Chapter 1

Introduction

Liquid crystals are states of matter having symmetries between those of crystals and liquids [1, 2, 6, 7]. They can be broadly classified as thermotropic liquid crystals and lyotropic liquid crystals. In thermotropic liquid crystals the liquid crystalline phase occurs when the temperature is varied. They consist of long rod like molecules or disc like molecules. In this thesis we will be discussing only thermotropic liquid crystals consisting of rod like molecules.

1.1 Nematic liquid crystals

The simplest liquid crystalline phase exhibited by long rod like organic molecules is the nematic phase. A schematic representation of the arrangement of the molecules in a nematic liquid crystal is shown in Fig. 1.1b. The molecules possess long range orientational order of the long axes of the molecules about some direction. A unit vector' along this axis is known as the director and is denoted by n which is apolar in character. In other words n and $-\mathbf{n}$ are physically equivalent. Hence the nematic phase is not ferroelectric [1].

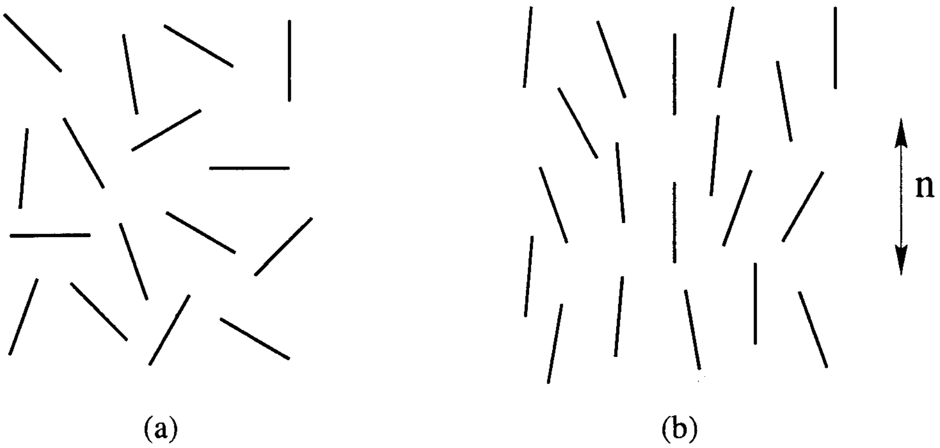


Fig. 1.1: Schematic representation of the arrangement of the molecules a) in the isotropic phase and b) in the nematic phase.

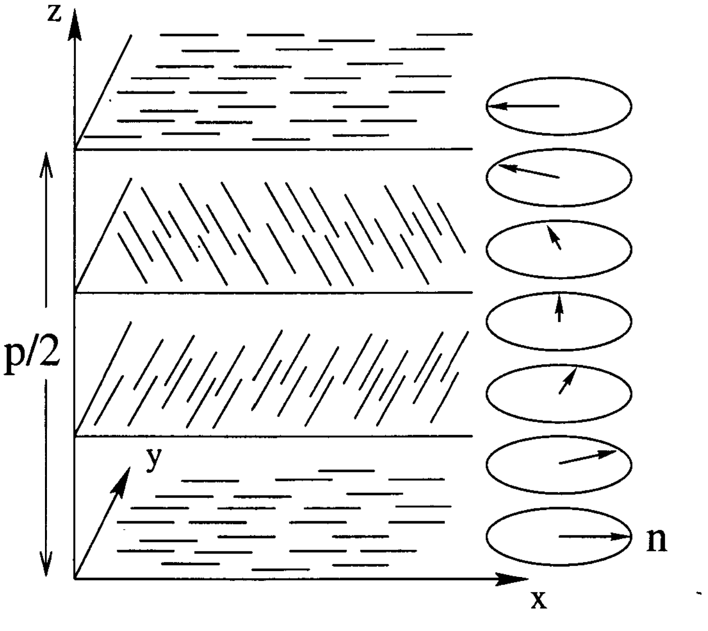


Fig. 1.2: Schematic representation of the helical structure of the apolar director n in the cholesteric phase.

1.2 Cholesteric liquid crystals

Cholesteric liquid crystals or chiral nematic liquid crystals are formed by optically active molecules. The director is no longer constant in space because of the inherent chirality of the medium and forms a helical structure as shown in Fig. *1.2.* The helical structure is described by a director field: $n_x = \cos \mathrm{a}$, $n_y = \sin \mathrm{a}, n_z = 0$. The helix axis is parallel to the z-axis with $\mathrm{a} = q_0 z + \mathrm{constant}$ where $q_0 = 2\pi/p$ and the pitch p is defined as twice the distance along the helical axis over which n turns by π. The sign of q_0 distinguishes between left-handed and right-handed helices. Due to the apolar nature of n the periodicity of the medium along the helix axis is $p/2$.

