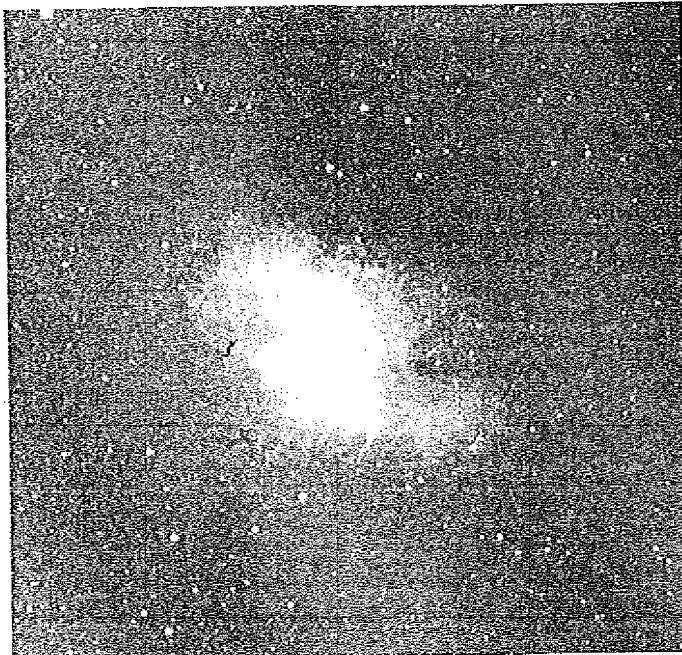


## CHAPTER 9

# Statistical Mechanics



The Crab Nebula is the result of a supernova explosion that was observed in A.D. 1054. The explosion left behind a star believed to consist entirely of neutrons. Statistical mechanics is needed to understand the properties of neutron stars.

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| <p><b>9.1 STATISTICAL DISTRIBUTIONS</b><br/><i>Three different kinds</i></p> <p><b>9.2 MAXWELL-BOLTZMANN STATISTICS</b><br/><i>Classical particles such as gas molecules obey them</i></p> <p><b>9.3 MOLECULAR ENERGIES IN AN IDEAL GAS</b><br/><i>They vary about an average of <math>\frac{1}{2}kT</math></i></p> <p><b>9.4 QUANTUM STATISTICS</b><br/><i>Bosons and fermions have different distribution functions</i></p> <p><b>9.5 RAYLEIGH-JEANS FORMULA</b><br/><i>The classical approach to blackbody radiation</i></p> <p><b>9.6 PLANCK RADIATION LAW</b><br/><i>How a photon gas behaves</i></p> | <p><b>9.7 EINSTEIN'S APPROACH</b><br/><i>Introducing stimulated emission</i></p> <p><b>9.8 SPECIFIC HEATS OF SOLIDS</b><br/><i>Classical physics fails again</i></p> <p><b>9.9 FREE ELECTRONS IN A METAL</b><br/><i>No more than one electron per quantum state</i></p> <p><b>9.10 ELECTRON-ENERGY DISTRIBUTION</b><br/><i>Why the electrons in a metal do not contribute to its specific heat except at very high and very low temperatures</i></p> <p><b>9.11 DYING STARS</b><br/><i>What happens when a star runs out of fuel</i></p> |
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The branch of physics called statistical mechanics considers how the overall behavior of a system of many particles is related to the properties of the particles themselves. As its name implies, statistical mechanics is not concerned with the actual motions or interactions of individual particles, but instead with what is most likely to happen. While statistical mechanics cannot help us find the life history of one of the particles in a system, it is able to tell us, for instance, the probability that the particle has a certain amount of energy at a certain moment.

Because so many phenomena in the physical world involve systems of great numbers of particles, the value of a statistical approach is clear. Owing to the generality of its arguments, statistical mechanics can be applied equally well to classical systems (notably molecules in a gas) and to quantum-mechanical systems (notably photons in a cavity and free electrons in a metal), and it is one of the most powerful tools of the theoretical physicist.

## 9.1 STATISTICAL DISTRIBUTIONS

### *Three different kinds*

What statistical mechanics does is determine the most probable way in which a certain total amount of energy  $E$  is distributed among the  $N$  members of a system of particles in thermal equilibrium at the absolute temperature  $T$ . Thus we can establish how many particles are likely to have the energy  $\epsilon_1$ , how many to have the energy  $\epsilon_2$ , and so on.

The particles are assumed to interact with one another and with the walls of their container to an extent sufficient to establish thermal equilibrium but not so much that their motions are strongly correlated. More than one particle state may correspond to a certain energy  $\epsilon$ . If the particles are not subject to the exclusion principle, more than one particle may be in a certain state.

A basic premise of statistical mechanics is that the greater the number  $W$  of different ways in which the particles can be arranged among the available states to yield a particular distribution of energies, the more probable is the distribution. It is assumed that each state of a certain energy is equally likely to be occupied. This assumption is plausible but its ultimate justification (as in the case of Schrödinger's equation) is that the conclusions arrived at with its help agree with experiment.

The program of statistical mechanics begins by finding a general formula for  $W$  for the kind of particles being considered. The most probable distribution, which corresponds to the system's being in thermal equilibrium, is the one for which  $W$  is a maximum, subject to the condition that the system consists of a fixed number  $N$  of particles (except when they are photons or their acoustic equivalent called phonons) whose total energy is some fixed amount  $E$ . The result in each case is an expression for  $n(\epsilon)$ , the number of particles with the energy  $\epsilon$ , that has the form

$$\text{Number of particles of energy } \epsilon \quad n(\epsilon) = g(\epsilon)f(\epsilon) \quad (9.1)$$

- where     $g(\epsilon)$  = number of states of energy  $\epsilon$   
                   = statistical weight corresponding to energy  $\epsilon$   
      $f(\epsilon)$  = distribution function  
                   = average number of particles in each state of energy  $\epsilon$   
                   = probability of occupancy of each state of energy  $\epsilon$

When a continuous rather than a discrete distribution of energies is involved,  $g(\epsilon)$  is replaced by  $g(\epsilon) d\epsilon$ , the number of states with energies between  $\epsilon$  and  $\epsilon + d\epsilon$ .

We shall consider systems of three different kinds of particles:

1 Identical particles that are sufficiently far apart to be distinguishable, for instance, the molecules of a gas. In quantum terms, the wave functions of the particles overlap to a negligible extent. The **Maxwell-Boltzmann distribution function** holds for such particles.

2 Identical particles of 0 or integral spin that cannot be distinguished one from another because their wave functions overlap. Such particles, called **bosons** in Chap. 7, do not obey the exclusion principle, and the **Bose-Einstein distribution function** holds for them. Photons are in this category, and we shall use Bose-Einstein statistics to account for the spectrum of radiation from a blackbody.

3 Identical particles with odd half-integral spin ( $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ ) that also cannot be distinguished one from another. Such particles, called **fermions**, obey the exclusion principle, and the **Fermi-Dirac distribution function** holds for them. Electrons are in this category, and we shall use Fermi-Dirac statistics to study the behavior of the free electrons in a metal that are responsible for its ability to conduct electric current.

## 9.2 MAXWELL-BOLTZMANN STATISTICS

*Classical particles such as gas molecules obey them*

The Maxwell-Boltzmann distribution function states that the average number of particles  $f_{MB}(\epsilon)$  in a state of energy  $\epsilon$  in a system of particles at the absolute temperature  $T$  is



Ludwig Boltzmann (1844–1906) was born in Vienna and attended the university there. He then taught and carried out both experimental and theoretical research at a number of institutions in Austria and Germany, moving from one to another every few years. Boltzmann was interested in poetry, music, and travel as well as in physics; he visited the United States three times, something unusual in those days.

Of Boltzmann's many contributions to physics, the most important were to the kinetic theory of gases, which he developed independently of Maxwell, and to statistical mechanics, whose foundations he established. The constant  $k$  in the formula  $\frac{3}{2}kT$  for the average energy of a gas molecule is named after him in honor of his work on the distribution of molecular energies in a gas. In 1884 Boltzmann derived from thermodynamic considerations the Stefan-Boltzmann law  $R = \sigma T^4$  for the radiation rate of a blackbody. Josef Stefan, who had been one of Boltzmann's

teachers, had discovered this law experimentally 5 years earlier. One of Boltzmann's major achievements was the interpretation of the second law of thermodynamics in terms of order and disorder. A monument to Boltzmann in Vienna is inscribed with his formula  $S = k \log W$ , which relates the entropy  $S$  of a system to its probability  $W$ .

Boltzmann was a champion of the atomic theory of matter, still controversial in the late nineteenth century because there was then only indirect evidence for the existence of atoms and molecules. Battles with nonbelieving scientists deeply upset Boltzmann, and in his later years asthma, headaches, and increasingly poor eyesight further depressed his spirits. He committed suicide in 1906, not long after Albert Einstein published a paper on brownian motion that was to convince the remaining doubters of the atomic theory of its correctness. Boltzmann had not been alone in his despair over doubters of the reality of atoms. Planck was driven to an extreme of pessimism: "A new scientific truth does not triumph by convincing its opponents and making them see the light, but rather because its opponents eventually die and a new generation grows up that is familiar with it."

Maxwell-Boltzmann distribution function

$$f_{MB}(\epsilon) = A e^{-\epsilon/kT} \quad (9.2)$$

The value of  $A$  depends on the number of particles in the system and plays a role here analogous to that of the normalization constant of a wave function. As usual,  $k$  is Boltzmann's constant, whose value is

Boltzmann's constant  $k = 1.381 \times 10^{-23} \text{ J/K} = 8.617 \times 10^{-5} \text{ eV/K}$

Combining Eqs. (9.1) and (9.2) gives us the number  $n(\epsilon)$  of identical, distinguishable particles in an assembly at the temperature  $T$  that have the energy  $\epsilon$ :

$$\text{Maxwell-Boltzmann} \quad n(\epsilon) = A g(\epsilon) e^{-\epsilon/kT} \quad (9.3)$$

### Example 9.1

A cubic meter of atomic hydrogen at  $0^\circ\text{C}$  and at atmospheric pressure contains about  $2.7 \times 10^{25}$  atoms. Find the number of these atoms in their first excited states ( $n = 2$ ) at  $0^\circ\text{C}$  and at  $10,000^\circ\text{C}$ .

Solution

(a) The constant  $A$  in Eq. (9.3) is the same for atoms in both states, so the ratio between the numbers of atoms in the  $n = 1$  and  $n = 2$  states is

$$\frac{n(\epsilon_2)}{n(\epsilon_1)} = \frac{g(\epsilon_2)}{g(\epsilon_1)} e^{-(\epsilon_2 - \epsilon_1)/kT}$$

From Eq. (7.14) we know that the number of possible states that correspond to the quantum number  $n$  is  $2n^2$ . Thus the number of states of energy  $\epsilon_1$  is  $g(\epsilon_1) = 2$ ; a 1s electron has  $l = 0$  and  $m_l = 0$  but  $m_s$  can be  $-\frac{1}{2}$  or  $+\frac{1}{2}$ . The number of states of energy  $\epsilon_2$  is  $g(\epsilon_2) = 8$ ; a 2s ( $l = 0$ ) electron can have  $m_s = \pm\frac{1}{2}$  and a 2p ( $l = 1$ ) electron can have  $m_l = 0, \pm 1$ , in each case with  $m_s = \pm\frac{1}{2}$ . Since the ground-state energy is  $\epsilon_1 = -13.6 \text{ eV}$ ,  $\epsilon_2 = \epsilon_1/n^2 = -3.4 \text{ eV}$  and  $\epsilon_1 - \epsilon_2 = 10.2 \text{ eV}$ . Here  $T = 0^\circ\text{C} = 273 \text{ K}$ , so

$$\frac{\epsilon_2 - \epsilon_1}{kT} = \frac{10.2 \text{ eV}}{(8.617 \times 10^{-5} \text{ eV/K})(273 \text{ K})} = 434$$

The result is

$$\frac{n(\epsilon_2)}{n(\epsilon_1)} = \left(\frac{8}{2}\right) e^{-434} = 1.3 \times 10^{-188}$$

Thus about 1 atom in every  $10^{188}$  is in its first excited state at  $0^\circ\text{C}$ . With only  $2.7 \times 10^{25}$  atoms in our sample, we can be confident that all are in their ground states. (If all the known matter in the universe were in the form of hydrogen atoms, there would be about  $10^{78}$  of them, and if they were at  $0^\circ\text{C}$  the same conclusion would still hold.)

(b) When  $T = 10,000^\circ\text{C} = 10,273 \text{ K}$ ,

$$\frac{\epsilon_2 - \epsilon_1}{kT} = 11.5$$

and  $\frac{n(\epsilon_2)}{n(\epsilon_1)} = \left(\frac{8}{2}\right) e^{-11.5} = 4.0 \times 10^{-5}$

Now the number of excited atoms is about  $10^{21}$ , a substantial number even though only a small fraction of the total.

**Example 9.2**

Obtain a formula for the populations of the rotational states of a rigid diatomic molecule.

**Solution**

For such a molecule Eq. (8.9) gives the energy states in terms of the rotational quantum number  $J$  as

$$\epsilon_J = J(J + 1) \frac{\hbar^2}{2I}$$

More than one rotational state may correspond to a particular  $J$  because the component  $L_z$  in any specified direction of the angular momentum  $L$  may have any value in multiples of  $\hbar$  from  $J\hbar$  through 0 to  $-J\hbar$ , for a total of  $2J + 1$  possible values. Each of these  $2J + 1$  possible orientations of  $L$  constitutes a separate quantum state, and so

$$g(\epsilon) = 2J + 1$$

If the number of molecules in the  $J = 0$  state is  $n_0$ , the normalization constant  $A$  in Eq. (9.3) is just  $n_0$ , and the number of molecules in the  $J = J$  state is

$$n_J = Ag(\epsilon)e^{-\epsilon/kT} = n_0(2J + 1)e^{-J(J+1)\hbar^2/2kT}$$

In carbon monoxide, to give an example, this formula shows that the  $J = 7$  state is the most highly populated at 20°C. The intensities of the rotational lines in a molecular spectrum are proportional to the relative populations of the various rotational energy levels.

**9.3 MOLECULAR ENERGIES IN AN IDEAL GAS**

*They vary about an average of  $\frac{3}{2}kT$*

We now apply Maxwell-Boltzmann statistics to find the distribution of energies among the molecules of an ideal gas. Energy quantization is inconspicuous in the translational motion of gas molecules, and the total number of molecules  $N$  in a sample is usually very large. It is therefore reasonable to consider a continuous distribution of molecular energies instead of the discrete set  $\epsilon_1, \epsilon_2, \epsilon_3, \dots$ . If  $n(\epsilon) d\epsilon$  is the number of molecules whose energies lie between  $\epsilon$  and  $\epsilon + d\epsilon$ , Eq. (9.1) becomes

Number of  
molecules with  
energies between  $\epsilon$   
and  $\epsilon + d\epsilon$

$$n(\epsilon) d\epsilon = [g(\epsilon) d\epsilon] [f(\epsilon)] = Ag(\epsilon)e^{-\epsilon/kT} d\epsilon \quad (9.4)$$

The first task is to find  $g(\epsilon) d\epsilon$ , the number of states that have energies between  $\epsilon$  and  $\epsilon + d\epsilon$ . This is easiest to do in an indirect way. A molecule of energy  $\epsilon$  has a momentum  $p$  whose magnitude  $p$  is specified by

$$p = \sqrt{2m\epsilon} = \sqrt{p_x^2 + p_y^2 + p_z^2}$$

Each set of momentum components  $p_x, p_y, p_z$  specifies a different state of motion. Let us imagine a momentum space whose coordinate axes are  $p_x, p_y, p_z$ , as in Fig. 9.1.

