Mechanical strains and electric fields applied to topologically imprinted elastomers

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We analyze and predict the behavior of a chirally imprinted elastomer under a mechanical strain and an electric field, applied along the helical axis. As the strain and/or field increases, the system is deformed from a conical or transverse imprinted state towards an ultimately nematic one. At a critical strain and/or field there is a first-order transition to a low imprinting efficiency state. This transition is accompanied by a discontinuous global rotation of the director toward the axis of the imprinted helix, measured by the cone angle, θ. We show that the threshold electric field required for switching this transition can be conveniently low, provided an appropriate prestrain is imposed. We suggest that these properties may give rise to a "chiral pump."

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I. INTRODUCTION

By crosslinking a nematic polymer melt in the presence of a chiral solvent, an elastomer may be created with a topologically imprinted director profile which follows a helix [1–4]. This topological memory may or may not be strong enough to preserve a helical structure on removal of the chiral solvent and hence the induced chirality. A theoretical model of this imprinting process [5,6] predicts a relationship between the various system parameters, and the efficiency of the imprinting (defined as fraction of helical twists retained after removal of the chiral solvent). One important system parameter is the angle θ between the nematic director and the axes of the imprinted helix, known as the "cone angle." At formation $\theta=\pi/2$ typically, the director is perpendicular to the helix axis (the "transverse case"). The original model [5] assumes that the sample is clamped or otherwise restrained such that θ remains at $\pi/2$. The later work [6] examines the stress-free relaxation of θ, and predicts a first-order transition in imprinting efficiencies coupled with discontinuous jumps in the cone angle θ. In this paper we extend the previous analysis by considering an additional mechanical strain and an electric field along the axes of the imprinted helices. In particular, we analyze the interplay between the mechanical and electrical fields. We show that an applied electric field can switch an elastomer between an imprinted conical state and an "unwound" conical, or a globally nematic state. The threshold electric field required may be considerably lowered by applying an appropriate prestrain, giving rise to the possibility of an ultraefficient "chiral pump."

Before proceeding we briefly clarify the meanings of particularly important terms. The imprinting process aims to leave the elastomer with an internal helical structure. After removal of the chiral solvent the pitch of the helices will either remain unchanged, in which case the elastomer is referred to as "imprinted," or it will lengthen, in which case the imprinting efficiency is lowered and the elastomer is referred to as "unwound." It is in the nature of the system that if unwinding occurs, it does so dramatically. The helical state is further characterized by θ, the cone angle, so described because the tilted helical director field traces out a cone. The elastomer can be in a transverse state ($\theta=\pi/2$), a conical state ($0<\theta<\pi/2$), or a nematic state ($\theta=0$). In the absence of local (spatially dependent) shearing, the conical state is energetically unfavorable.

A. Review of model

In the basic underlying model [5,6] (without fields or applied strain), the proposed free energy of an imprinted elastomer consists of two competing components. First, there is the "Frank" free energy, which accounts for the energy cost of distorting the natural nematic ordering of the liquid crystal molecules embedded in the elastomer. Second, there is the nematic rubber elastic free energy, which gives the cost of deforming away from the imprinted chiral structure. This second term depends not only on the configuration of the director field, but also the deformation gradient tensor which describes the mechanical relaxation of the elastomer after formation. The overall free energy is then minimized in two steps: first, over the parameters within the deformation gradient tensor, and then over the director configuration.

There are three main predictions obtained from this underlying model. First, while in the imprinted regime (all imprinted twists retained) and provided the costs of nematic bend and twist distortion remain such that their ratio $\kappa<2$, the elastomer will relax into a conical state. Second, an abrupt transition from fully imprinted to very low efficiency occurs when the effective chiral power, a dimensionless function of system parameters including the cone angle, exceeds $2/\pi$. The transition is accompanied by a discontinuous jump in the cone angle. Note that the value $2/\pi$ has no intuitive physical meaning beyond that which it takes from its derivation using elliptic integrals. The third prediction relates to the case where $\kappa>2$, when the conical state does not appear while the helices are imprinted, i.e., the director remains transverse to the helix axes. If $\kappa>2.226$, then upon the effective chiral power exceeding a critical value, the cone angle discontinuously changes from $\pi/2$ to 0, and the internal structure of the elastomer becomes uniformly nematic. If $\kappa\in[2,2.226]$, then the system parameters may be tuned to obtain a discontinuous transition from the transverse imprinted state to a conical low-efficiency state.

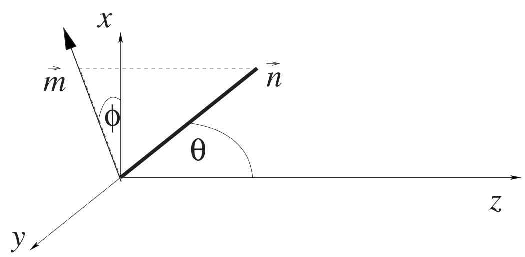

FIG. 1. The director in spherical polars.

B. Modifications

In accounting for mechanical strains, we do not need any formal modifications to the free energy. This is the case because in the basic model we assumed two (mathematically convenient) modes of elastic relaxation: a global volume-preserving stretch along the axial direction of the helices, and also local shearing. Fixing the stretch, rather than minimizing it, is thus equivalent to the application of a strain. To account for the effects of a static electric field, we must add the field-energy density, and then minimize the total free energy.

