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Patterning-induced surface chirality and modulation of director twist in a nematic cell

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A substrate coated with a polyimide alignment layer is scribed bidirectionally with the stylus of an atomic force microscope to create an easy axis for liquid-crystal orientation. The resulting noncentrosymmetric topography breaks two-dimensional inversion symmetry and results in a spatial amplitude modulation of an imposed twisted nematic state. This is observed optically as spatially periodic light and dark stripes. When the alignment layer is scribed unidirectionally the centrosymmetric topography maintains inversion symmetry, and no stripes are observed. The appearance of the twist modulation is consistent with a chiral term in the free energy.

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Chirality plays a central role in the behavior of soft materials, particularly in liquid crystals [1,2] and at interfaces [3]. Over the years a number of spectacular effects have been discovered that owe their existence to broken inversion symmetry. For example, some 35 years ago Meyer *et al.*, demonstrated the existence of a spontaneous electric polarization in a chiral smectic-*C* phase composed of chiral molecules [4]. Twelve years ago Link *et al.*, demonstrated the existence of chiral smectic domains formed from bent-shaped inherently achiral molecules [5], which in turn can give rise to macroscopic electric polarizations. Supramolecular organization of molecules has been shown to create two-dimensional (2D) chiral domains in small clusters and thin films [3,6], where "2D (surface) chirality" means that an object cannot be rotated into its mirror image when confined to a plane; the letter "**F**" is chiral in two dimensions, whereas the letter "**E**" is achiral. In this Rapid Communication we demonstrate that 2D chirality can be induced by appropriate patterning of an achiral polymer-coated substrate by means of scribing with the stylus of an atomic force microscope. When covered with a thin layer of nematic liquid crystal, we observe a signature of this 2D chirality, viz., the appearance of a striped optical texture when a twist is imposed externally on the liquid crystal, e.g., using a standard "twisted nematic" cell.

The cell was composed of two glass microscope slides. Both substrates were cleaned in detergent, acetone, and ethanol and spin-coated with a thin layer of the achiral polyamic acid RN-1175 (Nissan Chemical Industries, Ltd.), which is used for low pretilt planar alignment. The slides subsequently were prebaked for 5 min at 80 °C and then fully baked for 60 min at 230 °C to achieve a high degree of imidization. After baking, the polyimide-coated substrates were rubbed unidirectionally using a cotton cloth with a strength $n_f=4.6\times10^5$ cm^{-1}; details are given elsewhere [7,9]. One of the substrates then was scribed [7,8] with the stylus (TAP-300 Si) of a Topometrix Explorer atomic force microscope (AFM). Schematic representations of the AFM-scribing patterns (each covering an area of 100×100 μm^2) are depicted in Figs. 1(a) and 1(b). The spine of the chevron is denoted by dashed arrows in Fig. 1, with angles $\alpha_0=\pm30°$, $\pm45°$, $\pm60°$, and $\pm75°$ between the scribing directions and the spine. The cantilever remains parallel to the chevron spine when scribing the patterns; thus, the movement of the cantilever is oblique to its orientation. For each pattern scribed at angle α_0, we prepared two types of nanopatterned surfaces, viz., bidirectional [Fig. 1(a)] and unidirectional [Fig. 1(b)] scribing. For bidirectional scribing, adjacent lines were scribed in an antiparallel fashion with the stylus moving back and forth, whereas for undirectional scribing the adjacent lines are parallel. We fixed the distance D [shown in Fig. 1(a)] at 200 nm and used a scribing force of 4.4 ± 0.1 μN. Note that the actual separation d between adjacent lines is $d=D\sin\alpha_0$ and that the AFM-scribed surface always corresponds to the bottom substrate of the cell, i.e., the side of the cell for which the microscope illumination is incident.

