CHAPTER SIXTEEN

Some Specific Applications of the Statistical Distribution Laws

In the last chapter we derived expressions for the statistical distribution laws of quantum particles. These expressions contain a parameter α that must be determined in each specific case. The general approach for doing it is discussed in this chapter. The important cases of a Fermion gas and a photon gas are emphasized.

16.1 THE MAXWELL–BOLTZMANN DISTRIBUTION

In the case of particles obeying Maxwell–Boltzmann statistics we obtain directly from (15.46) after using $\beta=(kT)^{-1}$, $\Gamma(\frac{3}{2})=\sqrt{\pi}/2$:

$$\alpha=\ln\left(\frac{2\pi^{3/2}Vm(2m)^{1/2}}{h^3N}(kT)^{3/2}\right) \tag{16.1}$$

where N is the number of particles, m is their mass, and V is the volume to which they are confined.

The fraction of the total number of atoms with energy ε_i (or more exactly, which are in the energy "bin" i) is obtained from (15.23):

$$\begin{aligned} f_i &= \frac{n_i}{\sum ns} \\ &= \frac{g_i e^{-\alpha-\beta\varepsilon_i}}{\sum\limits_s g_s e^{-\alpha-\beta\varepsilon_s}} \\ &= \frac{g_i e^{-\varepsilon_i/kT}}{\sum\limits_s g_s e^{-\varepsilon_s/kT}} \end{aligned} \tag{16.2}$$

and is independent of α. The ratio of the populations of any two levels, say i and j, is thus

$$\frac{f_i}{f_j} = \frac{g_i}{g_j} e^{-(\varepsilon_i-\varepsilon_j)/kT} \tag{16.3}$$

and is known as the Boltzmann ratio.

16.2 FERMI–DIRAC DISTRIBUTION

The distribution function of identical, indistinguishable particles of half-odd-integral spin (Fermions) is given in (15.24) as

$$n_s = \frac{g_s}{e^{\alpha+\beta\varepsilon_s}+1} \tag{16.4}$$

Using $\beta = (kT)^{-1}$ and defining

$$\mu \equiv -\alpha kT$$

we may rewrite (16.4) as

$$n_s = \frac{g_s}{e^{(\varepsilon_s-\mu)/kT}+1} \tag{16.5}$$

If we use the label s to denote a bin containing but a single state (rather than the set of g_s degenerate states having an energy ε_s), then $g_s = 1$ and (16.5) becomes

$$n(\varepsilon) \equiv f(\varepsilon) = \frac{1}{e^{[\varepsilon-\mu(T)]/kT}+1} \tag{16.6}$$

The quantity μ is called the chemical potential of the system of particles. The function $f(\varepsilon)$, the Fermi–Dirac distribution law, gives the probability that the quantum state ε is occupied. It follows that $f(\varepsilon) \leq 1$.

Figure 16.1 shows a plot of $f(\varepsilon)$ at $T=0$ and also at some finite temperature. At $T=0$, $f(\varepsilon)=1$ for $\varepsilon<\mu$ and $f(\varepsilon)=0$ for $\varepsilon>\mu$. In words: At zero temperature the states whose energies lie below the chemical potential $\mu(0)$ are occupied, while those above it are empty. At finite temperatures the

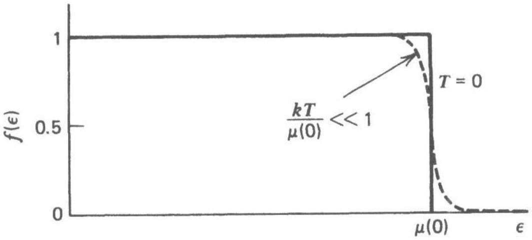

Figure 16.1 Sketch of the Fermi–Dirac distribution function at absolute zero and at a low temperature. The width of the transition region between $f(\varepsilon) \simeq 1$ and $f(\varepsilon) \simeq 0$ is of the order of kT.

transition from occupied states is "fuzzed" over a region of width $\sim kT$, as shown in the figure.

