

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 range¹ $d\mathbf{v}$ about \mathbf{v} as $f_B(\mathbf{v}) d\mathbf{v}$, where

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

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 electrons³ the Pauli exclusion principle requires the replacement of the Maxwell-Boltzmann distribution (2.1) with the Fermi-Dirac distribution:

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

Here \hbar is Planck's constant divided by 2π , and T_0 is a temperature that is determined by the normalization condition⁴

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

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 i th 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).

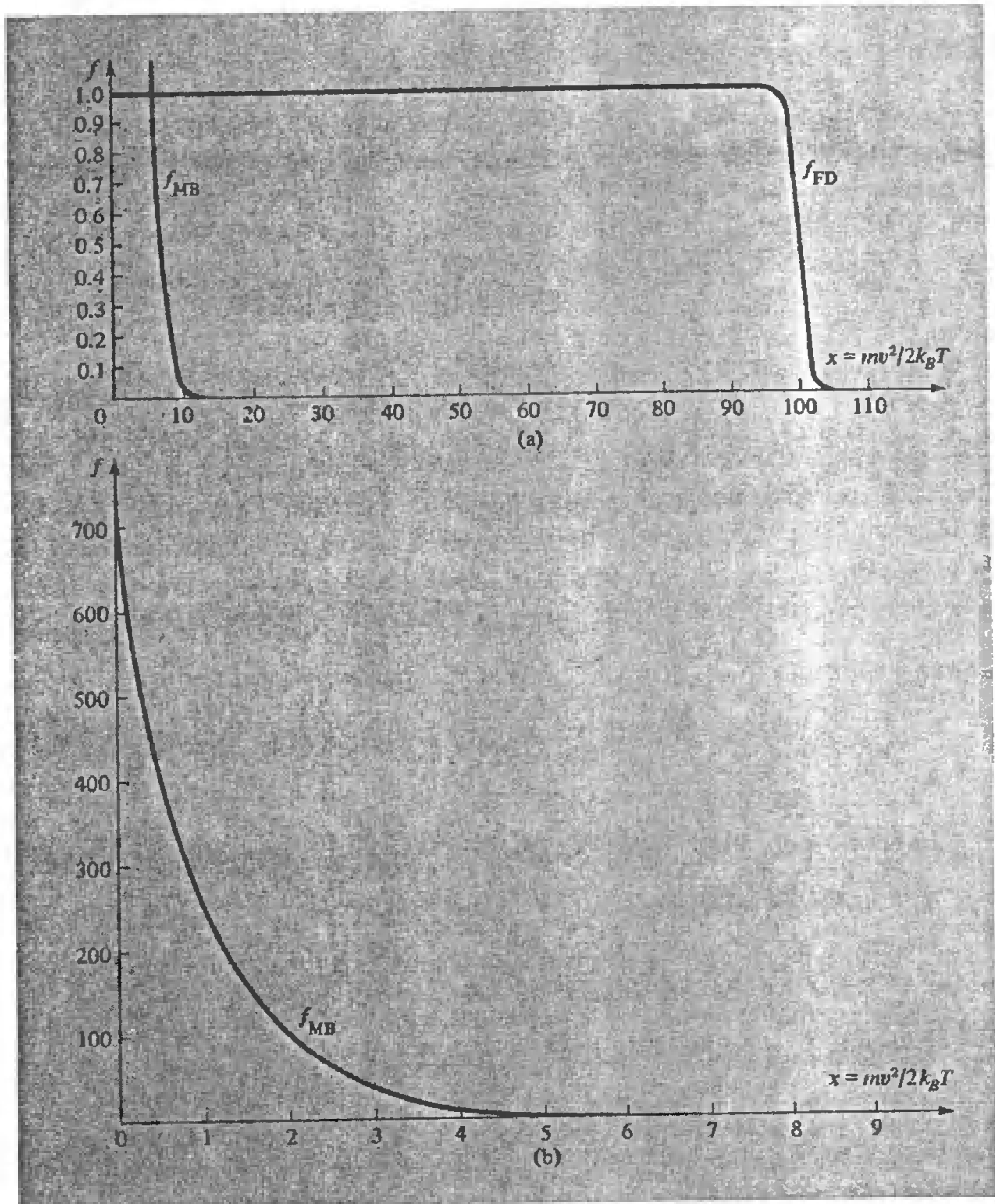


Figure 2.1

(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 ϵ satisfies the time-independent Schrödinger equation⁷:

