

Pretransitional Surface Ordering and Disordering of a Liquid Crystal

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Using the evanescent-wave ellipsometry technique, we have observed the growth of a disordered liquid-crystal layer adjacent to a SiO_x -coated surface near the nematic-isotropic transition. We have also observed the pretransitional growth of a planar-oriented liquid-crystal layer in the isotropic phase of the same system, with a negative orientational order parameter. Both behaviors can be explained quantitatively by the Landau-de Gennes theory.

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Recently there has been great theoretical and experimental interest in the phenomenon of wall-induced orientational order in a liquid-crystal (LC) medium [1-4]. Understanding the orientational ordering induced in a liquid-crystal film by various substrate treatments is of crucial importance for technological applications. The behavior of the surface ordered layer near the nematic-isotropic ($N-I$) transition is also of fundamental interest from the statistical-mechanics point of view. For the case of induced surface order in the isotropic phase, an interesting set of behaviors has been predicted and observed [1-4]. In that case, a convenient variable for describing the surface order is the adsorption parameter Γ , defined by $\Gamma = \int_0^\infty dz [Q(z) - Q_b]$, where $Q(z)$ is the orientational order parameter near the wall at $z=0$ and Q_b is the usual bulk scalar order parameter [5]. It was found that if the surface order parameter $Q_0 = Q(0)$ at the transition temperature T_c is greater than a certain threshold value, Γ diverges logarithmically as $T \rightarrow T_c$. Otherwise, Γ remains finite [6]. These results can be understood on the basis of Landau-de Gennes (LdG) or other mean-field theories [1,3,4] and both behaviors have been experimentally observed [2,4].

LdG theory can also be applied to the nematic side of the transition where a new phenomenon, surface-induced disordering, is now possible. Unfortunately, the large birefringence of the nematic bulk has made optical detection of the surface disorder difficult. Nevertheless, there is some fairly convincing circumstantial evidence for the existence of a disordered layer at the LC/ SiO_x interface [7-9]. That the SiO_x surface should induce disorder in an adjacent liquid crystal is understandable since electron microscope studies have shown that the SiO_x surface is rough on the scale of the bulk correlation length (≈ 100 Å) [10]. Faetti *et al.* [7] and Yokoyama, Kobayashi, and Kamei [8] have measured the azimuthal and polar anchoring energy of the 5CB/ SiO_x system, and found a nearly critical decrease of the anchoring energy coefficient as $T \rightarrow T_c$ from below. Although as yet there is no satisfactory microscopic theory of the anchoring energy, it seems reasonable that this behavior results from a decrease of the surface order parameter as $T \rightarrow T_c$. Later, Yokoyama [9] studied very thin films of 5CB (< 100 nm) between SiO_x -coated substrates, using an ellipsometric technique. He found that the phase shift of polarized light transmitted through the sample decreased

continuously to zero at the $I-N$ transition, beginning to decrease $\sim 0.1^\circ\text{C}$ before the transition. This behavior is almost certainly due to the growth of a disordered surface layer of liquid crystal near T_c . Yokoyama also measured a downward shift in the transition temperature of the system as the 5CB film thickness was reduced, a finite-size effect predicted for confined systems showing surface-induced disordering [11]. In this paper we report the first direct experimental determination of the temperature dependence of the adsorption parameter $\Gamma(T)$ for the semi-infinite 5CB/ SiO_x system. We have detected the growth of a disordered 5CB layer at the interface as $T \rightarrow T_c$ from the nematic side. The order parameter Q_0 at the surface is positive, measured with respect to the bulk director, which is parallel to the surface for the SiO_x -induced homogeneous alignment. This indicates that the surface layer remains homogeneously aligned along the bulk director, but the magnitude of the surface order parameter is reduced below the bulk order parameter. We have also observed the pretransitional growth of a planar-oriented 5CB layer in the isotropic phase of the same system. In the planar surface layer, the order parameter Q_0 is negative, measured with respect to the surface normal. Both results can be explained quantitatively by the LdG theory.

We used the evanescent-wave ellipsometry technique [2] to measure the phase shift $\Delta\phi_c$ between the p - and s -polarized components of a laser beam ($\lambda = 633$ nm) totally reflected from an LC sample oriented at the critical angle θ_c with respect to the incident beam. The technique is particularly sensitive to the optical properties of the interfacial region, even when the bulk medium is strongly birefringent. The sample cell consisted of a $130\text{-}\mu\text{m}$ film of 5CB sandwiched between an SiO_x -coated glass prism (Schott glass LaSF 9, $n = 1.84$ at 633 nm) and a glass plate. The SiO_x layer was evaporated onto the glass prism and plate at a rate of ≈ 15 Å/s at an angle of 60° to the surface normal to a thickness of 138 Å. The quality of the resulting homogeneous alignment was assured by microscope observation before the sample was loaded into an oven with $\pm 1\text{-mK}$ temperature stability.