We will describe the details of these calculations in the next sections. In brief, we find that mechanical straining causes the director to rotate smoothly toward the helix axis, with a small discontinuous rotation at the transition between the imprinted and low efficiency states. Applying an electric field also induces an increasingly conical state, but a much larger discontinuous rotation is seen at the transition. When the bend-twist ratio $\kappa > 2$, then over a broad range of physically realistic model parameters we see a dramatic transition from a conical (θ of order 1) imprinted state to a globally nematic state at a critical applied field. Calculation combining the mechanical and electrical fields shows that, by applying an appropriate pre-strain, it is feasible to control the imprinting efficiency transition by a conveniently small electric field, giving rise to many potential applications.

II. IMPOSED MECHANICAL STRAINS

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

$$\vec{n} = \sin\theta\cos\phi\vec{x} + \sin\theta\sin\phi\vec{y} + \cos\theta\vec{z}. \tag{1}$$

The director at formation is typically transverse

$$\vec{n}_0 = \cos(q_0 z)\vec{x} + \sin(q_0 z)\vec{y}, \tag{2}$$

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 reasonable and convenient approximation in order to make analytical progress.

Once a sample has been crosslinked and the chiral solvent removed, it is allowed to undergo spontaneous elastic deformation, or relaxation. This deformation is taken to be a global volume–preserving elongation (by a factor of R along $\vec{z}$) plus local shearing, described by the tensor

$$\underline{\underline{\mathbf{R}}} = \left(R - \frac{1}{\sqrt{R}}\right)\vec{z}\vec{z} + \frac{1}{\sqrt{R}}\underline{\underline{\delta}} + R_{mz}\vec{m}\vec{z}, \tag{3}$$

where the vector $\vec{m}$ is the unit vector aligned with the projection of the current director (after removal of the solvent) onto the (x,y) plane (see Fig. 1).

Suppose that we then stretch the sample along the helix axis, allowing the same kind of spontaneous shearing in response. Such a deformation may be described by the tensor

$$\underline{\underline{\lambda}} = \left(\lambda - \frac{1}{\sqrt{\lambda}}\right)\vec{z}\vec{z} + \frac{1}{\sqrt{\lambda}}\underline{\underline{\delta}} + \lambda_{mz}\vec{m}\vec{z}, \tag{4}$$

where λ is imposed, e.g., by clamps, but λ_{mz} is free to vary. The total deformation of the sample from its imprinted configuration will then be

$$\underline{\underline{\mathbf{T}}} = \underline{\underline{\lambda}} \cdot \underline{\underline{\mathbf{R}}}. \tag{5}$$

$\underline{\underline{\mathbf{T}}}$ describes global volume-preserving elongations and contractions plus local shearing. The element $[\underline{\underline{\mathbf{T}}}]_{zz}$, gives the fractional change in the length of the sample since formation.

Rather than calculate the effects of relaxation followed by the effects of straining, it is mathematically convenient to assume that the sample has a stretch factor T imposed on it with respect to formation. (With respect to a relaxed sample, imposing a strain λ would involve a compression of the sample if T was less than the elongation R which would occur naturally through relaxation.) In order to find the stretch factor that one would need to apply to an already relaxed sample, we extract $\underline{\underline{\lambda}}$ from (5) as $\underline{\underline{\lambda}} = \underline{\underline{\mathbf{T}}} \cdot \underline{\underline{\mathbf{R}}}^{-1}$. Written out explicitly this tensor takes the form

$$\underline{\underline{\lambda}} = \left(\frac{T}{R} - \sqrt{\frac{R}{T}}\right)\vec{z}\vec{z} + \sqrt{\frac{R}{T}}\underline{\underline{\delta}} + \left(\frac{T_{mz}}{R} - \frac{R_{mz}}{\sqrt{TR}}\right)\vec{m}\vec{z}, \tag{6}$$

from which we see that if we calculate the theoretical effects of stretching a sample from its formation length by a factor T, then this corresponds to a stretch factor of T/R for the already relaxed sample. It was shown in (6) that the cube of the spontaneous relaxation R is

$$R^3 = \frac{r - (r-1)\sin^2\theta_R}{2r}(r(r+1) - (r-1)\sin^2\theta_R \times\{1 + (r-1)\cos^2[\phi(z) - q_0 z]\}), \tag{7}$$

where r is the anisotropy of the Gaussian chain model for the nematic polymer, and θ_R is the physical value of the relaxed cone angle. Recall that $\phi(z)$ describes the rotation of the director field about the pitch axis, and is thus given by $\phi(z) = q_0 z$ in the imprinted state [assuming the projection of the director field onto the (x,y) plane is parallel with the x-axis at $z=0$]. Deviation from this configuration represents unwinding (or tightening) of the helix. In this case expression (7) contains an oscillating z-dependent component where no such dependence appeared in our definition (3). The elastic compatibility condition

$$\partial_k \lambda_{ij} = \partial_j \lambda_{ik} \tag{8}$$

then implies that since $\lambda_{xx} \equiv \lambda_{yy} = 1/\sqrt{\lambda(z)}$ has a z dependence (arising from the constant volume constraint), then we expect the terms $\lambda_{xz}(x)$ and $\lambda_{yz}(y)$. Fortunately this problem will not concern us here because the cases of interest to us are where the relaxed sample has retained its imprinted helices, i.e., $\phi(z)=q_0z$.

