3 Collections of particles in gases and solids

3.1 Introduction

We have so far discussed only properties of single, isolated particles. As soon as we turn our attention to whole collections of many such interacting particles, for example to consider molecules in a gas or electrons in a solid, it is no longer practicable to describe the detailed dynamics of the system by the application of Newton's laws to each particle. The detailed properties of individual microscopic components could be specified only at a particular time and would change continuously. Further, because of the vast numbers of particles involved in a typical gas or solid, a microscopic treatment would be too cumbersome to be readily solvable or physically meaningful.

Fortunately, we are usually more interested in the macroscopic or bulk behaviour of large numbers of particles, to predict such properties as currents, pressures, and so on. A statistical treatment that describes the average rather than detailed properties of a typical component of the complete assembly of particles is most useful, since the behaviour of the group of particles can then be deduced directly.

In order to determine the average value of, say, the velocity of a molecule in a gas or the energy of an electron in a solid, it is necessary to know first of all how the velocities or energies are distributed throughout the collection of particles. The type of statistics developed to describe such distributions depends not only on the type of particle present but also on the possible interactions between them. For instance, in a neutral gas, molecules can interchange energy by collisions but there is no restriction on the energy of individual molecules. On the other hand, when electrons interact in a solid their allowed energies are restricted by the Pauli exclusion principle, which permits only one electron to occupy a particular quantum state, and a different type of statistics applies.

We shall initially consider collections of neutral particles and develop a statistical method of treatment that not only will be useful in describing some of the properties of gases and plasmas but also is applicable to many other electronic materials. We shall then study the statistics of collections of

interacting particles that obey the exclusion principle, since this is necessary for later discussion of the electrical and thermal properties of solids.

3.2 Assemblies of classical particles—ideal gases

Let us consider an ideal gas of neutral molecules containing N molecules per cubic metre. Individual molecules have a random motion and undergo many collisions with other molecules and container walls, which result in changes in the magnitude and direction of their velocity. There is no restriction on the velocity of a particle at a particular time; it may be zero at one instant or relatively high at another, and the energy of each molecule is independent of that of the others. We wish to find how the various velocities and hence energies are distributed between individual molecules.

At any instant, the position of a molecule can be specified by a set of coordinates, (x, y, z) say, and its velocity v can also be resolved into components, (v_x, v_y, v_z), in the x, y and z directions, where

$$v^2 = v_x^2 + v_y^2 + v_z^2 \tag{3.1}$$

Hence, the velocity of each particle can be represented by a vector on a three-dimensional graph with axes v_x, v_y and v_z. Such a *velocity space* is illustrated in Fig. 3.1 A few typical velocity vectors are shown and the dots represent the tips of the velocity vectors of the remaining molecules. The problem of finding the distribution of velocities among the particles is reduced to finding the density of such dots in velocity space. This dot density will have spherical symmetry, since there are no preferred velocity directions, and it can

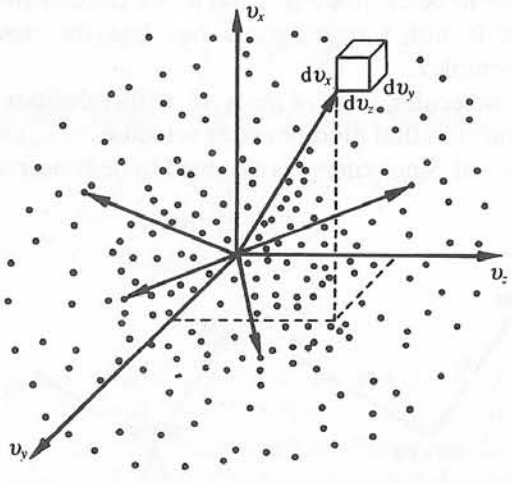

Fig. 3.1 Particles in velocity space.

be written $P(v^2)$. Thus, considering the elemental volume shown in Fig. 3.1, the number of molecules per unit volume, $\mathrm{d}N_{xyz}$, with velocity components in the range $v_x \rightarrow v_x + \mathrm{d}v_x$, $v_y \rightarrow v_y + \mathrm{d}v_y$ and $v_z \rightarrow v_z + \mathrm{d}v_z$ is

$$\mathrm{d}N_{xyz} = P(v^2)\,\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z \tag{3.2}$$

Alternatively, the number of molecules per unit volume with *speeds* ranging from $v \rightarrow v + \mathrm{d}v$, $\mathrm{d}N_v$, is equal to the number of vector tips (points in Fig. 3.1) that lie in a spherical shell of radius v and thickness $\mathrm{d}v$ in velocity space, or

$$\mathrm{d}N_v = P(v^2)4\pi v^2\,\mathrm{d}v \tag{3.3}$$

The loosely termed dot density, $P(v^2)$, is called the distribution function for speeds; it gives the number density in velocity space of molecules with a certain speed, v. Notice that in all cases the number of particles in a given range equals the distribution function multiplied by the size of the range.

Since each particle must be represented somewhere in velocity space, the integral of the number in a given range over all velocity space must equal the total number of particles per unit volume. For example

$$\int_0^\infty \mathrm{d}N_v = \int_0^\infty P(v^2)4\pi v^2\,\mathrm{d}v = N \tag{3.4}$$

3.2.1 The distribution function, $P(v^2)$

The method we use to determine $P(v^2)$ and hence the distribution of velocities in a neutral gas is not very rigorous but has the merit of not being mathematically complex.

Consider two molecules, each of mass M, with velocities v_1 and v_2, which suffer an elastic collision that modifies their velocities to v_3 and v_4 respectively, as shown in Fig. 3.2(a). Since energy is assumed to be conserved in the collision

$$v_1^2 + v_2^2 = v_3^2 + v_4^2 \tag{3.5}$$

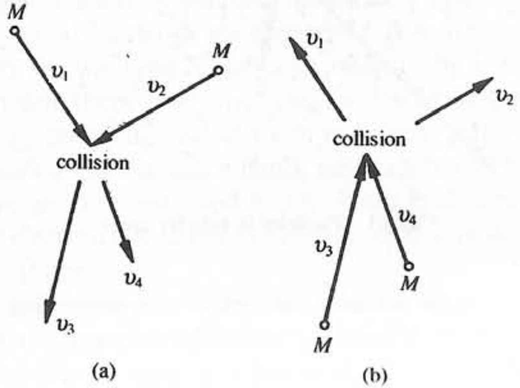

Fig. 3.2 Elastic collisions between gas molecules.

Now, the number of molecules having velocity v_1 is proportional to the distribution function evaluated at this velocity, $P(v_1^2)$. Similarly, the number of molecules with velocity v_2 is proportional to $P(v_2^2)$. Thus, the likelihood of two such particles colliding is proportional to the number in each class, and

$$\text{collison probability} \propto P(v_1^2)P(v_2^2) \tag{3.6}$$

The probability of reverse collisions occurring between molecules with velocities v_3 and v_4 to produce particles with velocities v_1 and v_2 as depicted in Fig. 3.2(b) is, by similar argument, proportional to $P(v_3^2)P(v_4^2)$. Thus, provided the geometry remains constant and the system is in equilibrium, the probability of collisions of either type must be the same, and

$$P(v_1^2)P(v_2^2) = P(v_3^2)P(v_4^2) \tag{3.7}$$

Now the only type of solution that satisfies Eqs (3.5) and (3.7) simultaneously is

$$P(v^2) = A\exp(-\beta v^2) \tag{3.8}$$

which can be verified by substitution.

Equation (3.8) is the general form of the distribution function for speeds, and all that remains is to find the values of the constants A and β. First, the expression for $P(v^2)$ can be substituted in the normalizing equation (3.4) to obtain a relationship between A and β as follows:

$$N = 4\pi A \int_0^\infty \exp(-\beta v^2)v^2\,\mathrm{d}v \tag{3.9}$$

It may be verified from tables of definite integrals that

$$\int_0^\infty \exp(-\beta v^2)v^2\,\mathrm{d}v = \pi^{1/2}/(4\beta^{3/2})$$

which can be substituted in Eq. (3.9) to give

$$A = (\beta/\pi)^{3/2}N \tag{3.10}$$

We now require a further relationship so that A and β can be obtained explicitly. We shall make use of the fact that the temperature of the gas, T, is defined in such a way that the mean particle energy per degree of freedom is $\frac{1}{2}kT$. Thus, since there are N molecules per cubic metre in the gas, each having three degrees of freedom, the total energy per unit volume is $\frac{3}{2}NkT$. Now, the number of particles in the speed range between v and $v + \mathrm{d}v$ is given by Eq. (3.3), where $P(v^2)$ is now given by Eq. (3.8), and each particle in the range has energy $\frac{1}{2}Mv^2$. Thus, the total energy per unit volume is

$$\int_0^\infty (\tfrac{1}{2}Mv^2)\,[A\exp(-\beta v^2)]\,4\pi v^2\,\mathrm{d}v = \tfrac{3}{2}NkT \tag{3.11}$$

