Sommerfeld model

Classical Drude model assumed classical statistics for the electron gas:

Maxwell-Boltzmann distribution

\[ f_{MB}(\vec{v}) = \frac{m}{2\pi k_B T}^{3/2} e^{-m\vec{v}^2/2k_B T} \]

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, would instead behave according to Fermi-Dirac statistics

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

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

\[ \int d^3 N \frac{d}{d^3 N} f_{FD}(\vec{v}) = n \text{ total conduction electron density} \]
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

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

which has solutions

\[
\psi_k(r) = A e^{i \mathbf{k} \cdot \mathbf{r}} \quad \text{with energy } \varepsilon_k = \frac{\hbar^2 k^2}{2m}
\]

normalization constant

The wave function is also an eigenstate of momentum

\[-i \nabla \psi_k = \mathbf{p} \psi_k \implies \mathbf{p} = \hbar \mathbf{k}
\]

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

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 $\psi_k(\mathbf{r})$ cannot satisfy this boundary condition.

We can make eigenstates which satisfy $\psi=0$ on the walls by taking an appropriate linear superposition of the degenerate eigenstates $\psi_k$ with $|\psi| = \sqrt{2mE/\hbar^2}$ constant. To get

$$\psi_k = (A \sin k_x x)(\sin k_y y)(\sin k_z z)$$

where $k_\mu$ must satisfy

$$k_\mu = \nu \mu \pi \frac{\lambda}{L} \quad \text{with } \nu \mu \text{ integer} \quad \mu=x,y,\text{ or } z$$

But this $\psi_k$ is not an eigenstate of momentum. It describes a "standing wave" whose expectation value of momentum is always

$$\langle \hat{\mathbf{p}} \rangle = 0$$

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.

$$\psi(x + L, y, z) = \psi(x, y, z)$$
$$\psi(x, y + L, z) = \psi(x, y, z)$$
$$\psi(x, y, z + L) = \psi(x, y, z)$$

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

In 1-d, this boundary condition is equivalent
to describing the system by a loop of length $L$.

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

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 allow for situations in which a current can be flowing.

The periodic boundary conditions restrict the solutions
\[
\psi_k = A e^{i k \cdot \mathbf{r}}
\]

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,
\[
\psi(x + L, y, z) = A e^{i [k_x L] x + k_y y + k_z z - i]
\]
\[
= A e^{i k_x L} e^{i (k_x x + k_y y + k_z z) - i}
\]
\[
= e^{i k_x L} \psi(x, y, z)
\]

The allowed values of \( k \) therefore satisfy
\[
k_x = \frac{2\pi \mu_x}{L} \quad \text{with } \mu_x \text{ an integer}
\]
\[
k = \left( \frac{2\pi \mu_x}{L}, \frac{2\pi \mu_y}{L}, \frac{2\pi \mu_z}{L} \right)
\]
We can represent these allowed states as points in $\mathbf{k}$-space.

\[
(\Delta k)^3 = \left( \frac{2\pi}{L} \right)^3 = \frac{8\pi^3}{V}
\]

so a region of volume $\Omega$ has

\[
\frac{\Omega}{(\Delta k)^3} = \frac{\sqrt[3]{\Omega}}{8\pi}
\]

states for large $\Omega$.

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 single electron states $\mathbf{k}$, putting two electrons in each $\mathbf{k}$-state (corresponding to spin up or spin down).

Since $E_\mathbf{k}$ 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"

\[
\begin{align*}
\mathcal{E}_F &= \frac{\hbar^2 k_F^2}{2m} \quad \text{is the "Fermi energy"}
\end{align*}
\]

\[
\begin{align*}
\mathcal{P}_F &= \hbar k_F \quad \text{is the "Fermi momentum"}
\end{align*}
\]

\[
\begin{align*}
\mathcal{V}_F &= \frac{\hbar k_F}{m} \quad \text{is the "Fermi velocity"}
\end{align*}
\]

$\mathcal{E}_F$, $\mathcal{P}_F$, $\mathcal{V}_F$ are the energy, momentum, and speed of the most energetic electrons in the ground state.

