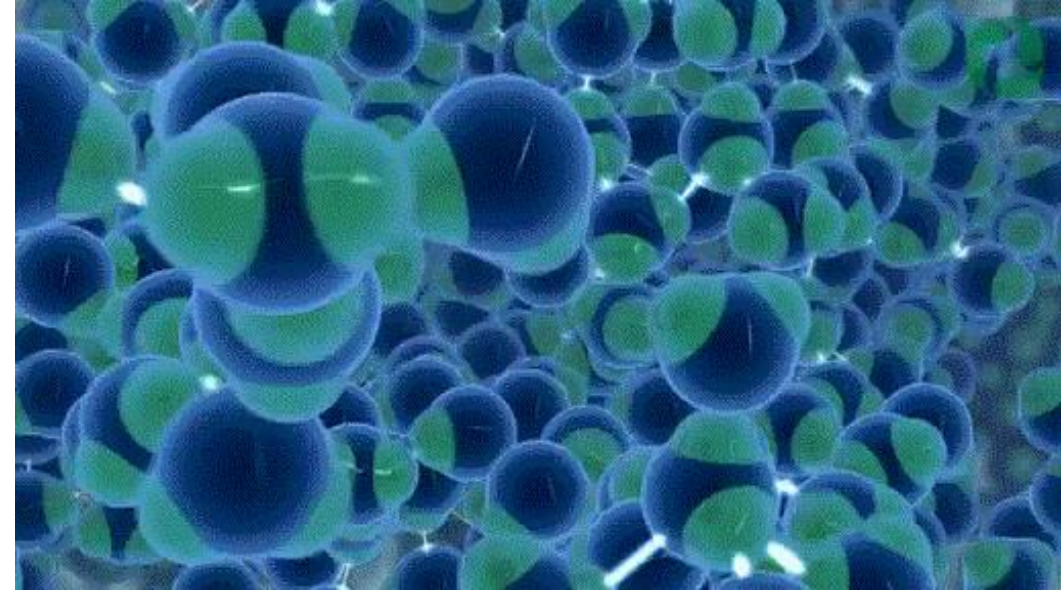# PEN205
MODERN PHYSICS

Molecules and Solids – II

Prof. Dr. H. Gül YAĞLIOĞLU – Dr. Öğr. Üyesi Çağıl KADEROĞLU

OUTLINE

- Molecular Bonds

- Energy States and Spectra of Molecules

- Bonding in Solids

- Free-Electron Theory of Metals

- Band Theory of Solids

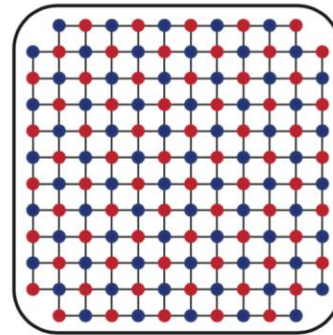- Electrical Conduction in Metals, Insulators, and Semiconductors

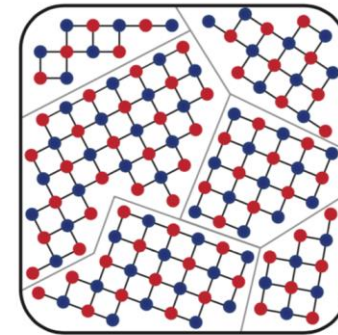# Classification of Solids

Crystalline Solids

Monocrystalline (Single Crystal)

Polycrystalline

Amorphous Solids

Crystalline

Polycrystalline
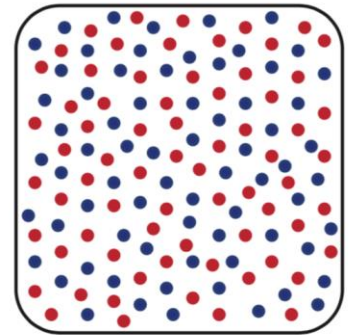
Amorphous

Crystalline Solids

grain boundary
grain
50 μm

→ consists of a large number of atoms arranged in a regular array, forming a periodic structure.

Monocrystalline (Single Crystal): crystal lattice of the entire sample is continuous and unbroken to the edges of the sample, with no grain boundaries.

Polycrystal: materials made up of an aggregate of many small single crystals (also called crystallites or grains).

The grains are usually 100 nm - 100 microns in diameter.

Polycrystals with grains that are <10 nm in diameter are called *nanocrystalline*

The Arkenstone, iRocks.com
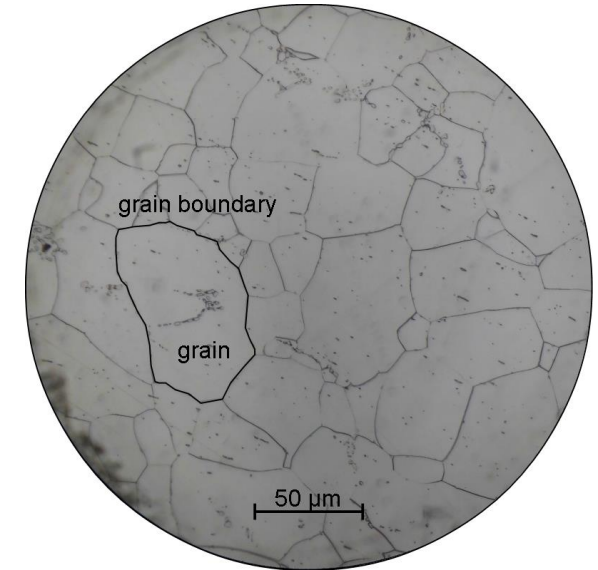
Amorphous (non-crystalline) Solids

→ composed of randomly orientated atoms, ions, or molecules that do not form defined patterns or lattice structures.

