

## X-Ray Scattering Study of the Smectic- $A_1$ to Smectic- $A_2$ Transition

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X-ray scattering measurements are reported for critical smectic- $A_2$  fluctuations along a line of second-order transitions between the smectic- $A_1$  and smectic- $A_2$  phases in mixtures of hexylphenyl cyanobenzoyloxy benzoate ( $DB_6$ ) and terephthal-*bis*-butylaniline (TBBA). The measured exponents  $\gamma = 1.46 \pm 0.05$  and  $\nu_{\parallel} = \nu_{\perp} = 0.74 \pm 0.03$  are constant along the second-order line and agree with recent heat-capacity measurements and the scaling law,  $3\nu + \alpha = 2$ . They disagree with current theoretical expectations.

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The smectic- $A$  phase, which corresponds to the establishment of a one-dimensional density wave in a three-dimensional (3D) liquid, is a system precisely at its lower marginal dimension and consequently does not have true long-range order (LRO) but instead has only quasi long-range order (QLRO).<sup>1</sup> The concept of QLRO in a correlation function has broad importance in equilibrium statistical physics and interest is particularly acute for the smectic- $A$  phase.<sup>2</sup> This phase continues to be one of the most important systems in which QLRO can be studied. The one-dimensional density wave can result in either a monolayer smectic- $A_1$  phase where the periodicity corresponds to the molecular length,  $l$ , or a bilayer smectic- $A_2$  phase where the periodicity corresponds to twice the molecular length,  $2l$ .<sup>3</sup> Very recently systems with a smectic- $A_1$  to smectic- $A_2$  ( $A_1A_2$ ) transition were discovered by Hardouin and co-workers.<sup>4,5</sup> This transition is of great intrinsic interest since it corresponds to a transition between two systems with QLRO.<sup>6-8</sup>

The  $A_1A_2$  transition is also relevant to the nematic to smectic- $A$  (NA) transition which, despite considerable experimental and theoretical effort, remains one of the principal unsolved problems in equilibrium statistical physics.<sup>9-11</sup> Complications in the NA transition include the divergent phase fluctuations of the smectic- $A$  order parameter which produce QLRO, strong coupling between the nematic director and the smectic layering, and the anisotropy ( $\nu_{\parallel} \neq \nu_{\perp}$ ) of divergences in the correlation lengths parallel ( $\xi_{\parallel} \sim t^{-\nu_{\parallel}}$ ) and perpendicular ( $\xi_{\perp} \sim t^{-\nu_{\perp}}$ ) to the nematic director. All materials which have been studied appear to obey the anisotropic hyperscaling relation,  $\nu_{\parallel} + 2\nu_{\perp} + \alpha = 2$  (where  $\alpha$  is the heat-capacity exponent).<sup>10</sup> However, there is no viable explanation for the anisotropy ( $\nu_{\parallel} - \nu_{\perp} \sim 0.1-0.2$  for all measured materials) or for the increase in the observed values of  $\nu_{\parallel}$  ( $\nu_{\parallel} \sim 0.7-0.8$  for the transitions which are currently thought to be representative of NA critical behavior)

relative to the theoretically predicted value ( $\nu_{\parallel} \sim 0.66$ ). The origin of this puzzling anisotropy has been widely attributed to the divergent phase fluctuations<sup>9</sup> but it has not been previously possible to test this hypothesis directly. The  $A_1A_2$  transition allows an indirect test since the smectic- $A_2$  phase fluctuations are quenched by the presence of the established smectic- $A_1$  density wave.

In this Letter we report the first high-resolution x-ray scattering studies of the  $A_1A_2$  transition. We measured the susceptibility and correlation lengths for a series of mixtures of hexylphenyl cyanobenzoyloxy benzoate ( $DB_6$ ) and terephthal-*bis*-butylaniline (TBBA) with  $A_1A_2$  transitions and found that these transitions are isotropic with correlation-length exponents,  $\nu_{\parallel} = \nu_{\perp} = 0.74 \pm 0.03$ , elevated compared to the theoretically predicted value ( $\nu = 0.63$ ).<sup>8</sup> This strongly supports the hypothesis that the phase fluctuations are responsible for the anisotropy in the NA transition.

