

Simultaneous Observation of Electric Field Coupling to Longitudinal and Transverse Ferroelectricity in a Chiral Liquid Crystal

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We report novel odd-even layering effects in freely suspended films of the chiral liquid crystal MHPOBC in its antiferroelectric smectic phase. Films with an odd number of smectic layers are characterized by transverse ferroelectricity (molecular tilt plane perpendicular to applied electric field \mathbf{E}), while films with an even number of layers exhibit longitudinal ferroelectricity (molecular tilt plane parallel to \mathbf{E}). This is the first observation of the simultaneous electric field manipulation of longitudinal and transverse ferroelectric polarization in liquid crystals. [S0031-9007(96)01148-9]

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Macroscopic polarization along the average molecular long axis [longitudinal polarization (LP)] is generally not observed in liquid crystals, a consequence of disorder with respect to end-for-end molecular flips and the consequent averaging effects. The possibility of obtaining spontaneous breaking of this symmetry and thereby manifestation of LP has been discussed theoretically for some time [1–4], but so far the only unambiguous observations of LP have been at surfaces, where the symmetry is broken by the interface [5,6]. To date there has been only a single instance of electric field manipulation of LP, at the free surface of an isotropic liquid crystal droplet covered with a few surface antiferroelectric layers [6].

The antiferroelectric SmC_A^* liquid crystal phase was identified in 1989 by Chandani *et al.* [7] in the chiral material MHPOBC [4-(1-methylheptyloxycarbonyl)phenyl 4'-octyloxybiphenyl-4-carboxylate], its distinguishing characteristic being tristable switching and a double P - E hysteresis loop. Further experiments using conoscopy [8] indicated that SmC_A^* is a tilted smectic phase, in which the local mean molecular long axis, given by the director \mathbf{n} , is tilted through an equilibrium angle ψ_0 relative to the smectic layer normal, and the tilt arrangement is anticlinic (i.e., adjacent layers are tilted in opposite directions). In 1990 Galerne and Liebert [6] made detailed observations of the thin smectic film floating on the free surface of an isotropic droplet of the liquid crystal material MHTAC [9] on a glass slide, and concluded that experimental parity effects of the number of smectic layers provided strong evidence for a layer-by-layer alternating tilt structure in this material. Subsequently, it was confirmed that their SmO and the SmC_A^* are, in fact, the same phase. Bahr *et al.* [10] found in 1993 that the transition from the SmC^* phase to the SmC_A^* phase in two and three layer films of MHPOBC takes place by inverting the tilt and polarization direction in a single smectic layer. This provided direct evidence that tilt and polarization alternate in a layer-by-layer fashion in the SmC_A^* phase. Combined, these experiments have led to the acceptance of an anticlinic structure for SmC_A^* in which the director

tilt direction and hence the sign of the transverse polarization alternate from one layer to the next, each individual layer being SmC^* like.

We report parity effects in freely suspended films of MHPOBC and demonstrate conclusively that while SmC_A^* films with an odd number of layers (N odd) indeed possess transverse ferroelectricity, films with an even number of layers (N even) exhibit *longitudinal* ferroelectricity.

Smectic liquid crystals can be drawn into freely suspended films of locally well-defined layer number N for $N = 1, 2, 3, \dots$, making them extremely well suited for the investigation of interface and finite size effects in liquid crystals [11]. In our experiments, freely suspended (S)-MHPOBC films from 2 to 15 layers thick were drawn over a 3 mm \times 10 mm hole in a glass cover slip. In the field experiments we used a bipolar square wave voltage to apply fields ranging from 4 to 25 V/mm in the sample plane, at frequencies between a few and several hundred Hz. These applied fields are much smaller than the ~ 1.5 kV/mm field required to induce a SmC_A^* to SmC^* transition at these temperatures in the SmC_A^* phase [12]. The layer number N was determined using laser reflectivity [13]. Bulk MHPOBC has the following phase diagram on heating: Cryst \rightarrow (84 $^\circ\text{C}$) \rightarrow SmC_A^* \rightarrow (118.4 $^\circ\text{C}$) \rightarrow SmC_γ^* \rightarrow (119.2 $^\circ\text{C}$) \rightarrow SmC^* \rightarrow (120.9 $^\circ\text{C}$) \rightarrow SmC_α^* \rightarrow (122 $^\circ\text{C}$) \rightarrow SmA^* \rightarrow (148 $^\circ\text{C}$) \rightarrow Iso [7]. Films could be formed in the SmA^* , SmC^* , and SmC_A^* phases.

