CHAPTER I

INTRODUCTION

Liquid crystals are states of matter that are intermediate between a solid crystal and an isotropic liquid. Many organic compounds with molecules having shape anisotropy are known to exhibit these phases (de Gennes, 1975; Chandrasekhar, 1977). Liquid crystals have some anisotropic properties like that of crystals; for example, the optical, dielectric and diamagnetic properties are anisotropic. Some other properties like the ability to flow and to form a miniscus are reminiscent of liquids. Thermotropic liquid crystals occur because of thermal effects, i.e., either by heating a crystal or by cooling a liquid. In this thesis, we report our experimental studies on thermotropic liquid crystals made of rod-like chiral molecules. As in most organic materials, one of the simplest ways to get the chirality of the molecule in a liquid crystal is by using a chiral carbon center. A substituted carbon atom will have a mirror plane if any two of the four substituents are the same. For example, in figure 1.1, if B and D are the same groups, the AC plane containing the carbon atom will be a mirror plane. But an asymmetrically substituted carbon atom does not have any mirror planes and is hence chiral. In the second, third and fourth chapters, we discuss our results on electromechanical coupling in cholesteric liquid
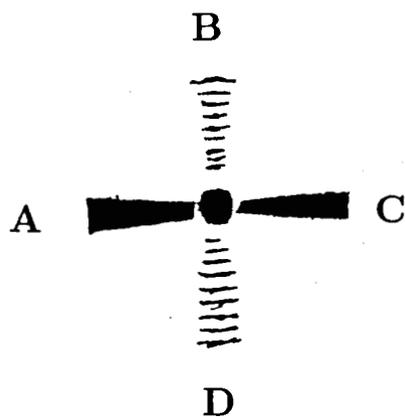
Figure 1.1. An asymmetrically substituted carbon atom (dark circle) is chiral

crystals. In the fifth and sixth chapters we discuss the electroclinic effect in the smectic A phase exhibited by some ferroelectric materials, made of chiral molecules.

In this chapter we briefly describe different types of liquid crystals that we use in our experiments and summarise their relevant physical properties.

1.1 Nematic Liquid Crystals

In this phase, the molecules exhibit an orientatiorial order, but they do not have positional order (Fig.1.2). The molecules can easily slide past one another which is characteristic of a fluid phase. The molecules obviously have a potential energy minimum when they are aligned along the direction of *average* orientation. This direction is represented by a unit vector called the director ($\hat{n}$). The director is apolar, i.e., $\hat{n}$ and $-\hat{n}$ are indistinguishable. Tlierefore the orientational order parameter is a second rank tensor and is defined as (Tsvetkov, 1942)

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

where θ is the angle made by the molecular long axis with the director $\hat{n}$. The angular brackets denote a statistical average. Generally a nematic liquid crystal is optically uniaxial, positive and strongly birefringent.

1.2 Cholesteric Liquid Crystals

This is also basically a nematic liquid crystal except that it is composed of optically active molecules. In this case the minimum energy configuration between two molecules occurs when there is a small angle between their long axes. The director twists about an orthogonal axis to produce a helical arrangement (Fig.1.3). This helical arrangement has a specific handedness. It can be right-handed or left-handed
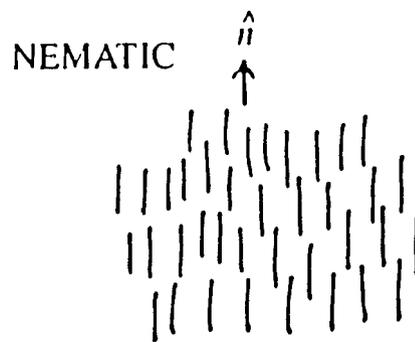
NEMATIC $\hat{n}$

Figure 1.2. Schematic representation of the molecular arrangement
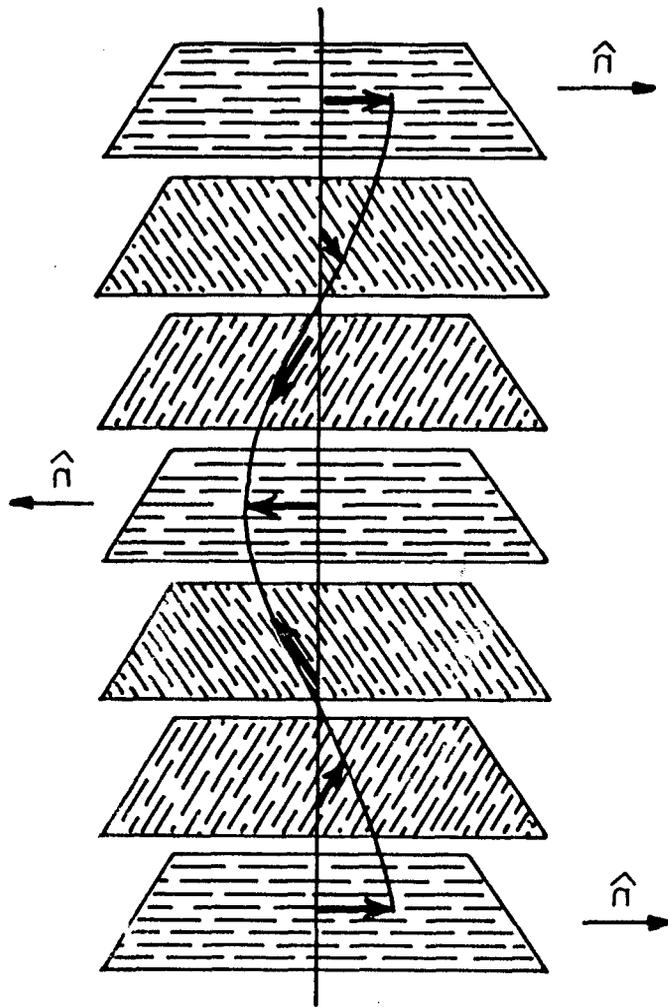in the nematic liquid crystalline phase.

Figure **1.3.** Schematic representation of the molecular arrangement in the cholesteric liquid crystalline phase.

depending on the chemical nature of the compounds. The handedness changes when the structure is reflected in a mirror, i.e., the reflected image of a left-handed structure looks like a right handed one and vice versa. It is not possible to superimpose the given structure on its mirror image, i.e., the cholesteric structure lacks mirror symmetry. The helical structure can be described by the director field of the following form

$$n_x = \cos(qz)$$
$$n_y = \sin(qz)$$

and $\quad n_z = 0$,

where q is the wavevector of the helix which is parallel to the z-axis. The distance over which the director turns through an angle 2π is defined as the pitch $P(= 2\pi/q)$ (Fig.1.3). The pitch of the helix is often of the order of the wavelength of visible light and the medium produces selective reflection of visible light. The cholesteric is optically uniaxial, negative with the optic axis along the helical axis.

When a left-handed cholesteric and a right-handed cholesteric are mixed together the pitch of the mixture becomes sensitive to temperature and composition. It is possible to have certain compositions for which the handedness of the helix changes sign at a particular temperature. At that temperature, there is an exact compensation of the right- and left-handed forms of helix and the mixture is said to be a *compensated cholesteric*. Friedel (1922) noted that at that temperature, the mixture exhibits the properties of a nematic.

1.3   Smectic Liquid Crystals

Smectic liquid crystals are characterised by one degree of translational order with the molecules arranged in layers. Depending upon the molecular arrangement within a layer, there are several types of smectics.

