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Chapter 1

1.1 Liquid Crystals

During the process of melting, some organic compounds pass through one or more turbid and fluid phases, before they transform to a clear isotropic liquid. This was first observed by Reinitzer in 1888. These intermediate phases possess liquid like properties such as viscosity and surface tension. At the same time, they exhibit many anisotropic properties like optical birefringence, anisotropy in conductivity, dielectric and diamagnetic susceptibilities. As their physical properties are intermediate between those of crystals and liquids, such phases are called liquid crystals or mesophases. The mesomorphism occurs in compounds made of molecules with shape *anisotropy*, which may be like rods, discs and bent-cores. In liquid crystals the anisotropic molecules exhibit long range orientational order. In some of the phases one or two dimensional positional order of centers of mass of the molecules are also observed.

There are two classes of liquid crystals, viz. thermotropic and lyotropic. In thermotropic liquid crystals the mesomorphic behaviour is manifested as a function of temperature. Lyotropic liquid crystals are found when amphiphilic molecules are dissolved in a solvent like water and form molecular assemblies which also exhibit mesophases. This thesis deals with the study of several physical properties of some thermotropic liquid crystals made of rod-like and bent-core molecules.

Classification of Thermotropic Liquid Crystals

Depending on the shape anisotropy of the molecule, thermotropic liquid crystals are classified into three categories. (i) **Calamitic**, (ii) **Discotic** and (iii) **Banana** liquid crystals composed of rod-like, disc-like and bent-core molecules, respectively.

1.2 Liquid Crystals Made of Rod-shaped Molecules

1.2.1 Nematic Liquid Crystals

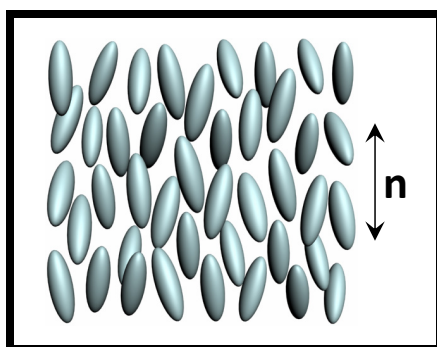


FIGURE 1.1: Schematic diagram of the molecular distribution in the nematic phase. The arrow represents the direction of average orientation of the long axes of the rod-like molecules and \mathbf{n} is the director.

The nematic (N) phase is the simplest known phase among all the liquid crystalline phases. The distribution of the centers of the mass of the molecules in the medium is liquid like. 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 have cylindrical symmetry i.e. *uniaxial*. The long axes of the molecules are on an average oriented about a specific direction, which is denoted by a unit vector \mathbf{n} , called the **director** as shown in Fig 1.1. The nematic director \mathbf{n} is a dimensionless *apolar* vector[1] i.e., \mathbf{n} and $-\mathbf{n}$ are indistinguishable.

1.2.2 Smectic Liquid Crystals

The smectic phase is characterized by a one dimensional translational order which arises from a layered arrangement of the molecules. In addition to the orientational order there is one dimensional density modulation parallel to the layer normal. Within the layers the centers of mass of the molecules are random i.e., liquid like. The *one dimensional* periodicity along the layer normal gives rise to large thermal fluctuations of the layers [1]. The periodic structure is described by a sinusoidal density wave given by,

$$\rho = \rho_0 [1 + \text{Re}\{|\psi|e^{i(q_0z+\phi)}\}] \quad (1.1)$$

where z is along the layer normal, ρ_0 is the average density, $|\psi|$ is the amplitude of the density wave, $q_0(= 2\pi/d)$ is the wave vector, ϕ is an arbitrary phase and d is the layer thickness. Depending upon the molecular orientation in the layer, smectics can be classified in the following categories:

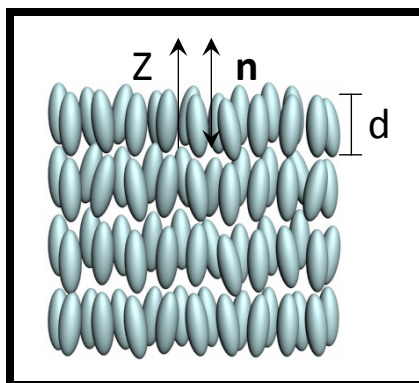


FIGURE 1.2: Schematic diagram of the molecular arrangement in the layers of the smectic-A phase. The director \mathbf{n} is parallel to the layer normal Z .

1.2.3 Smectic-A (SmA) Liquid Crystals

In the smectic-A phase the long axes of the molecules are parallel to the layer normal with their centers of gravity irregularly spaced like in a liquid, within the layer. The interlayer attractions are relatively weak and the layers can slide over one another relatively easily and each layer behaves as a 2 dimensional liquid[2]. Hence this phase has fluid properties, though it is much more viscous than nematic. The medium has uniaxial symmetry. If the molecules are symmetric and non-polar, in the smectic-A phase the layer spacing (d) is approximately equal to the molecular length (l). If the molecules have a strong longitudinal dipole moment there will be near-neighbour anti-parallel correlations and this can change the structure. This will be described in Chapter 3 and Chapter 6.

1.2.4 Reentrant Liquid Crystalline Phases

The symmetry of a liquid crystalline phase which occurs at a lower temperature is also expected to be lowered: For example, the SmA phase has a lower symmetry than the nematic phase and most of the liquid crystals follow the normal (Isotropic (I) – N – SmA – Crystal) phase sequence as the temperature is lowered. In 1975 Cladis[3] first observed that in a certain mixture the nematic phase re-appears below the smectic-A phase, with the following phase sequence: I – N – SmA – 2nd N – Crystal. The lower temperature nematic has been named as the **reentrant** nematic phase (N_r). Compounds whose molecules have strongly polar cyano or nitro end groups exhibit the re-entrant nematic phase. Cladis *et al.* also found N_r phase in a pure compound, *viz.* 8OCB at elevated pressures[4]. Later pure compounds were found which exhibited the N_r phase at atmospheric pressure[5, 6]. We will present some physical measurements on some systems consisting of dimeric compounds which exhibit the reentrant nematic phase. This will be described in Chapter 6.

