Chapter 1

INTRODUCTION

She wished to make all one immense embrace
That she might house in it all living things
Raised into a splendid point of seeing light...

-Sri Aurobindo in Savitri, -p362

1.1 Introduction

Liquid Crystals were first discovered by Reinitzer in 1888 [1, 2]. They occur thermodynamically in between the crystalline and liquid states of matter. Hence, they are also called Mesophases. Liquid Crystals are so named since they combine in them the properties of liquids and crystals alike. These mesophases may exist in a single component system with highly shape anisotropic molecules. Mesophases induced by heating are called Thermotropic Liquid Crystals. These mesophases can also exist in multicomponent systems where they can be obtained by varying the relative concentration of different components. These are known as Lyotropic Liquid Crystals.

Liquid crystals are further classified based on the underlying continuous and discrete symmetries. In fact, the isotropic liquid is highly symmetric. It is invariant under translations and rotations. On the other hand, a crystal possesses discrete translational and rotational symmetries. In crystals there is both long range positional order and orientational order in the arrangement of molecules on a lattice. In case of plastic crystals there is only the positional order. Liquid crystalline phases possess long range orientational order and in some cases a restricted low dimensional
In addition to the shape anisotropy, the molecule can also possess a chiral center, breaking the inversion symmetry of the resulting phase. In the absence of such a chiral center, the phase is called an Achiral liquid crystal. In the presence of a chiral center, the phase develops an overall global twist and the phase is called a Chiral liquid crystal. The same thing happens if the achiral liquid crystal is doped with chiral molecules.

1.2 Structure of Liquid Crystals

We discuss in this section the structure of a few important achiral and chiral liquid crystals.

1.2.1 Achiral liquid crystals

**Calamatic nematic**: In this phase rod like molecules tend to align along a certain direction leading to an orientational order but with no positional order. A schematic representation of this phase is shown in figure 1.1 (a). The unique direction of preferred alignment is described by a unit vector $\mathbf{n}$ called the director. From symmetry we can see that $\mathbf{n}$ and $-\mathbf{n}$ are both physically equivalent states. Further, in this case the physical properties are anisotropic and the medium has cylindrical symmetry about $\mathbf{n}$.

**Discotic nematic**: This phase is observed when the system is made of disc-like molecules. The unique direction is nearly perpendicular to the plane of the molecule as shown in figure 1.1 (b). Here also the medium is cylindrically symmetric about $\mathbf{n}$ and the physical properties are again anisotropic.

**Smectic A**: In this phase, apart from nematic like orientational order the medium also possesses a positional ordering in the form of one dimensional density modulation in the direction of the director. This leads to a layered structure as depicted in figure 1.2 (a). Here the average orientation of the molecule is perpendicular to the layers.
Figure 1.1: The two nematic phases. (a) Nematic phase with rod like molecules. (b) Nematic phase with disc like molecules. \( \mathbf{n} \) is the director.

**Smectic C**: This phase is often obtained when smectic \( A \) is cooled. Here the average molecular orientation is in a plane at an angle to the layer normal. The projection of the director onto the layers is called the c-director. A schematic representation of the phase is shown in figure 1.2 (b)

Figure 1.2: Schematic representation of the two smectic phases. (a) Smectic A phase with the director(\( \mathbf{n} \)) parallel to the layer normal (\( \mathbf{N} \)) (b) Smectic C phase with the director(\( \mathbf{n} \)) at an angle \( \theta \) to the layer normal(\( \mathbf{N} \)). Also shown is c-director, the projection of the director \( \mathbf{n} \) onto the plane.

1.2.2 **Chiral liquid crystals**

**Cholesteric**: The cholesteric phase is formed when the constituent molecules are chiral or a nematic has a chiral dopant. Here the director \( \mathbf{n} \) rotates in space along
a direction perpendicular to itself. The schematic representation of the phase is depicted in figure 1.3 (a). As the figure shows each layer, **locally**, is nematic like. Hence one could look upon this phase as a twisted nematic phase.

**Chiral Smectic C**: This phase is a twisted phase of smectic $C$. Here the director is tilted within the layers with respect to the layer normal and in addition the director rotates about the layer normal. This phase is schematically shown in figure 1.3 (b).

![Figure 1.3](image)

(a) Cholesteric phase. The twist axis is along z-axis and $q_0$ is the wavevector of the periodicity of the cholesteric. (b) Chiral smectic C phase. The director which is at an angle to the layer normal precesses about this axis and $l$ is the layer spacing. $P_0$ is the pitch of the twisted structure.

## 1.3 Optics of Liquid Crystals

Liquid crystals can be classified, based on the optical properties, as uniaxial or biaxial. Nematic has one optic axis which is along the director $\mathbf{n}$ and it is a uniaxial phase. In case of smectic C there are two optic axes and it is biaxial optically. The two optic axes will be in a plane perpendicular to the c-director. In weakly anisotropic media the laser field does not influence the physical properties of the medium.
1.3.1 Homogeneous anisotropic media

Uniaxial media:
The electrodynamics of such anisotropic media in the general case is very well known. It is described by the dielectric tensor, $\varepsilon_{ij}$, which reduces to a diagonal form in the coordinate system attached to the system. In the uniaxial phase the $\varepsilon_{\parallel}$ is the dielectric tensor component parallel to the optic axis and $\varepsilon_{\perp}$ is the component perpendicular to the optic axis. The difference of these two, $\varepsilon_a = (\varepsilon_{\parallel} - \varepsilon_{\perp})$ is the dielectric anisotropy.

