

Chapter 1

Introduction

1.1 What are Liquid crystals ?

Most crystals melt into the isotropic liquid on heating, in which the long range positional order of the molecules or atoms is destroyed. In the isotropic liquid, the average distribution of molecules is invariant under continuous rotations and translations and hence it has the highest symmetry. But some materials made up of molecules with anisotropic shapes exhibit intermediate states in which the symmetry is higher than that of a three-dimensional crystal but lower than that of the isotropic liquid. Because the molecules are geometrically anisotropic, the crystalline phase

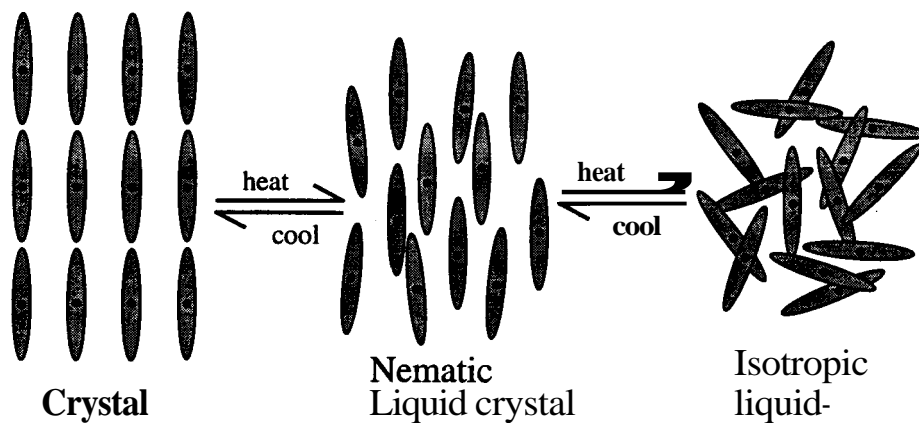


Figure 1.1: Schematic diagram showing an intermediate liquid crystalline state that can occur when a crystal made of anisotropic molecules is heated. In this, the long-range orientational order in the crystal is retained while the long-range positional correlations are lost.

will have a long range orientational as well as positional order. On heating such crystals, these two orders may be destroyed at different temperatures. Depending on the sequence in which the positional order and the orientational order are destroyed, there are two distinct possibilities. In one case, the positional order of the centers of mass of the molecules is retained while the orientational order is lost. Such a state is called a **Plastic Crystal**. The other possibility is that the orientational order is retained but the long-range positional correlations are destroyed along one or more directions. Such states are exhibited by compounds whose molecules have a very large shape anisotropy. A material in such a state is called a **Liquid Crystal**. Liquid crystals are ordered fluids and are sometimes referred to as **Mesophases**. The simplest form of liquid crystals is the nematic. A schematic diagram showing the crystal–nematic–isotropic sequence is shown in Fig. 1.1.

Liquid crystals can exhibit both crystal-like as well as liquid-like properties. They exhibit elastic properties and can transmit torques. Most of their physical properties are highly anisotropic. For example, they show very strong birefringence. Yet, they can flow like ordinary liquids, but the viscosities may be large and highly anisotropic. Because of some of these special properties, they are very useful in making low power consuming displays and tunable optical devices.

Liquid crystals can be broadly classified into two categories. Pure compounds and mixtures of compounds made of highly anisotropic molecules which exhibit various liquid crystalline states as a function of temperature are called **Thermotropic** liquid crystals. On the other hand, **Lyotropic** liquid crystals are formed by dissolving amphiphilic molecules in an isotropic liquid. Typically, these molecules have a hydrophilic head group connected to a hydrophobic 'tail' and form self organised structures when dissolved in a suitable solvent. These systems exhibit various liquid crystalline phases as a function of both temperature and concentration.

In thermotropics alone, more than thirty distinct liquid crystalline phases have been discovered so far. A detailed description of many of these can be found in references [1, 2, 3]. In this thesis, we will be dealing with only a few of them which are briefly described in the next few sections.

1.1.1 Nematics

The nematic (N) is the simplest example of a liquid crystal. This phase is usually exhibited by compounds composed of either 'rod-like' or 'disc-like' molecules. When the molecules are disc-shaped, the nematic phase formed by them is called a **Discotic nematic** [4]. The molecular structure of a compound (p-azoxyanisole) which shows a nematic phase is given in Fig. 1.2.

