Chapter - 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 (*meso*phases) 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 [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

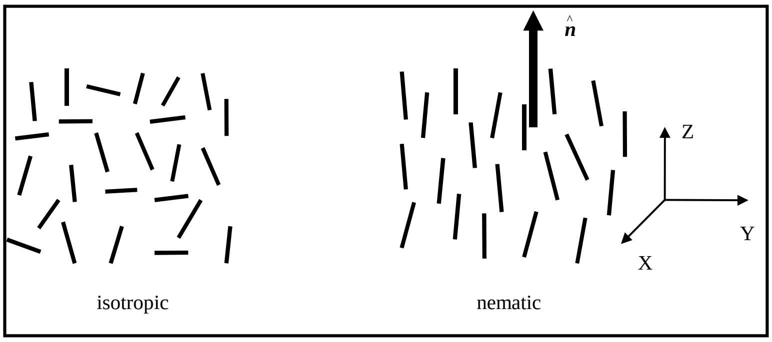


Figure - 1.1. Schematic representation of the ordering of the rod-like molecules in the isotropic and the nematic phases. The director $\hat{n}$ and the choice of axes in the laboratory frame of reference are also shown.

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

1. The ~~nematic~~ 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 $\hat{\boldsymbol{n}}$. 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 $\hat{\boldsymbol{n}}$ and -$\hat{\boldsymbol{n}}$ 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

$$S_{ij}^{\alpha\beta} = \tfrac{1}{2}\langle 3 i_\alpha j_\beta - \delta_{\alpha\beta}\delta_{ij}\rangle \qquad (1.1)$$

where, the tensor indices α and β 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 δ_{ij} are the Kronecker deltas and the brackets ⟨ ⟩ denote the thermal average. $S_{ij}^{\alpha\beta}$ is symmetric in *i,j* and in α,β . 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,

$$S_{ij}^{ZZ} = -2\, S_{ij}^{XX} = -2\, S_{ij}^{YY} = S_{ij} \qquad (1.2)$$

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

$$S_{ij} = \begin{bmatrix} -S/2 & 0 & 0 \\ 0 & -S/2 & 0 \\ 0 & 0 & S \end{bmatrix} \qquad (1.3)$$

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

$$S = \tfrac{1}{2}\langle 3\cos^2\theta_i - 1\rangle \qquad (1.4)$$

where θ_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

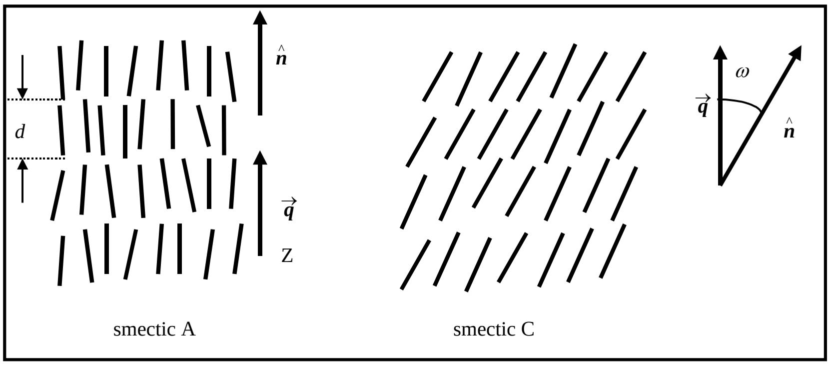


Figure -1.2. Schematic representation of ordering of rod-like molecules in the smectic A and the smectic C phases, showing the nematic director $\hat{n}$, the average spacing *d* between the layers, the wave vector $\vec{q}$ representing the density wave along the layer normal. $\vec{q}$ and $\hat{n}$ 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 ω.

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).

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

$$\rho(z) = \rho_o[1+\tau\cos(qz)] \tag{1.5}$$

where ρ_o is the average density of the medium, $\vec{\boldsymbol{q}}$ is the wave vector along the layer normal with $q = |\vec{\boldsymbol{q}}| = 2\pi/d$ 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 τ, given by

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

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 ρ_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 $\vec{\boldsymbol{q}} \| \hat{\boldsymbol{n}}$, *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, $\vec{\boldsymbol{q}}$ and $\hat{\boldsymbol{n}}$ are not parallel (see figure-1.2). The angle ω between $\vec{\boldsymbol{q}}$ and $\hat{\boldsymbol{n}}$ 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 various 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, *i.e.,* the algebraic sum of all the charges in a given molecule is zero. When the electronegativities 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 *permanent* electric dipole moments, called *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

$$p = q\, l \tag{1.7}$$

where q 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}esu). The SI unit is coulomb-metre (C m) and 1D=1/3 x 10^{-29} 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

Group or bond	Direction of moment	Magnitude of moment (D)
C – H	C ∏ H	0.44
C – N	N ∏ C	0.68
C – O	O ∏ C	1.24
O – H	O ∏ H	1.76

N – H	N ∏ H	1.84
C ≡ N	N ∏ C	4.37
NO_2	O_2 ∏ N	4.4

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.