1.2.5 Smectic-C (SmC) Liquid Crystals

In the Smectic-C phase the molecules take random positions within the layers as in SmA, but have a tilt angle with respect to the layer normal. The structure has *biaxial* symmetry. The *tilt* (polar) angle θ reduces the layer thickness. The azimuthal angle ϕ [see Figure 1.3] does not affect the layer thickness. So at any temperature, the amplitudes of the θ fluctuations of the

director are small compared with those of the ϕ fluctuations. Because of this and the anisotropic polarizability, SmC becomes optically biaxial[2]. In SmC the tilt plane is a plane of reflection symmetry [see Figure 1.3].

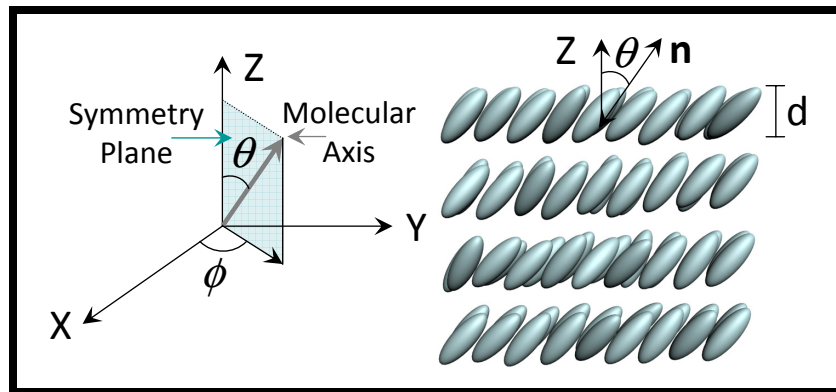


FIGURE 1.3: Schematic diagram of the molecular arrangement in the layers in the smectic-C phase. The director \mathbf{n} is tilted with respect to the layer normal.

1.3 Liquid Crystals Made of Disc-Shaped Molecules

In 1977 Chandrasekhar *et al.*[7] discovered a new class of liquid crystals in which disc-like molecules are stacked one above the other to form liquid columns. Further these columns arrange in hexagonal and other two dimensional lattices to exhibit new types of mesophases (Figure 1.4). The disc like molecules can also arrange to form a nematic phase (Discotic-Nematic N_D phase) which exhibits a pure orientational order.

1.4 Liquid Crystals Made of Bent-Core Molecules

Vorlander[8] first synthesized a compound made of bent-core (BC) molecules. Such molecules were termed “*Bad Rods*” and the liquid crystals were not characterized. In 1996 Niori *et al.* [9] reported a breakthrough ferroelectric switching behaviour in a compound composed of achiral bent-core molecules. The bent-core molecules are strongly polar and biaxial in shape and thus strongly deviate from cylindrical symmetry. Liquid crystals exhibited by bent-core molecules also

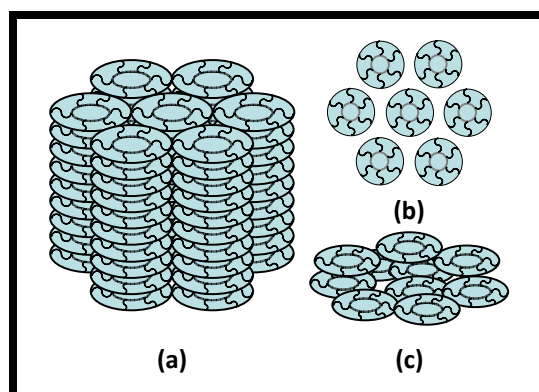


FIGURE 1.4: Schematic diagram of the molecular arrangement in discotic LCs (a) side view and (b) top view of the Columnar phase and (c) nematic phase.

show nematic, lamellar and columnar phases, and the phases are somewhat different from the ones exhibited by rod-like and disc-like molecules. Compounds made of bent-core molecules are now known to exhibit more than 10 different types of liquid crystalline phases which are designated as B_1, B_2, \dots . The letter B stands for banana or bent-core or bow shaped molecules, and the suffix number indicates the chronological order of discovery[10] of the different B phases. We will describe a few interesting B phases.

