1
The Drude Theory of Metals

Metals occupy a rather special position in the study of solids, sharing a variety of striking properties that other solids (such as quartz, sulfur, or common salt) lack. They are excellent conductors of heat and electricity, are ductile and malleable, and display a striking luster on freshly exposed surfaces. The challenge of accounting for these metallic features gave the starting impetus to the modern theory of solids.

Although the majority of commonly encountered solids are nonmetallic, metals have continued to play a prominent role in the theory of solids from the late nineteenth century to the present day. Indeed, the metallic state has proved to be one of the great fundamental states of matter. The elements, for example, definitely favor the metallic state: over two thirds are metals. Even to understand nonmetals one must also understand metals, for in explaining why copper conducts so well, one begins to learn why common salt does not.

During the last hundred years physicists have tried to construct simple models of the metallic state that account in a qualitative, and even quantitative, way for the characteristic metallic properties. In the course of this search brilliant successes have appeared hand in hand with apparently hopeless failures, time and again. Even the earliest models, though strikingly wrong in some respects, remain, when properly used, of immense value to solid state physicists today.

In this chapter we shall examine the theory of metallic conduction put forth by P. Drude[1] at the turn of the century. The successes of the Drude model were considerable, and it is still used today as a quick practical way to form simple pictures and rough estimates of properties whose more precise comprehension may require analysis of considerable complexity. The failures of the Drude model to account for some experiments, and the conceptual puzzles it raised, defined the problems with which the theory of metals was to grapple over the next quarter century. These found their resolution only in the rich and subtle structure of the quantum theory of solids.

BASIC ASSUMPTIONS OF THE DRUDE MODEL

J. J. Thomson's discovery of the electron in 1897 had a vast and immediate impact on theories of the structure of matter, and suggested an obvious mechanism for conduction in metals. Three years after Thomson's discovery Drude constructed his theory of electrical and thermal conduction by applying the highly successful kinetic theory of gases to a metal, considered as a gas of electrons.

In its simplest form kinetic theory treats the molecules of a gas as identical solid spheres, which move in straight lines until they collide with one another.[2] The time taken up by a single collision is assumed to be negligible, and, except for the forces coming momentarily into play during each collision, no other forces are assumed to act between the particles.

Although there is only one kind of particle present in the simplest gases, in a metal there must be at least two, for the electrons are negatively charged, yet the metal is electrically neutral. Drude assumed that the compensating positive charge was at-

---

[1]   *Annalen der Physik* **1**, 566 and **3**, 369 (1900).

[2]   Or with the walls of the vessel containing them, a possibility generally ignored in discussing metals unless one is interested in very fine wires, thin sheets, or effects at the surface.
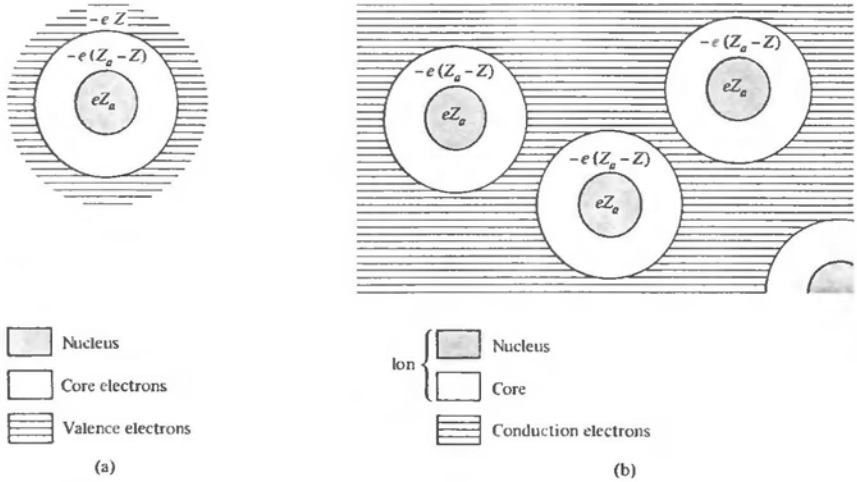
Figure 1.1
(a) Schematic picture of an isolated atom (not to scale). (b) In a metal the nucleus and ion core retain their configuration in the free atom, but the valence electrons leave the atom to form the electron gas.

tached to much heavier particles, which he considered to be immobile. At his time, however, there was no precise notion of the origin of the light, mobile electrons and the heavier, immobile, positively charged particles. The solution to this problem is one of the fundamental achievements of the modern quantum theory of solids. In this discussion of the Drude model, however, we shall simply assume (and in many metals this assumption can be justified) that when atoms of a metallic element are brought together to form a metal, the valence electrons become detached and wander freely through the metal, while the metallic ions remain intact and play the role of the immobile positive particles in Drude's theory. This model is indicated schematically in Figure 1.1. A single isolated atom of the metallic element has a nucleus of charge eZ_a, where Z_a is the atomic number and e is the magnitude of the electronic charge[3]: $e = 4.80 \times 10^{-10}$ electrostatic units (esu) $= 1.60 \times 10^{-19}$ coulombs. Surrounding the nucleus are Z_a electrons of total charge $-eZ_a$. A few of these, Z, are the relatively weakly bound valence electrons. The remaining $Z_a - Z$ electrons are relatively tightly bound to the nucleus, play much less of a role in chemical reactions, and are known as the core electrons. When these isolated atoms condense to form a metal, the core electrons remain bound to the nucleus to form the metallic ion, but the valence electrons are allowed to wander far away from their parent atoms. In the metallic context they are called conduction electrons.[4]

---

[3] We shall always take e to be a positive number.

[4] When, as in the Drude model, the core electrons play a passive role and the ion acts as an indivisible inert entity, one often refers to the conduction electrons simply as "the electrons," saving the full term for times when the distinction between conduction and core electrons is to be emphasized.

Drude applied kinetic theory to this "gas" of conduction electrons of mass m, which (in contrast to the molecules of an ordinary gas) move against a background of heavy immobile ions. The density of the electron gas can be calculated as follows:

A metallic element contains 0.6022×10^{24} atoms per mole (Avogadro's number) and ρ_m/A moles per cm^3, where ρ_m is the mass density (in grams per cubic centimeter) and A is the atomic mass of the element. Since each atom contributes Z electrons, the number of electrons per cubic centimeter, $n = N/V$, is

$$n = 0.6022 \times 10^{24} \frac{Z\rho_m}{A}. \tag{1.1}$$

Table 1.1 shows the conduction electron densities for some selected metals. They are typically of order 10^{22} conduction electrons per cubic centimeter, varying from 0.91×10^{22} for cesium up to 24.7×10^{22} for beryllium.[5] Also listed in Table 1.1 is a widely used measure of the electronic density, r_s, defined as the radius of a sphere whose volume is equal to the volume per conduction electron. Thus

$$\frac{V}{N} = \frac{1}{n} = \frac{4\pi r_s^3}{3}; \quad r_s = \left(\frac{3}{4\pi n}\right)^{1/3}. \tag{1.2}$$

Table 1.1 lists r_s both in angstroms (10^{-8} cm) and in units of the Bohr radius $a_0 = \hbar^2/me^2 = 0.529 \times 10^{-8}$ cm; the latter length, being a measure of the radius of a hydrogen atom in its ground state, is often used as a scale for measuring atomic distances. Note that r_s/a_0 is between 2 and 3 in most cases, although it ranges between 3 and 6 in the alkali metals (and can be as large as 10 in some metallic compounds).

These densities are typically a thousand times greater than those of a classical gas at normal temperatures and pressures. In spite of this and in spite of the strong electron-electron and electron-ion electromagnetic interactions, the Drude model boldly treats the dense metallic electron gas by the methods of the kinetic theory of a neutral dilute gas, with only slight modifications. The basic assumptions are these:

1. Between collisions the interaction of a given electron, both with the others and with the ions, is neglected. Thus in the absence of externally applied electromagnetic fields each electron is taken to move uniformly in a straight line. In the presence of externally applied fields each electron is taken to move as determined by Newton's laws of motion in the presence of those external fields, but neglecting the additional complicated fields produced by the other electrons and ions.[6] The neglect of electron-electron interactions between collisions is known as the *independent electron approximation*. The corresponding neglect of electron-ion interactions is known as the *free electron approximation*. We shall find in subsequent chapters that

---

[5] This is the range for metallic elements under normal conditions. Higher densities can be attained by application of pressure (which tends to favor the metallic state). Lower densities are found in compounds.

[6] Strictly speaking, the electron-ion interaction is not entirely ignored, for the Drude model implicitly assumes that the electrons are confined to the interior of the metal. Evidently this confinement is brought about by their attraction to the positively charged ions. Gross effects of the electron-ion and electron-electron interaction like this are often taken into account by adding to the external fields a suitably defined internal field representing the average effect of the electron-electron and electron-ion interactions.

Table 1.1

FREE ELECTRON DENSITIES OF SELECTED METALLIC ELE-MENTS[a]

ELEMENT	Z	$n\,(10^{22}/\mathrm{cm}^3)$	$r_s(\text{Å})$	r_s/a_0
Li (78 K)	1	4.70	1.72	3.25
Na (5 K)	1	2.65	2.08	3.93
K (5 K)	1	1.40	2.57	4.86
Rb (5 K)	1	1.15	2.75	5.20
Cs (5 K)	1	0.91	2.98	5.62
Cu	1	8.47	1.41	2.67
Ag	1	5.86	1.60	3.02
Au	1	5.90	1.59	3.01
Be	2	24.7	0.99	1.87
Mg	2•	8.61	1.41	2.66
Ca	2	4.61	1.73	3.27
Sr	2	3.55	1.89	3.57
Ba	2	3.15	1.96	3.71
Nb	1	5.56	1.63	3.07
Fe	2	17.0	1.12	2.12
Mn (α)	2	16.5	1.13	2.14
Zn	2	13.2	1.22	2.30
Cd	2	9.27	1.37	2.59
Hg (78 K)	2	8.65	1.40	2.65
Al	3	18.1	1.10	2.07
Ga	3	15.4	1.16	2.19
In	3	11.5	1.27	2.41
Tl	3	10.5	1.31	2.48
Sn	4	14.8	1.17	2.22
Pb	4	13.2	1.22	2.30
Bi	5	14.1	1.19	2.25
Sb	5	16.5	1.13	2.14

[a] At room temperature (about 300 K) and atmospheric pressure, unless otherwise noted. The radius r_s of the free electron sphere is defined in Eq. (1.2). We have arbitrarily selected one value of Z for those elements that display more than one chemical valence. The Drude model gives no theoretical basis for the choice. Values of n are based on data from R. W. G. Wyckoff, *Crystal Structures*, 2nd ed., Interscience, New York, 1963.

although the independent electron approximation is in many contexts surprisingly good, the free electron approximation must be abandoned if one is to arrive at even a qualitative understanding of much of metallic behavior.

2. Collisions in the Drude model, as in kinetic theory, are instantaneous events that abruptly alter the velocity of an electron. Drude attributed them to the electrons bouncing off the impenetrable ion cores (rather than to electron-electron collisions. the analogue of the predominant collision mechanism in an ordinary gas). We shall find later that electron-electron scattering is indeed one of the least important of the several scattering mechanisms in a metal, except under unusual conditions. However,
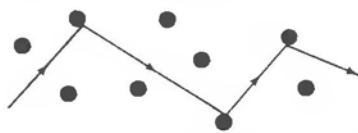
Figure 1.2
Trajectory of a conduction electron scattering off the ions, according to the naive picture of Drude.

the simple mechanical picture (Figure 1.2) of an electron bumping along from ion to ion is very far off the mark.[7] Fortunately, this does not matter for many purposes: a qualitative (and often a quantitative) understanding of metallic conduction can be achieved by simply assuming that there is *some* scattering mechanism, without inquiring too closely into just what that mechanism might be. By appealing, in our analysis, to only a few general effects of the collision process, we can avoid committing ourselves to any specific picture of how electron scattering actually takes place. These broad features are described in the following two assumptions.

3.   We shall assume that an electron experiences a collision (i.e., suffers an abrupt change in its velocity) with a probability per unit time $1/\tau$. We mean by this that the probability of an electron undergoing a collision in any infinitesimal time interval of length dt is just dt/τ. The time τ is variously known as the relaxation time, the collision time, or the mean free time, and it plays a fundamental role in the theory of metallic conduction. It follows from this assumption that an electron picked at random at a given moment will, on the average, travel for a time τ before its next collision, and will, on the average, have been traveling for a time τ since its last collision.[8] In the simplest applications of the Drude model the collision time τ is taken to be independent of an electron's position and velocity. We shall see later that this turns out to be a surprisingly good assumption for many (but by no means all) applications.

4.   Electrons are assumed to achieve thermal equilibrium with their surroundings only through collisions.[9] These collisions are assumed to maintain local thermodynamic equilibrium in a particularly simple way: immediately after each collision an electron is taken to emerge with a velocity that is not related to its velocity just before the collision, but randomly directed and with a speed appropriate to the temperature prevailing at the place where the collision occurred. Thus the hotter the region in which a collision occurs, the faster a typical electron will emerge from the collision.

In the rest of this chapter we shall illustrate these notions through their most important applications, noting the extent to which they succeed or fail to describe the observed phenomena.

DC ELECTRICAL CONDUCTIVITY OF A METAL

According to *Ohm's law*, the current I flowing in a wire is proportional to the potential drop V along the wire: $V = IR$, where R, the resistance of the wire, depends on its

---

[7]   For some time people were led into difficult but irrelevant problems connected with the proper aiming of an electron at an ion in each collision. So literal an interpretation of Figure 1.2 is strenuously to be avoided.

[8]   See Problem 1.

[9]   Given the free and independent electron approximation, this is the only possible mechanism left.

dimensions, but is independent of the size of the current or potential drop. The Drude model accounts for this behavior and provides an estimate of the size of the resistance.

One generally eliminates the dependence of R on the shape of the wire by introducing a quantity characteristic only of the metal of which the wire is composed. The resistivity ρ is defined to be the proportionality constant between the electric field $\mathbf{E}$ at a point in the metal and the current density $\mathbf{j}$ that it induces[10]:

$$\mathbf{E} = \rho\mathbf{j}. \tag{1.3}$$

The current density $\mathbf{j}$ is a vector, parallel to the flow of charge, whose magnitude is the amount of charge per unit time crossing a unit area perpendicular to the flow. Thus if a uniform current I flows through a wire of length L and cross-sectional area A, the current density will be $j = I/A$. Since the potential drop along the wire will be $V = EL$, Eq. (1.3) gives $V = I\rho L/A$, and hence $R = \rho L/A$.

If n electrons per unit volume all move with velocity $\mathbf{v}$, then the current density they give rise to will be parallel to $\mathbf{v}$. Furthermore, in a time dt the electrons will advance by a distance $v\,dt$ in the direction of $\mathbf{v}$, so that $n(v\,dt)A$ electrons will cross an area A perpendicular to the direction of flow. Since each electron carries a charge $-e$, the charge crossing A in the time dt will be $-nevA\,dt$, and hence the current density is

$$\mathbf{j} = -ne\mathbf{v}. \tag{1.4}$$

At any point in a metal, electrons are always moving in a variety of directions with a variety of thermal energies. The net current density is thus given by (1.4), where $\mathbf{v}$ is the average electronic velocity. In the absence of an electric field, electrons are as likely to be moving in any one direction as in any other, $\mathbf{v}$ averages to zero, and, as expected, there is no net electric current density. In the presence of a field $\mathbf{E}$, however, there will be a mean electronic velocity directed opposite to the field (the electronic charge being negative), which we can compute as follows:

Consider a typical electron at time zero. Let t be the time elapsed since its last collision. Its velocity at time zero will be its velocity $\mathbf{v}_0$ immediately after that collision plus the additional velocity $-e\mathbf{E}t/m$ it has subsequently acquired. Since we assume that an electron emerges from a collision in a random direction, there will be no contribution from $\mathbf{v}_0$ to the average electronic velocity, which must therefore be given entirely by the average of $-e\mathbf{E}t/m$. However, the average of t is the relaxation time τ. Therefore

$$\mathbf{v}_{\text{avg}} = -\frac{e\mathbf{E}\tau}{m}; \quad \mathbf{j} = \left(\frac{ne^2\tau}{m}\right)\mathbf{E}. \tag{1.5}$$

This result is usually stated in terms of the inverse of the resistivity, the conductivity $\sigma = 1/\rho$:

$$\boxed{\mathbf{j} = \sigma\mathbf{E}; \quad \sigma = \frac{ne^2\tau}{m}.} \tag{1.6}$$

---

[10] In general, $\mathbf{E}$ and $\mathbf{j}$ need not be parallel. One then defines a resistivity *tensor*. See Chapters 12 and 13.

This establishes the linear dependence of **j** on **E** and gives an estimate of the conductivity σ in terms of quantities that are all known except for the relaxation time τ. We may therefore use (1.6) and the observed resistivities to estimate the size of the relaxation time:

$$\tau = \frac{m}{\rho n e^2}. \tag{1.7}$$

Table 1.2 gives the resistivities of several representative metals at several temperatures. Note the strong temperature dependence. At room temperature the resistivity is roughly linear in T, but it falls away much more steeply as low temperatures are

Table 1.2
ELECTRICAL RESISTIVITIES OF SELECTED ELEMENTS[a]

ELEMENT	77 K	273 K	373 K	$\dfrac{(\rho/T)_{373\ \text{K}}}{(\rho/T)_{273\ \text{K}}}$
Li	1.04	8.55	12.4	1.06
Na	0.8	4.2	Melted	
K	1.38	6.1	Melted	
Rb	2.2	11.0	Melted	
Cs	4.5	18.8	Melted	
Cu	0.2	1.56	2.24	1.05
Ag	0.3	1.51	2.13	1.03
Au	0.5	2.04	2.84	1.02
Be		2.8	5.3	1.39
Mg	0.62	3.9	5.6	1.05
Ca		3.43	5.0	1.07
Sr	7	23		
Ba	17	60		
Nb	3.0	15.2	19.2	0.92
Fe	0.66	8.9	14.7	1.21
Zn	1.1	5.5	7.8	1.04
Cd	1.6	6.8		
Hg	5.8	Melted	Melted	
Al	0.3	2.45	3.55	1.06
Ga	2.75	13.6	Melted	
In	1.8	8.0	12.1	1.11
Tl	3.7	15	22.8	1.11
Sn	2.1	10.6	15.8	1.09
Pb	4.7	19.0	27.0	1.04
Bi	35	107	156	1.07
Sb	8	39	59	1.11

[a] Resistivities in microhm centimeters are given at 77 K (the boiling point of liquid nitrogen at atmospheric pressure), 273 K, and 373 K. The last column gives the ratio of ρ/T at 373 K and 273 K to display the approximate linear temperature dependence of the resistivity near room temperature.

