Chapter 1

Introduction

1.1   Liquid Crystals

Liquid crystals are states of condensed matter whose symmetries lie between those of 3-dimensionally ordered crystals and completely disordered isotropic liquids. In the liquid crystalline phase the anisotropic molecules exhibit long range orientational order. In some liquid crystals an additional 1-d (one-dimensional) or 2-d translational order is also observed. Liquid crystals like crystals exhibit anisotropies in physical properties such as refractive indices, dielectric constants and diamagnetic susceptibilities and flow like liquids, and hence get the name *liquid crystals*.

Many organic compounds exhibit mesophases as a function of temperature. Such liquid crystals are called **thermotropic** liquid crystals. Certain amphiphilic molecules dissolved in solvents like water form supramolecular assemblies which in turn exhibit mesophases. These are termed as **lyotropic** liquid crystals. As our interest of study is in the properties of **thermotropic** liquid crystals we describe only structures of some thermotropic liquid crystals.

Classification

The liquid crystalline phase is exhibited by shape anisotropic molecules. Depending on the shape anisotropy of the molecule they are classified into:

♦ **Calamitic** liquid crystals made of rod-like molecules,

♦ **Discotic** liquid crystals made of disc-like molecules,

♦ **Banana** liquid crystals made of bent-core molecules.

Friedel classified the thermotropic liquid crystals made of rod-like molecules into mainly three classes based on the symmetry of the medium:

• **Nematics**

• **Cholesterics**

• **Smectics**

1.2 Nematics

The uniaxial nematic (N) phase is the simplest known phase among all the mesophases. In the nematic phase the molecules have a long range orientational order but no translational order. Usually, nematic liquid crystals made of rod-like molecules exhibit uniaxial cylindrical symmetry. On an average the long axes of the molecules are oriented along a particular direction called the director denoted by $\hat{n}$ as shown in Figure 1.1. The director $\hat{n}$ is a dimensionless *apolar* unit vector i.e. $\hat{n}$ and - $\hat{n}$ are physically equivalent [1]. Even when the molecules are made of highly polar end groups the medium is still apolar as the molecules orient such that there is no net polarisation in the medium.
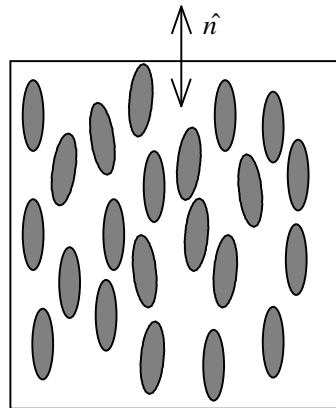

Figure 1.1: Schematic representation of molecular arrangement in a nematic liquid crystal, where $\hat{n}$ represents the director.

1.21 Order Parameter

The order parameter gives a measure of the distribution of the rod-like molecules about the director. In view of the apolar nature of the director $\hat{n}$ the orientational order parameter characterising the nematic phase cannot be a vector. The order parameter is a second rank traceless symmetric tensor and is given by $Q_{ij} = S(n_i n_j - \delta_{ij}/3)$, where i,j = x,y,z. The magnitude of orientational order parameter is denoted by $S = \frac{1}{2}\left\langle 3\cos^2\theta - 1 \right\rangle$, where θ is the angle between the long axis of the molecule and the director and $< >$ denote statistical average [1,2]. The order parameter $S = 0$ in the isotropic phase and $S \neq 0$ in the liquid crystalline phase, increasing from 0.3 to 0.8 with decreasing temperature.

1.22 Birefringence

In the case of uniaxial nematic and smectic A liquid crystals the direction of optic axis is along the director $\hat{n}$. The anisotropy of nematic liquid crystals causes a light beam polarised along the director to propagate at a different velocity than the one polarised perpendicular to the director. The uniaxial nematic phase has two principal refractive indices μ_e and μ_o. μ_e is the extraordinary refractive index for a light wave propagating normal to the director $\hat{n}$ with electric vector parallel to $\hat{n}$. μ_o is the ordinary refractive index for a light wave propagating orthogonal to $\hat{n}$ with electric vector perpendicular to $\hat{n}$. The birefringence is given by $\Delta\mu=(\mu_e-\mu_o)$. The $\Delta\mu$ data can be used to calculate the approximate orientational order parameter S of nematic liquid crystals using the relation $S\approx\Delta\mu/\Delta\mu_0$, where $\Delta\mu_0$ is the birefringence of the medium in the fully aligned state.
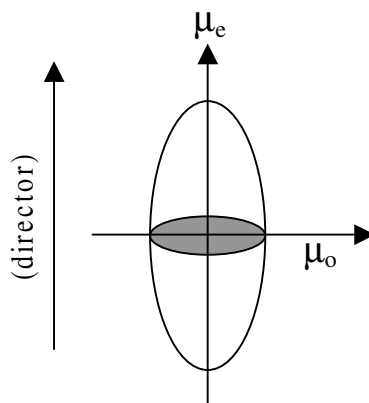

Figure 1.2: Refractive index ellipsoid, with the arrows indicating the polarisation directions of the light beam.

1.23 Dielectric Anisotropy

The dielectric constant ε is a measure of the response of the material to an external electric field. It depends on the intrinsic properties of the material like distribution of charges in the molecules as well as intermolecular interactions. The dielectric constant depends on temperature as well as frequency of the applied electric field. For mesogens with polar molecules in addition to the induced polarisation an orientational polarisation occurs due to the tendency of the permanent dipole moments to orient parallel to the electric field. The orientational polarisation in liquid crystals can contribute significantly to the dielectric constant. On the other hand, in a

solid crystal the orientational polarisation does not contribute significantly to the permittivity due to the fixed orientations of the molecules. In liquid crystals, the dielectric constants $\varepsilon_\parallel$ and $\varepsilon_\perp$ are measured with electric field parallel and perpendicular to the director ($\hat{n}$) respectively. The dielectric anisotropy is given by $\Delta\varepsilon = \varepsilon_\parallel$ - $\varepsilon_\perp$.

