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"Soft elasticity" — deformation without resistance in liquid crystal elastomers

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Abstract. — Polymeric nematic liquid crystals crosslinked into elastomers (solid liquid crystals) are shown to display novel and complex elasticity. The internal (nematic) direction can experience a barrier to its rotation which couples to standard elasticity. We predict a new phenomena unique to anisotropic rubber – a "soft elastic response"; uniaxial strain is developed without resistance below a critical deformation λ^* due to the relaxation of related shear strains and reorientation of the nematic director. We discuss possible experiments to verify this prediction and interpret the existing experimental observation in terms of the concept of "soft elasticity".

1. Introduction.

Anisotropic (liquid crystalline) elastomers have attracted a considerable attention in recent years due to their unique properties. de Gennes [1] first recognized that the most dramatic effect of molecular shape change coupling to orientational order would take place in these materials. Like conventional elastomers such "solid liquid crystals" can sustain very large deformations causing 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. There exist molecular models [2, 3] explaining such effects as mechanical critical points, memory of crosslinking, shifts in phase equilibria and stress-strain relations. At the heart of these descriptions is that nematic and hence anisotropic chains lead to a straightforward modification of the conventional Gaussian elastomer theory. The theory can be further developed, as in conventional networks, to account for junction point fluctuations [3] and other effects, but to understand the startling new effects visible in nematic elastomers these elaborations are not necessary.

Several important experiments have been performed and most basic effects have been observed, for instance shifts in the phase transition temperatures with both crosslinking density and crosslinking state (i.e. nematic or isotropic) [4], unusual stress-strain relations in the region

of the N-I transition for the elastomer, strong deviations from classical stress-optical laws and mechanical influences on the phase transition itself [5].

We continue here an investigation of the complex elasticity of such elastomers deep in the nematic phase, in particular when the principal stress-strain axes are not coincident with the initial nematic direction. A linear, continuum picture has been sketched by de Gennes [6] who described the anisotropy of such media, the coupling of strain to nematic order and the resistance to rotation. In recent publications [7, 8] we have reported results, showing that this rotational resistance is extremely subtle and is dependent on geometrical constraints. Molecular theory [8], in contrast to linear continuum theory, can describe the non-linear regimes where the discontinuous transitions are predicted to occur. The non-linear analysis within the framework of a molecular theory of Gaussian chains and anisotropic rubber elasticity, presented in this paper, results in a completely unexpected conclusion — that at straining with minimal constraints on the overall sample shape, nematic rubber can extend with little or no resistance, i.e. with the imposition of little stress.

The impetus for this theory comes from experiments on nematic monodomains. The first experiment on (microscopic) monodomains of elastomers was carried out by Zentel [9] where reorientation of the director under applied electric fields was seen under some circumstances — but not under others. Although not involving imposed stresses or strains, these experiments are crucial to our understanding of nematic rubber elasticity. Freely suspended samples respond readily with shape changes to modest electric fields. In contrast, samples constrained by electrodes do not change their shape in response to similar fields. Evidently the response, when all or most components of the distortion $\underline{\underline{\lambda}}$ are free to relax, is in some sense soft. It hardens to values conventionally found in elastomers when constraints are applied. We examine this anomalous electro–mechanical response in another paper. However these experiments appear to support the main conclusion of the present paper, namely that elastic deformations can occur without resistance in certain geometries.

Recently large nematic monodomain samples have become available in practice. Such single crystal samples can be made by crosslinking in a field oriented nematic melt [10], or alternatively by two-stage crosslinking and stressing the intermediate state [11]. Large monodomain elastomers lend themselves to the mechanical experiments corresponding to the theory described in [8]. Already Mitchell *et al.* [12] have performed applied strain measurements on monodomain rubbers far below their N-I transition. With stress applied perpendicular to the original director they find the predicted new mechanical transition where at a critical strain the director jumps by $\pi/2$ to the principal applied stress direction.

All particular expressions involved are presented in terms of intrinsic anisotropy of the polymer chains that underly the network before deformation, $l^0_\parallel/l^0_\perp$. Theory [2, 3, 8] shows simply that an anisotropic network, heated to the isotropic state, will suffer a spontaneous shape change $\lambda_c = (l^0_\parallel/l^0_\perp)^{1/3}$ on cooling back to the initial state. This ratio $l^0_\parallel/l^0_\perp$ is thus an observable quantity [4] and therefore the current analysis does not involve any model parameter at all. Since we shall find calculations of some algebraic complexity, we first describe the theory in general terms, including the scheme of imposition of strain and the response of chains, stating and interpreting the key results. The detailed derivations will follow in later sections so that they do not mask an understanding of the underlying effects we shall find.