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

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 cube⁹ 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 generalized⁹ 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

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m},\tag{2.7}$$

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,

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

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 the parallelepiped.

with eigenvalue $\mathbf{p} = \hbar \mathbf{k}$, for

$$\frac{\hbar}{i} \frac{\partial}{\partial \mathbf{r}} e^{i\mathbf{k} \cdot \mathbf{r}} = \hbar \mathbf{k} e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (2.10)$$

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 $\psi_{\mathbf{k}}(\mathbf{r})$ has a definite momentum proportional to \mathbf{k} :

$$\mathbf{p} = \hbar \mathbf{k}. \quad (2.11)$$

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

$$\mathbf{v} = \frac{\hbar \mathbf{k}}{m}. \quad (2.12)$$

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

$$\varepsilon = \frac{p^2}{2m} = \frac{1}{2} m v^2. \quad (2.13)$$

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 $\mathbf{k} \cdot \mathbf{r} = \text{constant}$) and it is periodic along lines parallel to \mathbf{k} , with wavelength

$$\lambda = \frac{2\pi}{k}, \quad (2.14)$$

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

$$e^{ik_x L} = e^{ik_y L} = e^{ik_z L} = 1. \quad (2.15)$$

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:

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

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.

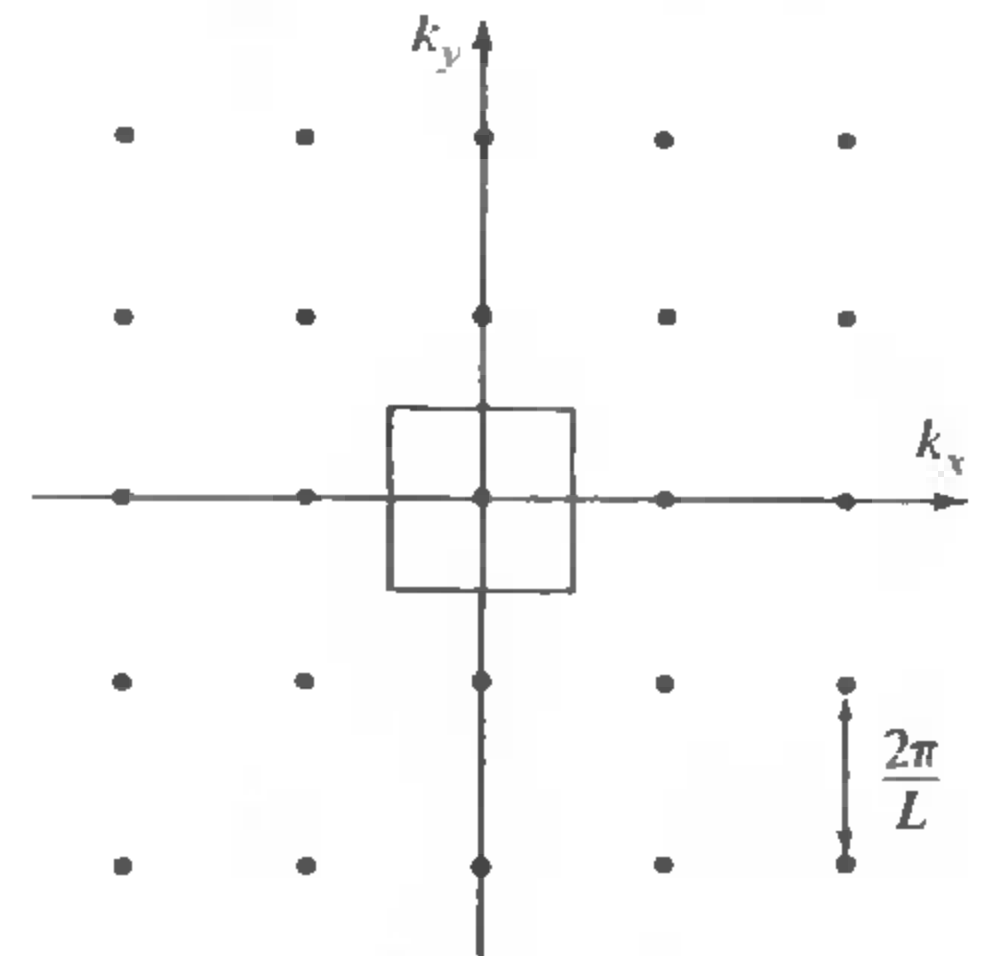
Generally the only practical use one makes of the quantization condition (2.16) is this: One often needs to know how many allowed values of \mathbf{k} are contained in a region of k -space that is enormous on the scale of $2\pi/L$, and that therefore contains a vast number of allowed points. If the region 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 \mathbf{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

