

Isotropic-to-cholesteric transition in liquid crystal elastomers

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A liquid crystal elastomer tries to spontaneously elongate on entering the locally nematic phase, but may have to twist to reduce its Frank elastic energy. The extremes are a conventional, transverse cholesteric structure (where it reduces its Frank energy), and a uniformly aligned state (where it can maximally spontaneously extend and reduce its elastic energy). Between these it can adopt a conical state where there is also bend but equally a partial satisfaction of the elastic requirements. A line of first-order transitions between conical and transverse states ends and becomes a line of second-order transitions, depending on chain anisotropy, the ratio of the Frank bend and twist constants, and on the elastic modulus reduced by the bend energy. Continuous and discontinuous variation of cone angles, and spontaneous elongations and shears are given, as are analytic forms for the singular variation of director as cones are lost to the transverse state. The variation of the multicritical point with the ratio of Frank constants is also given.

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I. INTRODUCTION

We address the question of the conformations of a block of chiral rubber which on cooling tries to enter the nematic or cholesteric states. Nonchiral rubber is known to extend by up to several hundred percents on entering the monodomain nematic state. The network chains become elongated by the nematic orientational field and then strain the network which they comprise. When the chains are chiral, they would like to form a cholesteric state where the director twists helically instead. Although a rubber can in general allow cholesteric, monodomain order [1], a rubber starting from the isotropic state suffers an energy cost since the spontaneous nematic strains would be in different directions at different places along the helix and a compromise strain must be found.

This problem has recently been addressed by Pelcovits and Meyer [2]. They employed elasticity theory in the linear continuum limit which is a qualitatively excellent way to proceed. It may give inaccuracies at the high spontaneous strains observed in liquid crystal elastomers and constancy of volume is difficult to implement in their approach. Deformations must be volume preserving in soft solids. Their predictions must, however, be qualitatively correct. We resolve the problem using nonlinear rubber elasticity theory which removes these quantitative quibbles.

Since the first classical proposals to subject cholesteric liquid crystals to external fields [3,4], there has been interest in the so-called conical state. Fields along the helix axis induce the director to rotate out of the perpendicular plane onto the surface of a cone that is explored as one moves down the helix. The reduction in field energy associated with conical alignment towards the field is resisted by the creation of bend Frank elastic energy plus an increase in the twist energy. There are difficulties in observing the conical state in fluids [3]. Solid cholesterics additionally offer mechanical strain fields to couple to the helix. Strains along the helix have been analyzed and are predicted [5,6] to produce a conical state. However, for geometrical reasons longitudinal strains are also difficult to apply to monodomain cholesteric elastomers. Their helix axes are perpendicular to the flat sur-

face of the monodomain strips produced by the Freiburg technique [1]. This was another reason why Pelcovits and Meyer were interested in the isotropic to cholesteric transition where there may be grounds for expecting a conical state to form spontaneously.

Consider a block of elastomer deforming by $\underline{\lambda}$ on transforming from the isotropic to the ordered state. Let the pitch axis be the pseudovector $\hat{\mathbf{p}}$, if there is a cholesteric ordering, and this will be the $\hat{\mathbf{z}}$ axis if a specific coordinate system is chosen.

The director in these coordinates is

$$\hat{\mathbf{n}} = \sin(\theta)\cos(\phi)\hat{\mathbf{x}} + \sin(\theta)\sin(\phi)\hat{\mathbf{y}} + \cos(\theta)\hat{\mathbf{z}}, \quad (1)$$

where $\phi = qz$ is the azimuthal angle and θ is the cone angle (our definition of θ is the complement of that of Pelcovits and Meyer). The director in this conical cholesteric advances uniformly, tracing out a helix of pitch $p = 2\pi/q$. Since $\hat{\mathbf{p}}$ is a pseudovector, ϕ is a scalar, and $\hat{\mathbf{p}} \rightarrow -\hat{\mathbf{p}}$ does not change the sense of the helix. There is a twofold symmetry axis perpendicular to the helix and $\hat{\mathbf{n}} \rightarrow -\hat{\mathbf{n}}$ invariance is also respected. Thus, although termed ‘‘conical,’’ this type of cholesteric cannot be polar along their helix axis as a result of its director tilt. (For this, biaxiality misaligned with the local principal axes would be required.) Since the system is invariant under $\hat{\mathbf{n}} \rightarrow -\hat{\mathbf{n}}$ and $\hat{\mathbf{p}} \rightarrow -\hat{\mathbf{p}}$, it might be more appropriate to term it an ‘‘hour-glass’’ phase. We shall retain the name conical.