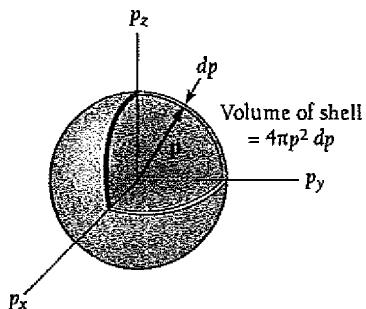


Figure 9.1 The coordinates in momentum space are  $p_x$ ,  $p_y$ ,  $p_z$ . The number of momentum states available to a particle with a momentum whose magnitude is between  $p$  and  $p + dp$  is proportional to the volume of a spherical shell in momentum space of radius  $p$  and thickness  $dp$ .

The number of states  $g(p) dp$  with momenta whose magnitudes are between  $p$  and  $p + dp$  is proportional to the volume of a spherical shell in momentum space  $p$  in radius and  $dp$  thick, which is  $4\pi p^2 dp$ . Hence

$$\text{Number of momentum states} \quad g(p) dp = Bp^2 dp \quad (9.5)$$

where  $B$  is some constant. [The function  $g(p)$  here is not the same as the function  $g(\epsilon)$  in Eq. (9.4).]

Since each momentum magnitude  $p$  corresponds to a single energy  $\epsilon$ , the number of energy states  $g(\epsilon) d\epsilon$  between  $\epsilon$  and  $\epsilon + d\epsilon$  is the same as the number of momentum states  $g(p) dp$  between  $p$  and  $p + dp$ , and so

$$g(\epsilon) d\epsilon = Bp^2 dp \quad (9.6)$$

Because

$$p^2 = 2m\epsilon \quad \text{and} \quad dp = \frac{m d\epsilon}{\sqrt{2m\epsilon}}$$

Eq. (9.6) becomes

$$\text{Number of energy states} \quad g(\epsilon) d\epsilon = 2m^{3/2} B\sqrt{\epsilon} d\epsilon \quad (9.7)$$

The number of molecules with energies between  $\epsilon$  and  $d\epsilon$  is therefore

$$n(\epsilon) d\epsilon = C\sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon \quad (9.8)$$

where  $C (= 2m^{3/2} AB)$  is a constant to be evaluated.

To find  $C$  we make use of the normalization condition that the total number of molecules is  $N$ , so that

$$\text{Normalization} \quad N = \int_0^\infty n(\epsilon) d\epsilon = C \int_0^\infty \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon \quad (9.9)$$

From a table of definite integrals we find that

$$\int_0^\infty \sqrt{x} e^{-ax} dx = \frac{1}{2a} \sqrt{\frac{\pi}{a}}$$

Here  $a = 1/kT$ , and the result is

$$N = \frac{C}{2} \sqrt{\pi} (kT)^{3/2}$$

$$C = \frac{2\pi N}{(\pi kT)^{3/2}} \quad (9.10)$$

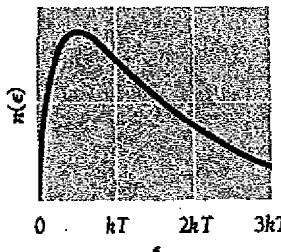


Figure 9.2 Maxwell-Boltzmann energy distribution for the molecules of an ideal gas. The average molecular energy is  $\bar{\epsilon} = \frac{3}{2}kT$ .

and, finally,

Molecular energy distribution  $n(\epsilon) d\epsilon = \frac{2\pi N}{(\pi kT)^{3/2}} \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon \quad (9.11)$

This formula gives the number of molecules with energies between  $\epsilon$  and  $\epsilon + d\epsilon$  in a sample of an ideal gas that contains  $N$  molecules and whose absolute temperature is  $T$ .

Equation (9.11) is plotted in Fig. 9.2 in terms of  $kT$ . The curve is not symmetrical about the most probable energy because the lower limit to  $\epsilon$  is  $\epsilon = 0$  while there is, in principle, no upper limit (although the likelihood of energies many times greater than  $kT$  is small).

### Average Molecular Energy

To find the average energy per molecule we begin by calculating the total internal energy of the system. To do this we multiply  $n(\epsilon)d\epsilon$  by the energy  $\epsilon$  and then integrate over all energies from 0 to  $\infty$ :

$$E = \int_0^\infty \epsilon n(\epsilon) d\epsilon = \frac{2\pi N}{(\pi kT)^{3/2}} \int_0^\infty \epsilon^{3/2} e^{-\epsilon/kT} d\epsilon$$

Making use of the definite integral

$$\int_0^\infty x^{3/2} e^{-ax} dx = \frac{3}{4a^2} \sqrt{\frac{\pi}{a}}$$

we have

Total energy of  $N$  gas molecules  $E = \left[ \frac{2\pi N}{(\pi kT)^{3/2}} \right] \left[ \frac{3}{4} (kT)^2 \sqrt{\pi kT} \right] = \frac{3}{2} N k T \quad (9.12)$

The average energy of an ideal-gas molecule is  $E/N$ , or

Average molecular energy  $\bar{\epsilon} = \frac{3}{2} k T \quad (9.13)$

which is independent of the molecule's mass: a light molecule has a greater average speed at a given temperature than a heavy one. The value of  $\bar{\epsilon}$  at room temperature is about  $0.04 \text{ eV}, \frac{1}{21} \text{ eV}$ .

## Equipartition of Energy

A gas molecule has three degrees of freedom that correspond to motions in three independent (that is, perpendicular) directions. Since the average kinetic energy of the molecule is  $\frac{3}{2}kT$  we can associate  $\frac{1}{2}kT$  with the average energy of each degree of freedom:  $\frac{1}{2}mv_x^2 = \frac{1}{2}mv_y^2 = \frac{1}{2}mv_z^2 = \frac{1}{2}kT$ . This association turns out to be quite general and is called the **equipartition theorem**:

The average energy per degree of freedom of any classical object that is a member of a system of such objects in thermal equilibrium at the temperature T is  $\frac{1}{2}kT$ .

Degrees of freedom are not limited to linear velocity components—each variable that appears squared in the formula for the energy of a particular object represents a degree of freedom. Thus each component  $\omega_i$  of angular velocity (provided it involves a moment of inertia  $I_i$ ) is a degree of freedom, so that  $\frac{1}{2}I_i\omega_i^2 = \frac{1}{2}kT$ . A rigid diatomic molecule of the kind described in Sec. 8.6 therefore has five degrees of freedom, one each for motions in the x, y, and z directions and two for rotations about axes perpendicular to its symmetry axis.

A degree of freedom is similarly associated with each component  $\Delta s_i$  of the displacement of an object that gives rise to a potential energy proportional to  $(\Delta s_i)^2$ . For example, a one-dimensional harmonic oscillator has two degrees of freedom, one that corresponds to its kinetic energy  $\frac{1}{2}mv^2$  and the other to its potential energy  $\frac{1}{2}K(\Delta x)^2$ , where K is the force constant. Each oscillator in a system of them in thermal equilibrium accordingly has a total average energy of  $2(\frac{1}{2}kT) = kT$  provided that quantization can be disregarded. To a first approximation, the constituent particles (atoms, ions, or molecules) of a solid behave thermally like a system of classical harmonic oscillators, as we shall see shortly.

The equipartition theorem also applies to nonmechanical systems, for instance to thermal fluctuations ("noise") in electrical circuits.

## Distribution of Molecular Speeds

The distribution of molecular speeds in an ideal gas can be found from Eq. (9.11) by making the substitutions

$$\epsilon = \frac{1}{2}mv^2 \quad d\epsilon = mv \, dv$$

The result for the number of molecules with speeds between  $v$  and  $v + dv$  is

$$\text{Molecular-speed distribution} \quad n(v) \, dv = 4\pi N \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} \, dv \quad (9.14)$$

This formula, which was first obtained by Maxwell in 1859, is plotted in Fig. 9.3.

The speed of a molecule with the average energy of  $\frac{3}{2}kT$  is

$$\text{RMS speed} \quad v_{\text{rms}} = \sqrt{\bar{v}^2} = \sqrt{\frac{3kT}{m}} \quad (9.15)$$

since  $\frac{1}{2}\bar{mv}^2 = \frac{3}{2}kT$ . This speed is denoted  $v_{\text{rms}}$  because it is the square root of the average of the squared molecular speeds—the root-mean-square speed—and is not the same as the simple arithmetical average speed  $\bar{v}$ . The relationship between  $\bar{v}$  and  $v_{\text{rms}}$  depends on the distribution law that governs the molecular speeds in a particular system. For a Maxwell-Boltzmann distribution the rms speed is about 9 percent greater than the arithmetical average speed.

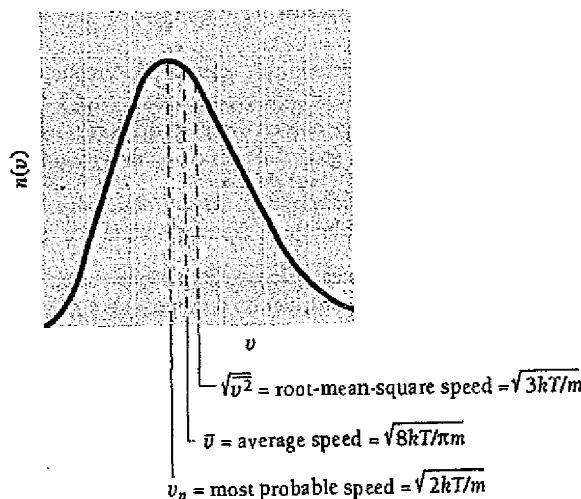


Figure 9.3 Maxwell-Boltzmann speed distribution.

**Example 9.3**

Verify that the rms speed of an ideal-gas molecule is about 9 percent greater than its average speed.

**Solution**

Equation (9.14) gives the number of molecules with speeds between  $v$  and  $v + dv$  in a sample of  $N$  molecules. To find their average speed  $\bar{v}$ , we multiply  $n(v) dv$  by  $v$ , integrate over all values of  $v$  from 0 to  $\infty$ , and then divide by  $N$ . (See the discussion of expectation values in Sec. 5.5.) This procedure gives

$$\bar{v} = \frac{1}{N} \int_0^\infty v n(v) dv = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_0^\infty v^3 e^{-mv^2/2kT} dv$$

If we let  $a = m/2kT$ , we see that the integral is the standard one

$$\int_0^\infty x^3 e^{-ax^2} dx = \frac{1}{2a^2}$$

and so  $\bar{v} = \left[ 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \right] \left[ \frac{1}{2} \left( \frac{2kT}{m} \right)^2 \right] = \sqrt{\frac{8kT}{\pi m}}$

Comparing  $\bar{v}$  with  $v_{rms}$  from Eq. (9.15) shows that

$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3\pi}{8}} \bar{v} \approx 1.09 \bar{v}$$

Because the speed distribution of Eq. (9.14) is not symmetrical, the most probable speed  $v_p$  is smaller than either  $\bar{v}$  or  $v_{rms}$ . To find  $v_p$ , we set equal to zero the derivative of  $n(v)$  with respect to  $v$  and solve the resulting equation for  $v$ . The result is

Most probable speed  $v_p = \sqrt{\frac{2kT}{m}}$  (9.16)

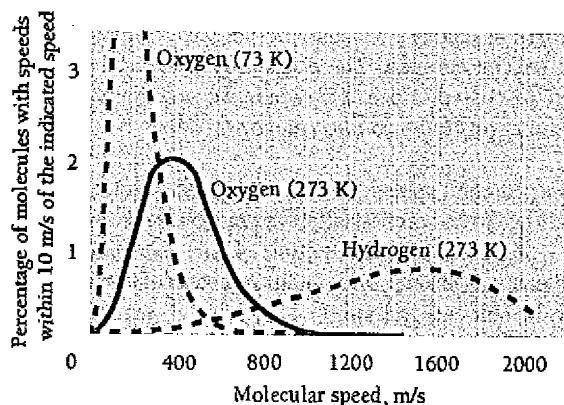


Figure 9.4 The distributions of molecular speeds in oxygen at 73 K, in oxygen at 273 K, and in hydrogen at 273 K.

Molecular speeds in a gas vary considerably on either side of  $v_p$ . Figure 9.4 shows the distribution of speeds in oxygen at 73 K ( $-200^\circ\text{C}$ ), in oxygen at 273 K ( $0^\circ\text{C}$ ), and in hydrogen at 273 K. The most probable speed increases with temperature and decreases with molecular mass. Accordingly molecular speeds in oxygen at 73 K are on the whole less than at 273 K, and at 273 K molecular speeds in hydrogen are on the whole greater than in oxygen at the same temperature. The average molecular energy is the same in both oxygen and hydrogen at 273 K, of course.

#### Example 9.4

Find the rms speed of oxygen molecules at  $0^\circ\text{C}$ .

##### Solution

Oxygen molecules have two oxygen atoms each. Since the atomic mass of oxygen is 16.0 u, the molecular mass of  $\text{O}_2$  is 32.0 u which is equivalent to

$$m = (32.0 \text{ u})(1.66 \times 10^{-27} \text{ kg/u}) = 5.31 \times 10^{-26} \text{ kg}$$

At an absolute temperature of 273 K, the rms speed of an  $\text{O}_2$  molecule is

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3(1.38 \times 10^{-23} \text{ J/K})(273 \text{ K})}{5.31 \times 10^{-26} \text{ kg}}} = 461 \text{ m/s}$$

This is a little over 1000 mi/h.

## 9.4 QUANTUM STATISTICS

### Bosons and fermions have different distribution functions

As mentioned in Sec. 9.1, the Maxwell-Boltzmann distribution function holds for systems of identical particles that can be distinguished one from another, which means particles whose wave functions do not overlap very much. Molecules in a gas fit this

description and obey Maxwell-Boltzmann statistics. If the wave functions do overlap appreciably, the situation changes because the particles cannot now be distinguished, although they can still be counted. The quantum-mechanical consequences of indistinguishability were discussed in Sec. 7.3, where we saw that systems of particles with overlapping wave functions fall into two categories:

- 1 Particles with 0 or integral spins, which are **bosons**. Bosons do not obey the exclusion principle, and the wave function of a system of bosons is not affected by the exchange of any pair of them. A wave function of this kind is called **symmetric**. Any number of bosons can exist in the same quantum state of the system.
- 2 Particles with odd half-integral spins ( $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ ), which are **fermions**. Fermions obey the exclusion principle, and the wave function of a system of fermions changes sign upon the exchange of any pair of them. A wave function of this kind is called **antisymmetric**. Only one fermion can exist in a particular quantum state of the system.

We shall now see what difference all this makes in the probability  $f(\epsilon)$  that a particular state of energy  $\epsilon$  will be occupied.

