



Liquid State

Prof. (Dr) Suryawanshi V.S.

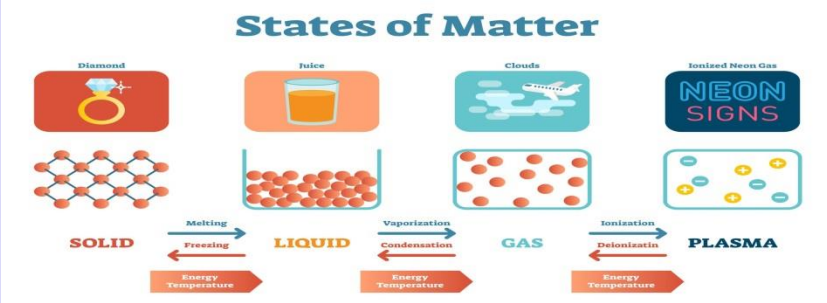
Dept. of Chemistry,
Shri Chhatrapati Shivaji College, Omerga.



Liquid State

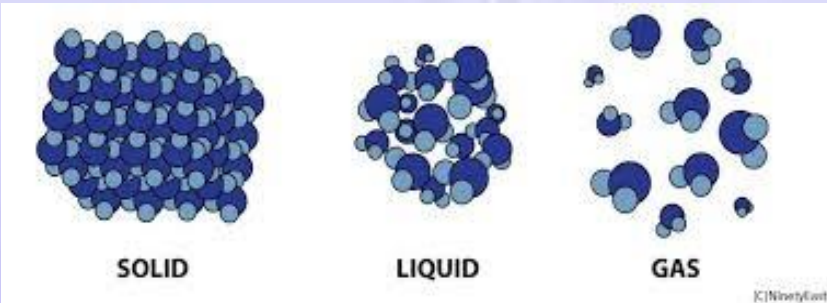
Introduction:
Properties of Liquid:

1.



Four different phases of matter are familiar to us - **Solid, liquid, gas and plasma.**

2.



A **solid is rigid** while **fluids do not** possess the property of rigidity.

3.



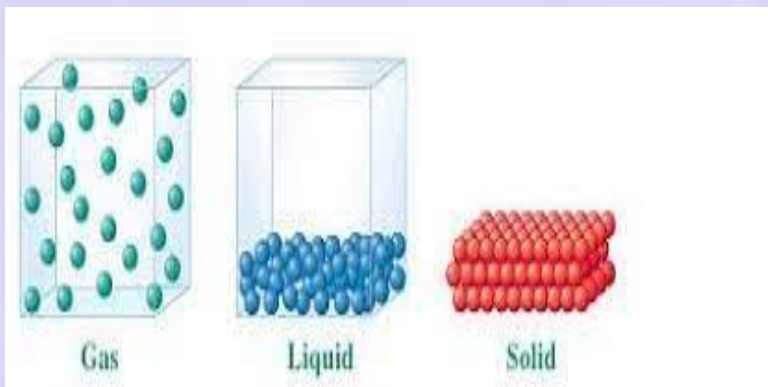
The **same material** exists differently, either as a solid, a liquid or a gas, **under different conditions of temperature and pressure.**

4.



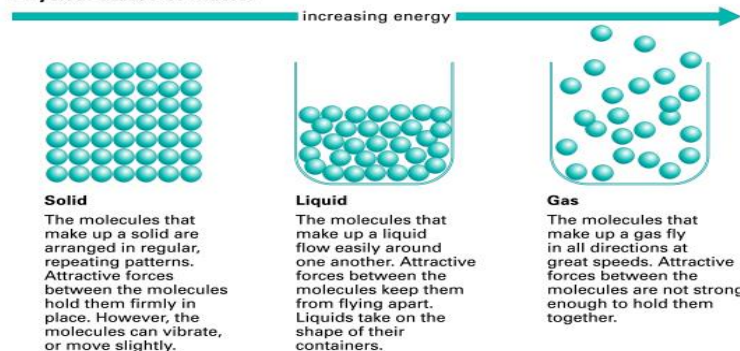
Intermolecular forces are **stronger in liquid state** than in gaseous state.

➤ Molecules in liquids are so close that there is **very little empty space** between them and under normal conditions Liquids are **denser than gases**.



Molecules in liquids are **so close** that there is **very little empty space** between them and under normal conditions **Liquids are denser than gases**.

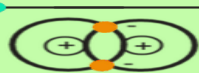
Physical states of matter



Molecules of liquids **can move fast** one another freely.

Some of the **physical properties** of the liquids such as vapor pressure, surface tension, density and viscosity.

Bonding



ionic

Viscosity

low high

Vapor Pressure

low high

Boiling/Melting Point

low high

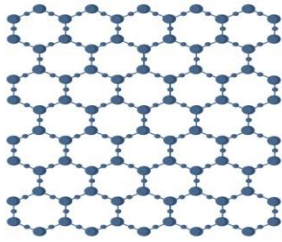
Surface Tension

low high

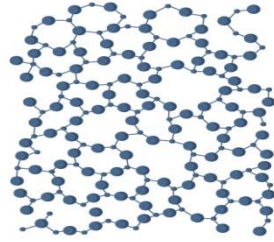
Strong Intermolecular Forces

8.

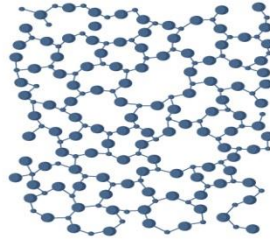
The Puzzle of Glass



In a **crystal**, molecules form an ordered, rigid lattice.



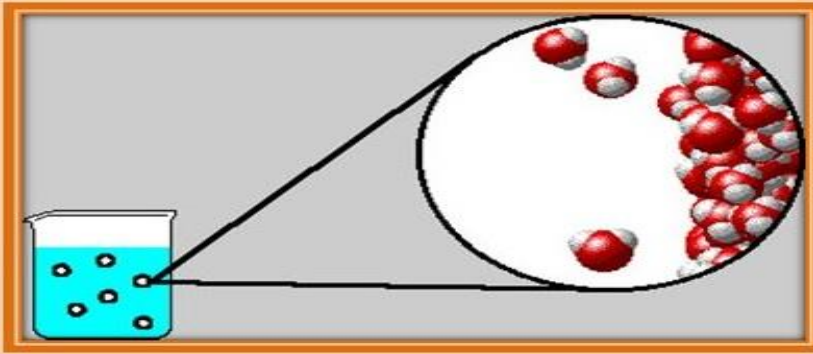
In a **liquid**, molecules are disordered and free-flowing.



Strangely, **glass** has disordered molecules like a liquid, yet is solid and rigid like a crystal.

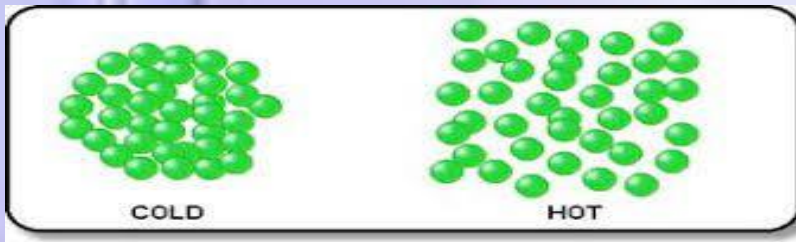
The arrangement of atoms in a liquid is more **disordered** than in a crystal.

9.



