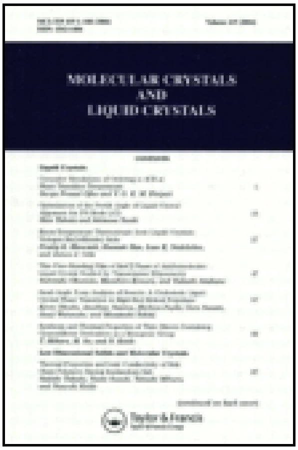

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Director Bend Mode Behavior Near a Nematic to Smectic-A Phase Transtion

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To cite this article: J. D. Litster (1977): Director Bend Mode Behavior Near a Nematic to Smectic-A Phase Transtion, Molecular Crystals and Liquid Crystals, 42:1, 33-41

To link to this article: http://dx.doi.org/10.1080/15421407708084493

Mol. Cryst. Liq. Cryst., 1977, Vol. 42, pp. 33–41
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Printed in Holland

Director Bend Mode Behavior Near a Nematic to Smectic-A Phase Transition*

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(*Received December 18, 1976*)

Measurements of the intensity and spectrum of light scattered by bend mode director fluctuations near the smectic-A to nematic phase transition of cyanobenzylidene octyloxyaniline are presented and analyzed. The longitudinal correlation length in the nematic phase appears to diverge as $(T - T_c)^{-0.75}$ and the data are consistent with the Jähnig–Brochard scaling function up to $q\xi_{\parallel} = 10$. The bend viscosity diverges as $(T - T_c)^{-0.5}$ when corrections for background and Arrhenius temperature dependence are included.

INTRODUCTION AND BACKGROUND

In this paper we report a study of the intensity and spectrum of light scattered by director fluctuations (bend mode) in the nematic phase of cyanobenzylidence octyoxyaniline (CBOOA) just above the transition to a smectic-A phase. It was originally pointed out by McMillan[1] and Kobayashi[2] that this phase transition could be second order; a focus for efforts to understand the phase transition has been provided by de Gennes' model[3] and subsequent developments by McMillan[4] and Jähnig and Brochard.[5,6] In this model the structure of the free energy is isomorphous to that for the Ginsburg–Landau

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* Supported by the National Science Foundation under grant GH33635 and the Office of Naval Research under Contract No. N0001467-A-0204-0062.

model of superconductivity and de Gennes predicted[3] a pretransitional stiffening of the nematic phase twist and bend elastic constants analogous to fluctuation diamagnetism above the superconducting critical temperature. Subsequent work[4–6] also includes predictions for dynamical behavior near the phase transition.

There has been much experimental study of nematic phase behavior of the compound CBOOA. The divergence of the bend elastic constant has been observed by means of a magnetically induced elastic deformation (Freedericksz transition)[7–9] while the twist elastic constant has been studied by quasielastic light scattering.[10,11] The diverging transport coefficient (the twist viscosity) has been studied by ultrasonics,[9] and a dynamical Freedericksz transition;[12] also the dynamics of the twist director mode has been studied by light scattering.[11,13] Our work is the first light scattering study of pretransitional behavior of the bend director mode and includes the critical non-hydrodynamic regime[14] up to $q\xi = 10$, thus permitting a test of the dynamical theories.[4–6] Also, previously reported smectic phase measurements[15] were carried out on the same sample; thus a meaningful comparison of modes on both sides of the transition can be made.

