

# Chapter 15

## Statistical Mechanics

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\*These sections can be skipped without loss of continuity.

### 15.1 Introduction

Statistical mechanics is the mechanics of systems with very large numbers of constituent particles — a liter of air with some  $10^{22}$  molecules of  $N_2$  and  $O_2$ , a cup of water with some  $10^{25}$  water molecules, a meter of copper wire with some  $10^{23}$  conduction electrons. There are classical and quantum versions of statistical mechanics. While both have applications under the heading of “modern physics,” it is the quantum version that is the more important and, rather surprisingly, the simpler. This chapter is a brief introduction to statistical mechanics, with an emphasis on the quantum version.

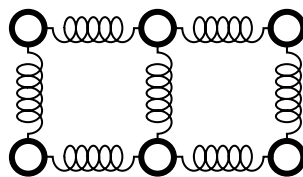
The name “statistical mechanics” reflects that because of the huge number of particles involved, we can treat them *statistically*, ignoring the detailed motion of the individual particles. This has the surprising consequence that problems in statistical mechanics (either classical or quantum) are often actually easier than problems involving only three or four particles whose motions need to be followed in detail. The detailed specification of the microscopic state, or **microstate**, of any system of  $N$  particles involves giving the wave functions of all  $N$  particles (in the quantum case) or the positions and velocities of all  $N$  particles (in the classical case). When  $N$  is large, this represents an appalling amount of information; to write down the microstate of a mole of gas would require more than the world’s total supply of paper! Fortunately, in statistical mechanics, we have no desire to know the microstate of a system. Rather, we want to know just a small number of *macroscopic* variables that are statistical averages over the many microscopic variables. For example, to specify the macroscopic state, or **macrostate**, of a container of helium gas, we have only to give the volume  $V$ , the number of atoms  $N$ , and the total energy  $E$  (or, equivalently — as we will see — the temperature  $T$ ). Statistical mechanics is the study of the relation between the observable macrostates and the underlying, but unobservable and ultimately uninteresting, microstates.

## 15.2 Temperature

We begin by discussing the meaning of temperature, a key idea in statistical mechanics. What is temperature? Before the development of statistical mechanics and kinetic theory (Section 3.7), temperature was defined in a purely pragmatic manner as “the thing that thermometers measure.” But this definition shed no light on the physical microscopic meaning of temperature. Before kinetic theory was established, physicists could say only that hot things have higher temperature, cold things have lower temperature, and one can define a temperature scale that everyone agrees on, so that different thermometers give consistent results. But what, microscopically, is the difference between hot objects and cold objects? What happens to water as it is heated? The appearance and mass of the water remain unchanged. What property is your body sensing when you dip your hand in water and feel hot or cold? It was a mystery.

Today, we understand that temperature is a measure of thermal energy — the random, microscopic energy of atoms. You can think of temperature as a measure of the “jiggling” of atoms. At  $T = 0$  K, the atoms of a material have no energy, or more precisely, they have as little energy as possible, with the system residing in its quantum ground state. A classical description of a solid material at  $T = 0$  is an assembly of stationary atoms, rigidly fixed in position. As the temperature rises, the atoms begin to vibrate about their equilibrium positions, gently jostling their neighbors. As the temperature rises further, the atoms jiggle more energetically, crashing against their neighbors until the chemical bonds between atoms begin to break and the atoms slide past each other — the phenomenon of melting. With the proper conditions of high temperature and low pressure, the atoms enter a gaseous state, with weakly interacting atoms flying in straight lines between collisions. In this state, higher temperature means more kinetic energy of the flying atoms. When the hand is dipped in hot water the sensation of heat is caused by jiggling water molecules pounding against the atoms of delicate skin cells. The atoms of the cells vibrate in response, sending complex chemical messages along our nerves.

To quantify this notion of jiggling atoms, this microscopic energy, and to give a precise definition of temperature, we must first introduce the concept of **degrees of freedom**. A degree of freedom is a kind of microscopic repository of energy, a mode in which an atom can store energy. In the context of statistical mechanics, the number of degrees of freedom is defined as the number of squared terms in the detailed expression for the total energy. For example, a single atom in an ideal gas has only kinetic energy (no potential energy) and it can move in any of three orthogonal directions  $x$ ,  $y$ , and  $z$ , so its energy is  $E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$ . There are three quadratic terms in this expression, so we say that the atom has three degrees of freedom. An ideal gas of  $N$  atoms has  $3N$  degrees of freedom — three degrees of freedom for each atom. A particle on a spring, moving in one dimension only, has both kinetic energy and potential energy (stored in the spring). The energy is  $E = \frac{1}{2}mv^2 + \frac{1}{2}kx^2$ . Here there are two quadratic terms, and hence, two degrees of freedom. A solid consisting of  $N$  atoms held in place by springlike chemical bonds between nearest neighbors (Figure 15.1) has  $6N$  degrees of freedom because the energy of each atom can be written as



**FIGURE 15.1**

Ball-and-spring model of a solid.

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}kx^2 + \frac{1}{2}ky^2 + \frac{1}{2}kz^2$$

where  $(x, y, z)$  is the displacement from the equilibrium position.

We can now state an important theorem in statistical mechanics called the **equipartition theorem**. The equipartition theorem says that for a classical system in thermal equilibrium, on average, the total energy of the system is shared, or “partitioned,” *equally* among the various degrees of freedom. As an example, consider a gas of atoms. At any instant, the atoms possess a wide variety of velocities. Some atoms are fast, some are slow, a few are moving very nearly along the  $x$ -axis, others are moving in other directions. As the atoms collide, they exchange energy, and a given atom has a rapidly fluctuating energy and velocity as it zigzags from one collision to the next. However, in the long run, each degree of freedom of each atom, has exactly the same *average* energy. This situation can be likened to a box of marbles being violently shaken. All the marbles shake with the same average energy. This will be true even if the marbles have different masses. If one of the marbles in the box is unusually massive, it will move about with a smaller than average speed, but its average kinetic energy ( $\frac{1}{2}mv^2$ ) will be the same as the other marbles. If we arrange things so that the marbles on the right half of the box are moving much faster than the marbles on the left half (if the total energy is not shared equally among the available degrees of freedom), the system is *not* in thermal equilibrium. But the random shaking of the box will quickly even out the energy distribution, and equilibrium will be achieved.

As another example of the equipartition theorem, consider a mass on a spring, constrained to move in one dimension. The energy has two terms  $E = \frac{1}{2}mv^2 + \frac{1}{2}kx^2$ ; there are two degrees of freedom. If the mass–spring system is shaken, the energy will sometimes be all kinetic (when  $x = 0$ ) and sometimes all potential (when  $v = 0$  and the mass is at the turning point). But on average, the energy is shared equally between the two terms.

Although we have not proved the equipartition theorem, we hope it seems plausible. A semirigorous proof is explored in Problem 15.9. There is one detail in the statement of the theorem that is easy to overlook, but will be important later. The equipartition theorem begins: “For a *classical* system in thermal equilibrium . . . ” This caveat means that quantum effects are ignored. In particular, the equipartition theorem assumes that the total energy of the system is continuous — not quantized, not discrete. We will see later that the quantization of energy in quantum systems can lead to a breakdown of the classical equipartition theorem and an unequal sharing of energy among the degrees of freedom.

Now that we understand the concept of degrees of freedom and the equipartition theorem, we can give a precise definition of temperature. The temperature  $T$  of a classical system in thermal equilibrium is defined by the relation

$$\frac{1}{2}kT = (\text{average energy in each degree of freedom}) \quad (15.1)$$

where  $k$  is called Boltzmann’s constant\* and has the experimentally determined value

$$k = 1.38 \times 10^{-23} \text{ J/K} = 8.62 \times 10^{-5} \text{ eV/K}$$

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\*Boltzmann’s constant  $k$  must not be confused with either the Coulomb constant  $k = 1/(4\pi\epsilon_0)$  or the wave number  $k = 2\pi/\lambda$ . Almost invariably, Boltzmann’s constant appears next to the absolute temperature in the combination  $kT$ , so the notation is usually clear. When there is any danger of confusion, we will use the symbol  $k_B$  for Boltzmann’s constant.

The factor  $\frac{1}{2}$  appears in (15.1) so that another equation (the Boltzmann relation, below) does *not* contain a factor of 2. The physically important concept here is that temperature is proportional to the average energy per degree of freedom, the amount of atomic “jiggling.”

### Example 15.1

What is the average translational kinetic energy of a nitrogen molecule in air at room temperature,  $T \approx 293$  K? What is the molecule’s rms speed?

The translational kinetic energy of a gas molecule is  $E = \frac{1}{2}mv^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$ , where  $v$  is the speed and  $v_x$ ,  $v_y$ , and  $v_z$  are the components of the velocity. (In addition to translational kinetic energy, diatomic molecules, such as nitrogen or oxygen, can have rotational kinetic energy. See Section 15.9). There are three degrees of freedom in this expression, and each has an average energy of  $\frac{1}{2}kT$ . The total average kinetic energy is therefore

$$\frac{3}{2}kT = \frac{3}{2}(1.38 \times 10^{-23}) \times (293) \approx 6.1 \times 10^{-21} \text{ J} = 0.038 \text{ eV}$$

Notice that the answer does not depend on any of the properties of the molecule, such as mass. *Any* molecule in a gas at temperature  $T$  will have an average translational kinetic energy of  $\frac{3}{2}kT$ . In estimating thermal energies like this, it is worth remembering that the factor  $kT$ , which characterizes thermal atomic energy, has the approximate value 0.025 eV at room temperature.

The average kinetic energy is often written  $\langle \frac{1}{2}mv^2 \rangle = \frac{1}{2}m\langle v^2 \rangle$ , where the brackets  $\langle \dots \rangle$  indicate an average over thermally fluctuating values. As discussed in Section 3.8, the root-mean-square (rms) value of the speed  $v$  is defined as  $v_{\text{rms}} = \sqrt{\langle v^2 \rangle}$ . Setting the average kinetic energy equal to  $\frac{3}{2}kT$ , we have

$$\frac{3}{2}kT = \frac{1}{2}m\langle v^2 \rangle$$

Solving for  $v_{\text{rms}}$  and recalling that the mass of an  $\text{N}_2$  molecule is 28 atomic mass units, we get (using SI units)

$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3 \times (1.38 \times 10^{-23}) \times (293)}{28 \times (1.66 \times 10^{-27})}} = 510 \text{ m/s}$$

This speed is comparable to, but somewhat greater than, the speed of sound. This is not surprising since sound is a pressure wave in air, propagating by collisions among the air molecules. Like a message being passed from person to person, the pressure disturbance in air (the sound wave) would be expected to travel at about the speed of the messengers, the air molecules.

### Example 15.2

What is the rms average speed of a diatomic bromine molecule ( $\text{Br}_2$ , atomic number  $Z = 35$ ) in air at room temperature?

By the equipartition theorem, the average kinetic energies of bromine molecules and  $\text{N}_2$  molecules are identical, at the same temperature.

$$\left(\frac{1}{2}mv^2\right)_{\text{Br}} = \left(\frac{1}{2}mv^2\right)_{\text{N}} = \frac{3}{2}kT$$

We can then set up the following ratio:

$$\frac{v_{\text{Br}}}{v_{\text{N}}} = \sqrt{\frac{m_{\text{N}}}{m_{\text{Br}}}} = \sqrt{\frac{14}{70}} = 0.447$$

Using the result from Example 15.1, we have

$$v_{\text{Br}} = 0.447v_{\text{N}} = 0.447 \times (510 \text{ m/s}) = 228 \text{ m/s}$$

At any given temperature, the heavier bromine molecules travel more slowly, on average.

### 15.3 The Boltzmann Factor

We now come to the central result of statistical mechanics, which, oddly enough, has no standard name. We will call it the Boltzmann relation,\* a name used in some textbooks. The Boltzmann relation was established before the development of quantum mechanics; however, we will give the quantum version of this equation because it is actually simpler than the original classical version. We begin by stating this relation without proof; in Section 15.5, we will explore its derivation.

For a system in equilibrium at temperature  $T$ , the probability that the system is in a particular quantum state  $i$ , a *particular microstate*, with energy  $E_i$ , is proportional to  $e^{-E_i/kT}$ :

$$P(\text{state } i) = C e^{-E_i/kT} \quad (15.2)$$

where  $P$  represents probability, and  $C$  is a constant of proportionality.

The factor  $e^{-E_i/kT}$  is called the **Boltzmann factor**, after Ludwig Boltzmann, one of the great pioneers of kinetic theory and statistical mechanics. The constant  $C$  is determined by the following normalization argument: The system must certainly occupy *one* of the possible states  $i$ . Thus the sum over all  $i$  of the probabilities (15.2) must equal 1.

$$\sum_i P(\text{state } i) = C \sum_i e^{-E_i/kT} = 1$$

and hence,

$$C = \frac{1}{\sum_i e^{-E_i/kT}}$$

We can then rewrite (15.2) as the **Boltzmann relation**

$$P(\text{state } i) = \frac{e^{-E_i/kT}}{\sum_j e^{-E_j/kT}} \quad (15.3)$$

\*We cannot call it the “Boltzmann equation” because that phrase is already used to refer to an equation in transport theory. Boltzmann was prolific.

Notice the use of two different indexes ( $i$  and  $j$ ) in this equation to avoid confusion: We consider a *particular* state  $i$ , but we sum over *all* states  $j$ . The sum

$$\sum_j e^{-E_j/kT} \quad (15.4)$$

depends on the energies  $E_j$  and is called the **partition function** because it describes how the total energy of the system is *partitioned* among the various available states. Notice that the partition function is a dimensionless number. This number turns out to be proportional to the number of different quantum states that the system is likely to be found in. See Problem 15.12.

The great power of the Boltzmann relation lies in its generality. The “system” under study might be a hydrogen atom or a neutron star, a block of metal or one electron in that metal, a mole of gas molecules in a container or one molecule in that gas. For this relation to apply, only two conditions must be met: The system must be in thermal equilibrium at temperature  $T$ , and the system must contain a definite number of particles. For systems in which the number of particles can change, a modified version of (15.3) must be used, a version beyond the scope of our discussion.\*

Since the Boltzmann factor  $e^{-E/kT}$  is a monotonically decreasing function of  $E$ , a particular state of higher energy is always less likely to occur than a given state of lower energy, at a given temperature. However, it does not follow that higher energies are less likely than lower energies. The probability  $P(\text{state } i)$  that a system is in a quantum state  $i$  with energy  $E_i$  is not the same as the probability  $P(\text{energy } E_i)$  that the system has energy  $E_i$ . As we have seen before, quantum states can be *degenerate*; that is, there can be several states with the same energy. In this case, the probability  $P(E)$  that the system has energy  $E$  is the sum of the probabilities that the system is in any of the states with that energy.

$$P(E) = \sum_{\substack{\text{states } i \\ \text{with energy } E}} P(i) \quad (15.5)$$

But all the states  $i$  with the same energy  $E$  have the same probability  $P(i)$ , given by (15.3), so the Boltzmann relation can be rewritten

$$P(E) = g(E)P(i) = \frac{g(E)e^{-E/kT}}{\sum_j e^{-E_j/kT}} \quad (15.6)$$

where  $g(E)$  is the degeneracy of the energy level  $E$ .

An analogy with playing cards may be useful. Consider the 52 cards in a deck of cards to represent 52 quantum states, and the 4 suits (hearts, clubs, spades, and diamonds) to be 4 different energies. The degeneracy of each energy is 13 (ace, two,  $\dots$  jack, queen, king). The probability of drawing a particular card, say, five of hearts, is  $1/52$ , but the probability of drawing a heart is

$$P(\text{heart}) = 13 \times \frac{1}{52} = \frac{1}{4}$$

an example of  $P(E) = g(E)P(i)$ .

### Ludwig Edward Boltzmann

(1844–1906, Austrian)



Boltzmann developed the kinetic theory of gases and invented the science of statistical mechanics. At a time when many scientists did not believe in atoms, Boltzmann's work was controversial and it was subjected to strong attacks, as well as great praise, throughout his career. He was known as an inspiring lecturer, and sometimes his classes had to be moved to larger and larger auditoriums to accommodate growing crowds of listeners. Suffering from episodes of depression all his life, he finally committed suicide, in part because he could not bear the criticism from his colleagues. Engraved on his tombstone is the equation  $S = k \ln W$  (Boltzmann used the symbol  $W$  for the multiplicity  $g$ ).

\*In cases where the number of particles is not fixed, but is a variable number  $N$ , one must introduce a *chemical potential*  $\mu$ , and the Boltzmann factor becomes  $e^{(N\mu - E)/kT}$  — but this is a topic for a later course.



