

CHAPTER-3

1. EXTENSION OF M-S THEORY

1.1 Review of Maier-Saupe theory for the N-I transition

As described in the previous chapter, the nematic (N) liquid crystal is characterized by a long range orientational order of their centres of mass. 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 scalar order parameter S defined as

$$S = \frac{1}{2} \langle 3 \cos^2 \theta_i - 1 \rangle = \langle P_2(\cos \theta_i) \rangle \quad (3.1)$$

Where θ_i is the angle between the long axis of the i th molecule and the director, P_2 is the second Legendre polynomial and $\langle \rangle$ 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.

Maier and Saupe (MS) (1959) developed a molecular mean field theory of the nematic phase. In the theory, each molecule is assumed to be in an average orienting field due to its environment, but otherwise uncorrelated with its neighbours. MS assumed that the anisotropic dispersion forces are entirely responsible for the orientational order and ignored the shape anisotropy of the molecules. Using the mean field approximation, MS wrote the single particle potential for the i^{th} molecule as

$$U_i = -U_0 S P_2(\cos\theta_i) \quad (3.2)$$

where U_0 is an interaction parameter and S is the nematic order parameter defined in equation 3.1 above. The parameter U_0 depends on the structural details of the constituent molecules and the molar volume of the compound. The molar internal energy is given by

$$U = \frac{N}{2} \langle U_i \rangle = -\frac{N}{2} U_0 S^2 \quad (3.3)$$

where N is the Avogadro number and $\langle \rangle$ denote a statistical average. The factor (1/2) arises since each molecule is counted twice while finding the average. The molar entropy is

$$\xi = -Nk_B \langle \ln f(\cos\theta) \rangle \quad (3.4)$$

where k is the Boltzmann constant and $f(\cos\theta)$ is the normalised orientational distribution function. The molar Helmholtz free energy is written as

$$F = U - T \xi. \quad (3.5)$$

The orientational distribution function found by minimising F is given by

$$f(\cos\theta) = Z^{-1} \exp(-U_i/kT) \quad (3.6)$$

where Z is the normalising integral. The orientational order parameter is calculated using

$$S = \int_0^1 d(\cos\theta) f(\cos\theta) P_2(\cos\theta) \quad (3.7)$$

It can be verified that minimising the free energy with respect to S also leads to the same expression for S . Using equations 3.1 to 3.7, the free energy per particle can be written in the dimensionless form as

$$\frac{F}{Nk_B T} = + \frac{U_0}{2k_B T} S^2 - \ln Z. \quad (3.8)$$

For a given value of $(U_0/k_B T)$, equation 3.7 is solved for self consistency and the free energy is calculated using equation 3.8. This represents the excess free energy over that of the isotropic phase, due to the onset of orientational order. Hence, the solutions resulting in $F < 0$ correspond to the stable nematic phase. This procedure is repeated for different values of $(U_0/k_B T)$. The nematic-isotropic transition occurs when the calculated free energy becomes zero. MS showed that the calculations lead to a first order N-I transition at

$S_{NI} = 0.4292$ and found that

$$U_0/k_B T_{NI} = 4.541 \quad (3.9)$$

where T_{NI} is the N-I transition temperature.

1.2 Extension of M-S Theory for nematic 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 the order parameter 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 propose a simple extension of Maier-Saupe (M-S) theory to account for the enhancement.

In our model, a molecule near the surface is assumed to feel the mean field potential (M-S type) and also surface induced potential. This is included in M-S theory. Our calculations are in better agreement with the experimental data (Surajit Dhara et.al. 2004, B Malrison et.al. 1980 I Lelidis 1993).

1.2.1 Theoretical Model

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 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

$$U_{is} = -U_s e^{-\frac{z}{r_0}} \quad (3.10)$$

where U_s is surface potential at $z = 0$ and r_o 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 (Sutajit Dhara et.al. 2004). Hence, for M-S type mean field also, we use S_z . The average value of the order parameter is

$$\langle S \rangle = \frac{\int_0^{\frac{t}{2}} S_z dz}{\int_0^{\frac{t}{2}} dz} \quad (3.11)$$

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 values of S .

