CHAPTER-2

1. LITERATURE SURVEY AND OBJECTIVE

1.1 Review of earlier experimental work

In many experimental studies, nematic LC are sandwiched between two parallel glass plates, which are pretreated for planar alignment (de Gennes etal.;1993). Such cells are used in display applications. The typical thickness used for this purpose is ~5μm. In the reflective mode displays, it is about 2 μm. Because of the fluid nature of the medium, the response time is relatively slow and is given by $\tau = \eta d^2/\pi^2 K$ where η is an effective viscosity, K an effective curvature elastic constant and d the sample thickness. The response time can be considerably reduced by reducing the sample thickness which are being investigated in recent years (Schadt M et.al. 1971). When the sample thickness is reduced, the surface–to–volume ratio is increased and the bulk properties are significantly influenced by the confining surfaces. Studies of LC in confined geometries are particularly important both from fundamental and technological points of view. Several experimental and theoretical studies on the confinement effects on the orientation order parameter (S) of nematic LC have been undertaken (Qian T.Z et.al. 1997, Sheng P. 1976,1982, Miyano K.1979, Mada H.1979 Sobha et.al.1998 F Beaubois et.al. 1979). It is found that the order parameter at the surface of the substrate as well as in the interior of the sample increases with decreasing cell thickness. This is considered in the next section.

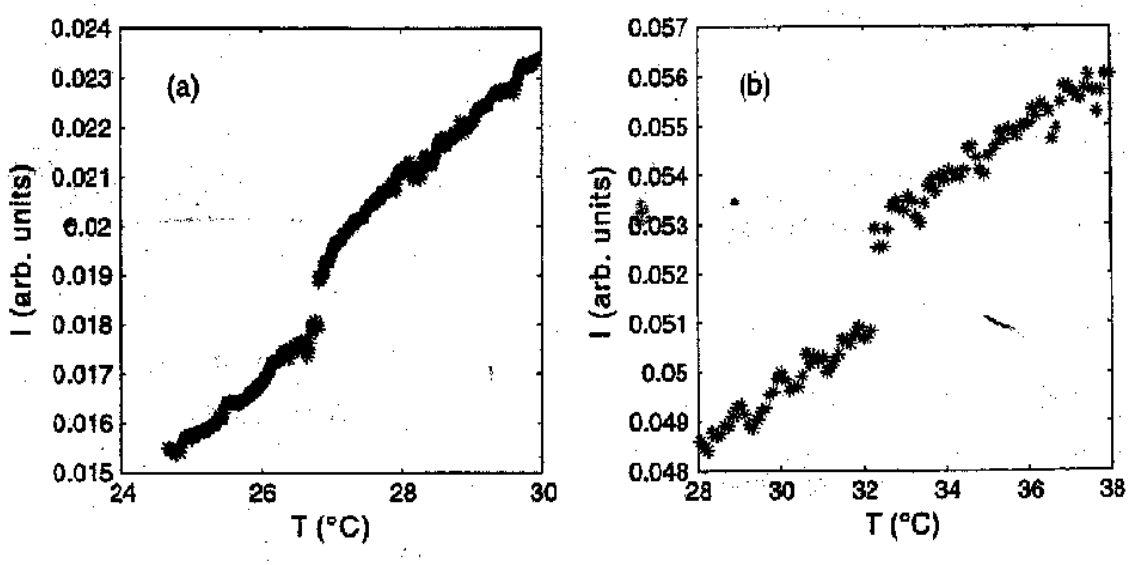

Fig. 2.1. Transmitted intensity profile as a function of temperature for cells of thickness (a) 3μm and (b) 1.9μm respectively. A jump in 'I' signifies a jump in Δn α S. Note a larger jump in (b)