In a uniaxial medium the index ellipsoid is an ellipsoid of revolution. In order to describe the propagation of polarised light in a uniaxial medium, we find the central cross-section of the index ellipsoid perpendicular to the direction of propagation. The axes of the ellipse represent the eigendirections in the medium. One of the axes is always equal to the $\sqrt{\varepsilon_{\perp}}$ and the other axes depends on the direction of propagation with respect to the optical axis. Any wave polarised along one of these directions is transmitted unaltered. Such a beam acquires only a phase on propagation. In case the direction of the electric vector is not along one of these axes, it is resolved into components along these two axes. Since these two waves acquire a phase difference on propagation a linearly polarised light becomes an elliptically polarised light [5].

The three different cases of light propagation through a uniaxial medium is shown in figure 1.4. Also shown in the figure are the various cross-sections for different directions of propagation.

Biaxial media:
In a biaxial medium the index ellipsoid is a general triaxial ellipsoid. Here all the axes are unequal. In this case, to describe the propagation of light in such a medium, we again find the central cross-section of the index ellipsoid perpendicular to the direction of propagation. Here both the axes change as the direction of propagation changes. As said above the incident wave polarised along one of these directions preserves its polarisation. In other cases the beam becomes elliptically polarised.

Theory:
The Maxwell's wave equation in isotropic media for light propagating along z-axis
Figure 1.4: (a) The index ellipsoid of a uniaxial medium. (b), (c), and (d) show the central cross-sections of the index ellipsoid perpendicular to the direction of propagation \( k \) for directions of propagation parallel to the optic axis (z-axis), perpendicular to the optic axis and at any other angle respectively.
can be written as

\[ \frac{d^2 \mathcal{E}(z)}{dz^2} + \left( \frac{\omega \mu}{c} \right)^2 \mathcal{E}(z) = 0 \]  

(1.1)

where \( \mathcal{E}(z) \) is the electric field, \( \omega \) is the angular frequency, \( c \) is the velocity of light, and \( \mu \) is the refractive index. In a uniform medium the wave equation has solutions as the well-known plane wave. These are written as: \( \mathcal{E}(z) = exp(ikz) \), where \( k = \frac{2\pi}{\lambda} \mu \), is the wavevector and \( \lambda \) is the wavelength of light. In an anisotropic medium the displacement vector is not parallel to the electric vector inside the medium. This leads to electric vector components inside the medium if the incident linear polarisation is not along one of the eigendirections. Yet, the polarisation could be preserved on propagation through the medium. In such cases the solution in a homogeneous medium for the electric field components are given by [6]:

\[
\begin{align*}
\mathcal{E}_x &= A(\epsilon_\perp + \epsilon_a \sin^2 \phi)^{\frac{1}{4}} \exp[-i k_0(\epsilon_\parallel \epsilon_\perp)^{\frac{1}{2}}(\epsilon_\perp + \epsilon_a \sin^2 \phi)^{-\frac{1}{2}}(1 - \frac{t}{t_0})] \\
\mathcal{E}_z &= -A \frac{\epsilon_a \sin \phi \cos \phi}{(\epsilon_\perp + \epsilon_a \sin^2 \phi)^{\frac{1}{2}}} \exp[-i k_0(\epsilon_\parallel \epsilon_\perp)^{\frac{1}{2}}(\epsilon_\perp + \epsilon_a \sin^2 \phi)^{-\frac{1}{2}}(1 - \frac{t}{t_0})]
\end{align*}
\]

(1.2)

where, \( t \) is the sample thickness, \( \epsilon_a = \epsilon_\parallel - \epsilon_\perp \), \( k_0 = \omega/c \), \( A \) is the amplitude of the light wave and \( \phi \) is the angle between the director \( \mathbf{n} \) and the \( \mathcal{E} \) vector. When anisotropy \( \epsilon_a \) is very small we can considerably simplify equation (1.2). We use equation (1.2) to work out the effect of a laser field on the orientation of the director \( \mathbf{n} \).

### 1.3.2 Inhomogeneous media

We consider next systems wherein the refractive index varies in one particular direction. This happens when \( \mathbf{n} \) varies in space. We take this direction of variation to be the direction of light propagation. We can generalise the above solution in an anisotropic media. We assume that the director distortions are confined to \( x - z \) plane, i.e., \( \mathbf{n} \) varies along \( z \) only. The Maxwell's wave equation can be solved in the approximation that the scale of distortions in the medium are on a length scale large compared to the wavelength of light. Then solutions to the wave equation become [7, 8]:

\[
\mathcal{E}_x(z) = A(\epsilon_\perp + \epsilon_a \sin^2 \phi)^{\frac{1}{4}} \exp[-i k_0(\epsilon_\parallel \epsilon_\perp)^{\frac{1}{2}} \int \left( \epsilon_\perp + \epsilon_a \sin^2 \phi \right)^{-\frac{1}{2}}dz']
\]

(1.3)
\[ \mathcal{E}_a(z) = -A \frac{\epsilon_a \sin \phi \cos \phi}{(\epsilon_{\perp} + \epsilon_a \sin^2 \phi)^{1/2}} \exp[-i k_o(\epsilon_{||} + \epsilon_a \sin^2 \phi)^{-1/2} \int \epsilon_{\perp} + \epsilon_a \sin^2 \phi] \frac{dz}{dz} \]

where, \( \phi \equiv \phi(z) \) is now a function of \( z \). We use this solution of the Maxwell’s wave equation in the analysis of structural solitons in the director field of nematics and ferronematics (see chapter 6).

