

## Surface Ordering Transitions at a Liquid Crystal–Solid Interface above the Isotropic Smectic-A Transition

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The degree of orientational order induced by confining cylindrical surfaces is monitored via deuteron nuclear magnetic resonance linesplitting and linewidth above the smectic-A to isotropic phase transition. The orientational order strongly depends on the length of the surfactant coupling molecule, on the surface coverage, and on the liquid crystal. Continuous and stepwise growth of orientational order and surface-induced orientational order transitions found in the isotropic phase are explained in terms of a simplified model of surface-induced layering and molecular self-diffusion.

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Liquid crystals (LC) exhibit surface-induced order at temperatures where the bulk phase is disordered [1]. Wetting phenomena [2] occur since both orientational (nematic) and translational (smectic) order easily propagate away from an aligning surface. Wetting behaviors at surfaces above the nematic to isotropic (NI) transition have been studied using evanescent wave ellipsometry, nonlinear optics, magnetic resonance, and calorimetry [3–7]. Studies above the smectic to isotropic transition include x-ray reflectivity and calorimetry [8–11]. Bahr and co-workers found prewetting transitions in smectics and nematics [12]. Models have been developed to explain the discrete progression of smectic layers in cooling towards the smectic-A to isotropic (AI) bulk transition [13–16]. With increased surface coupling, a transition from partial-to-complete wetting occurs [5]. As the nematic (or smectic) phase is approached from the isotropic phase, an ordered surface layer appears with a finite (partial wetting) or infinite (complete wetting) limiting thickness phenomena known in LC as orientational wetting [5]. A wetting review is found in Ref. [17].

We present deuteron nuclear magnetic resonance (DNMR) measurements of steplike (discontinuous) and continuous growth of the orientational order parameter above the AI transition for smectic LC confined to cylindrical pores. The results depend on the length of the surfactant molecule, on the amount of surfactant surface coverage, and on the smectic LC used.

The cyanobiphenyls 10CB and 12CB are confined to alumina Anopore membranes ( $d = 200$  nm diameter pores) [18]. The surface-confined LC interaction is adjusted with aliphatic acids,  $C_nH_{2n+1} - COOH$ , which chemically bond to the surface. Samples are prepared by immersing  $\sim 20$  Anopore strips of  $4 \times 25$  mm size in a 2% hexane solution of the surfactant for 1–2 min, and then baked in a vacuum oven for over 1 h at  $130^\circ\text{C}$ . The strips are filled with isotropic LC and stacked on top of each other inside a thin-walled NMR glass tube. Samples

for studies with different surface coverage are similarly prepared but with a different percent hexane solution. Homeotropic anchoring is promoted by varying the aliphatic tail length with carbon numbers ranging from  $n = 7$  up to  $n = 30$ . 10CB- $\alpha d_2$  and 12CB- $\alpha d_2$ , deuterated at the alpha position, have an AI transition temperature  $T_{AI}$  of  $50.5$  and  $58.4^\circ\text{C}$ , respectively.

DNMR is sensitive to the local degree of orientational order,  $Q(\vec{r})$ , and to the molecular ordering direction (director field),  $\vec{n}(\vec{r})$ , through the quadrupole splitting frequency  $\delta\nu(\vec{r}) = \delta\nu_0 Q(\vec{r})[3 \cos^2\theta(\vec{r}) - 1]/2$  [5,7,11]. Here  $\delta\nu_0$  is the quadrupole splitting of a perfectly orientationally ordered phase ( $\delta\nu_0 \sim 90$  kHz for alpha-deuterated cyanobiphenyls) and  $\theta(\vec{r})$  is the angle between the local director and the magnetic field  $\vec{B}$  [19]. The magnetic coherence length is larger than  $d$ ; thus, there is no influence of the  $4.7T$  field on the local director [5,18,19]. In all instances, the director field in the SmA phase is surface induced and it is planar radial [5].

For  $T > T_{AI}$ , the quadrupole splitting frequency  $\langle\delta\nu\rangle$  is diffusion averaged since the characteristic molecular displacement caused by the molecule diffusion on the time scale of the DNMR experiment is comparable to  $d$  [19,20]. Thus,  $\langle\delta\nu\rangle$  directly measures the orientational wetting of the surface with the ordered phase and is characterized by the adsorption parameter  $\Gamma = \int_0^\infty Q(z)dz$ , with  $z$  the distance from the order-inducing surface [5]. If  $\Gamma$  diverges as  $T_{AI}$  is neared, the orientational wetting is known as complete; if  $\Gamma$  increases rapidly in cooling but remains finite, the wetting is partial.