Now let us carry out the calculation to find the configuration of a sample which is clamped at formation and then has a mechanical stretch T imposed. The elastic free energy must be minimized over the spontaneous shears T_{mz} (see Appendix A for details), leading to

$$f_{\text{elast}} = \frac{D_1}{2}\left(a(\theta)T^2 + \frac{b(\theta)}{T}\right) - \frac{D_1}{2T}\sin^2\theta\cos^2[\phi(z) - q_0 z]. \tag{9}$$

The definitions of D_1 and the dimensionless functions 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.

The Frank free energy density is

$$f_{\text{Frank}} = \tfrac{1}{2}\{K_1(\nabla\cdot\vec{n})^2 + K_2[\vec{n}\cdot(\nabla\wedge\vec{n})]^2 + K_3[\vec{n}\wedge(\nabla\wedge\vec{n})]^2\}, \tag{10}$$

where $K_{1,2,3}$, respectively, measures the energy penalty for splay, twist, and bend, the three modes of nematic director distortion. In our system splay is not present in the geometry, and using our definition (1) of the director the Frank energy becomes

$$f_{\text{Frank}} = \frac{\phi'^2(z)}{2}[K_2\sin^4\theta + K_3\cos^2\theta\sin^2\theta]. \tag{11}$$

There is no natural twist since the chiral solvent has been removed. The system pays a rubber elastic penalty if $\phi(z)$ deviates from q_0z according to Eq. (9), but $\phi(z)\neq\text{const}$ incurs the above Frank energy. The full free-energy density is $f_{\text{Frank}}+f_{\text{elast}}$ and the free energy per unit area perpendicular to the helix axis for a sample of length L is obtained by integrating over z from 0 to L. This integral is brought into a particularly simple form by changing the length scale and transforming to a new polar variable ψ

$$\psi = q_0 z - \phi + \frac{\pi}{2} \tag{12}$$

$$u = \frac{z}{\xi(\theta)} \tag{13}$$

$$\xi(\theta) = \left(\frac{T(K_2\sin^2\theta + K_3\cos^2\theta)}{D_1}\right)^{1/2} \tag{14}$$

$$\alpha_0 = q_0\left(\frac{K_2}{D_1}\right)^{1/2} \tag{15}$$

$$\alpha(\theta) = q_0\xi(\theta), \tag{16}$$

then

$$F(L) = \frac{LD_1}{2}\left(a(\theta)T^2 + \frac{b(\theta)}{T}\right) + \frac{D_1\xi(\theta)\sin^2\theta}{2T} \times\int_0^{L/\xi(\theta)} du\{[\psi' - \alpha(\theta)]^2 - \sin^2\psi\}, \tag{17}$$

where the dash denotes differentiation with respect to u. 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 [5] where director rotations θ and elastic deformation were ignored, i.e., $\theta=\pi/2$, $T=1$. In that work α_0 was introduced [5] as the chiral power, and its value determined the efficiency of the imprinting process e_0 which is defined as the fraction of twists retained

$$e_0 = \frac{N_0 - N_{\text{lost}}}{N_0}, \tag{18}$$

where N_0 is the initial total number of twists in the sample, and N_{lost} is number lost. It was found that $\alpha_0<2/\pi$ gave rise to a high-efficiency imprinted regime, whereas $\alpha_0>2/\pi$ resulted in a low efficiency (loss of helical twists).

We now seek to minimize the total free energy, Eq. (17), with respect to director orientation $\psi(u)$, following the methods introduced in [5,6], the relevant details of which are given in Appendix B. We discuss the main results below.

For $\alpha(\theta)<2/\pi$, the imprinted helices are retained, and the solution is referred to as "localized." For $\alpha(\theta)>2/\pi$, the helices begin to be lost, and the solution is referred to as "delocalized." We refer to $\alpha(\theta)$ as the *effective chiral power* because it plays the same role as the chiral power α_0 does when θ, elastic relaxation and straining are ignored [5]. In our present case, the effective chiral power is coupled to the cone angle θ which varies to minimize the total free energy. This coupling gives rise to several possible scenarios which we shall discuss with physical predictions. It was shown in [5,6] that the loss of helical twists at the transition from localized to delocalized is discontinuous, and the same is true here. That is, when $\alpha(\theta)=(2/\pi)^-$ then all helical twists are retained, but at $\alpha(\theta)=(2/\pi)^+$ twists are quickly lost.

