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High-Resolution X-Ray Study of a Second-Order Nematic–Smectic-*A* Phase Transition

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We have carried out a high-resolution x-ray–scattering study of the critical fluctuations in the nematic phase associated with the nematic–smectic-*A* transition in N-*p*-cyanobenzylidene-*p*-octyloxyanilene (CBOOA). It is shown that for $8\times10^{-5}\lesssim T/T_c-1\lesssim2\times10^{-2}$ the transverse and longitudinal correlation lengths diverge with identical exponents, that is, $|\nu_L-\nu_T|<0.03$. As one approaches T_c the system appears to crossover from helium– to mean-field critical behavior at a reduced temperature of $\sim10^{-3}$.

Liquid crystals present a fascinating array of phase transitions associated with the orientational and spatial order of the rodlike liquid-crystal molecules.[1] Recently, considerable attention has been directed towards the nematic–smectic-*A* (*N*-*A*) transition in which, in the oriented liquid, a one-dimensional sinusoidal density wave is established. The general phenomenology of the behavior around the *N*-*A* transition seems to be well understood.[1] There are, however, a number of disturbing quantitative conflicts both within and between various theoretical models[2-4] and experimental measurements[5-8] of the critical behavior at the *N*-*A* transition. Most importantly, a number of experiments,[6] especially those in N-*p*-cyanobenzylidene-*p*-octyloxyanilene (CBOOA), suggest that the *N*-*A* transition is characterized by *two*, rather than *one*, divergent lengths. This would seem to conflict with current ideas on scaling near second-order transitions. Further it greatly complicates any attempt at a coherent theoretical description of the *N*-*A* transition.

In this Letter we report a detailed high-resolution x-ray study of the *N*-*A* transition in CBOOA. As emphasized by McMillan,[5] x rays couple directly to the smectic-*A* mass-density fluctuations so that one measures the relevant transverse and longitudinal correlation lengths, ξ_T and ξ_L, respectively, directly rather than indirectly as in most other measurements. Our salient result is that ξ_L and ξ_T diverge with identical exponents: More quantitatively, $|\nu_L-\nu_T|<0.03$ for $8\times10^{-5}\leq T/T_c-1\leq2\times10^{-2}$. This result thence represents a major simplification of the *N*-*A* problem. We believe that previous measurements have implied $\nu_L\neq\nu_T$ either because of limited accuracy or because of difficulties in interpretation. We find in addition the following results which are important in understanding the physics of CBOOA itself. Firstly, there is an apparent crossover from helium– to mean-field–like behavior, at $T/T_c-1\simeq10^{-3}$. Secondly, critical-exponent-η effects are seen to be negligible throughout the critical region. Thirdly, in our sample the transition is second order to within $T/T_c-1\lesssim3\times10^{-5}$.

The experiments were carried out on a two-crystal x-ray spectrometer with use of Cu-$K\alpha$ radiation from a Rigaku 12-kW rotating-anode source. The experimental setup is shown schematically in Fig. 1. We postpone any detailed discussion of the apparatus and the x-ray techniques to a later publication. Here it is sufficient to note that using germanium–single-crystal techniques it is possible to measure the liquid-crystal mass-density–fluctuation spectrum with a spatial resolution expressed as half-widths at half-maximum of 4.2×10^{-4} Å^{-1} in the longitudinal direction (in this case, perpendicular to the smectic layers), of $<2\times10^{-5}$ Å^{-1} in the transverse direction, and of 1.8×10^{-2} Å^{-1} in the direction perpendicular to the scattering plane. The scattering diagram in reciprocal space together with the in-plane resolution ellipse and the critical fluctuation half-intensity contour at $t=T/T_c-1=0.00116$ are shown in the bottom half of Fig. 1. The liquid crystal was contained in a flat rectangular vessel $12\times12\times1.5$ mm^3, with Kapton windows coated with SiO to provide planar alignment in the smectic phase. An applied magnetic field of 400 G provided alignment in the nematic phase. Only the center 1×3 mm^2 was illuminated with x rays. The liquid-crystal holder was mounted in

