

# Modern Materials- Contents

- Fundamental Principles
- Bonding in solids
- Polymers
- Liquid Crystals
- Composites
- Thin Films
- Nano materials

# Learning Objectives

- Understand the fundamental principles of material science
- Explain how functional needs are related to structure & bonding
- Apply experimental design techniques to material production
- Define liquid crystal phases & give specific examples
- Understand the essential concepts used in nanomaterial synthesis
- Applications of nanomaterials in different fields

# Fundamental principles of materials

Materials - substances used in the primary production or manufacturing of goods.

Different substances have different properties

- Contain different elements & different combinations of elements.
- Contain different types of chemical bonds
- Have different sizes of units
- The solid state structure may contain different types of assemblies  
e.g., molecular packing arrangement may be different or the geometry of linkage in an extended 3D structure may vary.

Non-metals such as C, Si, B, N, O, and P, and metals such as Al, Mg, Ti, Sn, Fe, Cu, Cr and Ni.

Other elements such as Cd, Ga, Ge, Pt, Ag and Au are also used in smaller quantities and for specialized applications.

**Material science involves the study of the relationship between structure and properties of materials.**

**Structure:** The structure relates to the arrangement of its internal components

At the atomic level:

arrangement of atoms in different ways.

Ex. two allotropes of carbon, graphite and diamond show, different properties.

At the microscopic level:

arrangement of small grains of material provides different optical properties.

# Properties:

Properties of materials are grouped into six categories

- *Mechanical*
- *Electrical*
- *Magnetic*
- *Thermal* (transmission of heat, heat capacity)
- *Optical* (absorption, transmission and scattering of light)
- *Chemical stability* in contact with the environment (like corrosion resistance).

# Classification of materials

```
graph TD; A[Classification of materials] --- B[Solid materials]; A --- C[Advanced materials]; A --- D[Nanomaterials];
```

Solid materials

Advanced materials

Nanomaterials

# **1)Solid materials:**

These materials have been conveniently grouped into three basic classifications based on chemical makeup and atomic structure

- Metals and alloys
- Ceramics,
- Polymers



## *Metals and alloys:*

- Metals are elements which can lose their outer electrons.
- spread in an 'electron sea' that "glues" the metal ions together.

Metals are usually strong, malleable, ductile, good electrical and thermal conductors and are opaque to light but-exhibit typical metallic luster. Example: aluminum, steel, brass, gold.

## *Ceramics:*

A ceramic is an inorganic, non-metallic solid prepared by the action of heat and subsequent cooling.

They are usually combinations of metals or semiconductors with oxygen, nitrogen or carbon forming corresponding oxides, nitrides, and carbides. Examples: glass, porcelain, fire brick.

## ***Polymers:***

- Substances of high molecular mass formed by the joining together of monomers.
- They are bound by covalent bonds and also by weak van der Waals forces, and usually synthetic polymers have a backbone of C-C bonds

## ***Composites;***

- Composed of two or more constituent materials with significantly different properties.
- The design goal of a composite is to achieve a combination of properties that are not displayed by any individual materials, and also to incorporate the best characteristics of each of the component materials.

## 2. Advanced materials

- Have superior properties such as toughness, hardness, durability and elasticity when compared to conventional materials.
- Materials that are used in high-technology applications are sometimes termed advanced materials. Advanced materials include

### ***Semiconductors:***

- Building blocks of modern electronics including transistors, solar cells, light emitting diodes and integrated circuits.

Examples: Si, Ge, Ga, As.

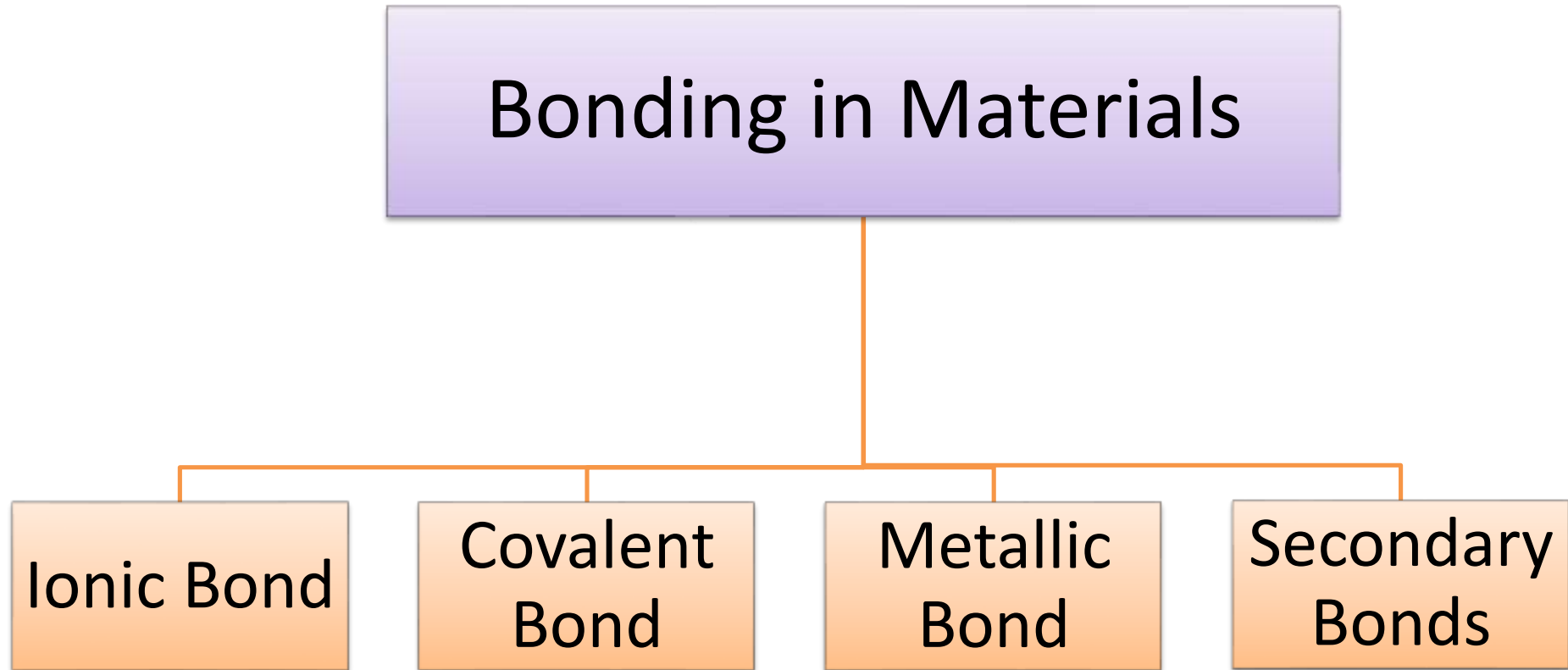
## ***Biomaterials***

- material that has a biomedical or biological application. They might have a therapeutic use or a diagnostic use and the material must have properties that meet the demands of that applications.

### **Nanomaterials:**

Nanomaterials are defined as materials with at least one external dimension in the size range from 1-100 nanometers.

**Chemical bond** is defined as a force that acts between two or more atoms to hold them together in a stable arrangement

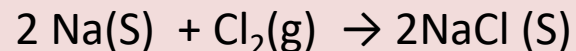


# Ionic Bond

The electrostatic attraction between the cation & anion produced by electron transfer



electrovalent bond

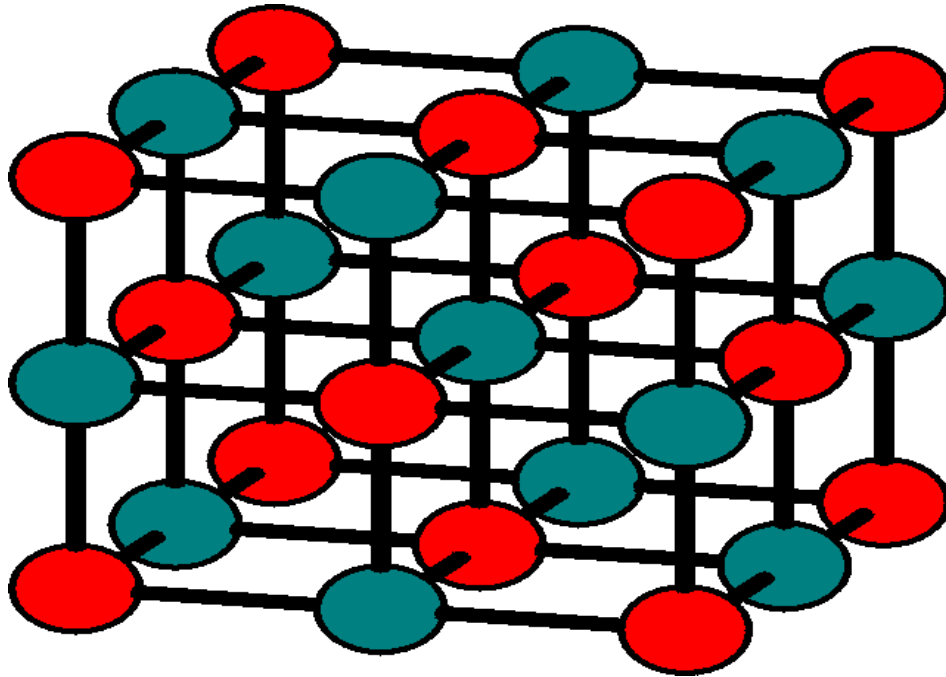


## The characteristic properties of ionic compounds

- They are solids at room temperature
  - Crystals of ionic solids are hard and brittle.
  - They possess high melting points and high boiling points.
  - They do not conduct electricity in the solid state.
- They are good conductors of electricity when they are in the molten state or in aqueous solution.
- They are soluble in polar solvents but insoluble in nonpolar solvents.
  - They do not exhibit isomerism.

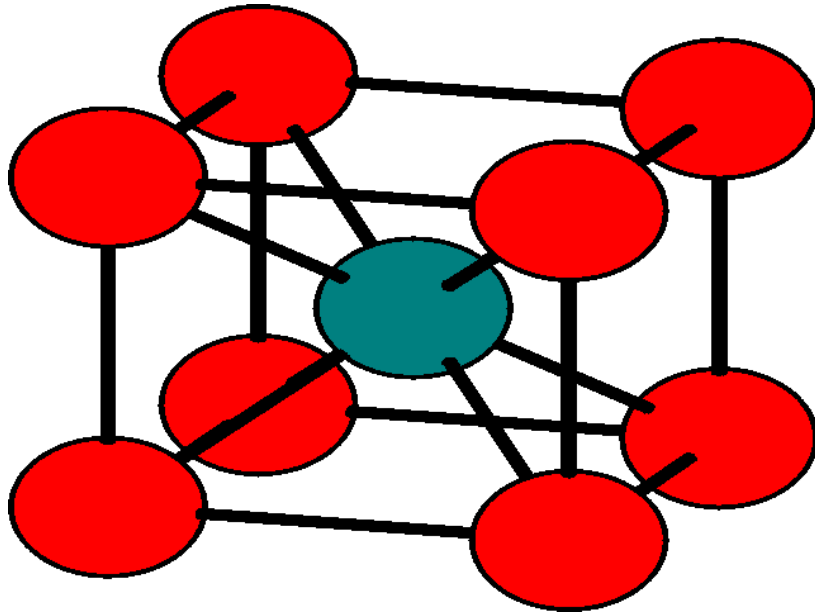


## The Rock Salt, or NaCl, structure



The sodium cations (green) occupy the octahedral holes in the fcc lattice of chloride anions (red).

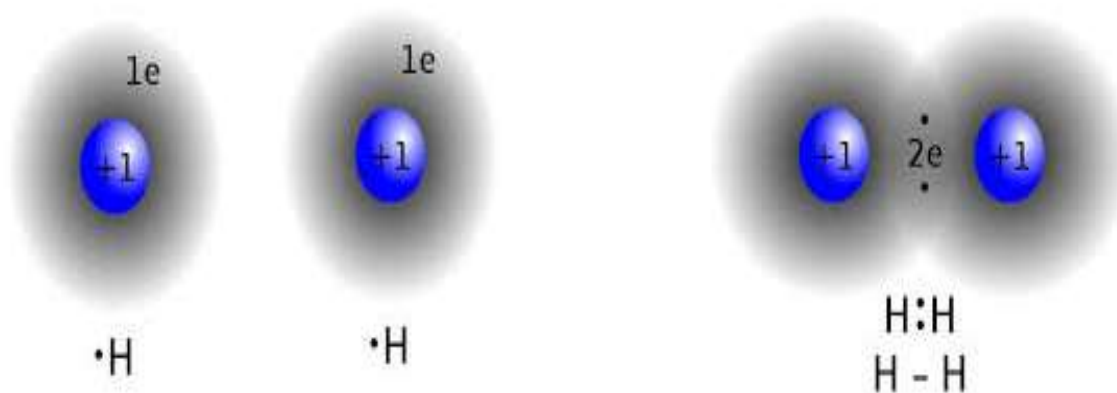
## Cesium Chloride structure (bcc)

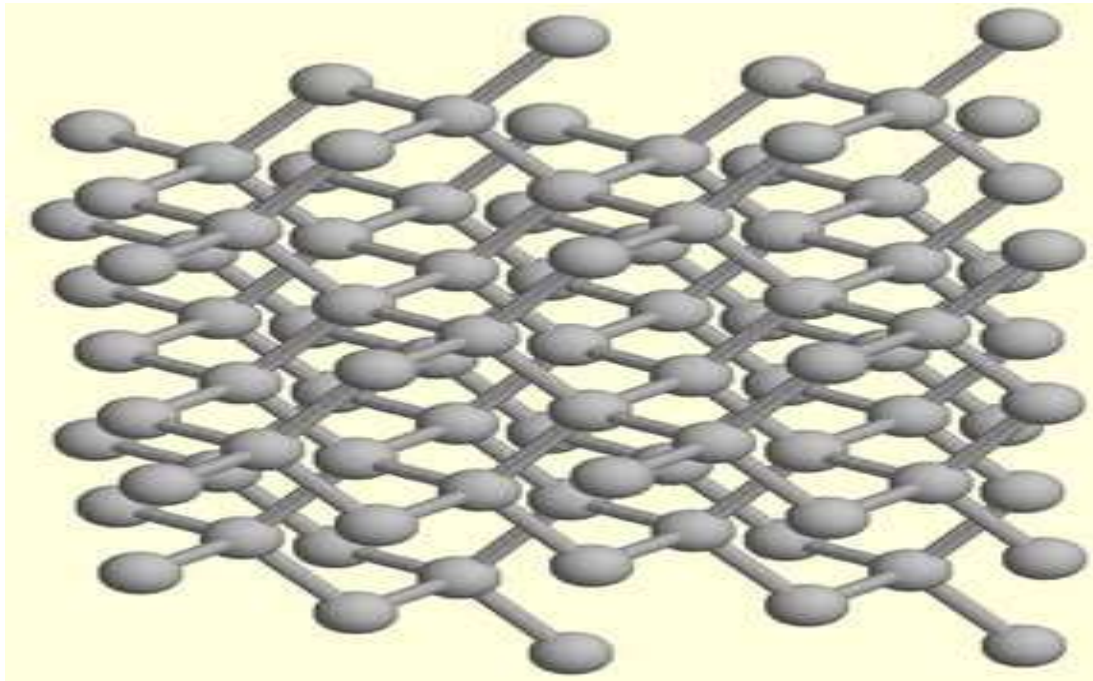
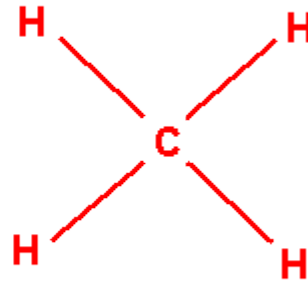
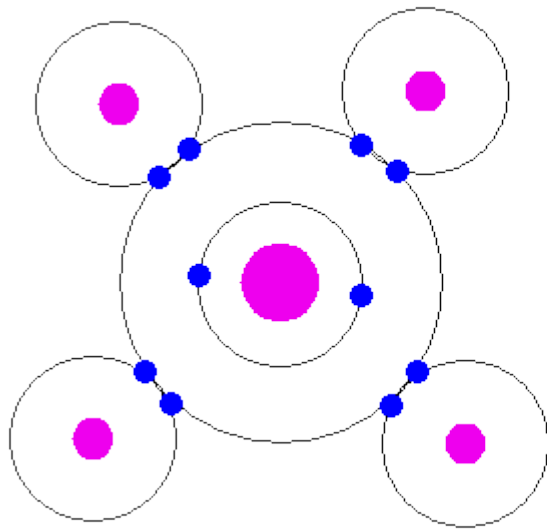


The simple cubic array of chloride anions (red) has a cesium cation (green) at the center of the cube

# Covalent Bond

Formed by overlap of atomic orbitals & mutual sharing of electrons.





