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Deformation–induced orientational transitions in liquid crystals elastomer

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Abstract. — Solid liquid crystals, formed by crosslinking polymeric nematics into elastomers 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 investigate this elasticity by considering imposed strains and demonstrate several new orientational phase transitions, caused by the interaction between applied stress fields and bulk barriers to rotation.

1. Introduction.

We find that by stretching a liquid crystalline elastomer obliquely to its optical axis continuous and discontinuous transitions of the rotation of this axis ensue. This new type of nematic transition has now been observed experimentally.

Polymer liquid crystals (PLC's) are long chain molecules composed of monomers capable themselves of forming nematic or more complex mesophases. When concatenated as polymers they combine the orientational order of nematics and the entropy driven aspects of high polymers. In particular such polymers 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 effect of molecular 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 Abramchuk et al. [2] and Warner et al. [3] have constructed molecular models of these effects and obtained an understanding of mechanical critical points, memory of crosslinking, shifts in phase equilibria and stress-strain relations. 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. This theory (and later theory directed towards biaxial effects [4]) was mostly concerned with phenomena around the spontaneous nematic-isotropic (N-I) transition — including the effect of applied stress on the transition. Experiments performed after the initial molecular theories [2, 3] have seen the basic effects, for instance shifts in the phase transition temperatures with both crosslinking density and crosslinking state (i.e. nematic or isotropic) [5], 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 [6].

Here we shall look at the complex elasticity of the nematic phase, including the effect of imposing stress and strain on elastomers deep in the nematic phase, with the principal stress-strain axes not coincident with the initial nematic direction. A linear, continuum picture has been sketched by de Gennes [7] who described the anisotropy of such media, the coupling of strain to nematic order and the resistance to rotation. We shall find this rotational resistance to be extremely subtle and dependent on geometrical constraints. A preliminary account of the present molecular theory predicting novel effects in the nematic phase has been published recently [8]. A molecular theory, in contrast to linear continuum theory can describe non-linear regimes where we find discontinuous transitions. The intimate relationship between rubber elasticity and geometry allows us to interpret these effects, including the role of constraints.

The impetus for this theory comes from experiments on nematic monodomains. The misalignment and interactions of differently oriented domains partly obscures the underlying physics of nematic solids. Indirect methods [6] could, for instance, estimate the spontaneous mechanical distortion of an elastomer undergoing a thermally induced phase transition. At the same time it was observed that a universal value of applied stress was required in order to induce the polydomain sample to form a monodomain.

More recently nematic monodomain samples have become available. Such single crystal samples can be made by crosslinking in a field oriented nematic melt [9], or alternatively by two-stage crosslinking and stressing the intermediate state [10]. Internal stresses in the latter method also give instabilities, but of a different type from those discussed in this paper. Large monodomain elastomers lend themselves to the mechanical experiments corresponding to the predictions of our theory [8] and are explored in detail in this paper. Already Mitchell et al. [11] have performed applied strain measurements on monodomain rubbers far below their N-I transition. With stress applied perpendicular to the original director they find that at a critical strain the director jumps by $\pi/2$ to the principal applied stress direction.

In nematic elastomers mechanical (stress-strain) fields, nematic fields and electromagnetic fields are all coupled. Nematic elastomers offer a barrier to the rotation of the current director away from the direction of the initial director. Internal rotational barriers and the concomitant resistance to strains interacting with these internal degrees of freedom is reminiscent of the Cosserat "couple-stress" elasticity [12]. In respect of nematic elastomers the full linear continuum theory involving strains, nematic director gradients and electric fields has been developed recently [13]. The non-linear analysis that follows shows that nematic elastomers and any rotational barriers are in fact more complex — a variety of continuous and discontinuous orientational transitions take place when subject to large strains, i.e. they exhibit unusual behaviour found only in the region of great non-linearity. Such transitions induced by application of stress are in some sense the opposite of the conventional Fredericks transition: a simple nematic is anchored by its surfaces and subjected to a field in a perpendicular direction, acting throughout its bulk. Here in nematic solids the resistance to rotation is associated with barriers in the bulk. The director remains therefore uniform.

We extend classical rubber elasticity theory to the case of networks formed from intrinsically
anisotropic polymer melts. Chain shape clearly depends on the magnitude of the nematic order and can be calculated by many methods. The simplest is to treat the chain as a sequence of orientable freely jointed rods. This limits the extent of anisotropy to \( l^0 < 3^0 \) where \( l^0 \) is the effective step length in the isotropic state and \( l^0 \parallel \) is the value along the director in the nematic state. Often the anisotropy induced by the nematic order is greater than this, for instance \( l^0 \parallel \sim 10^0 \) in main chain systems [14]. An alternative is to use a worm-like chain model to calculate chain shape. In this paper we can avoid the need to calculate the chain anisotropy explicitly. In some geometries we find that the instabilities in a strain experiment depend only on initial chain anisotropy and not that stemming from applied fields. In other geometries the instabilities depend on the current chain anisotropy, that is the equilibrium magnitude and direction of order after strains have been imposed. However, experiments are often performed deep in the nematic state far from \( T_N \) where the ordering is strong. We assume that the magnitude of the order parameter does not change, but simply the principal ordering directions rotate to a new equilibrium under the application of stress. Under this restriction all instabilities, phase transitions and soft deformations can be described in terms of the initial anisotropy and the imposed fields. The vital measure of the network anisotropy at formation, \( (t^0 \cdot t^0)^{1/3} \), is the spontaneous distortion, \( \lambda_c \), on stress-free cooling of the network from its isotropic phase back to its formation temperature. This quantity can easily be measured by neutron scattering [14], or macroscopically by observing the spontaneous distortion [11]. Thus our predictions are independent of detailed microscopic theories and measurements of nematic polymer shape.

We have assumed that deformations, leading to new nematic order, are imposed at the same temperature as network formation. It is frequently the case that the network is formed at one temperature, \( T_X \), and deformed at another, lower temperature, \( T_d \). In lowering the temperature the network will spontaneously deform, altering the initial network anisotropy. We show in Appendix that it is simple to account for this spontaneous deformation. All the results derived in this paper hold, but with a new definition of the initial network anisotropy, which encompasses both the crosslinking anisotropy and the spontaneous deformation.

Due to some algebraic complexity of calculations involved this paper is organized as follows. The next section outlines the basic concepts of the molecular theory of Gaussian anisotropic networks and describes the geometry of strains and director orientation in considered characteristic cases. Section 3 presents the results, illustrating transitions and instabilities that take place. After that, in section 4, we include some technical details and calculations and the discussion of whether approximations are involved. This section, probably, can be skipped at the first reading of the paper so that elaborations do not mask the qualitative understanding of underlying effects we describe here.

