

Handout 1

The Drude and Sommerfeld models of metals

This series of lecture notes covers all the material that I will present via transparencies during this part of the C3 major option. However, throughout the course **the material that I write on the blackboard will not necessarily be covered in this transcript**. Therefore I strongly advise you to take good notes on the material that I present on the board. In some cases a different approach to a topic may be presented in these notes – this is designed to help you understand a topic more fully.

I recommend the book *Band theory and electronic properties of solids*, by John Singleton (Oxford University Press, 2001) as a primary textbook for this part of the course. Dr Singleton lectured this course for a number of years and the book is very good. You should also read other accounts in particular those in *Solid State Physics*, by N.W Ashcroft and N.D. Mermin (Holt, Rinehart and Winston, New York 1976) and *Fundamentals of semiconductors*, by P. Yu and M. Cardona (Springer, Berlin, 1996). You may also find *Introduction to Solid State Physics*, by Charles Kittel, seventh edition (Wiley, New York 1996) and *Solid State Physics*, by G. Burns (Academic Press, Boston, 1995) useful. The lecture notes and both problem sets are on the website <http://www2.physics.ox.ac.uk/students/course-materials/c3-condensed-matter-major-option>. You will find that this first section is mainly revision, but it will get you ready from the new material in the lectures.

We start the course by examining metals, the class of solids in which the presence of charge-carrying electrons is most obvious. By discovering why and how metals exhibit high electrical conductivity, we can, with luck, start to understand why other materials (glass, diamond, wood) do not.

1.1 What do we know about metals?

To understand metals, it is useful to list some of their properties, and contrast them with other classes of solids. I hope that you enjoy the course!

1. The metallic state is favoured by elements; $> \frac{2}{3}$ are metals.
2. Metals tend to come from the left-hand side of the periodic table; therefore, a metal atom will consist of a rather tightly bound “noble-gas-like” ionic core surrounded by a small number of more loosely-bound valence electrons.
3. Metals form in crystal structures which have relatively large numbers n_{nn} of nearest neighbours, *e.g.*

hexagonal close-packed $n_{nn} = 12$;

face-centred cubic $n_{nn} = 12$

body-centred cubic $n_{nn} = 8$ at distance d (the nearest-neighbour distance) with another 6 at $1.15d$.

These figures may be compared with typical ionic and covalent systems in which $n_{nn} \sim 4 - 6$).

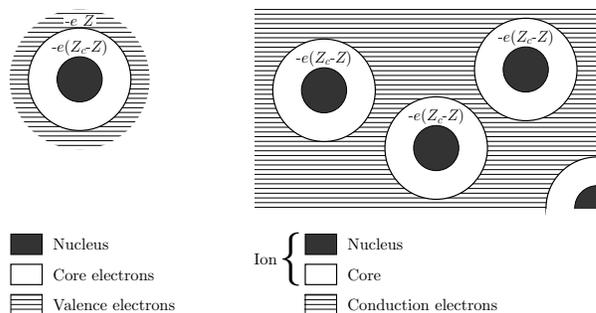


Figure 1.1: Schematic representations of a single, isolated metal atom and a solid metal. The atom (left) consists of a nucleus (size greatly exaggerated!) of charge $+eZ_c$ surrounded by the core electrons, which provide charge $-e(Z_c - Z)$, and Z valence electrons, of charge $-eZ$. In the solid metal (right), the core electrons remain bound to the nucleus, but the valence electrons move throughout the solid, becoming conduction electrons.

The large coordination numbers and the small numbers of valence electrons (~ 1) in metals imply that the outer electrons of the metal atoms occupy space between the ionic cores rather uniformly. This suggests the following things.

4. The bonds that bind the metal together are rather unidirectional; this is supported by the malleability of metals. By contrast, ionic and covalent solids, with their more directional bonds (deduced from the smaller number of nearest neighbours mentioned above) are brittle.
5. There is a lot of “empty space” in metals; *e.g.* Li has an interatomic distance of 3 \AA , but the ionic radius is only $\sim 0.5 \text{ \AA}$. This implies that there is a great deal of volume available for the valence (conduction) electrons to move around in.¹

We therefore picture the metal as an array of widely spaced, small ionic cores, with the mobile valence electrons spread through the volume between (see Figure 1.1). The positive charges of the ionic cores provide charge neutrality for the valence electrons, confining the electrons within the solid (see Figure 1.2).

1.2 The Drude model

1.2.1 Assumptions

The Drude model was the first attempt to use the idea of a “gas” of electrons, free to move between positively charged ionic cores; the assumptions were

- a *collision* indicates the scattering of an electron by (and only by) an ionic core; *i.e.* the electrons do not “collide” with anything else;
- between collisions, electrons do not interact with each other (*the independent electron approximation*) or with ions (*the free electron approximation*);
- collisions are instantaneous and result in a change in electron velocity;
- an electron suffers a collision with probability per unit time τ^{-1} (*the relaxation-time approximation*); *i.e.* τ^{-1} is the scattering rate;
- electrons achieve thermal equilibrium with their surroundings only through collisions.

¹This is actually one of the reasons why solid metals are stable; the valence electrons have a much lower zero-point energy when they can spread themselves out through these large volumes than when they are confined to one atom.

