Electrons in a Solid - Electronic properties of solids

Introduction to Solids: Structure and bonding in solids: Overview of crystal lattices and their role in defining material properties. Classification of solids into metals, semiconductors, and insulators based on bonding and electron behavior.

Electronic Properties of Materials: Band theory explaining conduction, valence bands, and energy gaps in different material types. Detailed examination of Fermi level, density of states, and their implications for electronic behavior.

Phonons and Thermal Properties: The role of lattice vibrations (phonons) in thermal and electronic properties. Concepts like specific heat and thermal conductivity in relation to material structure and temperature.

Electrons in a solid

The Resistivity of Materials (ohm m)

10^{-9}	10^{-7}	10^{-5}	10^{-3}	10^{-1}	10^{1}	10^{3}
Ag Cu Al Au	Ni Fe	Sb Bi Graphite	Ge (doped)	Ge (pure)		Si (pure)

← Metals → ← Semiconductors →

10^{5}	10^{7}	10^{9}	10^{11}	10^{13}	10^{15}	10^{17}
Window glass		Bakelite	Porcelain Diamond Rubber, Nylon Polyethylene	Lucite Mica	PVC	SiO_2 (pure)

← Insulators →

Electrical resistivity (or conductivity) is one of the most remarkable of all physical properties: it varies over 25 orders of magnitude.

Electrical properties of materials

OHM'S LAW

relates the current I to the applied voltage *V*

$$V = R\,I$$

R = resistance of the material through which current is passing

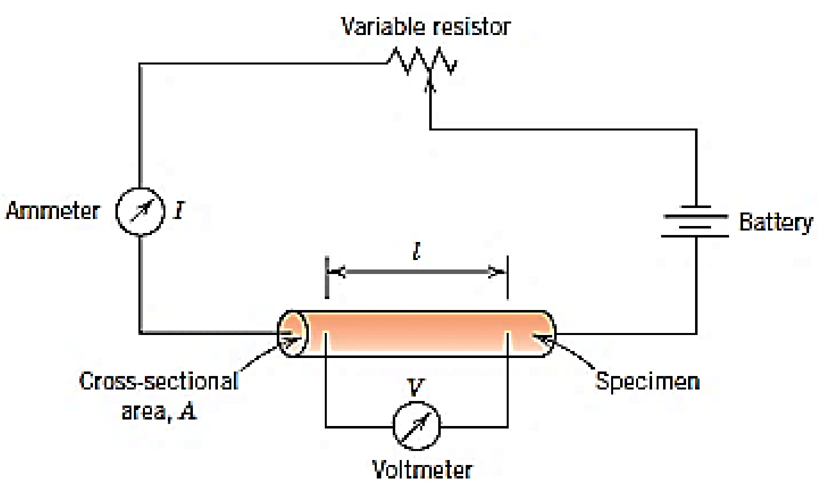
R is influenced by specimen configuration, but independent of current for many materials

ELECTRICAL RESISTIVITY

Independent of specimen geometry, but related to *R*

$$\text{Resistivity } \boldsymbol{\rho} = \frac{\boldsymbol{RA}}{\boldsymbol{l}} = \frac{\boldsymbol{VA}}{\boldsymbol{Il}}$$

$$\text{Conductivity } \boldsymbol{\sigma} = \frac{\mathbf{1}}{\boldsymbol{\rho}}$$



Energy band structures in solids

For many solids, there is only **electronic conduction.**

σ **depends on** the number of electrons participating in the conduction process.

The number of participating electrons is related to

1. arrangement of electron states or levels with respect to energy,
2. the manner in which these states are occupied by electrons.

Energy band structures in solids

In individual atoms

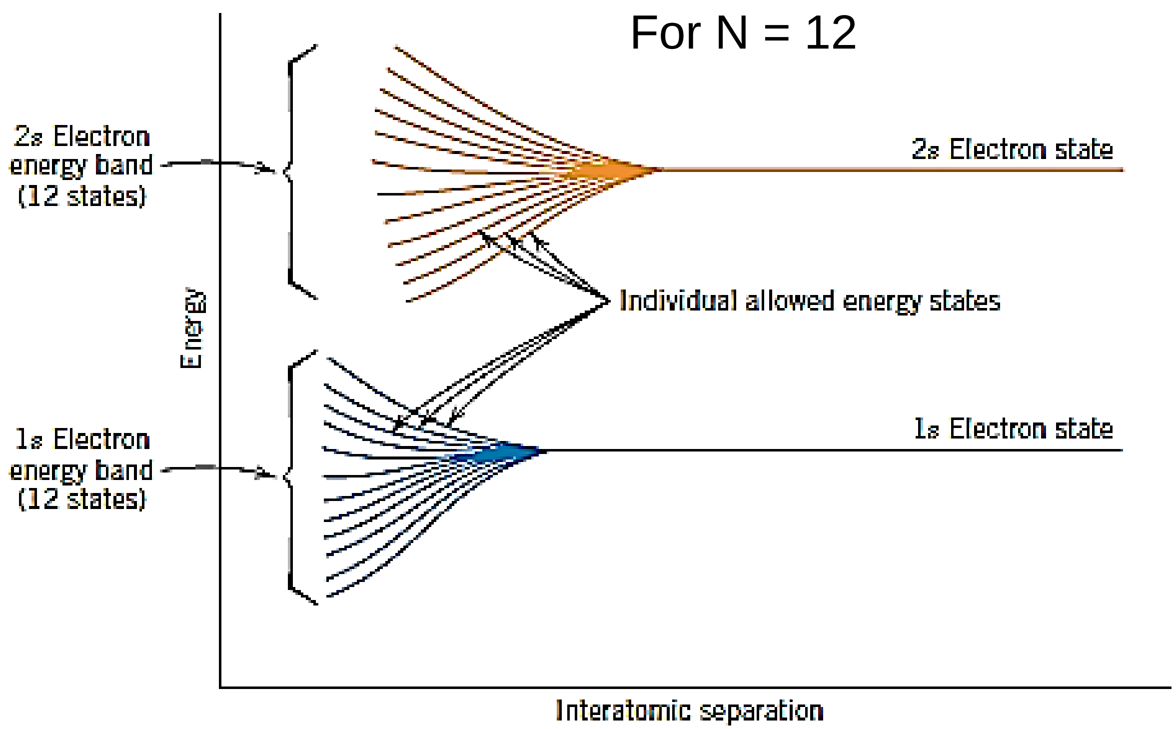
Discrete energy levels that may be occupied by electrons, arranged into shells and subshells.

Shell	Sub-shell	No. of States			
		s	*p*	*d*	*f*
1, 2, 3 etc.	*s, p, d, f*	1	3	5	7

Electrons fill only the states having the lowest energies, two electrons of opposite spin per state, in accordance with Pauli exclusion principle.

