# Light-Scattering Study of Bond Orientational Order in a Tilted Hexatic Liquid-Crystal Film

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We report a light-scattering study of the development of bond-orientational (BO) order in a thick, monodomain, freely suspended film. Our static results are consistent with a three-dimensional Landau free energy, and show an approximately linear increase of the BO elastic constant through the ordered phase. Our dynamic results show a hydrodynamic mode, which exhibits critical slowing down at the liquid to BO phase transition, and a nonhydrodynamic mode which is associated with the BO phase.

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In recent years, the discovery of a phase of matter intermediate between a liquid and a positionally ordered solid has greatly expanded our understanding of melting.[1,2] The phase we refer to exhibits long-range bond-orientational (BO) correlations along directions which become the crystal axes when the lattice crystallizes. The first definitive observations of a BO phase were made with x rays on the smectic-*B* phase of a liquid crystal.[2] Only quite recently, however, have quantitative measurements of BO order been performed on single-domain smectic samples.[3,4] In such samples the molecular long axis (director) is tilted with respect to the layer normal, and coupling between the molecular tilt and the BO order parameter induces monodomain BO order.[3] X-ray scattering experiments[3] exploit the effect of this coupling to measure quantitatively the BO order parameter. In addition, light scattering has been used on a very thin smectic film[4] to show a strong director-BO coupling, leading to a nonhydrodynamic mode in the bond-tilt field fluctuations.

The present work reports a quasielastic light-scattering study of the liquid ($S_C$) to BO ordered ($S_I$) phase transition in a thick monodomain film. We establish the validity of a simple free energy for the transition by quantitative analysis of the $q^2$ dependence of the scattering, as well as by confirming the predicted nonhydrodynamic mode. In the liquid phase of thick films, we observe layer-coupling effects in both the amplitude and relaxation time of the director-field fluctuations, and measure a dramatic critical slowing down of the hydrodynamic fluctuations at the transition. Additionally, we find that the temperature dependence of the BO elasticity in the $S_I$ phase scales like the square of the positional correlation length in a hexatic layer.

Our sample was a several-micron-thick film of racemic 4-(2-methylbutylphenyl)-4′-(octyloxy)-1,1′-biphenyl-4-carboxylate (8OSI) pulled across a 6.4-mm hole in a 0.51-mm-thick stainless-steel sample holder. The film was maintained in a clean $N_2$ atmosphere at $\simeq 100$ Torr inside a two-stage optical oven with 1-mK short-term temperature stability. The tilt field was aligned by cooling from the $S_A$ to the $S_C$ phase ($T_{AC} \simeq 133\,^\circ$C) in a $\simeq 1$ kOe magnetic field. Tilt alignment was carefully monitored for the duration of the experiment, and the tilt mosaic in the $S_C$ phase was estimated optically to be $< 2^\circ$. The film was illuminated with $\simeq 50$ mW of 5145-Å laser light. The experiment measured the intensity and the autocorrelation function of the light scattered by director fluctuations at a series of temperatures through the $S_C \rightarrow S_I$ transition. At each temperature, $q^2$ in the plane of the layers and along the tilt direction was scanned between $7\times10^7$ and $3\times10^9$ cm$^{-2}$; this geometry corresponds to the in-plane director bend mode.[5] Transition-temperature drift was estimated to be $< 0.2$ mK/h over a 5-d experiment.

To calculate the light scattering, we begin with a simple free-energy density $F$ which includes both the tilt order parameter $\Phi \equiv \Phi_0 e^{i\phi}$ and the BO order parameter $\psi \equiv \psi_0 e^{6i\theta}$. Here $\Phi_0$ is the angle the director makes with the layer normal, and $\phi$ describes the orientation of the in-plane director component. The phase $\theta$ in $\psi$ represents fluctuations in the sixfold in-plane bond orientation about a reference axis. For our experimental geometry, $F$ can be written[6] as

$$F = \tfrac{1}{2}a_1\Phi_0^2 + \tfrac{1}{4}c_1\Phi_0^4 + \cdots + \tfrac{1}{2}a_6\psi_0^2 + \tfrac{1}{4}c_6\psi_0^4 + h\Phi_0^6\psi_0 + \cdots + \tfrac{1}{2}K_A(\nabla_\perp\theta)^2 + \tfrac{1}{2}K_A'(\partial_z\theta)^2 + \tfrac{1}{2}K(\nabla_\perp\phi)^2 + \tfrac{1}{2}K'(\partial_z\phi)^2 + 18h\Phi_0^6\psi_0(\phi-\theta)^2. \quad (1)$$

