Chapter-3

A Molecular Theory for Phase Diagrams Involving Smectic and Nematic Phases Exhibited by Strongly Polar Compounds.

3.1 Introduction

As described in chapter-1 (see section 1.2), in the uniaxial nematic (N) liquid crystal composed of rod like molecules, the long axes of the rods tend to be aligned along the director represented by the unit vector \( \hat{n} \) (see figure 1.1, chapter-1). The extent of orientational order is represented by the order parameter \( S \) defined as

\[
S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle = \langle P_2(\cos \theta) \rangle
\]  

(3.1)

where \( \theta \) is the angle between the long axis of the \( i^{th} \) molecule and the director, \( P_2 \) is the second Legendre polynomial and \( \langle \rangle \) denote a statistical average.

In smectic liquid crystals, the centres of mass of the rods have an additional quasi long range one dimensional periodic order. 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 smectic density wave can be represented by

\[
\rho(z) = \rho_0 [1 + \tau \cos(qz)]
\]

(3.2)

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. We choose the laboratory frame of reference with the Z-axis along the layer normal. The extent of layering (smectic) order is measured by the normalised amplitude of this density wave, called the smectic order parameter \( \tau \), given by

\[
\tau = \langle \cos(2\pi z/d) \rangle
\]

(3.3)

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 \( \rho_0 \), corresponding to the
nematic or the isotropic phase. Different variations of layering and inlayer order are possible leading to different types of smectic liquid crystals. If $\mathbf{d} \parallel \mathbf{n}$, i.e., the director is normal to the layers, it is termed as the smectic A (SmA) liquid crystal (see figure 1.2, chapter-1). In this chapter, we describe various phase transitions involving SmA and nematic liquid crystals in highly polar compounds. We begin with a review of the experimental results.

### 3.1.1 The SmA-N transition

As explained in chapter-1 (see section 1.4), on cooling mesogenic compounds from the isotropic (I) phase, before transforming into a solid crystal (K), the shorter homologues exhibit the nematic (N) phase while the longer homologues exhibit the smectic A phase also. i.e., the usual sequences of phase transitions are: I $\rightarrow$ N $\rightarrow$ K or I $\rightarrow$ N $\rightarrow$ SmA $\rightarrow$ K or I $\rightarrow$ SmA $\rightarrow$ K. Often, the shorter homologues of the smectogens exhibit a second order SmA-N transition at which the order parameter $\tau$ continuously goes to zero. As the chain length is increased, the nature of the transition changes over to first order and also the temperature range of the N phase decreases and finally vanishes. Very long homologues exhibit a first order SmA-I transition. A typical phase diagram illustrating the vanishing of the N phase for higher homologues is shown in figure 3.1.

**Figure - 3.1.** Plot of liquid crystal transition temperatures against the number of carbon atoms ($n$) in the chain for $n$-alkoxy benzylidene amino biphenyls [1]. $\lambda$, $\sigma$, $\nu$ and $5$ represent N-I, SmA-N, SmA-I and C-N or C-
SmA transition respectively, where C denotes the solid crystal. The two branches in the N-I transition curve correspond to the odd (lower branch) and even (upper branch) values of \( n \).

Liquid crystals made of strongly polar molecules exhibit some unusual phase sequences. We describe these in the next few sections.

### 3.1.2 Nematic reentrance

The structural formula of the strongly polar compound \( n \)-alkoxy cyano biphenyl (\( n \)OCB), where \( n \) stands for the number of carbon atoms in the alkoxy chain, is shown below.

![Structural formula of 6OCB](image)

The sequence of phase transitions is I (78) N (56) K for 6OCB and I (79.5) N (67) SmA (54) K for 8OCB, where the numbers in the parenthesis represent the transition temperatures in °C.

Cladis [2] found that mixtures of certain compounds with strongly polar cyano or nitro end groups, on cooling from the isotropic phase, exhibit the sequence of transitions: I \( \land \) N \( \land \) SmA \( \land \) \( N_R \) \( \land \) K. The second nematic phase that occurs at temperatures lower than the range of occurrence of smectic phase is called the re-entrant nematic (\( N_R \)) phase (eg, 6OCB and 8OCB mixture, figure 3.2a). A similar phenomenon was found later on in pure compounds under elevated pressures (eg., 8OCB) [3] (figure 3.2b). Subsequently such a phase sequence has been found in some pure compounds at normal pressures also, for eg., in Octyloxybenzyloxy-benzylidene-cyanoaniline (OBBC) [4].

### 3.1.3 Double reentrance

On cooling further, below the \( N_R \) phase, another smectic phase re-enters in some pure compounds or binary mixtures leading to the sequence: I \( \land \) N \( \land \) SmA\( _d \) \( \land \) \( N_R \) \( \land \) SmA\( _1 \) \( \land \) K. This phenomenon is called double re-entrance. The lower temperature re-entrant smectic phase, called the smectic-A\( _1 \) (SmA\( _1 \)) phase, is found to have a layer spacing \( d \approx l \), whereas the higher temperature smectic phase, called the smectic-A\( _d \) (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 and hence the suffix ‘d’ is used to denote dimers and the suffix ‘1’ for the monomers (see section 1.6.5, chapter-1).

Figure - 3.2. (a) A typical temperature($T$) - concentration ($X$) phase diagram of a binary mixture of polar compounds with $X$ as wt% of 6OCB in 8OCB showing the nematic reentrance. The reentrant nematic occurs in the super cooled regime and the melting line is not shown [5]. (b) A reentrant phase sequence in pressure ($p$) - temperature ($T$) phase diagram for 8OCB [3].
Figure - 3.3. (a) The temperature (T) - concentration phase diagram for binary mixtures of n-alkyloxybenzoyloxy-cyano-stilbene (n shown along the X- axis) showing the double reentrance with the bounded SmA\textsubscript{d} phase [6]. (b) The pressure (p) - temperature (T) phase diagram [7] of the homologue with n = 8 showing similar features.

For example the compound octyloxybenzoyloxy cyano- stilbene (T8) shows double reentrance [8]:

\[
\begin{align*}
I & \leftrightarrow 283^\circ C \\
N & \leftrightarrow 247^\circ C \\
\text{SmA}_d & \leftrightarrow 138.9^\circ C \\
N_R & \leftrightarrow 96^\circ C \\
\text{SmA}_1 & \leftrightarrow 95^\circ C \\
K &
\end{align*}
\]

When the relative concentration in case of a binary mixture or the pressure applied to a pure compound is varied, the SmA\textsubscript{d} phase gets bounded. This is shown in figure 3.3

### 3.1.4 Multiple reentrance and reentrant nematic lake

A few pure compounds, show a quadruple re-entrant sequence \textit{viz.} I\text\cap\text{N}\text\cap\text{SmA}_d \text\cap\text{N}_{R}\text\cap\text{SmA}_{dR}\text\cap\text{N}_{R}\text\cap\text{SmA}_1 as the temperature is lowered. Multiple reentrance in the pure compound DB\textsubscript{9}ONO\textsubscript{2} (the ninth homologue of n-alkoxyphenyl-nitrobenzoyloxybenzoate, DB\textsubscript{n}ONO\textsubscript{2}) at atmospheric pressure was first reported by Tinh \textit{et al} [9] though they did not identify all the phases. Later, DB\textsubscript{9}ONO\textsubscript{2} was found to show the sequence [10],

\[
\begin{align*}
\text{N} & \leftrightarrow 195^\circ C \\
\text{SmA}_d & \leftrightarrow 156^\circ C \\
\text{SmA}_{dR} & \leftrightarrow 138.5^\circ C \\
\text{SmA}_1 & \leftrightarrow 124^\circ C \\
\text{SmC}_2 & \leftrightarrow 121.5^\circ C \\
\text{SmC}_2 & \leftrightarrow 96^\circ C \\
\text{SmA}_2 & \leftrightarrow 100^\circ C \\
\text{SmC} & \downarrow \\
\end{align*}
\]

In the above, it may be noted that, apart from the SmA phases, the compound also exhibits the SmC\text{C} phase which has, in the layers with tilted arrangement of molecules, the aromatic and the aliphatic parts alternating with some periodicity. The SmA\textsubscript{2} phase has $d\approx2l$ and SmC\textsubscript{2} is the tilted version of SmA\textsubscript{2}. In our theoretical models we do not consider the SmC\text{C}, SmA\text{2} and the SmC\text{2} phases. The 10\textsuperscript{th} homologue (DB\textsubscript{10}ONO\textsubscript{2}) exhibits a similar sequence at higher pressures (see figure 3.4a) [11]. This behaviour is also seen in some mixtures over a very narrow range of concentrations (\textit{eg.}, ~50% molar mixture of DB\textsubscript{8}ONO\textsubscript{2} and DB\textsubscript{10}ONO\textsubscript{2}) [10] (see
The temperature-concentration phase diagrams of mixtures of polar compounds not belonging to the same homologous series show other interesting features like a re-entrant nematic lake surrounded by the SmA phase [12] or a SmAd island surrounded by the nematic region [13] (figure 3.4c, d). A detailed review of various experimental studies on the SmAd-SmA1 phase transition boundary and the NR region has been given by Shashidhar et al [14]. We do not specifically discuss SmAd-SmA2 critical point on the basis of our theory. Experimentally this transition has been studied in detail by Shashidhar et al [15].

Figure 3.4(a) The pressure-temperature phase diagram showing multiple reentrance and different smectic phases in DB_{10}ONO_{2} [11]. (b) Similar phenomenon in temperature-concentration (X) plane in binary mixtures,
with $X$ as the mole % of DB$_{10}$ONO$_2$ in DB$_8$ONO$_2$ [10]. In (a) and (b), SmA$_1$, SmA$_d$ and SmA$_2$ are denoted as $A_1$, $A_2$ and $A_d$ respectively. (c) Re-entrant nematic lake surrounded by the SmA phase [12] where, 10.O.NCS is decyloxy isothiocyanatophenyl benzoate and 11OPCBOB is undecyloxyphenyl cyanobenzylxybenzoate. (d) SmA$_d$ (denoted as $S_{Ad}$) island surrounded by the nematic region where $nBCB$ is cyano biphenylyl $n$-alkylbenzoate and $nCN$ is cyanophenyl $n$-alkyl benzoate [13]. In all the diagrams, the reentrant nematic is denoted as $N_{re}$.

There have been many attempts to explain double reentrance using phenomenological as well as molecular theories. Prost has developed a very successful Landau theory of the various phases exhibited by such compounds [16]. We have given a brief review of this theory in chapter-1 (see section 1.6.4). In the next section, we give some of the phase diagrams predicted by an extension of this theory by Prost and Toner [17].