We again turn to tables of definite integrals to confirm that

$$\int_0^\infty \exp(-\beta v^2)v^4\,\mathrm{d}v = 3\pi^{1/2}/8\beta^{5/2} \tag{3.12}$$

Making use of this fact in Eq. (3.11) and eliminating first A and then β from the resulting equation and Eq. (3.10) gives

$$\beta = M/(2kT) \tag{3.13}$$

and

$$A = N\left(\frac{M}{2\pi kT}\right)^{3/2} \tag{3.14}$$

which can be substituted in Eq. (3.7) to give

$$P(v^2) = N\left(\frac{M}{2\pi kT}\right)^{3/2} \exp\left(-\frac{Mv^2}{2kT}\right) \tag{3.15}$$

3.2.2 Maxwell–Boltzmann distribution function

The number of molecules in the speed range v to $v + \mathrm{d}v$ is given by Eq. (3.3). We can now be more explicit and include the expression for $P(v^2)$ given in Eq. (3.15), to obtain

$$\mathrm{d}N_v = 4\pi N\left(\frac{M}{2\pi kT}\right)^{3/2} \exp\left(-\frac{Mv^2}{2kT}\right)v^2\,\mathrm{d}v \tag{3.16}$$

This can be simplified by writing

$$\mathrm{d}N_v = Nf(v)\,\mathrm{d}v \tag{3.17}$$

where

$$f(v) = 4\pi\left(\frac{M}{2\pi kT}\right)^{3/2} \exp\left(-\frac{Mv^2}{2kT}\right)v^2 \tag{3.18}$$

The function $f(v)$ is called the normalized Maxwell–Boltzmann distribution function for speeds. It is evident from the defining Eq. (3.17) that $f(v)$ is the fraction of the total number of molecules per unit volume in a given speed range, per unit range of speed.

A graph of $f(v)$ versus v is shown in Fig. 3.3(a). Areas under such a graph represent fractional numbers of molecules in given speed ranges. For example, the area of the region of length $\mathrm{d}v$ shown is $f(v)\mathrm{d}v$, which, by referring to Eq. (3.17), is seen to be equal to $\mathrm{d}N_v/N$, the fraction of the total number of molecules per unit volume in the speed range $\mathrm{d}v$. As a further example, the fraction of the total number of molecules with speeds less than v' shown on Fig. 3.3(a) is equal to the area under the curve to the left of v'.

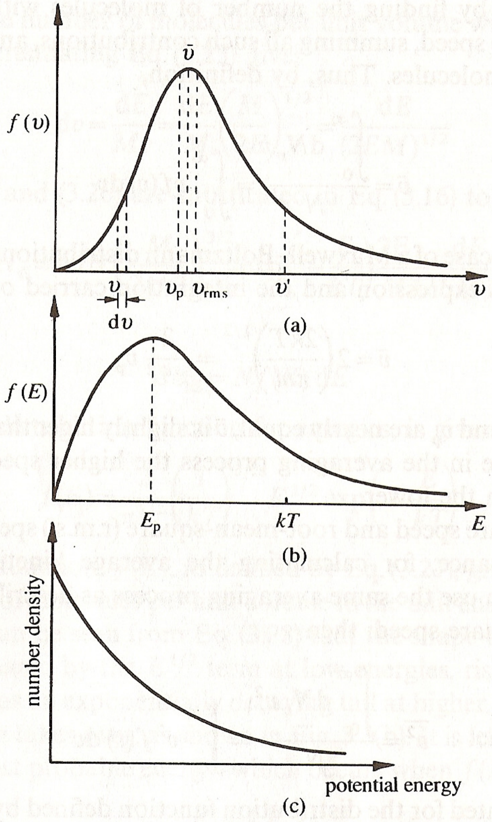

Fig. 3.3 (a) and (b) Maxwell–Boltzmann distributions for speed and energy; (c) Boltzmann distribution of particles in a field of force.

3.2.3 Use of distribution functions to calculate average values

We have determined the distribution of speeds among the constituent molecules of an ideal gas, in terms of a normalized distribution function $f(v)$, and are now able to use this to evaluate average values of speeds and velocities, which in turn can describe bulk properties of the gas, as discussed earlier. It should be pointed out that the averaging procedures developed are quite general and can be applied to *any* distribution function, even though we shall be specifically concerned with the speed distribution function.

What is the most probable speed of a molecule, v_p, in a gas obeying Maxwell–Boltzmann statistics? The defining Eq. (3.17) indicates that this occurs when $f(v)$ is maximum, as shown in Fig. 3.3(a). Hence v_p can be found by differentiation of Eq. (3.18), which gives

$$v_p = (2kT/M)^{1/2} \tag{3.19}$$

We next turn our attention to the average speed of a molecule in the gas, $\bar{v}$. This may be obtained by finding the number of molecules with a given speed, multiplying by the speed, summing all such contributions, and dividing by the total number of molecules. Thus, by definition,

$$\bar{v}=\frac{\int_0^\infty \mathrm{d}N_v v}{N}=\int_0^\infty v f(v)\,\mathrm{d}v \tag{3.20}$$

For the particular case of a Maxwell–Boltzmann distribution, Eq. (3.18) can be substituted in this expression and the integration carried out to give

$$\bar{v}=2\left(\frac{2kT}{\pi m}\right)^{1/2}=\frac{2}{\pi^{1/2}}v_\mathrm{p} \tag{3.21}$$

Thus, although $\bar{v}$ and v_p are nearly equal, $\bar{v}$ is slightly higer than v_p, as shown in Fig. 3.3(a), because in the averaging process the higher speeds are weighted more heavily than the lower.

The mean-square speed and root-mean-square (r.m.s.) speed, v_rms, are often required, for instance, for calculating the average kinetic energy of gas molecules. We can use the same averaging process as described previously to define a mean-square speed; then

$$\overline{v^2}=\frac{\int_0^\infty \mathrm{d}N_v v^2}{N}=\int_0^\infty v^2 f(v)\,\mathrm{d}v \tag{3.22}$$

This can be evaluated for the distribution function defined by Eq. (3.18), again making use of tables of definite integrals, to give

$$\overline{v^2}=3kT/M \tag{3.23}$$

and the root-mean-square speed is then

$$v_\mathrm{rms}=(\overline{v^2})^{1/2}=(3kT/M)^{1/2}=(\sqrt{\tfrac{3}{2}})v_\mathrm{p} \tag{3.24}$$

as shown on Fig. 3.3(a).

It will be noticed in passing that Eq. (3.23) can be rearranged to show that the average value of the kinetic energy of a molecule, $M\overline{v^2}/2$, is equal to $3kT/2$, which is consistent with our earlier assumption.

3.2.4 Energy distribution function

We now study how the energy of molecules is distributed throughout the ensemble. We make use of the fact that the translational kinetic energy of a particular molecule, designated E, is given by

$$E=Mv^2/2 \tag{3.25}$$

We consider energies in the range between E and $E+\mathrm{d}E$ and require an

expression for the number of molecules per unit volume with energies in this range $\mathrm{d}N_E$. Differentiating Eq. (3.25) gives

$$\mathrm{d}v=\frac{\mathrm{d}E}{Mv}=\frac{\mathrm{d}E}{M}\left(\frac{M}{2E}\right)^{1/2}=\frac{\mathrm{d}E}{(2EM)^{1/2}} \tag{3.26}$$

Equations (3.25) and (3.26) are substituted in Eq. (3.16) to give

$$\mathrm{d}N_E=4\pi N\left(\frac{M}{2\pi kT}\right)^{3/2}\exp\left(-\frac{E}{kT}\right)\frac{2E}{M}\frac{\mathrm{d}E}{(2EM)^{1/2}}$$

or

$$\mathrm{d}N_E=Nf(E)\,\mathrm{d}E \tag{3.27}$$

where $f(E)$, the distribution function for energies, is given by

$$f(E)=\frac{2}{\pi^{1/2}}\left(\frac{1}{kT}\right)^{3/2}E^{1/2}\exp\left(-\frac{E}{kT}\right) \tag{3.28}$$

The distribution function, $f(E)$, as defined by Eq. (3.27), gives the fraction of the total number of molecules per unit volume in the unit energy range centred on energy E. It can be seen from Eq. (3.28) that the shape of the $f(E)$ versus E curve is dominated by the $E^{1/2}$ term at low energies, rises to a maximum value, and then has an exponentially decaying tail at higher energies when the $\exp(-E/kT)$ term takes over, as shown in Fig. 3.3(b). It is left as an exercise to show that the most probable energy, which occurs when $f(E)$ is maximum, is

$$E_\mathrm{p}=kT/2$$

3.2.5 Boltzmann distribution

We have assumed previously that the gas molecules are not acted on by any external forces. Under these conditions, the energy E refers to the kinetic energy (KE) of a molecule; also, the density of the gas does not vary from point to point.