AMORPHOUS SOLIDS	CRYSTALLINE SOLIDS
Amorphous solids do not have an ordered structure	Crystalline solids have an ordered structure
Do not have a sharp melting point	Have a sharp melting point
Have no characteristic heat of fusion	Have a definite heat of fusion
Isotropic since they have the same physical properties in all directions	Anisotropic since their physical properties are different in different directions
Have covalently bonded networks	Have covalent bonds, ionic bonds, van der Waal's bonds and metallic bonds

Bonds in Solids

Let's remember the bonding types in/between molecules from previous lesson;

Primary Bonds → (Chemical bonds, strong)
- Ionic
- Covalent
- Metallic

Secondary Bonds→ (Physical bonds, weaker)
- Van der Waals
- Hydrogen

Three different types of chemical (primary) bonds are found in solids.
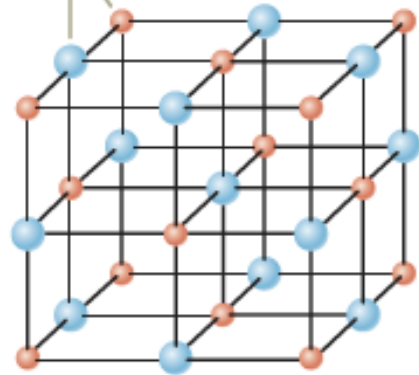
Depending on the bond structure solids are classified into three category →

- Ionic solids
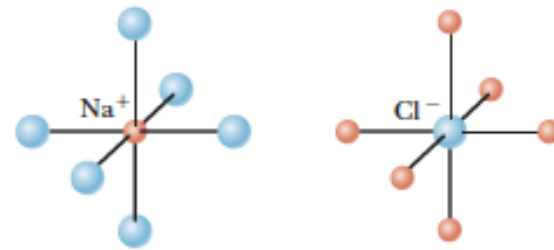- Covalent solids
- Metallic solids

Ionic Solids

the dominant interaction between ions is the **<u>Coulomb force</u>**

The blue spheres represent Cl⁻ ions, and the red spheres represent Na⁺ ions.

Crystalline structure of NaCl

- Each positive sodium ion (Na^+) is surrounded by six negative chlorine ions (Cl^-);

$$\text{Attractive potential energy} = -6\frac{k_e e^2}{r}$$

k_e : Coulomb constant
r : Separation distance between each Na^+ and Cl^-

- Also, there are 12 next-nearest-neighbor Na^+ atoms for every Na^+ ;

$$\text{Repulsive potential energy} = 12\frac{k_e e^2}{\sqrt{2}r}$$

The net effect of all these interactions is a <u>resultant negative electric potential energy</u> : $\boxed{U_{attractive} = -\alpha k_e \frac{e^2}{r}}$ α: Modelung constant
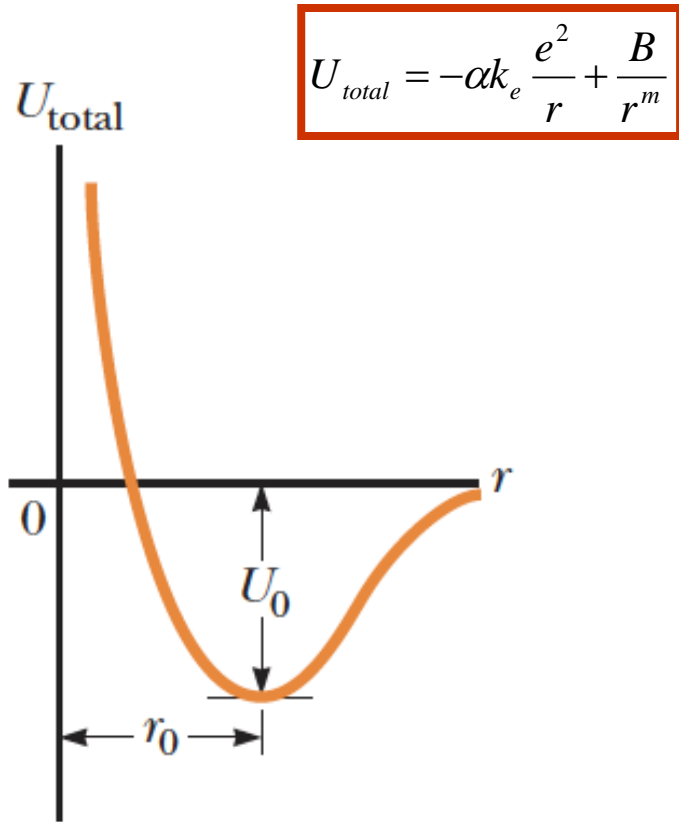
If atoms get very close to each other, inner shells try not to come closer due to exclusion principle.

→ Repulsive potential energy term: $\boxed{U_{repulsive} = \frac{B}{r^m}}$ ⟶ A small integer number

$$\boxed{U_{total} = -\alpha k_e \frac{e^2}{r} + \frac{B}{r^m}}$$

U_{total}

$$U_{total} = -\alpha k_e \frac{e^2}{r} + \frac{B}{r^m}$$

Total potential energy versus ion separation distance for an ionic solid;

U_0 : ionic cohesive energy
r_0: equilibrium separation distance between ions

The potential energy has its minimum value (U_0) at the equilibrium separation $r = r_0$

This minimum energy U_0 is called the **ionic cohesive energy.**

(Its value for NaCl is -7.84 eV per ion pair)

$$|U_0| : \begin{array}{l} \text{Required energy to break the solid} \\ \text{into positive and negative ions} \end{array}$$

atomic cohesive energy: binding energy relative to the energy of the neutral atoms

$Na^+ \rightarrow Na$: 5.14 eV

$Cl^- \rightarrow Cl$: 3.62 eV

atomic cohesive energy of NaCl : − 7.84 + 5.14 − 3.62 = -6.32 eV

Properties of Ionic Solids;

Properties of some ionic solids

Crystal	Equilibrium Separation (Å)	Atomic Cohesive Energy (eV per atom pair)	Melting Point (K)
LiF	2.01	8.32	1143
NaCl	2.82	6.31	1074
RbF	2.82	7.10	1068
KCl	3.15	6.48	1043
CsI	3.95	5.36	621

• stable and hard crystals

• poor electrical conductors → because no available free electrons

• fairly high melting and boiling points → high thermal energy must be added to the crystal to overcome the large cohesive energy.