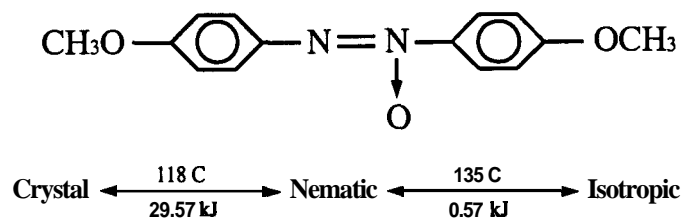


Figure 1.2: The molecular structure of a compound which exhibits the nematic phase.

The nematic phase is characterised by the following properties:

- There is a long range orientational order of the rod-like molecules. Thus, the continuous rotational symmetry of the isotropic liquid is broken (see Fig. 1.3).
- The centers of mass of the molecules have a liquid-like distribution. Thus, there is a continuous translational symmetry along all directions.
- Xray scattering shows two pairs of diffuse peaks, one corresponding to the short range order along the molecular length and the other to that along the molecular width.

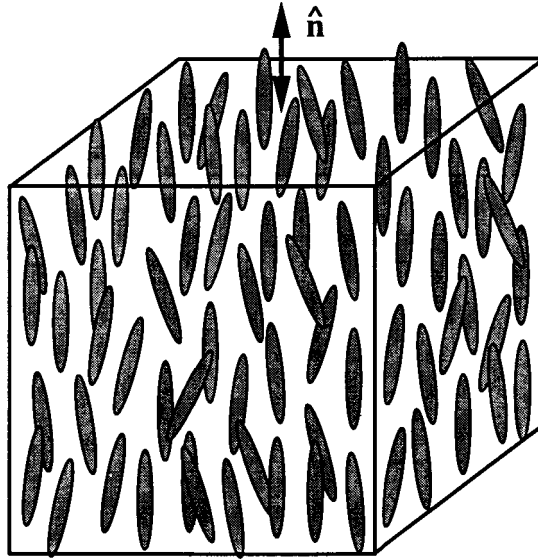


Figure 1.3: Schematic representation of the distribution of the molecules in the nematic phase.

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- The molecules are in general polar, but on the average there are an equal number of molecules which are pointing up or down. Therefore, the average orientation of the molecules is represented by an *apolar unit-vector* $\hat{\mathbf{n}}$, usually called the **Frank-director** or just **director**.
 - Though the molecules are in general biaxial, the medium has a uniaxial symmetry.
 - The point symmetry is $D_{\infty h}$.

Due to some of the properties mentioned above, the nematic phase is usually described by an order parameter which is a second rank tensor with components

$$S_{\alpha\beta} = S(n_{\alpha}n_{\beta} - \frac{1}{3}\delta_{\alpha\beta}); \quad \alpha, \beta = x, y, z. \quad (1.1)$$

The scalar S is a measure of the alignment of the long axes of the molecules and is defined as

$$S = \left\langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right\rangle, \quad (1.2)$$

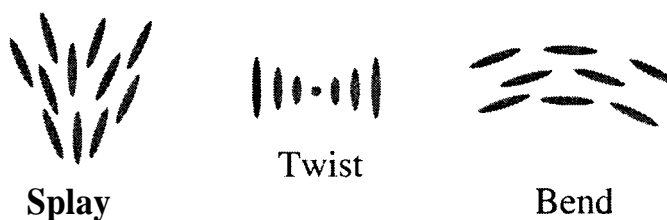


Figure 1.4: Schematic representation of the three principal deformations that can occur in the director field of a bulk nematic.

where θ is the angle made by the molecule with respect to the director. In the isotropic liquid the molecular long axes are randomly distributed and hence $\mathbf{S} = \mathbf{0}$. $\mathbf{S} = \mathbf{1}$ corresponds to a perfectly aligned nematic.

1.1.1.1 Elastic properties

Since the nematic is orientationally ordered, it exhibits curvature elasticity. The three principal deformations that can occur in a bulk nematic are 'splay', 'twist' and 'bend'. These three types of distortions are schematically shown in Fig. 1.4. The elastic free energy density is written as

$$f_N = \frac{1}{2} \left[K_{11}(\nabla \cdot \hat{\mathbf{n}})^2 + K_{22}(\hat{\mathbf{n}} \cdot \nabla \times \hat{\mathbf{n}})^2 + K_{33}(\hat{\mathbf{n}} \times \nabla \times \hat{\mathbf{n}})^2 \right], \quad (1.3)$$

where K_{11} , K_{22} and K_{33} are the elastic constants for the splay, twist and bend deformations, respectively. For the compound whose molecular structure is shown in Fig. 1.2, $K_{11} = 0.7 \times 10^{-6}$, $K_{22} = 0.43 \times 10^{-6}$ and $K_{33} = 1.7 \times 10^{-6}$ dynes at 120°C [1].