FORMULATION OF THE THEORY. — We should like to address the interested reader to our previous paper [8] on this subject, where the detailed formulation of the theory is given and all relevant approximations are discussed in some detail. Here we shall briefly recall the main concepts and equations used.

We use the following general scheme for notation. We use a superscript ^{0} to denote quantities

in initial (undeformed) states. Hence the initial nematic director is denoted by $\mathbf{n}^0$, which evolves under a deformation to $\mathbf{n}$. To describe tensors we use either suffix notation or a double underscore e.g. $\underline{\underline{\lambda}} \equiv \lambda_{ij}$. When describing uniaxial tensors, subscripts $_\perp$ and $_\parallel$ are used to differentiate between the two distinct axes. In their principal frame, the $_\parallel$ component is taken to lie along the $\hat{z}$ axis of that frame. As an example, the tensor used to describe the anisotropic step length characterizing the network chains in the initial (undeformed) state is $\underline{\underline{l}}^0$, which has eigenvalues $l^0_\parallel$ and $l^0_\perp$ in its principal frame. With this tensor the average square form of the networking points positions (i.e. end-to-end distance of polymer strands) is $\langle R^0_i R^0_j \rangle = \frac{1}{3} L l^0_{ij}$ where L is the contour length of the network strand. The effective step lengths of the random walk, and thus the overall average shape, are functions of the nematic order parameter Q_{ij}. Uniaxial nematic order Q_{ij} is characterized by both a magnitude Q and (most importantly) the current orientation of the director $\mathbf{n}$.

We employ the affine deformation assumption, an assumption that pervades network theory. Thus the current network span is defined as $R_i = \lambda_{ij} R^0_j$ with λ_{ij} the macroscopic deformation of the whole block of rubber. We consider deformations λ_{ij} imposed with respect to the initial crosslinking state. Strictly speaking, if the temperature has been changed since the crosslinking, the initial sample shape before deformation is determined by a spontaneous strain tensor $\underline{\underline{\lambda}}_c$. This requires a trivial re-definition of the deformation λ_{ij}, which has been been discussed at some length in [8].

Since the shear modulus of rubber is around 10^6 N/m^2 and that for the volume change is typically 10^{10} N/m^2, deformations of elastomers are at constant volume (to within 10^{-4} accuracy), that is: $\mathrm{Det}[\lambda_{ij}] = 1$. Taking the usual quenched average $F_{\mathrm{el}}/k_{\mathrm{B}}T = -\langle \ln P(\mathbf{R}) \rangle_{P_0(\mathbf{R}^0)}$ one obtains for the elastic free energy per network strand [8]:

$$\frac{F_{\mathrm{el}}}{k_{\mathrm{B}}T} = \frac{1}{2}\left[\mathrm{Tr}[\underline{\underline{l}}^0 \ \ \underline{\underline{\lambda}}^T \ \ \underline{\underline{l}}^{-1} \ \ \underline{\underline{\lambda}}] - \ln\left(\frac{\mathrm{Det}[\underline{\underline{l}}^0]}{\mathrm{Det}[\underline{\underline{l}}]} \right) \right] \tag{1}$$

where l_{ij} is the anisotropic step length tensor after the deformation, which in general may differ from l^0_{ij} in both magnitude and orientation of its principal values [8].

We are interested here in the case where an imposed deformation $\underline{\underline{\lambda}}$ has principal axes not coincident with $\mathbf{n}^0$, thereby creating an equilibrium state with $\mathbf{n}$ at some angle θ with respect to $\mathbf{n}^0$. We shall determine θ as a function of the magnitude of deformation and the orientation of the frame of the imposed deformation λ_{ij} with respect to $\mathbf{n}^0$. To do this we shall minimize F_{el} with respect to any free components of $\underline{\underline{\lambda}}$ and with respect to Q and θ, which characterize the underlying nematic order $\underline{\underline{Q}}$.