Let us consider a system of two particles, 1 and 2, one of which is in state  $a$  and the other in state  $b$ . When the particles are distinguishable there are two possibilities for occupancy of the states, as described by the wave functions

$$\psi_1 = \psi_a(1)\psi_b(2) \quad (9.17)$$

$$\psi_{11} = \psi_a(2)\psi_b(1) \quad (9.18)$$

- When the particles are not distinguishable, we cannot tell which of them is in which state, and the wave function must be a combination of  $\psi_1$  and  $\psi_{11}$  to reflect their equal likelihoods. As we found in Sec. 7.3, if the particles are bosons, the system is described by the **symmetric wave function**

$$\text{Bosons} \quad \psi_B = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)] \quad (9.19)$$

and if they are fermions, the system is described by the **antisymmetric wave function**

$$\text{Fermions} \quad \psi_F = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)] \quad (9.20)$$

The  $1/\sqrt{2}$  factors are needed to normalize the wave functions.

Now we ask what the likelihood in each case is that both particles be in the same state, say  $a$ . For distinguishable particles, both  $\psi_1$  and  $\psi_{11}$  become

$$\psi_M = \psi_a(1)\psi_a(2) \quad (9.21)$$

to give a probability density of

$$\text{Distinguishable particles} \quad \psi_M^* \psi_M = \psi_a^*(1)\psi_a^*(2)\psi_a(1)\psi_a(2) \quad (9.22)$$

For bosons the wave function becomes

$$\psi_B = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_a(2) + \psi_a(1)\psi_a(2)] = \frac{2}{\sqrt{2}} \psi_a(1)\psi_a(2) = \sqrt{2}\psi_a(1)\psi_a(2) \quad (9.23)$$

to give a probability density of

$$\text{Bosons} \quad \psi_B^* \psi_B = 2\psi_a^*(1)\psi_a^*(2)\psi_a(1)\psi_a(2) = 2\psi_M^*\psi_M \quad (9.24)$$

Thus the probability that both bosons be in the same state is twice what it is for distinguishable particles!

For fermions the wave function becomes

$$\text{Fermions} \quad \psi_F = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_a(2) - \psi_a(1)\psi_a(2)] = 0 \quad (9.25)$$

It is impossible for both particles to be in the same state, which is a statement of the exclusion principle.

These results can be generalized to apply to systems of many particles:

- 1 In a system of bosons, the presence of a particle in a certain quantum state increases the probability that other particles are to be found in the same state;
- 2 In a system of fermions, the presence of a particle in a certain state prevents any other particles from being in that state.

### Bose-Einstein and Fermi-Dirac Distribution Functions

The probability  $f(\epsilon)$  that a boson occupies a state of energy  $\epsilon$  turns out to be

$$\text{Bose-Einstein distribution function} \quad f_{BE}(\epsilon) = \frac{1}{e^{\alpha e^{\epsilon/kT}} - 1} \quad (9.26)$$

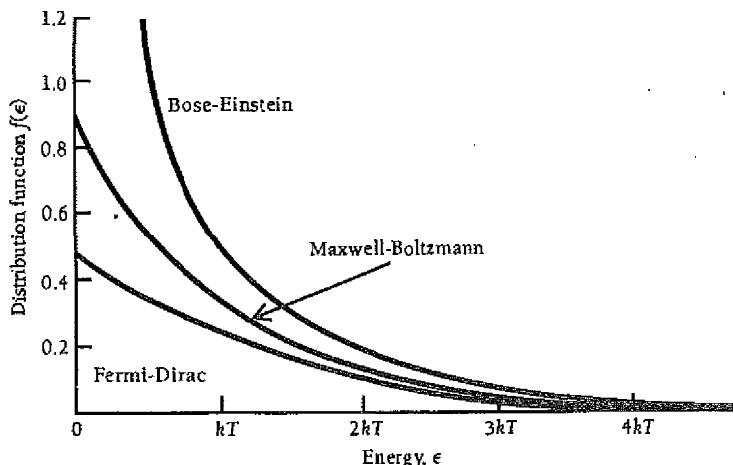
and the probability for a fermion turns out to be

$$\text{Fermi-Dirac distribution function} \quad f_{FD}(\epsilon) = \frac{1}{e^{\alpha e^{\epsilon/kT}} + 1} \quad (9.27)$$

### Names of the Functions

The Indian physicist S. N. Bose in 1924 derived Planck's radiation formula on the basis of the quantum theory of light with indistinguishable photons whose number is not conserved. His paper was rejected by a leading British journal. He then sent it to Einstein, who translated the paper into German and submitted it to a German journal where it was published. Because Einstein extended Bose's treatment to material particles whose number is conserved, both names are attached to Eq. 9.26. Two years later Enrico Fermi and Paul Dirac independently realized that Pauli's exclusion principle would lead to different statistics for electrons, and so Eq. 9.27 is named after them.

Figure 9.5 A comparison of the three distribution functions for the same value of  $\alpha$ . The Bose-Einstein function is always higher than the Maxwell-Boltzmann one, which is a pure exponential, and the Fermi-Dirac function is always lower. The functions give the probability of occupancy of a state of energy  $\epsilon$  at the absolute temperature  $T$ .



The quantity  $\alpha$  depends on the properties of the particular system and may be a function of  $T$ . Its value is determined by the normalization condition that the sum over all energy states of  $n(\epsilon) = g(\epsilon)f(\epsilon)$  be equal to the total number of particles in the system. If the number of particles is not fixed, as in the case of a photon gas, then from the way  $\alpha$  is defined in deriving Eqs. (9.26) and (9.27),  $\alpha = 0$ ,  $e^\alpha = 1$ .

The  $-1$  term in the denominator of Eq. (9.26) expresses the increased likelihood of multiple occupancy of an energy state by bosons compared with the likelihood for distinguishable particles such as molecules. The  $+1$  term in the denominator of Eq. (9.27) is a consequence of the uncertainty principle: No matter what the values of  $\alpha$ ,  $\epsilon$ , and  $T$ ,  $f(\epsilon)$  can never exceed 1. In both cases, when  $\epsilon \gg kT$  the functions  $f(\epsilon)$  approach that of Maxwell-Boltzmann statistics, Eq. (9.2). Figure 9.5 is a comparison of the three distribution functions. Clearly  $f_{BE}(\epsilon)$  for bosons is always greater at a given ratio of  $\epsilon/kT$  than it is for molecules, and  $f_{FD}(\epsilon)$  for fermions is always smaller.

From Eq. (9.27) we see that  $f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon-\epsilon_F)/kT} + 1}$  for an energy of

$$\text{Fermi energy } \epsilon_F = -\alpha kT \quad (9.28)$$

This energy, called the **Fermi energy**, is a very important quantity in a system of fermions, such as the electron gas in a metal. In terms of  $\epsilon_F$  the Fermi-Dirac distribution function becomes

$$\text{Fermi-Dirac } f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon-\epsilon_F)/kT} + 1} \quad (9.29)$$

To appreciate the significance of the Fermi energy, let us consider a system of fermions at  $T = 0$  and investigate the occupancy of states whose energies are less than  $\epsilon_F$  and greater than  $\epsilon_F$ . What we find is this:

$$T = 0; \epsilon < \epsilon_F: \quad f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon-\epsilon_F)/kT} + 1} = \frac{1}{e^{-\infty} + 1} = \frac{1}{0 + 1} = 1$$

$$T = 0; \epsilon > \epsilon_F: \quad f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon-\epsilon_F)/kT} + 1} = \frac{1}{e^{\infty} + 1} = 0$$

### Bose-Einstein Condensate

Under ordinary conditions, the wave packets that correspond to individual atoms in a gas of atoms are sufficiently small in size relative to their average spacing for the atoms to move independently and be distinguishable. If the temperature of the gas is reduced, the wave packets grow larger as the atoms lose momentum, in accord with the uncertainty principle. When the gas becomes very cold, the dimensions of the wave packets exceed the average atomic spacing so that the wave packets overlap. If the atoms are bosons, the eventual result is that all the atoms fall into the lowest possible energy state and their separate wave packets merge into a single wave packet. The atoms in such a Bose-Einstein condensate are barely moving, are indistinguishable, and form one entity—a superatom.

Although such condensates were first visualized by Einstein in 1924, not until 1995 was one actually created. The problem was to achieve a cold enough gas without it becoming a liquid or solid first. This was accomplished by Eric Cornell, Carl Wieman, and their coworkers in Colorado using a gas of rubidium atoms. The atoms were first cooled and trapped by six intersecting beams of laser light. The frequency of the light was adjusted so that the atoms moving against one of the beams would “see” light whose frequency was doppler-shifted to that of one of rubidium’s absorption lines. Thus the atoms would only absorb photons coming toward them, which would slow the atoms and thereby cool the assembly as well as pushing the atoms together and away from the warm walls of the chamber. To get the assembly still colder, the lasers were turned off and a magnetic field held the slower atoms together while allowing the faster ones to escape. (Such evaporative cooling is familiar in everyday life when the faster molecules of a liquid, for instance perspiration, leave its surface and so reduce the average energy of the remaining molecules.) Finally, when the temperature was down to under  $10^{-7}$  K—a tenth of a millionth of a degree above absolute zero—about 2000 rubidium atoms came together in a Bose-Einstein condensate 10  $\mu\text{m}$  long that lasted for 10 s.

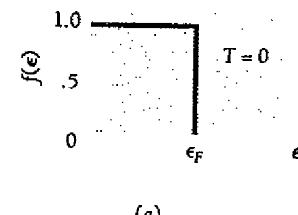
Soon after this achievement other groups succeeded in creating Bose-Einstein condensates in lithium and sodium. One condensate in sodium contained about 5 million atoms, was shaped like a pencil 8  $\mu\text{m}$  across and 150  $\mu\text{m}$  long, and lasted for 20 s. Still larger condensates were later produced, including one that consisted of  $10^8$  hydrogen atoms. It proved possible to extract from condensates beams of atoms whose behavior confirmed that they were coherent, with all the atomic wave functions in phase just like the light waves in the coherent beam from a laser. Bose-Einstein condensates are extremely interesting from a number of points of view both fundamental and applied—for example, for possible use in ultrasensitive measurements of various kinds.

Thus at absolute zero all energy states up to  $\epsilon_F$  are occupied, and none above  $\epsilon_F$  (Fig. 9.6a). If a system contains  $N$  fermions, we can calculate its Fermi energy  $\epsilon_F$  by filling up its energy states with the  $N$  particles in order of increasing energy starting from  $\epsilon = 0$ . The highest state to be occupied will then have the energy  $\epsilon = \epsilon_F$ . This calculation will be made for the electrons in a metal in Sec. 9.9.

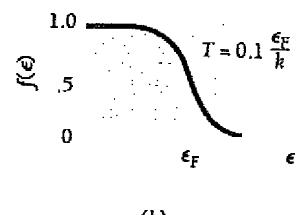
As the temperature is increased above  $T = 0$  but with  $kT$  still smaller than  $\epsilon_F$ , fermions will leave states just below  $\epsilon_F$  to move into states just above it, as in Fig. 9.6b. At higher temperatures, fermions from even the lowest state will begin to be excited to higher ones, so  $f_{FD}(0)$  will drop below 1. In these circumstances  $f_{FD}(\epsilon)$  will assume a shape like that in Fig. 9.6c, which corresponds to the lowest curve in Fig. 9.5.

The properties of the three distribution functions are summarized in Table 9.1. It is worth recalling that to find the actual number  $n(\epsilon)$  of particles with an energy  $\epsilon$ , the functions  $f(\epsilon)$  must be multiplied by the number of states  $g(\epsilon)$  with this energy:

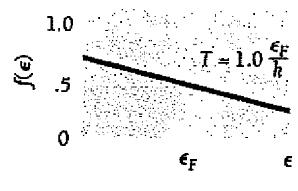
$$n(\epsilon) = g(\epsilon)f(\epsilon) \quad (9.1)$$



(a)



(b)

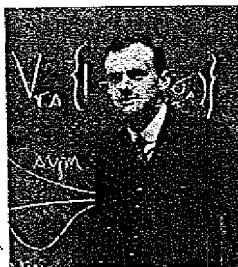


(c)

Figure 9.6 Distribution function for fermions at three different temperatures. (a) At  $T = 0$ , all the energy states up to the Fermi energy  $\epsilon_F$  are occupied. (b) At a low temperature, some fermions will leave states just below  $\epsilon_F$  and move into states just above  $\epsilon_F$ . (c) At a higher temperature, fermions from any state below  $\epsilon_F$  may move into states above  $\epsilon_F$ .

Table 9.1 The Three Statistical Distribution Functions

	Maxwell-Boltzmann	Bose-Einstein	Fermi-Dirac
Applies to systems of	Identical, distinguishable particles	Identical, indistinguishable particles that do not obey exclusion principle	Identical, indistinguishable particles that obey exclusion principle
Category of particles	Classical	Bosons	Fermions
Properties of particles	Any spin; particles far enough apart so wave functions do not overlap	Spin 0, 1, 2, ...; wave functions are symmetric to interchange of particle labels	Spin $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \dots$ ; wave functions are antisymmetric to interchange of particle labels
Examples	Molecules of a gas	Photons in a cavity; phonons in a solid; liquid helium at low temperatures	Free electrons in a metal; electrons in a star whose atoms have collapsed (white dwarf stars)
Distribution function (number of particles in each state of energy $\epsilon$ at the temperature $T$ )	$f_{MB}(\epsilon) = Ae^{-\epsilon/kT}$	$f_{BE}(\epsilon) = \frac{1}{e^{\epsilon/kT} - 1}$	$f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon - \epsilon_F)/kT} + 1}$
Properties of distribution	No limit to number of particles per state	No limit to number of particles per state; more particles per state than $f_{MB}$ at low energies; approaches $f_{MB}$ at high energies	Never more than 1 particle per state; fewer particles per state than $f_{MB}$ at low energies; approaches $f_{MB}$ at high energies



Paul A. M. Dirac (1902–1984) was born in Bristol, England, and studied electrical engineering there. He then switched his interest to mathematics and finally to physics, obtaining his Ph.D. from Cambridge in 1926. After reading Heisenberg's first paper on quantum mechanics in 1925, Dirac soon devised a more general theory and the next year formulated Pauli's exclusion principle in quantum-mechanical terms. He investigated the statistical behavior of particles that obey the Pauli principle, such as electrons, which Fermi had done independently a little earlier, and the result is called Fermi-Dirac statistics in honor of both. In 1928 Dirac joined special relativity to quantum theory to give a theory of the electron that not only permitted its spin and magnetic moment to be calculated but also predicted the existence of positively charged electrons, or positrons, which were discovered by Carl Anderson in the United States in 1932.

In an attempt to explain why charge is quantized, Dirac in 1931 found it necessary to postulate the existence of magnetic monopoles, isolated N or S magnetic poles. More recent theories show that magnetic monopoles should have been created in profusion just after the Big Bang that marked the beginning of the universe; the predicted monopole mass is  $\sim 10^{16}$  GeV/c<sup>2</sup> ( $\sim 10^{-8}$  g). As Dirac said in 1981, "From the theoretical point of view one would think that monopoles should exist, because of the prettiness of the mathematics. Many attempts to find them have been made, but all have been unsuccessful. One should conclude that pretty mathematics by itself is not an adequate reason for nature to have made use of a theory."

