CHAPTER -1

1. INTRODUCTION

1.1 Liquid Crystals

In a solid crystal the molecules are organised in a regular three dimensional lattice, i.e., the centres of mass of the molecules have long range three dimensional translational order. Usually the molecules are not spherical. 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.

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 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 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 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 polymeric liquid crystals (P.G.de Gennes et.al. 1993).

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 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

![Nematic liquid crystals]

Fig. 1.1. 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. 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-1.1).

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

\[
S_{\alpha\beta}^{ij} = \frac{1}{2} \left< 3i_\alpha j_\beta - \delta_{\alpha\beta} \delta_{ij} \right>
\]  

(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. \(S_{\alpha\beta}^{ij}\) is symmetric in \(i,j\) and in \(\alpha,\beta\) . It is also a traceless tensor with respect to either pair \(i.e.,\) \(S_{\alpha}^{\alpha\alpha} = S_{\beta}^{\alpha\beta} = 0\), 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,

\[
S_{\gamma\gamma}^{zz} = -2 \ S_{\gamma}^{xx} = -2 \ S_{\gamma}^{yy} = S_{\gamma}
\]  

(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 X 3) matrix $S_{ij}$ represented as

$$\begin{pmatrix}
-S/2 & 0 & 0 \\
0 & -S/2 & 0 \\
0 & 0 & S
\end{pmatrix}$$

(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 dissertation any further.

1.2.2 Smectic liquid crystals

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-1.2).
Fig. 1.2. 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 $\omega$.

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 (de Gennes P.G et.al. 1993) 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. 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

$$\rho(z) = \rho_o[1 + \tau \cos(qz)]$$

(1.5)

where $\rho_o$ 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
\[ \tau = \langle \cos(2\pi z_i / d) \rangle \]  

(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 \( \rho_o \) 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 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..

1.2.3 Compounds exhibiting only the nematic liquid crystalline phase

(a) Pentyl Cyanobiphenyl (5CB) (Landau L.D et. al. 1980)

(b) P-azoxyanisole (PAA) (de Gennes, P.G 1971)

(c) Quinquephenyl (Peter J.Collings, 2002)
The compound 5CB (structure (a) above) has two phenyl rings without any bridging group in between. It has a strong \textit{longitudinal} dipole moment due to the \(\text{C} \equiv = \text{N}\) group. The nematic phase is stable over a small range at low temperatures. The compound PAA (structure (b) above) has a strong dipole moment due to the NO group inclined at a large angle (\(\approx 60^\circ\)) 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.

\subsection*{1.2.4 Compounds exhibiting the smectic A 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 \textit{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.
In some molecules it can be observed 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.

1.3 Theories of phase transitions

1.3.1 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 $\sigma$ (Landau L.D etal., 1980). In the absence of any external fields the expansion is given by

$$F(T, \sigma) = F_0 + \frac{A}{2} \sigma^2 + \frac{B}{3} \sigma^3 + \frac{C}{4} \sigma^4 + \frac{D}{5} \sigma^5 + \frac{E}{6} \sigma^6 \ldots$$  \hspace{1cm} (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 minimising $F(T, \sigma)$ 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

$$A = a(T - T^*)$$  \hspace{1cm} (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

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

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

(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 explained later.

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.
1.3.2 Landau-de Gennes theory of the N-I transition

de Gennes (de Gennes P.G 1971) 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

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

(1.11)

where $T^*$ is the hypothetical second order transition temperature below which the isotropic phase cannot 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

$$S = 0 \quad \text{(isotropic phase)}$$

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

(1.12)

where $S_+$ 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 superheating 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.

### 1.3.3 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 (deGennes P.G et.al. 1993)

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

(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 $\tau$:

$$F_A = \frac{1}{2} A_A \tau^2 + \frac{1}{4} C_A \tau^2 + \ldots$$

(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 (de Gennes P.G., 1993)

$$S = S_0(T) + \delta S$$

(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

\[
F_s = \frac{1}{2} a_A (T - T_o) \tau^2 + \frac{1}{4} C_A \tau^4 - \gamma \tau^2 \delta S + \frac{1}{2\chi} (\delta S)^2 + F_N(S_o)
\]  

(1.21)

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

\[
\delta S = \chi \gamma \tau^2
\]  

(1.22)

which upon substituting into the equation 1.21 gives

\[
F_s = \frac{1}{2} a_A (T - T_o) \tau^2 + \frac{1}{4} C^* \tau^4 + F_N(S_o)
\]  

(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 \( \tau^6 \) 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

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

(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

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

(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 (Chandrasekhar et al. 1979).

In the next chapter we review the experimental and earlier theoretical results regarding the enhancement of nematic order in thin cells.