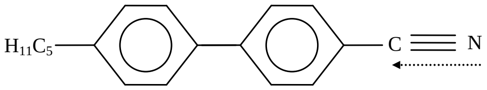
1.4 *Typical examples of rod-like mesogenic compounds*

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 ≈ 20Å and width ≈ 5Å.

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 ^{0}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.

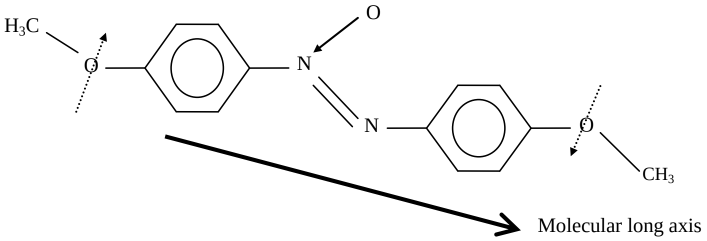
1.4.1 Compounds exhibiting only the nematic liquid crystalline phase

(a) Pentyl **c**yano**b**iphenyl(5CB) [3]



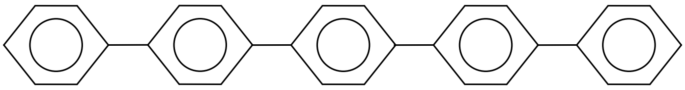
$$\text{Solid} \xleftrightarrow[17.2\ \text{kJ}]{22.5^0\ \text{C}} \text{N} \xleftrightarrow[0.8\ \text{kJ}]{35^0\ \text{C}} \text{I}$$

(b) ***p*-a**zoxy**a**nisole (PAA) [4]



$$\text{Solid} \xleftrightarrow[29.57\ \text{kJ}]{118.2^0\ \text{C}} \text{N} \xleftrightarrow[0.57\ \text{kJ}]{135.3^0\ \text{C}} \text{I}$$

(c) Quinquephenyl [5]



$$\text{Solid} \xleftrightarrow{401^0\ \text{C}} \text{N} \xleftrightarrow{445^0\ \text{C}} \text{I}$$

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 $C\equiv N$ 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 ($\approx 60^0$) 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 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.

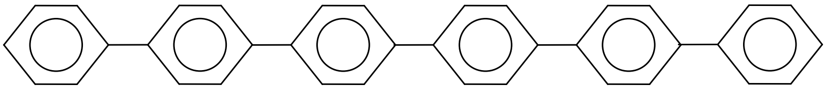
A series of compounds which differ only in the number of carbon atoms in the end chain(s) with the rest of the structure being the same, are called *homologues*. Usually, the shorter homologues of typical mesogenic compounds exhibit only the I and N phases before solidifying. The longer homologues exhibit 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]

$$\text{Solid} \xleftrightarrow[25.3\ \text{kJ}]{24^0\ \text{C}} \qquad \xleftrightarrow[0.13\ \text{kJ}]{34^0\ \text{C}} \text{N} \xleftrightarrow[0.97\ \text{kJ}]{42.6^0\ \text{C}} \text{I}$$

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.

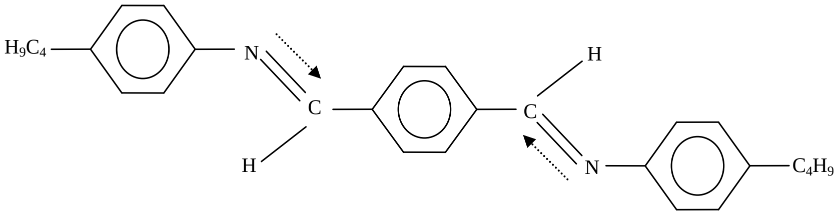
There are rare examples of molecules without any chain resulting in the SmA phase. As an example sexiphenyl that has the phase sequence solid-SmA-N-I, is shown below.



$$\text{Solid} \xleftrightarrow{435^0\ \text{C}} \text{SmA} \xleftrightarrow{465^0\ \text{C}} \text{N} \xleftrightarrow{565^0\ \text{C}} \text{I}$$

1.4.3 Compounds exhibiting the smectic C phase

The compounds exhibiting the smectic C phase usually have a *lateral* component of dipole moment. A typical example is terepthal-bis-butyl aniline(TBBA) whose structural formula is shown below.



$$\text{Solid} \xleftrightarrow{144.1^0\ C} \text{SmC} \xleftrightarrow{172.5^0\ C} \text{SmA} \xleftrightarrow{198.3^0\ C} \text{N} \xleftrightarrow{236.5^0\ C} \text{I}$$

