

## Light-scattering studies on the single-layer smectic *p*-butoxybenzilidene *p*-octylaniline

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An analysis of the intensity of the spectrum of light scattered from the director fluctuations of butoxybenzilidene octylaniline around the nematic to smectic-*A* transition shows the critical properties of this single-layer material to be wholly analogous to the well-studied bilayer smectics, i.e., the He analogy holds only for the nematic phase while it breaks down for  $T < T_c$ . The unusually large temperature dependence of the splay elastic constant  $K_1$  can be partly understood on the basis of an enhancement of the nematic order parameter  $S$  by the smectic ordering.

### INTRODUCTION

The nematic to smectic-*A* liquid-crystal phase transition has been of considerable experimental and theoretical interest over the past few years. The focus of this interest has been on the proposed analogy with superconducting or superfluid transitions<sup>1, 2</sup> of the *XY* model. The order-parameter fluctuations for the smectic-*A* to nematic transition can be directly studied by x-ray scattering. In addition, light scattering is an ideal tool to study the static and dynamic behavior of nematic director fluctuations<sup>3</sup> (the Goldstone modes resulting from nematic order). As de Gennes points out,<sup>1</sup> it is possible to learn a great deal about the smectic order-parameter fluctuations by studying the director modes. Nematic ( $T > T_c$ ) anomalies are expected in the bend ( $K_3$ ) and twist ( $K_2$ ) elastic constants. If  $\xi_{\parallel}$  and  $\xi_{\perp}$  are correlation lengths along and transverse to the director for smectic short-range-order fluctuations, then one expects  $K_3 \sim \xi_{\parallel}$ ,  $K_2 \sim \xi_{\perp}^2/\xi_{\parallel}$ , and both to diverge as  $(T - T_c)^{2/3}$  in the *XY* analogy. Extension to dynamical behavior also predicts the twist viscosity  $\gamma_1$  to diverge as  $\xi_{\perp}^{1/2} \sim (T - T_c)^{1/3}$ .<sup>4, 5</sup>

Light scattering, x-ray scattering, and thermal measurements<sup>6, 7</sup> confirm qualitative similarities to the superfluid analogy but also reveal slight quantitative discrepancies. The most accurate experiments suggest the exponent  $\nu_{\parallel}$  for the divergence of  $\xi_{\parallel}$  is close to the predicted value of 0.67, but that  $\nu_{\perp}$  is somewhat smaller. The heat-capacity measurements<sup>7</sup> give a divergence characterized by exponents  $\alpha = \alpha' \approx 0.25$  rather than the predicted logarithmic ( $\alpha = 0$ ) divergence. In the smectic phase the elastic constants  $B$  (for layer compression, analogous to the superfluid density) and  $D$  (formolecular tilt with respect to the layers) show behavior completely at variance with any theoretical prediction.

All of the above results come from experiments on compounds whose smectic density wave has a period roughly two molecular lengths—that is the

smectic “layers” are two molecules thick. From symmetry considerations one would not expect the behavior to be any different for “monolayer” smectics; in order to verify this we have carried out a detailed light-scattering study of director modes in both the nematic and smectic-*A* phase of butoxybenzylidene octylaniline (40.8).

### SAMPLE PREPARATION

The samples were prepared in planar or homogeneous alignment (director in the plane of the sample). Previously in this laboratory we have used skew evaporation of SiO to achieve this alignment. Since surface relief gratings have been demonstrated to provide effective liquid-crystal alignment<sup>8</sup> we used the assistance of the Massachusetts Institute of Technology Submicron Structures Laboratory to prepare gratings of 1- $\mu\text{m}$  period with approximately 300- $\text{\AA}$  depth and square wave profile. The grating pattern was generated by photolithographic contrast printing using a conformable Cr mask.<sup>9</sup> The mask was produced by holographic exposure of resist, and the chromium etched chemically. Relief gratings were etched into the SiO<sub>2</sub> substrate with an Ar-ion beam. We found the gratings performed best when coated with trimethoxysilane<sup>10</sup> (Corning product Z-6020) to reduce the tendency of the 40.8 molecules to align themselves perpendicular to the glass as well as to reduce the danger of sample contamination by water. Alignment by surface relief gratings offers the advantage that the sample may be allowed to enter the *B* phase or even crystallize and the alignment is recovered on warming to the *A* or nematic phase. We intend to publish detailed results of our experiments on alignment using surface relief gratings in the near future.

