The Drude model is inadequate in many respects, e.g., it gets the specific heat of metals wrong. Many of these errors occur because the electron’s velocity and energy are deduced from a classical distribution. Sommerfeld theory is a modified Drude model; the only significant difference being that the velocity of electrons is found from quantum statistical mechanics.

First, let us quickly derive the Fermi-Dirac distribution from statistical mechanics (canonical ensemble picture) and the Pauli exclusion principle.

1 Deriving the Fermi distribution

We work in the canonical ensemble with the number of particles fixed to be \( N \). We now deal with many indistinguishable particles, assuming that we have an indexed set of energy levels that can either be occupied or empty. For clarity, we will use the word ‘level’ to denote a single particle state, e.g., \((l, m, n, s)\) states in a hydrogen atom. We will use the word ‘configuration’ to denote the state of all \( N \) particles, i.e., we specify how many particles are present in each level.

The probability of a given configuration is given by

\[
P_N(E) = \frac{e^{-\beta Epsilon}}{\sum \alpha e^{-\beta E_{\alpha}}}.
\]

(1)

The sum in the denominator is over all \( N \)-particle configurations. The denominator is also called the partition function and is written as \( e^{-\beta F_N} \), so that

\[
P_N(E) = e^{-\beta (E - F_N)},
\]

(2)

where \( F_N \) is the Helmholtz free energy of the system \((F = U - TS)\).

Now, the probability that a level is occupied is given by

\[
f_i^N = \sum_{\alpha: N, occ, i} P_N(E_\alpha);
\]

(3)

the sum is over configurations \( \alpha \) in which the level \( i \) is occupied.

Pauli’s exclusion principle tells us that there are only two possibilities: \( i \) is either empty or occupied. We rewrite the above as

\[
f_i^N = 1 - \sum_{\beta: N, emp, i} P_N(E_\beta),
\]

(4)
the sum is now over configurations with \( i \) empty.

We now rewrite the sum in a clever way. Instead of counting \( N \)-particle configurations with \( i \) empty, we count \( N+1 \)-particle configurations with \( i \) occupied – there is a one-to-one and onto mapping between both these sets of configurations. The energy of the new configuration is now higher by \( \epsilon_i \), there energy of level \( i \).

\[
f_i^N = 1 - \sum_{\gamma;N+1;\text{occ.}i} P_N(E_\gamma - \epsilon_i).
\]  

(5)

We now use the compare the definition of \( P_N(E) \) in Eq. 2 to that of \( P_{N+1}(E) \),

\[
P_N(E_\gamma - \epsilon_i) = e^{-\beta(E_\gamma - \epsilon_i - F_N)},
\]  

(6)

\[
P_{N+1}(E_\gamma) = e^{-\beta(E_\gamma - F_{N+1})}.
\]  

(7)

Comparing the two, we can write

\[
P_N(E_\gamma - \epsilon_i) = e^{\beta(\epsilon_i - \mu)} P_{N+1}(E_\gamma),
\]  

(8)

where \( \mu = F_{N+1} - F_N \), the difference in free energy when one extra particle is added to the system.

We can thus write

\[
f_i^N = 1 - \sum_{\gamma;N+1;\text{occ.}i} e^{\beta(\epsilon_i - \mu)} P_{N+1}(E_\gamma)
\]  

\[
= 1 - e^{\beta(\epsilon_i - \mu)} f_i^{N+1}.
\]  

(9)

(10)

If \( N \) is large, we can argue that \( f_i^N \) shouldn’t change if we increase the total number of particles by 1. We expect that probability of occupation of level \( i \) to be a smooth function of \( N \) with a well-defined large-\( N \) limit.

Rearranging this equation, we obtain the Fermi-Dirac distribution:

\[
f(n) = \frac{1}{\exp(\epsilon_n - \mu) + 1}.
\]  

(11)

It is not often not emphasized that the Fermi-Dirac distribution is very different from the Maxwell-Boltzmann distribution or the canonical ensemble probability (\( \propto e^{-\beta E} \)). The latter two give us the probability of occurrence of a many particle configuration. In other words, we have to specify an entire configuration of \( N \) particles and then ask for its probability. The Fermi distribution, however, is the average occupation of a single level.