Source: G. W. C. Kaye and T. H. Laby, *Table of Physical and Chemical Constants*, Longmans Green, London, 1966.

reached. Room temperature resistivities are typically of the order of microhm centi-meters (μohm-cm) or, in atomic units, of order 10^{-18} statohm-cm.[11] If ρ_μ is the resistivity in microhm centimeters, then a convenient way of expressing the relaxation time implied by (1.7) is

$$\tau = \left(\frac{0.22}{\rho_\mu}\right)\left(\frac{r_s}{a_0}\right)^3 \times 10^{-14} \text{ sec.} \tag{1.8}$$

Relaxation times calculated from (1.8) and the resistivities in Table 1.2 are displayed in Table 1.3. Note that at room temperatures τ is typically 10^{-14} to 10^{-15} sec. In considering whether this is a reasonable number, it is more instructive to contemplate the mean free path, $\ell = v_0\tau$, where v_0 is the average electronic speed. The length ℓ measures the average distance an electron travels between collisions. In Drude's time it was natural to estimate v_0 from classical equipartition of energy: $\frac{1}{2}mv_0^2 = \frac{3}{2}k_BT$. Using the known electronic mass, we find a v_0 of order 10^7 cm/sec at room tem-perature, and hence a mean free path of 1 to 10 Å. Since this distance is comparable to the interatomic spacing, the result is quite consistent with Drude's original view that collisions are due to the electron bumping into the large heavy ions.

However, we shall see in Chapter 2 that this classical estimate of v_0 is an order of magnitude too small at room temperatures. Furthermore, at the lowest tempera-tures in Table 1.3, τ is an order of magnitude larger than at room temperature, while (as we shall see in Chapter 2) v_0 is actually temperature-independent. This can raise the low-temperature mean free path to 10^3 or more angstroms, about a thousand times the spacing between ions. Today, by working at sufficiently low temperatures with carefully prepared samples, mean free paths of the order of centimeters (i.e., 10^8 interatomic spacings) can be achieved. This is strong evidence that the electrons do not simply bump off the ions, as Drude supposed.

Fortunately, however, we may continue to calculate with the Drude model without any precise understanding of the cause of collisions. In the absence of a theory of the collision time it becomes important to find predictions of the Drude model that are independent of the value of the relaxation time τ. As it happens, there are several such τ-independent quantities, which even today remain of fundamental interest, for in many respects the precise quantitative treatment of the relaxation time remains the weakest link in modern treatments of metallic conductivity. As a result, τ-inde-pendent quantities are highly valued, for they often yield considerably more reliable information.

Two cases of particular interest are the calculation of the electrical conductivity when a spatially uniform static magnetic field is present, and when the electric field

---

[11]   To convert resistivities from microhm centimeters to statohm centimeters note that a resistivity of 1 μohm-cm yields an electric field of 10^{-6} volt/cm in the presence of a current of 1 amp/cm^2. Since 1 amp is 3×10^9 esu/sec, and 1 volt is $\frac{1}{300}$ statvolt, a resistivity of 1 μohm-cm yields a field of 1 statvolt/cm when the current density is $300 \times 10^6 \times 3 \times 10^9$ esu-cm^{-2}-sec^{-1}. The statohm-centimeter is the electrostatic unit of resistivity, and therefore gives 1 statvolt/cm with a current density of only 1 esu-cm^{-2}-sec^{-1}. Thus 1 μohm-cm is equivalent to $\frac{1}{9} \times 10^{-17}$ statohm-cm. To avoid using the statohm-centimeter, one may evaluate (1.7) taking ρ in ohm meters, m in kilograms, n in electrons per cubic meter, and e in coulombs. (*Note:* The most important formulas, constants, and conversion factors from Chapters 1 and 2 are sum-marized in Appendix A.)

Table 1.3
DRUDE RELAXATION TIMES IN UNITS OF 10^{-14} SECOND[a]

ELEMENT	77 K	273 K	373 K
Li	7.3	0.88	0.61
Na	17	3.2	
K	18	4.1	
Rb	14	2.8	
Cs	8.6	2.1	
Cu	21	2.7	1.9
Ag	20	4.0	2.8
Au	12	3.0	2.1
Be		0.51	0.27
Mg	6.7	1.1	0.74
Ca		2.2	1.5
Sr	1.4	0.44	
Ba	0.66	0.19	
Nb	2.1	0.42	0.33
Fe	3.2	0.24	0.14
Zn	2.4	0.49	0.34
Cd	2.4	0.56	
Hg	0.71		
Al	6.5	0.80	0.55
Ga	0.84	0.17	
In	1.7	0.38	0.25
Tl	0.91	0.22	0.15
Sn	1.1	0.23	0.15
Pb	0.57	0.14	0.099
Bi	0.072	0.023	0.016
Sb	0.27	0.055	0.036

[a] Relaxation times are calculated from the data in Tables 1.1 and 1.2, and Eq. (1.8). The slight temperature dependence of n is ignored.

is spatially uniform but time-dependent. Both of these cases are most simply dealt with by the following observation:

At any time t the average electronic velocity $\mathbf{v}$ is just $\mathbf{p}(t)/m$, where $\mathbf{p}$ is the total momentum per electron. Hence the current density is

$$\mathbf{j} = -\frac{ne\mathbf{p}(t)}{m}. \tag{1.9}$$

Given that the momentum per electron is $\mathbf{p}(t)$ at time t, let us calculate the momentum per electron $\mathbf{p}(t + dt)$ an infinitesimal time dt later. An electron taken at random at time t will have a collision before time $t + dt$, with probability dt/τ, and will therefore survive to time $t + dt$ without suffering a collision with probability $1 - dt/\tau$. If it experiences no collision, however, it simply evolves under the influence of the force $\mathbf{f}(t)$ (due to the spatially uniform electric and/or magnetic fields) and will therefore

acquire an additional momentum[12] $\mathbf{f}(t)\,dt - O(dt)^2$. The contribution of all those electrons that do not collide between t and $t + dt$ to the momentum per electron at time $t + dt$ is the fraction $(1 - dt/\tau)$ they constitute of all electrons, times *their* average momentum per electron, $\mathbf{p}(t) + \mathbf{f}(t)dt + O(dt)^2$.

Thus neglecting for the moment the contribution to $\mathbf{p}(t + dt)$ from those electrons that *do* undergo a collision in the time between t and $t + dt$, we have[13]

$$\mathbf{p}(t + dt) = \left(1 - \frac{dt}{\tau}\right)\left[\mathbf{p}(t) + \mathbf{f}(t)dt + O(dt)^2\right]$$
$$= \mathbf{p}(t) - \left(\frac{dt}{\tau}\right)\mathbf{p}(t) + \mathbf{f}(t)dt + O(dt)^2. \tag{1.10}$$

The correction to (1.10) due to those electrons that have had a collision in the interval t to $t + dt$ is only of the order of $(dt)^2$. To see this, first note that such electrons constitute a fraction dt/τ of the total number of electrons. Furthermore, since the electronic velocity (and momentum) is randomly directed immediately after a collision, each such electron will contribute to the average momentum $\mathbf{p}(t + dt)$ only to the extent that it has acquired momentum from the force $\mathbf{f}$ since its last collision. Such momentum is acquired over a time no longer than dt, and is therefore of order $\mathbf{f}(t)dt$. Thus the correction to (1.10) is of order $(dt/\tau)\mathbf{f}(t)dt$, and does not affect the terms of linear order in dt. We may therefore write:

$$\mathbf{p}(t + dt) - \mathbf{p}(t) = -\left(\frac{dt}{\tau}\right)\mathbf{p}(t) + \mathbf{f}(t)\,dt + O(dt)^2. \tag{1.11}$$

where the contribution of *all* electrons to $\mathbf{p}(t + dt)$ is accounted for. Dividing this by dt and taking the limit as $dt \to 0$, we find

$$\frac{d\mathbf{p}(t)}{dt} = -\frac{\mathbf{p}(t)}{\tau} + \mathbf{f}(t). \tag{1.12}$$

This simply states that the effect of individual electron collisions is to introduce a frictional damping term into the equation of motion for the momentum per electron.

We now apply (1.12) to several cases of interest.

HALL EFFECT AND MAGNETORESISTANCE

In 1879 E. H. Hall tried to determine whether the force experienced by a current carrying wire in a magnetic field was exerted on the whole wire or only upon (what we would now call) the moving electrons in the wire. He suspected it was the latter, and his experiment was based on the argument that "if the current of electricity in a fixed conductor is itself attracted by a magnet, the current should be drawn to one side of the wire, and therefore the resistance experienced should be increased."[14] His

---

[12]   By $O(dt)^2$ we mean a term of the order of $(dt)^2$.

[13]   If the force on the electrons is not the same for every electron, (1.10) will remain valid provided that we interpret $\mathbf{f}$ as the *average* force per electron.

[14]   *Am. J. Math.* **2**, 287 (1879).

efforts to detect this extra resistance were unsuccessful,[15] but Hall did not regard this as conclusive: "The magnet may *tend* to deflect the current without being able to do so. It is evident that in this case there would exist a state of stress in the conductor, the electricity pressing, as it were, toward one side of the wire." This state of stress should appear as a transverse voltage (known today as the Hall voltage), which Hall was able to observe.

Hall's experiment is depicted in Figure 1.3. An electric field E_x is applied to a wire extending in the x-direction and a current density j_x flows in the wire. In addition, a magnetic field H points in the positive z-direction. As a result the Lorentz force[16]

$$-\frac{e}{c}\mathbf{v} \times \mathbf{H} \tag{1.13}$$

acts to deflect electrons in the negative y-direction (an electron's drift velocity is *opposite* to the current flow). However the electrons cannot move very far in the y-direction before running up against the sides of the wire. As they accumulate there, an electric field builds up in the y-direction that opposes their motion and their further accumulation. In equilibrium this transverse field (or Hall field) E_y will balance the Lorentz force, and current will flow only in the x-direction.
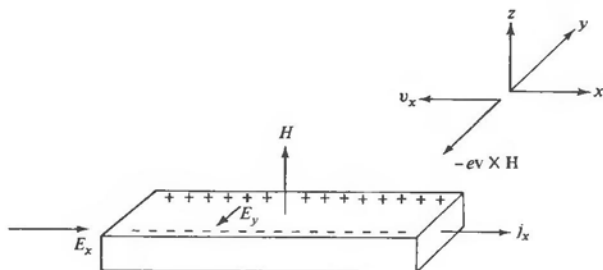

Figure 1.3
Schematic view of Hall's experiment.

There are two quantities of interest. One is the ratio of the field along the wire E_x to the current density j_x,

$$\rho(H) = \frac{E_x}{j_x}. \tag{1.14}$$

This is the magnetoresistance,[17] which Hall found to be field-independent. The other is the size of the transverse field E_y. Since it balances the Lorentz force, one might expect it to be proportional both to the applied field H and to the current along the

---

[15]   The increase in resistance (known as the magnetoresistance) does occur, as we shall see in Chapters 12 and 13. The Drude model, however, predicts Hall's null result.

[16]   When dealing with nonmagnetic (or weakly magnetic) materials, we shall always call the field H, the difference between B and H being extremely small.

[17]   More precisely, it is the transverse magnetoresistance. There is also a longitudinal magneto-resistance, measured with the magnetic field parallel to the current.

wire j_x. One therefore defines a quantity known as the Hall coefficient by

$$R_H = \frac{E_y}{j_x H}. \tag{1.15}$$

Note that since the Hall field is in the negative y-direction (Figure 1.3), R_H should be negative. If, on the other hand, the charge carriers were positive, then the sign of their x-velocity would be reversed, and the Lorentz force would therefore be unchanged. As a consequence the Hall field would be opposite to the direction it has for negatively charged carriers. This is of great importance, for it means that a measurement of the Hall field determines the sign of the charge carriers. Hall's original data agreed with the sign of the electronic charge later determined by Thomson. One of the remarkable aspects of the Hall effect, however, is that in some metals the Hall coefficient is positive, suggesting that the carriers have a charge opposite to that of the electron. This is another mystery whose solution had to await the full quantum theory of solids. In this chapter we shall consider only the simple Drude model analysis, which though incapable of accounting for positive Hall coefficients, is often in fairly good agreement with experiment.

To calculate the Hall coefficient and magnetoresistance we first find the current densities j_x and j_y in the presence of an electric field with arbitrary components E_x and E_y, and in the presence of a magnetic field H along the z-axis. The (position independent) force acting on each electron is $\mathbf{f} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{H}/c)$, and therefore Eq. (1.12) for the momentum per electron becomes[18]

$$\frac{d\mathbf{p}}{dt} = -e\left(\mathbf{E} + \frac{\mathbf{p}}{mc} \times \mathbf{H}\right) - \frac{\mathbf{p}}{\tau}. \tag{1.16}$$

In the steady state the current is independent of time, and therefore p_x and p_y will satisfy

$$0 = -eE_x - \omega_c p_y - \frac{p_x}{\tau}, \tag{1.17}$$

$$0 = -eE_y + \omega_c p_x - \frac{p_y}{\tau},$$

where

$$\omega_c = \frac{eH}{mc}. \tag{1.18}$$

We multiply these equations by $-ne\tau/m$ and introduce the current density components through (1.4) to find

$$\sigma_0 E_x = \omega_c \tau j_y + j_x,$$
$$\sigma_0 E_y = -\omega_c \tau j_x + j_y, \tag{1.19}$$

where σ_0 is just the Drude model DC conductivity in the absence of a magnetic field, given by (1.6).

---

[18] Note that the Lorentz force is not the same for each electron since it depends on the electronic velocity $\mathbf{v}$. Therefore the force $\mathbf{f}$ in (1.12) is to be taken as the average force per electron (see Footnote 13). Because, however, the force depends on the electron on which it acts only through a term *linear* in the electron's velocity, the average force is obtained simply by replacing that velocity by the average velocity, $\mathbf{p}/m$.

The Hall field E_y is determined by the requirement that there be no transverse current j_y. Setting j_y to zero in the second equation of (1.19) we find that

$$E_y = -\left(\frac{\omega_c \tau}{\sigma_0}\right) j_x = -\left(\frac{H}{nec}\right) j_x. \tag{1.20}$$

Therefore the Hall coefficient (1.15) is

$$R_H = -\frac{1}{nec}. \tag{1.21}$$

This is a very striking result, for it asserts that the Hall coefficient depends on no parameters of the metal except the density of carriers. Since we have already calculated n assuming that the atomic valence electrons become the metallic conduction electrons, a measurement of the Hall constant provides a direct test of the validity of this assumption.

In trying to extract the electron density n from measured Hall coefficients one is faced with the problem that, contrary to the prediction of (1.21), they generally do depend on magnetic field. Furthermore, they depend on temperature and on the care with which the sample has been prepared. This result is somewhat unexpected, since the relaxation time τ, which can depend strongly on temperature and the condition of the sample, does not appear in (1.21). However, at very low temperatures in very pure, carefully prepared samples at very high fields, the measured Hall constants do appear to approach a limiting value. The more elaborate theory of Chapters 12 and 13 predicts that for many (but not all) metals this limiting value is precisely the simple Drude result (1.21).

Some Hall coefficients at high and moderate fields are listed in Table 1.4. Note the occurrence of cases in which R_H is actually positive, apparently corresponding to carriers with a positive charge. A striking example of observed field dependence totally unexplained by Drude theory is shown in Figure 1.4.

The Drude result confirms Hall's observation that the resistance does not depend on field, for when $j_y = 0$ (as is the case in the steady state when the Hall field has been established), the first equation of (1.19) reduces to $j_x = \sigma_0 E_x$, the expected result for the conductivity in zero magnetic field. However, more careful experiments on a variety of metals have revealed that there is a magnetic field dependence to the resistance, which can be quite dramatic in some cases. Here again the quantum theory of solids is needed to explain why the Drude result applies in some metals and to account for some truly extraordinary deviations from it in others.

Before leaving the subject of DC phenomena in a uniform magnetic field, we note for future applications that the quantity $\omega_c \tau$ is an important, dimensionless measure of the strength of a magnetic field. When $\omega_c \tau$ is small, Eq. (1.19) gives $\mathbf{j}$ very nearly parallel to $\mathbf{E}$, as in the absence of a magnetic field. In general, however, $\mathbf{j}$ is at an angle ϕ (known as the Hall angle) to $\mathbf{E}$, where (1.19) gives $\tan \phi = \omega_c \tau$. The quantity ω_c, known as the cyclotron frequency, is simply the angular frequency of revolution[19]

---

[19]   In a uniform magnetic field the orbit of an electron is a spiral along the field whose projection in a plane perpendicular to the field is a circle. The angular frequency ω_c is determined by the condition that the centripetal acceleration $\omega_c^2 r$ be provided by the Lorentz force, $(e/c)(\omega_c r)H$.

Table 1.4
**HALL COEFFICIENTS OF SELECTED ELEMENTS
IN MODERATE TO HIGH FIELDS[a]**

| METAL	VALENCE	$-1/R_H nec$
Li	1	0.8
Na	1	1.2
K	1	1.1
Rb	1	1.0
Cs	1	0.9
Cu	1	1.5
Ag	1	1.3
Au	1	1.5
Be	2	−0.2
Mg	2	−0.4
In	3	−0.3
Al	3	−0.3

[a] These are roughly the limiting values assumed by R_H as the field becomes very large (of order 10^4 G), and the temperature very low, in carefully prepared specimens. The data are quoted in the form n_0/n, where n_0 is the density for which the Drude form (1.21) agrees with the measured R_H: $n_0 = -1/R_H ec$. Evidently the alkali metals obey the Drude result reasonably well, the noble metals (Cu, Ag, Au) less well, and the remaining entries, not at all.

of a free electron in the magnetic field H. Thus $\omega_c \tau$ will be small if electrons can complete only a small part of a revolution between collisions, and large if they can complete many revolutions. Alternatively, when $\omega_c \tau$ is small the magnetic field deforms the electronic orbits only slightly, but when $\omega_c \tau$ is comparable to unity or larger, the effect of the magnetic field on the electronic orbits is quite drastic. A useful numerical evaluation of the cyclotron frequency is

$$\nu_c \,(10^9 \text{ hertz}) = 2.80 \times H \text{ (kilogauss)}, \qquad \omega_c = 2\pi\nu_c. \qquad (1.22)$$

Figure 1.4
The quantity $n_0/n = -1/R_H nec$, for aluminum, as a function of $\omega_c \tau$. The free electron density n is based on a nominal chemical valence of 3. The high field value suggests only one carrier per primitive cell, with a positive charge. (From R. Lück, *Phys. Stat. Sol.* **18**, 49 (1966).)
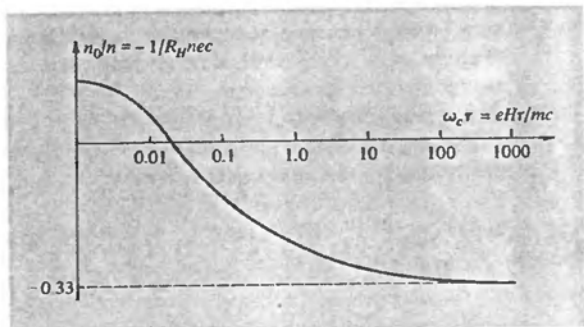
AC ELECTRICAL CONDUCTIVITY OF A METAL

To calculate the current induced in a metal by a time-dependent electric field, we write the field in the form

$$E(t) = \text{Re} \, (E(\omega)e^{-i\omega t}). \tag{1.23}$$

The equation of motion (1.12) for the momentum per electron becomes

$$\frac{d\mathbf{p}}{dt} = -\frac{\mathbf{p}}{\tau} - e\mathbf{E}. \tag{1.24}$$

We seek a steady-state solution of the form

$$\mathbf{p}(t) = \text{Re} \, (\mathbf{p}(\omega)e^{-i\omega t}). \tag{1.25}$$

Substituting the complex $\mathbf{p}$ and $\mathbf{E}$ into (1.24), which must be satisfied by both the real and imaginary parts of any complex solution, we find that $\mathbf{p}(\omega)$ must satisfy

$$-i\omega\mathbf{p}(\omega) = -\frac{\mathbf{p}(\omega)}{\tau} - e\mathbf{E}(\omega). \tag{1.26}$$

Since $\mathbf{j} = -ne\mathbf{p}/m$, the current density is just

$$\mathbf{j}(t) = \text{Re} \, (\mathbf{j}(\omega)e^{-i\omega t}),$$
$$\mathbf{j}(\omega) = -\frac{ne\mathbf{p}(\omega)}{m} = \frac{(ne^2/m)\mathbf{E}(\omega)}{(1/\tau) - i\omega}. \tag{1.27}$$

One customarily writes this result as

$$\mathbf{j}(\omega) = \sigma(\omega)\mathbf{E}(\omega), \tag{1.28}$$

where $\sigma(\omega)$, known as the frequency-dependent (or AC) conductivity, is given by

$$\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau}, \quad \sigma_0 = \frac{ne^2\tau}{m}. \tag{1.29}$$

Note that this correctly reduces to the DC Drude result (1.6) at zero frequency.

