the energy U' and U. Note that we consider U' to be a macroscopic energy, though the same derivation could be used to obtain the distribution of microscopic energies. The probability of U' is given by:

$$P(U') \quad \Omega(U',N,V)\Omega_R(U_t-U',N_t-N,V_t-V)=e^{S(U')/k+S_R(U_t-U')/k} \tag{1.3.39}$$

In the latter form we ignore the fixed arguments N and V. We expand the logarithm of this expression around the expected value of energy U:

$$\begin{aligned} &S(U')+S_R(U_t-U') \\ &= S(U)/k+S_R(U_t-U)/k+\frac{1}{2k}\frac{d^2S(U)}{dU^2}(U-U')^2+\frac{1}{2k}\frac{d^2S(U_t-U)}{dU_t^2}(U-U')^2 \end{aligned} \tag{1.3.40}$$

where we have kept terms to second order. The first-order terms, which are of the form $(1/kT)(U'-U)$, have opposite signs and therefore cancel. This implies that the probability is a maximum at the expected energy U. The second derivative of the entropy can be evaluated using:

$$\frac{d^2S(U)}{dU^2}=\frac{d}{dU}\frac{1}{T}=-\frac{1}{T^2}\frac{1}{dU/dT}=-\frac{1}{T^2C_V} \tag{1.3.41}$$

where C_V is known as the specific heat at constant volume. For our purposes, its only relevant property is that it is an extensive quantity. We can obtain a similar expression for the reservoir and define the reservoir specific heat C_{VR}. Thus the probability is:

$$P(U') \quad e^{-(1/2kT^2)(1/C_V+1/C_{VR})(U-U')^2} \approx e^{-(1/2kT^2)(1/C_V)(U-U')^2} \tag{1.3.42}$$

where we have left out the (constant) terms that do not depend on U'. Because C_V and C_{VR} are extensive quantities and the reservoir is much bigger than the small system, we can neglect $1/C_{VR}$ compared to $1/C_V$. The result is a Gaussian distribution (Eq. (1.2.39)) with a standard deviation

$$\sigma = T\sqrt{kC_V} \tag{1.3.43}$$

This describes the characteristic deviation of the energy U' from the average or typical energy U. However, since C_V is extensive, the square root means that the deviation is proportional to $\sqrt{N}$. Note that the result is consistent with a random walk of N steps. So for a large system of $N \quad 10^{23}$ particles, the possible deviation in the energy is smaller than the energy by a factor of (we are neglecting everything but the N dependence) 10^{12}—i.e., it is undetectable. Thus the energy of a thermodynamic system is very well defined. ■

1.3.3 *Kinetic theory of gases and pressure*

In the previous section, we described the microscopic analog of temperature and entropy. We assumed that the microscopic analog of energy was understood, and we developed the concept of free energy and its microscopic analog. One quantity that we have not discussed microscopically is the pressure. Pressure is a Newtonian concept—the force per unit area. For various reasons, it is helpful for us to consider the microscopic origin of pressure for the example of a simplified model of a gas called an ideal gas. In Question 1.3.2 we use the ideal gas as an example of the thermodynamic and statistical analysis of materials.

An ideal gas is composed of indistinguishable point particles with a mass m but with no internal structure or size. The interaction between the particles is neglected, so that the energy is just their kinetic energy. The particles do interact with the walls of the container in which the gas is confined. This interaction is simply that of reflection—when the particle is incident on a wall, the component of its velocity perpendicular to the wall is reversed. Energy is conserved. This is in accordance with the expectation from Newton's laws for the collision of a small mass with a much larger mass object.

To obtain an expression for the pressure, we must suffer with some notational hazards, as the pressure P, probability of a particular velocity $P(v)$ and momentum of a particular particle $\mathbf{p}_i$ are all designated by the letter P but with different case, arguments or subscripts. A bold letter $\mathbf{F}$ is used briefly for the force, and otherwise F is used for the free energy. We rely largely upon context to distinguish them. Since the objective of using an established notation is to make contact with known concepts, this situation is sometimes preferable to introducing a new notation.

Because of the absence of collisions between different particles of the gas, there is no communication between them, and each of the particles bounces around the container on its own course. The pressure on the container walls is given by the force per unit area exerted on the walls, as illustrated in Fig. 1.3.5. The force is given by the action of the wall on the gas that is needed to reverse the momenta of the incident particles between t and $t + \Delta t$:

$$P = \frac{|\mathbf{F}|}{A} = \frac{1}{A\Delta t}\left|\sum_i m\Delta\mathbf{v}_i\right| \tag{1.3.44}$$

where $|\mathbf{F}|$ is the magnitude of the force on the wall. The latter expression relates the pressure to the change in the momenta of incident particles per unit area of the wall. A is a small but still macroscopic area, so that this part of the wall is flat. Microscopic roughness of the surface is neglected. The change in velocity Δv_i of the particles during the time Δt is zero for particles that are not incident on the wall. Particles that hit the wall between t and $t + \Delta t$ are moving in the direction of the wall at time t and are near enough to the wall to reach it during Δt. Faster particles can reach the wall from farther away, but only the velocity perpendicular to the wall matters. Denoting this velocity component as v , the maximum distance is v Δt (see Fig. 1.3.5).

If the particles have velocity only perpendicular to the wall and no velocity parallel to the wall, then we could count the incident particles as those in a volume Av Δt. We can use the same expression even when particles have a velocity parallel to the surface, because the parallel velocity takes particles out of and into this volume equally.

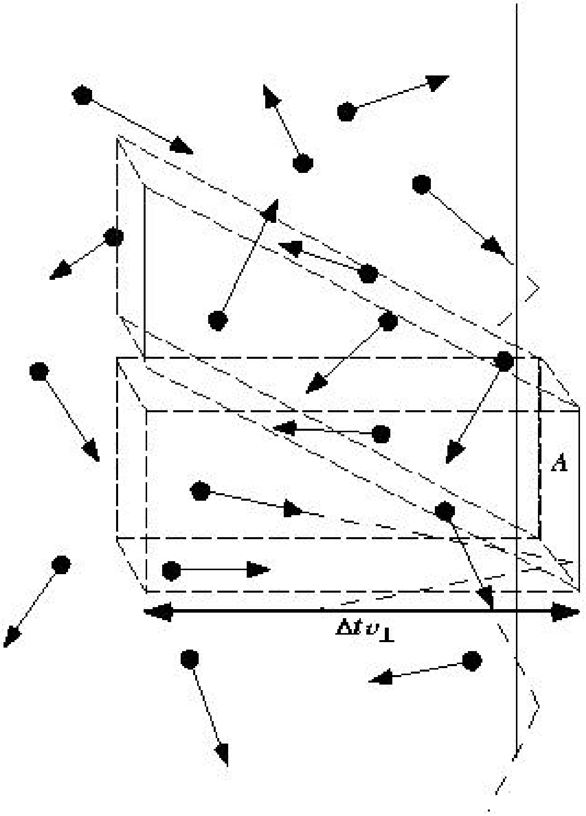


Figure 1.3.5 Illustration of a gas of ideal particles in a container near one of the walls. Particles incident on the wall are reflected, reversing their velocity perpendicular to the wall, and not affecting the other components of their velocity. The wall experiences a pressure due to the collisions and applies the same pressure to the gas. To calculate the pressure we must count the number of particles in a unit of time Δt with a particular perpendicular velocity v that hit an area A. This is equivalent to counting the number of particles with the velocity v in the box shown with one of its sides of length $\Delta t v$. Particles with velocity v will hit the wall if and only if they are in the box. The same volume of particles applies if the particles also have a velocity parallel to the surface, since this just skews the box, as shown, leaving its height and base area the same. ∎

Another way to say this is that for a particular parallel velocity we count the particles in a sheared box with the same height and base and therefore the same volume. The total number of particles in the volume, $(N / V)Av \ \Delta t$, is the volume times the density (N / V).

Within the volume $Av \ \Delta t$, the number of particles that have the velocity v is given by the number of particles in this volume times the probability $P(v)$ that a particle has its perpendicular velocity component equal to v. Thus the number of particles incident on the wall with a particular velocity perpendicular to the wall v is given by

$$\frac{N}{V} A P(v\ ) v\ \Delta t \qquad (1.3.45)$$

The total change in momentum is found by multiplying this by the change in momentum of a single particle reflected by the collision, $2mv$, and integrating over all velocities.

$$\left| \sum_i m \Delta \mathbf{v}_i \right| = \frac{1}{V} N A \Delta t \int_0^\infty dv\ P(v\ ) v\ (2mv\ ) \qquad (1.3.46)$$

Divide this by $A\Delta t$ to obtain the change in momentum per unit time per unit area, which is the pressure (Eq. (1.3.44)),

$$P = \frac{1}{V} N \int_0^\infty dv\ P(v\ ) v\ (2mv\ ) \qquad (1.3.47)$$

We rewrite this in terms of the average squared velocity perpendicular to the surface

$$P = \frac{N}{V} m 2 \int_0^\infty dv\ P(v\ ) v\ ^2 = \frac{N}{V} m \int_{-\infty}^\infty dv\ P(v\ ) v\ ^2 = \frac{N}{V} m < v\ ^2 > \qquad (1.3.48)$$

where the equal probability of having positive and negative velocities enables us to extend the integral to $-\infty$ while eliminating the factor of two. We can rewrite Eq.(1.3.48) in terms of the average square magnitude of the total velocity. There are three components of the velocity (two parallel to the surface). The squares of the velocity components add to give the total velocity squared and the averages are equal:

$$< v^2 > = < v\ ^2 + v_2^2 + v_3^2 > = 3 < v\ ^2 > \qquad (1.3.49)$$

where v is the magnitude of the particle velocity. The pressure is:

$$P = \frac{N}{V} m \frac{1}{3} < v^2 > \qquad (1.3.50)$$

Note that the wall does not influence the probability of having a particular velocity nearby. Eq. (1.3.50) is a microscopic expression for the pressure, which we can calculate using the Boltzmann probability from Eq. (1.3.29). We do this as part of Question 1.3.2.

Question 1.3.2 Develop the statistical description of the ideal gas by obtaining expressions for the thermodynamic quantities Z, F, U, S and P, in terms of N, V, and T. For hints read the first three paragraphs of the solution.

Solution 1.3.2 The primary task of statistics is counting. To treat the ideal gas we must count the number of microscopic states to obtain the entropy, or sum over the Boltzmann probability to obtain Z and the free energy. The ideal gas presents us with two difficulties. The first is that each particle has a continuum of possible locations. The second is that we must treat the particles as microscopically indistinguishable. To solve the first problem, we have to set some interval of position at which we will call a particle here different from a particle there. Moreover, since a particle at any location may have many different velocities, we must also choose a difference of velocities that will be considered as distinct. We define the interval of position to be Δx and the interval of momentum to be Δp. In each spatial dimension, the positions between x and $x+\Delta x$ correspond to a single state, and the momenta between p and $p+\Delta p$ correspond to a single state. Thus we consider as one state of the system a particle which has position and momenta in a six-dimensional box of a size $\Delta x^3 \Delta p^3$. The size of this box enters only as a constant in classical statistical mechanics, and we will not be concerned with its value. Quantum mechanics identifies it with $\Delta x^3 \Delta p^3 = h^3$, where h is Planck's constant, and for convenience we adopt this notation for the unit volume for counting.

There is a subtle but important choice that we have made. We have chosen to make the counting intervals have a fixed width Δp in the momentum. From classical mechanics, it is not entirely clear that we should make the intervals of fixed width in the momentum or, for example, make them fixed in the energy ΔE. In the latter case we would count a single state between E and $E+\Delta E$. Since the energy is proportional to the square of the momentum, this would give a different counting. Quantum mechanics provides an unambiguous answer that the momentum intervals are fixed.

To solve the problem of the indistinguishability of the particles, we must remember every time we count the number of states of the system to divide by the number of possible ways there are to interchange the particles, which is $N!$.

