Mechanically generated surface chirality at the nanoscale

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A substrate coated with an achiral polyimide alignment layer was scribed bidirectionally with the stylus of an atomic force microscope to create an easy axis for liquid crystal orientation. The resulting non-centrosymmetric topography resulted in a chiral surface that manifests itself at the molecular level. To show this unambiguously, a planar-aligned negative dielectric anisotropy achiral nematic liquid crystal was placed in contact with the surface and subjected to an electric field $E$. The nematic director was found to undergo an azimuthal rotation approximately linear in $E$. This so-called “surface electroclinic effect” is a signature of 2D chirality and was not observed when the polyimide was treated for a centrosymmetric topography, and therefore was nonchiral.

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Chirality plays a central role in both large scale and small scale systems. On large scales, technologies such as the mechanical screw date back to antiquity. On microscopic and nanoscopic scales, chirality plays a central role in physics and biology, and is crucial for the existence of life. Most often macroscopic consequences of chirality, such as optical rotatory power in a bulk material, occur as a result of the absence of inversion symmetry of the constituent components, such as molecules or self-assembled structures. But this is not an absolute requirement for bulk chirality. In fact, achiral molecules have been shown to self-organize into macroscopically chiral phases [1–3], which often can occur at interfaces due to the specifics of the molecule / substrate interactions. Chiral molecules such as DNA also have been used as templates to induce chirality in inherently achiral materials [4, 5]. In this paper we demonstrate nanoscale mechanical generation of chirality in two dimensions by nanoscribing, where 2D chirality is defined as the inability to superpose an object onto its mirror image by rotation and translation within a plane; the letter “F” is chiral in 2D, whereas the letter “E” is achiral. Chiral surface patterns such as a multi-turn or multi-arm spiral (the latter similar to certain spiral galaxies or an Eastern religious symbol) have been created by several techniques, such as lithography [6] and vacuum evaporation [7]. These patterns tend to have large length scales, however, typically several to hundreds of micrometers. In a recent paper we examined bidirectional scribing of an inherently achiral polymer-coated substrate using the stylus of an atomic force microscope (AFM) [8]. The sequential “pulling” and “pushing” actions of the AFM stylus and the resulting transport of material resulted in a non-centrosymmetric topography, and thus a non-centrosymmetric interaction potential with the adjacent liquid crystal. In fact, because of the different effects of pulling and pushing, we conjectured that the resulting topographically non-centrosymmetric axis (perpendicular to the scribing axis) and the scribing axis itself form a two-dimensional basis that lacks 2D inversion symmetry. When coated with a thin layer of nematic liquid crystal, the liquid crystal displayed a striped texture. On the other hand, when the substrate was scribed unidirectionally, resulting in a centrosymmetric topography, stripes were not observed. These observations suggested — but did not prove — the mechanical generation of surface chirality. Nevertheless, other phenomena also could have been responsible for the stripes, such as coupling between splay elasticity and a soft mode [9, 10] or saddle-splay elasticity [11–13]. In this paper we conclusively demonstrate nanoscopic scribing-induced
chirality at a polymer surface by detecting an electric field-induced rotation of an achiral nematic liquid crystal adjacent to the surface.

Three decades ago Meyer and Garoff demonstrated [14] an “electroclinic effect” in the bulk smectic-A phase of a chiral liquid crystal, whereby an electric field applied parallel to the smectic layer planes induces a polar rotation of the liquid crystal director about the electric field axis. This effect requires the absence of mirror symmetry in the liquid crystal molecules. Li, et al observed a related bulk nematic electroclinic effect [15] due to the presence of smectic fluctuations in a chiral nematic phase. Chirality-based phenomena at liquid crystal / substrate interfaces also have been well-studied. There have been numerous reports of layer tilt in the chiral smectic-A phase at a rubbed surface [16–19]. A group at Chalmers University in Sweden developed polymerizable chiral smectic-C* liquid crystals to use as fixed pretilt alignment layers. In what they refer to as an “electrically commanded surface,” an applied field reorients the smectic-C* surface layer, which couples elastically to the bulk liquid crystal [20, 21]. Tripathi, et al observed a linear electrooptic effect [22] — in essence, a type of electroclinic effect — at the interface between an achiral substrate and a chiral nematic liquid crystal. More recently it was shown that an achiral nematic tilts by an angle $\beta$ with respect to the rubbing direction at a molecularly chiral alignment layer [23, 24]. This effect arises from the biased molecular rotation and resulting polarization at, and normal to, the interface. If the surface is achiral the tilt can be either clockwise or counterclockwise with equal probability, resulting in zero net tilt; if the surface is chiral, one tilt direction is preferred and a net tilt may be observed, although its magnitude depends on the liquid crystal, the alignment layer, and the degree of chiral coupling. Moreover, application of an electric field normal to the surface would couple to the polarization and modify the tilt — again, this is one manifestation of the electroclinic effect. The ingredient required for all of these tilt phenomena is the breaking of mirror symmetry. Thus, the observation of a liquid crystal electroclinic effect at the interface would serve as a sensitive proof of mechanically generated chirality at the surface.