• transparent to visible radiation → the shells formed by the electrons in ionic solids are so tightly bound that visible radiation does not possess sufficient energy to promote electrons to the next allowed shell.

• infrared radiation is absorbed strongly → the vibrations of the ions have natural resonant frequencies in the low-energy infrared region.

• generaly quite soluble in polar liquids such as water → The water molecule, which has a permanent electric dipole moment, exerts an attractive force on the charged ions, which breaks the ionic bonds and dissolves the solid.

Covalent (Network) Solids

→ Solids that are held together by covalent bonds.

From previous lesson → the covalent bond is very strong. So, they have localized electrons (shared between the atoms) and the atoms are arranged in fixed geometries.

electronic configuration of atomic carbon : $1s^2 2s^2 2p^2$

it lacks four electrons with respect to a filled shell ($2p^6$).

So, in the diamond structure, each carbon atom is covalently bonded to four other carbon atoms to form a stable closed-shell structure.
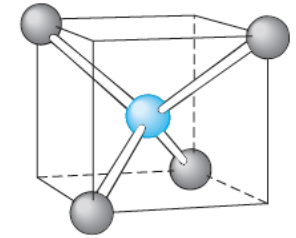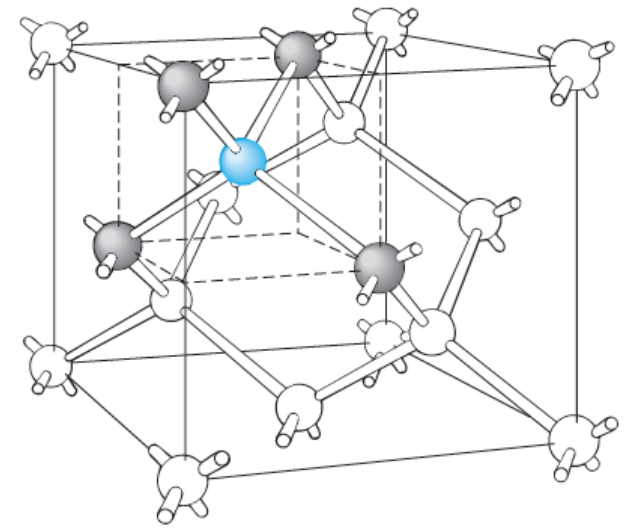
Carbon is interesting → it can form several different types of structures;

Graphite   Graphene   Carbon nanotube   Fullerene   Diamond
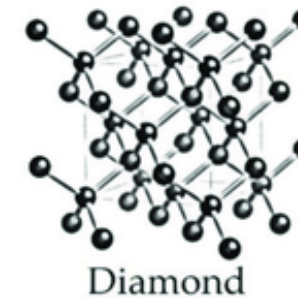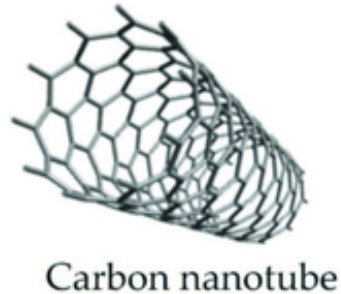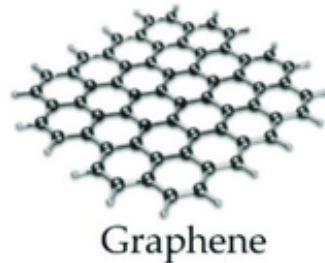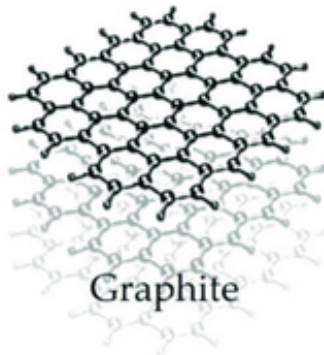
Properties of some covalent solids

Properties of some ionic solids

Crystal	Atomic Cohesive Energy (eV/atom)*	Melting Point (K)
C (diamond)	7.37	~4000
SiC	6.15	2870
Si	4.63	1687
Ge	3.85	1211

Crystal	Equilibrium Separation (Å)	Atomic Cohesive Energy (eV per atom pair)	Melting Point (K)
LiF	2.01	8.32	1143
NaCl	2.82	6.31	1074
RbF	2.82	7.10	1068
KCl	3.15	6.48	1043
CsI	3.95	5.36	621

Since covalent atomic cohesive energies are given in electron volts per atom, they should be multiplied by 2 for a proper comparison

the covalent atomic cohesive energies are greater than for ionic solids

In general, covalently bonded solids are very hard and have high melting points → high cohesive energy

good insulators → the electrons are tightly bound in localized bonds.

many covalent solids do not absorb visible light and so appear transparent → electrons are so tightly bound there is insufficient energy in visible light to raise electrons to excited states.
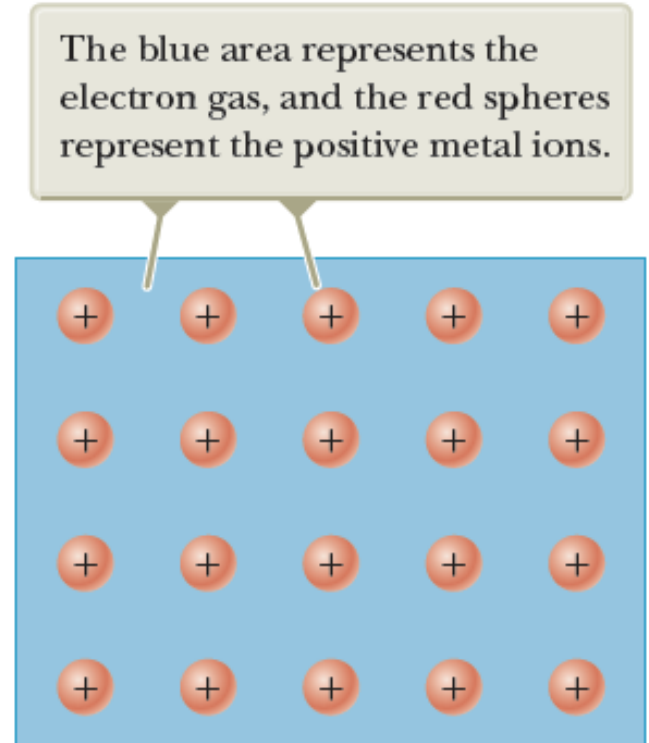
Metallic Solids

The outer electrons in the atoms of a metal are relatively free to move throughout the material, and the number of such mobile electrons in a metal is large.

