Novel Stripe Textures in Nonchiral Hexatic Liquid-Crystal Films

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A novel macroscopic stripe texture has been observed in freely suspended films of nonchiral liquid crystal; uniform stripes of alternating molecular orientation form spontaneously at the smectic-C–to–surface-hexatic phase transition and broaden with decreasing temperature. The stripes are identified as splay domains whose formation is attributed to the polar symmetry of the hexatic surface layers. Transverse (director bend) walls, which lead to an additional modulation of the basic one-dimensional pattern, are manifested inside thick circular islands as twelve-armed star defects.

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Many low-dimensional systems exhibit unidirectionally modulated (stripe domain) states whose characteristic modulation period is set by the balance of a short-ranged "domain wall" energy and a long-ranged, repulsive interaction which may be magnetostatic, electrostatic, or elastic in origin [1–3]. In particular, the appearance of stripe textures in freely suspended films of *chiral* liquid crystal (LC) materials is well documented and may also be understood within the general framework of competing interactions [4–6]. In this article, we report the observation and initial characterization of a stable, macroscopic stripe texture in films composed of *nonchiral* materials. We propose an explanation of the stripe formation based on the breaking of up-down (inversion) symmetry in these films. In addition, we discuss the striking similarity of the observed textures to those predicted to occur in the smectic-L phase, a hexatic phase of chiral symmetry which has so far been positively identified only in a single lyotropic system [7].

Freely suspended films 3 mm in diameter were drawn in the smectic-C (SC) phase, inside a temperature controlled hot stage, the smectic layers orienting parallel to the film plane [8, 9]. In the SC, the director is tilted away from the layer normal and the in-plane positional ordering of the molecules is liquidlike. Several LC materials were investigated, including a new terphenyl ester FTE1 and the well-known Schiff's base homologs 7O.4, 5O.6, and 7O.7 [10]. Freely suspended films of all of these compounds exhibit the SC and some tilted hexatic phases [a class which includes the smectic I (SI), smectic F (SF), and smectic L (SL)] and they *all* show the same textural features, to be described below. Because of its superior chemical stability, however, the terphenyl compound was found to be better suited to extended experimentation than the hydrolysis-prone Schiff's base materials [11]. Images were recorded using a polarizing microscope in reflection mode, with slightly decrossed polarizers and white light illumination. Optical diffraction patterns were obtained by imaging incident laser light ($\lambda = 543$ nm) in the back-focal plane of a 20x objective with the aid of a Bertrand lens. All photomicrographs in this paper are of FTE1 films.

We have made careful studies of the textures of films of several thicknesses while cooling through the SC-hexatic transition. The texture well in the SC phase is characterized by rapid fluctuations in the $\hat{\mathbf{c}}$-director field, $\hat{\mathbf{c}}(x,y)$, which is the projection of the molecular director field onto the smectic layer plane [8]. Broad, fluctuating extinction brushes emanating from point defects represent typical features of this phase. Upon cooling to just above the hexatic transition, there is a dramatic increase in the magnitude of the director fluctuations [9, 12]. Simultaneously, we observe transient, anisotropic correlation regions, which are typically about 100 μm in extent, developing perpendicular to $\hat{\mathbf{c}}(x,y)$. With further cooling, director fluctuations are largely quenched, leaving a large-scale, frozen texture of fairly uniform domains separated by walls. The walls are presumably generated as a response of the director topology inherited from the SC phase to the hexatic bond-orientational ordering field in a manner similar to that leading to star defects in some SI films [13]. In the material 7O.7 these phenomena occur at 78 °C, the temperature at which x-ray measurements reveal that the two outermost layers of the film undergo a transition into the SI phase [14].

At slightly lower temperature, this texture transforms into a phase of parallel, uniform stripes of well-defined, temperature-dependent periodicity d, initially of the order of 3 μm. The stripes form parallel to $\hat{\mathbf{c}}(x,y)$ and comprise two distinct director orientations (the $\hat{\mathbf{c}}$-director azimuth ϕ jumping by about $\pm 34°$ between stripes) separated by sharp, weakly undulating walls. When the film is left to equilibrate, within a few hours the stripes form defect-free regions basically spanning the film and this texture is extremely stable. The resulting periodic structure gives rise to several orders of Bragg scattering of visible light. A typical "young" striped film is shown in Fig. 1(a).