The most important application of this result is to the propagation of electromagnetic radiation in a metal. It might appear that the assumptions we made to derive (1.29) would render it inapplicable to this case, since (a) the E field in an electromagnetic wave is accompanied by a perpendicular magnetic field H of the same magnitude,[20] which we have not included in (1.24), and (b) the fields in an electromagnetic wave vary in space as well as time, whereas Eq. (1.12) was derived by assuming a spatially uniform force.

The first complication can always be ignored. It leads to an additional term $-e\mathbf{p}/mc \times H$ in (1.24), which is smaller than the term in E by a factor v/c, where v is the magnitude of the mean electronic velocity. But even in a current as large as 1 amp/mm², $v = j/ne$ is only of order 0.1 cm/sec. Hence the term in the magnetic field is typically 10^{-10} of the term in the electric field and can quite correctly be ignored.

---

[20]   One of the more appealing features of CGS units.

The second point raises more serious questions. Equation (1.12) was derived by assuming that at any time the same force acts on each electron, which is not the case if the electric field varies in space. Note, however, that the current density at point **r** is entirely determined by what the electric field has done to each electron at **r** since its last collision. This last collision, in the overwhelming majority of cases, takes place no more than a few mean free paths away from **r**. Therefore if the field does not vary appreciably over distances comparable to the electronic mean free path, we may correctly calculate $\mathbf{j}(\mathbf{r}, t)$, the current density at point **r**, by taking the field everywhere in space to be given by its value $\mathbf{E}(\mathbf{r}, t)$ at the point **r**. The result,

$$\mathbf{j}(\mathbf{r}, \omega) = \sigma(\omega)\mathbf{E}(\mathbf{r}, \omega), \tag{1.30}$$

is therefore valid whenever the wavelength λ of the field is large compared to the electronic mean free path ℓ. This is ordinarily satisfied in a metal by visible light (whose wavelength is of the order of 10^3 to 10^4 Å). When it is not satisfied, one must resort to so-called nonlocal theories, of greater complexity.

Assuming, then, that the wavelength is large compared to the mean free path, we may proceed as follows: in the presence of a specified current density **j** we may write Maxwell's equations as[21]

$$\nabla \cdot \mathbf{E} = 0; \quad \nabla \cdot \mathbf{H} = 0; \quad \nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{H}}{\partial t};$$

$$\nabla \times \mathbf{H} = \frac{4\pi}{c}\mathbf{j} + \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t}. \tag{1.31}$$

We look for a solution with time dependence $e^{-i\omega t}$, noting that in a metal we can write **j** in terms of **E** via (1.28). We then find

$$\nabla \times (\nabla \times \mathbf{E}) = -\nabla^2\mathbf{E} = \frac{i\omega}{c}\nabla \times \mathbf{H} = \frac{i\omega}{c}\left(\frac{4\pi\sigma}{c}\mathbf{E} - \frac{i\omega}{c}\mathbf{E}\right), \tag{1.32}$$

or

$$-\nabla^2\mathbf{E} = \frac{\omega^2}{c^2}\left(1 + \frac{4\pi i\sigma}{\omega}\right)\mathbf{E}. \tag{1.33}$$

This has the form of the usual wave equation,

$$-\nabla^2\mathbf{E} = \frac{\omega^2}{c^2}\epsilon(\omega)\mathbf{E}, \tag{1.34}$$

with a complex dielectric constant given by

$$\epsilon(\omega) = 1 + \frac{4\pi i\sigma}{\omega}. \tag{1.35}$$

If we are at frequencies high enough to satisfy

$$\omega\tau \gg 1, \tag{1.36}$$

---

[21]   We are considering here an electromagnetic wave, in which the induced charge density ρ vanishes. Below we examine the possibility of oscillations in the charge density.

then, to a first approximation, Eqs. (1.35) and (1.29) give

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}. \tag{1.37}$$

where ω_p, known as the plasma frequency, is given by

$$\omega_p^2 = \frac{4\pi n e^2}{m}. \tag{1.38}$$

When ϵ is real and negative ($\omega < \omega_p$) the solutions to (1.34) decay exponentially in space; i.e., no radiation can propagate. However, when ϵ is positive ($\omega > \omega_p$) the solutions to (1.34) become oscillatory, radiation can propagate, and the metal should become transparent. This conclusion is only valid, of course, if our high-frequency assumption (1.36) is satisfied in the neighborhood of $\omega = \omega_p$. If we express τ in terms of the resistivity through Eq. (1.8), then we can use the definition (1.38) of the plasma frequency to compute that

$$\omega_p \tau = 1.6 \times 10^2 \left(\frac{r_s}{a_0}\right)^{3/2} \left(\frac{1}{\rho_\mu}\right). \tag{1.39}$$

Since the resistivity in microhm centimeters, ρ_μ, is of the order of unity or less, and since r_s/a_0 is in the range from 2 to 6, the high frequency condition (1.36) will be well satisfied at the plasma frequency.

The alkali metals have, in fact, been observed to become transparent in the ultraviolet. A numerical evaluation of (1.38) gives the frequency at which transparency should set in as

$$v_p = \frac{\omega_p}{2\pi} = 11.4 \times \left(\frac{r_s}{a_0}\right)^{-3/2} \times 10^{15} \text{ Hz} \tag{1.40}$$

or

$$\lambda_p = \frac{c}{v_p} = 0.26 \left(\frac{r_s}{a_0}\right)^{3/2} \times 10^3 \text{ Å}. \tag{1.41}$$

In Table 1.5 we list the threshold wavelengths calculated from (1.41), along with the

Table 1.5
OBSERVED AND THEORETICAL WAVELENGTHS BELOW WHICH THE ALKALI METALS BECOME TRANSPARENT

ELEMENT	THEORETICAL[a] λ (10^3 Å)	OBSERVED λ (10^3 Å)
Li	1.5	2.0
Na	2.0	2.1
K	2.8	3.1
Rb	3.1	3.6
Cs	3.5	4.4

[a] From Eq. (1.41).
Source: M. Born and E. Wolf, *Principles of Optics*, Pergamon, New York, 1964.

observed thresholds. The agreement between theory and experiment is rather good. As we shall see, the actual dielectric constant of a metal is far more complicated than (1.37) and it is to some extent a piece of good fortune that the alkali metals so strikingly display this Drude behavior. In other metals different contributions to the dielectric constant compete quite substantially with the "Drude term" (1.37).

A second important consequence of (1.37) is that the electron gas can sustain charge density oscillations. By this we mean a disturbance in which the electric charge density[22] has an oscillatory time dependence $e^{-i\omega t}$. From the equation of continuity,

$$\nabla \cdot \mathbf{j} = -\frac{\partial \rho}{\partial t}, \quad \nabla \cdot \mathbf{j}(\omega) = i\omega\rho(\omega), \tag{1.42}$$

and Gauss's law,

$$\nabla \cdot \mathbf{E}(\omega) = 4\pi\rho(\omega), \tag{1.43}$$

we find, in view of Eq. (1.30), that

$$i\omega\rho(\omega) = 4\pi\sigma(\omega)\rho(\omega). \tag{1.44}$$

This has a solution provided that

$$1 + \frac{4\pi i\sigma(\omega)}{\omega} = 0, \tag{1.45}$$

which is precisely the condition we found above for the onset of propagation of radiation. In the present context it emerges as the condition the frequency must meet if a charge density wave is to propagate.

The nature of this charge density wave, known as a plasma oscillation or plasmon, can be understood in terms of a very simple model.[23] Imagine displacing the entire electron gas, as a whole, through a distance d with respect to the fixed positive background of the ions (Figure 1.5).[24] The resulting surface charge gives rise to an electric field of magnitude $4\pi\sigma$, where σ is the charge per unit area[25] at either end of the slab.

Figure 1.5
Simple model of a plasma oscillation.

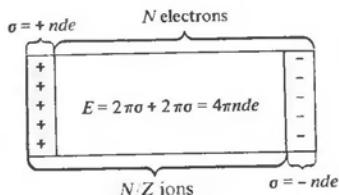
22 The charge density ρ should not be confused with the resistivity, also generally denoted by ρ. The context will always make it clear which is being referred to.

23 Since the field of a uniform plane of charge is independent of the distance from the plane, this crude argument, which places all of the charge density on two opposite surfaces, is not as crude as it appears at first glance.

24 We observed earlier that the Drude model does take the electron-ion interaction into account by acknowledging that the attraction to the positively charged ions confines the electrons to the interior of the metal. In this simple model of a plasma oscillation it is precisely this attraction that provides the restoring force.

25 The surface charge density σ should not be confused with the conductivity, also generally denoted by σ.

Consequently the electron gas as a whole will obey the equation of motion:

$$N m \ddot{d} = -Ne|4\pi\sigma| = -Ne\,(4\pi nde) = -4\pi ne^2 Nd, \qquad (1.46)$$

which leads to oscillation at the plasma frequency.

Few direct observations have been made of plasmons. Perhaps the most notable is the observation of energy losses in multiples of $\hbar\omega_p$ when electrons are fired through thin, metallic films.[26] Nevertheless, the possibility of their excitation in the course of other electronic processes must always be borne in mind.

THERMAL CONDUCTIVITY OF A METAL

The most impressive success of the Drude model at the time it was proposed was its explanation of the empirical law of Wiedemann and Franz (1853). The Wiedemann-Franz law states that the ratio, κ/σ, of the thermal to the electrical conductivity of a great number of metals is directly proportional to the temperature, with a proportionality constant which is to a fair accuracy the same for all metals. This remarkable regularity can be seen in Table 1.6, where measured thermal conductivities are given for several metals at 273 K and 373 K, along with the ratios $\kappa/\sigma T$ (known as the Lorenz number) at the two temperatures.

In accounting for this the Drude model assumes that the bulk of the thermal current in a metal is carried by the conduction electrons. This assumption is based on the empirical observation that metals conduct heat much better than insulators do. Thus thermal conduction by the ions[27] (present in both metals and insulators) is much less important than thermal conduction by the conduction electrons (present only in metals).

To define and estimate the thermal conductivity, consider a metal bar along which the temperature varies slowly. If there were no sources and sinks of heat at the ends of the bar to maintain the temperature gradient, then the hot end would cool and the cool end would warm, i.e., thermal energy would flow in a sense opposite to the temperature gradient. By supplying heat to the hot end as fast as it flows away, one can produce a steady state in which both a temperature gradient and a uniform flow of thermal energy are present. We define the thermal current density $\mathbf{j}^q$ to be a vector parallel to the direction of heat flow, whose magnitude gives the thermal energy per unit time crossing a unit area perpendicular to the flow.[28] For small temperature gradients the thermal current is observed to be proportional to ∇T (Fourier's law):

$$\mathbf{j}^q = -\kappa\,\nabla T. \qquad (1.47)$$

The proportionality constant κ is known as the thermal conductivity, and is positive, since the thermal current flows opposite to the direction of the temperature gradient.

---

[26]   C. J. Powell and J. B. Swan, *Phys. Rev.* **115**, 869 (1959).

[27]   Although the metallic ions cannot wander through the metal, there *is* a way in which they can transport thermal energy (though not electric charge): the ions can vibrate a little about their mean positions, leading to the transmission of thermal energy in the form of elastic waves propagating through the network of ions. See Chapter 25.

[28]   Note the analogy to the definition of the electrical current density **j**, as well as the analogy between the laws of Ohm and Fourier.

Table 1.6
EXPERIMENTAL THERMAL CONDUCTIVITIES AND LORENZ NUMBERS OF SELECTED METALS

ELEMENT	273 K		373 K	
	κ (watt/cm-K)	$\kappa/\sigma T$ (watt-ohm/K^2)	κ (watt/cm-K)	$\kappa/\sigma T$ (watt-ohm/K^2)
Li	0.71	2.22×10^{-8}	0.73	2.43×10^{-8}
Na	1.38	2.12		
K	1.0	2.23		
Rb	0.6	2.42		
Cu	3.85	2.20	3.82	2.29
Ag	4.18	2.31	4.17	2.38
Au	3.1	2.32	3.1	2.36
Be	2.3	2.36	1.7	2.42
Mg	1.5	2.14	1.5	2.25
Nb	0.52	2.90	0.54	2.78
Fe	0.80	2.61	0.73	2.88
Zn	1.13	2.28	1.1	2.30
Cd	1.0	2.49	1.0	
Al	2.38	2.14	2.30	2.19
In	0.88	2.58	0.80	2.60
Tl	0.5	2.75	0.45	2.75
Sn	0.64	2.48	0.60	2.54
Pb	0.38	2.64	0.35	2.53
Bi	0.09	3.53	0.08	3.35
Sb	0.18	2.57	0.17	2.69

Source: G. W. C. Kaye and T. H. Laby, *Table of Physical and Chemical Constants*, Longmans Green, London, 1966.

As a concrete example let us examine a case where the temperature drop is uniform in the positive x-direction. In the steady state the thermal current will also flow in the x-direction and have a magnitude $j^q = -\kappa\, dT/dx$. To calculate the thermal current we note (assumption 4, page 6) that after each collision an electron emerges with a speed appropriate to the local temperature; the hotter the place of the collision, the more energetic the emerging electron. Consequently, even though the mean electronic velocity at a point may vanish (in contrast to the case when an electric current flows) electrons arriving at the point from the high-temperature side will have higher energies than those arriving from the low-temperature side leading to a net flow of thermal energy toward the low-temperature side (Figure 1.6).

To extract a quantitative estimate of the thermal conductivity from this picture, consider first an oversimplified "one-dimensional" model, in which the electrons can only move along the x-axis, so that at a point x half the electrons come from the high-temperature side of x, and half from the low. If $\mathcal{E}(T)$ is the thermal energy per electron in a metal in equilibrium at temperature T, then an electron whose last collision was at x' will, on the average, have a thermal energy $\mathcal{E}(T[x'])$. The electrons arriving at x from the high-temperature side will, on the average, have had their last collision at
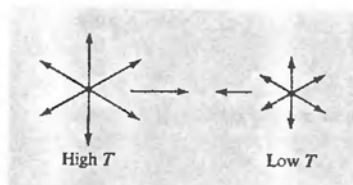
Figure 1.6
Schematic view of the relation between temperature gradient and thermal current. Electrons arriving at the center of the bar from the left had their last collision in the high-temperature region. Those arriving at the center from the right had their last collision in the low-temperature region. Hence electrons moving to the right at the center of the bar tend to be more energetic than those moving to the left, yielding a net thermal current to the right.

$x - v\tau$, and will therefore carry a thermal energy per electron of size $\mathcal{E}(T[x - v\tau])$. Their contribution to the thermal current density at x will therefore be the number of such electrons per unit volume, $n/2$, times their velocity, v, times this energy, or $(n/2)v\mathcal{E}(T[x - v\tau])$. The electrons arriving at x from the low-temperature side, on the other hand, will contribute $(n/2)(-v)[\mathcal{E}(T[x + v\tau])]$, since they have come from the positive x-direction and are moving toward negative x. Adding these together gives

$$j^q = \tfrac{1}{2}nv[\mathcal{E}(T[x - v\tau]) - \mathcal{E}(T[x + v\tau])]. \tag{1.48}$$

Provided that the variation in temperature over a mean free path ($\ell = v\tau$) is very small,[29] we may expand this about the point x to find:

$$j^q = nv^2\tau \frac{d\mathcal{E}}{dT}\left(-\frac{dT}{dx}\right). \tag{1.49}$$

To go from this to the three-dimensional case we need only replace v by the x-component v_x of the electronic velocity $\mathbf{v}$, and average over all directions. Since[30] $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \tfrac{1}{3}v^2$, and since $n\, d\mathcal{E}/dT = (N/V)d\mathcal{E}/dT = (dE/dT)/V = c_v$, the electronic specific heat, we have:

$$\mathbf{j}^q = \tfrac{1}{3}v^2\tau c_v(-\nabla T) \tag{1.50}$$

or

$$\kappa = \tfrac{1}{3}v^2\tau c_v = \tfrac{1}{3}\ell v c_v, \tag{1.51}$$

where v^2 is the mean square electronic speed.

We emphasize the roughness of this argument. We have spoken rather glibly about the thermal energy per electron carried by a particular group of electrons, a quantity one might be hard pressed to define with precision. We have also been quite careless about replacing quantities, at various stages of the calculation, by their thermal averages. One might object, for example, that if the thermal energy per electron depends on the direction the electrons come from, so will their average speed, since this too depends on the temperature at the place of their last collision. We shall note below that this last oversight is canceled by yet another oversight, and in Chapter 13

---

[29]   Its change in ℓ is (ℓ/L) times its change in the sample length L.

[30]   In equilibrium the velocity distribution is isotropic. Corrections to this due to the temperature gradient are exceedingly small.

we shall find by a more rigorous argument that the result (1.51) is quite close to (and, in special circumstances, precisely) the correct one.

Given the estimate (1.51), we can derive another result independent of the mysteries buried in the relaxation time τ, by dividing the thermal conductivity by the electrical conductivity (1.6):

$$\frac{\kappa}{\sigma} = \frac{\frac{1}{3}c_v m v^2}{n e^2}. \tag{1.52}$$

It was natural for Drude to apply the classical ideal gas laws in evaluating the electronic specific heat and mean square velocity. He therefore in effect took c_v to be $\frac{3}{2}n k_B$ and $\frac{1}{2}m v^2$ to be $\frac{3}{2}k_B T$, where k_B is Boltzmann's constant, 1.38×10^{-16} erg/K. This leads to the result

$$\frac{\kappa}{\sigma} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2 T. \tag{1.53}$$

The right side of (1.53) is proportional to T and depends only on the universal constants k_B and e, in complete agreement with the law of Wiedemann and Franz. Equation (1.53) gives a Lorenz number[31]

$$\frac{\kappa}{\sigma T} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2 = 1.24 \times 10^{-13} \; (\text{erg/esu-K})^2$$
$$= 1.11 \times 10^{-8} \; \text{watt-ohm/K}^2, \tag{1.54}$$

which is about half the typical value given in Table 1.6. In his original calculation of the electrical conductivity, Drude erroneously found half the correct result (1.6), as a result of which he found a value $\kappa/\sigma T = 2.22 \times 10^{-8}$ watt-ohm/K^2, in extraordinary agreement with experiment.