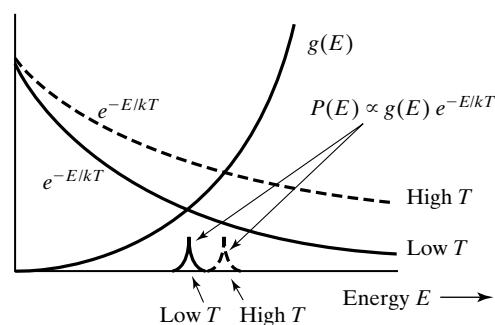


FIGURE 15.2

A highly schematic view of the competition between two factors in the Boltzmann relation (15.6).

In physical systems the degeneracy factor  $g(E)$  that appears in (15.6) is almost always an increasing function of energy. For instance, in Section 15.8, we will show that for the case of a single particle in a 3-D quantum gas,  $g(E) \propto E^{1/2}$ . In Section 15.5 we will see that for many-particle systems, the degeneracy  $g(E)$  grows *very* rapidly, typically  $g(E) \propto E^N$ , where  $N$  is the number of particles. While  $g(E)$  is an increasing function of energy, the Boltzmann factor  $e^{-E/kT}$  is a rapidly decreasing function of energy. The most probable energy of a system at temperature  $T$  is determined by the competition between these two factors, as indicated schematically in Fig. 15.2. When the temperature is increased, the Boltzmann factor curve in Fig. 15.2 moves up to the dashed position, resulting in a higher most probable energy for the system. Higher temperatures mean higher energies.

### Example 15.3

Consider a gas of hydrogen in equilibrium at room temperature,  $T \approx 293$  K. What is the ratio of the number of atoms in the first excited state to the number of atoms in the ground state?

The number ratio is the ratio of the probabilities given by (15.6). In this case the “system” is a single hydrogen atom. The ground-state energy is  $E_1 = -13.6$  eV; the first excited-state energy is  $E_2 = (E_1/4) = -3.4$  eV. At room temperature,  $kT = 0.0252$  eV. The degeneracy of the ground state is  $g(E_1) = 2$  since the two spin states of the electron have equal energy; the degeneracy of the first excited state is  $g(E_2) = 8$  since there is a single  $2s$  state, three  $2p$  states, and a factor of 2 from spin. When we take the ratio of the probabilities, the partition function factor,  $\sum_j e^{-E_j/kT}$ , cancels out, leaving

$$\frac{P(E_2)}{P(E_1)} = \frac{g(E_2)e^{-E_2/kT}}{g(E_1)e^{-E_1/kT}} = \frac{g(E_2)}{g(E_1)} e^{-(E_2-E_1)/kT} = \frac{8}{2} e^{-405} \approx 10^{-176}$$

This is such a fantastically small number that if the observable universe were filled with hydrogen gas at 1 atm of pressure, then at room temperature there would not be even one hydrogen atom in the first excited state.

In problems such as this one, where the Boltzmann factor is used to compute relative probabilities, it is expedient to set up a ratio so that the partition function cancels out. In all but the simplest cases, the partition function is quite difficult to compute exactly, so we avoid that task wherever possible.

**Example 15.4**

In hydrogen gas, at what temperature is the ratio of the number of atoms in the first excited state to the number of atoms in the ground state equal to 1/100; that is, how hot does hydrogen gas have to be for a significant fraction of the atoms to be in excited states?

Proceeding as in Example 15.3,

$$\frac{P(E_2)}{P(E_1)} = \frac{g(E_2) e^{-E_2/kT}}{g(E_1) e^{-E_1/kT}} = 4e^{-\Delta E/kT} = \frac{1}{100}$$

therefore,  $\Delta E/kT = \ln(400)$ , or

$$kT = \frac{\Delta E}{\ln(400)} = \frac{10.2 \text{ eV}}{5.99} = 1.70 \text{ eV}$$

This corresponds to a temperature of  $T \approx 20,000 \text{ K}$ . The universe was at this temperature about 100,000 years after the “big bang.” At that time, in addition to excited hydrogen atoms, there was a substantial density of free electrons and protons. These charged particles scatter light strongly, and so during that epoch the universe was opaque; light could not travel far before scattering. At about 300,000 years after the big bang, when the universe had cooled to 3000 K, virtually all free electrons and protons had combined to form hydrogen atoms in the ground state. Ground-state hydrogen atoms are completely transparent to low-energy photons (since photons of energy less than 10.2 eV cannot be absorbed), so light could travel freely without scattering. Today, some 15 billion years later, astronomers have observed that space is filled with microwave background radiation. This photon gas, which is at a temperature of 3 K, is the Doppler-shifted light from that time 300,000 years after the big bang, when matter and radiation “decoupled.”

**Example 15.5**

Consider a particle with spin half and a magnetic moment  $\mu$  in an external magnetic field  $\mathbf{B}$ . Two orientations of the moment with respect to the field are allowed, corresponding to spin up and spin down. Find the probability that the moment is aligned with the field, in terms of the temperature  $T$  and field  $B$ . What is this probability at room temperature (300 K) in a field of  $B = 1.0 \text{ T}$ ?

As described in Section 9.6, an electron in an external magnetic field has two energy states: a ground state with the moment aligned with the field and a first excited state with the moment anti-aligned with the field. The separation of the energy levels is  $\varepsilon = 2\mu_B B$  where  $\mu_B$  is the Bohr magneton. This is an example of a two-level system, a system with exactly two states, a ground state and an excited state. A two-level system is one of the few systems for which it is easy to write down the partition function (15.4) exactly. If we set the zero of energy at the ground-state energy, then the two levels have energies 0 and  $\varepsilon$  [see Fig. 15.3(a)], and the partition function becomes

$$\sum_j e^{-E_j/kT} = 1 + e^{-\varepsilon/kT}$$



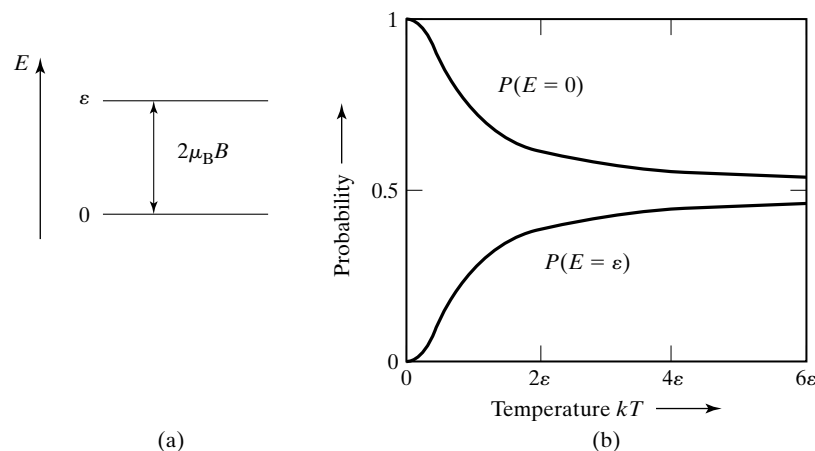


FIGURE 15.3

(a) The energy spectrum of an electron in a magnetic field, an example of a two-level system. (b) Probabilities that the electron is found in the ground state and in the excited state, as functions of  $kT$ .

The probabilities of the two states are then, according to (15.3)

$$P(E = 0) = \frac{1}{1 + e^{-\varepsilon/kT}} \quad \text{and} \quad P(E = \varepsilon) = \frac{e^{-\varepsilon/kT}}{1 + e^{-\varepsilon/kT}} = \frac{1}{e^{+\varepsilon/kT} + 1}$$

These two probabilities are plotted in Fig. 15.3(b). The upper curve is the probability  $P(E = 0)$  that the system is in the ground state, with the magnetic moment aligned with the field; the lower curve is the probability that the system is in the excited state. In the high-temperature limit ( $kT \gg \varepsilon$ ), both probabilities approach 0.5 and the system is equally likely to be in either state.

At  $B = 1.0$  T, the energy-level separation is  $2\mu_B = (2)(5.79 \times 10^{-5} \text{ eV/T})(1\text{T}) = 1.16 \times 10^{-4} \text{ eV}$ , and the ground-state probability at  $T = 300 \text{ K}$  ( $kT = 0.252 \text{ eV}$ ) is

$$P(E) = \frac{1}{1 + e^{-\varepsilon/kT}} = \frac{1}{1 + e^{-2\mu_B/kT}} = \frac{1}{1 + e^{-(1.16 \times 10^{-4})/(0.252)}} = 0.5012$$

At room temperature, we are in the high-temperature regime ( $kT \gg 2\mu_B$ ) and the populations of the two levels are almost equal. There is a preference for the moments to be aligned with the B field, but the degree of alignment (or polarization) is only about 1 part in 500.

## 15.4 Counting Microstates: The Equal-Probability Hypothesis

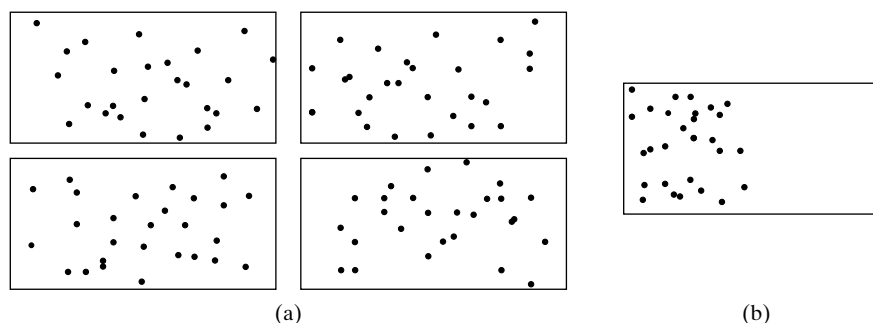
The whole of statistical mechanics, including the Boltzmann relation, rests upon a single axiom — an axiom that, like the Boltzmann relation, has no standard name. We will call it the

### EQUAL-PROBABILITY HYPOTHESIS

For an isolated system (that is, one with constant energy, constant number of particles, and so forth.) in thermal equilibrium, all microstates accessible to the system occur with equal probability.

FIGURE 15.4

Some microstates of a gas in a container. The seemingly peculiar state (b) is just as likely as any specific one of the states in (a), but there are *far* fewer states of the type (b) than of the type (a).



By *accessible* microstates, we mean those microstates that are consistent with the macroscopic constraints on the system — constraints such as the total energy, the total number of particles, and, in the case of a gas, the volume and shape of the container. These constraints define the *macrostate*. Thus, another way to state this hypothesis is this: All microstates corresponding to a given macrostate occur with equal probability. There is no known proof of this assumption; we believe it is true because it leads to many predictions that are all verified by experiment. We will see in the next section how this hypothesis leads to the Boltzmann relation.

As an example of the equal probability of accessible microstates, consider a gas of  $N$  particles in a container of volume  $V$ . The macrostate is given by  $(N, E, V)$ , where  $E$  is the total energy of the system. Classically, a microstate is specified by the positions and velocities of each of the  $N$  particles. In Fig. 15.4(a) four microstates are shown all corresponding to the same macrostate  $(N, E, V)$ . There is no reason for the system to prefer any of these states over the others, and they all occur with equal probability. Now consider the microstate in Figure 15.4(b), also a state with the same  $(N, E, V)$  as the others. This state appears unusual because all of the particles are in the left half of the container. However, strange as it may seem, this “left-side-only” microstate is just as likely as any other *particular* microstate. The reason we never observe gas molecules spontaneously clustering on one side of a container is because the microstates with the particles evenly dispersed *vastly* outnumber the microstates in which the particles cluster together. If a microstate is chosen at random, there is an overwhelming likelihood that it will be one with roughly uniform density.

To get some feeling for microstates and macrostates, we again resort to a playing-card analogy. There are a total of  $T = 52$  cards in a deck, but only  $N = 5$  cards in a poker hand. Specifying  $N$  defines the macrostate; in this analogy the macrostate is “a hand of 5 cards” — somewhat akin to specifying “5 mol of gas at standard temperature and pressure.”\* A microstate is a *particular* hand, for instance the hand

$$(3\spadesuit, J\heartsuit, 10\clubsuit, 4\spadesuit, 6\clubsuit)$$

Note that in specifying a hand, the order of the cards is irrelevant. The hand

$$(J\heartsuit, 3\spadesuit, 10\clubsuit, 4\spadesuit, 6\clubsuit)$$

\*Of course, in poker there is no clear analogue to temperature or pressure. We cannot push this analogy too far.

is the same microstate as the first hand; same cards, just different order. Likewise, in a gas of indistinguishable particles, interchanging two particles leads to the same microstate. (Indistinguishability was discussed in Ch. 10 and is further reviewed below.) There are many possible poker hands, many possible microstates, all of which are equally likely to be dealt from a well-shuffled deck. A royal flush

$$(10\clubsuit, J\clubsuit, Q\clubsuit, K\clubsuit, A\clubsuit)$$

is just as likely to occur as any *particular* “junk” hand

$$(3\diamondsuit, J\heartsuit, 10\spadesuit, 4\clubsuit, 6\clubsuit)$$

The reason junk hands are found so much more often than royal flushes is that there are only 4 possible royal flush hands (corresponding to the 4 suits), but there are more than a million possible junk hands.

To compute the probability of being dealt a royal flush, we need to know how many possible microstates (hands) there are. The number or “multiplicity”  $g$  of five-card hands ( $N = 5$ ) that can be dealt from a deck with  $T = 52$  cards is given by

$$g = \frac{T!}{(T-N)!N!} \text{ (number of ways of choosing } N \text{ objects from among } T \text{)} \quad (15.7)$$

This formula, which is called the binomial coefficient, can be understood as follows: The first card dealt in the 5-card hand can be any one of 52 cards; the second card can be any one of the remaining 51, and likewise for the third, and so on. The number of different *ordered* 5-card hands is then

$$52 \times 51 \times 50 \times 49 \times 48 = \frac{52!}{47!} = \frac{52!}{(52-5)!}$$

But we have overcounted the number of hands, because the order of the cards is irrelevant. There are  $5 \times 4 \times 3 \times 2 \times 1 = 5!$  ways of ordering 5 cards, so we must divide the expression above by 5! to get the number of distinct hands. The multiplicity  $g$  is then

$$g = \frac{T!}{(T-N)!N!} = \frac{52!}{(52-5)!5!} = 2,598,960$$

Out of all these hands, only 4 are royal flushes, so the probability of dealing a royal flush is

$$P = \frac{4}{2598960} \approx 1.54 \times 10^{-6}$$

This is a very small probability, but not as small as, say, the probability of winning a large state lottery ( $P \approx 10^{-8}$ ) and not nearly as small as the probabilities often encountered in statistical mechanics.

There is a small probability that the air molecules around you will spontaneously cluster in a corner of the room, leaving you to suffocate as you read these words. You need not worry; the probability of this occurring, although

nonzero, is *fantastically* small, as we now demonstrate. Consider a mole of gas molecules in a container. Any molecule can be anywhere in the container; of all the possible states (position and velocity) that a single molecule can occupy, there are as many on the right half of the container as on the left half. If we choose a state, *at random*, for a molecule to occupy, the probability that the one molecule will be on the left is  $P(1) = 1/2$ . If we randomly choose 2 states for 2 molecules, the probability that both particles will be on the left is the same as getting 2 heads in 2 coin flips,  $P(2) = (1/2)(1/2) = 1/4$ . The probability of choosing  $N$  states randomly and finding all  $N$  states on the left is

$$P(N) = \frac{1}{2^N} \quad (15.8)$$

For a mole of gas molecules,  $N = 6 \times 10^{23}$ , and  $P(N) = 0.5^N = 10^{-N \ln 2 / \ln 10} \approx 10^{-2 \times 10^{23}}$  (see Problem 15.22). It is difficult to describe how tiny this number is. If you wanted to write this number in decimal form as 0.000000...001, you would have to write  $2 \times 10^{23}$  zeroes. If you could write a 100,000 zeroes per second, it would take you the age of the universe ( $\approx 10^{10}$  years) to write all those zeroes.

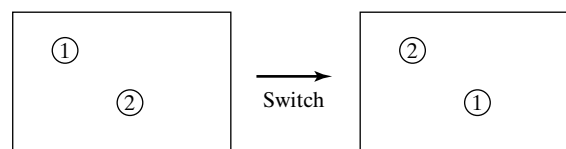
Exactly how one counts the microstates of a gas of molecules depends on whether the molecules are *distinguishable* or *indistinguishable*. Recall from Section 10.5 that in classical mechanics, identical particles are distinguishable, meaning that it is possible, in principle, to keep track of which particle is which by following their trajectories. In quantum mechanics, however, it is not possible, even in principle, to keep track of which particle is which because the wave functions of particles can overlap. We saw in Section 10.5 that this indistinguishability of identical particles has a profound effect on the symmetry of many-particle wave functions. When two indistinguishable particles in a gas have their positions interchanged, all observable properties must be unchanged; in particular, we must have  $|\psi(1, 2)|^2 = |\psi(2, 1)|^2$ .<sup>\*</sup> All particles can be classified as either *fermions* or *bosons*, depending on whether or not the wave function changes sign under particle exchange. For fermions,  $\psi(1, 2) = -\psi(2, 1)$ , which leads to the Pauli exclusion principle: No two fermions can exist in the same quantum state. For bosons,  $\psi(1, 2) = +\psi(2, 1)$  and there is no constraint on the number of particles that can exist in the same quantum state.

