# Anchoring and Orientational Wetting Transitions of Confined Liquid Crystals

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Deuterium magnetic resonance of cylindrically confined liquid crystals reveals a structural transition driven by a homeotropic-to-planar anchoring transition in the nematic phase and an orientational wetting (quasicomplete-to-partial) transition in the isotropic phase as the molecular length of the surface coupling agent is decreased. A simple phenomenological description reveals a weak positive surface order parameter in the homeotropic case and a negative one in the planar case. The absence of a symmetry breaking transition in the planar case is attributed to weak interfacial coupling.

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In recent years a lot of research has been devoted to surface phenomena; particularly, the liquid-crystal–solid interface because orientational ordering exhibits a rich variety of exciting physical behaviors: orientational wetting [1], wetting transitions [2], symmetry breaking Berezinskii-Kosterlitz-Thouless (BKT) transitions [3–5], disordered surface layers [6], surface melting [7,8], anchoring transitions [9,10], memory effects [11], ordering in microconfined systems [12], etc. Shen and co-workers [13] have applied nonlinear optics and evanescent-wave ellipsometry to investigate ordering and disordering behaviors at the surface close to the nematic-isotropic (*N-I*) phase transition. Recently deuterium nuclear magnetic resonance ($^2$H-NMR) was used to probe ordering of liquid-crystal molecules near the surfaces of porous membranes [14].

The growing number of theoretical predictions and limited experimental evidence has stimulated this first comprehensive study of anchoring, wetting, and ordering close to the *N-I* phase transition. In the general context of statistical mechanics, the possibility of a BKT transition characteristic of systems possessing symmetry of a two-dimensional *x-y* model is particularly attractive. We describe experiments to systematically control the liquid-crystal–solid interaction by varying the length of the coupling agent molecule ($C_nH_{2n+1}$-COOH) used to treat the surface of the cylindrical channels (diameter of 200 ± 20 nm) of alumina membranes [15]. The deuterated liquid-crystal compound 4′-pentyl-4-cyanobiphenyl (5CB-$\alpha d_2$) is filled into the treated channels. $^2$H-NMR is used to probe the liquid-crystal–solid interface for different carbon numbers ($n=15$, 9, 7, 6, and 5) of the coupling agent. Supporting optical observations are made on 20 $\mu$m thick nematic films between treated alumina substrates oriented so that their birefringent effects are compensated.

The confinement breaks the symmetry of the bulk phase and the resulting structure depends on elastic forces, surface coupling, and external field. $^2$H-NMR probes the local nematic director field $\mathbf{n}(r)$ and degree of order $S(r)$ via the quadrupole splitting frequency [14] $\delta\nu=\delta\nu_b S(r)[3\cos^2\theta(\mathbf{r})-1]/2S_b$, where the subscript $b$ denotes bulk nematic values, and $\theta(r)$ is the angle between $\mathbf{n}(r)$ and the magnetic field $\mathbf{B}$. This simple description is justified because no biaxial phase is found. The influence of the 4.7 T $\mathbf{B}$ field on $\mathbf{n}(r)$ is negligible since the 1.5 $\mu$m magnetic coherence length is substantially larger than cavity diameters. The $^2$H-NMR line shape in the nematic phase reflects details of $\mathbf{n}(r)$ inside the cavities since the molecules only diffuse ~20 nm (much less than the cavity diameter) during the NMR measurement [14]. This spectrum is not sensitive to inhomogeneities of the order parameter near the cavity wall because of the large splitting $\sim\delta\nu_b$. However, this is different above the *N-I* transition temperature ($T_{NI}$) where only order near the surface is present. Complete motional averaging over the cylinder is realized when $\mathbf{B}$ is parallel to the symmetry axis because the molecule migrates > 100 nm (approximately the cavity radius) during the NMR measurement [14]. The resulting splitting $\langle\delta\nu\rangle$ is a direct measure of the adsorption parameter $\Gamma=\int_0^\infty[S(z)-S_b]dz=RS_b\langle\delta\nu\rangle/2\delta\nu_b$, which characterizes the orientational wetting behaviors [2,13].

