Theoretical Studies on Phase Transitions in Liquid Crystals

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DECLARATION

I hereby declare that the entire work embodied in this thesis is the result of the investigations carried out by me independently in the Liquid Crystal Laboratory, Raman Research Institute, Bangalore, under the supervision of Prof. N. V. Madhusudana. No part of the subject matter presented in this thesis has previously been formed the basis of any Degree, Diploma, Associateship, Fellowship or any other similar title in any other university.

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CERTIFICATE

This is to certify that the thesis entitled **Theoretical Studies on Phase Transitions in Liquid Crystals** submitted by A. S. Govind for the award of the degree of DOCTOR OF PHILOSOPHY of Bangalore university, is his original work. This has not been published or submitted to any other University for any other Degree or Diploma.

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Preface

Liquid crystals are fluids characterised by long-range orientational order without long-range three dimensional translational molecular order [1,2]. They have some properties of liquids (for example, they can flow) as well as some of those of crystals (for example, birefringence). They consist of molecules having a pronounced shape anisotropy (rod-like, disc-like or with a bent-core). Liquid crystals obtained by heating the solid crystals are called *thermotropic* liquid crystals.

In this thesis, we consider only some thermotropic liquid crystals (nematic, smectic A and smectic C) made of rod-like molecules. We develop *molecular* theories of various liquid crystalline phases exhibited by a medium consisting of ***strongly polar*** molecules with *longitudinal* components of dipole moments. Also, we propose a molecular theory of the SmC phase exhibited by a medium consisting of polar molecules with *lateral* components of dipole moments. The thesis is divided into six chapters.

The nomenclature of liquid crystals is based on the type of order present in the medium. We describe the classification of the relevant mesophases in chapter-1. The simplest of the liquid crystalline phases exhibited by rod-like molecules is the uniaxial nematic (N) which has only a long range orientational order of the long axes of the rods. Since the director $\hat{n}$, which is a unit vector along the average orientation direction of the long axes of the rods, is *apolar* in nature, the relevant order parameter is a second rank tensor. In smectic A (SmA) liquid crystals, the centres of mass of the rods develop a quasi long range one dimensional periodic order whose wave vector ($|\vec{q}| = 2\pi/d$, d being the layer spacing) is parallel to $\hat{n}$. In smectic C (SmC) liquid crystals, the 'tilt' angle ω between $\vec{q}$ and $\hat{n}$ is nonzero [1] (figure-1).
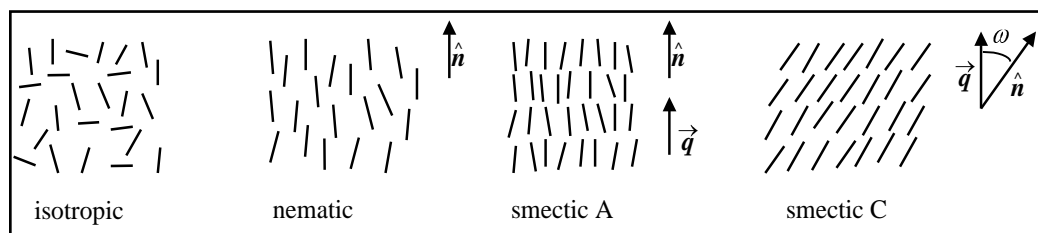
Figure-1. Schematic representation of ordering of rod-like molecules in the isotropic liquid and the nematic, the smectic A and the smectic C liquid crystals. The director $\hat{n}$ and the wave vector $\vec{q}$ representing the density wave along the layer normal are shown. $\vec{q}$ and $\hat{n}$ are parallel in the smectic A liquid crystals whereas in the smectic C liquid crystals, $\hat{n}$ is tilted with respect to $\vec{q}$ at an angle ω.

Typical examples of mesogenic compounds consist of rod-like organic molecules having a few phenyl rings with or without bridging groups and end chains. In chapter-1, we give some examples of compounds exhibiting nematic, SmA and SmC liquid crystals. These examples illustrate that the presence of end chains plays an important role in stabilizing the smectic phases. The compounds exhibiting the smectic C liquid crystals usually have a *lateral* component of dipole moment.

When a typical mesogenic compound is cooled, the more ordered phases, *i.e.,* the phases having lower symmetries, are expected to occur at lower temperatures. Accordingly, in most of the liquid crystals, the usual sequence of phase transitions is (with K for solid crystal): $I \wedge N \wedge K$ or $I \wedge N \wedge SmA \wedge K$. However, liquid crystals composed of molecules having *strongly polar* end groups show some unusual phase sequences. Cladis [3] 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: $I \wedge N \wedge SmA \wedge N_R \wedge K$. 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. 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: $I \wedge N \wedge SmA_d \wedge N_R \wedge SmA_1 \wedge K$ [4]. 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 [5] the SmA$_1$ liquid crystal has a layer spacing $d \approx l$, whereas the SmA$_d$ liquid crystal has $l < d < 2l$, where l is the molecular length. The latter *partial bilayer* arrangement is

understood on the basis of formation of appropriate antiparallel dimers of the molecules (see figure-2). Hence the suffix 'd' is used to denote *dimers* and the suffix '1' for the *monomers*.

There have been many attempts to explain double reentrance using phenomenological as well as molecular theories. Prost has developed a very successful *phenomenological* theory of various phases exhibited by such compounds. In view of this, we give a general review of the Landau theory of phase transitions in chapter-1.

The Landau theory is a phenomenological theory that helps in analysing a phase transition using appropriate model parameters. 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 [6]. In the absence of any external fields the expansion is given by

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

where F_0 is the free energy of the disordered phase ($\sigma = 0$).

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. If the symmetry of the system allows for odd powers of σ , then, a first order transition results when $B \neq 0$ and $C > 0$ (for $B < 0$, $\sigma > 0$). As an example, in chapter-1, we describe the Landau-deGennes theory of the first order N-I transition.

A change in the nature of the phase transition from second order to first order is possible as a function of some parameter and is called *tricritical* behaviour. As an example of this behaviour, we review in chapter-1, the Landau-deGennes theory of the N-SmA transition. We also give a brief review of the phenomenological theory developed by Prost [7] to explain double reentrance. He argued that the 'natural' length is the molecular length *l* and there is a 'competition' between this length and the other incommensurate length (see figure 2) in forming the smectic phase, leading

to frustration. Based on this idea, he developed a successful Landau theory of these unusual phase transitions. 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".