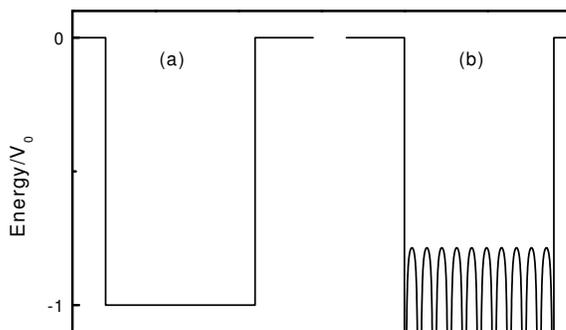


Figure 1.2: Schematic of the electronic potential assumed in the Drude and Sommerfeld models of metals (a). The small-scale details of the potential due to the ionic cores (shown schematically in (b)) are replaced by an average potential $-V_0$. In such a picture, the ionic cores merely maintain charge neutrality, hence keeping the electrons within the metal; the metal sample acts as a “box” containing electrons which are free to move within it.

These assumptions should be contrasted with those of the kinetic theory of conventional gases.² For example, in conventional kinetic theory, equilibrium is achieved by collisions *between* gas molecules; in the Drude model, the “molecules” (electrons) do not interact with each other at all!

Before discussing the results of the Drude model, we examine how the scattering rate can be included in the equations of motion of the electrons. This approach will also be useful in more sophisticated treatments.

1.2.2 The relaxation-time approximation

The current density \mathbf{J} due to electrons is

$$\mathbf{J} = -nev = -\frac{ne}{m_e}\mathbf{p}, \quad (1.1)$$

where m_e is the electron mass, n is the electron density and \mathbf{p} is the average electron momentum. Consider the evolution of \mathbf{p} in time δt under the action of an external force $\mathbf{f}(t)$. The probability of a collision during δt is $\frac{\delta t}{\tau}$, *i.e.* the probability of surviving without colliding is $(1 - \frac{\delta t}{\tau})$. For electrons that don’t collide, the increase in momentum $\delta\mathbf{p}$ is given by³

$$\delta\mathbf{p} = \mathbf{f}(t)\delta t + O(\delta t)^2. \quad (1.2)$$

Therefore, the contribution to the average electron momentum from the electrons that do not collide is

$$\mathbf{p}(t + \delta t) = (1 - \frac{\delta t}{\tau})(\mathbf{p}(t) + \mathbf{f}(t)\delta t + O(\delta t)^2). \quad (1.3)$$

Note that the contribution to the average momentum from electrons which *have* collided will be of order $(\delta t)^2$ and therefore negligible. This is because they constitute a fraction $\sim \delta t/\tau$ of the electrons and because the momentum that they will have acquired since colliding (each collision effectively randomises their momentum) will be $\sim \mathbf{f}(t)\delta t$.

Equation 1.3 can then be rearranged to give, in the limit $\delta t \rightarrow 0$

$$\frac{d\mathbf{p}(t)}{dt} = -\frac{\mathbf{p}(t)}{\tau} + \mathbf{f}(t). \quad (1.4)$$

²See *e.g.* *Three phases of matter*, by Alan J. Walton, second edition (Clarendon Press, Oxford 1983) Chapters 5-7.

³The $O(\delta t)^2$ comes from the fact that I have allowed the force to vary with time. In other words, the force at time $t + \delta t$ will be slightly different than that at time t ; *e.g.* if δt is very small, then $\mathbf{f}(t + \delta t) \approx \mathbf{f}(t) + (d\mathbf{f}/dt)\delta t$.

In other words, the collisions produce a frictional damping term. This idea will have many applications, even beyond the Drude model; we now use it to derive the electrical conductivity.

The electrical conductivity σ is defined by

$$\mathbf{J} = \sigma \mathbf{E}, \quad (1.5)$$

where \mathbf{E} is the electric field. To find σ , we substitute $\mathbf{f} = -e\mathbf{E}$ into Equation 1.4; we also set $\frac{d\mathbf{p}(t)}{dt} = 0$, as we are looking for a steady-state solution. The momentum can then be substituted into Equation 1.1, to give

$$\sigma = ne^2\tau/m_e. \quad (1.6)$$

If we substitute the room-temperature value of σ for a typical metal⁴ along with a typical $n \sim 10^{22} - 10^{23}\text{cm}^{-3}$ into this equation, a value of $\tau \sim 1 - 10$ fs emerges. In Drude's picture, the electrons are the particles of a classical gas, so that they will possess a mean kinetic energy

$$\frac{1}{2}m_e\langle v^2 \rangle = \frac{3}{2}k_B T \quad (1.7)$$

(the brackets $\langle \rangle$ denote the mean value of a quantity). Using this expression to derive a typical classical room temperature electron speed, we arrive at a mean free path $v\tau \sim 0.1 - 1$ nm. This is roughly the same as the interatomic distances in metals, a result consistent with the Drude picture of electrons colliding with the ionic cores. However, we shall see later that the Drude model very seriously underestimates typical electronic velocities.

