Chapter 1

Introduction

1.1 Liquid Crystals

Liquid Crystals (LC), as the name suggests, are states of matter in which the degree of ordering is in between the three dimensionally ordered solid and the isotropic liquid [1-12]. The LC state was discovered more than 100 years ago by Friedrich Reinitzer [13] and Otto Lehmann [14]. Similar to crystals, these intermediate phases, also known as mesophases, exhibit anisotropy in their optical, magnetic, and electrical properties. At the same time they possess some of the mechanical properties of a fluid, e.g., inability to support shear, formation and coalescence of droplets, and low viscosity.

Exhibited mostly by organic materials, these mesophases appear owing to either the action of temperature or the action of a suitable solvent. A well known example of the former category, termed thermotropic liquid crystal is, para azoxy anisole. Mixtures of alkali-n-alkonoates with water are an exhaustively studied example of the latter category, known as lyotropic liquid crystals. A detailed account of both these varieties may be found in several books and monographs [1-12].

To form a liquid crystalline phase, the molecules should possess shape anisotropy. This however is a necessary but not a sufficient condition. Typically the structure consists of a central rigid core with two or more aromatic rings and one or more flexible alkyl chains. Some of the well known mesogenic shapes are rod-like (calamitic) [15], disc-like
In this thesis we are concerned with thermotropic liquid crystals only and therefore limit the following description to phases exhibited by this category.

1.2 Classification of liquid crystals

The primary classification of the different calamitic liquid crystalline phases, nematic, smectics and cholesteric is due to G. Friedel [20].

1.2.1 Nematic and Cholesteric

The simplest of the liquid crystalline phases is the nematic (N) phase, the name derived from the Greek word meaning thread, owing to the fact that when observed under crossed polarizers, the phase exhibits thread like defects. In mesogenic materials, upon cooling the isotropic phase, the first phase to condense often is the nematic, characterized by a long-range orientational order of the molecules without any long-range translational order. A simplified picture of the molecular arrangement in this phase is shown in Figure 1.1. The molecules are spontaneously oriented with their long axes parallel to some preferred direction termed as the director and denoted by a unit vector \( \mathbf{n} \). The preferred direction may vary from point to point in the medium, but a homogeneously aligned sample is optically uniaxial and birefringent. [Nematics with biaxial symmetry have also been reported, see, e.g., [21, 22]. For a summary of the recent status on this topic, see [23]]. The positions of the molecular centres of mass remain randomly distributed as they are in the isotropic phase. Rotations about an axis perpendicular to \( \mathbf{n} \) leaves the N phase unchanged, and further, the structure has an up-down symmetry about the director, making \( \mathbf{n} \) apolar i.e., \( \mathbf{n} = -\mathbf{n} \).

If each molecule is regarded as a rigid rod whose long axis makes an angle \( \theta \) with respect to \( \mathbf{n} \), then a measure of the degree of order in the nematic phase is provided by the
second order Legendre polynomial,

\[ S = \langle P_2(\cos \theta) \rangle = \frac{\langle 3\cos^2 \theta - 1 \rangle}{2} \]

where S is the order parameter. For a perfectly oriented situation (\( \theta = 0 \)), S=1, while for random orientations (\( \theta \) taking all positive values), S=0 (isotropic phase). In the N phase, S takes an intermediate value which is strongly temperature dependent.

If the constituent molecules are chiral, the nematic phase is called chiral nematic (N*) or cholesteric phase. In this phase, the structure is essentially that of the nematic except that there is a screw axis imposed normal to the director. The resulting helix has a well defined pitch and is responsible for some unique optical properties, e.g., selective reflection of circularly polarized light, high optical rotatory power, etc.
1.2.2 Smectics

The smectic phase exhibits, in addition to the orientational order of the molecular long axis, a one-dimensional positional order in which the centers of gravity of the molecules are, on an average, arranged in equidistant planes resulting in a layered structure. Depending on the order within the layer and the orientation of the molecules with respect to the layer normal, the smectics are classified into several types. We shall look at three of them here.

