Theory of nematic surface ordering via a Berezinskii-Kosterlitz-Thouless phase transition

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For a surface interaction quadratic in the magnitude of the order parameter and favoring an in-plane molecular orientation, it is shown that a nematic surface state with quasi-two-dimensional order can exist in a narrow temperature range above the bulk transition point. This phase is characterized by fully biaxial order and the transition between it and the fully disordered one is via the Berezinskii-Kosterlitz-Thouless (BKT) mechanism. The BKT transition temperature is calculated as are the elastic and inelastic light-scattering intensities. The latter is a possible technique for observing the transition and confirming its BKT character. Numerical estimates indicate that systems having the surface interactions required to exhibit this type of nematic phase transition can be prepared.

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I. INTRODUCTION

The possibility of observing two-dimensional phase transitions in liquid-crystal systems has been of long-standing interest [1]. However, while a great deal of attention, both theoretical and experimental, has been devoted to the transitions in thin smectic layers, much less has been paid to the intrinsically simpler nematic system. The principal reason for this is that free-standing smectic films are mechanically stable over relatively long time periods while nematic ones are not.

On the other hand, a properly prepared bounding surface can preferentially orient liquid-crystal molecules in the vicinity of the interface [2] even when there is no bulk order (i.e., for $T > T_c$, where T_c is the bulk critical temperature at which a weak first-order phase transition from the isotropic to the uniaxially ordered nematic state occurs). Of course, such nematic-type surface ordering decays rapidly with distance from the boundary. There have been a number of studies in this area [3–10] due to the importance of surface ordering for liquid-crystal device applications and also for fundamental research.

Here we shall consider a type of interface coupling, which leads to surface ordering in an otherwise isotropic liquid-crystal phase. We shall show that this coupling, under specified conditions, can result in *fully biaxial order* within a surface layer and that this order appears via a continuous phase transition from the disordered phase. This naturally leads to the possibility that this phase, which is quasi-two-dimensional, disorders via defect unbinding, i.e., through the Berezinskii-Kosterlitz-Thouless (BKT) mechanism [11,12]. Our study is therefore a comprehensive development of earlier work by Sluckin and Poniewierski [6], who noted that particular surface potentials could result in surface ordering and BKT-type phase transitions.

A crucial ingredient in realizing such a phase transition is the character of the coupling between the liquid-crystal molecules and the bounding surface. In order to quantify this, we shall use a macroscopic description based upon a second-order traceless-tensor order parameter [13]. A convenient choice is

$$\epsilon_{ij} = \epsilon_{ij}^D - \tfrac{1}{3}\mathrm{Tr}(\epsilon^D)\delta_{ij} , \tag{1}$$

where ϵ_{ij}^D is the dielectric tensor. We take $z = 0$ as the bounding surface and consider potentials wherein (a) there is isotropy within this surface and (b) the molecules prefer to lie in the plane. Specifically, we shall be interested in the case wherein the dominant surface coupling contribution to the free energy has the form

$$F_s = -\tfrac{1}{2} \int g_1 \epsilon_{\alpha\beta}^2 \delta(z) d^3r . \tag{2}$$

Here $\alpha, \beta = 1, 2$ and g_1 (> 0) is a coupling parameter.

We shall show that this surface interaction, for sufficiently large g_1 and temperatures $T_s > T > T_c$, leads to quasi-two-dimensional order essentially characterized by

$$\epsilon_{\alpha\beta} = \sqrt{2}\epsilon_b(n_\alpha n_\beta - \tfrac{1}{2}\delta_{\alpha\beta}) ,$$
$$\epsilon_{i3} = \epsilon_{3j} = 0 , \tag{3}$$

where $\hat{n}$ is the nematic director and $i, j = 1, 2, 3$. It will follow that the phase transition at $T = T_s$ is of the BKT type.

We note, however, a surface coupling satisfying the two conditions noted above can have the more general form

$$\tilde{F}_s = \int g\epsilon_{33}\delta(z)d^3r - \tfrac{1}{2}\int g_1 \epsilon_{\alpha\beta}^2 \delta(z) d^3r , \tag{4}$$

with $g > 0$ a second coupling parameter [6]. Then (3) generalizes to

$$\epsilon_{ij} = \begin{bmatrix} \epsilon_{\alpha\beta} - \frac{1}{2}\epsilon_{33}\delta_{\alpha\beta} & 0 \\ 0 & \epsilon_{33} \end{bmatrix} , \tag{5}$$

and, among possible configurations, we can consider as limiting cases

$$\epsilon_{11} = -\epsilon_{22}, \quad \epsilon_{12} = \epsilon_{21} = \epsilon_{33} = 0 , \tag{6a}$$

$$2\epsilon_{11} = -\epsilon_{22} = -\epsilon_{33}, \quad \epsilon_{12} = \epsilon_{21} = 0 , \tag{6b}$$

$$2\epsilon_{33} = -\epsilon_{11} = -\epsilon_{22}, \quad \epsilon_{12} = \epsilon_{21} = 0 . \tag{6c}$$