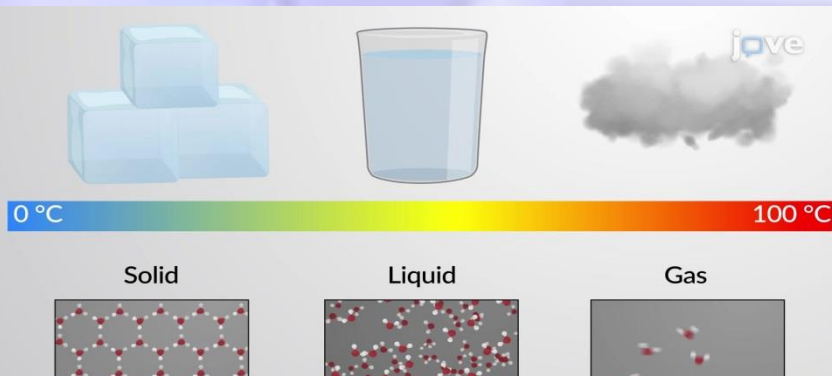
A liquid is made up of tiny vibrating particles of matter, such as atoms and molecules, held together by intramolecular bonds.

10.



When a liquid is heated, the atoms or molecules gain kinetic energy, and vice versa after cooling.

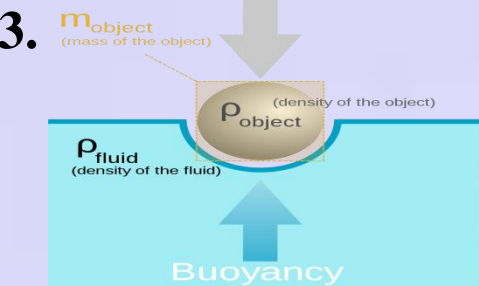
11.



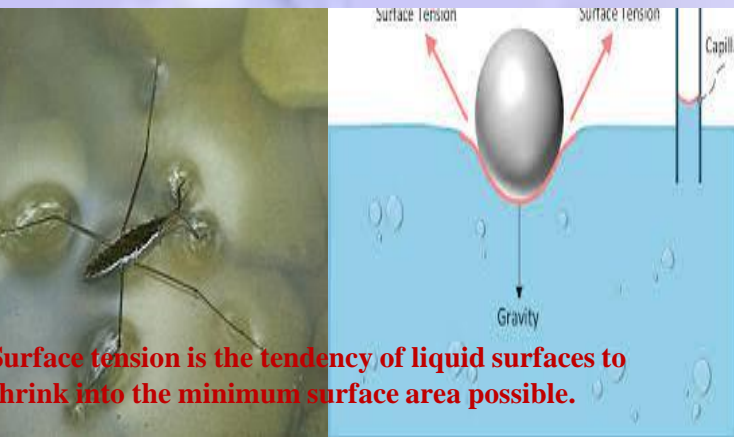
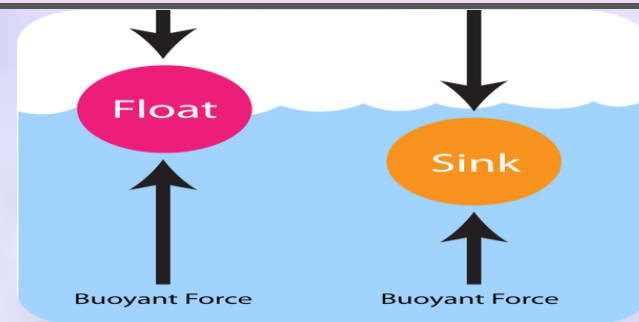
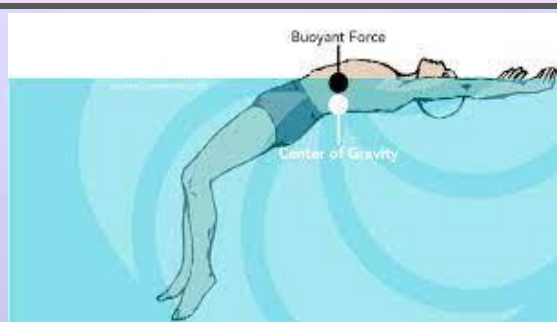
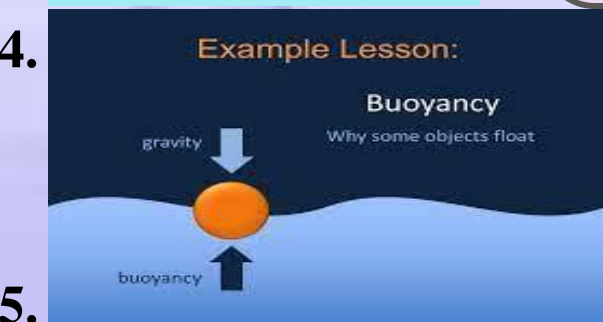
If the temperature becomes sufficiently high, the liquid becomes a gas, or it may react with chemicals in the environment.



Pressure: In a gravitational field, liquids exert pressure on the sides of a container as well as on anything within the liquid itself.



Buoyancy or up thrust : It is an upward force exerted by a fluid that opposes the weight of a partially or fully immersed object.

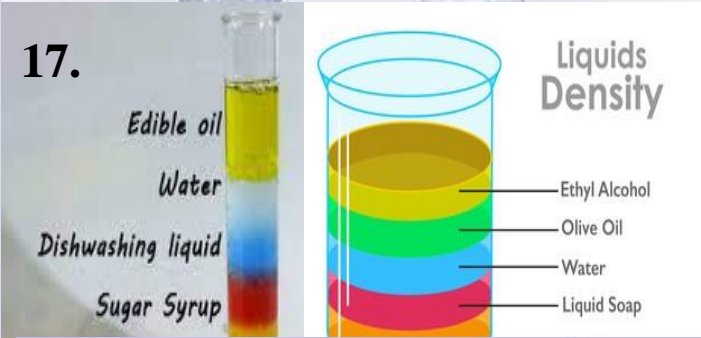


Surface tension is the tendency of liquid surfaces to shrink into the minimum surface area possible.

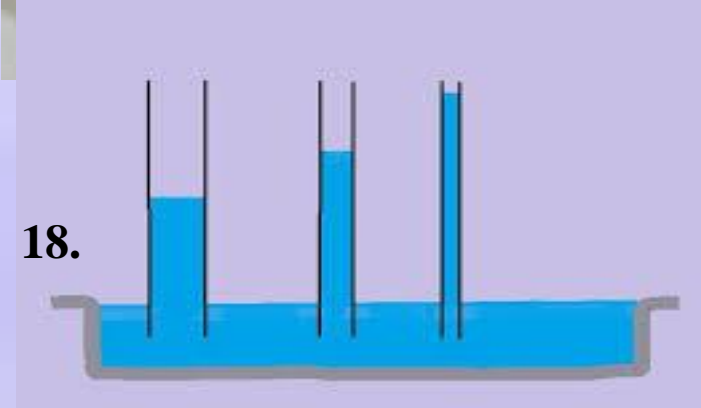
Surface Tension: This is because a molecule at a surface possesses bonds with other liquid molecules only on the inner side of the surface, which implies a net force pulling surface molecules inward with fixed amount of energy associated with forming a surface of a given area. This quantity is a material property called the surface tension.



Viscosity: The viscosity of a fluid is a **measure of its resistance to deformation at a given rate**. For liquids, it corresponds to the informal concept of "thickness". It is an internal frictional force that arises between adjacent layers of fluid that are in relative motion. **Viscosity denotes opposition to flow**. The reciprocal of the **viscosity** is called the fluidity, a measure of the ease of flow.