We now relax this assumption and consider the assembly of molecules to be in a field that causes each molecule to experience a force, which, athough it may vary spatially, is identical for each constituent. For example, the molecular gas may be in a gravitational field or the ensemble may be electrons under the influence of an electric field. In either case, a more general theory shows that Eq. (3.28) is still applicable, provided E is the total energy and includes a potential energy (PE) term. The distribution function is then

$$f(E)\propto\exp(-E/kT)\propto\exp[-(\mathrm{KE}+\mathrm{PE})/kT] \tag{3.29}$$

This expression is quite general and applies to any assembly of particles that interact infrequently. For example, consider a collection of electrons that originally has a Maxwellian distribution, say. When it is subjected to an electric field, applied such that the potential energy, eV, varies with position, the electron distribution everywhere still remains Maxwellian but the energy distribution function has an additional multiplying factor, $\exp(-eV/kT)$, which affects the local electron density. The electron densities n_1 and n_2, at two points where the potential energies are eV_1 and eV_2, respectively, are then related by

$$n_2/n_1=\exp[-e(V_2-V_1)/kT] \tag{3.30}$$

Hence, the electron density decreases exponentially with increasing potential energy. Such a relationship between particle density and potential energy is called a *Boltzmann distribution* and is of the form shown in Fig. 3.3(c). It has general applicability to many systems other than the ones mentioned.

3.3 Collections of particles that obey the exclusion principle

We have discussed assemblies of particles in which each constituent is independent of any other in the sense that it can take up any energy value; in other words, several molecules can exist in the same quantum state. We now turn our attention to collections of particles, electrons in particular, that interact quantum mechanically with each other in such a way that the occupancy of a particular state is restricted by the Pauli exclusion principle, i.e. no two electrons are allowed to occupy the same state. The ensemble must again be treated statistically, but the additional restriction leads to distribution functions of a form different from those encountered previously. The distribution function to be derived is most important, since it is applicable to free electrons in metals and semiconductors and allows many electrical phenomena in such materials to be understood, which otherwise could not be explained using classical concepts.

The arguments leading to a distribution function are similar to those followed previously, but this time, since we are dealing with quantum-mechanical systems, the uncertainty principle suggests that, rather than assign definite energy values to each particle, the probability that an energy state is occupied should be considered. Accordingly, let us consider a particular state, E_1, and let the probability of this level being occupied be $p(E_1)$. As a consequence, the probability that there are electrons at two different levels, E_1 and E_2, *simultaneously* is $p(E_1)\,p(E_2)$. Now, suppose two such electrons interact in such a way that they are transferred to two other energy levels, E_3 and E_4. The precise nature of the interaction will be discussed in later chapters. Energy will be assumed to be conserved by this process, and

$$E_1+E_2=E_3+E_4 \tag{3.31}$$

The exclusion principle implies that such an interaction is permissible only if vacant energy levels exist at E_3 and E_4. Now, the probability that level E_3 is *not* occupied is $1-p(E_3)$ and the probability that states E_3 and E_4 are vacant simultaneously is $[1-p(E_3)][1-p(E_4)]$. Thus, the probability that two electrons in states E_1 and E_2 interact and are transferred to states E_3 and E_4 is

$$p(E_1)p(E_2)[1-p(E_3)][1-p(E_4)]$$

Since the system is assumed to be in thermal equilibrium, the probability of the reverse process, that is, two electrons in the E_3 and E_4 states interact and are transferred to E_1 and E_2 states, must be the same, and hence

$$p(E_1)p(E_2)[1-p(E_3)][1-p(E_4)]=p(E_3)p(E_4)[1-p(E_1)][1-p(E_2)]$$

or

$$\left(\frac{1}{p(E_1)}-1\right)\left(\frac{1}{p(E_2)}-1\right)=\left(\frac{1}{p(E_3)}-1\right)\left(\frac{1}{p(E_4)}-1\right) \tag{3.32}$$

The solution that satisfies both this equation and the energy conservation condition, Eq. (3.31), is of the form

$$[1/p(E)]-1=A\exp(\beta E) \tag{3.33}$$

where A and β are constants. That this function simultaneously satisfies both equations can be verified by substitution.

Equation (3.33) can be rearranged to give

$$p(E)=1/[1+A\exp(\beta E)] \tag{3.34}$$

For high-energy states, the exponential term dominates the denominator and

$$p(E)\simeq A\exp(-\beta E) \tag{3.35}$$

Thus, at high energies the distribution approaches the Boltzmann distribution of Eq. (3.29) and hence the constant β can be identified with $1/kT$. That the two distribution functions become almost identical for high-energy states, even though one system (Boltzmann) allows multiple occupancy of states and that at present being discussed does not, is plausible on physical grounds. At high energies the number of electrons distributed over many available states is small and there are many more energy levels than electrons to occupy them. Under these conditions there is little chance of two or more electrons occupying the same state and whether the exclusion principle is included in the statistics or not becomes irrelevant to the form of the distribution function.

Equation (3.34) therefore becomes

$$p(E)=1/[1+A\exp(E/kT)] \tag{3.36}$$

Finally, it is customary to assume, without any loss of generality, that the constant A is redefined such that

$$A=\exp(-E_F/kT)$$

where the new constant, E_F, is called the *Fermi energy*; the physical significance of this constant energy will become apparent later. Meanwhile, Eq. (3.36) becomes

$$p(E) = \frac{1}{1+\exp[(E-E_F)/kT]} \tag{3.37}$$

This is the *Fermi–Dirac function*; it gives, for any ensemble obeying the exclusion principle, the probability that a particular state E is occupied. That the form of the function is consistent with the exclusion principle is apparent from (3.37); $p(E)$ can never exceed unity since the exponential term is always positive; hence the probability of occupancy of a particular state cannot exceed unity and no more than one electron per quantum state is allowed.

The nature of the probability function is best appreciated by plotting $p(E)$ versus E at various temperatures, as in Fig. 3.4. At 0 K the exponential in Eq. (3.37) has a value of 0 or ∞, depending on the sign of $(E-E_F)$. Thus, if $E<E_F$, the probability function is equal to unity and for $E>E_F$, the function equals zero, as shown in Fig. 3.4(a). Physically, what this implies is that at 0 K all available states up to an energy level E_F are filled, whereas all levels above E_F are empty, i.e. no electrons can possibly have energy greater than E_F. This serves as a preliminary definition of E_F and explains why it is alternatively called the *Fermi brim*.

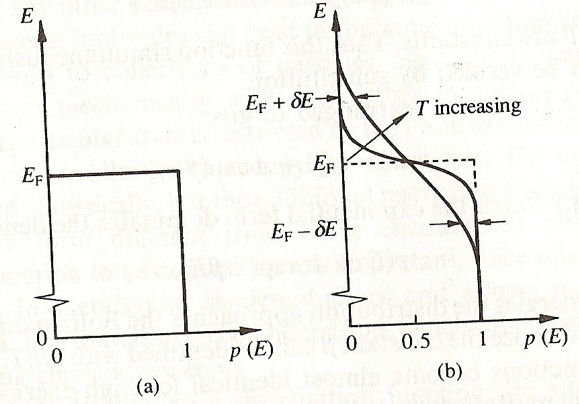

Fig. 3.4 **Fermi–Dirac probability function (a) at 0 K and (b) at *T* K.**

When the temperature is increased to T K, there is a possibility that electrons that were originally at levels near to the maximum possible energy at 0 K, namely the Fermi level E_F, can now occupy states for which E is greater than E_F. However, energy cannot be transferred to those electrons in low-energy states because there are no unoccupied energy levels immediately above for them to move into and the probability function at these energies remains substantially as it was for $T=0$ K. These arguments are substantiated by the shape of the probability function for $T>0$ K, as shown in Fig. 3.4(b). It will be seen that at low temperatures there is a small but finite probability that

electrons will occupy available states for which $E>E_F$ but the probability rapidly decreases with increasing energy. As the temperature is increased, this *tail* of the probability function becomes more pronounced and the probability of occupancy of higher energy states is correspondingly increased.

