

Sommerfeld model

Classical Drude model assumed classical statistics for the electron gas:

Maxwell Boltzmann distribution

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

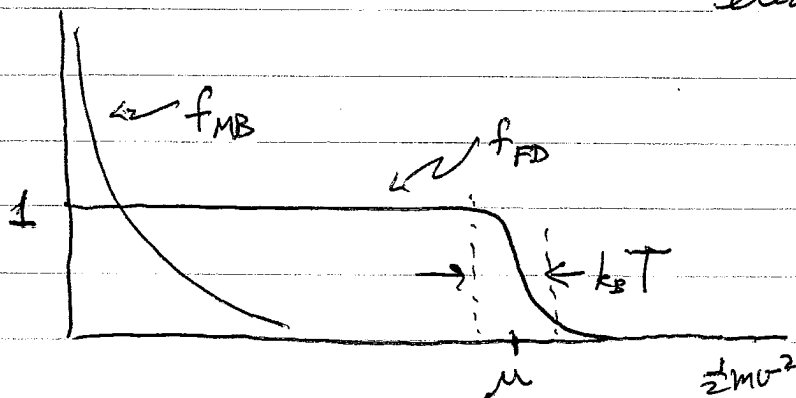
density of electrons per unit volume with velocity \vec{v}

Once quantum mechanics was developed, Sommerfeld realized that the electrons, which obey the Pauli exclusion principle, will 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 Schrodinger's Equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = \epsilon \psi$$

which has solutions

$$\psi_{\mathbf{k}}(\vec{r}) = \underset{\substack{\uparrow \\ \text{normalization constant}}}{A} e^{i\vec{k}\cdot\vec{r}} \quad \text{with energy } \epsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}$$

This wavefunction is also an eigenstate of momentum

$$-i\hbar \vec{\nabla} \psi_{\mathbf{k}} = \vec{p} \psi_{\mathbf{k}} \quad \Rightarrow \quad \vec{p} = \hbar \vec{k}$$

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 $\psi_{\vec{k}}(\vec{r})$ cannot satisfy this boundary condition.
~~except for the trivial case~~

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

$$\psi_{\vec{k}} = (A \sin k_x x)(\sin k_y y)(\sin k_z z)$$

where k_{μ} must satisfy

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

But this $\psi_{\vec{k}}$ is not an eigenstate of momentum. It describes a "standing wave" whose expectation value of momentum is always

$$\langle \psi_{\vec{k}} | \vec{p} | \psi_{\vec{k}} \rangle = 0$$

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 ψ to equal itself on opposite walls of the box, i.e.

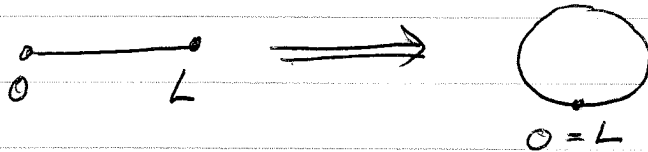
$$\psi(x+L, y, z) = \psi(x, y, z)$$

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

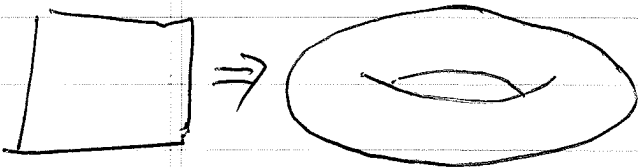
$$\psi(x, y, z+L) = \psi(x, y, z)$$

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

The periodic boundary conditions restrict the solutions

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

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

$$e^{ik_x L} = e^{ik_y L} = e^{ik_z L} = 1$$

since, for example,

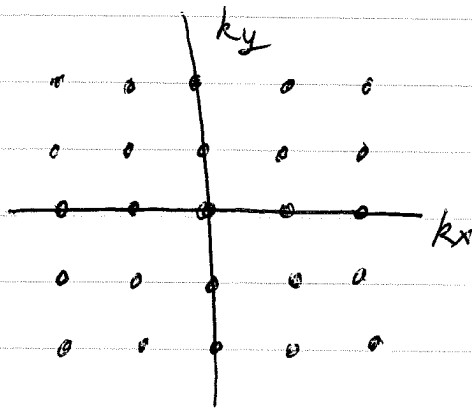
$$\begin{aligned}\psi(x+L, y, z) &= A e^{i(k_x+L)x + k_y y + k_z z} \\ &= A e^{ik_x L} e^{i(k_x x + k_y y + k_z z)} \\ &= e^{ik_x L} \psi(x, y, z)\end{aligned}$$

The allowed values of \vec{k} therefore satisfy

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

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

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 $\frac{\Omega}{(\Delta k)^3} = \frac{\sqrt{\Omega}}{8\pi^3}$ states

for large Ω .