To prepare samples for light scattering a sandwich using two gratings, as described above, separated by 125  $\mu\text{m}$  was loaded with 40.8 (used as obtained from Dr. G. A. Lorenzo at Organix,

Avon, N. Y.) under dry Ar and sealed in a vacuum-tight brass sample holder.

### EXPERIMENTAL RESULTS AND DISCUSSIONS

Despite all precautions the transition temperatures tended to decrease by 2–10 mK per hour starting from a high value of  $T_c = 63.950^\circ\text{C}$ .  $T_c$  was measured by observing the vanishing of the director fluctuations through a polarizing microscope mounted on top of the scattering setup. The resulting accuracy was 5–10 mK, depending on the sample quality.  $T_c$  was measured before and after each run and then linearly interpolated for each data point individually. Over a period of six weeks during which the transition temperature changed by two degrees no significant change of the exponents could be observed. In the following analysis we therefore give all the temperatures relative to  $T_c$ .

(a) *Results for mode 1:* In the smectic phase for  $q_z/q_x \ll 1$  the autocorrelation function of the scattered electric field  $\langle E^*(q, 0) E(q, \tau) \rangle$  is proportional to

$$\langle \delta\epsilon_{zx}^*(q, 0) \delta\epsilon_{zx}(q, \tau) \rangle = \frac{\epsilon_a^2 k_B T}{K_1 q_x^2 + B(q_z/q_x)^2} e^{-\Gamma\tau}, \quad (1)$$

$$\Gamma = \frac{K_1 q_x^2 + B(q_z/q_x)^2}{\eta_{\text{splay}} + \eta'(q_z/q_x)^2},$$

where the unperturbed director  $\vec{n}_0 \parallel z$  and  $\vec{q}$  is in the  $(x, z)$  plane. Both the linewidth  $\Gamma$  and the intensity  $I = \langle E^*(q, 0) E(q, 0) \rangle$  were measured for nine values of  $q_z$  around  $q_z = 0$  ( $q_x \approx \text{const}$ ) at every temperature  $T$ .  $B/K_1$  was determined by fitting  $\Gamma(q_z)$  and  $\epsilon_a^2/I(q_z)$  to a parabola. Within experimental error both fits yield identical values of  $B/K_1$ . The minima of the parabolas give values for  $K_1/\eta_{\text{splay}}$  and the temperature dependence of  $K_1$  as shown in Fig. 1. Both these quantities show an unusually large temperature dependence compared to previous observations in bilayer com-

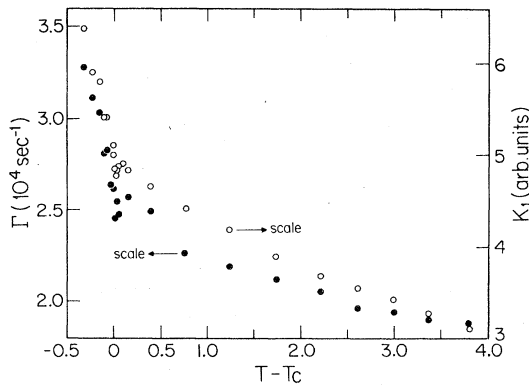


FIG. 1. Temperature dependence of  $K_1$  and  $K_1/\eta$ .

pounds, and from the data of Fig. 1 it appears that it is  $K_1$  rather than  $\eta_{\text{splay}}$  which is changing. D'Humières and Léger have also noted a pretransitional increase in  $K_1$  in their Fredericks transition measurements<sup>11</sup> on 40.8, which is about the same size as we observe. From both their data and ours it appears unlikely this increase in  $K_1$  is a strong power-law divergence. At least part of the increase in  $K_1$  can be understood as the result of a rather large coupling of the nematic order parameter  $S$  to the smectic ordering.<sup>12</sup> Assuming  $K_1 \sim S^2$  the observed increase of  $S$  down to 1 degree below  $T_c$  would lead to approximately

$$\frac{\Delta K_1}{K_1} = \frac{K_1(T_c - 1) - K_1(T_c)}{K_1(T_c)} \approx 15\%$$

while the change in  $K_1$  observed by light scattering is roughly twice as large. At present we have no theoretical explanation for this apparent discrepancy. The similar behavior of  $K_1$  and  $K_1/\eta_{\text{splay}}$  shows as expected  $\eta_{\text{splay}}$  is regular across the transition.

