X-Ray Study of Fluctuations near the Nematic–Smectic-A–Smectic-C Multicritical Point

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We present the results of a high-resolution x-ray-scattering study of the pretransitional fluctuations above the nematic–to–smectic-C phase boundary in the $\bar{7}$S5/8OCB system. The fluctuations are well described by the Lifshitz-point model of Chen and Lubensky with minimal adjustable parameters. We have located the line along which the x-ray cross section $\sigma(\mathbf{q})$ exhibits pure $q_\perp^{-4}$ fluctuations. Close to the nematic–smectic-A–smectic-C point this line is simply related to the smectic-A–smectic-C transition boundary.

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The phase-transition behavior of liquid-crystal systems exhibiting a confluence of nematic (N), smectic-A (S_A), and smectic-C (S_C) phases has been the subject of extensive investigation for the past decade.[1-5] In spite of this effort, a satisfactory experimental and theoretical description has not yet emerged. Experiments suggest that the N, S_A, and S_C phases come together at a single triple point, labeled the NAC multicritical point, with phase boundaries exhibiting universal geometrical behavior.[5] Much less is known about the nature of the mass-density fluctuations in the vicinity of the NAC point. This is an important shortcoming since the different theoretical models[1,2] make rather different predictions for the q dependence of the smectic susceptibility $\sigma(\mathbf{q})$.

Currently, the most extensive experimental information is available for the system $\bar{7}S5_x$-$\bar{8}S5_{1-x}$ (heptyloxy- and octyloxy-p'-pentylphenylthiol benzoate) which initially was viewed as prototypical.[3,4] However, recent work by Johnson and co-workers[4,5] indicates that the NAC multicritical region is unusually narrow in $\bar{7}$S5-$\bar{8}$S5. It is essential that detailed measurements be made on systems within the universal *NAC multicritical region* discovered by Brisbin *et al.*[5] and confirmed by Shashidhar, Ratna, and Krishna Prasad.[5] In this paper we report detailed microscope and high-resolution x-ray studies of mixtures of octyloxycyanobiphenyl (8OCB) and heptyloxypentylthiol benzoate ($\bar{7}$S5). We show from microscope studies that this system exhibits the "universal NAC diagram" of Brisbin *et al.* Further, from our x-ray studies in the nematic phase, we find that the smectic mass-density fluctuations are always well described by the simple Liftshitz form[6] proposed by Chen and Lubensky.[1] This is in partial contrast to the results of Ref. 3 where in the immediate vicinity of the NAC point the fluctuations are Lorentzian. We have located the Lifshitz line along which the coefficient of the transverse gradient squared term vanishes and we find that its locus mirrors that of the S_A-S_C boundary. Thus the NAC system is now experimentally the most completely characterized Lifshitz system; however, as we shall discuss, important theoretical issues remain unresolved.

We discuss first the $\bar{7}$S5-8OCB phase diagram. Using a polarizing microscope we studied 32 different mixtures; the phase boundaries could be identified by an abrupt change in the texture. The nature of the phases and the locations of the phase boundaries were confirmed for eleven of the mixtures by use of x rays. The phase diagram so obtained is shown in Fig. 1. Comparison with the data in Ref. 5 shows that the $\bar{7}$S5-8OCB system exhibits the generic NAC phase diagram with an extended multicritical region. The NAC point occurs for a molar fraction of 8OCB of $X_{8OCB} = 0.0217$ at the temperature $T_{NAC} = 41.8$ °C. Explicit fits by the crossover form suggested by Brisbin *et*

