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Nematic bend-splay elasticity near the nematic–smectic-A transition

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Magnetic-field-induced bend-splay deformation experiments are presented which show that the linear Frank-Oseen theory of nematic curvature elasticity is valid near a continuous nematic–smectic-A transition where smectic fluctuations dominate the bend elasticity. The results are compared with the Chu-McMillan criterion for the limit of linear response based on the smectic-A superconductivity analogy. It is shown that the success of the linear theory may be due to the unexpectedly small values of the longitudinal and transverse correlation lengths found in recent x-ray experiments.

I. INTRODUCTION

The linear theory of nematic curvature elasticity[1] has been tested near a continuous nematic–smectic-A (NA) phase transition by means of a magnetic deformation experiment. This theory had been tested earlier[2,3] for the nematic far from any smectic transition, but this is the first test of it in the regime where smectic fluctuations dominate the curvature elastic properties. In this regime the difference in the free-energy density functional between the distorted and undistorted nematic in a magnetic field $\vec{H}$ has been predicted by de Gennes[4] to be

$$f=f_c+f_s\,, \tag{1}$$

where f_c, the unrenormalized contribution due to distortions of the preferred nematic orientation axis, is

$$f_c=\tfrac{1}{2}K_{11}(\mathrm{div}\hat{n})^2+\tfrac{1}{2}K_{22}(\hat{n}\cdot\mathrm{curl}\hat{n})^2+\tfrac{1}{2}K_{33}(\hat{n}\times\mathrm{curl}\hat{n})^2-\tfrac{1}{2}\chi_a(\hat{n}\cdot\vec{H})^2\,. \tag{2}$$

K_{11}, K_{22}, and K_{33} are, respectively, the splay, twist, and bend elastic curvature coefficients of the Frank-Oseen theory,[1] which describes the preferred nematic orientation through the use of the unit vector $\hat{n}(\vec{r})$. $\chi_a=\chi_\parallel-\chi_\perp$ is the anisotropy of the diamagnetic susceptibility. The contribution due to smectic fluctuations and their coupling to the director $\vec{n}(\vec{r})$ is given by[4,5]

$$f_s=\alpha|\psi|^2+\frac{\beta}{2}|\psi|^4+\frac{1}{2M_v}\left|\frac{\partial\psi}{\partial z}\right|^2+\frac{1}{2M_T}\,|(\vec{\nabla}_T-iq_s\delta\vec{n})\psi|^2\,, \tag{3}$$

where the change in sign of α at $T=T_c$ induces a continuous NA transition if we take $\beta>0$. Thus below T_c the smectic-order parameter ψ grows continuously from zero. It is given by the complex number

$$\psi=|\psi|e^{i\phi}\,,\quad \phi=q_s u\,, \tag{4}$$

the magnitude of which is the amplitude of the smectic density wave originally introduced by McMillan[6] to describe the smectic layering. u is the normal component of the layer displacement and describes spatial distortion of the layers whose equilibrium separation is $d=2\pi/q_s$. $1/2M_{v,T}$ are related to the temperature-dependent parallel and perpendicular coherence lengths of the smectic fluctuations

$$\xi_\parallel(t)=(2M_v\alpha)^{-1/2}\,, \tag{5}$$

$$\xi_\perp(t)=(2M_T\alpha)^{-1/2}\,, \tag{6}$$

where

$$\alpha=\alpha_0 t=\alpha_0[(T-T_c)/T_c]\,. \tag{7}$$

M_T also enters the so-called penetration depths $\lambda_{2,3}$ for twist and bend distortions given, respectively, by

$$\lambda_2=q_s^{-1}(M_T K_{22}\beta/|\alpha|)^{1/2}\,, \tag{8}$$

$$\lambda_3=q_s^{-1}(M_T K_{33}\beta/|\alpha|)^{1/2}\,. \tag{9}$$

Equation (3) is strikingly similar to the Ginzburg-Landau free-energy density functional for a superconductor.[7] This fact led de Gennes to the by now well-known superconductivity–smectic-A analogy. We will discuss our experimental results in the light of this analogy.

A central feature of the analogy and the one we have focused on in the study reported here is related to the superconducting Meissner effect. It is well known that supercurrents near the surface of a superconductor shield the interior from an applied magnetic field and produce $\vec{B}=0$ at interior points more than a few penetration depths from the surface. The Meissner effect follows since the penetration depth is typically only a few thousand angstroms. In superconductors a precursor to the Meissner effect has been found[8] above T_c in the form of a fluctuation enhancement of the diamagnetic susceptibility.

Recently the analog of this fluctuation diamagnetism has been found in the suppression of bend and twist curvature fluctuations above the nematic–smectic-A transition. In the work reported here we show that the nonlinear regime which dominates the superconducting fluctuation spectrum for all but the lowest magnetic fields is absent from the liquid crystal even at very large bend distortions. These results are discussed in terms of the criterion for the onset of the nonlinear regime predicted by Eq. (1)–(3). In Sec. II we introduce this criterion and compare it with the analogous superconductivity criterion. In Sec. III we describe the experiment and the results and in Sec. IV we discuss the results in light of the superconductor analogy.

