CHAPTER 6: FREE ELECTRON FERMI GAS

In a theory which has given results like these,
there must certainly be a great deal of truth.

H. A. Lorentz

We can understand many physical properties of metals, and not only of the simple metals, in terms of the free electron model. According to this model, the valence electrons of the constituent atoms become conduction electrons and move about freely through the volume of the metal. Even in metals for which the free electron model works best, the charge distribution of the conduction electrons reflects the strong electrostatic potential of the ion cores. The utility of the free electron model is greatest for properties that depend essentially on the kinetic properties of the conduction electrons. The interaction of the conduction electrons with the ions of the lattice is treated in the next chapter.

The simplest metals are the alkali metals—lithium, sodium, potassium, cesium, and rubidium. In a free atom of sodium the valence electron is in a 3s state; in the metal this electron becomes a conduction electron in the 3s conduction band.

A monovalent crystal which contains N atoms will have N conduction electrons and N positive ion cores. The Na^+ ion core contains 10 electrons that occupy the 1s, 2s, and 2p shells of the free ion, with a spatial distribution that is essentially the same when in the metal as in the free ion. The ion cores fill only about 15 percent of the volume of a sodium crystal, as in Fig. 1. The radius of the free Na^+ ion is 0.98 Å, whereas one-half of the nearest-neighbor distance of the metal is 1.83 Å.

The interpretation of metallic properties in terms of the motion of free electrons was developed long before the invention of quantum mechanics. The classical theory had several conspicuous successes, notably the derivation of the form of Ohm's law and the relation between the electrical and thermal conductivity. The classical theory fails to explain the heat capacity and the magnetic susceptibility of the conduction electrons. (These are not failures of the free electron model, but failures of the classical Maxwell distribution function.)

There is a further difficulty with the classical model. From many types of experiments it is clear that a conduction electron in a metal can move freely in a straight path over many atomic distances, undeflected by collisions with other conduction electrons or by collisions with the atom cores. In a very pure specimen at low temperatures, the mean free path may be as long as 10^8 interatomic spacings (more than 1 cm).

Why is condensed matter so transparent to conduction electrons? The answer to the question contains two parts: (a) A conduction electron is not

deflected by ion cores arranged on a *periodic* lattice because matter waves can propagate freely in a periodic structure, as a consequence of the mathematics treated in the following chapter. (b) A conduction electron is scattered only infrequently by other conduction electrons. This property is a consequence of the Pauli exclusion principle. By a **free electron Fermi gas**, we shall mean a gas of free electrons subject to the Pauli principle.

ENERGY LEVELS IN ONE DIMENSION

Consider a free electron gas in one dimension, taking account of quantum theory and of the Pauli principle. An electron of mass m is confined to a length L by infinite barriers (Fig. 2). The wavefunction $\psi_n(x)$ of the electron is a solution of the Schrödinger equation $\mathcal{H}\psi = \epsilon\psi$; with the neglect of potential energy we have $\mathcal{H} = p^2/2m$, where p is the momentum. In quantum theory p may be represented by the operator $-i\hbar \, d/dx$, so that

$$\mathcal{H}\psi_n = -\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} = \epsilon_n\psi_n \ , \tag{1}$$

where ϵ_n is the energy of the electron in the orbital.

We use the term **orbital** to denote a solution of the wave equation for a system of only one electron. The term allows us to distinguish between an exact quantum state of the wave equation of a system of N interacting electrons and an approximate quantum state which we construct by assigning the N electrons to N different orbitals, where each orbital is a solution of a wave equation for one electron. The orbital model is exact only if there are no interactions between electrons.

The boundary conditions are $\psi_n(0) = 0$; $\psi_n(L) = 0$, as imposed by the infinite potential energy barriers. They are satisfied if the wavefunction is sinelike with an integral number n of half-wavelengths between 0 and L:

$$\psi_n = A \sin\left(\frac{2\pi}{\lambda_n}x\right) \ ; \qquad \tfrac{1}{2}n\lambda_n = L \ , \tag{2}$$

where A is a constant. We see that (2) is a solution of (1), because

$$\frac{d\psi_n}{dx} = A\left(\frac{n\pi}{L}\right)\cos\left(\frac{n\pi}{L}x\right) \ ; \qquad \frac{d^2\psi_n}{dx^2} = -A\left(\frac{n\pi}{L}\right)^2 \sin\left(\frac{n\pi}{L}x\right) \ ,$$

