

10 The Boltzmann Distribution Law

Statistical Mechanics Gives Probability Distributions for Atoms and Molecules

Now we begin statistical mechanics, the modeling and prediction of the properties of materials from the structures of the atoms and molecules of which they are composed. The core of statistical mechanics is modeling the probability distributions of the energies of atoms and molecules. The various averages over those distributions are what experiments measure. For example, to compute the properties of gases, you need the distributions of their energies and velocities (Chapter 11). You can predict chemical reaction equilibria if you know the distributions of the energies of the reactants and products (Chapter 13). And you can predict the average number of ligands bound to a DNA molecule if you know the distribution of energies of all the ligation states (Chapter 28).

The central result of this chapter is the Boltzmann distribution law, which gives probability distributions from the underlying energy levels. We derive this result by bringing together the two main threads from earlier chapters. First, the principles of thermodynamics in Chapters 6-9 describe how to predict the state of equilibrium. Second, Chapter 5 relates a macroscopic property of the equilibrium (the entropy) to a microscopic property, the probability distribution.

Here's the kind of problem we want to solve. Example 8.2 describes a two-dimensional model of a four-bead polymer chain that has four open conformations and one compact conformation. In that example, we computed the free

energies of the open and compact states. Now we want to compute the probability distribution, the fraction of molecules that are in each conformation.

To begin, we need to define the system and its *energy levels*. The system is one four-bead chain that has two energy levels (see Figure 10.1). Each energy level represents the number of bead-bead contacts that the chain can make. Let's use the convention that zero is the lowest energy, the lowest rung on the ladder. Conformations with the maximum number of bead-bead contacts have zero energy. Breaking a contact increases the energy by an amount $\varepsilon = \varepsilon_0 > 0$. We use ε to indicate the energy in general and ε_0 to represent some particular constant value. We seek the distribution of probabilities p_1, p_2, \dots, p_5 that the four-bead chain is in its various conformations.

The state of lowest energy is called the *ground state*. States of higher energy are called *excited states*. Each of the five configurations is called a *microstate*, to distinguish it from a *state* or *macrostate*, which is a collection of microstates. Each microstate is a snapshot of the system. When you measure system properties, you measure averages over multiple microstates. In Figure 10.1, you can see two macrostates of a one-chain system: the open macrostate, composed of four microstates, and the compact macrostate, composed of one microstate. For a lattice gas, a particular arrangement of N particles on M lattice sites is one microstate. A corresponding macrostate could include, for example, all such arrangements of particles that have the same density N/M .

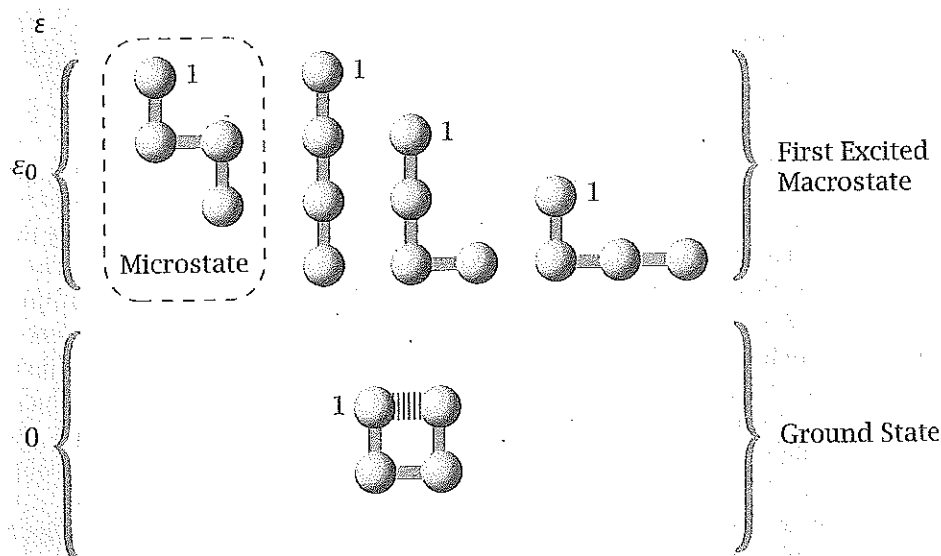


Figure 10.1 The five conformations of the four-bead chain in Example 8.2 are grouped on an energy ladder. Conformations with one bead-bead contact, $n_C = 1$, are taken to have energy $\varepsilon = 0$. The other four conformations have no bead-bead contacts, so $\varepsilon = \varepsilon_0$, where ε_0 is a constant. The number 1 next to the first bead indicates that the chain has a head and a tail. (Sometimes symmetry matters. Here, we counted only left turns. The numbers are different if you also count right turns separately. Here, for illustrating general principles, it doesn't matter.)

We will compute the probability distribution for this four-bead chain after we derive the Boltzmann law. But first, let's look at a more general version of the problem that we are trying to solve. Consider a complex system having N particles. Each particle has some *internal* energy due to its intrinsic properties. For example, different internal energies result from different rotational or vibrational states of molecules, or from the different conformations like the four-bead polymer molecule. In addition, there may be *interaction* energies between pairs or triples or larger collections of particles. The sum total of all the internal and interaction energies, taken for one particular arrangement j of the whole system, is E_j . The lowest energy over all the possible arrangements of the system is E_1 . The next lowest energy arrangement will have energy E_2 , etc. We will use two different notations for the energy: E_j for any system in general, no matter how complex, and ϵ_j for the specific simple case of independent particles (such as ideal gas atoms).

Now we derive the probability distribution for any system with known energy level spacings. We do this by combining the definition of entropy, $S/k = -\sum p_j \ln p_j$, with the definition of equilibrium. We focus here on a system with variables (T, V, N) . Our approach follows the dice problems of Chapter 5, but now, instead of knowing an average score, you know the average energy of the system.

The Boltzmann Distribution Law Describes the Equilibria Among Atoms and Molecules

Consider a system having N particles. (To make the math simple in this chapter, consider N particles of a single type, rather than a set of $N = (N_1, N_2, \dots, N_M)$ particles of multiple types.) Suppose the system has t different energy levels, E_j , $j = 1, 2, 3, \dots, t$, defined by the physics of the problem that you want to solve. A given energy level will be composed of many different microstates. Energies may be equally spaced, as in the polymer problem above, or they may be spaced differently. They may come from quantum mechanics, as we'll see in Chapter 11. Given the energies E_j , we aim to compute the probabilities p_j that the system is in each level j . (Computing these populations of the energy levels is metaphorically like computing the fraction of dice rolls that have a particular score j .) Suppose (T, V, N) are held constant. Then the condition for equilibrium is $dF = dU - T dS = 0$. Apply the Lagrange multiplier method as in Chapter 5. We need dS and dU .

To get dS , use Equation (5.2) for the entropy as a function of the probabilities p_j :

$$\frac{S}{k} = -\sum_{j=1}^t p_j \ln p_j.$$

Differentiating with respect to p_j (holding the $p_{i \neq j}$'s constant) gives

$$dS = -k \sum_{j=1}^t (1 + \ln p_j) dp_j. \quad (10.1)$$

To get dU , we postulate that the internal energy U , which is the macroscopic quantity from thermodynamics, is the average over all the microscopic states (see Equation (1.35)):

$$U = \langle E \rangle = \sum_{j=1}^t p_j E_j. \quad (10.2)$$

Now take the derivative of Equation (10.2):

$$dU = d\langle E \rangle = \sum_{j=1}^t (E_j dp_j + p_j dE_j). \quad (10.3)$$

Like the macroscopic energy U , the energy levels $E_j = E_j(V, N)$ depend on V and N . But, unlike U , the energy levels E_j do not depend on S or T . We take as a fundamental principle of quantum mechanics that only the populations $p_j(T)$, and not the energies E_j , depend on temperature. However, the *average energy* $\langle E \rangle = \sum p_j(T) E_j$ does depend on temperature. $dE_j = (\partial E_j / \partial V) dV + (\partial E_j / \partial N) dN = 0$ because both V and N are held constant here, and Equation (10.3) becomes

$$d\langle E \rangle = \sum_{j=1}^t E_j dp_j. \quad (10.4)$$

The First Law of Thermodynamics gives $dU = \delta q + \delta w$, which reduces to $d\langle E \rangle = dU = \delta q$ when V and N are constant. Because Equation (10.4) applies when V is constant, it follows that the term $\sum_j E_j dp_j$ is the heat and $\sum_j p_j dE_j$ is the work.