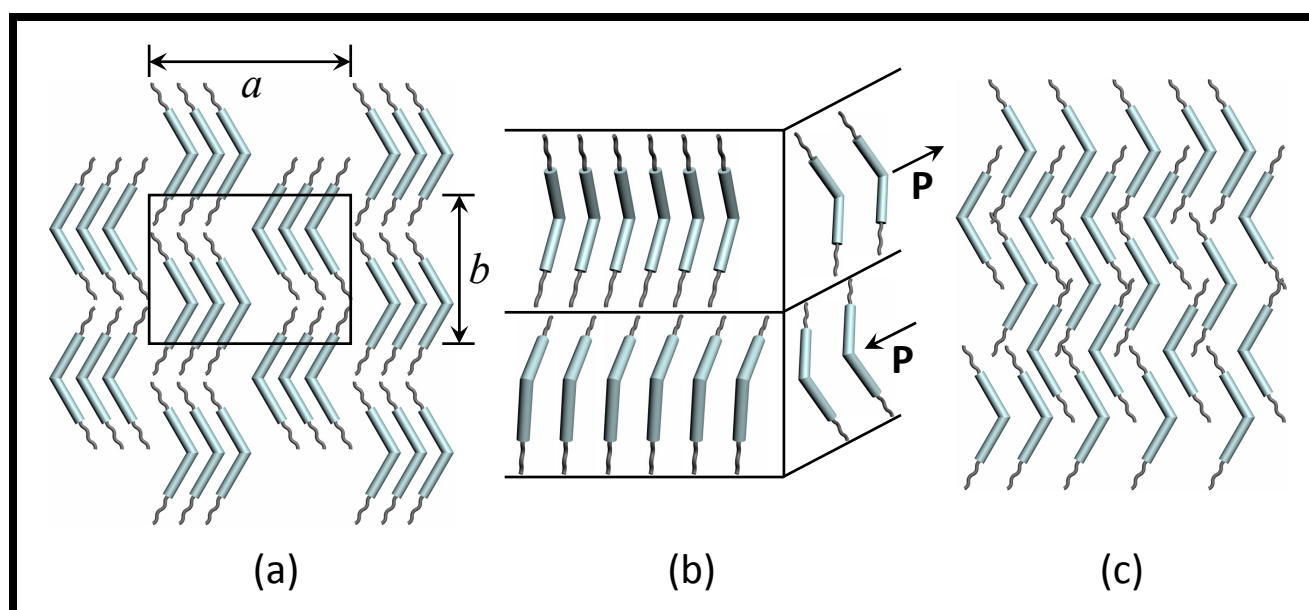


FIGURE 1.5: Schematic diagram of three B phases. (a) B_1 phase, (b) B_2 and (c) B_6 phase

1.4.1 B_1 , B_2 and B_6 Phases

B_1 : In this phase the bent-core molecules are arranged in a *2D rectangular columnar* structure [see Figure 1.5(a)]. a and b are the two lattice parameters. These columns are polarized and the polarization is generally perpendicular to the column axis but can also be parallel. Anti-ferroelectric order is observed between neighbouring columns. Aromatic cores and alkyl chains of the molecules overlap only near column boundaries. The molecules generally do not switch under an electric field.

B_2 : If the alkyl chain is long, the liquid crystal has a *layered* structure. The molecules cannot rotate (due to packing constraints) about the long axes and this gives rise to *layer polarization*. The intermolecular dipolar interaction is on an average repulsive and this can be reduced by a *tilting* about the *arrow* axes, as in the case of SmC phase [see Figure 1.5(b)] . The layer has no mirror planes and becomes *chiral* even though the molecules are *achiral*. As the symmetry is broken spontaneously, structures of opposite chirality are equally probable[11].

B_6 : In this phase the molecules form an *intercalated fluid lamellar* (smectic) structure with layer spacing equal to half the length of the molecules with short chains. Cores and chains overlap significantly [see Figure 1.5(c)]. A weak transverse anti-ferroelectric order is observed. The molecules do not switch under an electric field.

1.4.2 Biaxial Smectic-A Phase

In the orthogonal biaxial smectic-A phase the molecules are not tilted as in SmC, nevertheless there are two transverse directions in which the properties are different. This phase was first seen in mixtures of a polymer with a lateral naphthalene group in the side chain[12]. In this thesis, we are interested only in the biaxial smectic-A phase exhibited by low molecular weight liquid crystals. This was discovered in some mixtures of bent-core and rod-like molecules[13, 14]. The rod-like molecules themselves exhibit the SmA phase and the arrangement of the bent-core molecules in the SmA phase gives rise to a biaxial smectic-A phase. Detailed studies in this phase have shown that the *arrow* axes of the BC molecules are aligned along the layer normal (see Figure 1.6). Our

main interest will be to study these systems which at higher temperatures exhibit the nematic phase. This will be described in Chapter 3 of this thesis.

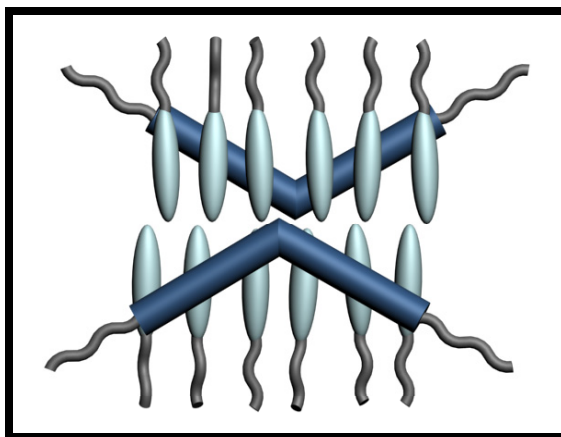


FIGURE 1.6: Side view of the biaxial SmA phase

1.5 Liquid Crystals Made of Dimeric Molecules

Dimeric molecules contain two conventional mesogenic groups linked via flexible spacers (Figure 1.7). The physical properties of nematic liquid crystals made of dimeric molecules are expected to be different from those made of monomers. We will present some studies on such compounds in Chapter 6.

