Chiral-mechanical transitions in topologically imprinted elastomers

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We extend a previous model for chirally imprinted monodomain nematic elastomers to allow a director rotation (by an angle $\pi/2-\theta$) towards the pitch axes of the imprinted helices. We find that provided the rubber matrix is allowed to spontaneously deform, the director array will make use of this additional degree of freedom, relaxing into a conical state in both the low and high imprinting efficiency regimes. Consequently, the transition between the regimes of differing imprinting efficiency is coupled to angle θ. This interdependence is nontrivial and involves discontinuous director rotation at the transitions.

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I. INTRODUCTION

Just as conventional rubbers, nematic elastomers are formed by cross-linking long chain polymer molecules. However, unlike conventional rubbers, the long chains incorporate rod-like liquid crystal molecules (mesogens) along their length, and as a result these materials exhibit interesting behavior. This has stimulated much research in recent years [1].

The idea of chiral imprinting was mooted by de Gennes [2]. He suggested that liquid crystalline order might be set up in networks by first dissolving polymers in a liquid crystalline phase, and then cross linking. In contrast to liquid crystal elastomers, the polymers envisaged by de Gennes would not have had liquid crystal molecules embedded.

Inspired by de Gennes' idea, successful experimental efforts have been made to imprint nematic elastomers with a local helical structure [3,4]. These imprinted monodomain elastomers were manufactured by adding a chiral solvent to a nematic polymer melt to create a cholesteric phase. Cross linking then "locks" in this helical structure by making permanent topologies between the chains. Achieving monodomain involved techniques such as multistage crosslinking, and ongoing experimental effort is very much guided by potential applications [3,4]. Evidence of successful imprinting was provided by absorption spectra obtained from the elastomer after the solvent had been completely removed. These showed a characteristic peak at a wavelength corresponding to the chiral pitch. The removal of solvent with twisting power leaves behind it a competition: the essentially nematic matrix now has to pay a Frank elastic penalty for having a twisted (helical) director distribution. But relieving this by unwinding means that the director has to move with respect to the elastic matrix in which it is embedded. There is a rubber-elastic penalty for performing the untwisting. If the untwisting penalty is too high, the system remains helical—the imprinting is stable. If the Frank penalty is too high, it unwinds and the imprinting efficiency is less that 100%. A theoretical model of this chiral imprinting was proposed by Mao and Warner [5]. In this model the free energy of an imprinted elastomer is expressed in terms of the configuration of its unit director field [7], $\vec{n}(\vec{r})$, after the chiral solvent is removed, and also its configuration at formation. The free energy is then minimized to find the current physical configuration. The efficiency of the process, defined as the ratio of helical twists retained after removal of the solvent to the number present before, is then found in terms of known and tunable physical parameters. These represent the extent of cross linking, the resistance to distortion of nematic ordering, and the pitch of the rubber in the presence of the chiral solvent. The model predicts an abrupt transition from a fully imprinted to a very low efficiency state when a simple combination of these parameters reaches a critical value of $2/\pi$.

The assumption is made in Ref. [5] that the director remains perpendicular to the helix axis after the solvent is removed. In the present paper, we extend this model to allow the director freedom to rotate toward this axis. In doing so we find that if we do not allow for any local or global mechanical relaxation in response, then the helix remains upright [8]. However, by allowing a limited class of relaxations we find that the director array will make use of this extra degree of freedom, relaxing into the conical state in both the imprinted and low imprinting efficiency regimes. As a result, the abrupt transition between the regimes becomes dependent on the extent of this new rotation. In the appendixes, where the detailed analysis is presented, the approximations we have used are discussed. These are principally that the conical angle does not vary with position along the helix, and simplification in the form of the spontaneous strain which then is not totally compatible.

II. FREE ENERGY OF A RELAXED IMPRINTED ELASTOMER

The free energy of a chirally imprinted nematic elastomer contains two competing components. First, there is a cost associated with distorting the natural nematic order of the material, the Frank free energy density:

$$f_{\mathrm{Frank}}=\frac{1}{2}\{K_1(\vec{\nabla}\cdot\vec{n})^2+K_2[\vec{n}\cdot(\vec{\nabla}\wedge\vec{n})]^2+K_3[\vec{n}\wedge(\vec{\nabla}\wedge\vec{n})]^2\}, \tag{1}$$

where $K_{1,2,3}$, respectively, measure the energy penalty for splay, twist, and bend, the three modes of nematic director

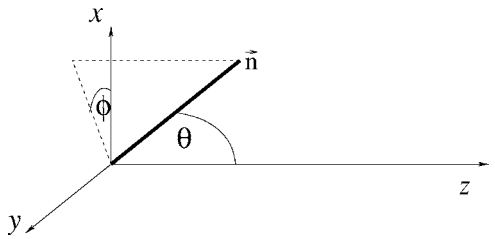

FIG. 1. The director in spherical polars.

distortion. In our problem splay will play no part.

Second, there is a cost to be paid for deforming away from the imprinted chiral structure, given by the nematic rubber elastic free energy which may be written [1]

$$f_{\text{elast}} = \frac{\mu}{2}\text{Tr}(\underline{\underline{\ell}}_0 \cdot \underline{\underline{\lambda}}^T \cdot \underline{\underline{\ell}}^{-1} \cdot \underline{\underline{\lambda}}), \tag{2}$$

with μ being the linear shear modulus. The step length tensors, $\underline{\underline{\ell}}_0$ and $\underline{\underline{\ell}}$, characterize the Gaussian chain shape before and after the solvent is removed. Tensor $\underline{\underline{\lambda}}$ describes the mechanical deformation of the elastomer since cross linking.