We want the probability distribution that satisfies the equilibrium condition $dF = d\langle E \rangle - T dS = 0$ subject to the constraint that the probabilities sum to one, $\sum_{j=1}^t p_j = 1$. The constraint can be expressed in terms of a Lagrange multiplier α :

$$\alpha \sum_{j=1}^t dp_j = 0. \quad (10.5)$$

Substitute Equations (10.1) and (10.3)–(10.5) into $dF = dU - T dS = 0$ to get

$$dF = \sum_{j=1}^t [E_j + kT(1 + \ln p_j^*) + \alpha] dp_j^* = 0. \quad (10.6)$$

According to the Lagrange multiplier equation (4.31), the term in the brackets in Equation (10.6) must equal zero for each value of j , so you have t equations of the form

$$\ln p_j^* = -\frac{E_j}{kT} - \frac{\alpha}{kT} - 1. \quad (10.7)$$

Exponentiate Equation (10.7) to find

$$p_j^* = e^{-E_j/kT} e^{(-\alpha/kT)-1}. \quad (10.8)$$

To eliminate α from Equation (10.8), write the constraint equation

$$\sum_{j=1}^t p_j^* = 1$$

as

$$1 = \sum_{j=1}^t e^{-E_j/kT} e^{(-\alpha/kT)-1}.$$

Divide Equation (10.8) by this form of the constraint equation, to get the **Boltzmann distribution law**

$$p_j^* = \frac{e^{-E_j/kT}}{\sum_{j=1}^t e^{-E_j/kT}} = \frac{e^{-E_j/kT}}{Q}, \quad (10.9)$$

where Q is the **partition function**,

$$Q = \sum_{j=1}^t e^{-E_j/kT}. \quad (10.10)$$

The relative populations of particles in energy levels i and j at equilibrium are given by

$$\frac{p_i^*}{p_j^*} = e^{-(E_i - E_j)/kT}. \quad (10.11)$$

Equation (10.9) gives an exponential distribution law, just as Equation (5.17) does, but here the energy levels E_j replace the scores on individual die rolls.

It is interesting to compare Equation (10.7), which we obtained by minimizing the free energy, with Equation (5.15), which we obtained by the conceptually identical procedure of maximizing the entropy subject to a constraint of the form of Equation (10.4). This comparison shows that the Lagrange multiplier that enforces the constraint of average energy is $\beta = 1/(kT)$.

The Boltzmann distribution says that more particles will have low energies and fewer particles will have high energies. Why? Particles don't have an intrinsic preference for lower energy levels. Fundamentally, all energy levels are equivalent. Rather, *there are more arrangements of the system that way*. It is extremely unlikely that one particle would have such a high energy that it would leave all the others no energy. There are far more arrangements in which most particles have energies that are relatively low, but nonzero. If each particle takes only a small fraction of the total energy, it leaves a great many more ways for the other particles to distribute the remaining energy.

Applications of the Boltzmann Law

Example 10.1 illustrates an application of the Boltzmann distribution law. We compute how the atmospheric pressure depends on the altitude above the Earth's surface.

EXAMPLE 10.1 Barometric pressure of the atmosphere. The energy ε of a gas molecule in the Earth's gravitational field is a function of altitude z :

$$\varepsilon(z) = mgz, \quad (10.12)$$

where g is the gravitational acceleration constant and m is the molecular mass. In this case, the energy is a continuous function (of z), not a discrete ladder, but Boltzmann's law still applies. We assume that the atmosphere is in equilibrium and is at constant temperature (valid only approximately; see below). The populations, or numbers, of molecules $N(z)$ at altitude z relative to the number $N(0)$ at sea level are given by the Boltzmann law, Equation (10.11):

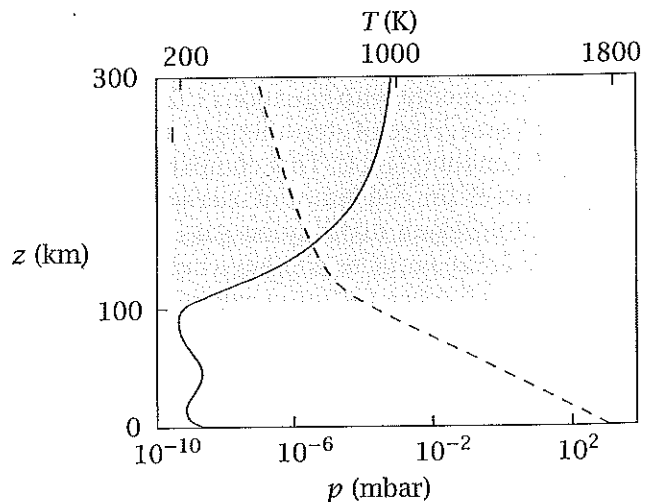
$$\frac{N(z)}{N(0)} = e^{-[\varepsilon(z) - \varepsilon(0)]/kT} = e^{-mgz/kT}. \quad (10.13)$$

If the gas is ideal and the temperature is constant, the pressure $p(z)$ is proportional to the number of molecules per unit volume, so the pressure should decrease exponentially with altitude:

$$\frac{p(z)}{p(0)} = \frac{N(z)kT/V}{N(0)kT/V} = \frac{N(z)}{N(0)} = e^{-mgz/kT}. \quad (10.14)$$

Figure 10.2 shows experimental evidence that the temperature is reasonably constant for the Earth's atmosphere up to about 100 km above the Earth's surface, and that the pressure decreases exponentially with altitude, as predicted. Above about 100 km, the equilibrium assumption no longer holds, because the atmosphere becomes too thin for normal wind turbulence to mix the gases, and the temperature is no longer independent of altitude.

Figure 10.2 The temperature T (—) of the atmosphere is approximately constant up to about 100 km in altitude z . The pressure p (---) decreases exponentially with altitude, following the Boltzmann law. Source: ML Salby, *Fundamentals of Atmospheric Physics*, Academic Press, San Diego, 1996. Data are from: *US Standard Atmosphere*, NOAA, US Air Force, US Government Printing Office, NOAA-S/T 76-1562, Washington, DC, 1976.



Example 10.2 gives another application of the Boltzmann distribution law: the distribution of the velocities of gas molecules. This is the basis for the kinetic theory of gases, a classical model of great historical importance. In our previous lattice modeling, our states have been discrete. We have evaluated discrete sums over Boltzmann factors. Now, we consider a continuous distribution of energies, so we replace sums by integrals.

EXAMPLE 10.2 The Maxwell-Boltzmann distribution of particle velocities. According to the kinetic theory, gases and liquids can be regarded as miniature billiard balls, i.e., Newtonian particles having mass m , velocity v , and kinetic energy ε , where

$$\varepsilon(v) = \frac{1}{2}mv^2.$$

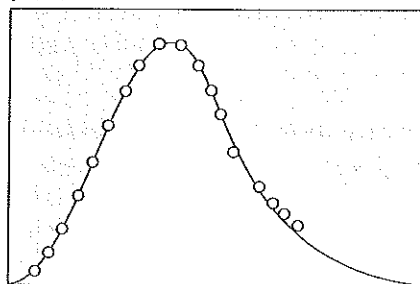
According to the Boltzmann law, the probability $p(v_x)$ that a particle in a container at constant volume and temperature will have velocity v_x in the x direction is

$$\begin{aligned} p(v_x) &= \frac{e^{-\varepsilon(v_x)/kT}}{\int_{-\infty}^{\infty} e^{-\varepsilon(v_x)/kT} dv_x} = \frac{e^{-mv_x^2/2kT}}{\int_{-\infty}^{\infty} e^{-mv_x^2/2kT} dv_x} \\ &= \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}, \end{aligned} \quad (10.15)$$

because $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\pi/a}$ (see Appendix K, Equation (K.1)) and $a = m/2kT$. This is called the *Maxwell-Boltzmann distribution*. Figure 10.3 shows the excellent agreement between this predicted distribution (multiplied by v^2 to convert to speeds) and experimental observations for the velocities of potassium atoms. The mean velocity is zero, because for any particular velocity v_x in the $+x$ direction, there is a corresponding velocity in the $-x$ direction. The *mean-square* velocity $\langle v^2 \rangle$ defines the width of the distribution:

$$\langle v_x^2 \rangle = \int_{-\infty}^{\infty} v_x^2 p(v_x) dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2} \int_{-\infty}^{\infty} v_x^2 e^{-mv_x^2/2kT} dv_x.$$

$v^2 p(v)$



Molecular Speed v

Figure 10.3 Experiments showing $v^2 p(v) = \text{constant} \times v^2 e^{-mv^2/2kT}$ versus average speed v , confirming the Maxwell-Boltzmann distribution of the speeds of potassium atoms in the gas phase. (The factor v^2 converts from velocity, which is a vector with a sign, to speed, which is not.) Source: DA McQuarrie and JD Simon, *Physical Chemistry a Molecular Approach*, University Science Books, Sausalito, 1997. Data are from RC Miller and P Kusch, *Phys Rev* **99**, 1314–1320 (1953).

