

Freely Suspended Ferroelectric Liquid-Crystal Films: Absolute Measurements of Polarization, Elastic Constants, and Viscosities

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The quenching by an electric field of molecular-orientation fluctuations in freely suspended ferroelectric smectic-C films has been studied by light scattering, allowing absolute measurements of polarization, elastic constants, and viscosities. Evidence is presented to demonstrate surface contributions to Frank elasticity and to show that Frank elasticity is nonlocal.

Smectic liquid crystals form freely suspended films which are quantized in thickness, consisting of some integral number of smectic layers, N . Such films can be made very thin ($N \geq 1$) and therefore present unique opportunities for the investigation of liquid-crystal surface and size effects. We have studied, in a ferroelectric smectic-C film of optically active *p*-decyloxybenzylidene-*p'*-amino-2-methylbutylcinnamate (DOBAMBC), the film-thickness dependence of the phenomenological parameters which characterize $\hat{n}(x,y)$, the two-dimensional director field that describes the local projection of the molecular long axes onto the film (x - y) plane.¹ The results provide the first evidence for several novel elastic effects operative at the liquid-crystal-air interface.

Freely suspended smectic-C films are formed by drawing the DOBAMBC over a rectangular hole (3 mm \times 9 mm) in a glass microscope cover slide. The molecules of a free smectic-C film are tilted with respect to the layer normal (z axis) through an angle $\theta_T(N)$ [Fig. 1(a)] which can be determined via ellipsometry.² Since DOBAMBC is optically active, its smectic-C films are ferroelectric with the permanent polarization per unit film area, \vec{P}_0 , locally normal to the two-dimensional director $\hat{n}(x,y)$.³ A small d.c. electric field, $E_a \sim 4$ V/cm, is applied parallel to the film plane to uniformly align $\hat{n}(x,y)$ such that $\vec{P}_0 \parallel \vec{E}$, minimizing $-\vec{P}_0 \cdot \vec{E}$, and establishing the average

director orientation \hat{n}_0 . The geometry of the sample and experiment is shown in Fig. 1 of Ref. 1.

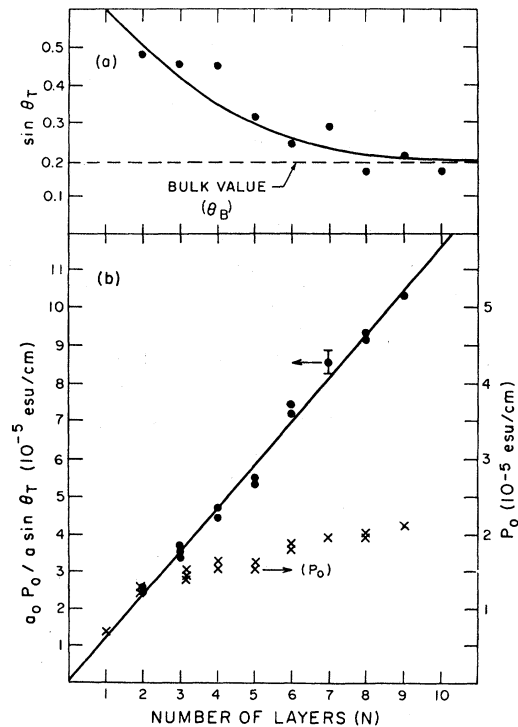


FIG. 1. (a) Tilt angle θ_T vs N [after Ref. 2] at $T = 91.5^\circ\text{C}$. The solid curve is used for scaling purposes throughout this paper. (b) Polarization data vs N at $T = 91.5^\circ\text{C}$. Note the linear dependence of $a_0 P_0 / a \sin \theta_T$, indicating equal contributions from each layer. The slope of the solid line yields $\rho_B / \sin \theta_T = 37 \pm 4$ esu/cm².