Various molecular theories have been proposed to explain the origin of the 'two lengths' assumed by Prost. The molecular origin of the partial bilayer structure was explained, before the discovery of double reentrance, as follows: An early experimental observation [8] on a cyano compound shows that the average dielectric constant has a *positive* jump as the temperature is increased across the N-I transition point. To explain this, it was proposed that [9] the interaction between the permanent dipoles favours an antiparallel configuration of the nearest neighbours. Later X-ray [5,10] and neutron scattering [11] studies on strongly polar compounds in the nematic phase have shown that they have a SmA like short range order, with a typical layer spacing ≈ 1.4 times the molecular length *i.e.,* there is a *partial bilayer* arrangement. This was interpreted [10] to be the result of the overlap of the aromatic parts of the neighbouring antiparallel molecules due to the strong dispersion interactions. An example of this arrangement of octyloxybenzoyloxy cyano- stilbene (or T8) molecules, which exhibit double reentrance, is shown in figure-2.
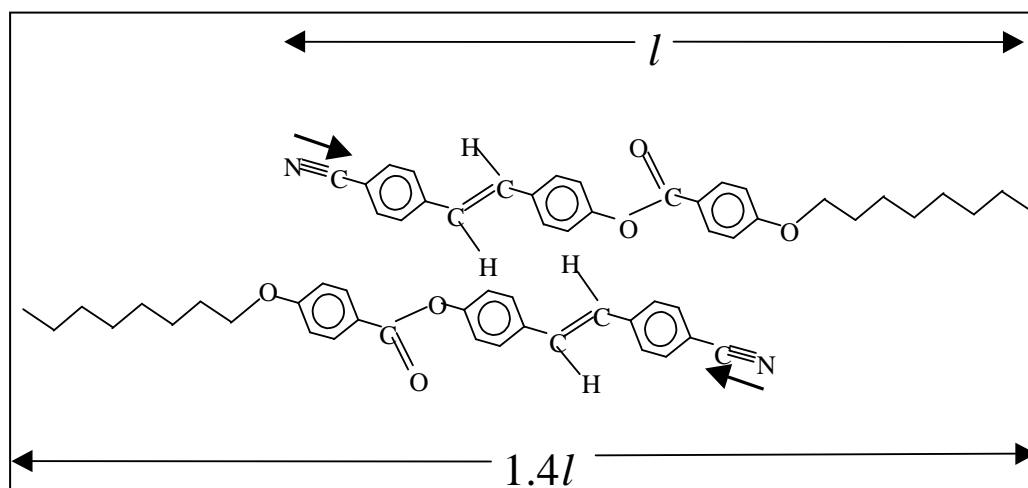
Figure-2. Schematic diagram showing the mutual configuration in an antiparallel pair of octyloxybenzoyloxy cyano- stilbene (or T8) molecules resulting in a partial bilayer arrangement. The zig-zag lines represent the aliphatic chain. Carbon and hydrogen atoms in the chain and in the phenyl rings are not shown. The thick arrow near the C ≡N group of the molecular structure represents the permanent dipole of the cyano group.

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. In the compounds which show double reentrance, the lower temperature smectic phase (SmA$_1$) has the monolayer structure [5]. Hence, as the temperature is decreased, the partial bilayer arrangement of molecules changes over to the monolayer arrangement. Many molecular theories have been proposed to explain the decrease in the smectic layer spacing associated with double reentrance. In all these theories, the SmA$_d$ structure is assumed to arise from the antiparallel dimers shown in figure-2.

In one of the models, the packing effects are assumed to destabilise the SmA$_d$ liquid crystals when the dimers come closer and intercalate [12, 13]. In other models, or the dimers are assumed to breakup into monomers [14] or to have a fully overlapping antiferroelectric arrangement [15]. The molecular model widely referred to in the literature is the frustrated spin gas model [16] in which molecular triplets are considered. In chapter-1, we give a critical review of these theories and point out their drawbacks.

A simple model to explain the molecular origin of the 'two lengths' assumed in the Prost's phenomenological model [7] was proposed by Madhusudana and Jyothsna Rajan [17]. The model, with suitable modifications, gives a variety of phase diagrams. Since we adopt this model for various extensions, we give a detailed discussion of this model in chapter-2.

In this model, the origin of the two incommensurate lengths is explained as follows: The interaction between permanent dipoles favours an antiparallel orientation (A) between neighbouring molecules [9]. This interaction energy is $\propto 1/r^3$ where r is the intermolecular separation. The strongest intermolecular interaction arises from the anisotropic dispersion energy between the aromatic cores resulting in the partial bilayer structure mentioned earlier (Figure-3a).

If the polar molecules are parallel, the dipolar interaction is repulsive. However, in view of the strong polarisability of the conjugated aromatic core to which the dipole is attached, the latter induces an oppositely oriented dipole moment in the neighbouring molecule thus reducing the net dipole moment of each molecule (Figure-3b). Further, in this 'parallel' or (P) configuration, the chains are in close

proximity, adding to the attractive interaction. Both these effects are $\propto 1/r^6$. Hence, as the density is increased, *i.e.,* the temperature is lowered, one can expect a change in the configuration of the pairs from 'A' type to 'P' type.
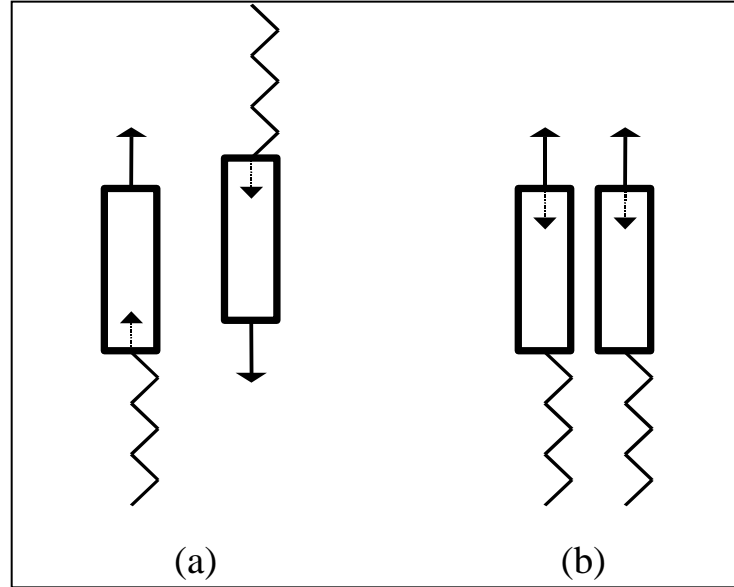
Figure-3. Schematic diagram showing (a) the antiparallel configuration of two molecules favoured at intermediate molecular separations and (b) the parallel configuration favoured at relatively low values of intermolecular separation. The arrow with solid line represents the permanent dipole moment and the one with dotted line, the induced one. (For the sake of clarity, the relative separation in (a) is exaggerated).

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

$$\Delta E = E_A - E_P = R_1 k_B T_{NI} \left(\frac{R_2}{T_R} -1 \right) \tag{2}$$

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

The two configurations shown in Figure-3 naturally account for the two length scales in the Landau theory developed by Prost [7]. A molecular theory of double reentrance has been developed in [17] including ΔE and considering the medium to be a mixture of A and P type of pairs . In reference [17], the authors have extended the

McMillan theory of SmA phase [18], which is itself an extension of the Maier-Saupe (MS) theory of the N-I transition [19]. We have reviewed the MS theory and the McMillan theory in chapter-2 and chapter-3 respectively. In this model [17], the McMillan parameters, which are effectively the strengths of the layering potentials for A-type (α_A) and P-type (α_P) configurations, are written as

$$\alpha_A = 2 \exp(- [\pi r_o / (r_o + 2c)]^2) \tag{3}$$

and

$$\alpha_P = 2 \exp(-[\pi r_o / (r_o + c)]^2) \tag{4}$$

where r_o and c are the lengths of the aromatic and chain moieties of the molecule respectively. Recent experiments [20] showing the presence of *polar* short range order at low temperatures support this model.

