CHAPTER - 1

INTRODUCTION
Introduction

1.1 Liquid Crystals

In a solid crystal the molecules are organized in a regular three dimensional lattice, *i.e.*, the centres of mass of the molecules have long range three dimensional translational orders. Usually the molecules are not spherical by symmetric. Thus, we can define the orientation of their long axis. In a solid crystal, the average orientations of the molecules within a unit cell are fixed in specific directions, *i.e.*, the molecules also have long range orientational order. On the other hand, in an isotropic liquid, there is no *long-range* order either in positions or in orientations of the molecules. A solid crystal, on heating, usually looses both the translational and orientational order at a well defined temperature (the melting point) and transforms into an isotropic liquid. But certain crystalline solids pass through one or more intermediate phases (*mesophases*) before transforming into an isotropic liquid.

In the crystalline solid state, as represented in figure 1.1, the arrangement of molecules is regular, with a regularly repeating pattern in all directions. (Molecules of substances with a liquid crystal state are generally oblong and rigid, that is, rod-shaped.) The molecules are held in fixed positions by intermolecular forces. As the temperature of a substance increases, its molecules vibrate more vigorously. Eventually, these vibrations overcome the forces that hold the molecules in place, and the molecules start to move.

![Arrangement of molecules in a solid crystal.](image)

Figure 1.1. Arrangement of molecules in a solid crystal.

In the liquid state, this motion overcomes the intermolecular forces that maintain acrystalline state, and the molecules move into random positions, without pattern in location or orientation, as represented in figure1.2.
In materials that form liquid crystals, the intermolecular forces in the crystalline solid are not the same in all directions; in some directions the forces are weaker than in other directions. When such a material is heated, the increased molecular motion overcomes the weaker forces first, but its molecules remain bound by the stronger forces. This produces a molecular arrangement that is random in some directions and regular in others. The arrangement of molecules in one type of liquid crystal is represented in figure 1.3. The molecules are still in layers, but within each layer, they are arranged in random positions, although they remain more or less parallel to each other. With in layers, the molecules can slide around each other, and the layers can slide over one another. This molecular mobility produces the fluidity which is the characteristic of a liquid.

If the molecules are globular in shape, on heating the solid crystal, the orientations of the molecules may become random before the positional ordering is lost. This results in an orientationally disordered, positionally ordered mesophase called plastic crystal. On the other hand, if the molecules have a pronounced shape anisotropy (rod-like, disc-like or with a bent-
core), then, the positions become random (in one, two or three dimensions) resulting in a liquid that still retains a long-range orientational order. Such phases, characterised by long-range orientational order without long-range three dimensional translational molecular order are called \textit{liquid crystals}, since they have some properties of liquids (for example, they can flow) as well as those of crystals (for example, birefringence).

Liquid crystals obtained purely by the thermal process mentioned above, are called \textit{thermotropic} liquid crystals. Liquid crystalline phases may also be induced by solvents, in which one of the components consists of amphiphilic molecules (molecules having lyophilic and lyophobic groups at the two opposite ends). Such mesophases are called \textit{lyotropic} liquid crystals in which, the parameter which brings about the phase transition is the relative concentration of the components. Certain long chain polymers exhibit liquid crystalline behaviour and are called \textit{polymeric} liquid crystals [1,2].

In this thesis, we consider only some thermotropic liquid crystals made of low molecular weight rod-like molecules. Their nomenclature is based on the type of order present in the phase. In the next section, we describe the classification of the mesophases relevant to the work reported in this thesis.
1.2 Classification of liquid crystals

It is now known that [1,2] liquid crystals can exhibit more than about 35 types of symmetries. Mainly, there are two fundamentally different types of liquid crystals made of rod-like molecules namely, the nematic and the smectic.

1.2.1 Nematic liquid crystals

Figure.1.4. Schematic representation of the ordering of the rod-like molecules in the isotropic and the nematic phases. The director \( \hat{n} \) and the choice of axes in the laboratory frame of reference are also shown.

The nematic liquid crystal (N) has the following characteristics[1]:

1. The medium has a long-range orientational order and no long-range translational order of the molecules \( i.e., \) the centres of mass of the molecules are randomly arranged in three dimensions, whereas the long axes of the rod-like molecules are approximately aligned (see figure-1.4).

2. The preferred axis of orientation in the nematic liquid crystal, called the director, is represented by the unit vector \( \hat{n} \). The orientational ordering in the nematic liquid crystal is different from that found in a solid ferroelectric crystal. In the latter, the molecular dipole moments have a long range correlation. This results in the formation of rigid domains having a net electric polarisation. Hence, the ‘up’ and ‘down’ configurations of the molecules are energetically different, leading to a long range polar orientational order. In the nematic liquid crystal, there is no such polar long range correlation, \( i.e., \) the ‘up’ and ‘down’ configurations of the molecules are equally probable. Hence the director is apolar, \( i.e., \) the states of the director \( \hat{n} \) and \( -\hat{n} \) are indistinguishable and the system is not ferroelectric.
3. The apolar orientational order, in general, is represented by even rank tensors. The most important one is the second rank tensor which can be represented as

\[ S_{ij}^{\alpha\beta} = \frac{1}{2} \langle 3i_\alpha j_\beta - \delta_{\alpha\beta} \delta_{ij} \rangle \]  

(1.1)

where, the tensor indices \( \alpha \) and \( \beta \) represent the orthogonal axes (X, Y, Z) in the laboratory frame of reference (see figure-1.1), while \( i, j \) represent the orthogonal axes (X', Y', Z') in the molecular frame of reference. \( \delta_{\alpha\beta} \) and \( \delta_{ij} \) are the Kronecker deltas and the brackets \( \langle \rangle \) denote the thermal average. \( S_{ij}^{\alpha\beta} \) is symmetric in \( i,j \) and in \( \alpha,\beta \). It is also a traceless tensor with respect to either pair \( i.e., S_{ij}^{\alpha\alpha} = S_{ii}^{\alpha\beta} = 0 \), where the repeated tensor indices imply the usual summation convention. The usual uniaxial nematic medium is cylindrically symmetric about the director taken to be along the Z axis and the X-Y plane is a plane of reflection for the structure. Hence,

\[ S_{ij}^{ZZ} = -2 S_{ij}^{XX} = -2 S_{ij}^{YY} = S_{ij} \]  

(1.2)

If the molecules are assumed to be cylindrically symmetric, the state of alignment of the molecules is described by a symmetric, diagonal and traceless \((3 \times 3)\) matrix \( S_{ij} \) represented as

\[
S_{ij} = \begin{bmatrix}
-S/2 & 0 & 0 \\
0 & -S/2 & 0 \\
0 & 0 & S \\
\end{bmatrix}
\]  

(1.3)

Hence, the extent of orientational order of the uniaxial nematic liquid crystal is represented by the so-called scalar order parameter \( S \) defined as

\[ S = \frac{1}{2} \langle 3\cos^2 \theta_i - 1 \rangle \]  

(1.4)

Where, \( \theta_i \) is the angle between the long axis of the \( i^{th} \) molecule and the director. The order parameter takes a maximum value equal to 1 when all the rods are perfectly aligned and is zero when all the orientations of the long axes are equally probable (in the isotropic phase).