whence the energy ϵ_n is given by

$$\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 \ . \tag{3}$$

We want to accommodate N electrons on the line. According to the **Pauli exclusion principle**, no two electrons can have all their quantum numbers
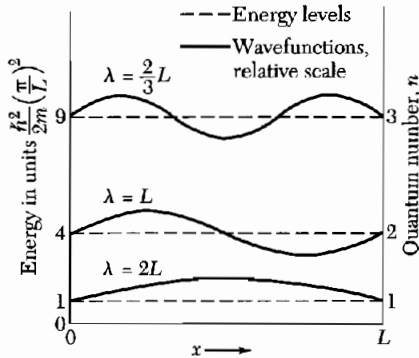
Figure 2 First three energy levels and wavefunctions of a free electron of mass m confined to a line of length L. The energy levels are labeled according to the quantum number n which gives the number of half-wavelengths in the wavefunction. The wavelengths are indicated on the wavefunctions. The energy ϵ_n of the level of quantum number n is equal to $(h^2/2m)(n/2L)^2$.

identical. That is, each orbital can be occupied by at most one electron. This applies to electrons in atoms, molecules, or solids.

In a linear solid the quantum numbers of a conduction electron orbital are n and m_s, where n is any positive integer and the magnetic quantum number $m_s = \pm\frac{1}{2}$, according to spin orientation. A pair of orbitals labeled by the quantum number n can accommodate two electrons, one with spin up and one with spin down.

If there are six electrons, then in the ground state of the system the filled orbitals are those given in the table:

n	m_s	Electron occupancy	n	m_s	Electron occupancy
1	↑	1	3	↑	1
1	↓	1	3	↓	1
2	↑	1	4	↑	0
2	↓	1	4	↓	0

More than one orbital may have the same energy. The number of orbitals with the same energy is called the **degeneracy.**

Let n_F denote the topmost filled energy level, where we start filling the levels from the bottom ($n = 1$) and continue filling higher levels with electrons until all N electrons are accommodated. It is convenient to suppose that N is an even number. The condition $2n_F = N$ determines n_F, the value of n for the uppermost filled level.

The **Fermi energy** ϵ_F is defined as the energy of the topmost filled level in the ground state of the N electron system. By (3) with $n = n_F$ we have in one dimension:

$$\epsilon_F = \frac{\hbar^2}{2m}\left(\frac{n_F\pi}{L}\right)^2 = \frac{\hbar^2}{2m}\left(\frac{N\pi}{2L}\right)^2 \, . \tag{4}$$

EFFECT OF TEMPERATURE ON THE FERMI-DIRAC DISTRIBUTION

The ground state is the state of the N electron system at absolute zero. What happens as the temperature is increased? This is a standard problem in elementary statistical mechanics, and the solution is given by the Fermi-Dirac distribution function (Appendix D and *TP*, Chapter 7).

The kinetic energy of the electron gas increases as the temperature is increased: some energy levels are occupied which were vacant at absolute zero, and some levels are vacant which were occupied at absolute zero (Fig. 3). The **Fermi-Dirac distribution** gives the probability that an orbital at energy ϵ will be occupied in an ideal electron gas in thermal equilibrium:

$$f(\epsilon) = \frac{1}{\exp[(\epsilon - \mu)/k_B T] + 1} \cdot \tag{5}$$

The quantity μ is a function of the temperature; μ is to be chosen for the particular problem in such a way that the total number of particles in the system comes out correctly—that is, equal to N. At absolute zero $\mu = \epsilon_F$, because in the limit $T \to 0$ the function $f(\epsilon)$ changes discontinuously from the value 1 (filled) to the value 0 (empty) at $\epsilon = \epsilon_F = \mu$. *At all temperatures* $f(\epsilon)$ *is equal to* $\frac{1}{2}$ *when* $\epsilon = \mu$, for then the denominator of (5) has the value 2.
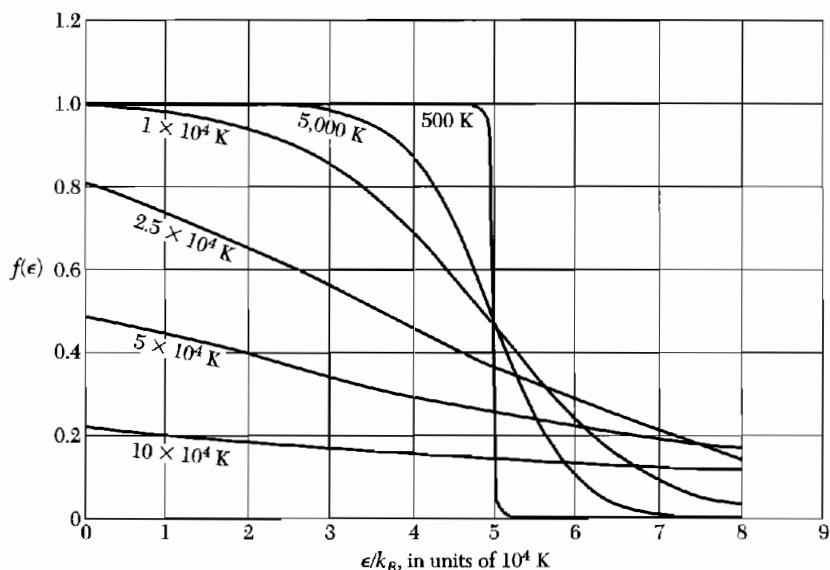

