From Gasiorowicz ← Free-electron gas and density of states
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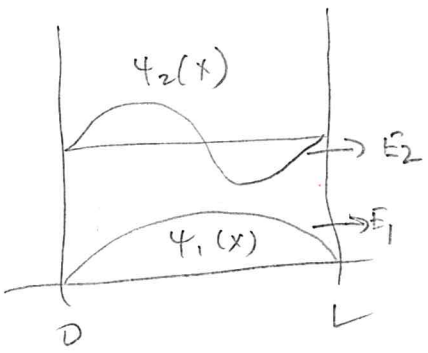
Recall the 1D infinite well soln

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2} \qquad \psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$



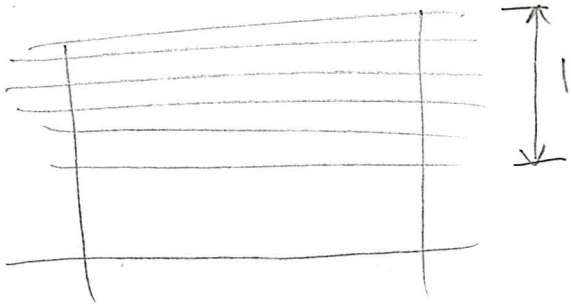
$E_n \propto n^2$

Ex 1 $L = 1\,mm$ (crystal size)

What value of n corresponds to a state of $E_n = 0.01\,eV$

$$n^2 = \frac{2mL^2 E_n}{\hbar^2 \pi^2} = 2.65 \times 10^8 \Rightarrow n \sim 1.6 \times 10^4$$

If we think that only 1 electron can occupy per state.



Define density of states $\frac{\Delta n}{\Delta E}$ or $\frac{dn}{dE}$

as number of states per unit energy:

Total number of states in, say, 0.0001 eV range around 0.01 eV

$$N = \left.\frac{dn}{dE}\right|_{0.01=n} \Delta n \qquad \Delta n = 0.0001$$

Since $E \propto n^2$ for 1D infinite well

$$\ln E = 2 \ln n$$

$$\Rightarrow \frac{1}{E} = \frac{2}{n}\frac{dn}{dE} \Rightarrow \frac{dn}{dE} = \frac{n}{2E} = \frac{n}{2E}; \quad \frac{1}{2\sqrt{E}}$$

$n = 1.6 \times 10^4$; $E = 0.01$

$\frac{dn}{dE} \sim 10^6$ states/eV.

In 0.0001 eV range, there are about 100 states available.

Lets move to 3D infinite pot + enforce Pauli exclusion principle

$$E_{n_x,n_y,n_z} = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2+n_y^2+n_z^2) = E_{nx} + E_{ny} + E_{nz}.$$

$$\psi(x,y,z) = \left(\frac{2}{L}\right)^{3/2} \sin\frac{n_1\pi x}{L} \sin\frac{n_2\pi y}{L} \sin\frac{n_3\pi z}{L}$$

$$= \psi_{n_1}(x)\,\psi_{n_2}(y)\,\psi_{n_3}(z) \qquad n_x \to 1,2,3\cdots \quad n_z \to 1,2,3$$
$$n_y \to 1,2,3\cdots$$

we shall assume electrons are non-interacting but only subject to Pauli exclusion.

set of mutually commuting observables

There is also a lot of degeneracy in 3D as H_x, H_y, H_z commute

Ground state energy $\to \frac{\hbar^2\pi^2}{2mL^2}(1^2+1^2+1^2) = \frac{3\hbar^2\pi^2}{2mL^2} \longrightarrow$ single state

First excited state $\to (1,1,2) \leftrightarrow (2,1,1) \leftrightarrow (1,2,1) \to E_n = \frac{\hbar^2\pi^2}{2mL^2}(6)$

$\hookrightarrow$ 3 states.

Q what is the lowest energy of a set of 24 electrons in units of $\frac{\hbar^2\pi^2}{2mL^2}$ subject to Pauli exclusion principle.