Using Maier and Meier's theory the expressions for the dielectric constants [3] can be written as follows

$$\varepsilon_\parallel = 1 + 4\pi \frac{N_A \rho h F}{M}\left\{\overline{\alpha} + \frac{2}{3}\Delta\alpha S + \frac{Fp^2}{3k_B T}\left[1 - \left(1 - 3\cos^2\beta\right)S\right]\right\} \qquad 1.1$$

$$\varepsilon_\perp = 1 + 4\pi \frac{N_A \rho h F}{M}\left\{\overline{\alpha} - \frac{1}{3}\Delta\alpha\ S + \frac{Fp^2}{3k_B T}\left[1 + \frac{1}{2}\left(1 - 3\cos^2\beta\right)S\right]\right\} \qquad 1.2$$

where $\Delta\alpha\ (=\alpha_l - \alpha_t)$ is the anisotropy of polarizability of a perfectly oriented medium, N_A is the Avagadro number, ρ the density, M the molecular weight, $h = \frac{3\overline{\varepsilon}}{(2\overline{\varepsilon}+1)}$, is the cavity field factor and $F = \frac{1}{(1 - f\overline{\alpha})}$ where $f = \frac{(\overline{\varepsilon}-1)}{\left[2\pi a^3\left(2\overline{\varepsilon}+1\right)\right]}$ is the reaction field factor for spherical cavity and $\overline{\alpha}$, is the average polarizability, p is the molecular dipole moment. β is the angle between the direction of dipole moment and the long axis of the molecule. The average dielectric constant $\overline{\varepsilon}$ can be obtained from equations (1.1) and (1.2) as

$$\overline{\varepsilon} = 1 + \frac{4\pi N_A \rho h F}{M}\left(\overline{\alpha} + \frac{Fp^2}{3k_B T}\right) \qquad 1.3$$

The dielectric anisotropy is given by

$$\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp = 4\pi\frac{N_A \rho h F}{M}\left[\Delta\alpha - F\left(\frac{p^2}{2k_B T}\right)\left(1 - 3\cos^2\beta\right)\right]S \qquad 1.4$$

The relative magnitude of the two terms within the square brackets of equation (1.4) determines the sign of $\Delta\varepsilon$. When $\beta < 55^0$, the two terms add up and the compound exhibits a strong positive dielectric anisotropy. For $\beta \sim 55^0$, the second term vanishes and only $\Delta\alpha$ contributes to $\Delta\varepsilon$. For $\beta > 55^0$, $\Delta\varepsilon > 0$ or < 0, depending on whether the dipolar contribution is less or more than the contribution due to polarizability anisotropy.

1.24   Curvature Elasticity

In a non-uniformly oriented nematic the orientation of director varies continuously in space. Any elastic deformation can be written as a combination of the three basic curvature deformations. They are

- **Splay**
- **Twist**
- **Bend**

The deformation free energy density is defined as

$$F_d = \frac{K_{11}}{2}\left(\nabla \cdot \hat{n}\right)^2 + \frac{K_{22}}{2}\left(\hat{n} \cdot \nabla \times \hat{n}\right)^2 + \frac{K_{33}}{2}\left(\hat{n} \times \nabla \times n\right)^2 \qquad 1.5$$

where K_{11}, K_{22} and K_{33} are the splay, twist and bend elastic constants respectively. Since $\hat{n}$ is a dimensionless unit vector, the elastic constants K_{11}, K_{22} and K_{33} have units of energy/length and are of the order of $k_B T_{NI}/a$, where k_B is the Boltzmann constant, T_{NI} is the nematic isotropic transition temperature and a is a typical molecular length. Usually the order of magnitude of elastic constants is $\sim 10^{-7}$ dynes. The pictorial representation of the three basic curvature deformations are shown in Figure 1.3.
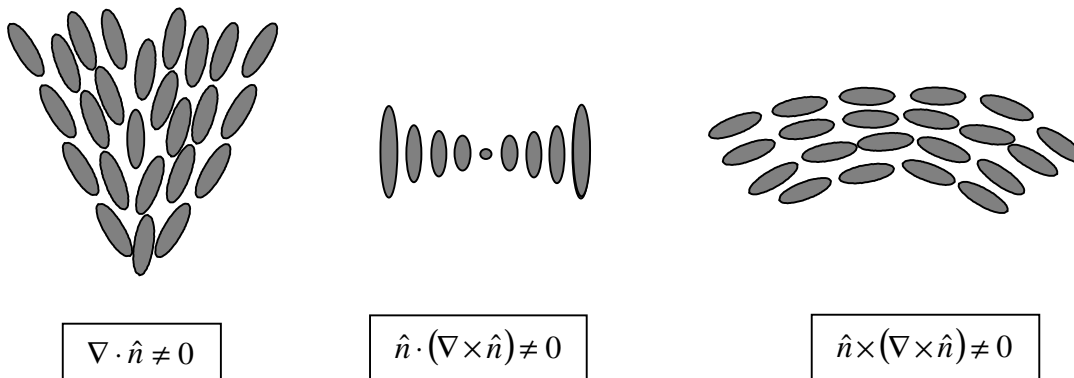

$$\boxed{\nabla \cdot \hat{n} \neq 0} \qquad \boxed{\hat{n} \cdot \left(\nabla \times \hat{n}\right) \neq 0} \qquad \boxed{\hat{n} \times \left(\nabla \times \hat{n}\right) \neq 0}$$

Figure 1.3: The three basic elastic deformations of the director in a nematic liquid crystal: (i) Splay (ii) Twist and (iii) Bend.