In the smectic **A** phase which is referred to as the *A* phase (Fig.1.4), the average orientation of the long axes of the molecules is along the layer normal whereas tlie centres of molecules in each layer are arranged randomly. It can be considered as a one-dimensional crystal and two-dimensional liquid. It is optically uniaxial with the optic axis lying normal to the plane of the layers.

The smectic C phase (Fig.1.5) is similar to smectic **A** except that the molecules are tilted with respect to the layer normal. This tilted orientation gives rise to optical biaxiality in the smectic C phase.

In a smectic C phase composed of chiral molecules (srnectic C* phase), the chiral interactions lead to the formation of a helical arrangement. The helix is formed by a precession of the tilt direction about an axis perpendicular to the layers witli a characteristic pitch P as shown in figure 1.6. Depending on the chirality of the constituent molecules, the helix can be either right-handed or left-handed. This is the natural state of the structure without any influence of external fields or surface effects, for the chiral smectic C phase. The helix of the srnectic C* can be unwound either by surface interactions or by the application of a strong electric or magnetic field. Figure 1.7 shows a non-helicoidal smectic C* structure.
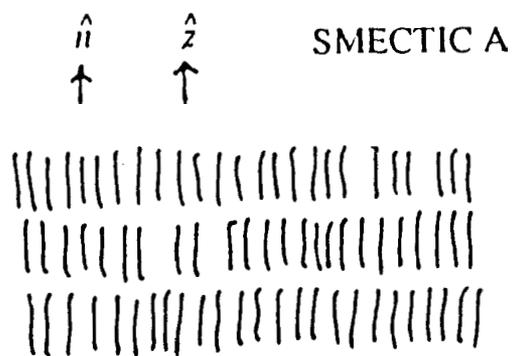
Figure 1.4. Schematic representation of the molecular arrangement in the srnectic A phase.
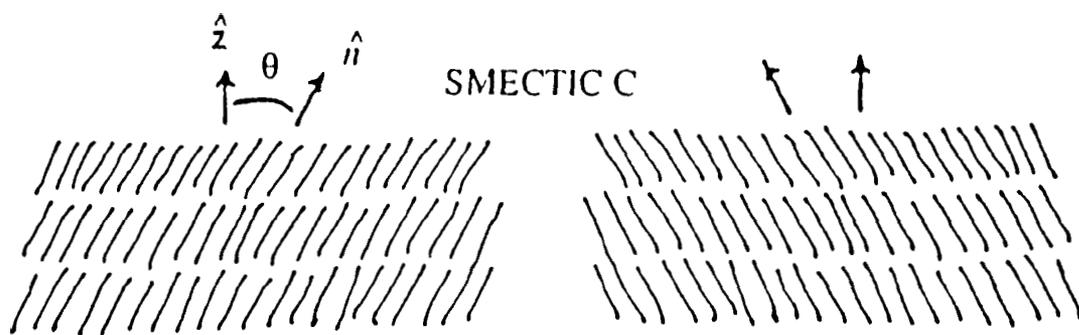

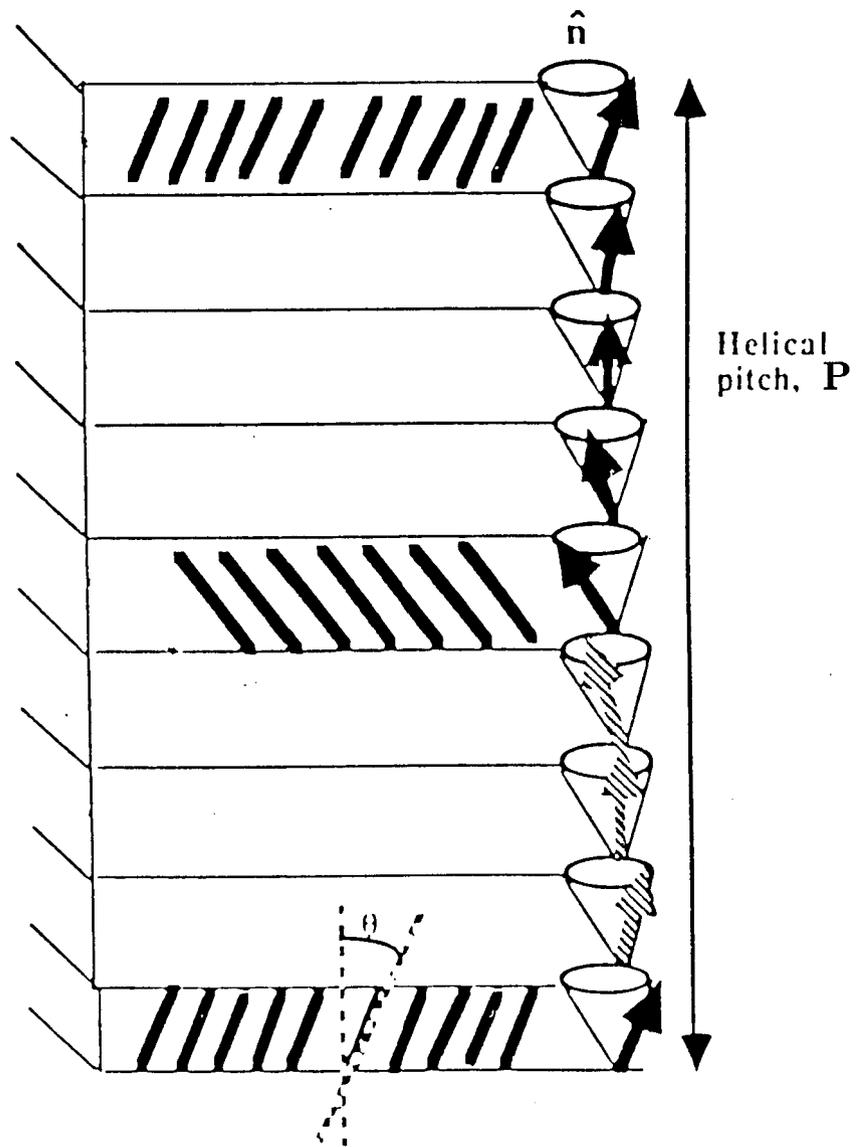**Figure 1.5.** Schematic representation of the molecular arrangement in the smectic C phase.

Figure 1.6. Twisted smectic C^* phase.
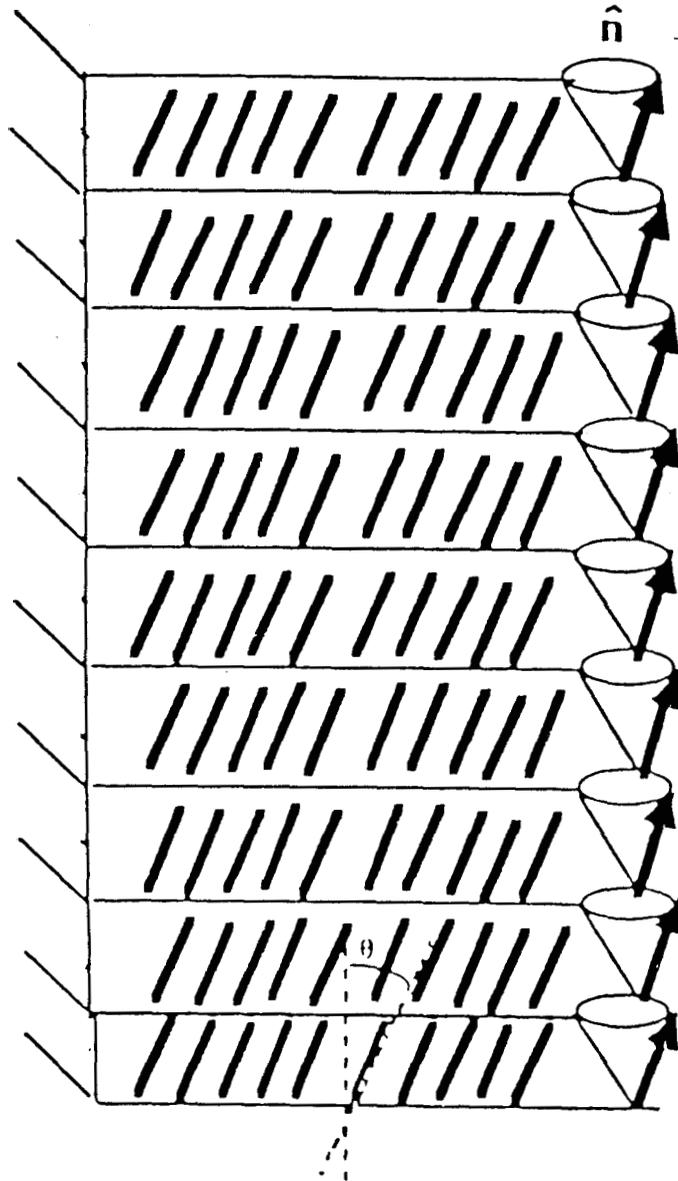
Figure **1.7.** Unwound smectic C* structure.