The energy of the ideal gas is given by the kinetic energy of all of the particles:

$$E(\{x,p\}) = \sum_{i=1}^{N} \frac{1}{2} m v_i^2 = \sum_{i=1}^{N} \frac{p_i^2}{2m} \tag{1.3.51}$$

where the velocity and momentum of a particle are three-dimensional vectors with magnitude v_i and p_i respectively. We start by calculating the partition function (Boltzmann normalization) Z from Eq. (1.3.29)

$$Z = \frac{1}{N!} \sum_{\{x,p\}} e^{-\sum_{i=1}^{N} \frac{p_i^2}{2mkT}} = \frac{1}{N!} \int e^{-\sum_{i=1}^{N} \frac{p_i^2}{2mkT}} \prod_{i=1}^{N} \frac{d^3x_i d^3p_i}{h^3} \tag{1.3.52}$$

where the integral is to be evaluated over all possible locations of each of the N particles of the system. We have also included the correction to over-counting, $N!$. Since the particles do not see each other, the energy is a sum over each particle energy. The integrals separate and we have:

$$Z = \frac{1}{N!}\left(\frac{1}{h^3}\int e^{-\frac{p^2}{2mkT}} d^3x\,d^3p\right)^N \tag{1.3.53}$$

The position integral gives the volume V, immediately giving the dependence of Z on this macroscopic quantity. The integral over momentum can be evaluated giving:

$$\begin{aligned}\int e^{-\frac{p^2}{2mkT}} d^3p &= 4\pi\int_0^\infty p^2 dp\,e^{-\frac{p^2}{2mkT}} = 4\pi(2mkT)^{3/2}\int_0^\infty y^2 dy\,e^{-y^2}\\ &= 4\pi(2mkT)^{3/2}\left(-\frac{\partial}{\partial a}\bigg|_{a=1}\right)\int_0^\infty dy\,e^{-ay^2} = 4\pi(2mkT)^{3/2}\left(-\frac{\partial}{\partial a}\bigg|_{a=1}\right)\frac{1}{2}\sqrt{\frac{\pi}{a}}\\ &= (2\pi mkT)^{3/2}\end{aligned} \tag{1.3.54}$$

and we have that

$$Z(V,T,N) = \frac{V^N}{N!}\left(2\pi mkT/h^2\right)^{3N/2} \tag{1.3.55}$$

We could have simplified the integration by recognizing that each component of the momentum p_x,p_y and p_z can be integrated separately, giving $3N$ independent one-dimensional integrals and leading more succinctly to the result. The result can also be written in terms of a natural length λ(T) that depends on temperature (and mass):

$$\lambda(T) = (h^2/2\pi mkT)^{1/2} \tag{1.3.56}$$

$$Z(V,T,N) = \frac{V^N}{N!\lambda(T)^{3N}} \tag{1.3.57}$$

From the partition function we obtain the free energy, making use of Sterling's approximation (Eq. (1.2.36)):

$$F = kTN(\ln N - 1) - kTN\ln(V/\lambda(T)^3) \tag{1.3.58}$$

where we have neglected terms that grow less than linearly with N. Terms that vary as $\ln(N)$ vanish on a macroscopic scale. In this form it might appear that we have a problem,since the $N\ln(N)$ term from Sterling's approximation to the factorial does not scale proportional to the size of the system, and F is an extensive quantity. However, we must also note the $N\ln(V)$ term, which we can combine with the $N\ln(N)$ term so that the extensive nature is apparent:

$$F = kTN[\ln N\lambda(T)^3/V) - 1] \tag{1.3.59}$$

It is interesting that the factor of $N!$,and thus the indistinguishability of particles,is necessary for the free energy to be extensive. If the particles were distinguishable,then cutting the system in two would result in a different counting, since we would lose the states corresponding to particles switching from one part to the other. If we combined the two systems back together, there would be an effect due to the mixing of the distinguishable particles (Question 1.3.3).

The energy may be obtained from Eq. (1.3.38) (any of the forms) as:

$$U = \frac{3}{2} NkT \tag{1.3.60}$$

which provides an example of the equipartition theorem, which says that each degree of freedom (position-momentum pair) of the system carries $kT/2$ of energy in equilibrium.Each of the three spatial coordinates of each particle is one degree of freedom.

The expression for the entropy ($S = (U - F)/T$)

$$S = kN[\ln(V/N\lambda(T)^3) + 5/2] \tag{1.3.61}$$

shows that the entropy per particle S/N grows logarithmically with the volume per particleV/N. Using the expression for U, it may be written in a form $S(U,N,\mathrm{V})$.

Finally, the pressure may be obtained from Eq.(1.3.20), but we must be careful to keep N and S constant rather than T. We have

$$P = -\left.\frac{\partial U}{\partial V}\right|_{N,S} = -\frac{3}{2} Nk \left.\frac{\partial T}{\partial V}\right|_{N,S} \tag{1.3.62}$$

Taking the same derivative of the entropy Eq. (1.3.61) gives us (the derivative of S with S fixed is zero):

$$0 = \frac{1}{V} - \frac{3}{2}\left.\frac{\partial T}{\partial V}\right|_{N,S} \tag{1.3.63}$$

Substituting, we obtain the ideal gas equation of state:

$$PV = NkT \tag{1.3.64}$$

which we can also obtain from the microscopic expression for the pressure—Eq.(1.3.50). We describe two ways to do this.One way to obtain the pressure from the microscopic expression is to evaluate first the average of the energy

$$U = < E(\{x,p\}) > = \sum_{i=1}^{N} \frac{1}{2} m < v_i^2 > = N \frac{1}{2} m < v^2 > \tag{1.3.65}$$

This may be substituted in to Eq. (1.3.60) to obtain

$$\frac{1}{2}m<v^2> = \frac{3}{2}kT \tag{1.3.66}$$

which may be substituted directly in to Eq. (1.3.50). Another way is to obtain the average squared velocity directly. In averaging the velocity, it doesn't matter which particle we choose. We choose the first particle:

$$<v_1^2> = 3<v_1^2> = \frac{\frac{1}{N!}\int 3v_1^2\, e^{-\sum\limits_{i=1}^{N}\frac{p_i^2}{2mkT}} \prod\limits_{i=1}^{N}\frac{d^3x_i d^3p_i}{h^3}}{\frac{1}{N!}\int e^{-\sum\limits_{i=1}^{N}\frac{p_i^2}{2mkT}} \prod\limits_{i=1}^{N}\frac{d^3x_i d^3p_i}{h^3}} \tag{1.3.67}$$

where we have further chosen to average over only one of the components of the velocity of this particle and multiply by three. The denominator is the normalization constant Z. Note that the factor $1/N!$, due to the indistinguishability of particles, appears in the numerator in any ensemble average as well as in the denominator, and cancels. It does not affect the Boltzmann probability when issues of distinguishability are not involved.

There are $6N$ integrals in the numerator and in the denominator of Eq. (1.3.67). All integrals factor into one-dimensional integrals.Each integral in the numerator is the same as the corresponding one in the denominator, except for the one that involves the particular component of the velocity we are interested in. We cancel all other integrals and obtain:

$$<v_1^2> = 3<v_1^2> = 3\frac{\int v_1^2\, e^{-\frac{p_1^2}{2mkT}}dp_1}{\int e^{-\frac{p_1^2}{2mkT}}dp_1} = 3\left(\frac{2kT}{m}\right)\frac{\int y^2 e^{-y^2}dy}{\int e^{-y^2}dy} = 3\left(\frac{2kT}{m}\right)\left(\frac{1}{2}\right) \tag{1.3.68}$$

The integral is performed by the same technique as used in Eq.(1.3.54). The result is the same as by the other methods. ▮

Question 1.3.3 An insulated box is divided into two compartments by a partition. The two compartments contain two different ideal gases at the same pressure P and temperature T. The first gas has N_1 particles and the second has N_2 particles. The partition is punctured. Calculate the resulting change in thermodynamic parameters (N, V, U, P, S, T, F). What changes in the analysis if the two gases are the same, i.e., if they are composed of the same type of molecules?

Solution 1.3.3 By additivity the extrinsic properties of the whole system before the puncture are (Eq. (1.3.59)–Eq. (1.3.61)):

$$\begin{aligned} U_0 &= U_1 + U_2 = \frac{3}{2}(N_1 + N_2)kT \\ V_0 &= V_1 + V_2 \\ S_0 &= kN_1[\ln(V_1/N_1\lambda(T)^3) + 5/2] + kN_2[\ln(V_2/N_2\lambda(T)^3) + 5/2] \\ F_0 &= kTN_1[\ln(N_1\lambda(T)^3/V_1) - 1] + kTN_2[\ln(N_2\lambda(T)^3/V_2) - 1] \end{aligned} \tag{1.3.69}$$

The pressure is intrinsic, so before the puncture it is (Eq. (1.3.64)):

$$P_0 = N_1kT/V_1 = N_2kT/V_2 \tag{1.3.70}$$

After the puncture, the total energy remains the same, because the whole system is isolated. Because the two gases do not interact with each other even when they are mixed, their properties continue to add after the puncture. However, each gas now occupies the whole volume, $V_1 + V_2$. The expression for the energy as a function of temperature remains the same,so the temperature is also unchanged. The pressure in the container is now additive: it is the sum of the pressure of each of the gases:

$$P = N_1kT/(V_1 + V_2) + N_2kT/(V_1 + V_2) = P_0 \tag{1.3.71}$$

i.e., the pressure is unchanged as well.

The only changes are in the entropy and the free energy. Because the two gases do not interact with each other, as with other quantities, we can write the total entropy as a sum over the entropy of each gas separately:

$$\begin{aligned} S &= kN_1[\ln((V_1 + V_2)/N_1\lambda(T)^3) + 5/2] \\ &\quad + kN_2[\ln((V_1 + V_2)/N_2\lambda(T)^3) + 5/2] \\ &= S_0 + (N_1 + N_2)k\ln(V_1 + V_2) - N_1k\ln(V_1) - N_2k\ln(V_2) \end{aligned} \tag{1.3.72}$$

If we simplify to the case $V_1 = V_2$, we have $S = S_0 + (N_1 + N_2)k \ln(2)$. Since the energy is unchanged, by the relationship of free energy and entropy (Eq. (1.3.33)) we have:

$$F = F_0 - T(S - S_0) \tag{1.3.73}$$

If the two gases are composed of the same molecule,there is no change in thermodynamic parameters as a result of a puncture. Mathematically, the difference is that we replace Eq. (1.3.72) with:

$$S = k(N_1 + N_2)[\ln((V_1 + V_2)/(N_1 + N_2)\lambda(T)^3) + 5/2] = S_0 \tag{1.3.74}$$

where this is equal to the original entropy because of the relationship $N_1/V_1 = N_2/V_2$ from Eq. (1.3.70). This example illustrates the effect of indistinguishability. The entropy increases after the puncture when the gases are different, but not when they are the same. ▮

Question 1.3.4 An ideal gas is in one compartment of a two-compartment sealed and thermally insulated box. The compartment it is in has a volume V_1. It has an energy U_0 and a number of particles N_0. The second compartment has volume V_2 and is empty. Write expressions for the changes in all thermodynamic parameters (N, V, U, P, S, T, F) if

a. the barrier between the two compartments is punctured and the gas expands to fill the box.

b. the barrier is moved slowly, like a piston, expanding the gas to fill the box.

Solution 1.3.4 Recognizing what is conserved simplifies the solution of this type of problem.

a. The energy U and the number of particles N are conserved. Since the volume change is given to us explicitly, the expressions for T (Eq. (1.3.60)), F (Eq. (1.3.59)), S (Eq. (1.3.61)), and P (Eq. (1.3.64)) in terms of these quantities can be used.

$$\begin{gathered}
N = N_0 \\
U = U_0 \\
V = V_1 + V_2 \\
T = T_0 \\
F = kTN[\ln(N\lambda(T)^3/(V_1 + V_2)) - 1] = F_0 + kTN\ \ln(V_1 + V_2)) \\
S = kN[\ln((V_1 + V_2)/N\lambda T)^3) + 5/2] = S_0 + kN\ \ln((V_1 + V_2)/V_1) \\
P = NkT/V = NkT/(V_1 + V_2) = P_0 V_1/(V_1 + V_2)
\end{gathered} \tag{1.3.75}$$

b. The process is reversible and no heat is transferred, thus it is adiabatic—the entropy is conserved. The number of particles is also conserved:

$$\begin{gathered}
N = N_0 \\
S = S_0
\end{gathered} \tag{1.3.76}$$

Our main task is to calculate the effect of the work done by the gas pressure on the piston. This causes the energy of the gas to decrease, and the temperature decreases as well. One way to find the change in temperature is to use the conservation of entropy, and Eq. (1.3.61), to obtain that $V/\lambda(T)^3$ is a constant and therefore:

$$T \quad V^{-2/3} \tag{1.3.77}$$

Thus the temperature is given by:

$$T = T_0 \left(\frac{V_1 + V_2}{V_1}\right)^{-2/3} \tag{1.3.78}$$

Since the temperature and energy are proportional to each other (Eq. (1.3.60)), similarly:

$$U = U_0 \left(\frac{V_1 + V_2}{V_1}\right)^{-2/3} \tag{1.3.79}$$

The free-energy expression in Eq. (1.3.59) changes only through the temperature prefactor:

$$F = kTN[\ln(N\lambda(T)^3/V) - 1] = F_0 \frac{T}{T_0} = F_0 \left(\frac{V_1 + V_2}{V_1}\right)^{-2/3} \tag{1.3.80}$$

