MD. ANISUR RAHMAN
Assistant Professor of Physics
University of Asia Pacific

Crystalline and amorphous Solids

The solids in which the constituent particles of matter are arranged and organized in a specific manner are called Crystalline Solids. Crystalline Solids are also known as True Solids as they don't tend to flow like pseudo solids. As crystalline solids have low potential energy, they are the most stable form of solids. Almost all solids fall in the category of crystalline solids including metallic elements (iron, silver, and copper) and non-metallic elements (Phosphorus, Sulphur, and iodine).

The solids in which the constituent particles of matter are arranged in a random manner are called amorphous solids. Amorphous Solids are also called Pseudo-solids or Supercooled Liquids because they don't form crystalline structure and has the ability to flow. Most solids are amorphous in nature. One of the most common examples of amorphous solids is glass.
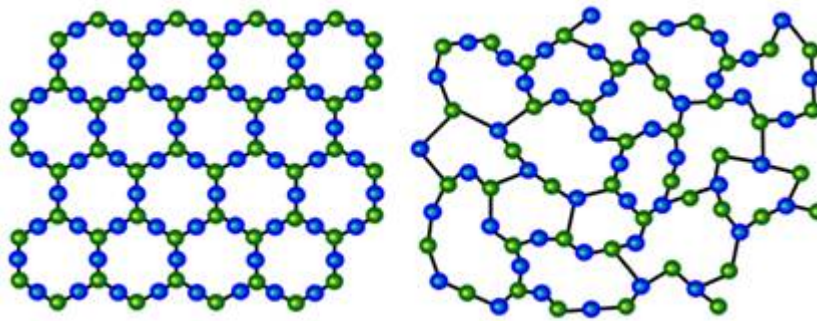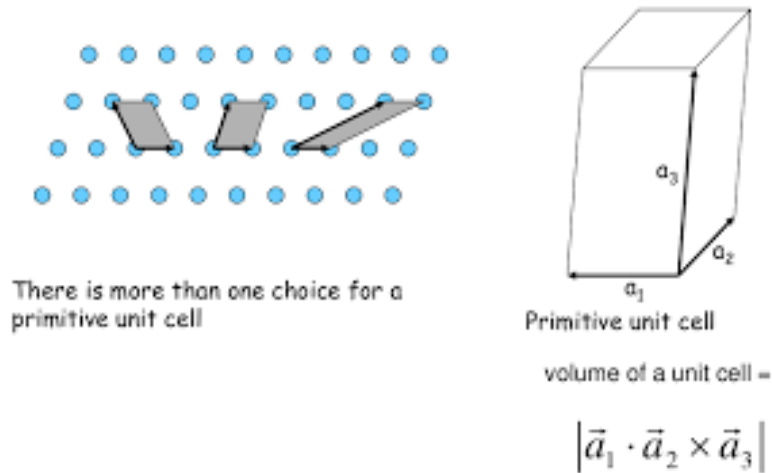

Single and polycrystalline solids

Single crystals have infinite periodicity, polycrystals have local periodicity, and amorphous solids (and liquids) have no long-range order. An ideal single crystal has an atomic structure that repeats periodically across its whole volume. Even at infinite length scales, each atom is related to every other equivalent atom in the structure by translational symmetry.