1.4   Dielectric anisotropy

When an electric field $\vec{E}$ is applied to a nematic liquid crystal, the resulting dielectric displacement $\vec{D}$ is given by (de Gennes, 1975)

$$\vec{D} = \epsilon_\perp \vec{E} + (\epsilon_\parallel - \epsilon_\perp)(\hat{n} \cdot \vec{E})\,\hat{n} \qquad (1.2)$$

where $\epsilon_\parallel$ and $\epsilon_\perp$ are the principal dielectric constants parallel and perpendicular to the director respectively. The dielectric anisotropy $At = (\epsilon_\parallel - \epsilon_\perp)$ is positive when the molecule is non-polar or carries a permanent dipole moment parallel to its long axis. By attaching a strongly polar group at one end of the molecule, we can have materials with a large positive value of At. When there is a permanent dipole moment which is nearly normal to the molecular long axis, At is negative $(\epsilon_\parallel < \epsilon_\perp)$. The anisotropy $\Delta\epsilon$ is strongly dependent on temperature and frequency.

In cholesterics, the dielectric constant measured along the helical axis is given by $\epsilon_\perp$. When measured normal to the helical axis, it takes the average value $\frac{1}{2}(\epsilon_\parallel + \epsilon_\perp)$. If $(\epsilon_\parallel > \epsilon_\perp)$, this average value becomes larger than $\epsilon_\perp$ and the helical axis prefers to be normal to the applied electric field.

1.5   Electrical Conductivity

A nematic usually has a weak electrical conductivity due to residual ionic impurities. By doping a nematic sample with appropriate ions, its conductivity can be varied in the range 10^{-9} to 10^{-6} ohm$^{-1}m^{-1}$. The conductivity is anisotropic. Usually the parallel conductance $\sigma_\parallel$ which is parallel to $\hat{n}$ is larger than the perpendicular conductance $\sigma_\perp$. This is connected with the greater freedom of motion of ions along $\hat{n}$ than perpendicular to $\hat{n}$. The current density for an electric field acting in an

arbitrary direction is given by

$$\vec{J} = \sigma_\perp \vec{E} + \Delta\sigma(\hat{n} \cdot \vec{E})\hat{n} \; . \tag{1.3}$$

In the smectic A and C liquid crystalline phases, the mobility of the ions in the plane of the liquid layer is greater than that across it. Therefore the conductivity anisotropy is negative in these cases.

1.6 Curvature Elasticity

In a uniformly oriented monodomain sample of a nematic liquid crystal, the direction of the director $\hat{n}$ is the same throughout the sample. The nematic sample with such a configuration has the lowest free energy. However, the director can be easily deformed by an external torque such as a magnetic or an electric one. In tlie distorted sample, $\hat{n}(r)$ represents the preferred orientation at any point r. In such a case elastic torques come into play within the sample, tending to restore $\hat{n}$ to tlie original undistorted state.

The curvature of tlie director can be classified into three basic deformations, viz., splay, twist and bend (Fig.1.8). They are characterised by the elastic constants K_{11}, K_{22} and K_{33} respectively (Frank, 1958). These constants are positive and $\approx 10^{-11}$ newton. The elastic free energy density of a deformed nematic sample in terms of director and its gradients is given by (Ericksen, *1962)*

$$F^{el} = \frac{1}{2}\left[K_{11}(div\hat{n})^2 + K_{22}(\hat{n} \cdot curl\hat{n})^2 + K_{33}(\hat{n} \times curl\hat{n})^2\right] \tag{1.4}$$
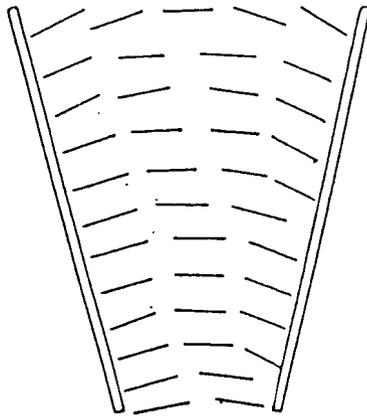
In the absence of external fields, the condition for equilibrium can be obtained by minimizing tlie total distortion energy with respect to all variations of tlie director $\hat{n}(\vec{r})$, with the constraint $n^2 = 1$. Taking this constraint into account by using the

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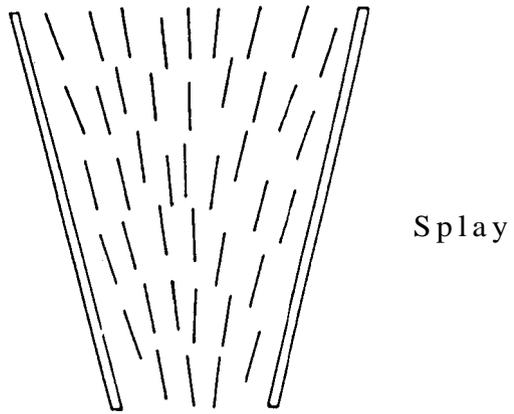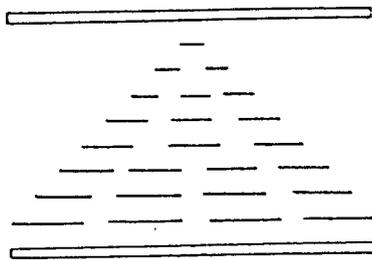
Figure 1.8. The three principal types of deformations in
a nematic (after Chandrasekhar, 1977).

rule of Lagrange, the condition for equilibrium (see de Gennes) is given by

$$h_i = -\left(\frac{\partial F^d}{\partial n_i}\right) + \partial_j \left(\frac{\partial F^d}{\partial g_{ji}}\right) = -C(\vec{r})n_i \tag{1.5}$$

where $\partial_j = \frac{\partial}{\partial x_j}$, $g_{ji} = \partial_j n_i$ and $C(\vec{r})$ is an arbitrary function of $\vec{r}$, and $\vec{h}$ is called the molecular field. Equation 1.5 states that, in equilibrium condition the director must be parallel to the molecular field at each point. $\vec{h}^d = \vec{h}^s + \vec{h}^t + \mathrm{h}^b$, where the three parts refer to splay, twist and bend respectively and are given by (de Gennes, 1975)

$$
\begin{aligned}
\vec{\mathrm{h}}^s &= K_1 \mathrm{grad}(div\,\hat{n}) \\
\vec{h}^t &= -K_2[A\ \mathrm{curl}\,\hat{n} + curl(A\hat{n})] \\
\vec{h}^b &= K_3[\vec{B} \times curl\,\hat{n} + curl(\hat{n} \times \vec{B})]
\end{aligned}
\tag{1.6}
$$

where $A = \hat{n} \cdot \mathrm{curl}\,\hat{n}$ and $\vec{\mathrm{B}} = \hat{n} \times \mathrm{curl}\,\hat{n}$.

