Lecture 6

Review of free electron gas

We assume that our solid is a rectangular box with dimensions l_x, l_y, and l_z ,and that the electrons inside only experience the potential associated with impenetrable walls, i.e.

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

The normalized wave functions are

$$\psi_{n_x, n_y, n_z} = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi}{l_x} x\right) \sin\left(\frac{n_y \pi}{l_y} y\right) \sin\left(\frac{n_z \pi}{l_z}\right),$$

and the allowed energies are

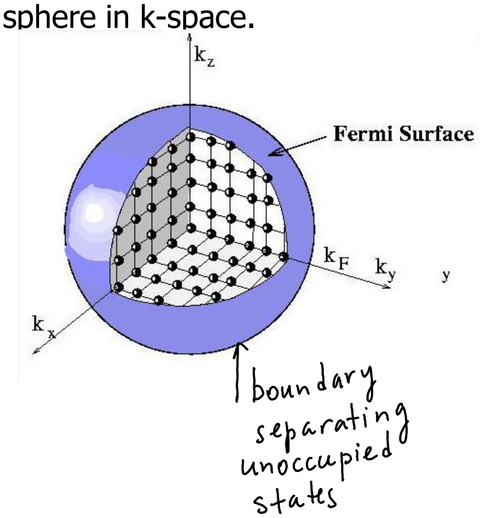
$$E = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2}{2m} k^2$$

wave vector $\vec{k} = (k_x, k_y, k_z)$

$$E = \frac{\hbar^2 \pi^2}{2m}\left\{ \frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right\}$$

Suppose our solid contains N atoms with each atom contributing q free electrons and our solid is in its collective ground state (no thermal excitations). We can say that electrons will fill up one octant (i.e. 1/8 part, see picture) of a sphere in k-space.

$$\rho = \frac{Nq}{V}$$



The radius of this sphere is

$$k_F = (3\pi^2 \rho)^{1/3}.$$

Free electron density

The energy of the highest state (Fermi energy) is

$$E_F = \frac{\hbar^2}{2m} k_F^2$$

The total energy of the free electron gas is

$$E_{tot} = \frac{\hbar^2 k_F^5 V}{10 \pi^2 m}$$

Continuing with our Exercise 1 from Lecture 5:

(c) At what temperature would the characteristic thermal energy (k_BT, where k_B is Boltzman constant and T is Kelvin temperature) equal the Fermi energy for copper?

$$k_B = 1.38 \times 10^{-23}\ J/K$$

$$\boxed{E_F = k_B T_F \Rightarrow T_F = \frac{E_F}{k_B} = \frac{11.2 \times 10^{-19}\ J}{1.38 \times 10^{-23}\ J/K} \simeq 8.1 \times 10^4\ K}$$

Comment: This is called Fermi temperature. As long as the actual temperature is substantially below the Fermi temperature, the material can be regarded as cold. Since the melting point of copper is 1356 K, solid copper is always cold.

Degeneracy pressure

$$E_{tot} = \frac{\hbar^2 k_F^5 V}{10\pi^2 m} = \frac{\hbar^2 (3\pi^2 Nq)^{5/3}}{10\pi^2 m} V^{-2/3}$$

This quantum mechanics energy is similar to the internal thermal energy U on the ordinary gas. It exerts a pressure on the walls since if the box expands by dV, the total energy will decrease:

$$dE = \frac{dE}{dV} dV = -\frac{2}{3} E_{tot} \frac{dV}{V}$$

This shows up as work $dW = PdV$ done on the outside by the quantum pressure P.

$$P = \frac{2}{3}\frac{E_{tot}}{V} = \frac{(3\pi^2)^{2/3}\hbar^2}{5m} \rho^{5/3}$$

This pressure is sometimes called degeneracy pressure.

