CHAPTER 1
LIQUID CRYSTALS AND THEIR CHARACTERISTIC PROPERTIES

1.1 Introduction

Liquid crystals are molecular fluids whose structural symmetry and physical properties are intermediate between crystalline solids and isotropic liquids. These molecules, in their crystalline phase exhibit orientational order as well as three-dimensional order, but lack both in the liquid phase. Thus, liquid crystals have been termed as “orientationally ordered liquids” which combine certain properties of both the crystalline (anisotropy of certain physical properties) and liquid (ability to flow) states [1, 2]. The schematic arrangement of molecules in the crystal, liquid crystal and liquid states are shown in Figure 1.1.

![Figure 1.1: Schematic representation of molecular arrangement in crystal, liquid crystal and liquid states [3]](image)

The discovery of liquid crystals dates back to 1888, when an Austrian botanist, Friedrich Reinitzer observed a very unusual melting phenomenon in the case of a newly synthesized compound, cholesterol benzoate. He noticed that the compound appeared to have two melting points. The white crystals of the compound melted at 145.5 °C to form a opaque liquid and at 178.5 °C the opacity disappeared to give a clear liquid [4]. Similar behaviour was also observed by Lehmann in silver iodide in 1890, between the temperatures 146 °C and 450 °C [5]. From subsequent studies it became clear that these turbid states flow like liquids and also exhibit anisotropic physical properties as in crystalline solids. Hence Lehmann referred to them as “Fliessende Krystalle” i.e., flowing or fluid crystals. In recent years, they are well known as “Liquid Crystals” or “mesophases”.

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The constituent molecules of liquid crystals which have shapes other than spherical may possess the following three types of order:

1) *Positional order:* Positional order refers to the extent to which an average molecule or group of molecules shows translational symmetry (as in crystalline state).

2) *Orientational order:* The symmetry axes of the molecules tend to orient or align along the particular preferred direction called the director, denoted by unit vector $\hat{n}$.

3) *Bond orientational order:* It describes an order in line joining the centers of nearest-neighbour molecules without requiring a regular spacing along that line.

The combinations of these orders in various proportions give rise to different liquid crystalline phases.

### 1.2 Classification of Liquid crystals

Depending on the way in which the liquid crystals are derived, they are broadly classified into two types:

a) *Thermotropic Liquid crystals:* Liquid crystals obtained by thermal process i.e., by heating a crystal or by cooling an isotropic liquid.

b) *Lyotropic Liquid crystals:* Liquid crystals obtained by the influence of solvents.

### 1.3 Thermotropic Liquid crystals

Thermotropic liquid crystals are those that exhibit liquid crystalline phase(s) in a certain temperature range. The constituent molecules exhibit geometric anisotropy in shape, such as rod-like, disc-like, bent core, etc. On the basis of molecular assemblage, Friedel in 1922 proposed the classification of thermotropic liquid crystals formed of rod-like molecules into three types namely, smectic, nematic and cholesteric phases [6].

Only rod-like thermotropic systems are studied in the present work and hence the other types of liquid crystals are discussed briefly for the sake of completeness.
1.3.1 Thermotropics with rod-like molecules

1.3.1.1 Smectic liquid crystals [7,8]

The word *smectic* is derived from the Greek word *smectos* meaning soap-like. The mesophase possess properties reminiscent of those found in soaps. In smectics, the molecules are arranged in layers with their long axes parallel to one another exhibiting correlations in their positions in addition to the orientational ordering. The stratified structure of smectics results in a well defined spacing between the layers. Due to the weak interaction between the layers of the smectics, the layers slide over one another relatively easily giving rise to the fluid property of the system. Based on the molecular arrangement and orientation within the layers, smectics are further classified into Sm A, Sm B, Sm C, Sm E, Sm F, Sm G, Sm H, Sm I, Sm J and Sm K. Among them some smectic phases like Sm B, Sm E, Sm G, Sm H, Sm J, and Sm K exhibit three dimensional order, hence they are also known as “crystal smectics” or “soft crystals”. They are denoted as Cr B, Cr E, Cr G, Cr H, Cr J and Cr K.

The Sm A phase possesses least order among all the smectic polymorphs. The molecules are arranged in layers with their long axes perpendicular to the planes of the layers. The distribution of the molecules within each layer is random and they are able to rotate freely about their long axes [9, 10]. Although the picture of Sm A phase is simple, a detailed X-ray investigation of Sm A phase lead to the discovery of various Sm A phases like monolayer Sm A phase (Sm A₁), bilayer Sm A phase (Sm A₂) [11], partial bilayer or interdigitated Sm A phase (Sm A₃) [12, 13], Sm A antiphase (Sm A) (phase composed of regions having both bilayer and monolayer structure) [14-16], etc.