Out of equilibrium, when $\hat{n}$ arid $\vec{h}^d$ the molecular field due to deformation are not parallel, the director experiences a torque which acts in a direction such that $\vec{h}^d$ and $\hat{n}$ become collinear. The torque density is given by

$$\vec{\Gamma}^d = \hat{n} \times \vec{h}^d \tag{1.7}$$

Using appropriate molecular fields, we can describe the influence of external fields acting on a nematic liquid crystal. In addition to $\vec{\mathrm{h}}^d$, contributions to the molecular field from each of these external fields have to be taken into account. The dielectric contribution to the free energy density is given by

$$F^\epsilon = -\frac{\epsilon_\perp E^2}{8\pi} - \frac{\Delta\epsilon(\hat{n} \cdot \vec{E})^2}{8\pi} \tag{1.8}$$

The corresponding molecular field $\vec{h}^\epsilon$ can be calculated using an equation analogous to (1.5). In such a case, the equilibrium condition is that $\hat{n}$ rnust be parallel to the total molecular field $\vec{h} = \vec{h}^d + \vec{h}^\epsilon$.
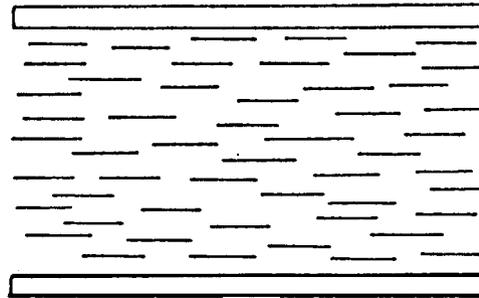
1.7   Alignment of Nematics

In order to conduct easily interpretable experiments, a monodomain nematic sample with a well defined alignment has to be used. In general, the orientation of the molecules on the surface is characterized by two parameters, viz., the average angle θ_o of the director with the plane of the surface and the anchoring energy W. $\theta_o = 0$, $\theta_o = \pi/2$ and $0 < \theta_o < \pi/2$ define the conditions for planar, homeotropic and tilted orientations respectively. In a *planar* or a *hornogeneously* aligned sample, tlie director is parallel to the enclosing glass surfaces (Fig.1.9a). It can be obtained by unidirectional rubbing (Chatelain, 1955; Guyon and Urbach, 1976) of a glass plate which is coated with an appropriate polyimide layer. This creates grooves on the surface along the direction of rubbing. The nematic is oriented with the director along this direction. Homogeneous alignment can also be obtained by oblique deposition of silicon monoxide on the glass plates such that the glancing angle of incidence is about 35° (Janning 1972). Here the shadowing effect effectively produces grooves on tlie surface, and the director aligns in a direction normal to the plane of SiO coating.

In a homeotropically aligned sample the director is aligned perpendicular to tlie surfaces (Fig.1.9b). This is obtained by treating the surface of the glass plates with certain polymers which have chemical groups that can attach themselves to the surface and have long chains that stick out of the surface.

Once a layer of the liquid crystal is coupled to the substrate along a certain direction, its average orientation is transmitted through the bulk via the orientation-dependent intermolecular forces which are responsible for tlie liquid crystalline phase itself.

Tlie other parameter which characterises surface alignment is the anchoring en-

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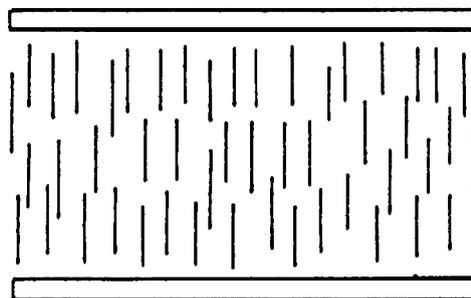
Figure 1.9. (a) Homogeneous alignment
and (b) homeotropic alignment of the
director in a nematic liquid crystal.

ergy W which usually has a finite magnitude. It is $\sim 10^{-5} joule/m^2$ or less for *weak* anchoring. de Gennes (1975) has shown that the anchoring energy can be expressed in terms of an *extrapolation length* L which is defined as

$$L = \frac{K}{W} \ ,$$ (1.9)

where K is an appropriate curvature elastic constant. Further if $\tilde{w}$ is the anisotropic part of tlie interaction between the wall and one molecule lying at the wall arid $'a'$ represents an average molecular dimension, then $W \sim \frac{\tilde{w}}{a^2}$. Now $K \sim \frac{w_1}{a}$, where w_1 is the nematic-nematic molecular interaction energy. Then from equation (1.9)

$$L \sim a \frac{w_1}{\tilde{w}}$$ (1.10)

If $\tilde{w}$ is comparable to w_1, the extrapolation length L becomes comparable to molecular dimensions a as given by equation (1.10). This situation corresponds to the case of strong anchoring. Here, the director is firmly fixed at the boundary and any applied field has very little effect on it.

If $w \leq w_1$, then $L \geq a$, i.e., the extrapolation length is much larger than the molecular dimension $'a'$. An external field can cause a disturbance of the surface alignment in this case and hence it is appropriately called *weak anchoring.*

1.8   The Freedericksz Transition

As mentioned earlier, in a nematic medium, the director is apolar. Nematic liquid crystals usually have a positive anisotropy of diamagnetic susceptibility. Therefore when a magnetic field is applied perpendicular to the alignment direction of a nematic liquid crystal which is strongly anchored at the bounding surfaces, tlie uniform pattern is distorted (Fig.1.10). The orienting effect of tlie field conflicts with tlie orientations imposed by the surface effect. There will riot be any distortion of the
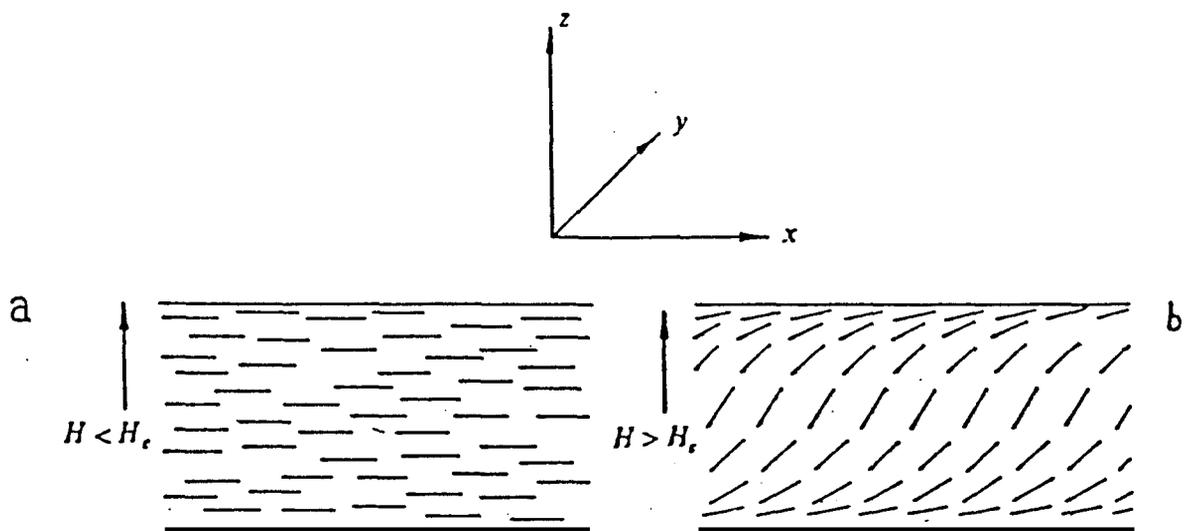
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Figure 1.10. Geometry for studying Freedericksz transition related to splay distortion. Molecular alignment (a) when the field is below H_c and (b) when the field is above H_c, the threshold field.

