

Free Electron Model

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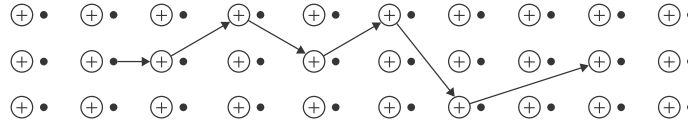
CHAPTER OUTLINE

3.1 The Classical (Drude) Model of a Metal	71
3.2 Sommerfeld Model	73
3.2.1 Introduction	73
3.2.2 Fermi Distribution Function	74
3.2.3 Free Electron Fermi Gas	77
3.2.4 Ground-State Energy of the Electron Gas	79
3.2.5 Density of Electron States	81
3.3 Fermi Energy and the Chemical Potential	82
3.4 Specific Heat of the Electron Gas	84
3.5 DC Electrical Conductivity	86
3.6 The Hall Effect	87
3.7 Failures of the Free Electron Model	89
Problems	90
References	93

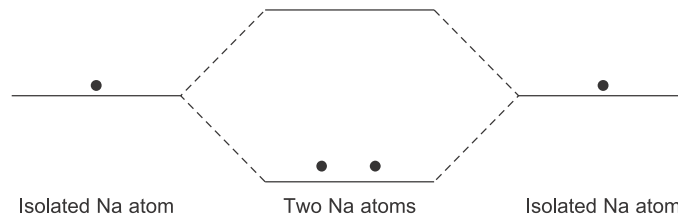
3.1 THE CLASSICAL (DRUDE) MODEL OF A METAL

Around 1900, Drude developed the theory of electrical and thermal conductivity of metals by considering a metal as a classical gas of electrons, the properties of which were governed by Maxwell–Boltzmann statistics. According to his model, the electrons were wandering around in a metal with a background of immobile but heavy positive charges. A sketch of his model is shown in [Figure 3.1](#).

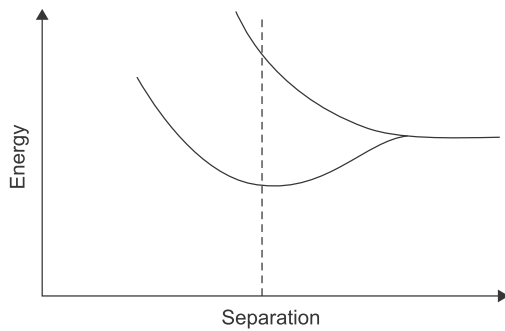
Drude had no idea as to the nature or origin of these positive charges, although he recognized that in order to be electrically neutral, a metal would have to have an equal number of positive and negative charges. Later, these heavy positive immobile charges were identified as the ions (constituted of the nucleus and the surrounding core electrons) of the neutrally charged atom stripped of its valence electron(s). The conduction electrons in a metal were the valence electrons stripped from their parent atoms because of the strong attractive interaction between the valence electron(s) of an atom and the positively charged ions surrounding it. In what follows, we will treat these positive charges as the ions described previously, although this concept was introduced by Bohr in his model of the atom long after Drude formulated a theory of metals. This concept of a sea of valence electrons moving around in a background of static positively charged ions and holding them together like a glue was in a sense an extension of the model of a hydrogen molecule in which the

**FIGURE 3.1**

Drude model of scattering of electrons in a metal.

**FIGURE 3.2a**

A system of two sodium atoms.

**FIGURE 3.2b**

The energy levels of two 3s electrons of sodium atoms as function of separation.

two valence electrons were stripped from their parent atoms and moving around the positively charged protons, thereby forming a strong bond.

An example of formation of bands in a sodium atom is shown [Figure 3.2](#). [Figure 3.2a](#) shows a system of two sodium atoms. The two 3s electrons occupy a lower energy level than the isolated atoms.

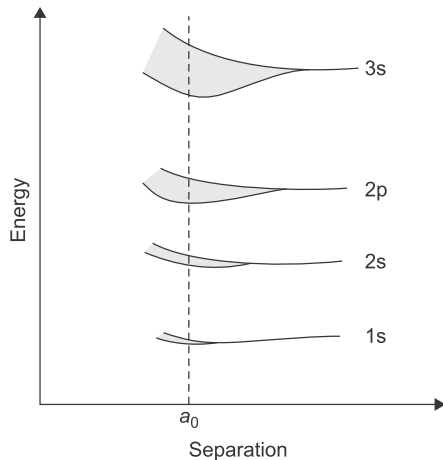
[Figure 3.2b](#) shows the energy levels of the outer 3s electrons in a pair of sodium atoms as a function of the separation between the two atoms. This figure shows how the energy level widens with smaller distance.

When there are N sodium atoms, where N is a very large number, these energy levels form bands. In [Figure 3.2c](#), we show the 1s, 2s, 2p,

and 3s energy bands of sodium. However, the bands become wider for electrons that are less tightly bound to the parent nucleus. We note the significant difference between the 1s and the 3s bands.

Drude introduced the concept of electron density $n = N/V$, where V is the volume of the metal and N is the number of atoms per mole (the Avogadro's number). He also introduced the electron density r_s , which is defined as the radius of a sphere of which the volume is equal to the available volume for each conduction electron. According to his model,

$$\frac{1}{n} = \frac{4\pi r_s^3}{3} = \frac{V}{N}, \quad (3.1)$$

**FIGURE 3.2c**

The formation of 1s, 2s, 2p, and 3s energy bands in sodium. Note that 1s is in the lowest energy state, whereas 3s is in the highest energy state.

from which it follows that

$$r_s = \left(\frac{3}{4\pi n} \right)^{1/3}. \quad (3.2)$$

Drude applied the kinetic theory of gas to these conduction electrons even though their electron densities are approximately a thousand times greater than those of a classical gas at normal pressure and temperature. He introduced several interesting approximations (in his kinetic theory model) to develop theories of both electrical and thermal conductivity of metals. First, the electron gas was assumed to be free and independent in the sense that there was no electron–electron or electron–ion interactions. An electron moved in a straight line (as per Newton’s law) in the absence of an external electric field. Second, when an external field is applied, the electron continues to move in a straight line between collisions with the ions (the collisions with other electrons were neglected in his theory). The velocity of an electron

would change immediately after a collision, which was assumed to be an instantaneous event. Third, the time between two collisions was the same value τ (often known as the relaxation time) for each electron. Fourth, immediately after each collision, an electron’s velocity was not related to the velocity with which it was traveling before the collision. The new speed of the electron depended on the temperature at the time of collision, and the direction of the new velocity was randomly directed. In a sense, the electron achieved thermal equilibrium with its surroundings.

The two major achievements of Drude’s model were the derivation of electrical and thermal conductivity (see problems) in a very simplistic way. However, it had several drawbacks. Some of these were solved by Sommerfeld, who recognized the fact the free electrons in a metal were not classical but quantum gas, for which the application of Fermi–Dirac statistics (instead of Maxwell–Boltzmann statistics) was appropriate.

