10

Statistical Physics

Chapter Outline

Thermodynamics is based on macroscopic or bulk properties, such as temperature and pressure of a gas. In this chapter we explain thermodynamic properties in terms of the motion of individual atoms. The goal of this microscopic approach, known as statistical physics, or statistical mechanics, is to explain the relationships between thermodynamic bulk properties using a more fundamental atomic picture. It is possible in principle to calculate the detailed motion of individual atoms from Newton's laws or the Schrödinger equation. The number of atoms in the average size sample ($\approx 10^{22}$ atoms/cm^3), however, makes such calculations impractical, and we must rely on a statistical approach.

In this chapter we introduce the laws of statistical physics and discuss systems of particles that obey either classical or quantum mechanics. We will show how a fixed amount of energy may be shared or distributed among a large number of particles in thermal equilibrium at temperature T. We investigate this energy distribution by calculating the average number of particles with a specific energy or, what is essentially the same thing, by finding the probability that a single particle has a certain energy.

10.1 THE MAXWELL–BOLTZMANN DISTRIBUTION

The satisfying explanation of thermodynamics in terms of averages over atomic properties was given in the second half of the 1800s by three physicists: James Clerk Maxwell, Ludwig Boltzmann, and Josiah Willard Gibbs. Maxwell, a Scottish professor at Cambridge, was extremely impressed by the work of Rudolf Clausius in explaining the apparent contradiction between the high speed of gas molecules at room temperature (about 400 m/s) and the slow diffusion rate of a gas. Clausius had explained this riddle by reasoning that gas molecules do not all travel at a single high speed, but that there is a well-defined distribution of molecular speeds in a gas that depends on the gas temperature; furthermore, the gas molecules collide and hence follow long zigzag paths from one spot to another. Building on this idea, Maxwell was able to derive the functional form of the equilibrium speed distribution, which is the number of gas molecules per unit volume having speeds between v and $v + dv$ at a specific temperature. Applying the theory of statistics to this distribution, Maxwell was able to calculate the temperature dependence of quantities such as the average molecular speed, the most probable speed, and the dispersion, or width, of the speed distribution.

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In 1872, Boltzmann, an Austrian professor at the University of Vienna, profoundly impressed with Darwin's ideas on evolution, took Maxwell's work a step further. He not only wanted to establish the properties of the equilibrium or most probable distribution but he also wished to describe the evolution in time of a gas toward the Maxwellian distribution—the so-called approach-to-equilibrium problem. With the use of a time-dependent speed distribution function and his kinetic equation, Boltzmann was able to show that a system of particles that starts off with a non-Maxwellian speed distribution steadily approaches and eventually achieves an equilibrium Maxwellian speed distribu-

Is the universe a gambling casino? (*Courtesy of Tropicana Casino And Resort*)

Ludwig Boltzmann (1844–1908), an Austrian theoretical physicist. (*Courtesy AIP Niels Bohr Library, Lande Collection*)

tion. Boltzmann, a staunch advocate of the reality of molecules, was subjected to personal attacks at the hands of critics who rejected the molecular theory of matter in the late 1800s. Depressed over the lack of universal acceptance of his theories, he committed suicide in 1908.

Gibbs, in contrast to Boltzmann, led a rather sheltered and secluded life as a professor at Yale. The son of a Yale professor, he lived his adult life in the same house in New Haven in which he had grown up, quietly establishing statistical mechanics and the kinetic theory of gases on a rigorous mathematical basis. Gibbs published his work in the obscure *Transactions of the Connecticut Academy of Arts and Sciences,* and his work remained relatively unknown during his lifetime.

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Having briefly discussed the contributions of Maxwell, Boltzmann, and Gibbs to statistical mechanics, let us examine the underlying assumptions and explicit form of the Maxwell–Boltzmann distribution for a system of particles. The basic assumptions are:

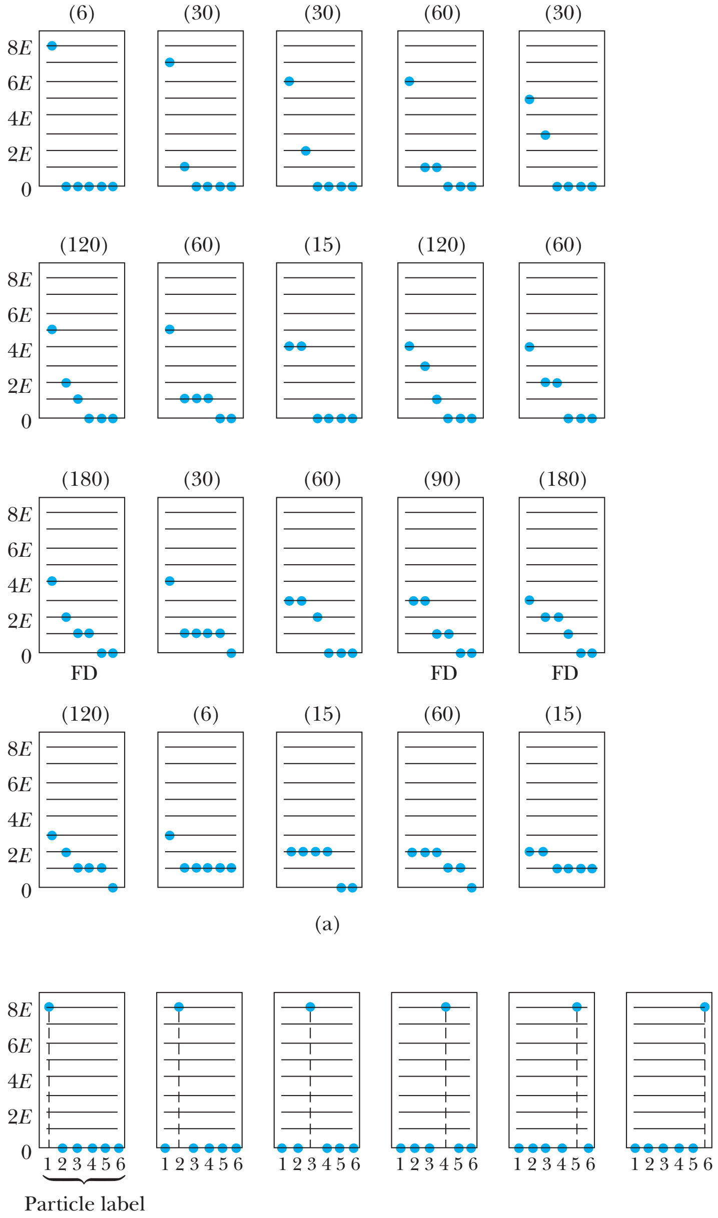
Assumptions of the Maxwell–Boltzmann distribution

- The particles are identical in terms of physical properties but distinguishable in terms of position, path, or trajectory. It will be demonstrated later in this chapter that this assumption is equivalent to the statement that the particle size is small compared with the average distance between particles.
- The equilibrium distribution is the most probable way of distributing the particles among various allowed energy states subject to the constraints of a fixed number of particles and fixed total energy.
- There is no theoretical limit on the number of particles in a given energy state, but the density of particles is sufficiently low and the temperature sufficiently high that no more than one particle is likely to be in a given state at the same time.

To make these assumptions concrete, let us consider the analysis of a manageable-sized system of distinguishable particles. In particular, consider the distribution of a total energy of $8E$ among six particles where E is an indivisible unit of energy. To work with a diagram of reasonable size, Figure 10.1a enumerates the 20 possible ways of sharing an energy of $8E$ among six *indistinguishable* particles. Since we are actually interested in *distinguishable* particles, each of the 20 arrangements can be decomposed into many distinguishable substates, or **microstates,** as shown explicitly for one arrangement in Figure 10.1b. The number of microstates for each of the 20 arrangements is given in parentheses in Figure 10.1a and may be computed from the relation

$$N_{\mathrm{MB}} = \frac{N!}{n_1!n_2!n_3!\ .\ .\ .} \tag{10.1}$$

where N_{MB} is the Maxwell–Boltzmann number of microstates, N is the total number of particles, and n_1, n_2, n_3, . . . are the numbers of particles in *occupied* states of a certain energy. This result may be understood by arguing that the first energy level may be assigned in N ways, the second in $N - 1$ ways, and so on, giving $N!$ in the numerator. The factor in the denominator of Equation 10.1 corrects for indistinguishable order arrangements when more than one particle occupies the same energy level. As an example of the use of Equation 10.1, consider the energy distribution of six particles, with two having energy $1E$, one having energy $6E$, and three having energy 0. This energy distribution is shown in the fourth diagram from the left in the top row of Figure 10.1a. In



(a)

(b)

Figure 10.1 (a) The 20 arrangements of six *indistinguishable* particles with a total energy of 8*E*. (b) The decomposition of the upper left-hand arrangement of part (a) into six distinguishable states for *distinguishable* particles.

this case, $N = 6$, $n_1(0E) = 3$ (that is, the number of particles in the 0 energy state is 3), $n_2(1E) = 2$, $n_3(2E) = 0$, $n_4(3E) = 0$, $n_5(4E) = 0$, $n_6(5E) = 0$, $n_7(6E) = 1$, $n_8(7E) = 0$, and $n_9(8E) = 0$. Since only the numbers of particles in occupied levels appear in the denominator of Equation 10.1, we find that the number of distinguishable microstates for this case is

$$N_{\mathrm{MB}} = \frac{6!}{3!2!1!} = 60$$

in agreement with the number in parentheses in the diagram.

To find the average number of particles with a particular value of energy, say E_j, we sum the number of particles with energy E_j in each arrangement weighted by the probability of realizing that arrangement:

$$\overline{n_j} = n_{j_1}p_1 + n_{j_2}p_2 + \cdots \tag{10.2}$$

Here $\overline{n_j}$ is the average number of particles in the jth energy level, n_{j_1} is the number of particles found in the jth level in arrangement 1, n_{j_2} is the number of particles found in the jth level in arrangement 2, p_1 is the probability of observing arrangement 1, p_2 is the probability of arrangement 2, and so on. **Using the basic postulate of statistical mechanics, that any individual microstate is as likely as any other individual microstate,** we may go on to calculate the various p's and $\overline{n_j}$'s. For example, since there are a total of 1287 microstates (the sum of all the numbers in the parentheses), and 6 distinguishable ways of obtaining arrangement 1 (the leftmost arrangement in row 1 in Fig. 10.1a), we see that $p_1 = 6/1287$. Using these ideas and Equation 10.2, we calculate the average number of particles with energy 0 as follows:

$$\begin{aligned}\overline{n_0} = {} & (5)(6/1287) + (4)(30/1287) + (4)(30/1287) + (3)(60/1287) \\ & + (4)(30/1287) + (3)(120/1287) + (2)(60/1287) + (4)(15/1287) \\ & + (3)(120/1287) + (3)(60/1287) + (2)(180/1287) \\ & + (1)(30/1287) + (3)(60/1287) + (2)(90/1287) + (2)(180/1287) \\ & + (1)(120/1287) + (0)(6/1287) + (2)(15/1287) \\ & + (1)(60/1287) + (0)(15/1287) \\ = {} & 2.307\end{aligned}$$

Now notice that it is easy to calculate the probability of finding a particle with energy 0 if we imagine reaching randomly into a box containing the six particles with total energy $8E$. This probability, $p(0)$, is simply the average number of particles with energy 0 divided by the total number of particles:

$$p(0) = \frac{\overline{n_0}}{6} = \frac{2.307}{6} = 0.385$$

It is left as a problem (Problem 1) to show that the probabilities of finding a particle with energies from $1E$ through $8E$ are as follows:

$$p(1E) = 0.256$$

$$p(2E) = 0.167$$

$$p(3E) = 0.0978$$

$$p(4E) = 0.0543$$

$$p(5E) = 0.0272$$

$$p(6E) = 0.0117$$

$$p(7E) = 0.00388$$

$$p(8E) = 0.000777$$

These results, which are plotted in Figure 10.2, show that this simple system follows an approximately exponential decrease in probability with energy. (See Problem 5.) The rapid decrease in probability with increasing energy shown in Figure 10.2 indicates that we are more likely to find the energy uniformly distributed among many particles of the system rather than concentrated in a few particles.

