Contents

Chapter 1
Solids

Matter- Anything that which occupies space and possesses rest mass is matter.

States of matter-

There are four fundamental phases, or states, of matter: **Solids**, **Liquids**, **Gases** and **Plasma**.

The main difference in the structures of each state is in the densities of the particles.

❖ Matter in the **solid state** maintains a fixed volume and shape, with component particles (atoms, molecules or ions) close together and fixed into place.

❖ Matter in the **liquid state** maintains a fixed volume, but has a variable shape that adapts to fit its container. Its particles are still close together but move freely.

❖ Matter in the **gaseous state** has both variable volume and shape, adapting both to fit its container. Its particles are neither close together nor fixed in place.

❖ Matter in the **plasma state** has variable volume and shape, but as well as neutral atoms, it contains a significant number of ions and electrons, both of which can move around freely.

o Unlike gases, plasmas are electrically conductive, produce magnetic fields and electric currents, and respond strongly to electromagnetic forces.

- A gas is usually converted to plasma in one of two ways. e .g. either from a huge voltage difference between two points, or by exposing it to extremely high temperatures.

- At very high temperatures, such as those present in stars, it is assumed that essentially all electrons are "free", and that very high-energy plasma is essentially bare nuclei swimming in a sea of electrons. This forms the so-called fully ionised plasma.

Solids are broadly classified into **crystalline solids** and **amorphous solids (glassy solids)**

❖ Amorphous solids are called **super cooled liquids** because of their slow tendency to flow. This is the reason why glass panes of windows are thicker at the bottom than at the top.

❖ Concepts like Lattice and motif thus cannot be used in glasses. This automatically implies that many of the properties of a glasses will be drastically different as compared to the corresponding crystal (thought he composition may be identical and the density not very different).

❖ In a simplistic picture, glass can be thought of as a *time snapshot* of the liquid.

❖ In glasses the atoms do not have long range order (LRO), though they may have short range order (SRO).

❖ Most of the solid matter in nature is crystalline because ordered arrangement has lower energy as compared to irregular packing of atoms.

❖ **Crystals** are solids that **consist of a periodic array of atoms, ions, or molecules.**

Difference between Crystalline and Amorphous (Glassy) solids

Crystalline Solids:

- ❖ They have a *regular three dimensional arrangement of atoms*, ions or molecules due to which they have well defined geometrical shape.
- ❖ Examples- Fibre glass, Teflon, Poly Vinyl Chloride, Naphthalene.
- ❖ They *have long range order* of atoms.
- ❖ They *have sharp melting point* i.e., they melt at a particular temperature because all bonds are equally strong; so on heating these bonds gets ruptured at the same temperature.
- ❖ They have *high and fixed heat of fusion,* i.e., high energy is required to melt 1 mole of crystalline solid.
- ❖ They *are anisotropic*, i.e., they have different optical and electrical properties like refractive index, mechanical strength, thermal conductivity and electrical conductivity in different directions.

- ❖ They are *true solids*, i.e., they show all the characteristic properties of solids because of its property of incompressibility and rigidity.
- ❖ Crystalline solids *cleavage along particular direction* at fixed cleavage planes.
- ❖ When crystalline solids are rotated about an axis, their appearance does not change. This shows that they are symmetrical.
- ❖ All the crystalline solids have definite value of interfacial angle.
- ❖ These solids are almost incompressible.

Amorphous Solid:

- ❖ They *do not have regular arrangement of particles*; therefore do not have well defined particles.
- ❖ Examples- Fibre glass, Teflon, Poly Vinyl Chloride, Naphthalene
- ❖ They *have short range order* of atoms.
- ❖ They *do not have sharp melting point* i.e., they melt over a range of temperature because all bonds are not equally strong. So when they are heated, weaker bonds get ruptured at lower temperature and stronger ones at higher temperature.
- ❖ They *do not have fixed heat of fusion*.
- ❖ They *are isotropic*, i.e., they have same properties in all directions like refractive index, mechanical strength, thermal conductivity and electrical conductivity
- ❖ They are *pseudo – solids*, i.e., they do not show all the characteristic properties of

solids because they are compressible to some extent.

- Amorphous solids *don't break at fixed cleavage planes.*
- Amorphous solids are unsymmetrical.
- They don't possess interfacial angle.