A quite general distortion is, in these coordinates,

$$\underline{\lambda} = \begin{pmatrix} 1/\sqrt{\lambda} & 0 & \lambda_{xz} \\ 0 & 1/\sqrt{\lambda} & \lambda_{yz} \\ 0 & 0 & \lambda \end{pmatrix}. \quad (2)$$

It is trivial to see that $\det(\underline{\lambda}) = 1$, that is the constancy of volume during deformation has been built in. Uniform extension ($\lambda > 1$) or compression ($\lambda < 1$) along the helix, and compression/extension ($1/\sqrt{\lambda}$) in the plane perpendicular to

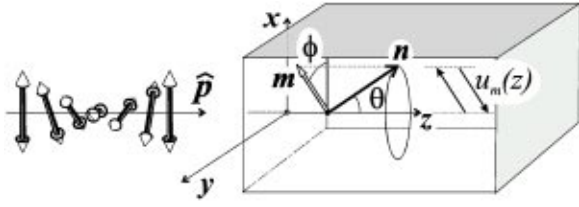


FIG. 1. The cholesteric conical state. The angle θ of the director $\hat{\mathbf{n}}$ is measured from the pitch axis $\hat{\mathbf{p}}$. The vector $\hat{\mathbf{m}}$ is along the projection of $\hat{\mathbf{n}}$ in the plane perpendicular to $\hat{\mathbf{p}}$. Displacement \mathbf{u} in the $\hat{\mathbf{m}}$ direction, varying in the z direction ($\hat{\mathbf{p}}$), gives rise to shears $\lambda_{mp}(z)$. For clarity these are shown shifted along the helix axis from where they are actually occurring.

the helix axis, is assumed—variation of any of these strains would cause problems with compatibility. See Ref. [5] for a discussion of this strain in this context. No compatibility problem with shears $\lambda_{xz}(z)$ and $\lambda_{yz}(z)$ arises from their variation with z along the helical pitch. By contrast, their conjugate strains λ_{zx} and λ_{zy} , which would also have to vary with z , leads to a serious compatibility mismatch, e.g., $\partial\lambda_{zx}/\partial z = \partial\lambda_{zz}/\partial x$. Let the direction of the projection of $\hat{\mathbf{n}}$ onto the plane perpendicular to $\hat{\mathbf{p}}$ be $\hat{\mathbf{m}}$. By symmetry the shears λ_{xz} and λ_{yz} can only be projections onto the x - y coordinates of the shear $\lambda_{mp}\hat{\mathbf{m}}\hat{\mathbf{p}}$ in the p - m plane. In a coordinate-free representation we thus have for $\underline{\lambda}$,

$$\underline{\lambda} = (\lambda - 1/\sqrt{\lambda})\hat{\mathbf{p}}\hat{\mathbf{p}} + 1/\sqrt{\lambda}\hat{\underline{\delta}} + \lambda_{mp}\hat{\mathbf{m}}\hat{\mathbf{p}}. \quad (3)$$

The requirement of compatibility is in effect that the well-defined, spatially varying displacements of the matrix exist. The suitable ones, $u_m\hat{\mathbf{m}}$ in the local $\hat{\mathbf{m}}$ direction, are shown in Fig. 1.

When the rubber spontaneously forms the cholesteric state, an underlying nematic order, Q (we assume it is locally approximately uniaxial in character), will be established. With it comes the necessity of spontaneous mechanical distortions and the onset of Frank elasticity, both of which we calculate below. The system finds the optimal degree of nematic order. Since the energy scale for nematic ordering is dominant, we shall for simplicity assume that the ordering is given (we indicate below the points at which it enters), rather than calculating it explicitly as Pelcovits and Meyer [2] did in their consideration of this problem. However, the director configurations and elastic distortions that are adopted on transition are not necessarily the optimal ones that would be found in a naturally uniform system because of the geometrical competitions between twist, bend, and elongation.

II. CHOLESTERIC TWIST AND BEND ENERGY

The Frank twist-bend elastic energy density is

$$F_{\text{Fr}} = \frac{1}{2}K_2[\hat{\mathbf{n}} \cdot (\nabla \times \hat{\mathbf{n}}) + q_0]^2 + \frac{1}{2}K_3[\hat{\mathbf{n}} \times (\nabla \times \hat{\mathbf{n}})]^2. \quad (4)$$

When the latter, bend term is absent and elastic effects play no role, the twist energy will be minimized when twist takes its natural value, that is $\hat{\mathbf{n}} \cdot (\nabla \times \hat{\mathbf{n}}) = -q_0$. The Frank twist

and bend elastic constants are, respectively, K_2 and K_3 . They depend on the degree of underlying nematic order Q . The natural cholesteric state is where the director is transverse to $\hat{\mathbf{p}}$, that is where the conical angle $\theta = \pi/2$. The twist wave number in the natural state is $q_0 = 2\pi/p$, where p is the pitch of the helix.

