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Birefringence investigation of the smectic-*A* —hexatic-*B* phase transition

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Birefringence meaurements of *n*-hexyl 4′-*n*-pentyloxbiphenyl-4-carboxylate (65OBC) near the smectic-*A* —hexatic-*B* transition are reported. It is found that the anomalous part of the birefringence $\delta(\Delta n)$ due to long-range hexatic order exhibits a critical exponent 0.38 ±0.05. The relationship between $\delta(\Delta n)$ and the hexatic order parameter is discussed.

Several years ago Halperin and Nelson proposed a theory of two-dimensional (2D) melting[1] in which a "hexatic" phase, possessing quasi-long-range in-plane bond orientational order but short-range positional order, lies between the high-temperature isotropic and low-temperature crystalline phases. Birgeneau and Litster then suggested[2] that a three-dimensional (3D) smectic-*B* liquid-crystal structure, composed of stacked 2D hexatic layers, could exhibit similar hexatic behavior, but with real long-range bond order. It would melt at higher temperatures into a smectic-*A* phase, the 3D analog to Halperin and Nelson's 2D isotropic phase. Using freely suspended films of 65OBC, Pindak *et al.* performed x-ray[3] and mechanical[4] measurements to demonstrate that the 3D hexatic phase does, in fact, exist in a liquid-crystalline system. Thus the smectic-*A* —hexatic-*B* (*A*-Hex) liquid-crystal phase transition provides an excellent experimental system in which to investigate a 3D analog to 2D hexatic melting.

With this in mind, Huang *et al.*[5] measured the heat capacity of 65OBC at the *A*-Hex transition and found it to diverge with a critical exponent $\alpha = \alpha' = 0.64 \pm 0.04$. Although most models predict $\alpha \simeq 0$, the two-dimensional four-state Potts model predicts $\alpha \simeq 0.67$ (Ref. 6); nevertheless, they ruled out this interpretation in light of an x-ray experiment[3] which indicates a herringbone structure[7] for the molecular packing. Despite their important results, however, a complete picture of 2D melting, in general, and the *A*-Hex transition, in particular, has yet to emerge. The purpose of this Communication, then, is to report on birefringence measurements of the *A*-Hex phase transition. If the nematic order parameter S (and thus the birefringence) and the bond orientational parameter Ψ are coupled, this measurement should provide the first determination of the critical behavior of Ψ at the *A*-Hex transition.

Samples of 65OBC were synthesized for us by J. W. Goodby and used without further purification. The material was placed between two microscope slides separated by 50 ± 5 μm with a Mylar spacer. The sandwich was then inserted in a 5.3-cm-diam brass cylinder which served as the oven. The light portholes were 3 mm in diameter. Long-term temperatures stability was 3 mK and the temperature gradient across the laser spot (Spectra Physics model 124 He-Ne laser attenuated to 3.5 μW) was 14 mK.

Owing to the absence of a nematic phase between the isotropic and smectic-*A* phases, planar alignment was achieved by cooling the sample through the smectic-*A* —isotropic (SI) transition in a magnetic field of 155 kOe. It was found that 100 kOe was insufficient; the sample broke up into arrays of parabolic focal conics[8] (PFC's) which created "wings" of intense scattered light at angles up to 3° about the central laser spot. After cooling in the higher field no such scattering was observed, although upon transfer to another oven suitable for microscopy, telltale signs of extremely weak PFC's were seen, perhaps arising from the transfer process. Nevertheless, the lack of any observable scattered light in the birefringence oven and the reproducibility of the data indicate that, in the case of 155 kOe, PFC's if indeed they were present, were unimportant.

