

## Critical Fluctuations near a Nematic-Smectic-A-Smectic-C Multicritical Point

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We report a high-resolution x-ray study of the fluctuations in a system exhibiting nematic, smectic-A, and smectic-C phases, with emphasis on the NAC multicritical region. We find that the transverse mass density fluctuations are always Lorentzian in character in explicit disagreement with the Lifshitz model for this system. Unexpectedly, both the mass density fluctuations and the tilt order parameter exhibit isotropic heliumlike critical exponents near the NAC point.

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Smectic-A and smectic-C liquid crystals may be simply described as orientationally ordered fluids with one-dimensional mass density waves either along (A) or at an angle (C) to the unique orientational axis.<sup>1</sup> In appropriate binary liquid-crystal mixtures it is possible to have lines of second-order nematic-smectic-A (NA) and smectic-A-smectic-C (AC) transitions crossing over to a line of first-order nematic-smectic-C transitions.<sup>2</sup> The point at which these three lines meet is labeled the NAC multicritical point. A variety of theoretical models have been proposed for this system,<sup>3</sup> the most intriguing being that due to Chen and Lubensky which predicts that the NAC point should be a realization of an  $m=2$  Lifshitz model.<sup>4</sup> As we shall discuss below this model predicts novel behavior for the mass density fluctuations; the latter are probed directly with x rays.<sup>1,5</sup> In this paper we report a high-resolution x-ray scattering study of the critical fluctuations in the NAC region in mixtures of octyl- and heptyloxy-*p'*-pentyphenyl thiolbenzoate (8S5<sub>1-x</sub>-7S5<sub>x</sub>). Complementary thermodynamic studies have been carried out by Johnson and co-workers.<sup>2</sup>

We begin with a brief discussion of the theory. A number of mean-field or Landau-Ginzburg models have been proposed for the global NAC phase diagram.<sup>3</sup> In this paper we shall emphasize those two theories which make explicit predictions for the  $\vec{q}$ -dependent mass density fluctuations. In the first, due to Chen and Lubensky,<sup>3</sup> the smectic-C tilt order parameter is described through the transverse gradient of the smectic mass density. A smectic-C phase occurs when the coefficient of the gradient-squared term is

negative, the equilibrium tilt thence being determined by the competition between the second- and fourth-order gradient terms. In this theory at the NAC point the coefficient of the gradient-squared term is zero. Thus the NAC point is an example of an  $m=2$  Lifshitz point,<sup>4</sup> which, in turn, has a lower marginal dimensionality of 3 so that especially interesting fluctuation effects should occur. The Chen-Lubensky model thus makes the dramatic prediction that near the NAC point the transverse mass density fluctuations should have a  $q_{\perp}^4$  dependence rather than conventional Lorentzian  $q_{\perp}^2$  behavior. Specifically, they predict for the x-ray cross section along the NA line

$$S(\vec{q}) = \frac{A \xi_{\parallel}^2}{1 + \xi_{\parallel}^2 (q_{\parallel} - q_0)^2 + \xi_{\perp}^2 q_{\perp}^2 + d_{\perp} q_{\perp}^4}, \quad (1)$$

with  $\xi_{\perp} \rightarrow 0$  as one approaches the NAC region. An alternative approach is taken by Chu and McMillan<sup>3</sup>: In their theory, the tilt occurs parasitically as a result of an in-plane orientational ordering of the liquid-crystal molecules due to the dipole-dipole interactions. Thus the tilt enters as an independent order parameter. This theory, as well as a number of other closely related models,<sup>3</sup> predicts  $q_{\perp}^2$  tails throughout the nematic region on either side of the NAC concentration with no special behavior in  $\xi_{\perp}$ .