$(1,1,1) \to 3 \to$ 2 states $= 2$

$(2,1,1) \to 6 \to 3\times2 = 6$

$(2,2,1) \to 9 \to 3\times2 = 6$

$(3,1,1) \to 11 \to 3\times2 = 6$

$(2,2,2) \to 12 \to 1\times2 = 2$

$(3,2,1) \to 6\times2 = 12$

Total energy for 24 electrons

$3\times2^{2} + 6\times6^{8} + 6\times9^{14} + 6\times11^{20} + 2\times12^{22}$

$+ 2\times12 = 214$

So how many triplets (→ states) are there when we have N electrons such that $E = \frac{\hbar^2\pi^2}{2mL^2}(n_1^2+n_2^2+n_3^2) \leq E_F$

Say $n_1^2+n_2^2+n_3^2 = R^2 \Rightarrow E_F = \frac{\hbar^2\pi^2R^2}{2mL^2}$

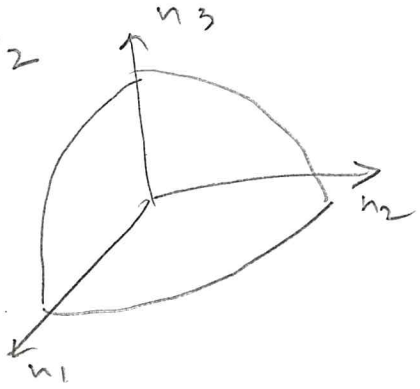
$$\Rightarrow R^2 = \frac{2mL^2}{\hbar^2\pi^2}E_F$$

No of lattice point for $n_1, n_2, n_3 \geq 0$

$$N = 2 \cdot \frac{1}{8}\cdot\frac{4\pi}{3}R^3 = \frac{1}{8}\cdot\frac{4}{3}\pi\left(\frac{2mL^2}{\hbar^2\pi^2}E_F\right)^{3/2}$$

2 ↓ spin deg

$\frac{1}{8}\cdot\frac{4\pi}{3}R^3$ ↓ volume of 1st quadrant



$$N = \frac{\pi}{3}L^3\left(\frac{2mE_F}{\hbar^2\pi^2}\right)^{3/2}$$

Say $n = \frac{N}{L^3}$ $n \rightarrow$ density $\quad E_F = \frac{\hbar^2\pi^2}{2m}\left(\frac{3n}{\pi}\right)^{2/3} = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3}$

E_F is the Fermi energy.

If n is the number of states with energy $\leq \epsilon$ then

$$\epsilon = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3} \quad \text{or} \quad n = \frac{1}{3\pi^2}\left(\frac{2m\epsilon}{\hbar^2}\right)^{3/2}$$

Therefore $\frac{dn}{d\epsilon} = \frac{3}{2}\cdot\frac{1}{3\pi^2}\left(\frac{2m\epsilon}{\hbar^2}\right)^{1/2} = \frac{1}{2\pi^2}\left(\frac{2m\epsilon}{\hbar^2}\right)^{1/2}$

Similarly define K_F, the Fermi wave vector such that

$$E_F = \frac{\hbar^2 K_F^2}{2m} \Rightarrow K_F = \left(3\pi^2 n\right)^{1/3}$$

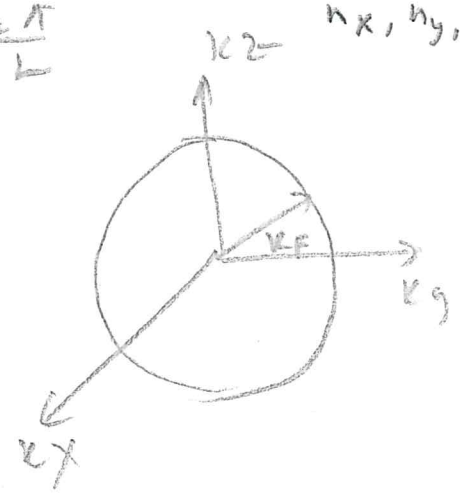
$$\frac{dN}{d\epsilon} = V\frac{dn}{d\epsilon} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\epsilon^{1/2} \rightarrow \text{Density of states}$$

Kittel approach

3D wave fn:- $\left(\frac{2}{L}\right)^{3/2} \sin(k_x x)\sin(k_y y)\sin(k_z z)$ cube of Length L

$k_x = \frac{n_x \pi}{L}$; $k_y = \frac{n_y \pi}{L}$; $k_z = \frac{n_z \pi}{L}$ $\quad n_x, n_y, n_z > 0$

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



~~1-3D~~ we require wavefns be periodic in x-y-z with period L

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

We can also write

$\psi_k(\vec{r}) = \frac{1}{\sqrt{V}} e^{ik\cdot r}$ as the soln of the 3D particle in a box.