Assuming the elastomer is unconstrained after solvent removal, the elastic energy must be minimized with respect to $\underline{\underline{\lambda}}$ (see Appendix A for details), leading to

$$f_{\text{elast}} = \frac{1}{2}D_1\gamma(\theta)\{a(\theta) - b(\theta)\cos^2[\phi(z) - q_0 z]\}^{2/3}, \tag{3}$$

where θ and $\phi(z)$ specify, respectively, the polar and azimuthal angles of the director in spherical polar coordinates (see Fig. 1), and z defines the helical axes. $\phi(z)$ varies along the helical axes z whereas θ, known as the helical cone angle, is assumed to be constant. The definitions of D_1 and the dimensionless γ, a, and b can be found in Appendix A. D_1 measures the penalty for rotations of the director with respect to the elastic matrix. In the small distortion limit it corresponds to a de Gennes modulus of continuum theory. γ, a, and b are simple functions of $\sin^2\theta$ and of the anisotropy r of the locally nematic phase into which helical director arrangement has been imprinted.

The Frank free energy density for our system reduces to

$$f_{\text{Frank}} = \frac{\phi'^2(z)}{2}[K_2\sin^4\theta + K_3\cos^2\theta\sin^2\theta], \tag{4}$$

as splay is not present in the geometry. The full free energy density is $f_{\text{Frank}} + f_{\text{elast}}$. In order to write this in a succinct way, we introduce

$$\kappa = K_3/K_2, \tag{5}$$

$$\omega(\theta) = (\sin^4\theta + \kappa\sin^2\theta\cos^2\theta), \tag{6}$$

where the constant κ measures the relative cost of bend to that of twist distortion, and is typically $\sim$1–5. Using these definitions, the free energy per unit area perpendicular to the helix axis, for a sample of length L, is

$$F(L) = \frac{1}{2}\int_0^L dz(K_2\omega\ \phi'^2(z) + D_1\gamma\{a - b\cos^2[\phi(z) - q_0 z]\}^{2/3}), \tag{7}$$

where we have left out the θ dependence of our newly defined functions in the interests of notational simplicity.

The Euler-Lagrange equations taken directly from this integral are not analytically tractable. The situation is simplified by writing part of the second term as a Fourier cosine series [6]

$$\{a(\theta) - b(\theta)\cos^2[\phi(z) - q_0 z]\}^{2/3} = \beta_0(\theta) + \sum_{n=1}^{\infty}\beta_{2n}(\theta)\cos\{2n[\phi(z) - q_0 z]\}. \tag{8}$$

The free energy may be brought into a particularly simple form if we take only the first two nonzero terms of the series. In order to convince ourselves of the veracity of the predictions we make using this approximation, it is essential to have a measure of how accurate it is for given values of its arguments. Clearly the quality of the approximation increases with the ratio $a(\theta)/[b(\theta)\cos^2(\phi - q_0 z)]$ (cf. binomial expansion), so it will be at its least accurate when $\phi(z) = q_0 z$, since in this case $\cos^2[\phi(z) - q_0 z] = 1\ \forall z$. With this in mind we set $\cos^2[\phi(z) - q_0 z] = 1$ and define the following function:

$$\Delta(\theta) = [\beta_0(\theta) + \beta_2(\theta)] - [a(\theta) - b(\theta)]^{2/3}, \tag{9}$$

which gives an upper bound to the error in our approximation. This function will later allow us to show that the minima of the free energy which we numerically determine are not simply artifacts of the approximation.

We now make the changes of variables:

$$\psi = q_0 z - \phi + \frac{\pi}{2}, \tag{10}$$

$$\xi(\theta) = \left(\frac{K_2}{D_1}\right)^{\frac{1}{2}}\left(\frac{-\omega(\theta)}{2\gamma(\theta)\beta_2(\theta)}\right)^{1/2}, \tag{11}$$

$$u = \frac{z}{\xi(\theta)}, \tag{12}$$

$$\alpha_0 = q_0\left(\frac{K_2}{D_1}\right)^{1/2}, \tag{13}$$

$$\alpha(\theta) = q_0\xi(\theta) \tag{14}$$

which lead to

$$F(L) = \frac{LD_1\gamma(\beta_0 - \beta_2)}{2} - D_1\gamma\beta_2\xi\int_0^{L/\xi} du[(\psi' - \alpha)^2 - \sin^2\psi]. \tag{15}$$

Notice that the integral component of this has the form of a Lagrangian for a particle in a sine squared potential. This property is shared by the free energy derived in Ref. [5]

where director rotations, θ, and elastic deformation were ignored. α_0 was introduced [5] as the *chiral power*. When rotations θ and elastic relaxation are ignored then the value of α_0 determines the efficiency of the imprinting process: $\alpha_0 < 2/\pi \Rightarrow$ imprinted, $\alpha_0 > 2/\pi \Rightarrow$ low efficiency, that is, loss of helical twists. Three elements compete to give the chiral power, see Eq. (13). If a strongly twisting solvent was added, the pitch of the helix at cross linking was short and the wave vector q_0 large. The Frank penalty for twist incurred when the solvent is removed, $\frac{1}{2}K_2 q_0^2$, is thereby greater and leads to unwinding (α_0 larger). Equally, if the Frank penalty K_2 for twist is large then untwisting is also more likely. Conversely, if the penalty D_1 for rotating the director with respect to the matrix is high (α_0 smaller) then untwisting is less likely to occur.