You can evaluate such integrals using Equations (K.1) and (K.3) of Appendix K:

$$\langle x^2 \rangle = \frac{\int_{-\infty}^{\infty} x^2 e^{(-ax^2)} dx}{\int_{-\infty}^{\infty} e^{(-ax^2)} dx} = \frac{1/2a\sqrt{\pi/a}}{\sqrt{\pi/a}} = \frac{1}{2a}. \quad (10.16)$$

Because $a = m/(2kT)$, you have

$$\langle v_x^2 \rangle = \frac{kT}{m} \implies \frac{1}{2}m\langle v_x^2 \rangle = \frac{1}{2}kT.$$

Now suppose that instead of measuring the x component of velocity, you measure the three-dimensional velocity v , where $v^2 = v_x^2 + v_y^2 + v_z^2$. In an ideal gas, the components are independent of each other, so $\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$, leading to:

$$\frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}kT. \quad (10.17)$$

Because the velocity components are independent, the probabilities multiply, giving

$$\begin{aligned} p(v) &= p(v_x)p(v_y)p(v_z) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/2kT} \\ &= \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}. \end{aligned} \quad (10.18)$$

Equations (10.17) and (10.18) are the central results of the kinetic theory of gases, describing the motions of atoms in terms of the kinetic energies of Newtonian particles. They provide a fundamental relationship between temperature and the velocities of the gas molecules.

What Does a Partition Function Tell You?

The partition function is the connection between macroscopic thermodynamic properties and microscopic models. It is a sum of *Boltzmann factors* $e^{-E_j/kT}$ that specify how *particles are partitioned* throughout the accessible states. Equation (10.10) gives

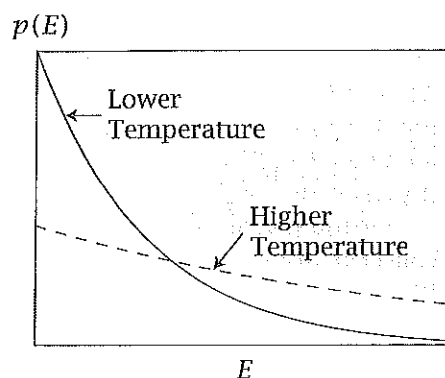
$$Q = \sum_{j=1}^t e^{-E_j/kT} = e^{-E_1/kT} + e^{-E_2/kT} + e^{-E_3/kT} + \dots + e^{-E_t/kT}. \quad (10.19)$$

It is also common to express Q in an alternative form. Experiments rarely give information about absolute energies; they give information about energy differences. So, it is often convenient to define the ground-state energy as zero, $E_1 = 0$, and write the partition function instead in terms of energy differences:

$$Q = 1 + e^{-(E_2-E_1)/kT} + e^{-(E_3-E_1)/kT} + \dots + e^{-(E_t-E_1)/kT}. \quad (10.20)$$

Both forms give exactly the same results for probabilities, which are the quantities we are interested in.

Figure 10.4 According to the Boltzmann distribution, states of lower energy are more populated than states of higher energy. As temperature increases, higher energy states become more populated.



Here's an intuitive way to think about the partition function. Think of Q as the number of states that are *effectively* accessible to the system. To see this, look at the limiting values (see Figures 10.4 and 10.5). When the energies are small, or the temperature is high, all the states become equally populated:

$$\left. \begin{array}{l} E_j \rightarrow 0 \\ \text{or} \\ T \rightarrow \infty \end{array} \right\} \Rightarrow \frac{E_j}{kT} \rightarrow 0 \Rightarrow p_j^* \rightarrow \frac{1}{t} \Rightarrow Q \rightarrow t. \quad (10.21)$$

In this case, all t states become accessible.

At the other extreme, as the energy intervals become large or as the temperature approaches zero, the particles occupy only the ground state:

$$\left. \begin{array}{l} E_{j \neq 1} \rightarrow \infty \\ \text{or} \\ T \rightarrow 0 \end{array} \right\} \Rightarrow \frac{E_{j \neq 1}}{kT} \rightarrow \infty \Rightarrow \left\{ \begin{array}{l} p_1^* \rightarrow 1 \\ \text{and} \\ p_{j \neq 1}^* \rightarrow 0 \end{array} \right. \Rightarrow Q \rightarrow 1. \quad (10.22)$$

In this case, only the ground state becomes accessible.

The magnitude of E_j/kT determines whether or not the state j is 'effectively accessible.' So kT is an important reference unit of energy. States that have energies higher than kT are relatively inaccessible and unpopulated at temperature T , while states having energies lower than kT are well populated. Increasing the temperature makes the higher energy levels effectively more accessible.

The number of *effectively accessible states* is not the same as the number of accessible states, which is always t . The number t is fixed by the underlying physics of the system. In contrast, the effective accessibility Q also depends on the temperature.

The Density of States

Sometimes you may want to compute different probabilities than the ones we computed above. Sometimes, there are intrinsically a different number of ways that a system can occupy one energy level than another. For example, for the four-bead polymer, each configuration shown in Figure 10.1 is one microstate. But for experiments, a more meaningful grouping may be into two macrostates: the *open* state (four microstates) or the *compact* state (one microstate). We have previously defined the quantity W as the multiplicity of

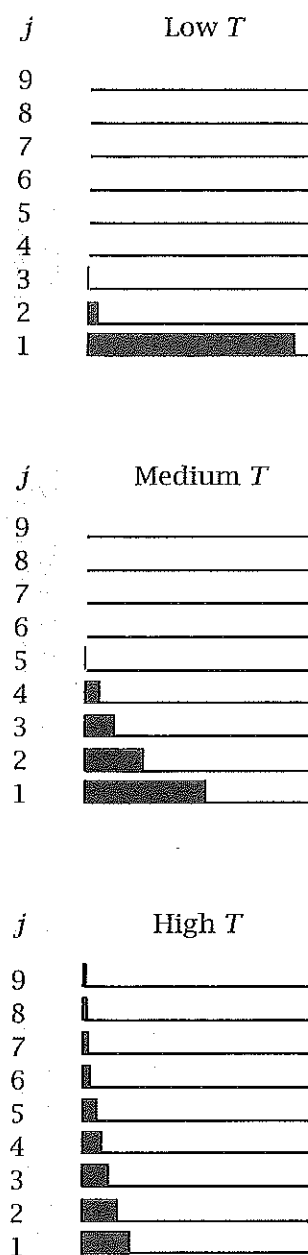


Figure 10.5 The Boltzmann distribution law. At low temperatures T , only the lowest energy states j are populated. Increasing T increases populations of higher energy states. The distribution is exponential.

states. We now generalize this. We now define $W(E)$ to be the *density of states*; that is, $W(E)$ is the total number of ways a system can occur in energy level E . When $W(E) > 1$, an energy level is called *degenerate*. (Think of an unusual die that has nine faces: three faces are 1's, two faces are 2's, and one face each has numbers 3–6. Its density of states would be $W(1) = 3$; $W(2) = 2$; $W(3) = W(4) = W(5) = W(6) = 1$.)

For the four-bead chain, there is one compact conformation and four open conformations (see Figure 10.1), so the density of states is $W(0) = 1$ and $W(\varepsilon_0) = 4$. Since W is the number of microstates per level, the partition function can be expressed as a sum over the two levels (open and compact, in this case), rather than over the five microstates:

$$Q = 1e^{-0/kT} + 4e^{-\varepsilon_0/kT},$$

where the first term describes the one microstate in level 1 ($\varepsilon = 0$) and the second describes the four microstates in level 2 ($\varepsilon = \varepsilon_0$).

When you have a density of states, you can express the partition function as a sum over energy levels $\ell = 1, 2, \dots, \ell_{\max}$ as

$$Q = \sum_{\ell=1}^{\ell_{\max}} W(E_\ell) e^{-E_\ell/kT}. \quad (10.23)$$

The factor of $W(E_\ell)$ in this expression counts the number of microstates in the given macrostate. You can compute the probability that the system is in macrostate energy level ℓ as

$$p_\ell = Q^{-1} W(E_\ell) e^{-E_\ell/kT}. \quad (10.24)$$

You are free to choose whether to focus on microstates or energy levels, or some other alternative, depending on what is most convenient for the problem that you are trying to solve. Examples 10.3 and 10.4 illustrate the density of states with the lattice polymer collapse model.

