

## CHAPTER-4

### 1. A MOLECULAR THEORY FOR PHASE DIAGRAMS INVOLVING SMECTIC AND NEMATIC PHASES

#### 1.1 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

$$S = \frac{1}{2} \langle 3\cos^2 \theta_i - 1 \rangle = \langle P_2(\cos \theta_i) \rangle \quad (4.1)$$

where  $\theta_i$  is the angle between the long axis of the  $i^{\text{th}}$  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. This results in a one-dimensional density wave. The molecular centres are, on average, arranged in equidistant planes, leading to what is loosely called a layer structure. In fact, the “layer” suggests far too much because the deviations from the equilibrium positions in the smectic planes can be quite large in these phases. Taking the density wave along the  $z$  axis, the distribution function now depends on the co-ordinate  $z$  as well. 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

$$\rho(z) = \rho_o [1 + \tau \cos(qz)] \quad (4.2)$$

where  $\rho_o$  is the average density of the medium,  $\vec{q}$  is the wave vector along the layer normal with  $q = |\vec{q}| = 2\pi/d$  and  $d$  is the average spacing of the layers. 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

$$\tau = \langle \cos(2\pi z_i/d) \rangle \quad (4.3)$$

where,  $z_i$  is the  $z$  coordinate of the centre of mass of the  $i^{\text{th}}$  molecule. When there is no layering order,  $\tau = 0$  and the medium has uniform density  $\rho_o$  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  $\vec{q} \parallel \hat{n}$ , *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). The characteristics of smectic liquid crystals is discussed in section 1.2.2

In this chapter, we describe phase transitions involving SmA and nematic liquid crystals in thin cells.

## 1.2 The Sm A-N Transition

As explained in chapter 1 (see section 1.2.4), 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 *ie.*, the usual sequences of phase transitions are

$$I \rightarrow N \rightarrow K \text{ or } I \rightarrow N \rightarrow \text{SmA} \rightarrow K \text{ or } I \rightarrow \text{SmA} \rightarrow K.$$

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.

## 1.3 Theory of the Smectic A –Nematic transition

The first molecular statistical treatment of the smectic-nematic transition has been given by Kobayishi (1970, 1971) on the basis of a rather ad hoc model, namely the Maier-

Saupe (MS) model with an additional isotropic intermolecular interaction. A similar but more explicit approach was followed by McMillan (1971), who discussed the SmA-N transition in terms of the MS model using, however, the additional constraint that the director is perpendicular to the smectic planes. This condition is necessary because the existence of the smectic phase requires a coupling of the orientations of the molecules with orientations of the intermolecular distance vectors and evidently such a coupling is not present in the MS model. Before discussing the McMillan approach, however an even simpler treatment of the SmA-N transition due to Meyer and Lubensky (1976) can be mentioned. The ML model limits the discussion of the SmA-N transition to the case of ideal orientational order, i.e., the temperature dependence of the orientation of the molecules is neglected. In the ML model, the molecules are assumed to be perfectly oriented in a given direction, say z direction, whereas their centres of mass are situated on planes, parallel to the xy plane.

#### 1.4 Review of the McMillan theory of SmA liquid crystals

McMillan extended the Maier and Saupe (MS) theory by including a potential corresponding to the one dimensional translational order of SmA liquid crystals. As explained in chapter-1 (see section 1.2.4), 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  $i^{\text{th}}$  molecule as

$$U_i(\cos \theta_i, z_i) = -U_o [1 + \alpha \sigma \cos(2\pi z_i / d) S(3 \cos^2 \theta_i - 1) / 2] \quad (4.4)$$

where  $U_o$  is the MS interaction parameter,  $\theta_i$  the angle between the long axis of the  $i^{\text{th}}$  molecule and the director,  $S$  the orientational order parameter defined in equation 4.1 above,  $d$  the layer spacing,  $z_i$  the coordinate of the centre of the  $i^{\text{th}}$  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

$$\sigma = \left\langle \cos(2\pi z_i / d) (3 \cos^2 \theta_i - 1) / 2 \right\rangle \quad (4.5)$$

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

$$\alpha = 2 \exp[-(\pi r_0 / d)^2] \quad (4.6)$$

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

$$U = \frac{N}{2} \langle U_i \rangle = -\frac{N}{2} U_0 (S^2 + \alpha \sigma^2) \quad (4.7)$$

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

$$S = -Nk_B \langle \ln f(z, \cos \theta) \rangle \quad (4.8)$$

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

$$F = U - TS. \quad (4.9)$$

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

$$f(z_i, \cos \theta_i) = Z^{-1} \exp(-U_i / k_B T) \quad (4.10)$$

where  $Z$  is the normalising integral. The order parameters  $S$  and  $\sigma$  are calculated using

$$S = \frac{1}{d} \int_{-d/2}^{+d/2} dz \int_0^1 d(\cos \theta) f(\cos \theta) P_2(\cos \theta) \quad (4.11)$$

$$\sigma = \frac{1}{d} \int_{-d/2}^{+d/2} dz \int_0^1 d(\cos \theta) f(\cos \theta) \cos(2\pi z/d) P_2(\cos \theta) \quad (4.12)$$