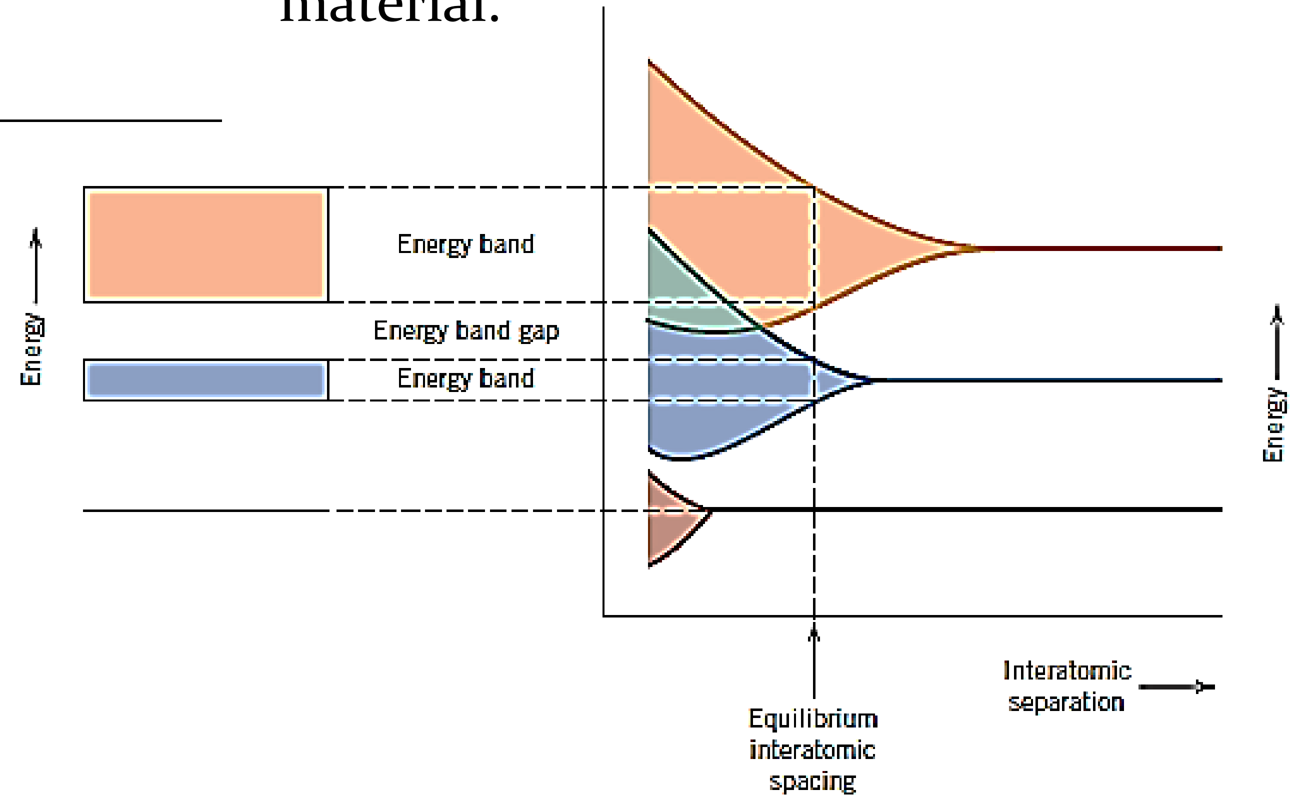
Electron configuration of an isolated atom represents the arrangement of the electrons within the allowed states.

Energy band structures in solids

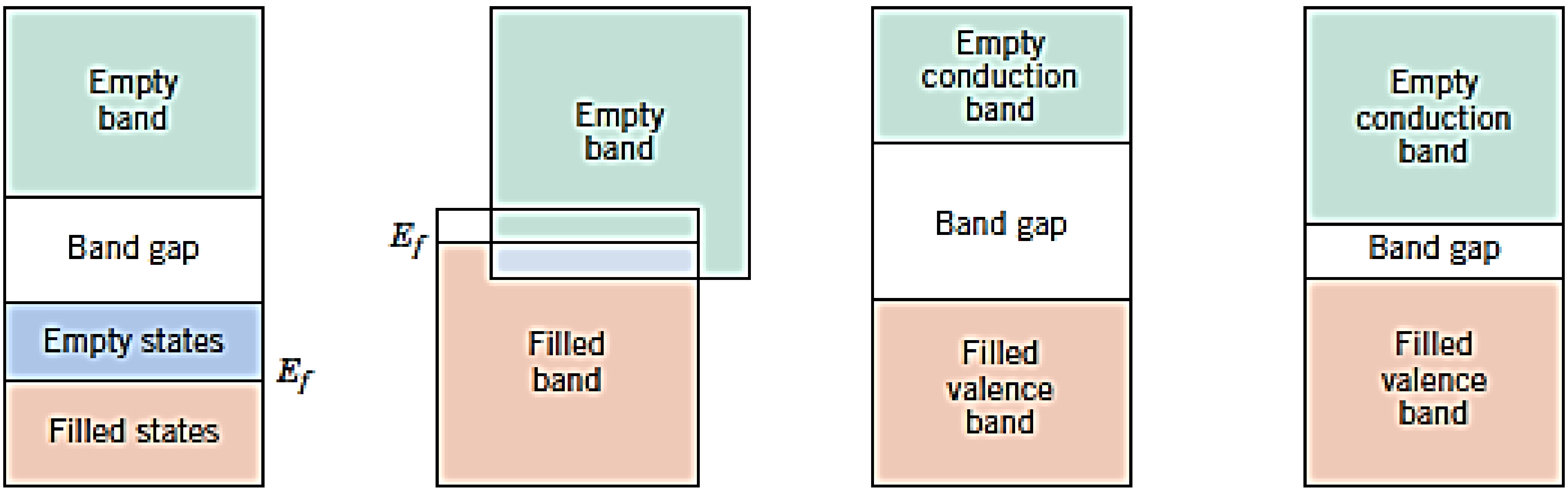


A solid → consists of a large number of atoms initially separated from one another.

All atoms are brought together and bonded to form the ordered atomic arrangement found in the crystalline material.



Possible band structures in solids at 0K



Metals like Cu

Solids like Mg

Insulators
Band gap > 2 eV

Semiconductors

Free electron theory – Electron Gas

Outermost electrons are not bound to a specific atom:
Free to move inside a solid

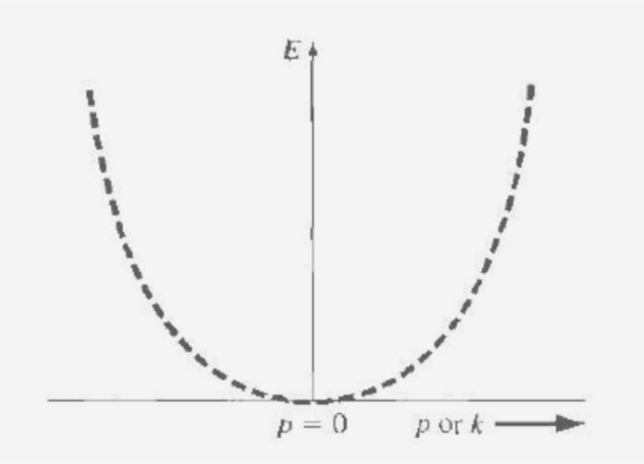
Potential due to ion cores is uniform everywhere:
Electron has the same PE everywhere in the solid.

Wave – Particle duality

$$\lambda = \frac{h}{mv} \quad \Rightarrow k = \frac{2\pi}{\lambda} = \frac{2\pi\, mv}{h} = \frac{p}{\hbar}$$

Energy (kinetic)

$$E = \frac{1}{2}mv^2 = \frac{h^2k^2}{8\pi^2 m} = \frac{\hbar^2 k^2}{2m}$$



Electrical properties of materials

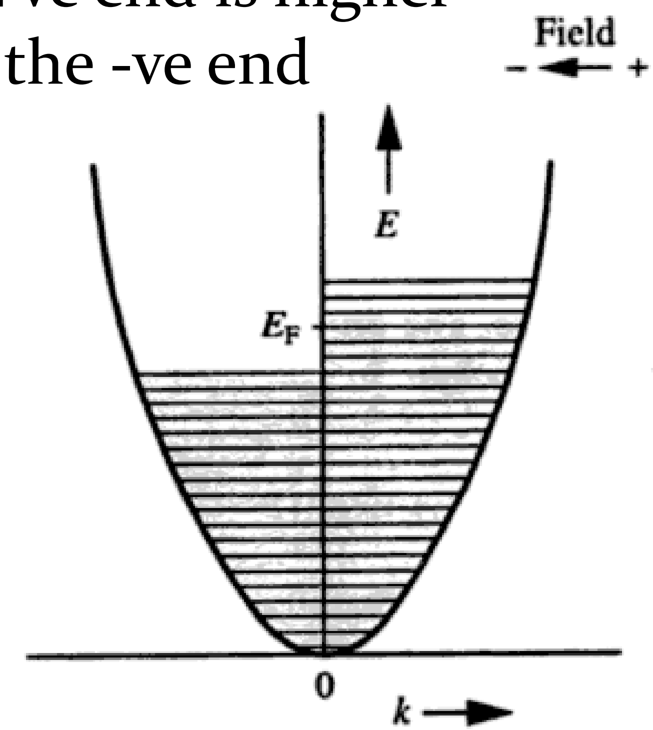
CONDUCTION BY FREE ELECTRON

For each electron moving with some velocity in a certain direction, there is another electron moving with the same speed but in the opposite direction.