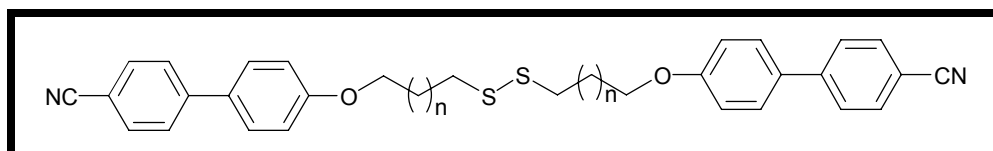


FIGURE 1.7: Molecular structure of a dimeric molecule

1.6 Properties of Nematic Liquid Crystals

1.6.1 Orientational Order Parameter

When some symmetry is broken one needs to introduce a variable called order parameter to describe the state of the system. An order parameter is a measure of the degree of order in a system; the minimum value is 0 for total disorder and 1 for complete order. The nematic phase is characterized by an average orientational order of the long axes of the molecules about a specific axis called the **director**. In order to define a nematic order parameter we use the following procedure[15]. Let us make the simplifying assumption that the molecules are rigid rods. To define the local orientation of the long axes of the molecules at a point $\vec{r} = (x, y, z)$, we consider a unit vector \hat{a} along the long axis. We consider the thermal averages of the relevant tensors which are composed of \hat{a} , over a microscopic volume around the point \vec{r} . As the average $\langle \hat{a} \cdot \hat{a} \rangle$ is a constant, a scalar order parameter (tensor rank zero) is not useful. So the next choice is vector order parameter $\langle \hat{a} \rangle$. This is analogous to the magnetization of the ferromagnet. A non-zero value of $\langle \hat{a} \rangle$ violates the equivalence of \mathbf{n} and $-\mathbf{n}$, and describes the polar nematic phase which has not yet been observed. The next possible choice is a second rank tensor S , the elements of which are given by,

$$S_{\alpha\beta} = \langle a_{\alpha}a_{\beta} \rangle - \frac{1}{3}\delta_{\alpha\beta}, \quad \alpha, \beta = x, y, z \quad (1.2)$$

where xyz is a laboratory fixed coordinate system and the Kronecker delta term ensures $S_{\alpha\beta}$ is zero in the isotropic phase as $\langle a_{\alpha}^2 \rangle = 1/3$. The tensor order parameter S is symmetric and traceless and thus has in general five independent elements. By choosing a principal coordinate system this tensor can be diagonalized. If two diagonal elements are equal this describes an uniaxial phase, and a biaxial phase requires that all the three diagonal elements are different. For the uniaxial case, denoting the average direction of alignment of the molecules by the director \mathbf{n} , the most general form of the order parameter field in the nematic phase is given by,

$$S_{\alpha\beta}(\vec{r}) = S \left(n_{\alpha}(\vec{r})n_{\beta}(\vec{r}) - \frac{1}{3}\delta_{\alpha\beta} \right) \quad (1.3)$$

Where S measures the degree of alignment of the long axes of the molecules along $\mathbf{n}(\vec{r})$. In a

well aligned nematic, \mathbf{n} is independent of \vec{r} .

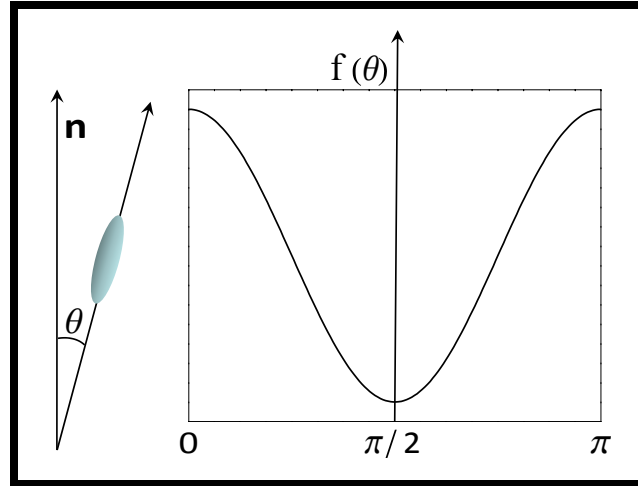


FIGURE 1.8: The distribution function $f(\theta)$ for a system of rod-like molecules in the nematic phase. $f(\theta)$ is large around $\theta = 0, \pi$ and is small for $\theta = \pi/2$.

Let the average orientation of the molecules be specified by a distribution function $f(\theta)$, where $f(\theta) 2\pi \sin \theta d\theta$ is the fraction of the molecules on a cone making an angle between θ and $\theta + d\theta$ with \mathbf{n} . A schematic representation of the distribution function of the rod-like molecules is shown in Fig 1.8. For cylindrically symmetric molecules the scalar order parameter is defined as,

$$S = \frac{3\langle \cos^2 \theta \rangle - 1}{2} \quad (1.4)$$

Where θ is the angle made by a molecule with the director. $S = 0$ and 1 correspond to isotropic and perfectly aligned phases respectively. When the temperature of a nematic liquid crystal is raised, S decreases monotonically and drops to *zero* discontinuously at the nematic-isotropic transition point (T_{NI}). The abrupt drop in the value of S at T_{NI} is a consequence of a first order transition.

The assumption that the molecule is cylindrically symmetric is not always valid for real systems. Therefore the use of a single order parameter is not adequate. Most of the molecules are lath-shaped (thin strips) and have a biaxial character. So two order parameters are necessary to

describe the *uniaxial nematic phase made of biaxial molecules*. The molecular biaxiality and the two associated order parameters will be discussed in the 4th chapter of this thesis.

1.6.2 Polarizability Anisotropy and Birefringence

The order parameter can be directly related to a few experimentally determined quantities viz, diamagnetic anisotropy, dielectric anisotropy, birefringence etc. Let us choose a space-fixed coordinate system xyz with z parallel to \mathbf{n} .