From this derivation, you may have noticed some key requirements for the applicability of the Fermi distribution:

- Clearly labelled level structure – we should first be able to identify the levels that will be occupied by fermions. This is not always an easy task. Imagine a test tube with \( \text{He}^3 \), a fermionic fluid. It would be difficult to identify the levels that are occupied by He atoms.
Figure 1: Fermi-Dirac distribution at low temperatures. The x-axis is $\epsilon_n - \mu$ and the y-axis is $f(n)$.

- Non-interacting fermions. The energy of the $N$ particle system is given by $\epsilon_1 + \epsilon_2 + \cdots$, the sum of the energies of the occupied levels. We have implicitly used this in the above derivation.

- Thermodynamic limit – We should have a large number of particles in the system. For instance, consider two electrons in a He atom. We cannot use the Fermi distribution to determine the occupation of the 2s level.

2 Properties of the Fermi Dirac distribution

The average number of electrons in a level $n$ is given by

$$f(n) = \frac{1}{\exp(\epsilon_n - \mu) + 1}. \quad (12)$$

The energy of the level $n$ is given by $\epsilon_n$. $\mu$ is the chemical potential which is chosen so that we get the required total number of electrons, $N = \sum_n f(n)$ on average. The expectation value of the number of particles in a state must lie between 0 and 1, as they are the only values allowed by Pauli’s exclusion principle. The Fermi-Dirac distribution is plotted in Fig. 1 for low temperatures. At zero temperature, all states with $\epsilon_n - \mu < 0$ are occupied and all states with $\epsilon_n - \mu > 0$ are empty. The chemical potential at zero temperature $\mu_{T=0}$ is also called the Fermi energy $\epsilon_F$. At temperatures above zero but much below $\epsilon_F$, this distribution is slightly modified with a small number of particles shifted from below $\epsilon_F$ to above $\epsilon_F$.

In order to correctly apply the Fermi distribution to electrons in metals, we first need to identify the single-particle states which can be occupied by electrons. We naïvely imagine that the electrons are described by a free Schrödinger
equation.

\[ H = -\frac{\hbar^2}{2m} \nabla^2 \psi = \epsilon \psi. \]  \hspace{2cm} (13)

This is a drastic assumption. It is consistent with the free-electron and independent electron approximations, i.e., we are neglecting both electron-ion and electron-electron interactions. When we later discuss Bloch’s theorem, we will treat this in a somewhat more sophisticated manner. Later we will see that we will only need translational symmetry in order to index levels by the momentum quantum number. To find the solutions of the Schrödinger equation, we first need to specify the boundary conditions obeyed by the electrons. We assume that the metal is a \( L \times L \times L \) cube with periodic boundaries. That is, if we move a distance \( L \) along the \( x \) axis, we come back to the same point where we started. While this boundary condition may not be physically meaningful, it is a convenient theoretical tool.

Taking the wavefunction to be of the form \( \frac{1}{\sqrt{V}} e^{-\mathbf{k} \cdot \mathbf{r}} \), we obtain solutions of the wavefunction. The boundary conditions further constrain the values of \( \mathbf{k} \) to be

\[ \mathbf{k} = (m, n, p) \frac{2\pi}{L}, \{m, n, p\} \in \mathbb{Z}. \]  \hspace{2cm} (14)

It can easily be seen that these values of \( \mathbf{k} \) make the wave function periodic with period \( L \) in the \( x, y \) and \( z \) directions.

By applying the momentum operator \(-i\hbar \nabla\), we can identify \( \mathbf{k} \) as the momentum eigenvalue. Thus, the single particle states are labelled by momentum eigenvalues, which are themselves given by three integers. The energy of each state is given by \( \epsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m} \).