The first of these is identical to (3)—it describes a fully biaxial state. The other two describe uniaxial states, with the direction $\hat{n}$ lying, respectively, within and perpendicular to the boundary plane. Of course, ϵ_{ij} can in general have intermediate biaxiality, with two (rather than one) independent amplitudes at a point **r**.

Which order parameter configuration is the stable one depends upon the parameters g_1 and g and the temperature. In the following section, we shall calculate the total free energy and show, for $g = \epsilon_{33} = 0$, that (6a) is the stable surface state where g_1 is sufficiently large. We then find the transition temperature T_s at which this state becomes unstable via a BKT mechanism. Next, we show that such a phase transition is stable with respect to the corrections arising when g and ϵ_{33} are small. We estimate the magnitudes of these corrections as well as those arising from an external field applied normal to the surface (for the case of negative anisotropy).

In Sec. III, we consider the effect of fluctuations on the intensity of light scattering near the BKT phase transition. For this type of transition, disclinations can play a role, resulting in the renormalization of the parameters appearing in the order parameter correlation function which, in turn, determines the scattered-light intensity. We calculate both elastic and inelastic light-scattering intensities.

In the final section, we review our results and introduce typical values for the parameters appearing in our calculation. These numerical estimates indicate that this phase transition is indeed possible. We conclude by discussing techniques for confirming this experimentally by observing the fully biaxial BKT surface state in nematic liquid-crystal systems.

II. THE SURFACE-INDUCED PHASE TRANSITION

A. The basic model

Consider a nematic liquid crystal confined to the half-space $z > 0$. The appropriate Landau–de Gennes free energy, assuming that the surface interaction has the form $\tilde{F}_s$ given in (4), is then [13]

$$F = \int d^3r \left[\frac{1}{2}(a\epsilon_{ij}^2 + c_1\epsilon_{ij,l}^2 + c_2\epsilon_{ij,i}\epsilon_{lj,l}) \right.$$
$$- \beta\epsilon_{ij}\epsilon_{yl}\epsilon_{li} + \gamma(\epsilon_{ij}^2)^2 + g\epsilon_{33}\delta(z)$$
$$\left. - \frac{1}{2}g_1\epsilon_{\alpha\beta}^2\delta(z) \right] , \tag{7}$$

where a is proportional to a reduced temperature; c_1, c_2, β, and γ are temperature-independent constants;

$\epsilon_{ij,l} \equiv \partial\epsilon_{ij}/\partial x_l$; and we sum on repeated indices. As before, latin indices (i,j,l) run from 1 to 3 and greek (α,β) from 1 to 2.

We simplify our notation by setting

$$\epsilon_{ij} = s\mu_{ij}, \quad s = \beta/\sqrt{6}\gamma, \quad f = F/(\beta^4/36\gamma^3) ,$$

$$\frac{1}{4}t = (3\gamma/\beta^2)a, \quad \frac{1}{4}\xi^2 = (3\gamma/\beta^2)c_1, \quad \rho = c_2/c_1 , \tag{8}$$

$$g = (\beta^3/6\sqrt{6}\gamma^2)\xi v, \quad g_1 = (\beta^2/6\gamma)\xi v_1 .$$

Then (7) becomes

$$f = \int d^3r \left\{ \frac{1}{4}[t\mu_{ij}^2 + \xi^2(\mu_{ij,l}^2 + \rho\mu_{ij,i}\mu_{lj,l})] \right.$$
$$- \sqrt{6}\mu_{ij}^3 + (\mu_{ij}^2)^2 + \xi v\mu_{33}\delta(z)$$
$$\left. - \frac{1}{2}\xi v_1\mu_{\alpha\beta}^2\delta(z) \right\} . \tag{9}$$

We now assume that the system is uniform in the x-y plane [i.e., $\mu_{ij} = \mu_{ij}(x)$]. Setting $\zeta = z/\xi$ then gives

$$f/A\xi = \int_{0-}^{\infty} d\zeta[\frac{1}{4}(t\mu_{ij}^2 + \mu_{ij,3}^2 + \rho\mu_{3j,3}^2)$$
$$- \sqrt{6}\mu_{ij}^3 + (\mu_{ij}^2)^2 + v\mu_{33}\delta(\zeta)$$
$$- \frac{1}{2}v_1\mu_{\alpha\beta}^2\delta(\zeta)] , \tag{10}$$

where differentiation is now with respect to ζ. The usual (first-order) transition to an ordered bulk phase occurs at $t = 1$.