In the real world, particles obey quantum mechanics and identical particles are always indistinguishable. Interchanging the positions of indistinguishable particles leads to the *same* microstate. In classical mechanics, however, switching identical but distinguishable particles leads to a *different* (though physically identical) microstate. See Fig. 15.5. We now show that, although distinguishability has a big effect on the number of microstates, it often has no effect on computed probabilities, such as (15.8).

Once again, we compute the probability that all the gas molecules in a box will, quite by chance, cluster in the left half of the box. We repeat this

**FIGURE 15.5**

A box containing two identical particles, labeled 1 and 2. Since the particles are identical, the labeling occurs in our imagination only. In classical mechanics the particles are *distinguishable*, so that if the particle positions are switched, we have a new microstate. This new state, although physically identical to the first, can be distinguished from the first by its history. In quantum mechanics, the particles are *indistinguishable*, so that switching particles produces the same microstate. In general, the new state cannot be distinguished from the original, even by looking at its history.



<sup>\*</sup>As in Ch. 10, we use 1 and 2 to represent the appropriate coordinates for particles 1 and 2. For example, for a spin-half particle,  $1 = (\mathbf{r}_1, m_{s1})$ .

exercise to show how probabilities are computed by counting microstates and to show that in the classical regime we get the same probability regardless of whether or not the particles are distinguishable. We consider  $N$  identical particles in a sealed container and assume that the particles can move freely between the left and right halves of the container. To keep the math uncomplicated, we will model the quantum states of this system very simply: We assume that there are  $H$  different single-particle quantum states on the left half of the box, that is, states with wave functions localized on the left, and there are another  $H$  states on the right. Hence, there are a total of  $2H$  different quantum states that any of the  $N$  particles can occupy (see Fig. 15.6). We also assume that  $H \gg N$ , which means there are many more quantum states than particles, so the particles are not crowded into a few states. (This is the *nondegenerate, classical regime* described in Section 13.11.) If the particles are fermions, then no more than one particle can occupy any of the  $2H$  states. If the particles are bosons, any number of particles can exist in any of the quantum states. Here we solve the problem for the case of fermions; the boson case is left as an exercise (Problem 15.26).

The probability that all the particles will cluster on the left is the ratio of the number of ways of arranging the  $N$  particles among the  $H$  states on the left to the total number of ways of arranging the particles among all  $2H$  states.

$$P(\text{left side only}) = \frac{\text{number of ways of arranging } N \text{ particles among } H \text{ states of left half}}{\text{number of ways of arranging } N \text{ particles among all } 2H \text{ states.}} \quad (15.9)$$

This equation is true because all arrangements, all microstates, occur with equal probability.

Whether the particles are distinguishable or indistinguishable affects the counting of the microstates. Let us first assume, as a nineteenth-century classical physicist would, that the particles are distinguishable. As we know, this assumption is *incorrect*, but let us proceed anyway.

The number of ways of arranging  $N$  *distinguishable* particles among  $H$  states, with no more than one particle per state is

$$g(N, H) = \frac{H!}{(H - N)!} \quad (\text{distinguishable particles}) \quad (15.10)$$

To see this, imagine placing  $N$  balls in  $H$  slots. The first ball can go into any of  $H$  slots. The second ball can go into any of the remaining  $(H - 1)$  slots, and so on. The total number of arrangements is  $H \cdot (H - 1) \cdot (H - 2) \cdots (H - N + 1)$ , which is equal to (15.10). Similarly, the total number of arrangements of  $N$  distinguishable particles among  $2H$  states is  $g(N, 2H) = (2H)! / (2H - N)!$ . We can now compute the ratio (15.9), and we find

$$P(\text{left side only}) = \frac{H!}{(2H)!} \frac{(2H - N)!}{(H - N)!} \quad (15.11)$$

This is the probability that all  $N$  distinguishable particles will spontaneously cluster on the left. We now show that this is also the probability that  $N$  *indistinguishable* particles will cluster on the left.

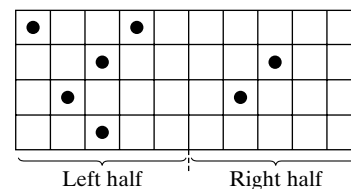


FIGURE 15.6

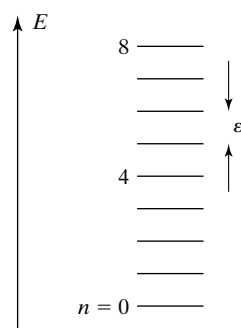
Seven particles ( $N = 7$ ) in a box with  $2H = 40$  quantum states. There are  $H = 20$  states in the left half of the box and another  $H$  states in the right. The counting of microstates in this system depends on whether the particles are distinguishable or not.

We repeat the calculation with *indistinguishable* particles. The number of ways of arranging  $N$  indistinguishable particles among  $H$  states, with no more than one particle per state, is

$$g(N, H) = \frac{H!}{N!(H - N)!} \quad (\text{indistinguishable particles}) \quad (15.12)$$

This is the same as (15.7), the poker hand multiplicity equation —  $N$  cards from a 52-card deck, or  $N$  particles among  $H$  states, the counting argument is the same. Note that the only difference between equations (15.10) and (15.12) is an extra factor of  $1/N!$  in (15.12) because there are  $N!$  ways of ordering  $N$  particles. For the case of indistinguishable particles, these  $N!$  arrangements all correspond to the same state. In exactly the same way, there is an extra factor of  $1/N!$  in the probability  $P(N, 2H)$ .

When we now recompute the ratio (15.9), we have an extra factor of  $1/N!$  in both numerator and denominator. The extra factors cancel and we get exactly the same answer as before, Eq. (15.11). This formula for the probability looks rather formidable, but it can be shown that it reduces to the simpler formula (15.8) in the limit  $H \gg N \gg 1$ . (See Problem 15.25.) We conclude that in the low-density classical regime, in which  $H \gg N$ , the probability is not affected by the distinguishability of the particles. (There are situations, however, in which distinguishability does make a difference. One such case is treated in Problem 15.36.)



**FIGURE 15.7**  
The energy spectrum of a simple quantum system.

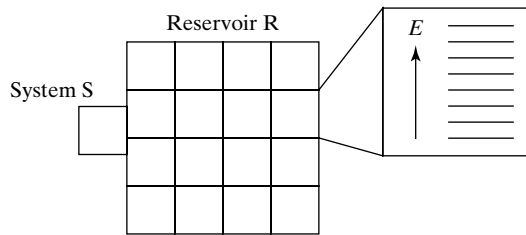
## 15.5 The Origin of the Boltzmann Relation\*

\*This section contains rather difficult arguments and can be omitted if you are satisfied to accept the Boltzmann relation (15.3) without proof.

Our goal in this section is to understand how the Boltzmann relation arises from the equal-probability hypothesis. Although the Boltzmann relation applies to any quantum system, we will consider the special case of a system with a very simple energy spectrum: a set of uniformly-spaced, nondegenerate energy levels given by  $E_n = n\varepsilon$ , where  $\varepsilon$  is a fixed energy and  $n$  is any non-negative integer:  $n = 0, 1, 2, \dots$ . (See Fig. 15.7.) This happens to be the energy-level spectrum of the 1-D simple harmonic oscillator described in Section 7.9, but the details of the system are irrelevant here; all we need to know is the energy spectrum.

We assume that this model microscopic system is in thermal equilibrium with a large thermal reservoir at temperature  $T$ . By **thermal reservoir**, we mean some large macroscopic system with a very large number of degrees of freedom, with which our microscopic system can exchange energy. Temperature is a macroscopic concept; it makes no sense to talk about the temperature of an *isolated* microscopic system, such as a single atom. The temperature of a microscopic system is the temperature of the thermal reservoir with which it is in equilibrium. The thermal reservoir is assumed to be so large that the exchange of energy with our micro-system has negligible effect on the reservoir's temperature, that is, on its average energy per degree of freedom. Finally, we assume that the reservoir and the system are thermally isolated from everything else. Hence, the sum of the energies of the reservoir and our system is fixed. It is this model “universe” of (system + reservoir) to which we will apply the equal-probability hypothesis.



**FIGURE 15.8**

A system  $S$  in contact with a thermal reservoir  $R$ . The reservoir is a collection of identical quantum systems, each with the same simple energy spectrum.

The thermal reservoir, also called a “heat bath,” can be modeled as a collection of a large number  $N$  of microscopic quantum systems in thermal contact. To keep things as simple as possible, we assume that each of the  $N$  quantum systems making up the reservoir is identical to our original microscopic system, with the simple energy spectrum  $E_n = n\varepsilon$ . Our universe of (system + reservoir) then consists of  $N + 1$  quantum systems, all in thermal contact, freely exchanging energy among themselves, as in Fig. 15.8. Let us denote the total energy of the (system + reservoir) by  $m\varepsilon$ , where  $m$  is some integer, equal to the number of energy quanta of size  $\varepsilon$ . Since the total energy of the (system + reservoir) is fixed, when the system has energy  $E_S = s\varepsilon$ , the reservoir must have energy  $E_R = r\varepsilon = (m - s)\varepsilon$ .

When the system is in some *particular* microstate  $s$  with energy  $E_S$ , the reservoir can be in *any* microstate with energy  $E_R = (m - s)\varepsilon$ . According to the equal-probability hypothesis, all microstates of the (system + reservoir) are equally likely; hence, the probability that the system is in state  $s$  is proportional to the number of microstates of the (system + reservoir) that have the system in the state  $s$ . This is just the number of microstates of the reservoir that have energy  $E_R = (m - s)\varepsilon$ . We conclude that the probability that the system is in state  $s$  is proportional to the degeneracy (the multiplicity) of the reservoir when it has energy  $E_R = (m - s)\varepsilon$ . Or, in symbols,  $P[\text{system is in particular state } s] = P[\text{reservoir is in any state with energy } (m - s)\varepsilon]$ ,

$$P(s) \propto g_R(m - s) \quad (15.13)$$

The key point here is to realize that the equal-probability hypothesis applies to the (system + reservoir); we cannot apply it to the microscopic system alone since the microsystem is not an isolated system; it exchanges energy with the heat bath. Our job now is to show that Eq. (15.13) is equivalent to the Boltzmann relation (15.2).

The multiplicity of the reservoir  $g_R(r)$  grows very rapidly with the number  $r$  of energy quanta. For example, if there are  $N = 100$  systems in the reservoir, and only one ( $r = 1$ ) quantum of energy, then the number of reservoir microstates is  $g(r = 1) = 100$  corresponding to the single energy quantum being in any one of the 100 systems. If there are  $r = 2$  energy quanta, then there are  $(100 \cdot 99)/2$  different microstates with two of the 100 systems containing one quantum each, plus another 100 microstates with both quanta in one of the 100 systems. Hence,  $g(2) = (100 \cdot 99)/2 + 100 = 5050$ . The general formula for the multiplicity, when there are  $r$  indistinguishable quanta distributed among  $N$  distinct systems, is

$$g(r) = \frac{(N + r - 1)!}{r!(N - 1)!} \quad (15.14)$$

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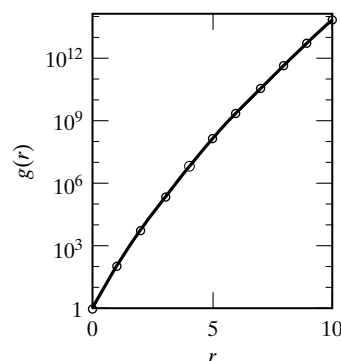


FIGURE 15.9

The number of ways of placing  $r$  identical objects in  $N = 100$  containers.

The proof of this formula, which is very similar to the proof of (15.7), is explored in Problem 15.29. A graph of  $g(r)$  for the case  $N = 100$  is shown in Figure 15.9. Note that  $g(r)$  grows *extremely* rapidly with increasing  $r$ . In the limit  $r \gg N$ , which corresponds to the high-temperature limit where there are many energy quanta per system, Eq. (15.14) becomes approximately  $g(r) \approx r^N \propto E^N$ , where  $E = r\varepsilon$  is the total energy of the system. (See Problem 15.30.)

We can now understand an important qualitative feature of the Boltzmann factor,  $e^{-E/kT}$ . According to the Boltzmann relation (15.2), a particular state  $i$  of lower energy  $E_i$  is always more likely to occur than a particular state  $j$  of higher energy  $E_j$ . When the microscopic system has low energy (small  $s$ ), the reservoir has more energy [larger  $(m - s)$ ]. When the reservoir has more energy, there are more ways to divide up that energy, resulting in a larger number of accessible microstates, a greater multiplicity, and a greater probability. Therefore, low-energy states of the system are more probable.

With the multiplicity of the reservoir (15.14) known, the probability (15.13) that the system is in a given state  $s$  can be written as

$$P(s) \propto g_R(m - s) = \frac{[N + (m - s) - 1]!}{(m - s)!(N - 1)!} \quad (15.15)$$

We leave it as an exercise (Problem 15.31) to show that, in the limit of large  $m \gg s$  (a big reservoir) and  $m \gg N$  (a high temperature), (15.15) can be rewritten as

$$P(s) \propto e^{-s/(m/N)} \quad (15.16)$$

This is none other than the Boltzmann relation (15.2) with the system energy  $E = s\varepsilon$  and temperature  $kT = (m/N)\varepsilon$ . To see how temperature enters, recall that according to the equipartition theorem, the energy per degree of freedom is  $\frac{1}{2}kT$ . For the  $N$  oscillators of the reservoir, there are  $2N$  degrees of freedom (two degrees of freedom for each simple harmonic oscillator). The total energy available is  $m\varepsilon$ , so we have

$$\frac{1}{2}kT = \frac{\text{energy}}{\text{number of degrees of freedom}} = \frac{m\varepsilon}{2N}$$

or  $kT = (m/N)\varepsilon$ . We have imposed the condition  $m \gg N$ , so that the mean energy per oscillator in the thermal reservoir is large compared to the energy quantum  $\varepsilon$ , in which case the energy can be regarded as a quasi-continuum and the classical equipartition theorem applies.\*

\*The Boltzmann relation is true always, even at very low temperatures where the equipartition theorem does not apply. However, when the equipartition theorem does not apply, we need a more general definition of temperature than the one we have given in Eq. (15.1). The more general definition relates temperature to the entropy  $S$  and the internal energy  $U$ , namely  $1/T = \partial S/\partial U$ . [See, for instance, *Thermal Physics* (Ed.) by C. Kittel and H. Kroemer, W H Freeman & Co., 1980.]

## 15.6 Entropy and the Second Law of Thermodynamics\*

\*This section assumes some previous exposure to thermodynamics and can be omitted.

The multiplicity, or degeneracy,  $g$  of a system is directly related to its *entropy*  $S$ . In thermodynamics the change in the entropy of a system is defined by the relation

$$dS = \frac{dQ}{T} \quad (15.17)$$

where  $dQ$  is the heat added or removed from the system and  $T$  is the absolute temperature in kelvins. This equation applies only to *reversible* processes, that is, processes in which the whole system remains in thermal equilibrium so that it has a well-defined temperature  $T$ . Before the development of statistical mechanics, the thermodynamic entropy defined by (15.17) was a mysterious quantity. One could compute its value (or at least *changes* in its value), but one could not say what it was microscopically. This uncomfortable situation was reminiscent of the incomplete understanding of temperature that existed before the advent of kinetic theory and the atomic hypothesis.

It was Boltzmann who first saw clearly the connection between macroscopic thermodynamics and microscopic statistical mechanics. Boltzmann showed that the thermodynamic entropy  $S$  of a macrostate is related to the natural logarithm of the multiplicity  $g$  by the equation

$$S = k \ln(g), \quad (15.18)$$

where  $k$  is Boltzmann's constant, so named in honor of the intellectual breakthrough represented by this equation. The multiplicity  $g$  is the number of microstates available to the system. With this equation, we can now understand better why entropy is often called the "disorder" of a system. A disordered state, like a junk hand, has a larger multiplicity  $g$  and hence a larger entropy than a highly ordered state, like a royal flush.