II. THEORY

Just above the superconducting transition fluctuations in the Cooper pair density are expected to enhance the diamagnetic susceptibility χ as a precursor to the Meissner effect.[7,8] Schmid[9] has calculated this fluctuation contribution in the Ginzburg-Landau approximation in the limit of weak fields. He finds

$$\delta\chi = (1/6\pi)(e/\hbar c)^2 k_B T \xi_{\mathrm{GL}} = (\pi/6)\Phi_0^{-2} k_B T \xi_{\mathrm{GL}}\,, \quad (10)$$

where ξ_{GL} is the temperature-dependent coherence length and Φ_0 is the flux quantum. In a series of definitive experiments Gollub *et al.*[8] have detected and measured this fluctuation diamagnetism as a function of both temperature and magnetic field. These experiments, although establishing the qualitative correctness of Eq. (10), have also shown that the Ginzburg-Landau approximation breaks down everywhere except very near T_c in the limit of weak field.

The liquid crystal analog of the fluctuation diamagnetism that precedes the full Meissner effect in superconductors is the fluctuation enhancement of the bend and twist elastic curvature coefficients of the nematic as a precursor to the full expulsion of bend and twist distortions in the smectic A. This happens because bend and twist distortions in the smectic do not preserve the smectic layer spacing d, and therefore couple to the lower-order layer dilation elasticity. The expressions for the divergence of the bend and twist elastic coefficients analogous to the diverging diamagnetic susceptibility given in Eq. (10) are[4]

$$\delta K_{22} = (\pi/6) k T d^{-2} (\xi_\perp^2/\xi_\parallel)\,, \quad (11)$$

$$\delta K_{33} = (\pi/6) k T d^{-2} \xi_\parallel\,, \quad (12)$$

where $\xi_\parallel$ and $\xi_\perp$ are given in Eqs. (5) and (6). Comparison of Eqs. (11) and (12) with Eq. (10) reveals that the smectic layer spacing d is analogous to the flux quantum Φ_0. Physically these are related as follows. The line integral of the scaled magnetic vector potential $\vec{A}/\Phi_0$ around a closed loop in a superconductor measures the flux enclosed in units of the flux quantum; similarly the line integral of the scaled director $\hat{n}/d$ around a closed loop in a smectic A measures the layer dilation in units of the layer spacing and therefore counts the equivalent number of line discontinuities in the layer structure. We will employ this interpretation below in the discussion of the limit of linear response. Both light scattering and magnetic field deformation experiments[10] have shown that the bend and twist coefficients do diverge as the nematic–smectic-A transition is approached from above as predicted by Eqs. (11) and (12). Furthermore, a combination of x-ray scattering measurements of $\xi_\parallel$ and light scattering measurements of δK_{33} have recently confirmed that δK_{33} does in fact diverge as $\xi_\parallel$ to within a constant of order unity,[11] in agreement with Eq. (12). So it appears that, at least in the linear approximation, the superconductor–smectic-A analogy predicts the observed behavior. But for superconductors Gollub *et al.*[8] found that the regime of linear diamagnetic response extended only to very low fields, which raises the question of whether we may also expect nonlinear elastic response for relatively gentle bend or twist distortions in liquid crystals. To answer that question it is necessary to examine the limit of validity of the weak-field calculation of Schmid.[9] He found the limit of the linear response regime to be given by

$$B \ll (\pi/2)(\Phi_0/\xi_{\mathrm{GL}}^2)\,, \quad (13)$$

which means physically that the flux linking a loop of radius equal to the coherence length must be much less than a few flux quanta. Chu and McMillan[12] have derived an analogous liquid crystal criterion for linear bend and twist elastic response based on a Landau expansion[5] equivalent to Eq. (3). They find for bend

$$|\hat{n}\times \mathrm{curl}\hat{n}| \ll (1/3\pi g)(d/\xi_\parallel \xi_\perp) \quad (14)$$

and for twist

$$|\hat{n}\cdot \mathrm{curl}\hat{n}| \ll (1/3\pi g)(d/\xi_\perp^2)\,, \quad (15)$$

where $g = 0.4683$. Physically this means that the layer dilation induced by the bend or twist over a region bounded by a loop of linear dimensions equal to an appropriate correlation length [$\xi_\perp$ for twist and $(\xi_\parallel \xi_\perp)^{1/2}$ for bend] must be much less than that which would be relaxed by an edge or screw dislocation in the layer structure. In the experiment reported here we originally thought we would be able, as we shall show, to magnetically induce a bend sufficiently large to violate the inequality (14); yet we observed no breakdown of the linear elastic theory of Eq. (2). The implications of this are discussed in Sec. IV, where an explanation for the unexpected success of the linear theory is given.

III. EXPERIMENT

The experiment performed is an extension of the usual bend Freedericksz transition experiment[13] to magnetic fields far beyond the threshold value H_c, given by

$$H_c = \frac{\pi}{D}\left(\frac{K_{33}}{\chi_a}\right)^{1/2}, \tag{16}$$

where D is the sample thickness. Above H_c the initial bend distortion appears. The geometry of this experiment is illustrated in Fig. 1, where the means of detection is also shown, namely the optical detection of the distortion induced birefringence.