The most unconstrained deformation is when the strain λ is imposed in one direction $\mathbf{u}$ with all other strains free to relax. This is equivalent to imposing a uniaxial stress on a sample at an arbitrary angle α to the original director, that is, along $\mathbf{u}$ of figure 1.. We find the astonishing result that $\mathbf{n}$ rotates with increasing λ but that the free energy does not rise until $\mathbf{n}$ lies along the principal direction $\mathbf{u}$ of $\underline{\underline{\lambda}}$. Thereafter the free energy rises as for a classical isotropic elastomer starting its deformation at this point. Variants of this imposed stress, where one of the shear strains in the plane spanned by the stress and $\mathbf{n}^0$ is fixed at zero are treated in our previous paper [8] and yield very different, "hard response", results albeit with discontinuous transitions.

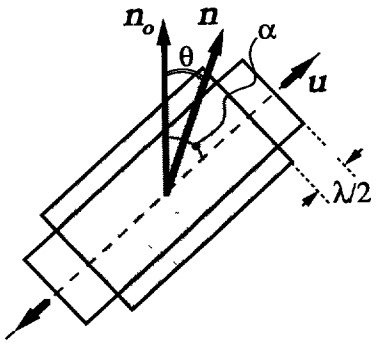

Fig. 1. — Alignment geometry in the (x, z) plane for an unconstrained extension $\mathbf{n}_0$; and $\mathbf{n}$ are initial and current directors respectively; unit vector $\mathbf{u}$ defines the principal axes of deformation.

2. Results.

Henceforth we use a coordinate system (z, x, y) based on $\mathbf{u} \equiv \hat{z}$ rotated by α about $\hat{y}$ from the original (principal) frame of $\underline{\underline{l}}^0$, figure 1.. The tensors $\underline{\underline{l}}^0$ and $\underline{\underline{l}}^{-1}$ have to be rotated by angles α and $\Delta = \alpha - \theta$ from their principal frames. One can recognize the relevant plane that includes the initial director $\mathbf{n}^0$, current director $\mathbf{n}$ and the direction of strain, $\mathbf{u}$.

If one applies a stress σ normal to one face of a body, along the $\hat{z}$ direction of a coordinate system at an angle α to $\mathbf{n}^0$, the distortion λ_{zz} relaxes to a particular value, say λ. All the other deformations in $\underline{\underline{\lambda}}$ also relax. On general grounds of symmetry we expect that all out–of–plane components of strain, $\lambda_{yx} = \lambda_{xy} = \lambda_{yz} = \lambda_{zy} = 0$. Given the misalignment (by angle α) of $\mathbf{n}^0$ and the principal direction of stress σ, there will be non-trivial values of λ_{xx}, λ_{yy}, λ_{xz} and λ_{zx}. Since in tensors the $\hat{y}$-direction has no coupling with this $\hat{x} - \hat{z}$ plane, in expressions that follow we can use the yy components and (2×2) $\hat{x} - \hat{z}$ tensors. Such second rank (2×2) tensors, for instance $\underline{\underline{l}}^0$, will be characterized by their mean $\overline{l^0} = (l^0_{\|} + l^0_{\perp})/2$ and anisotropy $\delta l^0 = (l^0_{\|} - l^0_{\perp})/2$ of their principal values and similarly for $\underline{\underline{l}}^{-1}$. We consider the strain $\lambda_{zz} \equiv \lambda$ to be imposed. We must minimize $F_{\rm el}$ with respect to the four relaxing deformations while keeping density constant, that is $\mathrm{Det}[\underline{\underline{\lambda}}] = 1 = \lambda_{yy}(\lambda_{xx}\lambda - \lambda_{xz}\lambda_{zx})$. *Post hoc* one can then find the stress required to impose the deformation λ:

$$\sigma(\lambda) = \frac{1}{\lambda_{xx}(\lambda)\lambda_{yy}(\lambda)} \left(\frac{\mathrm{d}F_{\rm el}}{\mathrm{d}\lambda}\right) \tag{2}$$

With such great freedom to relax this is a problem of some algebraic complexity which we analyze in detail in the following section. The remarkable result obtained is that the elastomer, with its initial director at general angle α to $\mathbf{u}$, deforms at constant free energy $2F_{\rm el}/k_{\rm B}T = 3$ until $\mathbf{n}$ has rotated through angle α from $\mathbf{n}^0$ to the direction of $\mathbf{u}$. Thereafter the energy rises and a finite stress is required in order to create further strain.

