

Ordering and Self-Diffusion in the First Molecular Layer at a Liquid-Crystal-Polymer Interface

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^2H NMR of a liquid crystal confined to submicron cylindrical cavities, in a 17-K interval above the nematic-isotropic transition, reveals a weakly orientationally ordered molecular layer at the cavity wall governed by local interactions. The order ($S_0=0.02$) is temperature independent so that a partial wetting is realized with no prewetting transition expected. A molecular exchange rate between the surface layer and the bulk is measured to be $\sim 10^3 \text{ s}^{-1}$. The coherence length measuring the order penetrating further into the cavity is described by $\alpha=0.4$ and $\xi_0=0.6 \text{ nm}$.

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Interfacial phenomena in thermotropic liquid crystals are presently attracting a lot of attention. Besides their relevance to basic physics of dispersion systems, their importance for the applications in electro-optic devices^{1,2} is the main driving force. The surface-induced ordering is usually described in terms of wetting³ or more precisely orientational wetting⁴ in the case of a nematic-liquid-crystal-solid interface. On approaching the isotropic-nematic transition temperature T_{NI} from above, an ordered surface layer appears with either a finite or infinite limiting thickness corresponding to partial or complete wetting,⁴ respectively. For a certain strength of the surface interactions, a prewetting transition^{3,4} to a phase with an oriented boundary layer⁵ is expected to occur.

Theories based on the Landau-de Gennes,⁵⁻⁸ Maier-Saupe,⁴ and molecular⁹ approaches have been developed to predict orientational ordering close to a surface. Experimental studies to determine the surface order parameter S_0 include wall-induced pretransitional birefringence,^{6,10} evanescent-wave ellipsometry,¹¹ second-harmonic generation,¹² field-induced twist,¹³ and combined optical and capacitance measurements.¹⁴ For different surface treatments, S_0 was found to be between 0.01 and 0.8 corresponding to partial or complete wetting. Only the data of Shen and co-workers¹¹ give some insight into the order penetration into the isotropic phase. There is no information about mobility of the molecules in the ordered layers.

We introduce ^2H NMR as a powerful tool to study the nematic ordering close to the isotropic-liquid-crystal-solid interface. In addition to the degree of the surface-induced order and its decay in the isotropic phase the method gives us information about the mobility of the molecules close to the surface. We report on surface-induced orientational order of a liquid crystal in the isotropic phase confined to submicron-size cylindrical cavities. The cylindrical pores of polycarbonate Nuclepore membranes¹⁵ are permeated with 4'-pentyl-4-cyanobiphenyl (5CB- βd_2) deuterated in the β position of the hydrocarbon chain. The large surface-to-volume ratio and high density of pores allow surface studies to be accessible with ^2H NMR. The ^2H -NMR spectra show a

strong quadrupole splitting in the isotropic phase which is sensitive to the order and the dynamics imposed by the surface. There is particular sensitivity to the first molecular layer which is found to have an exchange rate with the bulk substantially reduced from diffusion rates in the bulk of the cavity, yielding a value for the time a molecule resides on the surface. The order of the first molecular layer is found to be small with a temperature dependence governed by local molecular interactions at the surface.

The pores are well-defined cylindrical cavities treated with polyvinyl-pyrrolidone,¹⁶ oriented, on the average, perpendicular to the membrane surface and penetrating through its 10- μm thickness. Different pore sizes with radii ranging from 0.05 to 0.3 μm were used. The complete filling of the pores with 5CB- βd_2 was reached after approximately 1 h at 40°C in an oven. The films were then removed from the oven and pressed between two Whatman filtration papers to remove the excess liquid crystal from the surface. Approximately 200 4-mm-wide strips were uniformly stacked and placed in a 5-mm Norell precision thin-walled NMR tube. The experiments were performed on a home-built NMR spectrometer with a $B=4.7 \text{ T}$ Nalorac superconducting magnet.

The magnetic correlation length defined by $\xi_m = (\mu_0 K / \Delta\chi)^{1/2} / B$, reported for 5CB, is about 1.0 μm and thus much larger than pore radii for reported values of $\Delta\chi$, the anisotropy of the diamagnetic susceptibility, and K the elastic constant.² Therefore, the magnetic field has a negligible effect on the nematic director configuration inside the cylinder.

