Sommerfeld model

Classical Drude model assumed classical statistics for the electron gas:

Maxwell Boltzmann distribution

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

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

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

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

$$\int d^3v \, f_{FD}(\vec{v}) = n \quad \text{total conduction electron density}$$
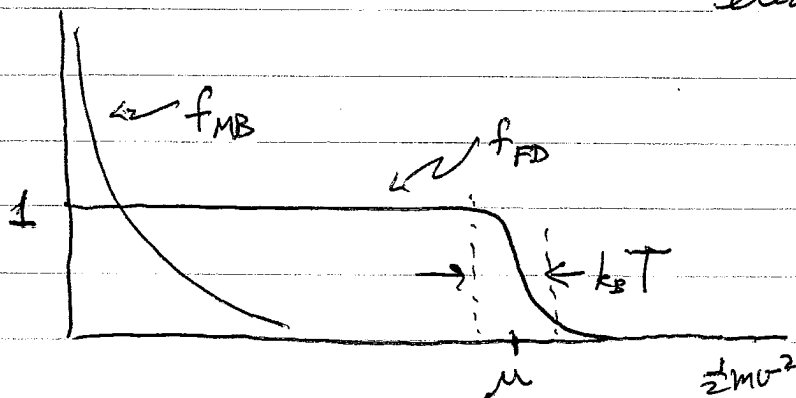
Review of quantum mechanics of a free electron gas

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

$$\psi_k(\vec{r}) = A e^{i \vec{k} \cdot \vec{r}} \qquad \text{with energy } \varepsilon_k = \frac{\hbar^2 k^2}{2m}$$

$\uparrow$
normalization constant

This wavefunction is also an eigenstate of momentum

$$-i \vec{\nabla} \psi_k = \vec{p} \psi \quad \Rightarrow \quad \vec{p} = \hbar \vec{k}$$
$$\text{with velocity } \vec{v} = \frac{\hbar \vec{k}}{m}$$

For electrons in a finite volume V, we also need to specify the boundary conditions on ψ 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 $\psi_k(\vec{r})$ cannot satisfy this boundary condition. ~~except for the trivial~~

We can make eigenstates which satisfy $\psi = 0$ on the walls by taking an appropriate linear superposition of the degenerate eigenstates ψ_k with $|\vec{k}| = \sqrt{2m\mathcal{E}/\hbar^2}$ constant. to get

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

where k_μ must satisfy

$$k_\mu = n_\mu \frac{\pi}{L} \qquad \text{with } n_\mu \text{ integer}$$
$$\mu = x, y, \text{ or } z$$

But this ψ_k is not an eigenstate of momentum. It describes a "standing wave" whose expectation value of momentum is always
$$\langle \psi_k | \vec{p} | \psi_k \rangle = 0$$

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 wavefunction 4 to equal itself on opposite walls of the box, ie
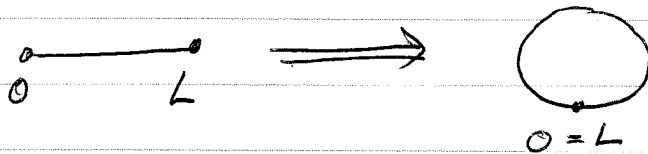
$$\Psi(x+L, y, z) = \Psi(x, y, z)$$
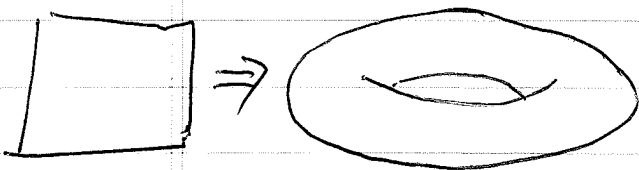$$\Psi(x, y+L, z) = \Psi(x, y, z)$$
$$\Psi(x, y, z+L) = \Psi(x, y, z)$$

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 2d, 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 ~~describe~~ allow for situations in which a current can be flowing.

The periodic boundary conditions restrict the solutions

$$\psi_k = A e^{i \vec{k} \cdot \vec{r}}$$

to values of $\vec{k}$ that obey the conditions

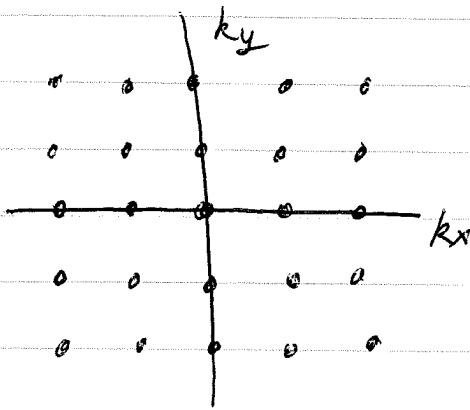$$e^{i k_x L} = e^{i k_y L} = e^{i k_z L} = 1$$

since, for example,

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

The allowed values of $\vec{k}$ therefore satisfy

$$k_\mu = \frac{2\pi n_\mu}{L} \qquad \text{with } n_\mu \text{ an integer}$$

$$\vec{k} = \left(\frac{2\pi n_x}{L}, \frac{2\pi n_y}{L}, \frac{2\pi n_z}{L} \right)$$

We can represent these allowed states as points in $\vec{k}$-space

volume of $\vec{k}$-space per state is

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

so a region of volume Ω has $\dfrac{\Omega}{(\Delta k)^3} = \dfrac{V\Omega}{8\pi^3}$ states for large Ω.

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

To find the ground state of N non interacting elections, we just fill up the lowest energy single election states $\vec{k}$, putting two elections in each $\vec{k}$-state (corresponding to spin up and ~~spin~~ down).