Finally, the pressure (Eq. (1.6.64)):

$$P = NkT/V = P_0 \frac{TV_0}{T_0 V} = P_0 \left(\frac{V_1 + V_2}{V_1}\right)^{-5/3} \tag{1.3.81}$$ ∎

The ideal gas illustrates the significance of the Boltzmann distribution. Consider a single particle. We can treat it either as part of the large system or as a subsystem in its own right. In the ideal gas, without any interactions, its energy would not change. Thus the particle would not be described by the Boltzmann probability in Eq. (1.3.29). However, we can allow the ideal gas model to include a weak or infrequent interaction (collision) between particles which changes the particle's energy. Over a long time compared to the time between collisions, the particle will explore all possible positions in space and all possible momenta. The probability of its being at a particular position and momentum (in a region $d^3x d^3p$) is given by the Boltzmann distribution:

$$\frac{e^{-\frac{p^2}{2mkT}} d^3p d^3x / h^3}{\int e^{-\frac{p^2}{2mkT}} d^3p d^3x / h^3} \tag{1.3.82}$$

Instead of considering the trajectory of this particular particle and the effects of the (unspecified) collisions, we can think of an ensemble that represents this particular particle in contact with a thermal reservoir. The ensemble would be composed of many different particles in different boxes. There is no need to have more than one particle in the system. We do need to have some mechanism for energy to be transferred to and from the particle instead of collisions with other particles. This could happen as a result of the collisions with the walls of the box if the vibrations of the walls give energy to the particle or absorb energy from the particle. If the wall is at the temperature T, this would also give rise to the same Boltzmann distribution for the particle. The probability of a particular particle in a particular box being in a particular location with a particular momentum would be given by the same Boltzmann probability.

Using the Boltzmann probability distribution for the velocity, we could calculate the average velocity of the particle as:

$$< v^2 > = 3 < v^2 > = 3\frac{\int v^2 e^{-\frac{p^2}{2mkT}} d^3p d^3x / h^3}{\int e^{-\frac{p^2}{2mkT}} d^3p d^3x / h^3} = \frac{\int v^2 e^{-\frac{p^2}{2mkT}} dp}{\int e^{-\frac{p^2}{2mkT}} dp} = \frac{3kT}{m} \quad (1.3.83)$$

which is the same result as we obtained for the ideal gas in the last part of Question 1.3.2. We could even consider one coordinate of one particle as a separate system and arrive at the same conclusion.Our description of systems is actually a description of coordinates.

There are differences when we consider the particle to be a member of an ensemble and as one particle of a gas. In the ensemble, we do not need to consider the distinguishability of particles. This does not affect any of the properties of a single particle.

This discussion shows that the ideal gas model may be viewed as quite close to the basic concept of an ensemble.Generalize the physical particle in three dimensions to a point with coordinates that describe a complete system. These coordinates change in time as the system evolves according to the rules of its dynamics.The ensemble represents this system in the same way as the ideal gas is the ensemble of the particle. The lack of interaction between the different members of the ensemble,and the existence of a transfer of energy to and from each of the systems to generate the Boltzmann probability, is the same in each of the cases. This analogy is helpful when thinking about the nature of the ensemble.

1.3.4 *Phase transitions—first and second order*

In the previous section we constructed some of the underpinnings of thermodynamics and their connection with microscopic descriptions of materials using statistical mechanics. One of the central conclusions was that by minimizing the free energy we can find the equilibrium state of a material that has a fixed number of particles, volume and temperature. Once the free energy is minimized to obtain the equilibrium state of the material, the energy, entropy and pressure are uniquely determined. The free energy is also a function of the temperature, the volume and the number of particles.

One of the important properties of materials is that they can change their properties suddenly when the temperature is changed by a small amount. Examples of this are the transition of a solid to a liquid, or a liquid to a gas. Such a change is known as a phase transition. Each well-defined state of the material is considered a particular phase. Let us consider the process of minimizing the free energy as we vary the temperature. Each of the properties of the material will, in general, change smoothly as the temperature is varied. However, special circumstances might occur when the minimization of the free energy at one temperature results in a very different set of properties of the material from this minimization at a slightly different temperature. This is illustrated in a series of frames in Fig. 1.3.6, where a schematic of the free energy as a function of some macroscopic parameter is illustrated.

The temperature at which the jump in properties of the material occurs is called the critical or transition temperature, T_c. In general, all of the properties of the material except for the free energy jump discontinuously at T_c. This kind of phase transition is known as a first-order phase transition. Some of the properties of a first-order phase transition are that the two phases can coexist at the transition temperature so that part of the material is in one phase and part in the other. An example is ice floating in water. If we start from a temperature below the transition temperature—with ice—and add heat to the system gradually, the temperature will rise until we reach the transition temperature. Then the temperature will stay fixed as the material converts from one phase to the other—from ice to water. Once the whole system is converted to the higher temperature phase, the temperature will start to increase again.

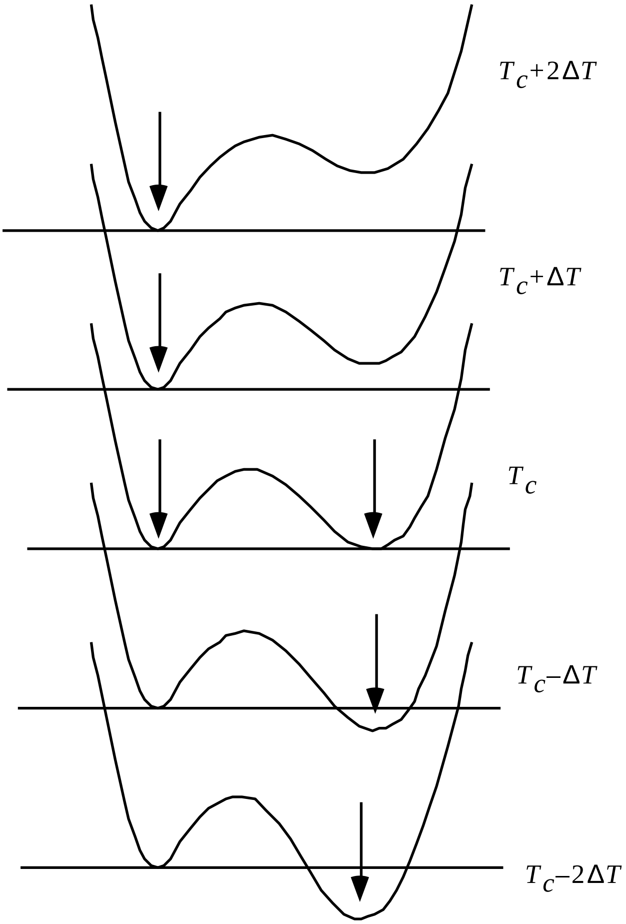


Figure 1.3.6 Each of the curves represents the variation of the free energy of a system as a function of macroscopic parameters. The different curves are for different temperatures. As the temperature is varied the minimum of the free energy all of a sudden switches from one set of macroscopic parameters to another. This is a first-order phase transition like the melting of ice to form water, or the boiling of water to form steam. Below the ice-to-water phase transition the macroscopic parameters that describe ice are the minimum of the free energy, while above the phase transition the macroscopic parameters that describe water are the minimum of the free energy. ▮

The temperature T_c at which a transition occurs depends on the number of particles and the volume of the system. Alternatively, it may be considered a function of the pressure. We can draw a phase-transition diagram (Fig. 1.3.7) that shows the transition temperature as a function of pressure. Each region of such a diagram corresponds to a particular phase.

There is another kind of phase transition, known as a second-order phase transition, where the energy and the pressure do not change discontinuously at the phase-transition point. Instead, they change continuously, but they are nonanalytic at the transition temperature. A common way that this can occur is illustrated in Fig. 1.3.8. In this case the single minimum of the free energy breaks into two minima as a function of temperature. The temperature at which the two minima appear is the transition temperature. Such a second-order transition is often coupled to the existence of first-order transitions. Below the second-order transition temperature, when the two minima exist, the variation of the pressure can change the relative energy of the two minima and cause a first-order transition to occur. The first-order transition occurs at a particular pressure $P_c(T)$ for each temperature below the second-order transition temperature. This gives rise to a line of first-order phase transitions. Above the second-order transition temperature, there is only one minimum, so that there are

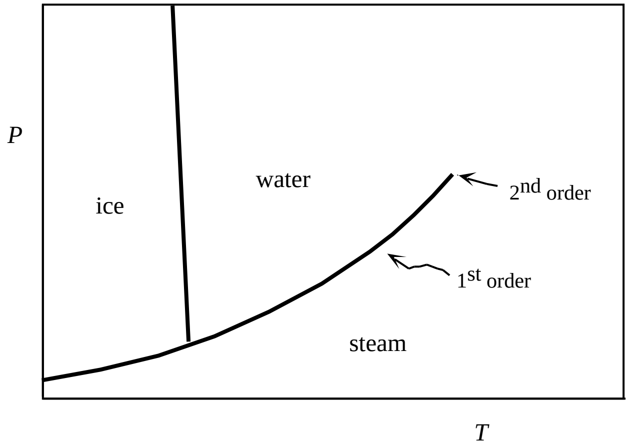


Figure 1.3.7 Schematic phase diagram of H_2O showing three phases — ice, water and steam. Each of the regions shows the domain of pressures and temperatures at which a pure phase is in equilibrium. The lines show phase transition temperatures, $T_c(P)$, or phase transition pressures, $P_c(T)$. The different ways of crossing lines have different names. Ice to water: melting; ice to steam: sublimation; water to steam: boiling; water to ice: freezing; steam to water: condensation; steam to ice: condensation to frost. The transition line from water to steam ends at a point of high pressure and temperature where the two become indistinguishable. At this high pressure steam is compressed till it has a density approaching that of water, and at this high temperature water molecules are energetic like a vapor. This special point is a second-order phase transition point (see Fig. 1.3.8). ▮

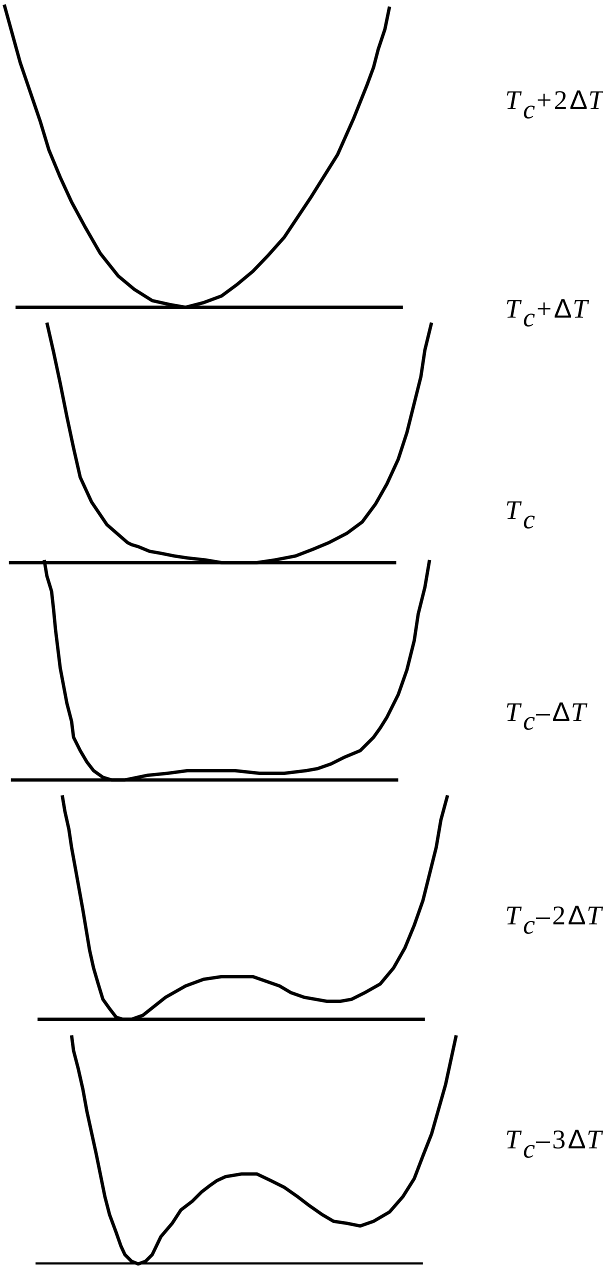


Figure 1.3.8 Similar to Fig. 1.3.6, each of the curves represents the variation of the free energy of a system as a function of macroscopic parameters. In this case, however, the phase transition occurs when two minima emerge from one. This is a second-order phase transition. Below the temperature at which the second-order phase transition occurs, varying the pressure can give rise to a first-order phase transition by changing the relative energies of the two minima (see Figs. 1.3.6 and 1.3.7). ❚

also no first-order transitions. Thus, the second-order transition point occurs as the end of a line of first-order transitions.A second-order transition is found at the end of the liquid-to-vapor phase line of water in Fig. 1.3.7.

