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Brief Reports

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Landau theory of wall-induced phase nucleation and pretransitional birefringence at the isotropic-nematic transition

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The Landau–deGennes theory is used to study the isotropic-nematic phase transition of a semi-infinite system having a wall which induces local nematic order. Analytic solutions are obtained and it is found that (1) for sufficient surface order, the birefringence-induced optical phase shift diverges at the transition rather than at the supercooling limit, and (2) the regions of superheating and supercooling are severely restricted.

The boundary conditions and nature of the molecular ordering and interaction at a surface have been a matter of interest in liquid-crystal systems for years.[1] It has long been known that a variety of substrate treatments, including rubbing, surfactant films, ion bombardment, and Si-O deposition, can select a direction at the surface along which the liquid-crystal molecules will preferentially orient. The way in which the local ordering thus created at the surface evolves spatially and the effect of this ordering on the pretransitional behavior near the bulk first-order isotropic-nematic phase transition of a semi-infinite sample are investigated in this work, using the Landau-deGennes theory.[2,3] The results are that the surface-induced ordering does not shift the transition temperature from that of the infinite system, but restricts the possible ranges of superheating and supercooling, essentially acting like a spontaneous nucleation site for the stable phase. Further, if the surface ordering is sufficiently high, the spontaneous spread of the local ordering away from the surface as the bulk transition temperature T_C is approached from above results in a logarithmic divergence of the optical retardation *at* T_C *rather than at the bulk supercooling limit.* We believe this to be the first example of pretransitional divergence at the temperature of a first-order transition.

The primary motivation for this work has been the birefringence measurements of Miyano[4] and his numerical analysis based on the same model used here. In addition to birefringence experiments to measure the temperature dependence of the divergence at T_C, light-scattering experiments should show enhanced scattering from the nucleation. Other experiments such as static dielectric-constant measurements should also be of interest. Thus it is expected that the behavior predicted here can be quantitatively tested.

We begin by assuming the Landau–deGennes theory for the isotropic-nematic transition, which has been widely used and gives a phenomenological expression for the free-energy density. For systems in which the director may be assumed fixed, the free-energy density reduces to a function of a single parameter, Q, equivalent to the Maier-Saupe order parameter.[5] Macroscopically, Q may be related to the anisotropy of the magnetic or electric susceptibilities while microscopically Q is determined by the degree of local orientational order. If we assume the wall to be the plane located at $z=0$ and the sample to fill the infinite half-space $z>0$, the free-energy density varies spatially only with z and is given by

$$f\left(Q, \frac{dQ}{dz}\right) = \frac{A}{2} Q^2 - \frac{B}{3} Q^3 + \frac{C}{4} Q^4 + \frac{L}{2}\left(\frac{dQ}{dz}\right)^2 . \qquad (1)$$

Equilibrium or metastable values of $Q(z)$ are those which minimize the total free energy [i.e., the integral of Eq. (1) over the volume of the sample].

The coefficient A is assumed to be $A_0(T - T^*)$ where T is the temperature and T^* the bulk supercooling limit, while B, C, and L are positive constants. Numerical values for A_0, T^*, B, C, and L may be obtained by comparison with experiment.[6] A final characteristic quantity is the zero-temperature coherence length, ξ_0, defined by $\xi_0^2 = L/A_0T^*$.

Solutions for the equilibrium and metastable states of Eq. (1) are well known for an infinite

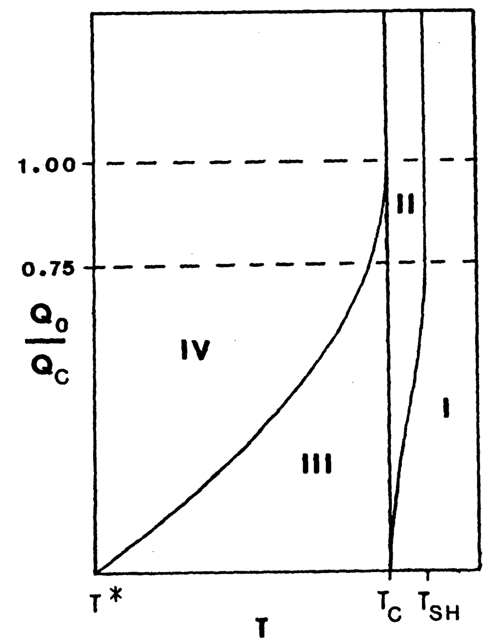

FIG. 1. For a semi-infinite system, the existence and stability of various solutions for the nematic order depend on the boundary value Q_0 and temperature. For $Q_\infty = 0$, solutions are stable in regions I and II, and metastable in III. Solutions for which $Q_\infty = Q_2 \neq 0$ are metastable in region II but stable in regions III and IV.