Here $\nabla_\perp \equiv \hat{\mathbf{x}}\partial_x + \hat{\mathbf{y}}\partial_y$ for in-plane coordinates $x,y$; $\hat{\mathbf{z}}$ lies along the layer normal. The elastic constants $K,K'$ measure respectively the elasticity of in-plane bend distortions and out-of-plane twist distortions of $\phi$. $K_A,K_A'$ correspond to similar distortions of $\theta$. $K'$ and $K_A'$ are thus effective layer coupling constants. The terms in $h$ represent a conjugate field to the BO order arising from the molecular tilt.[1]

To obtain the fluctuations in $\phi$ which scatter light, we diagonalize (1) by defining normal modes $\Delta=\theta-\phi$ and $\rho=\theta+b\phi$.[1] After projecting out the $\phi$ component of each mode, we obtain

$$\frac{\langle\delta\phi^2(q_\perp)\rangle}{k_BT}=\frac{1}{(K+K_A)q_\perp^2}+\frac{1}{(K+K_A)q_\perp^2+(K'+K_A')\pi^2/t^2}+\frac{1}{H(1+K/K_A)^2+K(1+K/K_A)q_\perp^2}$$
$$\equiv\frac{1}{Aq_\perp^2}+\frac{1}{C+Aq_\perp^2}+\frac{1}{B+Dq_\perp^2}, \tag{2}$$

where $H\equiv 36h\Phi_0^6\psi_0$. We have taken $q_z=\pi/t$ ($t$ = film thickness) as the dominant contribution from twist fluctuations,[7] which, because of the finite thickness of the film, $t\simeq 5\lambda$, we expect to see even for a scattering geometry that selects only pure in-plane fluctuations. (In our experiment, $q_z^2$ was always $<15\%$ of the minimum $q_\perp^2$.) In (2), the first two terms come from the $\rho$ mode and the third from the $\Delta$ mode.

We first compare the $q_\perp^2$ dependence of our intensity data with (2), and the temperature dependence of the associated parameters with their expected behavior. In the $S_C$ phase ($T>T_{CI}$, where $T_{CI}=S_C\rightarrow S_I$ transition temperature), we expect for small BO elasticity ($K_A\rightarrow 0$) $B\sim HK^2/K_A^2$, and $D\sim K^2/K_A$, so that the last term in (2) is negligible compared to the second term. Hence,

$$\frac{\langle\delta\phi^2(q_\perp)\rangle}{k_BT}\simeq\frac{1}{Aq_\perp^2}+\frac{1}{C'+B'q_\perp^2} \tag{3}$$

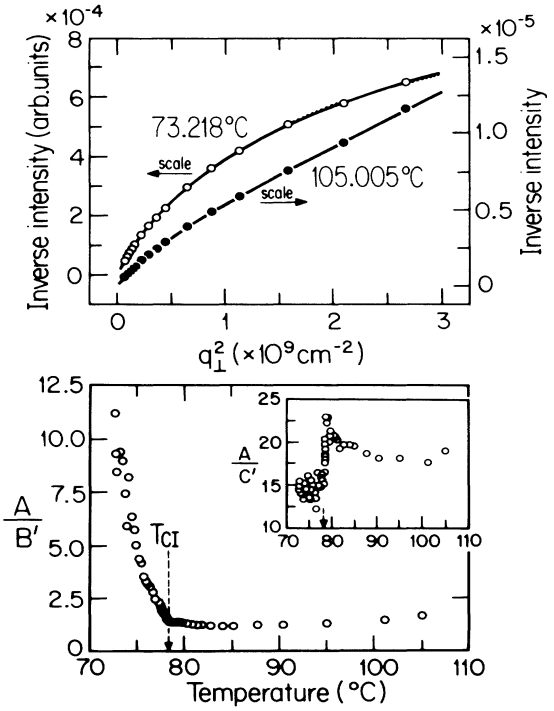


FIG. 1. Top: Inverse intensity vs $q_\perp^2$ fitted by (3) in the $S_C$ phase (bottom curve) and by (2) (dotted line) and (3) (solid line) in the $S_I$ phase (top curves). Bottom: The ratios $A/B'$ and (inset) $A/C'$ vs temperature. See (3) and accompanying text.

for the $S_C$ phase, with $C'\simeq C$ and $B'\simeq A$. The top panel of Fig. 1 shows a typical fit of (3) to data for the scattered intensity in the $S_C$ phase ($T\simeq 105\,^\circ$C); we find that (3) describes the $q_\perp^2$ dependence of the scattering well throughout the $S_C$ phase. The magnitude of $C$ is consistent with a sample thickness $t\simeq 1$ $\mu$m and typical values for $K'$. The bottom panel shows that in the liquid phase

$$A/C'\simeq A/C\sim(K+K_A)/(K'+K_A')\sim K/K'$$

is approximately constant and $A\simeq B'$, as expected.