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

$$g_{\text{loc}}(\theta) = \frac{\sin^2\theta}{T}[\alpha(\theta)^2 - 1] + \left(aT^2 + \frac{b}{T}\right), \tag{19}$$

and

$$g_{\text{deloc}}(\theta) = \frac{\sin^2\theta}{T}[\alpha(\theta)^2 - \tilde{c}^2] + \left(aT^2 + \frac{b}{T}\right), \tag{20}$$

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

$$2c\mathcal{E}(c^{-1}) = \alpha(\theta)\pi. \tag{21}$$

It is useful to introduce the dimensionless parameter $\kappa=K_3/K_2$, which measures the relative cost of bend to that of twist distortion. In terms of this parameter we may write $\alpha(\theta)=\alpha_0[T(\sin^2\theta+\kappa\cos^2\theta)]^{1/2}$ so that the form of the

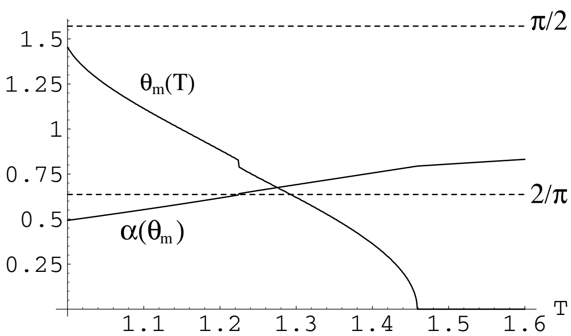

FIG. 2. The physical value of the helix cone angle θ_m and also the effective chiral power $\alpha(\theta_m)$ as a function of the stretch factor T when $\kappa=1.8$, $r=2$, and $\alpha_0=0.49$.

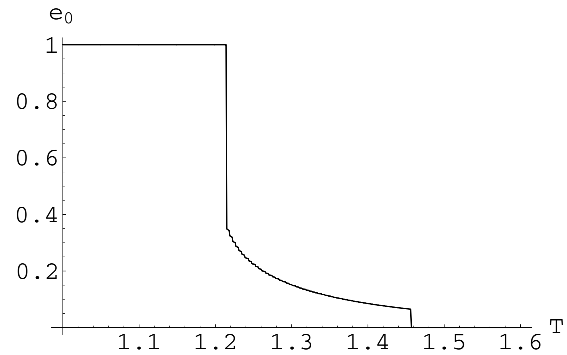

FIG. 3. The imprinting efficiency e_0 as a function of the stretch factor T when $\kappa=1.8$, $r=2$, and $\alpha_0=0.49$.

dimensionless free energy depends only on the four dimensionless parameters α_0, T, κ, and r. Typically [7], $K_i \sim 2-4 \times 10^{-12} N$ with $K_3 > K_2$, $2 < r < 4$, and $\alpha_0 \approx O(1)$.

The physical value, θ_m, of the cone angle is found numerically by minimizing the dimensionless free energy. We are interested in its dependence on the strain T for given α_0, r, and κ.

It was found in [5,6] that there is a qualitative difference in the form of the free energy of the underlying model between the cases $\kappa < 2$ and $\kappa > 2$. In the latter case a local minimum exists in the Frank energy at $\theta = \pi/2$, which prevents the conical state from appearing in the relaxed system. We find here that, although straining can generate a conical imprinted state, the local minimum is able to hold the director in the transverse state for small strains. No such transverse state appears when $\kappa < 2$. We therefore consider the two cases separately.

A. $\kappa < 2$ case

We are interested in the effects of straining a relaxed sample which has retained its imprinted structure. We therefore seek numerical values for α_0, r, and κ which ensure that the relaxed sample is imprinted. Suppose we take $\kappa=1.8$, $r=2$, and $\alpha_0=0.49$, then it may be shown using the methods developed in [6] that the sample remains imprinted, and that the relaxed cone angle is

$$\theta_R(\alpha_0 = 0.49, \kappa = 1.8, r = 2) = 1.252, \tag{22}$$

which corresponds to an elongation due to relaxation of

$$R(\alpha_0 = 0.49, \kappa = 1.8, r = 2) = 1.048. \tag{23}$$

Figure 2 shows the numerically determined cone angle and the associated effective chiral power $\alpha(\theta_m)$ as a function of the total elongation T with respect to formation. Imprinting fails when $\alpha(\theta_m) > 2/\pi$, which occurs when $T=1.223$, corresponding to the application of a strain $\lambda=1.167$ to an already relaxed system. While the total elongation is less than this transition value, the pitch of the imprinted helices is the same as at formation, and the elastomer is in a twisted nematic state. As T exceeds 1.223, there is a discontinuous loss of pitch [5,6], or imprinting efficiency. This is illustrated in Fig. 3, which shows e_0 as a function of T in this case. (Note that $e_0=0$ once the director is aligned with the helix axis.)

From Fig. 2 we see that associated with this transition at $T=1.223$ is a discontinuity in θ_m, and hence in $\alpha(\theta_m)$, which is too small to be visible. This is due to the presence of two local minima in the free energy, i.e., it is a first-order transition induced by an imposed mechanical strain.

For any given κ, r, this mechanical strain-driven discontinuity is only observable over a certain range of values of the chiral power. If α_0 is too small, then the effect of straining is to force the cone angle down to zero before the effective chiral power exceeds $2/\pi$. A cone angle of zero corresponds to the globally nematic state, such that all imprinted chiral structure is lost. If α_0 is too large, then the effective chiral power is greater than $2/\pi$ for all strains $T>1$, that is, helical twists were already being lost before a stretch is imposed.

B. $\kappa > 2$ case

To illustrate the behavior of the system in this case we take $\kappa=2.5$, $\alpha_0=0.45$, and keep $r=2$. Figure 4 shows the results of the numerical minimization to find θ_m.

