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Optical Studies of Pretransitional Surface Ordering and Disordering in Liquid Crystals

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OPTICAL STUDIES OF PRETRANSITIONAL SURFACE ORDERING AND DISORDERING IN LIQUID CRYSTALS

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Abstract The Landau-deGennes theory predicts interesting pretransitional surface behavior at the interface between a liquid crystal and a smooth or rough substrate. In the former case, we propose a simple form for the liquid crystal-substrate interaction which yields enhanced surface ordering in the nematic and a uniaxial-biaxial transition in the isotropic phase. For the experimentally accessible range of liquid crystal-substrate interaction strengths, the experimentally observed pretransitional behavior in the isotropic phase is in excellent agreement with the theory. For the case of a rough substrate, pretransitional surface disordering in the nematic is predicted and measured directly by evanescent-wave ellipsometry, while pretransitional random-planar surface ordering occurs in the isotropic phase.

Surface ordering in liquid crystals (LCs) is a subject of both practical and basic scientific interest. Several recent experiments have demonstrated the existence of a surface layer having enhanced orientational order, whose thickness increases as the isotropic-nematic (I-N) transition is approached from above.[1,2] The results are usually explained in terms of the Landau-deGennes (LdG) theory,[3] which predicts that the thickness of the ordered surface layer either remains finite (partial wetting) or diverges

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(complete wetting) as $T \rightarrow T_c^+$, depending on the strength of the LC-substrate interaction. LdG theory predicts analogous surface pretransitional phenomena in the nematic, where the presence of an ordered or a disordered surface layer is possible depending on the surface boundary condition. In the first part of this paper, we present a simple model for the interaction between a LC and a substrate favoring random-planar ordering.[4] In the isotropic phase, the theory predicts a uniaxial-biaxial surface transition near T_{NI}, above a threshold value of the LC-substrate interaction strength, and a pretransitional uniaxial surface layer with negative order parameter below that threshold. The latter prediction shows good agreement with experiment carried out with evanescent-wave ellipsometry. In the second part, we present direct experimental observation of the disordered surface layer at the nematic LC-rough substrate interface using the evanescent-wave ellipsometry technique.[5] Random-planar surface wetting is observed in the isotropic phase. Both nematic and isotropic pretransitional phenomena are explained quantitatively with LdG theory, using a LC-substrate interaction appropriate for a rough substrate.

We begin by considering the problem of the orientational ordering in a semi-infinite LC medium in the half-space $z > 0$, adjacent to a smooth substrate at $z = 0$ favoring random-planar alignment. We first note that although the bulk is uniaxial, spontaneous symmetry-breaking may result in a biaxial surface layer. We are therefore obliged to consider a biaxial tensor order parameter of the form[6,7]

$$Q_{ij} = S\,(n_i\, n_j - \delta_{ij}/3) + P\,(l_i\, l_j - m_i\, m_j) \tag{1}$$

where $(\underline{l}, \underline{m}, \underline{n})$ are orthonormal unit vectors. We expect the biaxial order parameter P to vanish as $z \rightarrow \infty$, so we recover the usual expression for the order parameter of a uniaxial nematic,[8] where $\underline{n}$ is the director. The LC-substrate interaction H_S, in the spirit of Landau theory, is given by the lowest order scalar formed from Q and $\underline{e}$, the surface normal:

$$H_S = G\,[S\,(\underline{n}.\,\underline{e})^2 - 1/3) + P(\underline{l}.\,\underline{e})^2]\,\delta(z) \tag{2}$$

Here we have chosen $\underline{l}$ in the ne-plane, and assumed that the range of the interaction is short. The positive constant G describes the strength of the interaction. The LdG expression for the bulk free energy density, in the Sluckin-Poniewierski model,[7] is given by

$$f = p(S, P, T) + L\left(\frac{dS}{dz}\right)^2 + G\,\delta(z)\,[(S - P)\cos^2\psi + (P - S/3)] \tag{3}$$