3.2 SOMMERFELD MODEL

3.2.1 Introduction

The major failure of Drude’s theory was the prediction that the specific heat of a metal was $C_v = 3/2 N k_B$, where N is the number of electrons in a metal and k_B is the Boltzmann constant. In practice, the specific heat of a metal was more than 100 times smaller than this value at room temperature. This anomaly was explained by Sommerfeld only after the introduction of quantum mechanics. The Pauli exclusion principle requires that no two electrons can have identical quantum numbers, which implies that a quantum state can be occupied by at most one electron. Sommerfeld recognized the significance of the Pauli exclusion principle, and as a consequence, the Fermi–Dirac statistics (instead

of the classical Maxwell–Boltzmann statistics) were applicable to a system of identical electron gas (or other fermions) in thermal equilibrium. Sommerfeld essentially adapted Drude’s model of the metal as a free electron gas moving in a background of static positively charged ions but modified it by using the Fermi–Dirac distribution function for the electron velocity. In the process, he was able to explain the (apparently) anomalous low specific heat of the electron gas as well as other thermal properties.

3.2.2 Fermi Distribution Function

(a) Grand Canonical Ensemble

The Fermi distribution function is easily derived from the concept of a Grand Canonical Ensemble, which is an ensemble of \mathbb{N} identical systems (labeled as $1, 2, \dots, \mathbb{N}$) mutually sharing a total number of particles $\mathbb{N}\bar{N}$ and a total amount of energy $\mathbb{N}\bar{E}$. If $n_{r,s}$ denotes the number of systems that have, at any time t , the number \mathbb{N}_r of particles and the amount of energy E_s ($r, s = 0, 1, 2, \dots$),

$$\sum_{r,s} n_{r,s} = \mathbb{N}, \quad (3.3)$$

$$\sum_{r,s} n_{r,s} N_r = \mathbb{N}\bar{N}, \quad (3.4)$$

$$\sum_{r,s} n_{r,s} E_s = \mathbb{N}\bar{E}. \quad (3.5)$$

We consider this ensemble of \mathbb{N} identical systems that are characterized by a Hamiltonian operator \hat{H} . At any time t , the physical states of the various systems in the ensemble are characterized by the wave functions $\psi(\mathbf{r}, t)$. Let $\psi^k(\mathbf{r}, t)$ denote the normalized wave function characterizing the physical state in which the k th state of the system of the ensemble happens to be at the time. We can write

$$\hat{H}\psi^k(\mathbf{r}, t) = i\hbar \dot{\psi}^k(\mathbf{r}, t). \quad (3.6)$$

We introduce a complete set of orthonormal functions $\phi_n(\mathbf{r}) \equiv \phi_n(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ and express

$$\psi^k(\mathbf{r}, t) = \sum_n a_n^k(t) \phi_n(\mathbf{r}). \quad (3.7)$$

We can write

$$a_n^k(t) = \int \phi_n^*(\mathbf{r}) \psi^k(\mathbf{r}, t) d\tau, \quad (3.8)$$

where $d\tau$ is the volume element of the coordinate space of the system. Thus, $a_n^k(t)$ are the probability amplitudes for the various systems of the ensemble to be in the states $\phi_n(\mathbf{r})$, and $|a_n^k(t)|^2$ represents the probability that a measurement of time t finds the k th system of the ensemble to be in the particular state $\phi_n(\mathbf{r})$. Thus, we obtain

$$\sum_n |a_n^k(t)|^2 = 1 \quad \text{for all } k. \quad (3.9)$$

Eq. (3.9) can also be derived from Eq. (3.7) in a straightforward manner. From Eq. (3.7), we obtain

$$\begin{aligned} \int |\psi^k(\mathbf{r}, t)|^2 d\tau &= \sum_{n,m} a_n^{k*}(t) a_m^k(t) \int \phi_n^*(\mathbf{r}) \phi_m(\mathbf{r}) d\tau \\ &= \sum_{n,m} a_n^{k*}(t) a_m^k(t) \delta_{n,m} = \sum_n |a_n^k(t)|^2 = 1. \end{aligned} \quad (3.10)$$

(b) Density Operator

The density operator $\hat{\rho}(t)$ is defined by the matrix elements

$$\rho_{mn}(t) = \frac{1}{\mathbb{N}} \sum_{k=1}^{\mathbb{N}} \{a_m^k(t) a_n^{k*}(t)\}. \quad (3.11)$$

The diagonal element $\rho_{nn}(t)$, which is the ensemble average of the probability $|a_n^k(t)|^2$, represents the probability of a system, chosen at random from the ensemble at time t , and is found to be in the state ϕ_n . From Eqs. (3.10) and (3.11), we obtain

$$\sum_n \rho_{nn} = 1. \quad (3.12)$$

One can show that if the system is in a state of equilibrium,⁸

$$i\hbar \dot{\hat{\rho}} = [\hat{H}, \hat{\rho}] = 0, \quad (3.13)$$

$$\langle \hat{G} \rangle = \text{tr}(\hat{\rho} \hat{G}), \quad (3.14)$$

and

$$\text{tr}(\hat{\rho}) = 1, \quad (3.15)$$

where $\langle \hat{G} \rangle$ is the expectation value of a physical quantity G .

In the Grand Canonical Ensemble, the density operator $\hat{\rho}$ operates on a Hilbert space in an indefinite number of particles. Therefore, the density operator commutes not only with the Hamiltonian operator \hat{H} , but also with a number operator \hat{n} of which the eigenvalues are 0, 1, 2. We can write⁸

$$\hat{\rho} = \frac{1}{Z(\mu, V, T)} e^{-\beta(\hat{H} - \mu \hat{n})}, \quad (3.16)$$

where the Grand partition function $Z(\mu, V, T)$ is defined as

$$Z(\mu, V, T) = \sum_{r,s} e^{-\beta(E_r - \mu N_s)} = \text{tr} \left\{ e^{-\beta(\hat{H} - \mu \hat{n})} \right\}. \quad (3.17)$$

The chemical potential μ is defined as

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V,N}, \quad (3.18)$$

where F is the Helmholtz free energy defined by the relation

$$F = E - TS. \quad (3.19)$$

Here, E is the energy, S is the entropy, T is the absolute temperature, and V is the volume.

