Sommerfeld model

Classical Drude model assumed classical statistics for the electron gas:

Maxwell-Boltzmann distribution

\[ f_{MB}(\vec{v}) = \frac{m}{\sqrt{2\pi knT}} \left( \frac{m}{2\pi knT} \right)^{3/2} e^{-\frac{mv^2}{2knT}} \]

density of electrons per unit volume with velocity \( \vec{v} \)

Once quantum mechanics was developed, Sommerfeld realized that the electrons, which obey the Pauli exclusion principle, use instead behavior according to Fermi-Dirac statistics

\[ f_{FD}(\vec{v}) = \frac{(\frac{m}{2\pi knT})^3}{4\pi^2} \frac{1}{e^{(\frac{\frac{1}{2}mv^2 - \mu}{kT})} + 1} \]

where \( \mu \) is the chemical potential (to be discussed in the following).

\[ \int d^3\vec{r} f_{FD}(\vec{v}) = \rho \]

electron density

\[ \int d^3\vec{r} f_{MB}(\vec{v}) \]

electron density
Review of quantum mechanics of a free electron gas

A single electron in a metal will be modeled as a free electron in a box of volume \( V = L^3 \)

The states of the electron are given by the eigenstates of Schrödinger's equation:

\[
-\frac{\hbar^2}{2m} \nabla^2 \psi = E \psi
\]

which has solutions:

\[
\psi_n(\mathbf{r}) = R e^{i \mathbf{k} \cdot \mathbf{r}} \quad \text{with energy} \quad E_n = \frac{\hbar^2 k^2}{2m}
\]

Normalization constant

The wave function is also an eigenstate of momentum:

\[
-i \hbar \nabla \psi = \mathbf{p} \psi \quad \Rightarrow \quad \mathbf{p} = \hbar \mathbf{k}
\]

with velocity \( \mathbf{v} = \frac{\hbar \mathbf{k}}{m} \)

For electrons in a finite volume \( V \), we also need to specify the boundary conditions on \( \psi \) at the walls: \( x=0,L \), \( y=0,L \), and \( z=0,L \)

One natural boundary condition is to choose \( \psi = 0 \) on the walls since there is no probability to find the electron outside the box.
The \( \psi_n(x) \) cannot satisfy the boundary condition.

We can make eigenstates which satisfy \( \psi = 0 \)
on the walls by taking an appropriate linear
superposition of the degenerate eigenstates
\( \psi_n \) with \( |k_l| = \sqrt{2mE/\hbar^2} \) constant to get

\[
\psi_n = (A \sin k_l x)(\sin k_y y)(\sin k_z z)
\]

where \( k_n \) must satisfy

\[
k_n = \frac{\mu \pi}{L} \quad \text{with } \mu \text{ integer}
\]

\( \mu = x, y, \text{ or } z \).

But this \( \psi_n \) is not an eigenstate of momentum.

It describes a "standing wave" whose expectation
value of momentum is always

\[
\langle \psi_n | \hat{p} | \psi_n \rangle = 0
\]

Since we will want to describe states of a metal
that carry a current, these standing wave solutions
corresponding to the \( \psi = 0 \) boundary condition
are not convenient.
Instead we use periodic boundary conditions requiring the wave function \( \psi \) to equal itself on opposite walls of the box, i.e.

\[
\begin{align*}
\psi(x+L, y, z) &= \psi(x, y, z) \\
\psi(x, y+L, z) &= \psi(x, y, z) \\
\psi(x, y, z+L) &= \psi(x, y, z)
\end{align*}
\]

These are also known as the Born–von Karman boundary conditions.

In 1-d, this boundary conditions is equivalent to describing the system by a loop of length \( L \).

\[
\begin{array}{ccc}
0 & \rightarrow & L \\
& \downarrow & \\
0 & \rightarrow & L
\end{array}
\]

In 2-d, it is equivalent to making the system the surface of a torus

\[
\begin{array}{ccc}
& \Rightarrow & \\
\square & \Rightarrow & \bigcirc
\end{array}
\]

In 3-d, it is the surface of a 3d torus (I won't try to sketch it!)

An electron hitting the wall at, say, \( x=L \) leaves the metal and simultaneously comes...
back in at the corresponding point on the opposite wall at $x=0$. This, therefore, is a convenient boundary condition to describe allow for situations in which a current can be flowing.