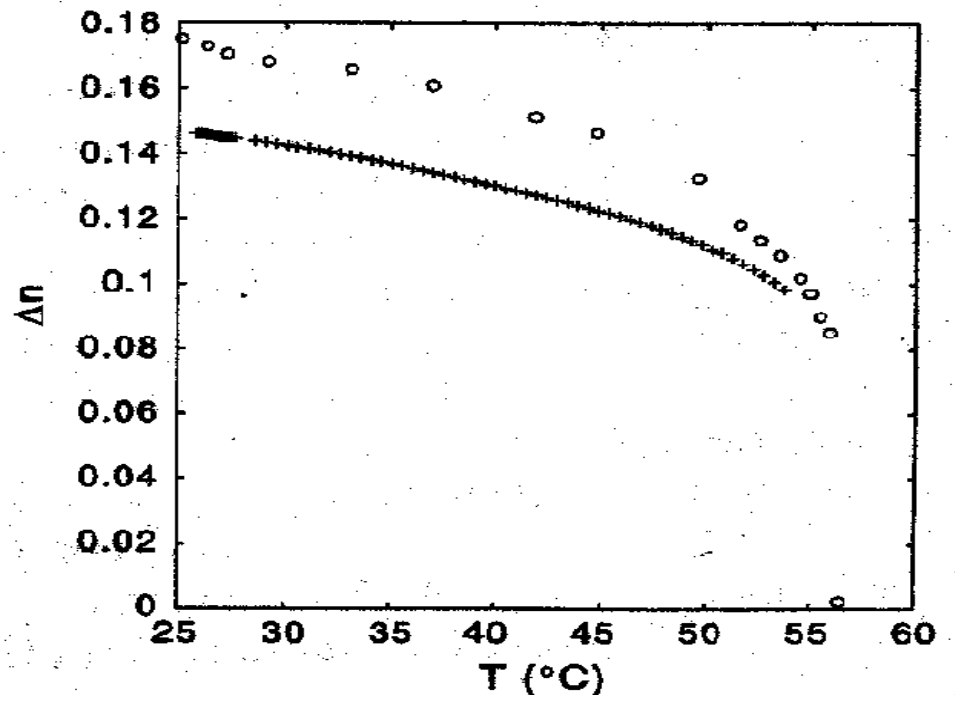

Fig.2.2. Δn with temperature for the compound CP7B o: cell of thickness ~ 1.5μm and +: cell of thickness ~ 25μm.

Sobha et.al. (1998) reported that the birefringence ($\Delta n \propto S$) is enhanced by a measurable amount in thin cells (1.5μm) compared to that in thick cells (25μm) in p-cyanophenyl p-n-heptylbenzoate (CP7B) as shown in fig 2.2. They also found that the nematic–nematic (N-N) transition in CP7B is found to shift to higher temperatures when the thickness of the cell is reduced from 3μm to 1.9μm as shown in fig 2.1. They argued that the shift in the N-N transition temperature is a clear consequence of the significant enhancement of the order parameter as the cell thickness is decreased. The variations of Δn of CN as functions of temperature are studied for cells of three different thicknesses namely, 1.5μm, 2.2μm, and 14μm. This compound exhibits the nematic phase at high temperatures (105.5 to 154.2^0C). The temperature dependence of Δn can be analysed using the formula $\Delta n= \Delta n_0[1-(T/T_1)]^{\beta}$ where T_1 and β are adjustable parameters and Δn_0 is the birefringence of the perfectly aligned sample (I Haller 1975). Least squares fits to the experimental data on CN with the above equation are shown for three different cell thicknesses in figure2.3a. It is noticed that the fitted birefringence for 1.5μm cell is slightly higher (by 5%) than that in 2.2 and 14μm cells. The fit parameter T_1 is higher by 0.1^0 in the 1.5μm cell than that in the 14μm cell. This indicates that T_{NI} increases as the thickness is decreased as predicted by the Landau theory (P Sheng 1982) Similar measurements have been made for a 50:50 wt % of compound CN and BAN(Surajit Dhara etal.,2004). It is found that at fixed temperature, Δn increases with decreasing cell thickness as shown in fig 2.3.(b). A comparative study of the increase in the order parameter in cells of different thickness have been made in (table2.1). It is found that the increase in S is considerable in thin cells.

