Free electron model

Kittel Ch. 6

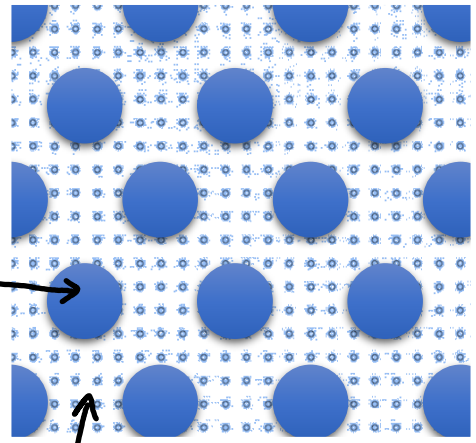
Starting Point for Understanding Electrons in Solids

application of Kinetic Theory of gases to metals by considering them as a "gas of electrons"

[but e- must obey Pauli exclusion principle!]

Metals

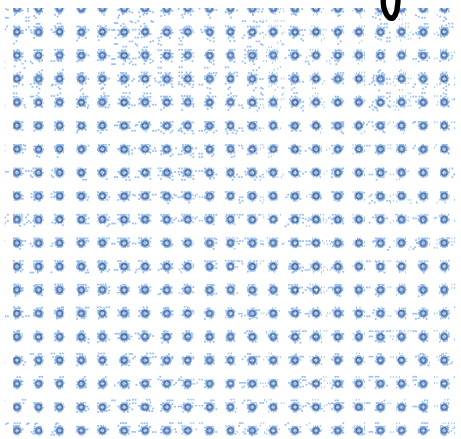
metal



sea of electrons

(valence e- of the constituent atoms become conduction e- that travel free through the crystal)

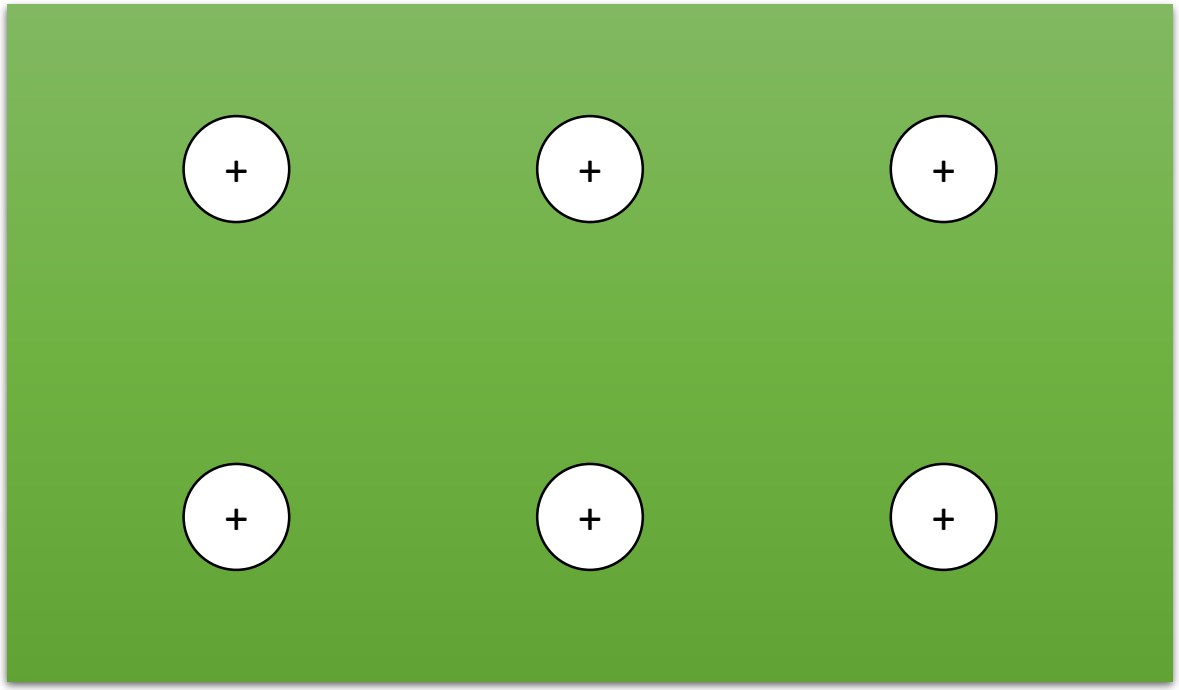
Free electron gas



- e- are free to more through crystal
- nuclei are replaced by smooth background

Alkali metals – How many conduction electrons?