The above equations have the following solutions:

$S = 0, \sigma = 0$ , corresponding to the isotropic phase,

$S \neq 0, \sigma = 0$ , corresponding to the nematic phase,

$$S \neq 0, \sigma \neq 0, \text{ corresponding to the SmA phase.} \quad (4.13)$$

The MS condition is given by

$$U_0/k_B T_{NI} = 4.541 \quad (4.14)$$

where  $T_{NI}$  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 4.6 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 4.2).

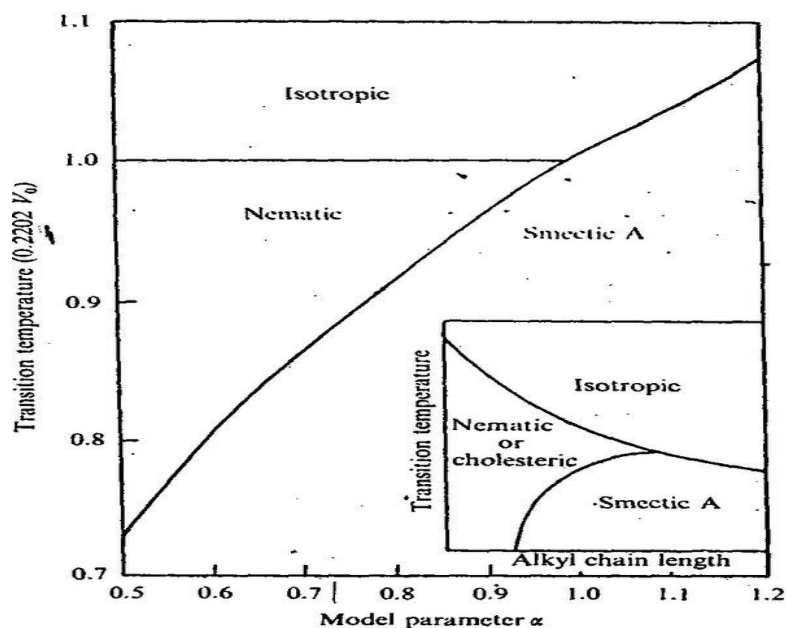


Fig. 4.1. Phase diagram for theoretical model parameter  $\alpha$  ; Inset: typical phase diagram for homologues series of compounds showing transition temperatures versus length of the alkyl end-chains (After McMillan).

### 1.5 Extension of Mc-Millan Theory for thin cell

Assuming a perfect orientational order at the surface, calculations based on the Landau-de-Gennes theory show that the thickness averaged enhancement of  $S$  increases as

the temperature is close to the nematic-isotropic transition temperature ( J.V. Selinger et.al. 1988). The measured order parameter  $S$  is further enhanced in thin cells because of the stiffening of the elastic constant. This reduces the thermal fluctuations of the nematic director. Even the combined effect is too small at low temperatures to account for the experimental data (Surajit Dhara et.al.2004). Experiments of Ocko et.al. (1986) show that liquid crystal systems in the isotropic phase can often show smectic order close to the free surfaces. We consider a similar induced smectic phase near the surface of a cell due to the surface potential. This in turn enhances the nematic order parameter near the surface and hence the thickness averaged order parameter.

In our model, a molecule near the surface is assumed to feel the mean field potential (M-S type) and also the surface induced potential. We have earlier extended M-S theory including such a potential to account for the enhancement of nematic order parameter in thin cells ( chapter-3). In this Chapter, we propose a simple extension of McMillan theory, to include the surface potential.

### 1.5.1 Theoretical Model

The distance from the surface of the cell, into the medium is taken along the Z-axis. The medium is imagined to be made up of layers of thickness  $dz$  parallel to the cell wall. All calculations are made for a layer and then integrated over  $z$ .  $U_i$  is the molecular mean field potential of  $i^{\text{th}}$  molecule at  $z$ .  $S_z$  and  $\tau_z$  are the nematic and smectic order parameters for molecules in the layer between  $z$  and  $z+dz$ .  $F/N$  is the average Helmholtz free energy per molecule in the layer between  $z$  and  $z +dz$ .

A molecule at  $z$  feels the mean field potential (M-S type) and also surface induced potential. The exact nature of the variation of surface potential with respect  $z$  is not known experimentally. The potential has to be maximum at  $z = 0$  and zero at large distances from the surface. Thus, as in chapter 3, the surface induced potential is taken empirically to decay exponentially as

$$U_{is} = -U_s e^{-\frac{z}{r_o}} \quad (4.15)$$

where  $U_s$  is surface potential at  $z = 0$  and  $r_o$  is the characteristic length.

