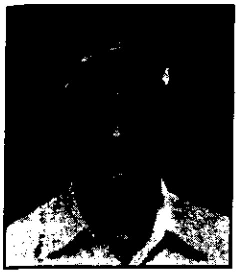

LIQUID CRYSTALS: PHASES OF MATTER IN WHICH ORDER AND DISORDER COEXIST

N.V. Madhusudana

We live in a material world. The air that we breathe, the water that we drink, the food that we eat, the earth on which we live, the sun from which we get all our energy, and the countless stars that we see in the night sky and the millions of cells with their incredible biological machinery which make up our bodies, are all made of materials. It is very clear that properties like say density, or ability to flow etc, of different materials can be widely different. One obvious classification of matter is: living and non living. The former type are quite complex in their structures. They are born, grow making use of food and other types of energy inputs from outside, usually produce offspring, and finally and inevitably die.

The non-living types of matter are much less complex and their physical properties have been studied in great quantitative detail. We learn in our school that such materials can occur in three states or 'phases': solids, liquids and gases. Solids, like common salt, quartz, ice, etc, are rigid and usually have regular shapes as well. On the other hand liquids like water or petrol flow, i.e, they are not rigid but have a well defined volume which can be measured, a useful property exploited in the water or petrol meters. A gas like air can occupy any available volume and is obviously much less denser than a liquid. The same material can exist in all the three phases, depending on its temperature. Water can be frozen to the crystalline ice in a freezer. Ice melts to water at 0 degree C. Water can be boiled at about 100 degreeC, to get steam, which is gaseous. The reason for the occurrence of matter in these 3 forms is now well understood. The medium is ultimately made of independent water molecules, each molecule made of one oxygen and two hydrogen atoms, which are held together by strong interatomic interactions. At high temperatures, the water molecules have a large root mean square velocity: They move more or less independently, with occasional direct collisions. As the temperature is lowered below the boiling point, the average speed decreases and the intermolecular attractive energy can now hold the molecules in close proximity, increasing the density of the medium which is in the liquid state. The kinetic energy of motion of the molecules is however quite large and they move from one neighbourhood of molecules to another rather frequently and the medium flows. As the temperature is lowered, the kinetic energy decreases further and below the freezing point, the molecules are held together in a regular

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geometrical arrangement or a lattice which minimizes the overall energy. The motion of a molecule now consists of relatively small amplitude oscillations about the position at which the potential energy has a minimum, with an occasional escape from that position. The geometrical arrangement adopted by the molecules depends on the chemical nature of the given material and many different arrangements are possible. As the temperature is lowered in the crystalline phase, the kinetic energy keeps decreasing and indeed it can practically tend to zero at about - 273.2°C which is really the zero of the absolute or Kelvin scale of temperature.

It is clear that the arrangement of molecules is dramatically different between the crystalline and liquid states. In the latter, properties like refractive index are isotropic: it has the same value independent of the direction of propagation of the light beam and its polarization state. On the other hand, in ice the refractive index becomes 'anisotropic', its value depending on the direction of light propagation and the polarization state of the light beam. More importantly, a single crystal which has a well defined shape resists any change in its shape: it has shear modulus. On the other hand, a liquid just takes the shape of the container. The crystal to liquid phase transition is said to correspond to a change in the symmetry of the medium.

Water is a small molecule with just three atoms. What happens if the molecular size is increased? Carbon atom which is tetravelent can form strong covalent bonds with a large number of atoms in the periodic table including carbon itself (diamond and graphite result from the latter type of bonds). The resulting organic molecules can have a very wide range of sizes and more importantly, shapes. While methane (CH_4) is a small molecule which is almost spherical in shape, long chains of repeating units form polymers like teflon or nylon which are linear molecules. Indeed this propensity of carbon to form an endless variety of molecules is perhaps responsible for the fact that all living matter is made of carbon compounds (like DNA, amino acids, lipids, etc) and also for the origin of the phrase 'organic molecules'. Of course not all organic molecules have biological significance.

However, even relatively small organic molecules with shape anisotropy can give rise to a remarkable new property: they can exhibit liquid crystalline phases.

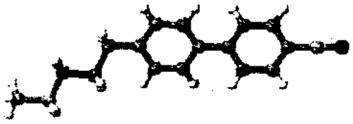

Fig. 1: The rod-like molecular structure of pentyl cyanobiphenyl. Hydrogen atoms are represented by light gray, carbons by dark gray and nitrogen by black shades.