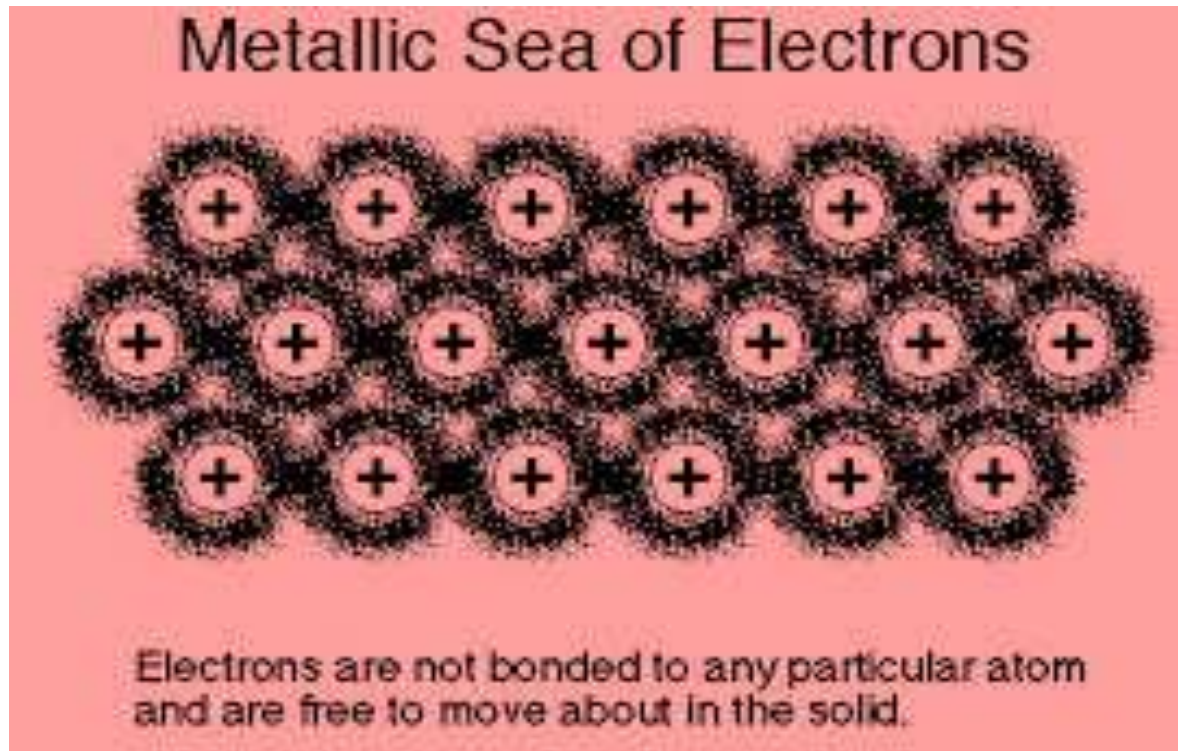
Diamond

## The characteristic properties of covalent compounds

- ☐ They are gases, liquids or solids at room temperature
- ☐ They are soft and much readily broken
- ☐ They have low melting points and boiling points
- ☐ They are soluble in organic solvents
- ☐ They are rigid and directional; causes stereoisomerism
- ☐ They do not conduct electricity in any state

# Metallic bond

The bonding which holds the metal atoms firmly together by force of attraction between metal ions & the mobile electrons



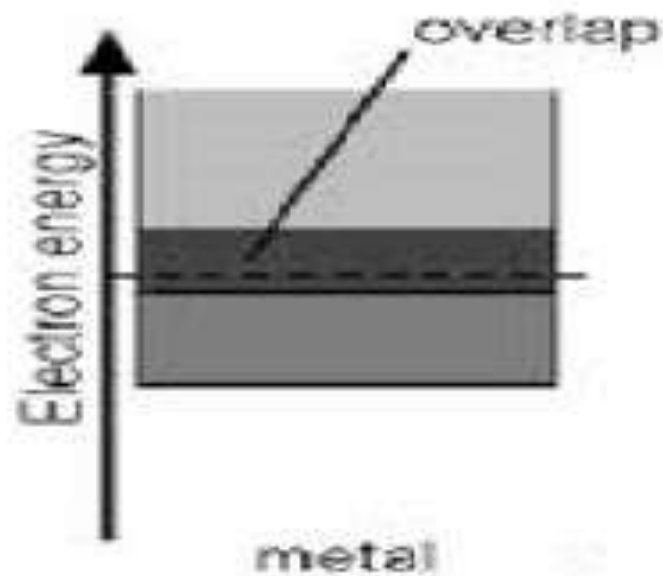
A block of metal can be thought of as an array of positive ions immersed in a sea of delocalized electrons.

The great cohesive forces resulting from the delocalization is responsible for the great strength in metals.

In a metals, overlap of large number of outer orbitals of atom to form a very large number of molecular orbitals that are delocalized over the metal. A large number of closely spaced energy levels form 'bands'

Conduction  
band

Valence  
band





## Properties of metals;

- They have bright metallic lustre
- They are malleable and ductile
- They have high electrical and thermal conductivity
- The melting points vary according to the efficiency of metallic bonding

# Secondary Bonds

```
graph TD; A[Secondary Bonds] --> B[Hydrogen Bonds]; A --> C[Dipole-dipole Bonds]; A --> D[Dipole-Induced dipole Bonds]; A --> E[London Forces];
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Hydrogen  
Bonds

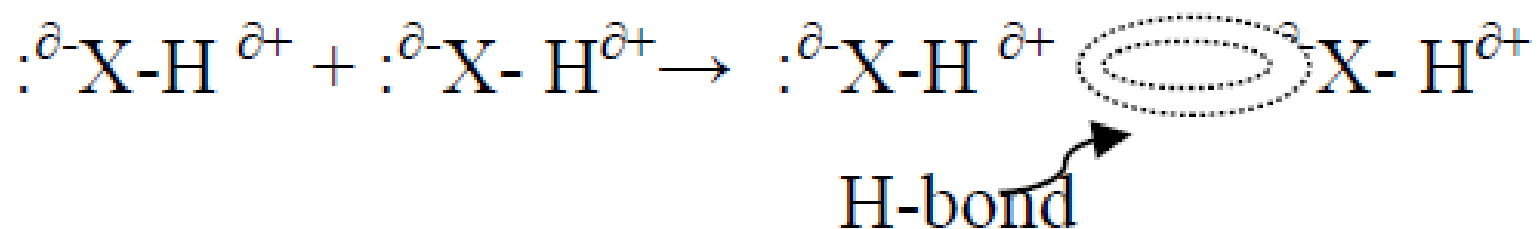
Dipole-dipole  
Bonds

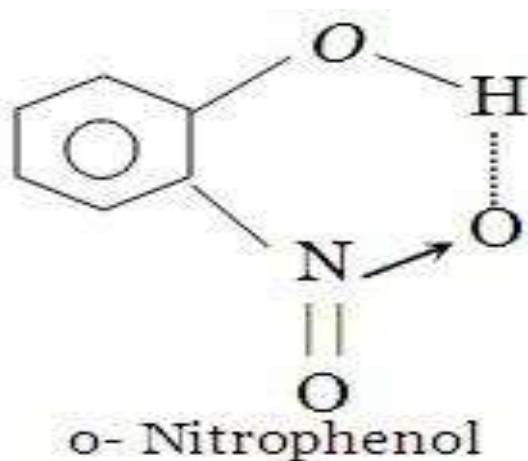
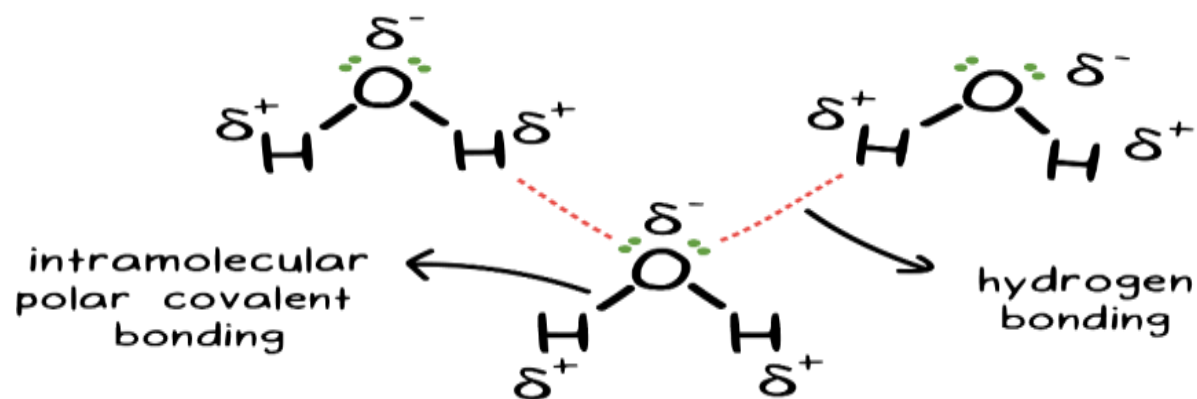
Dipole-Induced  
dipole Bonds

London Forces

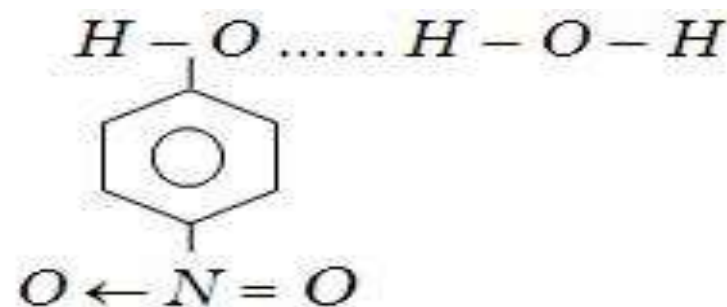
**Hydrogen bonds:** The electrostatic attraction between an H-atom covalently bonded to a highly electronegative atom X such as nitrogen, oxygen or fluorine and a lone pair of electrons on X in another molecule is called hydrogen bonding.

The hydrogen-bond attraction can occur between molecules (*intermolecular*) or within different parts of a single molecule (*intramolecular*).





Due to chelation,  $-OH$  group is not available to form hydrogen bond with water hence it is sparingly soluble in water.



p-Nitrophenol

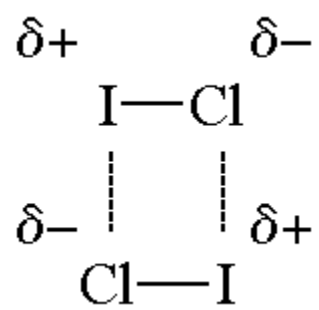
$-OH$  group available to form hydrogen bond with water, hence it is completely soluble in water.

### ***Dipole-dipole bonds:***

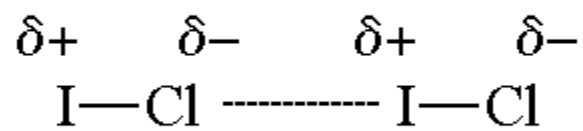
The strongest secondary bonding type exists between adjacent polar molecules.

HCl is an example of polar molecule. The positive end of one dipole attracts the negative end of the other. There is a net attraction between the polar molecules. Generally such attractions are about 1 % as strong as a covalent bond.



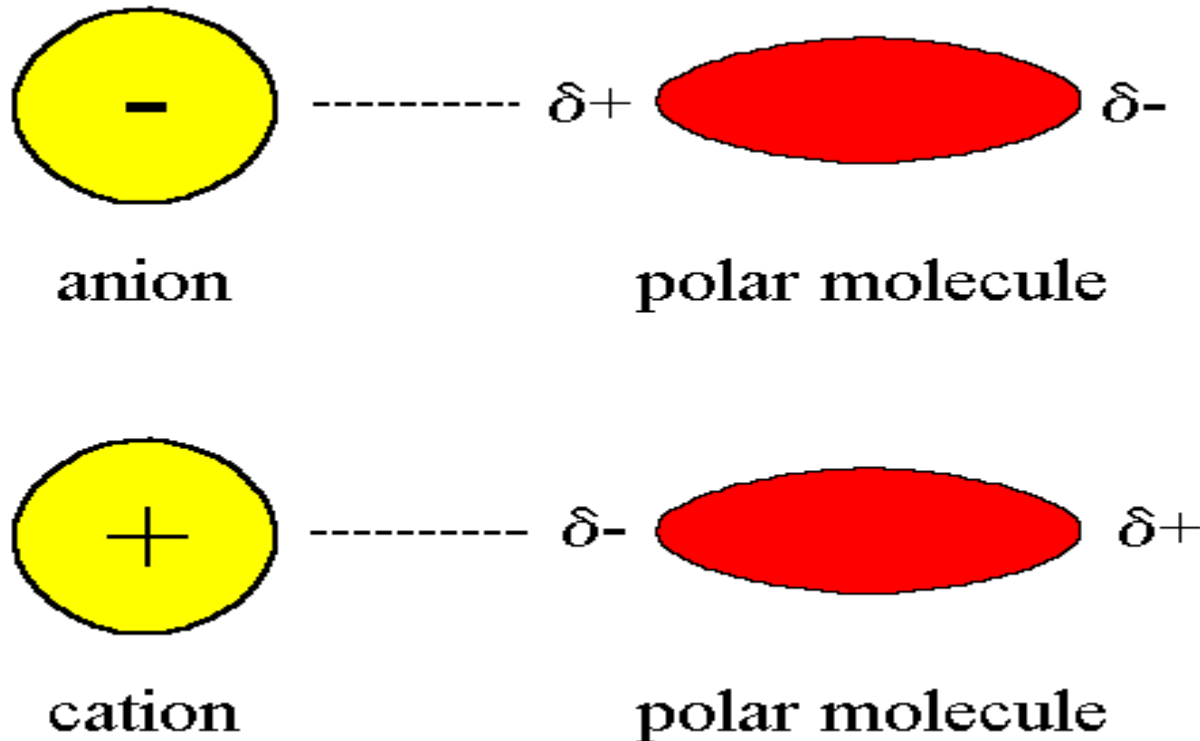


or



## Ion-Dipole Forces

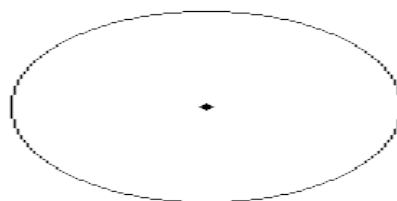
This type of force exists between an ion and the partial charge on the end of a polar molecule, e.g. KBr/NaCl in water



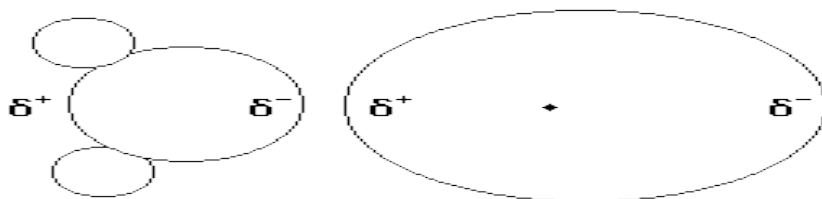
### ***Dipole-induced dipole bonds:***

polar molecules will induce a dipole in adjacent nonpolar molecules, and a bond will form as a result of attractive forces between the dipole and induced dipole.

Eg. solution of polar solutes in nonpolar solvents.



**Spherical atom with no dipole.  
The dot indicates the location  
of the nucleus.**

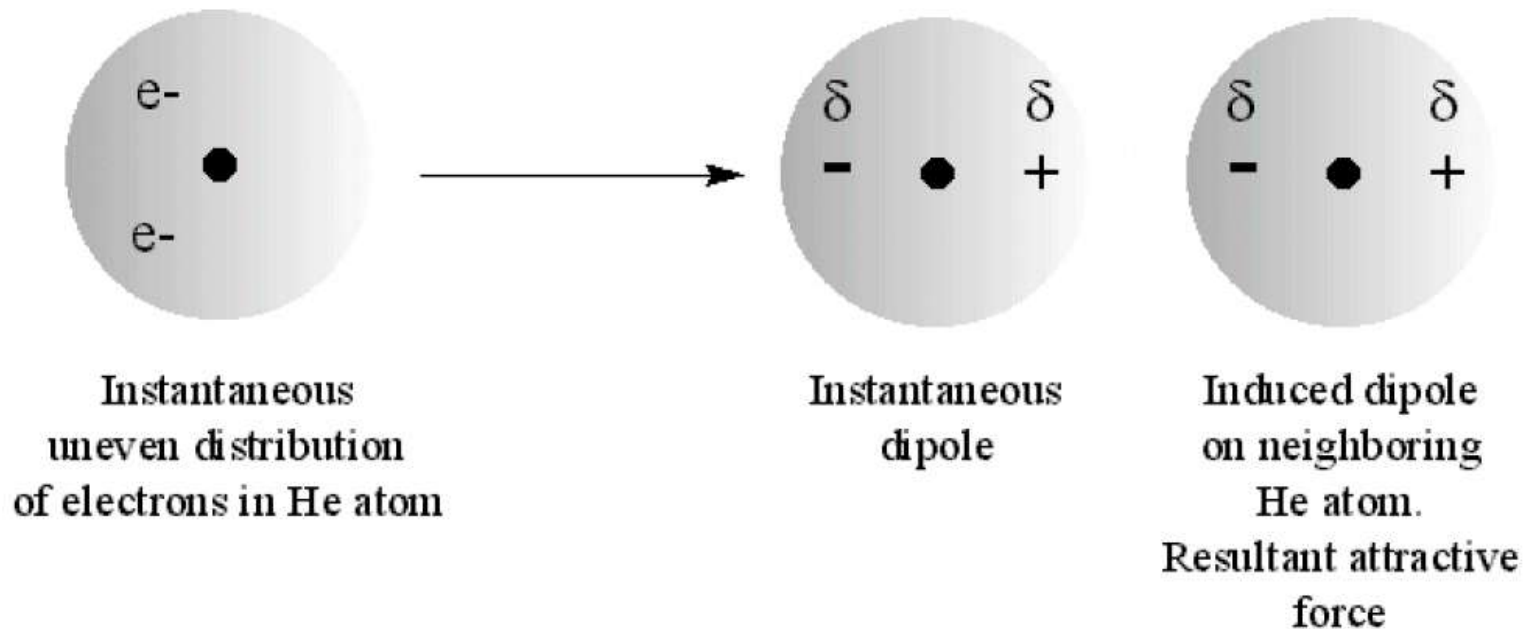
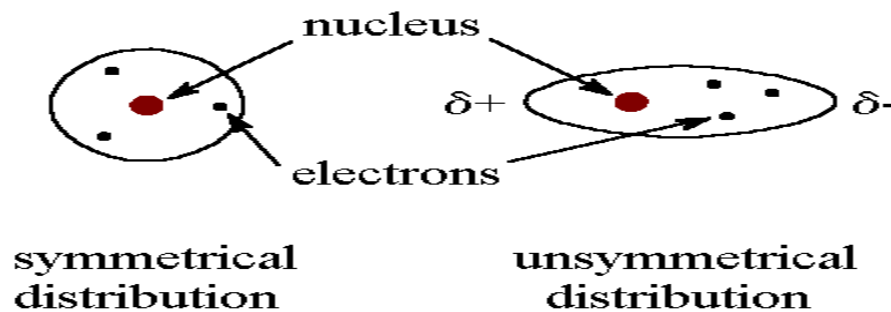


**Upon approach of a molecule with a  
dipole, electrons in the atom respond  
and the atom develops a dipole.**



## London forces:

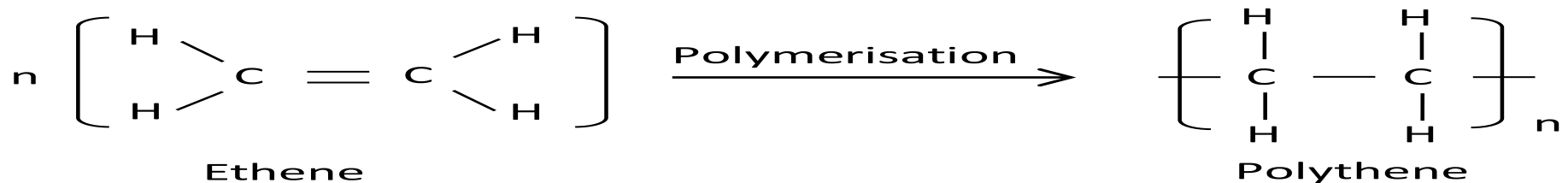
The momentary attraction between the molecules of a liquid caused by instant dipole and induced dipole are called London Forces.



- i) Upon cooling at very low temperature both  $\text{Cl}_2$  and  $\text{Br}_2$  form solids
  - ii) At room temperature, chlorine ( $\text{Cl}_2$ ) is a gas whereas bromine ( $\text{Br}_2$ ) is a liquid.
- 
- i) Due to London dispersion forces . As the elements are cooled, the kinetic energy of the  $\text{Cl}_2$  and  $\text{Br}_2$  molecules decreases and the London forces are strong enough to overcome the kinetic energy and hold the molecules in a solid.
  - ii) London dispersion forces between the larger  $\text{Br}_2$  molecules are sufficient to cause them to form a liquid at  $25^\circ\text{C}$ , whereas London dispersion forces between the smaller  $\text{Cl}_2$  molecules are not.

# Polymers

- Macro molecules formed by linking smaller structural units, called *monomers* interconnected by covalent bonds.



- Degree of polymerization:** The number of repeating units (n) in the chain.
- Polymers with low degree of polymerization are called oligomers.
- Functionality:** The number of reactive sites or bonding sites.



# Classification of polymers