1.25   Freedericks Transition

The apolar nature of $\hat{n}$ also has the consequence that an external electric field couples to the medium through its dielectric anisotropy $\Delta\varepsilon$. The orientational part of the energy density F_{diel} is given by - $\varepsilon_0 \Delta\varepsilon(\hat{n} . \vec{E})^2/2$, where ε_0 is the vacuum dielectric constant. On application of an external field (electric or magnetic) to an uniformly

aligned sample the orienting effect of the boundaries can conflict with the orienting effect of applied field, and hence a distortion of the original director field takes place. In a uniformly aligned $s$ample when an electric field is applied transverse to the director a distortion takes place only when the strength of applied field exceeds a certain well defined threshold value. This type of transition is called Freedericks transition. The threshold voltage is given by (independent of the sample thickness t) $V_{th}=\pi[K_{11}/(\varepsilon_0\Delta\varepsilon)]^{1/2}$ where K_{11} is the splay elastic constant, relevant to the initial distortion of the director in a planar aligned cell (Figure 1.4).
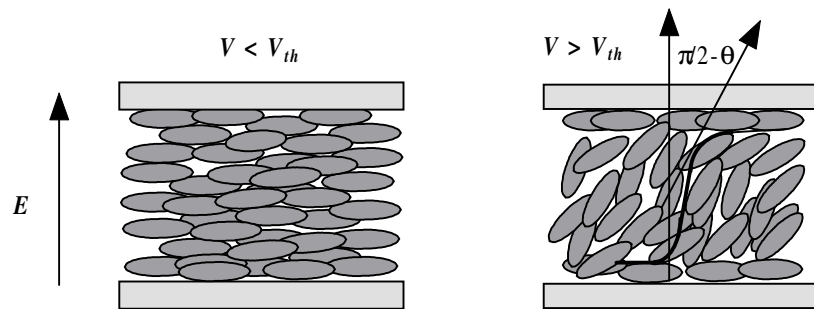

Figure 1.4: Schematic representation of the director configuration (a) for $V < V_{th}$ and (b) for $V > V_{th}$.

Consider a sample with positive dielectric anisotropy taken between two ITO (Indium Tin Oxide) coated glass plates aligned homogeneously as shown in Figure 1.4. When an electric field is applied to the sample (Figure 1.4), the molecules tend to align parallel to the electric field. Beyond the threshold voltage the orientation of the medium gets distorted near the center of the cell and molecules make an angle with respect to the glass substrate. The transmitted intensity from a sample placed between crossed polarisers with the optic axis at an angle of 45^0 with respect to the polariser is proportional to the optical phase difference of the sample $\Delta\phi=2\pi\overline{\Delta\mu}\ t/\lambda$, where $\overline{\Delta\mu}$ is the average value of the birefringence, t is the sample thickness and λ the wavelength of incident light. The intensity profile as a function of applied voltage at a given temperature in the nematic range typically looks like that shown in Figure 1.5. As the applied voltage is increased the distortion of the orientation in the medium increases leading to a decrease in the average value of the birefringence. With increase in the applied voltage the rate of variation of transmitted intensity decreases. At high values of applied voltages of ~ 5V and above, the intensity profile flattens out (Figure 1.5) as the average value of the birefringence $\overline{\Delta\mu}$ is negligible. Hence using this method the absolute value of optical phase difference can be found.
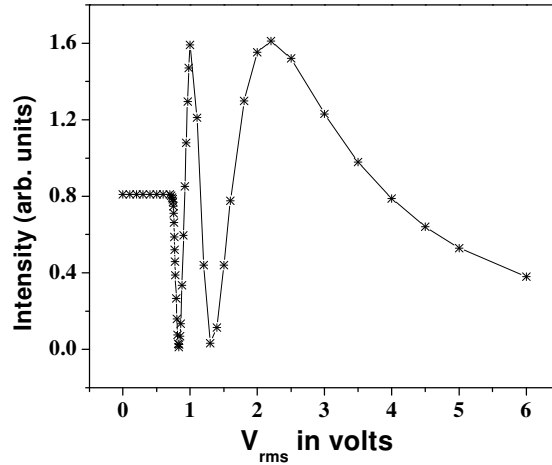
Figure 1.5: Variation of transmitted intensity as a function of applied voltage, freq: 4111Hz.

1.3 Cholesterics

The cholesteric phase (N*) is made of optically active or chiral molecules. The director $\hat{n}$ is no longer constant in space but precesses in a helical fashion along the z-axis as shown in Figure 1.6. As $\hat{n}$ is physically equivalent to $-\hat{n}$, the periodicity of medium along helix axis is $P/2$, where P represents the pitch of the medium.
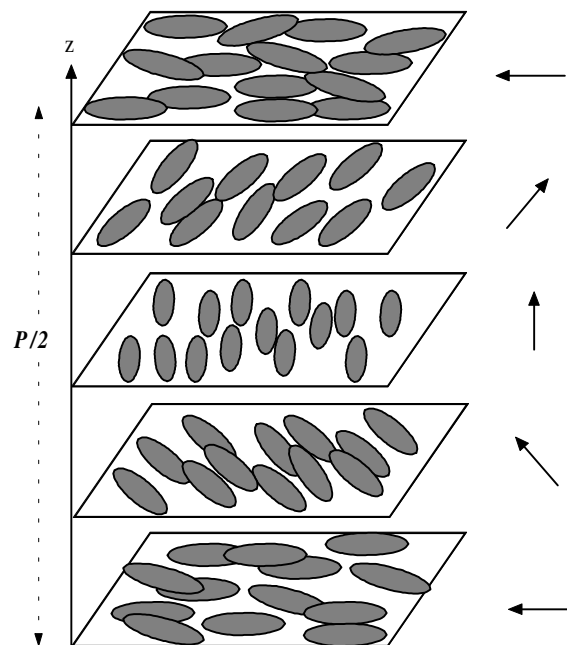

Figure 1.6: Schematic representation of molecular arrangement in the cholesteric phase. The arrows indicate the orientation of director $\hat{n}$.

