Theory of nonlinear elastic behavior of nematic liquid crystals near the nematic–smectic-A phase transition*

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We calculate the smectic order-parameter contribution to the nematic elastic energy near a second-order nematic–smectic-A phase transition and show that the elastic behavior is nonlinear for large strains. We show that the Fredericksz transition in a magnetic field becomes first order to a highly strained state within 0.1 °C of the phase transition under typical experimental conditions.

I. INTRODUCTION

de Gennes[1] has predicted a dramatic increase in the bend and twist elastic constants of nematic liquid crystals near a second-order nematic–smectic-A phase transition. For the renormalized bend elastic constant he finds

$$\tilde{K}_{33}=K_{33}+\frac{\pi KT}{6d^2}\,\xi_{\parallel},\quad \xi_{\parallel}\equiv\xi_{\parallel}(T-T_{SN}) \tag{1}$$

where K_{33} is the bare bend elastic constant, d is the smectic interplanar spacing, and $\xi_{\parallel}$ is the (longitudinal) smectic correlation length. A similar expression holds for twist elastic constant K_{22}. This effect has been observed experimentally by Rayleigh light scattering,[2-4] Fredericksz transition,[5-7] and other methods.[8,9] In the Fredericksz experiment one orients the liquid crystal homeotropically (director normal to the glass surfaces) by a suitable coating of the glass slides and applies a magnetic field perpendicular to the director. One can show easily from the free energy, Eq. (3), that above a critical field H_c the liquid crystal tilts over in the direction of the field. The transition is second order with

$$H_c=\frac{\pi}{l}\left(\frac{\tilde{K}_{33}}{\chi_a}\right)^{1/2} \tag{2}$$

where χ_a is the anisotropic part of the susceptibility and l is the sample thickness. The tilt angle at the center of the sample is given by

$$\theta(\tfrac{1}{2}l)=\text{const.}\times(H-H_c)^{1/2}.$$

This second-order behavior is observed when one is not too close to the nematic–smectic-A phase transition, and this experiment is one way of measuring $\tilde{K}_{33}/\chi_a$. However under typical experimental conditions within 0.1 K of the phase transition, the liquid crystal does not behave in the expected manner. Rather than a uniform tilted condition, one observes a "striped" texture[10] in the microscope and the elastic constant measurement fails.

In this paper we examine the elastic behavior near the nematic–smectic-A phase transition theoretically and show that, while Eq. (1) is correct for weak deformations, for large deformations the elastic behavior is nonlinear. Cladis and Torza[10] have already discussed this nonlinearity in physical terms. The transition temperature is reduced in the presence of a bend distortion and substitution of the reduced T_{SN} into Eq. (1) gives the nonlinear elastic behavior. Our derivation (Sec. II) shows that this procedure is correct to within a numerical constant. We then show that near the phase transition the Fredericksz transition becomes first order to a state with $\theta(\frac{1}{2}l)\approx\frac{1}{2}\pi$. These nonlinear effects become important about 0.1 K above the phase transition. However the tilted state is still spatially uniform, and the theory does not explain the appearance of the striped texture. Cladis and Torza explain the "stripes" as a corrugation of the smectic–nematic interface which should appear below T_{SN} in pure material.

II. NONLINEAR ELASTIC BEHAVIOR

We first study the elastic behavior of a nematic liquid crystal near a second-order nematic–smectic-A phase transition and derive an expression for the elastic free energy in the nonlinear regime.

We begin with the free-energy expression used previously by de Gennes[1] and McMillan.[11] The Oseen-Frank nematic free energy is

$$F_1=\int d^3r\{\tfrac{1}{2}K_{11}(\vec{\nabla}\cdot\vec{n})^2+\tfrac{1}{2}K_{22}[\vec{n}\cdot(\vec{\nabla}\times\vec{n})]^2+\tfrac{1}{2}K_{33}[\vec{n}\times(\vec{\nabla}\times\vec{n})]^2-\tfrac{1}{2}\chi_a(\vec{n}\cdot\vec{H})^2\}, \tag{3}$$

where $\vec{n}(\vec{r})$ is the nematic director, K_{11}, K_{22}, and K_{33} are the unrenormalized splay, twist, and bend elastic constants, and $\vec{H}$ is the magnetic field. The smectic-A free energy is

$$F_2=\int d^3r\,[a|\psi|^2+\tfrac{1}{2}b|\psi|^4 + c_\parallel|(\vec{n}\cdot\vec{\nabla}-iq_0)\psi|^2+c_\perp|\vec{n}\times\vec{\nabla}\psi|^2], \tag{4}$$