One may rigorously derive the Maxwell–Boltzmann distribution for a system in thermal equilibrium at the absolute temperature T containing a *large* number of particles by using calculus (see reference 1 in Suggestions for Further Reading at the end of this chapter). The expression for the number of ways of distributing the particles among the allowed energy states is maximized subject to two constraints. These constraints are (1) that the total number of particles is constant at any temperature and (2) that the total system energy is fixed at a given temperature. One finds an exponential form

Maxwell–Boltzmann distribution

$$f_{\mathrm{MB}} = Ae^{-E_i/k_{\mathrm{B}}T} \tag{10.3}$$

where f_{MB} is the Maxwell–Boltzmann probability of finding a particle with energy E_i, or in the language of statistical mechanics, the probability that a state with energy E_i is occupied at the absolute temperature T. If the number of states with the same energy E_i is denoted by g_i (g_i is called the **degeneracy** or **statistical weight**), then the number of particles, n_i, with energy E_i is equal to the product of the statistical weight and the probability that the state E_i is occupied, or

$$n_i = g_i f_{\mathrm{MB}} \tag{10.4}$$

The parameter A in Equation 10.3 is a normalization coefficient, which is similar to the normalization constant in quantum physics. A is determined by requiring the number of particles in the system to be constant, or

$$N = \sum n_i \tag{10.5}$$

where N is the total number of particles in the system.

When the allowed energy states are numerous and closely spaced, the discrete quantities are replaced by continuous functions as follows:

$$g_i \longrightarrow g(E)$$

$$f_{\mathrm{MB}} \longrightarrow Ae^{-E/k_{\mathrm{B}}T}$$

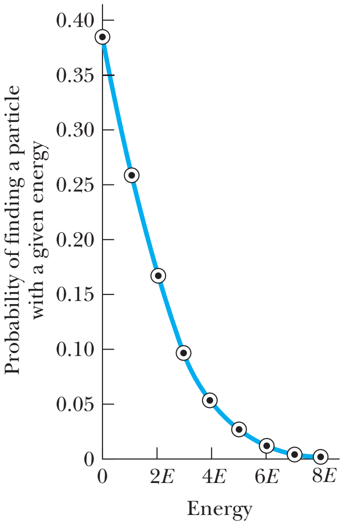


Figure 10.2 The distribution function for an assembly of six distinguishable particles with a total energy of 8E.

where $g(E)$ is the **density of states** or the number of energy states per unit volume in the interval dE. In a similar manner, Equations 10.4 and 10.5 may be replaced as follows:

Number of particles per unit volume with energy between E and $E + dE$

$$n_i = g_i f_{\mathrm{MB}} \longrightarrow n(E)\ dE = g(E)\ f_{\mathrm{MB}}(E)\ dE \tag{10.6}$$

$$N = \sum n_i \longrightarrow \frac{N}{V} = \int_0^\infty n(E)\ dE = \int_0^\infty g(E) f_{\mathrm{MB}}(E)\ dE \tag{10.7}$$

where $n(E)\,dE$ is the number of particles per unit volume with energies between E and $E + dE$. Note that Equations 10.6 and 10.7 may also be used for a system of quantum particles, provided that $g(E)$ and $f_{\mathrm{MB}}(E)$ are replaced with the appropriate density of states and quantum distribution functions.

EXAMPLE 10.1 Emission Lines from Stellar Hydrogen

(a) Find the populations of the first and second excited states *relative* to the ground state for atomic hydrogen at room temperature, assuming that hydrogen obeys Maxwell–Boltzmann statistics.

Solution For a gas at ordinary pressures, the atoms maintain the discrete quantum levels of isolated atoms. Recall that the discrete energy levels of atomic hydrogen are given by $E_n = (-13.6/n^2)$ eV and the degeneracy by $g_n = 2n^2$. Thus we have

Ground state:	$E_1 = -13.6$ eV	$g_1 = 2$
First excited state:	$E_2 = -3.40$ eV	$g_2 = 8$
Second excited state:	$E_3 = -1.51$ eV	$g_3 = 18$

Using Equation 10.4 gives

$$\frac{n_2}{n_1} = \frac{g_2 A e^{-E_2/k_B T}}{g_1 A e^{-E_1/k_B T}} = \frac{g_2}{g_1} e^{(E_1-E_2)/k_B T}$$

$$= \frac{8}{2} \exp\{(-10.2 \text{ eV})/(8.617 \times 10^{-5} \text{ eV/K})(300 \text{ K})\}$$

$$= 4e^{-395} \approx 0$$

The ratio of n_3/n_1 will be even smaller. Therefore, essentially all atoms are in the ground state at 300 K.

(b) Find the populations of the first and second excited states relative to the ground state for hydrogen heated to 20,000 K in a star.

Solution When a gas is at very high temperatures (as in a flame, under electric discharge, or in a star), detectable numbers of atoms are in excited states. In this case, $T = 20{,}000$ K, $k_B T = 1.72$ eV, and we find

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} e^{(E_1-E_2)/k_B T} = 4e^{-10.2/1.72} = 0.0107$$

$$\frac{n_3}{n_1} = \frac{g_3}{g_1} e^{(E_1-E_3)/k_B T} = 9e^{-12.1/1.72} = 0.0807$$

(c) Find the emission strengths of the spectral lines corresponding to the transitions $E_3 \rightarrow E_1$ and $E_3 \rightarrow E_2$ relative to $E_2 \rightarrow E_1$ at 20,000 K, assuming equal probability of transition for $E_3 \rightarrow E_1$, $E_3 \rightarrow E_2$, and $E_2 \rightarrow E_1$.

Solution The strength of an emission or absorption line is proportional to the number of atomic transitions per unit time. For particles obeying Maxwell–Boltzmann statistics, the number of transitions per unit time from some initial state (i) to some final state (f) equals the product of the population of the initial state and the probability for the transition i → f. Note that *the transition rate for particles obeying MB statistics depends only on the initial population, since there are no restrictions on the number of particles in the final state.* Returning to the calculation of the emission strength, S, we find the relative values:

$$\frac{S(3 \rightarrow 1)}{S(2 \rightarrow 1)} = \frac{n_3 P(3 \rightarrow 1)}{n_2 P(2 \rightarrow 1)}$$

$$\frac{S(3 \rightarrow 2)}{S(2 \rightarrow 1)} = \frac{n_3 P(3 \rightarrow 2)}{n_2 P(2 \rightarrow 1)}$$

In reality, the transition probabilities depend on the wavefunctions of the states involved, but to simplify matters we assume equal probabilities of transition; that is, $P(2 \rightarrow 1) = P(3 \rightarrow 1) = P(3 \rightarrow 2)$. This yields

$$\frac{S(3 \rightarrow 1)}{S(2 \rightarrow 1)} = \frac{n_3}{n_2} = \frac{g_3}{g_2} e^{(E_2-E_3)/k_B T} = \frac{18}{8} e^{-1.89/1.73}$$

$$= 0.75$$

$$\frac{S(3 \rightarrow 2)}{S(2 \rightarrow 1)} = 0.75$$

If the emission lines are narrow, the measured heights of the 3 → 1 and 3 → 2 lines will be 75% of the height of the 2 → 1 line, as shown in Figure 10.3. For broader lines, the area under the peaks must be used as the experimental measure of emission strength.

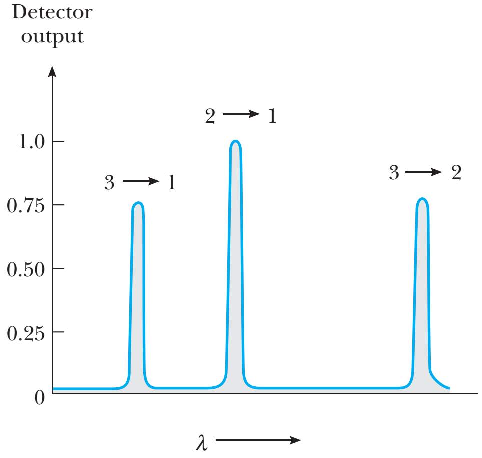


Figure 10.3 The predicted emission spectrum for the 2 → 1, 3 → 1, and 3 → 2 transitions for atomic hydrogen at 20,000 K.

The Maxwell Speed Distribution for Gas Molecules in Thermal Equilibrium at Temperature T

Maxwell's important formula for the equilibrium speed distribution, or the number of molecules with *speeds* between v and $v + dv$ in a gas at temperature T, may be found by using the Maxwell–Boltzmann distribution in its continuous form (Eqs. 10.6 and 10.7). In particular, we shall show that

$$n(v)\,dv = \frac{4\pi N}{V}\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-mv^2/2k_B T}\,dv \tag{10.8}$$

where $n(v)\,dv$ is the number of gas molecules per unit volume with speeds between v and $v + dv$, N/V is the total number of molecules per unit volume, m is the mass of a gas molecule, k_B is Boltzmann's constant, and T is the absolute temperature. This speed distribution function is sketched in Figure 10.4. The v^2 term determines the behavior of the distribution as $v \to 0$, and the exponential term determines what happens as $v \to \infty$.

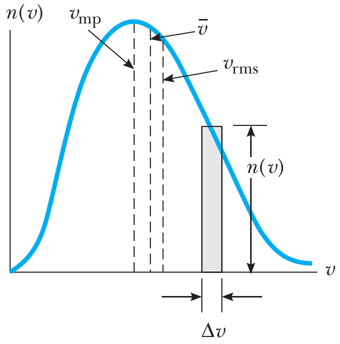


Figure 10.4 The speed distribution of gas molecules at some temperature. The number of molecules in the range Δv is equal to the area of the shaded rectangle, $n(v)\Delta v$. The most probable speed, v_{mp}, the average speed, $\bar{v}$, and the root mean square speed, v_{rms}, are indicated.

