CHAPTER-5

1. A MOLECULAR THEORY OF THE NEMATIC TO NEMATIC PHASE TRANSITION IN STRONGLY POLAR COMPOUNDS

1.1 Introduction

As described in the previous chapter, the nematic (N) liquid crystal is characterised by a long range orientational order of the long axes of the molecules without a long range positional order of their centres of mass (see section 1.2.1, chapter-1). The preferred axis of orientation in the nematic liquid crystal, called the director, is represented by the unit vector \( \hat{n} \). The extent of orientational order in a cylindrically symmetric nematic liquid crystal is given by the so-called scalar order parameter \( S \) defined as

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

(5.1)

where \( \theta_i \) is the angle between the long axis of the \( i^{th} \) molecule and the director, \( P_2 \) is the second Legendre polynomial and \( \langle \cdots \rangle \) denote a statistical average. The order parameter takes a maximum value equal to 1 when all the rods are perfectly aligned and is zero when all the orientations of the long axes are equally probable i.e., in the isotropic phase.

When heated, usually a nematic liquid crystal undergoes a transition to the isotropic liquid. Since the nematic liquid crystal differs from the isotropic liquid only in an orientational order, one would not normally expect any other variation in the transition sequence. However, such variations have been observed in some special cases. For example, as described in chapter-1, in case of compounds consisting of molecules with polar end groups, when the reentrant nematic liquid crystal is heated, it undergoes a transition to the SmA\(_d\) liquid crystal. Some liquid crystal compounds consisting of strongly polar molecules show the nematic-nematic (N-N) transition associated with a jump in the order parameter. Experimentally, the first example of the N-N transition was found in a binary mixture.
of polar compounds DB₈ONO₂ and DB₁₀ONO₂ where, DBₙONO₂ denotes the homologues of n-alkyloxyphenyl-nitrobenzoxyloxybenzoate. The transition was discovered by high resolution calorimetric (see figure 5.1a) and X-ray diffraction techniques. The X-ray measurements indicated a jump in the short range smectic like order associated with the N-N transition. In fact, in the temperature -concentration phase diagram, the N-N transition line appears as a continuation of the SmA₁-SmA₃ transition line (see figure 5.1b). Hence the transition is denoted as N₁-N₃ transition. Here, the suffix ‘d’ denotes *dimers* and the suffix ‘1’ *monomers* characterising the short range order.

The N₁-N₃ transition has been subsequently observed in a single component system also (Sobha et al., 1998). In this experiment, the strongly polar compound p-cyanophenyl p-n heptylbenzoate (CP7B) contained in a *thin* cell was studied optically and a jump in the transmitted intensity indicating a jump in the orientational order parameter associated with the N₁-N₃ transition was detected (see figure 5.2). Note that the N₁-N₃ transition in this case is not associated with the smectic phase.

![Figure 5.1](image-url)

Figure 5.1. (a) Variation $C_p$ for a sample with $X = 53.7\%$, where $X$ is the mole percent concentration of DB₁₀ONO₂ in DB₈ONO₂. The strong peak in the middle corresponds to the N₀-N₁ transition and the small peak marked by the right arrow corresponds to SmA₃-N₃ transition and the left arrow to SmA₁-N₁ transition. (b) Detail of the $T$-$X$ phase diagram for the same mixture for $X$ between 51% and 55%. 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, 1$^{st}$ order ones. TCP marks the tricritical point. (Nounesis, G et al., 1991, 1994).
Fig. 5.2. Variation in the transmitted intensity as a function of temperature for the compound CP7B for cell thickness of 1.9 \( \mu \)m (Sobha et al. 1998). Note the jump around 33\(^{0}\)C.

