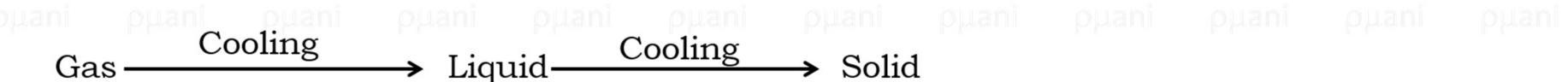


Lecture 17

In this lecture we will learn about “Liquid State”



Liquid state is the “intermediate state”, thus, possess properties of both gaseous state and solid state.

Gaseous state: Molecules are in chaotic motion due to very little cohesive forces and potential energy is negligible.

Solid state: Molecules are “tied together” in a regular pattern due to strong cohesive force, free motion is almost forbidden.

Liquid state: Molecules have intermediate order of potential energies, cohesive forces and free motion.



- (a) There is relatively small increase in volume on fusion. Thus, near the melting point the density of liquid do not appreciably alter from that of the solid.
- (b) Near the freezing point the specific heat of solid and liquid approach each other.
- (c) Whereas, the latent heat of fusion and latent heat of vaporisation are quite different from each other.
- (d) The compressibilities of solids and liquids are of the order of 10^{-6} and 10^{-5} per atmosphere. Thus, solids and liquids are relatively incompressible compared to gas (compressibility factor ~ 1 per atmosphere). Compressibility of gas is reciprocal to the pressure.

(e) Gases and liquids lack rigidity in comparison to the solid. Neither liquid nor gas can offer permanent resistance to shearing stress and thus takes the shape of the container.

⇒ Thus, the liquid state possess some properties of gaseous state and some of the solid state.

Compactness and cohesion observed in liquid are similar to that of solid → structural aspect

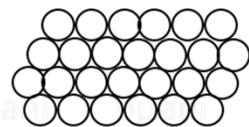
Comparative case with which liquids flow or diffuse is similar to that of gas → disordered random structural aspect.

However, the nature of motion and arrangement of molecules in liquid state resemble more to that of solid than the gaseous state.

| Substance | Density (g/cc) | | Latent heat (Joule/g) | | Specific heat (Cal/°A/mol) | |
|------------------|----------------|--------|-----------------------|--------------|----------------------------|--------|
| | Solid | Liquid | Fusion | Vaporisation | Solid | Liquid |
| Hg | 14.19 | 13.60 | 11 | 296 | 6.7 | 6.7 |
| H ₂ O | 0.915 | 1.00 | 334 | 2230 | 8.82 | 18.14 |

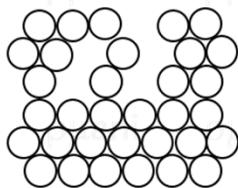
In a crystal, molecules are in (neat) perfect and well ordered arrangement throughout the entire mass. Each molecule is surrounded by a set of equal number of other molecules in a symmetrical pattern. On melting the crystal expands only about 10% in volume and 3% in intermolecular spacing. This means thermal motion introduces a disorder in geometrical arrangement. However, the extent of disorder is small on melting. The disorder causes disturbance in the long range and destroy crystalline arrangement.

J. D. Bernal's approach: Two dimensional model

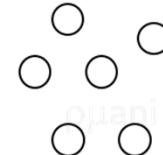


Crystal

(Each atom is surrounded
by six other atom)



Liquid



Gas

Small 'perturbation' caused by thermal disorder disrupts one atom out of the six atoms arrangement in the crystal. The disorder must first appear in the long range in all directions whereas small range order still remains. Thus, in the liquid short range order and long range disorder persists. Short range order in liquid structure changes continuously because of thermal motions.

Stewart's model: In a liquid there remains large number of well-order groups, each containing a few hundred molecules. These regularly ordered small groups are known as '**cybotactic groups**'. In between cybotactic groups there remains disordered chaotically moving molecules. These groups are however not permanent and there remains dynamic equilibrium between cybotactic groups and disordered molecules.

⇒ In both the models, there exists short range order in the liquid.