4. The nematic phase occurs only in materials whose molecules do not have handedness, \( i.e., \) either each constituent molecule must be identical to its mirror image (nonchiral) or, if it is not, the system must be a racemic (1:1) mixture of the right- and left-handed species. The molecules become chiral if they have an asymmetrically substituted carbon atom. Then, the medium becomes optically active and the structure acquires a spontaneous twist about an axis.
perpendicular to the director. The resulting phase is called cholesteric liquid crystal denoted as N*\(^*\). The cholesteric phase is not considered in this thesis any further.

1.2.2 Smectic liquid crystals

Figure 1.5. Schematic representation of ordering of rod-like molecules in the smectic A and the smectic C phases, showing the nematic director \( \hat{n} \), the average spacing \( d \) between the layers, the wave vector \( \vec{q} \) representing the density wave along the layer normal. \( \vec{q} \) and \( \hat{n} \) are parallel in the smectic A liquid crystals whereas in the smectic C liquid crystals, \( \hat{n} \) is tilted with respect to \( \vec{q} \) by an angle \( \omega \).

The smectic liquid crystal (Sm) has the following characteristics:

1. The centres of mass of the molecules are approximately arranged in layers, the lateral arrangement within the layers being random. The Z axis is taken along the layer normal (see figure-1.5).

2. The medium has a density modulation along the Z axis. It is known that a true one dimensional order in three dimensional space is not possible since it leads to Landau-Peierls instability [1] and the mean square displacement diverges logarithmically with the linear size of the sample. However, samples having a linear size of a few hundred metres are required to have the root mean square displacement of the order of the lattice spacing [1]. This size is much bigger than that of the experimental samples. The X-ray scattering by a sample of small size shows quasi-Bragg peaks corresponding to quasi-long range one dimensional order. Hence, in addition to the long range orientational order, the smectic liquid crystal has quasi-long range one dimensional translational order.
3. The resulting density modulation, on Fourier analysis, can be expressed in a series of sinusoidal functions. Of these, the dominant one is the first harmonic. Hence, the density wave can be represented by

$$\rho(z) = \rho_0 [1 + \tau \cos(qz)]$$  \hspace{1cm} (1.5)

Where, $\rho_0$ is the average density of the medium, $\vec{q}$ is the wave vector along the layer normal with $q = |\vec{q}| = 2\pi/d$ and $d$ is the average spacing of the layers. The extent of layering (smectic) order is measured by the normalised amplitude of this density wave, called the smectic order parameter $\tau$, given by

$$\tau = \langle \cos(2\pi z_i / d) \rangle$$  \hspace{1cm} (1.6)

where, $z_i$ is the z coordinate of the centre of mass of the $i$th molecule. When there is no layering order, $\tau = 0$ and the medium has uniform density $\rho_0$ as in a nematic liquid crystal.

4. Different variations of the layering and inlayer order are possible leading to different types of smectic liquid crystals. If $\vec{q} \parallel \hat{n}$, i.e., the nematic director is normal to the layers, it is termed as the smectic A (SmA) liquid crystal. In this thesis, apart from the N and the SmA liquid crystals, we also consider the smectic C (SmC) liquid crystal. In SmC liquid crystals, $\vec{q}$ and $\hat{n}$ are not parallel (see figure-1.2). The angle $\omega$ between $\vec{q}$ and $\hat{n}$ represents the average tilt of the long axes of the rod-like molecules with respect to the layer normal.

In this thesis, we develop molecular theories of nematic and smectic liquid crystalline phases exhibited by polar compounds. The presence of polar bonds in the molecules is important in the formation of some liquid crystals. It is known that the liquid crystals composed of strongly polar molecules exhibit some unusual phase sequences (see section 1.5). In the next section, we give examples of some polar bonds and their dipole moments.
1.3 Examples of polar bonds and their dipole moments

Generally, molecules are electrically neutral, \textit{i.e.}, the algebraic sum of all the charges in a given molecule is zero. When the electro negativities of the two neighbouring atoms forming a bond are unequal, the common electron pair of the covalent bond is shifted towards the more electronegative atom. Hence, the centres of the positive and the negative charges do not coincide. This results in molecules with \textit{permanent} electric dipole moments, called \textit{polar} molecules. The direction of this electric dipole moment (\(\vec{p}\)) is, by convention, taken from the negative charge towards the positive charge. The magnitude (\(p\)) is defined as

\[
p = g l
\]

where, \(g\) is the magnitude of the equal and opposite point charges having the separation \(l\).

The electric dipole moment is usually expressed in debye (1D=10^{-18} \text{esu}). The SI unit is coulomb-metre (C m) and 1D=1/3 \times 10^{-29} \text{C m}. One electron charge displaced by one angstrom results in 4.8D. Magnitudes and directions of permanent electric dipole moments of some polar bonds are given in table 1.1.

Table 1.1

<table>
<thead>
<tr>
<th>Group or bond</th>
<th>Direction of moment</th>
<th>Magnitude of moment (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C – H</td>
<td>C (\rightarrow) H</td>
<td>0.44</td>
</tr>
<tr>
<td>C – N</td>
<td>N (\rightarrow) C</td>
<td>0.68</td>
</tr>
<tr>
<td>C – O</td>
<td>O (\rightarrow) C</td>
<td>1.24</td>
</tr>
<tr>
<td>O – H</td>
<td>O (\rightarrow) H</td>
<td>1.76</td>
</tr>
<tr>
<td>N – H</td>
<td>N (\rightarrow) H</td>
<td>1.84</td>
</tr>
<tr>
<td>C \equiv N</td>
<td>N (\rightarrow) C</td>
<td>4.37</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>O(_2) (\rightarrow) N</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Magnitudes and directions of permanent electric dipole moments of some polar bonds.

In the next section, we consider some typical examples of rod-like mesogenic compounds.
1.4 Typical examples of rod-like mesogenic compounds

Typical examples of mesogenic compounds consist of rod-like organic molecules having a few phenyl rings with or without bridging groups and end chains. A typical mesogenic molecule can be roughly taken as a rigid rod of length $\approx 20 \text{Å}$ and width $\approx 5 \text{Å}$.

