

TOPIC 7: FREE-ELECTRON THEORY OF METALSREADING ASSIGNMENT

“The Free-Electron Theory of Metals”, from *Solid State and Semiconductor Physics*, J.P. McKelvey

LECTURE PROGRAM

1. Boltzmann Equation and the Mean Free Path
 - a. Distribution function $f(x,y,z,p_x,p_y,p_z)$
 - b. Change df occurring in time dt due to force $\mathbf{F}=d\mathbf{p}/dt$ acting on particles at x,y,z
 - c. Change due to collisions or scattering interactions $(\partial f/\partial t)_{\text{coll}}$
 - d. Boltzmann equation
 - e. Relaxation time or mean free time τ
 - f. Restoring effect of collisions
 - g. Drift velocity, current density, conductivity
 - h. Mean free path
2. Electron Conductivity of a Free-Electron Gas
 - a. Conditions
 - b. Form of the Boltzmann equation
 - c. Electrical current density, mobility, conductivity (Maxwell-Boltzmann distribution)
 - d. Conductivity and mobility (Fermi-Dirac distribution)
3. Thermal Conductivity
 - a. Conditions
 - b. Boltzmann equation
 - c. Electrical current density
 - d. Thermal current density
 - e. Thermoelectric effect
 - f. Wiedemann-Franz law
4. Scattering Processes
 - a. Collision mechanisms
 - b. Effective relaxation time
 - c. Effective mobility
5. Hall Effect
6. Thermal Capacity of Free-Electron Systems

CHAPTER 7

THE FREE-ELECTRON THEORY OF METALS

7.1 INTRODUCTION

The idea that the large electrical and thermal conductivity of metallic substances might be explained by the presence of large concentrations of mobile *free electrons* in these materials was first proposed by Drude¹ in 1900. The implications of this hypothesis were exhaustively investigated subsequently by Lorentz.² Drude and Lorentz assumed that the free electrons in a metal could be treated as an ideal gas of free particles which, when in thermal equilibrium, would obey Maxwell-Boltzmann statistics. In order to examine what might happen when electric or thermal currents were allowed to flow, thus establishing a nonequilibrium state, it was necessary to investigate how the equilibrium distribution would be modified by a (small) electrical or thermal current. It was also necessary to consider the kinetic behavior of the electrons as being that of free particles subject to instantaneous collisions which serve to return the distribution to the equilibrium condition, and to express the final result for electrical and thermal conductivity in terms of a mean free path or mean free time between these randomizing collisions. The Drude-Lorentz theory accounted satisfactorily for the well known experimental law of Wiedemann and Franz,³ according to which the ratio of electrical to thermal conductivity for most metals is nearly the same. In addition, the magnitudes of the electrical and thermal conductivity could be obtained using values for the mean free path which were quite reasonable.

The free-electron theory in its simplest form, however, led to a prediction of the electronic component of the specific heat which (assuming that the Debye theory for the lattice component is right) was in serious disagreement with experimental results. This difficulty (along with certain others) was resolved by Sommerfeld⁴ by the use of Fermi-Dirac statistics rather than the classical Boltzmann statistics. The Fermi-Dirac free-electron picture serves as a very simple and conceptually quite direct way of discussing and visualizing transport effects in metals. Since it starts with a preconceived notion of what a metal is like, it is of no value in explaining just *why* some substances are metals and have free electrons in abundance and others are insulators with few, if any, free electrons. For an explanation of these underlying questions, one must begin by examining the quantum-mechanical behavior of electrons in periodic potential fields, thus discussing essentially the same subject on a much more fundamental level. The latter approach will be postponed until the next chapter, where it will be shown that

¹ P. Drude, *Ann. Physik* **1**, 566 (1900).

² H. A. Lorentz, *The Theory of Electrons*, Teubner Verlag, Leipzig (1909).

³ Wiedemann and Franz, *Ann. Physik* **89**, 497 (1853).

⁴ A. Sommerfeld, *Z. Physik*, **47**, 1 (1928).

the properties of metals and insulators can be understood in terms of quantum theory, and that the foundations upon which the free-electron theory rests, are, for the most part, compatible with the requirements of quantum mechanics.

7.2 THE BOLTZMANN EQUATION AND THE MEAN FREE PATH

In any problem of statistical mechanics it is of central importance to know the form of the distribution function. In a system in thermal equilibrium, of course, the distribution function will be one of those which have been discussed in Chapter 5, but if the state of the system is not one of equilibrium (for example, if a current is flowing or if a temperature gradient is present), then the distribution function will be somewhat different. In the limit where the perturbation from the equilibrium condition vanishes, naturally, the nonequilibrium distribution function must approach the appropriate equilibrium distribution. As a preliminary to any statistical discussion of nonequilibrium processes, then, one must find a way of evaluating the distribution function when the system is in a nonequilibrium state. This is accomplished by means of the Boltzmann equation.

To derive this equation, consider a region of phase space about the point (x, y, z, p_x, p_y, p_z) . The number of particles entering this region in time dt is equal to the number which were in the region of phase space at $(x - v_x dt, y - v_y dt, z - v_z dt, p_x - F_x dt, p_y - F_y dt, p_z - F_z dt)$ at a time dt earlier. Here \mathbf{F} represents the force acting on the particles of the distribution at the point (x, y, z) and time t , and it follows from Newton's Law that $\mathbf{F} = d\mathbf{p}/dt$. If $f(x, y, z, p_x, p_y, p_z)$ is the distribution function, which expresses the number of particles per quantum state in the region, then the change df which occurs during time dt due to the motion of the particles in coordinate space and due to the fact that force fields acting on the particles tend to move them from one region to another in momentum space is

$$df = f(x - v_x dt, y - v_y dt, z - v_z dt, p_x - F_x dt, p_y - F_y dt, p_z - F_z dt) - f(x, y, z, p_x, p_y, p_z). \quad (7.2-1)$$

This, using Taylor's expansion and retaining only first-order terms in the limit $dt \rightarrow 0$ may be written

$$df = \left(-v_x \frac{\partial f}{\partial x} - v_y \frac{\partial f}{\partial y} - v_z \frac{\partial f}{\partial z} - F_x \frac{\partial f}{\partial p_x} - F_y \frac{\partial f}{\partial p_y} - F_z \frac{\partial f}{\partial p_z} \right) dt$$

$$\text{or} \quad \frac{df}{dt} = -\mathbf{v} \cdot \nabla f - \mathbf{F} \cdot \nabla_p f, \quad (7.2-2)$$

where the symbol ∇_p refers to the gradient operator in the momentum space (p_x, p_y, p_z) . So far, only the change in the distribution function due to the motion of the particles in coordinate space and due to the momentum changes arising from force fields

acting on the particles have been accounted for. Particles may also be transferred into or out of a given region of phase space by *collisions* or *scattering interactions* involving other particles of the distribution or scattering centers external to the assembly of particles under consideration. If the rate of change of the distribution function due to collisions or scattering is denoted by $(\partial f / \partial t)_{\text{coll}}$, then the total rate of change of f may be obtained by simply adding this quantity to the right-hand side of (7.2-2), giving

$$\frac{df}{dt} = -\mathbf{v} \cdot \nabla f - \mathbf{F} \cdot \nabla_p f + \left(\frac{\partial f}{\partial t} \right)_{\text{coll}}. \quad (7.2-3)$$

This is the Boltzmann equation. If the force field \mathbf{F} and the rate of change $(\partial f / \partial t)_{\text{coll}}$ are known, then the differential equation (7.2-3) can, in principle, be solved for the distribution function.

To actually do this, of course, one must adopt some model for the scattering interaction which can be made to yield the rate at which particles may enter or leave any region in phase space due to collisions. For example, one may assume steady state conditions, whereby $df/dt = 0$, and in addition specify that there are no force fields acting on the particles, and that the particles of the distribution are hard, perfectly elastic spheres of given radius, which undergo collisions that may be treated mechanically by the classical laws of motion to obtain an average value for $(\partial f / \partial t)_{\text{coll}}$. This mechanical calculation yields essentially a *cross-section* for scattering by a particle of the distribution. In this case it can be shown that the Boltzmann equation leads directly to the Maxwell-Boltzmann distribution of Chapter 5.

The Boltzmann equation is more commonly used to discuss the properties of a system which is displaced from equilibrium by a small perturbing force, such as an electric field or a temperature gradient, when the distribution function f_0 which is the equilibrium distribution function in the absence of the perturbation is known. In such cases, it is frequently assumed that the collision term has the form

$$\left(\frac{\partial f}{\partial t} \right)_{\text{coll}} = -\frac{f - f_0}{\tau} \quad (7.2-4)$$

where τ is a parameter called the relaxation time or mean free time. Equation (7.2-4) represents the rate at which the distribution function approaches the equilibrium condition (the perturbing force having been suddenly removed) as being proportional at any time to the deviation from the equilibrium condition.

For example, suppose that an electric field E_0 sets up a current in a circuit, which is composed of a uniform metallic substance, so that f is the same at all points and hence $\nabla f = 0$. As long as the field is on, the force \mathbf{F} in (7.2-3) must be represented as $-eE_0$, but if the field is suddenly removed, say at $t = 0$, then for positive values of t , $F = 0$ and Boltzmann's equation, using the relaxation time approximation (7.2-4) becomes

$$\frac{df}{dt} = \left(\frac{\partial f}{\partial t} \right)_{\text{coll}} = -\frac{f - f_0}{\tau}, \quad (t > 0) \quad (7.2-5)$$

which can easily be solved to obtain

$$f - f_0 = (\text{const.})e^{-t/\tau} \quad (t > 0). \quad (7.2-6)$$

The distribution function thus approaches the equilibrium distribution function exponentially with time constant τ , and the current in the circuit will be found to decrease from its initial value in essentially the same way, approaching zero exponentially with time constant τ .

