Macroscopic Orientation Patterns in Smectic-*C* Films

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An experimental study of electrostatically stabilized disclination walls is reported in the two-dimensional director field of freely suspended ferroelectric smectic-*C* films. This Letter presents measurements of the dependence of the wall width on applied field and the collapse rate of walls forming closed circular loops. These are the first measurements of macroscopic orientation patterns in a physical *XY* system.

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Smectic liquid crystals can form freely suspended films as thin as two molecular layers.[1,2] In a smectic-*C* film the molecules have an average tilt angle, θ_T, from the layer normal and the in-plane direction of molecular orientation is characterized by the angle $\varphi(x,y)$, or equivalently by a two-dimensional (2D) unit vector $\hat{n}(x,y)$ as indicated in Fig. 1. The theoretical model relevant to the space-time behavior of $\hat{n}(x,y)$ is the continuous *XY* model.[3] Smectic-*C* films offer unique opportunities for the study of *XY* systems in that direct microscopic observation permits the mapping of the spatial variation of $\hat{n}(x,y)$ over the entire film surface at any particular time. In this Letter we report the first such studies.

The experimental arrangement is shown in Fig. 1(a). Films are drawn over a 6 mm×6 mm hole in a 0.15-mm-thick glass slide and polarized reflection microscopy is used to measure the spatial variation of $\hat{n}(x,y)$. The film is illuminated with nearly normally incident polarized light from an argon-ion laser ($\lambda_0 = 5145$ Å) and the reflected light is imaged through an analyzer. Because the liquid-crystal molecules are optically anisotropic, the reflection coefficient for incident light polarized parallel to $\hat{n}(x,y)$ will be different (larger) from that for the perpendicular polarization and the reflected-light polarization vector will be rotated toward $\hat{n}(x,y)$. In the limit that the film thickness $h \ll \lambda_0$, the reflected light intensity, $I(\varphi)$, after the crossed (ideal) analyzer is given by

$$I(\varphi)/I_0 \equiv R(\varphi) \cong [2\pi(h/\lambda_0)(n_\parallel^2 - n_\perp^2)\sin(2\varphi)]^2, \quad (1)$$

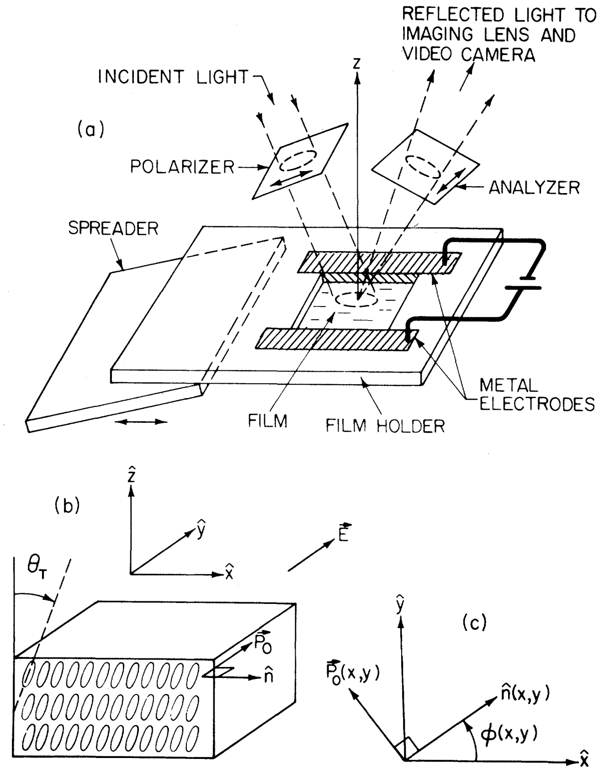

FIG. 1. Freely suspended smectic-film geometry. (a) Schematic of film holder and optical arrangement. (b) Structure of a three-layer smectic-*C* film. The molecules are tilted in the $\hat{x}\hat{z}$ plane through an angle θ_T. Shown are the directions for the in-plane molecular orientation, $\hat{n}$, and the polarization, $\vec{P}_0$, in an applied electric field, $\vec{E} = E\hat{y}$. (c) Angular displacement, $\varphi(x,y)$, of $\hat{n}(x,y)$ and $\vec{P}_0(x,y)$ in the $\hat{x}\hat{y}$ plane from their field aligned direction ($\varphi = 0$).