3 Zero temperature properties

At zero temperatures, we know that states below the \( E_F \) are fully occupied and states above are completely empty. With our spherically symmetric dispersion relation, we know that energy depends on the modulus of the momentum. Effectively, we have a ‘Fermi sphere’ with radius \( k_F \). All \( \mathbf{k} \)-points inside the sphere are occupied; all outside are empty.

We are interested in calculating expectation values of quantities like energy and electron number. To this end, it is convenient to introduce the density of states. We first note that each allowed momentum eigenvalues occupies a volume of \( (2\pi/L)^3 = 8\pi^3/V \) in \( \mathbf{k} \)-space. We have denoted the total volume in real space as \( V \). If we have a large volume \( \Omega \) in \( \mathbf{k} \)-space, the number of momentum values in the volume is approximately given by \( 2\Omega V/(8\pi^3) \) – we have multiplied this by a factor of 2 to account for the two-fold spin degeneracy. Since we work in the thermodynamic limit with \( N \gg 1 \) particles, we will always work with large volumes in \( \mathbf{k} \)-space. We will always count the number of allowed \( \mathbf{k} \) points, by dividing the volume by the density of momentum values. There may be small \( \mathcal{O}(1) \) errors in our calculations, but we will neglect them.
How many momentum-levels do we have with momentum amplitude between $k$ and $k + dk$? The volume in k-space occupied by such points is $(4\pi k^2 dk)$. The number of such states is given by $(4\pi k^2 (4\pi^3)$. If we denote $\epsilon = \hbar^2 k^2 / 2m$, this is also the number of states with energy between $\epsilon$ and $\epsilon + d\epsilon$. This number is taken to be equal to $g(\epsilon) d\epsilon$, where $g(\epsilon)$ is called the ‘density of states’. We have

$$
(4\pi k^2 dk) \times V/(4\pi^3) = g(\epsilon) d\epsilon.
$$

(15)

We rewrite $k^2 = 2m\epsilon / \hbar^2$ and $d\epsilon = \hbar^2 k dk / m = \hbar^2 (\sqrt{2m\epsilon / \hbar}) dk / m$. Rearranging terms, we obtain

$$
g(\epsilon) = (\sqrt{\epsilon}).
$$

(16)

Using this expression for the density of states, we can write energy and number of electrons as

$$
E = \int d\epsilon g(\epsilon) \epsilon f(\epsilon),
$$

(17)

$$
N = \int d\epsilon g(\epsilon) f(\epsilon).
$$

(18)

Exercise: (a) Show that the energy per particle in the metal is given by $E/N = 3\epsilon_F / 5$.

(b) Show that pressure $P = 2E/3V$, proportional to energy density.

(c) Show that the bulk modulus $B = 5P/3$. The bulk modulus measures the change in pressure when the system is subjected to isotropic pressure. It is a measure of the resistance of the metal to change in volume. The estimate for the bulk modulus from the free-electron gas picture turns out to be in remarkable agreement with experiment for many metals (see table in book). This is a reflection of the fact that all contact between objects in our everyday experience comes from Coulomb interactions between electrons. When you squeeze a metal with your fingers, it is the electrons in your finger which are interacting with the electrons in the metal. Nuclear forces are practically irrelevant for everyday contact processes.

4 Non-zero (low) temperatures

We will do a low temperature expansion for the properties of the metal. We will present a somewhat tedious derivation. However, we will be able to understand the results qualitatively from simple a posteriori arguments. Consider two quantities, energy and number of electrons at non-zero temperatures:

$$
u = \int d\epsilon g(\epsilon) f(\epsilon),
$$

(19)

$$
n = \int d\epsilon g(\epsilon) f(\epsilon).
$$

(20)
We have evaluated these quantities at zero temperature. At non-zero temperatures, the Fermi energy $\epsilon_F$ provides us with an energy scale which helps to expand in small temperatures with respect to $\epsilon_F$. We should keep in mind that $\epsilon_F \sim 10^4 K$ in metals which is comparable to the metal’s melting temperature itself. Thus, any metal in the solid state is practically in the low temperature limit.