The metallic structure can be viewed as a "sea" or a "gas" of nearly free electrons surrounding a lattice of positive ions.

The bonding mechanism in a metal is the attractive force between the entire collection of positive ions and the electron gas.

cohesive energy ~ 1–4 eV per atom (< ionic or covalent solids)

The blue area represents the electron gas, and the red spheres represent the positive metal ions.

Crystal	Atomic Cohesive Energy (eV/atom)*	Melting Point (K)
Fe	4.28	2082
Cu	3.49	1631
Au	3.81	1338
Ag	2.95	1235
Pb	2.04	874
Zn	1.35	693

- high electrical conductivity

- the nondirectional nature of the metallic bond allows many different types of metal atoms to be dissolved in a host metal in varying amounts ➔ ALLOYS

- nonmetallic solids tend to fracture when stressed. Fracturing results because bonding in nonmetallic solids is primarily with nearest-neighbor ions or atoms.

but

bonding in metals is between all the electrons and all the positive Ions → metals tend to bend when stressed

Why do metallic surfaces look shiny?

Light interacts strongly with the free electrons in metals.

Hence, visible light is absorbed and re-emitted quite close to the surface of a metal, which accounts for the shiny nature of metal surfaces.

- Crystals of a given material form when the liquid state of that material is cooled sufficiently.

    eg. water forms crystals when cooled to 0 °C.

- if a liquid is cooled slowly → more perfect crystals form
    Slow cooling allows the molecules to relax gradually to states having minimum potential energy.

- rapid cooling of a liquid → causes many dislocations in the resulting lattice structure.
    If the cooling is rapid enough, almost any liquid can form an amorphous solid (or glass) without long-range order
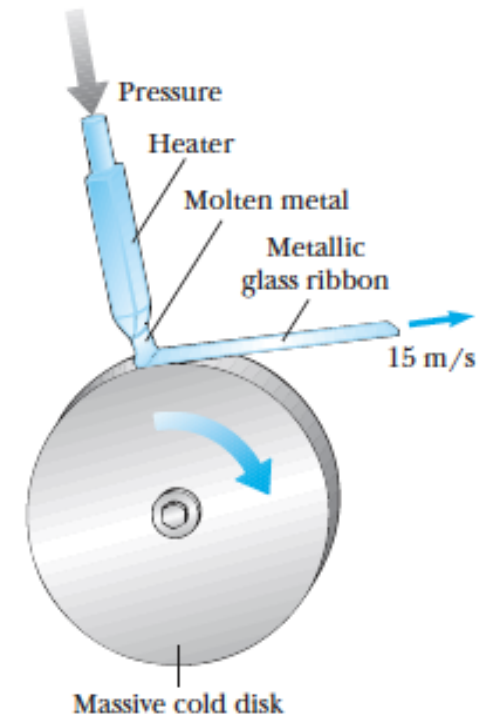

Crystal   Glass   Gas
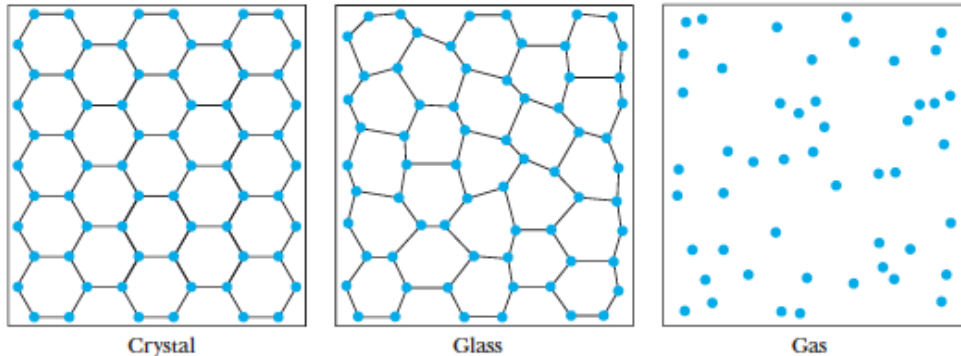
amorphous solid ;

→ there is no long-range order

→ there is extensive short-range order

➜ **Metals can be made to solidify in an amorphous form (called a metallic glass) if the metal in the liquid state can be cooled by 1000 K in about 1 millisecond.**

Pressure
Heater
Molten metal
Metallic glass ribbon
15 m/s
Massive cold disk

The main experimental techniques for determining the distribution of atoms in crystalline and amorphous solids ;

- x-ray diffraction
- electron diffraction
- neutron diffraction.

Preparing an amorphous metal ribbon by **melt spinning**

Free-Electron Theory of Metals

discovery of e⁻ → 1897, Thomson

Drude and Thomson proposed the free electron theory of metals

According to this theory, a metal is modeled as a classical gas of
conduction electrons moving through a fixed lattice of ions.

predicts the correct functional
form of Ohm's law

not predict the correct values of
electrical and thermal conductivities

shortcomings of the classical model can be remedied only by taking
into account the wave nature of the electron

(quantum particle under boundary conditions analysis model)

- outer-shell electrons are free to move through the metal
  (mobile electrons)

- Mobile electrons trapped within a three-dimensional box
  formed by the metal surfaces. Therefore, each electron is
  represented as **a particle in a box**.