For a precise structure determination in the nematic phase ($T=24\,^\circ$C), spectra are recorded for the cylinder axis oriented parallel to $\mathbf{B}$ ($\theta_B=0^\circ$) and perpendicular to $\mathbf{B}$ ($\theta_B=90^\circ$). The line shapes (Fig. 1) reveal a radical structure change between $n=6$ and 7. For $n=7$, 9, and 15, the line shapes are all similar and characteristic of the planar nematic director field orthogonal to the cylindrical axis. For $n=6$ and 5, the director field is completely uniform and oriented along the cylinder axis because the splitting at $\theta_B=0^\circ$ is $\delta\nu_B$ and $\delta\nu_B/2$ at $\theta_B=90^\circ$.

To interpret our data in the nematic phase where $S(r)=S_b$ can be assumed, a simple deformation free energy density $f_v=\frac{1}{2}K\{(\nabla\cdot\mathbf{n})^2+(\nabla\times\mathbf{n})^2\}$ is used where the average elastic constant $K$ is $7\times10^{-12}$ J/m for 5CB. The well known surface free energy density $f_s=W_0\times\sin^2\theta_s/2$ is used where $\theta_s$ is the angle between the preferred and actual anchoring direction and $W_0$ is the anchoring strength. For $n=15$, $W_0$ is not expected to differ from lecithin treated ($W_0\sim10^{-5}$ J/m$^2$) surfaces [16] where the carbon number of the surface coupling molecules is comparable. The ratio $RW_0/K<1$ indicates

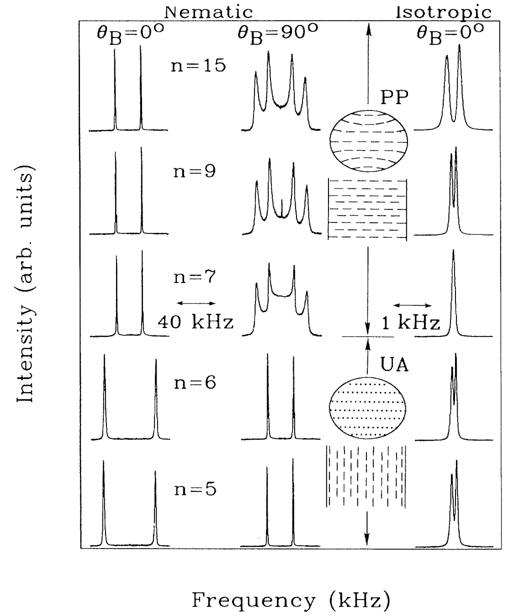

FIG. 1. $^2$H-NMR line shapes of 5CB-$\alpha d_2$ confined to the modified cavities of Anopore membranes accumulated in the nematic phase at $T_{NI}-T=10.5$ K and isotropic phase at $T-T_{NI}=2.5$ K. Illustrations of nematic director fields: planar polar (PP) and uniform axial (UA).

weak anchoring where the anchoring direction substantially deviates from the preferred direction to reduce the deformation of the director field.

Using free energy considerations [16], one finds that for planar anchoring the uniform-axial structure (UA in Fig. 1) and for homeotropic anchoring (perpendicular to the surface) the planar-polar structure (PP in Fig. 1) are stable. The UA structure completely describes the $n=5$ and 6 spectra while the PP structure describes the $n=7$, 9, and 15 spectra at $\theta_B=0°$. For $\theta_B=90°$, "cylindrical" NMR spectral patterns show that the symmetry axes of the PP director fields are randomly distributed, indicating random deviations away from the circular cross section. A free energy estimate shows that deviations of a few percent are enough to prevent the **B** field from orienting the PP director fields, and do not allow us to use the full power of NMR for the determination of the anchoring strength $W_0$.