The critical vector which characterizes both twist and bend is $\nabla \times \hat{\mathbf{n}} = -\sin\theta\phi'(\cos\phi, \sin\phi, 0)$. It is then straightforward to derive the Frank-free energy density:

$$F_{\text{Fr}} = \frac{1}{2}K_3q_0^2[\gamma^{-1}(\tilde{q} - 1 - \tilde{q}\cos^2\theta)^2 + \tilde{q}^2\cos^2\theta(1 - \cos^2\theta)]. \quad (5)$$

We have extracted an energy density scale $\frac{1}{2}K_3q_0^2$ which leaves behind the dimensionless reduced wave number $\tilde{q} = q/q_0$ and elastic constant ratio $\gamma = K_3/K_2$ (following the notation of Pelcovits and Meyer).

We now minimize with respect to the reduced wave vector $\partial F_{\text{tot}}/\partial\tilde{q} = 0$. A simple relation between reduced wave vector and cone angle emerges

$$\tilde{q} = \frac{1}{1 + (\gamma - 1)\cos^2\theta}. \quad (6)$$

Take $\gamma > 1$, that is $K_2 < K_3$ —the physically realistic regime. Inverting Eq. (6) to give $\cos^2\theta = [(1 - \tilde{q})/\tilde{q}][1/(\gamma - 1)]$, shows that \tilde{q} is restricted to $1/\gamma \leq \tilde{q} \leq 1$, to ensure that $\cos\theta$ is real and ≤ 1 . If the pitch changes at all, it lengthens. We have solved a restricted part of the problem: if a cholesteric spiral has a conical distortion imposed upon it, what is the resulting optimal period of the helix?

At the optimal period, the free energy density for a fixed cone angle is

$$F_{\text{Fr}} = \frac{1}{2}K_3q_0^2 \frac{\cos^2\theta}{\sin^2\theta + \gamma\cos^2\theta}. \quad (7)$$

When the cone angle $\theta = \pi/2$ the free energy is zero (the natural twisted state is achieved) and when $\theta = 0$ the free energy density is $1/\gamma$ in reduced units, or equivalently $\frac{1}{2}K_2q_0^2$ in real units (there is neither twist nor bend present and a penalty is paid for not being at the natural state of twist, q_0). The state of the system will be somewhere between these extremes because of the competition with the rubber elastic energy which we consider below.

III. RUBBER ELASTIC ENERGY

A classical, Gaussian model for the rubber elastic free energy, generalized to nematic elastomers and valid for large distortions up to many 100%, is [5]

$$F_{\text{el}} = \frac{1}{2}\mu \text{Tr}(\underline{\ell}_0 \cdot \underline{\lambda}^T \cdot \underline{\ell}^{-1} \cdot \underline{\lambda}), \quad (8)$$

where μ is the shear modulus for small distortions in the isotropic state. The shape ellipsoids characterising the Gaussian chain shape in the isotropic and in the locally nematic ordered cholesteric states are, respectively,

$$\underline{\underline{\ell}}_0 = a \underline{\underline{\delta}}, \quad (9)$$

$$\underline{\underline{\ell}}^{-1} = (1/\ell_{\perp}) \underline{\underline{\delta}} + (1/\ell_{\parallel} - 1/\ell_{\perp}) \hat{\mathbf{n}}\hat{\mathbf{n}} \quad (10)$$

(the latter being given as its inverse). The chain anisotropy $r = \ell_{\parallel}/\ell_{\perp}$, the ratio of the effective step lengths parallel and perpendicular to the director, will be important. At isotropy, $r = 1$ and both these step lengths are equal to a . A factor of ℓ_{\parallel} can be extracted from $\underline{\underline{\ell}}^{-1}$ to leave behind $r \underline{\underline{\delta}} - (r-1) \hat{\mathbf{n}}\hat{\mathbf{n}}$. The nematic order induces shape anisotropy via the ratio r : in general for small order $r-1 \sim Q$. For the simple freely jointed rod model of polymers one has $\ell_{\parallel} = a(1+2Q)$ and $\ell_{\perp} = a(1-Q)$ for all values of the order. Inserting the shape tensors in F_{el} one obtains

$$F_{\text{el}} = \frac{1}{2} \mu \frac{a}{\ell_{\parallel}} \text{Tr} \left[\left(\lambda - \frac{1}{\sqrt{\lambda}} \right) \hat{\mathbf{p}}\hat{\mathbf{p}} + \frac{1}{\sqrt{\lambda}} \underline{\underline{\delta}} + \lambda_{\text{mp}} \hat{\mathbf{p}}\hat{\mathbf{m}} \right] \cdot [r \underline{\underline{\delta}} - (r-1) \hat{\mathbf{n}}\hat{\mathbf{n}}] \cdot \left[\left(\lambda - \frac{1}{\sqrt{\lambda}} \right) \hat{\mathbf{p}}\hat{\mathbf{p}} + \frac{1}{\sqrt{\lambda}} \underline{\underline{\delta}} + \lambda_{\text{mp}} \hat{\mathbf{m}}\hat{\mathbf{p}} \right]. \quad (11)$$