Consider now the special case $g = v = 0$. (The relaxation of this constraint will be discussed later.) The form of the order parameter which will certainly be relevant when v_1 is sufficiently large [with respect to the coefficient of the cubic term in (10) is the two-dimensional one of (6a). We therefore consider the ansatz

$$\mu_{ij}^{(b)} = \frac{1}{\sqrt{2}}\mu_b(z) \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{bmatrix} , \tag{11}$$

and, from (1),

$$f_b/A_\xi = \int_{0-}^{\infty} d\zeta[\frac{1}{4}t\mu_b^2 + \frac{1}{4}(\mu_b')^2 + \mu_b^4 - \frac{1}{2}v_1\mu_b^2\delta(\zeta)] , \tag{12}$$

where the prime denotes $d/d\zeta$. Note particularly that the cubic contribution to f_b vanishes; the phase transition to $\mu_{ij}^{(b)} \neq 0$ can be of second order.

Setting the variation $\delta f_b = 0$ yields the Euler-Lagrange equation

$$\frac{1}{2}\mu_b'' - \frac{1}{2}t\mu_b - 4\mu_b^3 = 0 , \tag{13}$$

whose solution is

$$\mu_b = \frac{\sqrt{t}}{2\sinh(\sqrt{t}\zeta + \psi_b)} . \tag{14}$$

The constant of integration ψ_b is fixed by the boundary condition

$$-\mu_b'(\zeta = 0) = v_1\mu_b(\zeta = 0) \tag{15a}$$

to be

$$\coth\psi_b = v_1/\sqrt{t} . \tag{15b}$$

Since coth $\psi_b \geq 1$, we immediately find that a surface state characterized by $\mu_b \neq 0$ can exist (according to Landau theory) whenever

$$1 < t < v_1^2 . \tag{16}$$

As an extreme alternative to the above ordering, consider the uniaxial order parameter given in (6b). In our present notation

$$\mu_{ij}^{(u)} = \frac{1}{\sqrt{6}} \mu_u(z) \begin{bmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} , \tag{17}$$

with, from (10),

$$f_u / A \tilde{\xi} = \int_{0^-}^{\infty} d\zeta \left[\frac{1}{4} t \mu_u^2 + \frac{1}{4}(\mu_u')^2 - \mu_u^3 + \mu_u^4 \right.$$

$$\left. - \frac{5}{12} \tilde{v}_1 \mu u_u^2 \delta(\zeta) \right] . \tag{18}$$

Here $\tilde{\xi} = \xi \sqrt{1+\rho/6}$, $\tilde{v}_1 = v_1/\sqrt{1+\rho/6}$, and $\zeta = z/\tilde{\xi}$. Proceeding as before, we have the Euler-Lagrange equation

$$\frac{1}{2}\mu_u'' - \frac{1}{2} t \mu_u + 3\mu_u^2 - 4\mu_u^3 = 0 , \tag{19}$$

whose solution is

$$\mu_u = \frac{t}{2[1 + \sqrt{t-1} \sinh(\sqrt{t}\,\xi + \psi_u)]} . \tag{20}$$

The constant of integration ψ_u is found from the boundary condition

$$\mu_u'(\zeta=0) = \frac{5}{6}\tilde{v}_1 \mu_u(\zeta=0) \tag{21a}$$

to be

$$\psi_u = \ln \left[\frac{a_0 - (a_0^2 + a_1^2 - 1)^{1/2}}{1 - a_1} \right] , \tag{21b}$$

with

$$a_0 = \frac{5\tilde{v}_1}{6\sqrt{t(t-1)}}, \quad a_1 = \frac{5\tilde{v}_1}{6\sqrt{t}} . \tag{21c}$$