In light of equation (15.18), we can also better understand one of the most profound achievements of nineteenth-century physics, the second law of thermodynamics. The second law, also called the law of increase of entropy, states that the entropy of a closed system never decreases; it can only increase or stay constant. For instance, when an internal constraint, such as a barrier between the two halves of a container of gas, is removed, the entropy always increases. From (15.18) we see that this is because the number of accessible microstates always increases when constraints are removed.

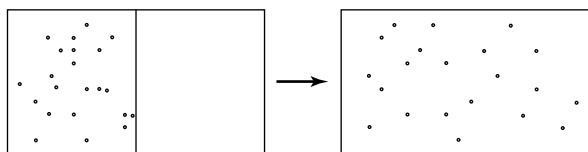
### Example 15.6

A well-insulated container is divided in half by a thin barrier. In the left half of the container is an ideal gas of  $N$  particles at some temperature  $T$ ; the right half of the container is empty. The barrier breaks, doubling the volume of the gas from  $V_0$  to  $2V_0$ , as shown in Figure 15.10. What is the increase in entropy of the system resulting from this adiabatic expansion of the gas? (An **adiabatic** process is one in which no heat is added to or removed from the system.)

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FIGURE 15.10

Adiabatic expansion of a gas.



This problem can be solved in two ways: by counting microstates and using (15.18), or by a thermodynamic calculation using (15.17).

**Method I, counting microstates.** If  $g_0$  is the original multiplicity of the system before the barrier broke, then after the volume of the system doubles, the new multiplicity is  $2^N g_0$ . We show this by the following classical argument: If the gas consisted of only a single particle, the number of microstates  $g$  would double because for every single-particle state on the left, there is a corresponding state on the right. If the gas consisted of two particles, the multiplicity would increase by a factor  $2^2 = 4$ , since each particle can be in either a right state or the corresponding left state and there are  $2 \times 2$  possible combinations. With  $N$  particles, the multiplicity increases by  $2^N$ , from  $g_0$  to  $2^N g_0$ . The final entropy is then

$$S = k \ln(2^N g_0) = k \ln(g_0) + k \ln(2^N) = k \ln(g_0) + Nk \ln(2)$$

Thus, the increase in entropy is

$$\Delta S = Nk \ln(2) \quad (15.19)$$

**Method II, thermodynamics.** In the free expansion of the gas, no heat was added or removed ( $dQ = 0$ ) and no work was done ( $dW = 0$ ), so the internal energy  $U$  of the gas remains unchanged ( $dU = dQ + dW = 0$ ). For an ideal gas,  $U = (3/2)NkT$ , and so the temperature is also unchanged. The free expansion of a gas is a nonreversible process, but equation (15.17)  $dS = dQ/T$  applies only to reversible (equilibrium) processes. So to use (15.17), we must imagine some reversible process that results in the same final state of the system. One such process is this: The barrier is slowly moved right, like a piston head, and at the same time the temperature of the system is held fixed by slowly adding heat to the system to compensate for the work done on the piston ( $dQ = -dW$ , so  $dU = 0$ ). During this reversible, constant-temperature expansion,  $dQ = -dW = p dV$ , and so

$$\frac{dQ}{T} = \frac{p}{T} dV$$

whence,

$$\Delta S = \int \frac{dQ}{T} = \int_{V_0}^{2V_0} \frac{p}{T} dV = \int_{V_0}^{2V_0} \frac{Nk}{V} dV = Nk \ln\left(\frac{2V_0}{V_0}\right) = Nk \ln(2)$$

in agreement with the result of Method I, (15.19). (The third equality follows from  $pV = NkT$ .)

The second law of thermodynamics gives direction to the arrow of time. In this world, the sequence of events is always more order, then less order —

lower entropy, then higher entropy. Buildings eventually fall down and become rubble; we die and become dust. But one never sees the reverse; a field of dirt never spontaneously rearranges its molecules to form a house or a human. Such a miracle could occur without violating conservation of energy or momentum, just as a large pocket of vacuum could spontaneously occur in a gas, or a ball could, of its own accord, roll up hill by becoming cooler than its surroundings. But these incredible events *would* violate the second law. They would result in a decrease in the entropy of the universe and are therefore fantastically unlikely to occur — not impossible, but so unlikely that they would never occur in a trillion trillion trillion (put in as many trillions as you like) years. Of all the microstates of the field of dirt, there are many many more “rubble” states than there are “house” states, many more junk hands than royal flushes. If you pick a state at random, you are overwhelmingly likely to find rubble.

So the second law of thermodynamics says that decay is the way of the world; all things, left to themselves, eventually become more disordered. Heterogeneous structures become more uniform, sources of heat cool, houses and humans turn to dust. Why is it then, that here on earth, we are surrounded by complex, highly ordered structures, structures of low entropy, like computers and cities and books and people? It is because these structures did not arise from spontaneous fluctuations in isolated systems. They were built at great expense. In order to reduce the entropy in some part of the universe, the entropy elsewhere must be increased, for the total entropy of the universe can only increase. In our corner of the universe, the Sun is the local entropy factory, becoming more disordered at a terrific rate. Rest-mass energy, tightly locked in compact hydrogen nuclei, is being converted into gamma rays by thermonuclear reactions and then into visible photons by scattering from ions. These photons pour out into space, spreading the Sun’s energy over an immense volume. There are many many more ways to spread the immense number of photons about in space than there are ways to arrange the few hydrogen nuclei that produced those photons in the Sun’s interior. And so the multiplicity and entropy of the Sun’s energy are increasing all the time. However, as the visible light photons produced on the 6000 K surface of the Sun spread out through space, some are captured by photosynthesizing plants, which feed people, who build houses. Most of the energy taken in by plants and people is eventually expelled as heat in the form of low-energy infrared photons corresponding to a temperature near 300 K. Thus, a few high-energy visible photons moving away from the Sun are turned into many, low-energy infrared photons moving in random directions, resulting in an overall entropy increase. Biological structures and all the other wonders of the world are thermodynamically possible because they are *open* systems, *metabolizing* systems, taking in low entropy structures and expelling high entropy ones. You can create order in some places, but only by making more disorder elsewhere. We exist because we leave chaos in our wake.

## 15.7 The Quantum Ideal Gas — a Many-Particle System

As an example of a macroscopic system that can, in principle, be described in complete microscopic detail, we consider the quantum-mechanical problem of an ideal gas:  $N$  *noninteracting* particles in a cubical box. The problems of a single particle in a 2-D square box and in a 3-D cubical box were treated in Section 8.3. We begin by reviewing briefly the results of that section.

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The Schrödinger equation for a single particle of mass  $M$  in a three-dimensional box is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = \frac{2M}{\hbar^2} [U - E] \psi \quad (15.20)$$

where the potential  $U(x, y, z)$  is zero inside the cubical region  $0 \leq x \leq a$ ,  $0 \leq y \leq a$ ,  $0 \leq z \leq a$ , and is infinite everywhere outside. The wave function  $\psi = \psi(x, y, z)$  must be zero at the boundaries of the box, since  $\psi$  must be continuous and it is zero outside the box. This problem is solved by the technique of separation of variables, in which one seeks solutions of the form

$$\psi(x, y, z) = X(x)Y(y)Z(z) \quad (15.21)$$

Plugging the assumed form (15.21) into equation (15.20) and performing some algebra (Problem 15.37), we find the solution

$$\psi(x, y, z) = A \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right) \quad (15.22)$$

where the quantum numbers  $n_x$ ,  $n_y$ , and  $n_z$  are any positive integers ( $n_x = 1, 2, 3, \dots$  etc.) and the constant  $A$  is determined by the normalization condition. Corresponding to these solutions are the allowed energies,

$$E = E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2M a^2} (n_x^2 + n_y^2 + n_z^2) \quad (15.23)$$

Some economy of notation is achieved by defining a “ $k$  value” associated with each value of  $n$ ,

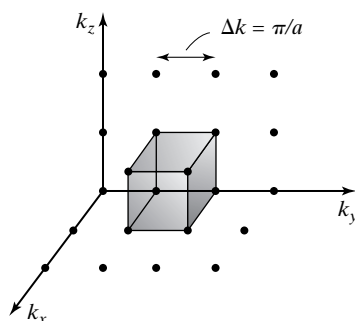
$$k_x = \frac{n_x \pi}{a} \quad (15.24)$$

and similarly for  $k_y$  and  $k_z$ . Our wave functions and their energies are then written,

$$\psi(x, y, z) = A \sin(k_x x) \sin(k_y y) \sin(k_z z),$$

with energy

$$E = \frac{\hbar^2}{2M} (k_x^2 + k_y^2 + k_z^2) \quad (15.25)$$



**FIGURE 15.11**

The states of a particle in a cubical box of side  $a$  are identified by points in  $k$  space. The allowed points form a cubic array with nearest-neighbor distance equal to  $\pi/a$ .

Each of our solutions to the single-particle Schrödinger equation is completely described by the set of three quantum numbers ( $n_x, n_y, n_z$ ) or equivalently, by the three  $k$  values ( $k_x, k_y, k_z$ ). Each allowed set of  $k$  values ( $k_x, k_y, k_z$ ) can be represented by a point in an abstract three-dimensional space called  $k$  space, which we represent with three mutually perpendicular axes  $k_x$ ,  $k_y$ , and  $k_z$ , as shown in Figure 15.11. In  $k$  space the allowed points ( $k_x, k_y, k_z$ ) form a cubic array of evenly spaced points. According to (15.24), as we move along a direction parallel to the  $k_x$  axis, the allowed points have the  $k_x$  values  $\pi/a, 2\pi/a, 3\pi/a$ , and so forth so the spacing of adjacent points is



$\Delta k = \pi/a$ . Notice that in  $k$  space, “distance” has the units of 1/(length). One can think of  $k_x$ ,  $k_y$ , and  $k_z$  as the three components of a vector  $\mathbf{k}$ , whose magnitude  $k = \sqrt{k_x^2 + k_y^2 + k_z^2}$  is the “distance” from the point  $(k_x, k_y, k_z)$  to the origin. Notice also that, according to (15.25), the energy of an allowed state is proportional to this distance squared,  $k_x^2 + k_y^2 + k_z^2$ , so that points further from the origin correspond to states of higher energy.

It may seem strange to refer to these  $k$ 's as if they were real. It may even seem strange that we use the term  $k$ , rather than some name. As mentioned in Section 6.6, physicists sometimes refer to  $k$  as “the wave number,” but most often, it is simply called  $k$ . Physically, the  $k$  value is related to the momentum of a particle by  $p = \hbar k$  and it is related to the de Broglie wavelength of the particle by  $k = 2\pi/\lambda$ . Large  $k$  means short wavelength, large momentum, and large energy. A particular point in the  $k$  space array represents a particular solution to the single-particle Schrödinger equation. Like all things new, it takes some getting used to.

So far, we have considered only a single particle in our cubical box. What now happens when we place  $N$  particles in the box and form a many-particle system? To answer this question, we must begin by assuming that the interactions between the particles are sufficiently weak that the particles can be regarded as noninteracting. This means that the wave function of a single, given particle in the system of many particles can still be written as (15.22) with an energy given by (15.23). We assume that the presence of other particles in other states has negligible effect on this single-particle description. Perhaps surprisingly, this *independent-particle approximation* is accurate in many real, physical systems. For instance, in Chapter 13, we saw that conduction electrons in a metal behave like a gas of noninteracting particles. This is quite surprising since electrons interact via the Coulomb force, which is both strong and long range. However, in a metal, the negatively charged conduction electron gas coexists with an array of positively charged ions, and the two signs of charges effectively cancel.

If we have many noninteracting particles in our box, each particle in the system is described by a point in the lattice of allowed  $k$ -space points. A microstate of this many-particle system is a set of occupied  $k$ -space points, or equivalently, a complete set of quantum numbers  $(n_{1x}, n_{1y}, n_{1z}, n_{2x}, n_{2y}, n_{2z}, \dots)$  describing the state of every particle. Which states are likely to be occupied depends on the temperature and, possibly, on the particle type — fermion or boson. We consider first the high-temperature case.

If the temperature of our system of noninteracting particles is sufficiently high, and the density of particles is sufficiently low, then our gas is in the nondegenerate, classical regime, described in Section 13.11 (see Problem 15.40). In this regime the occupied  $k$ -space points are widely scattered among a nearly empty array. As shown in Figure 15.12(a), in  $k$  space, the particles form a sparse cloud with a mean radius  $k_{\text{rms}}$  given by

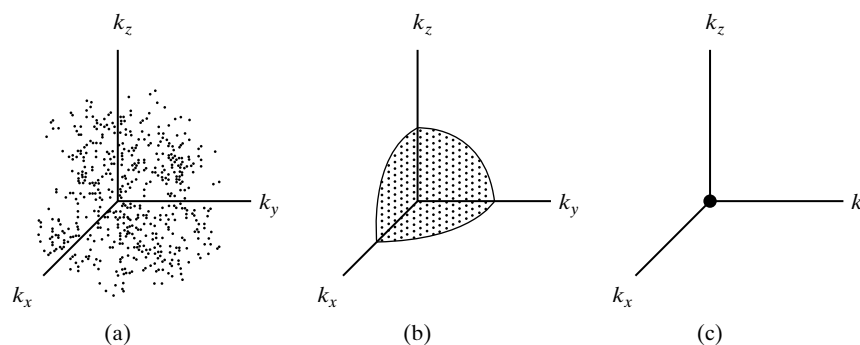
$$(\text{mean energy per particle}) = \frac{3}{2}kT = \frac{\hbar^2 k_{\text{rms}}^2}{2m} \quad (15.26)$$

Each particle has many unoccupied states to choose from, and particles seldom vie for the same single-particle state — the same point in  $k$  space. Consequently, the particle type, fermion or boson, is largely irrelevant. Ordinary gases, such as air at STP, are in this classical regime.

**FIGURE 15.12**

The  $k$ -space picture of an ideal gas in three different regimes. Each dot represents the state of one particle, given by the three numbers  $k_x$ ,  $k_y$ , and  $k_z$ , all of which are positive.

**(a)** The classical, nondegenerate regime occurring at high temperature and low density.  
**(b)** A degenerate gas of fermions at low temperature and high density. The  $N$  fermions occupy the  $N$  states of lowest energy, that is the  $N$  allowed points closest to the origin.  
**(c)** A degenerate gas of bosons, also at very low temperature and high density. All  $N$  bosons occupy the single state of lowest energy.



If we now lower the temperature so that the average energy per particle drops, then occupied states begin to crowd near the origin of  $k$  space, and particles compete for a limited number of  $k$ -space points. As discussed in Section 13.11, in this low-temperature, *degenerate quantum gas* limit, the behavior of the system depends critically on the type of particle involved. Bosons will happily share occupancy of a  $k$ -space point with an unlimited number of other particles. In contrast, fermions obey the Pauli exclusion principle and allow no more than one particle per  $k$ -space point if we neglect the particles' spin. If the particles have spin half, then two particles are allowed at each  $k$ -space point, one spin up and one spin down.

If the particles are fermions, then the  $N$  particles will fill the  $N$  lowest energy states nearest the origin. The filled states occupy an eighth of a sphere in  $k$  space, as in Figure 15.12(b). In this case the average energy per particle is very roughly equal to the Fermi energy, the energy of the highest occupied states, and is independent of the temperature. (More exactly, at  $T = 0$ , the average energy per particle and the Fermi energy are related by  $\langle E \rangle = (3/5)E_F$ ; see Problem 15.39.) Recall from Chapter 13 that examples of degenerate Fermi gases include electrons in a metal, electrons in a white dwarf star, and neutrons in a neutron star.

If the particles are bosons, then as the absolute temperature is lowered to zero, all particles crowd into the lowest energy single-particle state, the state nearest the origin, as indicated in Figure 15.12(c). This many-particle system is then a Bose–Einstein condensate, as described in Section 13.12. Such an exotic state requires extremely low temperatures and is not normally encountered in nature; examples of degenerate boson gases include superconductors and superfluids. For the remainder of this chapter, we will consider only ordinary gases in the classical nondegenerate regime.

## 15.8 Energy and Speed Distributions in an Ideal Gas

In this section we apply the Boltzmann relation (15.6) to a *single* particle in the 3-D ideal gas described in the previous section. Because all particles in a gas are statistically identical in behavior, any one particle is representative of the behavior of all particles. We will derive expressions for the distribution of energies and the distribution of speeds of the particles of a gas in the classical, nondegenerate regime.

The Boltzmann relation in the form (15.6) applies to any quantum system with a discrete spectrum of energies. A particle in a 3-D quantum ideal gas has a discrete energy spectrum; however, for a large container of gas, the energy states are so numerous and so closely spaced that it is appropriate to view

the states as a continuum. In our  $k$ -space picture of the gas (Figure 15.11), the single-particle quantum states are a distance  $\Delta k = \pi/a$  apart, where  $a$  is the edge length of the cubical container. If the box is macroscopic, then on an atomic scale the edge length  $a$  is very large and  $\Delta k = \pi/a$  is very small. There are many many quantum states densely packed in  $k$  space. Recalling that the energy of a state is proportional to the square of the  $k$ -space distance to the origin, we see that there is a nearly continuous distribution of energies.