Figure 3 Fermi-Dirac distribution function (5) at the various labelled temperatures, for $T_F \equiv \epsilon_F/k_B = 50{,}000$ K. The results apply to a gas in three dimensions. The total number of particles is constant, independent of temperature. The chemical potential μ at each temperature may be read off the graph as the energy at which $f = 0.5$.

The quantity μ is the **chemical potential** (*TP*, Chapter 5), and we see that at absolute zero the chemical potential is equal to the Fermi energy, defined as the energy of the topmost filled orbital at absolute zero.

The high energy tail of the distribution is that part for which $\epsilon - \mu \gg k_B T$; here the exponential term is dominant in the denominator of (5), so that $f(\epsilon) \cong \exp[(\mu - \epsilon)/k_B T]$. This limit is called the Boltzmann or Maxwell distribution.

FREE ELECTRON GAS IN THREE DIMENSIONS

The free-particle Schrödinger equation in three dimensions is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi_\mathbf{k}(\mathbf{r}) = \epsilon_\mathbf{k}\,\psi_\mathbf{k}(\mathbf{r}) \ . \tag{6}$$

If the electrons are confined to a cube of edge L, the wavefunction is the standing wave

$$\psi_n(\mathbf{r}) = A \sin(\pi n_x x/L) \sin(\pi n_y y/L) \sin(\pi n_z z/L) \ , \tag{7}$$

where n_x, n_y, n_z are positive integers. The origin is at one corner of the cube.

It is convenient to introduce wavefunctions that satisfy periodic boundary conditions, as we did for phonons in Chapter 5. We now require the wavefunctions to be periodic in x, y, z with period L. Thus

$$\psi(x + L, y, z) = \psi(x, y, z) \ , \tag{8}$$

and similarly for the y and z coordinates. Wavefunctions satisfying the free-particle Schrödinger equation and the periodicity condition are of the form of a traveling plane wave:

$$\boxed{\psi_\mathbf{k}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) \ ,} \tag{9}$$

provided that the components of the wavevector $\mathbf{k}$ satisfy

$$k_x = 0 \ ; \quad \pm\frac{2\pi}{L} \ ; \quad \pm\frac{4\pi}{L} \ ; \quad \ldots , \tag{10}$$

and similarly for k_y and k_z.

Any component of $\mathbf{k}$ of the form $2n\pi/L$ will satisfy the periodicity condition over a length L, where n is a positive or negative integer. The components of k are the quantum numbers of the problem, along with the quantum number m_s for the spin direction. We confirm that these values of k_x satisfy (8), for

$$\exp[ik_x(x + L)] = \exp[i2n\pi(x + L)/L]$$
$$= \exp(i2n\pi x/L)\exp(i2n\pi) = \exp(i2n\pi x/L) = \exp(ik_x x) \ . \tag{11}$$

On substituting (9) in (6) we have the energy ϵ_k of the orbital with wavevector **k**:

$$\epsilon_k = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) \ . \tag{12}$$

The magnitude k of the wavevector is related to the wavelength λ by $k = 2\pi/\lambda$.

The linear momentum **p** may be represented in quantum mechanics by the operator $\mathbf{p} = -i\hbar\nabla$, whence for the orbital (9)

$$\mathbf{p}\psi_k(\mathbf{r}) = -i\hbar\nabla\psi_k(\mathbf{r}) = \hbar\mathbf{k}\psi_k(\mathbf{r}) \ , \tag{13}$$

so that the plane wave ψ_k is an eigenfunction of the linear momentum with the eigenvalue $\hbar\mathbf{k}$. The particle velocity in the orbital **k** is given by $\mathbf{v} = \hbar\mathbf{k}/m$.