This success, though wholly fortuitous, was so impressive as to spur further investigations with the model. It was, however, quite puzzling, since no electronic contribution to the specific heat remotely comparable to $\frac{3}{2}n k_B$ was ever observed. Indeed, at room temperature there appeared to be no electronic contribution to the specific heat measured at all. In Chapter 2 we shall find that the classical ideal gas laws cannot be applied to the electron gas in a metal. Drude's impressive success, aside from his factor-of-two mistake, is a consequence of two errors of about 100 that cancel: at room temperature the actual electronic contribution to the specific heat is about 100 times smaller than the classical prediction, but the mean square electronic speed is about 100 times larger.

We shall examine the correct theory of the equilibrium thermal properties of the free electron gas in Chapter 2, and shall return to a more correct analysis of the thermal conductivity of a metal in Chapter 13. Before leaving the subject of thermal transport, however, we should correct one oversimplification in our analysis that obscures an important physical phenomenon:

We calculated the thermal conductivity by ignoring all manifestations of the temperature gradient except for the fact that the thermal energy carried by a group

---

[31] Since (joule/coulomb)^2 = (watt/amp)^2 = watt-ohm, the practical units in which Lorenz numbers are quoted are often called watt-ohm/K^2, instead of (joule/coulomb-K)^2.

of electrons depends on the temperature at the place of their last collision. But if electrons emerge from a collision with higher energies when the temperature is higher, they will also have higher speeds. It would therefore appear that we should let the electron's speed v as well as its contribution to the thermal energy depend on the place of the last collision. As it turns out such an additional term only alters the result by a factor of the order of unity, but we were in fact quite right to ignore such a correction. It is true that immediately after the temperature gradient is applied there will be a nonvanishing mean electronic velocity directed toward the low-temperature region. Since the electrons are charged, however, this velocity will result in an electric current. But thermal conductivity measurements are performed under open-circuit conditions, in which no electric current can flow. Therefore the electric current can continue only until enough charge has accumulated at the surface of the sample to build up a re-tarding electric field that opposes the further accumulation of charge, and hence precisely cancels the effect of the temperature gradient on the electronic mean ve-locity.[32] When the steady state is reached there will be no electric current flow, and we were therefore correct in assuming that the mean electronic velocity at a point vanished.

In this way we are led to consider another physical effect: A temperature gradient in a long, thin bar should be accompanied by an electric field directed opposite to the temperature gradient. The existence of such a field, known as the thermoelectric field, has been known for some time (the Seebeck effect). The field is conventionally written as

$$E = Q\nabla T, \tag{1.55}$$

and the proportionality constant Q is known as the thermopower. To estimate the thermopower note that in our "one-dimensional" model the mean electronic velocity at a point x due to the temperature gradient is

$$v_Q = \tfrac{1}{2}[v(x - v\tau) - v(x + v\tau)] = -\tau v \frac{dv}{dx}$$

$$= -\tau \frac{d}{dx}\left(\frac{v^2}{2}\right). \tag{1.56}$$

We can again generalize to three dimensions[33] by letting $v^2 \to v_x^2$, and noting that $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \tfrac{1}{3}v^2$. so that

$$v_Q = -\frac{\tau}{6}\frac{dv^2}{dT}(\nabla T). \tag{1.57}$$

The mean velocity due to the electric field is[34]

$$v_E = -\frac{eE\tau}{m}. \tag{1.58}$$

---

[32] See the analogous discussion of the genesis of the Hall field on page 12.
[33] Cf. the discussion leading from Eq. (1.49) to Eq. (1.50).
[34] See the discussion on page 7.

To have $\mathbf{v}_Q + \mathbf{v}_E = 0$, we require that

$$Q = -\left(\frac{1}{3e}\right)\frac{d}{dT}\frac{mv^2}{2} = -\frac{c_v}{3ne}. \tag{1.59}$$

This result is also independent of the relaxation time. Drude evaluated it by another inappropriate application of classical statistical mechanics, setting c_v equal to $3nk_B/2$ to find that

$$Q = -\frac{k_B}{2e} = -0.43 \times 10^{-4} \text{ volt/K}. \tag{1.60}$$

Observed metallic thermopowers at room temperature are of the order of microvolts per degree, a factor of 100 smaller. This is the same error of 100 that appeared twice in Drude's derivation of the Wiedemann-Franz law, but being now uncompensated, it offers unambiguous evidence of the inadequacy of classical statistical mechanics in describing the metallic electron gas.

With the use of quantum statistical mechanics one removes this discrepancy. However, in some metals the sign of the thermopower—the direction of the thermo-electric field—is opposite to what the Drude model predicts. This is as mysterious as the discrepancies in the sign of the Hall coefficient. The quantum theory of solids can account for a sign reversal in the thermopower as well, but one's sense of triumph is somewhat tempered in this case, for a really quantitative theory of the thermo-electric field is still lacking. We shall note in later discussions some of the peculiarities of this phenomenon that make it particularly difficult to calculate with precision.

These last examples have made it clear that we cannot proceed very far with a free electron theory without a proper use of quantum statistics. This is the subject of Chapter 2.

PROBLEMS

1. *Poisson Distribution*

In the Drude model the probability of an electron suffering a collision in any infinitesimal interval dt is just dt/τ.

(a)   Show that an electron picked at random at a given moment had no collision during the preceding t seconds with probability $e^{-t/\tau}$. Show that it will have no collision during the next t seconds with the same probability.

(b)   Show that the probability that the time interval between two successive collisions of an electron falls in the range between t and $t + dt$ is $(dt/\tau)e^{-t/\tau}$.

(c)   Show as a consequence of (a) that at any moment the mean time back to the last collision (or up to the next collision) averaged over all electrons is τ.

(d)   Show as a consequence of (b) that the mean time between successive collisions of an electron is τ.

(e)   Part (c) implies that at any moment the time T between the last and next collision averaged over all electrons is 2τ. Explain why this is not inconsistent with the result in (d). (A

thorough explanation should include a derivation of the probability distribution for T.) A failure to appreciate this subtlety led Drude to a conductivity only half of (1.6). He did not make the same mistake in the thermal conductivity, whence the factor of two in his calculation of the Lorenz number (see page 23).

2.   Joule Heating

Consider a metal at uniform temperature in a static uniform electric field E. An electron experiences a collision, and then, after a time t, a second collision. In the Drude model, energy is not conserved in collisions, for the mean speed of an electron emerging from a collision does not depend on the energy that the electron acquired from the field since the time of the preceding collision (assumption 4, page 6).

(a)   Show that the average energy lost to the ions in the second of two collisions separated by a time t is $(eEt)^2/2m$. (The average is over all directions in which the electron emerged from the first collision.)

(b)   Show, using the result of Problem 1(b), that the average energy loss to the ions per electron per collision is $(eE\tau)^2/m$, and hence that the average loss per cubic centimeter per second is $(ne^2\tau/m)E^2 = \sigma E^2$. Deduce that the power loss in a wire of length L and cross section A is I^2R, where I is the current flowing and R is the resistance of the wire.

3.   Thomson Effect

Suppose that in addition to the applied electric field in Problem 2 there is also a uniform temperature gradient ∇T in the metal. Since an electron emerges from a collision at an energy determined by the local temperature, the energy lost in collisions will depend on how far down the temperature gradient the electron travels between collisions, as well as on how much energy it has gained from the electric field. Consequently the power lost will contain a term proportional to $E \cdot \nabla T$ (which is easily isolated from other terms since it is the only term in the second-order energy loss that changes sign when the sign of E is reversed). Show that this contribution is given in the Drude model by a term of order $(ne\tau/m)(d\varepsilon/dT)(E \cdot \nabla T)$, where ε is the mean thermal energy per electron. (Calculate the energy lost by a typical electron colliding at r, which made its last collision at $r - d$. Assuming a fixed (that is, energy-independent) relaxation time τ, d can be found to linear order in the field and temperature gradient by simple kinematic arguments, which is enough to give the energy loss to second order.)

4.   Helicon Waves

Suppose that a metal is placed in a uniform magnetic field H along the z-axis. Let an AC electric field $Ee^{-i\omega t}$ be applied perpendicular to H.

(a)   If the electric field is circularly polarized ($E_y = \pm iE_x$) show that Eq. (1.28) must be generalized to

$$j_x = \left(\frac{\sigma_0}{1 - i(\omega \mp \omega_c)\tau}\right)E_x, \quad j_y = \pm ij_x, \quad j_z = 0. \tag{1.61}$$

(b)   Show that, in conjunction with (1.61), Maxwell's equations (1.31) have a solution

$$E_x = E_0e^{i(kz - \omega t)}, \quad E_y = \pm iE_x, \quad E_z = 0, \tag{1.62}$$

provided that $k^2c^2 = \epsilon\omega^2$, where

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega}\left(\frac{1}{\omega \mp \omega_c + i/\tau}\right). \tag{1.63}$$

(c)   Sketch $\epsilon(\omega)$ for $\omega > 0$ (choosing the polarization $E_y = iE_x$) and demonstrate that solutions to $k^2c^2 = \epsilon\omega^2$ exist for arbitrary k at frequencies $\omega > \omega_p$ and $\omega < \omega_c$. (Assume the high field condition $\omega_c\tau \gg 1$, and note that even for hundreds of kilogauss, $\omega_p/\omega_c \gg 1$.)

(d)   Show that when $\omega \ll \omega_c$ the relation between k and ω for the low-frequency solution is

$$\omega = \omega_c\left(\frac{k^2c^2}{\omega_p^2}\right). \tag{1.64}$$

This low-frequency wave, known as a helicon, has been observed in many metals.[35] Estimate the helicon frequency if the wavelength is 1 cm and the field is 10 kilogauss, at typical metallic densities.

5.   Surface Plasmons

An electromagnetic wave that can propagate along the surface of a metal complicates the observation of ordinary (bulk) plasmons. Let the metal be contained in the half space $z > 0$, $z < 0$ being vacuum. Assume that the electric charge density ρ appearing in Maxwell's equations vanishes both inside and outside the metal. (This does not preclude a surface charge density concentrated in the plane $z = 0$.) The surface plasmon is a solution to Maxwell's equations of the form:

$$\begin{aligned}
E_x &= Ae^{iqx}e^{-Kz}, \quad E_y = 0, \quad E_z = Be^{iqx}e^{-Kz}, \quad z > 0; \\
E_x &= Ce^{iqx}e^{K'z}, \quad E_y = 0, \quad E_z = De^{iqx}e^{K'z}, \quad z < 0; \\
&\quad q, K, K' \text{ real}, \quad K, K' \text{ positive}.
\end{aligned} \tag{1.65}$$

(a)   Assuming the usual boundary conditions ($E_\|$ continuous, $(\epsilon E)_\perp$ continuous) and using the Drude results (1.35) and (1.29) find three equations relating q, K, and K' as functions of ω.

(b)   Assuming that $\omega\tau \gg 1$, plot q^2c^2 as a function of ω^2.

(c)   In the limit as $qc \gg \omega$, show that there is a solution at frequency $\omega = \omega_p/\sqrt{2}$. Show from an examination of K and K' that the wave is confined to the surface. Describe its polarization. This wave is known as a surface plasmon.

---

35   R. Bowers et al., *Phys. Rev. Letters* **7**. 339 (1961).

2
The Sommerfeld Theory of Metals

Fermi-Dirac Distribution

Free Electrons

Density of Allowed Wave Vectors

Fermi Momentum, Energy, and Temperature

Ground-State Energy and Bulk Modulus

Thermal Properties of a Free Electron Gas

Sommerfeld Theory of Conduction

Wiedemann-Franz Law

In Drude's time, and for many years thereafter, it seemed reasonable to assume that the electronic velocity distribution, like that of an ordinary classical gas of density $n = N/V$, was given in equilibrium at temperature T by the Maxwell-Boltzmann distribution. This gives the number of electrons per unit volume with velocities in the range[1] $d\mathbf{v}$ about $\mathbf{v}$ as $f_B(\mathbf{v}) \, d\mathbf{v}$, where

$$f_B(\mathbf{v}) = n \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T}.$$ (2.1)

We saw in Chapter 1 that in conjunction with the Drude model this leads to good order of magnitude agreement with the Wiedemann-Franz law, but also predicts a contribution to the specific heat of a metal of $\frac{3}{2}k_B$ per electron that was not observed.[2]

This paradox cast a shadow over the Drude model for a quarter of a century, which was only removed by the advent of the quantum theory and the recognition that for electrons[3] the Pauli exclusion principle requires the replacement of the Maxwell-Boltzmann distribution (2.1) with the Fermi-Dirac distribution:

$$f(\mathbf{v}) = \frac{(m/h)^3}{4\pi^3} \frac{1}{\exp\left[(\frac{1}{2}mv^2 - k_B T_0)/k_B T\right] + 1}.$$ (2.2)

Here h is Planck's constant divided by 2π, and T_0 is a temperature that is determined by the normalization condition[4]

$$n = \int d\mathbf{v} f(\mathbf{v}),$$ (2.3)

and is typically tens of thousands of degrees. At temperatures of interest (that is, less than 10^3 K) the Maxwell-Boltzmann and Fermi-Dirac distributions are spectacularly different at metallic electronic densities (Figure 2.1).

In this chapter we shall describe the theory underlying the Fermi-Dirac distribution (2.2) and survey the consequences of Fermi-Dirac statistics for the metallic electron gas.

Shortly after the discovery that the Pauli exclusion principle was needed to account for the bound electronic states of atoms, Sommerfeld applied the same principle to the free electron gas of metals, and thereby resolved the most flagrant thermal anomalies of the early Drude model. In most applications Sommerfeld's model is nothing more than Drude's classical electron gas with the *single* modification that the electronic velocity distribution is taken to be the quantum Fermi-Dirac distribution

---

[1] We use standard vector notation. Thus by v we mean the magnitude of the vector $\mathbf{v}$; a velocity is in the range $d\mathbf{v}$ about $\mathbf{v}$ if its ith component lies between v_i and $v_i + dv_i$, for $i = x, y, z$; we also use $d\mathbf{v}$ to denote the volume of the region of velocity space in the range $d\mathbf{v}$ about $\mathbf{v}$: $d\mathbf{v} = dv_x dv_y dv_z$ (thereby following the practice common among physicists of failing to distinguish notationally between a region and its volume, the significance of the symbol being clear from context).

[2] Because, as we shall see, the actual electronic contribution is about 100 times smaller at room temperature, becoming smaller still as the temperature drops.

[3] And any other particles obeying Fermi-Dirac statistics.

[4] Note that the constants in the Maxwell-Boltzmann distribution (2.1) have already been chosen so that (2.3) is satisfied. Equation (2.2) is derived below; see Eq. (2.89). In Problem 3d the prefactor appearing in Eq. (2.2) is cast in a form that facilitates direct comparison with Eq. (2.1).
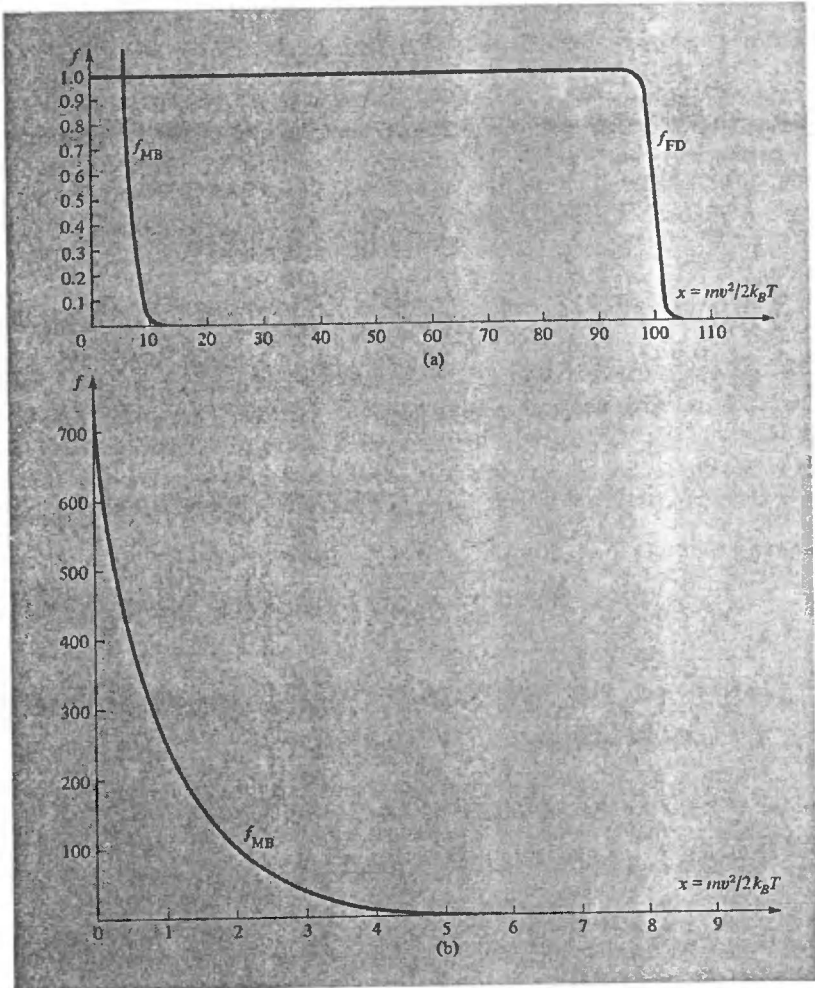
Figure 2.1
(a) The Maxwell-Boltzmann and Fermi-Dirac distributions for typical metallic densities at room temperature. (Both curves are for the density given by $T = 0.01 T_0$.) The scale is the same for both distributions, and has been normalized so that the Fermi-Dirac distribution approaches 1 at low energies. Below room temperature the differences between the two distributions are even more marked. (b) A view of that part of (a) between $x = 0$ and $x = 10$. The x-axis has been stretched by about a factor of 10, and the f-axis has been compressed by about 500 to get all of the Maxwell-Boltzmann distribution in the figure. On this scale the graph of the Fermi-Dirac distribution is indistinguishable from the x-axis.

rather than the classical Maxwell-Boltzmann distribution. To justify both the use of the Fermi-Dirac distribution and its bold grafting onto an otherwise classical theory, we must examine the quantum theory of the electron gas.[5]

For simplicity we shall examine the ground state (i.e., $T = 0$) of the electron gas before studying it at nonzero temperatures. As it turns out, the properties of the ground state are of considerable interest in themselves: we shall find that room temperature, for the electron gas at metallic densities, is a very low temperature indeed, for many purposes indistinguishable from $T = 0$. Thus many (though not all) of the electronic properties of a metal hardly differ from their values at $T = 0$, even at room temperature.