Before preparing the closed cell, we investigated the topography of the scribed surface in noncontact AFM mode. Figures 2(a) and 2(b) show two-dimensional images of the topography for bidirectional and unidirectional scribing, respectively. Figure 2(c) shows the topography across the line shown in the bidirectionally scribed pattern [Fig. 2(a)], where the sequential "pulling" and "pushing" actions of the AFM in scribing mode and the resulting movement of material gouged out by the stylus results in a noncentrosymmetric topography. On the other hand, unidirectional scribing [Fig. 2(d)] results in a centrosymmetric topography, whether it involves pulling or pushing of the stylus. A more detailed study

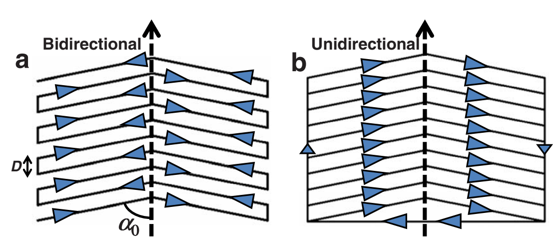

FIG. 1. (Color online) Schematic representation of scribing pattern of bottom substrate for (a) bidirectional and (b) unidirectional scribing. $d=D\sin\alpha_0$, where d is the gap between the centers of adjacent lines and α_0 is the angle between the scribing and the "spine" of the chevron.

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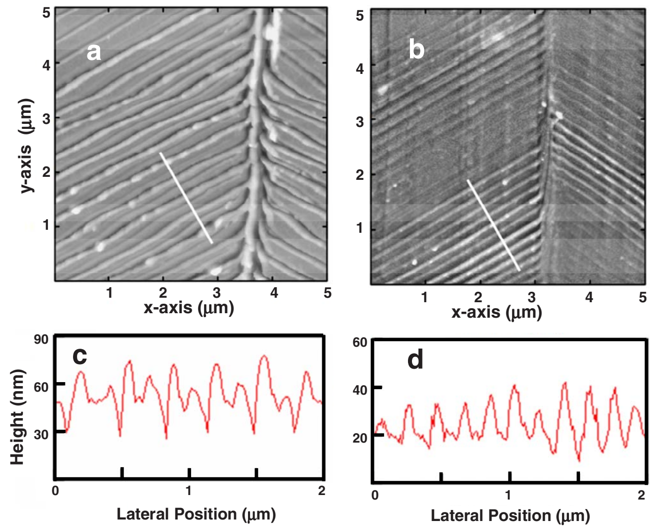

FIG. 2. (Color online) (a) 2D topographical image of bidirectional scribing and (b) 2D topographical image of unidirectional scribing. (c) and (d) Topographical profiles along the lines indicated in (a) and (b), respectively.

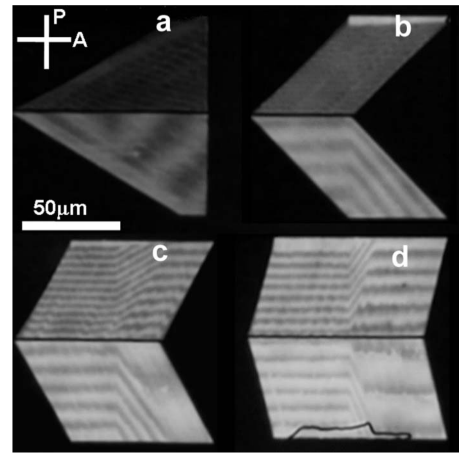

FIG. 3. Polarized microscope images of the twisted cell for angles (a) $\alpha_0=30°$, (b) 45°, (c) 60°, and (d) 75° between the scribing directions and the symmetry axes. Exit polarizer (analyzer A) is parallel to the chevrons' spine and the incident polarizer (P) is rotated by 90°.

of the differences between pulling and pushing the AFM stylus and the resulting topographies can be found in Ref. [10]. Thus, the only nontrivial difference between the two types of scribing is the absence of centrosymmetry of the bidirectional topography vs the centrosymmetry of the unidirectional topography. In fact, because of the different effects of pulling and pushing in the bidirectional case, the topographically noncentrosymmetric axis that is perpendicular to the scribing axis [i.e., the white lines in Figs. 2(a)] and the scribing axis itself form a two-dimensional coordinate system that lacks 2D inversion symmetry. In other words, it is two dimensionally chiral. Moreover, the chiral handedness of one wing of a chevron is opposite to that of the other. It is important to note, however, that—although we measure the topography—the *shape* of the surface itself may not be the primary driver of the observed stripes. Rather, the topography is related to the induced orientation of the polyimide backbone [11], and thus to the interaction potential between the substrate and the liquid crystal [12]. Thus, the symmetry of the topography corresponds to the symmetry of the interaction potential.