Optical microscopy¹⁷ and ^2H -NMR studies¹⁸ verify perpendicular anchoring conditions in Nuclepore membranes permeated with 5CB in the nematic phase. From cases where ordering is low and limited only to the relatively thin surface layer, we expect that the director field is radial everywhere and no escape characteristic for the nematic phase¹⁹ can occur. Deuterium NMR provides a direct measure of orientational order on a molecular level via the time-averaged quadrupole interaction of a selectively deuterated liquid-crystal compound.²⁰ In a local region of the cylinder represented by the position

vector \mathbf{r} , a compound deuterated in a specific site will yield a spectrum of two sharp lines separated by

$$\delta\nu(r) = [S(\mathbf{r})/S_B] \delta\nu_B \left[\frac{3}{2} \cos^2\theta(\mathbf{r}) - \frac{1}{2} \right], \quad (1)$$

where $\theta(\mathbf{r})$ is the angle between the local nematic director and the magnetic field, $S(\mathbf{r})$ is the local order parameter, S_B is the order parameter of the bulk nematic, and $\delta\nu_B$ is the corresponding quadrupole splitting. The observed quadrupole splitting for a 0.2- μm -diam pore is ~ 20 kHz in the nematic phase and ~ 200 Hz in the isotropic phase. The distance that the molecule migrates in the isotropic phase during a NMR measurement $\sqrt{D/\delta\nu}$ is in our case ($D \sim 3 \times 10^{-7} \text{ cm}^2/\text{s}$) on the order of the cylinder size and the motional averaging by translational self-diffusion must be taken into account. The general equation of a free-induction decay describing such a system of molecules is given by the expression²¹

$$G(t) = \left\langle \exp \left[i\pi \int_0^t \delta\nu(\mathbf{r}(t')) dt' \right] \right\rangle, \quad (2)$$

where $\delta\nu(\mathbf{r})$ is given by Eq. (1) and $\langle \rangle$ stands for the statistical average.

To incorporate diffusion into the calculation of Eq. (2) a simple ring model was devised. A cylinder of radius R can be divided into N equally spaced rings. The probabilities of a molecule diffusing from ring i to ring $i+1$ and ring i to ring $i-1$ are assumed to be $P(i \rightarrow i+1) = D/(R/N)^2$ and $P(i \rightarrow i-1) = [(i-1)/i]D/(R/N)^2$. It is also assumed that all molecules within one ring have the same frequency given by Eq. (1). The NMR spectra are calculated by using the inversion matrix method discussed by Abragam.²¹

The bulk 5CB- βd_2 material used in this experiment has a nematic-isotropic transition temperature T_{NI} of 35°C. A temperature depression between 1 and 2 K (depending on cylinder radius) is observed. It is mostly due to impurities introduced by the Nuclepore filters and to a lesser degree due to elastic distortions caused by the small cylinder size.^{17,22} Selected ^2H -NMR spectra for various pore sizes in the isotropic phase with the long axes of the cylinders parallel or perpendicular to the magnetic field are shown in Fig. 1. As the cylinder size decreases the quadrupole splitting increases because of the increased surface-to-volume ratio. This is seen in the inset of Fig. 1 where the quadrupole splitting at $T = 33.75^\circ\text{C}$ is plotted as a function of the radius of the pore. The small splitting (100 times smaller than in the bulk nematic phase) indicates that a number of molecules which are ordered is small and their degree of ordering is low. This suggests the use of a simple Landau-de Gennes formalism developed for the description of a nematic liquid crystal in contact with a flat surface.⁵⁻⁸ Following Sheng⁵ the simplest form for the surface free-energy density associated with orientational wetting is $f_s = -GS_0$, where G is a constant describing the strength of the interaction and S_0 is the value of the order parameter on the surface. In the limit of weak sur-