### 3.1.5 Phase diagrams predicted by Prost’s phenomenological theory

Different types of phase diagrams have been predicted by the phenomenological theory developed by Prost [16, 17] depending on the parameters used. In the theory, two coupled smectic order parameters corresponding to the molecular length $l$ and another incommensurate length $l' \text{ such that } l < l' < 2l$, have been used. Some of the phase diagrams predicted by this model are shown in the figures 3.5 and 3.6.
Figure- 3.5. Phase diagrams involving SmA$_1$, SmA$_d$ and N phases, predicted by the dislocation loop melting theory of Prost and Toner [17] without considering fluctuations. The thick and the dashed lines indicate first and the second order phase transitions respectively and C denotes a critical point. $r$ and $\delta r$ are general variables which can be mapped to pressure and temperature or pressure and concentration etc.

As de Gennes and Prost remark [16], “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 discuss the molecular origin of the ‘two lengths’ assumed by Prost.
3.1.6 Molecular origin of the ‘two lengths’ assumed in Prost’s model

Various theories have been proposed to explain the molecular origin of the ‘two lengths’ assumed by Prost. In all the molecular theories, the SmA\textsubscript{d} structure is explained by assuming that the medium consists of antiparallel dimers [18] having the overlap of the aromatic parts. In the compounds which show double reentrance, the lower temperature smectic liquid crystals (SmA\textsubscript{1}) has the monolayer structure [19]. We have reviewed several molecular models which have been proposed for the strongly polar compounds in section 1.6.5, chapter-1. We have also described in chapter-2, a simple model proposed by Madhusudana and Jyothsna Rajan [20], to explain the molecular origin of the ‘two lengths’ assumed in the Prost’s phenomenological model [16]. The basic idea in this model is that the molecular pairs can change over from the anti-parallel (A) to the parallel (P) configuration as the intermolecular separation (£r$) is reduced due to cooling or due to increase of pressure. This change over occurs due to a competition between the repulsive dipole-dipole interaction and the attractive dipole-induced dipole and chain-chain interactions (see section 2.2, chapter-2). Recent experiments [21] showing the presence of polar short range order at low temperatures support this model. The model [20], with suitable modifications, gives a variety of phase diagrams. In chapter-2, we adopted this model for describing the N\textsubscript{i}-N\textsubscript{d} transition. In this chapter, we extend this model and develop a molecular theory of smectic mixtures, on the basis of the McMillan [22] theory of SmA liquid crystals. In the next section we give a brief review of the McMillan theory.

3.2 The McMillan theory of SmA liquid crystals

McMillan extended the Maier and Saupe (MS) [23] theory by including a potential corresponding to the one dimensional translational order of SmA liquid crystals. As explained in chapter-1 (see section 1.4.2), the compounds exhibiting the SmA phase usually have a central aromatic core and flexible alkyl chains at the two ends. The dispersion interaction energy is very strong between the aromatic moieties since they have large polarisabilities. Thus the aromatic parts of the neighbours tend to overlap and arrange themselves in a layer. The layer-structure is stabilised if the alkyl chains, which separate the layers, are sufficiently long. This is the physical idea
behind the model proposed by McMillan. Starting from an anisotropic pair interaction energy, and restricting the expansion to only one Fourier component, McMillan wrote the single particle potential of the $i^{th}$ molecule as

$$U_i(\cos \theta, z_i) = -U_0 \left[ 1 + \alpha \sigma \cos(2\pi z_i/ld) \right] S (3 \cos^2 \theta - 1)/2$$

(3.4)

where $U_0$ is the MS interaction parameter, $\theta$ the angle between the long axis of the $i^{th}$ molecule and the director, $S$ the orientational order parameter defined in equation 3.1 above, $d$ the layer spacing, $z_i$ the coordinate of the centre of the $i^{th}$ molecule measured along the layer normal and $\sigma$ the coupled order parameter, which is a measure of the amplitude of the density wave in the SmA phase, defined by

$$\sigma = \langle \cos(2\pi z_i/ld) (3 \cos^2 \theta - 1)/2 \rangle.$$  

(3.5)

in which $\langle \rangle$ denote a statistical average. The McMillan parameter $\alpha$ is given by

$$\alpha = 2 \exp\left[ -\left( \pi r_0/d \right)^2 \right]$$

(3.6)

where $r_0$ which represents the ‘range’ of the dispersion interaction is of the order of the length of the rigid core of the molecules.

The molar internal energy is given by

$$U = \frac{N}{2} \langle U_i \rangle = -\frac{N}{2} U_0 (S^2 + \alpha \sigma^2)$$

(3.7)

where $N$ is the Avogadro number. The factor (1/2) arises since each molecule is counted twice while finding the average. The molar entropy is written as

$$S = -N k_B \langle \ln f(z, \cos \theta) \rangle$$

(3.8)

where $k_B$ is the Boltzmann constant and $f(z, \cos \theta)$ is the normalised single particle distribution function. The molar Helmholtz free energy is written as

$$F = U - T S$$

(3.9)

The normalised distribution function found by minimising the free energy is given by

$$f(z, \cos \theta) = Z^{-1} \exp(-U/k_B T)$$

(3.10)

where $Z$ is the normalising integral. The order parameters $S$ and $\sigma$ are calculated using
\begin{align*}
S &= \frac{1}{d} \int_{-d/2}^{+d/2} \int_{0}^{1} d(z) f(\cos \theta) P_2(\cos \theta). \tag{3.11}
\end{align*}

\begin{align*}
\sigma &= \frac{1}{d} \int_{-d/2}^{+d/2} \int_{0}^{1} d(z) f(\cos \theta) \cos(2\pi z/d) P_2(\cos \theta). \tag{3.12}
\end{align*}

The above equations have the following solutions:

(i) \quad S = 0, \quad \sigma = 0 \quad \text{corresponding to the isotropic phase},

(ii) \quad S \neq 0, \quad \sigma = 0, \quad \text{corresponding to the nematic phase},

(iii) \quad S \neq 0, \quad \sigma \neq 0, \quad \text{corresponding to the SmA phase}. \tag{3.13}

The MS condition is given by

\begin{align*}
U_0/k_B T_{N1} = 4.541 \tag{3.14}
\end{align*}

where $T_{N1}$ is the N-I transition temperature. Hence, $U_0$ just fixes the N-I transition temperature. The McMillan parameter $\alpha$ is a measure of the strength of the layering potential. It is clear from equation 3.6 that, for a given core length $r_0$, the value of $\alpha$ increases with an increase of the layer spacing $d$, i.e., $\alpha$ increases with the increase of chain length in a homologous series. Thus the temperature- $\alpha$ phase diagrams of the McMillan theory are compared with the temperature-chain length phase diagrams obtained in experiments.

McMillan showed that, $\alpha < 0.7$ results in a second order SmA-N transition, which becomes first ordered in nature for $\alpha \geq 0.7$, i.e., the phase diagram has a tricritical point at $\alpha = 0.7$. Further, the SmA phase has a direct transition to the isotropic phase for $\alpha \geq 0.98$. The theoretical phase diagram broadly reflects the experimental trends (see figure 3.1) in a homologous series.

We now extend the McMillan theory to develop a theory for smectic liquid crystals made of strongly polar compounds. For simplicity, we first consider the nematic order to be saturated, i.e., $S=1$. 
3.3 Theory of smectic liquid crystals made of strongly polar compounds with a saturated nematic order

3.3.1 Theoretical model

3.3.1.1 Assumptions

In order to simplify the calculations, the following assumptions are made.

1. As mentioned above, the nematic order is taken to be saturated and only the smectic interactions are considered.

2. For the sake of simplicity, as explained in chapter-2, we assume that the medium consists of pairs of molecules which have either an antiparallel (A) or parallel (P) configuration.

3. As we described in chapter-2, the A-type (P-type) configuration is favoured at lower (higher) densities (see section 2.2, Chapter-2). The energy difference between the two configurations is written as

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

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, \( T^* \) is some reference temperature, \( R_1 k_B T^* \) is an interaction parameter and \( T_R = T/T^* \) 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.

4. The McMillan parameters for A-type (\( \alpha_A \)) and P-type (\( \alpha_P \)) configurations can be written as

\[
\alpha_A = 2 \exp(- \left[ \pi r_o / (r_o + 2c) \right]^2)
\]

and

\[
\alpha_P = 2 \exp(- \left[ \pi r_o / (r_o + c) \right]^2)
\]

where \( r_o \) and \( c \) are the lengths of the aromatic and chain moieties of the molecule respectively. \( \alpha_P \) can be expressed in terms of \( \alpha_A \) using
\[
\frac{c}{r_0} = \frac{1}{2} \left[ \frac{\pi}{\sqrt{\ln(2/\alpha_A)}} - 1 \right].
\] (3.18)

(5) It is clear that the geometrical parameters of the A and P types of configurations are different. Hence, as in case of nematic potential used in chapter-2, we assume the mutual smectic interaction parameter

\[
\alpha_{AP} = \alpha_{PA} = \alpha_{E} = Q \sqrt{\alpha_A \alpha_P}
\] (3.19)

where \( Q \neq 1 \) indicates a deviation from the geometric mean (GM) approximation for the mutual smectic interaction and \( (Q - 1) \) is a measure of this deviation.

(6) In the previous chapter, \( \Delta E \) was taken to be a function of temperature only (see equation 3.15 above). But, we note that the nematic lake is found in mixtures of chemically dissimilar compounds. Hence, an exact description of this phenomenon requires a general theory of mixtures. However, for the sake of simplicity we assume that the McMillan parameter \( \alpha_A \) (or \( \alpha_P \)) is adequate to represent a given concentration in such mixtures. In a homologous series, the chain length of the molecule and hence \( \alpha \) vary. The chain-chain interaction energy and hence \( E_P \) can also be expected to vary with \( \alpha \). We assume that

\[
\Delta E \propto (\alpha_A)^n
\] (3.20)

As in chapter-2, the value of \( \Delta E \) is calculated for \( r = 0.5 \) nm for various values of chain length \( c \), with the core length equivalent to that of 10 carbon bonds, dipole moment \( p = 6 \) Debye = \( 2 \times 10^{-29} \) Cm, polarisability of the core \( = 20 \) \( \text{Å}^3 \) = \( 20 \times 10^{-30} \) m\(^3\) and chain-chain interaction constant \( \approx 1.1 \times 10^{-77} \) SI units/carbon bond (see section 2.2, chapter-2 for details). \( \alpha_A \) is calculated using equation 3.16 above. By plotting \( \ln(\Delta E/10^{-19}) \) as a function of \( \ln(\alpha_A) \), it is seen that the slope \( \approx 4 \) for the range of \( \alpha_A \).
relevant in our calculations (see figure-3.7).