The properties of second-order phase transitions have been extensively studied because of interesting phenomena that are associated with them. Unlike a first-order phase transition, there is no coexistence of two phases at the phase transition, because there is only one phase at that point. Instead, there exist large fluctuations in the local properties of the material at the phase transition. A suggestion of why this occurs can be seen from Fig. 1.3.8, where the free energy is seen to be very flat at the phase transition. This results in large excursions (fluctuations) of all the properties of the system except the free energy. These excursions, however, are not coherent over the whole material. Instead, they occur at every length scale from the microscopic on up. The closer a material is to the phase transition, the longer are the length scales that are affected. As the temperature is varied so that the system moves away from the transition temperature,the fluctuations disappear, first on the longest length scales and then on shorter and shorter length scales. Because at the phase transition itself even the macroscopic length scales are affected,thermodynamics itself had to be carefully rethought in the vicinity of second-order phase transitions. The methodology that has been developed, the renormalization group, is an important tool in the investigation of phase transitions. We will discuss it in Section 1.10. We note that, to be consistent with Question 1.3.1, the specific heat C_V must diverge at a second-order phase transition, where energy fluctuations can be large.

1.3.5 *Use of thermodynamics and statistical mechanics in describing the real world*

How do we generalize the notions of thermodynamics that we have just described to apply to more realistic situations? The assumptions of thermodynamics—that systems are in equilibrium and that dividing them into parts leads to unchanged local properties—do not generally apply. The breakdown of the assumptions of thermodynamics occurs for even simple materials, but are more radically violated when we consider biological organisms like trees or people. We still are able to measure their temperature. How do we extend thermodynamics to apply to these systems?

We can start by considering a system quite close to the thermodynamic ideal—a pure piece of material that is not in equilibrium. For example, a glass of water in a room. We generally have no trouble placing a thermometer in the glass and measuring the temperature of the water. We know it is not in equilibrium, because if we wait it will evaporate to become a vapor spread out throughout the room (even if we simplify by considering the room closed). Moreover, if we wait longer (a few hundred years to a few tens of thousands of years),the glass itself will flow and cover the table or flow down to the floor, and at least part of it will also sublime to a vapor. The table will undergo its own processes of deterioration. These effects will occur even in an idealized closed room without considerations of various external influences or traffic through the room. There is one essential concept that allows us to continue to apply thermodynamic principles to these materials,and measure the temperature of the water, glass or table, and generally to discover that they are at the same (or close to the same) temperature. The concept is the separation of time scales. This concept is as basic as the other principles of thermodynamics. It plays an essential role in discussions of the dynamics of physical systems and in particular of the dynamics of complex systems. The separation of time scales assumes that our observations of systems have a limited time resolution and are performed over a limited time. The processes that occur in a material are then separated into fast processes that are much faster than the time resolution of our observation, slow processes that occur on longer time scales than the duration of observation,and dynamic processes that occur on the time scale of our observation. Macroscopic averages are assumed to be averages over the fast processes. Thermodynamics allows us to deal with the slow and the fast processes but only in very limited ways with the dynamic processes. The dynamic processes are dealt with separately by Newtonian mechanics.

Slow processes establish the framework in which thermodynamics can be applied. In formal terms,the ensemble that we use in thermodynamics assumes that all the parameters of the system described by slow processes are fixed. To describe a system using statistical mechanics, we consider all of the slowly varying parameters of the system to be fixed and assume that equilibrium applies to all of the fast processes. Specifically, we assume that all possible arrangements of the fast coordinates exist in the ensemble with a probability given by the Boltzmann probability. Generally, though not always, it is the microscopic processes that are fast. To justify this we can consider that an atom in a solid vibrates at a rate of 10^{10}–10^{12} times per second,a gas molecule at room temperature travels five hundred meters per second. These are, however, only a couple of select examples.

Sometimes we may still choose to perform our analysis by averaging over many possible values of the slow coordinates. When we do this we have two kinds of ensembles—the ensemble of the fast coordinates and the ensemble of the different values of the slow coordinates. These ensembles are called the annealed and quenched ensembles. For example, say we have a glass of water in which there is an ice cube. There are fast processes that correspond to the motion of the water molecules and the vibrations of the ice molecules,and there are also slow processes corresponding to the movement of the ice in the water. Let's say we want to determine the average amount of ice. If we perform several measurements that determine the coordinates and size of the ice, we may want to average the size we find over all the measurements even though they are measurements corresponding to different locations of the ice. In contrast, if we wanted to measure the motion of the ice, averaging the measurements of location would be absurd.

Closely related to the discussion of fast coordinates is the ergodic theorem. The ergodic theorem states that a measurement performed on a system by averaging a property over a long time is the same as taking the average over the ensemble of the fast coordinates. This theorem is used to relate experimental measurements that are assumed to occur over long times to theoretically obtained averages over ensembles. The ergodic theorem is not a theorem in the sense that it has been proven in general, but rather a statement of a property that applies to some macroscopic systems and is known not to apply to others. The objective is to identify when it applies. When it does not apply, the solution is to identify which quantities may be averaged and which may not, often by separating fast and slow coordinates or equivalently by identifying quantities conserved by the fast dynamics of the system.

Experimental measurements also generally average properties over large regions of space compared to microscopic lengths. It is this spatial averaging rather than time averaging that often enables the ensemble average to stand for experimental measurements when the microscopic processes are not fast compared to the measurement time. For example, materials are often formed of microscopic grains and have many dislocations. The grain boundaries and dislocations do move, but they often change very slowly over time. When experiments are sensitive to their properties, they often average over the effects of many grains and dislocations because they do not have sufficient resolution to see a single grain boundary or dislocation.

In order to determine what is the relevant ensemble for a particular experiment, both the effect of time and space averaging must be considered. Technically, this requires an understanding of the correlation in space and time of the properties of an individual system. More conceptually, measurements that are made for particular quantities are in effect made over many independent systems both in space and in time, and therefore correspond to an ensemble average. The existence of correlation is the opposite of independence. The key question (like in the case of the ideal gas) becomes what is the interval of space and time that corresponds to an independent system. These quantities are known as the correlation length and the correlation time. If we are able to describe theoretically the ensemble over a correlation length and correlation time, then by appropriate averaging we can describe the measurement.

In summary, the program of use of thermodynamics in the real world is to use the separation of the different time scales to apply equilibrium concepts to the fast degrees of freedom and discuss their influence on the dynamic degrees of freedom while keeping fixed the slow degrees of freedom. The use of ensembles simplifies consideration of these systems by systematizing the use of equilibrium concepts to the fast degrees of freedom.

1.3.6 *From thermodynamics to complex systems*

Our objective in this book is to consider the dynamics of complex systems. While, as discussed in the previous section, we will use the principles of thermodynamics to help us in this analysis, another important reason to review thermodynamics is to recognize what complex systems are not. Thermodynamics describes macroscopic systems without structure or dynamics. The task of thermodynamics is to relate the very few macroscopic parameters to each other. It suggests that these are the only relevant parameters in the description of these systems. Materials and complex systems are both formed out of many interacting parts. The ideal gas example described a material where the interaction between the particles was weak. However, thermodynamics also describes solids, where the interaction is strong. Having decided that complex systems are not described fully by thermodynamics, we must ask, Where do the assumptions of thermodynamics break down? There are several ways the assumptions may break down, and each one is significant and plays a role in our investigation of complex systems. Since we have not yet examined particular examples of complex systems, this discussion must be quite abstract. However, it will be useful as we study complex systems to refer back to this discussion. The abstract statements will have concrete realizations when we construct models of complex systems.

The assumptions of thermodynamics separate into space-related and time-related assumptions. The first we discuss is the divisibility of a macroscopic material. Fig. 1.3.2 (page 61) illustrates the property of divisibility. In this process,a small part of a system is separated from a large part of the system without affecting the *local* properties of the material. This is inherent in the use of extensive and intensive quantities. Such divisibility is not true of systems typically considered to be complex systems. Consider, for example, a person as a complex system that cannot be separated and continue to have the same properties. In words, we would say that complex systems are formed out of not only interacting, but also interdependent parts. Since both thermodynamic and complex systems are formed out of interacting parts, it is the concept of interdependency that must distinguish them. We will dedicate a few paragraphs to defining a sense in which “interdependent” can have a more precise meaning.

We must first address a simple way in which a system may have a nonextensive energy and still not be a complex system. If we look closely at the properties of a material, say a piece of metal or a cup of water, we discover that its surface is different from the bulk. By separating the material into pieces, the surface area of the material is changed. For macroscopic materials,this generally does not affect the bulk properties of the material.A characteristic way to identify surface properties, such as the surface energy, is through their dependence on particle number. The surface energy scales as $N^{2/3}$, in contrast to the extensive bulk energy that is linear in N. This kind of correction can be incorporated directly in a slightly more detailed treatment of thermodynamics, where every macroscopic parameter has a surface term. The presence of such surface terms is not sufficient to identify a material as a complex system. For this reason, we are careful to identify complex systems by requiring that the scenario of Fig. 1.3.2 is violated by changes in the local (i.e., everywhere including the bulk) properties of the system, rather than just the surface.

It may be asked whether the notion of “local properties” is sufficiently well defined as we are using it. In principle,it is not. For now, we adopt this notion from thermodynamics. When only a few properties, like the energy and entropy, are relevant, “affect locally”is a precise concept.Later we would like to replace the use of local thermodynamic properties with a more general concept—the behavior of the system.

How is the scenario of Fig. 1.3.2 violated for a complex system? We can find that the local properties of the small part are affected without affecting the local properties of the large part.Or we can find that the local properties of the large part are affected as well. The distinction between these two ways of affecting the system is important, because it can enable us to distinguish between different kinds of complex systems. It will be helpful to name them for later reference. We call the first category of systems complex materials, the second category we call complex organisms.

Why don't we also include the possibility that the large part is affected but not the small part? At this point it makes sense to consider generic subdivision rather than special subdivision. By generic subdivision, we mean the ensemble of possible subdivisions rather than a particular one. Once we are considering complex systems, the effect of removal of part of a system may depend on which part is removed. However, when we are trying to understand whether or not we have a complex system, we can limit ourselves to considering the generic effects of removing a part of the system. For this reason we do not consider the possibility that subdivision affects the large system and not the small. This might be possible for the removal of a particular small part, but it would be surprising to discover a system where this is generically true.

Two examples may help to illustrate the different classes of complex systems. At least superficially, plants are complex materials, while animals are complex organisms. The reason that plants are complex materials is that the cutting of parts of a plant, such as leaves, a branch, or a root, typically does not affect the local properties of the rest of the plant, but does affect the excised part. For animals this is not generically the case. However, it would be better to argue that plants are in an intermediate category, where some divisions, such as cutting out a lateral section of a tree trunk, affect both small and large parts, while others affect only the smaller part. For animals, essentially all divisions affect both small and large parts. We believe that complex organisms play a special role in the study of complex system behavior. The essential quality of a complex organism is that its properties are tied to the existence of all of its parts.

How large is the small part we are talking about? Loss of a few cells from the skin of an animal will not generally affect it. As the size of the removed portion is decreased, it may be expected that the influence on the local properties of the larger system will be reduced. This leads to the concept of a robust complex system. Qualitatively, the larger the part that can be removed from a complex system without affecting its local properties, the more robust the system is. We see that a complex material is the limiting case of a highly robust complex system.

The flip side of subdivision of a system is aggregation. For thermodynamic systems, subdivision and aggregation are the same, but for complex systems they are quite different. One of the questions that will concern us is what happens when we place a few or many complex systems together. Generally we expect that the individual complex systems will interact with each other. However, one of the points we can make at this time is that just placing together many complex systems, trees or people, does not make a larger complex system by the criteria of subdivision. Thus, a collection of complex systems may result in a system that behaves as a thermodynamic system under subdivision—separating it into parts does not affect the behavior of the parts.

