

## Spontaneous Anchoring-Mediated Topography of an Orientable Fluid

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A topography in a Newtonian fluid occurs if there is a disturbance near the surface. But what if there is no such disturbance? We show by optical profilometry that a thin nematic film resting on a topological-defect-patterned substrate can exhibit a hill or divot at the opposing free (air) interface *in the absence of a topological disturbance at that interface*. We propose a model that incorporates several material properties and that predicts the major experimental features. This work demonstrates the importance of, in particular, anisotropic surface interactions in the creation of a free surface topography.

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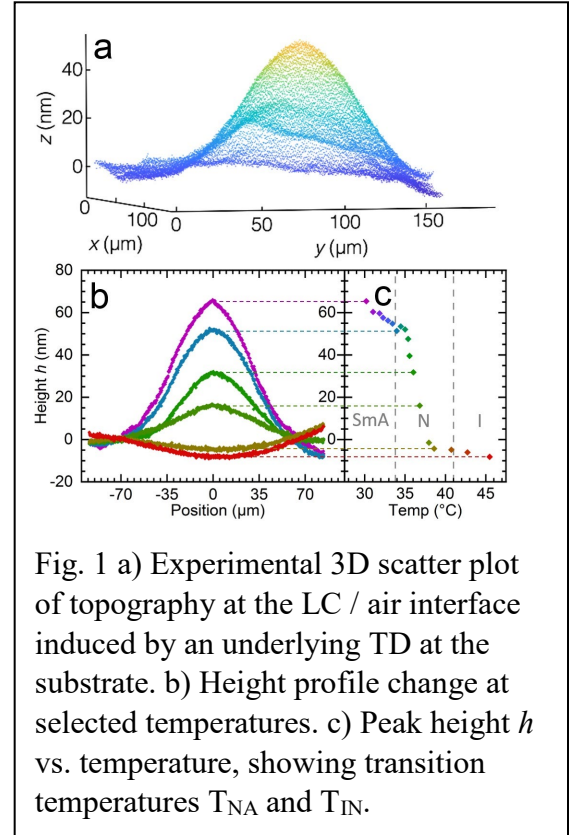
Freely flowing Newtonian fluids are, in general, unable to support an equilibrium topography at an interface with another fluid. Nevertheless, there has been an ongoing effort to find counterexamples. Under certain conditions it is known that an orientable Newtonian fluid, examples of which are nematic (but not smectic [1]) liquid crystals (LCs), certain polymers, and aqueous mixtures of tobacco mosaic virus, can support a topography when there is a disturbance near the interface. This can occur, for example, with small anisometric structures such as vesicles and tactoids [2,3,4,5,6], inclusions or defects residing at the free surface [7,8,9,10], or topological defects (TDs) that completely traverse the fluid film's thickness and that have reached the air interface. Such TDs can be pinned to the solid substrate as, observed by Virga and Schadt [11,12], or associated with mismatched boundary conditions in a chiral nematic LC [13,14]. But it is surprising that an orientable Newtonian fluid can possess an equilibrium free-surface topography *in the absence of a disturbance* at or near that surface. Why should this be? What sort of long range interactions could induce an “action-at-a-distance” [15] variation in the free-surface topography?

In this Letter we show experimentally and theoretically that a topological defect of strength  $m = +1$  (a so-called “boojum”) localized at the underlying substrate in a nematic LC can create a topography at the opposing nematic LC / air interface in the absence of any singularity traversing the film. Our “hybrid” boundary conditions (nominally planar at the substrate and vertical at the air interface) result in a topography at the fluid / air interface based on a tradeoff among elasticity, the isotropic component of the surface energy (surface tension), and its anisotropic part (anchoring), providing the first equilibrium topography of a Newtonian fluid in the absence of a singularity at the perturbed free surface and that is based solely on the material properties of the film and its interfaces.

Experimental details are described in Supplemental Material online [16,17]. A sample was prepared by AFM scribing a TD pattern of strength  $m=+1$ ,  $\varphi=0^\circ$  (radial) having a “confinement radius”  $\ell$  on a polymer-coated substrate [18]. A thin layer of liquid crystal 8CB was then spin-coated on the substrate. The LC’s free-surface topography was measured by optical profilometry.