For a free electron gas,

$$\hat{H} = \sum_{\mathbf{k}} \varepsilon(\mathbf{k}) c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} \quad (3.20)$$

and

$$N_s = 0 \text{ or } 1. \quad (3.21)$$

Therefore,

$$\begin{aligned} E_r &= N_s \varepsilon(\mathbf{k}) \\ &= 0 \text{ or } \varepsilon(\mathbf{k}). \end{aligned} \quad (3.22)$$

From Eqs. (3.17) and (3.20) through (3.22), we obtain (omitting spin $[\sigma]$),

$$Z_k = 1 + e^{-\beta(\varepsilon(\mathbf{k})-\mu)} \quad (3.23)$$

and

$$\hat{\rho}_k = \frac{1}{Z_k} e^{-\beta(\varepsilon(\mathbf{k})-\mu)} c_{\mathbf{k}}^\dagger c_{\mathbf{k}}. \quad (3.24)$$

The average number in state \mathbf{k} is

$$\begin{aligned} \bar{n}_{\mathbf{k}} &= \text{tr}\{n_{\mathbf{k}} \hat{\rho}_k\} = \sum_{n_{\mathbf{k}}} \langle n_{\mathbf{k}} | n_{\mathbf{k}} \hat{\rho}_k | n_{\mathbf{k}} \rangle = \langle 1 | \hat{\rho}_k | 1 \rangle \\ &= \frac{e^{-\beta(\varepsilon(\mathbf{k})-\mu)}}{1 + e^{-\beta(\varepsilon(\mathbf{k})-\mu)}} = \frac{1}{e^{\beta(\varepsilon(\mathbf{k})-\mu)} + 1} = f(\varepsilon(\mathbf{k}), T). \end{aligned} \quad (3.25)$$

Here, $f(\varepsilon(\mathbf{k}), T)$ is the Fermi distribution, which is a function of energy and temperature. The Fermi distribution function $f(\varepsilon(\mathbf{k}), T)$ gives the probability that a state at energy ε_i is occupied in an ideal electron gas in thermal equilibrium. We also note that the Fermi distribution is an eigenvalue of the statistical operator $\hat{\rho}_k$.

In practice, because the electrons in an electron gas are indistinguishable and are constantly moving around, the probability that a state is occupied by an electron is the average number of electrons in the state and

$$\sum_i f(\varepsilon_i) = N, \quad (3.26)$$

where N is the total number of electrons in the free electron gas (note that we do not include the core electrons of the atoms that are bound to the parent nuclei and are not free to move around). In Eq. (3.26), ε_i are the energy levels. In semiconductor physics, μ is also called the Fermi level.

The Fermi energy ε_F is defined as the energy of the topmost filled level of the electron states at $T=0$. All the electron states having energy greater than the Fermi energy are empty (there are no electrons in these states) at $T=0$. From Eq. (3.26), we note that the alternate definition of the Fermi energy at $T=0$ is

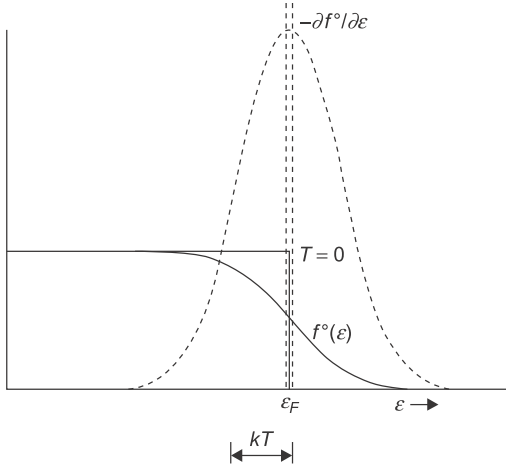
$$\begin{aligned} f(\varepsilon_i) &= 1, \quad \varepsilon_i \leq \varepsilon_F, \\ &= 0, \quad \varepsilon_i > \varepsilon_F. \end{aligned} \quad (3.27)$$

We also note from Eq. (3.23) that

$$\begin{aligned} \lim_{T \rightarrow 0} f(\varepsilon_i) &= 1, \quad \varepsilon_i \leq \mu, \\ &= 0, \quad \varepsilon_i > \mu. \end{aligned} \quad (3.28)$$

Comparing Eqs. (3.27) and (3.28), we note that at $T=0$, $\varepsilon_F = \mu$. Thus, in the limit $T \rightarrow 0$, when $\varepsilon_i = \varepsilon_F = \mu$, the Fermi–Dirac distribution function changes abruptly from 1 to 0. At higher temperatures ($T > 0$), $f(\varepsilon_i) = 1/2$ when $\varepsilon_i = \mu$. The distribution of the Fermi distribution function and its derivative at $T=0$ and at finite temperature is shown in Figure 3.3.

From Figure 3.3, we note that the Fermi distribution function at a large temperature T is significantly different from that at zero temperature. When the metal is heated from $T=0$, electrons are transferred from the region $\varepsilon/\mu < 1$ to the region $\varepsilon/\mu > 1$. The rest of the electrons deep inside the

**FIGURE 3.3**

Fermi distribution function and its derivative at $T=0$ and at a finite temperature.

move inside this cube. There are no other interactions, either with other electrons or with the positively charged background (the lattice). Because there is no potential energy term, the Schrodinger equation for an electron in state \mathbf{k} can be written as

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_{\mathbf{k}}(\mathbf{r}) = \epsilon(\mathbf{k}) \psi_{\mathbf{k}}(\mathbf{r}). \quad (3.29)$$

Here, $\psi_{\mathbf{k}}(\mathbf{r})$ is the wave function and $\epsilon(\mathbf{k})$ is the energy of the electron in the state \mathbf{k} . The normalized solution of Eq. (3.29) is easily obtained, by requiring $\psi_{\mathbf{k}}(\mathbf{r})$ to vanish at the surface of the cube (the particle in a box problem in quantum mechanics), as

$$\psi_{\mathbf{k}}(\mathbf{r}) = (8/V)^{1/2} \sin(n_1 \pi x/L) \sin(n_2 \pi y/L) \sin(n_3 \pi z/L), \quad (3.30)$$

where L is the side of the cubic metal of volume $V(V=L^3)$ and n_1, n_2 , and n_3 are positive integers. For simplicity, we have considered the metal as a cube, although we could have chosen a parallelepiped, which would yield the same results but the derivation would have been more complicated. However, we note that the solutions obtained in Eq. (3.30) are standing-wave solutions and the probability density $|\psi_{\mathbf{k}}(\mathbf{r})|^2$ of the electron in \mathbf{k} state varies with its position in real space, thereby yielding an unrealistic picture for free electrons. To obtain more realistic solutions for free electron gas, we introduced the Born–von Karman (or periodic) boundary conditions. These conditions are

$$\begin{aligned} \psi(x+L, y, z) &= \psi(x, y, z), \\ \psi(x, y+L, z) &= \psi(x, y, z), \\ \psi(x, y, z+L) &= \psi(x, y, z). \end{aligned} \quad (3.31)$$

These periodic boundary conditions were imposed by imagining that each face of the cube is joined to the face opposite it. When an electron meets the surface of the metal, instead of being reflected

Fermi level are not affected when the electron gas is heated. However, as the temperature increases, there is a significant change in the Fermi distribution function. We will discuss this in Section 3.3. On the other hand, each electron in a classical electron gas would gain energy when the system is heated. This immediately explains the anomalous results for the specific heat of the electron gas. As we will see, this property of the fermions is very significant in the derivation of other physical quantities of metals.

3.2.3 Free Electron Fermi Gas

By definition, a free electron gas consists of N independent electrons confined in a volume V . There are positively charged static ions inside the metal to keep it electrically neutral. For simplicity, we will consider this volume to be a cube of side L . An electron is completely free to

by the surface, it emerges at an equivalent point on the opposite surface. This is obviously an improbable situation in a three-dimensional solid, but the periodic boundary conditions yield free electron wave functions for the free electron gas. It may be noted that these approximations hold good as long as one is not considering the physical properties of the electrons on or close to the surface, in which case they have to be modified. It may be further noted that it is not necessary to consider the metal as a cube of side L ; the results would still hold good for a parallelepiped.