By comparing the free energies f_b and f_u, we can determine which order parameter configuration, $\mu_{ij}^{(b)}$ or $\mu_{ij}^{(u)}$, is necessarily irrelevant at a given point (t, v_1). This is most easily done by using the connection between the derivative term and the remainder of the bulk free-energy density given by the first integrals of the Euler-Lagrange equations (13) and (19). We obtain

$$f_b / A \xi = \frac{t^{3/2}}{24} \left[\coth\psi_b - 1 - 2\cosh\psi_b / \sinh^3\psi_b \right] , \tag{22a}$$

$$f_u / A \xi = \frac{\sqrt{(1+\rho/6)(t-1)} t^{5/2}}{24} \left\{ \left[-2/d^3 - 1/2td^2 - (2t-3)/2t^2 d \right] \cosh\psi_u - (2t-3)/2(t-1)^{1/2} t^2 \right.$$

$$\left. + \frac{3(t-1)^{1/2}}{t^{5/2}} \left[\text{arctanh} \left[\frac{1-\sqrt{t-1}}{\sqrt{t}} \right] - \text{arctanh} \left[\frac{\tanh(\psi_u/2) - \sqrt{t-1}}{\sqrt{t}} \right] \right] \right\} , \tag{22b}$$

with ψ_b and ψ_u given by (15b) and (21b), respectively.

In Fig. 1, we show, for $\rho=0$ and 1, the phase diagram in the $(t>1, v_1)$ plane when the only allowed ground states are $\mu_{ij}=0$ (the disordered state), $\mu_{ij}^{(b)}$, and $\mu_{ij}^{(u)}$. As expected, $\mu_{ij}^{(b)}$ is irrelevant for $v_1 \gtrsim 2$ while $\mu_{ij}^{(u)}$ does not exist at larger v_1 values. This is easily understood physically—for large v_1, the surface term in f dominates the cubic one. Since the numerical coefficient multiplying v_1 is greater for the case of $\mu_{ij}^{(b)}$ than for $\mu_{ij}^{(u)}$, the former is therefore energetically favored. For small values of v_1, the opposite is true.

Of course, the above analysis does not prove, even within Landau theory, that either $\mu_{ij}^{(b)}$ or $\mu_{ij}^{(u)}$ is necessarily the ground-state anywhere. In fact, it is easy to see that neither rigorously fulfills this role. For example, consider the modified order parameter

$$\mu_{ij} = \frac{1}{\sqrt{2}} \begin{bmatrix} \mu_b + \alpha & 0 & 0 \\ 0 & -\mu_b + \alpha & 0 \\ 0 & 0 & -2\alpha \end{bmatrix} , \tag{23}$$

with $\alpha(z) \ll \mu_b(z)$. To $O(\alpha^2)$, we have

$$f = f_b + \int_{0^-}^{\infty} d\zeta \left[\frac{3}{4} t \alpha^2 + \frac{3}{4}(1 + \frac{2}{3}\rho)(\alpha')^2 \right.$$

$$\left. - 3\sqrt{3}\alpha\mu_b^2 - \frac{1}{2} v_1 \alpha^2 \delta(\zeta) \right] , \tag{24}$$

and setting $\delta_\alpha f = 0$ gives the Euler-Lagrange equation

$$-(1 + \frac{2}{3}\rho)\alpha'' + t\alpha = 2\sqrt{3}\mu_b^2 . \tag{25}$$

It is clear from (25) that $\alpha=0, \mu_b \neq 0$ is not a rigorous solution for the ground state, even when $g = v = 0$. However, it is also evident that, to lowest order, α is not linearly proportional to μ_b and that the continuous character of the disordered-to-$\mu_{ij}^{(b)}$ phase transition is therefore unaffected by this admixture. We conclude that this transition will still be of the BKT type and that, close to the phase boundary, the $\alpha=0$ approximation to the order parameter is a reasonable one. $O(\alpha)$ corrections will be estimated in Sec. II C.

B. BKT phase transition

As we have shown, a phase characterized essentially by the order parameter $\mu_{ij}^{(b)}$ exists for $v_1 \gtrsim 2$ and $1 < t < t_s$, where $t_s(v_1)$, is the phase boundary between the surface ordered and disordered phases. We now calculate this
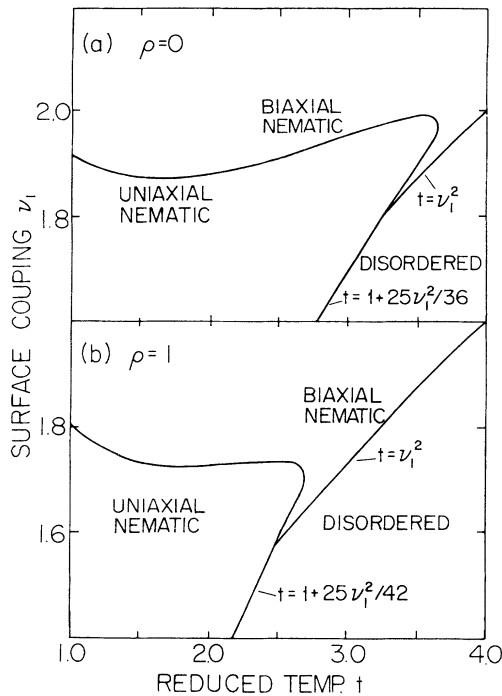
FIG. 1. Phase diagram in the (t, v_1) space with (a) $\rho = 0$ and (b) $\rho = 1$. The system is restricted to be in one of three possible states, the disordered one $(\mu_{ij} = 0)$, the fully biaxial one $(\mu_{ij}^{(b)})$, and the uniaxial one $(\mu_{ij}^{(u)})$.

temperature by considering the BKT mechanism, which is relevant to continuous phase transitions in two-dimensional systems [11,12].