**Figure- 3.7. Plot of ln(\(\Delta E/10^{-19}\)J ) with ln(\(\alpha_A\)). The slope \(\approx 4\).**

Hence we take

\[
\Delta E \propto (\alpha_A)^4
\]

(3.21)

Since \(\Delta E\) linearly depends on the interaction parameter \(R_1\), we assume that

\[
R_1 = R_1^*(\alpha_A)^4
\]

(3.22)

where \(R_1^*\) is an input parameter. As will be discussed later (section 3.3.3.3 and section 3.4.2.3), inclusion of this variation of \(\Delta E\) results in phase diagrams containing an \(N_R\) lake. Though the above calculation has been made for variation of chain length in a homologous series, the strong dependence of \(\Delta E\) with respect to \(\alpha_A\) appears to be valid only in case of mixtures of chemically dissimilar compounds which show the \(N_R\) lake in the temperature-concentration plane (see figure 3.4c). Mixtures of compounds belonging to the same homologous series show only SmA\(_1\)-SmA\(_d\) transition and not an \(N_R\) lake. \(R_2\) can also be expected to depend weakly on the chain length in a homologous series \(i.e.,\) on the McMillan parameter \(\alpha\). We ignore this dependence of \(R_2\) with \(\alpha\).

(7) As we have described in chapter-2, most experimental phase diagrams on binary mixtures of nematogens correspond to a negative deviation from the geometric mean (GM) approximation for the mutual interaction between the components and the deviation increases as the molecular structures of the two components become more dissimilar. Further, in chapter-2, we have shown that a negative deviation is necessary to get a nematic to nematic phase transition in polar compounds. We can expect a similar negative deviation in the mutual smectic interaction also, \(i.e.,\) for the McMillan parameter \(\alpha_{AP}\).

As we have discussed, the P-type and A-type configurations give rise to the SmA\(_1\) and SmA\(_d\) phases respectively. There have been some experiments on binary mixtures of polar compounds [24] in which one component shows SmA\(_1\) and the other shows SmA\(_d\). In these cases, the smectic-nematic transition line has an appreciable concave shape, especially when the components have a large difference in the layer spacings, indicating a strong negative deviation from the GM approximation for the mutual interaction \(i.e.,\) \(Q < 1\) in equation 3.19. As the chain length in a homologues series is
increased, the numerical value of $\alpha_A$ as also the structural dissimilarity between the P- and A-types of pairs is enhanced. Hence it is reasonable to assume that as $\alpha_A$ increases the deviation $|Q - 1|$ from GM rule increases, or $Q (< 1)$ decreases. Since both $\alpha_A$ and $\alpha_P$ vary in a homologous series, we expect $Q$ to depend on the ratio $\alpha_A/\alpha_P$ (which is a rough measure of the dissimilarity) and we assume

$$Q = Q^* (\frac{\alpha_A}{\alpha_P})$$

(3.23)

where $Q^*$ is a constant chosen such that $Q < 1$ in the entire range of $\alpha_A$ used. Since $\alpha_P$ increases with the chain length more rapidly than $\alpha_A$, the ratio $\alpha_A/\alpha_P$ decreases moderately, and leads to results which can be compared with experimental data. For example, with $Q^* \approx 0.12$, we get $Q \approx 0.6$ for $\alpha_A \approx 0.4$ while $Q \approx 0.4$ for $\alpha_A \approx 1$.

In chapter-5, where a hybrid model is developed including the hard core interactions, we show that the excluded volume effects cause the negative deviation from the GM approximation and that the magnitude of the deviation increases as the two components become geometrically more dissimilar. In our present calculations where the hard core interactions are not taken into account, as in the previous chapter, the assumed negative deviation reflects the excluded volume effects.

### 3.3.1.2 Expressions for the free energy and the order parameters

Extending the McMillan theory to the case of mixtures and considering only the smectic interactions, the potential energy of the $i^{th}$ A-type of pair can be written as

$$U_{Ai} = - U_0 X_A \alpha_A \tau_A \cos(2\pi \alpha_A/d) - U_0 X_P \alpha_P \tau_P \cos(2\pi \alpha_P/d)$$

(3.24)

where $X_A$, $X_P$ and $\tau_A$, $\tau_P$ are the mole fractions and translational order parameters of the A- and P-types of pairs respectively, and $d$ is the average layer spacing given by

$$d = X_A d_A + X_P d_P,$$

with

$$d_A = r_0 + 2c$$

and

$$d_P = r_0 + c.$$

(3.25)

Similarly for a P-type pair,

$$U_{Pj} = - U_0 X_P \alpha_P \tau_P \cos(2\pi \alpha_P/d) - U_0 X_A \alpha_A \tau_A \cos(2\pi \alpha_A/d)$$

(3.26)
The internal energy of one mole of the pairs obtained by averaging over the
distribution functions is

\[
2U = \frac{NX_A}{2} \langle U_A \rangle + \frac{NX_P}{2} \langle U_P \rangle - NX_P \Delta E
\]

\[
= -\frac{N U_0}{2} \left[ X_A^2 \alpha_A \tau_A^2 + X_P^2 \alpha_P \tau_P^2 + 2 \alpha_P X_A X_P \tau_A \tau_P \right] - NX_P \Delta E \tag{3.27}
\]

where \( N \) is the Avogadro number, \( \langle \rangle \) indicate statistical averages and the factor 2 on
the left hand side reminds that we have a mole of pairs. The last term is the
concentration dependent part of the configurational energy.

The molar entropy is given by

\[
2S = -N k_B \left[ X_A \int_{-d/2}^{d/2} dz_A \ln f_{A_i} + X_P \int_{-d/2}^{d/2} dz_P \ln f_{P_j} \right]
- N k_B \left( X_A \ln X_A + X_P \ln X_P \right) \tag{3.28}
\]

where the last term is the entropy of mixing and \( f_A \) and \( f_P \) are the normalised
translational distribution functions of A and P types of pairs respectively. The
Helmholtz free energy is given by:

\[
F = U - TS \tag{3.29}
\]

The normalised distribution functions \( f_A \) and \( f_P \) and the expression for \( X_A \) found by
minimising \( F \) are,

\[
f_{A_i}(z) = \frac{1}{Z_A} \exp(-U_A/k_B T) \tag{3.30}
\]

\[
f_{P_j}(z) = \frac{1}{Z_P} \exp(-U_P/k_B T) \tag{3.31}
\]

and

\[
X_A = \frac{1}{1 + \frac{Z_P}{Z_A} \exp(\Delta E/k_B T)} \tag{3.32}
\]
where $Z_A$ and $Z_P$ are the appropriate normalising integrals. The expressions for the smectic order parameters are given by,

$$
\tau_A = \langle \cos(2\pi \zeta_A/d) \rangle = \int_0^1 d\zeta f_A(\zeta) \cos(\pi \zeta_A) \tag{3.33}
$$

$$
\tau_P = \langle \cos(2\pi \zeta_P/d) \rangle = \int_0^1 d\zeta f_P(\zeta) \cos(\pi \zeta_P) \tag{3.34}
$$

where we have used the reduced coordinate $\zeta = 2z/d$.

### 3.3.1.3 Specific heat at constant volume

The molar specific heat at constant volume is given by

$$
C_V = \left( \frac{\partial U}{\partial T} \right)_V
$$

$$
= -\frac{NU_0}{2} \left[ \frac{\partial X_A}{\partial T} \left( X_A \phi_A \tau_A^2 - X_P \phi_P \tau_P^2 + \alpha \tau_A \tau_P (X_P - X_A) \right) + \frac{\partial \tau_A}{\partial T} \left( X_A^2 \phi_A + \alpha \tau_A X_P \tau_P \right) + \frac{\partial \tau_P}{\partial T} \left( X_P^2 \phi_P + \alpha \tau_P X_A \tau_A \right) \right] + \frac{\partial X_A}{\partial T} N \Delta E. \tag{3.35}
$$

Note that in the above expression, as explained in chapter 2, we have not differentiated $\Delta E$ with respect to $T$ as it depends really on volume and the temperature dependence is taken only for convenience. Expressions for the derivatives of $X_A$, $\tau_A$ and $\tau_P$ are obtained by differentiating the relevant parameters in the equations 3.32, 3.33 and 3.34 respectively, with respect to $T$. We get,

$$
\frac{\partial X_A}{\partial T} \left[ \frac{U_0}{k_B T}(-\alpha \tau_A^2 - \alpha \tau_P^2 + 2 \phi_{\tau_A} \tau_A \tau_P) + \frac{1}{X_A X_P} \right]
$$

$$
+ \frac{\partial \tau_A}{\partial T} \left[ \frac{U_0}{k_B T} (\alpha \phi_A \tau_A^2 - \alpha \phi_P \tau_P^2 + \alpha \phi_{\tau_A} \tau_A \tau_P) \right] + \frac{\partial \tau_P}{\partial T} \left[ \frac{U_0}{k_B T} (\alpha \phi_P \tau_P^2 - \alpha \phi_{\tau_P} \tau_P \tau_A) \right]
$$

$$
+ \frac{U_0}{k_B T^2} \left[ \alpha \phi_A X_A \tau_A^2 - \alpha \phi_P X_P \tau_P^2 + \alpha \phi_{\tau_A} \tau_A \tau_P (X_P - X_A) \right] - \frac{\Delta E}{k_B T^2} = 0. \tag{3.36}
$$
\[
\frac{\partial X_A}{\partial T} \left[ \frac{U_0}{k_B T} (\alpha_A \tau_A - \alpha_E \tau_P) \right] + \frac{\partial \tau_A}{\partial T} \left[ \frac{U_0}{k_B T} \alpha_A X_A - \frac{1}{\Delta AS} \right] + \frac{\partial \tau_P}{\partial T} \left[ \frac{U_0}{k_B T} \alpha_E X_P \right] \nonumber \\
- \frac{U_0}{k_B T^2} \left[ \alpha_A X_A \tau_A + \alpha_E X_P \tau_P \right] = 0. \tag{3.37}
\]

\[
\frac{\partial X_A}{\partial T} \left[ \frac{U_0}{k_B T} (\alpha_E \tau_A - \alpha_P \tau_P) \right] + \frac{\partial \tau_A}{\partial T} \left[ \frac{U_0}{k_B T} \alpha_E X_A \right] + \frac{\partial \tau_P}{\partial T} \left[ \frac{U_0}{k_B T} \alpha_P X_P - \frac{1}{\Delta PS} \right] \\
- \frac{U_0}{k_B T^2} \left[ \alpha_P X_P \tau_P + \alpha_E X_A \tau_A \right] = 0. \tag{3.38}
\]

where, we have used,

\[
\Delta AS = \left\langle \left[ \cos(2\pi \alpha_A l/d) \right]^2 \right\rangle - \tau_A^2
\]

and \[
\Delta PS = \left\langle \left[ \cos(2\pi \alpha_P l/d) \right]^2 \right\rangle - \tau_P^2 \tag{3.39}
\]

The relevant derivatives are obtained by solving the three simultaneous equations 3.36, 3.37 and 3.38 and used to calculate \( C_V \).