For each data run, $\Delta\phi_c$ was measured at a series of temperatures monotonically approaching T_c . The bulk phase transition temperature could be clearly identified by the sudden increase in scattered light and change in the critical angle. The width of the coexistence region

between isotropic and nematic phases of our 5CB sample was 30 mK. All data runs were taken within three days of the assembly of the cell; the shape of the $\Delta\phi_c$ curves only began to change after about six days, presumably due to the migration of impurities to the 5CB/SiO_x interface. The error in $\Delta\phi_c$ was due primarily to a long-term system drift, no more than 0.5 mrad/day.

The phase shift $\Delta\phi_c$, as has been noted before [2], is very closely proportional to the adsorption parameter Γ when the thickness of the surface ordered layer is much smaller than an optical wavelength. Therefore the $\Delta\phi_c(T)$ curve provides a visual indication of the induced surface disordering. A typical curve for 5CB in the nematic phase is shown in Fig. 1, where a decrease of Γ as T approaches T_c is a clear manifestation of surface-induced disordering. The behavior of Γ near T_c is most interesting, since it allows us to distinguish the cases of complete and partial dewetting (wetting of the interface by the disordered layer). For complete dewetting, we expect a logarithmic divergence of Γ at T_c whereas in partial dewetting, Γ remains finite. Uncertainty in the exact value of T_c (owing to the finite width of the I - N coexistence region) may make a logarithmic divergence hard to identify. However, the observed change in Γ in the last 0.25°C before the transition is much smaller (by a factor of 2 or more) than that predicted by the theory of complete dewetting described below, even allowing for a 30-mK uncertainty in T_c . Therefore we can conclude that the observed dewetting is partial in the nematic 5CB/SiO_x system.

In the isotropic phase of the same sample we observe negative Γ , indicating that molecules in the interfacial layer prefer to lie along the surface with $Q(z) < 0$ referring to the surface normal. A typical curve is displayed in Fig. 2. The pretransitional growth of a single-domain

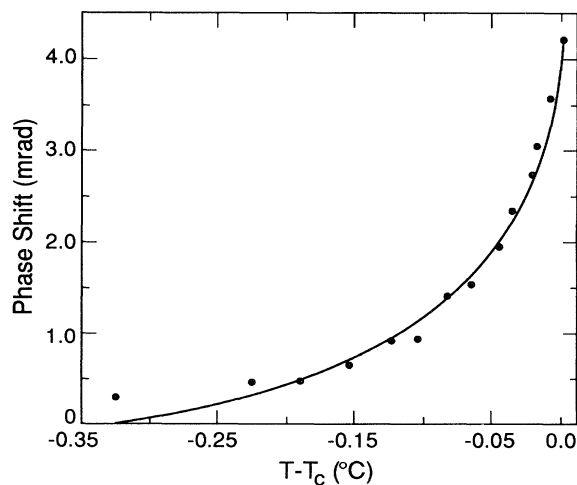


FIG. 1. Nematic-phase temperature variation of $\Delta\phi_c - (\Delta\phi_c)_0$, where $(\Delta\phi_c)_0$ is the value of the phase shift at the critical angle at the lowest measured temperature. The solid line is a theoretical fit by LdG theory. To 1% accuracy, $\Gamma(\text{in } \text{Å}) = -1.82 \times \Delta\phi_c$.

homogeneous layer (molecules aligned in a preferred direction along the surface) near the wall could account for the observed $\Delta\phi_c(T)$ curve. To test this possibility, we performed a transmission ellipsometry measurement on a similar 5CB sample sandwiched between two glass plates. We found the transmitted phase shift to be constant with temperature and with respect to azimuthal rotation of the cell, indicating that the surface-induced ordered (or disordered) layer is not a single-domain homogeneous texture. Two possible structures can give the azimuthal symmetry as well as a negative $\Delta\phi_c$. First, the wall-induced layer may have a true negative order parameter Q_0 , in such a way that the director is along the surface normal but the long molecular axes of 5CB are randomly oriented in the surface plane. Second, the layer may be composed of many small homogeneous domains. In each domain the molecules preferentially lie along a director parallel to the surface plane. The domains, which may be macroscopic though much smaller than the 2-mm laser beam spot, are randomly oriented in the surface plane. In our measurements, both structures appear azimuthally symmetric about the surface normal, but the first is described by a negative order parameter along the surface normal whereas the second has a positive order parameter along the direction of each domain. We have attempted to fit both behaviors with the LdG theory (described below), and found that the only model capable of fitting both nematic and isotropic phases of 5CB gave a negative order parameter for $T > T_c$. This makes us believe that with the bulk in the isotropic phase, the surface layer is *not* composed of macroscopic homogeneously aligned domains, but has molecules oriented randomly in the surface plane with a negative order parameter about a director along the surface normal.