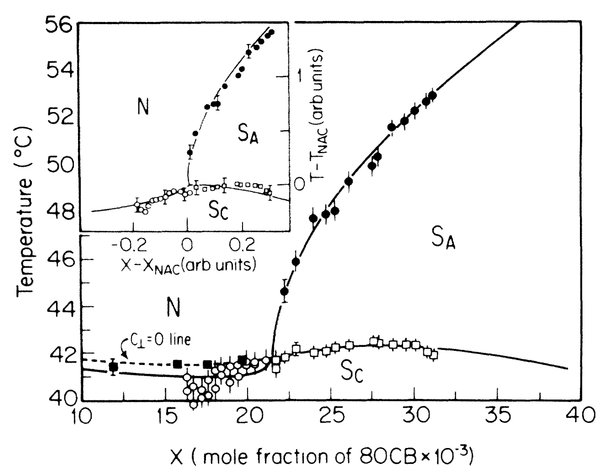

FIG. 1. NAC phase diagram obtained from the polarizing microscope studies. Solid circles, T_{NA}; open squares, T_{AC}; open circles, T_{NC}; and solid squares, $T(C_\perp = 0)$. The solid lines are the results of fits by Eq. (1) as discussed in the text. For the N-S_C transition which is hysteretic we show transition temperatures on both heating (upper) and cooling (lower). Inset: The data superimposed on the universal NAC curve of Ref. 5 with temperature and concentration rescaled by 0.124 and 0.033, respectively, and $B = 0$. Only the N-S_C transitions on heating are displayed in the inset.

al.,[5]

$$T_\alpha - T_{\rm NAC} = A_\alpha |X - X_{\rm NAC}|^{1/\phi_\alpha} + B(X - X_{\rm NAC}), \quad (1)$$

where α = NA, NC, and AC with $\phi_{\rm NA} = \phi_{\rm NC}$, give $1/\phi_{\rm NA} = 0.5 \pm 0.05$, $1/\phi_{\rm AC} = 1.6 \pm 0.1$, $A_{\rm NA} = 80.5 \pm 10$, $A_{\rm NA}/A_{\rm NC} = -4 \pm 2$, $A_{\rm AC} = 2240$, and $B = 174 \pm 130$. These agree well with the values obtained previously[5] in five different systems. The ratio $A_{\rm NA}/A_{\rm NC}$ is poorly determined because of uncertainties connected with hysteresis at the N-C boundary. In the inset to Fig. 1 we show the "universal form" of Brisbin *et al.*[5] for the NAC boundaries with $B=0$ superimposed on our data; clearly the agreement is good and could be improved by explicit fitting of B, etc. The exponents and amplitude ratio themselves, however, remain unexplained.

We carried out x-ray studies on eleven separate samples with molar concentrations $X_{\rm 8OCB} = 0$, 0.0069, 0.0097, 0.0119, 0.0158, 0.0176, 0.0197, 0.0217, 0.0219, 0.0261, and 0.0346. The first seven samples exhibit single N-S_C transitions. Experiments on each sample took about three weeks. The experimental configuration was essentially identical to that discussed by Safinya and co-workers.[3] For S_A pretransitional scattering one observes a single Lorentzian peak centered about $(0,0,q_\parallel^0)$ while for S_C fluctuations one observes a diffuse ring centered about $(q_\perp^0 \cos\phi, q_\perp^0 \sin\phi, q_\parallel^0)$; the scattering is independent of the azimuthal angle ϕ. In the S_C fluctuation region we took four x-ray scans per temperature point, a transverse scan varying $q_\perp$ at fixed $q_\parallel^0$ and three longitudinal scans varying $q_\parallel$ at fixed $q_\perp = 0, \pm q_\perp^0$. For the samples $X_{\rm 8OCB} = 0$ and 0.0069 the pretransitional scattering in the nematic phase up to 8° above $T_{\rm NC}$ has an S_C character, that is, $q_\perp^0$ is nonzero. However, five samples, $X_{\rm 8OCB} = 0.0097$, 0.0119, 0.0158, 0.0176, and 0.0197, show a crossover from S_A- to S_C-type fluctuations as the temperature is decreased. Representative scans for $X_{\rm 8OCB} = 0.0158$ spanning the crossover region in the nematic phase are shown in Fig. 2.