Prost developed a mean field model for the  $A_1A_2$  transition which introduces complex order parameters  $\psi_1$  and  $\psi_2$  corresponding to density fluctuations at  $\mathbf{q}_0 = (2\pi/2l)\hat{z}$  and  $2\mathbf{q}_0 = (2\pi/l)\hat{z}$ , respectively.<sup>6,7</sup> In this model the NA transition is a normal NA transition in which  $\psi_2$  develops QLRO. At the  $A_1A_2$  transition  $\psi_1$  develops in the presence of a nonzero  $\psi_2$ . Because of the coupling  $\psi_1^* \psi_2^*$  between  $\psi_1$  and  $\psi_2$ , the phase of  $\psi_1$  is locked to that of  $\psi_2$ . Consequently only the amplitude  $|\psi_1|$  has critical behavior at the  $A_1A_2$  transition, and the mean-field model predicts that the transition will be in the 3D Ising class. A more accurate description notes that the "Ising" transition occurs on a smectic- $A_1$  "lattice" (with QLRO) rather than on a true 3D crystal lattice (with LRO). This presents all the complications inherent in the smectic- $A$  phase: QLRO, anisotropy, and coupling between smectic layering and nematic director. Wang and Lubensky<sup>8</sup> have studied a model which includes all of these effects. To first order in the  $\epsilon$  expansion they

find the  $A_1A_2$  transition to be in the same universality class as the Ising model with isotropic correlation length exponents  $\nu_{\parallel} = \nu_{\perp} = 0.63$ . However, a nonuniversal susceptibility exponent ( $\gamma$ ) of order 0.1 to 0.2 less than the Ising value<sup>12</sup> of 1.242 is predicted.

The x-ray source was a Rigaku RU-200 rotating-anode generator with a  $0.3 \times 0.3$ -mm<sup>2</sup> effective source size. Germanium (220) monochromator and analyzer crystals provided a longitudinal resolution of  $1.6 \times 10^{-4} \text{ \AA}^{-1}$  [half width at half maximum (HWHM)] in the scattering plane. The transverse in-plane resolution was effectively perfect while the transverse out-of-plane resolution was set by slits to be  $0.06 \text{ \AA}^{-1}$  (HWHM). The dispersion of the monochromator induced a spatial separation of the Cu  $K\alpha$  doublet, which allowed the  $K\alpha_2$  ( $\lambda = 1.55439 \text{ \AA}$ ) line to be eliminated by a slit. Only the  $K\alpha_1$  ( $\lambda = 1.54056 \text{ \AA}$ ) component was incident on the sample. The scattered intensity was normalized to the signal from a beam monitor between the monochromator and sample. The sample was contained in a beryllium cell inside a two-stage oven with a dry nitrogen atmosphere. The measured temperature uniformity over the illuminated sample volume (typically 1–2-mm linear dimensions) was better than 2 mK and the stability was about 0.5 mK over a period of several hours. The nematic director was aligned with a 4.3-kG field provided by samarium-cobalt permanent magnets. Typical sample mosaics in the smectic- $A_1$  phase were about  $0.6^\circ$  FWHM.

Pretransitional fluctuations above  $T_c$  ( $T_c$  is the  $A_1A_2$  transition temperature) give rise to critical scattering which can be described by an x-ray structure factor

$$S(\mathbf{q}) = \sigma / [1 + \xi_{\parallel}^2 (q_{\parallel} - q_0)^2 + \xi_{\perp}^2 q_{\perp}^2], \quad (1)$$