For an ideal gas of point particles (no internal structure and no interactions between particles), the energy of each molecule consists only of translational kinetic energy and we have

$$E = \tfrac{1}{2}mv^2$$

for each molecule. Since the gas molecules have speeds that are continuously distributed from 0 to ∞, the energy distribution of molecules is also continuous and we may write the number of molecules per unit volume with energy between E and $E + dE$ as

$$n(E)\,dE = g(E) f_{MB}(E)\,dE = g(E) A e^{-mv^2/2k_B T}\,dE$$

To find the density of states, $g(E)$, we introduce the concept of **velocity space.** According to this idea, the velocity of each molecule may be represented by a velocity vector with components v_x, v_y, and v_z or by a *point* in velocity space with coordinate axes v_x, v_y, and v_z (Fig. 10.5). From Figure 10.5 we note that the number of states $f(v)\,dv$ with speeds between v and $v + dv$ is proportional to the volume of the spherical shell between v and $v + dv$:

$$f(v)\,dv = C4\pi v^2\,dv \tag{10.9}$$

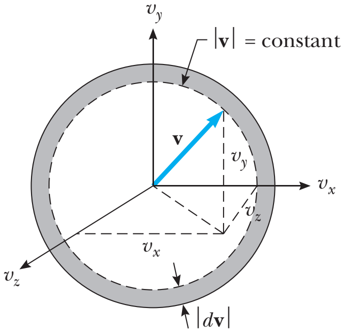


Figure 10.5 Velocity space. The number of states with speeds between v and $v + dv$ is proportional to the volume of a spherical shell with radius v and thickness dv.

where C is some constant. Because $E = \frac{1}{2}mv^2$, each speed v corresponds to a single energy E, and the number of energy states, $g(E)\,dE$, with energies between E and $E + dE$ is the same as the number of states with speeds between v and $v + dv$. Thus,

$$g(E)\,dE = f(v)\,dv = C4\pi v^2\,dv$$

Substituting this expression for $g(E)\,dE$ into our expression for $n(E)\,dE$, we obtain

$$n(E)\,dE = A4\pi v^2 e^{-mv^2/2k_B T}\,dv$$

where the constant C has been absorbed into the normalization coefficient A. Since the number of molecules with energy between E and $E + dE$ equals the number of molecules with speed between v and $v + dv$, we may write

$$n(E)\,dE = n(v)\,dv = A4\pi v^2 e^{-mv^2/2k_B T}\,dv \tag{10.10}$$

To find A we use the fact that the total number of particles per unit volume is N/V:

$$\frac{N}{V} = \int_0^\infty n(v)\,dv = \int_0^\infty 4\pi A v^2 e^{-mv^2/2k_BT}\,dv \tag{10.11}$$

Because

$$\int_0^\infty z^{2j} e^{-az^2}\,dz = \frac{1\cdot 3\cdot 5\cdots(2j-1)}{2^{j+1}a^j}\sqrt{\frac{\pi}{a}} \qquad j = 1, 2, 3, \ldots$$

we find with $j = 1$ and $a = m/2k_BT$

$$\frac{N}{V} = \frac{(4\pi A)}{2^2(m/2k_BT)}\sqrt{\frac{\pi 2k_BT}{m}} = A\left(\frac{2\pi k_BT}{m}\right)^{3/2}$$

or

$$A = \frac{N}{V}\left(\frac{m}{2\pi k_BT}\right)^{3/2}$$

Therefore, the normalization coefficient A depends on the number of particles per unit volume, the particle mass, and the temperature. Substituting this value for A into Equation 10.10, we finally obtain Maxwell's famous 1859 result:

$$n(v)\,dv = \frac{4\pi N}{V}\left(\frac{m}{2\pi k_BT}\right)^{3/2} v^2 e^{-mv^2/2k_BT}\,dv \tag{10.8}$$

To find the average speed, $\overline{v}$, indicated in Figure 10.4, we multiply $n(v)\,dv$ by v, integrate over all speeds from 0 to ∞, and divide the result by the total number of molecules per unit volume:

$$\overline{v} = \frac{\displaystyle\int_0^\infty v n(v)\,dv}{N/V} = \frac{4\pi(N/V)(m/2\pi k_BT)^{3/2}\displaystyle\int_0^\infty v^3 e^{-mv^2/2k_BT}\,dv}{N/V}$$

Using the definite integral formula

$$\int_0^\infty z^3 e^{-az^2}\,dz = \frac{1}{2a^2}$$

gives

$$\overline{v} = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}\left(\frac{1}{2}\right)\left(\frac{2k_BT}{m}\right)^2 = \sqrt{\frac{8k_BT}{\pi m}} \tag{10.12}$$

This important result, first proved by Maxwell, shows that the average speed of the molecules in a gas is proportional to the square root of the temperature and inversely proportional to the square root of the molecular mass. The root mean square speed may be found by finding the average of v^2, denoted $\overline{v^2}$, and then taking its square root. Consequently, we have

$$\overline{v^2} = \frac{\displaystyle\int_0^\infty v^2 n(v)\,dv}{N/V} = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}\int_0^\infty v^4 e^{-mv^2/2k_BT}\,dv$$

Using the definite integral formula

$$\int_0^\infty z^4 e^{-az^2}\,dz = \frac{3}{8a^2}\sqrt{\frac{\pi}{a}}$$

gives

$$\overline{v^2} = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\left[\frac{3}{8(m/2k_B T)^2}\right]\left(\frac{2\pi k_B T}{m}\right)^{1/2} = \frac{3k_B T}{m} \qquad (10.13)$$

Since the root mean square speed, v_{rms}, is defined as $v_{\text{rms}} = \sqrt{\overline{v^2}}$, we have

$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}} \qquad (10.14)$$

Note that v_{rms} is *not* the same as the average speed, $\overline{v}$, but is about 10% greater, as indicated in Figure 10.4. The derivation of the most probable speed, v_{mp}, is left to Problem 2.

The Equipartition of Energy

As a final remark to this section, we observe that Equation 10.13 may be rewritten as

$$\tfrac{1}{2}m\overline{v^2} = \overline{K} = \tfrac{3}{2}k_B T$$

In this form, Equation 10.13 is consistent with the result known as the **equipartition of energy,** or the **equipartition theorem.** According to this theorem, **a classical molecule in thermal equilibrium at temperature T has an average energy of $k_B T/2$ for each independent mode of motion or so-called degree of freedom.** In this case there are 3 degrees of freedom corresponding to translational motion of the molecule along the independent x, y, and z directions in space; hence the average kinetic energy in each independent direction is $k_B T/2$:

Equipartition of energy

$$\tfrac{1}{2}m\overline{v_x^2} = \tfrac{1}{2}m\overline{v_y^2} = \tfrac{1}{2}m\overline{v_z^2} = \tfrac{1}{2}k_B T$$

The total average kinetic energy consequently equals 3 times $k_B T/2$, in agreement with Equation 10.13:

$$\tfrac{1}{2}m\overline{v^2} = \tfrac{1}{2}m\overline{v_x^2} + \tfrac{1}{2}m\overline{v_y^2} + \tfrac{1}{2}m\overline{v_z^2} = \tfrac{3}{2}k_B T$$

Note that degrees of freedom are not only associated with translational velocities. A degree of freedom is also associated with each rotational velocity as well so that $\frac{1}{2}I_1\overline{\omega_1^2} = \frac{1}{2}k_B T$ for a molecule with moment of inertia I_1 rotating about an axis with angular velocity ω_1. In fact, **each variable that occurs squared in the formula for the energy of a particular system represents a degree of freedom subject to the equipartition of energy.** For example, a one-dimensional harmonic oscillator with $E = \frac{1}{2}mv_x^2 + \frac{1}{2}kx^2$ has 2 degrees of freedom, one associated with its kinetic energy and the variable v_x^2 and the other with its potential energy and the variable x^2. Thus, each oscillator in a group in thermal equilibrium at T has $\overline{K} = \frac{1}{2}m\overline{v_x^2} = \frac{1}{2}k_B T$ and $\overline{U} = \frac{1}{2}k\overline{x^2} = \frac{1}{2}k_B T$. The average total energy of each one-dimensional harmonic oscillator is then $\overline{E}_{\text{total}} = \overline{K} + \overline{U} = k_B T/2 + k_B T/2 = k_B T$. This result will be of use to us shortly when we model the atoms of a solid as a system of vibrating harmonic oscillators.

Exercise 1 (a) Show that the formula for the number of molecules with energies between E and $E + dE$ in an ideal gas at temperature T is given explicitly in terms of E by

$$n(E)\,dE = \frac{2\pi(N/V)}{(\pi k_B T)^{3/2}} E^{1/2} e^{-E/k_B T}\,dE$$

(b) Use this result to show that the total energy per unit volume of the gas is given by

$$E_{\text{total}} = \frac{3}{2}\frac{NkT}{V}$$

in agreement with the equipartition theorem.

Exercise 2 Confirm Maxwell's 1859 result that the "spread-outness" of the speed distribution increases as $\sqrt{T}$. Do this by showing that the standard deviation of the molecular speeds is given by

$$\sigma_v = \sqrt{3 - \frac{8}{\pi}} \cdot \sqrt{\frac{k_B T}{m}}$$

10.2 UNDER WHAT PHYSICAL CONDITIONS ARE MAXWELL–BOLTZMANN STATISTICS APPLICABLE?

If we reexamine the assumptions that led to the Maxwell–Boltzmann distribution for classical particles, keeping the quantum mechanical wave nature of particles in mind, we immediately find a problem with the assumption of distinguishability. Since particles exhibit wave-like behavior, they are necessarily fuzzy and are not distinguishable when they are close together because their wavefunctions overlap. (See Section 9.4, "Exchange Symmetry and the Exclusion Principle," for a review of this issue.) If trading molecule A for molecule B no longer counts as a different configuration, then the number of ways a given energy distribution can be realized changes, as does the equilibrium or most probable distribution. Thus the classical Maxwell–Boltzmann distribution must be replaced by a quantum distribution when there is wavefunction overlap or when the particle concentration is high. The MB distribution is a valid approximation to the correct quantum distribution, however, in the common case of gases at ordinary conditions. Quantum statistics are required for cases involving high particle concentrations, such as electrons in a metal[1] or photons in a blackbody cavity.

It is useful to develop a criterion to determine when the classical distribution is valid. We may say that the **Maxwell–Boltzmann distribution is valid when the average distance between particles, d, is large compared with the quantum uncertainty in particle position, Δx, or**

$$\Delta x \ll d \tag{10.15}$$

To find Δx we use the uncertainty principle and evaluate Δp_x for a particle of mass m. For such a particle that is part of a system of particles in thermal

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[1] The density of conduction electrons in a metal is several thousand times the density of molecules in a gas at standard temperature and pressure.

equilibrium at temperature T, $\overline{p_x} = 0$ and $\overline{p_x^2}/2m = k_BT/2$ from the equipartition theorem. Thus

$$\Delta p_x = \sqrt{\overline{p_x^2} - (\overline{p_x})^2} = \sqrt{mk_BT} \tag{10.16}$$

Substituting this expression for Δp_x into $\Delta p_x \, \Delta x \geq \hbar/2$, we find

$$\Delta x \geq \frac{\hbar}{2\sqrt{mk_BT}} \tag{10.17}$$

As mentioned before, the uncertainty in particle position, Δx, must be much less than the average distance, d, between particles if the particles are to be distinguishable and the Maxwell–Boltzmann distribution is to hold. Substituting $d = (V/N)^{1/3}$ and $\Delta x = \hbar/2\sqrt{mk_BT}$ into the relation $\Delta x \ll d$ gives

$$\frac{\hbar}{2\sqrt{mk_BT}} \ll \left(\frac{V}{N}\right)^{1/3}$$

or cubing both sides,

$$\left(\frac{N}{V}\right)\frac{\hbar^3}{8(mk_BT)^{3/2}} \ll 1 \tag{10.18}$$

Criterion for the validity of Maxwell–Boltzmann statistics

Equation 10.18 shows that the Maxwell–Boltzmann distribution holds for low particle concentration and for high particle mass and temperature.