3	Li	Lithium 6.941
11	Na	Sodium 22.990
19	K	Potassium 39.098
37	Rb	Rubidium 84.468



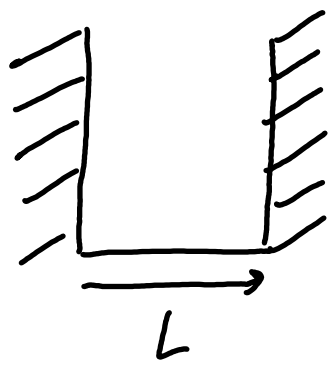
Na

Free atom: $1s^2 2s^2 2p^6 3s^1$ $1e^-$

In the metal, this e^- becomes a conduction e^-

Monovalent crystal: N atoms $\Rightarrow$ N conduction electrons

Free electrons in 1D



1 e⁻ of mass m confined to a length L by ∞-potential barriers

$$\mathcal{H}\psi_n(x) = E_n\psi_n(x)$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} = E_n\psi_n(x)$$

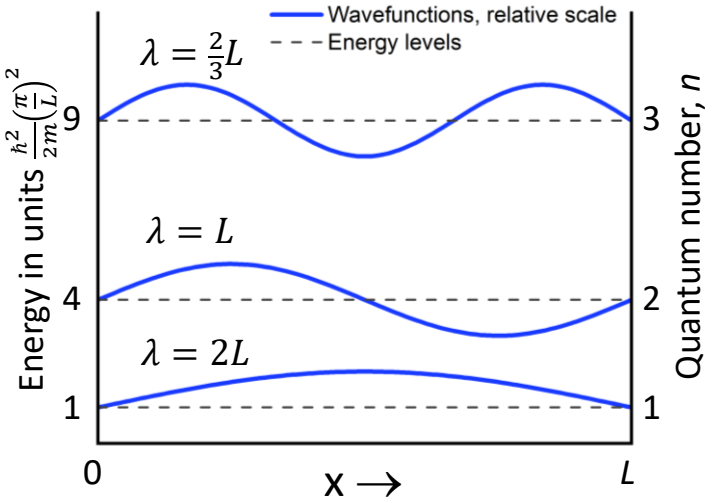
E_n ← energy of the e⁻ ie the orbital

boundary conditions $\psi(0) = \psi(L) = 0$

solution $\psi_n(x) = A \cdot \sin\left(\frac{\pi n}{L} \cdot x\right)$ n = integer

A ↑ constant

Eigenvalues (Energy) $E = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$

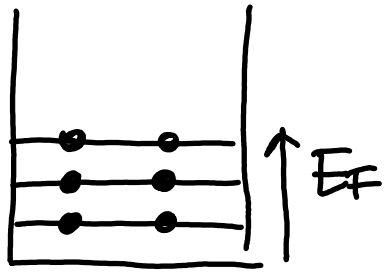


Free electrons in 1D - electron occupancy

N valence electrons

- must obey Pauli exclusion principle
- electronic state in 1D: quantum numbers → n (describes $\psi_n(x)$); $m_s = \pm \frac{1}{2}$
- each orbital Label n accommodates $2e^-$
- n_F: highest filled energy level

$$2 \cdot n_F = N$$



→ Fermi Energy = Energy of the highest occupied orbital $E_{F_{1D}} = \frac{\hbar^2}{2m}\left(\frac{\pi N}{2L}\right)^2$