We define the “tilt plane” to contain \mathbf{n} and the layer/film normal, and a 2D “ \mathbf{c} -director” unit vector field \mathbf{c} as locally parallel to the intersection of the tilt plane and the layers. The \mathbf{c} -director can be visualized using depolarized reflected light microscopy (DRLM) [14] as follows: When linearly polarized light is normally incident on a uniformly oriented, optically thin film with an in-plane anisotropy of the refractive index, the polarization of the reflected light is, in general, rotated slightly toward the optic axis of higher refractive index. In thin films where the spontaneous helixing of the \mathbf{c} -director can be neglected, the reflected intensity

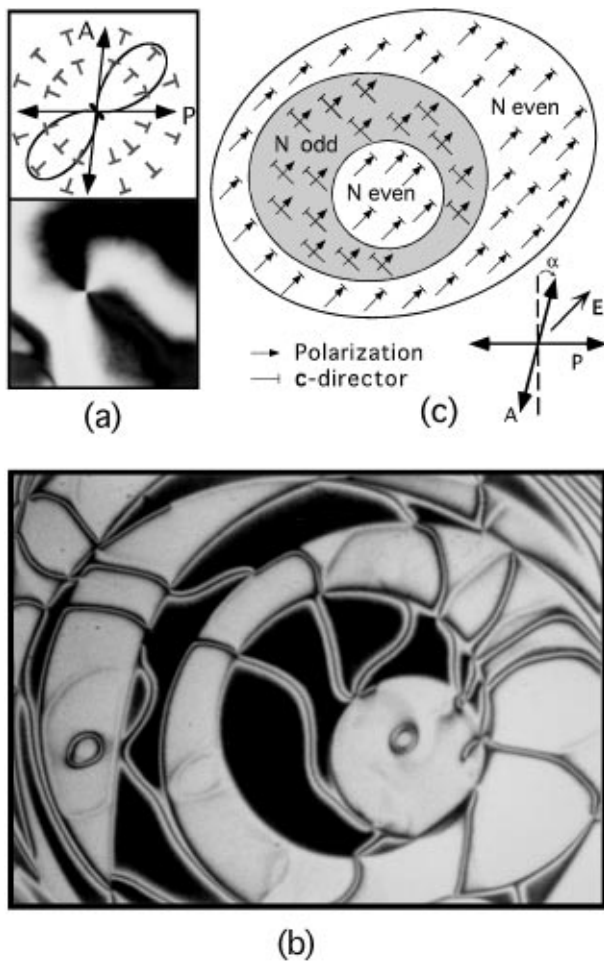


FIG. 1. Field-induced director orientation in an inhomogeneous antiferroelectric film. (a) The small sketch and photograph of a point defect demonstrate how orthogonal orientations of the \mathbf{c} -director can be distinguished using depolarized reflected light microscopy. (b) A typical inhomogeneous film of antiferroelectric MHPOBC in an applied electric field of 10 V/mm viewed between decrossed polarizers. The horizontal dimension is about 700 μm . (c) Regions with an odd number of layers have a transverse spontaneous polarization so that the \mathbf{c} -director is aligned perpendicular to the applied field, while regions with an even number of layers possess a spontaneous longitudinal polarization so that the \mathbf{c} -director is aligned parallel to the field.

with polarizer and analyzer decreased by an angle α is twofold symmetric in the azimuth φ , with maxima at $(\pi/4 - \alpha/2)$ and $(5\pi/4 - \alpha/2)$. Figure 1(a) shows this intensity distribution around a point defect, where the \mathbf{c} -director orientation is in the range $0^\circ < \varphi < 360^\circ$.

The photograph in Fig. 1(b) shows the typical texture of a freshly drawn SmC_A^* film that has regions of different thickness, photographed in an electric field $\mathbf{E} \cong 10 \text{ V/mm}$. The polarizer, analyzer, and \mathbf{E} -field directions, as well as the \mathbf{c} -director, are indicated in Fig. 1(c). The approximately concentric rings are “layer steps,” and the radial double stripes seen in both dark and light regions are “ 2π walls.” These are structures often observed in ferroelectric films in which the \mathbf{E} -field

stabilized \mathbf{c} -director orientation φ changes by 2π [14]. In an alternating applied field this entire pattern is dynamic, with the areas between the 2π walls reorienting by π upon field reversal [15]. Regions with N even are bright, implying that the \mathbf{c} -director is aligned *parallel* to \mathbf{E} , while regions with N odd are dark, implying that the \mathbf{c} -director is *perpendicular* to \mathbf{E} . Figure 1(c) shows the polarization and \mathbf{c} -director orientations in the even and odd layer regions. We conclude from this observation that *while the net spontaneous polarization in films with N odd is transverse* (normal to \mathbf{c} and the tilt plane), *the polarization in N even films is longitudinal* (parallel to \mathbf{c} and the tilt plane). The applied field simultaneously orients both longitudinal and transverse spontaneous polarization in the film of Fig. 1(b).

