

Enhancement of the orientational order parameter of nematic liquid crystals in thin cells

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Abstract. We report measurements of birefringence (Δn) of several nematic liquid crystals having transverse as well as longitudinal dipole moments in thin (1.4 to 2.3 μm) and thick (7 to 16 μm) cells. Rubbed polyimide-coated glass plates are used to get planar alignment of the nematic director in these cells. We find significant enhancement (6 to 18%) of Δn ($\propto S$, where S is the orientational order parameter) in thin cells in all compounds with *aromatic cores* even at temperatures far ($\sim 20^\circ\text{C}$) below the nematic-isotropic transition point. The enhancement is larger in compounds having several phenyl rings and lower if the number of phenyl rings is reduced. In a compound that does not have an aromatic core no significant enhancement is observed, implying that the strength of the surface potential depends on the aromaticity of the cores. Assuming a perfect orientational order at the surface, calculations based on the Landau-de Gennes theory show that the thickness averaged enhancement of S is sharply reduced as the temperature is lowered in the nematic phase. The *measured* order parameter S is further enhanced in thin cells because of the stiffening of the elastic constant which reduces the thermal fluctuations of the nematic director. The combined effect is however too small at low temperatures to account for the experimental data.

PACS. 61.30.-v Liquid crystals – 61.30.Pq Microconfined liquid crystals: droplets, cylinders, randomly confined liquid crystals, polymer dispersed liquid crystals, and porous systems – 61.30.Hn Surface phenomena: alignment, anchoring, anchoring transitions, surface-induced layering, surface-induced ordering, wetting, prewetting transitions, and wetting transitions

1 Introduction

Organic molecules with anisotropic shape exhibit a variety of liquid-crystalline phases. The least ordered of liquid crystals is the nematic (N), in which the long axes of the rod-like molecules are spontaneously aligned on average along a specific direction called the director, \hat{n} , a dimensionless unit vector [1]. It is *apolar* in nature which requires that the orientational order parameter of a nematic is a second rank tensor given by $Q_{\alpha\beta} = S(3n_\alpha n_\beta - \delta_{\alpha\beta})/2$, where $S = \langle 3 \cos^2 \theta - 1 \rangle / 2$ is the magnitude of the order parameter, θ being the angle made by the long axis of the molecule with \hat{n} . In many experimental studies nematic liquid crystals are sandwiched between two parallel glass plates, which are pretreated for planar alignment [1]. Such cells are also used in display (LCD) applications. The typical thickness used for this purpose is $\sim 5 \mu\text{m}$. In the reflective mode displays, it is about $2 \mu\text{m}$. Because of the fluid nature of the medium the response time is relatively slow

and is given by $\tau = \eta d^2 / \pi^2 K$ [1] where η is an effective viscosity, K an effective curvature elastic constant and d the sample thickness. The response time can be reduced considerably by reducing the sample thickness. In bistable displays, which are being investigated in recent years, the thickness has to be quite small, about $2 \mu\text{m}$ [2]. 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 liquid crystals in confined geometries are very important both from fundamental and technological points of view. Several studies have been undertaken to make physical measurements and to investigate the influence of different types of confinement [2]. There are several theoretical and a few experimental studies on the confinement effects on the orientational order parameter of nematic liquid crystals [3–7]. Ping Sheng [3] 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)

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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 [3,4]. 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. Experimentally, Miyano [5] measured the wall-induced birefringence in pentyl cyanobiphenyl (5CB) above the N-I transition temperature both in homeotropically and planar aligned samples. In the former case, the sample was viewed at an angle with respect to the optic axis. It was found that the pretransition birefringence diverges in the homeotropic cell while there is no such dependence in the planar cell. Mada *et al.* [6] reported the measurement of surface and bulk order parameters in the nematic as well as in the isotropic phase as functions of temperature using an interferometric method [8] in heptyl cyanobiphenyl (7CB). They used plates which were pretreated by oblique evaporation of SiO. The surface order parameter was found to be ~ 0.15 just above T_{NI} and had finite values even at temperatures further above T_{NI} . In the nematic phase the surface order parameter was found to be always 25% higher than the bulk order parameter.

Sobha *et al.* [7] reported that Δn is enhanced by a measurable amount in thin cells ($1.5\ \mu\text{m}$) compared to that in thick cells ($25\ \mu\text{m}$) in *p*-cyanophenyl *p*-*n*-heptylbezoate (CP7B). This compound is highly polar and the authors found a nematic-nematic (N-N) transition in thin cells ($3\ \mu\text{m}$) though such a transition was not found in the bulk. Interestingly, the N-N transition in CP7B is found to shift to higher temperatures when the thickness of the cell is reduced to $1.9\ \mu\text{m}$. 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. In the bulk, the N-N transition which is a consequence of a jump in the short-range order from a monolayer to a partial bilayer structure [1,9] is pre-empted by the crystallisation of the sample. Using the Landau-de Gennes theory they described a uniaxial nematic made of biaxial particles, which gives rise to relatively large values for the correlation length of the order parameter in a suitable parameter range [10]. The large correlation length can give rise to a significant enhancement of the order parameter in thin cells. More recently, Manjula *et al.* have confirmed that the N-N transition in the bulk of CP7B occurs above the ambient temperature under high pressures [11]. They also found that in a binary mixture, in which the N-N transition in the bulk occurs above the ambient temperature, the transition temperature increases as the thickness of the cell is decreased [12].