1.3 Smectic liquid crystals

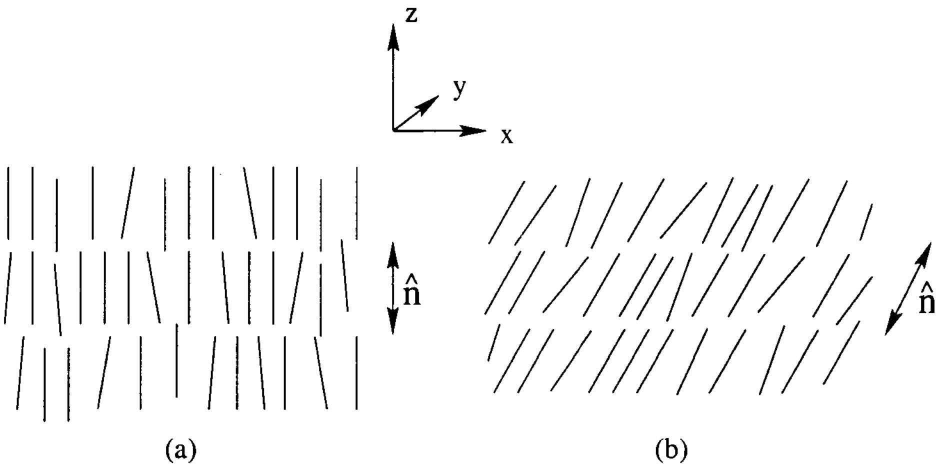
Smectic liquid crystals exhibit orientational order like the nematic liquid crystals but they possess a one dimensional quasi-long range positional order unlike nematics. The centres of molecules are, on the average, arranged in equidistant planes.

1.3.1 Smectic A liquid crystals

In the smectic A phase the molecules are arranged in layers with a thickness about the length of one molecule (see Fig. 1.3a). In each layer the molecules are random positions but are directionally ordered with their long axes on average normal to the plane of the layer. The medium has rotational symmetry about the director.

1.3.2 Smectic C liquid crystals

Smectic C liquid crystals are similar to smectic A liquid crystals except that the molecules are tilted with respect to the layer normal. Fig. 1.3b shows the corresponding packing of molecules in different layers. The tilt direction can be described



(a) (b)

Fig. 1.3: Schematic representation of the arrangement of the molecules a) in the smectic A phase and b) in the smectic C phase.

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by a C-director $\mathbf{c}$ which is the projection of $\mathbf{n}$ on the layer plane. While $\mathbf{n}$ and $-\mathbf{n}$ are still equivalent, such a symmetry operation does not hold for the C-director.

1.3.3 Smectic C* liquid crystals

The chiral smectic C* phase is formed by optically active molecules or when smectic C liquid crystals are doped with a chiral substance. They have a helical structure with the twist axis perpendicular to the layers as shown in Fig. 1.4. The chirality of the molecules removes the mirror plane from the symmetry group C_{2h} of the smectic C phase and the local point symmetry of the smectic C* layer is C_2. This lower symmetry of the smectic C* layers allows them to be transversely polarised along the C_2 axis and hence smectic C* is also referred to as a ferroelectric liquid crystal.

1.4 Twist grain boundary phase

When the smectic A phase is formed by chiral molecules, the chiral interactions favour a helical configuration. Due to the layered structure of the smectic A phase,

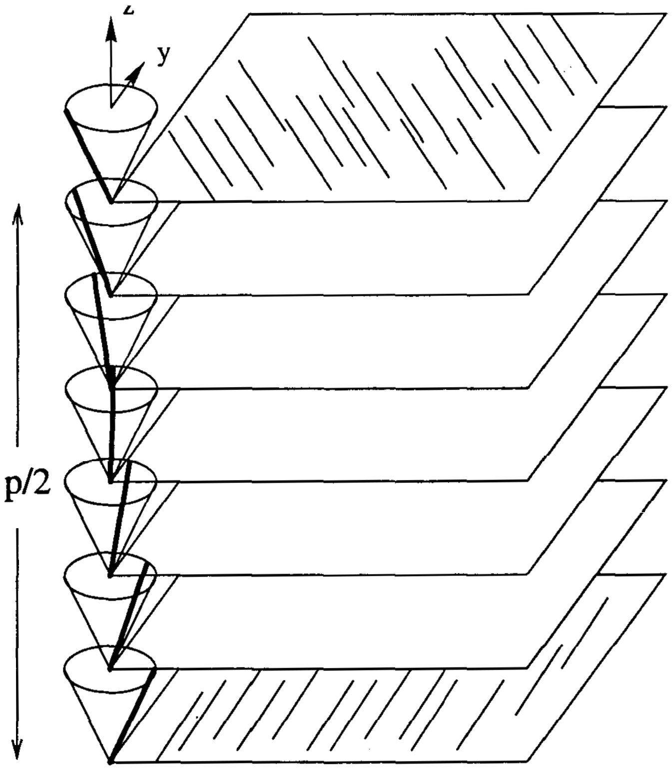

Fig. 1.4: Schematic representation of the arrangement of the molecules in the smectic C* phase.