In chapter-2, we develop a simple theory for a nematic mixture consisting of these two types of pairs, by extending the MS theory [19]. The single particle orienting potential used in the MS theory for the ith molecule is of the form

$$U_i = - U_0 S (3\cos^2\theta_i - 1)/2 \tag{5}$$

where U_0 is an interaction parameter and the nematic order parameter $S=\langle 3\cos^2\theta_i - 1\rangle/2$ where θ_i is the angle between the long axis of the ith molecule and the director and $\langle \, \rangle$ indicate the thermal average. U_0 can be expressed as $4.541 k_B T_{NI}$ [19] where k_B is the Boltzmann constant and T_{NI} is the nematic-isotropic transition temperature. Since the A and P types of pairs are geometrically dissimilar, we assume that the orientational potential for A-type of pairs (U_{AA}) and P-type of pairs (U_{PP}) are be different. We write,

$$U_{PP} = Y \, U_{AA} \tag{6}$$

and the mutual interaction potential

$$U_{AP} = U_{PA} = P \sqrt{U_{AA} \, U_{PP}} \tag{7}$$

where $P \neq 1$ indicates a deviation from the geometric mean (GM) rule. We write the orienting potential of the ith A-type of pair as

$$U_{Ai} = - U_{AA} X_A S_A P_2 (\cos\theta_{Ai}) - U_{AP} X_P S_P P_2 (\cos\theta_{Ai}) \tag{8}$$

where X_A, X_P, and S_A, S_P are the molefractions and orientational order parameters of A and P types of pairs respectively and P_2 is the second Legendre polynomial. Similarly

for a P-type pair, $U_{\mathrm{p}j}$ is written by interchanging suffixes A and P in equation (8). The internal energy of one mole of pairs can be written as

$$2U = \frac{NX_{\mathrm{A}}}{2} \langle U_{\mathrm{A}i} \rangle + \frac{NX_{\mathrm{P}}}{2} \langle U_{\mathrm{P}j} \rangle - NX_{\mathrm{P}} \Delta E \tag{9}$$

where N is the Avogadro number 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

$$2\mathcal{S} = - N k_{\mathrm{B}} [\, X_{\mathrm{A}} \int f_{\mathrm{A}i} \ln f_{\mathrm{A}i} \, \mathrm{d}(\cos \theta_{\mathrm{A}i}) + X_{\mathrm{P}} \int f_{\mathrm{P}j} \ln f_{\mathrm{P}j} \, \mathrm{d}(\cos \theta_{\mathrm{P}j}) \,]$$

$$- N k_{\mathrm{B}} (\, X_{\mathrm{A}} \ln X_{\mathrm{A}} + X_{\mathrm{P}} \ln X_{\mathrm{P}}) \tag{10}$$

where the last term is the entropy of mixing and f_{A} and f_{P} are the normalised distribution functions of A and P types of pairs respectively. The Helmholtz free energy is given by

$$F = U - T\mathcal{S} \tag{11}$$

The distribution functions f_{A} and f_{P} and also X_{A} are found by minimising F. We evaluate the necessary integrals using a 32-point Gaussian quadrature technique in double precision.

For certain ranges of the model parameters, we get a first order N-N transition ending in a critical point [21]. The N-N transition corresponds to a jump in X_{A} (see figure 4-i). We have also calculated the specific heat anomaly around the transition region (see figure 4-ii).

Usually, the mutual interaction energy between the two different species in a mixture is assumed to be the geometric mean of the interaction energies of the pure species (*i.e.*, $P=1$, see equation 7). We show that $P<1$ is required to get the N-N transition. Experimentally, the first example of the N-N transition was found in a binary mixture [22] and has been subsequently observed in a single component system also [23]. We discuss the theoretical results in comparison with the available experimental data on the N-N transition.

(i)   **(ii)**
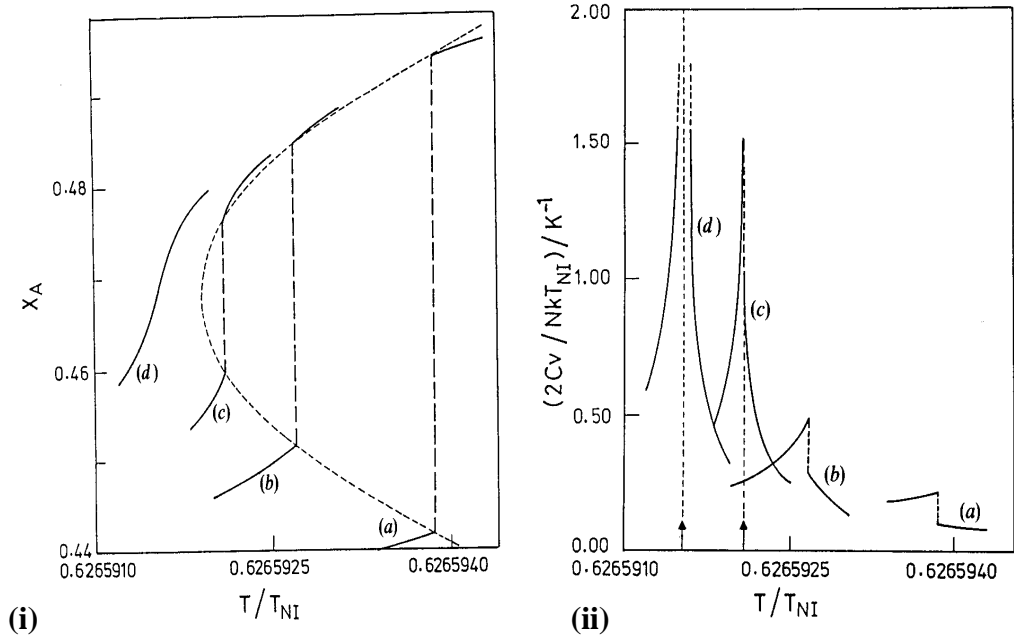
Figure-4. (i) Relative concentration of the A- type of pairs (X_A) and (ii)specific heat at constant volume per mole of pairs, plotted as functions of T/T_{NI} for $Y = 1.4$, with (a) $P= 0.6954$, (b) $P = 0.6956$, (c) $P = 0.6957$ and (d) $P = 0.6958$.

In chapter-3, we extend the above theory to binary mixtures of smectic liquid crystals based on the McMillan model [18].Following Katriel and Kventsel [24], the decoupled form of the McMillan potential is,

$$U_M(\theta_i, z_i) = -U_o \left[1 + \alpha \, \tau \cos(2\pi z_i / d)\right] S \, (3 \cos^2 \theta_i - 1)/2 \qquad (12)$$

where the translational order parameter $\tau = \langle \cos(2\pi z_i / d)\rangle$. We consider the layering potential of the A type of pairs to be different from that of the P type of pairs as in [17]. The mutual interaction parameter

$$\alpha_{AP} = \alpha_{PA} = \alpha_E = Q \sqrt{\alpha_A \, \alpha_P} \qquad (13)$$

where $Q \neq 1$ indicates a deviation from the geometric mean rule in the smectic interaction. Initially, we treat the nematic order to be saturated. We write the single particle potential the ith A-type of pair as

$$U_{Ai} = -U_0 X_A \, \alpha_A \tau_A \cos (2\pi Z_{Ai}/d) - U_0 X_P \, \alpha_{AP} \tau_P \cos (2\pi Z_{Ai}/d) \qquad (14)$$

where τ_A, τ_P are the translational order parameters of A and P types of pairs respectively. Since the deviation increases as the molecular structures of the two components in a mixture become more dissimilar, we write,

$$Q = Q^* \, (\alpha_A/\alpha_P) \tag{15}$$

where Q^* is a constant chosen such that Q is < 1 in the range of α used. Considering the variation of pairing energies with the chain length of the molecules, we show that $\Delta E \propto (\alpha_A)^4$ in the range of α_A relevant in our calculations and we write