We have studied the dependence of the intensity of light, scattered by thermal molecular-orientation fluctuations, on the applied electric field. This intensity is determined by the free energy of distortion of the two-dimensional director field \hat{n} , associated with local reorientation of \hat{n} about z through the azimuthal angle $\varphi(x, y)$.¹ Fourier transformation of $\varphi(x, y)$ and application of equipartition yields the intensity of depolarized light scattered by fluctuations of wave vector \vec{q} :

$$I(\vec{q}) \propto \langle |\varphi \vec{q}|^2 \rangle \propto (K_b q_{\parallel}^2 + K_s q_{\perp}^2 + 2\pi P_0^2 |q_{\parallel}| + P_0 E)^{-1}, \quad (1)$$

where q_{\perp} and q_{\parallel} are the components of \vec{q} which are normal and parallel to \hat{n}_0 , respectively, and K_b and K_s are the two-dimensional Frank elastic constants for the pure bend ($\vec{q} \parallel \hat{n}_0$) and splay ($\vec{q} \perp \hat{n}_0$) distortions of \hat{n} .

We first studied the bend-mode scattered intensity $I_{\parallel} = I(q_{\parallel}, q_{\perp} = 0)$ as a function of q_{\parallel} ($2000 \text{ cm}^{-1} < q_{\parallel} < 6000 \text{ cm}^{-1}$) and E . A large rectangular pulsed electric field of amplitude $E_0 = 300 \text{ V/cm}$ and duration 1.8 ms was added to the small aligning field E_a thereby quenching the fluctuations [see Eq. (1)]. The scattered light intensity was monitored using photon-counting techniques and a multichannel analyzer which signal averaged the time profiles of the scattered intensity for many pulses to give $I_{\parallel}(t)$. Taking I_{off} to be the intensity with $E = E_a$ and I_{on} to be the intensity with $E = E_0 + E_a$, we can extract from $I_{\parallel}(t)$ the quantity $I_{\parallel}(q_{\parallel})$, which from Eq. (1) is simply related to K_b and P_0 :

$$L_{\parallel}(q_{\parallel}) = \frac{E_a}{q_{\parallel}} \left(\frac{I_{\text{on}}}{I_{\text{off}} - I_{\text{on}}} - \frac{E_a}{E_0} \right) = \frac{K_b}{P_0} q_{\parallel} + 2\pi P_0. \quad (2)$$

Note that $L_{\parallel}(q_{\parallel})$ depends only on the ratio $I_{\text{on}}/I_{\text{off}}$ so that the geometric and cross-section factors in I drop out. Measurements of $L(q_{\parallel})$ vs q_{\parallel} therefore yield absolute values for P_0 and K_b . In calculating L_{\parallel} the electric field amplitude E_0 was determined from the applied voltage and an electrostatic model based on the experimental electrode configuration. Measurements of $L_{\parallel}(q_{\parallel})$ agree well with the prediction of Eq. (2), being linear in q_{\parallel} and independent of E_0 to better than 2% for $E_0 < 600 \text{ V/cm}$.

The dynamic response of the scattered intensity to a step voltage change is exponential, with a decay rate $2\Gamma_{\parallel}$ equal to twice that for correlations in thermal orientation fluctuations of the same wave vector. The time profiles may thus

be used to determine the bend-mode viscosity via Eq. (5b) of Ref. 1.

Once P_0 is determined from $L_{\parallel}(q_{\parallel})$, \vec{q} is rotated through 90° and the splay-mode intensity, $I_{\perp}(t)$, and hence $L_{\perp}(q_{\perp})$ are studied. A procedure analogous to that outlined for the bend mode yields K_s and η_s . Measurements were made on DOBAMBC films at $T = 91.5^\circ\text{C}$ for N in the range $2 \leq N \leq 9$.