Notice that the probability that an electron occupies the Fermi level, i.e. $E=E_F$, is always 0.5, independent of the temperature. Another interesting fact is that the probability function is symmetrical about the value ($E=E_F$, $p(E)=0.5$). This can be shown as follows. Consider an energy level that is δE *above* the Fermi level, as shown in Fig. 3.4(b). The probability that the level is occupied is, using Eq. 3.37

$$p(E_F+\delta E) = \frac{1}{1+\exp[(E_F+\delta E-E_F)/kT]} = \frac{1}{1+\exp(\delta E/kT)} \tag{3.38}$$

Now consider the level that is δE *below* E_F. The probability that this level is *not* occupied is

$$1-p(E_F-\delta E) = 1-\frac{1}{1+\exp(-\delta E/kT)} = \frac{1}{1+\exp(\delta E/kT)} \tag{3.39}$$

Comparison of Eqs (3.38) and (3.39) demonstrates the symmetry of the probability about E_F, since the probability that a level at a particular energy increment above E_F is occupied equals the probability that a level below E_F by the same energy increment is empty.

Finally, it should be pointed out that in many solids E_F is typically of the order of a few electronvolts and at ordinary temperature kT is only a fraction of an electronvolt. Thus, since the probability function goes from nearly unity to nearly zero over an energy range near E_F of only a few kT, the ordinate of the probability curve in Fig 3.4(b) has been artificially compressed so that details of the variation of $p(E)$ near to $E=E_F$ are not lost.

Problems

1. For a hypothetical gas the number of molecules per unit volume dN_v in the speed range from v to $v+dv$ is given by

$$dN_v = Kv\,dv \qquad v_0>v>0$$
$$dN_v = 0 \qquad v>v_0$$

where K is a constant. The total number of molecules per unit volume is N. Draw a graph of the distribution function and find the constant K in terms of v_0 and N. Compute the average, r.m.s. and most probable speeds in terms of v_0.

Ans. $2N/v_0^2$, $2v_0/3$, $v_0/\sqrt{2}$, v_0

2. A hypothetical gas with N molecules per cubic metre has a speed

distribution function

$$f(v)=Cv^2 \qquad \text{for } v_0>v>0$$
$$f(v)=0 \qquad \text{for } v>v_0$$

Find the mean-square fluctuation of the speeds, which is defined as the mean-square speed minus the square of the mean speed.

Ans. $0.04v_0^2$

3. Show that the Maxwell–Boltzmann distribution function for the speeds of molecules in a gas can be written in terms of a most probable speed v_p, thus

$$f(v)=\frac{4}{\sqrt{\pi}}\frac{v^2}{v_p^3}\exp\left(-\frac{v^2}{v_p^2}\right)$$

Use this expression to find the mean speed and the r.m.s. speed in terms of v_p. Assume

$$\int_0^{\infty}\exp(-ax^2)x^{2k+1}\,dx=\frac{k!}{2a^{k+1}}$$

and

$$\int_0^{\infty}\exp(-ax^2)x^{2k}\,dx=\frac{1,3,5\ldots(2k-1)}{2^{k+1}}\left(\frac{\pi}{a^{2k+1}}\right)^{1/2}$$

Ans. $2v_p/\sqrt{\pi}$, $(\sqrt{\tfrac{3}{2}})v_p$.

4. In a Maxwellian gas the number of particles colliding with unit surface area of its container per second is

$$\frac{N}{4}\left(\frac{8kT}{\pi M}\right)$$

Caesium atoms are contained within a furnace at temperature T K. There is also a hot tungsten wire (radius r, length l) inside the furnace and caesium atoms striking this wire became singly ionized. The resulting ions are collected on a nearby negative electrode. Show that the ion current I to this electrode is given by

$$I=erlp(2\pi/kTM)^{1/2}$$

where p is the vapour pressure of the caesium at temperature T and M the mass of the caesium atom. Can you suggest a practical use for this device?

5. A gas possesses a Maxwellian velocity distribution. Show that the fraction of molecules in a given volume that possess a velocity component v_x whose magnitude is greater than some selected value v_{0x} is given by

$$\exp(\tfrac{1}{2}-\pi^{-1/2})\int_0^{mv_{0x}^2/2kT}\exp\left(\frac{-mv_{0x}^2}{2kT}\right)d\left(\frac{mv_{0x}^2}{2kT}\right)^{1/2}$$

The definite integral $\int_0^{\infty}\exp(-\beta s^2)ds=\frac{1}{2}(\pi/\beta)^{1/2}$ will be required.

6. Show that the most probable energy of a molecule in a Maxwellian gas is $kT/2$.

7. Show that the number of molecules, N_0, in a Maxwellian gas whose energies lie between zero and E_0, where $E_0 \ll kT$, is given approximately by

$$\frac{N_0}{N}=\frac{4}{3\sqrt{\pi}}\left(\frac{E_0}{kT}\right)^{3/2}$$

Hence calculate approximately the percentage of molecules whose energies are less than 1 per cent of kT.

8. At $T=0$ K the electron energy levels in a metal are all occupied for $E<E_F$ and are empty for $E>E_F$. The energy distribution is then of the form

$$\Delta N/N=CE^{1/2}\Delta E \qquad \text{for } E<E_F$$
$$\Delta N/N=0 \qquad \text{for } E>E_F$$

where C is a constant. Find (a) the average electron energy under these conditions and (b) the percentage of the total number of electrons with energies between $0.1E_F$ and $0.2E_F$.

Ans. $0.6E_F$, 5.8 per cent.

4 Conduction in metals

4.1 Introduction

In this chapter we shall be considering the conduction of electricity in good conductors, typically metals. We shall see that in such materials the valence electrons are no longer associated with any one particular ion core but are free to wander about the lattice under the influence of external forces. The metal is then considered simply as a 'container' of free electrons, which are only trapped within the boundaries of the metal. Earlier arguments about bound particles would suggest that confining the electrons in this manner leads to a set of discrete energy eigenvalues, much the same as for electrons trapped in the one-dimensional well of Sec. 2.2. Further, since electrons in the metal will be subject to the exclusion principle, Fermi rather than Maxwell–Boltzmann statistics will be applicable to them.

4.2 A simple model of a conductor

The potential energy of an electron located at some distance r from the nucleus of a single, isolated metal atom will be of the general form shown in Fig. 2.3(a). Consequently, there will be a set of allowed electron energy levels associated with the atom, each specified by a particular set of quantum numbers, similar to that shown in Fig. 2.3(a). Electrons are trapped within the potential energy well and are thus bound to the atom; not even the outermost valence electrons usually have sufficient energy to escape.

When such atoms are incorporated in the lattice of a metal, the potential energy distribution between neighbouring atoms is different from that of the individual atoms, as shown in Fig. 4.1. Since potential energy is a scalar quantity, the potential energies of the individual atoms add and the net energy profile is depressed, i.e. is made more negative, as shown in the figure. This causes some of the less tightly bound electrons, lying in the outermost levels of the individual atoms, for example those in E_4 of Fig. 4.1, to have energies higher than the binding energies of atoms in the lattice. Such valence electrons can no longer be associated with a particular atom and are free to move about the lattice in the vicinity of any ion core. Notice that electrons occupying the lower energy states are unaffected by the atoms being incorporated into the metal and remain bound to the parent nucleus. We can estimate the number density of free electrons by assuming, conservatively, that each atom provides only one such electron. A typical lattice constant of 0.1 nm then suggests a number density of $[(10^{-10})^{-1}]^3 = 10^{30}$ atoms per cubic metre and a similar minimum number of free electrons in the same volume.

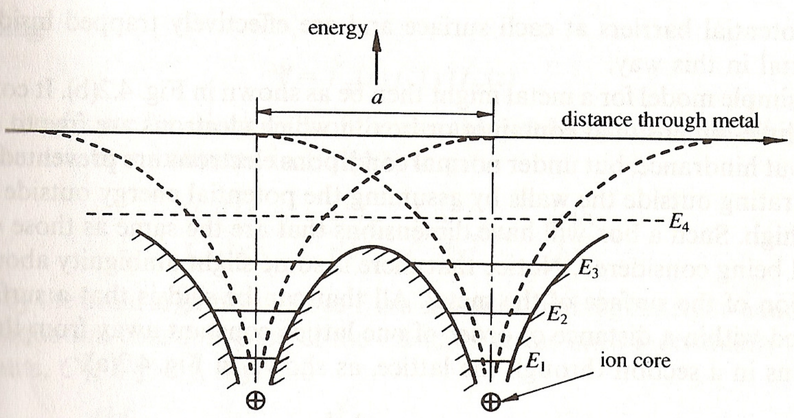

Fig. 4.1 **Potential energy and energy levels of neighbouring atoms in a metal lattice.**

The situation is somewhat different near the surface of the metal. Consider a section of the metal lattice shown in Fig. 4.2(a). The nearest atom to a particular surface obviously has no neighbouring atom outside the metal and the potential energy is not depressed as in the interior of the metal. Hence, potential barriers exist at each surface, as shown, which are normally unsurmountable by electrons. Thus, although electrons are considered to be free to wander unimpeded about the inside of the metal, they are reflected by