We multiply this out, using $\hat{\mathbf{n}} \cdot \hat{\mathbf{p}} = \cos \theta$ and $\hat{\mathbf{n}} \cdot \hat{\mathbf{m}} = \sin \theta$ and $\hat{\mathbf{m}} \cdot \hat{\mathbf{p}} = 0$,

$$F_{\text{el}} = \frac{1}{2} \mu \frac{a}{\ell_{\parallel}} \left[r \left(\lambda^2 + \frac{2}{\lambda} + \lambda_{\text{mp}}^2 \right) - (r-1) \left(\cos^2 \theta \left(\lambda^2 - \frac{1}{\lambda} \right) + 2 \sin \theta \cos \theta \lambda_{\text{mp}} \lambda + \frac{1}{\lambda} + \lambda_{\text{mp}}^2 \sin^2 \theta \right) \right]. \quad (12)$$

The shear λ_{mp} obtains by minimizing F over λ_{mp} ,

$$\lambda_{\text{mp}} = \frac{(r-1) \sin \theta \cos \theta}{r - (r-1) \sin^2 \theta}. \quad (13)$$

The shear vanishes naturally for a transition to a uniform nematic ($\theta=0$) and also to a standard, transverse cholesteric ($\theta=\pi/2$) that we shall denote by T . One can return the shear to the free energy to yield a resultant energy dependent upon only the cone angle and elongation along the pitch axis,

$$F_{\text{el}} = \frac{1}{2} \mu \frac{a}{\ell_{\parallel}} \left[\frac{r \lambda^2}{r - (r-1) \sin^2 \theta} + \frac{2r - (r-1) \sin^2 \theta}{\lambda} \right]. \quad (14)$$

This energy can in turn be minimized over elongations λ at fixed cone angle and yields a spontaneous distortion λ_{m} conditional on the choice of cone angle θ ,

$$\lambda_{\text{m}}^3 = \frac{1}{2r} [r - (r-1) \sin^2 \theta] [2r - (r-1) \sin^2 \theta]. \quad (15)$$

One can check that it yields the usual result for the spontaneous distortion $\lambda_{\text{m}} = r^{1/3}$ for the isotropic to uniform nematic case, when $\sin \theta = 0$. If the cholesteric energy dominates and $\sin^2 \theta = 1$ (cone angle $\theta = \pi/2$), then the rubber is twisted

to the classical transverse cholesteric state. There is a contraction along $\hat{\mathbf{p}}$ of $\lambda_{\text{m}} = [(r+1)/2r]^{1/3} < 1$ associated with this transition.

Returning $\lambda_{\text{m}}(\sin^2 \theta)$ to F one finally obtains a free energy density that only depends on angle:

$$F_{\text{el}} = \frac{1}{2} \mu \frac{3a}{\ell_{\parallel}} \frac{r^{1/3}}{2^{2/3}} \left[\frac{[2r - (r-1) \sin^2 \theta]^2}{r - (r-1) \sin^2 \theta} \right]^{1/3}. \quad (16)$$

Before the addition of Frank elastic terms, the rubber elastic free energy is minimal at $\theta=0$, that is a uniform state which has optimally elongated on entering the nematic state.

IV. MINIMIZATION OF THE TOTAL FREE ENERGY DENSITY

We add together the liquid crystal and rubber elastic free energy densities that have been optimized over all but the cone angle θ :

$$F_{\text{tot}} = \frac{1}{2} K_3 q_0^2 \left\{ \frac{\cos^2 \theta}{1 + (\gamma - 1) \cos^2 \theta} + \zeta \frac{3}{(r-1)^2} \left[\frac{[r + 1 + (r-1) \cos^2 \theta]^2}{1 + (r-1) \cos^2 \theta} \right]^{1/3} \right\}. \quad (17)$$

The energy scale $K_3 q_0^2/2$ has been extracted as a prefactor. The ratio of the rubber elastic to the Frank elastic energy scales is denoted by

$$\zeta = [\mu(r-1)^2 / (K_3 q_0^2)] \left[\frac{a}{\ell_{\parallel}} \frac{r^{1/3}}{2^{2/3}} \right]. \quad (18)$$

We refer to this simply as the reduced modulus.