According to BKT, phase transitions occur due to long-wavelength in-plane distortions (fluctuations) in a two-dimensional layer. The standard form for the relevant free energy associated with such distortions is [14]

$$F_{BKT} = \tfrac{1}{2}K \int d^2r (\nabla n_\alpha)^2 , \qquad (26)$$

where n_α $(\alpha = 1,2)$ are the in-plane components of the nematic director and K is a stiffness (elastic) coefficient.

Our surface-ordered nematic system can also be regarded as effectively two dimensional with an effective stiffness coefficient K_b arising from the bulk elastic constants c_1 and c_2. To see this, we return to (9) and consider arbitrary fluctuations about the ground-state configuration $\mu_{ij}^{(b)}$. We then obtain [15] a term having the form (26) with

$$K_b/c_1\xi = (2\beta^2/3\gamma^2)(1 + \rho/2)\int_0^\infty d\zeta\, \mu_b^2$$
$$= (\beta^2/6\gamma^2)(1 + \rho/2)(v_1 - \sqrt{t}) . \qquad (27)$$

As there is no purely two-dimensional system underlying the ordered surface layer, the critical temperature associated with the BKT phase transition is given by [16]

$$\lim_{T \to T_S-} K_b = \frac{8}{\pi} k_B T_S , \qquad (28)$$

where k_B is Boltzmann's constant. Using (27), we obtain finally

$$(v_1 - \sqrt{t_s}) = 48\gamma^2 k_B T_s/\beta^2(1 + \rho/2)\pi c_1\xi . \qquad (29)$$

We shall evaluate (29) numerically in the final section.

C. Modifications to the basic model

We have already noted that even with only a quadratic surface term, the order parameter is not fully biaxial due to the cubic invariant in the bulk free energy. Here we examine this and two other sources of modifications of the order parameter—the second surface energy term [proportional to v in (9)] and the effect of an external electric field applied along $\hat{z}$ when the nematic material has a negative dielectric (or, for the equivalent care of an applied magnetic field, magnetic) anisotropy.

In an external field, there is a further contribution to f of the form

$$f_a/A\xi = \int d\zeta\, \mu_{33}e^2 , \qquad (30a)$$

where

$$e = |3\gamma^2/2\pi\beta^3|^{1/2}E \qquad (30b)$$

or

$$e = |6\gamma^2\chi_{33}/\beta^3\epsilon_{33}|^{1/2}H \qquad (30c)$$

for the case of an electric or magnetic field, respectively. [For the latter, χ_{33} is an element of the traceless part of the magnetic susceptibility tensor χ_{ij}. The algebraic sign of the integral in (30a) is connected with the system's negative dielectric or magnetic anisotropy.]

We now examine the effect of these modifications on $\mu_{ij}^{(b)}$. Considering an order parameter having the form (23) with α now arbitrary. Adding (30a) to (10), the corresponding free energy is

$$f/A\xi = f_b + \int_{0-}^\infty d\zeta[\tfrac{3}{4}t\alpha^2 + \tfrac{3}{4}(1 + \tfrac{2}{3}\rho)(\alpha')^2 - 3\sqrt{3}\alpha\mu_b^2$$
$$- 5\sqrt{3}\alpha^3 + 6\alpha^2\mu_b^2 + 9\alpha^4 - 2e^2\alpha$$
$$- \tfrac{1}{2}v_1\alpha^2\delta(\xi) - 2v\alpha\delta(\xi)] . \qquad (31)$$

In general, the coupled Euler-Lagrange equations for μ_b and α obtained from (31) can only be solved numerically. However, the lowest-order corrections to K_b arising from $\alpha \neq 0$ can be easily calculated and the self-consistency of neglecting them verified. Neglecting terms of $O(\alpha^3)$ or higher (including $\alpha^2\mu_b^2$) in (31) and setting $\delta_\alpha f = 0$, we obtain

$$-(1 + \tfrac{2}{3}\rho)\alpha'' + t\alpha = \tfrac{4}{3}e^2 + 2\sqrt{3}\mu_b^2 , \qquad (32a)$$

where μ_b is the solution given in (14) and (15). The associated boundary condition is

$$-(1 + \tfrac{2}{3}\rho)\alpha'(z = 0) = \tfrac{2}{3}[v + v_1\alpha(z = 0)] . \qquad (32b)$$