2. Formulation of the theory.

In this paper we use the following general scheme for notation. We use a superscript \( ^0 \) to denote quantities in initial (undeformed) states. Hence the initial director is denoted by \( n^0 \), which evolves under a deformation to \( n \). To describe tensors we use either suffix notation or a double underscore e.g. \( \lambda_{ij} \equiv \lambda_{ij} \). 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 \( l^0 \parallel \), which has eigenvalues \( l^0 \parallel \) and \( l^0 \perp \) in its principal frame.

In a nematic monodomain with director \( n^0 \) coincident with the \( \hat{z} \) axis, we assume a poly-
mer chain sufficiently long that spans $\mathbf{R}^0$ between network points have, at the moment of crosslinking, a Gaussian distribution:

$$P_0(\mathbf{R}^0) \sim \text{Det}[l_{ij}^0]^{-1/2} \exp \left( -\frac{3}{2L} R_i^0 (l_{ij}^0)^{-1} R_j^0 \right)$$

(1)

Summation over repeated indices has been assumed. The matrix $l_{ij}^0$ of effective step lengths defines the chain shape parallel and perpendicular to the director $\mathbf{n}^0$ for a uniaxial phase, that is $\langle R_i^0 R_j^0 \rangle = \frac{1}{3} L l_{ij}^0$, where $L$ is the chain contour length. The effective step lengths of the random walk, and thus the overall average shape, are functions of the nematic order. For a uniaxial nematic the order parameter $Q_{ij}$:

$$Q_{ij} = \frac{1}{2} Q \left( 3n_i^0 n_j^0 - \delta_{ij} \right) \equiv \begin{pmatrix} Q & 0 & 0 \\ 0 & -Q/2 & 0 \\ 0 & 0 & -Q/2 \end{pmatrix}$$

in a principal frame. We shall find occasion to discuss both the magnitude $Q$ and principal direction $\mathbf{n}$ of this order parameter. The inverse effective step length matrix in (1) is:

$$(l_{ij}^0)^{-1} = 1/l_{ij}^0 \delta_{ij} + (1/l_{ij}^0 - 1/l_{ii}^0) n_i^0 n_j^0 \equiv \begin{pmatrix} 1/l_{ii}^0 & 0 & 0 \\ 0 & 1/l_{ii}^0 & 0 \\ 0 & 0 & 1/l_{ii}^0 \end{pmatrix}$$

(2)

with eigenvalues $1/l_{ii}^0$ and $1/l_{ii}^0$ in its principal frame dependent on the order parameter $Q^0$. We shall confine ourselves to uniaxial formation states (in the two-step method [10] of achieving monodomains this need not always be the case). The effective step lengths are related to the mean square chain size by $\langle (R_i^0)^2 \rangle = \frac{1}{3} L l_{ii}^0$ and $\langle (R_i^0)^2 \rangle = \frac{2}{3} L l_{ii}^0$. In highly ordered main-chain melts $l_{ii} \gg l_\perp$ [14].

We employ the affine deformation assumption, an assumption that pervades network theory. Junction point fluctuations are damped by connectivity compelling junctions to deform in geometric proportion to the whole. Junction point fluctuations are easily handled and alter the elastic free energy by the trivial multiplicative factor $(1-2/\phi)$, where $\phi$ is the junction point functionality. This modification has been demonstrated for nematic elastomers in reference [3]. It is not essential to the new phenomena we introduce here. Using the affine deformation assumption we define the current network span to be $R_n = \lambda_{ij} R_i^0$ with $\lambda_{ij}$ the macroscopic deformation of the whole block of rubber. We consider deformations $\lambda_{ij}$ imposed with respect to the initial crosslinking state. 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: $\text{Det}[\lambda_{ij}] = 1$. In general the current temperature may be different from that of the formation state. Span probabilities are governed by a distribution, $P(\mathbf{R})$, differing from $P_0(\mathbf{R}^0)$ in equation (1) in that the $(l_{ij})^{-1}$ tensor, describing the current chain shape, depends on the current ordering tensor $Q$. Taking the usual quenched average $F_{el}/k_B T = -\langle \ln P(\mathbf{R}) \rangle_{R_0(\mathbf{R}^0)}$ one obtains for the elastic free energy per network strand:

$$\frac{F_{el}}{k_B T} = \frac{3}{2L} \langle l_{ik}^{-1} (R_k R_i)_0 \rangle = \frac{3}{2L} \langle l_{ik}^{-1} (\lambda_{kj} R_j^0 \lambda_{li} R_i^0)_0 \rangle$$

$$= \frac{1}{2} \text{Tr}[(\mathbf{I}^0)^T \mathbf{A}^{-1} \mathbf{A}] ,$$

(3)

where we have used $\langle R_i^0 R_j^0 \rangle = \frac{1}{3} L l_{ij}^0$ from equation (1). There is also an additional term which
arises from the normalization of $P(\mathbf{R})$. Including this term, the free energy is:

$$
\frac{F_{\text{el}}}{k_B T} = \frac{1}{2} \left[ \text{Tr} \left( \frac{P_0}{\lambda^2} \right) + \frac{1}{\lambda} \ln \left( \frac{\text{Det}(P_0)}{\text{Det}(\lambda)} \right) \right]
$$

(4)

The resultant elastic free energy will depend on the nematic order at formation through $P_0$ and on the nematic order in the current state through $P$, that is $F_{\text{el}} = F_{\text{el}}(Q_0, Q)$. In turn $Q$ will depend on the imposed $\lambda$ through both magnitude $Q$ and direction $n$ of the current nematic order. It is the purpose of this paper to specify how $Q$ and $n$ depend on the imposed strain. As a result of applying $\lambda$, minimizing the free energy will yield new $Q$ and $n$, differing from $Q_0$ and $n_0$, and hence a new equilibrium shape $P$. Thus the current director, $n$, is in general not coincident with the initial $n_0$, except if $\lambda$ has the same principal frame as $n_0$ and is a uniaxial extension. In this latter case $\lambda_\parallel = \lambda$, $\lambda_\perp = 1/\sqrt{\lambda}$ and

$$
\frac{F_{\text{el}}}{k_B T} = \frac{P_0}{l_\parallel} \lambda^2 + \frac{P_0}{l_\perp} \frac{1}{\lambda}
$$

(5)

Allowing $\lambda$ in (5) to relax to its equilibrium (i.e. zero-stress) value, that is taking $\partial F_{\text{el}}/\partial \lambda = 0$, gives the spontaneous shape change $\lambda_m = \left(\frac{l_\parallel P_0}{P_0 l_\perp} \right)^{1/3}$ due to a change in the current nematic order with respect to its initial state [3].

