Almost Critical Behavior of the Anchoring Energy at the Interface between a Nematic Liquid Crystal and a SiO Substrate

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The anchoring energy at the interface between the nematic liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl (5CB) and a glass plate treated by oblique evaporation of SiO is studied by measurement of the torque exerted on the surface by the nematic subject to an orienting magnetic field. The anchoring energy is sharply reduced as the clearing temperature is approached. The experiment provides the first direct evidence of a strong reduction of the surface order parameter for this system in the anisotropic phase.

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In recent years there has been a growing interest in the physical interactions at interfaces.[1] Particular interest has focused on the interfacial properties of nematic liquid crystals (LC),[2] and in particular on the orientational properties of an interface between a nematic LC and a different medium. Minimization of the surface free energy imposes an easy axis on the liquid-crystal director **n** at the interface. In our experiment the easy axis is the x axis in the x-y plane of the interface; this is known as homogeneous parallel alignment. The surface excess free energy when the director makes an angle ϕ with the x axis in the x-y plane is

$$\gamma(\phi)=\gamma_0+W(\phi)\,, \tag{1}$$

where γ_0 and $W(\phi)$ represent the isotropic and anisotropic part of the surface excess free energy. $W(\phi)$ is a positive function which vanishes for $\phi=0$. Usually one assumes[3] that

$$W(\phi)=W_0\sin^2\phi\,, \tag{2}$$

where W_0 is the "*torsion anchoring energy coefficient*,"[2] although recent experimental and theoretical evidence[4–7] indicates that the ϕ dependence of $W(\phi)$ can be more complicated.

In this Letter we report a detailed experimental investigation of the temperature dependence of the anchoring energy coefficient W_0 near the nematic-isotropic transition temperature T_{NI}. We study the interface between the nematic liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl (5CB) and a glass plate on which a thin (200 Å) SiO layer has been deposited by oblique evaporation.[8] This physical treatment gives a homogeneous parallel alignment of the director[8] with a high anchoring energy coefficient.[2] We obtain the anchoring energy by making a direct measurement of the elastic torque exerted by a twisted nematic on the glass plate. This torque depends both on the twist elastic constant K_{22} and on the anchoring coefficient W_0. Our measurements are sufficient to determine both of these quantities. We have demonstrated the reliability of this new technique by measuring K_{22} in 5CB as a function of temperature.[9] In this Letter we investigate the physical behavior of the SiO-nematic interface very close to the clearing temperature T_{NI} of 5CB. The anchoring energy exhibits a roughly linear dependence on temperature, greatly decreasing as the phase transition is approached.

The experimental setup used to measure the surface torque has been described in detail in a previous paper.[9] We describe here the crucial features of the experiment. A circular glass plate (diameter 15 mm, thickness 0.7 mm) is suspended by a thin (diameter 30 μm) quartz wire and is dipped in a nematic LC sample (5CB). Both plane surfaces of the circular glass plate are treated by oblique evaporation of SiO[8] in such a way as to induce a uniform orientation of the director along the x axis in the x-y horizontal plane parallel to the glass plate. The whole apparatus is thermostatically controlled with an accuracy of ±10 mK and the temperature is measured by means of a linear thermoresistor. A magnetic field **H** can be applied in the horizontal plane along a direction which makes an angle $\alpha=18°$ with the y axis. When the field is switched on, the director field is twisted near the interface,[10] subjecting the glass plate to an elastic torque. The rotation $\Delta\theta$ of the torsion pendulum is related to the torque τ by the simple relation

$$\tau=k\Delta\theta\,, \tag{3}$$

where $k=0.2073\pm0.0014$ dyn cm rad^{-1} is the torsion elastic constant of the quartz wire. The surface torque is obtained by measurement of $\Delta\theta$ by an optical method; $\Delta\theta$ is accurate to within $\sim10^{-4}$ rad.

The director distortion close to the interface and the torque can be easily calculated by use of the Frank-Eriksen theory.[10] After simple calculations one obtains the following equations for the surface torque τ and for the angle ϕ between the director and the easy axis x at the interface:

$$\tau=(K_{22}\chi_{\alpha})^{1/2}HS\cos(\alpha+\Delta\theta+\phi)\ , \tag{4}$$

$$\tau/S=\partial W(\phi)/\partial\phi\ , \tag{5}$$

where χ_{α} is the anisotropy of the diamagnetic susceptibility and S is the total surface of the glass plate. In the following we will assume for $W(\phi)$ the simple form of Eq. (2). For $W_0/(K_{22}\chi_{\alpha})^{1/2}H \gg 1$ (strong anchoring), the magnetic field does not modify the surface director polar angle appreciably. Thus, for $\Delta\theta \ll 1$, the elastic torque is an almost linear function of the magnetic field. However, for weak anchoring, the angle ϕ is an increasing function of the field and the H dependence of τ is no longer linear. Hence one can obtain both $K_{22}\chi_{\alpha}$ and the anchoring coefficient W_0 by the best fit of the experimental data. More details of the experimental procedure can be found in Ref. 9.