where $\psi(\vec{r})$ is the complex smectic-A phase order parameter, $q_0=2\pi/d$ where d is the smectic interplanar spacing, and one assumes $a=a'(T-T_{SN})$ with the other constants independent of temperature. The total free energy is the sum of Eqs. (3) and (4). We want to calculate the way in which the elastic behavior in the nematic phase is affected by smectic order-parameter fluctuations just above T_{SN}. We will therefore calculate the free energy of the fluctuations in the presence of a fixed bend distortion of the director. We assume $\vec{n}=\hat{z}+\delta\vec{n}$, $\delta\vec{n}=\epsilon z\hat{y}$, which gives a uniform bend distortion of magnitude $|\vec{n}\times(\vec{\nabla}\times\vec{n})|=\epsilon$ near the origin ($\vec{r}=0$). Then writing $\psi(\vec{r})=\phi(\vec{r})e^{iq_0z}$ we have

$$F_2=\int d^3r\,\phi^*\left[a-c_\parallel\frac{\partial^2}{\partial z^2}-c_\perp\frac{\partial^2}{\partial x^2}-c_\perp\left(\frac{\partial}{\partial y}-iq_0\epsilon z\right)^2\right]\phi. \tag{5}$$

We neglect the ψ^4 term in the nematic phase. We next find the eigenfunctions and eigenvalues of the operator in the square brackets. The solution is well known from the Landau diamagnetism problem:

$$\left[a-c_\parallel\frac{\partial^2}{\partial z^2}-c_\perp\frac{\partial^2}{\partial x^2}-c_\perp\left(\frac{\partial}{\partial y}-iq_0\epsilon z\right)^2\right]\phi_{n,k_x,k_y} = E_{n,k_x,k_y}\phi_{n,k_x,k_y} \tag{6}$$

with

$$\phi_{n,k_x,k_y}=\chi_n(z)e^{ik_xx+ik_yy}. \tag{7}$$

The eigenvalues are

$$E_{n,k_x,k_y}=a+c_\perp k_x^2+(2n+1)(c_\parallel c_\perp)^{1/2}q_0\epsilon. \tag{8}$$

The function $\chi_n(z)$ is centered at $z=k_y/q_0\epsilon$. Writing

$$\phi(\vec{r})=\sum_{n,k_x,k_y}C_{n,k_x,k_y}\phi_{n,k_x,k_y}(\vec{r}) \tag{9}$$

we have

$$F_2=\sum_{n,k_x,k_y}|C_{n,k_x,k_y}|^2E_{n,k_x,k_y} \tag{10}$$

assuming that ϕ_{n,k_x,k_y} are normalized.

We now integrate over the smectic order-parameter fluctuations to find the partition function:

$$Z\equiv\int\left(\prod_{n,k_x,k_y}d^2C_{n,k_x,k_y}\right)e^{-F_2/kT} = \prod_{n,k_x,k_y}\frac{\pi kT}{E_{n,k_x,k_y}}. \tag{11}$$

The partition function is a function of ϵ, and we find a nematic elastic free energy due to smectic order-parameter fluctuations

$$\tilde{F}_2\equiv-kT\ln Z=-kT\sum_{n,k_x,k_y}\ln\left(\frac{\pi kT}{E_{n,k_x,k_y}}\right). \tag{12}$$

The eigenvalue is independent of k_y, and we have $\sum_{k_y}=q_0\epsilon/2\pi$. The free energy is then

$$\tilde{F}_2=\frac{kTq_0\epsilon}{2\pi}\sum_n\int\frac{dk_x}{2\pi}\ln[a+2(n+\tfrac{1}{2})(c_\parallel c_\perp)^{1/2}q_0\epsilon+c_\perp k_x^2]. \tag{13}$$

The integral

$$\frac{kTq_0\epsilon}{2\pi}\int dx\int\frac{dk_x}{2\pi}\ln[a+2x(c_\parallel c_\perp)^{1/2}q_0\epsilon+c_\perp k_x^2] \tag{13a}$$

is a constant (independent of ϵ) and after subtracting (13a) from (13) we obtain a convergent expression for $\tilde{F}_2$.

$$\tilde{F}_2=\frac{kTq_0\epsilon}{2\pi}\int_0^1dx\sum_n\int\frac{dk_x}{2\pi}\ln\left(\frac{a+2(n+\frac{1}{2})(c_\parallel c_\perp)^{1/2}q_0\epsilon+c_\perp k_x^2}{a+2(n+x)(c_\parallel c_\perp)^{1/2}q_0\epsilon+c_\perp k_x^2}\right)+\text{const.} \tag{14}$$