At energies ε such that $(\varepsilon - \mu) \gg kT$, $f(\varepsilon) \sim e^{-(\varepsilon - \mu(T)/kT}$. This exponential dependence of the occupation probability is the same as that of the Boltzmann law (16.3) so that in this limit the statistical behavior of fermions and of classical particles is similar.

To evaluate the chemical potential $\mu(0)$, we consider the case of a free electron gas that is confined to a volume V. The number of available electron states in $d\varepsilon$ is obtained from (15.44):

$$g(\varepsilon)\, d\varepsilon = \frac{8\pi V m (2m)^{1/2}}{h^3} \varepsilon^{1/2}\, d\varepsilon \tag{16.7}$$

P.188

[The factor of 2 difference between (16.7) and (15.44) is due to the fact that, in the case of electrons, each spatial wavefunction is associated with two associated quantum states, one with $m_s = \frac{1}{2}$ "spin up" and one with $m_s = -\frac{1}{2}$.] The number of occupied states in the energy interval $d\varepsilon$ is given by the product of the number of such states $g(\varepsilon)\, d\varepsilon$ and $f(\varepsilon)$, the occupation probability. Since the total number of electrons N is fixed, it follows that

$$\int_0^\infty g(\varepsilon) f(\varepsilon)\, d\varepsilon = N$$

which, using (16.6) and (16.7), becomes

$$N = \frac{8\pi V m (2m)^{1/2}}{h^3} \int_0^\infty \varepsilon^{1/2} \frac{1}{e^{[\varepsilon - \mu(T)]/kT} + 1}\, d\varepsilon \tag{16.8}$$

At zero temperature $f(\varepsilon) = 1$ for $\varepsilon < \mu$, and $f(\varepsilon) = 0$ for $\varepsilon > \mu$, so that the last integral becomes

$$\lim_{T \to 0} \int_0^\infty \varepsilon^{1/2} \frac{d\varepsilon}{e^{[\varepsilon - \mu(0)]/kT} + 1} = \int_0^{\mu(0)} \varepsilon^{1/2}\, d\varepsilon = \tfrac{2}{3} \mu^{3/2}(0)$$

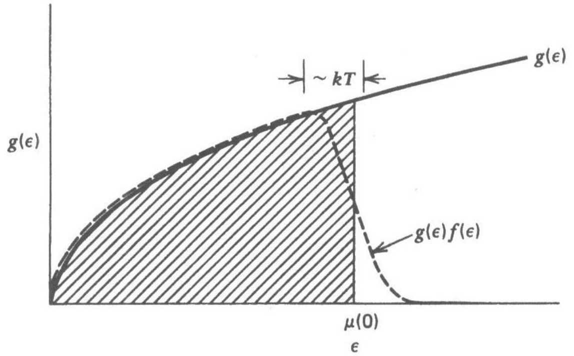

Figure 16.2 Plot of density of states $g(\varepsilon)$ and the density of electrons $g(\varepsilon)f(\varepsilon)$, as a function of energy. At absolute zero the states up to $\mu(0)$ are filled. The dotted curve indicates the density of filled states at a temperature $T \ll \mu(0)/k$.

and after substituting in (16.8)

$$\mu(0)=\frac{\hbar^2}{2m}\left[3\pi^2\left(\frac{N}{V}\right)\right]^{2/3} \tag{16.9}$$

The chemical potential μ, often called the Fermi energy, plays a key role in the theories of metals and semiconductors. The behavior of many metals can often be explained to a good approximation using a model of a free electron gas. According to this model at very low temperatures all the electron states with energies up to $\varepsilon=\mu$ are filled, and those above it are empty. At higher temperatures, levels within $\sim kT$ of μ are only partially filled. This situation is depicted in Fig. 16.2.