The ratio $\sqrt{K}/\mu(r-1)^2$ (taking a representative Frank constant K) is the nematic penetration depth ξ , since it determines how deeply the surface orientation can penetrate into a bulk of a different orientation by the influence of Frank elasticity. Mostly, the rubber modulus presents a much larger energy than that associated with Frank elasticity [5]. The combination $\mu(r-1)^2$ is essentially D_1 , the de Gennes nematic rubber elastic modulus [7] resisting director rotation with respect to the elastic background. The deviation $r-1$ from isotropy drives the elastic anchoring. ξ is typically very short, about 10^{-8} m, unless the rubber modulus or the anisotropy are very low. The β of Pelcovits and Meyer corresponds as $\beta \sim 1/\sqrt{\zeta}$ to our ratio ζ with the assorted Q -dependent constants in the $[\dots]$ of our ζ corresponding to the order parameter-dependent constants in the expression for β .

Thus the measure of the relative energy scales is $\zeta \sim 1/(q_0 \xi)^2$ with some constants that scale harmlessly with Q in the second $[\dots]$ in ζ . We expand this out to see the size of the reduced modulus

$$\zeta = \left(\frac{p_0}{2\pi\xi} \right)^2 = \left(\frac{p_0}{2\pi} \right)^2 \frac{\mu(r-1)^2}{K_3} \sim 60(r-1)^2. \quad (19)$$

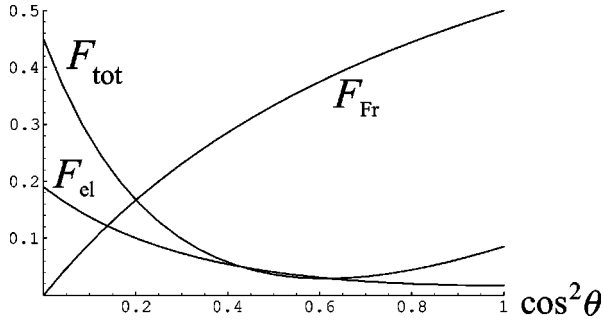


FIG. 2. The separate reduced Frank (F_{Fr}) and elastic (F_{el}) free energies as functions of $\cos^2\theta$ for $r=3$ and $\gamma=2$. Their total ($F_{tot}-9$) is shown for reduced elastic modulus $\zeta=5$. The shifts in two of the free energies are simply to put them on the same graph.

This estimate is for representative values $K_3=10^{-11}$ N for the bend modulus, $\mu=10^5$ N m $^{-2}$ for the rubber modulus and $p_0=5\times 10^{-7}$ m for the intrinsic cholesteric pitch. The factor r can be estimated from the gel's spontaneous elongation in analogous untwisted nematic phases. For the mechanically very weakly anisotropic gels of Mitchell, $r-1\sim 0.2$ and $\zeta\sim 1$ can be possible. It is easily possible, if we take modified estimates of $K_3=2\times 10^{-11}$ N and of $\mu=5\times 10^4$ N m $^{-2}$, to obtain $\zeta\sim 15(r-1)^2$. For mechanically strong anisotropic gels, for instance main chain elastomers, $(r-1)\sim 60$ and ζ can be large. On the other hand less anisotropic gels in this limit could have $\zeta<1$.

The equilibrium cone angle is given by $\partial F_{tot}/\partial(\cos^2\theta)=0$, that is

$$\frac{1}{[1+(\gamma-1)\cos^2\theta]^2} = \zeta \frac{1-\cos^2\theta}{[r+1+(r-1)\cos^2\theta]^{1/3}[1+(r-1)\cos^2\theta]^{4/3}}. \quad (20)$$

We show in Fig. 2 the two parts of the reduced free energy $F_{Fr}=\cos^2\theta/(1+(\gamma-1)\cos^2\theta)$ and $F_{el}=\{[r+1+(r-1)\cos^2\theta]^2/[1+(r-1)\cos^2\theta]\}^{1/3}$ [with the $3\zeta/(r-1)^2$ factor omitted] separately to emphasize the competition. The former is minimal in the transverse cholesteric at $\cos^2\theta=0$ ($\theta=\pi/2$). The latter is minimal in the uniform elongated state, $\cos^2\theta=0$ ($\theta=0$). Their sum $F_{tot}(\cos^2\theta)$ has two qualitatively different behaviors depending on r , γ , and ζ which we examine separately below. However, the uniform state (where the cone is lost altogether) is *never* stable since at the upper end of the range ($\cos^2\theta=1$) the derivative $\partial F_{tot}/\partial(\cos^2\theta)=1/\gamma^2>0$, independently of any elastic effects which find their absolute minimum there (one sees from Fig. 2 that here F'_{tot} comes entirely from F'_{Fr}). For large modulus μ , and hence large reduced modulus ζ , the resulting cone angle θ is clearly small but nonzero—a conical helix results from the slightest chiral perturbation because the transverse shears that it induces as it induces a cone angle correspond to soft elasticity [2]. Expanding relation (20) for small θ and large ζ one obtains at lowest order,