Let us repeat the salient features of de Gennes' model. The order parameter for the smectic A (SmA) phase is related to a density wave along the z direction (perpendicular to the smectic layers); thus the density is

$$\rho = \rho_0[1 + \mathrm{Re}(\psi e^{iq_0 z})] \tag{1}$$

where $a = 2\pi/q_0$ is the layer spacing and $\psi = |\psi| e^{iq_0 u}$ is the SmA order parameter. Thus ψ is a two component order parameter analogous to the order parameter of superfluids; when the phase of ψ is written as $q_0 u$, u represents a displacement of layers in the z direction. Then de Gennes suggested a free energy density of the Ginsburg–Landau form

$$\begin{aligned} F = F_0 &+ \alpha|\psi|^2 + (\beta/2)|\psi|^4 + (1/2M_v)|\partial_z \psi|^2 \\ &+ (1/2M_t)|(\partial_x + iq_0 n_x)\psi|^2 + (1/2M_t)|(\partial_y + iq_0 n_y)\psi|^2 \\ &+ (K_1/2)[\partial_x n_x + \partial_y n_y]^2 + (K_2/2)[\partial_x n_y - \partial_y n_x]^2 \\ &+ (K_3/2)[(\partial_z n_x)^2 + (\partial_z n_y)^2] \end{aligned} \tag{2}$$

In (2), the unperturbed director $\mathbf{n}_0$ lies along z and K_1, K_2, K_3 are, respectively, the splay, twist, and bend Frank elastic constants. In the SmA phase $\langle|\psi|\rangle = \psi_0 = (-\alpha/\beta)^{1/2}$; if we take $|\psi|$ to be spatially uniform then (2) becomes

$$\begin{aligned} F = F_0 &+ 1/2\{-\alpha^2/\beta + B(\partial_z u)^2 + D[(n_x + \partial_x u)^2 + (n_y + \partial_y u)^2] \\ &+ K_1[(\partial_x n_x) + (\partial_y n_y)]^2 + K_2[\partial_x n_y - \partial_y n_x]^2 \\ &+ K_3[(\partial_z n_x)^2 + (\partial_z n_y)^2]\} \end{aligned} \tag{3}$$

Taking the Fourier transform of (3) and applying the equipartition theorem leads to expressions for the mean squared fluctuations in the director. If we choose the wave vector **q** to lie in the $x-z$ plane we obtain

$$\langle n_x^2(q)\rangle = kT[K_1 q_x^2 + K_3 q_z^2 + B(q_z/q_x)^2\{1 + (B/D)(q_z/q_x)^2\}^{-1}]^{-1} \quad (4a)$$

$$\langle n_y^2(q)\rangle = kT[D + K_2 q_x^2 + K_3 q_z^2]^{-1} \quad (4b)$$

The coefficients $B = \psi_0^2 q_0^2/M_v$ and $D = \psi_0^2 q_0^2/M_t$ physically give, respectively, the restoring forces for fluctuations in the phase of ψ (i.e. layer thickness) and fluctuations in molecular orientation away from the normal to the layers. Equation (4) with $B = D = 0$ describes the usual director fluctuations in the nematic phase.[16] The presence of fluctuations in the smectic order parameter on both sides of the SmA–N transition modifies the Frank elastic constants. By carrying over the results of Schmid[17] for fluctuation diamagnetism in superconductors de Gennes obtained[3] the expressions

$$K_2 = K_2^0 + (kT/24\pi)q_0^2(\xi_\perp^2/\xi_\parallel) \quad (5a)$$

$$K_3 = K_3^0 + (kT/24\pi)q_0^2\xi_\parallel \quad (5b)$$

Here K_i^0 is the normal nematic phase value of the elastic constant. The longitudinal and transverse coherence lengths for fluctuations in $|\psi|$ are respectively given by (in the nematic phase): $\xi_\parallel^2 = 1/(2\alpha M_v)$ and $\xi_\perp^2 = 1/(2\alpha M_t)$.