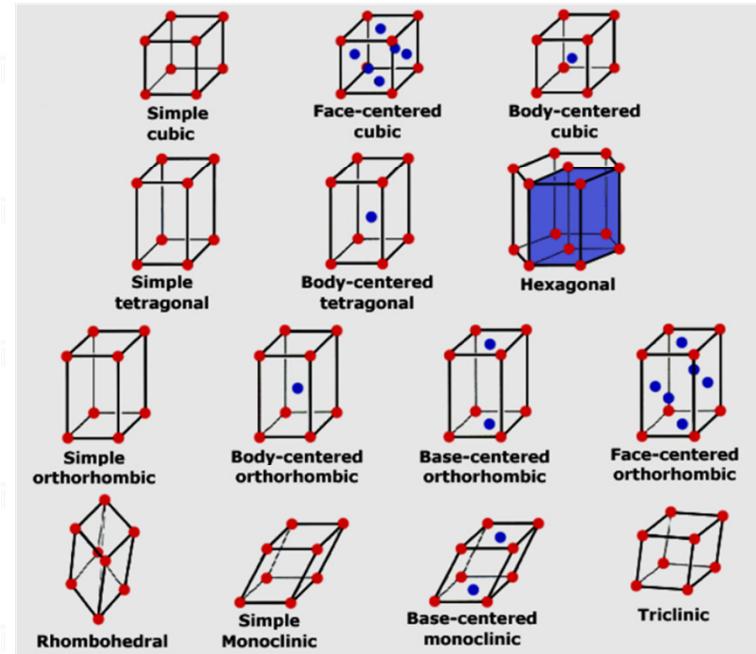
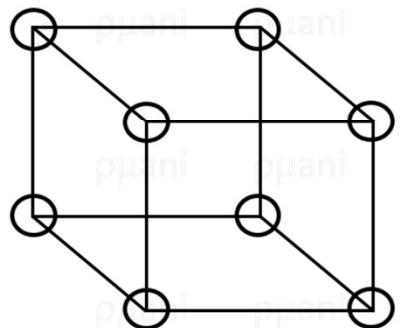
There are many other models that you will study later, e.g. Eyring model etc.

Radial distribution function: (Advanced topic)

The average relative locations of particles of a liquid are expressed in terms of the radial distribution function $g(r)$. This function is defined so that $g(r) r^2 dr$ is the probability that a molecule will be found in the range ' dr ' at a distance ' r ' from another molecule.

In a perfect crystal $g(r)$ is a periodic array of sharp spikes, representing a certainty that molecule or ions or atoms occupy definite locations.

Thus in the solid state long range order persists (in absence of thermal motions & defects).



Question: How will the $g(r)$ plots for these unit-cells will look like?

Picture courtesy: Google

What happens when the crystals melt?

When the crystal melts, long range order is lost.

Whenever we look, at long distance from a particular molecule there is equal probability of finding a second molecule close to the first molecule though the nearest neighbours may still adopt approximately the same original relative position.

And there remains a finite probability that same vacated position may be taken up by a new one because of dynamic equilibrium.

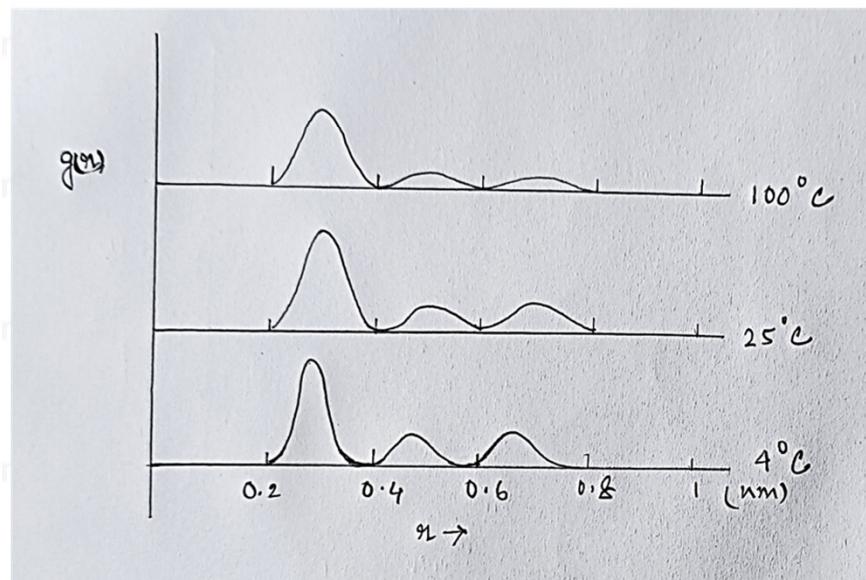
Thus, a sphere of nearest neighbours can be observed at a distance r_1 .