The observed anchoring transition which drives the structural transformation can be described by two simple limiting models of a more general description [10]: (i) $W_0$ decreases as $n$ decreases, supporting homeotropic anchoring until $W_0$ changes sign between $n=6$ and 7 and begins to support planar anchoring or (ii) a continual change of the preferred anchoring angle $\theta_0$ (measured from surface normal) from $\theta_0=0$ to $\pi/2$ similar to the observation of Porte [17]. The latter model reveals a PP↔UA transition at $\theta_0 \sim 61°$ where the free energy of the PP structure, $W_0 R[1-2\sin(2\theta_0)/\pi]/2$, equals that of the UA structure, $\pi W_0 R\cos^2\theta_0$, in the weak anchoring limit. Our conoscopy studies of alignment of 5CB on $n=15$, 9, and 7 surfaces show a Maltese black cross characteristic of homeotropic anchoring and a symmetric hyperbolic pattern for $n=5$ and 6 surfaces characteristic of planar alignment which helps us to select model (i) that predicts a discrete homeotropic-to-planar anchoring transition. The structural transition thus occurs at $W_0=0$ where the free energies of the PP and UA structures cross. According to theory [10], this indicates the dominance of short range surface interactions rather than quadrupolar ones.

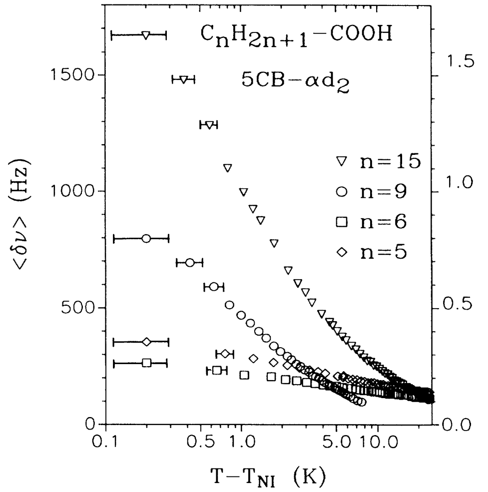

FIG. 2. The adsorption parameter Γ as a function of temperature derived directly from the averaged quadrupole splitting frequency $\langle \delta\nu \rangle$.

To get further insight into this transition, the $^2$H-NMR line shapes in the isotropic phase are studied (Fig. 1). For $n=7$, 9, and 15 surfaces which induce homeotropic anchoring, $\langle \delta\nu \rangle$ clearly decreases as $n$ decreases. The unresolvable splitting for $n=7$ indicates the presence of very weak interfacial coupling. The splitting is again resolvable for $n=5$ and 6 where anchoring is planar. The temperature dependence of the line splitting $\langle \delta\nu \rangle$ which is proportional to the adsorption parameter Γ exhibits a relatively strong increase on approaching $T_{NI}$ (Fig. 2). Within experimental error, it appears that this increase could lead to a weak logarithmic divergence corresponding to complete wetting [2] caused by short range interactions [18]. However, for $n=5$ and 6, Γ definitely remains finite and weakly temperature dependent corresponding to partial wetting. No splitting is observed for $n=7$, implying that $\langle \delta\nu \rangle$ is smaller than the linewidth ($<200$ Hz) and $\Gamma < 0.2$ nm, indicating weak partial wetting or no wetting.

We interpret our results using Landau-de Gennes (LdG) theory [1,19]. Since anchoring is either homeotropic or planar and the data are not indicating a transition to a highly ordered biaxial surface layer, the free energy density in terms of the scalar orientational order parameter $S$ is used: $f(S)=a(T-T^*)S^2/2-bS^3/3$

$+cS^4/4-L(dS/dr)^2/2$, where $a=0.13\times10^6$ J/m$^3$K, $b=1.6\times10^6$ J/m$^3$, $c=3.9\times10^6$ J/m$^3$, $L=1.7\times10^{-11}$ J/m, and $T_{NI}-T^*=2b^2/9ac=1.1$ K are material parameters [20]. We assume a contact nature for the surface interactions and derive the adsorption parameter $\Gamma_{\mathrm{LdG}}$ [19]:

$$\Gamma_{\mathrm{LdG}}=4\xi[a(T-T^*)/2c]^{1/2}\ln\left(\frac{[2/a(T-T^*)c]^{1/2}(R+b/3)+1}{[2/a(T-T^*)c]^{1/2}(R+b/3)-1}\right) \tag{1}$$

with

$$R(S_0)=S_0^{-1}[2a(T-T^*)]^{1/2}[a(T-T^*)/2-bS_0/3+cS_0^2/4]^{1/2}+a(T-T^*)/S_0-b/3\,,$$