where $n_{\parallel}$ and $n_{\perp}$ are refractive indices parallel and perpendicular to $\hat{n}$ and where the incident light, I_0, is polarized along the x direction. $R(\varphi)$ exhibits four equal intensity maxima for a φ rotation of 360° permitting the determination of φ modulo 90°. This fourfold degeneracy may be removed in two steps. First, by slightly uncrossing the analyzer alternate maxima (say $\varphi = 45°$, $225°$) are equally increased in intensity and the ones in between ($\varphi = 135°, 315°$) are equally decreased. Next, the film may be tilted about the y axis rendering the maxima at $\varphi = 45°$ and $\varphi = 225°$ nonequivalent. Hence optical reflectivity is sufficient to uniquely characterize the x, y behavior of φ.

Because light levels were low ($R_{\max} \sim 10^{-5}$), dynamic recording required that the film be imaged onto the face of a TIVICON video camera. Also, to minimize stray light, the optical system was comprised of a binocular microscope having *separate* illumination and collection optical paths. Experiments were carried out at a fixed temperature $T = 54$ °C on smectic-C films made from the optically active compound n-(4-n-octyloxybenzylidene)-4-(2-methylbutyl) aniline (8O.5*). N (the number of molecular layers) was varied from 2 to 5.

In the absence of an applied field the molecular orientation varies nearly continuously over the film surface in "swirl patterns". These patterns are interrupted by a small number ($\sim 5/\mathrm{cm}^2$) of stable point defects. The typical appearance of a point defect is shown in Fig. 2(a). These are identified as $+2\pi$ point disclinations in which $\hat{n}$ points radially out from the defect core.

An electric field, $\vec{E} = E\hat{y}$, may be applied in the film plane with use of deposited electrodes. Since 8O.5* is optically active its smectic-C films are ferroelectric.[4] They possess a permanent electric dipole density $\vec{P}_0$ in the film plane locally normal to $\hat{n}$ (Fig. 1). An applied electric field will orient $\hat{n}$ such that $\vec{P}_0$ and $\vec{E}$ are parallel ($\varphi = 0$) minimizing the electrostatic energy $U_E = -\vec{P}_0 \cdot \vec{E}$. The orientation induced by the sudden application of an electric field occurs by two processes. First, the major portion of the film area will reorient to minimize U_E trapping and "squeezing" disoriented regions into distinct 2π line disclination walls. Any 2π point defect on the film will necessarily be the point of termination of one of these 2π line disclinations. The formation of a 2π line disclination wall in the vicinity of a 2π point defect as E is increased is shown in Figs. 2(a)–2(d). For the largest E [Fig. 2(d)] the molecular orientation φ is nearly uniform except at the disclination wall where it undergoes a continuous 2π rotation as the wall is crossed (along the line $\overline{ab}$). 2π walls are found to terminate both at 2π point defects and at the film edge or may form closed loops as shown in Fig. 2(e). The disclination walls are free to move via molecular rotation, and will do so to minimize their length and, thereby, excess energy. Consequently, the second step in the orientation of a film is the disappearance of the disclination walls either by being "sucked" off at the edge or by the collapse of closed loops as shown in Figs. 2(e)–2(g).