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 ∧ N ∧ K or I ∧ N ∧ SmA ∧ 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∧ N ∧ SmA ∧ N_R ∧ 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, **o**ctyl**o**xy **c**yano **b**iphenyl (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: $I \wedge N \wedge SmA_d \wedge N_R \wedge SmA_1 \wedge K$, as for example in octyloxybenzoyloxy 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 (SmA_1) phase and the higher temperature smectic phase is called the smectic-A_d (SmA_d). X-ray measurements show that [10] the SmA_1 phase has a layer spacing $d \approx l$, whereas the 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 (see figure-1.3 in section 1.6.5). 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: $I \wedge N \wedge SmA_d \wedge N_R \wedge SmA_{dR} \wedge N_R \wedge SmA_1$ as for example, DB_9ONO_2 [11], the ninth homologue of *n* alkyloxy phenyl-nitro benzoyloxy benzoate, denoted in general as DB_nONO_2. This behaviour is also seen in a few mixtures over a very narrow range of concentrations, as in ≈50% molar mixture of DB_8ONO_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 undecyloxyphenyl cyanobenzyloxy benzoate (11OPCBOB) and nonyloxybiphenyl cyanobenzoate (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 various liquid crystalline phases (described in section 1.5) 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. Also, in this thesis, we propose a molecular theory of the SmC phase exhibited by a medium consisting of molecules with *lateral* components of dipole moments. Experimental data of the temperature variations of the order parameter and the specific heat, associated with the SmC to SmA transition, have been often analysed on the basis of the phenomenological Landau 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 σ, characterising the phase of lower symmetry, continuously goes to zero at a 2nd order phase transition. As σ is extremely small near the transition point, it is assumed that, the free energy density F can be expanded in powers of σ [18]. In the absence of any external fields the expansion is given by

$$F(T, \sigma) = F_0 + \frac{A}{2}\sigma^2 + \frac{B}{3}\sigma^3 + \frac{C}{4}\sigma^4 + \frac{D}{5}\sigma^5 + \frac{E}{6}\sigma^6 \;\ldots\ldots \qquad (1.8)$$

where F_0 is the free energy of the disordered phase ($\sigma = 0$). The term linear in σ 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 σ.

$A > 0$ 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

$$A = a(T - T^*) \tag{1.9}$$

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

$$\sigma = \left(\frac{a(T^* - T)}{C}\right)^{\frac{1}{2}}. \tag{1.10}$$

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 σ, then, a first order transition results when a third ordered term in σ 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

de Gennes [19] proposed a phenomenologial 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 $\hat{\boldsymbol{n}}$ while for $S<0$ they are nearly perpendicular to $\hat{\boldsymbol{n}}$. 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

$$F(T, S) = F_0 + \frac{a(T-T^*)}{2}S^2 - \frac{B}{3}S^3 + \frac{C}{4}S^4 \tag{1.11}$$

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

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

$$\text{and } S_{\pm} = \frac{B}{2C}\left[1 \pm \left(1 - \frac{4Ca(T-T^*)}{B^2}\right)^{1/2}\right] \tag{1.12}$$

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 $S = S_{\mathrm{NI}}$). With these conditions imposed on F, equation 1.11 gives,

$$S_{\mathrm{NI}} = \frac{2B}{3C} \tag{1.13}$$

$$T_{\mathrm{NI}} = T^* + \frac{2B^2}{9aC}\,. \tag{1.14}$$

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

$$T^{\,h} = T^* + \frac{B^2}{4aC} > T_{NI}\,. \tag{1.15}$$

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 (*eg*: ≈ 0.8 kJ/mol for 5CB) compared to that of the crystal - melting transition (*eg*: ≈ 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]:

$$\rho(z) = \rho_o\,[1 + \tau\cos(2\pi z/d + \phi) + \ldots\ldots] \tag{1.16}$$

where τ is the amplitude of the first harmonic of the density wave and ϕ is an orbitrary phase which can be taken as zero by a suitable choice of the origin. τ is zero in the nematic phase. Hence, τ 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 τ:

$$F_A = \frac{1}{2}A_A\tau^2 + \frac{1}{4}C_A\,\tau^4 + \ldots \tag{1.17}$$

Only even powers of τ 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],

$$S = S_0(T) + \delta S \tag{1.18}$$

where, $S_0(T)$ is the orientational order parameter in the absence of the layering and δS 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

$$F_{\mathrm{AN}} = -\gamma\tau^2\delta S \tag{1.19}$$

where γ is positive. The nematic free energy which is minimum when $\delta S = 0$ is given by

$$F_{\mathrm{N}} = F_{\mathrm{N}}(S_0) + \frac{1}{2\chi}(\delta S)^2 \tag{1.20}$$

where, χ is a response function. The overall free energy of the smectic phase obtained by adding F_{A} , F_{AN} and F_{N} is

$$F_{\mathrm{S}} = \frac{1}{2}a_{\mathrm{A}}(T - T_0)\ \tau^2 + \frac{1}{4}C_{\mathrm{A}}\ \tau^4 - \gamma\tau^2\delta S + \frac{1}{2\chi}(\delta S)^2 + F_{\mathrm{N}}(S_0). \tag{1.21}$$