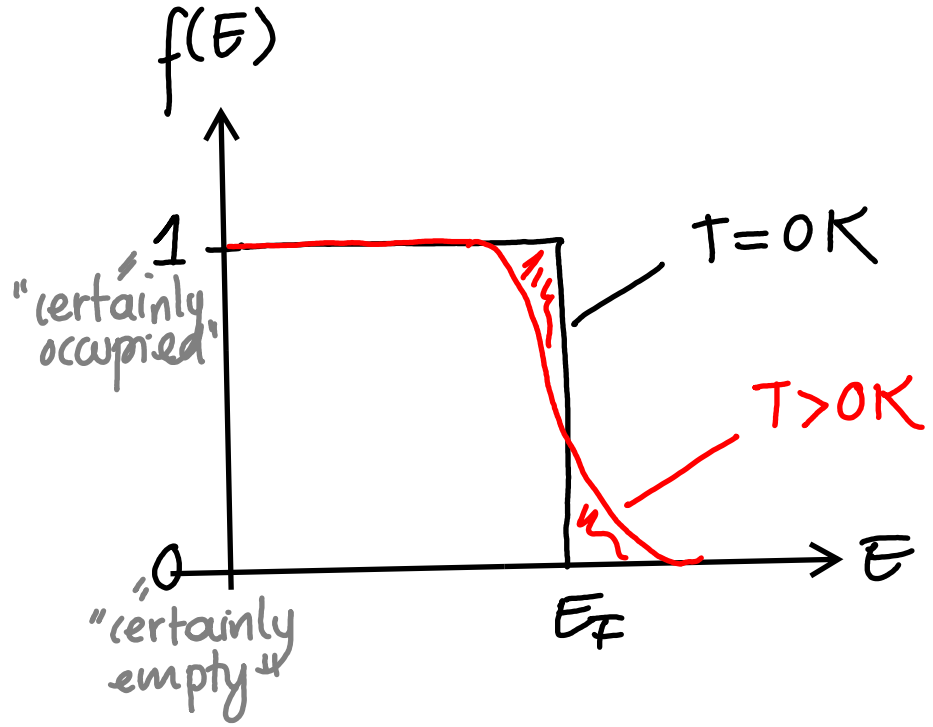
→ in metals $E_F \sim 5eV$

Fermi distribution

$f(E)$ = distribution function
= distribution of e^- among levels

As T↑, Kinetic energy of e^- ↑
⟹ only e^- close to E_F can be excited (Pauli Principle!)