GROUND-STATE PROPERTIES OF THE ELECTRON GAS

We must calculate the ground-state properties of N electrons confined to a volume V. Because the electrons do not interact with one another (independent electron approximation) we can find the ground state of the N electron system by first finding the energy levels of a single electron in the volume V, and then filling these levels up in a manner consistent with the Pauli exclusion principle, which permits at most one electron to occupy any single electron level.[6]

A single electron can be described by a wave function $\psi(\mathbf{r})$ and the specification of which of two possible orientations its spin possesses. If the electron has no interactions, the one electron wave function associated with a level of energy $\mathcal{E}$ satisfies the time-independent Schrödinger equation[7]:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) = \mathcal{E}\psi(\mathbf{r}). \tag{2.4}$$

We shall represent the confinement of the electron (by the attraction of the ions) to the volume V by a boundary condition on Eq. (2.4). The choice of boundary condition, whenever one is dealing with problems that are not explicitly concerned with effects of the metallic surface, is to a considerable degree at one's disposal and can be determined by mathematical convenience, for if the metal is sufficiently large we should expect its *bulk* properties to be unaffected by the detailed configuration of its surface.[8] In this spirit we first select the shape of the metal to suit our analytic convenience. The time-honored choice is a cube[9] of side $L = V^{1/3}$.

Next we must append a boundary condition to the Schrödinger equation (2.4).

---

[5]   Throughout this chapter we shall take "electron gas" to mean a gas of free and independent electrons (see page 4) unless we are explicitly considering corrections due to electron-electron or electron-ion interactions.

[6]   Note that here and later we shall reserve the term "state" for the state of the N-electron system, and the term "level" for a one-electron state.

[7]   We also make the free electron approximation, so that no potential energy term appears in the Schrödinger equation.

[8]   This is the approach that is almost universally followed in theories of macroscopic matter. Rigorous proofs that bulk properties are independent of the boundary conditions can now be constructed in a variety of contexts. The work most pertinent to solid state physics is by J. L. Lebowitz and E. H. Lieb, *Phys. Rev. Lett.* **22**, 631 (1969).

[9]   We shall subsequently find it far more convenient to take not a cube but a parallelepiped with

reflecting the fact that the electron is confined to this cube. We also make this choice in the belief that it will not affect calculated bulk properties. One possibility is to require the wave function $\psi(\mathbf{r})$ to vanish whenever $\mathbf{r}$ is on the surface of the cube. This, however, is often unsatisfactory, for it leads to standing-wave solutions of (2.4), while the transport of charge and energy by the electrons is far more conveniently discussed in terms of running waves. A more satisfactory choice is to emphasize the inconsequence of the surface by disposing of it altogether. We can do this by imagining each face of the cube to be joined to the face opposite it, so that an electron coming to the surface is not reflected back in, but leaves the metal, simultaneously reentering at a corresponding point on the opposite surface. Thus, if our metal were one-dimensional, we would simply replace the line from 0 to L to which the electrons were confined, by a circle of circumference L. In three dimensions the geometrical embodiment of the boundary condition, in which the three pairs of opposite faces on the cube are joined, becomes topologically impossible to construct in three-dimensional space. Nevertheless, the analytic form of the boundary condition is easily generalized. In one dimension the circular model of a metal results in the boundary condition $\psi(x + L) = \psi(x)$, and the generalization to a three-dimensional cube is evidently

$$
\begin{aligned}
\psi(x, y, z + L) &= \psi(x, y, z), \\
\psi(x, y + L, z) &= \psi(x, y, z), \\
\psi(x + L, y, z) &= \psi(x, y, z).
\end{aligned}
\tag{2.5}
$$

Equation (2.5) is known as the Born-von Karman (or periodic) boundary condition. We shall encounter it often (sometimes in a slightly generalized[9] form).

We now solve (2.4) subject to the boundary condition (2.5). One can verify by differentiation that a solution, neglecting the boundary condition, is

$$
\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}},
\tag{2.6}
$$

with energy

$$
\mathcal{E}(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}.
\tag{2.7}
$$

where $\mathbf{k}$ is any position independent vector. We have picked the normalization constant in (2.6) so that the probability of finding the electron *somewhere* in the whole volume V is unity:

$$
1 = \int d\mathbf{r} \, |\psi(\mathbf{r})|^2.
\tag{2.8}
$$

To see the significance of the vector $\mathbf{k}$, note that the level $\psi_{\mathbf{k}}(\mathbf{r})$ is an eigenstate of the momentum operator,

$$
\mathbf{p} = \frac{\hbar}{i}\frac{\partial}{\partial\mathbf{r}} = \frac{\hbar}{i}\nabla, \quad \left(p_x = \frac{\hbar}{i}\frac{\partial}{\partial x}, \quad \text{etc.} \right).
\tag{2.9}
$$

edges not necessarily equal or perpendicular. For the moment we use a cube to avoid minor geometrical complexities, but it is a useful exercise to verify that all the results of this section remain valid for t⁻ parallelepiped.

with eigenvalue $p = \hbar k$, for

$$\frac{\hbar}{i} \frac{\partial}{\partial \mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}} = \hbar \mathbf{k} \, e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{2.10}$$

Since a particle in an eigenstate of an operator has a definite value of the corresponding observable given by the eigenvalue, an electron in the level $\psi_k(\mathbf{r})$ has a definite momentum proportional to $\mathbf{k}$:

$$\mathbf{p} = \hbar \mathbf{k}, \tag{2.11}$$

and a velocity $\mathbf{v} = \mathbf{p}\,m$ of

$$\mathbf{v} = \frac{\hbar \mathbf{k}}{m}. \tag{2.12}$$

In view of this the energy (2.7) can be written in the familiar classical form,

$$\varepsilon = \frac{p^2}{2m} = \tfrac{1}{2}mv^2. \tag{2.13}$$

We can also interpret $\mathbf{k}$ as a wave vector. The plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$ is constant in any plane perpendicular to $\mathbf{k}$ (since such planes are defined by the equation $\mathbf{k}\cdot\mathbf{r} = $ constant) and it is periodic along lines parallel to $\mathbf{k}$, with wavelength

$$\lambda = \frac{2\pi}{k}, \tag{2.14}$$

known as the de Broglie wavelength.

We now invoke the boundary condition (2.5). This permits only certain discrete values of $\mathbf{k}$, since (2.5) will be satisfied by the general wave function (2.6) only if

$$e^{ik_x L} = e^{ik_y L} = e^{ik_z L} = 1. \tag{2.15}$$

Since $e^z = 1$ only if $z = 2\pi i n$, where n is an integer,[10] the components of the wave vector $\mathbf{k}$ must be of the form:

$$k_x = \frac{2\pi n_x}{L}, \quad k_y = \frac{2\pi n_y}{L}, \quad k_z = \frac{2\pi n_z}{L}. \qquad n_x, n_y, n_z \text{ integers.} \tag{2.16}$$

Thus in a three-dimensional space with Cartesian axes k_x, k_y, and k_z (known as k-space) the allowed wave vectors are those whose coordinates along the three axes are given by integral multiples of $2\pi/L$. This is illustrated (in two dimensions) in Figure 2.2.

Generally the only practical use one makes of the quantization condition (2.16) is this: One often needs to know how many allowed values of $\mathbf{k}$ are contained in a region of k-space that is enormous on the scale of $2\pi/L$, and that therefore contains a vast number of allowed points. If the region is very large,[11] then to an excellent approximation the number of allowed points is just the volume of k-space contained within the region, divided by the volume of k-space per point in the network of

---

[10]   We shall always use the word "integer" to mean the negative integers and zero, as well as the positive integers.

[11]   And not too irregularly shaped; only a negligible fraction of the points should be within $O(2\pi/L)$ of the surface.

Figure 2.2
Points in a two-dimensional k-space of the form $k_x = 2\pi n_x/L$, $k_y = 2\pi n_y/L$. Note that the area per point is just $(2\pi/L)^2$. In d dimensions the volume per point is $(2\pi/L)^d$.
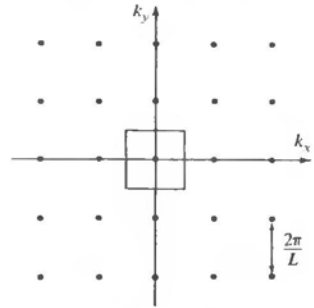
allowed values of k. That latter volume (see Figure 2.2) is just $(2\pi/L)^3$. We therefore conclude that a region of k-space of volume Ω will contain

$$\frac{\Omega}{(2\pi/L)^3} = \frac{\Omega V}{8\pi^3} \tag{2.17}$$

allowed values of k, or, equivalently, that the number of allowed k-values per unit volume of k-space (also known as the k-space density of levels) is just

$$\frac{V}{8\pi^3}. \tag{2.18}$$

In practice we shall deal with k-space regions so large ($\sim 10^{22}$ points) and so regular (typically spheres) that to all intents and purposes (2.17) and (2.18) can be regarded as exact. We shall begin to apply these important counting formulas shortly.

Because we assume the electrons are noninteracting we can build up the N-electron ground state by placing electrons into the allowed one-electron levels we have just found. The Pauli exclusion principle plays a vital role in this construction (as it does in building up the states of many electron atoms): we may place at most one electron in each single electron level. The one-electron levels are specified by the wave vectors k and by the projection of the electron's spin along an arbitrary axis, which can take either of the two values $h/2$ or $-h/2$. Therefore associated with each allowed wave vector k are *two* electronic levels, one for each direction of the electron's spin.

Thus in building up the N-electron ground state we begin by placing two electrons in the one-electron level $k = 0$, which has the lowest possible one-electron energy $\varepsilon = 0$. We then continue to add electrons, successively filling the one-electron levels of lowest energy that are not already occupied. Since the energy of a one-electron level is directly proportional to the square of its wave vector (see (2.7)), when N is enormous the occupied region will be indistinguishable from a sphere.[12] The radius of this sphere is called k_F (F for Fermi), and its volume Ω is $4\pi k_F^3/3$. According to (2.17) the number of allowed values of k within the sphere is

$$\left(\frac{4\pi k_F^3}{3}\right)\left(\frac{V}{8\pi^3}\right) = \frac{k_F^3}{6\pi^2} V. \tag{2.19}$$

---

[12] If it were not spherical it would not be the ground state, for we could then construct a state of lower energy by mov... ~g the electrons in levels farthest away from $k = 0$ into unoccupied levels closer to the origin.

Since each allowed k-value leads to two one-electron levels (one for each spin value), in order to accommodate N electrons we must have

$$N = 2 \cdot \frac{k_F^3}{6\pi^2} V = \frac{k_F^3}{3\pi^2} V. \tag{2.20}$$

Thus if we have N electrons in a volume V (i.e., an electronic density $n = N/V$), then the ground state of the N-electron system is formed by occupying all single-particle levels with k less than k_F, and leaving all those with k greater than k_F unoccupied, where k_F is given by the condition:

$$n = \frac{k_F^3}{3\pi^2}. \tag{2.21}$$

This free and independent electron ground state is described by some rather unimaginative nomenclature:

The sphere of radius k_F (the *Fermi wave vector*) containing the occupied one electron levels is called the *Fermi sphere*.

The surface of the Fermi sphere, which separates the occupied from the unoccupied levels is called the *Fermi surface*. (We shall see, starting with Chapter 8, that the Fermi surface is one of the fundamental constructions in the modern theory of metals; in general it is not spherical.)

The momentum $\hbar k_F = p_F$ of the occupied one-electron levels of highest energy is known as the *Fermi momentum*; their energy, $\mathcal{E}_F = \hbar^2 k_F^2/2m$ is the *Fermi energy*; and their velocity, $v_F = p_F/m$, is the *Fermi velocity*. The Fermi velocity plays a role in the theory of metals comparable to the thermal velocity, $v = (3k_BT/m)^{1/2}$, in a classical gas.

All these quantities can be evaluated in terms of the conduction electron density, via Eq. (2.21). For estimating them numerically it is often more convenient to express them in terms of the dimensionless parameter r_s/a_0 (see page 4), which varies from about 2 to 6 in the metallic elements. Taken together, Eqs. (1.2) and (2.21) give

$$k_F = \frac{(9\pi/4)^{1/3}}{r_s} = \frac{1.92}{r_s}, \tag{2.22}$$

or

$$k_F = \frac{3.63}{r_s/a_0} \text{ Å}^{-1}. \tag{2.23}$$

Since the Fermi wave vector is of the order of inverse angstroms, the de Broglie wavelength of the most energetic electrons is of the order of angstroms.

The Fermi velocity is

$$v_F = \left(\frac{\hbar}{m}\right) k_F = \frac{4.20}{r_s/a_0} \times 10^8 \text{ cm/sec.} \tag{2.24}$$

This is a substantial velocity (about 1 percent of the velocity of light). From the viewpoint of classical statistical mechanics this is quite a surprising result, for we are

describing the ground state ($T = 0$), and all particles in a classical gas have zero velocity at $T = 0$. Even at room temperature the thermal (i.e., average) velocity for a classical particle with the electronic mass is only of order 10^7 cm/sec.

The Fermi energy is conveniently written in the form (since $a_0 = \hbar^2/me^2$)

$$\mathcal{E}_F = \frac{\hbar^2 k_F^2}{2m} = \left(\frac{e^2}{2a_0}\right)(k_F a_0)^2. \tag{2.25}$$

Here $e^2/2a_0$, known as the rydberg (Ry), is the ground-state binding energy of the hydrogen atom, 13.6 electron volts.[13] The rydberg is as convenient a unit of atomic energies as the Bohr radius is of atomic distances. Since $k_F a_0$ is of the order of unity, Eq. (2.25) demonstrates that the Fermi energy has the magnitude of a typical atomic binding energy. Using (2.23) and $a_0 = 0.529 \times 10^{-8}$ cm, we find the explicit numerical form:

$$\mathcal{E}_F = \frac{50.1 \text{ eV}}{(r_s/a_0)^2}, \tag{2.26}$$

indicating a range of Fermi energies for the densities of metallic elements between 1.5 and 15 electron volts.

Table 2.1 lists the Fermi energy, velocity, and wave vector for the metals whose conduction electron densities are given in Table 1.1.

To calculate the ground-state energy of N electrons in a volume V we must add up the energies of all the one-electron levels inside the Fermi sphere[14]:

$$E = 2 \sum_{k < k_F} \frac{\hbar^2}{2m} k^2. \tag{2.27}$$

Quite generally, in summing any smooth function $F(\mathbf{k})$ over all allowed values of $\mathbf{k}$, one may proceed as follows:

Because the volume of k-space per allowed $\mathbf{k}$ value is $\Delta \mathbf{k} = 8\pi^3/V$ (see Eq. (2.18)) it is convenient to write

$$\sum_{\mathbf{k}} F(\mathbf{k}) = \frac{V}{8\pi^3} \sum_{\mathbf{k}} F(\mathbf{k}) \, \Delta \mathbf{k}, \tag{2.28}$$

for in the limit as $\Delta \mathbf{k} \to 0$ (i.e., $V \to \infty$) the sum $\Sigma F(\mathbf{k}) \, \Delta \mathbf{k}$ approaches the integral $\int d\mathbf{k} \, F(\mathbf{k})$, provided only that $F(\mathbf{k})$ does not vary appreciably[15] over distances in k-space of order $2\pi/L$. We may therefore rearrange (2.28) and write

$$\lim_{V \to \infty} \frac{1}{V} \sum_{\mathbf{k}} F(\mathbf{k}) = \int \frac{d\mathbf{k}}{8\pi^3} F(\mathbf{k}). \tag{2.29}$$

In applying (2.29) to finite, but macroscopically large, systems one always assumes that $(1/V) \Sigma F(\mathbf{k})$ differs negligibly from its infinite volume limit (for example, one

---

[13]   Strictly speaking, the rydberg is the binding energy in the approximation of infinite proton mass. An electron volt is the energy gained by an electron crossing a potential of 1 volt; 1 eV $= 1.602 \times 10^{-12}$ erg $= 1.602 \times 10^{-19}$ joule.

[14]   The factor of 2 is for the two spin levels allowed for each $\mathbf{k}$.

[15]   The most celebrated case in which F fails to satisfy this condition is the condensation of the ideal Bose gas. In applications to metals the problem never arises.

Table 2.1
FERMI ENERGIES, FERMI TEMPERATURES, FERMI WAVE VECTORS, AND FERMI VELOCITIES FOR REPRESENTATIVE METALS[a]

ELEMENT	r_s/a_0	$\mathcal{E}_F$	T_F	k_F	v_F
Li	3.25	4.74 eV	5.51×10^4 K	1.12×10^8 cm^{-1}	1.29×10^8 cm/sec
Na	3.93	3.24	3.77	0.92	1.07
K	4.86	2.12	2.46	0.75	0.86
Rb	5.20	1.85	2.15	0.70	0.81
Cs	5.62	1.59	1.84	0.65	0.75
Cu	2.67	7.00	8.16	1.36	1.57
Ag	3.02	5.49	6.38	1.20	1.39
Au	3.01	5.53	6.42	1.21	1.40
Be	1.87	14.3	16.6	1.94	2.25
Mg	2.66	7.08	8.23	1.36	1.58
Ca	3.27	4.69	5.44	1.11	1.28
Sr	3.57	3.93	4.57	1.02	1.18
Ba	3.71	3.64	4.23	0.98	1.13
Nb	3.07	5.32	6.18	1.18	1.37
Fe	2.12	11.1	13.0	1.71	1.98
Mn	2.14	10.9	12.7	1.70	1.96
Zn	2.30	9.47	11.0	1.58	1.83
Cd	2.59	7.47	8.68	1.40	1.62
Hg	2.65	7.13	8.29	1.37	1.58
Al	2.07	11.7	13.6	1.75	2.03
Ga	2.19	10.4	12.1	1.66	1.92
In	2.41	8.63	10.0	1.51	1.74
Tl	2.48	8.15	9.46	1.46	1.69
Sn	2.22	10.2	11.8	1.64	1.90
Pb	2.30	9.47	11.0	1.58	1.83
Bi	2.25	9.90	11.5	1.61	1.87
Sb	2.14	10.9	12.7	1.70	1.96

[a] The table entries are calculated from the values of r_s/a_0 given in Table 1.1 using $m = 9.11 \times 10^{-28}$ grams.

assumes that the electronic energy per unit volume in a 1-cm cube of copper is the same as in a 2-cm cube).

Using (2.29) to evaluate (2.27), we find that the energy density of the electron gas is:

$$\frac{E}{V} = \frac{1}{4\pi^3} \int_{k < k_F} d\mathbf{k} \frac{\hbar^2 k^2}{2m} = \frac{1}{\pi^2} \frac{\hbar^2 k_F^5}{10m}. \tag{2.30}$$

To find the energy per electron, E/N, in the ground state, we must divide this by $N/V = k_F^3/3\pi^2$, which gives

$$\frac{E}{N} = \frac{3}{10} \frac{\hbar^2 k_F^2}{m} = \frac{3}{5} \mathcal{E}_F. \tag{2.31}$$

We can also write this result as

$$\frac{E}{N} = \frac{3}{5} k_B T_F \tag{2.32}$$

where T_F, the *Fermi temperature*, is

$$T_F = \frac{\varepsilon_F}{k_B} = \frac{58.2}{(r_s/a_0)^2} \times 10^4 \text{ K.} \tag{2.33}$$

Note, in contrast to this, that the energy per electron in a classical ideal gas, $\frac{3}{2}k_B T$, vanishes at $T = 0$ and achieves a value as large as (2.32) only at $T = \frac{2}{3}T_F \approx 10^4$ K.