This result may seem at first to contradict experimental evidence, but it really does not, since the decay constant τ under ordinary circumstances is very short—typically of the order of 10^{-13} sec. More careful consideration will serve to verify the plausibility of (7.2-6), since the action of the electric field is to give the electrons in the circuit a drift velocity opposite the direction of the current, which, by the law of inertia, *must* persist for a short time after the removal of the force, until the electrons in the wire undergo processes which randomize their velocity, reducing the average drift velocity to zero. It is clear that the collisions exert an influence upon a distribution which is perturbed in one way or another, which tends to *restore* it to the equilibrium state, and that if the perturbation is removed, this restoration is accomplished in a time of the order of the relaxation time τ . The details of the scattering process determine the relaxation time which is in general a function of energy due to the fact that scattering cross-section may depend upon energy.

This restraining effect of collisions can be seen to be essential in determining the law relating current density and electric field in an ordinary conductor. If a system containing perfectly free electrons is acted upon by a constant electric field, in the absence of collisions, the electrons, subject to a constant force, acquire a constant acceleration, thus a linearly *increasing* velocity. With a given field, the current density in a long conductor would then be greater than in a short one, since the average velocity of electrons starting from rest at one end and flowing to the other would be larger over a long path than over a short one. This, of course, is not what happens at all. In reality an electron starting from rest is accelerated by the field and acquires a linearly increasing drift velocity for a short time, but then undergoes a collision which (on the average) reduces its drift velocity to zero, whereupon the process is repeated. The electron, over a period of time, can be assigned a *constant average drift* velocity, proportional to the field and inversely proportional to the relaxation time. This leads at once to Ohm's law, wherein the current density is proportional to electric field strength. A crude estimate of the conductivity can be made on the basis of this picture. The force on an electron is $-eE_0$ where E_0 is the applied field, whereby the acceleration is $-eE_0/m$, with m the electron mass. If the force acts for time t , it produces a drift velocity $-eE_0t/m$, and if the average time between randomizing collisions is τ , the average drift velocity is given by

$$\bar{v} = -\frac{eE_0\tau}{2m}, \quad (7.2-7)$$

assuming, of course, that the drift velocity is on the average reduced to zero by a collision. If the free electron density is n_0 , the current density I will be, by definition,

$$I = -n_0e\bar{v} = \frac{n_0e^2\tau}{2m} E_0 = \sigma E_0 \quad (7.2-8)$$

with the conductivity σ expressed by

$$\sigma = \frac{n_0e^2\tau}{2m}. \quad (7.2-9)$$

Equation (7.2-8) is simply Ohm's law; this simple-minded approach, which neglects the niceties of averaging yields a value for σ which is too low by a factor of 2, as we shall soon see.

The justification for regarding the relaxation time τ as the mean free time between randomizing collisions can be obtained by examining a group which consists initially of n_0 particles at time $t = 0$, each of which may be expected to undergo a collision which completely randomizes its velocity with probability dt/τ in any time interval dt . Suppose that at some time t there remain $n(t)$ particles which have not yet experienced collision. The number colliding in a time dt about t is then, on the average, $n(t)dt/\tau$, so that

$$\frac{dn(t)}{dt} = -\frac{n(t)}{\tau}, \quad (7.2-10)$$

which upon integration (demanding that $n = n_0$ at $t = 0$) gives

$$n(t) = n_0 e^{-t/\tau}. \quad (7.2-11)$$

The number of particles in the original group thus decays exponentially, returning to the equilibrium distribution according to (7.2-11). This is exactly the behavior predicted by the Boltzmann equation in the relaxation time approximation (7.2-6). Furthermore, the distribution of free times, according to (7.2-11) is also exponential, such that the number of free times $dn(t)$ in an interval dt about t is simply

$$dn(t) = \frac{n_0}{\tau} e^{-t/\tau} dt. \quad (7.2-12)$$

The *average* free time may be computed in the usual way, giving

$$\bar{t} = \frac{\int_0^\infty t \, dn(t)}{\int_0^\infty dn(t)} = \frac{\int_0^\infty t e^{-t/\tau} dt}{\int_0^\infty e^{-t/\tau} dt} = \tau. \quad (7.2-13)$$

We may conclude, then, that the assumption of a collision probability which for a given particle is *constant* with time leads to the same result as the relaxation time approximation in the Boltzmann equation, and that the relaxation time of the Boltzmann equation is identical with the mean free time between collisions. In the above development we have assumed that a single collision is sufficient to return a particle to the equilibrium distribution. If this is not so (for example, if several collisions are required to completely randomize the velocity of a particle) then the relaxation time must be interpreted as referring to the time required, on the average, for a particle to acquire a completely random velocity, even though this may be several times larger than the actual mean time between collisions.

In the above discussion it is assumed that the *initial* group of particles all have the same energy. If the cross-section for collision varies with incident particle energy, as it often does, then the relaxation time will be different for each value of particle energy,

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and τ will be a function of energy. It is also possible for the relaxation time to be nonisotropic, varying with the direction of the particle momentum vector. We shall, however, limit ourselves to discussing in detail only the isotropic case where τ may be a function of energy but not of direction.

The mean free path between collisions may be defined in the same manner as the relaxation time. If the probability for a single particle to undergo collision in traversing a distance dx is the constant value dx/λ , and if there are $n(x)$ particles of an initial group numbering n_0 remaining after having travelled a distance x , the number colliding in a path interval dx about x will be $n(x)dx/\lambda$, whence

$$\frac{dn(x)}{dx} = -\frac{n(x)}{\lambda} \quad (7.2-14)$$

As before, this leads to

(7.2-11)

$$n(x) = n_0 e^{-x/\lambda} \quad (7.2-15)$$

Again, the distribution of path lengths $dn(x)$ in an interval dx about x is simply

$$dn(x) = \frac{n_0}{\lambda} e^{-x/\lambda} dx \quad (7.2-16)$$

and the average free path is given by

$$\bar{x} = \frac{\int_0^\infty x dn(x)}{\int_0^\infty dn(x)} = \frac{\int_0^\infty x e^{-x/\lambda} dx}{\int_0^\infty e^{-x/\lambda} dx} = \lambda \quad (7.2-17)$$

The quantity λ , which from the discussion above is seen to be the reciprocal of the probability of collision per unit distance, is called the mean free path.

The mean free path is also defined with reference to a group of particles all of which have the same initial energy, and must in general be regarded as a function of energy. For the case of elastic mutual interactions between hard spheres or elastic collisions between rigid spherical particles and fixed hard sphere scattering centers it is easily seen that the mean free path is simply a geometric property of the system and is therefore *independent* of energy. We shall see that scattering of electrons by acoustical mode phonons in metals and semiconductors can be approximated by this model, and hence may be described in terms of a velocity-independent mean free path. Any individual free path l and the corresponding free time t are, of course, related by

$$l = vt, \quad (7.2-18)$$

but the relation between the *mean* free path λ and the *mean* free time τ must be obtained by averaging over the distribution of velocities and will depend in detail upon the way in which the mean free path and relaxation time depend upon energy.

7.3 ELECTRICAL CONDUCTIVITY OF A FREE-ELECTRON GAS

The Boltzmann equation will now be used to predict the electrical and thermal conductivity of a free-electron gas. We shall consider first a uniform isotropic substance at constant temperature in a steady-state condition under the influence of a constant applied electric field E_0 . Since the system is in a steady state, $df/dt = 0$, and since the material is uniform and at constant temperature, the distribution function must be the same in every part of the sample, whereby $\nabla f = 0$. Under these conditions, the force upon an electron is $-eE_0$ and the Boltzmann equation in the relaxation time approximation may, using (7.2-3) and (7.2-4), be written as

$$eE_0 \cdot \nabla_p f = \frac{f - f_0}{\tau}. \quad (7.3-1)$$

If the coordinate system is chosen so that the z -axis is in the direction of E_0 , then E_0 has only a z -component, and the above equation may be written

$$\frac{eE_0\tau}{m} \frac{\partial f}{\partial v_z} = f - f_0. \quad (7.3-2)$$

In this equation the difference between f and f_0 is assumed to be quite small, so that $\partial f / \partial v_z$ can be approximated by $\partial f_0 / \partial v_z$. If the equilibrium state of the system is a Maxwell-Boltzmann distribution of the form (5.4-15), then Boltzmann distribution of the form (5.4-15), then

$$\frac{\partial f_0}{\partial v_z} = -\frac{mv_z}{kT} f_0. \quad (7.3-3)$$

Under these conditions, the Boltzmann equation becomes

$$f = f_0 \left(1 - \frac{eE_0\tau v_z}{kT} \right) = f_0 \left(1 - \frac{eE_0\tau}{kT} v \cos \theta \right), \quad (7.3-4)$$

since $v_z = v \cos \theta$, where θ is the angle between the polar z -axis and the direction v .