The general solutions of Eq. (3.29) are the well-known plane waves

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (3.32)$$

In general, \mathbf{k} is a continuous variable in the reciprocal space. However, if we invoke the periodic boundary conditions as stated in Eq. (3.31), we obtain only discrete values of \mathbf{k} , i.e.,

$$e^{ik_x L} = e^{ik_y L} = e^{ik_z L} = 1. \quad (3.33)$$

Eq. (3.33) implies that k_x , k_y , and k_z are discrete variables,

$$k_x = \frac{2\pi n_1}{L}, \quad k_y = \frac{2\pi n_2}{L}, \quad k_z = \frac{2\pi n_3}{L}. \quad (3.34)$$

Here, n_1 , n_2 , and n_3 are integers (zero, positive, or negative). Thus, the components of the wave vector \mathbf{k} are discrete in the k -space and, along with the spin components m_s , are the quantum numbers of the problem.

We also obtain from Eqs. (3.29) and (3.32),

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}. \quad (3.35)$$

The plane wave is also an eigenfunction of the linear momentum \mathbf{p} ,

$$\mathbf{p}\psi_{\mathbf{k}}(\mathbf{r}) = -i\hbar\nabla \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}} = \hbar\mathbf{k}\psi_{\mathbf{k}}(\mathbf{r}). \quad (3.36)$$

Thus, the electron velocity \mathbf{v} in the state \mathbf{k} is given by

$$\mathbf{v} = \hbar\mathbf{k}/m. \quad (3.37)$$

We can now use Eq. (3.34) to build the k -space. The k -space is a three-dimensional space with an extremely large number (N) of allowed discrete k points. Figure 3.4 illustrates the points in a two-dimensional k -space that are separated by $\frac{2\pi}{L}$ in both k_x and k_y directions (as per Eq. 3.34).

As seen in Figure 3.4, the discrete k values are separated by $2\pi/L$ in each dimension. In a three-dimensional k -space, the volume per each \mathbf{k} -point is $(2\pi/L)^3 = 8\pi^3/V$, where the volume of the metal $V = L^3$. Therefore, a k -space of volume Ω will contain $\Omega V/8\pi^3$ allowed values of \mathbf{k} .

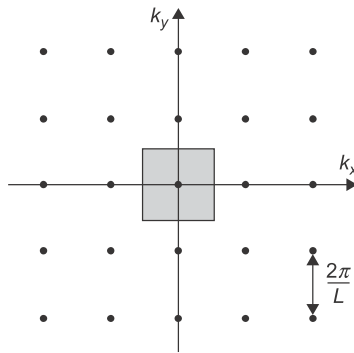
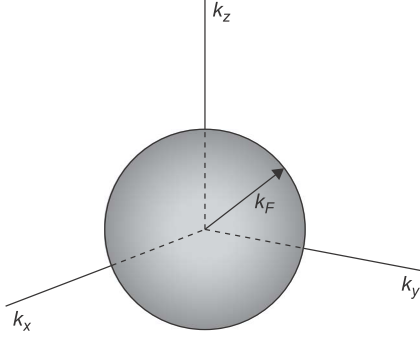


FIGURE 3.4

Points in a two-dimensional k -space.

**FIGURE 3.5**

Schematic diagram of the Fermi sphere.

Thus, the density of states, ρ , in the k -space (number of allowed k -values per unit volume of k -space) is

$$\rho = V/8\pi^3. \quad (3.38)$$

We note that each \mathbf{k} state can contain exactly two electrons (spin up or spin down) at zero temperature as per the Fermi–Dirac distribution function in Eq. (3.25). Thus, when we build the filled k -space at zero temperature in three dimensions, we are essentially filling up these discrete \mathbf{k} states starting with the lowest energy, which is zero. Because the \mathbf{k} states are densely packed and the total number of electrons is N , which is a huge number ($\sim 10^{23}$), the constant

energy levels of the electrons can be considered as the surface of a sphere (as per Eq. 3.33). Thus, all the N electrons will fill a sphere of volume $\Omega = 4\pi/3 k_F^3$, which is known as the Fermi sphere. k_F , the radius of the sphere, is known as the Fermi wave vector. The surface of the Fermi sphere that separates the filled \mathbf{k} states from the empty \mathbf{k} states (at zero temperature) is known as the Fermi surface. The energy of an electron on the Fermi surface is called the Fermi energy $\epsilon_F = \frac{\hbar^2 k_F^2}{2m}$, and the momentum $\mathbf{p}_F = \hbar \mathbf{k}_F$ is known as the Fermi momentum. A schematic diagram of the Fermi sphere is shown in Figure 3.5.

The volume of the Fermi sphere is $\Omega = 4\pi k_F^3/3$ and, as shown earlier, a k -space of volume Ω will contain $\Omega V/8\pi^3$ allowed values of \mathbf{k} . Hence, the allowed values of \mathbf{k} in the Fermi sphere are

$$\frac{\Omega V}{8\pi^3} = \left(\frac{V}{8\pi^3} \right) \left(\frac{4\pi k_F^3}{3} \right) = \frac{k_F^3 V}{6\pi^2}. \quad (3.39)$$

Because there are two electrons per each \mathbf{k} state and the total number of electrons is N , we obtain from Eq. (3.39)

$$\frac{N}{2} = \frac{k_F^3 V}{6\pi^2}. \quad (3.40)$$

The electron density $n \equiv N/V$ is easily obtained from Eq. (3.40),

$$n = \frac{k_F^3}{3\pi^2}. \quad (3.41)$$

3.2.4 Ground-State Energy of the Electron Gas

To make a summation over allowed values of \mathbf{k} , we use the following procedure. If $F(\mathbf{k})$ is a function of \mathbf{k} states, we can write, using Eq. (3.38),

$$\sum_{\mathbf{k}} F(\mathbf{k}) = \frac{V}{8\pi^3} \sum_{\mathbf{k}} F(\mathbf{k}) \Delta \mathbf{k}. \quad (3.42)$$

In the limit $V \rightarrow \infty$, $\Delta \mathbf{k} \rightarrow 0$ and the summation over \mathbf{k} on the right side, $\sum_{\mathbf{k}} F(\mathbf{k}) \Delta \mathbf{k}$ approaches the integral $\int F(\mathbf{k}) d\mathbf{k}$. Thus, we can write Eq. (3.42) in the alternate form

$$\lim_{V \rightarrow \infty} \sum_{\mathbf{k}} F(\mathbf{k}) = \frac{V}{8\pi^3} \int F(\mathbf{k}) d\mathbf{k}. \quad (3.43)$$

In general, the approximation $V \rightarrow \infty$ is fairly good because the volume of a metal is infinitely large compared to the volume of a primitive cell.