A polycrystalline solid or polycrystal is comprised of many individual grains or crystallites. Each grain can be thought of as a single crystal, within which the atomic structure has long-range order.
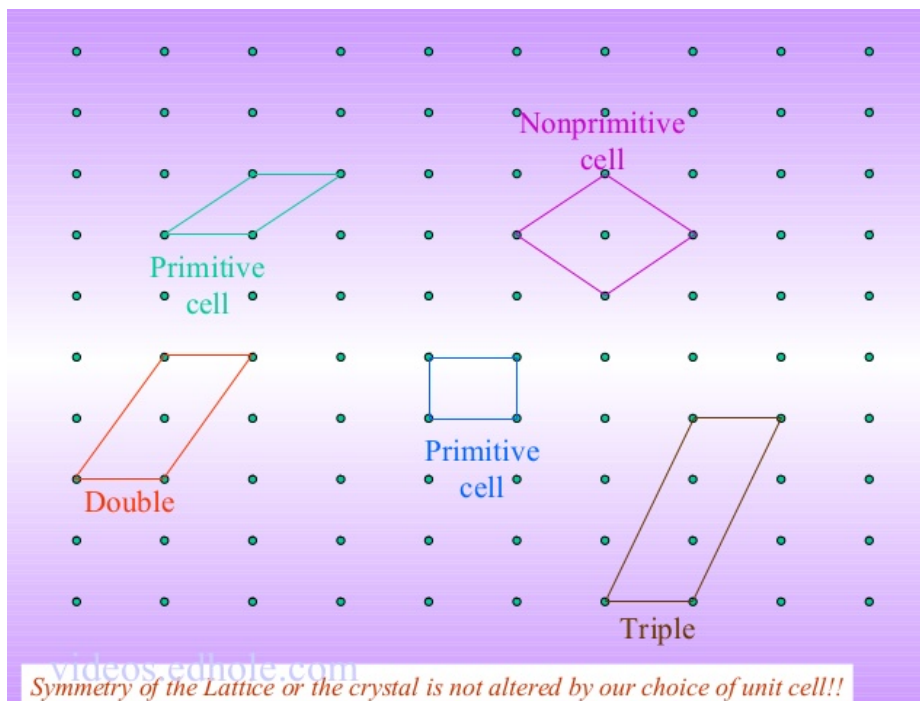

Single crystal	Polycrystal	Amorphous solid
Periodic across the whole volume.	Periodic across each grain.	Not periodic.
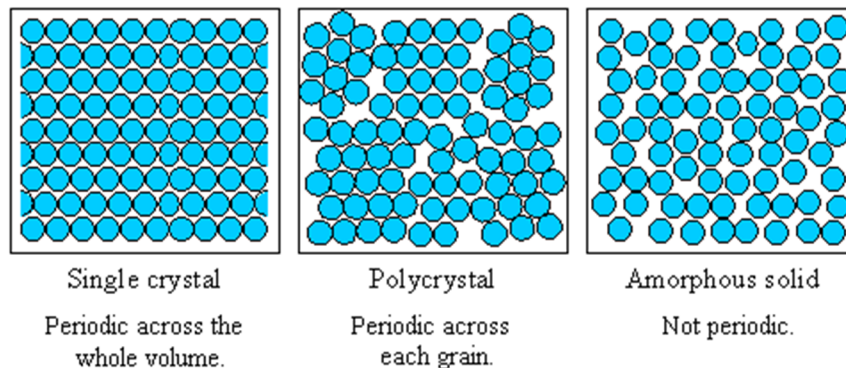
Unit cell

The smallest group of particles in the material that constitutes the repeating pattern is the unit cell of the structure. The unit cell completely defines the symmetry and structure of the entire crystal lattice.

There is more than one choice for a primitive unit cell

Primitive unit cell

volume of a unit cell =

$$\left| \vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3 \right|$$

There are two distinct types of unit cell: primitive and non-primitive. Primitive unit cells contain only one lattice point, which is made up from the lattice points at each of the corners. Non-primitive unit cells contain additional lattice points, either on a face of the unit cell or within the unit cell, and so have more than one lattice point per unit cell.

Nonprimitive cell

Primitive cell

Double

Primitive cell

Triple

videos.edhole.com

Symmetry of the Lattice or the crystal is not altered by our choice of unit cell!!

Crystal system	Bravais lattices			
	primitive	base-centered	body-centered	face-centered
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$				
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = \frac{\pi}{2} \neq \beta$				
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = \frac{\pi}{2}$				
Trigonal $a = b = c$ $\alpha = \beta = \gamma \neq \frac{\pi}{2}$				
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = \frac{\pi}{2}$				
Hexagonal $a = b \neq c$ $\alpha = \beta = \frac{\pi}{2}$ $\gamma = \frac{2\pi}{3}$				
Cubic $a = b = c$ $\alpha = \beta = \gamma = \frac{\pi}{2}$				

A lattice is defined as a discrete but infinite regular arrangement of points (lattice sites) in a vector space. lattices which exhibit a translational symmetry can be represented by any translation vector given by

$$T_{mno} = ma_1 + na_2 + oa_3$$

is referred to as a *Bravais lattice*.

A crystal is defined as a lattice with a basis added to each lattice site. Usually the basis consists of an atom, a group of atoms or a molecule.