$-\frac{\hbar^2}{2m}\nabla^2 \psi_k(\vec{r}) = \frac{\hbar^2 k^2}{2m}\psi_k(r)$

$\psi(x+L, y, z) \Rightarrow e^{ik_x L} = e^{i2n\pi} \Rightarrow k_x = \pm\frac{2\pi n}{L}$, $n = 0, 1, 2\cdots$

$\frac{1}{V}\int_V dx\,dy\,dz\, e^{-ik\cdot r} e^{+ik\cdot r} = 1$

For a system of N electrons, the occupied states may be represented as points inside a sphere in k-space.

$\epsilon_F = \frac{\hbar^2}{2m} k_F^2$; $\epsilon_k = \frac{\hbar^2}{2m} k^2$ $\quad |k| = 2\pi/\lambda$

There is only one allowed wave vector - that is, one distinct triplet of q.nos. k_x, k_y, k_z for the volume element $(2\pi/L)^3$ of k space. So the total # of states $= 2 \cdot \frac{\frac{1}{8}\cdot\frac{4}{3}\pi k_F^3}{(2\pi/L)^3} = \frac{V}{3\pi^2} k_F^3 = N \Rightarrow k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3}$

$$\epsilon_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

Momentum at Fermi level :- $\hbar k_F$

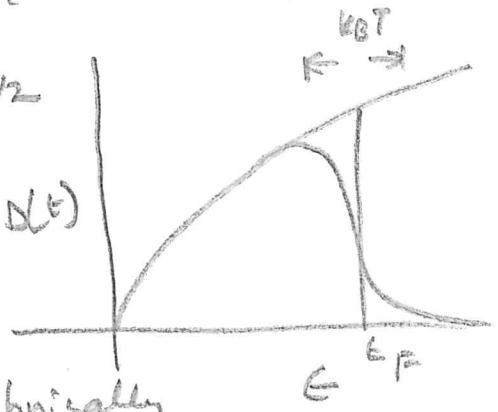
Velocity at " " $v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3}$

Temperature " " " $T_F = \frac{\epsilon_F}{k_B}$

Typical values:-

	N/V ($/cm^3$)	k_F (cm^{-1})	v_F cm/s	ϵ_F (eV)	T_F (K)
Na	2.5×10^{22}	1.1×10^8	1.1×10^8	3.1	3.7×10^4
Cu	8.5	1.35	1.56	7.0	8.2×10^4

$$D(\epsilon) = \frac{dN}{d\epsilon} = \frac{\pi V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\epsilon^{1/2}$$



Pauli exclusion principle

At absolute zero, all states are filled upto ϵ_F. At finite T, all electrons technically have k_BT energy classically. But quantum-mechanically only a fraction of electrons can do something about it. This is due to Pauli exclusion principle. This is because for most electrons a states within $\sim k_BT$ energy are already occupied. Only states that are $\sim k_BT$ away from Fermi energy are thermally excited.

This drastically modifies the thermal, magnetic, and electrical properties of metals and solid state systems.

Point (1) Only a fraction T/T_F of electrons are excited thermally. each electron has $\sim k_B T$ energy.

So Total electronic thermal energy $\sim \left(N \frac{T}{T_F}\right) k_B T = E_{el}$

$\Rightarrow$ Specific heat $\frac{\partial E_{el}}{\partial T} = N k_B \frac{T}{T_F}$

This value is much smaller than classical calculation of sp. heat $= \frac{\partial}{\partial T}\left(N \frac{3}{2} k_B T\right) = \frac{3N}{2} k_B$ by a factor $\frac{T}{T_F}$

Since $T_F \sim 5 \times 10^4$ deg $\quad T \sim 300$ K $\quad \frac{T}{T_F} \sim 10^{-2} = 0.01$ 1%.

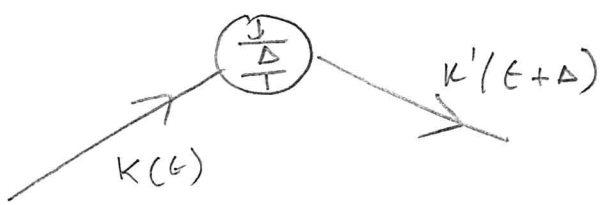
Detailed calculation will require Fermi - Dirac statistics

A simplified derivation (F. Bloch)

Consider an inelastic collision of a conduction electron with a "two-level" impurity atom with which the electron may interact. Impurity atom has 2 energy states "0" and "Δ" with probability $p(0)$, $p(\Delta)$.