A pair of glass substrates coated with a semitransparent layer of indium-tin-oxide (ITO) was cleaned sequentially in detergent, acetone, and ethanol. One substrate was spin coated for 20 s at 2000 rpm with a layer of the polyamic acid RN-1175 (Nissan Chemical Industries), then imidized by baking according to the manufacturer’s specifications at 250° C for 60 min. The thickness of the alignment layer $t_A$ was measured by a mechanical profilometer
and found to be \( t_A = 200 \pm 20 \) nm. Several squares of size \( 100 \times 100 \) \( \mu \)m were scribed into the polyimide surface by the stylus (TAP-300 Si) of a Topometrix Explorer AFM. Two different patterns were scribed several times each, in close proximity to each other: A bidirectional pattern involved translating the stylus back and forth (i.e., pulling and pushing) at an angle \( \theta = 60^\circ \) with respect to the cantilever orientation, as shown in Fig. 1a. We remark that the details of the scribed pattern must be on length scales comparable to, or smaller than, the liquid crystal’s extrapolation length \( L \), which corresponds to a characteristic distance over which the nematic director remains correlated in the presence of spatial variations in the surface patterning [25]. The quantity \( L = K/W_2 \), where \( K \) is an elastic modulus for some combination of splay and bend and \( W_2 \) is the spatially-averaged quadratic coefficient for in the surface free energy expansion in powers of the director’s angular deviation from the scribed axis [26]. The magnitude of \( L \) typically is many hundreds nanometers for strong scribing (large \( W_2 \)) and 1 \( \mu \)m or more for weak scribing forces [27]. Given this condition, we used a \( d = 200 \) nm spacing between adjacent lines. Figure 1c shows the cross-sectional topography obtained in non-contact AFM mode, which clearly is non-centrosymmetric, a topography that has been observed previously [8, 28]. Taking into account the vector associated with, e.g., the pulling direction, we believe that this topography (and the resulting interfacial potential) are chiral in two dimensions; it is the goal of this work to confirm this conjecture. The unidirectional pattern, which involved only lateral translation of the stylus, is shown in Fig. 1b. The cross-sectional topography, shown in Fig. 1d, is on average centrosymmetric and therefore its surface must be achiral.

The opposing substrate was spin coated with polymethylmethacrylate (PMMA) dissolved in 66% vol. propylene glycol methyl ether acetate with 33% vol. \( \gamma \)-butyrolactone and baked at \( 80^\circ \) C for 120 min. The thickness \( t_{PMMA} \) of the PMMA layer was measured to be approximately 1000 \( \mu \)m. The PMMA provides a planar-degenerate surface for alignment of the liquid crystal, where the azimuthal orientation at the PMMA “slave” surface is controlled initially by the RN-1175 coated “master” surface [29]. Over several hours a memory effect [30] develops at the PMMA substrate, and the initial orientation of the liquid crystal becomes fixed at that substrate. The two substrates were placed together, separated by Mylar spacers, and cemented. The thickness \( t_{LC} \) of the gap between the alignment layers was measured by interferometry and found to be \( t_{LC} = 6.0 \pm 0.1 \) \( \mu \)m. After attaching wires to the ITO electrodes, the cell gap was filled with the negative dielectric anisotropy and low
resistivity liquid crystal methoxybenzylidine butylanaline (MBBA) in its isotropic phase at a temperature 53° C. The cell then was cooled into the nematic phase and stabilized at room temperature, approximately 22° C. We note that the deviation angle $\beta$ of the director at the supposedly chiral surface was too small to detect — $\beta$ was well under 1° — indicating weak coupling to the chirality.

Before proceeding, let us consider the application of a low frequency voltage across the cell, which reached as high as $V_{app} = 145$ V rms at frequency $f = 2$ Hz. If an electroclinic effect were present at the presumed chiral surface, the director would undergo a small twist from the fixed PMMA substrate to the chiral RN-1175 substrate. The low frequency was used to ensure that the director profile would follow the ac voltage adiabatically. Ordinarily, a negative anisotropy liquid crystal such as MBBA would exhibit an instability at low frequencies at a relatively small voltage [25]; this was not observed in our cell, however. The reason is that at low frequencies the two alignment layers and the liquid crystal layer behave as resistors, rather than capacitors, in series. To determine the effective voltage drop $V_{LC}$ across the liquid crystal layer we constructed another cell having the same gap $t_{LC}$ but without the alignment layers and filled it with MBBA, which in this cell was in direct contact with the ITO. Using an electrometer, we measured the dc resistance across the MBBA-only cell and the cell having the two alignment layers, finding resistances of $1.4 \times 10^6$ Ω and $4 \times 10^8$ Ω, respectively. Thus the voltage drop across the liquid crystal was much smaller than that across the alignment layers ($V_{LC} \approx 0.0035V_{app}$), and was insufficient to induce the instability.

