A mechanical strain field applied to a monodomain cholesteric elastomer will unwind the helical director distribution. There is an analogy with the classical problem of an electric field applied to a cholesteric liquid crystal, but with important differences. Frank elasticity is of minor importance unless the gel is very weak. The interplay is between director anchoring to the rubber elastic matrix and the external mechanical field. Stretching perpendicular to the helix axis induces the uniform unwound state via the elimination of sharp, pinned twist walls above a critical strain. Unwinding through conical director states occurs when the elastomer is stretched along the helical axis.

Monodomain cholesteric elastomers are formed by crosslinking mesogenic chiral polymers in the cholesteric state with a properly formed helical director twist. The subsequent retention of the helical state as an elastic equilibrium \( \phi = \frac{q_0}{\lambda} \) is a natural consequence of topological imprinting of textures in the crosslinked network, seen in a number of other elastomers with liquid crystalline order and other microstructure. Recently an interesting aspect of chiral imprinting was established by crosslinking nematic polymers in a chiral state purely induced by a chiral solvent \( \lambda \); on removal of the solvent, the network of chemically achiral nematic chains remains macroscopically cholesteric. Such an imprinting has been envisaged long time ago \( \phi \) on phenomenological grounds. It is now important to consider the mechanical possibilities of such solids with a helical microstructure, expecting new transitions and instabilities characteristic of liquid crystalline elastomers. Additionally there are obvious device applications of such materials, which combine all the optical properties of twisted nematic liquids with the remarkable mechanical characteristics of rubbers. There is some experimental evidence \( \phi \) that such effects are indeed observable and our hope is that this theoretical work will stimulate more studies in this field.

Consider a monodomain cholesteric elastomer with an ideal helically twisted director \( \mathbf{n}_0(z) \) in the \( xy \) plane, initially making angle \( \phi_0 = q_0 z \) with the \( x \) axis, Fig. 1. We shall examine two specific cases of imposed uniaxial extension: (i) the transverse deformation \( \lambda_{xx} = \lambda \) in the plane including \( \mathbf{n}_0 \), and (ii) the longitudinal deformation along the helix axis \( \lambda_{zz} = \lambda \).

The symmetry obvious from Fig. 1 requires that in the case (i) the director remains in the \( xy \) plane, characterised by the azimuthal angle \( \phi(z) \), while in the case (ii) one may expect a conical texture with \( \mathbf{n}(z) \) inclined towards the stretching axis \( z \) and, therefore, described by two angles \( \theta \) and \( \phi \) (cf. Fig. 2 below). In ordinary liquid cholesterics subjected to, e.g., a magnetic field \( H_z \), such conical states are not generally seen, preempted by the 90°-switching of the helix axis and then untwisting in the “transverse” geometry \( \phi \). We shall see that in elastomers, due to the chiral imprinting, this regime is not possible and the conical director configurations should occur.

An elastic material with a microstructure represented by an independently mobile director orientation is analogous to the Cosserat medium. In the limit of linear elasticity the relative rotation coupling between the director rotation \( \omega = [\mathbf{n} \times \tilde{\mathbf{n}}] \) and the antisymmetric part of strain, \( \Omega_i = \epsilon_{ijk} \ell_{jk} \),

\[
\frac{1}{2} D_1 [\mathbf{n} \times (\Omega - \omega)]^2 + D_2 \mathbf{n} : \varepsilon^{(s)} : [\mathbf{n} \times (\Omega - \omega)], \quad (1)
\]

has been first written down phenomenologically by de Gennes \( \phi \); \( \varepsilon^{(s)} \) being the symmetric part of the small strain defined as \( \tilde{\varepsilon} = \frac{1}{2} (\mathbf{e} - \mathbf{e}) \). This symmetry-based expression is only valid for small deformations, having only linear and quadratic terms in the local relative rotation.

