COMMENTARY

Prepatterned liquid crystal elastomers as a step toward artificial morphogenesis

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Morphogenesis, a biological process that translates nanoscale details of molecular organization into a macroscopic shape of an organism, is a marvel of nature. Morphogenesis starts with a placement of predesigned molecules of different chemical structure into predetermined locations, with subsequent out-of-equilibrium interactions and developments fueled by an influx of energy. It inspires scientists to learn how to create complex molecular architectures that yield nontrivial 3D shapes when actuated by external stimuli. A popular approach is to prepare a 2D precursor and then fold along certain directions into a 3D shape (1–3). The information about the desired 3D shape must be preinscribed into the initial 2D structure. Some solutions are borrowed from the ancient Japanese art of paper folding. In one technique, called origami (literally "fold-paper" in Japanese) the feat is achieved by inscribing a pattern of creases. Folding a piece of paper along strategically placed creases yields 3D structures, without cutting or gluing. In the case of mesoscale and nanoscale materials, creases are achieved by spatially varying chemical composition (4). In kirigami (literally "cut-paper" in Japanese), the 2D precursor can contain cuts that guide buckling and folding. The challenge to origami and kirigami that operate with isotropic materials, such as paper, is that bending and folding preserve the intrinsic geometrical properties of the surface. The facets of resulting 3D shapes remain locally flat, like the original piece of paper they are made of. Most surfaces of interest, such as a face, however, are clearly nonflat, with local "valleys" and "elevations" smoothly connected with each other without obvious creases. These smooth surfaces are much harder to produce than a regular origami. The paper in PNAS by Aharoni et al. (5) demonstrates how one can preprogram a flat film in such a way that it develops a smoothly curved replica of a face upon activation by heat. The crucial enabling feature is the anisotropic nature of the material, which represents the so-called "liquid crystal elastomer" (LCE). What enables the desired 2D-to-3D transformation is the predesigned pattern of molecular orientation that varies from point to point in the plane of the film.

To understand the advantage of an LCE over a regular isotropic material such as paper, consider the main geometrical characteristics of a thin film (3). A surface can be characterized by its metric that describes the distances between the neighboring points. A good approximation of the metric of a paper is a square grid of mutually perpendicular equidistant lines. When the paper is bent, the distances and angles between the lines are preserved. Arbitrary bending of paper preserves the metric and also the so-called "intrinsic curvature," universally known as the Gaussian curvature.

The Gaussian curvature and the mean curvature are two important characteristics of a curved surface. Both are introduced through the principal curvatures κ_1 and κ_2 defined at each point of the surface (6). To find these, one cuts the surface by a plane that contains a normal to this surface. The intersection is approximated by a circular arc. The curvature is the reciprocal of the radius of this arc. Among all curvatures at a given point, one can identify the minimum and maximum values κ_1 and κ_2; these are the principal curvatures. They can be negative or positive, depending on orientation of the arc with respect to chosen normal. The mean curvature is the average quantity, $H = (\kappa_1 + \kappa_2)/2$, while the Gaussian curvature is the product, $K = \kappa_1 \kappa_2$. Obviously, a flat paper has zero mean and Gaussian curvature. If the paper is bent, H becomes nonzero, but $K = 0$. A good example is a cylinder with only one finite principal curvature. It turns out that arbitrary bending of a piece of paper cannot change its Gaussian curvature. Thus, origami and kirigami shapes with a nontrivial $K \neq 0$ could be approached only approximately, through the introduction of many small facets connected by a network of folding lines or properly placed cuts (3).