Applied the electric field $\rightarrow$ net velocity in a particular direction

Electrons are accelerated towards the +ve end.

The velocity of fastest-moving electron towards the +ve end is higher than the velocity of fastest-moving electron towards the -ve end



This is possible only when there are empty states available just above the Fermi level.

Example: metals

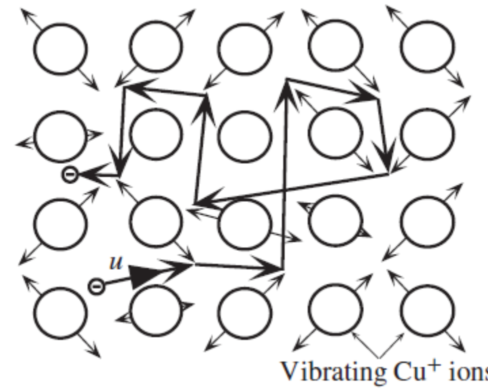
Conduction by free electrons

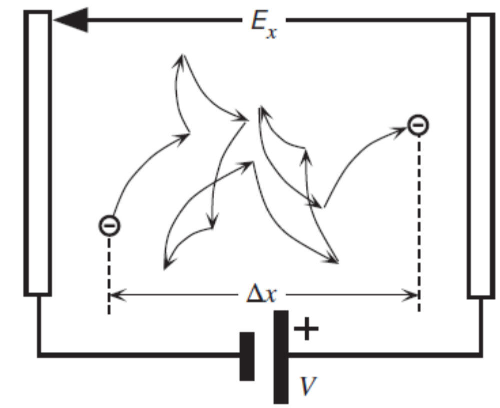
$e\varepsilon = ma$

ε = Applied field gradient

m = mass of electron

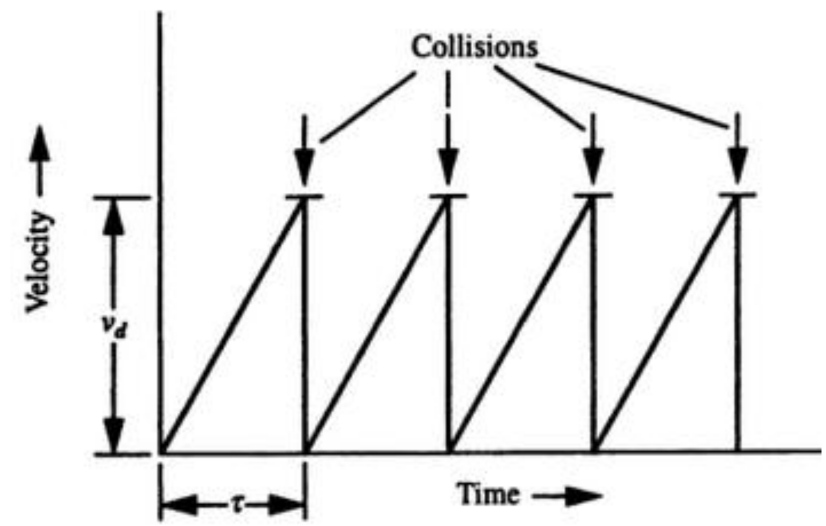
a = acceleration of the electron due to the field





Velocity does not increase continuously!

The average increment in velocity between successive collisions is called the drift velocity.



Drift velocity

= extra velocity over and above normal velocity with no field.

Conduction by free electrons

τ = Average collision time, v_d = drift velocity

$$\frac{mv_d}{\tau} = Ee \qquad \Longrightarrow v_d = \frac{Ee\tau}{m}$$

Flux due to flow of electrons (current density)

$$J = nev_d = \frac{ne^2\tau E}{m} = \sigma E$$

Conductivity is the flux per unit potential gradient.

$$\sigma = \frac{ne^2\tau}{m}$$

MOBILITY

Drift velocity

- Av. electron velocity in the direction of force imposed by the applied field.

$v_d \propto E$

proportionality constant = **electron mobility**

$v_d = \mu_e E$

$\boxed{\Rightarrow \sigma = n\mu_e e}$

μ_e is an indication of the frequency of the scattering events;

Its unit is $m^2/V.s$

Electrons in a solid – Electron Gas – Classical ideal gas

This assumption (the electron gas in the solid was considered to be the ideal gas) gave accurate predictions, which matched the experiments.

$$\frac{1}{2}mv^2 = \frac{3}{2}k_B T$$

Independent electron approximation: Interaction between the electrons is neglected.

Free electron approximation: Interaction between the electrons and cores is neglected.

Electrons in a solid – Electron Gas – Classical ideal gas

Incorrect expression for thermal conductivity.

Incorrect temperature and conc. dependence of σ.

Cannot explain electrical conductivity of semiconductors or insulators.

Failure to predict correct sign for Hall coefficients and thermo power coefficients for all materials

Fails to explain superconducting properties of metals.

Failure to predict specific heat of material even metals

Predicted larger Susceptibility

Ferromagnetism could not be explained

Electrons in a solid – Electron Gas – Quantum gas

Assumption: Electrons behave like a quantum gas

To understand a system we must know how particles are distributed within it:

Total energy, $E = n_1(E_1) \times E_1 + n_2(E_2) \times E_2 + n_3(E_3) \times E_3 + \dots\dots\dots\dots$

$$E = \sum_i n_i(E_i) \times E_i$$

Where,

$n_i(E_i)$: Number of particles having energy E_i

$n_1(E_1) + n_2(E_2) + n_3(E_3) + \dots\dots\dots = N$, Total number of particles

For solids, we are dealing with 10^{22} electrons/cm^3!!

Electrons in a solid – Electron Gas – Quantum gas

We use Statistical Mechanics:

$$n(E) = g(E)\, f(E)$$

n(E): No. of particles in an energy range E to E + dE.

g(E): No. of states of energy E, ***density of states***

f(E): probability of occupancy of state of energy E, ***Distribution Function.***

$$N = \int n(E) dE \qquad E = \int n(E)\, E\, dE$$

Fermi-Dirac distribution function

Distribution Function: Probability of occupancy of a state of energy

Electrons are spin-half quantum particles that follow Pauli's Exclusion Principle.