The stripe period increases with decreasing temperature in the manner displayed in Fig. 2. The stripe broadening is reversible and the original texture is maintained provided that the temperature is changed slowly. How-

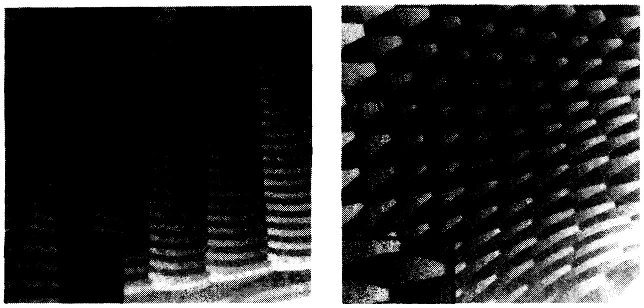

FIG. 1. Stripe textures in hexatic films: (a) stripes near film edge, modulated by perpendicular string defects (brick-wall texture) (~ 73 °C); (b) honeycomb pattern at low temperature (~ 65 °C) . The horizontal dimension of each frame is about 130 μm. The insets show details of the texture near bend walls.

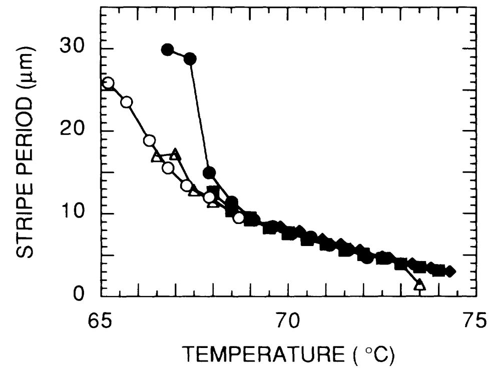

FIG. 2. Temperature dependence of stripe period on temperature, $d(T)$, in a grey film (~ 15 layers). Although stripes were discernible from about 65 °C–75 °C, a reliable measure of the period at the two extremes was not obtained. The period was measured directly (○, ●) and by light scattering (△, ▲, ■, and ◆) in different regions near the center of the film. Open symbols denote cooling runs, solid symbols heating. The stripe period was quite insensitive to film thickness.

ever, rapid heating leads to buckling, a response known from magnetic systems to reduce the stripe period without having to introduce new stripes [15].

We have seen no indication (such as overlapping domains) of independent director orientations on the two film surfaces, and the high degree of optical contrast between the stripes suggests that they are structures which propagate through the thickness of the film. SC-like director fluctuations are observable in the background throughout the stripe phase, although they become less visible with decreasing temperature. Stripes occur in films containing between about 10 and at least 60 layers as estimated from their interference colors, which range from black to green [14]. There was no significant dependence of stripe width on film thickness in this range. However, in a 5O.6 film estimated to be less than 10 layers thick, *no* stripes were observed throughout the SI/SC range, the film retaining instead the coarse texture of large-scale correlation regions frozen in from the SC phase.

The stripe phase persists down to about 73 °C in 7O.7, the temperature at which the x-ray experiments show the entire film transforming into the SI phase [14]. At this point the director fluctuations and domain wall undulations are finally quenched and the stripes slowly expand to the broad, rather featureless bands characteristic of many SI and SF films.

Important additional defect structures are frequently seen in the stripe phase: stringlike defects [16] first appearing in the SC and persisting into the stripe phase, as well as condensed walls generated at the hexatic transition, cause additional modulations of the basic one-dimensional stripe pattern described above. When oriented perpendicular to the stripes, as is usually the case, they appear as sharp domain walls across *every other* stripe and lead to long-wavelength modulations of the director field along the stripe direction. Remarkably, they also cause the stripe orientation to be distorted locally into a cusp. An array of such "walls" generates a film texture resembling a brick wall [Fig. 1(a)], which evolves into a honeycomb texture [Fig. 1(b)] on cooling.

Lateral temperature gradients or surplus material present while the film is being drawn can lead to the spontaneous formation of circular islands, which are thicker, uniform regions floating on the film. In the SC phase, a point singularity in the director field appears spontaneously near the middle of each island because of the symmetry imposed by the circular boundary. Decrossing the polarizers slightly shows that the basic orientation of the $\hat{\mathbf{c}}$ director in these islands is *circumferential*, i.e., the point defect forms the center of a *bend* distortion [17]. Transient (anisotropic) correlation regions forming near the SC-hexatic transition are extended radially inside these islands. Upon cooling, fluctuations cease, concentric stripes appear, and a *twelve-armed* radial star defect forms in each island (Fig. 3). The arms terminate at the edge of the island and are often curved. The fact that stripes always form *concentrically* in islands with central defects implies that they correspond fundamentally to *splaylike* distortions of the director. Modulations *along* the stripes are therefore *bendlike*.