When considering a system with a continuum of allowed energies, instead of asking what is the probability  $P(E)$  that the system has a specific energy  $E$ , we should rather ask what is the probability that the system has some energy in a small range from  $E$  to  $E + dE$ . The probability *distribution*  $p(E)$  is defined by the relation

$$p(E) dE = (\text{probability system has energy in the range } E \text{ to } E + dE)$$

Similarly, in place of the degeneracy  $g(E)$ , we use a **density of states**  $D(E)$  defined by the relation

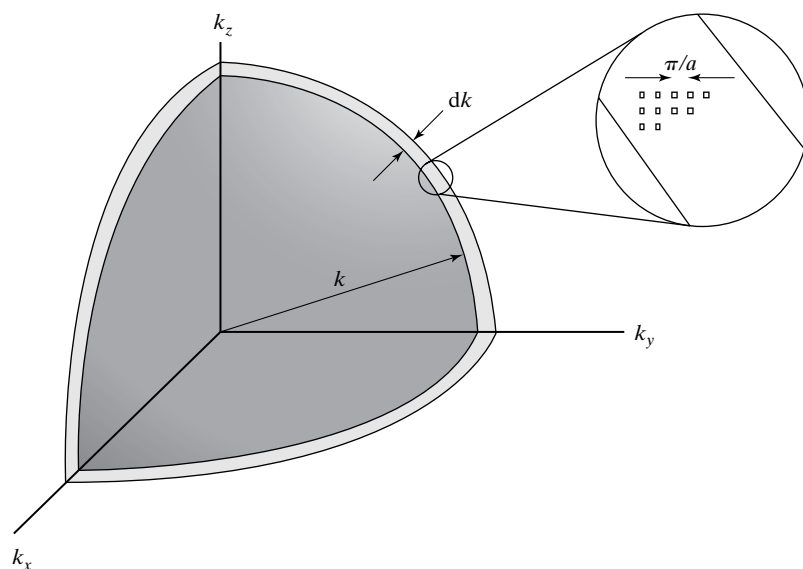
$$D(E) dE = \text{number of states with energies in the range } E \text{ to } E + dE$$

The Boltzmann relation (15.6), when applied to a system with a continuum of energies, then becomes

$$p(E) dE = \frac{D(E)e^{-E/kT} dE}{\int_0^\infty D(E)e^{-E/kT} dE} \quad (15.27)$$

As in (15.3), the normalization condition  $\int_0^\infty p(E) dE = 1$  produces the constant  $\int_0^\infty D(E)e^{-E/kT} dE$  in the denominator of (15.27).

We now compute the density of states  $D(E)$  for a particle in a 3-D quantum ideal gas. Our strategy is first to compute how many states have  $k = \sqrt{k_x^2 + k_y^2 + k_z^2}$  in a range  $k$  to  $k + dk$ , and then to change variables from  $k$  to  $E$ . In  $k$  space we consider a shell of radius  $k$  and thickness  $dk$ , as shown in Figure 15.13. Since the states within this shell are all nearly the same



**FIGURE 15.13**

A shell of nearly constant energy in  $k$  space.

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distance from the origin, these states have nearly the same energy. As described in Section 15.7, the states within the shell form a cubic array of points. These points are separated by a distance  $\Delta k = \pi/a$ , so that corresponding to each point is a  $k$ -space volume  $\Delta k^3 = (\pi/a)^3 = \pi^3/V$ , where  $V = a^3$  is the volume of the box containing the gas. The number of single-particle quantum states within this shell is given by

$$\begin{aligned} \left( \frac{\text{number of states in}}{\text{range } k \text{ to } k + dk} \right) &= \frac{\text{volume of the shell}}{\text{volume per } k\text{-space point}} \\ &= \frac{(1/8)4\pi k^2 dk}{(\pi/a)^3} = \frac{V}{2\pi^2} k^2 dk \quad (15.28) \end{aligned}$$

The factor of  $(1/8)$  in the volume of the shell arises because only one octant of the full sphere appears in  $k$  space, as in Figure 15.13.

We now change variables from  $k$  to energy  $E$ . Corresponding to the wave number  $k$  is an energy  $E = \hbar^2 k^2/2m$ . Corresponding to the  $k$  increment  $dk$  is an energy increment

$$dE = \frac{dE}{dk} dk = \frac{\hbar^2 k}{m} dk$$

We substitute  $dk = (m/\hbar^2 k) dE$  and  $k = \sqrt{2mE}/\hbar$  into (15.28) and note that the number of states in the range  $k$  to  $k + dk$  is the same as the number of states in the corresponding energy interval  $E$  to  $E + dE$ , which is  $D(E) dE$ . Therefore, (15.28) becomes

$$D(E) dE = \frac{V}{2\pi^2} \sqrt{2} \frac{m^{3/2}}{\hbar^3} \sqrt{E} dE \quad (15.29)$$

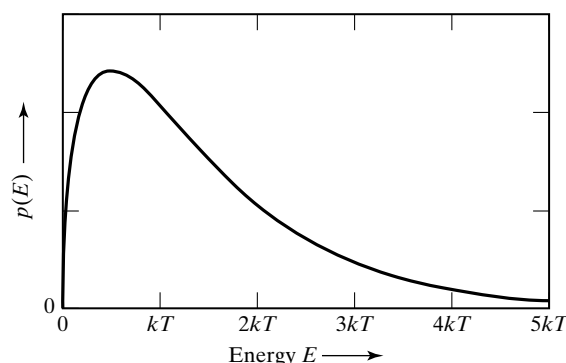
Inserting this expression for  $D(E) dE$  into (15.27) yields the energy probability distribution

$$p(E) dE = \frac{\sqrt{E} e^{-E/kT} dE}{\int_0^\infty \sqrt{E} e^{-E/kT} dE} \quad (15.30)$$

Notice that the messy constant  $(V/\sqrt{2\pi^2})m^{3/2}\hbar^{-3}$  appearing in (15.29) cancels out in (15.30). The integral in the denominator of (15.30) is given in Appendix B, leading to our final expression for the probability distribution of single-particle energies in an ideal gas,

$$p(E) dE = \frac{2}{\sqrt{\pi}(kT)^{3/2}} \sqrt{E} e^{-E/kT} dE \quad (15.31)$$

This distribution is plotted in Figure 15.14. We see that a small fraction of the gas molecules have energies near zero, corresponding to molecules that are momentarily near rest. The peak in the distribution occurs at roughly energy  $E = kT$ . There is a long tail out to high energies, but very few molecules have energies greater than several  $kT$ .



**FIGURE 15.14**  
Distribution of single-particle energies in an ideal gas.

Computing the distribution of speeds of the gas molecules from the distribution of energies is mathematically straightforward, as we show below, but is conceptually subtle. Shifting from a description of energies to a description of speeds requires a delicate mixing of quantum and classical language. We have been describing a *quantum* ideal gas whose single-particle states are described by wave functions extending over the entire volume of the container. These wave functions are stationary states, standing wave states with a definite energy  $E$  and a definite wavelength  $\lambda$ . How do we reconcile our quantum-mechanical view of stationary, delocalized states with our classical view of localized particles moving with some velocity? The key to reconciling these apparently contradictory descriptions is wave packets.

As described in Section 6.7, wave-packet states have a spread in wavelengths  $\Delta\lambda$  and a corresponding spread in momenta  $\Delta p = \Delta(h/\lambda)$ , as well as a spread in angular frequencies  $\Delta\omega$  and a corresponding spread in energies  $\Delta E = \hbar \Delta\omega$ . Although the wave packets do not have a single definite energy (as the stationary states do), they do have a well-defined average energy  $E$ . And though they do not possess a single definite momentum, they do have an average momentum  $p$  and a corresponding average speed  $v = p/m$ . As shown in Section 6.10, the average energy  $E$  and average speed  $v$  of the wave packet are related in the usual classical manner  $E = \frac{1}{2}mv^2$ .

Without further ado, let us write  $E = \frac{1}{2}mv^2$  and perform a change of variables from  $E$  to  $v$  to transform the energy distribution (15.31) into a distribution of speeds. Corresponding to every energy  $E$  is a speed  $v = \sqrt{2E/m}$  and corresponding to  $p(E) dE$ , the probability of finding a particle in a state with some energy between  $E$  and  $E + dE$ , is  $p(v) dv$ , the probability of finding the particle with corresponding speed between  $v$  and  $v + dv$ . Furthermore, since  $E = \frac{1}{2}mv^2$ ,

$$dE = \frac{dE}{dv} dv = \frac{d}{dv} \left( \frac{1}{2}mv^2 \right) dv = mv dv$$

Substituting for  $E$ ,  $\sqrt{E}$ , and  $dE$  in (15.31) yields

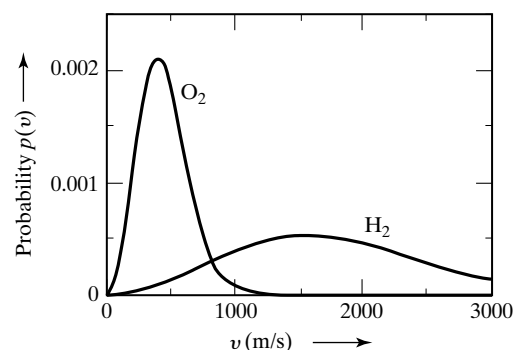
$$p(v) dv = \sqrt{\frac{2}{\pi}} \left( \frac{m}{kT} \right)^{3/2} v^2 e^{-mv^2/2kT} dv \quad (15.32)$$

This expression is called the **Maxwell speed distribution** because it was first derived by Maxwell, using an entirely different approach before the development of either quantum mechanics or statistical mechanics.

**James Clerk Maxwell**  
(1831–1879, Scottish)



A child prodigy with wide interests in math and physics, young Maxwell published important papers on geometry, the rings of Saturn, elastic solids, and the perception of color. Shy, quiet, and unassuming, he amazed colleagues with the breadth of his knowledge. Though a brilliant lecturer, he was once turned down for a university position because he lacked “the power of oral exposition proceeding on the supposition of imperfect knowledge or even total ignorance on the part of pupils.” Maxwell’s theory of electromagnetism, which describes light as an electromagnetic wave, is probably the greatest accomplishment of nineteenth-century physics. His pioneering work in the kinetic theory of gases helped establish statistical mechanics and the atomic hypothesis.

**FIGURE 15.15**

Speed distribution of oxygen and hydrogen gas at  $T = 300$  K.

The Maxwell speed distribution (15.32) is plotted in Figure 15.15 for both  $O_2$  molecules and lighter, faster  $H_2$  molecules. The distribution of speeds is seen to be qualitatively similar to the energy distribution. There is a peak near the speed  $v$  at which  $\frac{1}{2}mv^2 = \frac{3}{2}kT$ . There is a tail out to higher speeds, but few molecules have speeds higher than about three times the most probable speed, which would correspond to an energy nine times the most probable energy. This figure explains why there is almost no hydrogen in the earth's atmosphere. For hydrogen, the tail of the speed distribution extends beyond the earth's escape speed (about 10 km/s) just enough so that any hydrogen in the atmosphere eventually leaks into space. Smaller astronomical bodies, such as the moon and asteroids, have such low escape velocities that all gases on their surfaces escape to space.

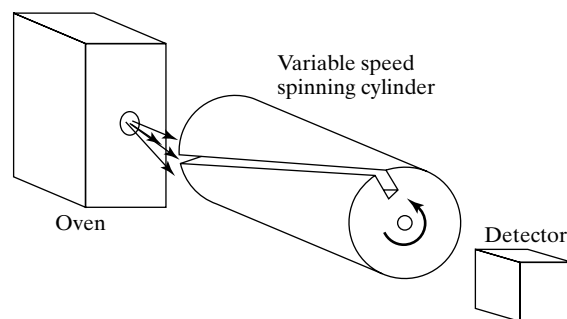
The Maxwell speed distribution has been experimentally verified with apparatus of the type shown in Fig. 15.16. An oven, containing a known gas at a well-controlled temperature, has a small hole through which gas molecules can escape into an evacuated test chamber. For a given rotation rate of the spinning cylinder, only molecules of a particular speed can pass through the slot of the spinning cylinder and strike the detector. The speed distribution is determined by measuring the detector signal as a function of the rotation rate of the cylinder.

Given the probability distributions  $p(E)$  and  $p(v)$ , we can compute the average energy or mean energy  $\langle E \rangle$  and mean speed  $\langle v \rangle$  of a particle by using the expectation-value formula (7.69),

$$\langle E \rangle = \int_0^{\infty} E p(E) dE$$

and

$$\langle v \rangle = \int_0^{\infty} v p(v) dv$$

**FIGURE 15.16**

Apparatus to measure the speed distribution of gas molecules.



These are often called the “thermal average” values. We leave it as exercises (Problems 15.47 and 15.48) to show that the thermal average values of  $E$  and  $v$  are

$$\langle E \rangle = \int_0^{\infty} E p(E) dE = \frac{3}{2} kT$$

and

$$\langle v \rangle = \int_0^{\infty} v p(v) dv = \sqrt{\frac{8kT}{\pi m}}$$

Of course, we already knew the first result,  $\langle E \rangle = \frac{3}{2} kT$ , from the equipartition theorem.

It is not hard to show that for an ideal gas, the rms speed  $v_{\text{rms}} = \sqrt{\langle v^2 \rangle}$  is given by  $v_{\text{rms}} = \sqrt{3kT/m}$ , which is slightly larger than the mean speed  $\langle v \rangle$ . The rms average speed is often a more useful quantity than the mean speed because the rms speed is more clearly related to the mean energy via the equation  $\langle E \rangle = \frac{1}{2} m \langle v^2 \rangle$ .

## 15.9 Heat Capacities

The energy levels of atoms or molecules in the gaseous state can be readily determined by measuring the spectrum of light emitted when the gas is heated. Each line in the spectrum corresponds to a transition between a pair of discrete energy levels in the atom or molecule. In contrast, it is quite difficult to measure directly the energy spectrum of many-particle condensed-matter systems such a block of copper or a container of liquid helium — systems in which the energy levels are so closely spaced that they form a continuum. However, important clues about the energy spectrum can be gleaned from a measurement of the system’s heat capacity. The heat capacity  $C$  of a system is defined as

$$C = \frac{d\langle E \rangle}{dT} \quad (15.33)$$

where  $\langle E \rangle$  is the thermal average energy of the system. To raise the temperature of a system by a small amount  $\delta T$ , we must input an amount of energy  $\delta E = C \delta T$ . Usually the energy is added to the system in the form of heat, so the heat capacity  $C$  is the amount of heat absorbed (or released) when the temperature is raised (or lowered) by one degree Kelvin. As we will see, the dependence of the heat capacity on temperature yields information on the spectrum of quantum energy levels of the system.

The heat capacity of a monatomic ideal gas has a very simple form. According to the equipartition theorem (15.1), the energy per degree of freedom of a gas is  $\frac{1}{2} kT$ . In a gas, the number of degrees of freedom per atom is 3 (one each for translational motion in the  $x$ ,  $y$ , and  $z$  directions). If the total number of atoms is  $N$ , the total energy  $\langle E \rangle$ , which we write as\*  $U$  is

$$\begin{aligned} U &= (\text{number of degrees of freedom}) \times (\frac{1}{2} kT \text{ per degree of freedom}) \\ &= (3N)(\frac{1}{2} kT) = \frac{3}{2} NkT \end{aligned}$$

\*As is traditional in chemistry and statistical mechanics, we use the symbol  $U$  to represent the total internal energy, which in this case is the same as  $\langle E \rangle$ . Be careful not confuse this with our previous use of  $U$  for potential energy.

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The heat capacity of a monatomic ideal gas is then

$$C = \frac{dU}{dT} = \frac{3}{2}Nk = \frac{3}{2}nR$$

where  $R$  is the universal gas constant  $R = N_A k = 8.31 \text{ J/mole} \cdot \text{K}$  and  $n = N/N_A$  is the number of moles. This temperature-independent value  $\frac{3}{2}R$  per mole for the heat capacity of an ideal gas has been abundantly confirmed by experiment.

The heat capacity of a solid is more complicated than that of a gas. A solid can store energy in more ways than a gas can — it has more degrees of freedom — and, as we will see, the heat capacity of a solid is temperature-dependent. A crystalline solid with its springlike chemical bonds between atoms can store energy in the vibrations of the atomic lattice, leading to a “lattice heat capacity.” In addition, if the solid is a metal, the conduction electrons can store energy and contribute to the total heat capacity. This electronic heat capacity is absent in electrical insulators, and even in metals it is generally small compared to the lattice heat capacity. Here, we will consider insulating solids only.