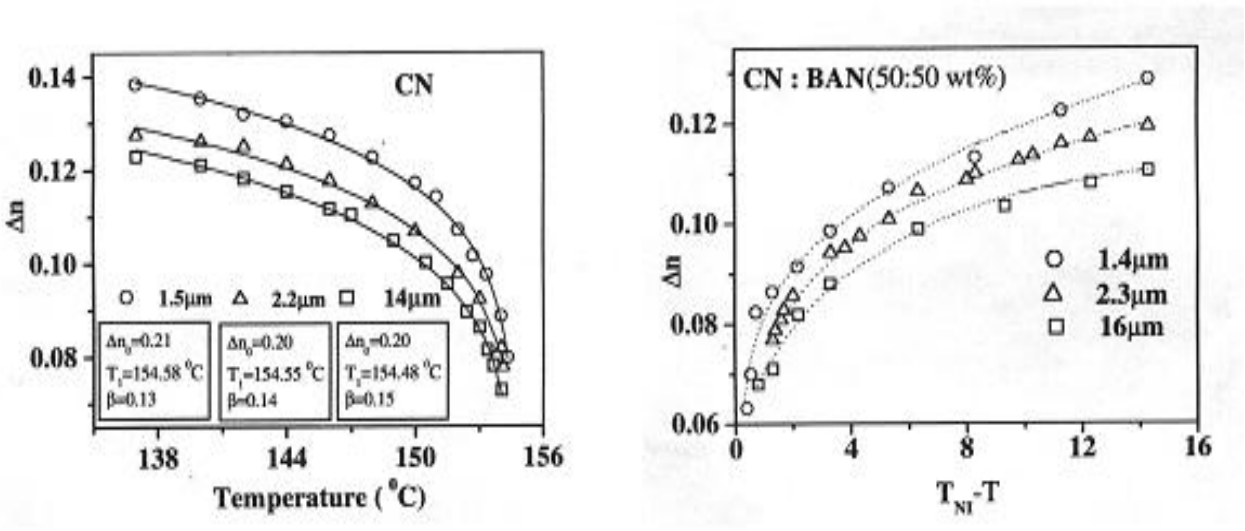

Fig.2.3(a). The variations of birefringence (Δn α S) of CN as a function of temperature are shown for cells of 3 different thickness: 1.5 μm (open circles) 2.2 μm (open triangles) and 14 μm (open squares).

Fig2.3(b) Variations of Δn as functions of temperature of the mixture of CN and BAN in three different cell thicknesses, namely 1.4 μm (open circles).

Table 2.1 Comparison of Δn in thin and thick cells

Compound	Thickness of the thin and thick cells (μm)	$(T_{NI}-T)$ in ^0C	$\frac{(\Delta n_{thin} - \Delta n_{thick})}{\Delta n_{thick}} \times 100$
S1014	1.5 and 6.7	12	15%
CN	1.5 and 14	12	11%
Mixture (50:50) wt %	1.4 and 16	12	13%
PCH5	1.4 and 7	12	6%
CCN47	1.4 and 7	12	no significant enhancement

From the graphs we find $\Delta n \propto S$ increases with decreasing thickness. In case of mixture also $\Delta n \propto S$, is higher by 6% and 13% in 2.3μm and 1.4μm as compared to 16 μm. Reasons for this enhancement in Δn is not well understood.

Two possibilities have been invoked to explain the observations: A) The suppression of the thermal fluctuations of the director in thin cells can enhance the order parameter compared to that in the thicker cells; B) The effect of a strong surface potential which increases the order parameter at the surfaces. This will be discussed in the next section.

1.2 Review of earlier theoretical work

1.2.1 Considering the effect of surface orientation potential

Orientation potential already exists in nematic liquid crystal. Stronger orientation potential implies more order. The orientation potential may be large near the surface. Surface effect penetrates up to certain depths. This may affect the bulk order parameter (P. Sheng 1982). Mada etal., (1979) reported the measurements of the anisotropy of the refractive index for heptyl cyanobiphenyl (7CB) at the surface as well as in the bulk by the interferometeric method. The experimental setup is as shown in the fig (2.4)

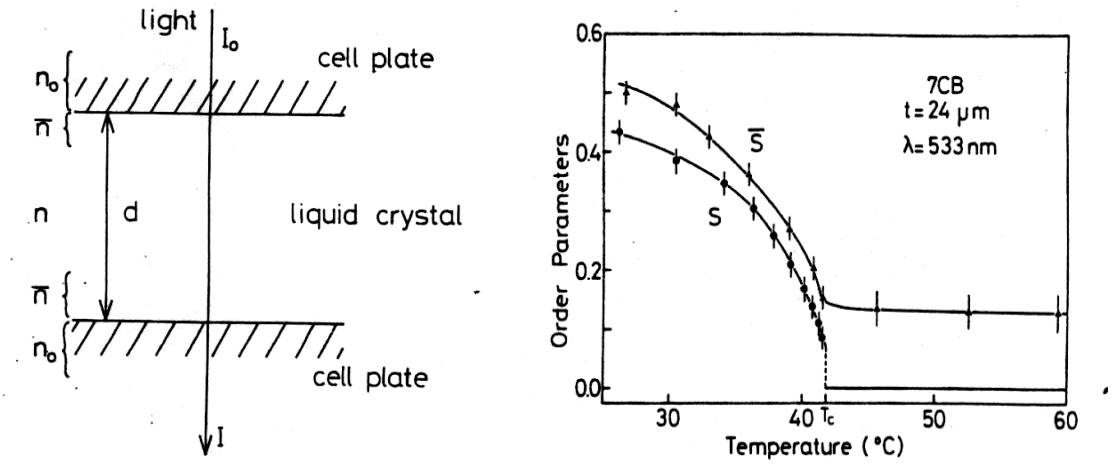

Fig. 2.4. Cross section of a sample cell.Hatched region is SiO evaporated film: n_o, n and $\bar{n}$ are the refractive indices of the cell plates, bulk of LC, and LC near the surface, respectively.