EXAMPLE 10.3 The collapse distribution for the four-bead polymer chain. How does the population of collapsed conformations change as the temperature is changed? We focus here on the two macrostates, open and compact, rather than on the individual microstates, so the partition function for this two-state system is

$$Q = 1 + 4e^{-\varepsilon_0/kT},$$

where $\varepsilon_0 > 0$ is the energy increase if the bond is broken. At low temperatures, $T \rightarrow 0$, $Q \rightarrow 1$, so only the compact state is populated. But as the temperature increases, $T \rightarrow \infty$, $Q \rightarrow 5$, indicating that all conformations become equally populated. Cooling collapses the chain. The fractions of the molecules p_0 that

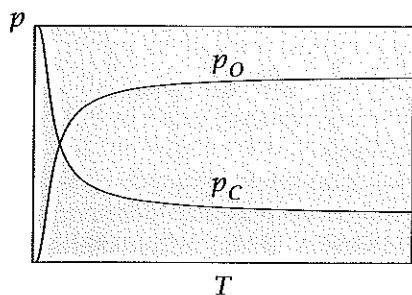


Figure 10.6 In the four-bead-chain polymer collapse model of Example 10.3, the collapsed population (probability p_C) diminishes with temperature T while the population of open conformations (probability p_O) grows.

are open and p_C that are compact are

$$p_C = \frac{1}{Q} \quad \text{and} \quad p_O = \frac{4e^{-\epsilon_0/kT}}{Q} = \frac{4e^{-\epsilon_0/kT}}{1 + 4e^{-\epsilon_0/kT}}.$$

Figure 10.6 shows how the populations change with temperature. This figure describes a series of different experiments, each one at a fixed temperature. This kind of curve is sometimes called an *unfolding* or *denaturation* profile for a polymer or protein [1]. If you define $Q_C = 1$ as the partition function for the compact state alone and $Q_O = 4 \exp(-\epsilon_0/kT)$ for the open state alone, then you can compute free energies using $F = -kT \ln Q$. At the cross-over point, where $p_C = p_O = 1/2$, the free energy of collapse is zero: $\Delta F = F_C - F_O = -kT \ln(Q_C/Q_O) = 0$.

Another example is the collapse of a six-bead chain.

EXAMPLE 10.4 Collapse of the six-bead polymer chain. For the six-bead chain shown in Figure 10.7, there are three equally spaced energy levels because a chain can have 0, 1, or 2 bead-bead contacts, corresponding to energies $\epsilon = 2\epsilon_0, 1\epsilon_0$, and 0. The density of states is $W(0) = 4$, $W(\epsilon_0) = 11$, and $W(2\epsilon_0) = 21$. The partition function is

$$Q = 4 + 11e^{-\epsilon_0/kT} + 21e^{-2\epsilon_0/kT},$$

and the populations $p(\ell)$ of energy levels $\ell = 0, 1, 2$ are

$$p(0) = \frac{4}{Q}, \quad p(1) = \frac{11e^{-\epsilon_0/kT}}{Q}, \quad p(2) = \frac{21e^{-2\epsilon_0/kT}}{Q}.$$

Figure 10.8 shows the populations versus temperature for the collapse of the six-bead polymer. This six-bead model differs from the four-bead model in having an *intermediate* state that is populated near the middle of the transition from C at low temperatures to O at high temperatures.

Partition Functions for Independent and Distinguishable Particles

The Boltzmann distribution law applies to systems of any degree of complexity. The probabilities p_j can represent states $j = 1, 2, 3, \dots, t$ of atoms in ideal gases. Or the probabilities can represent states with energies that depend on the complex intermolecular system configurations. Calculations are simplest whenever

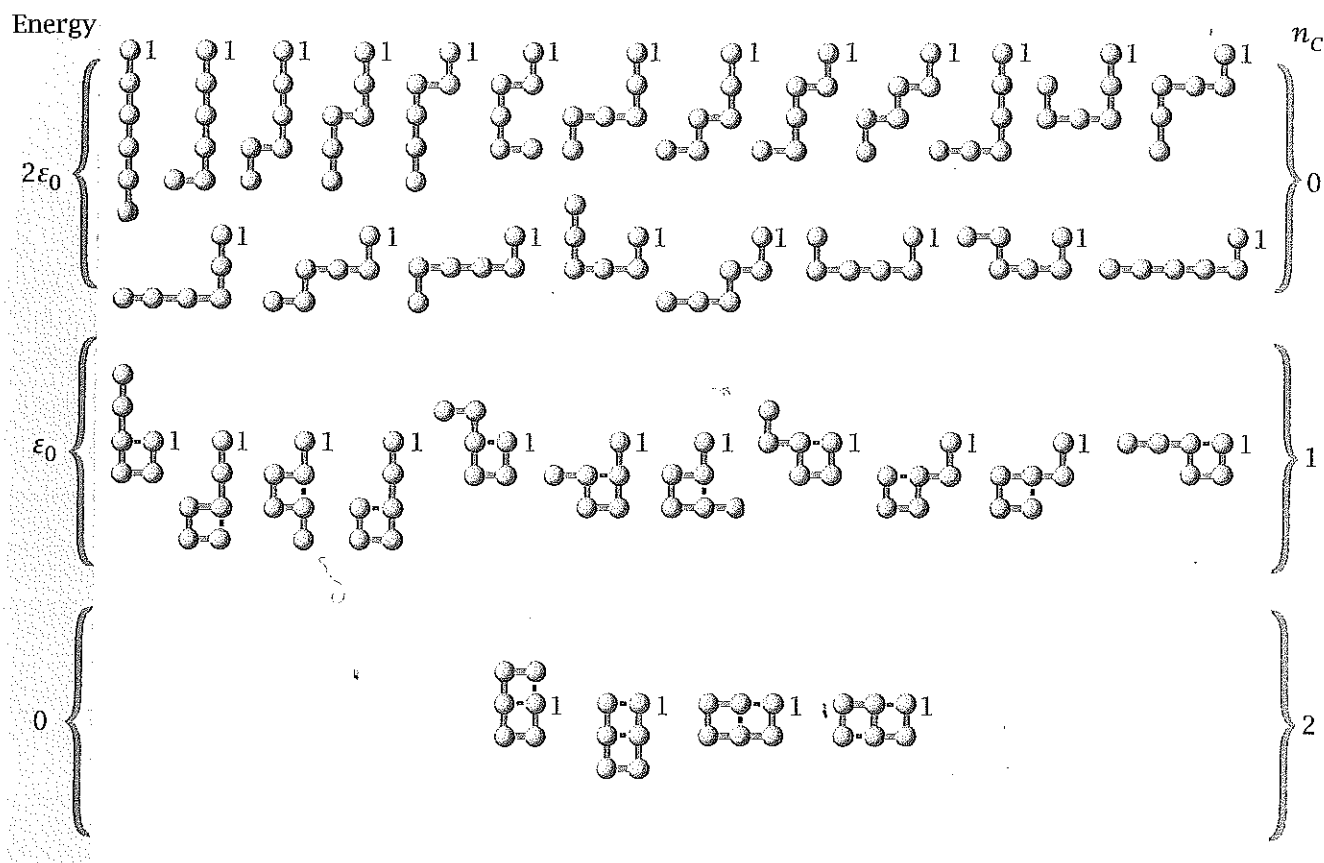
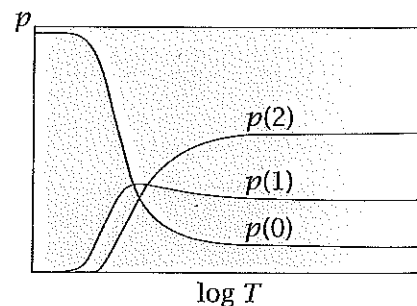


Figure 10.7 For the six-bead polymer chain, there are $W(0) = 4$ microstates having $n_C = 2$ contacts (contacts are shown as short dashes), $W(\epsilon_0) = 11$ microstates having 1 contact, and $W(2\epsilon_0) = 21$ microstates having 0 contacts.

Figure 10.8 Six-bead-chain polymer collapse of Example 10.4. At low temperatures T , the ground state is most stable ($p(0)$ is largest). At high temperatures, the open state is most stable ($p(2)$ is largest). Near the middle of the thermal transition, the intermediate state is most populated ($p(1)$ is largest).



a system is composed of independent subsystems. For example, each molecule in an ideal gas is independent of every other molecule. Or suppose you have N four-bead polymer molecules that do not interact with each other. In such cases, the system energy is the sum of the energies of each of the particles, and the system partition function is the product of particle partition functions.

In this section, we show this, first for the case of *distinguishable*, then for *indistinguishable*, particles. What is the difference? The atoms in a crystal are spatially distinguishable because each one has its own private location in the

crystal over the timescale of a typical experiment. Its location serves as a marker that distinguishes one particle from another. In contrast, according to quantum mechanics, the particles in a gas are indistinguishable from each other over the typical experimental timescale. Particles can interchange locations, so you cannot tell which particle is which.