1.4   Smectics

In the smectic phases along with the orientational order of the molecules there is a 1-dimensional translational order. This gives rise to a layered structure. In the layer plane the arrangement of molecules is liquid like.
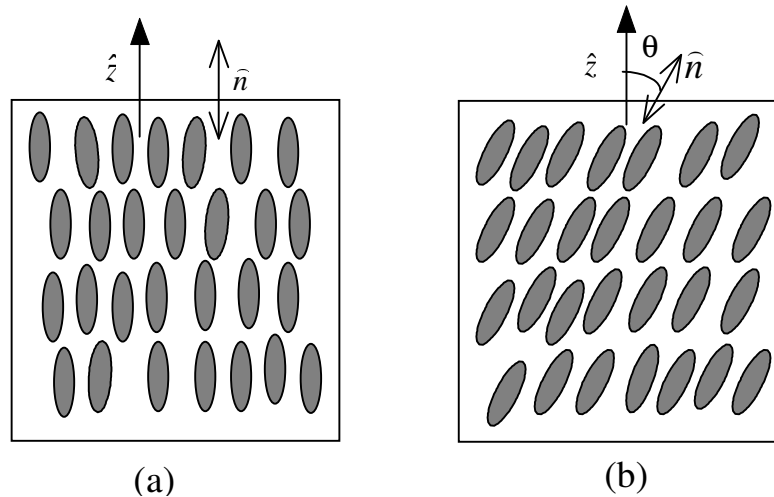

$$(a) \qquad\qquad (b)$$

Figure 1.7: Schematic representation of molecular arrangement in (a) Smectic A and (b) Smectic C phases.

In Smectic A (SmA) the long axes of molecules are parallel on an average to the layer normal $\hat{z}$ i.e. $\hat{n}$ is parallel to $\hat{z}$ as shown in Figure 1.7a. The layer thickness can vary from monomolecular length to twice the molecular length depending on the nature of molecular interactions.

In Smectic C (SmC) the long axes of the molecules are tilted with respect to layer normal $\hat{z}$ as shown in Figure 1.7b. The projection of $\hat{n}$ onto the plane of layers is denoted by $\vec{c}$, which is a *polar* vector. The medium is biaxial in nature.

1.41   Smectic C[*] Liquid Crystals

 SmC phase made of optically active molecules forms a helical structure. The helix is formed by precession of the tilt direction about an axis perpendicular to the layers with a characteristic pitch as shown in Figure 1.8. Depending on the chirality of the molecule, the helix can be either left-handed or right-handed. The symmetry of the SmC[*] layers allows them to be transversely polarized and hence SmC[*] is also referred to as a ferroelectric liquid crystal [4].
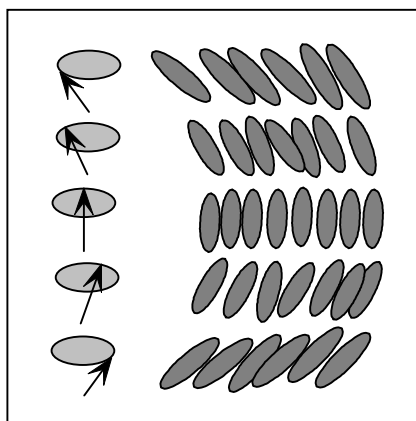
Figure 1.8: Schematic representation of molecular arrangement in the smectic C* phase. The tilt direction rotates between successive layers as represented by arrows.

1.42   Biaxial Smectic A Phase

The liquid crystalline compounds made of molecules with a large bent-core (with a bend angle of ~120^0) are known as banana or bow-shaped liquid crystal compounds (Figure 1.9). Unlike the rod-like molecules, which rotate freely about their long axis, the bent–core molecules with a large bend angle cannot rotate freely. Compounds composed of these molecules exhibit distinctive phases which are usually denoted by B$_i$, where i =1, 2, etc.
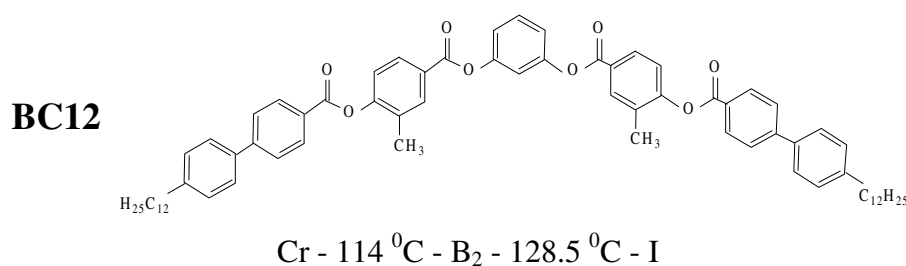
BC12

Cr - 114 ^{0}C - B$_2$ - 128.5 ^{0}C - I

Figure 1.9: Chemical structure and transition temperatures of the banana shaped compound BC12 (1,3-phenylene bis[4-(3-methylbenzoyloxy)] 4′-n-dodecylbiphenyl 4′-carboxylate).