In the ground state of a system of N free electrons, the occupied orbitals may be represented as points inside a sphere in **k** space. The energy at the surface of the sphere is the Fermi energy; the wavevectors at the Fermi surface have a magnitude k_F such that (Fig. 4):

$$\epsilon_F = \frac{\hbar^2}{2m} k_F^2 \ . \tag{14}$$

From (10) we see that there is one allowed wavevector—that is, one distinct triplet of quantum numbers k_x, k_y, k_z—for the volume element $(2\pi/L)^3$ of **k** space. Thus in the sphere of volume $4\pi k_F^3/3$ the total number of orbitals is

$$2 \cdot \frac{4\pi k_F^3/3}{(2\pi/L)^3} = \frac{V}{3\pi^2} k_F^3 = N \ , \tag{15}$$

where the factor 2 on the left comes from the two allowed values of the spin quantum number for each allowed value of **k**. Then (15) gives

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3} , \tag{16}$$

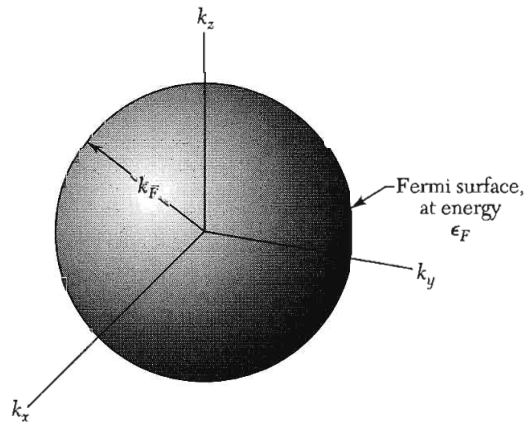which depends only on the particle concentration.

Figure 4 In the ground state of a system of N free electrons the occupied orbitals of the system fill a sphere of radius k_F, where $\epsilon_F = \hbar^2 k_F^2/2m$ is the energy of an electron having a wavevector k_F.

Table 1 Calculated free electron Fermi surface parameters for metals at room temperature

(Except for Na, K, Rb, Cs at 5 K and Li at 78 K)

Valency	Metal	Electron concentration, in cm^{-3}	Radius[a] parameter r_n	Fermi wavevector, in cm^{-1}	Fermi velocity, in cm s^{-1}	Fermi energy, in eV	Fermi temperature $T_F \equiv \epsilon_F/k_B$, in deg K
1	Li	4.70×10^{22}	3.25	1.11×10^8	1.29×10^8	4.72	5.48×10^4
	Na	2.65	3.93	0.92	1.07	3.23	3.75
	K	1.40	4.86	0.75	0.86	2.12	2.46
	Rb	1.15	5.20	0.70	0.81	1.85	2.15
	Cs	0.91	5.63	0.64	0.75	1.58	1.83
	Cu	8.45	2.67	1.36	1.57	7.00	8.12
	Ag	5.85	3.02	1.20	1.39	5.48	6.36
	Au	5.90	3.01	1.20	1.39	5.51	6.39
2	Be	24.2	1.88	1.93	2.23	14.14	16.41
	Mg	8.60	2.65	1.37	1.58	7.13	8.27
	Ca	4.60	3.27	1.11	1.28	4.68	5.43
	Sr	3.56	3.56	1.02	1.18	3.95	4.58
	Ba	3.20	3.69	0.98	1.13	3.65	4.24
	Zn	13.10	2.31	1.57	1.82	9.39	10.90
	Cd	9.28	2.59	1.40	1.62	7.46	8.66
3	Al	18.06	2.07	1.75	2.02	11.63	13.49
	Ga	15.30	2.19	1.65	1.91	10.35	12.01
	In	11.49	2.41	1.50	1.74	8.60	9.98
4	Pb	13.20	2.30	1.57	1.82	9.37	10.87
	Sn(w)	14.48	2.23	1.62	1.88	10.03	11.64

[a]The dimensionless radius parameter is defined as $r_n = r_0/a_H$, where a_H is the first Bohr radius and r_0 is the radius of a sphere that contains one electron.