An insulating solid with  $N$  atoms has  $6N$  degrees of freedom. Recall (Section 15.2) that in a solid, each atom has six degrees of freedom because the total energy of each atom has three kinetic energy terms ( $\frac{1}{2}mv_x^2, \frac{1}{2}mv_y^2, \frac{1}{2}mv_z^2$ ) and three potential energy terms ( $\frac{1}{2}kx^2, \frac{1}{2}ky^2, \frac{1}{2}kz^2$ ). The equipartition theorem then leads us to predict that for *any* solid with  $N$  atoms, the total energy and lattice heat capacity are given by

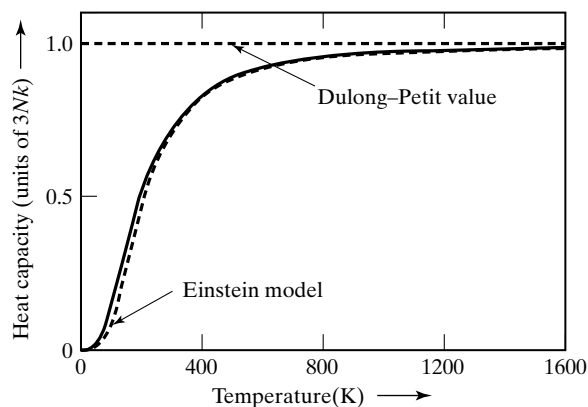
$$U = (6N)(\frac{1}{2}kT) = 3NkT$$

and

$$C = \frac{dU}{dT} = 3Nk = 3nR$$

This result for the heat capacity of solids is called the **Dulong–Petit law**. It is found to agree with experiment at high temperatures, but at low temperatures, typically somewhat below room temperature, the heat capacity falls rapidly as the temperature is lowered and approaches zero as  $T \rightarrow 0 \text{ K}$ , as shown in Fig 15.17.

This disagreement between theory and experiment was deeply puzzling to physicists of the early twentieth century. It was Einstein who showed that the discrepancy is due to a quantum effect that causes a breakdown of the classical



**FIGURE 15.17**

Measured heat capacity of germanium (solid line) and the predictions of the Einstein model and Dulong–Petit.

equipartition theorem. Recall that the equipartition theorem assumes that the energy of the system is continuous, not discrete. Real physical systems obey quantum mechanics and have quantized energies. If the temperature is high enough that  $kT \gg \Delta E$ , where  $\Delta E$  is the separation between adjacent energy levels, then the energy spectrum can be approximated as a continuum and the equipartition theorem applies. But when the temperature is so low that  $kT < \Delta E$ , the equipartition theorem does not apply and the energy quantization has a profound effect on the heat capacity. The vanishing of the heat capacity at low temperatures in quantum systems can be understood qualitatively as follows: If the temperature is so low that  $kT \ll \Delta E$ , where  $\Delta E$  is the energy gap between the ground state and the first excited state, then the system will almost always be in its ground state. A small increase in temperature will not give the system enough thermal energy to jump up to the first excited state and it will remain in the ground state. The excited states are said to be “frozen out.” There will be (almost) no increase in the mean energy  $\langle E \rangle$  when the temperature is increased, so  $C = d\langle E \rangle/dT \approx 0$ .

To explain in detail the low-temperature heat capacity of solids (Fig. 15.17), we need a quantum calculation of the thermal average energy  $U = \langle E \rangle$  of an atom in a solid. This calculation was first performed by Einstein.

### **The Einstein Model of Heat Capacity**

An atom in a solid can be modeled as a simple 3-D harmonic oscillator — a mass  $m$  with potential energy  $U = \frac{1}{2}kr^2$ , where  $r$  is the distance from the equilibrium position and the spring constant  $k$  depends on the strength of the chemical bonds with neighboring atoms. We will begin by computing the heat capacity of a 1-D harmonic oscillator and then will generalize to 3-D. As described in Section 7.9, the energy levels of a 1-D harmonic oscillator are given by  $E_n = (n + \frac{1}{2})\hbar\omega$ , where  $n = 0, 1, 2, \dots$  and  $\omega = \sqrt{k/m}$ . To simplify things, we can reset the zero of energy so that  $E_n = n\varepsilon$ , where  $\varepsilon = \hbar\omega$ . Using the Boltzmann relation (15.3), we have (all sums shown are over  $n = 1, 2, \dots$ )

$$\begin{aligned} \langle E \rangle &= \frac{\sum E_n e^{-E_n/kT}}{\sum e^{-E_n/kT}} = \frac{\sum n\varepsilon e^{-n\varepsilon/kT}}{\sum e^{-n\varepsilon/kT}} \\ &= \frac{\varepsilon e^{-\varepsilon/kT} [1 + 2(e^{-\varepsilon/kT}) + 3(e^{-\varepsilon/kT})^2 + \dots]}{1 + e^{-\varepsilon/kT} + (e^{-\varepsilon/kT})^2 + \dots} \end{aligned}$$

The last expression can be simplified by making use of the following identities

$$\frac{1}{(1-x)} = 1 + x + x^2 + x^3 + \dots \quad \text{and} \quad \frac{1}{(1-x)^2} = 1 + 2x + 3x^2 + \dots \quad (15.34)$$

(See Problem 15.51.) The mean energy is then

$$\langle E \rangle = \frac{\varepsilon e^{-\varepsilon/kT}}{1 - e^{-\varepsilon/kT}} = \frac{\varepsilon}{e^{+\varepsilon/kT} - 1} \quad (15.35)$$

And the heat capacity of a single 1-D harmonic oscillator is

$$C_{1D} = \frac{d\langle E \rangle}{dT} = k \left( \frac{\varepsilon}{kT} \right)^2 \frac{e^{\varepsilon/kT}}{(e^{\varepsilon/kT} - 1)^2} \quad (15.36)$$

where  $\varepsilon = \hbar\omega$ . Notice that Boltzmann's constant  $k$  has the units of heat capacity (recall  $E = kT$ , and hence  $k = E/T$ ), so (15.36) is written as  $k$  multiplied by dimensionless quantities.

A 3-D simple harmonic oscillator can be regarded as three independent 1-D harmonic oscillators (one each for the  $x$ ,  $y$ , and  $z$  directions). The total energy of the 3-D oscillator is just the sum of the energies of the three 1-D oscillators, and we conclude that the heat capacity of a 3-D harmonic oscillator, which we use to model a single atom in a solid, is three times the expression in (15.36),  $C_{\text{atom}} = 3C_{1D}$ .

Einstein made the simplifying assumption that the atoms in a solid could be treated as *independent* 3-D harmonic oscillators, so that the total energy of the collection of  $N$  atoms is just the sum of the energies of the  $N$  independent atoms,  $\langle E \rangle_{\text{solid}} = N\langle E \rangle_{\text{atom}}$  and the total heat capacity of the solid is simply

$$C_{\text{solid}} = \frac{d}{dT} \langle E \rangle_{\text{solid}} = NC_{\text{atom}} = 3NC_{1D}$$

There is an unknown parameter in this model, namely the value of  $\varepsilon = \hbar\omega$ , the energy-level spacing of the simple harmonic oscillator used to approximate the vibrational behavior of an atom. The parameter  $\varepsilon$  is regarded as a *fitting parameter*, and its value is adjusted to give the best agreement between theory and experiment. The resulting **Einstein model of heat capacity** is plotted in Fig. 15.17 along with experimental data on the heat capacity of germanium. We see that the model gives a very good fit with a temperature-independent heat capacity at high temperatures ( $T > \hbar\omega$ ), and a vanishing heat capacity at low temperatures. At very low temperatures, ( $0 < T \ll \hbar\omega$ ), the Einstein model does not give accurate quantitative results, because of a failure of the independent-oscillator approximation; nevertheless, the qualitative success of the model in explaining the heat capacity of solids was one of the earliest successes of quantum theory.

#### Example 15.7

Consider again the two-level system described in Example 15.5. Compute the heat capacity  $C$  of the system as a function of temperature.

A two-level system, such as a spin magnetic moment in an external magnetic field, has a ground state with energy  $E = 0$  and a single excited state with energy  $E = \varepsilon$ . The mean thermal energy of such a system at temperature  $T$  is

$$\langle E \rangle = \frac{\sum E_i e^{-E_i/kT}}{\sum e^{-E_i/kT}} = \frac{0 + \varepsilon e^{-\varepsilon/kT}}{1 + e^{-\varepsilon/kT}} = \frac{\varepsilon}{e^{+\varepsilon/kT} + 1} \quad (15.37)$$

Both sums are over two states only:  $i = 1, 2$ .

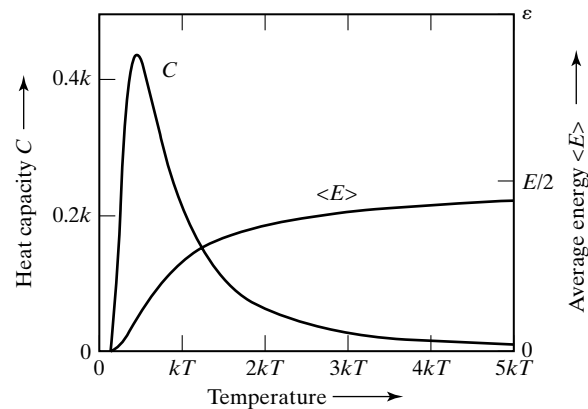


FIGURE 15.18

Heat capacity and average energy of a two-level system.

The heat capacity is then

$$C = \frac{d\langle E \rangle}{dT} = k \frac{(\epsilon/kT)^2 e^{\epsilon/kT}}{(1 + e^{\epsilon/kT})^2} \quad (15.38)$$

Notice the similarity between these expressions and the corresponding expressions (15.35) and (15.36) for a harmonic oscillator. (But notice that the minus sign in the harmonic-oscillator formulas has been replaced by a plus sign for the two-level system.) The heat capacity (15.38) is plotted in Fig. 15.18 along with the mean energy (15.37). Notice that the peak in the heat capacity  $C = d\langle E \rangle/dT$  occurs where the slope of  $\langle E \rangle$  versus  $T$  is maximum.

### Diatomic Gases

At the beginning of this section, we argued that the heat capacity of an ideal monatomic gas is  $\frac{3}{2}Nk$ , where the factor of  $\frac{3}{2}$  came from the fact that each of the three degrees of freedom (motion in the  $x$ ,  $y$ , and  $z$  directions) of a gas atom contributes  $\frac{1}{2}kT$  to the energy. It may come as a surprise then to learn that at room temperature the heat capacity of oxygen and nitrogen, the principle components of air, is  $\frac{5}{2}Nk$ , not  $\frac{3}{2}Nk$ . (When dealing with molecular gases,  $N$  is the number of molecules in the gas, not the number of atoms.) The reason is that molecules with two or more atoms have **internal degrees of freedom**. Oxygen and nitrogen, as well as hydrogen, chlorine, and many other gases, form *diatomic* molecules, and these multi-atom molecules can rotate and vibrate, as well as translate. Rotation contributes two degrees of freedom, since a dumbbell-shaped diatomic molecule can rotate about two orthogonal axes (Fig. 15.19). Vibration contributes two more degrees of freedom, radial kinetic energy and elastic potential energy, similar to a simple 1-D mass on a spring.

So, in addition to the three translational degrees of freedom, we have four internal degrees of freedom, for a total of seven degrees of freedom. The corresponding seven quadratic terms in the energy are

$$U = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}I\omega_x^2 + \frac{1}{2}I\omega_y^2 + \frac{1}{2}\mu(dr/dt)^2 + \frac{1}{2}k(r - r_0)^2$$

(Can you identify each term and the meaning of each symbol?) With seven degrees of freedom, why then is the heat capacity not  $(7/2)Nk$ ? At sufficiently high temperature, it is! The heat capacity of diatomic molecules is temperature-dependent. Recall that a degree of freedom, which is often called a “mode,”

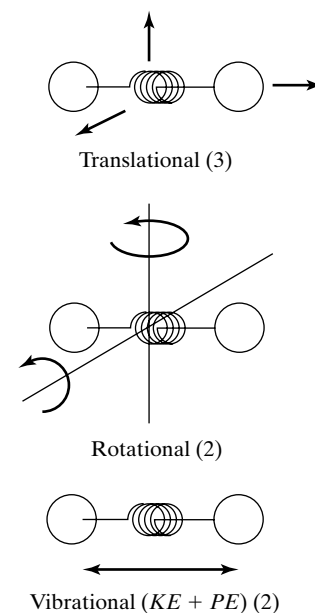
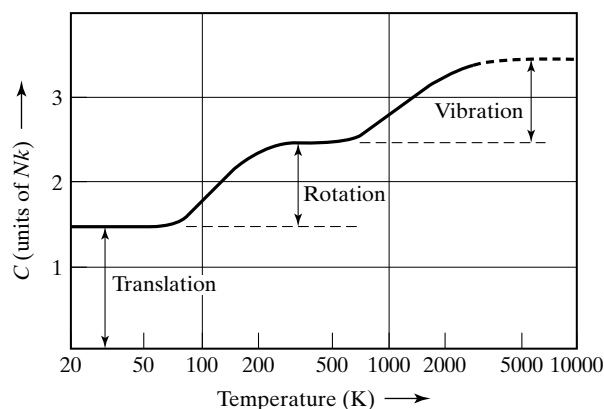


FIGURE 15.19

The seven degrees of freedom of a diatomic molecule.

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**FIGURE 15.20**

Heat capacity of hydrogen, a diatomic gas as a function of temperature. The hydrogen molecule dissociates at high temperatures, before the vibrational modes are fully excited.

fully contributes to the heat capacity only when  $kT \gg \Delta E$ , where  $\Delta E$  is the energy-level spacing for the quantum levels associated with that mode. At very low temperatures ( $T \approx 100$  K) both the rotational and vibrational degrees of freedom are frozen out, and the heat capacity is  $\frac{3}{2}Nk$ , since only the center-of-mass kinetic energy contributes to the heat capacity. We saw in Chapter 12 that the energy-level spacing for the rotational modes of molecules are smaller than the level spacing for the vibrational modes. At intermediate temperatures — around room temperature — the two rotational degrees of freedom become thermally activated, but the vibrational degrees are still frozen out, leading to a heat capacity of  $\frac{5}{2}Nk$ . At sufficiently high temperatures,  $kT$  is greater than the quantum of excitation of the vibrational modes and all degrees of freedom contribute to the heat capacity  $\frac{7}{2}Nk$ . Fig. 15.20 shows the temperature dependence of the heat capacity of hydrogen gas, which clearly exhibits these three regimes. We leave it as exercises (Problems 15.61 and 15.62) to estimate the temperatures at which the vibrational and rotational degrees of freedom are activated.

## CHECKLIST FOR CHAPTER 15

CONCEPT	DETAILS
Microstates and macrostates	Complete specification of all microscopic variables versus specification of statistical averages of a few macroscopic variables. (Section 15.1)
Degrees of freedom	Number of quadratic terms in detailed expression of total energy. (Section 15.2)
Equipartition theorem	The total energy of a classical system is shared equally among its degrees of freedom. (Section 15.2)
Temperature	Amount of atomic “jiggling.” $\frac{1}{2}kT =$ energy per degree of freedom in a classical system (15.1)
Boltzmann relation: probability that a system is in a particular quantum state $i$	$P(\text{state } i) = \frac{e^{-E_i/kT}}{\sum_j e^{-E_j/kT}} \quad (15.3)$
Probability that a system has an energy $E$	$P(E) = g(E)P(i) \quad (15.6)$
Equal-probability hypothesis	All accessible microstates are equally likely to occur. (Section 15.4)



Counting microstates	The probability of a situation = $\frac{\text{(number of ways that situation can occur)}}{\text{(total number of possible situations)}} \quad \text{(Section 15.4)}$
Number of ways of choosing $N$ indistinguishable objects from among $T$ objects	$g = \frac{T!}{(T - N)!N!} \quad (15.7)$
Origin of the Boltzmann relation $\star$	For an isolated (system + reservoir), if the system is in a state $i$ with more energy, then the reservoir has less energy and therefore fewer microstates. (Section 15.5)
Entropy and the second law $\star$ thermodynamic definition of entropy statistical definition of entropy	The entropy of a closed system cannot decrease. (Section 15.6) $dS = dQ/T \quad (15.17)$ $S = k \ln g \quad (15.18)$
Quantum ideal gas	Each one-particle state is specified by a point in $k$ space. (Section 15.7)
Density of states $D(E)$ of ideal gas	$D(E) dE = \text{number of states with energies between } E \text{ and } E + dE, D(E) \propto \sqrt{E} \quad (15.29)$
Maxwell speed distribution $p(v)$	$p(v) dv = \text{probability that particle has speed between } v \text{ and } v + dv \quad (15.32)$
Heat capacity Dulong–Petit law	$C = d\langle E \rangle/dT \quad (15.33)$ For a classical solid, energy $U = 3NkT$ , so $C = dU/dT = 3Nk$ (Section 15.9)
Einstein model of heat capacity	When $kT \ll \Delta E$ , the excited modes of a quantum solid are frozen out, leading to a vanishingly small heat capacity. (Section 15.9)
diatomic gases	In addition to translational modes, the rotational and vibrational modes can contribute to the heat capacity. (Section 15.9)

## PROBLEMS FOR CHAPTER 15

### SECTION 15.1 (Introduction)

- 15.1** • Neon is a noble element and therefore forms a gas of monatomic molecules at all but the lowest temperatures. However, neon freezes and forms a crystalline solid at temperatures below  $T = 26$  K. Classically, how many degrees of freedom are in **(a)** a mole of neon gas at room temperature? **(b)** A mole of solid neon at  $T = 10$  K?

