

# 880:174 Physics of Modern Materials

## Chapter 4: The Free-Electron Theory of Metals

### 1. Electrons in Metals

Electrons do not pop out of a piece of copper lying on the table. Clearly, the “free” electrons in a metal are trapped inside the surface, at least at room temperature. In other words, there is a potential barrier at the surface that prevents electrons from escaping at ordinary temperatures. In a crystalline metallic solid, there are positive ions at the lattice sites. Due to the Coulomb interaction, these positive ions give rise to an attractive potential energy for an electron. Of course, the electrons repel each other. The overall potential for a single electron within the metal is a superposition of the potentials due to the positive ions and the other electrons. A *square-well* potential is a useful first model for the net potential that an electron experiences. Electron-electron interactions in many cases play a minor role because the mobile electrons tend to avoid each other due to the Pauli principle. Thus, each electron is essentially independent of the others, i.e., it is nearly free. The potential inside the metal due to the ion cores varies rapidly but “averages out” due to the motion of the electron to an approximately constant value. This is a first approximation for the treatment of electrons in metals.

### 2. Density of States

For an infinite square well in one dimension, the allowed energies are given by

$$E_n = n^2 \frac{\hbar^2 \pi^2}{2mL^2}, \quad n = 1, 2, 3, 4, \dots \quad (4.1)$$

For a three-dimensional square well, Eq. (4.1) applies for each dimension and the total energy is the sum of all three terms:

$$E = (n_x^2 + n_y^2 + n_z^2) \frac{\hbar^2 \pi^2}{2mL^2}, \quad n_x, n_y, n_z = 1, 2, 3, 4, \dots \quad (4.2)$$

Thus, there is an allowed value of energy corresponding to each distinct set of values for the quantum numbers  $n_x$ ,  $n_y$  and  $n_z$ . Let us rewrite Eq. (4.2) in this way:

$$n_x^2 + n_y^2 + n_z^2 = \frac{2mL^2 E}{\hbar^2 \pi^2}. \quad (4.3)$$

We can regard the quantum numbers as the orthogonal coordinates of a three-dimensional coordinate system. The values of the coordinates are restricted to positive integers. Since each distinct set of values for  $n_x$ ,  $n_y$  and  $n_z$  corresponds to one allowed energy value, it follows that a unit cube in our quantum-number space contains exactly one allowed energy or one allowed quantum state. Now, the L.H.S. of Eq. (4.3) corresponds to the square of the radius  $r_q$  of our quantum-number space (Pythagorean theorem). The total volume of the space is then

$$V_q = \frac{1}{8} \left( \frac{4}{3} \pi r_q^3 \right) = \frac{\pi}{6} \left( \frac{2mL^2 E}{\hbar^2 \pi^2} \right)^{3/2}. \quad (4.4)$$

The factor of 1/8 is present because the quantum numbers can assume only positive values, so the allowed volume is one-eighth of a sphere. Since a unit cube contains exactly one state, then the total volume  $V_q$  is equal to the total number of states. If we insert a factor of 2 because of spin, then the total number of states  $N_q$  is given by

$$N_q = 2 \times \frac{\pi}{6} \left( \frac{2mL^2 E}{\hbar^2 \pi^2} \right)^{3/2} = \frac{\pi}{3} \left( \frac{2mL^2 E}{\hbar^2 \pi^2} \right)^{3/2}. \quad (4.5)$$

The density of states  $Z(E)$  is defined to be the number of states per unit energy interval. Thus,

$$Z(E) = \frac{dN_q}{dE} = \frac{8\pi L^3 (2m^3)^{1/2}}{h^3} E^{1/2}. \quad (4.6)$$

(Recall that  $\hbar = h / 2\pi$ .) Thus, the number states in an energy interval  $dE$  is

$$Z(E)dE = \frac{dN_q}{dE} dE = \frac{8\pi L^3 (2m^3)^{1/2}}{h^3} E^{1/2} dE. \quad (4.7)$$