III. PHYSICAL PREDICTIONS

We now seek to minimize the total free energy, Eq. (15), with respect to director orientation $\psi(u)$, following the method introduced in Ref. [5] the relevant details of which are given in Appendix B. The results are as follows.

For $\alpha(\theta) < 2/\pi$, the imprinted helices are retained, and the solution is referred to as "localised." For $\alpha(\theta) > 2/\pi$, the helices begin to be lost, and the solution is referred to as "delocalised." The rubber is not perfectly imprinted. We refer to $\alpha(\theta)$ as the *effective chiral power* because it plays the same role as the chiral power α_0 does when changes in θ and elastic relaxation are ignored [5].

Dimensionless minimized energy densities for the (de)localized regimes are, respectively,

$$g_{\mathrm{loc}}(\theta) = \alpha_0^2 \omega(\theta) + \gamma(\theta)[a(\theta) - b(\theta)]^{2/3}, \tag{16}$$

$$g_{\mathrm{deloc}}(\theta) = \gamma(\theta)\{\beta_0(\theta) - \beta_2(\theta)[3 - 2\tilde{c}^2(\alpha(\theta))]\}, \tag{17}$$

where $\tilde{c}$ is the solution of

$$2c\mathcal{E}(c^{-1}) = \alpha(\theta)\pi. \tag{18}$$

Physically, θ may take on any value in the interval $[0, \pi]$. The value of θ which minimizes g over this interval is the physical value we expect to see in a relaxed sample.

The dimensionless free energy of Eqs. (16) and (17) may be evaluated numerically in MATHEMATICA, its form depending on the choice of the three parameters α_0, κ, and r. Typically [1], $K_i \sim 2\text{–}4 \times 10^{-12} N$ with $K_3 > K_2$, and $2 < r < 4$. Making the choices $\kappa = 1.3$ and $r = 2$, we may find the angle θ_m which minimizes $g(\theta)$ numerically, as a function of the chiral power α_0. Figure 2 shows the results of this calculation, along with the corresponding effective chiral power $\alpha(\theta_m)$.

From the figure we see that the director array relaxes into a conical state while in the imprinted regime for $\alpha_0 > 0$, rotating further toward the helix axis as the chiral power is increased. This is explained as follows: When $\alpha_0 = 0$ then the dimensionless free energy is

$$g_{\mathrm{loc}}(\theta) = \gamma(\theta)[a(\theta) - b(\theta)]^{2/3}, \tag{19}$$

which is a monotonically decreasing function of θ for $\theta \in [0, \pi/2]$. Hence $\theta_m(\alpha_0 = 0) = \pi/2$. If we now increase the chiral power then $\omega(\theta)$ begins to play a role. For $\kappa < 2, \omega$ is a monotonically increasing function of θ for $\theta \in [0, \pi/2]$, so that provided its maximum at $\theta = \pi/2$ has a steeper curvature than the minimum of the anchoring term, then θ_m will be shifted away from $\pi/2$. We can check this by Taylor expanding g_{loc} to second order about $\theta = \pi/2$:

$$g_{\mathrm{loc}}(\pi/2 + \epsilon) \approx \alpha_0^2 + \frac{3r}{(r-1)^2} + \alpha_0^2(\kappa - 2)\epsilon^2 + \text{higher-order terms}. \tag{20}$$

Since this is a decreasing function of ϵ (because $\kappa < 2$) then an increase in α_0 will lead to a shifting of θ_m away from $\pi/2$.

As α_0 passes through 0.518, θ_m undergoes a jump. This is due to the presence of two local minima of equal depths in $g(\theta)$. As the chiral power passes through its critical value, the localized minimum becomes shallower than the delocalized minimum, and the system jumps to the untwisted state. Figure 3 shows the form of the dimensionless free energy for $\alpha_0 = 0.52$ which is just above the transition value.

Between the two local minima of g there is a pronounced discontinuity due to the fact that we are using the Fourier approximation in the delocalized regime. Since the discontinuity is of the order of the depth of the delocalized minimum, then it is clearly essential that we check that the minimum is not an artifact of our approximation. When $\alpha_0 = 0.52$ the boundary between the localized and delocalized regimes is at $\theta_{\mathrm{disc}} = 0.717$, and the discontinuity is $\delta g = 5.81 \times 10^{-4}$. The upper bound for the error in g is

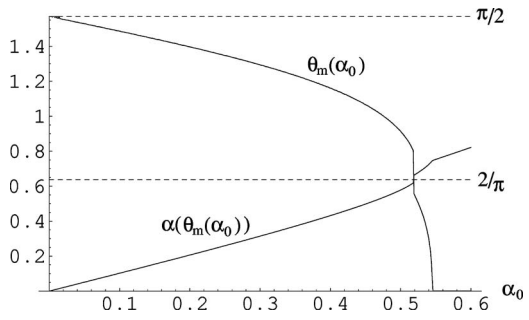

FIG. 2. The physical value of the helix cone angle θ rad as a function of α_0 when $\kappa = 1.3$ and $r = 2$.