### 3.3.2 Method of calculation

The smectic interaction parameter is assumed to be \( U_0 \alpha \) with \( U_0 = 4.541 \times 500k_B \) i.e., \( T^* = 500K \), which corresponds numerically to the value of \( T_{NI} \) used in the previous chapter. We use \( Q < 1 \) i.e., \( \alpha_E < \sqrt{\alpha_A \alpha_P} \) in equation 3.19 to take into account the negative deviation from the GM approximation. At any reduced temperature \( T_R \), consistent values of \( \tau_A \) and \( \tau_P \) are found as \( X_A \) is varied from 0 to 1 for the assumed set of the four parameters of the problem, \( \alpha_A, R_1^*, R_2, \alpha_A, \) and \( Q^* \). The free energy is calculated in each case. Near the minimum of \( F \) with respect to \( X_A \), equation 3.32 is used to find the consistent value of \( X_A \). We usually get more than one set of self consistent values of \( X_A, \tau_A \) and \( \tau_P \). The stable solution corresponds to the one with the lowest value of \( F \). Calculations have been made for \( R_1^* = 8 \) and \( R_2 \) around 0.7 which are very reasonable values as described in chapter-2. We evaluate all the necessary integrals numerically using a 32 point Gaussian quadrature method in double precision.

We look for the following types of solutions:
(i) \( \tau_\Lambda = \tau_\rho = 0 \) corresponding to the nematic phase, and,

(ii) \( \tau_\Lambda \neq \tau_\rho \neq 0 \) corresponding to smectic phase which is SmA\(_1\) if \( X_\Lambda \) is relatively small and SmA\(_d\) if \( X_\Lambda \) is relatively large.

### 3.3.3 Results and discussion

Depending on the values of the parameters used, our calculations give the following results: (i) a first order SmA\(_1\)-SmA\(_d\) transition changing to a continuous SmA\(_1\) to SmA\(_d\) evolution beyond a critical point (ii) a re-entrant nematic lake associated with the SmA\(_1\)-SmA\(_d\) transition, and (iii) the re-entrant nematic lake merging with the nematic sea. We discuss these in the following subsections.

#### 3.3.3.1 First order SmA\(_1\)-SmA\(_d\) transition ending in a critical point

Since the SmA\(_1\) and the SmA\(_d\) phases have the same symmetry, we can expect a first order SmA\(_1\)-SmA\(_d\) transition or a continuous evolution of SmA\(_1\) to SmA\(_d\) beyond a critical point. The temperature-\( \alpha_\Lambda \) phase diagram obtained with \( Q^* = 0.22 \) and \( R_2 = 0.7 \) is shown in figure 3.8. Keeping \( R_1^* \) and \( R_2 \) fixed, if a lower value of \( Q \) is used, \textit{i.e.}, the deviation from the GM rule is slightly larger, the critical point \( C_1 \) of the SmA\(_1\)-SmA\(_d\) transition is shifted to a lower value of \( \alpha_\Lambda \) while the rest of the diagram does not change perceptibly. This is shown by a dashed line in figure 3.8 for \( Q^* = 0.2 \) for which the critical point is at \( \alpha_\Lambda = 0.945 \) and \( T_R = 0.60867 \).
Figure – 3.8. Calculated phase diagram showing the SmA$_1$-SmA$_d$ critical point $C_1$ for $R_1^* = 8$, $R_2=0.7$ and $Q^* =0.22$. The open circle shows the critical point which is shifted to a lower value of $\alpha_A$ when $Q^*$ = 0.2. The rest of the diagram does not change perceptibly when $Q^*$ is reduced from 0.22 to 0.2.

It can be seen that the first order SmA$_1$- SmA$_d$ boundary ends at a critical point $C_1$ as $\alpha_A$ is decreased. This can be understood as follows. For low values of $\alpha_A$, the free energy has a single minimum with respect to $X_A$. For higher values of $\alpha_A$, the structural dissimilarity between the A-type of pairs and the P-type of pairs is large, leading to a large negative deviation from GM rule (see equation 3.23), i.e., the mutual interaction between the A-type of pairs and the P-type of pairs is relatively weak. Hence the ‘middle’ concentrations (i.e., $X_A \approx 0.5$) are not favoured and this causes a ‘hump’ in the variation of the free energy with respect to $X_A$ resulting in two minima. This is shown in figure 3.9 for $\alpha_A =1.1$. At $T_R \approx 0.6383$, the two minima in free energy become equal resulting in a first order SmA$_1$-SmA$_d$ transition with a jump in $X_A$. The latter along with the jumps in the order parameters are shown in figure 3.10. In the narrow range of temperatures around $T_{A1-Ad}$ shown in the figure 3.10, the order parameter $\tau_P$ does not have an appreciable dependence on temperature. Over a wider range, $\tau_P$ generally decreases with increase of temperature.
Figure – 3.9. Molar Helmholtz free energy difference \( (F_{\text{smectic}} - F_{\text{nematic}}) \) as a function of relative concentration of the A-type of pairs \( (X_A) \) at three temperatures near \( T_{A1-Ad} \) for \( R_1^* = 8, R_2 = 0.7, Q^* = 0.22 \) and \( \alpha_A = 1.1 \)

(a) \( T/T^* = 0.6373 \) (b) \( T/T^* = 0.6383 \) and (c) \( T/T^* = 0.6393 \).

Figure – 3.10. Relative concentration of the A-type of pairs \( (X_A) \), smectic order parameter for the A-type of pairs \( (\tau_A) \) and for P-type of pairs \( (\tau_P) \) as functions of \( T/T^* \) near \( T_{A1-Ad}/T^* = 0.6383 \). Other parameters are the same as in figure 3.9.

As \( \alpha_A \) is decreased, the dissimilarity between the A- and P-types of pairs is reduced. Hence the SmA_1-SmA_4 transition becomes weaker and at a specific value of \( \alpha_A \) \( (\approx 1.01) \) the first order SmA_1-SmA_4 line ends in a critical point \( C_1 \) for \( T_R = 0.62238 \) (see figure 3.8). As the critical point is reached, as expected, the jumps in \( X_A, \tau_A, \tau_P \) and the internal energy approach zero (figure 3.11).
Figure – 3.11. (i) Relative concentration of the A-type of pairs ($X_A$), (ii) smectic order parameter of the A-type of pairs ($\tau_A$), (iii) smectic order parameter of the P-type of pairs ($\tau_P$) and (iv) internal energy per mole of pairs ($2U$) as functions of $T/T^*$ near the critical point $C_1$ of figure 3.8 for $R_1^* = 8$, $R_2 = 0.7$, $Q^* = 0.22$ and (a) $\alpha_A = 1.01$, (b) $\alpha_A = 1.02$, (c) $\alpha_A = 1.03$, (d) $\alpha_A = 1.04$.

Over a narrow range of temperatures close to the critical point, the value of $X_A$ increases rapidly with temperature. As $X_A$ increases, the effective smectic interaction potential of the A-type of pairs ($X_A\alpha_A$) and the mutual interaction ($X_A\alpha_A\tau_P$) increase. This results in an increase of both $\tau_A$ and $\tau_P$ with temperature. However, over a wider range of temperatures, $\tau_A$ and $\tau_P$ generally decrease as the temperature is increased.
This variation is similar to that in the average orientational order parameter near the $N_1-N_d$ transition for $Y<1$ (i.e., the orienting potential of the P-type pairs less than that of the A-type of pairs) discussed in chapter-2 (see section 2.4.3.3 and figures 2.16 and 2.17).

As the critical point is reached, the specific heat ($C_V$) peak becomes stronger and finally diverges as shown in figure 3.12. Note that $C_V$ shown in figure 3.12 is obtained as $\left(\frac{\partial U}{\partial T}\right)_V$ without differentiating $\Delta E$ with respect to $T$ (see section 3.3.1.3), while the variation of $U$ shown in figure 3.11(iv) includes the variation of $\Delta E$ with respect to $T$.

![Figure 3.12](image)

**Figure – 3.12.** Specific heat at constant volume per mole of pairs ($2C_v$) as a function of $T/T^*$ near the critical point $C_1$ of figure 3.18. The parameters corresponding to (a) ,(b), (c) and (d) are the same as in figure 3.11

### 3.3.3.2 Two SmA$_1$-SmA$_d$ transition lines ending in critical points $C_1$ and $C_2$

A further lowering of $Q$ results in other interesting results. With $Q^* = 0.19$, we have extended the calculations for $\alpha_A$ values much lower than that corresponding to $C_1$. At some low value of $\alpha_A$, the SmA$_1$-SmA$_d$ transition *reappears* below another
critical point $C_2$ (see figure 3.13). This indicates that, at low values of $T_R$ and $\alpha_A$, the free energy again has two equal minima with respect to $X_A$. This can be understood as follows.

![Phase Diagram](image)

**Figure – 3.13.** Calculated phase diagram showing two SmA$_1$-SmA$_d$ critical points $C_1$ and $C_2$ for $R_1^* = 8$, $R_2 = 0.7$, and $Q^* = 0.19$. Near $C_2$, SmA$_1$ and SmA$_d$ are denoted as A$_1$ and A$_d$ respectively.

It can be seen from figure 3.14 that, for higher values of $\alpha_A$, a steep variation of $X_A$ with $T_R$ occurs at $T_R \approx R_2$, whereas when $\alpha_A$ has a low value, it occurs at $T_R$ considerably lower than $R_2$.

$\Delta E$ varies as $\alpha_A^4$ (see equation 3.21) and at any given value of $T_R$, $\Delta E$ is very low for low values of $\alpha_A$. Further, when $\alpha_A$ is decreased, $\alpha_P$ decreases more rapidly than $\alpha_A$ and hence the ratio $\alpha_P/\alpha_A$ (which is $> 1$) is large thus favouring the A-type configuration. Hence $X_A$ is relatively large even when $T_R$ is much less than $R_2$. However, as the temperature is further decreased, $\Delta E$ becomes sufficiently strong to lower the value of $X_A$. 
Figure – 3.14. Relative concentration of the A-type of pairs \((X_A)\) plotted as a function of \(T/T^*\) for \(R_1^* = 8, R_2 = 0.7, Q^* = 0.18\) and (a) \(\alpha_A = 0.43\), (b) \(\alpha_A = 0.865\). Note that in (a), the rather low value of \(\Delta E\) leads to a significant decrease in \(X_A\) as \(T/T^*\) is increased beyond 0.3.

Since \(\Delta E\) is small for low values of \(\alpha_A\), even though \(X_A\) has a steep variation, the free energy does not vary much over a wide range of \(X_A\) (see equations 3.27 and 3.29). Hence, for lower values of \(\alpha_A\), the free energy has a flat minimum with respect to \(X_A\) (see figure 3.15) while it has a deeper minimum for larger values of \(\alpha_A\). Therefore, at low values of \(\alpha_A\), even a small negative deviation from GM rule is sufficient to cause a ‘hump’ in the free energy minimum, resulting in two minima with respect to \(X_A\). This leads to SmA\(_1\)-SmA\(_d\) transition. Thus, even though the deviation from the GM rule (i.e., \(|Q - 1|\) decreases as \(\alpha_A\) is decreased (see equation 3.23 and figure 3.15), the SmA\(_1\)-SmA\(_d\) transition reappears below some values of \(\alpha_A\), i.e., below another critical point \(C_2\). If the negative deviation from GM rule is stronger (i.e., as \(Q\) is lowered), the critical point \(C_2\) is shifted to higher value of \(\alpha_A\) and \(T_R\). For \(Q^* = 0.19\), \(C_2\) is at \(\alpha_A = 0.385\) and \(T_R \approx 0.1693\) (figure 3.13). For \(Q^* = 0.18\), \(C_2\) is at \(\alpha_A \approx 0.43\) and \(T_R \approx 0.2316\) as indicated by vanishing of two minima(figure 3.15).
In general as $Q^*$ is lowered, both $C_1$ and $C_2$ approach each other. For a sufficiently low value of $Q^*$ we can expect them to merge. But, much before this happens, a nematic lake appears in the middle which is discussed in the next subsection.