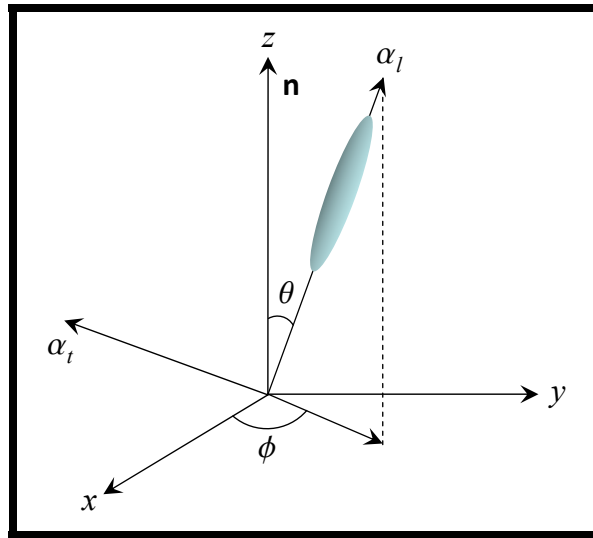


FIGURE 1.9: Schematic representation of the principal components of the polarizabilities of the molecule.

If α_l and α_t are the principal polarizabilities of the molecule along its long and short axes, the average z component of the polarizability in the nematic phase can be written as,

$$\alpha_z = \alpha_l \langle \cos^2 \theta \rangle + \alpha_t \langle \sin^2 \theta \rangle \quad (1.5)$$

Using equations (1.4) and (1.5) we get,

$$\alpha_z = \left(\bar{\alpha} + \frac{2}{3} \Delta\alpha_0 S \right) \quad (1.6)$$

It can be shown that,

$$\alpha_x = \alpha_y = \left(\bar{\alpha} - \frac{1}{3} \Delta\alpha_0 S \right) \quad (1.7)$$

where $\bar{\alpha} = (\alpha_l + 2\alpha_t)/3$, and $\Delta\alpha_0 = (\alpha_l - \alpha_t)$, is the polarizability anisotropy of a perfectly aligned medium. The absolute value of the order parameter is expressed as,

$$S = \frac{(\alpha_z - \alpha_x)}{(\alpha_l - \alpha_t)} = \frac{\Delta\alpha}{\Delta\alpha_0} \quad (1.8)$$

Refractive index is the property of a material that determines the relative speed of light in the material. In the case of uniaxial nematic liquid crystals the direction of optic axis is along the director \mathbf{n} . The uniaxial nematic phase has two principal refractive indices called n_e and n_o . n_e is the extraordinary refractive index for a light wave propagating with electric vector parallel to \mathbf{n} . n_o is the ordinary refractive index for a light wave propagating with electric vector perpendicular to \mathbf{n} . The birefringence is given by,

$$\Delta n = n_e - n_o \quad (1.9)$$

Δn can be used to calculate the approximate orientational order parameter S of nematic liquid crystals using the relation,

$$S \simeq \frac{\Delta n}{\Delta n_o} \quad (1.10)$$

where Δn_o is the birefringence of the medium in the fully aligned state. The exact relationship between the principal polarizabilities α_e and α_o and the refractive indices n_e and n_o is not known in strongly anisotropic media like liquid crystals. In the Vuks approach, the local field is considered to be isotropic and the Lorentz-Lorentz formula works fairly well for the *average* polarizability of strongly anisotropic organic molecules. The relation is given by,

$$\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} = \frac{4\pi}{3} \nu \bar{\alpha} \quad (1.11)$$

where ν is the number of molecules/cc and

$$\frac{1}{\bar{n}^2} = \frac{n_x^2 + n_y^2 + n_z^2}{3} \quad \text{and} \quad \bar{\alpha} = \frac{\alpha_x + \alpha_y + \alpha_z}{3} \quad (1.12)$$

n_x , n_y and n_z are the principal refractive indices of the crystal and α_x , α_y and α_z are the corresponding principal polarizabilities.

In the isotropic medium, the polarization \vec{P} is given by,

$$\vec{P} = \frac{n^2 - 1}{4\pi} \vec{E} \quad \text{where } \vec{E} \text{ is the applied field.}$$

$$\text{Also } \vec{P} = \alpha \nu \vec{F} = \alpha \nu \frac{n^2 + 2}{3} \vec{E}$$

where $\vec{F} = \frac{n^2 + 2}{3} \vec{E}$ is the internal field

For an anisotropic medium,

$$P_i = \frac{(n_{ik}^2 - \delta_{ik})}{4\pi} E_k \quad i, k = x, y, z$$

Assuming that the internal field is isotropic, we can write

$$P_i = \frac{\nu}{3} (\bar{n}^2 + 2) \alpha_{ik} E_k$$

From these equations we get,

$$\frac{n_i^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \nu \alpha_i \quad (1.13)$$

which is the Vuks formula. Equation (1.11) follows from Equation (1.13). From Equations (1.8), (1.11) and (1.13) we get,

$$S = \frac{\Delta\alpha}{\Delta\alpha_0} = \frac{\bar{\alpha}}{\Delta\alpha_0} \frac{n_e^2 - n_o^2}{n^2 - 1}$$

(1.14)