All the compounds used in the above-mentioned studies have large longitudinal dipole moments. In order to check if the enhancement of the orientational order parameter in thin cells is a general feature of nematic liquid crystals, we have made such measurements on systems with different chemical structures having both longitudinal and transverse dipole moments. In this paper we report the measurement of Δn of nematic liquid crystals in thin and thick cells which are pretreated with

polyimide and rubbed unidirectionally. We show that Δn and hence the orientational order parameter is enhanced considerably in thin cells with respect to that in thick cells in all the compounds with *aromatic cores*. The enhancement is higher in compounds having several phenyl rings like, 2-cyano 4-heptylphenyl-4'-pentyl-4-biphenyl carboxylate (S1014) and 4-cyanophenyl 3'-methyl 4'-(4''-*n*-decylbenzoyloxy) benzoate (CN) (see Fig. 1). In trans-4-pentyl-(4-cyanophenyl)-cyclohexane (PCH5), which has only one aromatic ring, the enhancement is decreased. In 4'-butyl-4 heptyl-biclohexyl-4-carbonitrile (CCN47), which does not have any aromatic core, no significant enhancement is observed except close to T_{AN} , the nematic-smectic transition temperature. This implies that the surface potential on the molecules with aromatic cores is stronger than that on molecules without any aromatic cores. We show that the Landau-de Gennes theory can partially account for this effect if a strong surface potential is assumed which gives perfect order at the surfaces. This also leads to an increase in the elastic constant which results in a reduction in the fluctuation amplitude of the nematic director, and hence contributes to the larger *measured* value of the order parameter in the thinner cells. The calculated enhancement drastically decreases as the temperature is lowered, in contrast to the experimental trend.

2 Experimental

We have chosen a number of compounds with different chemical structures in which the dipole moments make different angles with the long axes of the molecules. The chemical structures and phase sequences of the compounds are shown in Figure 1. The first compound (S1014) is obtained from Merck. It is highly polar and the direction of the permanent dipole moment makes a large angle with the long axis and hence the dielectric anisotropy is negative ($\Delta\epsilon = \epsilon_{||} - \epsilon_{\perp} < 0$). The nematic phase occurs over a wide temperature range and can be supercooled to room temperature. It also has a smectic-C-like short-range order (cybotactic groups) in the entire nematic range [13]. The second compound (CN) is also highly polar with a long alkyl chain. It exhibits the nematic phase at relatively high temperatures. The direction of the permanent dipole moment in this molecule is along the long axis and hence the dielectric anisotropy is positive. The third compound (BAN) is made of banana-shaped molecules and is highly biaxial. This compound does not exhibit the nematic phase. The mixture with 50 : 50 wt% of compounds CN and BAN gives rise to a uniaxial nematic with positive dielectric anisotropy. This mixture was studied to explore the effect of molecular biaxiality on the order parameter measured in thin cells. The compounds CN and BAN were synthesized in our chemistry laboratory. The fourth compound (PCH5) also obtained from Merck, is highly polar. It exhibits a nematic phase at room temperature and is widely used in display applications. The direction of the permanent dipole moment in this molecule is along the long axis and hence the dielectric anisotropy is positive. The last compound (CCN47) was obtained from Merck

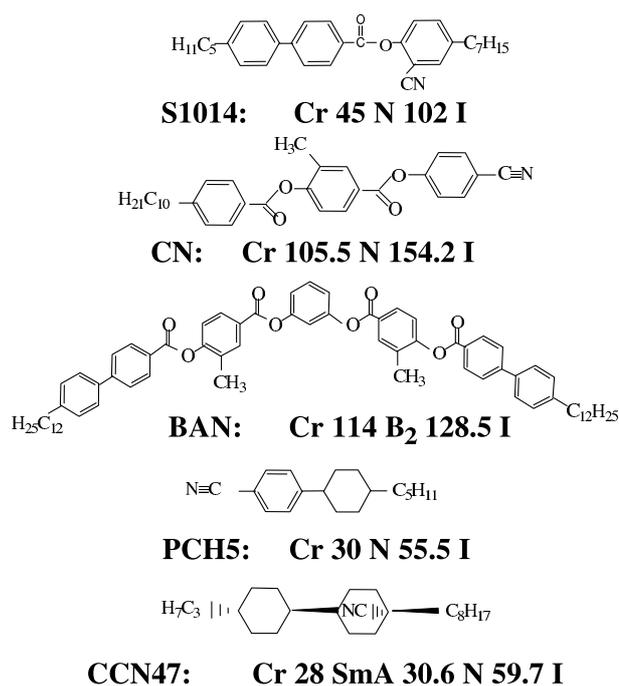


Fig. 1. Chemical structures, phase sequences and transition temperatures of the compounds used in thin-cell experiments. The transition temperatures are given in degree Celsius.

and is highly polar with a negative dielectric anisotropy, but does not have an aromatic core.