As an example we calculate the chemical potential (Fermi energy) of a metal with 10^{29} electrons/m^3. Using this result in (16.9) gives

$$\begin{aligned}\mu(0)&=1.257\times10^{-18}\text{ joules}\\&=7.85\text{ eV}\end{aligned}$$

(It is useful to recall here that it is the Pauli exclusion principle that causes the energy levels in the metal, even at $T=0$, to be filled up to $\varepsilon\simeq7.85$ eV. In a system of bosons, for example, where a given state may be occupied by any number of particles at zero temperature, the particles will all "condense" to $\varepsilon=0$). Electrons near the top of the occupied states move with velocities v_F such that at $T=0$

$$\tfrac{1}{2}mv_F^2=\mu(0)$$

In the above example, $v_F\simeq1.67\times10^8$ cm/s. It is important to note that these high velocities persist even at zero temperature, and the explanation of their existence is *purely quantum mechanical.*

A very simple yet important significance of the chemical potential $\mu(T)$ is that it corresponds to the *increase* of the *total energy of the system when one particle is added to it*, that is,

$$\mu(T)=\frac{\partial}{\partial N}\int_0^\infty \varepsilon g(\varepsilon)f(\varepsilon)\,d\varepsilon \tag{16.10}$$

P.191

This statement follows directly from the Fermi–Dirac distribution law (16.6). Since the states up to $\mu(T)$ are occupied [here we ignore the small transition region of width $\sim kT$ near $\mu(T)$], any additional particle must be placed at an energy $\mu(T)$. It will be assigned as an exercise to show that at $T=0$

$$\frac{\partial E}{\partial N}=\frac{\partial E}{\partial \mu(0)}\frac{\partial \mu(0)}{\partial N}=\mu(0) \tag{16.11}$$

where $E=\int_0^{\mu(0)}\varepsilon g(\varepsilon)\,d\varepsilon$ is the energy of the N-particle system (at zero temperature). It follows that if two materials with different chemical potentials are brought into contact with one another, particles will flow from the region of high μ to that of low μ. Equilibrium will be reestablished when the chemical potential has a single uniform value throughout the sample, since otherwise the total energy may be lowered by transferring particles from regions of high chemical potential to those where it is lower.

The general dependence of $\mu(T)$ on temperature can be obtained using (16.8) P.192 by taking $T\neq 0$. We will not derive the result (the interested reader can consult any basic text in statistical mechanics or solid state physics[1]), but merely state it:

$$\mu(T)\cong\mu(0)\left[1-\left(\frac{\pi^2}{12}\right)\left(\frac{kT}{\mu(0)}\right)^2\right] \tag{16.12}$$

Another important consequence of the Pauli exclusion principle manifests itself in the heat capacity of an electron gas. Viewed as a classical particle, each electron would have a total energy $3kT/2$, so that the energy per unit volume in a sample with an electron density (N/V) is $U=\frac{3}{2}(N/V)kT$ and the heat capacity per unit volume is $C=\partial U/\partial T=\frac{3}{2}(N/V)k$. This result is bigger by some two orders of magnitude than the measured values of the heat capacity at room temperature.

We can understand the nature of this discrepancy by referring to Fig. 16.2. The total energy of the electron system is given by

$$E=\int_0^\infty g(\varepsilon)f(\varepsilon)\varepsilon\,d\varepsilon$$

Most of the value of this integral comes from the fully occupied states $[f(\varepsilon)=1]$ below the chemical potential. Their contribution to U is thus a

---

[1] See, for example, C. Kittel, *Introduction to Solid State Physics*, 5th ed. (J. Wiley & Sons, New York, 1976).

constant that does not depend on temperature, so that their heat capacity

$$C = \partial E / \partial T$$

is zero. The main contribution to C is thus due to the fraction $\sim kT/\mu$ of the electrons with energies within kT of the chemical potential μ. These may be considered approximately as classical particles with an energy per particle of $\frac{3}{2}kT$. The contribution to the total energy due to these electrons is, per unit volume,

$$E' \sim \left(\frac{N}{V}\right)\left(\tfrac{3}{2}kT\right)\frac{kT}{\mu(0)}$$

so that the heat capacity becomes

$$C = \frac{\partial E}{\partial T} \simeq \frac{\partial E'}{\partial T} = 3\left(\frac{N}{V}\right)k\frac{kT}{\mu(0)}$$

An exact analysis[2] yields

$$C = \frac{\pi^2}{2}\left(\frac{N}{V}\right)k\frac{kT}{\mu(0)} \tag{16.13}$$

In the case of the numerical example considered above and for $T = 300°\text{K}$, $kT/\mu(0) \sim \frac{1}{300}$. This factor is of the order of magnitude of the discrepancy between the experimental data and the prediction of classical theory.