Pratibha et al [5] have reported the phase diagram of binary mixtures of the banana compound BC12 and a compound made of rod shaped molecule viz. 4-biphenylyl 4″-n-undecyloxybenzoate (BO11) exhibiting interesting phase transitions.

In the composition range of 4 to 13mol% of the banana compound the binary mixtures exhibit the phase sequence: I - N - SmA_2 - SmA_{2b} [5], where SmA_2 and SmA_{2b} correspond to uniaxial smectic and biaxial smectic phases respectively (with layer spacing d being twice the molecular length in both the cases). In homeotropically aligned samples the uniaxial nematic presents a dark field of view between crossed polarisers. However, strong fluctuations of the director can be observed, which abruptly cease at the N-SmA_d transition point. As the sample is cooled below this temperature another transition takes place, and the sample exhibits a schlieren texture between crossed polarisers, in which dark brushes emerge from some points. The texture shows that the medium is an orthogonal biaxial smectic liquid crystal [5]. Recently there are reports [6] of pure banana compounds exhibiting biaxial smectic A phase.

Pratibha et al [7] have also studied another system of binary mixtures of the banana compound BC12 with a different rod-shaped molecule viz., 4-cyano-4-octyloxy biphenyl (8OCB). This system of binary mixtures in a concentration range of 10 to 15 mol% of BC12 exhibits the following phase sequence: I - N - SmA_d - SmA_{db} [7]. We have studied the effect of pressure on this phase sequence in a binary mixture with 14 mol% of BC12 which will be reported in chapter 5.

1.5   Reentrant Nematic Phase

The normal expectation is that with decreasing temperature the symmetry of the lower temperature phase is lower than that of the higher temperature phase. Hence the SmA phase which has a lower symmetry than the nematic phase is expected to occur at lower temperatures. Indeed most of the liquid crystals exhibit this phase sequence. However, Cladis in 1975 [8] discovered that a certain mixture of polar mesogens exhibits the following phase sequence with decreasing temperature: Isotropic (I) - N - SmA – re-entrant nematic (N_r)- Crystal (Cr). The lower temperature nematic phase (N_r) has been named as the re-entrant nematic phase. Subsequently, in 1977 Cladis et al [9] found that a polar mesogen viz. 8OCB at elevated pressures, shows a similar phase sequence. Later pure compounds [10-11] were found which exhibited the re-entrant nematic phase even at atmospheric pressure. Some experiments on such systems will be reported in chapters 5 and 6.
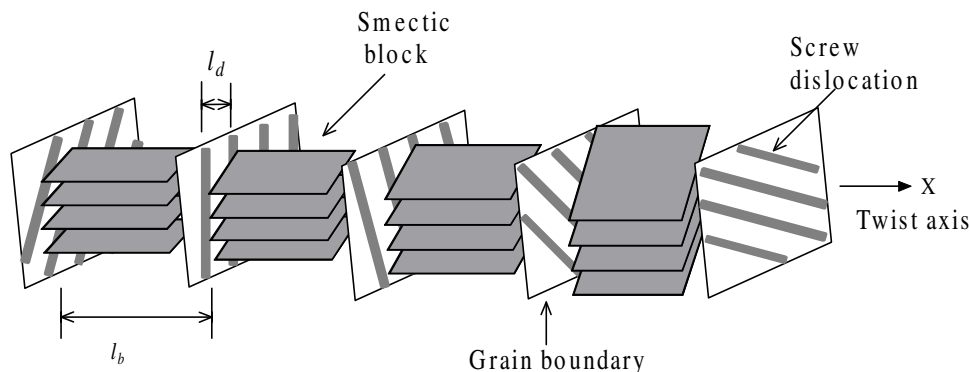
1.6   Twist Grain Boundary Phases

Figure 1.10: Schematic representation of the structure of TGB$_A$ phase, where l_d is the distance between two dislocations and l_b the distance between two grain boundaries.

The twist grain boundary (TGB) phase is formed by the competing interaction between the smectic like order and chiral interaction between the molecules giving rise to a twisted structure. The TGB phase is analogous to the vortex state in a type II superconductor under a strong magnetic field. This analogy was pointed out by de Gennes [12]. The detailed structure of TGB phase was theoretically predicted by Renn and Lubensky [13]. The TGB$_A$ phase consists of a regular twisted arrangement of SmA blocks separated by grain boundaries made of arrays of screw dislocations. Goodby et al [14] reported the first observation of TGB phase in some highly chiral liquid crystals. Depending on the local smectic order, the TGB phases are classified as TGB$_A$, TGB$_C$, TGB$_C^*$ etc. A schematic representation of a TGB$_A$ phase is shown in Figure 1.10.

