Dynamics of Thin Tilted Hexatic Liquid Crystal Films

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We have used quasielastic light scattering to measure the bond-orientational elasticity and viscosity of thin tilted hexatic liquid crystal films. Our results agree well with a microscopic model of the dynamics of a hexatic. We have also discovered a novel optical mode corresponding to the out-of-phase motion of the tilt field and bond-angle field. This mode softens dramatically at the structural phase transition from hexatic I to hexatic F.

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Hexatic can occur as intermediate phases between the solid and liquid during the melting of two-dimensional (2D) crystals. They have translational symmetry due to short-range positional correlations but broken rotational symmetry due to quasi-long-range hexagonal bond-orientational correlations. Their Goldstone mode consists of excitations of the bond-angle field characterized by a bond-orientational elastic constant, K_A, and a bond-orientational viscosity, ν_A. K_A is predicted[1-6] to be proportional to the diverging positional correlation length squared, ξ^2, near the hexatic to crystal transition and should jump discontinuously to zero when rotational symmetry is restored at the disclination unbinding transition to an isotropic liquid.

Free-standing liquid crystal films are an ideal system for the study of the hexatic phase. The molecules may either be oriented normal to the layers or tilted by a fixed angle. The orientation with respect to a fixed reference axis of the projection of the local tilt into the layer plane can be described by a 2D director field, $\hat{\mathbf{n}}(\mathbf{r})$. Tilt-bond coupling generally exists which constrains the local tilt to point either along the local bond directions (hexatic I) or between them (hexatic F), and distorts the short-range positional symmetry from hexagonal to rectangular. Consequently, tilted hexatics should possess two Goldstone modes corresponding to splaylike and bendlike coupled in phase motions of the tilt- and bond-angle fields. Since the tilt itself breaks rotational symmetry, the disclination unbinding transition leads to an anisotropic liquid, the smectic-C phase, with similar Goldstone modes as in the tilted hexatic but only involving tilt-field distortions.

We have extended our earlier observations[7] of the qualitative temperature dependence of K_A by using quasielastic light scattering to make the first quantitative measurements of the bond-orientational elasticities and viscosities of a tilted hexatic. Our results are in good agreement with a microscopic theory[4,5] which models the dynamic properties of a hexatic as those of a heavily dislocated solid. We also present evidence for a novel optic mode in tilted hexatics corresponding to the out-of-phase motion of the tilt and bond fields. This mode shows a strong softening and enhanced susceptibility at the structural phase transition from hexatic-I to hexatic-F, indicating a dramatic reduction in tilt-bond coupling.

The liquid-crystal compound studied was the chiral material (*S*)-4-(2′-methylbutyl)phenyl 4-(*n*-octyl)biphenyl-4-carboxylate. Two-layer films of this chiral compound have the phase sequence[8] smectic-A–smectic-C^*–hexatic-I^*–crystal-J^*–crystal-G^*. The tilted phases are marked by an asterisk to indicate that they develop a spontaneous in-plane ferroelectric polarization. Free-standing films are drawn in the smectic-C^* phase across a 1-mm-diam hole in a metal slide in an oven with 10-mK temperature stability and optical access. Single-domain samples were produced by the application of a 1.3-kG magnetic field at a 45° angle from the normal to the film. The sample alignment during measurements was monitored with use of depolarized microscopy.[7] A 20-mW laser beam was incident on the film and both the average intensity and intensity autocorrelation function of the depolarized scattered light were measured. Fluctuations with wave vectors, $\mathbf{q}$, either parallel, $q_\parallel$, or perpendicular, $q_\perp$ to $\hat{\mathbf{n}}$ were probed at a range of wave vectors from 1000 to 6000 cm^{-1}. We could not obtain data in the immediate vicinity of the weakly first-order smectic-C^*–to–hexatic-I^* transition because of the presence of a two-phase coexistence region.

The inverse intensity of depolarized light scattered by thermal molecular-orientation fluctuations is proportional to their energy:

$$\langle I\rangle^{-1} \sim K_S q_\perp^2 + K_B q_\parallel^2 + 2\pi P_0^2 |q_\parallel| . \tag{1}$$

In the smectic C^* phase, K_S and K_B are the Frank elastic constants for splay and bend distortions of $\hat{\mathbf{n}}$. In the hexatic phase, they are the sum of the director and bond-orientational elasticities. The last term is a space-charge contribution due to the permanent dipole moment, P_0, of the chiral molecules. Application of an electric field across the film adds the term $P_0|E|$ to Eq. (1). By measuring the change in intensity when an electric field is applied across the film[9] we have determined

$P_0 = 1.0 \times 10^{-5}$ esu/cm. Knowledge of P_0 allows us to calibrate the scattering intensity and thus determine absolute values for the elastic constants in the smectic-C^* and hexatic phases.