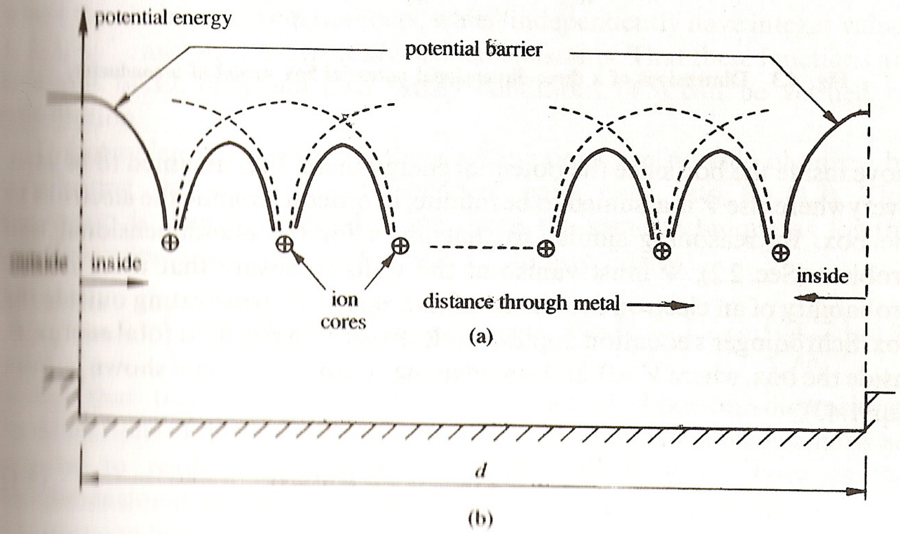

Fig. 4.2 **(a) Section through a metal lattice; (b) potential box model.**

the potential barriers at each surface and are effectively trapped inside the material in this way.

A simple model for a metal might then be as shown in Fig. 4.2(b). It consists of a three-dimensional container or box in which electrons are free to move without hindrance, but under normal conditions electrons are prevented from penetrating outside the walls by assuming the potential energy outside to be very high. Such a box will have dimensions that are the same as those of the metal being considered. Notice that there is some slight ambiguity about the position of the surface of the metal. All that can be said is that a surface is located within a distance of order of one lattice constant away from the last nucleus in a section through the lattice, as shown in Fig. 4.2(a).

4.3 Electrons trapped in a three-dimensional potential box

If the free-electron model of a metal is assumed, the electron energy states will be the same as those for electrons trapped in a three-dimensional potential box. Consider a box with dimensions shown in Fig. 4.3. Electrons are free to move inside the box since the potential energy there, V, is assumed to be zero. Everywhere else V is assumed to be infinite, in order to confine the electrons to the box. By reasoning similar to that given for the one-dimensional well problem (Sec. 2.2), Ψ must vanish at the walls to ensure that there is zero probability of an electron acquiring infinite energy by penetrating outside the box. Schrödinger's equation applied to electrons with constant total energy, E, inside the box, where $V=0$, and stated in the coordinate system shown is, from Eq. (1.43),

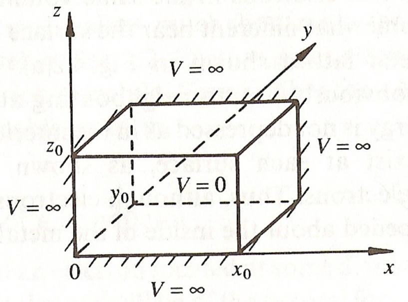

Fig. 4.3 **Dimensions of a three-dimensional potential box model of a conductor.**

$$\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}+\frac{2m}{\hbar^2}E\Psi=0 \tag{4.1}$$

This equation can be solved by the separation-of-variables technique by

assuming

$$\Psi=f_x(x)f_y(y)f_z(z) \tag{4.2}$$

where the f's are functions only of the variable used as a subscript. This trial solution can be substituted in Eq. (4.1) to give

$$\frac{1}{f_x}\frac{\mathrm{d}^2f_x}{\mathrm{d}x^2}+\frac{1}{f_y}\frac{\mathrm{d}^2f_y}{\mathrm{d}y^2}+\frac{1}{f_z}\frac{\mathrm{d}^2f_z}{\mathrm{d}z^2}=-\frac{2mE}{\hbar^2} \tag{4.3}$$

Then, by the usual arguments, since E is a constant, making the right-hand side of the equation constant, each of the left-hand terms must individually equal constants, C_1^2, C_2^2, C_3^2, say, and

$$\frac{\mathrm{d}^2f_x}{\mathrm{d}x^2}=C_1^2f_x \qquad \frac{\mathrm{d}^2f_y}{\mathrm{d}y^2}=C_2^2f_y \qquad \frac{\mathrm{d}^2f_z}{\mathrm{d}z^2}=C_3^2f_z \tag{4.4}$$

As has been established already, the boundary conditions on the wavefunctions require that $\Psi=0$ at the walls of the box. Hence

$$\begin{aligned}\Psi=0 \qquad &\text{at } x=0 \text{ and } x=x_0\\ &y=0 \text{ and } y=y_0\\ &z=0 \text{ and } z=z_0\end{aligned} \tag{4.5}$$

Possible solutions to Schrödinger's equation, given by Eq. (4.4) and also satisfying the boundary conditions (4.5), are then

$$\begin{aligned}f_x&=A\sin(n_x\pi x/x_0)\\ f_y&=B\sin(n_y\pi y/y_0)\\ f_z&=C\sin(n_z\pi z/z_0)\end{aligned} \tag{4.6}$$

where the n's are quantum numbers, which independently have integer values 1, 2, 3, 4, ..., and A, B, C are newly defined constants. That these functions are solutions of Eq. (4.4) and also satisfy conditions (4.5) can be verified by substitution.

The complete expression for the wavefunctions can now be obtained by substituting the x-, y- and z-dependent parts back into Eq. (4.3). This expression is then normalized, using much the same technique as for the one-dimensional potential well in Sec. 2.2, to give finally

$$\Psi_{n_xn_yn_z}=\left(\frac{2}{x_0}\right)^{1/2}\sin\left(\frac{n_x\pi x}{x_0}\right)\left(\frac{2}{y_0}\right)^{1/2}\sin\left(\frac{n_y\pi y}{y_0}\right)\left(\frac{2}{z_0}\right)^{1/2}\sin\left(\frac{n_z\pi z}{z_0}\right) \tag{4.7}$$

Notice that this wavefunction is the product of three one-dimensional wavefunctions of the type encountered in Sec. 2.2. (This result may come as no surprise to readers familiar with electromagnetic theory, since as the one-dimensional potential well is analogous to a short-circuited resonant transmission line, the three-dimensional potential box has its electromagnetic equivalent in a short-circuited resonant cavity.)

The wavefunction expression of Eq. (4.7) is next substituted back into Schrödinger's equation to obtain the permitted quantized energy levels of electrons in the box, to give

$$E_{n_x n_y n_z} = \frac{\hbar^2}{2m}\left[\left(\frac{n_x \pi}{x_0}\right)^2 + \left(\frac{n_y \pi}{y_0}\right)^2 + \left(\frac{n_z \pi}{z_0}\right)^2\right] \qquad (4.8)$$

where n_x, n_y, n_z are three quantum numbers that specify a particular electronic energy state.

The problem is simplified if the containing volume is considered to be a cube of side d. The expression for the energy eigenvalues given by Eq. (4.8) then simplifies to

$$E = \frac{h^2}{8md^2}(n_x^2 + n_y^2 + n_z^2) \qquad (4.9)$$

Finally, if we write

$$n^2 = n_x^2 + n_y^2 + n_z^2 \qquad (4.10)$$

the expression for eigenvalues of electrons in a cubical potential box is

$$E = \frac{h^2}{8md^2} n^2 \qquad (4.11)$$

which is of the same form as that obtained for the one-dimensional potential well (Eq. (2.6)).

4.4 Maximum number of possible energy states

It is instructive to find the maximum number of possible energy states for which n, as defined by Eq. (4.10), is less than some maximum value, n_F say. The discussion and result will be most pertinent to later consideration of the distribution of electron energies on a metal.