Pramod et al [15] in 1997 reported a new defect phase called Undulating Twist Grain Boundary (UTGB$_C^*$) phase with SmC* like block structure in a binary mixture of a chiral compound and a nonchiral compound. A schematic representation of the structure of UTGB$_C^*$ phase is shown in Figure 1.11. In addition to a helical structure within the smectic blocks, this phase is also characterised by a two-dimensional undulation of the grain boundaries orthogonal to the TGB twist axis. This structure has twist deformation along all the three mutually orthogonal directions. High pressure studies on this system will be described in chapter 5.
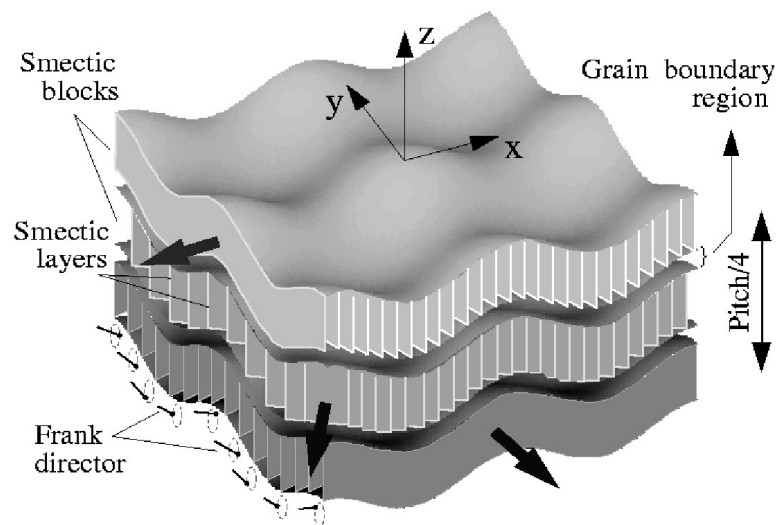
Figure 1.11: Schematic representation of the structure of UTGB$_C^*$ phase. The smectic layer normals (large arrows) rotate from block to block. Within each block the Frank director precesses along the layer normal direction as represented by the nails (from reference 15).

1.7   Cell Preparation

1.71   Alignment of Liquid Crystals

In an unaligned sample, the director $\hat{n}$ varies from point to point. For measuring the anisotropic physical properties like birefringence $\Delta\mu$ one needs a monodomain sample of the liquid crystal in which director $\hat{n}$ is uniform throughout the sample. Generally either a planar or homeotropic alignment is used. A planar or homogeneous sample is one in which the director is unidirectional and is parallel to the enclosing surfaces. On the other hand, in a homeotropically aligned sample the director is perpendicular to the enclosing surfaces. A review on different alignment techniques is given by Cognard [16]. A schematic representation of both the orienting geometries is given in Figure 1.12.

- **Homogeneous or Planar Alignment**

The sample cell is prepared using Indium Tin Oxide (ITO) coated glass plates, which serve as transparent electrodes. The ITO plate is coated with polyimide and cured at 280 ^{0}C for about an hour. And then the plate is rubbed unidirectionally using

a soft tissue. The cell is prepared such that the rubbing directions of both the plates are parallel to each other giving a planar alignment.
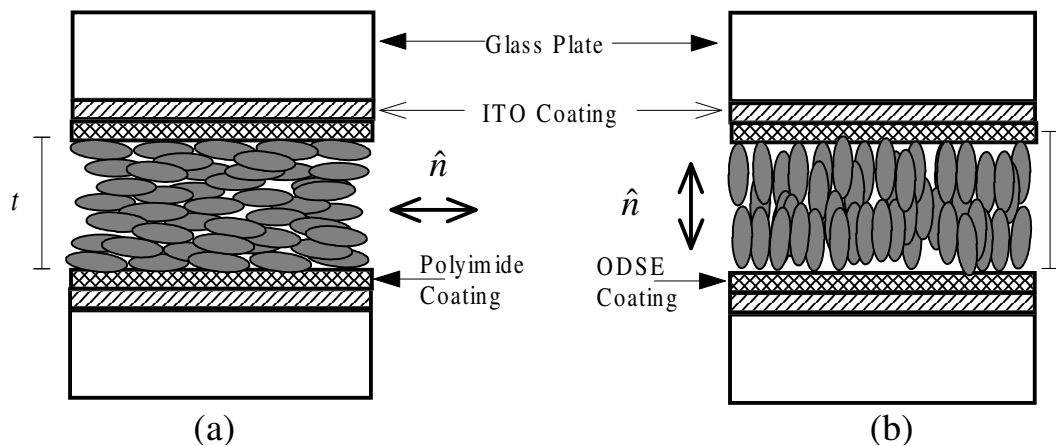

Figure 1.12: Schematic diagram of the (a) homogeneous and (b) homeotropic alignment of the molecules, where $\hat{n}$ represents the director.

• **Homeotropic Alignment**

For homeotropic alignment of the molecules the ITO coated glass plate is coated with a surfactant like octadecyl triethoxy silane (ODSE) and cured at 150 ^{0}C for about an hour. ODSE is a long chained molecule which is amphiphilic in nature having a polar group and an aliphatic chain. The polar end group is attracted to the surface of the glass plate and the long aliphatic chain interacts with the alkyl chain of the liquid crystal molecules thus giving rise to perpendicular orientation of the director with respect to the glass plate.

1.72 Preparation of Liquid Crystal Cell

The glass plates which are pretreated for the required alignment are placed one above the other such that pretreated surfaces face each other. A little gap is left at both the ends so that in required cases electrical connections to apply the electric field can be made (Figure 1.13). The sides are sealed using a special kind of glue viz. epoxy glue meant for liquid crystal displays (LCD) which does not react with liquid crystals. The thickness of the cell is fixed using either mylar spacers or glass beads. The sealed cell is cured for about an hour at 150 ^{0}C.
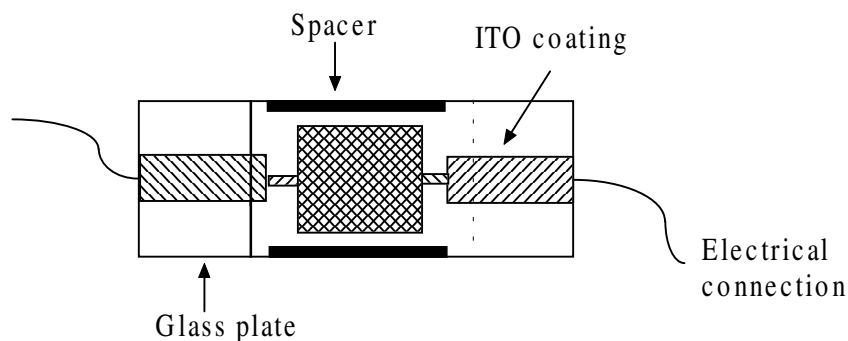
Figure 1.13: Schematic representation of a liquid crystal sample cell (top view). The central rectangular region is the effective electrode area.