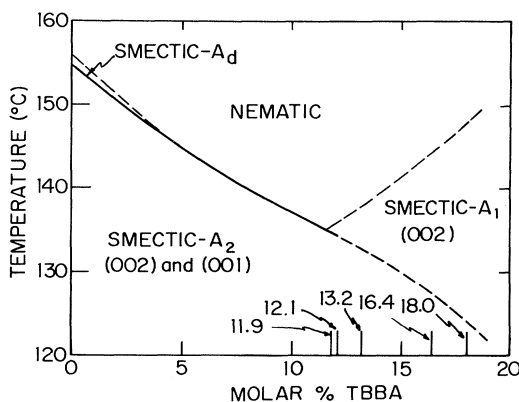


FIG. 1. Phase diagram for mixtures of  $DB_6$  with TBBA. The quasi-Bragg reflection from the bilayer ordering is indexed (001) and the monolayer ordering is indexed (002). The dashed lines indicate second-order phase transitions and the solid lines indicate first-order transitions. The order of the  $A_dA_2$  phase boundary has not been determined. The five mixtures reported in this study are indicated.

where  $q_0 = 2\pi/2l$  is the wave number corresponding to the bilayer spacing ( $2l$ ) and  $\parallel$  and  $\perp$  indicate directions with respect to the nematic director. Longitudinal scans (vary  $q_{\parallel}$  at  $q_{\perp} = 0$ ) and transverse scans (vary  $q_{\perp}$  at  $q_{\parallel} = q_0$ ) were done at a series of temperatures close to the transition. Simultaneous fits of the longitudinal and transverse scans by Eq. (1) (appropriately convolved with the instrumental resolution and corrected for sample mosaic which was directly measured using the monolayer peak at  $2q_0$ ) yielded  $\sigma$ ,  $\xi_{\parallel}$ , and  $\xi_{\perp}$ . The results of the structure factor fits were then fitted by the power laws  $\sigma(t) = \sigma^0 t^{-\gamma}$ ,  $\xi_{\parallel}(t) = \xi_{\parallel}^0 t^{-\nu_{\parallel}}$ ,  $\xi_{\perp}(t) = \xi_{\perp}^0 t^{-\nu_{\perp}}$  [where  $t = (T - T_c)/T_c$ ] to obtain the critical exponents. The transition temperature,  $T_c$ , was determined to within  $\pm 3$  mK as the temperature below which the widths of longitudinal and transverse scans were resolution and mosaic limited.

The phase diagram for the  $DB_6$ -TBBA system is shown in Fig. 1. The  $A_1A_2$  transitions, for five mixtures chosen to span the second-order to first-order crossover, were studied and are reported here. A complete study including the  $NA_1$ ,  $NA_2$ ,  $NA_d$ , and  $A_dA_2$  transitions will be published separately. The 18.0-, 16.4-, and 13.2-mol% TBBA mixtures had second-order transitions while the 12.1- and 11.9-mol% mix-

