magnitude is noticeable between a silica glass and soda-lime-silica (window glass). This striking difference is a result of the ionic conductivity of window glass. The relatively loosely-bound sodium and calcium cations in soda-lime glass diffuse and conduct much more readily, as compared to the tightly-bound immobile silicon cations in pure silica. Ionic conduction and ionic diffusivity are closely related phenomena, recall Sec. 8.6.

14.2   The Free Electron Theory

The conducting properties of a solid are not a function of the total number of electrons in the solid, as only the *outermost electrons* of the atoms can take part in conduction. In the free electron model, the outermost electrons of an atom are not bound to that atom, but are *free to move through the whole solid*. These electrons have been variously called the free electron cloud, the free electron gas or the Fermi gas.

In the free electron theory, the basic assumption is that *the potential field due to the ion cores is uniform* throughout the solid. The free electrons have the same potential energy everywhere in the solid. Due to the electrostatic attraction between a free electron and the ion cores, this potential energy will be a finite negative value. As we are interested only in energy differences, we can assume this constant potential to be zero. Then the only energy that we have to consider is the *kinetic energy*. This kinetic energy is substantially lower than that of the bound electrons in an isolated atom, as the field of motion for the free electron is considerably enlarged in the solid as compared to the field around an isolated atom. This effect is explained below.

Electrons have both particle-like and wave-like characteristics. The de Broglie wavelength of an electron λ is related to its momentum mv as

$$\lambda = \frac{h}{mv} \tag{14.1}$$

where h is Planck's constant, m is the mass of the free electron and v is its velocity. The wavelength is inversely related to the magnitude of the wave number vector **k**:

$$k = \frac{2\pi}{\lambda} \tag{14.2}$$

As the velocity of the free electrons is much smaller than that of light, we can ignore relativistic effects and use the classical relation for kinetic energy E:

$$E = \frac{1}{2} mv^2 \tag{14.3}$$

Substituting Eqs. (14.1) and (14.2) into Eq. (14.3), we obtain

$$E = \frac{h^2 k^2}{8\pi^2 m} \tag{14.4}$$

The kinetic energy E increases as the square of the wave number. This parabolic relationship between E and k is shown in Fig. 14.1. As λ is inversely related to k, the electron with the largest de Broglie wavelength will have the lowest kinetic energy. With the enlarged field of motion in the solid, the electrons can have larger wavelengths and hence lower kinetic energies.
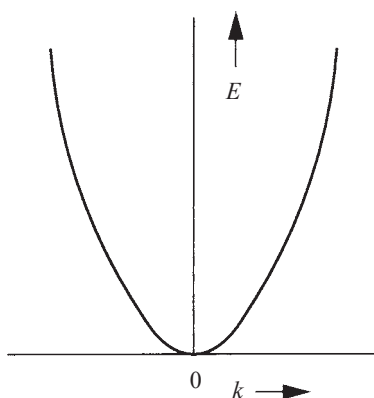

Fig. 14.1   The parabolic relationship between the kinetic energy E of a free electron and its wave number k.

Even though the variation in the kinetic energy E is shown to be continuous in Fig. 14.1, these are in fact *very closely spaced discrete energy levels*, as the quantum restrictions arising from the Pauli exclusion principle apply to the free electrons as well. Let us consider a solid, in which the electron motion is unidirectional. Let L be the length of this axis of motion. The longest wavelength that is permissible for the free electron is equal to twice this length as shown in Fig. 14.2, as the amplitude of the wave should be zero *at both ends*
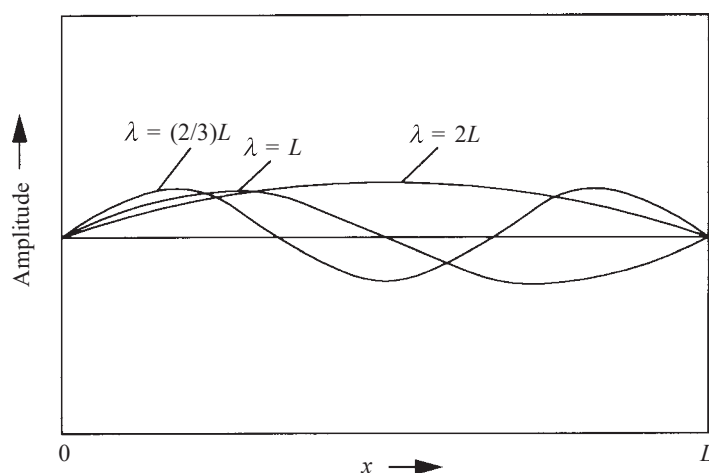

Fig. 14.2   The de Broglie wavelengths of the first few electrons moving along x.

of this length. The next smaller wavelength that is permissible is equal to L, the third one is equal to $(2/3)L$, and so on. The corresponding values of the wavenumber k are π/L, $2\pi/L$, …, as obtained from Eq. (14.2).