Given the ground-state energy E, one can calculate the pressure exerted by the electron gas from the relation $P = -(\partial E/\partial V)_N$. Since $E = \frac{3}{5}N\varepsilon_F$ and ε_F is proportional to k_F^2, which depends on V only through a factor $n^{2/3} = (N/V)^{2/3}$, it follows that[16]

$$P = \frac{2}{3}\frac{E}{V}. \tag{2.34}$$

One can also calculate the compressibility, K, or bulk modulus, $B = 1/K$, defined by:

$$B = \frac{1}{K} = -V\frac{\partial P}{\partial V}. \tag{2.35}$$

Since E is proportional to $V^{-2/3}$, Eq. (2.34) shows that P varies as $V^{-5/3}$, and therefore

$$B = \frac{5}{3}P = \frac{10}{9}\frac{E}{V} = \frac{2}{3}n\varepsilon_F \tag{2.36}$$

or

$$B = \left(\frac{6.13}{r_s/a_0}\right)^5 \times 10^{10} \text{ dynes/cm}^2. \tag{2.37}$$

In Table 2.2 we compare the free electron bulk moduli (2.37) calculated from r_s/a_0, with the measured bulk moduli, for several metals. The agreement for the heavier alkali metals is fortuitously good, but even when (2.37) is substantially off, as it is in

Table 2.2
BULK MODULI IN 10^{10} DYNES/CM² FOR SOME TYPICAL METALS[a]

METAL	FREE ELECTRON B	MEASURED B
Li	23.9	11.5
Na	9.23	6.42
K	3.19	2.81
Rb	2.28	1.92
Cs	1.54	1.43
Cu	63.8	134.3
Ag	34.5	99.9
Al	228	76.0

[a] The free electron value is that for a free electron gas at the observed density of the metal, as calculated from Eq. (2.37).

---

[16]   At no   temperatures the pressure and energy density continue to obey this relation. See (2.101).

the noble metals, it is still of about the right order of magnitude (though it varies from three times too large to three times too small, through the table). It is absurd to expect that the free electron gas pressure alone should completely determine the resistance of a metal to compression, but Table 2.2 demonstrates that this pressure is at least as important as any other effects.

THERMAL PROPERTIES OF THE FREE ELECTRON GAS: THE FERMI-DIRAC DISTRIBUTION

When the temperature is not zero it is necessary to examine the excited states of the N-electron system as well as its ground state, for according to the basic principles of statistical mechanics, if an N-particle system is in thermal equilibrium at temperature T, then its properties should be calculated by averaging over all N-particle stationary states, assigning to each state of energy E a weight $P_N(E)$ proportional to $e^{-E/k_B T}$:

$$P_N(E) = \frac{e^{-E/k_B T}}{\sum e^{-E_\alpha^N/k_B T}}. \tag{2.38}$$

(Here E_α^N is the energy of the αth stationary state of the N-electron system, the sum being over all such states.)

The denominator of (2.38) is known as the partition function, and is related to the Helmholtz free energy, $F = U - TS$ (where U is the internal energy and S, the entropy) by

$$\sum e^{-E_\alpha^N/k_B T} = e^{-F_N/k_B T}. \tag{2.39}$$

We can therefore write (2.38) more compactly as:

$$P_N(E) = e^{-(E-F_N)/k_B T}. \tag{2.40}$$

Because of the exclusion principle, to construct an N-electron state one must fill N different one-electron levels. Thus each N-electron stationary state can be specified by listing which of the N one-electron levels are filled in that state. A very useful quantity to know is f_i^N, the probability of there being an electron in the particular one-electron level i, when the N-electron system is in thermal equilibrium.[17] This probability is simply the sum of the independent probabilities of finding the N-electron system in any one of those N-electron states in which the ith level is occupied:

$$f_i^N = \sum P_N(E_\alpha^N) \quad \begin{array}{l}\text{(summation over all } N\text{-electron} \\ \text{states } \alpha \text{ in which there is an elec-} \\ \text{tron in the one-electron level } i).\end{array} \tag{2.41}$$

We can evaluate f_i^N by the following three observations:

1. Since the probability of an electron being in the level i is just one minus the probability of no electron being in the level i (those being the only two possibilities

---

[17]   In the case we are interested in the level i is specified by the electron's wave vector $\mathbf{k}$ and the projection s of its spin along some axis.

allowed by the exclusion principle) we could equally well write (2.41) as

$$f_i^N = 1 - \sum P_N(E_\gamma^N)$$ (summation over all N-electron states γ in which there is *no* electron in the one-electron level i).   (2.42)

2.   By taking any $(N + 1)$-electron state in which there *is* an electron in the one-electron level i, we can construct an N-electron state in which there is *no* electron in the level i, by simply removing the electron in the ith level, leaving the occupation of all the other levels unaltered. Furthermore, *any* N-electron state with no electron in the one-electron level i can be so constructed from just one $(N + 1)$-electron state *with* an electron in the level i.[18] Evidently the energies of any N-electron state and the corresponding $(N + 1)$-electron state differ by just ε_i, the energy of the only one-electron level whose occupation is different in the two states. Thus the set of energies of all N-electron states with the level i unoccupied is the same as the set of energies of all $(N + 1)$-electron states with the level i occupied, provided that each energy in the latter set is reduced by ε_i. We can therefore rewrite (2.42) in the peculiar form

$$f_i^N = 1 - \sum P_N(E_\alpha^{N+1} - \varepsilon_i)$$ (summation over all $(N + 1)$-electron states α in which there *is* an electron in the one-electron level i).   (2.43)

But Eq. (2.40) permits us to write the summand as

$$P_N(E_\alpha^{N+1} - \varepsilon_i) = e^{(\varepsilon_i - \mu)/k_B T} P_{N+1}(E_\alpha^{N+1}),$$ (2.44)

where μ, known as the chemical potential, is given at temperature T by

$$\mu = F_{N+1} - F_N.$$ (2.45)

Substituting this into (2.43), we find:

$$f_i^N = 1 - e^{(\varepsilon_i - \mu)/k_B T} \sum P_{N+1}(E_\alpha^{N+1})$$ (summation over all $(N + 1)$-electron states α in which there *is* an electron in the one-electron level i).   (2.46)

Comparing the summation in (2.46) with that in (2.41) one finds that (2.46) simply asserts that

$$f_i^N = 1 - e^{(\varepsilon_i - \mu)/k_B T} f_i^{N+1}.$$ (2.47)

3.   Equation (2.47) gives an exact relation between the probability of the one-electron level i being occupied at temperature T in an N-electron system, and in an $(N + 1)$-electron system. When N is very large (and we are typically interested in N of the order of 10^{22}) it is absurd to imagine that by the addition of a single extra electron we could appreciably alter this probability for more than an insignificant handful of one-electron levels.[19] We may therefore replace f_i^{N+1} by f_i^N in (2.47), which

---

[18]   Namely the one obtained by occupying all those levels occupied in the N-electron state *plus* the ith level.

[19]   For a typical level, changing N by one alters the probability of occupation by order $1/N$. See Problem 4.

makes it possible to solve for f_i^N:

$$f_i^N = \frac{1}{e^{(\mathcal{E}_i - \mu)/k_B T} + 1}.$$ (2.48)

In subsequent formulas we shall drop the explicit reference to the N dependence of f_i, which is, in any event, carried through the chemical potential μ; see (2.45). The value of N can always be computed, given the f_i, by noting that f_i is the mean number of electrons in the one-electron level[20] i. Since the total number of electrons N is just the sum over all levels of the mean number in each level,

$$N = \sum_i f_i = \sum_i \frac{1}{e^{(\mathcal{E}_i - \mu)/k_B T} + 1},$$ (2.49)

which determines N as a function of the temperature T and chemical potential μ. In many applications, however, it is the temperature and N (or rather the density, $n = N/V$) that are given. In such cases (2.49) is used to determine the chemical potential μ as a function of n and T, permitting it to be eliminated from subsequent formulas in favor of the temperature and density. However the chemical potential is of considerable thermodynamic interest in its own right. Some of its important properties are summarized in Appendix B.[21]

THERMAL PROPERTIES OF THE FREE ELECTRON GAS: APPLICATIONS OF THE FERMI-DIRAC DISTRIBUTION

In a gas of free and independent electrons the one-electron levels are specified by the wave vector $\mathbf{k}$ and spin quantum number s, with energies that are independent of s (in the absence of a magnetic field) and given by Eq. (2.7); i.e.,

$$\mathcal{E}(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}.$$ (2.50)

We first verify that the distribution function (2.49) is consistent with the ground-state ($T = 0$) properties derived above. In the ground state those and only those levels are occupied with $\mathcal{E}(\mathbf{k}) \leqslant \mathcal{E}_F$, so the ground-state distribution function must be

$$\begin{aligned} f_{\mathbf{k}s} &= 1, \quad \mathcal{E}(\mathbf{k}) < \mathcal{E}_F; \\ &= 0, \quad \mathcal{E}(\mathbf{k}) > \mathcal{E}_F. \end{aligned}$$ (2.51)

---

[20]   *Proof:* A level can contain either 0 or 1 electron (more than one being prohibited by the exclusion principle). The mean number of electrons is therefore 1 times the probability of 1 electron plus 0 times the probability of 0 electrons. Thus the mean number of electrons in the level is numerically equal to the probability of its being occupied. Note that this would not be so if multiple occupation of levels were permitted.

[21]   The chemical potential plays a more fundamental role when the distribution (2.48) is derived in the grand canonical ensemble. See, for example, F. Reif, *Statistical and Thermal Physics*, McGraw-Hill, New York, 1965, p. 350. Our somewhat unorthodox derivation, which can also be found in Reif, uses only the canonical ensemble.

On the other hand, as $T \to 0$, the limiting form of the Fermi-Dirac distribution (2.48) is

$$\lim_{T \to 0} f_{k} = 1, \quad \mathcal{E}(k) < \mu; \\ = 0, \quad \mathcal{E}(k) > \mu. \tag{2.52}$$

For these to be consistent it is necessary that

$$\lim_{T \to 0} \mu = \mathcal{E}_F. \tag{2.53}$$

We shall see shortly that for metals the chemical potential remains equal to the Fermi energy to a high degree of precision, all the way up to room temperature. As a result, people frequently fail to make any distinction between the two when dealing with metals. This, however, can be dangerously misleading. In precise calculations it is essential to keep track of the extent to which μ, the chemical potential, differs from its zero temperature value, $\mathcal{E}_F$.

The most important single application of Fermi-Dirac statistics is the calculation of the electronic contribution to the constant-volume specific heat of a metal,

$$c_v = \frac{T}{V}\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial u}{\partial T}\right)_V, \quad u = \frac{U}{V}. \tag{2.54}$$

In the independent electron approximation the internal energy U is just the sum over one-electron levels of $\mathcal{E}(k)$ times the mean number of electrons in the level[22]:

$$U = 2 \sum_{k} \mathcal{E}(k) f(\mathcal{E}(k)). \tag{2.55}$$

We have introduced the *Fermi function* $f(\mathcal{E})$ to emphasize that f_k depends on k only through the electronic energy $\mathcal{E}(k)$:

$$\boxed{f(\mathcal{E}) = \frac{1}{e^{(\mathcal{E}-\mu)/k_B T} + 1}.} \tag{2.56}$$

If we divide both sides of (2.55) by the volume V, then (2.29) permits us to write the energy density $u = U/V$ as

$$u = \int \frac{dk}{4\pi^3} \mathcal{E}(k) f(\mathcal{E}(k)). \tag{2.57}$$

If we also divide both sides of (2.49) by V, then we can supplement (2.57) by an equation for the electronic density $n = N/V$, and use it to eliminate the chemical potential:

$$n = \int \frac{dk}{4\pi^3} f(\mathcal{E}(k)). \tag{2.58}$$

In evaluating integrals like (2.57) and (2.58) of the form

$$\int \frac{dk}{4\pi^3} F(\mathcal{E}(k)), \tag{2.59}$$

---

[22] As usual, the factor of 2 reflects the fact that each k-level can contain two electrons of opposite spin orientations.

one often exploits the fact that the integrand depends on $\mathbf{k}$ only through the electronic energy $\varepsilon = \hbar^2 k^2/2m$, by evaluating the integral in spherical coordinates and changing variables from k to ε:

$$\int \frac{d\mathbf{k}}{4\pi^3} F(\varepsilon(\mathbf{k})) = \int_0^\infty \frac{k^2\,dk}{\pi^2} F(\varepsilon(\mathbf{k})) = \int_{-\infty}^\infty d\varepsilon\,g(\varepsilon)F(\varepsilon). \qquad (2.60)$$

Here

$$g(\varepsilon) = \frac{m}{\hbar^2\pi^2}\sqrt{\frac{2m\varepsilon}{\hbar^2}}, \quad \varepsilon > 0;$$
$$= 0, \qquad\qquad \varepsilon < 0. \qquad (2.61)$$

Since the integral (2.59) is an evaluation of $(1/V)\sum_{\mathbf{k}s} F(\varepsilon(\mathbf{k}))$, the form in (2.60) shows that

$$g(\varepsilon)\,d\varepsilon = \left(\frac{1}{V}\right) \times \begin{array}{l}\text{[the number of one-electron}\\ \text{levels in the energy range}\\ \text{from } \varepsilon \text{ to } \varepsilon + d\varepsilon\text{].}\end{array} \qquad (2.62)$$

For this reason $g(\varepsilon)$ is known as the density of levels per unit volume (or often simply as the density of levels). A dimensionally more transparent way of writing g is

$$g(\varepsilon) = \frac{3}{2}\frac{n}{\varepsilon_F}\left(\frac{\varepsilon}{\varepsilon_F}\right)^{1/2}, \quad \varepsilon > 0;$$
$$= 0, \qquad\qquad \varepsilon < 0, \qquad (2.63)$$

where ε_F and k_F are *defined* by the zero-temperature equations (2.21) and (2.25). A quantity of particular numerical importance is the density of levels at the Fermi energy, which (2.61) and (2.63) give in either of the two equivalent forms:

$$\boxed{g(\varepsilon_F) = \frac{mk_F}{\hbar^2\pi^2}} \qquad (2.64)$$

or

$$\boxed{g(\varepsilon_F) = \frac{3}{2}\frac{n}{\varepsilon_F}.} \qquad (2.65)$$

Using this notation, we rewrite (2.57) and (2.58) as:

$$u = \int_{-\infty}^\infty d\varepsilon\,g(\varepsilon)\varepsilon f(\varepsilon) \qquad (2.66)$$

and

$$n = \int_{-\infty}^\infty d\varepsilon\,g(\varepsilon)f(\varepsilon). \qquad (2.67)$$

We do this both for notational simplicity *and* because in this form the free electron approximation enters only through the particular evaluation (2.61) or (2.63) of the density of levels g. We can define a density of levels, via (2.62), in terms of which (2.66)
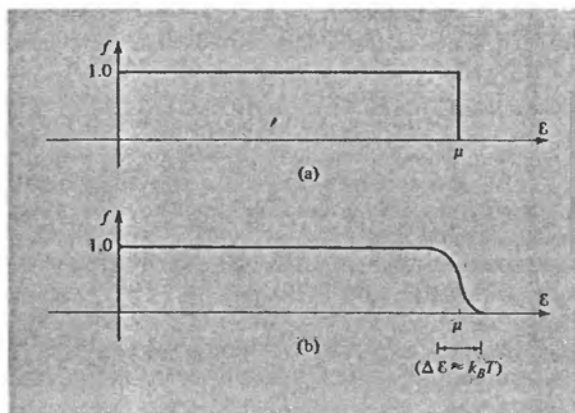
Figure 2.3
The Fermi function, $f(\varepsilon) = 1/[e^{\beta(\varepsilon-\mu)} + 1]$ versus ε for given μ, at (a) $T = 0$ and (b) $T \approx 0.01\mu$ (of order room temperature, at typical metallic densities). The two curves differ only in a region of order $k_B T$ about μ.

and (2.67) remain valid for any set of noninteracting (that is, independent) electrons.[23] Thus we shall later be able to apply results deduced from (2.66) and (2.67) to considerably more sophisticated models of independent electrons in metals.

In general, the integrals (2.66) and (2.67) have a rather complex structure. There is, however, a simple systematic expansion that exploits the fact that at almost all temperatures of interest in metals, T is very much smaller than the Fermi temperature (2.33). In Figure 2.3 the Fermi function $f(\varepsilon)$ is plotted at $T = 0$ and at room temperature for typical metallic densities ($k_B T/\mu \approx 0.01$). Evidently f differs from its zero temperature form only in a small region about μ of width a few $k_B T$. Thus the way in which integrals of the form $\int_{-\infty}^{\infty} H(\varepsilon)f(\varepsilon) \, d\varepsilon$ differ from their zero temperature values, $\int_{-\infty}^{\varepsilon_F} H(\varepsilon) \, d\varepsilon$, will be entirely determined by the form of $H(\varepsilon)$ near $\varepsilon = \mu$. If $H(\varepsilon)$ does not vary rapidly in the energy range of the order of $k_B T$ about μ, the temperature dependence of the integral should be given quite accurately by replacing $H(\varepsilon)$ by the first few terms in its Taylor expansion about $\varepsilon = \mu$:

$$H(\varepsilon) = \sum_{n=0}^{\infty} \frac{d^n}{d\varepsilon^n} H(\varepsilon) \bigg|_{\varepsilon=\mu} \frac{(\varepsilon - \mu)^n}{n!}. \tag{2.68}$$

This procedure is carried out in Appendix C. The result is a series of the form:

$$\int_{-\infty}^{\infty} H(\varepsilon)f(\varepsilon) \, d\varepsilon = \int_{-\infty}^{\mu} H(\varepsilon) \, d\varepsilon + \sum_{n=1}^{\infty} (k_B T)^{2n} a_n \frac{d^{2n-1}}{d\varepsilon^{2n-1}} H(\varepsilon) \bigg|_{\varepsilon=\mu} \tag{2.69}$$

which is known as the Sommerfeld expansion.[24] The a_n are dimensionless constants of the order of unity. The functions H one typically encounters have major variations on an energy scale of the order of μ, and generally $(d/d\varepsilon)^n H(\varepsilon)|_{\varepsilon=\mu}$ is of the order of $H(\mu)/\mu^n$. When this is the case, successive terms in the Sommerfeld expansion are

---

[23] See Chapter 8.