### 1.3.3 Chiral media

Cholesterics and chiral smectic \( C \) are examples of spontaneously twisted media. This leads to periodic modulation of the refractive index of the medium. In such periodic liquid crystals we consider two geometries viz., the Bragg mode and the diffraction mode. When light is propagating along the direction of the helix, it is known as the Bragg mode and when light propagates perpendicular to the helix axis it is referred to as the diffraction mode. We summarise below the well known results for various regimes in the Bragg geometry [4].

(i) \( \lambda \ll \Delta \mu P \) (\( \Delta P = \) local birefringence, \( P = \) Pitch of the structure)

In this limit the eigenstates have their electric vectors either parallel or perpendicular to the local director everywhere in the medium. This limit is also known as the Mauguin limit or the adiabatic limit.

(ii) \( \Delta \mu P < \lambda < \mu P \) (\( \mu = \) average refractive index)

In this limit the eigenstates are right and left circular polarised waves propagating with different velocities. Here the system exhibits a very large optical rotation. This limit is known in the standard literature as the de Vries limit.

(iii) \([\mu P - (\Delta \mu P/2)] < \lambda < [\mu P + (\Delta \mu P/2)]\)

In this band of wavelengths we get the Bragg band. Eigenstates are again right and left circularly polarised waves. The circularly polarised wave that has the same sense as the helix suffers total reflection. The orthogonal component state goes through unaltered but for a phase change. In the case of Bragg reflected circular wave a standing wave is set up inside the medium by interference of the forward and the backward propagating waves. The net wave is linearly polarised whose polarisation rotates along the twist axis following the local director. The electric vector of this
standing wave is, in general, at an angle to the local director everywhere inside the medium. In a medium with positive optical dielectric anisotropy, at the short wavelength edge of the Bragg band this electric field is parallel to the director while it is perpendicular to the director at the long wavelength edge.

(iv) $\lambda \gg \mu P$

Here also the right and left circularly polarised waves are the eigenstates. Again the system exhibits optical rotation but of opposite sign and it is very small compared to that found under (ii).

The Mauguin limit can be easily realised experimentally by adding chiral molecules to an achiral medium. In this limit the electric vector follows the director twist inherent in the cholesteric. It may be mentioned in passing that it is in this limit that the twisted nematic displays work.

### 1.4 Elasticity of Liquid Crystals

In a well aligned nematic, the molecules are on the average along one common direction $\pm n$. However, due to the presence of confining boundaries or external fields deformations in the alignment sets in. These deformations or spatial variations in $n$ can be resolved into three main types of deformations. They are splay, bend and the twist type distortions. The typical boundary conditions which lead to these distortions are shown in the figure 1.5. These distortions can be described by a vector field.

![Figure 1.5: The three types of director distortions: (a) Splay (b) bend and (c) twist](image)

Figure 1.5: The three types of director distortions: (a) Splay (b) bend and (c) twist

which can be obtained as gradients in the director, $n$. The splay type of distortion is associated with non-vanishing values for $(V \cdot n)$. The bend type of distortions result
in a non-zero \((n \times V \times n)\) and finally for twist type of distortions \((n \cdot V \times n)\) is non-zero.

### 1.4.1 Nematic

The elasticity of nematic liquid crystal can be described by writing down the free-energy density due to these deformations. The theory of describing elasticity in terms of the director distortions was initiated by Oseen [9] and Zocher [10]. It was further developed by Frank [11] and Ericksen [12]. The free-energy density is a quadratic form in the said gradients of \(n\). Hence, the free-energy density of a nematic will involve the three terms associated with the three types of distortions described above. Each of these term is associated with an elastic constant. This free-energy is at times referred to as Frank free-energy in the literature. The Frank free-energy density is then [3].

\[
\mathcal{F}_{\text{elastic}} = \frac{1}{2} \left[ K_1 (\nabla \cdot n)^2 + K_2 (n \cdot \nabla \times n)^2 + K_3 (n \times \nabla \times n)^2 \right]
\]

where \(K_1, K_2, K_3\) are splay, twist and bend elastic constants respectively. Generally, these elastic constants satisfy the inequality \(K_2 < K_1 < K_3\). The magnitude of these elastic constants is of the order of \(10^{-8} \text{dyne}\) which is very small. Thus director deformations can be induced very easily in these systems. In many situations, to describe the phenomena qualitatively, we use the so called 'one – constant approximation'. In this case we have \(K_1 = K_2 = K_3 \equiv K\); and the Frank free-energy density (1.4) becomes:

\[
\mathcal{F}_{\text{elastic}} = \frac{K}{2} \left[ (\nabla \cdot n)^2 + (\nabla \times n)^2 \right]
\]

### 1.4.2 Smectic

As already described they are layered structures. Thus one of the deformations in these systems are described by the layer displacement variable \(u(r)\) [3]. The variable \(u(r)\) can be related to the nematic director in smectic \(A\) in the following way:

\[
n_x = -\frac{\partial u}{\partial x}; \quad n_y = -\frac{\partial u}{\partial y}
\]

The first type of distortions is a layer compression or dilation (see figure 1.6 (a)).
Figure 1.6: The two basic distortions in smectics: (a) layer compression or dilation (b) layer curvature

This is described by the gradients in the variable \( 'u(\mathbf{r})' \) and is of the form,

\[
\frac{B}{2} \left( \frac{\partial u}{\partial r} \right)^2
\]

where \( B \) is the corresponding elastic constant and is of the order of \( 10^8 \) dyne/cm².

The second type of distortion involves the layer curvature. This results in the curvature of layers as shown in the figure 1.6 (b). It leads to splay deformations in the local director which is similar to nematic director. This is described by a term in the free-energy density of the form:

\[
\frac{K_1}{2} \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right)^2
\]

The magnitude of \( K_1 \) is same as in the nematic phase. These are the two main contributions to the elastic free-energy density in smectics.