The electrical current density I_z is by definition

$$I_z = -ne\bar{v}_z \quad (7.3-5)$$

and \bar{v}_z may be expressed as

$$\bar{v}_z = \frac{\int v_z f(v) g(v) d^3v}{\int f(v) g(v) d^3v}, \quad (7.3-6)$$

where $g(v)$ is the density of states per unit volume of velocity space and d^3v is an appro-

priate volume element in velocity space. The notation we shall adopt, and use consistently hereafter, is that a barred quantity, $\bar{\alpha}$, refers to an average over the *actual* nonequilibrium distribution, while a bracketed quantity, $\langle \alpha \rangle$, refers to the average of that quantity taken over the *equilibrium* distribution function. The single exception is the thermal velocity, which according to this convention should really be written $\langle v \rangle$, but for which, in deference to convention, we shall retain the notation \bar{v} . Since we shall find it most convenient to integrate over spherical coordinates (v, θ, ϕ) in velocity space, we must use the volume element $d^3v = v^2 \sin \theta dv d\theta d\phi$. Using this volume element in conjunction with the density of states in velocity space as given by (5.4-17) and the distribution function (7.3-4), noting that $v_z = v \cos \theta$, we may write (7.3-6) as

$$(7.3-1) \quad \bar{v}_z = \frac{\int_0^\infty \int_0^\pi f_0(v) \left(1 - \frac{eE_0\tau}{kT} v \cos \theta\right) v^3 \cos \theta \sin \theta dv d\theta}{\int_0^\infty \int_0^\pi f_0(v) \left(1 - \frac{eE_0\tau}{kT} v \cos \theta\right) v^2 \sin \theta dv d\theta}. \quad (7.3-7)$$

In (7.3-7) the integration over ϕ from 0 to 2π has already been performed. Since the integrands are both independent of ϕ the factors 2π obtained in numerator and denominator cancel. Also, since $\langle v_z \rangle$ is zero (for the equilibrium condition) the integral involving only f_0 in the numerator of (7.3-7) must be zero; furthermore, in the field dependent term in the denominator an angular integral of $\cos \theta \sin \theta = \frac{1}{2} \sin 2\theta$ over the range $0 < \theta < \pi$ appears, and hence this term also integrates to zero. Equation (7.3-7) can thus be reduced to

$$(7.3-2) \quad \bar{v}_z = - \frac{\frac{eE_0}{kT} \int_0^\infty \int_0^\pi v^2 \tau(v) \cdot f_0(v) v^2 \cos^2 \theta \sin \theta dv d\theta}{\int_0^\infty \int_0^\pi f_0(v) \cdot v^2 \sin \theta dv d\theta}. \quad (7.3-8)$$

The angular integrals can easily be evaluated, giving

$$(7.3-3) \quad \bar{v}_z = - \frac{eE_0}{3kT} \frac{\int_0^\infty v^2 \tau(v) \cdot v^2 f_0(v) dv}{\int_0^\infty v^2 f_0(v) dv} = - \frac{eE_0}{3kT} \langle v^2 \tau \rangle, \quad (7.3-9)$$

the remaining integrals representing simply the average $\langle v^2 \tau(v) \rangle$ over the equilibrium distribution function. But, in a Boltzmann gas of free particles, the average kinetic energy per particle is $3kT/2$, so that

$$(7.3-4) \quad \langle \frac{1}{2} m v^2 \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT, \quad (7.3-5)$$

whence

$$(7.3-6) \quad kT = \frac{1}{3} m \langle v^2 \rangle. \quad (7.3-10)$$

Substituting this into (7.3-9), we may write, finally

$$\bar{v}_z = -\frac{eE_0\bar{\tau}}{m} \quad (7.3-11)$$

where

$$\bar{\tau} = \frac{\langle v^2\tau \rangle}{\langle v^2 \rangle}. \quad (7.3-12)$$

The result of this more accurate treatment is in agreement with (7.2-7), which was obtained in a very crude fashion, except for a factor of 2, and except for the fact that the quantity $\bar{\tau}$ as given by (7.3-12) and (7.3-9) is not precisely equal to τ except when τ is independent of v .

It is quite common in this connection to define the *mobility* of a particle as the magnitude of the average drift velocity per unit field. From (7.3-11), the mobility μ must be given by

$$\mu = \left| \frac{\bar{v}_z}{E_0} \right| = \frac{e\bar{\tau}}{m}. \quad (7.3-13)$$

The unit of mobility is velocity per unit field, which in the cgs-gaussian system is $\text{cm}^2 \text{volt}^{-1} \text{sec}^{-1}$. The current density I_z is, by (7.3-5) and (7.3-11)

$$I_z = -ne\bar{v}_z = \frac{ne^2\bar{\tau}}{m} E_0 = \sigma E_0 \quad (7.3-14)$$

whereby

$$\sigma = \frac{ne^2\bar{\tau}}{m}. \quad (7.3-15)$$

It should be noted that these results can be also stated in terms of the mobility as

$$I_z = \sigma E_0 = ne\mu E_0 \quad (7.3-16)$$

whence

$$\sigma = ne\mu. \quad (7.3-17)$$

To evaluate σ explicitly in terms of the relaxation time τ , it is necessary to specify the dependence of τ upon v . If τ is independent of v , then, from (7.3-9) and (7.3-12) $\bar{\tau} = \tau$. For the case where the mean free path is independent of velocity, $\tau = \lambda/v$ and (7.3-12), (7.3-10), and (5.4-20) lead to

$$\bar{\tau} = \frac{\lambda\langle v \rangle}{\langle v^2 \rangle} = \frac{\lambda\bar{c}}{3kT/m} = \frac{8}{3\pi} \frac{\lambda}{\bar{c}}. \quad (7.3-18)$$

In the preceding discussion we assumed, as did Drude and Lorentz, that the

electron gas could be described adequately by a Maxwell-Boltzmann distribution of energies. Actually, of course, since the electrons obey the Pauli exclusion principle, we should really use the Fermi-Dirac distribution function if the results we obtain are to be perfectly correct. If the equilibrium distribution is the Fermi-Dirac distribution (5.5-20) we should write, in place of (7.3-3),

$$\frac{\partial f_0}{\partial v_z} = \frac{\partial f_0}{\partial \varepsilon} \frac{\partial \varepsilon}{\partial v_z} = -\frac{mv_z}{kT} \frac{e^{\varepsilon - \varepsilon_f/kT}}{(1 + e^{\varepsilon - \varepsilon_f/kT})^2} = \frac{-mv_z}{kT} f_0(1 - f_0). \quad (7.3-19)$$

Substituting this result into (7.3-2), again assuming that $\partial f/\partial v_z$ can be replaced by $\partial f_0/\partial v_z$, one finds

$$f = f_0 - \frac{eE_0\tau}{kT} f_0(1 - f_0)v \cos \theta. \quad (7.3-20)$$

Using this as the distribution function in (7.3-6) and noting that the integral involving the first term of (7.3-20) in the numerator and the integral involving the second term of (7.3-20) in the denominator of the resulting expression vanish exactly as before, we are led after integrating over the angular coordinates to

$$\bar{v}_z = -\frac{eE_0}{3kT} \frac{\int_0^\infty v^4 \tau(v) f_0(1 - f_0) dv}{\int_0^\infty v^2 f_0 dv}. \quad (7.3-21)$$

Although it is impossible to evaluate these integrals over the Fermi-Dirac distribution function analytically in the general case, it is quite easy to obtain an approximate result which is very nearly correct for $T \ll T_F$, which, of course, is usually the case for most metallic conductors under conditions which are encountered in practice.

To accomplish this, it is most convenient to express the integrals in (7.3-21) as integrals over energy rather than velocity, whereby we obtain

$$\bar{v}_z = -\frac{2eE_0}{3mkT} \frac{\int_0^\infty \varepsilon^{3/2} \tau(\varepsilon) f_0(\varepsilon)(1 - f_0(\varepsilon)) d\varepsilon}{\int_0^\infty \varepsilon^{1/2} f_0(\varepsilon) d\varepsilon}. \quad (7.3-22)$$

It must now be noted that for $T \ll T_F$ (i.e., $kT \ll \varepsilon_f$) the Fermi function $f_0(\varepsilon)$ is very small for ε significantly in excess of ε_f and the complementary function $1 - f_0$ is very small for values of ε which are substantially smaller than ε_f . The product function $f_0(1 - f_0)$ is therefore very small *except* in the neighborhood of $\varepsilon = \varepsilon_f$, as shown in Figure 7.1. It is easy to show analytically, from (7.3-19), that $f_0(1 - f_0)$ is a maximum at $\varepsilon = \varepsilon_f$, at which point $f_0(1 - f_0) = \frac{1}{4}$, and that the width of the region over which $f_0(1 - f_0)$ is not small compared to this maximum value is of the order of kT . There will thus be no significant contribution to the integral in the numerator of (7.3-22) except where ε takes on values within a few kT units of ε_f . If $\varepsilon^{3/2} \tau(\varepsilon)$ is a function which does not change much over this energy range, we may then regard $f_0(1 - f_0)$

as essentially a Dirac δ -function of $\varepsilon - \varepsilon_f$, and write⁵

$$f_0(\varepsilon)(1 - f_0(\varepsilon)) \cong A\delta(\varepsilon - \varepsilon_f) \quad (7.3-23)$$

where A is a normalizing factor which must be chosen in such a way that when (7.3-23) is integrated over energy the correct value for the integral on the left-hand side is obtained.

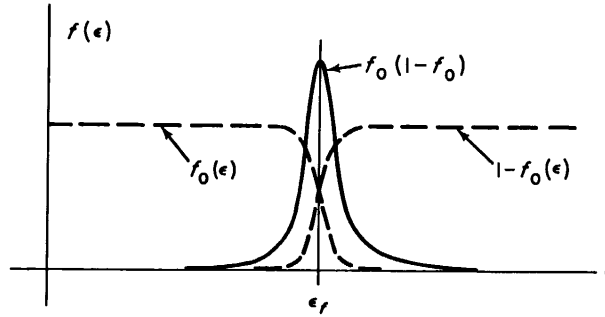


FIGURE 7.1. The functions $f_0(\varepsilon)$, $1 - f_0$ and $f_0(1 - f_0)$ for a Fermi system, plotted as a function of energy. The vertical scale factor for the $f_0(1 - f_0)$ curve is not the same as for the other curves.