The ground-state energy of N free electrons in a metal is calculated by adding the energies of the \mathbf{k} states inside the Fermi sphere and multiplying by 2 (because each \mathbf{k} state has two electrons of opposite spin),

$$E = 2 \sum_{\mathbf{k}} \varepsilon(\mathbf{k}). \quad (3.44)$$

From Eqs. (3.35) and (3.44),

$$E = 2 \sum_{k \leq k_F} \frac{\hbar^2 k^2}{2m}. \quad (3.45)$$

From Eqs. (3.43) and (3.45),

$$E = \frac{V}{4\pi^3} \int_{k \leq k_F} d\mathbf{k} \frac{\hbar^2 k^2}{2m}. \quad (3.46)$$

Because $d\mathbf{k} = 4\pi k^2 dk$, Eq. (3.46) can be easily integrated, and we obtain

$$E = \frac{V \hbar^2 k_F^5}{10\pi^2 m}. \quad (3.47)$$

Here, E is the total energy of the electron gas. To find the energy per electron, E/N , we obtain from Eqs. (3.40) and (3.47),

$$\frac{E}{N} = \frac{3\hbar^2 k_F^2}{10m}, \quad (3.48)$$

which can be written in the alternate form

$$\frac{E}{N} = \frac{3}{5} \varepsilon_F. \quad (3.49)$$

The average energy of an electron at zero temperature, derived in Eq. (3.49), differs significantly from the energy of a classical ideal gas, which is zero at $T=0$. This significant difference is due to the fact that the electrons obey the Pauli exclusion principle, and therefore, the Fermi–Dirac distribution function has to be applied to the electron gas instead of the Maxwell–Boltzmann distribution function, which is applicable for a classical ideal gas.

We now define the Fermi temperature using the relation

$$\varepsilon_F = k_B T_F. \quad (3.50)$$

From Eqs. (3.49) and (3.50), we obtain

$$T_F = \frac{5E}{3Nk_B}. \quad (3.51)$$

The Fermi temperature T_F is of the order of 10^4 K for simple metals (see Problem 3.7), an incredibly large value for the temperature of the electrons on the Fermi surface. We note that for a classical ideal gas, the temperature $T = 0$ irrespective of the location of the gas molecule.

The wavelength of an electron at the Fermi surface is given by

$$\lambda_F = \frac{2\pi}{k_F}. \quad (3.52)$$

3.2.5 Density of Electron States

Because the \mathbf{k} states are discrete variables, normally one makes a summation over all the \mathbf{k} states. In Eq. (3.43), we approximated the summation of a function $F(\mathbf{k})$ over all the \mathbf{k} states as an integration over the \mathbf{k} states. An alternate way to consider the summation over all the \mathbf{k} states is to consider the same summation as integration over the energy levels. Such integrations over the energy levels are done by using the concept of the density of electron states.

As an example, we consider the summation $\sum_{\mathbf{k}} F(\epsilon(\mathbf{k}))$, where $F(\epsilon(\mathbf{k}))$ is a function of the energy of the electrons in the filled \mathbf{k} states. We can write Eq. (3.43) in the alternate form

$$\frac{1}{V} \sum_{\mathbf{k}} F(\epsilon(\mathbf{k})) = \frac{1}{4\pi^3} \int d\mathbf{k} F(\epsilon(\mathbf{k})). \quad (3.53)$$

We note that because each \mathbf{k} state has two electrons with the same energy, we have multiplied the right side of Eq. (3.43) by a factor of 2. Because $\epsilon(\mathbf{k}) = \hbar^2 k^2 / 2m$, we can write

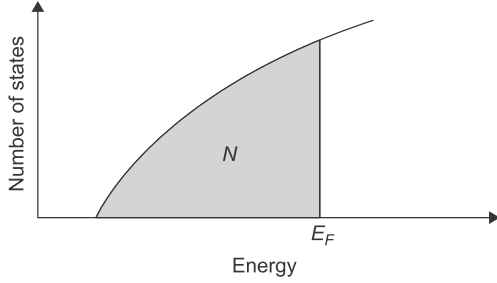
$$d\mathbf{k} = 4\pi k^2 dk. \quad (3.54)$$

From Eqs. (3.53) and (3.54), we obtain

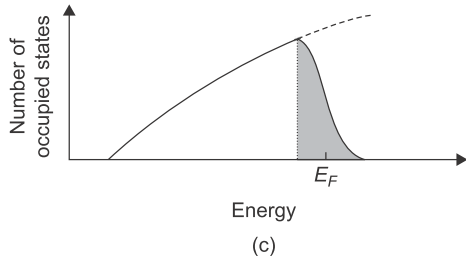
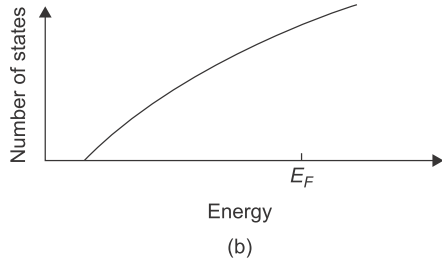
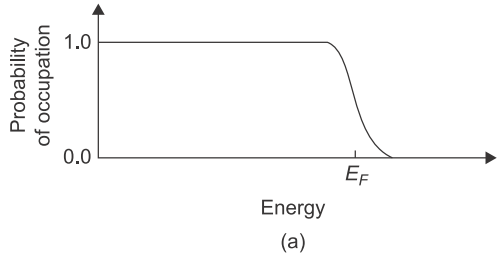
$$\begin{aligned} \frac{1}{4\pi^3} \int d\mathbf{k} F(\epsilon(\mathbf{k})) &= \int_0^\infty \frac{k^2 dk}{\pi^2} F(\epsilon(\mathbf{k})) \\ &= \int_{-\infty}^\infty d\epsilon g(\epsilon) F(\epsilon). \end{aligned} \quad (3.55)$$

Here,

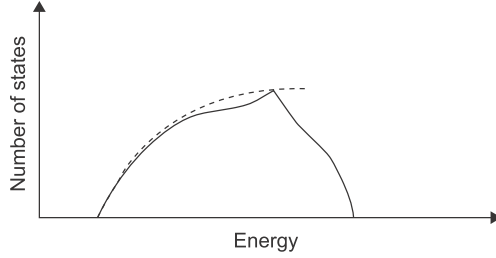
$$\begin{aligned} g(\epsilon) &= \frac{m}{\pi^2 \hbar^2} \sqrt{\frac{2m\epsilon}{\hbar^2}}, \quad \epsilon > 0 \\ &= 0, \quad \epsilon \leq 0. \end{aligned} \quad (3.56)$$

**FIGURE 3.6**

Density of states versus energy.

**FIGURE 3.8**

The density of occupied states (c) obtained from the Fermi–Dirac distribution (a) and the density of states (b).

**FIGURE 3.7**

Comparison of density of states for a typical metal (solid line) with the predicted value (dashed curve).

Thus, the density of electron states $g(\epsilon)d\epsilon$ is defined as the number of one-electron levels per unit volume of the metal in the energy range ϵ and $\epsilon + d\epsilon$. From Eqs. (3.41) and (3.56), we can rewrite $g(\epsilon)$ in the alternate form

$$g(\epsilon) = \frac{3n}{2} \left(\frac{\epsilon}{\epsilon_F^3} \right)^{1/2}, \quad \epsilon > 0 \quad (3.57)$$

$$= 0, \quad \epsilon \leq 0.$$

The number of single electron states N is equal to the area under the density of states curve $g(\epsilon)$ up to the Fermi energy. The plot of $g(\epsilon)$ versus ϵ is shown in Figure 3.6.