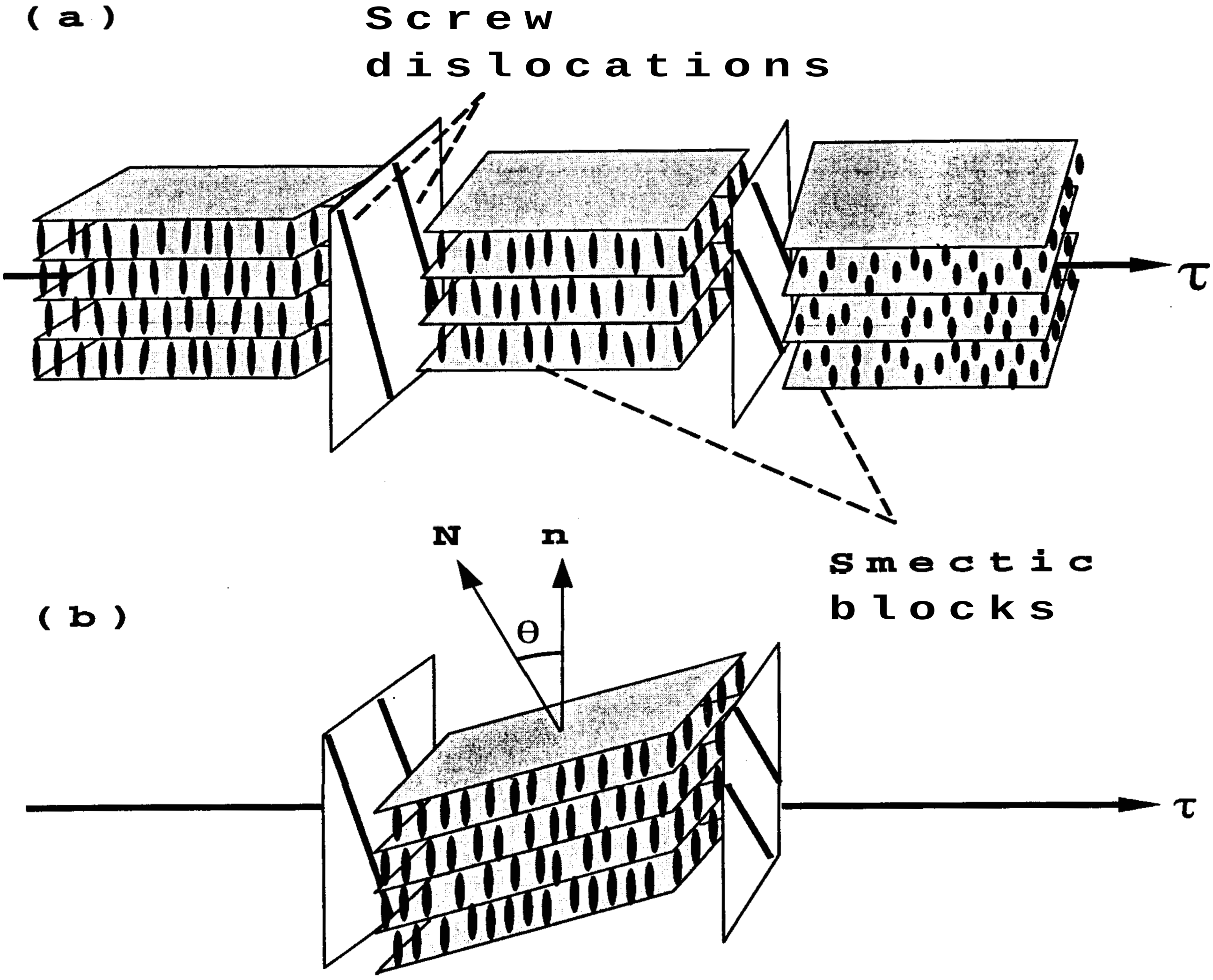

Fig. 1.5: (a) Schematic representation of the TGB$_A$ structure. (b) Schematic representation of the TGB$_C$ structure. 'N' is the layer normal, 'n' is the director and τ is the helical **axis.**