EXAMPLE 10.2 When Can We Use Maxwell–Boltzmann Statistics?

(a) Are Maxwell–Boltzmann statistics valid for hydrogen gas at standard temperature and pressure (STP)?

Solution Under standard conditions of 273 K and 1 atmosphere, 1 mol of H_2 gas (6.02×10^{23} molecules) occupies a volume of $22.4 \times 10^{-3}\ \text{m}^3$. Using $m_{H_2} = 3.34 \times 10^{-27}$ kg, and $k_BT = 3.77 \times 10^{-21}$ J, we find

$$\left(\frac{N}{V}\right)\frac{\hbar^3}{8(mk_BT)^{3/2}} = \left(\frac{6.02 \times 10^{23}}{22.4 \times 10^{-3}\ \text{m}^3}\right) \times \frac{(1.055 \times 10^{-34})^3\ (\text{J}\cdot\text{s})^3}{8[(3.34 \times 10^{-27}\ \text{kg})(3.77 \times 10^{-21}\ \text{J})]^{3/2}} = 8.83 \times 10^{-8}$$

This is much less than 1, and from the condition given by Equation 10.18, we conclude that even hydrogen, the lightest gas, is described by Maxwell–Boltzmann statistics.

(b) Are Maxwell–Boltzmann statistics valid for conduction electrons in silver at 300 K?

Solution Silver has a density of $10.5\ \text{g/cm}^3$ and a molar weight of 107.9 g. Assuming one free electron per silver atom, the density of free electrons in silver is found to be

$$\frac{10.5\ \text{g/cm}^3}{107.9\ \text{g/mol}}(6.02 \times 10^{23}\ \text{electrons/mol}) = 5.86 \times 10^{22}\ \text{electrons/cm}^3 = 5.86 \times 10^{28}\ \text{electrons/m}^3$$

Note that the density of free electrons in silver is about 2000 times greater than the density of hydrogen gas molecules at STP; that is,

$$\frac{(N/V)\text{electrons in Ag}}{(N/V)_{H_2\ \text{at STP}}} = \frac{5.86 \times 10^{28}\ \text{m}^{-3}}{2.69 \times 10^{25}\ \text{m}^{-3}} = 2180$$

Using $\hbar^3 = 1.174 \times 10^{-102}\ (\text{J}\cdot\text{s})^3$, $m_e = 9.109 \times 10^{-31}$ kg, and $k_BT = 4.14 \times 10^{-21}$ J (at $T = 300$ K), we find

$$\left(\frac{N}{V}\right)\frac{\hbar^3}{8(m_ek_BT)^{3/2}} = 4.64$$

Comparing this result to the condition given by Equation 10.18, we conclude that the Maxwell–Boltzmann distribution *does not hold* for electrons in silver because of the small mass of the electron and the high free electron density. We shall see that the correct quantum distribution for electrons is the Fermi–Dirac distribution.

10.3 QUANTUM STATISTICS

Wavefunctions and the Bose–Einstein Condensation and Pauli Exclusion Principle

Maxwell–Boltzmann statistics apply to systems of *identical, distinguishable* particles. As mentioned in the previous section, in quantum terms this means the wavefunctions of the particles do not overlap. If the individual particle wavefunctions do overlap, then the particles become indistinguishable or interchangeable, and this forces the system wavefunction to be either even or odd under particle exchange (see Section 9.4). In order to understand the important connection between wavefunctions and distribution functions, as well as the origin of the Bose–Einstein condensation for a system of particles with no actual attractive physical forces between particles, we look at a simple system of two particles with two possible quantum states to expose the essential features.

Consider two independent particles—particle 1 located at the position $\mathbf{r}_1$ and particle 2 located at $\mathbf{r}_2$—and two quantum states—state a and state b. For distinguishable particles there exist two possible system wavefunctions, which are simple products of normalized single particle wavefunctions:

$$\psi_A = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)$$

$$\psi_B = \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)$$

Now we ask for the probability that both particles are in the same state, say a. In this case, both ψ_A and ψ_B are the same, and we find the probability of two distinguishable particles described by the Maxwell–Boltzmann distribution to be in the same state to be given by

$$\psi_{MB}^* \psi_{MB} = \psi_a^*(\mathbf{r}_1)\psi_a^*(\mathbf{r}_2)\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2) = |\psi_a(\mathbf{r}_1)|^2\,|\psi_a(\mathbf{r}_2)|^2$$

If the particles are *indistinguishable*, we can't tell if a given particle is in state a or b, and to reflect this fact, the system wavefunction must be a *combination* of the distinguishable wavefunctions ψ_A and ψ_B. As mentioned in Section 9.4 and Problem 9.16, bosons have a symmetric wavefunction, ψ_B, given by

$$\psi_B = \frac{1}{\sqrt{2}}\left[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)\right]$$

where we have added $\frac{1}{\sqrt{2}}$ as the normalization constant. Fermions have an antisymmetric wavefunction ψ_F, where

$$\psi_F = \frac{1}{\sqrt{2}}\left[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) - \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)\right]$$

For comparison to the case of distinguishable particles, we now recalculate the probability that two bosons or fermions occupy the *same* state. For bosons the wavefunction becomes

$$\psi_B = \frac{1}{\sqrt{2}}\left[\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2) + \psi_a(\mathbf{r}_2)\psi_a(\mathbf{r}_1)\right] = \sqrt{2}\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2)$$

and the probability for two bosons to be in the same state is

$$\psi_B^*\psi_B = 2|\psi_a(\mathbf{r}_1)|^2\,|\psi_a(\mathbf{r}_2)|^2 = 2\psi_{MB}^*\,\psi_{MB}$$

Thus we have the amazing result that bosons are twice as probable to occupy the same state as distinguishable particles! This is an entirely quantum mechanical effect and it is *as if* there were a force attracting additional bosons once a boson occupies a state, even though there are no actual attractive physical forces, such as electromagnetic intermolecular forces, present. Einstein was the first to point out that an *ideal* gas of bosons (with no attractive intermolecular forces!) could still undergo a strange kind of condensation at low-enough temperatures called a **Bose–Einstein condensation (BEC).** A Bose–Einstein condensation is a single cooperative state with all individual particle wavefunctions in phase in the ground state. In 1995 Einstein's prediction was directly confirmed by a group at the University of Colorado led by Eric Cornell and Carl Wieman who observed a BEC in a cloud of rubidium atoms cooled to less than 100 nK (see the guest essay by Steven Chu at the end of this chapter for details).

For fermions, as in Chapter 9, we find a probability of zero for two fermions to be in the same state since the wavefunction is zero:

$$\psi_F = \frac{1}{\sqrt{2}}\left[\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2) - \psi_a(\mathbf{r}_2)\psi_a(\mathbf{r}_1)\right] = 0$$

This is just the Pauli exclusion principle again.

Bose–Einstein and Fermi–Dirac Distributions

As we have seen there are two distributions for indistiguishable particles that flow from parity requirements on the system wavefunctions, the **Bose–Einstein distribution** and the **Fermi–Dirac distribution.** To obtain the Bose–Einstein distribution, we retain the MB assumption of no theoretical limit on the number of particles per state. Particles that obey the Bose–Einstein distribution are called **bosons** and are observed to have **integral spin.** Some examples of bosons are the alpha particle ($S = 0$), the photon ($S = 1$), and the deuteron ($S = 1$). To obtain the Fermi–Dirac distribution we stipulate that only one particle can occupy a given quantum state. Particles that obey the Fermi–Dirac distribution are called **fermions** and are observed to have **half integral spin.** Some important examples of fermions are the electron, the proton, and the neutron, all with spin $\frac{1}{2}$.

To see the essential changes in the distribution function introduced by quantum statistics, let us return to our simple system of six particles with a total energy of $8E$. First we consider the Bose–Einstein case; the particles are indistinguishable and there is no limit on the number of particles in a particular energy state. Figure 10.1a was drawn to represent this situation. Since the particles are indistinguishable, each of the 20 arrangements shown in Figure 10.1a is equally likely, so the probability of each arrangement is 1/20. The average number of particles in a particular energy level may be calculated by again using Equation 10.2. The average number of particles in the zero energy level is found to be

$$\begin{aligned}\overline{n_0} = {} & (5)(1/20) + (4)(1/20) + (4)(1/20) + (3)(1/20) + (4)(1/20)\\ & + (3)(1/20) + (2)(1/20) + (4)(1/20) + (3)(1/20) + (3)(1/20)\\ & + (2)(1/20) + (1)(1/20) + (3)(1/20) + (2)(1/20) + (2)(1/20)\\ & + (1)(1/20) + (0)(1/20) + (2)(1/20) + (1)(1/20) + (0)(1/20)\\ = {} & 49/20 = 2.45\end{aligned}$$

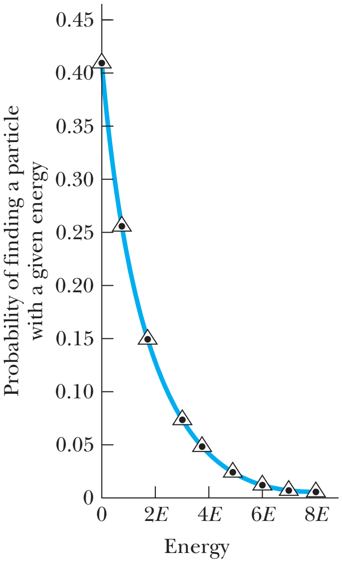

Figure 10.6 The distribution function for six indistinguishable particles with total energy 8*E* (bosons).

Similarly, we find $\overline{n_1} = 31/20 = 1.55$, $\overline{n_2} = 18/20 = 0.90$, $\overline{n_3} = 9/20 = 0.45$, $\overline{n_4} = 6/20 = 0.30$, $\overline{n_5} = 3/20 = 0.15$, $\overline{n_6} = 2/20 = 0.10$, $\overline{n_7} = 1/20 = 0.05$, and $\overline{n_8} = 0.05$. Once again using the idea that the probability of finding a particle with a given energy, $p(E)$, is simply the average number of particles with that energy divided by the total number of particles, we find

$$p(0) = \frac{\overline{n_0}}{6} = \frac{2.45}{6} = 0.408$$

In like manner we find: $p(1E) = 0.258$, $p(2E) = 0.150$, $p(3E) = 0.0750$, $p(4E) = 0.0500$, $p(5E) = 0.0250$, $p(6E) = 0.0167$, $p(7E) = 0.00833$, and $p(8E) = 0.00833$. A plot of these values in Figure 10.6 shows that the Bose–Einstein distribution gives results similar, but not identical, to the Maxwell–Boltzmann distribution. In general, the Bose–Einstein distribution tends to have more particles in the lowest energy levels. At higher energies, the curves come together and both exhibit a rapid decrease in probability with increasing energy.