The SmA-SmA transition is associated with a jump in the layer spacing. This has been successfully explained by the phenomenological theory developed by Prost (de Gennes, P G. et al., 1993, Prost J ,1987) using two coupled smectic order parameters corresponding to ‘two competing lengths’. This theory predicts the general phase diagrams showing the \( N_1-N_d \) transition as a continuation of the SmA-SmA transition line (see figure 5.3) in agreement with the experimental result of figure 5.1b. Hence it is clear that the \( N_1-N_d \) transition is also associated with the two competing lengths characterising the short range smectic like order.
A simple model to explain the molecular origin of the ‘two lengths’ assumed in the Prost’s phenomenological model was proposed by Madhusudana and Jyothsna Rajan (1990). The basic concept in this model is that the molecular pairs can change over from anti-parallel (A) to parallel (P) configuration as the intermolecular separation \((r)\) is reduced due to cooling or due to increase of pressure. The medium is treated as an equilibrium mixture of the A and P types of pairs. Experiments (Basappa et al., 1998) showing the presence of polar short range order at low temperatures support this model. In this chapter, we extend this model to develop a molecular theory of polar liquid crystal in thin cells. We begin with a description of this model.

### 1.2 Model for molecular pairs with parallel dipole moments at low temperatures

In the model proposed by Madhusudana and Jyothsna Rajan (1990), the origin of the two incommensurate lengths is explained as follows: the permanent dipolar interaction favours an antiparallel arrangement between the neighbouring mesogenic molecules (Madhusudhana N.V et al., 1973) However, the aromatic part of the antiparallel neighbours overlap due to the strong dispersion interaction between them leading to the partial bilayer...
arrangement (see figure 5.4a). In this configuration, the alkyl chains of the two molecules, which lie on opposite sides of the core region, do not have a significant interaction.

On the other hand, if the molecules are parallel, the permanent dipolar interaction is repulsive. However, the aromatic cores have strong polarizabilities and the induced dipole moment due to a neighbouring polar molecule would weaken the net dipole moment of any given molecule in this configuration (see figure 5.4b). Further, the chains of the two neighbours are now in close proximity and the dispersion interaction between them would favour this arrangement. The repulsive dipolar interaction is \( \propto \frac{1}{r^3} \) where \( r \) is the intermolecular separation, while both the dipole-induced dipole and the dispersion interactions are \( \propto \frac{1}{r^6} \) and are attractive in nature. Hence there can be a change from the antiparallel to the parallel configuration as the intermolecular separation is decreased below some value as the density is increased due to a lowering of temperature or an increase of pressure.

![Fig. 5.4. 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 a solid line represents the permanent dipole moment and the one with a dotted line, the induced one. (For the sake of clarity, the relative separation in (a) is exaggerated).](image)

The following calculations show that the change over from the A-type configuration to the P-type configuration occurs for reasonable values of the molecular parameters. Considering an antiparallel pair (see figure 5.4a), the induced dipole moment in a molecule is given by
\[ \vec{p}_1 = \chi \vec{E} \]  \hspace{1cm} (5.2)

where \( \chi \) is the longitudinal component of the polarisability of the part of the core which is close to the dipole of the neighbour which generates an electric field \( \vec{E} \). We have, for short dipoles,

\[ \vec{E} = \frac{1}{4\pi\varepsilon_0} \frac{(p+p_1)}{r^3} \]  \hspace{1cm} (5.3)

where \( \varepsilon_0 \) is the absolute permittivity of free space, \( p \) is the permanent dipole moment, \( (p+p_1) \) is the net dipole moment of one of the molecules in the A-type configuration (see figure 5.4a) and \( r \) is the intermolecular separation. From equations 5.2 and 5.3, we have

\[ (p+p_1) = \frac{p}{1 - \frac{\chi}{4\pi\varepsilon_0 r^3}} \]  \hspace{1cm} (5.4)

The pairing energy for an antiparallel pair is given by

\[ E_A = - \frac{1}{4\pi\varepsilon_0} \frac{(p+p)^2}{r^3} \]

\[ = - \frac{1}{4\pi\varepsilon_0 r^3} \frac{p^2}{(1-\frac{\chi}{4\pi\varepsilon_0 r^3})^2} E_p \]  \hspace{1cm} (5.5)

For a P-type of pair (see figure 5.4b), the pairing energy is

\[ E_p = + \frac{1}{4\pi\varepsilon_0 r^3} \frac{p^2}{(1+\frac{\chi}{4\pi\varepsilon_0 r^3})^2} - \frac{Kc^2}{r^5} \]  \hspace{1cm} (5.6)

where \( K \) is the chain-chain interaction parameter and \( c \) is the chain length. We do not explicitly include the energy due to the dispersion interaction between the cores as it is supposed to be the same in the A and P configurations.