$$R_1 = R_1^*(\alpha_A)^4 \tag{16}$$

where R_1^* is an input parameter. With this, we write the expressions for free energy and X_A as explained in chapter-2. Depending on the model parameters, we get the following results [25]: i) first order SmA_1-SmA_d transition which changes over to a continuous Sm_{A1}-Sm_{Ad} evolution beyond a critical point in two regimes of the McMillan parameter α, ii) a re-entrant nematic lake associated with the SmA_1-SmA_d boundary, and iii) the merger of the re-entrant nematic lake with the nematic sea (see figure-5). We discuss the results in comparison with experiments [26] and other theoretical models.
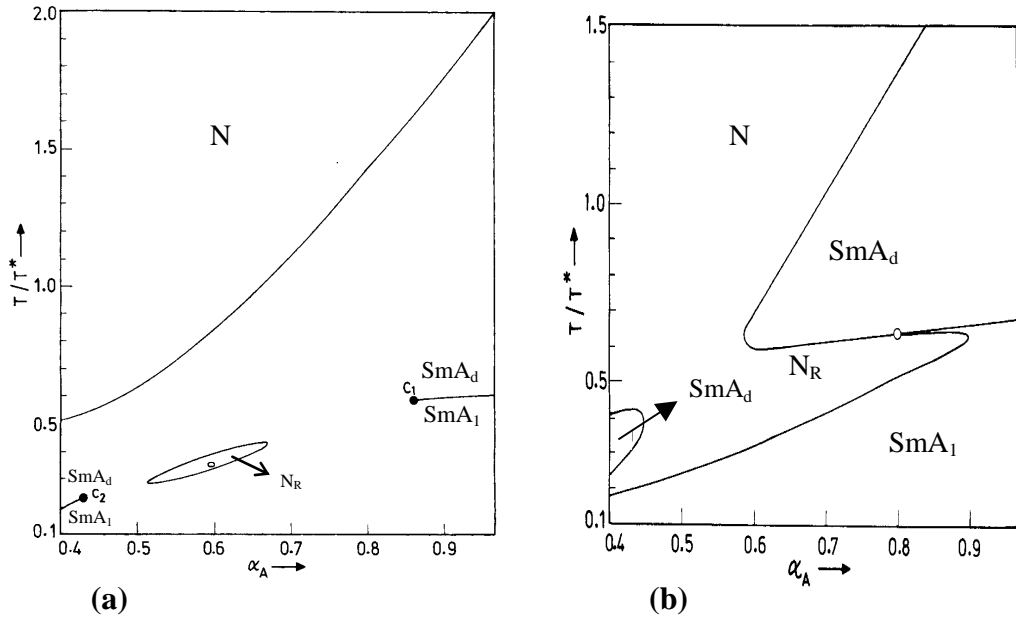
Figure-5. (a) Calculated phase diagram for $R_1^* = 8$, $R_2 = 0.7$ showing the re-entrant nematic (N_R) lake for $Q^* = 0.18$. The small loop within the N_R lake is for $Q^* = 0.188$, for which the N_R lake just appears. C_1 and C_2 are the SmA_1-SmA_d critical points.(b) Calculated phase diagram showing the 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 SmA_1-SmA_d transition line meets the N_R boundary.

Next, we extend the theory to include the temperature dependence of the nematic order also [27]. Since P and Q always occur together in the terms representing the

mutual interaction in all the equations, it is sufficient to consider the variation of P only and as in equation(15), P is written as $P*(\alpha_A/\alpha_P)$. We get the N-N transition in the reentrant nematic range and denote it as N_{Rd}- N_{R1} transition. We show that, as the McMillan parameter α_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 (see figure-6), as seen in an experiment [22]. Also for a range of values of α_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 α_A values.
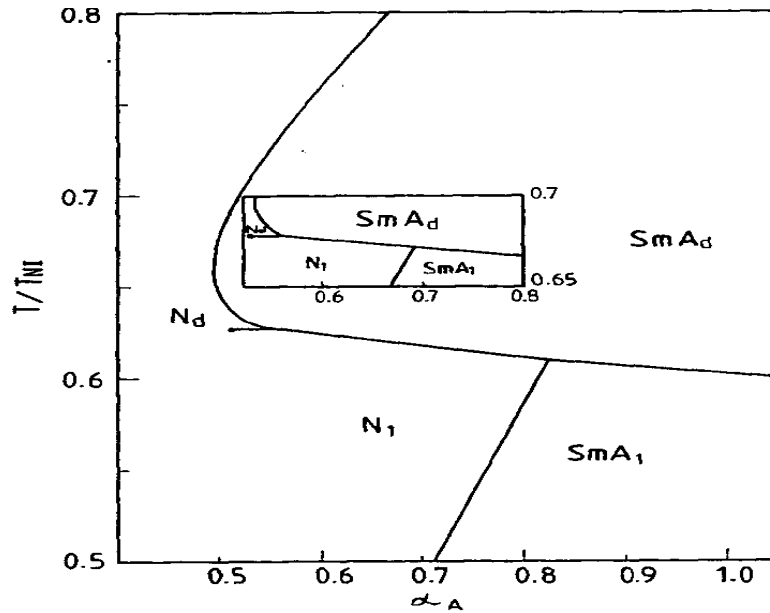
Figure-6. Calculated phase diagram with $R_1 = 15$, $R_2 = 0.6$, $P* =0.15$, $Y=1.4$, $Q = 1$, showing the reentrant N_d- N_1 (indicated in the text as N_{Rd} - N_{R1}) transition line starting from a critical point, which continues as SmA_d -N_1 line and extends as SmA_d - SmA_1 line as α_A is increased. 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 α_A values.

In chapter-4, we extend the model to include the effect of an external electric field. The electric field can in general be expected to enhance the density of the medium (electrostriction). The 'direct' effect arises from the pressure due to the field, and yields $\delta\rho/\rho \sim 10^{-5}$ for the highest field that is used in experiments [28]. The nematic director aligns parallel to the applied field when the medium consisting of polar molecules has a large positive dielectric anisotropy. The additional orienting potential due to the external field ($\mathcal{E}$) results in an increase of the nematic order

parameter $\delta S \propto \mathcal{E}^2$. This results in another contribution to the electrostriction and yields $\delta \rho / \rho \sim 10^{-3}$. Hence the intermolecular separation decreases with $\mathcal{E}^2$, and this can in turn be expected to change R_2 in equation (2). Hence we write

$$R_2(\mathcal{E}) = R_2(0) + C\mathcal{E}^2. \tag{17}$$

The value of C is estimated from the earlier calculation of the variation of ΔE given by equation (2) [17] and is found to be $\sim 10^{-8}$ cgs units.

Though there is no long *range* polar order in the medium, the P-type of pairs have a polar *short range* order. In the presence of an external electric field ($\vec{\mathcal{E}}$), this contributes a term linear in $\vec{\mathcal{E}}$, to the orienting potential of P-type of pairs. Also, due to the anisotropy in the polarisability of the aromatic cores, *both* A and P types of pairs have an orienting potential proportional to $\mathcal{E}^2$.