They follow Fermi-Dirac distribution function - Fermions

$f_{FD}(E)$ = Fermi-Dirac distribution function

$$f_{FD}(E) = \frac{1}{1 + e^{(E-E_f)/kT}}$$

E_f: Fermi Energy,

k: Boltzmann Constant = 1.38 x 10^{-23} J/K

$$T = 0,\ \epsilon < \epsilon_F: \qquad f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon-\epsilon_F)/kT} + 1} = \frac{1}{e^{-\infty} + 1} = \frac{1}{0 + 1} = 1$$

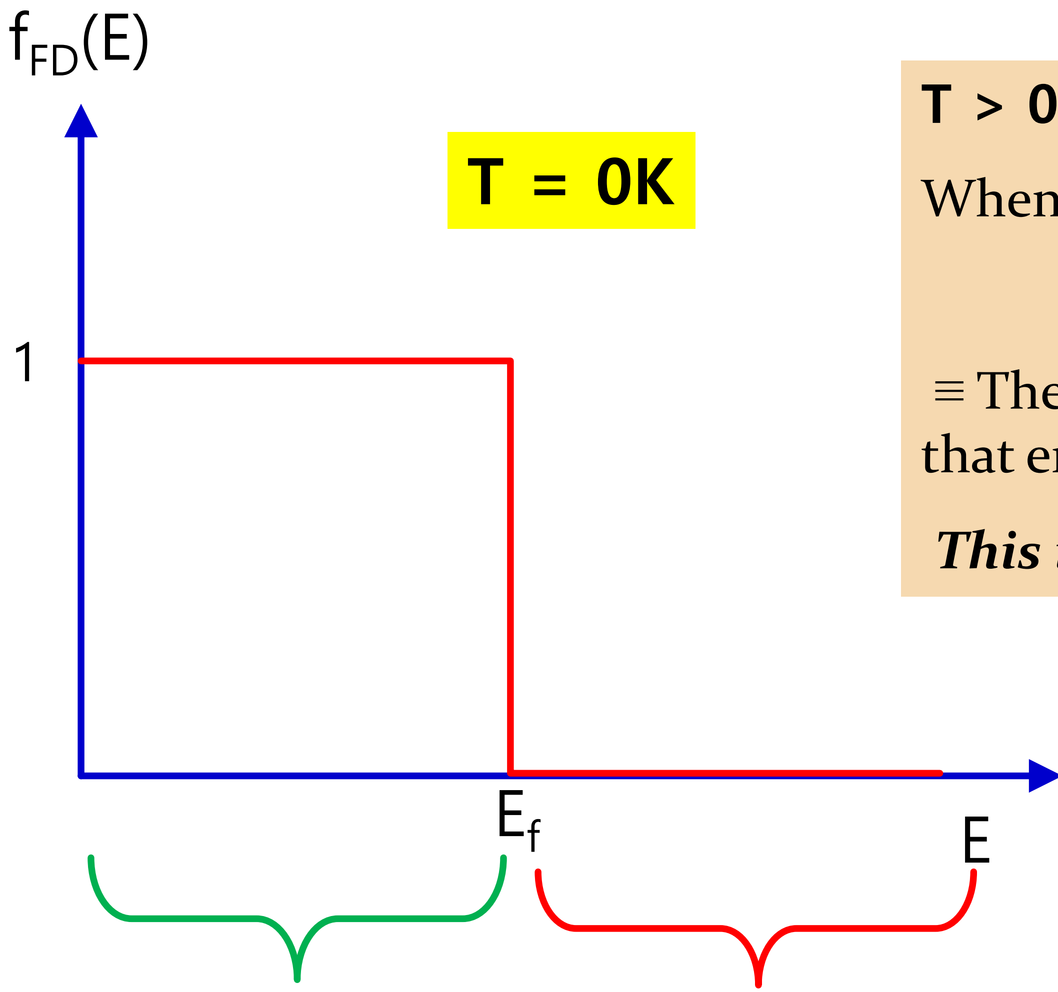
All states below the level E_f are **occupied.**

$$T = 0,\ \epsilon > \epsilon_F: \qquad f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon-\epsilon_F)/kT} + 1} = \frac{1}{e^{\infty} + 1} = 0$$

All states above the level E_f are **Empty.**

Fermi level (E_f) separates occupied from unoccupied levels at T = 0K

Fermi-Dirac distribution function



T > 0K

When $E = E_f$,

$$f(E_f) = ½$$

≡ The probability of finding the electron is ½ at that energy

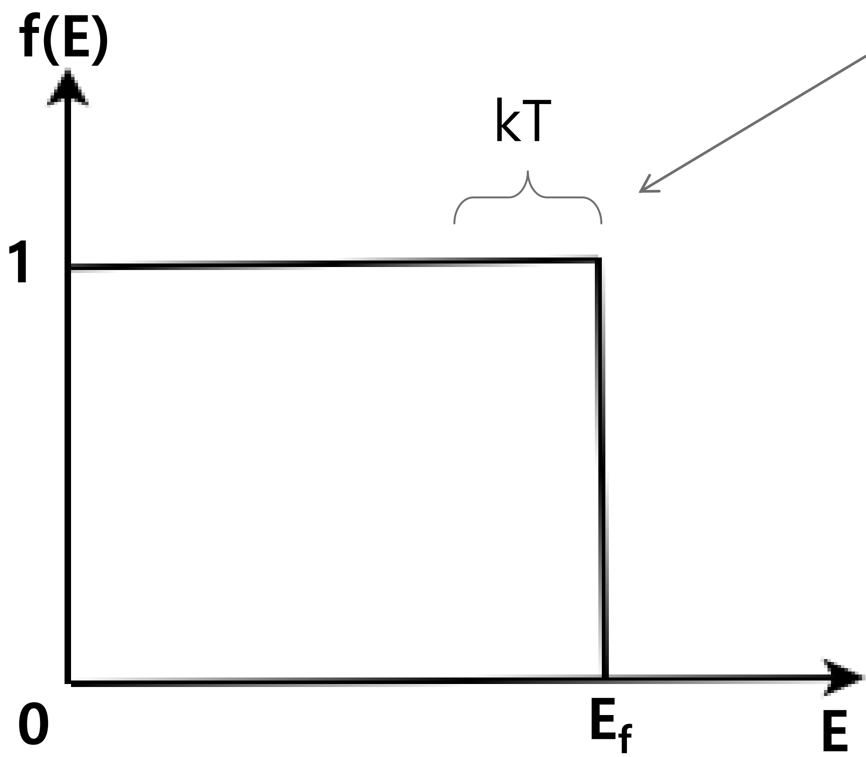
This is the definition of the Fermi energy.

Probability of occupancy is 1
These levels are all occupied

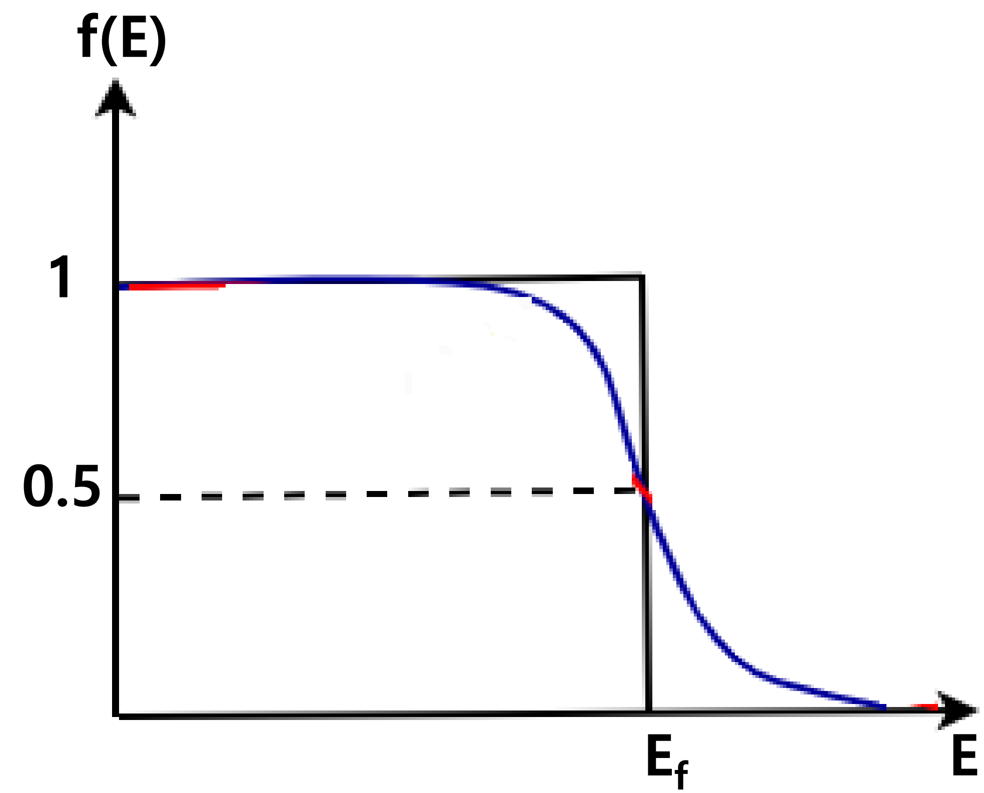
Probability of occupancy is 0.
These levels are all empty