DNMR spectra as a function of  $T$ , LC material, and surfactant chain length are seen in Fig. 1 (Fig. 2) for 12CB (10CB). At  $T \gg T_{AI}$ , the DNMR spectra is a small but measurable splitting rather than a single absorption peak expected in bulk. The confined DNMR small frequency splitting,  $\langle\delta\nu_1\rangle \cong 100\text{--}200$  Hz [Fig. 1(a)] increases weakly with decreasing  $T$ . Cooling towards  $T_{AI}$ ,

the small splitting coexists [21] and eventually gives way to a 10 times larger frequency splitting,  $\langle\delta\nu_2\rangle \sim 1.5$  kHz [Figs. 1(b) and 1(c)]. This second splitting is at first weakly dependent on temperature, but near  $T_{AI}$  it shows a nearly steplike increase to  $\langle\delta\nu_3\rangle \sim 3$  kHz. Cooling further into the confined smectic-*A* phase finally yields a quadrupole splitting of  $\sim 35$  kHz (not shown), which is one-half that of the aligned bulk SmA phase at the same  $T$ . The pattern indicates that the confined configuration is of the planar-radial type [5,18,22]. The  $T$  dependence of  $\langle\delta\nu\rangle$  for several surfactant molecules (Fig. 1) reveals two temperatures at which (e.g., for  $n = 15$ ) there is either a discontinuity (near  $63^\circ\text{C}$ ) or a very sharp increase (close to  $60^\circ\text{C}$ ) in its growth with decreasing  $T$ . The temperature location of the discontinuous (sharp) rise depends on the length of the chain of the surfactant molecule. For both LC and short chain lengths ( $n \leq 8$ ), there is no measurable splitting. Thus, there is either no surface-induced orientational order or the spectrum is diffusion averaged and a splitting cannot be resolved. For 12CB, the growth of  $\langle\delta\nu\rangle$  is discrete for all chain lengths. For 10CB (Fig. 2), it is discontinuous for surfactants with chain lengths  $8 < n < 12$  and  $n \geq 21$ ; for the other chain lengths, the surface-induced quadrupole splitting seen in the isotropic phase continuously increases with decreasing  $T$ . Differences in surface-induced alignment for 10CB and 12CB are not unusual [3].

The 12CB pretransitional order is qualitatively explained assuming weak anchoring at the surface and that the surface-LC interaction increases with surfactant treatment. For short chain lengths, the interaction increases but does not overcome high- $T$  disordering effects. For longer  $n$ , the interaction is strong enough and the surfactant molecules are rigidly attached that the surface

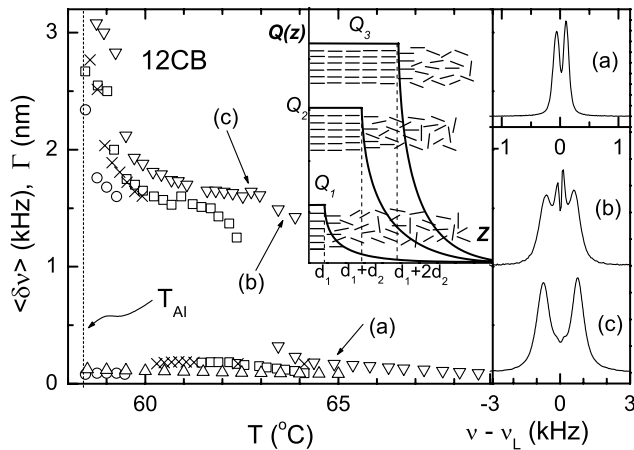


FIG. 1.  $\langle\delta\nu\rangle$  vs  $T$  for 12CB- $\alpha d_2$  in Anopore with the pore's axis parallel to  $\vec{B}$  for several surfactants:  $n = 8$  ( $\Delta$ ), 9 ( $\circ$ ), 11 ( $\square$ ), 15 ( $\nabla$ ), and 21 ( $\times$ ). Typical spectra at selected temperatures and  $\Gamma$  are also plotted. Because of numerical rounding, the scale for  $\Gamma$  roughly coincides with that of  $\langle\delta\nu\rangle$ . Inset: The aligned prenematic ( $d_1$ ), presmectic ( $d_2$ ) bilayers, and the  $Q$  dependence on the distance  $z$  from the wall for three different  $T > T_{AI}$ .