In the examples given below, the single headed arrows in the structural formulae indicate the direction of the dipole moment. The double headed arrows below the structure indicate phase transitions. The number above the double headed arrow gives the transition temperature in $^\circ\text{C}$. The latent heats (in kilojoule per mole) are given below the arrow in those cases for which the data are available. The carbon and the hydrogen atoms in the phenyl rings are not shown.

1.4.1 Compounds exhibiting only the nematic liquid crystalline phase

(a) Pentylenobiphenyl(5CB) [3]

(b) p-azoxyanisole (PAA) [4]
The compound 5CB (structure (a) above) has two phenyl rings without any bridging group in between. It has a strong longitudinal dipole moment due to the C≡N group. The nematic phase is stable over a small range at low temperatures. The compound PAA (structure (b)) has a strong dipole moment due to the NO group inclined at a large angle (≈60°) with respect to the molecular long axis. Note that the nematic phase of PAA is stable over a larger range at higher temperatures compared to that of 5CB. The compound (c) has no chains or bridging groups and very nearly resembles a long rigid rod. Also, it has no permanent dipole moment. Note that the transition temperatures are quite high. These examples illustrate that the molecular shape (length to breadth ratio) plays a more important role in stabilizing the nematic phase than the presence of the bridging groups, end chains or the permanent dipoles. However, the presence of end chains plays an important role in stabilizing the smectic phase, as illustrated in the following examples.

1.4.2 Compounds exhibiting the smecticA liquid crystalline phase

Compounds exhibiting the SmA phase usually have 2 or 3 phenyl rings, with sufficiently long end chains. The electrons in the phenyl rings (aromatic cores) are relatively free within the ring due to resonant configurations. Hence, the aromatic cores of the neighbouring molecules overlap due to the strong dispersion interaction and tend to arrange themselves in layers. If the chains are sufficiently long, they act as separators between such cores and the layered structure (SmA) is stabilised.

A series of compounds which differ only in the number of carbon atoms in the end chain(s) with the rest of the structure being the same, are called homologues. Usually, the shorter homologues of typical mesogenic compounds exhibit only the I and N phases before solidifying. The longer homologues exhibit the smectic phase also. For example, the longer
homologues of 5CB (structure ‘a’ above), in general denoted as $n$CB having $n$ carbon atoms in the end chain with $n \geq 8$, exhibit SmA phase.

For 8CB we have [3]

$$
\text{Solid} \quad 24^\circ C \quad 25.3 \text{ kJ} \quad \text{SmA} \quad 34^\circ C \quad 0.13 \text{ kJ} \quad \text{N} \quad 42.6^\circ C \quad 0.97 \text{ kJ} \quad \text{I}
$$

Note that the first order SmA-N transition is weaker than the N-I transition. Often, the shorter homologues of the smectogens exhibit a second order SmA-N transition. As the chain length of the homologues is increased, the nature of the transition changes over to first order, the temperature range of the N phase decreases and finally vanishes. Very long homologues exhibit a first order SmA-I transition.

There are rare examples of molecules without any chain resulting in the SmA phase. As an example sexiphenyl that has the phase sequence solid-SmA-N-I, is shown below.

$$
\text{Solid} \quad 435^\circ C \quad \text{SmA} \quad 465^\circ C \quad \text{N} \quad 565^\circ C \quad \text{I}
$$

Some compounds exhibit a variety of smectic phases before transforming into the nematic phase [1]. However, in this thesis, we consider only the SmC, SmA and the N phases. Strongly polar compounds exhibit some unusual phase sequences. This is described in the next section.
1.5 Re-entrant phases and smectic polymorphism exhibited by strongly polar compounds

When a typical mesomorphic compound is cooled from the isotropic (I) phase, the usual sequence of phase transitions is (with K for solid crystal): $I \rightarrow N \rightarrow K$ or $I \rightarrow N \rightarrow \text{SmA} \rightarrow K$. In other words, the more ordered phases, i.e., the phases having lower symmetries, are expected to occur at lower temperatures. Indeed, this sequence is followed in most of the liquid crystals. However, liquid crystals composed of molecules having strongly polar end groups show some unusual phase sequences. This is illustrated in the following examples.

1.5.1 Nematic reentrance

Cladis [6] found that mixtures of certain compounds with strongly polar cyano or nitro end groups, on cooling from the isotropic phase, exhibit the following sequence of transitions: $I \rightarrow N \rightarrow \text{SmA} \rightarrow N_R \rightarrow K$. The second nematic phase that occurs at temperatures below the range of existence of the smectic phase is called the re-entrant nematic ($N_R$) phase. Later, she found a similar phenomenon in pure compounds, as for example, octyloxy cyano biphenyl (or 8OCB) under elevated pressures [7]. Subsequently, such a phase sequence has been found in case of pure compounds at normal pressures also [8].

1.5.2 Double and Multiple reentrance

In some strongly polar pure compounds or binary mixtures, at temperatures below the range of existence of the re-entrant nematic phase, another smectic phase re-enters leading to the sequence: $I \rightarrow N \rightarrow \text{SmA}_d \rightarrow N_R \rightarrow \text{SmA}_1 \rightarrow K$, as for example in octyloxy benzoyloxy cyano- stilbene or T8 [9]. This phenomenon is called double re-entrance. The lower temperature re-entrant smectic phase is called the smectic-A$_1$ ($\text{SmA}_1$) phase and the higher temperature smectic phase is called the smectic-A$_d$ ($\text{SmA}_d$). X-ray measurements show that [10] the $\text{SmA}_1$ phase has a layer spacing $d = l$, whereas the $\text{SmA}_d$ phase has $l < d < 2l$, where $l$ is the molecular length. This partial bilayer arrangement is understood on the basis of formation of appropriate antiparallel dimers of the molecules. Hence the suffix ‘d’ is used to denote dimers and the suffix ‘1’ for the monomers.