In the mean field approximation $\alpha = \alpha_0(T - T_c)$ and a second order SmA–N phase transition occurs at T_c. The free energy of (2) might be expected to provide an approximate description for a non-classical (i.e. non-mean field) phase transition if the temperature dependence of α, M_v, and M_t are suitably modified.[5]

We summarize the dynamical behavior to be expected for the director modes[16] under various conditions in the nematic phase. When $q_z = 0$, we have

$$\langle n_x^*(\mathbf{q}, 0)n_x(\mathbf{q}, \tau)\rangle = (kT/K_1 q_x^2)\exp(-\Gamma_s\tau) \quad (6a)$$

$$\Gamma_s = K_1 q_x^2/[\gamma_1 - (\gamma_1 + \gamma_2)^2/4\eta_1] \quad (6b)$$

$$\langle n_y^*(\mathbf{q}, 0)n_y(\mathbf{q}, \tau)\rangle = (kT/K_2 q_x^2)\exp(-\Gamma_t\tau) \quad (7a)$$

$$\Gamma_t = K_2 q_x^2/\gamma_1 \quad (7b)$$

Equations (6) and (7) represent modes which are pure splay and twist, respectively. When $q_x = 0$, both modes are identical and become pure bend:

$$\langle \delta n_y^*(q, 0)\delta n_y(\mathbf{q}, \tau)\rangle = (kT/K_3 q_z^2)\exp(-\Gamma_b\tau) \quad (8a)$$

$$\Gamma_b = K_3 q_z^2/[\gamma_1 - (\gamma_1 - \gamma_2)^2/4(\eta_1 - \gamma_2)] \quad (8b)$$

The viscosity coefficients are discussed in detail by de Gennes;[18] γ_1 is the twist viscosity for the director, γ_2 is the flow alignment viscosity, and η_1 is the shear viscosity that would be measured with the velocity along the director and the velocity gradient transverse to it. All of these viscosity coefficients involve motion of the liquid crystal molecules across the smectic planes and thus show divergences at the SmA–N phase transition; i.e. $\gamma_1 = \gamma_1^0 + \tilde{\gamma}_1$ where $\tilde{\gamma}_1$ is the divergent part due to fluctuations in the smectic order parameter and γ_1^0 is the background nematic phase twist viscosity. The divergent parts of γ_2 and η_1 are predicted to be identical to that of γ_1; thus $\gamma_2 = \gamma_2^0 + \tilde{\gamma}_1$ and $\eta_1 = \eta_1^0 + \tilde{\gamma}_1$. The divergence of γ_1 is given by

$$\tilde{\gamma}_1 = \eta^0 \xi_{\parallel} \tag{9a}$$

or

$$\tilde{\gamma}_1 = \eta^0 (\xi_{\parallel})^{1/2} \tag{9b}$$

where (9a) comes from a mean field model[4] and (9b) results from dynamic scaling arguments.[4,19]

In CBOOA, neither K_1 nor Γ_s show any anomalous behavior near the SmA–N transition. The behavior of K_2 and Γ_t have been studied by light scattering,[10,11,13] and we now present the results of our quasielastic light scattering measurements of K_3 and Γ_b.

EXPERIMENTAL DISCUSSION AND RESULTS

CBOOA was obtained from Eastman Organic Chemicals and purified by recrystallization from heptane. The samples were prepared in the planar configuration (molecules parallel to the glass plates) between microscope slides treated by shew evaporation[20] of SiO; the sample was about 40 μ thick. It was placed in an oven whose short term stability was 0.5 mK/hr and long term stability was ~2 mK/day; the temperature gradient across the sample (as observed at the nematic–isotropic transition) was less than 10 mK.

Incident light was 750 μW at 6328 Å polarized normal to the scattering vector $\mathbf{q}$ (which was chosen to lie along the director); thus we had $q_x = 0$, $q_z = 7.37 \times 10^4\ \mathrm{cm}^{-1}$. As the refractive indices changed with temperature[21] slight changes in scattering angle were necessary to keep $q_x = 0$; we corrected for the consequent changes in q_z as well as the collection solid angle for intensity measurements.