The AFM-scribed bottom substrate and the cloth-rubbed-only top substrate were cemented together, separated by a Mylar spacer of nominal thickness 3 μm, with the top and bottom substrate axes parallel to each other, i.e., their relative azimuthal angle $\psi=0$. This creates a twist structure within the two "wings" of the chevron, where the rubbing and scribing directions of the top and bottom substrates are rotated with respect to each other by an angle $+\alpha_0$ in one wing and $-\alpha_0$ in the other. The thickness of the cell was measured to be $t=4.2\pm0.1$ μm by interferometry. The cell was placed into an oven, heated to a temperature of 85 °C (well above the nematic-isotropic transition temperature of 74 °C), and filled with the achiral liquid-crystal heptyloxy cyanobiphenyl (7OCB, Merck) in its isotropic phase. The sample then was cooled into the nematic phase and stabilized at a temperature of 65 °C. [We note that several experiments also were performed with the achiral liquid-crystal pentyl cyanobiphenyl (5CB, Merck), with results qualitatively consistent with those using 7OCB.]

The cell was observed using a polarizing optical microscope. Figure 3 shows the cell with bidirectional AFM scribing, where the orientation of the analyzer (A) is parallel to the rubbing direction of the top substrate, and that of the polarizer (P) is at 90° with respect to the analyzer. Dark and light stripes can be seen for all α_0. For each of the four scribing orientations α_0, we then rotated the incident polarizer while keeping the analyzer fixed to minimize the total light intensity for one wing; this condition is met when the polarizer is *approximately* parallel to the scribing direction α_0. Then, on rotating the polarizer by angles $\pm\Delta\alpha$, we observed that the dark and light stripes are interchanged. This indicates that the director twist through the cell is modulated spatially, where the twist is a little smaller in one stripe and larger in the adjacent stripe, with a modulation amplitude of $\Delta\alpha$. Note that such a modulation also requires the presence of splay and/or bend. $\Delta\alpha$ was found to have no systematic dependence on α_0 and has a typical value of approximately 5° [13]. Additionally, we found that the wavelength λ of the stripes could be varied by changing the angle α_0 between the rubbing directions of the two substrates, such that λ decreases with increasing α_0 up to $\alpha_0\sim60°$, beyond which it apparently begins to increase; this behavior can be seen in Fig. 3. Importantly, for $\alpha_0=90°$—this corresponds to the cantilever moving perpendicular to its axis, where there no longer is a distinction between pushing and pulling and thus no chirality—the stripes vanish completely. It also is important to reiterate that stripes were not observed in any of the unidirectionally scribed cells.