Figure 1a shows a 3D reconstruction of the surface profile of the LC / air interface for film thickness  $d=610\pm30$  nm above an underlying  $m=+1$ ,  $\varphi=0^\circ$  (radially) patterned surface. Immediately visible is a hill-like protrusion rising above a nearly flat nematic surface. Reflecting the underlying pattern, the hill is azimuthally symmetric, and its height  $h$  above the background increases monotonically toward  $r=0$ , reaching a peak height  $h=52\pm4$  nm. This corresponds to 9% of the film’s total thickness. (Note that we have observed  $h/d$  as large as 0.21 in the nematic phase.)

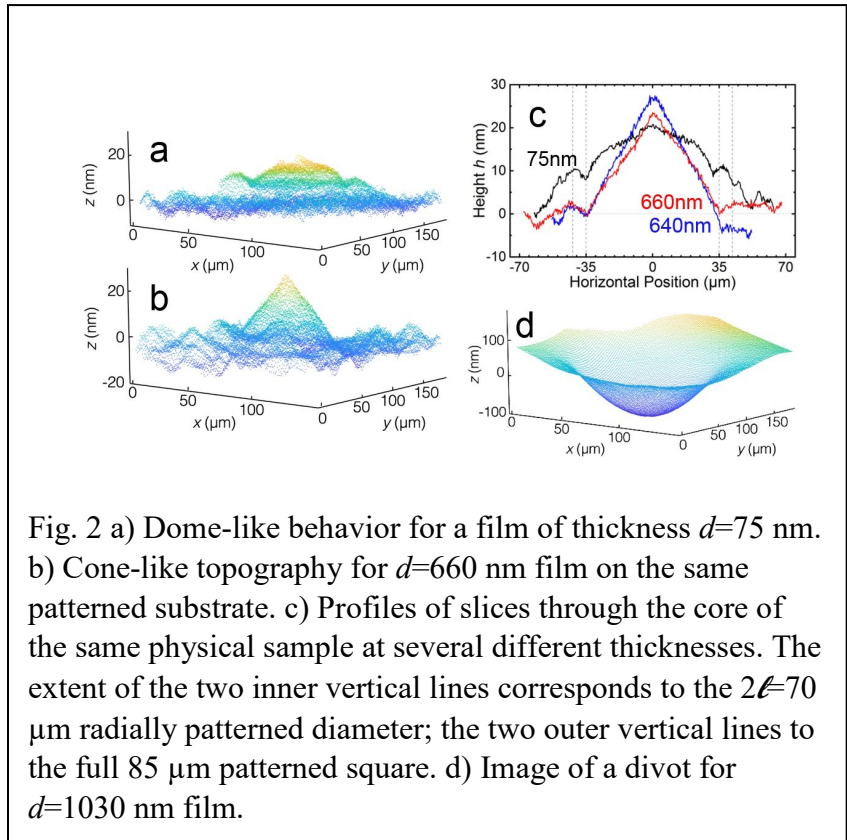
The height distribution  $h(r)$  changes significantly with temperature (Fig. 1b). It is virtually flat above the I–N transition temperature  $T_{NI} \sim 41^\circ\text{C}$ , with a tiny divot observed in Fig. 1b (in this sample only) due to a dust particle beyond  $r = \ell$ . A small hill becomes visible at the core after cooling below  $T_{NI}$ . This hill grows in height as we cool further into the nematic, which is our focus. Figure 1c shows the peak height  $h$  vs. temperature, including the pretransitional behavior on approaching  $T_{NA}$ . Although effects in the SmA phase are beyond the scope of the current work and will be published elsewhere, we note



several features specific to the SmA phase and distinct from the nematic: formation of *curved* oily streak defects [Error! Bookmark not defined.] transverse to the patterned easy axis; significant transfer of LC to beyond the patterned region with a hill rising above the patterned region, all of which is now depressed from the surrounding area; and an extremely sharp cone whose apex height ( $66 \pm 5$  nm) now reaches 10% of the film's asymptotic thickness. These smectic cones have been observed with absolute heights as large as  $h=200$  nm (for  $d=1200$  nm) and relative heights as large as 65% ( $h=50$  nm,  $d=75$  nm).