To evaluate \( E_A \) and \( E_p \), the following typical values (Mahasudhana N.V etal., 1990) are used:

\[ p = 4 \text{ Debye} = 4/3 \times 510^{-29} \text{C m}, \quad \chi / (4\pi\varepsilon_0) = 20.5 \times 10^{-30} \text{m}^3, \quad Kc^2 = 6.65 \times 10^{-76} \text{SI units.} \]

The pairing energy difference
\[ \Delta E = E_A - E_P \]  \hspace{1cm} (5.7)

is calculated for various values of \( r \). A graph of \( \Delta E \) against \( r \) is shown in figure 5.5. Note that the energy of two dipoles of strength 1D each separated by a distance of 1Å \( i.e., \) \( 1D^2/\text{Å}^3 \) in CGS units is equal to \( 10^{-19} \) J in SI units.

It can be seen that, for \( r \leq 5.47 \) Å, \( \Delta E > 0, \) \( i.e., \) \( E_P < E_A \) or the P-type configuration has lower energy than the A-type of configuration. This clearly shows that, as the intermolecular separation is decreased, the P-type configuration is favoured over the A-type configuration.

For simplicity, the above calculations are carried out restricting the interaction to two near neighbours. In the liquid crystal medium, many near neighbours interact. More than two molecules can have an all-parallel configuration, whereas many near neighbours cannot be mutually antiparallel. In reference (Madhusudana N.V. et.al.,1990), as an example, molecules arranged in a two dimensional hexagonal lattice is considered for calculation of \( E_A, \) \( E_P \) and \( \Delta E \). The resulting graph of \( \Delta E \) against \( r \) is very similar to that shown in fig 5.5

![Graph showing \( \Delta E \) against \( r \)](image)

Fig. 5.5. The pairing energy difference \( \Delta E = E_A - E_P \) (in \( 10^{-19} \)J) between the antiparallel and parallel configurations plotted as a function of the intermolecular separation \( r \) (in Å) (Govind A.S et.al. 1997)
Even though more than two near neighbours can have parallel configuration, for simplicity, as in reference (Madhusudhana N.V et.al. 1990). We consider the medium to be a mixture of A and P types of pairs. Incorporating these ideas, we develop a molecular theory for the nematic-nematic transition has been developed. For this, we extend the Maier-Saupe theory of nematic liquid crystals to develop a theory of nematic mixtures.

This concept has already been used by Govind and Madhusudana (1997) to explain \( N_1-N_d \) transition, double and quadruple re-entrance, effect of electric field etc (Geetha Basappa et al; 1997).

The model has been recently extended to explain the decrease of \( T_{NI} \) due to UV exposure (Suresha et al. 2011). The model is also extended to explain photo-induced smectic phase considering the medium with saturated nematic order (Suresha et al., 2011) and with unsaturated nematic order (Govind A.S. et al. 2012).

### 1.3 Polar liquid crystals in thin cells.

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. The combined effect is too small at low temperatures to account for the experimental data (Surajit Dhara et al. 2004). We have earlier proposed a simple extension of Maier-Saupe (M-S) theory to account for the enhancement, in which, a molecule near the surface is assumed to feel the mean field potential (M-S type) and also surface induced potential (chapter -3). In the earlier theory (chapter 3) the variation in the density of the medium due to the variation of \( S \) was ignored. It is to be noted that, the experimental compounds (Surajit Dhara et al. 2004) consist of polar molecules. A molecular mean field model has been developed (Madhusudhana et al. 1990) assuming the medium with polar molecules to consist of inter-converting anti-parallel and parallel pairs to explain the molecular origin of “two lengths”. The model was used to explain double re-entrance, effect of electric field on \( T_{NI} \) etc. In the present chapter, the change in the relative proportion of the parallel pairs due to change in the density of the medium is included in the M-S theory with the surface potential. Our
calculations are in better agreement with the experimental data in ref (Surajit Dhara et.al. 2004).