However, the density of states for a typical metal, which is plotted in Figure 3.7, is different from the curve shown in Figure 3.6.

3.3 FERMI ENERGY AND THE CHEMICAL POTENTIAL

We will derive an expression between the chemical potential μ and the Fermi energy ϵ_F at a reasonably low temperature (we note that $\mu = \epsilon_F$ at $T = 0$).

The electron density $n = N/V$ can be written in the form

$$n = \frac{1}{4\pi^3} \int d\mathbf{k} f(\epsilon(\mathbf{k})). \quad (3.58)$$

From Eqs. (3.55) and (3.58), we obtain

$$n = \int_{-\infty}^{\infty} g(\varepsilon) f(\varepsilon) d\varepsilon. \quad (3.59)$$

Using the Sommerfeld expansion (Problem 3.8) and retaining terms of the order T^2 , we obtain

$$n = \int_{-\infty}^{\infty} g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F). \quad (3.60)$$

From Eqs. (3.57) and (3.60), we obtain

$$n = \int_0^{\mu} g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F). \quad (3.61)$$

Eq. (3.61) can be written in the alternate form

$$n = \int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon + \int_{\varepsilon_F}^{\mu} g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F). \quad (3.62)$$

We note that at zero temperature, the electron density n can also be expressed as

$$n = \int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon. \quad (3.63)$$

In addition, at low temperatures, $g(\varepsilon) \approx g(\varepsilon_F)$ in the small energy range of ε_F to μ and the integration of $g(\varepsilon)$ in this range can be approximated as

$$\int_{\varepsilon_F}^{\mu} g(\varepsilon) d\varepsilon \approx (\mu - \varepsilon_F) g(\varepsilon_F). \quad (3.64)$$

From Eqs. (3.62) through (3.64), we obtain

$$(\mu - \varepsilon_F) g(\varepsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F) = 0. \quad (3.65)$$

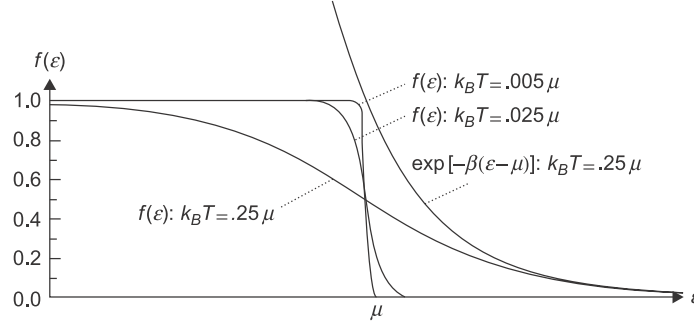
From Eq. (3.65), the chemical potential μ can be expressed as

$$\mu = \varepsilon_F - \frac{\pi^2}{6} (k_B T)^2 \frac{g'(\varepsilon_F)}{g(\varepsilon_F)}. \quad (3.66)$$

From Eqs. (3.64) and (3.66), we obtain

$$\mu = \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right)^2 \right]. \quad (3.67)$$

Eq. (3.67) expresses the chemical potential μ in terms of the Fermi energy ε_F (up to the order of T^2).

**FIGURE 3.9**

Variation of the Fermi–Dirac distribution function with temperature.

The variation of the Fermi–Dirac distribution function for various values of $k_B T$ is shown in Figure 3.9. The Fermi function differs slightly from a step function around the chemical potential μ . It differs significantly from 0 or 1 in the region in which the width is $k_B T$. For $\varepsilon \gg \mu$, it is hard to distinguish the Fermi function from the classical Boltzmann distribution function $e^{-\beta\varepsilon}$.

3.4 SPECIFIC HEAT OF THE ELECTRON GAS

At a finite temperature T , the \mathbf{k} states will be filled by $2 f(\varepsilon(\mathbf{k}))$ electrons, where $f(\varepsilon(\mathbf{k}))$ is the Fermi–Dirac distribution function, which determines the probability that a \mathbf{k} state is occupied by an electron. The factor 2 is multiplied because each \mathbf{k} state can have two electrons of opposite spin as prescribed by the Pauli exclusion principle. Thus, the total internal energy of the electrons at temperature T is given by

$$E_{el}(T) = 2 \sum_{\mathbf{k}} \varepsilon(\mathbf{k}) f(\varepsilon(\mathbf{k})). \quad (3.68)$$

The electronic specific heat of the metal is given by

$$C_{el} = \frac{1}{V} \left(\frac{\partial E_{el}}{\partial T} \right)_N. \quad (3.69)$$

By converting the summation over \mathbf{k} states to integration and following the procedure outlined in Eq. (3.53), we can rewrite Eq. (3.68) as

$$\frac{E_{el}}{V} = \frac{1}{4\pi^3} \int d\mathbf{k} \varepsilon(\mathbf{k}) f(\mathbf{k}). \quad (3.70)$$

From Eqs. (3.55) and (3.70), we obtain

$$\frac{E_{el}}{V} = \int_{-\infty}^{\infty} \varepsilon g(\varepsilon) d\varepsilon. \quad (3.71)$$

By using the Sommerfeld expansion (Problem 3.8), we obtain from Eq. (3.71)

$$\frac{E_{el}}{V} = \int_{-\infty}^{\mu} \varepsilon g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 \frac{d}{d\varepsilon} (\varepsilon g(\varepsilon)) \big|_{\varepsilon=\mu} + \text{higher order terms in } T. \quad (3.72)$$

We note from Eq. (3.57) that the density of one-electron levels $g(\varepsilon) = 0$ for $\varepsilon \leq 0$. Using this condition, we rewrite Eq. (3.72) as

$$\frac{E_{el}}{V} = \int_0^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon + \int_{\varepsilon_F}^{\mu} \varepsilon g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 [g(\mu) + \mu g'(\mu)] + \text{higher order terms in } T. \quad (3.73)$$

From Eqs. (3.67), which specifies the relation between μ and ε_F , retaining the second-order terms in T , we obtain

$$\int_{\varepsilon_F}^{\mu} \varepsilon g(\varepsilon) d\varepsilon \approx \varepsilon_F (\mu - \varepsilon_F) g(\varepsilon_F). \quad (3.74)$$

Substituting Eq. (3.74) in Eq. (3.73) and consistently retaining terms only up to the second order in T $g(\mu) \approx g(\varepsilon_F)$ and $\mu \approx \varepsilon_F$ in Eq. (3.73), we obtain

$$\frac{E_{el}}{V} = \int_0^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 g(\varepsilon_F) + \varepsilon_F \left\{ (\mu - \varepsilon_F) g(\varepsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F) \right\}. \quad (3.75)$$

From Eqs. (3.65) and (3.75),

$$\frac{E_{el}}{V} = \int_0^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 g(\varepsilon_F). \quad (3.76)$$

From Eqs. (3.69) and (3.76), noting that the first term on the right side of Eq. (3.76) is independent of temperature for constant N , we obtain an expression for the electronic specific heat for a free electron gas in the metal,

$$C_{el} = \frac{\pi^2}{3} k_B^2 T g(\varepsilon_F). \quad (3.77)$$

From Eqs. (3.57) and (3.77),

$$C_{el} = \frac{n \pi^2 k_B^2 T}{2 \varepsilon_F}. \quad (3.78)$$

We note the result for the electronic specific heat obtained by using Fermi–Dirac statistics is significantly different and approximately 100 times smaller than Drude’s result for a classical electron gas ($C_v = 3/2 n k_B$) obtained by using Maxwell–Boltzmann statistics. The major difference

is that while each electron in a classical gas gains an energy $3/2 k_B T$ when heated to a temperature T , only the electrons in a range $k_B T$ near the Fermi level are excited to the higher energy states, whereas the rest of the electrons inside the Fermi surface are unaffected.