$k_F$ depends on the density of electrons $\mathcal{N} = \mathcal{N}/V$ in the gas, as follows:

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

$$N = \frac{Q V}{4\pi^3} = \frac{4}{3} \pi k_F^3 \frac{V}{4\pi^3} = \frac{k_F^3}{3\pi^2} \frac{V}{\hbar^2}$$

$$\Rightarrow m = \frac{N}{V} = \frac{k_F^3}{3\pi^2} \Rightarrow k_F = \left(\frac{3\pi^2 m}{2}\right)^{1/3}$$

How big is $k_F$?

Using our density parameter $r_s$, where $\frac{4}{3} \pi r_s^3 = \frac{1}{m}$

$$k_F = \left(\frac{9\pi^4}{r_s^3}\right)^{1/3} = \frac{1.92}{r_s} = \frac{3.63}{(r_s/a_0)} \text{ Å}^{-1} \approx \text{Å}^{-1}$$

de Broglie wavelength

$$\lambda_F = \frac{\hbar}{k_F} \approx \text{Å}$$

$$\nu_F = \frac{\lambda_F}{\hbar} k_F = 4.20 \times 10^8 \text{ cm/sec} \approx 10^8 \text{ cm/sec} \approx 0.01 \text{ c}$$

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

$$\langle v \rangle \approx \sqrt{\frac{3 k_B T}{m}} \approx 10^7 \text{ cm/sec}$$

Fermi energy

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2ma_0^2} (k_F a_0)^2 = \left(\frac{e^2}{2a_0}\right)(k_F a_0)^2$$

where $\frac{e^2}{2a_0} = 13.6 \text{ eV} = 1 \text{ Rydberg}$

$$a_0 = \frac{\hbar^2}{m e^2} \approx 0.529 \times 10^{-8} \text{ cm}$$
\[ \varepsilon_F = (13.6) (k_F a_0)^2 \text{ ev} \approx (13.6) \left( \frac{1.92}{r_s/a_0} \right)^2 \]

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

\[ \varepsilon_F \text{ is the magnitude of typical atomic binding energies} \]

"Fermi temperature"

\[ T_F = \frac{\varepsilon_F}{k_B} = \frac{58.2 \times 10^4 \text{ K}}{(r_s/a_0)^2} \sim 3 \times 10^4 \text{ K} \quad \Rightarrow \text{ room temperature} \]

Total ground state energy,

\[ E = 2 \sum_{|k| < k_F} \varepsilon_k = 2 \sum_{|k| < k_F} \frac{\hbar^2 k^2}{2m} \]

\[ \uparrow \text{ two spin states for each } k \]

as \( L \to \infty \), the spacing \( \Delta k = \frac{2 \pi L}{L^2} \to 0 \) and we can approximate the sum by an integral

\[ \frac{1}{3} \frac{1}{L^3} \sum P(k) = \frac{1}{3} \frac{1}{L^3} \int 4 \pi \delta^3 (\vec{k}) \text{ ev} \]
For any quantity \( F(k) \) we have as \( \Delta k \to 0 \)

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

So

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

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

So total energy

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

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

\[
E = \frac{V \hbar^2 k_F^5}{2\pi^2 m} \frac{5}{5}
\]

Energy per particle

\[
\frac{E}{N} = \frac{V}{N} \frac{\hbar^2 k_F^5}{2m 5\pi^2} = \frac{1}{M} \left( \frac{\hbar^2 k_F^2}{2m} \right) \frac{k_F^3}{5\pi^2}
\]

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

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

energy per particle

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

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

\[
\sum \sum \frac{F(E_k)}{V} = \frac{V}{\frac{4\pi^3}{k^3}} \int \frac{d^3k}{k} F(E_k)
\]

\( \sum \) over spin states

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

\[
\frac{1}{V} \sum \sum \frac{F(E_k)}{k} = \frac{1}{4\pi^3} \int \frac{d^3k}{k} = g(E) dE
\]

\( \frac{1}{V} \sum \sum \frac{F(E_k)}{k} \) over \( \vec{k} \) such that \( E < E_k < E + dE \)

Then \( \frac{1}{V} \sum \sum \frac{F(E_k)}{k} = \int dE g(E) F(E) \)

When \( E_k \) depends on \( \vec{k} \) only through \( |\vec{k}| \), we can write

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

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

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