LdG theory is the simplest formalism for describing transitional phenomena in liquid crystals and has been successfully used to explain surface-induced ordering in

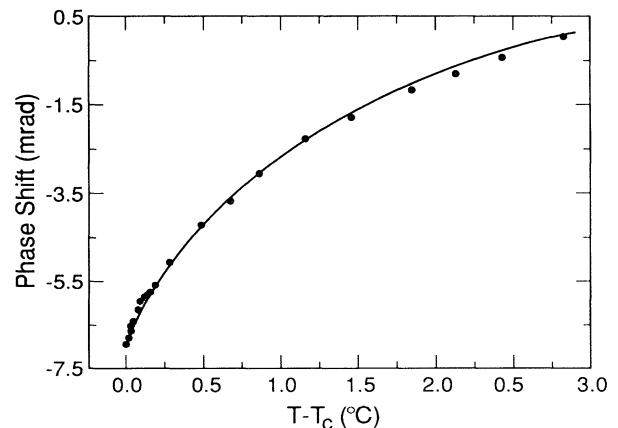


FIG. 2. Isotropic-phase temperature variation of $\Delta\phi_c - (\Delta\phi_c)_0$, where $(\Delta\phi_c)_0$ is the value of the phase shift at the critical angle at the highest measured temperature. The solid line is a theoretical fit by LdG theory. To 1% accuracy, $\Gamma(\text{in } \text{Å}) = 0.252 \times \Delta\phi_c$.

the isotropic phase [1-4]. For these reasons we interpret our data in terms of LdG theory extended to the nematic side of the transition, and we find that the theory can account quantitatively for our results. Following Tarczon and Miyano [4] and ignoring possible surface biaxiality [12], we assume a δ -function surface potential and minimize a Sheng free-energy functional [3] to find the profile of the order parameter $Q(z)$ and its surface value Q_0 . We find

$$Q(z) - Q_b = \frac{2a'R(Q_0 - Q_b)e^{z/\xi}}{[R(Q_0 - Q_b)e^{z/\xi} + b'/3]^2 - a'c/2}, \quad (1)$$

where

$$R(Q_0 - Q_b) = Q_0^{-1} [2a']^{-1/2} \left[\frac{1}{2} a' - \frac{1}{3} b' Q_0 + \frac{1}{4} c Q_0^2 \right]^{1/2} + a'/Q_0 - \frac{1}{3} b',$$

$$\xi = (2L/a')^{1/2}, \quad a' = a(T - T^*) - 2bQ_b + 3cQ_b^2,$$

$$b' = b - 3cQ_b.$$

Here a , b , c , L , and T^* are material constants of the LC [13] and Q_0 and Q_b are the surface and bulk order parameters. Note that the functional form of $Q(z)$ is identical to that obtained in Ref. [4] for the isotropic case with the Landau constants transformed and Q_0 replaced by $Q_0 - Q_b$. The temperature dependence of Q_0 is given by minimizing the interfacial free energy, as described in Ref. [3]. The adsorption parameter Γ is calculated by direct integration of the order-parameter profile. The functional form of Γ is again identical to that obtained in the isotropic case and the exact expression can be read off from Ref. [4] with the above-mentioned substitutions. When the limit $T \rightarrow T_c$ is taken, we find

$$\Gamma = \begin{cases} 2\sqrt{L/c} \ln(|Q_0|/Q_c) + \dots, & Q_0 \neq 0, \\ \sqrt{L/c} \ln[(T_c - T)/T_c] + \dots, & Q_0 = 0, \end{cases} \quad (2)$$

where the temperature dependence of Q_0 has been temporarily ignored. This result has an appealingly simple physical interpretation. For $Q_0 = 0$, the thickness of the disordered layer diverges to infinity as $T \rightarrow T_c$ from below (complete dewetting), since the quasi-isotropic layer is stabilized by the the $Q = 0$ minimum of the bulk free energy. This is perfectly analogous to the result for the isotropic side of the transition, where complete wetting occurs when the surface order parameter Q_0 exceeds the threshold value Q_c of the nematic bulk order parameter at T_c . In that case, the macroscopically thick nematiclike layer is stabilized by the $Q = Q_c$ minimum of the bulk free energy. Though derived within the framework of LdG theory, it seems reasonable to suppose that the qualitative result obtained here is model independent.