```
graph TD; A[Classification of polymers] --> B[Origin]; A --> C[Structure]; A --> D[Methods of formation]; A --> E[Response to heat]; A --> F[Applications]
```

**Origin**

**Structure**

**Methods  
of  
formation**

**Response  
to heat**

**Applications**

Based on the *origin*, polymers are broadly classified as

(a) Natural polymers

(b) synthetic polymers.

Based on *molecular structure*, the polymers further can be classified as follows

(a) Linear

(b) Branched

(c) Cross-linked

*homopolymer.*

e.g., .....- M – M – M – M – M – M – M - .....

Block copolymer

e.g., .....- M – M – M – M - M<sub>1</sub> – M<sub>1</sub> - M<sub>1</sub> - M<sub>1</sub> - M – M – M – M –

The polymers can be classified as follows, on the basis of the *method of formation*

(a) Addition polymers

(b) condensation polymers

The polymers can be classified on the basis of the *response to heat* as follows.

(a) Thermo softening

(b) Thermosetting

The polymers can be classified on the basis of their *applications* as follows.

(a) Plastics      (b) Elastomers      (c) Fibers      (d) Resins

Plastics are the polymers, which are soft enough at some temperature to be moulded into a desired shape and hardened on cooling so that they can retain that shape. Examples: poly styrene, poly vinyl chloride & poly methyl methacrylate.

Elastomers are polymers in which the structural units are either zig zag or helical chains. They undergo elastic changes when subjected to an external force, but readily regain their original shape when the force is withdrawn. Examples: natural rubber & silicone rubbers.

Fibres are characterized by their molecular chains arranged parallel to each other in a spiral or helical pattern which do not undergo stretching or deformation and the molecular length is at least 100 times its diameter.

Examples: nylons & terylene.

Resins are much lower molecular weight polymers either in liquid or solid form used as adhesives or moulding powders. It has a glossy appearance. Resins constitute the major essential part of the plastics.

Examples: polysulphide sealants & epoxy adhesives.



# Polymerization

## ADDITION POLYMERISATION      CONDENSATION POLYMERISATION

- Monomers undergo self addition to each other without loss of by products
- Unsaturated vinyl compounds undergo addition polymerization
- Monomers are linked together through C – C covalent linkages
- Monomers undergo intermolecular condensation with continuous elimination of by products-  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{HCl}$ .
- Monomers containing the functional groups ( $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{NH}_2$ ) undergo this polymerization
- Covalent linkages are through their functional groups

# Structure & properties of polymers

- **Strength**
- **Plastic deformation**
- **Crystallinity**
- **Chemical Resistance**
- **Elasticity**

# Molecular weight of polymers

## *Number-average molecular weight*

- Number fraction
- Lower value
- Determined by colligative properties

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

## *Weight-average molecular weight*

- Weight fraction
- Higher value
- Determined by ultracentrifugation & light scattering expts

$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

## Application

# Numerical Problems

- Calculate the number average & weight average molecular weight of a polymer sample in which 40 % molecules have molecular mass of 25000, 20 % have molecular mass of 30000 & rest have molecular mass of 55000.
- A polymer sample contains 1,2,3 & 4 molecules having molecular weight  $10^5$ ,  $2 \times 10^5$  &  $4 \times 10^5$  respectively.  
Calculate the number average & weight average molecular weight of the polymer.

# Liquid Crystals

- Find application in display systems of modern electronic gadgets.
- Liquid crystal displays have the advantage of low power consumption
- widely used in display devices of mobile communication appliances, aircraft cockpit, laptops and other electronic equipment.

Liquid crystalline (LC) state is the intermediate state between solid and liquid states

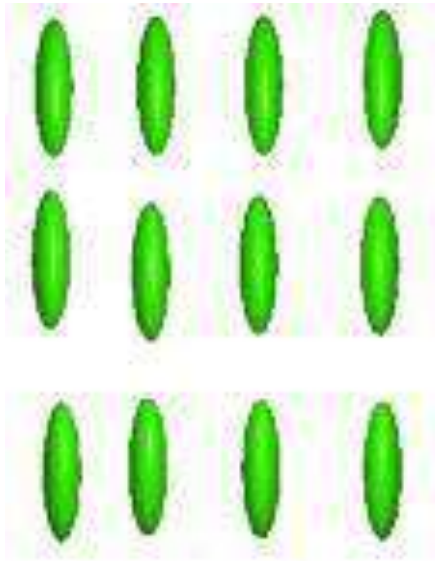
LCs exhibits both the properties of solids and liquids

The three fundamental states of matter are

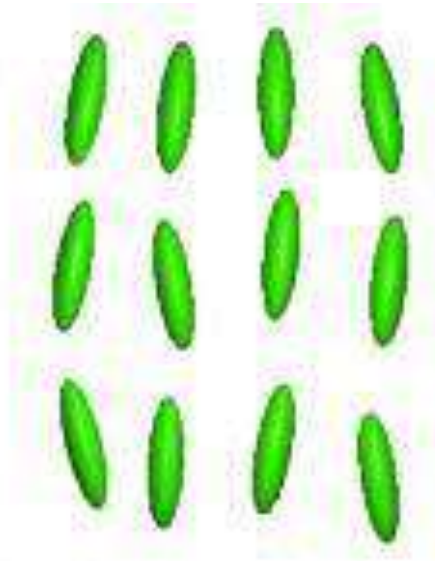
❖ Solid

❖ Liquid

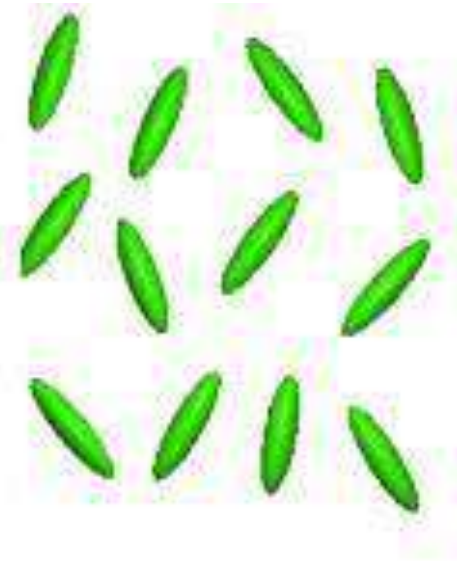
❖ Gas



**Solid**



**Liquid Crystal**



**Liquid**

Arrangement of molecules in different states

**Solids** are having long range orientational order

**Liquids** are disordered

In a liquid crystal, the molecules possess orientational order, i.e., the molecules tend to remain oriented in a particular direction

direction of preferred orientation in a liquid crystal is called the **director** ( $\bar{n}$ )

Are all the molecules exhibit liquid crystallinity?

No

What is the primary requirement for a molecule to be a mesogenic (or LC)?

**Anisotropy:** Properties of a material vary with different crystallographic orientations, the material is said to be anisotropic.

Due to geometrical anisotropy, these may pass through one or more intermediate states before they transform into isotropic liquids

Isotropic: Properties of a material are the same in all directions



The transitions to these intermediate states may be brought by

*Thermal processes*

or

*Influence of solvents*

**Thermotropic Liquid Crystals**

**Lyotropic Liquid Crystals**

# Classification

## Based on the response to temperature or concentration

- Thermotropic
- Lyotropic

## Based on the shape

- *Calamitic*
- *Discotic*
- *Polycatenar*
- *Bent (Banana )*