Minimising this with respect to δS gives

$$\delta S = \chi\gamma\tau^2 \tag{1.22}$$

which upon substituting into the equation 1.21 gives

$$F_{\mathrm{S}} = \frac{1}{2}a_{\mathrm{A}}(T - T_0)\ \tau^2 + \frac{1}{4}C^*\tau^4 + F_{\mathrm{N}}(S_0) \tag{1.23}$$

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

$$C^* = C_{\mathrm{A}} - 2\gamma^2\chi\,. \tag{1.24}$$

If T_0 is close to T_{NI}, *i.e.*, when the nematic range is small, S_0 is relatively small and hence χ is large and C^* is negative. Then the term in τ^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 $T_{\mathrm{AN}}>T_0$. 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 χ is small and C^* is positive. This leads to a second order N-SmA transition at a temperature $T_{\mathrm{AN}} = T_0$. 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 τ^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

$$\tau \propto (T_0 - T)^{1/4}. \qquad (1.26)$$

The tricritical behaviour may be observed experimentally by varying χ. 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 smectic A 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 $d \approx l$, 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 ρ 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,

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

$$\text{and} \quad \rho = \frac{1}{\sqrt{2}}[\,\psi_2 \exp(i\ \vec{\boldsymbol{q}}\cdot\vec{\boldsymbol{r}}) + \text{complex conjugate}] \qquad (1.27)$$

in which ϕ corresponds to the partial bilayer order and ρ to the monolayer order, ψ_1 and ψ_2 are the corresponding amplidues and $\vec{\boldsymbol{q}}$ is the wave vector of the one dimentional density wave in the SmA phase. An appropriate form of the free energy density is given by

$$F = \frac{A_1}{2}\phi^2 + \frac{C_1}{4}\phi^4 + \frac{A_2}{2}\rho^2 + \frac{C_2}{4}\rho^4 + A_{12}\,\phi\rho - \frac{B_{12}}{\sqrt{2}}\phi^2\rho + \frac{C_{12}}{3}\rho^2\phi^2. \qquad (1.28)$$

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

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

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

where,

$$a_1 = (T - T_1^*)\,,\quad a_2 = (T - T_2^*) \qquad (1.30)$$

$\Delta = \partial^2/\partial z^2$ if the layers are condensed along the Z-axis and $q_1 = 2\pi/l_d$, $q_2 = 2\pi/l_1$, ensuring that ϕ condenses with a wave vector q_1, and ρ 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, $l_d \approx l_1$ and the ($\rho\phi$) term dominates. In the SmA$_2$ phase, $l_d \approx 2l$ 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 behaviours, SmA$_1$-SmA$_d$ critical point *etc.,* in the appropriate parameter space [1]. Some of the phase diagrams predicted by this theory will be reproduced later in chapter-2 and chapter-3.

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.

1.6.5 Review of theories of reentrant phases based on attractive molecular potential

As described in section 1.5, the phenomenon of reentrance is exhibited by strongly *polar* compounds. Hence, the *dipolar interaction* is important in any molecular theory describing this phenomenon. Indeed, Max Born [22], who was the first to propose a molecular theory for the N-I transition, assumed an alignment of permanent dipoles in the nematic phase and predicted the nematic phase to be ferroelectric. However, as described in section 1.2.1, the theory is not valid since the nematic phase is exhibited even if the compound is non polar and the nematic liquid crystal is not ferroelectric even if the compound has polar molecules.

An important property of a liquid crystal is the dielectric anisotropy. It is defined as the difference in the dielectric constants[†] measured with the electric field applied ~~in the directions~~ parallel and perpendicular to the ~~molecular long axis~~director, *i.e.*,

$$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}. \tag{1.31}$$

Usually, a medium with nonpolar rod-like molecules will have a small positive $\Delta\varepsilon$ (<1) due to the anisotropy in the polarisability of the molecules. However, when the molecule has one or more permanent dipoles, the orientational contribution to the polarisability becomes important. When a low frequency external electric field is applied, the molecular reorientation in a liquid crystal is relatively easy compared to that in a solid. This results in a large value of $\Delta\varepsilon$. For nematic liquid crystals consisting of polar molecules with dipoles *along* the long axes, $\Delta\varepsilon$ can be as large as +20 or ~~more~~higher. This helps in decreasing the operating voltage in twisted

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[†] Note that, in SI units, absolute permittivity is denoted as ε and the relative permittivity (or dielectric constant) is denoted as ε_r. For the sake of convenience we omit the subscript ‘r’ and use ε for dielectric constant.

nematic display devices. Due to ~~its~~their technological importance, a large number of polar compounds have been synthesised and studied.