A particular value of n, which has components n_x, n_y and n_z, all positive integers, can be visualized in n space as shown in Fig. 4.4(a). In order to count the number of possible combinations of (n_x, n_y, n_z) up to the maximum value n_F, which will then automatically specify the possible energy levels via Eq. (4.9), it is easiest first of all to assume n_x fixed at some value, n_{x0} say, and consider a plane that is a section through n space as shown in Fig. 4.4(b). Each point in the diagram represents a particular combination of quantum numbers n_y and n_z. Notice that any area on this plane is numerically equal to the number of possible combinations of n's enclosed by the area. For example, the section indicated by broken lines is 12 units of area in extent and encloses 12 combinations of n_y and n_z. Now, for the fixed quantum number n_{x0}, the other quantum numbers are related by

$$n^2 - n_{x0}^2 = n_y^2 + n_z^2$$

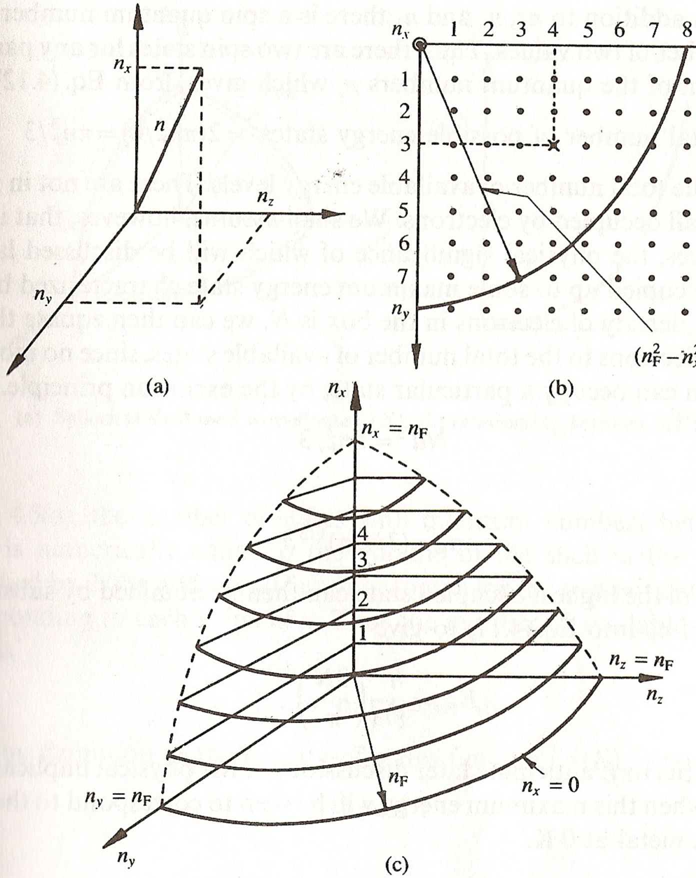

Fig. 4.4 **Diagrams illustrating the evaluation of the maximum number of energy states of electrons trapped in a potential box.**

and thus the maximum number of possible combinations of n_y and n_z for $n \leqslant n_F$ must lie within a circle centred at the origin and of radius $(n_F^2 - n_{x0}^2)^{1/2}$, as shown; by our previous argument this number of combinations must be numerically equal to the area of the circle in the first quadrant.

If n_x is now allowed to assume other values the total number of possible combinations of (n_x, n_y, n_z) is included in a series of slices through n space, each corresponding to different integer values of n_x, as shown diagrammatically in Fig. 4.4(c). It follows that the total number of possible combinations of the quantum numbers for $n \leqslant n_F$ is numerically equal to that volume of a sphere of radius n_F that is contained in the first quadrant of n space. This latter condition is necessary since the n's are always positive integers. Hence

$$\text{total number of combinations of } (n_x, n_y, n_z) = \tfrac{1}{8}(\tfrac{4}{3}\pi n_F^3) = \pi n_F^3/6 \qquad (4.12)$$

Now, in general, each electron energy state is characterized by four quantum numbers; in addition to n_x, n_y and n_z there is a spin quantum number, which can have either of two values. Thus, there are two spin states for any particular combination of the quantum numbers n, which gives, from Eq. (4.12),

$$\text{total number of possible energy states } = 2(\pi n_F^3/6) = \pi n_F^3/3 \qquad (4.13)$$

This gives the total number of available energy levels. These are not in general necessarily all occupied by electrons. We shall assume, however, that in some circumstances, the physical significance of which will be discussed later, all states are occupied up to some maximum energy state characterized by n_F. If the number density of electrons in the box is N, we can then equate the total number of electrons to the total number of available states, since no more than one electron can occupy a particular state, by the exclusion principle. Hence

$$Nd^3 = \pi n_F^3/3$$

or

$$n_F = (3N/\pi)^{1/3} d \qquad (4.14)$$

The energy of the highest occupied state can then be obtained by substituting this value of n_F into Eq. (4.11) to give

$$E_{F0} = \frac{h^2}{8m}\left(\frac{3N}{\pi}\right)^{2/3} \qquad (4.15)$$

The subscripts to E anticipate later discussions of the physical implications of the result, when this maximum energy will be seen to correspond to the Fermi energy of a metal at 0 K.

4.5 The energy distribution of electrons in a metal

In order to find out the manner in which energy is distributed among the free electrons in a metal, it is first necessary to determine the energy distribution of allowed energy levels that are available for occupation by the electrons. In other words, the number of available energy states lying in a range of energies, say between E and $E + dE$, is required.

It is found to be convenient to define a function $S(E)$, called the *density distribution of available states* or simply the *density of states*, which is defined in such a way that $S(E)\,dE$ is the number of available states per unit volume in the energy range considered; the problem is then modified to that of finding the form of $S(E)$.

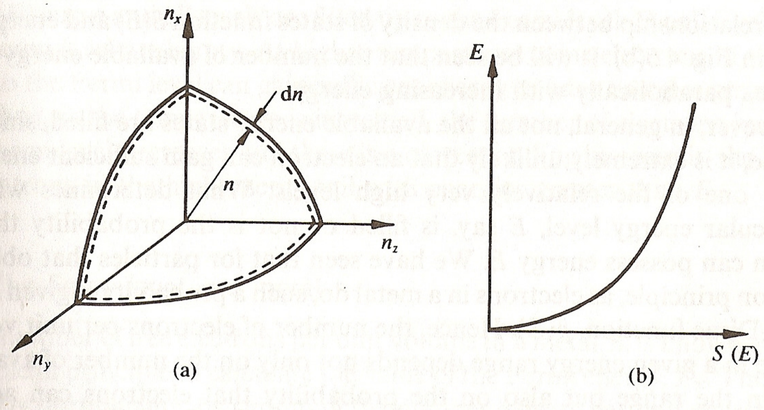

Fig. 4.5 **(a) Spherical shell used to evaluate $S(E)$; (b) relationship between $S(E)$ and energy E.**

The relationship between the energy of a state, E, and its quantum number designation, n, for a metal cube of side d is given in Eq. (4.11). In the energy range dE there will be a corresponding range of quantum numbers, dn say. We can evaluate the number of states in the range by finding the volume that the range dn occupies in n space, as was explained in the previous section. Thus, considering a spherical shell in n space of radius n and thickness dn, as shown in Fig. 4.5(a), the number of states with quantum numbers between n and $n + dn$ is numerically equal to the volume of the shell in the first octant, multiplied by 2; the additional factor accounts for the two possible spin states corresponding to each value of n. Thus the number of available states in the range is

$$2(4\pi n^2\,dn)/8 = \pi n^2\,dn \qquad (4.16)$$

which by definition of the density-of-states function, $S(E)$, is equal to

$$S(E)\,dE\,d^3$$

Hence

$$S(E) = \frac{\pi n^2\,dn}{d^3\,dE} \qquad (4.17)$$

Equation (4.11) can be differentiated to give

$$n^2\frac{dn}{dE} = \frac{(8\sqrt{2})m^{3/2}\,d^3\,E^{1/2}}{h^3}$$

which can be substituted in Eq. (4.17) to provide the following expression for the density of available states:

$$S(E) = \frac{(8\sqrt{2})\pi m^{3/2}}{h^3}E^{1/2} \qquad (4.18)$$

To reiterate, the total number of *available* energy levels per unit volume in a given energy range, dE, is obtained by multiplying this distribution function, $S(E)$, by the size of the range. Thus an alternative definition of $S(E)$ is that it is the number of available states per unit volume, per unit of energy centred at E. Notice that Eq. (4.18) is independent of d; the expression for $S(E)$ is quite general and is independent of dimensions.

The relationship between the density of states function $S(E)$ and energy E is shown in Fig. 4.5(b). It will be seen that the number of available energy levels increases parabolically with increasing energy.