The electron state is labeled by its wavevector k, ϵ

$$\psi_k(r) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \qquad \epsilon_n = \frac{\hbar^2 k^2}{2m}$$



We examine inelastic collisions which connect the electron state $\vec{k}$ at energy ϵ to k' with energy $\epsilon + \Delta$

The final state k' must be vacant if the scattering event is to take place (Pauli exclusion principle)

Let us assume there is a distribution $f(\epsilon)$ that the electron will follow.

$f(\epsilon)$ is the probability that the initial state k is occupied

Probability ~~that electron e~~ of the entire event.

electron at k, impurity atom in state Δ, and electrons in state $f(\epsilon+\Delta)$ → so that it can give up energy Δ to electron.

→ probability this state is unoccupied.

$$f(\epsilon)\, p(\Delta)\, [1 - f(\epsilon+\Delta)]$$

Probability of the reverse event :-

$k' \longrightarrow k$ $\quad f(\epsilon+\Delta)\, p(\Delta)\, [1 - f(\epsilon)]$

In thermal equilibrium $k \to k'$ process happens with same probability as $k' \to k$

$$\Rightarrow f(\epsilon)\, p(\Delta)[1 - f(\epsilon+\Delta)] = f(\epsilon+\Delta)\, p(\Delta)\, [1 - f(\epsilon)]$$

Boltzmann distribution applies for the impurity atom

$$\frac{p(\Delta)}{p(0)} = \exp(-\Delta/k_B T)$$

$$f(\epsilon)\, p(0) \exp(-\Delta/k_B T)\, [1 - f(\epsilon+\Delta)] = f(\epsilon+\Delta)\, p(0)\, [1 - f(\epsilon)]$$

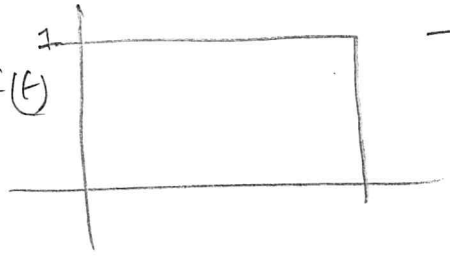
$$\Rightarrow \exp(-\Delta/k_B T) = \left[\frac{f(\epsilon+\Delta)}{1 - f(\epsilon+\Delta)}\right]\left[\frac{1 - f(\epsilon)}{f(\epsilon)}\right]$$

It can be shown that this equation can be solved for all T if $\frac{1-f(\epsilon)}{f(\epsilon)} = e^{(\epsilon-\mu)/k_B T}$

$$\Rightarrow \boxed{f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_B T}+1}} \rightarrow \text{Fermi Dirac dist.}$$

μ is called the chemical potential and has to be chosen such that # of particles in the system $= N$.

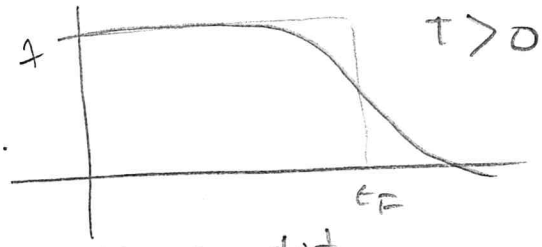
At $T=0$ $\mu = \epsilon_F$



At $T \Rightarrow 0$ $f(\epsilon) = 1/2$ at $\epsilon = \mu = \epsilon_F$

$f(\epsilon) = 1$ $\epsilon < \epsilon_F$

$f(\epsilon) = 0$ $\epsilon > \epsilon_F$.



At all T $f(\epsilon) = 1/2$ when $\epsilon = \mu$.

for $\epsilon - \mu \gg kT$ $f(\epsilon) \approx e^{(\mu-\epsilon)/k_B T}$ → Boltzmann dist.

If the energy levels are ϵ_i, then we must have

$\sum_i f(\epsilon_i) = N$ (probability of the state being occupied. How many states at ϵ.)

In integral form, $\int_0 d\epsilon\, f(\epsilon)\, D(\epsilon) = N$

If $f(\epsilon) = 1$ then $\int D(\epsilon)\, d\epsilon = N$ which is what we are used to previously.