The mean field is not provided by the bulk medium since the interaction beyond few layers is negligible. Also the effect of gradient  $dS/dz$  and its elastic energy effects are shown to be very small (Surajit Dhara et al., 2004). Hence, for M-S type mean field also, we use  $S$  instead of  $S_z$  and similarly  $\tau$  instead of  $\tau_z$ . Variation in the density of the medium due to the variation of  $S$  is ignored.

The nematic order parameter, averaged over the full thickness of the cell is

$$\langle S \rangle = \frac{\int_0^{\frac{t}{2}} S_z dz}{\int_0^{\frac{t}{2}} dz} \quad (4.16)$$

where  $t$  is the cell thickness. The integration is done upto half the cell thickness since the other half is symmetric. This is to be compared with the experimental value of  $S$ .

Surface potential at  $z = 0$  is  $U_s = AU_o$  where  $A$  is a constant and  $U_o$  is the constant in M-S theory with

$$\frac{U_o}{kT_{NI}} = 4.541 \quad (4.17)$$

$k$  being the Boltzmann constant and  $T_{NI}$  the nematic -isotropic transition temperature.

### 1.5.2 Expression for Free energy and order parameter

We extend McMillan theory as modified by Kventzel (1983) with decoupled order parameters.

As explained above, the potential of the  $i^{\text{th}}$  molecule at  $z$  is written as

$$U_i = -U_o S P_2(\cos \theta_i) \left[ 1 + \alpha \tau \cos \left( \frac{2\pi z_i}{d} \right) \right] + U_{is} \quad (4.18)$$

$U_o$  is the MS interaction parameter,  $\theta_i$  is the angle between the long axis of the  $i^{\text{th}}$  molecule and the nematic director,  $S$  is the nematic order parameter,  $d$  is the layer spacing,  $z_i$  the co-ordinate of the centre of mass of the  $i^{\text{th}}$  molecule. The extent of layering order is

measured by the smectic order parameter  $\tau$  given by  $\tau = \langle \cos 2\pi z / d \rangle$ . It is to be noted that the calculations are done in steps of  $z/r_0$  (see eq.4.15). The size of  $r_0$  is taken as  $0.01 \mu\text{m}$ , which is much larger than a smectic layer. Thus, the surface potential is almost constant with in a smectic layer and does not affect the statistical average done over a layer to calculate  $\tau$ .

The McMillan parameter  $\alpha$  is given by

$\alpha = 2 \exp[-(\pi r_c / d)^2]$  where  $r_c$  which represents the range of the dispersion interaction is of the order of the length of the rigid core of the molecules.

The average internal energy per molecule is

$$\frac{U}{N} = -\frac{U_0 S^2 (1 + \alpha \tau^2)}{2} - U_s e^{-\frac{z}{r_0}} S \quad (4.19)$$

where  $N$  is the Avagadro number.

The Molar entropy is  $\zeta = -Nk \langle \ln f_N f_S \rangle$  where  $f$  is the probability distribution function. Subscripts N and S represent nematic and smectic and phases respectively. These distribution functions are found by minimising the free energy.

The average Helmholtz free energy per molecule is

$$\frac{F}{NkT} = -\frac{U_0 S^2 (1 + \alpha \tau^2)}{2kT} - \frac{U_s}{kT} e^{-\frac{z}{r_0}} S + \langle \ln f_N f_S \rangle \quad (4.20)$$

where  $\langle \ln f_N f_S \rangle = \iint (f_N f_S) \ln(f_S f_N) dx dy$  with  $x = \cos \theta$  and  $y = z/d$

Hence the order parameters S and  $\tau$  are calculated using

$$\begin{aligned} S &= \int_0^1 f_N P_2(x) dx \\ \tau &= \frac{1}{d} \int_{-d/2}^{d/2} f_S \cos(2\pi z / d) dz = \int_{-1/2}^{1/2} f_S \cos(2\pi y) dy \end{aligned} \quad (4.21)$$

minimizing  $F$  w.r.t  $f_N$  and  $f_S$  we get,

$$f_N = \frac{e^{\frac{U_0}{kT} \left( S(1 + \alpha \tau^2) + A e^{-\frac{z}{r_0}} \right) P_2(x)}}{Z_N}$$



$$Z_N = \int_0^1 f_N dx$$

$$Z_S = \int_{-1/2}^{1/2} f_S dy$$

$$f_S = \frac{e^{\frac{U_0}{kT} S^2 \alpha \tau \cos(\pi y)}}{Z_S}$$
(4.22)

where  $Z_N$  and  $Z_S$  are the partition functions for nematic and smectic orders respectively.