If ~~the~~ ε ~~i~~arises only ~~due to~~ from the polarisability of the molecules, a small decrease in the average ε is expected across the N-I transition due to a small increase in volume. However, an early experimental observation [23] on a cyano compound shows that the average ε has a *positive* jump as the temperature is increased across the N-I transition point. To explain this, it is proposed that [24] the interaction between the permanent dipoles favours an antiparallel configuration of the nearest neighbours. Later ~~of~~ X-ray [9,25] and neutron scattering [26] studies on the strongly polar compounds in the nematic phase have shown that they have a SmA like short range order, with a typical ~~the~~ layer spacing ≈ 1.4 times the molecular length *i.e.*, there is a *partial bilayer* arrangement. This is interpreted [25~~18~~] to be the result of the overlap of the aromatic parts of the neighbouring antiparallel molecules due to the strong dispersion interactions (see figure-1.3). This picture also accounts for the 'incommensurate length' of the SmA$_d$ liquid crystals, used in Prost's phenomenological theory based on two coupled order parameters (see previous section). ~~However, during~~ In the compounds which show double reentrance, the lower temperature smectic phase (SmA$_1$) has the monolayer structure [9]. Hence, as the temperature is decreased, the partial bilayer arrangement of molecules changes over to the monolayer arrangement. We consider a few molecular models which attempt to explain the origin of these 'two lengths' assumed in Prost's phenomenological theory [21] of ~~during~~ double reentrance.

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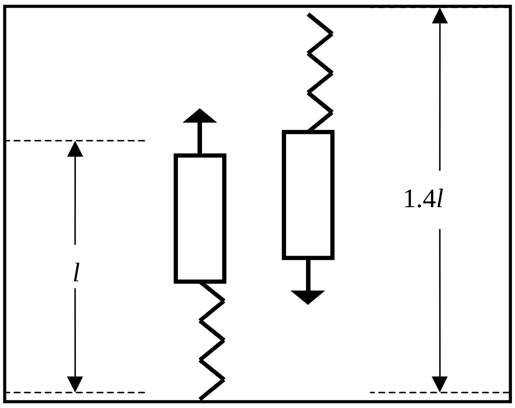

Figure -1.3. Schematic diagram showing the mutual configuration in an antiparallel pair of molecules resulting in a partial bilayer arrangement. The zig-zag line represents the aliphatic chain, t~~T~~he rectangular box attached to it represents the aromatic part and the arrow at the end represents the permanent dipole.

1.6.5.1 Molecular model by Cladis and its extensions

The first attempt to develop a molecular ~~picture~~ model for reentrance was by Cladis [27]. In this, the medium is assumed to consist of antiparallel pairs. Since the antiparallel pairs have ~~the~~ 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-1.4a. When the nematic liquid crystal (figure- 1.4b) is cooled, the number of dimers increases and they come closer. The ~~overlapping of cores and a~~ layering order of the ~~molecules~~ dimers (figure- 1.4c) leads to a lowering of internal energy which more than compensates for the decrease of entropy due to ordering. This leads to the SmA_d phase with a partial bilayer structure. On further cooling, the pairs come still closer. The bulky central parts of the dimers can not be accommodated in the central plane of the layers, thus destroying the layering arrangement (figure- 1.4d) leading to a re-entrant nematic phase. When this is further cooled, a still closer packing leads to a the SmA_1 phase with $d \approx l$ (figure- 1.4e). This is only a pictorial model. The proposed packing in the SmA_1 phase is solid-like and hence can not describe the SmA_1 liquid crystal which is a fluid.

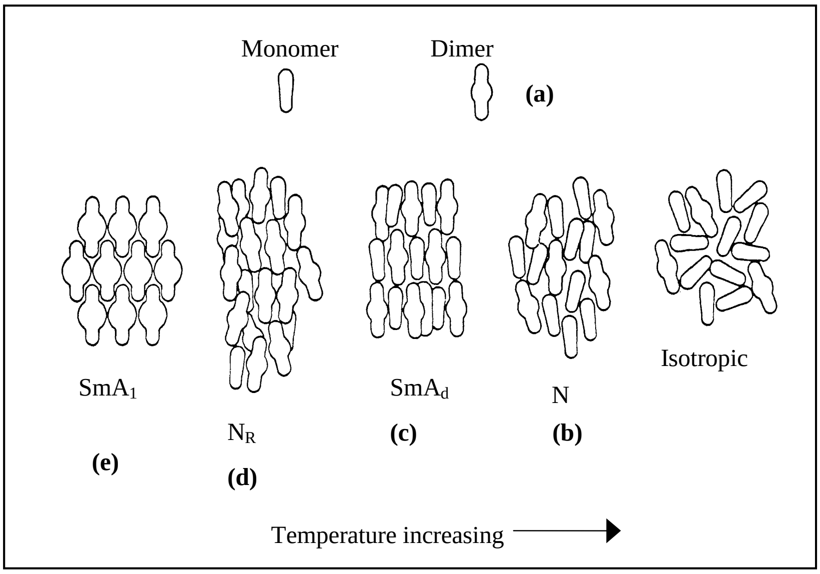

Figure-1.4. Pictorial model given by Cladis [27] for double rentrance. (a)Effective shape of an antiparallel dimer. The figures (b), (c), (d) and (e) represent the organisation of monomers and dimers in the higher temperature nematic (N) phase, SmA$_d$ phase with partial bilayer structure, lower temperature reentrant nematic (N$_R$) phase and the SmA$_1$ phase with a mono layer structure respectively.