The periodic boundary conditions restrict the solutions

$$u_k = A e^{i k \cdot \mathbf{r}}$$

to values of $k$ that obey the conditions

$$e^{i k_x L} = e^{i k_y L} = e^{i k_z L} = 1$$

since, for example,

$$u(x+L, y, z) = A e^{i k_x L} e^{i (k_x x + k_y y + k_z z)}$$

$$= A e^{i k_x L} u(x, y, z)$$

The allowed values of $k$ therefore satisfy

$$k_x = \frac{2\pi n_x}{L} \quad \text{with} \quad n_x \text{ an integer}$$

$$k = \left( \frac{2\pi n_x}{L}, \frac{2\pi n_y}{L}, \frac{2\pi n_z}{L} \right)$$
We can represent these allowed states as points in \( \mathbf{k} \)-space:

\[
\begin{align*}
\text{volume of } \mathbf{k} \text{-space per state } & \propto (\Delta k)^3 \\
& = \left( \frac{2\pi}{L} \right)^3 = \frac{8\pi^3}{V} \\
\text{so a region of volume } S^2 & \text{ has } \frac{S^2}{(\Delta k)^3} = \frac{\sqrt{S}}{8\pi^2} \text{ states } \\
& \text{for large } S^2.
\end{align*}
\]

To describe a state of \( N \) non-interacting electrons, we need to give the value of \( \mathbf{k} \) and electron spin \( s \), for each electron (electrons have intrinsic spin that can take two possible values—"spin up" or "spin down"). Because electrons are fermions that obey the Pauli Exclusion Principle, no two electrons can have the same values of both \( \mathbf{k} \) and \( s \).

To fill the ground state of \( N \) non-interacting electrons, we just fill up the lowest energy electron states \( \mathbf{k} \), putting two electrons in each \( \mathbf{k} \)-state (corresponding to spin up and spin down).

Since \( E \) depends only on \( |\mathbf{k}| \), for \( N \) large, the set of \( \mathbf{k} \) values that will get filled...
in the ground state will correspond to the states inside the surface of a sphere of fixed radius \( k_F \).

\( k_F \) is the "Fermi wave vector." The sphere of radius \( k_F \) is the "Fermi sphere." The surface of the Fermi sphere is the "Fermi surface".

\[
\begin{align*}
\varepsilon_F &= \frac{\hbar^2 k_F^2}{2m} \quad \text{the "Fermi energy"} \\
p_F &= \hbar k_F \quad \text{the "Fermi momentum"} \\
V_F &= \frac{\hbar k_F}{m} \quad \text{the "Fermi velocity"}
\end{align*}
\]

\( \varepsilon_F, p_F, V_F \) are the energy, momentum, and speed of the most energetic electrons in the ground state.

\( k_F \) depends on the density of electrons \( n \) in the gas, as follows:

\[
\alpha = \frac{n}{V} \text{ in the gas, as follows:}
\]

In a \( k \)-space volume \( \Omega = \frac{4\pi}{3} k_F^3 \) (sphere of radius \( k_F \)), the number of allowed values of \( k \) are \( \frac{\Omega V}{8\pi^3} \). Then the number of allowed electron states are \( 2 \times \frac{\Omega V}{8\pi^3} = \frac{\Omega V}{4\pi^3} \) since each allowed value of \( k \) can hold two spin states ("up" and "down")
Therefore, the number of electrons in the volume \( V \) is

\[
N = \frac{\Omega V}{4\pi} = \frac{4}{3} \pi k_F^2 \frac{V}{4\pi} = \frac{k_F^3 V}{3\pi^2}
\]

\[
\Rightarrow n = \frac{N}{V} = \frac{k_F^3}{3\pi^2} \quad \Rightarrow k_F = (\frac{3\pi^2 n}{m})^{1/3}
\]

How big is \( k_F \)?

Using our density parameter \( r_s \), where \( \frac{4}{3} \pi r_s^3 = \frac{n}{m} \)

\[
k_F = \frac{(3\pi^2/4)^{1/3}}{r_s} \frac{1}{r_s} \frac{3.63}{(r_s/a_0)} \approx A^{-1}
\]

\( a_0 \) = Bohr radius

\[
a_0 = \frac{0.529 \times 10^{-8} \text{ cm}}{0.529 \text{ A}}
\]

\( \lambda_F = 2\pi/k_F \sim A \)

\( v_F = \frac{\frac{4}{3} k_F}{m} \sim 4 \times 10^8 \text{ cm/sec} \sim 10^8 \text{ cm/sec} \sim 0.01c \)

Compare this to thermal velocity at room temperature of a classical gas

\( v_T \approx \sqrt{\frac{3k_B T}{m}} \approx 10^7 \text{ cm/sec} \)

\( \text{Fermi energy} \quad E_F = \frac{\hbar^2}{2m} \left( k_F a_0 \right)^2 = \frac{(e^2)}{(2a_0)} \left( k_F a_0 \right)^2 \)

\( \quad \left( \frac{e^2}{2a_0} = 13.6 \text{ eV} = 1 \text{ Rydberg} \right) \quad a_0 = \frac{\hbar^2}{m e^2} = \frac{1.29 \times 10^{-8}}{5.29 \times 10^{-8} \text{ cm}} \)
\[ E_F = (13.6) \left( \frac{k_F a_0}{2} \right)^2 \text{ eV} \approx (13.6) \left( \frac{1.92}{r_s/a_0} \right)^2 \]

\[ = \frac{50.1 \text{ eV}}{(r_s/a_0)^2} \sim 1.5 \text{ to } 15 \text{ eV depending on density} \]

\( E_F \) is the magnitude of typical atomic binding energies.