The cell is constructed using two ITO (indium tin oxide) coated glass plates which are treated with polyimide and cured at a temperature of 280 °C for 90 minutes. After curing, the plates are rubbed for homogeneous alignment of the nematic director. Glass beads are mixed with an epoxy glue, which is spread outside the electrode region to get the required cell thickness $> 2 \mu\text{m}$. However, to make cells of thicknesses $< 2 \mu\text{m}$ we do not use any spacers. The glue used does not affect the liquid crystals and is usually used for making liquid-crystal displays. The thickness of the cell is measured carefully at several positions using an interferometric technique, with the help of the Ocean Optics spectrometer (model, S2000). Several cells are made at a time and those with uniform thickness (within $\sim 1\%$) are selected for the experiment. To test if the cell thickness changes with temperature, we heated the empty cell up to 150 °C and measured the thickness at several temperatures and found no noticeable change. The cell is filled with the sample in the isotropic phase by capillary action. A heating stage (INTEC HS1) is used to control the temperature to an accuracy of ~ 10 mK. The heater is kept on the rotating stage of a polarizing microscope (Leitz, ORTHOPLAN). A helium-neon laser beam ($\lambda = 632.8$ nm) is used to illuminate the sample. A tilting compensator (Leitz, 5 λ) is used to measure Δn . We could also measure Δn from the transmitted optical intensity. In thick cells the variation of optical intensity shows maxima and minima as a function of temperature between two crossed polarizers. However in thin cells ($< 2 \mu\text{m}$) the variation of optical intensity shows only one broad maximum

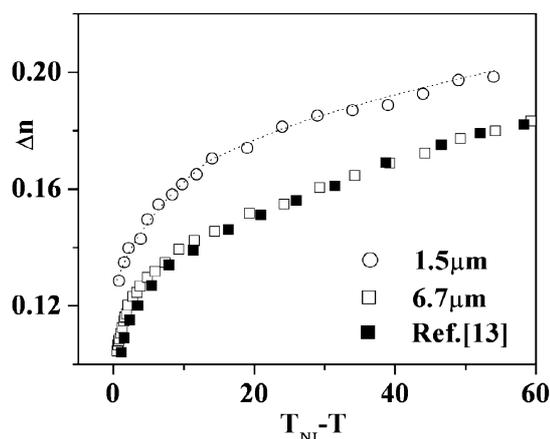


Fig. 2. Variations of Δn of S1014 in 1.5 μm (open circles) and 6.7 μm (open squares) thick cells as functions of temperature. The dotted line is drawn as guide to the eye. Data corresponding to the filled squares are obtained from reference [13].

and it is not possible to calibrate the intensity and hence measure Δn accurately. Therefore, Δn values in all the cells are measured by using the tilting compensator. The measurements are made while cooling the samples from the isotropic phase.

3 Results and discussion

The variations of birefringence (Δn) of S1014 measured in two cells of thickness 1.5 μm and 6.7 μm , respectively, are shown as functions of temperature in Figure 2. The Δn values measured using the tilting compensator in the thick cell compares well with the data of reference [13] (filled squares, Fig. 2) in which n_e (extraordinary refractive index) and n_o (ordinary refractive index) have been measured separately using a goniometer. Δn measured in the thin cell (1.5 μm) is larger at all temperatures than that in the thick cell (6.7 μm) and at lower temperatures the two curves are roughly parallel (Fig. 2). It should be pointed out that S1014 has also a smectic-C-like short-range order throughout the nematic range [13].

The variations of Δn of CN as functions of temperature are shown for cells of three different thicknesses, namely 1.5 μm , 2.2 μm and 14 μm in Figure 3. This compound exhibits the nematic phase at high temperatures (105.5 to 154.2 °C). Again, at a fixed temperature, Δn increases with decreasing cell thickness. For example, at $T = 142$ °C, Δn is higher by 6% and 11%, respectively, in the 2.2 μm and 1.5 μm cells compared to that in the cell of thickness 14 μm . For this compound we analyse the temperature dependence of Δn , which can be approximated well for nematic liquid crystals by the formula $\Delta n = \Delta n_o (1 - T/T_1)^\beta$ here T_1 and β are adjustable parameters and Δn_o is the birefringence of the perfectly aligned sample [14]. Least-squares fits to the experimental data on CN with the above equation are shown for the three different cell thicknesses in Figure 3.

