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Transitions and instabilities in liquid-crystal elastomers

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Solid nematic liquids, formed by cross-linking polymer liquid crystals into elastomers, are shown to display novel and complex elasticity. The internal (nematic) direction suffers a barrier to its rotation and this couples to standard elasticity. By considering imposed strains we illuminate this elasticity and also demonstrate an entirely new nematic phase transition. At a critical strain there is a discontinuity of director rotation.

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Polymer liquid crystals (PLC's) are long chain molecules composed of monomers capable of forming nematic or more complex mesophases. They combine the orientational order of nematic liquid crystals and the entropy-driven aspects of high polymers. In particular, they change their shape on orientationally ordering. Given that most properties unique to polymers depend on their shape, it is clear that new properties can arise in these unusual materials.

Long ago de Gennes [1] recognized that the most dramatic manifestation of shape-change coupling to orientational order would be in elastomeric networks of PLC's. Like conventional elastomers these materials can sustain very large deformations, which cause molecular extension and orientation, but, conversely, spontaneous alignment, or a nematic phase induced by applied stress, can lead to spontaneous distortion or a jump in a stress-strain relation.

More recently molecular models of these effects have been constructed (Abramchuk and Khokhlov [2], Warner, Gelling, and Vilgis [3]), and an understanding of mechanical critical points, memory of cross-linking, shifts in phase equilibria, and stress-strain relations obtained. Experiments before and after these theories have seen these basic effects [4], including nematic solid monodomains [5]. Such single-crystal samples are made by cross-linking in a field-oriented nematic melt, or by two-stage cross-linking and stressing the intermediate state. Internal stresses in the latter method also give instabilities, but of a different type from those proposed in this article. An initial phenomenological theory of the coupling between elastic, nematic, and electromagnetic fields has been set up by Brand [6] and a complete (group-theoretical) analysis of the linear elastic and piezoelectric possibilities carried out by Terentjev [7].

In this Rapid Communication we wish to sketch some new, complex elastic phenomena that seem to be unique to nematic solids. Networks cross-linked as nematic monodomains retain a memory of their initial state, characterized by the initial value of the order parameter, Q^0_{ij}, say. The order parameter tensor for uniaxial nematic liquid crystals is $Q_{ij} = Q^0(n_i n_j - \frac{1}{3}\delta_{ij})$ with $Q^0 = \langle P_2(\cos\beta)\rangle$ (where β is the local chain direction). It was shown earlier [3] that the *magnitude* Q^0 of the order at cross-linking determines the increase in the phase transition temperature above the melt value. Here we show that the principal axis $\mathbf{n}^0$ of Q^0_{ij} gives the solid an extra direction and that there is a barrier to the rotation of the current director from this direction. Internal rotational barriers and the concomitant resistance to strains interacting with these internal angular degrees of freedom yield the so-called "couple-stress" elasticity of the Cosserat form [8]. We shall demonstrate that the interplay between elastic-nematic memory and strain yields phase transitions and instabilities. Imposition of a bulk strain with principal axis not coincident with those of Q^0_{ij} causes deformations of $\mathbf{n}^0$, which can be continuous, or display a threshold, depending on the geometry. These are in some sense bulk versions of Fréedericksz transitions (where the barriers stem from the surfaces).

In a nematic monodomain with director $\mathbf{n}^0$ coincident with the $\mathbf{z}$ axis, spans $\mathbf{R}^0$ of polymer chain between network points have at the moment of cross-linking a Gaussian distribution:

$$P_0(R^0) \sim \mathrm{Det}[l^0_{ij}]^{-1/2} \exp\left(-\frac{3}{2L} R^0_i (l^0_{ij})^{-1} R^0_j\right), \qquad (1)$$

where summation over repeated indices has been assumed. L is the contour length of the chain strand, and the matrix l^0_{ij} of the inverse effective step lengths defining the chain shape parallel and perpendicular to the director $\mathbf{n}^0$ for a uniaxial phase is

$$(l^0_{ij})^{-1} = 1/l^0_\perp \delta_{ij} + (1/l^0_\parallel - 1/l^0_\perp) n^0_i n^0_j, \qquad (2)$$