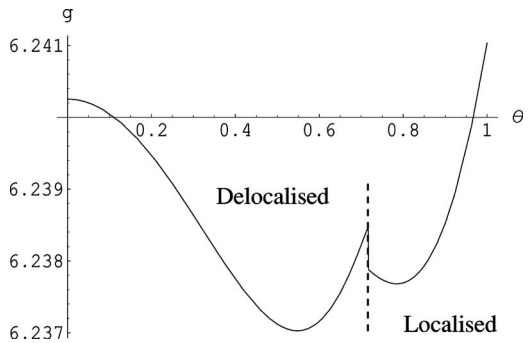

FIG. 3. The two local minima in the dimensionless free energy, responsible for the discontinuous change in θ_m. Here $\kappa = 1.3$, $r = 2$, and $\alpha_0 = 0.52$.

$$\gamma(\theta_{\text{disc}})\Delta(\theta_{\text{disc}}) = 5.86 \times 10^{-4}, \tag{21}$$

which is consistent with δg.

We now wish to check that the size of the error is significantly smaller than the depth of the delocalized minimum with respect to $g(0)$. The minimum lies at $\theta_m = 0.548$, so it has a depth $g(0) - g(0.548) = 3.22 \times 10^{-3}$. At the minimum, $\gamma(\theta_m)\Delta(\theta_m) = 2.09 \times 10^{-4}$, which is approximately 6% of its depth. We conclude that our predictions about the behavior of θ_m are qualitatively correct.

The jump in θ_m due to the two local minima produces the discontinuity in the effective chiral power we see in Fig. 2. A key difference from the predictions of the original paper [5] is that the imprinted to untwisted transition no longer occurs at $\alpha_0 = 2/\pi$, but rather when $\alpha(\theta_m) = 2/\pi$. It is the case that $\alpha(\theta) > \alpha_0 \forall\, \theta \in [0, \pi/2]$ and $r, \kappa > 1$ so the transition will always occur for a lower value of α_0 than it does when $\theta = \pi/2$ and distortions $\underline{\underline{\lambda}}$ are forbidden [5].

Increasing α_0 further beyond the transition shifts the delocalized minimum toward $\theta_m = 0$ as shown in Fig. 2. At each value of α_0 we find that the upper bound on the error is less than 10% of the depth, so we can again be confident that our predictions are qualitatively correct. The behavior is explained as follows: The unwinding of the helix associated with delocalized solutions dramatically reduces the importance of the Frank term, which is proportional to $\phi'^2(z)$, so that the elastic term becomes the dominant contribution to the free energy. Within the elastic term

$$F_{\text{elast}}(L) = \frac{1}{2}\int_0^L dz D_1 \gamma\{a - b\cos^2[\phi(z) - q_0 z]\}^{2/3}, \tag{22}$$

unwinding makes the argument of the cos-squared term nonzero. Where pure unwinding is the only effect of delocalization, then the average value of F_{elast} would not depend on its extent, because the argument of the cos-squared term would be linear in z allowing us to approximate it with an average value $\cos^2[\phi(z) - q_0 z] \approx 1/2$. However, the coarsening of the helix increases the average size of the $\cos^2$ term and the minimum of the full free energy is determined by the size of a relative to the average of $b\cos^2[\phi(z) - q_0 z]$ within Eq. (22).

The extent to which lengthening occurs gives the efficiency of the imprinting process e_0 defined as the fraction of twists retained

$$e_0 = \frac{N_0 - N_{\text{lost}}}{N_0}, \tag{23}$$

where N_0 is the initial total number of twists in the sample, and N_{lost} is number lost. This can be derived analytically for both localized and delocalized regimes (see Appendix C for details). Figure 4 shows the efficiency for the case we have been considering. An important point to note is that the infinite negative slope of e_0 at the localized/delocalized transition point ($\alpha_0 \approx 0.518$) would be present even without the discontinuity in the effective chiral power-in the nonconical case there is infinite slope but with no jump. Beyond $\alpha_0 \approx 0.545$, the director is globally aligned with the z axis, that is $\theta = 0$. Then imprinted structure is entirely lost, i.e.,

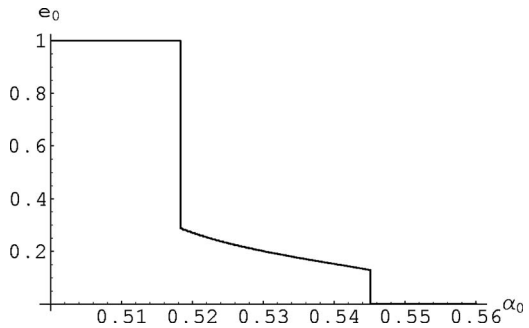

FIG. 4. The efficiency of the imprinting process as a function of α_0 when $\kappa = 1.3$ and $r = 2$. Note that for lower values of α_0 the efficiency remains equal to unity.

$$e_0 = 0 \text{ if } \theta_m = 0. \tag{24}$$

The dependence of θ_m on the chiral power has a qualitatively different form when $\kappa > 2$. In this case the coefficient of $\phi'(z), \omega(\theta)$, which sets the structure of the Frank component of the energy possesses two local minima: $\omega(0) = 0$ and $\omega(\pi/2) = 1$. Let us consider the imprinted regime. The anchoring term is monotonically decreasing on $[0, \pi/2]$ so that $\theta_m(\alpha_0 = 0) = \pi/2$. If we increase α_0 from zero [so that $\omega(\theta)$ plays a role] the minimum will remain at $\pi/2$ because $\omega(\theta)$ possesses a local minimum there. The system will remain in this state as we increase α_0, until a deeper minimum appears somewhere else.