The Sm B phase is more ordered than the Sm A phase. There are two types of Sm B phases namely, hexatic (Hex B or Sm B_{hex}) phase and crystalline (Cr B or Sm B_{cr}) phase. The constituent molecules of Hex B phase are arranged within the layers in a hexagonally close-packed array with their molecular long axes perpendicular to the layer planes. They exhibit short-range in-plane positional order but quasi long-range six fold bond orientational order [17, 18]. In the Cr B phase, the long-range positional order exists within the layers and also from layer to layer. The molecular centers are packed with hexagonal symmetry within the layers and they are free to rotate about the normal to the layers [19, 20].
In Sm C phase, the molecules are tilted with respect to the layer normal planes. The molecules within the layers are packed in an unstructured way, and therefore it is usually referred to as a tilted analogue of Sm A phase [8, 21].

Cr E phase exhibits herringbone-structure, with highly ordered molecules adopting an orthorhombic close-packing. The long axes of the molecules are orthogonal to the layer planes. This phase is characterized by the rotational disorder of the molecules around the long axis [22, 23].

The Sm F and Sm I phases are tilted analogues of the Hex B phase. The molecules within the layers of Sm F phase are oriented in two-dimensional lattice with hexagonal packing. This phase exhibits bond-orientational order with long range orientational order of hexagons and short range positional order of the molecules within the layer but no interlayer positional correlation. The director in Sm F phase is tilted towards the sides of the hexagonal net [24]. In Sm I phase, it is tilted towards the apex of the hexagonal packing net [25].

The Cr G and Cr J phases are tilted analogues of Cr B phase. In Cr G phase the long axes of the molecules are tilted and exhibits pseudo-hexagonal close packing in the plane right angles to the tilt direction within the layers. The tilt direction is towards the side of the hexagonal net. The inter-layer correlation is well established in Cr G phase. In Cr J phase, the structural features are same as Cr G phase, except that the tilt direction is towards the apex of the hexagonal net. Both Cr G and Cr J phases exhibit long range orientational and positional ordering and the molecules undergo free rotation about their long axes [26, 27].

Cr H and Cr K phases are tilted analogues of Cr E phase exhibiting long range positional and orientational ordering. The packing arrangement is monoclinic. The direction is towards the shorter edge of the packing net in Cr H phase and to the longer edge of the packing array in Cr K phase. The reorientational motion of the molecules is restricted as in Cr E phase [28, 29].

The molecular arrangement in some of the smectic phases discussed above are shown in Figure 1.2.

Chiral smectic phase comprises molecules that are non-superimposable on their mirror image and exhibit different liquid crystalline properties compared to their achiral analogues. The chiral smectic phases are designated with an asterik (*) symbol over the letter which are used to specify nonchiral smectic phases such as Sm C*,
Sm I*, Sm F*, Cr J*, Cr G*, Cr K* and Cr H*. These phases arise due to molecular chirality of the constituent molecules. Chiral phases can be obtained in achiral molecules by doping with chiral additive.

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**Figure 1.2:** Schematic representation of molecular arrangement in side and plan views of different smectic mesophases [7]. Triangles or arrows are used to represent tilt direction.
The helical structure of Sm C* phase was first recognized in early 1970s [30]. Its helical structure is formed by the precession of the director around the layer normal and the tilt direction of the molecules rotates through an angle in the same direction when going from layer to layer [Figure 1.3 (a)]. The presence of helical structure in the Sm C* phase leads to spontaneous polarization and this is responsible for its unique optical and ferroelectric properties. Hence they are also referred to as ferroelectric phases. The ferroelectric properties of chiral phases enhance the electro-optic effects [31] and form the basis for many applications [32]. The different molecular arrangements within these chiral smectic phases may result in antiferroelectric phase and ferrielectric phase. In antiferroelectric phase, the molecules in the neighbouring layers tilt to almost opposite direction and the polarization direction in subsequent layers point in opposite direction [Figure 1.3 (b)]. In ferrielectric phases, there are more layers of one tilt direction than the other [Figure 1.3 (c)]. These phases are currently the subject of wide research due to their unique optical properties and hold a great potential for display devices [33, 34].