We return to equation (1) with matrices $\underline{\underline{l}}^0$ and $\underline{\underline{l}}^{-1}$ defined in the (x, z) plane, by elements a, b, c and d, e, f:

$$\underline{\underline{l}}^0 = \begin{pmatrix} a & c \\ c & b \end{pmatrix}, \qquad \underline{\underline{l}}^{-1} = \begin{pmatrix} d & f \\ f & e \end{pmatrix}. \tag{3}$$

These coefficients, a, b, c and d, e, f, depend on the angles α and $\Delta = \alpha - \theta$. Matrices in (3) are given in the (2×2) form, each of them also has a diagonal element in the $\hat{y}$ direction, l^0_y

and l_y^{-1} respectively. With these definitions $F_{\rm el}$ takes the form:

$$\begin{aligned}\frac{2F_{\rm el}}{k_{\rm B}T} &= ad\lambda^2 + be\lambda_{xx}^2 + ae\lambda_{xz}^2 + bd\lambda_{zx}^2 + 2af\lambda\lambda_{xz} + 2cd\lambda\lambda_{zx} + \\ &\quad 2cf\lambda\lambda_{xx} + 2ce\lambda_{xx}\lambda_{xz} + 2bf\lambda_{xx}\lambda_{zx} + 2cf\lambda_{xz}\lambda_{zx} + r\lambda_{yy}^2\end{aligned} \tag{4}$$

where $r = l_y^0/l_y$. A solution minimizing the free energy is quite simple (see the following section for details). The relaxing strains attain the following values:

$$\begin{aligned}\lambda_{zx} &= -\frac{c}{b}\lambda\,, \qquad \lambda_{xz} = -\frac{f}{e}\lambda\,, \qquad \lambda_{yy} = \left(\frac{be}{r}\right)^{1/4}\frac{1}{\sqrt{\lambda}}\,, \\ \lambda_{xx} &= \frac{cf}{be}\lambda + \left(\frac{r}{be}\right)^{1/4}\frac{1}{\sqrt{\lambda}}\end{aligned} \tag{5}$$

The free energy becomes a function of the combination (be) alone,

$$\frac{2F_{\rm el}}{kT} = \frac{\lambda^2}{be} + \frac{2(be)^{1/2}}{\lambda} \tag{6}$$

Through (be) this is a function of θ which must be minimized to find the equilibrium orientation of the nematic director. On minimization one obtains $be = \lambda^2$.

When the system adopts the optimal angle given by this condition $be = \lambda^2$, the free energy is $(2F_{\rm el}/k_{\rm B}T)_{\rm min} = 3$. This is exactly the energy per strand of an undistorted network! Thus the energy of the network does not rise as an extension λ is imposed in a particular direction, all other distortions being permitted to relax.

Writing out the condition $be = \lambda^2$ for the angle θ in full,

$$\lambda^2 = (\overline{l_0} - \delta l_0 \cos 2\alpha)(\overline{l^{-1}} - \delta l^{-1}\cos 2\Delta)\,, \tag{7}$$

shows that this solution is only valid for $\lambda = 1$ if the network anisotropy vanishes ($\delta l_0 = \delta l^{-1} = 0$), that is, these effects are limited to anisotropic networks. The optimal value of $\Delta = \alpha - \theta$ is obtained from (7):

$$\cos 2\Delta = \frac{4\lambda^2 - \left(1 + \frac{1}{\lambda_{\rm c}^3}\right)\left[(\lambda_{\rm c}^3 + 1) - (\lambda_{\rm c}^3 - 1)\cos 2\alpha\right]}{\left(1 - \frac{1}{\lambda_{\rm c}^3}\right)\left[(\lambda_{\rm c}^3 + 1) - (\lambda_{\rm c}^3 - 1)\cos 2\alpha\right]} \tag{8}$$

where we have used the definitions of $\overline{l_0}$, etc. from above, and taken ratios $l_\parallel^0/l_\perp^0$ in order to express the result in terms of $\lambda_{\rm c}^3 = l_\parallel^0/l_\perp^0$, the cube of the observed spontaneous distortion on cooling the rubber from the isotropic to the nematic state.