Smectic A

In the Smectic A (SmA) phase, the director is along the layer normal. The order within the layer plane is liquid-like with no long range translational order (Figure 1.2). Considering a one-dimensional mass density wave is a more rigorous way to treat such a layer arrangement [24-26]. In the SmA phase the wave vector of this mass density wave is along the layer normal direction. The inter layer correlation does not have true long-range order, but exhibits an algebraic decay [27], a feature referred to as quasi long-range order giving
rise to Landau-Peierls' instability [28]. In the Schoenflies notation the symmetry of the structure is denoted by the $D_{nah}$ point group.

If the constituent molecules are chiral, the phase is termed chiral SmA or SmA* and this phase exhibits interesting features, such as as electroclinic effect, in which an electric field applied in the plane of the layers induces a tilt of the molecules [29]. This phenomenon has implications in technology with possibilities for field-controlled grey scale in spatial light modulators.

**Smectic C**

The smectic C (SmC) is a tilted phase with the director inclined relative to the layer normal making an angle $\theta$, called the polar tilt angle. It has a symmetry lower than that of the SmA phase since the tilted molecules pick out a special direction in the smectic plane, i.e., their projections in the xy-plane are along a common direction denoted by a unit vector $c$, called the in-plane or c-director (Figure 1.3). The SmC phase is optically biaxial, and is described by $C_{2h}$ symmetry. In a generalized description, the tilt of the molecule is depicted in terms of the polar tilt angle $\theta$, and an azimuthal angle $\phi$. For a uniformly aligned sample, $\phi$ is the same within and between each layer.

**Smectic C***

If the constituent molecules are chiral, the smectic C is referred to as smectic C* or SmC* (Figure 1.4). Just as in the case of the N* phase, the chirality superimposes a screw axis, or a helix. But in the SmC* case, the axis of the helix is along the layer normal direction. Like in the SmC phase, the azimuthal angle of all the molecules (the c-director) within the layer is the same and the symmetry is $C_2$. However, the c-director precesses around the layer normal (z axis), on moving from one layer to the next giving rise to a helical structure. The interesting outcome of this is that the electric polarization which is normal to the tilt-plane (plane containing $n$ and $z$) also precesses. This effectively cancels out the polarization in...
the helical state. But if the helix can be unwound by some means, such as, e.g., an electric field, the system exhibits a macroscopic polarization. The SmC* with the helix structure intact is macroscopically, optically uniaxial.

Figure 1.4: Schematic representation of the molecular arrangement in the SmC* phase. $P_s$ represents the spontaneous polarization of this phase.
1.3 Polar liquid crystals

A molecule that has a net electric dipole moment in the absence of an external field is called a polar molecule. A large number of compounds exhibiting LC phases have polar molecules. In contrast, a non-polar molecule is one in which the distributions of the positive and negative charges are centered at the same point, resulting in the absence of a permanent dipole moment. Figure 1.5 gives examples of non-polar (terephthal-bisbutylaniline: TBBA), weakly polar (4-n-pentyloxyphenyl 4-n-decyloxybenzoate: POPDOB) and strongly polar (octylcyanobiphenyl: 8CB) liquid crystal molecules. POPDOB has a net dipole moment transverse to the long molecular axis due to the COO group whereas there is a strong longitudinal dipole moment due to the CN group in 8CB.

\[
\text{TBBA} \quad (a)
\]

\[
\text{POPDOB} \quad (b)
\]

\[
\text{8CB} \quad (c)
\]

Figure 1.5: Examples of (a) non-polar, (b) weakly polar, and (c) strongly polar liquid crystalline molecules.

There has been much research activity on the molecular interactions responsible for the stability of the nematic phase, which is the simplest of the liquid crystalline phases. In
fact, the first molecular field theory proposed in 1916 by Max Born [30], considered that
the interactions between the permanent dipole moments of the molecules are essential for
the stabilization of the nematic phase. Though this attempt was theoretically consistent,
the basic assumption was not correct because it was soon shown that non-polar molecules
also exhibit liquid crystal phases [31]. However, liquid crystals composed of strongly polar
molecules exhibit certain unusual properties and phase sequences, some examples of which
are provided in the next section.

1.3.1 Some special properties exhibited by compounds with highly polar end groups

As pointed out earlier, the absence of ferroelectricity in the N phase shows that there is
equal probability of any permanent dipole existing along the length of the molecule point-
ing along $n$ or $-n$. Thus it is assumed that the contribution of the permanent dipoles is
negligible. However, it has been found, especially in strongly polar molecules, that the in-
teraction between neighboring dipoles is not trivial. In the following, we point out certain
consequences of such interactions.