The microscopic statistical-mechanical theory of nematic rubber elasticity, e.g. \( \phi \), obtains a generalisation of the classical rubber-elastic energy density in the form of a complete frame-independent expression

\[
F = \frac{1}{2} \mu \; \text{Tr} \left( \tilde{\varepsilon} : \varepsilon^{-1} \right), \quad (2)
\]

plus the constraint of material incompressibility, expressed by the condition \( \text{Det} (\lambda) = 1 \) on the strain.
tensor. Apart from the strain tensor, the other entries in the Eq. (4) are \( \ell_n = \ell_y - \ell_y + (\ell_x - \ell_z) \mathbf{n}_n \) and \( \ell_{-1} = (1/\ell_1) \delta + (1/\ell_1 - 1/\ell_1) \mathbf{n} \mathbf{n}_n \), the reduced shape and inverse shape tensors characterising the Gaussian distribution of nematic polymer chains before and after the distortion \( \mathbf{A} \). The rubber shear modulus \( \mu = n_s k_b T \) (with \( n_s \) the number density of network strands, proportional to the crosslink density) is that characteristic of the underlying isotropic rubber and sets the energy scale of distortions. The free energy density Eq. (2) is known to be valid up to large strains and correctly predicts the opto-mechanical responses and the soft elasticity of nematic elastomers. The free energy \( F \) is a function only of the chain anisotropy \( r = \ell_2/\ell_1 \), the ratio of the effective step lengths parallel and perpendicular to the director. It is an independently measured parameter accessible from neutron scattering or from spontaneous mechanical distortions on going from the nematic to isotropic phase. Unless there is a large nematic order change induced by the deformation, in spite of the apparent anisotropy along the pitch of affine contraction of the helical pitch so that \( \tilde{q} \propto \cos \phi \), \( \lambda \) diverges as the linear dimension of the sample. We accordingly conclude that the transverse contractions are uniform. Such deformations, e.g., \( \lambda_{xx} \) and \( \lambda_{yy} \), are equal in the first approximation, in spite of the apparent anisotropy along the pitch axis \( z \). Each deformation generates the same energy per chain independently of its alignment with respect to the director) and are thus both equal to \( 1/\sqrt{\lambda} \).

(i) Transverse elongation \( \lambda_{xx} = \lambda \). We consider the strain tensor in the following form:

\[
\mathbf{A} = \begin{pmatrix} \lambda & 0 & 0 \\ 0 & 1/\sqrt{\lambda} & 0 \\ 0 & 0 & 1/\sqrt{\lambda} \end{pmatrix}.
\]

Although one expects the director rotation in the azimuthal plane (cf. Fig. 3), there are no associated shear strains. Such shears, \( \lambda_{xy} \) and \( \lambda_{yx} \), would both lead to elastic compatibility problems (e.g., a generated shear \( \lambda_{xx} \propto y \), the sample dimension) and we assume they are suppressed. The shears \( \lambda_{xx} \) and \( \lambda_{xx} \) are not subject to compatibility requirements. However, they should not appear on symmetry grounds, which is easily confirmed by direct minimisation. Now \( \mathbf{n}_x = \{ \cos \phi_0, \sin \phi_0, 0 \} \) and the rotated director after deformation is \( \mathbf{n} = \{ \cos \phi, \sin \phi, 0 \} \). Note that the helix is \( \phi_0 = \phi_0 z \) in the initial undistorted material. After deformation, because of the affine contraction \( \lambda_{xx} = 1/\sqrt{\lambda} \), the material frame shrinks: \( z \to z/\sqrt{\lambda} \). This has an effect of affine contraction of the helical pitch so that \( \tilde{q} = \sqrt{\lambda} q_0 \) in all expressions below. With the \( \ell_n \) and \( \ell_{-1} \) implied by these \( \mathbf{n}_n \) and \( \mathbf{n} \), the free energy density Eq. (4) yields

\[
F_{\perp} = \frac{1}{2} \mu \left( \lambda^2 + \frac{2}{\lambda} + \frac{r-1}{r} \left[ \lambda^2 (r c_0^2 s^2 - c^2 s_0^2) \right. \right.
\]

\[
+ \left. \frac{1}{\lambda} (r c^2 s_0^2 - s^2 c_0^2) - 2 \sqrt{\lambda} (r-1) s_0 c_0 s c \right) \right),
\]