Performing the k_x integration we have

$$\tilde{F}_2=\text{const.}+\frac{kTq_0\epsilon}{2\pi\sqrt{c_\perp}}\int_0^1dx\sum_n\{[a+2(n+\tfrac{1}{2})(c_\parallel c_\perp)^{1/2}q_0\epsilon]^{1/2}-[a+2(n+x)(c_\parallel c_\perp)^{1/2}q_0\epsilon]^{1/2}\}, \tag{15}$$

which is still exact. We will evaluate Eq. (15) in two limits. First, if the bend distortion is small $[\epsilon\ll a/(c_\parallel c_\perp)^{1/2}q_0]$, we can expand the second square root in Eq. (15) in powers of x, keeping terms up to second order. We then find

$$\tilde{F}_2=\text{const.}+\frac{kTq_0^2\epsilon^2}{48\pi}\left(\frac{c_\parallel}{a}\right)^{1/2}, \quad \epsilon\ll a/(c_\parallel c_\perp)^{1/2}q_0 \tag{16}$$

which is de Gennes' result since $\xi_\parallel\equiv(c_\parallel/a)^{1/2}$.

This result is valid only for weak bend distortions. For large bend distortion $[\epsilon \gg a/(c_\parallel c)^{1/2} q_0]$ we can neglect a in Eq. (15), and we find

$$\tilde{F}_2 = \text{const.} + \frac{kTq_0^2\epsilon^2}{48\pi}\left(\frac{c_\parallel}{g(c_\parallel c_\perp)^{1/2} q_0 \epsilon}\right)^{1/2}, \quad \epsilon \gg a/(c_\parallel c_\perp)^{1/2} q_0, \quad (17)$$

where

$$g^{-1/2} \equiv 24 \sum_{n=0}^{\infty} [(n+\tfrac{1}{2})^{1/2} - \tfrac{2}{3}(n+1)^{3/2} + \tfrac{2}{3} n^{3/2}] = 1.4613.$$

Thus we find that for large bend distortion the free energy increases as $\epsilon^{3/2}$. A suitable interpolation formula between these two limits is

$$\tilde{F}_2 = \text{const.} + \frac{kTq_0^2\epsilon^2}{48\pi}\left(\frac{c_\parallel}{a + g(c_\parallel c_\perp)^{1/2} q_0 \epsilon}\right)^{1/2}. \quad (18)$$

Note that $a = a'(T - T_{SN})$, so that nonlinear effects become important at smaller distortions near the phase transition.

The bend distortion ϵ has dimensions of an inverse length which is physically the distance over which the director rotates by 1 rad. The present calculation is valid provided it is carried out in a box of linear dimensions greater than the correlation length. In order to have a uniform bend over a box of this size, we require $\epsilon \xi_\parallel \ll 1$, which sets an upper limit on the bend distortion. The crossover from linear to nonlinear elastic behavior occurs at a much smaller value of bend distortion $\epsilon \sim d/\xi_\parallel^2$ so that the nonlinear calculation is valid over a wide range of ϵ.

The transition to the smectic phase in the presence of a bend distortion occurs when the lowest eigenvalue of (8) goes to zero. This occurs for

$$T = T_{SN} - (c_\parallel c_\perp)^{1/2} q_0 \epsilon / a'. \quad (19)$$

Substituting this transition temperature into de Gennes' expression, Eq. (1), gives the nonlinear free energy, Eq. (18), except for the numerical factor g.

For twist distortion a similar calculation yields

$$\tilde{F}_2 = \text{const.} + \frac{kTq_0^2\epsilon^2}{48\pi}\left(\frac{c_\perp^2}{c_\parallel(a + g c_\perp q_0 \epsilon)}\right)^{1/2}, \quad (20)$$

where $\epsilon = |\vec{n} \cdot (\vec{\nabla} \times \vec{n})|$. There is no contribution for splay distortion.

III. FREDERICKSZ TRANSITION

In this section we calculate the Fredericksz-transition behavior including the nonlinear elastic behavior. Far from the phase transition the Fredericksz transition is second order, the distortion near the critical field is weak, and H_c is not affected by the nonlinearity at large distortions.