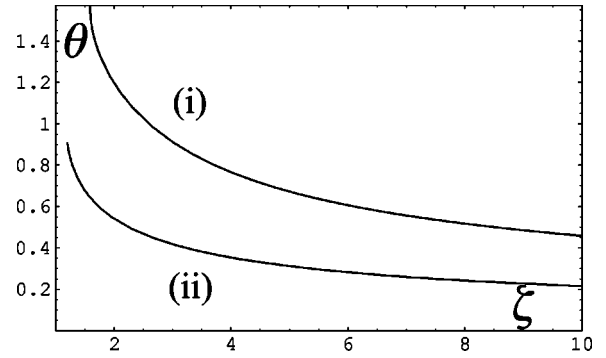


FIG. 3. Cone angle θ against reduced elastic coupling ζ for (i) $r=3$, $\gamma=2$ —note the $\sqrt{\quad}$ singularity as the classical T state is approached. (ii) $r=2$, $\gamma=3$, where the transition from conical to transverse is now discontinuous. Metastable conical states exist beyond the jump but are not shown.

$$\theta^2 \sim \frac{2^{4/3} r^{5/3}}{\gamma^2} \frac{1}{\zeta} \equiv \theta^2 \sim \frac{K_2 q_o^2}{\mu} \frac{4}{\gamma} \frac{r^{4/3}}{(r-1)^2} \frac{\ell_{\parallel}}{a} \sim \frac{K_2 q_o^2}{\mu}. \quad (21)$$

The development of the cone angle depends on the ratio of elastic to *twist* energies. We denote the conical state by C and now examine the two regimes of its development and loss to the T state.

(i) *Continuous conical-transverse (C-T) transition.* The minimum near $\theta=0$, that is $\cos^2\theta=1$, for large ζ moves as in Fig. 2 to smaller $\cos^2\theta$ as ζ decreases. The slope of $F_{tot}(\cos^2\theta)$ against $\cos^2\theta$ at $\cos^2\theta=0$ is $\partial F_{tot}/\partial \cos^2\theta|_0=1-\zeta/(r+1)^{1/3}$. Thus $F'_{tot}<0$ here for large ζ . If the minimum approaches $\cos^2\theta=0$ as $F'(0)$ changes sign, then F_{tot} simply has its smallest value at the end of its range, the T state at $\cos^2\theta=0$. Thus the critical value of ζ is

$$\zeta_c=(r+1)^{1/3} \equiv \mu_c=K_3 q_o^2 \frac{(r+1)^{1/3}}{(r-1)^2} \frac{\ell_{\parallel}}{a} \frac{2^{2/3}}{r^{1/3}}, \quad (22)$$

for the stability of the transverse cholesteric when elastic effects are small compared with those of *bend*. Recall that r is the intrinsic shape anisotropy of the network polymers, with $r=1$ representing isotropy, and $r-1\sim Q$ representing the nematic order.

The T state has been approached continuously from the C state. For the example of $r=3$, $\gamma=2$, Fig. 3 shows $\theta(\zeta)$. The $\sqrt{\quad}$ singularity as $\theta\rightarrow\pi/2$ comes from transforming from $\cos^2\theta$ to θ as a variable. One can solve Eq. (20) analytically around $\cos^2\theta\rightarrow 0$, that is, $\theta\rightarrow\pi/2$, to obtain this $\sqrt{\quad}$ singularity,

$$\cos^2\theta \sim \frac{1}{2} \frac{(\zeta/\zeta_c - 1)}{2r^2 + 2r - 1 - (\gamma - 1)},$$

or

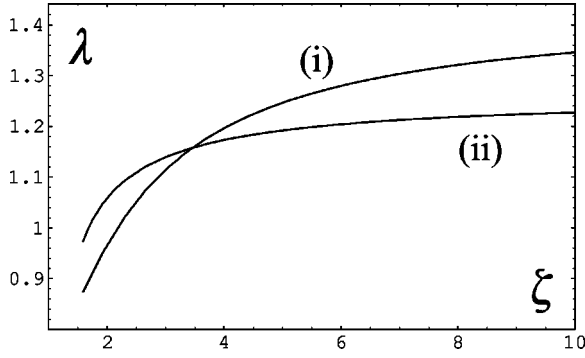


FIG. 4. Spontaneous distortion λ against reduced elastic coupling ζ for (i) $r=3$, $\gamma=2$. (ii) $r=2$, $\gamma=3$, where the final jump is to $\lambda=0.909$.

$$\delta = \pi/2 - \theta \sim \frac{\sqrt{\zeta/\zeta_c - 1}}{\sqrt{2 \left[\frac{2r^2 + 2r - 1}{3(r+1)} - (\gamma - 1) \right]^{1/2}}}. \quad (23)$$