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

allowed values of \mathbf{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

$$\frac{V}{8\pi^3} \quad (2.18)$$

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 \mathbf{k} and by the projection of the electron's spin along an arbitrary axis, which can take either of the two values $\hbar/2$ or $-\hbar/2$. Therefore associated with each allowed wave vector \mathbf{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 $\mathbf{k} = 0$, 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 \mathbf{k} within the sphere is

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

¹² If it were not spherical it would not be the ground state, for we could then construct a state of lower energy by moving the electrons in levels farthest away from $\mathbf{k} = 0$ 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

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

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:

$$n = \frac{k_F^3}{3\pi^2}. \quad (2.21)$$

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, $\varepsilon_F = \hbar^2 k_F^2 / 2m$ 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, $v = (3k_B T / m)^{1/2}$, 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

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

or

$$k_F = \frac{3.63}{r_s / a_0} \text{ \AA}^{-1}. \quad (2.23)$$

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

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

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 $a_0 = \hbar^2/me^2$)

$$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m} = \left(\frac{e^2}{2a_0} \right) (k_F a_0)^2. \quad (2.25)$$

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:

$$\varepsilon_F = \frac{50.1 \text{ eV}}{(r_s/a_0)^2}, \quad (2.26)$$

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 sphere¹⁴:

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

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 $\Delta k = 8\pi^3/V$ (see Eq. (2.18)) it is convenient to write

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

for in the limit as $\Delta k \rightarrow 0$ (i.e., $V \rightarrow \infty$) the sum $\sum F(\mathbf{k}) \Delta k$ approaches the integral $\int d\mathbf{k} F(\mathbf{k})$, provided only that $F(\mathbf{k})$ does not vary appreciably¹⁵ over distances in k -space of order $2\pi/L$. We may therefore rearrange (2.28) and write

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

In applying (2.29) to finite, but macroscopically large, systems one always assumes that $(1/V) \sum F(\mathbf{k})$ 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; $1 \text{ eV} = 1.602 \times 10^{-12} \text{ erg} = 1.602 \times 10^{-19} \text{ joule}$.

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	ϵ_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:

$$\frac{E}{V} = \frac{1}{4\pi^3} \int_{k < k_F} dk \frac{\hbar^2 k^2}{2m} = \frac{1}{\pi^2} \frac{\hbar^2 k_F^5}{10m}. \quad (2.30)$$

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

$$\frac{E}{N} = \frac{3}{10} \frac{\hbar^2 k_F^2}{m} = \frac{3}{5} \epsilon_F. \quad (2.31)$$

We can also write this result as

$$\frac{E}{N} = \frac{3}{5} k_B T_F \quad (2.32)$$

where T_F , the *Fermi temperature*, is

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

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 that¹⁶

$$P = \frac{2}{3} \frac{E}{V}. \quad (2.34)$$

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

$$B = \frac{1}{K} = -V \frac{\partial P}{\partial V}. \quad (2.35)$$

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

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

or

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

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).