director up to a *critical* field H_c as tlie stabilizirig elastic torque is larger than tlie destabilizing magnetic torque. At H_c, the medium undergoes a transition to the distorted state called Freedericksz transition (Freedericksz, 1933). Beyond H_c, tlie distortion in the sample increases with the increase in the field.

For a fixed value of field the stable equilibrium state can be found by minimizing the free energy with respect to the variations in the director profile. The expression for tlie critical field is given by

$$H_c = \frac{\pi}{d}\left(\frac{K_{ii}}{\Delta\chi}\right)^{1/2} \tag{1.11}$$

where $K_{ii} = K_{11}$, K_{22} or K_{33}, depending on the geometry of the experiment.

The electric analogue of the Freedericksz transition is well known since the days of Freedericksz and Zvetkov (1934). The formula for the threshold field is given by

$$E_c = \frac{\pi}{d}\left(\frac{K_{ii}}{\epsilon_o\Delta\epsilon}\right)^{1/2}. \tag{1.12}$$

1.9 Defects

Characteristic *defects* in unaligned liquid crystal samples are seen when they are viewed under a microscope. Many of these are cliaracterised by an abrupt change in the orientation of the director.

The term disclination was used by Frank to explain the defects caused by discontinuities in the director field $\hat{n}(r)$. It represents a discontinuity in the inclination of the director. The discontinuity may be located at a point or on a line (Fig.1.11). Point defects are less common than line defects.

The lines usually lie along the viewing direction and under a polarizing microscope with crossed polarisers, points can be observed which have usually two or four
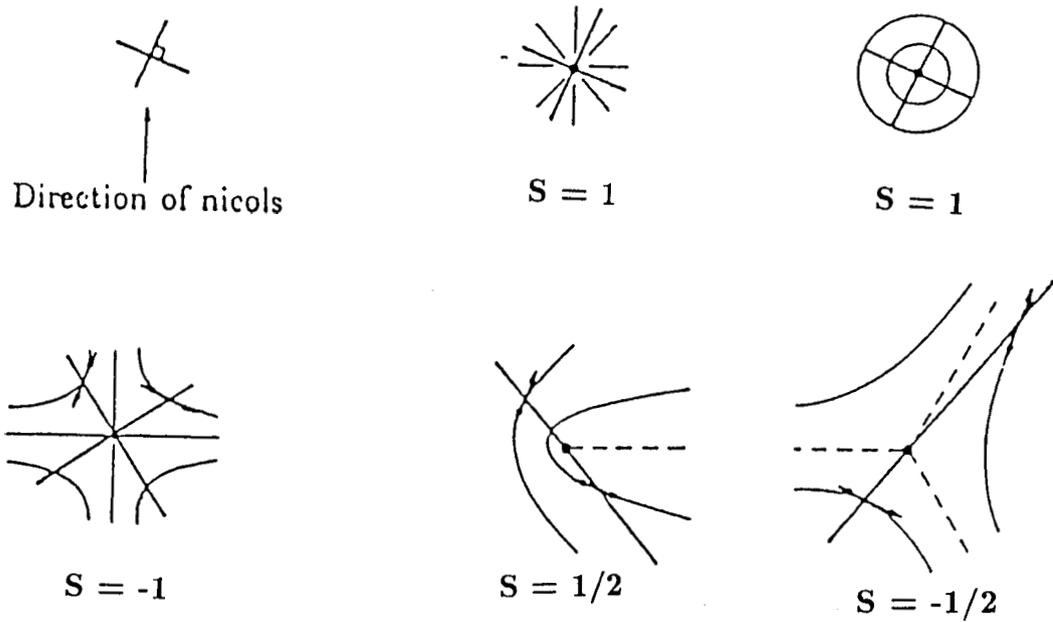
Direction of nicols

S = 1

S = 1

S = -1

S = 1/2

S = -1/2

Figure 1.11. Geometrical arrangement of the director, in the case of line defects. The thick lines give the regions of extinction between crossed polarisers.

brushes radiating from them. Around these points, the director changes its orientation through an angle which is a multiple of π. The brushes are regions in which the director is either parallel or perpendicular to the plane of polarisation of the incident light. The polarisation of the light beam remains unaltered as it passes through the sample in these regions. When the polarisers are rotated simultaneously, the brushes are seen to rotate continuously. This shows that whereas the points themselves remain unchanged, the orientation of the director changes continuously around these points. When the direction of rotation is the same as that of the polarisers, they are said to be positive disclinations and if they are opposite, negative disclinations. The various types of disclinations are defined by the *strength S* which is equal to $\frac{1}{4}\times$ *number of brushes.*

In disclination lines of half-integral strength ($S = \pm\frac{1}{2}$), which arise due to the apolar character of the director, $\hat{n}$ is confined to a plane orthogonal to the disclination line which has a singularity associated with it.

On the other hand, a disclination line of integral strength is unstable. The distortions around this line are continuously transformed into a smooth structure with no singular line (Meyer, 1973; Cladis and Kleman, 1972). The director *escapes* into the third dimension giving rise to the smooth pattern as shown in figures 1.12.