And may be another set of spheres at a distance r_2 .

Thus, there exists short range order in liquids.

Thus, radial distribution function can be expected to oscillate at short distance with a peak at r_1 , a smaller peak at r_2 and so on.

The radial distribution function can be experimentally determined by X-ray diffraction. $g(r)$ can be extracted from the diffused diffraction pattern characteristic of liquid samples. The shells of local structures for water has been shown below:



Radial distribution function of oxygen atom in liquid water.

At 4°C, there remains one intense sharp peak at 0.3 nm and other small peaks at ~0.5, ~0.7 nm. With increase in temperature, the sharp peak broadens. Even at 100 °C, intermolecular forces (H-bonding etc.) are strong enough to hold the local structure.

IR spectra for H_2O shows that about 90% of hydrogen bonds are intact at the melting point of ice and 20% at the boiling point.

Information about liquid structure can be obtained by Scattering experiments (e.g, Raman scattering or neutron scattering).

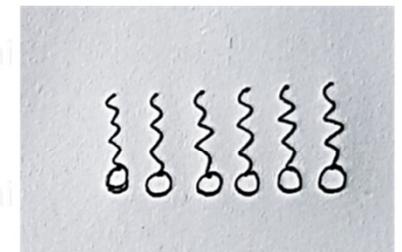
Liquid crystals:

All crystalline solids (except cubic systems) are **anisometric and also anisotropic** in nature. This means the value of any physical property (magnetic, optical, electrical) are different in different direction. In contrast, liquids are isotropic having identical properties in different directions.

For certain substances like cholesteryl benzoate when melted first forms a translucent mobile state. This new phase flows like a liquid but are anisotropic in nature. This intermediate phase is known as '**mesophase**' or **liquid crystal**. It possesses **liquid like imperfect long-range order** at least in one direction in space but positional or orientational order in at least one other direction.

Mesophase can be of two types: (i) Lyotropic

- (ii) Thermotropic –
 - (a) Smectic
 - (b) Nematic
 - (c) Cholesteric



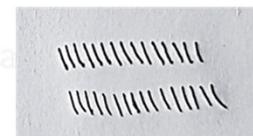
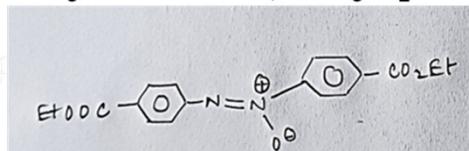
Lyotropic – a combination of two different components, one is polar another nonpolar → micelles etc.

Lyotropic → shows phase transition with change in temperature and concentration of the liquid crystal molecules.

Thermotropic → shows phase transition as temperature is changed. These are of three types, e.g.

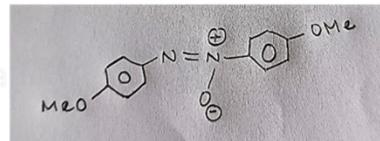
- (a) Smectic, (b) Nematic, (c) Cholesteric.

(a) Smectic phase: (Greek word: soapy) [generally forms at lower temperature than nematic phase] Molecules align them in layers, different phases or sheets glide over one another. For molecules like ethyl p-azoxy benzoate, ethyl p-azoxy cinnamate, smectic phases are observed.

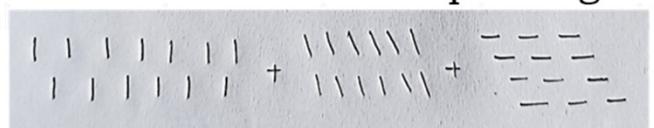


→ More order, higher viscosity

(b) Nematic phase: (Greek word: thread) No layer structure (Rod like) but parallel arrangement remains. Molecules like p-azoxy anisole etc. form this kind of phase.



(c) Cholesteric (Chiral nematic) phase: (Greek word: bile solid) Molecules lie in sheets that change slightly between each other. Thus they form helical structure with a pitch that depends on temperature. Thus cholesteric liquid crystals diffract light and have different colours depending on temperature. Cholesteryl esters show this kind of behaviour.



Pitch of a liquid crystal: Pitch refers to the distance over which liquid crystal molecules undergo 360° twist (P and $\frac{P}{2}$). Strongly anisotropic optical properties of nematic liquid crystals and their response to electric fields have found its application in LCDs.

There are other types of liquid crystals, e.g. Metallotropic , Discotic etc. phases.