First, consider distinguishable particles in a system with energy levels E_j . Suppose the system has two independent subsystems (e.g., two particles), distinguishable by labels A and B , with energy levels ε_i^A and ε_m^B , respectively, $i = 1, 2, \dots, a$ and $m = 1, 2, \dots, b$. The system energy is

$$E_j = \varepsilon_i^A + \varepsilon_m^B.$$

Because the subsystems are independent, you can write partition functions q_A for subsystem A and q_B for subsystem B according to Equation (10.10):

$$q_A = \sum_{i=1}^a e^{-\varepsilon_i^A/kT} \quad \text{and} \quad q_B = \sum_{m=1}^b e^{-\varepsilon_m^B/kT}. \quad (10.25)$$

The partition function Q for the entire system is the sum of Boltzmann factors $e^{-E_j/kT}$ over all $j = ab$ energy levels:

$$Q = \sum_{j=1}^t e^{-E_j/kT} = \sum_{i=1}^a \sum_{m=1}^b e^{-(\varepsilon_i^A + \varepsilon_m^B)/kT} = \sum_{i=1}^a \sum_{m=1}^b e^{-\varepsilon_i^A/kT} e^{-\varepsilon_m^B/kT}. \quad (10.26)$$

Because the subsystems are independent and distinguishable by their labels, the sum over the i levels of A has nothing to do with the sum over the m levels of B . The partition function Q in Equation (10.26) can be factored into subsystem partition functions q_A and q_B :

$$Q = \sum_{i=1}^a e^{-\varepsilon_i^A/kT} \sum_{m=1}^b e^{-\varepsilon_m^B/kT} = q_A q_B. \quad (10.27)$$

More generally, for a system having N independent and distinguishable particles, each with partition function q , the partition function Q for the whole system will be

$$Q = q^N. \quad (10.28)$$

Partition Functions for Independent and Indistinguishable Particles

Gas molecules are *indistinguishable*. They have *no labels* A or B that distinguish them from each other. For a system of two indistinguishable particles, the total energy is

$$E_j = \varepsilon_i + \varepsilon_m,$$

where $i = 1, 2, \dots, t_1$ and $m = 1, 2, \dots, t_2$. The system partition function is

$$Q = \sum_{j=1}^t e^{-E_j/kT} = \sum_{i=1}^{t_1} \sum_{m=1}^{t_2} e^{-(\varepsilon_i + \varepsilon_m)/kT}, \quad (10.29)$$

You cannot now factor the system partition function into particle partition functions as we did before. Here's the problem. If one particle occupied energy

level 27 and other particle occupied energy level 56, you could not distinguish that from the reverse. Because of this indistinguishability, you would have overcounted by a factor of $2!$.¹

For this system, you have $Q = q^2/2!$ to a good approximation. For N indistinguishable particles, this argument generalizes to give a system partition function Q ,

$$Q = \frac{q^N}{N!}. \quad (10.30)$$

We will use Equation (10.30) for gases.

If you know the partition function for a system or model, you can compute all the macroscopic thermodynamic properties.

Thermodynamic Properties Can Be Predicted from Partition Functions

Computing the Internal Energy from the Partition Function

Consider a system having fixed (T, V, N) . To get the internal energy for a system with energies E_j , substitute Equation (10.9) for p_j^* into Equation (10.2):

$$\begin{aligned} U &= \sum_{j=1}^t p_j^* E_j \\ &= Q^{-1} \sum_{j=1}^t E_j e^{-\beta E_j}, \end{aligned} \quad (10.31)$$

where $\beta = 1/kT$ is a useful quantity for simplifying the next few steps. Notice that the sum on the right-hand side of Equation (10.31) can be expressed as a derivative of the partition function in Equation (10.10):

$$\left(\frac{dQ}{d\beta} \right) = \frac{d}{d\beta} \sum_{j=1}^t e^{-\beta E_j} = - \sum_{j=1}^t E_j e^{-\beta E_j}. \quad (10.32)$$

Substituting Equation (10.32) into (10.31) simplifies it:

$$U = -\frac{1}{Q} \left(\frac{dQ}{d\beta} \right) = - \left(\frac{d \ln Q}{d\beta} \right). \quad (10.33)$$

¹That's close, but not exactly right. Suppose *both* particles were in energy level 27: then you would need no indistinguishability factor correction, because there's only one way to have that happen. To compute Equation (10.29) correctly in general for indistinguishable particles is challenging. But fortunately a most important case is simple. Suppose you have a huge number of energy levels, say 100,000, and only two particles. The chance that those particles would have coincident energies is exceedingly small, so the $2!$ correction would be a very good approximation. In reality, this is often valid: the number of accessible states is often much larger than the number of particles. You will see in Chapter 11 that translational partition functions are of the order of 10^{30} , while usually the number of particles is much smaller, 10^{20} or less. Therefore you are often justified in neglecting this small correction.

Since $\beta = 1/kT$, you have

$$\left(\frac{d\beta}{dT}\right) = -\frac{1}{kT^2}. \quad (10.34)$$

So you can multiply the left side of Equation (10.33) by $-1/kT^2$ and the right side by $d\beta/dT$ to get

$$\frac{U}{kT^2} = \left(\frac{d \ln Q}{dT}\right). \quad (10.35)$$

A useful alternative expression is $U/kT = d \ln Q / d \ln T = (T/Q) dQ/dT$.

Computing the Average Particle Energy

If particles are independent and distinguishable ($Q = q^N$), Equation (10.35) gives the average energy $\langle \epsilon \rangle$ per particle:

$$\begin{aligned} \langle \epsilon \rangle &= \frac{U}{N} = \frac{kT^2}{N} \left(\frac{\partial \ln q^N}{\partial T} \right)_{V,N} \\ &= kT^2 \left(\frac{\partial \ln q}{\partial T} \right) = - \left(\frac{\partial \ln q}{\partial \beta} \right). \end{aligned} \quad (10.36)$$

Computing the Entropy

The entropy of a system is defined by Equation (5.2):

$$\frac{S}{k} = - \sum_{j=1}^t p_j \ln p_j.$$

Substituting the Boltzmann distribution $p_j^* = Q^{-1} e^{-E_j/kT}$ from Equation (10.9) into Equation (5.2) gives

$$\frac{S}{k} = - \sum_{j=1}^t \left(\frac{1}{Q} e^{-E_j/kT} \right) \left[\ln \left(\frac{1}{Q} \right) - \frac{E_j}{kT} \right]. \quad (10.37)$$

Substituting Equation (10.10) for Q and Equation (10.31) for U into Equation (10.37) gives

$$S = k \ln Q + \frac{U}{T} = k \ln Q + kT \left(\frac{\partial \ln Q}{\partial T} \right). \quad (10.38)$$

For systems of N independent distinguishable particles, for which $Q = q^N$,

$$S = kN \ln q + \frac{U}{T}. \quad (10.39)$$

Because S increases linearly with N , the system entropy is the sum of the entropies of the independent particles.

Table 10.1 Thermodynamic quantities derived from the partition function for constant (T, V, N) .

Internal energy U	$U = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N}$	(10.40)
Entropy S	$S = k \ln Q + \frac{U}{T}$	(10.41)
Helmholtz free energy F	$F = U - TS = -kT \ln Q$	(10.42)
Chemical potential μ	$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = -kT \left(\frac{\partial \ln Q}{\partial N} \right)_{T,V}$	(10.43)
Pressure p	$p = - \left(\frac{\partial F}{\partial V} \right)_{T,N} = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{T,N}$	(10.44)

Computing the Free Energy and Chemical Potential

From U and S in Equations (10.35) and (10.38), thermodynamic relationships can produce the rest—the Helmholtz free energy, chemical potential, and pressure, for example. Table 10.1 lists the main relationships.

Now we illustrate these relationships by computing the thermodynamic properties of one of the simplest statistical mechanical models, the two-state model.

EXAMPLE 10.5 The Schottky two-state model. Consider a system that has N distinguishable particles with two energy levels for each particle: a ground state with energy zero and an excited state with energy $\varepsilon = \varepsilon_0 > 0$. This model is useful for describing many different problems: our polymer or dimer lattice models in Chapter 8, the behaviors of atoms or molecules that are excited by electromagnetic radiation, conduction of electrons in semiconductors, or the behavior of spins in magnetic fields (see Example 10.6).