It is helpful to classify crystal structures according to its symmetry. Besides the translational symmetry, there is another symmetry known as point symmetry, i.e. the group of symmetry operations that leaves at least one point unchanged. These comprise rotations, reflections, inversions or any combinations of these. They are the basis of the classification of crystals.

The structures of all crystals can be classified according to the symmetry of the unit cells. There are in total 7 groups, collectively called Crystal Systems: Tricinic, Monoclinic, Orthorhombic, Tetragonal, Trigonal, Hexagonal, and Cubic. The Bravais lattices into 7 crystal systems which are defined by the lengths a, b, c and angles α, β, γ between the primitive translation vectors.

Coordination number and packing factor

The coordination number, also called ligancy, of a central atom in a molecule or crystal is the number of atoms, molecules or ions bonded to it. The ion/molecule/atom surrounding the central ion/molecule/atom is called a ligand.

In crystallography, atomic packing factor (APF), packing efficiency or packing fraction is the fraction of volume in a crystal structure that is occupied by constituent particles. It is a dimensionless quantity and always less than unity. By convention, the APF is determined by assuming that atoms are rigid spheres.

For one-component crystals (those that contain only one type of particle), the packing fraction is represented mathematically by

$$\text{atomic packing factor} = \frac{N_{particle} V_{particle}}{V_{unit\ cell}}$$

where $N_{particle}$ is the number of particles in the unit cell, $V_{particle}$ is the volume of each particle, and $V_{unit\ cell}$ is the volume occupied by the unit cell.

Miller Indices (hkl)

The orientation of a surface or a crystal plane may be defined by considering how the plane (or indeed any parallel plane) intersects the main crystallographic axes of the solid. a set of numbers which quantify the intercepts and thus may be used to uniquely identify the plane or surface.

Crystallographic Planes

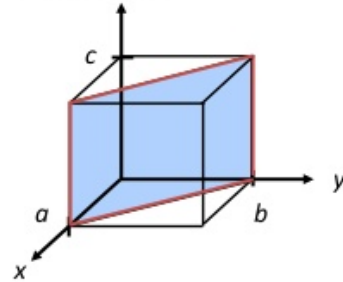|	example	a	b	c
1.	Intercepts	1/2	1	3/4
2.	Reciprocals	1/½	1/1	1/¾
		2	1	4/3
3.	Reduction	6	3	4
4.	Miller Indices	(634)		
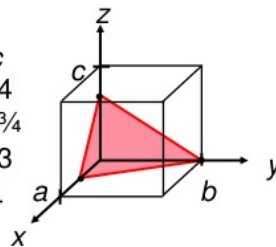
Family of Planes {*hkl*}

Ex: {100} = (100), (010), (001), ($\bar{1}$00), (0$\bar{1}$0), (00$\bar{1}$)

52

Crystallographic Planes

example		a	b	c
1.	Intercepts	1	1	∞
2.	Reciprocals	1/1	1/1	1/∞
		1	1	0
3.	Reduction	1	1	0
4.	Miller Indices	(110)		

example		a	b	c
1.	Intercepts	1/2	∞	∞
2.	Reciprocals	1/½	1/∞	1/∞
		2	0	0
3.	Reduction	2	0	0
4.	Miller Indices	(200)		
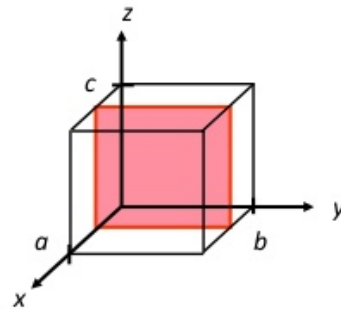
19

Bragg's Law

The atoms in crystals interact with X-ray waves in such a way as to produce interference. The interaction can be thought of as if the atoms in a crystal structure reflect the waves. But, because a crystal structure consists of an orderly arrangement of atoms, the reflections occur from what appears to be planes of atoms.

Let's imagine a beam of X-rays entering a crystal where the spacing between the atomic planes occurs over the distance, d. Wave 2 reflects off of the upper atomic plane at an angle θ equal to its angle of incidence. Similarly, Wave 1 reflects off the lower atomic plane at the same angle θ. The path difference between the two reflected waves along is $BC + BD$.