$$p(S, P, T) = a\,(T - T^*)\,(S^2 + 3P^2) - B\,S\,(S^2 - 9P^2) + C\,(S^2 + 3P^2)^2$$

where ψ is the angle between the director $\underline{n}$ and the substrate normal $\underline{e}$, T^* is the minimum supercooling temperature, and a ,B , C, and L are material constants. For the liquid crystal 4'-n-pentyl-4-cyanobiphenyl (5CB),[9] $a = .065$ J/cm^3/K, $B = .53$ J/cm^3, $C = .98$ J/cm^3, and $L = 4.5 \times 10^{-14}$ J/cm. We may transform to dimensionless variables by $u = C\,S/B$, $v = C\,P/B$, $\xi = B\,z/\sqrt{C\,L}$, $t = a\,C\,(T - T_{NI})/B^2$, $g = C^{3/2}\,G/B^2\,\sqrt{L}$, and $T_{NI} = T^* + B^2/4aC$. Then the dimensionless surface layer free energy F we will minimize is given by

$$F = g\left[\left(v_S - \frac{u_S}{3}\right) + (u_S - v_S)\cos^2\psi\right] + \int_0^\infty d\xi\left[p(u, v, t) - p(u_B, 0, t) + \left(\frac{du}{d\xi}\right)^2\right] \qquad (4)$$

Here $u_S = u(z = 0)$ and $v_S = v(z = 0)$ are surface order parameters, and u_B is the bulk order parameter. The bulk order parameter is found as usual by minimizing the bulk free energy density $p(u_B, 0, t)$ with respect to u_B.

The surface phase behavior may be obtained from the minimization of the surface layer free energy. One finds that the surface phase diagram is determined by the magnitude of the LC-substrate interaction parameter g (see Fig. 1). The theory predicts a threshhold value $g_c = .126$. For $g < g_c$, the interface is partially wet in the isotropic phase by a uniaxial, random-planar layer. In the nematic phase, the surface and bulk alignment is homogeneous ($\psi = \pi/2$) with no difference between surface and bulk order parameters. For $g > g_c$, there is a temperature range above T_{NI} for which the surface layer is biaxial. The biaxial surface layer thickness diverges as $T \rightarrow T_c^+$. In the nematic phase, the interface is partially wet by a uniaxial surface layer ($\psi = \pi/2$) of enhanced order as $T \rightarrow T_c^-$. Finally, for $g > g_o = 1.109 > g_c$, the surface layer behavior remains qualitatively the same, but the uniaxial-biaxial surface phase transition occurs below T_{NI}.

For the special case $v = 0$, the Euler-Lagrange equation resulting from the minimization of equation (4) can be solved exactly. The result is

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$$u(\xi) = u_B - \frac{2\beta A}{\alpha A - \sqrt{\beta}\, A^2 \exp\left(\sqrt{\beta}\,\xi\right) + \left(\sqrt{\beta} - \dfrac{\alpha^2}{4\sqrt{\beta}}\right)\exp\left(-\sqrt{\beta}\,\xi\right)} \tag{5}$$

where $\alpha = 4\,u_B - 1$

$$\beta = 6\,u_B^2 - 3\,u_B + t + \frac{1}{4}$$

$$A = \frac{\sqrt{\beta} + \sqrt{(u_S - u_B)^2 + \alpha\,(u_S - u_B) + \beta}}{u_S - u_B} + \frac{\alpha}{2\sqrt{\beta}}$$

and the surface order parameter u_S can be found by minimizing (4) with respect to u_S.

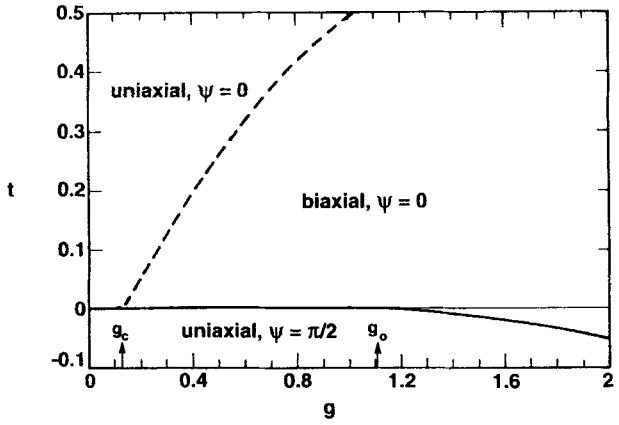

FIGURE 1 Boundary-layer phase diagram as a function of t and g. The solid line denotes a first-order phase transition, and the dashed line denotes a second-order phase transition.