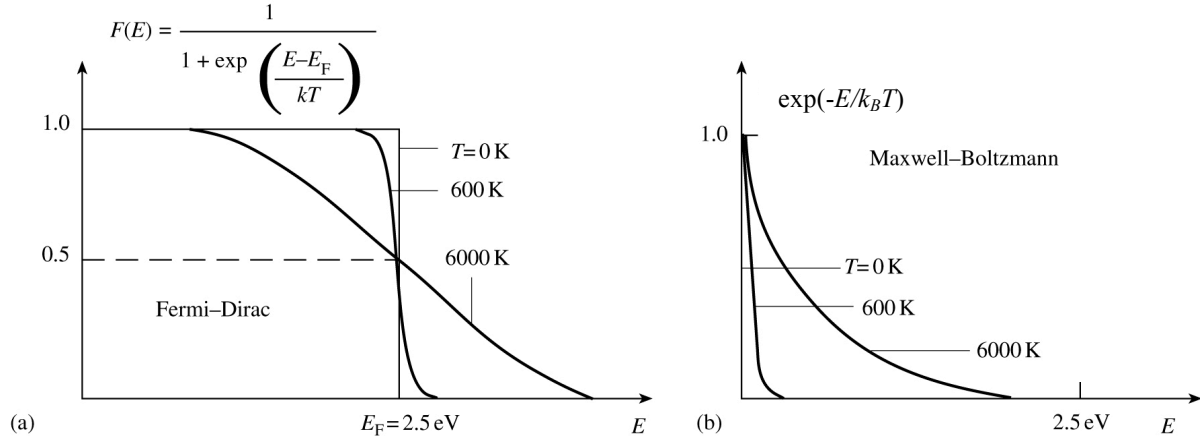
### 3. Fermi-Dirac Distribution Function

The probable number of electrons that occupy a given quantum state at a certain temperature is governed by a distribution function called the Fermi-Dirac (FD) distribution function. The FD function incorporates the Pauli principle – a quantum state can be occupied by at most one electron, i.e., the state has either one electron or zero. Thus, the probable number of electrons in a state is always less than or equal to one, i.e., the probable number of electrons in a state is equal to the probability of occupation of that state. In addition, all electrons are treated as identical and indistinguishable. A more familiar distribution function is the Maxwell-Boltzmann (MB) distribution function, which governs the distribution of speeds of gas molecules at a given temperature. Recall that at any given temperature, the speeds of the molecules of a gas are distributed on a Gaussian (bell) curve. Some molecules are faster than the average; others are slower. Most molecules have speeds in the vicinity of the average. The MB distribution function gives the probable number of molecules that have a certain speed.

For a quantum system at absolute temperature  $T$  whose quantum states are occupied by electrons, the probable number of electrons occupying a state of energy  $E$  is given by the FD distribution function

$$F(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1}, \quad (4.8)$$

where  $E_F$  is the Fermi energy and  $k_B$  is Boltzmann's constant. The Fermi energy is the energy at which the occupation probability is exactly 0.5, as can be seen by substituting  $E = E_F$  in Eq. (4.8). Note that at  $T = 0$  K,  $F(E) = 1$  for  $E < E_F$  and  $F(E) = 0$  for  $E > E_F$ . Thus,  $F(E)$  is a step function, with all states below the Fermi energy occupied and all states above it unoccupied. For  $T > 0$ ,  $F(E) < 1$  for  $E < E_F$  and  $F(E) > 0$  for  $E > E_F$ . Also, the function changes more gradually in the region of the Fermi energy. The rapidity of the change depends on the temperature.  $F(E)$  goes from a value of 0.9 to 0.1 between  $E_F - 2.2k_B T$  and  $E_F + 2.2k_B T$ . Note that whatever the temperature,  $F(E) = 0.5$  for  $E = E_F$ . At room temperature ( $\sim 300$  K),  $F(E)$  is not much different from the step function when  $T = 0$ . Only electrons in the vicinity of the Fermi energy are thermally excited to empty states immediately above  $E_F$ . At low energies, the states are still occupied and there are no empty states in their vicinity that these electrons could be excited into by a relatively small amount of energy. Thus, these low-energy electrons do not play a significant role in the thermal properties of metals. It should be noted that  $E_F$  is a function of temperature. For temperatures  $k_B T \ll E - E_F$ , its value changes little and is very nearly the same as its  $T = 0$  K value. However, for higher temperatures,  $E_F$  decreases in value.