(d) Calculate degeneracy pressure of copper, in the electron gas model.

$$\hbar = 1.055 \times 10^{-34}\ J\cdot s$$
$$m_e = 9.20 \times 10^{-31}\ kg$$
$$1eV = 1.602 \times 10^{-19}\ J$$

We already calculated free electron density to be

$$\rho = 8.49 \times 10^{28} / m^3.$$

$$p = \frac{(3\pi^2)^{2/3}\hbar^2}{5m_e}\rho^{5/3} = \frac{(3\cdot 3.14^2)^{2/3}}{5\cdot 9.20\times10^{-31}\,kg}\left(1.055\times10^{-34}\,J\cdot s\right)^2$$

$$\times\left(8.49\times10^{28}\,\frac{1}{m^3}\right)^{5/3} = 3.8\times10^{10}\,\frac{J^2\cdot s^2}{kg}\,\frac{1}{m^5} = 3.8\times10^{10}\,N/m^2$$

Checking units

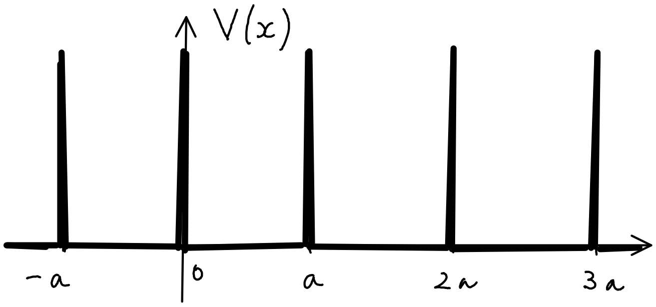
$[J]\equiv[N\cdot m]$

$$\left[\frac{J\cdot N\cdot \cancel{m}\cdot s^2}{kg\cdot m^{\cancel{5}4}}\right] = \left[\frac{\cancel{kg}\cdot \cancel{m^2}\cdot N\cdot \cancel{s^2}}{\cancel{s^2}\cdot \cancel{kg}\cdot m^{\cancel{4}2}}\right] = \left[\frac{N}{m^2}\right] \text{ ok.}$$

Hint: units are supposed to be N/m^2.

Band structure

Model # 2: we include the forces exerted on the electron by the regularly spaced, positively charged, essentially stationary nuclei. Important part of this model is that potential is periodic. The qualitative behavior of solids is largely determined by the periodicity of the potential.
We consider one-dimensional Dirac comb. Such potential consist of evenly spaced delta-function spikes (for simplicity we let delta-functions go up).



Periodic potential:

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

Bloch's theorem:

For a periodic potential $V(x+a) = V(x)$ the solutions of the Schrödinger equation

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

can be taken to satisfy the condition

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

for some constant K (that means that K does not depend on x, it well may depend on something else, like energy).

Proof:

We take D to be a displacement operator

$$Df(x) = f(x+a)$$

If the potential is periodic $[D, H] = 0 \Rightarrow$

we can chose simultaneous eigenfunctions of H and D: $D\psi = \lambda\psi = \psi(x+a)$

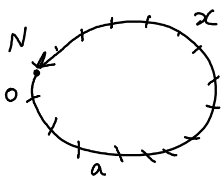
$\lambda \neq 0$ (since that would mean $\psi = 0$).

Any non-zero complex number can be expressed as exponential:

$$\lambda = e^{iKa}$$

for some constant K.

All solids have boundaries, i.e. they don't just continue forever, so the periodicity will end somewhere that will render Bloch's theorem inapplicable. There is a nice way around it: number of atoms is so large so edge effects can not affect electrons that are deeply inside the solid too much. So we just wrap our x-axis in a circle and connect it to its tail after a really large number of periods (assume on the order of Avogadro's number). That gives us the boundary condition:



N is very large.

$$\boxed{\psi(x+Na) = \psi(x)}$$

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

$$\psi(x+Na) = e^{iKNa}\psi(x) = \psi(x) \Rightarrow$$

$$e^{iKNa} = 1 \Rightarrow NKa = 2\pi \quad \text{and}$$

$$K = \frac{2\pi n}{Na} \quad (n = 0, \pm 1, \pm 2, \dots), \text{ i.e.}$$

K in this case is real.

