P423 – Lecture 14 Solids: Fermi gas and periodic potentials (Bloch's theorem)

The free electron gas (Fermi gas)

Consider N non-interacting Fermions in a 3d box:

$$V(\vec{r}) = \begin{cases} 0 & \text{if } 0<x<l_x,\ 0<y<l_y,\ 0<z<l_z \\ \infty & \text{otherwise} \end{cases}$$

The Schrödinger eqn

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

is separable: $\psi = X(x)\,Y(y)\,Z(z)$ with

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}X = E_x X\ ;\quad -\frac{\hbar^2}{2m}\frac{d^2}{dy^2}Y = E_y Y\ ,\quad -\frac{\hbar^2}{2m}\frac{d^2}{dz^2}Z = E_z Z,$$

with $E = E_x + E_y + E_z$.

Let $k_x = \frac{\sqrt{2mE_x}}{\hbar}$, $k_y = \frac{\sqrt{2mE_y}}{\hbar}$, $k_z = \frac{\sqrt{2mE_z}}{\hbar}$ and the general sols are:

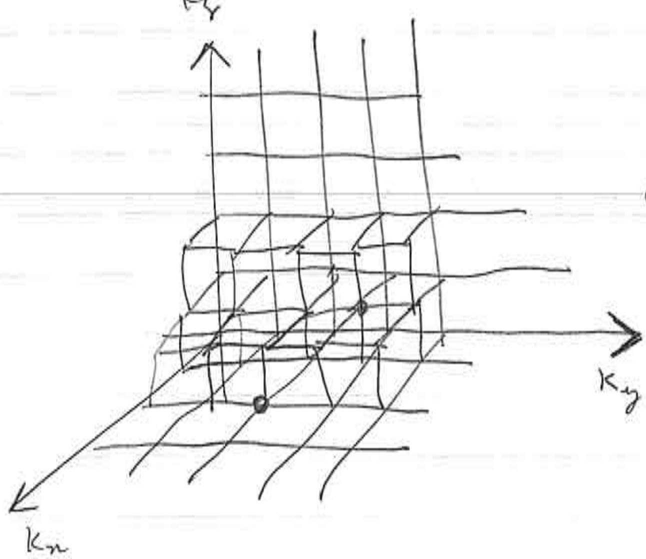
$$X(x) = A_x \sin(k_x x) + B_x \cos(k_x x)\ ,\quad Y(y) = A_y \sin(k_y y) + B_y \cos(k_y y)\ ,\ \dots$$

Because $X(x=0) = 0$ and $X(x=l_x) = 0$ (same for Y, Z) we get:

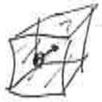
$$\psi_{n_x,n_y,n_z}(\vec{r}) = \sqrt{\frac{8}{l_x l_y l_z}}\ \sin\Big(\underbrace{\frac{n_x\pi}{l_x}}_{k_x} x\Big)\sin\Big(\underbrace{\frac{n_y\pi}{l_y}}_{k_y} y\Big)\sin\Big(\underbrace{\frac{n_z\pi}{l_z}}_{k_z} z\Big)$$

$$E_{n_x,n_y,n_z} = \frac{\hbar^2}{2m}\left[\left(\frac{n_x\pi}{l_x}\right)^2 + \left(\frac{n_y\pi}{l_y}\right)^2 + \left(\frac{n_z\pi}{l_z}\right)^2\right] = \frac{\hbar^2}{2m}\left(\vec{k}\right)^2$$

It's convenient to label each state (n_x, n_y, n_z) by its $\vec{k}$ vector. In $\vec{k}$ space consider planes drawn at $k_x = \frac{\pi}{l_x}, \frac{2\pi}{l_x}, \frac{3\pi}{l_x}, \ldots$ and same for k_y, k_z:



Each intersection point represents a state of the particle in the box.

Each intersection point can be associated to a cube of volume $\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V}$ (associate the cube along $(1,1,1)$  . Note that this is a 1:1 correspondence.