We also examined qualitatively the effects of varying the scribed line spacing $d=D\sin\alpha_0$, cell thickness t, temperature, and introducing a nonzero angle ψ between the rubbing direction of the top substrate and chevron spine of the bottom (scribed) substrate. With increasing D out to $D=600$ nm, we found that the period of the stripes becomes larger (λ is approximately $\propto D$) and that the twist amplitude $\Delta\alpha$ becomes smaller. This correlates with a less asymmetric topography associated with a decoupling of the push- and pull-created grooves and the associated material displaced from the grooves when D becomes large. Although such a large value of D might suggest that the push- and pull-created grooves should be decoupled completely, in reality the sequential scribing of each line and material carried by the stylus results in a small degree of noncentrosymmetry, even for large D. Turning to cell thickness t and temperature T, we found the wavelength λ to be nearly independent of t for t=3.0, 5.3, 8.5, and 13.4 μm and we found $\Delta\alpha$ to be a very weakly decreasing function of t. Very little, if any, variation was found with temperature throughout most of the nematic range, 56 °C<T<74 °C, although we did not examine the behavior close to the smectic-A phase transition. That the stripes appeared unchanged on cycling through the nematic-isotropic phase transition suggests that they are either pinned or controlled by the director orientation $\hat{n}$ just outside the scribed regions. As for ψ, we found that the stripe pattern in the two wings were similar for $\psi=0$; in fact, that stripes are observed in both wings (having opposite handedness) is due to the fact that the sense of the twist rotation also is interchanged in the two wings. For $\psi \neq 0$ we found that the stripe patterns in each of the two wings become less similar with increasing ψ. This is as expected, as the angle between the rubbing direction of the top substrate and the scribing direction in one wing is $\alpha_0+\psi$ and that in the other wing is $\alpha_0-\psi$. For $\psi=\alpha_0$, i.e., when the cloth rubbing direction of the top substrate was parallel to the scribing direction in one of the wings (i.e., no macroscopically imposed twist), stripes were not observed. However, we do not believe that the absence of observed stripes is due to the absence of an imposed twist. To show this, we fabricated a cell in which the top surface was coated with an unrubbed layer of the planar-degenerate alignment material polymethyl methacrylate [14]. The cell was filled in the nematic phase along the bidirectional scribing axis, and the resulting average alignment was parallel to this axis, with no macroscopic twist. However, a striped pattern with moderately long λ was observed.

Stripe patterns in liquid crystals generally have been explained using a continuum approach. Although a surfacelike saddle-splay mechanism [15–17] involving the surface elastic constant K_{24} (which can be different at the two surfaces) in principle can play a role in stripe formation, the stripes' disappearance when $\alpha_0=90°$ and mirror symmetry is restored argues against this mechanism being responsible for the observed stripes in the chirally patterned cell. Selinger *et al.* suggested [18] and Maclennan and Seul experimentally found [19] that modulated patterns can appear as a result of a coupling between bend or splay on a surface and a scalar soft mode. The required soft mode may exist in our system, viz., the (small) projection of the director $\hat{n}$ onto the surface normal $\hat{S}$, which is resisted only by the polar anchoring as characterized by the quadratic polar anchoring strength coefficient W_2^θ [20]. Given the absence of *any* symmetry in our surface, this soft mode can couple to some surface specific combination of bend and splay, e.g., there should be an energy term of the form

$$\int \hat{S}\cdot\hat{n}(a\hat{S}\cdot\nabla\times\hat{n}+b\,\nabla\cdot\hat{n})d^2r, \tag{1}$$

where the first term is chiral term and therefore requires either a chiral liquid crystal or a chiral surface or both, while the second term is nonchiral and also is allowed. For our case we believe that the first term, i.e., the chiral term, is dominant, as on purely empirical grounds the stripes are absent when the surface is achiral after being scribed unidirectionally. It is important to note, however, that we are not certain of the actual interactions responsible for the chiral term. Specifically such a term can arise from direct interactions at the surface. On the other hand, intricate chiral surface patterning may result in complicated director textures in a region near the surface of thickness comparable to d. In general, the free energy of such a texture will depend on its nature far from the surface and can be expanded in powers of gradients of the order parameter far from the surface. Terms having no gradient correspond to the usual anchoring terms [20] and terms proportional to the first power of the gradient are those in Eq. (1). Assuming that the usual elastic free energy applies in this surface region, the interaction between the elastic distortions in the surface region due to the periodic scribing and the twist due to the large-scale modulation implies that $a\sim K_{22}\langle\hat{n}\cdot\nabla\times\hat{n}\rangle$, where $\langle\cdots\rangle$ corresponds to an average of the integral of the argument through the surface layer. Similarly, from the interaction between the corresponding bend distortions, $b\sim K_{33}\langle\hat{S}\cdot\hat{n}\times\nabla\times\hat{n}\rangle$. Here, K_{22} and K_{33} are the twist and bend elastic moduli. Note that macroscopic twist or bend distortions, such as our imposed uniform twist, will result in changes in these averages, i.e., in the magnitudes of a and/or b, and thus in λ, consistent with our observations. As the perturbations associated with the surface pattern extend a distance of approximately d into the bulk, we expect that $a\sim K_{22}\langle\hat{n}\cdot\nabla\times\hat{n}\rangle\sim K_{22}\sigma_\varphi$, where σ_φ is the standard deviation of the director about its average orientation $\Delta\varphi$. Here, $\Delta\varphi$ is the chirality-induced angle between the average director orientation at the surface and the scribing direction, even in the absence of an imposed twist, i.e., $\psi=\alpha_0$ [21,22]. For a fixed surface anchoring, σ_φ will (generally) grow with increasing d.