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overcomes the disorder aligning the LC. The surface-LC interaction increases with  $n$ , achieving a maximum at  $n \approx 15$ . Longer surfactants also rigidly bond to the surface but are more flexible and disorder sets in. This flexibility introduces elastic strains and smectic bilayers are difficult to form. The largest surface-LC interaction, identified with the chain length for which the first discontinuous rise occurs at the highest  $T$ , is when the surfactant length is approximately one-half that of the smectic LC bilayer.

A detailed theoretical description will appear in a longer paper; we discuss some of its most salient features. For  $T \gg T_{AI}$  where the small splitting is seen, the surface-induced orientational order parameter profile would follow that used in describing the NI transition; the magnitude of the orientational order associated with this splitting ( $\sim 100$  Hz) is too small to be consistent with the formation of smectic layers. At this  $T$  the surfaces induce only prenematic ordering: a weakly orientationally ordered molecular layer of thickness  $d_1$  (comparable to a molecular length), characterized by a constant orientational order parameter  $Q_1$  that is followed by an exponential decay of order. In the Landau-de Gennes approach it is given by  $Q_1 \exp[-(z - d_1)/\xi]$ , where  $z > d_1$  and  $\xi = \xi_0(T/T^* - 1)^{-1/2}$  is the nematic correlation length depending on the material constants  $\xi_0$ , the zero-temperature coherence length, and the supercooling limit temperature  $T^*$  [5,11].

Cooling towards  $T_{AI}$  the prenematic yields, continuously or stepwise, a larger  $\sim 1.5$  kHz splitting. We assume that as a function of substrate-LC interaction there is a prenematic to presmectic surface transition. The surface layer is orientationally ordered enough and can be taken to be smecticlike, or presmectic: a smectic bilayer of thickness  $d_2$  (approximately two molecular lengths) has formed. In our picture (inset in Fig. 1), the presmectic surface layer of thickness  $d_1 + d_2$  has uniform order

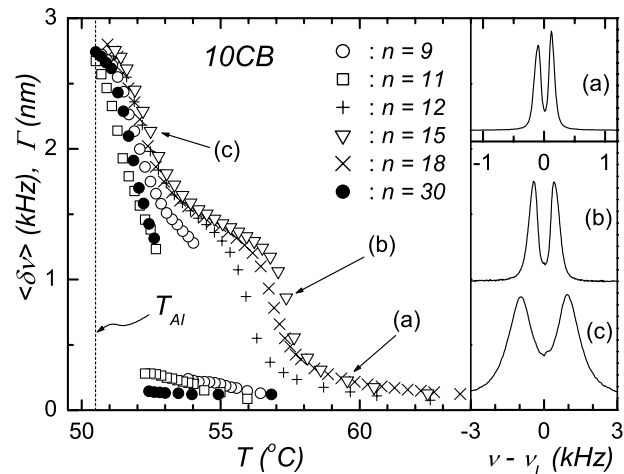


FIG. 2.  $\langle\delta\nu\rangle$  vs  $T$  for 10CB- $\alpha d_2$  in Anopore with the pore's axis parallel to  $\vec{B}$  for several surfactants. Unlike for 12CB, here  $\langle\delta\nu\rangle$  grows continuously for  $11 < n < 21$ .

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$Q_2 \gg Q_1$ , followed by a “nematic tail” decaying according to  $Q_2 \exp[-(z - d_1 - d_2)/\xi]$ . Closer to  $T_{AI}$  a second large increase in splitting occurs (always continuously) signaling the formation of a second smectic bilayer. The induced orientational order profile is given by a uniform  $Q_3$  in a layer of thickness  $d_1 + d_2 + d_2$  followed by a  $Q_3 \exp[-(z - d_1 - 2d_2)/\xi]$  decay in the nematic tail.

In the presmectic range the line splitting is small that for  $R = 100$  nm radius pores, the condition for motional averaging  $\frac{2D}{\langle \delta\nu \rangle} > R^2$  is satisfied [7,19];  $D$  is the translational molecular diffusion constant,  $\sim 5 \times 10^{-11} \text{ m}^2 \text{ sec}^{-1}$  in these materials. Averaging over the cylinder  $(\pi R^2)^{-1} \int_0^R \delta\nu(r) 2\pi r dr$ , as  $R \gg (2d_2 + d_1 + \xi)$ , the linesplitting becomes:

$$\langle \delta\nu_m \rangle \simeq \frac{1}{R} \delta\nu_0 Q_m [d_1 + (m-1)d_2 + \xi(T)],$$

$$m = 1, 2, 3. \quad (1)$$

Fitting the experimental results to Eq. (1) yields information on our orientational order parameters  $Q_1$ ,  $Q_2$ , and  $Q_3$  characterizing the three regions of orientational wetting near  $T_{AI}$ . Preliminary results for  $Q_m$  (Table I) indicate that order drastically increases in going from nematic to smectic wetting, but it is not very sensitive to the number of smectic bilayers.