Fig. 2.5. Temperature dependence of order parameters in the bulk and at the surface.

n is the mean value of the refractive index throughout the bulk and $\bar{n}$ is the refractive index near the surface layer which has a thickness of the order of the wavelength of light. Using these data, order parameters S at the surface and in the bulk were calculated.

Result is shown in fig 2.5. The bulk order parameter S goes to zero at T_C but $\bar{S}$, at the surface is higher and not equal to zero even after T_C. which implies, near the surface there is a greater orientational potential.

Ping Sheng (1982) calculated the order parameter profile in thin cells using the Landau de Gennes theory assuming a surface potential which enhances the order parameter at the surface. He found that within a limited range of surface potentials a surface transition can occur at a temperature higher than that of the bulk transition. Close to the nematic-isotropic (N-I) transition point, the surface-induced order decays to the bulk value over a length scale, which is an order of magnitude larger than the order parameter correlation length (P Sheng 1976; K.Miyano 1979). In the nematic phase the order parameter at the surface of the substrate as well as in the interior of the sample increases with the decreasing cell thickness.

Selinger et.al.(1988) calculated the variation of the order parameter from the surface to the bulk assuming a strong surface potential ($V_S=10V_0$, where V_0 is the Maier Saupe orientation potential between the molecules). They found that, at the surface, the order parameter is saturated ie. S(0)=1. However they did not extend the calculation to the nematic phase (fig2.6)

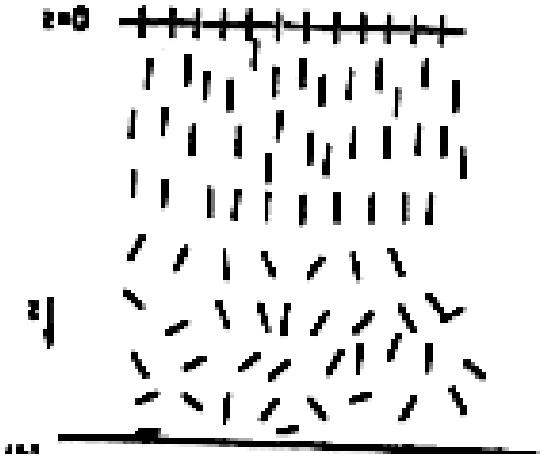

Fig. 2.6. Nematic order near a free surface of the bulk isotropic phase

1.2.1.1 Limitations

One limitation of this model is it uses unrealistically simple intermolecular potential.

A more serious limitation of this model may be due to the fact that a mean field theory neglects fluctuation in Sm phase.

Recent calculation (Surajit Dhara et.al.2004) show that this effect is not sufficient to produce the required enhancement.

1.2.2 Considering the Quenching of director fluctuations in thin cells

In the nematic phase thermal fluctuations of the director are quite strong. The suppression of the thermal fluctuations of the director in thin cells can enhance the order parameter compared to that in thicker cells. It is well known that under the application of an external strong field the director fluctuations are partially quenched resulting in the enhancement of the order parameter (B.Malraison etal.,1980 I.Lelidis etal., 1993). Recent studies have shown that the quenching of director fluctuations significantly influences the thermodynamics of the nematic-paranematic phase transition under an external field. Surajit Dhara et.al.(2004) have reported that this effect increases the order parameter by ~0.1% in a 1μm cell compared to that in a 10 μm cell.

1.2.2.1 Limitations

Experimentally it is found in the first four compounds (Table 2.1) the enhancement of the order parameter in thin cells is nearly 6% to 13% compared to that in thicker cells. As such the enhancement of the order parameter due to partial quenching of the director fluctuations in thin cells cannot explain the experimental results.

1.2.3 Combined effect

The two independent effects discussed above cannot account for the enhancement of the order parameter. Calculations with the combined effect has been tried using Landau-de-Gennes formulation (Surajit Dhara et.al. 2004). The enhancement of the order parameter due to the reduction of cell thickness has two aspects. Firstly, the number of fluctuation modes are reduced which increase the order parameter by ~0.1% when the thickness is decreased from 10 to 1μm. Secondly with a strong surface ordering potential, the thickness averaged value of the order parameter ($\bar{S}$) in thin cells is enhanced. This increased value of $\bar{S}$ in turn

leads to an increase in the effective curvature elastic constant ($K \propto S_0^2$) which results in the reduction in the fluctuation amplitude. The calculated values of S_{meas} in cells of thickness 1μm and 10μm at few temperatures are shown in table 2.2. S_{meas} is less than mean field order parameter S_0 due to the director fluctuations in both the 10μm and 1μm cells. However the relative enhancement of S_{meas} in a cell of thickness 1μm is larger.