After field cooling through the SI transition, the magnetic field was turned off and all subsequent measurements were made in zero field. The birefringence apparatus is described in detail elsewhere.[9] Briefly, it consisted of a pair of Glan-Thomson polarizers with an extinction ratio better than 10^{-6}; the sample and a Pockels cell (Lasermetrics LMA-4) were placed between the two crossed polarizers (see Fig. 1). An ac voltage at $\nu_0 = 530$ Hz was then applied to the Pockels cell to modulate its birefringence. For sufficiently small total birefringence the signal V from the detector had three frequency components, at $\nu = 0$, ν_0, and $2\nu_0$, such that $V_{\nu_0} \propto (\delta_s - \delta_p)$. δ_s and δ_p were the dc phase shifts due to the sample and Pockels cell birefringences,

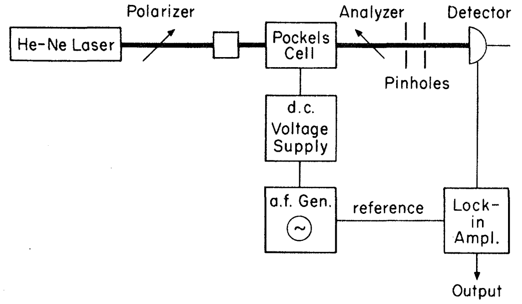

FIG. 1. Experimental apparatus.

respectively, and $\delta_s = k\Delta nd$. For our experiment, the sample thickness $d = 5.0 \times 10^{-3}$ cm and $k = 9.93 \times 10^4$ cm^{-1}. To measure δ_s, and therefore Δn, a dc voltage proportional δ_p as applied to the Pockels cell to cancel δ_s and thereby null out V_{ν_0}, as measured on a lock-in amplifier. Sensitivity in δ was conservatively estimated to be 10^{-3}, equivalent to $\Delta n = 2 \times 10^{-6}$.

Since the quantity of interest is the incremental birefringence, Δn was arbitrarily chosen to be zero several degrees above the A-Hex transition. Measurements of Δn were always made on cooling because heating through the A-Hex transition induced PFC's accompanied by intense scattered light. A typical set of data is shown in Fig. 2. At temperatures several degrees above the transition temperature T_c, $|d(\Delta n)/dT|$ is approximately 4.1×10^{-4} K^{-1}, similar to behavior found in other materials[10]; in the neighborhood of T_c, $|d(\Delta n)/dT| \gtrsim 1.2 \times 10^{-2}$ K^{-1}. Although the transition appears to be second order[5] with an expected diverging derivative at T_c, this small smearing of the transition is due most likely to the temperature gradient across the sample. Finally, by microscopic observation of the liquid-crystal air interface in an unaligned bulk sample, an anomalous increase in the thermal expansion coefficient was observed near T_c; the density change was crudely estimated to be $\Delta\rho/\rho_0 = 2 \times 10^{-3}$ over a ±0.5-K temperature change about T_c. (This value is similar to thermal expansion coefficients in the smectic-A phase of other materials near the second-order or weakly first-order nematic transition.[11]) Although such a contraction could, in principle, distort the alignment in the experiment, cooling was slow and no distortion, on cooling through T_c, was observed. Moreover, birefringence results were reproducible for each of the three samples used in the experiment. A measurement of the expansion coefficient should nevertheless be performed for a complete understanding of the birefringence.