where \( c_0 \) and \( s_0 \) are shorthand for \( \cos \phi_0 \) and \( \sin \phi_0 \); analogously, \( c \) and \( s \) stand for \( \cos \phi \) and \( \sin \phi \). The appearance of terms linear and quadratic in \( \phi \) (or rather
$\sin \phi$ because all values of the azimuthal angle will be found along the cholesteric helix) indicate that rotations can always lower the energy for $\lambda \neq 1$. Minimization of $F_L$ with respect to $\phi$ results in the expression for the local director angle $\phi(z)$ at a given imposed extension $\lambda$, depending on the phase of cholesteric helix:

$$\tan 2\phi = \frac{2\lambda^{3/2}(r-1)\sin 2\tilde{q}z}{(r-1)(\lambda^3+1)\cos 2\tilde{q}z + (r+1)(\lambda^3-1)} \quad (6)$$

Initially, all directors at $0 < \tilde{q}z < \pi/2$ are induced to rotate “backward” towards $\phi = 0$, and all directors at $-\pi/2 < \tilde{q}z < 0$ rotate “forward” towards $\phi = \pi$, as the imposed deformation $\lambda$ increases, see Fig. 2. Although $\phi = 0$ and $\pi$ describe equivalent directors, the twist wall between these two states becomes more and more sharp. Due to the helix imprinting, the orientations $\phi = 0$ at $\tilde{q}z = 0$ and $\phi = \pi$ at $\tilde{q}z = \pi$ are pinned, as is the midpoint of the twist wall at $\tilde{q}z = \pi/2$. As a result, no change of the helical pitch can occur. This is in contrast with cholesteric liquid crystals, where in a classical problem of helix unwinding by electric or magnetic field one finds an increase in cholesteric pitch along with the coarsening of the helix.

![FIG. 2. The director angle $\phi$ against the cholesteric helix phase $q_0z$ for increasing strain $\lambda = 1$ (open circle), 1.15 (triangle), 1.23 (open square), 1.25 (shaded square) and 1.5 (shaded circle). The polymer chain anisotropy is $r = 1.9$ and thus the critical strain is $\lambda_c = r^{1/3} \approx 1.24$ (see text). At $\lambda > \lambda_c$, the director pinning at $\phi = \pi/2$ breaks down and a discontinuous transition occurs, after which the director continuously rotates towards the final uniform $\phi = 0.$](image)

Examining the Eq. (6) one finds that the denominator changes sign and remains negative in the region of the twist wall, centered at $\tilde{q}z = \pi/2$ between the values $\phi = \pi/4$ and $3\pi/4$. The width of such a wall is

$$w \simeq \frac{2}{q_0} \sqrt{\frac{r-\lambda^3}{(r-1)(\lambda^3+1)}}.$$

As the increasing applied strain reaches a critical value $\lambda_c = r^{1/3}$, the wall width $w \to 0$ and the discontinuous transition occurs. The director in the mid-point of the wall breaks away from the pinning and jumps from $\phi = \pi/2$ to $\phi = 0$, along the strain axis, thus removing the topologically constrained twist wall. From this point there is no barrier for director rotation towards the final uniform orientation with $\phi = 0$, as the last two curves in Fig. 2 indicate. The bifurcation occurs between the family of $\phi(z)$ curves at $\lambda < \lambda_c$ and those at $\lambda > \lambda_c$. They are separated by the critical curve $\phi_c$ given by $\tan 2\phi_c = -2 \left( \frac{\sqrt{r}}{\lambda+1} \right) \tan \tilde{q}z$.

A discontinuous director jump at a critical strain has been predicted, and indeed observed in nematic elastomers stretched at 90° to their initial director $n_0$. It was also found that even small deviations from the exact perpendicular geometry, or the possibility of soft shears in stripe domains lead to a continuous director rotation. However, in the present cholesteric case the shears are prohibited by compatibility constraints and one always finds an exact phase angle $\phi = \pi/2$ along the helix – where the center of narrowing twist wall becomes pinned from both sides. It is this point that experiences a discontinuous jump in order to allow the system to proceed to its final uniform equilibrium state.