Substituting for  $\langle f_N f_S \ln(f_N f_S) \rangle$  we get

$$\frac{F}{NkT} = \frac{U_0 S^2}{2kT} (1 + 3\alpha \tau^2) - \ln(Z_N Z_S)$$
(4.23)

Minimizing  $F$  w. r. t  $S$  and  $\tau$ , we get

$$S = \int f_N P_2(x) dx$$

$$\tau = \int_{-1/2}^{1/2} f_S \cos(2\pi y) dy$$
(4.24)

which satisfy the self consistency condition.

### 1.5.3 Method of Calculation

The necessary integrals are evaluated numerically using 32 point Gaussian quadrature method in double precision. Numerical iteration is used to adjust  $S$  and  $\tau$  for self consistency. The constant  $A$  is taken to be 10 as in (Surajit Dhara et.al. 2004) and in chapter- 3.

We look for the following types of solutions:

$S = 0, \tau = 0$ , corresponding to the isotropic phase,

$S \neq 0, \tau = 0$ , corresponding to the nematic phase,

$S \neq 0, \tau \neq 0$ , corresponding to the smectic phase.

The stable phase is the one having lower free energy. The temperature at which any two solutions have the same free energy gives the corresponding transition temperature.

The thickness average value of  $S$  is found using equation-4.16, for different values of  $T$ , for thicknesses  $1 \mu\text{m}$  and  $10 \mu\text{m}$  respectively. In each case the percentage change in nematic order parameter  $dS_1 \%$ ,  $dS_2 \%$  and  $dS \%$  are calculated using

$$\begin{aligned} dS_1 \%/_{(1\mu\text{m})} &= \frac{\langle S \rangle_{1\mu\text{m}} - S_b}{S_b} \times 100 \\ dS_2 \%/_{(10\mu\text{m})} &= \frac{\langle S \rangle_{10\mu\text{m}} - S_b}{S_b} \times 100 \\ dS \%/ &= \frac{\langle S \rangle_{1\mu\text{m}} - \langle S \rangle_{10\mu\text{m}}}{\langle S \rangle_{10\mu\text{m}}} \times 100 \end{aligned} \quad (4.25)$$

where  $S_b$  is the bulk value, corresponding to large value of  $z$  at which  $U_{is}$  has become negligible.

#### 1.5.4 Results and Discussion.

Initially, we have carried out the calculations without considering the surface potential. The resulting phase diagram as a function of  $Tr$  and  $\alpha$  is shown in fig-4.2. The arrow indicates  $\alpha = 0.95$  which is chosen for the rest of the calculations. It is to be noted that, at  $\alpha = 0.95$ , smectic phase exists for  $Tr < 0.95$ , which corresponds to  $T = T_{NI} - 15^0$  for a typical  $T_{NI}$  of  $300\text{K}$ . Thus, down to the least temperature in our calculations ( $T = T_{NI} - 12^0$ ), the bulk medium is only in the nematic phase. However, smectic phase is

induced near the surface due to the surface potential causing an enhancement of  $S_z$ , as shown below.