The topic of bringing together many pieces or subdividing into many parts is also quite distinct from the topic of subdivision by removal of a single part. This brings us to a second assumption we will discuss. Thermodynamic systems are assumed to be composed of a very large number of particles. What about complex systems? We know that the number of molecules in a cup of water is not greater than the number of molecules in a human being. And yet, we understand that this is not quite the right point. We should not be counting the number of water molecules in the person, instead we might count the number of cells, which is much smaller. Thus appears the problem of counting the number of components of a system. In the context of correlations in materials, this was briefly discussed at the end of the last section. Let us assume for the moment that we know how to count the number of components. It seems clear that systems with only a few components should not be treated by thermodynamics. One of the interesting questions we will discuss is whether in the limit of a very large number of components we will always have a thermodynamic system. Stated in a simpler way from the point of view of the study of complex systems, the question becomes how large is too large or how many is too many. From the thermodynamic perspective the question is, Under what circumstances do we end up with the thermodynamic limit?

We now switch to a discussion of time-related assumptions. One of the basic assumptions of thermodynamics is the ergodic theorem that enables the description of a single system using an ensemble. When the ergodic theorem breaks down, as discussed in the previous section, additional fixed or quenched variables become important. This is the same as saying that there are significant differences between different examples of the macroscopic system we are interested in. This is a necessary condition for the existence of a complex system. The alternative would be that all realizations of the system would be the same, which does not coincide with intuitive notions of complexity. We will discuss several examples of the breaking of the ergodic theorem later. The simplest example is a magnet. The orientation of the magnet is an additional parameter that must be specified, and therefore the ergodic theorem is violated for this system. Any system that breaks symmetry violates the ergodic theorem. However, we do not accept a magnet as a complex system. Therefore we can assume that the breaking of ergodicity is a necessary but not sufficient condition for complexity. All of the systems we will discuss break ergodicity, and therefore it is always necessary to specify which coordinates of the complex system are fixed and which are to be assumed to be so rapidly varying that they can be assigned equilibrium Boltzmann probabilities.

A special case of the breaking of the ergodic theorem, but one that strikes even more deeply at the assumptions of thermodynamics, is a violation of the separation of time scales. If there are dynamical processes that occur on every time scale, then it becomes impossible to treat the system using the conventional separation of scales into fast, slow and dynamic processes. As we will discuss in Section 1.10, the techniques of renormalization that are used in phase transitions to deal with the existence of many spatial scales may also be used to describe systems changing on many time scales.

Finally, inherent in thermodynamics, the concept of equilibrium and the ergodic theorem is the assumption that the initial condition of the system does not matter. For a complex system, the initial condition of the system does matter over the time scales relevant to our observation. This brings us back to the concept of correlation time. The correlation time describes the length of time over which the initial conditions are relevant to the dynamics. This means that our observation of a complex system must be shorter than a correlation time. The spatial analog, the correlation length, describes the effects of surfaces on the system. The discussion of the effects of subdivision also implies that the system must be smaller than a correlation length. This means that complex systems change their internal structure—adapt—to conditions at their boundaries. Thus, a suggestive though incomplete summary of our discussion of complexity in the context of thermodynamics is that a complex system is contained within a single correlation distance and correlation time.

1.4 Activated Processes (and Glasses)

In the last section we saw figures (Fig. 1.3.7) showing the free energy as a function of a macroscopic parameter with two minima. In this section we analyze a single particle system that has a potential energy with a similar shape (Fig. 1.4.1). The particle is in equilibrium with a thermal reservoir. If the average energy is lower than the energy of the barrier between the two wells, then the particle generally resides for a time in one well and then switches to the other. At very low temperatures, in equilibrium,it will be more and more likely to be in the lower well and less likely to be in the higher well. We use this model to think about a system with two possible states, where one state is higher in energy than the other. If we start the system in the higher energy state, the system will relax to the lower energy state. Because the process of relaxation is enabled or accelerated by energy from the thermal resevoir, we say that it is activated.

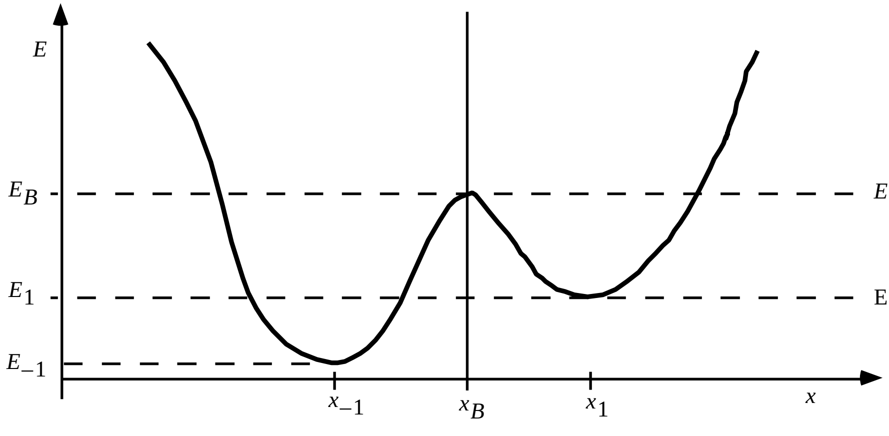


Figure 1.4.1 Illustration of the potential energy of a system that has two local minimum energy configurations x_1 and x_{-1}. When the temperature is lower than the energy barriers $E_B - E_{-1}$ and $E_B - E_1$, the system may be considered as a two-state system with transitions between them. The relative probability of the two states varies with temperature and the relative energy of the bottom of the two wells. The rate of transition also varies with temperature. When the system is cooled systematically the two-state system is a simple model of a glass (Fig. 1.4.2). At low temperatures the system can not move from one well to the other, but is in equilibrium within a single well. ▮

1.4.1 *Two-state systems*

It might seem that a system with only two different states would be easy to analyze. Eventually we will reach a simple problem. However, building the simple model will require us to identify some questions and approximations relevant to our understanding of the application of this model to physical systems (e.g. the problem of protein folding found in Chapter 4). Rather than jumping to the simple two-state problem (Eq. (1.4.40) below), we begin from a particle in a double-well potential. The kinetics and thermodynamics in this system give some additional content to the thermodynamic discussion of the previous section and introduce new concepts.

We consider Fig. 1.4.1 as describing the potential energy $V(x)$ experienced by a classical particle in one dimension. The region to the right of x_B is called the right well and to the left is called the left well. A classical trajectory of the particle with conserved energy would consist of the particle bouncing back and forth within the potential well between two points that are the solution of the equation $V(x) = E$, where E is the total energy of the particle. The kinetic energy at any time is given by

$$E(x,p) - V(x) = \frac{1}{2}mv^2 \tag{1.4.1}$$

which determines the magnitude of the velocity at any position but not the direction. The velocity switches direction every bounce. When the energy is larger than E_B, there is only one distinct trajectory at each energy. For energies larger than E_1 but smaller than E_B, there are two possible trajectories, one in the right well—to the right of x_B — and one in the left well. Below E_1, which is the minimum energy of the right well, there is again only one trajectory possible, in the left well. Below E_{-1} there are no possible locations for the particle.

If we consider this system in isolation, there is no possibility that the particle will change from one trajectory to another. Our first objective is to enable the particle to be in contact with some other system (or coordinate) with which it can transfer energy and momentum. For example, we could imagine that the particle is one of many moving in the double well—like the ideal gas. Sometimes there are collisions that change the energy and direction of the motion. The same effect would be found for many other ways we could imagine the particle interacting with other systems. The main approximation, however, is that the interaction of the particle with the rest of the universe occurs only over short times. Most of the time it acts as if it were by itself in the potential well. The particle follows a trajectory and has an energy that is the sum of its kinetic and potential energies (Eq.(1.4.1)). There is no need to describe the energy associated with the interaction with the other systems. All of the other particles of the gas (or whatever picture we imagine) form the thermal reservoir, which has a well-defined temperature T.

We can increase the rate of collisions between the system and the reservoir without changing our description. Then the particle does not go very far before it forgets the direction it was traveling in and the energy that it had. But as long as the collisions themselves occur over a short time compared to the time between collisions, any time we look at the particle, it has a well-defined energy and momentum. From moment to moment,the kinetic energy and momentum changes unpredictably. Still,the position of the particle must change continuously in time. This scenario is known as diffusive motion. The different times are related by:

collision (interaction) time << time between collisions << transit time

where the transit time is the time between bounces from the walls of the potential well if there were no collisions—the period of oscillation of a particle in the well. The particle undergoes a kind of random walk, with its direction and velocity changing randomly from moment to moment. We will assume this scenario in our treatment of this system.

When the particle is in contact with a thermal reservoir, the laws of thermodynamics apply. The Boltzmann probability gives the probability that the particle is found at position x with momentum p:

$$
\begin{gathered}
P(x,p)=e^{-E(x,p)/kT}/Z \\
Z=\sum_{x,p} e^{-E(x,p)/kT}=\frac{1}{h}\int dx dp\, e^{-E(x,p)/kT}
\end{gathered}
\tag{1.4.2}
$$

Formally, this expression describes a large number of independent systems that make up a canonical ensemble. The ensemble of systems provides a formally precise way of describing probabilities as the number of systems in the ensemble with a particular value of the position and momentum. As in the previous section, Z guarantees that the sum over all probabilities is 1. The factor of h is not relevant in what follows, but for completeness we keep it and associate it with the momentum integral, so that $\Sigma_p \to \int dp/h$.

If we are interested in the position of the particle,and are not interested in its momentum, we can simplify this expression by integrating over all values of the momentum. Since the energy separates into kinetic and potential energy:

$$
P(x)=\frac{e^{-V(x)/kT}\int (dp/h)e^{-p^2/2mkT}}{\int dx\, e^{-V(x)/kT}\int (dp/h)\,e^{-p^2/2mkT}}=\frac{e^{-V(x)/kT}}{\int dx\, e^{-V(x)/kT}}
\tag{1.4.3}
$$

The resulting expression looks similar to our original expression. Its meaning is somewhat different,however, because $V(x)$ is only the potential energy of the system. Since the kinetic energy contributes equivalently to the probability at every location, $V(x)$ determines the probability at every x. An expression of the form $e^{-E/kT}$ is known as the Boltzmann factor of E. Thus Eq.(1.4.3) says that the probability $P(x)$ is proportional to the Boltzmann factor of $V(x)$. We will use this same trick to describe the probability of being to the right or being to the left of x_B in terms of the minimum energy of each well.

To simplify to a two-state system, we must define a variable that specifies only which of the two wells the particle is in. So we label the system by $s = \pm 1$, where $s = +1$ if $x > x_B$ and $s = -1$ if $x < x_B$ for a particular realization of the system at a particular time, or:

$$s = \mathrm{sign}(x - x_B) \tag{1.4.4}$$

Probabilistically, the case $x = x_B$ never happens and therefore does not have to be accounted for.