To illustrate the distinctive shape of the Fermi–Dirac distribution, again consider our simple example of six indistinguishable particles with energy 8*E*. Since the particles are fermions, we impose the constraint that no more than two particles can be assigned to a given energy state (corresponding to electrons with spin up and down). There are only three arrangements (denoted by FD) out of the 20 shown in Figure 10.1a that meet this additional constraint imposed by the Pauli exclusion principle. Since each of these arrangements is equally likely, each has a probability of occurrence of 1/3, and we again use Equation 10.2 to calculate the average number of fermions in the zero energy level, as follows:

$$\overline{n_0} = (2)(1/3) + (2)(1/3) + (2)(1/3) = 2.00$$

Similarly, we find for the average number of fermions with energies of 1*E* through 8*E* the following:

$$\overline{n_1} = 5/3 = 1.67, \overline{n_2} = 3/3 = 1, \overline{n_3} = 3/3 = 1, \overline{n_4} = 1/3 = 0.33,$$
$$\overline{n_5} = \overline{n_6} = \overline{n_7} = \overline{n_8} = 0$$

Finally, we obtain the probabilities of finding a fermion with energies 0 through 8*E*:

$$p(0) = 2.00/6 = 0.333, p(1E) = 0.278, p(2E) = 0.167, p(3E) = 0.167,$$
$$p(4E) = 0.0550, \text{and } p(5E) = p(6E) = p(7E) = p(8E) = 0$$

When this distribution is plotted, we discover a distinctly different shape from the Maxwell–Boltzmann or Bose–Einstein curves (Fig. 10.7). The results show a leveling off of probability at both low and high energies. Although it is not entirely clear that the points plotted in Figure 10.7 conform to the smooth curve drawn, consideration of systems with more than six particles proves this to be the case (see Problem 10.11).

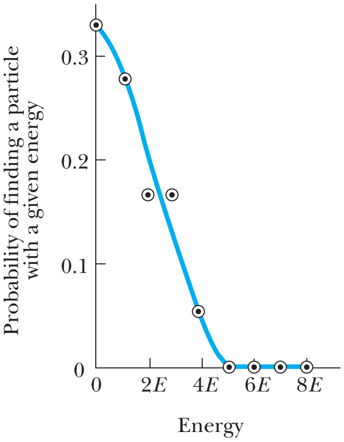

Figure 10.7 The distribution function for six indistinguishable particles with total energy 8*E* constrained so that no more than two particles occupy the same energy state (fermions).

When large numbers of quantum particles are considered, *continuous* distribution functions may be rigorously derived for both the Bose–Einstein (BE) and Fermi–Dirac (FD) cases. By maximizing the number of ways of distributing the indistinguishable quantum particles among the allowed energy states, again subject to the two constraints of a fixed number of particles and a fixed total energy, we find the distribution functions to have the explicit forms:

$$f_{\mathrm{BE}}(E) = \frac{1}{Be^{E/k_{\mathrm{B}}T} - 1} \tag{10.19}$$

$$f_{\mathrm{FD}}(E) = \frac{1}{He^{E/k_{\mathrm{B}}T} + 1} \tag{10.20}$$

where $f(E)$ is the probability of finding a particle in a particular state of energy E at a given absolute temperature T. As noted earlier, the number of particles per unit volume with energy between E and $E + dE$ is given by

$$n(E)\ dE = g(E) f_{\mathrm{BE}}(E)\ dE \tag{10.21}$$

or

$$n(E)\ dE = g(E) f_{\mathrm{FD}}(E)\ dE \tag{10.22}$$

Thus the parameters B and H in Equations 10.19 and 10.20 may be determined from the total number of particles, N, since integrating Equations 10.21 and 10.22 yields

$$\left(\frac{N}{V}\right)_{\text{bosons}} = \int_0^\infty \frac{g(E)}{Be^{E/k_{\mathrm{B}}T} - 1}\, dE \tag{10.23}$$

and

$$\left(\frac{N}{V}\right)_{\text{fermions}} = \int_0^\infty \frac{g(E)}{He^{E/k_{\mathrm{B}}T} + 1}\, dE \tag{10.24}$$

In general we find that B and H depend on the system temperature and particle density as shown by Equations 10.23 and 10.24. For a system of bosons that are not fixed in number with temperature, Equation 10.23 no longer serves to determine B. By maximizing the ways of distributing the bosons among allowed states subject to the single constraint of fixed energy, it can be shown that the coefficient B in Equation 10.19 is equal to 1. This is a particularly important case since both photons in a blackbody cavity and phonons in a solid are bosons whose numbers per unit volume increase with increasing temperature. (We define phonons shortly.) Thus,

$$f(E) = \frac{1}{e^{E/k_{\mathrm{B}}T} - 1} \qquad \text{(for photons or phonons)}$$

For the case of the Fermi–Dirac distribution, H depends strongly on temperature and is often written in an explicitly temperature-dependent form as $H = e^{-E_{\mathrm{F}}/k_{\mathrm{B}}T}$, where E_{F} is called the **Fermi energy.**[2] With this substitution, Equation 10.20 changes to the more common form

$$f_{\mathrm{FD}}(E) = \frac{1}{e^{(E-E_{\mathrm{F}})/k_{\mathrm{B}}T} + 1} \tag{10.25}$$

Fermi–Dirac distribution

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[2] If we force the functional form of H to be $H = e^{-E_{\mathrm{F}}/k_{\mathrm{B}}T}$, E_{F} will itself have a weak dependence on T. Fortunately, this dependence of E_{F} on T is so weak that we can ignore it here.

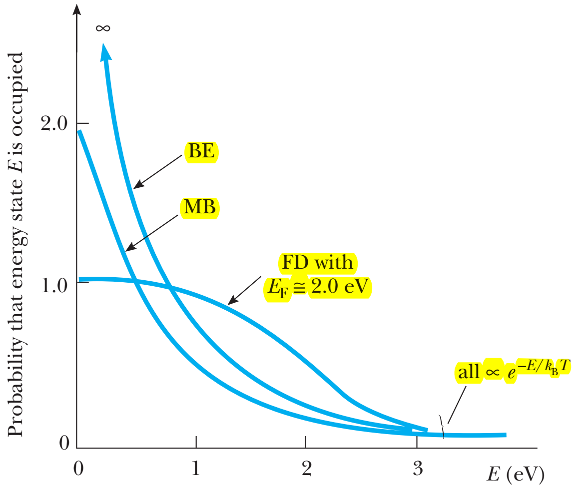

Figure 10.8 A comparison of Maxwell–Boltzmann, Bose–Einstein, and Fermi–Dirac distribution functions at 5000 K.

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This expression shows the meaning of the Fermi energy: The probability of finding an electron with an energy equal to the Fermi energy is exactly 1/2 at any temperature.

A plot comparing the Maxwell–Boltzmann, Bose–Einstein, and Fermi–Dirac distributions as functions of energy at a common temperature of 5000 K is shown in Figure 10.8. Note that for large E, all occupation probabilities decrease to zero as e^{-E/k_BT}. For small values of E, the FD probability saturates at 1 as required by the exclusion principle, the MB probability constantly increases but remains finite, and the BE probability tends to infinity. This very high probability for bosons to have low energies means that at low temperatures most of the particles drop into the ground state. When this happens, a new phase of matter with different physical properties can occur. This change in phase for a system of bosons is called a **Bose–Einstein condensation (BEC),** and it occurs in liquid helium at a temperature of 2.18 K. Below 2.18 K liquid helium becomes a mixture of the normal liquid and a phase with all molecules in the ground state. The ground-state phase, called liquid helium II, exhibits many interesting properties, one being zero viscosity. For more on Bose condensation and applications of this remarkable state of matter, see the essay by Steven Chu at the end of this chapter.

The history of the discovery of the quantum distributions is interesting. The first quantum distribution to be discovered was the Bose–Einstein function introduced in 1924 by Satyendranath Bose (Indian physicist, 1894–1974), working in isolation. He sent his paper, which contained a new proof of the Planck formula for blackbody radiation, to Einstein. In this paper, Bose applied the normal methods of statistical mechanics to light quanta but treated the quanta as absolutely indistinguishable. Einstein was impressed by Bose's work and proceeded to translate the paper into German for publication in the *Zeitschrift für Physik.*[3] To obtain the quantum theory of the ideal gas,

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[3] S. N. Bose, *Z. Phys.,* 26:178, 1924.

Einstein extended the method to molecules in several papers published in 1924 and 1925.

The exclusion principle

In 1925, Wolfgang Pauli, after an exhaustive study of the quantum numbers assigned to atomic levels split by the Zeeman effect, announced his new and fundamental principle of quantum theory, the exclusion principle: Two electrons in an atom cannot have the same set of quantum numbers. In 1926, Enrico Fermi obtained the second type of quantum statistics that occurs in nature by combining Pauli's exclusion principle with the requirement of indistinguishability. Paul Dirac is also credited for this work, since he performed a more rigorous quantum mechanical treatment of these statistics in 1926. The empirical observation that particles with integral spin obey BE statistics and particles with half-integral spin obey FD statistics was explained much later (in 1940) by Pauli, using relativity and causality arguments.

10.4 APPLICATIONS OF BOSE–EINSTEIN STATISTICS

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Blackbody Radiation

In this section we apply BE statistics to the problem of determining the energy density (energy per unit volume) of electromagnetic radiation in an enclosure heated to temperature T, now treating the radiation as a gas of photons. (In Chapter 3 we discussed the importance of this blackbody problem for quantum physics.) Since photons have spin 1, they are bosons and follow Bose–Einstein statistics. The number of photons per unit volume with energy between E and $E + dE$ is given by $n(E)\ dE = g(E)f_{\mathrm{BE}}(E)\ dE$. The *energy density* of photons in the range from E to $E + dE$ is

$$u(E)\ dE = En(E)\ dE = \frac{g(E)E\ dE}{e^{E/k_{\mathrm{B}}T} - 1} \tag{10.26}$$

To complete our calculation, we need the factor $g(E)$, the density of states for photons in an enclosure. This important calculation, given in Web Appendix 1 on our Web site, shows that the number of photon states per unit volume with frequencies between f and $f + df$ is

$$N(f)\ df = \frac{8\pi f^2\ df}{c^3} = \frac{8\pi(hf)^2\ d(hf)}{(hc)^3} = \frac{8\pi E^2\ dE}{(hc)^3}$$

using $E = hf$ for photons. Since the number of photon states per unit volume with frequencies between f and $f + df$ is equal to the number of photon states with energies between E and $E + dE$, we have

$$N(f)\ df = \frac{8\pi E^2\ dE}{(hc)^3} = g(E)\ dE$$

Thus we find that the density of states for photons is

$$g(E) = \frac{8\pi E^2}{(hc)^3} \tag{10.27}$$

Substituting Equation 10.27 into Equation 10.26 gives the expression for the energy density:

$$u(E)\ dE = \frac{8\pi}{(hc)^3}\,\frac{E^3\ dE}{e^{E/k_{\mathrm{B}}T} - 1} \tag{10.28}$$

Converting from photon energy to frequency using $E = hf$ in Equation 10.28, we immediately retrieve the Planck blackbody formula:

$$u(f, T) = \frac{8\pi h}{c^3}\,\frac{f^3}{e^{hf/k_{\mathrm{B}}T} - 1} \tag{3.9}$$

Thus the Planck formula for a blackbody follows directly and simply from Bose–Einstein statistics.