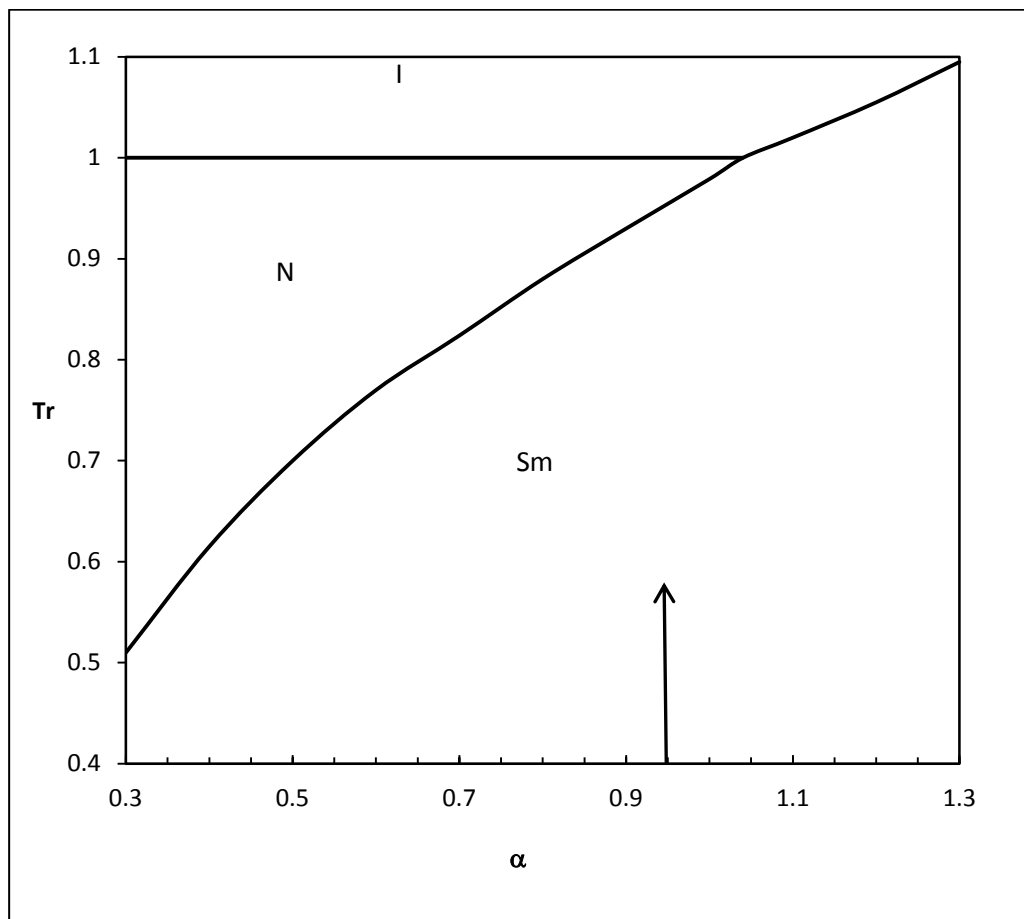


Fig. 4.2. Calculated phase diagram as a function of  $Tr$  and  $\alpha$  without considering the surface potential. Arrow indicates  $\alpha = 0.95$  which is chosen for the rest of the calculations.

With  $\alpha = 0.95$ , calculated variation of order parameter ( $S_z$ ) with distance from surface ( $z$ ) for a cell of thickness  $1\mu\text{m}$  at  $T = T_{NI} - 1^\circ$ , with  $r_0 = 0.01\mu\text{m}$  is shown in Fig- 4.3. Note that, the  $S_z$  at the surface is nearly 0.98 as in chapter-3 since the surface potential at  $z = 0$  is strong. It decreases to the bulk value away from the surface. The middle of cell corresponds to  $z/r_0 = 50$  and the other half is symmetric. The graph is shown upto  $z/r_0 = 30$  since  $S_z$  has already reached the bulk value. Due to increased orientational order, the smectic phase is stabilised near the surface. The arrow indicates  $z/r_0 = 4$  at which smectic becomes nematic. A change of slope in the corresponding  $S_z$  at this point can be noted. The

calculated variation of  $S_z$  with  $z$  considering only the nematic phase (chapter-3) is also shown for comparison. Since the nematic order in the smectic phase is stronger than that in the nematic phase, the induced smectic phase has increased  $S_z$  over some range of  $z/r_0$  compared to the earlier (chapter-3) values thus leading to a higher value of the thickness averaged 'S'.

This calculation is repeated for different temperatures. The distance from the surface at which Sm-N transition takes place decreases as the temperature is increased as expected. Calculated distance-temperature phase diagram involving smectic (Sm), nematic (N), paranematic ( $N_p$ ) and isotropic (I) phases is shown in fig.4.4. Since  $T_r$  is defined as  $T/T_{NI}$ , the nematic phase is stable in the bulk upto  $T_r = 1$  and hence the  $N_p$  or the I phase does not appear even at large values of  $z/r_0$ .

At  $T = T_{NI} - 10^0$ , the Sm-N transition occurs at  $z/r_0 = 5$ . The corresponding variation of the order parameters  $S$  and  $\tau$  is shown in fig.4.5