There are some rare examples of pure polar compounds which, on cooling, show the quadruple reentrant sequence: $I \rightarrow N \rightarrow \text{SmA}_d \rightarrow N_R \rightarrow \text{SmA}_{dR} \rightarrow N_R \rightarrow \text{SmA}_1$ as for example, DB$_9$ONO$_2$[11], the ninth homologue of nalkyloxy phenyl-nitro benzoyloxy benzoate, denoted in general as DB$_n$ONO$_2$. This behaviour is also seen in a few mixtures over a very narrow
range of concentrations, as in ≈50% molar mixture of DB$_8$ONO$_2$ and DB$_{10}$ONO$_2$ [12]. Apart from these, the pressure-temperature and temperature-concentration phase diagrams show a first order SmA$_1$ - SmA$_d$ transition ending in a critical point, SmA$_1$ - SmA$_2$ transition etc., where the SmA$_2$ phase has $d \approx 2l$. The occurrence of different types of SmA phases is in general called smectic A polymorphism. Some mixtures of strongly polar compounds also show a re-entrant nematic lake surrounded by the SmA$_d$ region [13] or a SmA$_d$ island surrounded by the nematic region [14] or a weak first order nematic-nematic transition [15]. A general review of phase transitions and critical phenomena in polar compounds has been given by Chandrasekhar [2] and Shashidhar et al [16]. The most detailed study of the first order SmA$_d$ - SmA$_2$ transition ending in a critical point in temperature-concentration phase diagram has been reported by Shashidhar et al [17] in the binary mixtures of undecyloxyphenylcyanobenzylxybenzoate (11OPCBOB) and nonyloxybiphenylcyanobenzoate (9OBCB).

There have been many attempts to explain these phenomena theoretically. In the next section, we briefly review some of the theories of phase transitions in liquid crystals.
1.6 Review of some theories of phase transitions in liquid crystals

In this thesis, we first develop molecular theories of Nematic and Smectic liquid crystalline phases exhibited by a medium consisting of strongly polar molecules with longitudinal components of dipole moments. Prost has developed a very successful phenomenological theory of various phases exhibited by such compounds. Our model provides a molecular basis for some of the assumptions made in the phenomenological theory. A general review of the Landau theory of phase transitions is given below.

1.6.1 Landau theory of phase transitions

The Landau theory was initially developed to describe 2nd order phase transitions. The order parameter \( \sigma \), characterising the phase of lower symmetry, continuously goes to zero at a 2nd order phase transition. As \( \sigma \) is extremely small near the transition point, it is assumed that, the free energy density \( F \) can be expanded in powers of \( \sigma \)[18]. In the absence of any external fields the expansion is given by

\[
F(T, \sigma) = F_0 + \frac{A}{2} \sigma^2 + \frac{B}{3} \sigma^3 + \frac{C}{4} \sigma^4 + \frac{D}{5} \sigma^5 + \frac{E}{6} \sigma^6 + \ldots
\]  

(1.8)

Where, \( F_0 \) is the free energy of the disordered phase (\( \sigma = 0 \)). The term linear in \( \sigma \) is absent to ensure the stability of the disordered phase. The linear term can be non zero when an external symmetry breaking field is introduced. The magnitude of the order parameter near the phase transition is determined by minimizing \( F(T, \sigma) \) with respect to \( \sigma \).

\( A > 0 \) ensures that \( \sigma = 0 \) corresponding to the higher temperature phase has a minimum in \( F \) and \( A < 0 \) corresponds to the lower temperature phase with \( \sigma \neq 0 \). Landau assumed that

\[
A = a(T - T^*)
\]  

(1.9)

Where, \( T^* \) is the transition temperature. The coefficients \( a, B, C \ldots \) are normally assumed to be independent of temperature. For a system in which the free energy is independent of the sign of \( \sigma \), i.e., \( F(\sigma) = F(-\sigma) \), as for example, in a ferromagnetic system, the cubic and higher odd powers in \( \sigma \) are not allowed. Hence, with \( B = 0, C > 0 \) and neglecting the terms with higher powers in \( \sigma \), a second order phase transition is obtained between the states \( \sigma = 0 \) and \( \sigma \neq 0 \) at \( T = T^* \). Minimising \( F \) with respect to \( \sigma \) gives

\[
\sigma = \left( \frac{a(T^* - T)}{C} \right)^{\frac{1}{2}}.
\]  

(1.10)
The above argument can be extended to describe weakly first order phase transitions. If the symmetry of the system prevents the presence of odd ordered terms \((i.e., B = D = 0)\), then, a first order transition can be obtained by having \(C < 0\). In that case, a sixth order term with a positive coefficient \((i.e., E > 0)\) is required for stability. If \(C > 0\), the transition is of second order.

In some cases with \(B = D = 0\) and \(E > 0\), the coefficient of the fourth order term \((C)\) may depend on some parameter \(x\) (for example, the concentration in a binary mixture or the chain length in a homologous series). Then, as a function of \(x\), the positive coefficient \(C\) may tend to zero or even change sign. This leads a change in the nature of the phase transition from second order to first order as a function of the parameter \(x\). The point on the transition line in the \(T-x\) phase diagram at which this happens is called the tricritical point. This trend is seen in the N-SmA transition and is discussed in section 1.6.3.

If the symmetry of the system allows for odd powers of \(\sigma\), then, a first order transition results when a third ordered term in \(\sigma\) is retained with \(C > 0\). This is described in the next section, taking the N-I transition as an example.

### 1.6.2 Landau- de Gennes theory of the N-I transition

deGennes [19] proposed a phenomenological description of the N-I transition on the basis of the Landau theory of phase transitions. The nematic order parameter \(S\) is basically a second rank tensor (see section 1.2.1). It is clear from equation 1.4 that \(S > 0\) represents a structure with the molecular long axes nearly parallel to \(\hat{n}\) while for \(S < 0\) they are nearly perpendicular to \(\hat{n}\). Since these two arrangements are energetically different, the expansion of the free energy density for the nematic phase should include the cubic term in \(S\).

The free energy density for the nematic phase is hence written as

\[
F(T, S) = F_0 + \frac{a(T-T^*)}{2}S^2 - \frac{B}{3}S^3 + \frac{C}{4}S^4
\]  

Where, \(T^*\) is the hypothetical second order transition temperature below which the isotropic phase can not be supercooled. The cubic term is assumed to be negative to get \(S > 0\) in the nematic phase for \(B > 0\). Minimising \(F(T, S)\) with respect to \(S\) gives the solutions

\[
S = 0 (\text{isotropic phase})
\]

and \(S_{\pm} = \frac{B}{2C} \left[ 1 \pm \left( 1 - \frac{4Ca(T-T^*)}{B^2} \right)^{1/2} \right] \)  

(1.12)
where, $S_\pm$ corresponds to the free energy maximum and is not an acceptable solution, while, $S_+$ corresponding to the free energy minimum represents the stable phase. At the N-I transition temperature ($T_{NI}$), we have, $F(T,S)=F_0$. Also, the equilibrium condition, $(\partial F/\partial S) = 0$, is valid at the transition value of $S$ (i.e., at $S=S_{NI}$). With these conditions imposed on $F$, equation 1.11 gives,

$$S_{NI} = \frac{2B}{3C}$$

(1.13)

$$T_{NI} = T^* + \frac{2B^2}{9aC}$$

(1.14)

Equation 1.12 has solutions only when $B^2 > 4Ca(T-T^*)$, leading to an upper temperature limit for super heating the nematic phase. This temperature $T^h$ is

$$T^h = T^* + \frac{B^2}{4aC}T_{NI}$$

(1.15)

Thus when the third order term is present, the N-I transition is first order in nature. Typically, the order parameter at the transition point $S_{NI} \approx 0.3$, which is not very small. However, from the thermodynamic point of view, the N-I transition is a weakly first order transition since the heat of transition is very small (e.g., $\approx 0.8$ kJ/mol for 5CB) compared to that of the crystal-melting transition (e.g., $\approx 17$ kJ/mol for 5CB). The coefficients $a$, $B$ and $C$ for a given liquid crystal compound can be found using the values of $S_{NI}$, $T_{NI}$ and the heat of transition.

