

Long-Range Order in Two- and Three-Dimensional Smectic-*B* Liquid-Crystal Films

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This Letter presents x-ray studies of freely suspended smectic liquid-crystal films from 2 to >100 layers thick. Smectic-*B* thick films of butyloxybenzylidene octylaniline (4O.8) have three-dimensional long-range order while thin films are two-dimensional crystals. Large diffuse scattering is observed from soft shear waves, propagating perpendicular to the layers, and three new low-temperature phases with different interlayer order in thick films are found.

Freely suspended films of smectic liquid crystals are attractive systems for the study of the effects of reduced structural dimensionality. Success in optical experiments¹ has led to attempt x-ray studies of intermolecular correlations in the various smectic phases and at phase transitions. The film technique is unique for two reasons. First, uniform, stable, large-area (1 cm²) films can be made which consist of two molecular layers ($N=2$). These films are the first truly two-dimensional (2D) systems which allow the study of structural correlations. Second, the film thickness may be increased to study the evolution to 3D. For thick films ($N>100$), this technique eliminates layer pinning at sample-cell walls and extraneous forces of alignment fields. In the smectic-*B* phase, the films are single crystals with negligible mosaic spread.

The principal motivation for the present work was to investigate the 2D melting process (i.e., the smectic *B* → *A* transition) and the interlayer correlations with increasing thickness. A 2D lattice possesses both conventional long-range bond-orientational order and power-law decay of positional correlations.² The δ -function Bragg scattering of a 3D solid is replaced by the structure factor

$$S(\vec{q}) \sim (\vec{q} - \vec{G})^{-2+\eta_{\vec{G}}(T)}, \quad (1)$$

where \vec{G} is a 2D reciprocal-lattice vector and $\eta_{\vec{G}}(T)$ is wave-vector and temperature dependent. During our experiments Halperin and Nelson,³ building upon ideas of Kosterlitz and Thouless,⁴ showed that melting could occur in two steps. With increasing temperature, one would first observe a transition to an intermediate "hexatic" phase with power-law decay of bond order and short-range positional order. This state would have a Lorentzian structure factor

$$S(\vec{q}) \sim [\xi_{\parallel}^2 (\vec{q} - \vec{G})^2 + 1]^{-1}, \quad (2)$$

where ξ_{\parallel} is the in-plane positional correlation length. Then in an additional transition at higher

temperatures, this phase would transform to a 2D liquid. Later Birgeneau and Litster⁵ proposed that a 3D system of stacked hexatic layers would have long-range orientational order and exponential decay of both in-plane and interlayer positional correlations. They offered this explanation for previous x-ray observations^{6,7} suggesting finite interlayer correlations in smectic-*B* phases.

Here we present our progress in the study of films of butyloxybenzylidene octylaniline (4O.8), which has a bulk smectic *B* → *A* transition at $T_{AB} = 49^{\circ}\text{C}$. This material was chosen because previous work⁶ on the *B* phase suggested the behavior described above. However our results prove that the bulk smectic-*B* phase of 4O.8 does *not* have a short ξ_{\perp} and the Birgeneau-Litster model does not apply. Thin films in the smectic-*B* temperature range are 2D crystals and not the intermediate hexatic phase discussed by Halperin and Nelson, although this phase may occur at temperatures above 49°C .

Our experiments used a spectrometer based on a 50-kW rotating-Cu-anode x-ray generator. A vertically bent pyrolytic graphite(002) crystal focused Cu $K\alpha$ x rays to a 1×3 -mm² spot on the film and scattered radiation was analyzed with a flat pyrolytic graphite(002) crystal and scintillation detector. Our resolution function is Gaussian with full widths at half maxima given by

$$\Delta q_x = 0.046 \cos\theta \text{ \AA}^{-1},$$

$$\Delta q_y = 0.046 \sin\theta \text{ \AA}^{-1},$$

$$\Delta q_z \approx 0.1 \text{ \AA}^{-1},$$

where \hat{x} , \hat{y} are in the scattering plane, parallel and perpendicular, respectively, to the nominal momentum transfer, \vec{Q} , and \hat{z} is perpendicular to the scattering plane.