Suppose we apply this model to a material with N atoms, each atom having q valence electrons. There will be a total of Nq electrons in this "electron gas". No electron can go in the same state, so we can only put 2 electrons in each $\vec{k}$ ($\uparrow$ or $\downarrow$). Nq is a very large number $\Rightarrow$ Fill up one octant of the "$\vec{k}$ sphere" up to $|\vec{k}| = k_F$, the Fermi vector. To determine k_F use:

$$Nq = \underbrace{2}_{\uparrow \text{ or } \downarrow} \times \frac{\underbrace{\frac{1}{8}}_{\text{one octant}}\overbrace{\left(\frac{4}{3}\pi k_F^3\right)}^{\text{volume of sphere}}}{\frac{\pi^3}{V}} \Rightarrow \boxed{\underbrace{\frac{Nq}{V}}_{\text{electron density}} = \rho} = \frac{1}{3\pi^2} k_F^3 \Rightarrow \boxed{k_F = \left(3\pi^2 \rho\right)^{\frac{1}{3}}}.$$

The energy of the top-most electron is called Fermi energy:

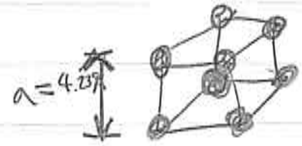
$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}\left(3\pi^2 \rho\right)^{2/3} .$$

And the associated temperature scale is called Fermi temperature: $k_B T_F = E_F$ or

$$T_F = \frac{E_F}{k_B} .$$

Metals have a lot of electrons in them. Consider for example Na. At room temperature

it forms a bcc lattice (body centered cell) with side $a = 4.23\,\text{Å}$:



$$Na = [Ne]\,3s^1 \quad \Rightarrow q = 1 \text{, so}$$

$$\rho = \frac{\frac{1}{8}\times 8 + 1}{a^3} \times 1 = \frac{2}{a^3} = \frac{2}{(4.23)^3}\,\frac{1}{(10^{-8}\,cm)^3} = 2.64 \times 10^{22}\ cm^{-3}$$

$\Rightarrow$ 2.64×10^{22} electrons per $1\,cm^3$ sample.

$$\Rightarrow \begin{cases} k_F = 9.2 \times 10^7\, cm^{-1} \\ E_F = 3.24\, eV \\ T_F = 3.77 \times 10^4\, K \end{cases}$$

T_F is quite high! Means that even at $T \simeq 300\,K$ we can treat a metal as if it was

at $T = 0$.

All this happens because of Pauli exclusion.

Calculate total energy: Electrons in a shell with wavevector k have energy $\frac{\hbar^2}{2m}k^2$.

There are $\dfrac{2 \times \frac{1}{8}(4\pi k^2)\, dk}{\pi^3/V}$ electrons in each shell, thus

$$dE = \frac{\hbar^2 k^2}{2m} \frac{2 \times \frac{1}{8} 4\pi k^2 dk}{\frac{\pi^3}{V}} = \frac{\hbar^2 k^2}{2m} \frac{V}{\pi^2} k^2 dk = \frac{\hbar^2}{2m\pi^2} V k^4 dk$$

$$E_{Total} = \int_0^{E_F} dE = \frac{\hbar^2}{2m\pi^2} V \int_0^{k_F} dk\, k^4 = \frac{\hbar^2}{2m\pi^2} V \frac{k_F^5}{5} = \frac{\hbar^2}{10m\pi^2} V \left[3\pi^2 \rho\right]^{5/3}$$

$$E_{Total} = \frac{\hbar^2}{10m\pi^2} 3^{5/3} \pi^{10/3} \frac{V N^{5/3} q^{5/3}}{V^{5/3}} = \frac{\hbar^2 (3\pi^2 N q)^{5/3}}{10\pi^2 m} V^{-2/3} = \frac{3}{5} N E_F .$$

This shows that the Fermi gas exerts pressure on the walls of the box: If we expand the volume, energy decreases, i.e. the gas does work on the walls of the box.

$$P = -\left(\frac{\partial E_{Total}}{\partial V}\right)_{T=0} = -\left[-\frac{2}{3} \frac{E_{Total}}{V}\right] = \frac{2}{3} \frac{\hbar^2}{10m\pi^2} \left[3\pi^2 \rho\right]^{5/3} \propto \rho^{5/3} .$$

Note how this pressure has nothing to do with collisions of the particles with the wall, or ~~between themselves~~.