### 1.6.3 Landau-de Gennes theory for the N - SmA transition

As described in section 1.2.2, the SmA phase is characterised by a density modulation in a direction $\vec{z}$ orthogonal to the layers [1].

$$\rho(z) = \rho_0 [1 + \tau \cos(2\pi z/d + \phi) + \ldots . ]$$

(1.16)

Where, $\tau$ is the amplitude of the first harmonic of the density wave and $\phi$ is an arbitrary phase which can be taken as zero by a suitable choice of the origin. $\tau$ is zero in the nematic phase. Hence, $\tau$ is the natural order parameter for the smectic phase.

In the vicinity of the N-SmA transition, the free energy density can be expanded in powers of $\tau$:
\[ F_A = \frac{1}{2} A_A \tau^2 + \frac{1}{4} C_A \tau^4 +... \] (1.17)

Only even powers of \( \tau \) are required since \( \pm \tau \) differ only in the choice of the origin of the Z-axis. \( A_A = a_A(T-T_0) \) and \( C_A \) are the usual Landau coefficients. This leads to a second order transition at a temperature \( T_{AN} = T_0 \) if \( C_A > 0 \). However, the appearance of smectic order usually increases the degree of alignment of the molecular long axes. Hence, we have [1],

\[ S = S_0(T) + \delta S \] (1.18)

where, \( S_0(T) \) is the orientational order parameter in the absence of the layering and \( \delta S \) is the additional orientational ordering due to the onset of the layering order. The lowest order coupling term of the translational order and the orientational order must have the form

\[ F_{AN} = -\gamma \tau^2 \delta S \] (1.19)

Where, \( \gamma \) is positive. The nematic free energy which is minimum when \( \delta S = 0 \) is given by

\[ F_N = F_N(S_0) + \frac{1}{2\chi}(\delta S)^2 \] (1.20)

where, \( \chi \) is a response function. The overall free energy of the smectic phase obtained by adding \( F_A, F_{AN} \) and \( F_N \) is

\[ F_S = \frac{1}{2}a_A(T-T_0) \tau^2 + \frac{1}{4} C_A \tau^4 - \gamma \tau^2 \delta S + \frac{1}{2\chi}(\delta S)^2 + F_N(S_0). \] (1.21)

Minimising this with respect to \( \delta S \) gives

\[ \delta S = \chi \tau^2 \] (1.22)

which upon substituting into the equation 1.21 gives

\[ F_S = \frac{1}{2}a_A(T-T_0) \tau^2 + \frac{1}{4} C^* \tau^4 + F_N(S_0) \] (1.23)

where the modified coefficient \( C^* \) of the fourth ordered term is given by

\[ C^* = C_A - 2\gamma^2 \chi. \] (1.24)

If \( T_0 \) is close to \( T_{NI}, i.e., \) when the nematic range is small, \( S_0 \) is relatively small and hence \( \chi \) is large and \( C^* \) is negative. Then the term in \( \delta S \) with a positive coefficient must be included in the equation 1.17 to ensure stability. This results in a first order N-SmA transition at a temperature \( T_{AN} > T_0 \). On the other hand, if \( T_0 \) is significantly smaller than \( T_{NI}, i.e., \) when
the nematic range is large, \( S_0 \) is practically saturated and \( \chi \) is small and \( C^* \) is positive. This leads to a second order N-SmA transition at a temperature \( T_{AN} = T_0 \). In this case, for \( T < T_0 \) near the transition, as in equation 1.10, we have

\[
\tau \propto (T_0 - T)^{1/2}. \tag{1.25}
\]

The point at which \( C^* = 0 \) is the tricritical point. This is a point on the transition line, where the first order nature of the transition changes to second order. With \( C^* = 0 \), and with a positive term in \( \tau^6 \), a second order N-SmA transition results at a temperature \( T_{AN} = T_0 \). For \( T < T_0 \) near the transition, unlike the equation 1.25, we have

\[
\tau \propto (T_0 - T)^{1/4}. \tag{1.26}
\]

The tricritical behaviour may be observed experimentally by varying \( \chi \). This is possible by varying the length of the end chain, or by preparing mixtures, or by the application of pressure [20].

The phenomenological theory explains the appearance of the smectic phase as the nematic liquid crystal is cooled. However, as described earlier, experiments on strongly polar compounds show that the nematic phase reenters when the smectic liquid crystal is cooled further. Also, the smectic phase can be stabilised with various layer spacings. In order to explain the phenomenon of smecticA polymorphism and multiple reentrances, Prost extended the Landau theory using two coupled order parameters for the smectic phase. In the next section we briefly describe this theory.

### 1.6.4 Phenomenological theory with two coupled smectic order parameters

As described in section 1.5.2, X-ray measurements show that [9] the lower temperature re-entrant smectic phase (SmA\(_1\)) has a layer spacing \( d = l \), whereas the higher temperature smectic phase (SmA\(_d\)) has \( l < d < 2l \), where \( l \) is the molecular length. Prost [21] argued that the ‘natural’ length is the molecular length \( l \) and there is a ‘competition’ between this length and the other incommensurate length in forming the smectic phase, leading to frustration. Based on this idea, he developed a successful Landau theory of these unusual phase transitions. A brief review of this theory is given in this section. The molecular origin of the ‘two lengths’ is discussed later.