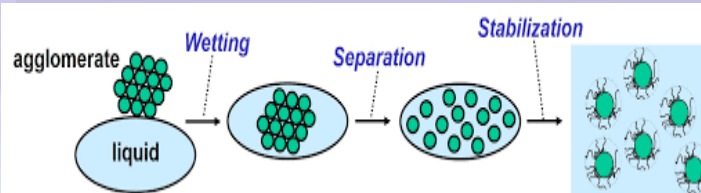


Density: The **density** of water is roughly 1 gram per milliliter i.e. $d=M/V$ but, this changes with temperature or if there are substances dissolved in it. Ice is less dense than **liquid** water which is why your ice cubes float in your glass.



Capillary action (capillarity or wicking) is the **process of a liquid to flow in narrow spaces** without the assistance of, or even in opposition to, external forces like gravity.

The narrower the bore of the capillary tube, the higher the water rises.



Wetting agent or surfactant, is a liquid or chemical substance that increases the spreading and penetrating properties of a **liquid** by lowering its surface tension—that is, the tendency of its molecules to adhere to each other.

Intermolecular forces:

- Intermolecular forces are the **forces of attraction and repulsion** between interacting particles (atoms and molecules). It **not** includes the **electrostatic forces** that exist between the two oppositely charged ions. e.g. Covalent bonds.
- Attractive intermolecular forces are known as **van der Waals forces**.

There are **three types of Intermolecular forces**

1. Dipole-dipole forces or interactions.
 2. Dispersion forces or London forces.
 3. Dipole-induced dipole forces.
- A particularly **strong type of dipole-dipole interaction is hydrogen bonding**. Only a few elements can participate in hydrogen bond formation.
 - Attractive forces between an ion and a dipole are known as ion-dipole forces and these are **not van der Waals forces**.

1) Dipole - dipole forces or interactions:

- Dipole-dipole forces act between the molecules possessing permanent dipole.
- The polar molecules interact with neighboring molecules.
- This interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved.
- The attraction between opposite charge is greater than repulsion between the like poles.
- The attractive force decreases with the increase of distance between the dipoles.
- The interaction energy is inversely proportional to distance between polar molecules.

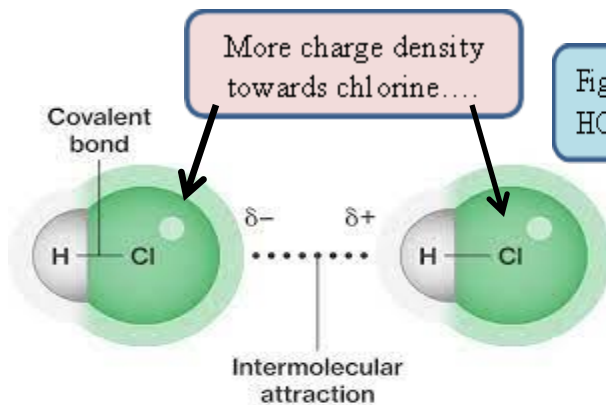


Fig.4.1 Distribution of electron cloud in HCl, a polar molecule.

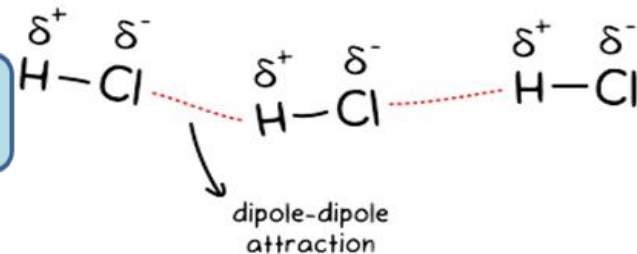
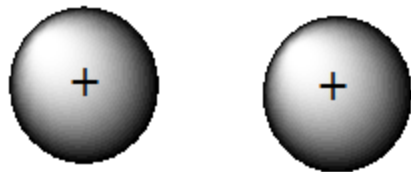


Fig.4.2 Dipole-dipole interaction between two HCl molecules.

Dispersion forces or London forces: (German physicist fritz london)

- Atoms and nonpolar molecules are electrically symmetrical and have no dipole moment because their electronic charge cloud is symmetrically distributed. But a dipole may develop momentarily.
- It may so happen that momentarily electronic charge distribution in one of the atoms, say 'A', becomes unsymmetrical *i.e.*, the charge cloud is more on one side than the other (Fig. 4.4 and 4.5).



Atom 'A'

Atom 'B'

Fig.4.3 Symmetrical distribution of electronic charge cloud

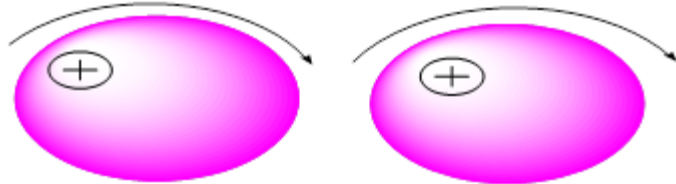


Fig.4.4 (A) Atom 'A' with instantaneous dipole, more electron density on the right hand side.
Fig.4.4 (B) Atom 'B' with induced dipole.

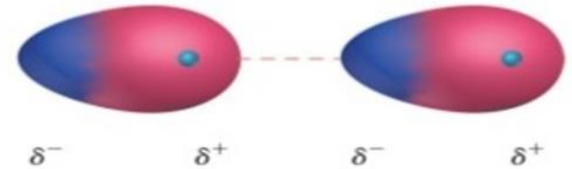


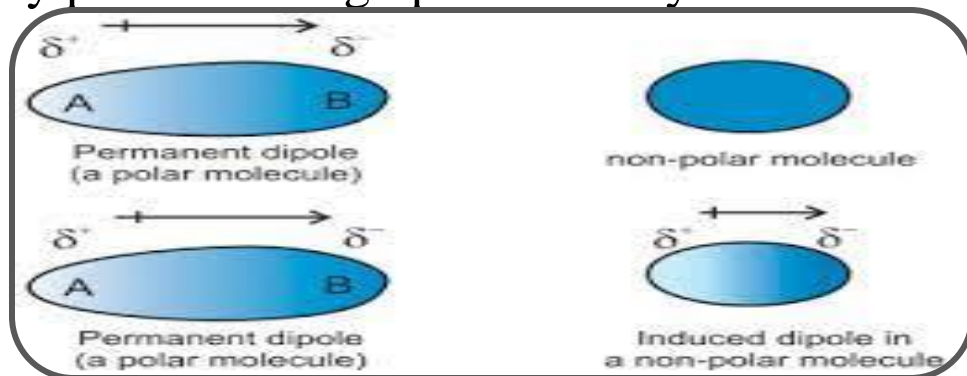
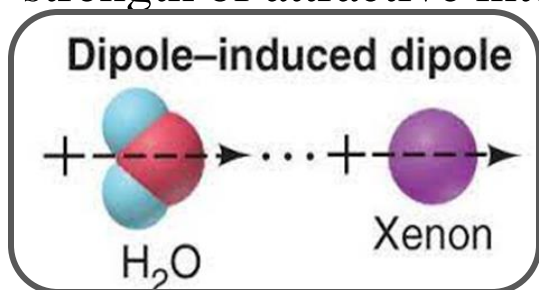
Fig.4.5 (A) Atom 'A' more electron density on the left hand side
Fig.4.5 (B) Atom 'B' with induced dipole.