Fermi level (E_f) separates occupied from unoccupied levels at $T = 0K$

Fermi-Dirac distribution function

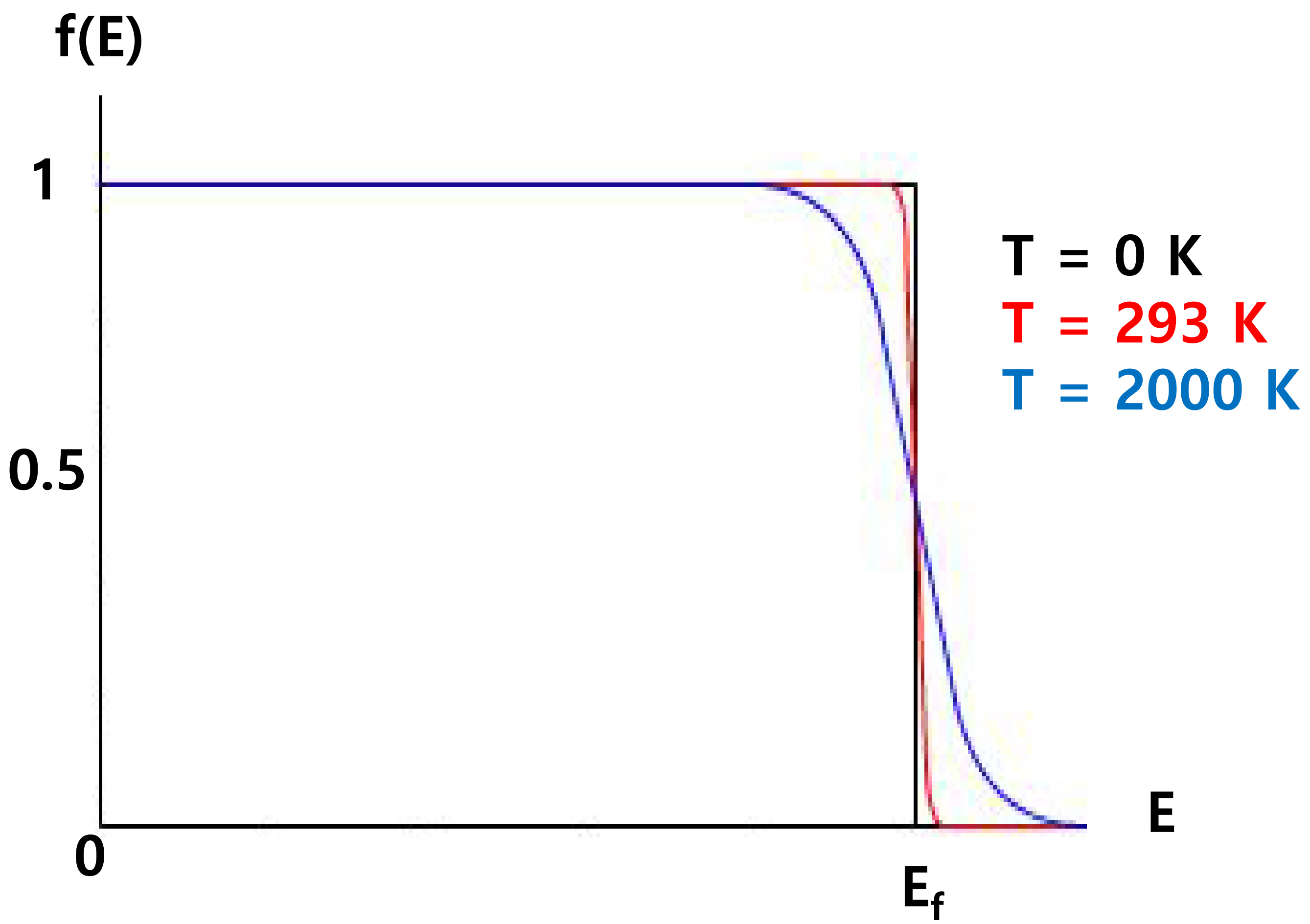


At T ≠ 0 K, only these electrons have states available that they can move into.



Electrons leave states below E_f and move to states just above it

Fermi-Dirac distribution function



300 K = 26 meV

Density of States

If the electron has no interactions, one electron wave function will satisfy the Schrödinger equation:

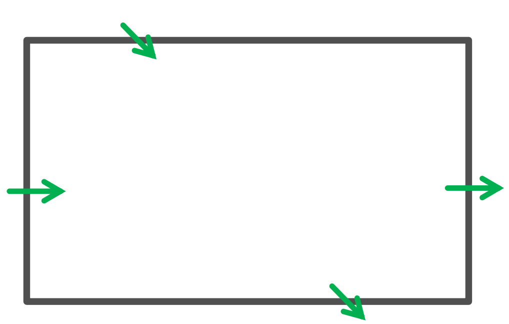
$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\,\psi(x)$$

Solution can be of form: $\psi(x) \sim e^{ikx}$ when $k^2 = \frac{2mE}{\hbar^2}$

Boundary Conditions:

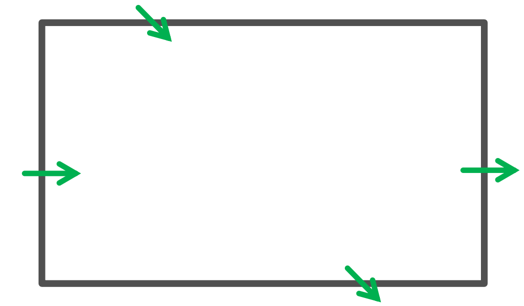
- The electron is confined to a solid.
- Electrons move under applied potentials.
- Boundary conditions cannot be the same as that we used for an electron in a box, $\psi(0) = 0$ and $\psi(L) = 0$; L: dimension of the solid
- These boundary conditions result in only stationary solutions.

• The transport properties: properties due to the flow of electrons cannot be explained.