Surface potential at $z = 0$ is $U_s = AU_0$ where A is a constant and U_0 is the constant in M-S theory

$$\frac{U_0}{kT_{NI}} = 4.541 \quad (3.12)$$

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

1.2.2 Expression for Free energy and order parameter

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

$$U_i = -U_0 S P_2(\cos \theta_i) + U_{is} \quad (3.13)$$

where P_2 is the 2nd Legendre polynomial and θ_i is the angle between nematic director and the long axis of the i^{th} molecule.

The average internal energy per molecule is

$$\frac{U}{N} = -\frac{U_0 S^2}{2} - U_s e^{-\frac{z}{r_o}} S_z \quad (3.14)$$

where N is the Avagadro number and

$S_z = \langle P_2 \cos \theta_i \rangle$ at z , with $\langle \rangle$ representing the statistical average.

The Molar entropy is $\xi = Nk \langle \ln f \rangle$ where f is the probability distribution function.

The average Helmholtz free energy per molecule is

$$\frac{F}{NkT} = -\frac{U_o S_z^2}{2kT} - \frac{U_s}{kT} e^{-\frac{z}{r_o}} S_z + \langle \ln f \rangle \quad (3.15)$$

where $\langle \ln f \rangle = \int_0^1 f \ln f dx$ with $x = \cos \theta$

Hence the order parameter is

$$S_z = \int_0^1 f P_2(x) dx \quad (3.16)$$

minimizing F w.r.t f we get,

$$f = \frac{e^{\frac{U_o}{kT} \left(S + A e^{-\frac{z}{r_o}} \right) P_2(x)}}{Z} \quad (3.17)$$

where $Z = \int_0^1 f dx$ is the partition function.

Substituting for $\langle f \ln f \rangle$ we get

$$\frac{F}{NkT} = \frac{U_o S^2}{2kT} - \ln z \quad (3.18)$$

Minimizing F w. r. t S , we get

$$S = \int f P_2(x) dx \quad (3.19)$$

which satisfies the self consistency condition.

1.2.3 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 for self consistency. The constant A is taken to be 10 as in (J.V.Selinger et.al.1988). The average value of S is found for different values of T_{NI} , for a given thickness (t) using equation 3.11

The value of $\langle S \rangle$ is also found 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

$$dS_1 \%_{0(1\mu\text{m})} = \frac{\langle S \rangle_{1\mu\text{m}} - S_b}{S_b} \times 100$$

$$dS_2 \%_{0(10\mu\text{m})} = \frac{\langle S \rangle_{10\mu\text{m}} - S_b}{S_b} \times 100$$

$$dS \% = \frac{\langle S \rangle_{1\mu\text{m}} - \langle S \rangle_{10\mu\text{m}}}{\langle S \rangle_{10\mu\text{m}}} \times 100 \quad (3.20)$$

Where S_b is the bulk value, in the absence of surface effect.

We have tried for another surface induced potential with inverse square dependence of the type

$$U_i = U_s \frac{1}{1+(z/r_0)^2} \quad (3.21)$$

Minimising the free energy per molecule we get

$$f = \frac{e^{\frac{u_o}{kT} \left[S + A \frac{1}{(1+z/r_0)^2} \right] P_2(x)}}{z}$$

The value of $\langle S \rangle$ and various $dS\%$ are also found for different values of T , for thicknesses $1\mu\text{m}$ and $10\mu\text{m}$ respectively as earlier.

1.2.4 Results and Discussion.

Calculated variations of order parameter (S_z) with distance from surface (z) for a cell of thickness $1\mu\text{m}$ and $10\mu\text{m}$, at $T = T_{NI} - 1^0$ and $T = T_{NI} - 10^0$ are shown below in Fig 3.1 and Fig 3.2. The variations are plotted upto middle of cell since the other half is symmetric. The X-axis is taken as z/r_0 , with $r_0 = 0.01 \mu\text{m}$.

Note that, the S_z 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.