The magnetic-field-induced director distortion can be calculated in the regime of linear response by finding the director configuration $\hat{n}(\vec{r}, \vec{H})$ that minimizes the Frank-Oseen free-energy functional. Therefore, the object of the experiment is to determine whether the field-induced birefringence, as measured by the phase shift $\delta(H)$ between the extraordinary and ordinary rays, is consistent with any field-induced director distortion that minimizes Eq. (2) for reasonable values of the elastic and optical coefficients. Any failure of Frank-Oseen theory to explain the data in this way would mean a breakdown of the linear theory itself, assuming that one can effectively rule out other explanations such as field-dependent boundary conditions, temperature gradients, etc. To analyze the $\delta(H)$ data in this way, it is necessary to set forth the predictions of the Frank-Oseen theory for the experiment described by Fig. 1.

A. Data analysis

For the geometry of Fig. 1 we assume by symmetry that Eq. (2) may be written as

$$f_c = \tfrac{1}{2}K_{11}\sin^2\theta\left(\frac{d\theta}{dz}\right)^2 + \tfrac{1}{2}K_{33}\cos^2\theta\left(\frac{d\theta}{dz}\right)^2 - \tfrac{1}{2}\chi_a H^2 \sin^2\theta\,, \tag{17}$$

where θ is the angle between the distorted and the undistorted director and $\theta(0) = \theta(D) = 0$ are the boundary conditions. The undistorted director is parallel to the z axis and $\vec{H}$ is along the y axis as shown in Fig. 1. Minimizing f_c with respect to the function $\theta(z)$ generates an Euler equation which may be integrated once since f_c does not contain z explicitly. The resulting first-order differential equation has solutions $\theta(z) \neq 0$ only for $H > H_c$ given in Eq. (16). Integrating the Euler equation over half the sample thickness and making a variable change gives

$$H = \frac{2H_c}{\pi}\int_0^{\pi/2}\left(\frac{1 + K'\eta\sin^2\psi}{1 - \eta\sin^2\psi}\right)^{1/2} d\psi\,, \tag{18}$$

where

$$K' \equiv K_{11}/K_{33} - 1\,, \tag{19}$$

$$\eta = \sin^2\theta_m\,,\quad \theta_m = \theta(D/2)\,. \tag{20}$$

For a sample of thickness D the birefringence induced by a finite bend-splay distortion gives

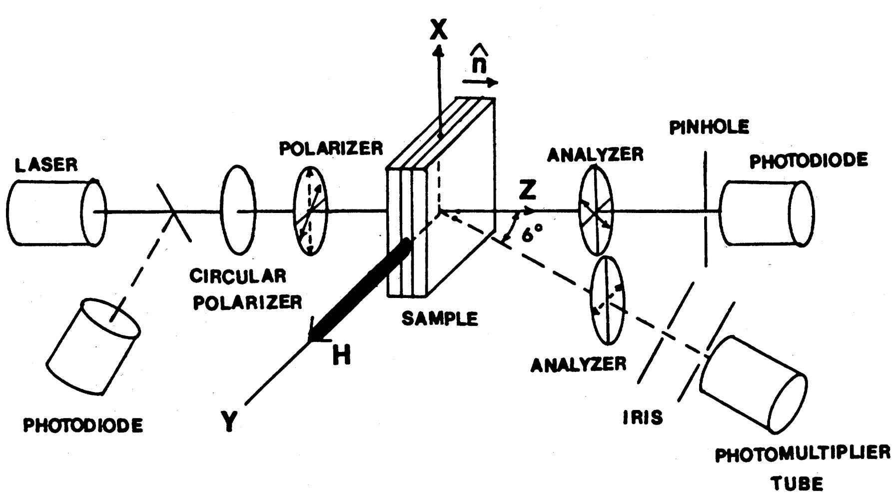

FIG. 1. Schematic illustrating geometry of the magnetic deformation and light scattering experiments. The undistorted nematic director $\hat{n}$ is along the z axis; at right angles to the magnetic field. The dashed orientation of the polarizer corresponds to the light scattering experiment.

rise to a phase shift between the ordinary and extraordinary rays given by[14]

$$\delta(H)=\frac{2\pi}{\lambda}\int_0^D dz\left(\frac{n_e n_0}{(n_e^2\cos^2\theta+n_0^2\sin^2\theta)^{1/2}}-n_0\right), \qquad (21)$$

where $\lambda = 6328$ Å (He-Ne laser), n_0 is the ordinary index of refraction, n_e is the extraordinary index of refraction, and $\theta=\theta(z,H)$. Thus for $H>H_c$ we have a distortion that may be detected optically through the field-dependent phase shift $\delta(H)$, the light intensity at the photodiode being given by