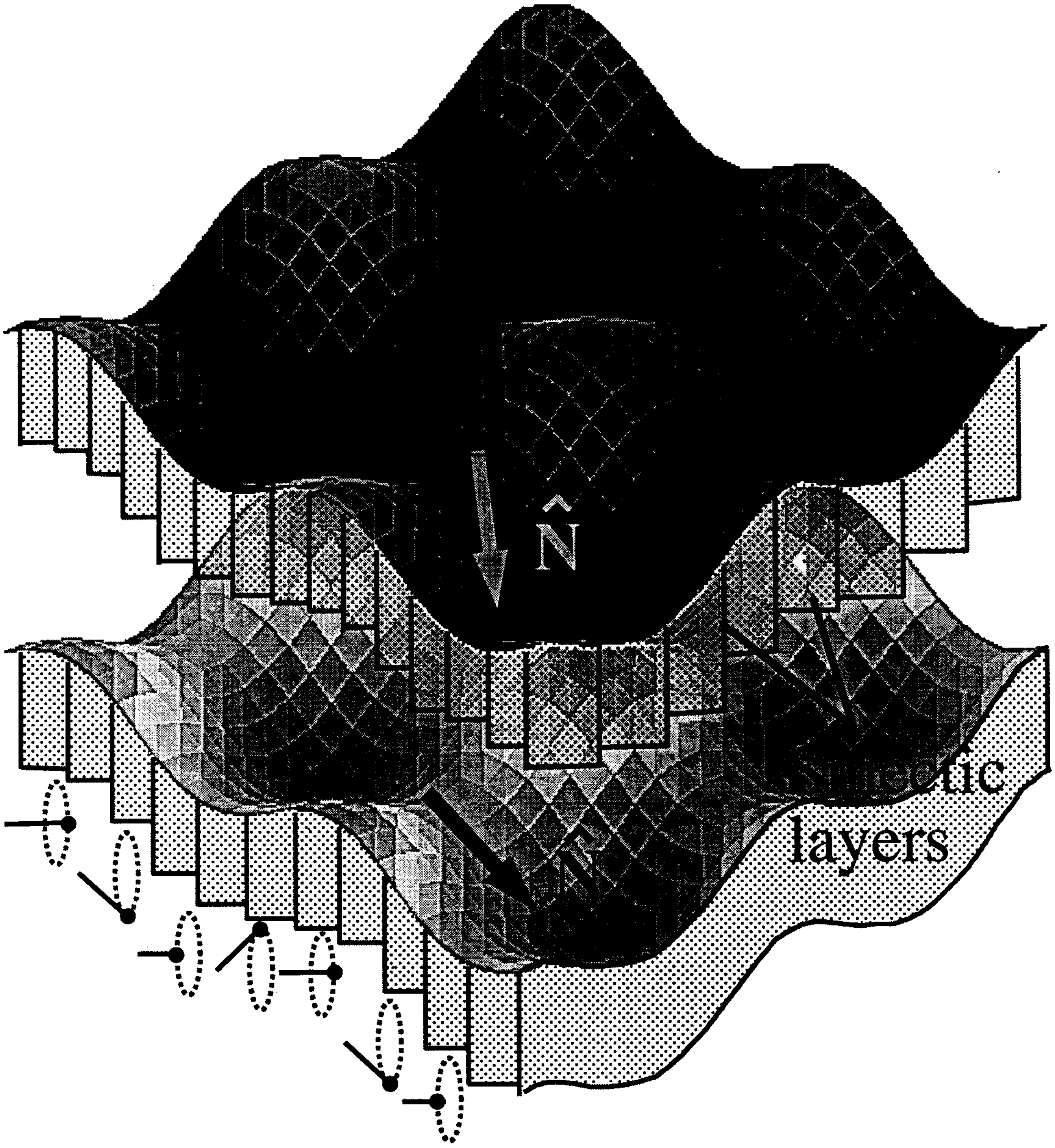

Fig. 1.6: Schematic representation of the proposed structure in the UTGB$_C$* phase (taken from Ref.[5]). The 2D-undulations in both the blocks have the same orientations of the wave vectors. The orientation of the smectic layer normal (large arrows) is different in the two neighbouring smectic C* blocks. The helicity of the director in the lower smectic C* block is shown by that of the 'nails'.

twist deformations cost too much energy as it involves changes in the layer spacing. The twist grain boundary (TGB) phase is formed by the competing interaction between the smectic like order and the chiral interaction between the molecules giving rise to a twisted structure [3].

The analogy between superconductors and smectic liquid crystals was established by deGennes [8]. The director n in smectic A liquid crystals plays the same role as the magnetic vector potential **A** in a superconductor and twist/bend deformations involving (V x n) (see equation 1.8 in the later section 1.6) as the magnetic induction $(\mathrm{B} = \mathrm{V} \times \mathbf{A})$. Both systems are described by complex order parameters, the Cooper-pair wave function in the case of superconductors and the mass-density wave normal to the layers in the case of smectic A. For superconductors, the Ginzburg parameter is defined as $\kappa = \lambda/\xi$, where λ is the magnetic field penetration depth and ξ is the superconducting coherence length for the Cooper-pair wave function. For type I superconductors $\kappa < 1/\sqrt{2}$ while for type II superconductors $\kappa > 1/\sqrt{2}$. For smectics too, one can define two important lengths, namely, the twist penetration length λ and the smectic order parameter coherence length ξ, the ratio of the two $\kappa = \lambda/\xi$ is the analogue of the Ginzburg parameter. If $\kappa < 1/\sqrt{2}$ then it is called type I smectic. If the smectic is of type II, $\kappa > 1/\sqrt{2}$. In type I smectic A liquid crystals twist deformations are expelled while type I superconductors expel magnetic lines of force. The type I smectic A resists twist/bend deformations until a critical value of the stress at which it melts into a nematic. The type I superconductors expel the field completely till a critical value of the field above which it transforms to a normal metal. In type II superconductors, beyond a critical field H_{c1}, there can be an intermediate state between the perfect superconductor and the normal metal, in which the magnetic lines of force partially penetrate as a lattice of flux vortices. When the field is increased beyond H_{c2}, where $H_{c2} > H_{c1}$, the superconductor transforms into a normal metal. For type II smectic A the twist/bend deformations can penetrate the smectic in the form of screw/edge dislocations when the stress is increased beyond a critical value. Thus, screw/edge dislocations are the liquid crystalline analogues of the magnetic flux tubes in superconductors. Unlike in superconductors where the quantised flux tubes form a triangular lattice, in smectics the screw dislocations do not form such a network. The geometry of parallel screw dislocations is not permitted for the following reasons [9]: For a circular contour of radius R around a spatially uniform lattice of parallel screw dislocations, the gradient in the displacement of the smectic layers increases with R. As R $\rightarrow \infty$, $|\nabla u| \rightarrow \infty$ and hence does not have a well defined thermodynamic limit.