Dielectric properties and antiferroelectric short-range order

The average dielectric constant in the nematic phase is given by $\varepsilon_{\text{avg}} = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$, where
$\varepsilon_\parallel$ and $\varepsilon_\perp$ are the dielectric constants parallel and perpendicular to the director. Schadt [32]
found an unusual feature in the measured values of $\varepsilon_{\text{avg}}$, having a sharp increase by 2%
across $T_{NI}$ instead of a decrease in the value as is expected from the small (0.5%), but abrupt
lowering across the NI transition. This was interpreted by a model [33] which invokes
antiferroelectric short-range order but is also consistent with the non-polar character of the
medium. This behavior in the dielectric constant across the NI transition is not observed
for the non-polar molecules. The antiparallel character of the local ordering in the N and
I phases has been directly evidenced in X-ray and neutron scattering experiments [34].

Chapter 6 of the thesis throws more light on the behavior of the dielectric constant and its relation to the molecular structure in strongly polar materials, antiferroelectric order, and cybotactic groups.

**Reentrant liquid crystalline phase**

When a liquid crystalline compound is cooled from the isotropic phase, the more ordered phases, i.e., the phases having lower symmetries, for e.g., smectic A, etc. are expected to occur at temperatures lower than that of the nematic. Indeed this rule is followed more often than not. The first exception in this regard was discovered by Cladis in 1975 [35] in a binary mixture of two strongly polar compounds, which exhibited, on cooling, the phase sequence, isotropic – nematic – smectic A – reentrant nematic. The reemergence of the higher symmetry nematic phase below the smectic, and therefore termed reentrant, in fact completes de Gennes’ analogy [2] between the normal – superconductivity sequence and the nematic – smectic A transition. Later, the phenomenon was found in pure compounds, under elevated pressures [36]. Subsequently, such a phase sequence has not only been found in pure compounds at atmospheric pressures [37, 38], but double and triple reentrance sequences [39, 40] have also been observed. The reentrance of the nematic phase has been observed in polymeric [41] as well as dimeric materials [42]. Incidentally, the field of liquid crystals not only augmented, but added new dimensions [43-51] to the phenomenon of reentrance observed in condensed matter systems [52].

**Smectic A polymorphism**

Another unique feature exhibited by strongly polar molecules is the phenomenon referred to as polymorphism of smectic A and smectic C phases [53, 54]. This feature has been studied quite exhaustively from both theoretical and experimental points of view. The essential point that governs the appearance of polymorphic forms of these phases, is the
competition between two length scales in the system and the resulting frustration. While the length of a single molecule is the natural length, \( l \), the other arises because of the length formed to satisfy the dipolar interaction between a pair of molecules. If the layer thickness \( d \) is comparable to \( l \), the formed SmA is referred to as monolayer SmA\(_1\), if \( 1 < d < 2l \), it is partially bilayer SmA\(_{d} \), and if \( d \approx 2l \), a bilayer phase. Corresponding variations exist for the SmC phase also. Subtle change in the molecular interactions which govern the appearance and temperature range of these phases has led to many interesting observations in the area of critical phenomenon, such as critical point, critical end point, a nematic island surrounded by SmA phases etc.

The three topics covered in this section are concerned with the effects in non-chiral liquid crystals. Polar effects manifest in a variety of ways in systems composed of chiral entities also. We have already mentioned two such effects, namely the existence of spontaneous polarization and electroclinic effect. In fact the chiral liquid crystals exhibit a rich spectrum of polar phases showing ferroelectric, antiferroelectric, and ferrielectric structures [55].

1.4 Scope of the thesis

In the following we briefly describe the contents of the chapters outlining the essential results.