### 1.4.3 Cholesteric

**Usual elasticity:**

As described earlier cholesterics can be considered as a twisted nematic phase. Thus the Frank free-energy density for the nematic can be used to describe distortions in the cholesteric also. Due to spontaneous chirality in the system there is a spontaneous twist. This can be described by adding to the free-energy density a linear term in \( \mathbf{n} \cdot \nabla \times \mathbf{n} \). Then the free-energy density for cholesterics can be written as [3],

\[
\mathcal{F}_{\text{elastic}} = \frac{1}{2} \left[ K_1 (\nabla \cdot \mathbf{n})^2 + K_2 (\mathbf{n} \cdot \nabla \times \mathbf{n} - q_o)^2 + K_3 (\mathbf{n} \times \nabla \times \mathbf{n})^2 \right]
\]
Here $q_0 = 2\pi/P_o$ with pitch $P_o$.

Coarse-grained approximation:

In the unperturbed state the cholesteric can be considered as made of layers. The layers are equidistant (equal to pitch $P_o$) and parallel. In the weak distortion limit, each layer is displaced by an amount $'u(r)'$ along $z$; $'u(r)'$ is a slowly varying function of $r$. In the coarse-grained approximation free-energy density must be as in smectic A:

$$\mathcal{F}_{cg} = \frac{B}{2} \left( \frac{\partial u}{\partial z} \right)^2 + \frac{K}{2} \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right)^2$$  \hspace{1cm} (1.9)

We can get values of $B$ and $K$ in terms of $K_1$, $K_2$ and $K_3$. It can be shown [3] that $B = K_2 q_0^2$ and $K = \frac{3}{8} K_3$.

1.5 Field Induced Deformations in Liquid Crystals

As described earlier, the curvature elastic constants being very small director distortions can be easily induced in liquid crystals. These are anisotropic dielectric and diamagnetic materials and thus respond to external static electric and magnetic fields. The anisotropy in these liquid crystals lead to dielectric and diamagnetic torques which affect the director orientation. The dielectric free-energy density is given by [3],

$$F_{elec} = -\frac{\epsilon^s}{8\pi} E^2 - \frac{\epsilon^a}{8\pi} (n \cdot E)^2$$  \hspace{1cm} (1.10)

where $\epsilon^s_\parallel$ and $\epsilon^s_\perp$ are the static dielectric constants parallel and perpendicular to $n$ and $\epsilon^a = \epsilon^s_\parallel - \epsilon^s_\perp$ is the static dielectric anisotropy. The diamagnetic free-energy density can be similarly written as:

$$F_{mag} = -\frac{\chi^s_\perp}{2} H^2 - \frac{\chi^a}{2} (n \cdot H)^2$$  \hspace{1cm} (1.11)

Here, $\chi_\parallel$ and $\chi_\perp$ are the diamagnetic susceptibility components parallel and perpendicular to the director and $\chi_a = \chi_\parallel - \chi_\perp$ is the diamagnetic anisotropy. It is easy to see from equation (1.10) and (1.11) that in an unbounded nematic with positive dielectric or diamagnetic anisotropy director aligns itself parallel to the external field and perpendicular to the field if the material has negative dielectric or diamagnetic
anisotropy. The form of free-energy density in an external field is similar even in cholesteric. This is due to the fact that cholesteric can be looked upon as a nematic locally. In smectic too the same free-energy density holds good. Here the local orientation of molecule is described by a director similar to the nematic director. We consider below the field induced distortions in various configurations in nematics, cholesterics and smectics.

1.5.1 Kinks or walls

Topological defects form an important component of studies in condensed matter physics. Walls or kink states are permitted defect states in electric or magnetic fields. These exist due to the degeneracy in the orientation of the director with respect to the external field. This results in wall type of defects. Such defects were first discussed by Helfrich [13]. In a nematic due to $\mathbf{n}$ being equivalent to $-\mathbf{n}$, the resulting topological winding could be any integral multiple of $\pi$. The defect configuration connecting $\mathbf{n}$ and $-\mathbf{n}$ states is naturally distorted and is thus associated with an elastic distortion energy. These are static walls in a nematic in the presence of an external magnetic field. There could be pure twist walls or splay-rich or bend-rich walls. In each case the director turns through $180^\circ$ along a direction normal to the wall as shown in figure 1.7.

In case of nematics doped with aligned ferromagnetic grains with magnetisation along $\mathbf{n}$ (say), the $\mathbf{n}$ and $-\mathbf{n}$ equivalence is lost and then the topological winding is $2\pi$. In such walls the director distortions are in 1D and are often called planar solitons in literature [14]. Yet, unlike true solitons these do not preserve their shape and velocity.
after a pair-wise collision. They are rather structurally like kinks. Kinks also appear naturally in the form of a lattice [15, 16] near a electric or magnetic field induced transition of a cholesteric to a nematic state. However, optical effects that can occur when a laser is used for probing topological defects appear to have not attracted as much attention. In chapter 6 we address ourselves to nonlinear optical effects on topological walls.