Including this, the internal energy of one mole of pairs in presence of electric field can be written as

$$2U = \frac{NX_A}{2} \langle U_{Ai} \rangle + \frac{NX_P}{2} \langle U_{Pj} \rangle - NX_P \Delta E$$

$$- N\gamma \mathcal{E}^2 (X_A \langle \cos^2 \theta_{Ai} \rangle + X_P \langle \cos^2 \theta_{Pj} \rangle) - Np \mathcal{E} \langle \cos \theta_{Pj} \rangle \tag{18}$$
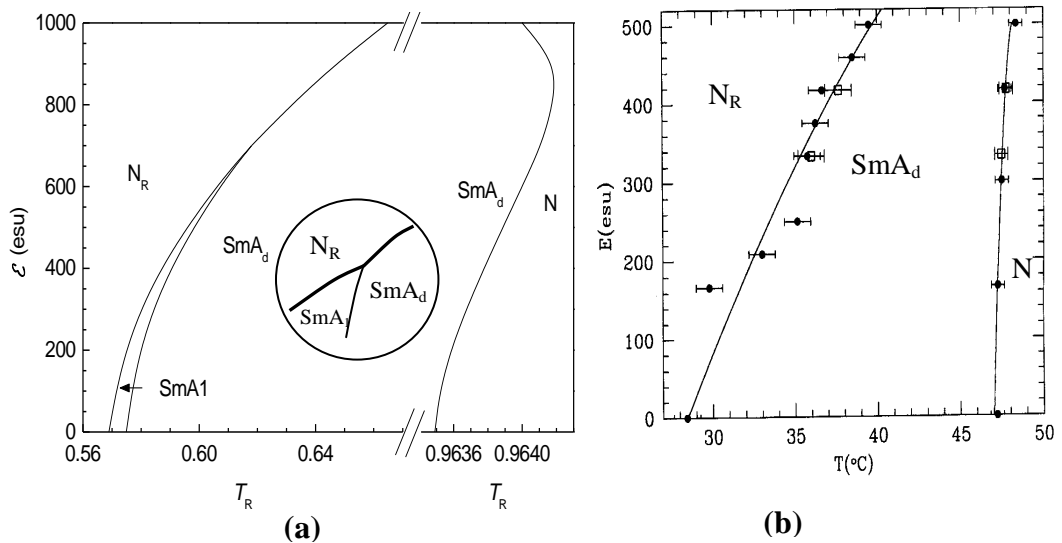
where γ is a constant which is estimated from the known dielectric anisotropy. We get, for a mole of *pairs*, $N\gamma \sim 1000$ cgs units where N is the Avogadro number.

Proceeding as in the previous chapters, we show that the temperatures of nematic-para nematic transition, N-N transition, SmA_d-N_R transition and SmA_1-SmA_d transition increase with the field [28]. Further, we show that the temperature range of the SmA_d phase decreases and finally vanishes with increasing field, resulting in a bounded SmA_d region in the electric field-temperature phase diagram. For suitable parameters, we also predict that either a nematic-nematic transition line can branch off from the SmA_d-N_R transition line or a smectic A-smecticA transition line can meet the SmA_d-N_R transition line at an appropriate field (see figures 7 and 8). We compare some of the results with the available experimental data (see figure-8b).
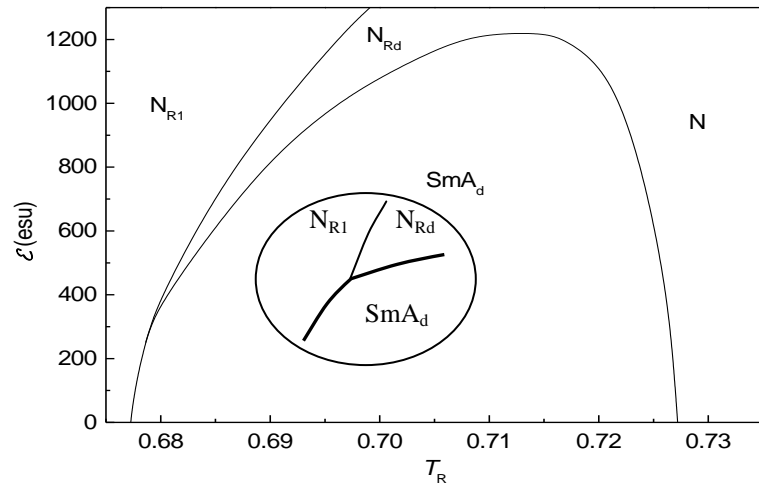
Figure-7. Calculated phase diagram showing the N$_{R1}$-N$_{Rd}$ transition line branching off from the N$_R$ -SmA$_d$ line at $\int$ $\approx$300 esu and $T_R$$\approx$0.679, for R_1=15, R_2(0)= 0.6, P = 0.7935, Y = 2, α_A=0.56 and C = 10^{-8} cgs units. The inset shows the topology near the branching point on an exaggerated scale.

(a)   **(b)**

Figure-8. (a) Calculated phase diagram showing the SmA$_1$-SmA$_d$ transition line meeting the N$_R$-SmA$_d$ transition line at $\mathcal{E}$ $\approx$700 esu and $T_R$$\approx$0.618, for R_1=15, R_2(0)=0.6, P=Y=1, Q=0.55, α_A =0.97 and C = 8Δ10^{-8} cgs units. Note that the temperature scale for the SmA$_d$-N transition is different from that for the N$_R$-SmA$_d$ transition. The inset shows the topology near the branching point on an exaggerated scale. (b)Experimental phase diagram for the 6OCB-8OCB mixture [28]. Circles and open squares are data obtained from light scattering and electrical impedance measurements respectively. The solid lines are guides to the eye. Note the change of slope in the N$_R$-SmA$_d$ transition points at $\mathcal{E}$ $\approx$ 200 esu.

In chapter-5, we extend the model to include the effect of external pressure on various phase transitions. When a medium is compressed, the molecules come closer. When the pressure is applied at a fixed temperature, the thermal energy is not changed and the size and shape of the molecules have to be taken into account in describing the phase diagrams. Hence the hard rod features and the effect of excluded volume on packing are included in the theory to explain the effect of pressure. In this chapter, we develop a hybrid model by including the hard rod features as well as the attractive interactions. We extend the hard rod model developed by Kimura *et.al* [29] to include the mean field attractive potential and the pairing potential as described earlier.

In chapter-5, for the sake of notational convenience, we use the suffix '1' to represent the P-type pair and '2' the A-type of pair. We write the energy difference between the A and the P type configurations as

$$\Delta E = E_2 - E_1 = A\, k_B T * \left(\frac{\eta}{\eta *} - 1 \right) \qquad (19)$$

where, A is a dimensionless interaction parameter, $T*$ some reference temperature, η the packing fraction, $\eta*$ the packing fraction at which $E_2 = E_1$. The expression for the hard rod component of the free energy per pair in units of $k_B T$ is found to depend on the kinetic energy contributions, the lengths, the volume fractions, the number densities and the number of P- and A-type of pairs respectively. We carry out the calculations assuming the medium to have a saturated nematic order. We consider the sinusoidal density perturbation in the SmA phase and also add the attractive component of the smectic potential. As in the previous chapters, we find the appropriate distribution function by minimising the free energy. We expand the free energy in terms of the smectic density amplitudes limiting the expansion to quadratic terms.

We calculate the pressure-temperature phase diagrams which show the N-N transition, double re-entrance with a bounded SmA$_d$ region and the N-N transition associated with double reentrance. We have also calculated pressure versus A (a parameter in equation 19, which increases with chain length in a homologous series) phase diagrams. These show the N$_R$ lake associated with the SmA$_1$-SmA$_d$ transition, N-N transition occurring inside such an N$_R$ lake, quadruple reentrance at constant pressure, and widening and merging of the N$_R$ lake with the main nematic sea [30]

(see figures 9,10). As we have mentioned earlier, using the simple model described in chapter-2, in which the hard rod effects have not been taken into account, a negative deviation from the geometric mean rule for the mutual interaction is *necessary* to get the N-N transition. In this chapter, the change over between A-type and P-type of configurations with the *inclusion* of the steric effects of packing naturally lead to the N-N transition without the necessity of any such deviation. We show that the hard core interaction is the physical origin for this negative deviation and this effect increases as the two components become more dissimilar. We discuss the results in comparison with the available experimental data (see figure 9-ii) and other theoretical models (see figure-11).

