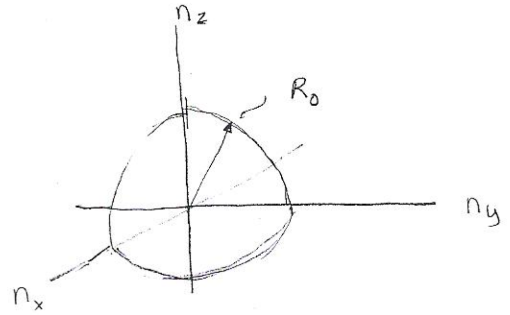
In which states do the electrons exist? In which energy levels

Density of States

Say E_{n_x, n_y, n_z} = some value, E_0, how many quantum states are there with energy E_0 or less?

$$E_{n_x n_y n_z} = \frac{h^2}{8mL^2}\underbrace{(n_x^2 + n_y^2 + n_z^2)}_{\Rightarrow \text{ some value, say } R_0^2} = E_0$$

$R_0^2 = n_x^2 + n_y^2 + n_z^2$, defines a circle with radius R_0 on n_x, n_y, n_z orthonormal co-ordinates.



all q.s with $n_x^2 + n_y^2 + n_z^2 < R_0^2$ have $E < E_0$

each of those q.s. can be represented as a unit volume in the sphere

(# states within sphere of radius R_0) $= \frac{4}{3}\pi R_0^3$.

consider only one octant $(n_x, n_y, n_z > 0) \Rightarrow \div$ by 8

$$N_{q.s.} = \frac{\pi}{6} R_0^3$$

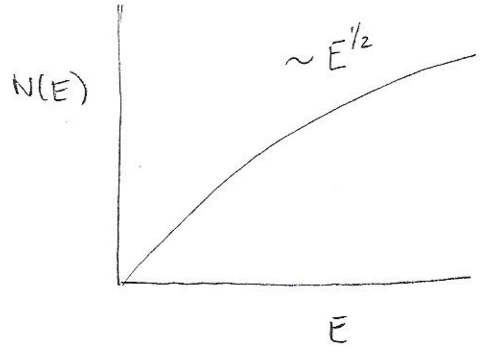
from above: $R_0 = L\left(\frac{8m}{h^2}\right)^{1/2} E_0^{1/2}$

$$N_{q.s} = L^3 \frac{\pi}{6}\left(\frac{8m}{h^2}\right)^{3/2} E^{3/2}$$ ← let E_0 be arbitrary

$$N(E) = \frac{dN_{q.s.}}{dE} = L^3 \frac{\pi}{4}\left(\frac{8m}{h^2}\right)^{3/2} E^{1/2}$$

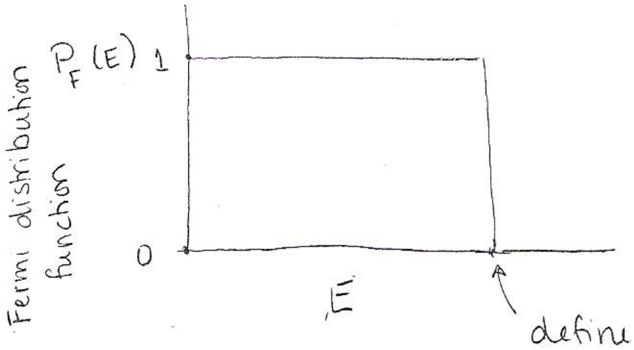
↑ states between E and $E + dE$

Density of States



Distribution of electrons within available states.

Electrons obey Pauli exclusion principle : Fermions
Probability that an energy level is occupied, P(E)



0 Kelvin

States are (sequentially) occupied until no more electrons to fill them

↑ define as ε_f : Fermi energy.

Free electron metal: ε_f simply fixed by # of electrons available to fill the states.

electrons $= N_0 = N_{qs}(\varepsilon_f) \times 2$ ← spin.

N_{qs} → # states up to energy ε_f

$$\Rightarrow N_0 = L^3 \frac{\pi}{3} \left(\frac{8m}{h^2}\right)^{3/2} \varepsilon_F^{3/2}$$

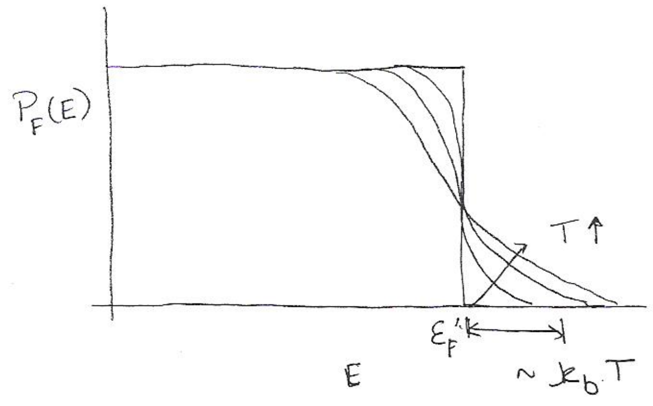
$$\Rightarrow \varepsilon_F = \frac{h^2}{8m} \left(\frac{3}{\pi} \frac{N_0}{L^3}\right)^{2/3}$$