1.1.2 Cholesterics

A molecule is said to be chiral if it lacks mirror symmetry (non-centrosymmetric). This, for example, can be achieved by substituting four different atoms or groups to one of the carbon atoms in the alkyl chain as schematically shown in Fig. 1.5. The chemical structure of a chiral molecule is shown in Fig. 1.6.

When the molecules are chiral or when chiral molecules are added to a nematic,

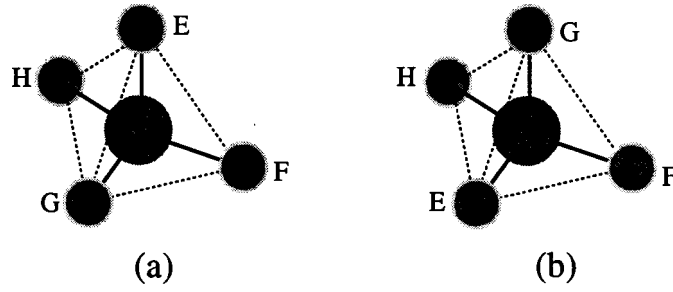


Figure 1.5: Schematic representation of the two chiral enantiomers formed by substituting different groups to carbon atoms.

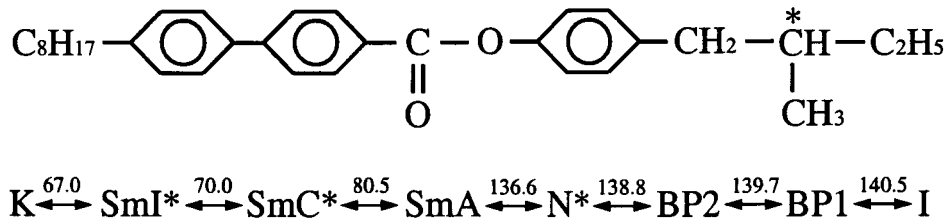


Figure 1.6: Molecular structure of a chiral compound which forms blue phases, cholesteric and smectic phases, which are described in the text. The chiral carbon atom is marked by a star and the transition temperatures are in $^{\circ}C$.

it develops a twisted structure and is then called a cholesteric (N^*). This is because the chiral interactions prefer adjacent molecules to be oriented at an angle with respect to each other. In the cholesteric phase the nematic director is confined to planes which are parallel to the XY-plane and its orientation varies continuously along the Z-axis as represented in Fig. 1.7. The director distribution can be represented as

$$\hat{\mathbf{n}} \equiv [\cos(q_0 z + \phi), \sin(q_0 z + \phi), 0]. \quad (1.4)$$

The pitch, $p = 2\pi/q_0$, of the cholesteric is the distance over which the director orientation changes by 2π . But, the effective periodicity is half the pitch because of the $\hat{\mathbf{n}} \equiv -\hat{\mathbf{n}}$ symmetry. The pitch can be of the order of sub-microns and hence most cholesterics Bragg reflect light in the visible range. Also the pitch decreases with increase in temperature. This property is used in making temperature sensors.

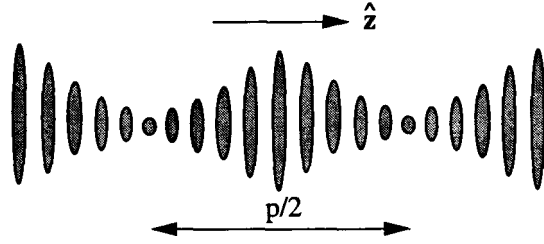


Figure 1.7: Schematic diagram showing the variation of the projection of the average molecular orientation on to the plane of the paper in a cholesteric. The twist axis is along \hat{z} .