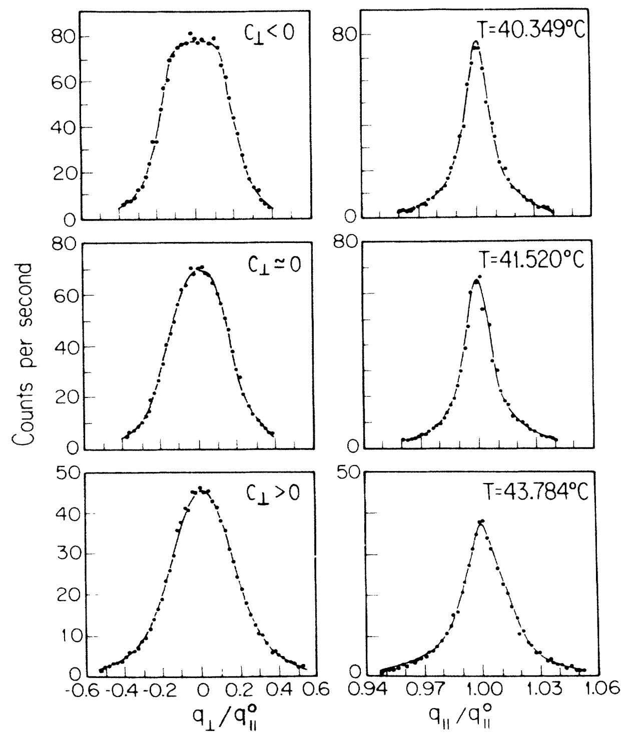

FIG. 2. Longitudinal and transverse x-ray scans in the crossover region for the $X_{\rm 8OCB} = 0.0158$ sample. The longitudinal scans are all through the position $q_\perp = 0.1$. The solid lines are the results of fits to the Chen-Lubensky form Eq. (2).

In order to discuss quantitatively the x-ray results we must first specify the appropriate form for the x-ray cross section $\sigma(\mathbf{q})$. In the Chen-Lubensky infinite-dimensional order-parameter model[1] the tilt ($q_\perp^0 \neq 0$) enters through the gradient of the mass-density wave. The Ornstein-Zernike expression then is

$$\sigma(\mathbf{q}) = \frac{\sigma_0}{1 + \xi_\parallel^2 (1 + K q_\perp^2)(q_\parallel - q_\parallel^0)^2 + C_\perp q_\perp^2 + D_\perp q_\perp^4}, \quad (2)$$

where for $C_\perp > 0$ the fluctuations are S_A-like, for $C_\perp < 0$ the fluctuations are S_C-like, and $C_\perp = 0$ defines the Lifshitz line.[6] The higher-order cross term $q_\perp^2 (q_\parallel - q_\parallel^0)^2$ is necessitated by the data. The Lifshitz point is defined by $C_\perp = 0$, $\sigma_0 \to \infty$. The cross section for the independent tilt models is more complicated. For Lorentzian mass-density fluctuations about a fixed local configuration one obtains,[2] after averaging over the tilt azimuthal angle ϕ,

$$\sigma(\mathbf{q}) = \frac{\sigma_0}{[1 + \xi_\parallel^2 (q_\parallel - q_\parallel^0)^2 + \xi_\perp^2 (q_\perp - q_\perp^0)^2]^{1/2} [1 + \xi_\parallel^2 (q_\parallel - q_\parallel^0)^2 + \xi_\perp^2 (q_\perp + q_\perp^0)^2]^{1/2}}. \quad (3)$$

If one includes a $D_\perp q_\perp^4$ term in the mass-density fluctuations one obtains an expression like (3) but algebraically more complicated. This form, which we do not quote explicity here, was derived on a phenomenological basis by Safinya[3] and from a formal two–order-parameter theory by Andereck and Patton.[2] Here the adjustable parameters are σ_0, $\xi_\parallel$, $\xi_\perp$, $q_\perp^0$, and $D_\perp$.

The solid lines shown in Fig. 2 are the results of fits by Eq. (2). It is evident that this model, which has as adjustable parameters σ_0, $\xi_\parallel$, K, $C_\perp$, and $D_\perp$, works very well in the S_A, Lifshitz, and S_C regions. The goodness-of-fit parameter χ^2 is typically 1 for all temperatures and concentrations. Fits by Eq. (3) are completely unsuccessful in the S_C fluctuation region as found previously by Safinya and co-workers[3] in $\overline{7}S5$-$\overline{8}S5$. This is because the transverse scans fall off much faster than $q_\perp^2$. Fits by the Safinya-Andereck-Patton form which includes the $D_\perp q_\perp^4$ are more successful. Nevertheless, the χ^2 obtained from fits to this model are about three times larger than those found for the Chen-Lubensky model,[1] Eq. (2), for scans near the N-S_C boundary. Furthermore, near the Lifshitz point Eq. (3) with the $q_\perp^4$ correction fails completely while Eq. (2) describes the data quite well. This should be regarded as strong but not absolute evidence for the Chen-Lubensky approach since Eq. (3) and its isomorphs only represent one limit for the two-parameter models—that in which the tilt amplitude is fixed.