"Fermi temperature"
\[ T_F = \frac{E_F}{k_B} = \frac{58.2}{(r_s/a_0)^2} \times 10^4 \text{ K} \sim 3 \times 10^4 \text{ K} \]

\( \Rightarrow \text{room temperature} \)

Total ground state energy
\[ E = \frac{\pi^2}{3} \sum_{|k| < k_F} \frac{\hbar^2 k^2}{2m} \]

up \( |k| < k_F \)

\( \text{two spin states for each } k \)

as \( L \to \infty \), the spacing \( \Delta k = \frac{2\pi}{L} \to 0 \) and we can approximate the sum by an integral
\[ \int_{k_1}^{k_2} \frac{\hbar^2 k^2}{2m} \]
For any quantity \( F(k) \) we have as \( \Delta k \rightarrow 0 \)

\[
\frac{\sum}{\Delta k} F(k) (\Delta k)^3 = \int d^3k F(k)
\]

So

\[
\sum_{k} F(k) = \frac{1}{(\Delta k)^3} \int d^3k F(k) = \frac{(\Delta k)^2}{(2\pi)^2} \int d^3k F(k)
\]

\[
= \frac{V}{8\pi^3} \int d^3k F(k)
\]

So, total energy

\[
E = 2 \sum \frac{k^2}{2m} \frac{k}{k_F} = 2 \cdot \frac{V}{8\pi^3} \frac{k^2}{2m} \int d^3k k^2
\]

\[
= \frac{V k^2}{8\pi^3 m} 4\pi \int_0^k k^4 k^2 k^2 \text{ convert } d^3k \text{ to spherical coordinates and integrate over angles}
\]

\[
E = \frac{V k^2}{8\pi^3 m} \frac{k_F^5}{5}
\]

Energy per particle

\[
\frac{E}{N} = \frac{V}{N} \frac{k^2}{2m} \frac{k_F^5}{5\pi^2} = \frac{1}{m} \left( \frac{k^2}{2m} \right) \frac{k_F^2}{5\pi^2}
\]

\[
= \frac{(3\pi^2)}{k_F^3} \left( \frac{k_F^2}{2m} \right) \frac{k_F^3}{5\pi^2} = \frac{3}{5} E_F
\]

\[
\frac{E}{N} = \frac{3}{5} E_F, \quad \frac{E}{V} = \frac{3}{5} m E_F
\]

energy per particle    energy per volume
Density of states \( g(E) \)

Often we want to sum a quantity that depends on \( k \) only through the energy \( E_k \), i.e.

\[
\sum_k \sum_i F(E_k) = \frac{2}{\mathcal{V}} \sum_i F(E_k) = \frac{\mathcal{V}}{\pi^2} \int d^3k \, F(E_k)
\]

\[\text{sum over spin states} \]

Define \( g(E) \) as the number of states per unit energy per unit volume, i.e.

\[
\frac{1}{\mathcal{V}} \sum_k \sum_i = \frac{1}{\pi^2} \int d^3k = g(E) \, dE
\]

\[\text{such that}\]

\[E \leq E_k \leq E + dE\]

Then

\[
\frac{1}{\mathcal{V}} \sum_k \sum_i F(E_k) = \int dE \, g(E) \, F(E)
\]

\[\text{When } E_k \text{ depends on } \mathbf{k} \text{ only through } |\mathbf{k}|, \text{ we can write}\]

\[
\frac{1}{4\pi^3} \int d^3k = \frac{4\pi}{4\pi^3} \int d\mathbf{k} \, k^2 = \frac{1}{\pi^2} \int dk \, k^2 = \int g(E) \, dE
\]

\[
\frac{1}{\pi^2} k^2 \, dk = g(E) \, dE
\]

\[
g(E) = \frac{1}{\pi^2} \frac{k^2 \, dk}{dE}
\]
For free electrons $E = \frac{\hbar^2 k^2}{2m}$

$$g(E) = \frac{1}{\pi^2 \hbar^2} \frac{2mE}{\hbar^2} \frac{1}{e^{E/E_F}}$$

$$= \frac{2mE}{\pi^2 \hbar^2} \frac{1}{2mE} = \frac{2mE}{\pi^2 \hbar^2} \frac{k}{2E}$$

$$= \frac{m}{\pi^2 \hbar^2} \sqrt{\frac{2mE}{\hbar^2}}$$

$$g(E) = \frac{m}{\pi^2 \hbar^2} \sqrt{\frac{2mE}{\hbar^2}} \propto \sqrt{E}$$

Total Energy

$E = \sum_{n} E_n$

Write $g(E) = C \sqrt{E}$ where $C$ is appropriate constant

Density of electrons

$M = \frac{1}{V} \sum_{k} \sum_{s} 1$ count states

$= \frac{E_F}{\hbar} \int dE g(E) = C \int_0^{E_F} dE \sqrt{E} = \frac{2}{3} C E_F^{3/2}$