(ii) STRETCHING ALONG THE PITCH AXIS $\lambda_{zz} = \lambda$. We now take (cf. Fig. 3)

$$\lambda = \begin{pmatrix} 1/\sqrt{\lambda} & 0 & \lambda_{zz} \\ 0 & 1/\sqrt{\lambda} & \lambda_{yz} \\ 0 & 0 & \lambda \end{pmatrix} \quad (7)$$

No compatibility problem with shears $\lambda_{zz}(z)$ and $\lambda_{yz}(z)$ arises from their variation with $z$ along the helical pitch. By contrast, their conjugate strains $\lambda_{xz}$ and $\lambda_{xy}$, which would also have to vary with $z$, would lead to a serious compatibility mismatch, e.g. $\partial \lambda_{zz}/\partial z = \partial \lambda_{xx}/\partial x$. We therefore assume $\lambda_{xz}$ and $\lambda_{xy}$ are suppressed even though in other settings these are the generators of soft elastic response.

![FIG. 3. (a) The geometry of director rotation in response to stretching $\lambda_{zz}$ along the helix axis. (b) The angle $\theta$ of director tilt plotted against the imposed strain $\lambda$, Eq. (11) for $r = 1.3$ (triangle) and $r = 1.9$ (circle). Strain varies from 1 to $\lambda_2 = r^{2/3}$ at which point the alignment is $\theta = \pi/2$, uniformly along the former pitch axis.](image)
in the corresponding expansion of the cholesteric pitch: \( q = q_0/\lambda \). With the \( \ell_x \) and \( \ell_z \) defined by the axes \( n_0 \) and \( n \), the free energy density Eq. (2) now becomes a function of three variables: the director tilt angle \( \theta \) and the two shear strains \( \lambda_{xz}(z) \) and \( \lambda_{yz}(z) \) (we continue to neglect the effects of director gradients and Frank elasticity). Algebraic minimisation over these components of strain tensor is not difficult and results in

\[
\left( \frac{\lambda_{xz}}{\lambda_{yz}} \right) = \frac{r_1 (r_1 - 1) \sin 2\theta}{r_1 + 1 - (r_1 - 1) \cos 2\theta} \left( \frac{\cos q \bar{q}_z}{\sin q \bar{q}_z} \right),
\]

(8)

in phase with the azimuthal angle along the helical pitch. Eq. (8) describes small distortions in the \( xy \) plane, perpendicular to the helix axis, rotating following the initial orientation \( n_0 \). On substitution of these optimal shears back into the free energy density one obtains

\[
F_\parallel = \frac{1}{2} \mu \left( \frac{\lambda^2}{1 + (r_1 - 1) \sin^2 \theta} + 2 + (r_1 - 1) \sin^2 \theta \right) \lambda \]

(9)

\( F_\parallel \) expands at small tilt angle \( \theta \) as

\[
F_\parallel \approx \frac{1}{2} \mu \lambda^2 + 2/\lambda - 1 \frac{1}{2} \mu \lambda^2 (r_1 - 1) (r_1 - 1)/\lambda),
\]

(10)

that is the director starts to rotate down to define a cone of semiangle \( \pi/2 - \theta \) immediately as the strain \( \lambda > 1 \) is imposed. The equilibrium director tilt is obtained by minimisation of the full free energy density \( F_\parallel (\theta) \):

\[
\sin^2 \theta = \frac{\lambda^2/2 - 1}{r_1 - 1}; \quad \theta = \arcsin \frac{\lambda^2/2 - 1}{r_1 - 1}.
\]

(11)

The director rotation starts and ends in a characteristically singular fashion Fig. (b) (reminiscent of the universal opto-mechanical response seen in nematic elastomers [11]). The rotation is complete with the director aligned along the extension axis (\( \theta = \pi/2 \)) at \( \lambda = r_1^{2/3} \) which, for some elastomers, can be a very large extension.