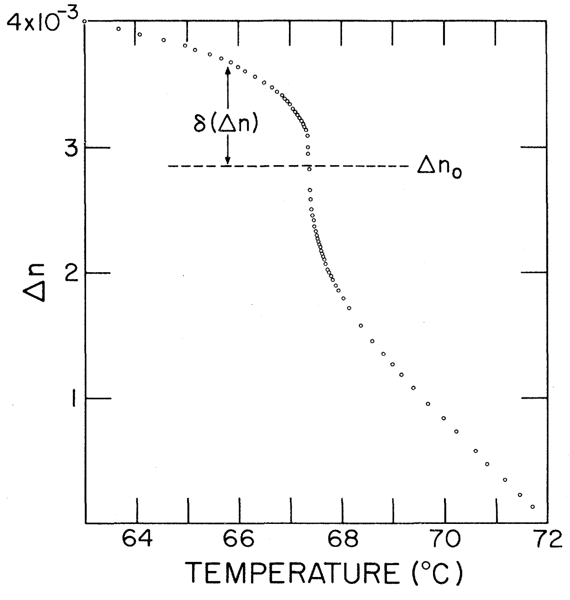

FIG. 2. Birefringence (above an arbitrary zero point) vs temperature. Δn_0 is the birefringence at T_c and $\delta(\Delta n)$, the anomalous part of the birefringence, $\equiv \Delta n - \Delta n_0$. Error bars in temperature are approximately ±5 mK, and in Δn approximately $\pm 5 \times 10^{-6}$. The temperature gradient is 14 mK across the beam spot.

The relevant parameter for sixfold bond orientational order is $e^{6i\theta(\vec{r})}$ (Ref. 2), where $\theta(\vec{r})$ is the orientation, relative to some axis, of a bond between two nearest-neighbor molecules at position $\vec{r}$. In the crystalline phase the correlation function[1] $C(r) = \langle e^{6i\theta(0)} e^{-6i\theta(\vec{r})} \rangle$ approaches some nonzero value at large r given by $|\langle e^{6i\theta(\vec{r})} \rangle|^2$. In the 2D hexatic phase, however, $C(\vec{r})$ decays algebraically to zero as $r^{-\eta(T)}$, and $\langle e^{6i\theta(\vec{r})} \rangle$ is rigorously zero when averaged over the entire plane. Birgeneau and Litster pointed out,[2] however, that interlayer couplings should result in true long-range order, rather than an algebraic decay of $\langle e^{6i\theta(\vec{r})} \rangle$; thus, in the 3D hexatic phase, $\langle e^{6i\theta(\vec{r})} \rangle$ is some nonzero complex number. (True long-range order in the hexatic phase has been verified by x rays.[3]) Using the formalism of Bruinsma and Nelson,[12] an order parameter Ψ with fluctuations can be defined for this phase, such that

$$\Psi = \langle e^{6i\theta(\vec{r})} \rangle + \delta\Psi(\vec{r}) = \Psi_0 e^{6i\theta_0} + \delta\Psi(\vec{r}) \ ,$$

where Ψ_0 and θ_0 are both real and $\delta\Psi$ represents a complex fluctuating quantity. Finally, in the smectic-A phase, $C(r)$ decays as $r^{-1/2} e^{-r/\xi_H}$, where ξ_H is the hexatic correlation length and $\Psi_0 = 0$.

If coupling exists between the nematic order parameter S and Ψ, an enhancement of S, and thus the birefringence, can occur. To maintain rotational invariance, $\Psi\Psi^*$ is the relevant quantity which couples to the nematic order. Then, in analogy with de Genne's theory[13] of the nematic–smectic-A transition, but including fluctuations, the anomalous part of the birefringence $\delta(\Delta n)$ (proportional to the anomalous part of S) should scale as $\langle \Psi\Psi^* \rangle$.

For $T > T_c$, Ψ_0 vanishes and the anomalous increase in the Δn arises solely from fluctuation, i.e., $\delta(\Delta n)$ ($\equiv \Delta n - \Delta n_0$) scales as $\langle \delta\Psi\delta\Psi^* \rangle$. By fitting $|\delta(\Delta n)| = |\Delta n - \Delta n_0|$ to the form $-Qt^{\Omega}$, where $t = (T - T_c)/T_c$, and the parameters T_c, Δn_0, Q, and Ω are adjustable, a best fit was obtained[14] with $T_c = 67.370 \pm 0.005\,^{\circ}\mathrm{C}$, $\Delta n_0 = (2.85 \pm 0.05) \times 10^{-3}$, $Q = (1.26 \pm 0.10) \times 10^{-2}$, and $\Omega = 0.40 \pm 0.05$. (Note that the fractional errors in Ω and Q represent a composite from several experimental runs.) A log-log plot of $|\delta(\Delta n)|$ is shown in Fig. 3 (×). Since the critical part of the correlation function for short ranges exhibits behavior characterized by the form $-Ct^{(1-\alpha)}$ (Refs. 15 and 16), we find by equating $1 - \alpha$ with Ω that $\alpha = 0.60 \pm 0.05$. This is consistent with a value $\alpha = 0.64 \pm 0.04$ found in Ref. 5.