16.3 THE BOSE–EINSTEIN DISTRIBUTION

We conclude this chapter by considering the case of the Bose–Einstein distribution law (15.25). To determine α in this case, one must invoke, as in the case of the other distributions, the constancy of the number of particles in the system. This involves a good deal of specialized calculation. There exists, however, a very important yet simple case we can use to demonstrate the basic principles. This is the case of electromagnetic radiation at thermal equilibrium. We have already considered this case in Chapter 12. In that treatment, the elementary particles of the system were the radiation modes (oscillators) that, due to their distinguishability, obey the Boltzmann distribution law (16.2).

We may, alternatively, consider the photons, rather than the oscillators, as the elementary particles of the radiation fields. The one-particle states are taken as the electromagnetic modes

$$\psi(\mathbf{r}) \propto e^{i\mathbf{k}\cdot\mathbf{r}} \tag{16.14}$$

which were considered in Section 12.2. A "particle" (photon) in state $\mathbf{k}$ thus has an energy $h\nu$ ($\nu = kc/2\pi$). The photon is characterized, in addition to the

---

[2] Kittel, *ibid.*

propagation vector **k**, as well as by its "spin" state $s=1$, $m_s=\pm 1$. The quantum numbers $m_s=\pm 1$ describe the two senses of circular polarization associated with a given direction of propagation **k**. The photons being indistinguishable and possessing an integral ($s=1$) spin obey the Bose–Einstein distribution law (15.25):

$$n_s=\frac{g_s}{e^{\alpha+\epsilon_s/kT}-1} \tag{16.15}$$

where we used $\beta=(kT)^{-1}$. We recall that the parameter α was introduced into the formalism [see for example (15.18)], in the process of insuring that the number of particles N in the system be a constant. The total number of photons (particles), however, is not restricted.

(This is a very subtle point and deserves amplification. If the field energy is increased, then, using the radiation modes as the basic "particles" of the system, we need merely increase the energy of the modes, keeping their number a *constant*. If we choose instead to take the field particles as photons, then an increase in the excitation of the system results in an increase of the number of photons per mode. The number of photons is thus not conserved.)

Since the number of particles is not fixed, the auxiliary condition (15.13) that gave rise to α in the distribution laws is now meaningless, so that in (16.15) $\alpha=0$ and

$$n_s=\frac{g_s}{e^{h\nu_s/kT}-1} \quad \text{(for photons)} \tag{16.16}$$

Let g_s in (16.16) be the number of states **k** whose frequencies lie within an interval $d\nu$ centered on ν. The number of such states was given by (12.35) P. 135 as

$$g_s=\frac{8\pi\nu^2 n^3 V}{c^3}\,d\nu$$

The number of particles (photons) in this range is from (16.16):

$$n_s=\frac{8\pi\nu^2 n^3 V}{c^3\left(e^{h\nu/kT}-1\right)}\,d\nu$$

Multiplying the last expression by the energy $h\nu$ per photon, we obtain (after dividing by the enclosure volume V) an expression for the energy density of a black body radiation field due to frequencies between ν and $\nu+d\nu$:

$$\rho(\nu)\,d\nu=\frac{8\pi h\nu^3 n^3}{c^3\left(e^{h\nu/kT}-1\right)}\,d\nu \tag{16.17}$$

in agreement with (12.37). P. 135

PROBLEMS

1. Show that at equilibrium the "temperature" of a mixture of three types of particles is the same.
2. Derive the Fermi energy of a two-dimensional electron gas confined to an area of $a \times b$.
3. Show that the two orthogonally plane-polarized states of an electromagnetic wave propagating along some arbitrary direction can be considered, equivalently, as two waves with opposite senses of circular polarization.

   Hint: Show that we can express each representation as a linear superposition of the modes of the other.
4. Prove Eq. (16.11).
5. Derive the black body energy density formula (16.17)

   $$\rho(\nu) = \frac{8\pi h\nu^3 n^3}{c^3(e^{h\nu/kT} - 1)}$$

   considering the electromagnetic modes, rather than the photons, as the "particles."

   Clue: Are the modes distinguishable?