Figure 4 shows the spontaneous elongation-contraction along the helix axis. Asymptotically, the unwound state would give $\lambda=r^{1/3}=1.44$ relative to its isotropic starting point. The unwound state is far away from the reduced moduli we display. The C state is evidently stable over a wide range of modulus μ compared with the intrinsic bend energy scale $K_3 q_0^2$. The T state contracts relative to the isotropic state by $[(r+1)/2r]^{1/3}=0.874$. Returning the spontaneous distortion λ_m of Eq. (15) to Eq. (13) gives the optimal shear $\lambda_{mp}(\zeta)$, shown in Fig. 5. Although the shear is very large for a wide range of reduced moduli, ζ , (but vanishing in the T state for $\zeta < \zeta_c$ and in the untwisted state for $\zeta \rightarrow \infty$) it will be hard to see. It corresponds to displacements in the plane perpendicular to the helix, but in a direction \mathbf{m} which rotates with a period along the helix axis corresponding to the current wave-vector \tilde{q} of Eq. (6), that is a period $p = p_0 [1 + (\gamma - 1) \cos^2 \theta(\zeta)]$. Thus the displacement pattern is fine (submicron) and of amplitude $\sim \lambda_{mp} p_0$, that is rather small. It is compellingly visualised by Pelcovits and Meyer [2].

(ii) *Multicritical C-T transition.* One can see from Eq.

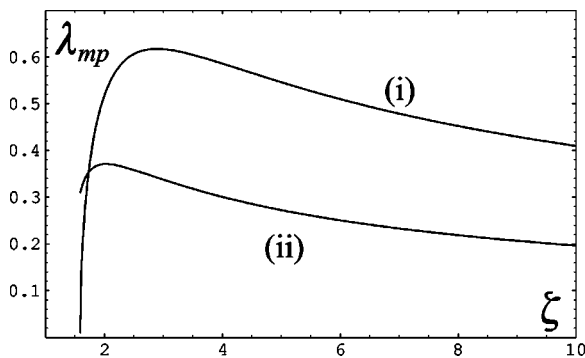


FIG. 5. Spontaneous shear λ_{mp} against reduced elastic coupling ζ on making the transition from the isotropic to cholesteric state for (i) $r=3$, $\gamma=2$; (ii) $r=2$, $\gamma=3$, where the final vanishing of shear occurs discontinuously as ζ is reduced.

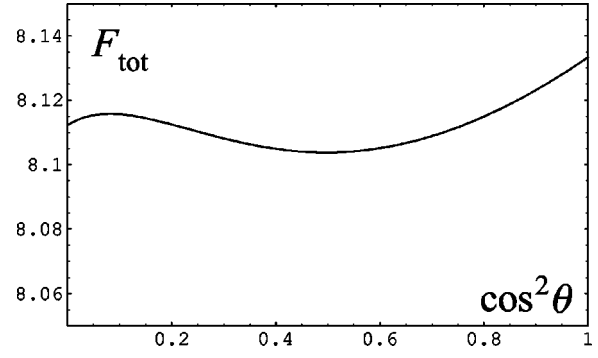


FIG. 6. Free energy F_{tot} against $\cos^2 \theta$ for case (ii) $r=2$, $\gamma=3$, where discontinuities arise as ζ is reduced.

(23) that the $\delta \sim (\zeta/\zeta_c - 1)^{1/2}$ solution for $\theta \rightarrow \pi/2$ fails at an r_{mc} given by the solution of the quadratic

$$\gamma = 1 + \frac{2r^2 + 2r - 1}{3(r+1)}. \quad (24)$$

It is straightforward to reanalyze the solution to Eq. (20) around $\theta = \pi/2$ and one obtains

$$\delta = (\zeta/\zeta_c - 1)^{1/4} / g^{1/4}(r_{mc}), \quad (25)$$

where the function $g(r_{mc})$ is relatively simple and has the property that $g(r_{mc}) > 0$ for $r_{mc} > 1$. Thus for each γ there is a multicritical point (that depends on the value of γ) where the approach to the transverse cholesteric state with varying coupling ζ takes on the power dependence $1/4$ rather than $1/2$.

(iii) *Discontinuous C-T transition.* Below the multicritical point $r < r_{mc}$ the behavior is quite different in that when the slope $F'_{\text{tot}}(\cos^2 \theta = 0)$ becomes negative with ζ decreasing below $\zeta_c = (1+r)^{1/3}$, there is still a minimum in F_{tot} for $\cos^2 \theta > 0$ which can be lower. An example of such a free energy is shown in Fig. 6 for which $r=2$, $\gamma=3$. When the $\cos^2 \theta_{\text{min}} \neq 0$ minimum gives a free energy equal to $F_{\text{tot}}(\cos^2 \theta_{\text{min}} = 0)$, then the system jumps from C to T state. For this pair of r and γ the jump occurs at a $\zeta^* = 1.256$ which is easily obtained by solving the condition $F_{\text{tot}}(0) = F_{\text{tot}}(\cos^2 \theta_{\text{min}})$ above. This ζ^* is markedly less than $\zeta_c = (1+r)^{1/3} = 1.442$. The corresponding variation of cone angle $\theta(\zeta)$ with reduced elastic modulus is given in Fig. 3 which shows the end of stability at ζ^* and a continuing set of metastable conical states down to $\zeta = 1.2$ that one indeed expects below a first-order transition (it is hard to resolve the metastable interval on the figure since the ζ range is so large). Figures 4 and 5 similarly show the jumps in the spontaneous distortion (to $\lambda_m = [(r+1)/2r]^{1/3} = 0.909$) and the shear (to zero) at the end of the C state.