We can calculate the probability $P(s)$ of the system having a value of $s = +1$ using:

$$P(1) = \frac{\int_{x_B}^{\infty} dx\, e^{-V(x)/kT}}{\int dx\, e^{-V(x)/kT}} \tag{1.4.5}$$

The largest contribution to this probability occurs when $V(x)$ is smallest. We assume that kT is small compared to E_B, then the value of the integral is dominated by the region immediately in the vicinity of the minimum energy. Describing this as a two-state system is only meaningful when this is true. We simplify the integral by expanding it in the vicinity of the minimum energy and keeping only the quadratic term:

$$V(x) = E_1 + \tfrac{1}{2} m\omega_1^2 (x - x_1)^2 + \quad = E_1 + \tfrac{1}{2} k_1 (x - x_1)^2 + \tag{1.4.6}$$

where

$$k_1 = m\omega_1^2 = \left. \frac{d^2 V(x)}{dx^2} \right|_{x_1} \tag{1.4.7}$$

is the effective spring constant and ω_1 is the frequency of small oscillations in the right well. We can now write Eq. (1.4.5) in the form

$$P(1) = \frac{e^{-E_1/kT} \int_{x_B}^{\infty} dx\, e^{-k_1 (x - x_1)^2 /2kT}}{\int dx\, e^{-V(x)/kT}} \tag{1.4.8}$$

Because the integrand in the numerator falls rapidly away from the point $x = x_1$, we could extend the lower limit to $-\infty$. Similarly, the probability of being in the left well is:

$$P(-1) = \frac{e^{-E_{-1}/kT} \int_{-\infty}^{x_B} dx\, e^{-k_{-1} (x - x_{-1})^2 /2kT}}{\int dx\, e^{-V(x)/kT}} \tag{1.4.9}$$

Here the upper limit of the integral could be extended to ∞. It is simplest to assume that $k_1 = k_{-1}$. This assumption, that the shape of the wells are the same, does not significantly affect most of the discussion (Question 1.4.1–1.4.2). The two probabilities are proportional to a new constant times the Boltzmann factor $e^{-E/kT}$ of the energy at the bottom of the well. This can be seen even without performing the integrals in Eq. (1.4.8) and Eq. (1.4.9). We redefine Z for the two-state representation:

$$P(-1) = \frac{e^{-E_{-1}/kT}}{Z_s} \tag{1.4.10}$$

$$P(1) = \frac{e^{-E_1/kT}}{Z_s} \tag{1.4.11}$$

The new normalization Z_s can be obtained from:

$$P(1) + P(-1) = 1 \tag{1.4.12}$$

giving

$$Z_s = e^{-E_1/kT} + e^{-E_{-1}/kT} \tag{1.4.13}$$

which is different from the value in Eq. (1.4.2). We arrive at the desired two-state result:

$$P(1) = \frac{e^{-E_1/kT}}{e^{-E_1/kT} + e^{-E_{-1}/kT}} = \frac{1}{1 + e^{(E_1 - E_{-1})/kT}} = f(E_1 - E_{-1}) \tag{1.4.14}$$

where f is the Fermi probability or Fermi function:

$$f(x) = \frac{1}{1 + e^{x/kT}} \tag{1.4.15}$$

For readers who were introduced to the Fermi function in quantum statistics,it is not unique to that field, it occurs anytime there are exactly two different possibilities. Similarly,

$$P(-1) = \frac{e^{-E_{-1}/kT}}{e^{-E_1/kT} + e^{-E_{-1}/kT}} = \frac{1}{1 + e^{(E_{-1} - E_1)/kT}} = f(E_{-1} - E_1) \tag{1.4.16}$$

which is consistent with Eq. (1.4.12) above since

$$f(x) + f(-x) = 1 \tag{1.4.17}$$

Question 1.4.1 Discuss how $k_1 \neq k_{-1}$ would affect the results for the two-state system in equilibrium. Obtain expressions for the probabilities in each of the wells.

Solution 1.4.1 Extending the integrals to ±∞, as described in the text after Eq. (1.4.8) and Eq. (1.4.9), we obtain:

$$P(1) = \frac{e^{-E_1/kT}\sqrt{2\pi kT/k_1}}{\int dx\, e^{-V(x)/kT}} \tag{1.4.18}$$

$$P(-1) = \frac{e^{-E_1/kT}\sqrt{2\pi kT/k_{-1}}}{\int dx\, e^{-V(x)/kT}} \tag{1.4.19}$$

Because of the approximate extension of the integrals, we are no longer guaranteed that the sum of these probabilities is 1. However, within the accuracy of the approximation, we can reimpose the normalization condition. Before we do so, we choose to rewrite $k_1 = m\omega_1^{\;2} = m(2\pi\nu_1)^2$, where ν_1 is the natural frequency of the well. We then ignore all common factors in the two probabilities and write

$$P(1) = \frac{\nu_1^{-1} e^{-E_1/kT}}{Z_s'} \tag{1.4.20}$$

$$P(-1) = \frac{\nu_{-1}^{-1} e^{-E_{-1}/kT}}{Z_s'} \tag{1.4.21}$$

$$Z_s' = \nu_{-1}^{-1} e^{-E_1/kT} + \nu_{-1}^{-1} e^{-E_{-1}/kT} \tag{1.4.22}$$

Or we can write, as in Eq. (1.4.14)

$$P(1) = \frac{1}{1 + (\nu_1/\nu_{-1})e^{(E_1 - E_{-1})/kT}} \tag{1.4.23}$$

and similarly for $P(-1)$. ∎

Question 1.4.2 Redefine the energies E_1 and E_{-1} to include the effect of the difference between k_1 and k_{-1} so that the probability $P(1)$ (Eq. (1.4.23)) can be written like Eq. (1.4.14) with the new energies. How is the result related to the concept of free energy and entropy?

Solution 1.4.2 We define the new energy of the right well as

$$F_1 = E_1 + kT\ln(\nu_1) \tag{1.4.24}$$

This definition can be seen to recover Eq. (1.4.23) from the form of Eq. (1.4.14) as

$$P(1) = f(F_1 - F_{-1}) \tag{1.4.25}$$

Eq. (1.4.24) is very reminiscent of the definition of the free energy Eq. (1.3.33) if we use the expression for the entropy:

$$S_1 = -k\ln(\nu_1) \tag{1.4.26}$$

Note that if we consider the temperature dependence, Eq. (1.4.25) is not identical in its behavior with Eq.(1.4.14). The free energy, F_1, depends on T, while the energy at the bottom of the well, E_1, does not. ∎

In Question 1.4.2, Eq. (1.4.24), we have defined what might be interpreted as a free energy of the right well. In Section 1.3 we defined only the free energy of the system as a whole. The new free energy is for part of the ensemble rather than the whole ensemble. We can do this quite generally. Start by identifying a certain subset of all possible states of a system. For example, $s = 1$ in Eq. (1.4.4). Then we define the free energy using the expression:

$$F_s(1) = -kT \ln\Big(\sum_{\{x,p\}} \delta_{s,1}\, e^{-E(\{x,p\})/kT}\Big) = -kT \ln(Z_1) \tag{1.4.27}$$

This is similar to the usual expression for the free energy in terms of the partition function Z, but the sum is only over the subset of states. When there is no ambiguity, we often drop the subscript and write this as $F(1)$. From this definition we see that the probability of being in the subset of states is proportional to the Boltzmann factor of the free energy

$$P(1) \quad e^{-F_s(1)/kT} \tag{1.4.28}$$

If we have several different subsets that account for all possibilities, then we can normalize Eq. (1.4.28) to find the probability itself. If we do this for the left and right wells, we immediately arrive at the expression for the probabilities in Eq.(1.4.14) and Eq. (1.4.16), with E_1 and E_{-1} replaced by $F_s(1)$ and $F_s(-1)$ respectively. From Eq.(1.4.28) we see that for a collection of states, the free energy plays the same role as the energy in the Boltzmann probability.

We note that Eq. (1.4.24) is not the same as Eq.(1.4.27). However, as long as the relative energy is the same, $F_1 - F_{-1} = F_s(1) - F_s(-1)$, the normalized probability is unchanged. When $k_1 = k_{-1}$, the entropic part of the free energy is the same for both wells. Then direct use of the energy instead of the free energy is valid, as in Eq.(1.4.14). We can evaluate the free energy of Eq. (1.4.27), including the momentum integral:

$$\begin{aligned} Z_1 &= \int_{x_B}^{\infty} dx \int (dp/h)\, e^{-E(x,p)/kT} = \int_{x_B}^{\infty} dx e^{-V(x)/kT} \int (dp/h) e^{-p^2/2mkT} \\ &\approx e^{-E_1/kT} \int_{x_B}^{\infty} dx\, e^{-k_1(x-x_1)^2/2kT} \sqrt{2\pi mkT}/h \approx e^{-E_1/kT} \sqrt{m/k_1}\, 2\pi kT/h \\ &= e^{-E_1/kT} kT/h\nu_1 \end{aligned} \tag{1.4.29}$$

$$F_s(1) = E_1 + kT \ln(h\nu_1/kT) \tag{1.4.30}$$

where we have used the definition of the well oscillation frequency above Eq.(1.4.20) to simplify the expression. A similar expression holds for Z_{-1}. The result would be exact for a pure harmonic well.

The new definition of the free energy of a set of states can also be used to understand the treatment of macroscopic systems, specifically to explain why the energy is determined by minimizing the free energy. Partition the possible microstates by the value of the energy, as in Eq. (1.3.35). Define the free energy as a function of the energy analogous to Eq. (1.4.27)

$$F(U) = -kT \ln\left(\sum_{\{x,p\}} \delta_{E(\{x,p\}),U}\, e^{-E(\{x,p\})/kT}\right) \tag{1.4.31}$$

Since the relative probability of each value of the energy is given by

$$P(U) \quad e^{-F(U)/kT} \tag{1.4.32}$$

the most likely energy is given by the lowest free energy. For a macroscopic system, the most likely value is so much more likely than any other value that it is observed in any measurement. This can immediately be generalized. The minimization of the free energy gives not only the value of the energy but the value of any macroscopic parameter.

1.4.2 *Relaxation of a two-state system*

To investigate the kinetics of the two-state system, we assume an ensemble of systems that is not an equilibrium ensemble. Instead,the ensemble is characterized by a time-dependent probability of occupying the two wells:

$$\begin{aligned} P(1) &\rightarrow P(1;t) \\ P(-1) &\rightarrow P(-1;t) \end{aligned} \tag{1.4.33}$$

Normalization continues to hold at every time:

$$P(1;t)+P(-1;t)=1 \tag{1.4.34}$$

For example, we might consider starting a system in the upper well and see how the system evolves in time. Or we might consider starting a system in the lower well and see how the system evolves in time. We answer the question using the time-evolving probabilities that describe an ensemble of systems with the same starting condition. To achieve this objective, we construct a differential equation describing the rate of change of the probability of being in a particular well in terms of the rate at which systems move from one well to the other. This is just the Master equation approach from Section 1.2.4.

The systems that make transitions from the left to the right well are the ones that cross the point $x = x_B$. More precisely, the rate at which transitions occur is the probability current per unit time of systems at x_B, moving toward the right. Similar to Eq. (1.3.47) used to obtain the pressure of an ideal gas on a wall,the number of particles crossing x_B is the probability of systems at x_B with velocity v, times their velocity:

$$J(1|-1)=\int_0^\infty (dp/h)vP(x_B,p;t) \tag{1.4.35}$$

where $J(1|-1)$ is the number of systems per unit time moving from the left to the right. There is a hidden assumption in Eq. (1.4.35). We have adopted a notation that treats all systems on the left together. When we are considering transitions,this is only valid if a system that crosses $x = x_B$ from right to left makes it down into the well on the left, and thus does not immediately cross back over to the side it came from.

We further assume that in each well the systems are in equilibrium, even when the two wells are not in equilibrium with each other. This means that the probability of being in a particular location in the right well is given by:

$$\begin{aligned} P(x,p;t) &= P(1;t)e^{-E(x,p)/kT}/Z_1 \\ Z_1 &= \int_{x_B}^{\infty} dxdp\ e^{-E(x,p)/kT} \end{aligned} \tag{1.4.36}$$

In equilibrium, this statement is true because then $P(1) = Z_1/Z$. Eq.(1.4.36) presumes that the rate of collisions between the particle and the thermal reservoir is faster than both the rate at which the system goes from one well to the other and the frequency of oscillation in a well.

In order to evaluate the transition rate Eq.(1.4.35), we need the probability at x_B. We assume that the systems that cross x_B moving from the left well to the right well (i.e., moving to the right) are in equilibrium with systems in the left well from where they came. Systems that are moving from the right well to the left have the equilibrium distribution characteristic of the right well. With these assumptions, the rate at which systems hop from the left to the right is given by:

$$\begin{aligned} J(1|-1) &= \int_0^{\infty} (dp/h)(p/m)\left(P(-1;t)e^{-(E_B+p^2/2m)/kT}/Z_{-1}\right) \\ &= P(-1;t)e^{-E_B/kT}(kT/h)/Z_{-1} \end{aligned} \tag{1.4.37}$$

We find using Eq. (1.4.29) that the current of systems can be written in terms of a transition rate per system:

$$\begin{aligned} J(1|-1) &= R(1|-1)P(-1;t) \\ R(1|-1) &= \nu_{-1}e^{-(E_B-E_{-1})/kT} \end{aligned} \tag{1.4.38}$$

Similarly, the current and rate at which systems hop from the right to the left are given by:

$$\begin{aligned} J(-1|1) &= R(-1|1)P(1;t) \\ R(-1|1) &= \nu_1 e^{-(E_B-E_1)/kT} \end{aligned} \tag{1.4.39}$$

When $k_1 = k_{-1}$ then $\nu_1 = \nu_{-1}$. We continue to deal with this case for simplicity and define $\nu = \nu_1 = \nu_{-1}$. The expressions for the rate of transition suggest the interpretation that the frequency ν is the rate of attempt to cross the barrier. The probability of crossing in each attempt is given by the Boltzmann factor, which gives the likelihood that the energy exceeds the barrier. While this interpretation is appealing, and is often given, it is misleading. It is better to consider the frequency as describing the width of the well in which the particle wanders. The wider the well is, the less likely is a barrier crossing. This interpretation survives better when more general cases are considered.