$$I(H)=I_0\sin^2\tfrac{1}{2}\delta(H). \qquad (22)$$

Making use of the Euler equation allows us to rewrite Eq. (21) as

$$\delta=\frac{2\pi n_0 D}{\lambda}\left[\int_0^{\pi/2}\left(\frac{1+K'\eta\sin^2\psi}{(1+\nu\eta\sin^2\psi)(1-\eta\sin^2\psi)}\right)^{1/2}d\psi\Big/\int_0^{\pi/2}\left(\frac{1+K'\eta\sin^2\psi}{1-\eta\sin^2\psi}\right)^{1/2}d\psi-1\right], \qquad (23)$$

where

$$\nu=(n_e/n_0)^2-1. \qquad (24)$$

Equations (18) and (23) are coupled integral equations which relate the observed phase shift $\delta(H)$ to the applied magnetic field H. The exact experimental technique for measuring $\delta(H)$ vs H is described below. Four unknown parameters K', H_c, D, and ν couple Eqs. (18) and (23) in a nonlinear way and must be fitted self-consistently. We have reduced the number of adjustable parameters in the fit by independently measing n_e and n_0 as a function of temperature on an Abbe refractometer, thus determining ν. The results are shown in Fig. 2. The nonlinear least-squares fitting procedure used is a modification of Marquardt's compromise.[15] It allows us to determine the parameters K', H_c, and D at each temperature at which the relationship $\delta(H)$ is experimentally determined. The best fits were taken to be those that minimized the square of the standard deviation defined as

$$\sigma^2=\sum_{i=1}^{N}[\delta_i-\delta(H_i)]^2\frac{1}{N-P}, \qquad (25)$$

where N is the number of data points and P is the number of adjustable parameters ($P=3$). Since δ is related to H through the implicit variable $\eta(H)$, it is necessary to determine the set $\{\eta_i(H)_i\}$ for each set of trial parameters $\{\tilde{K}', \tilde{H}_c, \tilde{D}\}$ by fitting Eq. (18). After this preliminary procedure one can calculate $\delta_i(H_i)$ and thus determine σ^2. We will not go into the technique used for adjusting the parameters after each iteration because it is a

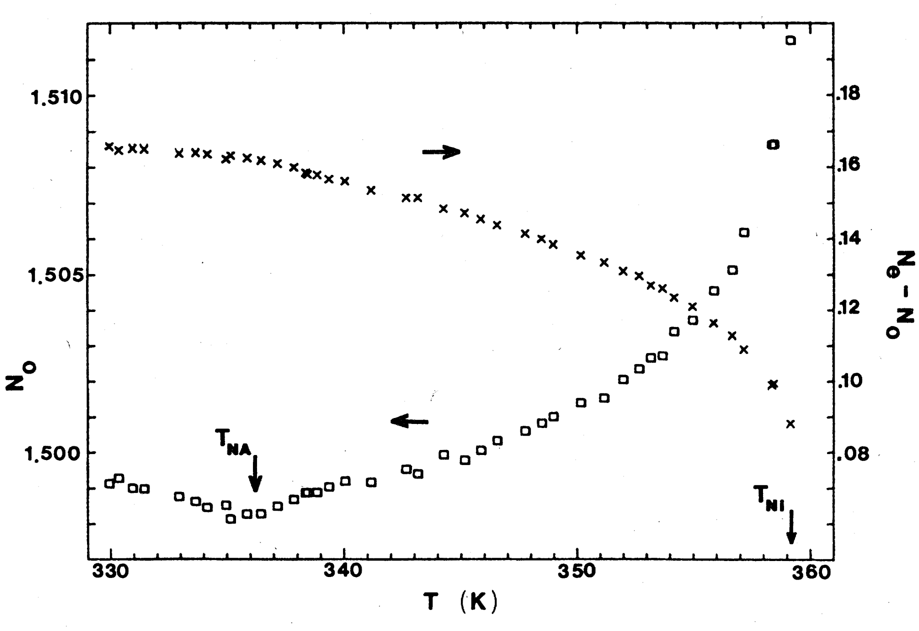

FIG. 2. The ordinary index of refraction N_0 and the birefringence $N_e - N_0$ vs temperature over the nematic and smectic-A ranges. T_{NI} and T_{NA} are the nematic–isotropic and nematic–smectic-A transition temperatures, respectively. N_e and N_0 data were taken with the aid of an Abbe refractometer augmented by an orientable polarizer on the eyepiece. The liquid crystal was homeotropically aligned between the prisms with the aid of the surfactant XZ2-2300 (see Ref. 17).