In order to relate <u>microscopic properties to macroscopic properties</u>, statistical physics can be applied.

In the case of electrons, it is necessary to use <u>quantum statistics</u>;

Statistics of Particles

In dealing with large number of particles, we are interested only in the statistical behavior of the group as a whole, rather than in the behavior of each individual particle.

In determining the statistical behavior of particles, we must consider the laws of probabilities they obey. There are three distribution laws determining the distribution of particles among available energy states:

Maxwell - Boltzmann	Bose - Einstein	Fermi - Dirac
Identical distinguishable	Indistinguishable no Pauli principle	Indistinguishable Pauli principle
Classical particles	bosons	fermions
Any spin Ψ do not overlap	Spin 0,1,2,… Ψ overlap Ψ symmetric	Spin 1/2, 3/2, 5/2, … Ψ overlap Ψ antisymmetric
e.g. gas molecules	e.g. cavity photons (laser) Liquid He at low T	e.g. free e^- in metals e^- in white dwarfs
Unlimited number of particles per state	Unlimited number of particles per state	Never more than 1 particle per state

At low particle concentrations and high temperature, most systems are well described by Maxwell–Boltzmann statistics.

Exclusion Principle → each state of the system can be occupied by only two electrons (↑↓)

For electrons; Fermi-Dirac Statistics

At a given temperature T, the probability of finding an electron on a given state with energy E is given by
Fermi-Dirac distribution function:
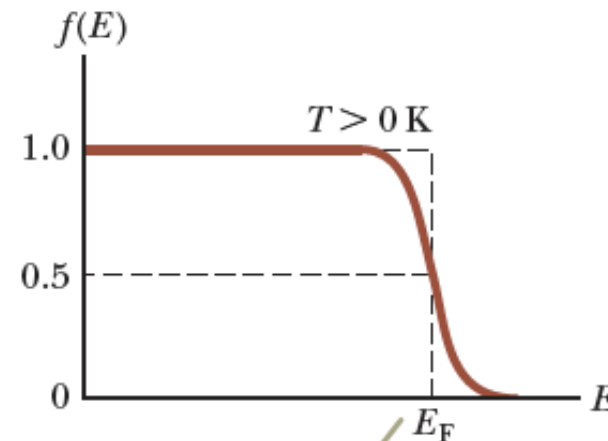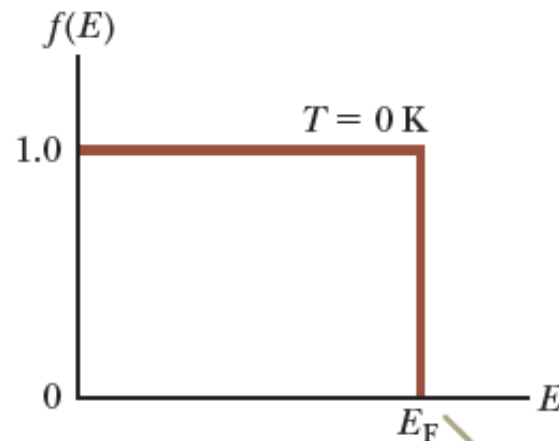
$$f(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1}$$

E_F → Fermi energy

$f(E)$ → Fermi-Dirac distribution function

Probability of each state to be filled is $f(E)$

$f(E) = 1$ for $E < E_F$

$f(E) = 0$ for $E > E_F$

The energy E_F is the Fermi energy.

all states having energies less than the Fermi energy are occupied and all states having energies greater than the Fermi energy are vacant.

Because of thermal excitation, states near and below E_F lose population and states near and above E_F gain population.

The Fermi energy E_F also depends on temperature, but the dependence is weak in metals.
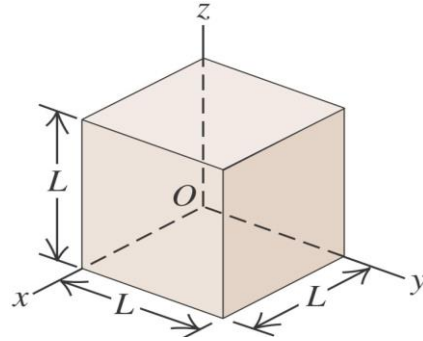
Remember from previous lessons;

if a particle of mass m is confined to move in a one-dimensional box of length L, the allowed states have quantized energy levels

$$E_n = \left(\frac{h^2}{8mL^2}\right)n^2 = \left(\frac{\hbar^2\pi^2}{2mL^2}\right)n^2 \quad n = 1, 2, 3, \ldots$$

Lets imagine ;

- A piece of metal in the shape of a solid cube of sides L and volume L³
- focus on one electron that is free to move anywhere in this volume

$$E = \frac{\hbar^2\pi^2}{2m_e L^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

Quantum numbers

Therefore, the electron is modeled as a particle in a three-dimensional box →

$$n_x = n_y = n_z = 1 \quad\longrightarrow\quad 3\hbar^2\pi^2/2m_e L^2$$

For ground state

This energy level can be occupied by two electrons (↑↓)

L is macroscopic → energy levels for the electrons are very close together → quantum numbers can be treated as continuous variables

Under this assumption, the number of allowed states per unit volume that have energies between E and E + dE is ;

$$g(E)\,dE = \frac{8\sqrt{2}\,\pi m_e^{3/2}}{h^3}E^{1/2}\,dE$$

density-of-states function

If a metal is in thermal equilibrium;

the number of electrons per unit volume N(E) dE that have energy between E and E + dE	=	product of the number of allowed states per unit volume and the probability that a state is occupied

$$N(E) \, dE = g(E)f(E) \, dE$$

$$N(E) \, dE = \left(\frac{8\sqrt{2}\,\pi m_e^{3/2}}{h^3} E^{1/2} \right) \left(\frac{1}{e^{(E-E_F)/k_B T} + 1} \right) dE$$

$$n_e = \int_0^\infty N(E) \, dE = \frac{8\sqrt{2}\,\pi m_e^{3/2}}{h^3} \int_0^\infty \frac{E^{1/2} \, dE}{e^{(E-E_F)/k_B T} + 1}$$