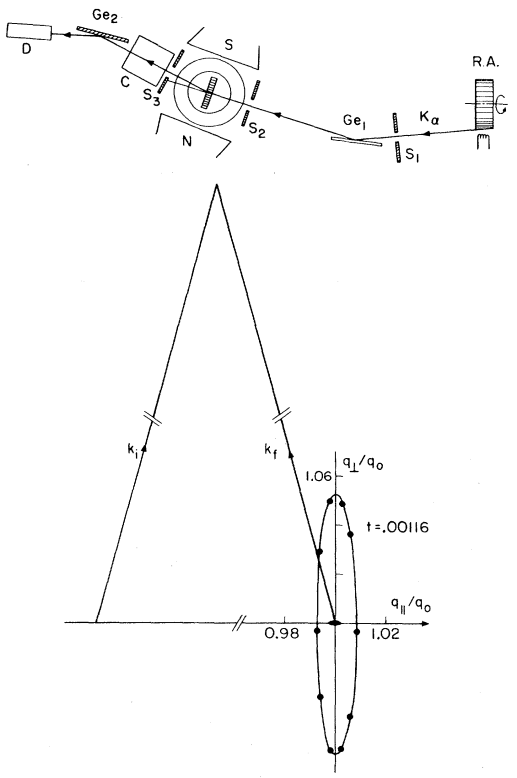

FIG. 1. Upper panel: schematic diagram of x-ray spectrometer with S_i = slits, Ge_i = perfect germanium crystals, C = horizontal Soller slits, D = sodium iodide detector. Lower panel: scattering diagram in reciprocal space showing critical scattering half-intensity contour at $t = 0.001\,16$; the solid ellipse in the center is the instrumental resolution function.

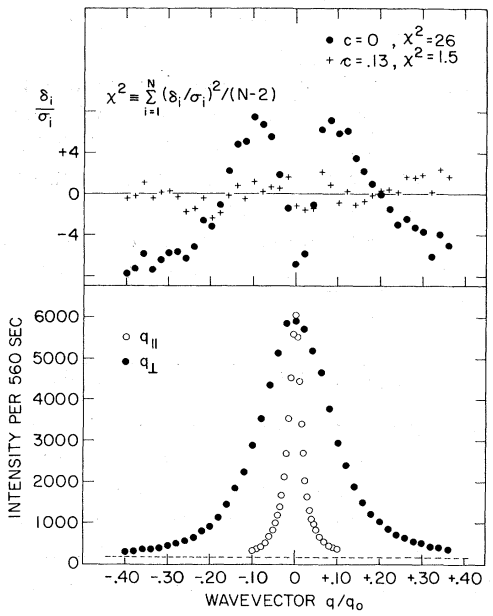

FIG. 2. Lower panel: transverse and longitudinal scans at $t = 0.0052$; upper panel: deviations for the best of fits of Eq. (1) to the transverse scan with the fourth-order term (i) fixed at 0, (ii) allowed to vary as a free parameter.

the center of a two-stage servo-controlled oven; typically temperature was constant to within 2×10^{-3} K during an x-ray scan. Finally, a He-Ne laser, photomultiplier, and associated optics were mounted on the x-ray table so that simultaneous *in situ* light-scattering studies could be performed.

The experimental results are rather similar to those reported originally by McMillan[5] except, of course, that the much higher resolution provided by our single-crystal spectrometer together with the improved temperature control enables us to probe much closer to T_c. As noted in Fig. 1(b) the critical scattering takes the form of an ellipsoid with aspect ratio 5.8:1 centered about the position $(0,0,q_0)$, where q_0 is the wave vector of the ultimate smectic ordering at T_c. In CBOOA $q_0 = 0.179$ Å^{-1}, independent of temperature in the nematic phase. Typical longitudinal ($q_\parallel$) and transverse scans ($q_\perp$) are shown in the bottom part of Fig. 2 for $t = 0.0052$. As $t \to 0$, the lines narrow and the peak intensity grows corresponding to the divergences of the transverse and longitudinal correlation lengths and the smectic susceptibility, respectively.