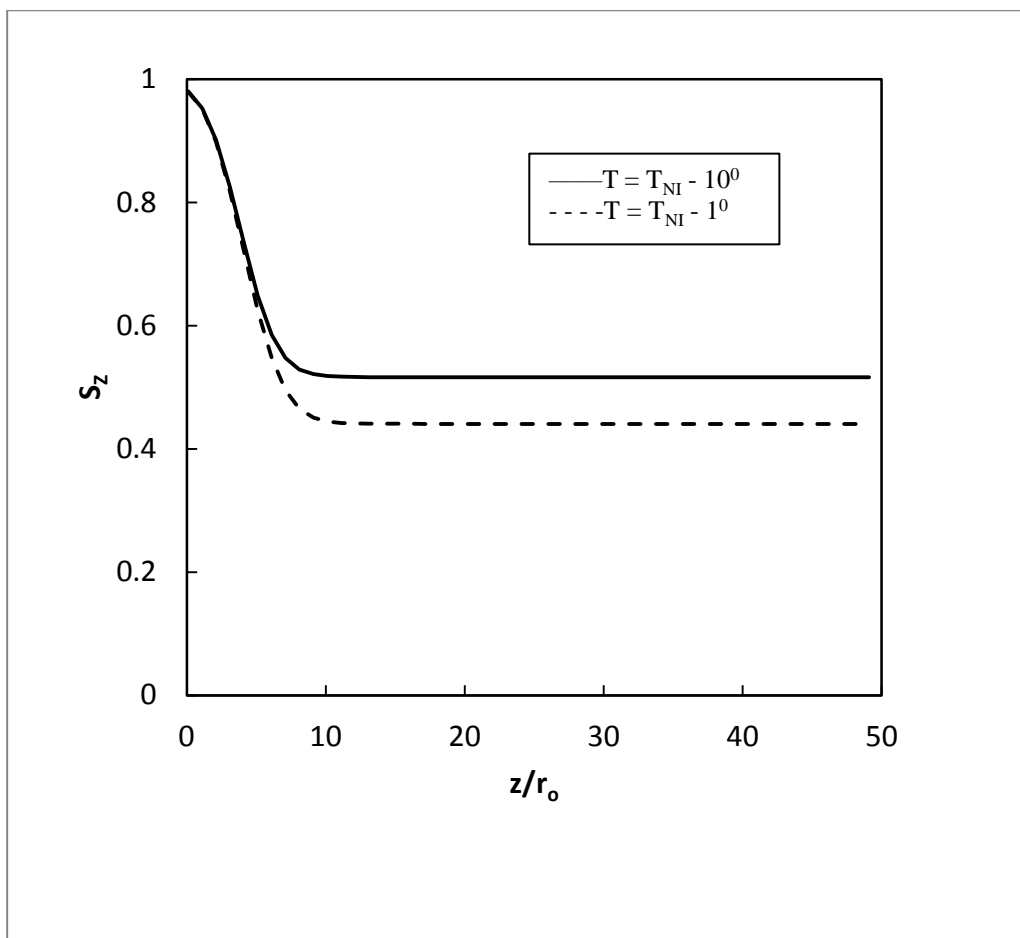


Fig. 3.1. Variation of order parameter (S_z) with distance from surface (z) for a cell of thickness $1\mu\text{m}$, upto middle of cell, with $r_0 = 0.01\mu\text{m}$, at $T = T_{NI} - 1^0$ and $T_{NI} - 10^0$.