We show that near the phase transition the Fredericksz transition is strongly first order to a state which is highly distorted. We simplify the problem somewhat by neglecting the unrenormalized elastic constants K_{ii}. Near the phase transition $\tilde{K}_{33}$ in an order of magnitude larger than K_{33} so this approximation is justified. The undistorted state has free energy $F = 0$. In the distorted state the distortion is large, and we use Eq. (17) for the free energy

$$F = \int d^3 r [\tfrac{1}{2} K'_{33} |\vec{n} \times (\vec{\nabla} \times \vec{n})|^{3/2} - \tfrac{1}{2}\chi_a (\vec{n} \cdot \vec{H})^2], \quad (21)$$

where

$$K'_{33} = \frac{kTq_0^{3/2}(c_\parallel/c_\perp)^{1/4}}{24\pi g^{1/2}}.$$

Writing

$$\vec{n} = \cos\theta\, \hat{z} + \sin\theta\, \hat{x}, \quad (22)$$

and $\vec{H} = H\hat{x}$, the free energy per unit area is

$$f = \tfrac{1}{2} K'_{33} \left(\frac{\pi}{l}\right)^{3/2} \int_0^\pi dz \left(-\alpha \sin^2\theta + \left|\frac{\partial \sin\theta}{\partial z}\right|^{3/2}\right). \quad (23)$$

Where l is the sample thickness, and $\alpha = \chi_a H^2 l^{3/2} / K'_{33} \pi^{3/2}$. The boundary conditions on the tilt angle θ at the glass surfaces are $\theta(0) = \theta(\pi) = 0$. Expanding $\theta(z)$ in a Fourier series,

$$\theta(z) = \sum_{n \text{ odd}} \theta_n \sin nz. \quad (24)$$

We can find the free energy as a function of the parameters θ_n. Since we seek the state of lowest free energy, we can treat the θ_n as variational parameters and minimize the free energy with re-

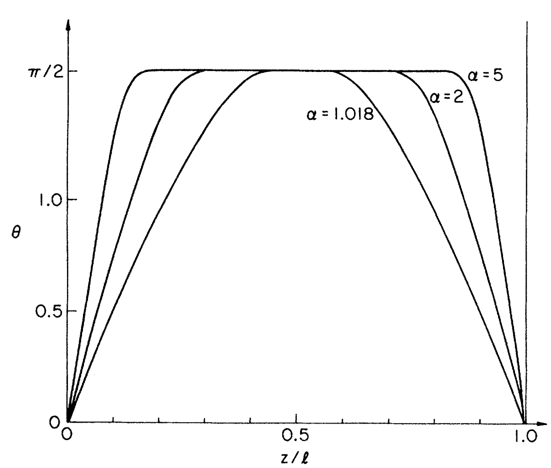

FIG. 1. Tilt angle $\theta(z)$ versus position at the critical field ($\alpha = 1.018$) and at higher fields.

spect to the θ_n. The minimization problem is a nonlinear one, and we use the standard trick of guessing a trial solution, linearizing the equations for the θ_n about the trial values θ_n^0, and solving the linearized problem. We then take the new solution as a trial solution and iterate this procedure until it converges. Keeping ten terms in the Fourier expansion, we find that the distorted state has negative free energy (and is thermodynamically stable) provided $\alpha > \alpha_c = 1.018$. Thus we have a first-order critical field

$$H_1 = \left(\frac{1.018 K'_{33}}{\chi_a}\right)^{1/2} \left(\frac{\pi}{l}\right)^{3/4} \tag{25}$$

which is a function of material parameters but independent of temperature. The tilt angle $\theta(z)$ in the distorted state at $H = H_1$ is shown in Fig. 1. The tilt angle in the middle of the sample is $\approx \frac{1}{2}\pi$ and rises discontinuously from zero at $H = H_1$.

When $H_1 < H_c$ one will not observe the second-order Fredericksz transition and the elastic-constant measurement fails. This occurs when $\xi_{\parallel} = 0.4(ld)^{1/2}$ (using $c_{\parallel}/c_{\perp} \approx 4$). For CBOOA[4] $\xi_{\parallel} \approx 24/(T/T_{SN} - 1)^{1/2}$Å and $d = 35$Å; so for a sample thickness of 50 μ the crossover occurs 0.07 °C above the phase transition. Thus the nonlinear elastic behavior explains the appearance of anomalous behavior in the Fredericksz experiment ≈ 0.1 °C above the phase transition.

IV. CONCLUSIONS

We have derived the nonlinear elastic behavior of a nematic liquid crystal near a second-order nematic–smectic-A phase transition and have shown that the Fredericksz transition behavior is modified.

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