Unfortunately, the usual LdG bulk free-energy density, with constant coefficients determined from measurements on the isotropic phase, seriously overestimates the nematic

bulk order parameter. To remedy this problem, Yokoyama has adopted for the nematic phase a Landau free energy with temperature-dependent coefficients [9,10], chosen to match the experimentally measured temperature dependence of the bulk nematic order parameter [14], as well as the usual LdG free energy at $T = T_c^+$ and the known entropy discontinuity at $T = T_c$. As shown below, this modified LdG free energy for the bulk used in our calculation can yield a good quantitative description of our experimental results.

In order to fit the temperature dependence of Γ on both sides of the transition, it is necessary to choose a specific form for the surface free-energy density. We use the Sluckin-Poniewierski form [1,12],

$$F_0(Q_0) = (-GQ_0 + \frac{1}{2} U_1 Q_0^2) \delta(z),$$

which may be regarded as the first two terms of a Landau expansion of the surface free energy. Note that for $G < 0$ and $U_1 > 0$, the surface energy will be lowered by reducing Q_0 (assuming $Q_0 > 0$), so the model predicts dewetting or surface disordering in the nematic phase. To generate our theoretical curves, we used the following procedure. At each temperature, we calculated Q_0 by minimizing the interfacial free energy [3], and then determined the entire order-parameter profile $Q(z)$ using Eq. (1) for $T < T_c$ or the corresponding equation (Ref. [4]) for $T > T_c$. We inferred the profile of the dielectric tensor $\epsilon(z)$ using the relation $\Delta\epsilon(z) = Q(z)(\Delta\epsilon)_{\max}$, where $\Delta\epsilon = \epsilon_{\perp} - \epsilon_{\parallel}$ is the dielectric anisotropy [14]. Finally, the phase shift at the critical angle $\Delta\phi_c$ is calculated by numerical integration of Maxwell's equations, using a 4×4 matrix method [15].

By adjusting the surface free-energy parameters G and U_1 , we could match the observed temperature dependence of Γ on both sides of the transition temperature (see Figs. 1 and 2). Contrary to the anchoring energy experiments [8,9], we find that our data can be fitted only with $G < 0$; specifically, $G = -6.8 \times 10^{-9}$ J/cm² and $U_1 = 9.0 \times 10^{-9}$ J/cm² give the best fit [16]. With these parameter values, $Q_0(T_c^-) = 0.14$ and $Q_0(T_c^+) = -0.047$. Our value of $Q_0(T_c^-)$ is substantially larger than those inferred from the anchoring energy experiments [$Q_0(T_c^-)_{\text{Yokoyama}} = 0.04$, $Q_0(T_c^-)_{\text{Faetti}} = 0.008$]. This may be due to our use of a thinner SiO_x aligning layer [17], chosen to minimize the temperature-independent phase contribution from the SiO_x. The discrepancy may also result from theoretical difficulties in inferring the surface order parameter from the anchoring energy. The deviation of the experimental Γ points from the theoretical prediction at low temperatures in Fig. 1 should be noted. Our use of a truncated power series for the nematic free energy is probably responsible, since this approximation worsens as $T_c - T$ increases, especially when Q_b and Q_0 are not small.

In summary, we have observed pretransitional surface-induced ordering (with a negative order parameter) and

disordering of 5CB adjacent to a SiO_x -coated surface. This compliments the previous studies of surface-induced ordering in isotropic LCs [2,4] and confirms that LdG theory for surface-induced effects can be quantitatively correct even in the nematic regime. Future work should complete the picture by examining *enhanced* order at the nematic-wall interface, expected for systems showing complete wetting in the isotropic phase. The observation of surface biaxiality would also be interesting, since all experiments to date have used the simple theory with a scalar order parameter, although the more correct theory involves a tensor order parameter. Finally, any effect of external fields on the pretransitional wetting behavior would be very interesting. LdG theory predicts a critical point in the bulk I - N transition [18] at a critical electric field of $\approx 13 \text{ V}/\mu\text{m}$ applied along the nematic director, with complete wetting going over to partial wetting as the bulk transition goes from first to second order. The effect of the field on the wetting behavior should be observable at much lower fields however. The problem of pretransitional wetting in LCs is a very rich one, with much experimental work yet to be done.

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