Interpretation of these results can be made with the aid of Fig. 2. Here we indicate a few layers in the bulk of a SmC_A^* phase, and the layer structure of even (four layer) and odd (three layer) films. Both the longitudinal and transverse polarization densities, $\mathbf{P}_L(z)$ and $\mathbf{P}_T(z)$, of a bulk SmC_A^* monodomain with layer normal along z can be characterized in terms of the spatial densities of their components, $P_{Lx}(z)$ and $P_{Ty}(z)$, respectively, obtained by averaging the responsible molecular dipoles over molecular orientational and translational fluctuations and over end-for-end flips. For example, possible spatial variations of $P_{Lx}(z)$ and $P_{Ty}(z)$ which reflect the necessary symmetries of these distributions in the bulk are shown in Fig. 2(a): in the bulk SmC_A^* phase, $\mathbf{P}_T(z)$ [$\mathbf{P}_L(z)$] must be symmetric [antisymmetric] about the layer center (a consequence of the C_{2y} symmetry about the layer midplanes) and antisymmetric [symmetric] about the interlayer interfaces (a consequence of the sign change of the director tilt in adjacent layers). The integrated polarization density is zero for all components in the bulk. In the three and four layer films, both $P_{Lx}(z)$ and $P_{Ty}(z)$ are modified near the surfaces, leading to a crucial modification of the symmetries of the polarization densities. Notice that in the three layer film $\langle P_{Lx} \rangle \equiv \int dz P_{Lx}(z) = 0$ even with these modifications but that $\langle P_{Ty} \rangle \equiv \int dz P_{Ty}(z) \neq 0$, in general. For the four layer film, $\langle P_{Ty} \rangle = 0$ even with the surface modifications, but $\langle P_{Lx} \rangle \neq 0$ because of the surface modifications. Thus the nonzero $\langle P_{Lx} \rangle$ and $\langle P_{Ty} \rangle$ observed, respectively, in even and odd layer number films are required by their symmetries. In the limit that the surface modification of $P_{Lx}(z)$ and $P_{Ty}(z)$ is small, we have $\langle P_{Ty} \rangle \cong P_1$, the polarization of a single layer, and $\langle P_{Ty} \rangle$ in an N layer odd film is $\langle P_{Ty} \rangle \cong P_1/N$; and $\langle P_{Lx} \rangle \ll \langle P_{Ty} \rangle$.

Inhomogeneous films such as the one shown in Fig. 1(b) have a tendency to evolve into films containing large regions with only odd numbers of layers or only even numbers of layers. Boundaries where the difference in layer number, ΔN , is even appear to be energetically favored over boundaries where ΔN is odd, so that in time a film that originally has mostly layer steps with