~~molecular picture and a proper thermodynamic calculation is required to assess the feasibility of this.~~

Luckhurst and Timimi [28] 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 α in the McMillan theory [29] of the SmA phase, see section 3.2 of chapter-3 for a description of the McMillan theory) is taken to be temperature dependent. If α 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 α is sufficient to stabilise the SmA phase at low temperatures. To incorporate this trend, α 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 ~~proper~~ suitable choice of the dependence of α on temperature~~-~~, they are able to obtain double reentrance. They suggested that the assumed form of the temperature dependence of α may be due to structural changes in the molecular dimers which have not been worked out.

The ~~A~~first microscopic theory of the reentrant nematic phase exhibited by polar liquid crystals was proposed by Longa and de Jeu [30] extending McMillan's theory [29] 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.*,[31] 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[30], this repulsion plays the main role. In the~~is~~ 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 ~~remaining unchanged~~ and hence the McMillan parameter α 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 1.4e. They have ignored the smectic interaction between the monomers assuming it to be small, and have assumed that the McMillan parameter α_d for dimers remains constant up to some critical monomer concentration. Below this concentration, the intercalation starts decreasing the layer thickness and α_d starts decreasing. The assumed variation of α is ad hoc as in the case of Luckhurst and Timimi model [28] described above.~~appears artificial.~~

Mirantsev [32] has extended the model of Longa and de Jeu [30], 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 [33], 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 claculations 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, recent experiments [34] showing the presence of *polar* short range order at low temperatures do not support this arrangement of molecules.

More recently, Luckhurst *et.al.*,[35] have developed a model extending McMillan's model [29] 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 α, this leads to the reentrant nematic phase. On further cooling, the SmA$_1$ phase consisting mostly of the monomers is stabilised. 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 can not explain the recent experimental observation [34] showing the presence of polar short range order at low temperatures.

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The molecular model which is often referred to in the literature is the frustrated spin gas model. We describe this in the next section.

1.6.5.2 Frustrated spin-gas model

The frustrated spin gas model was proposed by Berker *et.al* [36]. The key ~~factor~~ aspect in this model is that, when a third polar molecule comes near an antiparallel dimer, its orientation can not be antiparallel to both the molecules in the dimer leading to frustration in orientation. To incorporate this idea, they consider triplets of molecules in a two dimensional triangular lattice with the molecular long axes having an ideal orientational order in a direction perpendicular to the lattice plane. The molecules are free to have only the axial displacement. Positional fluctuations transverse to the molecular axes are ignored. Each molecule is assumed to have notches which create potential barriers to prevent free movement of neighbours axially. The number of notches is assumed to be related to the number of carbon atoms in the alkyl chain. ~~Along with~~The terminal axial dipoles lead to antiparallel near-neighbour interaction and also the frustration of a third molecule. They develop the theory incorporating different 'up' and 'down' arrangements of the molecules in a triplet with different extents of axial overlapping of the notches. Presence of smaller 'sub-notches' allows for slight axial vibrations. The effective averaged couplings between the molecules in each triplet are classified as 'strong', 'moderate' and 'weak'. They develop the model in analogy with the spin gas theory of ferromagnetism using a two dimensional distorted triangular Ising model [37].~~is obtained.~~ If the moderate coupling has strength close to that of the strong coupling, then, according to the theory, the molecular triplets form a two dimensional 'polymer' with long range anti-ferroelectric order in the plane perpendicular to the direction of the nematic director. This phase is interpreted as ~~leads to~~ a stable smectic phase. In the absence of such a correlation, ~~, otherwise,~~ the stable phase is taken to be the nematic. The relative weights of these couplings depend on the number of notches *etc.* By adjusting these, they get various phase diagrams showing

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~~The model predicts~~ double, quadruple, sextuple and octuple re-entrances. The phase diagrams are calculated with the variation of intermolecular separation and number of notches (chain length). With suitable conversions, these diagrams can be compared with experimental ~~–~~temperature-concentration or pressure-temperature phase diagrams. The topology of the theoretical phase diagrams as well as the predicted specific heat variation compare well with experimental ones. But, the theory has the following drawbacks:

- As de Gennes and Prost [1] remark, the model is two dimensional. Hence, the piling of layers can not be considered *i.e.*, the phase identified as the SmA$_1$ could be SmA$_2$ or longitudinal ferroelectric as well. Also, since the model corresponds to a two dimensional system, the transitions are strongly displaced towards low temperatures as compared to what they should be in a three dimensional system. As the authors themselves remark, the temperatures calculated do not directly correspond to experimental values.