1.1.3 Smectics

Smectic liquid crystals have a layered arrangement of rod-like molecules. Within each layer the order is liquid-like. X-ray diffraction shows quasi-Bragg peaks corresponding to the smectic layering. Only the first-order diffraction maxima are prominent. This indicates that the mass density modulation along the layer normal is almost sinusoidal. Therefore, the density variation along the layer normal, \hat{N} , assumed to be along the \hat{z} direction can be expressed as

$$\rho(z) \simeq \rho_o + \psi e^{i\mathbf{q}_A \cdot \mathbf{z}}; \quad \mathbf{q}_A = \frac{2\pi\hat{z}}{d}, \quad (1.5)$$

where ρ_o is the average density, d is the layer spacing and \hat{z} is the unit vector along the Z -axis. This defines an order parameter ψ , which is a complex number with an amplitude and a phase, that can be written as

$$\psi = |\psi_o| e^{-i\phi} \quad (1.6)$$

This order parameter is zero in the nematic phase and becomes non-zero below the nematic to smectic-A (NA) transition point.

Smectics can have several modifications depending on the structure within the layers.

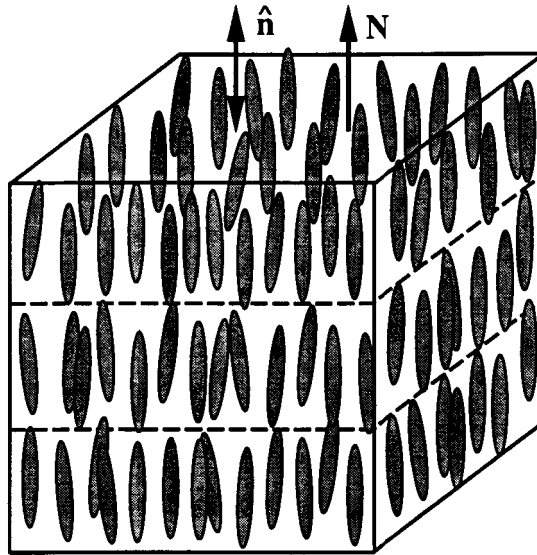


Figure 1.8: Schematic diagram showing the molecular arrangement in the smectic-A phase.

1.1.3.1 Smectic-A

The simplest of the smectics is the smectic-A (*SmA*) (Fig. 1.8). In this phase, the continuous translational symmetry of the nematic is broken along the Frank-director. The long-axes of the molecules are on the average oriented along the layer normal. The layer spacing usually corresponds to the molecular length. The medium is uniaxial with the point symmetry $D_{\infty h}$.

1.1.3.2 Smectic-C

In the case of smectic-C (*SmC*), the average orientation of the molecules is tilted with respect to the layer normal (Fig. 1.9). This phase is exhibited by compounds whose molecules have strong lateral dipole moments. The tilt order shows long-range correlations. The tilt order is usually represented by a two-dimensional vector called the c-vector, which is the projection of \hat{n} onto the plane of the layers. The layer spacing is equal to the projection of the molecular length along the layer normal. The anisotropy in thermal fluctuations makes the medium slightly biaxial, though for most practical purposes it can be considered as uniaxial along \hat{n} . The point

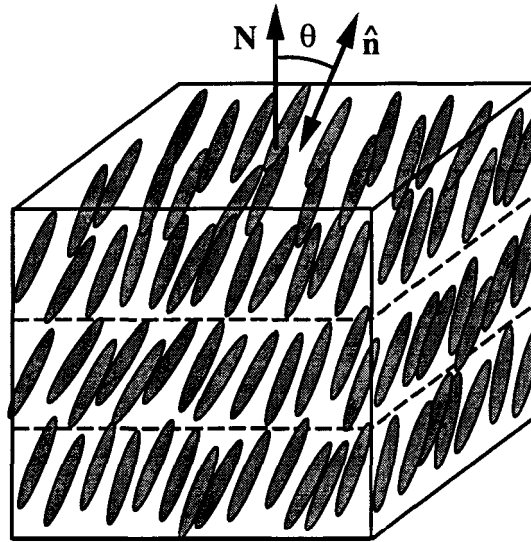


Figure 1.9: Schematic diagram showing the tilted arrangement of the molecules in the smectic-C phase.

symmetry is C_{2h}

1.1.3.3 Smectic- C^*

In the presence of chiral molecules, the smectic-C phase develops a spontaneous helical structure and is then known as the smectic- C^* (SmC^*) phase (Fig. 1.10). In this phase, the tilt direction (c-vector) varies continuously along the layer normal. The director distribution can be described as

$$\hat{\mathbf{n}} \equiv (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta), \quad (1.7)$$

where θ is the amplitude of the tilt order and ϕ its phase. The presence of chiral molecules removes the mirror plane symmetry of the layers and the point symmetry is reduced to C_2 . It was first realised by R. B. Meyer et al. [5] that the C_2 point symmetry of the layers allows the medium to sustain a permanent polarisation along the C_2 -axis in each layer. Since the tilt direction has a periodic variation along the layer normal the medium is helielectric.