Since by direct integration (using the substitution $u = (\varepsilon - \varepsilon_f)/kT$) it is possible to show that

$$\int_0^\infty f_0(1 - f_0) d\varepsilon = kT \int_{-\varepsilon_f/kT}^\infty \frac{e^u du}{(1 + e^u)^2} = \frac{kT}{1 + e^{-\varepsilon_f/kT}} \cong kT \quad (7.3-24)$$

and since the integral of the δ -function is unity, it is clear that we must take $A = kT$ in (7.3-23), whereby

$$f_0(\varepsilon)(1 - f_0(\varepsilon)) \cong kT\delta(\varepsilon - \varepsilon_f) \quad (kT \ll \varepsilon_f). \quad (7.3-25)$$

Using this in (7.3-22), and evaluating the integral in the denominator of that equation by regarding $f_0(\varepsilon)$ to be unity for $0 < \varepsilon < \varepsilon_f$ and zero for $\varepsilon > \varepsilon_f$, which is a good approximation for $kT \ll \varepsilon_f$, we obtain

$$\bar{v}_z = -\frac{2eE_0}{3m} \frac{\int_0^\infty \varepsilon^{3/2} \tau(\varepsilon) \delta(\varepsilon - \varepsilon_f) d\varepsilon}{\int_0^{\varepsilon_f} \varepsilon^{1/2} d\varepsilon} = -\frac{eE_0 \tau(\varepsilon_f)}{m}. \quad (7.3-26)$$

The current density $I_z = -ne\bar{v}_z$ and the conductivity σ can be evaluated as before, in

⁵ See Appendix A for a definition and discussion of the Dirac δ -function.

connection with (7.3-15), giving

$$(7.3-23) \quad \sigma = \frac{ne^2\tau(\epsilon_f)}{m} = ne\mu \quad \text{with} \quad \mu = \frac{e\tau(\epsilon_f)}{m}. \quad (7.3-27)$$

It is apparent that these results are the same as those which were found for the Maxwell-Boltzmann case (7.3-11) etc. except that the average mean free time τ is represented by the value of $\tau(v)$ at the "Fermi velocity" v_f , where

$$\frac{1}{2}mv_f^2 = \epsilon_f. \quad (7.3-28)$$

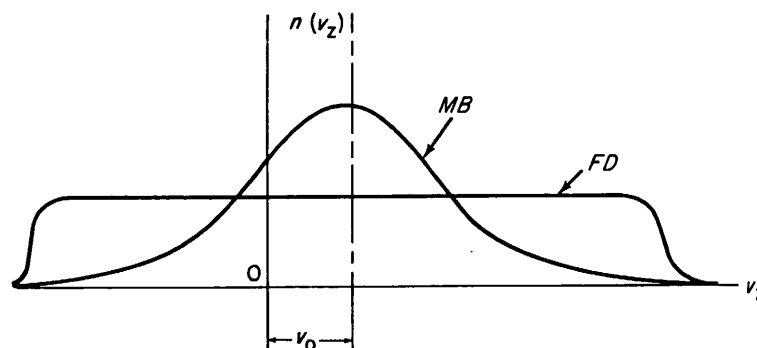


FIGURE 7.2. The Maxwell-Boltzmann (MB) and Fermi-Dirac (FD) z -velocity component distributions in the presence of an electric field.

The statistics in this instance makes a difference only in the details of averaging, and does not affect the conductivity by orders of magnitude. This is understandable on physical grounds, since the effect of the field in either case is simply to superimpose a drift velocity of the order of $eE_0\tau/m$ upon all the electrons of the distribution as shown in Figure 7.2, irrespective of the details of their distribution in energy. In any case the introduction of Fermi-Dirac statistics, while altering some of the details, preserves the essential features of the Drude-Lorentz-Boltzmann free electron picture of electrical conduction, which are basically correct. As we shall see in due time, however, the *thermal capacities* predicted by Maxwell and Fermi-Dirac statistics for the free electrons in metals are very different indeed, and in this case the use of Fermi-Dirac statistics is essential in explaining the experimental findings.

7.4 THERMAL CONDUCTIVITY AND THERMOELECTRIC EFFECTS IN FREE-ELECTRON SYSTEMS

In discussing the thermal conductivity of free electrons, it is necessary to consider a sample wherein there is no electric current, but in which there exists a temperature gradient. The distribution function at any point is then characterized by the local temperature, and must be regarded as a function of position as well as energy. As

before, we shall assume that we are dealing with a homogeneous, isotropic sample, and for simplicity we assume that the temperature varies only along the z -direction. We shall work with Fermi-Dirac statistics from the outset; the case of Maxwell-Boltzmann statistics may be obtained as a special case of the Fermi-Dirac result when the Fermi energy is allowed to become large and negative.

Under these conditions in the steady state, using the usual relaxation time approximation with $\tau = \tau(v)$, the Boltzmann equation can be written as

$$\frac{df}{dt} = 0 = -v_z \frac{\partial f_0}{\partial z} + \frac{eE_0}{m} \frac{\partial f_0}{\partial v_z} - \frac{f - f_0}{\tau(v)}. \quad (7.4-1)$$

In this equation the derivatives of the actual distribution function with respect to z and v_z have been approximated by the values of the corresponding equilibrium distribution function, in analogy with the reasoning used in connection with Equation (7.3-2). The field E_0 is assumed to have only a z -component. The above equation may be rewritten as

$$f = f_0 + \tau \left(\frac{eE_0}{m} \frac{\partial f_0}{\partial v_z} - v_z \frac{\partial f_0}{\partial z} \right). \quad (7.4-2)$$

Using the expression (5.5-20) to represent f_0 , and remembering that ϵ_f is a function of temperature, we may with the aid of (7.3-19) write the quantity $\partial f_0 / \partial z$ as

$$\begin{aligned} \frac{\partial f_0}{\partial z} &= \frac{\partial f_0}{\partial T} \frac{\partial T}{\partial z} = \frac{\partial}{\partial T} \left(\frac{1}{1 + e^{\frac{\epsilon - \epsilon_f}{kT}}} \right) \frac{\partial T}{\partial z} = \frac{1}{kT} \left[\frac{\epsilon - \epsilon_f}{T} + \frac{\partial \epsilon_f}{\partial T} \right] \frac{e^{\frac{\epsilon - \epsilon_f}{kT}}}{\left(1 + e^{\frac{\epsilon - \epsilon_f}{kT}}\right)^2} \frac{\partial T}{\partial z} \\ &= \frac{f_0(1 - f_0)}{kT} \left[\frac{\epsilon - \epsilon_f}{T} + \frac{\partial \epsilon_f}{\partial T} \right] \frac{\partial T}{\partial z} = \left[T \frac{\partial}{\partial T} \left(\frac{\epsilon_f}{T} \right) + \frac{\epsilon}{T} \right] \frac{f_0(1 - f_0)}{kT} \frac{\partial T}{\partial z}. \end{aligned} \quad (7.4-3)$$

The Boltzmann Equation can then be written in the form

$$f = f_0 - \frac{v_z \tau}{kT} f_0(1 - f_0) \left[eE_0 + \left(T \frac{\partial(\epsilon_f/T)}{\partial T} + \frac{\epsilon}{T} \right) \frac{\partial T}{\partial z} \right]. \quad (7.4-4)$$

As before, the electrical current density I_z will be

$$I_z = -en\bar{v}_z = -en \frac{\int v_z f(v, z) g(v) d^3v}{\int f(v, z) g(v) d^3v}, \quad (7.4-5)$$

while the thermal current density Q_z will be represented by the energy carried per particle times the z -component of its velocity times the particle density, thus,

$$Q_z = n(\overline{\epsilon v_z}) = n \frac{\int \epsilon v_z f(v, z) g(v) d^3v}{\int f(v, z) g(v) d^3v}. \quad (7.4-6)$$

Upon substituting the distribution function (7.4-4) into (7.4-5) and (7.4-6), one obtains expressions analogous to (7.3-7). For exactly the same reasons discussed in connection with that equation the integral of the first term in the numerator of these expressions (involving f_0) must vanish, and the integral of the second term in the denominator (involving $f_0(1 - f_0)$) must also vanish. We have then

$$I_z = \frac{en \int \frac{v_z^2 \tau}{kT} f_0(1 - f_0) \left[eE_0 + \left(T \frac{\partial(\epsilon_f/T)}{\partial T} + \frac{\epsilon}{T} \right) \frac{\partial T}{\partial z} \right] d^3v}{\int f_0(v) d^3v} \quad (7.4-7)$$

and

$$Q_z = \frac{-n \int \frac{v_z^2 \tau}{kT} f_0(1 - f_0) \left[eE_0 \epsilon + \left(\epsilon T \frac{\partial(\epsilon_f/T)}{\partial T} + \frac{\epsilon^2}{T} \right) \frac{\partial T}{\partial z} \right] d^3v}{\int f_0(v) d^3v} \quad (7.4-8)$$

Without going into the details involved in evaluating these integrals, it is clear from the results of the preceding section that these equations may be expressed as

$$I_z = \frac{en}{m} \left[\left(eE_0 + T \frac{\partial(\epsilon_f/T)}{\partial T} \frac{\partial T}{\partial z} \right) \bar{\tau} + \frac{1}{T} \frac{\partial T}{\partial z} \overline{(\epsilon \tau)} \right] \quad (7.4-9)$$

and

$$Q_z = \frac{-n}{m} \left[\left(eE_0 + T \frac{\partial(\epsilon_f/T)}{\partial T} \frac{\partial T}{\partial z} \right) \overline{(\epsilon \tau)} + \frac{1}{T} \frac{\partial T}{\partial z} \overline{(\epsilon^2 \tau)} \right] \quad (7.4-10)$$

where the quantities over which a bar has been written are averages defined by

$$\bar{\alpha} = \frac{\int \frac{mv_z^2}{kT} \alpha(v) f_0(1 - f_0) d^3v}{\int f_0(v) d^3v} \quad (7.4-11)$$