## Based on the phase structures

- Nematics
- Smectics
- Columnar
- Cubic

Thermotropic phases occur in a certain temperature range. If the temperature rise is too high, thermal motion will destroy the delicate cooperative ordering of the LC phase, convert the material into a conventional isotropic liquid phase. At too low temperature, most LC materials will form a conventional crystal

Based on the shape of the constituting molecules,  
the Thermotropic Liquid Crystals can be classified as

Calamitic LCs – rod like

Discotic LCs – disc like


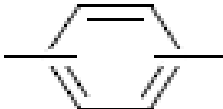
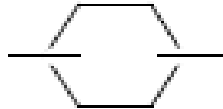
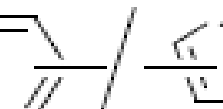
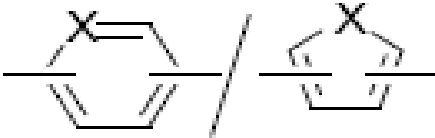
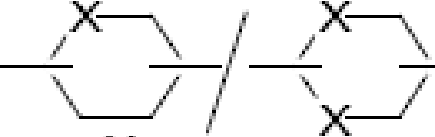
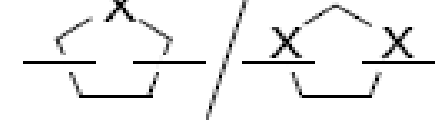
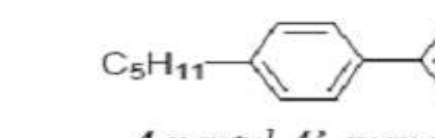
Banana LCs – bent like

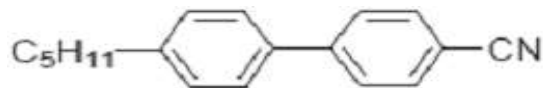
Polycatenar – Half rod like and disc like

Calamitic, i.e. rod-shaped, molecules show a large difference in length and breadth, thus delivering the required anisotropy

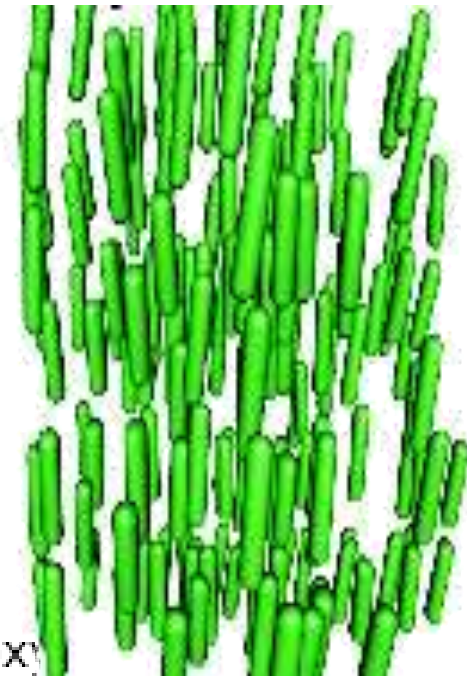
The general molecular formulae of **Calamitic** LC s



	L	R'/R''
	N=C	CN
	N=N	NO <sub>2</sub>
	COO	Alkyl
	COS	Alkyloxy
	C≡C	F/Cl/Br/I
	C=C	Fluorinated Alkyl
		Fluorinated Alkyloxy

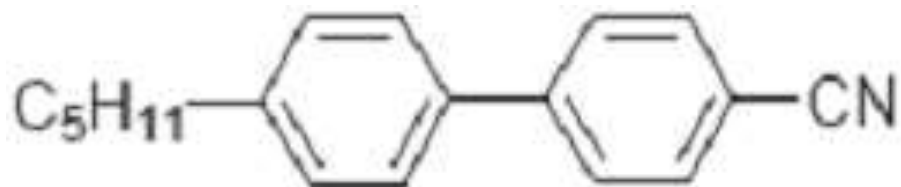
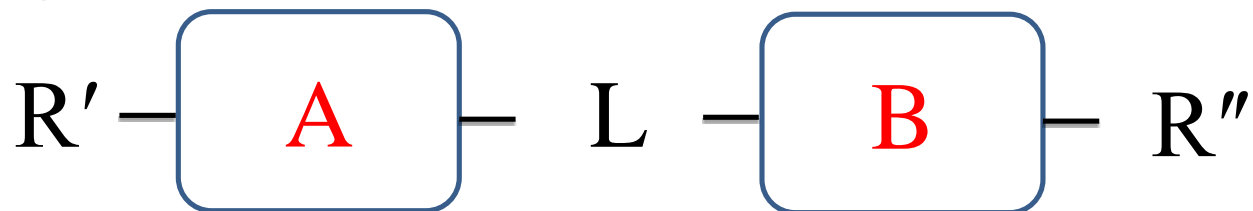


*4-pentyl-4'-cyanobiphenyl*

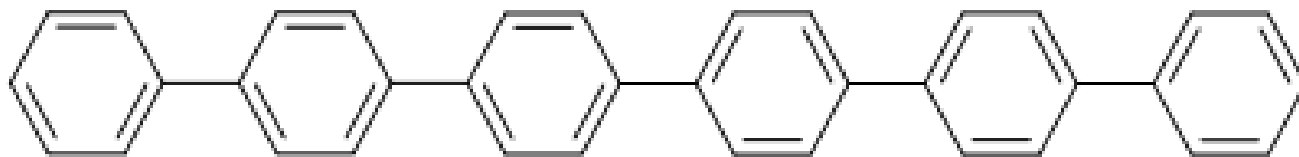


# Mol. Structures & examples

## Calamitic



*4-pentyl-4'-cyanobiphenyl*

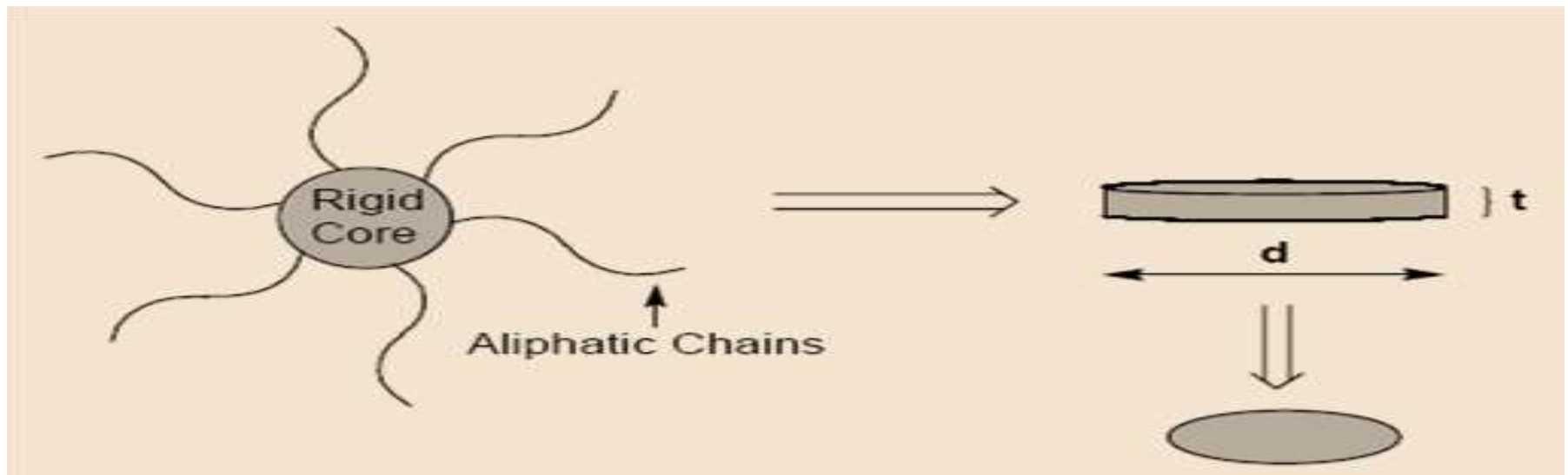


*p-sexiphenyl*

## Discotic LCs

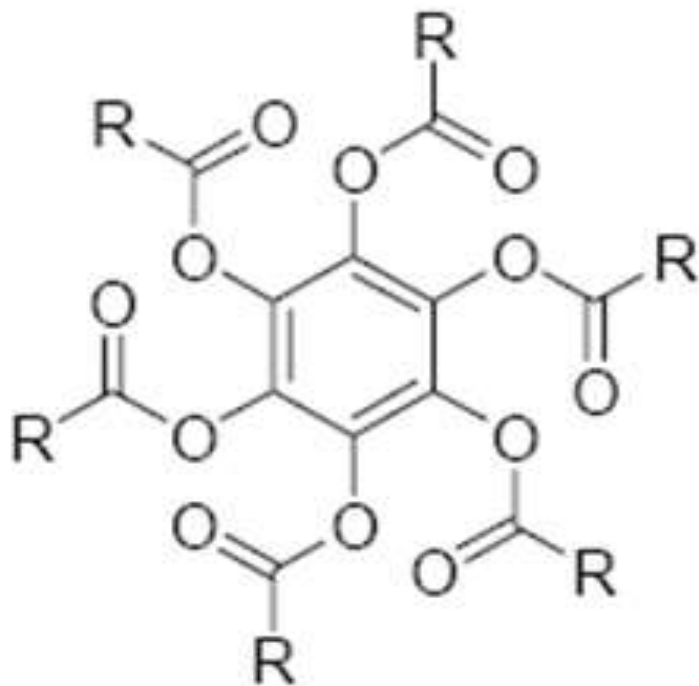
In 1977, a second type of mesogenic structure, based on discotic (disc-shaped) molecular structures was discovered. The first series of discotic compounds to exhibit mesophase belonged to the hexa-substituted benzene derivatives synthesised by S. Chandrasekhar et al.

Discotic LCs possess a general structure comprising a planar (usually aromatic) central rigid core surrounded by a flexible periphery, represented mostly by pendant chains (usually four, six, or eight),



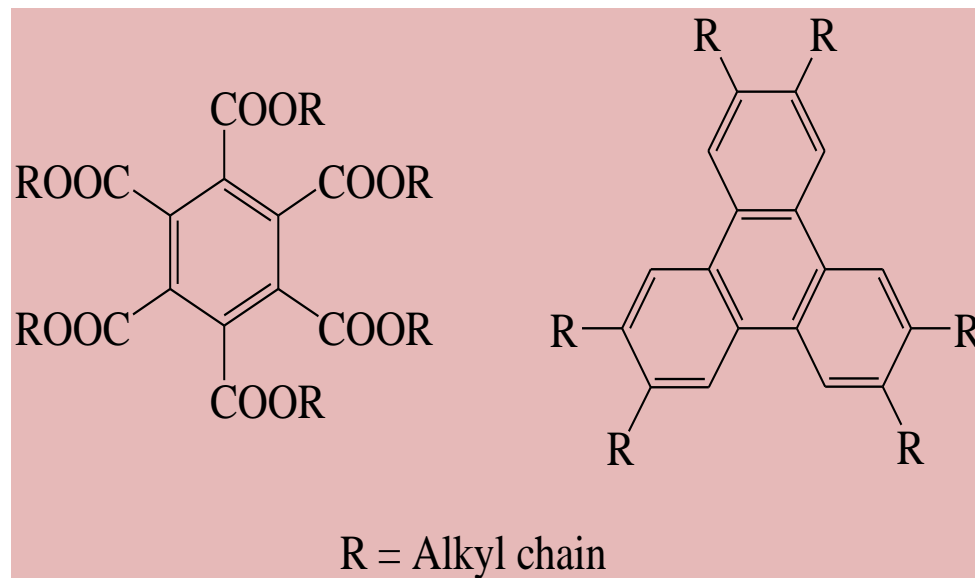
the molecular diameter ( $d$ ) is much greater than the disc thickness ( $t$ ) to form anisotropy and packed one upon another to form columns





$R = C_4H_9 \text{ to } C_9H_{19}$

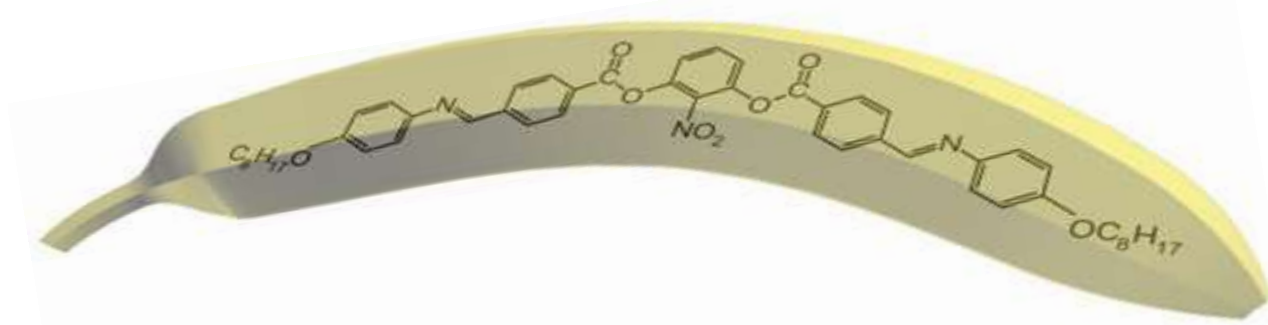
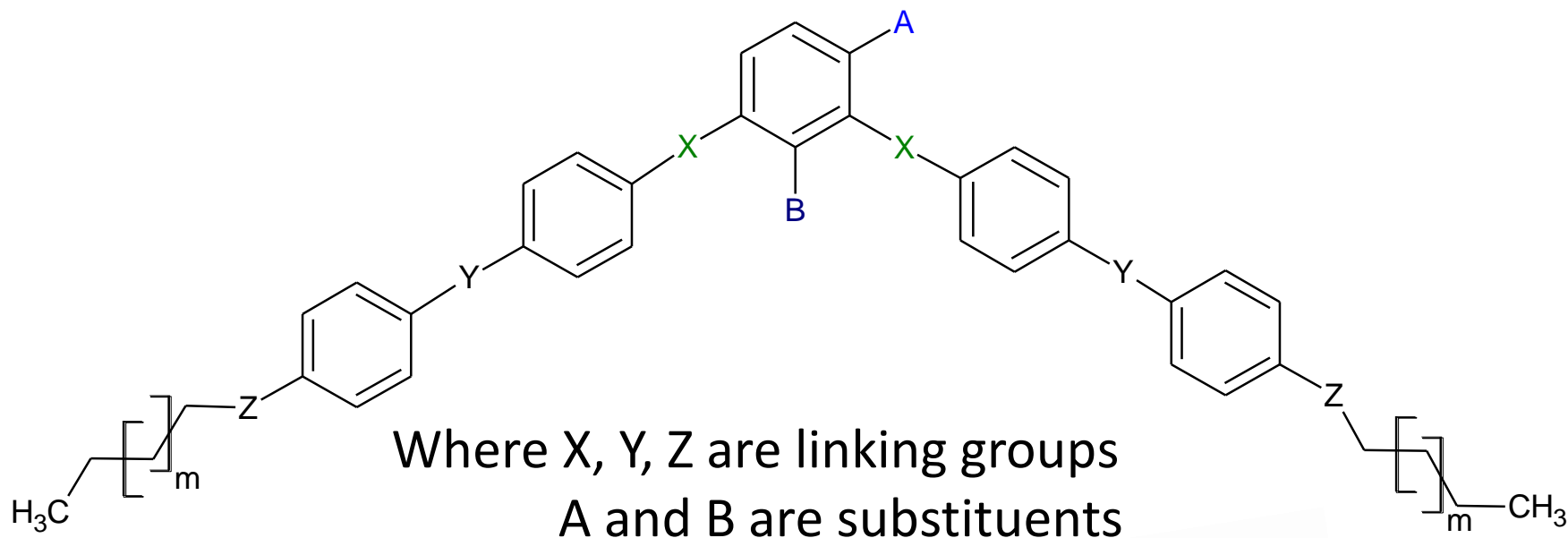
Molecular structure of first series of discotic LCs  
discovered *Benzene hexa n-alkanoate*  
*derivatives*



# Bent Core LCs

- Banana shaped liquid crystals are also known as bent core mesogen.
- Compound composed of a bent central aromatic part (1,3 substituted benzene) and two flexible tails.

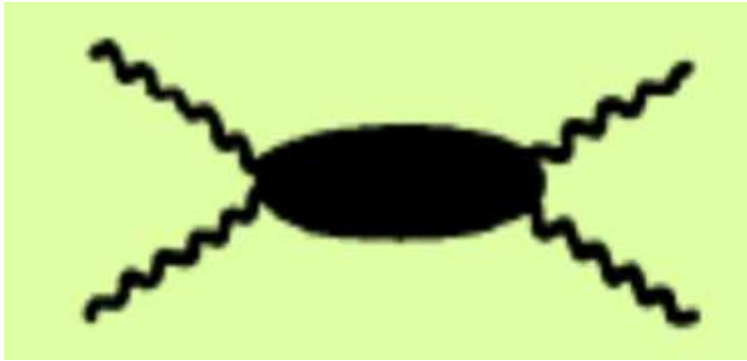
# The general molecular structure of bent core mesogens



# Polycatenar

represent a hybrid class of thermotropic LCs, intermediate molecular features between classical rod-like and disc-like mesogens

comprises a calamitic region, with half-discs on the extremities



2,2-polycatenary mesogen  
(hemiphasmidic)



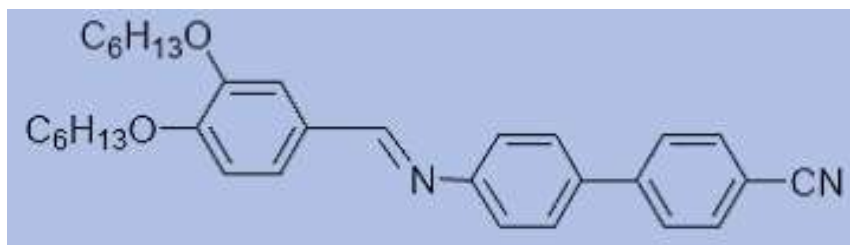
3,1-polycatenary mesogen  
(hemiphasmidic)



3,2-polycatenary mesogen  
(Forked hemiphasmidic)



3,3-polycatenary mesogen (Phasmidic)



## Lyotropic LCs

Lyotropic LCs are two-component systems where an amphiphile is dissolved in a solvent.

Thus, lyotropic mesophases are concentration and solvent dependent.

The amphiphilic compounds are characterized by two distinct moieties, a hydrophilic polar “head” and a hydrophobic “tail”.

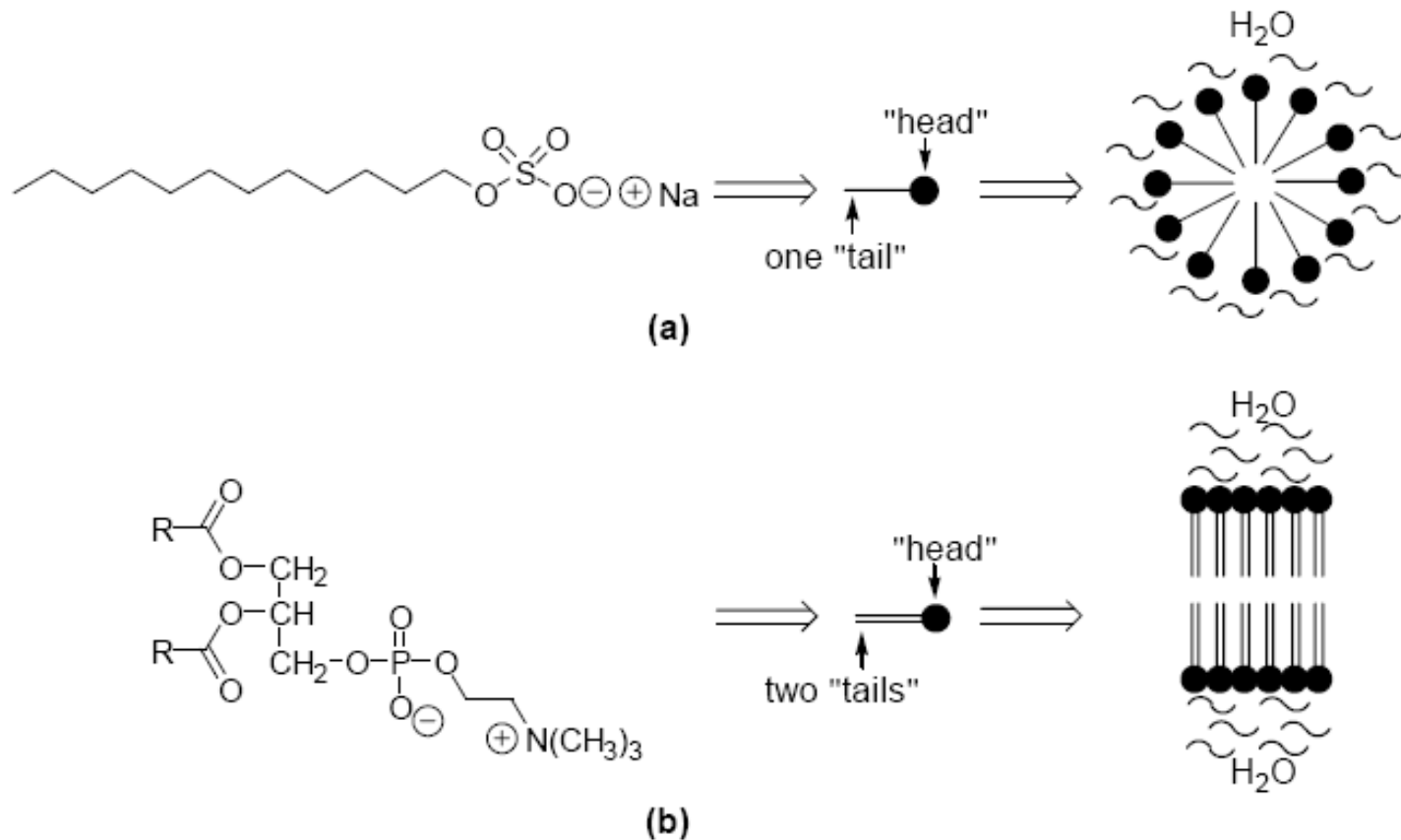
Examples of these kinds of molecules are soaps and various phospholipids like those present in cell membranes

A lyotropic liquid crystal consists of two or more components that exhibit liquid-crystalline properties in certain concentration ranges.

In the lyotropic phases, solvent molecules fill the space around the compounds to provide fluidity to the system. In contrast to thermotropic liquid crystals, these lyotropics have another degree of freedom of concentration that enables them to induce a variety of different phases.

Soap + **polar solvent like water**- micelle formation

Soap + **non polar solvent like hexane** – inverted micelle

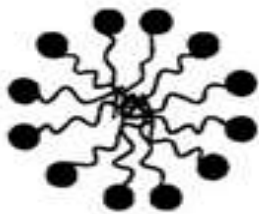


**Figure 2.** Chemical structure and cartoon representation of (a) sodium dodecylsulfate (soap) forming micelles, and (b) a phospholipid (lecithine), present in cell membranes, in a bilayer lyotropic liquid crystal arrangement.

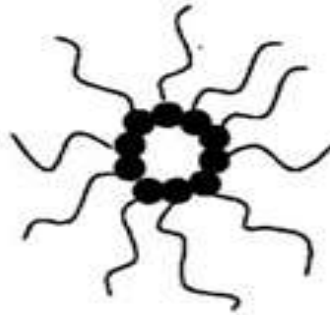


# Micellar aggregates and phases formed by Lyotropic liquid crystals

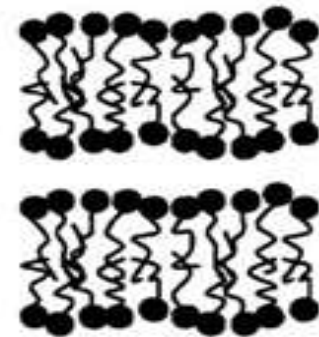
Under certain conditions, these micelles further aggregate to form more complicated assemblies, such as lamellar and hexagonal phases, which generate lyotropic liquid crystal phases.



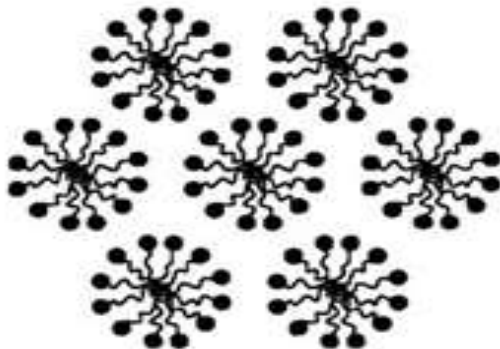
a.) micelle



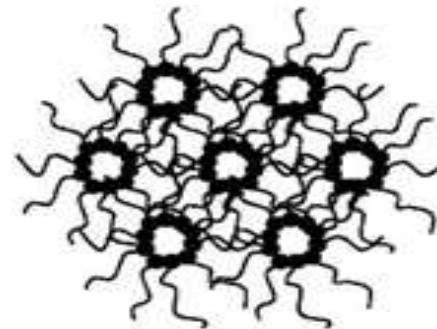
b.) inverse micelle



c.) lamellar



d.) hexagonal phase (H<sub>1</sub>)



e.) inverse hexagonal phase (H<sub>2</sub>)

## Based on the phase structures

The most important phase structures (mesophases) of liquid crystals are

Nematic

Smectic

Columnar

Cubic

*Nematic:* The most liquid like structure in which, one or two molecular axes are oriented parallel to one another, resulting in an orientational long-range order.

*Smectic:* Layer structures with many possibilities of the state of order inside the layers and different possibilities of mutual arrangement of the layers, showing long range orientational and more or less positional order