In cholesterics, the disclination lines parallel to the helical axis are called χ *lines.* In the case of a χ line of strength 1, as the average orientation of the director twists around the helical axis, the director pattern gradually changes between radial and tangential arrangements (Fig.1.13). Even in this case, the director can escape into the third dimension removing the singularity (de Gennes, 1975). In chapter II we will come across χ line defects which occur in cholesteric droplets.
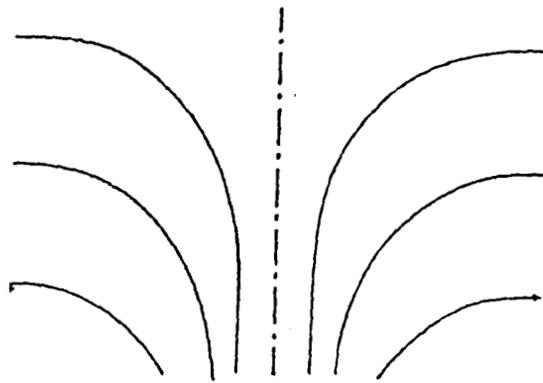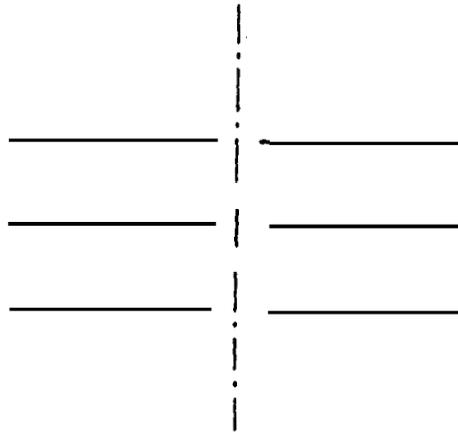
Figure 1.12. Disclination of strength $+1$. (a) The arrangement near the centre has discontinuity. (b) Escape of the director in the third dimension removing the singularity.
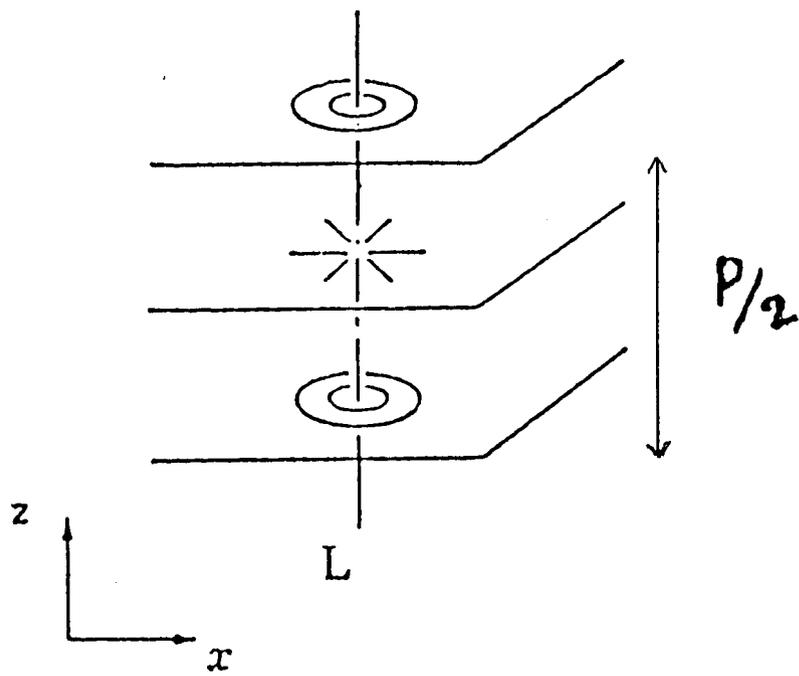
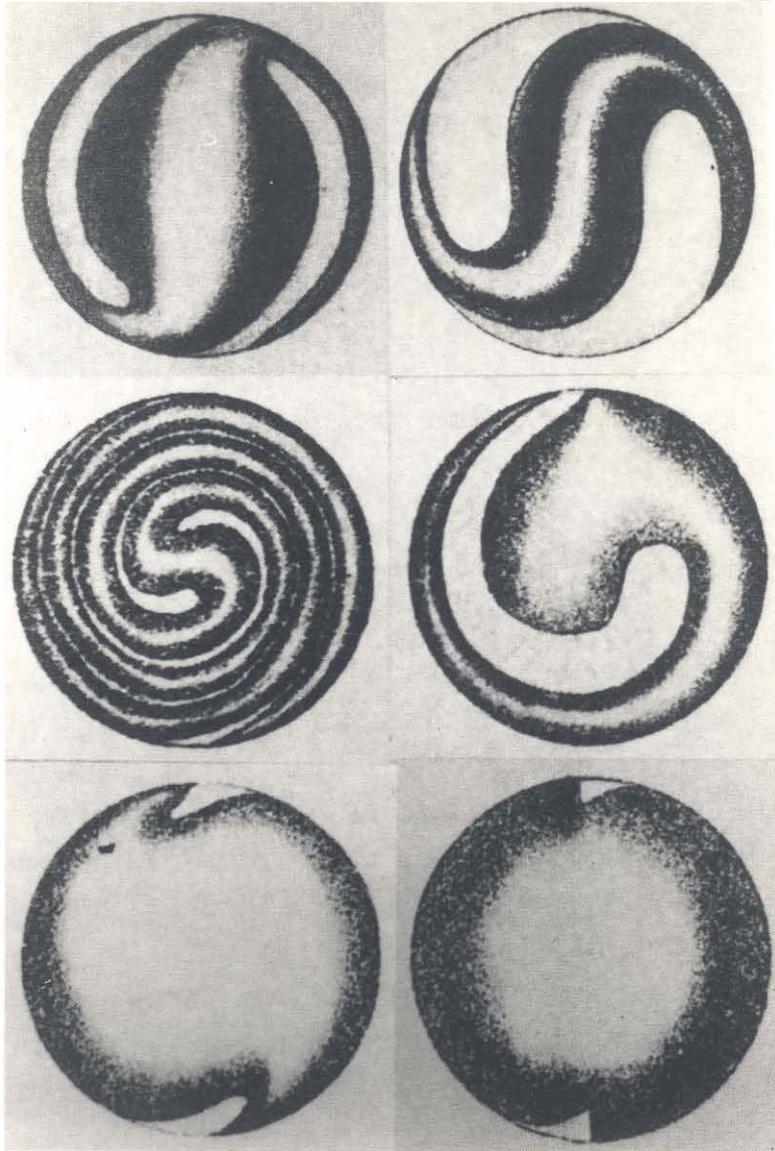**Figure 1.13.** Structure of a χ-line of strength $+1$, normal to the cholesteric plane.

Figure 1.14. Lehmann's diagrams illustrating the rotation phenomenon in open cholesteric droplets heated from below (From Chandrasekhar, 1977).

1.10 Hydrodynamics of Cholesterics

In parity violating chiral systems, the Curie (or Von Neumann) principle allows unusual cross couplings between fluxes and dissipative forces (Pomeau, 1971). However, studies on the effect of chirality on dissipative systems are rare. These cross coupling effects are rather small and difficult to detect in the isotropic liquid phase in which each chiral molecule is essentially independent. The cooperative nature of the chiral interactions in cholesteric liquid crystals can be expected to result in relatively large cross coupling effects which are clearly observable.

In fact, we may note that the thermotropic liquid crystalline phase itself was discovered by Reinitzer in 1888 in cholesteric benzoate which forms the cholesteric phase. The very first physical study on liquid crystals was also made on a cholesteric liquid crystal. Lehmann discovered in 1900 that drops of a cholesteric liquid crystal material exhibited a very unusual rotation phenomenon. Oseen (1933) summarised Lehmann's observations as follows: *He found that in certain cases a substance spread out between two glass surfaces would be put into motion, when influenced by a flow of heat coming from below, during which motion the different drops of liquid seemed to be in violent rotation. Further investigations convinced Lehmaizn that in this case it was not the drop itself, but the* **Structure** *that moved.* As mentioned earlier, it appears that the cooperative nature of the chiral interactions in a cholesteric gives rise to a magnification of the unusual cross couplings. Lehmann has drawn sketches of a large number of structures that he could see, many of them in vivid colours. In figure 1.14 we have reproduced a sequence of his sketches.

This phenomenon could be explained theoretically only after the hydrodynamic theories of the cholesteric phase were developed. A study of hydrodynamic properties of anisotropic fluids was made for the first time by Anzelius (1931) and then

by Oscen (1933). Ericksen (1966) and Leslie (1968, 1979) analysed the coupling between orientation and flow in tlie case of nematic and cholesteric liquid crystals. Leslie's theory gives solutions that describe the Lehmann rotation phenomenon in the cholesteric phase.