The optical setup consisted of a beam from a Nd-YaG laser at wavelength 532 nm that passed through a polarizer, through the sample with the PMMA side facing the laser, a second polarizer oriented at 45° with respect to the first polarizer, a microscope lens to create an enlarged real image (magnification $\sim 20X$) of the liquid crystal sample downstream, a 500 μm diameter pinhole, and into a photodiode detector. The detector output was fed into a lock-in amplifier operating in amplitude/phase ($R/\theta$) mode and referenced to $V_{app}$. The signal from the lock-in amplifier (1 s time constant filter) was computer recorded. The MBBA cell was oriented so that the director was parallel to the initial polarizer. (Because the unidirectional and bidirectional axis orientations were different, the cell had to be rotated when examining the two different surface scribing.) We chose this optical configuration to exclude an undesired consequence of a coupling between the applied field and the two surface
polarizations: If we had used a standard optical retardation arrangement involving crossed polarizers and the liquid crystal director at 45° with respect to the two polarizers, the voltage-induced variation of the MBBA orientational order parameter at the two dissimilar surfaces would have resulted in a variation at frequency $f$ of the optical retardation through the cell, and thus the intensity at the detector [31–33]. Our geometry excludes this effect because, even though the MBBA order parameter at the surfaces can vary slightly with applied field, only the extraordinary optical mode propagates through the cell and thus the resulting signal is insensitive to changes in retardation. But, if the azimuthal orientation $\alpha$ of the director at the supposedly chiral surface were to vary with the applied voltage, as it should on symmetry grounds, the director would undergo a small twist from its perturbed orientation at the chiral scribed substrate to its (nearly) pinned orientation at the PMMA substrate. The optical polarization would adiabatically rotate with the spatially slow variation of the director through the cell. Thus, the resulting intensity of light that passes through the second polarizer would vary approximately linearly with $\delta \alpha$ at frequency $f$. This is the signal that we observe.

The voltage $V_{app}$ applied to the cell was increased from zero to 145 V rms in steps of 0.65 V, with a dwell time $\tau = 10$ s at each step. Figure 2a shows a typical result for the bidirectionally-scribed surface: field-induced tilt $\delta \alpha$ vs. $V_{app}$ along the lower axis, with the approximate voltage drop $V_{LC}$ across the liquid crystal shown along the upper axis. The azimuthal deviation $\delta \alpha$ was obtained from the intensity data by noting that, neglecting reflections, the intensity $I = I_0 \cos^2 \alpha = I_0 \cos^2 \left( \frac{\pi}{4} + \delta \alpha \right)$, where $I_0$ is the incident intensity of light. For small $\delta \alpha$, $I \approx I_0 \left( \frac{1}{2} - \delta \alpha \right)$. Thus, the ratio of the ac signal at frequency $f$ to the dc signal corresponds to $-2\delta \alpha$. Experiments were performed at several bidirectionally-scribed squares, with similar qualitative results. We note, however, that the slope could vary by more than a factor of two from one run to the next, indicative of variations in the strength of the chiral environment due to experimental inconsistencies in the scribing process. We then examined the unidirectionally-scribed squares that exhibit a centrosymmetric topography; these squares are not expected to be chiral in 2D. Figure 2b shows a typical result. Notice that there is no systematic variation in the signal at frequency $f$, indicating the absence of an electroclinic effect.

The appearance of an electroclinic effect at the bidirectionally-scribed surface and its absence at the unidirectionally-scribed surface is an unambiguous signature of mechanically
generated two dimensional chirality at the bidirectionally-scribed surface. To be sure, the demonstrated effect is small, as typical values for $\delta \alpha$ were well under a milliradian and that there was no clear deviation $\beta$ of the equilibrium director orientation from the scribing direction, as had been observed in Refs. [23] and [24]. Nevertheless, that this chirality manifests itself at the molecular level suggests that other patterns such as dividing a region into subregions, each with uniform scribing but with an overall nonzero curl [34]; imprinting a grid of parallelograms [35]; unidirectional scribing with forces varying sequentially as ABCABCABC...; or scribing 2D chiral step-like patterns. These may provide a significantly larger response at the molecular scale.

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FIG. 1: Schematic representation of scribing pattern for a) bidirectional scribing and b) unidirectional scribing. The orientation of the AFM cantilever is shown. Panel c) shows a typical topographical profile (along the dashed line in panel a) for the bidirectional scribing, and panel d) shows a typical topographical profile (along the dashed line in panel b) for the unidirectional scribing.

FIG. 2: Experimental results for a) bidirectionally-scribed (2D chiral) surface and b) for unidirectionally-scribed (achiral) surface. Note that the signal does not vanish at zero voltage, as the lock-in amplifier was operated in $R/\theta$ mode. Close circles correspond to data on increasing the voltage with time, and open triangles correspond to decreasing the voltage with time. No hysteresis was observed.

[35] H. Yokoyama, private communication
AFM cantilever

$\theta = 60^\circ$

d = 200nm

Position ($\mu$m)

Height (nm)

Position ($\mu$m)

Height (nm)