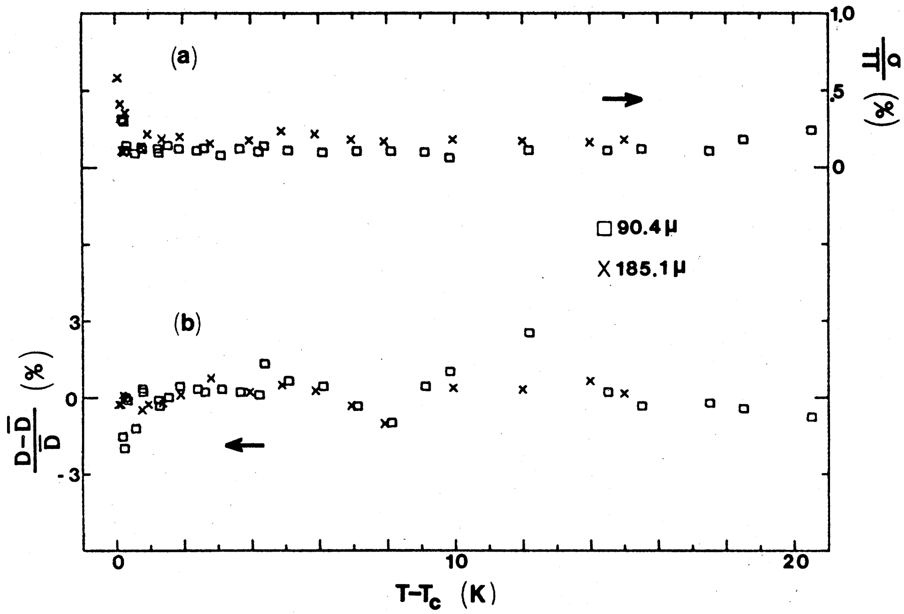

FIG. 3. (a) σ/π is the root-mean-square deviation σ of the phase-shift data from the best-fit curve [see Eq. (25)] normalized by π, the phase shift between successive extrema in $I(H)$ [see Eq. (22)]. T-T_c is the interval in temperature above the nematic–smectic-A transition T_c. Examination of deviation plots (not shown) indicates that the σ/π arise almost entirely from random deviations of the data, δ_i, about the best-fit curve $\delta(H_i)$. (b) Percent deviation of the film thickness D from the average value $\bar{D}$ where T_c is the nematic–smectic-A transition temperature. The fitted value of D should be independent of temperature in the linear regime.

straightforward generalization of the Marquardt method.

This fitting procedure yields best values for K', H_c, and D at each temperature for which $\delta(H)$ is experimentally determined. Figures 3–5 display these results as a function of $\Delta T = T - T_c$, where T_c is the NA transition temperature determined separately by the disappearance at T_c of the light

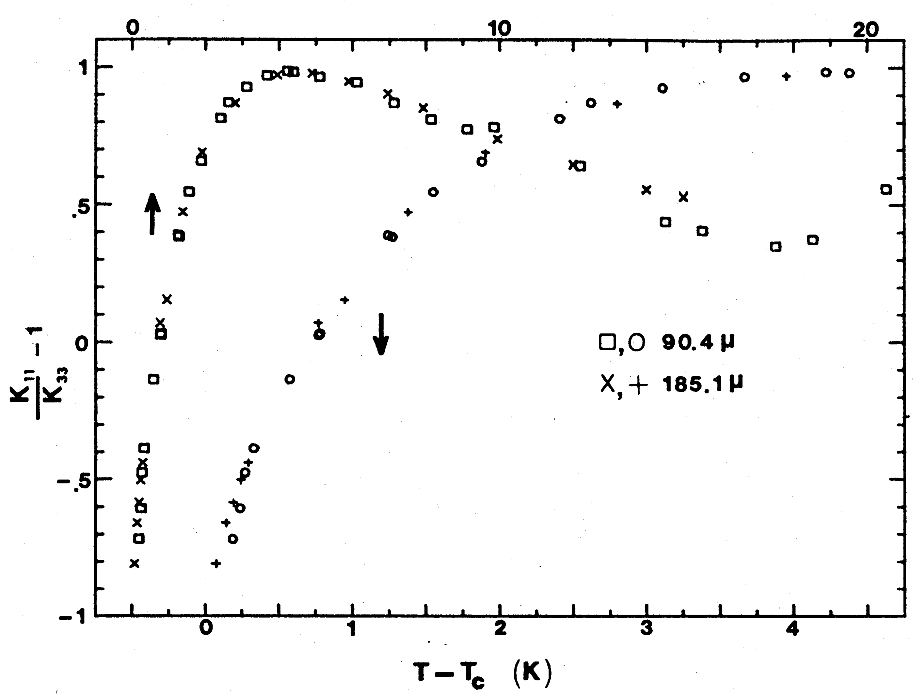

FIG. 4. Fit parameter $K' \equiv K_{11}/K_{33} - 1$ vs T-T_c, where T_c is the nematic–smectic-A transition temperature. Consistency with the linear theory and the superconducting analogy requires that K' be independent of film thickness and that it tend toward minus one as T-T_c goes to zero.