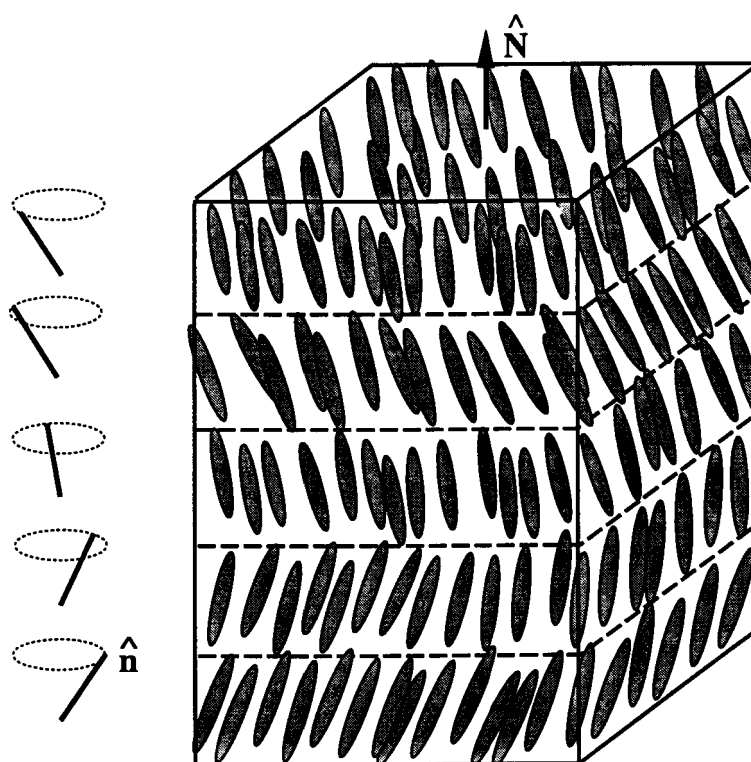


Figure 1.10: In the smectic-C* phase the tilt direction rotates on passing from one layer to another as represented. The periodicity is usually of the order of a micron.

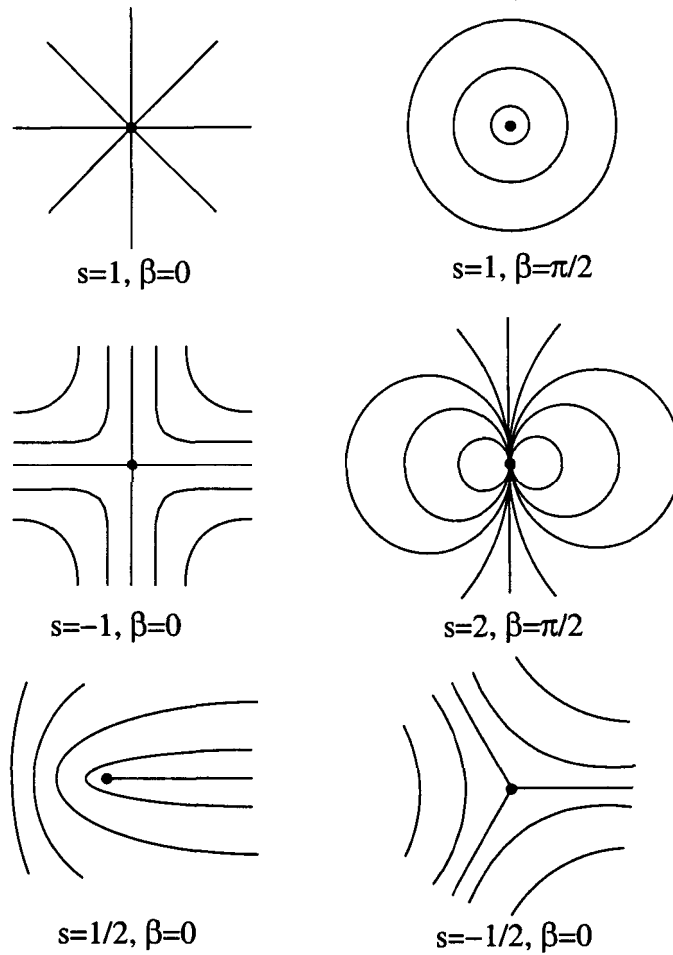


Figure 1.11: Schematic drawings of a few disclinations that can occur in a nematic if the director is confined to the plane of the paper. In a bulk nematic the $s = 1$ structures can 'escape' out of the plane of the paper to form non-singular defects. The $s = 1/2$ structures reflect the $\hat{\mathbf{n}} \equiv -\hat{\mathbf{n}}$ symmetry of the medium. These half integer disclinations are forbidden in the c-vector field of the smectic-C phase.