Net number stays constant

Density of States



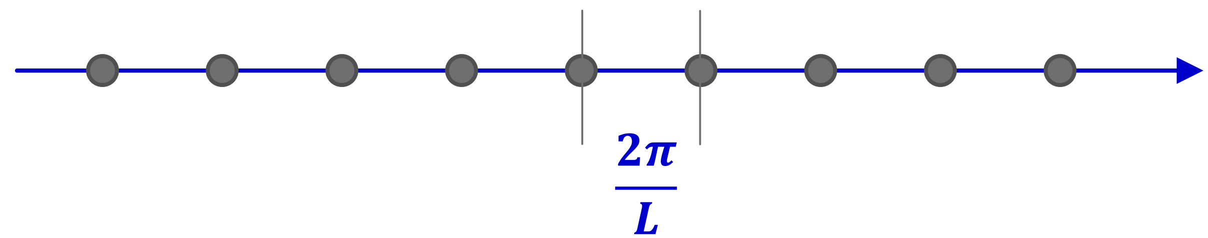
Periodic Boundary conditions

Wave function should be periodic with dimension of solid ≡ L

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

Hence, $e^{ik(x+L)} = e^{ikx}$, The solution is a travelling wave.

$$\Rightarrow e^{ikL} = 1 = e^{i2n\pi}$$



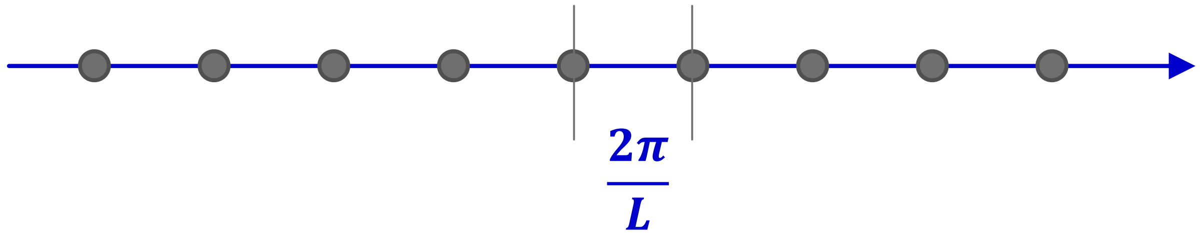
$$\Rightarrow k = \frac{2n\pi}{L}$$

$$\Rightarrow E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{2n\pi}{L}\right)^2 \qquad E_n = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 n^2$$

E depends on n^2

The finite size of the solid in real space has resulted in quantization of k-space.

Density of States

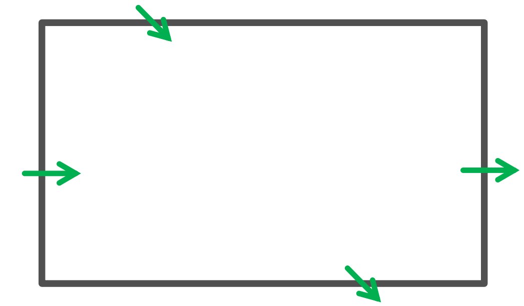


- Electrons can only exist at the location of a k-state.
- Each k-state can accommodate two electrons of opposite spins.
- No of k-states will be half of number of electrons.

Density of States

In 3-Dimension

Wave function should be periodic with dimension of solid ≡ L



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

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

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

Solving as before,

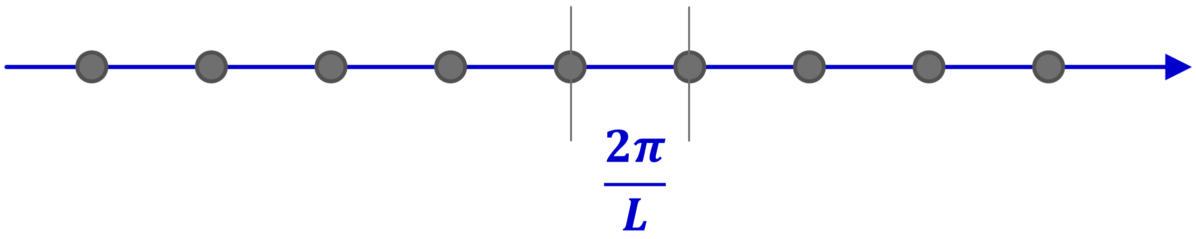
$$\Rightarrow k_x = \frac{2nx\pi}{L} \qquad k_y = \frac{2ny\pi}{L} \qquad k_z = \frac{2nz\pi}{L}$$

$$\Rightarrow \boldsymbol{E_k = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 \left(n_x^2 + n_y^2 + n_z^2\right)}$$

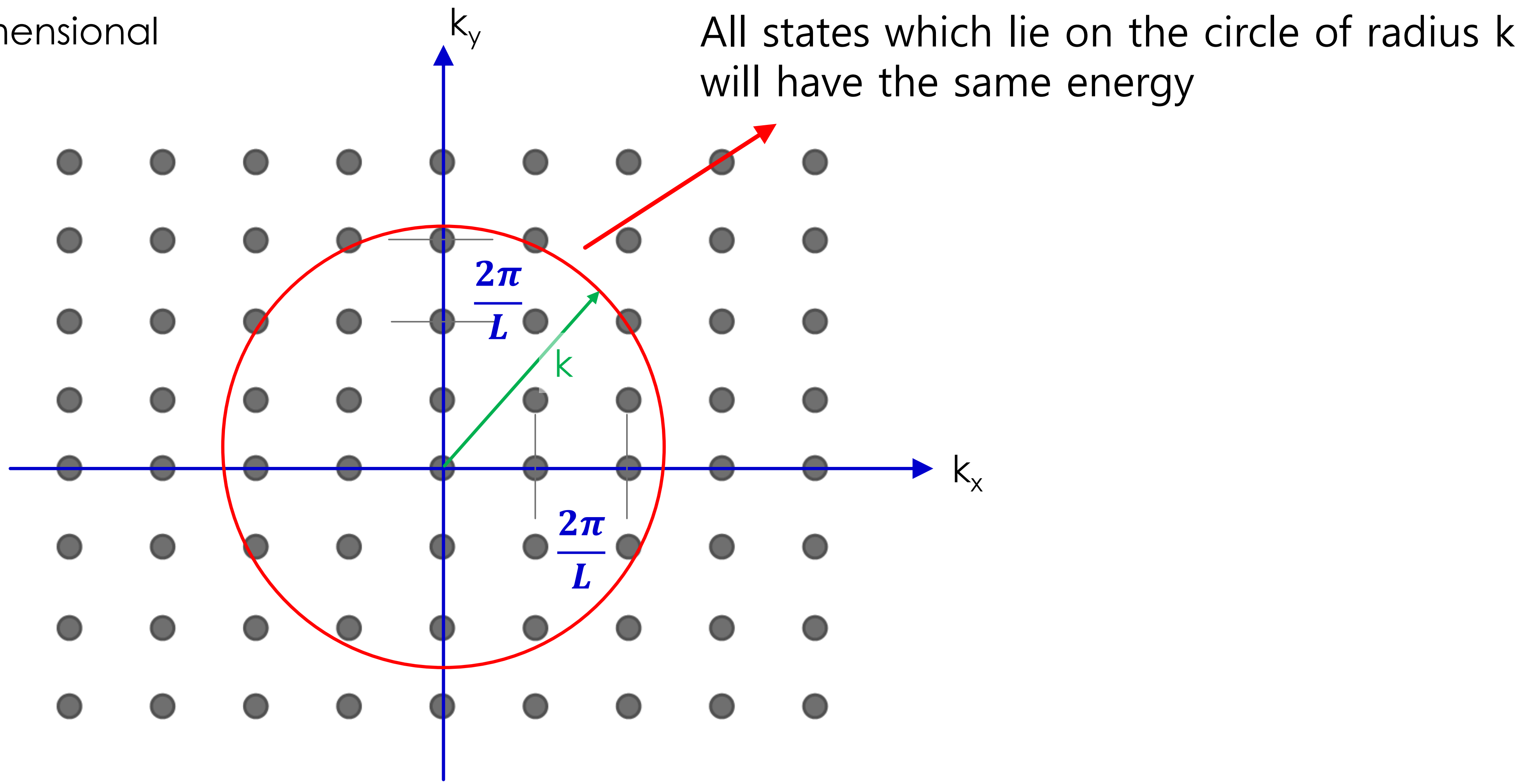
n_x, n_y, n_z = 0,1,2… (but not simultaneously 0)