Returning to nematic films, the height, shape, and even the sign of the topography are found to depend on the film thickness  $d$ : Thinner films exhibit taller hills as a fraction of the film thickness, with  $h$  generally decreasing with increasing film thickness.

Additionally, for thinner films ( $d \sim 100$  nm), we observe that hills are more likely to have a dome-like (rather than cusp-like) shape (Fig. 2a), but become more conical with a

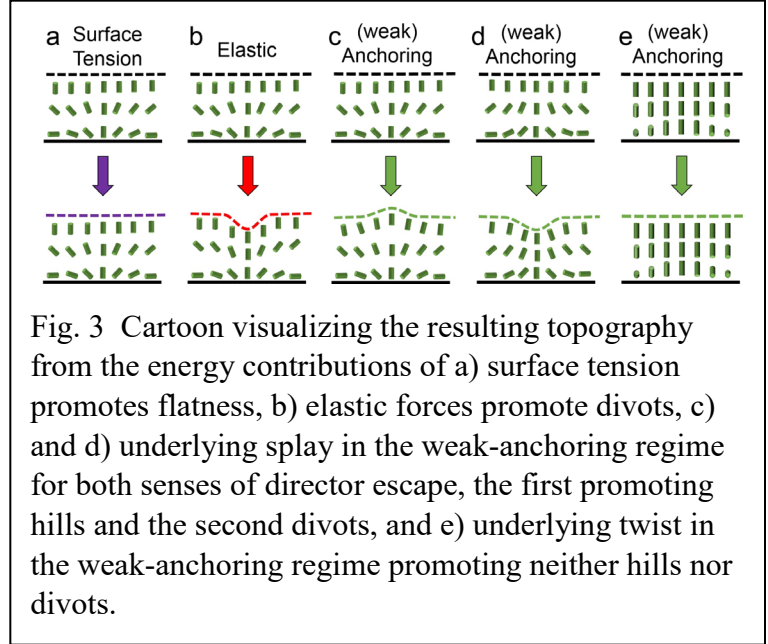


singularity at the peak for thicker films ( $\sim 600$  nm, Fig. 2b,c). For the dome-like topography, its rounded shape in conjunction with the vertical boundary conditions at the air interface ensure that variations in the director at the substrate smooth out rapidly with increasing  $z$ . Thus no

disclination line projects from the patterned surface defect through the LC to the top surface. This behavior is due to an energy balance and is borne out by our modeling below. *Thus, the dome-like behavior indicates the presence of a boojum at the patterned surface, and that the free-surface topography is **not** generated by a local surface defect or transmitted by a bulk disclination line — this is unlike the case reported in Refs. 11,12,13, and 14. Instead the topography is mediated through anchoring, as well as elastic forces from the patterned substrate to the free surface.* We also note that the height of the hill also depends on  $\ell$ , the distance out to which the radial ( $m=+1, \varphi=0^\circ$ ) TD is patterned:  $h$  increases monotonically with pattern diameter  $2\ell$  in the SmA phase ( $h=8, 10$ , and  $14\pm 2$  nm for  $\ell=15, 25$ , and  $35$   $\mu\text{m}$ , respectively for  $d=500\pm 20$  nm just below  $T_{NA}$ ), with similar but smaller (and thus noisy) results in the nematic phase as well. Finally, Fig. 2d shows a divot.

We also compared our nematic results to a region of the same substrate that had been patterned with an underlying  $m=+1, \varphi=\pi/2$  topological defect — this corresponds to an alignment pattern of concentric circles. This pattern exhibits no significant topography, suggesting that the source of the topography is not simply elastic relaxation near the core — indeed, both the radial and concentric circle patterns have the same total 2D elastic energy density (in the single elastic constant approximation) at the defect core.