We first discuss results for $P_0(N)$, shown in Fig. 1(b). If we take the film to be simply a slab of bulk material having a uniform tilt angle $\theta_T(N)$, then the scaled film polarization, $a_0 P_0(N)/[a(N) \times \sin\theta_T(N)]$ should be equal to $(\mathcal{P}_B/\sin\theta_B)Na_0$, where \mathcal{P}_B is the bulk polarization per unit volume, θ_B is the bulk tilt angle.⁴ Here the layer thickness is $a(N) = a_0 \cos\theta_T(N)$ with $a_0 = 33 \text{ \AA}$.⁵ Figure 1(b) shows that the measured scaled film polarization is proportional to N and that it compares well with the previously reported bulk values of $\mathcal{P}_B/\sin\theta_B$ of 36 (Ref. 6) and 33 (Ref. 7) esu/cm².

The measured elastic constants K_s and K_b are shown in Fig. 2. Neglecting surface effects and assuming nematic bulk behavior the two-dimensional parameters K_s , K_b , η_s , and η_b may be related to bulk quantities as $K_{s,b} = h \sin^2\theta_T \mathcal{K}_{s,b}$ and $\eta_{s,b} = h \sin^2\theta_T u_{s,b}$ where the appropriate three-dimensional elastic constants $\mathcal{K}_{s,b}$ are given in Eq. (2) of Ref. 1 and the three-dimensional viscosities $u_{s,b}$ in Eq. (5.80) of de Gennes.⁸ Here h is the film thickness and is equal to $Na(N)$.

The first feature to note in Fig. 2 is that $K_s \sim 10K_b$. \mathcal{K}_{11} (effective bulk splay elastic constant) is obtained from K_s , h , and by using Eq. (2) of Ref. 1. The results for all N show that $\mathcal{K}_{11} \geq 1.5 \times 10^{-5} \text{ erg/cm}$, which is ≥ 30 times typically observed Frank splay elastic constants. We have considered possible additional contributions to K_s and offer the explanation that this phenomenon is due to the preferential orientation and resulting electrostatic interaction of surface molecular dipoles. In the layers adjacent to both surfaces of the film the asymmetric DOBAMBC molecules will align to maximize the distance R of the molecular dipole moment \vec{P}_m from the surface since this orientation minimizes dipole surface energy $U \cong [(\epsilon - 1)/(\epsilon + 2)]P_m^2/R^3$. This preferential orientation produces a surface dipole density $\vec{P}^s(x, y)$ on one surface and $-\vec{P}^s(x, y)$ on the other surface. Director fluctuations will result in a spatial variation of $\hat{n}(x, y)$ and therefore of $\vec{P}^s(x, y)$, creating surface polarization charges of opposite sign on the two surfaces of the film and, for $qh \ll 1$, the additional contribution K_s^P to the elastic constant

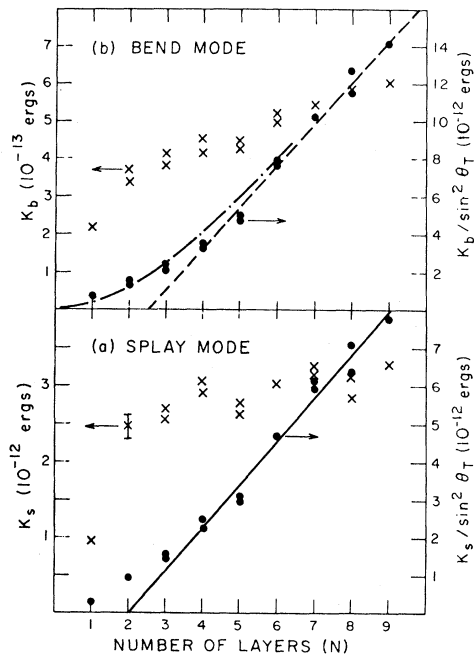


FIG. 2. Elastic constants vs N at $T=91.5^\circ\text{C}$. (a) The dash-dot curve is $K_b/\sin^2\theta_T$ calculated using the simplest theory of nonlocal nematic elasticity (see text) and is asymptotic to the dashed line at large N . The dashed and solid lines emphasize the linear dependence of $K/\sin^2\theta_T$ at large N , and the reduced contribution of the surface layers. The data for $N=1$ were obtained from only one film and scaled using $\sin\theta_T$ from the solid curve of Fig. 1(a).