Although ten- and fourteen-armed defects occasionally occur, the overwhelming preference for forming *twelve* arms suggests that each arm preferentially mediates an average change of director orientation of about 30°. Each stripe is apparently able to pass through every other radial arm unchanged, as can be seen in the figure. As a result, the stripes are modulated along their length such that each alternate stripe appears azimuthally rotated half a "modulation period" relative to its neighbors. This configuration implies that the arms of the star are topologically equivalent to the wall defects crossing linear

FIG. 3. Island with concentric stripes modulated by a twelve-armed star defect ($\sim$ 71 °C). The horizontal dimension is about 250 μm.

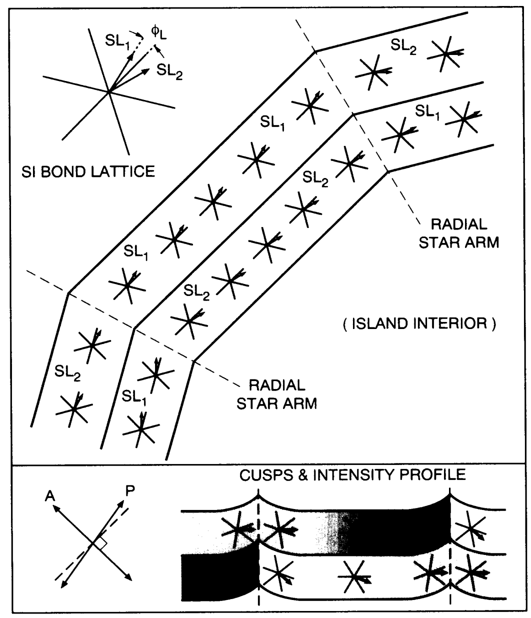

FIG. 4. Schematic proposed director field in a striped island with twelve-armed SL star defect. Each arm of the star mediates a change in SL chirality. When $\phi_L = 15°$, there is no optically detectable change across every other arm. The inset shows the director field in cusp regions.

stripes [(Fig. 1(a)]. As discussed below, the specific intensity patterns displayed in the brick wall texture strongly constrain possible models of the director configuration.

Upon further cooling, the stripe phase disappears. At this stage, six-armed stars with straight arms, reminiscent of those recently seen inside hexagonal domains in tilted hexatic Langmuir monolayers [18], usually appear.

Modulated textures have previously been reported only in LC films of tilted chiral materials [4, 13], which are intrinsically ferroelectric and lack mirror symmetry. These modulations can be accounted for by elastic theories which predict the spontaneous formation of parallel bands of director bend (i.e., polarization splay) in chiral materials [5, 6].

For films of nonchiral materials entirely in the SC phase, both LC-air interfaces must be physically equivalent. Strict up-down symmetry permits only continuous *bend* distortions of the director field ($\nabla \times \hat{\mathbf{c}}$) to propagate unchanged through the film: *Splay* deformations ($\nabla \cdot \hat{\mathbf{c}}$) effectively change sign when passing from one surface to the other and are therefore normally disallowed [5]. There are, however, exceptions to this rule [6, 19, 20]. In particular, suspending a smectic film between two different fluids removes up-down symmetry, which, as pointed out by Hinshaw and co-workers. [6], is mathematically equivalent to imposing chiral symmetry on the film and leads to the spontaneous formation of director splay domains. A related situation exists in films of amphiphilic molecules adsorbed "heads down" at the air-water interface [18].

We propose that the stripe domains in our films represent a modulated phase resulting from breaking of up-down symmetry coupled with the incomplete wetting of the air-SC interface by a newly appearing surface hexatic phase. The latter phenomenon has been demonstrated explicitly by x-ray scattering in the materials 7O.7 and 5O.6 [12, 14], where films up to a thickness of about 35 layers were found to form SI surface layers initially, prior to bulk condensation into the SI and later the SF phase.

To explain the intensity distribution of our linear and circular stripe patterns decorated by transverse bend walls, we have found that the simple splay walls allowed [21] in the SI phase are insufficient. Specifically, the magnitude ($\pm 34°$) of the observed jump in director orientation across our splay walls appears to be incompatible with the pseudosixfold symmetry of the bond-angle field to which $\hat{\mathbf{c}}$ is locked in the SI phase. In the smectic-*L* (SL) phase, however, the director is offset from the symmetric SI configurations by an angle $\pm\phi_L$, implying chiral symmetry breaking within each surface layer. An interpretation of the stripes consistent with all our observations is that they correspond to alternating SL domains, SL_1 and SL_2. Each radial arm and stripe boundary would, in this model, mediate a change in *chirality*, analogous to SL stripe structures recently proposed by Selinger [21]. In general, the domain walls $SL_1 \to SL_2$ and $SL_2 \to SL_1$ have different energies, a property consistent with the appearance of the honeycomb texture in Fig. 1(b). The general sequence of textural changes seen in our films and, particularly, the striking similarity of the island textures to the twelve-leafed SL petal structure proposed by Selinger and Nelson [22] provide additional support for this interpretation.