- The model produces only phase diagrams and does not give the order parameters and their temperature dependences.

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- Only ‘up’ and ‘down’ spins are considered and extensions are not made to include unsaturated nematic order. Hence, the theory can not explain the nematic-nematic transition which has been confirmed experimentally [14]. Also, the phase diagrams can not contain the isotropic phase.

- The notches are identified with the zig-zag nature of the alkyl chain. As Cladis remarks [38] ~~[31], ,~~ the pressure data showing universality depending only on the number of benzene rings, suggests that chains may not be the most important molecular entities determining the reentrance.

- As Garland [39] has pointed out, the re-entrant nematic loop (or lake) found in experiments is associated with the SmA$_1$ - SmA$_d$ transition, whereas in the spin-gas theory this is not found to be true.

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1.7 A ~~New~~ molecular model based on pairs with parallel dipole moments at low temperatures~~to explain the reentrant sequences:~~

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 Jyothsna Rajan [40]. The basic concept in this~~our~~ model is that the molecular pairs can change over from anti-parallel (A) to parallel (~~–~~P~~–~~) configuration as the intermolecular separation (*r*) is reduced due to cooling or due to increase of pressure. The medium is treated as an equilibrium *mixture* of the A and P types of pairs. The formation of 'two lengths' assumed in Prost's model [21], the temperature variation of dimer concentration, the variation of the McMillan parameter α assumed in Luckhurst and Timimi model [28] and reentrant phase diagrams are explained as natural consequences of the temperature variation of the relative concentration of the two species. The model, with suitable modifications gives a variety of phase diagrams. Since we adopt this model for various extensions, a detailed discussion of this model is given in the next chapter.

~~We treat the medium as a *mixture* of the A and P type of pairs. We extend the Maier Saupe and the McMillan theories including this concept and develop a mean field theory for the nematic and the smectic phases. The different possible extensions of this are discussed in subsequent chapters of the thesis.~~ In the next section, we give an outline of the contents of different chapters of the thesis.

1.8 Scope of the thesis

In the next chapter (chapter-2), we describe the model proposed Madhusudana and Jyothsna Rajan [40] for double reentrance. In this model, t~~consider the dipole-dipole, dipole induced dipole, chain-chain and aromatic core dispersion interactions with reasonable values of dipole moment, polarisability *etc.* we show that, as the intermolecular separation is decreased, the parallel(P) configuration of pairs is energetically favoured over the anti-parallel(A) configuration. To reflect this, a suitable form of the temperature dependence of the pairing energy is assumed.~~ he medium is considered to be a mixture of A and P types of pairs. We develop a simple theory for nematic mixtures consisting of these two types of pairs by extending the Maier-Saupe theory [41]. We 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 consequence of a deviation from this approximation is investigated. Under certain ranges of the model parameters, a~~A~~ first order N-N transition ending in a critical point is predicted [42]. Also, the jump in the relative concentration of the A and P types of pairs, the jump in the order parameters and the variation of the specific heat at constant volume are calculated near the N-N transition. The results are discussed in comparison with a few available experimental data on the N-N transition.

In chapter-3, the above theory is extended to binary mixtures of smectic liquid crystals based on the McMillan model [29]. We consider the layering potential of the A-type of pairs to be different from that of the P-type of pairs as in reference [40]. Initially, we treat the nematic order to be saturated. With this, various phase diagrams showing first order SmA$_1$-SmA$_d$ transition ending in a critical point, N$_R$ lake associated with the SmA$_1$-SmA$_d$ boundary and the merger of the N$_R$ lake with the main nematic sea are obtained [43]. Next, the temperature dependence of the nematic order is also included [44]. For different ranges of the model parameters, in addition to the earlier results with a saturated nematic order, the calculated phase diagrams show the N-N transition associated ~~along with~~with the SmA$_1$-SmA$_d$ transition and the phase sequence N-SmA$_d$-N$_{Rd}$-N$_{R1}$-SmA$_1$ on cooling. The results are discussed in comparison with experimental data and other theoretical models.

In chapter-4, the model is extended to include the effect of an external electric field. The nematic director aligns parallel to the applied field since the medium consisting of molecules with strong longitudinal dipoles has a large positive dielectric anisotropy.~~medium tends to have an orientational order due to orientational polarisability of the medium with polar molecules, or due to anisotropic polarisability of the medium with molecular dielectric anisotropy.~~ ~~Since~~ T~~t~~he additional orienting potential due to the external field results in an increase of the nematic order parameter. Indeed, the external electric field produces a weak orientational order even in the otherwise isotropic phase (paranematic phase). The nematic-isotropic transition temperature, which now becomes the nematic-paranematic transition temperature, increases with field. A~~A~~s the field is further increased, the first order nature of the nematic-paranematic transition becomes weaker and finally results in a continuous change-over from a strongly oriented to a weakly oriented phase beyond some critical field, as also described by the Landau theory. Our calculations show that the temperatures of N-N transition, SmA_d-N_R transition and SmA_1 - SmA_d transition also increase with the field. Further, we show that the temperature range of the SmA_d phase decreases and finally vanishes with an increase of the field, resulting in a bounded SmA_d region in the electric field-temperature phase diagram. ~~All these effects and also on the basis of our model in chapter 4.~~E~~ E~~lectric field-temperature phase diagrams are calculated for various ranges of the model parameters [45]. Some of the results are compared with the available experimental data.