What makes an LCE better than paper in creating a nonzero Gaussian curvature out of a flat film? The short answer is that the metric of an LCE can be made spatially varying.
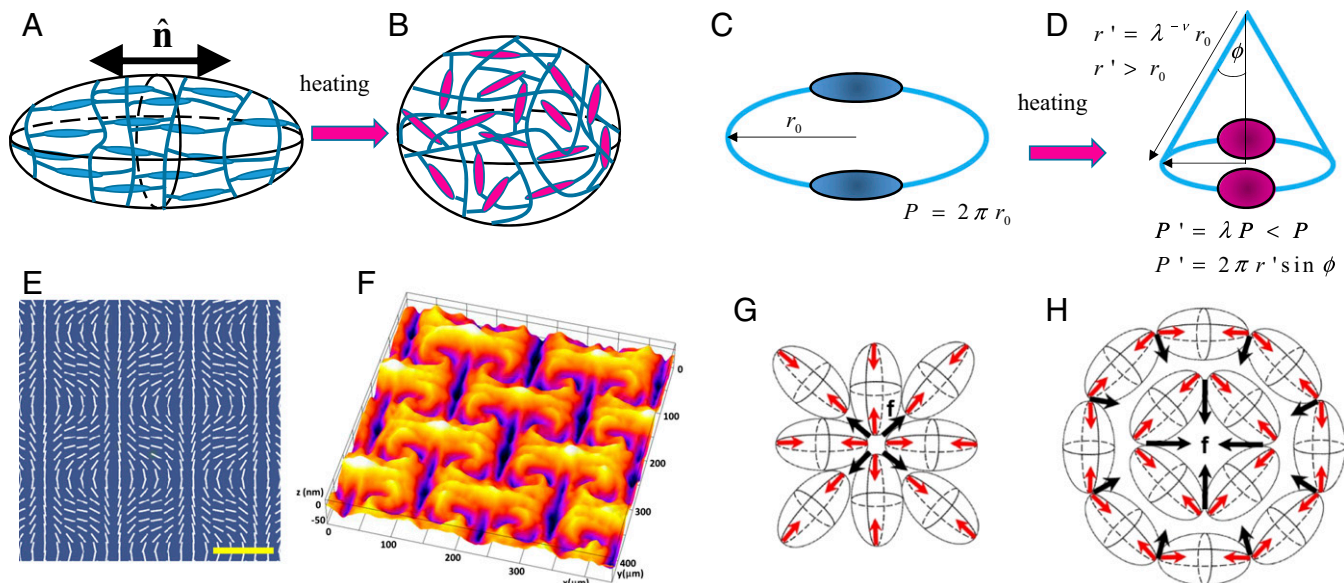
Fig. 1. (*A*) Prolate ellipsoid of an LCE network with the long axis along the director. (*B*) Upon heating, the ellipsoid shrinks along the long axis because of the reduction of orientational order. (*C* and *D*) LCE sheet with a circular director transforms into a cone upon heating. Modified with permission from ref. 9. Copyright 2010 by the American Physical Society. (*E* and *F*) Patterned smooth director produces elevations and valleys in an LCE coating upon heating. Image courtesy of Greta Babakhanova (Kent State University, Kent, OH). (*G* and *H*) Map of forces moving the material within the LCE coating as a result of shrinking of ellipsoids upon heating. Scale bar in *E* corresponds to 100 μm.

An LCE is an anisotropic rubber. It is formed by cross-linked polymeric chains with rod-like mesogenic segments (Fig. 1*A*). These segments are similar to the molecules forming low-molecular-weight liquid crystals (7, 8). In the so-called "nematic state" of an LCE, the segments are oriented along a nonpolar direction called the director $\hat{\mathbf{n}} \equiv -\hat{\mathbf{n}}$. Cross-linked polymeric chains are structurally anisotropic because of their coupling to the orientational order. The coupling enables the mechanical response of LCEs to external factors, such as temperature. The mechanism can be illustrated by imagining an LCE as composed of "blobs" of polymer chains (Fig. 1*A*). At room temperature, the mesogenic units are aligned predominantly along $\hat{\mathbf{n}}$; thus, the ellipsoid is prolate, with $\hat{\mathbf{n}}$ being its axis of symmetry. If the temperature is raised, the directions of the mesogenic units randomize; thus, the ellipsoid shrinks along $\hat{\mathbf{n}}$ and expands in perpendicular directions (Fig. 1*B*). If the director is uniformly aligned, shrinking of ellipsoids upon heating results in shrinking of the entire LCE film that behaves as an artificial muscle (7). An even more interesting response to heating occurs when the director varies in space.