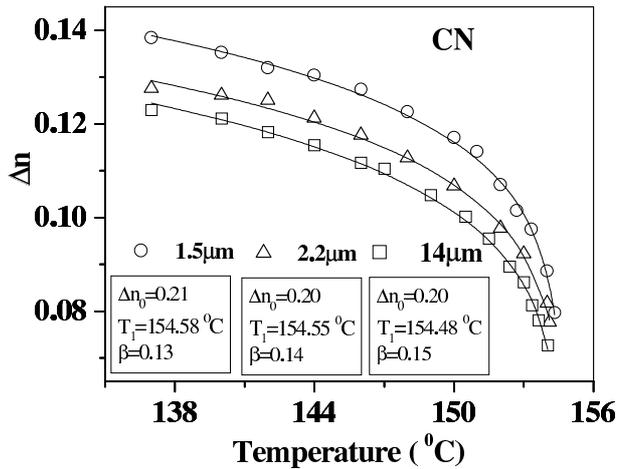


Fig. 3. Variations of Δn of CN as functions of temperature in cells of three different thicknesses: $1.5 \mu\text{m}$ (open circles) $2.2 \mu\text{m}$ (open triangles) and $14 \mu\text{m}$ (open squares). The continuous lines are the theoretical fits to the functional form of $\Delta n = \Delta n_0(1 - T/T_1)^\beta$. The relevant fit parameters are shown in the insets.

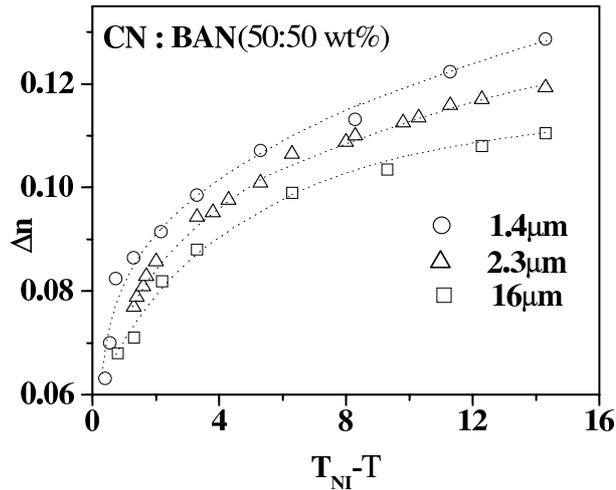


Fig. 4. Variations of Δn as functions of temperature of the mixture of CN and BAN in three different cell thicknesses, namely $1.4 \mu\text{m}$ (open circles) $2.3 \mu\text{m}$ (open triangles), $16 \mu\text{m}$ (open squares). Dotted lines are drawn as guides to the eye.

It is noticed that the fitted birefringence of the completely ordered sample in $1.5 \mu\text{m}$ is slightly higher (by 5%) than that in 2.2 and $14 \mu\text{m}$ cells. The fit parameter T_1 is higher by 0.1° in the $1.5 \mu\text{m}$ cell than that in the $14 \mu\text{m}$ cell. This indicates that T_{NI} increases as the thickness is decreased as predicted by the Landau theory [3] and hence T_1 , which is slightly above T_{NI} , is also increased. However our main interest is to study the effect of confinement on the orientational order parameter and we have not carefully measured the enhancement of T_{NI} at reduced thicknesses of the samples. The value of β is 0.13 in the $1.5 \mu\text{m}$ thin cell and increases to 0.15 in the $14 \mu\text{m}$ thick cell. Similar values of β are obtained in several other nematics [1].

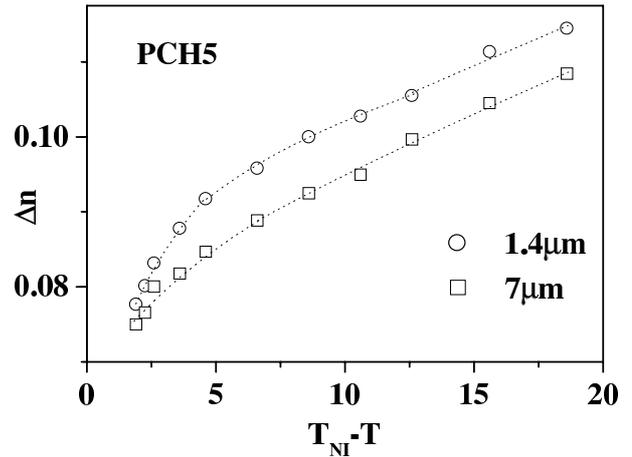


Fig. 5. Variations of Δn of PCH5 measured in $1.4 \mu\text{m}$ (open circles) and $7 \mu\text{m}$ (open squares) thick cells as functions of temperature. Dotted lines are drawn as guides to the eye.

The variations of Δn in the 50 : 50 wt% mixture of CN and BAN are shown as functions of temperature in Figure 4 for three thicknesses. Close to the transition temperature the data points are noisy because this mixture exhibits a nematic-isotropic coexistence range $\simeq 1^\circ\text{C}$. Therefore in this mixture Δn is measured while heating the sample. Again, at a fixed temperature, Δn increases with decreasing cell thickness. For example, at $T_{\text{NI}} - T = 12^\circ$, Δn is higher by 6% and 13%, respectively, in the $2.3 \mu\text{m}$ and $1.4 \mu\text{m}$ cells compared to that in the cell of thickness of $16 \mu\text{m}$.