In the Δ ABC, $sin\theta = \frac{BC}{AB}$

$BC = AB \sin \theta = d \sin \theta$

Similarly, $BD = AB \sin \theta = d \sin \theta$

Path difference $= 2d \sin\theta$

If this path difference is an integral multiple of wavelength, then constructive interference will occur between the reflected beams and they will reinforce each other. Therefore, the reflected

beam to be of maximum intensity, $2d \sin \theta = n\lambda$, where n = 1, 2, 3, etc. This is Bragg's equation and represents Bragg's law.
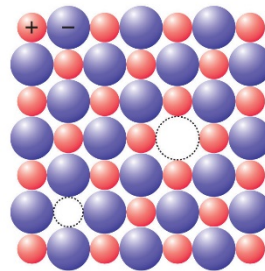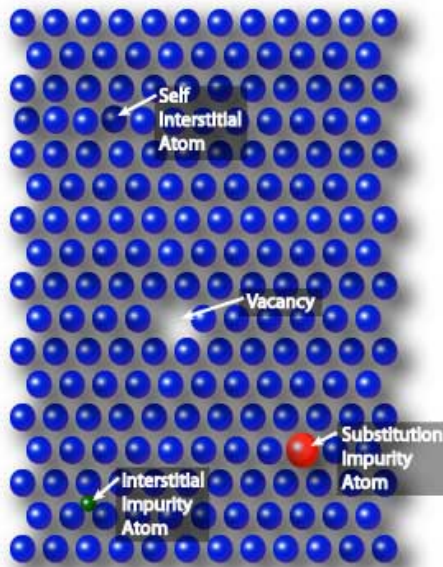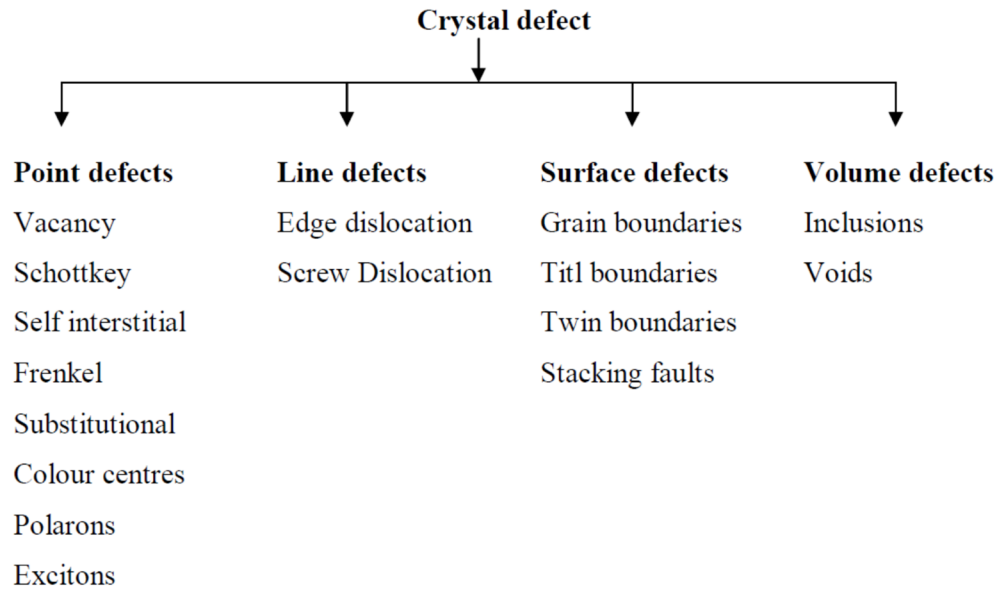