Since there are two different lengths at which the SmA density modulation can take place, the Landau free energy density is expanded in terms of the two order parameters \( \rho \) and
φ corresponding to these two lengths and it is necessary to consider the phase of the modulation (see equation 1.16). This is conveniently written using complex notation following Prost [21] as,

\[
\phi = \frac{1}{\sqrt{2}} \{ \psi_1 \exp(i \vec{q} \cdot \vec{r}) + \text{complex conjugate} \}
\]

and \( \rho = \frac{1}{\sqrt{2}} \{ \psi_2 \exp(i \vec{q} \cdot \vec{r}) + \text{complex conjugate} \} \) (1.27)

in which \( \phi \) corresponds to the partial bilayer order and \( \rho \) to the monolayer order, \( \psi_1 \) and \( \psi_2 \) are the corresponding amplitudes and \( \vec{q} \) is the wave vector of the one dimensional density wave in the SmA phase. An appropriate form of the free energy density is given by

\[
F = \frac{A_1}{2} \phi^2 + \frac{C_1}{4} \phi^4 + \frac{A_2}{2} \rho^2 + \frac{C_2}{4} \rho^4 + A_{12} \phi \rho - \frac{B_{12}}{\sqrt{2}} \phi^2 \rho + \frac{C_{12}}{3} \rho^2 \phi^2 .
\]

(1.28)

As the two order parameters correspond to two different periodicities, it is appropriate to write

\[
A_1 \phi^2 = a_1 \phi^2 + A_{01}((\Delta + q_1^2)\phi)^2
\]

and \( A_2 \rho^2 = a_2 \rho^2 + A_{02}((\Delta + q_2^2)\rho)^2 \) (1.29)

where,

\[
a_1 = (T-T_1^*) , a_2 = (T-T_2^*)
\]

\( \Delta = \frac{\partial^2}{\partial z^2} \) if the layers are condensed along the Z-axis and \( q_1 = 2\pi / l_d \), \( q_2 = 2\pi / l_1 \), ensuring that \( \phi \) condenses with a wave vector \( q_1 \), and \( \rho \) with \( q_2 \). This very general expression can give rise to many different structures depending on the relative importance of the coupling terms [1].

In the SmA\(_1\) phase, \( l_d=l_1 \) and the \( (\rho \phi) \) term dominates. In the SmA\(_2\) phase, \( l_d=2l \) which results from the dominance of the \( \phi^2 \rho \) term, while the \( (\rho \phi) \) term is negligible. Satisfying these two tendencies simultaneously is not possible, hence the name frustrated smectics. Similarly, with suitable dependences of the constants \( A_1 \) and \( A_2 \) on temperature and concentration or temperature and pressure, and with proper weightages given to the other constants, the equation 1.28 leads to single and double reentrant behaviors, SmA\(_1\)-SmA\(_d\) critical point etc., in the appropriate parameter space [1].
As de Gennes and Prost remark [1], “if the phenomenological approach provides a unifying framework for the description of the frustrated smectics, it does not give much detail on what is happening at a molecular scale”. In the next section, we give a brief review of some of the molecular theories of reentrant phases.

1.6.4.1 Molecular model by Cladis and its extensions

The first attempt to develop a molecular model for reentrance was by Cladis [22]. In this, the medium is assumed to consist of antiparallel pairs. Since the antiparallel pairs have overlapping aromatic parts, the cores of the pairs are more bulky than the end chains. Hence, the pairs have an effective shape as shown in figure-1.6a. When the nematic liquid crystal (figure- 1.6b) is cooled, the number of dimers increases and they come closer. The layering order of the dimers (figure- 1.6c) leads to a lowering of internal energy which more than compensates for the decrease of entropy due to ordering. This leads to the SmA\textsubscript{d} phase with a partial bilayer structure. On further cooling, the pairs come still closer. The bulky central parts of the dimers cannot be accommodated in the central plane of the layers, thus destroying the layering arrangement (figure- 1.6d) leading to a re-entrant nematic phase. When this is further cooled, a still closer packing leads to a SmA\textsubscript{1} phase with \( d \approx l \) (figure-1.6e). This is only a pictorial model. The proposed packing in the SmA\textsubscript{1} phase is solid-like and hence cannot describe the SmA\textsubscript{1} liquid crystal which is a fluid.
Figure 1.6. Pictorial model given by Cladis [27] for double reentrance. (a) Effective shape of an antiparallel dimer. The figures (b), (c), (d) and (e) represent the organisation of monomers and dimers in the higher temperature nematic (N) phase, SmA phase with partial bilayer structure, lower temperature reentrant nematic (N_R) phase and the SmA_1 phase with a mono layer structure respectively.

Luckhurst and Timimi [23] have also developed a qualitative model assuming that the medium consists of loose dimers whose structure may change with temperature. Hence the strength of layering interaction (the parameter $\alpha$ in the McMillan theory [24] of the SmA phase, see section 4.2 of chapter-4 for a description of the McMillan theory) is taken to be temperature dependent. If $\alpha$ decreases with temperature, the SmA phase becomes unstable and the nematic phase reenters. Further decrease of temperature would again stabilise the SmA phase, since a lower $\alpha$ is sufficient to stabilise the SmA phase at low temperatures. To incorporate this trend, $\alpha$ is assumed to decrease with temperature over the middle range of temperatures whereas it is taken to be a constant over the higher and lower ranges of temperatures. By a suitable choice of the dependence of $\alpha$ on temperature, they are able to obtain double reentrance. They suggested that the assumed form of the temperature
dependence of $\alpha$ may be due to structural changes in the molecular dimers which have not been worked out.

The first microscopic theory of the reentrant nematic phase exhibited by polar liquid crystals was proposed by Longa and de Jeu [25] extending McMillan’s theory [24] of the SmA phase. In this model, the medium is assumed to be a mixture of monomers and dimers which interact through attractive soft interactions as well as hard-core repulsions. They have shown that the higher temperature smectic phase is stabilised because of dimers having a stronger layering interaction than that of monomers. On cooling, more dimers are formed and the dimers have bulky central parts. Hence, due to difficulty in packing into layers, as proposed by Cladis, the repulsive steric forces dominate and thus the nematic phase reenters. However, in the model, the equilibrium concentration of dimers at a given temperature is an input parameter based on the permittivity data and is not calculated in a self consistent manner. Also, the calculations are restricted to the case of ideal orientational order. Further, the appearance of the SmA$_1$ phase below the N$_R$ phase is not discussed.