1.73 **Measurement of Cell Thickness**

The thickness of an empty cell is measured using an interferometric technique. The schematic diagram of the setup is shown in Figure 1.14. The miniature fiber optic spectrometer (Ocean Optics) is controlled through a computer. The illuminating and read fibers are made of optical fibers. The reflection probe consists of 7 optical fibers, out of which the *central* fiber is the read fiber and the surrounding 6 fibers are the illuminating fibers. The light incident on the cell through the 6 illuminating fibers will get reflected back from the cell to the read fiber of the reflection probe and the signal is sensed through the spectrometer (Ocean Optics model S 2000) which in turn will display the interference pattern on the screen of the computer monitor. The light reflected by the two internal glass surfaces interfere to produce the interference pattern. We use this interferometer to make precise measurements of cell thickness at various positions.
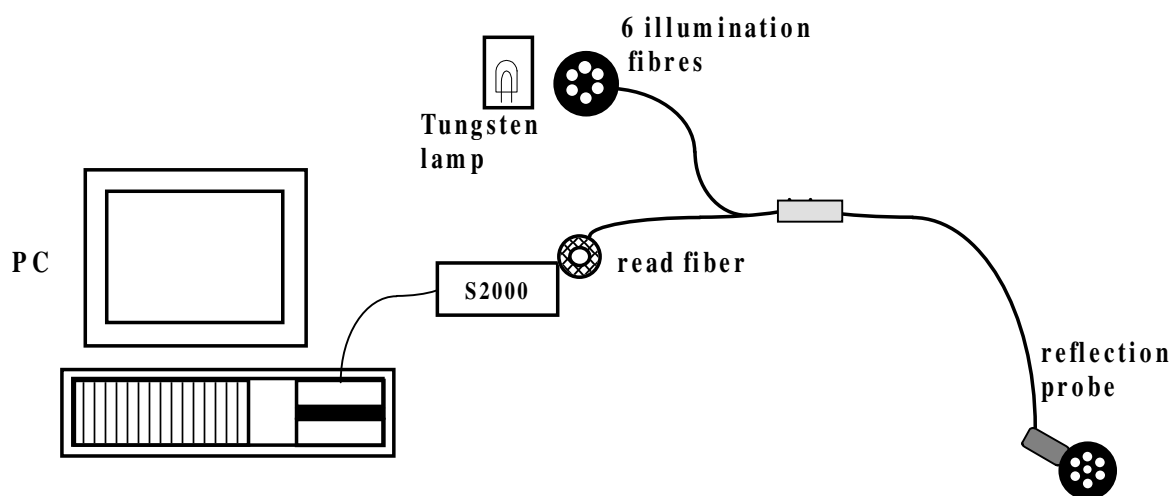

Figure 1.14: Schematic diagram of the setup used for measuring the thickness of the empty cell.

The interference pattern consists of maxima and minima corresponding to constructive and destructive interference. The thickness of the cell 't' is calculated by measuring the air gap between the two glass plates of the cell using the formula given below.

$$t = \frac{(m-n)}{2} \frac{(\lambda_m \times \lambda_n)}{(\lambda_m - \lambda_n)} \qquad 1.7$$

where λ_m and λ_n are wavelengths corresponding to m^{th} and n^{th} minima or maxima.

1.8   Theoretical Background

1.81   Landau Theory of Phase Transitions

The Landau theory is a phenomenological theory originally developed for describing second order phase transitions. The order parameter increases continuously across the transition point, and close to the transition point the order parameter is very small. Landau, speculated that near the second order phase transition the free energy density F can be expanded in powers of order parameter S which characterises the lower symmetry phase [17].

$$F(P,T,S) = F_0 + \frac{A}{2} S^2 + \frac{B}{3} S^3 + \frac{C}{4} S^4 \qquad 1.8$$

where F_0 is the free energy density when $S = 0$. The absence of the linear term in S (equation 1.8) ensures the stability of the higher temperature phase. In the lower symmetric phase occurring at low temperatures ($S \neq 0$), the minimum in F is ensured by assuming $A < 0$ and in the higher symmetric phase ($S = 0$) the minimum in F is ensured by assuming $A > 0$. Landau assumed that $A = \alpha(T - T^*)$ and T^* is the second order transition temperature and α, B, C are constants which do not depend on temperature. For a system in which F is independent of the sign of order parameter S (e.g. ferromagnetic system) i.e. $F(S) = F(-S)$ and the cubic and the higher odd powers of S are not allowed. Thus $B = 0$, and with $C > 0$ a second order phase transition takes place between the states $S = 0$ and $S \neq 0$ at the temperature $T = T^*$. The free energy density is

$$F(P,T,S) = F_0 + \frac{\alpha}{2}(T - T^*) S^2 + \frac{C}{4} S^4 \qquad 1.9$$

The equilibrium value of the order parameter is found by using $F' = 0$ and $F'' > 0$ (each prime denotes a differentiation with respect to S).

$$S = \sqrt{\frac{\alpha(T^* - T)}{C}}$$ 1.10

The order parameter profile is continuous with temperature for the second order phase transition.