©1998 Encyclopaedia Britannica, Inc.
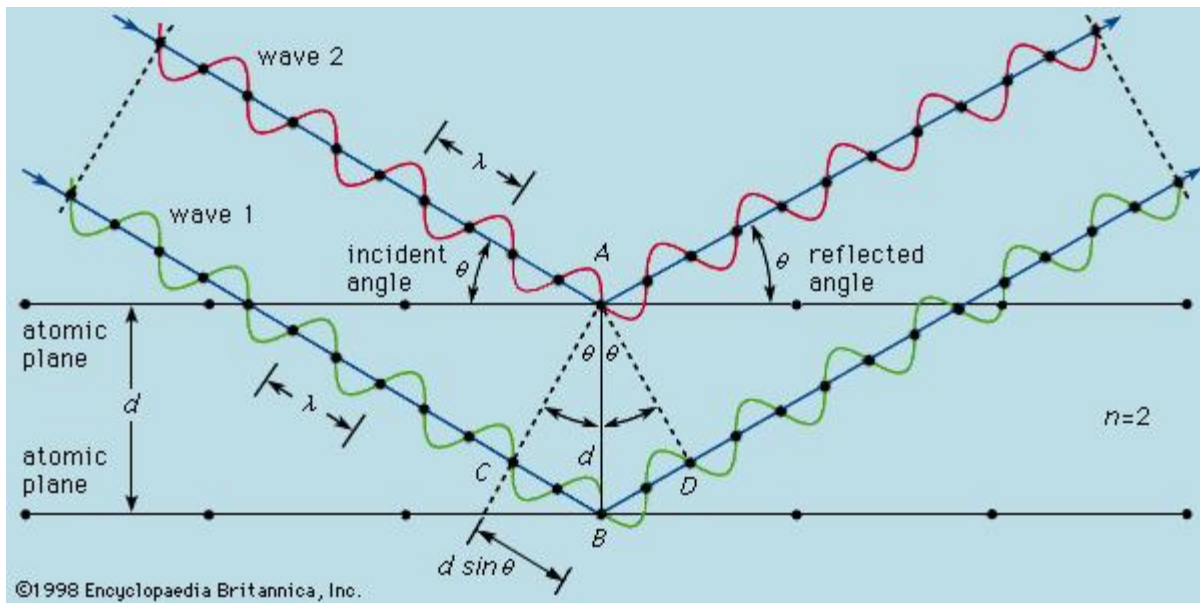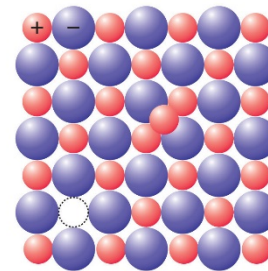
Defects in solids

Any deviation from the perfect atomic arrangement in a crystal is said to contain imperfections or defects. Crystal imperfections have strong influence upon many properties of crystals, such as strength, electrical conductivity and hysteresis loss of ferromagnets. The conductivity of some semiconductors is due entirely to trace amount of chemical impurities. Color, luminescence of many crystals arise from impurities and imperfections. Mechnical and plastic properties are usually controlled by imperfections.

Imperfections in crystalline solids are normally classified according to their dimension as follows
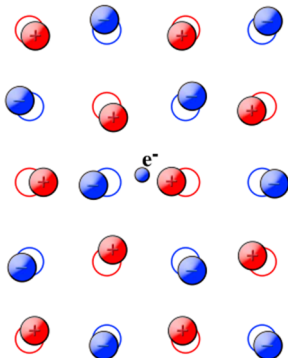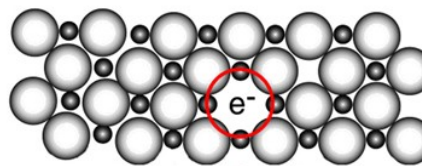
1. Point imperfections (Zero dimensional defects)

2. Line imperfections (one dimensional defects)

3. Plane or surface imperfections (Two dimensional defects)

4. Volume imperfections (three dimensional defects)

Crystal defect

Point defects	Line defects	Surface defects	Volume defects
Vacancy	Edge dislocation	Grain boundaries	Inclusions
Schottkey	Screw Dislocation	Titl boundaries	Voids
Self interstitial		Twin boundaries	
Frenkel		Stacking faults	
Substitutional			
Colour centres			
Polarons			
Excitons			

(a) Schottky defect (b) Frenkel defect

Color Center

MD. ANISUR RAHMAN
Assistant Professor of Physics
University of Asia Pacific

1.   Point Defects

Point defects are where an atom is missing or is in an irregular place in the lattice structure. Point defects include self-interstitial atoms, interstitial impurity atoms, substitutional atoms and vacancies. A **self-interstitial** atom is an extra atom that has positioned itself into an interstitial void in the crystal structure. A **substitutional impurity** atom is an atom of a different type than the bulk atoms, which has replaced one of the bulk atoms in the lattice. The combination of anion cation vacancies (in pairs) is called **Schottkey imperfections**. The combination of a vacancy and interstitial is called a **Frankel imperfection**.