Consider, for example, pentyl cyanobiphenyl (Fig 1). The molecule has a distinctly anisotropic, rod like shape. When the crystal melts at 22 degreeC, the periodic arrangement of the molecules is lost, but the rods remain roughly parallel to one another (Fig. 2).

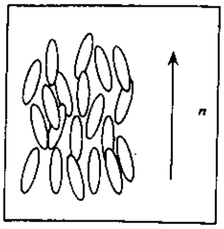

Fig 2: Schematic representation of the orientational order of rod-like molecules abour the direction 'n' in a nematic liquid crystal.

The medium flows and needs a container like any liquid, but the parallel alignment (ie., orientational order) of the rods gives rise to anisotropic properties: the refractive index is larger for light polarized parallel to the rods than for the one polarized in a perpendicular direction. Such anisotropic properties are reminiscent of those of crystals. Indeed it is this combination of crystal like and liquid like properties that justifies the name 'liquid crystals' given to the melt. It is the simplest kind of liquid crystal, known as nematic (N). If pentyl cyanobiphenyl is heated to 3 5^{0}C, the rod like molecules acquire enough kinetic energy to lose even the orientational order and the medium becomes an ordinary 'isotropic' liquid like water.

The nematic phase of pentyl cyanobiphenyl also has anisotropic dielectric properties: the molecules prefer to orient along an external electric field. This is exploited in liquid crystal display (LCD) devices. The liquid crystal is taken between two conducting glass plates which are separated by ~5 μm, and is oriented with the long axes of the molecules parallel to the plates. An electric field applied between the electrodes reorients the molecules along the field if it is above a threshold value. The two orientations have very different optical properties and can be converted to very different transmitted intensities in the two cases. Electrooptic effects like this are used in all LCDs. The transparent electrodes on the two plates can be suitably patterned and 'addressed' to get any picture that is to be displayed. As the power consumption and space requirement of the LCDs are extremely low, they are used in all portable devices like watches, calculators, laptop computers, cell phones etc. The cost of LCDs has come down recently and it is displacing the cathode ray tube (CRT) monitors even from table top computers and colour television sets as well.

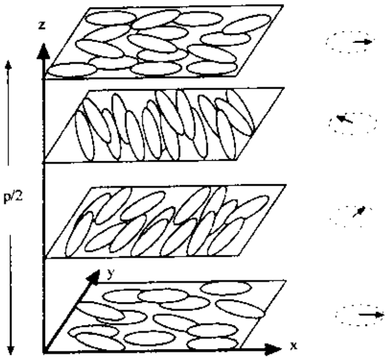

Fig 3: Schematic representation of the helical winding of the orientation direction in a cholesteric liquid crystal. *P* is the pitch of the helix.

An image of the pentyl cyanobiphenyl molecule in a mirror looks exactly similar to the original molecule: it has 'mirror symmetry'. Organic molecules without such a mirror symmetry can also be synthesized because of the tetravalent nature of the carbon atom. Such compounds have a 'handedness' like in a helical spring or screw. The molecules are usually called 'chiral' molecules. The intermolecular interactions between chiral molecules generates a helical structure in the orientation of the long axes in the liquid crystal medium (Fig. 3). Typical organic compounds with chiral molecules which exhibit liquid crystals are derivatives of cholesterol and the medium is called a 'cholesteric' liquid crystal. Indeed the liquid crystalline phase was discovered in 1888 by Renitzer, an Australian botanist in the compound cholesteryl benzoate. The pitch of the helix in a cholesteric liquid crystal can be less than half a pm, which corresponds to the wavelength of visible light. Consequently, coloured light in strongly reflected by the cholesteric liquid crystal. Moreover if the temperature is increased, the pitch decreases, and the reflected wavelength shifts towards blue. This phenomenon is exploited in thermography, i.e, measurement of temperatures (like in a clinical thermometer).

Octylcyanophenyl has 3 additional CH_2 groups in the alkyl chain compared to pentyl cyanobiphenyl. The former compound exhibits the nematic phase when it is cooled below 40 degee C. On further cooling below ~ 32 degree C, it undergoes a phase transition to a different type of liquid crystal called the smectic A (SmA) phase. In this pilase, in addition to the orientational order of the long axes, the molecules are arranged in layers so that there is a one dimensional periodicity alonq the layer normal (Fig 4). Smectic liquid crystals are thus 1 dimensional crystals. The medium has to be cooled below ~ 21°C for it to become a 3dimensional crystal. The smectic liquid crystal can still flow, but not with as much ease as a nematic liquid crystal. There are a few different types of smectic liquid crystals, depending as the detailed arrangement of the rod?like molecules in the layers. Further, if the molecules are chiral, some new types of smectic phases with novel properties arise.

