Anomalous Viscoelastic Response of Nematic Elastomers

S. M. Clarke,[1,2] A. R. Tajbakhsh,[1] E. M. Terentjev,[1] and M. Warner[1]

[1] *Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, United Kingdom*
[2] *The BP Institute, University of Cambridge, Madingley Rise, Cambridge CB3 0EZ, United Kingdom*

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We report a combined theoretical and experimental study of linear viscoelastic response in oriented monodomain nematic elastomers. The model predicts a dramatic decrease in the dynamic modulus in certain deformation geometries in an elastic medium with an independently mobile internal degree of freedom, the nematic director with its own relaxation dynamics. Dynamic mechanical measurements on monodomain nematic elastomers confirm our predictions of dependence on shear geometry and on nematic order, and also show a very substantial mechanical loss clearly associated with director relaxation.

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The equilibrium mechanical response of liquid crystalline elastomers can be soft or hard depending on the relation between the imposed strains and the nematic director. With such unusual equilibrium elasticity one might expect dynamical response to be equally nontrivial. If the elastic forces are small, then the return to equilibrium could be driven more weakly than in conventional systems. How does internal director rotation, and the corresponding softening of rubber-elastic response, determine the dynamic mechanical response of a nematic rubber to a small amplitude oscillatory shear?

Equilibrium elastic properties of monodomain nematic rubbers are well studied, both theoretically and experimentally. The small-deformation limit of elastic energy takes the form (cf. recent review [1])

$$\begin{aligned} F = {} & C_1(\boldsymbol{n}\cdot\tilde{\underline{\underline{\varepsilon}}}\cdot\boldsymbol{n})^2 + 2C_2\,\mathrm{Tr}[\underline{\underline{\varepsilon}}]\,(\boldsymbol{n}\cdot\tilde{\underline{\underline{\varepsilon}}}\cdot\boldsymbol{n}) + C_3(\mathrm{Tr}[\underline{\underline{\varepsilon}}])^2 \\ & + 2C_4[\boldsymbol{n}\times\tilde{\underline{\underline{\varepsilon}}}\times\boldsymbol{n}]^2 + 4C_5([\boldsymbol{n}\times\tilde{\underline{\underline{\varepsilon}}}\cdot\boldsymbol{n}])^2 \\ & + \tfrac{1}{2}D_1[\boldsymbol{n}\times(\boldsymbol{\Omega}-\boldsymbol{\omega})]^2 + D_2\boldsymbol{n}\cdot\tilde{\underline{\underline{\varepsilon}}}\cdot[\boldsymbol{n}\times(\boldsymbol{\Omega}-\boldsymbol{\omega})]. \end{aligned} \tag{1}$$

where $\boldsymbol{n}$ is the undistorted nematic director. $\tilde{\varepsilon}_{ik}$ is the traceless part of linear symmetric strain tensor, $\varepsilon_{ik} - \frac{1}{3}\mathrm{Tr}[\underline{\underline{\varepsilon}}]\delta_{ik}$ with $\varepsilon_{ik} = \frac{1}{2}(\partial_k \boldsymbol{u}_i + \partial_i \boldsymbol{u}_k)$, cf. [2]. In a system with an internal orientational degree of freedom $\boldsymbol{n}$, the antisymmetric part of the strain, expressed by the local rotation vector $\boldsymbol{\Omega} = \frac{1}{2}\,\mathrm{curl}\boldsymbol{u}$, also contributes to the physical properties when it deviates from the director rotation vector $\boldsymbol{\omega} = [\boldsymbol{n}\times\delta\boldsymbol{n}]$. It is this relative rotation [3] that causes a number of unique effects in nematic elastomers.

In a rubber or dense polymer melt, the bulk modulus C_3 is comparable to liquid values, $C_3 \sim 10^{10}$ Pa and is much larger than penalties for shear. We, therefore, shall consider only deformations with no bulk compression: $\mathrm{Tr}[\underline{\underline{\varepsilon}}] = 0$. In general, all other constants in the elastic energy density Eq. (1) are of the same order of magnitude, similar to the isotropic rubber modulus $\mu \simeq c_x k_B T \sim 10^5$ Pa, with c_x the effective crosslinking density. A molecular model of an ideal nematic elastomer, that is, with simplest Gaussian and nematic effects, cf. [1], gives specific values for these constants:

$$\begin{aligned} C_1 &= 2C_4 = c_x k_B T, & C_5 &= \tfrac{1}{8}c_x k_B T\,\frac{(r+1)^2}{r}, \\ D_1 &= c_x k_B T\,\frac{(r-1)^2}{r}, & D_2 &= c_x k_B T\,\frac{1-r^2}{r}, \end{aligned} \tag{2}$$