Equation (32) can be solved explicitly (in fact, analytically for $\rho = 0$) and we summarize the lowest-order corrections to K_b arising from the α component of the order parameter. These are

$$\delta K^{(1)}/K_b = O(1/v_1^2) \ , \tag{33a}$$

$$\delta K^{(2)}/K_b = O(v/v_1^3; v^2/v_1^4) \ , \tag{33b}$$

$$\delta K^{(3)}/K_b = O(e^4/v_1^6) \ . \tag{33c}$$

Here $\delta K^{(1)}$ is the additional contribution to K_b existing even when $v = e = 0$, as discussed in Sec. II B. The other two, $\delta K^{(2)}$ and $\delta K^{(3)}$, arise from $v \neq 0$ and $e \neq 0$, respectively. Any of these corrections, when sufficiently large, suppresses the transition to a BKT phase.

For self-consistency, we therefore require that all $\delta K^{(i)}/K_b$ be small. Clearly, the strictest constraint is that on $\delta K^{(1)}$ as this correction is intrinsic. We therefore conclude that a BKT-type phase transition is possible provided that $v_1^2 \gg 1$. Since, as shown in Fig. 1, we require $v_1 \gtrsim 2$ in any case, it is clear that this constraint can, in principle, be satisfied.

III. FLUCTUATIONS AND LIGHT SCATTERING

We now consider the effect of fluctuations on the behavior of our system near the BKT phase transition point T_s. It is well known [12] that, in this region, all thermodynamic quantities scale as powers of the correlation length ξ_+ (defined as the length over which order persists for $T > T_s$) and that ξ_+ has an essential singularity at T_s of the form

$$\xi_+ = \xi \exp\left[-\frac{\text{const}}{|T - T_s|^{1/2}} \right], \quad T > T_s \ . \tag{34}$$

For $T < T_s$, $\xi_+ = \infty$.

It is convenient to parametrize the two-dimensional director field n_α by an angle θ [$\hat{n} = (\cos\theta, \sin\theta)$]. When T exceeds T_s, the BKT mechanism results in a finite density of free disclinations which inhibit nematic order in the surface layer. It is therefore necessary to take such disclinations into account. This has been done for the case of the smectic-$C - A$ transition in freely suspended thin films [17]. With slight modifications, we can use the expression given in [17] for the director angle correlation function

$$G(\mathbf{q}, \omega) \equiv \langle \theta(\mathbf{q}, \omega)\theta(-\mathbf{q}, -\omega) \rangle$$

$$= \frac{2\Gamma k_B T}{\omega^2 + \Gamma^2 K_b^2(q^2 + \xi_+^{-2})^2} \ . \tag{35}$$

Here $\theta(\mathbf{q}, \omega)$ is the Fourier component of $\theta(\mathbf{r}, t)$ with wave vector $\mathbf{q}$ and frequency ω and Γ is the usual kinetic coefficient (which has no singularity at T_s) characterizing the relaxation of θ. Its inverse Γ^{-1} has the dimension (and physical meaning) of the torsional viscosity γ_1 in nematic liquid crystals. Note that the coefficients Γ and K_b in (35) are both renormalized by disclinations.

To obtain the light-scattering cross section, we must evaluate the correlation function $\langle \epsilon_{\alpha\beta}(\mathbf{r}, t), \epsilon_{\gamma\delta}(0,0) \rangle$. Consider, for example, an experimental configuration wherein the light is in the x-z plane and is initially polarized along y. Then the intensity $I(\mathbf{q}, \omega)$ of scattered light due to orientational fluctuations is dominated by the correlation function

$$I(\mathbf{q}, \omega) = M \langle \cos[2\theta(\mathbf{q}, \omega)] \cos[2\theta(-\mathbf{q}, -\omega)] \rangle \ , \tag{36}$$

where $M = \epsilon_a^2 \omega^4 / 8\pi^2 c^4$ (ϵ_a is the dielectric anisotropy and c the velocity of light) is the usual factor relating the light-scattering intensity to the correlation function of the fluctuations.