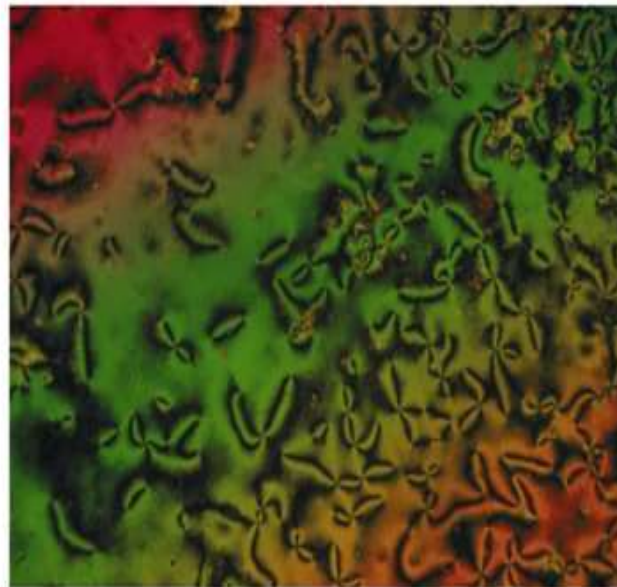
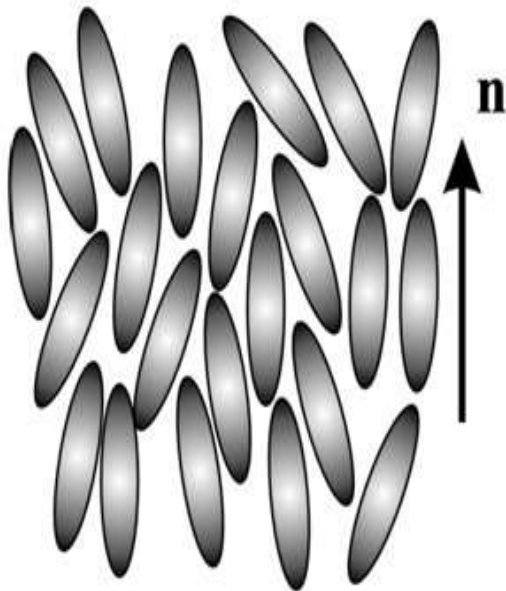
*Columnar:* Structures with columns consisting of parallel arranged disc-like molecules.

*Cubic:* Structures with micellar lattice units or complicated interwoven networks.

## Nematic phase:

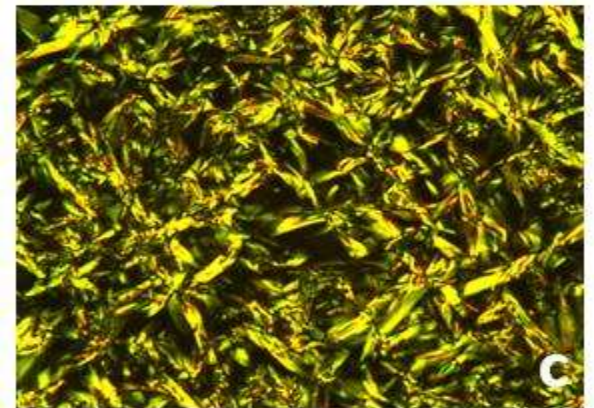
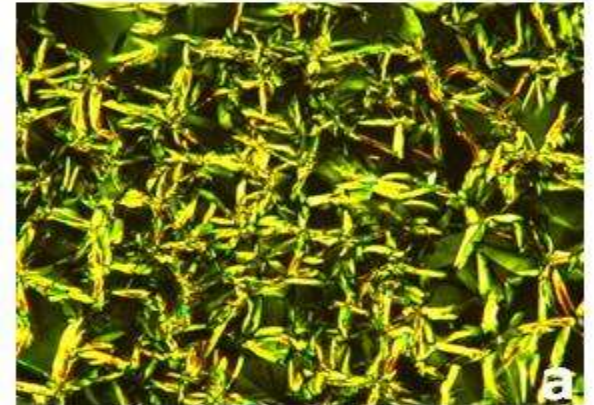
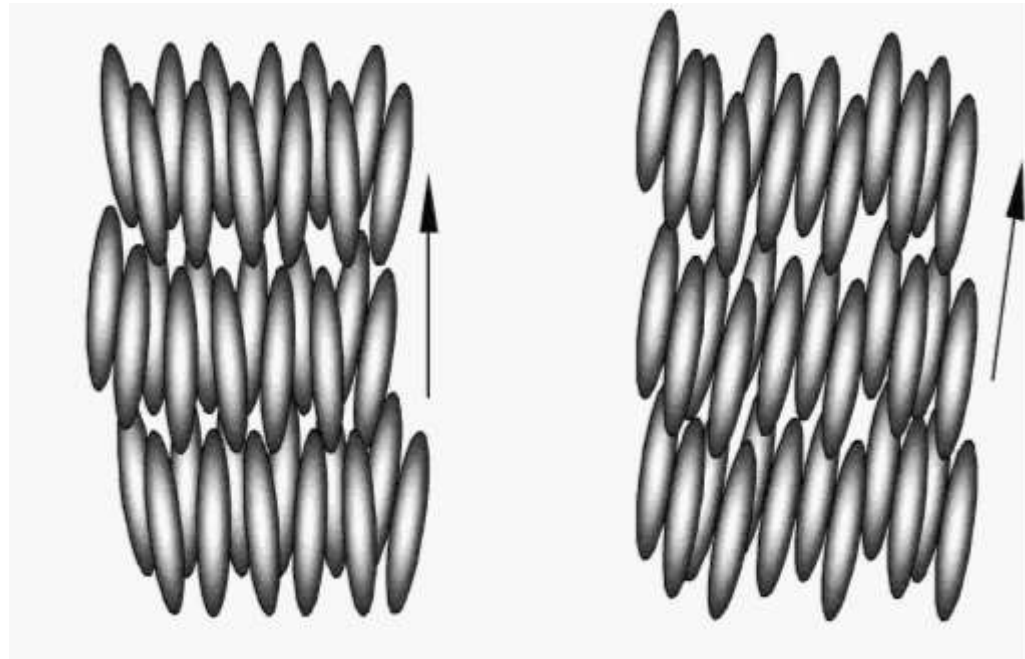


The least ordered mesophase (the closest to the isotropic liquid state) is the nematic (N) phase, where the molecules have only an orientational order



# Smectic phases

In smectic (S) phase, in addition to the orientational order the molecules possess less or more positional order, such that the molecules organize in layered structures.

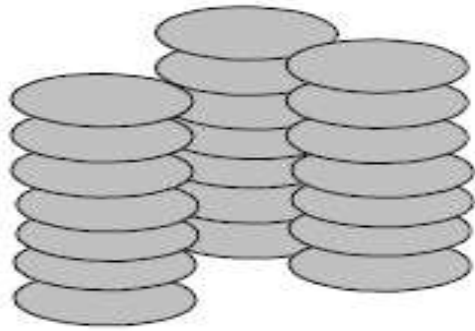


# Columnar Phases

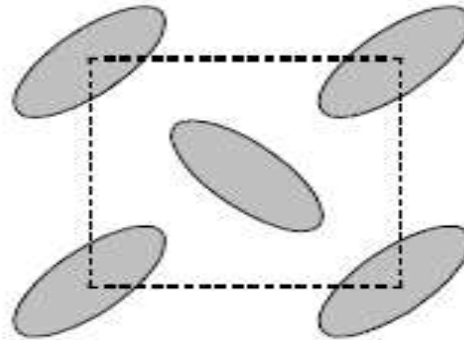
Columnar (Col) phases are more ordered. Here the disc-shaped cores have a tendency to stack one on the top of another, forming columns

Arrangement of these columns into different lattice patterns gives rise to a number of columnar mesophases, namely columnar rectangular ( $\text{Col}_r$ ) and columnar hexagonal ( $\text{Col}_h$ )

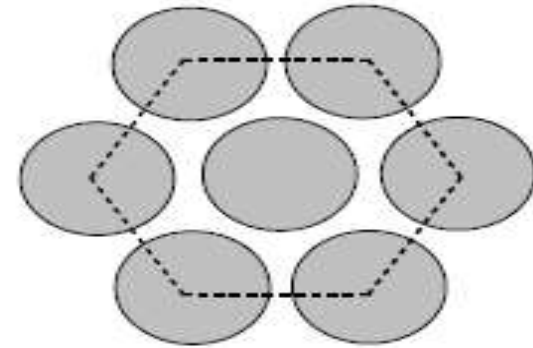




(a)



(b)



(c)

(a) the general structure of Col phases, where the molecules are aligned in the same orientation and, in addition, form columns,  
 (b) representation of Col<sub>r</sub>, and (c) representation of Col<sub>h</sub>.

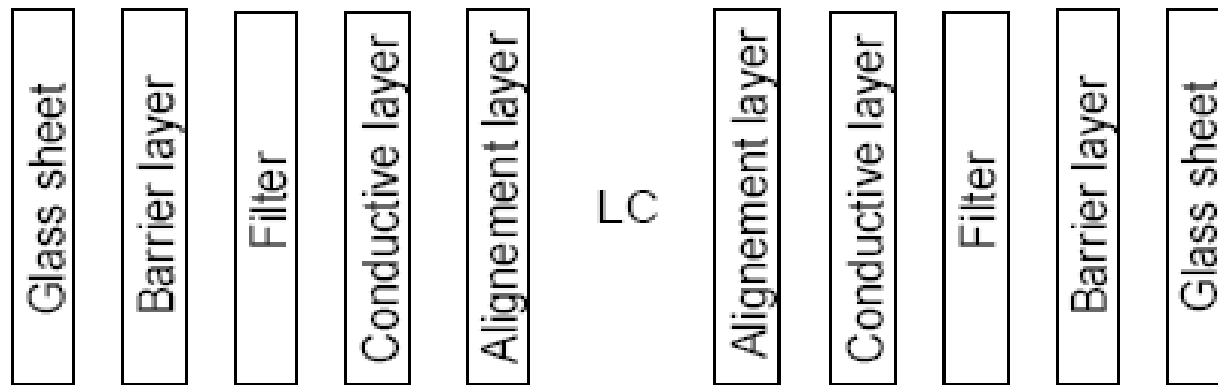
# LCs - Properties

- LC behavior should be at RT & the entire temp.range of the device operation
- Chemically, electrochemically, photochemically & thermally stable
- High electrical resistance
- Either low or high birefringence anisotropy, depending upon the type of device
- Permanent electric dipole to possess dielectric anisotropy, either a positive or negative.
- Possess easily polarizable substituents



## Liquid Crystals in Display systems

used in displays for more than thirty years starting with the simple passive-matrix displays to the technologically advanced multiplex active-matrix displays.



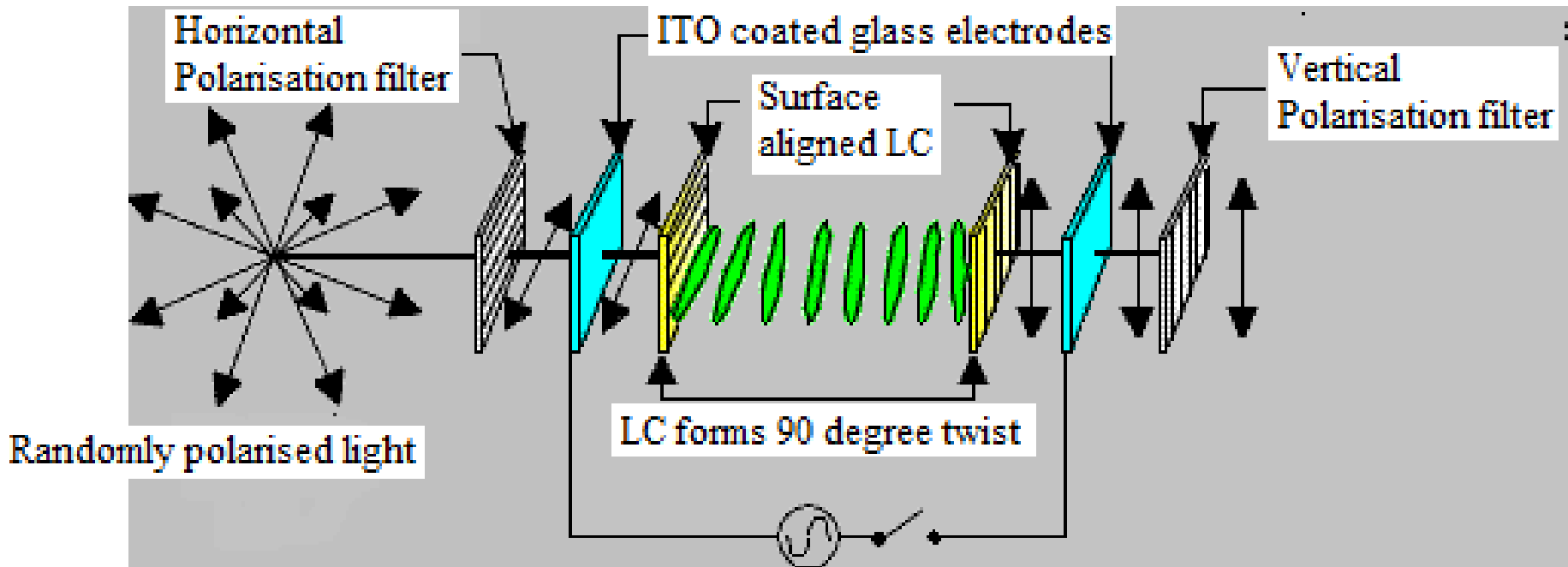
*Scheme of the sequence of the most common parts used for the fabrication*

Layer	Material	Function
Barrier	Silica	Prevention of contaminants from the glass to the LC film
Filter	Dyed polymer/ photographic emulsion	Colour
Conductive	Indium tin oxide (ITO)	Activation of the display
Alignment	Polyimide	Direction of orientation of the LC molecular director

The electro-optic effect of liquid crystals controls brightness/darkness of the light emerging from its elements, this is used in information displays

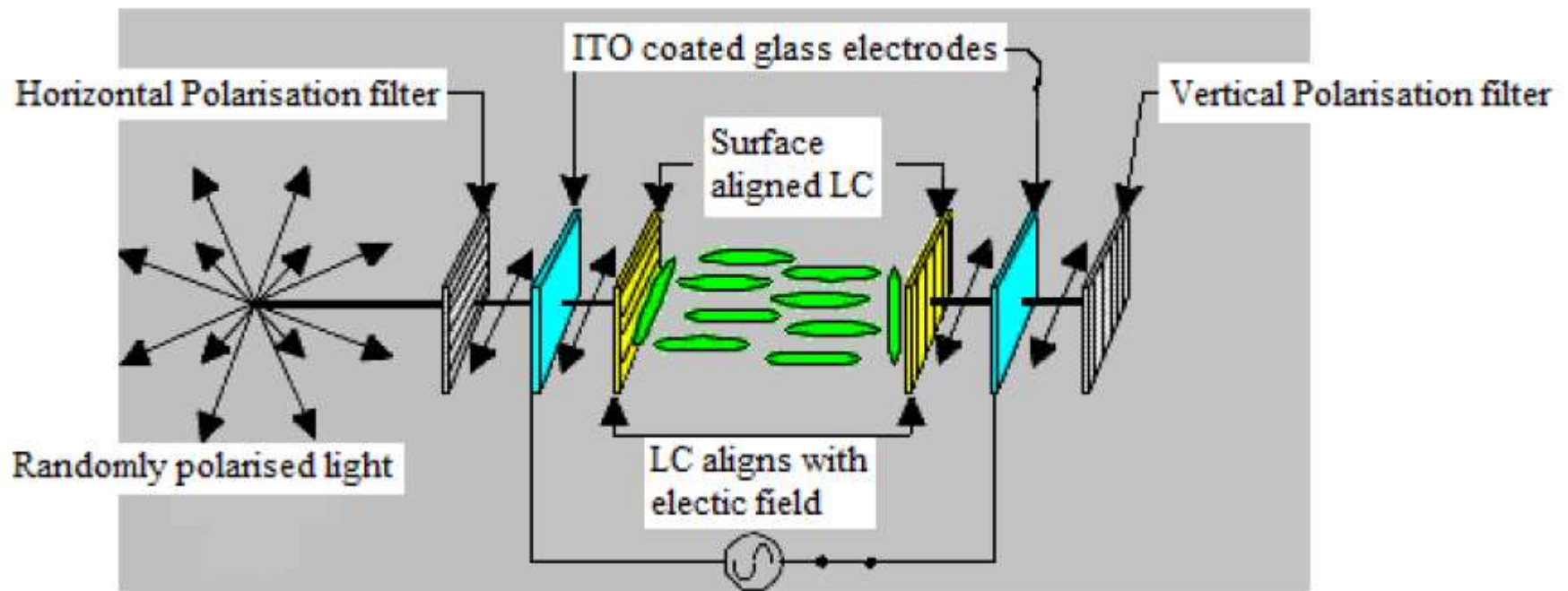
In the most common types of displays two polarisers, one on each side of this unit completes the display construction.

# LC Displays - working



LCD pixel with 'OFF' state

In the absence of an external electric field, linearly polarized light enters the device, the LC film acts as an optical wave guide rotating the polarization of the light by  $90^\circ$ . Thus, the light reaches the second polarizer (analyzer/reflector) with its polarization plane parallel to the polarizer axis and is transmitted. In this configuration the display appears bright (off-state)



when an electric field is applied (on-state), the LC molecules reorient in order to align the molecular director with the external electric field, Here, light passing through the LC film, is not guided through  $90^\circ$ , and is not able to pass through the second polarizer. The observer sees a black character on a silver gray background

When the electric field is turned off, the molecules relax back to their  $90^\circ$  twist structure

# Applications of liquid crystals

**Liquid crystal displays:** display devices such as watches, calculators, mobile telephones, laptop computers and clocks.

2. **Liquid crystal thermometers:** Nematic LCs reflect light and the color reflected is dependent upon temperature.

3. **In medicine:** LCs can be used to detect tumors. As tumor cells are warmer than normal cells, show a different color than normal cells on LCs.

4. **Optical Imaging and recording:** LC cell is placed between two layers of photoconductor. When light is applied, it increases the conductivity of material. This causes an electric field to develop in the LC corresponding to the intensity of light. The electric pattern can be transmitted by an electrode, which enables the image to be recorded.

5. **mechanical testing of materials:** LCs have tendency to change color when stretched or stressed. Thus, LC sheets are often used in industry to look for hot spots, map heat flow, measure stress distribution patterns and so on.

# COMPOSITES

- Composed of two or more materials of the categories namely metals, ceramics & polymers. These are artificially produced multiphase materials having a desirable combination of the best properties of the constituent phases  
Usually one phase (the matrix) is continuous and completely surrounds the other (the dispersed phase)

Properties of composite materials are determined by three factors.

i) The materials used as component phases in the composite

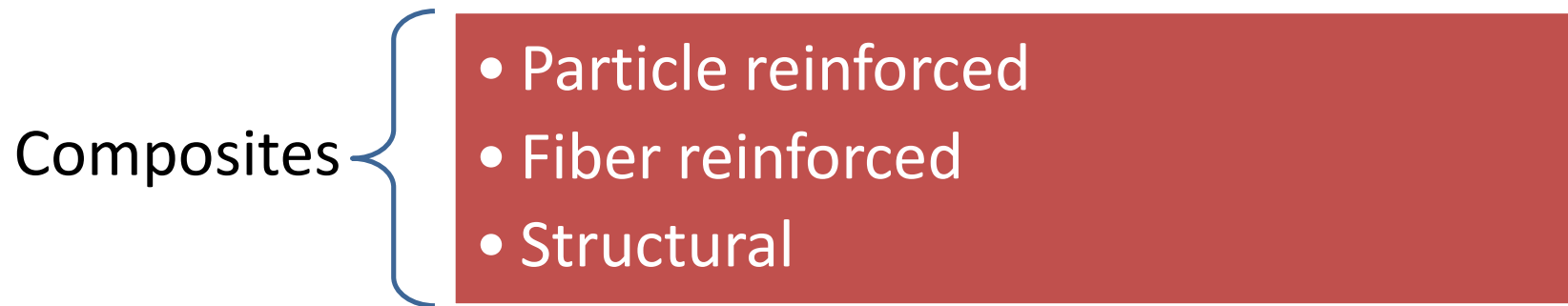
ii) The geometric shapes of the constituents

iii) The manner in which the phases interact with one another



# Classification of composites

According to the matrix material & the reinforcement geometry



# Particle reinforced

Properties are isotropic

The dispersed phase for particle reinforced composites is equiaxed (i.e., particle dimensions are approximately the same in all directions)