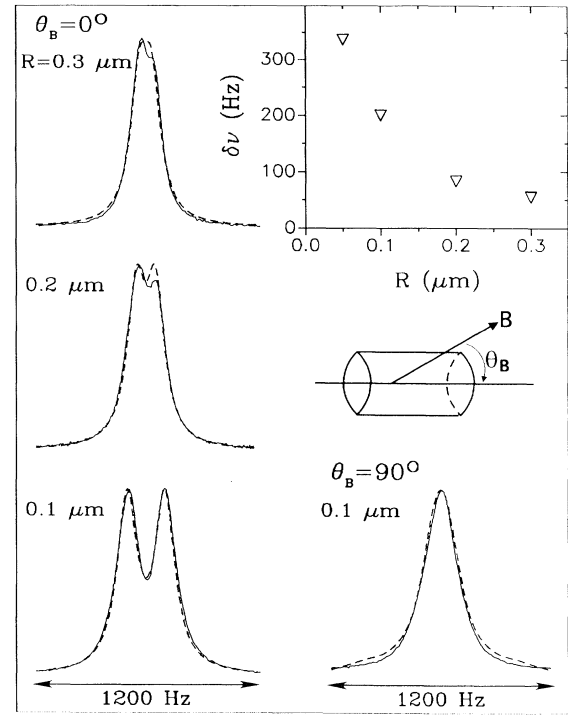


FIG. 1. Some fitted deuterium NMR spectra of Nuclepore filters permeated with 5CB- βd_2 recorded in the isotropic phase at $T = 33.75 \pm 0.03^\circ\text{C}$ with theoretical fit (---) where the molecular long axis is taken as oriented (on the average) perpendicular to the wall. Inset: The effect of pore size on the quadrupole splitting.

face coupling ($S_0 \ll 1$ for $T > T_{\text{NI}}$) one finds

$$S(r) \approx S_0 e^{-(R-r)/\xi}, \quad (3)$$

where $S_0 = G\xi/2L$ and $\xi = \xi_0 / [(T - T^*)/T^*]^{-\alpha}$ with $\alpha = \frac{1}{2}$. Further, T^* is the supercooling limit temperature which is $2B^2/9aC$, below T_{NI} bulk, and $\xi_0 = (aT^*/L)^{-\alpha}$ is the zero-temperature coherence length. The conventional Landau-de Gennes coefficients, a , B , C , and L are material constants. For pure 5CB one has $L = 1.7 \times 10^{-11} \text{ J/m}$, $a = 0.132 \times 10^6 \text{ J/m}^3\text{K}$, $T_{\text{NI}} - T^* \sim 1.1 \text{ K}$, and $\xi_0 = (K/aT^*)^{1/2} = 0.65 \text{ nm}$. Using the above theoretical predictions in the calculation of the NMR spectra leads to a much faster decrease of the line splitting $\delta\nu$ with increasing temperature than our data show (see Fig. 2). This indicates that the above description of the orientational wetting is not adequate. A weaker temperature dependence of the splitting could be obtained by assuming a noncritical (in first approximation temperature independent) surface order parameter S_0 . Such a behavior is expected when the dominant ordering interactions are local in nature. A better agreement with the data is obtained assuming a constant order within a thin surface layer. Therefore, we use the model where order parameter is constant (equal to S_0) in a first

molecular layer with the thickness equal to the molecular length $l_0 \sim 2$ nm followed by an exponential decay described by Eq. (3), where $\xi(T)$ is assumed to behave according to the Landau-de Gennes predictions (see the inset in Fig. 2). Additional evidence for a different behavior of the first molecular surface layer comes from the positional dependence of the diffusion constant which was determined by the simultaneous fitting of the data for the different cylinder diameters with the same fitting parameters. The use of the spatially independent D required its dependence on the cylinder diameter which is not reasonable. We obtained the best fit (see Figs. 1 and 2) with D equal to the bulk isotropic value (3×10^{-7} cm²/s) everywhere in the cylinder except in the surface layer introduced above, where $D_s = 1 \times 10^{-10}$ cm²/s. Further, we find $S_0 = 0.02 \pm 0.004$ for the entire temperature range and the temperature dependence of the correlation length to be described by the parameters $\xi_0 = 0.7 \pm 0.1$ nm, $T_{NI} - T^* = 1.4 \pm 0.2$ K, and $\alpha = 0.4 \pm 0.04$ for the best fit obtained in Fig. 2. These values of $T_{NI} - T^*$, α , and ξ_0 are in good agreement with Shen's results and close to the corresponding values 1.1 K, 0.5, and 0.65 nm predicted by the Landau-de Gennes model and cannot be assumed as real free parameters. From the value for D_s , the time $\Delta\tau$ a molecule resides on the surface is estimated to be $l_0^2/D_s \approx 1.0$ ms, consistent with that estimated by Žumer *et al.*²³ from direct measurements of the self-diffusion constant in nematic droplets of polymer-dispersed liquid-crystal (PDLC) materials. So the only real free parameter is S_0 . Our value $S_0 = 0.02$ is much smaller than the one obtained by Shen and co-workers¹¹ ($S_0 \sim 0.2$) on a silane-treated glass substrate, but larger than the value 0.01 reported by Yokoyama, Kobayashi, and Kamei^{10,14} just above T_{NI} for a 5CB-evaporated SiO interface. The difference in measured order parameters can be attributed to the