Dynamic fluctuations of the director and bond-angle fields relax diffusively with a decay rate given by

$$\Gamma = D_S q_\perp^2 + D_B q_\parallel^2 + (2\pi P_0^2/\nu_B)\,|q_\parallel|, \tag{2}$$

where the diffusion coefficient D_S is given by the ratio of the elastic constant to the viscosity, K_S/ν_S, and similarly for D_B. Combined with our absolute determination of the elasticities, we are thus able to deduce absolute values for the viscosities.

Our measuremenst of the elasticities and viscosities of a two-layer film are presented in Fig. 1. Note that both increase by 1 or 2 orders of magnitude in going from smectic-C^* to hexatic-I^*. Thus the effective elasticity and viscosity of the coupled tilt-field plus bond field are dominated by the bond-field values. Theory[1] requires K_A to be greater than $K_A^* = 72kT_{IC}/\pi$ in order for the hexatic phase to be stable. We find this condition to be satisfied.

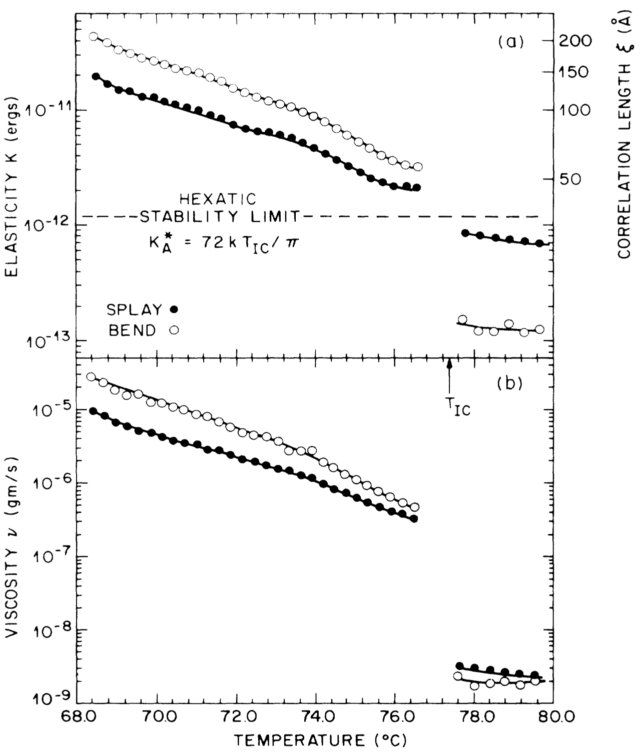

FIG. 1. Temperature dependence of the (a) elasticity and (b) viscosity of a two-layer film in the smectic-C^* and hexatic-I^* phases for both the splay and bend modes. The smectic-C^*-to-hexatic-I^* transition temperature, T_{IC}, is indicated. The hexatic-I^*-to-crystal-J^* transition occurs at $\simeq 63\,^\circ$C. The stability limit on the elasticity for an isotropic hexatic is indicated. The equivalent positional correlation lengths in the hexatic phase, derived from the Ostlund-Toner-Zippelius model as discussed in the text, are shown at the right in (a).

The results of Fig. 1 reveal significant anisotropy in the elastic constants in the smectic-C^* phase. This anisotropy is comparable in magnitude to what was previously observed[9] in a different compound and attributed to space-charge effects. In the hexatic-I^* phase, both the elastic constants and the viscosities are anisotropic and, in addition, the anisotropy is of opposite sign from the smectic-C^* phase.

The magnitude and anisotropy of the tilted hexatic elasticities can be understood with the microscopic theory of Ostlund, Toner, and Zippelius,[5] which models the dynamic properties of a tilted hexatic as those of a heavily dislocated solid. In this model, the elastic constants are given by

$$K_{S(B)} = kT/n_{f_{\perp(\parallel)}} = kT\xi^2_{\perp\parallel}/a_0^2, \tag{3}$$

where $n_{f_{\perp(\parallel)}}$ is the density of free dislocations with Burger's vectors perpendicular or parallel to $\hat{\mathbf{n}}$, a_0 is a dislocation core diameter, and $\xi_{\perp(\parallel)}$ is the positional correlation length perpendicular or parallel to $\hat{\mathbf{n}}$. Using Eq. (3) and taking a_0 to be the average in-plane lattice constant,[10] we find that our measured elastic constants imply correlation lengths ranging from $\simeq 50$ to $\simeq 200$ Å, as indicated on the right-hand axis of Fig. 1(a). They agree well, both in magnitude and anisotropy, with x-ray measurements[11] on tilted hexatic thin films of a different liquid crystal.