(i)   **(ii)**
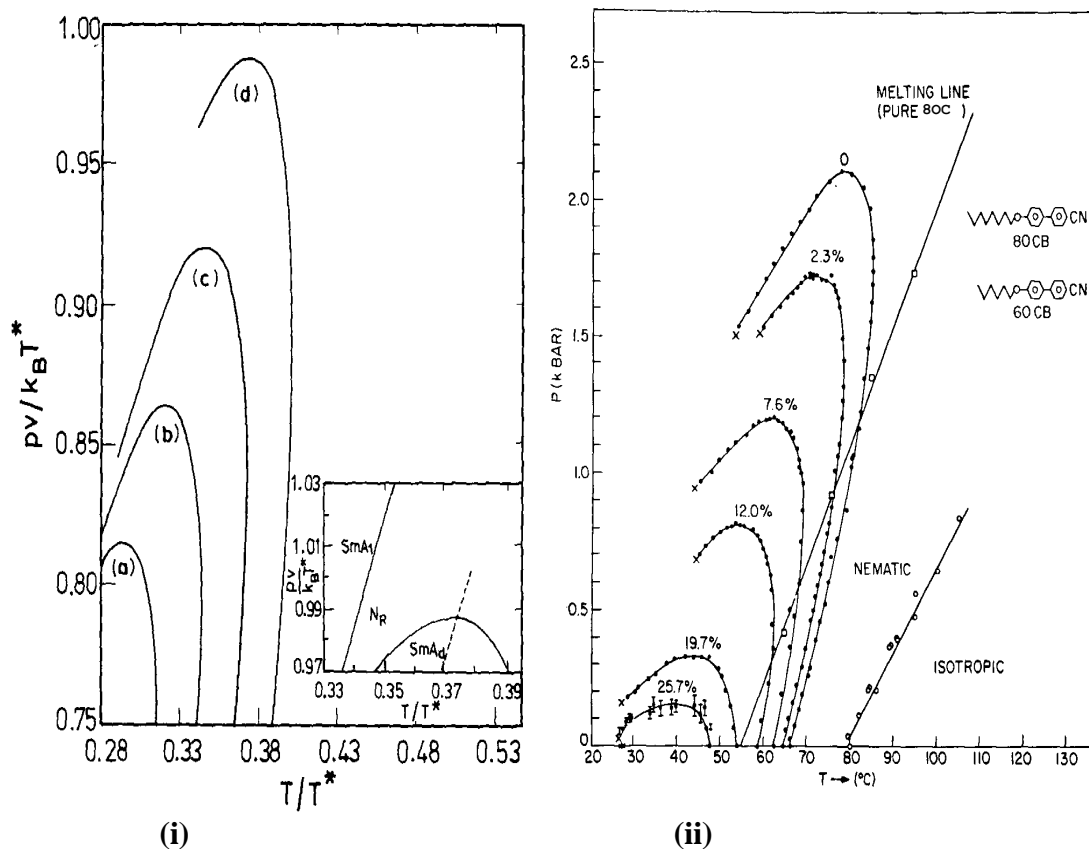
Figure-9. (i) The *p-T* phase diagram obtained for *A* = 1.5, η^* = 0.5, *q* =1.8 for different values of α_2. (a) α_2 = 0.048, (b) α_2 = 0.054, (c) α_2 = 0.06 and (d) α_2 = 0.066. The inset shows the reentrant part of the phase diagram in a magnified scale along the pressure axis for α_2 = 0.066. The axis of the parabolic SmA$_d$ boundary (the dashed line) and the SmA$_1$-N$_R$ line are roughly parallel. (ii) Experimental *p-T* phase diagram [31] for 8OCB-6OCB mixtures. The numbers indicate the concentration of the lower homologue 6OCB.
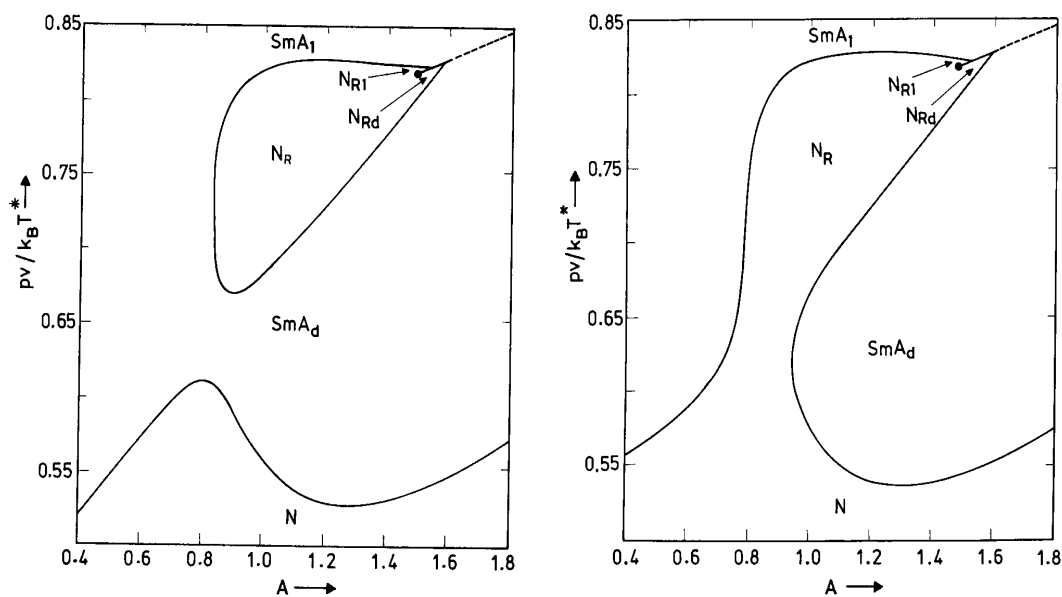
Figure-10. (a) The p - A phase diagram showing a reentrant nematic (N_R) lake having the N_{R1}-N_{Rd} transition line for $\eta^* = 0.5$, $q = 1.8$, $T_R = 0.28$, $\alpha_2 = 0.0475$. The values of (p,T) which are indicative of a SmA_1- SmA_d transition are shown by a dashed line. The filled circle indicates the N_{R1} - N_{Rd} critical point. (b) The p - A phase diagram when α_2 is increased to 0.047, showing the opening of the reentrant nematic lake creating a 'bay'.
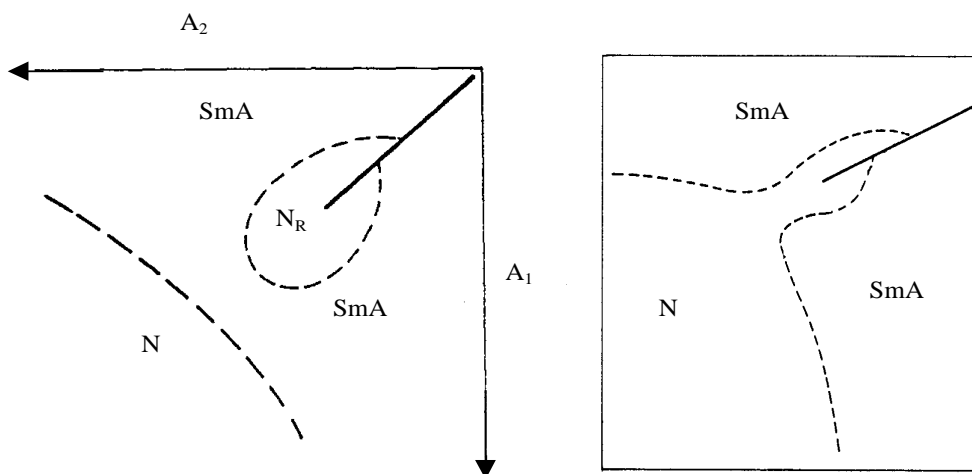
Figure-11. Phase diagrams predicted by the dislocation loop melting theory of Prost and Toner [1]. A_1 and A_2 are general variables which can be mapped to pressure and temperature or pressure and concentration *etc.*

In chapter-6, the subject matter is different from that of the previous chapters. We no longer consider molecules with *longitudinal* components of dipole moments. We discuss the molecular theory of the SmC phase which is exhibited by compounds whose molecules have *lateral* components of electric dipole moments. We give

examples of some typical compounds which exhibit SmC liquid crystals. We first review various earlier molecular theories of the SmC-SmA transition. We conclude, in agreement with Goossens [32], that there is no satisfactory molecular theory for the SmC-SmA transition.