The constant free energy solution persists until $\mathbf{n}$ is along the extension direction, that is $\Delta = 0$, and the l.h.s. of the equation (8) reaches its maximum value of 1. This is achieved at a critical strain $\lambda^*(\alpha)$ given by:

$$\lambda^*(\alpha)^2 = \frac{1}{2}\left[\lambda_{\rm c}^3 + 1 - (\lambda_{\rm c}^3 - 1)\cos 2\alpha\right] \tag{9}$$

When λ exceeds λ^*, the solution of $\mathrm{d}F/\mathrm{d}\Delta = 0$ gives the minimum free energy at $\theta = \alpha$, corresponding to $\mathbf{n}$ parallel to $\mathbf{u}$. The free energy for $\lambda > \lambda^*$ takes the form

$$\frac{2F_{\rm el}}{k_{\rm B}T} = \frac{\lambda^2}{\lambda^{*2}} + 2\frac{\lambda^*}{\lambda} \tag{10}$$

This branch of the free energy has a minimum of 3 at $\lambda = \lambda^*$ and behaves like a classical elastomer [with an apparent natural shape of $\lambda = \lambda^*(\alpha)$] for $\lambda > \lambda^*$ — see figure 2.

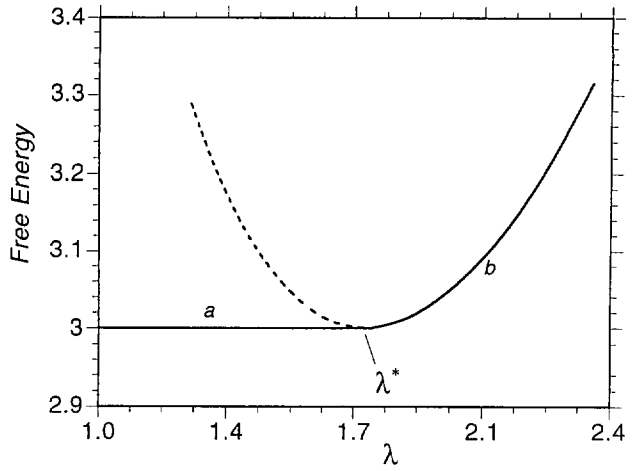

Fig. 2. — The elastic free energy (in $\frac{1}{2}k_BT$ units) per network strand plotted against a distortion λ imposed at an angle $\alpha = \pi/2$ to the original director. The free energy is flat [branch (a)] for $1 < \lambda < \lambda^*$ with the critical λ^* depending on the misorientation α (see text). For $\lambda > \lambda^*$ the free energy increases as for a classical rubber about the point $\lambda = 1$ [branch (b)].

INTERPRETATION. — It is a clear expectation [6] that crosslinking chains into a network while they are anisotropic in shape will create a memory of this anisotropy and its direction. Our calculations [8] partially affirm this expectation in that there is sometimes a resistance to director rotation. Recall that the direction of chain anisotropy is related to the nematic director and that in a rubber macroscopic deformation is coupled with the chain shape. What is unexpected is the existence of initial deformations at which there are discontinuities in the director, and that under some circumstances the rotational barrier does not exist. These rather different phenomena suggest that the ideas of rotational barriers arising from the constraint of attachment to other chains is incomplete. An additional constraint is that of incompressibility so that changes of shape in certain direction impose shape changes in others. The more constrained the deformation, the less freedom a chain has to adopt a high entropy, low free energy distribution. This is seen in the constrained geometries [8] where the energy rises when chains are distorted in a direction different to their principal direction. At some critical strain λ a new director can be found where relatively more freedom for the chain exists. The chains and hence the director and extensions thus jump. The "rotational barrier" is thus dependent on the geometrical constraints put upon other components of the chain shape tensor.

In the unconstrained case considered here the great freedom of a chain, even with the ever–present incompressibility constraint, means that its initially anisotropic Gaussian distribution can be distorted at no cost to the entropy, and the free energy does not rise as the director (the signature of this anisotropic distribution) rotates. In the next section we prove that in this "soft elasticity" regime effects are purely entropic.