When we go to small non-zero temperature, the change comes in through the Fermi function. The Fermi function itself is approximately the same as the zero temperature function except in the vicinity of the Fermi energy. As can be seen in Fig. 1, a little weight is shifted from immediately below $\epsilon_F$ to immediately above $\epsilon_F$. Suppose we want to evaluate some quantity of the form

$$\langle H(\epsilon) \rangle = \int_{-\infty}^{\infty} d\epsilon H(\epsilon)f(\epsilon),$$

this quantity will depend on the values of $H(\epsilon)$ in the vicinity of $\epsilon = \epsilon_F$. Note that $H(\epsilon)$ contains both the function of interest and the density of states. The above quantity can be written using the Taylor series expansion of $H(\epsilon)$ as follows:

$$\int_{-\infty}^{\infty} d\epsilon H(\epsilon)f(\epsilon) = \int_{-\infty}^{\mu} d\epsilon H(\epsilon) + \sum_{n=1}^{\infty} (k_B T)^{2n} a_n \left. \frac{d^{2n-1}}{d\epsilon^{2n-1}} H(\epsilon) \right|_{\epsilon = \mu}. \quad (22)$$

This is the Sommerfeld expansion. Note that the chemical potential $\mu$ may be different from $\epsilon_F$, the zero temperature value – more on this below. The constants $a_n$ are dimensionless and of order unity. (see Appendix C in Ashcroft and Mermin for derivation). We may assume that the typical function $H(\epsilon)$ changes significantly over an energy range comparable to $\mu$, so that $(d/d\epsilon)^n H(\epsilon) |_{\mu} \sim H(\mu)/\mu^n$. The successive terms in the Sommerfeld expansion are of the order $O(k_B T/\mu)^n$. Thus, in the low temperature limit, we may retain the first few terms only.

5 Deriving the Sommerfeld expansion

To lowest order, we have

$$\int_{-\infty}^{\infty} d\epsilon H(\epsilon)f(\epsilon) \approx \int_{-\infty}^{\mu} d\epsilon H(\epsilon) + \frac{\pi^2}{6} (k_B T)^2 H'(\mu). \quad (23)$$

Let us present a brief derivation here. We want to evaluate

$$\langle H \rangle = \int_{-\infty}^{\infty} d\epsilon H(\epsilon)f(\epsilon)$$

Since the major contribution to this integral comes from near $\mu$, we can Taylor expand both $f(\epsilon)$ and $H(\epsilon)$ about $\mu$. We will get terms of the form $\int d\epsilon (\epsilon - \mu)^n$.
\(\mu^{2n}(d^m f / de^m)(d^{n-m}H / de^{n-m})\). The Sommerfeld expansion simplifies this by grouping all derivatives but one with \(H(\epsilon)\). Let us first denote

\[
K(\epsilon) = \int_{-\infty}^{\epsilon} \text{d}\epsilon' H(\epsilon'),
\]

so that

\[
H(\epsilon) = \frac{dK}{d\epsilon}.
\]  

(25)

We can rewrite

\[
\langle H \rangle = \int_{-\infty}^{\infty} \text{d}\epsilon d\epsilon K(\epsilon) \left[ \frac{df}{d\epsilon} \right].
\]  

(26)

We have integrated by parts using \(\lim_{\epsilon \to \infty} f(\epsilon) = 0\) and \(\lim_{\epsilon \to -\infty} H(\epsilon) = 0\) (due to density of states being zero).