where $\xi=\xi_0(T/T^*-1)^{-\alpha}$ is the correlation length with $\alpha=0.5$ and $\xi_0=0.65$ nm for 5CB, and $S_0$ is the value of the order parameter at the surface. It should be stressed that the elastic free energy caused by the curvature constraint is a factor $(\xi/R)^2\ll1$ less than the term of $f(S)$ including $dS/dr$. In droplets of comparable radii [12], this results in $T_{NI}$ shifts below our temperature resolution (0.1 K). Therefore, the elastic effects of the curved geometry are neglected in our study of the isotropic phase. $\Gamma_{\mathrm{LdG}}$ exhibits a logarithmic singularity $\ln[T/(T-T_{NI})]$ on approaching $T_{NI}$ if $S_0>2b/3c=0.27$ for 5CB. In a quantitative comparison of our data with theory we must account for the finite length of the molecules [14] by assuming a constant $S_0$ in the first molecular layer followed by a continuous profile predicted by the LdG theory. The thickness of the first layer $l_0$ is estimated by averaging over the squares of the molecular length $q$ and the molecular diameter $d$ to be $\langle l_0\rangle=[(q^2+2d^2)/3+2S_0(q^2-d^2)/3]^{1/2}\sim1.2$ nm independent of temperature and anchoring direction since $q=2.0$ nm, $d=0.5$ nm, and $S_0\ll1$. Following the usual treatment of surface ordering [11,13], the temperature dependence of $S_0$ (Fig. 3) is obtained by comparing $\Gamma$ (Fig. 2) to $\Gamma_{\mathrm{LdG}}+\langle l_0\rangle S_0$.

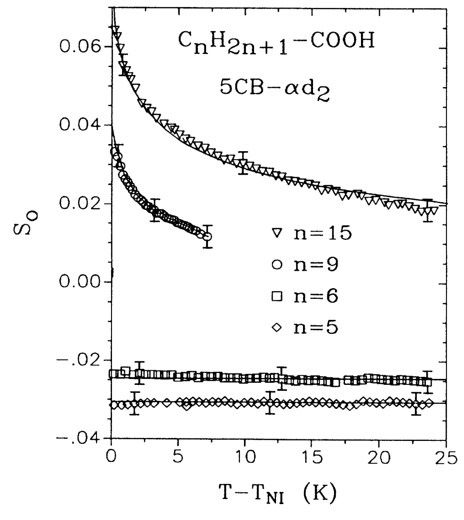

FIG. 3. The surface-induced orientational order parameter vs reduced temperature for various chain lengths ($n$) of the surface coupling molecule. The solid line denotes the theoretical fit.

Since NMR cannot distinguish between negative and positive solutions for $n=15$ and 9 we simply take into account that homeotropic anchoring requires $S_0>0$. For the planar anchoring a weak $S_0<0$ ordering far from $T_{NI}$ and possible symmetry breaking transition to a biaxially ordered surface layer [3-6] on approaching $T_{NI}$ are predicted. The lack of evidence for such a transition in our data leads us to select the $S_0<0$ solution for $n=5$ and 6 cases. $S_0$ shows a strong critical increase for $n=15$ and 9 while noncritical behavior for $n=5$ and 6.

In the fitting procedure for $n=5$ and 6, $\alpha=0.4\pm0.02$ was used instead of 0.5 to compensate for the small but nonphysical increase of $S_0$ as temperature increases obtained when describing the subtle temperature dependence by our simplified LdG model. The $n=9$ and 15 values of $S_0$ show a sharp increase on approaching $T_{NI}$, but within our temperature range $T-T_{NI}>0.2$ K they are still much smaller than the threshold value 0.27 needed for the divergence of $\Gamma_{\mathrm{LdG}}$. To decipher whether our case corresponds to complete or quasicomplete wetting, we follow Nobili and Durand [21] and choose $g(S_0-S_S)^2$ for the surface free energy density to cover positive and negative ordering and the absence of the symmetry breaking transition. The surface coupling parameter $g$ and preferred degree of order $S_S$ are determined such that the theoretical $S_0(T)$ dependence corresponds to the minimum of the total free energy and yield the best fit to $S_0$ obtained from $\Gamma$ (Fig. 3). Results are summarized in Table I. It is seen that $S_0(T_{NI})$ cannot reach the critical value of 0.27 and wetting for $n=9$ and 15 surface within LdG theory is only quasicomplete.