1.4 Extension of the model to polar model to liquid crystals in thin cells.

We now extend this molecular theory of highly polar compounds to include the effect of surface potential. Many of the assumptions made in this model have already been discussed in the earlier papers (Govind A.S 2002, Geetha Basappa et.al. 1997, Suresha B.L et.al. 2011). We recall the assumptions relevant for the present theory.

1.4.1 Assumptions

(1) As explained above, the medium is assumed to consist of pairs of molecules having either antiparallel (A) or parallel (P) configurations. The difference between the pairing energy of the A-type \( E_A \) and the P-type \( E_P \) configurations is written as

\[
\Delta E = E_A - E_P = R_1 k T_N I \left( \frac{R_2}{T_R} - 1 \right)
\]

where \( R_1 \) is an interaction parameter and \( R_2 \) is the reduced temperature at which the density of the medium is such that \( \Delta E \) becomes zero, \( k \) is the Boltzmann constant, \( T_N \) the nematic -istropic transition temperature and the reduced temperature \( T_R = T/T_N \).

(2) The orientational potential for A-type of pairs \( (U_{AA}) \) and P-type of pairs \( (U_{PP}) \) are assumed to be different.

\[
U_{PP} = Y U_{AA}
\]

and the mutual interaction potential

\[
U_{AP} = U_{PA} = P \sqrt{U_{AA} U_{PP}}
\]

where \( P \neq 1 \) indicates a deviation from the geometric mean (GM) approximation.

The following are the additional assumptions made to incorporate the effect of surface potential.

(3) The distance from the surface of the cell, into the medium is taken along the \( Z \)-axis. The medium is assumed 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 \( i^{th} \) molecule at \( z \). \( S_z \) is the order parameter 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 to $z$ is not known experimentally. The potential has to be maximum at $z = 0$ and zero at large distances from the surface. Thus, the surface induced potential is taken empirically to decay exponentially as

$$U_{S} = -U_{S}e^{-\frac{z}{r_0}}$$

(5.11)

where $U_{S}$ is surface potential at $z = 0$ and $r_0$ is the characteristic length. The layer thickness is taken to be quite small, comparable to molecular 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 $S_{r}$.

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

$$\langle S \rangle = \frac{\int_{0}^{t} S_{z}dz}{\int_{0}^{t} dz}$$

(5.12)

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

Surface potential at $z = 0$ is $U_{S} = AU_{AA}$ where $A$ is a constant and $U_{AA}$ is the constant in M-S theory, taken for A-type of pairs with

$$\frac{U_{AA}}{kT_{NI}} = 4.541$$

(5.13)

(4) As we mentioned, the surface potential enhances the order parameter of the medium. This results in an increase in the density which in turn decreases intermolecular separation. This increases the fraction of parallel pairs and hence increases $R_{2}$. Thus, $R_{2}$ at some distance $z$ from the cell wall ($R_{2}(z)$) is greater than $R_{2}$ of the bulk ($R_{2B}$). Thus, we can write:
\[ R_2(z) = R_{2B} + \delta(z) \]  

(5.14)

where, \( \delta(z) \) represents the change in \( R_2 \) because of change in density.

We assume

\[ \delta(z) = \delta_0 e^{-\frac{cz}{\tau_0}} \]  

(5.15)

The estimation of the constants \( \delta_0 \) and \( c \) is explained in the next section.

1.4.2 Free energy and order parameters

Extending the Maier-Saupe theory for mixtures, the potential energy of the \( i^{th} \) A-type of pair can be written as

\[
\begin{align*}
U_{Ai} &= - U_{AA} X_A S_A P_2 (\cos \theta_{Ai}) - U_{AP} X_P S_P P_2 (\cos \theta_{Ai}) \\
\text{and } U'_{Ai} &= - U_{SP} X_P S_P P_2 (\cos \theta_{Ai})
\end{align*}
\]  

(5.16)

where \( X_A, X_P, S_A, S_P \) are the mole fractions, orientational order parameters of A and P types of pairs respectively. Similarly for a P-type pair, \( U_{pj} \) is obtained by interchanging suffixes A and P in equation 5.16. The surface potential \( U'_{Pi} \) being apolar, is the same for A and P types of pairs. The internal energy of one mole of pairs can be written as

\[ 2U = \frac{N}{2} X_A \left( U_{Ai} \right) + \frac{N}{2} X_P \left( U_{pj} \right) + N \langle U'_{Ai} \rangle - N X_P \Delta E \]  