Films were drawn inside an oven with 0.05°C temperature control, evacuated to 500 mTorr to minimize the background. Since the scattering from a 100-Å thick film of hydrocarbons is small, it was crucial to have no windows within the scat-

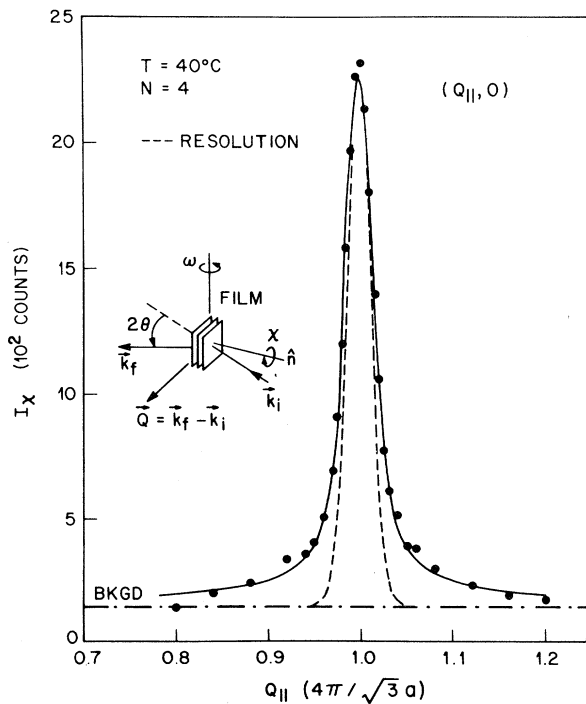


FIG. 1. Intensity integrated over a $60^\circ \chi$ segment for a four-layer film, vs the in-plane momentum transfer $Q_{||}$. The solid line represents the structure factor described in the text. The inset describes the experimental geometry, with \hat{n} being the film normal.

tering volume. Typically the beam-on, no-film background was less than 0.025 count per second.

Our data are obtained as scans in the hexagonal reciprocal lattice where $a^* [4\pi/(3^{1/2}a)]$ varies linearly from 1.4457 \AA^{-1} at 25°C to 1.4360 \AA^{-1} at 49°C and $C^* (2\pi/c) = 0.217 \text{ \AA}^{-1}$ essentially independent of temperature. Momentum transfers $\vec{Q} = (Q_{||}, Q_{\perp})$ are defined by their components parallel and perpendicular to the smectic layer plane (see inset to Fig. 1). In thin films we find well-defined lattice orientational order as evidenced by narrow peaks in a χ scan. However, there is often more than one such peak in a $60^\circ \chi$ segment. Since the beam area is large, $\sim 3 \text{ mm}^2$, we conclude that the film consists of a few well-ordered domains. In thin films the orientation of these domains varies slowly with time. At temperatures near 48°C (43°C) the peak rotates 2° in χ in about 20 minutes (1.5 hours). This domain structure and dynamics provide evidence that the 2D film can support mobile dislocations.

To establish the extent of in-plane positional correlations with moving domains, we employed a rotational averaging technique to obtain the data in Fig. 1. At each value of momentum trans-

fer, the intensity was integrated over a $60^\circ \chi$ segment. Successive scans were accumulated until fluctuations due to counting statistics dominated the random errors due to the averaging procedure. To compare with experiment, structure factors (1) and (2) have been integrated over the angle χ and convoluted with the measured resolution. Equally good fits can be obtained by either form provided $\xi_{||} > 800 \text{ \AA}$. The fact that this length is so large argues strongly against the applicability of the hexatic description in favor of the 2D crystal interpretation. Such a model for 2D films predicts that thick films would have conventional 3D order.