In the case $\kappa = 2.5$, numerical investigation reveals that for all values of $r \in [1, 4]$ this deeper minimum always appears at $\theta = 0$, so that the system makes a jump from the imprinted transverse state to the nematic state. It is possible to calculate the critical value of α_0 at which this transition takes place by considering the values of g at the two minima:

$$g_{\text{loc}}(\pi/2) = \alpha_0^2 + \frac{3r}{(r-1)^2}, \tag{25}$$

$$g(0) = \frac{3[r(1+r)]^{2/3}}{2^{2/3}(r-1)^2}. \tag{26}$$

Solving $g(0) = g_{\text{loc}}(\pi/2)$ we find the critical value of the chiral power:

$$\alpha_{0c}(r) = \frac{1}{r-1}\sqrt{\frac{3[r(1+r)]^{2/3}}{2^{2/3}} - 3r}. \tag{27}$$

Provided that the effective chiral power, $\alpha[\theta_m(=\pi/2)]$, has not reached $2/\pi$ before the chiral power reaches α_{0c} then we see a discontinuous jump in the cone angle (θ) of $\pi/2$ at α_{0c}. This is shown in Fig. 5, where $r = 2$ so $\alpha_{0c} = 0.490$. Notice that the effect of the rotation is to shift the effective chiral power into the delocalized regime, but this is not of any physical consequence since at $\theta_m = 0$ the ordering is globally nematic.

It is natural to ask if there are any conditions under which the effective chiral power reaches $2/\pi$ before the chiral power reaches α_{0c}. Noting that

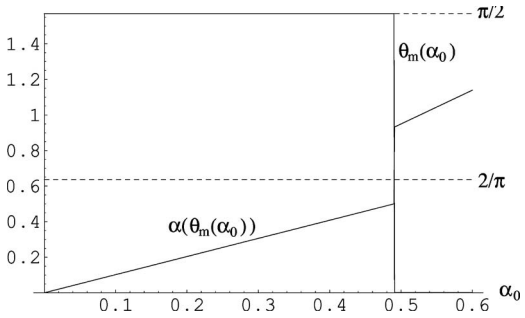

FIG. 5. θ_m and $\alpha(\theta_m)$ as a functions of α_0 when $\kappa=2.5$ and $r=2$.

$$\alpha(\pi/2) = \alpha_0 \frac{(1+r)^{1/3}}{(4r)^{1/6}}, \tag{28}$$

then the condition for unwinding to occur before α_{0c} is reached is then

$$\alpha_{0c}(r) \frac{(1+r)^{1/3}}{(4r)^{1/6}} > \frac{2}{\pi}. \tag{29}$$

It is straightforward to show that the function of r on the left-hand side is $\leqslant (1/2) \forall r > 1$, so the condition can never be met for prolate elastomers.

By reducing κ so that it is close to 2, and r so that it is close to unity, it is possible to generate a conical low efficiency state. This is illustrated in Fig. 6 which shows θ_m and $\alpha(\theta_m)$ as a functions of α_0 when $\kappa=2.01$ and $r=1.01$. Numerical investigations show that the largest value of κ with which such a state may be generated is $\kappa=2.226$.

IV. CONCLUSIONS

We have shown that if an imprinted elastomer is allowed to undergo elastic deformation in response to changes in its director configuration, then provided $\kappa<2$, it will relax into the conical state. There is a discontinuity in the director angle θ_m at a critical value of α_0, corresponding to the transition between the imprinted and untwisted states. For values of $\kappa>2$ (i.e., $K_3>2K_2$) the θ dependence of the Frank and anchoring terms in the free energy prevent the conical state from appearing, and we find that the array switches from the perfectly imprinted to the pure untwisted nematic state at a critical value of α_0.

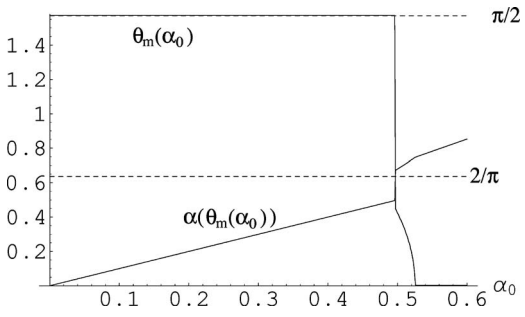

FIG. 6. θ_m and $\alpha(\theta_m)$ as a functions of α_0 when $\kappa=2.01$ and $r=1.01$.

When the system is on the brink of transition then the application of even modest strains might have a profound mechanical and director response. The possibility of this effect merits further investigation experimentally and analytically.

APPENDIX A: MINIMIZING ELASTIC ENERGY

The step length tensors $\underline{\underline{\ell}}_0$ and $\underline{\underline{\ell}}$ are given by

$$\underline{\underline{\ell}}_0 = \underline{\underline{\delta}} + (r-1)\vec{n}_0\vec{n}_0, \tag{A1}$$

$$\underline{\underline{\ell}}^{-1} = \underline{\underline{\delta}} + \left(\frac{1}{r} - 1\right)\vec{n}\vec{n}, \tag{A2}$$

where $\vec{n}_0$ and $\vec{n}$ are the director before and after the solvent is removed, and r is the chain anisotropy, being the ratio of effective step length parallel and perpendicular to the director. Local and global mechanical deformations of the elastomer are described by the elastic deformation gradient tensor $\underline{\underline{\lambda}}$. We take the axes of the imprinted helices to lie along the z direction, and adopt a form

$$\underline{\underline{\lambda}} = \left(\lambda - \frac{1}{\sqrt{\lambda}}\right)\vec{z}\vec{z} + \frac{1}{\sqrt{\lambda}}\underline{\underline{\delta}} + \lambda_{mz}\vec{m}\vec{z}, \tag{A3}$$

where the vector $\vec{m}$ is the unit vector aligned with the projection of the current director (after removal of solvent) onto the (x,y) plane. This representation is thus independent of the x and y coordinates. $\underline{\underline{\lambda}}$ represents a volume preserving relaxation by $\lambda \equiv \lambda_{zz}$ along z accompanied by $1/\sqrt{\lambda}$ along x and y, plus a limited class of z-dependent shears, λ_{mz}, with displacements in the $\vec{m}$ direction. Such shears are known to drastically reduce the cost of director rotation. The triangular form (A3) only has its diagonal elements involved in the constant volume constraint. The z-spatial dependence in $\lambda_{mz}(z)$ does not raise problems with elastic compatibility.