(5.17)

where the angular brackets indicate statistical average, the factor 2 on the left hand side reminds that we have a mole of pairs, the factor \( \frac{1}{2} \) appears in the first two terms since each pair is counted twice while averaging over the mutual interactions and we have also added the concentration dependent part of the configurational energy. The molar entropy is given by:

\[
2\zeta = -Nk \left[ X_A \int_{-d/2}^{+d/2} dz_{Ai} \int_{0}^{1} d (\cos \theta_{Ai}) f_{Ai} \ln f_{Ai} + X_P \int_{-d/2}^{+d/2} dz_{pj} \int_{0}^{1} d (\cos \theta_{pj}) f_{pj} \ln f_{pj} \right]
\]

\[ -Nk \left( X_A \ln X_A + X_P \ln X_P \right) \]  

(5.18)

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:

\[ F = U - T\zeta \]  

(5.19)
The orientational distribution functions of the A-type of pairs \( f_A \) and \( f_P \) are found by minimising \( F \). We have

\[
f_A = \frac{1}{Z_A} \exp \left\{ \left( \frac{U_{AA}}{kT} \right) \left[ X_A S_A + P \sqrt{Y} X_P S_P + A e^{-z/r_0} \right] P^2(\cos \theta_A) \right\}
\]

\[
f_P = \frac{1}{Z_P} \exp \left\{ \left( \frac{U_{AA}}{kT} \right) \left[ Y X_P S_P + P \sqrt{Y} X_A S_A + A e^{-z/r_0} \right] P^2(\cos \theta_P) \right\}
\]

(5.20)

where \( Z_A \) and \( Z_P \) are the appropriate normalising integrals. Hence the order parameters are given by:

\[
S_A = \int_0^1 d(\cos \theta_A) P^2(\cos \theta_A) f_A
\]

(5.21)

where \( S_P \) is obtained by interchanging the suffixes A and P in equation 14. The free energy per mole of pairs can now be written in the simplified form

\[
2F = + \frac{N U_{AA}}{2} \left[ X_A^2 S_A^2 + Y X_P^2 S_P^2 + 2P \sqrt{Y} X_A S_A S_P \right] - Nk_B T X_A \ln \left( \frac{Z_A}{X_A} \right)
\]

\[- Nk_B T X_P \ln \left( \frac{Z_P}{X_P} \right) - N X_P \Delta E
\]

(5.22)

The terms of surface potential depending on \( P_2(\cos \theta) \) in equation 5.16 cancel in \( F \) on substituting equations 5.20 in equation 5.18 for entropy. However, it affects \( S_A \) and \( S_P \) and hence \( F \) through \( f_A \) and \( f_P \) (see equations 5.20 and 5.21).

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

\[
\frac{X_P}{X_A} = \frac{Z_P}{Z_A} \exp \left\{ \frac{\Delta E}{kT} \right\}
\]

(5.23)

The average value of \( S \) including both A and P type of pairs is

\[
S_{av} = X_A S_A + X_P S_P
\]

(5.24)
1.4.3 Calculations

Calculations have been made for $R_{2B} = 0.8$ with $R_1 = 10$, $P = 0.822$ and $Y = 0.8$ which are reasonable as explained in ref (Geetha Basappa et al; 1997). The values are chosen such that the bulk medium is in the nematic phase up to $T_R = 1$. We evaluate all the necessary integrals using a 32 point Gaussian quadrature method in double precision. We look for the following types of solutions:

- $S_A, S_P \neq 0$ leading to nematic phase and
- $S_A, S_P = 0$ leading to isotropic phase.

The stable phase is the one having lower free energy.