For $T < T_c$, both fluctuations and long-range order contribute to $\delta(\Delta n)$. The exponent β, which characterizes Ψ_0, can easily be extracted since $\delta(\Delta n) = D|t|^{2\beta} - Q'|t|^{(1-\alpha')}$, where D is a constant. The first term is the long-range order contribution to $\delta(\Delta n)$ and the second term is the fluctuation contribution to $\delta(\Delta n)$. Ideally, a five-parameter fit (D, β, Q', α', and T_c) should be performed; however, since $1 - \alpha$ and 2β turn out to be nearly equal, such a fit would be virtually impossible. Instead, we have used the well-known relationships[15] $\alpha = \alpha'$ and $Q/Q' = A/A'$, where A/A' is the ratio of coefficients appearing in the specific-heat divergence above (A) and below (A') T_c. The quantity $1 - \alpha'$ is thus equal to $\Omega = 0.40$ and, from Ref. 5, Q' is expected to equal $Q/0.83$. Then, from the data above T_c, $Q' = 1.53 \times 10^{-2}$. In Fig. 3, a log-log plot of $\delta(\Delta n) + Q'|t|^{(1-\alpha')}$ (●) is shown, displaying a critical exponent $\tau' = 0.38 \pm 0.05$. Finally, equating τ' with 2β, we immediately see that $\beta = 0.19 \pm 0.03$. We note in passing that β is relatively insensitive to Q'; a 50% change in Q' would still keep β well within the stated error. This value of β, like the value of α obtained in Ref. 5, is inconsistent with a 2D or 3D n-vector model. Moreover, a value $\beta = 0.19$ is inconsistent with the 2D four-state Potts model[6] which predicts $\beta = 0.083$.

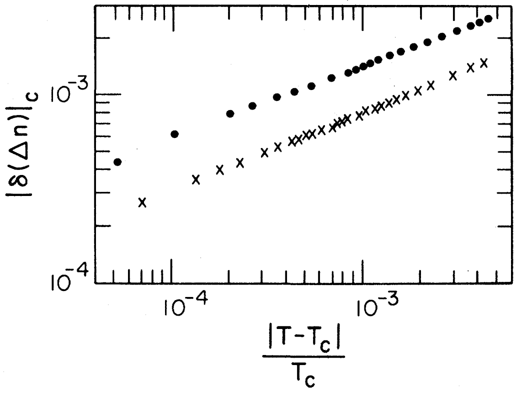

FIG. 3. Log-log plot of the quantity $|\delta(\Delta n)|_C$, which is defined as the fluctuation contribution to $|\delta(\Delta n)|$ for $T > T_c$(×) and the long-range order contribution for $T < T_c$ (●). (See text for details.) Error bars are as in Fig. 2.

Finally, we point out that, although the coupling mechanism between the nematic order and bond order is still not well understood, the onset of herringbone packing[7] could serve as a mediating mechanism.[17] It has been suggested[18] that the A-Hex transition in 65OBC may be near a herringbone-induced tricritical point, thus accounting for the unusual critical exponents. Using the data of Ref. 5 and that presented herein, the scaling relationship $\alpha + 2\beta + \gamma = 2$ is found to be consistent with a tricritical exponent $\gamma = 1$. (However, the values for α and β apparently differ from the tricritical values because of nonuniversal corrections.[18]) This herringbone hypotesis requires further study.

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