Rather than calculating $I(\mathbf{q}, \omega)$ directly from (36), consider the first $I(\mathbf{r}, t)$. As a consequence of the Gaussian distribution of the θ fluctuations

$$I(\mathbf{r}, t) = M \exp\{ -4[G(0,0) - G(\mathbf{r}, t)] \} \ , \tag{37}$$

where $G(\mathbf{r}, t)$ is the Fourier transform of $G(\mathbf{q}, \omega)$, i.e.,

$$
\begin{aligned}
G(\mathbf{r}, t) &= \frac{2\Gamma k_B T}{(2\pi)^3} \int \int \frac{d\omega\, d^2q \exp(-i\omega t + i\mathbf{q}\cdot\mathbf{r})}{\omega^2 + \Gamma^2 K_b^2(q^2 + \xi_+^{-2})^2} \\
&= \frac{k_B T}{4\pi^2 K_b} \int \frac{d^2q}{q^2 + \xi_+^{-2}} \\
&\quad \times \exp[-\Gamma K_b(q^2 + \xi_+^{-2})t + i\mathbf{q}\cdot\mathbf{r}] \ .
\end{aligned}
\tag{38}
$$

Setting $g(\mathbf{r}, t) = G(0,0) - G(\mathbf{r}, t)$, (38) gives

$$
\begin{aligned}
g(\mathbf{r}, t) = \frac{k_B T}{4\pi^2 K_b} \int \frac{d^2q}{q^2 + \xi_+^{-2}} \\
\times \{ 1 - \exp[-\Gamma K_b(q^2 + \xi_+^{-2})t \\
+ i\mathbf{q}\cdot\mathbf{r}] \}
\end{aligned}
\tag{39a}
$$

and

$$
\begin{aligned}
\frac{\partial g(\mathbf{r}, t)}{\partial t} &= \frac{\Gamma k_B T}{4\pi^2} \int d^2q \exp\{ [-\Gamma K_b(q^2 + \xi_+^{-2})t + i\mathbf{q}\cdot\mathbf{r}] \} \\
&= \frac{k_B T}{4\pi K_b t} \exp(-\Gamma K_b \xi_+^{-2}t - r^2/4\Gamma K_b t) \ .
\end{aligned}
\tag{39b}
$$

We then have

$$
\begin{aligned}
g(\mathbf{r}, t) = g(\mathbf{r}, 0) + \frac{k_B T}{4\pi K_b} \int_0^t \frac{1}{t'} \exp(-\Gamma K_b \xi_+^{-2}t' \\
- r^2/4\pi\Gamma K_b t') dt' \ .
\end{aligned}
\tag{39c}
$$

We obtain finally for the scattered-light intensity

$$I(\mathbf{q}, \omega) = M \int d^2r\, dt \exp[-4g(\mathbf{r}, t) + i\omega t - i\mathbf{q}\cdot\mathbf{r}] \ . \tag{40}$$

While we cannot evaluate (40) analytically, we can obtain the dependence of $I(\mathbf{q}, \omega)$ on $\mathbf{q}$ and ω in some limiting cases. First, we note from (39) that the single-time correlation function $g(\mathbf{r}, 0)$ has the following limiting forms:

$$g(\mathbf{r}, 0) = \frac{k_B T}{2\pi K_b} \ln\left| \frac{r}{l} \right|, \quad r \ll \xi_+ \tag{41a}$$

$$g(\mathbf{r}, 0) = \frac{k_B T}{2\pi K_b} \ln(\xi_+/l), \quad r \gg \xi_+ \ , \tag{41b}$$

where l is the usual short-length cutoff for logarithmically divergent integrals [like that in (39c)]. In our case, $l \approx \xi$, which characterizes the thickness of the surface ordered layer.

From (40) and (41), it follows that the integrated intensity $I(q) = \int d\omega\, I(q,\omega)$ is

$$I(q) \approx \begin{cases} \dfrac{\text{const}}{q^{2-x}} & \text{for } q\xi_+ \gg 1 \\[2ex] \dfrac{\text{const}}{\xi_+^x q^2} & \text{for } q\xi_+ \ll 1 \ , \end{cases} \tag{42a}$$

where the exponent x is

$$x = 2k_B T / \pi K_b \ . \tag{42b}$$

It follows from (15) that, at the phase transition point T_s, $x = \frac{1}{4}$.