- This results in the development of instantaneous dipole on the atom 'A' for a very short time.
- This instantaneous distorts the electron density of the other atom 'B', which is close to it and as a consequence a dipole is induced in the atom 'B'.

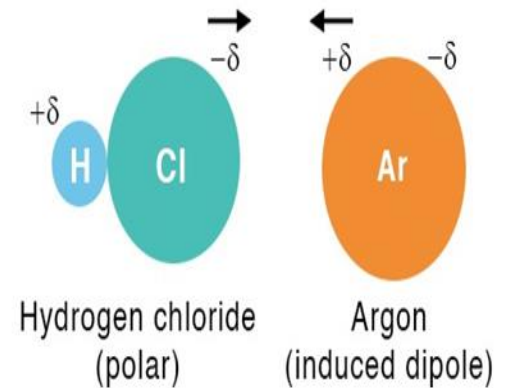
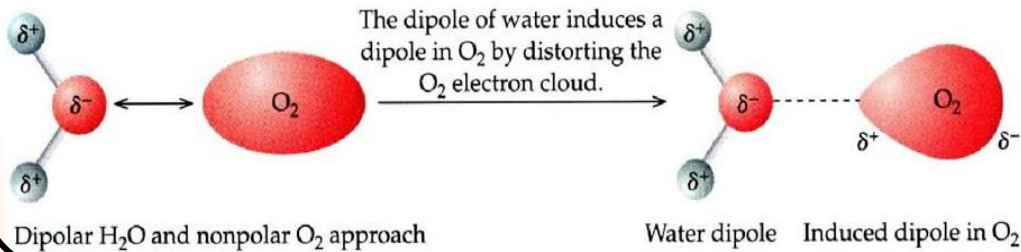
- The temporary dipoles of atom 'A' and 'B' attract each other. Similarly temporary dipoles are induced in molecules also.
- These forces are important only at short distances.

Dipole-induced dipole forces:

- Attractive forces operates between the polar molecules having permanent dipole and the molecules lacking permanent dipole.
- Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming its electronic cloud (Fig. 5.3). Thus an induced dipole is developed in the other molecule.
- Molecules of larger size can be easily polarized. High polarisability increases the strength of attractive interactions.

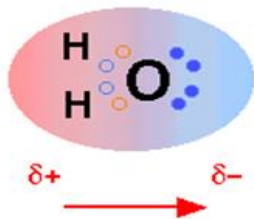


- When a **non-polar** molecule approaches a **polar** molecule (with a permanent dipole), a **dipole** will be induced in the non-polar molecule.



Hydrogen bonding:

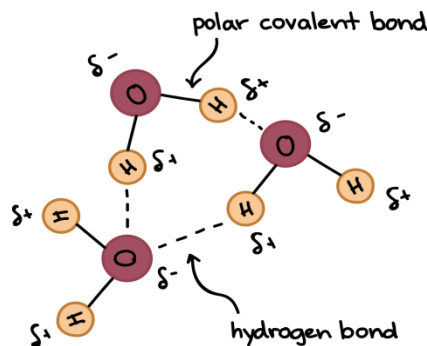
- The **electrostatic force of attraction** that occurs between molecules when **one molecule contains hydrogen covalently bonded to a highly electronegative atom.**
- The molecules in which highly polar **N–H, O–H or H–F** bonds are common.
- The **H₂O** molecule is electrically **neutral**, but the positive and negative **charges are not distributed uniformly.** This charge displacement constitutes an **electric dipole.**



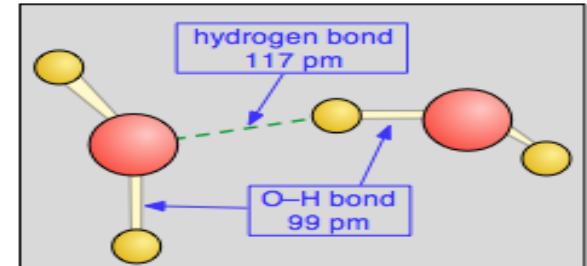
- Energy of hydrogen bond varies between **10 to 100 kJ mol⁻¹**. hydrogen bonds are **powerful force** in determining the **structure and properties** of many compounds.
- Hydrogen bonding in proteins and nucleic acids.

(There are a total of 44,955 **H-bonds in protein-DNA** complexes and 77,947 **H-bonds in protein-RNA** complexes. ... In the 77,947 **H-bonds** of **protein-RNA** complexes, there are 59,796 **hydrogen donors** and 18,151 **hydrogen acceptors** in amino **acids**.)

- **Hydrogen bonds** are responsible for specific base-pair formation in the **DNA** double helix and a **major** factor to the stability of the **DNA**.
- A hydrogen bond in water occurs between the hydrogen atom of **one water molecule** and the **lone pair of electrons on an oxygen** atom of a neighboring water molecule.



- The hydrogen bond (shown by the dashed green line) is somewhat **longer than the covalent O-H bond**. It is also **much weaker**, about 23 kJ mol^{-1} compared to the **O–H** covalent bond strength of 492 kJ mol^{-1}



Structure of liquids (a qualitative description):

- Short range intermolecular force exists while the long range forces are negligible. Therefore, liquids have structure similar to that of crystal.
- The ordered arrangement of molecule extends over a short region instead of over the whole mass. This is called short range order. It continuously changing due to the thermal motions.
- In X-ray diffraction, instead of getting harp lines a few broad bands are observed. This indicates regular order.
- As the temperature of the liquid is raised the bonds become less pronounced (not definite) and the pattern resembles those of a gas.

Henry Eyring, in 1933 (vacancy model for a liquid.)

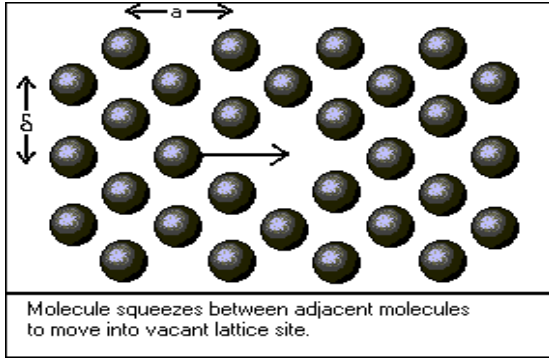
➤ In the liquid **most** of the space is **occupied by the molecules** and only a **small fraction** of the total liquid is **free**. This void space is called **free volume**.



Henry Eyring 1901-1981

- Vapors contain an only a few molecules moving randomly and thus have large free volume.
- With rise in temperature, the vaporized molecule increases causing an increase in the vacancies of the liquid.
- Density of vapor increases while that of liquid decreases. At critical temperature density of vapor and liquid becomes equal.
- According to Eyring, the free volume is distributed randomly and the vacancies are approximately of molecular size.

- Molecules adjacent to a vacancy possess gas like property. While molecule away from the vacancy would be having solid like property.



Difference between solids, liquids and gases:

S.N.	Basis for comparison	Solid	Liquid	Gas
01	Meaning	Has structural rigidity and has a firm shape which cannot be changed easily.	Flows freely, having a definite volume but no permanent shape.	Do not have any shape but conform to the shape of the container, completely, in which it is put in.
02	Shape and Volume	Fixed shape and volume.	No fixed shape but has volume.	Neither definite shape nor volume.