In contrast to conventional cholesteric liquid crystals, we have altogether ignored effects of Frank elastic energy. The most compelling evidence for this is the very stability of the imprinted helical state in the face of the Frank penalty \( \frac{1}{2} K q_0^2 \). The argument for this relies upon the great difference in characteristic length scales, the elastomer penetration depth, more accurately expressed as \( \xi \approx \frac{1}{r_1} \sqrt{K/\mu} \) [cf. Eq. (3)], and the director modulation wavelength estimated by the helical pitch \( p = \pi/q_0 \gg \xi \). There are two possibilities to alter this inequality – by increasing the penetration depth \( \xi \) (either by making a weaker gel, or a less anisotropic one), or by locally increasing the director gradient (for instance, in the ever narrowing twist wall, Fig. 3).

One can estimate how weak a gel must be for the Frank elasticity to intervene in our analysis. When \( \xi \sim p \), for example with a pitch \( p \sim 4 \times 10^{-7} \text{m} \), then a rubber modulus of only \( \mu \sim 60 \text{J/m}^3 \) is required (assuming \( r_1 - 1 \sim 1 \)). Nematic elastomers typically have \( \mu \sim 10^3 - 10^4 \text{J/m}^3 \) and their cholesteric analogues would clearly find Frank-elastic effects minor. However, an elastomer with a reasonable \( \mu \sim 10^3 \text{J/m}^3 \) would feel the director gradients when its polymer chain anisotropy becomes as low as \( r = \ell_y/\ell_z \sim 1.25 \). Such a value is easily reached in side-chain liquid crystal polymers, especially near the clearing point [1].

Another interesting test of the role of Frank elasticity is in the twist wall described in our case (i). The width of the wall decreases to zero, and the Frank energy density grows, being maximal at the centre of the wall. There it is \( \frac{1}{2} K q_0^2 \lambda^3 (r_1 - 1/2)(r_1 - \lambda^3) \) and diverges at the critical strain \( \lambda_c \). Therefore, the local analysis of Eqs. (12)-(14) is only valid outside the region of strain \( \Delta \lambda \gg \frac{1}{3} \pi/2 \pi \rho \xi^2 \) around \( \lambda_c \). In a typical hard nematic rubber this is a narrow region of \( \Delta \lambda \leq 0.01 \), but in a weak gel with low chain anisotropy it may become more substantial. Moreover, the finite width of the twist wall, demanded by the Frank gradient energy, raises the question of topological mechanism for eliminating the twist stored in the cholesteric helix, perhaps by a disclination loop expansion.

To summarise, we have predicted a qualitatively new response of an elastomer with chiral cholesteric microstructure to applied fields that is different from classical cholesteric liquids. Likewise, the chiral imprinting and its modification by elastic fields is a new effect in rubbers and solids. One could envisage tuning these effects by the use of solvents (with or without chiral power) and by other fields affecting the director, for instance electric.

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\[1\] G. Maxein, S. Mayer and R. Zentel, Macromolecules 32, 5747 (1999).
\[2\] C.D. Hasson, F.J. Davis and G.R. Mitchell, Chem. Commun., 2515 (1998).
\[3\] P.G. de Gennes, Phys. Lett. 28A, 11 (1969).
\[4\] R. Zentel, Liq. Cryst. 3, 531 (1988).
\[5\] R.B. Meyer, Appl. Phys. Lett. 12, 281 (1968).
\[6\] P.G. de Gennes in: Liquid Crystals of One- and Two-Dimensional Order, ed. W. Helfrich and G. Heppke, Springer, Berlin, p.231 (1980).
\[7\] M. Warner and E.M. Terentjev, Progr. Polym. Sci. 21, 853 (1996).
\[8\] P.D. Olmsted, J. Phys. II 4, 2215 (1994).
\[9\] P.G. de Gennes, Solid State Commun. 6, 163 (1968).
\[10\] G.R. Mitchell, F.J. Davis and W. Guo, Phys. Rev. Lett. 71, 2947 (1993).
\[11\] H. Finkelmann, I. Kundler, E.M. Terentjev and M. Warner, J. Phys. II 7, 1059 (1997).