K_s is

$$K_s^P = 4\pi(\vec{P}^s \cdot \hat{n})^2 h = 4\pi(P^s)^2 h \sin^2\theta_T. \quad (3)$$

Assuming reasonable values for DOBAMBC of $P_m \sim 0.7$ D and $R = 5 \text{ \AA}$ we find $U \sim k_B T$ implying substantial surface ordering and possible partial ordering in the second and third layers. From Eq. (3), for $N=3$, we obtain $K_s^P \sim 1.4 \times 10^{-12}$ erg, which is large enough to account for the observed K_s . Evidence for this effect is shown in Fig. 2(b), where the measured $K_s(N)$ do not exhibit the linear dependence on h expected from Eq. (3) but behave as $K_s/\sin^2\theta_T \propto h - (66 \pm 15) \text{ \AA}$ at large N , indicating that the mean location of P^s is $\sim 33 \text{ \AA}$ (approximately one layer) into the film.

Turning to K_b , we have plotted in Fig. 2(a), $K_b' = K_b/\sin^2\theta_T$ which should scale as h .¹ The data show that for large h , $K_b' = \mathcal{K}_b(h - h_0)$ with $\mathcal{K}_b = 6.5 \times 10^{-6}$ erg/cm and $h_0 = 82 \text{ \AA}$. In the bulk ($h \rightarrow \infty$) limit we thus find a \mathcal{K}_b which is only slightly

greater than that calculated from typical bulk values of \mathcal{K}_{22} and \mathcal{K}_{33} .¹ We note that there are no surface dipole contributions to K_b . To lowest order in φ , fluctuations in \hat{n} produce a $\delta\hat{n}$ (and hence $\delta\vec{P}^s$) perpendicular to \hat{n}_0 . Hence an effective charge distribution ($\nabla \cdot \vec{P}^s$) exists only for modes (K_s) where $\vec{q} \perp \hat{n}_0$. Therefore the dependence of K_b' on h , although qualitatively similar to that of K_s' , must also arise from bulk interactions. We can understand the h dependence of K_b' by introducing nonlocal nematic elasticity to account explicitly for the finite range ξ of intermolecular interactions. This leads naturally to a reduced elasticity contribution of the surface layers.

To show this we generalize the usual nematic Frank free energy $F = \int_V d^3r \frac{1}{2} \mathcal{K} [\nabla\varphi(x, y)]^2$ to the nonlocal form⁹

$$F = \frac{1}{2} An^2 \iint_V d^3r_1 d^3r_2 [\varphi(\vec{r}_1) - \varphi(\vec{r}_2)]^2 G(\vec{r}_1 - \vec{r}_2), \quad (4)$$

where we have taken a director distortion $\delta n(\vec{r})$ characterizable by the rotation angle $\varphi(\vec{r})$. For the periodic distortion $\varphi(\vec{r}) = \varphi_{\vec{q}} \cos \vec{q} \cdot \vec{r}$ we find an effective q -dependent Frank elastic constant $\mathcal{K}(q)$ given by

$$\mathcal{K}(q) = (2An^2/q^2)[G(0) - G(q)], \quad (5)$$

$$G(q) = \int d^3r e^{i\vec{q} \cdot \vec{r}} G(\vec{r}),$$

for which, if we assume for simplicity spherical symmetry for $G(r)$, we get

$$\lim_{q \rightarrow 0} \mathcal{K}(q) = \mathcal{K} = \frac{4}{3} \pi An^2 \int_0^\infty G(r) r^4 dr.$$