We can now go back to the consideration of our Dirac comb potential:

$$V(x) = \alpha \sum_{j=0}^{N-1} \delta(x - ja) \quad \leftarrow N^{th} \text{ spike is at } x = -a$$

The beautiful part about the Bloch's theorem is that we only need to solve Schrödinger equation in one "cell" of the potential $0 < x < a$.

The potential is zero at this interval. $\Rightarrow$

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

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad k \equiv \frac{\sqrt{2mE}}{\hbar}$$

The general solution, as we reviewed during the last lecture is

$$\psi(x) = A\sin(\kappa x) + B\cos(\kappa x), \quad 0 < x < a$$

The Bloch's theorem states that in the next cell to the left the solution must be:

$$\psi(x) = e^{-iKa}\left[A\sin\kappa(x+a) + B\cos\kappa(x+a)\right] \quad -a < x < 0$$

At $x=0$ ψ must be continuous $\Rightarrow$

$$e^{-iKa}\left[A\sin(\kappa a) + B\cos(\kappa a)\right] = A\overset{0}{\cancel{\sin 0}} + B\overset{1}{\cancel{\cos 0}}$$

$$\boxed{B = e^{-iKa}\left[A\sin(\kappa a) + B\cos(\kappa a)\right]} \leftarrow \text{Eq. (1)}$$

From PHYS 424 lecture on delta-function potential, we get (see Eq. 2.125 in the book)

$$\Delta\left(\frac{d\psi}{dx}\right) = +\frac{2m\alpha}{\hbar^2}\psi(0)$$

sign is "+" since we have δ-function spike up rather than down.

$$\Delta\left(\frac{d\psi}{dx}\right) \equiv \left.\frac{\partial\psi}{\partial x}\right|_{+\varepsilon} - \left.\frac{\partial\psi}{\partial x}\right|_{-\varepsilon} \quad \text{(at the boundary)}$$

$$\left[\frac{d\psi}{dx}\right]_+ = \frac{d}{dx}\left(A\sin\kappa x + B\cos\kappa x\right)\Big|_{x=0}$$

$$= \left(\kappa A\cos\kappa x - \kappa B\sin\kappa x\right)\Big|_{x=0} = \kappa A$$

$$\left[\frac{d\psi}{dx}\right]_- = \frac{d}{dx}\left\{e^{-iKa}\left(A\sin\kappa(x+a) + B\cos\kappa(x+a)\right)\right\}\Big|_{x=0}$$

$$= e^{-iKa}\left(\kappa A\cos\kappa(x+a) - \kappa B\sin\kappa(x+a)\right)\Big|_{x=0}$$

$$= e^{-iKa}\kappa\left(A\cos\kappa a - B\sin\kappa a\right)$$

$$\text{Eq.}(2) \rightarrow \quad kA - e^{-iKa} k\left[A\cos(ka) - B\sin(ka)\right] = \frac{2m\alpha}{\hbar^2} B$$

$\psi(0) = B$

Combining Eq. (1) $B = e^{-iKa}\left(A\sin(ka) + B\cos(ka)\right)$ and Eq.(2) gives