We now discuss the results obtained from the fits by the Chen-Lubensky form. For each N-S_C sample we obtained σ_0, K, $\xi_\parallel$, $C_\perp$, and $D_\perp$ over a range of temperatures down to the N-S_C boundary. For the samples $X_{8OCB}=0$ and 0.0069 the fits give $C_\perp < 0$ over the range studied ($\sim 8°$ above T_{NC}). For the remaining N-S_C samples we explicitly observe a continuous evolution of $C_\perp$ from positive to negative values with decreasing temperature. Results for the $X_{8OCB} = 0.0158$ and 0.0197 samples are shown in Fig. 3. The data are most dramatic for the 0.0197 sample which is quite close to the NAC concentration. As is evident in Fig. 3, $C_\perp$ increases continuously as if one were headed towards a transition into an S_A phase ($C_\perp \sim \xi_\perp^2$). However, approximately 1° above T_{NC}, $C_\perp$ reaches a maximum and then decreases rapidly through zero. There is then a weakly first-order transition into the S_C phase at $T_{NC}=41.53$ °C.

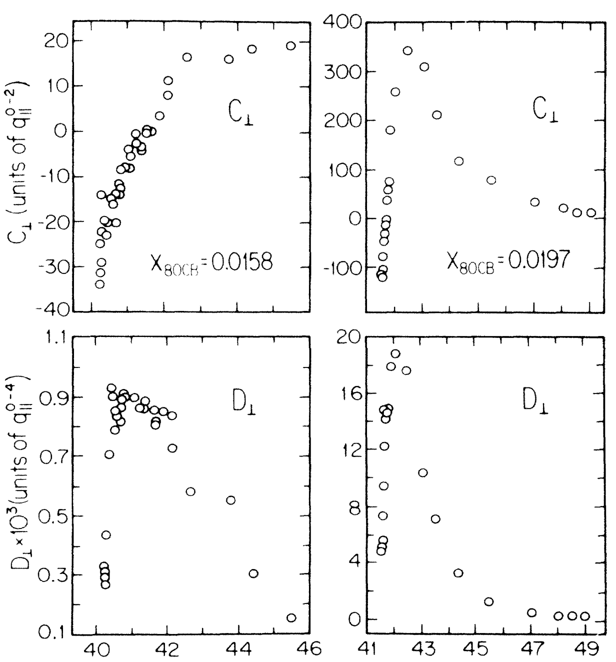

FIG. 3. Best-fit coefficients, $C_\perp$ and $D_\perp$ of Eq. (2), for the 0.0158 and 0.0197 samples.

The fitted transverse and longitudinal correlation lengths for the $X_{8OCB}=0.0197$ sample are shown in Fig. 4. Here $\xi_\perp$ is defined as the inverse half width at half maximum of the transverse scan while $\xi_\parallel$ is the inverse of the HWHM at $q_\perp=0$ for $C_\perp \geq 0$ and $q_\perp = q_\perp^0$ for $C_\perp < 0$. It is notable that in the crossover region $\xi_\parallel/\xi_\perp \simeq 50$ and the correlated regions are approximately $3000 \times 60 \times 60$ Å^3 in size. We do not know if this extreme anisotropy is generic. The temperatures at which $C_\perp = 0$ are shown in Fig. 1. The dashed line is just the inverse of the AC boundary, that is, Eq. (1) with $A_{C_\perp=0} = -A_{AC}$; this is an interesting phenomenological observation which, hopefully, will stimulate theory for the Lifshitz line. We note that the $C_\perp = 0$ line rises dramatically for $X_{8OCB} < 0.01$ (not shown in Fig. 1) implying that one is departing from the N_{AC} multicritical region.