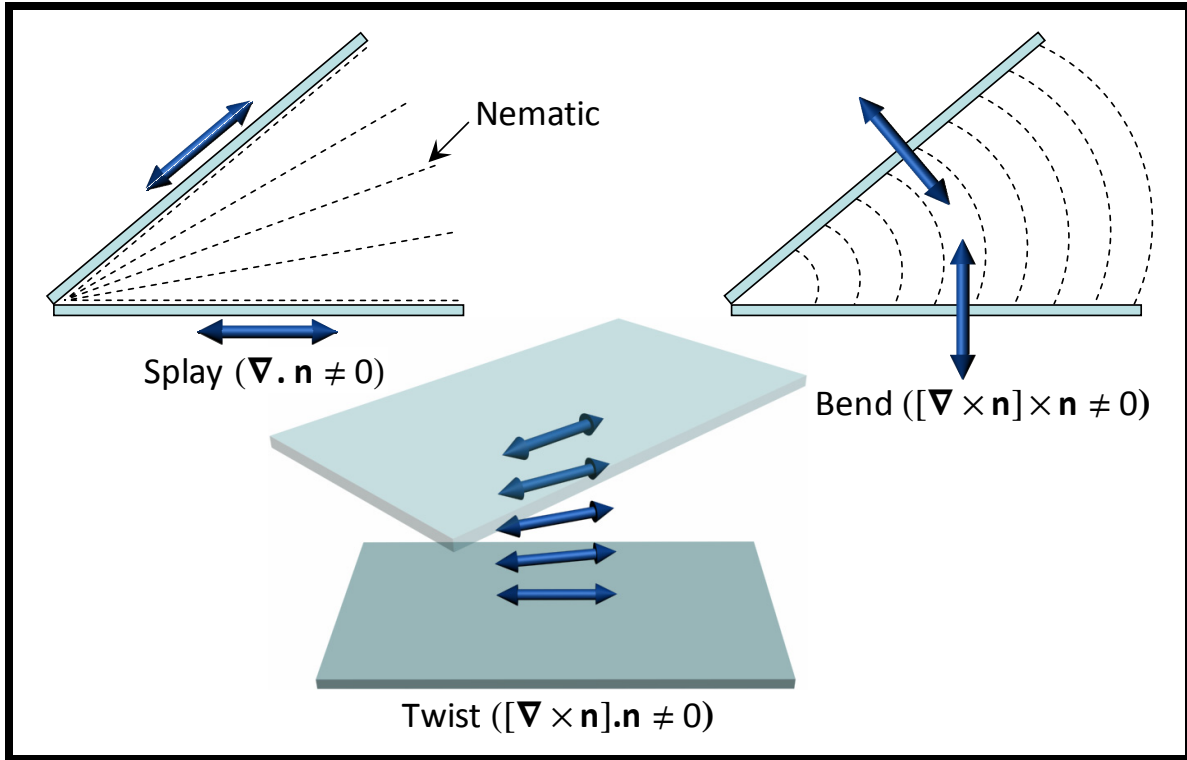


FIGURE 1.10: Schematic representation of the splay, twist and bend deformations.

1.6.3 Curvature Elasticity

A nematic liquid crystal possesses curvature elasticity. In a uniformly orientated, mono-domain sample of nematic liquid crystal, the director \mathbf{n} is in the same direction throughout the medium. When a distortion is induced in $\mathbf{n} = \mathbf{n}(\mathbf{r})$ and the derivatives of \mathbf{n} exist, an elastic restoring torque comes into play tending to restore \mathbf{n} to the undistorted state. Any deformation is a combination of three basic curvature deformations. These are called **splay**, **twist** and **bend**. The deformation free energy density is defined as,

$$F_d = \frac{1}{2} K_{11} [\nabla \cdot \mathbf{n}]^2 + \frac{1}{2} K_{22} [\mathbf{n} \cdot \nabla \times \mathbf{n}]^2 + \frac{1}{2} K_{33} [\mathbf{n} \times \nabla \times \mathbf{n}]^2 \quad (1.15)$$

where K_{11} , K_{22} and K_{33} are the splay, twist and bend elastic constants respectively. The constants are positive and usually $K_{33} > K_{11} > K_{22}$. The typical magnitudes of these constants are $\sim 10^{-12}$ Newton. A schematic representation of these three curvature deformations is shown

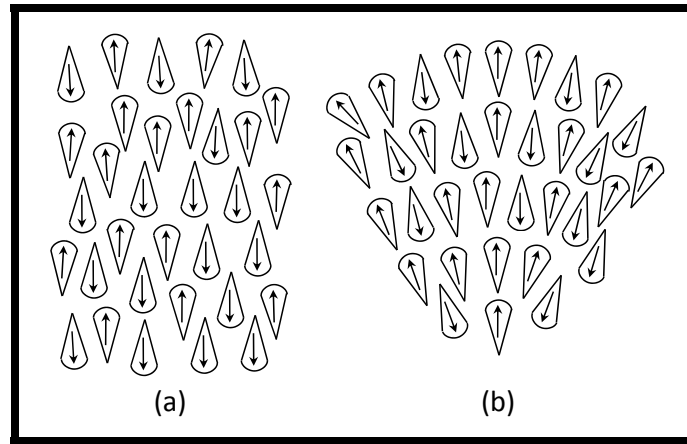


FIGURE 1.11: A nematic consisting of pear-shaped molecules with longitudinal dipole moments becomes polarized under splay deformation

in Fig 1.10.

1.6.4 Flexoelectricity

The nematic medium does not exhibit spontaneous polarization due to the **apolar** nature of the director. A macroscopic polarization can be induced in a nematic liquid crystal by splay and bend distortions of the director field. This was first shown by Meyer (1969)[16]. The flexoelectric polarization is given by,

$$\mathbf{P} = e_{11} (\nabla \cdot \mathbf{n}) \mathbf{n} + e_{33} (\nabla \times \mathbf{n}) \times \mathbf{n} \quad (1.16)$$

where e_{11} and e_{33} are the two flexoelectric coefficients corresponding to splay and bend distortions respectively. According to Meyer's model only nematics made of polar molecules with shape anisotropy can be expected to exhibit flexoelectricity. For example, a nematic consisting of pear shaped molecules with longitudinal dipole moments become polarized under splay distortion (see Figure 1.11) and a nematic made of banana shaped molecules with transverse dipole moments becomes polarized under bend distortion (see Figure 1.12). In the undistorted state, the dipole moments of the molecules are oriented with equal probability in opposite directions. They cancel each other and the net dipole density is zero.