The variations of Δn of PCH5 measured in two cells of thickness $1.4 \mu\text{m}$ and $7 \mu\text{m}$, respectively, are shown as functions of temperature in Figure 5. The values of Δn of the $7 \mu\text{m}$ thick cell agree well with those calculated from earlier measurements of n_e and n_o [15]. Close to the isotropic-to-nematic transition point ($T_{\text{NI}} - T < 2^\circ$) Δn measured in the two cells are comparable. At lower temperatures, there is a clear enhancement of Δn in the thinner cell. For example, it is 6% higher than in the thicker cell at 5° below T_{NI} .

The variations of Δn as functions of temperature are shown for CCN47 in two different cell thicknesses, namely $1.5 \mu\text{m}$ and $6.7 \mu\text{m}$ in Figure 6. Interestingly, no significant enhancement is noticed between the two curves corresponding to the two thicknesses in the nematic phase down to $T_{\text{NI}} - T \simeq 20^\circ$. There is an enhancement of Δn in both the cells as the temperature approaches T_{AN} , due to the coupling of the orientational and translation order parameters [1]. The relative enhancement in the thinner cell increases at lower temperatures. For example, at T_{AN} in the thinner cell Δn is $\sim 10\%$ higher than that in the thicker cell.

We summarise the experimental results of Δn on all the five systems studied in Table 1 (at $T_{\text{NI}} - T = 12^\circ$) in which the relative enhancement of Δn in thin cells with respect to thick cells is shown. We notice that in the first four systems Δn is enhanced considerably in thin cells compared to that in thick cells. It is also noticed from the

Table 1. Comparison of Δn in thin and thick cells.

Compound	Thickness of the thin and thick cells (μm)	$(T_{\text{NI}} - T)$ in $^{\circ}\text{C}$	$\frac{\Delta n_{\text{thin}} - \Delta n_{\text{thick}}}{\Delta n_{\text{thick}}} \times 100$
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

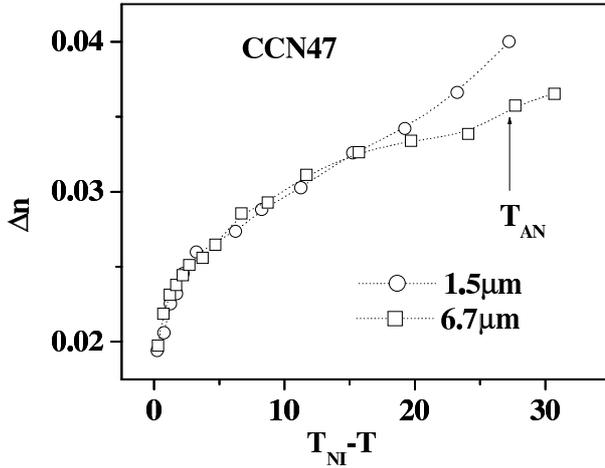


Fig. 6. Variations of Δn of CCN47 in $1.5 \mu\text{m}$ (open circles) and $6.7 \mu\text{m}$ (open squares) cells as functions of temperature. Note that the separation between the two curves increases as T_{AN} (smectic-to-nematic transition temperature) is approached. Dotted lines are drawn as guides to the eye.

table that due to the addition of biaxial molecules in the mixture, the enhancement of Δn in thin cells does not change significantly from that of CN. Thus, the effect of molecular biaxiality on the orientational order parameter in thin cells may not be significant.

The orientational order parameter in thin cells in the first three systems studied is considerably larger compared to that in the thick cells irrespective of the molecular structure, temperature range and orientation of the permanent dipole moments in the molecules. In PCH5, which has only one phenyl ring, the relative enhancement is smaller than in the other compounds with more than one phenyl ring. CCN47 has no aromatic rings and also does not exhibit any significant dependence of Δn on the thickness except close to T_{AN} . The data on Δn in the thicker cells of both S1014 and PCH5 agree well with those calculated from the n_e and n_o measurements of earlier workers. This shows that in the cells used by us the nematic has a planar alignment, without any significant pretilt. To understand the enhancement of the orientational order parameter in thin cells two possibilities can be invoked: 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. First, we will discuss the effect of

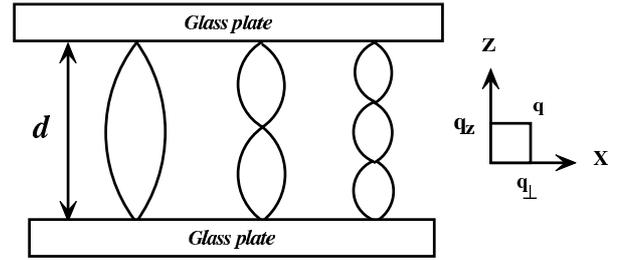


Fig. 7. Schematic representation of a few allowed fluctuation modes between the two plane surfaces.

thermal fluctuations of the director on the magnitude of the scalar order parameter in thin cells.