In 1932 Dirac became Lucasian Professor of Mathematics at Cambridge, the post Newton had held two and a half centuries earlier, and in 1933 shared the Nobel Prize in physics with Schrödinger. He remained active in physics for the rest of his life, after 1969 in the warmer climate of Florida, but as is often the case in science he will be remembered for the brilliant achievements of his youth.

## 9.5 RAYLEIGH-JEANS FORMULA

### *The classical approach to blackbody radiation*

Blackbody radiation was discussed briefly in Sec. 2.2, where we learned about the failure of classical physics to account for the shape of the blackbody spectrum—the “ultraviolet catastrophe”—and how Planck’s introduction of energy quantization led to the correct formula for this spectrum. Because the origin of blackbody radiation is such a fundamental question, it deserves a closer look.

Figure 2.6 shows the blackbody spectrum for two temperatures. To explain this spectrum, the classical calculation by Rayleigh and Jeans begins by considering a blackbody as a radiation-filled cavity at the temperature  $T$  (Fig. 2.5). Because the cavity walls are assumed to be perfect reflectors, the radiation must consist of standing em waves, as in Fig. 2.7. In order for a node to occur at each wall, the path length from wall to wall, in any direction, must be an integral number  $j$  of half-wavelengths. If the cavity is a cube  $L$  long on each edge, this condition means that for standing waves in the  $x$ ,  $y$ , and  $z$  directions respectively, the possible wavelengths are such that

$$\begin{aligned} j_x &= \frac{2L}{\lambda} = 1, 2, 3, \dots = \text{number of half-wavelengths in } x \text{ direction} \\ j_y &= \frac{2L}{\lambda} = 1, 2, 3, \dots = \text{number of half-wavelengths in } y \text{ direction} \quad (9.30) \\ j_z &= \frac{2L}{\lambda} = 1, 2, 3, \dots = \text{number of half-wavelengths in } z \text{ direction} \end{aligned}$$

For a standing wave in any arbitrary direction, it must be true that

$$\begin{array}{lll} \text{Standing waves} & j_x^2 + j_y^2 + j_z^2 = \left(\frac{2L}{\lambda}\right)^2 & j_x = 0, 1, 2, \dots \\ \text{in a cubic cavity} & & j_y = 0, 1, 2, \dots \\ & & j_z = 0, 1, 2, \dots \end{array} \quad (9.31)$$

in order that the wave terminate in a node at its ends. (Of course, if  $j_x = j_y = j_z = 0$ , there is no wave, though it is possible for any one or two of the  $j$ ’s to equal 0.)

To count the number of standing waves  $g(\lambda) d\lambda$  within the cavity whose wavelengths lie between  $\lambda$  and  $\lambda + d\lambda$ , what we have to do is count the number of permissible sets of  $j_x, j_y, j_z$  values that yield wavelengths in this interval. Let us imagine a  $j$ -space whose coordinate axes are  $j_x, j_y$ , and  $j_z$ ; Fig. 9.7 shows part of the  $j_x-j_y$  plane of such a space. Each point in the  $j$ -space corresponds to a permissible set of  $j_x, j_y, j_z$  values and thus to a standing wave. If  $j$  is a vector from the origin to a particular point  $j_x, j_y, j_z$ , its magnitude is

$$j = \sqrt{j_x^2 + j_y^2 + j_z^2} \quad (9.32)$$

The total number of wavelengths between  $\lambda$  and  $\lambda + d\lambda$  is the same as the number of points in  $j$  space whose distances from the origin lie between  $j$  and  $j + dj$ . The volume of a spherical shell of radius  $j$  and thickness  $dj$  is  $4\pi j^2 dj$ , but we are only interested in the octant of this shell that includes non-negative values of  $j_x, j_y$ , and  $j_z$ . Also, for each standing wave counted in this way, there are two perpendicular

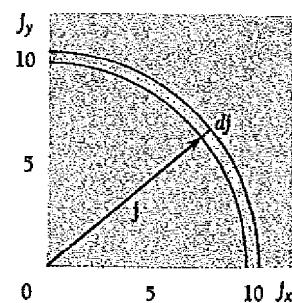


Figure 9.7 Each point in  $j$  space corresponds to a possible standing wave.

directions of polarization. Hence the number of independent standing waves in the cavity is

$$\begin{array}{ll} \text{Number of} & g(j) dj = (2)(\frac{1}{8})(4\pi j^2 dj) = \pi j^2 dj \\ \text{standing waves} & \end{array} \quad (9.33)$$

What we really want is the number of standing waves in the cavity as a function of their frequency  $\nu$  instead of as a function of  $j$ . From Eqs. (9.31) and (9.32) we have

$$j = \frac{2L}{\lambda} = \frac{2L\nu}{c} \quad dj = \frac{2L}{c} d\nu$$

and so

$$\begin{array}{ll} \text{Number of} & g(\nu) d\nu = \pi \left( \frac{2L\nu}{c} \right)^2 \frac{2L}{c} d\nu = \frac{8\pi L^3}{c^3} \nu^2 d\nu \\ \text{standing waves} & \end{array} \quad (9.34)$$

The cavity volume is  $L^3$ , which means that the number of independent standing waves per unit volume is

$$\begin{array}{ll} \text{Density of} & G(\nu) d\nu = \frac{1}{L^3} g(\nu) d\nu = \frac{8\pi\nu^2 d\nu}{c^3} \\ \text{standing waves} & \end{array} \quad (9.35)$$

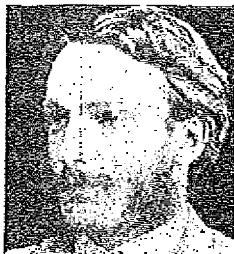
in a cavity

Equation (9.35) is independent of the shape of the cavity, even though we used a cubical cavity to facilitate the derivation. The higher the frequency, the shorter the wavelength and the greater the number of standing waves that are possible, as must be the case.

The next step is to find the average energy per standing wave. Here is where classical and quantum physics diverge. According to the classical theorem of equipartition of energy, as already mentioned, the average energy per degree of freedom of an entity that is part of a system of such entities in thermal equilibrium at the temperature  $T$  is  $\frac{1}{2}kT$ . Each standing wave in a radiation-filled cavity corresponds to two degrees of freedom, for a total  $\bar{\epsilon}$  of  $kT$ , because each wave originates in an oscillator in the cavity wall. Such an oscillator has two degrees of freedom, one that represents its kinetic energy and one that represents its potential energy. The energy  $u(\nu) d\nu$  per unit volume in the cavity in the frequency interval from  $\nu$  to  $\nu + d\nu$  is therefore, according to classical physics,

$$\begin{array}{ll} u(\nu) d\nu = \bar{\epsilon} G(\nu) d\nu = kT G(\nu) d\nu & \\ \text{Rayleigh-Jeans} & = \frac{8\pi\nu^2 kT d\nu}{c^3} \\ \text{formula} & \end{array} \quad (9.36)$$

The Rayleigh-Jeans formula, which has the spectral energy density of blackbody radiation increasing as  $\nu^2$  without limit, is obviously wrong. Not only does it predict a spectrum different from the observed one (see Fig. 2.8), but integrating Eq. (9.36) from  $\nu = 0$  to  $\nu = \infty$  gives the total energy density as infinite at all temperatures. The discrepancy between theory and observation was at once recognized as fundamental. This is the failure of classical physics that led Max Planck in 1900 to discover that only if light emission is a quantum phenomenon can the correct formula for  $u(\nu) d\nu$  be obtained.



Lord Rayleigh (1842–1919) was born John William Strutt to a wealthy English family and inherited his title on the death of his father. After being educated at home, he went on to be an outstanding student at Cambridge University and then spent some time in the United States. On his return Rayleigh set up a laboratory in his home. There he carried out both experimental and theoretical research except for a five-year period when he directed the Cavendish Laboratory at Cambridge following Maxwell's death in 1879.

For much of his life Rayleigh's work concerned the behavior of waves of all kinds, and he made many contributions to acoustics and optics. One of the types of wave an earthquake produces is named after him. In 1871 Rayleigh explained the blue color of the sky in terms of the preferential scattering of short-wavelength sunlight in the atmosphere. The formula for the resolving power of an optical instrument is another of his achievements.

At the Cavendish Laboratory, Rayleigh completed the standardization of the volt, the ampere, and the ohm, a task Maxwell had begun. Back at home, he found that nitrogen prepared from air is very slightly denser than nitrogen prepared from nitrogen-containing compounds. Together with the chemist William Ramsay, Rayleigh showed that the reason for the discrepancy was a hitherto unknown gas that makes up about 1 percent of

the atmosphere. They called the gas argon, from the Greek word for "inert," because argon did not react with other substances. Ramsay went on to discover the other inert gases neon ("new"), krypton ("hidden"), and xenon ("stranger"). He was also able to isolate the lightest inert gas, helium, which had thirty years earlier been identified in the sun by its spectral lines; *helios* means "sun" in Greek. Rayleigh and Ramsay won Nobel Prizes in 1904 for their work on argon.

What was possibly Rayleigh's greatest contribution to science came after the discovery of argon and took the form of an equation that did not agree with experiment. The problem was accounting for the spectrum of blackbody radiation, that is, the relative intensities of the different wavelengths present in such radiation. Rayleigh calculated the shape of this spectrum; because the astronomer James Jeans pointed out a small error Rayleigh had made, the result is called the Rayleigh-Jeans formula. The formula follows directly from the laws of physics known at the end of the nineteenth century—and it is hopelessly incorrect, as Rayleigh and Jeans were aware. (For instance, the formula predicts that a blackbody should radiate energy at an infinite rate.) The search for a correct blackbody formula led to the sounding of the quantum theory of radiation by Max Planck and Albert Einstein, a theory that was to completely revolutionize physics.

Despite the successes of quantum theory and of Einstein's theory of relativity that followed soon afterward, Rayleigh, after a lifetime devoted to classical physics, never really accepted them. He died in 1919.

## 9.6 PLANCK RADIATION LAW

### *How a photon gas behaves*

Planck found that he had to assume that the oscillators in the cavity walls were limited to energies of  $\epsilon_n = nh\nu$ , where  $n = 0, 1, 2, \dots$ . He then used the Maxwell-Boltzmann distribution law to find that the number of oscillators with the energy  $\epsilon_n$  is proportional to  $e^{-\epsilon_n/kT}$  at the temperature  $T$ . In this case the average energy per oscillator (and so per standing wave in the cavity) is

$$\bar{\epsilon} = \frac{h\nu}{e^{h\nu/kT} - 1} \quad (9.37)$$

instead of the energy-equipartition average of  $kT$  which Rayleigh and Jeans had used. The result was

$$\text{Planck radiation formula} \quad u(\nu) d\nu = \bar{\epsilon} G(\nu) d\nu = \frac{8\pi h}{c^3} \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1} \quad (9.38)$$

which agrees with the experimental findings.

Although Planck got the right formula, his derivation is, from today's perspective, seriously flawed. We now know that the harmonic oscillators in the cavity walls have

the energies  $\epsilon_n = (n + \frac{1}{2})\hbar\nu$ , not  $n\hbar\nu$ . Including the zero-point energy of  $\frac{1}{2}\hbar\nu$  does not lead to the average energy of Eq. (9.37) when Maxwell-Boltzmann statistics are used. The proper procedure is to consider the em waves in a cavity as a photon gas subject to Bose-Einstein statistics, since the spin of a photon is 1. The average number of photons  $f(\nu)$  in each state of energy  $\epsilon = \hbar\nu$  is therefore given by the Bose-Einstein distribution function of Eq. (9.26).

The value of  $\alpha$  in Eq. (9.26) depends on the number of particles in the system being considered. But the number of photons in a cavity need not be conserved: unlike gas molecules or electrons, photons are created and destroyed all the time. Although the total radiant energy in a cavity at a given temperature remains constant, the number of photons that incorporate this energy can change. As mentioned in Sec. 9.4, the nonconservation of photons means that  $\alpha = 0$ . Hence the Bose-Einstein distribution function for photons is

$$\text{Photon distribution function} \quad f(\nu) = \frac{1}{e^{\hbar\nu/kT} - 1} \quad (9.39)$$

Equation (9.35) for the number of standing waves of frequency  $\nu$  per unit volume in a cavity is valid for the number of quantum states of frequency  $\nu$  since photons also have two directions of polarization, which corresponds to two orientations of their spins relative to their directions of motion. The energy density of photons in a cavity is accordingly

$$u(\nu) d\nu = \hbar\nu G(\nu)f(\nu) d\nu = \frac{8\pi\hbar}{c^3} \frac{\nu^3 d\nu}{e^{\hbar\nu/kT} - 1}$$

which is Eq. (9.38).

### Example 9.5

How many photons are present in  $1.00 \text{ cm}^3$  of radiation in thermal equilibrium at  $1000 \text{ K}$ ? What is their average energy?

#### Solution

(a) The total number of photons per unit volume is given by

$$\frac{N}{V} = \int_0^\infty n(\nu) d\nu$$

where  $n(\nu) d\nu$  is the number of photons per unit volume with frequencies between  $\nu$  and  $\nu + d\nu$ . Since such photons have energies of  $\hbar\nu$ ,

$$n(\nu) d\nu = \frac{u(\nu) d\nu}{\hbar\nu}$$

with  $u(\nu) d\nu$  being the energy density given by Planck's formula, Eq. (9.38). Hence the total number of photons in the volume  $V$  is

$$N = V \int_0^\infty \frac{u(\nu) d\nu}{\hbar\nu} = \frac{8\pi V}{c^3} \int_0^\infty \frac{\nu^2 d\nu}{e^{\hbar\nu/kT} - 1}$$

If we let  $h\nu/kT = x$ , then  $\nu = kTx/h$  and  $d\nu = (kT/h) dx$ , so that

$$N = 8\pi V \left( \frac{hT}{hc} \right)^3 \int_0^\infty \frac{x^2 dx}{e^x - 1}$$

The definite integral is a standard one equal to 2.404. Inserting the numerical values of the other quantities, with  $V = 1.00 \text{ cm}^3 = 1.00 \times 10^{-6} \text{ m}^3$ , we find that

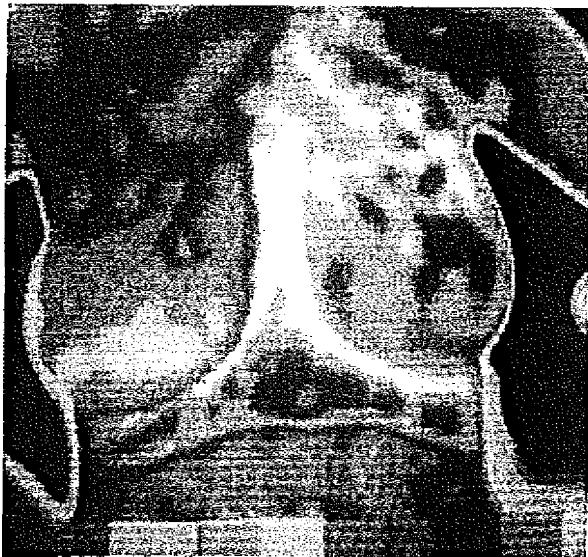
$$N = 2.03 \times 10^{10} \text{ photons}$$

(b) The average energy  $\bar{\epsilon}$  of the photons is equal to the total energy per unit volume divided by the number of photons per unit volume:

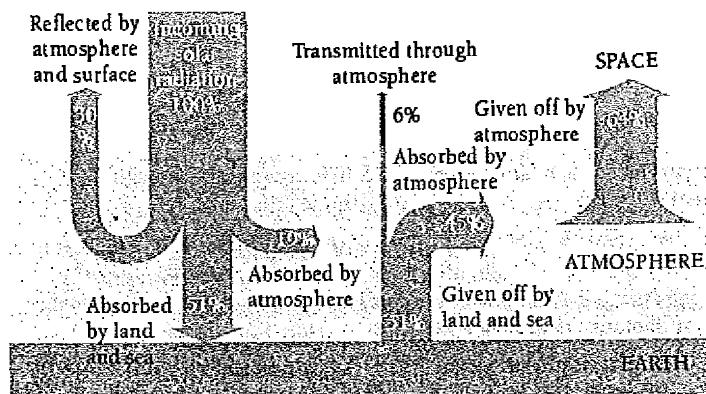
$$\bar{\epsilon} = \frac{\int_0^\infty u(\nu) d\nu}{n(\nu) d\nu} = \frac{aT^4}{N/V}$$

Since  $a = 4\sigma/c$  (see the discussion of the Stefan-Boltzmann law later in this section) and  $N = (2.405) [8\pi V(kT/hc)^3]$ ,

$$\bar{\epsilon} = \frac{\sigma c^2 h^3 T}{(2.405)(2\pi k^3)} = 3.73 \times 10^{-20} \text{ J} = 0.233 \text{ eV}$$



A thermograph measures the amount of infrared radiation each small portion of a person's skin emits and presents this information in pictorial form by different shades of gray or different colors in a thermogram. The skin over a tumor is warmer than elsewhere (perhaps because of increased blood flow or a higher metabolic rate), and thus a thermogram is a valuable diagnostic aid for detecting such maladies as breast and thyroid cancer. A small difference in skin temperature leads to a significant difference in radiation rate.