For the $S_I$ phase, returning to (2), we note that for large $K_A$, $K_A'$, and $\psi_0^2$, $A\sim K_A$, $C\sim K_A'$, and $D\sim K$. We also expect[8] $B\sim\Phi_0^6\psi_0\sim\psi_0^2$. Since three of these parameters should increase for $T\lesssim T_{CI}$, we might expect $B+Dq_\perp^2$ and $C+Aq_\perp^2$ to be highly correlated in the $S_I$ phase. In fact, (2) and (3) fit our data equally well near $T_{CI}$ and for $T<T_{CI}$. The top panel Fig. 1 shows $S_I$ intensity data ($T\simeq 73.2\,^\circ$C) fitted by (2) and by (3). In the bottom panel, we show $A/C'$ and $A/B'$ for the $S_I$ phase obtained from fits by (3), which gives the most reliable parameters. To understand these ratios, we examine the limiting behavior of the full result (2). At low $q_\perp^2$, we find $\langle\delta\phi^2\rangle\simeq(Aq_\perp^2)^{-1}+1/C'$ with

$$C'=CB[C+B]^{-1}\sim K_A'\psi_0^2(K_A'+\psi_0^2)^{-1}.$$

Thus, for $K_A'\sim K_A$, $A/C'\sim\psi_0^{-2}(K_A'+\psi_0^2)$ should be approximately independent of $T$, as shown for the $S_I$ phase in Fig. 1. At high $q_\perp^2$, (2) gives $\langle\delta\phi^2\rangle\simeq(Aq_\perp^2)^{-1}+(B'q_\perp^2)^{-1}$ with $B'=AD[A+D]^{-1}$, so that $A/B'$

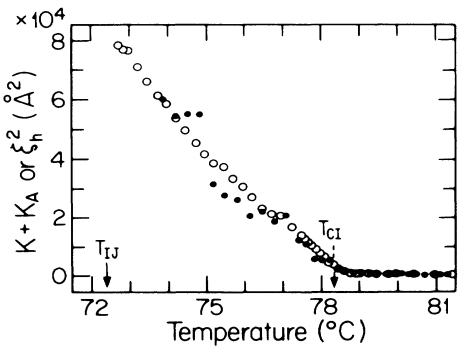


FIG. 2. Temperature dependence of $K+K_A$ (open circles) scaled to data for $\xi_h^2$ (solid circles) obtained by Brock *et al.* (Ref. 3), on the assumption that $K+K_A=K+C\xi_h^2$.

$\sim 1+A/D \sim K_A/K$ for large $K_A$. Thus $A/B'$ should increase sharply in the $S_I$ phase, as Fig. 1 demonstrates.

We now discuss the temperature dependence of $K+K_A$ obtained from the parameter $A$ in fits by (3). We have considered both $K_A \sim \psi_0^2$ and $K_A \sim \xi_h^2$, where $\xi_h$ is the in-layer positional correlation length along the molecular tilt direction.[9] The latter prediction holds rigorously in 2D,[9] but may hold in 3D if the finite thickness of the film suppresses the formation of lattice dislocation loops cutting through the layers. In particular, if in 3D the dislocations extend across layers in isolated lines whose length is fixed by the film thickness, the dislocation energy would still scale with $\xi_h$ like $\xi_h^2$.

