Liquid crystals – Old and new

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A brief summary of the developments during the past two decades in the rapidly growing subject of liquid crystals is given. In particular, the R & D activities in different institutions in India are cited.

Liquid crystals are states of matter having symmetries intermediate between those of crystals with 3-D translational order and the isotropic liquid. The constituent units can have different forms: (a) thermotropic liquid crystals are made of small organic molecules which have shape anisotropy. Liquid crystals made of rod-like molecules were discovered by Reinitzer about 106 years ago while those made of disc-like were found by Chandrasekhar *et al.* 17 years ago in our laboratory. (b) If amphiphilic molecules with a hydrophilic polar head group and a hydrophobic alkyl chain are dissolved in water and/or oil they self-assemble in the form of micelles. In a certain concentration range the micelles become anisotropic in shape and give rise to lyotropic liquid crystals. Many natural phospholipids form such structures. These liquid crystals have been known for about 150 years. (c) A number of polymeric molecules also form liquid crystals: In main chain polymers mesogenic units are linked together by flexible parts. The mesogenic units can also be suspended as pendant units from a backbone structure to form side-chain polymers. These have been known for over 30 years.

We may note that both in de Gennes' book[1] which was published in 1974 and in Chandrasekhar's book[2] published three years later only four types of thermotropic liquid crystals were described: the uniaxial nematic with pure orientational order of rod-like molecules, the cholesteric with chiral molecules, and the smectic with periodic stacking of liquid layers. Smetic A has upright molecules while smectic C has tilted molecules in the layers.

In the past couple of decades the subject has grown enormously and we now know more than 20 types of thermotropic liquid crystals. Of course much of this growth is due to the fact that thermotropic liquid crystals are used in display devices which consume the lowest power of all known devices. These have found ever-increasing applications and are expected to replace the CRT in home television in the years to come. Practically all of the displays use twisted nematic devices and one would like to optimize various physical properties of the material like the dielectric anisotropy, the viscosity and the curvature elastic constants. The associated developments in materials led to discoveries of the reentrant nematic phase[3], multiple reentrance[4], polymorphism of smectic A[5], and in turn to Prost's Landau theory[6] with two coupled order parameters and various molecular models including one from our laboratory[7].

Of course not all advances owe their origin to applications. For example, Meyer[8] realized that the symmetry of a chiral smectic C liquid crystal allows it to have transverse polarization in a 'liquid' direction in the smectic layers. The later demonstration[9] that it is possible to use a surface stabilized book-shelf structure in fast switching display devices with memory in turn led to a veritable deluge of work on these systems. A large number of new ferroelectric materials have been synthesized and characterized, in which our laboratory has also made some useful contributions[10], including some interesting investigations on their optical properties[11], Coming back to ferroelectric LCDs, it was soon realized that it is not easy to get the bookshelf geometry: The surface anchoring of the molecules which is basically a polar interaction gives rise to a chevron structure in which the layers tilt at an angle to the glass plates which in turn leads to the zig-zag defects[12] and much effort has gone into understanding and eliminating these undesirable features. There are no commercial ferroelectric displays yet, but the Canon Company is reported to be building a large factory in Japan for producing such LCDs. Of course, this effort resulted in many dividends for pure science: many new liquid crystals like the TGB phase[13], the antiferroelectric and ferrielectric phases[14] were discovered in the last four or five years in chiral smectic materials. In turn, it is now felt that the antiferroelectric phase may itself have a good potential for application in display devices.

The TGB phase is the analogue of the Abirkosov phase in a type II superconductor under a magnetic field. A somewhat different arrangement of dislocations was predicted to occur by de Gennes in his classic paper[15] on the A-N transition. Incidentally all the smectic phases are subject to the Landau–Peierls instability and because of this, and in view of the fact that in general div n is not zero, the analogy with the superconductor-normal transition is not exact and the A/-N translation is not considered to be completely understood.

The theoretical studies by Renn and Lubensky lead to the result that it should be possible to have TGBA, TGBC (tilted but untwisted layers) and TGBC* (tilted and twisted layers) phases. The first two have been found, and in TGBC as both tilt angle (i.e. layer spacing) and the pitch vary with temperature, it is possible to find commensurate as well as incommensurate structures[16].

There are other defect lattices amongst liquid crystals. For example, short pitched cholesterics exhibit at least three types of blue phases within a couple of degrees of the transition to the isotropic phase[17]. The natural tendency for the medium to twist in two orthogonal directions leads to frustration and disclinations in the medium. The disclinations can arrange themselves in a cubic lattice. Much work has been done on these systems in the past couple of decades.

A very simple 2-dimensional defect lattice was predicted to occur by de Gennes at the nematic air interface subjected to a magnetic field[18]. Though that has not yet been found, we found that it can be easily produced at the nematic–isotropic interface[19]. In 2-D systems, the Kosterlitz-Thouless theory of melting was developed by Nelson and Halperin[20] to predict a bond orientationally ordered (BOO) hexatic phase. Subsequent careful experimental studies on free standing films led to an unambiguous identification of such phases in liquid crystals[21]. In 3-D systems, BOO has long range characteristics. We also now know that many phases which were originally identified as liquid crystals are actually crystals with 3-D translational order. Some work on the nature of the hexatic smectic I to smectic C transition has been carried out in our laboratory[22].