Correcting the values of  $B/K_1$  for the temperature dependence of  $K_1$  we obtain the temperature dependence of  $B$  from the extrapolated correlation function (intensity data) shown in Fig. 2. We find this vanished with an exponent,  $B \sim (T_c - T)^\phi$ ,  $\phi = 0.32 \pm 0.03$ . This is in complete agreement with previous results<sup>6</sup> in bilayer compounds.

(b) *Results from  $q_x = 0$  (modes 1 and 2 degenerate).* In the nematic phase we have

$$\langle \delta\epsilon_{zx}^*(y, 0) \delta\epsilon_{zx}(y, \tau) \rangle = \frac{\epsilon_a^2 k_B T}{K_3 q_z^2} e^{-\Gamma_b \tau}, \quad (2)$$

$$\Gamma_b = \frac{K_3 q_z^2}{\eta_{\text{splay}}}.$$

Since we enter the nonhydrodynamic regime above  $T_c$  we have to analyze the intensity

$$I \sim \frac{\epsilon_a^2 T}{K_3 q_z^2} \cong \text{const} \frac{\epsilon_a^2}{K_3}$$

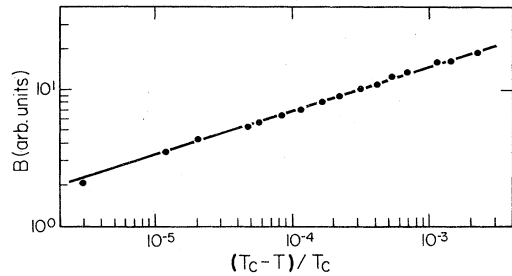


FIG. 2. Temperature dependence of  $B$  obtained from the extrapolated correlation functions to zero delay. The full line represents a least-squares fit to the data which yields  $\phi = 0.32 \pm 0.03$  for the exponent  $B$ .

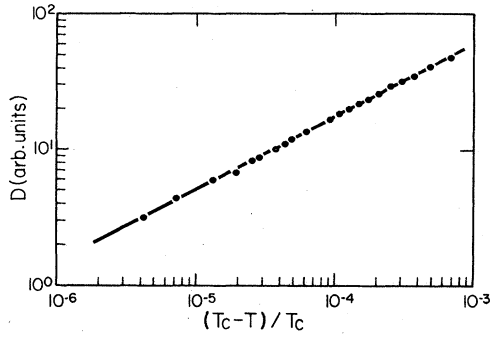


FIG. 3. Temperature dependence of  $D$  obtained after the background subtraction ( $K_3 q_z^2$ ) described in the text. The full line shows a least-squares fit giving  $\phi' = 0.54 \pm 0.04$ .

using the Jähmig-Brochard formula<sup>5</sup> for  $K_3$ :

$$K_3 = K_3^0 + \frac{kT q_0^2}{8q_z} \left[ \left( 1 + \frac{1}{X^2} \right) \tan^{-1} X - \frac{1}{X} \right], \quad (3)$$

$$X = \frac{1}{2} q_z \xi = \frac{1}{2} q_z \xi_0 t^{-\nu_{\parallel}}.$$

$K_3^0$  turns out to be negligible in the temperature range considered and  $kT q_0^2 / 8q_z$  can be taken to be constant to a very good approximation. A fit to the data in only the hydrodynamic regime ( $T - T_c \lesssim 0.1$  K) gives  $\nu_{\parallel} = 0.69 \pm 0.03$ . For  $\xi_0 = 4$  Å, Eq. (3) then yields a good fit over the whole nematic temperature range.

In the smectic phase this mode becomes nonhydrodynamic and instead of Eq. (2) we have