Substrate stabilized presmectic order has been found in several LC [11]. Its evolution with decreasing  $T$  is often associated with a discrete growth of the smectic layer resulting in a discontinuity in  $\langle \delta\nu \rangle$ . To date, discrete layering transitions have been seen only in long chain LC (11CB and 12CB); the discontinuous transitions disappeared for short chain LC such as 8CB which also possesses the nematic phase. While our work agrees with that picture, the observation of discrete layering transition over a narrow range of surface interactions for 10CB which also lacks a nematic phase suggests that additional effects are present.

The dynamic molecular exchange at  $T > T_{AI}$  between the ordered surface layers and disordered regions in the core of the pores is quantified by monitoring the linewidth (full width at half maximum  $\Delta$ ) of the DNMR

absorption peak (Fig. 3) for both LC. It is known for confined nematic LC [7] that such a process can be described via an exchange between an ordered surface layer (consisting of  $m$  presmectic or prenematic layers) of order parameter  $Q_m$  and disordered regions with  $Q = 0$ .  $\Delta_m$  can be interpreted as the spin-spin relaxation rate  $(T_2^{-1})_m$ ; for  $\theta = 90^\circ$  is approximately equal to  $(\frac{\pi}{2} \delta\nu_0 Q_m)^2 \tau_m$  with  $\tau_m$  representing the effective time during which the molecules are in the ordered layer. As a function of temperature,  $\Delta$  behaves like  $\langle \delta\nu \rangle$ ; transitions in  $\Delta$  cooling towards  $T_{AI}$  mimic those found in  $\langle \delta\nu \rangle$  occurring at the same temperature at which prenematic to presmectic transitions occur. Yet the steps in  $\Delta$  are larger than the ones expected from the changes in  $Q_m$  since  $\tau_m$  strongly depends on the surface layer thickness.

Within our simplified model, for each  $m$  one can approximate  $\tau_m$  with a translational diffusion time  $\tau_m = \frac{1}{2D} [d_1 + (m-1)d_2 + \xi]^2$ . This is the time required to travel through the ordered layer and that allows to relate the linewidths with the corresponding linesplittings:  $\Delta_m = (\pi \delta\nu_m R)^2 / 8D$ . For both 12CB and 10CB and different surfactants, the previous relation can be fit for all cases with the same  $D \simeq (4.5 \pm 0.5) \times 10^{-11} \text{ m}^2 \text{ sec}^{-1}$ , a value very close to the one found experimentally. For the  $m = 3$  region, the equality  $\Delta_m / \Delta_{m-1} = (\delta\nu_m / \delta\nu_{m-1})^2$  is satisfied to within a 15% error; the relation is not applicable for  $m = 2$  since  $(\delta\nu_2 / \delta\nu_1) \sim 7$  yields  $\Delta_1 \sim 10$  Hz or much smaller than the measured linewidth which in this temperature range is dominated by other mechanisms. Yet it can be concluded that the simple model of presmectic surface-induced ordering is not too far from reality. The behavior of our modeled  $Q$  is schematically shown in Fig. 1, with some results found in Table I.

Identical behavior is seen by varying the surface coverage at a fixed surfactant as exemplified for 10CB and  $n = 15$ . Samples were prepared with hexane solutions ranging from 0.3% to  $\leq 10\%$  [23] and their spectra measured as a function of  $T$ . Figure 4 shows the  $T$  dependence of  $\langle \delta\nu \rangle$  at  $T > T_{AI}$  for several surface coverages; comparing with Fig. 2 where the surface-LC interaction changed with  $n$ , the behavior is identical.

TABLE I. Experimental data for three selected points in regions  $m = 1, 2$ , and 3, fitted to our model to obtain the corresponding parameters,  $Q_m$ , to test the relation between  $\Delta_m$  and  $\delta\nu_m$ , and to determine the molecular self-diffusion constant. Three combinations of surfactant chain length and LC are used: (a) 12CB and  $n = 15$ ; (b) 12CB and  $n = 11$ ; (c) 10CB and  $n = 15$ .  $D \simeq (4.5 \pm 0.5) \times 10^{-11} \text{ m}^2 \text{ sec}^{-1}$  was obtained by minimizing the deviations of  $8D\Delta_m / (\pi R \delta\nu_m)^2$  from unity. Typical cyanobiphenyl parameters were used:  $d_1 = 1.6$  nm,  $d_2 = 3.2$  nm,  $\xi(T_{AI}) = 5$  nm, and  $T^* = T_{AI} - 1$ .