3.5 DC ELECTRICAL CONDUCTIVITY

We have shown in Eq. (3.36) that

$$\mathbf{p} = \hbar \mathbf{k}. \quad (3.79)$$

Using Newton's second law, we can see the force \mathbf{F} on the electron with momentum \mathbf{p} is

$$\mathbf{F} = \frac{d\mathbf{p}}{dt} = \hbar \frac{d\mathbf{k}}{dt}. \quad (3.80)$$

In an external electric field \mathbf{E} , the force on each electron of charge $-e$ is

$$\mathbf{F} = -e\mathbf{E}. \quad (3.81)$$

From Eqs. (3.80) and (3.81), we obtain

$$\hbar \frac{d\mathbf{k}}{dt} = -e\mathbf{E}. \quad (3.82)$$

If the electric field \mathbf{E} is applied to the metal at time $t=0$, after a time τ , the center of the Fermi sphere (within which all the electrons are located at $T=0$), which was at the origin of the \mathbf{k} space, would shift by

$$\Delta \mathbf{k} = -\frac{e\mathbf{E}\tau}{m}. \quad (3.83)$$

The displacement of the Fermi sphere due to an applied electric field is shown in Figure 3.10.

Because the change of momentum of each electron is

$$\Delta \mathbf{p} = \hbar \Delta \mathbf{k} = m \Delta \mathbf{v}, \quad (3.84)$$

and the electric current density of n electrons per unit volume is

$$\mathbf{j} = -ne\Delta \mathbf{v}, \quad (3.85)$$

we obtain from Eqs. (3.83) through (3.85)

$$\mathbf{j} = \frac{ne^2\tau}{m} \mathbf{E}. \quad (3.86)$$

The electrical conductivity σ is defined by (note that conductivity is a tensor, but we are treating it here as a scalar quantity)

$$\mathbf{j} = \sigma \mathbf{E}. \quad (3.87)$$

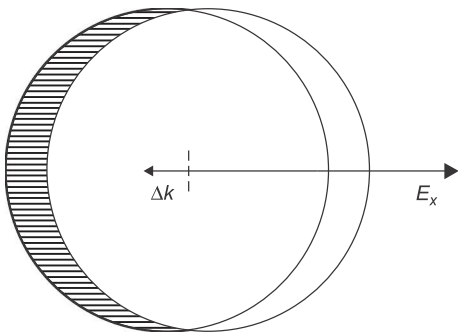


FIGURE 3.10

Displacement of the Fermi sphere in an applied electric field.

From Eqs. (3.86) and (3.87), we obtain

$$\sigma = \frac{ne^2\tau}{m}. \quad (3.88)$$

Eq. (3.88) for the electrical conductivity σ , derived by considering the displacement of the Fermi sphere in an electric field, is identical to the expression derived by using Drude's theory of metals (Problem 3.1), in which electrons were treated as a classical electron gas. However, one significant difference is that although the relaxation time defined by Drude was the average collision time between the electrons and the static positively charged ions while in the present model, the collisions of the electrons with impurities, lattice imperfections, and phonons can be included. The two results appear identical because of the approximation of a relaxation time τ in both models.

The following are the major drawbacks of the theory of DC electrical conductivity. First, it may be noted that in this derivation, the average relaxation time τ was not properly defined, although it was implicitly borrowed from the concept of the relaxation time defined by Drude. Second, because the origin of the collision time was left unanswered, the temperature dependence of the DC conductivity in metals could be explained only by introducing a temperature dependence in the relaxation time τ . Third, the current density \mathbf{j} is not parallel to the electric field \mathbf{E} in some metals, and the DC conductivity depends on the orientation of the metal with respect to \mathbf{E} .

3.6 THE HALL EFFECT

Here, we consider a conductor in the shape of a rod that has a rectangular cross-section, which is placed under a magnetic field \mathbf{B} in the z direction. There is a longitudinal electric field E_x . The electric and magnetic fields are so adjusted that the current cannot flow out of the rod in the y direction ($j_y = 0$). This configuration is shown in Figure 3.11.

The equation of motion of the displacement $\delta\mathbf{k}$, a Fermi sphere of particles acted on a force \mathbf{F} , is given by

$$\mathbf{F} = \hbar \left(\frac{d}{dt} + \frac{1}{\tau} \right) \delta\mathbf{k}, \quad (3.89)$$

where τ is the relaxation time. The Lorentz force on carrier of charge q (which can be positive or negative) in an electric field \mathbf{E} and a magnetic field \mathbf{B} is

$$\mathbf{F} = q \left(\mathbf{E} + \frac{1}{c} \mathbf{V} \times \mathbf{B} \right). \quad (3.90)$$

Here, we note that $q = -e$ for electrons, but the Hall effect is equally applicable for determining the sign of other carriers in a solid.

If $\hbar \delta\mathbf{k} = m\delta\mathbf{V}$, Eq. (3.90) can be written as

$$m \left(\frac{d}{dt} + \frac{1}{\tau} \right) \delta\mathbf{V} = q \left(\mathbf{E} + \frac{1}{c} \delta\mathbf{V} \times \mathbf{B} \right). \quad (3.91)$$

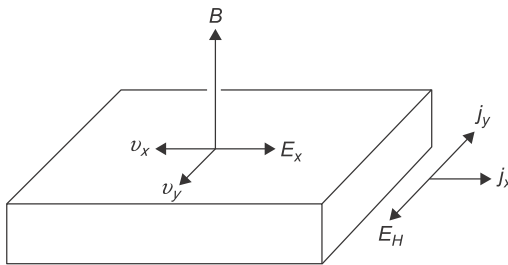


FIGURE 3.11

The geometry of the Hall effect.