Different types of crystalline Solids-

Ionic Solids:

- The ionic crystal structure consists of **alternating positively-charged cations and negatively-charged anions.** The ions may either be monatomic or polyatomic.
- Poor conductors of heat and electricity.
- Relatively high melting point
- Hard but brittle; shatter under stress
- Relatively dense
- Examples: NaCl , CaF_2

Metallic Solids:

- Metallic crystals consist of **metal cations surrounded by a "sea" of mobile valence electrons**. These electrons, also referred to as delocalized electrons, do not belong to any one atom, but are capable of moving through the entire crystal.
- Good conductors of heat and electricity
- Melting points depend strongly on electron configuration

- ❖ Easily deformed under stress; ductile and malleable
- ❖ Usually high density
- ❖ Examples: Hg , Na, Au, W

Covalent Solids

- ❖ A covalent network crystal consists of atoms at the lattice points of the crystal, with each atom being **covalently bonded** to its nearest neighbour atoms.
- ❖ The covalently bonded network is three-dimensional and contains a very large number of atoms. Network solids include diamond, quartz, many metalloids, and oxides of transition metals and metalloids.
- ❖ Poor conductors of heat and electricity
- ❖ High melting point
- ❖ Very hard and brittle
- ❖ Low density
- ❖ Example: Diamond, Graphite, SiO_2

Molecular Solids

- ❖ Molecular crystals typically **consist of molecules** at the lattice points of the crystal, held together by relatively **weak intermolecular forces**.
- ❖ The intermolecular forces may be dispersion forces in the case of non polar crystals, or dipole-dipole forces in the case of polar crystals.

- Some molecular crystals, such as ice, have molecules held together by hydrogen bonds.
- Poor conductors of heat and electricity
- Low melting point
- Soft
- Low density
- Examples: H_2, I_2 ,NH_3, H_2O

Liquid Crystal

- In 1888, an Austrian plant physiologist, Friedrich Reinitzer, working in Prague, attempted to measure the melting point of a cholesterol derivative that he had extracted from a plant. To his surprise, he found that this substance appeared to have *two* melting points. At 145° C the crystalline solid first melted into a cloudy liquid, and then at 178° the cloudiness suddenly disappeared, leaving the clear, transparent liquid that one ordinarily expects after melting.
- Liquid crystal state is a hybrid state.
- Liquid crystals are matter in a state which has properties between those of conventional liquids and those of solid crystals. For instance, a liquid crystal may flow like a liquid, but its molecules may be oriented in a crystal-like way.
- A liquid crystal phase has many of the physical attributes of a liquid, but its molecular units are sufficiently ordered to

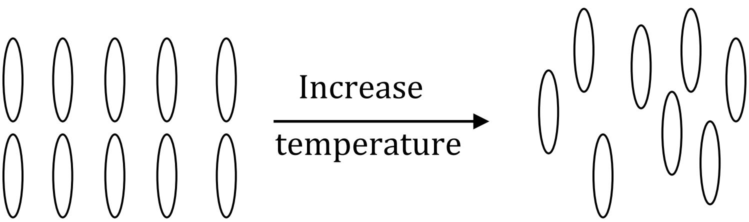
give rise to some anisotropy, most notably in their optical properties.

Definition:

There are some organic crystalline solids which on heating don't convert directly into liquid phase but at a certain temperature range between the solid and the crystalline phase, they become fluid and retain their anisotropic property and have long range orientation order. They are called liquid crystals.

Properties:

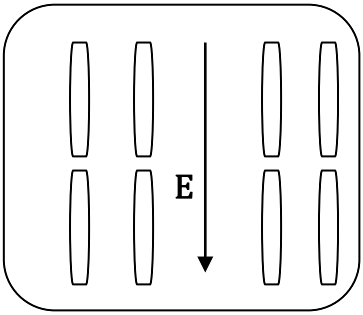
- Liquid crystals are characterised by their *high orientation* and *low positional* molecular order. Liquid crystals have the orienting properties of solids but flow like liquids. Within layers, the molecules can slide over each other. This molecular mobility produces the fluidity of a liquid.



Crystal Liquid Crystal

- Liquid crystal molecules are typically 'rod shaped' – long and thin with a rigid centre that allows them to maintain their shape. They also have flexible ends, which mean that they can still flow past each other with ease. Molecules with this shape are known as *calamitic* liquid crystals.

- The molecules of liquid crystals have a permanent dipole which on applying an electric field rotates the dipole & establishes order within the collection of molecules.