sample with no surface, and their regions of existence are shown in Fig. 1. The order parameter Q is independent of z and the equilibrium value jumps discontinuously from 0 to $2B/3C = Q_C$ as the temperature decreases to $T_C = T^* + 2B^2/9A_0C$. The equilibrium expressions for Q are

$$Q_1 = 0, \quad T > T_C$$
$$Q_2 = \tfrac{3}{4} Q_C(1+\phi), \quad T < T_C. \tag{2}$$

Here ϕ is $(1 - 8A/9A_C)^{1/2}$ and $A/A_C = (T - T^*)/(T_C - T^*)$. The supercooled metastable state is Q_1 for $T^* < T < T_C$ while the superheated metastable state is Q_2 for $T_C < T < T_{SH} = T^* + \frac{9}{8}(T_C - T^*)$.

For the case of the semi-infinite system, the Euler-LaGrange equation for Q is obtained by minimizing the volume integral of Eq. (1), resulting in

$$L\frac{d^2Q}{dz^2} - AQ + BQ^2 - CQ^3 = 0. \tag{3}$$

This form may be multiplied by dQ/dz and integrated over z to obtain the simpler form

$$\frac{L}{2}\left(\frac{dQ}{dz}\right)^2 = f(Q,0) - f(Q_\infty,0), \tag{4}$$

where Q_∞ is $Q(z=\infty)$ and it is assumed that $Q(z)$ approaches Q_∞ asymptotically with $(dQ/dz)_\infty = 0$ as z goes to infinity. Equation (4) can be solved analytically to obtain the following solutions which are summarized in Fig. 1.

(1) An equilibrium solution which decays from $Q(z=0) = Q_0$ to $Q(\infty) = Q_1 = 0$, valid for $T_C < T$ and any boundary value of Q, is

$$\frac{Q}{Q_C} = \frac{A}{A_C}\left[1 + R_1 \sinh\left(\frac{t^{1/2}z}{\xi_0} + \epsilon_1\right)\right]^{-1}. \tag{5}$$

Here $R_1 = |A/A_C - 1|^{1/2}$, $t = (T - T^*)/T^*$, and $\epsilon_1 = \sinh^{-1}\{[(Q_C A/Q_0 A_C) - 1]/R_1\}$. Note that as T goes to T_C, the phase shift ϵ_1 goes to $-\infty$ if $Q_0 > Q_C$ but to $+\infty$ if $Q_0 < Q_C$. For $Q_0 > Q_C$, this results in the spontaneous growth of a "knee" in $Q(z)$ as $T \to T_C$. This is illustrated in Fig. 2, and describes the nucleation of the nematic phase by the surface. The width of the nucleated nematic layer is given by the new characteristic length, $|\epsilon_1|\xi_0$, which, although it scales as ξ_0, diverges at T_C rather than at T^*, the divergence temperature of the usual coherence length, $\xi \equiv \xi_0 t^{-1/2}$, describing second-order transitions.

(2) A metastable supercooled solution which decays from Q_0 to 0 and is valid for $T < T_C$ and $Q_0/Q_C < 1 - R_1$ is

$$\frac{Q}{Q_C} = \frac{A}{A_C}\left[1 + R_1 \cosh\left(\frac{t^{1/2}z}{\xi_0} + \epsilon_2\right)\right]^{-1}, \tag{6}$$

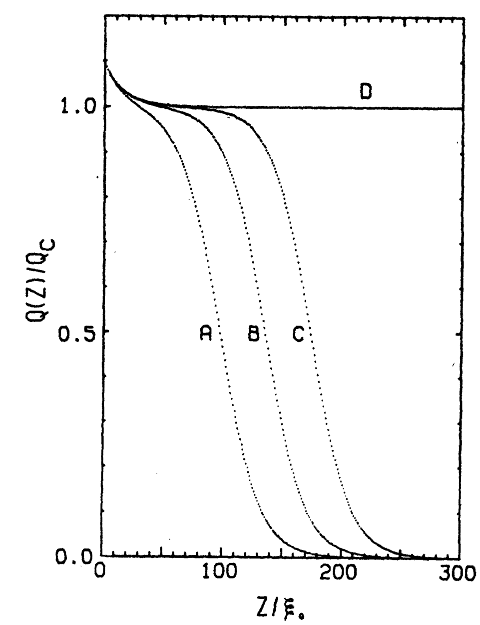

FIG. 2. Illustrated are curves showing equilibrium states of $Q(z)$ at a series of temperatures when $Q_0 Q_C = 1.1$. As A/A_C decreases, the plateau in $Q(z)$ grows resulting in a smooth crossover to a finite Q_∞ at $A/A_C = 1$. For curves A, B, C, and D the corresponding A/A_C values are 1.001, 1.0001, 1.00001, and 0.999. Values of A_0, B, and C are for 5CB (Ref. 6).