The transition rates enable us to construct the time variation of the probability of occupying each of the wells. This gives us the coupled equations for the two probabilities:

$$\begin{aligned} \dot{P}(1;t) &= R(1|-1)P(-1;t) - R(-1|1)P(1;t) \\ \dot{P}(-1;t) &= R(-1|1)P(1;t) - R(1|-1)P(-1;t) \end{aligned} \tag{1.4.40}$$

These are the Master equations (Eq. (1.2.86)) for the two-state system. We have arrived at these equations by introducing a set of assumptions for treating the kinetics of a single particle. The equations are much more general, since they say only that there is a rate of transition between one state of the system and the other. It is the correspondence between the two-state system and the moving particle that we have established in Eqs. (1.4.38) and (1.4.39). This correspondence is approximate. Eq. (1.4.40) does not rely upon the relationship between E_B and the rate at which systems move from one well to the other. However, it does rely upon the assumption that we need to know only which well the system is in to specify its rate of transition to the other well. On average this is always true, but it would not be a good description of the system, for example, if energy is conserved and the key question determining the kinetics is whether the particle has more or less energy than the barrier E_B.

We can solve the coupled equations in Eq. (1.4.40) directly. Both equations are not necessary, given the normalization constraint Eq.(1.4.34). Substituting $P(-1;t) = 1 - P(1;t)$ we have the equation

$$\dot{P}(1;t) = R(-1|1) - P(1;t)(R(1|-1) + R(-1|1)) \tag{1.4.41}$$

We can rewrite this in terms of the equilibrium value of the probability. By definition this is the value at which the time derivative vanishes.

$$P(1;\infty) = R(-1|1)/(R(1|-1) + R(-1|1)) = f(E_1 - E_{-1}) \tag{1.4.42}$$

where the right-hand side follows from Eq.(1.4.38) and Eq.(1.4.39) and is consistent with Eq. (1.4.13), as it must be. Using this expression, Eq. (1.4.24) becomes

$$\dot{P}(1;t) = (P(1;\infty) - P(1;t))/\tau \tag{1.4.43}$$

where we have defined an additional quantity

$$1/\tau = (R(1|-1) + R(-1|1)) = \nu(e^{-(E_B - E_1)/kT} + e^{-(E_B - E_{-1})/kT}) \tag{1.4.44}$$

The solution of Eq. (1.4.43) is

$$P(1;t) = (P(1;0) - P(1;\infty))e^{-t/\tau} + P(1;\infty) \tag{1.4.45}$$

This solution describes a decaying exponential that changes the probability from the starting value to the equilibrium value. This explains the definition of τ, called the relaxation time. Since it is inversely related to the sum of the rates of transition between the wells,it is a typical time taken by a system to hop between the wells. The relaxation time does not depend on the starting probability. We note that the solution of Eq.(1.4.41) does not depend on the explicit form of $P(1;\infty)$ or τ. The definitions implied by the first equal signs in Eq.(1.4.42) and Eq.(1.4.44) are sufficient. Also, as can be quickly checked, we can replace the index 1 with the index −1 without changing anything else in Eq (1.4.45). The other equations are valid (by symmetry) after the substitution $1 \leftrightarrow -1$.

There are several intuitive relationships between the equilibrium probabilities and the transition rates that may be written down. The first is that the ratio of the equilibrium probabilities is the ratio of the transition rates:

$$P_1(\infty)/P_{-1}(\infty) = R(-1|1)/R(1|-1) \qquad (1.4.46)$$

The second is that the equilibrium probability divided by the relaxation time is the rate of transition:

$$P_1(\infty)/\tau = R(-1|1) \qquad (1.4.47)$$

Question 1.4.3 Eq. (1.4.45) implies that the relaxation time of the system depends largely on the smaller of the two energy barriers $E_B - E_1$ and $E_B - E_{-1}$. For Fig. 1.4.1 the smaller barrier is $E_B - E_1$. Since the relaxation time is independent of the starting probability, this barrier controls the rate of relaxation whether we start the system from the lower well or the upper well. Why does the barrier $E_B - E_1$ control the relaxation rate when we start from the lower well?

Solution 1.4.3 Even though the rate of transition from the lower well to the upper well is controlled by $E_B - E_{-1}$, the fraction of the ensemble that must make the transition in order to reach equilibrium depends on E_1. The higher it is,the fewer systems must make the transition from $s = -1$ to $s = 1$. Taking this into consideration implies that the time to reach equilibrium depends on $E_B - E_1$ rather than $E_B - E_{-1}$. ▮

1.4.3 *Glass transition*

Glasses are materials that when cooled from the liquid do not undergo a conventional transition to a solid. Instead their viscosity increases,and in the vicinity of a particular temperature it becomes so large that on a reasonable time scale they can be treated as solids. However, on long enough time scales,they flow as liquids. We will model the glass transition using a two-state system by considering what happens as we cool down the two-state system. At high enough temperatures, the system hops back and forth between the two minima with rates given by Eqs.(1.4.38) and (1.4.39). ν is a microscopic quantity; it might be a vibration rate in the material. Even if the barriers are higher than the temperature, $E_B - E_{\pm 1} >> kT$, the system will still be able to hop back and forth quite rapidly from a macroscopic perspective.

As the system is cooled down, the hopping back and forth slows down. At some point the rate of hopping will become longer than the time we are observing the system. Systems in the higher well will stay there. Systems in the lower well will stay there. This means that the population in each well becomes fixed. Even when we continue to cool the system down, there will be no change, and the ensemble will no longer be in equilibrium. Within each well the system will continue to have a probability distribution for its energy given by the Boltzmann probability, but the relative populations of the two wells will no longer be described by the equilibrium Boltzmann probability.

To gain a feeling for the numbers, a typical atomic vibration rate is 10^{12}/sec. For a barrier of 1eV, at twice room temperature, $kT \approx 0.05$eV (600°K), the transition rate would be of order 10^{3}/sec. This is quite slow from a microscopic perspective, but at room temperature it would be only 10^{-6}/sec, or one transition per year.

The rate at which we cool the system down plays an essential role. If we cool faster, then the temperature at which transitions stop is higher. If we cool at a slower rate, then the temperature at which the transitions stop is lower. This is found to be the case for glass transitions, where the cooling rate determines the departure point from the equilibrium trajectory of the system, and the eventual properties of the glass are also determined by the cooling rate. Rapid cooling is called quenching. If we raise the temperature and lower it slowly, the procedure is called annealing.

Using the model two-state system we can simulate what would happen if we perform an experiment of cooling a system that becomes a glass. Fig. 1.4.2 shows the probability of being in the upper well as a function of the temperature as the system is cooled down. The curves depart from the equilibrium curve in the vicinity of a transition temperature we might call a freezing transition, because the kinetics become frozen. The glass transition is not a transition like a first- or second-order transition (Section 1.3.4) because it is a transition of the kinetics rather than of the equilibrium structure of the system. Below the freezing transition, the relative probability of the system being in the upper well is given approximately by the equilibrium probability at the transition.

The freezing transition of the relative population of the upper state and the lower state is only a simple model of the glass transition; however, it is also more widely applicable. The freezing does not depend on cooperative effects of many particles. To find examples, a natural place to look is the dynamics of individual atoms in solids. Potential energies with two wells occur for impurities, defects and even bulk atoms in a solid. Impurities may have two different local configurations that differ in energy and are separated by a barrier. This is a direct analog of our model two-state system. When the temperature is lowered, the relative population of the two configurations becomes frozen. If we raise the temperature, the system can equilibrate again.

It is also possible to artificially cause impurity configurations to have unequal energies. One way is to apply uniaxial stress to a crystal—squeezing it along one axis. If an impurity resides in a bond between two bulk atoms, applying stress will raise the energy of impurities in bonds oriented with the stress axis compared to bonds perpendicular to the stress axis. If we start at a relatively high temperature, apply stress and then cool down the material, we can freeze unequal populations of the impurity. If we have a way of measuring relaxation, then by raising the temperature gradually and observing when the defects begin to equilibrate we can discover the barrier to relaxation. This is one of the few methods available to study the kinetics of impurity reorientation in solids.

The two-state system provides us with an example of how a simple system may not be able to equilibrate over experimental time scales. It also shows how an equi-

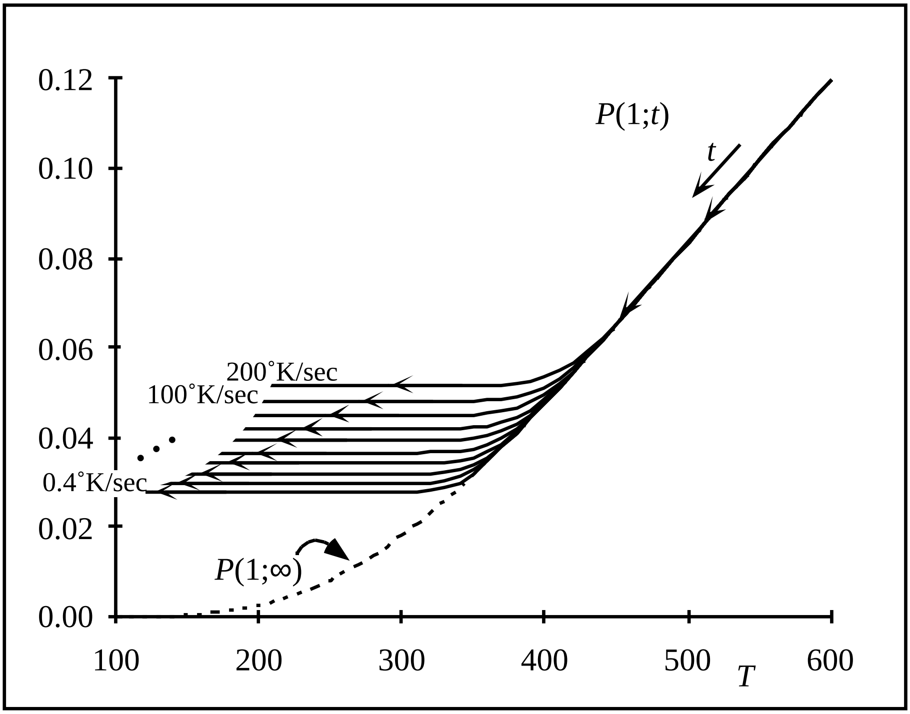


Figure 1.4.2 Plot of the fraction of the systems in the higher energy well as a function of temperature. The equilibrium value is shown with the dashed line. The solid lines show what happens when the system is cooled from a high temperature at a particular cooling rate. The example given uses $E_1 - E_{-1} = 0.1\mathrm{eV}$ and $E_B - E_{-1} = 1.0\mathrm{eV}$. Both wells have oscillation frequencies of $\nu = 10^{12}/\mathrm{sec}$. The fastest cooling rate is 200°K/sec and each successive curve is cooled at a rate that is half as fast, with the slowest rate being 0.4°K/sec. For every cooling rate the system stops making transitions between the wells at a particular temperature that is analogous to a glass transition in this system. Below this temperature the probability becomes essentially fixed. ∎

librium ensemble can be used to treat relative probabilities within a subset of states. Because the motion within a particular well is fast,the relative probabilities of different positions or momenta within a well may be described using the Boltzmann probability. At the same time, the relative probability of finding a system in each of the two wells depends on the initial conditions and the history of the system—what temperature the system experienced and for how long. At sufficiently low temperatures, this relative probability may be treated as fixed. Systems that are in the higher well may be assumed to stay there. At intermediate temperatures, a treatment of the dynamics of the transition between the two wells can (and must) be included. This manifests a violation of the ergodic theorem due to the divergence of the time scale for equilibration between the two wells. Thus we have identified many of the features that are necessary in describing nonequilibrium systems: divergent time scales, violation of the ergodic theorem, frozen and dynamic coordinates. We have illustrated a method for treating systems where there is a separation of long time scales and short time scales.

Question 1.4.4 Write a program that can generate the time dependence of the two-state system for a specified time history. Reproduce Fig. 1.4.2. For an additional "experiment," try the following quenching and annealing sequence:

a. Starting from a high enough temperature to be in equilibrium, cool the system at a rate of 10°K/sec down to $T = 0$.

b. Heat the system up to temperature T_a and keep it there for one second.

c. Cool the system back down to $T = 0$ at rate of 100°K/sec.

Plot the results as a function of T_a. Describe and explain them in words. ▮

1.4.4 *Diffusion*

In this section we briefly consider a multiwell system. An example is illustrated in Fig. 1.4.3, where the potential well depths and barriers vary from site to site. A simpler case is found in Fig. 1.4.4, where all the well depths and barriers are the same. A concrete example would be an interstitial impurity in an ideal crystal. The impurity lives in a periodic energy that repeats every integral multiple of an elementary length a.