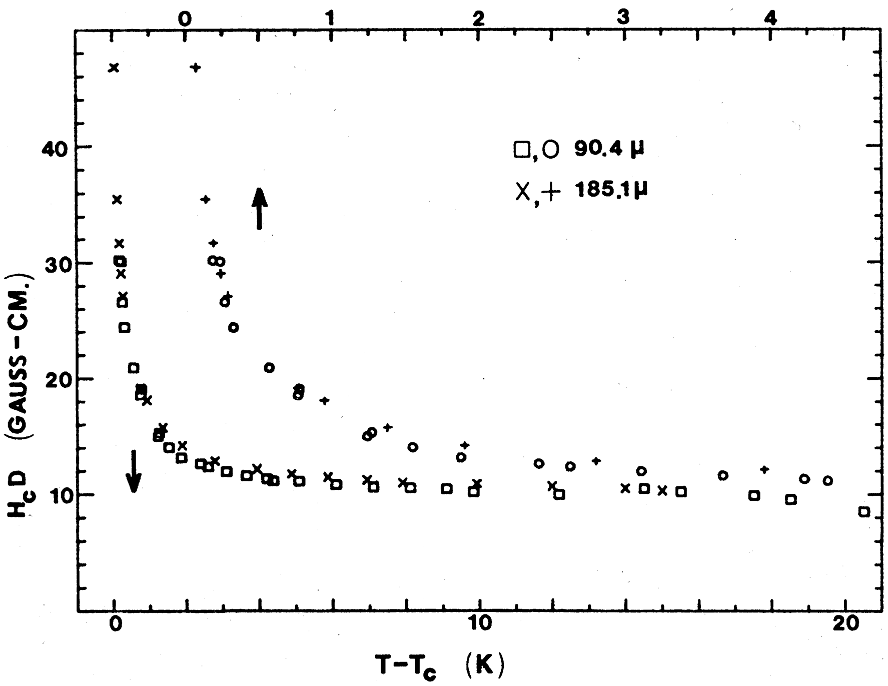

FIG. 5. H_cD, the product of critical field H_c and film thickness D vs $T-T_c$, where T_c is the nematic–smectic-A transition temperature. The linear theory predicts that H_cD should be independent of film thickness; see Eq. (16).

scattered by the bend-twist director mode.[10] The light scattering geometry is illustrated in Fig. 1. Figure 3(a) shows the root-mean-square deviation of the data from the best-fit curve as a function of ΔT. These deviation data are plotted in units of π, which is the phase shift between successive extrema of the transmitted light. Only the extrema of the $I(H)$ data were used in the fit because of the envelope superimposed on the $I(H)$ fringes due to many spurious effects; that is, I_0 of Eq. (22) is actually very weakly field dependent but not enough to significantly affect the positions of the extrema.

The question of whether the results displayed in Figs. 3–5 imply any deviation from the linear elastic theory of nematics will be discussed in Sec. IV.

B. Samples and apparatus

The liquid crystal used in this experiment was 4-n-pentylphenylthiol-4′-n-octyloxybenzoate ($\bar{8}$S5), which has nematic, smectic A, smectic C, smectic B, and biaxial smectic B phases. Its purity has been estimated[16] to exceed 99.9%. Homeotropic alignment of the director was achieved through the use of the surfactant XZ2-2300,[17] and was verified conoscopically under the polarizing microscope. Two samples of nominal thickness 100 and 200 μ were studied.

Enclosing the sample in an aluminum block inside a vacuum allowed for temperature control of better than 0.0005 K. The gradients near the center of the window where the laser beam passed through the sample was determined experimentally to be $\lesssim$0.008 K/mm. Pinholing the input to the photodiode reduced the sample portion of the beam to approximately one-tenth of its total cross sectional diameter of ~1.0 mm. Thus the portion of the sample studied is isothermal to within 0.0001 K. To avoid domains of reverse tilt, the sample director was aligned approximately 0.2° off the perpendicular to the magnetic field, with a precision of 0.025°, by making use of a 3-m optical lever and the observation of tilt domains that form at the Freedericksz transition when the director is within 0.1° of the perpendicular.

The photomultiplier tube of Fig. 1 collected light scattered by bend-twist director fluctuations. The dc output of the photomultiplier and the spectral distribution were both measured. The disappearance of the bend-twist mode on decreasing temperature signaled the NA transition and allowed a measurement of T_c to within ±0.002 K. Such measurements of T_c were made frequently during the course of the experiment and T_c was found to decrease at a rate of 0.005 K/day.

The $I(H)$ measurements were made at each temperature by ramping the magnetic field very slowly, typically 0.5 g/min near H_c to 10 g/min far from H_c, to ensure the quasistatic distortion of the director. The ramp was stopped periodically to detect any lag between the director and field. Ramping the field down showed no observable hysteresis. The magnetic field ranged from 0 to 0.6 T and was measured with a precision of 0.25%

by a Bell 620 gaussmeter. This information was input to the x axis of an x-y recorder. Photodiode 2 detected $I(H)$ and its output was displayed on the y axis of the recorder. Thus the $I(H)$-vs-H fringes were displayed on the x-y recorder. Photodiode 1 was used to detect any drift of I_0, which was always negligible. Finally, the values of H_i for $\delta_i = i\pi$ were found from the positions of the maxima and minima of $I(H)$ vs H as indicated in Eq. (22) and the data set $\delta_i = i\pi$ vs H_i were fitted in the manner described above.