For a cholesteric subjected to a temperature gradient, the entropy production rate is given by TS, where T is the temperature and S is the entropy density. One of the causes for the dissipative loss of energy is the rotation of the director and its contribution to $T\dot{S}$ is given by $\vec{h} \cdot \vec{N}$, where $\vec{h}$ is the molecular *field*; $\vec{N}$ is the rate of change of the director with respect to the background fluid, i.e., $\vec{N} = (\partial \hat{n} / \partial t)$, if there are no velocities. The molecular field in a cholesteric is given by (Leslie, 1968)

$$\vec{h} = \vec{h}^N + \nu \vec{n} \times \vec{E} \quad . \tag{1.13}$$

Here $\vec{h}^N$ denotes the contribution from the hydrodynamics of nematics. ν is the thermo- or electro-mechanical coupling coefficient, and E is the applied field. TS which denotes the dissipation of energy is a scalar. $\vec{h} \cdot \vec{N}$ should be a scalar as it is the dot product of two polar vectors. We have to note however that $\hat{n} \times \vec{E}$ in equation (1.13) is an axial vector which changes sign when the coordinate system is reflected in a mirror. Hence ν, the cross-coupling coefficient should be a pseudoscalar which should also change sign in the reflected system. In other words, this coefficient can have a non-zero value only for chiral systems. In the hydrodynamic limit, the relevant chirality is the macroscopic chirality represented by the wave vector q of the helix which also changes sign under reflection. In the lowest approximation, the cross-coupling coefficient must be proportional to q, the wavevector of the helix as its handedness changes sign under mirror reflection. As a convention, tlie sign of q is taken to be positive for a right-handed helix and negative for a left handed helix. Then according to the hydrodynamic theory, the cross-coupling does not

exist for a system with q = 0 such as in the case of a nematic or a compensated cholcsteric. The cross-coupling between a thermal gradient and mechanical effect results in the rotation phenomenon observed by Lehmann. The analogous effect that exists between the ion flow and electric field is called the electromechanical effect. Although the cholesteric is characterized by two thiermo- (electro-) mechanical couplirig coefficients, in our thesis we will be discussing only one of them in chapters II, III and IV .

1.11   Ferroelectric Liquid Crystals

Using a symmetry argument, Meyer et *al.* (1975) showed that the smectic C* phase should be ferroelectric. His argument can be summarised as follows.

Let us consider a vertical cross section of the smectic C structure passing through the layer normal $\vec{z}$ and the clircctor $\hat{n}$ (Fig.1.15). This structure has the following syrnmetry elements: (i) a two-fold rotation axis about X; (ii) a mirror plane lying in the YZ plane. These symmetry elements are consistent with the apolar nature of the director. If the molecules are chiral, as in the case of smectic C* phase, the YZ plane is no longer a mirror plane. So the medium is left with only a two-fold axis as the symmetry element. The two-fold axis sustains the properties described by a polar vector along that axis. When the molecules have permanent transverse dipole moments, then there can be a polarisation $\vec{P}$ along the two-fold axis, i.e., the medium can become ferroelectric. The dipole moment and hence the polarisation is normal to the plane containing the director and the layer normal and hence such a ferroclcctric is called *transverse ferroelectric.* The first compound to be synthesised with the requisite features was p-decyloxybenzylidene p-amino-2-methylbutyl cinnamate ($C_{10}H_{21}O\Phi CHN\Phi CHCHCOOCH_2^*CH(CH_3)C_2H_5$) or DOBAMBC for short.
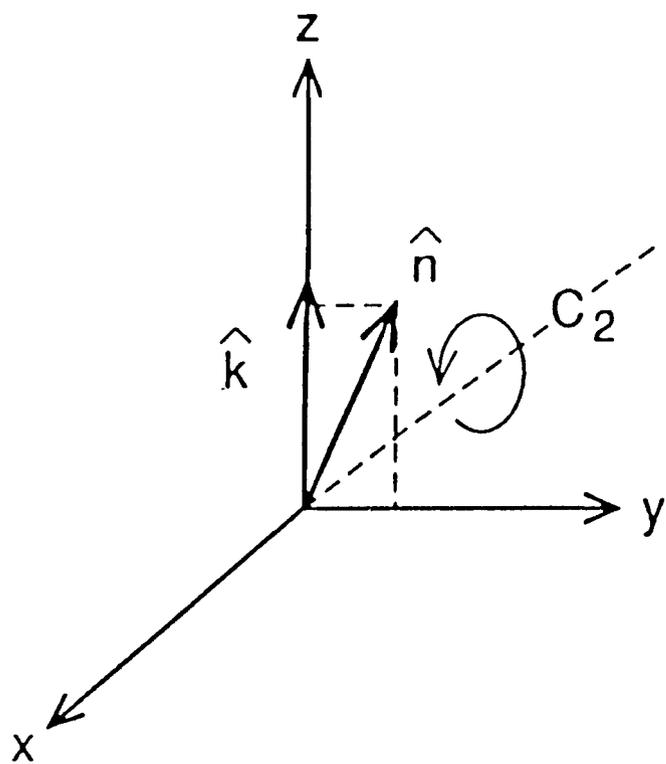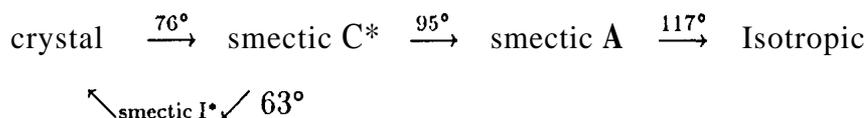
Figure 1.15. The FLC C_2 symmetry operation.

The phase sequence for this compound is as follows:

crystal $\xrightarrow{76°}$ smectic C* $\xrightarrow{95°}$ smectic **A** $\xrightarrow{117°}$ Isotropic

$\nwarrow$ smectic I*$\nearrow$ 63°

For this compound, the ferroelectric polarisation and the hysteresis loop in the electric displacement D versus the electric field E curve were demonstrated. We can get the C* phase either by synthesising a chiral variant of a molecule which has a stable C phase or by doping a smectic C liquid crystal with any chiral compound soluble in it. To obtain the transverse polarisation the molecules are to be tilted in the layers as in the smectic C phase. The smectic **A** phase cannot have transverse ferroelectricity as the upright molecules freely rotate about their long axes. The cholesteric phase is not ferroelectric, as the local director which is orthogonal to the twist axis has a 2-fold rotational symmetry.