### 3.3.3.3 Re-entrant nematic lake

When $Q^*$ is 0.188, the nematic phase just re-enters over narrow ranges of $\alpha_A$ (between 0.585 and 0.593) and temperature ($T_R$ between 0.352 and 0.358). On lowering $Q^*$ to 0.18, the $N_R$ region widens as a lake occupying larger ranges of $\alpha_A$ and temperature (figure 3.16). The appearance of the $N_R$ can be understood as follows.

In a binary mixture of polar compounds, since the $\Delta E$ values of the components are different, the average $\Delta E$ per pair can be expected to change with composition. As explained earlier, in our model, $\alpha_A$ is taken to represent a given concentration and $\Delta E$ is assumed to vary as $\alpha_A^4$. Therefore, $\Delta E$ is very low for small values of $\alpha_A$. But, in our model, the re-entrance of the nematic phase on cooling is due to the rapid changeover of A-type of pairs to P-type of pairs at a temperature not low enough to
stabilise the SmA$_1$ phase. However, when $\Delta E$ is very low, as discussed in the previous subsection, and shown in figure 3.14, this changeover occurs at temperatures low enough for the SmA$_1$ phase to be stable. Therefore, as the temperature is varied at low values of $\alpha_A$, the smectic phase is stable without the intervening N$_R$ region. On the other hand, at intermediate value of $\alpha_A$, $\Delta E$ is strong enough to bring about the ‘A’ to ‘P’ changeover at a higher temperature, thus resulting in double re-entrance.

Figure – 3.16. Calculated phase diagram for $R_1^* = 8$, $R_2 = 0.7$ showing the re-entrant nematic (N$_R$) lake for $Q^* = 0.18$. C$_1$ and C$_2$ are the SmA$_1$-SmA$_d$ critical points. The small loop within the N$_R$ lake is for $Q^* = 0.188$, for which the N$_R$ lake just appears.

Larger values of $\alpha_A$ also lead to larger values of $\alpha_R$. Hence the SmA phase is stable even when $X_A$ is small, leading again to the disappearance of the N$_R$ phase. Hence, the N$_R$ region appears as a lake over a range of intermediate values of $\alpha_A$ or equivalently, over a range of intermediate concentrations in a mixture. In general, we can see that, in the presence of a strong negative deviation from GM rule, the smectic phase is destabilised in the ‘middle’ concentrations, whereas the ‘pure’ components have only smectic phases. Indeed, experiments [6, 11, 25] on binary mixtures show
that the N\textsubscript{R}-lake appears around a concentration of 50\%.
Further, the N\textsubscript{R}-lake appears in association with SmA\textsubscript{1}-SmA\textsubscript{d} boundary in the experimental studies also (for example, see figure 3.4c above).

A further increase of the negative deviation ($Q^* = 0.15$) obviously widens the N\textsubscript{R} lake and also as discussed earlier, brings the critical points C\textsubscript{1} and C\textsubscript{2} closer (figure 3.17a). In this case, near the extreme values of $\alpha$ the N\textsubscript{R} phase occurs below the SmA\textsubscript{d}-SmA\textsubscript{1} transition line. For still lower value of $Q$ ($Q^* = 0.12$, see figure 3.17b) or when $\Delta E$ is increased using a higher value of $R_2 = 0.72$, (see figure 3.18a), the N\textsubscript{R}-lake becomes still wider and swallows one or both the SmA\textsubscript{1}-SmA\textsubscript{d} critical points.

When $\Delta E$ is increased further, the nematic lake becomes much wider and eventually merges with the nematic sea creating a ‘nematic gap’ over a range of $\alpha$ values (figure 3.18b). Obviously, the nematic gap widens as $Q^*$ is further decreased or equivalently, the components in a binary mixture become structurally more dissimilar. This agrees with the appearance and widening of the nematic gap in experiments [24] on binary mixtures of 8OCB with one of the homologues of nDBT ($n$ alkyl isothiocyanatophenyl dioxane) exhibiting SmA\textsubscript{d} and SmA\textsubscript{1} phases respectively. With the lower values of $n$, the components have larger ratio of smectic layer spacing and are structurally more dissimilar. For mixtures of 8OCB and 7DBT, the layer spacing ratio $r = 1.46$ and the nematic gap is over a small concentration range of $X = 0.4$ to 0.75 of 8OCB, whereas for mixtures of 8OCB and 4DBT, $r = 1.76$ and the nematic gap is wider, between $X = 0.3$ to 0.9 [24]. Also, we note that the calculated N-SmA\textsubscript{d}-N\textsubscript{R} boundary is parabolic (figure 3.18b) as seen in the experimental phase diagrams [24].

Experimentally it is possible to measure the temperature variation of the smectic layer spacing. We plot in figure 3.19 the calculated values of the relative layer spacing

$$
\frac{dl}{dp} = \frac{(Xd_A + Xpdp)}{dp}
$$

(3.40)
as functions of relative temperature for three values of the McMillan parameter $\alpha_A$ corresponding to the phase diagram shown in figure 3.17a. Note that $d$ shows a maximum value as the temperature is increased in the SmA\textsubscript{d} phase. This trend reflects the temperature variation of $X_A$ (see figure 3.14). The increase in layer spacing from SmA\textsubscript{1} to SmA\textsubscript{d} has been experimentally measured [19].
Figure 3.17. Calculated phase diagram showing a wide re-entrant nematic (NR) lake for $R_1^* = 8, R_2 = 0.7$. (a) $Q^* = 0.15$. $C_1$ and $C_2$ are the SmA$_1$-SmA$_d$ critical points. SmA$_1$ is indicated as A$_1$ at the bottom left corner of the figure. (b) $Q^* = 0.12$. The point where first-order SmA$_1$-SmA$_d$ transition line meets the boundary of NR lake is shown by the open circle.
Figure –3.18. (a) Calculated phase diagram showing a wide re-entrant nematic (\(N_R\)) lake for \(R_1^* = 8\), \(R_2 = 0.72\) and \(Q^* = 0.15\). In this case, the first order Sm\(A_1\)-Sm\(A_d\) transition line merges with the boundary of the lake in the lower range of \(\alpha_A\). (b) Calculated phase diagram showing the re-entrant nematic (\(N_R\)) lake merging with the nematic sea creating a nematic gap, for \(R_1^* = 8\), \(R_2 = 0.75\), \(Q^* = 0.12\). The open circle indicates the point where the Sm\(A_1\)-Sm\(A_d\) transition line meets the \(N_R\) boundary. In some parts of the figures, Sm\(A_1\) and Sm\(A_d\) are indicated as \(A_1\) and \(A_d\) respectively.
Figure – 3.19. The ratio of average layer spacing $d$ to the molecular length $d_P$ as a function of $T/T^*$ for (a) $\alpha_\lambda = 0.5$, (b) $\alpha_\lambda = 0.6$ and (c) $\alpha_\lambda = 0.75$ corresponding to the phase diagram of figure 3.17a. The dotted lines in the N$_R$ phase represent the $d$ values of smectic like short range order. The dashed lines indicate jumps in $d$ at the first order SmA$_1$-SmA$_d$ transitions.

3.3.3.4 Comparison with other theoretical models

The dislocation loop melting theory developed by Prost and Toner [17] predicts different types of topologies showing a first order SmA$_1$-SmA$_d$ transition boundary ending at a critical point, the N$_R$-lake associated with SmA$_1$-SmA$_d$ transition and the N$_R$-lake merging with the main nematic sea as shown in figures 3.5 and 3.6. These topologies are similar to those obtained by our theoretical calculations. Note that, figure 3.6 shows a nematic-nematic transition also. As described in the previous chapter (see chapter-2, section 2.4.3), taking into account only the orientation dependent part of the interactions, a nematic-nematic transition can be obtained only if we assume a negative deviation from the geometric mean (GM) rule for the mutual
orienting potential. But, in the present calculations such a transition is not possible since the nematic order is taken to be saturated. In the next section, we extend the theory to include an unsaturated nematic order and discuss the results. The microscopic theory using the frustrated spin-gas model developed by Berker et al. [26] predicts the possibility of double re-entrance, quadruple re-entrance, SmA$_1$-SmA$_d$ transition, N$_R$-lake surrounded by the SmA$_d$ region etc. However, as noted by Garland et al. [27], the N$_R$-lake predicted by the frustrated spin-gas model does not occur in association with the SmA$_1$-SmA$_d$ transition whereas the experiments [25, 27] and also the Landau theory by Prost and Toner [17] indicate that the N$_R$-lake occurs in association with the SmA$_1$-SmA$_d$ transition line and eventually replaces the SmA$_1$-SmA$_d$ critical point. This feature is brought out in our molecular model. However, the predicted temperature range of N$_R$-lake is much larger than the experimental one.

We now extend the theory to include the orientational interactions also.

### 3.4 Extension of the theory to include unsaturated nematic order

In the previous section, we have developed a theory of smectic mixtures to describe the SmA$_1$-SmA$_d$ transition assuming a saturated nematic order is, i.e., $S = 1$. Depending on the values of the parameters used, our calculations have shown the possibility of (i) a first order SmA$_1$-SmA$_d$ transition changing to a continuous SmA$_1$ to SmA$_d$ evolution beyond a critical point (ii) a re-entrant nematic lake associated with the SmA$_1$-SmA$_d$ transition, and (iii) the re-entrant nematic lake merging with the nematic sea.

In chapter-2, we have described the nematic-nematic transition considering only the orientational interactions. The nematic-nematic transition found experimentally in a system [28] occurs in the reentrant nematic range associated with SmA$_1$-SmA$_d$ transition. In order to describe this feature, we extend our model to include both the nematic and smectic interactions. In the next section, the theoretical model is presented.
3.4.1 Theoretical model

3.4.1.1 Assumptions

We have made the following modifications of our assumptions mentioned in section 3.3.1.1.

(1) As explained in chapter 2, the energy difference between the A and P type configurations is written in terms of the N-I transition temperature $T_{NI}$

$$\Delta E = E_A - E_P = R_1 k_B T_{NI} \left( \frac{R_2}{T_R} - 1 \right)$$  \hspace{1cm} (3.41)

(2) Since the A and P type of pairs are geometrically dissimilar, as in chapter 2, we assume that the orientational potential for A-type of pairs $U_{AA}$ and P-type of pairs $U_{PP}$ to be different. We write,

$$U_{PP} = Y U_{AA}$$  \hspace{1cm} (3.42)

and the mutual interaction potential

$$U_{AP} = U_{PA} = P \sqrt{U_{AA} U_{PP}}$$  \hspace{1cm} (3.43)

where $P \neq 1$ indicates a deviation from the geometric mean (GM) rule in the orientational part of the mutual interaction potential.