It has to do with Pauli Exclusion! It's called Fermi pressure or "degeneracy pressure".

Band structure

To describe solids more realistically, let's introduce the potential produced by atoms in a lattice. The main feature of this lattice potential is that it is periodic:

$$V(x+a) = V(x)$$

where a is the period of the lattice.

Bloch's theorem:

The solutions of the Schrödinger eqn

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi + V(x)\psi = \epsilon\,\psi$$

for a periodic potential $\left(V(x+a) = V(x)\right)$ can be taken to satisfy the condition:

$$\psi(x+a) = e^{iKa}\,\psi(x)$$

where K is a real constant (independent of x but dependent on ϵ and the state's quantum numbers).

K is called "Bloch wavevector" and as we shall see in a moment it is a "good quantum number" to describe states in a periodic potential.

Proof:

Define the displacement operator:

$$\hat{D}(a)\,f(x) = f(x+a).$$

(b)

Because $\hat{H}$ is invariant under displacements by a (or na with n an integer)

we get
$$\hat{D}^\dagger \hat{H} \hat{D} = \hat{H} \quad \text{or} \quad [\hat{H}, \hat{D}] = 0 .$$

We say that H has "discrete translation symmetry".

Hence, we can diagonalize H simultaneously with $\hat{D}$: $\begin{cases} H|\psi\rangle = E|\psi\rangle \\ \hat{D}(a)|\psi\rangle = \lambda|\psi\rangle \end{cases}$

But we know that $\hat{D}(a) = e^{\frac{i}{\hbar}\hat{p}_x a}$ (use Taylor expansion!), so that $\hat{D}(a)\hat{D}^\dagger(a) = 1$

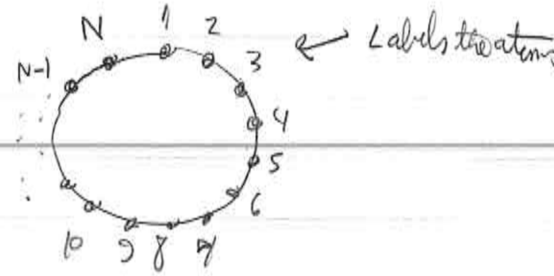
(Note that $\hat{D}^\dagger(a) = \hat{D}(-a)$ so that $\hat{D}(-a)\psi(x) = \psi(x-a)$, so $\hat{D}(a)\hat{D}(-a) = 1$).

Now: $\left.\begin{matrix} \hat{D}(a)|\psi\rangle = \lambda|\psi\rangle \\ \langle\psi|\hat{D}^\dagger(a) = \langle\psi|\lambda^* \end{matrix}\right\} \Rightarrow \langle\psi|\hat{D}^\dagger(a)\hat{D}(a)|\psi\rangle = |\lambda|^2\langle\psi|\psi\rangle = |\lambda|^2 \Rightarrow |\lambda|^2 = 1 \Rightarrow \boxed{\lambda = e^{iKa}}$

for some real K.

Which K's are allowed? Assume periodic boundary conditions so that

$$\psi(x + Na) = \psi(x)$$



But $\psi(x+Na) = [\hat{D}(a)]^N \psi(x) = e^{iNKa}\psi(x)$

$$\Rightarrow e^{iNKa} = 1 \Rightarrow Ka = 0, \frac{2\pi}{N}, \frac{2\pi}{N}\times 2, \frac{2\pi}{N}\times 3, \ldots$$

$$\Rightarrow K = \frac{2\pi}{Na} m \quad (m = \ldots, -2, -1, 0, 1, 2, 3, \ldots)$$