To test this behavior we studied interlayer correlations as a function of film thickness. As shown in Fig. 2 the slowly varying layer interference function characteristic of a four-layer film evolves continuously into a spectrum of sharp Bragg peaks riding on a large diffuse background. We note that peak widths are fully accounted for

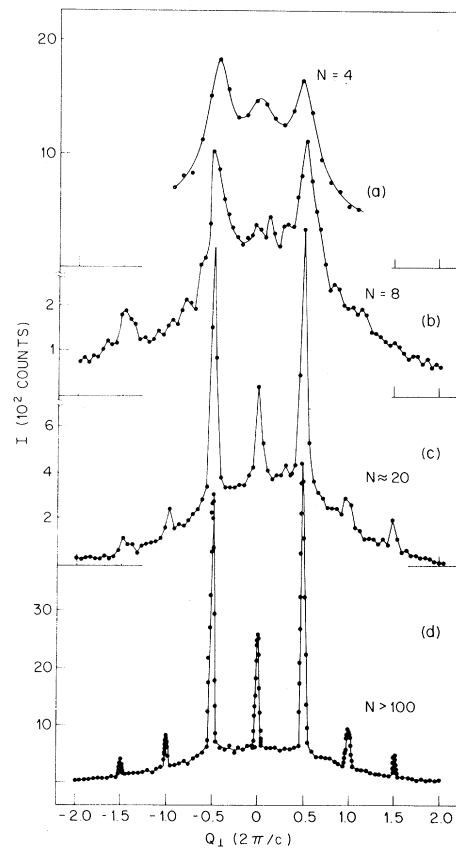


FIG. 2. Scans taken at $\vec{Q} = (1, Q_{\perp})$ for four different film thicknesses show the development of interlayer correlations. The data for the $N=4$ film was integrated over χ .

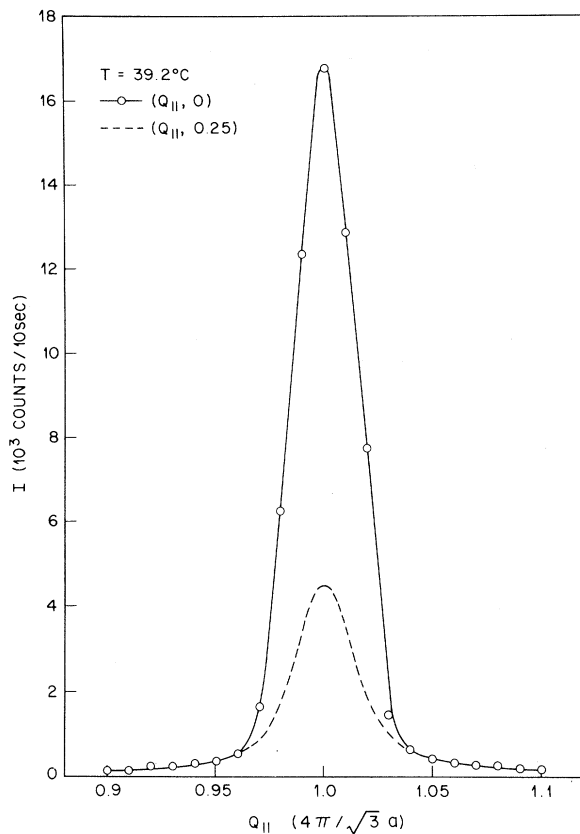


FIG. 3. Longitudinal scans through the Bragg peak at $\vec{Q} = (1, 0)$ (solid line) and through the diffuse scattering at $\vec{Q} = (1, 0.25)$ (dashed line) for a thick film with $N > 100$.

by a combination of resolution and the finite number of layers for $N = 4, 8,$ and 20 . For the case $N > 100$ the peaks are limited solely by resolution and have profiles which are identical within experimental error to those produced by a perfect Ge single crystal. There is *no doubt* that this smectic- B phase has conventional 3D long-range order. The spectrum of peaks indexes on half-integer units of the single-layer reciprocal lattice constant. Intensity arguments and systematic extinction rules imply that the interlayer ordering consists of 3D hexagonal-close-packed ($ABAB$) stacking.

The large diffuse scattering seen in Fig. 2 is clearly distinguished from the Bragg scattering as the number of layers increases. For a thick film, Fig. 3 shows longitudinal scans both through a Bragg point ($Q_{\perp} = 0$) and through the diffuse scattering only ($Q_{\perp} = 0.25$). Subtraction of the two scans shows that the coherent Bragg scattering is identical to the Gaussian resolution function within experimental error (5% in FWHM).

