

Design of Chiral Domains by Surface Confinement of Liquid Crystals



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Spatial confinement of water-based lyotropic chromonic liquid crystals made of achiral molecules produces chiral structures with alternating left and right twists.

Chirality, or absence of mirror symmetry, is a fascinating attribute of inanimate and living objects, which inspires artists and fascinates scientists in various disciplines, from physics to mathematics, biology to chemistry and crystallography. Producing and controlling the sense of handedness in systems formed by mirror-symmetric elements or containing an equal amount of left- and right-twisted elements is usually a nontrivial task. In this issue of *ACS Central Science*, Geonhyeong Park et al.¹ demonstrate that a slab of a lyotropic chromonic liquid crystal (LCLC), formed by achiral molecules dispersed in water, can produce a periodic array of domains with left- and right-handed twists of the orientation of molecular aggregates. The twist develops over macroscopic regions of tens of microns in size and is caused by a balance of two facets of the orientational order pertinent to liquid crystals: the elastic response to deformations of orientation and anisotropy of surface interactions at confining boundaries.

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The studied LCLC is an aqueous solution of disodium cromoglycate (DSCG), a material known under a commercial name “Cromolyn” or “Cromolyn sodium” and used as an active ingredient in drugs that prevent allergy- and asthma-related symptoms.² In water, DSCG molecules stack face-to-face, shielding their hydrophobic cores from the polar environment. This self-assembly produces elongated cylindrical aggregates of a diameter about 2 nm and a stacking distance 0.34 nm, which makes them similar to a double-stranded DNA (dsDNA). However, while dsDNA is chiral, the DSCG molecules are not and show no persistent twist along the aggregate’s axis. This molecular-scale difference exhibits itself spectacularly at the macroscopic level. In aqueous solution, the dsDNA molecules twist with respect to each other, forming a so-called cholesteric liquid crystal with a macroscopic pitch on the order of microns. The subtle nature of the relationship between the molecular and macroscopic chirality is still a subject of current investigation.³ In contrast, achiral aggregates of DSCG in water align parallel to each other, forming a mirror-symmetric nematic liquid crystal with a preferred direction \hat{n} , called the director.

While chiral packings of chiral molecules are ubiquitous, chiral packings of achiral molecules are rare. A macroscopically broken mirror symmetry of a liquid crystal formed by achiral molecules requires special spatial confinement. Charles-Victor Mauguin, who was inspired to explore crystallography and liquid crystals after attending lectures in Paris by Pierre Curie on symmetry in physical effects and by



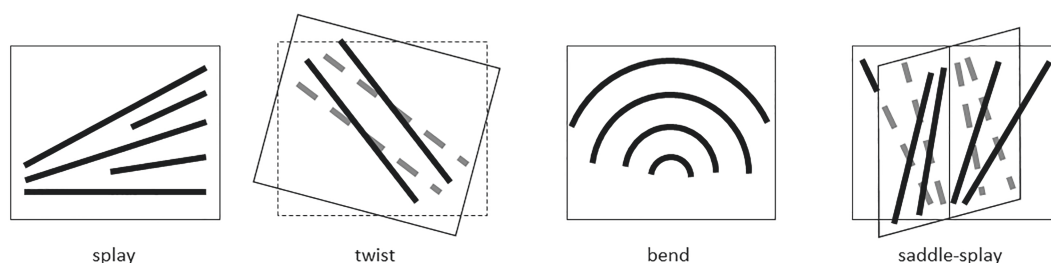


Figure 1. Director deformations of various types in a nematic liquid crystal.

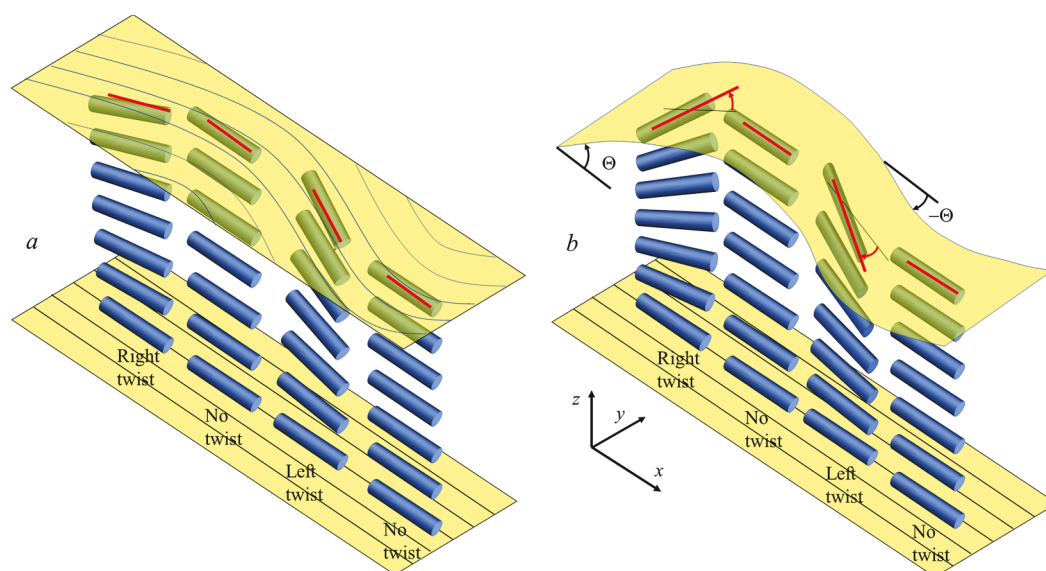


Figure 2. Patterning the surface anchoring direction (a) or the shape of the top plate (b) could produce an array of alternating left- and right-twisted domains in a nematic liquid crystal.