The constants $\delta_0$ and $c$ in equation 5.15 are estimated as in ref (Geetha Basappa et al; 1997) as follows:

The change in the density of the medium can be written as

$$\delta \rho = \left[ \frac{\partial \rho}{\partial S} \right]_T \delta S(U_{IS})$$

(5.25)

where, $\delta S(U_{IS})$ is the change in $S$ due to the surface potential. In our earlier calculations (chapter 3), the maximum enhancement of $S$ near the surface compared to the bulk is $\delta S \approx 0.1$. Horn (1979) has measured the order parameter of pentyl cyanobiphenyl as a function of pressure and it is found that $[\partial \rho / \partial S]_T \approx 0.3$. Using these values in equation 5.25, since $\rho \approx 1 \text{gm/cc}$, we have, maximum $\delta \rho / \rho \approx 0.03$.

As $\rho$ increases, the intermolecular separation $r$ decreases and hence $\Delta E$ increases (see figure 2). From our earlier calculation (Govind A. S, Thesis 2002) of the variation in $\Delta E$ with $r$, for $r \approx 5 \text{Å}$ it is found that

$$\partial (\Delta E) / \partial r \approx 10^{-19} \text{J/Å}.$$ 

(5.26)

We have, $\delta \rho / \rho = 3 \delta r / r \approx 0.03$. Hence, $\delta r / r \approx 0.01$ and for $r \approx 5 \text{Å}$, we have $\delta r \approx 5 \times 10^{-2} \text{Å}$. With this, equation 5.26 yields $\partial (\Delta E) \approx 5 \times 10^{-21} \text{J} \approx 1.5 k T_{NI}$ at $T_{NI} \approx 300 \text{ K}$. Using equation 7 in equation 1, the maximum increase in $\Delta E$ due to $\delta (z)$ is given by

$$\delta (\Delta E) = R_1 k T_{NI} \delta_0.$$ 

(5.27)

Using $R_1 = 10$, we have $\delta_0 = 0.15$. The value of $c$ is arbitrary and is taken as 0.1. Thus, equation 7 becomes,
\[ R_2(z) = R_{2B} + 0.15 e^{-\frac{0.1z}{\tau_0}} \]  

(5.28)

We have not taken into account the possible volume-dependence of the orientational potential, the effect of which will be much smaller than the one discussed above.

The constant A is taken to be 10 as in (Selinger et al; 1988) and (chapter -3). After calculating \( S_{av} \) at different values of z, the thickness average value <S> is found for a given thickness (t) using equation 5.12. This is repeated for different values of T and also for thicknesses 1 \( \mu \)m and 10 \( \mu \)m respectively. In each case the percentage change in nematic order parameter \( dS_1 \% , dS_2 \% \) and \( dS \% \) are calculated using

\[ dS_1 \% = \frac{\langle S \rangle_{1\mu m} - \langle S \rangle_{10\mu m}}{\langle S \rangle_{10\mu m}} \times 100 \]  

(5.29)

\[ dS_2 \% = \frac{\langle S \rangle_{10\mu m} - S_b}{S_b} \times 100 \]  

(5.30)

\[ dS_1 \% = \frac{\langle S \rangle_{1\mu m} - S_b}{S_b} \times 100 \]  

(5.31)

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

1.4.4 Results and Discussion.

Calculated variations of order parameter (\( S_{av} \)) with distance from surface (z) for a cell of thickness 1 \( \mu \)m and 10 \( \mu \)m, at \( T = T_{NI} - 1^0 \) and \( T = T_{NI} - 10^0 \) are shown below in Fig 5.6. The variations are plotted upto middle of cell since the other half is symmetric. The X-axis is taken as \( z/r_0 \), with \( r_0 = 0.01 \mu m \).

Note that, the \( S_{av} \) at the surface is nearly 0.98 since the surface potential at \( z = 0 \) is strong. It decreases to the bulk value away from the surface.
Fig. 5.6. Calculated variation of $S_{av}$ and $X_P$ as a function of distance from the cell wall ($z/r_0$). In the legend, ‘1’ corresponds to $T = T_{NI} - 0.2^0$ and ‘2’ to $T = T_{NI} - 10^0$.

Fig. 5.7. Calculated variation of weighted order parameters $X_A S_A$ and $X_P S_P$ and the average order parameter $S_{av}$ as a function of distance from the cell wall ($z/r_0$).

