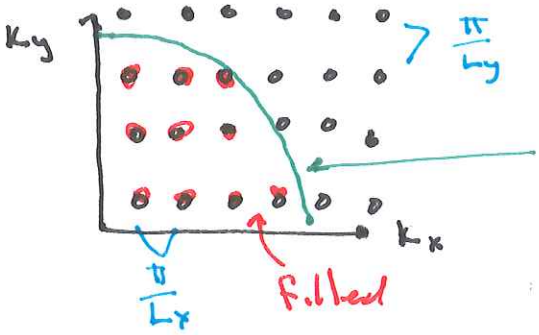
Drude et al: metals as a nearly non-interacting gas of e^-

$\psi \sim \sin\left(\frac{n_x \pi}{L_x} x\right) \sin\left(\frac{n_y \pi}{L_y} y\right) \sin\left(\frac{n_z \pi}{L_z} z\right) \sim e^{i \vec{k} \cdot \vec{r}}$

$k = \left(\frac{n_x \pi}{L_x}, \frac{n_y \pi}{L_y}, \frac{n_z \pi}{L_z}\right)$

Lattice of states — fill low energy states first



$E = \frac{\hbar^2}{2m} \vec{k}^2$

Fermi energy ↓ E_F

Sphere radius k_F ; E_F

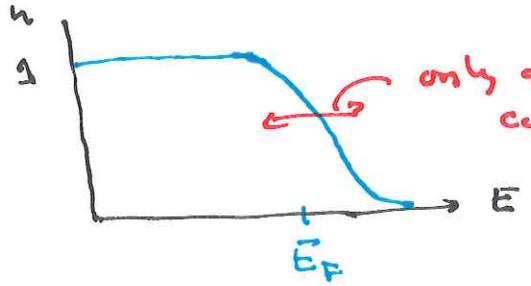
Classical Thermo: avg energy in a quadratic degree of freedom = $\frac{1}{2} kT$ ← Boltzmann constant

Eg most solids 6 degrees of freedom (KE & PE of 3d sho) ⇒ molar specific heat = 3R "Dulong Petit" (modern vibrations)

but electron gas should add to this → Not so.

Fermi-Dirac $\bar{n}_i = \frac{1}{e^{(E_i - \mu)/kT} + 1}$ ← "Bose Einstein"

↑ chem potential



only a fraction of electrons can change energy — small specific heat

also explains rare scattering (long mfp)

2 center problem (H_2^+ molecule)

gerade bonding $\Sigma \Pi \Delta - L_z$

ungerade antibonding

N>2 → the idea that wave functions span molecular frame does not sit well with chemist who think in terms of bond = pair shared e⁻ between nuclei

exception: "resonance" as in benzene

hopping freq relates to bandwidth relates to overlap

Bloch thm (Floquet / Hill etc) ← if potential periodic

$\psi = e^{ik\cdot r} u_k(r)$

$e^{ik\cdot r}$: reduce to Brillouin zone; $u_k(r)$: periodic

density of states

Brillouin zone 1d example: consider a lattice spacing "a"

$e^{i\frac{2\pi n}{a}x}$ is a periodic function of x. Wolog:

$e^{ik\cdot r} = e^{i(k-\frac{2\pi n}{a})x} \; e^{i\frac{2\pi}{a}x}$

$e^{ik\cdot r}$: u_k; $e^{i\frac{2\pi}{a}x}$: u_k; product: new periodic function.

Result: we can always consider $-\frac{\pi}{a} \le k \le \frac{\pi}{a}$ as simply reconsider u_k (reduce k by $\frac{2\pi}{a}$) if k is outside that region.

So E(k) with several "bands" which come from k beyond the Brillouin zone.

Insulator: Completely filled band – energy gap between bands required to free an electron

Conductor: partially filled band – unoccupied state available at nearly zero energy cost

Semiconductor – energy gap not huge cf kT