Ostlund, Toner, and Zippelius also predict an isotropic

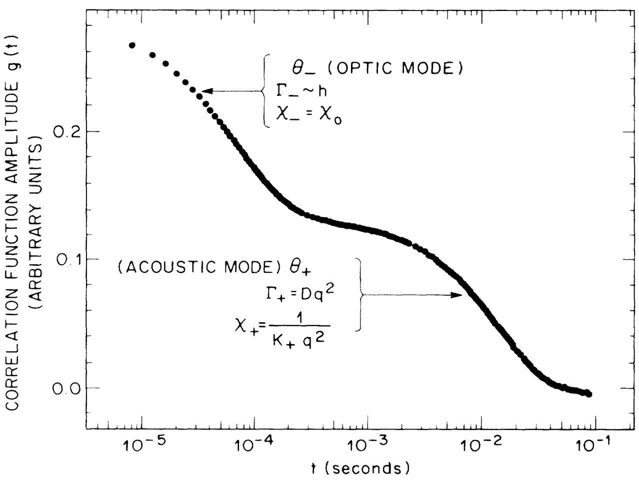

FIG. 2. Dynamic correlation function for a five-layer film in the hexatic-I^* phase 1.2 K below the smectic-C^* phase. The optic mode, θ_-, and the acoustic mode, θ_+, are indicated along with the q dependence of their relaxation rate, Γ, and their susceptibility, χ. $q_\perp = 3000$ cm^{-1}. Similar spectra are observed for $\mathbf{q} \parallel \hat{\mathbf{n}}$.

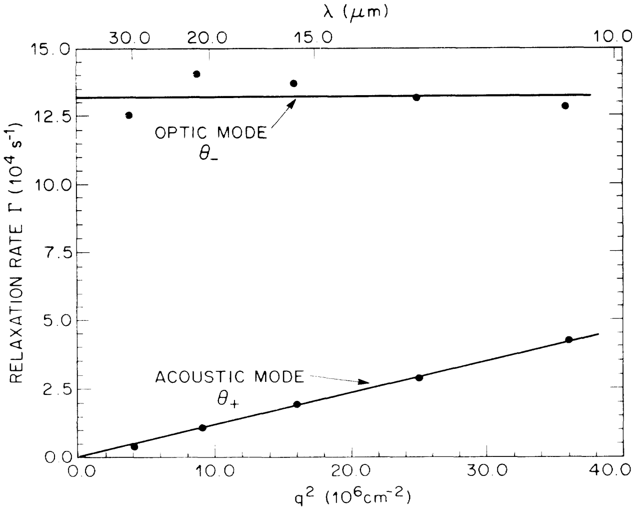

FIG. 3. Wave-vector dependence of the relaxation rates of the optic mode and the acoustic mode for a five-layer film in a 3.7-kG magnetic field in the hexatic-I^* phase 1.0 K below the smectic-C^* phase. Results for splay distortions are shown. Similar results are obtained for bend distortions.

bond orientational viscosity given by

$$\nu=\frac{kT}{2D}\left(\frac{1}{n_\perp}+\frac{1}{n_\parallel}\right)=\frac{kT}{2Da_0^2}\left(\xi_\perp^2+\xi_\parallel^2\right), \qquad (4)$$

where D is the dislocation diffusion coefficient. As shown in Fig. 1(b), we find that ν is actually anisotropic, indicating different diffusion coefficients for climb and glide of dislocations. The viscosities also increase $\simeq$3–4 times faster than the elasticities with decreasing temperature, in contrast to the predictions of Eqs. (3) and (4). This indicates that the dislocation diffusion coefficients are actually temperature dependent.

We next report our discovery of an additional relaxation process in tilted hexatics. In Fig. 2 we show the dynamic correlation function for a five-layer film in the hexatic-I^* phase. There are clearly two distinct single-exponential relaxations. We show the dispersion relations for these two modes in Fig. 3. We identify the slower mode as the in-phase fluctuation of the tilt field plus bond field discussed above. Its relaxation rate is proportional to q^2 and its intensity, or susceptibility, is proportional to $1/q^2$, as expected for a hydrodynamic mode. The faster mode, however, has a relaxation rate and susceptibility which are independent of q, as expected for an optic mode.