### SECTION 15.2 (Temperature)

- 15.2** • What is the temperature in kelvins that corresponds to an energy of  $kT$  equal to **(a)** 0.001 eV **(b)** 0.1 eV **(c)** 10 eV **(d)** 1000 eV?
- 15.3** • **(a)** What is the rms speed of a helium atom in a sample of pure helium gas at room temperature ( $T \approx 293$  K)? **(b)** How do you expect the speed of sound in helium gas to compare with that in air at the same temperature?
- 15.4** • Radon is a heavy inert gas, with atomic number  $Z = 86$ . What is the rms speed of radon atoms in air at room temperature ( $T \approx 293$  K)? Is the rms speed

of the atoms in pure radon gas greater than, less than, or the same as that of radon atoms mixed in air?

- 15.5** • A water droplet in a cloud is typically 5 microns in diameter (1 micron =  $1 \mu\text{m} = 10^{-6}$  m). What is the rms speed of such a droplet at room temperature ( $T \approx 293$  K)?
- 15.6** • **(a)** What is the ratio of the kinetic energies of  $\text{O}_2$  molecules to that of  $\text{N}_2$  molecules in air at room temperature? **(b)** What is the ratio of the rms speed of  $\text{O}_2$  molecules to that of  $\text{N}_2$  molecules in air at room temperature? **(c)** Are these ratios temperature-dependent?
- 15.7** •• **(a)** What is the total energy  $E_{\text{tot}}$  of a mole of helium gas at room temperature,  $T \approx 293$  K? [*Hint:* This is just  $N\langle K \rangle$ , where  $N$  is the number of atoms and  $\langle K \rangle$  is the average kinetic energy per atom.] **(b)** By how many kelvins would this energy raise the temperature of a cup of water (200 grams, say)?
- 15.8** •• **(a)** Write an expression for the total energy  $E_{\text{tot}}$  of a mole of a monatomic gas at temperature  $T$ . (See Problem 15.7.) **(b)** Use this to find the constant-

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volume) molar specific heat  $C_v$  of the gas. This is the energy needed to raise the temperature of 1 mol by 1 K, so is equal to  $dE_{\text{tot}}/dT$ .

- 15.9 •••** In his *Feynman Lectures in Physics* (Vol. 1), Richard Feynman gives the following proof of the equipartition theorem for the special case of molecules in an ideal gas: Consider two molecules of masses  $m_1$  and  $m_2$  with initial velocity vectors  $v_1$  and  $v_2$ , prior to collision. The velocity of the center of mass  $\mathbf{v}_{\text{cm}}$  is defined by the equation  $(m_1 + m_2)\mathbf{v}_{\text{cm}} = (m_1\mathbf{v}_1 + m_2\mathbf{v}_2)$ .

The relative velocity  $\mathbf{w}$  of molecules is defined as  $\mathbf{w} = (\mathbf{v}_1 - \mathbf{v}_2)$ . One can argue that if the system is in thermal equilibrium, the direction of the center-of-mass motion is completely uncorrelated to the direction of the relative velocity, so that  $\langle \mathbf{w} \cdot \mathbf{v}_{\text{cm}} \rangle = 0$ , where the brackets  $\langle \dots \rangle$  represents an average over all pairs of molecules. (Since the directions are random, the dot-product is positive as often as negative and it averages to zero.) Use this relation to argue that

$$\frac{1}{2}m_1\langle v_1^2 \rangle = \frac{1}{2}m_2\langle v_2^2 \rangle$$

## SECTION 15.3 (The Boltzmann Factor)

- 15.10 •** Consider the quantum-mechanical system consisting of a particle of mass  $m$  in a one-dimensional rigid box of length  $a$ , (often called an infinite square well), as described in Section 7.4. Assume that the system is in thermal equilibrium at temperature  $T$ . **(a)** Write an expression for the ratio  $P(E_2)/P(E_1)$ , that is, the ratio of the probability that the system is in the first excited state to that in the ground state. **(b)** What is the approximate temperature below which the system is unlikely to be found in any of its excited states?

- 15.11 •** Consider a gas of hydrogen atoms at a temperature  $T$ . At what temperature is the ratio of the number of atoms in the first excited state to the number of atoms in the ground state equal to 1/10; that is, at what temperature is  $P(E_2)/P(E_1) = 1/10$ ? [Don't forget that these states have degeneracies.]

- 15.12 ••** *Physical interpretation of the partition function.* Consider a single-particle quantum system whose states are labeled with an index  $i = 1, 2, 3, \dots$  with corresponding energies  $E_1, E_2, E_3, \dots$ . Set the zero of energy at the ground-state energy so that  $E_1 = 0$ . Argue that if the absolute temperature  $T$  is such that  $kT = E_n$ , where  $n$  is some integer, then  $n$  is the approximate value of the partition function (15.4). Therefore, the partition function is equal to the number of states that are likely to be occupied.

- 15.13 ••** A pocket compass with a magnetized iron needle is at rest in the earth's magnetic field,  $B \approx 10^{-4}$  T. **(a)** Given that the mass of the needle is 0.2 grams, estimate its magnetic moment. Assume that each atom in the needle has a magnetic moment of one Bohr magneton and that the moments of all the atoms are fully aligned. **(b)** Find the ratio of the probability that the needle is pointing along the earth's field to that of its pointing in the opposite direction. [It is

legitimate to use the Boltzmann relation in this classical situation.]

- 15.14 ••** Consider an electron in an external magnetic field of 1.0 T, and recall that the energy of an electron in a magnetic field is given by Eq. (9.18) as  $E = m\mu_B B$ , where  $m = \pm 1/2$ . **(a)** Make a plot of the ratio of the probability that the electron's moment is aligned with the field (the low-energy state) to the probability that it is anti-aligned (the high-energy state) versus the absolute temperature  $T$ . **(b)** What is the ratio at room temperature? **(c)** How low does the temperature have to be in order for this ratio to be 2?
- 15.15 ••** At what temperature would one be just as likely to find a hydrogen atom in its first excited level as in its ground level? [Don't forget about degeneracies.]
- 15.16 ••** As described in Section 7.9, a 1-D quantum-mechanical harmonic oscillator has a particularly simple spectrum of energies:  $E_n = (n + \frac{1}{2})\hbar\omega$ , where  $n = 0, 1, 2, \dots$ ,  $\omega$  is a constant, and all the states are nondegenerate. **(a)** At temperature  $T$ , what is the ratio  $P(E_0)/P(E_1)$ , that is, the ratio of the probability that the system is in the ground ( $n = 0$ ) state to the probability that it is in the first excited ( $n = 1$ ) state? **(b)** Sketch the ratio  $P(E_0)/P(E_1)$  as a function of the parameter  $kT/\hbar\omega$ .
- 15.17 •••** Consider the 1-D harmonic oscillator of the previous problem. **(a)** Write down the partition function (15.4) for this system and sum the infinite series. [Remember that  $1 + x + x^2 + x^3 + \dots = 1/(1 - x)$ .] **(b)** Sketch the probabilities  $P(E_0)$  and  $P(E_1)$  as functions of  $T$ .
- 15.18 •••** Consider a quantum system consisting of two spin-half particles in a magnetic field  $B$ . This system has four possible states, which we can indicate schematically as (1)  $\uparrow\uparrow$ , (2)  $\downarrow\downarrow$ , (3)  $\uparrow\downarrow$ , and (4)  $\downarrow\uparrow$ . States 3 and 4 both have energy  $E = 0$ , state 2 has energy  $E = +\varepsilon$ , and state 1 has energy  $E = -\varepsilon$ , where  $\varepsilon = 2\mu_B B$ . **(a)** Write down an expression for the partition function for this system. [Note that the  $E = 0$  state has a degeneracy of two.] **(b)** Write expressions for the probabilities that the system is in each of the three energy levels  $E = +\varepsilon, 0, -\varepsilon$ , as a function of temperature. **(c)** Sketch these probabilities as a function of the parameter  $kT/\varepsilon$ .

## SECTION 15.4 (Counting Microstates: The Equal-Probability Hypothesis)

- 15.19 •** **(a)** What is the probability that in a deal of 2 cards from a randomly shuffled deck you will get 2 hearts? **(b)** What is the probability of turning up 2 hearts if the first card is replaced and the deck shuffled before the second card is turned?
- 15.20 •** **(a)** What is the probability that in a roll of 5 dice you will get 5 sixes? **(b)** What is it that you will get no sixes?
- 15.21 ••** **(a)** What is the probability that, from a randomly shuffled deck, you will be dealt a hand of 5 cards that are all hearts. **(b)** What is the probability that you will be dealt 4 kings and an ace in that order (4 kings followed by an ace)?

**15.22** •• A coin is flipped  $N$  times. The probability that the coin will come up heads all  $N$  times is  $P(N) = 1/2^N$ . **(a)** Show that this probability can also be written as  $P(N) = 10^{-N \ln 2 / \ln 10}$ . [Hint: Note that  $x = e^{\ln x} = 10^{\log x}$ , from which it follows that  $\ln x = \ln[10^{\log x}] = (\log x)(\ln 10)$ .] **(b)** For what value of  $N$  does the probability of  $N$  heads in a row fall below  $10^{-8}$ ? ( $10^{-8}$  is about the probability of winning a large state lottery.)

**15.23** •• **(a)** What is the probability that, from a randomly shuffled deck, you will be dealt the cards (A♦, A♥, A♠, A♣, K♣) in that order? **(b)** What is the probability that, from a randomly shuffled deck, you will be dealt the same 5 cards in any order?

**15.24** •• For very large numbers, the factorial of  $N$  can be estimated by Stirling's approximation  $N! \approx (\sqrt{2\pi N}) N^N e^{-N}$ . **(a)** What is the fractional error in this approximation for  $N = 25$  and  $N = 60$ ? **(b)** Stirling's approximation can also be written as  $\ln(N!) \approx \frac{1}{2} \ln(2\pi) + \frac{1}{2} \ln N + N \ln N - N$ . Often, to simplify calculations, a further approximation is made and the formula is written as  $\ln(N!) \approx N \ln N - N$ . If  $N = 10^{23}$ , how do the values of these two versions of Stirling's approximation compare? What percent error is made in the computation of  $\ln(N!)$  by using the shorter, more approximate version compared to the longer, more precise version (for  $N = 25$  and 60 again)? [See also Problem 15.63.]

**15.25** •• Show that Eq. (15.11)

$$P(\text{left side only}) = \frac{H!}{(2H)!} \frac{(2H - N)!}{(H - N)!}$$

reduces to the simpler equation (15.8)  $P(N) = 1/2^N$  in the limit  $H \gg N \gg 1$ . [Hint: To compute the factorial of large numbers, use Stirling's approximation:  $\ln N! \approx N \ln N - N$ . Note also that if  $H \gg N$ , then  $\ln(H - N) \approx \ln H$ .]

**15.26** ••• Consider  $N$  identical indistinguishable bosons in a sealed container, and assume that the particles can move freely between the left and right halves of the container. As in Section 15.4, model the quantum states of this system in the following simple manner: Assume that there are  $H$  different single-particle quantum states on the left half of the box, that is, states with wave functions localized on the left, and there are another  $H$  states on the right. Compute the probability that all  $N$  bosons will be found in the left half of the box. [Hint: See Problem 15.29.]

**15.27** ••• Consider a room full of air molecules. Each molecule can be considered to be in one of two states: in the right half of the room or in the left half. The probability of each of these states is  $1/2$ . If there are  $N$  distinguishable molecules in the room, then the total number of ways of arranging the molecules is  $2^N$ . **(a)** Argue that the number of ways of arranging the  $N$  distinguishable molecules with  $N_L$  molecules on the left is

$$P_L = \frac{N!}{(N - N_L)! N_L!}$$

**(b)** If there are 100 molecules in the room, what is the ratio  $(P_L = 0.5)/(P_L = 0.6)$ ; that is, how much more likely is it that the molecules are evenly distributed compared to having 60 on the left and 40 on the right? **(c)** If there are  $10^{25}$  molecules in the room, what is the ratio  $(P_L = 0.500)/(P_L = 0.501)$ ? To compute the factorial of large numbers, use Stirling's approximation:  $\ln N! \approx N \ln N - N$ .

**15.28** ••• Continuing with the situation in the previous problem, the number of molecules in the right and left halves of a room containing  $N$  molecules can be written as  $N_R = (N/2)(1 + \Delta)$ ,  $N_L = (N/2)(1 - \Delta)$ . For  $N$  large, we expect the number of molecules in the two halves to be nearly equal so  $\Delta \ll 1$ . **(a)** Show that the probability of a fractional discrepancy of  $2\Delta$  more molecules on the right than on the left is given by

$$P(\Delta) = C e^{-\Delta^2 N}$$

where  $C$  is a constant that does not depend on  $\Delta$ . [Hint: You will need to use Stirling's approximation,  $\ln N! \approx N \ln N - N$ , and the relation  $\ln(1 + x) \approx x$ , valid for  $x \ll 1$ . Begin by writing  $P = N!/(N_R! N_L!)$  and take the  $\ln$  of both sides.] **(b)** For a room containing  $10^{25}$  molecules, what is the ratio  $P(\Delta = 0.001)/P(\Delta = 0)$ ? **(c)** What values of  $\Delta$  are likely to actually occur in a room?

### SECTION 15.5 (The Origin of the Boltzmann Relation\*)

**15.29** •• Prove Eq. (15.14),

$$g(r) = \frac{(N + r - 1)!}{r!(N - 1)!}$$

where  $g(r)$  is the number of ways of placing  $r$  indistinguishable objects in  $N$  distinct boxes. A particular arrangement of the objects among the boxes can be represented schematically by a series of  $r$  dots sprinkled among  $N + 1$  lines, like so:

$$|\bullet||| |\bullet\bullet|$$

The figure above represents  $r = 4$  objects placed in  $N = 6$  boxes. Note that the two lines on the far right and far left must remain fixed on the outside positions, but the remaining  $(N - 1)$  lines and  $r$  dots can occur in any order.

**15.30** •• Show that Eq. (15.14),

$$g(r) = \frac{(N + r - 1)!}{r!(N - 1)!}$$

is approximately equal to  $r^N$  in the limit  $r \gg N \gg 1$ . [Hint: Use Stirling's approximation:  $\ln N! \approx N \ln N - N$ . You will need to make several approximations along the way, including, for instance,  $\ln(N + r - 1) \approx \ln(r)$ .]

**15.31** ••• Show that Eq. (15.16)  $P(s) \propto e^{-s/(m/N)}$  can be derived from Eq. (15.15),

$$P(s) \propto g_R(m - s) = \frac{[N + (m - s) - 1]!}{(m - s)!(N - 1)!}$$

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in the limit of large  $N$  and  $m \gg N \gg 1$  and  $m \gg s$ . [Hint: Use *Stirling's approximation*:  $\ln N! \approx N \ln N - N$ , valid for large  $N$ . Also, note that, if  $x \ll 1$ , then  $\ln(1 + x) \approx x$ .]

## SECTION 15.6 (Entropy and the Second Law of Thermodynamics\*)

**15.32** • Consider Example 15.6 in which a gas is allowed to expand from a volume  $V_0$  into a volume  $2V_0$  when a barrier is broken. Using both of the methods given in that example, find the change in entropy if the gas is allowed to expand in this way from volume  $V_0$  to  $3V_0$ .

**15.33** •• An ideal gas of  $N$  spinless monatomic atoms is at temperature  $T$  and volume  $V$ . What is the entropy increase of the gas when the temperature is doubled at constant volume? [Hint: Use a thermodynamic argument, not a statistical mechanical one, and remember that for a monatomic ideal gas, the average energy per atom is  $\frac{3}{2}kT$ .]