IV. DISCUSSION

In this section we discuss the implications of the results displayed in Figs. 2–5 making use of the superconductivity analogy. Nonlinear diamagnetism arises above the superconducting transition when the field-induced magnetization ceases to depend linearly on field owing to the suppression of superconducting fluctuations by the field. Analogous behavior above the smectic-A transition arises when the elastic-restoring torque of the medium ceases to depend linearly on the bend, $\hat{n}\times \mathrm{curl}\hat{n}$, or twist, $\hat{n}\cdot \mathrm{curl}\hat{n}$. In superconductors nonlinearity becomes manifest in a field-dependent susceptibility $\chi(H)$, which is measured directly.[8] The experiment described in the previous section, on the other hand, is *not* a direct measurement of torque vs bend.

The nonlinearity would instead be detected indirectly by a failure of the Frank-Oseen theory to correctly account for the functional form of an imposed nonuniform bend. Competition between the homeotropic boundary conditions and the magnetic field results in a nonuniform director distortion $\theta(z)$ for $H > H_c$, hence the nonuniform bend $\cos\theta(z)\, d\theta/dz$ [see Eq. (17)]. The nonuniformity of the bend would, in the nonlinear regime, introduce z dependence into the bend coefficient K_{33}, since in that regime K_{33} is bend dependent. Such a spatially dependent K_{33} is not included in the linear theory; therefore, Eq. (18) and (23) should fail to account for the observed results. If, on the other hand, the linear theory is to give a satisfactory account of the $\delta(H)$-vs-H data, the fits of these data to Eqs. (18) and (23) must meet the following conditions.

(1) Equations (18) and (23) should fit the $\delta(H)$-vs-H data to within the experimental uncertainty.

(2) The best-fit value of the film thickness D should be independent of temperature, i.e., of $\Delta T \equiv T - T_c$.

(3) The best-fit value of the parameter $K' \equiv K_{11}/K_{33} - 1$ should be independent of film thickness D and should tend toward the value -1 as $\Delta T \to 0$. The latter condition arises because K_{33} diverges upon approaching the NA transition, while K_{11} does not.

(4) The fit parameter H_c should diverge with K_{33} as indicated in Eqs. (12) and (16), assuming that χ_a depends only weakly on temperature near the NA transition. In the first approximation χ_a is proportional to the birefringence Δn shown in Fig. 2. Both χ_a and Δn are expected to scale as the nematic-order parameter, which is nearly saturated far below the nematic-isotropic transition. Finally, the quantity H_cD should be independent of film thickness as indicated in Eq. (16).

Beginning with the first condition, Fig. 3(a) shows that the root-mean-square deviation of the phase-shift data, $\{\delta_i\}$, from the best fit is on the average less than 2% of π, the difference in phase shift between adjacent extrema of the $I(H)$ fringes. A sampling of deviation plots revealed no apparent systematic deviation of the data, $\{\delta_i\}$, from the fitted curve $\delta(H)$. Furthermore, with the possible exception of a few points nearest T_c, Fig. 3(a) exhibits no apparent systematic increase of σ/π as ΔT approaches zero. We conclude that Eqs. (18) and (23) in fact fit the data to within rather small experimental uncertainty. The question remains, however, whether the best-fit parameters D, K', and H_c meet the *a priori* criteria for being reasonable imposed by conditions (2)–(4).

Figure 3(b) reveals that the film thickness is independent of ΔT to within an average of less than 1% for both samples studied, thus satisfying the second condition. The average thicknesses found were 90.4 ± 0.8 and 185.1 ± 0.8 μ, which is consistent with less accurate mechanical measurements. This result is not only consistent with the linear theory but also indicates that the boundary conditions were not violated by the strong distortions applied.

Figure 4 indicates that the fit parameter $K' = K_{11}/K_{33} - 1$ satisfies both conditions under statement (3). First, it is seen that K' is experimentally independent of sample thickness. Second, it is clear that the ratio K_{11}/K_{33} decreases rapidly with ΔT as the NA transition is approached. The expanded version shows that the data are consistent with $\lim_{\Delta T\to 0} K' = -1$ as expected.

Figure 5 shows that H_cD appears to diverge as $T \to 0$, in agreement with the first of the two conditions set forth in statement (4). Furthermore, Fig. 5 shows that except for a small systematic deviation the relationship H_cD vs ΔT is very nearly the same for both films studied, in substantial agreement with Eq. (16) and therefore the second condition of statement (4).

We conclude that the overall agreement between the data and the linear theory is excellent.

TABLE I. Evaluation of the Chu-McMillan criterion [see Eq. (28b)] for linear elastic curvature response at various reduced temperatures $t \equiv (T - T_c)/T_c$, where T_c is the nematic–smectic-*A* transition temperature. According to Eq. (28b) linear response requires that numbers in column 4 be much less than 1.