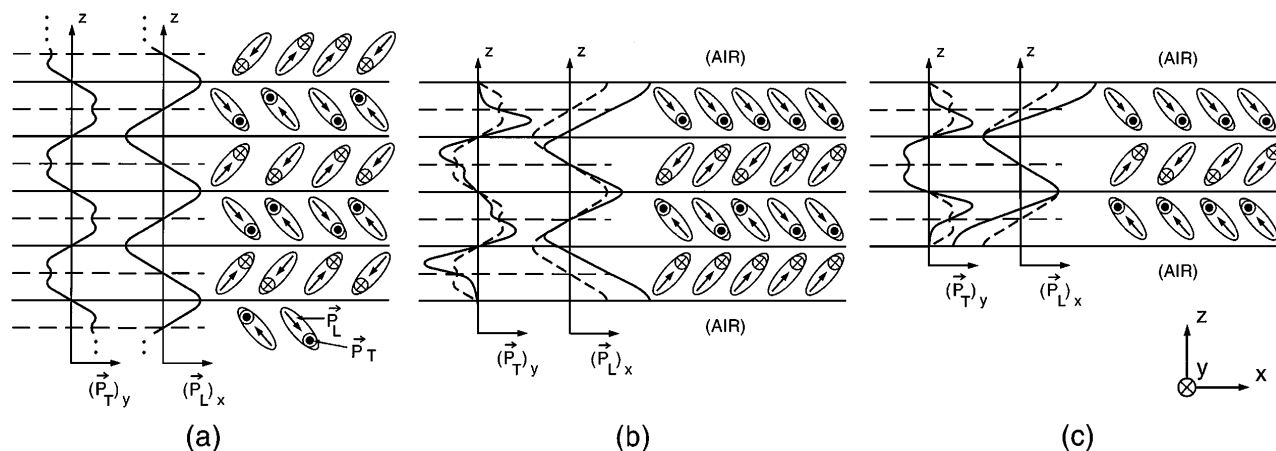


FIG. 2. A depiction of the longitudinal and transverse polarization densities as required by the symmetry of the SmC_A^* phase. In the bulk, (a), the phase is antiferroelectric and the net spontaneous polarization is zero. In freely suspended films, the symmetry breaking at the liquid crystal-air interface results in ferroelectric ordering. In (b) and (c) the solid line shows the polarization densities of the film. The bulk polarization density (dashed line) is shown for comparison. For films with an even layer number, (b), the increase in the transverse polarization density at one surface is canceled by a corresponding decrease at the other surface, while the changes in the longitudinal polarization density add constructively, resulting in a net spontaneous longitudinal polarization $\langle P_{Lx} \rangle$. For films with an odd layer number, (c), the situation is reversed and the net polarization $\langle P_{Ty} \rangle$ is transverse to the tilt plane.

$\Delta N = 1$ will be dominated by $\Delta N = 2$ boundaries. This is illustrated in the several hours old SmC_A^* film shown in Fig. 3. The (dark) upper left part of the image shows regions with N equal to 4, 6, and 8, while the (bright) lower right part shows regions with N equal to 11 and 13. The SmC^* to SmC_A^* phase transition temperature upon cooling decreases with decreasing N : in this film first the 13 layer region becomes antiferroelectric, followed by the 11, 8, 6, and 4 layer regions as T decreases. This is contrary to Bahr's observations of mixtures of (R)- and (S)-MHPOBC with enantiomeric excess $ee = 0.8$, which show the usual elevation of phase transition temperatures with decreasing film thickness [11]. A similar decrease of the SmC^* to SmC_A^* transition temperature with thickness has also been found by Demikhov in films of a

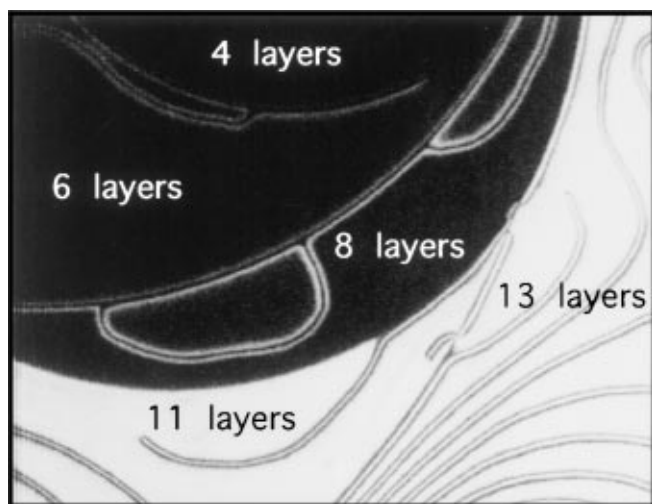


FIG. 3. Segregation of a freely suspended film of MHPOBC into regions of odd and even layer numbers, indicating that the preferred layer number step is a multiple of 2.

different liquid crystal at $ee = 1$ [16].