Density of States

1-Dimensional



2-Dimensional



Density of States

<u>3-Dimensional</u>

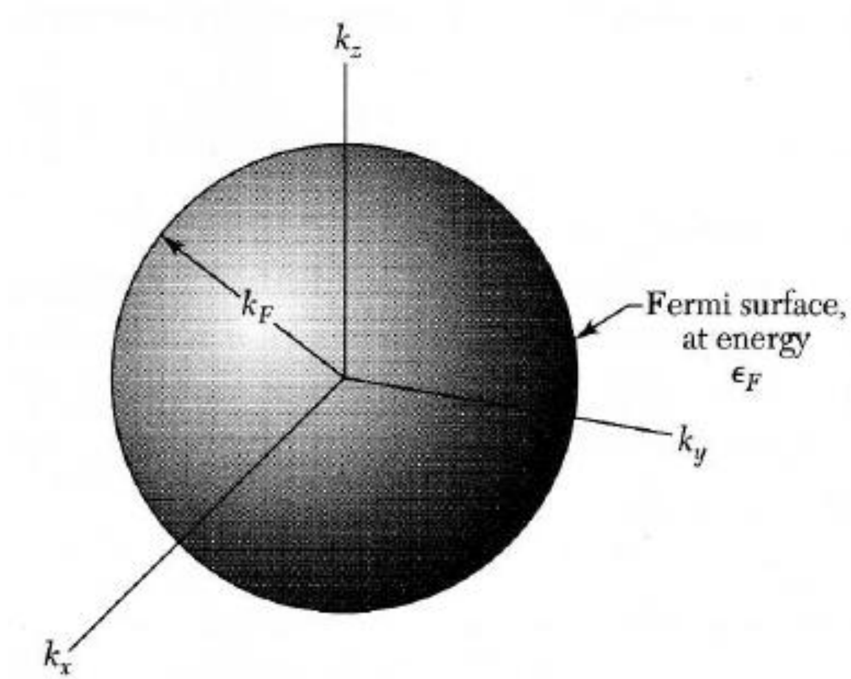
All states which lie on the surface of a sphere of radius k will have the same energy.

In the ground state of a system of N free electrons, the occupied orbitals are represented as points inside a sphere in k space.

The energy at the surface of the sphere is the Fermi energy (E_f)

$$E_f = \frac{\hbar^2 k_f^{\ 2}}{2m}$$

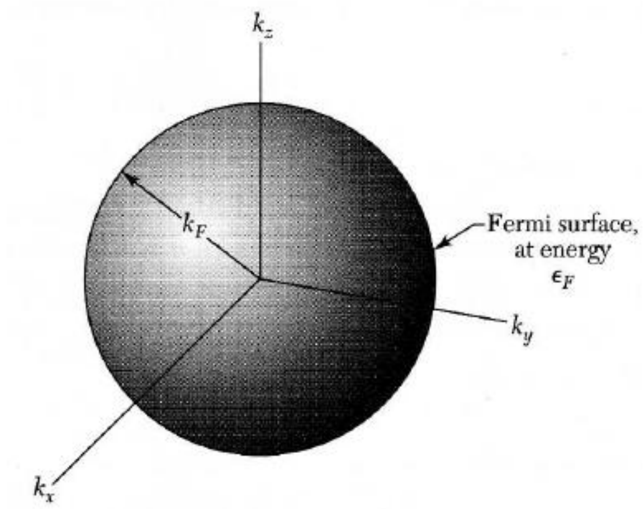
No. of k-states inside fermi-sphere = ?



Density of States

Volume of Fermi sphere = $\frac{4}{3}\pi k_f^3$

Volume of one k-state = $(2\pi/L)^3 = \frac{8\pi^3}{V}$



No. of k-states inside Fermi-sphere $= \frac{\text{Volume of Fermi sphere}}{\text{Volume of one k-state}} = \frac{\frac{4}{3}\pi k_f^3}{\frac{8\pi^3}{V}} = \frac{N}{2}$

$$\frac{N}{2} = \frac{k_f^3}{6\pi^2}\mathrm{V} \qquad \Rightarrow \frac{N}{V} = n = \frac{k_f^3}{3\pi^2}$$

$$E_f = \frac{\hbar^2}{2m}k_f^2 = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$$

$n = z\,N_d$

z: Valency

N_d: Number density = No. of atoms/Volume

= (density • N_A)/ Atomic mass

Density of States

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

For any ***N*** number of electrons, if the levels are filled up to E.

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

Density of states ≡ number of states per unit energy

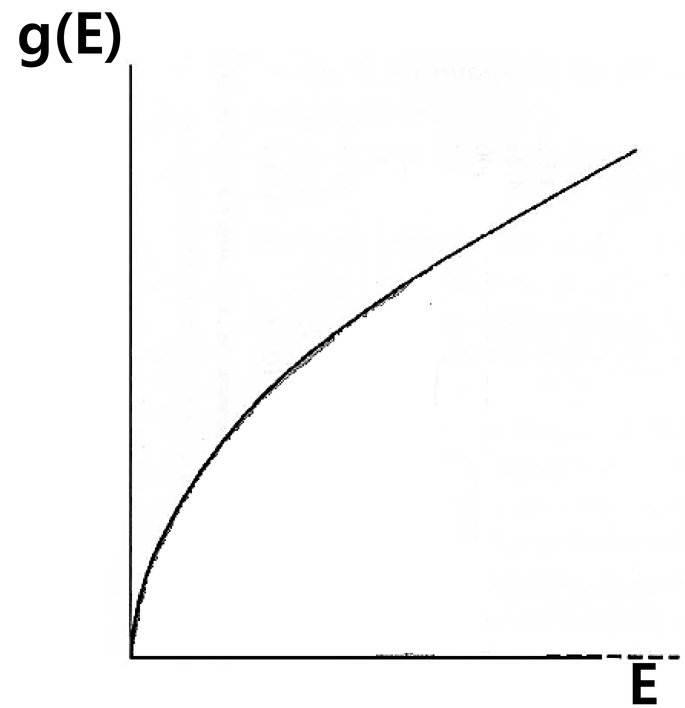
$$D(E) = \frac{d\boldsymbol{N}}{dE} = \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

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

g(E): density of states is independent of the size of sample, property of material.

Density of States

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



Density of states at Fermi energy

$$N = \frac{V}{3\pi^2}\left(\frac{2mE}{\hbar^2}\right)^{3/2} = A(E)^{3/2}$$

$$\ln N = \frac{3}{2}\ln E + \ln A$$

$$\frac{dN}{N} = \frac{3}{2}\frac{dE}{E}$$

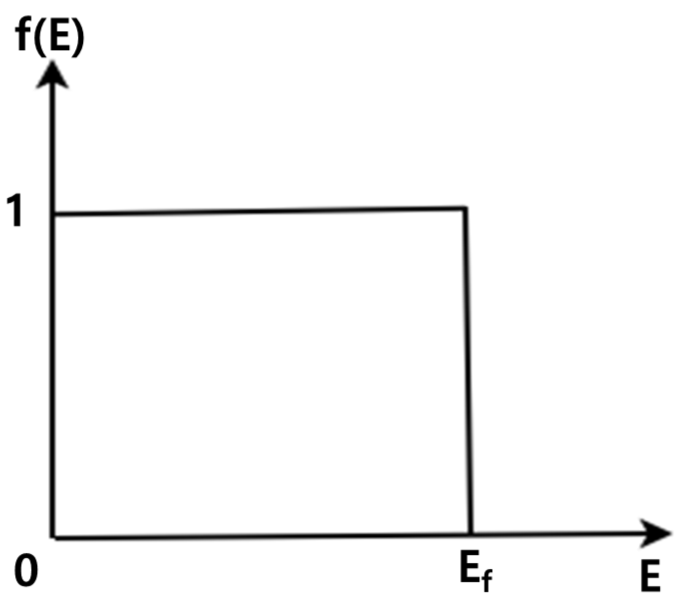
$$\Longrightarrow \frac{dN}{dE} = \frac{3}{2}\frac{N}{E} \Longrightarrow \boxed{g(E = E_F) = \frac{3}{2}\frac{n}{E_f}}$$