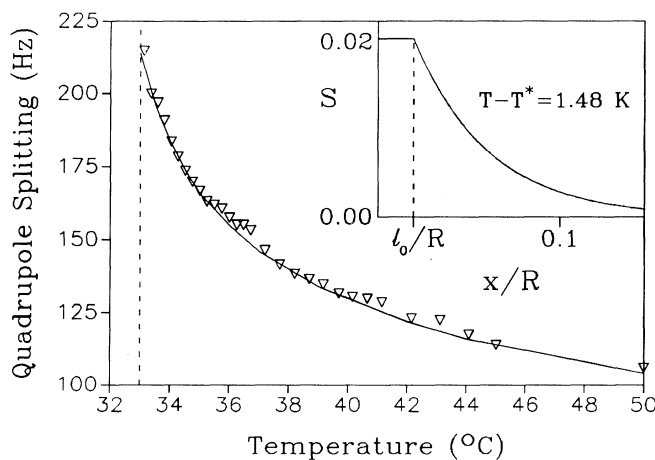


FIG. 2. Quadrupolar splitting order vs temperature measured for $R = 0.1 \mu\text{m}$. The solid line, theory, is based on the order-parameter profile illustrated in the inset for 33.1°C .

different surface treatments. Our small value of S_0 indicates that surface coupling with the orientational order parameter of Sheng's type,⁵ if it exists, is very weak. Using the relation $S_0 = G\xi/2L$ and our experimentally determined S_0 one can estimate the upper boundary for G . The resulting value 1.5×10^{-5} J/m² is much smaller than the value 4×10^{-4} J/m² needed for the existence of the prewetting transition, which is in agreement with the fact that it is not observed here or elsewhere.⁵

As mentioned earlier, there is an impurity-induced depression of the transition temperature which does not affect the critical behavior but only slightly rescales the temperature and can thus be described by a small change in the material constants. Further, there are two competing mechanisms: surface-induced ordering which tends to increase the transition temperature, and the geometry-introduced elastic deformation which tends to decrease the transition temperature. Only the latter effect can be simply described in terms of the T^* shift which is of the order L/R^2a ($\ll 1$ for $R > 0.1 \mu\text{m}$). The detailed description of these phenomena is far beyond the scope of this Letter. Therefore, we can only use the analogy of the planar nematic cell^{5,10} where the effects of both competing mechanisms have been discussed in detail and where only the ordering mechanism is important. We conclude that for cylinders with $R > 0.1 \mu\text{m}$ the transition-temperature shifts are expected to be smaller than the impurity-induced ones so that the approach we have applied is adequate to describe the interesting physics of the weak pretransitional nematic ordering in our cylindrical system.

We have shown how NMR enables us to study surface-induced nematic ordering in a very broad temperature range not accessible before. It is shown that at the polyvinylpyrrolidone/5CB interface there is a weakly ordered molecular layer where the degree of order is within the error constant over the temperature range studied. Thus it is governed by the local interactions where only a noncritical Boltzmann-type temperature dependence can be expected. The weak surface order indicates that partial wetting is realized similarly as was found by Shen and co-workers¹¹ for 5CB and silane-treated surfaces. The weak ordering also indicates that the surface coupling G to the collective order parameter S is smaller than 4×10^{-4} J/m² and thus cannot induce a prewetting transition. The decay of the order away from the surface layer is well described by the Landau-de Gennes approach where the exponent $\alpha = 0.4$, slightly smaller than the theoretical 0.5, is used. A complete agreement cannot be expected even if a more detailed Landau-de Gennes description of the transition in a cylinder were worked out since fluctuations are neglected within a mean-field-type theory. Further, the molecular exchange time between the surface layer and the rest of the cylinder is shown to be compatible with the predictions obtained from a magnetic-relaxation study of a nematic droplet in the polymer matrix.²³ The surface ordering is

expected to depend on surfactants used on the substrate. Therefore, studies are in progress on treating the cylindrical cavities with various surfactants to investigate the effect on S_0 and D_s . The direct measure of orientational order and the sensitivity to molecular mobility demonstrates the unique effectiveness of ^2H NMR to investigate the statistics and dynamics of interfacial phenomena of liquid crystals confined to restricted geometries.

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