$m$	3			2			1		
	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
$\delta\nu_m$ (kHz)	3.10	2.70	2.75	1.68	1.50	1.80	0.20	0.18	0.27
$\Delta_m$ (kHz)	2.55	2.30	2.25	0.68	0.60	0.63	0.20	0.2	0.20
$Q_m$	0.27	0.24	0.24	0.25	0.22	0.23	0.06	0.05	0.09
$\frac{\Delta_m}{(\delta\nu_m)^2} \frac{8D}{(\pi R)^2}$	0.96	1.14	1.08	0.87	0.98	1.01			

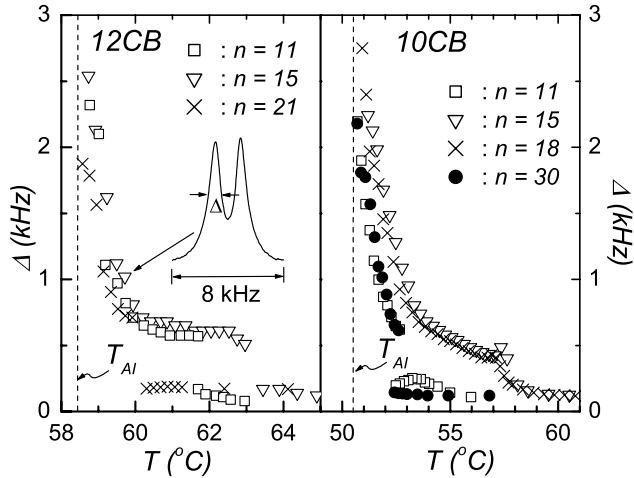


FIG. 3. The width at half maximum  $\Delta$  of the absorption peaks as a function of  $T$  for several surfactant molecules.

Specifically, as a function of surface coverage,  $\langle \delta\nu \rangle$  evolves from exhibiting no pretransitional order for coverages below 0.3%. Such a surfactant coverage is too small to cover much of the surface; LC molecules intercalate between the few distant surfactant molecules and are aligned parallel to the pore axis. Increasing the surfactant coverage coats the pores almost completely (nearing a monolayer coverage), the surface interaction is large and discrete prenematic to presmectic transitions occur; this coverage range is narrow as was the case when changing  $n$ . Further surfactant coverage increase (equivalent to longer chain lengths) yields continuous transitions; another increase and stepwise transitions are recovered.

In short, depending on the surface-LC interaction, adjusted by changing the length of the surfactant molecule or the surface coverage for a given surfactant, there is a prenematic layer which in cooling towards  $T_{AI}$  evolves continuously or discretely depending on the LC and/or surface interaction into presmectic bilayers. This transition is always stepwise for 12CB, but may be continuous (still sharp) for 10CB. A simple model describes the experimental linesplitting and linewidths for 12CB; a more complete one is needed for 10CB.

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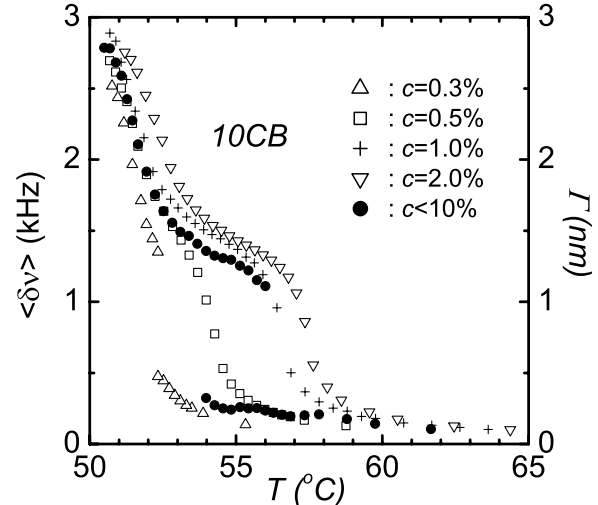


FIG. 4.  $\langle \delta\nu \rangle$  vs  $T$  for 10CB- $ad_2$  in Anopore with the pore's axis parallel to  $\vec{B}$  for  $n = 15$  and several surface coverages  $c$ .

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- [21] Temperature gradients are on the order of millidegrees; the splittings coexist over one degree.
- [22] The SmA DNMR pattern at  $\theta = 90^\circ$ , not shown, is a cylindrical pattern powder pattern.
- [23] For the 10% solution, the membranes were washed in distilled water removing freely moving surfactant molecules; the surface coverage is thus less than 10%.