Here we briefly sketch the kink solution in a nematic in the presence of external magnetic field. The relevant free-energy density is:

$$\mathcal{F} = \frac{K}{2} \left( \frac{\partial \phi}{\partial z} \right)^2 - \frac{\chi_a H^2}{2} \cos^2 \phi$$  \hspace{1cm} (1.12)

where $\phi(z)$ is the angle between the magnetic field and the director. The minimisation of the total free-energy density gives the elastic equilibrium equation:

$$K \frac{\partial^2 \phi}{\partial z^2} = \chi_a H^2 \sin \phi \cos \phi \hspace{1cm} (1.13)$$

$$\frac{\partial^2 \phi}{\partial \eta^2} = \sin \phi \cos \phi$$
where $\eta = z/\xi$ and $\xi = \sqrt{\frac{K}{\chi_0 H^2}}$, is the coherence length over which most of the distortions in the medium take place. The above equation is a 'sine – Gordon' equation which permits soliton solutions. We impose the boundary conditions:

$$\phi(-\infty) = 0, \quad \phi(\infty) = \pi; \quad \frac{\partial \phi}{\partial z}(\pm \infty) = 0$$

With these boundary conditions we obtain a kink solution:

$$\phi(z) = 2 \arctan \left[ \exp \left( z/\xi \right) \right]$$

(1.14)

A typical kink solution is shown in figure 1.8.

### 1.5.2 Soliton lattices

**Cholesteric in a magnetic field:**

A cholesteric-nematic transition is possible in an external electric or magnetic field. This was first suggested by de Gennes [15] and R.B. Meyer [17] independently. In an external field there are internal distortions in the helical structure. The initial situation for low field is represented in figure 1.9 (a) and that for intermediate fields in figure 1.9 (b). In regions $A, A',...$ the molecules are favourably aligned along the field. In regions such as $B, B',...$ the molecules are unfavourably oriented with respect

![Figure 1.9: The various stages in the cholesteric to nematic transition in a magnetic field are shown. (a) Uniform cholesteric (b) Soliton lattice at a field below the critical field $H_c$ for helix unwinding and (c) Uniform nematic or completely unwound cholesteric at a field greater than the critical field.](image)
to the field. Thus if the field becomes strong enough region A will expand. Region B, on the other hand, cannot contract very much, since this would have to counter the twist. The overall result is an increase of the pitch $P$ with field. At higher fields, this leads to a succession of $180^\circ$ kinks separating large widely uniform regions. Each kink has a finite thickness, of the order of $2\xi$, where $\xi$ is defined as $\xi = \sqrt{K_2/\chi_0} H$. This structure is referred to as a soliton or a kink lattice. Finally, at a certain critical field $H_c$, the walls become infinitely separated ($P \to \infty$) and we obtain a nematic structure. The pitch variation with the increase of field is shown in the figure 1.10. As shown in the figure the pitch is essentially undisturbed at low fields. At higher

![Figure 1.10: The variation of the pitch $P$ as the magnetic field is varied. Pitch diverges at a critical field $H_c$.](image)

Figure 1.10: The variation of the pitch $P$ as the magnetic field is varied. Pitch diverges at a critical field $H_c$.

fields $P$ increases and finally diverges at the critical field.

We could also study this transition from the point of view of existence of a single wall in an infinite nematic medium. Assuming always a one-dimensional situation of pure twist, where

$$n_x = \cos \phi(z), \quad n_y = \sin \phi(z), \quad n_z = 0,$$

we find the equilibrium equation (as discussed earlier),

$$\xi^2 \frac{\partial^2 \phi}{\partial z^2} = \sin \phi \cos \phi$$

(1.15)
The first integral to this equation is

\[ \xi^2 \left( \frac{\partial \phi}{\partial z} \right)^2 = \sin^2 \phi \]  

(1.16)

ensuring that \( \frac{\partial \phi}{\partial z} \to 0 \) as \( \phi \to \pi \).

The free-energy (per unit area) of the wall, compared to the energy of nematic conformation, is then

\[ F_{\text{wall}} = \int \left\{ \frac{K_2}{2} \left[ \left( \frac{\partial \phi}{\partial z} - q_o \right)^2 - q_o^2 \right] + \frac{\chi_a H^2}{2} \sin^2 \phi \right\} dz \]  

(1.17)

Using equation (1.16) we find that the first and the third term are equal and the energy of the wall becomes:

\[ \frac{F_{\text{wall}}}{\chi_a H^2} = \int \xi^2 \frac{d\phi}{dz} \bigg|_0^\pi d\phi - q_o \xi \int \frac{d\phi}{dz} \bigg|_0^\pi d\phi = 2 - \pi q_o \xi \]  

(1.18)

Here, \( \xi = \sqrt{\frac{K_2}{\chi_a H^2}} \). Thus it becomes unfavourable to have kinks when this energy becomes positive i.e.,

\[ \xi(H) < 2/\pi q_o \]

In terms of the field this corresponds to a critical field

\[ H_c = \frac{\pi}{2} \sqrt{\frac{K_2}{\chi_a}} q_o = \pi^2 \sqrt{\frac{K_2}{\chi_a}} \frac{1}{P_o} \]  

(1.19)

where \( P_o \) is the unperturbed pitch.

Typically, \( K_2 \approx 10^{-6} \) dyne, \( \chi_a = 10^{-7} \) cgs, \( P_o = 20 \mu m \) which gives for \( H_c = 15000 G \).

Incidentally, this transition is a thermodynamic second-order phase transition.

**Nematic in a static electric field**

We next consider a nematic made of either pear-shaped or banana shaped molecules. In such nematics a new type of contribution to the free-energy density is possible. It is well known that in certain solids, a strain will induce a polarisation \( P \). The sources of the strain is usually external pressure and this effect is referred
Figure 1.11: (a) The pear shaped molecules and a splay distortion resulting in a non-zero polarisation. (b) The banana shaped molecules and a bend distortion which leads to a non-zero polarisation.