However, in general, not all the available energy states are filled, since, for example, it is extremely unlikely that an electron can gain sufficient energy to occupy one of the relatively very high levels. What determines whether a particular energy level, E say, is filled or not is the probability that an electron can possess energy E. We have seen that for particles that obey the exclusion principle, as electrons in a metal do, such a probabilty is given by the Fermi–Dirac function, $p(E)$. Hence, the number of electrons per unit volume that are in a given energy range depends not only on the number of available states in the range but also on the probability that electrons can acquire sufficient energy to occupy the states, or

number of electrons per unit volume with energies between E and $E+\mathrm{d}E$
= (number of available states per unit volume in the range E to $E+\mathrm{d}E$)
× (probability that a state of energy E is occupied)

and

$$N(E)\,\mathrm{d}E = S(E)\,\mathrm{d}E\,p(E)$$

where $N(E)$ is the number of electrons per unit volume per unit of energy centred at E. Thus, the number density of electrons in a unit energy range is obtainable from the distribution function of available states and the probability function since

$$\boxed{N(E) = S(E)p(E)} \tag{4.19}$$

The number density of electrons as a function of energy can thus be deduced from Eq. (4.19) and Figs 3.4 and 4.5(b), and is plotted at 0 K and some higher temperature in Fig. 4.6. At 0 K, $N(E)$ increases parabolically with E, following

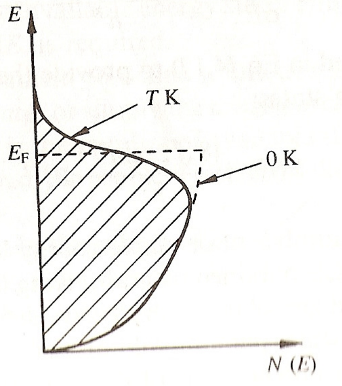

Fig. 4.6 Number density of free electrons in a metal.

the $S(E)$ curve and all levels are filled up to the Fermi level, E_F; all levels above the Fermi level are empty. At higher temperature some electrons in the levels near to the Fermi level can gain sufficient energy to have energies greater than E_F. Thus, as the temperature is increased, the number of electrons just below the Fermi level decreases and there is a corresponding increase in the number of electrons in the high-energy tail with energies greater than E_F.

4.6 The Fermi level in a metal

If the number of free electrons per unit volume in a metal, n, is known, it is then possible in principle to calculate the value of the Fermi energy, E_F. This can be done by normalizing, by summing the number density per unit energy, $N(E)$, over all possible energies and equating to n, thus

$$n = \int_0^\infty N(E)\,\mathrm{d}E \tag{4.20}$$

Writing $N(E)$ in terms of the density-of-states function, $S(E)$, and the probability function, $p(E)$, using Eq. (4.19), and including the more specific expressions of Eqs (4.18) and (3.37) give

$$n = \int_0^\infty S(E)p(E)\,\mathrm{d}E = \frac{(8\sqrt{2})\pi m^{3/2}}{h^3}\int_0^\infty \frac{E^{1/2}\,\mathrm{d}E}{1+\exp[(E-E_F)/kT]} \tag{4.21}$$

This integral is difficult to evaluate except when $T = 0$ K; then $p(E)$ equals unity for all $E \leqslant E_{F0}$ and is zero elsewhere, and

$$n = \frac{(8\sqrt{2})\pi m^{3/2}}{h^3}\int_0^{E_{F0}} E^{1/2}\,\mathrm{d}E$$

The Fermi energy at 0 K is thus given by

$$E_{F0} = \frac{h^2}{8m}\left(\frac{3n}{\pi}\right)^{2/3} = 3.65\times 10^{-19}\,n^{2/3}\ \mathrm{eV} \tag{4.22}$$

a result that was anticipated in Eq. (4.15).

Typical values for the Fermi energy at 0 K as calculated from Eq. (4.22) and a knowledge of n are: for silver, $E_{F0} = 5.5$ eV; for copper, $E_{F0} = 7.0$ eV; and for aluminium, $E_{F0} = 11.7$ eV. Thus, the Fermi energy for a good conductor is of the order of a few electronvolts. This emphasizes an essential difference between a classical gas and the electron-gas model of a metal at 0 K; in the former all particles have zero energy while in the latter all electron energies up to the Fermi energy are possible.

At temperatures other than 0 K, the Fermi energy can be obtained from Eq. (4.21) by numerical integration. At room temperature it can be shown that a reasonably good approximation for E_F is

$$E_F = E_{F0}\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{E_{F0}}\right)^2\right] \tag{4.23}$$

This equation shows that, whereas E_F decreases with increasing temperature, since kT is usually much smaller than E_{F0}, E_F is not far removed from E_{F0} and is fairly insensitive to temperature changes.

4.7 Conduction processes in metals

We shall first examine electrical conduction in terms of the free-electron model of a metal. Although there are drawbacks to the treatment, which will be discussed subsequently, what follows will serve as a simple introduction to the essential features of conduction processes.

Conduction in electrical conductors is governed by a fundamental experimental law, Ohm's law, which in its most general form may be written

$$J = \sigma\mathscr{E} \tag{4.24}$$

where J is the current density, in a material of conductivity σ, produced by the application of an electric field $\mathscr{E}$. If we assume that the current flow is due to the movement of n free electrons per unit volume, each of charge $-e$ and travelling with velocity v, we can write

$$J = -nev \tag{4.25}$$

Now, an electron subjected to an electric field, $\mathscr{E}$, by definition experiences an accelerating force, $-e\mathscr{E}$. Thus, in the absence of any restraining force the free electrons in a metal with an externally applied electric field accelerate progressively, and as a consequence of Eq. (4.25) the current density increases with time. This is clearly at variance with Ohm's law, which requires the current to be constant for a particular applied field. It is evident that, for the two expressions for current density to be compatible, the electron velocity must remain constant for any particular applied field. The constant velocity can be explained in terms of 'collisions' of the electrons with the crystal structure in which they move. The precise mechanism of the collisions will be discussed more fully later. Meanwhile, it is sufficient to say that a free electron can be accelerated from rest by the application of an external electric field, acquires a linearly increasing velocity for a short time, but then undergoes some form of collision that reduces its velocity to zero; the process then repeats itself. As a consequence, the electron acquires a constant average drift velocity in the direction of the accelerating force, which is superimposed on to its random thermal motion. This situation is shown diagrammatically in Fig. 4.7.

The effect of collisions in this case, and, incidentally, for similar processes in semiconductors which are considered in following chapters, is thus to introduce a viscous or frictional force, which inhibits the continual acceleration of the carriers by the field and limits the velocity to some average drift velocity, v_D.

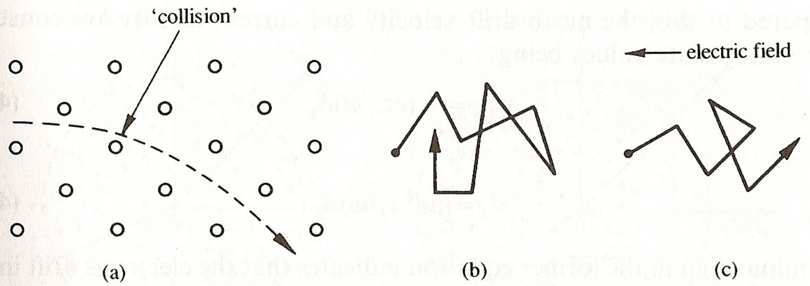

Fig. 4.7 **(a) Random motion of an electron through the crystal lattice; (b) as for (a) but on a larger scale; and (c) drift motion of an electron under the influence of an external electric field.**

If the average time between collisions is τ_r, then the number of collisions per second is $1/\tau_r$ and the average rate of change of momentum or the frictional force on the carriers due to collision is mv_D/τ_r. The equation of motion of an electron subject to an applied field in the x direction, $\mathscr{E}_x$, is then

$$-e\mathscr{E}_x = m\frac{\mathrm{d}}{\mathrm{d}t}(v_{Dx}) + \frac{m(v_{Dx})}{\tau_r} \tag{4.26}$$

The solution of this equation is

$$v_{Dx} = \frac{-e\tau_r\mathscr{E}_x}{m}[1 - \exp(-t/\tau_r)] \tag{4.27}$$

which may be verified by substitution. We can now substitute this value of v_{Dx} in Eq. (4.25) to obtain the current density

$$J = n(-e)v_{Dx} = \frac{ne^2\tau_r\mathscr{E}_x}{m}[1 - \exp(-t/\tau_r)] \tag{4.28}$$

We see that the electron drift velocity and the current density both rise exponentially with time to become constant in a time comparable to τ_r.

We can understand the significance of τ_r further if we suppose that after some initial application of the field it is suddenly reduced to zero. Equation (4.26) indicates that the decay of drift velocity from its initial value at $t = 0$, v_{D0}, back to the thermal equilibrium state when $v_D = 0$ is then governed by the equation

$$v_D = v_{D0}\exp(-t/\tau_r) \tag{4.29}$$

The time constant, τ_r, is often referred to as the electron *relaxation time*, since it controls the exponential way in which electron drift velocity and hence current relax back to zero when the field is suddenly removed. It is typically of order 10^{-14} s and so, for any time after the application of an electric field that is long compared to this, the mean drift velocity and current density are constant, their steady-state values being

$$v_{Dx} = -(e\tau_r/m)\mathscr{E}_x \tag{4.30}$$

and

$$J_x = (ne^2\tau_r/m)\mathscr{E}_x \tag{4.31}$$

The minus sign in the former equation indicates that the electrons drift in the negative x direction, in the opposite direction to the field. This corresponds to a conventional current flow in the opposite direction, so J_x remains positive.