If we note that $mv_z^2 = mv^2 \cos^2 \theta$, and if we assume that α is independent of angular variables, we may integrate over angles in (7.4-11) to obtain

$$\bar{\alpha} = \frac{m}{3kT} \frac{\int v^2 \alpha(v) f_0(1 - f_0) \cdot v^2 dv}{\int f_0 \cdot v^2 dv} = \frac{2}{3kT} \frac{\int \epsilon^{3/2} \alpha(\epsilon) f_0(1 - f_0) d\epsilon}{\int \epsilon^{1/2} f_0 d\epsilon} \quad (7.4-12)$$

It is easy to see from (7.4-12) and (7.3-10) that when the Fermi distribution reduces to a Maxwellian one (whereupon $1 - f_0 \cong 1$ and $f_0 = Ae^{-\epsilon/kT}$) the average $\bar{\alpha}$ reduces to

$$\bar{\alpha} = \frac{\langle v^2 \alpha \rangle}{\langle v^2 \rangle} = \frac{\langle \epsilon \alpha \rangle}{\langle \epsilon \rangle} \quad (7.4-13)$$

in analogy to (7.3-12), the averages being taken over the Maxwell-Boltzmann distribution. Likewise, if the distribution is a Fermi distribution for which $kT \ll \epsilon_f$, we may use (7.3-25) to represent $f_0(1 - f_0)$, whereupon, by the same methods used to arrive at (7.3-26), it is a simple matter to show that

$$\bar{\alpha} = \alpha(\epsilon_f). \quad (7.4-14)$$

If no electric current flows, then $I_z = 0$, whereby, from (7.4-9) we must have

$$eE_0 + T \frac{\partial(\epsilon_f/T)}{\partial T} \frac{\partial T}{\partial z} = -\frac{1}{T} \frac{\partial T}{\partial z} \frac{\overline{(\epsilon\tau)}}{\bar{\tau}}, \quad (7.4-15)$$

whence

$$E_0 = -\frac{1}{e} \left[\frac{1}{T} \frac{\overline{(\epsilon\tau)}}{\bar{\tau}} + T \frac{\partial(\epsilon_f/T)}{\partial T} \right] \frac{\partial T}{\partial z}. \quad (7.4-16)$$

If the temperature dependences of the averages $\bar{\tau}$ and $\overline{(\epsilon\tau)}$ may be neglected (and this is *not* always possible), equation (7.4-16) may be written in the form

$$E_0 = T \frac{\partial}{\partial T} \left[\frac{\overline{(\epsilon\tau)} - \epsilon_f \bar{\tau}}{e \bar{\tau} T} \right] \frac{\partial T}{\partial z}. \quad (7.4-17)$$

From this it appears that even in the absence of current, there must be an electric field if a temperature gradient is present. This is indeed the case, and the above equation is the fundamental description of the *thermoelectric effect*. Phenomenologically one may define the *Thomson coefficient* as the coefficient of proportionality relating the electric field and the temperature gradient from which it arises, as follows;

$$E_0 = -\mathcal{T} \frac{\partial T}{\partial z} \quad (7.4-18)$$

whereby the Thomson coefficient \mathcal{T} must be given by

$$\mathcal{T} = -T \frac{\partial}{\partial T} \left[\frac{\overline{(\epsilon\tau)} - \epsilon_f \bar{\tau}}{e \bar{\tau} T} \right]. \quad (7.4-19)$$

From (7.4-9) and (7.4-10) it is obvious also that if there is an applied electric field which causes an electric current to flow, then even when $\partial T/\partial z = 0$ the heat current Q_z does not vanish. There is instead a heat current which is proportional to the electric field E_0 and hence to the electric current. This effect is known as *Thomson heating*, and is quite distinct from the ordinary irreversible Joule heating associated with the passage of current through a resistive medium. The voltage developed per unit temperature difference by a thermocouple is expressed as the difference in the *thermoelectric powers* associated with the two constituents of the couple. It can be shown by a simple thermodynamic argument⁶ that the absolute thermoelectric power

⁶ M. W. Zemansky, *Heat and Thermodynamics*, McGraw-Hill Book Co., Inc., New York (1951) p. 301.

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FREE-ELECTRON THEORY OF METALS

\mathcal{P} of a substance is related to the Thomson coefficient by

$$\mathcal{T} = T \frac{\partial \mathcal{P}}{\partial T}, \quad (7.4-20)$$

whence, from (7.4-19), we must have

$$\mathcal{P} = \frac{\varepsilon_f \bar{\tau} - (\overline{\varepsilon \tau})}{e \bar{\tau} T}.$$

If $I_z = 0$, then by using (7.4-15) the term involving the electric field plus a contribution involving the temperature gradient and the temperature derivative of the Fermi energy can be eliminated from (7.4-10) to give

$$Q_z = -\sigma_t \frac{\partial T}{\partial z} = -\frac{n}{mT} \left[\frac{\bar{\tau}(\overline{\varepsilon^2 \tau}) - (\overline{\varepsilon \tau})^2}{\bar{\tau}} \right] \frac{\partial T}{\partial z} \quad (7.4-21)$$

whereby the thermal conductivity σ_t is simply

$$\sigma_t = \frac{n}{mT} \left[\frac{\bar{\tau}(\overline{\varepsilon^2 \tau}) - (\overline{\varepsilon \tau})^2}{\bar{\tau}} \right]. \quad (7.4-22)$$

It is clear from this that the Fermi free electron theory and the Boltzmann free electron picture differ only in details of averaging, and that both approaches lead to a thermal conductivity of the same order of magnitude, just as both predict about the same electrical conductivity.

According to the experimental investigations of Wiedemann and Franz, the ratio $\sigma_t/(T\sigma_e)$, where σ_e is the electrical conductivity, is about the same for nearly all metallic conductors, independent of temperature. Since $\sigma_e = ne^2 \bar{\tau}/m$, the Wiedemann-Franz ratio can be expressed as

$$L = \frac{\sigma_t}{T\sigma_e} = \frac{1}{e^2 T^2} \frac{\bar{\tau}(\overline{\varepsilon^2 \tau}) - (\overline{\varepsilon \tau})^2}{\bar{\tau}^2}. \quad (7.4-23)$$

From this it is apparent that if $\tau(\varepsilon)$ is the same function of energy for all metallic substances, the Wiedemann-Franz ratio will be the same for all materials. Since each factor of ε contributes kT to the averages, the Wiedemann-Franz ratio will be independent of temperature. As a matter of fact, if $\tau(\varepsilon)$ is slowly-varying with respect to ε , the Wiedemann-Franz ratio will be nearly the same even if $\tau(\varepsilon)$ is not the same function of energy for all substances. In particular, if the mean free path λ is independent of energy, then, by (7.3-18), using the classical Boltzmann free-electron picture of Drude and Lorentz, the thermal conductivity is just given by

$$\sigma_t = \frac{nm\lambda}{4T} \frac{\langle v \rangle \langle v^5 \rangle - \langle v^3 \rangle^2}{\langle v \rangle \langle v^2 \rangle} = \frac{4}{3} n\lambda k \sqrt{\frac{2kT}{\pi m}} \quad (7.4-24)$$

while the Wiedemann-Franz ratio becomes

$$L = \frac{m^2}{4e^2 T^2} \frac{\langle v \rangle \langle v^5 \rangle - \langle v^3 \rangle^2}{\langle v \rangle^2} = \frac{2k^2}{e^2}, \quad (7.4-25)$$

independent of the mean free path or the temperature. The magnitude of L as given by (7.4-25) is in fair agreement with experimentally determined values for most pure metals.

If we attempt to evaluate the thermal conductivity and the Wiedemann-Franz ratio using Fermi statistics and the average values as calculated according to (7.4-14), we obtain the result $\sigma_t = L = 0$! This rather surprising state of affairs arises simply because the representation of $f_0(1 - f_0)$ as a δ -function and the rather crude treatment of the Fermi integral in the denominator (as in (7.3-26)) of the expressions for the averages, which leads to (7.4-14), is not quite accurate enough for these calculations. If ε_f is expressed as kT_F in (7.4-23), it becomes apparent that what is involved here is really a small difference between two very large quantities of the order of $(k^2/e^2)(T_F/T)^2$, and the two quantities themselves must be expressed quite accurately in order that their difference be even approximately correct. A more precise treatment, such as that given by Smith,⁷ leads to the result

$$\sigma_t = \frac{\pi^2 n k^2 T \tau(\varepsilon_f)}{3m} \quad (7.4-26)$$

and

$$L = \frac{\sigma_t}{T \sigma_e} = \frac{\pi^2 k^2}{3 e^2}. \quad (7.4-27)$$

7.5 SCATTERING PROCESSES

In all the foregoing discussions the idea of free electrons undergoing instantaneous collisions which tend to return them to the equilibrium distribution has been of central importance, but up to this point we have studiously avoided answering the question, "collisions with what?" It is the purpose of this section to discuss in a qualitative way the answer to this question. As we shall see in detail in the next chapter, free electrons moving independently in a *perfectly periodic* crystal lattice potential are subject to *no scattering interactions* at all with the atoms of the lattice. Furthermore, since in elastic collisions between electrons themselves energy and each component of momentum is conserved, there is no resulting net change either in electrical or heat current. Therefore, the collision mechanisms which do result in randomizing the electron distribution must be associated with impurities, imperfections or aperiodicities of one sort or another in the crystal.

⁷ R. A. Smith, *Wave Mechanics of Crystalline Solids*, Chapman and Hall, London (1961) p. 328.