in which case the condition for ideal soft elasticity holds, $C_5^R = C_5 - \frac{1}{8}D_2^2/D_1 = 0$ [4]: shears governed by C_5 and with complete director relaxation cost no energy. The measure of renormalized shear modulus $C_5^R \neq 0$ is the characteristic parameter of semisoftness, or nonideality of nematic networks, essentially, the deviation from Eqs. (2). Model expressions for elastic constants depend, apart from the universal rubber-elastic energy scale μ, on a single parameter r. In an ideal nematic network $r = \ell_{\|}/\ell_{\perp}$, the ratio of principal step lengths of the anisotropic backbone [or $r = (R_{\|}/R_{\perp})^2$ for the principal gyration radii]. In more complex, nonideal elastomers this parameter may be less clearly defined. Nevertheless, it has to be a function of nematic order parameter $Q(T)$, satisfying a linear limit $r \approx 1 + \alpha Q$ at small Q. In the isotropic phase, at $Q = 0$ and $r = 1$, the elastic constants become, as expected: $C_1 = 2C_4 = 2C_5 = \mu$, $D_1 = D_2 = 0$ and the elastic energy (1) reduces to a classical Lamé expression.

In an incompressible material, all deformations are essentially shears. We shall examine two relevant simple shear geometries, ***D*** and ***V***, as shown in Fig. 1. These are the geometries that one achieves in a typical dynamic-mechanical experiment since in all known cases the director is confined to the sample plane. The geometry of uniaxial extension, more commonly found in studies of

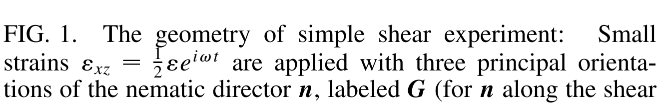

FIG. 1. The geometry of simple shear experiment: Small strains $\varepsilon_{xz} = \frac{1}{2}\varepsilon e^{i\omega t}$ are applied with three principal orientations of the nematic director $\boldsymbol{n}$, labeled ***G*** (for $\boldsymbol{n}$ along the shear gradient), ***D*** (displacement), and ***V*** (vorticity). The director changes by $|\delta\boldsymbol{n}| \approx \theta$.

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equilibrium stress-strain, is less appropriate for an oscillating regime because of possible slow relaxation [5] and incomplete sample recovery. The simple oscillating shear $\varepsilon(t)$, externally applied to the sample, is the single xz component of the full Cauchy strain, the same for each director orientation in Fig. 1. It also automatically satisfies the necessary incompressibility constraint.

The issue of possible director gradients and corresponding Frank elasticity in nematic elastomers has been discussed in the literature [1,6]. It is known that, unless there are special reasons for a director singularity (such as in disclinations or narrow domain walls), the Frank elastic effects play a minor role in the free energy balance and can be neglected. Perhaps this approximation needs to be reconsidered if a sheared sample is very thin in the z direction. However, in a practical situation with a sample thickness $d \sim 100\ \mu$m and more, ignoring the effect of nematic director gradients is a reasonable first approximation.

The elastic free energy density, Eq. (1), takes the form, in the cases $\boldsymbol{D}$ and $\boldsymbol{V}$ of Fig. 1:

$$\begin{aligned} F_D &= (C_5 + \tfrac{1}{8}[D_1 + 2D_2])\varepsilon^2 \\ &\quad - \tfrac{1}{2}(D_1 + D_2)\varepsilon\theta + \tfrac{1}{2}D_1\theta^2, \\ F_V &= C_4\varepsilon^2, \end{aligned} \tag{3}$$

where the small change in director orientation $\delta\mathbf{n}$ is taken equal to the angle θ. Clearly, one does not expect director rotation to occur in the "log-rolling" geometry $\boldsymbol{V}$.

Signs of unusual elastic response arise immediately. If the director is allowed to rotate, θ adopts its optimal value, minimizing F for a given deformation ε. Returning the resulting $\theta(\varepsilon)$ to Eqs. (3), the free energy at a given strain is also optimal:

$$\theta_D = \frac{D_1 + D_2}{2D_1}\,\varepsilon, \qquad F_D \to \left(C_5 - \frac{D_2^2}{8D_1}\right)\varepsilon^2. \tag{4}$$

Notice that if the nematic elastomer is ideal, then the free energy in the geometry $\boldsymbol{D}$ (and $\boldsymbol{G}$, for that matter) vanish ($C_5 - D_2^2/8D_1 = 0$) because the director can internally relax. Case $\boldsymbol{V}$ remains elastically hard. In fact, because of the chosen restricted strain geometry, the response of even ideal elastomers is actually quartic, rather than completely soft (true softness requires some unconstrained extension as well as shear [4]). Molecular models [1,7] yield the quartic penalty $F = \frac{1}{2}\mu\frac{r^2}{(r-1)^2}\varepsilon^4$, which we neglect in the present linear-response analysis.