One particular case of this is essential. If one heats the nematic rubber so that the current state is isotropic, its step length tensor is $l = 6\delta_{kk}$. The spontaneous distortion is then $\lambda_m = (l_\parallel P_0/l_\perp)^{1/3}$, which will in general be less than one, a flattening, if the crosslinking state was prolate uniaxial. This is a useful experiment since it is a direct measure of the chain anisotropy and is pivotal in what follows. The inverse experiment would be the cooling the initially isotropic rubber down to the nematic state with $Q = Q_0$. This gives the spontaneous distortion $\lambda_c = 1/\lambda_m > 1$, an elongation of the sample that can be easily measured. In general we envisage performing elasticity experiments at the formation temperature, or at lower temperatures where $\lambda_m > 1$, i.e. further chain ordering causes a spontaneous elongation of the sample. Returning the value of $\lambda_m$ to (5) gives the elastic free energy as a function of $l$ and $P_0$: $F_{\text{el}}(Q) = F_{\text{el}}(\lambda_m, l_\perp P_0)$ which represents an addition to the Landau-de Gennes free energy of the nematic order, quartic in the current order parameter $Q$ if the crosslinking is done in the isotropic state, quartic and quadratic in $Q$ if the crosslinking was performed in the nematic state — see [3] for a detailed discussion. The free energy $F_{\text{el}}(\lambda_m, l_\perp P_0)$ then is minimized with respect to $Q$ in order to totally solve the problem.

We are interested here in the case where an imposed deformation $\lambda$ has principal axes not coincident with $n_0$, thereby creating an equilibrium state with $n$ at some angle $\theta$ with respect to $n_0$. In separate papers we shall consider applied (uniaxial) stress and electric fields, both of which lead to novel counter intuitive effects. We shall determine $\theta$ as a function of the magnitude of deformation and the orientation of the frame of the imposed deformation $\lambda_{ij}$ with respect to $n_0$. To do this we shall proceed essentially as above, minimizing $F_{\text{el}}$ with respect to any free components of $\lambda$ and with respect to $Q$ and $\theta$, which characterize $Q$.

We consider several types of deformations in increasing order of complexity taking two principal axes of distortion to define the $(x, z)$ plane. For these distortions we show below that the director rotates about the $\hat{y}$ axis and remains in the $(x, z)$ plane, therefore one can effectively operate with $(2 \times 2)$ anisotropic matrices. Each type of deformation produces characteristic instabilities. Some produce "soft elasticity" phenomenon hitherto unknown in rubber theories.
Fig. 1. — Alignment geometry in the \((x, z)\) plane for (a) constrained extension [Sect. 3.1]; (b) imposed extension experiment by Mitchell et al. [Sect. 3.2]; (c) simple shear [Sect. 3.3]. \(\mathbf{n}_0\) 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.

and which we discuss in a separate paper. We list here each type of deformation and analyze them later in separate sections.

(A) Uniaxial extension at an angle \(\alpha\) with respect to \(\hat{z}\) (coincident with the initial director \(\mathbf{n}^0\)), figure 1a. In terms of the unit vector \(\mathbf{u}\) of the direction of extension, the deformation tensor at a constant volume is \(\lambda_{ij} = (1/\sqrt{\lambda})\delta_{ij} + (\lambda - 1/\sqrt{\lambda})u_iu_j\). This is simple conceptually but difficult to apply in practice since biaxial stresses are needed to create uniaxial deformation in a misaligned but naturally uniaxial system. The simplicity of \(\lambda\) however allows one to see the hallmark of instabilities occurring in more complex geometries. We find a jump in the director at a critical strain applied at \(\alpha = \pi/2\). For \(\alpha < \pi/2\), the director moves continuously away from \(\mathbf{n}^0\) as \(\lambda\) increases.

(B) Extension applied at an angle \(\alpha\) with respect to \(\mathbf{n}^0\), but normal transverse relaxation permitted (giving in general a biaxial \(\lambda\)). Relaxation via simple shear strains is prohibited by symmetry, figure 1b. This geometry is that employed experimentally by Mitchell et al. [11]. We again find a discontinuity in the direction of \(\mathbf{n}\) with \(\lambda\), but now over a range of \(\alpha\) around \(\pi/2\). As one reduces \(\alpha\) below \(\pi/2\) eventually these transitions terminate at a critical point. There is mechanical hysteresis where the transitions are discontinuous.
3. Results.

Henceforth we use a coordinate system \((z, x, y)\) based on \(u_i = \hat{z}\) rotated by \(\alpha\) about \(\hat{y}\) from the original (principal) frame of \(\xi_0\). This will be a principal frame, for instance, for imposed uniaxial strain and a simple frame in which to consider shear. The tensors \(\xi^0\) and \(\xi^{-1}\) have to be rotated by angles \(\alpha\) and \(\Delta = \alpha - \theta\) from their principal frames. Second rank \((2 \times 2)\) tensors, for instance \(\xi_0\), will be characterized by their mean \(\bar{\xi}_0 = (\xi_0^0 + \xi_0^1)/2\) and anisotropy \(\delta\xi^0 = (\xi_0^0 - \xi_0^1)/2\) of their principal values and similarly for \(\xi^{-1}\) and \(\lambda\). Details of calculations are to be found in the following section 4.

3.1 Uniaxial Extension. — Using the expressions for \(\xi_0^0\) and \(\xi^{-1}\) given by equation (2) with the corresponding orientation of the director in each case, and taking the uniaxial form

\[
\lambda = \begin{pmatrix}
\lambda & 0 \\
0 & 1/\sqrt{\lambda}
\end{pmatrix},
\]

one obtains for the elastic part of the free energy (with \(\lambda_y = 1/\sqrt{\lambda}\))

\[
\frac{2F_{el}}{k_B T} = \frac{\xi_0^0}{\xi_0^0} \frac{1}{\lambda} + 2\delta\xi^{-1} \left[ C_1 \cos 2\Delta + C_2 \sin 2\Delta \right] + C_3
\]

(6)

where the coefficients of the angularly varying terms depend simply on \(\xi_0^0\), \(\lambda\) and angle \(\alpha\). The variation of \(F_{el}\) with the relative orientation of the current director, \(\Delta\), is through the \(C_1\) and \(C_2\) terms. Taking the minimal free energy, at \(\partial F/\partial \Delta = 0\), and inserting \(\lambda\), \(\delta\lambda\), \(\bar{\xi}_0\) and \(\delta\xi^0\), one obtains for the equilibrium orientation:

\[
\tan 2\Delta = \frac{2(\lambda_0^2 - 1)\sqrt{\lambda} \sin 2\alpha}{(\lambda_0^3 + 1)(\lambda_0^2 - 1/\lambda) + (\lambda_0^2 - 1)(\lambda_0^2 + 1/\lambda) \cos 2\alpha}
\]

(7)

where \(\lambda_0 = (\xi_0^0/\xi_0^1)^{1/3}\) specifies the anisotropy of the initial strand conformation.