with eigenvalues $1/l^0_\perp$ and $1/l^0_\parallel$ in its principal frame. The effective step lengths are related to the radii of gyration by $\langle (R^0_\parallel)^2\rangle = l^0_\parallel(Q^0)L$, etc. (often $l_\parallel \gg l_\perp$). Chain shape clearly depends on the nematic order parameter $Q^0 = \langle P_2(\cos\beta)\rangle$, with β the local chain direction. Let the current span be $R_i = \lambda_{ij} R^0_j$, with λ_{ij} the macroscopic deformation of the whole block of rubber. We employ the affine deformation assumption. We consider deformations λ_{ij} imposed with respect to the initial cross-linking state. Throughout this paper we assume the incompressibility of rubber, i.e., $\mathrm{Det}[\lambda_{ij}] = 1$. In general, the current temperature may be different from that of the formation state. Span probabilities are governed by a distribution $P(R)$ differing from that in Eq. (1) only in the $(l_{ij})^{-1}$ tensor, which describes the current chain shape. Taking $F_{\rm el}/k_BT = -\langle \ln P(R)\rangle_{P_0(R^0)}$, that is, the usual quenched average, one obtains for the elastic free energy per network strand

$$\frac{2F_{\rm el}}{k_BT} = l^0_{ij}\lambda_{kj}(l_{kl})^{-1}\lambda_{li} \equiv {\rm Tr}[\underline{\underline{l}}^0 \cdot \underline{\underline{\lambda}}^T \cdot \underline{\underline{l}}^{-1} \cdot \underline{\underline{\lambda}}] \tag{3}$$

(here and below the $\underline{\underline{\lambda}}$ notation symbolizes the diadic tensor form of λ). The current director, denoted by $\mathbf{n}$, is coincident with the initial $\mathbf{n}^0$ if λ_{ij} has the same principal frame. Minimization of Eq. (3) gives the spontaneous relaxation of deformations and one recovers the previous result for the shape change $\lambda_m = (l_\| l^0_\perp / l^0_\| l_\perp)^{1/3}$ [3].

We are interested here in the case where an imposed deformation λ_{ij} has principal axes not coincident with $\mathbf{n}^0$, thereby causing the equilibrium state to have $\mathbf{n}$ at some angle θ with respect to $\mathbf{n}^0$. We now determine this angle as a function of the magnitude of deformation and the orientation of the frame of λ_{ij} with respect to $\mathbf{n}^0$. What is revealed is an unusual elasticity with an internal barrier to rotation, and phase transitions of $\mathbf{n}$. We consider:

(i) Uniaxial extension at an angle α with respect to $\mathbf{z}$ (coincident with the initial director $\mathbf{n}^0$). Figure 1(a) shows the geometry. In terms of the unit vector $\mathbf{u}$ of the direction of extension, the deformation tensor at a constant volume is $\lambda_{ij} = (1/\sqrt{\lambda})\delta_{ij} + (\lambda - 1/\sqrt{\lambda})u_iu_j$.

(ii) Simple shear at an angle α, Fig. 1(b). In terms of unit vectors along the direction of shear $\mathbf{u}$, and along the gradient $\mathbf{v}$, the deformation is $\lambda_{ij} = \delta_{ij} + \lambda u_i v_j$.

It is clear [for $\lambda > 1$ in Fig. 1(a) and for general λ in Fig. 1(b)] that $\mathbf{n}$ must be in the plane of $\mathbf{z}$ (i.e., of $\mathbf{n}^0$) and $\mathbf{u}$, and it is sufficiently general to consider a 2×2 problem in (x,z). The current conformations l_{ij} depend on the current order parameter Q (which may be much larger than Q^0 if temperature has dropped since fabrication). In general, since the axes of λ_{ij} are not coincident with those of l^0_{ij}, the distortion forces the phase to be biaxial, with a second-order parameter X, so that l_{ij} has three distinct elements l_x, l_y, and l_z depending on Q and X. Strictly speaking the total free energy $F_{\rm total} = F_{\rm nem} + F_{\rm el}$ must be minimized with respect to Q, X, and θ for each λ_{ij} imposed. Experience shows that X is generally small [9]. However, it turns out that the optimal angle θ does not depend on Q and X (although $F_{\rm el}$ and $F_{\rm nem}$ do): since it is sufficient to consider a 2×2 problem, we can always write l^{-1}_{ij} in the form of Eq. (2) with $l_\| \to l_z$, $l_\perp \to l_x$, ignoring the third dimension $(1/l_y)\hat{\mathbf{y}}\hat{\mathbf{y}}$. Then the only part of the free energy (3) that depends on the current orientation $\mathbf{n}$ [or on the angle $\Delta = \alpha - \theta = \cos^{-1}(\mathbf{n}\cdot\mathbf{u})$] is the second term below:

$$F_{\rm el} = F_0(Q,\lambda) + \frac{k_BT}{2}\left(\frac{1}{l_\|} - \frac{1}{l_\perp}\right) {\rm Tr}[\underline{\underline{l}}^0 \cdot (\mathbf{n}\cdot\underline{\underline{\lambda}})^T \cdot (\mathbf{n}\cdot\underline{\underline{\lambda}})].$$

The dependence on order parameter is in the prefactor and is irrelevant when we minimize this free energy with respect to θ. If we only want the orientation of $\mathbf{n}$ we can ignore the self-consistency problem (the minimization) in Q and X.