The above model has been extended to describe *weakly first order* phase transitions. One way of obtaining a first order phase transition is to have a third order term. If the symmetry of the system prevents the presence of a third order term i.e. $B = 0$, then a first order transition can be obtained by having $C < 0$. In that case a stabilising sixth order term with co-efficient $E > 0$ is required.

1.82 Landau-de Gennes Theory for the Nematic to Isotropic (N-I) Phase Transition

The Landau theory for the nematic isotropic phase transition has been reviewed in detail by Gramsbergen et al [18]. The orientational order parameter of nematic liquid crystal is defined as $S = \frac{1}{2}\langle 3\cos^2 \theta - 1 \rangle$ where θ is the angle between the long axes of the molecules and the director $\hat{n}$. The order parameter S can take any value between 1 to –1/2. The two extreme values of S describe two distinct physical situations of the system. The first one corresponds to a situation with $\theta = 0$ and the second one with $\theta = \pi/2$. The positive and negative values of S arise in general from different distribution functions, and hence $F(S) \neq F(-S)$. Thus the free energy density of the nematic phase must include the cubic power of S and is given by

$$F(P,T,S) = F_0 + \frac{\alpha}{2}(T - T^*)\, S^2 - \frac{B}{3}S^3 + \frac{C}{4}S^4$$ 1.11

where T^* is now the hypothetical second order transition temperature below which the isotropic phase cannot be supercooled. The negative sign of the cubic term has been assumed to get a lower free energy for $S > 0$.

Minimising equation 1.11 with respect to S we get three solutions

$$S = 0$$

and
$$S_{\pm} = \frac{B}{2C} \pm \frac{\sqrt{B^2 - 4C\alpha(T - T^*)}}{2C}$$
1.12

$S = 0$ corresponds to the isotropic phase. S_- corresponds to a maximum in the free energy density and hence not an acceptable solution. S_+ corresponds to a minimum in the free energy and hence is a stable solution characterising the nematic phase. The nematic-isotropic transition temperature T_{NI} can be calculated by equating the free energy density in the nematic phase to that of the isotropic phase i.e. $F(p, T, S) = F_0$, which gives

$$\frac{\alpha}{2}(T_{NI} - T^*) S_{NI}^2 - \frac{B}{3} S_{NI}^3 + \frac{C}{4} S_{NI}^4 = 0$$
1.13

where S_{NI} is the order parameter at the transition point. The equilibrium condition yields

$$\alpha(T - T^*) S - BS^2 + CS^3 = 0$$
1.14

Equation 1.14 is also valid at T_{NI}, where $S = S_{NI}$.

From equations (1.13) and (1.14) at $T = T_{NI}$, we get

$$S_{NI} = \frac{2B}{3C}$$
1.15

and

$$T_{NI} = T^* + \frac{2B^2}{9\alpha C}$$
1.16

Equation 1.14 has a real solution only when $B^2 - 4C\alpha(T - T^*) > 0$, leading to an upper temperature limit above which the nematic phase cannot exist. This temperature T^{**} is given by

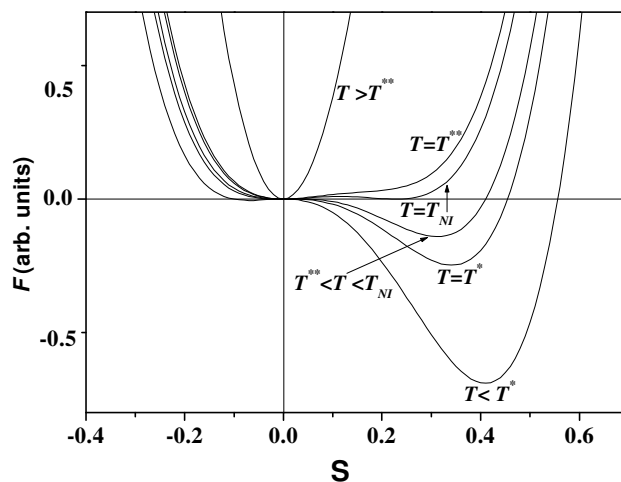$$T^{**} = \frac{B^2}{4\alpha C} + T^*$$
1.17

Figure 1.15: Variation of the free energy density as a function of order parameter S at various temperatures near the nematic-isotropic transition point.

The variations of the free energy density as functions of order parameter for various temperatures are shown in Figure 1.15. For temperatures $T > T^{**}$ there is only one minimum in the free energy curve corresponding to $S=0$, i.e. the isotropic phase. At temperature $T=T^{**}$ an inflection is observed in the free energy density curve. For $T_{NI} < T < T^{**}$ there are two minima one of which corresponds to the isotropic phase with $S=0$ and the other one corresponds to the superheated nematic phase. There are two minima of equal energy density at $T=T_{NI}$. Thus a first order phase transition takes place from $S=0$ to $S=S_{NI}$. For $T^* < T < T_{NI}$ there are again two minima, the absolute minimum corresponds to the nematic phase i.e. $S > 0$. Below temperature T^* the isotropic phase can not be supercooled. At $T=T^*$ there is only one minimum corresponding to $S > S_{NI}$ and an inflection point at $S=0$. For temperatures $T < T^*$, there is a second minimum for $S < 0$, but the corresponding energy is higher than that for $S > 0$. Thus the inclusion of non - zero third order term explains a first order phase transition observed in all nematogens. Typically the corresponding jump in the order parameter S_{NI} is ~ 0.3. However from a thermodynamical point of view NI transition is a weakly first order transition as the heat of transition ΔH and the volume change ΔV occurring at the NI transition are very small in comparison to those at a crystal melting transition.

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