Here, $\delta\mathbf{V}$ is the average of \mathbf{V} over the Fermi sphere. In the steady state, the acceleration $\frac{d\delta\mathbf{V}}{dt} = 0$. We can write Eq. (3.91) in the steady state (writing \mathbf{V} for $\delta\mathbf{V}$ for convenience),

$$\mathbf{V} = \frac{q\tau}{m} (\mathbf{E} + \mathbf{V} \times \mathbf{B}). \quad (3.92)$$

Because the static electric field \mathbf{E} lies in the xy plane and \mathbf{B} is along the z axis (Figure 3.7), we can write the components of Eq. (3.92) as

$$V_x = \frac{q\tau}{m} E_x - \omega_c \tau V_y, \quad (3.93)$$

and

$$V_y = \frac{q\tau}{m} E_y + \omega_c \tau V_x. \quad (3.94)$$

Here,

$$\omega_c \equiv \frac{-qB}{mc} \quad (3.95)$$

is the cyclotron frequency, usually defined for free electrons (in which case $q = -e$). By solving Eqs. (3.93) and (3.94), we obtain

$$V_x = \frac{q\tau/m}{1 + (\omega_c \tau)^2} (E_x - \omega_c \tau E_y), \quad (3.96)$$

and

$$V_y = \frac{q\tau/m}{1 + (\omega_c \tau)^2} (E_y + \omega_c \tau E_x). \quad (3.97)$$

The conductivity is

$$\sigma_0 = \frac{nq^2\tau}{m}, \quad (3.98)$$

and the components of charge current density from Eqs. (3.96) through (3.98),

$$j_x = nqV_x = \frac{\sigma_0}{1 + (\omega_c \tau)^2} (E_x - \omega_c \tau E_y), \quad (3.99)$$

$$j_y = nqV_y = \frac{\sigma_0}{1 + (\omega_c \tau)^2} (E_y + \omega_c \tau E_x), \quad (3.100)$$

and because the z-component of the current is not affected by the magnetic field,

$$j_z = nqV_z = \sigma_0 E_z. \quad (3.101)$$

In the Hall effect, the external fields are $E = E_x$ and $B_z = B$. There is a drift of the charges in the y direction due to the magnetic field B . However, no current can flow in this direction because of lack

of circuit continuity. Instead, the charges pile up on the surface of the sample, thereby setting up an electric field E_y . This field, which nullifies the Lorentz force, is known as the “Hall field.”

The Hall field is obtained by setting

$$j_y = nqv_y = 0. \quad (3.102)$$

From Eqs. (3.100) and (3.102), we obtain

$$\frac{\sigma_0}{1 + \omega_c^2 \tau^2} (\omega_c \tau E_x + E_y) = 0, \quad (3.103)$$

which yields

$$E_y = E_H = -\omega_c \tau E_x = \frac{qB}{m} \tau E_x. \quad (3.104)$$

From Eqs. (3.99) and (3.104), we obtain

$$j_x = \frac{\sigma_0}{1 + \omega_c^2 \tau^2} (E_x + \omega_c^2 \tau^2 E_x) = \sigma_0 E_x. \quad (3.105)$$

The Hall coefficient R_H is defined as

$$R_H = \frac{E_H}{j_x B} = \frac{q\tau}{\sigma_0 m} = \frac{1}{nq}. \quad (3.106)$$

The Hall resistance is defined as

$$\mathfrak{R}_H = \frac{V_y}{I_x}. \quad (3.107)$$

The sign of the Hall coefficient is determined by the charge carrier q , and for metals, these are the electrons of which the charge is $-e$. Later, we will see the impact of the Hall effect in determining the sign of the charge carriers in semiconductors as well as study the importance of the quantum Hall effect.

3.7 FAILURES OF THE FREE ELECTRON MODEL

The failures of the free electron model can be briefly summarized as follows:

- a. The temperature and the directional dependence of the DC electrical conductivity could not be adequately explained by the Sommerfeld theory.
- b. The free electron model explains the contribution of the linear term in T to the specific heat of metals, but the magnitude of this contribution is inadequate for many metals in the sense that it is either too large or too small. In addition, there is a cubic term (T^3) that contributes to the specific heat of metals but cannot be explained by the free electron model.
- c. The major failure of the free electron model is that it does not explain the significant difference between metals, insulators, and semiconductors. To be specific, it fails to explain why some elements crystallize as good conductors (metals) of which the conductivity decreases with the increase of temperature, some others crystallize as insulators that are very poor conductors, and the rest

crystallize as semiconductors of which the conductivity is very poor at low temperatures but increases with increase of temperature unlike that of metals. In fact, it has been commented that the difference of electrical resistivity at room temperature between that of good conductors (10^{-10} – 10^{-6}) ohm-cm and of good insulators (10^{14} – 10^{22}) ohm-cm is one of the widest range of any physical property ever found in nature. In contrast, the electrical resistivity of semiconductors at room temperature is in the range (10^{-2} – 10^9) ohm-cm but is strongly dependent on temperature.

To understand this major classification of solids, we have to include the effect of the positively charged stationary ions that are arranged in a periodic array. As we will show, the periodic array of ions leads to a periodic potential that results in the band theory of solids. The band theory of solids explains the difference between the electrical properties of metals, semiconductors, and insulators. In addition, it distorts the spherical Fermi surface to a more complex shape, and as we have noted, the Fermi surface determines many physical properties of the solid.

There are other significant deficiencies in the free electron model. First, it introduces the relaxation time of the electrons in an unrealistic manner in the sense that the role of the background positive ions is confined only to scatter an electron moving in an external field. Second, it ignores the electron–electron interactions, which has significant contribution to some physical properties. Third, the positively charged ions are not stationary but oscillate around their equilibrium position. Since these ions are positively charged, they affect the motion of the negatively charged electrons (the electron–phonon interaction). Fourth, the free electron model completely ignores the effects of lattice defects and lattice impurities. Fifth, the free electron model ignores the surface effects because of the periodic boundary condition invoked as a necessary condition of the model.

PROBLEMS

- 3.1. Show that in Drude’s model, the average electron velocity in an external electric field \mathbf{E} is

$\mathbf{v}_{avg} = -\frac{e\mathbf{E}\tau}{m}$ and the current density $\mathbf{j} = -nev = \left(\frac{ne^2\tau}{m}\right)\mathbf{E}$. Here, n is the number of electrons per unit volume. Because $\mathbf{j} = \sigma\mathbf{E}$, where σ is the DC electrical conductivity of the metal, show that $\sigma = \frac{ne^2\tau}{m}$.

- 3.2. The basic assumption of the Drude model is that the thermal current in a metal is carried by the conduction electrons. If we define the thermal current density $\mathbf{j}^q = -\kappa\nabla T$, where κ is the thermal conductivity, it can be easily shown that $\kappa = \frac{1}{3}v^2\tau c_v$, where c_v is the electronic specific heat. By applying classical ideal gas laws to the electron gas, $c_v = \frac{3}{2}nk_B$, and $\frac{1}{2}mv^2 = \frac{3}{2}k_B T$ (where k_B is the Boltzmann constant), show that

$$\frac{\kappa}{\sigma} = \frac{3}{2} \left(\frac{k_B}{e} \right)^2 T.$$

This relation between the electrical and thermal conductivities of a metal is known as the Wiedemann–Franz law.

- 3.3. Show that the Fermi–Dirac distribution function reduces to the Maxwell–Boltzmann distribution function $f(\epsilon) = e^{-(\epsilon-\mu)/k_B T}$ for very high temperatures when $\epsilon \ll \mu$. An alternate condition to make this classical approximation is $e^{-\mu/k_B T} \gg 1$.