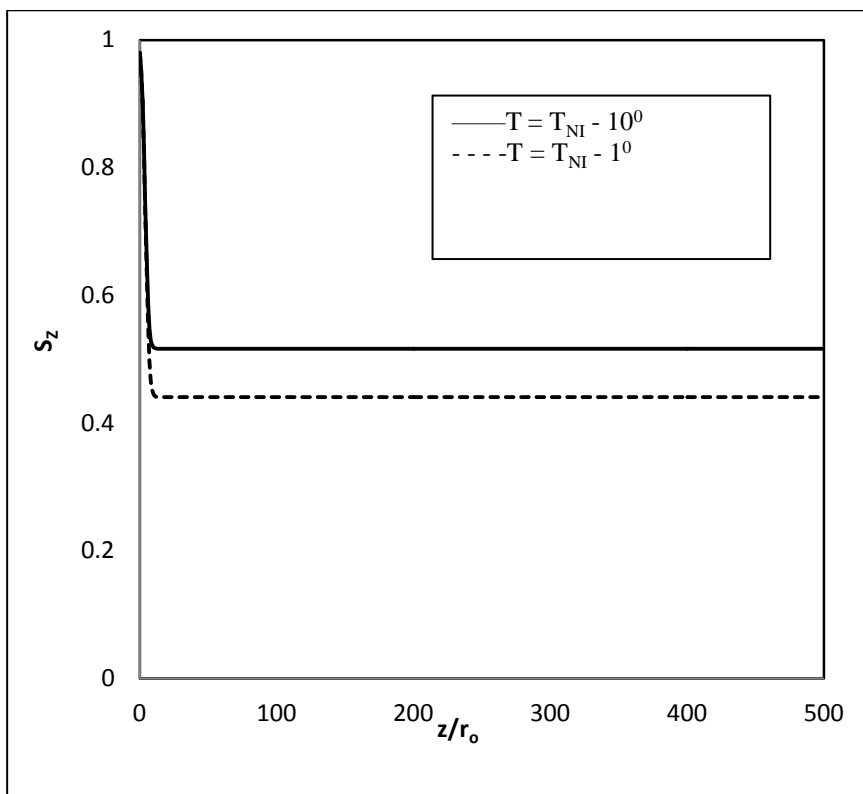


Fig. 3.2. Variation of order parameter (S_z) with distance from surface (z) for a cell of thickness $10\mu\text{m}$, upto middle of cell, with $r_0 = 0.01\mu\text{m}$, at $T = T_{NI} - 1^0$ and $T_{NI} - 10^0$.

Table 3.1: Comparison of calculated values of order parameters (S) in cells of thicknesses 1 μ m and 10 μ m for first potential (exponential decay)

Temp	S_b^*	S_b	$\langle S_1 \rangle$	$\langle S_2 \rangle$	$dS_1 \%$	$dS_2 \%$	$dS \%$	$dS \%$ *
$T_{NI} - 0.2^0$	0.297	0.4311	0.4835	0.4363	12.15%	1.21%	10.8%	30%
$T_{NI} - 1^0$	0.373	0.4407	0.4918	0.4458	11.58%	1.16%	10.3%	9%
$T_{NI} - 5^0$	0.566	0.4799	0.5257	0.4845	9.55%	0.96%	8.5%	1.5%
$T_{NI} - 10^0$	0.714	0.5165	0.5578	0.5206	8%	0.8%	7.1%	0.6%

*Ref:Surajit Dhara etal.,(2004)

Table 3.2: Comparison of calculated values of order parameters (S) in cells of thicknesses 1 μ m and 10 μ m for the second potential (inverse square type)

Temp	S_b^*	S_b	$\langle S_1 \rangle$	$\langle S_2 \rangle$	$dS_1 \%$	$dS_2 \%$	$dS \%$	$dS \%$ *
$T_{NI} - 0.2^0$	0.297	0.4311	0.5136	0.4403	16.67%	2.11%	16.49%	30%
$T_{NI} - 1^0$	0.373	0.4407	0.5192	0.4494	15.66%	1.95%	15.53%	9%
$T_{NI} - 5^0$	0.566	0.4799	0.5257	0.4871	12.36%	1.479%	12%	1.5%
$T_{NI} - 10^0$	0.714	0.5165	0.5726	0.5225	10%	1.142%	9.6%	0.6%

*Ref: Surajit Dhara etal.,(2004)

Table 3.3: Comparison of dS % in first and second potential

Compound	Thickness of the thin and thick cells (μm)	dS %*	dS % (first potential)	dS % (second potential)
S1014	1.5 and 6.7	15%	3.85%	10.10%
CN	1.5 and 14	11%	4.26%	12.58%

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

Tables 3. 2 and 3. 3 show the variation of S_b and dS % at different temperatures near T_{NI} . The experimental values are as reported in Surajit Dhara et.al. (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 is reduced. Experimentally it is found (Surajit Dhara et.al.2004) that the enhancement is not significantly reduced at lower temperatures. Considering the first potential (exponential decay) the percentage enhancement of the order parameter between thick and thin cells reduces by 1.5 times with the decrease in temperature, while for the second potential (inverse square law) the reduction is 1.7 times. 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 give results which are in better agreement with experimental data compared to earlier theories (Surajit Dhara et.al. 2004). Of the two potentials used, the second potential is better than the first as seen by table-3. This gives an insight about the realistic variation of surface effects which may be investigated more rigorously

1.2.5 Conclusions:

Experimental observations show that the nematic order parameter is significantly enhanced as the thickness of the cell is reduced. Calculations of earlier theories do not agree well with the experimental data.

The simple empirical equations 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). Of the two potentials used, (exponential and inverse square type) the second potential (inverse square type) is better than the first as seen by table-3.

MS theory fails to explain the phase transitions in case of smectic materials because in case of smectics, along with the order potential parameter we have to consider the layering potential parameter also into account. This modification was done by McMillan in his model which will be discussed in detail in next chapter.