**15.34** •• A bar of ferromagnetic material consists of  $N$  atoms, each with spin half. The spin of each atom can point in one of two directions: up or down. When the bar is fully magnetized, all the spins point in the same directions, like so:  $\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow$ ; it is completely demagnetized when the spins are in random directions, like so:  $\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow$ . (a) How many different ways  $g$  can the  $N$  spins be arranged? (Note that these are  $N$  distinguishable spins since they are on a fixed lattice.) (b) What is the increase in entropy of the bar magnet when it is taken from a fully magnetized state to a fully demagnetized state? (c) Repeat part (b), but with a magnet made of spin  $\frac{3}{2}$  atoms, which can exist in any one of four states  $\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ .

**15.35** ••• An ideal gas of  $N$  spinless monatomic atoms is at a temperature  $T$  and volume  $V$ . (a) What is the entropy increase of the gas when the volume of the gas is doubled isothermally (at constant temperature)? (b) What is the entropy change of the gas when the volume of the gas is doubled reversibly (slow, steady volume change) and adiabatically (no heat allowed into or out of the gas)?

**15.36** ••• *Entropy of Mixing*. Consider a box containing  $N$  particles. A partition separates the right and left halves of the box and there are  $N/2$  particles to the right of the partition and  $N/2$  particles to the left. Suddenly, the partition breaks allowing the particles on the right and left to freely mix. If the particles are indistinguishable, there is no change in the entropy of the system when the partition breaks. However, if the particles are distinguishable (for instance, if the right and left halves contain different isotopes of the same inert gas) then there is an increase in entropy, called the entropy of mixing, equal to  $\Delta S = kN \ln 2$ . Prove these statements.

In the nineteenth century, before the development of quantum mechanics and the notion of indistinguishability, physicists thought that identical particles were distinguishable and that there should therefore be an increase in entropy when identical gases mix. Experimentally, no such increase was observed and this puzzling state of affairs was called Gibbs's paradox.

## SECTION 15.7 (The Quantum Ideal Gas — A Many-Particle System)

**15.37** • Use the technique of separation of variables to verify that the wave functions (15.22) with energies (15.23) are solutions of the Schrödinger Eq. (15.20).

**15.38** •• As in Fig. 15.10(b), the ground state of a gas of fermions consists of one-eighth of a sphere of states in  $k$  space, with all states filled up to a maximum energy, called the *Fermi energy*. (a) For a gas of  $N$  spin- $\frac{1}{2}$  noninteracting fermions in a container of volume  $V = a^3$ , derive an expression for the Fermi energy. (b) Compute the approximate value of the Fermi energy in eV for the case of an electron gas in a metal. Assume one conduction electron per atom, and a lattice constant (distance between nearest-neighbor atoms) of 0.3 nm.

**15.39** •• Show that for a degenerate gas of fermions at  $T = 0$ , the average energy per particle and the Fermi energy  $E_F$  (the energy of the highest occupied states) are related by  $\langle E \rangle = (3/5)E_F$ . [Hint: Avoid writing any messy constants in your calculation, by noting that we can write

$$\langle E \rangle = \frac{\int_0^{E_F} p(E)E dE}{\int_0^{E_F} p(E) dE}$$

where  $p(E) = C\sqrt{E}$  and  $C$  is a constant that you don't need to know because it cancels.]

**15.40** ••• Consider a quantum ideal gas of  $N$  spinless particles in a container of volume  $V = a^3$ . If the temperature is sufficiently high and the density is sufficiently low, the gas is in the classical nondegenerate regime, in which the probability that any particular point in  $k$  space is occupied is much less than one, corresponding to Fig. 15.12(a). In this high-temperature, low-density limit, the properties of the gas are the same regardless of whether the particles of the gas are fermions or bosons. (a) Show that this classical regime occurs when the number density (number per volume)  $n$  obeys  $n \ll (3kTm)^{3/2}/6\pi^2\hbar^3$ , where  $m$  is the mass of a gas molecule. [Hint: From the equipartition theorem, the average kinetic energy of a single particle is  $\frac{3}{2}k_B T$ , and so a typical value of  $k = |\mathbf{k}|$  for a particle is given roughly by  $\hbar^2 k^2/2m \approx \frac{3}{2}k_B T$ . Also, recall that the density of points in  $k$  space is 1 point per  $(\pi/a)^3$ .] (b) For a gas of helium atoms at atmospheric pressure, below what temperature (roughly) does the gas become degenerate? (c) For a conduction electron gas in a metal, how high a temperature would be necessary for the electrons to be in the classical regime? Is such a temperature possible? Assume 1 conduction electron per atom, and a volume per atom of about  $(0.3 \text{ nm})^3$ .

## SECTION 15.8 (Energy and Speed Distributions in an Ideal Gas)

**15.41** • (a) In an ideal monatomic gas at temperature  $T$ , what is the ratio of the probabilities that a particle has speeds  $2v$  and  $v$ , that is, what is  $p(2v)/p(v)$ ?



(b) For a gas of helium atoms at  $T = 300 \text{ K}$ , what is this ratio when  $v$  is the rms speed  $\sqrt{3kT/m}$ ?

**15.42 ••** Protons on the surface of the sun can be considered to be a gas of noninteracting particles. (a) Calculate the escape speed from the surface of the sun. ( $M_{\text{sun}} = 1.99 \times 10^{30} \text{ kg}$ ,  $R_{\text{sun}} = 6.96 \times 10^8 \text{ m}$ ). (b) Assume that the protons at the sun's surface are in thermal equilibrium at  $T = 6000 \text{ K}$ . Argue that none of the protons on the surface of the sun has a speed greater than the escape speed. (See, however, Problem 15.67.)

**15.43 ••** Eq. (15.29) is the distribution of single-particle energies in a three-dimensional ideal gas. Derive the corresponding expression for the case of a two-dimensional ideal gas. [Hint: Instead of considering a shell of states in 3-D  $k$  space, consider a ring of states in 2-D  $k$  space.] (A physical example of a 2-D gas is the electron gas that forms at the interface between doped GaAs layers in some semiconductor devices.)

**15.44 ••** (a) At what value of the molecular speed  $v$  does the Maxwell-Boltzmann distribution of speeds have its maximum? (b) Show that this most probable speed corresponds to a kinetic energy  $kT$ .

**15.45 ••** In an ideal gas, at a given instant in time, roughly what fraction of the molecules have average kinetic energies  $\text{KE} < 0.1 kT$ ? [Hint: If  $E \ll kT$ , then  $e^{-E/kT} \approx 1$ .]

**15.46 ••** The standard deviation of a random variable  $x$  is defined as  $\Delta x = \sqrt{\langle (x - \langle x \rangle)^2 \rangle}$ . Note that this is a measure of the "spread" of values of  $x$  about the mean value. (a) Show that the standard deviation can also be written as  $\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$ . (b) What is the standard deviation  $\Delta v$  of the distribution of speeds of an atom in an ideal monatomic gas at temperature  $T$ ? (c) What is the ratio  $\Delta v/v_{\text{rms}}$ ?

**15.47 ••** Prove that for the particles of an ideal monatomic gas,  $\langle E \rangle = \int_0^\infty E p(E) dE = \frac{3}{2} kT$ , where  $p(E)$  is the energy distribution given by (15.31).

**15.48 ••** Prove that for an ideal gas,  $\langle v \rangle = \int_0^\infty v p(v) dv = \sqrt{8kT/(\pi m)}$ , where  $p(v)$  is the Maxwell speed distribution given by (15.32).

**15.49 ••** Derive expressions for  $\langle v \rangle^2$  and  $\langle v^2 \rangle$  in an ideal gas, where  $v$  is the speed of the molecules. (The equipartition theorem and probability distribution  $p(v)$  given by (15.32) will be useful here.) Which expression is larger, and why?

### SECTION 15.9 (Heat Capacities)

**15.50 •** (a) How much energy is required to raise the temperature of a mole of an ideal monatomic gas by  $1^\circ\text{C}$  at constant volume? Give your answer in both J/mol and

eV/atom. (b) How much energy is required to raise the temperature of 1 kg of aluminum by  $1^\circ\text{C}$  at room temperature (where the Dulong-Petit law applies)?

**15.51 ••** Prove the two identities in (15.34):

$$\frac{1}{(1-x)} = 1 + x + x^2 + x^3 + \dots$$

and

$$\frac{1}{(1-x)^2} = 1 + 2x + 3x^2 + \dots$$

**15.52 ••** Show that the average energy of a system can be written as  $\langle E \rangle = -d(\ln Z)/d\beta$ , where  $\beta = 1/kT$  and  $Z$  is the partition function  $Z = \sum_i g_i e^{-\beta E_i}$ .

**15.53 ••** Show that the heat capacity of a system can be written as  $C = T d^2(kT \ln Z)/dT^2$ , where  $Z$  is the partition function  $Z = \sum_i g_i e^{-\beta E_i}$ . [Hint: Use the results of Problem 15.52.]

**15.54 ••** Consider a three-level quantum system, with non-degenerate energy levels  $0, +\varepsilon$ , and  $+2\varepsilon$ . (A physical example of such a system is a spin  $S = 1$  magnetic moment in a magnetic field.) (a) Write down the partition function  $Z$  for this system. (b) Write down the expression for the thermal average energy  $\langle E \rangle$  of this system. (c) Show that in the low-temperature limit  $kT \ll \varepsilon$ , the energy and specific heat of this system are identical to those of a two-level system. (d) Show that in the high-temperature limit  $kT \gg \varepsilon$ , the heat capacity of this system, like that of a two-level system, approaches zero.

**15.55 ••** The argument leading to the Dulong-Petit law treats the lattice vibrations classically, that is, the spectrum of energies is assumed to be continuous. This would be expected to break down once the thermal energy ( $\sim k_B T$ ) is comparable to, or less than, the quantized level spacing  $\Delta E = \hbar\omega_c$  of the lattice vibrations. Given that the latter is of order  $0.03 \text{ eV}$ , estimate the temperature below which the Dulong-Petit law should fail. Compare your answer with Fig. 15.17.

**15.56 ••** The Dulong-Petit law predicts that the molar specific heats (that is, the heat capacity *per mole*) of elemental solids should all have the same value,  $C = 3R$ . On the other hand, the ordinary specific heats  $c$ , defined as the energy per degree *per mass*, can be quite different. (a) Prove that the specific heats,  $c$ , of elemental solids obeying the Dulong-Petit law are inversely proportional to the atomic masses. (b) Given the following data, check the accuracy of this prediction.

Solid:	Aluminum	Silver	Gold
$c[\text{cal}/(\text{g} \cdot \text{K})]$ :	0.214	0.0558	0.0312

**15.57 ••** (a) Assuming their molar specific heats are given by the Dulong-Petit law, predict the specific heats, in  $\text{cal}/(\text{g} \cdot \text{K})$ , of Al, Ag, and Au. (b) Find the percent discrepancies between your predictions and the measured values given in Problem 15.56.

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- 15.58 ••** Compare the measured specific heat of ice [ $c_{\text{ice}} = 0.49 \text{ cal}/(\text{g} \cdot \text{K})$  at temperatures somewhat below freezing] with that expected from the Dulong–Petit law. From this comparison, can you estimate how many internal degrees of freedom of the ice molecule are contributing to the heat capacity?
- 15.59 ••** Consider a dilute gas of  $N$  noninteracting atoms, in which the atoms have a nondegenerate ground state with energy  $E_0 = 0$  and a first excited level that has an energy  $E_1 = \varepsilon$  and degeneracy  $g$ . Assume that the second excited state has an energy very high compared with the thermal energy; that is, assume  $kT \ll E_2$ , so that the level  $E_2$  and all higher levels can be ignored. **(a)** At temperature  $T$ , what is the ratio of the number of atoms in the first excited level (degeneracy  $g$ ) to the number in the ground state? **(b)** What is the average energy of an atom in this gas? **(c)** What is the total energy of the gas? **(d)** What is the specific heat of the gas?
- 15.60 •••** Consider a simple solid, such as aluminum, consisting of  $N$  identical atoms. Assume that the Einstein approximation correctly describes the vibrational motion of the atom. **(a)** Assume that the vibrational level spacing has the value  $\varepsilon = 0.037 \text{ eV}$  (a typical value in a solid). Consider the probability that an atom of the solid is in its ground state. At what temperature is this probability equal to 0.1? **(b)** For a given  $N$  and  $\varepsilon$ , at what temperatures is the average number of atoms in the ground state less than one? That is, how high does the temperature have to be to ensure that all atoms are in an excited state? Is this temperature achievable in an ordinary sample of a solid?
- 15.61 ••** Make an order-of-magnitude estimate of the temperature at which the internal vibrational mode of a nitrogen molecule becomes appreciably excited. Recall that the energy of the first excited state of a simple harmonic oscillator is  $\hbar\omega$ , where  $\omega = \sqrt{k/m}$  is the classical angular frequency,  $k$  is the spring constant, and  $m$  is the mass. Recall also that the energy of the oscillator can be written as  $U = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2x^2$ . Finally, note that we can expect a typical chemical bond energy  $U(x) \sim 3 \text{ eV}$  when  $x$  is a typical atomic distance  $x \approx 0.1 \text{ nm}$ . The moral of this question is that the vibrational modes of air molecules are largely “frozen out” at room temperature.
- 15.62 ••** Make an order-of-magnitude estimate of the temperature at which the rotational modes of a nitrogen molecule become excited. Recall that the kinetic energy of a rotating system is  $U = \frac{1}{2}I\omega^2 = \frac{1}{2}L^2/I$ , where  $I = \sum m_i r_i^2$  is the moment of inertia and  $L = I\omega$  is the angular momentum. Recall that for a quantum system, the first excited state has  $L^2 \approx \hbar^2$ . Based on your answer, would you expect the rotational modes of air molecules to contribute to the heat capacity of air at room temperature?



## COMPUTER PROBLEMS

- 15.63 ••** (Section 15.4) For very large numbers, the factorial of  $N$  can be estimated by *Stirling's approximation*  $N! \approx (\sqrt{2\pi N})N^N e^{-N}$ , which can also be written as  $\ln(N!) \approx \frac{1}{2}\ln(2\pi N) + N \ln N - N$ . Often, to simplify calculations, a further approximation is made and the formula is written as  $\ln(N!) \approx N \ln N - N$ . **(a)** Plot  $\ln(N!)$  versus  $N$  for  $N = 1, 2, \dots, 10$ , and on this same plot, graph the long version of Stirling's approximation. **(b)** Make a graph showing how the long and short versions of Stirling's approximation compare over the range of 10 to 100. Consider carefully what plot will show this comparison to best effect.
- 15.64 ••** (Section 15.8) Reproduce Figure 15.14, the distribution of single-particle energies in an ideal gas, for the case of helium gas at room temperature.
- 15.65 ••** (Section 15.8) Reproduce Figure 15.15, showing the Maxwell speed distributions, for the cases of  $\text{N}_2$  and He gases at room temperature.
- 15.66 ••** (Section 15.8) The temperature of the uppermost reaches of the earth's atmosphere, called the thermosphere, is approximately 600 K during the day (the high temperature is due to efficient absorption of solar radiation). **(a)** At 600 K, what fraction of hydrogen molecules have thermal speeds greater than the earth's escape velocity? **(b)** What fraction of the hydrogen molecules have speeds greater than the escape velocity at room temperature, about 300 K? [*Hint:* You need the computer to do the required integration.]
- 15.67 ••** (Section 15.8) The outer atmosphere of the sun, called the corona, consists mostly of protons and extends out to distances of two to three times the radius of the sun. The temperature of the corona is extraordinarily high, approximately 1 million degrees Kelvin (the cause of this high temperature is still not well understood). **(a)** Compute the approximate escape speed for particles in the outer corona. ( $M_{\text{sun}} = 1.99 \times 10^{30} \text{ kg}$ ,  $R_{\text{sun}} = 6.96 \times 10^8 \text{ m}$ ) **(b)** Approximately what fraction of the protons in the outer corona have a thermal speed greater than the escape speed? [Protons escaping from the corona cause the “solar wind.”]
- 15.68 •• (a)** (Section 15.9) Plot the Einstein specific heat of a solid as a function of temperature and thus reproduce Figure 15.17. Assume that the vibrational level spacing has the value  $\varepsilon = 0.037 \text{ eV}$  (a typical value in a solid). **(b)** Using the value  $\varepsilon = 0.037 \text{ eV}$ , at what temperature is the heat capacity of the solid given by 0.9 times the Dulong–Petit value?
- 15.69 ••** (Section 15.9) Reproduce Figure 15.18, showing the average energy and heat capacity, for the case of a three-level system with nondegenerate energy levels 0,  $+\varepsilon$ , and  $+2\varepsilon$ .