Figure 2 shows our data for $K+K_A$ scaled to x-ray scattering data[3] for $\xi_h^2$ obtained for a thick film of the same liquid crystal. We note a strong qualitative correspondence and an approximately linear behavior in the $S_I$ phase, in sharp contrast to the x-ray data[3] for $\psi_0^2$. In 2D $\xi_h$ is expected[10] to diverge dramatically at the hexatic-to-solid transition ($T-T_{IJ}$); neither the x-ray nor light-scattering results show this divergence in 3D. However, neither experiment obtained data for $T-T_{IJ} \lesssim 0.3\,^\circ$C. We note that $K+K_A$ reported here changes by a factor $\sim 10^2$ through the $S_I$ phase, in good agreement with the x-ray data for $\xi_h^2$ and with the result for $K+K_A$ obtained in very thin films.[4]

We now turn to the dynamics of the director fluctuations. For the three components of Eq. (2), we expect[11] three overdamped modes, characterized by linewidths

$$\Gamma_\rho^1 = \frac{(Kq_\perp^2 + K'\pi^2/t^2)^2}{\eta_\rho(K+K_A)q_\perp^2 + \eta_\rho'(K'+K_A')\pi^2/t^2}$$

and $\Gamma_\rho^0 = K^2 q_\perp^2 [\eta_\rho(K+K_A)]^{-1}$ for the $\rho$ modes with $q_z = \pi/t$ and $q_2 = 0$, respectively, and

$$\Gamma_\Delta = [H + KK_A(K+K_A)^{-1} q_\perp^2]\eta_\Delta^{-1}$$

for the $\Delta(q_z = 0)$ mode. The transport coefficients associated with the three modes are $\eta_\rho$, $\eta_\rho'$, and $\eta_\Delta$; in general, we expect $\eta_\rho \neq \eta_\rho'$.

In the $S_C$ phase, on the basis of the scattered intensity analysis above, the linewidths should be those of the $\rho$ mode. Moreover, from the forms of $\Gamma_\rho^0$ and $\Gamma_\rho^1$, we expect very similar time scales for the corresponding correlation function decays except when $q_\perp^2 \lesssim \pi^2/t^2$. We show this to be the case in Fig. 3. The top panel shows the $q_\perp^2$ dependence of the $\rho$ mode in the $S_C$ phase ($T \simeq 105\,^\circ$C) and the $S_I$ phase ($T \simeq 73.2\,^\circ$C). For the range of $q_\perp^2$ we could study, we could not reliably separate $\Gamma_\rho^0$ and $\Gamma_\rho^1$ in either phase; instead, we extracted a single decay $\Gamma_\rho$ using a cumulant analysis of the correlator data. The evidence for multiple linewidths then comes from the larger variance in $\Gamma_\rho$ obtained for $q_\perp^2 \lesssim \pi^2/t^2$, and from the fact that $\Gamma_\rho$ does not go to zero as $q_\perp^2$ for $q_\perp \to 0$ in the $S_C$ phase, as shown in the top panel of Fig. 3. We observe that this does not occur in the $S_I$ phase; in fact, the intercept disappears at $T \sim T_{CI}$. Thus, for $T \lesssim T_{CI}$, $\Gamma_\rho^0 = \Gamma_\rho^1$ and the $\rho$ mode is hydrodynamic within the accuracy of our experiment. We conjecture that $\eta_\rho'/\eta_\rho \to 0$ near $T_{CI}$.

The bottom panel of Fig. 3 shows the temperature dependence of the slope and intercept obtained from fits

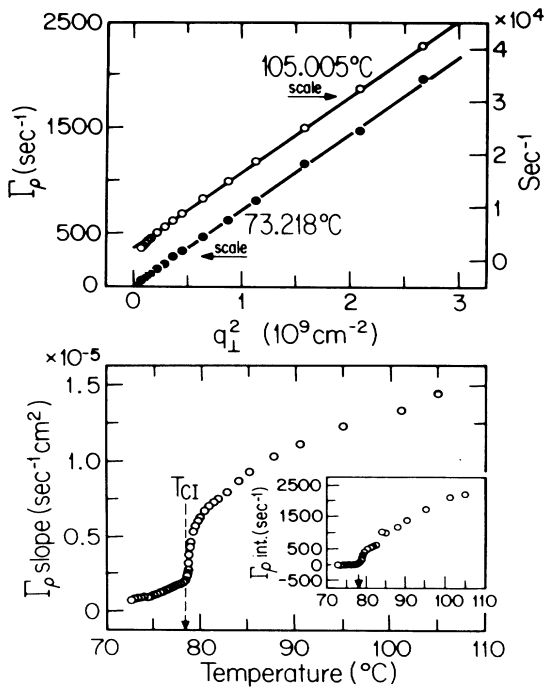


FIG. 3. Top: $\Gamma_\rho$ (see text) vs $q_\perp^2$ fitted by a line in the $S_C$ phase (top curve) and $S_I$ phase (bottom curve). Bottom: Temperature dependence of the fitted slope and intercept.