We examine the three major terms of the free energy: surface tension, elastic forces, and anchoring. In both the radial and concentric circle geometries, **surface tension** at the free surface tends to minimize curvature, promoting a uniformly flat topography (Fig. 3a). Next are **elastic forces**, with the director constrained (nearly) normal



to the free surface. Focusing on the radial easy axis pattern, very close to  $r=0$  the director must melt; become biaxial [19,20,21] when tightly confined in specific geometries [22,23,24], a condition that is not met in our experiments; or become vertically-aligned at the substrate. The latter scenario is effectively the common escaped radial configuration [25,26] and is consistent with our setup. For the latter case the far-field region beyond  $r > \ell$  finds its polar orientation  $\theta$  undergoing a bend/splay distortion along the  $z$ -axis to meet the hybrid-alignment boundary conditions. The total energy of this far-field region can be reduced by increasing the local film thickness to spread the distortion over a larger  $z$ -distance. With a constant volume constraint, material must be transported away from the core region near  $r=0$ , thus promoting a divot for both configurations (Figs. 2d and 3b). We note that these nematic divots derive from very different physics than those in the SmA phase [27,28].

The third term, **anchoring**, is the source of the hill-like behavior (Fig. 3c) for the radial pattern. Due to the hybrid boundary conditions, there is a director torque at the surfaces, and the LC must be pretilted slightly, by angle  $\theta_f(r)$ , from the normal at the free surface (vanishing as

$r \rightarrow 0$ ). This pretilt anchoring cost can be mitigated by a deformation of the free surface to form a hill (Fig. 3c) or a divot (Fig. 3d), depending on the sense of pretilt at the substrate. Figure 3e shows the case of a concentric circle easy axis pattern, with a twist distortion along an axis passing through  $r=0$  at the substrate. Elastic energy relaxation requires that  $\nabla h$  be azimuthal, although owing to azimuthal symmetry  $\nabla h=0$ . Thus free-surface anchoring promotes neither hill nor divot, leaving elasticity as the main driving force for the topography. That the topography is negligible for  $m=+1$ ,  $\varphi=\pi/2$  (Fig. 3e) suggests that the elastic forces are weak.

The relative tradeoff among the three energy contributions determines the magnitude of  $h$  and its sign. We observed the pretilt phenomenon experimentally, wherein heating and cooling through  $T_{NI}$  randomly nucleates the sense of pretilt – this is due to the bi-directional scribing – thereby interchanging hill and divot. We note that scribing the patterns uni-directionally predisposes one sense of substrate pretilt, with hills for radially-inward scribing and divots for outward scribing. Thus, the shape of the topography depends on force balance, with anchoring typically dominating. This, in turn, depends on the LC's materials parameters, the scribing pattern, the scribing radius  $\mathcal{L}$  and the film thickness  $d$ .

We now turn to an overview of the modeling with a patterned defect at the substrate; a more extensive exposition will be published elsewhere. The free energy of the system consists of the usual surface tension, elastic, and anchoring contributions,

$$F = \frac{1}{2} \int_{\Omega} f(\mathbf{n}, \nabla \mathbf{n}) dV + \int_{\partial\Omega} \left[ \sigma - \frac{W}{2} (\mathbf{n} \cdot \mathbf{n}_e)^2 \right] dA, \quad (1)$$

where  $\sigma$  is the surface tension; the elastic contribution is  $f = K_{11}(\nabla \cdot \mathbf{n})^2 + K_{22}(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_{33}|\mathbf{n} \times \nabla \times \mathbf{n}|^2$ ;  $K_{11} = K_{22} = K_{33} = K$  are the splay, twist and bend elastic constants in the equal constant approximation; and  $W$  is the anchoring strength coefficient. The second integral is taken over the free surface with the director  $\mathbf{n}$  fixed at the lower substrate.

Two length scales,  $\zeta = K/\sigma$  and  $\xi = K/W$ , characterize the relative influence of the three terms. Far above the  $N - \text{SmA}$  transition, approximate values for these are  $\zeta \sim 0.4 \text{ nm} \ll \xi \lesssim 100 \text{ nm}$ ; hence the upper surface remains flat and the director adopts the configuration in Fig. 3a. Note that the director deviates slightly from vertical above the pattern due to the finite anchoring strength. As the nematic approaches the  $N - \text{SmA}$  transition, two effects occur: First,  $K_{22}$  and  $K_{33}$  diverge [29]; second, the SmA phase grows inward from the substrate [30], enhancing surface order and, importantly, increasing the surface anchoring  $W$  [31,32]. This tends to enhance  $h$  for both hills and divots on nearing  $T_{NA}$ .