The rotation \(\theta\) of \(n\) is shown as a function of the imposed \(\lambda\) at constant \(\alpha\) in figure 2a. Figure 2b shows \(\theta(\alpha)\) for various (fixed) \(\lambda\). When \(\lambda\) is imposed at an angle \(\alpha = \pi/2\) an internal barrier prevents any rotation of \(n\) until \(\lambda \geq \lambda_c\). The system then breaks symmetry and jumps to \(\theta = \pi/2\). For smaller \(\alpha < \pi/2\) there is no degeneracy in the direction of rotation and the director is continuously dragged around towards \(\alpha\).

One would expect that the discontinuous jump in the director orientation is due purely to a symmetry argument that there is a degeneracy at \(\alpha = \pi/2\). In fact we shall see in the next subsection that the reason for such discontinuity is more subtle and it may persist for some region of finite \(\alpha < \pi/2\). The discontinuity in \(\theta(\alpha)\) is seen in a different guise in some of the other geometries, below.

The curves for different \(\alpha\) cross and this is more easily seen in figure 2b where, for a given \(\lambda < \lambda_c\), the \(\theta(\alpha)\) curves have maxima, which disappear with a singularity at the critical extension \(\lambda = \lambda_c\).
3.2 IMPOSED EXTENSION. — The geometry of imposed extension $\lambda_{zz} = \lambda$ for an experiment with arbitrary $\alpha$ allowing transverse normal relaxation only is shown in figure 1b where $\lambda_{zz} = \lambda_{xx} = 0$. (More complicated setups could be envisaged, for instance the biaxial relaxometer frame with rollers [15] so that $\lambda_{zz}$ becomes fixed as well). When $\alpha \neq 0$ or $\pi/2$, shear relaxation is in general needed. The experimental geometry restricts such shear strains to a (hopefully) small region of non-uniform deformation near the clamps (shown in Fig. 1b). The bulk of the sample can only relax in $\lambda_{zz}$, with $\lambda_y = 1/\lambda_{xx} \lambda$ fixed by incompressibility.

Again rotating tensors to the $(\hat{z}, \hat{z}, \hat{y})$ frame, one obtains for the elastic energy, now with $\lambda_{zz}$ appearing,

$$\frac{2F_{el}}{kT} = ad\lambda^2 + be\lambda_{xx}^2 + 2cf\lambda\lambda_{xx} + \frac{r}{\lambda_{zz}^2\lambda^2}$$

(8)

The coefficients $a - f$ arise from writing $\hat{r}_z = \begin{pmatrix} a \\ c \\ b \end{pmatrix}$ and $\hat{l}_z^{-1} = \begin{pmatrix} d & f \\ f & e \end{pmatrix}$ and depend on the angles $\alpha$ and $\Delta$. The coefficient $r = l_y^0/l_y$ and is equal to unity if the magnitude of the order parameter remains constant.

Given that we fix only $\lambda$, we minimize the free energy (8) with respect to $\lambda_{xx}$ to obtain a condition for $\lambda_{xx}$.

$$be\lambda_{xx}^4 + cf\lambda\lambda_{xx}^2 - \frac{r}{\lambda^2} = 0$$

(9)

This quartic yields the equilibrium $\lambda_{xx}(\Delta, \lambda, \alpha)$ as a function of $\Delta = \alpha - \theta$, i.e. as a function of the as yet undetermined angle $\theta$ of the director. Minimizing over choices of the director angle $\theta$, which appears in coefficients $d, e$ and $f$, that is $\partial F/\partial \Delta = 0$, we obtain

$$\tan 2\Delta = \frac{2\delta^0 \lambda\lambda_{xx} \sin 2\alpha}{\delta^0 (\lambda^2 - \lambda_{xx}^2) + \delta^0 (\lambda^2 + \lambda_{xx}^2) \cos 2\alpha}$$

(10)

Equilibrium strain relaxation and orientation are specified by equations (9) and (10). We consider some specific cases.
Fig. 3. — a) Director orientation under imposed strain, θ vs. λ, is shown for initial anisotropy λ_{zz}^0 = l_||^0/l_\perp^0 = 3. The different curves correspond to different (fixed) values of α. Curve (a) α = 90 deg, (b) 87.5 deg, (c) 85 deg, (d) 82.5 deg. b) Plot of the transverse strain under imposed strain, λ_{xx} vs. λ, for the same values of α and l_||^0/l_\perp^0 as above. The upper and lower boundaries of the hysteresis region are λ_{c'} and λ_{c''}, respectively.

(i) Specializing to α = π/2, one has c = 0, a = l_\perp^0 and b = l_\parallel^0. The quartic (9) is trivial and the transverse dimensions become

\[ \lambda_{xx} = \left( \frac{r}{be} \right)^{1/4} \frac{1}{\sqrt{\lambda}}; \quad \lambda_{yy} = \left( \frac{be}{r} \right)^{1/4} \frac{1}{\sqrt{\lambda}}. \]

Inserting the equilibrium values of the λ’s into (8) yields

\[ \frac{2F_{el}}{k_BT} = ad\lambda^2 + 2\sqrt{rbe} \lambda \]  

(11)

Although the final strains are not uniaxial (\(\lambda_{xx} \neq \lambda_{yy}\)) (11) is reminiscent of the classical uniaxial result. For α = π/2 the solutions of (10) for the equilibrium director orientation θ are θ = 0 or π/2. The direction θ = 0 becomes unstable when \(\partial^2F/\partial\theta^2|_{\theta=0} \rightarrow 0\), which occurs at \(\lambda = \lambda_c\). We thus predict a jump in θ from 0 to π/2 at \(\lambda = \lambda_c\). The turning point in \(F\) at \(\theta = \pi/2\) first becomes a minimum at \(\lambda = \sqrt{\lambda_c}\), a significantly smaller distortion. As one might expect for a discontinuous phase transition there is a hysteresis. On releasing strain after achieving the jump from \(\theta = 0\) to \(\theta = \pi/2\) at \(\lambda_c\), we predict that the system should remain with \(\theta = \pi/2\) until \(\lambda = \sqrt{\lambda_c}\) is achieved, whereupon it jumps back to \(\theta = 0\). The hysteresis region is thus \(\lambda \in (\sqrt{\lambda_c}, \lambda_c)\).