For temperatures such that  $k_B T \ll E - E_F$  and for energies above the Fermi energy, the 1 in the denominator of the FD function is negligible. Thus, the occupation probability decreases exponentially:

$$F(E) \approx e^{-(E-E_F)/k_B T}. \quad [T \ll (E - E_F) / k_B]$$
 (4.9)

In this regime, the FD distribution approaches the MB distribution for classical particles.

One can calculate  $E_F$  using the FD distribution function at  $T = 0$ . The density of states times the FD function times  $dE$  equals the number of electrons in states with energies between  $E$  and  $E + dE$ . Let  $N$  be the number of electrons per unit volume. Thus, the total number of electrons  $NL^3$  is given by

$$NL^3 = \int_0^{\infty} F(E)Z(E)dE. \quad (4.10)$$

The integral is easy to do at  $T = 0$  because the FD function is simple. Recall that at  $T = 0$  K,  $F(E) = 1$  for  $E < E_F$  and  $F(E) = 0$  for  $E > E_F$ . Thus,

$$NL^3 = \frac{8\pi L^3 (2m^3)^{1/2}}{h^3} \int_0^{E_F} (1)E^{1/2} dE. \quad (4.11)$$

Performing the integral and solving for  $E_F$  gives

$$E_F = \frac{h^2}{8m} \left( \frac{3N}{\pi} \right)^{2/3}. \quad (4.12)$$

Fermi energies for typical metals are usually in the range 1-10 eV. (See table 6-1 in textbook.)

#### 4. Electronic Contribution to Specific Heat

We are interested in finding how the free electrons in a metal contribute to the specific heat. The electronic specific heat at constant volume is the energy per electron necessary to change the temperature of the metal by one unit (e.g., one Kelvin degree) with the volume held constant. We should note that the vibrations of the ions in the crystal lattice also contribute to the specific heat of the metal. In fact, the contribution of the ions dominates that of the electrons, except at low temperatures.

The classical equipartition theorem holds that each electron has a kinetic energy of  $\frac{3}{2}k_B T$  in three dimensions. In the free-electron model, the potential energy of an electron is a constant, so

there is no thermal contribution from the potential energy. Within our free-electron model, if a metal is heated from absolute zero to a temperature  $T$ , only those electrons within  $\sim 2 k_B T$  of the Fermi energy can gain thermal energy and be excited to higher energy states. These electrons will gain energy  $\sim (3/2)k_B T$ . If the temperature is not too high ( $k_B T \ll E_F$ ), we can easily calculate (approximately) the fraction of electrons that will be excited. As we saw from Eq.

(4.10), the total number of electrons  $n$  can be calculated from  $n = NL^3 = \int_0^\infty F(E)Z(E)dE$ . Since

the energies for which there are excited electrons are within a very small range  $\sim 2 k_B T$  around  $E_F$  and the FD function at these temperatures is not very different from the step function at  $T = 0$ , we approximate the number of excited electrons by

$$\Delta n \approx Z(E_F)F(E_F)\Delta E \approx Z(E_F)\left(\frac{1}{2}\right)(2k_B T) = Z(E_F)k_B T.$$

The *fraction* of excited electrons is then

$$\frac{\Delta n}{n} = \frac{Z(E_F)k_B T}{n} = \frac{\left[ \frac{8\pi L^3 (2m^3)^{1/2}}{h^3} E_F^{1/2} \right] (k_B T)}{\left[ \frac{\pi L^3}{3} \left( \frac{8m}{h^2} \right)^{3/2} E_F^{3/2} \right]} = \frac{3}{2} \frac{k_B T}{E_F}.$$