1.3 The failure of the Drude model

1.3.1 Electronic heat capacity

The Drude model predicts the electronic heat capacity to be the classical “equipartition of energy” result⁵ *i.e.*

$$C_{\text{el}} = \frac{3}{2}nk_B. \quad (1.8)$$

This is independent of temperature. Experimentally, the low-temperature heat capacity of metals follows the relationship (see Figures 1.3 and 1.4)

$$C_V = \gamma T + AT^3. \quad (1.9)$$

The second term is obviously the phonon (Debye) component, leading us to suspect that $C_{\text{el}} = \gamma T$. Indeed, even at room temperature, the electronic component of the heat capacity of metals is much smaller than the Drude prediction. This is obviously a severe failing of the model.

1.3.2 Thermal conductivity and the Wiedemann-Franz ratio

The thermal conductivity κ is defined by the equation

$$\mathbf{J}_q = -\kappa \nabla T, \quad (1.10)$$

where \mathbf{J}_q is the flux of heat (*i.e.* energy per second per unit area). The Drude model assumes that the conduction of heat in metals is almost entirely due to electrons, and uses the kinetic theory expression⁶ for κ , *i.e.*

$$\kappa = \frac{1}{3}\langle v^2 \rangle \tau C_{\text{el}}. \quad (1.11)$$

⁴Most metals have resistivities ($1/\sigma$) in the range $\sim 1 - 20 \mu\Omega\text{cm}$ at room temperature. Some typical values are tabulated on page 8 of *Solid State Physics*, by N.W Ashcroft and N.D. Mermin (Holt, Rinehart and Winston, New York 1976).

⁵See any statistical mechanics book (*e.g.* *Three phases of matter*, by Alan J. Walton, second edition (Clarendon Press, Oxford 1983) page 126; *Statistical Physics*, by Tony Guenault (Routledge, London 1988) Section 3.2.2).

⁶See any kinetic theory book, *e.g.* *Three phases of matter*, by Alan J. Walton, second edition (Clarendon Press, Oxford 1983) Section 7.3.

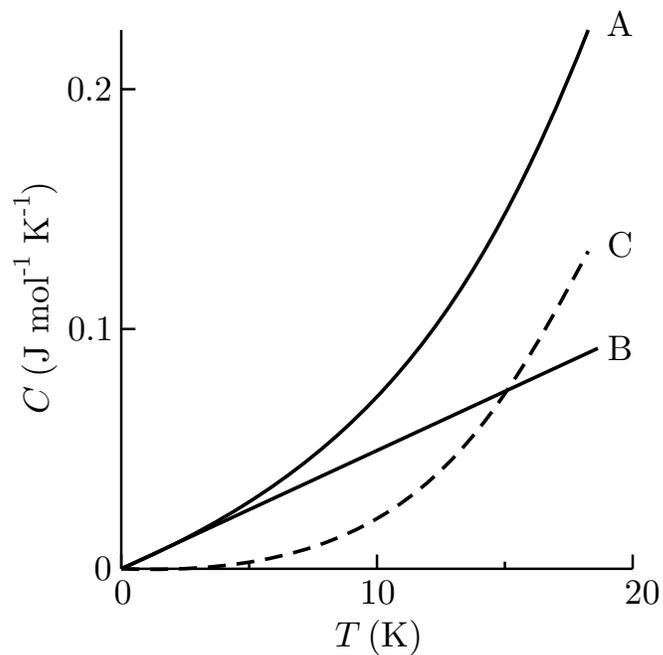


Figure 1.3: Heat capacity of Co at low temperatures. A is the experimental curve, B is the electronic contribution γT and C is the Debye component AT^3 . (Data from G. Duyckaerts, *Physica* **6**, 817 (1939).)

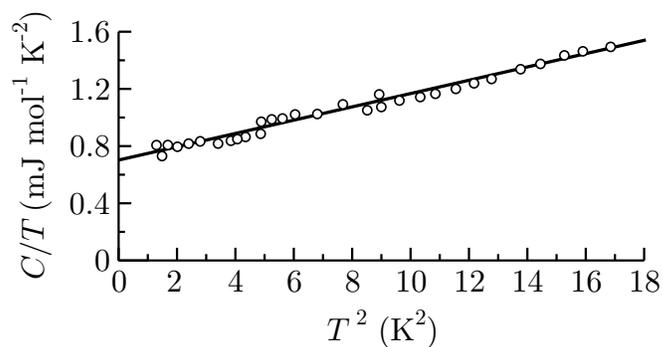


Figure 1.4: Plot of C_V/T versus T^2 for Cu; the intercept gives γ . (Data from W.S. Corak *et al.*, *Phys. Rev.* **98**, 1699 (1955).)

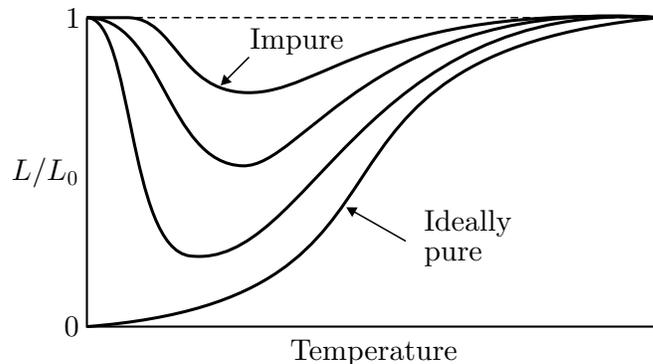


Figure 1.5: Schematic of experimental variation of $L = \kappa/(\sigma T)$ with temperature; L_0 is the theoretical value of L derived in later lectures. The high temperature limit of the figure represents room temperature.