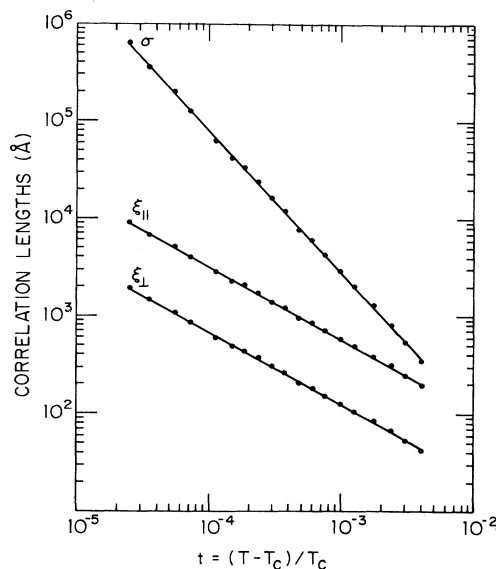


FIG. 2. Measured evolution of the  $A_2$  fluctuations in the  $A_1$  phase for the 16.4-mol% mixture. The divergence of the susceptibility ( $\sigma = \sigma^0 t^{-\gamma}$ ), longitudinal correlation length ( $\xi_{\parallel} = \xi_{\parallel}^0 t^{-\nu_{\parallel}}$ ), and transverse correlation length ( $\xi_{\perp} = \xi_{\perp}^0 t^{-\nu_{\perp}}$ ) is shown. The units for the susceptibility are arbitrary and  $q_0 = 0.1171 \text{ \AA}^{-1}$ . The exponents determined by a simultaneous power-law fit for  $\gamma$ ,  $\nu_{\parallel}$ , and  $\nu_{\perp}$  are  $\gamma = 1.46 \pm 0.05$ ,  $\nu_{\parallel} = 0.75 \pm 0.03$ , and  $\nu_{\perp} = 0.74 \pm 0.03$ . The transition temperature  $T_c$  ( $\sim 127^\circ \text{C}$ ) was allowed to vary in the fits.

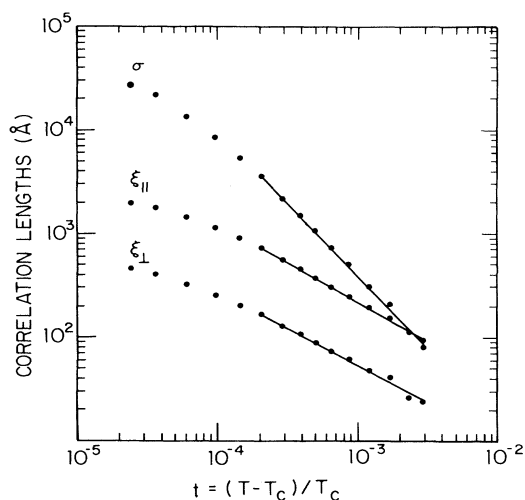


FIG. 3. Measured evolution of the  $A_2$  fluctuations in the  $A_1$  phase for the 12.1-mol% mixture. The susceptibility ( $\sigma$ ), longitudinal correlation length ( $\xi_{||}$ ), and transverse correlation length ( $\xi_{\perp}$ ) are shown. The units for the susceptibility are arbitrary and  $q_0 = 0.1185 \text{ \AA}^{-1}$ . Power-law fits over the range  $t > 2 \times 10^{-4}$  yielded  $\gamma = 1.41$ ,  $\nu_{||} = 0.76$ , and  $\nu_{\perp} = 0.72$ .

tures had first-order transitions.

Figure 2 shows the measured susceptibility and correlation lengths for the 16.4-mol% sample, together with the power-law fits. In the fits the transition temperature was allowed to vary as a free parameter; it never deviated by more than 3 mK from the value determined from simple inspection of the linewidths of the raw data. For this mixture the resulting critical exponents are  $\gamma = 1.46 \pm 0.05$ ,  $\nu_{||} = 0.75 \pm 0.03$ , and  $\nu_{\perp} = 0.74 \pm 0.03$ . The quoted errors are almost entirely systematic, reflecting uncertainties in the corrections for mosaic, background, and instrumental resolution. Table I lists the results for all of the mixtures.

The results for the 12.1-mol% sample are shown in

Fig. 3. The data could not be fitted with simple power laws using the transition temperature identified by linewidth inspection. The presence, near  $T_c$ , of a sharp resolution-limited peak superposed on diffuse fluctuation scattering indicated a first-order transition with a small coexistence region. An extrapolation of the data yielded an asymptotic transition temperature about 20 mK below the beginning of the coexistence. Power-law fits to the data over the reduced temperature range  $t > 2 \times 10^{-4}$  yielded exponents comparable to those obtained for the other mixtures (see Table I). The 11.9-mol% mixture was unambiguously first order; there was a sudden transition (within 3 mK) and no observed coexistence.

We tested the effect of including a fourth-order term of the form  $c\xi_{\perp}^4 q_{\perp}^4$  in the denominator of the structure factor in Eq. (1). Other workers have found this to be necessary to account for anomalous transverse tails observed in the NA transition.<sup>13</sup> We found no measurable effect on the quality of the line-shape fits (the  $\chi^2$  were typically 1.0 to 1.5) and in all cases the coefficient  $c$  was consistent with zero within a statistical uncertainty many times larger than the best-fit value.