$D(\epsilon)$

Density of orbitals, relative scale
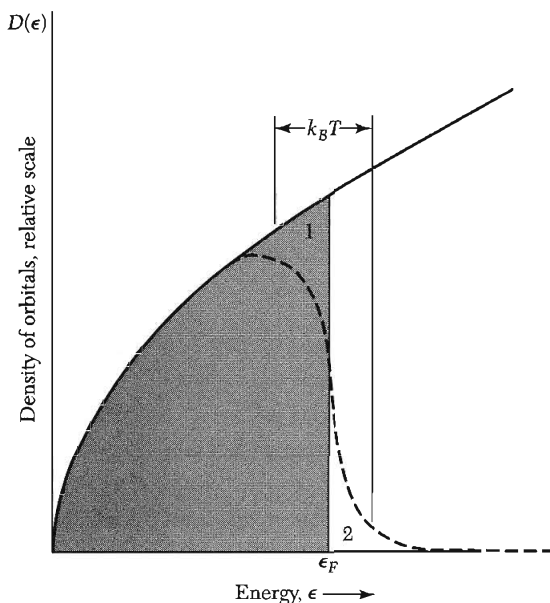
Energy, $\epsilon \longrightarrow$

Figure 5 Density of single-particle states as a function of energy, for a free electron gas in three dimensions. The dashed curve represents the density $f(\epsilon, T)D(\epsilon)$ of filled orbitals at a finite temperature, but such that k_BT is small in comparison with ϵ_F. The shaded area represents the filled orbitals at absolute zero. The average energy is increased when the temperature is increased from 0 to T, for electrons are thermally excited from region 1 to region 2.

Using (14) and (16),

$$\epsilon_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} . \tag{17}$$

This relates the Fermi energy to the electron concentration N/V. The electron velocity v_F at the Fermi surface is

$$v_F = \left(\frac{\hbar k_F}{m}\right) = \left(\frac{\hbar}{m}\right)\left(\frac{3\pi^2 N}{V}\right)^{1/3} . \tag{18}$$

Calculated values of k_F, v_F, and ϵ_F are given in Table 1 for selected metals; also given are values of the quantity T_F which is defined as ϵ_F/k_B. (The quantity T_F has nothing to do with the temperature of the electron gas!)

We now find an expression for the number of orbitals per unit energy range, $D(\epsilon)$, called the **density of states**.[1] We use (17) to obtain the total number of orbitals of energy $\leq\epsilon$:

$$N = \frac{V}{3\pi^2}\left(\frac{2m\epsilon}{\hbar^2}\right)^{3/2} , \tag{19}$$

so that the density of states (Fig. 5) is

$$D(\epsilon) \equiv \frac{dN}{d\epsilon} = \frac{V}{2\pi^2} \cdot \left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot \epsilon^{1/2} . \tag{20}$$

[1]Strictly, $D(\epsilon)$ is the density of one-particle states, or density of orbitals.

This result may be expressed more simply by comparing (19) and (20) to obtain at ϵ

$$D(\epsilon) \equiv \frac{dN}{d\epsilon} = \frac{3N}{2\epsilon} \ . \tag{21}$$

Within a factor of the order of unity, the number of orbitals per unit energy range at the Fermi energy is the total number of conduction electrons divided by the Fermi energy, just as we would expect.

HEAT CAPACITY OF THE ELECTRON GAS

The question that caused the greatest difficulty in the early development of the electron theory of metals concerns the heat capacity of the conduction electrons. Classical statistical mechanics predicts that a free particle should have a heat capacity of $\frac{3}{2}k_B$, where k_B is the Boltzmann constant. If N atoms each give one valence electron to the electron gas, and the electrons are freely mobile, then the electronic contribution to the heat capacity should be $\frac{3}{2}Nk_B$, just as for the atoms of a monatomic gas. But the observed electronic contribution at room temperature is usually less than 0.01 of this value.

This important discrepancy distracted the early workers, such as Lorentz: How can the electrons participate in electrical conduction processes as if they were mobile, while not contributing to the heat capacity? The question was answered only upon the discovery of the Pauli exclusion principle and the Fermi distribution function. Fermi found the correct result and he wrote, "One recognizes that the specific heat vanishes at absolute zero and that at low temperatures it is proportional to the absolute temperature."

When we heat the specimen from absolute zero, not every electron gains an energy $\sim k_B T$ as expected classically, but only those electrons in orbitals within an energy range $k_B T$ of the Fermi level are excited thermally, as in Fig. 5. This gives an immediate qualitative solution to the problem of the heat capacity of the conduction electron gas. If N is the total number of electrons, only a fraction of the order of T/T_F can be excited thermally at temperature T, because only these lie within an energy range of the order of $k_B T$ of the top of the energy distribution.

Each of these NT/T_F electrons has a thermal energy of the order of $k_B T$. The total electronic thermal kinetic energy U is of the order of

$$U_{el} \approx (NT/T_F)k_B T \ . \tag{22}$$

The electronic heat capacity is given by

$$C_{el} = \partial U/\partial T \approx Nk_B(T/T_F) \tag{23}$$

and is directly proportional to T, in agreement with the experimental results discussed in the following section. At room temperature C_{el} is smaller