It should be emphasized that this unusual result is not simply that we have a body rotation about the $\hat{y}$ axis (the form of $\underline{\underline{\lambda}}$ given above is different). It would seem that with sufficient freedom to relax, macroscopic distortions can be achieved by rotating anisotropic chains until they are aligned with $\mathbf{u}$. Thereafter elastic distortions at microscopic level, involving entropy and nematic order changes, must occur and the energy rises accordingly. Evidently such an exact cancellation of any resistance to an external stress (in a certain region of deformations

$\lambda < \lambda^*$) is the feature of this theory specifically based on Gaussian chains and affine deformations approximations. In practice one would observe a small resistance caused by other effects — in more sophisticated models of rubber elasticity, involving entanglements and correlations, probably some resistance will be created. Experimental evidence from nematic elastomers subjected to electric fields suggests that these effects are indeed small. This is an observation of central importance to models of conventional elastomers, where the complications of entanglements and correlations have been discussed for over 50 years. Thus our prediction offers a method of examining these effects in isolation since the crossover at $\lambda = \lambda^*$, figure 2., should be clearly detectable by experiment.

3. Calculations.

We present here more technical details omitted in the previous section. At the same time we shall discuss when results are exact and when they involve approximations.

Rotating $\underline{\underline{l}}^0$ and $\underline{\underline{l}}^{-1}$ into the frame of $\underline{\underline{\lambda}}$ gives explicit forms for the elements $a - f$:

$$\begin{aligned} a &= \overline{l^0} + \delta l^0 \cos 2\alpha\,; \quad b = \overline{l^0} - \delta l^0 \cos 2\alpha\,; \quad c = -\delta l^0 \sin 2\alpha \\ d &= \overline{l^{-1}} + \delta l^{-1} \cos 2\Delta\,; \quad e = \overline{l^{-1}} - \delta l^{-1} \cos 2\Delta\,; \quad f = -\delta l^{-1} \sin 2\Delta \\ r &= l_y^0 / l_y \end{aligned} \tag{11}$$

We demonstrate that when only one strain is fixed (namely $\lambda_{zz} = \lambda$), resulting from an applied normal stress in the $\hat{z}$ direction, the elastomer is "soft". With λ set, the other strains relax to minimize the free energy. Setting the derivatives of (4) with respect to the unconstrained variables equal to zero yields:

$$be\lambda_{xx} + cf\lambda + ce\lambda_{xz} + bf\lambda_{zx} - \Lambda\lambda_{yy}\lambda = 0 \tag{12}$$

$$ae\lambda_{xz} + af\lambda + ce\lambda_{xx} + cf\lambda_{zx} + \Lambda\lambda_{yy}\lambda_{zx} = 0 \tag{13}$$

$$bd\lambda_{zx} + cd\lambda + bf\lambda_{xx} + cf\lambda_{xz} + \Lambda\lambda_{yy}\lambda_{xz} = 0 \tag{14}$$

$$r\lambda_{yy} - \Lambda(\lambda\lambda_{xx} - \lambda_{xz}\lambda_{zx}) = 0 \tag{15}$$

The constraint $\mathrm{Det}[\underline{\underline{\lambda}}] = 1$ has been included in the free energy with a Lagrange multiplier: $\Lambda[\lambda_{yy}(\lambda\lambda_{xx} - \lambda_{xz}\lambda_{zx}) - 1]$. Inserting (12) into (13) and (14) and solving for λ_{zx} gives a condition yielding two solutions

$$\left(D^0 D - (\Lambda\lambda_{yy})^2\right)\left(\lambda_{zx} + \frac{\lambda c}{b}\right) = 0 \tag{16}$$

where D^0 and D are the determinants of $\underline{\underline{l}}^0$ and $\underline{\underline{l}}^{-1}$. $D^0 = ab - c^2$, $D = de - f^2$. Leaving for the moment the solution containing the determinants (first bracket), we obtain for λ_{xz}, λ_{zx} and λ_{xx}

$$\lambda_{zx} = -\frac{\lambda c}{b} \tag{17}$$

$$\lambda_{xz} = -\frac{\lambda f}{e} \tag{18}$$

$$\lambda_{xx} = \frac{\lambda}{be}(\Lambda\lambda_{yy} + cf) \tag{19}$$

Inserting (17-19) in (15) then gives

$$\Lambda^2 = \frac{rbe}{\lambda^2} \tag{20}$$

Taking the (physically relevant) positive root of this solution and using the constraint condition $\mathrm{Det}[\underline{\underline{\lambda}}] = 1$ gives for λ_{yy}

$$\lambda_{yy} = \left(\frac{be}{r}\right)^{1/4} \frac{1}{\sqrt{\lambda}} \tag{21}$$

and hence for λ_{xx}

$$\lambda_{xx} = \frac{cf}{be}\lambda + \left(\frac{r}{be}\right)^{1/4} \frac{1}{\sqrt{\lambda}} \tag{22}$$