← total number of electrons per unit volume

At T = 0 K → $$n_e = \frac{8\sqrt{2}\,\pi m_e^{3/2}}{h^3} \int_0^{E_F} E^{1/2} \, dE = \frac{2}{3} \frac{8\sqrt{2}\,\pi m_e^{3/2}}{h^3} E_F^{3/2}$$

$$E_F(0) = \frac{h^2}{2m_e} \left(\frac{3n_e}{8\pi} \right)^{2/3}$$

Fermi energy at 0 K

Kinetic energy of an electron at Fermi level : $\dfrac{1}{2}mv_f^2 = E_F$

Fermi velocity

Thermal energy of an electron at Fermi level: $k_B T = E_F$

Fermi temperature

Table 10.1 Calculated Values of Various Parameters for Metals Based on the Free Electron Theory

Metal	Electron Concentration (m^{-3})	Fermi Energy (eV)	Fermi Speed (m/s)	Fermi Temperature (K)
Li	4.70×10^{28}	4.72	1.29×10^6	5.48×10^4
Na	2.65×10^{28}	3.23	1.07×10^6	3.75×10^4
K	1.40×10^{28}	2.12	0.86×10^6	2.46×10^4
Cu	8.49×10^{28}	7.05	1.57×10^6	8.12×10^4
Ag	5.85×10^{28}	5.48	1.39×10^6	6.36×10^4
Au	5.90×10^{28}	5.53	1.39×10^6	6.41×10^4
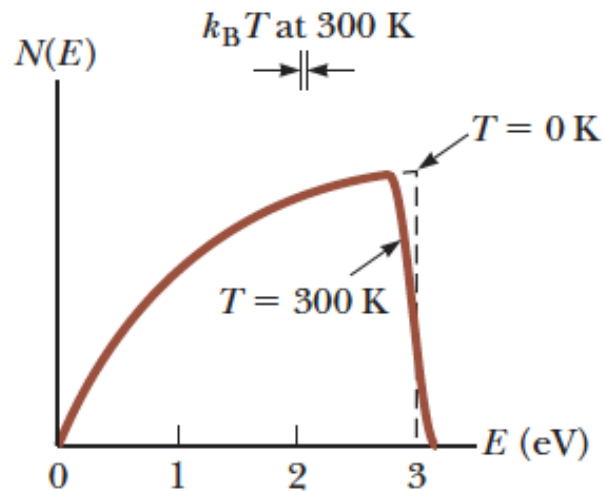
Free Electron Theory of Metals-Summary:

➢ Metals have many free electrons and energy levels.

➢ Electrons occupy these levels from $E=0$ to E_F.

➢ All the energy levels are filled bellow Fermi level at T=0K.

➢ All the energy levels are empty above Fermi level at T=0K.

➢ Energy levels are quantized but they are so close to each other that they are considered continuous.

➢ A small fraction of free electrons are excited above Fermi energy level at T=300K.

EXAMPLE: Assuming each gold atom contributes one free electron to the Fermi gas, find
     a) Fermi energy
     b) Fermi velocity,
     c) Fermi temperature of gold.

(Free electron density of gold $n_e=5,9x10^{28}$ m^{-3})

a)
$$E_F(0) = \frac{h^2}{2m_e}\left(\frac{3n_e}{8\pi}\right)^{2/3} = \frac{(6,626\times10^{-34}\,J.s)^2}{2(9,11\times10^{-31}\,kg)}\left(\frac{3\times5,9\times10^{28}\,m^{-3}}{8\pi}\right)^{2/3}$$

$$E_F(0) = 8,85\times10^{-19}\,J = 5,53eV$$

b)
$$v_f = \sqrt{2\frac{E_F}{m_e}} = \sqrt{\frac{2\times5,58\times10^{-19}\,J}{9,11\times10^{-31}\,kg}} = 1,39\times10^6\,m/s$$

c)
$$T_F = \frac{E_F}{k_B} = \frac{8,85\times10^{-19}\,J}{1,38\times10^{-23}\,J/K} = 6,41\times10^4\,K$$

A **gas of classical particles** would have to be heated to about 64,000 K to have an average energy per particle equal to the Fermi energy at 0 K!

Band Theory of Solids

(a)

(b)

(c)

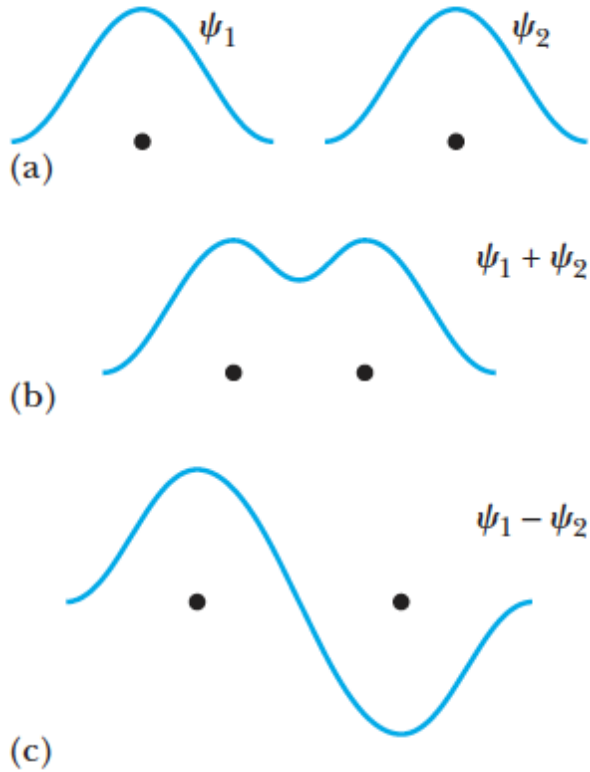Let's consider an atom that has a single *s* electron outside of a closed shell.