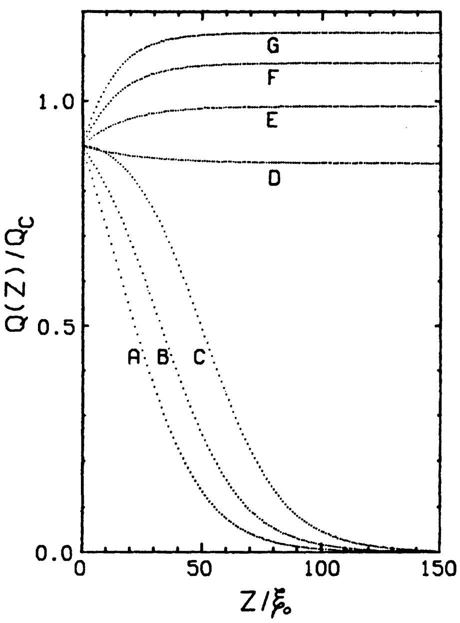

FIG. 3. Equilibrium and metastable states for $Q(z)$ with $Q_0/Q_C = 0.9$ are shown. Curves A, B, F, and G are stable solutions having A/A_C values of 1.1, 1.01, 0.9, and 0.8, respectively. Curves C, D, and E are metastable and correspond to A/A_C equal to 0.99, 1.1, and 1.01, respectively. A_0, B, and C are the same as in Fig. 2.

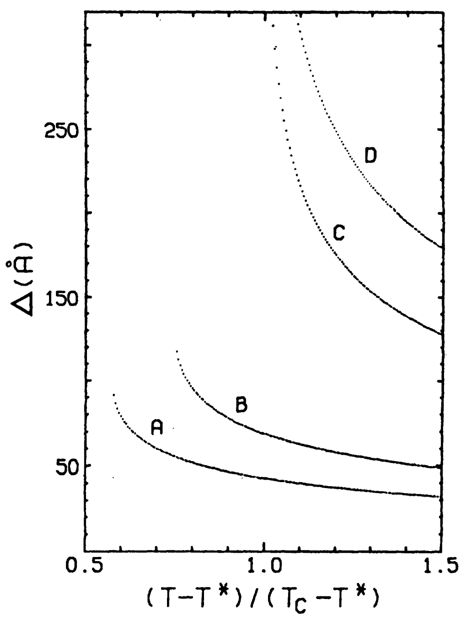

FIG. 4. Optical retardation, Δ, versus reduced temperature for various values of Q_0/Q_C. For Q_0/Q_C greater than one, Δ diverges logarithmically at $T = T_C$, while for Q_0/Q_C less than one, it does not diverge but has a square root cusp at the supercooling limit. Values of Q_0/Q_C are 0.35, 0.5, 1.1, and 1.5 for curves A, B, C, and D, respectively, and ξ_0 is assumed to be 6 Å.

where $\epsilon_2 = \cosh^{-1}\{[(Q_C A/Q_0 A_C) - 1]/R_1\}$. We stress that no supercooled solution exists for $Q_0/Q_C > 1 - R_1$. Thus, as shown in Fig. 1, there is no supercooling for $Q_0 > Q_C$, while for $Q_0 < Q_C$ there is restricted supercooling depending upon Q_0. A typical solution is shown in Fig. 3.

(3) A metastable superheated solution which has $Q_\infty = Q_2$ and is valid for $T_C < T < T_{SH}$ and $Q_0/Q_C > \frac{1}{4}(1-3\phi) + \frac{1}{2}(1-3\phi)^{1/2}$ is

$$\frac{Q}{Q_C} = \frac{3}{4}(1+\phi) + \frac{9}{2}\frac{\phi(1+\phi)}{(3\phi+1)}\left[-1 \pm R_2 \cosh\left(\frac{az}{\xi_0} + \epsilon_3\right)\right]^{-1}, \tag{7}$$

where $R_2 = |1 - 9\phi(1+\phi)/(3\phi+1)^2|^{1/2}$, $a^2 = 9\phi(1+\phi) \times (T_C - T^*)/4T^*$, $\epsilon_3 = \cosh^{-1}(\pm R_3/R_2)$, and

$$R_3 = 1 + 9\phi(1+\phi)/\{2(3\phi+1)[Q_0/Q_C - 3(1+\phi)]\}.$$

The upper (+) sign is used if $Q_0 > Q_2$ while the lower (−) sign is relevant for $Q_0 < Q_2$. Here we find restricted superheating for $Q_0 < Q_2$ depending upon Q_0, as shown in Fig. 1. A characteristic solution is shown in Fig. 3.