A director configuration that is qualitatively consistent with observed intensity distributions and explicitly realizes the requisite jumps in chirality is sketched in Fig. 4. Cusps [as in Fig. 1(a)] would form to minimize the director bend across the arm, so that the cusp angle would be directly related to ϕ_L (Fig. 4 inset). The spontaneous domain structures induced in the hexatic surfaces are propagated elastically through the SC film interior in our model. The broadening of the stripes with decreasing temperature shown in Fig. 2 would be consistent with an increase in elastic stiffness of the surface layers [23].

Whatever the actual thermodynamic phase of the striped films, a fundamental question concerns the molecular origin of the repulsive interaction stabilizing the array of walls. We believe that a contribution to such a term results from dipole-dipole interactions. We have argued that each frozen hexatic surface layer of our films exists in an asymmetric environment which, given a finite molecular dipole moment, will generally result in a surface polarization [24]. Indeed, the presence of permanent dipoles even in the SC phase is confirmed by the *polar* response of the LC to weak applied electric fields seen in preliminary experiments on FTE1 films just above the hexatic transition.

We have described the spontaneous formation of a periodic stripe texture in hexatic films of nonchiral liquid crystal. We identify the stripes as domains of uniform director orientation separated from one another by splay walls which arise from the breaking of up-down symmetry in hexatic surface layers. Additional lateral modulations result from transverse bend walls. An explicit model of the director configuration requires the introduction of chiral symmetry breaking consistent with that expected in the SL phase, with domain walls mediating a change in chirality. X-ray or electron diffraction experiments are desirable to confirm the thermodynamic phase and probe the precise molecular ordering of the striped texture.

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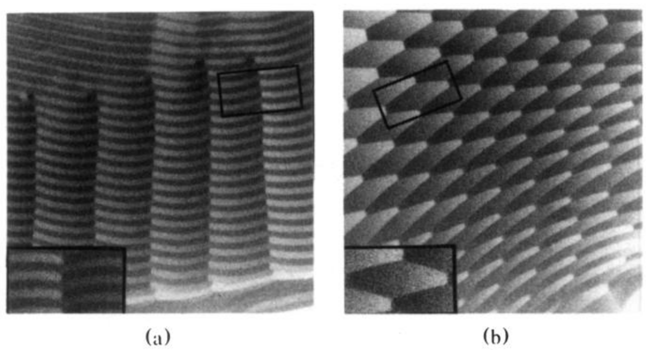

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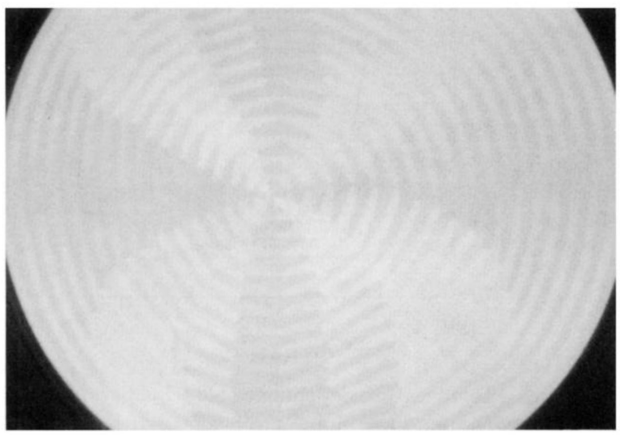

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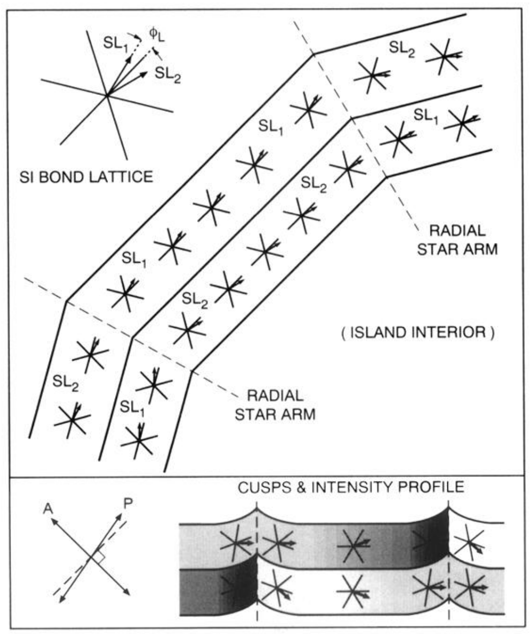

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