For the case of $g < g_c$, equation (5) predicts partial wetting of the LC-substrate interface by a random-planar aligned surface layer above T_{NI}. This prediction was verified experimentally using the evanescent-wave ellipsometry technique.[1] The measured quantity was the phase shift $\Delta\phi_c$ between p- and s-polarized components of a HeNe laser beam reflected from the glass/LC interface at the critical angle θ_c. The sample cell was prepared by sandwiching a 130 μm film of 5CB between a high refractive index glass prism and a glass plate. The prism surface in contact with the LC was either acid-cleaned

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or acid-cleaned and coated with a layer of the surfactant MAP. The phase shift $\Delta\phi_c$ can be shown to be proportional to the integrated birefringence Γ at the interface,

$$\Delta\phi_c = 2\,\kappa\sqrt{L/C}\,\Gamma, \text{ where}$$

$$\Gamma = \int_o^\infty d\xi\,[u(\xi) - u_B] = \ln\left(\frac{\alpha - 2\sqrt{\beta}\,(1+A)}{\alpha + 2\sqrt{\beta}\,(1-A)}\right) \qquad (6)$$

and $\kappa = 3.37 \times 10^{-3}$ Å^{-1} depends only on the material optical constants. The phase shift was measured at a series of temperatures approaching T_{NI} from above (see Fig. 2). The values of the LC-substrate interaction parameter g can be deduced from the theoretical fits to the data. The fits yield g = .033 for the clean glass surface and g = .036 for the MAP-coated surface. For these values of the interaction parameter, the theory predicts partial wetting of the interface by a uniaxial, random-planar layer in the isotropic phase, and no enhanced surface ordering in the nematic.

We next consider surface disordering at the interface between a LC and a rough substrate. We chose to study the interface between 5CB and an evaporated layer of silicon monoxide, since previous work has indicated the existence of a disordered surface layer.[10,11] We present the first measurement of the temperature dependence of the integrated birefringence from the interfacial region, a direct optical signature of the surface disordering.

Using evanescent-wave ellipsometry, we have measured the phase shift $\Delta\phi_c$ at a series of temperatures approaching the I-N transition (see Fig. 3). The prism surface in contact with the LC was coated with a 130 Å film of SiO_x deposited obliquely at an incident angle of 60° to the substrate normal. The resulting homogeneous monodomain alignment was confirmed by microscope observation. The marked increase in the phase shift as $T \rightarrow T_c^-$ indicates the growth of the disordered surface layer. From our fit to LdG theory, we conclude that the observed disordering is partial; the disordered surface layer thickness remains finite at the bulk transition.

We observed partial wetting of the interface by a random-planar surface layer in the isotropic phase for the same sample (see Fig. 4). Both nematic and isotropic phase pretransional behaviors are predicted by equation (5),[5] using the Sluckin-Poniewierski model[2] for the surface free energy density:

$$F_S = (-G\,S + 1/2\,U\,S^2)\,\delta(z) \qquad (7)$$

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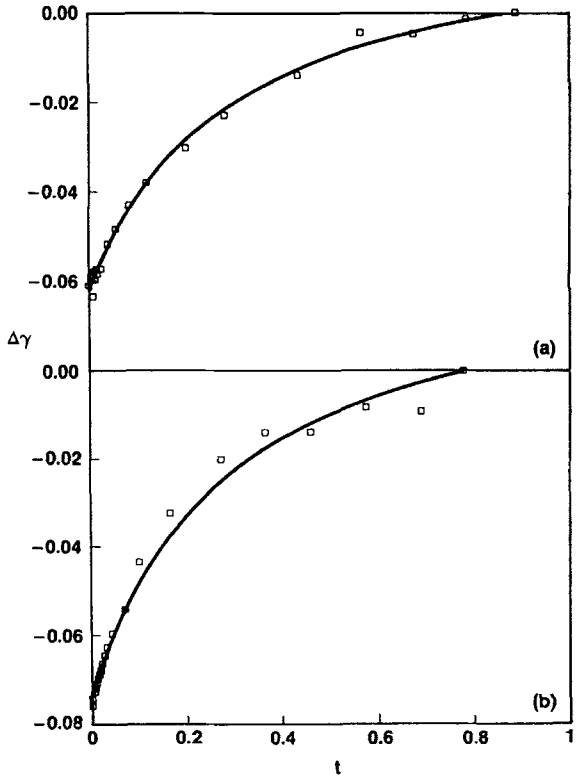

FIGURE 2 Temperature variation of $\Delta\gamma = \Gamma - \Gamma_0$, where Γ_0 is the value of Γ at the highest measured temperature. The solid lines are the one-parameter fits to the LdG theory. (a) Clean glass substrate. (b) MAP substrate.