3.1 Quenching of director fluctuations in thin cells

In the nematic phase thermal fluctuations of the director are quite strong. These fluctuations cause strong scattering of light and the nematic is turbid in appearance. In the one elastic constant approximation the mean-square fluctuation at any wave vector q is given by [1]

$$\langle |n_{\perp}(q)|^2 \rangle = \frac{k_{\text{B}}T}{VKq^2}, \quad (1)$$

where k_{B} is the Boltzmann constant, T the temperature, V the volume, and K the elastic constant. 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 [16, 17]. In a recent study we have shown that the quenching of director fluctuations also significantly influences the thermodynamics of the nematic-paranematic phase transition under an external electric field [18]. In that case the fluctuation amplitude is reduced due to the external field. In thin cells the number of modes are reduced due to the finite cell thickness. The wave vector \vec{q} can be decomposed into q_z , along the z -axis and q_{\perp} , which is in the xy plane (Fig. 7). When the thickness is decreased the number of allowed modes along the z -axis is reduced. Any mode which has wavelength longer than twice the cell thickness d is not allowed, due to the confinement along the z -direction.

In principle, to calculate the r.m.s. fluctuation in real space, we have to sum over the allowed modes along the z -direction [19]. However, as the smallest gap d used in our experiment is $> 1 \mu\text{m}$ which is much larger than the

intermolecular distance a ($\approx 2 \times 10^{-7}$ cm), we will replace the summation by an integration over the appropriate limits. In real space the mean-square fluctuation amplitude is given by

$$\langle |n_{\perp}(r)|^2 \rangle = \frac{k_B T}{8\pi^3 K} \int_{\pi/d}^{q_{\max}} dq_z \int_0^{q_{\max}} \frac{2\pi q_{\perp} dq_{\perp}}{q_{\perp}^2 + q_z^2}, \quad (2)$$

where $q_{\max} \approx 2\pi/a$, is the cut-off wave vector. As $d \approx 1 \mu\text{m}$, $q_{\max} d \approx 10^3$. We use this to simplify the above integral to get

$$\langle |n_{\perp}(r)|^2 \rangle \approx \frac{k_B T}{8\pi^2 K} \left[q_{\max} \left(\ln 2 + \frac{\pi}{2} \right) + \frac{2\pi}{d} \left\{ \ln \left(\frac{\pi}{dq_{\max}} \right) - 1 \right\} \right]. \quad (3)$$

It is noticed from equation (3) that the fluctuation amplitude is reduced with the reduction of the sample thickness. Using equation $\langle n_z^2 \rangle = 1 - 2\langle n_{\perp}^2 \rangle$, the measured value of the order parameter can be written as $S_{\text{meas}} = S_0(3\langle n_z^2 \rangle - 1)/2$, where S_0 is the order parameter in the absence of director fluctuations as calculated, for example, in a mean-field theory. We get the order parameter in a cell of finite thickness d as $S_{\text{meas}} = S_0(1 - 3\langle |n_{\perp}^2(r)| \rangle)$. Using equation (3) it can be written as

$$S_{\text{meas}} = S_0 \left[1 - \frac{3k_B T}{8\pi^2 K} \left[q_{\max} \left(\ln 2 + \frac{\pi}{2} \right) + \frac{2\pi}{d} \left\{ \ln \left(\frac{\pi}{dq_{\max}} \right) - 1 \right\} \right] \right]. \quad (4)$$

Using $K \simeq 5 \times 10^{-7}$ dynes, $a \simeq 20 \text{ \AA}$, and $T = 330 \text{ K}$, we find that the order parameter increases by $\sim 0.1\%$ in a $1 \mu\text{m}$ cell compared to that in a $10 \mu\text{m}$ cell. On the other hand, experimentally, we find in the first four compounds (see Tab. 1) that the enhancement of the order parameter in thin cells is nearly 6 to 13% compared to that in the thicker cells. As such, the enhancement of the order parameter due to the partial quenching of the director fluctuations in thin cells cannot explain our experimental result. Now we consider the effect of confinement on the order parameter of nematic liquid crystals due to the surface potential. As mentioned earlier using the Landau-de Gennes theory Ping Sheng calculated the order parameter profile in thin cells [3]. He restricted the calculation between $T_{\text{NI}} - 0.12^\circ$ to $T_{\text{NI}} + 0.36^\circ$. We extend the calculation to a few degrees below T_{NI} .