Solutions (17), (18), (21) and (22) correspond to (5) and minimization with respect to θ remains to be done. Returning the optimized distortions to F_{el} one obtains

$$\frac{2F_{\mathrm{el}}}{k_{\mathrm{B}}T} = \frac{D^0 D}{be}\lambda^2 + \frac{2(rbe)^{1/2}}{\lambda} \tag{23}$$

where, recall, $D^0 = \mathrm{Det}[\underline{\underline{l}}^0] = ab - c^2$ and $D = \mathrm{Det}[\underline{\underline{l}}^{-1}] = de - f^2$.

This expression is valid for general director orientation θ (that is $\Delta = \alpha - \theta$) and order parameter Q (which enter through the elements of $\underline{\underline{l}}^{-1}$). We should minimize with respect to all these quantities, which define the new nematic order of the distorted state.

If we adopt for a moment the simplifying assumption that $\underline{\underline{l}}$ is merely a rotated version of $\underline{\underline{l}}^0$, that is only $\mathbf{n}$ in the order parameter $\underline{\underline{Q}}$ changes direction but the magnitude Q is unchanged, then (23) is only a function of Δ and, furthermore, $D^0 D = 1$ and $r = 1$. We then obtain the result (6) of the previous section. We must minimize (6) with respect to change in the direction of $\mathbf{n}$, that is angle θ or equivalently $\Delta = \theta - \alpha$. $\mathrm{d}F/\mathrm{d}\Delta$ simplifies to:

$$\frac{\mathrm{d}F}{\mathrm{d}\Delta} = \frac{\partial F}{\partial(be)}\frac{\mathrm{d}(be)}{\mathrm{d}\Delta} = \frac{\mathrm{d}(be)}{\mathrm{d}\Delta}\left(-\frac{\lambda^2}{(be)^2} + \frac{1}{\sqrt{be}\lambda}\right) = 0 \tag{24}$$

Setting the final bracket equal to zero gives the minimization condition $(be) = \lambda^2$ used for $\lambda < \lambda^*$. When λ exceeds the critical value λ^*, the solution of $\mathrm{d}F/\mathrm{d}\Delta = 0$ derives from $\mathrm{d}(be)/\mathrm{d}\Delta = 0$ in (24). It is simple to check that this is only satisfied by $\theta = \alpha$ or $\theta = \alpha - \pi/2$.

It might be argued that the avoidance of self-consistency (our failure to minimize with respect to order parameter Q) could nullify the "soft elasticity" result. In fact the result $2F_{\mathrm{el}}/k_{\mathrm{B}}T = 3$ is already the free energy of an undistorted network with its nematic energy at a minimum. There can be no reduction below this value (otherwise mechanical instability ensues!) and hence there is actually no need to minimize with respect to Q and it remains at its formation value, Q^0 say. After λ exceeds λ^* this statement is no longer true and there may be further falls in F_{el} below (10) on optimizing over Q. This effect, however, is hardly relevant as it goes on the background of a standard rubber elasticity response. Since for $\lambda \leq \lambda^*$, F_{nem} is already at an optimal $Q = Q^0$ then changes as λ exceeds λ^* must be at second order and one initially expects changes in Q small in $(\lambda - \lambda^*)$.

Thus *post hoc* one sees that the neglect of the variation in the magnitude of the nematic order parameter Q is not an approximation at all. Given then that the nematic component of the free energy is unchanged, the unchanging total free energy implies that the entropic contribution of the (anisotropic) Gaussian distribution is also unchanged under distortions and rotations with $\lambda < \lambda^*$. This is the basis of the assertion of constant entropy in the discussion of the previous section about the "soft elasticity" response. It may seem miraculous when comparing with isotropic Gaussians that always suffer a drop in entropy on distortion (the basis of classical rubber elasticity), but calculations in this section prove that some particular distortions at constant entropy are possible for anisotropic Gaussian chains.