Figure 1 shows some experimental values of the surface torque per unit surface versus the magnetic field for some different values of the temperature close to the clearing temperature $T_{\rm NI}$ of the nematic LC 5CB ($T_{\rm NI}=35.3=-0.1\,^{\circ}$C). The solid lines correspond to the best fit obtained by use of the theoretical dependence given in Eqs. (4) and (5). Notice that the dependence of τ/S on H becomes increasingly nonlinear as one approaches the clearing temperature. This clearly indicates that the anchoring energy coefficient W_0 decreases. Great care was devoted to making sure that the nematic LC had reached thermal equilibrium; it was necessary to wait several hours between two successive measurements.

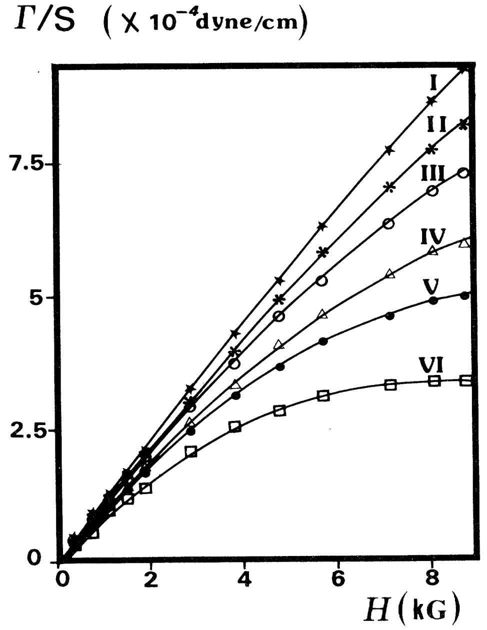

FIG. 1. Torque per unit surface vs the magnetic field for temperatures close to $T_{\rm NI}$. Curve I, $T_{\rm NI}-T=720$ mK; curve II, $T_{\rm NI}-T=410$ mK; curve III, $T_{\rm Ni}-T=220$ mK; curve IV, $T_{\rm NI}-T=90$ mK; curve V, $T_{\rm NI}-T=40$ mK; and curve VI, $T_{\rm NI}-T=10$ mK. Solid lines correspond to the best fits of the experimental points are obtained by use of Eqs. (4) and (5). The two parameters of the best fit are $A=K_{22}\chi_{\alpha}$ and W_0, where W_0 is the anchoring energy coefficient defined by Eq. (2).

Figure 2 represents the dependence of $K_{22}\chi_{\alpha}$ and W_0 versus temperature near the clearing temperature $T_{\rm NI}$. Both of these parameters are obtained by the best fit of the experimental results of Fig. 1 and of other experimental results not shown in Fig. 1. The accuracy on the temperature values and on the clearing-temperature value is ±10 mK. Notice that the anchoring energy coefficient close to the nematic-isotropic transition decreases dramatically: For theoretical reasons discussed below we have fitted the experimental points by a curve

$$W_0=[a+b(T_{\rm NI}-T)^{1/2}]^2\ . \tag{6}$$

The values of a and b obtained by the best fit are $a=1.5\times10^{-2}$ erg$^{1/2}$/cm and $b=3.7\times10^{-2}$ erg$^{1/2}$/cm·K$^{1/2}$.

It is significant that when $T_{\rm NI}-T=10$ mK (curve VI in Fig. 1), the value of W_0 is very low [$W_0=(3.5\pm0.3)\times10^{-4}$ erg/cm^2] and the ϕ angle of the director at the maximum field (8.8 kG) differs appreciably from 0 ($\phi\sim\pi/4$). In this case the director explores regions far away from the parabolic minimum of the free-energy well $W(\phi)$. It is thus possible to detect deviations of $W(\phi)$ from the simple $\sin^2\phi$ behavior of Eq. (2). However, within our accuracy, such deviations were not observed.

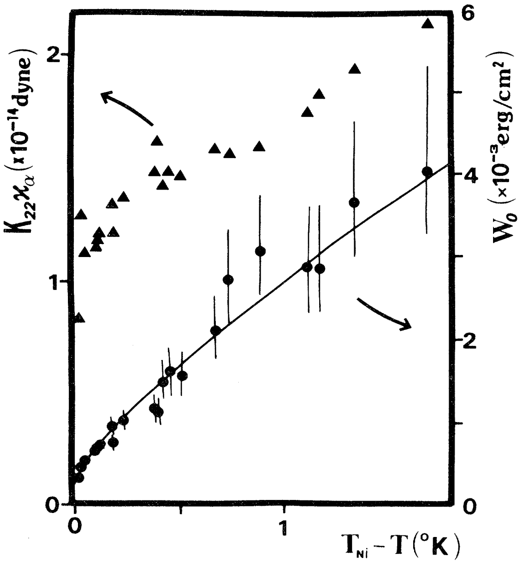

FIG. 2. $K_{22}\chi_{\alpha}$ and W_0 vs the temperature difference $T_{\rm NI}-T$. $K_{22}\chi_{\alpha}$ and W_0 are obtained by the best fit of the experimental dependence of the torque per unit surface vs the magnetic field according to Eqs. (4) and (5). The solid curve represents the best linear fit according to Eq. (10) with $a=1.5\times10^{-2}$ erg$^{1/2}$/cm and $b=3.7\times10^{-2}$erg$^{1/2}$/cm·K$^{1/2}$.