We choose to work in spherical polar coordinates, Fig. 1, in which the director is given by

$$\vec{n} = \sin\theta\cos\phi\vec{x} + \sin\theta\sin\phi\vec{y} + \cos\theta\vec{z} \tag{A4}$$

and the director at formation is transverse

$$\vec{n}_0 = \cos(q_0 z)\vec{x} + \sin(q_0 z)\vec{y}, \tag{A5}$$

and describes a perfect helix with pitch wave number $q_0 \equiv \pi/s_0$ where s_0 is the distance along the z direction between equivalent director configurations. Although we allow the angle ϕ to depend on z, we treat θ as a constant throughout the sample so that any rotations of the director toward the helix axis must be global. This is a convenient approximation in order to make analytical progress.

Using $\vec{n}_0\cdot\vec{z}=0$, $\vec{n}_0\cdot\vec{n}=\sin\theta\cos(\phi-q_0 z)$, $\vec{n}\cdot\vec{z}=\cos\theta$, $\vec{n}\cdot\vec{m}=\sin\theta$, and $\vec{m}\cdot\vec{z}=0$, we find that

$$f_{\text{elast}} = \frac{\mu}{2}\left(\lambda^2 + \frac{2}{\lambda} + \lambda_{mz}^2\right) - \frac{\mu(r-1)}{2r}\left[\left(\lambda^2 - \frac{1}{\lambda}\right)\cos^2\theta + 2\sin\theta\cos\theta\lambda_{mz}\lambda + \frac{1}{\lambda} + \lambda_{mz}^2\sin^2\theta - \frac{r-(r-1)\sin^2\theta\cos^2[\phi(z)-q_0 z]}{\lambda}\right].$$

We do not impose a distortion on the system but instead allow it to mechanically relax in response to changes in the director field. Thus we must minimize this expression over the parameters which describe the distortion to find the spontaneous relaxation. Minimizing over λ_{mz} we obtain the spontaneous shear:

$$\lambda_{mz} = \frac{(r-1)\lambda\sin\theta\cos\theta}{r-(r-1)\sin^2\theta}. \tag{A6}$$

Substituting this back into f_{elast}, we obtain

$$f_{\text{elast}} = \frac{\mu\lambda^2}{2[r-(r-1)\sin^2\theta]} + \frac{\mu r(r+1)}{2r\lambda} - \frac{\mu(r-1)\sin^2\theta\{1+(r-1)\cos^2[\phi(z)-q_0 z]\}}{2r\lambda}. \tag{A7}$$

We may now minimize over λ to obtain the spontaneous elongation:

$$\lambda^3 = \frac{r-(r-1)\sin^2\theta}{2r}(r(r+1)-(r-1)\sin^2\theta\{1+(r-1)\cos^2[\phi(z)-q_0 z]\}). \tag{A8}$$

Notice that this expression contains an oscillating z dependent elastic component where no such dependence appeared in our definition (A3). The compatibility condition

$$\partial_k\lambda_{ij} = \partial_j\lambda_{ik} \tag{A9}$$

then implies that since $\lambda_{xx} \equiv \lambda_{yy} = 1/\sqrt{\lambda(z)}$ have a z dependence (arising from the constant volume constraint) then we expect the terms $\lambda_{xz}(x)$ and $\lambda_{yz}(y)$, which in fact we ignore. Such a modulation in the transverse (x,y) plane is, however, known to be a problem in cholesteric elastomers (in their photonic behavior) and our observation is perhaps at the core of this behavior. The ratio of the size of this component to the z independent part is $(r-1)^2:(r^2+1)$, which for a typical value of $r=2$ is 1:5, so that the oscillating part should be considerably smaller.

Returning this λ to Eq. (A7) results in an elastic free energy just as a function of θ and $\phi(z)$:

$$f_{\text{elast}} = \frac{1}{2}D_1\gamma[a - b\cos^2(\phi - q_0 z)]^{2/3}, \tag{A10}$$

where

$$D_1 = \mu\frac{(r-1)^2}{r}, \tag{A11}$$

$$\gamma(\theta) = \frac{3r}{(r-1)^2(2r)^{2/3}[r-(r-1)\sin^2\theta]^{1/3}}, \tag{A12}$$

$$a(\theta) = r(r+1) - (r-1)\sin^2\theta, \tag{A13}$$

$$b(\theta) = (r-1)^2\sin^2\theta. \tag{A14}$$

APPENDIX B: MINIMIZATION OVER $\psi(u)$

The free energy per unit area for a sample of length L where relaxation to a conical state was *not* permitted, up to a multiplicative constant, was found to be [5]

$$\int_0^{L/\chi} ds\{[\psi'(s) - \alpha_0]^2 - \sin^2\psi(s)\}, \tag{B1}$$

α_0 and ψ being the same as in Sec. II, and s being defined by $z=\chi s$ where $\chi \approx \xi(\pi/2)$. The approach taken to minimizing this over ψ was to write down the first integral for ψ' involving a constant of integration c, substitute back into the integral, and then integrate over a single period to find an energy density per period as a function of c. Dividing this by the period then gives us an energy density which may be minimized over c. Note that the period varies as chiral power changes.