We can now replace \(K(\epsilon)\) with its Taylor expansion about \(\mu\).

\[
K(\epsilon) = K(\mu) + \sum_{n=1}^{\infty} \left[ \frac{(\epsilon - \mu)^n}{n!} \right] \left[ \frac{d^n K}{d\epsilon^n} \right]_{\epsilon=\mu}.
\]  

(27)

We substitute this in the expression for \(\langle H \rangle\) to obtain. We use \(\int_{-\infty}^{\infty} (-\partial f / \partial \epsilon) \text{d}\epsilon = 1\). Also, we only keep even \(n\), since \(\partial f / \partial \epsilon\) is an even function of \((\epsilon - \mu)\).

\[
\int_{-\infty}^{\infty} \text{d}\epsilon H(\epsilon) = \int_{-\infty}^{\mu} H(\epsilon) + \sum_{n=1}^{\infty} \int_{-\infty}^{\infty} \text{d}\epsilon \left[ \frac{(\epsilon - \mu)^{2n}}{2n!} \right] \left( -\frac{\partial f}{\partial \epsilon} \right) \left[ \frac{d^{2n-1}H}{d\epsilon^{2n-1}} \right]_{\epsilon=\mu},
\]

(28)

\[
\Rightarrow \int_{-\infty}^{\infty} \text{d}\epsilon H(\epsilon) = \int_{-\infty}^{\mu} H(\epsilon) + \sum_{n=1}^{\infty} a_n (k_B T)^{2n} \left[ \frac{d^{2n-1}H}{d\epsilon^{2n-1}} \right]_{\epsilon=\mu},
\]  

(29)

where \(a_n\) are constants of order unity (see Appendix C of Ashcroft and Mermin for numbers).

6 Low temperature properties

Let us now calculate the density of electrons using the leading order term:

\[
n \approx \int_{-\infty}^{\mu} \text{deg}(\epsilon) + \frac{\pi^2}{6} (k_B T)^2 g'(\mu),
\]  

(30)

\[
\approx \int_{-\infty}^{\epsilon_F} \text{deg}(\epsilon) + \left\{ (\mu - \epsilon_F)g(\epsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\epsilon_F) \right\}.
\]  

(31)

The fact that \(\mu\) need not be the same as its zero temperature value \(\epsilon_F\) enters here. We have assumed that \(g'(\mu)\) is roughly constant at \(\mu\). Demanding that
the density is the same as its zero temperature value, we find that the terms in
the braces must vanish. This determines \( \mu \) to be

\[
\mu = \epsilon_F - \frac{\pi^2}{6} (k_B T)^2 \frac{g'(\epsilon_F)}{g(\epsilon_F)},
\]

with a \( \mathcal{O}(T^2) \) correction.

The energy of the system is given by

\[
u \approx u_0 + \frac{\pi^2}{6} (k_B T)^2 g(\epsilon_F).
\]

The specific heat is given by

\[
c_v \approx \frac{\partial u}{\partial T} n \approx \frac{\pi^2}{3} (k_B T)^2 g(\epsilon_F).
\]

Unlike the classical gas result, it is linear proportional to \( T \) and is very small. In
general, we expect to see a linear \( T \)-dependence in specific heat for a good metal.
Note that the coefficient of the linear term is proportional to the density of states
at the Fermi level; this is important information that helps us understand several
properties of the metal.

Typically, when a new material is synthesised, its basic characterisation in-
cludes a measurement of specific heat vs. temperature. For a metal, this data
is typically fit to the form \( c_v = \gamma T + \beta T^3 \) – see Fig. 2. The linear contribution
is interpreted as coming from the electrons as we have shown above. The cubic
part is attributed to phonons (more on this later in the course). The coefficient
\( \gamma \) is then interpreted as a measure of the density of states at the Fermi level.

**Thermal conductivity**

\[
\kappa = \frac{1}{3} \nu^2 \tau c_v.
\]

Here, we take \( \nu^2 \approx \nu_F^2 = 2\epsilon_F/m \). We see that \( \kappa \sim T \) is linear in \( T \). We can
easily show that Wiedemann Franz law is still obeyed.

Similarly, thermopower (\( E = Q \nabla T, Q = -c_V/3ne \)) is also linear in \( T \).
Using the Drude model and the Sommerfeld expansion, we have mainly been concerned with transport properties, e.g., electrical conductivity, thermal conductivity, etc. Towards the end of this course, we will attempt a somewhat more sophisticated approach to transport properties using semi-classical equations of motion.