This result is approximately the same as the ratio of the excitation energy range and the Fermi energy, which is approximately equal to the area of the difference between the  $T = 0$  and the  $T \neq 0$  curve for  $F(E)$  divided by the area under the  $T = 0$  curve. [Show the curves and illustrate.] The thermal energy gained per electron is then approximately

$$\langle E \rangle = \frac{\Delta n}{n} \langle \Delta E \rangle = \frac{3}{2} \frac{k_B T}{E_F} \left( \frac{3}{2} k_B T \right) = \frac{9k_B^2 T^2}{4E_F}.$$

The specific heat at constant volume is then calculated as

$$c_v = \frac{d\langle E \rangle}{dT} = \frac{9k_B^2}{2E_F} T. \quad (\text{Approx.}) \quad (4.13)$$

We find that the specific heat is proportional to the absolute temperature, which is what is found experimentally. The result of a more precise (and laborious) calculation is

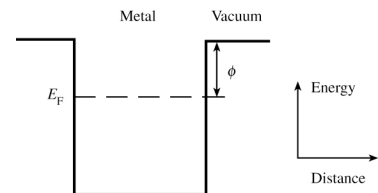
$$c_v = \frac{\pi^2}{2} \frac{k_B^2}{E_F} T, \quad (4.14)$$

which is not very different from our result. [Exp. data from Kittel.]

## 5. Thermionic Emission

Our model of free electrons in a metal treats them as independent particles moving in a square well. At temperatures that are not too high, the electrons have filled all the levels up to the Fermi energy and there are few electrons at energies above  $E_F$ . Thus, the most energetic electrons have an energy  $\approx E_F$ .

These electrons remain trapped inside the metal by the potential wall. Let us take the height of the potential wall *above*  $E_F$  to be  $\phi$ . This energy difference is called the *work function*. At room temperature,  $k_B T \ll \phi$  and so the probability that an electron will be excited over the barrier and



into the vacuum is virtually zero. However, as the temperature increases, more electrons are excited into higher energy states above the Fermi energy and at sufficiently high temperatures, the probability that an electron will be excited over the barrier and escape the metal becomes significant. This process of electron ejection from a metal at high temperatures is called *thermionic emission*. The emission current density can be calculated using the density of states (as a function of momentum rather than energy) and the FD function. The expression is

$$J = \frac{e}{m} \int_{p_{x0}}^{\infty} [(1 - r(p_x))] p_x F(p_x) Z(p_x) dp_x, \quad (4.15)$$

where  $p_x$  is the component of the electron's momentum that is in the direction of the surface,  $p_{x0}$  is the minimum momentum necessary for escape, and  $r(p_x)$  is the reflection coefficient at the surface (which generally depends on the energy, and therefore the momentum, of the electron). The textbook gives the details of the calculation. The result is

$$J = A_0 (1 - r) T^2 e^{-\phi/k_B T}, \quad (4.16)$$

where  $A_0$  is a constant and  $r$  has been treated as a constant for simplicity. Thus the thermionic emission current is exponentially dependent on the ratio of the work function and the temperature. This explains the experimental sensitivity of the emission current to changes in temperature or work function. Work function values for metals typically lie in the range 2–6 eV.

## 6. Contact Potential Difference

Different metals have different Fermi energies and work functions. Thus, the electrons near the Fermi energy in one metal will generally have significantly different energies (relative to the lowest vacuum energy) than electrons near the Fermi energy of another metal. Hence, when two dissimilar metals are placed in contact, the electrons near the Fermi energy in one metal will have lower energies than corresponding electrons in the other metal. To lower the energy of the system, electrons at higher energies in metal 1 (see diagrams below) will cross the junction into empty lower-energy states near the Fermi energy in metal 2. The net electron transfer will continue until the total energy is minimized.

This equilibrium situation occurs when the Fermi energies are equal. The transfer of electrons means that one metal becomes negatively charged and the other positively charged. Thus, an electric field and associated electric potential difference is created across the junction. The resulting potential difference is called the *contact potential difference*. The contact potential difference is equal to  $(\phi_2 - \phi_1) / e$ . Note that when equilibrium is established, there is no *net* flow of electrons, i.e., equal numbers of electrons flow across the junction in both directions. The electrons in metal 2 can slide down the potential-energy hill into metal 1, and sufficiently energetic electrons from metal 1 can climb up the hill into metal 2.