Otto Lehmann on liquid crystals, presented the first example in 1911.⁴ Namely, Mauguin discovered that a nematic liquid crystal could be aligned unidirectionally between two glass plates when melted from a sufficiently large solid single crystal. Rotating the plates with respect to each other, he produced a twisted structure. The experiment is a direct illustration of Pierre Curie's principle: "the symmetries of the causes are to be found in the effects", since a chiral input, the rotated plates, generates a chiral output, a twisted nematic. Decades later, Mauguin's "twisted nematic" cells were reincarnated as electrically driven pixels in liquid crystal displays.⁵ In the absence of the electric field, the twisted nematic cell is optically active; i.e., it rotates the plane of polarization of propagating light, again demonstrating Pierre Curie's principle. A unidirectionally applied electric field realigns the liquid crystal molecules parallel to itself so that the polarization of the transmitted light does not rotate anymore. The field-switchable optical activity translates into a "bright–dark" switchable appearance of the pixels sandwiched between two polarizers of the display.

Nematics could offer a more sophisticated mechanism of confinement-induced chirality, in which the "input" is not

chiral. Imagine a spherical nematic droplet. The spherical shape is obviously not chiral, and there are no chiral molecules; however, such a droplet could show a twisted director structure and optical activity.⁶ The reason is in the elastic nature of the nematic: the twist relieves other modes of deformations that are imposed by the spherical confinement, such as splay, bend, and saddle-splay. The droplet behaves similarly to an elastic rod under axial loading. The rod and the loading are both uniaxial and cylindrically symmetric, yet the rod would buckle into an asymmetric shape when the load exceeds some threshold. The symmetry of the "cause" is preserved only in the sense that the bulge develops along any direction perpendicular to the compression direction; i.e., it is the multitude of all possible bulged shapes that preserves axial symmetry.

The present work¹ deals with this next level of complexity in the relationship between symmetries of phenomenon and causes since the confinement shows no chirality. It is the nematic elasticity that responds in a chiral manner to the confinement. Differently from the nematic droplets, in which the entire structure is of a certain handedness, the proposed symmetry-breaking geometry creates a periodic array of

left- and right-twisted domains. The material is sandwiched between two plates, one of which produces Mauguin's unidirectional planar alignment; the second plate allows \hat{n} to orient in any direction within its surface. Moreover, the slab is pierced by air columns extending from one plate to the other; the nematic–air interface aligns \hat{n} tangentially to itself. The director needs to curve in space to satisfy conflicting boundary conditions and to minimize the elastic energy of these curvatures. Different types of director distortions, splay, bend, twist, and saddle-splay (Figure 1), carry different elastic energy costs. For example, if the aggregates are infinitely rigid, bend would be impossible. If the aggregates are infinitely long, splay and saddle-splay would be prohibited as these deformations create voids that should be filled by ends of other aggregates, and there would be no ends available. The twist deformation of a nematic LCLC, and of many other lyotropic liquid crystals,⁷ is associated with the smallest elastic constant. Whenever the confinement requires the director to curve in space, the system seeks to replace the energetically costly splay and bend distortions with twist. The chirality of domains disappears if the nematic is heated into an isotropic fluid.

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The periodic pattern with twists observed by Geonhyeong Park et al.¹ contains an approximately equal amount of left- and right-handed domains, as expected, since there are no chiral molecules, and the energies of the two states are the same. Periodic arrays of left- and right-twisted domains can be produced in other geometries that do not require air bubbles and, thus, avoid multiple interfaces (Figure 2). In the simplest case, one can combine a unidirectionally rubbed plate with a flat plate that sets a wavy direction of alignment (Figure 2a). This might require a special technique of director alignment. One can instead use a wavy shape of the bounding plate, in combination with a unidirectionally treated substrate (Figure 2b). The tilts of the top plate with

respect to the bottom plate create splay director deformations if the director remains in the vertical xz plane. However, when the ratio of the twist elastic constant K_2 to the constant of splay K_1 is small, then any surface tilt by an angle $\Theta < \sqrt{K_2/K_1}$ would produce a twist of \hat{n} .⁸ The twist regions would be of left- or right-handedness, depending on the direction of the local tilt of the top surface in Figure 2b, and will be separated from each other by walls of an untwisted nematic.

The elegant design of arrays of alternating left- and right-twisted domains by Geonhyeong Park et al.¹ suggests a number of interesting research extensions. Chiral molecules, such as L-amino acids or D-nucleotides, can be added to the nematic LCLC to make it a cholesteric with a certain handedness. Would the array of left and right twists amplify the excess of molecular chirality to the macroscopic scale, so that the presence of even minute amounts of chiral molecules could be detected optically, say, by observations between crossed polarizers?⁹ Would there be a concentration that sets a homochiral twist, and if so, how is the frustration between the surface anchoring and bulk elasticity resolved? How fast would chiral molecules of certain handedness diffuse in left- and right-twisted domains? One could also add a racemic mixture of left- and right-handed molecules; could the connectedness of the right and left twists separate these chiral enantiomers in space? Would the confinement-induced chirality affect the dynamics of chiral microswimmers such as bacteria with helicoidal flagella¹⁰ and their artificial analogues? All these questions could be addressed with the approach described by Geonhyeong Park et al.¹

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