$$\boxed{\cos(Ka) = \cos(ka) + \frac{m\alpha}{\hbar^2 k}\sin(ka)}$$

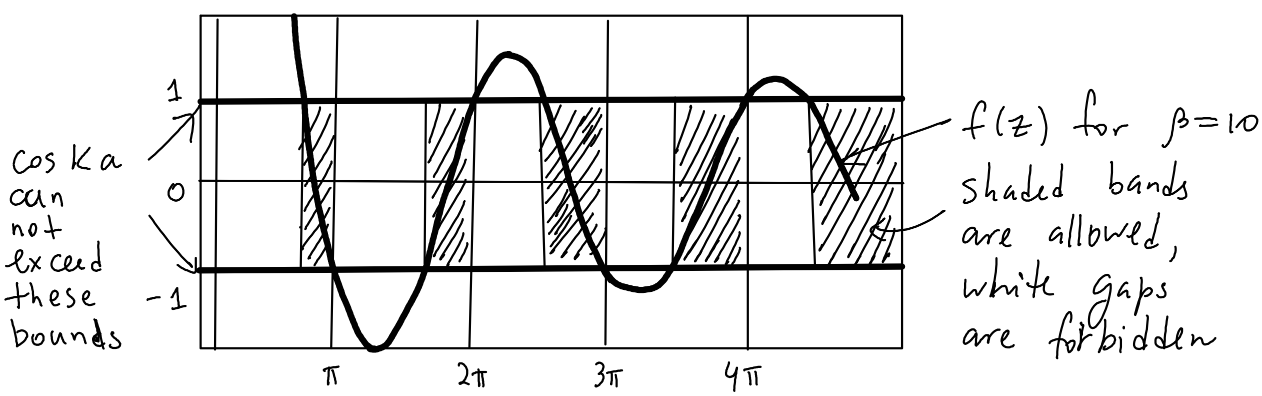
capital K

This equation determines possible values of k, and; therefore, allowed values of energy.

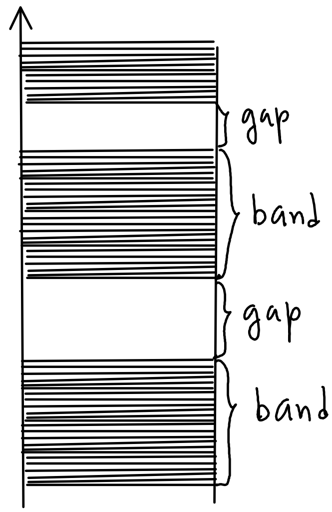
For simplicity, we use

$$\left.\begin{aligned} z &\equiv ka \\ \beta &= \frac{m\alpha a}{\hbar^2} \end{aligned}\right\} \quad \underbrace{\cos(ka) + \frac{m\alpha}{\hbar^2 k}\sin(ka)}_{\Downarrow} \equiv f(z)$$

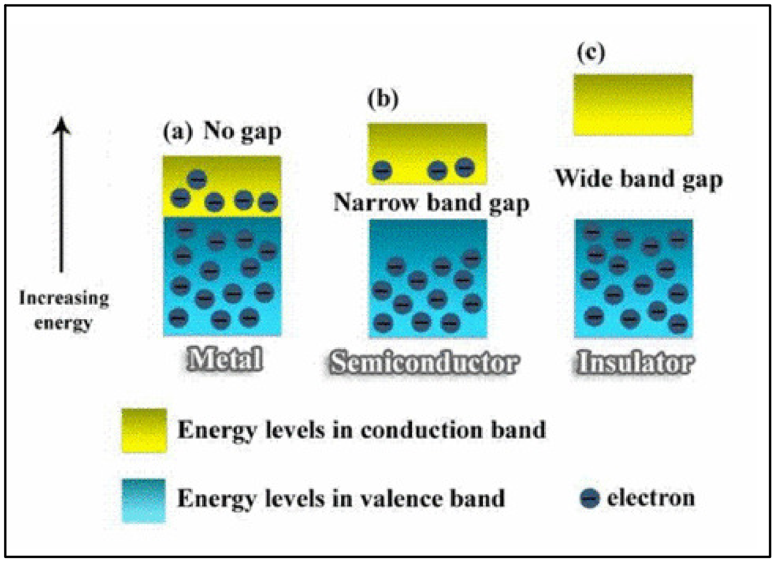
$$f(z) \equiv \cos(z) + \beta\,\frac{\sin(z)}{z}$$



Since $|\cos Ka|$ can not exceed one, not all energies are allowed. As a result, we get gaps of forbidden energies and bands of allowed energies.



The allowed energies for a periodic potential form essentially continuous bands.



Simulation: band structure

http://phet.colorado.edu/simulations/sims.php?sim=Band_Structure