In lyotropic liquid crystals, the realization of smectic colloids, i.e. lamellar phases with a layer spacing $\sim 1\ \mu m$ has led to the verification of the theoretical model due to Helfrich that entropy can stabilize such lamellar phases[23]. It has also led to the discovery of the sponge phase in these systems[24]. Pandit[25] has worked on an Ising model to describe the phase diagram of lyotropic systems. Ramaswamy[26] has worked on hydrodynamics of the lamellar phases. Manoharan[27] has found some novel lyotropic systems and possibly a system which behaves like a spin glass. Some synthetic work on amphiphilic compounds has been started recently by Bhattacharya.

Polymeric liquid crystals have potentially many applications. Kevlar fibres which have high strength and high modulus are drawn from a liquid crystalline phase. An indigenous process for making the fibres has been developed at NAL. Polymeric liquid crystals are being synthesized in IISc, RRL (Trivandrum), as well as in NCL (Pune). It would be useful if someone made liquid crystalline elastomers, which can have rather interesting physical properties.

Many biological systems including water solutions of DNA exhibit lyotropic liquid crystalline phases. There is hardly any work on such systems in our country, though Usha Deniz of BARC has been studying some aspects of phospholipid bilayers and membranes.

As for applications, the know-how for the manufacture of TN displays was generated as a collaborative effort between RRI scientists and Bharat Electronics engineers. Now BE is manufacturing custom-made displays which can be multiplexed at a relatively low level. The state of the art is high level multiplexing using thin film transistor-backed active addressing schemes, which has found applications in small portable TV sets and computer displays. But there is no local effort for developing such displays – it requires substantial investment and R & D effort which are hard to find. However, with the development of supertwisted nematic (STN) displays of twist angles of $\sim 240°$ and materials with low viscosity which respond relatively fast, an addressing scheme essentially developed in RRI by Ruckmongathan[28] is finding increasing application. This scheme in which several rows are addressed simultaneously is complex, and specialized IC chips are now being developed in Japan to exploit its advantages.

Another recent development is the polymer dispersed liquid crystal display in which small nematic droplets (~ 2 m in diameter) are formed in a polymer matrix by a suitable phase separation technique. The extraordinary index of the nematic (~ 1.7 to 1.8) is much higher than that of the matrix so that the composite scatters light. On application of a sufficiently strong electric field, the nematic director gets aligned in the drops and as the ordinary index matches with that of the matrix, the cell becomes transparent. There are several advantages in using this device in large area optical shutters. Some work to develop such displays is going on both in NPL and RRI. It is clear that the subject of liquid crystals is interdisciplinary: organic chemists, experimental and theoretical physicists and electronic engineers have been contributing to the growth of this area.

From a fundamental point of view it is clear that not all the possible symmetries have been discovered. Further, physicists working in the theory of strings believe that the latter have analogies with the nematic threads, which are the topological defects of the nematic phase. Pattern formation is quite natural in liquid crystals: electrohydrodynamic instabilities and growth phenomena produce some novel patterns[29]. Freely suspended smectic films are as good 2-D systems as any other one can find.

In RRI we are interested in practically all aspects of thermotropic liquid crystals and we are hoping that some activity will be initiated in polymeric systems in the coming years. IISc has several theorists and chemists interested in liquid crystals especially of the lyotropic and polymeric variety. Bangalore will also be fortunate in having another centre for liquid crystal research which Prof. Chandrasekhar has started and as it is associated with Bharat Electronics, hopefully R & D on applications will get a boost from this new centre. Yashwant Singh of BHU has systematically developed the density functional theory of nematics[30] and Saha and others at the Calcutta University have been active in developing molecular theories of different types of liquid crystals. Synthetic work on liquid crystals is being carried out both in our Institute and the M.S. University of Baroda.

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Chemistry and physics of dispersions

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Here we consider the importance of dispersions in industry and academics to make an attempt to evolve a frontline research programme which would be relevant but yet challenging. Examples are given to point out the emergence of new disciplines which combine rheology, phase transitions and chemical reactions which include some biological systems too. These developments are likely to lead to important industrial consequences.

We discuss here some of the fascinating areas in the field of dispersions with the main stress on solid/liquid and liquid/liquid dispersions[1]. Dispersions have recently been considered as a branch of Condensed Matter Science – the 'Soft Matter' or 'Complex Fluids'. Uniqueness of this branch of science is that it is close to a number of industrial systems and is therefore of great relevance in applications. This character offers an opportunity to discuss science starting from applications – *down to earth, but yet challenging science*. This is the strategy used here.

Solid–liquid dispersions are of great interest in paints, pharmaceuticals, pesticides, waste treatment, etc. These basically consist of solid particles dispersed in water or hydrocarbon medium. One of the main characteristics of these systems is the large interfacial area. Any small change in the interfacial structure makes dramatic macroscopic changes in the structure and properties of the system. For example, the viscosity of dispersions with say about 40% solids would be extremely high (> 10^4 cP)