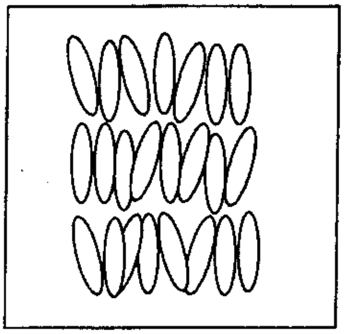

Fig 4: Schematic representation of the layered arrangement of rod-like molecules in a smectic a liquid crystal.

It is possible to synthesise molecules with a different type of shape anisotropy, which look like discs. Some of these compounds exhibit the nematic phase. More interestingly, it was discovered in 1977 in the Raman Research Institute that they can exhibit columnar structures in which the discs are stacked on each other but without any periodicity in the columns. However, the columns can themselves pack in a 2 dimensional lattice, like a hexagonal lattice (Fig. 5). The resulting columnar liquid crystals are 2 dimensional crystals. Again the medium has to be cooled for it to have a phase transition to a 3 dimensional crystal.

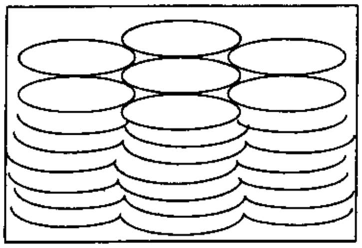

Fig 5: Schematic representaion of the 2-dimensionally periodic structure in columnar liquid crystals exhibited by disc-like molecules.

At present scientists working in the field of liquid crystals are excited about molecules with a third type of shape anisotropy. These are bent core or banana shaped molecules (Fig 6). Compounds with such molecules were found to exhibit novel liquid crystalline phases by the

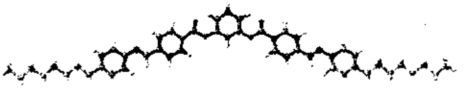

Fig 6: The chemical structure of a typical banana-shaped molecule exhibiting liquid crystalline phases.

Japanese scientists in 1996. The molecules usually pack in layers but with a 'polar' order with the tips of bent cores pointed in the same direction. One of the quirks of this type of ordering is that helical structures can be obtained with non chiral molecules. About 10 different new types of liquid crystals have been identified in the compounds with bentcore molecules.

All together, more than 40 different type of liquid crystals have been discovered in about 80,000 organic compounds which have been synthesized so far with molecules having the 3 types of shapes mentioned above. A vast majority of them of course are made of rod?like molecules.

The rod like or disc like units can also be joined together with flexible spacer units to form long chain like molecules i.e, polymers. N' any such polymers also exhibit different types of liquid crystals. The orientational order in the nematic phase helps to get a better aligned polymerwhich can then be solidified to get a very tough structure.

The liquid crystals that we described above are obtained in pure compounds in well defined temperature ranges and are called 'thermotropic' liquid crystals. A different class, called 'lyotropic' liquid crystals results from the formation of supra molecular structures by self assembly of a special type of organic molecules in solvents like water. These molecules have polar head groups which like water, hydrophilic. They also have long alkyl chains which do not like to be in water, and are hence hydrophobic. The molecules are called amphiphilic which have two different parts which like water and oil respectively, though the latter two do not mix by themselves, as the proverb says. Good examples of such compounds are soap molecules like potassium octanoate

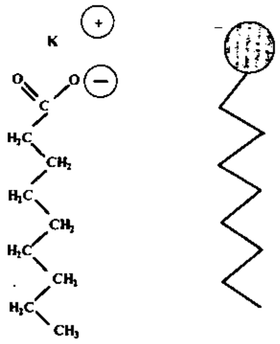

Fig 7: (Left) - Chemical structure of potassium octanoate which has a polar head group which is made of the positive potassium ion and the negative COO group. (Right) - Cartoon of an amphiphilic molecule in which the polar head the group is indicated by the shaded area.