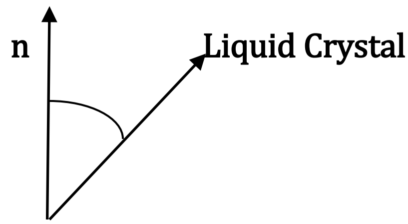
- Molecules are long and narrow structures and orient themselves in a particular direction.

- Liquid crystal phases are generally cloudy in appearance, which means that they scatter light in much the same way as colloids such as milk. These light scatterings are a consequence of fluctuating regions of non-uniformity as small groups of molecules form and disperse.

- The intermolecular forces are not same in all directions.

- The anisotropy of liquid crystals causes them to exhibit *birefringence*. That is, light that enters the crystal is broken up into two oppositely-polarized rays that travel at different velocities. Observation of a birefringent material between crossed polarizing filters reveals striking patterns and color effects.

- Due to their distinctive shape calamitic liquid crystal molecules undergo stronger attractive forces when arranged parallel to one another. They therefore tend to align themselves pointing along one particular direction; this is a known as the *director* vector and is given the notation **n**. The angle between individual liquid crystal molecules and the director gives an indication of the *orientational order* of the system, which can be calculated using the following formula:



$$Order\ parameter\ Q = (3 < cos^2\theta > -1)/2$$

When $Q = 1$ the liquid crystal has complete orientational order;

When $Q = 0$ it has no orientational order and has behaves as isotropic liquid.

In general, calamitic liquid crystals can be divided into three different *mesophases*: They are defined by their differing degrees of positional order.

Nematic Liquid Crystal:

- Nematic liquid crystals have *no positional order* – they only have orientational order.
- In a *nematic phase* (the term means "thread-like") the molecules are aligned in the same direction but are free to drift around randomly, very much as in an ordinary liquid. Owing to their polarity, the alignment of the rod-like molecules can be controlled by applying an electric field; this is the physical basis for liquid crystal displays and certain other electro optic devices
- They scatter light strongly.
- These molecules are not arranged in layers.
- Examples: p-Azoxyanisole, p-Azoxyphenetole

Smectic Liquid Crystal:

- Smectic liquid crystals consist of molecules arranged into separate layers. However, there is no further positional order within the layers themselves.
- In *smectic* ("soap-like") phases the molecules are arranged in layers, with the long molecular axes approximately perpendicular to the laminar planes. The only long-range order extends along this axis, with the result that individual layers can slip over each other (hence the "soap-like" nature) in a manner similar to that observed in graphite. Within a layer there is a certain amount of short-range order. There are a large number of sub-categories of smectic phases.

- A smectic substance can be easily transformed into nematic substance at high temperature.
- Examples: Ethyl p-azoxy benzoate, Ethyl p-azoxy cinnamate

Chiral Liquid Crystal (Cholesteric):

- In chiral nematic liquid crystals we see a helical structure, where the *director vector* is rotated slightly in each subsequent layer of molecules – the distance along the axis between two molecules with parallel director vectors is called the *pitch* of the liquid crystal.
- Their name derives from the fact that they are easily made by mixing a nematic with a chiral substance (which does not have to be a liquid crystal itself). Historically, they were also known as *cholesteric* liquid crystals as the first molecules found to display these properties were those related to cholesterol.

Solid	Liquid	Nematic	Smectic
Both Orientation Periodicity	Neither Orientation Nor Periodicity	Only Orientation No Periodicity	Orientation with some Periodicity

Applications of Liquid Crystal:

Used in liquid crystal displays like watches, calculators (alkyl cyano biphenyl) which rely on the optical properties of certain liquid crystalline substances in the presence or absence of an E field.

✓ Used in liquid crystal thermometers-(cholesterol esters) because they show a change in colour with temperature.

✓ Used in detecting tumours in the body (cholesterol liquids)

✓ Used in optical imaging

✓ Used in non destructive mechanical testing of materials under stress.

✓ Used as liquid crystal lasers where the lasing medium is distributed feedback mechanism instead of external mirrors.

✓ Used in industries as lubricants.

Advantage of Liquid Crystal:

- ✓ Consumes less power, Cheaper, Easy to manufacture in any size, shape and colours.

Disadvantage of Liquid Crystal:

✓ They operate in very limited range.

✓ They have comparatively large response time and short life span.

✓ In high temperature environments there is loss of contrast.