(3) Following Kventsel et al [29], we decouple the translational and orientational parts in the McMillan’s ‘mixed’ order parameter ($\sigma$) and write

$$\sigma = \langle P_2(\cos \theta) \rangle \langle \cos(2\pi l/d) \rangle$$

i.e., \hspace{0.5cm} $\sigma = S \tau$  \hspace{1cm} (3.44)

(4) As explained in section 3.3.1.1, a negative deviation from the geometric mean (GM) approximation for the mutual interaction between the components can be assumed to be valid. Hence we can assume both $P$ and $Q$ to be < 1. The deviation increases as the molecular structures of the two components in a mixture become more dissimilar. As the chain length in a homologues series is increased, the numerical value of $\alpha_A$ and also the structural dissimilarity between the P-and A-types of pairs is enhanced. Hence it is reasonable to assume that, as $\alpha_A$ increases, the deviations ($|1-P|$ and $|1-Q|$) from GM approximation increase, or $P$ and $Q$ decrease.
Since \( P \) and \( Q \) always occur together in the expressions involving the mutual interaction in all the equations, it is enough to consider the variation of \( P \) with respect to \( \alpha_A \), i.e., we do not use the equation 3.23 above. Since both \( \alpha_A \) and \( \alpha_P \) vary in a homologous series, as explained earlier, we expect \( P \) to depend on the ratio \( \alpha_A/\alpha_P \) and we assume, as in equation 3.23

\[
P = P^* \left( \frac{\alpha_A}{\alpha_P} \right) \tag{3.45}
\]

where \( P^* \) is a constant chosen such that \( P < 1 \) in the entire series.

### 3.4.1.2 Free energy and order parameters

The medium is assumed to consist of a mixture of A-type pairs and P-type pairs. Extending the McMillan theory to the case of mixtures, the potential energy of the \( i \)-th A-type of pair can be written as

\[
U_{AI} = -U_{AA} X_A S_A P_2 \cos(\theta_A) \left[ 1 + \alpha_A \tau_A \cos(2\pi A/d) \right] - U_{AP} X_P S_P P_2 \cos(\theta_P) \left[ 1 + \alpha_P \tau_P \cos(2\pi P/d) \right] \tag{3.46}
\]

where \( X_A, X_P, S_A, S_P \) and \( \tau_A, \tau_P \) are the mole fractions, orientational and translational order parameters of A and P types of pairs respectively and \( d \) the average layer spacing (see equation 3.25). Similarly for a P-type pair, \( U_{PI} \) is obtained by interchanging suffixes A and P in equation 3.46. Now, the internal energy of one mole of pairs can be written as

\[
2U = \frac{NX_A}{2} \langle U_{AI} \rangle + \frac{NX_P}{2} \langle U_{PI} \rangle - NX_P \Delta E
\]

\[
= -\frac{N}{2} U_{AA} X_A S_A^2 (1+\alpha_A \tau_A^2) + Y X_P^2 S_P^2 (1+\alpha_P \tau_P^2) + 2P \sqrt{Y} X_A X_P S_A S_P (1+\alpha_E \tau_A \tau_P \Delta E)
\]

where we have used the equations 3.42, 3.43 and the factor 2 on the left hand side reminds that we have a mole of pairs. We have also added the concentration dependent part of the configurational energy.

The molar entropy is given by:
where the last term is the entropy of mixing and \( f_A \) and \( f_P \) are the normalised distribution functions of A and P type of pairs respectively. The Helmholtz free energy is given by:

\[
F = U - T \mathcal{S} \tag{3.49}
\]

The distribution functions \( f_A \) and \( f_P \) are found by minimising \( F \). It can be shown that [29] the decoupling assumption (see equation 3.44) leads to the result

\[
f_A = f_{A0} f_{At}, \quad \text{and} \quad f_P = f_{P0} f_{Pt} \tag{3.50}
\]

where \( f_{A0} \) and \( f_{At} \) are the orientational and translational distribution functions of the A-type of pairs and \( f_{P0} \) and \( f_{Pt} \) are similar functions for the P-type of pairs. We have

\[
\begin{align*}
f_{A0} &= \frac{1}{Z_{A0}} \exp \left[ \frac{U_{AA}}{k_B T} \left( X_A S_A (1 + \alpha_A \xi_A^2) + P Y_X S_P (1 + \alpha_P \xi_P^2) \right) \right] \cos(\theta_A) \\
f_{P0} &= \frac{1}{Z_{P0}} \exp \left[ \frac{U_{AA}}{k_B T} \left( Y X_P S_P (1 + \alpha_P \xi_P^2) + P \sqrt{Y} X_A S_A (1 + \alpha_A \xi_A^2) \right) \right] \cos(\theta_P) \\
f_{At} &= \frac{1}{Z_{At}} \exp \left[ \frac{U_{AA}}{k_B T} \left( \alpha_A X_A S_A \xi_A + P \sqrt{Y} \alpha_P X_P S_P \xi_P \cos(2\pi \xi_A / d) \right) \right] \\
f_{Pt} &= \frac{1}{Z_{Pt}} \exp \left[ \frac{U_{AA}}{k_B T} \left( Y \alpha_P X_P S_P \xi_P + P \sqrt{Y} \alpha_A X_A S_A \xi_A \cos(2\pi \xi_P / d) \right) \right] \tag{3.51}
\end{align*}
\]

where \( Z_{A0} \), \( Z_{P0} \), \( Z_{At} \), and \( Z_{Pt} \) are the corresponding normalising integrals. The order parameters are given by:

\[
S_A = \int_0^1 d(\cos(\theta_A)) P_2(\cos(\theta_A)) f_{A0} \tag{3.52}
\]

and

\[
\tau_A = \int_0^1 d(\xi_A) \cos(\pi \xi_A) f_{At} \tag{3.53}
\]

where the reduced co-ordinate \( \xi_A = (2\xi_A / d) \) is used. \( S_P \) and \( \tau_P \) are obtained by interchanging the suffixes A and P in equations 3.52 and 3.53.
The free energy per mole of pairs can now be written in the simplified form as

\[
2F = \frac{NU_{AA}}{2} [X_A^2 S_A^2 (1 + 3 \alpha_A \tau_A^2) + Y X_P^2 S_P^2 (1 + 3 \alpha_P \tau_P^2) + 2\sqrt{Y} X_A S_A S_P (1 + 3 \alpha_E \tau_A \tau_P)] - N k_B T X_A \ln \left( \frac{Z_{\alpha_A} Z_{\alpha_P}}{X_A} \right) - N k_B T X_P \ln \left( \frac{Z_{\alpha_P} Z_{\alpha_A}}{X_P} \right) - N X_P \Delta E
\]

(3.54)

The equilibrium value of mole fraction \(X_A\) of the A-type of pairs is found by minimising \(F\) with respect to \(X_A\). We get (with \(X_P = 1 - X_A\))

\[
\frac{X_P}{X_A} = \frac{Z_{\alpha_P} Z_{\alpha_A}}{Z_{\alpha_A} Z_{\alpha_P}} \exp \left[ \frac{U_{AA}}{k_B T} \left[ \alpha_A X_A S_A^2 \tau_A^2 - Y \alpha_P X_P S_P^2 \tau_P^2 + P \sqrt{Y} \alpha_E S_A S_P \tau_A \tau_P (X_P - X_A) \right] + \frac{\Delta E}{k_B T} \right] \quad (3.55)
\]

### 3.4.1.3 Specific heat at constant volume

The molar specific heat at constant volume is given by

\[
C_V = \frac{\partial U}{\partial T} \bigg|_V = \frac{NU_{AA}}{2} \left[ \frac{\partial X_A}{\partial T} \left[ X_A S_A^2 (1 + \alpha_A \tau_A^2) - Y X_P S_P^2 (1 + \alpha_P \tau_P^2) + P \sqrt{Y} S_A S_P (1 + \alpha_E \tau_A \tau_P) \right] (X_P - X_A) \right]
\]

\[
+ \frac{\partial S_A}{\partial T} X_A [X_A S_A (1 + \alpha_A \tau_A^2) + P \sqrt{Y} X_P S_P (1 + \alpha_E \tau_A \tau_P)]
\]

\[
+ \frac{\partial S_P}{\partial T} X_P [Y X_P S_P (1 + \alpha_P \tau_P^2) + P \sqrt{Y} X_A S_A (1 + \alpha_E \tau_A \tau_P)]
\]

\[
+ \frac{\partial \tau_A}{\partial T} X_A S_A (\alpha_A X_A S_A \tau_A + P \sqrt{Y} \alpha_E X_P S_P \tau_P)
\]

\[
+ \frac{\partial \tau_P}{\partial T} X_P S_P (\alpha_P X_P S_P \tau_P + P \sqrt{Y} \alpha_E X_A S_A \tau_A)
\]

\[
+ \frac{\partial X_A}{\partial T} N \Delta E.
\]

(3.56)

Note that in the above expression, as explained earlier (see section 3.3.1.3), we have not differentiated \(\Delta E\) with respect to \(T\). Expressions for the derivatives of \(X_A\),
$S_A$, $S_P$, $\tau_A$ and $\tau_P$ and are obtained by differentiating the relevant parameters in the equations 3.52, 3.53 and 3.55 respectively, with respect to $T$. The five equations obtained after differentiation can be written in the matrix notation as,

$$
\begin{bmatrix}
C_{11} & C_{12} & C_{13} & C_{14} & C_{15} \\
C_{21} & C_{22} & C_{23} & C_{24} & C_{25} \\
C_{31} & C_{32} & C_{33} & C_{34} & C_{35} \\
C_{41} & C_{42} & C_{43} & C_{44} & C_{45} \\
C_{51} & C_{52} & C_{53} & C_{54} & C_{55}
\end{bmatrix}
\begin{bmatrix}
X'_A \\
S'_A \\
S'_P \\
\tau'_A \\
\tau'_P
\end{bmatrix}
=
\begin{bmatrix}
D_1 \\
D_2 \\
D_3 \\
D_4 \\
D_5
\end{bmatrix}

(3.57)

where the primes indicate the differentiation with respect to $T$. The expressions for the elements of the matrices are given in the appendix. The relevant derivatives are obtained by solving the five simultaneous equations and hence $C_V$ is calculated.

Apart from the trivial solution corresponding to the isotropic phase, we look for the following types of solutions:

1) $S_A, S_P \neq 0$, $\tau_A = \tau_P = 0$ leading to nematic phase which is $N_1$ if $X_A$ is small and $N_d$ if $X_A$ is large, and,

2) $S_A, S_P \neq 0$, $\tau_A, \tau_P \neq 0$ leading to the smectic phase which is SmA if $X_A$ is small and SmA$_d$ if $X_A$ is large.