Both of the following wave functions are valid for such an atom with atomic number Z

$$\psi_s^+(r) = +Af(r)e^{-Zr/na_0} \qquad \psi_s^-(r) = -Af(r)e^{-Zr/na_0}$$

Choosing either of these wave functions leads to the same value of probability density $|\Psi|^2$

both choices are equivalent !

**But, a difference arises when two atoms are combined → (b) and (c)**

➢ The positive–positive curve shows some probability of finding the electron at the midpoint between the atoms.
(the electron is more tightly bound - has lower energy)

➢ The positive–negative function shows no such probability.
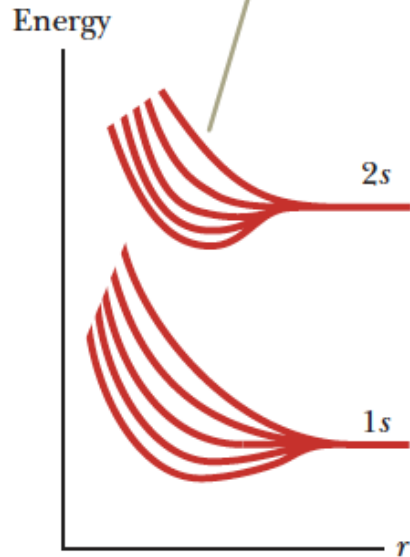(the electron is less tightly bound - has higher energy)

Energies of them are different!

Therefore, the **states are split into two** energy levels due to the two ways of combining the wave functions.
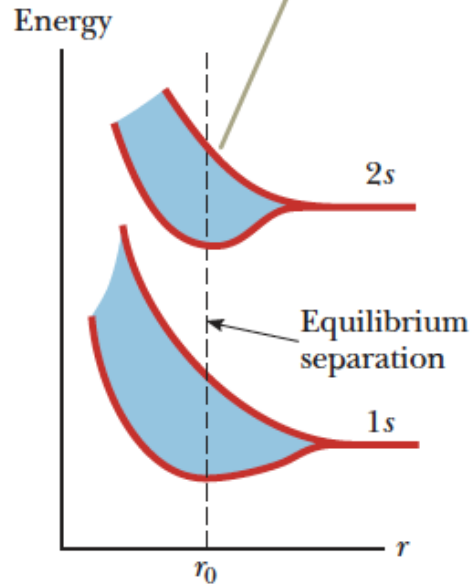
When two atoms are brought together, the 1s and 2s levels split into two components.
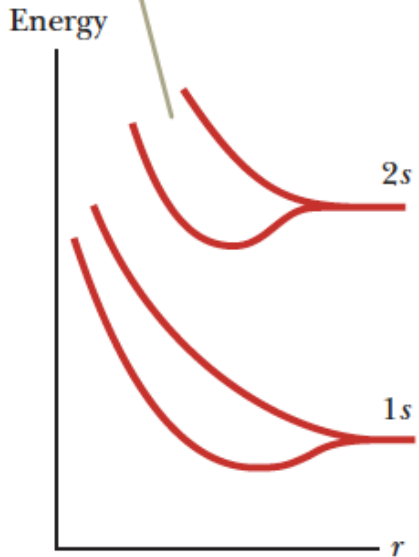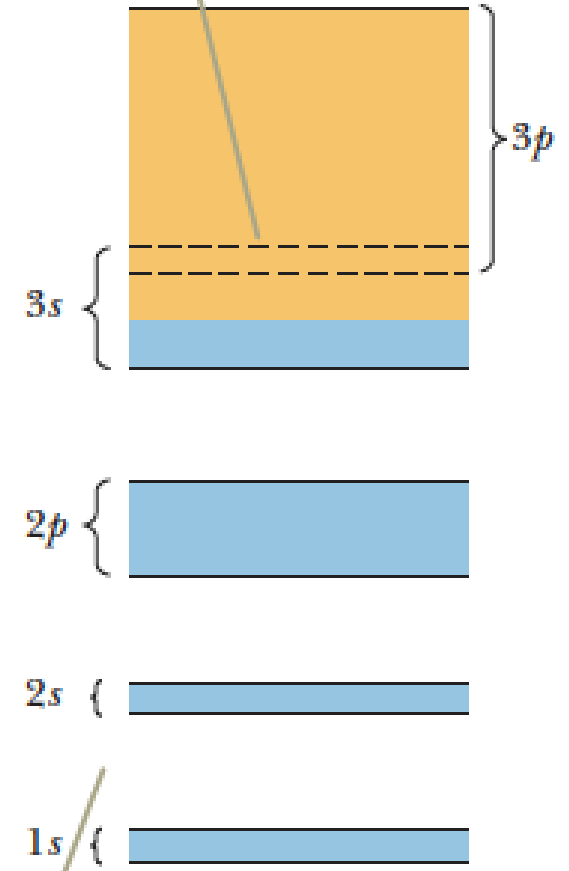
When five atoms are brought together, the 1s and 2s levels split into five components.

When a large number of atoms are brought together, the 1s and 2s levels spread into energy bands.

In some cases, the energy bands of previously separated atomic states overlap.

Energy

2s

1s

r

Energy

2s

1s

r

Energy

2s

Equilibrium separation

1s

r

r_0

3p

3s

2p

ENERGY

2s

1s

There are no states for electrons to occupy in the energy gaps.

splitting effect as a function of separation distance;

- For large separations r, the electron clouds do not overlap and there is no splitting.

- For small separations, the electron clouds overlap

- As the number of atoms grows, the number of combinations of wave functions grows

EXAMPLE: Lets consider 1 cm^3 of Silicon. How many atoms does this contain?