$10^3 t$	$(H/H_c)_{max}$	$(\sin\theta_m)_{max}$	$[3\pi^2 g(\xi_\parallel \xi_\perp/dD)(H/H_c)\sin\theta_m]_{max}$ [a]
		$D = 185.1\ \mu$	
0.199	2.10	0.999 993	6.77
0.577	3.40	0.999 998	3.27
0.878	3.99	0.999 999	1.77
2.28	4.88	0.999 997	0.61
4.098	5.80	0.999 998	0.33
8.33	8.17	1.000 00	0.18
17.5	6.00	0.999 994	0.05
35.7	6.31	0.999 999	0.02
		$D = 90.4\ \mu$	
0.560	1.69	0.987 32	2.48
0.979	2.59	0.999 55	2.04
2.29	3.10	0.999 45	0.79
4.60	4.30	0.999 89	0.43
9.25	4.89	0.999 92	0.34
21.2	5.29	0.999 97	0.07
46.1	4.52	0.999 96	0.04

[a] To evaluate this expression we have used Eqs. (29) taking $\xi_\parallel^0 = d = 25$ Å, $\xi_\parallel^0/\xi_\perp^0 = 5$ and $\nu = 0.67$. $(H/H_c)_{max}$ and $(\sin\theta_m)_{max}$ came from the present work.

Such close agreement was not expected. To see why, we evaluate both sides of the inequality of Eq. (14). This inequality sets an upper limit on the bend distortion in the linear regime where the bend is given by

$$|\hat{n} \times \text{curl}\hat{n}| = \frac{\pi}{D}\frac{H}{H_c}\left(\frac{\cos^2\theta - \cos^2\theta_m}{1 + K'\sin^2\theta}\right)^{1/2}\cos\theta \quad (26)$$

and H/H_c is given by Eq. (18).

Applying this to Eq. (14) gives

$$\frac{\pi}{D}\frac{H}{H_c}\left(\frac{\cos^2\theta - \cos^2\theta_m}{1 + K'\sin^2\theta}\right)^{1/2}\cos\theta \ll \frac{1}{3\pi g}\frac{d}{\xi_\parallel \xi_\perp}. \quad (27)$$

At the center of the film the bend vanishes ($\theta = \theta_m$) because $d\theta/dz$ changes sign. At the boundaries, where $\theta = 0$, the bend is greatest and is given by $|\hat{n} \times \text{curl}\hat{n}| = (\pi/D)(H/H_c)\sin\theta_m$. Therefore, at the boundaries Eq. (27) becomes

$$(\pi/D)(H/H_c)\sin\theta_m \ll (1/3\pi g)(d/\xi_\parallel \xi_\perp) \quad (28a)$$

or

$$3\pi^2 g(\xi_\parallel \xi_\perp/dD)(H/H_c)\sin\theta_m \ll 1. \quad (28b)$$

Equation (28) gives the criterion for the linear regime. Numerical evaluation of the left-hand side of Eq. (28a) requires only input from the experiments reported here; however, in order to evaluate the right-hand side of this inequality we need experimental values of d, $\xi_\parallel$, and $\xi_\perp$ at temperatures in the range of our measurements. All three of these quantities come most directly from x-ray measurements. Presently, however, there are no published x-ray data on $\overline{8}$S5, so we proceed by making the only reasonable assumptions that one can make in the absence of experimental data, namely, that the smectic layer spacing d is comparable with the length of a molecule, ~25 Å for $\overline{8}$S5, and that

$$\xi_\parallel = \xi_\parallel^0 t^{-\nu}, \quad (29a)$$

$$\xi_\perp = \xi_\perp^0 t^{-\nu}, \quad (29b)$$

where $\xi_\parallel^0 \sim d$, and $\xi_\parallel^0/\xi_\perp^0$ is comparable with the length-to-width ratio of the molecule; i.e., ~5 for $\overline{8}$S5. The exponent ν, which takes on the mean field value of $\frac{1}{2}$ in superconductors, is known to be closer to the critical value of $\frac{2}{3}$ in liquid crystals. Using these values of d, $\xi_\parallel^0$, and $\xi_\perp^0$, and ν, we can estimate the right-hand side of Eq. (28a) with the aid of Eq. (29). Finally the left-hand side of Eq. (28a) is determined by our own experiments and we are able to evaluate the left-hand side of Eq. (28b) for values of reduced temperature and H/H_c spanned by the experiments. For the maximum experimental value of H/H_c at several given reduced temperatures the results are shown in Table I, where the right-hand column is the left-hand side of Eq. (28b). Clearly there is a wide range of reduced temperature (nearly a decade) where nonlinear behavior would be expected but in fact did not materialize.

The well-known stripe instability[18] appeared at reduced temperatures just below the lowest ones listed in Table I ($\sim 10^{-4}$), thus limiting the experiment to $t \gtrsim 10^{-4}$ and suggesting that the stripe instability signals the *onset* of nonlinear behavior.

Although the success of the linear theory in explaining these experiments may seem surprising, recent x-ray data[19] suggest that perhaps it is to be expected. These data show that although our estimates of $\xi_{\parallel}^0/\xi_{\perp}^0$ and ν were close to the x-ray-determined values, the longitudinal coherence length amplitude $\xi_{\parallel}^0$ is actually only about one-fifth of the smectic layer spacing d. Thus our estimates in Table I of the left-hand side of Eq. (28b) may be high by an order of magnitude. This would explain the results.

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