$\therefore C = \frac{3}{2} \frac{m}{E_F^{3/2}}$

$$g(E) = \frac{3}{2} \frac{m}{E_F^{3/2}} \sqrt{\frac{E}{E_F}}$$
Total energy

\[
\frac{E}{V} = \int_0^{E_F} dE \frac{q(E)}{E} = C \int_0^{E_F} E^{3/2} = \frac{3}{5} C E_F^{5/2}
\]

\[
= \frac{3}{5} \frac{3}{2} \frac{m}{2} E_F^{3/2} = \frac{3}{5} m E_F
\]

\[
\frac{E}{V} = \frac{3}{5} m E_F \quad \text{same as we found before}
\]

We will see that \( q(E) \), and in particular \( q(E_F) \), is a very important quantity which determines the behavior of conduction electrons in a metal.

Pressure of conduction electrons in a metal

From thermodynamics

\[
dE = TdS - pdV
\]

at \( T = 0 \)

\[
dE = -pdV
\]

\[
P = -\left( \frac{dE}{dV} \right)
\]

Now:

\[
E = \frac{3}{5} V m E_F = \frac{3}{5} N E_F
\]

\[
E_F = \frac{1}{2} k_F^2 \quad \text{where} \quad k_F = \left( \frac{3 N^2 N}{V} \right)^{1/3}
\]

so

\[
E_F \propto V^{-2/3} \quad \text{for constant} \ N
\]
\[ E = \text{const} \, V^{-\frac{2}{3}} \]

\[ \text{const} = \frac{2}{3} N \frac{1}{2m} (3\pi^2 N)^{\frac{3}{2}} \]

\[ -\frac{dE}{dV} = \frac{2}{3} \text{const} \, V^{-\frac{5}{3}} = \frac{2}{3} \text{const} \, V^{-\frac{7}{3}} \]

\[ p = \frac{2}{3} \frac{E}{V} = \frac{2}{3} \frac{8}{5} m \varepsilon_F = \frac{2}{5} m \varepsilon_F \]

**Bulk modulus**

Anyone to a classical ideal gas where

\[ p = \frac{1}{3} \text{ class} \]

we now have:

\[ p = \frac{2}{3} \text{ class} \]

since \( T_F > T \) for a metal

\[ \text{Poisson's } \nu = \frac{1}{3} \text{ class} \]

**Bulk modulus**

\[ B = \frac{1}{k} \]

\[ K = \text{compressibility} \]

\[ B = -V \left( \frac{\partial P}{\partial V} \right)_N \]

\[ \text{derivative } \partial \text{ at constant } N \]

\[ P = \frac{2}{3} \frac{E}{V} \quad \text{and } E = \text{const} \, V^{-\frac{2}{3}} \]

\[ \Rightarrow p = \text{const} \, V^{-\frac{5}{3}} \]

\[ B = -V \left( \frac{\partial P}{\partial V} \right)_N = -V \frac{5}{3} \text{ const} \, V^{-\frac{7}{3}} = \frac{5}{3} \text{ const} \, V^{-\frac{5}{3}} \]

\[ \frac{5}{3} p = \frac{5}{3} \frac{2}{3} \text{ const } E = \frac{10}{9} E = \frac{10}{9} \frac{3}{5} m \varepsilon_F = \frac{2}{3} m \varepsilon_F \]
\[ B = \frac{2}{3} n^2 F \] 
\[ = \left( \frac{6.15 \times 10^{-10}}{a_0} \right)^5 \times 10^{10} \text{ dyne/cm}^2 \]

<table>
<thead>
<tr>
<th>Metal</th>
<th>( B - \text{theory} )</th>
<th>( B - \text{exp} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>23.9</td>
<td>11.5</td>
</tr>
<tr>
<td>Na</td>
<td>9.25</td>
<td>6.42</td>
</tr>
<tr>
<td>Ca</td>
<td>6.38</td>
<td>134.3</td>
</tr>
<tr>
<td>Ag</td>
<td>34.5</td>
<td>99.9</td>
</tr>
</tbody>
</table>

Our free electron model gives correct order of magnitude. Note that our calculation gives only the contribution to \( B \) from the conduction electrons, whereas the measured \( B \) in experiment has also a contribution from the lattice of ions. We see that the electronic contribution is clearly just as important as the ionic contribution.