Modes et al. (9) considered a thin LCE sheet in which the director forms a system of concentric lines; the configuration is called a topological defect of strength 1. Upon heating, the LCE shrinks along $\hat{\mathbf{n}}$ by a factor $\lambda < 1$ and expands in the perpendicular directions by a factor $\lambda^{-\nu}$ where ν is the thermal Poisson ratio. For a circular director field, heating means that the perimeter contracts, $P \rightarrow P' = \lambda P$, but the radii extend, $r_0 \rightarrow r' = \lambda^{-\nu} r_0$, which could be reconciled only if the initially flat film (Fig. 1*C*) morphs into a cone (Fig. 1*D*). The cone's tip carries localized positive Gaussian curvature $K = 2\pi(1 - \sin\phi)$, where ϕ is the cone opening angle (9). Away from the tip, the Gaussian curvature vanishes. However, defects that have a topological charge different from 1 could produce Gaussian curvature everywhere around their core (10). These theoretical considerations solve the "forward" design problem (i.e., finding the 3D shape of an activated LCE film when the director field inscribed in its 2D precursor is known). The predicted connection between the topological defects in 2D films and their 3D

buckling has been confirmed experimentally, as reviewed by White and Broer (8). A harder task is to solve an inverse design problem (i.e., to find a flat director field that would induce a desired 3D shape upon activation).

A big step forward in generalizing the theoretical insights into generation of the Gaussian curvature has been made by Aharoni et al. (11), who considered smoothly varying director fields. That paper (11) demonstrated that surfaces of revolution, such as spherical, pseudospherical, and toroidal surfaces, can be produced by patterning the 2D precursor with a smooth director field that depends only on one spatial coordinate. One other interesting feature in that study (11) was a recipe to remove degeneracy of 3D "bulging." As is clear from Fig. 1 *C* and *D*, a given distorted director field could make the 3D shape bulge either up or down upon heating. If the director is uniform across the film thickness, these two directions are equivalent. However, if the precursor is prepared with the director patterns at the top and the bottom surface slightly twisted with respect to each other, this degeneracy could be removed. The most important message of the work (11) was that the inverse design problem might be solvable even for more general geometries.

The study in PNAS by Aharoni et al. (5) combines a numerical approach based on the earlier paper by Aharoni et al. (11) with advanced experimental control of an elastomer preparation to demonstrate how the inverse design could produce an arbitrary desired shape, such as a face. The desired surface is first presented as a 3D triangulated mesh that is transformed numerically into a 2D mesh with triangles that carry a certain director orientation. The director varies from one triangle to another, as needed for faithful reconstruction of the 3D shape. At room temperature, the elastomer film is flat. Upon heating, the varying director field causes the triangular mesh to morph into a 3D structure that approximates the desired surface.

The experimental realization of the inverse design problem implies that the director pattern of the elastomer is preinscribed with great accuracy; small imperfections could produce disastrous

results, as evidenced by comparing the theoretically predicted director fields for a sphere and a torus (11). The experimental design used by Aharoni et al. (5) and developed by Yang and coworkers (12) relies on top-down microfabrication of a system of photopatterned microchannels. When these substrates are used to confine the liquid crystal in its fluid form (no cross-linking), the channels align the local director parallel to themselves. After the liquid crystal is aligned with the director pattern derived from numerical simulations, it is cross-linked to produce a 2D LCE precursor with a memorized director. Preparation also induces small twists of the director between the top and bottom surfaces to lift degeneracy of bulging (5, 11).

The demonstrated possibility of producing any 3D surface by preprogramming the director field of a 2D LCE (5) opens exciting perspectives for numerous technological applications, such as flexible electronic, medical, and aerospace devices. The approach can be expanded to elastomer-like materials of different chemical compositions, including the ones with an extraordinary tensile strength (13) and those that respond to stimuli other than temperature (8). A patterned director for controlled surface profiles can be also used in LCE coatings. Coatings differ from the films considered by Aharoni et al. (5, 11) in that one of their surfaces is affixed to a substrate. When the director is patterned (Fig. 1E), activation with heat leads to local redistribution of material, which results in spatially varying thickness (14) (Fig. 1F). Qualitatively, one can understand the mass transport by considering the shrinking LCE ellipsoid as being acted upon by a pair of forces at the poles. The sum **f** of these forces pushes the material within the plane of coating. For example, a radial deformation of the director causes a circular valley by moving the material toward the periphery (Fig. 1G), while the circular director produces an elevation (Fig. 1H). Programming arbitrary surface profiles of LCE coatings with variable thickness represents another challenging problem, the solving of which would expand the potential technological applications of LCEs.

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