**Figure 9.8** The greenhouse effect is important in heating the earth's atmosphere. Much of the short-wavelength visible light from the sun that reaches the earth's surface is reradiated as long-wavelength infrared light that is readily absorbed by  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the atmosphere. This means that the atmosphere heated mainly from below by the earth rather than from above by the sun. The total energy that the earth and its atmosphere radiate into space on the average equals the total energy that they receive from the sun.

It is worth noting again that every body of condensed matter radiates according to Eq. (9.38), regardless of its temperature. An object need not be so hot that it glows conspicuously in the visible region in order to be radiating. The radiation from an object at room temperature, for instance, is chiefly in the infrared part of the spectrum to which the eye is not sensitive. Thus the interior of a greenhouse is warmer than the outside air because sunlight can enter through its windows but the infrared radiation given off by the interior cannot escape through them (Fig. 9.8).

### Wien's Displacement Law

An interesting feature of the blackbody spectrum at a given temperature is the wavelength  $\lambda_{\max}$  for which the energy density is the greatest. To find  $\lambda_{\max}$  we first express Eq. (9.38) in terms of wavelength and solve  $dU(\lambda)/d\lambda = 0$  for  $\lambda = \lambda_{\max}$ . We obtain in this way

$$\frac{hc}{kT\lambda_{\max}} = 4.965$$

which is more conveniently expressed as

$$\text{Wien's displacement law} \quad \lambda_{\max}T = \frac{hc}{4.965k} = 2.898 \times 10^{-3} \text{ m} \cdot \text{K} \quad (9.40)$$

Equation (9.40) is known as **Wien's displacement law**. It quantitatively expresses the empirical fact that the peak in the blackbody spectrum shifts to progressively shorter wavelengths (higher frequencies) as the temperature is increased, as in Fig. 2.6.

---

**Example 9.6**

Radiation from the Big Bang has been doppler-shifted to longer wavelengths by the expansion of the universe and today has a spectrum corresponding to that of a blackbody at 2.7 K. Find the wavelength at which the energy density of this radiation is a maximum. In what region of the spectrum is this radiation?

**Solution**

From Eq. (9.40) we have

$$\lambda_{\max} = \frac{2.898 \times 10^{-3} \text{ m} \cdot \text{K}}{T} = \frac{2.898 \times 10^{-3} \text{ m} \cdot \text{K}}{2.7 \text{ K}} = 1.1 \times 10^{-3} \text{ m} = 1.1 \text{ mm}$$

This wavelength is in the microwave region (see Fig. 2.2). The radiation was first detected in a microwave survey of the sky in 1964.

---

**Stefan-Boltzmann Law**

Another result we can obtain from Eq. (9.38) is the total energy density  $u$  of the radiation in a cavity. This is the integral of the energy density over all frequencies,

$$u = \int_0^{\infty} u(\nu) d\nu = \frac{8\pi^5 k^4}{15c^3 h^3} T^4 = aT^4$$

where  $a$  is a universal constant. The total energy density is proportional to the fourth power of the absolute temperature of the cavity walls. We therefore expect that the energy  $R$  radiated by an object per second per unit area is also proportional to  $T^4$ , a conclusion embodied in the Stefan-Boltzmann law:

Stefan-Boltzmann  
law

$$R = e\sigma T^4 \quad (9.41)$$

The value of Stefan's constant  $\sigma$  is

Stefan's constant  $\sigma = \frac{ac}{4} = 5.670 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$

The emissivity  $e$  depends on the nature of the radiating surface and ranges from 0, for a perfect reflector which does not radiate at all, to 1, for a blackbody. Some typical values of  $e$  are 0.07 for polished steel, 0.6 for oxidized copper and brass, and 0.97 for matte black paint.

---

**Example 9.7**

Sunlight arrives at the earth at the rate of about  $1.4 \text{ kW/m}^2$  when the sun is directly overhead. The average radius of the earth's orbit is  $1.5 \times 10^{11} \text{ m}$  and the radius of the sun is  $7.0 \times 10^8 \text{ m}$ . From these figures find the surface temperature of the sun on the assumption that it radiates like a blackbody, which is approximately true.

### Solution

We begin by finding the total power  $P$  radiated by the sun. The area of a sphere whose radius  $r_e$  is that of the earth's orbit is  $4\pi r_e^2$ . Since solar radiation falls on this sphere at a rate of  $P/A = 1.4 \text{ kW/m}^2$ ,

$$P = \left(\frac{P}{A}\right)(4\pi r_e^2) = (1.4 \times 10^3 \text{ W/m}^2)(4\pi)(1.5 \times 10^{11} \text{ m})^2 = 3.96 \times 10^{26} \text{ W}$$

Next we find the radiation rate  $R$  of the sun. If  $r_s$  is the sun's radius, its surface area is  $4\pi r_s^2$  and

$$R = \frac{\text{power output}}{\text{surface area}} = \frac{P}{4\pi r_s^2} = \frac{3.96 \times 10^{26} \text{ W}}{(4\pi)(7.0 \times 10^8 \text{ m})^2} = 6.43 \times 10^7 \text{ W/m}^2$$

The emissivity of a blackbody is  $\epsilon = 1$ , so from Eq. (9.41) we have

$$T = \left(\frac{R}{\epsilon\sigma}\right)^{1/4} = \left(\frac{6.43 \times 10^7 \text{ W/m}^2}{(1)(5.67 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4)}\right)^{1/4} = 5.8 \times 10^3 \text{ K}$$

## 9.7 EINSTEIN'S APPROACH

### Introducing stimulated emission

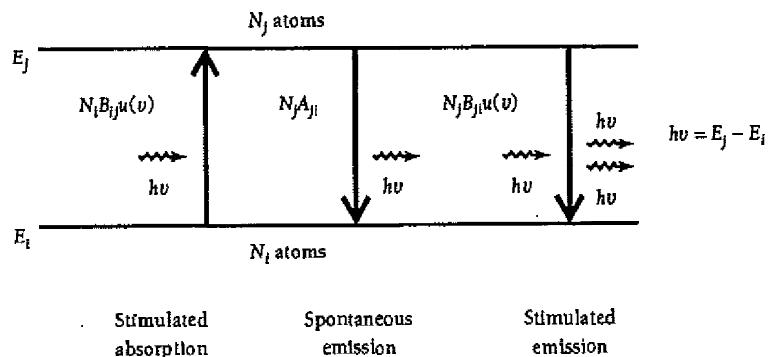
The stimulated emission of radiation was mentioned in Sec. 4.9 as the key concept behind the laser. In a 1917 paper Einstein introduced stimulated emission and used it to arrive at the form of Planck's radiation law in an elegantly simple manner. By the early 1920s this idea together with what had become known about the physics of the atom would have enabled the laser to have been invented then, but somehow nobody connected the dots until over thirty years later.

Let us consider two energy states in a particular atom, a lower one  $i$  and an upper one  $j$  (Fig. 9.9). If the atom is initially in state  $i$ , it can be raised to state  $j$  by absorbing a photon of frequency

$$\nu = \frac{E_j - E_i}{h} \quad (9.42)$$

Now we imagine an assembly of  $N_i$  atoms in state  $i$  and  $N_j$  atoms in state  $j$ , all in thermal equilibrium at the temperature  $T$  with light of frequency  $\nu$  and energy density  $u(\nu)$ . The probability that an atom in state  $i$  absorbs a photon is proportional to the

**Figure 9.9** Three kinds of transition between states of energies  $E_i$  and  $E_j$  in an atom. In spontaneous emission, the photon leaves the atom in a random direction. In stimulated emission, the photons that leave are in phase with each other and with the incident photon, and all the photons move in the same direction. The number of atoms that undergo each transition per second is indicated, where the quantity  $u(\nu)$  is the density of photons of frequency  $\nu$  and  $A_{ji}$ ,  $B_{ij}$ , and  $B_{ji}$  are constants that depend on the properties of the atomic states.



energy density  $u(\nu)$  and also to the properties of states  $i$  and  $j$ , which we can include in some constant  $B_{ji}$ . Hence the number  $N_{i \rightarrow j}$  of atoms per second that absorb photons is given by

$$\begin{array}{ll} \text{Number of atoms} & N_{i \rightarrow j} = N_i B_{ji} u(\nu) \\ \text{that absorb photons} & \end{array} \quad (9.43)$$

An atom in the upper state  $j$  has a certain probability  $A_{ji}$  to spontaneously drop to state  $i$  by emitting a photon of frequency  $\nu$ . We also suppose that light of frequency  $\nu$  can somehow interact with an atom in state  $j$  to induce its transition to the lower state  $i$ . An energy density of  $u(\nu)$  therefore means a probability for stimulated emission of  $B_{ji}u(\nu)$ , where  $B_{ji}$ , like  $B_{ij}$  and  $A_{ji}$ , depends on the properties of states  $i$  and  $j$ . Since  $N_j$  is the number of atoms in state  $j$ , the number of atoms per second that fall to the lower state  $i$  is

$$\begin{array}{ll} \text{Number of atoms} & N_{j \rightarrow i} = N_j [A_{ji} + B_{ji}u(\nu)] \\ \text{that emit photons} & \end{array} \quad (9.44)$$

As discussed in Sec. 4.9, stimulated emission has a classical analog in the behavior of a harmonic oscillator. Of course, classical physics often does not apply on an atomic scale, but we have not assumed that stimulated emission *does* occur, only that it *may* occur. If we are wrong, we will ultimately find merely that  $B_{ji} = 0$ .

Since the system here is in equilibrium, the number of atoms per second that go from state  $i$  to  $j$  must equal the number that go from  $j$  to  $i$ . Therefore

$$\begin{aligned} N_{i \rightarrow j} &= N_{j \rightarrow i} \\ N_i B_{ji} u(\nu) &= N_j [A_{ji} + B_{ji}u(\nu)] \end{aligned}$$

Dividing both sides of the latter equation by  $N_j B_{ji}$  and solving for  $u(\nu)$  gives

$$\begin{aligned} \left( \frac{N_i}{N_j} \right) \left( \frac{B_{ji}}{B_{ji}} \right) u(\nu) &= \frac{A_{ji}}{B_{ji}} + u(\nu) \\ u(\nu) &= \frac{A_{ji}/B_{ji}}{\left( \frac{N_i}{N_j} \right) \left( \frac{B_{ji}}{B_{ji}} \right) - 1} \end{aligned} \quad (9.45)$$

Finally we draw on Eq. (9.2) for the numbers of atoms of energies  $E_i$  and  $E_j$  in a system of these atoms at the temperature  $T$ , which we can write as

$$N_i = C e^{-E_i/kT}$$

$$N_j = C e^{-E_j/kT}$$

Hence

$$\frac{N_i}{N_j} = e^{-(E_i - E_j)/kT} = e^{(E_j - E_i)/kT} = e^{h\nu/kT} \quad (9.46)$$

and so

$$u(\nu) = \frac{A_{ji}/B_{ji}}{\left(\frac{B_{ij}}{B_{ji}}\right)e^{h\nu/kT} - 1} \quad (9.47)$$

This formula gives the energy density of photons of frequency  $\nu$  in equilibrium at the temperature  $T$  with atoms whose possible energies are  $E_i$  and  $E_j$ .

Equation (9.47) is consistent with the Planck radiation law of Eq. (9.38) if

$$B_{ij} = B_{ji} \quad (9.48)$$

and

$$\frac{A_{ji}}{B_{ji}} = \frac{8\pi h\nu^3}{c^3} \quad (9.49)$$

We can draw these conclusions:

- 1 Stimulated emission does occur and its probability for a transition between two states is equal to the probability for absorption.
- 2 The ratio between the probabilities for spontaneous and stimulated emission varies with  $\nu^3$ , so the relative likelihood of spontaneous emission increases rapidly with the energy difference between the two states.
- 3 All we need to know is one of the probabilities  $A_{ji}$ ,  $B_{ij}$ ,  $B_{ji}$  to find the others.

Conclusion 3 suggests that the process of spontaneous emission is intimately related to the processes of absorption and stimulated emission. Absorption and stimulated emission can be understood classically by considering the interaction between an atom and an electromagnetic waves, but spontaneous emission can occur in the absence of any such wave, yet apparently by a comparable interaction. This paradox is removed by the theory of quantum electrodynamics. As briefly described in Sec. 6.9, this theory shows that "vacuum fluctuations" in  $E$  and  $B$  occur even when  $E = B = 0$  classically, and these fluctuations, analogs of the zero-point vibrations of a harmonic oscillator, stimulate what is apparently spontaneous emission.

## 9.8 SPECIFIC HEATS OF SOLIDS

### *Classical physics fails again*

Blackbody radiation is not the only familiar phenomenon whose explanation requires quantum statistical mechanics. Another is the way in which the internal energy of a solid varies with temperature.

Let us consider the molar specific heat of a solid at constant volume,  $c_V$ . This is the energy that must be added to 1 kmol of the solid, whose volume is held fixed, to raise its temperature by 1 K. The specific heat at constant pressure  $c_p$  is 3 to 5 percent higher than  $c_V$  in solids because it includes the work associated with a volume change as well as the change in internal energy.