In chapter-5, the model is extended to include the effect of external pressure on the various phase transitions. When a medium is compressed, the molecules come closer. This effect is similar to that produced by cooling under constant pressure. ~~Hence, the phenomenon of multiple re-entrance and smectic polymorphism can be expected when pressure is applied over a nematic liquid crystal. At a fixed temperature, when pressure is increased on the nematic phase, a double re-entrant sequence N $\wedge$ SmA_d $\wedge$ N_R $\wedge$ SmA_1 is observed [8]. As the temperature is increased, the SmA_d region decreases. At high temperatures, the thermal energy is sufficient to destabilise the SmA_d phase and the phase disappears, *i.e.*, a typical pressure-temperature phase diagram shows a bounded SmA_d region.~~ When the pressure is applied at a fixed temperature, since the thermal energy is not changed, the size and shape of the molecules play an important role in stabilising the different phases. Hence the hard rod features and the effect of excluded volume on packing are to be included in the theory to explain the effect of pressure. In this chapter, a hybrid model is developed by including the hard rod features as well as the attractive interactions. The hard rod model developed by Kimura *et.al* [46] has been extended to include the mean field potential and short-range parallel or anti-parallel correlations. Calculations are carried out assuming the medium to have a saturated nematic order. ~~Calculations are carried out for smectic phase with saturated nematic order.~~The pressure-temperature phase diagrams calculated using this model show the N-N transition, double re-entrance with a bounded $\mathrm{SmA_d}$ region and the N-N transition associated with double reentrance. We have also calculated pressure versus *A* (a parameter which increases with chain length in a homologous series) phase diagrams. These show the $\mathrm{N_R}$ lake associated with the $\mathrm{SmA_1}$-$\mathrm{SmA_d}$ transition, N-N transition occurring inside such an $\mathrm{N_R}$ lake, quadruple reentrance at constant pressure, and widening and merging of the $\mathrm{N_R}$ lake with the main nematic sea [47]. As shown in chapters 2 and 3, if the hard rod effects are not taken into account, a negative deviation from the geometric mean approximation for the mutual attractive interaction is *necessary* to get the N-N transition. Our calculations including the hard core interactions in chapter-5 clearly show that, neglecting these interactions is equivalent to a negative deviation in the geometric mean approximation for the effective mutual interaction between A and P types of pairs and this deviation increases as the two components become structurally more dissimilar. The results are discussed in comparison with the available experimental data and other theoretical models.

In chapter-6, the subject matter is different from that of the previous chapters. W~~w~~e no longer consider molecules with *longitudinal* components of dipole moments. We discuss a molecular theory of the ~~SmA~~ SmC ~~transition~~phase ~~. As it is already mentioned in section 1.2, the SmC phase~~ which is exhibited by compounds whose molecules have *lateral* components of electric dipole moments (see section 1.4.3). ~~The SmC phase is characterised by long range one dimensional layering order and a long range orientational order with the director tilted with respect to the layer normal see figure 1.2). This phase stabilises on cooling the SmA phase. It is known by experiments that, on heating the SmC phase, the average tilt angle ω of the nematic director continuously decreases leading to a second order SmC -SmA transition or jumps to zero leading to a first order SmC-SmA transition.~~ In this chapter, various earlier molecular theories of the SmC-SmA transition are critically reviewed. As Goossens points out in his detailed criticism [48], these theories for the SmC -SmA transition are not satisfactory. We propose that the molecular origin of the tilt is the *off axis* location of the lateral dipole in the molecule. Using reasonable values of dipole moment *etc.*, we show that a tilted structure lowers the energy of the medium. An appropriate single particle potential is proposed to develop a molecular mean field model for the SmC phase.~~on the basis of this.~~ Phase diagrams calculated on the basis of the model show SmC-SmA-N-I transition sequence or a direct SmC-N or SmC-I transition [49]. Over an appropriate parameter space, nature of the SmC-SmA transition changes from first order to second order (tricritical behaviour). The results are discussed in comparison with experimental data. We also estimate the specific heat at constant volume. Close to a second order SmC-SmA transition, using the calculated temperature variation of the tilt angle, the Landau coefficients have been evaluated and are compared with those estimated from experimental data. Over a very narrow range of the parameters, a first order SmC-SmC transition ending in a critical point is also predicted. The calculations have been extended to include a higher order term in the tilting potential and to include the effect of different tilt angles of the core and the chain in the SmC phase. Some possible extensions of the model have been pointed out.

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