Consistent with Selinger *et al.*, we consider the possibility of a modulation of $\hat{n}$ both parallel and perpendicular to the surface normal and decaying over a distance κ^{-1} ($\propto\lambda$) into the bulk. We assume that this modulation decays into the bulk slowly, which occurs when λ is more or less comparable to t. When t is significantly larger than λ the modulation no longer is expected, as its elastic cost falls off more slowly with decreasing λ. In our observations t and λ are comparable, consistent with a modulation but requiring, in principle, a more detailed theory that accounts for these parameters. Using Eq. (1) with $b=0$ and the usual bulk elastic [1] and quadratic surface anchoring [20] energies, one can show that the energy per unit area favors a modulated state when $[a+cK_{22}(\alpha_0\pm\Delta\varphi)]^2 > t[K_aW_2^\theta+K_bW_2^\varphi+(2K_aK_bW_2^\theta W_2^\varphi)^{1/2}]$, where W_2^φ is the azimuthal quadratic anchoring strength coefficient, c is a constant of order unity when t is not much larger than λ, $\alpha_0\pm\Delta\varphi$ is the actual azimuthal twist through the cell—note that for most cases $\alpha_0 \gg \Delta\varphi$ (see Fig. 3) unless the imposed α_0 is small or zero, for which stripes are not observed—and K_a and K_b are appropriate combinations of, and of the same magnitude as, K_{22} and K_{33}. The inclusion of a nonzero b complicates this inequality somewhat but qualitatively adds a constant multiplied by b^2 to the left-hand side. We remark that while a nonzero value for b would be expected for our system, the observation that the modulation vanishes when the surface is nonchiral suggests that the chiral a term in Eq. (1) dominates in our system. It is also the case that an imposed uniform twist in the sample will, depending on its sign, linearly increase or decrease the tendency for modulation. This is because the modulation has a particular sense of helicity that couples with a uniform twist. In principle, if the modulation is in equilibrium and not controlled by the boundaries of the scribed area, then the angle the modulation direction makes with the director is controlled by the ratio b/a, as the a term favors bend and b favors splay. We do not believe this to be the case in our situation; rather we believe that the modulation direction is controlled by boundary conditions of the scribed area.

To summarize, we demonstrated that an inherently achiral alignment layer can be patterned with a noncentrosymmetric topography, and thus a noncentrosymmetric interaction potential, which is the key ingredient in the creation of a chiral surface environment. We observed a signature of this chiral environment, viz., a striped texture that arises from a modulation of the twist angle in a twisted nematic cell. On an empirical basis we find that the observed phenomenon cannot be due solely to a coupling with 2D splay nor with saddle-splay elasticity. Rather, a chiral term associated with bend distortion plays the dominant role. To be sure, there are many other patterns that can be scribed and that lack centrosymmetry symmetry, such as a zigzag pattern where the lengths of the "zigs" and "zags" are unequal, or a repeating series of parallel lines where the line spacing increases from one line to the next to some maximum value. The relationship between such patterns, chirality, and their effect on liquid crystals will be the subject of future investigation.

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