S.N.	Basis for comparison	Solid	Liquid	Gas
02	Energy	Lowest	Medium	Highest
03	Compressibility	Difficult	Nearly difficult	Easy
04	Arrangement of molecules	Regular and closely arranged.	Random and little sparsely arranged.	Random and more sparsely arranged.
05	Fluidity	Cannot flow	Flows from higher to lower level.	Flows in all directions.
06	Molecular motion	Negligible molecular motion	Brownian molecular motion	Free, constant and random molecular motion.
07	Intermolecular space	Very less	More	Large
08	Intermolecular attraction	Maximum	Medium	Minimum
09	Sound speed	Fastest	Faster than gas but slower than solid	Lowest among all
10	Molecular motion	Negligible molecular motion	Brownian molecular motion	Free, constant and random molecular motion.

S.N.	Basis for comparison	Solid	Liquid	Gas
11	Storage	Don't need container, for storage.	Cannot be stored without container.	Needs closed container for storage.
12	Density	Very high	Lower than solid but higher than gases	Very low density.
13	Diffusion	Can diffuse into liquids	Diffusion is higher than solids	Highly diffusible as particles move randomly at high speed.
14	K.E. of particles at a given temp.	Least energy	Higher than solids	Maximum energy
15	Inter particle space	Least	Lesser	More than others.
16	Expansion on heating	Low	More than solids	More than liquids.
17	Particle motion	Only vibrates thus only vibratory motion	Transversal, rotational and vibrational motion	Large transversal, rotational and vibratory motion.
18	Direction of motion of particles	About fixed position	Move around each other.	Move quickly in all directions.

Liquid crystals/ Mesomorphic states:

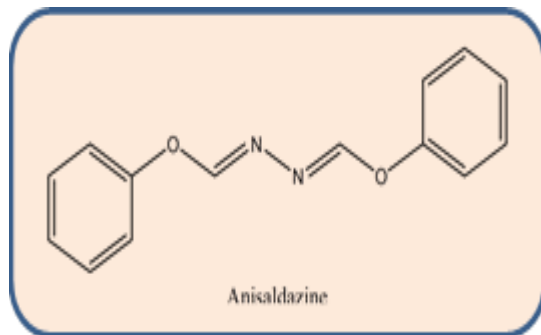
- Liquid crystals (LCs) are a state of matter which has **properties between those of conventional liquids and those of solid crystals**. For instance, a liquid crystal may flow like a liquid, but its molecules may be oriented in a crystal-like way.
- In some cases molecular or ionic clusters **do not lose their identity beyond the melting point of the solid**.
- In such a solid, the **breakdown of clusters in some directions is very slow** and they **yield very viscous cloudy liquids** at a more or less **sharp characteristics temp.** known as **transition point**.
- If the **temp. is increased beyond the transition point**, the cloudiness disappears again sharply at a new temp., known as **melting point** of solid.
- **Beyond the M.pt.**, the substance usually behaves as an **ordinary liquid**, between the temp. i.e. transition point and M.P. ,the cloud liquid shows double refraction, a behavior usually exhibited by crystalline solids.

- On this account the **cloudy liquid state** sometimes called **Mesomorphic state** or regarded to be made up of **liquid crystals**. (made up of liquid and crystals).
- Actually they are more **like liquids** in having properties such as **mobility, surface tension, viscosity etc.**

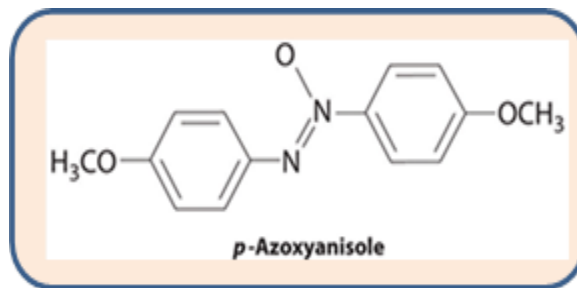
Example 1. para-cholesteryl benzoate



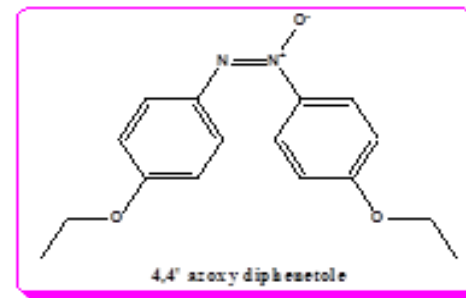
❑ Some other typical compounds showing liquid crystal are...



Anisaldazine



P-azoxyanisole



4,4' azoxydiphenetole

Classification of liquid crystal:

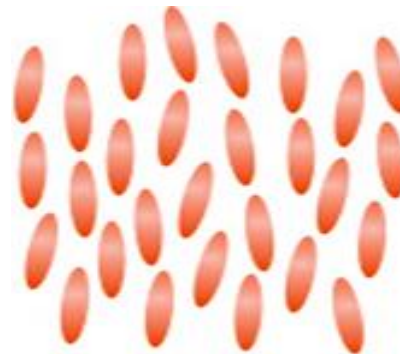
- An essential condition for liquid crystals to occur is that the molecule must be,
 1. Highly **geometrically anisotropic**,
 2. Usually **long and relatively narrow**.
- Depending on detail molecular geometry the system and before it is transformed into the isotropic liquid. Transitions to these intermediate states may be brought about by.
 1. Purely thermal process (**Thermotropic liquid crystals**)
 2. By the influence of solvents (**Lyotropic liquid crystals**).

Thermotropic liquid crystals are further classified into....

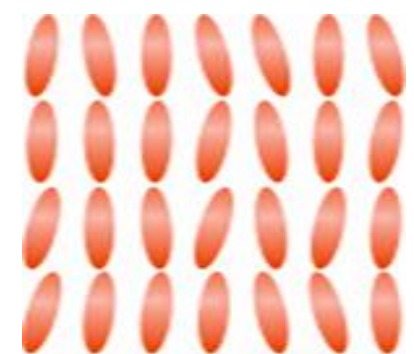
1. Nematic,
2. Cholesteric
3. Smectic liquid crystals.



Isotropic



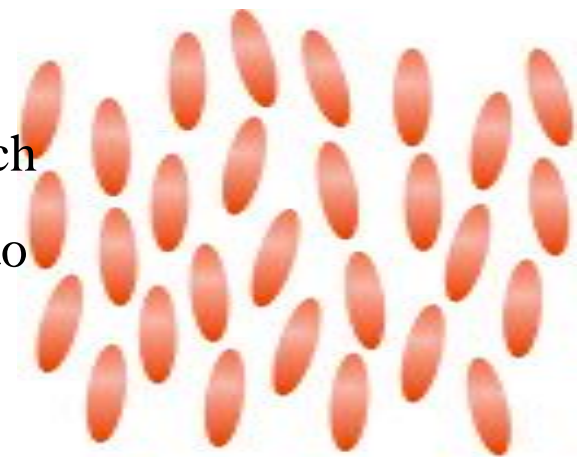
Nematic



Smectic

Structure of nematic phases:

- All molecules are aligned approximately parallel to each other. In each point a unit vector can be defined, parallel to the average direction of the long axis of the molecules in the immediate neighborhood.