### 3.4.2 Results and discussion

#### 3.4.2.1 $\Delta E$ and $P$ independent of $\alpha_A$: Double reentrance and SmA$_1$-SmA$_d$ transition

We have carried out the calculations, in the first instance, without including the variation of $\Delta E$ or $P$ with $\alpha_A$. A negative deviation from the GM approximation $(i.e., Q <1)$ is necessary to get a first order SmA$_1$ - SmA$_d$ transition. The phase diagram obtained with $R_1 = 15$, $R_2 = 0.6$, $Q = 0.62$ with $P = Y = 1$, is shown in figure 3.20.
Figure 3.20. The phase diagram obtained with $R_1 = 15$, $R_2 = 0.6$, $Q = 0.62$, $P = Y = 1$ and treating $\Delta E$ and $P$ to be independent of $\alpha_A$. The first order SmA$_1$-SmA$_d$ transition line ends in a critical point (shown by the filled circle). When $Q$ is decreased to 0.55, the SmA$_1$-SmA$_d$ transition line continues (as indicated by the dashed line) and meets the SmA-N$_R$ boundary (shown by the open circle). The remaining parts of the phase diagram do not change perceptibly on decreasing $Q$.

The first order SmA$_1$-SmA$_d$ transition ends in a critical point at $\alpha_A = 1.067$ and $T_R = 0.56855$ (shown by the filled circle). When $Q$ is decreased, the critical point is shifted to lower values of $\alpha_A$. For $Q = 0.55$, before ending in a critical point, the SmA$_1$-SmA$_d$ transition line meets the SmA-N$_R$ boundary at $\alpha_A = 0.907$ and $T_R = 0.5796$ (shown by the open circle). Note that the critical point is highly sensitive to the value of $Q$ while the other transition temperatures do not change perceptibly on changing the value of $Q$. This trend is similar to that got in the calculations with saturated nematic order, as already shown in section 3.3.3.1. If we consider $P = Q = Y = 1$, our model reduces to the model by Madhusudana et al., [20], which gives a similar $T$-$\alpha_A$ phase diagram showing double reentrance, which does not contain a SmA$_1$-SmA$_d$ transition line. In the next subsection, we present the results obtained when the variation of $P$ with $\alpha_A$ is included while $\Delta E$ is treated as constant with respect to $\alpha_A$. 
3.4.2.2 Variation of only $P$ with $\alpha_A$: $N - SmA_d - N_{Rd} - N_{R1} - SmA_1$ transition sequence

In this subsection, we treat $\Delta E$ constant with respect to $\alpha_A$ and include the variation of $P$ with $\alpha_A$. In this case, for a given set of parameters, the free energy has four local minima with respect to $X_A$, two corresponding to the nematic phase and two to the smectic phase. Of these, the phase corresponding to the absolute minimum is the stable one. Depending on which two of these four local minima are equal, we get the possibility of various phase transitions.

With $Y = 1.4$, $R_1 = 15$, $R_2 = 0.6$, $P^* = 0.15$ (recall equation 3.45) and $Q = 1$, we get the phase diagram shown in figure 3.21. We have already shown, considering a saturated nematic order, that the strong variation of $\Delta E$ with $\alpha_A$ (see section 3.3.3.2) leads to an $N_R$ lake associated with the SmA$_1$-SmA$_d$ transition in the temperature-$\alpha$ phase diagram which corresponds to the experimental temperature-concentration phase diagram. We have also pointed out that this variation is associated with the dissimilarity of the molecules of the two components in the mixture. As mentioned earlier, the strong variation of $\Delta E$ with $\alpha_A$ appears to be valid in case of binary mixtures of smectogenic compounds not belonging to the same homologous series which show the $N_R$ lake in the temperature-concentration phase diagram. In the mixtures of smectogenic compounds belonging to the same homologous series, which show only the SmA$_1$-SmA$_d$ transition, $\Delta E$ can be taken to be practically constant with respect to $\alpha_A$. As mentioned earlier, $\alpha_A$ is taken to represent the concentration in a mixture. Hence, our results obtained by neglecting the variation of $\Delta E$ with $\alpha_A$ can be compared with that obtained by experiments [28] (see figure 3.22a) on a mixture of two compounds DB$_8$ONO$_2$ and DB$_{10}$ONO$_2$ belonging to the same homologous series. In the phase diagram, $X$ denotes the mole percentage of the longer homologue (DB$_{10}$ONO$_2$). Obviously, increase of $X$ is equivalent to increase of the McMillan parameter $\alpha$. For example at $X = 53$, SmA$_d$-N$_{Rd}$-N$_{R1}$-SmA$_1$ sequence is seen on cooling. In our calculated phase diagram, for example, at $\alpha_A = 0.525$, we have N-(0.7)-SmA$_d$-(0.63)-N$_{Rd}$-(0.627)-N$_{R1}$-(0.323)-SmA$_1$ sequence on cooling, where we have indicated the transition $T_R$ values in parentheses. (For the sake of clarity, the part of the phase diagram below $T_R = 0.5$ is not shown in the figure 3.21). A reentrant $N_d$-$N_1$ transition line which ends at a critical point (at $\alpha_A = 0.5123$ and $T_R = 0.6266$) is
seen over a small range of $\alpha_A$ (0.5123 to 0.542). As $\alpha_A$ is increased above 0.542, the N_{Rd}-N_{R1} transition line continues as SmA$_d$ - N$_{R1}$ line (for a range of $\alpha_A = 0.542$ to 0.83) and extends as SmA$_d$ - SmA$_1$ line (for $\alpha_A > 0.83$). These features agree with the experimental trends [28], in which there is a reentrant N$_d$ - N$_1$ transition line which ends at a critical point for lower values of X (see figure 3.22a). As X is increased the N$_d$ - N$_1$ transition line becomes the SmA$_d$ - N$_{R1}$ transition line and finally continues as SmA$_d$ - SmA$_1$ transition line.

Keeping $R_1$, $R_2$, and $Q$ the same, if $Y$ and $P^*$ are increased to 2 and 0.18 respectively, we get a similar phase diagram shown in the inset of figure 3.21. In this case, the SmA$_d$-N$_{R1}$ transition occurs over a smaller range of $\alpha_A$ values. These diagrams are also similar to those predicted by the dislocation loop melting theory of Prost and Toner [17] (see figure 3.6 given earlier).

We have evaluated the variation of specific heat at constant volume across the SmA$_d$-N$_{Rd}$-N$_{R1}$-SmA$_1$ transition sequence at $\alpha_A = 0.513$ of figure 3.21. The calculated specific heat (figure 3.23) shows a strong peak at the N$_{R1}$-N$_{Rd}$ transition as seen in the experimental diagram (figure 3.22b). The corresponding variation of the order parameters and $X_A$ are shown in figure 3.24.
Figure 3.21. Calculated phase diagram with $R_1 = 15$, $R_2 = 0.6$, $P^* = 0.15$, $Y = 1.4$, $Q = 1$, and treating $P$ to be dependent on $\alpha_A$, showing the reentrant $N_d$-$N_1$ (indicated in the text as $N_{Rd}$-$N_{R1}$) transition line starting from a critical point. As $\alpha_A$ is increased the transition line continues as $SmA_d$-$N_1$ line and finally as $SmA_d$-$SmA_1$ line. The inset is a similar diagram with $P^*$ and $Y$ increased to 0.18 and 2 respectively, showing that $SmA_d$-$N_1$ transition occurs over a smaller range of $\alpha_A$ values.

Figure 3.22. (a) The $T$-$X$ phase diagram, where $X$ is the mole percent of DB$_{10}$ONO$_2$ in DB$_8$ONO$_2$ [28]. Filled circles, open circles and open squares represent calorimetric, X-ray scattering and optical measurements respectively. The dashed curves indicate 2$^{nd}$ order phase transitions and the solid curves, the 1$^{st}$ order ones. TCP marks the tricritical point. (b) Variation of $C_p$ across the $SmA_1$-$N_1$-$N_d$-$SmA_d$ transition for the mixture with $X = 53.7$. The strong peak in the middle corresponds to the $N_1$-$N_d$ transition and the small peak marked by the left arrow corresponds to $SmA_1$-$N_1$ and the right arrow to $SmA_d$-$N_d$ transition.
Figure - 3.23. Calculated temperature variation of the specific heat at constant volume ($C_v$) across the SmA$_d$-N$_{Rd}$-N$_{R1}$-SmA$_1$ transition at $\alpha_A=0.513$ as shown in figure 3.21. Note that the scales are different in the left and the right parts of the figure.

Figure - 3.24. Calculated temperature variations of the order parameters and $X_A$ across the SmA$_d$ - N$_{Rd}$ - N$_{R1}$ - SmA$_1$ transition at $\alpha_A = 0.513$ corresponding to figure 3.21. Note that the X-axis scales are different in the left and the right parts of the figure.
The calculated specific heat \( (2C_v/Nk_BT_{NI}) \) shows a jump \( \approx 0.28 \) for the \( \text{N}_{R1}-\text{N}_{Rd} \) transition. Taking \( T_{NI} = 500\text{K} \) and the gram molecular weight of \( \text{DB}_9\text{ONO}_2 \) to be \( \approx 500 \text{ gm} \), this value corresponds to \( \Delta C_v \approx 1 \text{ JK}^{-1}\text{g}^{-1} \). This roughly agrees with the experimental value of \( \Delta C_p \approx 2 \text{ JK}^{-1}\text{g}^{-1} \) (see figure 3.22b). Also, the experimental data indicates that the \( \Delta C_p \) corresponding to the \( \text{SmA}_1-\text{N}_{R1} \) transition is less than that for the \( \text{N}_{Rd}-\text{SmA}_d \) transition. Our calculations show that the jump in the specific heat at constant volume \( \Delta C_v \) at the \( \text{SmA}_1-\text{N}_{R1} \) transition is about 10 times less than that at the \( \text{N}_{Rd}-\text{SmA}_d \) transition (see figure 3.23). However, the calculated \( C_v \) values can not be expected to have a quantitative agreement with the experimental \( C_p \) data. Further, in the \( \text{SmA}_1 \) and the \( \text{N}_1 \) phases, the parallel molecules need not be restricted to pairs but can form larger clusters, which has not been taken into account in the theoretical treatment.

In the next subsection we discuss the effect of inclusion of the variation of \( \Delta E \) with \( \alpha_A \) while \( P \) is treated as constant with respect to \( \alpha_A \).