As shown by Johnson and co-workers<sup>2</sup> the binary mixture system 8S5<sub>1-x</sub>-7S5<sub>x</sub> exhibits an NAC multicritical point at  $x_{\text{NAC}} = 0.422 \pm 0.005$  mole fraction, with lines of second-order NA and AC transitions for  $x < x_{\text{NAC}}$ . We have carried out x-ray diffuse scattering studies for five concentrations  $x = 0, 0.15, 0.31, 0.41,$  and  $0.42$ ; in this

paper we shall emphasize the results in the latter two samples. The experimental techniques have been described previously.<sup>5</sup> By using a combination of horizontal and vertical slits together with perfect Si(111) crystals as monochromator and analyzer we obtain a resolution for Cu  $K\alpha$  radiation of  $1.2 \times 10^{-4} \text{ \AA}^{-1}$  half width at half maximum (HWHM) in the longitudinal direction, and  $\sim 10^{-5} \text{ \AA}^{-1}$  HWHM in the transverse in-plane direction. In the NA experiments the vertical resolution was  $4.8 \times 10^{-2} \text{ \AA}^{-1}$  (HWHM) while in the AC measurements where the vertical resolution requirement is more stringent, it was improved by about an order of magnitude. The liquid-crystal mixtures were contained in a vessel  $12 \times 12 \times 0.5 \text{ mm}^3$  with 0.25-mm Be windows. The illuminated area was typically  $1 \times 3 \text{ mm}^2$ . An applied magnetic field of 4000 Oe provided alignment of the director in the scattering plane. Temperature control of  $\sim 2 \text{ mK}$  during an x-ray scan was provided by a two-stage computer-controlled oven.

In the nematic phase the critical scattering was centered about the point  $(0, 0, q_0)$  in reciprocal space with  $q_0 \approx 0.2255 \text{ \AA}^{-1}$  in the NAC region. In all mixtures we carried out both longitudinal ( $q_{\parallel}$  varied,  $q_{\perp} = 0$ ) and transverse ( $q_{\perp}$  varied,  $q_{\parallel} = q_0$ ) scans for each reduced temperature  $t = (T - T_{NA})/T_{NA}$ . We show in Fig. 1 typical results for the sample<sup>6</sup> with  $x = 0.42$ . For this set of data the NA and AC transitions occurred at 322.99 and 322.71 K, respectively, with both transitions being sec-

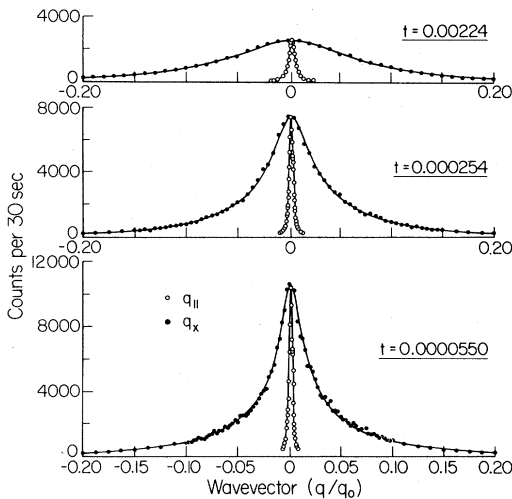


FIG. 1. Transverse and longitudinal scans through the position  $(0, 0, q_0)$  with  $q_0 = 0.2255 \text{ \AA}^{-1}$  in the sample with  $x = 0.42$ . The solid lines are the results of fits of Eq. (1) to the data as discussed in the text.

ond order to within 5 mK. From the phase diagram of DeHoff *et al.*<sup>2</sup> we estimate  $x_{NAC} - x \approx 0.002$ . Essentially identical data were obtained from the sample with  $T_{NA} - T_{AC} = 0.16 \text{ K}$ . Qualitatively, we note that the transverse scans look very much like Lorentzians. We note also that the lengths are quite anisotropic with  $\xi_{\parallel} \gg \xi_{\perp}$ . These results may be analyzed quantitatively by least-squares fits of Eq. (1) convoluted with the instrumental resolution function to the experimental data. The results of these fits are shown as the solid lines in Fig. 1. Both the longitudinal and transverse scans are nearly ideal Lorentzians; as observed previously in other NA studies there is a small transverse  $q_{\perp}^4$  term with  $C_{\perp} \approx 0.03$  but, as before,  $C_{\perp} \rightarrow 0$  as  $t \rightarrow 0$ ; here  $d_{\perp} = C_{\perp} \xi_{\perp}^4$ .