Chapter 2: Experimental investigations on de Vries type liquid crystal

The structural details of the SmA and the SmC liquid crystalline phases have been given in the previous sections. A phase that has certain features of both these phases is termed as the de Vries SmA (SmA\(_{dV}\)) and has the molecules tilted, but with only short-range azimuthal coherence. Chiral materials exhibiting this phase (SmA\(_{dV}\)) show large electroclinic tilt angles without the layer buckling feature, normally seen in ferroelectric
smectic C* liquid crystals. This is beneficial for obtaining fast gray-scale display devices with good contrast. Despite many reports on various aspects of the SmA_{dV} phase including a transition from the normal SmA to de Vries SmA phase, and also between two variants of de Vries phases, the structural aspects of this phase are yet to be fully understood. In this chapter, with the help of electrical, electro-optical and dielectric evidence we have demonstrated that in systems composed of molecules with hydrocarbon chain at one end, and a bulky terminal group at the other, the interlayer interaction is very strong at short scales, but very weak on a global scale. This results in an antiferroelectric structure for this phase. A model is also suggested to explain it, which should be common to systems having structurally incompatible termini, such as siloxane and hydrocarbon chains. While providing explanation to all the observed properties, the model also gives the basis for such molecules favoring the formation of the de Vries phase. A second aspect that is presented in the chapter concerns the universality class to which the transition from the SmA_{dV} to the globally tilt-correlated SmC* phase belongs to. Employing the range shrinking analysis it is found that the exponent describing the growth of the susceptibility increases monotonically from a near-mean field value far away from the transition to a value slightly higher than that predicted for the two dimensional Ising model. While the description by the Ising model is appropriate owing to the finite, but local, tilt of the SmA_{dV} phase, the slight deviation of the exponent from the standard 2D Ising prediction is suggested to be due to the antiferroelectric nature of the SmA_{dV} phase and to the change of the polar tilt angle across the transition to the SmC* phase.

Chapter 3: Electric field dictated phase diagram and accelerated dynamics of a reentrant nematic liquid crystal under photostimulation

A system is said to undergo a reentrant phase transition, if a monotonic variation in any thermodynamic field such as temperature or pressure results in two or more phase changes and finally attains a state which is macroscopically similar to the initial state. In a system containing photoactive molecules that exhibit light driven isomerization transfor-
mations, actinic light can diminish or enhance ordering to the extent that transitions from
the equilibrium to a more disordered/ordered phase can be brought about isothermally. This
feature enables light to be used as a thermodynamic-like parameter to investigate phase be-
havior and adds another dimension to the studies owing to the nonequilibrium character
of the isothermal transitions. Photoinduced isomerization and the resulting phase change
can drive the system away from equilibrium conditions providing a convenient situation to
study nonequilibrium phase transitions. The azobenzene molecular entity has proved to be
attractive for photoinduced phase transitions due to its easily accomplished geometric iso-
merization about the azo bond, converting the molecule from the E to Z isomer. Upon UV
irradiation the energetically more stable E configuration with an elongated rodlike molec-
ular form changes into the substantially bent Z configuration. The reverse transformation
can be brought about by illuminating with visible light. This latter change can also occur
spontaneously in the dark by a process known as “thermal back relaxation”. In our labora-
tory, it was recently found that an applied electric field can accelerate the relaxation to the
equilibrium phase. This relaxation was found to be faster than that by the visible light thus
reducing the complications of alignment of optics. Unique temperature-electric field phase
diagrams under such unusual light driven scenario are mapped out, revealing the influence
of the electric field on different phase transitions, the effect being maximum on the equi-
librium reentrant nematic to the photo-induced smectic A transformation. The dynamics of
the thermal back relaxation connected with this transformation is seen to be accelerated by
about 1000 times upon application of the electric field.

Chapter 4: Diminution of the ordering in plastic and liquid crystalline
phases by confinement

Understanding the behavior of finite-sized systems is important in many areas of sci-
ence from both theoretical and experimental points of view. In particular, the influence of
the size of the system on phase transitions, for example, freezing and melting, has received
interest for more than a century, although there is a lot of activity in the past two decades.
The dimensions over which the positional ordering of the molecules is observed, determines the nature - liquid crystalline or plastic - of the phase. The aim of these experiments was to introduce externally a length scale that competes with that in the medium in one or more dimensions. Liquid crystals are especially suitable for work in confined geometries for many reasons. Probing the influence using calorimetric and X-ray investigations, on a sample exhibiting the SmA-CrB transition confined in a porous environment, viz., Anopore membrane, we observe that confinement in cylindrical pores can have a strong effect on the transition from plastic to the liquid crystalline phase. Further, the direction of confinement brings about drastic changes, even to the extent of inducing a new phase in one case and lowering the positional ordering in the other.