... (text continues)
This leads to a flexoelectric lattice which involves alternate splay and bend distortions as shown in the figure 1.12.

![Figure 1.12: A nematic in the presence of a static electric field leads to a flexoelectric lattice. The lattice wavevector is parallel to z-axis. E is the static electric field.](image)

We observe that the free-energy density (1.21) is mathematically similar to the free-energy density in the case of cholesterics (see equation (1.17)). In fact, the equilibrium equations in both cases are identical. The wavevector associated with the periodicity of the structure is given by $q = \frac{\partial \phi}{\partial z}$ and is equal to $q = e E/K$. As this structure exists in an electric field, obviously the periodicity is a function of the field. Extending the analogy further we can consider the analogue of cholesteric-nematic transition. We find that this condition $\xi(H) < 2/\pi q_o$ reduces to

$$\sqrt{4\pi K/\epsilon_o E^2} < 2K/\pi e E$$

or $\epsilon_o < \pi^2 e^2/K$  \hspace{1cm} (1.23)

Thus we find that a flexoelectric lattice exists only when (1.23) is satisfied [19].

### 1.5.3 Undulation instability

**Cholesterics:**

We next examine the effect of a magnetic field acting along the helical axis of a cholesteric film. If boundary effects are such as to maintain the orientation of helical axis, then we expect a deformation where the director is tilted towards the field leading to conical type of distortion. It was realised by Helfrich that yet another type of deformation can set in [20]. This distortion is in the form of periodic distortion of layers. The layers are ripple-like along a direction parallel to the layers.
figure 1.13). Such a distortion has been experimentally observed both in magnetic

![Figure 1.13: The (a) geometry for the undulation instability in a cholesteric and (b) the corrugation of layers. The twist axis is along z-axis.](image)

and electric fields [21, 22]. The theory of this instability was worked out by Helfrich [20] and subsequently also by Hurault [23]. We briefly summarise the theory here.

We consider the description of cholesterics in the coarse-grained approximation as described earlier. The free-energy density for $u = u(z, x)$ is rewritten here for easy reference:

$$
F_{cg} = \frac{K_2}{2} q_z^2 \left( \frac{\partial u}{\partial z} \right)^2 + \frac{3K_3}{16} \left( \frac{\partial^2 u}{\partial x^2} \right)^2 - \frac{\chi_a H^2}{2} \left( \frac{\partial u}{\partial z} \right)^2
$$

(1.24)

We introduce perturbations in $u$: $u = u_0 \cos(q_x x) \cos(q_z z)$, where $q_z = \pi/t$. $t$ is the sample thickness. Minimising the total free-energy we get for the equilibrium equation

$$
\left( K q_z^2 q_x^2 + \frac{3}{8} K q_z^2 - \frac{\chi_a}{2} H^2 \right) u = 0
$$

(1.25)

where we have used the one-constant elastic approximation. The distortion comprises of two components bend and twist. The limit $q_x \to \infty$ excites the bend mode while $q_x \to 0$ excites the twist mode. The optimum wavevector corresponds to admixture of both modes and is given by

$$
q_z^4 = \frac{8}{3} q_x^2 q_x^2
$$

(1.26)

The threshold field for the instability to set in is given by:

$$
H_{Helfrich}^2 = \sqrt{6} K q_0 q_x / \chi_a
$$

(1.27)
For typical values of the material parameters $K = 10^{-6}$ dyne, $P_o = 20$ pm, $t = 100 \, \mu m$ and $\chi_a = 10^{-7}$ cgs, the critical field is of the order of $3 \, kG$.

**Smectics**

We should expect a similar instability in smectics as well. The critical field for the instability to set in and the wavevector of distortion are given by similar expressions. The critical field is given by

$$H_{Hel} = \sqrt{\frac{2\pi K}{\chi_a \sqrt{K/B \, t}}}$$

Here $K$ is the curvature elastic constant and $B$ is the elastic constant associated with the dilation of layers. The wavevector of lateral periodic distortion is given by:

$$q_x^2 = q_z / \lambda = \pi / \left( \sqrt{K/B \, t} \right)$$

For typical values of the material parameters and $t = 1 \, \text{mm}$ gives for the critical field $H_c \approx 50 \, kG$. It should be noted that even for large sample thickness the critical field is quite high.

### 1.6 Well Known Nonlinear Optical Processes in Liquid Crystals

In this section we present briefly the important nonlinear processes that are well established in liquid crystals viz., the laser induced director reorientation and thermal indexing. Some of the nonlinear optical effects in liquid crystals have already been reviewed by others [24, 25, 26, 27, 28].

**1.6.1 Laser induced director reorientation**

It was realised in 1980's that the electric field associated with a laser beam can simulate the effect of an external static or low frequency electric or magnetic field since the field effect is quadratic in the field strength. As a result, the director tends to align along the electric field $\mathcal{E}$ of the laser field. This in turn changes the refractive index as seen by the laser beam. This effect was first reported by B. Ya. Zeldovich and
his collaborators [8, 29, 30]. They reported a large nonlinear response from a nematic liquid crystal. Around the same time I. C. Khoo reported a large nonlinearit in an experiment on self-focusing and four wave mixing [31] a work based upon a suggestion made by Hermann and Serinko in an earlier paper [32]. It also appears that even A. Saupe in 1969 had studied the effect of a laser field but unfortunately he did not publish his views [33].