Equations (4.30) and (4.31) can be somewhat simplified if we assume that τ_r is independent of $\mathscr{E}_x$, which is usually permissible. We then notice that the drift velocity of electrons is directly proportional to the applied field. The constant of proportionality, usually designated μ, is called the *mobility*. Thus

$$v_D = -\mu\mathscr{E}_x \tag{4.32}$$

where the electron mobility

$$\mu = e\tau_r/m \tag{4.33}$$

The mobility is thus defined as the incremental average electron velocity per unit of electric field.

We can now rewrite the current equation in terms of the mobility, and Eq. (4.31) becomes

$$J_x = ne\mu\mathscr{E}_x \tag{4.34}$$

Comparing this equation with Eq. (4.24), it is seen that the conductivity of the metal, σ, can be expressed as

$$\sigma = ne\mu = ne^2\tau_r/m \tag{4.35}$$

This expression is quite general and holds for any conduction process, provided μ, n and m are specified for the particular process.

The discussion so far has excluded any mention of the distribution of allowed electron energy levels or the exclusion principle, which must apply to electrons in a metal. A graphical representation of the statistical distribution of the energies of conduction electrons will now be considered, since it gives more physical insight into the conduction process.

Each conduction electron occupies a particular energy state, which has an associated velocity that can be represented as a point in the three-dimensional velocity space shown in Fig. 4.8(a). In the absence of an applied electric field, the electron velocities are random; for every group of electrons travelling with a particular velocity, there will be a similar number travelling with the same speed but in the opposite direction, and the distribution in velocity space will have spherical symmetry. At zero temperature the distribution will be most compact and all levels will be occupied out to a velocity, v_F, corresponding to

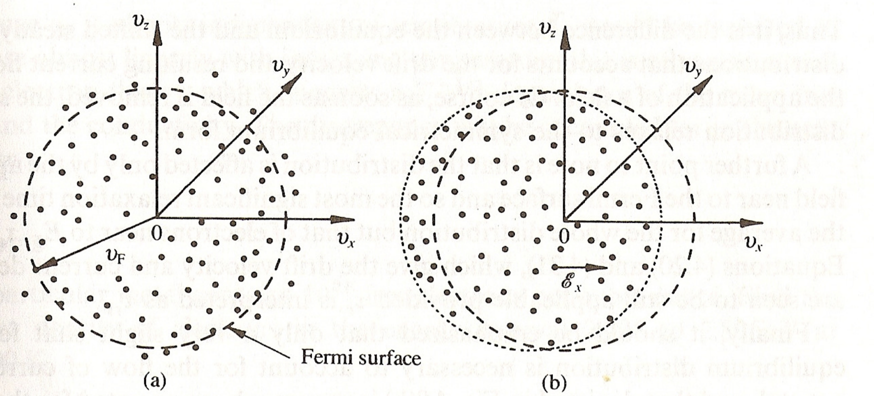

Fig. 4.8 Distribution of electrons in velocity space: (a) with no applied field and (b) with field $\mathscr{E}_x$ applied.

the Fermi energy. Moreover, since $E_F = \frac{1}{2}mv_F^2$, the outermost boundary containing all possible velocities will be a sphere, shown as a broken circle in Fig. 4.8(a). Such a boundary is called a *Fermi surface*, even when it is not spherical as it is in this diagram.

At more elevated temperatures the boundary of the distribution in velocity space becomes more diffuse since a small proportion of electrons now have velocities greater than v_F. This 'fuzzing' of the edges of the sphere is not very pronounced because the corresponding range of energies is only a few kT, which is generally much less than E_F.

When an electric field $\mathscr{E}_x$ is applied as shown in Fig. 4.8(b), all electrons in the distribution are subjected to a force $e\mathscr{E}_x$ in the $-x$ direction. Only those electrons near to the Fermi level can move, since only they have unoccupied energy levels immediately adjacent into which to move. Suppose for the moment that all electrons suffer a randomizing collision simultaneously at time $t = 0$ and that at this instant the electrons have the equilibrium velocity distribution shown in Fig. 4.8(a). At some time t later the distribution as a whole moves in the negative x direction by a velocity increment $e\mathscr{E}_x t/m$. After a further series of collisions the distribution will tend to revert to its equilibrium position. Of course, in a more realistic situation, collisions occur in a more random manner; some electrons are returning to their equilibrium position in velocity space after a collision while others are being accelerated by the field. Hence, on average, application of an electric field causes the entire equilibrium velocity distribution to be shifted slightly by an amount $e\mathscr{E}_x\tau_r/m$ in the opposite direction to the field as shown in Fig. 4.8(b). The velocity distribution is no longer symmetrical about the origin and the precise cancellation of electron velocity components in the direction of the field does not occur. There is now a slightly preferred electron velocity direction in the opposite direction to the field, which results in a drift velocity

$$v_D = -e\mathscr{E}_x\tau_r/m$$

Thus, it is the difference between the equilibrium and the shifted steady-state distributions that accounts for the drift velocity and resulting current flow on the application of a field. Of course, as soon as the field is removed, the steady distribution relaxes to the symmetrical equilibrium form.

A further point to note is that the distribution is affected only by the applied field near to the Fermi surface and so the most significant relaxation time is not the average for the whole distribution but that of electrons near to E_F, τ_{rF} say. Equations (4.20) and (4.31), which give the drift velocity and current density, are seen to be still applicable provided τ_r is interpreted as τ_{rF}.

Finally, it should be emphasized that only a very slight shift for the equilibrium distribution is necessary to account for the flow of current in a metal, and that depicted in Fig. 4.8(b) is very much exaggerated for the sake of clarity.

The free-electron model has been used successfully to explain many aspects of electronic conduction in metals, particularly when Fermi statistics is employed. There are, however, some details of the properties of electrical conductors that cannot be accounted for quantitatively by the simple model. For example, in order that the electron velocity be limited to a drift velocity, it has been found necessary to postulate some sort of collision mechanism followed by energy randomization. Early theories assumed that the collisions were between electrons and ion cores, which occupy most of the volume of a metal. That such a theory is unacceptable can be seen by estimating the mean free path or average distance between collisions, $\bar{l}$. For electrons near the Fermi level

$$\bar{l}_F = \tau_{rF} v_F \tag{4.36}$$

where v_F is the velocity of an electron with the Fermi energy. Since the Fermi energy is relatively insensitive to temperature, v_F is given approximately by

$$v_F \approx (2E_{F0}\, e/m)^{1/2}$$

If, for example, we consider copper, $E_{F0} \approx 7$ eV and $v_F \approx 10^6$ m s^{-1}. The relaxation time for copper can be estimated using Eq. (4.35); if a measured conductivity of 6×10^7 S m^{-1} and a free-electron density of 10^{29} are assumed, then τ_{rF} is of order 10^{-14} s. Hence the mean free path from Eq. (4.36) is of the order of tens of nanometres. This is very much longer than the lattice constant, which is of order 0.1 nm. Clearly, collisions are not occurring between electrons and metallic ions since this would inevitably lead to mean free paths of the same order as the lattice constant. A more accurate description of the nature of the collision process will be deferred until the next chapter.

Another property of conductors for which the simple model does not account quantitatively is the temperature dependence of resistivity. It is well known experimentally that the resistance of a metal increases almost linearly with temperature. Thus, since

and since v_F is almost independent of temperature, $\bar{l}_F$ would be expected to decrease almost linearly with increasing temperature; this is at variance with a free-electron theory, which suggests a $T^{-1/2}$ dependence of the mean free path and the conductivity. The discrepancy will be accounted for in the next chapter.

Problems

1. A particular metal contains 10^{28} free electrons per cubic metre. Find the number density of electrons in the energy interval 2.795 to 2.805 eV at $T = 300$ K.

Ans. 8×10^6 m^{-3}

2. The Fermi level in copper at 0 K is 7.0 eV. Estimate the number of free electrons per unit volume in copper at this temperature.

Ans. 8.4×10^{28} m^{-3}

3. Calculate the Fermi energy at 0 K in copper given that there is one conduction electron per atom, that the density of copper is 8920 kg m^{-3} and its atomic weight is 63.54.

Ans. 7.06 eV

4. Use the equation of motion of an electron in a metal under the influence of an electric field $\mathscr{E}$, Eq. (4.26), to show that if an alternating field $\mathscr{E}_0 \exp(j\omega t)$ is applied, the effective conductivity of a metal may be written

$$\sigma = \sigma_0/(1 + j\omega\tau_r)$$

where σ_0 is the low-frequency conductivity. [*Hint*: Write $C\exp(j\omega t)$ as a solution of the equation, where C is to be found.] What do you infer from the result?