EXAMPLE 10.3 Photons in a Box

(a) Find an expression for the number of photons per unit volume with energies between E and $E + dE$ in a cavity at temperature T.

Solution

$$n(E)\ dE = g(E)f(E)\ dE = \frac{8\pi E^2\ dE}{(hc)^3(e^{E/k_{\mathrm{B}}T} - 1)}$$

(b) Find an expression for the total number of photons per unit volume (all energies).

Solution

$$\frac{N}{V} = \int_0^\infty n(E)\ dE = \frac{8\pi(k_{\mathrm{B}}T)^3}{(hc)^3}\int_0^\infty \frac{(E/k_{\mathrm{B}}T)^2(dE/k_{\mathrm{B}}T)}{e^{E/k_{\mathrm{B}}T} - 1}$$

or

$$\frac{N}{V} = 8\pi\left(\frac{k_{\mathrm{B}}T}{hc}\right)^3 \int_0^\infty \frac{z^2\ dz}{e^z - 1}$$

(c) Calculate the number of photons/cm^3 inside a cavity whose walls are heated to 3000 K. Compare this with a cavity whose walls are at 3.00 K.

Solution From standard tables,

$$\int_0^\infty \frac{z^2\ dz}{e^z - 1} \approx 2.40$$

Therefore,

$$\frac{N}{V}\text{ (at 3000 K)} = (8\pi)\left[\frac{(8.62 \times 10^{-5}\ \text{eV/K})(3000\ \text{K})}{1.24 \times 10^{-4}\ \text{eV}\cdot\text{cm}}\right]^3 \cdot (2.40)$$

$$= 5.47 \times 10^{11}\ \text{photons/cm}^3$$

Likewise, N/V (at 3.00 K) $= 5.47 \times 10^2$ photons/cm^3. Therefore, the photon density decreases by a factor of 10^9 when the temperature drops from 3000 K to 3.00 K.

Einstein's Theory of Specific Heat

Recall that the molar specific heat of a substance, C, is the ratio of the differential thermal energy, dU, added to a mole of substance divided by the resulting differential increase in temperature, dT, or

$$C = \frac{dU}{dT} \tag{10.29}$$

Thus C has units of calories per mole per kelvin (cal/mol·K). To develop a theoretical expression for comparison to the experimental curves of C versus T measured for different elemental solids, we need an expression for U, the internal thermal energy of the solid, as a function of the solid's temperature, T. Differentiation of this expression will then yield the specific heat as a function of temperature.

To find an expression for U, let us model the solid as a collection of atoms vibrating *independently* on springs with equal force constants in the x, *y*, and *z* directions, each atom being represented by three identical one-dimensional harmonic oscillators. The internal energy of each atom may then be calculated from the classical equipartition theorem. A one-dimensional harmonic oscillator has 2 degrees of freedom: one for its kinetic energy and one for its potential energy. (Physically this means that thermal energy added to the atoms in a solid may go into atomic vibration or into work done to stretch the springs holding the atoms in place.) Because the equipartition theorem states that the average thermal energy per degree of freedom should be $k_B T/2$, the internal energy per atom of a solid should be ($k_B T/2$ per degree of freedom) × (2 degrees of freedom per one-dimensional oscillator) × (three oscillators per atom) $= 3k_B T$. As a mole contains Avogadro's number of atoms, N_A, the total internal energy per mole, U, is predicted to be

$$U = 3N_A k_B T = 3RT \tag{10.30}$$

where R is the universal gas constant given by $R = N_A k_B = 8.31\ \text{J/mol}\cdot\text{K} = 1.99\ \text{cal/mol}\cdot\text{K}$. Using $C = dU/dT$, we immediately see that C should be constant with temperature:

$$C = \frac{d}{dT}(3RT) = 3R = 5.97\ \text{cal/mol}\cdot\text{K} \tag{10.31}$$

The specific heat of many solids is indeed constant with temperature, especially at higher temperatures, as can be seen in Figure 10.9, showing good agreement with the classical idea that the average thermal energy is $k_B T/2$ per degree of freedom. However, as can also be seen in Figure 10.9, the specific heat of all solids drops sharply at some temperature and approaches zero as the temperature approaches 0 K.

The explanation of why classical physics failed to give the correct value of specific heat at all temperatures was given by Einstein in 1907. He realized that the quantized energies of vibrating atoms in a solid must be explicitly considered at low temperatures to secure agreement with experimental measurements of specific heat. Einstein assumed that the atoms of the solid

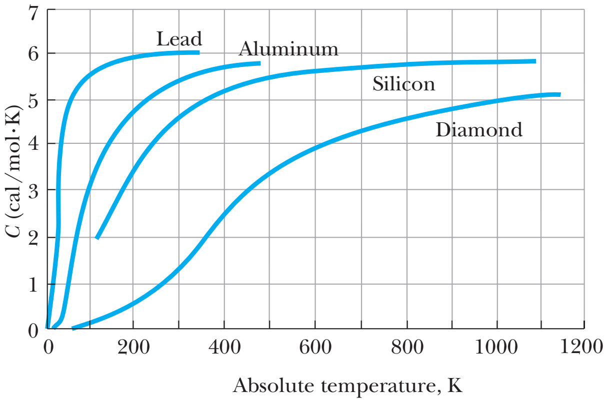

Figure 10.9 The dependence of specific heat on temperature for several solid elements.

could be modeled as a system of *independent* or *uncoupled* three-dimensional *quantum* harmonic oscillators with equal spring constants in the x, y, and z directions. He then showed that the average energy of a *one-dimensional* oscillator with frequency ω at temperature T was given by the Bose–Einstein distribution, or

$$\overline{E} = \frac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1}$$

Because the atoms are considered to be independent, he gave the internal energy of a mole of atoms, or N_A atoms, as

$$U = 3N_A\overline{E} = 3N_A\frac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1}$$

Finally, he obtained the molar specific heat:

$$C = \frac{dU}{dT} = 3R\left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{e^{\hbar\omega/k_BT}}{(e^{\hbar\omega/k_BT} - 1)^2} \tag{10.32}$$

It is left as an exercise to show that Equation 10.32 predicts that C approaches zero for small T as $e^{-\hbar\omega/k_BT}$, and that C approaches $3R$ for large T.

To understand Equation 10.32 qualitatively, consider the quantity $\overline{E}$, the average one-dimensional quantum oscillator energy at temperature, T:

$$\overline{E} = \frac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1} \tag{10.33}$$

Recall that the vibrating atoms of the solid have quantized energy levels spaced $\hbar\omega$ apart. For high temperatures such that $\hbar\omega \ll k_BT$, the energy level spacing $\hbar\omega$ is small relative to the average thermal energy per atom, and we can expect many atoms to be in excited energy levels. In fact, we can expand the exponential in the denominator of Equation 10.33 as $\exp(\hbar\omega/k_BT) = 1 + \hbar\omega/k_BT + \cdots$ to get

$$\overline{E} = \frac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1} \approx k_BT$$

In this case the atomic energies appear to be continuous and the classical result $C = 3R$ holds. For low temperatures such that $\hbar\omega \gg k_BT$, Equation 10.33 shows that the average thermal energy of an oscillator rapidly tends to zero. This means the average energy is much less than the spacing between adjacent atomic energy levels, $\hbar\omega$, and there is insufficient thermal energy to raise an atom out of its ground state to higher energy levels. In this case atoms are unable to absorb energy from the surroundings for a small increase in temperature, and the increase in internal energy with temperature or specific heat tends to zero.

A final point to note is that Equation 10.32 has only one adjustable parameter, ω, the harmonic oscillator vibration frequency, which is chosen to give the best fit of Equation 10.32 to the experimental heat capacity data. Frequently, ω is given in terms of an equivalent temperature T_E, called the **Einstein temperature,** where

$$\hbar\omega = k_BT_E \tag{10.34}$$

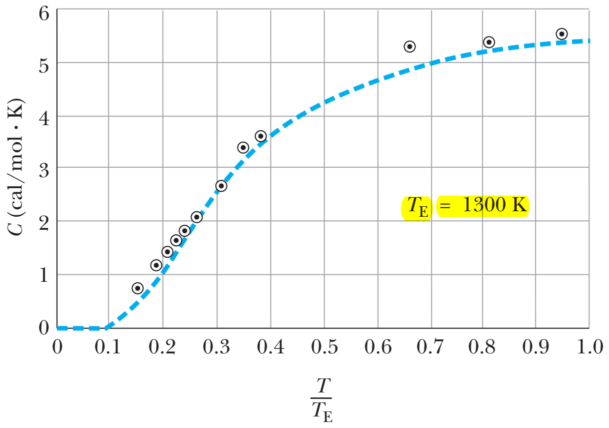

Figure 10.10 Einstein's specific heat formula fitted to Weber's experimental data for diamond. This figure is adapted from A. Einstein, *Ann. Physik.*, 4(22):180, 1907.

In his pioneering 1907 paper, Einstein found good agreement between his formula and Heinrich Weber's data on diamond, with $T_E = 1300$ K. This agreement is shown in Figure 10.10.

The too rapid falloff of the Einstein formula at low temperatures hinted at in Figure 10.10 was confirmed in 1911 by Hermann Nernst. Although it was generally felt that the problem with Einstein's result was the assumption that each atom vibrated independently of its neighbors at a single fixed frequency, no one really knew how to treat a band or spread of frequencies corresponding to groups of neighboring atoms interacting and moving together. In 1912, however, Peter Debye obtained the experimentally observed temperature dependence of $C \propto T^3$ for low temperatures by modeling a solid as a continuous elastic object whose internal energy was made up of the energy in standing sound (elastic) waves. These sound waves are both transverse and longitudinal in a solid and possess a range of frequencies from zero to some maximum value determined by the dependence of the minimum wavelength on the interatomic spacing. Furthermore, these elastic waves or lattice vibrations are *quantized,* like electromagnetic waves or photons. **A quantized elastic vibration of frequency ω, called a phonon, travels at the speed of sound in a solid, and carries a quantum of elastic energy $\hbar\omega$.** Debye was able to show that a "phonon gas" with a distribution of allowed frequencies was a better model of a solid at low temperatures than a system of independent harmonic oscillators all having the same frequency. Since the introduction of the idea of phonons by Debye, the concept has found many applications in condensed matter physics, including the electron–phonon interaction in superconductivity and the coupling of phonons to the motion of impurity atoms and molecules in a lattice.