### 3.4.2.3 Variation of only \( \Delta E \) with \( \alpha_A \): Reentrant nematic lake

We now include the variation of only \( \Delta E \) with \( \alpha_A \) \( (i.e., \Delta E \propto \alpha_A^4, \text{see equation 3.21}) \) and, for the sake of simplicity, ignore the variation of \( P \) and \( Q \) with respect to \( \alpha_A \). As already discussed, the results of this calculation are to be compared with those of experiments on mixtures of chemically dissimilar compounds. With \( R_1^* = 6, R_2 = 0.7, P = Q = Y = 1 \), the \( \text{N}_R \) lake obtained in the \( T_{R-\alpha_A} \) plane is shown in figure 3.25. In our earlier calculations with saturated nematic (section 3.3.3.3) order, we have already shown that the variation of \( \Delta E \) with \( \alpha_A \) leads to an \( \text{N}_R \) lake. The shape of the \( \text{N}_R \) lake boundary was elliptical, whereas experimentally it is not found to be so (see figure 3.4c). The shape of the \( \text{N}_R \) lake boundary obtained in the present calculations is also not elliptical, being wider in the lower \( \alpha_A \) side.

As explained in section 3.3.3.3, in this case also, an increase of \( R_1^* \) or \( R_2 \) leads to a wider lake as shown in figure 3.26 (for \( R_1^* = 7, R_2 = 0.7 \)) which finally merges with the main nematic sea (for \( R_1^* = 6, R_2 = 0.75 \)). Also, we have made several calculations including the variation of both \( \Delta E \) and \( P \) with \( \alpha_A \). It not possible in the
present theory to get $N_{R1}-N_{Rd}$ and SmA$_1$-SmA$_d$ transitions associated with an $N_R$ lake merging with the main nematic sea, as it is found in the experiment.

Figure - 3.25. The phase diagram calculated including the variation of
only $\Delta E$ with $\alpha_A$, showing the $N_R$ lake with $R_1^* = 6, R_2 = 0.7$ and $P=Q=Y=1$. Figure – 3.26. The phase diagram calculated including the variation of only $\Delta E$ with $\alpha_A$, showing the widening and merging of the $N_R$ lake with the nematic sea ($P = Q = Y = 1$). The solid curve is for $R_1^* = 7, R_2 = 0.7$ and the dashed one is for $R_1^* = 6, R_2 = 0.75$. 

While the topology of the calculated phase diagram agrees with the experimental one, the theory overestimates the temperature range of $N_R$. However, it is to be noted that experiments are done on a mixture of two components belonging to different chemical species. Our molecular theory is necessarily over simplified, and a quantitative comparison can not be made. A more detailed theory of mixtures of polar compounds might give results which are in closer agreement with the experimental data. We develop a hybrid model in chapter-5, including the hard rod features of the interactions and show that the resulting phase diagrams compare better with the experimental ones.

3.5 Conclusions

In this chapter, we treat the N and SmA liquid crystals made of highly polar molecules to consist of mixtures of parallel and antiparallel molecular pairs to develop a simple molecular mean field theory. We have argued that the configurational energy difference between the two types of pairs as well as the negative deviation from the GM rule for the mutual attractive interaction between them vary with the McMillan parameter $\alpha_A$. We first treat the nematic order to be saturated and calculate various phase diagrams as functions of model parameters. Our theory explains the phenomenon of double re-entrance, first order smectic $A_1$ to smectic $A_d$ transition ending at a critical point and the appearance of a re-entrant nematic lake associated with the SmA$_1$-SmA$_d$ transition [30]. Next, we have extended the theory [31] to include the orientational interactions and an appropriate deviation from the GM rule. It is shown that as the McMillan parameter $\alpha_A$ (and hence the chain length in a homologous series) is decreased, SmA$_d$ - SmA$_1$ line goes over to the SmA$_d$-$N_{R1}$ line which finally becomes the $N_{Rd}$-$N_{R1}$ transition line, the latter ending in a critical point, as seen experimentally. Also, for a range of values of $\alpha_A$, we get the possibility of $N$-SmA$_d$-$N_{Rd}$-$N_{R1}$-SmA$_1$ phase sequence on cooling. The $N_{Rd}$-$N_{R1}$ transition occurs over a very small range of $\alpha_A$. The shape of the boundary of the $N_R$ lake obtained after the
inclusion of the nematic interactions is in better agreement with the experimental results compared to that obtained with a saturated nematic order.

3.6 Appendix

Elements of the matrix (see equation 3.57) used to calculate the derivatives are as follows:

\[ C_{11} \text{ are the coefficients of } \frac{\partial X_A}{\partial T}, \]
\[ C_{11} = \frac{U_{AA}}{k_B T} \left[ 2P\sqrt{Y} \ A \ S_p (1+\alpha_A \tau_A \pi) - A^2 \left( 1+\alpha_A \tau_A^2 \right) - Y \ S_p^2 \left( 1+\alpha_p \tau_p^2 \right) \right] + \frac{1}{X_A X_p} \]
\[ C_{21} = \frac{U_{AA}}{k_B T} \left[ S_A (1+\alpha_A \tau_A^2) - P\sqrt{Y} \ A \ S_p \left( 1+\alpha_A \tau_A \pi \right) \right] \]
\[ C_{31} = \frac{U_{AA}}{k_B T} \left[ P\sqrt{Y} \ A \ S_p (1+\alpha_A \tau_A \pi) - Y \ S_p \left( 1+\alpha_p \tau_p^2 \right) \right] \]
\[ C_{41} = \frac{U_{AA}}{k_B T} S_A (1+\alpha_A \tau_A \pi) - P\sqrt{Y} \ A \ S_p \left( 1+\alpha_A \tau_A \pi \right) \]
\[ C_{51} = \frac{U_{AA}}{k_B T} S_p (1+\alpha_A \tau_A \pi) - P\sqrt{Y} \ A \ S_p \left( 1+\alpha_A \tau_A \pi \right) \]

\[ C_{12} \text{ are the coefficients of } \frac{\partial S_A}{\partial T}, \]
\[ C_{12} = \frac{U_{AA}}{k_B T} \left[ P\sqrt{Y} \ A \ S_p (1+\alpha_A \tau_A \pi) - X_A S_A \left( 1+\alpha_A \tau_A^2 \right) \right] \]
\[ C_{22} = \frac{U_{AA}}{k_B T} \left[ X_A (1+\alpha_A \tau_A^2) \right] - \frac{1}{\partial A} \]
\[ C_{32} = \frac{U_{AA}}{k_B T} \left[ P\sqrt{Y} \ A \left( 1+\alpha_A \tau_A \pi \right) \right] \]
\[ C_{42} = \frac{U_{AA}}{k_B T} \left[ 2 \alpha_A X_A S_A \tau_A + P\sqrt{Y} \ A \ S_p \left( 1+\alpha_A \tau_A \pi \right) \right] \]
\[ C_{52} = \frac{U_{AA}}{k_B T} \left[ P\sqrt{Y} \ A \ S_A \tau_A S_p \right] \]
Where we have used $\Delta A = \langle [P_2 \cos(\theta)]^2 \rangle - S_{A^2}$

$C_{13}$ are the coefficients of $\frac{\partial S_p}{\partial T}$,

$$C_{13} = \frac{U_{AA}}{k_B T} \{ YX_p S_p (1 + \alpha_p \tau_p) - P \sqrt{Y} X_p S_A (1 + \alpha_E \tau_A \tau_p) \}$$

$$C_{23} = \frac{U_{AA}}{k_B T} \{ P \sqrt{Y} X_p (1 + \alpha_E \tau_A \tau_p) \}$$

$$C_{33} = \frac{U_{AA}}{k_B T} \{ YX_p (1 + \alpha_p \tau_p^2) - \frac{1}{\Delta P} \}$$

$$C_{43} = \frac{U_{AA}}{k_B T} \{ P \sqrt{Y} \alpha_E X_p \tau_p S_A \}$$

$$C_{53} = \frac{U_{AA}}{k_B T} \{ 2Y \alpha_p X_p S_p \tau_p + P \sqrt{Y} \alpha_E X_A \tau_A \}$$

Where we have used $\Delta P = \langle [P_2 \cos(\theta)]^2 \rangle - S_p^2$

$C_{14}$ are the coefficients of $\frac{\partial \tau_A}{\partial T}$,

$$C_{14} = \frac{U_{AA}}{k_B T} \{ S_A (P \sqrt{Y} \alpha_E X_A S_p \tau_p - \alpha_A \tau_A X_A S_A) \}$$

$$C_{24} = \frac{U_{AA}}{k_B T} \{ P \sqrt{Y} \alpha_E X_p S_p \tau_p + 2X_A S_A \alpha_A \tau_A \}$$

$$C_{34} = \frac{U_{AA}}{k_B T} \{ P \sqrt{Y} \alpha_E X_A \tau_p \}$$

$$C_{44} = \frac{U_{AA}}{k_B T} \{ [\alpha_A X_A S_A^2] - \frac{1}{\Delta A S} \}$$

$$C_{54} = \frac{U_{AA}}{k_B T} \{ P \sqrt{Y} \alpha_E X_A S_A \tau_p \}$$

Where we have used $\Delta A S = \langle [\cos(2\pi x_j / l)]^2 \rangle - \tau_A^2$

$C_{15}$ are the coefficients of $\tau_A$ and

$$C_{15} = \frac{U_{AA}}{k_B T} \{ S_p (Y \alpha_p \tau_p X_p S_p - P \sqrt{Y} \alpha_E X_p S_A \tau_A) \}$$
\[ C_{25} = \frac{U_{AA}}{k_B T} [P\sqrt{Y} \alphaE X_p S_p \tau_a] \]
\[ C_{35} = \frac{U_{AA}}{k_B T} [P\sqrt{Y} \alphaE X_A S_A \tau_a + 2Y \alphaE X_p S_p \tau_p] \]
\[ C_{45} = \frac{U_{AA}}{k_B T} [P\sqrt{Y} \alphaE X_p S_p S_A] \]
\[ C_{55} = \frac{U_{AA}}{k_B T} [Y \alphaE X_p S_p^2] - \frac{1}{\Delta BS} \]

Where we have used \( \Delta BS = \langle \cos(2\pi p/d) \rangle - \tau_p^2 \)

\[ D_1 = \frac{U_{AA}}{k_B T^2} [YX_p S_p^2(1+\alphaE \tau_p^2) - X_A S_A^2(1+\alphaE \tau_a^2) - P\sqrt{Y} S_A S_p(1+\alphaE \tau_a \tau_p)(X_p - X_A)] + \]
\[ \frac{\Delta E}{k_B T^2} \]
\[ D_2 = \frac{U_{AA}}{k_B T^2} [X_A S_A(1+\alphaE \tau_a^2) + P\sqrt{Y} X_p S_p(1+\alphaE \tau_a \tau_p)] \]
\[ D_3 = \frac{U_{AA}}{k_B T^2} [YX_p S_p(1+\alphaE \tau_p^2) + P\sqrt{Y} X_A S_A(1+\alphaE \tau_a \tau_p)] \]
\[ D_4 = \frac{U_{AA}}{k_B T^2} [S_A(\alphaE X_A S_A \tau_a + P\sqrt{Y} \alphaE X_p S_p \tau_p)] \]
\[ D_5 = \frac{U_{AA}}{k_B T^2} [S_p(Y \alphaE X_p S_p \tau_p + P\sqrt{Y} \alphaE X_A S_A \tau_a)] \]

### 3.7 References for chapter-3