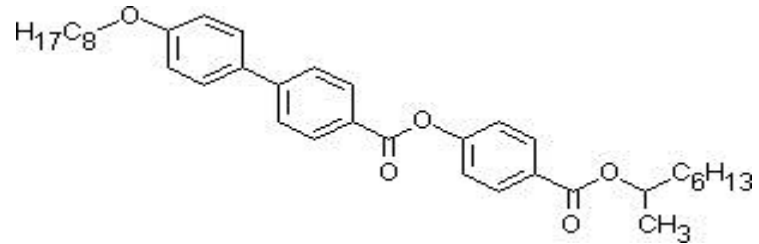
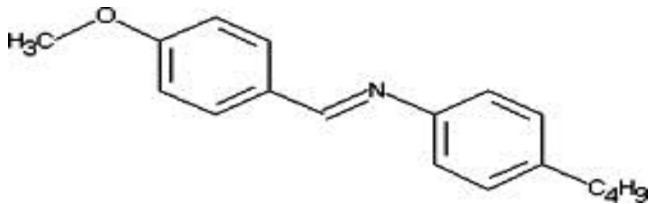


- The molecular structure of a typical rod-like liquid crystal molecule. It consists of two or more ring systems connected by a central linkage group.



- The presence of the rings provides the short range molecular forces needed to form the nematic phase, but also affects the electrical and elastic properties.
- The chemical stability of liquid crystals, their resistance to e.g. moisture or ultraviolet radiation, depends strongly on the central linkage group.

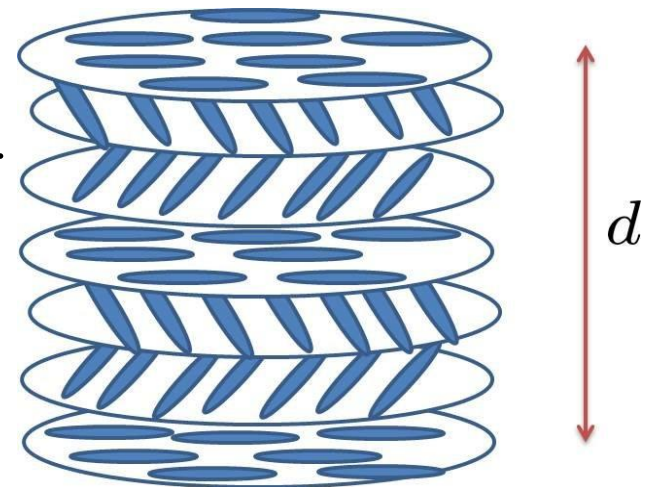
- Compounds with a **single bond in the center** are among the most stable ones. At one side of the rings there is a **long side chain** which **strongly influences** the **elastic constants** and the **transition temperature** of the liquid crystal phases.
- At the other end, a terminal group is connected, which determines the dielectric constant and its anisotropy.



1. *N*-(4-methoxybenzylidene)-4-butylaniline (MBBA)
2. 4-(1-methylheptyloxycarbonyl) phenyl 4-octyloxybiphenyl-4-carboxylate (MHPOBC)

Structure of cholestric phases:

- The molecule should have long and strongly attractive groups should be present to promote adhesion between adjacent molecules
- (ChLCD) It is a display containing a liquid crystal with a helical structure and which is therefore chiral.
- Shows some color effect under polarized light is observed.
- Optically active molecules the cholesteric state has a spontaneous twist about an axis.
- Long and strongly attractive groups present to promote adhesion between adjacent molecules.
- They organize in layers with no positional ordering within layers, but a director axis which varies with layers.
- Cholestric liquid crystals are also known as chiral nematic liquid crystals.



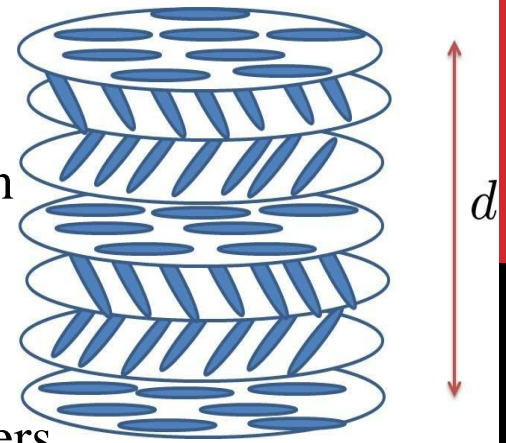
➤ This has intermolecular forces that favor alignment between molecules at a slight angle to one another.

➤ It is visualized as a stack of very thin 2-D nematic-like layers

with the director in each layer twisted with respect to those above and below forming a continuous helical pattern.

➤ The variation of the director axis tends to be periodic in nature.

➤ The period of this variation (the distance over which a full rotation of 360° is completed) is known as the pitch. This pitch determines the wavelength of light which is reflected.



Applications of liquid crystals :

1. Research on optical & electrical properties of these unique compounds attracted very much by scientific and industrial community. Example electro-magneto-optic characteristics and photoelectric properties of nematic and cholesteric type liquid crystals.
2. Liquid crystals when applied to the surface of the skin, have been used to locate veins, arteries, infections, tumors and the fetal placenta which are warmer than the surrounding tissues.
3. Nematic liquid crystals are useful research tools in the application of magnetic resonance.
4. Liquid crystals have been used in chromatographic separations¹³⁸ as solvents
5. They are widely used in cosmetic industry in manufacturing of liquid crystal makeup removers, lipsticks and lip glasses containing cholesteric liquid crystals.

6. Liquid crystals are using extensively in pharmaceutical industries.

7. Liquid crystal displays are common in calculators, digital watches, oscillaographic systems; television displays using L.C.D. screens have also been developed. Cholesteric liquid crystals have also been used for novelty items such as toys and decorative materials.

8. Liquid crystals have various industrial applications. E.g. Polyester liquid crystals were developed for fire resistant, and are used as coating for multifiber, optical cables due to good surface roughness, low coefficient of friction. Polyesters are used for moldings with improved elastic modulus.

Technological Application

Where are liquid crystals used?

Liquid crystals can be found in the following devices:

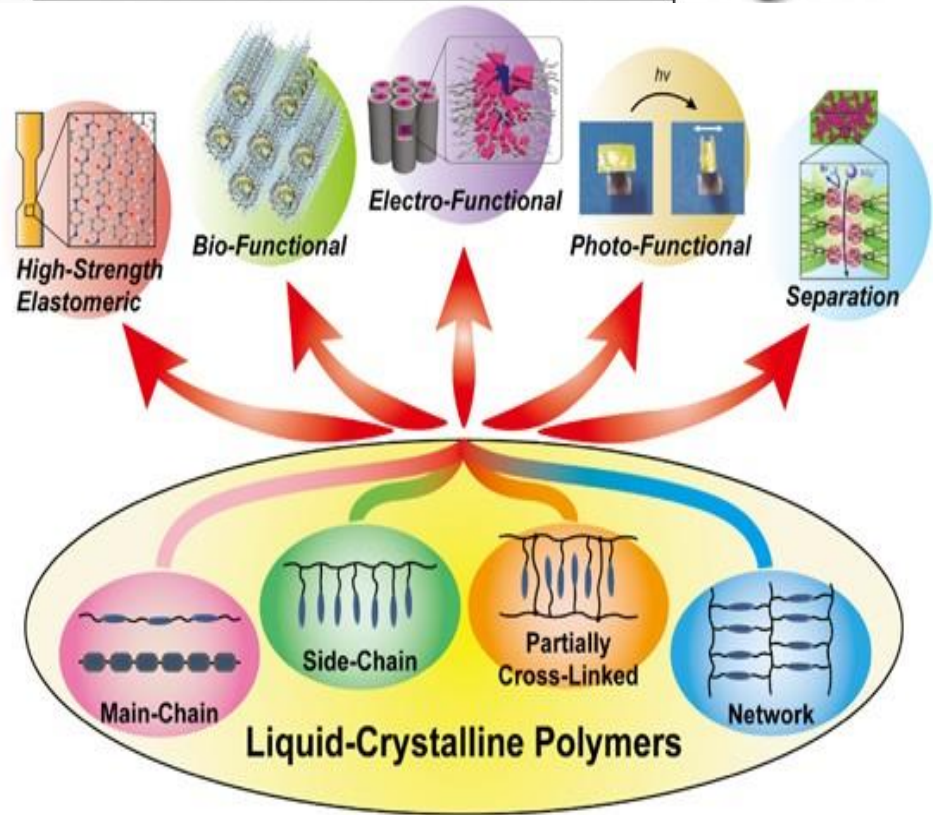
- Digital watches
- Pocket TVs
- Gas pumps
- Parking meters
- Telecommunications
- Cell phones and pagers
- High-speed computing
- Digital signs
- Electronic games
- Personal digital assistants
- Electronic books
- Calculators
- Digital cameras and camcorders
- Fishfinders
- Thermometers