For surfaces that prefer homeotropic anchoring conditions, $n=7$, 9, and 15, both $g$ and $S_S$ decrease as $n$ decreases but for $n=5$ and 6 the reversed trend is observed. This indicates that the interaction between the long alkyl chains and the liquid-crystal molecules is predominantly sterical, resulting in homeotropic ordering while, for short chain lengths, strong interactions between the alumina surface and the core of liquid-crystal molecules dominate and enforce planar ordering.

For comparison the corresponding values of ordering ($G$) and disordering ($U$) coupling constants describing the form of the surface free energy density $(-GS_0+US_0^2/2)\delta(z)$ used by Poniewierski and Sluckin [2] are presented in Table I. The constants $G$ and $U$ are related to $g$ and $S_S$ by the relations $G=2gS_S$, $U=2g$, and $S_S$

TABLE I. Estimated interfacial parameters for the coupling molecule $C_nH_{2n+1}$-COOH.

| $n$ | $T_{NI}-T^*$ (K) | $10^{-4}g$ (J/m$^2$) | $S_S$ | $10^{-4}G$ (J/m$^2$) | $10^{-3}U$ (J/m$^2$) |
|---|---|---|---|---|---|
| 15 | $1.1\pm0.2$ | $8.75\pm1.00$ | $0.11\pm0.02$ | $1.92\pm0.60$ | $1.75\pm2.00$ |
| 9 | $0.8\pm0.2$ | $7.80\pm0.75$ | $0.05\pm0.01$ | $0.78\pm0.25$ | $1.56\pm1.50$ |
| 7[a] | $1.1\pm0.3$ | $7.30\pm1.50$ | $0.008\pm0.002$ | $0.12\pm0.50$ | $1.46\pm3.00$ |
| 6[b] | $1.5\pm0.2$ | $>58.30$ | $-0.024\pm0.002$ | $>-1.22$ | $>11.1$ |
| 5[b] | $1.5\pm0.2$ | $>58.30$ | $-0.031\pm0.002$ | $>-1.00$ | $>11.1$ |

[a]Estimate based on linewidth measurements.

[b]Only lower bound on $g$, $G$, and $U$ attainable.

$=G/U$. The data of Moses and Shen [13] on substrates with planar anchoring yield values of $G=-6.8\times10^{-5}$ J/m$^2$, $U=9\times10^{-5}$ J/m$^2$, and $S_0=-0.047$ near $T_{NI}$. Their values of $S_0$ and $G$ compare well with our $n=5$ and 6 surfaces but $U$ does not because their sample exhibits a strong temperature dependence for $\Gamma$. Our large value of $U$ is related to noncritical temperature behavior of $S_0$ in our systems.

For the first time in a single system, a comprehensive study concerning anchoring, wetting, and ordering near the $N$-$I$ transition is presented. In summary, we stress our main conclusions. The discovered discrete homeotropic-to-planar anchoring transition occurring between $n=6$ and 7 indicates that interfacial coupling is dominated by short range interactions rather than quadrupolar ones [10]. The quasicomplete wetting for $n=15$ and 9 surfaces seems to be a result of short range surface interactions [18] rather than confinement [12,22]. The wetting transition from quasicomplete to partial is observed between $n=9$ and 7 (just above the anchoring transition) indicating a very strong dependence of the surface coupling on the length of the coupling agent. The weak temperature dependence of the surface order and its persistence deep in the isotropic phase shows the need for inclusion of nonlinear terms in the phenomenological description of surface coupling. The lack of the symmetry breaking BKT transition and other surface layer transitions indicates a relatively weak surface coupling. Unfortunately, none of the extensive theoretical treatments covers our situation [3-6]. A further search for stronger interfacial coupling allowing the occurrence of surface layer phase transitions is planned.

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