The intensity of the scattered light, proportional to $(K_3 q_z^2)^{-1}$, was measured both by direct measurement of the photomultiplier current and the zero intercept of the autocorrelation function of the scattered light. The

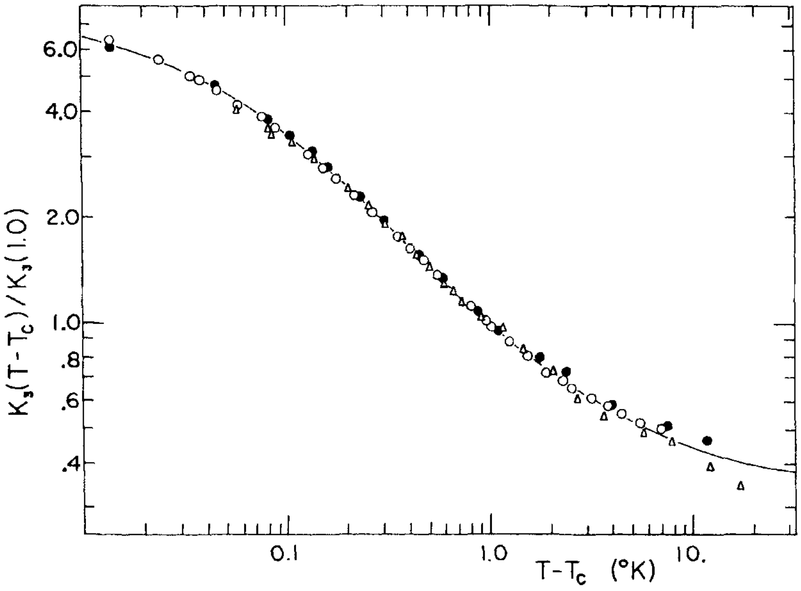

FIGURE 1 Temperature dependence of the bend elastic constant in nematic CBOOA. The symbols are for sample with different transition temperatures (solid circles, open circles, triangles have T_c = 82.51, 82.75, 83.00). The value of $K_3(1.0)$ is 1.79×10^{-6} dyne.

results were identical for each method within experimental error. In Figure 1 we plot the ratio of $K_3(T_c + 1K)$ to $K_3(T)$ deduced from these measurements. Data for several samples with different phase transition temperatures are seen to fall on the same curve. The divergence of K_3 appears to round off beginning at T_c + 0.2 K as a result of entering the critical region. An expression for K_3 for all values of $q\xi$ has been derived by Jähnig and Brochard.[5] They assumed the Ornstein–Zernike form for the generalized susceptibility and used Ferrell's decoupled mode approach[22] to carry out the calculation. Their result is (for $q_x = 0$)

$$K_3 = K_3^0 + \frac{kTq_0^2}{8q_z}\left[\left(1 + \frac{1}{X^2}\right)\tan^{-1} X - \frac{1}{X}\right] \tag{10}$$

where $X = (1/2)q_z\xi_{\parallel}$. We found our experimental results to be quite satisfactorily represented by equation (10). Since $q_0 = 1.80 \times 10^7\ \text{cm}^{-1}$ from x-ray measurements,[23] we may calculate the factor $kTq_0^2/8\pi q_z = 8.54 \times 10^{-6}$ dyne; this enables a numerical calibration of our data even though they are obtained from intensity measurements. The fit is shown as the solid line in Figure 1 and the resulting parameters are: $K_3^0 = 5.7 \times 10^{-7}$ dyne,