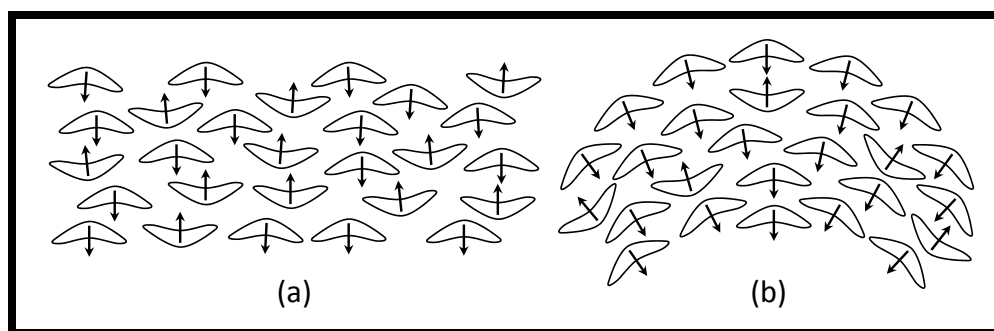


FIGURE 1.12: A nematic consisting of banana-shaped molecules with transverse dipole moments becomes polarized under bend deformation

Another microscopic model was developed by Prost and Marcerou[17] in which the flexoelectric effect arises due to quadrupolar moments of the molecules. The splay deformation develops a net dipole moment and the medium gets polarized. The quadrupolar contribution to flexoelectric effect is of the same magnitude as due to dipolar contribution. The quadrupolar contribution is independent of the shape of the molecules. Since all nematogenic molecules have finite quadrupole moments, flexoelectric effect is an universal property of nematics. Flexoelectricity will be described later in Chapter 5.

1.6.5 Dielectric Constants

Dielectric constant is a measure of the response of the given material to an external electric field. It depends on the intrinsic properties of the material like distribution of the charges in the molecules and also intermolecular interactions. The dielectric constant changes with the temperature and the frequency of the applied electric field. In a medium with polar molecules in addition to the induced polarization an orientational polarization occurs due to the tendency of the permanent dipole moments to orient parallel to the electric field. The *orientational polarization* in liquid crystals has a major contribution to the dielectric constants. But in a solid crystal the orientational polarization does not contribute significantly to the permittivity due to the fixed orientations of the molecules. In liquid crystals, ϵ_{\parallel} and ϵ_{\perp} represent the dielectric constants measured with an electric field parallel and perpendicular to the director \mathbf{n} respectively. The dielectric anisotropy is the difference of parallel and perpendicular dielectric constants i.e. $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$. The sign of $\Delta\epsilon$

depends upon the permanent dipole moments of the molecules. It is positive, if the component of the net dipole moment of the molecule along the long axis is larger than that along the transverse axis and vice versa.

Using Maier and Meier's theory the expressions of two dielectric constants[18] can be written as,

$$\epsilon_{\parallel} = 1 + 4\pi \frac{N_A \rho h F}{M} \left[\bar{\alpha} + \frac{2}{3} \Delta\alpha_0 S + \frac{F\mu^2}{3k_B T} \{1 - (1 - 3\cos^2 \beta)S\} \right] \quad (1.17)$$

$$\epsilon_{\perp} = 1 + 4\pi \frac{N_A \rho h F}{M} \left[\bar{\alpha} - \frac{1}{3} \Delta\alpha_0 S + \frac{F\mu^2}{3k_B T} \left\{ 1 + \frac{1}{2}(1 - 3\cos^2 \beta)S \right\} \right] \quad (1.18)$$

where $\Delta\alpha_0$ is the polarizability anisotropy of a perfectly oriented medium, N_A is the Avogadro number, ρ the density, M the molecular weight, $h = 3\bar{\epsilon}/(2\bar{\epsilon} + 1)$, is the cavity field factor and $F = 1/(1 - f\bar{\alpha})$ where, $f = (\bar{\epsilon} - 1)/[2\pi a^3(2\bar{\epsilon} + 1)]$ is the reaction field factor for a spherical cavity and $\bar{\alpha}$ is the average polarizability and β is the angle between permanent dipole moment μ and the long axis of the molecule. The average dielectric constant and dielectric anisotropy can be obtained from Equation (1.17) and Equation (1.18) as,

$$\bar{\epsilon} = \frac{\epsilon_{\parallel} + 2\epsilon_{\perp}}{3} = 1 + 4\pi \frac{N_A \rho h F}{M} \left[\bar{\alpha} + \frac{F\mu^2}{3k_B T} \right] \quad \text{and} \quad (1.19)$$

$$\Delta\epsilon = (\epsilon_{\parallel} - \epsilon_{\perp}) = 4\pi \frac{N_A \rho h F}{M} \left[\Delta\alpha_0 - \frac{F\mu^2}{2k_B T} (1 - 3\cos^2 \beta) \right] S \quad (1.20)$$

The relative magnitudes of the two terms within the square brackets of Equation (1.20) determine the sign of $\Delta\epsilon$. When $\beta < 54.7^\circ$, the two terms add up and the compound exhibits positive dielectric anisotropy. For $\beta \sim 54.7^\circ$, the second term vanishes and only $\Delta\alpha_0$ contributes to $\Delta\epsilon$. For $\beta > 54.7^\circ$, $\Delta\epsilon > 0$ or < 0 depending on whether the dipolar contribution is less or more than the contribution due to polarizability anisotropy. The dielectric displacement \mathbf{D} induced in a nematic liquid crystal by an electric field \mathbf{E} is given by,

$$\mathbf{D} = \epsilon_0 \epsilon_{\perp} \mathbf{E} + \epsilon_0 \Delta\epsilon (\mathbf{n} \cdot \mathbf{E}) \mathbf{n} \quad (1.21)$$

and the dielectric energy density of a nematic is given by,

$$W_{diel} = - \int_0^{\mathbf{E}} \mathbf{D} \cdot d\mathbf{E} = -\frac{1}{2}\epsilon_0 \epsilon_{\perp} E^2 - \frac{1}{2}\epsilon_0 \Delta\epsilon (\mathbf{n} \cdot \mathbf{E})^2 \quad (1.22)$$

It is clear that the dielectric energy is lowered by an alignment of \mathbf{n} with respect to \mathbf{E} , which depends on the sign of $\Delta\epsilon$.