3.2 Effect of a large surface orientation potential

We consider a nematic liquid crystal confined between two plane parallel surfaces separated by the distance d . The solid-liquid crystal interfaces are defined by $z = 0$ and $z = d$, respectively. The sample is assumed to be uniform in the x and y directions (Fig. 7). The substrates are treated such that the molecules experience a uniaxial aligning potential in a particular direction. It can be

assumed that the surface potential averaged over many molecules over a small volume is given by [3]

$$V = \langle \nu(\theta, z) \rangle = -G\delta(z)\langle P_2(\cos\theta) \rangle = -G\delta(z)S, \quad (5)$$

where the angular brackets represent a local average. As we have experimentally found that the enhancement of the order parameter in thin cells is very substantial, we assume the surface potential is so large that there is perfect order at the surfaces, *i.e.* $S(0) = S(d) = 1$. Selinger *et al.* [20] 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 *i.e.* $S(0) = 1$. However, they did not extend the calculation to the nematic phase. Following Sheng [3], we write the Landau-de Gennes free energy density

$$\phi = f(S) + L \left[\frac{dS}{dz} \right]^2, \quad (6)$$

where

$$f(S) = \frac{a}{2}(T - T^*)S^2 - \frac{B}{3}S^3 + \frac{C}{4}S^4; \quad (7)$$

$f(S)$ is the bulk free energy density and a, T^*, B, C are material parameters. L is the bare elastic constant. The total free energy density Φ which is the volume integral of ϕ can be minimised with the help of the Euler-Lagrange equation, $\partial\phi/\partial S = \nabla \cdot [\partial\phi/\partial \nabla S]$. The boundary conditions are: $S = 1$ at $z = 0, d$ and $(dS/dz)_{z=d/2} = 0$ and $S(d/2) = S_m$, where S_m is the minimum order parameter which is obtained at the mid-plane of the sample. Using the above boundary conditions and following the procedure given by Sheng [3], it can be shown that

$$\frac{z}{\xi_0} = \int_{S(z)}^1 \sqrt{\frac{1}{F(S) - F(S_m)}} dS, \quad (8)$$

where $\xi_0 = \sqrt{L/aT_{\text{NI}}}$ is the bare correlation length and $F(S) = f(S)/aT_{\text{NI}}$ and $F(S_m) = f(S_m)/aT_{\text{NI}}$. The material parameters a, B, C for PCH5 are assumed to be $a = 0.10 \text{ J/cm}^3 \text{ K}$, $B = 1.5 \text{ J/cm}^3$, $C = 3.8 \text{ J/cm}^3$, $T^* = 327.2 \text{ K}$, $T_{\text{NI}} = 328.5 \text{ K}$. The first three coefficients are of the same order as in other nematics [3]. The elastic constant L , is found by using the formula [21] $L = (K_1 + K_2 + K_3)/6S^2$ where K_1, K_2 and K_3 are the splay twist and bend elastic constants and taken from reference [22] for PCH5. L is estimated to be $\simeq 3 \times 10^{-13} \text{ J/cm}$. The estimated bare correlation length $\xi_0 \sim 10 \text{ \AA}$. Using these parameters we have numerically calculated the $S(z)$ profile for half the cell thickness at a few temperatures in the nematic phase. The variation of the calculated $S(z)$ at $T_{\text{NI}} - 1^\circ$ is shown as a function of z/ξ_0 in Figure 8. It is noticed that the order parameter decays to a value hardly different from S_m when $z/\xi_0 \sim 50$. The thickness averaged order parameter in the cell is calculated using

$$\bar{S} = \frac{1}{d} \int_0^d S(z) dz. \quad (9)$$

Table 2. Comparison of calculated values of the order parameters in $1\ \mu\text{m}$ cell using different approximations and the bulk values at a few temperatures.

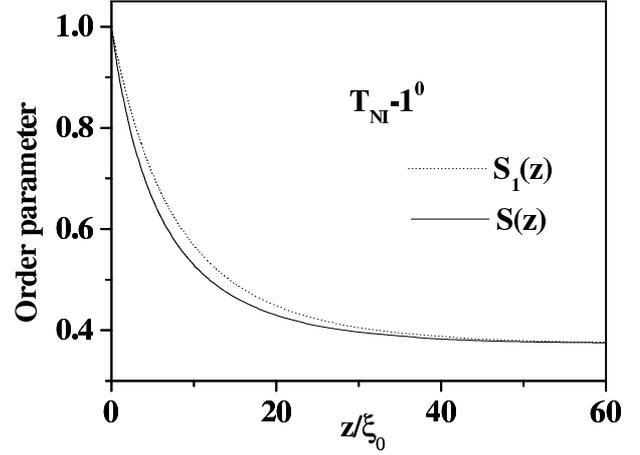
Temperature	S_b	\bar{S}	\bar{S}_1	$\frac{\bar{S}-S_b}{S_b} \times 100$	$\frac{\bar{S}_1-S_b}{S_b} \times 100$	$S_{\text{meas}}(10\ \mu\text{m})$	$S_{\text{meas}}(1\ \mu\text{m})$	$\frac{S_{\text{meas}}(1\ \mu\text{m})-S_{\text{meas}}(10\ \mu\text{m})}{S_{\text{meas}}(10\ \mu\text{m})} \times 100$
$T_{\text{NI}} - 0.2^\circ$	0.297	0.310	0.313	4.4%	5.2%	0.091	0.119	30%
$T_{\text{NI}} - 1^\circ$	0.373	0.383	0.385	2.7%	3.2%	0.209	0.228	9%
$T_{\text{NI}} - 5^\circ$	0.566	0.571	0.572	0.9%	1.1%	0.460	0.467	1.5%
$T_{\text{NI}} - 10^\circ$	0.714	0.716	0.717	0.3%	0.4%	0.631	0.635	0.6%