(Fig. 7). Beyond some concentration, the amphiphilic molecules form spherical micellar structures which expose the polar groups to water (Fig. 8), but hide the alkyl chains from water. As the concentration is increased, the micelles elongate forming cylindrical structures which organise themselves in a 2 dimensional hexagonal lattice, which is similar to the columnar liquid crystal phase which we described earlier. As the concentration is increased further, the amphiphilic molecules form flat bilayers which stack in a 'lamellar' phase with layers of water

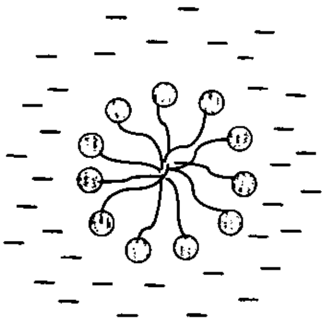

Fig 8: Schematic representation of the structure of a micelle formed by the self assembly of amphiphilic molecules in a solvent like water which is indicated by dashes.

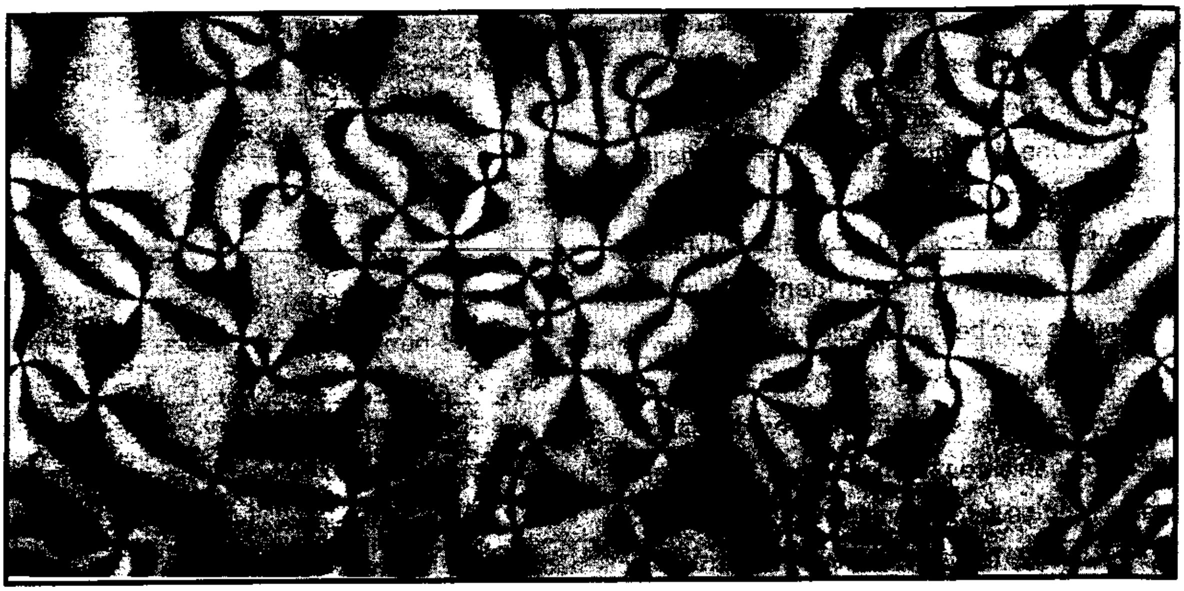

Fig 9: Microphotograph of the texture exhibited by a nematic liquid crystal (crossed polarizers).

between the exposed polar head groups. This phase is very similar to the smectic A phase described earlier.

Lipid molecules have a large polar head group attached to two hydrophobic chains. These self assemble to form vescicles, which are relatively large spherical objects with a bilayer of the lipids forming the skin. Such membrane like skins are found in all biological cells which are basic units of living organisms. The biologically active ingredients like DNA etc, are enclosed within the cell. Indeed lyotropic liquid crystals are ubiquitious in living organisms. For example, DNA itself forms both cholesteric and columnar phases. This is not very surprising as biological function needs organization of the relevant molecules but not in a rigid crystalline lattice which would prevent the essential mobility of the molecules.

Liquid crystals are very fascinating. They exhibit a variety of structures which keeps growing rapidly. Most of them exhibit beautiful textures which can be seen under a microscope (Fig. 9). They are technologically important in the display and cosmetic industries. And they probably play an important role in facilitating biological activity as well.

Science is intimately integrated with the whole social structure and cultural tradition. They mutually support one other - only in certain types of society can science flourish, and conversely without a continuous and healthy development and application of science such a society cannot function properly.

- **Talcott Parsons** (1902-79), U.S. sociologist.