C_{el} is taken from Equation 1.8 and the speed takes the classical thermal value, *i.e.* $\frac{1}{2}m_e\langle v^2 \rangle = \frac{3}{2}k_B T$.

The fortuitous success of this approach came with the prediction of the Wiedemann-Franz ratio, κ/σ . It had been found that the Wiedemann-Franz ratio divided by the temperature, $L = \kappa/(\sigma T)$,⁷ was close to the constant value $\sim 2.5 \times 10^{-8} \text{W}\Omega\text{K}^{-2}$ for many metals at room temperature.⁸ Substituting Equations 1.6 and 1.11 into this ratio leads to

$$\frac{\kappa}{\sigma T} = \frac{3}{2} \frac{k_B^2}{e^2} \approx 1.1 \times 10^{-8} \text{W}\Omega\text{K}^{-2}. \quad (1.12)$$

However, in spite of this apparent success, the individual components of the model are very wrong; *e.g.* C_{el} in the Drude model is at least two orders of magnitude bigger than the experimental values at room temperature! Furthermore, experimentally $\kappa/(\sigma T)$ drops away from its constant value at temperatures below room temperature (see Figure 1.5); the Drude model cannot explain this behaviour.

1.3.3 Hall effect

The Hall effect occurs when a magnetic field \mathbf{B} is applied perpendicular to a current density \mathbf{J} flowing in a sample. A *Hall voltage* is developed in the direction perpendicular to both \mathbf{J} and \mathbf{B} . We assume that the current flows parallel to the x direction and that \mathbf{B} is parallel to the z direction; the Hall voltage will then be developed in the y direction.

The presence of both electric and magnetic fields means that the force on an electron is now $\mathbf{f} = -e\mathbf{E} - e\mathbf{v} \times \mathbf{B}$. Equation 1.4 becomes

$$\frac{d\mathbf{v}}{dt} = -\frac{e}{m_e}\mathbf{E} - \frac{e}{m_e}\mathbf{v} \times \mathbf{B} - \frac{\mathbf{v}}{\tau}. \quad (1.13)$$

In steady state, the left-hand side vanishes, and the two components of the equation read

$$v_x = -\frac{e\tau}{m_e}E_x - \omega_c\tau v_y \quad (1.14)$$

and

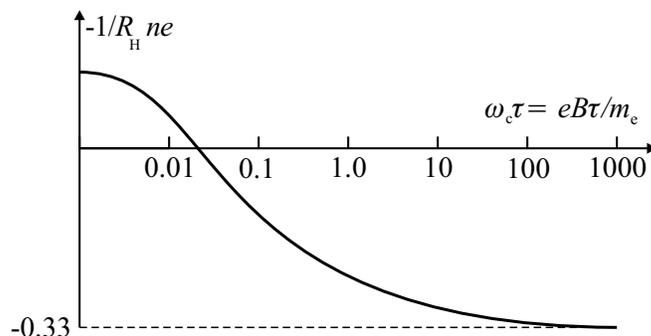
$$v_y = -\frac{e\tau}{m_e}E_y + \omega_c\tau v_x, \quad (1.15)$$

where we have written $\omega_c = eB/m_e$ (ω_c is of course the classical cyclotron angular frequency). If we impose the condition $v_y = 0$ (no current in the y direction) we have

$$\frac{E_y}{E_x} = -\omega_c\tau. \quad (1.16)$$

⁷ $L = \kappa/(\sigma T)$ is often referred to as the *Lorenz number*.

⁸Typical values of κ and σ for metals are available in *Tables of Physical and Chemical Constants*, by G.W.C. Kaye and T.H. Laby (Longmans, London, 1966); find the book and check out the Lorenz number for yourself!

Figure 1.6: $-1/(R_H ne)$ for Aluminium as a function of magnetic field.

Metal	Observed R_H	Calculated R_H	j
Li	-17.0	-13.1	1
Na	-25.0	-24.4	1
Cu	-5.5	-7.4	1
Ag	-8.4	-10.4	1
Zn	+4.1	-4.6	2
Cd	+6.0	-6.5	2

Table 1.1: Observed and calculated values of the Hall coefficient R_H in units of $10^{-11} \text{m}^3 \text{C}^{-1}$ for several metals. The calculated values assume j free electrons per atom.

Writing $J_x = -env_x$, Equations 1.14 and 1.16 can be combined to give

$$R_H \equiv \frac{E_y}{J_x B} = -\frac{1}{ne}. \quad (1.17)$$

R_H is known as the *Hall coefficient*.

The Drude model therefore predicts the surprising fact that R_H is independent of both the magnitude of B and the scattering time τ . In reality, however, R_H is found to vary with magnetic field (see Figure 1.6) In many cases (see Table 1.1) the Hall coefficient is even *positive*!