Here we'll keep the model general and won't specify ε_0 in terms of any particular microscopic structure or property. We want to find the average particle energy $\langle \varepsilon \rangle$, the heat capacity C_V , the entropy, and the free energy per particle from the partition function. The partition function for a two-level system is the sum of two Boltzmann factors, one for each level:

$$q = 1 + e^{-\beta \varepsilon_0}. \quad (10.45)$$

The partition function approaches 1 at low temperatures and 2 at high temperatures. The relative populations of the two states are given by the Boltzmann distribution, Equation (10.9):

$$p_1^* = \frac{1}{q} \quad \text{and} \quad p_2^* = \frac{e^{-\beta \varepsilon_0}}{q}. \quad (10.46)$$

The average energy is given by Equation (10.36):

$$\langle \epsilon \rangle = \sum p_j^* \epsilon_j = 0 p_1^* + \epsilon_0 p_2^* = \frac{\epsilon_0 e^{-\epsilon_0/kT}}{1 + e^{-\epsilon_0/kT}} \quad (10.47)$$

(or you can get this by taking the derivative $\langle \epsilon \rangle = -q^{-1}(\partial q / \partial \beta)$). Figure 10.9(a) shows the energy of the two-state system as a function of temperature. At low temperatures, most molecules are in the ground state, so the system has low energy. As the temperature increases, the energy of the system increases and approaches the value $\epsilon_0/2$ per particle because energy levels 0 and ϵ_0 become equally populated.

To compute the heat capacity, use the definition $C_V = (\partial U / \partial T)$ from thermodynamics. Using Equation (10.36) to convert the total energy to the average energy per particle, $U = N \langle \epsilon \rangle$, you have

$$C_V = N \left(\frac{\partial \langle \epsilon \rangle}{\partial T} \right)_{V,N} = N \left(\frac{\partial \langle \epsilon \rangle}{\partial \beta} \right) \left(\frac{d\beta}{dT} \right) = -\frac{N}{kT^2} \left(\frac{\partial \langle \epsilon \rangle}{\partial \beta} \right), \quad (10.48)$$

where the right-hand expressions convert from T to β to make the next step of the differentiation simpler. Take a derivative of the form $d(u/v) = (vu' - uv')/v^2$, where $u = \epsilon_0 e^{-\beta \epsilon_0}$ and $v = 1 + e^{-\beta \epsilon_0}$, to get

$$\begin{aligned} \left(\frac{\partial \langle \epsilon \rangle}{\partial \beta} \right) &= \frac{(1 + e^{-\beta \epsilon_0})(-\epsilon_0^2 e^{-\beta \epsilon_0}) - \epsilon_0 e^{-\beta \epsilon_0}(-\epsilon_0 e^{-\beta \epsilon_0})}{(1 + e^{-\beta \epsilon_0})^2} \\ &= \frac{-\epsilon_0^2 e^{-\beta \epsilon_0}}{(1 + e^{-\beta \epsilon_0})^2}. \end{aligned} \quad (10.49)$$

Substitute Equation (10.49) into the right side of Equation (10.48) to find the heat capacity C_V in terms of the energy level spacing ϵ_0 :

$$C_V = \frac{N \epsilon_0^2}{kT^2} \frac{e^{-\beta \epsilon_0}}{(1 + e^{-\beta \epsilon_0})^2}. \quad (10.50)$$

The heat capacity is plotted in Figure 10.9(b), and is discussed in more detail in Chapter 12. Heat capacity peaks are characteristic of bond-breaking and melting processes. At low temperatures, the thermal energy kT from the bath is too small to excite the system to its higher energy level. At intermediate temperatures, the system can absorb heat from the bath, and particles are excited into the higher-energy state. At the highest temperatures, the system takes up no further energy from the bath because it has already taken up the maximum energy it can contain.

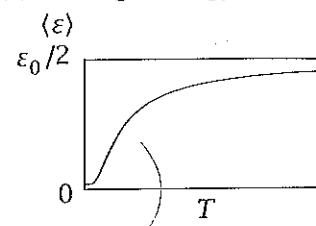
To get the entropy, substitute Equation (10.45) for q and $Q = q^N$ into Equations (10.41) and (10.40):

$$\frac{S}{N} = \frac{\epsilon_0 e^{-\beta \epsilon_0}}{T(1 + e^{-\beta \epsilon_0})} + k \ln(1 + e^{-\beta \epsilon_0}). \quad (10.51)$$

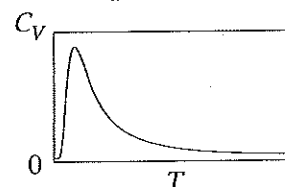
To get the free energy, substitute $Q = q^N$ into $F = -kT \ln Q$ (Equation (10.42)):

$$\frac{F}{NkT} = -\ln q = -\ln(1 + e^{-\beta \epsilon_0}). \quad (10.52)$$

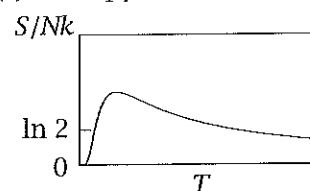
(a) Average Energy



(b) Heat Capacity



(c) Entropy



(d) Free Energy

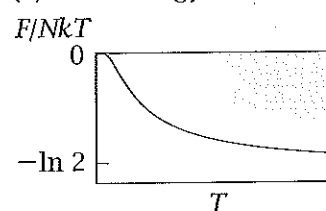


Figure 10.9 (a) The average energy per particle $\langle \epsilon \rangle$ for the Schottky model (Equation (10.47)) saturates at $\epsilon_0/2$ as temperature T approaches infinity. (b) The two-state model has a peak in the heat capacity C_V as a function of temperature (Equation (10.50)). (c) The entropy per particle divided by k has a peak and then approaches $\ln 2$ for large temperatures T (Equation (10.51)). (d) The free energy per particle divided by kT approaches $-\ln 2$ for large temperatures (Equation (10.52)).

As $\varepsilon_0 \rightarrow \infty$, the excited state becomes inaccessible, so $S \rightarrow 0$ and $F \rightarrow 0$. On the other hand, as $\varepsilon_0 \rightarrow 0$, both states become accessible, so $S \rightarrow Nk \ln 2$ and $F \rightarrow -NkT \ln 2$.

Now let's consider a specific example of a two-level system: a magnetic material in a magnetic field.

EXAMPLE 10.6 Curie's law of paramagnetism, a two-level system. Some materials are magnetic. Inside their atoms are unpaired spins (miniature magnets) that can be driven to align by an external magnetic force. The magnetic dipole moment describes the degree to which a spin aligns with a given magnetic field $B \geq 0$. Some materials, like refrigerator magnets, are ferromagnetic. They are magnetic even when there is no applied magnetic field. One spin points in a favored direction because its neighboring spins also point in that direction, helping to keep it oriented. Others, called paramagnets, are only aligned when a field is applied. In a paramagnet, the magnetic dipole-dipole interaction between neighboring atoms is small compared with the interaction with an applied field. Paramagnetic materials include hydrogen gas atoms and the heme iron atoms in hemoglobin. If you heat a paramagnet, it loses magnetization. The Schottky model illustrates this. Consider a simple paramagnetic material, in which every one of the N independent atoms has a magnetic dipole moment of magnitude $\mu_0 > 0$. (Don't confuse μ here with the chemical potential: the same symbol is used for both quantities, but they are unrelated.)

Here's a two-state model. Each spin can be either aligned or antialigned with the magnetic field (see Figure 10.10). The aligned spins have a lower energy than the antialigned spins. A spin that is parallel to the field is in the ground state, with energy $\varepsilon_1 = -\mu_0 B$. A spin that is antiparallel to the field is in the excited state, with higher energy: $\varepsilon_2 = +\mu_0 B$. Using the convention that the ground state defines the zero of energy, the energy difference between these two states is $+2\mu_0 B$, which defines the excited state energy, so the partition function is

$$q = 1 + e^{-2\mu_0 B/kT}. \quad (10.53)$$

We want to calculate the average magnetic moment (the material's magnetization) as a function of temperature. At equilibrium, the probability that an atom's magnetic moment is parallel to B is p_1^* and the probability that it is antiparallel is p_2^* :

$$p_1^* = \frac{1}{q} \quad \text{and} \quad p_2^* = \left(\frac{1}{q}\right) e^{-2\mu_0 B/kT}. \quad (10.54)$$

Because the magnetic moment of the aligned state is $+\mu_0$ and that of the antialigned state is $-\mu_0$, the average magnetic moment is

$$\begin{aligned} \langle \mu \rangle &= \sum_{j=1}^2 \mu_j p_j^* \\ &= \mu_0 p_1^* + (-\mu_0) p_2^* = \frac{\mu_0}{q} (1 - e^{-2\mu_0 B/kT}) = \mu_0 \frac{1 - e^{-2\mu_0 B/kT}}{1 + e^{-2\mu_0 B/kT}}. \end{aligned} \quad (10.55)$$

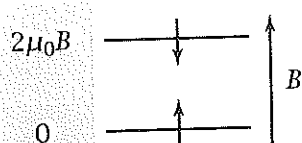


Figure 10.10 The two-state model of spins. The B arrow shows the direction of an externally applied magnetic field. The ground state occurs when an atomic spin is aligned with the direction of B . The excited state occurs when the atomic spin is anti-aligned with B .