Chapter 5: Enhancement of anisotropic conductivity, elastic and dielectric constants in a liquid crystal-gold nanorod system

Composites based on liquid crystals have been extensively investigated owing to their attractive electrical properties as well as interesting effects on different phase transitions. A dimension that has developed in such systems is the research on composites of liquid crystals with gold nanoparticles. This is owing to the fact that gold nanoparticles are the most stable metal nanoparticles and present fascinating size-related electronic, magnetic and optical properties. The study in this chapter brings out the attractive possibility of stabilizing/enhancing the anisotropic properties of the liquid crystal-metal particle system by having anisotropic gold nanoparticles. This chapter describes experimental results of electrical conductivity, dielectric constant, and elastic constant measurements carried out on the composites. Orders of magnitude higher absolute values of conductivity when compared to the pure liquid crystal was observed for the composites. Also observed are enhancement of the conductivity anisotropy, and the ratio of the splay and the bend elastic constants. Based on these observations, especially the fact that the presence of the nanoparticles results in a large increase in the electrical conductivity, the possibility of employing the composites to fabricate a conductivity switch is suggested.
Chapter 6: Pretransitional behavior in the vicinity of the isotropic-nematic transition of strongly polar compounds

The isotropic-nematic transition, being weakly first order, exhibits pretransitional effects signifying the appearance of the nematic-like regions in the isotropic phase. In the isotropic phase, strongly polar liquid crystals, such as the alkyl and alkoxy cyano biphenyl behave in a non-standard fashion. Far away from the transition the dielectric constant has a $1/T$ dependence, a feature seen for polar liquids also. But on approaching the nematic phase the trend reverses resulting in a maximum in the dielectric constant value, at a temperature slightly above the transition. This effect was observed experimentally and explained on the basis of antiparallel pairing of molecules. Specifically, molecules with a strong polar terminal group have a tendency to form antiparallel pairs in order to reduce the dipolar contribution to the free energy. This feature manifests as a convex shaped anomaly in the dielectric permittivity owing to the coupling between the antiparallel arrangement and the growing short-range nematic ordering. In this chapter, dielectric measurements on a number of liquid crystalline systems of varied molecular structures, exhibiting isotropic-nematic transitions are described. These studies reveal that the pretransitional behavior depends on not one but several factors including the magnitude of the dipole moment along the molecular axis.

Chapter 7: Photoflexoelectricity in azo-dye doped nematic liquid crystals

Flexoelectricity signifies macroscopic spontaneous polarization developed in orientationally deformed liquid crystals and is thus an electromechanical effect. In the inverse flexoeffect, curvature stresses are induced or modified by an external electric field. Photoflexoelectricity is an opto-electro-mechanical effect in nematics with 3 degrees of freedom: electrical, mechanical and notably an optical one. Among these, the optical degree of freedom is usually based upon E-Z isomerization of azo-bonds under UV illumination. In this chapter, using conoscopy as the optical technique, clear evidence of the UV light induced
photoflexoelectric effect has been realised. Further, dielectric measurements indicate that the bend elastic constant value decreases upon photoisomerization, suggesting how subtle changes in the molecular/structural changes can drastically affect the macroscopic properties.
1.5 List of Publications

The following is the list of publications resulting from the work carried out by the candidate, and in the order to be described in the thesis:


   Selected for IoP Collections, in which articles are chosen by journal editors for their novelty, significance and potential impact on future research. Also highlighted as a News item, Contradictions coexist in smectic liquid crystals, http://iopscience.iop.org/0953-8984/labtalk-article/45336.


   This paper has also been selected for the September 14, 2009 issue of "Virtual Journal of Nanoscale Science and Technology".


   This paper has also been selected for the October 18, 2010 issue of "Virtual Journal of Nanoscale Science and technology".

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In addition to the above publications, the candidate is also an author to the following articles which are not discussed in the thesis:

1. *Influence of single-walled carbon nanotubes (0.001 wt%) and/or zwitterionic phospholipid (SOPC) surface layer on the behaviour of the gradient flexoelectric and surface induced polarization domains arising in a homeotropic E7 (a mixture of 5CB, 7CB, 8OCB and 5CT)*, H. P. Hinov, J. I. Pavlic, Y. G. Marinov, A. G. Petrov, S.

References


[17] D. Vorländer, Ber. Dtsch. Chem. Ges. 62, 2831 (1929), is credited to have synthesized the first bent-core molecule. But the existence of LC phases in such systems was unequivocally established in the next ref.