Consider a uniform nematic as shown in figure 1.1. Let the incident linearly polarised laser light propagate at an angle to the director with its E in the (n, k) plane. The refractive index $\mu$ as seen by the electric field E is found from the crystal optics formula given by:

$$\frac{1}{\mu(\phi)^2} = \frac{\cos^2 \phi}{\mu^2_\parallel} + \frac{\sin^2 \phi}{\mu^2_\perp}$$

(1.28)

The optical field $E$, being at an angle to the director leads to director reorientation. After reorientation the refractive index and hence the phase acquired by the beam changes. This effect is similar to the familiar nonlinear optical effects where the laser affects the refractive index of a medium. The director reorientation also affects the laser beam itself. This is similar to self-action effects found in traditional nonlinear optics.

The process of director reorientation is a nonlinear process that is independent of the frequency of the incident laser field. Also the induced change in refractive index is proportional to intensity, and is thus similar to the classical Kerr process. Nonlinear optical effects due to the director reorientation process has been extensively studied by various groups. Many well known nonlinear optical effects like self-focusing, self-defocusing, self-phase modulation, pump-probe type of experiments, degenerate four-wave mixing, etc have been studied theoretically and demonstrated experimentally. But in liquid crystals there are certain nonlinear optical effects peculiar to them like hydrodynamic flows [34] and structural instabilities [8] associated with the director reorientation.

It should be mentioned here that the change in refractive index is very sensitive to the initial director orientation, sample preparation and polarisation of the
incident laser beam. For instance, if the electric field of the laser is parallel to the
director no director reorientation occurs and the nonlinearity due to this process is
absent. On the other hand, if the director is perpendicular to the electric field of the
laser the director experiences maximum torque and the nonlinearity is maximum. It
is also an example of saturation nonlinearity because the director reorientation torque
is zero after the director has aligned itself parallel to the laser field. In cases where the
director is rigidly anchored at 90° at the boundaries and the incident electric vector
of the laser is perpendicular to the director then again we find static field effects. The
director reorientation is absent up to a threshold intensity beyond which we get the
director reorientation.

Another feature must be mentioned here which makes this process different
from other familiar nonlinear processes. Usually a laser beam has a finite beam width
with a central peak intensity distribution. This yields maximum director reorientation
at the centre relative to the outer regions. This leads to non-local effects, due to the
inherent elasticity of liquid crystals, because of which the director reorientation occurs
even in regions outside the laser beam [35, 36].

The importance of laser induced director reorientation as a nonlinear process
can be appreciated by looking at the laser induced changes in the refractive index.
The birefringence of the liquid crystals is of the order of 0.1. Hence the maximum
change in the refractive index due to this process is 0.1 when the director turns
through 90°. Even when the director is anchored at the boundaries a change in
director orientation by 30° can easily be affected with an intensity of 50 W/cm².
This corresponds to a change in refractive index of the order of 0.01. In some cases
we can find the change to be even greater than this. If the refractive index is defined
as $\mu = \mu_o + \mu_2 I$, incorporating the intensity dependent part then $\mu_2$ corresponds
to the nonlinear coefficient. In the process of director reorientation $\mu_2$ is of the
order of $10^{-4}$ cm²/W. This should be compared with the nonlinear coefficient of
$10^{-12}$ cm²/W found for CS₂ one of the most optically nonlinear media. It is for this
reason B. Ya. Zeldovich and coworkers described the nonlinearity in liquid crystals
1.6.2 Thermal indexing

In addition to the process of director reorientation there can be an additional non-linear process due to laser absorption in the medium which heats the material with a consequent change in the refractive index. This process is referred to in the literature as Thermal Indexing. The refractive index change $\delta \mu$ is related to change in temperature $dT$ \[37\]:

$$
\delta \mu(T) = \frac{d\mu}{dT} \left( \frac{t^2 \chi}{\pi^2 \kappa} \right) I
$$

(1.29)

Here $t$ is the sample thickness, $\chi$ is the optical absorption coefficient, and $\kappa$ is the thermal conductivity of the medium. The raise in temperature could be as large as 10K for an absorption coefficient of 0.01 cm$^{-1}$ \[37\]. From symmetry considerations it is easy to see that in nematic liquid crystals which are uniaxial, the ordinary and extraordinary refractive indices should suddenly change to a single refractive index at the nematic-isotropic phase transition at which the medium becomes an isotropic liquid. In this process the extraordinary refractive index decreases and the ordinary refractive index increases with the raise of temperature. If the laser polarisation is such that the electric vector is parallel to the director the change in refractive index, $\delta \mu$ is negative. For an incident beam with intensity peak at the center if the electric vector of the laser beam is parallel to the director then an incident plane wavefront emerges as a convex wavefront. This leads to self-divergence as shown in figure 1.14 (a). If the electric vector of the laser beam is perpendicular to the director, the change in the refractive index is then positive. This converts an incident plane wavefront into a concave wavefront. This leads to self-focusing as shown in figure 1.14 (b). In the second case the director is assumed to be so strongly anchored that the process of director reorientation is absent. Incidentally, when the electric vector is at an angle $\phi$ to the director, in the plane of the electric field and the direction of propagation then the change in the refractive index is given by \[37\]:

$$
\frac{d\mu(\phi)}{dT} = \zeta(\phi) \frac{\mu_\perp}{\mu(\phi)} \frac{d\mu_\perp}{dT}
$$

(1.30)
Here, $\zeta(\phi) = \epsilon(\phi) \left[ \frac{\epsilon_{\parallel}}{\epsilon_{\perp}} \frac{a'_\parallel}{a'_\perp} - \frac{a'_\perp}{a'_\parallel} \right] \cos^2 \phi$ with $a'$ defined as: $\frac{du}{dt} = -a' \frac{d\phi}{dt}$, $a' > 0$, and $\mu(\phi)$ is the refractive index as seen by the optical beam when the director makes an angle with the electric vector. We note that for $\zeta(0) = 1$, $\frac{d\mu(0)}{dt} = \frac{d\mu}{dt}$ and for $\zeta(\pi/2) = -a'$, $\frac{d\mu(\pi/2)}{dt} = \frac{d\mu}{dt}$. Also there exists certain angle $\phi_0$ at which $\frac{d\mu(\phi_0)}{dt} = 0$.