1.2 Defects in liquid crystals

1.2.1 Disclinations

Because they have long range orientational order, liquid crystals can exhibit a class of topological defects called disclinations [1, 2, 6, 7]. Disclinations are classified based on the director field which produces them. The strength, s , of a disclination is defined as the angle by which the director orientation rotates along a closed loop enclosing the disclination divided by 2π . In the case where the director is confined

to a parallel set of planes,

$$\oint \frac{d\phi}{dl} dl = 2\pi s, \quad (1.8)$$

where ϕ defines the orientation of the director in a plane. The integral is usually taken in a counter-clock-wise sense.

In its simplest form, with a one elastic constant approximation, the elastic energy density given by Eq. 1.3 can be expressed as

$$f_{el} = \frac{1}{2} K (\nabla\phi)^2. \quad (1.9)$$

The Euler-Lagrange minimisation condition corresponding to Eq. 1.9 is

$$\nabla^2\phi = 0. \quad (1.10)$$

Equation 1.10 has solutions of the form

$$\phi = s \tan^{-1} \left(\frac{y}{x} \right) + constant = sa + \beta. \quad (1.11)$$

The allowed values for s depend on the symmetry of the medium. In the case of nematics, s can be any multiple of $\pm 1/2$ because of the $\hat{\mathbf{n}} \equiv -\mathbf{i}\mathbf{i}$ symmetry. Some examples with half-integer and integer values of s are represented in Fig. 1.11. For such structures, the elastic energy density given by Eq. 1.9 diverges as $r \rightarrow 0$, where $r = \sqrt{(x^2 + y^2)}$. In practice, a 'core' region around this point will be 'molten' when the elastic energy cost exceeds the energy cost for melting the medium in that region.

If the director is allowed to 'escape' from the plane of the paper as in a bulk nematic, the $+1$ defects take non-singular configurations [1, 2]. In this the director orientation can be defined at all points and hence there is no molten core.

In the case of smectic-C, the c -vector is polar, and hence only disclinations with integer values of s are allowed in the c -field. Moreover, the disclinations are always singular.

Like electrical charges, disclinations with the same sign repel and those with opposite signs attract each other. A disclination pair with equal and opposite signs produces a far-field distortion similar to that without any defects. The integral of Eq. 1.8 taken around a loop enclosing such a pair is equal to zero. They can, in fact, attract and annihilate each other.

Apart from these bulk disclinations, there can also be surface disclinations in the presence of interfaces at which the director makes a non-zero projection on to the plane of the interface. In the last chapter we describe a new organisation of surface disclinations in drops of a nematic liquid crystal doped with a polymer. These drops merge to form large domains in which the surface disclinations form periodic arrays. Such patterns are not observed in pure nematics.

In the second chapter we present the experimental observation of a new type of helical disclination lines in smectic-C domains co-existing with the nematic phase of a binary mixture. This new structure is an example of spontaneous chiral symmetry breaking as the constituent molecules are *achiral*. In the third chapter we discuss the stability of such a structure using a simple theory of elasticity.

1.2.2 Dislocations

Apart from disclinations, smectic liquid crystals can exhibit dislocations due to their layered structure. Consider smectic layers with the layer normal along the Z-axis. In the presence of a dislocation, the change in the layer displacement field, u , integrated along a closed loop enclosing the dislocation line is

$$\oint d\mathbf{u} = (nd)\hat{\mathbf{z}} = \mathbf{b} , \quad (1.12)$$

where d is the layer spacing and \mathbf{b} is called the Burgers vector of the dislocation.