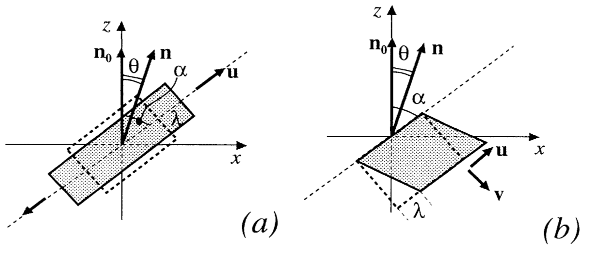

FIG. 1. Alignment geometry in the (x,z) plane for (a) extension and (b) simple shear. $\mathbf{n}_0$ and $\mathbf{n}$ are initial and current directors, respectively; unit vectors $\mathbf{u}$ ($\mathbf{u}$, $\mathbf{v}$ for simple shear) define the principal axes of deformation.

(i) Uniaxial Extension: After constructing the elastic free energy and minimizing with respect to θ one obtains the condition (recall $\Delta = \alpha - \theta$)

$$\tan 2\Delta = \frac{2(\lambda_c^3 - 1)\sqrt{\lambda}\sin 2\alpha}{(\lambda_c^3+1)(\lambda^2 - 1/\lambda) + (\lambda_c^3 - 1)(\lambda^2 + 1/\lambda)\cos 2\alpha},$$

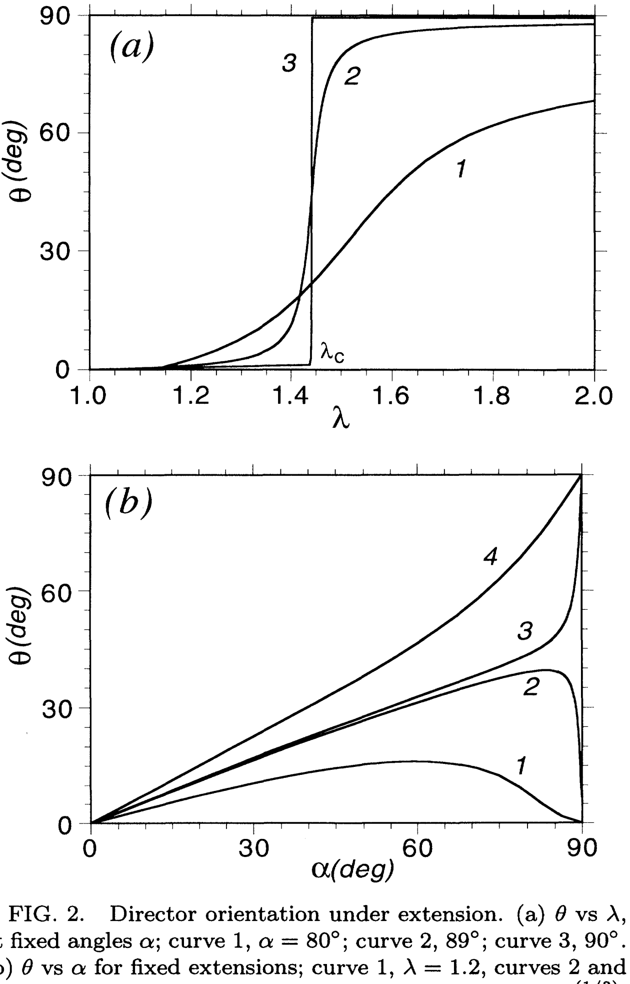

FIG. 2. Director orientation under extension. (a) θ vs λ, at fixed angles α; curve 1, $\alpha = 80°$; curve 2, 89°; curve 3, 90°. (b) θ vs α for fixed extensions; curve 1, $\lambda = 1.2$, curves 2 and 3 are for λ just below and above the critical value $\lambda_c = 3^{(1/3)}$, and curve 4, $\lambda = 2$. In all cases initial anisotropy $l^0_\|/l^0_\perp = 3$.

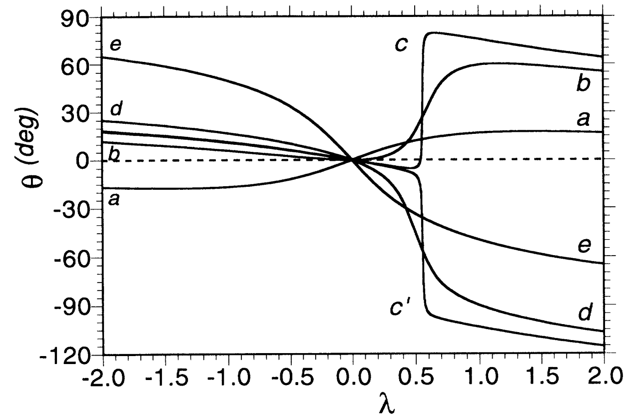

FIG. 3. Director orientation under shear, θ vs λ at initial anisotropy $l_{\|}^0/l_{\perp}^0 = 3$ for fixed angles α; curve a, $\alpha = 0°$; curve b 30°; curves c and c', α just below and above the critical $\alpha^* = 37.2°$; curve d, $\alpha = 45°$, and curve e 90°.