Also, the fraction of P type of pairs ($X_P$) near the surface is large. This is because, near the surface, the order parameter and hence the density is large resulting in reduced separation
of the molecules at which the P type of pairs are stable as seen from figures 5.6 and 5.7. As the distance from the surface increases, $X_P$ decreases to the bulk value. $X_P$ and hence $S_{av}$ are lower at higher temperature ($T_{NI} - 0.2^0$) since some of the P type of pairs are converted to A type due to the thermal energy. The weighted order parameters of A and P type of pairs as a function of distance from the cell wall are plotted in fig 5.7. Though $S_A$ is large near $z = 0$, the weighted average of A type is less since $X_A$ is small. Hence, there is a dip in it towards $z = 0$. The weighted average of P type has variation similar to $X_P$ as expected.

In table-5.1, we have shown the calculated values of percentage change in nematic order parameter $dS_1 \%, dS_2 \%$, $dS \%$ (see equation 5.29 to 5.31) and $S_b$ at different temperatures near $T_{NI}$ in comparison with e values in ref (Surajit Dhara et.al. 2004).
Table 5.1: Comparison of calculated values of order parameters (S) in cells of thicknesses 1 µm and 10 µm.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$S_b$</th>
<th>$S'_b$</th>
<th>$\langle S_1 \rangle$</th>
<th>$\langle S_2 \rangle$</th>
<th>d$S_1$%</th>
<th>d$S_2$%</th>
<th>d$S$% our cal</th>
<th>d$S$%* our cal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{ni} - 0.2^\circ$</td>
<td>0.297</td>
<td>0.43195</td>
<td>0.4915</td>
<td>0.4388</td>
<td>13.8%</td>
<td>1.5%</td>
<td>12.0%</td>
<td>30%</td>
</tr>
<tr>
<td>$T_{ni} - 1^\circ$</td>
<td>0.373</td>
<td>0.4419</td>
<td>0.4999</td>
<td>0.4486</td>
<td>13.1%</td>
<td>1.5%</td>
<td>11.4%</td>
<td>9%</td>
</tr>
<tr>
<td>$T_{ni} - 5^\circ$</td>
<td>0.566</td>
<td>0.4823</td>
<td>0.5349</td>
<td>0.4885</td>
<td>10.9%</td>
<td>1.2%</td>
<td>9.5%</td>
<td>1.5%</td>
</tr>
<tr>
<td>$T_{ni} - 10^\circ$</td>
<td>0.714</td>
<td>0.5203</td>
<td>0.5689</td>
<td>0.5262</td>
<td>9.35%</td>
<td>1.1%</td>
<td>8.1%</td>
<td>0.6%</td>
</tr>
</tbody>
</table>

*Ref: (SurajitDharaetal; 2004)
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 order in further enhancing it is reduced. Experimentally (Surajit Dhara et al; 2004) it is found that the enhancement is not significantly reduced at lower temperatures. The calculated percentage enhancement of the order parameter between thick and thin cells (dS%) reduces by 1.5 times with the decrease in temperature from to $T = T_{NI} - 0.2$ to $T = T_{NI} - 10$.

However, the reduction as per the calculations in ref (Surajit Dhara et al; 2004) is 50 times. Thus, the simple empirical equations used for the decay of surface potential gives results which are in better agreement with experimental data compared to earlier theories (Surajit Dhara et al; 2004). The calculated values of the present paper show slight improvement compared to our earlier paper (chapter -3) in which the polar nature of molecules is not considered. We have not come across any experimental evidence in support of the calculated variation of $X_P$ with distance from the cell wall shown in fig 5.6. The better agreement with experimental values imply that the empirical variation of surface effect considered in ref (chapter 3) as well as in the present chapter are close to the realistic variation, the cause which may be investigated more rigorously. Further work in this direction is under progress.

1.4.5 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 recently extended Maier-Saupe (M-S) theory (chapter 3) using an empirical variation of surface potential to account for the enhancement in which the variation in the density of the medium due to the variation of S was ignored. In the present paper, the change in the relative proportion of the parallel pairs due to change in the density of the medium is included in the M-S theory with the surface potential. Our calculations are in better agreement with the experimental data.