The nature of the dislocation depends on the relative orientations of \mathbf{b} and the dislocation line. If \mathbf{b} is parallel to the dislocation line, it is called a screw dislocation. In this, the smectic layers climb up or down by an integral number of

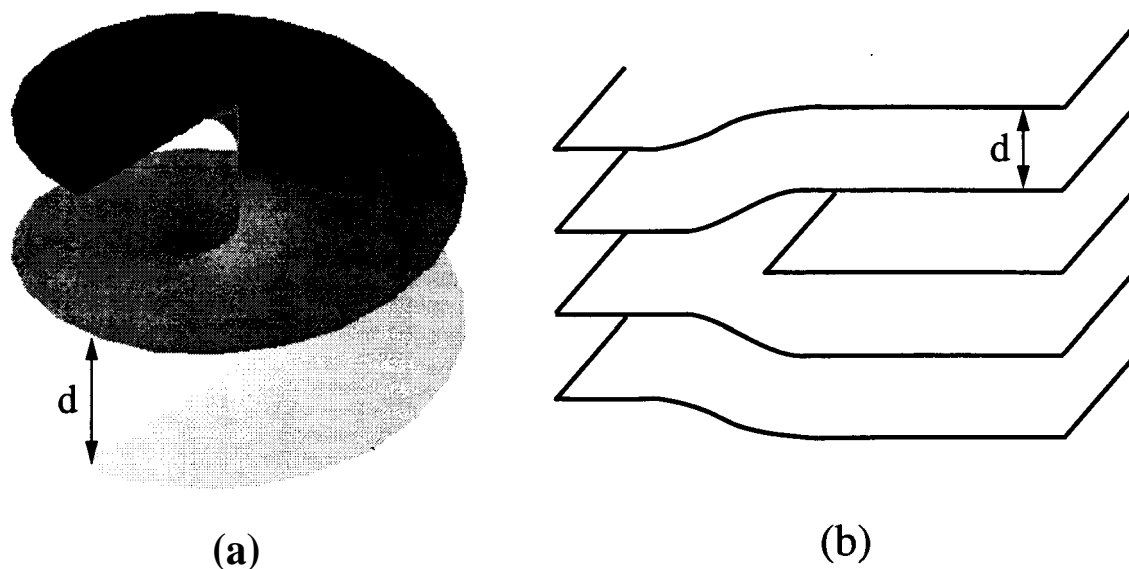


Figure 1.12: Schematic diagrams of the smectic layering close to a screw dislocation (a) and an edge dislocation (b) lines.

layer spacings on going round the dislocation line once. If b is perpendicular to the dislocation line, its called an **edge dislocation**. In this case, a certain number of layers are added or removed from one side of the dislocation line. These two types of dislocations are schematically shown in Fig. 1.12.

Like disclinations, dislocations with the same sign repel and those with opposite signs attract each other.

1.3 Defect induced phases in liquid crystals

Liquid crystals are rather soft, so soft that weak effects like chiral interactions can overcome elastic forces to produce highly non-uniform structures. In fact, the richness of the liquid crystalline structures arises partly due to the interplay between chirality which prefers a twist deformation in the Frank-director and elasticity which favours a uniform director field. Two such structures, namely, the cholesteric and the smectic-C*, have already been discussed. When the chiral strength is increased, some compounds show more complicated structures where defects proliferate in or-

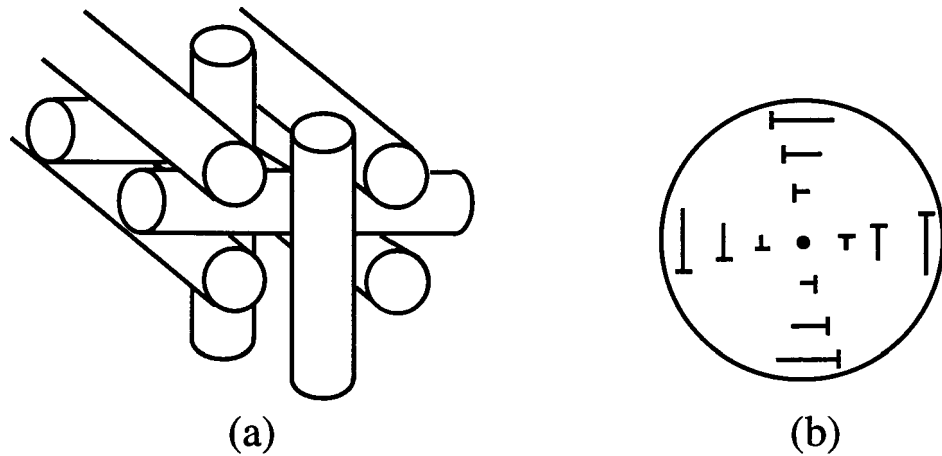


Figure 1.13: Schematic diagrams of (a) the arrangement of the double-twist cylinders in the BP2 phase and (b) the director arrangement in a double-twist cylinder viewed along its axis. The nails represent the projection of the director on to the plane of the figure with the nail head indicating the end which is closer to the observer.

der to gain chiral energy. Some of these remarkable structures are described below.