We can introduce an additional elastic term $L' \left(S \frac{\partial S}{\partial z} \right)^2$ in equation (6), where L' is also an elastic constant. This term is also allowed by the symmetry of the medium. Following a procedure similar to that given above and assuming $L = L'$, we find

$$\frac{z}{\xi_0} = \int_{S(z)}^1 \sqrt{\frac{1+S^2}{F(S)-F(S_m)}} dS. \quad (10)$$

Using the same material parameters a , B , C , T^* we calculate the variation of the order parameter $S_1(z)$ at a few temperatures where the suffix 1 indicates that an additional elastic term is used. The $S_1(z)$ profile, which is calculated at $T_{\text{NI}} - 1^\circ$ including the $L \left(S \frac{\partial S}{\partial z} \right)^2$ term in equation (6), is shown by a dotted line in Figure 8. We notice that the overall variation of $S_1(z)$ is similar to that of $S(z)$. The order parameter $S_1(z)$ is somewhat higher upto $z/\xi_0 \simeq 50$ than that of $S(z)$. We summarise the calculated values of the order parameter in the bulk S_b , obtained from equation (7), and in the $1\ \mu\text{m}$ cell at a few temperatures in Table 2. Close to T_{NI} the enhancement is large and decreases rapidly as the temperature is lowered. This trend is expected as the perfect order at the surface has a larger effect when the bulk order parameter is lower. The bulk order parameter is increased with decreasing temperature and the effect of surface order is reduced. On the other hand, experimentally, we find that the enhancement is not significantly reduced at lower temperatures (see Tab. 1).

The enhancement of the order parameter due to the reduction of the cell thickness has two aspects as discussed above. Firstly, the number of *fluctuation modes* are reduced (see Sect. 3.1). This increases the order parameter by $\sim 0.1\%$ when the thickness is decreased from 10 to $1\ \mu\text{m}$. 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 a reduction in the *fluctuation amplitude* (see Eq. (3)). To estimate this effect, we simply use the average value \bar{S}_1 in place of S_0 in equation (4) and use $\bar{K} = K_0(\bar{S}_1)^2$ to calculate S_{meas} . In this calculation we use $K_0 = 2 \times 10^{-6}$ dynes and $a = 20\ \text{\AA}$. The calculated values of S_{meas} in cells of thicknesses $1\ \mu\text{m}$ and $10\ \mu\text{m}$ at a few temperatures are also shown in Table 2. S_{meas} is less than the mean-field order parameter S_0 due to the director fluctuations in both the 10 and $1\ \mu\text{m}$ cells. However, the relative enhancement of S_{meas} in a cell of thickness $1\ \mu\text{m}$ is larger


Fig. 8. Variations of the calculated order parameters (continuous line: $S(z)$ and dotted line: $S_1(z)$) as functions of z/ξ_0 near one wall of the thin cell. Variations are shown only up to $z/\xi_0 = 60$ for clarity. ($1\ \mu\text{m}$ corresponds to $z/\xi_0 = 1000$.)

than that of \bar{S}_1 . Thus, the combined effect of the surface potential and the stiffening of the elastic constant has amplified the enhancement of S_{meas} in thin cells. Close to T_{NI} the enhancement in S_{meas} is very large and again decreases sharply as the temperature is lowered. On the other hand, the experimentally measured enhancement remains high as the temperature is lowered in the nematic phase (Figs. 2–5). Thus, the large enhancement well below T_{NI} is not accounted for by the model.

Our experiments show that the orientational order parameter of nematic liquid crystals in thin cells is enhanced considerably with respect to that in thick cells in all the compounds with *aromatic cores*. In PCH5, which has only one phenyl ring, the relative enhancement is smaller than that in compounds with more than one phenyl ring. In CCN47, which has no phenyl rings in the molecular structure, no enhancement is observed except close to T_{AN} . This implies that the surface potential on the molecules with aromatic cores on the polyimide coating is much larger than that on molecules without any aromatic cores. The Landau-de Gennes theory for the uniaxial medium partially accounts for the enhancement of the order parameter if the surface potential produces perfect order. Both the number of fluctuation modes as well as the fluctuation amplitude are reduced in thin cells. The latter effect is due to the stiffening of the elastic constant due to the enhanced order and has a larger influence on the “measured” order parameter. However, 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. Curiously, in CCN47 there is a significant enhancement of the experimentally measured order parameter in a thin cell near T_{AN} . The reason for this enhancement is not clear. Further theoretical work is required to understand these experimental results.

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