Exercise 3 Show that Equation 10.32 predicts that C approaches zero for small T as $e^{-\hbar\omega/k_B T}$ and that C approaches $3R$ for large T.

EXAMPLE 10.4 The Specific Heat of Diamond

As we have seen, a solid at temperature T can be viewed as a system of quantized harmonic oscillators with discrete energy levels separated by $\hbar\omega$. The oscillators can only absorb thermal energy, however, if the temperature is high enough that the average thermal energy of the oscillator, $\overline{E}$, is approximately equal to the oscillator energy-level spacing, $\hbar\omega$. For low temperatures such that $\overline{E} \ll \hbar\omega$, there is so little thermal energy available that the atoms cannot even be raised to the first excited state and the specific heat tends to zero. In the following example we show that the carbon atoms in diamond are effectively decoupled from thermal energy at room temperature but can absorb energy at a temperature of 1500 K.

(a) Calculate the vibration frequency of the carbon atoms in diamond if the Einstein temperature is 1300 K. Also find the energy-level spacing for the carbon atoms.

Solution Since $\hbar\omega = k_B T_E$, the frequency of vibration of carbon atoms in diamond is

$$\omega = \frac{k_B T_E}{\hbar} = \frac{(8.62 \times 10^{-5}\ \text{eV/K})(1300\ \text{K})}{6.58 \times 10^{-16}\ \text{eV}\cdot\text{s}}$$

$$= 1.70 \times 10^{14}\ \text{Hz}$$

The spacing between adjacent oscillator energy levels in carbon is

$$\hbar\omega = (6.58 \times 10^{-16}\ \text{eV}\cdot\text{s})(1.70 \times 10^{14}\ \text{Hz}) = 0.112\ \text{eV}$$

(b) Calculate the average oscillator energy $\overline{E}$ at room temperature and at 1500 K and compare this energy with the carbon energy-level spacing $\hbar\omega$. Is there sufficient thermal energy on average to excite carbon atoms at 300 K? at 1500 K?

Solution The average oscillator energy at room temperature (300 K) is

$$\overline{E} = \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

$$= \frac{0.112\ \text{eV}}{e^{0.112\ \text{eV}/(8.62\times10^{-5}\ \text{eV/K})(300\ \text{K})} - 1} = 0.00149\ \text{eV}$$

while the average oscillator energy at 1500 K is

$$\overline{E} = \frac{0.112\ \text{eV}}{e^{0.112\ \text{eV}/(8.62\times10^{-5}\ \text{eV/K})(1500\ \text{K})} - 1} = 0.0813\ \text{eV}$$

Comparing, we see that $\overline{E}$ at 300 K is about $0.01\hbar\omega$, and $\overline{E}$ at 1500 K is approximately equal to $\hbar\omega$. This means that at 300 K most carbon atoms are frozen into the oscillator ground state and the specific heat tends to zero.

Exercise 4 (a) Calculate the vibration frequency of lead atoms and their energy-level spacing if the Einstein temperature of lead is 70 K. (b) Explain the low Einstein temperature of lead relative to that for diamond in terms of the physical properties of lead. (c) Calculate the average one-dimensional oscillator energy in lead at room temperature. Is there enough energy to raise lead atoms out of the ground state at 300 K?

10.5 AN APPLICATION OF FERMI–DIRAC STATISTICS: THE FREE ELECTRON GAS THEORY OF METALS

Because the outer electrons are weakly bound to individual atoms in a metal, we can treat these outer conduction electrons as a gas of fermions trapped within a cavity formed by the metallic surface. Many interesting physical quantities, such as the average energy, Fermi energy, specific heat, and thermionic emission rate, may be derived from the expression for the concentration of electrons with energies between E and $E + dE$:

$$n(E)\ dE = g(E) f_{FD}(E)\ dE \qquad (10.22)$$

Recall that the probability of finding an electron in a particular energy state E is given by the Fermi–Dirac distribution function,

$$f_{FD}(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1}$$

Plots of this function versus energy are shown in Figure 10.11 for the cases $T = 0$ K and $T > 0$. Note that at $T = 0$ K, $f_{\text{FD}} = 1$ for $E < E_{\text{F}}$, and $f_{\text{FD}} = 0$ for $E > E_{\text{F}}$. Thus all states with energies less than E_{F} are completely filled and all states with energies greater than E_{F} are empty. This is in sharp contrast to the predictions of MB and BE statistics, in which all particles condense to a state of zero energy at absolute zero. In fact, far from having zero speed, a conduction electron in a metal with the cutoff energy E_{F} has a speed v_{F} which satisfies the relation

$$\tfrac{1}{2}m_{\text{e}}v_{\text{F}}^2 = E_{\text{F}} \tag{10.35}$$

where v_{F} is called the **Fermi speed.** Substituting a typical value of 5 eV for the Fermi energy yields the remarkable result that electrons at the Fermi level possess speeds of the order of 10^6 m/s at 0 K!

Figure 10.11b shows that as T increases, the distribution rounds off slightly, with states between E and $E - k_{\text{B}}T$ losing population and states between E and $E + k_{\text{B}}T$ gaining population. In general, E_{F} also depends on temperature, but the dependence is weak in metals, and we may say that $E_{\text{F}}(T) \approx E_{\text{F}}(0)$ up to several thousand kelvin.

Let us now turn to the calculation of the density of states, $g(E)$, for conduction electrons in a metal. Since the electrons may be viewed as a system of matter waves whose wavefunctions vanish at the boundaries of the metal, we obtain the same result for electrons as for electromagnetic waves confined to a cavity. In the latter case, we found (see our Web site at http://info.brookscole.com/mp3e) that the number of states per unit volume with wavenumber between k and $k + dk$ is

$$g(k)\ dk = \frac{k^2\ dk}{2\pi^2} \tag{3.44}$$

To apply this expression to electrons in a metal, we must multiply it by a factor of 2 to account for the two allowed spin states of an electron with a given momentum or energy:

$$g(k)\ dk = \frac{k^2\ dk}{\pi^2} \tag{10.36}$$

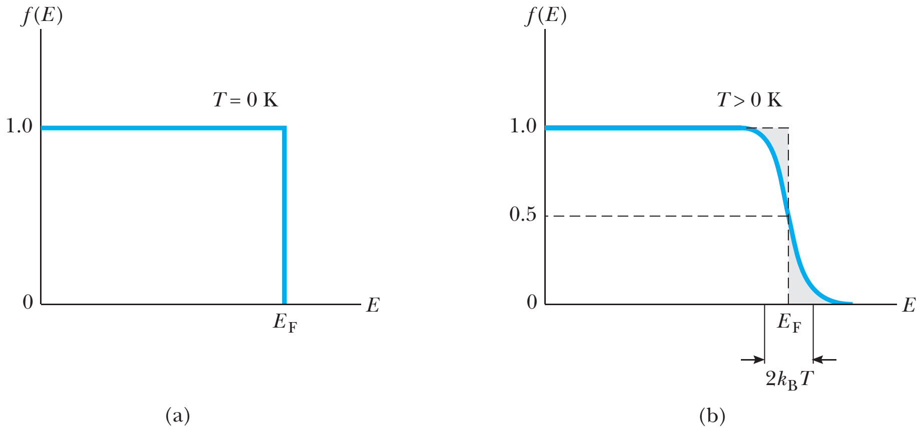

Figure 10.11 A comparison of the Fermi–Dirac distribution functions at (a) absolute zero and (b) finite temperature.

To obtain $g(E)$ from $g(k)$, we assume nonrelativistic free electrons. Thus

$$E = \frac{p^2}{2m_e} = \frac{\hbar^2 k^2}{2m_e}$$

or

$$k = \left(\frac{2m_e E}{\hbar^2}\right)^{1/2} \tag{10.37}$$

and

$$dk = \frac{1}{2}\left(\frac{2m_e}{\hbar^2}\right)^{1/2} E^{-1/2}\, dE \tag{10.38}$$

Substituting Equations 10.37 and 10.38 into Equation 10.36 yields

Density of states for conduction electrons

$$g(E)\ dE = DE^{1/2}\ dE \tag{10.39}$$

where

$$D = \frac{8\sqrt{2}\pi m_e^{3/2}}{h^3} \tag{10.40}$$

Thus the key expression for the number of electrons per unit volume with energy between E and $E + dE$ becomes

Number of electrons per unit volume with energy between E and $E + dE$

$$n(E)\ dE = \frac{DE^{1/2}\, dE}{e^{(E-E_F)/k_B T} + 1} \tag{10.41}$$

Figure 10.12 is a plot of $n(E)$ versus E, showing the product of an increasing density of states and the decreasing FD distribution. Because

$$\frac{N}{V} = \int_0^\infty n(E)\ dE = D\int_0^\infty \frac{E^{1/2}\ dE}{e^{(E-E_F)k_B T} + 1} \tag{10.42}$$

we can determine the Fermi energy as a function of the electron concentration, N/V. For arbitrary T, Equation 10.42 must be integrated numerically. At $T = 0$ K, the integration is simple since $f_{FD}(E) = 1$ for $E < E_F$ and is 0 for $E > E_F$. Therefore, at $T = 0$ K, Equation 10.42 becomes

$$\frac{N}{V} = D\int_0^{E_F} E^{1/2}\ dE = \tfrac{2}{3} DE_F^{3/2} \tag{10.43}$$

Substituting the value of D from Equation 10.40 into Equation 10.43 gives for the Fermi energy at 0 K, $E_F(0)$,

$$E_F(0) = \frac{h^2}{2m_e}\left(\frac{3N}{8\pi V}\right)^{2/3} \tag{10.44}$$

Equation 10.44 shows a gradual increase in $E_F(0)$ with increasing electron concentration. This is expected, because the electrons fill the available energy states, two electrons per state, in accordance with the Pauli exclusion principle up to a maximum energy E_F. Representative values of $E_F(0)$ for various metals calculated from Equation 10.44 are given in Table 10.1. This table also lists values of the Fermi speed and the **Fermi temperature,** T_F, defined by

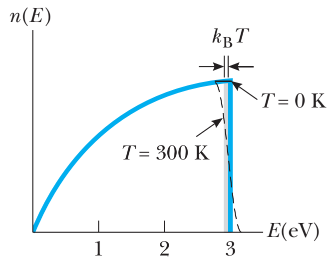

Figure 10.12 The number of electrons per unit volume with energy between E and $E + dE$. Note that $n(E) = g(E) f_{FD}(E)$.