The internal energy of a solid resides in the vibrations of its constituent particles, which may be atoms, ions, or molecules; we shall refer to them as atoms here for

convenience. These vibrations may be resolved into components along three perpendicular axes, so that we may represent each atom by three harmonic oscillators. As we know, according to classical physics a harmonic oscillator in a system of them in thermal equilibrium at the temperature  $T$  has an average energy of  $kT$ . On this basis each atom in a solid should have  $3kT$  of energy. A kilomole of a solid contains Avogadro's number  $N_0$  of atoms, and its total internal energy  $E$  at the temperature  $T$  accordingly ought to be

Classical internal energy of solid 
$$E = 3N_0kT = 3RT \quad (9.50)$$

where  $R = N_0k = 8.31 \times 10^3 \text{ J/Kmol} \cdot \text{K} = 1.99 \text{ kcal/kmol} \cdot \text{K}$

is the universal gas constant. (We recall that in an ideal-gas sample of  $n$  kilomoles,  $pV = nRT$ .)

The specific heat at constant volume is given in terms of  $E$  by

Specific heat at constant volume 
$$c_V = \left( \frac{\partial E}{\partial T} \right)_V$$

and so here

Dulong-Petit law 
$$c_V = 3R = 5.97 \text{ kcal/kmol} \cdot \text{K} \quad (9.51)$$

Over a century ago Dulong and Petit found that, indeed,  $c_V \approx 3R$  for most solids at room temperature and above, and Eq. (9.51) is known as the Dulong-Petit law in their honor.

However, the Dulong-Petit law fails for such light elements as boron, beryllium, and carbon (as diamond), for which  $c_V = 3.34, 3.85$ , and  $1.46 \text{ kcal/kmol} \cdot \text{K}$  respectively at  $20^\circ\text{C}$ . Even worse, the specific heats of all solids drop sharply at low temperatures and approach 0 as  $T$  approaches 0 K. Figure 9.10 shows how  $c_V$  varies with  $T$  for several elements. Clearly something is wrong with the analysis leading up to Eq. (9.51), and it must be something fundamental because the curves of Fig. 9.10 share the same general character.

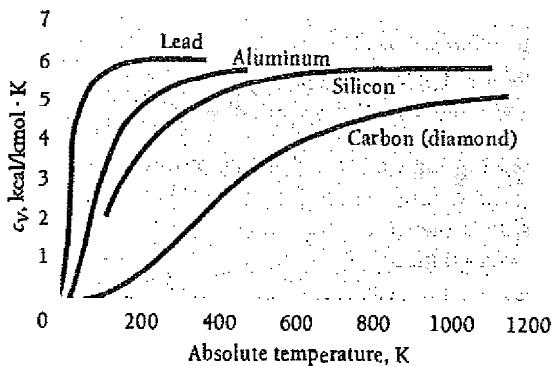


Figure 9.10 The variation with temperature of the molar specific heat at constant volume  $c_V$  for several elements.

### Einstein's Formula

In 1907 Einstein discerned that the basic flaw in the derivation of Eq. (9.51) lies in the figure of  $kT$  for the average energy per oscillator in a solid. This flaw is the same as that responsible for the incorrect Rayleigh-Jeans formula for blackbody radiation. According to Einstein, the probability  $f(\nu)$  that an oscillator have the frequency  $\nu$  is given by Eq. (9.39),  $f(\nu) = 1/(e^{h\nu/kT} - 1)$ . Hence the average energy for an oscillator whose frequency of vibration is  $\nu$  is

$$\text{Average energy per oscillator} \quad \bar{\epsilon} = h\nu f(\nu) = \frac{h\nu}{e^{h\nu/kT} - 1} \quad (9.52)$$

and not  $\bar{\epsilon} = kT$ . The total internal energy of a kilomole of a solid therefore becomes

$$\text{Internal energy of solid} \quad E = 3N_0\bar{\epsilon} = \frac{3N_0h\nu}{e^{h\nu/kT} - 1} \quad (9.53)$$

and its molar specific heat is

$$\text{Einstein specific heat formula} \quad c_V = \left( \frac{\partial E}{\partial T} \right)_V = 3R \left( \frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} \quad (9.54)$$

We can see at once that this approach is on the right track. At high temperatures,  $h\nu \ll kT$ , and

$$e^{h\nu/kT} \approx 1 + \frac{h\nu}{kT}$$

since  $e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$

Hence Eq. (9.52) becomes  $\bar{\epsilon} \approx h\nu(h\nu/kT) = kT$ , which leads to  $c_V \approx 3R$ , the Dulong-Petit value, as it should. At high temperatures the spacing  $h\nu$  between possible energies is small relative to  $kT$ , so  $\epsilon$  is effectively continuous and classical physics holds.

As the temperature decreases, the value of  $c_V$  given by Eq. (9.54) decreases. The reason for the change from classical behavior is that now the spacing between possible energies is becoming large relative to  $kT$ , which inhibits the possession of energies above the zero-point energy. The natural frequency  $\nu$  for a particular solid can be determined by comparing Eq. (9.54) with an empirical curve of its  $c_V$  versus  $T$ . The result in the case of aluminum is  $\nu = 6.4 \times 10^{12}$  Hz, which agrees with estimates made in other ways, for instance on the basis of elastic moduli.

Why is it that the zero-point energy of a harmonic oscillator does not enter this analysis? As we recall, the permitted energies of a harmonic oscillator are  $(n + \frac{1}{2})h\nu$ ,  $n = 0, 1, 2, \dots$ . The ground state of each oscillator in a solid is therefore  $\epsilon_0 = \frac{1}{2}h\nu$ , the zero-point value, and not  $\epsilon_0 = 0$ . But the zero-point energy merely adds a constant, temperature-independent term of  $\epsilon_0 = (3N_0)(\frac{1}{2}h\nu)$  to the molar energy of a solid, and this term vanishes when the partial derivative  $(\partial E / \partial T)_V$  is taken to find  $c_V$ .

### The Debye Theory

Although Einstein's formula predicts that  $c_V \rightarrow 0$  as  $T \rightarrow 0$ , as observed, the precise manner of this approach does not agree too well with the data. The inadequacy of Eq. (9.54) at low temperatures led Peter Debye to look at the problem in a different way in 1912. In Einstein's model, each atom is regarded as vibrating independently of its neighbors at a fixed frequency  $\nu$ . Debye went to the opposite extreme and considered a solid as a continuous elastic body. Instead of residing in the vibrations of individual atoms, the internal energy of a solid according to the new model resides in elastic standing waves.

The elastic waves in a solid are of two kinds, longitudinal and transverse, and range in frequency from 0 to a maximum  $\nu_m$ . (The interatomic spacing in a solid sets a lower limit to the possible wavelengths and hence an upper limit to the frequencies.) Debye assumed that the total number of different standing waves in a kilomole of a solid is equal to its  $3N_0$  degrees of freedom. These waves, like em waves, have energies quantized in units of  $\hbar\nu$ . A quantum of acoustic energy in a solid is called a phonon, and it travels with the speed of sound since sound waves are elastic in nature. The concept of phonons is quite general and has applications other than in connection with specific heats.

Debye finally asserted that a phonon gas has the same statistical behavior as a photon gas or a system of harmonic oscillators in thermal equilibrium, so that the average energy  $\bar{\epsilon}$  per standing wave is the same as in Eq. (9.52). The resulting formula for  $c_V$  reproduces the observed curves of  $c_V$  versus  $T$  quite well at all temperatures.

Peter Debye, who was Dutch, did original work in many aspects of both physics and chemistry, at first in Germany and later at Cornell University. Although Heisenberg, a colleague for a time, thought him lazy ("I could frequently see him walking around in his garden and watering the roses even during duty hours of the Institute"), he published nearly 250 papers and received the Nobel Prize in chemistry in 1936.

## 9.9 FREE ELECTRONS IN A METAL

*No more than one electron per quantum state*

The classical, Einstein, and Debye theories of specific heats of solids apply with equal degrees of success to both metals and nonmetals, which is strange because they ignore the presence of free electrons in metals.

As discussed in Chap. 10, in a typical metal each atom contributes one electron to the common "electron gas," so in 1 kilomole of the metal there are  $N_0$  free electrons. If these electrons behave like the molecules of an ideal gas, each would have  $\frac{1}{2}kT$  of kinetic energy on the average. The metal would then have

$$E_e = \frac{3}{2}N_0kT = \frac{3}{2}RT$$

of internal energy per kilomole due to the electrons. The molar specific heat due to the electrons should therefore be

$$c_{Ve} = \left( \frac{\partial E_e}{\partial T} \right)_V = \frac{3}{2}R$$

and the total specific heat of the metal should be

$$c_V = 3R + \frac{3}{2}R = \frac{9}{2}R$$

at high temperatures where a classical analysis is valid. Actually, of course, the Dulong-Petit value of  $3R$  holds at high temperatures, from which we conclude that the free electrons do not in fact contribute to the specific heat. Why not?

If we reflect on the characters of the entities involved in the specific heat of a metal, the answer begins to emerge. Both the harmonic oscillators of Einstein's model and the phonons of Debye's model are bosons and obey Bose-Einstein statistics, which place no upper limit on the occupancy of a particular quantum state. Electrons, however, are fermions and obey Fermi-Dirac statistics, which means that no more than one electron can occupy each quantum state. Although both systems of bosons and systems of fermions approach Maxwell-Boltzmann statistics with average energies  $\bar{\epsilon} = \frac{1}{2}kT$  per degree of freedom at "high" temperatures, how high is high enough for classical behavior is not necessarily the same for the two kinds of systems in a metal.

According to Eq. (9.29), the distribution function that gives the average occupancy of a state of energy  $\epsilon$  in a system of fermions is

$$\text{Average occupancy per state} \quad f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon - \epsilon_F)/kT} + 1} \quad (9.29)$$

What we also need is an expression for  $g(\epsilon) d\epsilon$ , the number of quantum states available to electrons with energies between  $\epsilon$  and  $\epsilon + d\epsilon$ .

We can use exactly the same reasoning to find  $g(\epsilon) d\epsilon$  that we used to find the number of standing waves in a cavity with the wavelength  $\lambda$  in Sec. 9.5. The correspondence is exact because there are two possible spin states,  $m_s = +\frac{1}{2}$  and  $m_s = -\frac{1}{2}$  ("up" and "down"); for electrons, just as there are two independent directions of polarization for otherwise identical standing waves.

We found earlier that the number of standing waves in a cubical cavity  $L$  on a side is

$$g(j) dj = \pi j^2 dj \quad (9.33)$$

where  $j = 2L/\lambda$ . In the case of an electron,  $\lambda$  is its de Broglie wavelength of  $\lambda = h/p$ . Electrons in a metal have nonrelativistic velocities, so  $p = \sqrt{2m\epsilon}$  and

$$j = \frac{2L}{\lambda} = \frac{2Lp}{h} = \frac{2L\sqrt{2m\epsilon}}{h} \quad dj = \frac{L}{h} \sqrt{\frac{2m}{\epsilon}} d\epsilon$$

Using these expressions for  $j$  and  $dj$  in Eq. (9.33) gives

$$g(\epsilon) d\epsilon = \frac{8\sqrt{2}\pi L^3 m^{3/2}}{h^3} \sqrt{\epsilon} d\epsilon$$

As in the case of standing waves in a cavity the exact shape of the metal sample does not matter, so we can substitute its volume  $V$  for  $L^3$  to give

$$\text{Number of electron states} \quad g(\epsilon) d\epsilon = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \sqrt{\epsilon} d\epsilon \quad (9.55)$$

### Fermi Energy

The final step is to calculate the value of  $\epsilon_F$ , the Fermi energy. As mentioned in Sec. 9.4, we can do this by filling up the energy states in the metal sample at  $T = 0$  with the  $N$  free electrons it contains in order of increasing energy starting from  $\epsilon = 0$ . The highest state to be filled will then have the energy  $\epsilon = \epsilon_F$  by definition. The number of electrons that can have the same energy  $\epsilon$  is equal to the number of states that have this energy, since each state is limited to one electron. Hence

$$N = \int_0^{\epsilon_F} g(\epsilon) d\epsilon = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \int_0^{\epsilon_F} \sqrt{\epsilon} d\epsilon = \frac{16\sqrt{2}\pi V m^{3/2}}{3h^3} \epsilon_F^{3/2}$$

and so

$$\text{Fermi energy} \quad \epsilon_F = \frac{\hbar^2}{2m} \left( \frac{3N}{8\pi V} \right)^{2/3} \quad (9.56)$$

The quantity  $N/V$  is the density of free electrons.

### Example 9.8

Find the Fermi energy in copper on the assumption that each copper atom contributes one free electron to the electron gas. (This is a reasonable assumption since, from Table 7.4, a copper atom has a single 4s electron outside closed inner shells.) The density of copper is  $8.94 \times 10^3 \text{ kg/m}^3$  and its atomic mass is 63.5 u.

#### Solution

The electron density  $N/V$  in copper is equal to the number of copper atoms per unit volume. Since  $1 \text{ u} = 1.66 \times 10^{-27} \text{ kg}$ ,

$$\begin{aligned} \frac{N}{V} &= \frac{\text{atoms}}{\text{m}^3} = \frac{\text{mass}/\text{m}^3}{\text{mass/atom}} = \frac{8.94 \times 10^3 \text{ kg}/\text{m}^3}{(63.5 \text{ u}) \times (1.66 \times 10^{-27} \text{ kg/u})} \\ &= 8.48 \times 10^{28} \text{ atoms}/\text{m}^3 = 8.48 \times 10^{28} \text{ electrons}/\text{m}^3 \end{aligned}$$

The corresponding Fermi energy is, from (9.56),

$$\begin{aligned} \epsilon_F &= \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})^2}{(2)(9.11 \times 10^{-31} \text{ kg/electron})} \left[ \frac{(3)(8.48 \times 10^{28} \text{ electrons}/\text{m}^3)}{8\pi} \right]^{2/3} \\ &= 1.13 \times 10^{-18} \text{ J} = 7.04 \text{ eV} \end{aligned}$$

At absolute zero,  $T = 0 \text{ K}$ , there would be electrons with energies of up to 7.04 eV in copper (corresponding to speeds of up to  $1.6 \times 10^6 \text{ m/s}$ ). By contrast, all the molecules in an ideal gas at 0 K would have zero energy. The electron gas in a metal is said to be degenerate.

### 9.10 ELECTRON-ENERGY DISTRIBUTION

*Why the electrons in a metal do not contribute to its specific heat except at very high and very low temperatures*

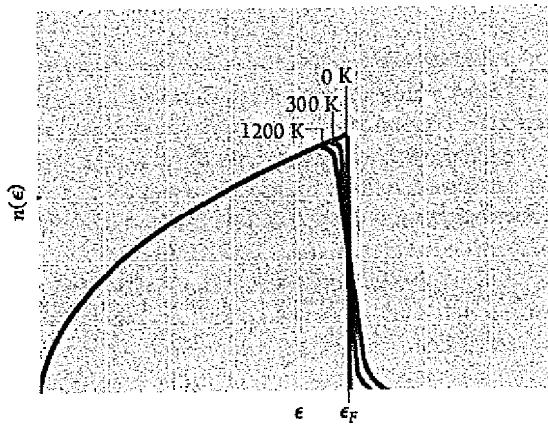


Figure 9.11 Distribution of electron energies in a metal at various temperatures.