To describe a state of N -noninteracting electrons, we need to give the value of \vec{k} and 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 \vec{k} and s .

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

Since $E_{\vec{k}}$ 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"

$$\left\{ \begin{array}{l} \mathcal{E}_F = \frac{\hbar^2 k_F^2}{2m} \text{ is the "Fermi energy"} \\ p_F = \hbar k_F \text{ is the "Fermi momentum"} \\ v_F = \hbar k_F / m \text{ is the "Fermi velocity"} \end{array} \right.$$

\mathcal{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 $\Omega = \frac{4}{3}\pi k_F^3$ (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 $\frac{2 \times \Omega V}{8\pi^3} = \frac{\Omega V}{4\pi^3}$ 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

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

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

How big is k_F ?

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

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

de Broglie wavelength

$$\lambda_F = 2\pi/k_F \sim \text{ \AA}$$

$$\begin{aligned} a_0 &= \text{Bohr radius} \\ &= 0.529 \times 10^{-8} \text{ cm} \\ &= 0.529 \text{ \AA} \end{aligned}$$

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

↑
speed of light

Compare this to thermal velocity at room

~~temp~~ Temperature of a classical gas

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

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

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

$$\begin{aligned} a_0 &= \frac{\hbar^2}{m e^2} \\ &= 0.529 \times 10^{-8} \text{ cm} \end{aligned}$$

$$E_F = (13.6) (k_F a_0)^2 \text{ eV} \approx (13.6) \left(\frac{1.92}{r_s/a_0} \right)^2$$

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

E_F is the magnitude of typical atomic binding energies

"Fermi temperature"

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

\gg room temperature

Total ground state energy

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

two spin states for each \vec{k}

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

$$\lim_{L \rightarrow \infty} \frac{1}{V} \sum_{\vec{k}} F(\vec{k}) = \int \frac{d^3k}{(2\pi)^3} F(\vec{k})$$

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

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

$$\begin{aligned} \text{So } \sum_{\vec{k}} F(\vec{k}) &= \frac{1}{(\Delta k)^3} \int d^3k F(\vec{k}) = \left(\frac{L}{2\pi}\right)^3 \int d^3k F(\vec{k}) \\ &= \frac{V}{8\pi^3} \int d^3k F(\vec{k}) \end{aligned}$$

So total energy

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

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

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

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

Energy per particle

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

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

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

energy per particle
energy per volume

Density of states $g(\epsilon)$

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

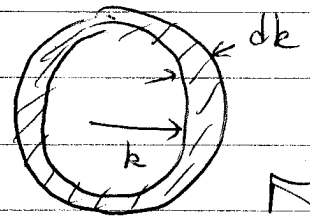
$$\sum_s \sum_{\vec{k}} F(\epsilon_k) = 2 \sum_{\vec{k}} F(\epsilon_k) = \frac{V}{4\pi^3} \int d^3k F(\epsilon_k)$$

\uparrow sum over spin states

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

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

\vec{k} such that
 $\epsilon \leq \epsilon_k \leq \epsilon + d\epsilon$



$$\text{Then } \frac{1}{V} \sum_s \sum_{\vec{k}} F(\epsilon_k) = \int d\epsilon g(\epsilon) F(\epsilon)$$

When ϵ_k depends on \vec{k} only through $|\vec{k}|$, ~~we~~ can write in \vec{k} -space a spherical shell of width dk and we can write

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

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

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

For free electrons $\epsilon = \frac{\hbar^2 k^2}{2m}$

$$g(\epsilon) = \frac{1}{\pi^2} \frac{2m\epsilon}{\hbar^2} \frac{1}{(d\epsilon/dk)}$$

$$= \frac{2m\epsilon}{\pi^2 \hbar^2} \frac{1}{\frac{2\hbar^2 k}{2m}} = \frac{2m\epsilon}{\pi^2 \hbar^2} \frac{k}{2\epsilon}$$