(4) An equilibrium solution which has $Q_\infty = Q_2$ and is valid for $T < T_C$ and any boundary value is

$$\frac{Q}{Q_C} = \frac{3}{4}(1+\phi) + \frac{9}{2}\frac{\phi(\phi+1)}{(3\phi+1)}\left[-1 \pm R_2 \sinh\left(\frac{az}{\xi_0} + \epsilon_4\right)\right]^{-1}, \tag{8}$$

where $\epsilon_4 = \sinh^{-1}(\pm R_3/R_2)$ and the upper and lower signs apply in the same manner as previously. See Fig. 2.

Finally, the mean-field behavior of the optical retardation is easily found by considering the phase difference, Δ, between the ordinary and extraordinary waves transmitted through a slab of thickness D,

$$\Delta \propto \int_0^D (n_e - n_0)\,dz\ , \tag{9}$$

where n_e and n_0 are the indices of refraction of the extraordinary and ordinary waves, respectively. If it is assumed that the independent molecule model is adequate so that the system polarizability is simply related to the molecular polarizability (i.e., local-field corrections are not too severe), then it is readily found that $n_e - n_0$ is proportional to $Q(z)$. Thus the phase shift may be found by analytically integrating Eq. (9). Using Eq. (5) for $Q(z)$ and taking the limit $D \to \infty$, the result for $T > T_C$ is

$$\int_0^\infty dz\, Q = \xi_0\left(\frac{T^*}{T_C - T^*}\right)^{1/2} \ln\left(\frac{[1+(1+R_1^2)^{1/2} - R_1][(1+R_1^2)^{1/2} - \tanh(\epsilon_1/2) + R_1]}{[(1+R_1^2)^{1/2} - 1 + R_1][(1+R_1^2)^{1/2} + \tanh(\epsilon_1/2) - R_1]}\right) . \qquad (10)$$

For $Q_0 > Q_C$, $\epsilon_1 \to -\infty$ as $T \to T_C$, and the knee develops, leading to a divergence of Δ, while for $Q_0 < Q_C$, $\epsilon_1 \to +\infty$ and Δ remains finite. Expanding for small R_1^2 and $Q_0 > Q_C$ we find $\Delta \propto -\ln R_1^2$. Therefore, Δ is expected to diverge logarithmically as $T \to T_C$ but only for $Q_0 > Q_C$, as shown in Fig. 4.

If $Q_0 < Q_C$, $\epsilon_1 \to +\infty$ as $T \to T_C$, and Δ continues smoothly below T_C as Q enters onto the supercooled branch as shown in Fig. 4. As the limit of supercooling is approached, dQ/dz goes to zero at the surface and Δ has a divergent derivative (a cusp), but no divergence. In particular, $\Delta \cong K_1 - K_2 |T - T_t|^{1/2}$ so $d\Delta/dT$ has a square-root cusp at $T = T_t$, the supercooling limit for $Q_0 < Q_C$. T_t is defined by $Q_0/Q_C = 1 - R_1$, and K_1 and K_2 are constants.

In conclusion, we have discussed a system in which there is a pretransitional divergence at the temperature of a first-order phase transition. The usual coherence length is still finite and the divergence is related to the second characteristic length $|\epsilon_1|\xi_0$ which is the "thickness" of the nucleated nematic layer. We stress that the experimental data of Miyano[4] strongly suggest a divergence at T_C. It would be interesting to know whether his data are consistent with a divergence which is both logarithmic and located at the bulk first-order transition temperature. Our calculation is valid only in the mean-field regime and the divergence may be altered if critical fluctuations are important.

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[6] As an example, values of A_0, T^*, B, and C for the compound 5*CB* are given by H. J. Coles, Mol. Cryst. Liq. Cryst. 49, 67 (1978). These values are used in the numerical data shown in Figs. 2, 3, and 4 and are $A_0 = 0.13 \times 10^6$ J m^{-3} K^{-1}, $B = 1.6 \times 10^6$ J m^{-3}, $C = 3.9 \times 10^6$ J m^{-3}, and $T^* = 34\,°$C.