Applications of liquid crystalline materials (LCs)

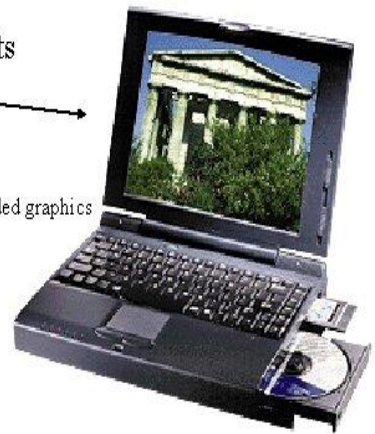


APPLICATIONS OF LIQUID CRYSTALS



Most important commercial products based on LCs are LCDs.

Present top LCD:
WUXGA (wide ultra extended graphics array) 1920 x 1200 pixels.

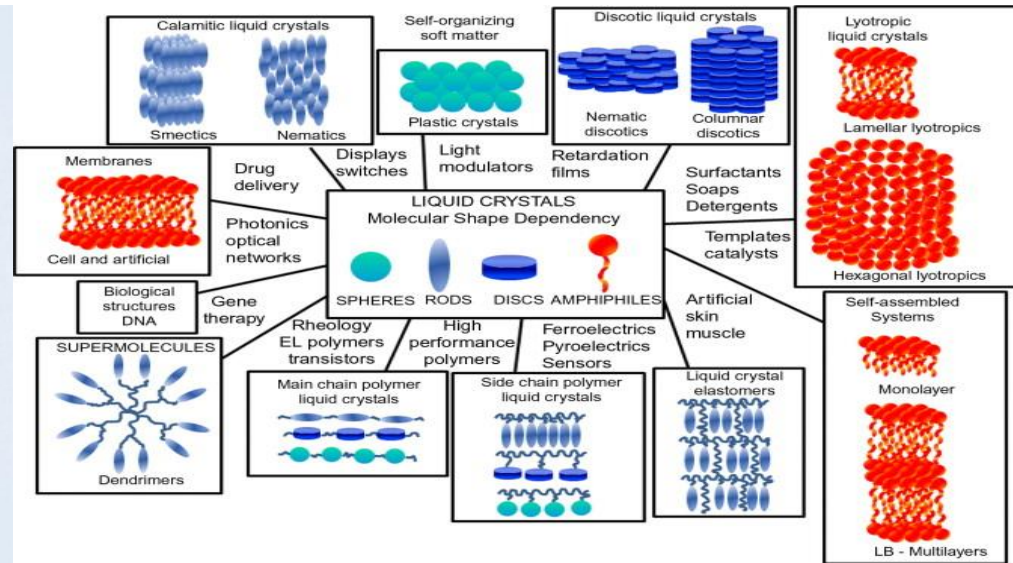


- Other applications:
- optical switching devices,
 - optical filters,
 - temperature and stress sensors,
 - special paints and colorants,
 - cosmetics,
 - etc.

Technological Application

Where are liquid crystals used?

- Liquid crystals can be found in the following devices:
- **Digital watches**
- **Pocket TVs**
- **Gas pumps**
- **Parking meters**
- **Telecommunications**
- **Cell phones and pagers**
- **High-speed computing**
- **Digital signs**
- **Electronic games**
- **Personal digital assistants**
- **Electronic books**
- **Calculators**
- **Digital cameras and camcorders**
- **Fishfinders**
- **Thermometers**



Salient Features

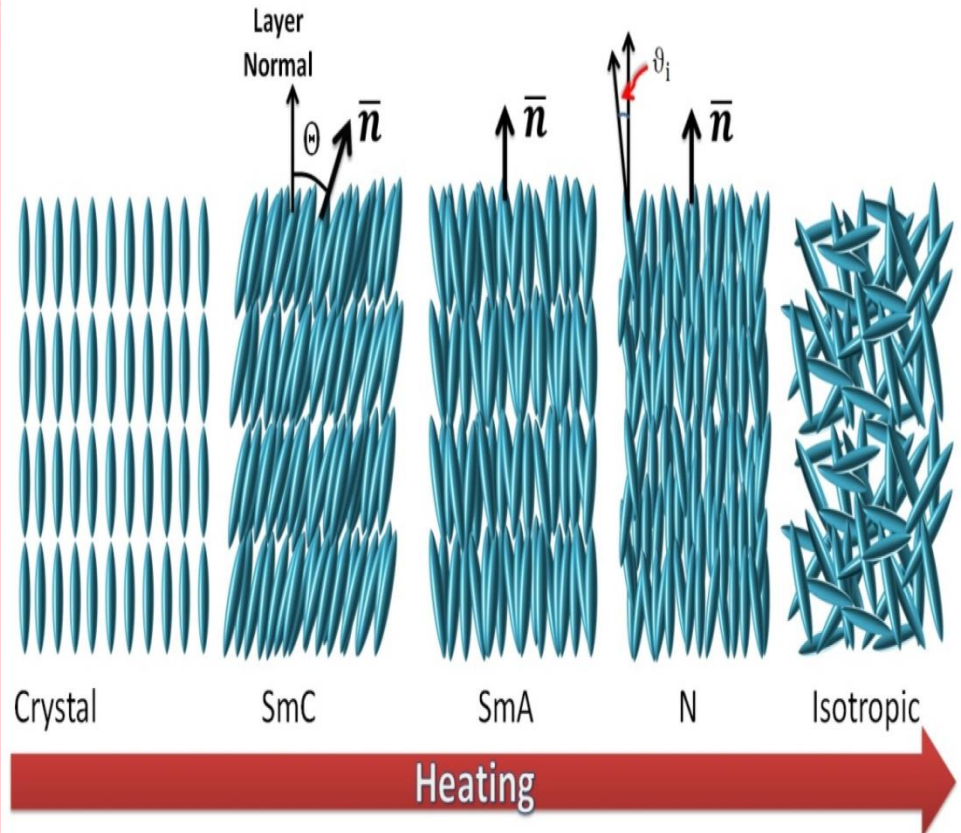
Tunable optical, electrical, morphological, and molecular properties