In a solid that is electrically neutral, a free electron having a certain speed in one direction will always be associated with another electron having the same speed but moving in the opposite direction. (If this were not so, there will be a net flow of electrons in one direction, even in the absence of an externally applied field.) In other words, the wave number k takes on both positive and negative values. Thus, for the first two states, we have k equal to $\pm\pi/L$ and $\pm2\pi/L$. In general, $k = \pm n\pi/L$, where the quantum number n takes on successively increasing integer values. Substituting $k = \pm n\pi/L$ in Eq. (14.4), we obtain

$$E = \frac{h^2 n^2}{8mL^2} \tag{14.5}$$

In a three-dimensional solid, the free electron can move in any direction in space. So, three quantum numbers n_x, n_y and n_z corresponding to the three coordinate axes are used to define each quantum state. n_x, n_y and n_z take on successively-increasing integer values. $(n_x^2 + n_y^2 + n_z^2)$ is substituted in place of n^2 used for the unidirectional motion. Equation (14.5) can be rewritten for three-dimensional motion as

$$E = h^2 \left(\frac{n_x^2 + n_y^2 + n_z^2}{8mL^2} \right) \tag{14.6}$$

Each distinct combination of n_x, n_y and n_z corresponds to a quantum state, where two electrons of opposite spins can reside. Several combinations of n_x, n_y and n_z can result in the same value of E. Quantum states with the same energy are said to be *degenerate*. The successive energy levels calculated from Eq. (14.6) are so close to one another that E can be considered to be varying continuously as illustrated for unidirectional motion in Fig. 14.1.

Example 14.1   Calculate the energy difference between the $n_x = n_y = n_z = 1$ level and the next higher energy level for free electrons in a solid cube of 10 mm × 10 mm × 10 mm.

Solution

$$L = 10 \text{ mm} = 10^{-2} \text{ m}$$

From Eq. (14.6),

$$E = \frac{(6.626 \times 10^{-34})^2 \ (1^2 + 1^2 + 1^2)}{8 \times 9.109 \times 10^{-31} \times (10^{-2})^2}$$

$$= 1.81 \times 10^{-33} \text{ J}$$

There are many equal energy quantum states above this energy level, with values of n_x, n_y and n_z as (1,1,2), (1,2,1), (2,1,1), … . For these states,

$$E = \frac{(6.626 \times 10^{-34})^2 \ (1^2 + 1^2 + 2^2)}{8 \times 9.109 \times 10^{-31} \times (10^{-2})^2}$$

$$= 3.62 \times 10^{-33} \text{ J}$$

The energy difference between the first and the next higher energy levels is extremely small, only 1.81×10^{-33} J, so that we are justified in assuming E to be continuously varying with k. Compare this energy difference with the value of thermal energy at temperature as low as 1 K, 1.38×10^{-23} J, which is ten orders of magnitude larger.

The wave forms for the free electrons starting from the lowest energy level are sketched in Fig. 14.2 for unidirectional motion. The probability of finding an electron at any point along the length is proportional to the square of the amplitude of the wave at that point. This means that, for the free electron with $\lambda = 2L$, the probability of finding it at the midpoint of the length is a maximum. This, however, is not an acceptable result, as the probability of finding the free electron must be the same anywhere within the solid. To overcome this difficulty, the waves are considered to be *travelling waves with a constant velocity, so that the time averaged probability of finding an electron is constant* throughout the solid.

In keeping with the minimum energy criterion and the Pauli exclusion principle, the free electrons occupy successive quantum states of increasing kinetic energy. The energy corresponding to the highest filled level at 0 K is called the *Fermi energy* E_F. At 0 K, the free electrons occupy all the levels up to the Fermi level, leaving all those above it empty. At temperatures above 0 K, due to *thermal excitation*, there is a finite probability of some of the electrons from below the Fermi level moving to levels above E_F. This probability is given by the *Fermi–Dirac statistics*, which takes into account the quantum restrictions due to the Pauli exclusion principle. The probability of occupation $P(E)$ of an energy level E by an electron is given by