As mentioned earlier, when $\kappa > 2$, the conical and yet fully imprinted state does not appear in the unstrained system due to the existence of a local minimum in the Frank free energy at $\theta = \pi/2$. At a critical value of α_0 and in the absence

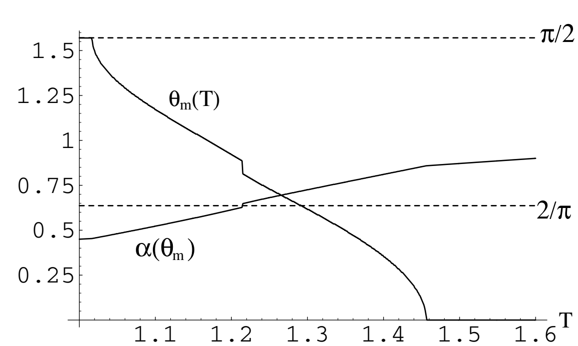

FIG. 4. The physical value of the helix cone angle θ_m and also the effective chiral power $\alpha(\theta_m)$ as a function of the stretch factor T when $\kappa=2.5$, $r=2$, and $\alpha_0=0.45$.

of imposed mechanical strain, the imprinted transverse state is abruptly lost and the system becomes either nematically ordered ($\theta_R=0$), or conical with low imprinting efficiency. For the parameter values we have chosen here the critical value is $\alpha_0=0.490$, at which point the system reverts to nematic ordering. Since $\theta_R=\pi/2$ when $\alpha_0=0.45$, and it can be shown that $R=1$ so that the sample does not undergo any shape relaxation, then $\lambda=T$. For $\alpha_0>0.490$, the sample will relax into the nematic state without the application of any strain, so it is not meaningful to consider the behavior of a sample clamped at formation.

The effect of the extra local minimum in the Frank term, which distinguishes from the $\kappa<2$ case when the system is strained, is that the director remains transverse for small values of T (Fig. 4). This may be explained in a quantitative way by writing $T=1+\epsilon$, expanding the localized energy density about $\theta=\pi/2$ and linearizing each term in ϵ to obtain

$$g_{loc}(\theta)=\alpha_0^2+\frac{3r}{(r-1)^2}+\left(\alpha_0^2(\kappa-2)-\frac{3r}{r-1}\epsilon\right)(\theta-\pi/2)^2+\cdots. \quad (24)$$

Provided that the coefficient of $(\theta-\pi/2)^2$ is positive, then $\theta=\pi/2$ is a local minimum. The condition for this is

$$\epsilon_{cr}=\frac{\alpha_0^2(r-1)(\kappa-2)}{3r}, \quad (25)$$

which for the parameter values we have chosen gives $\epsilon_{cr}=0.0169$. For larger strains than this, the system must shift to the conical state. This linearized approximation of the transition point agrees with the numerical calculation.

III. ELECTRIC FIELDS

We will assume that our liquid crystal elastomer is a perfect insulator. In such a nematic liquid crystal the static dielectric constants measured along ($\epsilon_\parallel$) and normal to ($\epsilon_\perp$) the nematic axis are different, and for a general director orientation, the relationship between electric field and electric displacement is

$$\vec{D}=\epsilon_0(\epsilon_\perp\vec{E}+(\epsilon_\parallel-\epsilon_\perp)(\vec{n}\cdot\vec{E})\vec{n}). \quad (26)$$

The contribution to the energy density due to electric fields in a dielectric is $-\frac{1}{2}\vec{D}\cdot\vec{E}$, which in the nematic elastomer becomes

$$-\frac{\epsilon_0}{2}(\epsilon_\perp\vec{E}\cdot\vec{E}+(\epsilon_\parallel-\epsilon_\perp)(\vec{n}\cdot\vec{E})^2). \quad (27)$$

The first term is independent of orientation and will contribute a constant to the free energy, so we need only consider the second term when minimizing. If the field is applied longitudinal to the helix axis then $\vec{n}\cdot\vec{E}=E\cos\theta$ and the second term becomes

$$-\frac{\Delta\epsilon\epsilon_0E^2\cos^2\theta}{2}, \quad (28)$$

where $\Delta\epsilon=\epsilon_\parallel-\epsilon_\perp$ is the dielectric anisotropy. We assume it is positive. For later convenience we define a *dimensionless field* δ by

$$\delta=\frac{\Delta\epsilon\epsilon_0E^2}{D_1}. \quad (29)$$

We assume that the electric field is applied to a relaxed sample which is not subject to any imposed mechanical strains. The total free-energy density per unit area perpendicular to the helix axis is then the sum of the density for a relaxed sample plus the field contribution. The density for the relaxed sample is derived as in the mechanical case, but in addition, we minimize over the longitudinal stretch factor. This calculation was carried out in [6] and we refer the reader to that paper for details. Since the field term is independent of the polar angle $\phi(z)$, then the minimization over $\phi(z)$ carried out in [6] may also be carried over directly. Therefore, the present case, with further complications arising from the field terms, can be first simplified using the procedures introduced previously. In order to quote the result we must first define three additional dimensionless functions

$$\gamma(\theta)=\frac{3r}{(r-1)^2(2r)^{2/3}[r-(r-1)\sin^2\theta]^{1/3}}, \quad (30)$$

$$c(\theta)=r(r+1)-(r-1)\sin^2\theta, \quad (31)$$

$$d(\theta)=(r-1)^2\sin^2\theta, \quad (32)$$

which in turn define two functions $\beta_0(\theta)$ and $\beta_2(\theta)$, the first two coefficients of the Fourier expansion

$$[c(\theta)-d(\theta)\cos^2x]^{2/3}=\beta_0(\theta)+\beta_2(\theta)\cos 2x+\cdots. \quad (33)$$