There will an explanation of these effects in later lectures, where the Hall effect will be treated much more rigorously.

1.3.4 Summary

Although the Drude model was a brave attempt to apply classical Kinetic Theory to the electrons in a metal, it is plainly flawed in many respects. In order to start to remedy the most severe failings (*e.g.* the electronic heat capacity, the thermal conductivity) we must treat the electrons as quantum-mechanical particles (fermions), rather than the molecules of a classical gas.

1.4 The Sommerfeld model

1.4.1 The introduction of quantum mechanics

Quantum mechanics tells us that we can only have a certain number of states N per unit volume of phase space, where

$$N = \left(\frac{1}{2\pi}\right)^j V_{kj} V_{rj}, \quad (1.18)$$

where j is the number of dimensions, V_{kj} is the k -space volume and V_{rj} is the r -space (*i.e.* real) volume. For example, in three dimensions

$$N = \left(\frac{1}{2\pi}\right)^3 V_{k3} V_{r3}. \quad (1.19)$$

Now we assume electrons free to move within the solid; once again we ignore the details of the periodic potential due to the ionic cores (see Figure 1.2(b)),⁹ replacing it with a mean potential $-V_0$ (see Figure 1.2(a)). The energy of the electrons is then

$$E(\mathbf{k}) = -V_0 + \frac{p^2}{2m_e} = -V_0 + \frac{\hbar^2 k^2}{2m_e}. \quad (1.20)$$

However, we are at liberty to set the origin of energy; for convenience we choose $E = 0$ to correspond to the average potential within the metal (Figure 1.2(a)), so that

$$E(\mathbf{k}) = \frac{\hbar^2 k^2}{2m_e}. \quad (1.21)$$

Let us now imagine gradually putting free electrons into a metal. At $T = 0$, the first electrons will occupy the lowest energy (*i.e.* lowest $|\mathbf{k}|$) states; subsequent electrons will be forced to occupy higher and higher energy states (because of Pauli's Exclusion Principle). Eventually, when all N electrons are accommodated, we will have filled a sphere of k -space, with

$$N = 2\left(\frac{1}{2\pi}\right)^3 \frac{4}{3}\pi k_F^3 V_{r3}, \quad (1.22)$$

where we have included a factor 2 to cope with the electrons' spin degeneracy and where k_F is the k -space radius (the *Fermi wavevector*) of the sphere of filled states. Rearranging, remembering that $n = N/V_{r3}$, gives

$$k_F = (3\pi^2 n)^{\frac{1}{3}}. \quad (1.23)$$

The corresponding electron energy is

$$E_F = \frac{\hbar^2 k_F^2}{2m_e} = \frac{\hbar^2}{2m_e} (3\pi^2 n)^{\frac{2}{3}}. \quad (1.24)$$

This energy is called the *Fermi energy*.

The substitution of typical metallic carrier densities into Equation 1.24,¹⁰ produces values of E_F in the range $\sim 1.5 - 15$ eV (*i.e.* \sim atomic energies) or $E_F/k_B \sim 20 - 100 \times 10^3$ K (*i.e.* \gg room temperature). Typical Fermi wavevectors are $k_F \sim 1/(\text{the atomic spacing}) \sim$ the Brillouin zone size \sim typical X-ray k -vectors. The velocities of electrons at the Fermi surface are $v_F = \hbar k_F/m_e \sim 0.01c$. Although the Fermi surface is the $T = 0$ groundstate of the electron system, the electrons present are enormously energetic!

The presence of the Fermi surface has many consequences for the properties of metals; *e.g.* the main contribution to the bulk modulus of metals comes from the Fermi "gas" of electrons.¹¹

1.4.2 The Fermi-Dirac distribution function.

In order to treat the thermal properties of electrons at higher temperatures, we need an appropriate distribution function for electrons from Statistical Mechanics. The Fermi-Dirac distribution function is

$$f_D(E, T) = \frac{1}{e^{(E-\mu)/k_B T} + 1}, \quad (1.25)$$

⁹Many condensed matter physics texts spend time on hand-waving arguments which supposedly justify the fact that electrons do not interact much with the ionic cores. Justifications used include "the ionic cores are very small"; "the electron-ion interactions are strongest at small separations but the Pauli exclusion principle prevents electrons from entering this region"; "screening of ionic charge by the mobile valence electrons"; "electrons have higher average kinetic energies whilst traversing the deep ionic potential wells and therefore spend less time there". We shall see in later lectures that it is the *translational symmetry* of the potential due to the ions which allows the electrons to travel for long distances without scattering from anything.

¹⁰Metallic carrier densities are usually in the range $\sim 10^{22} - 10^{23} \text{cm}^{-3}$. Values for several metals are tabulated in *Solid State Physics*, by N.W Ashcroft and N.D. Mermin (Holt, Rinehart and Winston, New York 1976), page 5. See also Problem 1.

¹¹See Problem 2; selected bulk moduli for metals have been tabulated on page 39 of *Solid State Physics*, by N.W Ashcroft and N.D. Mermin (Holt, Rinehart and Winston, New York 1976).