Similarly, one can find the dependence of $I(q,\omega)$ on q and ω in different limiting cases. We obtain

$$I(q,\omega) \approx \begin{cases} M\dfrac{1}{\omega q^{2-x}}, & q\xi_+ \gg 1, \quad \omega \gg \Gamma K_b \xi_+^{-1} q & \text{(43a)} \\[2ex] M\dfrac{1}{q^2(\Gamma K_b \xi_+^{-2})^{x/2}\omega^{1-(x/2)}}, & q\xi_+ \gg 1, \quad \Gamma K_b \xi_+^{-2} \ll \omega \ll \Gamma K_b q^2 & \text{(43b)} \\[2ex] M\dfrac{1}{\omega q^2}, & q\xi_+ \gg 1, \quad \omega \ll \Gamma K_b \xi_+^{-2} & \text{(43c)} \\[2ex] M\dfrac{1}{\omega \xi_+^x q^2} & q\xi_+ \ll 1 \text{ for all } \omega \ . & \text{(43d)} \end{cases}$$

Note that in all these expressions for $I(q,\omega)$, the critical behavior near the BKT phase transition enters only through the correlation length ξ_+.

IV. DISCUSSION

In Sec. II, we showed, for a particular type of surface interaction, that a phase transition to a BKT state with its characteristic two-dimensional order becomes possible. This state is expected to exist in a narrow temperature region (see below) above the bulk nematic ordering temperature.

However, a BKT phase is possible only when the reduced coefficient v_1 of the quadratic (in the order parameter) surface coupling interaction is sufficiently large ($\gtrsim 2$). In physical units

$$g_1 = (\beta^2 c_1/3\gamma)^{1/2} v_1 \ , \tag{44a}$$

and, taking as typical values [4,18], $\beta/\sqrt{6} = 0.53 \times 10^7$ erg/cm^3, $\gamma = 0.98 \times 10^7$ erg/cm^3, and $\frac{1}{2}c_1 = 4.5 \times 10^{-7}$ erg/cm, we have

$$g_1 = 2.3 v_1 \text{ erg/cm}^2 \ . \tag{44b}$$

We thus require an in-plane quadratic surface coupling of at least 5 erg/cm^2 in order for a BKT-type phase transition to be possible. This is well within the range of surface potentials which have been obtained by various surface treatments [2]. Interfaces characterized by interaction potential strengths sufficient for testing the predicted phase transition can therefore very likely be prepared.

However, an additional requirement was noted in Sec. II; i.e., the reduced coefficient v of the second symmetry-allowed surface interaction term should (when taken together with the lower bound on v_1 itself) satisfy

$$v/v_1 = (\beta/\sqrt{6}\gamma)(g/g_1) \lesssim 1 \ . \tag{45a}$$

Using the values noted above, this is equivalent to require that

$$g/g_1 \lesssim 0.1 \ . \tag{45b}$$

That is, g must be less than 0.5 erg/cm^2. In itself, this is not unreasonable; the crucial point, of course, is to achieve this while simultaneously having g_1 greater than 5 erg/cm^2. This dual requirement must be realized in order to make the observation of a BKT phase experimentally feasible.

Assuming that the required conditions are met, the BKT phase transition temperature is given by (29). (Of course, the mean field value for this phase transition is just $t = v_1^2$.) Using the typical values given above and assuming that $T_s \approx T_c \approx 350$ K, we obtain $\xi = 79$ Å and

$$v_1 - \sqrt{t_s} = 0.59/(1+\rho/2) \ . \tag{46a}$$

For $v_1 = 2$, we have

$$t_s = \begin{cases} 2.0 & \text{for } \rho = 0 \\ 2.6 & \text{for } \rho = 1 \ . \end{cases} \tag{46b}$$

Since the reduced unit of temperature $t = 1$ is of the order of 0.5–1 K [19], we find that the BKT phase should exist in a temperature region 1–2.5 K above the transition to the bulk nematic phase for $g_1 = 5$ erg/cm^2.

One possible technique for observing a surface phase transition is via evanescent-wave ellipsometry [7–9]. In this approach, one measures the phase difference Δ between p- and s-polarized incident laser light totally reflected from the liquid-crystal boundary at the critical angle. This phase difference is directly proportional to the integrated birefringence at the interface. In Landau theory

$$\Delta \sim \int_0^\infty d\zeta \mu_b(\zeta) \sim \ln \tanh(\psi_b/2)$$

$$\sim (v_1/\sqrt{t} - 1)^{1/2} \quad \text{as} \quad \psi_b \to \infty \ . \tag{47}$$

The critical behavior of Δ appears only through its dependence on the reduced temperature t. It follows that confirmation of a BKT character for the phase transition by this technique would be difficult. This is not surprising as the singularities associated with static critical behavior are very weak for this type of transition.

For this reason, dynamic critical behavior studies are likely to be more fruitful. Inelastic light-scattering measurements, together with the theoretical results given in Sec. III, could provide direct experimental confirmation of a BKT surface ordered state in nematic liquid crystals.

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