It was shown in [6] that truncating the Fourier expansion at this point is a sufficiently good approximation to preserve the essential shape of the free energy, and not to introduce spurious minima. Finally a new effective chiral power is defined

$$\alpha_R(\theta)=\alpha_0\sin\theta\left(\frac{-(K_2\sin^2\theta+K_3\cos^2\theta)}{2\gamma(\theta)\beta_2(\theta)}\right)^{1/2}, \quad (34)$$

where the definition of α_0 is the same as in the preceding section; see Eq. (15). Minimizing over $\phi(z)$, it is found [6] that when $\alpha_R(\theta)<2/\pi$, the imprinted helices are retained, and the solution is referred to as localized; when $\alpha_R(\theta)>2/\pi$, the helices begin to be lost, and the solution is referred to as delocalized. Energy densities are made dimensionless through multiplication by $2/D_1$, which in the case of the field term gives $-\delta\cos^2\theta$. Adding this to the dimensionless free-energy densities in the (de)localized regimes, we obtain

$$g_{\rm loc}(\theta)=\alpha_0^2(\sin^4\theta+\kappa\sin^2\theta\cos^2\theta)+\gamma(\theta)[c(\theta)-d(\theta)]^{2/3}-\delta\cos^2\theta, \quad (35)$$

and

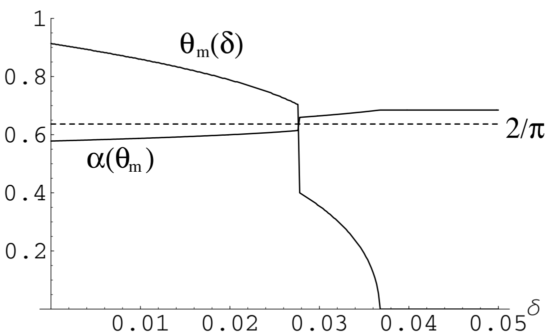

FIG. 5. The physical value of the helix cone angle θ_m and also the effective chiral power $\alpha(\theta_m)$ as a function of the dimensionless field δ when $\kappa=1.3$, $r=2$, and $\alpha_0=0.5$.

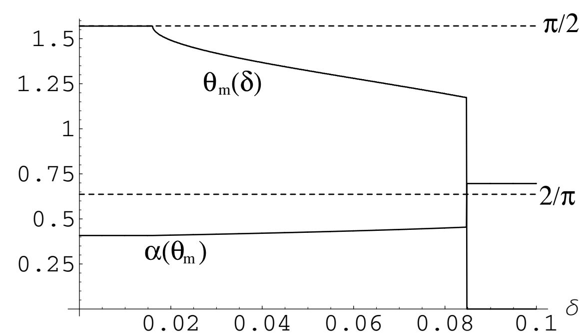

FIG. 6. The physical value of the helix cone angle θ_m and also the effective chiral power $\alpha(\theta_m)$ as a function of the dimensionless field δ when $\kappa=2.1$, $r=2$, and $\alpha_0=0.4$.

$$g_{\rm deloc}(\theta) = \gamma(\theta)\{\beta_0(\theta) - \beta_2(\theta)[3 - 2\tilde{c}^2(\alpha_R(\theta))]\} - \delta\cos^2\theta, \quad (36)$$

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

$$2c\mathcal{E}(c^{-1}) = \alpha_R(\theta)\pi. \quad (37)$$

We again discuss the $\kappa<2$ and $\kappa>2$ cases separately.

A. $\kappa<2$ case

Choosing the parameter values $\kappa=1.3$, $r=2$, and $\alpha_0=0.5$, we find the angle θ_m which minimizes $g(\theta)$ numerically, as a function of the dimensionless field δ. Figure 5 shows the results of this calculation, along with the associated chiral power, which makes a discontinuous jump to a value greater than $2/\pi$ at $\delta=0.0276$.

If we set $\delta=0$ and vary α_0, then we find that the imprinting efficiency transition occurs at $\alpha_0=0.518$. We have chosen the value of the chiral power to be close to this, so as to allow the transition to be induced for smaller fields. Note that δ of the order of 0.001 typically corresponds to a field of the order of 10^3 V/m.

After the unwinding transition the director remains in the conical state but is rapidly dragged down to the helix axis.