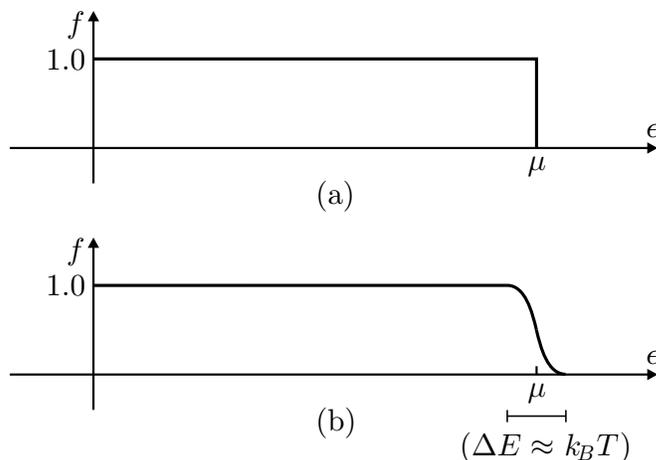


Figure 1.7: The Fermi-Dirac distribution function at $T = 0$ and at a finite temperature $T \ll E_F/k_B$.

where μ is the *chemical potential*; f_D gives the probability of occupation of a state of energy E . One of the definitions of the chemical potential¹² is that it is the energy at which the probability of occupation is $\frac{1}{2}$.

Figure 1.7 shows f_D at $T = 0$ and at a finite temperature $T \ll E_F/k_B$ (*e.g.* room temperature). Considering first the $T = 0$ figure, we see that

$$E_F \equiv \mu(T = 0). \quad (1.26)$$

This defines E_F .

Turning to the finite T figure, f_D only varies significantly within $k_B T$ of μ . This has two implications.

1. As $k_B T \ll E_F$, this implies that $\mu \approx E_F$.

In much of what follows, we shall make use of Fermi-Dirac statistics. Strictly the chemical potential μ is the fundamental energy used in the Fermi-Dirac distribution function f_D . However, for a typical metal at all accessible temperatures (*i.e.* until it melts) $\mu \approx E_F \equiv \mu(T = 0)$. The substitution $\mu \rightarrow E_F$ made in the thermodynamic analysis below (for convenience) results in minimal errors.

2. Only electrons with energies within $k_B T$ of μ , *i.e.* E_F , will be able to contribute to thermal processes, transport *etc.* Electrons further below μ will be unable to acquire sufficient thermal energy to be excited into empty states; states more than $\sim k_B T$ above μ will be empty.

1.4.3 The electronic density of states

It will be useful to have a function that describes the number of electron states in a particular energy range. We start by substituting a general value of k in Equation 1.22 instead of k_F . This gives $n(\mathbf{k})$, the number of states per unit volume of r -space with wavevectors less than $|\mathbf{k}|$. For free electrons, with energy $E = \hbar^2 \mathbf{k}^2 / 2m_e$, one can then define a density of states, $g(E)$, where $g(E)dE$ is the number of electrons per unit volume of r -space with energies between E and $E + dE$:

$$g(E) \equiv \frac{dn}{dE} = \frac{dn}{dk} \frac{dk}{dE} = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}}. \quad (1.27)$$

¹²The chemical potential is often (confusingly) referred to as *the Fermi level*. Although you will see this usage in other books, I have tried to stick to *chemical potential*, to avoid confusion with *the Fermi energy*. Furthermore, I find the term “Fermi level” defective, in that it implies that there is a quantum-mechanical state (level) present at that energy. As we shall see when we come to treat semiconductors, there need be no such state at that energy.

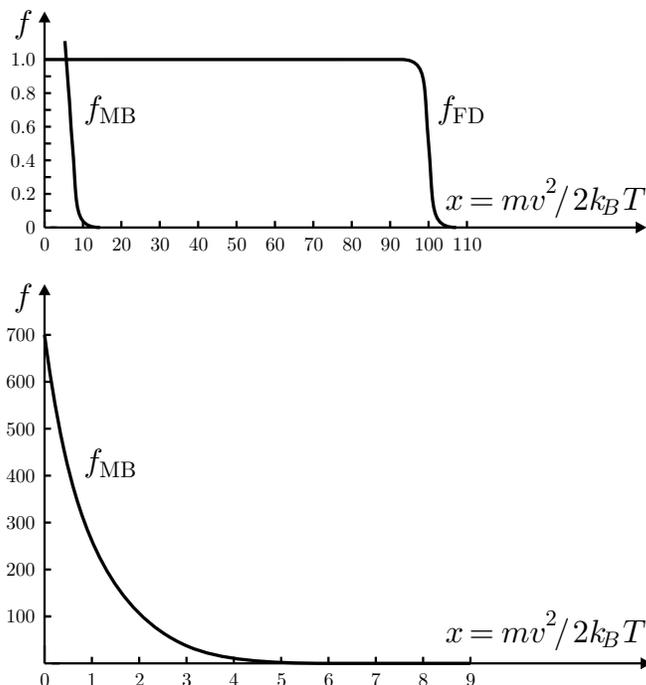


Figure 1.8: Comparison of the Maxwell–Boltzmann and Fermi–Dirac distribution functions using parameters relevant for a typical metal at room temperature. The concentration of filled states at low energies in the Maxwell–Boltzmann distribution is the reason why the Drude model fails to describe the thermal properties of metals.