We have measured the width and collapse rate

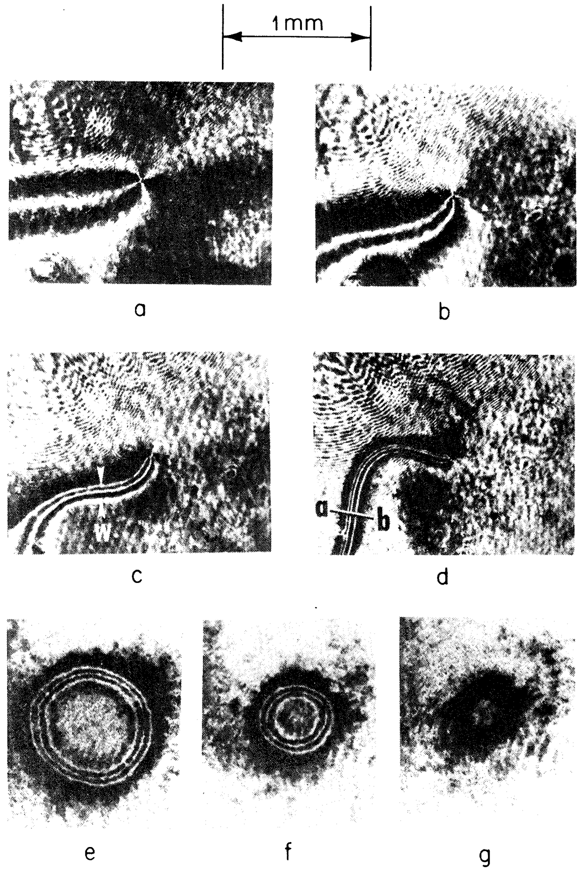

FIG. 2. Video records of disclination walls in a 75 Å thick ($N = 3$) freely suspended film of 8O.5* obtained by polarized reflection microscopy. The fine grained fringes are due to the coherent nature of the incident light, not the director variation. These images are *negatives*, with the bright bands corresponding to reflected intensity minima. (a)–(d) A 2π disclination wall terminating at a 2π point disclination as the applied electric field is increased. (e)–(g) The collapse and disappearance of a disclination wall forming a closed circular loop.

of these disclination walls. Fig. 3(a) shows the variation with applied electric field, $\vec{E}$, of the wall width, w, characterized by the distance between the two outermost reflected intensity minima [Fig. 3(c)]. We find that $w \propto E^{-1/2}$. This static dependence of w on E can be calculated via a minimization of the net free energy of distortion of $\hat{n}$ given in Eq. (1) of Ref. 2. This free energy contains both bend and splay elastic terms characterized by the 2D Frank constants K_b and K_s, an electrostatic term arising from polarization space charge accompanying the bend mode, and the polarization term $-\vec{P}_0 \cdot \vec{E}$. With use of the one constant approximation,[5] $K_s = K_b = K$, and neglecting (to be justified later) the space-charge term, the free energy, F, for a linear wall parallel to the $\hat{y}$ axis simplifies to $F = \int dx[-P_0E\cos\varphi + \frac{1}{2}K(\partial\varphi/\partial x)^2]$. Taking $\varphi = 0$ for $|x|$ large, the transcendental equation

$$\tan\tfrac{1}{4}\varphi = \pm\exp(-|x|/\xi) \qquad (2)$$

is obtained for the wall structure $\varphi(x)$, where the length $\xi = (K/P_0E)^{1/2}$. This equation gives $\varphi = \pm\pi/2$ at $|x| = 0.881\xi$ so that the wall width is $w = 1.76\xi = 1.76\,(K/P_0E)^{1/2} \propto E^{1/2}$. This result is thus in accord with our data and allows us to calculate K/P_0 from the slope of the w vs $E^{-1/2}$ curve. The result is $K/P_0 = 2.0 \times 10^{-7}$ statvolt·cm independent of film thickness within experimental error (±15%) for $N = 2$–5. This value of K/P_0 is consistent with our light-scattering results on 8O.5*[2] and with absolute measurements of K_s, K_b, and P_0 in DOBAMBC.[6]

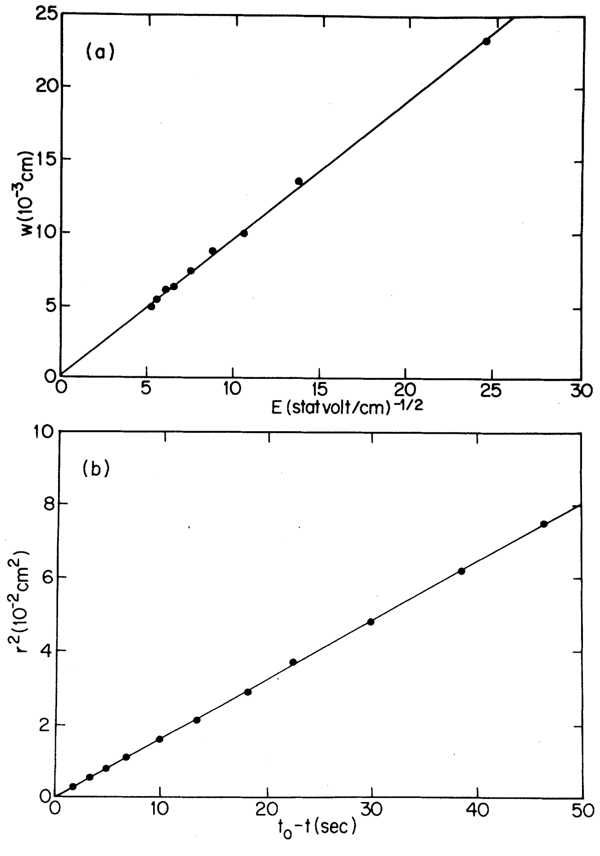

FIG. 3. (a) Typical dependence of wall width, w, on applied electric field, E. (b) Typical time dependence of the radius, r, of a circular closed-loop disclination wall. Both measurements were taken on a two-layer film.