(ii) Strain imposed at α ≠ π/2: contrary to expectations based on case (A) the discontinuities and hysteresis we predict continue to be displayed for a range of α < π/2. Figure 3a shows θ, the direction of \(\mathbf{n}\), as λ is increased. The upper and lower transition deformations, now denoted by \(\lambda_{c'}\) and \(\lambda_{c''}\), are indicated and are marked as solid lines for the α = π/2 case. For angles α < π/2, \(\lambda_{c'}\) diminishes rapidly and the hysteretic region narrows until α reaches a critical value when the transition becomes continuous. Explicit conditions for this critical
point are lengthy and complicated to solve analytically. Figure 3b shows how the associated relaxing strain $\lambda_{xx}$ varies with $\lambda$, suffering the same discontinuities and hysteresis as $\theta$.

The experiments of Mitchell et al. [11] were performed at 50 °C, about 70° below the N-I transition. We expect our assumption of the constancy of the magnitude $Q$ of the order parameter to apply very well to their experiments. Mitchell et al. indeed see the discontinuity in $\theta$ we discuss above. The thermal history of the sample must be accounted for if the crosslinking temperature is not that of the mechanical experiment. We discuss this in Appendix.

Figure 3b shows that the value of the jump in $\lambda_{xx}$ and $\theta$ depend sensitively on the alignment $\alpha$. To analyze Mitchell et al.'s experiments one needs a precise value of $\alpha$ and ideally measurements of $\lambda_c(\alpha)$ and $\lambda_{c'}(\alpha)$, the region of hysteresis in $\theta$, for a variety of angles $\alpha$. Since at these low temperatures our predictions are functions only of the one separately measurable quantity $\lambda_c$ and is not dependent on any parameters, detailed quantitative comparison of theory and experiment would be highly desirable.

3.3 Simple shear. — In the $(\hat{z}, \hat{x}, \hat{y})$ frame with $\hat{z}$ along the shear direction

$$\Delta = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \delta_{ij} + \lambda u_i v_j$$

(12)

Substituting equations (19) into (4) one again obtains a free energy of the form

$$\frac{2F_{el}}{k_B T} = \delta l^{-1} [C_1 \cos 2\Delta + 2C_2 \sin 2\Delta] + C_3$$

(13)

where the coefficients $C_k$ depend on $\alpha$, $\lambda$ and the anisotropy. Again we can minimize the free energy with respect to the director angle $\theta$ by taking $\partial F/\partial \theta = 0$ whereupon the relative angle $\Delta = \alpha - \theta$ is given by

$$\tan 2\Delta = 2C_2/C_1 = 2 \frac{(\lambda^3 - 1) [\sin 2\alpha + \lambda \cos 2\alpha] - \lambda(\lambda^3 + 1)}{\lambda^2(\lambda^3 + 1) + 2(\lambda^3 - 1) [(1 - \lambda^2/2) \cos 2\alpha - \lambda \sin 2\alpha]}$$

(14)

When the initial state is isotropic, $\lambda_c = 1$, we find that $\tan 2\Delta = -2/\lambda$ — the director follows the principal extensional component of the shear as expected. For a nematic monodomain with anisotropy $l_0/l_1 = 3$ at formation, the director orientation $\theta(\lambda)$ is shown in figure 4. For large enough initial angle $\alpha = \alpha^*$ between unit vectors $u$ and $n_0$ there is a discontinuity in $\theta(\lambda)$, another manifestation of that found in subsections (A) and (B).

The character of the director rotation $\theta(\lambda)$ and its discontinuities can be established analytically from (14), analysis that we present in the next section. A convenient measure of the anisotropy is $A = (\lambda^3 - 1)/(\lambda^3 + 1) \equiv (l_0^0 - l_0^1)/(l_0^0 + l_0^1)$.

The initial rotation $\theta(\lambda \to 0)$. Figure 4 shows this to be positive at small $\alpha$, i.e. when the direction of shear is close to the initial nematic orientation $n^0$. Approaching a critical value of $\alpha = \alpha_c$ the director can undergo a negative rotation as $\lambda$ rises from zero. This first happens at

$$\alpha_c = \frac{1}{2} \cos^{-1}(A) \equiv \frac{1}{2} \cos^{-1} \left( \frac{l_0^0 - l_0^1}{l_0^0 + l_0^1} \right)$$

(15)

For $\alpha < \alpha_c$ we have $\theta$ initially positive, that is $d\theta/d\lambda \bigg|_{\lambda=0} > 0$. For the value $\lambda_c = 3^{1/3}$ shown in figure 4 we have $\alpha_c = 30°$. For $\alpha > \alpha_c$ the initial rotation is negative. In the region $(\alpha_c, \alpha^*)$ the director rotation again becomes positive for large enough shears. The transition between negative and positive rotation $\theta$ becomes sharper as $\alpha$ increases toward $\alpha^*$. 
The critical \( \alpha^* \) where the director rotation angle \( \theta(\lambda) \) displays a discontinuity is given by

\[
\alpha^* = \frac{1}{2} \cos^{-1} \left( \frac{1 - \sqrt{1 - A^2}}{A} \right)
\]

with corresponding critical shear

\[
\lambda^* = \sqrt{2 \left( \frac{1}{(1 - A^2)^{1/2}} - 1 \right)}
\]


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. Cases will be in the order of previous sections.

It is clear, for \( \lambda > 1 \) in figure 1a, for general shear \( \lambda \) in figure 1c and for the stress and applied electric field cases, that the equilibrium \( \mathbf{n} \) must be in the plane of \( \hat{z} \) (i.e. of \( n^0 \)) and \( \mathbf{u} \). It is sufficiently general to consider a \( (2 \times 2) \) problem in the \( (x, z) \) plane. With the rotation of \( \mathbf{n} \) by the angle \( \theta \), the major principal direction of \( \frac{1}{2} \) also rotates. Seen in, say, the frame of \( \Lambda_z \), matrices \( \frac{1}{2} \) and \( \frac{1}{2} \) have off-diagonal elements in \( (x, z) \) only and none connecting \( \hat{y} \) with either \( \hat{z} \) or \( \hat{x} \). Thus in the free energy (4) there is an isolated term \( \lambda^2_{yy} \rho^0 / \rho_y \). In \( \text{Tr}[\frac{1}{2} \Lambda \Lambda^T \frac{1}{2} \Lambda] \) the tensors can now be thought of as \( (2 \times 2) \) tensors of the remaining elements \( (x, z) \). \( \Lambda_z \) and \( \frac{1}{2} \) have principal frames rotated respectively by angles \( \alpha \) and \( \theta \) away from that of \( \frac{1}{2} \).