Our data show critical exponents that are invariant along the second-order  $A_1A_2$  line. The correlation-length exponents are isotropic ( $\nu_{||} = \nu_{\perp}$ ) within the errors. The average values are  $\gamma = 1.46 \pm 0.05$  and  $\nu_{||} = \nu_{\perp} = 0.74 \pm 0.03$ . Although there is a change in the absolute lengths  $\xi_{||}^0$  and  $\xi_{\perp}^0$  with concentration (with smaller values closer to the tricritical point), within experimental uncertainty  $\xi_{||}^0 / \xi_{\perp}^0 \sim 4$  is invariant. This appears explicitly if the data for different concentrations are fitted with  $\nu_{||} = \nu_{\perp}$  held fixed at 0.74. Over the range of length scales and reduced temperatures measured, we find no indication of critical to tricritical crossover effects, as reported for the NA transition.<sup>10,11</sup>

Our exponents do not agree with the 3D Ising values

TABLE I. Summary of the power-law fits for the susceptibility ( $\sigma = \sigma^0 t^{-\gamma}$ ), longitudinal correlation length ( $\xi_{||} = \xi_{||}^0 t^{-\nu_{||}}$ ), and transverse correlation length ( $\xi_{\perp} = \xi_{\perp}^0 t^{-\nu_{\perp}}$ ) for each mixture. The units for the susceptibility are arbitrary. Except for the 12.1-mol% sample the reduced temperature range used in the fits was  $2 \times 10^{-5} \leq t \leq 8 \times 10^{-3}$ ; for the 12.1-mol% sample  $t > 2 \times 10^{-4}$ .

mol% TBBA	$\sigma^0$	$\gamma$	$\xi_{  }^0$ (Å)	$\nu_{  }$	$\xi_{\perp}^0$ (Å)	$\nu_{\perp}$
18.0	0.14	1.46 <sup>a</sup>	3.5	0.75 <sup>b</sup>	0.91	0.73 <sup>b</sup>
16.4	0.12	1.46	3.3	0.75	0.77	0.74
13.2	0.062	1.45	2.5	0.74	0.58	0.73
12.1	0.024	1.41	1.2	0.76	0.39	0.72

<sup>a</sup>The error on the susceptibility exponent,  $\gamma$ , is  $\pm 0.05$ .

<sup>b</sup>The error on the correlation length exponents,  $\nu_{||}$  and  $\nu_{\perp}$ , is  $\pm 0.03$ .

( $\gamma = 1.24$ ,  $\nu = 0.63$ ) but are consistent with the recent heat-capacity measurements by Chiang and Garland<sup>14</sup> and the scaling law  $3\nu + \alpha = 2$ . Combining their value of  $\alpha = -0.14 \pm 0.06$  with our values yields  $3\nu + \alpha = 2.08 \pm 0.15$  which agrees with the scaling law. Since the experiments do not agree with theoretical expectations, it is important to determine if the observed exponents are universal. Experiments on other systems with an  $A_1A_2$  transition are clearly needed to answer this question.

In conclusion, we note that the isotropic correlation-length exponents observed in these  $A_1A_2$  transitions provide the first experimental support for the widespread hypothesis that the divergent phase fluctuations of the smectic order parameter are responsible for the anisotropy in the NA transition. In addition, our observation that the pretransitional  $A_2$  fluctuations are well described by a pure Lorentzian form in both the longitudinal and transverse directions suggests that the inherent anisotropy in the NA transition is related to the anomalous  $q^4$  transverse tails. There is no understanding at the present time of the increase in the correlation-length exponents compared to the theoretically expected value, but it is suggestive that this behavior is found in both the NA ( $\nu_{\parallel}$ ) and  $A_1A_2$  transitions. The theoretically predicted decrease in the susceptibility exponent relative to the Ising value is also in disagreement with the observed increase. Clearly, continued experimental and theoretical work on the  $A_1A_2$  transition is needed.

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