The atomic mass of silicon is 28.1 g

Avagadro's number N is 6.02 x 10^{23} atoms/mol

The density of silicon: 2.3 x 10^3 kg/m^3

so 1 cm^3 of silicon weighs 2.3 gram and so contains

$$\frac{6.02 \times 10^{23}}{28.1} \times 2.3 = 4.93 \times 10^{22} \, atoms$$

This means that in a piece of silicon just 1 cm^3 in volume , each electron energy-level has split up into 4.93 x 10^{22} smaller levels !

# Electrical Conduction in Metals, Insulators, and Semiconductors

Metal

- Kinetic energy of electrons increase with the electrical field.
- Electrons are excited to empty states in the band.
- Electrons near Fermi level are excited with a little energy.
- Conduction gets lower with temperature.
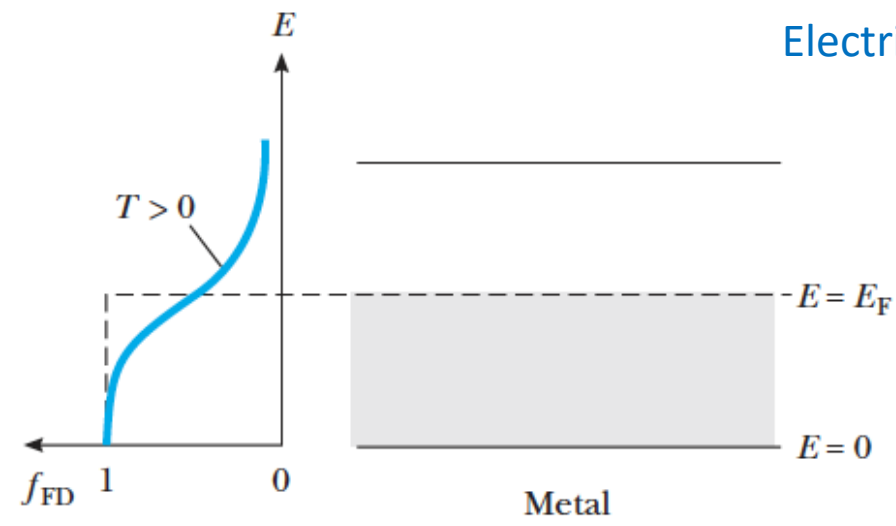
- Room temperature is $T=300K$ → $kT=0,025\ eV$, therefore it is difficult to excite electrons thermally to the conduction band.
- Although there are many empty energy levels in conduction band only a few electrons can be excited to there.

Insulator
$E_g \approx 10\ eV$
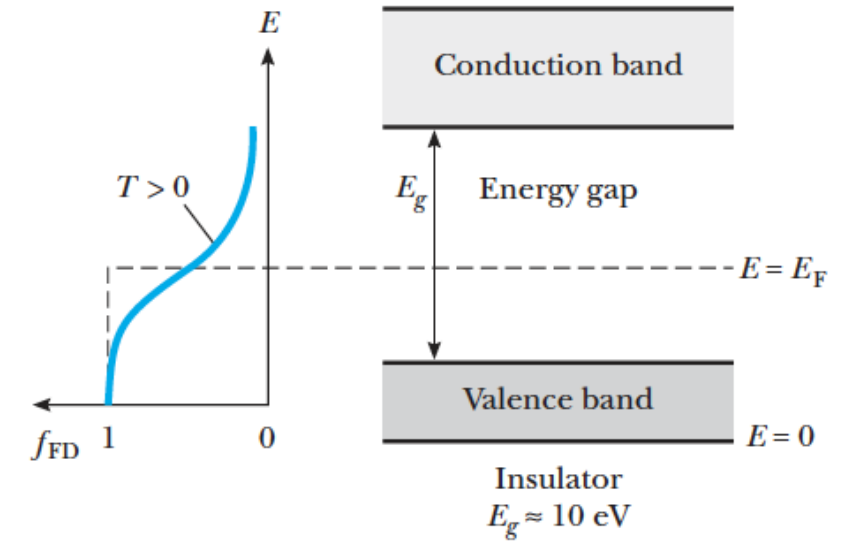
- All the electrons are in valance band at T=0K.
- They are not good conductor at low temperature.
- Electrons can be excited to conduction band thermally.
- Conductivity increases with temperature.

Semiconductor
$E_g \approx 1\ eV$
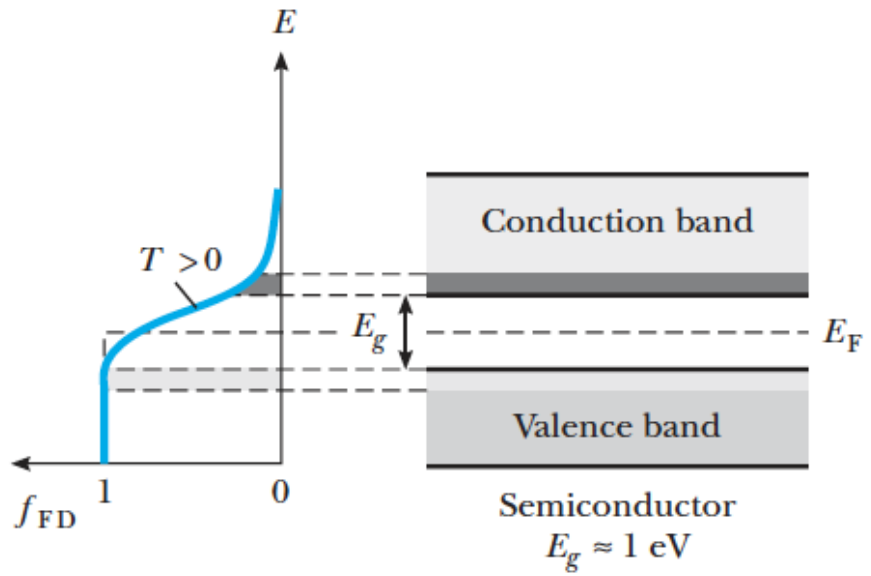
Homework:

Doped Semiconductors

Semiconductor Devices