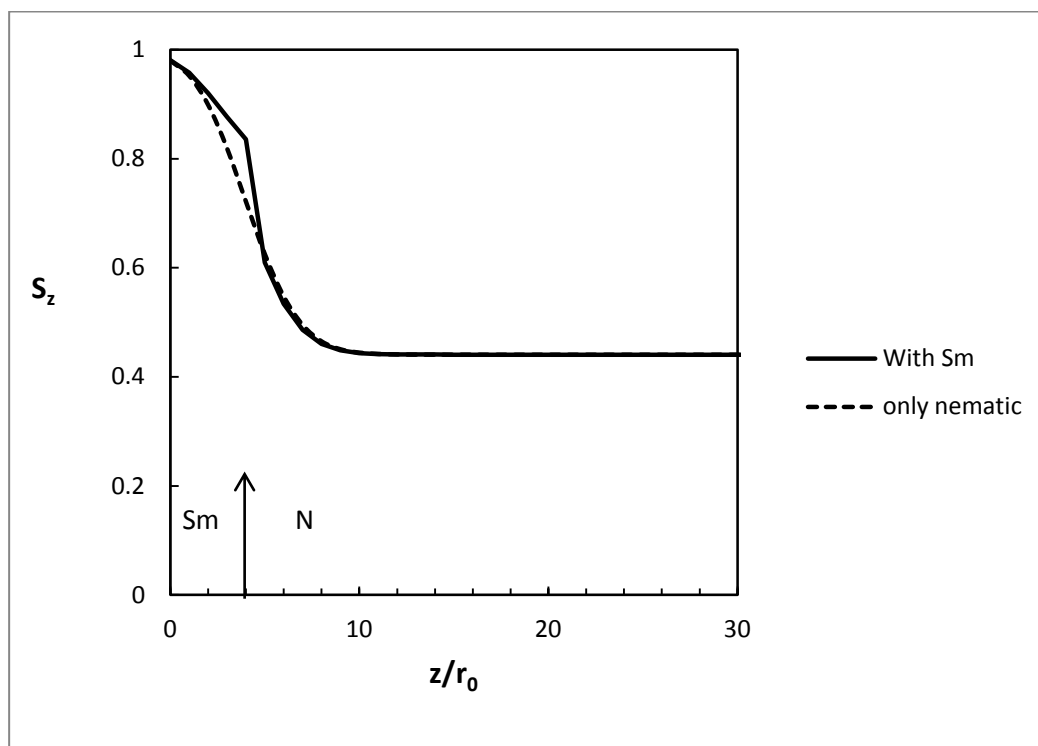


Fig. 4.3. The calculated variation of order parameter ( $S_z$ ) with distance from surface ( $z$ ) for a cell of thickness  $1\mu\text{m}$ , with  $r_0 = 0.01\mu\text{m}$ , at  $T = T_{NI} - 1^0$ , with  $\alpha = 0.95$ . The arrow indicates  $z/r_0 = 4$  at which smectic becomes nematic. The calculated variation of  $S_z$  with  $z$  considering only the nematic phase (chapter- 3) is also shown for comparison.

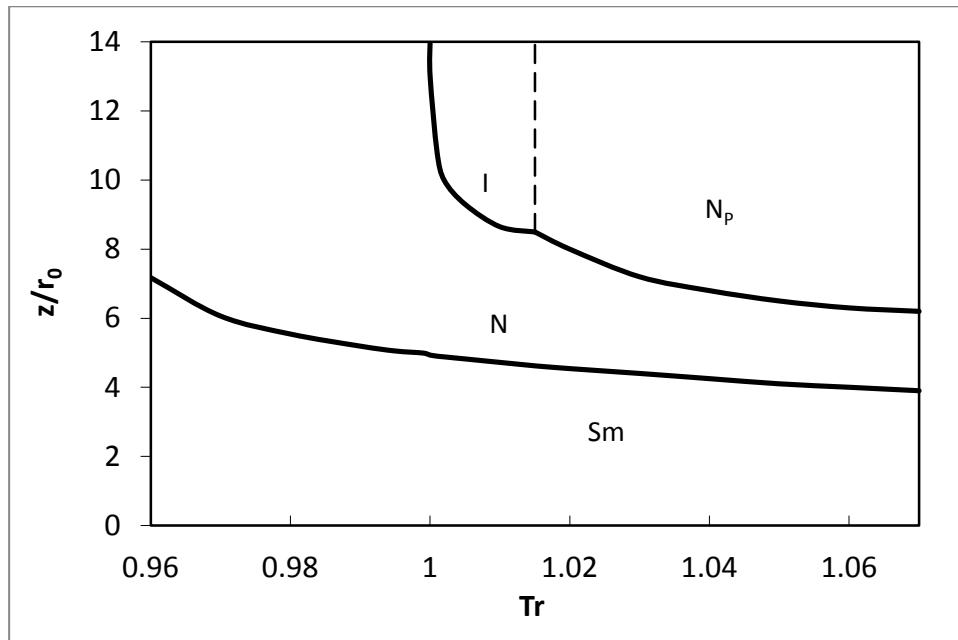


Fig.4.4. Calculated distance-temperature phase diagram showing smectic (Sm), nematic (N), para nematic(Np) and isotropic phases. The Np phase becomes isotropic for large values of  $z/r_0$  (not shown).