We can apply the same analysis from the previous section to describe what happens to a system that begins from a particular well at $x = 0$. Over time, the system makes transitions left and right at random,in a manner that is reminiscent of a random walk. We will see in a moment that the connection with the random walk is valid but requires some additional discussion.

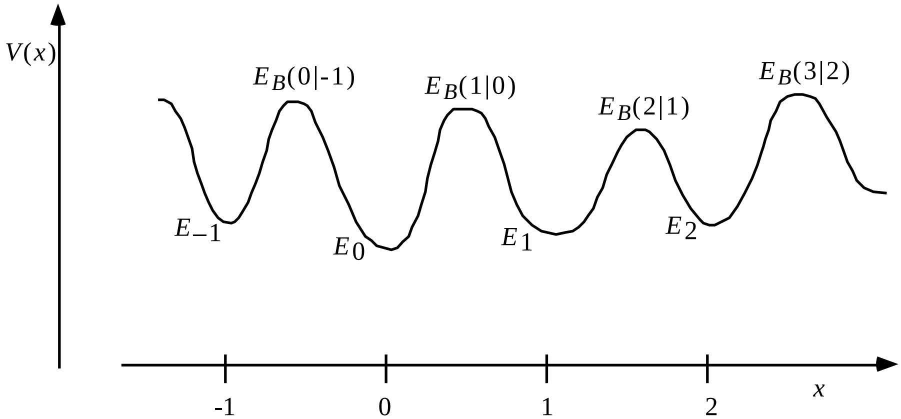


Figure 1.4.3 Illustration of a multiple-well system with barrier heights and well depths that vary from site to site. We focus on the uniform system in Fig. 1.4.4. ▮

The probability of the system being in a particular well is changed by probability currents into the well and out from the well. Systems can move to or from the well immediately to their right and immediately to their left. The Master equation for the *i*th well in Fig. 1.4.3 is:

$$\dot{P}(i;t) = R(i|i-1)P(i-1;t) + R(i|i+1)P(i+1;t) - (R(i+1|i) + R(i-1|i))P(i;t) \tag{1.4.48}$$

$$\begin{aligned} R(i+1|i) &= \nu_i e^{-(E_B(i+1|i)-E_i)/kT} \\ R(i-1|i) &= \nu_i e^{-(E_B(i|i-1)-E_i)/kT} \end{aligned} \tag{1.4.49}$$

where E_i is the depth of the *i*th well and $E_B(i+1|i)$ is the barrier to its right. For the periodic system of Fig. 1.4.4 ($\nu_i \rightarrow \nu$, $E_B(i+1|i) \rightarrow E_B$) this simplifies to:

$$\dot{P}(i;t) = R(P(i-1;t) + P(i+1;t) - 2P(i;t)) \tag{1.4.50}$$

$$R = \nu e^{-(E_B - E_0)/kT} \tag{1.4.51}$$

Since we are already describing a continuum differential equation in time,it is convenient to consider long times and write a continuum equation in space as well. Allowing a change in notation we write

$$P(i;t) \rightarrow P(x_i;t) \tag{1.4.52}$$

Introducing the elementary distance between wells *a* we can rewrite Eq. (1.4.50) using:

$$\begin{aligned} &\frac{(P(i-1;t) + P(i+1;t) - 2P(i;t))}{a^2} \\ &\rightarrow \frac{(P(x_i - a;t) + P(x_i + a;t) - 2P(x_i;t))}{a^2} \rightarrow \frac{\partial^2}{\partial x^2} P(x;t) \end{aligned} \tag{1.4.53}$$

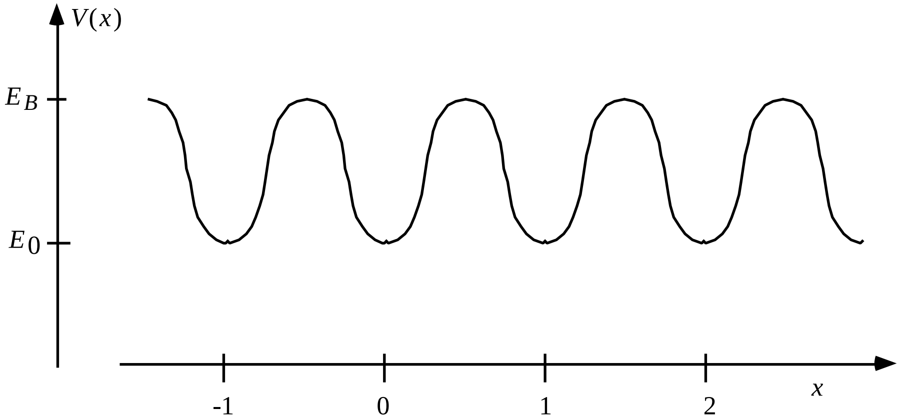


Figure 1.4.4 When the barrier heights and well depths are the same, as illustrated, the long time behavior of this system is described by the diffusion equation. The evolution of the system is controlled by hopping events from one well to the other. The net effect over long times is the same as for the random walk discussed in Section 1.2. ∎

where the last expression assumes a is small on the scale of interest. Thus the continuum version of Eq. (1.4.50) is the conventional diffusion equation:

$$\dot{P}(x;t) = D\frac{\partial^2}{\partial x^2}P(x;t) \tag{1.4.54}$$

The diffusion constant D is given by:

$$D = a^2 R = a^2 \nu e^{-(E_B - E_0)/kT} \tag{1.4.55}$$

The solution of the diffusion equation, Eq. (1.4.54), depends on the initial conditions that are chosen. If we consider an ensemble of a system that starts in one well and spreads out over time, the solution can be checked by substitution to be the Gaussian distribution found for the random walk in Section 1.2:

$$\begin{gathered} P(x,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt} = \frac{1}{\sqrt{2\pi}\,\sigma} e^{-x^2/2\sigma^2} \\ \sigma = \sqrt{2Dt} \end{gathered} \tag{1.4.56}$$

We see that motion in a set of uniform wells after a long time reduces to that of a random walk.

How does the similarity to the random walk arise? This might appear to be a natural result,since we showed that the Gaussian distribution is quite general using the central limit theorem. The scenario here,however, is quite different. The central limit theorem was proven in Section 1.2.2 for the case of a distribution of probabilities of steps taken at specific time intervals. Here we have a time continuum. Hopping events may happen at any time. Consider the case where we start from a particular well. Our differential equation describes a system that might hop to the next well at any time. A hop is an event, and we might concern ourselves with the distribution of such events in time. We have assumed that these events are uncorrelated. There are unphysical consequences of this assumption. For example, no matter how small an interval of time we choose,the particle has some probability of traveling arbitrarily far away. This is not necessarily a correct microscopic picture, but it is the continuum model we have developed.

There is a procedure to convert the event-controlled hopping motion between wells into a random walk that takes steps with a certain probability at specific time intervals. We must select a time interval. For this time interval, we evaluate the total probability that hops move a system from its original position to all possible positions of the system. This would give us the function $f(s)$ in Eq.(1.2.34). As long as the mean square displacement is finite,the central limit theorem continues to apply to the probability distribution after a long enough time. The generality of the conclusion also implies that the result is more widely applicable than the assumptions indicate. However, there is a counter example in Question 1.4.5.

Question 1.4.5 Discuss the case of a particle that is not in contact with a thermal resevoir moving in the multiple well system (energy is conserved).

Solution 1.4.5 If the energy of the system is lower than E_B, the system stays in a single well bouncing back and forth. A model that describes how transitions occur between wells would just say there are none.

For the case where the energy is larger than E_B, the system will move with a periodically varying velocity in one direction. There is a problem in selecting an ensemble to describe it. If we choose the ensemble with only one system moving in one direction, then it is described as a deterministic walk. This description is consistent with the motion of the system. However, we might also think to describe the system using an ensemble consisting of particles with the same energy. In this case it would be one particle moving to the right and one moving to the left. Taking an interval of time to be the time needed to move to the next well, we would find a transition probability of 1/2 to move to the right and the same to the left. This would lead to a conventional random walk and will give us an incorrect result for all later times.

This example illustrates the need for an assumption that has not yet been explicitly mentioned. The ensemble must describe systems that can make transitions to each other. Since the energy-conserving systems cannot switch directions, the ensemble cannot include both directions. It is enough, however, for there to be a small nonzero probability for the system to switch directions for the central limit theorem to apply. This means that over long enough times, the distribution will be Gaussian. Over short times,however, the probability distribution from the random walk model and an almost ballistic system would not be very similar. ▮

We can generalize the multiple well picture to describe a biased random walk. The potential we would use is a “washboard potential,” illustrated in Fig. 1.4.5. The Master equation is:

$$\dot{P}(i;t) = R_+ P(i-1;t) + R_- P(i+1;t) - (R_+ + R_-) P(i;t) \tag{1.4.57}$$

$$\begin{aligned} R_+ &= \nu_i e^{-\Delta E_+ /kT} \\ R_- &= \nu_i e^{-\Delta E_- /kT} \end{aligned} \tag{1.4.58}$$

To obtain the continuum limit, replace $i \rightarrow x$: $P(i+1;t) \rightarrow P(x+a,t)$, and $P(i-1;t) \rightarrow P(x-a,t)$, and expand in a Taylor series to second order in a to obtain:

$$\dot{P}(x;t) = -v \frac{\partial}{\partial x} P(x;t) + D \frac{\partial^2}{\partial x^2} P(x;t) \tag{1.4.59}$$

$$\begin{aligned} v &= a(R_+ - R_-) \\ D &= a^2 (R_+ + R_-)/2 \end{aligned} \tag{1.4.60}$$

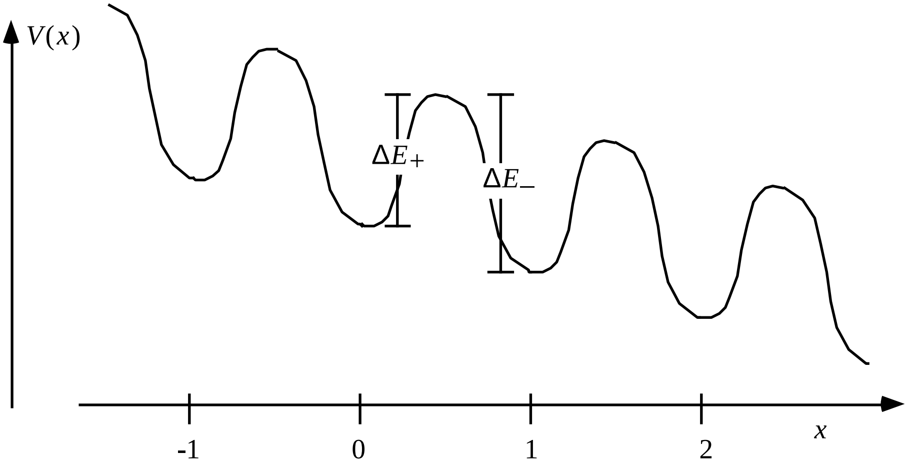


Figure 1.4.5 The biased random walk is also found in a multiple-well system when the illustrated washboard potential is used. The velocity of the system is given by the difference in hopping rates to the right and to the left. ▮

The solution is a moving Gaussian:

$$\begin{gathered} P(x,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-(x-vt)^2/4Dt} = \frac{1}{\sqrt{2\pi}\,\sigma} e^{-(x-vt)^2/2\sigma^2} \\ \sigma = \sqrt{2Dt} \end{gathered} \tag{1.4.61}$$

Since the description of diffusive motion always allows the system to stay where it is, there is a limit to the degree of bias that can occur in the random walk. For this limit set $R_- = 0$. Then $D = av/2$ and the spreading of the probability is given by $\sigma = \sqrt{avt}$. This shows that unlike the biased random walk in Section 1.2, diffusive motion on a washboard with a given spacing a cannot describe ballistic or deterministic motion in a single direction.

1.5 Cellular Automata

The first four sections of this chapter were dedicated to systems in which the existence of many parameters (degrees of freedom) describing the system is hidden in one way or another. In this section we begin to describe systems where many degrees of freedom are explicitly represented. Cellular automata (CA) form a general class of models of dynamical systems which are appealingly simple and yet capture a rich variety of behavior. This has made them a favorite tool for studying the generic behavior of and modeling complex dynamical systems. Historically CA are also intimately related to the development of concepts of computers and computation. This connection continues to be a theme often found in discussions of CA. Moreover, despite the wide differences between CA and conventional computer architectures,CA are convenient for