1.3.1 Blue phases

Blue phases (BP) occur over a narrow temperature range ($\sim 1^\circ\text{C}$) between the cholesteric and the isotropic phases. The simplest of the blue phases is perhaps the blue phase-2. Its structure consists of a regular packing of double twist cylinders as shown in Fig. 1.13. The medium has cubic symmetry and the periodicity is of the order of a few thousand angstroms. Hence most of them Bragg scatter light in the visible range.

1.3.2 Twist Grain Boundary phases

Smectic liquid crystals are incompatible with a simple cholesteric-like twist deformation of the Frank-director. This is because such a deformation necessarily involves changes in the spacing between the smectic layers. This is energetically very expensive. However, in some smectics, when the molecular chirality is strong enough, twist can penetrate in the form of screw dislocations. This possibility was pointed out by de Gennes based on a detailed analogy between the smectics and supercon-

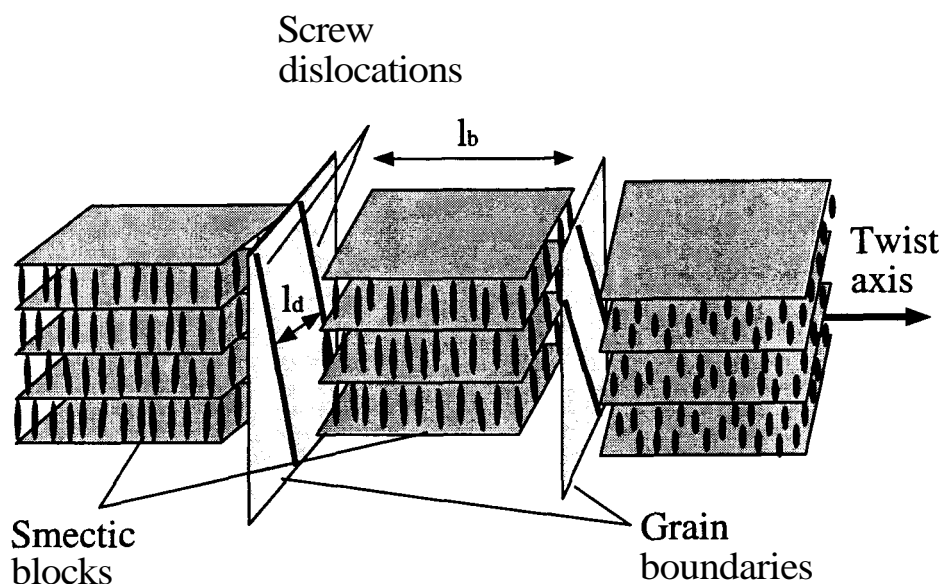


Figure 1.14: Schematic diagram of the TGB_A structure which was predicted by Renn and Lubensky [8] and discovered by Goodby *et al.* [9].

ductors [10, 1]. The possibility of a thermodynamically stable phase with a twisted smectic structure was shown by Renn and Lubensky [8] and was first observed by Goodby *et al* [9]. This phase which is referred to as the Twist Grain Boundary (TGB) phase consists of a helical arrangement of smectic blocks separated by grain boundaries as represented in Fig. 1.14. Each grain boundary is made of a linear array of parallel screw dislocations. Such an array of screw dislocations results in a rotation of the smectic layers across the grain boundary. This in turn generates a twist deformation in the Frank-director, and hence the medium gains chiral energy. Depending on the local smectic order TGB phases are classified as TGB_A , TGB_C and TGB_{C^*} . These will be discussed in some detail in chapter four. Very recently, there have been reports on other more complicated TGB-type structures as well [11, 12].

In the fourth chapter, we describe the observation of a new Undulating Twist Grain Boundary phase with smectic- C^* -like block structure ($UTGB_{C^*}$). Besides

having a helical structure within the smectic blocks, this phase is also characterised by a two-dimensional modulation of the grain boundaries orthogonal to the TGB twist axis. This structure has twist distortions along three mutually orthogonal directions and is reminiscent of the blue phases described earlier. A simple theoretical model which accounts for the stability of the $UTGB_{C^*}$ phase as well as the TGB_A and the TGB_C phases is presented in the fifth chapter.