![Diagram](image)

Figure 1.14: Effect of thermal indexing on beam width. (a) Light propagating in a homogeneously aligned nematic with the electric vector parallel to the director. The beam diverges on propagation. (b) Light propagating in the homogeneously aligned nematic with the electric vector perpendicular to the director. The beam converges on propagation.

In this thesis we have not considered some of the other phenomena which also contribute to the nonlinearities in liquid crystals. In the dye-doped liquid crystals it was realized by Janossy that with certain dyes known as anthraquinone dyes the process of director reorientation can be affected [38]. In fact they reported an order of magnitude higher nonlinear coefficients due to this process. This effect is also known as Janossy effect [39]. As this process is not yet completely understood and also is not a universal effect for all dye-doped systems we have not considered this process. In certain molecules the conformational transformation can also be induced by the laser beam. The molecules can undergo trans–cis isomerisation leading to nonlinear optical effects [40]. Again these effects are not considered since they are specific to
certain type of molecules.

1.7 Optical Solitons

We have briefly described in the previous section the static kinks or walls in the presence of external fields. These are to be distinguished from the optical solitons associated with light beams in nonlinear media. Optical solitons in liquid crystals have not received enough attention and the last chapter is devoted to beams propagating through liquid crystals. In this section we briefly present what is known of soliton formation and propagation in usual nonlinear media [41]. These optical solitons could be either spatial or temporal solitons. The optical nonlinearities of a medium will have to be considered along with not only the usual self-diffraction but also dispersion effects. In some media, self-divergence effects of diffraction or dispersion on a light beam are opposite in sense to that due to the nonlinearity. At a certain intensity the nonlinear effect can balance exactly the effect of diffraction or dispersion. This results in beams which travel in the medium without change of spatial intensity profile or pulse shape and width. If the nonlinearity balances the effects of dispersion, the resulting soliton is termed a **temporal soliton**. On the other hand, if the nonlinearity compensates the effects of diffraction then the resulting soliton is referred to as a **spatial soliton** [42, 43]. In case of spatial solitons it is possible that the nonlinearity could be either positive or negative. If the nonlinear coefficient is positive the resulting soliton will have a central peak with vanishing asymptotes. In literature this is called a **bright** soliton. On the other hand if the nonlinear coefficient is negative then the soliton solution has a central dip in the intensity on a uniform intense background. Such a soliton is called a **dark soliton** [44]. It should be remarked here that usually the term **soliton** refers to special solutions which preserve their shape after a **pairwise** collision. They are usually described by a system of differential equations which are completely **integrable**. It is known that only the Kerr nonlinearity leads to an integrable differential equation. But most of the nonlinearities in liquid crystals are not of the Kerr type and the resulting differential equations
are not integrable. Hence, they only possess solitary wave solutions. Unfortunately solitary waves are also sometimes referred to in the literature as solitons. However, optical solitons in liquid crystals has not been given enough attention. There are very few studies in this subject [45, 46, 47, 48].

Next we present the analysis of finding a spatial soliton solution when the usual Kerr nonlinearity is operating. At low intensities diffraction dominates while at high intensity self-focusing predominates. Hence at a particular intensity the two opposing effects annul each other. This leads to self-trapping of the laser beam with an unchanging profile. This was first studied by Talanov [49]. The governing one dimensional nonlinear equation is given by [44, 50]:

\[ 2i k_0 \mu_0 \frac{\partial \epsilon(X, Z)}{\partial Z} + \frac{\partial^2 \epsilon(X, Z)}{\partial X^2} + 2k_0^2 \mu_0 \mu_{nl}(I) \epsilon(X, Z) = 0 \]

where \( \epsilon \) is the envelope of the electric field, \( Z = k_0 Z \) is the scaled distance along the direction of propagation, \( X = k_0 X \) is the scaled transverse coordinate, \( \mu_0 \) is the linear refractive index and \( k_0 \) is wavevector of the laser beam. Incidentally, this is a nonlinear Schrodinger equation. The local nonlinearity is introduced by the function \( \mu_{nl}(I) \). Assume a solution of the form \( \epsilon(Z, X) = \psi(X) \exp(i \nu Z) \), where \( \psi(X) \) is a function of \( X \) only. In case of the usual Kerr nonlinearity the function \( n_{nl}(I) \) takes a simple form \( \mu_{nl}(I) = \mu_2 I \), where \( \mu_2 \) is a constant. The permitted spatial soliton is described by:

\[ \psi(X) = \left( \frac{2a}{b} \right) \frac{1}{\cosh(\sqrt{a} X)} \]

where \( a = 2 \mu_0 k_0 \nu \) and \( b = 2 \mu_0 k_0^2 \mu_2 \). Here \( \nu \) is a real positive parameter and \( 1/\sqrt{\nu} \) is directly related to the soliton width. In practice the width of the soliton depends on the full solution of the differential equation subject to the boundary condition that at \( Z = 0 \), the solution matches the input pulse profile. This parameter also determines the amplitude and the wavevector of the soliton along the propagation direction. In liquid crystals, however, \( \mu_{nl} \) takes a complicated structure and the corresponding solitons are very different structurally. Some of these studies are described in detail in the chapter 7.
Bibliography