Table 2.2 Comparision of calculated values of the order parameters in 1μm using different approximations and the bulk values at a few temperatures.(Surajit Dhara; 2004)

Temp	S_b bulk order parameter	$\bar{S}$	$\bar{S}_1$	$\frac{\bar{S}-S_b}{S_b}\times 100$	$\frac{\bar{S}_1-S_b}{S_b}\times 100$	S_{meas} (10 μm)	S_{meas} (1 μm)	$\frac{S_{meas}(1\mu m)-S_{meas}(10\mu m)}{S_{meas}(10\mu m)}\times 100$
T_{NI} -0.2^0	0.297	.310	.313	4.4%	5.2%	0.091	.119	30%
T_{NI} -1^0	0.373	.383	.385	2.7%	3.2%	0.209	.228	9%
T_{NI} -5^0	0.566	.571	.572	0.9%	1.1%	0.460	.467	1.5%
T_{NI} -10^0	0.714	.716	.717	0.3%	0.4%	0.631	.635	0.6%

1.2.3.1 Limitation

The calculated values of the enhancement of the order parameter decrease sharply as the temperature is lowered from T_{NI} . On the other hand, the experimental values do not decrease so drastically.

1.3 Motivation and Objective of the present work

Ping Sheng (1982) calculated the order parameter profile in thin cells using the Landau de Gennes theory assuming a surface potential which enhances the order parameter at the surface. He found that within a limited range of surface potentials a surface transition can occur at a temperature higher than that of the bulk transition. In the nematic phase the order parameter at the surface of the substrate as well as in the interior of the sample increases with decreasing cell thickness.

Selinger etal (1988) calculated the variation of the order parameter from the surface to the bulk assuming a strong surface potential ($V_S=10V_0$, where V_0 is the Maier-Saupe orientation potential between the molecules). They found that, at the surface, the order parameter is saturated ie. S(0)=1. However they did not extend the calculation to the nematic phase (Selinger et al 1988).

One limitation of this model is that it uses unrealistically simple intermolecular potential. A more serious limitation of this model may be due to the fact that the mean field theory neglects fluctuation in Sm phase.

Later calculations (Surajit Dhara et.al. 2004) show that this effect is not sufficient to produce the required enhancement.

In nematic phase the thermal fluctuations of the director are quite strong .It is well known that under the application of an external strong field, the director fluctuations are partially quenched and the order parameter is enhanced as a result. Recent studies have shown that the quenching of director fluctuations significantly influences the thermodynamics of the nematic-paranematic phase transition under an external field. Surajit Dhara etal (2004) have reported that this effect increases the order parameter by ~0.1% in a 1μm cell compared

to that in a 10μm cell. Experimentally the enhancement of the order parameter in thin cells is nearly 6 to 13% compared to that in thicker cells.

The enhancement of the order parameter due to reduction of cell thickness has two aspects. Firstly, with a strong surface ordering potential, the thickness averaged of the order parameter $\overline{S}$, in turn leads to an increase in the effective curvature elastic constant. Secondly the reduction in the number of fluctuation modes which enhances the order parameter by ~0.1% , when the thickness is reduced from 10μm to 1μm.

The combined effect of the surface potential and the stiffening of the elastic constant has amplified the S_{meas} in thin cells which is very large close to T_{NI} and decreases sharply as the temperature is lowered. On the other hand, the experimental values do not decrease so drastically. Further theoretical work is required to understand the experimental results.

In this thesis we theoretically investigate this significant enhancement of the nematic orientation order parameter S, in thin cells by proposing suitable variations of surface potential w.r.t the distance from the cell wall of the thin cell. Different theories are modified by including this potential to account for the enhancement

1.4 Importance of the study

1. Studies of LC are very important both from fundamental and technological point of view.

2. LC are used in display devices. The typical thickness used in bistable displays is about 2μm.

3. Twisted nematic LC is widely used in many display systems. The d/p ratio affects the switching time, where d is the cell thickness and p is the pitch.

4. The ratio d/p shows the deviation in thin cells. Such deviation is observed to increase as the cell thickness decreases and can be appreciable for $d \leq 7\mu m$. More recent experimental data show that the deviations tend to vanish in thicker cells (Tie-Zheng Qian et.al. 1997).This may involve some novel physics