Consider a crystal which contains no impurity atoms or structural imperfections whatsoever. If there were no thermal motion of the atoms about their equilibrium positions, the electric potential experienced by an electron within the crystal would be perfectly periodic and there would be no mechanism at all to return electrons acted on by external electric or magnetic forces to the thermal equilibrium state. Due to the thermal vibrations of the atoms, however, there exists at any given time a slight *aperiodicity* of the potential within the crystal which serves to scatter the conduction electrons, dissipating whatever drift velocity they might have acquired from externally applied fields and returning them to the thermal equilibrium state. Obviously the higher the temperature, the stronger the lattice vibrations and the higher the probability of scattering per unit time. This mechanism of scattering leads therefore to a mean free time [and thus, according to (7.3-15) to a conductivity] which *decreases* with rising temperature. This is in accord with experimental observations on pure metals.

Since the lattice vibrations can be thought of as particle-like quanta of vibrational energy (phonons), the scattering interaction between electrons and phonons can be described as a quasi-mechanical collision process involving the free electrons and phonons, the latter behaving like neutral particles whose mass is much greater than the electron mass.⁸ Because of the fact that the phonons are neutral, current is no longer conserved in these collisions. Because the phonon "mass" is much greater than the electronic mass, the fractional energy loss suffered by the electron in an electron-phonon interaction is quite small, although, of course, the electron momentum change can be quite large. Electrons can interact with either acoustical-mode or optical-mode phonons, although since much more thermal energy is required to excite optical-mode phonons, the chief interaction at moderate temperatures is likely to be with acoustical phonons. The two interactions are similar in their qualitative aspects, although they lead to certain quantitative differences in the transport coefficients, particularly the temperature dependence of the relaxation time (thus the temperature dependence of the mobility). At any given temperature, the number of available phonons is constant. Since the phonons behave like massive quasi-stationary particles, the probability of scattering per unit distance along the path of an electron is a purely geometrically determined quantity, dependent only on the effective geometrical cross-section associated with the phonon, and *independent* of the velocity of the electron. The mean free path is therefore independent of particle velocity under these circumstances, as noted in Section 7.2. The mean free time is then given by

$$\tau(v) = \frac{\lambda}{v} \quad (7.5-1)$$

where λ is independent of v , leading to the relation (7.3-18) between $\bar{\tau}$ and λ . Of course, since the number of available phonons is a function of temperature, λ will be a function of *temperature* despite the fact that it is independent of velocity. This *lattice scattering* or *phonon scattering* mechanism is the dominant scattering process in relatively pure and structurally perfect crystals, especially in the higher temperature ranges.

The presence of an impurity atom in a crystal will usually alter the electrostatic potential in the neighborhood and create an aperiodicity in the potential field within the crystal which can act to scatter conduction electrons. The details of the scattering

⁸ See, for example, Problem 4 at the end of Chapter 6.

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process will naturally depend upon the nature of the impurity atom, its ionic size, its valence, and the way it is bonded into the crystal lattice. The presence of impurity atoms in an otherwise pure crystal will thus decrease the mean free time between scattering events and lead to a decrease in electrical conductivity which will be proportional to impurity content. This effect is indeed observed experimentally in a large number of substances.⁹ The impurity scattering mechanism is usually dominant in crystals which are relatively impure, or even in very pure samples at very low temperatures, when the phonon mechanism is quite weak. Structural imperfections in the crystal lattice, such as lattice vacancies, interstitial atoms, dislocations, and grain boundaries also lead to aperiodicities in the crystal potential and hence to scattering centers with which the conduction electrons may interact. The transport properties of the crystal will thus be influenced to a greater or lesser extent by the structural perfection of the lattice. In some circumstances the scattering of electrons by the surfaces of the sample may also be significant. We have already seen (in Section 6.6) how surface scattering of phonons is sometimes an important factor in the lattice component of thermal conductivity at low temperatures.

If two independent scattering mechanisms (for example, lattice scattering and impurity scattering) operate simultaneously to thermalize the electron energy distribution function, then there will be two relaxation times, τ_1 and τ_2 , associated with the respective mechanisms. In the above example τ_1 may represent the mean free time between lattice scattering events and τ_2 the mean free time between impurity scatterings. Under these conditions the collision term of the Boltzmann equation can be written

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = -\frac{f-f_0}{\tau_1} - \frac{f-f_0}{\tau_2} = -\frac{f-f_0}{\tau} \quad (7.5-2)$$

where

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2}. \quad (7.5-3)$$

From this it is clear that the combined effect of the two scattering mechanisms can be represented by a *single* relaxation time τ related to τ_1 and τ_2 by the reciprocal addition formula (7.5-3). Likewise, if there are more than two mechanisms, their effect can be represented by a single relaxation time τ given by

$$\frac{1}{\tau} = \sum_i \frac{1}{\tau_i}. \quad (7.5-4)$$

Since mobilities, according to (7.3-13) are directly proportional to relaxation times, the mobilities arising from separate independent scattering mechanisms may be added reciprocally in the same way to give a combined mobility of the form

$$\frac{1}{\mu} = \sum_i \frac{1}{\mu_i}. \quad (7.5-5)$$

⁹ This is the reason why, for example, copper of very high purity is required for electrical conductors in commercial power transmission systems.

Mean free paths arising from separate scattering processes can also be added reciprocally to arrive at an overall mean free path. It should be noted, however, that the addition formulas (7.5-4) and (7.5-5) should be applied *before*, not after, averaging over velocity.

7.6 THE HALL EFFECT AND OTHER GALVANOMAGNETIC EFFECTS

So far, we have considered only cases where an electric field acts upon the particles of a free-electron system. If in addition there is a magnetic field, the force upon a particle of charge q is given by the Lorentz force

$$\mathbf{F} = q(\mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{B}) \quad (7.6-1)$$

and the Boltzmann equation in the steady state, using the relaxation time approximation becomes

$$\mathbf{v} \cdot \nabla f + q(\mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{B}) \cdot \nabla_p f + \frac{f - f_0}{\tau} = 0. \quad (7.6-2)$$

The solution of this equation exhibits a number of *galvanomagnetic effects* arising out of the interaction of electric and magnetic fields and thermal gradients with the particles of the distribution. We shall not go through the details of the solution of the Boltzmann equation at this point, but shall simply restrict ourselves to a phenomenological description of these effects. A more rigorous treatment of galvanomagnetic phenomena as applied to semiconductors, where it is easier to arrive at exact analytic solutions, will be given in a later chapter.

The most important of the galvanomagnetic effects is the *Hall Effect*, in which an electric field in the y -direction is produced as a result of a current flowing in the x -

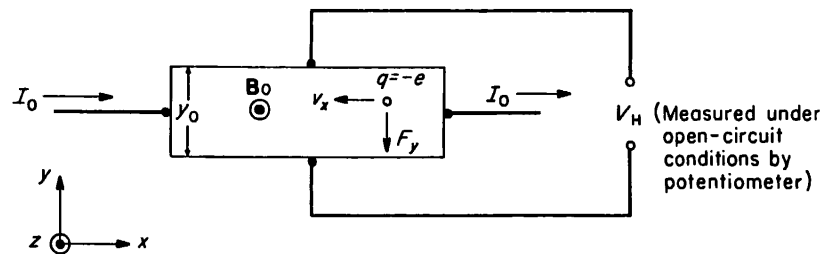


FIGURE 7.3. The geometry of the Hall effect experiment.

direction and a magnetic field along the z -direction, as shown in Figure 7.3. In that figure an electron moving with velocity v_x is subject to a downward thrust from the Lorentz force. In the steady state there can be no net force upon the electron, so what must happen is that an excess concentration of electrons builds up at the lower edge

of the sample until an electrostatic field E_y is generated which exactly balances the Lorentz force. Then

$$F_y = \frac{q}{c} (\mathbf{v} \times \mathbf{B}_0)_y - eE_y = \frac{ev_x B_0}{c} - eE_y = 0, \quad (7.6-3)$$

whence

$$E_y = \frac{v_x B_0}{c}. \quad (7.6-4)$$

But the current density I_0 is

$$I_0 = -nev_x. \quad (7.6-5)$$

Expressing v_x in (7.6-4) in terms of I_0 by (7.6-5) we may write the Hall field E_y as

$$E_y = \frac{-I_0 B_0}{nec} = RI_0 B_0 \quad (7.6-6)$$

where the *Hall coefficient* R is simply given by

$$R = -\frac{1}{nec}. \quad (7.6-7)$$

The Hall field is directly proportional to both I_0 and B_0 ; the Hall coefficient R is merely the proportionality constant between the Hall field and the product $I_0 B_0$. The Hall field can be obtained by measuring the Hall voltage V_H of Figure 7.3 potentiometrically. The Hall field and Hall voltage are then related by

$$V_H = E_y y_0 \quad (7.6-8)$$

where y_0 is the width of the sample. The Hall coefficient R can be determined if V_H , I_0 , and B_0 are known.

The Hall coefficient is inversely proportional to the density n of charge carriers in the sample, and a measurement of R affords a simple way of determining n . By combining measurements of the Hall coefficient and conductivity the mobility μ may be obtained, since from (7.6-7) and (7.3-17)

$$R\sigma = -\frac{1}{nec} (ne\mu) = -\frac{\mu}{c}$$

or

$$\mu = -R\sigma c. \quad (7.6-9)$$

The above analysis of the Hall effect is oversimplified in that all charge carriers do not have the same velocity component v_x , and hence one should average over the distribution of v_x . The effect of this is generally to change the value (7.6-7) for R by a small numerical factor.