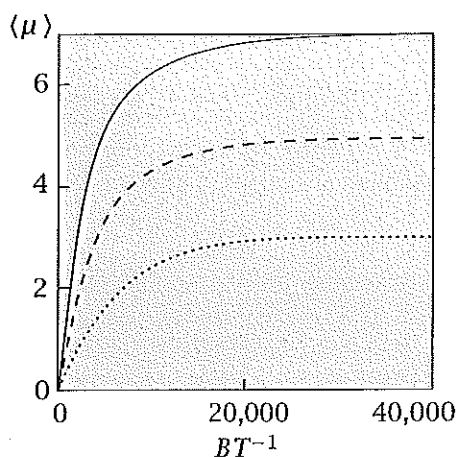


Figure 10.11 The average magnetic moment $\langle \mu \rangle$ saturates with increasing magnetic field B/kT . At low fields, $\langle \mu \rangle$ is linear in B/kT . Data for gadolinium sulphate octahydrate (—), ferric ammonium alum (---), chromium potassium alum (.....). Source: JD Fast, *Entropy; The Significance of the Concept of Entropy and Its Applications in Science and Technology*, McGraw-Hill, New York, 1962. Data are from CJ Gorter, WJ deHaas and J van den Handel, *Proc Kon Ned Akad Wetensch* **36**, 158 (1933) and WE Henry, *Phys Rev* **88**, 559 (1952).

The last equality follows from the definition of q in Equation (10.53). A concise way to express this relationship is through use of the hyperbolic tangent function,

$$\tanh x = \frac{1 - e^{-2x}}{1 + e^{-2x}}. \quad (10.56)$$

Using the hyperbolic tangent, the average magnetic moment is given by

$$\langle \mu \rangle = \mu_0 \tanh\left(\frac{\mu_0 B}{kT}\right). \quad (10.57)$$

In weak magnetic fields or at high temperatures, $\mu_0 B/kT \ll 1$. The Taylor series expansion for exponentials (see Appendix J, Equation (J.1)) gives $1 - e^{-2\mu_0 B/kT} \approx 2\mu_0 B/kT$ and $1 + e^{-2\mu_0 B/kT} \approx 2 - 2\mu_0 B/kT \approx 2$. At high temperatures or in weak fields, the total magnetic moment is inversely proportional to T , and Equation (10.57) becomes **Curie's law**:

$$\langle \mu \rangle = \frac{\mu_0^2 B}{kT}. \quad (10.58)$$

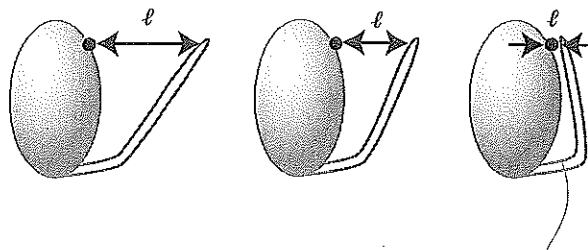
In contrast, at high fields ($B/kT \rightarrow \infty$), Equation (10.55) gives $\langle \mu \rangle = \mu_0$.

Figure 10.11 shows experimental evidence that the magnetization of a material increases with increasing magnetic field. High fields cause all the spins to align with the field. Cooling leads to magnetization (alignment of the spins) and heating leads to demagnetization (random orientations of the spins).

EXAMPLE 10.7 Modeling a protein loop. Let's use Boltzmann's law to model a peptide loop on a protein molecule. You probe the loop with fluorescence spectroscopy, which measures a distance ℓ from a point on the loop to a point on the protein (see Figure 10.12).

You model the loop as having three different conformations: (1) The loop sticks to the side of the protein, $\ell_1 = 1$ Å; define this as the ground state, with energy $\varepsilon_1 = 0$. (2) In a second conformation, the loop is more distant from

Figure 10.12 Three states of a protein loop in Example 10.7: 4 Å away from the protein, 2 Å away from the protein, or 1 Å away from the protein.



the protein, $\ell_2 = 2 \text{ Å}$, and the energy is higher by an amount $\varepsilon_2 = 1 \text{ kcal mol}^{-1}$. (3) In the third conformation, the loop flops far away from the protein, $\ell_3 = 4 \text{ Å}$, and the energy relative to the ground state is $\varepsilon_3 = 1.7 \text{ kcal mol}^{-1}$. At temperature $T = 300 \text{ K}$, the partition function for this model is

$$q = 1 + e^{-\varepsilon_2/RT} + e^{-\varepsilon_3/RT} = 1 + 0.19 + 0.06 = 1.25, \quad (10.59)$$

so the populations of the three states are

$$p_1 = \frac{1}{q} = 0.8, \quad p_2 = \frac{e^{-\varepsilon_2/RT}}{q} = 0.15, \quad p_3 = \frac{e^{-\varepsilon_3/RT}}{q} = 0.05. \quad (10.60)$$

The ideal test of your model would be measurements of the three populations in the distribution. However, usually experiments measure only averages, not full distributions. So, to compare with experiments, compute averages such as

$$\langle \ell \rangle = 0.8\ell_1 + 0.15\ell_2 + 0.06\ell_3 = 1.34 \text{ Å} \quad (10.61)$$

and

$$\langle \varepsilon \rangle = 0.8\varepsilon_1 + 0.15\varepsilon_2 + 0.06\varepsilon_3 = 0.25 \text{ kcal mol}^{-1} \quad (10.62)$$

You can also compute the variance of the loop distance, $\langle \ell^2 \rangle - \langle \ell \rangle^2$, the heat capacity C_V , the entropy and free energy, and other such properties that might be measurable. Increasing temperature will lead to increasing loop opening $\langle \ell \rangle$.

What Is an Ensemble?

A term commonly used in statistical mechanics is *ensemble*. We will use it in the following chapters. The term is usually used in one of two ways. First, it can refer to which set of variables you are controlling: 'the (U, V, N) ensemble' or 'the (T, p, N) ensemble,' for example. Some ensembles are so common that they have names. In this chapter, we have used the (T, V, N) ensemble, also called the *canonical ensemble*. (U, V, N) is called the *microcanonical ensemble*. (T, p, N) , is called the *isobaric-isothermal ensemble*. Another one that will be important later in Chapters 28 and 29 on ligand binding is (T, V, μ) , called the *grand canonical ensemble*. These are the four main named ensembles.

The term ensemble also has another meaning. An ensemble is the collection of all the possible microstates, or snapshots, of a system. For example, our four-bead polymer chain has an ensemble of five microstates and our six-bead chain has an ensemble of 36 microstates. Below, we briefly note some properties of the microcanonical ensemble.

The Microcanonical Ensemble

The microcanonical ensemble is qualitatively different from the canonical and grand canonical ensembles. In the canonical ensemble, the temperature is fixed, which is equivalent to fixing the average energy $U = \langle E \rangle$. The energy can fluctuate. But in the microcanonical ensemble, every microstate has exactly the same fixed energy, so $U = E$, and there are no fluctuations. For the microcanonical ensemble, it is more useful to focus on the $i = 1, 2, 3, \dots, W(E, V, N)$ different microstates of the system than on t different energy levels, since there is only one energy level. In the microcanonical ensemble, each microstate is equivalent. So you can express the probability that the system is in microstate $i = 1, 2, 3, \dots, W$ as

$$p_i^* = \frac{1}{W}. \quad (10.63)$$

Using the definition of the entropy, $S/k = -\sum_i p_i \ln p_i$, now summed over microstates, you get

$$\begin{aligned} \frac{S}{k} &= -\sum_{i=1}^W p_i \ln p_i = -\sum_{i=1}^W \left(\frac{1}{W}\right) \ln\left(\frac{1}{W}\right) \\ &= \ln W(E, V, N), \end{aligned} \quad (10.64)$$

as you expect from the Boltzmann expression.

Summary

Boltzmann's law gives the equilibrium distribution of atoms and molecules over their energy levels. Starting with a model for the ladder of energies accessible to the system, you can compute the partition function. From the partition function, you can compute the thermodynamic and averaged physical properties. In the next chapter, we illustrate how quantum mechanical models give the energy levels that can be used to predict the properties of gases and simple solids from their atomic structures.

Problems

1. **Statistical thermodynamics of a cooperative system.** Perhaps the simplest statistical mechanical system having 'cooperativity' is the three-level system in Table 10.2.