Before discussing the analysis of the data we consider our determination of T_c. Initially T_c was located by observing a discontinuity in $d(I_{\text{light scatering}})/dT$ at a scattering vector $q_\parallel \simeq 4 \times 10^{-4}$ Å^{-1}, where the discontinuity arises from the divergence of the Frank elastic constant K_3 at T_c. This gave $T_c = 83.195 \pm 0.010$°C and the transition was second order to well within the error limits. As an aside we note that the intensity of the scattered light was consistent with K_3 diverging proportional to ξ_L measured by the x rays, as predicted by de Gennes.[2] The transition manifested itself in several ways in the x-ray experiments. Firstly, at $T = T_c = 83.195 \pm 0.010$°C the transverse spectrum changed abruptly from a single Lorentzian to a multiple-peak structure with a slight shift in the center of gravity. We interpret this to mean that in the smectic phase the bulk smectic-layer orientation is noticeably influenced by the Kapton walls whereas in the nematic phase the applied field determines the bulk orientation. Discontinuities were also observed

in the temperature derivatives of the x-ray peak intensity and of the $q_\perp$ width at $T = T_c = 83.195 \pm 0.010$°C. Thus the x-ray and light-scattering data are each separately consistent with a second-order transition at $T_c = 83.195 \pm 0.010$°C; the error bars also include our estimate of the limits of any possible smearing of T_c.

We now consider the analysis of the x-ray data. The data were fitted to a cross section of the form (with $\vec{q} \equiv \vec{k}_i - \vec{k}_f$)

$$\sigma(\vec{q}) = \frac{a\xi^2}{1 + [\xi(q_\parallel - q_0)]^2 + b[(\xi q_\perp)^2 + c(\xi q_\perp)^4]}, \quad (1)$$

convoluted with the instrumental-resolution function. For this cross section, the susceptibility $\sigma(q_0) = a\xi^2$, the longitudinal correlation length $\xi_L = \xi$, and the transverse correlation length $\xi_T = \sqrt{b}\xi$. The $q_\perp^4$ term is dictated by the data, as we shall discuss below. It is useful to point out that in de Gennes's superfluid-helium model[2] for the N-A transition, $\xi \sim t^{-\nu}$ with $\nu = 0.66$, $\sigma(q_0) \sim t^{-\gamma}$ with $\gamma = 1.29$, and from the scaling relation $\gamma = \nu(2 - \eta)$, $a \sim t^{-\nu\eta}$ with $\eta = 0.04$. For mean-field theory[3] and for a tricritical point ignoring logarithmic corrections $\gamma = 1$, $\nu = \frac{1}{2}$, and $\eta = 0$. We should re-emphasize that previous experiments[5] have suggested that b is not a constant but rather approaches 0 as $T \to T_c$. For all scans, the goodness-of-fit parameter χ^2 is close to 1 so that Eq. (1) is indeed an adequate representation of the data. As illustrated in the upper part of Fig. 2 if we set $c = 0$, that is if we exclude the fourth-order term in $q_\perp$, then the χ^2 for the transverse scans increase drastically to typically 10–30. At $(q_\perp \xi_T) \simeq 1$ this fourth-order term is 5–10% of the second-order term in $q_\perp$. Such large fourth-order corrections are a novel feature of the nematic–smectic-A transition; most likely they originate from splay-mode director fluctuations and represent a clear precursor for the anticipated $q_\perp^{4-2x}$ line shape in the smectic phase.[9] We should emphasize that at a given $q_\perp$, because of the ξ^2 scaling factor, the wings are changing progressively from a $q_\perp^{-2}$ to a $q_\perp^{-4}$ shape as one approaches T_c.

The final parameters are shown in Fig. 3. The central result is contained in (c): The ratio $\xi_L/\xi_T = 5.8 \pm 0.8$ over the complete temperature range. From the data in Fig. 3(c) we can determine, as an upper limit, $|\nu_L - \nu_T| \leq 0.03$. Thus, *there is only one divergent length characterizing the nematic–smectic-A phase transition for* $T > T_c$. We should emphasize that the above ratio is given directly by the ratio of the widths of the transverse and longitudinal x-ray scans through $(0, 0, q_0)$ with only a minor correction for the $q_\perp^4$ term. Thus it is independent of any other detailed aspects of the critical behavior. We believe, therefore, that the constancy of $\xi_\parallel/\xi_\perp$ is a well-established and essential feature of the N-A transition. As we noted in the beginning of this paper, this result represents an important simplification of the N-A problem.