B. $\kappa>2$ case

The behavior of the system when $\kappa>2$ is of a qualitatively different form. In a similar way to the mechanical strain, the longitudinal electric field is able to drag the system out of the local minimum which pinned the relaxed and imprinted system to $\theta_R=\pi/2$. From Fig. 6, which shows θ_m and the effective chiral power as a function of the applied field, we see that the imprinted conical state appears abruptly at $\delta=0.016$. This transition value may be found analytically, in a similar way to the mechanical case, by expanding $g(\theta)$ about $\theta=\pi/2$. We are in the imprinted regime so this gives

$$g_{loc}(\pi/2-\epsilon) = \alpha_0^2 + \frac{3r}{(r-1)^2} + (\alpha_0^2(\kappa-2)-\delta)\epsilon^2 + \cdots \quad (38)$$

When $\delta<\alpha_0^2(\kappa-2)$ this is an increasing function of ϵ, and so will be minimized by $\theta_m=\pi/2$; however, when δ is larger than this, $g_{loc}(\pi/2-\epsilon)$ becomes a decreasing function of ϵ, leading to the shift of θ_m away from $\pi/2$ seen in Fig. 6. For the parameter values we have chosen the transition value is $\delta_{cr}=0.4^2\times(2.1-2)=0.016$, which agrees with the numerical calculation. The imprinting efficiency in this case will be a step function.

A third class of behavior is exhibited by the system if we set κ close to 2 and reduce the anisotropy r. In this case the conical state appears in the low-efficiency regime rather than the imprinted regime. Figure 7 shows an example of this behavior.

IV. ELECTRIC FIELDS WITH PRESTRAINING

We expect that the field and/or strain-induced switching between imprinted and low-efficiency states will have technological applications. Previous ideas of using electric field induced director switching in nematic elastomers have been hampered by the large magnitude of the required electric field, corresponding to $\delta\approx1$, typically over 10^5 V/m. In the case of electric fields applied to chiral elastomers, the onset of switching can be made small by fine–tuning system parameters to achieve a chiral power close to the transition value. However, manufacturing a sample with a uniform chiral power prescribed to below 1% accuracy is currently un-

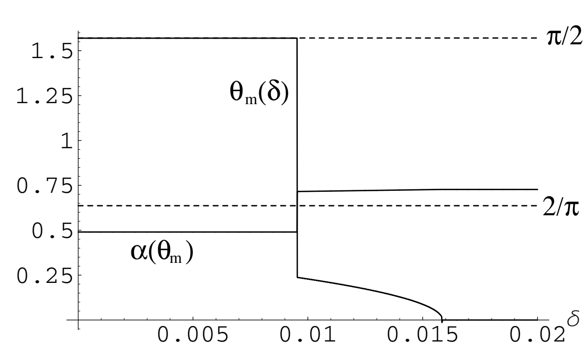

FIG. 7. The physical value of the helix cone angle θ_m and also the effective chiral power $\alpha(\theta_m)$ as a function of the dimensionless field δ when $\kappa=2.1$, $r=1.1$, and $\alpha_0=0.49$.

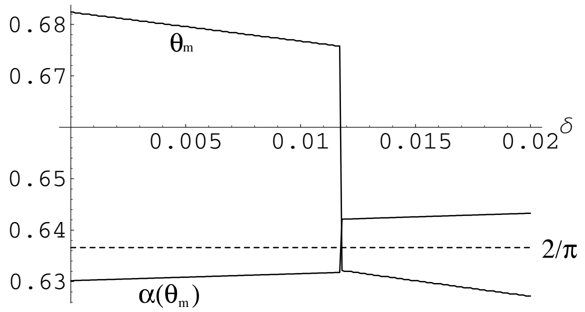

FIG. 8. The physical value of the helix cone angle θ_m and also the effective chiral power $\alpha(\theta_m)$ as a function of the dimensionless field δ when the sample is prestrained to $T=1.304$. The parameter values are $\kappa=2.5$, $r=2$, and $\alpha_0=0.4$.

feasible, and in fact unnecessary, if we consider the case where a sample is prestrained so that it is helped towards the transition point, before being subjected to the electric field.

The dimensionless free energy in the prestrained case is equal to the free energy with the mechanical strain of Eqs. (19) and (20), plus the electric field term $-\delta \cos^2\theta$. We choose the parameter values $\kappa=2.5$, $r=2$, and $\alpha_0=0.4$. In the absence of an electric field, the delocalization transition occurred at a strain of $T=1.306$. With this in mind we consider the case where the sample is prestrained to $T=1.304$, and is then subject to the electric field. Minimization of the free energy then reveals that delocalization occurs at $\delta\approx 0.01$ as shown in Fig. 8. Of course, this threshold electric field could be made even smaller if the prestrain can be controlled more accurately. The extent of this promotion of transition may be affected by the presence of defects within the sample, although current experimental techniques can already produce samples sufficiently defect-free to demonstrate clear mechanical and/or optical transitions. For comparison, this threshold value is close to 0.1 without the prestrain.

V. CONCLUSIONS

As one would intuitively expect, both mechanical strain and the electric field applied along the axes of imprinted helices force the director field to rotate toward those axes. This provides a valuable method of controlling the microscopic director profile via macroscopic fields. It also raises the possibility of an electro-mechanical device where the electric field may couple to mechanical deformation. Compared to piezoelectric materials, the elastomer deformation is much larger, providing a wider range of possible applications.