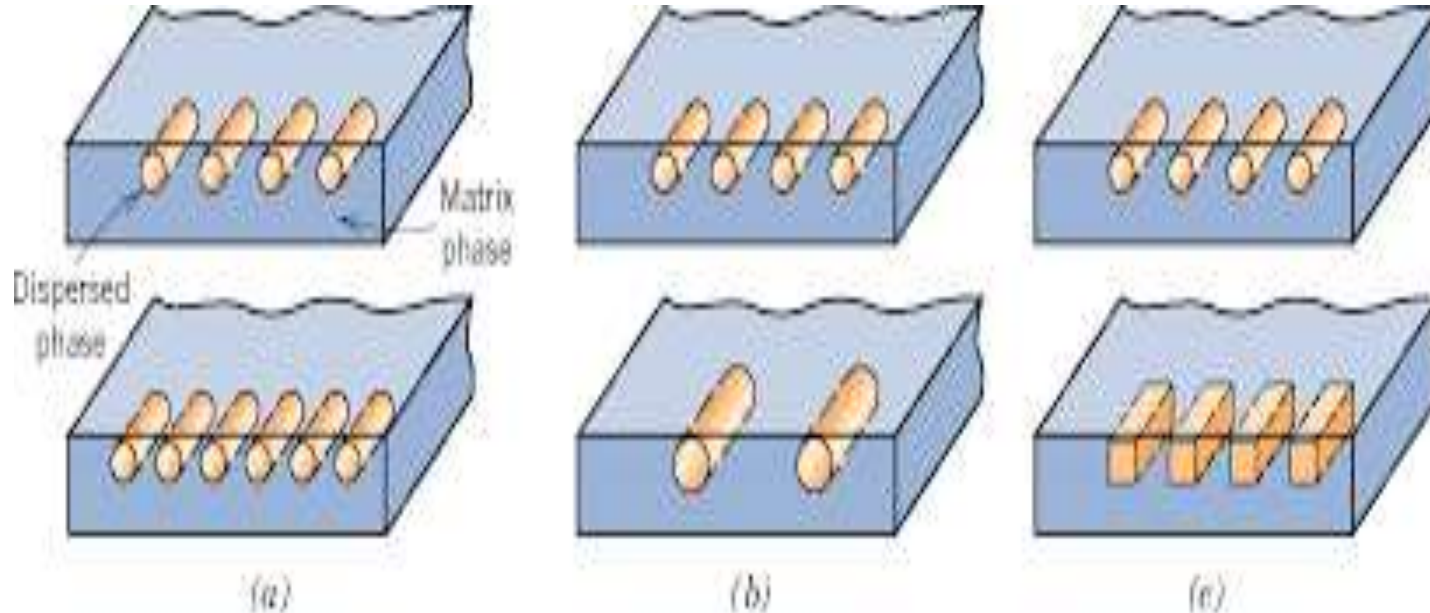
**Large particle**

**Dispersion strengthened**

# Particle reinforced

## Large particle

- the particulate phase is harder & stiffer than the matrix.



the particulate phase is harder and stiffer than the matrix. the matrix transfers some of the applied stress to the particles, which bear the friction of the load.

# Particle reinforced

## Dispersion strengthened

- the matrix bears the major portion of an applied load
- particles usually are much smaller
- the small dispersed particles hinder the motion of dislocations

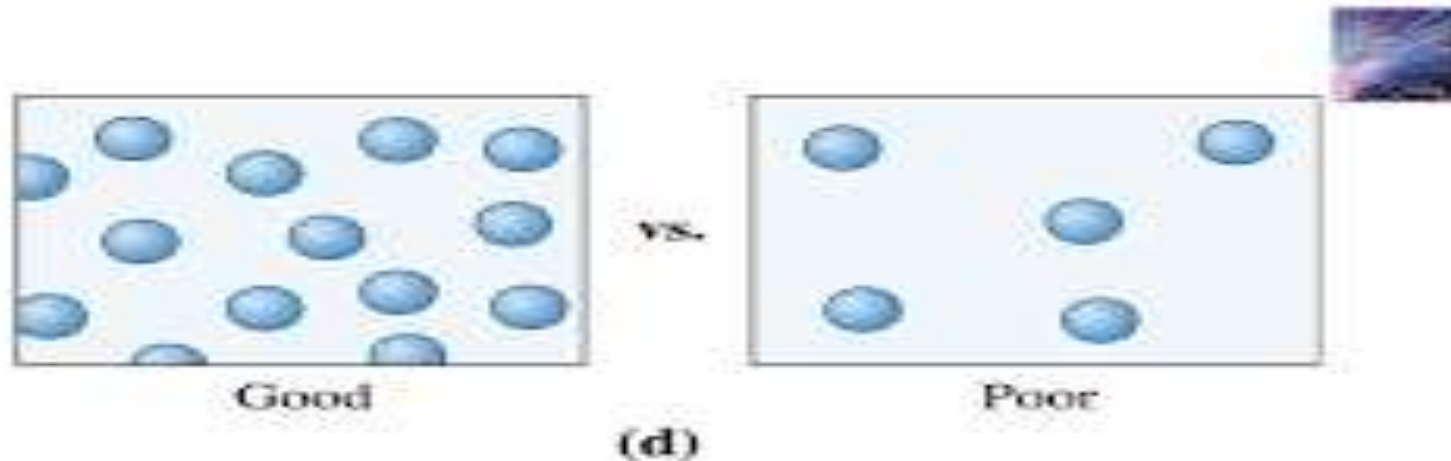


Figure 10.1 Considerations for effective dispersion strengthening: (d) Larger amounts of dispersed phase increase strengthening.

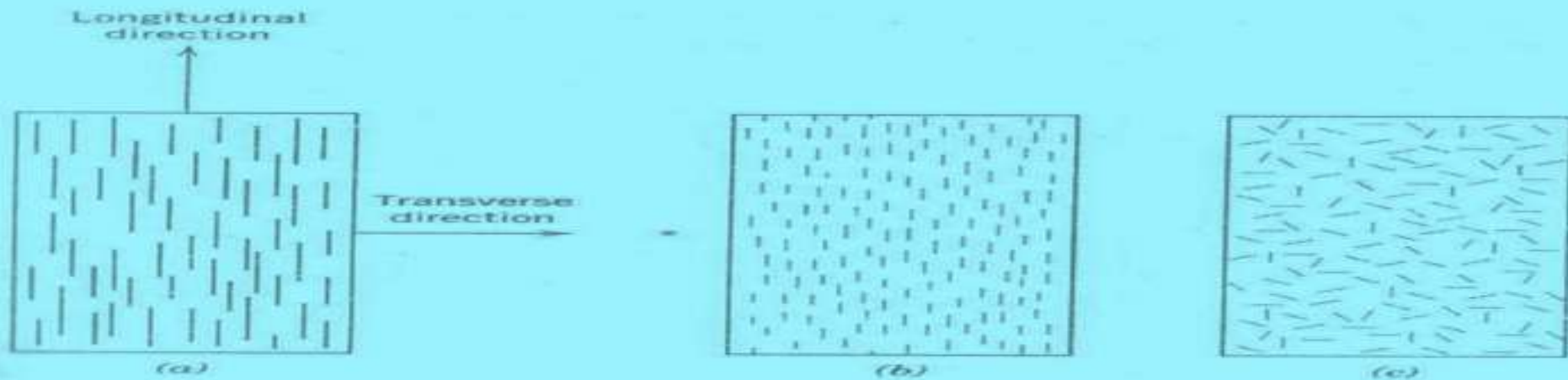
# Fiber reinforced

## Properties can be isotropic or anisotropic

The dispersed phase- in the form of a fiber.

An applied load is transmitted to & distributed among the fibers via the matrix phase.

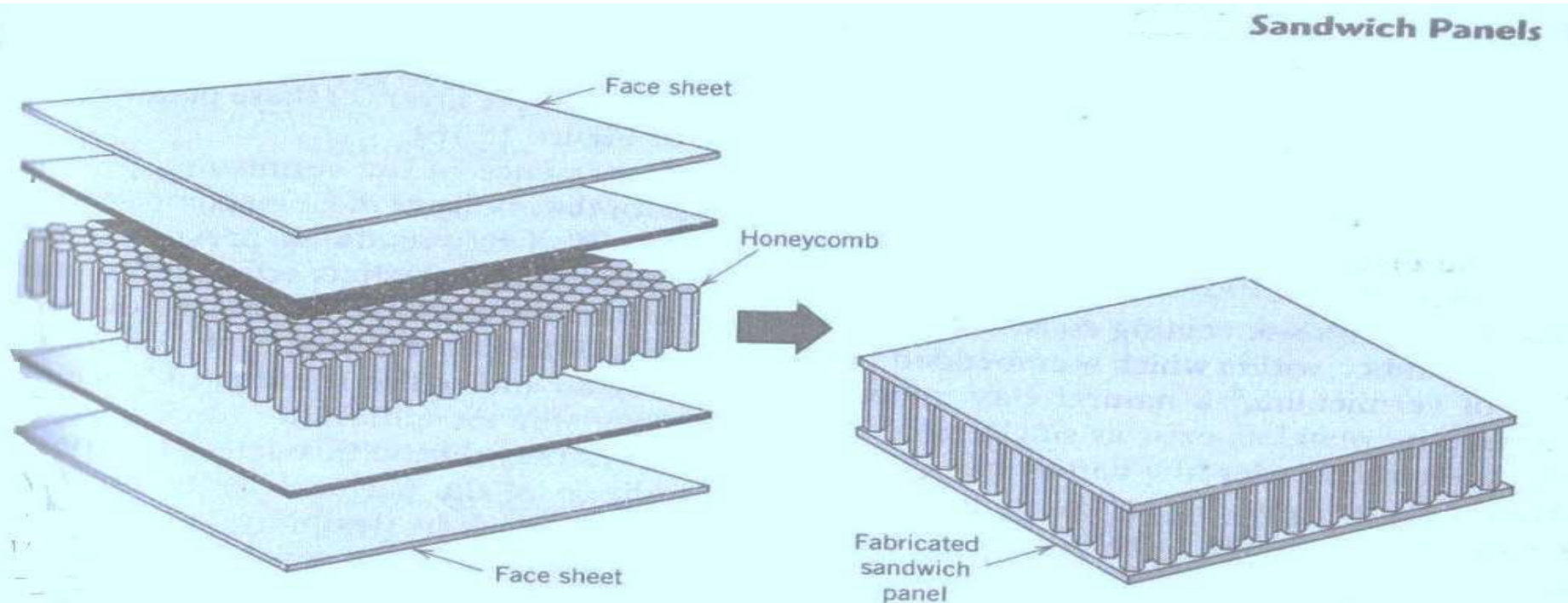
- Continuous (aligned)
- Discontinuous (short) ---- Aligned & Randomly oriented



Fiber orientation and concentration have a significant influence on the strength and other properties

# Structural

Based on build-up of sandwiches in layered form



Sandwich panels consist of two strong and stiff faces that are separated by a core material or structure. These structures combine relatively high strengths & stiffness with low densities.

# Composites

## Advantages

- Strong and stiff, yet very light in weight
- Better fatigue properties
- Can be designed that they do not corrode
- Possible to achieve combinations of properties not attainable with metals, ceramics, polymers alone

## Disadvantages

- More expensive than conventional materials
- Manufacturing methods for shaping composite materials are often slow
- polymer based composites subject to attack by chemicals or solvents
- anisotropic

# POLYMER COMPOSITES

## 2 components;

- Reinforcing materials- that are strong with low densities
- Matrix- usually a ductile or tough material

**Materials used**

**Advantages**

**Applications**



The fibre is most often glass, carbon fibre, or polyethylene. The matrix is usually a thermoset polymer like epoxy resin, polydicyclopentadiene or a polyimide.

The materials generally used are:

**Fibers** - Glass fibres, carbon fibres or aromatic polyimides (or aramids).

**Resins:** (a) thermosetting: polyesters and epoxides.

(b) thermoplastics: polyolefins, polyimides, vinylic polymers, polyacetals, polycarbonates and polyphenylenes.

**Additives:** For structural applications it is mandatory to achieve some degree of flame retardancy. FR additives are incorporated in the resin itself. Fillers and pigments are also used in the process.

## **Advantages of polymer composites:**

- Light weight, High strength to weight ratio.
- Durability, Good corrosion resistance.
- High fatigue strength, High temperature resistance.

## **Applications:**

- Composites of phenolic resins and nylon are used in heat shields for space crafts.
- used in automotive and railway applications.
- As structural material in construction industries.

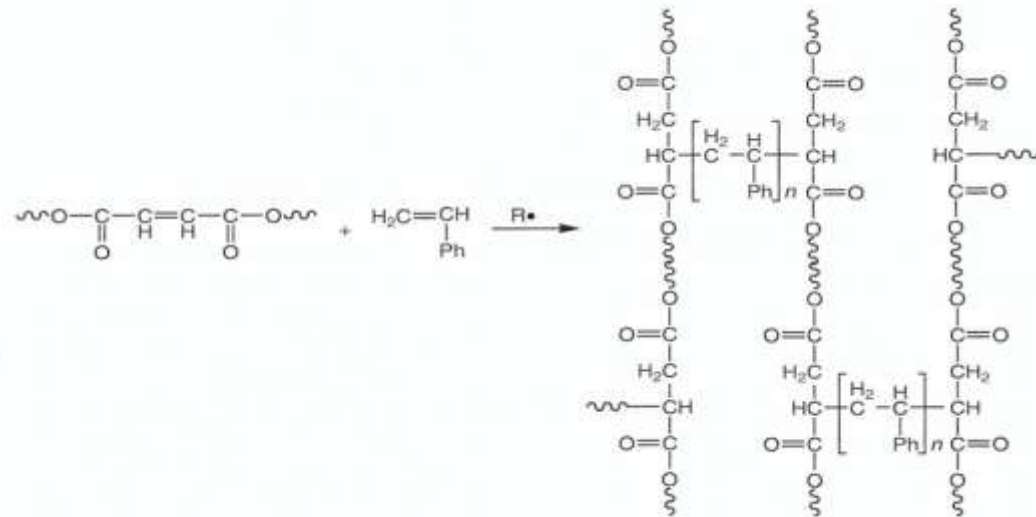
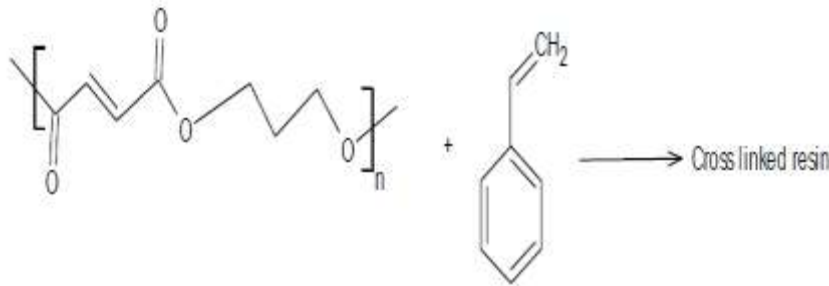
- i) Glass Fiber-Reinforced Polymer Composites,
- ii) Carbon Fiber-Reinforced Polymer Composites,  
and
- iii) Aramid Fiber-Reinforced Polymer Composites.

# Examples of polymer composites

## *Fibre glass or glass-reinforced plastic (GRP)*

**Matrix:** Made by reacting a polyester with carbon-carbon double bonds in its backbone and styrene- a mix of the styrene and polyester

**Fibre:** glass fibre



The glass fibre are trapped inside, where they act as a reinforcement. The matrix adds toughness to the composite, while fibres have good tensile strength

Applications: car engine components, aeroplane parts to boat hulls, sports equipments etc

# Aramid Fiber-Reinforced Polymer Composite

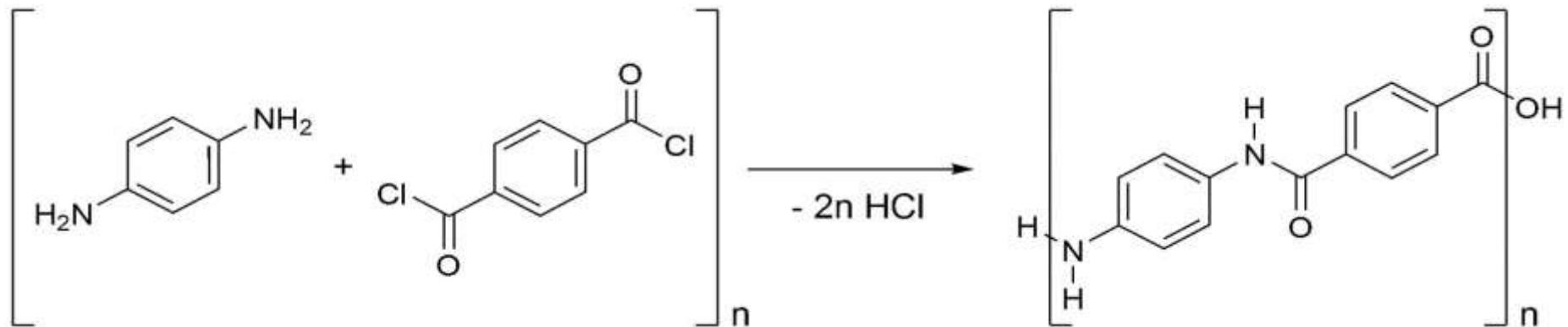
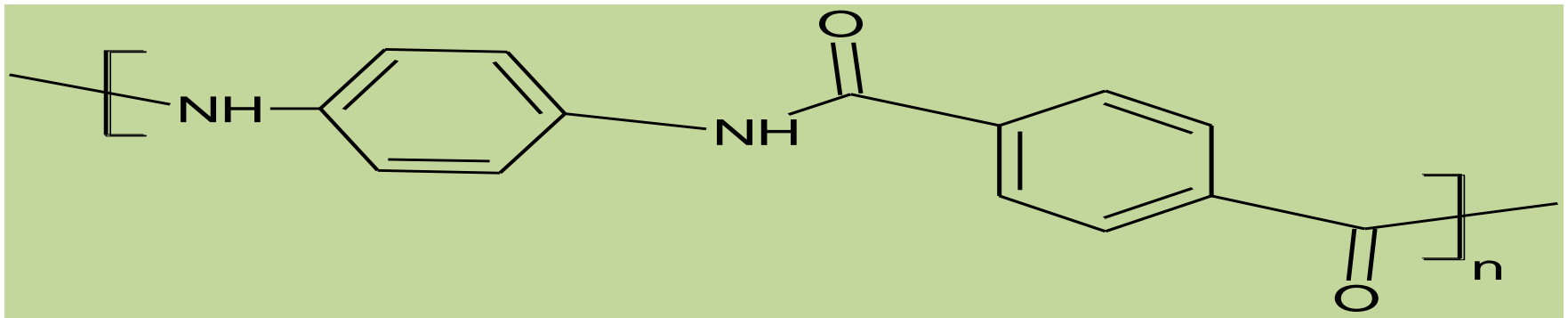
Aramid fibers - high-strength, high-modulus materials

desirable for their outstanding strength-to-weight ratios,  
which are superior to metals

Eg. Kevlar

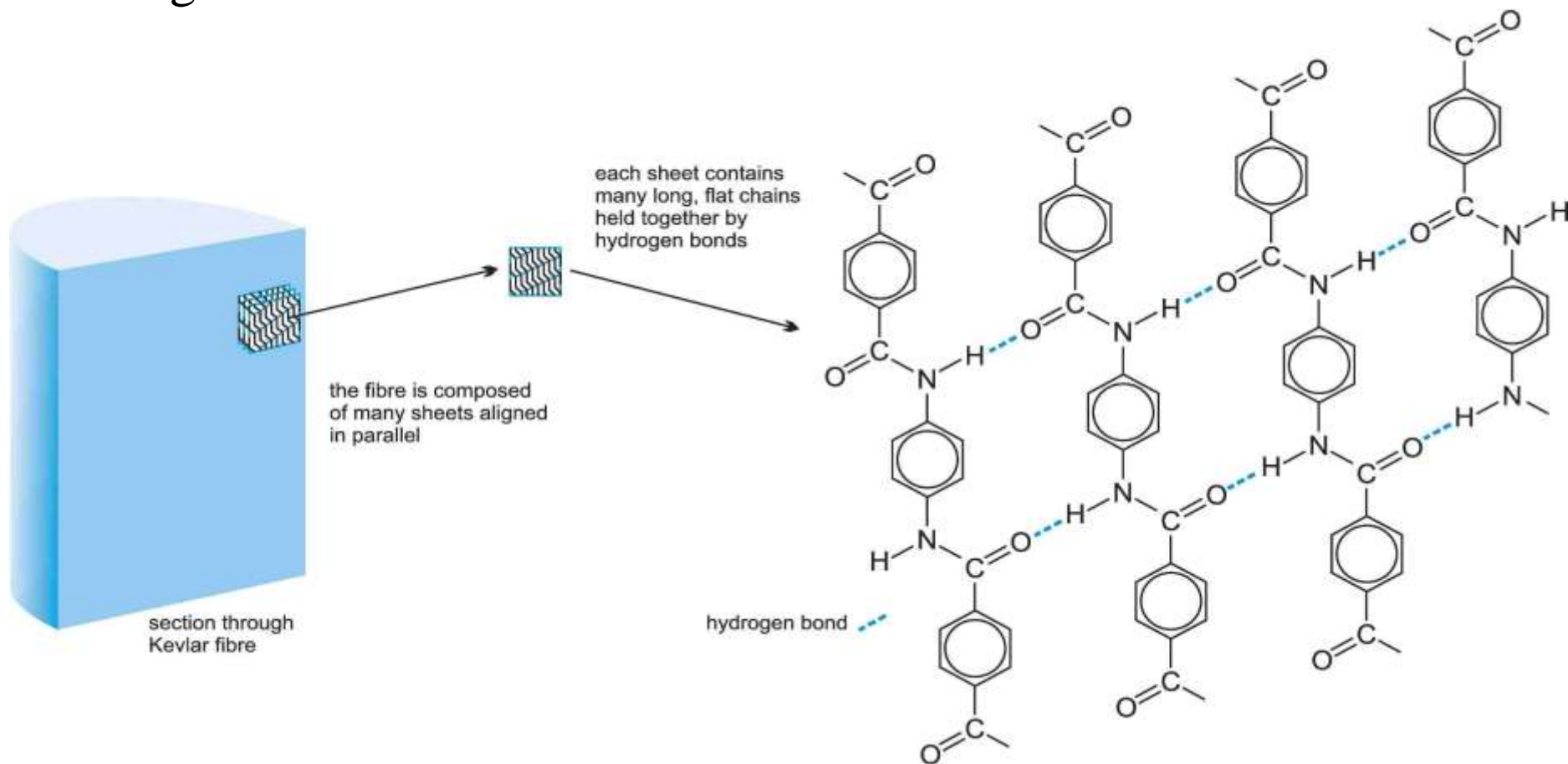
# Kevlar composites

- Kevlar is an aromatic polyamide. Chemically it is poly(para phenyleneterephthalamide).
- **Matrix:** Kevlar
- **Fibres:** carbon fibre or glass fibre as reinforcing agent.



# Kevlar composites

**Kevlar® 29** is used in the manufacture of body armour (panels) for lightweight military vehicles. A good example is the US Army's 'Bradley Fighting Vehicle'. This has been used extensively in Iraq and Afghanistan.



# Kevlar composites

**Advantages** Light weight, high strength, thermally stable, resistant to impact and abrasion damage. It can be used as protective layer on graphite laminates.

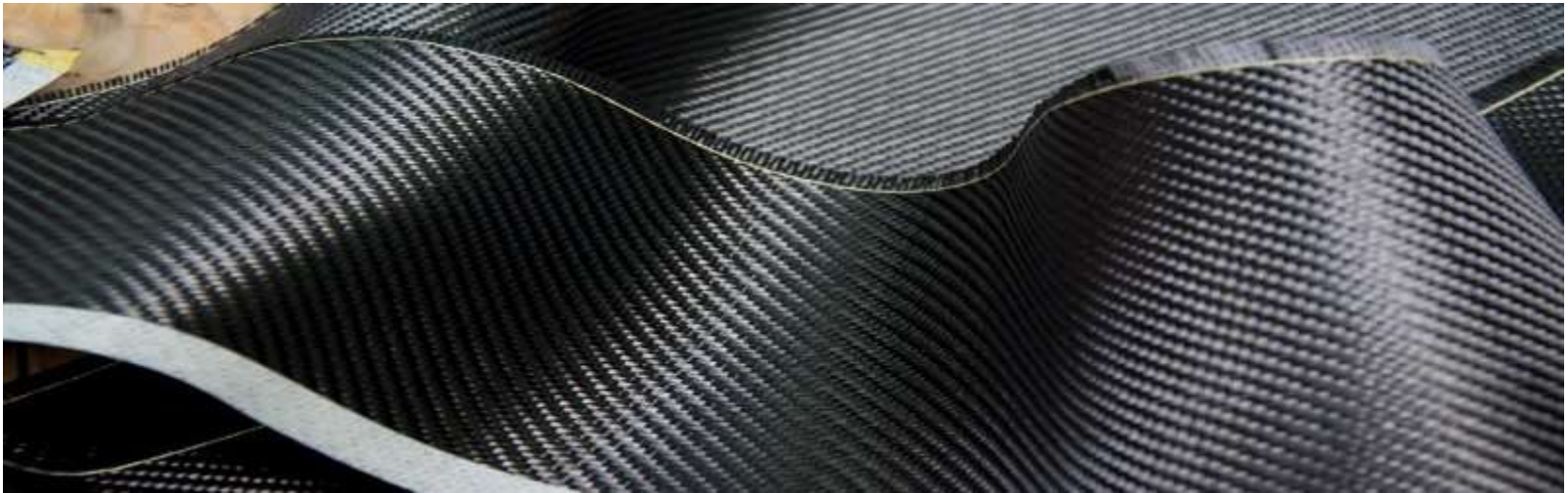
-Can be mixed with graphite to provide damage resistance and to prevent failure.

**Disadvantages:** Fibres themselves absorb moisture, Poor compression resistance



# Carbon fibre composites

- Carbon fibre is a fibre containing at least 90% carbon and 5–10 mm diameter
- Advantages including high stiffness, high tensile strength, low weight, high chemical resistance, high temperature tolerance



# Carbon fibre composites

- Obtained by controlled pyrolysis of appropriate fibres.
- Fibre precursors are used to produce carbon fibres of different morphologies & characteristics.

Precursors; e.g. polyacrylonitrile, cellulosic fibres or phenolic fibres.