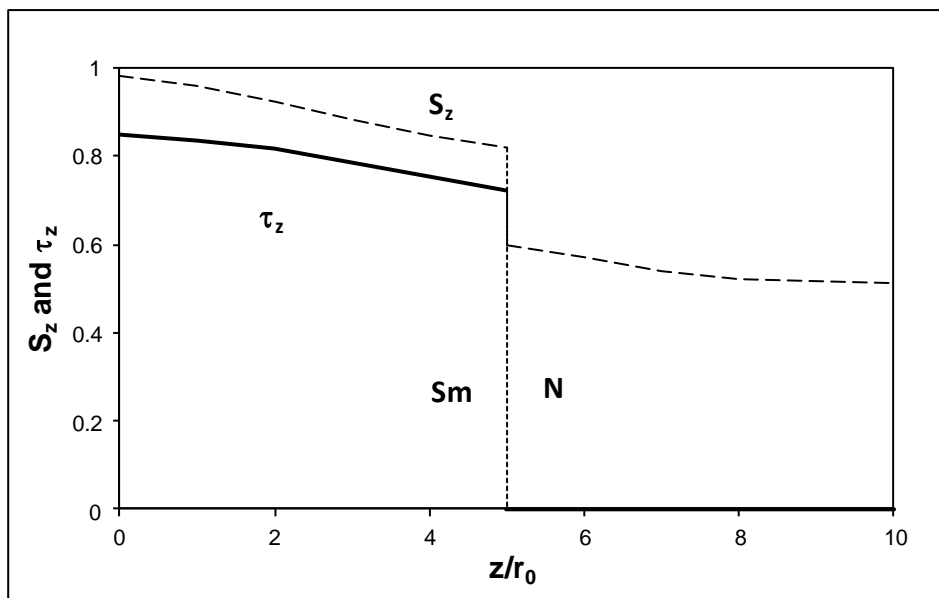


Fig 4.5. Calculated variation of nematic and smectic order parameters as a function of  $z/r_0$  showing the presence of smectic phase upto  $z/r_0 = 5$ , for  $\alpha = 0.95$  and  $T = T_{NI} - 10^0$  corresponding to the phase diagram in figure 4.4

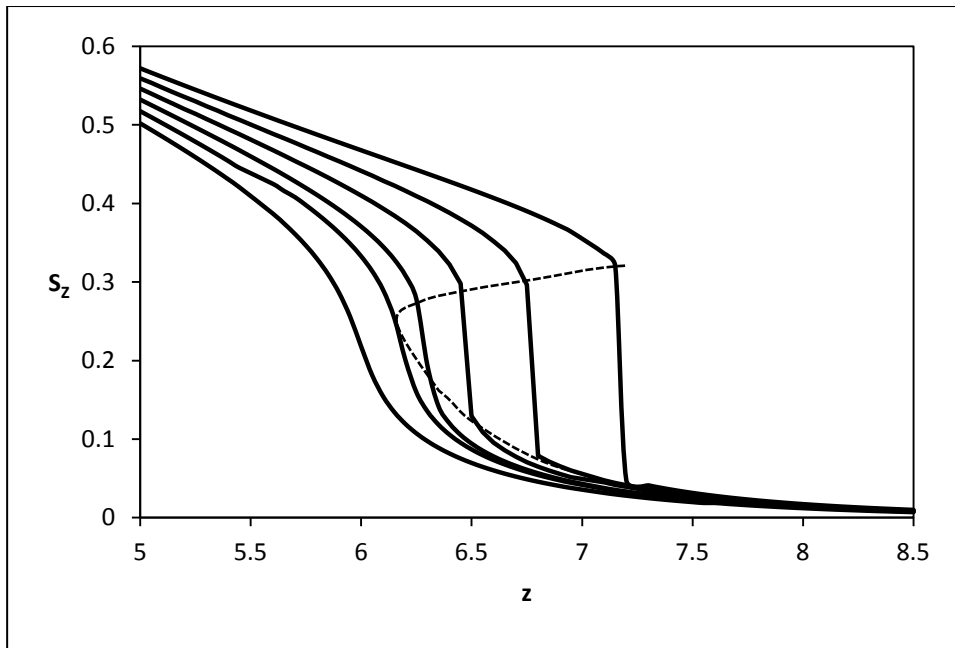


Fig. 4.6. Variation of  $S_z$  with  $z/r_0$  at different  $Tr$  corresponding to nematic to paranematic transitions shown in the phase diagram in figure 4.4. Solid lines from right to left correspond to  $Tr = 1.03$  to  $1.08$ . The dashed line shows decrease in  $S_z$  as  $Tr$  is increased.

Between  $Tr = 1$  to  $Tr = 1.015$ , the jump in  $S_z$  is large and there is direct N-I transition. The jump in  $S_z$  decreases as  $Tr$  is increased and there is continuous N-Np transition beyond  $Tr = 1.07$  as shown in fig.4.6 . The Np phase becomes isotropic for large values of  $z/r_0$  (not shown in fig.4.4).

In table-4.1, the calculated values of thickness averaged  $S$  and various  $dS\%$  as defined in equations 4.25, with only nematic potential from our earlier work (chapter-3) are shown in comparison with values in ref( Surajit Dhara et.al. 2004) .Table -4.2 shows the corresponding values with inclusion of smectic potential.