- Energy an e^- absorb thermally ~ K_BT (~ 0.025 eV at RT)
- E_F ~ 5eV

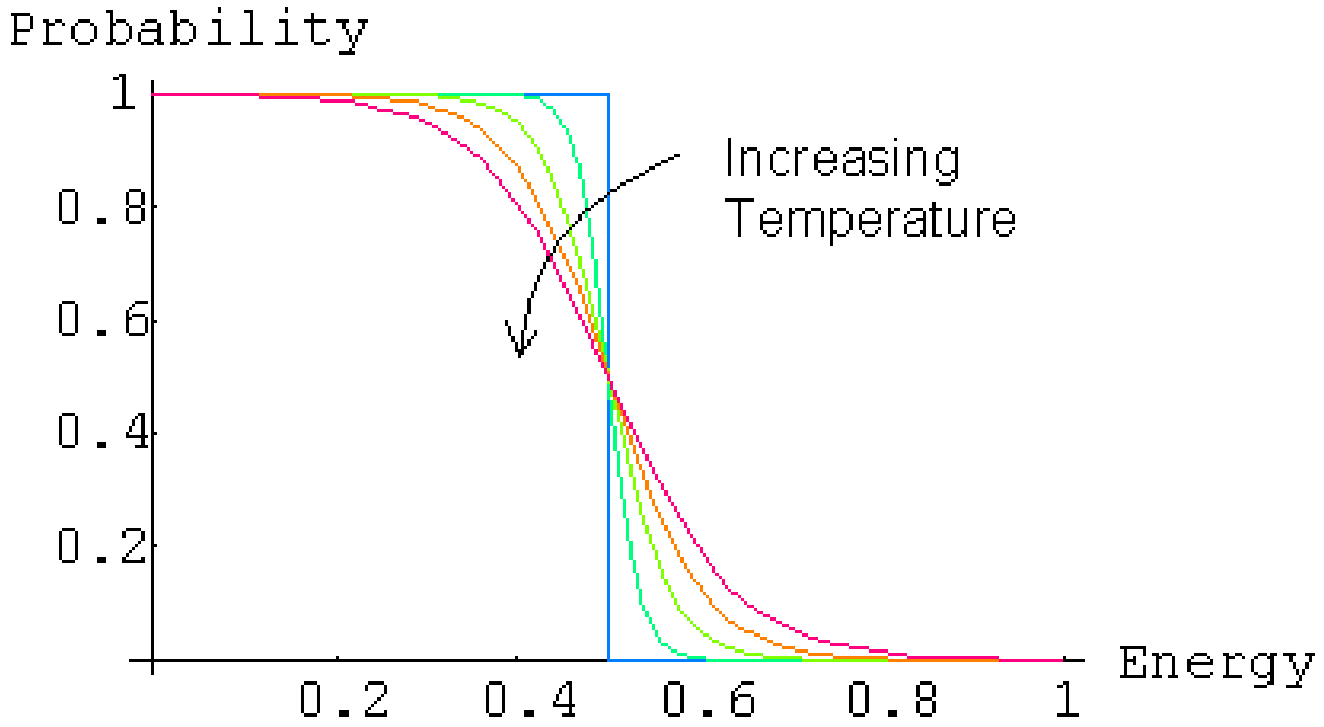


Fermi-Dirac distribution

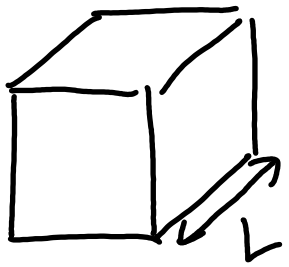
probability that an orbital of Energy E is occupied at thermal equilibrium.

$$f(E) = \frac{1}{\exp\left(\frac{E-\mu}{K_BT}\right)+1}$$

μ: chemical potential
(at 0K: $\mu = E_F$)


Probability
1
0.8
0.6
0.4
0.2
Increasing
Temperature
0.2
0.4
0.6
0.8
1
Energy

Free electrons in 3D



$$\mathcal{H}\Psi(\vec{r}) = -\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r}) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Psi(\vec{r}) = E\Psi(\vec{r})$$

- periodic boundary conditions i.e. x-axis $\Psi(x+L,y,z) = \Psi(x,y,z)$ (idem for other axis)

- Solutions : $\Psi_{\vec{K}}(\vec{r}) = A\exp(i\vec{K}\cdot\vec{r})$

with $K_i = \frac{2\pi}{L}n_i$ (i.e $K_x = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}\ldots$)

n_i : positive integers

- Energies for the orbital with $\vec{K}$

$$E_K = \frac{\hbar^2K^2}{2m} = \frac{\hbar^2}{2m}(K_x^2+K_y^2+K_z^2)$$

Free electrons in 3D

$$\psi_K = A \exp(i\vec{K}\cdot\vec{r})$$

* $\psi(\vec{r})$ are eigenfunctions of the momentum

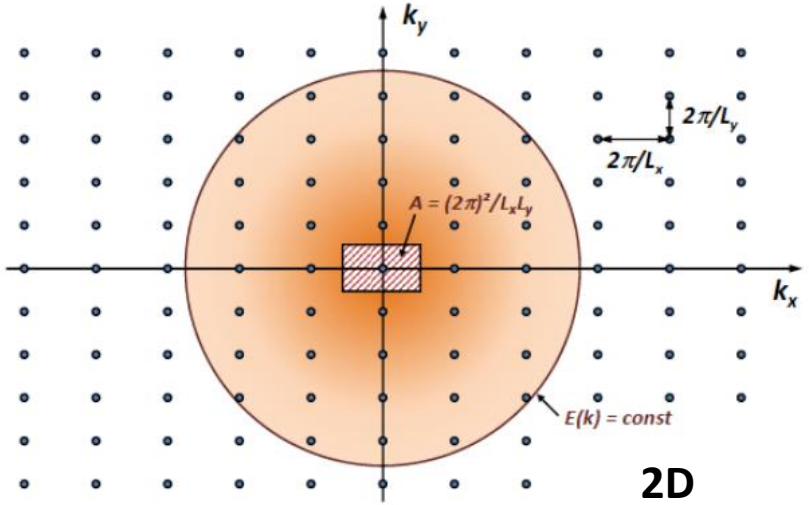
$$\vec{p}\,\psi_K(\vec{r}) = -i\hbar\nabla\psi_K(\vec{r}) = \underbrace{\hbar\vec{K}}_{\text{eigenvalue of the momentum}}\psi_K(\vec{r})$$

* velocity of the electron

$$\vec{v} = \frac{\vec{p}}{m} = \frac{\hbar\vec{K}}{m}$$

- Each $\vec{K}$ state occupies $\left(\frac{2\pi}{L}\right)^3$ in 3D

Here 2D example



2D