1.4.4 The electronic density of states at $E \approx E_F$

As only the electrons within $\sim k_B T$ of E_F are able to take part in thermal processes, only the density of electron states at the Fermi energy, $g(E_F)$, will be particularly important in many calculations. In the free-electron approximation, the Fermi energy is given by $E_F = \frac{\hbar^2}{2m_e} (3\pi^2 n)^{\frac{2}{3}}$ (see Equation 1.24). Taking natural logarithms gives

$$\ln(E_F) = \frac{2}{3} \ln(n) + \text{const.} \quad (1.28)$$

Differentiating (*i.e.* making infinitesimal changes in E_F and n) gives

$$\frac{dE_F}{E_F} = \frac{2}{3} \frac{dn}{n}. \quad (1.29)$$

We rearrange to obtain¹³

$$\frac{dn}{dE_F} \equiv g(E_F) = \frac{3}{2} \frac{n}{E_F}. \quad (1.30)$$

1.4.5 The electronic heat capacity

Let $U(T)$ be the energy of the electron system at temperature T . At absolute zero, the electronic states are filled up to $E = E_F$ and empty for higher energies. $U(0)$ can therefore be evaluated rather easily:

$$U(0) = \int_0^{E_F} E g(E) dE = \frac{E_F^{\frac{5}{2}}}{5\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{\frac{3}{2}}, \quad (1.31)$$

where $g(E)$ has been taken from Equation 1.27.

¹³Note that this expression contains only n and E_F ; the mass of the electron and the spin degeneracy (factor 2) which feature in the prefactor in Equation 1.24 do not show up. This means that Equation 1.30 has a rather wider applicability than its simple derivation might suggest; remember this when you come to do some of the questions!

At finite temperature, electrons are excited into higher levels, and the expression for the energy of the electron system becomes slightly more complicated

$$\begin{aligned} U(T) &= \int_0^\infty E g(E) f_D(E, T) dE \\ &= \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{E^{\frac{3}{2}}}{(e^{(E-\mu)/k_B T} + 1)} dE. \end{aligned} \quad (1.32)$$

The integral in Equation 1.32 is a member of the family of so-called *Fermi-Dirac integrals*

$$F_j(y_0) = \int_0^\infty \frac{y^j}{e^{(y-y_0)} + 1} dy. \quad (1.33)$$

There are no general analytical expressions for such integrals, but certain asymptotic forms exist. Comparison with Equation 1.32 shows that $y_0 \equiv \mu/k_B T$; we have seen that for all practical temperatures, $\mu \approx E_F \gg k_B T$. Hence, the asymptotic form that is of interest for us is the one for y_0 very large and positive:

$$F_j(y_0) \approx \frac{y_0^{j+1}}{j+1} \left(1 + \frac{\pi^2 j(j+1)}{6y_0^2} + O(y_0^{-4}) + \dots \right) \quad (1.34)$$

Using Equation 1.34 to evaluate Equation 1.32 in the limit $\mu \gg k_B T$ yields

$$U(T) = \frac{2}{5} \mu^{\frac{5}{2}} \left\{ 1 + \frac{5}{8} \left(\frac{\pi k_B T}{\mu} \right)^2 \right\} \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{\frac{3}{2}}. \quad (1.35)$$

We are left with the problem that μ is temperature dependent; μ is determined by the constraint that the total number of electrons must remain constant:

$$\begin{aligned} n &= \int_0^\infty g(E) f_D(E, T) dE \\ &= \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{E^{\frac{1}{2}}}{(e^{(E-\mu)/k_B T} + 1)} dE. \end{aligned} \quad (1.36)$$

This contains the $j = \frac{1}{2}$ Fermi-Dirac integral, which may also be evaluated using Equation 1.34 (as $\mu \gg k_B T$) to yield

$$\mu \approx E_F \left\{ 1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\mu} \right)^2 \right\}. \quad (1.37)$$

Therefore, using a polynomial expansion

$$\mu^{\frac{5}{2}} \approx E_F^{\frac{5}{2}} \left\{ 1 - \frac{5\pi^2}{24} \left(\frac{k_B T}{\mu} \right)^2 \dots \right\}, \quad (1.38)$$

Combining Equations 1.35 and 1.38 and neglecting terms of order $(k_B T/E_F)^4$ gives

$$\begin{aligned} U(T) &\approx \frac{2}{5} E_F^{\frac{5}{2}} \left\{ 1 - \frac{5\pi^2}{24} \left(\frac{k_B T}{\mu} \right)^2 \right\} \left\{ 1 + \frac{5}{8} \left(\frac{\pi k_B T}{\mu} \right)^2 \right\} \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{\frac{3}{2}} \\ &\approx \frac{2}{5} E_F^{\frac{5}{2}} \left\{ 1 + \frac{5}{12} \left(\frac{\pi k_B T}{\mu} \right)^2 \right\} \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{\frac{3}{2}}. \end{aligned} \quad (1.39)$$