Table 4.1: Comparison of calculated values of average order parameters ( $S$ ) in cells of thicknesses  $1\mu\text{m}$  and  $10\mu\text{m}$  with nematic phase only

Temperature	$S_b^*$	$S_b$	$\langle S_1 \rangle_{1\mu\text{m}}$	$\langle S_2 \rangle_{10\mu\text{m}}$	$dS_1\%$	$dS_2\%$	$dS\%$	$dS\%*$
$T_{NI} - 0.2^\circ$	0.297	0.4311	0.4835	0.4363	12.15%	1.21%	10.8%	30%
$T_{NI} - 1^\circ$	0.373	0.4407	0.4918	0.4458	11.58%	1.16%	10.3%	9%
$T_{NI} - 5^\circ$	0.566	0.4799	0.5257	0.4845	9.55%	0.96%	8.5%	1.5%
$T_{NI} - 10^\circ$	0.714	0.5165	0.5578	0.5206	8%	0.8%	7.1%	0.6%

\*(Ref: Surajit Dhara et.al. 2004)

Table 4.2: Comparison of calculated values of average order parameters ( $S$ ) in cells of thicknesses  $1\mu\text{m}$  and  $10\mu\text{m}$  with smectic near the surface.

Temp	$S_b$ *	$S_b$	$\langle S_1 \rangle_{1\mu\text{m}}$	$\langle S_2 \rangle_{10\mu\text{m}}$	$dS_1$ %	$dS_2$ %	$dS$ %	$dS$ %*
$T_{NI} - 0.2^\circ$	0.297	0.4311	0.4855	0.4367	12.61%	1.28%	11.18%	30%
$T_{NI} - 1^\circ$	0.373	0.4407	0.4938	0.4462	12.045%	1.27%	10.7%	9%
$T_{NI} - 5^\circ$	0.566	0.4799	0.53178	0.4857	10.791%	1.1985%	9.48%	1.5%
$T_{NI} - 10^\circ$	0.714	0.5165	0.5684	0.5218	10.05%	1.0232%	8.93%	0.6%

\*Ref: (Surajit Dhara 2004)



Table 4. 3: Comparison of  $dS$  % in first and second cases

Compound*	Thickness of the thin and thick cells ( $\mu m$ )	$dS$ % *	$dS$ % (only nematic)	$dS$ % (with smectic)
S1014	1.5 and 6.7	15%	3.85%	5.063%
CN	1.5 and 14	11%	4.26%	5.569%

\*Ref: (Surajit Dhara 2004)

Comparing the values of the nematic order parameter in table 4.1 and table 4.2 we find that the enhancement is larger in table 4.2. As mentioned earlier, higher values of the thickness averaged 'S' with smectic phase are due to the fact that the nematic order in the smectic phase is stronger than that in the nematic phase and the induced smectic phase has increased  $S_z$  over some range of  $z/r_0$  as seen in fig-4.3. Also, this effect is larger at lower temperatures, especially in thin cells. It can be seen that, close to  $T_{NI}$  the enhancement is large and decreases as the temperature is lowered. This trend is expected, as the surface potential has a larger effect in increasing the order parameter when the bulk order parameter is lower. The bulk order parameter increases with the decrease in temperature and the effect of surface potential in further increasing the order is reduced. Experimentally it is found (Surajit Dhara et al., 2004) that the enhancement is not significantly reduced at lower temperatures. Considering table-1, the percentage enhancement of the order parameter between thick and thin cells ( $dS\%$ ) reduces by 1.5 times with the decrease in temperature and after including the smectic potential (table-4.2) it is still better (1.2 times). However, the reduction as per the calculations in ref (Surajit Dhara et al., 2004) is 50 times. Of the two, the inclusion of smectic potential is better than the first as seen by table 4.3, which shows the  $dS\%$  values for different pairs of thicknesses at  $T = T_{NI} - 12^0$ . Thus, the simple empirical equation used for the decay of surface potential give results which are in better agreement with experimental data compared to earlier theories (Surajit Dhara et al., 2004). This gives an

insight about the realistic variation of surface effects which may be investigated more rigorously.

The trends agree only qualitatively and the actual dS% values are much less than the experimental values (Surajit Dhara et al., 2004) as seen in table-4.3. This may be due to the presence of polar short range order since the experimental molecules are polar. The effect of including polar short range order is being studied and further theoretical work in this direction is under progress.

### **1.5.5 Conclusions:**

Experimental observations show that the nematic order parameter is significantly enhanced as the thickness of the cell is reduced and that this enhancement does not significantly reduce as the temperature is lowered below  $T_{NI}$ . Calculations of earlier theories do not agree well with the experimental data. We have earlier used an empirical variation of surface potential and have proposed the simple extension of Maier-Saupe theory to account for the enhancement (chapter-3) which resulted in values with better agreement with experimental results. In the present paper, we consider that the increased orientational order near the surface can stabilise the smectic phase. This is discussed by including the surface potential to extend McMillan theory for the smectic phase. Our calculations lead to a surface induced smectic phase. This in effect has improved the qualitative agreement with experimental results.