Color centers are point defects associated with trapped electrons or holes in transparent materials. These centers cause the solid to become colored when the electronic ground state of the defect is excited to higher energy states by the absorption of visible light. An F-center or Farbe center (German Farbe means color) is a type of crystallographic defect in which an anionic vacancy is filled by electrons. Color centers can occur when heated to high temperature causing the ions become excited and are displaced from their normal crystallographic positions, leaving behind some electrons in the vacated spaces.

Polaron (Polarization caused by electron) is the electron moving through the constituent atoms of a solid material, causing the neighbouring positive charges to shift toward it and the negative charges to shift away. This distortion of the regular position of electrical charges constitutes a region of polarization that travels along with the moving electron. After the electron passes, the region returns to normal.

Exciton is the combination of an electron and a hole which is free to move through a nonmetallic crystal as a unit. Because the electron and the positive hole have equal but opposite charges, the exciton as a whole has no net electrical charge. When an electron in an exciton recombines with a positive hole, the original atom is restored, and the exciton vanishes. The energy of the exciton may be converted into light or it may be transferred to an electron of a neighbouring atom in the solid. If the energy is transferred to another electron, a new exciton is produced as this electron is forced away from its atom.

2.   Line Imperfections

In   linear defects, groups of atoms are in irregular positions. Any deviation from perfectly periodic arrangement of atoms along a line is called the line imperfection. The line imperfection acting as boundary between the slipped and unslipped region, lies in the slip plane and is called a dislocation. Dislocations are generated and move when a stress is applied.

Two types of dislocations are distinguished as

1. Edge dislocations

2. Screw dislocations.

An **edge dislocation** is a defect where an extra half-plane of atoms is introduced midway through the crystal. When enough force is applied from one side of the crystal structure, this extra plane passes through planes of atoms. The dislocation has two properties, a line direction, which is the direction running along the bottom of the extra half plane, and the Burgers vector which describes the magnitude and direction of distortion to the lattice. **Screw dislocation** is a dislocation in which the atoms are arranged in a helical pattern.
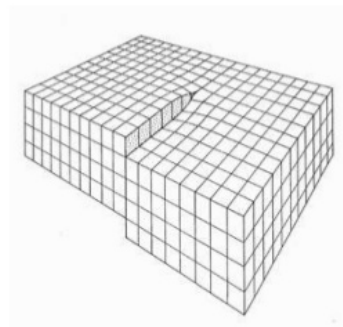
EDGE DISLOCATION

- POSITIVE DISLOCATION
- NEGATIVE DISLOCATION
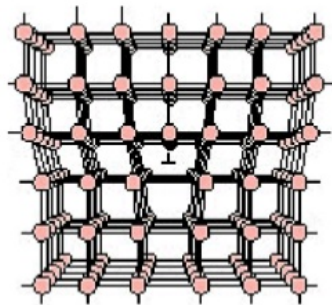
SCREW DISLOCATION

The lattice/atomic planes follow helical or spiral along the dislocation line.

Types of bonding in solids

1. Ionic bond 2. Covalent bond 3. Metallic bond 4. Weak bonds (hydrogen, Van Der Waals etc)

1.   An ionic bonding is the Attractive Force existing between positive ion and a negative ion when they are brought into close proximity or surrounding. They are formed when atoms of different elements lose or gain their electrons in order to achieve stabilized outermost electronic configuration. It forms between a metal and a non-metal. The electron transfer is from less electronegative atom to the more electronegative. Bonding force is the electrostatic attraction between opposite charged ions. Example: Ionic Bonding in NaCl.

Ionic solids are rigid, unidirectional and crystalline in nature. They have high melting and boiling points. Ionic solids are good insulators of electricity in their solid state and good conductor of electricity in their molten state. Ionic solids are soluble in water and slightly soluble in organic solvents.