For a nematic, molecular interactions are strictly short ranged, implying that $\mathcal{K}(q)$ has a Taylor series expansion around $q=0$, i.e., $\mathcal{K}(q) \approx \mathcal{K}(1 - (q\xi)^2)$ and implying via Eq. (5) the form $G(r) = (\mathcal{K}/8\pi An^2 \xi^4 r) e^{-r/\xi}$. The resulting effective two-dimensional elastic constant for a film of thickness h is

$$K' = \mathcal{K} \xi \left[x - \frac{3}{2}(1 - e^{-x}) + \frac{1}{2} x e^{-x} \right] \quad (x = h/\xi)$$

$$\approx \mathcal{K} (h - \frac{3}{2}\xi) \quad \text{for } h \gg \xi. \quad (6)$$

Equation (6), plotted as the dash-dotted curve of Fig. 2(a) for $\xi = 55 \text{ \AA}$, reproduces the observed behavior of K_b' .

The viscosities are shown in Fig. 3. The effective bulk viscosities obtained are $\approx 2 \times 10^{-2}$ g/cm sec, which is reasonable. The scaled viscosities show that the surface layers contribute less to the two-dimensional viscosities, a result to be expected given the similar behavior of the bend elasticity. The two-dimensional-orientational

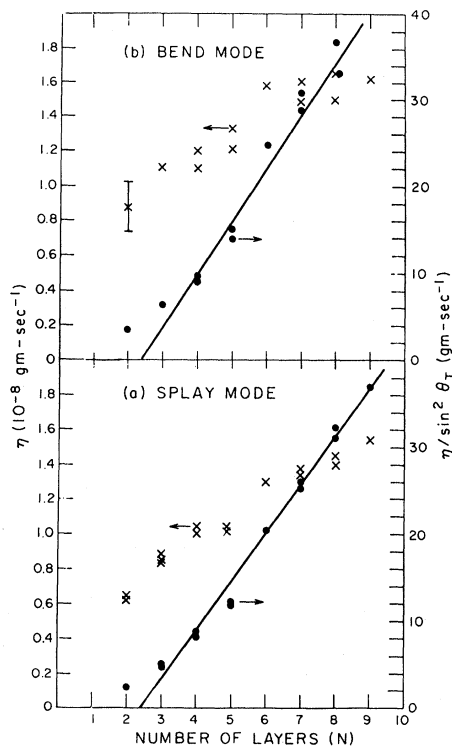


FIG. 3. Viscosity vs N at $T=91.5^\circ\text{C}$: The solid lines indicate the asymptotic linear dependence on η on h at large N , and the reduced contributions of the surface layers.

diffusion coefficients are $D_b = K_b/\eta_b \cong 4 \times 10^{-5}$ cm^2/sec for the bend mode and $D_s \cong 2 \times 10^{-4}$ cm^2/sec for the splay mode. The bend-mode value is quite typical where as D_s is more than an order of magnitude larger than the usual bulk value, a result of the surface-enhanced K_s .

Finally, it might be argued that the reduced surface-layer contributions to K_s , K_b , η_s , and η_b are a result of less dense surface layers. Our optical reflectivity and ellipsometry² measurements, however, show that the average layer

area per molecule, when corrected for tilt, is independent of N for $2 \leq N \leq 9$. Hence the surface layers to be less dense must be spread out along z . However, surface tension strongly promotes the smectic ordering of the surface layers as evidenced by the dramatic elevation of the nematic-smectic-A phase-transition temperature in freely suspended films. We thus expect the surface layers to have nearly the bulk density.

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⁴ ϕ_B is proportional to the first moment of $f(\psi, \theta_T)$ the distribution of molecular orientation ψ about their long axes. Expansion of $f(\psi)$ in spherical harmonics shows $\phi_B = \langle P_1(\psi) f(\psi, \theta_T) \rangle \propto \sin \theta_T$.

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⁹Here A is an intermolecular interaction energy and n is the number density.