We propose that the molecular origin of the tilt is the *off axis* location of the lateral dipole in the molecule. As the neighbouring molecules in a smectic layer freely rotate about their long axes, at a particular mutual orientation, the lateral dipoles face each other at close proximity. This contributes to a large repulsive energy especially when the molecular centres are at the same z' coordinate (figure -12a).
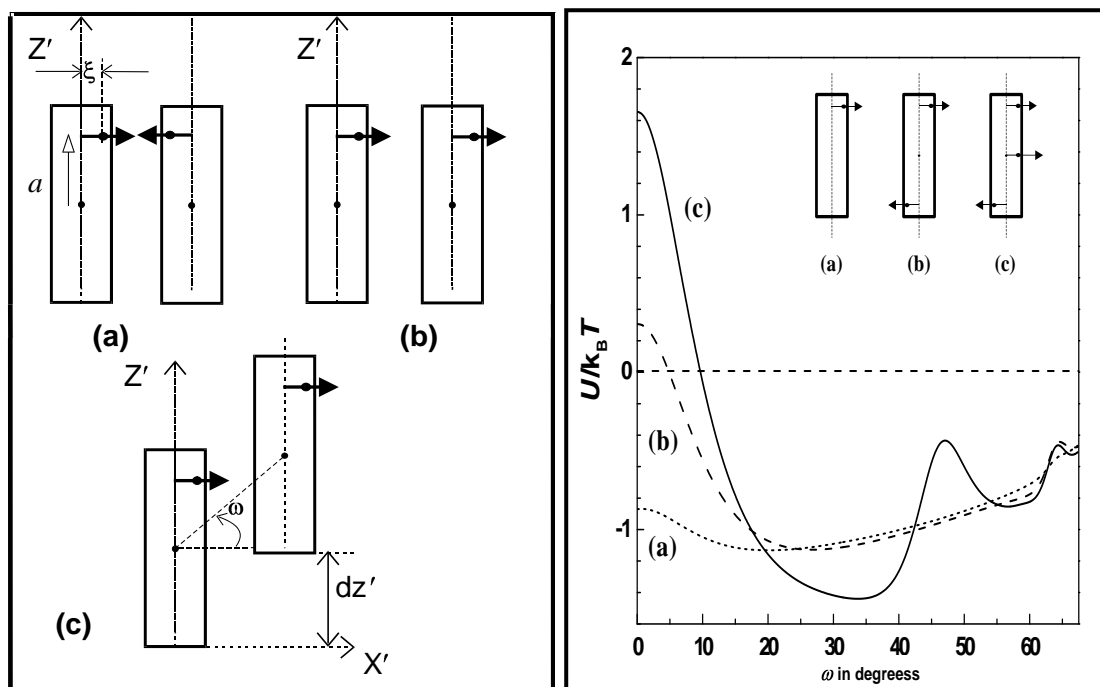

Figure-12   **Figure-13**

Figure-12. The proposed off-axis dipolar mechanism of tilt in smectic C layers. The repulsive energy of antiparallel configuration of dipoles (a) is much larger than the attractive energy of parallel configuration (b), resulting in a relative shift of the molecules (c).

Figure-13. The interaction energy $U/k_B T$ with T=290K is plotted against tilt angle ω in degrees.(a) single dipole, 1.5D at $a = 5\text{Å}$, $\xi =2\text{Å}$, (b) two opposite dipoles at $a=\pm5\text{Å}$, $\xi =\pm2\text{Å}$, (c) three dipoles, two as in (b) and one more of 2D at $a = 0$ and $\xi =2\text{Å}$. Note that the net energy at the minimum is always negative.

In the configuration shown in figure-12b, the dipole interaction is attractive. If the dipoles are *on* the molecular long axis,   the average energy would be zero when both the molecules are allowed to freely rotate about their long axes. Since the dipoles are *off axis*, their separation in the configuration shown in figure-12a is less than that in

figure-12b. Therefore the repulsive energy contribution is more than that of the attractive energy, leading to a net repulsive energy when averaged over molecular rotations. Hence, to lower the energy, the molecules tend to have a relative shift (dz') along their long axes (figure-12c). However, due to this shift, the attractive dispersion energy between the cores is reduced. We calculate the net interaction energy considering a pair of molecules in a smectic layer. We show that the average energy has a minimum when $dz'\neq0$.

Using reasonable values of dipole moment *etc.,* we show that a tilted structure lowers the energy of the medium (see figure-13).We give a comparison between the experimental and the calculated trends in the following table.

Table.1

Experimental observations [33,34]	Results of our calculation
1. Non-polar dialkylazobenzenes do not exhibit the SmC phase	For $p = 0$, U is lowest for $\omega = 0$ due to the contribution from dispersion energy only.
2. Replacement of one alkyl group by the polar alkoxy group gives rise to both SmA and SmC phases	If there is only one dipole of strength 1.5 Debye at $a = 5\text{Å}$ and $\xi = 2\text{Å}$, there is a broad minimum at $\omega \approx 19^0$ (figure-13a).
3. Replacement of both the alkyl groups by alkoxy groups gives rise to SmC and N phases	If there are two equal and opposite dipoles (at $a = 5\text{Å}$, $\xi = 2\text{Å}$ and $a = -5\text{Å}$ and $\xi = -2\text{Å}$), there is a sharper minimum at 27^0 (figure-13b).
4. Dialkoxyazoxy compounds exhibit N and SmC with a large value of ω [34]	A third dipole of strength 2 Debye near the molecular centre (at $a = 0$, $\xi = 2\text{Å}$) gives rise to an even sharper minimum at $\omega = 34^0$, in addition to a higher minimum at $\omega = 58^0$ (figure- 13c).

The theoretical trends thus reflect the experimental ones and the proposed model in which the origin of tilt is due to the *off-axis* lateral dipoles appears to be reasonable.