The molecules that form the A and C phases have a rigid and straight aromatic core and the alkyl chains at the two ends which have the lowest energy in the extended all-trans configuration make an angle with respect to the rigid core. In the smectic C phase the chains would prefer to make a small angle with respect to the layer normal, i.e., in figure 1.16, position 2 has higher energy than position 1 (Clark and Lagerwall, 1991). It means that there is a rotational bias in the C phase. But because of the mirror plane, we do not get polarisation in the smectic C phase. The molecular dipole can point out of the paper or into the paper with equal probability and there is a quadrupolar symmetry. We get polarisation if the dipoles are rigidly attached to chiral centres in the molecule. $\vec{P}$ is along $\vec{k}$ x $\hat{n}$, where $\vec{k}$ is a unit vector along the layer normal and $\hat{n}$ the director. $\vec{P}$ is taken to be positive and when it is in the opposite direction, it is taken to be negative.
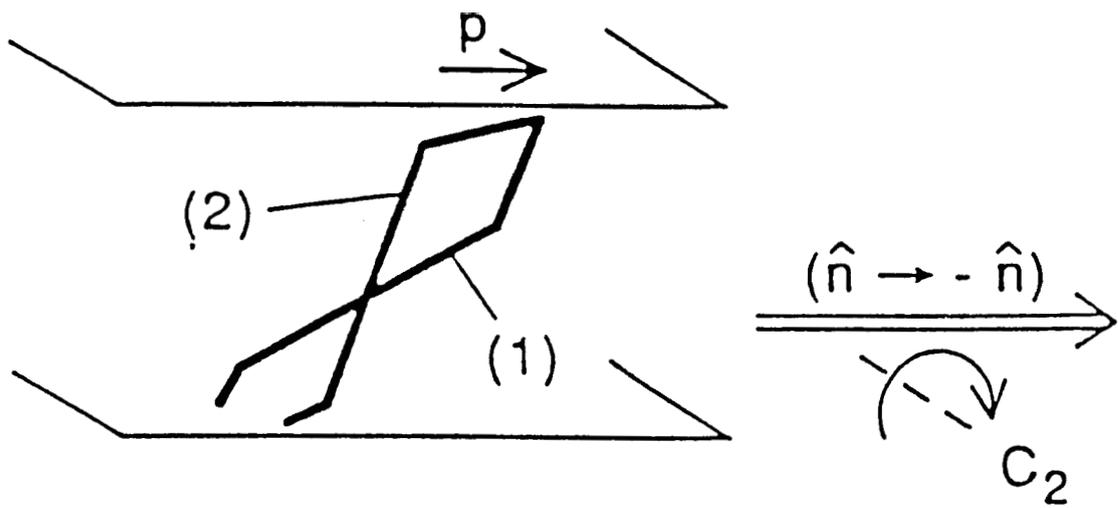
15

Figure 1.16. Two possible orientations of the molecules with chains in the smectic C phase.

In practice, $\vec{P}$ is found to be negative in most of the ferroelectrics. They are fluid ferroelectrics with ferroelectric polarisation in the plane of the fluid layers. Polarisation measurements indicate that the effective dipole moment P_m per molecule is quite small ($P_m \sim 10^{-2} Debye$). This is due to a weak polar bias in the rotation of the molecules around their long axes in smectic C* phase. The dipolar energy $P_m^2/a \sim 10^{-25} J$, where a is an intermolecular distance. This is much smaller than the thermal energy $k_B T \sim 10^{-21} J$. This means that the dipolar interactions do not produce the transition from A* to C* phase. The ferroelectric polarisation $\vec{P}$ is merely due to the symmetry of the C* phase. Hence the primary order parameter in the A* to C* transition is the tilt angle 0 as in the case of A to C transition of a non-chiral substance. The polarisation $\vec{P}$ is only a secondary order parameter.

As we have already discussed in the case of the cholesteric phase, in the C* phase also the tilt direction twists around the layer normal, resulting in a helicoidal structure. The polarisation $\vec{P}$ which is coupled to the tilt also twists around the helical axis $\vec{z}$ (Fig.1.17). The polarisation averages out to zero when the helix makes one full 360° turn. Hence in a macroscopic undisturbed sample which is free from any of the external forces, the polarisation averages to zero. However, if the helix is unwound by external forces such as surface interactions or by compensating the helix in a mixture, the phase will have non-zero polarisation. It is because of this reason that the smectic C* phase has often been described as *helielectric*.

Since the first ferroelectric liquid crystal was synthesised by Meyer *et al.* (1975) many properties of these ferroelectric liquid crystals are being investigated as they have some advantages over nematic liquid crystals in display applications. Based on an argument similar to that for ferroelectricity in chiral smectic liquid crystals, Garoff and Meyer (1977 arid 1979) predicted the existence of *the electroclinic effect*
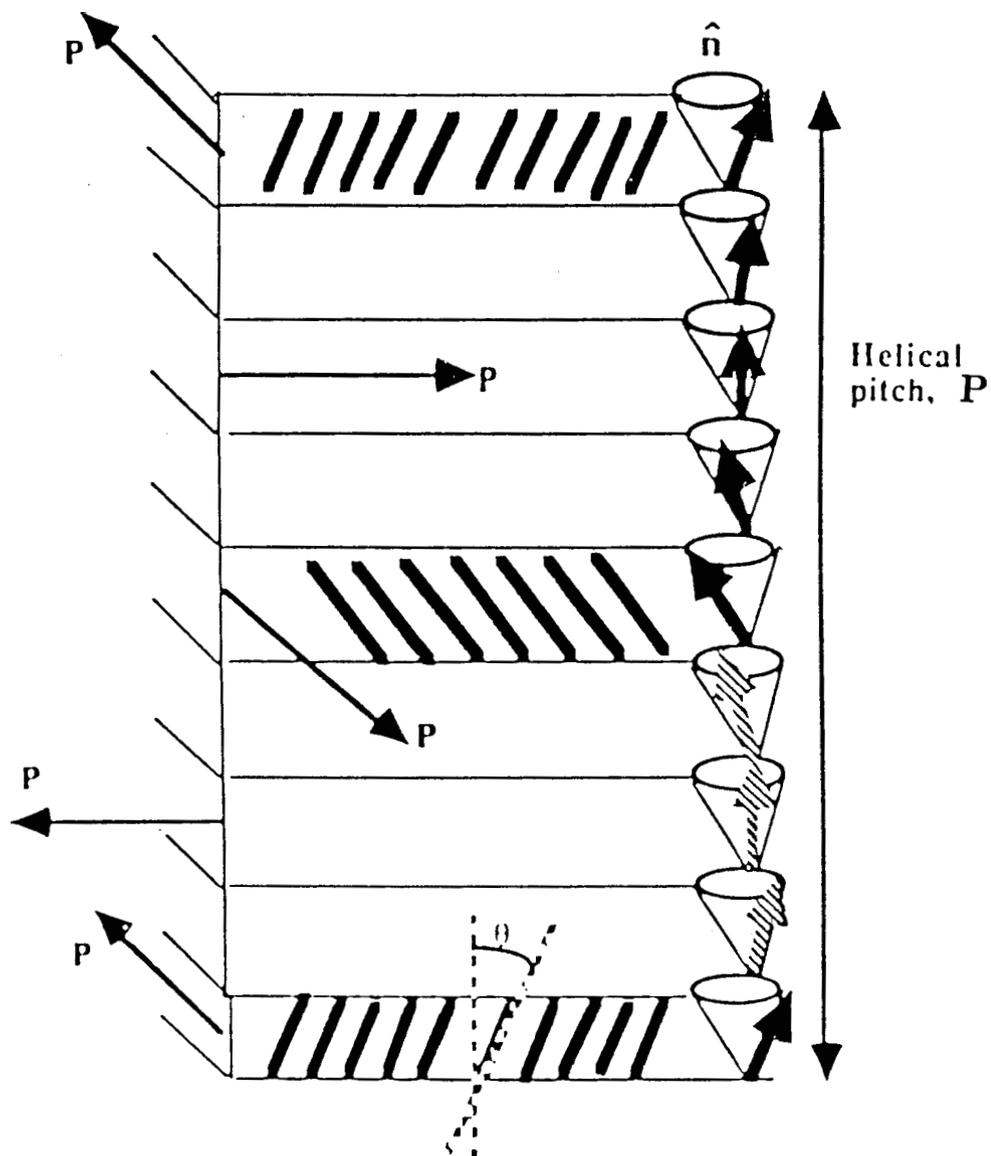
Figure 1.17. Twisted smectic C* phase.

in the smectic **A** phase of the liquid crystal composed of chiral molecules. In this phenomenon, by applying an electric field **E** parallel to the smectic layers, a molecular tilt angle, θ is induced relative to the layer normal in a plane orthogonal to E. We discuss the electroclinic response of some ferroelectric liquid crystals in chapters V and VI.

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