[24] The expansion is not always exact, but is highly reliable unless $H(\varepsilon)$ has a singularity very close to $\varepsilon = \mu$. If, for example, H is singular at $\varepsilon = 0$ (as is the free electron density of levels (2.63)) then the expansion will neglect terms of the order of $\exp(-\mu/k_B T)$, which are typically of order $e^{-100} \sim 10^{-43}$. See also Problem 1.

smaller by $O(k_B T/\mu)^2$ which is $O(10^{-4})$ at room temperature. Consequently, in actual calculations only the first and (very occasionally) the second terms are retained in the sum in (2.69). The explicit form for these is (Appendix C):

$$\int_{-\infty}^{\infty} H(\varepsilon) f(\varepsilon)\, d\varepsilon$$
$$= \int_{-\infty}^{\mu} H(\varepsilon)\, d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 H'(\mu) + \frac{7\pi^4}{360} (k_B T)^4 H'''(\mu) + O\left(\frac{k_B T}{\mu}\right)^6. \quad (2.70)$$

To evaluate the specific heat of a metal at temperatures small compared with T_F we apply the Sommerfeld expansion (2.70) to the electronic energy and number densities (Eqs. (2.66) and (2.67)):

$$u = \int_0^{\mu} \varepsilon g(\varepsilon)\, d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 [\mu g'(\mu) + g(\mu)] + O(T^4), \quad (2.71)$$

$$n = \int_0^{\mu} g(\varepsilon)\, d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 g'(\mu) + O(T^4). \quad (2.72)$$

Equation (2.72) as we shall presently see in detail, implies that μ differs from its $T = 0$ value, ε_F, by terms of order T^2. Thus, correctly to order T^2, we may write

$$\int_0^{\mu} H(\varepsilon)\, d\varepsilon = \int_0^{\varepsilon_F} H(\varepsilon)\, d\varepsilon + (\mu - \varepsilon_F) H(\varepsilon_F). \quad (2.73)$$

If we apply this expansion to the integrals in (2.71) and (2.72), and replace μ by ε_F in the terms already of order T^2 in these equations, we find

$$u = \int_0^{\varepsilon_F} \varepsilon g(\varepsilon)\, d\varepsilon + \varepsilon_F \left\{ (\mu - \varepsilon_F) g(\varepsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F) \right\}$$
$$+ \frac{\pi^2}{6} (k_B T)^2 g(\varepsilon_F) + O(T^4), \quad (2.74)$$

$$n = \int_0^{\varepsilon_F} g(\varepsilon)\, d\varepsilon + \left\{ (\mu - \varepsilon_F) g(\varepsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F) \right\}. \quad (2.75)$$

The temperature-independent first terms on the right sides of (2.74) and (2.75) are just the values of u and n in the ground state. Since we are calculating the specific heat at constant density, n is independent of temperature, and (2.75) reduces to

$$0 = (\mu - \varepsilon_F) g(\varepsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F), \quad (2.76)$$

which determines the deviation of the chemical potential from ε_F:

$$\mu = \varepsilon_F - \frac{\pi^2}{6} (k_B T)^2 \frac{g'(\varepsilon_F)}{g(\varepsilon_F)}. \quad (2.77)$$

Since for free electrons $g(\varepsilon)$ varies as $\varepsilon^{1/2}$ (see Eq. (2.63)), this gives

$$\mu = \varepsilon_F\left[1 - \frac{1}{3}\left(\frac{\pi k_B T}{2\varepsilon_F}\right)^2\right], \tag{2.78}$$

which is, as we asserted above, a shift of the order of T^2 and typically only about 0.01 percent, even at room temperature.

Equation (2.76) sets the term in braces in (2.74) equal to zero, thereby simplifying the form of the thermal energy density at constant electronic density:

$$u = u_0 + \frac{\pi^2}{6}(k_B T)^2 g(\varepsilon_F) \tag{2.79}$$

where u_0 is the energy density in the ground state. The specific heat of the electron gas is therefore

$$\boxed{c_v = \left(\frac{\partial u}{\partial T}\right)_n = \frac{\pi^2}{3} k_B^2 T g(\varepsilon_F)} \tag{2.80}$$

or, for free electrons (see (2.65)),

$$c_v = \frac{\pi^2}{2}\left(\frac{k_B T}{\varepsilon_F}\right) n k_B. \tag{2.81}$$

Comparing this with the classical result for an ideal gas, $c_v = 3nk_B/2$, we see that the effect of Fermi-Dirac statistics is to depress the specific heat by a factor of $(\pi^2/3)$ $(k_B T/\varepsilon_F)$, which is proportional to the temperature, and even at room temperature is only of order 10^{-2}. This explains the absence of any observable contribution of the electronic degrees of freedom to the specific heat of a metal at room temperature.

If one is willing to dispense with the precise numerical coefficient, one can understand this behavior of the specific heat quite simply from the temperature dependence of the Fermi function itself. The increase in energy of the electrons when the temperature is raised from $T = 0$ comes about entirely because some electrons with energies within $O(k_B T)$ below ε_F (the darkly shaded region of Figure 2.4) have been excited to an energy range of $O(k_B T)$ above ε_F (the lightly shaded region of Figure 2.4). The number of electrons per unit volume that have been so excited is the width, $k_B T$, of the energy interval times the density of levels per unit volume $g(\varepsilon_F)$. Furthermore, the excitation energy is of order $k_B T$, and hence the total thermal energy density is of order $g(\varepsilon_F)(k_B T)^2$ above the ground-state energy. This misses the precise result (2.79) by a factor of $\pi^2/6$, but it gives a simple physical picture, and is useful for rough estimates.

Figure 2.4
The Fermi function at nonzero T. The distribution differs from its $T = 0$ form because some electrons just below ε_F (darkly shaded region) have been excited to levels just above ε (lightly shaded region).

The prediction of a linear specific heat is one of the most important consequences of Fermi-Dirac statistics, and provides a further simple test of the electron gas theory of a metal, provided one can be sure that degrees of freedom other than the electronic ones do not make comparable or even bigger contributions. As it happens, the ionic degrees of freedom completely dominate the specific heat at high temperatures. However, well below room temperature their contribution falls off as the cube of the

Table 2.3
SOME ROUGH EXPERIMENTAL VALUES FOR THE COEFFICIENT OF THE LINEAR TERM IN T OF THE MOLAR SPECIFIC HEATS OF METALS, AND THE VALUES GIVEN BY SIMPLE FREE ELECTRON THEORY

ELEMENT	FREE ELECTRON γ (in 10^{-4} cal-mole^{-1}-K^{-2})	MEASURED γ	RATIO[a] (m^*/m)
Li	1.8	4.2	2.3
Na	2.6	3.5	1.3
K	4.0	4.7	1.2
Rb	4.6	5.8	1.3
Cs	5.3	7.7	1.5
Cu	1.2	1.6	1.3
Ag	1.5	1.6	1.1
Au	1.5	1.6	1.1
Be	1.2	0.5	0.42
Mg	2.4	3.2	1.3
Ca	3.6	6.5	1.8
Sr	4.3	8.7	2.0
Ba	4.7	6.5	1.4
Nb	1.6	20	12
Fe	1.5	12	8.0
Mn	1.5	40	27
Zn	1.8	1.4	0.78
Cd	2.3	1.7	0.74
Hg	2.4	5.0	2.1
Al	2.2	3.0	1.4
Ga	2.4	1.5	0.62
In	2.9	4.3	1.5
Tl	3.1	3.5	1.1
Sn	3.3	4.4	1.3
Pb	3.6	7.0	1.9
Bi	4.3	0.2	0.047
Sb	3.9	1.5	0.38

[a] Since the theoretical value of γ is proportional to the density of levels at the Fermi level, which in turn is proportional to the electronic mass m, one sometimes defines a specific heat effective mass m^* so that m^*/m is the ratio of the measured γ to the free electron γ. Beware of identifying this specific heat effective mass with any of the many other effective masses used in solid-state theory. (See, for example, the index entries under "effective mass.")

temperature (Chapter 23), and at very low temperatures it drops below the electronic contribution, which only decreases linearly with T. In order to separate out these two contributions it has become the practice to plot c_v/T against T^2, for if the electronic and ionic contributions together result in the low-temperature form,

$$c_v = \gamma T + AT^3, \tag{2.82}$$

then

$$\frac{c_v}{T} = \gamma + AT^2. \tag{2.83}$$

One can thus find γ by extrapolating the c_v/T curve linearly down to $T^2 = 0$, and noting where it intercepts the c_v/T-axis. Measured metallic specific heats typically contain a linear term that becomes comparable to the cubic one at a few degrees Kelvin.[25]

Specific heat data are usually quoted in joules (or calories) per mole per degree Kelvin. Since a mole of free electron metal contains ZN_A conduction electrons (where Z is the valence and N_A is Avogadro's number) and occupies a volume ZN_A/n, we must multiply the heat capacity per unit volume, c_v by ZN_A/n, in order to get the heat capacity per mole, C:

$$C = \frac{\pi^2}{3} ZR \frac{k_B T g(\mathcal{E}_F)}{n}, \tag{2.84}$$

where $R = k_B N_A = 8.314$ joules/mole $= 1.99$ calories/mole-K. Using the free electron density of levels (2.65) and the evaluation (2.33) of $\mathcal{E}_F/k_B$, we find a free electron contribution to the heat capacity per mole of $C = \gamma T$, where

$$\gamma = \frac{1}{2} \pi^2 R \frac{Z}{T_F} = 0.169 Z \left(\frac{r_s}{a_0} \right)^2 \times 10^{-4} \text{ cal-mole}^{-1}\text{-K}^{-2}. \tag{2.85}$$

Some rough, measured values of γ are displayed in Table 2.3, together with the free electron values implied by (2.85) and the values of r_s/a_0 in Table 1.1. Note that the alkali metals continue to be reasonably well described by free electron theory, as do the noble metals (Cu, Ag, Au). Note also, however, the striking disparities in Fe and Mn (experiment of the order of 10 times theory) as well as those in Bi and Sb (experiment of the order of 0.1 times theory). These large deviations are now qualitatively understood on fairly general grounds, and we shall return to them in Chapter 15.

THE SOMMERFELD THEORY OF CONDUCTION IN METALS

To find the velocity distribution for electrons in metals, consider a small[26] volume element of k-space about a point $\mathbf{k}$, of volume $d\mathbf{k}$. Allowing for the twofold spin

---

[25]   Since constant density is hard to arrange experimentally, one generally measures the specific heat at constant pressure, c_p. However, one can show (Problem 2) that for the metallic free electron gas at room temperature and below, $c_p/c_v = 1 + O(k_B T/\mathcal{E}_F)^2$. Thus at temperatures where the electronic contribution to the specific heat becomes observable (a few degrees Kelvin) the two specific heats differ by a negligible amount.

[26]   Small enough that the Fermi function and other functions of physical interest vary negligibly throughout the volume element, but large enough that it contains very many one-electron levels.

degeneracy, the number of one-electron levels in this volume element is (see (2.18))

$$\left(\frac{V}{4\pi^3}\right) d\mathbf{k}. \tag{2.86}$$

The probability of each level being occupied is just $f(\mathcal{E}(\mathbf{k}))$, and therefore the total number of electrons in the k-space volume element is

$$\frac{V}{4\pi^3} f(\mathcal{E}(\mathbf{k})) \, d\mathbf{k}, \qquad \mathcal{E}(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}. \tag{2.87}$$

Since the velocity of a free electron with wave vector $\mathbf{k}$ is $\mathbf{v} = \hbar\mathbf{k}/m$ (Eq. (2.12)), the number of electrons in an element of volume $d\mathbf{v}$ about $\mathbf{v}$ is the same as the number in an element of volume $d\mathbf{k} = (m/\hbar)^3 \, d\mathbf{v}$ about $\mathbf{k} = m\mathbf{v}/\hbar$. Consequently the total number of electrons per unit volume of real space in a velocity space element of volume $d\mathbf{v}$ about $\mathbf{v}$ is

$$f(\mathbf{v}) \, d\mathbf{v}, \tag{2.88}$$

where

$$f(\mathbf{v}) = \frac{(m/\hbar)^3}{4\pi^3} \frac{1}{\exp\left[(\frac{1}{2}mv^2 - \mu)/k_BT\right] + 1}. \tag{2.89}$$

Sommerfeld reexamined the Drude model, replacing the classical Maxwell-Boltzmann velocity distribution (2.1) by the Fermi-Dirac distribution (2.89). Using a velocity distribution constructed from quantum-mechanical arguments in an otherwise classical theory requires some justification.[27] One can describe the motion of an electron classically if one can specify its position and momentum as accurately as necessary, without violating the uncertainty principle.[28]

A typical electron in a metal has a momentum of the order of $\hbar k_F$, so the uncertainty in its momentum, Δp, must be small compared with $\hbar k_F$ for a good classical description. Since, from (2.22), $k_F \sim 1/r_s$, the uncertainty in position must satisfy

$$\Delta x \sim \frac{\hbar}{\Delta p} \gg \frac{1}{k_F} \sim r_s, \tag{2.90}$$

where, from (1.2), r_s is of the order of the mean interelectronic distance—i.e., angstroms. Thus a classical description is impossible if one has to consider electrons localized to within atomic distances (also of the order of angstroms). However, the conduction electrons in a metal are not bound to particular ions, but can wander freely through the volume of the metal. In a macroscopic specimen, for most purposes there is no need to specify their position to an accuracy of 10^{-8} cm. The Drude model assumes a knowledge of the position of an electron primarily in only the two following contexts:

---

[27] A detailed analytical justification is fairly complicated to construct, just as it is a fairly subtle matter to specify with generality and precision when the quantum theory can be replaced by its classical limit. The underlying physics, however, is straightforward.

[28] There is also a somewhat more specialized limitation on the use of classical mechanics in describing conduction electrons. The energy of motion of an electron in the plane perpendicular to a uniform applied magnetic field is quantized in multiples of $\hbar\omega_c$ (Chapter 14). Even for fields as large as 10^4 gauss, this is a very small energy, but in suitably prepared samples at temperatures of a few degrees Kelvin, these quantum effects become observable, and are, in fact, of great practical importance.

1. When spatially varying electromagnetic fields or temperature gradients are applied, one must be able to specify the position of an electron on a scale small compared with the distance λ over which the fields or temperature gradients vary. For most applications the applied fields or temperature gradients do not vary appreciably on the scale of angstroms, and the necessary precision of definition in the electron's position need not lead to an unacceptably large uncertainty in its momentum. For example, the electric field associated with visible light varies appreciably only over a distance of order 10^3 Å. If, however, the wave length is very much shorter than this (for example, X rays), one must use quantum mechanics to describe the electronic motion induced by the field.

2. There is also an implicit assumption in the Drude model that one can localize an electron to within substantially less than a mean free path ℓ, and one should therefore be suspicious of classical arguments when mean free paths much shorter than tens of angstroms occur. Fortunately, as we shall see below, mean free paths in metals are of the order of 100 Å at room temperature, and become longer still as the temperature drops.

There is thus a wide range of phenomena in which the behavior of a metallic electron is well described by classical mechanics. It is not, however, immediately evident from this that the behavior of N such electrons can be described by classical mechanics. Since the Pauli exclusion principle so profoundly affects the statistics of N electrons, why should it not have similarly drastic effects on their dynamics? That it does not follows from an elementary theorem, which we state without proof, since the proof, though simple, is notationally rather cumbersome:

Consider a system of N electrons whose interactions with one another are ignored, and which are exposed to an arbitrary space- and time-dependent electromagnetic field. Let the N-electron state at time 0 be formed by occupying a particular group of N one-electron levels, $\psi_1(0), ..., \psi_N(0)$. Let $\psi_j(t)$ be the level $\psi_j(0)$ would evolve into in time t under the influence of the electromagnetic field if there were only a single electron present, which was in the level $\psi_j(0)$ at time zero. Then the correct N-electron state at time t will be the one formed by occupying the set of N one-electron levels $\psi_1(t), ..., \psi_N(t)$.

Thus the dynamical behavior of N noninteracting electrons is completely determined by considering N independent one-electron problems. In particular, if the classical approximation is valid for each of these one-electron problems, it will also be valid for the whole N-electron system.[29]

The use of Fermi-Dirac statistics affects only those predictions of the Drude model that require some knowledge of the electronic velocity distribution for their evaluation. If the rate $1/\tau$ at which an electron experiences collisions does not depend on its energy, then only our estimate of the electronic mean free path and our calculation of the thermal conductivity and thermopower are at all affected by a change in the equilibrium distribution function.

---

[29] Note that this implies that any classical configuration consistent with the exclusion principle at time t = 0 (i.e., having less than one electron of each spin per unit volume, in any momentum space region of volume $d\mathbf{p} = (2\pi\hbar)^3/V$) will remain consistent with the exclusion principle at all future times. This result can also be proved by purely classical reasoning as a direct corollary of Liouville's theorem. See Chapter 12.

Mean Free Path Using v_F (Eq. (2.24)) as a measure of the typical electronic speed, we can evaluate the mean free path $\ell = v_F \tau$ from Eq. (1.8) as follows:

$$\ell = \frac{(r_s/a_0)^2}{\rho_\mu} \times 92 \text{ Å}. \tag{2.91}$$

Since the resistivity in microhm centimeters, ρ_μ, is typically 1 to 100 at room temperature, and since r_s/a_0 is typically 2 to 6, mean free paths of order a hundred angstroms long are possible even at room temperature.[30]

Thermal Conductivity We continue to estimate the thermal conductivity by Eq. (1.51):

$$\kappa = \tfrac{1}{3} v^2 \tau c_v. \tag{2.92}$$

The correct specific heat (2.81) is smaller than the classical guess of Drude by a factor of order $k_B T/\varepsilon_F$; the correct estimate of v^2 is not the classical thermal mean square velocity of order $k_B T/m$, but $v_F^2 = 2\varepsilon_F/m$, which is larger than the classical value by a factor of order $\varepsilon_F/k_B T$. Inserting these values in (2.92) and eliminating the relaxation time in favor of the conductivity through (1.6), we find

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \left(\frac{k_B}{e}\right)^2 = 2.44 \times 10^{-8} \text{ watt-ohm/K}^2. \tag{2.93}$$

This is remarkably close to Drude's fortuitously good value, thanks to the two compensating corrections of order $k_B T/\varepsilon_F$, and in excellent agreement with the data in Table 1.6. We shall see (Chapter 13) that this value of the Lorenz number is a far better one than the very rough derivation of (2.93) would suggest.

Thermopower Drude's overestimate of the thermopower is also resolved by the use of Fermi-Dirac statistics. Substituting the specific heat, from Eq. (2.81), into Eq. (1.59) we find

$$Q = -\frac{\pi^2}{6} \frac{k_B}{e} \left(\frac{k_B T}{\varepsilon_F}\right) = -1.42 \left(\frac{k_B T}{\varepsilon_F}\right) \times 10^{-4} \text{ volt/K}, \tag{2.94}$$

which is smaller than Drude's estimate (Eq. (1.60)) by $O(k_B T/\varepsilon_F) \sim 0.01$ at room temperature.

Other Properties Since the form of the electronic velocity distribution did not play a role in the calculation of the DC or AC conductivities, the Hall coefficient, or the magnetoresistance, the estimates given in Chapter 1 remain the same whether one uses Maxwell-Boltzmann or Fermi-Dirac statistics.

This is not the case, however, if one uses an energy-dependent relaxation time. If, for example, one thought the electrons collided with fixed scattering centers, then it would be natural to take an energy-independent mean free path, and hence a relaxation time $\tau = \ell/v \sim \ell/\varepsilon^{1/2}$. Shortly after Drude set forth the electron gas model of a

---

[30] It is perhaps just as well that Drude estimated ℓ using the very much lower classical thermal velocity, or he might have been sufficiently baffled by such long mean free paths to abandon further investigation.

metal, H. A. Lorentz showed, using the classical Maxwell-Boltzmann velocity distribution, that an energy-dependent relaxation time would lead to temperature dependence in the DC and AC conductivities, as well as to a nonvanishing magnetoresistance and a field- and temperature-dependent Hall coefficient. As one might now expect from the inappropriateness of the classical velocity distribution, none of these corrections were in any way able to bring the discrepancies of the Drude model into better alignment with the observed facts about metals.[31] Furthermore, we shall see (Chapter 13) that when the correct Fermi-Dirac velocity distribution is used, adding an energy dependence to the relaxation time has little significant effect on most of the quantities of interest in a metal.[32] If one calculates the DC or AC conductivities, the magnetoresistance, or the Hall coefficient assuming an energy-dependent $\tau(\mathcal{E})$, the results one finds are the same as those one would have calculated assuming an energy-independent τ, equal to $\tau(\mathcal{E}_F)$. In metals these quantities are determined almost entirely by the way in which electrons near the Fermi level are scattered.[33] This is another very important consequence of the Pauli exclusion principle, the justification of which will be given in Chapter 13.