Bose et.al.,[26] have developed a model more closely based on the molecular picture given by Cladis. They point out that the repulsion between the central parts is not absolutely essential for the reentrant phenomenon whereas in the model by Longa and de Jeu[25], this repulsion plays the main role. In the model by Bose et.al., the medium is assumed to be a mixture of monomers and dimers in chemical equilibrium. The dimers when arranged in layers leave void spaces which are filled by the monomers thus stabilising the high temperature SmA$_d$ phase. With lowering of temperature, more monomers combine to form dimers. The neighbouring layers intercalate for better packing. This results in a decrease of layer thickness without changing the core length of the dimers and hence the McMillan parameter $\alpha$ decreases, leading to nematic reentrance. As the temperature is further lowered, the medium mostly consists of dimers. Due to complete intercalation, this results in a smectic phase with the layer thickness comparable to the length of the monomers (SmA$_1$) as in figure 1.6e. They have ignored the smectic interaction between the monomers assuming it to be small, and have assumed that the McMillan parameter $\alpha_d$ for dimers remains constant up to some critical monomer concentration. Below this concentration, the intercalation starts decreasing the layer thickness and $\alpha_d$ starts decreasing. The assumed variation of $\alpha$ is ad hoc as in the case of Luckhurst and Timimi model [23] described above.
Mirantsev [27] has extended the model of Longa and de Jeu [25], including a self consistent calculation of the dimer concentration and modifying the mean field potential to allow for the smectic periodicities of both the monomer and dimer lengths. Later [28], he has developed a simple microscopic description of the reentrant phenomenon. In this model, it is assumed that each molecule not only feels a molecular mean field due to the long range anti-ferroelectric order, but also interacts with the nearest neighbours within the layers to produce a short range anti-ferroelectric order of the Ising type. It is shown that if the increase of the latter with decrease of temperature is sufficiently rapid, then the nematic phase reenters. The calculations are restricted to the case of saturated nematic order. In the SmA$_1$ phase, a short range anti-ferroelectric order is predicted. This means that the aromatic core of one molecule overlaps with the aliphatic chain of the neighbouring one, which is unlikely. Also, some experiments [29] showing the presence of polar short range order at low temperatures do not support this arrangement of molecules.

Luckhurst et al., [30] have developed a model extending McMillan’s model [24] of the SmA phase, considering isomerisation and dimerisation of molecules. In the model, lowering of temperature below that corresponding to the SmA$_d$ phase results in the dissociation of the dimers thus increasing the concentration of monomers and also increasing the total number of interacting particles. Since the monomers are assumed to have a lower value of the McMillan parameter $\alpha$, this leads to the reentrant nematic phase. On further cooling, the SmA$_1$ phase consisting mostly of the monomers is stabilized. In the model, the near neighbours interact and associate as dimers at higher temperatures. At lower temperatures, they dissociate and remain as monomers even though they are more closely spaced than at higher temperatures. This behaviour is obtained by choosing a suitable value of the equilibrium constant for monomer-dimer association. This model, which is opposite to that proposed by Cladis and others, appears artificial. Also, an increase in the number of monomers due to the lowering of temperature is not explained on any physical basis and cannot explain the recent experimental observation [28] showing the presence of polar short range order at low temperatures.
1.7 A molecular model based on pairs with parallel dipole moments at low temperatures

Various molecular theories have been proposed to explain the origin of the ‘two lengths’ assumed by Prost. The molecular origin of the partial bilayer structure was explained, before the discovery of double reentrance, as follows: An early experimental observation [31] on a cyano compound shows that the average dielectric constant has a positive jump as the temperature is increased across the N-I transition point. To explain this, it was proposed that [32] the interaction between the permanent dipoles favours an antiparallel configuration of the nearest neighbours. Later X-ray [10,33] and neutron scattering [34] studies on strongly polar compounds in the nematic phase have shown that they have a SmA like short range order, with a typical layer spacing $\approx 1.4$ times the molecular length i.e., there is a partial bilayer arrangement. This was interpreted [33] to be the result of the overlap of the aromatic parts of the neighbouring antiparallel molecules due to the strong dispersion interactions.

A simple model to explain the molecular origin of the ‘two lengths’ assumed in the Prost’s phenomenological model [21] was proposed by Madhusudana and JyothsnaRajan [35]. The model, with suitable modifications, gives a variety of phase diagrams. In this model, the origin of the two incommensurate lengths is explained as follows: The interaction between permanent dipoles favour an antiparallel orientation (A) between neighbouring molecules [32]. This interaction energy is $\propto 1/r^3$ where $r$ is the intermolecular separation. The strongest intermolecular interaction arises from the anisotropic dispersion energy between the aromatic cores resulting in the partial bilayer structure mentioned earlier (Figure-1.7a).

If the polar molecules are parallel, the dipolar interaction is repulsive. However, in view of the strong polarisability of the conjugated aromatic core to which the dipole is attached, the latter induces an oppositely oriented dipole moment in the neighbouring molecule thus reducing the net dipole moment of each molecule (Figure-3b). Further, in this ‘parallel’ or (P) configuration, the chains are in close proximity, adding to the attractive interaction. Both these effects are $\propto 1/r^6$. Hence, as the density is increased, i.e., the temperature is lowered, one can expect a change in the configuration of the pairs from ‘A’ type to ‘P’ type.
Figure 1.7. Schematic diagram showing (a) the antiparallel configuration of two molecules favoured at intermediate molecular separations and (b) the parallel configuration favoured at relatively low values of intermolecular separation. The arrow with solid line represents the permanent dipole moment and the one with dotted line, the induced one. (For the sake of clarity, the relative separation in (a) is exaggerated).

For the sake of simplicity, it is assumed that the energy difference between the two configurations has the following form

\[ \Delta E = E_A - E_P = R_1 k_B T_{NI} \left( \frac{R_2}{T_R} - 1 \right) \]  

(1.31)

where \( k_B \) is the Boltzmann constant, \( E_A \) and \( E_P \) are the configurational energies of the A-type and P-type pairs respectively, \( T_{NI} \) is the nematic-isotropic transition temperature of the A-type of pairs, \( R_1 k_B T_{NI} \) is an interaction parameter and \( T_R = T/T_{NI} \) is the reduced temperature. \( R_2 \) is the reduced temperature at which the density of the medium is such that \( \Delta E \) becomes zero. For \( T_R > R_2 \), the A-type configuration has the lower energy.

The two configurations shown in Figure 3 naturally account for the two length scales in the Landau theory developed by Prost [21]. A molecular theory of double reentrance has been
developed in [35] including $\Delta E$ and considering the medium to be a mixture of A and P type of pairs. In reference [35], the authors have extended the McMillan theory of SmA phase [36], which is itself an extension of the Maier-Saupe (MS) theory of the N-I transition [37]. This model has been extensively used to explain double reentrance, $N_1-N_d$ and SmA$_1$-SmA$_d$ transitions, effect of pressure and electric field on these transitions. The details are discussed in the respective chapter later.