- **Matrix material:** epoxy resin, phenolics, polyester or polyvinyls.

Uses: bicycles, used as a lightweight alternative to materials such as aluminium (twice as heavy)  
racing car, motorbike or powerboat

## **ii) Carbon Fiber Reinforced Polymer (CFRP) Composite:**

is a high-performance fiber material in advanced polymer matrix composites. The reasons for this are as follows:

1. Carbon fibers have the highest specific modulus and specific strength of all reinforcing fiber materials.
2. They retain their high tensile modulus and high strength at elevated temperatures; high-temperature oxidation, however, may be a problem.
3. At room temperature, carbon fibers are not affected by moisture or a wide variety of solvents, acids, and bases.
4. These fibers exhibit a diversity of physical and mechanical characteristics, allowing composites incorporating these fibers to have specific engineered properties.
5. Fiber and composite manufacturing processes have been developed that are relatively inexpensive and cost-effective.

# THIN FILMS

Properties

**Bonding**

Uses

**Techniques of deposition**

A thin film in general, refers to films with thickness ranging from 0.1  $\mu\text{m}$  to about 300  $\mu\text{m}$ .

Coatings such as paint or varnish are typically much thicker.

Thin film coatings have unique properties and hence make them desirable for a variety of reasons including materials conservation and design flexibility.

# Properties

- Chemically stable in the environment where it is used
- Adhere well to the substrate
- Uniform thickness
- Chemically pure or of controlled chemical composition
- Low density of imperfections
- Optical or magnetic properties, insulator or semiconductor as required for particular applications

# Uses of thin films

They are used as conductors, resistors and capacitors.

They are widely used as optical coatings on lenses to reduce reflection and to protect the softer glass against scratching.

Thin metallic films have been used as protective coatings on metals. Eg. Silver plating, chrome plating.

Metal tool surfaces are coated with ceramic thin films to increase their hardness. The top of the drill bit is normally coated with a thin film of tungsten carbide to impart hardness and wear resistance.

The films are applied to the glass to reduce scratching and abrasion and to increase lubricity.

# **Formation of thin films**

The process of applying a thin film to a surface is known as thin-film deposition or fabrication.

It is the technique for depositing a thin film of material onto a substrate or onto previously deposited layers.

Thin films are formed by different techniques

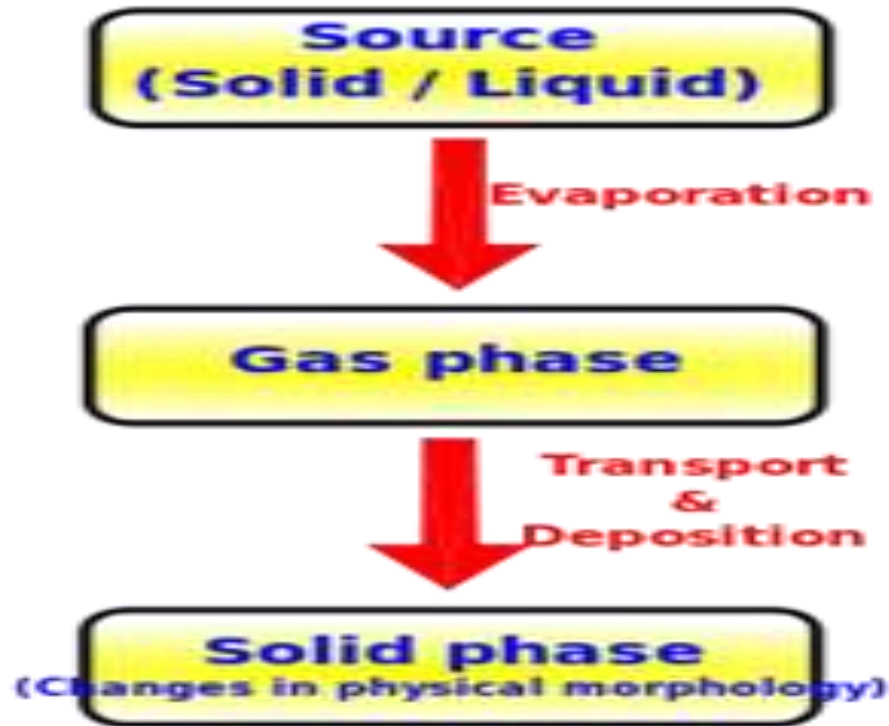
Physical vapor deposition (PVD)

Chemical vapor deposition (CVD).



In PVD there is no change in the chemical nature of the source and coated material whereas in CVD due to chemical reactions occurring, the chemical identity of the source and the coated thin film materials are different.

# Physical Vapor Deposition (PVD)



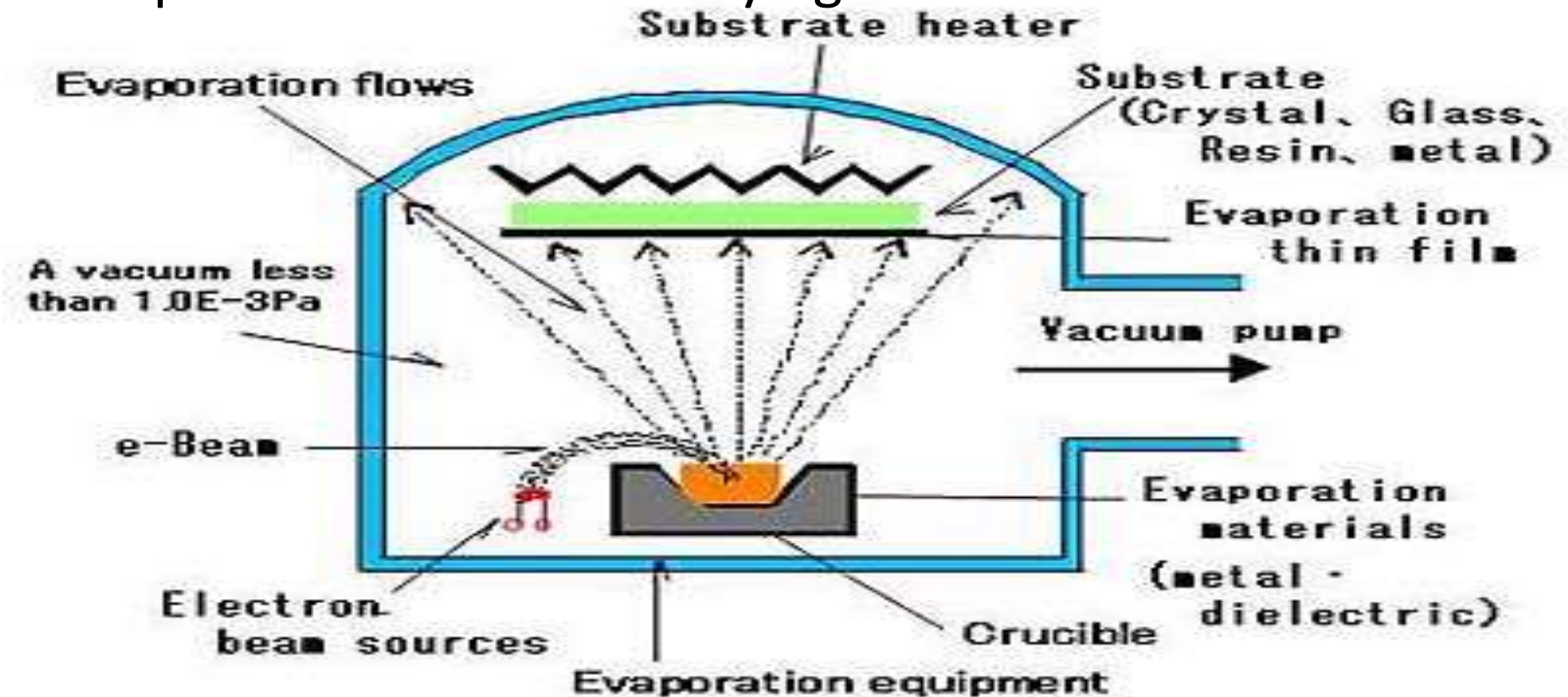
PVD processes are atomistic deposition processes in which material is vaporized to form a solid or liquid source in the form of atoms or molecules, transported as vapor through a vacuum or low pressure gaseous (or plasma) environment to the substrate where it condenses.

The chemical purity of evaporated films depends on the nature and level of impurities that

- (1)** are initially present in the source,
- (2)** contaminate the source from the heater, crucible, or support materials, and
- (3)** originate from the residual gases present in the vacuum system

# Vacuum deposition

This method is used to form thin films of substances that can be vaporized without destroying their chemical identities



Evaporation of target consisting of the material to be deposited is bombarded by a high energy source such as a beam of electrons or ions in a high vacuum chamber under pressure

**Vacuum deposition:** This method is used to form thin films of substances that can be vaporized without destroying their chemical identities.

Eg. Optical lenses are coated with inorganic materials such as  $\text{MgF}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ .

During evaporation, a target consisting of the material to be deposited is bombarded by a high energy source such as a beam of electrons or ions in a high vacuum chamber with a pressure of  $10^{-5}$  torr or less.

# PVD

## *Advantages*

- coatings harder & more corrosion resistant
- Have high temperature & good impact strength, excellent abrasion resistance & durable
- Able to use several types of inorganic & organic coating materials on diverse group of substrates using a wide variety of finishes.
- Eco-friendly than traditional processes
- Possible to change the target material from which the sputtered atoms arise without disturbing the system so that multilayer films can be formed.

## *Disadvantages*

- High capital cost
- Some processes operate at high vacuums & temperatures
- Requires appropriate cooling systems
- The rate of coating deposition quite slow

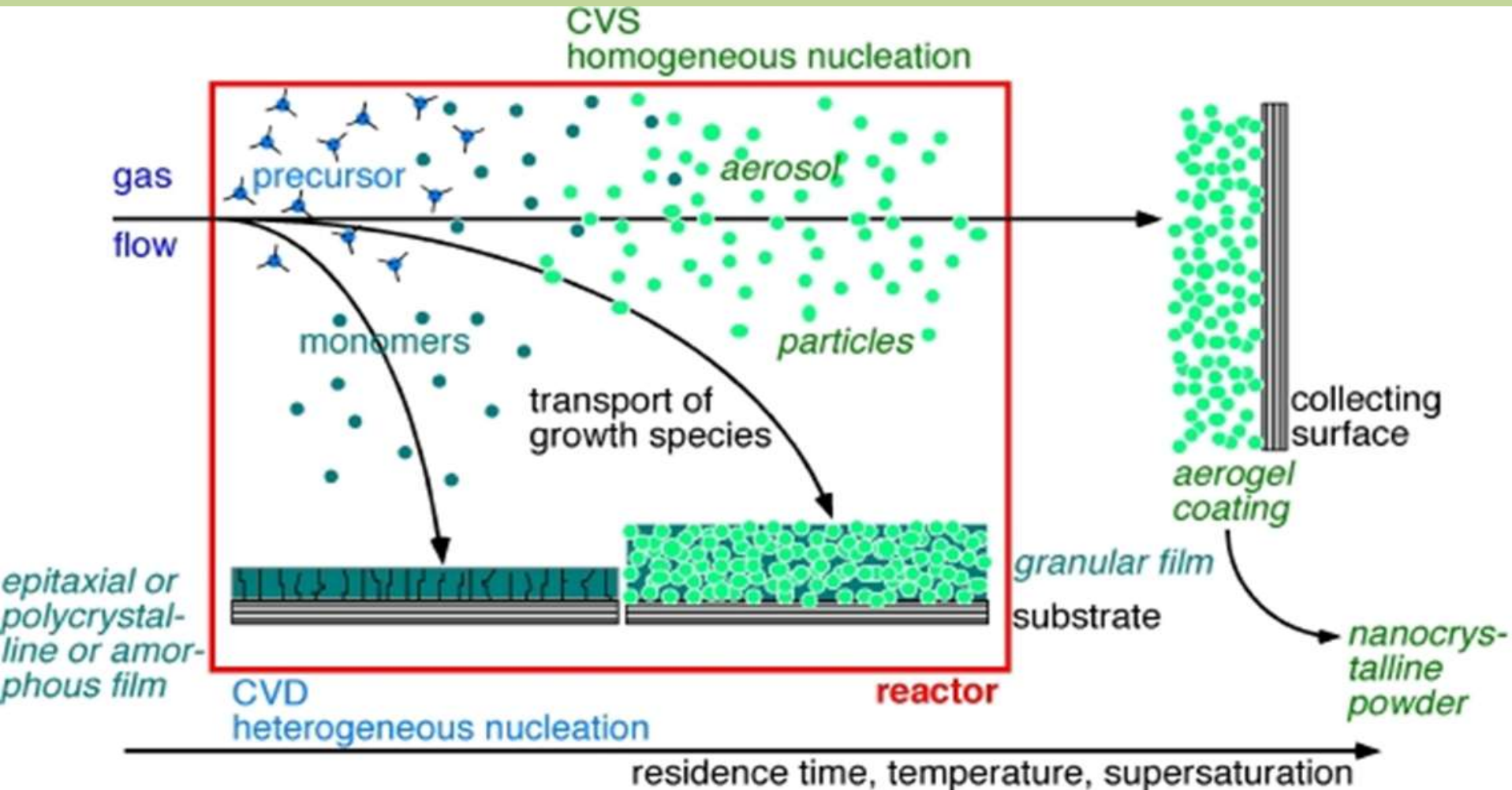
# Chemical Vapor Deposition (CVD)

- surface is coated with a volatile, stable chemical compound below the melting point of the surface. It involves the dissociation /chemical reactions of gaseous reactants in an activated (heat, light, plasma) environment, followed by the formation of a stable solid product

## *Main components of CVD equipment*

- ✓ Chemical vapor precursor supply system
- ✓ CVD reactor component
- ✓ Effluent gas handling system