![Figure 1.3: Schematic representation of molecular arrangement in (a) ferroelectric (b) antiferroelectric and (c) ferrielectric Sm C* phases [35]](image)

### 1.3.1.2 Nematic Liquid crystal

The word nematic stems from the Greek word, nematos meaning thread-like. The mesophase adopts a characteristic threaded texture when observed under
polarizing microscope. In the nematic phase the long axes of the molecules are aligned approximately about a preferred direction which is referred to as the director and denoted by the unit vector $\hat{n}$ [Figure 1.4(a)]. Nematics possess long range orientational order and no translational order. The distribution of the centers of the mass of the molecules exhibits short range order similar to isotropic liquids. The physical properties measured along $+\hat{n}$ and $-\hat{n}$ directions are equivalent.

### 1.3.1.3 Cholesteric liquid crystal

The cholesteric phase is a special case of the nematic phase formed of optically active molecules and is referred to as chiral nematic or twisted nematic. The molecules in this mesophase are arranged in layers with the long axes of the molecules being oriented about a particular preferred direction $(ii)$ in the plane of each layer, but this preferred direction rotates smoothly as one progresses from layer to layer along the normal to the layers [Figure 1.4 (b)]. The measured distance along the twist axis over which the direction of the alignment of the molecules rotates through a full cycle is called the pitch $p$ of the medium. The pitch is highly sensitive to temperature and it is responsible for unique optical properties, viz., selective reflection of circularly polarized light and its rotatory power is about one thousand times greater than that of an ordinary optically active substance. They have long range orientational order and no long-range order in the positions of the centers of mass of molecules.

*Figure 1.4:* Schematic representation of molecular arrangement in the (a) nematic phase and (b) cholesteric phase [36]
1.3.2 Discotic liquid crystals

Liquid crystals formed of disc shaped molecules are referred to as *discotic liquid crystals*. They are two types of discotic phases namely, nematic discotic and columnar discotic (Figure 1.5). In the nematic phase, the disc like molecules orient along a preferred director. In the columnar phase, the discs stack up one on top of the other. The molecular arrangement within the columns may be ordered or disordered. There are different types of columnar phases exhibited by discotics namely, hexagonal, rectangular and tilted.

![Diagram of nematic and columnar phases](image)

*Figure 1.5: Schematic representation of molecular arrangement in discotic (a) nematic and (b) columnar phases [37]*

1.3.3 Banana shaped or bent core liquid crystals

Liquid crystals composed of banana or bow shaped molecules are known as *bent core liquid crystals*. These mesogens consist of the same chemical composition and basic chemical architecture of conventional calamatic (rod-like) liquid crystals but with a sharp “kink” or bend within the linkage of the rigid core group (Figure 1.6). They exhibit distinctly different phases compared to other conventional liquid crystals. The banana phases are designated as $B_1$, $B_2$, ..., $B_8$, where ‘B’ stands for banana shaped molecules and the subscript corresponds to the sequence of discovery of the different phases (Figure 1.7). These liquid crystals have gained considerable interest due to the novel and peculiar polar switching properties in spite of comprising achiral molecules.
1.4 Lyotropic liquid crystals

Lyotropic liquid crystals are obtained on adding suitable solvents to amphiphilic materials. Amphiphilic materials such as soaps, phospholipids, etc., consist of molecules which possess hydrophilic polar groups that interact strongly with water and hydrophobic nonpolar groups which are water insoluble. Under suitable concentration ranges, the molecules tend to organize themselves forming aggregates of various well defined geometries such as micelles [Figure 1.8 (a)], hexagons [Figure 1.8 (b)], cubes [Figure 1.8 (c)], lamellar [Figure 1.8 (d)], etc.

1.5 Polymeric liquid crystals

Polymeric liquid crystals are synthesized by embedding mesogenic units in polymer systems. Such systems hence exhibit the properties of the constituent polymers as well as liquid crystals. The constituent molecules in these systems may be either rod-like, disc-like, rod and disc together, lyotropic, etc. There are two kinds of polymer liquid crystals namely: i) Main Chain Liquid Crystal Polymers (MCLCPs) in which the main chain consists of repeating mesogenic units [Figure 1.9 (a)] and ii) Side Chain Liquid Crystal Polymers (SCLCPs) in which the mesogenic units are
attached to the polymer chain as side groups [Figure 1.9 (b)]. The structural composition and degree of flexibility determine the properties of polymeric liquid crystals.