To understand the neglected space-charge term consider the energy of a periodic variation of φ of wave vector q. From Eq. (1) of Ref. 2 the free energy is proportional to $Kq^2 + 2\pi P_0^2|q| + P_0E$. The Frank and space-charge terms are equal at an inverse wave vector $\xi_c = K/2\pi P_0^2$. For large fields such that $\xi < \xi_c$, the Frank term dominates and $w \sim q^{-1} \propto (K/P_0E)^{1/2}$ as obtained above. For small fields, $\xi > \xi_c$ and we expect $w \sim q^{-1} \propto 2\pi P_0/E$. In our light-scattering experiment[2] on 8O.5* we clearly observed the effects of polarization space charge and found $\xi_c \simeq 10^{-3}$ cm. Since this value for ξ_c is smaller than our measured wall widths we should be in the space-charge-dominated regime even though the observed dependence of w on E indicates the *absence of a space-charge contribution.* We propose that the reason for this is the screening of polarization space charge by ionic impurities. The relaxation time for a 2D periodic ionic impurity fluctuation of wave vector q is $\tau(q) = (2\pi\sigma hq)^{-1}$, where σ is the bulk ionic conductivity. For a typical σ (10^{12} Ω cm), $\tau(q = 2\pi/w) \sim 0.1$ sec. This relaxation time is large compared to the orientation fluctuation times involved in the light scattering experiments but small compared to the time of formation and observation of the disclination walls. We have direct qualitative evidence for the accumulation of ionic impurities at walls in films of DOBAMBC. If, after a wall has been formed, the applied field is reversed, the wall will split and move to another part of the film. However, along its original path a "kink" in the molecular orientation will remain because of the electric field from the accumulated ionic charge. After a few minutes conduction will dissipate the ionic charge and all trace of the wall will disappear. In 8O.5* the same process occurs but on a faster time scale (larger σ).

Finally, we consider the collapse rate of disclination walls forming closed circular loops. Figure 3(b) shows the time dependence of the radius of a collapsing loop, $r(t)$. $r(t)$ is found to vary as $r \propto (t_0 - t)^{1/2}$ where t_0 is the time at which the loop disappears. The disclination wall will carry some excess energy per unit length which, by integration over the $\varphi(X)$ resulting from Eq. (2), is given by $U_W = 8K/\xi \propto E^{1/2}$. U_W has dimensions of force and may be viewed as an effective line tension acting on the wall locally tangent to it. The effective normal force per unit length, f, will be $f = U_W/r$ where r is the local radius of curvature. The disclination wall will move under this force which in steady state will be balanced by a viscous force per unit length, $f_V = -\beta\dot{r}$, arising because motion of the wall past a point on the film is accompanied by dissipative molecular rotation. Equating the two forces gives the equation $\dot{r}(t) = -(U_W/\beta)/r(t)$ for the local motion of a wall. This yields $r^2(t) = (2U_W/\beta)(t_0 - t)$ for a circular loop which is what we observe. Detailed calculation shows that $\beta = 8\eta/\xi$ where η is a 2D orientational viscosity. Hence the collapse rate constant $U_W/\beta = K/\eta$ *independent* of E. Our experimental results for K/η, obtained from the slope of the r^2 vs $(t_0 - t)$ curves, are $K/\eta = 9.2$ ($N = 2$), 7.3 ($N = 3$), 6.2 ($N = 4$), and 5.0 ($N = 5$); all are ± 1.0 in units of 10^{-5} cm^2/sec. These lie between K_b/η_b and K_s/η_s previously obtained from light scattering[2] and are independent of E as expected.

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[1] G. Friedel, Ann. Phys. (Paris) 18, 273 (1922).

[2] C. Y. Young, R. Pindak, N. A. Clark, and R. B. Meyer, Phys. Rev. Lett. 40, 773 (1978).