1.8 Gaussian Integration

The simplest form of Gaussian Integration is based on the use of an optimally chosen polynomial to approximate the integrand $f(t)$ over the interval [-1, +1]. The details of the determination of this polynomial, meaning determination of the coefficients of $t$ in this polynomial, are given in Schaum’s Series [38]. The simplest form uses a uniform weighting over the interval, and the particular points at which to evaluate $f(t)$ are the roots of a particular class of polynomials, the Legendre polynomials, over the interval. It can be shown that the best estimate of the integral is then:

$$\int_{-1}^{1} f(t) \, dt = \sum_{i=1}^{n} w_i f(t_i)$$

(1.32)

Where, $t_i$ is a designated evaluation point, and $w_i$ is the weight of that point in the sum. If the number of points at which the function $f(t)$ is evaluated is $n$, the resulting value of the integral is of the same accuracy as a simple polynomial method (such as Simpson's Rule) of about twice the degree (i.e., of degree $2n$). Thus the carefully designed choice of function evaluation points in the Gauss-Legendre form results in the same accuracy for about half the number of function evaluations, and thus at about half the computing effort.

Gaussian quadrature formulae are evaluating using abscissae and weights from a table like that included here. The choice of value of $n$ is not always clear, and experimentation is useful to see the influence of choosing a different number of points. When choosing to use $n$ points, we call the method an ``$n$-point Gaussian'' method.

We evaluate the necessary integrals using a 32-point Gaussian quadrature technique in double precision.
In the next section, we give an outline of the contents of different chapters of the thesis.

1.9 Scope of the thesis

In the next chapter (chapter-2), we review the experimental results on photo induced effects of light on the Liquid crystals. The photo induced effects are accomplished by employing azobenzene derivatives as a dopant in a liquid-crystal host material. The heart of the phenomenon in such systems is the reversible photo-induced shape transformation of the molecules containing the photo-chromic azo groups. Photo-isomerization [39] is the transformation of a chemical compound between two conformations having different absorption spectra. Upon UV irradiation (around 365 nm, corresponding to the p–p* bond of the azo group) the energetically more stable E or trans configuration, with an elongated rod-like molecular form changes into a bent Z or cis configuration. These two configurations differ in the direction of the central bonds as shown in the figure 1.8.

![Diagram of the azobenzene molecule in E and Z forms.](image)

Figure.1.8. Schematic diagram of the azobenzene molecule in the E and Z forms.

In the energetically more stable (by about 50kJ/mol) E state the two bonds linking the azo group to the aromatic rings are parallel, resulting in an elongated shape of the molecule. In the metastable cis state the angle between the two bonds is 120 degrees and the molecule adopts a bent banana-like confirmation. The reverse transformation can be brought about by illuminating with visible light (in the range 400–500 nm, corresponding to the n–p* bond). This latter change can also occur spontaneously in the ‘dark’ by a process known as thermal
back relaxation. In the case of the photoactive guest–non-photoactive host systems, the E form of the azo dopant, as it is rod-like, is favorable for the stabilization of the liquid-crystalline phase. On the other hand, the Z form, which is in bent form, acts like an ‘impurity’ and therefore destabilizes the liquid-crystalline phase. Hence, photo-isomerization from the E to the Z form causes, in general, a lowering of the transition temperature. If, for instance, the material exhibits a nematic–isotropic (N–I) transition and the UV irradiation is done in the nematic phase, the lowering of the transition temperature $T_{NI}$ could induce an isothermal N–I transition.

Photo induced transitions have been well studied in systems exhibiting nematic–isotropic and smectic C–smectic A transitions, reports on studies in the smectic C, TGB and the banana B2 phases also exist. Recently a reentrant nematic–smecticA transition induced by light has been reported.

In chapter 3, we describe the model proposed by Madhusudana and JyothsnaRajan [40] for reentrance. In this model, the medium is considered to be a mixture of A type (antiparallel) and P type (parallel) of pairs. A simple theory for nematic mixtures consisting of these two types of pairs has been developed by Maier-Saupe. As in [29], consider the orienting potential of the A-type of pairs to be different from that of the P-type of pairs. Usually, the mutual interaction between the two different species in a mixture is assumed to be the geometric mean of the interaction of the pure species. The incidence of UV rays changes the trans isomer (longer) to cis isomer (shorter). This is equivalent to an increase in shorter ‘P’ type of pairs. The ‘P’ type pairs which are shorter have lower orientational potential than ‘A’ type pairs. Thus, the medium with larger $X_p$ (mole fraction of P type molecule) has lower $T_{NI}$. Hence, UV irradiation results in lowering of $T_{NI}$. The thermal back relaxation is very slow and the relaxation of cis to trans and hence the decrease of $X_p$ due to this is ignored. As the intensity of UV radiation is increased, the fraction of trans available reduces. Thus, the variation of $\Delta T_{NI}$ with intensity is not linear. The slope decreases indicating that the cis isomers are gradually reaching saturation. The total energy received also depends on the time of illumination. We have plotted $\Delta T_{NI}$ with respect to energy and not power [41]. The theoretical diagrams show trends similar to experimental diagrams.

In chapter 4, we extend the model and develop a simple molecular theory for photo-induced smectic phase, on the basis of the McMillan theory of SmA liquid crystals. We consider the layering potential of the A-type of pairs to be different from that of the P-type of pairs. As in chapter 3, the incidence of UV radiation is assumed to increase $X_p$. Our main
interest is to discuss the smectic phase. Hence the nematic order is assumed to be saturated for simplicity. Experimentally, the concentration of C10 is chosen such that Sm-phase does not exist without incident light. Similarly, we have chosen \( \alpha = 0.5 \) at which Sm-phase does not exist. Note that the smectic boundary is parabolic.

The incidence of UV rays change the trans isomer (longer) to cis isomer (shorter). This is equivalent to an increase in shorter ‘p’ type of pairs. As mentioned earlier, this is equivalent to a decrease in \( \Delta E \). This reduces internal energy of smectic phase and hence free energy (note that \( \Delta E \) is negative for \( T_R < R_2 \)). This stabilizes the smectic phase. This is indirectly brought about through the variation of \( R_2 \) in our model. As mentioned earlier, the thermal back relaxation is very slow and the relaxation of cis to trans and hence the decrease of \( X_P \) is ignored. The calculated phase diagram showing induced smectic phase is plotted [42]. We notice that the upper \( T_{N_{sm}} \) curve is somewhat flat compared to lower \( T_{NR_{Sm}} \) making the Sm-region un-symmetric.

In chapter5, the above theory is extended to binary mixtures of smectic liquid crystals based on the McMillan model including nematic order. We consider the layering potential of the A-type of pairs to be different from that of the P-type of pairs as in chapter 4. Initially, we consider only the nematic order (i.e., \( \alpha = 0 \)) [43]. The theoretical diagrams show trends similar to experimental diagrams.
1.10 References