Our task is very similar: we seek to minimize the ψ dependent part of the free energy:

$$I(L) = -D_1\gamma(\theta)\beta_2(\theta)\xi(\theta)\int_0^{L/\xi(\theta)} du\{[\psi' - \alpha(\theta)]^2 - \sin^2\psi\},$$

over ψ. However, there is an important difference here, in that the variable α is no longer a constant. This means that the period of the solution to the first integral depends on θ as a well as c, and we must be careful to take account of this. The first integral is

$$\psi'^2 + \sin^2\psi = c^2. \tag{B2}$$

This equation has two types of solutions [5]. First, when $c^2 < 1$, the particle remains trapped within one of the wells of $\sin^2\psi$ and oscillates between $\psi = \pm\arcsin c$. We refer to this as a localized solution. When $c^2 > 1$, the particle has sufficient energy to escape the wells and traverses the potential landscape, and we refer to these solutions as delocalized.

Let us consider the localized case. It was shown in Ref. [5] that the period of oscillatory motion is

$$T_{u,\text{loc}} = 4\mathcal{K}(c), \tag{B3}$$

where $\mathcal{K}(c)$ is the complete elliptic integral of the first kind [9]. The subscripts on T refer to the fact that it is the period in terms of the variable u for the localized solutions. We may now perform the integral over this period, finding [5] that

$$\int_0^{4\mathcal{K}(c)} du\{[\psi' - \alpha(\theta)]^2 - \sin^2\psi\} = 4\mathcal{K}(c)\left[c^2 + \alpha(\theta)^2 - 2 + \frac{2\mathcal{E}(c)}{\mathcal{K}(c)}\right], \tag{B4}$$

where $\mathcal{E}(c)$ is the complete elliptic integral of the second

kind [10]. Thus after minimizing over ψ, averaging over one period we find

$$\frac{I(T_{z,\mathrm{loc}})}{T_{z,\mathrm{loc}}} = \frac{I(4\mathcal{K}(c)\xi(\theta))}{4\mathcal{K}(c)\xi(\theta)} = -D_1\gamma(\theta)\beta_2(\theta) \times \left[c^2 + \alpha(\theta)^2 - 2 + \frac{2\mathcal{E}(c)}{\mathcal{K}(c)}\right]. \tag{B5}$$

Since $c^2+2\mathcal{E}(c)/\mathcal{K}(c)$ is a monotonically decreasing function of c on $c\in[0,1]$ then the minimum in terms of c in the localized case is always at $c=1$. Thus after minimizing over c

$$\frac{I(T_{z,\mathrm{loc}})}{T_{z,\mathrm{loc}}} = -D_1\gamma(\theta)\beta_2(\theta)[\alpha(\theta)^2 - 1]. \tag{B6}$$

Now let us consider the delocalized solutions. The particle traverses the potential, so, to find the energy density we must calculate the "time" the particle takes to go from one peak to the next. This is

$$T_{u,\mathrm{deloc}} = 2c^{-1}\mathcal{K}(c^{-1}). \tag{B7}$$

Performing the integral over this period,

$$\int_0^{2c^{-1}\mathcal{K}(c^{-1})} du[(\psi' - \alpha(\theta))^2 - \sin^2\psi] = 2\left[[\alpha(\theta)^2 - c^2]\frac{2}{c}\mathcal{K}(c^{-1}) - \alpha(\theta)\pi + 2c\mathcal{E}(c^{-1})\right],$$

we find that the integral component of the free energy density, minimized over ψ and averaged over one period, is

$$\frac{I(T_{z,\mathrm{deloc}})}{T_{z,\mathrm{deloc}}} = -D_1\gamma(\theta)\beta_2(\theta) \times \left[\alpha(\theta)^2 - c^2 + \frac{c^2}{\mathcal{K}(c^{-1})}\left(2\mathcal{E}(c^{-1}) - \frac{\alpha(\theta)\pi}{c}\right)\right]. \tag{B8}$$

Using the identities

$$\frac{d\mathcal{K}(p)}{dp} = \frac{\mathcal{E}(p)}{p(1-p^2)} - \frac{\mathcal{K}(p)}{p}, \tag{B9}$$

$$\frac{d\mathcal{E}(p)}{dp} = \frac{\mathcal{E}(p) - \mathcal{K}(p)}{p} \tag{B10}$$

we may minimize Eq. (B8) in the $c>1$ range by setting its derivative with respect to c to zero. This yields the condition

$$2c\mathcal{E}(c^{-1}) = \alpha(\theta)\pi, \tag{B11}$$

which has no solution for $\alpha(\theta)<(2/\pi)$. When $\alpha(\theta)>(2/\pi)$ then the minimized energy density is obtained by solving the above condition (B11) numerically to find c as a function of $\alpha(\theta)$, and substituting this back into the density. We denote the solution to Eq. (B11) $\tilde{c}(\alpha(\theta))$. Since

$$\mathrm{sgn}\left[\frac{d}{dc}\frac{I(T_{z,\mathrm{deloc}})}{T_{z,\mathrm{deloc}}}\right]_{c=1} = \begin{cases} + & \text{if } \alpha(\theta) < 2/\pi \\ - & \text{if } \alpha(\theta) > 2/\pi, \end{cases} \tag{B12}$$

and

$$\lim_{c\to 1^-}\frac{I(T_{z,\mathrm{loc}})}{T_{z,\mathrm{loc}}} = \lim_{c\to 1^+}\frac{I(T_{z,\mathrm{deloc}})}{T_{z,\mathrm{deloc}}}, \tag{B13}$$

then the global minimum over c of the integral part of the free energy is at

$$c = \begin{cases} 1 & \text{if } \alpha(\theta) < 2/\pi \\ \tilde{c}(\alpha(\theta)) & \text{if } \alpha(\theta) > 2/\pi. \end{cases} \tag{B14}$$