With the help of Eqs. (9.29) and (9.55) we have for the number of electrons in an electron gas that have energies between  $\epsilon$  and  $\epsilon + d\epsilon$

$$n(\epsilon) d\epsilon = g(\epsilon)f(\epsilon) d\epsilon = \frac{(8\sqrt{2\pi}Vm^{3/2}/h^3)\sqrt{\epsilon} d\epsilon}{e^{(\epsilon-\epsilon_F)/kT} + 1} \quad (9.57)$$

If we express the numerator of Eq. (9.57) in terms of the Fermi energy  $\epsilon_F$  we get

$$\text{Electron energy distribution} \quad n(\epsilon) d\epsilon = \frac{(3N/2) \epsilon_F^{-3/2} \sqrt{\epsilon} d\epsilon}{e^{(\epsilon-\epsilon_F)/kT} + 1} \quad (9.58)$$

This formula is plotted in Fig. 9.11 for  $T = 0, 300$ , and  $1200$  K.

It is interesting to determine the average electron energy at  $0$  K. To do this, we first find the total energy  $E_0$  at  $0$  K, which is

$$E_0 = \int_0^{\epsilon_F} \epsilon n(\epsilon) d\epsilon$$

Since at  $T = 0$  K all the electrons have energies less than or equal to the Fermi energy  $\epsilon_F$ , we may let

$$e^{(\epsilon-\epsilon_F)/kT} = e^{-\infty} = 0$$

$$\text{and} \quad E_0 = \frac{3N}{2} \epsilon_F^{-3/2} \int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon = \frac{3}{5} N \epsilon_F$$

The average electron energy  $\bar{\epsilon}_0$  is this total energy divided by the number  $N$  of electrons present, which gives

$$\text{Average electron energy at } T = 0 \quad \bar{\epsilon}_0 = \frac{3}{5} \epsilon_F \quad (9.59)$$

**Table 9.2 Some Fermi Energies**

Metal		Fermi Energy, eV
Lithium	Li	4.72
Sodium	Na	3.12
Aluminum	Al	11.8
Potassium	K	2.14
Cesium	Cs	1.53
Copper	Cu	7.04
Zinc	Zn	11.0
Silver	Ag	5.51
Gold	Au	5.54

Since Fermi energies for metals are usually several electronvolts (Table 9.2), the average electron energy in them at 0 K will also be of this order of magnitude. The temperature of an ideal gas whose molecules have an average kinetic energy of 1 eV is 11,600 K. If free electrons behaved classically, a sample of copper would have to be at a temperature of about 50,000 K for its electrons to have the same average energy they actually have at 0 K!

The failure of the free electrons in a metal to contribute appreciably to its specific heat follows directly from their energy distribution. When a metal is heated, only those electrons near the very top of the energy distribution—those within about  $kT$  of the Fermi energy—are excited to higher energy states. The less energetic electrons cannot absorb more energy because the states above them are already filled. It is unlikely that an electron with, say, an energy  $\epsilon$  that is 0.5 eV below  $\epsilon_F$  can leapfrog the filled states above it to the nearest vacant state when  $kT$  at room temperature is 0.025 eV and even at 500 K is only 0.043 eV.

A detailed calculation shows that the specific heat of the electron gas in a metal is given by

$$\text{Electron specific heat} \quad c_{ve} = \frac{\pi^2}{2} \left( \frac{kT}{\epsilon_F} \right) R \quad (9.60)$$

At room temperature,  $kT/\epsilon_F$  ranges from 0.016 for cesium to 0.0021 for aluminum for the metals listed in Table 9.2, so the coefficient of  $R$  is very much smaller than the classical figure of  $\frac{3}{2}$ . The dominance of the atomic specific heat  $c_V$  in a metal over the electronic specific heat is pronounced over a wide temperature range. However, at very low temperatures  $c_{ve}$  becomes significant because  $c_V$  is then approximately proportional to  $T^3$  whereas  $c_{ve}$  is proportional to  $T$ . At very high temperatures  $c_V$  has leveled out at about  $3R$  while  $c_{ve}$  has continued to increase, and the contribution of  $c_{ve}$  to the total specific heat is then detectable.

## 9.11 DYING STARS

*What happens when a star runs out of fuel*

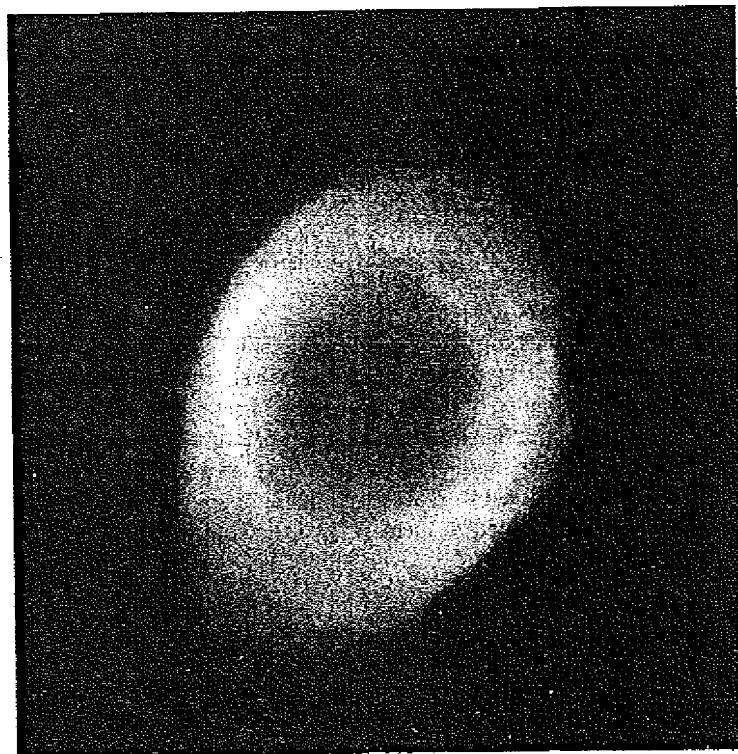
Metals are not the only systems that contain degenerate fermion gases—many dead and dying stars fall into this category also.

### White Dwarfs

Perhaps 10 percent of the stars in our galaxy are believed to be white dwarfs. These are stars in the final stages of their evolution with original masses that were less than about 8 solar masses. After the nuclear reactions that provided it with energy run out of fuel, such a star becomes unstable, swells to become a red giant, and eventually throws off its outer layer. The remaining core then cools and contracts gravitationally until its atoms collapse into nuclei and electrons packed closely together. A typical white dwarf has a mass of two-thirds that of the sun but is only about the size of the earth; a handful of its matter would weigh over a ton on the earth.

As a prospective white dwarf contracts, its volume  $V$  decreases and as a result the Fermi energy  $\epsilon_F$  of its electrons increases; see Eq. (9.56). When  $\epsilon_F$  exceeds  $kT$ , the electrons form a degenerate gas. A reasonable estimate for the Fermi energy in a typical white dwarf is 0.5 MeV. The nuclei present are much more massive than the electrons, and because  $\epsilon_F$  is inversely proportional to  $m$ , they continue to behave classically.

With the star's nuclear reactions at an end, the nuclei cool down and come together under the influence of gravitation. The electrons, however, cannot cool down since most of the low-energy states available to them are already filled; the situation corresponds to Fig. 9.6b. The electron gas becomes hotter and hotter as the star shrinks. Even though the total electron mass is only a small fraction of the star's mass, in time it exerts enough pressure to stop the gravitational contraction. Thus the size of a white dwarf is determined by a balance between the inward gravitational pull of its atomic nuclei and the pressure of its degenerate electron gas.



The Ring nebula in the constellation Lyra is a shell of gas moving outward from the star at its center, which is in the process of becoming a white dwarf.

### The Chandrasekhar Limit

The maximum white dwarf mass of  $1.4M_{\text{sun}}$  is called the **Chandrasekhar limit** after its discoverer, Subrahmanyan Chandrasekhar, who calculated it in 1930 at the age of nineteen on the ship bringing him from his native India to take up a fellowship at Cambridge. Two observations underlie the existence of the limit:

- 1 Both the internal energy of a dwarf and its gravitational potential energy vary in the same way ( $1/R$ ) with its radius.
- 2 Its internal energy is proportional to the mass  $M$  of the dwarf but its gravitational potential energy is proportional to  $M^2$ .

Because of (2), the inward gravitational pressure dominates for a sufficiently massive dwarf, which causes a contraction that cannot be stopped by the pressure of its electron gas as  $R$  decreases because of (1).

What becomes of dying stars with  $M > 1.4M_{\text{sun}}$ ? The answer then seemed to be total collapse into what today is called a black hole. (We know now that a neutron star can be somewhat more massive than a white dwarf and still be stable.) The noted Cambridge astrophysicist Arthur Eddington, one of Chandrasekhar's heroes, publicly derided the idea of total collapse as absurd, a humiliation that was one of the reasons Chandrasekhar later moved to the University of Chicago where he had a distinguished career. His work on white dwarfs led to a Nobel Prize in 1983.

In a white dwarf, only electrons with the highest energies can radiate, since only such electrons have empty lower states to fall into. As the states lower than  $\epsilon_F$  become filled, the star becomes dimmer and dimmer and in a few billion years ceases to radiate at all. It is now a **black dwarf**, a dead lump of matter, since the energies of its electrons are forever locked up below the Fermi level.

The greater the mass of a shrinking star, the greater the electron pressure needed to keep it in equilibrium. If the mass is more than about  $1.4M_{\text{sun}}$ , gravity is so overwhelming that the electron gas can never counteract it. Such a star cannot become a stable white dwarf.

### Neutron Stars

A star too heavy—more than about 8 solar masses—to follow the evolutionary path that leads to a white dwarf has a different fate. The large mass of such a star causes it to collapse abruptly when out of fuel, and then to explode violently. The explosion flings into space most of the star's mass. An event of this kind, called a **supernova**, is billions of times brighter than the original star ever was.

What is left after a supernova explosion may be a remnant whose mass is greater than  $1.4M_{\text{sun}}$ . As this star contracts gravitationally, its electrons become more and more energetic. When the Fermi energy reaches about 1.1 MeV, the average electron energy is 0.8 MeV, which is the minimum energy needed for an electron to react with a proton to produce a neutron. (The neutron mass exceeds the combined mass of an electron and a proton by the mass equivalent of 0.8 MeV) This point is reached when the star's density is perhaps 20 times that of a white dwarf. From then on neutrons are produced until most of the electrons and protons are gone. The neutrons, which are fermions, end up as a degenerate gas, and their pressure supports the star against further gravitational shrinkage.

## Discovery of Neutron Stars

In a paper published in 1934, only two years after the discovery of the neutron, the astronomers Walter Baade and Fritz Zwicky proposed that, at the end of its active life, an exceptionally heavy star undergoes a cataclysmic explosion that appears in the sky as a brilliant supernova. "We advance the view that a supernova represents the transition of an ordinary star into a neutron star, consisting mainly of neutrons. Such a star may possess a very small radius and an extremely high density [and would] represent the most stable configuration of matter as such."

Although several physicists developed the theory of neutron stars further in the next few years, it was not until pulsars were detected in 1967 that their existence was confirmed. In that year unusual radio signals with an extremely regular period of exactly 1.33730113 s were picked up that came from a source in the direction of the constellation Vulpecula. They were found by Jocelyn Bell (now Jocelyn Bell Burnell), then a graduate student at Cambridge University; her thesis advisor received the Nobel Prize in physics for the discovery. At first only radio emissions from pulsars were observed, but later flashes of visible light were detected from some pulsars that were synchronized with the radio signals.

The power output of a pulsar is about  $10^{26}$  W, which is comparable with the total power output of the sun. So strong a source of energy cannot possibly be switched on and off in a fraction of a second, which is the period of some pulsars, nor can it be the size of the sun. Even if the sun were to suddenly stop radiating, it would take an interval of 2.3 s before light stopped reaching us, because all parts of the sun that we see are not the same distance away. Nor could a sun-sized pulsar spin around in less than a second per turn. The conclusion is that a pulsar must have the mass of a star, in order to be able to emit so much energy, but it must be very much smaller than a star, in order that its signals fluctuate so rapidly. From these and other considerations it seems clear that pulsars are neutron stars in rapid rotation.

Neutron stars are thought to be 10 to 15 km in radius with masses between 1.4 and  $\sim 3M_{\text{sun}}$  (Fig. 9.12). If the earth were this dense, it would fit into a large apartment house. Stars called pulsars are believed to be neutron stars that are rotating rapidly. Most stars have magnetic fields, and as a star contracts into a neutron star, its surface field increases enormously. The magnetic field is produced by motions of the electrons that remain in its interior, and since they cannot lose energy (the gas they form is degenerate, with all the lowest states filled), the field should persist for a time long compared with the age of the universe.

The magnetic field of a pulsar traps tails of ionized gas that radiate light, radio waves, and x-rays. If the magnetic axis is not aligned with the rotational axis, a distant observer, such as an astronomer on the earth, will receive bursts of radiation as the pulsar spins. Thus a pulsar is like a lighthouse whose flashes are due to a rotating beam of light.

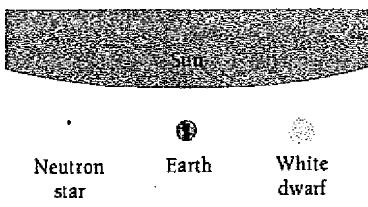
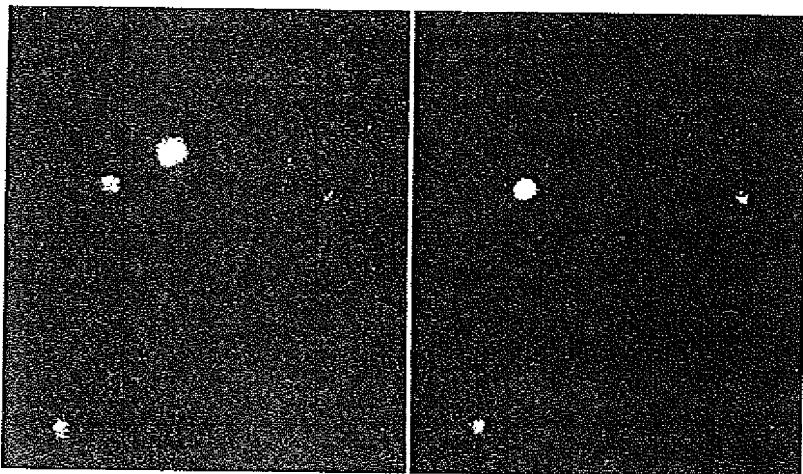


Figure 9.12 A comparison of a white dwarf and a neutron star with the sun and the earth. Both white dwarfs and neutron stars are thought to have masses similar to that of the sun.



The pulsar at the center of the Crab nebula flashes 30 times per second and is thought to be a rotating neutron star. These photographs were taken at maximum and minimum emission. The nebula itself is shown in the photograph at the start of this chapter; it is now about 10 light-years across and is still expanding.

Over 1000 pulsars have been discovered, all with periods between 0.0016 and 4 s. The best known pulsar, which is at the center of the Crab nebula, has a period of 0.033 s that is increasing at a rate of  $10^{-5}$  s per year as the pulsar loses angular momentum.