Before discussing the overall implications of these results we mention briefly the behavior on the N-S_A side of the NAC point. We find conventional N-S_A transitions with exponents $\gamma = 1.55 \pm 0.1$, $\nu_\parallel = 0.90 \pm 0.05$, and $\nu_\perp = 0.76 \pm 0.05$. Closely similar results for $\nu_\parallel$ have been independently obtained by Solomon and Litster[7] via light-scattering studies of the elastic response as discussed in the accompanying Letter. These exponents are close to but somewhat larger than those found in other N-S_A transitions.[8] The S_A-S_C transitions for the 0.0219, 0.0261, and 0.0346 samples are all consistent with mean-field behavior with a small

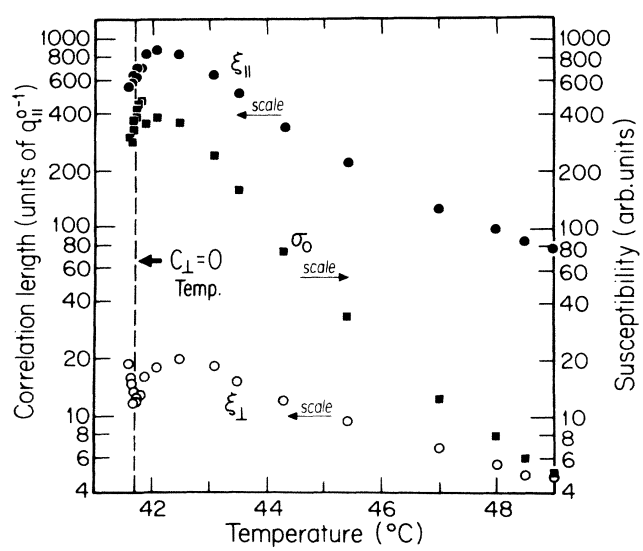

FIG. 4. Susceptibility and longitudinal and transverse correlation lengths as defined in the text for the $X_{8OCB}=0.0197$ sample; $q_\parallel^0 = 0.23195$ Å^{-1}

sixth-order term in the tilt free energy; the effective tilt exponent for all three samples is 0.44 ± 0.04.

These experiments, therefore, have shown that in a prototypical system $\overline{7}$S5-8OCB which exhibits the universal NAC phase diagram[5] the smectic susceptibility in the nematic phase is always well described by the simple Chen-Lubensky Lifshitz form. Further, the Lifshitz line appears to be a simple extension of the AC boundary. Conventional two-order-parameter theories[2] are shown to be invalid both by the geometry of the phase boundaries[5] and by the nature of $\sigma(\mathbf{q})$. As noted by Brisbin *et al.*,[5] the fact that the nematic-to-smectic transition is suppressed as the fluctuations become *C*-like is suggestive of the Brazovskii model applied to the N-S_C transition by Swift.[9] This is further substantiated by our results near the NAC point where, as shown in Fig. 4, the longitudinal correlation length actually *decreases* as the fluctuations change from S_A-like to S_C-like. This decrease in $\xi_\parallel$ also manifests itself in the Solomon and Litster[7] light-scattering experiments.

An alternative approach to the NAC problem has been given by Grinstein and Toner,[2] who predict that in $d=3$ the NAC point is a tetracritical point with decoupled mass-density and tilt orderings. Thus, close enough to the NAC point one should have the sequence of phases N $\rightarrow$ biaxial nematic $\rightarrow$ S_C. The x-ray cross section presumably should evolve from Eq. (2) to the Safinya-Andereck-Patton form. However, neither we nor other groups[5,7] find any evidence for the biaxial nematic phase nor for the anticipated evolution in the x-ray cross section. To make this more definite one requires explicit predictions for the magnitude of effects caused by the biaxial nematic ordering. The Chen-Lubensky model itself, however, presents the dilemma that an $m=2$ Lifshitz point is believed to be unstable in three dimensions[6]; nevertheless, this model appears to describe the smectic susceptibility quite well. We hope that these experiments will stimulate a renewed theoretical effort on this most subtle and interesting problem.

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