An alternative arrangement was predicted by Renn and Lubensky and is referred to as the twist grain boundary phase [9]. In this phase, the smectic like blocks are stacked in a helical fashion along an axis parallel to the smectic layers. The adjacent blocks are connected by a grain boundary within which the twist of the director is confined. ,Each such grain boundary consists of an array of parallel equispaced screw dislocations. The twist grain boundary phase can be TGB_A(see Fig. 1.5 (a)) , TGB_C (see Fig. 1.5 (b)) or TGB_{C^*} depending on whether these smectic blocks are Smectic A, Smectic C and Smectic C* respectively. In the recently discovered $UTGB_{C^*}$ phase (see Fig. 1.6) [5]the tilted molecules in the smectic blocks are arranged in a helical fashion like in the Smectic C* phase . In addition these slabs exhibit a 2D undulation in the form of a square lattice. The $UTGB_{C^*}$ phase is characterised by helical'axes both along and normal to the Smectic C* layers.

1.5 Orientational order parameter of nematics

The orientational order parameter should be consistent with the apolar nature of the director and a vector order parameter is not appropriate. The order parameter is a

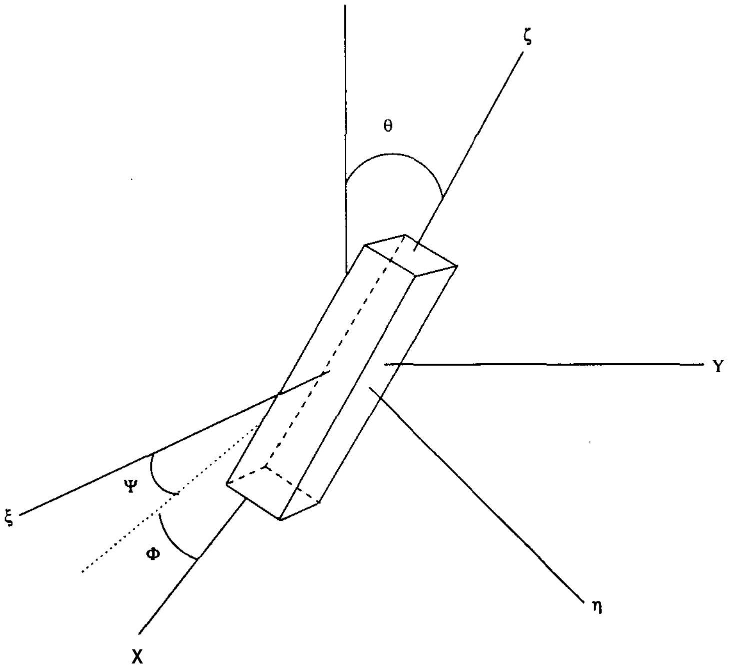

Fig. 1.7: Illustration of the Euler angles 8, ψ and ϕ

second rank symmetric traceless tensor. It should be nonzero in the nematic phase and should go to zero in the isotropic phase. For cylindrically symmetric molecules the order parameter is defined as

$$S = \frac{1}{2} < 3\cos^2\theta - 1 >, \tag{1.1}$$

where 8 is the angle between the director and the long axis of the rod like molecule and the angular brackets represent the ensemble average. However the assumption that the molecules are cylindrically symmetric is not valid in general. Hence for a molecule of arbitrary shape the generalised order parameter can be written as:

$$Q_{ij}^{\alpha\beta} = \frac{1}{2} < 3 i_\alpha j_\beta - \delta_{\alpha\beta}\delta_{ij} >, \tag{1.2}$$

where a, β=X, Y, Z refer to a laboratory fixed coordinate system. i, j=ξ, η, ζ refer to the frame linked to the molecule. i,, j_β denote the projection of the unit vectors i and j along α and β respectively. $\delta_{\alpha\beta}$ and δ_{ij} are the Kronecker deltas. The orientational state of the molecules is determined by the three Euler angles θ, ψ and ϕ (see Fig.1.7), where θ is the angle between the Z axis and the ζ axis, ψ is the angle made by the ξ axis of the biaxial molecule with the line of intersection of the $\xi\eta$ and XY planes, describing a rotation of the molecule around its long axis. ϕ is the angle between the X axis with the line of intersection of the $\xi\eta$ and XY planes, describing a rotation of the whole molecule around the director. In the uniaxial phase ϕ can take all values with equal probability. Choosing proper coordinate systems for the molecules as well as for the medium, the order parameter tensor can be written in the diagonal form. The nonzero components of this tensor using the Eulerian angles, are

$$Q_{\xi\xi} = \frac{1}{2} < 3\sin^2\theta \sin^2\psi - 1 > \tag{1.3}$$

$$Q_{\eta\eta} = \frac{1}{2} < 3\sin^2\theta \cos^2\psi - 1 > \tag{1.4}$$

$$Q_{\zeta\zeta} = \frac{1}{2} < 3\cos^2\theta - 1 > \tag{1.5}$$

The two independent order parameters x and y of a uniaxial nematic medium made up of biaxial molecules are defined as

$$\begin{aligned} x &= Q_{\zeta\zeta} & (1.6)\\ y &= Q_{\eta\eta} - Q_{\xi\xi} = \frac{3}{2} < \sin^2\theta \cos 2\psi > & (1.7)\end{aligned}$$

y=0 for cylindrically symmetric molecules.