$$P(E) = \frac{1}{1 + \exp\left[(E - E_F)/kT\right]} \tag{14.7}$$

If E_F is independent of temperature, $P(E)$ varies with E as shown in Fig. 14.3. At 0 K, $P(E)$ remains constant at unity with increasing E up to E_F, where it falls abruptly to zero. At $T_1 > 0$ K, some of the electrons just below the Fermi level are thermally excited to higher levels just above E_F. So, $P(E)$ is less than one just below the Fermi level and is greater than zero just above the Fermi level. At a still higher temperature, more electrons leave the lower energy levels and occupy higher levels. The cross-over point, where $P(E)$ is 0.5 for different temperatures in Fig. 14.3, occurs at the same value of the energy level which is E_F. This is true, provided that E_F is independent of temperature, an assumption valid for most ordinary temperatures. Under such conditions, *the Fermi level can be defined as that level which has a 50% probability of occupation by an electron at any temperature.*
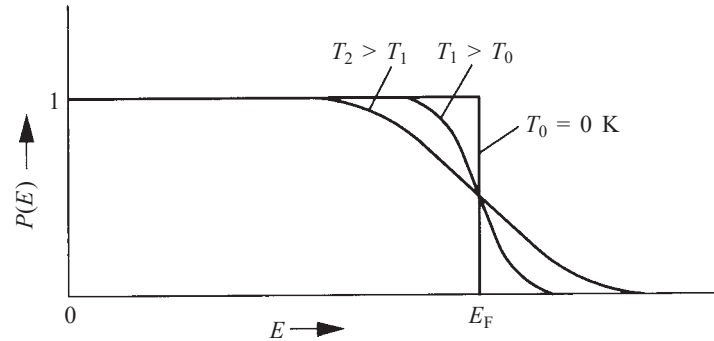
Fig. 14.3   The Fermi–Dirac distribution of free electrons at different temperatures.

14.3   Conduction by Free Electrons

We have already noted that the wave number k takes both positive and negative values. For every electron moving with a certain speed in a direction, there is another electron moving with the same speed in the opposite direction. This equal and opposite velocity distribution in a neutral solid can be biased by an *externally applied electric field* to yield a *net velocity* in one direction. With this biasing, the solid conducts electricity. Under an applied field, the *E–k* relationship of Fig. 14.1 gets modified to the distribution shown in Fig. 14.4. The negatively charged
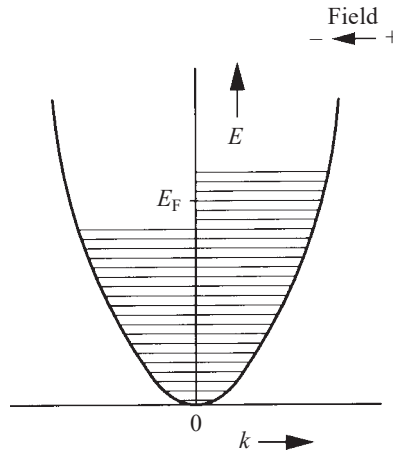

Fig. 14.4   Electrons moving towards the positive end of the applied field acquire extra velocity, while those moving in the opposite direction lose some velocity.

electrons are accelerated towards the positive end of the field. The velocity of the fastest electron moving in the direction of the positive end has a larger magnitude than that of the fastest electron moving towards the negative end of the field. Such redistribution is possible, *only when empty electron states are available immediately above the Fermi level*. This availability is a basic characteristic of conductors, as opposed to semiconductors and insulators.

The force experienced by an electron of charge e in an applied field of gradient ε can be equated to the force as defined in the classical law:

$$\varepsilon e = ma \tag{14.8}$$

where m is the mass of the electron and a is the acceleration due to the applied field. The electrons that are accelerated towards the positive end of the field do not continue to increase their velocity indefinitely. They collide with obstacles on their way. Depending on the time interval between two successive collisions, the electrons acquire an average increment of velocity called *drift velocity*, all of which they lose during a collision, as illustrated in Fig. 14.5. The drift velocity is the extra velocity that electrons acquire over and above their normal velocity in the absence of a field.
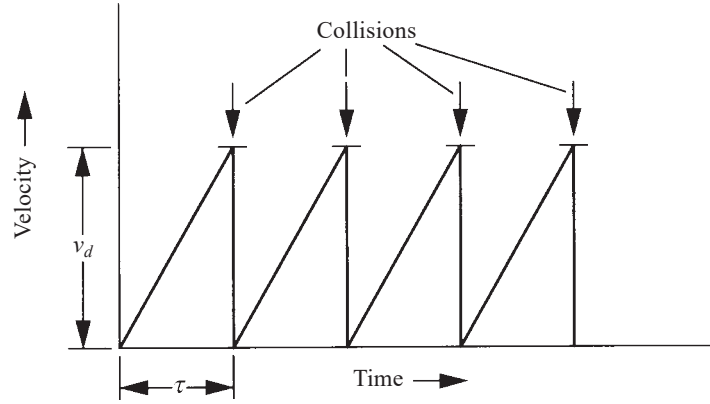

Fig. 14.5   The extra velocity acquired by an electron due to an applied field is lost on collision with an impurity, imperfection or phonon.

If the average collision time is τ and v_d is the drift velocity acquired by the electrons, Eq. (14.8) can be rewritten as

$$m(v_d/\tau) = \varepsilon e \tag{14.9}$$

or

$$v_d = \frac{\varepsilon e \tau}{m} \tag{14.10}$$

The flux J_e due to the flow of electrons is called the *current density*:

$$J_e = nev_d = \frac{ne^2 \tau \varepsilon}{m} \tag{14.11}$$

where n is the number of free electrons of charge e. This is in the form of Ohm's law. As conductivity σ is by definition the flux per unit potential gradient, we have

$$\sigma = \frac{ne^2 \tau}{m} \tag{14.12}$$

The electrical resistivity ρ is the reciprocal of conductivity.