$X = 0.216\ (T - T_c)^{-\nu_\parallel}$ with $\nu_\parallel = 0.745 \pm 0.04$. The uncertainties given for $\nu_\parallel$ result from doubling the error of the fit (χ^2 test). Thus if $\xi_\parallel = \xi_0(T/T_c - 1)^{-\nu_\parallel}$, we obtain $\xi_0 = 7.37$ Å and $\xi(T_c + 0.2\ K) = 1950 \pm 100$ Å which is in satisfactory agreement with x-ray measurements.[23] We therefore have $q\xi_\parallel = 0.43$ at $T_c + 1$K, enter the critical region ($q\xi_\parallel = 1$) at $T_c + 0.324$ K, and the lowest temperature points in Figure 1 have $q\xi_\parallel = 10$. The exponent $\nu_\parallel$ is somewhat higher than previous estimates[7–9] but close to the x-ray result[23] and recent optical measurements by Chu.[24] We have ignored the slight temperature dependence of K_3^0. Given that no clearly exponential temperature dependence can be seen in Figure 1 and all values must be obtained by fitting to Eq. (10), the agreement with results of Freedericks transition and x-ray measurements is striking. Our measurements were carried out during the same experiment as previously reported smectic phase studies,[15] and we may therefore make a numerical estimate $D = 6.3 \times 10^5(T_c - T)^{0\cdot 5}$ erg cm^{-3} in the smectic phase.

The spectrum of the scattered light was also measured with a Precision Devices and Systems Ltd. clipped digital autocorrelator using scaling in the clipped channel. We thereby obtained $\Gamma_b = K_3 q_z^2/\eta_{\text{bend}}$. Using $K_3 q_z^2$ from the intensity measurements we were able to deduce $\eta_{\text{bend}} = \gamma_1 - (\gamma_1 - \gamma_2)^2/4(\eta_1 - \gamma_2)$.

We expect $\eta_{\text{bend}} = \eta_b^0 + \tilde{\gamma}_1$; here our measurement offers some advantage over twist viscosity measurements because the background η_b^0 is small compared to γ_1^0. (We find $\eta_b^0 = 0.069$ poise at $T_c + 1K$ and Ref. 22 reports $\gamma_1^0 = 0.46$ poise.) In fact, a log–log plot of the "raw" values of η_{bend} appears quite linear for $T - T_c > 0.2$ K with a slope of 0.41. To assume this represents the divergence $\tilde{\gamma}_1$ would be in error, however. In both the mean field[4] and scaling law[19] estimates for $\tilde{\gamma}_1$, the power law divergence multiplies a bare viscosity, η^0 in Eq. (9), which has an Arrhenius dependence. From results quoted by Langevin[25] we expect the activation energy for this and any background viscosity to be about 2 kcal/mole (i.e. to vary as exp $5000/T$). Thus we expect our bend viscosity to be represented in the hydrodynamic region by

$$\eta_{\text{bend}} = Ae^{W/T}[(T - T_c)^{-x} + B] \tag{11}$$

Since we were able to find numerical values for K_3, we may also calculate numerical values for the viscosity from our measurements of Γ_b. If we take $W = 5000$, our best fit occurs with $A = 1.74 \times 10^{-7}$ poise, $B = 0.33$, and $x = 0.49$. Thi gives $\tilde{\gamma}_1(T_c + 1K) = 0.21$ poise, which agrees well with both the results of Langevin[25] and Huang, Pindak, and Ho.[2] Keeping W fixed, but allowing both B and x to vary to optimize the fit, we find $x = 0.49 \pm 0.09$; thus a conservative estimate favors the divergence predicted by mean field estimates. However, we must caution that the power law obtained depends upon the activation energy chosen. For example, an

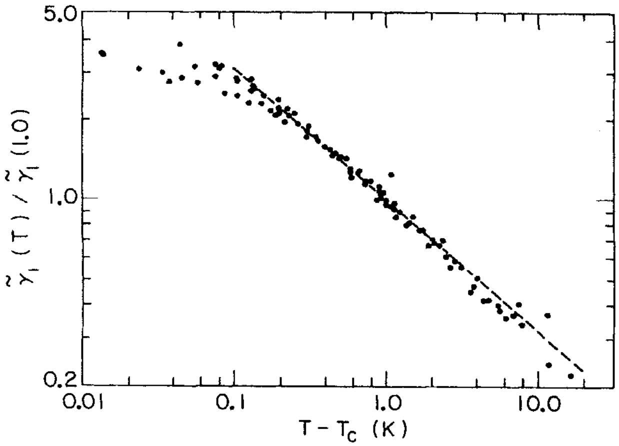

FIGURE 2 Temperature dependence of $\tilde{\gamma}_1$ obtained from the bend viscosity as described in the text and normalized to $T_c + 1K$ ($\tilde{\gamma}_1(1.0) = 0.21$ poise). The line has slope 0.49 and the Arrhenius temperature dependence has been removed.