1.6 Elasticity of nematics

The state of uniform director orientation is the configuration with the lowest free energy for a nematic. External forces can give rise to nonuniform changes in the

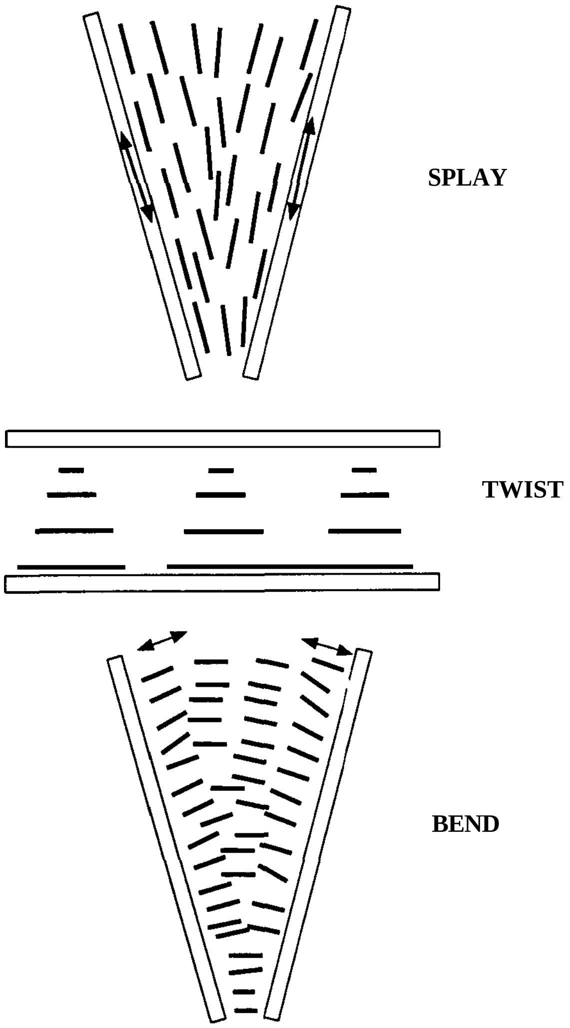

Fig. 1.8: The three curvature deformations of the nematic director field.

orientation of the director which in turn changes the free energy. This deformation produces restoring elastic torques in a nematic liquid crystal which oppose the change in the orientation of the director between neighbouring points.

The curvature deformations are three types, viz splay, twist and bend deformations which are shown in Fig. 1.8. The elastic free energy density (F_d) of a nematic liquid crystal is given by

$$F_d = \frac{1}{2}K_{11}(\nabla \cdot \mathbf{n})^2 + \frac{1}{2}K_{22}(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + \frac{1}{2}K_{33}(\mathbf{n} \times \nabla \times \mathbf{n})^2 \qquad (1.8)$$

where K_{11}, K_{22} and K_{33} are splay, twist and bend elastic constants respectively.

1.7 Anchoring

Anchoring of liquid crystals at interfaces is the orientation of the director by appropriately treated interfaces. When a mesophase is in contact with another phase an interfacial layer is formed whose symmetry is in general lower than that of the bulk medium. Interfaces are characterised by the normal vector.which is a polar vector. A liquid crystal layer near an interface is in principle, polar.

1.7.1 Easy axis

Easy axis is the direction of the director along which the surface free energy is minimised in the absence of external torques. The easy direction at the nematic solid interface is predetermined by a specific treatment of the solid surface.

1.7.2 Anchoring energy

Anchoring energy measures the strength of anchoring of the director along the easy axis. The surface free energy density becomes anisotropic due to the orientational order of nematic liquid crystals and it depends on the deviation of the director from the equilibrium orientation, i.e., the easy axis of the substrate. In general this deviation has two components, viz., in the tilt and azimuthal orientations. The anisotropic part of the surface free energy density is written as [10]

$$F_s(\theta) = \frac{1}{2} W_\theta \sin^2(\theta - \theta_o) \tag{1.9}$$

where θ and θ_o are the polar angles made by the director $\mathbf{n}$ and the easy axis with the surface normal respectively(see Fig. 1.9). W_θ is the anchoring energy for tilt orientation of the director.

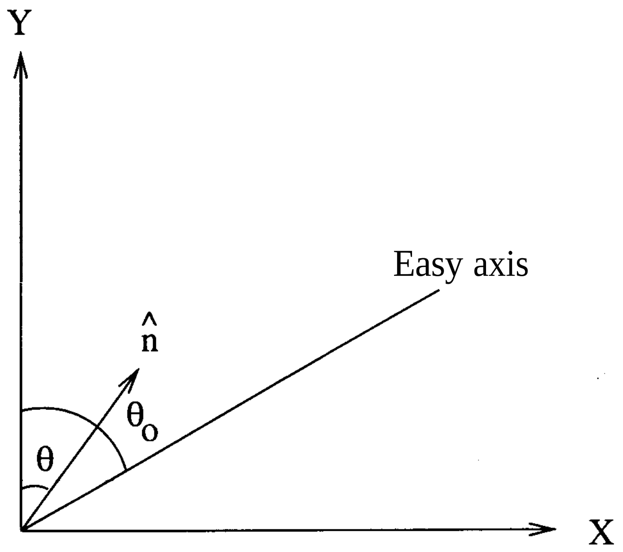

Fig. 1.9: Definition of the angles 6 and θ_o.