### Black Holes

An old star whose mass is less than  $1.4M_{\text{sun}}$  becomes a white dwarf and one whose mass is between 1.4 and  $\sim 3M_{\text{sun}}$  becomes a neutron star. What about still heavier old stars? Neither a degenerate electron gas nor a degenerate neutron gas can resist gravitational collapse when  $M > \sim 3M_{\text{sun}}$ . Does such a star end up as a point in space? This does not seem likely. One argument comes from the uncertainty principle,  $\Delta x \Delta p \geq \hbar/2$ . This principle prevents a hydrogen atom from collapsing beyond a certain size under the inward pull of the proton's electric field. The same principle ought to prevent a massive old star from collapsing beyond a certain size under an inward gravitational pull. Or perhaps the quarks of which neutrons and protons are composed (Chap. 13) have special properties that stabilize such a star when it reaches a certain density.

Whatever its final nature, as an old star of  $M > 3M_{\text{sun}}$  contracts it passes the Schwarzschild radius of Eq. (2.30) and from then on is a black hole (Sec. 2.9). We can receive no further information from the star because its gravitational field is too intense to permit anything, even photons, to escape past its event horizon.

Not only heavy stars end up as black holes. As time goes on, both white dwarfs and neutron stars attract more and more cosmic dust and gas. When they have gathered up enough additional mass, they too will become black holes. If the universe lasts long enough, then everything in it may be in the form of black holes.

**EXERCISES**

By the pricking of my thumbs / Something wicked this way comes. —William Shakespeare, *Macbeth*

**9.2 Maxwell-Boltzmann Statistics**

1. At what temperature would one in a thousand of the atoms in a gas of atomic hydrogen be in the  $n = 2$  energy level?
2. The temperature in part of the sun's atmosphere is 5000 K. Find the relative numbers of hydrogen atoms in this region that are in the  $n = 1, 2, 3$ , and 4 energy levels. Be sure to take into account the multiplicity of each level.
3. The  $3^2P_{1/2}$  first excited state in sodium is 2.093 eV above the  $3^2S_{1/2}$  ground state. Find the ratio between the numbers of atoms in each state in sodium vapor at 1200 K. (See Example 7.6.)
4. The frequency of vibration of the  $H_2$  molecule is  $1.32 \times 10^{14}$  Hz. (a) Find the relative populations of the  $v = 0, 1, 2, 3$ , and 4 vibrational states at 5000 K. (b) Can the populations of the  $v = 2$  and  $v = 3$  states ever be equal? If so, at what temperature does this occur?
5. The moment of inertia of the  $H_2$  molecule is  $4.64 \times 10^{-48}$  kg · m<sup>2</sup>. (a) Find the relative populations of the  $J = 0, 1, 2, 3$ , and 4 rotational states at 300 K. (b) Can the populations of the  $J = 2$  and  $J = 3$  states ever be equal? If so, at what temperature does this occur?
6. In a certain four-level laser (Sec. 4.9), the final state of the laser transition is 0.03 eV above the ground state. What fraction of the atoms are in this state at 300 K in the absence of external excitation? What is the minimum fraction of the atoms that must be excited in order for laser amplification to occur at this temperature? Why? How is the situation changed at 100 K? Would you expect cooling a three-level laser to have the same effect?

**9.3 Molecular Energies in an Ideal Gas**

7. Find  $\bar{v}$  and  $v_{rms}$  for an assembly of two molecules, one with a speed of 1.00 m/s and the other with a speed of 3.00 m/s.
8. Show that the average kinetic energy per molecule at room temperature (20°C) is much less than the energy needed to raise a hydrogen atom from its ground state to its first excited state.
9. At what temperature will the average molecular kinetic energy in gaseous hydrogen equal the binding energy of a hydrogen atom?
10. Show that the de Broglie wavelength of an oxygen molecule in thermal equilibrium in the atmosphere at 20°C is smaller than its diameter of about  $4 \times 10^{-10}$  m.
11. Find the width due to the Doppler effect of the 656.3-nm spectral line emitted by a gas of atomic hydrogen at 500 K.
12. Verify that the most probable speed of an ideal-gas molecule is  $\sqrt{2kT/m}$ .
13. Verify that the average value of  $1/v$  for an ideal-gas molecule is  $\sqrt{2m/\pi kT}$ . [Note:  $\int_0^\infty v e^{-\alpha v^2} dv = 1/(2\alpha)$ ]

14. A flux of  $10^{12}$  neutrons/m<sup>2</sup> emerges each second from a port in a nuclear reactor. If these neutrons have a Maxwell-Boltzmann energy distribution corresponding to  $T = 300$  K, calculate the density of neutrons in the beam.

**9.4 Quantum Statistics**

15. At the same temperature, will a gas of classical molecules, a gas of bosons, or a gas of fermions exert the greatest pressure? The least pressure? Why?
16. What is the significance of the Fermi energy in a fermion system at 0 K? At  $T > 0$  K?

**9.5 Rayleigh-Jeans Formula**

17. How many independent standing waves with wavelengths between 9.5 and 10.5 mm can occur in a cubical cavity 1 m on a side? How many with wavelengths between 99.5 and 100.5 mm? (Hint: First show that  $g(\lambda) d\lambda = 8\pi L^3 d\lambda/\lambda^4$ .)

**9.6 Planck Radiation Law**

18. If a red star and a white star radiate energy at the same rate, can they be the same size? If not, which must be the larger?
19. A thermograph measures the rate at which each small portion of a person's skin emits infrared radiation. To verify that a small difference in skin temperature means a significant difference in radiation rate, find the percentage difference between the total radiation from skin at 34° and at 35°C.
20. Sunspots appear dark, although their temperatures are typically 5000 K, because the rest of the sun's surface is even hotter, about 5800 K. Compare the radiation rates of surfaces of the same emissivity whose temperatures are respectively 5000 and 5800 K.
21. At what rate would solar energy arrive at the earth if the solar surface had a temperature 10 percent lower than it is?
22. The sun's mass is  $2.0 \times 10^{30}$  kg, its radius is  $7.0 \times 10^8$  m, and its surface temperature is  $5.8 \times 10^3$  K. How many years are needed for the sun to lose 1.0 percent of its mass by radiation?
23. An object is at a temperature of 400°C. At what temperature would it radiate energy twice as fast?
24. A copper sphere 5 cm in diameter whose emissivity is 0.3 is heated in a furnace to 400°C. At what rate does it radiate?
25. At what rate does radiation escape from a hole 10 cm<sup>2</sup> in area in the wall of a furnace whose interior is at 700°C?

26. An object at 500°C is just hot enough to glow perceptibly; at 750°C it appears cherry-red in color. If a certain blackbody radiates 1.00 kW when its temperature is 500°C, at what rate will it radiate when its temperature is 750°C?
27. Find the surface area of a blackbody that radiates 1.00 kW when its temperature is 500°C. If the blackbody is a sphere, what is its radius?
28. The microprocessors used in computers produce heat at rates as high as 30 W per square centimeter of surface area. At what temperature would a blackbody be if it had such a radiance? (Microprocessors are cooled to keep from being damaged by the heat they give off.)
29. Considering the sun as a blackbody at 6000 K, estimate the proportion of its total radiation that consists of yellow light between 570 and 590 nm.
30. Find the peak wavelength in the spectrum of the radiation from a blackbody at a temperature of 500°C. In what part of the em spectrum is this wavelength?
31. The brightest part of the spectrum of the star Sirius is located at a wavelength of about 290 nm. What is the surface temperature of Sirius?
32. The peak wavelength in the spectrum of the radiation from a cavity is 3.00  $\mu\text{m}$ . Find the total energy density in the cavity.
33. A gas cloud in our galaxy emits radiation at a rate of  $1.0 \times 10^{27} \text{ W}$ . The radiation has its maximum intensity at a wavelength of 10  $\mu\text{m}$ . If the cloud is spherical and radiates like a blackbody, find its surface temperature and its diameter.
34. (a) Find the energy density in the universe of the 2.7-K radiation mentioned in Example 9.6. (b) Find the approximate number of photons per cubic meter in this radiation by assuming that all the photons have the wavelength of 1.1 mm at which the energy density is a maximum.
35. Find the specific heat at constant volume of 1.00  $\text{cm}^3$  of radiation in thermal equilibrium at 1000 K.
- 9.9 Free Electrons in a Metal**
- 9.10 Electron-Energy Distribution**
36. What is the connection between the fact that the free electrons in a metal obey Fermi statistics and the fact that the photoelectric effect is virtually temperature-independent?
37. Show that the median energy in a free-electron gas at  $T = 0$  is equal to  $\epsilon_F/2^{2/3} = 0.630\epsilon_F$ .
38. The Fermi energy in copper is 7.04 eV. Compare the approximate average energy of the free electrons in copper at room temperature ( $kT = 0.025 \text{ eV}$ ) with their average energy if they followed Maxwell-Boltzmann statistics.
39. The Fermi energy in silver is 5.51 eV. (a) What is the average energy of the free electrons in silver at 0 K? (b) What temperature is necessary for the average molecular energy in an ideal gas to have this value? (c) What is the speed of an electron with this energy?
40. The Fermi energy in copper is 7.04 eV. (a) Approximately what percentage of the free electrons in copper are in excited states at room temperature? (b) At the melting point of copper, 1083°C?
41. Use Eq. (9.29) to show that, in a system of fermions at  $T = 0$ , all states of  $\epsilon < \epsilon_F$  are occupied and all states of  $\epsilon > \epsilon_F$  are unoccupied.
42. An electron gas at the temperature  $T$  has a Fermi energy of  $\epsilon_F$ . (a) At what energy  $\epsilon$  is there a 5.00 percent probability that a state of that energy is occupied? (b) At what energy is there a 95.00 percent probability that a state of that energy is occupied? Express the answers in terms of  $\epsilon_F$  and  $kT$ .
43. Show that, if the average occupancy of a state of energy  $\epsilon_F + \Delta\epsilon$  is  $f_1$  at any temperature, then the average occupancy of a state of energy  $\epsilon_F - \Delta\epsilon$  is  $f_2 = 1 - f_1$ . (This is the reason for the symmetry of the curves in Fig. 9.10 about  $\epsilon_F$ .)
44. The density of aluminum is 2.70 g/cm<sup>3</sup> and its atomic mass is 26.97 u. The electronic structure of aluminum is given in Table 7.4 (the energy difference between 3s and 3p electrons is very small), and the effective mass of an electron in aluminum is 0.97  $m_e$ . Calculate the Fermi energy in aluminum. (Effective mass is discussed at the end of Sec. 10.8.)
45. The density of zinc is 7.13 g/cm<sup>3</sup> and its atomic mass is 65.4 u. The electronic structure of zinc is given in Table 7.4, and the effective mass of an electron in zinc is 0.85  $m_e$ . Calculate the Fermi energy in zinc.
46. Find the number of electrons each lead atom contributes to the electron gas in solid lead by comparing the density of free electrons obtained from Eq. (9.56) with the number of lead atoms per unit volume. The density of lead is  $1.1 \times 10^4 \text{ kg/m}^3$  and the Fermi energy in lead is 9.4 eV.
47. Find the number of electron states per electronvolt at  $\epsilon = \epsilon_F/2$  in a 1.00-g sample of copper at 0 K. Are we justified in considering the electron energy distribution as continuous in a metal?
48. The specific heat of copper at 20°C is 0.0920 kcal/kg · °C. (a) Express this in joules per kilomole per kelvin (J/kmol · K). (b) What proportion of the specific heat can be attributed to the electron gas, assuming one free electron per copper atom?
49. The Bose-Einstein and Fermi-Dirac distribution functions both reduce to the Maxwell-Boltzmann function when  $e^\alpha e^{\epsilon/kT} \gg 1$ . For energies in the neighborhood of  $kT$ , this approximation holds if  $e^\alpha \gg 1$ . Helium atoms have spin 0 and so obey Bose-Einstein statistics. Verify that  $f(\epsilon) \approx 1/e^\alpha e^{\epsilon/kT} \approx Ae^{-\epsilon/kT}$  is valid for He at STP (20°C and atmospheric pressure, when the volume of 1 kmol of any gas is  $= 22.4 \text{ m}^3$ ) by showing that  $A \ll 1$  under these circumstances. To do this, use Eq. (9.55) for  $g(\epsilon) d\epsilon$  with a coefficient of 4 instead of 8 since a He atom does not have the two spin states of an electron, and employing the approximation, find  $A$  from the normalization condition  $\int_0^\infty n(\epsilon) d\epsilon = N$ , where  $N$  is the total number of atoms in the sample. (A kilomole of He contains Avogadro's number  $N_A$  of atoms, the atomic mass of He is 4.00 u, and  $\int_0^\infty \sqrt{\pi} e^{-\alpha x^2} dx = \sqrt{\pi}/a/2a$ )
50. Helium is a liquid of density 145 kg/m<sup>3</sup> at atmospheric pressure and temperatures under 4.2 K. Use the method of Exercise 49 to show that  $A > 1$  for liquid helium, so that it cannot be satisfactorily described by Maxwell-Boltzmann statistics.

51. The Fermi-Dirac distribution function for the free electrons in a metal cannot be approximated by the Maxwell-Boltzmann function at STP (see Exercise 49) for energies in the neighborhood of  $kT$ . Verify this by using the method of Exercise 49 to show that  $A > 1$  in copper if  $f(\epsilon) \approx Ae^{-\epsilon/kT}$ . As calculated in Sec. 9.9  $N/V = 8.48 \times 10^{28}$  electrons/m<sup>3</sup> for copper. Note that Eq. (9.55) must be used unchanged here.
- 9.11 Dying Stars
52. The sun has a mass of  $2.0 \times 10^{30}$  kg and a radius of  $7.0 \times 10^8$  m. Assume it consists of completely ionized hydrogen at a temperature of  $10^7$  K. (a) Find the Fermi energies of the proton gas and of the electron gas in the sun. (b) Compare these energies with  $kT$  to see whether each gas is degenerate ( $kT \ll \epsilon_F$ , so that few particles have energies over  $\epsilon_F$ ) or nondegenerate ( $kT \gg \epsilon_F$ , so that few particles have energies below  $\epsilon_F$  and the gas behaves classically).
53. Consider a white dwarf star whose mass is half that of the sun and whose radius is 0.01 that of the sun. Assume it consists of completely ionized carbon atoms (mass 12 u), so that there are six electrons per nucleus, and its interior temperature is  $10^7$  K. (a) Find the Fermi energies of the carbon nucleus gas and of the electron gas. (b) Compare these energies with  $kT$  to see whether each gas is degenerate or nondegenerate, as in Exercise 52.
54. The gravitational potential energy of a uniform-density sphere of mass  $M$  and radius  $R$  is  $E_g = -\frac{1}{5} GM^2/R$ . Consider a white dwarf star that contains  $N$  electrons whose Fermi energy is  $\epsilon_F$ . Since  $kT \ll \epsilon_F$ , the average electron energy is, from Eq.(9.51), about  $\frac{1}{3} \epsilon_F$  and the total electron energy is  $E_e = \frac{1}{3} N \epsilon_F$ . The energies of the nuclei can be neglected compared with  $E_e$ . Hence the total energy of the star is  $E = E_g + E_e$ . (a) Find the equilibrium radius of the star by letting  $dE/dR = 0$  and solving for  $R$ . (b) Evaluate  $R$  for a star whose mass is half that of the sun and consists of completely ionized carbon atoms, as in Exercise 53.