So far we have explored only one of the two solutions of the key equation (16). The second possibility in (16), namely $D^0D = (\Lambda\lambda_{yy})^2$, would appear to be an anisotropic remenant of a trivial (although little known) solution for conventional rubbers under compressive stress (for isotropic elastomers it is a simple rotation). Inserting $\Lambda\lambda_{yy} = \pm\sqrt{D^0D}$ into (15) and doing some algebra gives, in the limit where $r = 1$ and $D^0D = 1$,

$$\begin{aligned} \lambda_{yy} &= 1; \quad \lambda_{xx} = (1 + \lambda_{xz}\lambda_{zx})/\lambda \\ \lambda_{zx} &= -\frac{c}{b}\lambda \pm \frac{1}{b\sqrt{D}}\sqrt{be - \lambda^2}; \quad \lambda_{xz} = -\frac{f}{e}\lambda \mp \frac{\sqrt{D}}{e}\sqrt{be - \lambda^2} \end{aligned} \tag{25}$$

Returning these to $F_{\rm el}$ gives the result $2F_{\rm el}/k_{\rm B}T = 3$ as before. In contrast to the first solution, this result is achieved *without* any minimization with respect to Δ. The solution is clearly valid until $\lambda^2 = be$, the maximum value of be being when $\Delta = 0$ i.e. $be = \lambda^{*2}$ It is important to emphasize that under this condition equations (25) coincide with the previous solution (5), which therefore represents just a single (extremal) branch out of the continuous set (25) valid for all angles Δ. (Given that F is independent of Δ there is no criterion for selecting any particular orientation of the director). Despite $\lambda_{yy} = 1$, the solution (25) does not represent a body rotation about the y axis, but is a combination of simple shear and extension in the (x, z) plane. It can exist along any direction, given by an arbitrary angle $\Delta = \alpha - \theta$, but the magnitude of deformations depends on this direction through coefficients e and f. This represents a remarkable degeneracy in the "soft elasticity" phenomenon we are describing here, it corresponds to a natural fact that a given rotation of the director can be accomodated by a continuous set of possible deformations of the network — the smallest shear is required, obviously, when the initial director $\mathbf{n}^0$ was perpendicular to the direction of shear.

One branch out of this continuous set is special, it corresponds to the maximal possible extension λ^* (9) that can be accomodated by a nematic network without changing its free energy and the director rotation $\Delta(\lambda)$ given by (8). In any experiment that is based on constant stress, rather than constant strain conditions, only this branch would be observed – the system will deform freely under the applied stress until it reaches λ^*, when the elastic response will first appear. For this reason we have picked this extremal mode of deformations, equations (5), in our discussion of the "soft elasticity" above.

In the isotropic limit $\delta l^0 = \delta l^{-1} = 0$, $c = f = 0$, $be = 1$, $b = l^0$, $D = 1/(l^0)^2$ and the continuous set of equations (25) reduces to

$$\lambda_{yy} = 1; \quad \lambda_{xx} = (1 + \lambda_{xz}\lambda_{zx})/\lambda; \quad \lambda_{zx} = -\lambda_{xz} = \sqrt{1 - \lambda^2} \tag{26}$$

This is a trivial solution for a conventional elastomer: on applying a uniaxial compression, $\lambda < 1$, the system reacts by uniform body rotation ($\lambda \equiv \cos\psi$) about the $\hat{y}$ axis with no change in free energy.

4. Summary and conclusions.

Previous theory [7, 8] and experiment [12] suggest that nematic solids can behave in qualitatively new ways, not found in conventional liquid crystals and isotropic elastomers. Discontinuous nematic and elastic response to applied stresses was found and explained in terms of coupling between translational and orientational degrees of freedom in nematic polymers.

Here we have predicted another qualitatively new and completely counter-intuitive phenomenon: a softening response of the elastomer when stress (or other external field) is applied in sufficiently unconstrained geometries. We predict that strain should develop (with the application of low stress or electric field) until $\mathbf{n}$ is along the field direction, whereupon the material

will harden and attain the modulus characteristic of the elastomer in the isotropic or more constrained nematic state. Previously unexplained electric field experiments of Zentel on nematic elastomers suggest that this unusual behaviour does indeed occur. The magnitudes of the stresses or fields required in the soft regime (where our conventional approach to rubber elasticity predicts that zero stress or field is required) will be an indicator of just how significant more subtle effects in elastomers, such as entanglements and correlations, actually are.

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