$$I \sim \frac{\epsilon_a^2 k_B T}{D + K_3 q_z^2}. \quad (4)$$

Hence  $\epsilon_a^2 / I = \text{const} (D + K_3 q_z^2)$  and we can calcu-

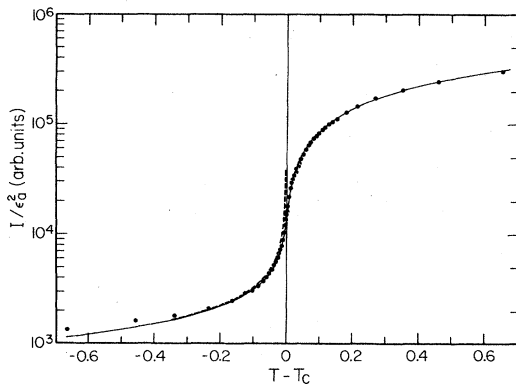


FIG. 4. Variation of the intensity of mode 2 with temperature. The full line gives the theoretical fit using the Jähmig-Brochard formula with parameters  $\nu_{\parallel} = \nu_{\parallel}^0 = 0.69$  and  $\xi_0$  and  $2\xi_0^2 = 4$  Å. The dashed curve shows the contribution of  $1/D$  to the total intensity in the smectic phase.

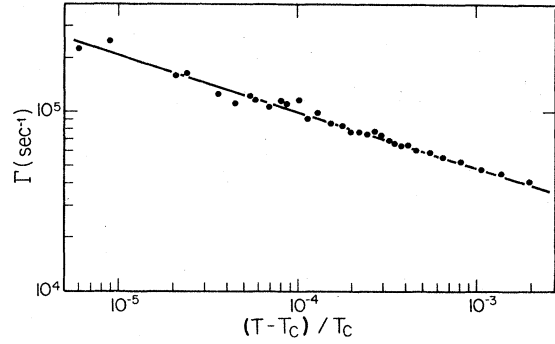


FIG. 5. Temperature dependence of the linewidth  $\Gamma_b = K_3 q_z^2 / \eta_{\text{bend}}$  in the nematic phase. The least-squares fit (full line) yields  $0.32 \pm 0.05$  for the exponent of  $\Gamma_b$ .

late the background term  $K_3 q_z^2$  using again Eq. (3) under the additional assumption  $\nu_{\parallel}' = \nu_{\parallel}$  and  $\xi_0' = \frac{1}{2} \xi_0$ . The proportionality constant follows from the fit in the nematic phase. This gives us the exponent for  $D$ :  $D \sim t^{\phi'}$ ,  $\phi' = 0.54 \pm 0.04$ . In order to get a straight line in the double log fit for  $D$  (Fig. 3)  $T_c$  had to be shifted by 2 mK with respect to the value used in the nematic phase. This is however well within the error limits ( $\pm 5$  mK) for  $T_c$  anyway. For the choice  $\xi_0' = \frac{1}{3} \xi_0$  this slight shift of  $T_c$  is not necessary while  $\phi'$  remains the same within the error limits.<sup>13</sup>

The full line in Fig. 4 shows the above described fit to the data. The dashed curve represents the contribution of  $1/D$  to the intensity. The background term  $K_3 q_z^2$  obviously gives a non-negligible contribution in the last 50 mK before the transition. The deviation between fit and data at the lowest temperatures can definitely be attributed to increasing strain in the sample which tends to enhance the total measured intensity due to elastic scattering. (The mode decays too rapidly for our correlator's 50-ns resolution so we had to make intensity measurements which integrated over all energies.)

Turning next to the bend viscosity in the nematic phase we find (Fig. 5):

$$\Gamma_b = \frac{K_3 q_z^2}{\eta_{\text{bend}}} \sim t^{-0.32 \pm 0.05}.$$

Thus we may say that within our experimental errors the bend viscosity behaves according to the helium model:  $\eta_{\text{bend}} \sim t^{-\nu/2}$ .

## CONCLUSIONS

Our main conclusion is that the critical behavior of single-layer smectics is identical to that of the well known double-layer smectics. In particular the He analogy holds to the same extent for the dynamic and the static properties in the nematic

phase, and the smectic phase shows the familiar deviations from scaling. The only significant difference between 40.8 and all bilayer smectics is the relatively strong temperature dependence of  $K_1$ . NMR measurements clearly show an enhancement of the nematic order parameter due to the onset of smectic ordering, although this seems unlikely to explain the whole change in  $K_1$ . In addition preliminary measurements on 40.7 indicate a similar temperature dependence of  $K_1$  despite the fact that the nematic range of 4.07 is much wider and therefore the coupling between  $S$  and  $\psi$  should be considerably smaller.

We have not attempted to measure  $\nu_\perp$  in this

work since the background contribution to the twist elastic constant  $K_2$  has generally proven to be too large to allow an unambiguous determination of  $\nu_\perp$ .<sup>6</sup>

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