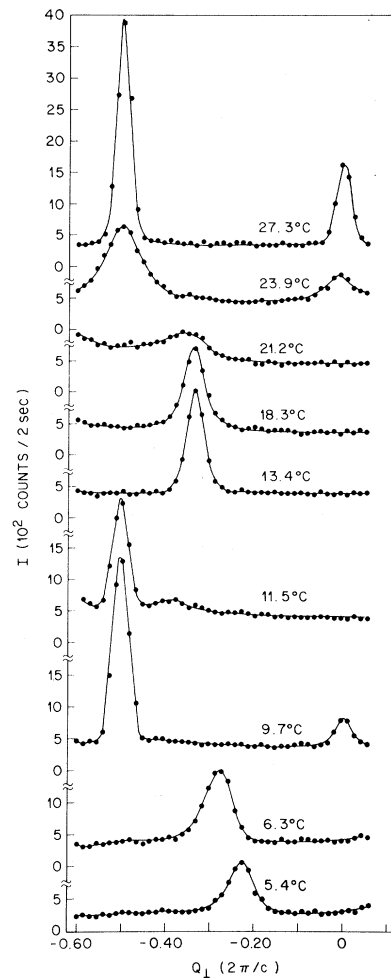


FIG. 4. Temperature dependence of the interlayer ordering in a thick film ($N > 100$) is monitored by transverse scans with $\vec{Q} = (1, Q_{\perp})$. Note phase transitions at about 22°C , 12°C , and 7°C .

The diffuse scattering is sharply peaked in Q_{\parallel} but is neither Gaussian nor of resolution width. It has long wings characteristic of scattering from phonons but its intensity is extraordinary compared with that from a normal solid. We believe that this scattering derives from soft shear waves propagating perpendicular to the layers. Neutron scattering experiments⁸ on terephthal-*bis*-butylaniline (TBBA) have shown the zone-boundary frequency for these TA $[00\xi]$ modes to be less than 1 MeV.

Having established that the smectic- B phase has 3D long-range order but anomalously soft TA $[00\xi]$ excitations, we believe that interlayer ordering, although present, is energetically weak. Unexpected evidence for weak interlayer forces is provided by a remarkable series of three first-

order phase transitions which occurs between 27°C and 5°C. In Fig. 4, transverse scans show that these transitions involve changes in the interlayer periodicity from two layers to three layers near 22°C and back to two layers again near 12°C. Finally below 7°C the lattice becomes monoclinic with the \vec{c}^* axis tilting as a function of temperature.

We conclude by emphasizing that our results on thick films clearly establish that the smectic-*B* phase of 4O.8 has 3D long-range order. Although it is apparently a solid, unusually low-frequency layer shear modes exist. Furthermore, the energy of interlayer ordering must be weak to account for the observed phase transitions below 27°C. In thin-film experiments we have shown that it is possible to use x-ray diffraction techniques which have thus far demonstrated that the smectic-*B* phase is a 2D crystal. From this basis it is now possible to approach the problem of 2D melting. Improved synchrotron-based x-ray experiments are now in progress.

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Neutron-Diffraction Study of Phases of CD₄ Monolayer Films on Graphite

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Neutron-diffraction studies have been carried out of the various two-dimensional phases of CD₄ physisorbed on graphite and a phase diagram has been constructed. Registered, expanded, and compressed solid phases and a disordered fluidlike phase have been identified. The lattice constant, intensity, and cluster size have been measured as functions of temperature and coverage and the nature of the transitions between the phases has been investigated.

The nature of the various phases of submonolayer atomic or molecular films physisorbed on solid surfaces, and of the transitions between such phases have recently received increasing experimental and theoretical attention.¹⁻³ The interactions between the adsorbed molecules themselves and with the substrate lead to a rich variety of ordered ("solid"-like) and disordered ("fluid"-like) two-dimensional (2D) phases which may be

commensurate or incommensurate with the substrate.

In this Letter, we present the results of a neutron-diffraction investigation of the various 2D phases of methane adsorbed on exfoliated graphite. Methane was chosen because it is the simplest (spherical) hydrocarbon molecule which can be thus studied and because no detailed information has been available regarding the 2D phases of