The existence of an effective chiral power which is a function of the cone angle (and also the strain in the mechanical case) means that the transition from an imprinted to a low-efficiency state may also be induced in this way. Such a field or strain-driven transition might provide a mechanism for a chiral pump. Such a device would consist of a permeable strip of elastomer imprinted with the pitch of the chiral molecules which are to be pumped. Immersed in a solution in which such molecules were present, the elastomer would selectively retain them. Once saturated, a small field or strain could be used to release the trapped molecules via the changes in internal structure we have described.

Our analysis has shown that the behavior of the elastomer under applied strain or field depends strongly on the choice of physical parameter values which characterize the system. As well as offering insight as to the kinds of physical effects one might expect to see, combined with the model of the underlying system, it provides a guide to tuning the system to obtain the particular behavior one requires for a given task.

APPENDIX A: MINIMIZING ELASTIC ENERGY OVER SHEARS

The nematic rubber elastic free energy may be written [7]

$$f_{\text{elast}} = \frac{\mu}{2}\,\mathrm{Tr}(\underline{\underline{\ell}}_0 \cdot \underline{\underline{\mathbf{T}}}^T \cdot \underline{\underline{\ell}}^{-1} \cdot \underline{\underline{\mathbf{T}}}), \tag{A1}$$

with μ being the linear shear modulus in the isotropic state. The step length tensors $\underline{\underline{\ell}}_0$ and $\underline{\underline{\ell}}$ characterize the Gaussian chain shape before and after the solvent is removed. The tensor $\underline{\underline{\mathbf{T}}}$ describes the total mechanical deformation of the elastomer since crosslinking.

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

$$\underline{\underline{\ell}}_0 = \underline{\underline{\delta}} + (r-1)\vec{n}_0\vec{n}_0, \tag{A2}$$

$$\underline{\underline{\ell}}^{-1} = \underline{\underline{\delta}} + \left(\frac{1}{r} - 1\right)\vec{n}\vec{n}, \tag{A3}$$

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.

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

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

Minimizing over T_{mz}, we obtain the spontaneous shear

$$T_{mz} = \frac{(r-1)T\sin\theta\cos\theta}{r-(r-1)\sin^2\theta}. \tag{A4}$$

Substituting this back into f_{elast}, we obtain

$$f_{\text{elast}} = \frac{\mu T^2}{2[r-(r-1)\sin^2\theta]} + \frac{\mu r(r+1)}{2rT} - \frac{\mu(r-1)\sin^2\theta\{1+(r-1)\cos^2[\phi(z)-q_0 z]\}}{2rT}. \tag{A5}$$

Defining

$$D_1 = \mu\frac{(r-1)^2}{r}, \tag{A6}$$

$$a(\theta) = \frac{r}{(r-1)^2[r-(r-1)\sin^2\theta]}, \tag{A7}$$

$$b(\theta) = \frac{1}{(r-1)^2}[r(r+1)-(r-1)\sin^2\theta], \tag{A8}$$

the elastic free energy becomes

$$f_{\text{elast}} = \frac{D_1}{2}\left(a(\theta)T^2 + \frac{b(\theta)}{T}\right) - \frac{D_1}{2T}\sin^2\theta\cos^2(\phi - q_0 z). \tag{A9}$$

APPENDIX B: MINIMIZING FREE ENERGY 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

$$I(L) = \frac{D_1\xi(\theta)\sin^2\theta}{2T}\int_0^{L/\xi(\theta)} du\{[\psi' - \alpha(\theta)]^2 - \sin^2\psi\},$$

over ψ. However, there is an important difference here, in that the variable α is not a constant. This means that the period of the solution to the first integral depends on θ as 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 [5] that the period of oscillatory motion is

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

where $\mathcal{K}(c)$ is the complete elliptic integral of the first kind [8]. The subscripts to P 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 [9]. Thus, after minimizing over ψ, averaging over one period we find

$$\frac{I(P_{z,\text{loc}})}{P_{z,\text{loc}}} = \frac{I[4\mathcal{K}(c)\xi(\theta)]}{4\mathcal{K}(c)\xi(\theta)} = \frac{D_1\sin^2\theta}{2T}\left[c^2 + \alpha(\theta)^2 - 2 + \frac{2\mathcal{E}(c)}{\mathcal{K}(c)}\right]. \tag{B5}$$

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

$$\frac{I(P_{z,\text{loc}})}{P_{z,\text{loc}}} = \frac{D_1\sin^2\theta}{2T}[\alpha(\theta)^2 - 1]. \tag{B6}$$

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

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

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

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

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 (B8) in the $c>1$ range by setting its derivative with respect to c to 0. 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 (B11) $\tilde{c}[\alpha(\theta)]$. Since

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

and

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

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 and 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 $\psi=az+\text{periodic}(z)$. From this we see that the physical director angle will be given by

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

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 (de)localized ($\alpha(\theta)>2/\pi$) regimes is

$$g_{\text{loc}}(\theta) = \frac{\sin^2\theta}{T}[\alpha(\theta)^2 - 1] + \left(aT^2 + \frac{b}{T}\right), \tag{B16}$$

and

$$g_{\text{deloc}}(\theta) = \frac{\sin^2\theta}{T}[\alpha(\theta)^2 - \tilde{c}^2] + \left(aT^2 + \frac{b}{T}\right). \tag{B17}$$

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