Table 10.1 Calculated Values of Various Parameters for Metals Based on the Free Electron Theory

Metal	Electron Concentration (m^{-3})	Fermi Energy (eV)	Fermi Speed (m/s)	Fermi Temperature (K)
Li	4.70×10^{28}	4.72	1.29×10^{6}	5.48×10^{4}
Na	2.65×10^{28}	3.23	1.07×10^{6}	3.75×10^{4}
K	1.40×10^{28}	2.12	0.86×10^{6}	2.46×10^{4}
Cu	8.49×10^{28}	7.05	1.57×10^{6}	8.12×10^{4}
Ag	5.85×10^{28}	5.48	1.39×10^{6}	6.36×10^{4}
Au	5.90×10^{28}	5.53	1.39×10^{6}	6.41×10^{4}

$$T_F \equiv \frac{E_F}{k_B} \tag{10.45}$$

As a final note, it is interesting that a long-standing puzzle concerning the anomalously small contribution of the conduction electron "gas" to the heat capacity of a solid has a qualitative solution in terms of the Fermi–Dirac distribution. If conduction electrons behaved classically, warming a gas of N electrons from 0 to 300 K should result in an average energy increase of $3k_BT/2$ for *each* particle, or a total thermal energy per mole, U, given by

$$U = N_A\left(\tfrac{3}{2}k_BT\right) = \tfrac{3}{2}RT$$

Thus the electronic heat capacity per mole should be given by

$$C_{el} = \frac{dU}{dT} = \tfrac{3}{2}R$$

assuming one free electron per atom. An examination of Figure 10.12, however, shows that on heating from 0 K, very few electrons become excited and gain an energy k_BT. Only a small fraction f within k_BT of E_F can be excited thermally. The fraction f may be approximated by the ratio of the area of a thin rectangle of width k_BT and height $n(E_F)$ to the total area under $n(E)$. Thus

$$f \approx \frac{\text{area of shaded rectangle in Figure 10.12}}{\text{total area under } n(E)}$$
$$= \frac{(k_BT)g(E_F)}{D\displaystyle\int_0^{E_F} E^{1/2}\,dE} = \frac{(k_BT)D(E_F)^{1/2}}{\frac{2}{3}DE_F^{3/2}} = \frac{3}{2}\,\frac{k_BT}{E_F} = \frac{3}{2}\,\frac{T}{T_F}$$

Since only fN of the electrons gain an energy of the order of k_BT, the actual total thermal energy gained per mole is

$$U = \left(\frac{3}{2}\,\frac{T}{T_F}\right)(N_Ak_BT) = \frac{3}{2}\,\frac{RT^2}{T_F}$$

From this result, we find that the electronic heat capacity is

$$C_{el} = \frac{dU}{dT} \approx 3R\,\frac{T}{T_F}$$

Substituting $T = 300$ K and $T_F = 5 \times 10^4$ K, we find a very small value for the electronic heat capacity at ordinary temperatures:

$$C_{el} \approx 3R\left(\frac{300\ \text{K}}{50{,}000\ \text{K}}\right) = 0.018R$$

Thus, the electrons contribute only $0.018R/1.5R$, or about 1% of the classically expected amount, to the heat capacity.

EXAMPLE 10.5 The Fermi Energy of Gold

(a) Calculate the Fermi energy of gold at 0 K.

Solution The density of gold is 19.32 g/cm^3, and its molar weight is 197 g/mol. Assuming each gold atom contributes one free electron to the Fermi gas, we can calculate the electron concentration as follows:

$$\begin{aligned}\frac{N}{V} &= (19.32\ \text{g/cm}^3)\left(\frac{1}{197\ \text{g/mol}}\right) \times (6.02 \times 10^{23}\ \text{electrons/mol})\\ &= 5.90 \times 10^{22}\ \text{electrons/cm}^3\\ &= 5.90 \times 10^{28}\ \text{electrons/m}^3\end{aligned}$$

Using Equation 10.44, we find

$$\begin{aligned}E_F(0) &= \frac{h^2}{2m_e}\left(\frac{3N}{8\pi V}\right)^{2/3}\\ &= \frac{(6.625 \times 10^{-34}\ \text{J}\cdot\text{s})^2}{2(9.11 \times 10^{-31}\ \text{kg})}\left(\frac{3 \times 5.90 \times 10^{28}\ \text{m}^{-3}}{8\pi}\right)^{2/3}\\ &= 8.85 \times 10^{-19}\ \text{J} = 5.53\ \text{eV}\end{aligned}$$

(b) Calculate the Fermi speed for gold at 0 K.

Solution Since $\frac{1}{2}m_e v_F^2 = E_F$,

$$\begin{aligned}v_F &= \left(\frac{2E_F}{m_e}\right)^{1/2} = \left(\frac{2 \times 5.85 \times 10^{-19}\ \text{J}}{9.11 \times 10^{-31}\ \text{kg}}\right)^{1/2}\\ &= 1.39 \times 10^6\ \text{m/s}\end{aligned}$$

(c) Calculate the Fermi temperature for gold at 0 K.

Solution The Fermi temperature is given by

$$\begin{aligned}T_F &= \frac{E_F}{k_B} = \frac{5.53\ \text{eV}}{8.62 \times 10^{-5}\ \text{eV/K}}\\ &= 64{,}000\ \text{K}\end{aligned}$$

Thus a gas of classical particles would have to be heated to about 64,000 K to have an average energy per particle equal to the Fermi energy at 0 K!

SUMMARY

Statistical physics deals with the distribution of a fixed amount of energy among a number of particles that are identical and indistinguishable in any way (quantum particles) or identical particles that are distinguishable in the classical limit of narrow particle wave packets and low particle density. In most situations, one is not interested in the energies of all the particles at a given instant, but rather in the time average of the number of particles in a particular energy level. The average number of particles in a given energy level is of special interest in spectroscopy because the intensity of radiation emitted or absorbed is proportional to the number of particles in a particular energy state.

For a system described by a continuous distribution of energy levels, the number of particles per unit volume with energy between E and $E + dE$ is given by

$$n(E)\,dE = g(E)f(E)\,dE \qquad (10.6)$$

where $g(E)$ is the density of states or the number of energy states per unit volume in the interval dE and $f(E)$ is the probability that a particle is in the energy state E. The function $f(E)$ is called the **distribution function.**

Three distinct distribution functions are used, depending on whether the particles are distinguishable and whether there is a restriction on the number of particles in a given energy state:

- **Maxwell–Boltzmann Distribution (Classical).** The particles are distinguishable, and there is no limit on the number of particles in a given energy state.

$$f_{\mathrm{MB}}(E) = Ae^{-E/k_{\mathrm{B}}T} \tag{10.3}$$

- **Bose–Einstein Distribution (Quantum).** The particles are indistinguishable, and there is no limit on the number of particles in a given energy state.

$$f_{\mathrm{BE}}(E) = \frac{1}{Be^{E/k_{\mathrm{B}}T} - 1} \tag{10.19}$$

- **Fermi–Dirac Distribution (Quantum).** The particles are indistinguishable, and there can be no more than one particle per quantum state.

$$f_{\mathrm{FD}}(E) = \frac{1}{e^{(E-E_{\mathrm{F}})/k_{\mathrm{B}}T} + 1} \tag{10.25}$$

where E_{F} is the **Fermi energy.** At $T = 0$ K, all levels below E_{F} are filled and all levels above E_{F} are empty.

At low particle concentrations and high temperature, most systems are well described by Maxwell–Boltzmann statistics. The criterion that determines when the classical Maxwell–Boltzmann distribution is valid is

$$\left(\frac{N}{V}\right)\frac{h^3}{(8mk_{\mathrm{B}}T)^{3/2}} << 1 \tag{10.18}$$

where N/V is the particle concentration, m is the particle mass, and T is the absolute temperature. For high particle concentration, low particle mass, and modest temperature, there is considerable overlap between the particles' wavefunctions, and quantum distributions must be used to describe these systems of indistinguishable particles.

A system of photons in thermal equilibrium at temperature T is described by the Bose–Einstein distribution with $B = 1$ and a density of states given by

$$g(E) = \frac{8\pi E^2}{(hc)^3} \tag{10.27}$$

Thus, the concentration of photons with energies between E and $E + dE$ is

$$n(E)\,dE = \frac{8\pi E^2}{(hc)^3}\left(\frac{1}{e^{E/k_{\mathrm{B}}T} - 1}\right)dE$$

Phonons, which are quantized lattice vibrations of a solid, are also described by the Bose–Einstein distribution with $B = 1$.

Free (conduction) electrons in metals obey the Pauli exclusion principle, and we must use the Fermi–Dirac distribution to treat such a system. The density of states for electrons in a metal is

$$g(E) = \frac{8\sqrt{2}\pi m_{\mathrm{e}}^{3/2}}{h^3}E^{1/2} \tag{10.39}$$

hence the number of electrons per unit volume with energy between E and $E + dE$ is

$$n(E)\,dE = \frac{8\sqrt{2}\pi m_e^{3/2}\,E^{1/2}}{h^3(e^{(E-E_F)/k_BT}+1)}\,dE \qquad (10.41)$$

An expression for the Fermi energy at 0 K as a function of electron concentration may be obtained by integrating Equation 10.41. One finds

$$E_F(0) = \frac{h^2}{2m_e}\left(\frac{3N}{8\pi V}\right)^{2/3} \qquad (10.44)$$

The small electronic contribution to the heat capacity of a metal can be explained by noting that only a small fraction of the electrons near E_F gain k_BT in thermal energy when the metal is heated from 0 K to T K.

SUGGESTIONS FOR FURTHER READING

1. A. Beiser, *Concepts of Modern Physics*, 5th ed., New York, McGraw-Hill Book Co., 1995.

More advanced treatments of statistical physics may be found in the following books:

2. P. M. Morse, *Thermal Physics*, New York, Benjamin, 1965.
3. C. Kittel, *Thermal Physics*, New York, Wiley, 1969.
4. D. Griffiths, *Introduction to Quantum Mechanics*, Englewood Cliffs, NJ, Prentice-Hall, 1994.

QUESTIONS

1. Discuss the basic assumptions of Maxwell–Boltzmann, Fermi–Dirac, and Bose–Einstein statistics. How do they differ, and what are their similarities?
2. Explain the role of the Pauli exclusion principle in describing the electrical properties of metals.

PROBLEMS

10.1 The Maxwell–Boltzmann Distribution

1. Verify that for a system of six distinguishable particles with total energy $8E$, the probabilities of finding a particle with energies $1E$ through $8E$ are: 0.256, 0.167, 0.0978, 0.0543, 0.0272, 0.0117, 0.00388, 0.000777.
2. Show that the most probable speed of a gas molecule is

$$v_{\mathrm{mp}} = \sqrt{\frac{2k_BT}{m}}$$

Note that the most probable speed corresponds to the point where the Maxwellian speed distribution curve, $n(v)$, has a maximum.

3. Figure P10.3 shows an apparatus similar to that used by Otto Stern in 1920 to verify the Maxwell speed distribution. A collimated beam of gas molecules from an oven, O, is allowed to enter a rapidly rotating cylinder when slit S is coincident with the beam. The pulse of molecules created by the rapid rotation of S then strikes and adheres to a glass plate detector, D. The velocity of a molecule may be determined from its position on the glass plate (fastest molecules to the right). The number of molecules arriving with a given velocity may be determined by measuring the density of molecules deposited on D at a given position. Suppose that

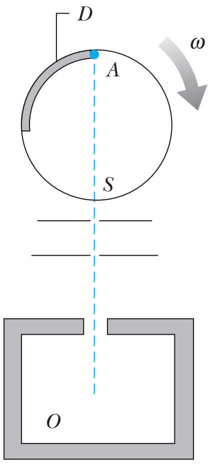

Figure P10.3 A schematic drawing of an apparatus used to verify the Maxwell speed distribution.