If $\alpha(\theta)<2/\pi$, then the solution to the Euler Lagrange equation for $\psi(u)$ has a divergent period and we may treat it as a constant, fixed by boundary conditions in the sample. The important consequence of this is that if we recall the relation between ψ the director angle ϕ: $\psi=q_0z-\phi+\pi/2$, we see that ϕ maintains the imprinted period. Hence localized solutions correspond to the imprinted state.

If $\alpha(\theta)>2/\pi$ then the solutions to the Euler-Lagrange equations describe a particle moving over a potential landscape. It is useful to make the schematic decomposition: $\psi=az+\mathrm{periodic}(z)$. From this we see that the physical director angle will be given by

$$\phi(z) = (q_0 - a)z - \mathrm{periodic}(z) + \pi/2, \tag{B15}$$

so that the pitch wave number is reduced and some of the twists in the imprinted helices are lost. Hence delocalized solutions correspond to the partially untwisted state. The periodic component of the solution corresponds to a coarsening of the imprinted helix, i.e., the tightness of the helical twists varies along z.

Combining the ψ dependent part of the free energy density, $I(L)$, minimized over ψ, with the ψ independent part, and dividing by $D_1/2$, we obtain a *dimensionless energy density* which in the delocalized ($\alpha(\theta)>2/\pi$) regime is

$$g_{\mathrm{deloc}}(\theta) = \gamma(\theta)\{\beta_0(\theta) - \beta_2(\theta)[3 - 2\tilde{c}^2(\alpha(\theta))]\}. \tag{B16}$$

In the localized regime there is no need to use the Fourier series approximation because since no unwinding has occurred then $\phi(z)=q_0z$. This means that we may set $\cos^2[\phi(z)-q_0z]=1$ and $\phi'=q_0$ in Eq. (7) and the integral becomes trivial. The dimensionless free energy in the localized [$\alpha(\theta)<2/\pi$] regime is then

$$g_{\mathrm{loc}}(\theta) = \alpha_0^2\omega(\theta) + \gamma(\theta)[a(\theta) - b(\theta)]^{2/3}. \tag{B17}$$

APPENDIX C: IMPRINTING EFFICIENCY

The efficiency, as introduced in the main text, is clearly unity in the localized regime, since no twists are lost. In the delocalized regime, since the modulation in ϕ is periodic, then the efficiency may be calculated by considering a single period of the modulation. The journey of our "particle" from one peak of the potential to the next corresponds to the loss of half a twist, since the peaks are separated by π. The "time" taken for the particle to make this journey corre-

sponds to the length (along the z direction) over which the director loses this half twist. This is just the period $T_{z,\mathrm{deloc}}$:

$$T_{z,\mathrm{deloc}} = \frac{\alpha(\theta_m) T_{u,\mathrm{deloc}}}{q_0} = \frac{2\alpha(\theta_m)\mathcal{K}(\tilde{c}^{-1})}{\tilde{c} q_0}. \tag{C1}$$

The initial number of twists present along this length is

$$N_{T_{z,\mathrm{deloc}}} = \frac{2\alpha(\theta_m)\mathcal{K}(\tilde{c}^{-1})/q_0}{2\pi\tilde{c}/q_0} = \frac{\alpha(\theta_m)\mathcal{K}(\tilde{c}^{-1})}{\tilde{c}\pi}, \tag{C2}$$

so the efficiency in the delocalized regime is

$$e_0 = \frac{N_{T_{z,\mathrm{deloc}}} - \frac{1}{2}}{N_{T_{z,\mathrm{deloc}}}} \tag{C3}$$

$$= \frac{2\alpha(\theta_m)\mathcal{K}(\tilde{c}^{-1}) - \tilde{c}\pi}{2\alpha(\theta_m)\mathcal{K}(\tilde{c}^{-1})}. \tag{C4}$$

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[6] The Fourier coefficients are $\beta_0 = (1/2\pi)\int_{-\pi}^{\pi} dx (a - b\cos^2 x)^{2/3} dx$ and $\beta_n = (1/\pi)\int_{-\pi}^{\pi} dx (a - b\cos^2 x)^{2/3}\cos(nx)$.

[7] The director field $\vec{n}(\vec{r})$ is the unit vector field aligned at each point $\vec{r}$ with the local average orientation of the rodlike liquid crystal molecules, $\vec{n}(\vec{r}) \equiv -\vec{n}(\vec{r})$.

[8] D. J. Burridge, Ph.D. thesis, University of Cambridge, Cambridge, England (2005).

[9] $\mathcal{K}(c) = \int_0^{\pi/2} (dy/\sqrt{1 - c^2\sin^2 y})$.

[10] $\mathcal{E}(c) = \int_0^{\pi/2} dy \sqrt{1 - c^2\sin^2 y}$.