Here we have neglected possible surface biaxiality. S is the scalar order parameter, and G and U are constants describing the strength of the substrate interaction. The previous expression (2) for the surface free energy density may not be used to describe a rough substrate since the angle ψ varies locally. From fits to the LdG theory, we obtain $G = -6.8 \times 10^{-9}$ J/cm^2, $U = 9.0 \times 10^{-9}$ J/cm^2, $S(T_c^-) = .14$, and $S(T_c^+) = -.047$.

LdG theory predicts a rich set of surface pretransitional phenomena. We have proposed a simple model for the LC-substrate interaction which predicts enhanced surface ordering in the nematic, as well as random-planar wetting and a uniaxial-biaxial

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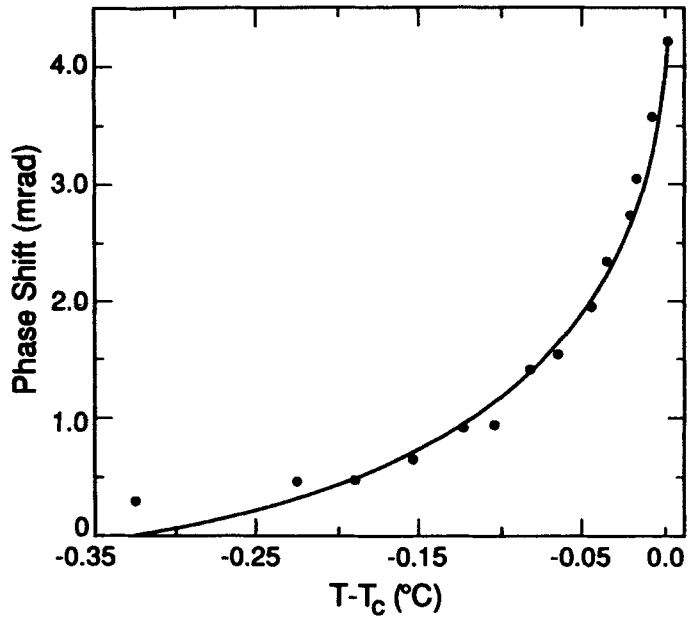

FIGURE 3 Nematic phase temperature variation of $\Delta\phi_c$ - $(\Delta\phi_c)_o$, where $(\Delta\phi_c)_o$ is the value of the phase shift at the lowest measured temperature. The solid line is a fit to LdG theory. To 1% accuracy, Γ (in Å) = - 1.82 x $\Delta\phi_c$.

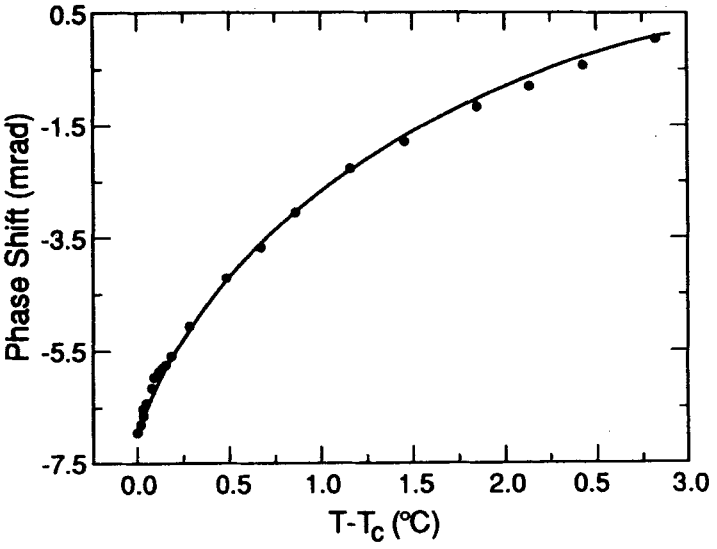

FIGURE 4 Isotropic phase temperature variation of $\Delta\phi_c$ - $(\Delta\phi_c)_o$, where $(\Delta\phi_c)_o$ is the value of the phase shift at the highest measured temperature. The solid line is a fit to LdG theory. To 1% accuracy, Γ (in Å) = 0.252 x $\Delta\phi_c$.

surface transition in the isotropic phase. Random-planar wetting on smooth and rough substrates in the isotropic phase and nematic surface disordering on rough substrates have been observed experimentally.

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