To understand the origin of the optic mode we consider the Hamiltonian for tilted hexatics neglecting elastic anisotropy,[2]

$$H=\tfrac{1}{2}\int d^2r[K_A(\nabla\theta)^2+K_1(\nabla\phi)^2] + h\int d^2r\cos6(\theta-\phi). \qquad (5)$$

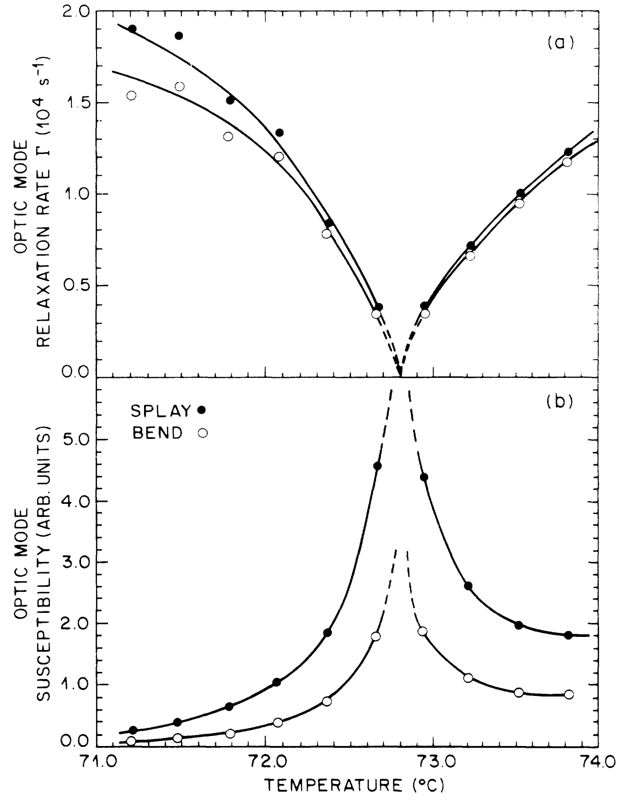

FIG. 4. Temperature dependence of the (a) relaxation rate and (b) susceptibility of the optic mode in a five-layer film showing the strong softening and divergent susceptibility at the structural phase transition from hexatic-I^* to hexatic-F^*. The smectic-C^*-to-hexatic-I^* transition occurs at 75.0 °C and the hexatic-to-crystal transition occurs at $\simeq$64 °C.

The first and second terms are the elastic energies for distortions of the bond-angle field, $\theta(\mathbf{r})$, and of the tilt-phase-angle field, $\phi(\mathbf{r})$, respectively. The last term is the sixfold potential which the tilt and bond fields exert on each other. It is revealing to rewrite[2] the Hamiltonian in terms of new variables, $\theta_+=\alpha\theta+\beta\phi$ and $\theta_-=\theta-\phi$, giving

$$H=\tfrac{1}{2}\int d^2r K_+(\nabla\theta_+)^2 + \int d^2r[\tfrac{1}{2}K_-(\nabla\theta_-)^2+h\cos(6\theta_-)]. \qquad (6)$$

The first term gives a hydrodynamic, or acoustic, mode, θ_+, which corresponds to the in-phase fluctuations of bond plus tilt discussed above with the elastic constant $K_+=K_A+K_1$. The second gives a nonhydrodynamic, or optic, mode, θ_-, which corresponds to the out-of-phase fluctuation of bond plus tilt. This mode has an energy at zero wave vector proportional to the coupling constant h and a dispersive contribution proportional to $K_-=K_1K_A/(K_1+K_A)$. We find $K_A \gg K_1$ so that $K_-\sim K_1$. We also find the θ_- mode to be overdamped with an undetectable dispersive part so that $h \gg K_1$. Our results represent the first observation of this novel optic mode in tilted hexatics and provide information on the size and nature of the coupling between tilt and bond angle.

We find that a transition from one tilted hexatic phase to another occurs in five-layer films at $\simeq 2.5$ K below the smectic-C^*-to-hexatic-I^* transition. Viewed by depolarized optical microscopy, the transition is characterized upon cooling by a phase front of changing tilt orientation sweeping across the film. Tilt disclination lines similar to the spiral defect discussed in Ref. 7 also appear in the immediate vicinity of the transition. It is most likely a hexatic-I^*-to-hexatic-F^* transition in which the molecular tilt rotates by $\pm 30°$ to a point between rather than along the bonds. Little is known about the nature of such hexatic to hexatic transitions or what the driving force for their occurrence is. If the transition is only weakly first order then it may be accompanied by a strongly reduced tilt-bond coupling. We have examined this possibility by studying the relaxation rate and susceptibility of the θ_- mode across the transition. As shown in Fig. 4, we do indeed find that the structural phase transition from hexatic-I^* to hexatic-F^* is accompanied by a strong softening of the θ_- mode and a large increase in its susceptibility. In contrast, the θ_+ mode shows only a monotonic temperature dependence. This result shows that a strong reduction in tilt-bond coupling accompanies the hexatic-I^*-to-hexatic-F^* transition and is the first experimental evidence for a microscopic mechanism for this type of transition. Additional theoretical work is needed to elucidate the microscopic nature of the tilt-bond coupling.

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Note added.—Subsequent to the submission of this paper, we learned that Sam Sprunt and David Litster have also observed the optic mode in thick films of a different material.

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