Table 10.2

Energies	$2\varepsilon_0$	ε_0	0
Degeneracies	γ	1	1

- (a) Write an expression for the partition function q as a function of energy ε , degeneracy γ (see page 178), and temperature T .
- (b) Write an expression for the average energy $\langle \varepsilon \rangle$ versus T .
- (c) For $\varepsilon_0/kT = 1$ and $\gamma = 1$, compute the equilibrium populations, or probabilities, p_1^* , p_2^* , p_3^* of the three levels of energy 0, ε_0 , $2\varepsilon_0$, respectively.
- (d) Now if $\varepsilon_0 = 2 \text{ kcal mol}^{-1}$ and $\gamma = 1000$, find the temperature T_0 at which $p_1 = p_3$.
- (e) Under condition (d), compute p_1^* , p_2^* , and p_3^* at temperature T_0 .
2. **The speed of sound.** The speed of sound in air is approximately the average velocity $\langle v_x^2 \rangle^{1/2}$ of the gas molecules. Compute this speed for $T = 0^\circ\text{C}$, assuming that air is mostly nitrogen gas.
3. **The properties of a two-state system.** Given a two-state system in which the low energy level is 600 cal mol^{-1} , the high energy level is $1800 \text{ cal mol}^{-1}$, and the temperature of the system is 300 K ,
- (a) What is the partition function q ?
- (b) What is the average energy $\langle \varepsilon \rangle$?
4. **Binding to a surface.** Consider a particle that has two states: bonded to a surface, or non-bonded (released). The non-bonded state is higher in energy by an amount ε_0 .
- (a) Explain how the ability of the particle to bond to the surface contributes to the heat capacity, and why the heat capacity depends on temperature.
- (b) Compute the heat capacity C_V in units of Nk if $T = 300 \text{ K}$ and $\varepsilon_0 = 1.2 \text{ kcal mol}^{-1}$ (which is about the strength of a weak hydrogen bond in water).
5. **Entropy depends on distinguishability.** Given a system of molecules at $T = 300 \text{ K}$, $q = 1 \times 10^{30}$, and $\Delta U = 3740 \text{ J mol}^{-1}$,
- (a) What is the molar entropy if the molecules are distinguishable?
- (b) What is the molar entropy if the molecules are indistinguishable?
6. **The Boltzmann distribution of uniformly spaced energy levels.** A system has energy levels uniformly spaced at $3.2 \times 10^{-20} \text{ J}$ apart. The populations of the energy levels are given by the Boltzmann distribution.

What fraction of particles is in the ground state at $T = 300 \text{ K}$?

7. **The populations of spins in a magnetic field.** The nucleus of a hydrogen atom, a proton, has a magnetic moment. In a magnetic field, the proton has two states of different energy: spin up and spin down. This is the basis of proton NMR. The relative populations can be assumed to be given by the Boltzmann distribution, where the difference in energy between the two states is $\Delta\varepsilon = g\mu B$, $g = 2.79$ for protons, and $\mu = 5.05 \times 10^{-24} \text{ J T}^{-1}$. For a 300 MHz NMR instrument, $B = 7 \text{ T}$.

- (a) Compute the relative population difference, $|N_+ - N_-|/(N_+ + N_-)$, at room temperature for a 300 MHz machine.
- (b) Describe how the population difference changes with temperature.
- (c) What is the partition function?

8. **Energy and entropy for indistinguishable particles.** Equations (10.36) for $\langle \varepsilon \rangle$ and (10.39) for S apply to distinguishable particles. Compute the corresponding quantities for systems of indistinguishable particles.

9. **Computing the Boltzmann distribution.** You have a thermodynamic system with three states. You observe the probabilities $p_1 = 0.9$, $p_2 = 0.09$, and $p_3 = 0.01$ at $T = 300 \text{ K}$. What are the energies ε_2 and ε_3 of states 2 and 3 relative to the ground state?

10. **The pressure reflects how energy levels change with volume.** If energy levels $\varepsilon_i(V)$ depend on the volume of a system, show that the pressure is the average

$$p = -N \left\langle \frac{\partial \varepsilon}{\partial V} \right\rangle.$$

11. **The end-to-end distance in polymer collapse.** Use the two-dimensional four-bead polymer of Example 10.3. The distance between the chain ends is 1 lattice unit in the compact conformation, 3 lattice units in the extended conformation, and $\sqrt{5}$ lattice units in each of the other three chain conformations. Plot the average end-to-end distance as a function of temperature if the energy is

- (a) $\varepsilon = 1 \text{ kcal mol}^{-1}$;
- (b) $\varepsilon = 3 \text{ kcal mol}^{-1}$.

12. **The lattice model of dimerization.** Use the lattice model for monomers bonding to form dimers, and assume large volumes $V \gg 1$.

- (a) Derive the partition function.
- (b) Compute $p_1(T)$ and $p_2(T)$, the probabilities of monomers and dimers as functions of temperature, and sketch the dependence on temperature.
- (c) Compute the bond breakage temperature T_0 at which $p_1 = p_2$.

13. **Deriving the Boltzmann law two different ways.** Use Equation (10.6) to show that the distribution of probabilities p_j^* that minimizes the free energy F at constant

T is the same one you get if instead you maximize the entropy S at constant $U = \langle E \rangle$.

14. Protein conformations. Assume a protein has six different discrete conformations, with energies given in Figure 10.13.

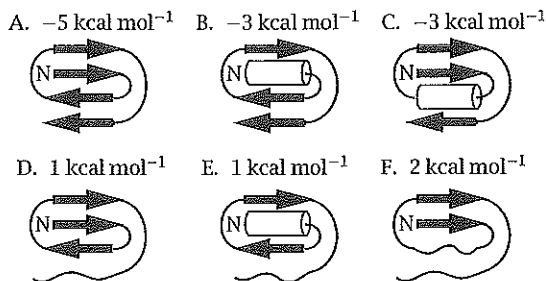


Figure 10.13

- Write an expression for the probability $p(i)$ of finding the protein in conformation i .
- Write an expression for the probability $p(E)$ of finding the protein having energy E .
- Use the expressions you wrote in (a) and (b) to calculate the following probabilities:

- $p(\text{State B})$.
- $p(\text{State A})$.
- $p(\text{State D})$.
- $p(1 \text{ kcal mol}^{-1})$.
- $p(-5 \text{ kcal mol}^{-1})$.

- What is the average energy of the ensemble of conformations?

15. Modeling ligand binding. A ligand is bound to a protein with a spring-like square-law energy $\varepsilon(x)$, where x is the distance between the ligand and protein as shown in Figure 10.14.

$$\varepsilon(x) = \frac{1}{2}cx^2$$

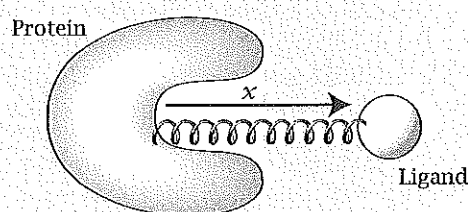


Figure 10.14

- For constant (T, V, N) , write an expression for the probability distribution $p(x)$ of the ligand separation from the protein.
- Sketch a plot of $p(x)$ versus x .
- Write an expression for the average location of the ligand, $\langle x \rangle$.
- Write an expression for the second moment of the location of the ligand, $\langle x^2 \rangle$.
- Calculate the average energy $\langle \varepsilon \rangle$ of the system.

16. Distribution of torsional angles. In a computer simulation that samples a molecular torsion angle θ , you observe a Gaussian distribution $p(\theta)$, shown in Figure 10.15:

$$p(\theta) = p_0 e^{-k_s(\theta - \theta_0)^2}$$

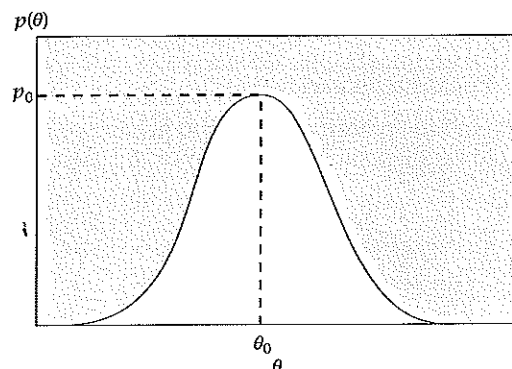


Figure 10.15

What is the underlying energy function $E(\theta)$ that gives rise to it?

17. Three-bead polymer chain model. Consider a three-bead polymer that can undergo conformational change from a nonlinear to a linear form, as shown in Figure 10.16. Both conformations have the same energy. Now suppose the X and Y atoms of the polymer can bind a ligand L (Figure 10.17). Breaking one bond increases the energy by ε and breaking two bonds increases the energy by 2ε . Assume that the ligand-bound conformation has the lowest energy.

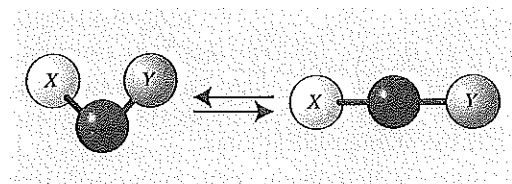


Figure 10.16

- Draw a picture showing the possible binding states.
- Calculate the equilibrium probabilities of these conformations.