We show in Fig. 2 the transverse correlation length  $\xi_{\perp}$  in reduced units at a series of reduced temperatures; we show also the evolution of the fourth-order coefficient  $C_{\perp}$ . It is evident that both quantities vary quite smoothly up to the NAC multicritical region with no evidence whatsoever of the Chen-Lubensky prediction of  $\xi_{\perp} \rightarrow 0$  at  $x_{NAC}$ . These results thence definitively rule out the

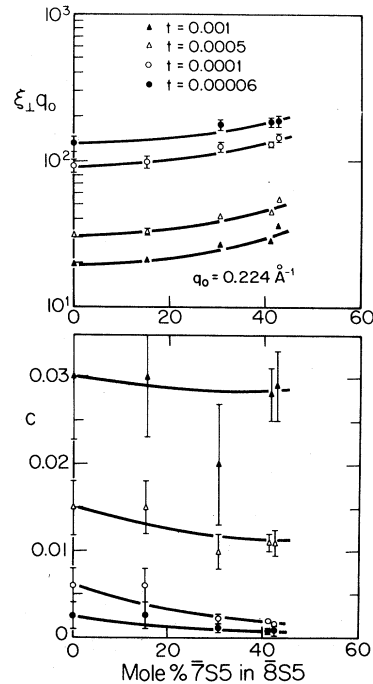


FIG. 2. Upper panel: transverse correlation length  $\xi_{\perp} q_0$  at several reduced temperatures in all samples studied. Lower panel: coefficient of  $\xi_{\perp}^4 q^4$  in Eq. (1) at a series of reduced temperatures in all samples studied. The solid lines are guides to the eye.

*Lifshitz model for the NAC multicritical region.* Before discussing alternative models we consider first the detailed NA critical behavior as well as the behavior of the tilt order parameter in the smectic-C phase.

We show in the upper panel of Fig. 3 the transverse and longitudinal correlation lengths and the smectic susceptibility for the  $x=0.41$  and  $x=0.42$  samples. Fits to single-power-law divergences over the reduced temperature range  $2 \times 10^{-3} > t > 5 \times 10^{-5}$  yield the exponents  $\gamma = 1.31 \pm 0.05$ ,  $\nu_{\parallel} = 0.69 \pm 0.03$ , and  $\nu_{\perp} = 0.67 \pm 0.03$  with  $\xi_{\parallel}/\xi_{\perp} = 32 \pm 2$  for  $x=0.42$ , and  $\gamma = 1.29 \pm 0.04$ ,  $\nu_{\parallel} = 0.66 \pm 0.03$ , and  $\nu_{\perp} = 0.63 \pm 0.02$  with  $\xi_{\parallel}/\xi_{\perp} = 30 \pm 2$  for  $x=0.41$ . These exponents agree within the errors with those for the superconducting analog model ( $d=3$ ,

$n=2$ ),  $\gamma \approx 1.32$ ,  $\nu_{\parallel} = \nu_{\perp} = 0.67$ , postulated for the pure NA transition.<sup>1</sup> We note that in pure  $\bar{8}S5$  we found  $\gamma = 1.53$ ,  $\nu_{\parallel} = 0.83$ , and  $\nu_{\perp} = 0.68$  in explicit disagreement with the  $d=3, n=2$  exponents. The ratio of lengths inside of  $10^{-3}$  is approximately five times the molecular length ratio of 6.3 determined from the ratio of the in-plane to between-plane peak  $q$  vectors.