Figure 1.8: Schematic representation of molecular arrangement in (a) micellar (b) hexagonal (c) cubic and (d) lamellar lyotropic mesophases [40]

Figure 1.9: Schematic representation of (a) main chain and (b) side chain polymeric liquid crystals [41]

1.6 Physical properties of liquid crystals

The degree of ordering of molecules present in liquid crystals distinguishes the physical properties of liquid crystals from that of liquids. The anisotropy of liquid crystals which arises due to the molecular shape and the order existing in the constituent molecules manifests itself in the elastic, electric, magnetic and optical properties. Many applications of liquid crystals rely on their anisotropic physical properties and their response to the external perturbations like temperature,
mechanical stress, electric, magnetic fields, etc. [34]. Hence, a detailed knowledge about the physical properties of liquid crystals such as orientational order parameter, birefringence, dielectric permittivity, electrical conductivity, magnetic susceptibilities, elasticity, viscosity, etc. are necessary to describe the applicability of liquid crystals in various fields. As the present thesis deals much with the systems exhibiting nematic and / or smectic phases, in what follows, the focus will be mainly on the different properties of these systems.

1.6.1 Birefringence

Due to the anisotropic nature of liquid crystals, they are optically inhomogeneous and exhibit birefringence. The optical anisotropy or birefringence is given by \( \Delta n = (n_e - n_o) = (n_{\parallel} - n_{\perp}) \), where \( n_e \) and \( n_o \) are extraordinary and ordinary refractive indices and, \( n_{\parallel} \) and \( n_{\perp} \) are the components parallel and perpendicular to the director respectively. Optical anisotropy is strongly dependent on temperature and wavelength. In nematics with rod-like molecules, \( n_{\parallel} > n_{\perp} \) and therefore \( \Delta n \) is positive. In the case of discotic molecules, \( n_{\parallel} < n_{\perp} \) and \( \Delta n \) is negative. Different mesophases are characterized by uniaxial, biaxial and / or helicoidal optical symmetries. Generally, nematics and orthogonal smectic and columnar phases are uniaxial while the tilted smectic and columnar phases are biaxial. Chiral nematic (i.e., cholesteric) and chiral smectic phases are associated with helicoidal optical symmetry. The birefringence associated with the nematic medium is generally quite large near the melting point, being usually in the range 0.05-0.5 and almost zero near the clearing point \( T_{NI} \).

1.6.2 Orientational order parameter

The order existing in the liquid crystalline phases determines the relationship between microscopic and macroscopic properties. The orientational order parameter gives a measure of the distribution of molecules about the director \( \hat{n} \) and is inherent in all mesophases. The order parameter ‘\( S \)’ is mathematically defined as,

\[
S = \left\langle \frac{3 \cos^2 \theta_i - 1}{2} \right\rangle
\]

where, \( \theta_i \) is the angle made by the \( i^{th} \) molecule with the director \( \hat{n} \) and the angular brackets indicate a statistical average. The order parameter \( S = 0 \) in the isotropic
liquid phase, in which there is a random distribution of molecules and $S = 1$ for a perfectly aligned phase (where all the angles equals to zero). The value of $S$ varies between 0.3 and 0.8 in liquid crystalline phases. The orientational order parameter can be directly related to experimentally determined quantities like birefringence, dielectric anisotropy, diamagnetic susceptibilities, etc. [7, 34].

1.6.3 Translational order parameter

While nematic phases possess orientational order, smectic phases possess positional order in addition. The order in nematics is usually quantified by orientational order parameter while that in smectics by translational order parameter. Different smectic phases are in fact characterized by varying degrees of orientational and translational order. Smectic translational order parameter for $l^{th}$ order layer reflection (0 0 $l$) along $z$-direction (the direction of the layer normal) is defined as,

$$\tau = \langle \cos(2\pi l z / d) \rangle$$

where $d$ is the layer spacing. Thus, $\tau$ is directly proportional to the amplitude of the cosine modulation in electron density along $z$ direction and gives the strength of the sinusoidal smectic ordering [7, 42]. The value of $\tau$ generally varies between 0.5 and 0.9 in various smectic phases.