The current conformations \( \frac{1}{2} \) depend on the current order parameter \( Q \) (which may be much larger than \( Q^0 \) if the temperature has dropped since fabrication). In general, since the axes of \( \Lambda_z \) are not coincident with those of \( \frac{1}{2} \) the distortion forces the network chains and hence the phase itself to be biaxial, with a second order parameter \( X \). In its principal frame \( \frac{1}{2} \) then has...
three distinct elements \( l_x, l_y \) and \( l_z \) depending on \( Q \) and \( X \). Strictly speaking the total free energy, the sum of the nematic and elastic contributions \( F_{\text{total}} = F_{\text{nem}} + F_{\text{el}} \) must be minimized with respect to \( Q, X \) and \( \theta \) for each \( \lambda, \sigma \) or \( E \) imposed. Experience shows that \( X \) is generally small [4]. For many geometries we show that the optimal angle \( \theta \) does not depend on \( Q \) and \( X \) (although \( F_{\text{el}} \) and \( F_{\text{nem}} \) do). We shall throughout simply minimize \( F_{\text{el}} \) with respect to the angle \( \theta \) of the new ordering, but not with respect to the new magnitudes \( Q \) and \( X \) of the order. This corresponds to temperatures well below the N-I transition where the order saturates and no further changes are induced by applied fields. We shall indicate in the detailed derivations the cases where this is exact, and discuss the procedure where it is approximate.

Since it is sufficient to consider a \( (2 \times 2) \) problem, we can always write \( l_i^{-1} \) in the form of equation (2), replacing \( l_x, l_y \) and \( l_z \) with \( l_\parallel \) and \( l_\perp \) respectively (the third component of the tensor for \( l \) can of course be different from \( l_\perp \)). Then the only part of the free energy (4) that depends on the current orientation \( n \) (or on the angle \( \Delta = \alpha - \theta = \cos^{-1}(n \cdot u) \)) if one instead measures angles from the principal frame of \( \lambda \) is the second term below:

\[
\frac{2F_{\text{el}}}{k_B T} = \frac{2}{k_B T} F_0(Q, \lambda yy) + \frac{k_B T}{2} \left( \frac{1}{l_\parallel} - \frac{1}{l_\perp} \right) \text{Tr}[\tilde{f}^0 (n_{\lambda}) \tilde{f}^0 (n_{\lambda})]
\]  

The additional component to the free energy, \( F_0 \), contains the \( \lambda_{yy} l_0^0 / l_y \) factor, independent of the frame rotations \( \alpha, \theta \) but dependent on \( Q^0, Q \) and \( X \). \( F_0 \) also contains \( \ln(\text{Det}[l_\parallel^0] / \text{Det}[l_y^0]) \) which has no explicit \( \lambda_{\lambda} \theta \) or \( \alpha \) dependence and only depends on \( Q \) and \( X \).

Calculations are performed in a coordinate system based on the distortion field \( \lambda \). On rotation by \( \alpha \) and \( \Delta = \alpha - \theta \) from their own principal frames to the frame of \( \lambda \), \( l_\parallel^0 \) and \( l_\perp^{-1} \) become

\[
l_\parallel^0 = \tilde{l}_\perp^{-1} + \delta l_\parallel^0 \left( \begin{array}{cc} \cos^2 \alpha & -\sin \alpha \cos \alpha \\ -\sin \alpha \cos \alpha & \sin^2 \alpha \end{array} \right)
\]

\[
l_\perp^{-1} = \tilde{l}_\parallel^{-1} + \delta l_\perp^{-1} \left( \begin{array}{cc} \cos^2 \Delta & -\sin \Delta \cos \Delta \\ -\sin \Delta \cos \Delta & \sin^2 \Delta \end{array} \right)
\]

The mean of the principal elements remains invariant on rotation, the anisotropies \( \delta l_\parallel^0 \) and \( \delta l_\perp^{-1} \) transform with angular factors to non-diagonal forms. The coefficients \( a \) through \( f \), arising when \( l_\parallel^0 \) and \( l_\perp^{-1} \) are written as \( 2 \times 2 \) matrices [see after (8)], are

\[
a = \tilde{l}_\parallel^0 + \delta l_\parallel^0 \cos 2\alpha; \quad b = \tilde{l}_\parallel^0 - \delta l_\parallel^0 \cos 2\alpha; \quad c = -\delta l_\parallel^0 \sin 2\alpha
\]

\[
d = \tilde{l}_\perp^{-1} + \delta l_\perp^{-1} \cos 2\Delta; \quad e = \tilde{l}_\perp^{-1} - \delta l_\perp^{-1} \cos 2\Delta; \quad f = -\delta l_\perp^{-1} \sin 2\Delta
\]

\[
r = l_y^0 / l_y
\]

4.1 UNIAXIAL EXTENSION. — Inserting in (18) the above elements of \( l_\parallel^0 \) and \( l_\perp^{-1} \) and the simple uniaxial form for \( \lambda \) one obtains for the coefficients \( C_k \) in (6)

\[
C_1 = 2\tilde{l}_\parallel^0 \lambda \delta \lambda + \delta l_\parallel^0 [\lambda^2 + (\delta \lambda)^2] \cos 2\alpha; \quad C_2 = \delta l_\parallel^0 [\lambda^2 - (\delta \lambda)^2] \sin 2\alpha
\]

\[
C_3 = 2\tilde{l}_\perp^{-1} (\tilde{l}_\parallel^0 [\lambda^2 + (\delta \lambda)^2] + 2\delta l_\parallel^0 \lambda \delta \lambda \cos 2\alpha)
\]

The mean and anisotropy of \( \lambda \) are \( \bar{\lambda} = (\lambda + 1/\sqrt{\lambda})/2 \) and \( \delta \lambda = (\lambda - 1/\sqrt{\lambda})/2 \).

The variation with the director angle \( \alpha - \theta \) is purely through the \( C_1 \) and \( C_2 \) terms of (6) and these terms have a common prefactor of \( \delta l \). Free energy is minimized at \( \Delta \) satisfying
\[ \tan 2\Delta = \frac{C_2}{C_1} \] and thus we have the resulting equation (7) which does not involve \( l^{-1} \) and hence does not involve \( Q \) or \( X \). In fact inspection of equation (18) shows that this is a general result. In (18) the dependence on the order parameters \( Q \) and \( X \) is restricted to the first term of the free energy and the prefactor of the trace which in turn contains only \( \theta \) and \( \alpha \). If all components of the the deformation \( \Lambda \) are imposed, that is there is no freedom to relax, then we can minimize this free energy with respect to \( \theta \) to obtain the orientation of \( n \) without considering the self-consistency problem (the minimization) in \( Q \) and \( X \). Accordingly the results of section 3.1 do not involve any approximation of \( Q \) and \( X \).