With use of high-resolution x-ray techniques<sup>5</sup> it is possible to measure both the tilt order parameter and the layer spacing simultaneously. In the simplest model these are related by  $d_C = d_A \cos \Phi$  where  $d_{A,C}$  is the layer spacing and  $\Phi$  is the tilt angle. This model gives  $d_A - d_C \sim 2\theta_C - 2\theta_A \sim \Phi^2$ , where  $2\theta$  is the scattering angle. We show in the bottom panel of Fig. 3 the tilt angle together with  $\Delta 2\theta = 2\theta_C - 2\theta_A$  for the  $x=0.42$  sample. Both quantities exhibit single-power-law behavior with exponents differing by a factor of 2 as expected. Further, the order-parameter exponent,  $\beta_{\Phi} = 0.34 \pm 0.02$ , again agrees with the helium value 0.346 within the errors. In pure  $\bar{8}S5$  Safinya *et al.*<sup>5</sup> find  $\beta_{\Phi} = 0.47 \pm 0.04$  and  $\beta_{2\theta} = 0.98 \pm 0.12$ ; they have rationalized this mean-field behavior using a Ginzburg criterion argument, that is, that the true critical region is inside of  $t = 10^{-5}$ . Evidently near the NAC point one observes true critical behavior out to  $3 \times 10^{-3}$ , presumably due to a reduced bare length.

We now discuss the significance of these results. It is evident that one important feature of the Chu-McMillan approach is correct, that is, that one has Lorentzian mass density fluctuations throughout the nematic phase and that these fluctuations vary smoothly across the NAC phase diagram. We have preliminary results that suggest that this holds into the NC region; the principal change is in the geometry of the configuration in reciprocal space about which these fluctuations occur—the points  $(0, 0, \pm q_0)$  in the NA region, and the rings  $(q_{\perp} \cos \varphi, q_{\perp} \sin \varphi, \pm q_0)$  in the NC region. At the same time there is convincing evidence that the McMillan model of the tilt being driven by in-plane orientational ordering of the molecules is not correct.<sup>2,3</sup> Indeed we know of no datum that requires that the tilt enter as a truly independent order parameter; rather the Chen-Lubensky approach of treating the tilt as the transverse gradient of the density wave is both physically persuasive and consistent with the empirical behavior. It seems evident therefore that a Landau-Ginzburg theory which is an amalgam of the Chen-Lubensky and Chu-McMillan approaches is required since both theories have as-

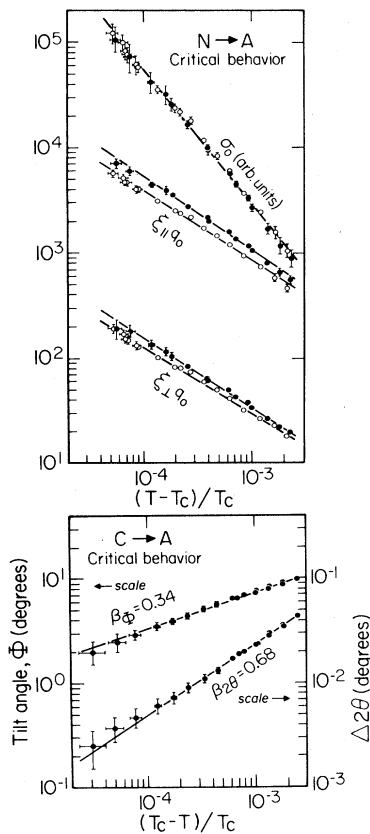


FIG. 3. Upper panel: critical behavior of  $\xi_{\parallel}$ ,  $\xi_{\perp}$ , and the smectic susceptibility  $\sigma(0)$  in the samples with  $x = 0.41$  (open circles) and  $x = 0.42$  (filled circles). The solid lines are single power laws with exponents given in the text. Above  $3 \times 10^{-3}$  the data deviate from the single-power-law behavior. Lower panel: tilt order parameter and change in scattering angle  $2\theta$  in the smectic-C phase for the sample with  $x = 0.42$ . The solid lines are single power laws with the exponents indicated.

