Sommerfeld model

Classical Drake model assumed classical statistics for the electron gas:

Maxwell-Boltzmann distribution

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

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, use instead behave according to Fermi-Dirac statistics

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

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

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

\[
\psi_k(r) = A e^{i \frac{k}{\hbar} \cdot r}
\]

with energy \( \varepsilon_k = \frac{\hbar^2 k^2}{2m} \)

The wave function is also an eigenstate of momentum

\[
-i \hbar \frac{\partial \psi}{\partial t} = \hat{p} \psi 
\rightarrow \hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial r}
\]

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 \( \Phi(\vec{r}) \) cannot satisfy this boundary condition.

We can make eigenstates which satisfy \( \nabla \cdot \Phi = 0 \)
on the walls by taking an appropriate linear superposition of the degenerate eigenstates
\( \Phi_k \) with \( |\vec{k}| = \sqrt{2mE/k^2} \) constant. To get

\[ \Phi_k = (A \sin k_x x)(\sin k_y y)(\sin k_z z) \]

where \( k_\mu \) must satisfy

\[ k_\mu = \frac{n_\mu \pi}{L} \quad \text{with } n_\mu \text{ integer} \quad \mu = x, y, \text{ or } z \]

But this \( \Phi_k \) is not an eigenstate of momentum.
It describes a "standing wave" whose expected value of momentum is always

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

Since we will want to describe states of a metal that carry a current, these standing wave solutions corresponding to the \( \Phi = 0 \) 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 $L$.

\[ \begin{array}{c}
0 \\
\hline
L \\
\end{array} \quad \Rightarrow \quad \bigcirc \quad o = L \]

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

\[ \Rightarrow \bigcirc \bigcirc \]

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 at 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

\[ \psi_k = A e^{-i k \cdot \mathbf{r}} \]

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,

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

The allowed values of \(k\) therefore satisfy

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

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

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

so a region of volume \( \Omega \) has

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

for large \( \Omega \).

To describe a state of \( N \)-non-interacting electrons, we need to give the value of \( \mathbb{k} \) 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 \( \mathbb{k} \) and \( s \).

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

Since \( E_k \) depends only on \( |\mathbb{k}| \) for \( N \) large, the set of \( \mathbb{k} \) 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".

$$E_F = \frac{\hbar^2 k_F^2}{2m} \quad \text{is the "Fermi energy"}$$

$$p_F = \hbar k_F \quad \text{is the "Fermi momentum"}$$

$$v_F = \frac{\hbar k_F}{m} \quad \text{is the "Fermi velocity"}$$

$E_F$, $p_F$, $v_F$ are the energy, momentum, and speed of the most energetic electrons in the ground state.

$k_F$ depends on the density of electrons $n = N/V$ in the gas, as follows:

In a $k$-space volume $\Omega = \frac{4\pi k_F^3}{3}$ (sphere of radius $k_F$), the number of allowed values of $k$ is

$$\frac{\Omega V}{8\pi^3}.$$ 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

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

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

How big is \( k_F \)?

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

\[
k_F = \left( \frac{9\pi^2}{4} \right)^{1/3} = 1.92 \left( \frac{r_s}{r_s} \right) = 3.13 \text{ Å}^{-1} = \text{Å}^{-1}
\]

\[
a_0 = \text{Bohr radius} = 0.529 \times 10^{-8} \text{ Å}
\]

de Broglie wavelength

\[
\lambda_p = \frac{2\pi}{k_F} \sim \text{Å}
\]

\[

\]
\[ \varepsilon_F = (13.6) \left( \frac{k_F a_0}{r_s/a_0} \right)^2 \text{ ev} \approx (13.6) \left( \frac{1.92}{r_s/a_0} \right)^2 \]

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

\[ \varepsilon_F \] is the magnitude of typical atomic binding energies.

"Fermi temperature"

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

\[ \Rightarrow \text{ room temperature} \]

Total ground state energy

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

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

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

\[ \frac{\hbar^2}{2m} \sum_{k} \psi_k \bar{\psi}_k = \frac{\hbar^2}{2m} \sqrt{\frac{L}{2\pi}} \int \psi_k \bar{\psi}_k \frac{d^2k}{(2\pi)^2} \]
For any quantity \( F(\mathbf{k}) \) we have as \( \Delta k \to 0 \)

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

So

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

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

So total energy

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

\[
= \frac{V}{8\pi^3} \frac{\hbar^2}{2m} \frac{k_F^5}{4\pi^2 \int d^3k \ k^2}
\]

\[
\text{convert } d^3k \text{ to spherical coords and integrate over angles}
\]

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

Energy per particle

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

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

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