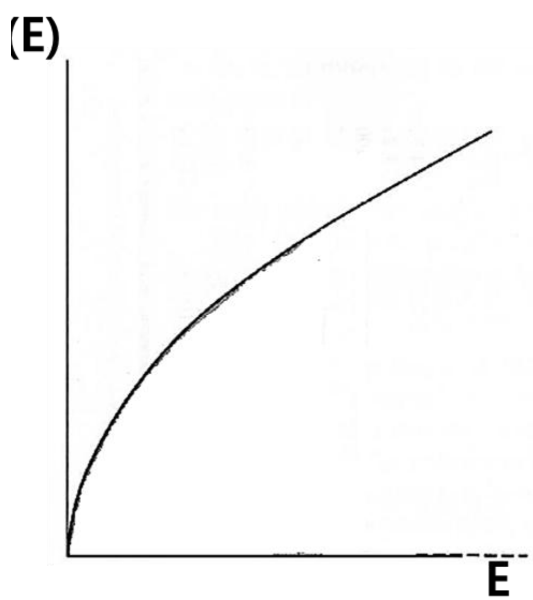
Electrons in a solid – Quantum Gas

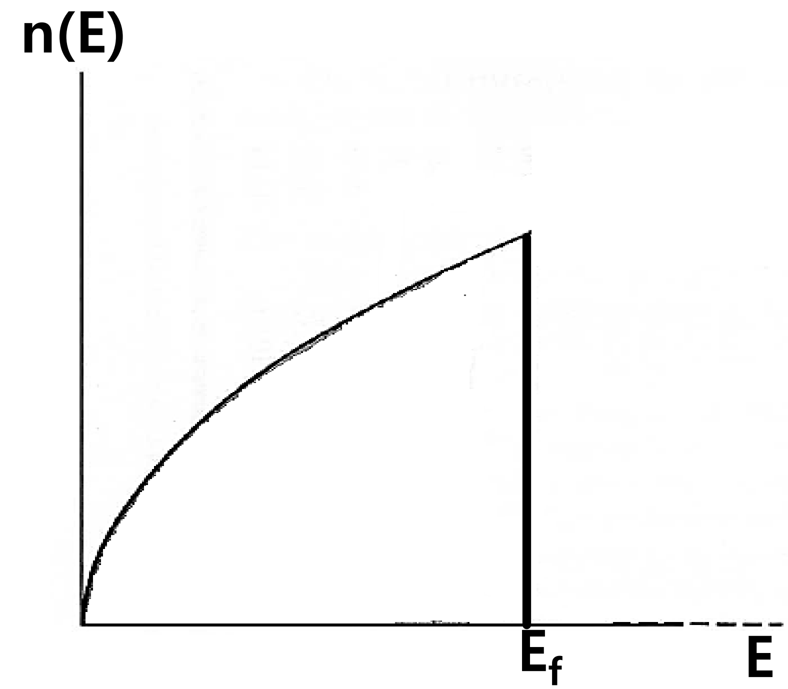
No. of electrons having energy E

$n(E) = g(E)\, f(E)$

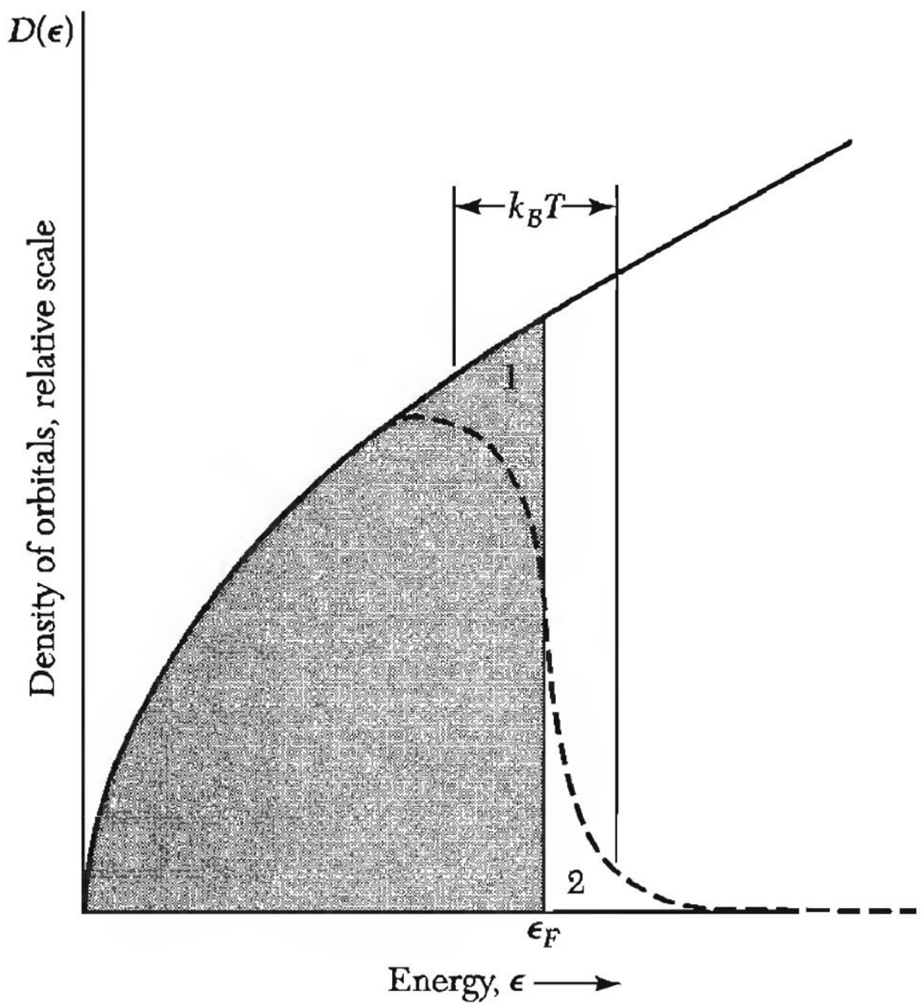
At T = 0 K







Electrons in a solid – Quantum Gas



Only electrons near the Fermi level (E_f) contribute to the conduction/transport phenomenon.

Velocity of conduction electrons
= v_f = Fermi velocity

Total energy, $$E = 2 \sum_{k<k_F} \frac{\hbar^2}{2m} k^2.$$

Solving for ground state energy per electron
= E/N

$$\frac{E}{N} = \frac{3}{10} \frac{\hbar^2 k_F^2}{m} = \frac{3}{5} \varepsilon_F.$$

Energy of conduction electrons in solids is independent of temperature.

Numerical Problem

Determine the kinetic energy, velocity, and momentum for conduction electrons in Silver. Also, determine its Fermi temperature and average energy per electron. (E_f = 5.5 eV)

$E = E_f$

$E_f = (mv_f^2)/2$

$1\ \text{eV} = 1.6 \times 10^{-19}\ \text{J},\ m = 9.1 \times 10^{-31}\ \text{kg}$

$P_f = mv_f$

$E = k_B T$

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

$$\bar{E} = \frac{3}{5} E_f$$