pects which are correct and aspects which disagree with experiment. We should also mention that a variant of the Chu-McMillan Landau theory has been given by Benguigi.<sup>3</sup> As discussed by DeHoff *et al.*<sup>2</sup> his Landau model yields a phase diagram closer to that observed experimentally; however, he predicts that the AC transition should become first order near the NAC point in contradiction with our experimental results. An interesting mean-field model which relies on induced dipole effects to produce the tilt has been given by Van der Meer and Vertogen<sup>3</sup>; this model has a number of appealing features. Unfortunately, it does not give the correct geometry for the phase boundaries around the NAC point. However, this may be an artifact of the mean-field approximation. A Landau-Ginzburg formulation of their model with more accurate calculations using, for example, renormalization-group techniques, would be most valuable.

Finally, we emphasize that the simple  $d=3, n=2$  critical behavior we observe for the NA and AC transitions near the NAC point is extremely surprising. Our high-resolution studies of other NA transitions in a variety of systems including  $\overline{8S5}$  consistently show  $\xi_{\parallel}$  and  $\xi_{\perp}$  diverging at different rates with  $\nu_{\parallel} - \nu_{\perp} \sim 0.15$ . The exponents  $\alpha$ ,  $\nu_{\parallel}$ ,  $\nu_{\perp}$ , and  $\gamma$  seem to vary smoothly with  $T_{NI}/T_{NA}$  but with substantial differences from the  $d=3, n=2$  values.<sup>5</sup> We do not have any plausible explanation for the simple behavior observed near the NAC point.

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<sup>1</sup>P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford Univ. Press, New York, 1977).

<sup>2</sup>D. L. Johnson, D. Allender, R. DeHoff, C. Maze, E. Oppenheim, and R. Reynolds, *Phys. Rev. B* **16**, 470 (1977). For more detailed work which establishes the nature of the phase boundaries near the NAC multicritical point, see R. DeHoff, R. Biggers, D. Brisbin, R. Mahmood, C. Gooden, and D. L. Johnson, preceding Letter [*Phys. Rev. Lett.* **47**, 664 (1981)]. It should also be noted that Sigaud *et al.*, *Solid State Comm.* **23**, 35 (1977), have discovered a system which may exhibit a different NAC phase boundary topology. However, much more detailed measurements analogous to those of DeHoff *et al.* must be performed on the system of Sigaud *et al.* before this is definitely established.

<sup>3</sup>J.-L. Chen and T. C. Lubensky, *Phys. Rev. A* **14**, 1202 (1976); K. C. Chu and W. L. McMillan, *Phys. Rev. A* **15**, 1181 (1977); L. Benguigi, *J. Phys. (Paris) Colloq.* **40**, C3-419 (1979); B. W. Van der Meer and G. Vertogen, *J. Phys. (Paris), Colloq.* **40**, C3-222 (1979).

<sup>4</sup>R. Hornreich, M. Luban, and S. Shtrikman, *Phys. Rev. Lett.* **35**, 1678 (1975).

<sup>5</sup>See, for example, J. D. Litster *et al.*, *J. Phys. (Paris), Colloq.* **40**, C3-339 (1979); C. R. Safinya *et al.*, *Phys. Rev. B* **21**, 4149 (1980); M. Kaplan, Ph.D. thesis, Massachusetts Institute of Technology, 1980 (unpublished); C. R. Safinya, Ph.D. thesis, Massachusetts Institute of Technology, 1981 (unpublished).

<sup>6</sup>We should note that in this sample the effective concentration evolved slightly over the time scale of one month, possibly because of degradation from the x-ray beam. The *A* region changed from unobservably small to 160 to 280 mK. We have confirmed that this has no important effect on the results.