Similarly let ϕ be the azimuthal angle made by the director with the plane containing the normal to the substrate and the easy axis. Then the anisotropic part of the surface free energy density corresponding to azimuthal deviation is written as

$$F_s(\phi) = \frac{1}{2} W_\phi \sin^2(\phi) \tag{1.10}$$

In the theoretical analysis described in this thesis we assume a planar director field or in other words at all points n is parallel to a plane. Hence we will consider only the anchoring energy for the tilt orientation of the director.

1.8 Alignment of liquid crystals

In order to measure several physical properties of liquid crystals, samples with a well defined, uniform director alignment are required. Mainly two types of alignment are important: a) homeotropic alignment and b) homogeneous alignment. In the case of homeotropic alignment the director is aligned perpendicular to the glass plates

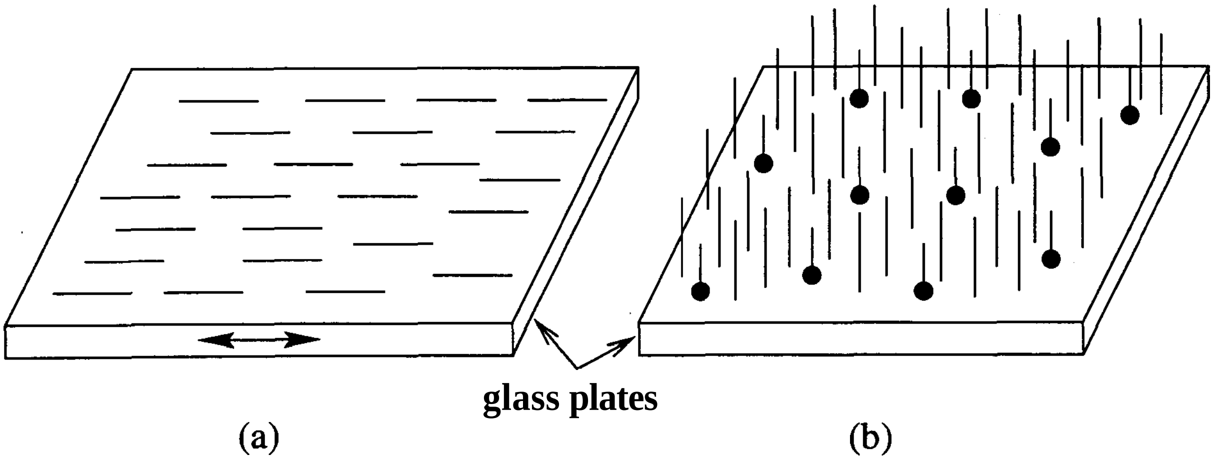

Fig. **1.10:** The director profile in the case of a) homogeneous alignment b) homeotropic alignment. The molecules with solid circles at the tip represent the ODSE molecules.

and the director makes an angle of 0^o with the surface normal. In the homogeneous case the director is aligned parallel to the glass plates or in other words the director make an angle of 90^o with the surface normal. Various treatments of the glass plates can be used to obtain either of the alignment. In all our experiments we have used glass plates coated with polyimide and rubbed for homogeneous alignment and glass plates treated with long ODSE(octadecyl triethyl silane) molecules for homeotropic alignment. The director profile in the case of homogeneous alignment and homeotropic alignment are shown in Fig. 1.10.

1.9 Flexoelectric polarisation

The nematic medium does not exhibit spontaneous polarisation due to the apolar nature of the director. In the absence of an external field the distribution of the dipoles in an undistorted nematic liquid crystal has a non-polar cylindrical symmetry. The inversion symmetry of the nematic can be broken by splay and bend distortions and a macroscopic polarisation can be induced in a nematic. This polarisation is known as flexoelectric polarisation $\mathbf{P}_f$: [4]

$$\mathbf{P}_f = e_1\mathbf{n}(\nabla \cdot \mathbf{n}) + e_3(\nabla \times \mathbf{n}) \times \mathbf{n} \tag{1.11}$$

where e_1 and e_3 are the two flexoelectric coefficients corresponding to splay and bend deformations respectively. We can see from the above equation that $\mathbf{P}_f$ is an even function of n and hence is consistent with the apolar nature of the director and $\mathbf{P}_f$ transforms like a polar vector. Both permanent dipoles associated with molecules whose shape deviates from cylindrical symmetry [4] and more generally the quadrupole moments of the molecules [11] contribute to the flexoelectric coefficients.

According to Meyer's model [4] nematics made up of polar molecules with shape asymmetry can be expected to exhibit flexoelectricity. For instance a nematic made up of polar pear shaped molecules with longitudinal dipoles when subjected to splay deformation, or a nematic made up of banana shaped molecules with transverse dipoles subjected to bend deformation can give rise to flexoelectric polarisation. There is no net polarisation in the undistorted state because of equal probability of opposite orientations of the dipole moments of the molecules.