4.2 IMPOSED EXTENSIONS (AT \( \alpha = \pi/2 \)). — Take \( \alpha = \pi/2 \) as an illustration of the process. With the explicit forms of coefficients \( a - f \) now given in (21), the collapse of the quartic equation (9) when the coefficient \( c(\alpha = \pi/2) \equiv 0 \) can now be clearly seen. Coefficients \( d \) and \( e \) become simple functions of \( \theta \): \( d = l^{-1} - \delta l^{-1} \cos 2\theta \) and \( e = l^{-1} + \delta l^{-1} \cos 2\theta \). Since \( F \) is a function of \( \cos 2\theta \),

\[ \partial^2 F / \partial \theta^2 \bigg|_{\theta = 0} = -4 \cos 2\theta \frac{\partial F}{\partial (\cos 2\theta)} \] (23)

This vanishes at

\[ \lambda^3 = \sqrt{\frac{rl_\parallel l_0^0}{(l_\parallel l_\perp)^2}} = \lambda_{c'}^3 \] (24)

(compare with \( \lambda_c \) appearing in Eq. (7)). Since \( F \) depends on \( \cos 2\theta \) it is clear that \( \theta = \pi/2 \) is also a turning point and at \( \lambda = \lambda_{c'} \) it is a minimum.

The stability of the other turning point is established from (23) by setting \( \partial F / \partial (\cos 2\theta) = 0 \) at \( \theta = \pi/2 \); it yields

\[ \lambda^3 = \sqrt{\frac{rl_\perp l_0^0}{(l_\perp l_\parallel)^2}} = \lambda_{c''}^3 \] (25)

This value \( \lambda_{c''} \) is smaller than the first instability at \( \lambda_{c'} \) associated with \( \theta = 0 \):

\[ \lambda_{c''} = \lambda_{c'} \left( \frac{l_\perp}{l_\parallel} \right)^{1/6} \] (26)

Note that, as expected, the limits to stability \( \lambda_{c'} \) and \( \lambda_{c''} \) involve components of the current tensor of the chain shape \( l \) and hence the current values of order parameters \( Q \) and \( X \). Self-consistency demands that one also minimizes with respect to the magnitudes of \( Q \) and \( X \). This will, in addition to the above determination of the orientation of \( n \) (i.e. \( \theta \)) of the tensor \( l^{-1} \), also fix the magnitudes \( l_\parallel \) and \( l_\perp \) (more accurately denoted by \( l_s \) and \( l_t \)) in the above. Imposing strains \( \Lambda \) not aligned with \( n_0 \) when near the N-I transition presumably has a profound effect on the order of a nematic elastomer. There is then no alternative but to optimize \( F_{el} \) with respect to \( Q \) and \( X \). Bladon and Warner [4] have seen this in an extreme form when describing uniaxial compressions to the isotropic phase of an elastomer near the N-I transition using the worm-like chain model for the nematic polymer. There is ultimately a transition to a biaxial nematic state with \( n \) perpendicular to the compression axis and large values of \( Q \) and \( X \) created.

At lower temperatures where the order is already high we adopt a simplifying assumption: with \( Q^0 \) large any further increase caused by \( \Lambda \) is minimal and the most that can be achieved is a rotation (by amount \( \theta \)) of \( l^{-1} \) with respect to the axis of \( l^0 \). Thus we have numerical equalities of the principal frame quantities \( l_\parallel = l_\parallel^0 \) and \( l_\perp = l_\perp^0 \) with the ratio \( r = l_\parallel^0 / l_\parallel = 1 \).
Under these conditions we have

\[
\lambda_{c'} = \left( \frac{\ell_0}{\ell_1} \right)^{1/3} = \lambda_c \quad \lambda_{c''} = \sqrt{\lambda_c},
\]

the results presented in the previous section 3.2.

4.3 Simple shear. — Adopting the form (12) for $\vec{A}$ and inserting it along with initial and current chain shape tensors $\ell_0$ and $\ell^{-1}$ in the free energy (18) gives for the coefficients $C_k$

\[
C_1 = \lambda^2 \ell_0 + 2 \delta \ell_0 \cos 2\alpha - 2 \lambda \delta \ell_0 \sin 2\alpha; \quad C_2 = -\ell_0^2 \alpha + \delta \ell_0 \sin 2\alpha + \lambda \delta \ell_0 \cos 2\alpha \\
C_3 = 2 \ell_0 \ell^{-1} + \lambda^2 \ell_0 \ell^{-1} - 2 \lambda \delta \ell_0 \ell^{-1} \sin 2\alpha - \lambda^2 \delta \ell_0 \ell^{-1} \cos 2\alpha
\]

(27)

Given that elements of $\ell^{-1}$ appear only as the common prefactor $\delta \ell^{-1}$ in (13) then, as in case (4.1) of uniaxial distortion, the current order does not determine the equilibrium angle $\theta$ of $\vec{n}$. Thus simple shear instabilities do not involve self consistency in $Q$ and $X$. The results quoted in the previous section 3.3 do not depend on the approximation of constant magnitude of the principal values of $\ell$.

The initial rotation. We expand (14) for $\lambda \to O^+$ yielding

\[
\tan 2\Delta = \tan 2\alpha \left[ 1 - \lambda \left( \frac{1/A - 1}{\sin 2\alpha} \right) + O(\lambda^2) \right]
\]

(28)

We have positive rotation if $\Delta < \alpha$, which is achieved if the coefficient of $\lambda$ is positive. The critical value of $\alpha$ determining the sign of the rotation of $\vec{n}$ is therefore determined by setting the coefficient to $\lambda$ equal to zero and gives the resulting equation (15).

Discontinuities in $\theta(\lambda)$. When the numerator $C_2$ in (14) changes sign as $\lambda$ is increased (at fixed $\alpha$), $\theta$ becomes greater than $\alpha$. We denote this point by $\lambda_2$. If at the same point the denominator $C_1$ is also very small, then the variation of $\tan 2\Delta$ will be very rapid. If $C_1 = 0$ also, then $\tan 2\Delta$ varies rapidly between $-\infty \to +\infty$, that is $2\Delta$ varies from $-\pi/2$ to $\pi/2$ or $\theta$ varies from $\alpha + \pi/4$ to $\alpha - \pi/4$. The discontinuity in $\theta$ is thus $\pi/2$ and occurs when the zeros of $C_1$ and $C_2$ fall at the same point. The zero of $C_2$ is

\[
\lambda_2(\alpha) = \frac{\sin 2\alpha}{(1/A - \cos 2\alpha)}
\]

(29)

and that of $C_1$ is

\[
\lambda_1(\alpha) = \sin 2\alpha \pm \frac{\sqrt{1 + \cos^2 2\alpha - 2(1/A) \cos 2\alpha}}{1/A - \cos 2\alpha}
\]

(30)

Only when $\alpha \geq \alpha^*$ [where $\alpha^*$ determines the zero of the square root in Eq. (30)] is $\lambda_1$ real. At $\alpha = \alpha^*$ we satisfy the desired condition that $\lambda_1 = \lambda_2$ for the instability. Setting $\lambda_1 = \lambda_2$ and solving this condition as an equation for $\alpha$ gives the final result of the previous section (16) for $\alpha^*$. Returning $\alpha^*$ to (29) or (30) gives the expression (17) for $\lambda^*$.