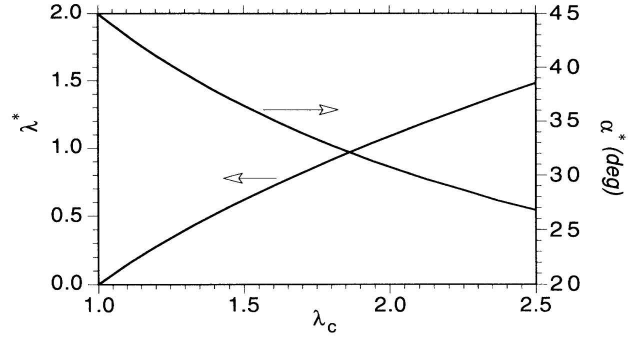

FIG. 4. Critical λ^* and critical angle α^* for the shear instability vs initial anisotropy $\lambda_c = (l_{\|}^0/l_{\perp}^0)^{1/3}$.

where $\lambda_c = (l_{\|}^0/l_{\perp}^0)^{1/3}$ is a parameter dependent on the anisotropy of the initial strand conformation. Analysis of this is straightforward, but we simply show the rotation θ as a function of the imposed λ at constant α [Fig. 2(a)] and $\theta(\alpha)$ for various λ [Fig. 2(b)]. When λ_{ij} is imposed at an angle $\alpha = \pi/2$ the internal barrier prevents any rotation until $\lambda \geq \lambda_c$. The system then breaks its symmetry and jumps to $\theta = \pi/2$. For smaller α there is no degeneracy in the direction of rotation and the **n** is continuously dragged around towards α. The curves for different α cross and this is more easily seen in Fig. 2(b), where, for a given $\lambda < \lambda_c$, the $\theta(\alpha)$ curves have maxima, which disappear with a singularity at the critical extension $\lambda = \lambda_c$. The discontinuity in $\theta(\lambda)$, caused by a degeneracy in the direction of rotation at $\alpha = \pi/2$, is seen again in a different guise in the simple shear results.

(ii) Simple Shear: Similar manipulation yields

$$\tan 2\Delta = 2\frac{(\lambda_c^3 - 1)\left[\sin 2\alpha + \lambda \cos 2\alpha\right] - \lambda(\lambda_c^3 + 1)}{\lambda^2(\lambda_c^3 + 1) + 2(\lambda_c^3 - 1)\left[(1 - \lambda^2/2)\cos 2\alpha - \lambda \sin 2\alpha\right]}.$$

Limits of this result are illuminating. When the initial state is isotropic, $\lambda_c = 1$, then $\tan 2\Delta = -2/\lambda$ with $2\Delta = -\pi/2$, that is, $\theta = \pi/4$, with $\lambda \to 0+$, i.e., **n** is induced to be along the the direction suffering the extensional component of the shear, as one would expect. For a nematic monodomain with anisotropy $l_{\|}^0/l_{\perp}^0 = 3$ at formation, the director orientation $\theta(\lambda)$ is presented in Fig. 3. For large enough initial angle α between unit vectors **u** and $\mathbf{n}_0$, so that the stretch diagonal can be brought to $\pi/2$ with respect to **n** (allowing for rotations of **n** as shear proceeds), there is a discontinuity also seen in (i). Analytical conditions for this transition will be presented elsewhere. Figure 4 shows how the critical shear λ^* and the critical angle α^* for this transition depend on the initial anisotropy of the chain, $\lambda_c = (l_{\|}^0/l_{\perp}^0)^{1/3}$.

We have demonstated that nematic solids are a qualitatively new type of elastic medium with an elastic barrier to the rotation of its internal direction **n**, a barrier which in turn couples with strain. We have illustrated this elasticity by considering the simple case of imposed deformation. Imposed stresses induce a most complex response, since director instabilities will be accompanied by strain instabilities. These are seen in a blurred form in stress-strain measurements on polydomain nematic elastomers [4]. Our work is an initial step to explaining this response.

We have given a microscopic basis to this new elasticity. Within the limitation of uniform directors and deformation, the linear phenomenological continuum expression for the free energy is given in [7]. We have demonstrated that new nematic transitions are possible in nematic solids using mechanical applied fields and having bulk rather than surface barriers to rotation.

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