Later Prost and Marcerou [11] suggested that flexoelectric polarisation can also result in nematic liquid crystals with non-polar molecules due to their quadrupolar nature. There is no net dipole density in the undistorted state because of the symmetry in the arrangement of the quadrupoles. But when there is a splay deformation, it gives rise to a net dipole density and hence to a polarisation. The quadrupolar contribution to flexoelectricity can arise in any nematic independent of the shape of the molecules. Flexoelectric effect is a universal property of nematics as all nematogenic molecules have finite quadrupole moments which is consistent with the symmetry of uniaxial phases. In the presence of an external field E the flexoelectric polarisation couples linearly with field giving rise to a free energy density

$$f^{fl} = -\mathbf{P_f} \cdot \mathbf{E} \tag{1.12}$$

1.10 Anisotropic physical properties

Nematics have anisotropic physical properties. The anisotropies in some physical properties which are relevant to the work presented in this thesis are described below.

1.10.1 Refractive index

The nematic liquid crystal is a uniaxial medium. It has two principal refractive indices, n_o and n_e. n_o is the ordinary refractive index for a light wave propagating orthogonal to n with electric vector perpendicular to n. n_e is the extraordinary refractive index for a light wave propagating normal to n with electric vector parallel to n. The birefringence is given by

$$\Delta n = n_e - n_o \tag{1.13}$$

and is positive for rod like molecules.

1.10.2 Electrical conductivity

In nematic liquid crystals impurity ions present in the sample give rise to a weak electrical conductivity of the medium. The conductivity anisotropy is given by

$$\Delta\sigma = \sigma_{||} - \sigma_{\perp}. \tag{1.14}$$

where $\sigma_{||}$ and $\sigma_{\perp}$ are the principal conductivities parallel and perpendicular to the director respectively. The current density for an applied electric field E is given by

$$\mathbf{J} = \sigma_{\perp}\mathbf{E} + \Delta\sigma(\mathbf{n} \cdot \mathbf{E})\mathbf{n}. \tag{1.15}$$

1.10.3 Dielectric constant

Dielectric studies are concerned with the response of matter to the application of an external electric field. In a material consisting of nonpolar molecules the field induces a polarisation, whereas in materials having polar molecules with permanent dipole moments, in addition to the induced polarisation, an orientational polarisation occurs due to the tendency of the permanent dipole moments to orient parallel to the field. The dielectric anisotropy $\Delta\epsilon$ is given by

$$\Delta\epsilon = \epsilon_{||} - \epsilon_{\perp} \tag{1.16}$$

where $\epsilon_{||}$ and $\epsilon_{\perp}$ are the principal dielectric constants parallel and perpendicular to the director respectively. For nematic liquid crystals consisting of polar molecules with strong dipoles along their long axes, $\Delta\epsilon$ usually has values between 10 to 20. The dielectric displacement D induced in a nematic liquid crystal by an electric field E is given by

$$\mathbf{D} = \epsilon_{\perp}\mathbf{E} + \Delta\epsilon(\mathbf{n}\cdot\mathbf{E})\mathbf{n}. \tag{1.17}$$

The dielectric energy density of a nematic is given by [1]

$$f^{\epsilon} = \frac{\epsilon_{\perp}E^2}{8\pi} - \frac{\Delta\epsilon(\mathbf{n}\cdot\mathbf{E})^2}{8\pi} \tag{1.18}$$

1.11 Dielectric relaxation

The dielectric permittivity of a liquid crystal becomes a dynamic permittivity when the dipoles undergo a reorientation process under the action of an AC field. This reorientation process takes a finite time interval. After the field is removed, orientation polarisation decays exponentially, with a characteristic time τ known as the relaxation time. At relatively high frequencies($> \tau^{-1}$) the orientation polarisation cannot follow the applied field. The difference in relaxation behaviour of $\epsilon_{||}$ and $\epsilon_{\perp}$

can provide information on the dynamic behaviour of the molecules in the liquid crystalline phase. The relaxation of $\epsilon_\perp$ corresponds to the reorientation about the long molecular axis and is independent of nematic order. Thus the relaxation process of $\epsilon_\perp$ is not influenced by the nematic potential. The relaxation of $\epsilon_{||}$ corresponds to the molecular reorientations about the short molecular axis. This relaxation process is effected by the nematic potential. Hence the relaxation of $\epsilon_{||}$ occurs at a much lower frequency (in the MHz region or even in the KHz region) than that of $\epsilon_\perp$ (in the GHz region).

1.12 Cell thickness measurement

The thickness of the cell is measured using channel spectrum. An optical interference technique is used in the channel spectrum. The white light reflected normally from the two surfaces bounding the air gap corresponding to the cell thickness is made to fall on a constant deviation spectroscope (Adam and Hilger Ltd.). A spectrum with alternate dark and bright fringes is seen due to interference of light reflected from the two surfaces of the cell forming the air film. The cell thickness is calculated using the expression

$$d = \frac{\lambda_m \times \lambda_n}{\lambda_m - \lambda_n} \times \frac{n - m}{2} \tag{1.19}$$

where λ_m and λ_n are the wavelengths corresponding to the m^{th} and n^{th} dark fringes respectively.