# Simplified CVD setup

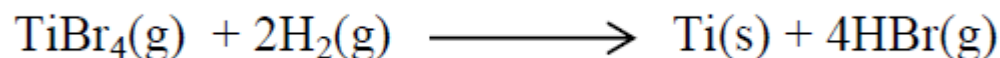


*Examples*



1. Generation of active gaseous reactant species
2. Transport of these gaseous species into the reaction chamber.
3. Gaseous reactants undergo gas phase reactions forming intermediate species
4. Absorption of gaseous reactants on to the heated substrate
5. The deposits will diffuse along the heated substrate surface forming the crystallization centre and growth of the film takes place.
6. Gaseous by-products are removed from the boundary layer through diffusion or convection

Ex.



# CVD

## Advantages

- produces highly dense & pure materials
- uniform films with good reproducibility & adhesion
- good throwing power
- control over crystal structure, surface morphology & orientation of the products
- Deposition rate can be adjusted
- Reasonable processing cost
- use a wide range of chemical precursors
- Relatively low deposition temperatures

## Drawbacks

- Chemical & safety hazards caused by the use of toxic, corrosive, flammable &/or explosive precursor gases
- Difficult to deposit multicomponent materials with well controlled stoichiometry using multisource precursors
- High fabrication cost

# Comparison between PVD & CVD

Features	PVD		CVD
	Vacuum evaporation	sputtering	
Mechanism of deposition	Thermal energy	Momentum transfer	Chemical reaction
Deposition rate	High	Low except for pure metals	Moderate
Deposited species	Atoms & ions	Atoms & ions	Precursor molecules dissociate into atoms
Energy of deposited species	Low (0.1-0.5 eV)	Can be high ( 1-100 eV)	Low; can be high with plasma-assisted CVD
Throwing power	Poor	Poor	Good

# Nanomaterials

- dimensions - 1 to 100 nm
- physical and chemical properties of nano-materials differ significantly from those of their bulk counterparts
- Large surface area to volume

# Classification

*Based on*

- **origin**
  - ✓ Natural
  - ✓ Artificial
- ✓ **Dimension**
  - ✓ Zero dimensional
  - ✓ 1 dimensional
  - ✓ 2 dimensional
  - ✓ 3 dimensional

- (i) *Zero dimensional*: Materials wherein all the dimensions are within the nanoscale range. Eg : quantum dots.
- (ii) *1 dimensional*: Two dimensions are at nanoscale range, other dimension is not. This leads to needle like shaped nanomaterials. Eg: nanotubes, nanorods, nanowires.
- (iii) *2 dimensional*: One dimension is at nanoscale range, other two dimensions are not. They exhibit plate like shapes. Eg : nanocoatings, nanofilms
- (iv) *3 dimensional*: Are not confined to the nanoscale in any dimension. These are characterized by having three arbitrarily dimensions above 100 nm. Also known as bulk nanomaterials

# Preparation of nano-materials

- Bottom up
  - ✓ Vapor deposition
  - ✓ Chemical synthesis
  - ✓ Electro-deposition
- Top down
  - ✓ Ball milling
  - ✓ Solution Combustion

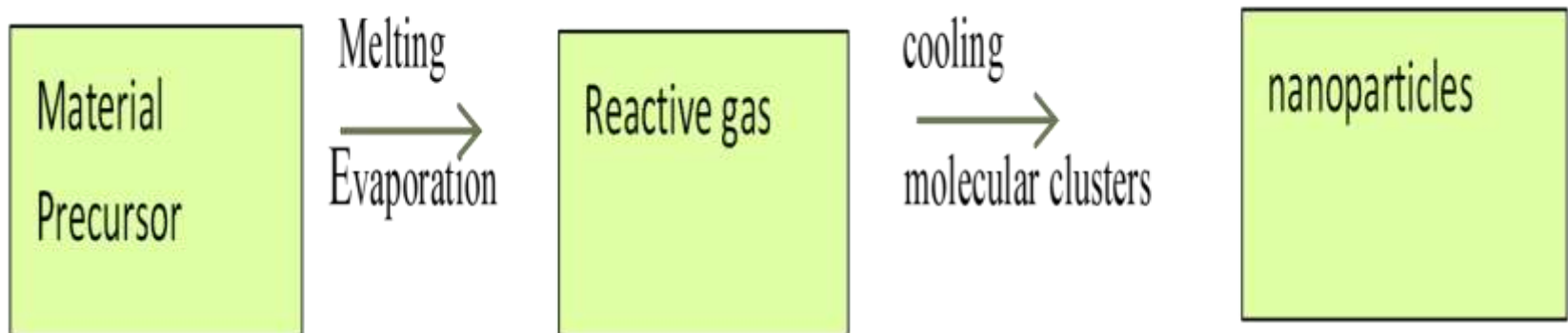
# Vapor deposition

Materials in the vapor state are condensed through chemical reactions to form a solid material

- PVD

Involves evaporation of solid metal followed by rapid condensation to form nanosized clusters that settle in the form of a powder.

Inert gases are used to prevent oxidation when creating metal nanoparticles, whereas a reactive oxygen atmosphere is used to produce metal oxide ceramic nanoparticles

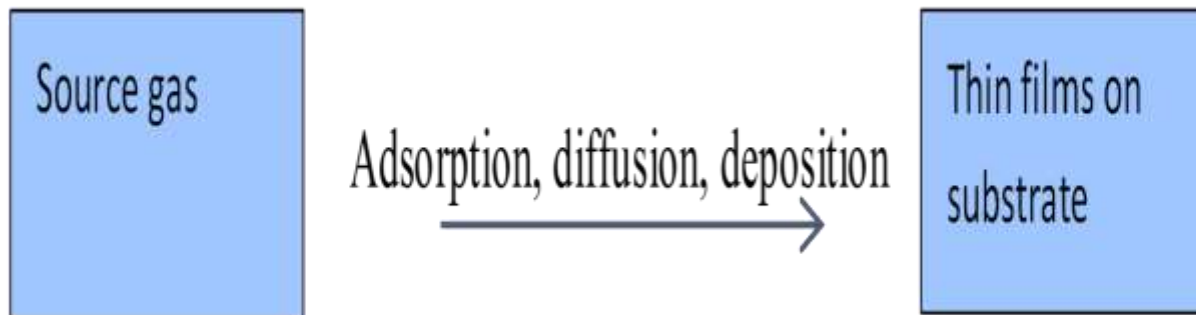




# Vapor deposition

## ***Chemical vapour deposition (CVD)***

the precursor gases are delivered to the reaction chambers at low temperatures. Chemical reactions occur on and/or near the heated substrate, resulting in the deposition of a thin film on the surface



# Chemical Synthesis

## ❖ Sol-gel method

wet-chemical technique used primarily for the fabrication of nanomaterials

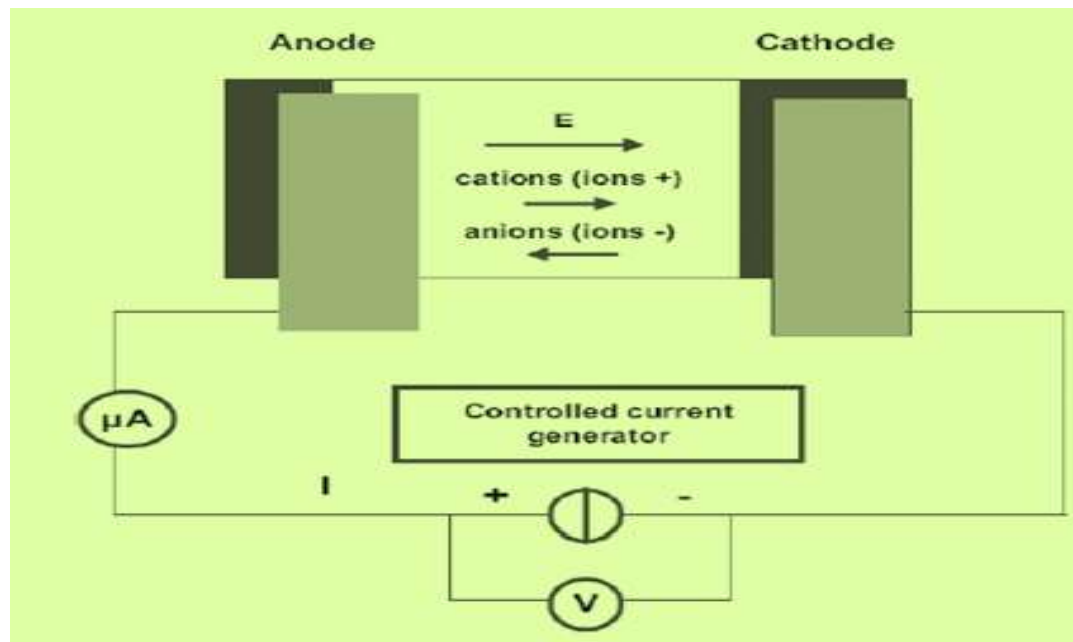
- *Preparation of a precursor solution:* The desired colloidal particles are dispersed in a liquid to form a sol. Typical precursors are metal alkoxides, which undergo various forms of hydrolysis and poly-condensation reactions
- *Deposition of the sol onto a substrate:* The sol solution is coated on a substrate by spraying, dipping or spinning.
- *Formation of gel:* The particles in the solid state are polymerised through the removal of the stabilizing components.
- *Drying process:* Removal of the remaining liquid (solvent) phase requires a drying process
- *Heat Treatment:* After drying, a thermal treatment, or firing process, is often necessary to favor further poly-condensation and enhance mechanical properties and structural stability

# Chemical Synthesis

## ❖ Reduction method

Metallic colloidal particles can be produced by reducing metal salts in solution by reagents such as formaldehyde

## Electrodeposition



Electro deposition can be carried out by either electroplating or electroless plating or multilayer plating technique.

# Ball milling

- small balls are allowed to rotate around the inside of a drum and drop with gravity force on to a solid enclosed in the drum
- The grinding of ceramics can reduce them to a fine powder with each individual particle having nanoscale dimensions
- can be readily implemented commercially



# Review questions

- How do you define a liquid crystal? Classify the liquid crystals based on shape of molecules.
- Describe how a cholesteric LC phase differs from a nematic phase.
- Explain CVD method using a schematic diagram.
- What are the disadvantages of PVD?
- List the advantages of cement as a construction material.
- Mention the applications of polymer composites.
- Justify: Liquid crystalline phases tend to be more viscous than the normal liquid phase of the same substance