For smaller γ , the r at which C-T transitions become discontinuous is smaller, for instance $\gamma=2$ has discontinuous transitions below a multicritical $r_{mc} = 1.5$, corresponding to condition Equation (24) above. The results can be summarized schematically in Fig. 7. The reduced modulus ζ_c is where the T state becomes stable and it varies with r as $(r+1)^{1/3}$. Trajectory (i) is a typical second-order transition

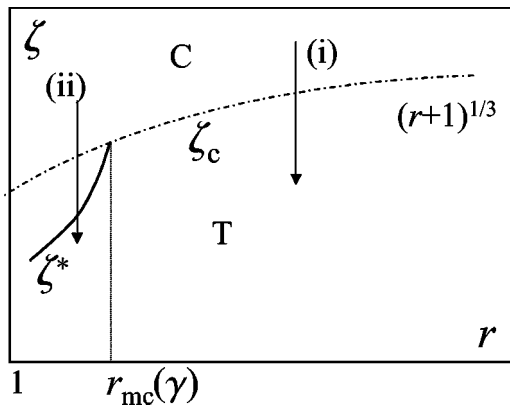


FIG. 7. Reduced elastic modulus ζ against chain anisotropy, r . The line $\zeta_c(r)$ separates conical (C) and transverse (T) cholesteric states with continuous transitions. For r and ζ below a multicritical point this line of second-order phase transitions ends and becomes first order, the line ζ^* separating the C and T states with a discontinuous transition. The location of the multicritical point varies with γ , the ratio of the bend to twist Frank elastic constants.

[case (i) discussed above] while (ii) is first order [case (ii)]. The multicritical anisotropy r_{mc} varies with γ by inverting Eq. (24) which is a simple quadratic in r .

A similar problem to this one of competition between elastic and twist-bend free energies arises when a cholesteric structure is crosslinked into an elastomer and then any chiral material removed. There is now no natural reason for director twist. Can the cost $\frac{1}{2}K_2q_0^2$ of retaining this twist be lost by untwisting and incurring some perhaps smaller mechanical elastic energy? This is the topological imprinting problem [8] that reveals a critical balance between μ and $K_2q_0^2$ where untwisting can occur. We stress that this is not a transition between a cholesteric and isotropic state as in this paper, but one induced by the removal of chiral solvent that induced the initial twist.

The converse of the thermal problem that we have asked here was posed by de Gennes [9]—will mechanical compatibility constraints on the spontaneous distortions in a cholesteric heated above the nematic-isotropic transition tempera-

ture prevent total isotropy being attained? The answer is theoretically yes, though experiments find the degree of chiral order surviving too small to detect [10].

We have shown that on leaving the isotropic state that (i) the untwisted nematic state is always unstable to cholesteric ordering, if only of a highly conical form. (ii) The period of twist depends on the cone angle but only varies between p_0 and γp_0 where p_0 is the natural cholesteric pitch and $\gamma = K_3/K_2$. (iii) There is a continuous conical to transverse transition if the reduced modulus ζ is lowered for suitable (r, γ) . The C-T transition becomes discontinuous beyond a multicritical point (r_{mc}, ζ_{mc}) , the location of which depends on γ , a dependence we specify. Variation of ζ , r , and γ is directly or indirectly possible—for instance r depends on the nematic order parameter and is known from spontaneous distortion and optical studies of related nematic elastomers to vary drastically. It could therefore be possible to observe a wide range of behaviors in making the transition from the isotropic state of fabrication to the cholesteric state.

Fabricating, in the isotropic state, elastomers that might undergo a transition to a monodomain C or T cholesteric state may simply require a variation of the Freiburg technique [1] of making cholesteric monodomain rubber. Biaxial stretch is effectively applied during the crosslinking process since solvent is lost while the rubber adheres to a rigid substrate. The helix axis is then directed perpendicular to the plane of stretch. In an isotropic variant of the technique, such a stretch would still take place. All directions in the plane being equal, monodomain cholesteric order could be induced by spontaneous distortions of the character of the $\underline{\lambda}$ of Eqs. (2) and (3) on entering the ordered phase. This technique, of prestretching during crosslinking, is also used in the Freiburg technique to produce monodomain nematic rubber, even when all processing is done in the isotropic state.

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