We interpret our results in terms of the Berremann model.[11] In this model the azimuthal anchoring energy is due to the grooved structure of the obliquely evaporated SiO film. When the molecules at the interface do not lie parallel to the grooves, there is an excess of free energy due to the presence of a distortion of the director field close to the surface. This distortion is confined to within a few characteristic lengths $h \simeq \lambda/2\pi$ from the interface, where λ is the average spacing between grooves. By assuming a sinusoidal profile of the SiO surface and isotropic elastic constants of the nematic LC ($K_{ii}=\overline{K}$), Berremann obtains

$$W_0=(2\pi^3 A^2/\lambda^3)\overline{K}\ , \tag{7}$$

where A represents the amplitude of grooves. We note also that generally $\overline{K} \propto Q^2$, where Q is the order parameter. In Eq. (7) it is assumed that the elastic constants maintain the same value everywhere in the nematic sample. However, there is strong circumstantial evidence[12] from surface birefringence experiments above T_{NI}[13,14] and contact-angle experiments[15] that the surface order parameter Q_s at the 5CB-oblique-SiO interface is lower than the bulk value Q_b (at other interfaces it is higher). Close to the interface there is a thin interfacial layer of thickness δ where there is less order than in the bulk; δ increases and may diverge as the temperature approaches the clearing value T_{NI}.[12] While a full theory of the anchoring energy should take into account the spatial variation of the order parameter, we make the simple phenomenological assumption that Eq. (7) remains valid so long as $\overline{K}$ in Eq. (7) is replaced by a surface elastic constant $K_s \propto Q_s^2$. Our experiments thus, for the first time, provide direct evidence of a reduction in Q_s below T_{NI}. Within this context an understanding of our results can be obtained in terms of a simple mean-field-theory model. If we decouple the director and order-parameter variations, then near the interface we can consider the free energy to be a functional of the local order parameter $Q(z)$. Sluckin and Poniewierski[12] have written the free energy per unit area of the interface (at $z=0$, the LC lies in the region $z>0$) as

$$\Phi=\int_0^\infty dz[\omega(Q(z))-\omega(Q_b)+L(dQ/dz)^2] -GQ_s+\tfrac{1}{2}U_1Q_s^2\ , \tag{8}$$

where $w(Q)$ is the free energy per unit volume of a uniform liquid crystal with order parameter Q, L is an effective elastic constant, and G and U_1 are surface free-energy parameters. Solution of the Euler-Lagrange equations of this free-energy functional gives rise to an equation for the surface order parameter Q_s,

$$\omega(Q_s)-\omega(Q_b)\propto[-G+U_1Q_s]^2\ , \tag{9}$$

which in turn, for large enough values of U_1, yields

$$Q_s^2 \propto W_0=[a+b(T_{\mathrm{NI}}-T)^{1/2}]^2\ , \tag{10}$$

where $a \propto G$. This model successfully describes the experimental results as shown above (Fig. 2).

The case of $G=0$ corresponds to complete wetting of the surface by the isotropic phase. Only in this case do we expect that $Q_s \to 0$ as $T \to T_{\mathrm{NI}}^-$ and that $Q_s=0$ for $T>T_{\mathrm{NI}}$. We find a nonzero a and hence a nonzero G, although a number of birefringence experiments[13,14] above T_{NI} have not found $Q_s \neq 0$. however, they find a residual birefringence due to the glass surfaces, which makes measurements of small values of Q_s difficult. In our experiments, with use of Eq. (7) ($A\sim 100$ Å, $\lambda \sim 300$ Å),[2] we can estimate $Q_s(T_{\mathrm{NI}})\sim 0.008$. The contact-angle experiments of Yokoyama, Kobayashi, and Kamei[15] also suggest a strongly reduced order parameter near the surface, in line with our results. Mada and Kobayashi,[16] on the other hand, find enhanced surface order for the system at all temperatures. Further experimental clarification of the surface order near T_{NI} is clearly desirable.

In conclusion, our experimental results furnish a direct evidence for the presence of reduced surface order close to the interface between a nematic LC and a grooved surface. This surface order greatly influences the anchoring at the interface. In particular the experimental value of the anchoring energy coefficient close to the clearing temperature is found to be some orders of magnitude lower than that obtained directly from Eq. (7). Consequently the anchoring model proposed by Berremann must be suitably modified in order to account for simultaneous spatial variations of director orientation and scalar order parameter.

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