Thus far, it was essential to keep the temperature dependence of μ in the algebra in order to get the prefactor of the temperature-dependent term in Equation 1.39 correct. However, Equation 1.37 shows that at temperatures $k_B T \ll \mu$ (e.g. at room temperature in typical metal), $\mu \approx E_F$ to a high degree of accuracy. In order to get a reasonably accurate estimate for $U(T)$ we can therefore make the substitution $\mu \rightarrow E_F$ in denominator of the second term of the bracket of Equation 1.39 to give

$$U(T) = U(0) + \frac{n\pi^2 k_B^2 T^2}{4E_F}, \quad (1.40)$$

where we have substituted in the value for $U(0)$ from Equation 1.31. Differentiating, we obtain

$$C_{\text{el}} \equiv \frac{\partial U}{\partial T} = \frac{1}{2}\pi^2 n \frac{k_{\text{B}}^2 T}{E_{\text{F}}}. \quad (1.41)$$

Equation 1.41 looks very good as it

1. is proportional to T , as are experimental data (see Figures 1.3 and 1.4);
2. is a factor $\sim \frac{k_{\text{B}}T}{E_{\text{F}}}$ smaller than the classical (Drude) value, as are experimental data.

Just in case the algebra of this section has seemed like hard work,¹⁴ note that a reasonably accurate estimate of C_{el} can be obtained using the following reasoning. At all practical temperatures, $k_{\text{B}}T \ll E_{\text{F}}$, so that we can say that only the electrons in an energy range $\sim k_{\text{B}}T$ on either side of $\mu \approx E_{\text{F}}$ will be involved in thermal processes. The number density of these electrons will be $\sim k_{\text{B}}Tg(E_{\text{F}})$. Each electron will be excited to a state $\sim k_{\text{B}}T$ above its groundstate ($T = 0$) energy. A reasonable estimate of the thermal energy of the system will therefore be

$$U(T) - U(0) \sim (k_{\text{B}}T)^2 g(E_{\text{F}}) = \frac{3}{2}nk_{\text{B}}T \left(\frac{k_{\text{B}}T}{E_{\text{F}}} \right),$$

where I have substituted the value of $g(E_{\text{F}})$ from Equation 1.30. Differentiating with respect to T , we obtain

$$C_{\text{el}} = 3nk_{\text{B}} \left(\frac{k_{\text{B}}T}{E_{\text{F}}} \right),$$

which is within a factor 2 of the more accurate method.

1.5 Successes and failures of the Sommerfeld model

The Sommerfeld model is a great improvement on the Drude model; it can successfully explain

- the temperature dependence and magnitude of C_{el} ;
- the approximate temperature dependence and magnitudes of the thermal and electrical conductivities of metals, and the Wiedemann–Franz ratio (see later lectures);
- the fact that the electronic magnetic susceptibility is temperature independent.¹⁵

It cannot explain

- the Hall coefficients of many metals (see Figure 1.6 and Table 1.1; Sommerfeld predicts $R_{\text{H}} = -1/ne$);
- the magnetoresistance exhibited by metals (see subsequent lectures);
- other parameters such as the thermopower;
- the shapes of the Fermi surfaces in many real metals;
- the fact that some materials are insulators and semiconductors (*i.e.* not metals).

Furthermore, it seems very intellectually unsatisfying to completely disregard the interactions between the electrons and the ionic cores, except as a source of instantaneous “collisions”. This is actually the underlying source of the difficulty; to remedy the failures of the Sommerfeld model, we must re-introduce the interactions between the ionic cores and the electrons. In other words, we must introduce the periodic potential of the lattice.

¹⁴The method for deriving the electronic heat capacity used in books such as *Introduction to Solid State Physics*, by Charles Kittel, seventh edition (Wiley, New York 1996) looks at first sight rather simpler than the one that I have followed. However, Kittel’s method contains a hidden trap which is not mentioned; it ignores $(d\mu/dT)$, which is said to be negligible. This term is actually of comparable size to all of the others in Kittel’s integral (see *Solid State Physics*, by N.W. Ashcroft and N.D. Mermin (Holt, Rinehart and Winston, New York 1976) Chapter 2), but happens to disappear because of a cunning change of variables. By the time all of this has explained in depth, Kittel’s method looks rather more tedious and less clear, and I do not blame him for wishing to gloss over the point!

¹⁵The susceptibility of metals in the Sommerfeld model is derived in Chapter 7 of *Magnetism in Condensed Matter*, by S.J. Blundell (OUP 2000).

1.6 Reading.

A more detailed treatment of the topics in this Chapter is given in *Solid State Physics*, by N.W Ashcroft and N.D. Mermin (Holt, Rinehart and Winston, New York 1976) Chapters 1-3 and *Band theory and electronic properties of solids*, by John Singleton (Oxford University Press, 2001) Chapter 1. Other useful information can be found in *Electricity and Magnetism*, by B.I. Bleaney and B. Bleaney, revised third/fourth editions (Oxford University Press, Oxford) Chapter 11, *Solid State Physics*, by G. Burns (Academic Press, Boston, 1995) Sections 9.1-9.14, *Electrons in Metals and Semiconductors*, by R.G. Chambers (Chapman and Hall, London 1990) Chapters 1 and 2, and *Introduction to Solid State Physics*, by Charles Kittel, seventh edition (Wiley, New York 1996) Chapters 6 and 7.