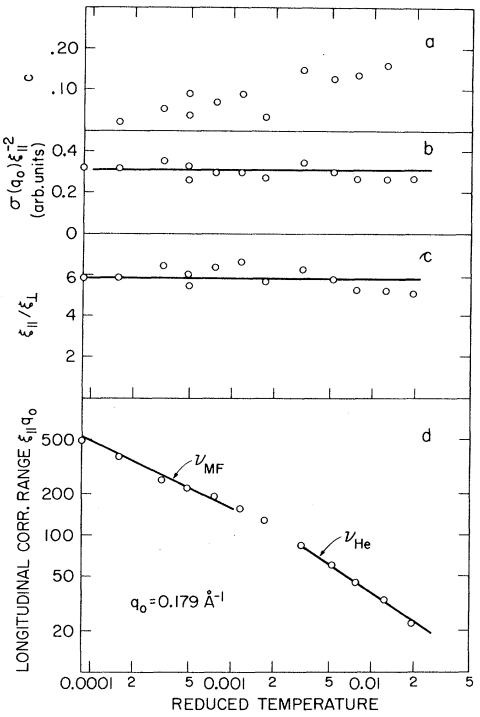

FIG. 3. Best-fit parameters obtained by fitting Eq. (1) to the experimental data. The helium and mean-field slopes $\nu_{He} = 0.66$ and $\nu_{MF} = 0.05$ are drawn as guides to the eye.

Finally, we consider our results for the detailed critical behavior in CBOOA. Firstly, the amplitude factor, shown as $\sigma(q_0)\xi^{-2}$ in Fig. 3, is temperature independent to within the errors. Quantitatively, we estimate from Fig. 3(b) that $\eta \leq 0.06$, consistent with both the helium and mean-field predictions. This constancy of $\sigma(q_0)\xi^{-2}$ also gives us strong confidence in the internal consistency of our analysis. The behavior for ξ and $\sigma(q_0) = a\xi^2$ is more complicated. As is evident in Fig. 3(d), ξ and concomitantly $\sigma(q_0)$ show apparent crossover behavior at a reduced temperature of $\sim 10^{-3}$. We emphasize once more that T_c is not an adjustable parameter but rather it is known to an accuracy of at least 3×10^{-5}. For t

$> 10^{-3}$, γ and ν are consistent with the helium-model values of 1.29 and 0.66, respectively. However, for $t < 10^{-3}$ there is a decrease in the slopes and indeed the asymptotic behavior seems to be mean-field-like,[10] that is, $\gamma \sim 1$ and $\nu \sim 0.5$. This is, to say the least, a rather unexpected result. Clearly further experiments on other CBOOA samples and also with varied boundary conditions are required to characterize fully this crossover effect; such experiments are now underway. Nevertheless, we believe that the results of Fig. 3 make comprehensible a variety of apparently contradictory results on CBOOA in the literature. We would like to conclude this paper with a simple theoretical conjecture concerning the critical behavior of CBOOA.

Following Chu and McMillian[7] we suggest that the CBOOA transition accidently occurs extremely close to a tricritical point. We then suggest that far from T_c we are observing a lambda line, that is, helium-dominated behavior, whereas close to T_c the tricritical point takes over, thence giving $\gamma = 1$, $\nu = \frac{1}{2}$, and $\eta = 0$. Subtle changes in chemistry, therefore, could drive a sample to either side of the tricritical point, thus making the transition either weakly first order or second order and heliumlike, consistent with various reported results. Finally, this tricritical model requires $\beta = \frac{1}{4}$, rather than $\frac{1}{2}$, for $T < T_c$, consistent at least with the light-scattering measurements of D by Birecki *et al.*[11] Clearly, much more work, especially in the smectic phase, remains to be done in CBOOA as well as in other materials before we can claim a full understanding of the nematic-smectic-*A* transition. Nevertheless, we can now proceed with confidence that above T_c there is only one divergent length in this problem.

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