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According to (7.6-7), if the charge carriers are electrons R should always be negative. Experimentally it has been found that R is *positive* for many metallic and semi-conducting substances. The occurrence of a positive Hall coefficient can be explained on the assumption that the charge carriers are positive rather than negative, but the free-electron theory of metals provides no reasonable way of accounting for the presence of positive charge carriers. The occurrence of positive Hall coefficients and the existence of positive charge carriers can be explained by the quantum theory, as we shall see in the next chapter.

In the experimental arrangement of Figure 7.3, a temperature gradient is set up along the y -direction along with the Hall field E_y . The reason for this is that since the downward force on the electrons is proportional to v_x , according to the Lorentz force law, the faster more energetic electrons experience a greater $\mathbf{v} \times \mathbf{B}_0$ force and hence tend to accumulate in the lower part of the sample, raising its temperature with respect to the top part where the "cooler" electrons remain. The resulting temperature gradient gives rise to a thermoelectric field in the y -direction, as given by (7.4-17) which results in an additional voltage, distinct from the Hall voltage, across the y -terminals of the sample. This effect is called the *Ettingshausen effect*, and in some instances it can interfere seriously with measurements of the Hall voltage. Its effect on Hall measurements can be eliminated by using an alternating sample current whose period is short compared to the thermal time constant of the sample, in conjunction with an ac detector.

When the electric current I_0 in the Hall effect experiment is replaced by a thermal current, one may still measure an electric field along the y -direction. In this case there is on the average, a net transport of faster electrons along the x -direction from the hot end to the cold end of the sample, and the $\mathbf{v} \times \mathbf{B}_0$ force acts upon them to produce an electric field in much the same way as the Hall field is produced when an electric current flows. This phenomenon is known as the *Nernst effect*. The Nernst field is accompanied by a temperature gradient along the y -direction just as is the Hall field; this causes an additional thermoelectric voltage analogous to the Ettingshausen voltage. The thermoelectric effect arising from the Nernst effect is called the *Righi-Leduc effect*.

Due to the fact that in the presence of a magnetic field the electrons travel in curved rather than straight paths, the conductivity is in general found to depend upon the magnetic field. This phenomenon is called *magnetoresistance* and will be dealt with in more detail in a later chapter.

7.7 THE THERMAL CAPACITY OF FREE-ELECTRON SYSTEMS

The classical Drude-Lorentz free-electron theory, in which the free electrons are assumed to obey Maxwell-Boltzmann statistics leads one to the conclusion that (assuming one free electron per atom) the heat capacity of the free electrons should be, as given by (5.4-11), $\frac{3}{2}nk$. The total heat capacity would then be the sum of the lattice contribution, given by the Debye theory, and the electronic contribution $\frac{3}{2}nk$, and at temperatures large compared to the Debye temperature the limiting value of the heat

capacity would be $\frac{3}{2}nk$. This conclusion is contradicted by experiment, however, the observations showing that the asymptotic value of the heat capacity for high temperatures differs little from the value $3nk$ predicted by the Debye theory for the lattice contribution alone. It would appear from this that the heat capacity of the free electrons is much smaller than the value predicted by the Drude-Lorentz-Boltzmann model. This was one of the major shortcomings of the original Drude-Lorentz model as first proposed.

It turns out, as we shall see, that when Fermi-Dirac statistics are used to describe the free-electron energy distribution, the calculated electronic heat capacity is much smaller than the value $\frac{3}{2}nk$ given by Boltzmann statistics, and is in fact negligible compared to the lattice contribution at moderate and high temperatures. The Fermi free-electron model is thus in much better accord with the experimental observations than the original Drude-Lorentz theory. The explanation of the electronic specific heat of metallic substances was one of the original triumphs of quantum statistics.

The reason for the much smaller heat capacity of the Fermi-Dirac free-electron system is that only the electrons within a few kT of the surface of the Fermi sphere can receive energy from an external heat source. Ordinarily a particle of an external heat bath at temperature T has an energy of only a few times kT to give to an electron of the Fermi free-electron system. Electrons deep inside the Fermi sphere are incapable of interacting with such external exciting bodies, because there are *no unoccupied states within a few times kT in energy into which they can be excited*. Only electrons near the Fermi surface where there are unoccupied states available can participate in interactions with an external heat source.

In order to make an accurate calculation of the heat capacity, it is necessary to take into account the first-order variation of the Fermi energy with temperature. In order to do this we shall have to evaluate the integral

$$I = \int_0^{\infty} f_0(\epsilon) \frac{\partial \phi(\epsilon)}{\partial \epsilon} d\epsilon. \quad (7.7-1)$$

where f_0 is the Fermi function and $\phi(\epsilon)$ is a function of ϵ which has the property that

$$\phi(0) = 0. \quad (7.7-2)$$

If (7.7-1) is integrated by parts, it is easy to see that I can be expressed in the form

$$I = \left[f_0(\epsilon) \phi(\epsilon) \right]_0^{\infty} - \int_0^{\infty} \phi(\epsilon) \frac{\partial f_0}{\partial \epsilon} d\epsilon = - \int_0^{\infty} \phi(\epsilon) \frac{\partial f_0}{\partial \epsilon} d\epsilon, \quad (7.7-3)$$

since the product $f_0(\epsilon)\phi(\epsilon)$ vanishes at both limits. Expanding $\phi(\epsilon)$ as a Taylor's series about the point $\epsilon = \epsilon_f$, we may write

$$\phi(\epsilon) = \phi(\epsilon_f) + (\epsilon - \epsilon_f) \left(\frac{\partial \phi}{\partial \epsilon} \right)_{\epsilon_f} + \frac{1}{2} (\epsilon - \epsilon_f)^2 \left(\frac{\partial^2 \phi}{\partial \epsilon^2} \right)_{\epsilon_f} + \dots, \quad (7.7-4)$$

whereby (7.7-3) can be expressed as

$$I = a_0 \phi(\epsilon_f) + a_1 \left(\frac{\partial \phi}{\partial \epsilon} \right)_{\epsilon_f} + a_2 \left(\frac{\partial^2 \phi}{\partial \epsilon^2} \right)_{\epsilon_f} + \dots, \quad (7.7-5)$$

where

$$a_n = -\frac{1}{n!} \int_0^\infty (\varepsilon - \varepsilon_f)^n \frac{\partial f_0}{\partial \varepsilon} d\varepsilon. \quad (7.7-6)$$

Now, if $kT \ll \varepsilon_f$, according to (7.3-19), $\partial f_0 / \partial \varepsilon$ is negligible for negative values of ε , and the limits of the integral (7.7-6) may be extended to ∞ and $-\infty$. If this is done, then we shall find

$$a_0 = - \int_{-\infty}^{\infty} \frac{\partial f_0}{\partial \varepsilon} d\varepsilon = \left[f_0 \right]_{-\infty}^{\infty} = 1 \quad (7.7-7)$$

$$a_1 = - \int_{-\infty}^{\infty} (\varepsilon - \varepsilon_f) \frac{\partial f_0}{\partial \varepsilon} d\varepsilon = 0 \quad (7.7-8)$$

$$a_2 = -\frac{1}{2} \int_{-\infty}^{\infty} (\varepsilon - \varepsilon_f)^2 \frac{\partial f_0}{\partial \varepsilon} d\varepsilon = \frac{(kT)^2}{2} \int_{-\infty}^{\infty} \frac{x^2 e^x dx}{(1 + e^x)^2} = \frac{\pi^2}{6} (kT)^2. \quad (7.7-9)$$

The integral in (7.7-8) vanishes because $\partial f_0 / \partial \varepsilon$ is an even function of $\varepsilon - \varepsilon_f$ and the integrand is thus an odd function of that argument, which when integrated from $-\infty$ to ∞ must yield zero. The integral of (7.7-9) is put into the form shown above by the substitution $x = (\varepsilon - \varepsilon_f) / kT$; this form is listed in most standard tables of definite integrals. Substituting these values into (7.7-5), the result is

$$I = \int_p^\infty f_0(\varepsilon) \frac{\partial \phi}{\partial \varepsilon} d\varepsilon = \phi(\varepsilon_f) + \frac{\pi^2}{6} (kT)^2 \left(\frac{\partial^2 \phi}{\partial \varepsilon^2} \right)_{\varepsilon_f} + \dots \quad (7.7-10)$$

This formula is convenient for working out approximate values of Fermi integrals where the δ -function approximation for $\partial f_0 / \partial \varepsilon$ is not good enough. It is restricted by the condition (7.7-2) and by the condition that $kT \ll \varepsilon_f$. This approach can be used to evaluate the Wiedemann-Franz ratio for a Fermi gas; the details are left as an exercise.