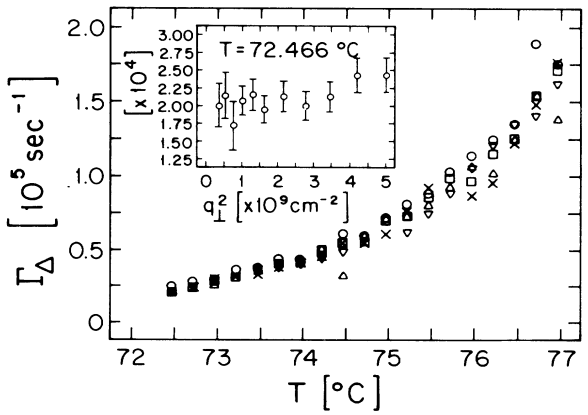


FIG. 4. Temperature and $q_\perp^2$ dependence of the $\Delta$ mode. Inset: $q_\perp^2$ dependence of $\Gamma_\Delta$ at $T = 72.466\,^\circ\text{C} \ll T_{CI}$. The highest $q_\perp^2$ value and the next four lower values in the inset correspond to the circles, squares, inverted triangles, and crosses, respectively.

of $\Gamma_\rho(q_\perp^2)$ by a line for the linear region of $\Gamma_\rho$. The slope is given by

$$\lim_{q_\perp \to \infty} \Gamma_\rho^0 q_\perp^{-2} = \lim_{q_\perp \to \infty} \Gamma_\rho^1 q_\perp^{-2} = K^2[\eta_\rho(K+K_A)]^{-1},$$

and the intercept by

$$\lim_{q_\perp \to 0} \Gamma_\rho^1 = (K'\pi/t)^2[\eta_\rho'(K'+K_A')]^{-1}.$$

The slope shows a critical slowing down of the $\rho$-mode fluctuations, as predicted for increasing $K_A$ (and possibly $\eta_\rho$) as $T \to T_{CI}^+$. The intercept shows a continuous decrease (to 0) as $T \to T_{CI}^+$, as expected, except for a jump at $T - T_{CI} \simeq 5\,^\circ$C. We have found this anomaly in other thick film samples, but do not yet have adequate data to understand it.

We now discuss the $\Delta$-mode dynamics. Since the intensity of the $\Delta(q_z = 0)$ mode is very weak for $T > T_{CI}$, we expect $\Gamma_\Delta$ to be difficult to measure in the $S_C$ phase. In fact, we could not detect $\Delta$-mode dynamics for $T > T_{CI}$. In the $S_I$ phase, however, we expect observable intensity, and $\Gamma_\Delta \to (H + Kq_\perp^2)\eta_\Delta^{-1} \simeq H\eta_\Delta^{-1}$ for large $\psi_0^2$. Indeed, the $\Delta$ mode appears as a fast component in the $S_I$-phase scattering and is shown in Fig. 4. For $T \ll T_{CI}$ we see that $\Gamma_\Delta$ is independent of $q_\perp^2$ within experimental error, as expected. We note that $\Gamma_\Delta$ increases about sevenfold with increasing $T$ over the range studied. Finally, we have not observed in thick films evidence of a hexatic-to-hexatic structural transition reported in very thin films.[4]

To summarize, we have demonstrated that a simple free energy explains the main static and dynamic features of the light scattered from director fluctuations in a three-dimensional film at the $S_C \to S_I$ phase transition. When the film thickness is comparable to the wavelength of light, scattering from the lowest-order twist mode produces observable nonhydrodynamic effects in the $S_C$ phase. In the $S_I$ phase, nonhydrodynamic behavior arises from the beating of the in-plane director against the BO order directions. Finally, even for films of several microns thickness, $K_A$ behaves qualitatively like the square of the correlation length in a BO layer. More complete measurements as well as further theoretical work are needed to understand fully the temperature dependence of the static and dynamic parameters associated with the development of BO order.

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[7]A simple calculation shows that 94% of the scattered intensity comes from the $q_z = 0$ components of the $\rho$ and $\Delta$ modes and the lowest-order ($q_z = \pi/t$) twist component of the $\rho$ mode.

[8]Minimizing Eq. (1) in $\psi_0$, we can replace $h\Phi_0^6$ with $a_6\psi_0$ to lowest order.

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