We propose an appropriate single particle potential and develop a molecular mean field model for the SmC phase. A general single particle tilting potential which is consistent with the biaxial symmetry of the medium can be written as

$$U_C(\theta_i, \phi_i) \propto -\sum_n \beta_n \eta_n \tau^2 \sin 2n\theta_i \cos\phi_i \tag{20}$$

where β_n would depend on the strength and the geometrical arrangement of the dipoles in the molecules, $\tau = \langle \cos(2\pi z/d) \rangle$ is the translational order parameter with z the position of the molecular centre along the layer normal $\hat{z}$ and d the layer spacing, the smectic C order parameter $\eta_n = \langle \sin 2n\theta \cos\phi \rangle$ with θ_i and ϕ_i the polar and azimuthal angles of the long axis of the ith molecule. The tilting potential is added to the layering potential of the McMillan theory (see equation 12). The theory based on equation (12) however does not specify the relative orientation between the director and the layer normal and all 'tilted' smectic A configurations have the same energy. The smectic A phase is favoured due to excluded volume effects. Goossens [35] has shown that for ellipsoids, the relevant contribution to the free energy is of the form

$$\delta F_{hr} = \gamma k_B T \tau^2 \sin^2 \omega \tag{21}$$

where γ is a parameter depending on the dimensions of the ellipsoid. δF_{hr} is entropic in origin and has a positive sign. Including this, we proceed in the usual manner to write an expression for the free energy. Minimising this, we obtain the relevant distribution functions.

On the basis of the model, we calculate phase diagrams showing SmC-SmA-N-I transition sequence or a direct SmC-N or SmC-I transition [36] (see figure-14). For the α and γ values as in figure-14 and for $\beta = 0.4$, the SmA-SmC transition is second ordered in nature (see figure-15a). Over an appropriate parameter space, we show that the nature of the SmC-SmA transition changes from first order to second order (tricritical behaviour). We discuss the results in comparison with experimental data. We estimate the specific heat at constant volume using the calculated values of the internal energy (see figure-15b).
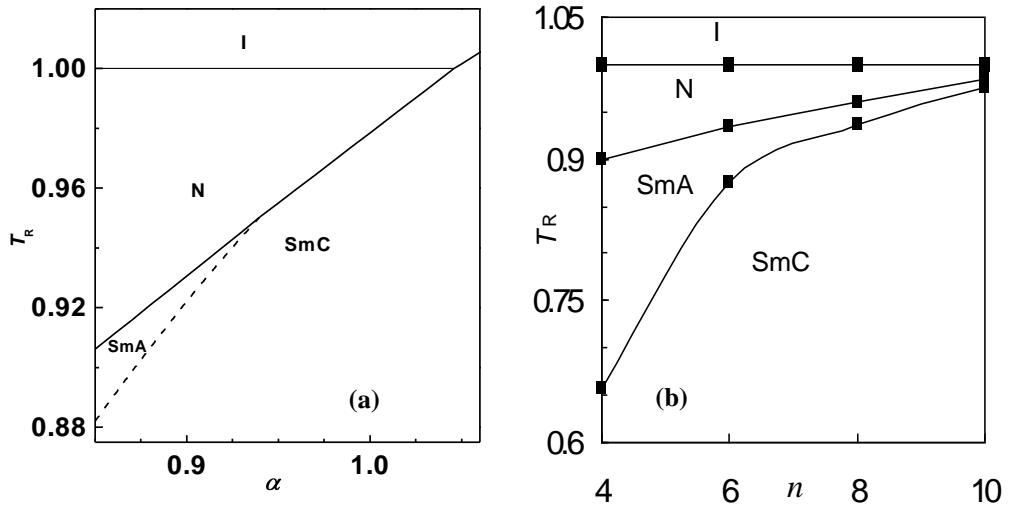
Fi gure 14- (a) Calculated phase diagram as a function of α, with T_R= T/T_{NI}, T_{NI} being the N-I transition temperature, γ = 3 and β =0.42. The dashed line indicates a second order transition and the solid line a first order transition. The jump in η at the first order SmC-N transition decreases to zero as the N-SmA-SmC point is reached. (b)Experimental phase diagram for the homologus seties of compounds 10OPEPOn plotted using data in reference [37]. The solid lines are guides to the eye.
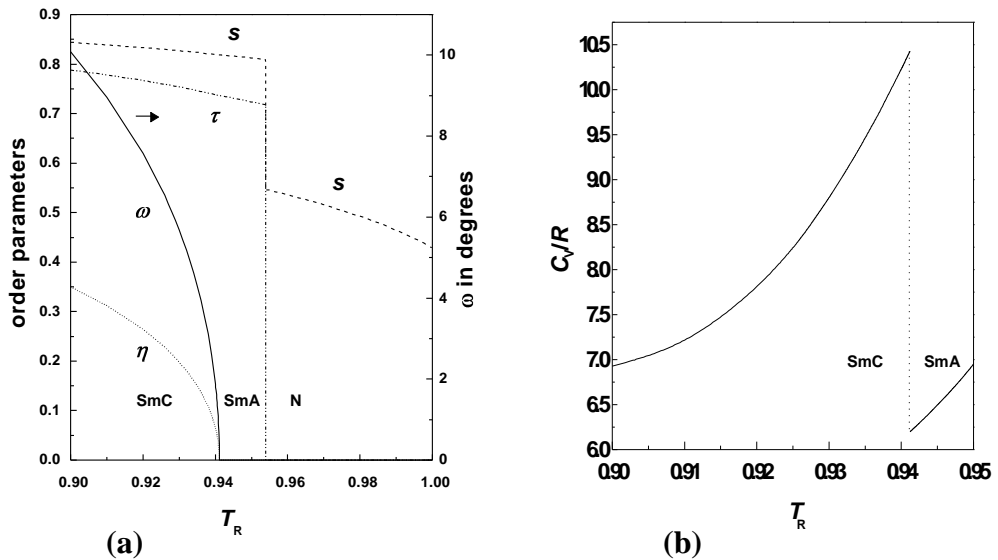
Figure-15. (a) Temperature variations of the order parameters S, τ, η and the tilt angle ω for α = 0.95, β = 0.4 and γ = 3.(b) Jump in the specific heat at constant volume C_V expressed in terms of the universal gas constant R, across the SmC-SmA transition point shown in (a).

In the Landau theory of the SmC-SmA transition, ω is taken as the order parameter and not η. The Landau theory with an unusually large sixth order term in ω has been used [38] to explain the specific heat data close to a second order SmC-SmA transition. We fit the calculated values of the free energy and ω and evaluate the Landau coefficients which compare favourably with the experimental results. We also predict a first order SmC-SmC transition ending in a critical point, over a very narrow range of parameters. We extend the calculations to include the next higher order term in the tilting potential and to include the effect of different tilt angles for the core and the chain in the SmC phase. We also point out some possible extensions of the model.

Many of the results discussed in the thesis are published in the following papers :

1. A simple molecular theory of a nematic-nematic phase transition in highly polar compounds, Govind, A. S., and Madhusudana, N. V., *Liq. Cryst.*, **14**, 1539, 1993.

2. A simple molecular theory of the SmA_1-SmA_d critical point and nematic lake in highly polar compounds, Govind, A. S., and Madhusudana, N. V., *Liq. Cryst.*, **23**, 327, 1997.

3. Effect of strong electric field on the reentrant nematic to smectic A_d phase transition, Geetha Basappa, Govind, A. S., and Madhusudana, N. V., *J. Phys. II France*., **7**, 1693, 1997.

4. A simple molecular model for N-SmA_d-N_{dRe}-N_{1Re}-SmA_1 phase sequence in highly polar compounds, Govind, A. S., and Madhusudana, N. V., *Liq. Cryst.*, **27**, 215, 2000.

5. A molecular theory including hard rod interactions of liquid crystalline phases exhibited by highly polar compounds, Govind, A. S., and Madhusudana, N. V., *Liq. Cryst.*, **27**, 1249, 2000.

6. A simple molecular theory of smectic C liquid crystals, Govind, A. S., and Madhusudana, N. V., *Eur.Phys.Lett.*, **55**, 505, 2001.

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