Since $\mathcal{E}_k$ depends only on $|\vec{k}|$, for N large the set of $\vec{k}$ 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"

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

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

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

ε_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 $\Omega = \frac{4}{3}\pi k_F^3$ (sphere of radius k_F)
the number of allowed values of $\vec{k}$ are
$\frac{\Omega V}{8\pi^3}$. Thus 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 $\vec{k}$ can hold two spin states ("up" and "down")

Therefore, the number of electrons in the volume Ω is

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

$$\Rightarrow \boxed{n = \frac{N}{V} = \frac{k_F^3}{3\pi^2} \qquad \Rightarrow k_F = (3\pi^2 n)^{1/3}}$$

How big is k_F?

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

$$k_F = \frac{(9\pi/4)^{1/3}}{r_s} = \frac{1.92}{r_s} = \frac{3.63}{(r_s/a_0)} \, \mathring{A}^{-1} \sim \mathring{A}^{-1}$$

$a_0 = $ Bohr radius
$= 0.529 \times 10^{-8}$ cm
$= 0.529 \, \mathring{A}$

de Broglie wavelength
$$\lambda_F = 2\pi/k_F \sim \mathring{A}$$

$$v_F = \frac{\hbar}{m} k_F = \frac{4.20 \times 10^8 \, \text{cm/sec}}{(r_s/a_0)} \sim 10^8 \, \text{cm/sec} \sim 0.01c$$

$\uparrow$
speed of light

Compare this to thermal velocity at room
Temperature of a classical gas
$$\langle v \rangle \simeq \sqrt{3 k_B T/m} \sim 10^7 \, \text{cm/sec}$$

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

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

$a_0 = \frac{\hbar^2}{me^2}$
$= .529 \times 10^{-8}$ cm

$$\varepsilon_F = (13.6)(k_F a_0)^2 \; ev \quad \simeq (13.6)\left(\frac{1.92}{r_s/a_0}\right)^2$$

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

ε_F is the magnitude of typical atomic binding energies

"Fermi temperature"

$$T_F = \varepsilon_F/k_B \quad = \frac{58.2}{(r_s/a_0)^2} \times 10^4 \; {}^\circ K \quad \sim 3 \times 10^4 \; {}^\circ K$$

$$\gg \text{room temperature}$$

Total ground state energy

$$E = 2 \sum_{|\vec{k}| < k_F} \varepsilon_k \quad = 2 \sum_{|\vec{k}| < k_F} \frac{\hbar^2 k^2}{2m}$$

two spin states for each $\vec{k}$

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

~~(illegible scribbled-out equation)~~

For any quantity $F(\vec{k})$ we have as $\Delta k \to 0$

$$\sum_{\vec{k}} F(\vec{k}) (\Delta k)^3 \simeq \int d^3k \; F(\vec{k})$$

So $\quad \sum_{\vec{k}} F(\vec{k}) = \frac{1}{(\Delta k)^3} \int d^3k \; F(\vec{k}) = \left(\frac{L}{2\pi}\right)^3 \int d^3k \; F(\vec{k})$

$$= \frac{V}{8\pi^3} \int d^3k \; F(\vec{k})$$

So total energy

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

$$= \frac{V \hbar^2}{8\pi^3 m} \; 4\pi \int_0^{k_F} dk \; k^2 \; k^2 \qquad$$

convert d^3k to
spherical coords
and integrate over
angles

$$\boxed{E = \frac{V \hbar^2}{2\pi^2 m} \frac{k_F^5}{5}}$$

Energy per particle

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

$$= \left(\frac{3\pi^2}{k_F^3}\right)\left(\frac{\hbar^2 k_F^2}{2m}\right) \frac{k_F^3}{5\pi^2} = \frac{3}{5}\varepsilon_F$$

$$\boxed{\frac{E}{N} = \frac{3}{5}\varepsilon_F \; , \quad \frac{E}{V} = \frac{3}{5} m \varepsilon_F}$$

energy per particle
energy per volume

Density of states $g(\varepsilon)$

Often we want to sum a quantity that depends on $\vec{k}$ only through the energy ε_k, ie

$$\sum_s \sum_{\vec{k}} F(\varepsilon_k) = 2\sum_{\vec{k}} F(\varepsilon_k) = \frac{V}{4\pi^3} \int d^3k \, F(\varepsilon_k)$$

$\uparrow$ sum over spin states

Define $g(\varepsilon)$ as the number of states per unit energy per unit volume, ie

$$\frac{1}{V}\sum_s \sum_{\vec{k}} = \frac{1}{4\pi^3} \int d^3k = g(\varepsilon)d\varepsilon$$

$\vec{k}$ such that
$\varepsilon \leq \varepsilon_k \leq \varepsilon + d\varepsilon$

Then $\qquad \frac{1}{V}\sum_s \sum_{\vec{k}} F(\varepsilon_k) = \int d\varepsilon \, g(\varepsilon) F(\varepsilon)$

When ε_k depends on $\vec{k}$ only through $|\vec{k}|$, we can write

$$\frac{1}{4\pi^3}\int d^3k = \frac{4\pi}{4\pi^3}\int dk \, k^2 = \frac{1}{\pi^2}\int dk \, k^2 = \int g(\varepsilon)d\varepsilon$$

$$\frac{1}{\pi^2} k^2 dk = g(\varepsilon)d\varepsilon$$

$$\boxed{g(\varepsilon) = \frac{1}{\pi^2} k^2 \frac{dk}{d\varepsilon}}$$