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

$$g(\epsilon) = \frac{m}{\pi^2 \hbar^3} \sqrt{2m\epsilon} \propto \sqrt{\epsilon}$$

Total energy

$$E = \int_0^{\epsilon_F} \epsilon g(\epsilon) d\epsilon$$

write $g(\epsilon) = C\sqrt{\epsilon}$ where C is appropriate const

Density of electrons

$$n = \frac{1}{V} \sum_{\mathbf{s}} \sum_{|\mathbf{k}| < k_F} 1 \quad \text{count states}$$

$$= \int_0^{\epsilon_F} d\epsilon g(\epsilon) = C \int_0^{\epsilon_F} d\epsilon \epsilon^{1/2} = \frac{2}{3} C \epsilon_F^{3/2}$$

$$\text{so } C = \frac{3}{2} \frac{n}{\epsilon_F^{3/2}}$$

$$g(\epsilon) = \frac{3}{2} \frac{n}{\epsilon_F} \sqrt{\frac{\epsilon}{\epsilon_F}}$$

Total energy

$$\frac{E}{V} = \int_0^{E_F} dE g(E) E = C \int_0^{E_F} dE E^{3/2} = \frac{2}{5} C E_F^{5/2}$$
$$= \frac{2}{5} \cdot \frac{3}{2} \frac{m}{E_F^{3/2}} E_F^{5/2}$$

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

We will see that $g(E)$, and in particular $g(E_F)$ is a very important quantity w/ determining the behavior of conduction electrons in a metal

Pressure of conduction electrons in a metal

From thermodynamics

$$dE = TdS - pdV$$

at $T=0$

$$dE = -pdV$$

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

$$\text{Now } E = \frac{3}{5} V m E_F = \frac{3}{5} N E_F$$

$$E_F = \frac{\hbar^2 k_F^2}{2m} \quad \text{where } k_F = \left(3\pi^2 \frac{N}{V} \right)^{1/3}$$

$$\text{so } E_F \propto V^{-2/3} \quad \text{for constant } N$$

$$E = \text{const } V^{-2/3}$$

$$\text{const} = \frac{3}{5} N \frac{\hbar^2}{2m} (3\pi^2 N)^{2/3}$$

$$-\frac{dE}{dV} = \frac{2}{3} \text{const } V^{-5/3} = \frac{2}{3} \text{const } \frac{V^{-2/3}}{V}$$

$$\boxed{p = \frac{2}{3} \frac{E}{V}} = \frac{2}{3} \frac{3}{5} m E_F = \frac{2}{5} m E_F$$

Bulk modulus Compare to a classical ideal gas where

$$p = m k_B T \quad \text{classical}$$

we now have:

$$p = \frac{2}{5} m k_B T_F \quad \text{quantum where } E_F = k_B T_F$$

since $T_F \gg T$ for a metal

$$p_{\text{quantum}} \gg p_{\text{classical}}$$

Bulk modulus $B \equiv 1/\kappa$, $\kappa = \text{compressibility}$

$$B = -V \left(\frac{\partial p}{\partial V} \right)_N \quad \leftarrow \text{derivative is at constant } N$$

$$p = \frac{2}{3} \frac{E}{V} \quad \text{and} \quad E = \text{const } V^{-2/3}$$

$$\Rightarrow p = \text{const } V^{-5/3}$$

$$B = -V \left(\frac{\partial p}{\partial V} \right)_N = +V \frac{5}{3} \text{const } V^{-7/3} = \frac{5}{3} \text{const } V^{-5/3}$$

$$= \frac{5}{3} p = \frac{5}{3} \cdot \frac{2}{3} \frac{E}{V} = \frac{10}{9} \frac{E}{V} = \frac{10}{9} \frac{3}{5} m E_F = \frac{2}{3} m E_F$$

$$\boxed{B = \frac{2}{3} n E_F} \quad \text{at } T=0$$

$$= \left[\frac{6.15}{(r_s/a_0)} \right]^5 \times 10^{10} \text{ dynes/cm}^2$$

<u>metal</u>	<u>B-theory</u>	<u>B-expt</u>	($\times 10^{10}$ dynes/cm ²)
Li	23.9	11.5	
Na	9.25	6.42	
Cu	63.8	134.3	
Ag	34.5	99.9	

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.