$\frac{N_0}{L^3}$ → $\eta \equiv$ # free electrons / unit volume

e.g. Ca metal ⇒ Ca^{2+} ⇒ 2 free electrons / atom

from density & structure : atoms / volume for $T > 0\,K$ use formal definition of $P_F(E)$

$$P_F(E) = \frac{1}{\exp\left(\frac{E-\varepsilon_F}{k_b T}\right) + 1}$$

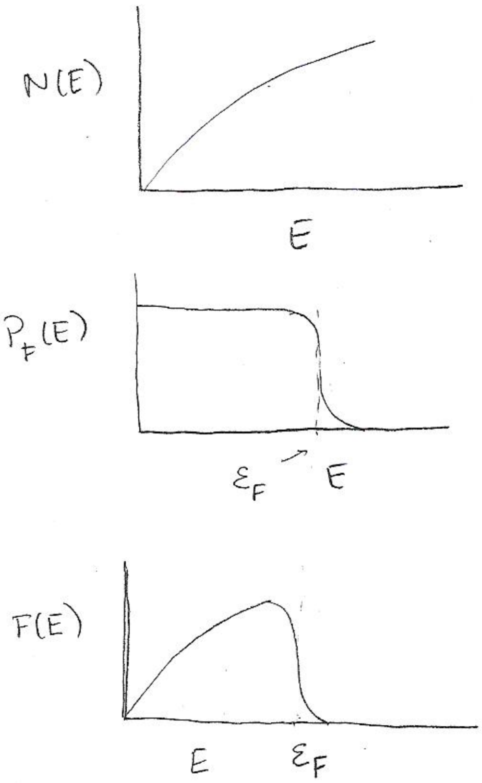


thermal excitation to higher energy states.

$P_F(\varepsilon_F) = 0.5$ at all T

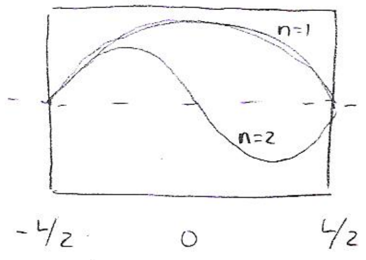
In which energy states are the electrons?

Electron distribution function: $F(E) = 2N(E) \cdot P_F(E)$



Now, consider atom cores.

recall: $\lambda_n = \frac{2L}{n}$

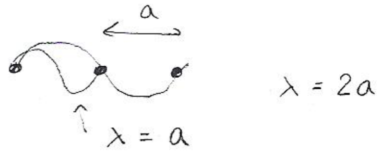


$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$ even

$\psi_n = \sqrt{\frac{2}{L}} \cos\left(\frac{n\pi x}{L}\right)$ odd

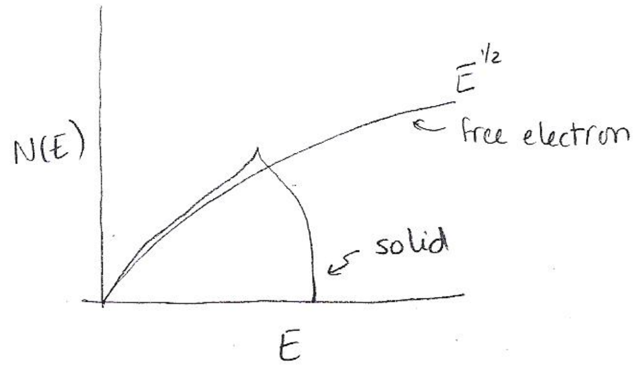
turns out at $\lambda = \frac{2a}{n}$ $\left(k = \frac{2\pi}{\lambda} = \frac{n\pi}{a}\right)$

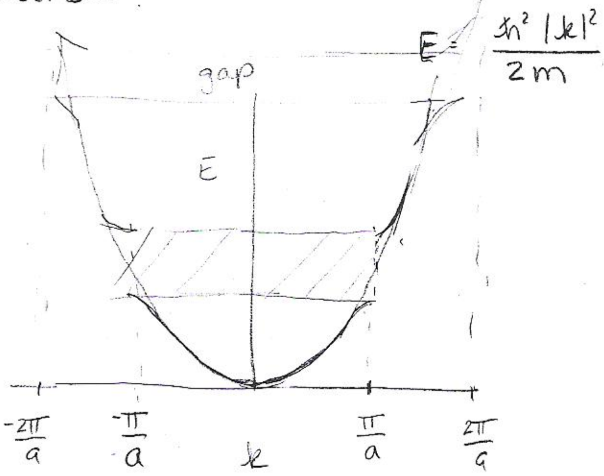
→ discontinuity in N(E)



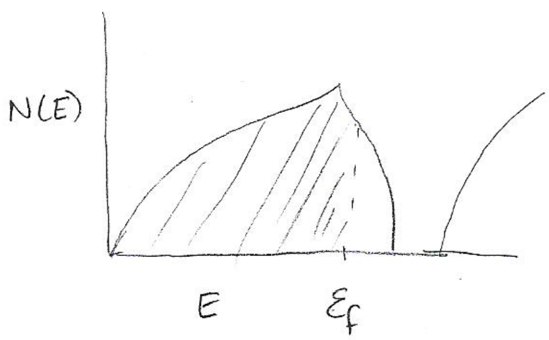
electrons are 'scattered' by atoms.

→ forbidden energies ⇒ bands.

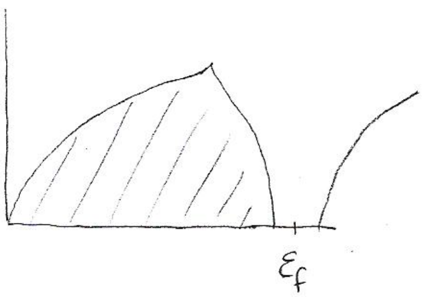




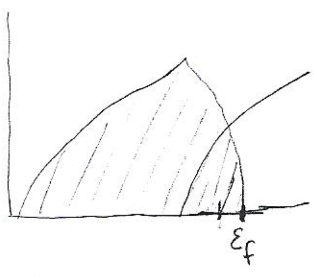
Extend E to higher E like E(k)
& fill states up to $\mathcal{E}_f$ → 3 possibilities (at 0 K)



metal



semiconductor/
insulator



metal

(alkaline
earth metal.