Sodium chloride (NaCl)
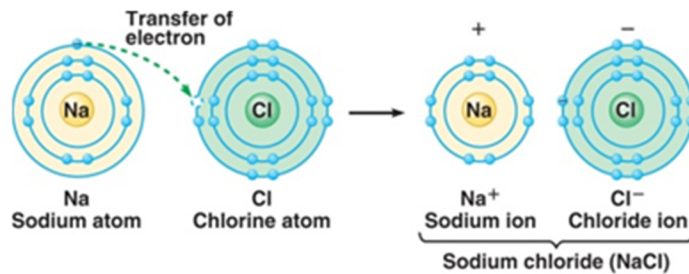
2.   A covalent bond is formed, when two or more electrons of an atom, in its outermost energy level, are shared by other atoms. Example: chlorine molecule, water molecule.

In this bonding a stable arrangement is achieved by sharing of electrons rather than transfer of electrons. Sometimes a covalent bond is also formed when two atoms of different non-metals share one or more pair of electrons in their outermost energy level.

Covalent compounds are bad conductors of electricity. They have low melting and boiling points but insoluble in water.

● Electron from hydrogen
● Electron from carbon
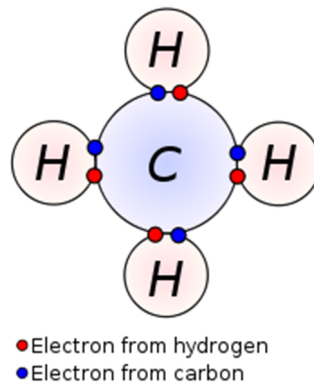
3.   It has been observed that in metal atoms, the electrons in their outermost energy levels are loosely held by their nuclei. Thus, a metal may be considered as a cluster of positive ions surrounded by a large number of free electrons, forming electron cloud. Example: all metals.

These materials have high thermal and electrical conductivity, low melting and boiling point temperature and have a bright lustre. Metallic solids are malleable and ductile.

Free Electrons from outer
shell of metal atoms

Metal ions
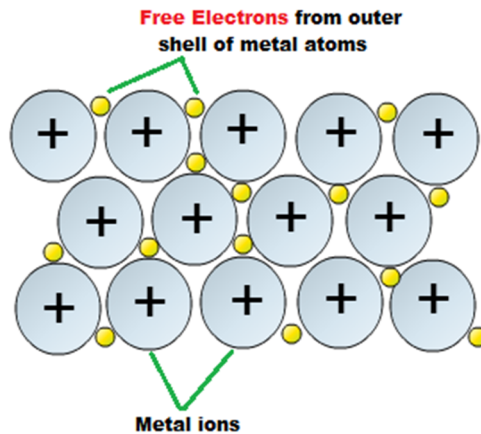
4.   Van der waals bond arises from atomic or molecular dipoles. In essence, an electric dipole exists whenever there is some separation of positive and negative portions of an atom or molecule. The bonding results from the coulombic attraction between the positive end of one dipole and the negative region of an adjacent one. Dipole interactions occur between induced dipoles, and polar molecules (which have permanent dipoles). Hydrogen bonding, a special type of secondary bonding, is found to exist between some molecules that have hydrogen as one of the constituents.

hydrogen bonding
between water molecules

δ^-

δ^+

δ^+

δ^+

δ^-

H bond

δ^+
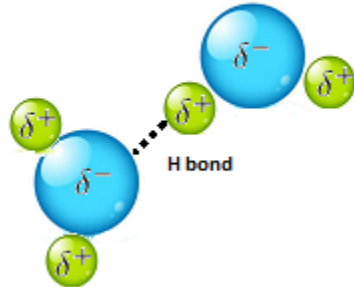
Arises from interaction between dipoles
• **Fluctuating dipoles**

asymmetric electron
clouds

ex: liquid H$_2$
H$_2$ → ← H$_2$

secondary
bonding

secondary
bonding
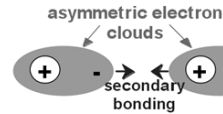
• **Permanent dipoles-molecule induced**

- **general case:** secondary
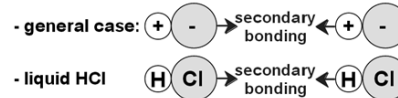bonding

- **liquid HCl** secondary
bonding

Figure 2.8. Fluctuating dipoles or permanent dipoles are the basis for weak Van-der-Waal bonding.