[3] J. M. Kosterlitz and D. J. Thouless, J. Phys. C 6, 1181 (1973); R. A. Pelcovits and B. I. Halperin, Phys. Rev. B 19, 4614 (1979); D. R. Nelson and B. I. Halperin, Phys. Rev. B (to be published).

[4] R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, J. Phys. 36, L69 (1975).

[5] Since between $\varphi = \pm\pi/2$ the wall contains equal amounts of bend and splay distortion, it is the average elastic constant $K = \frac{1}{2}(K_b + K_s)$ that determines w. Any difference between K_s and K_b is a negligibly small correction.

[6] C. Rosenblatt, R. Pindak, N. A. Clark, and R. B. Meyer, Phys. Rev. Lett. 1220 (1979). DOBAMBC refers to p-decyloxybenzylidene p'-amino 2-methylbutyl cinnamate.

Crystal Structure and Pair Potentials: A Molecular-Dynamics Study

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With use of a Lagrangian which allows for the variation of the shape and size of the periodically repeating molecular-dynamics cell, it is shown that different pair potentials lead to different crystal structures.

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Recent molecular-dynamics (MD) calculations[1] on homogeneous nucleation of a crystal out of a supercooled liquid phase have shown that the structure of the nucleated phase does depend on the pair potential. These calculations are time consuming because of the long-lived, glassy, metastable states which the system has to inhabit before nucleating. Here we present a very direct and relatively short calculation which relates the crystal structure to the pair potential in a simple manner.

Andersen[2] has shown how MD calculations can be modified to study systems under constant pressure by introducing the volume of the system as an additional dynamical variable. In this paper we show how a generalization of this idea leads to a powerful method for the study of crystal structures and their relation to pair potentials. We have performed MD calculations with a time-dependent metric tensor which allows the volume *and* the shape of the MD cell to vary with time.

Let the edges of the MD cell be $\vec{a}$, $\vec{b}$, and $\vec{c}$ (in a space-fixed coordinate system), and let them be time dependent. Periodically repeating MD cells will obviously fill up all space. Let $\underline{h}$ be the matrix formed by $\{\vec{a}, \vec{b}, \vec{c}\}$; $\Omega = \det\underline{h} \equiv a \cdot b \times c$

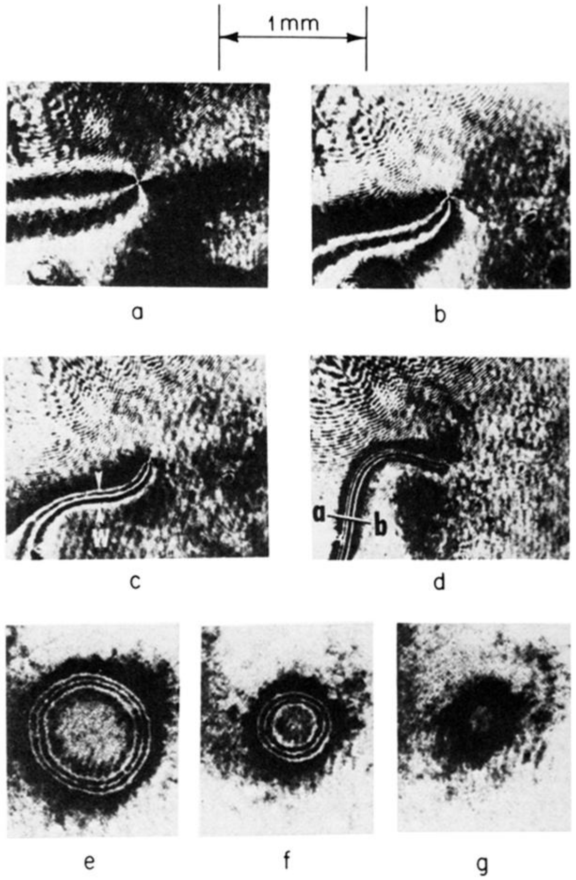

FIG. 2. Video records of disclination walls in a 75 Å thick ($N = 3$) freely suspended film of 80.5* obtained by polarized reflection microscopy. The fine grained fringes are due to the coherent nature of the incident light, not the director variation. These images are *negatives*, with the bright bands corresponding to reflected intensity minima. (a) – (d) A 2π disclination wall terminating at a 2π point disclination as the applied electric field is increased. (e) – (g) The collapse and disappearance of a disclination wall forming a closed circular loop.