Now suppose the free interface can vary. The **surface tension** term in Eq. 1 resists deformations (Fig. 3a). **Elastic** stresses tend to push the interface upwards to mitigate  $d\theta/dz$ : As described above, this leaves a divot near  $r=0$  where  $d\theta/dz=0$  (Fig. 3b). The **anchoring** term requires careful consideration: It is typically thought to promote alignment of the director with respect to a fixed easy axis  $\mathbf{n}_e$  defined relative to the surface normal. *Here we reverse the causality and investigate how a spatially changing  $\mathbf{n}$  can induce variations in  $\mathbf{n}_e$  and hence the topography of the surface.*

To do so, the free surface is parameterized in dimensionless (scaled by  $d$ ) cylindrical coordinates  $(\rho, u, Z)$  as  $\mathbf{X} = \{\rho, u, H(\rho)\}$  and hence the surface normal is  $\hat{\mathbf{s}} = \{-H'(\rho), 0, 1\}/(1 + H'(\rho)^2)$ . Here  $H = h/d$ ,  $L = \ell/d$ , and the prime denotes  $\partial/\partial\rho$ . Similarly, the director at the surface is parametrized to lie at a constant azimuthal angle  $\phi$  to the radial direction,  $\mathbf{n} \equiv \{n_\rho, n_u, n_z\} = \{\sin\theta(\rho)\cos\phi, \sin\theta(\rho)\sin\phi, \cos\theta(\rho)\}$ . Hence, the anchoring term in Eq. 2 becomes

$$F_w = -\pi W d \int_0^L \frac{(\cos\theta(\rho) - H'(\rho)\cos\phi\sin\theta(\rho))^2}{\sqrt{1+H'(\rho)^2}} \rho d\rho, \quad (2)$$



revealing a coupling between topography,  $H'(\rho)$ , and orientation  $\theta(\rho)$ . Notice that the coupling vanishes if  $\theta = 0$ , where the director is vertical, and similarly if  $\phi = \pi/2$ , where the director is azimuthal; here a spatially varying director does not induce topography.

Experimentally,  $H \ll 1$ , suggesting a perturbative approach. We therefore series expand about a solution where the director is nearly vertical at the free surface and fixed by elasticity,  $\theta \approx \alpha \theta_1(\rho)$ , and the interface is nearly flat,  $H(\rho) \approx \alpha H_1$ , where  $\alpha$  is an expansion parameter. We include the surface tension,

$$F_\sigma = 2\pi\sigma d \int_0^L \sqrt{1 + H'(\rho)^2} \rho d\rho$$

and a volume constraint  $2\pi\lambda d \int_0^L H(\rho) \rho d\rho$  but neglect the elastic stress as this has leading order  $\alpha^3$  while the other terms are of order  $\alpha^2$ . With these considerations, the linearized Euler-Lagrange equation is obtained,

$$(1 + w)(H_1' + \rho H_1'') + 2w\cos\phi(\theta_1 + \rho\theta_1') + \lambda\rho = 0, \quad (3)$$

where  $w = W/\sigma$ . A suitable ansatz for  $\theta_1$  is  $\theta_1 = \frac{\pi}{2} \tanh(\pi\rho/2)/(1 + \Gamma)$  where  $\Gamma = Wd/K$ .