1.6.4 Dielectric permittivity

The dielectric property of liquid crystals is a measure of collective response of liquid crystalline molecules to the applied electric field and it is a macroscopic property of the system. It is characterized by the dielectric permittivity $\varepsilon$ which depends on temperature and also on the frequency of the applied field. The dielectric properties of mesomorphic substances such as dielectric permittivity, dielectric loss, relaxation time, etc. provide an insight into the molecular structure of the system, nature and strength of intermolecular interactions. The degrees of orientational and translational order prevalent in different mesomorphic phases affect the short range dipole-dipole interactions. The dielectric anisotropy is given by $\Delta \varepsilon = \varepsilon_1 - \varepsilon_\perp$, where $\varepsilon_1$ and $\varepsilon_\perp$ are the permittivity components measured parallel and perpendicular to the director $\hat{n}$ respectively. The dielectric anisotropy may be positive or negative depending on the permanent dipole moment and polarizabilities of the molecules. The permittivity components depend on temperature and frequency. The study of
temperature variation of permittivity components (static studies) of liquid crystals usually shows abrupt changes in the vicinity of phase transitions which occur due to molecular reorganization while their frequency dependence (dispersion studies) gives information about the molecular polarizabilities, dipole moments and the influence of neighbouring molecules on molecular rotation [7, 34].

1.6.5 Electrical conductivity

The flow of ionic impurities gives rise to electrical conductivity in liquid crystals [43]. The anisotropy of the conductivity is given by $\Delta \sigma = \sigma_1 - \sigma_\perp$, where $\sigma_1$ and $\sigma_\perp$ are the conductivity components measured parallel and perpendicular to the director $\mathbf{n}$ respectively. These conductivity components depend on temperature and the frequency of the applied field. The conductivity anisotropy may be positive or negative depending upon the direction in which the ions can flow easily. Generally in the nematic phase, the ions flow easily in the direction parallel to the director and hence $\sigma_1 > \sigma_\perp$. In smectic phases, the movement of ions is favoured in the direction perpendicular to the smectic layer planes resulting in $\sigma_\perp > \sigma_1$ [44, 45].

1.7 Applications of liquid crystals

Liquid crystalline substances possess the properties of both anisotropic crystalline solids and isotropic liquids. They have the ability to detect extremely small changes in temperature, mechanical stress, electro-magnetic radiation, etc. Hence they play significant role in several fields such as scientific, technical, medical, etc.

One of the major applications of liquid crystals is in display technology. Liquid crystal displays (LCDs) are used in watches, calculators, computers, mobile phones, household electric appliances, etc. The first practical electro-optical flat panel LCD was reported by Heilmeier, Zanoni and Barton [46,47] at the RCA Laboratories in Princeton, New Jersey in 1968. Since then a wide variety of prototype and commercial LCDs have been developed based on the manipulation of liquid crystalline state by the electric field on the LCD geometry to modulate the intensity of light passing through the cell in the activated and nonactivated states [48-50]. More importantly, liquid crystals have dominated the displays market due to their extremely low power consumption, low-voltage operation, faster switching speed, high-contrast ratio, compactness and flexibility of size [51].
In addition to displays, liquid crystals have found numerous applications in various fields such as optical imaging and recording, industrial, scientific, technical, medical, etc. They are used for non-destructive mechanical testing of materials under stress and this technique is used for the visualization of radio frequency waves in waveguides. Low molar mass liquid crystalline polymers have been used in erasable optical disks, full color “electronic slide” for computer-aided drawing (CAD) and light modulators for color electronic imaging [52,53]. Cholesteric liquid crystals are used as temperature sensors in which the devices are based on the selective reflection of light by liquid crystal layers. These devices include thermometers (fever strips), hot warning indicators, battery testers, novelties such as ‘stress’ and ‘mood’ sensors. In medical field, attaching colour sensitive device to a part of the body produces a visual image of the temperature variations of the skin and helps in the diagnosis of circulation problems and cancerous growth [34]. This technique, known as medical thermography is also used in diagnosing deep vein thrombosis, acute paraproctitis, etc.; anesthetic recovery and several ophthalmologic practices [7]. Further, cholesterics have certain chromatographic applications where they are used to create anisotropic medium that promotes the separation of similar compounds. They can also be used as anisotropic solvents to control orientation or mobility for certain spectographic applications [54].

Liquid crystalline materials play a remarkable role in nanoscience and nanotechnology. Many lyotropic and thermotropic liquid crystals plays a major role in the synthesis and self assembly of nano structures of uniform size and shape. The molecular ordering and mobility properties of liquid crystals help in controlling orientation and reorientation (switching) of anisometric one-dimensional nanostructures leading to new electro-optical applications. Liquid crystal nanocomposites have greatly contributed to the nanotechnology revolution and have opened up a new avenue for high-tech applications in areas such as nanoscale electronics, electro-optics, optical memories and display devices [51,55].

Present work is concerned with the studies on the physical properties, viz., birefringence, orientational order, microstructural parameters, translational order, electrical conductivity and molecular structure of some thermotropic liquid crystals and crystals. The studies carried out are discussed in the following chapters.
References

Chapter 1