Easy interface with smart-electroactive advanced functionalized nanostructures

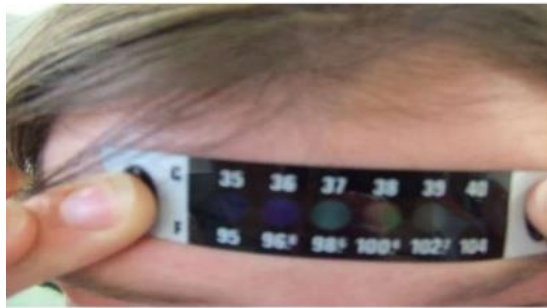


Applications

- Display
 - Flat screen television
 - Laptop screen
 - Wristwatch
 - Digital clock
 - Thermometer
 - Switchable windows
- Optical Switching devices
- Optical filters
- Temperature & strain sensor
- Special paints & Colorants
- Cosmetics

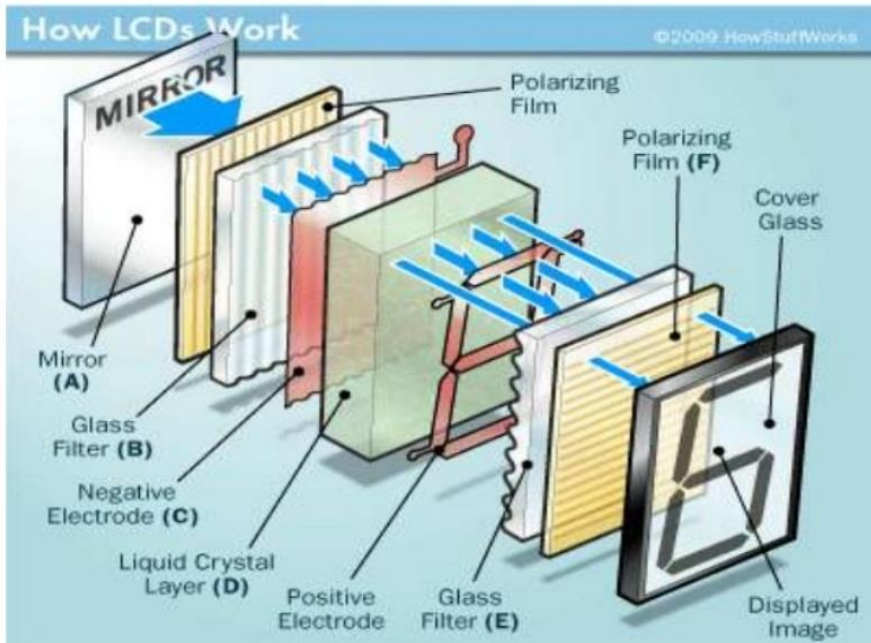


Liquid Crystal Thermometers



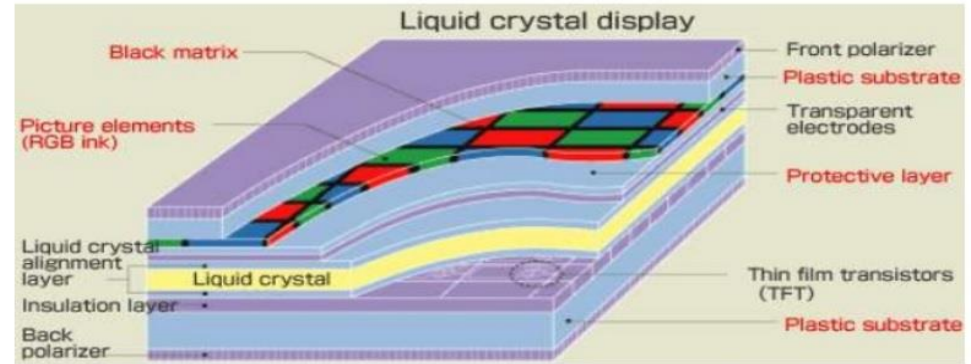
Liquid-crystal thermometers use liquid crystals that change color in response to temperature changes. Mixtures of liquid crystals are enclosed in separate partitions. Numbers on the partitions indicate temperatures according to the amount of heat present. Liquid-crystal thermometers include some indoor digital thermometers and fever thermometers, which are placed on the forehead.

How LCD Works



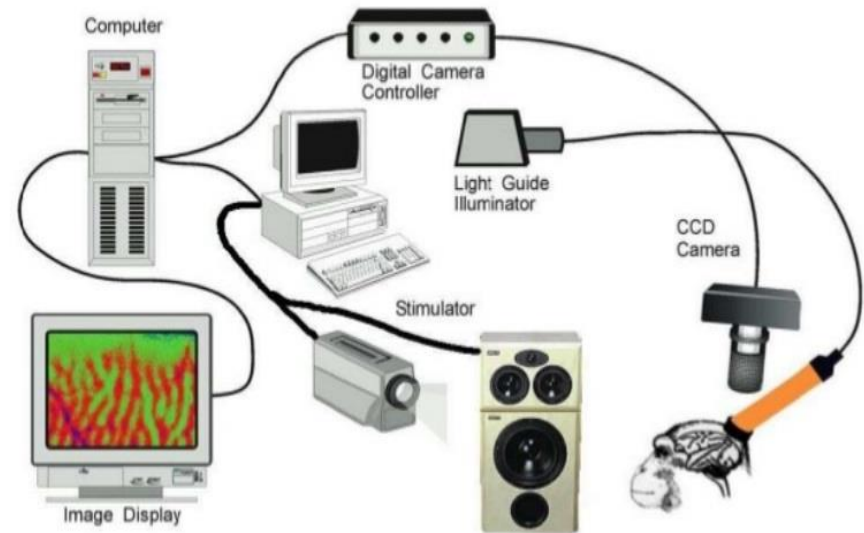
Liquid Crystal Displays

Clip slide



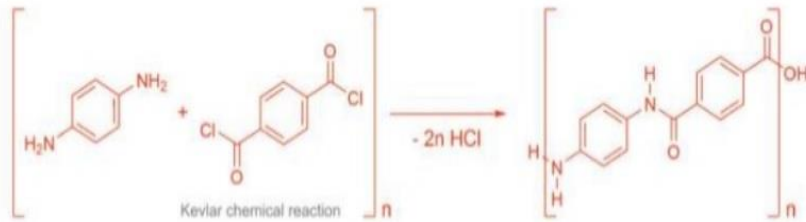
Liquid crystal display (LCD) is a flat electronic display panel used as a visual display aid. It uses liquid crystals to create visual effects on screen. Liquid crystal is a state of matter between solids and liquids. LCDs do not generate light on their own but rely on sunlight or room light to generate images with help of liquid crystal.

Optical Imaging



Helmets and Bullet-proof vests

- Long-chained rigid polymers that orient parallel to each other, with very strong inter-molecular interactions, strong enough to withstand the impact of bullets.



Slugs and Snails (nature)



- Nature beat us to the punch in making use of liquid crystals. The mucus secreted by slugs behaves like liquid crystals. Its rod-shaped molecules align in varying degrees to control the viscosity of the mucus to adapt to different ground conditions.
- Liquid crystals can also be found in biological cell-membranes

- We know today that many chemical compounds can exist in the liquid crystal state, such as cholesteryl benzoate. Thanks to the scientists that worked so diligently toward understanding this phenomenon, the world can focus on ways to make this product useful in society. Over the last century many applications such as the detection of hot points in microcircuits, the findings of fractures or tumors in humans and the conversion of infrared images have become accessible due to the understanding of pitch in a liquid crystal.

THANK
YOU