PROBLEMS

1. **The Free and Independent Electron Gas in Two Dimensions**
    (a) What is the relation between n and k_F in two dimensions?
    (b) What is the relation between k_F and r_s in two dimensions?
    (c) Prove that in two dimensions the free electron density of levels $g(\mathcal{E})$ is a constant independent of $\mathcal{E}$ for $\mathcal{E} > 0$, and 0 for $\mathcal{E} < 0$. What is the constant?
    (d) Show that because $g(\mathcal{E})$ is constant, every term in the Sommerfeld expansion for n vanishes except the $T = 0$ term. Deduce that $\mu = \mathcal{E}_F$ at any temperature.
    (e) Deduce from (2.67) that when $g(\mathcal{E})$ is as in (c), then

$$\mu + k_B T \ln \left(1 + e^{-\mu/k_B T}\right) = \mathcal{E}_F. \qquad (2.95)$$

    (f) Estimate from (2.95) the amount by which μ differs from $\mathcal{E}_F$. Comment on the numerical significance of this "failure" of the Sommerfeld expansion, and on the mathematical reason for the "failure."

2. **Thermodynamics of the Free and Independent Electron Gas**
    (a) Deduce from the thermodynamic identities

$$c_v = \left(\frac{\partial u}{\partial T}\right)_n = T\left(\frac{\partial s}{\partial T}\right)_n, \qquad (2.96)$$

---

[31] The Lorentz model is, however, of considerable importance in the description of semiconductors (Chapter 29).

[32] The thermopower is a notable exception.

[33] These assertions are correct to leading order in $k_B T/\mathcal{E}_F$, but in metals this is always a good expansion parameter.

from Eqs. (2.56) and (2.57), and from the third law of thermodynamics ($s \to 0$ as $T \to 0$) that the entropy density, $s = S/V$ is given by:

$$s = -k_B \int \frac{d\mathbf{k}}{4\pi^3} \left[f \ln f + (1-f) \ln (1-f) \right], \tag{2.97}$$

where $f(\mathcal{E}(\mathbf{k}))$ is the Fermi function (Eq. (2.56)).

(b)   Since the pressure P satisfies Eq. (B.5) in Appendix B, $P = -(u - Ts - \mu n)$, deduce from (2.97) that

$$P = k_B T \int \frac{d\mathbf{k}}{4\pi^3} \ln \left(1 + \exp \left[-\frac{(\hbar^2 k^2/2m) - \mu}{k_B T} \right] \right). \tag{2.98}$$

Show that (2.98) implies that P is a homogeneous function of μ and T of degree 5/2; that is,

$$P(\lambda\mu, \lambda T) = \lambda^{5/2} P(\mu, T) \tag{2.99}$$

for any constant λ.

(c)   Deduce from the thermodynamic relations in Appendix B that

$$\left(\frac{\partial P}{\partial \mu} \right)_T = n, \qquad \left(\frac{\partial P}{\partial T} \right)_\mu = s. \tag{2.100}$$

(d)   By differentiating (2.99) with respect to λ show that the ground-state relation (2.34) holds at any temperature, in the form

$$P = \tfrac{2}{3} u. \tag{2.101}$$

(e)   Show that when $k_B T \ll \mathcal{E}_F$, the ratio of the constant-pressure to constant-volume specific heats satisfies

$$\left(\frac{c_p}{c_v} \right) - 1 = \frac{\pi^2}{3} \left(\frac{k_B T}{\mathcal{E}_F} \right)^2 + O \left(\frac{k_B T}{\mathcal{E}_F} \right)^4.$$

(f)   Show, by retaining further terms in the Sommerfeld expansions of u and n, that correct to order T^3 the electronic heat capacity is given by

$$c_v = \frac{\pi^2}{3} k_B^2 T g(\mathcal{E}_F)$$
$$- \frac{\pi^4}{90} k_B^4 T^3 g(\mathcal{E}_F) \left[15 \left(\frac{g'(\mathcal{E}_F)}{g(\mathcal{E}_F)} \right)^2 - 21 \frac{g''(\mathcal{E}_F)}{g(\mathcal{E}_F)} \right]. \tag{2.102}$$

3.   The Classical Limit of Fermi-Dirac Statistics

The Fermi-Dirac distribution reduces to the Maxwell-Boltzmann distribution, provided that the Fermi function (2.56) is much less than unity for every positive $\mathcal{E}$, for in that case we must have

$$f(\mathcal{E}) \approx e^{-(\mathcal{E}-\mu)/k_B T}. \tag{2.103}$$

The necessary and sufficient condition for (2.103) to hold for all positive $\mathcal{E}$ is

$$e^{-\mu/k_B T} \gg 1. \tag{2.104}$$

(a)   Assuming that (2.104) holds, show that

$$r_s = e^{-\mu/3k_B T} \, 3^{1/3} \pi^{1/6} \hbar (2 m k_B T)^{-1/2}. \tag{2.105}$$

In conjunction with (2.104) this requires that

$$r_s \gg \left(\frac{\hbar^2}{2mk_BT}\right)^{1/2},\qquad(2.106)$$

which can also be taken as the condition for the validity of classical statistics.

(b) What is the significance of the length r_s must exceed?

(c) Show that (2.106) leads to the numerical condition

$$\frac{r_s}{a_0} \gg \left(\frac{10^5 \text{ K}}{T}\right)^{1/2}.\qquad(2.107)$$

(d) Show that the normalization constant $m^3/4\pi^3\hbar^3$ appearing in the Fermi-Dirac velocity distribution (2.2) can also be written as $(3\sqrt{\pi}/4)n(m/2\pi k_BT_F)^{3/2}$ so that $f_B(0)/f(0) = (4/3\sqrt{\pi})(T_F/T)^{3/2}$.

4. Insensitivity of the Distribution Function to Small Changes in the Total Number of Electrons

In deriving the Fermi distribution (page 41) we argued that the probability of a given level being occupied should not change appreciably when the total number of electrons is changed by one. Verify that the Fermi function (2.56) is compatible with this assumption as follows:

(a) Show, when $k_BT \ll \mathcal{E}_F$, that when the number of electrons changes by one at fixed temperature, the chemical potential changes by

$$\Delta\mu = \frac{1}{Vg(\mathcal{E}_F)},\qquad(2.108)$$

where $g(\mathcal{E})$ is the density of levels.

(b) Show, as a consequence of this, that the most the probability of any level being occupied can change by is

$$\Delta f = \frac{1}{6}\frac{\mathcal{E}_F}{k_BT}\frac{1}{N}.\qquad(2.109)$$

[Use the free electron evaluation (2.65) of $g(\mathcal{E}_F)$.] Although temperatures of millidegrees Kelvin can be reached, at which $\mathcal{E}_F/k_BT \approx 10^8$, when N is of order 10^{22} then Δf is still negligibly small.

3

Failures of the Free Electron Model

Free electron theory successfully accounts for a wide range of metallic properties. In the form originally put forth by Drude the most striking deficiencies of the model were due to the use of classical statistical mechanics in describing the conduction electrons. As a result, predicted thermoelectric fields and heat capacities were hundreds of times too large, even at room temperature. The difficulty was obscured by the fact that classical statistics fortuitously gave a form for the Wiedemann-Franz law that was not in such gross error. Sommerfeld's application of Fermi-Dirac statistics to the conduction electrons eliminated this class of difficulties while retaining all of the other basic assumptions of the free electron model.

However, the Sommerfeld free electron model still makes many quantitative predictions that are quite unambiguously contradicted by observation, and leaves many fundamental questions of principle unresolved. We list below those inadequacies of the free electron model that have emerged from the applications made in the preceding two chapters.[1]

DIFFICULTIES WITH THE FREE ELECTRON MODEL

1.   Inadequacies in the Free Electron Transport Coefficients

(a)   *The Hall Coefficient*   Free electron theory predicts a Hall coefficient which at metallic densities of electrons has the constant value $R_H = -1/nec$, independent of the temperature, the relaxation time, or the strength of the magnetic field. Although observed Hall coefficients have this order of magnitude, generally speaking they depend on both the magnetic field strength and the temperature (and presumably on the relaxation time, which is rather harder to control experimentally). Often this dependence is quite dramatic. In aluminum, for example, R_H (see Figure 1.4) never gets within a factor of three of the free electron value, depends strongly on the strength of the field, and at high fields does not even have the sign predicted by free electron theory. Such cases are not atypical. Only the Hall coefficients of the alkali metals come even close to behaving in accordance with the predictions of free electron theory.

(b)   *The Magnetoresistance*   Free electron theory predicts that the resistance of a wire perpendicular to a uniform magnetic field should not depend on the strength of the field. In almost all cases it does. In some cases (notably the noble metals, copper, silver, and gold) it can be made to increase apparently without limit as the field increases. In most metals the behavior of the resistance in a field depends quite drastically on the manner in which the metallic specimen is prepared and, for suitable specimens, on the orientation of the specimen with respect to the field.

---

[1]   These examples and the remarks making up the rest of this brief chapter are not intended to give a detailed picture of the limitations of the free electron model. That will emerge in the chapters that follow, together with the solutions to the difficulties posed by the model. Our purpose in this chapter is only to emphasize how varied and extensive the shortcomings are, thereby indicating why one must resort to a considerably more elaborate analysis.

(c) **The Thermoelectric Field**   The sign of the thermoelectric field, like the sign of the Hall constant, is not always what free electron theory predicts it should be. Only the order of magnitude is right.

(d) **The Wiedemann-Franz Law**   That great triumph of free electron theory, the Wiedemann-Franz law, is obeyed beautifully at high (room) temperatures and also quite probably at very low (a few degrees K) temperatures. At intermediate temperatures it fails, and $\kappa/\sigma T$ depends on the temperature.

(e) **Temperature Dependence of the DC Electrical Conductivity**   Nothing in free electron theory can account for the temperature dependence of the DC conductivity (revealed, for example, in Table 1.2). It has to be mechanically inserted into the theory as an *ad hoc* temperature dependence in the relaxation time τ.

(f) **Directional Dependence of the DC Electrical Conductivity**   In some (but by no means all) metals the DC conductivity depends on the orientation of the specimen (if suitably prepared) with respect to the field. In such specimens the current **j** need not even be parallel to the field.

(g) **AC Conductivity**   There is a far more subtle frequency dependence to the optical properties of metals than the simple free electron dielectric constant can hope to produce. Even sodium, in other respects a fairly good free electron metal, appears to fail this test in the detailed frequency dependence of its reflectivity. In other metals the situation is far worse. We cannot begin to explain the colors of copper and gold in terms of reflectivities calculated from the free electron dielectric constant.

2.   Inadequacies in the Static Thermodynamic Predictions

(a) **Linear Term in the Specific Heat**   The Sommerfeld theory accounts reasonably well for the size of the term linear in T in the low-temperature specific heat of the alkali metals, rather less well for the noble metals, and very poorly indeed for transition metals such as iron and manganese (much too small a prediction) as well as for bismuth and antimony (much too large a prediction).

(b) **Cubic Term in the Specific Heat**   There is nothing in the free electron model to explain why the low-temperature specific heat should be dominated by the electronic contribution. However, it is evident from experiment that the T^3 correction to the linear term is very definitely dominated by something else, since the simple Sommerfeld theory for the electronic contribution to the T^3 term has the wrong sign and is millions of times too small.

(c) **The Compressibility of Metals**   Although free electron theory does miraculously well in estimating the bulk moduli (or compressibilities) of many metals, it is clear that more attention must be paid to the ions and to electron-electron interactions if one is to achieve a more accurate estimate of the equation of state of a metal.

3.   Fundamental Mysteries

(a) **What Determines the Number of Conduction Electrons?**   We have assumed that the 'l valence electrons become conduction electrons, while the others

remain bound to the ions. We have given no thought to the question of why this should be, or how it is to be interpreted in the case of elements, like iron, that display more than one chemical valence.

(b)　*Why Are Some Elements Nonmetals?*　A more acute inadequacy of our rule of thumb for determining the number of conduction electrons is posed by the existence of insulators. Why, for example, is boron an insulator while its vertical neighbor in the periodic table, aluminum, an excellent metal? Why is carbon an insulator when in the form of diamond and a conductor when in the form of graphite? Why are bismuth and antimony such very poor conductors?

REVIEW OF BASIC ASSUMPTIONS

To make further progress with any of these problems we must reexamine the basic assumptions on which free electron theory rests. The most notable are these:

1.　**Free Electron Approximation**[2] The metallic ions play a very minor role. In between collisions they have no effect at all on the motion of an electron, and though Drude invoked them as a source of collisions, the quantitative information we have been able to extract about the collision rate has made no sense when interpreted in terms of electrons colliding with fixed ions. The only thing the ions really seem to do properly in the models of Drude and Sommerfeld is to maintain overall charge neutrality.

2.　**Independent Electron Approximation**[3] The interactions of the electrons with one another are ignored.

3.　**Relaxation-Time Approximation**[4] The outcome of a collision is assumed not to depend on the configuration of the electrons at the moment of collision.

All these oversimplifications must be abandoned if we are to achieve an accurate model of a solid. However, a remarkable amount of progress can be made by first concentrating entirely on improving some aspects of the free electron approximation while continuing to use the independent electron and relaxation time approximations. We shall return to a critical examination of these last two approximations in Chapters 16 and 17, limiting ourselves here to the following general observations:

There is a surprisingly wide range of circumstances in which the independent electron approximation does not drastically diminish the validity of the analysis. In resolving the problems of free electron theory listed above, improving on the independent electron approximation plays a major role only in the calculation of metallic compressibilities (2c).[5,6] An indication of why we apparently ignore electron-electron interactions is given in Chapter 17, together with further examples in which electron-electron interactions do play a direct and crucial role.

---

[2]　See page 4.

[3]　See page 4.

[4]　See page 6.

[5]　Numbers in parentheses refer to numbered paragraphs at the beginning of this chapter.

[6]　There are also some cases where a failure of the independent electron approximation (Chapter 10, p. 186 and Chapter 32) invalidates the simple distinction between metals and insulators that we shall draw in Chapters 8 and 12.

As for the relaxation time approximation, even in Drude's time there were methods in kinetic theory for correcting this oversimplification. They lead to a much more complex analysis and in many cases are primarily important in understanding metallic phenomena with greater precision. Of the difficulties described previously, only the problem of the Wiedemann-Franz law at intermediate temperatures (1d) has a resolution that requires abandoning the relaxation time approximation even at the most gross qualitative level of explanation.[7] In Chapter 16 we shall describe the form a theory must take if it is to go beyond the relaxation time approximation, together with further examples of problems requiring such a theory for their resolution.

The free electron approximation is the major source of the difficulties in the theories of Drude and Sommerfeld. It makes several simplifications:

(i)   The effect of the ions on the dynamics of an electron between collisions is ignored.
(ii) What role the ions play as a source of collisions is left unspecified.
(iii) The possibility that the ions themselves, as independent dynamical entities, contribute to physical phenomena (such as the specific heat or thermal conductivity) is ignored.

The failures of assumptions (ii) and (iii) play an essential role in accounting for deviations from the Wiedemann-Franz law at intermediate temperatures (1d) and the temperature dependence of the electrical conductivity (1e). The failure of assumption (iii) accounts for the cubic term in the specific heat (2b). Relaxing these two assumptions is also essential in accounting for a variety of phenomena yet to be discussed. Such phenomena are briefly described in Chapter 21, and the consequences of abandoning assumptions (ii) and (iii) are explored in detail in Chapters 22 to 26.

It is assumption (i), that the ions have no significant effect on the motion of electrons between collisions, that is responsible for most of the deficiencies of the Drude and Sommerfeld theories described above. The reader may well be perplexed at how one can distinguish between assumptions (i) and (ii), for it is far from clear that the effect of the ions on the electrons can be unambiguously resolved into "collisional" and "noncollisional" aspects. We shall find, however (especially in Chapters 8 and 12), that a theory that takes into account the detailed field produced by an appropriate static array of ions but ignores the possibility of ionic motion (the "static ion approximation") reduces under a wide range of circumstances to a relatively simple modification of the Drude and Sommerfeld free electron theories, in which collisions are entirely absent! It is only when one allows for ionic motion that their role as a source of collisions can be properly understood.

We shall therefore relax the free electron approximation in two stages. First we shall examine the wealth of new structure and the subsequent elucidation that emerges when the electrons are considered to move not in empty space, but in the presence of a specified static potential due to a fixed array of stationary ions. Only after that (from Chapter 21 onward) will we examine the consequences of the dynamical deviations of the ionic positions from that static array.

The single most important fact about the ions is that they are not distributed at random, but are arranged in a regular periodic array, or "lattice." This was first

---

[7]   It must also be abandoned to explain the detailed temperature dependence of the DC conductivity (1e).

suggested by the macroscopic crystalline forms assumed by many solids (including metals), first directly confirmed by X-ray diffraction experiments (Chapter 6) and subsequently reconfirmed by neutron diffraction, electron microscopy, and many other direct measurements.

The existence of a periodic lattice of ions lies at the heart of modern solid state physics. It provides the basis for the entire analytic framework of the subject, and without it comparatively little progress would have been made. If there is one reason why the theory of solids is so much more highly developed than the theory of liquids, even though both forms of matter have comparable densities, it is that the ions are arranged periodically in the solid state but are spatially disordered in liquids. It is the lack of a periodic array of ions that has left the subject of amorphous solids in so primitive a state compared with the highly developed theory of crystalline solids.[8]

To make further progress in the theory of solids, whether metallic or insulating, we must therefore turn to the subject of periodic arrays. The fundamental properties of such arrays are developed in Chapters 4, 5, and 7, without regard to particular physical applications. In Chapter 6 these concepts are applied to an elementary discussion of X-ray diffraction, which provides a direct demonstration of the periodicity of solids and is a paradigm for the wide variety of other wave phenomena in solids we shall subsequently encounter. Chapters 8 to 11 explore the direct consequences of the periodicity of the array of ions on the electronic structure of any solid, whether insulating or metallic. In Chapters 12 to 15 the resulting theory is used to reexplore the properties of metals described in Chapters 1 and 2. Many of the anomalies of free electron theory are thereby removed, and its mysteries are in large part resolved.

---

[8]   Although there has been a great burst of interest in amorphous solids (starting in the late 1960s), the subject has yet to develop any unifying principles of a power even remotely comparable to that provided by the consequences of a periodic array of ions. Many of the concepts used in the theory of amorphous solids are borrowed, with little if any justification, from the theory of crystalline solids, even though they are only well understood as consequences of lattice periodicity. Indeed, the term "solid state physics," if defined as the subject matter of solid state physics textbooks (including this one) is currently confined almost entirely to the theory of crystalline solids. This is in large part because the normal condition of solid matter is crystalline, and also because in its present form the subject of amorphous solids still lacks the kind of broad basic principles suitable for inclusion in an elementary text.