5. Summary and conclusions.

Nematic solids are qualitatively new types of liquid crystal and elastomeric media. Their novelty derives from the coupling of their orientational and translational degrees of freedom, a coupling that is absent in conventional liquid crystals and in conventional elastic media. The
coupling arises because nematic ordering in polymers leads to a molecular shape change, and in elastomers molecular shape change leads to macroscopic shape change. Since these macroscopic shape changes couple to stress, so we have the coupling of stress indirectly to nematic order.

It is a clear expectation [7] that crosslinking chains into a network while they are anisotropic in shape will create a memory of this anisotropy and its direction. Our calculations partially affirm this expectation in that there is 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. Imposing a certain strain tensor essentially means the imposition of constraints on chain shape. The more constrained the deformation, the less freedom a chain has to adopt a high entropy, low free energy distribution. This is seen in geometries (A) and (B) where the energy rises when chains are distorted in a direction different to their principal direction. At some critical strain \( \lambda \) a new director can be found where relatively more freedom for the chain exists. The chains and hence the director and extensions then jump. The “rotational barrier” is thus dependent on the geometrical constraints put upon components of the chain shape tensor. We have predicted a new nematic transition where a field (stress) applied to a surface acts therefore to rotate the director of the bulk. Such director jumps have been seen experimentally by Mitchell et al. [11]. The transition occurs at high strains well beyond the scope of linear models.

In separate papers we consider two others, previously unanticipated effects in nematic elastomers — the deformation without resistance in response to certain applied stress, and the soft response to applied electric field.

Problems for the future include those of polydomain samples and non-uniform distortions and orientations. Although monodomain samples are now readily available and offer cleaner paths to a fundamental understanding of nematic elastomers, polydomain materials offer many challenges, for instance why do they clear at universal values of stress?

Non-uniform nematics are governed by Frank curvature elasticity, non-uniform elastic bodies — by Lame (classical) elasticity. Nematic solids demand a generalization of both these free energies in that one can have coupling between \( \nabla n_1 \) and \( \lambda_{ij} \). The continuum theory of such coupling in nematic (and more complex) solids has been established recently [13]. A molecular understanding is also demanded. Since elastomers abound with non-linear effects (two unusual ones are presented here) we can perhaps expect a richness of new phenomena when considering non-uniform systems at high deformations.

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Appendix.

Thermal history effects on elastomers.

Our predictions of new types of instabilities, soft deformations and the critical strains and angles involved have all been presented in terms of intrinsic anisotropy of the polymer chains that underly the network before deformation, \( \lambda^3_c = \frac{r_0}{l_0} \). We have assumed that the deformation, leading to new nematic order and hence a new \( \frac{1}{2} \) shape tensor, was imposed at the same temperature as the network was formed. It is frequently the case that the network is formed at one temperature, \( T_X \), and deformed at the second, lower temperature, \( T_D \). In lowering the temperature the network will spontaneously deform by an amount we denote by \( m \lambda \) where,
since no external forces are applied, this deformation is uniaxial with principal elements $\lambda_m$, $1/\sqrt{\lambda_m}$, $1/\sqrt{\lambda_m}$. Subsequent deformation $\Lambda$ is seen experimentally as being applied from the cooled state as a starting point. Therefore it is the overall deformation $\Lambda = \lambda \cdot \lambda_m$, which must appear in the fundamental expression (3) for $F_{el}$:

$$\frac{2F_{el}}{k_B T} = \text{Tr}[I^{(X)}: \Lambda_m^T \Lambda^{-1} \Lambda_m]$$  \hspace{1cm} (31)

The quantity $I^{(X)}$ is the molecular shape tensor at the moment of crosslinking. If $\Lambda = 1$ — if there is no specific strain imposed at the lower temperature — then all the remaining tensors in (31) share a common principal frame and are uniaxial. In this case we identify $I = I_0^0$ as the natural shape at the current temperature $T_0$ in (31). We have then

$$\frac{2F_{el}}{k_B T} = \lambda_m^2 \frac{I^{(X)}_\parallel}{I_\parallel^0} + 2 \frac{I^{(X)}_\perp}{\lambda_m I_\perp^0}$$  \hspace{1cm} (32)

where the minimum of $F_{el}$ determines $\lambda_m = \left(I^{(X)}_\parallel / I_\parallel^0 \right)^{1/3}$ and $(2F_{el}/k_B T)_{\text{min}} = 3(I^{(X)}_\parallel I_\perp^0 / I_\perp^{02})^{1/3}$. The combination $\Lambda_m = I^{(X)} I_\parallel^0 \lambda_m I_\parallel^0$ in equation (31) is thus

$$I_\parallel^0 \text{eff} = \begin{pmatrix} \lambda_m^2 I^{(X)}_\parallel & 0 & 0 \\ 0 & I^{(X)}_\perp / \lambda_m & 0 \\ 0 & 0 & I^{(X)}_\perp / \lambda_m \end{pmatrix}$$

Thus the free energy expression (31) becomes $\text{Tr}[I_\parallel^0 \text{eff} : \Lambda_m^T \Lambda^{-1} \Lambda_m]$, which is the form we have used before [Eq. (3)] except that $\Lambda$ is the deformation applied in the mechanical phase of the experiment and that $I_\parallel^0 \text{eff}$ replaces $I_\parallel^0$ in $F_{el}$. It will be recalled that in previous sections all results were expressed in terms of $\lambda_c^3 = I_\parallel^0 / I_\parallel$, the spontaneous deformation observed when cooling a monodomain sample from the isotropic phase to the crosslinking temperature (where also the mechanical deformation was to be carried out). The same formulae will apply, but depend instead on $I_\parallel^0 / I_\parallel^0 = I^{(X)}_\parallel \lambda_m^3 / I^{(X)}_\perp$. Inserting the above expression for $\lambda_m$ one obtains

$$I_\parallel^0 / I_\parallel^0 = I_\parallel^0 / I_\parallel^0 \equiv \lambda_0^3$$

where now $\lambda_0$ refers to the elongation when cooling down from the isotropic state to the temperature at which mechanical experiments are to be performed. Thus where $T_X \neq T_0$ all the formulae and conclusions derived before pertain, but with a new definition of $\lambda$ (being the distortion with respect to the equilibrium state at the temperature of this mechanical phase of the experiment). The quantity $\lambda_c$ is replaced by $\lambda_0$ and contact with experiment is therefore straightforward.

References