1.6.6 Electrical Conductivity

The origin of electrical conductivity in liquid crystals is the mobility of the residual ionic impurities under the application of an electric field. The conductivity is usually of the order of 10^{-11} Ω/m . The conductivity anisotropy is given by,

$$\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp} \quad (1.23)$$

where σ_{\parallel} and σ_{\perp} are the principal components of conductivity parallel and perpendicular to \mathbf{n} respectively. The sign of $\Delta\sigma$ depends on the direction along which the ions can flow easily. Usually for nematics $\Delta\sigma$ is positive as the ions can move more freely along \mathbf{n} than perpendicular to it. In smectics usually $\Delta\sigma$ is negative as it is easier for the ions to flow in the layers than perpendicular to the layers. In usual liquid crystals, the ionic effects can be usually ignored for frequencies ≥ 1 kHz of the applied electric field.

1.6.7 Alignment of Liquid Crystals

In an unaligned liquid crystalline medium the director \mathbf{n} varies gradually from point to point. In order to measure physical properties, the director should be aligned in a specific direction in the cell. In general the director is aligned either parallel or perpendicular to the plane of the glass substrate, called homogeneous and homeotropic alignment respectively.

Homogeneous Alignment : A glass plate coated with a thin layer of polyimide and rubbed in a specific direction gives rise to planar or homogeneous alignment. The rubbing on polyimide generates micro-grooves along which the long axes of the molecules get aligned. Another method used to obtain homogeneous alignment is by evaporating SiO in vacuum onto the glass plate at

$\sim 32^\circ$ grazing angle of incidence. The molecules sit in the channels, formed by the shadowing effect. In uniaxial nematic liquid crystals the rubbing direction or channel direction orients the director, and hence the optic axis.

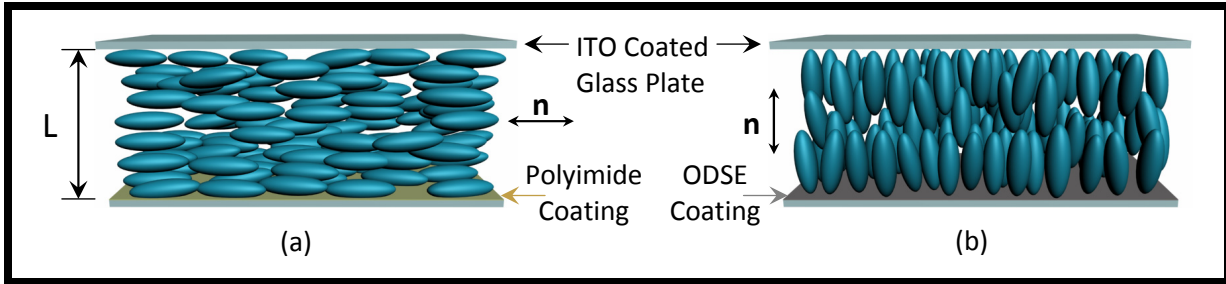


FIGURE 1.13: Schematic diagrams of the two types of alignment of the molecules

Homeotropic Alignment : A glass plate coated with a surfactant which has long chain molecules like ODSE (octadecyl triethoxy silane) gives rise to a homeotropic alignment. The molecules with long chains are amphiphilic in nature having a polar group and an aliphatic chain. The polar head group is attracted to the surface of the glass plate and the long aliphatic chain interacts with the alkyl chain of the liquid crystals giving rise to a perpendicular orientation of the director with respect to the glass plate (Figure 1.13b).

1.6.8 Anchoring Energy

The description of how strongly the director is aligned on the boundary surface is called anchoring. The anchoring energy measures the strength of anchoring of the director along a well defined direction, called as *easy axis* at the surface. The simplest surface energy density is of a form first proposed by Rapini and Papoular[19], and can be written as,

$$W_s(\theta) = \frac{1}{2} W_\theta \sin^2(\theta - \theta_0) \quad (1.24)$$

where θ and θ_0 are polar angles made by the director \mathbf{n} and the easy axis with the surface normal respectively. W_θ is the anchoring energy for tilt orientation of the director.

1.6.9 Fréedericksz Transition in Nematic Liquid Crystals

Competition between the effect of a wall and the effect of an external torque results in a director distribution that minimizes the free energy. The re-orienting torque arises due to a coupling between an external field and the corresponding susceptibility anisotropy. In a homogeneously (planar) aligned sample with positive $\Delta\epsilon$, when an electric field is applied perpendicular to the director, a distortion takes place only when the strength of the applied field exceeds a certain well defined threshold value. This transition is called Fréedericksz transition. The threshold voltage (independent of cell thickness) is given by,

$$V_{Th} = \pi \sqrt{\frac{K_{11}}{\epsilon_0 \Delta\epsilon}} \quad (1.25)$$

where K_{11} is the splay elastic constant and $\Delta\epsilon$ is the dielectric anisotropy of the medium. K_{11} can only be measured if the sample has a *positive dielectric anisotropy*. The director orientation above the threshold depends on both K_{33} and K_{11} and can be used to measure K_{33} also. This will be described in Chapters 2 and 3.