equally good fit (identical χ^2) is obtained with $W = 0$, $B = 0.05$, and $x = 0.43$. Thus, knowledge of W is a prerequisite for meaningful data analysis. The best fit with $W = 5000$ is shown in Figure 2. We find, therefore, that the divergence of $\tilde{\gamma}_1$ is close to that predicted from mean field estimates. This confirms the result of Chu and McMillan[11] and also the measurements of Langevin. Huang, Pindak, and Ho[12] find a smaller exponent (0.37 ± 0.05) which is to be expected since their analysis did not consider the temperature dependence of the bare viscosity; the latter may also explain the slowing down of the twist mode observed by Chu and McMillan.[11] It is not clear whether Langevin considered the temperature dependence of η^0 in her analysis.

Our analysis used only viscosity data for $T - T_c > 0.2$ K; closer to T_c, $q\xi > 1$ and a rounding off of the divergence can be seen in Figure 2. The scaling function for $\tilde{\gamma}_1(q\xi)$ has yet to be calculated, but it seems unlikely our data could provide a test of such a calculation. The relaxation times close to T_c are comparable to the resolution of our apparatus, which causes the large scatter seen in the data for $T < T_c + 0.2$.

CONCLUSIONS

From our measurements of K_3, we find the expression of Jähnig and Brochard to be valid in the non-hydrodynamic regime up to $q\xi = 10$, even though an Ornstein-Zernike form of susceptibility was used. This is consistent with the results of recent calculations by Tracy and McCoy[26] for the detailed form of the correlation function in magnetic systems.

There is also beginning to emerge a self consistency within a subset of experimental results in the nematic phase of CBOOA. The fact that the splay elastic constant K_1, and the splay mode relaxation time show no observable anomalous behavior[15] at T_c confirms the theoretical prediction that γ_1, γ_2, and η_1 all diverge in the same way. This work and Refs. 12, 13 and 25 seem to be consistent with $\tilde{\gamma}_1$ diverging as $(T - T_c)^{-0\cdot5}$. This work, Ref. 24, and the x-ray measurements[24] are consistent with $\xi_{\parallel}$ diverging as $(T - T_c)^{-0\cdot75}$. If the above divergence for $\tilde{\gamma}_1$ is assumed, then the light scattering results of Ref. 11 and the x-ray results are consistent with $\xi_{\perp}$ diverging as $(T - T_c)^{-0\cdot6}$. However, caution seems still to be in order. There remain unresolved disagreements with other experimental results, notably those of Refs. 7, 8, 9, 10, and 13. Although it does not show up in light scattering experiments, the SmA–N transition in CBOOA may be first order (but probably so weakly first order as to have little effect). The apparently different divergences for $\xi_{\parallel}$ and $\xi_{\perp}$ are disturbing since this is contrary to expectations from the scaling laws. All of the data analysis has been carried out within the framework of de Gennes' model; if it is missing some of the essential physics of the problem[15] then the true significance of the experiments may not be known. The best way to elucidate the situation is a careful direct measurement of correlation lengths by x-ray scattering in both the nematic and smectic A phases; such experiments are in progress at M.I.T.

Acknowledgements

We are grateful to Professor F. D. Greene and his students for help in purifying the CBOOA, Mr. A Colozzi and Professor C. G. Fonstad for aid in performing the skew evaporation. Ralph Schaetzing also assisted in sample preparation, and we appreciate helpful discussions with Professor W. McMillan.

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