Suppose now that we choose

$$\phi(\varepsilon) = \int_0^\varepsilon g(\varepsilon) d\varepsilon \quad (7.7-11)$$

$$\text{whence} \quad \partial \phi / \partial \varepsilon = g(\varepsilon) \quad \partial^2 \phi / \partial \varepsilon^2 = \partial g(\varepsilon) / \partial \varepsilon, \quad (7.7-12)$$

with $g(\varepsilon)$ as given by (5.2-22) for a free-electron system. Then, from (7.7-10),

$$n = \int_0^\infty f_0(\varepsilon) g(\varepsilon) d\varepsilon = \int_0^{\varepsilon_f(T)} g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (kT)^2 \left(\frac{\partial g}{\partial \varepsilon} \right)_{\varepsilon_f}. \quad (7.7-13)$$

But also, from (5.5-24),

$$n = \int_0^{\varepsilon_f(0)} g(\varepsilon) d\varepsilon. \quad (7.7-14)$$

Subtracting (7.7-14) from (7.7-13) we have

$$0 = \int_{\varepsilon_f(0)}^{\varepsilon_f(T)} g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (kT)^2 \left(\frac{\partial g}{\partial \varepsilon} \right)_{\varepsilon_f} \cong g(\varepsilon_f) [\varepsilon_f(T) - \varepsilon_f(0)] + \frac{\pi^2}{6} (kT)^2 \left(\frac{\partial g}{\partial \varepsilon} \right)_{\varepsilon_f} \quad (7.7-15)$$

In the above equation we have assumed that $g(\varepsilon)$ does not vary much in the interval from $\varepsilon_f(0)$ to $\varepsilon_f(T)$, which for $kT \ll \varepsilon_f$ will be only a small fraction of $\varepsilon_f(0)$. Since $g(\varepsilon)$ is of the form $c\varepsilon^{1/2}$ with c a constant, (7.7-15) can be written

$$\varepsilon_f(T) = \varepsilon_f(0) - \frac{\pi^2 (kT)^2}{12 \varepsilon_f(T)} \quad (7.7-16)$$

For $kT \ll \varepsilon_f$, the second term will be a small correction to be subtracted from the relatively large quantity $\varepsilon_f(0)$ and the difference between $\varepsilon_f(T)$ and $\varepsilon_f(0)$ will be small compared to $\varepsilon_f(0)$. Not much error will be made under these circumstances if $\varepsilon_f(T)$ in the correction term of (7.7-16) is replaced with $\varepsilon_f(0)$, giving finally

$$\varepsilon_f(T) = \varepsilon_f(0) \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{\varepsilon_f(0)} \right)^2 \right] \quad (7.7-17)$$

To evaluate the electronic specific heat, we shall choose

$$\phi(\varepsilon) = \int_0^\varepsilon \varepsilon g(\varepsilon) d\varepsilon \quad (7.7-18)$$

$$\text{whence} \quad \partial \phi / \partial \varepsilon = \varepsilon g(\varepsilon) \quad \text{and} \quad \partial^2 \phi / \partial \varepsilon^2 = \partial(\varepsilon g(\varepsilon)) / \partial \varepsilon. \quad (7.7-19)$$

Then, substituting in (7.7-10), we find

$$\int_0^\infty f_0(\varepsilon) \frac{\partial \phi}{\partial \varepsilon} d\varepsilon = \int_0^\infty \varepsilon g(\varepsilon) f_0(\varepsilon) d\varepsilon = U \quad (7.7-20)$$

and

$$U = \int_0^{\varepsilon_f(T)} \varepsilon g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (kT)^2 \left[\frac{\partial}{\partial \varepsilon} (\varepsilon g(\varepsilon)) \right]_{\varepsilon_f}$$

Again using the fact that $g(\varepsilon) = c\varepsilon^{1/2}$, this can be written as

$$\begin{aligned} U &= \int_0^{\varepsilon_f(0)} \varepsilon g(\varepsilon) d\varepsilon + \int_{\varepsilon_f(0)}^{\varepsilon_f(T)} \varepsilon g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (kT)^2 \cdot \frac{3}{2} g(\varepsilon_f) \\ &\cong U_0 + [\varepsilon_f(T) - \varepsilon_f(0)] \varepsilon_f(0) g(\varepsilon_f(0)) + \frac{\pi^2}{4} (kT)^2 g(\varepsilon_f(0)). \end{aligned} \quad (7.7-21)$$

Here U_0 is the absolute zero value of the internal energy as represented by the integral of $\varepsilon g(\varepsilon)$ from 0 to $\varepsilon_f(0)$, and the integral of this quantity over the small range $\varepsilon_f(0)$

to $\varepsilon_f(T)$ has been approximated by the same procedure which was used in connection with (7.7-15). In the last term of (7.7-21) $g(\varepsilon)$ is evaluated at $\varepsilon_f(0)$ rather than $\varepsilon_f(T)$, which introduces only a small error. Substituting the value given by (7.7-17) for $\varepsilon_f(T) - \varepsilon_f(0)$ into (7.7-21), one may write

(7.7-15)

$$U = U_0 + \frac{\pi^2}{6} (kT)^2 g(\varepsilon_f(0)). \quad (7.7-22)$$

From (5.2-22) and (5.5-25), $g(\varepsilon_f(0))$ may be expressed as

(7.7-16)

$$g(\varepsilon_f(0)) = \frac{8\sqrt{2}\pi}{h^3} m^{3/2} [\varepsilon_f(0)]^{1/2} = \frac{4\pi m}{h^2} \left(\frac{3n}{\pi}\right)^{1/3},$$

which, since from (5.5-25) the ratio m/h^2 equals $(3n/\pi)^{2/3}/(8\varepsilon_f(0))$, can be written

$$g(\varepsilon_f(0)) = \frac{3n}{2\varepsilon_f(0)} = \frac{3n}{2kT_F}, \quad (7.7-23)$$

where T_F is a "Fermi temperature" defined by the relation $\varepsilon_f(0) = kT_F$. Substituting this value into (7.7-22) gives finally

(7.7-17)

$$U = U_0 + \frac{\pi^2}{4} \frac{nkT^2}{T_F}. \quad (7.7-24)$$

The heat capacity is obtained in the usual way, the result being

(7.7-18)

(7.7-19)

$$C_v = \frac{\partial U}{\partial T} = \frac{\pi^2}{2} nk \left(\frac{T}{T_F}\right). \quad (7.7-25)$$

(7.7-20)

This expression differs from the classical result $\frac{3}{2}nk$ by a factor $(\pi^2/3)(T/T_F)$, which amounts to 0.03 for $T = 300^\circ\text{K}$ and $T_F = 30\,000^\circ\text{K}$ [a typical value for simple metals calculated from (5.5-25)]. The electronic component of specific heat as calculated using Fermi statistics thus amounts to only a small fraction of the Drude-Lorentz value $\frac{3}{2}nk$, and except at very low temperatures is small compared to the lattice contribution. At temperatures small compared to the Debye temperature, the lattice contribution becomes quite small, approaching zero like T^3 as $T \rightarrow 0$. In this range the electronic contribution is often a significant factor, and in certain temperature ranges may even be the dominant effect. It is easily recognized in the experimental data due to its *linear* temperature dependence, as exhibited in (7.7-25).

EXERCISES

(7.7-21)

1. Show that if τ is independent of v , the distribution function

$$f(v) = Ae^{-\frac{m(\mathbf{v} - \mathbf{v}_0)^2}{2kT}} \quad \left(\text{where } \mathbf{v}_0 = \frac{e\tau}{m} \mathbf{E}_0 \right)$$

the integral
range $\varepsilon_f(0)$

is an approximate solution of the Boltzmann equation in the case where the Maxwell-Boltzmann distribution represents the equilibrium distribution function and where $v_0 \ll (kT/m)^{1/2}$.

2. Assuming Maxwell-Boltzmann statistics, evaluate $\bar{\tau}$ from (7.3-12), assuming that the dependence of τ on energy is given by $\tau(\epsilon) = A\epsilon^{-s}$, where A and s are constants.

3. In a metal such as copper (resistivity 1.7×10^{-6} ohm-cm), what (approximately) is the maximum electric field for which the Drude or Fermi free-electron treatment of Section 7.3 might be expected to hold? What is the current density for this value of field?

4. Starting with (7.7-10) and (7.7-17) derive formulas (7.4-26) and (7.4-27) for the thermal conductivity and Wiedemann-Franz ratio of a Fermi free-electron gas, using the approximation $kT \ll \epsilon_f(0)$.

5. Adopting a Fermi free-electron picture of a metal surface as shown in the accompanying diagram, show that there is a thermionic-emission current which may flow out across the surface potential barrier, and that the thermionic current density is given by

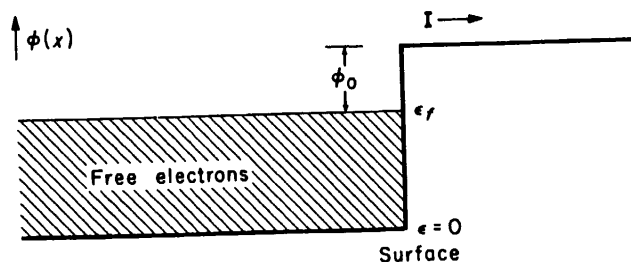
$$I = \frac{4\pi em(kT)^2}{h^3} e^{-\phi_0/kT} i_x.$$

Assume ϕ_0 , the work function, to be $\gg kT$.

6. Show that if the mean free path is independent of the velocity, the electrical conductivity of a Maxwell-Boltzmann free-electron gas may be expressed as

$$\sigma = \frac{4}{3} ne^2 \lambda / \sqrt{2\pi m k T}.$$

7. Describe physically the origin of the thermoelectric effect. (Hint: Consider a long bar, half of which is maintained at temperature T_1 , the other half at temperature T_2 ($> T_1$) and calculate the electron fluxes in either direction at the interface between the two regions. Use Maxwell-Boltzmann statistics.)



8. Assuming that the mean free path for electron-phonon interaction is independent of velocity, and that $T \gg \Theta$, show that the electrical conductivity of a Fermi-Dirac free electron gas for which $T \ll T_F$ is proportional to T^{-1} . Show that the electrical conductivity of a Maxwell-Boltzmann free electron gas under similar circumstances is proportional to $T^{-3/2}$. Note that the former result is in agreement with experimental data for pure metals, wherein Fermi statistics are applicable, and the latter agrees with experimental results in slightly impure semiconductors wherein the number of free electrons is essentially independent of temperature, and where Maxwell-Boltzmann statistics may be used. *Hint:* What is the total number of phonons, and how may the mean free path be expected to vary with this number, ignoring the dependence of scattering cross-section with temperature?

9. Show that for $kT \ll \epsilon_f(0)$ (i.e., $T \ll T_F$), the heat capacity of a two-dimensional Fermi free electron gas can be expressed approximately as $C_v = (\pi^2/3)nk(T/T_F)$.

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