In achiral and low-polarization SmC films, thermal orientation fluctuations in \mathbf{c} are easily observed using DRLM [17]. In both N odd and N even regions in the SmC^* phase of MHPOBC, visual observation shows that the director fluctuations are unusually small. When cooled into the SmC_A^* phase, though, there is a significant visible increase in the director fluctuations, although predominantly in the N even regions. To explain the increase in director fluctuations that occurs in regions with N even after the phase transition from SmC^* to SmC_A^* , it is necessary to consider the dependence of the director fluctuations not only on the elastic bend and splay constants, but also on the net spontaneous polarization. As was first proposed by Meyer *et al.* [18] and Young *et al.* [11], and observed by Rosenblatt *et al.* [19] and Lu *et al.* [20], spatial inhomogeneity of the spontaneous polarization, \mathbf{P} , gives rise to a space charge and the ensuing electrostatic energy contributes to a higher effective splay elastic constant K_s^{eff} given by $K_s^{\text{eff}} = K_s^0 + 2\pi P^2/q_x$. Here q_x is the x component of the wave vector describing bend fluctuations in the \mathbf{c} -director and K_s^0 is the bare elastic constant of the racemate. Lu *et al.* found that the elastic constant is, in fact, completely dominated by this polarization contribution and K_s^{eff} is much larger than K_s^0 . From this perspective, one may speculate that a large \mathbf{P} in all SmC^* films of MHPOBC results in a suppression of fluctuations. This can be taken as qualitative evidence that $\langle P_{Lx} \rangle_{\text{SmC}_A^*} \ll \langle P_{Ty} \rangle_{\text{SmC}_A^*} < \langle P_{Ty} \rangle_{\text{SmC}^*}$, indicating that the surface polar ordering is weak. Figure 4 provides further evidence for polarization charge screening effects in the N odd regions of an inhomogeneous film (a) with \mathbf{E} applied and (b) several seconds after the field is removed. When the \mathbf{E} field is applied, the 2π wall shrinks down to two narrow lines in both the N even and

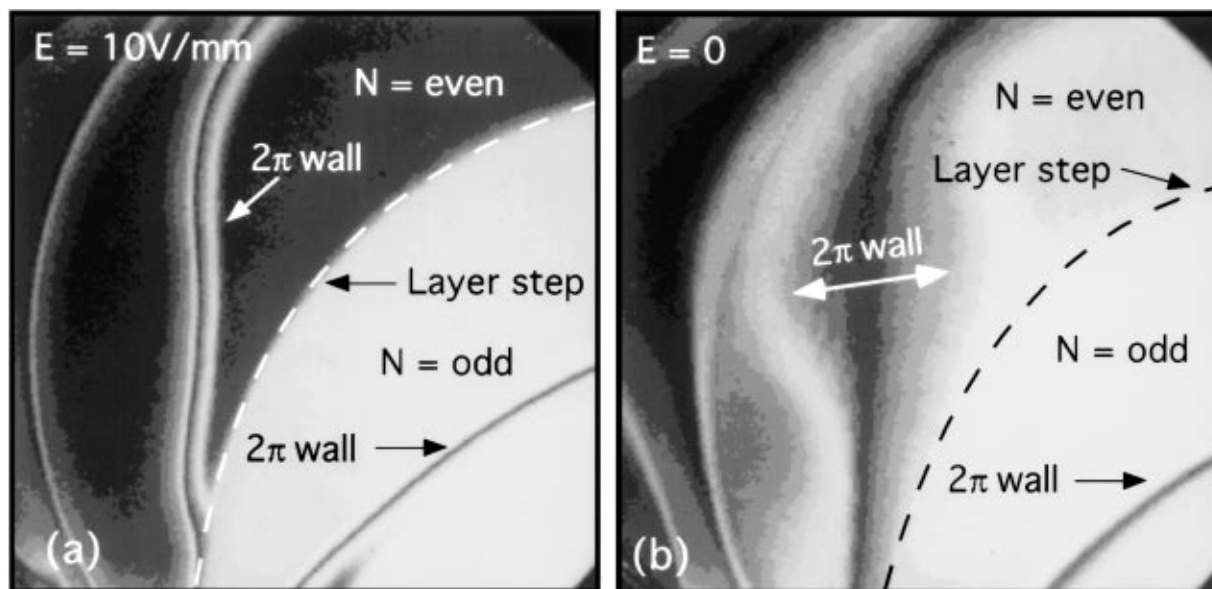


FIG. 4. 2π walls in an inhomogeneous MHPOBC film in the SmC_A^* phase. (a) In an applied electric field of 10 V/mm the compressed walls are of comparable width in both the even (dark) and odd (bright) layer regions. (b) A few seconds after removing the field, the 2π wall in the even region has already relaxed and spread out considerably while in the odd layer region the 2π wall remains narrow.

N odd regions of the film [8]. Once the field is removed, the 2π wall immediately reexpands in the N even region but is stabilized by ionic screening charge in the N odd region and remains narrow there.

In summary, we report the simultaneous observation of electric field coupling to longitudinal and transverse ferroelectricity and several other novel odd/even effects, in freely suspended films of a chiral liquid crystal. In the antiferroelectric phase, regions with odd layer number are characterized by transverse ferroelectricity and small director fluctuations comparable to the fluctuations in the SmC^* phase. In contrast, regions with even layer number have longitudinal ferroelectricity and significantly larger director fluctuations than the SmC^* phase.

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