Inserting this into Eq. 3, we obtain a solution,

$$H(R) = H_0 - \frac{\lambda\rho^2}{2\pi(1+w)} - \frac{2w\cos\phi \log[\cosh(\pi\rho/2)]}{(1+w)(1+\Gamma)}. \quad (4)$$

The constants  $\lambda$  and  $H_0$  are determined by imposing the boundary condition  $H'(L) = 0$  and volume constraint  $\int_0^L H(\rho) \rho d\rho = 0$ . From the solution (Eq. 4), the magnitude of the dimensionless topography  $\Delta H \equiv H(L) - H(0)$  may be estimated,

$$\Delta H = \frac{w\cos\phi[4\log(\cosh(\pi L/2)) - \pi L \tanh(\pi L/2)]}{2(1+w)(1+\Gamma)},$$

and solutions are plotted in Fig. 4a for different  $L$ . The profile becomes increasingly conical with increasing  $L$ . Thus, we have the following takeaways: i) our analytic model articulates the

mechanism(s) for the topography, ii) it predicts that a topography is observed only for the case of a radial surface pattern, consistent with experiment, and iii) it predicts that the topography scales with confinement distance  $L$ , also consistent with observation.

We also perform numerical simulations relaxing the strong assumptions of the above model. The full free energy (Eq. 1) with three elastic constants is minimized subject to a volume constraint both with respect to the director and the shape of the domain using one of the authors (TJA's) *morpho* code [33]; an initial 2D rectangular domain is used and all quantities are represented using linear interpolation on a triangular finite element mesh. The height is fixed at  $\rho = L$  on the right hand boundary. A typical height profile is displayed in Fig. 4b and closely resembles those from the analytical model despite the much less restrictive assumptions of the calculation. Additionally, we display the normal component of the generalized force  $\frac{\partial F}{\partial x_i} \cdot \hat{\mathbf{s}}$  on the  $i$ th boundary vertex due to the respective terms (Fig. 4c)

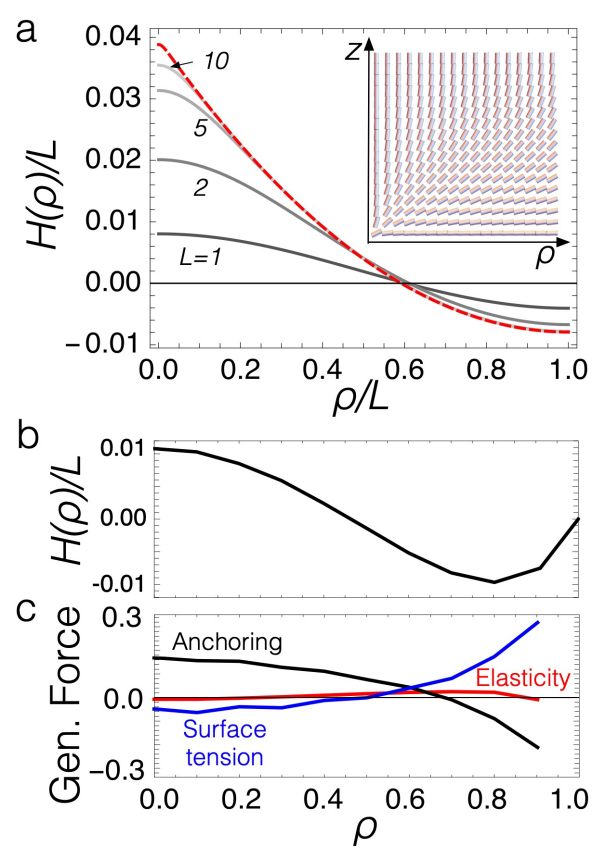


Fig. 4 a) Cartoon of flat interface solution (inset) and analytical height profile for different  $L$ ;  $w = 0.1$ ,  $\Gamma = 10$ ,  $\phi = 0$ . Asymptotic solution for  $L \rightarrow \infty$  is shown in red for comparison. b) Numerically minimized height profile with finite elements. c) Generalized forces on the boundary vertices due to different terms in the elastic energy.

To summarize, we have shown experimentally and theoretically that the topography of a nematic LC, *i.e.*, an orientable Newtonian fluid, at an air interface can be determined by the easy

axis pattern of the underlying substrate. The interplay of surface tension, elasticity, and especially anchoring alone determines the shape of the free-surface topography, without the need of a singular defect running from the substrate to the air interface.

### **Acknowledgments**

We thank Profs. Robin Selinger, Nigel Mottram, Emmanuelle Lacaze, and Samo Kralj for useful discussions. Support came from the NSF under grants DMR1910797 (AJF and CR) and DMR1654283 (TJA).

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