The generalized force driving the director rotation $\theta(t)$ is a torque, $\partial F/\partial\theta$. In F one implicitly finds the shear $\varepsilon(t)$, with its externally imposed time variation, which of course is the ultimate driving agent. The flatness of the free energy $F(\varepsilon)$ will give the resulting dynamical response its particular character in the geometries where director rotation is possible [8].

Simplified single-viscosity model.—In order to study the dynamics of mechanical response, one needs to model viscoelastic properties, essentially, the viscous dissipation. This, added to the equilibrium elastic free energy, would allow a description of the relaxation. As in the continuum theory of liquid crystals, much progress can be made phenomenologically, using the symmetries of variables contributing to the physical effects. In a subsequent longer paper, we present such a symmetry-based version of linear dissipation function for nematic elastomers—it turns out that a full analogy with the Leslie-Ericksen formalism [9] can be established.

A downside of such a full description is the necessarily large number (five) of independent viscous coefficients that enter the model. In this Letter, we present a much simplified version of the viscoelastic model, which ignores the viscous anisotropy and considers only a single rotational viscosity dissipation. Although approximate, this simple model highlights the principal physical mechanism behind the effect of shear softening on the dynamic rubber moduli.

An elastic torque acting on nematic director $\boldsymbol{n}$ in the deformation geometries $\boldsymbol{G}$ and $\boldsymbol{D}$ is resisted by a linear viscous torque $\gamma(\partial\theta/\partial t)$ with γ an appropriate rotational viscosity. The dynamical equation describing the evolution of the director approaching its equilibrium is, then, a balance of torques $\gamma\dot{\theta} = -\partial F/\partial\theta$. From Eqs. (3) we have for the case $\boldsymbol{D}$:

$$\gamma\dot{\theta} = -D_1\theta + \tfrac{1}{2}(D_1 + D_2)\varepsilon(t). \tag{5}$$

This linear inhomogeneous differential equation is easily solved. After the relaxation of the transient $\theta \simeq \theta_0 e^{-(D_1/\gamma)t}$ associated with starting the strain oscillations, the steady-state response is given by the particular solution with $\varepsilon \sim e^{i\omega t}$:

$$\theta_D(t) = \frac{(D_1 + D_2)}{2\gamma}\int_{-\infty}^{t} e^{-(D_1/\gamma)[t-t']}\varepsilon(t')\,dt'. \tag{6}$$

The characteristic time for relaxation is $\tau = \gamma/D_1$. At frequencies much lower than the Rouse scale one can neglect specific polymer/rubber viscoelastic contributions and concentrate only on the (much slower) director relaxation modes. The linear-response stress function $\sigma = \partial F/\partial\varepsilon$ at a given frequency of imposed strain becomes

$$\begin{aligned} \sigma_D &= 2(C_5 + \tfrac{1}{8}[D_1 + 2D_2])\varepsilon(\omega) \\ &\quad - \tfrac{1}{2}(D_1 + D_2)\theta(\omega), \\ \sigma_V &= 2C_4\varepsilon(\omega). \end{aligned} \tag{7}$$

In the $\mathbf{D}$ geometry, where director rotation is possible, the dynamic modulus is modified by the internal director relaxation. Substituting the Fourier transform of Eq. (6) into (7), we obtain the stress in the form $\sigma(\omega) = G(\omega)\varepsilon(\omega)$, that is,

$$\sigma_D = \left(2C_5 + \tfrac{1}{4}[D_1 + 2D_2] - \frac{(D_1 + D_2)^2}{4(D_1 - i\gamma\omega)}\right)\varepsilon(\omega). \tag{8}$$

The corresponding storage and loss moduli are given by the real and imaginary parts of the effective complex modulus

$G(\omega)$ in Eq. (8), which have a characteristic single-relaxation time behavior:

$$G' = \frac{2(C_5 - D_2^2/8D_1) + (2C_5 + \frac{1}{4}[D_1 + 2D_2])\,(\omega\tau_o)^2}{1 + (\omega\tau)^2}\,,$$
$$G'' = -\frac{(D_1 + D_2)^2}{4D_1}\,\frac{\omega\tau}{1 + (\omega\tau)^2}\,. \tag{9}$$

Equations (5)–(9) ignore all classical aspects of polymer chain relaxation in rubbers and look only at the additional effect of coupling to the independently rotating director. The effective response modulus in the "log-rolling" geometry $\boldsymbol{V}$ is unchanged by director rotation $G_V(\omega) = 2C_4$. We shall assume the classical frequency dependence is the same in the D_i and C_i and, thus, that it is revealed by $G_V(\omega)$. Normalizing G'_D by G'_V would then isolate the dynamics associated with the director.

At zero frequency strain the storage moduli G'_0 is equal to $2C_5^R \equiv 2(C_5 - D_2^2/8D_1)$. In the isotropic phase (at $r = 1$) the ideal G' value would be $2C_5 = \mu = 2C_4$; cf. Fig. 2(a). The high-frequency response increases to $G' \to 2C_5 + \frac{1}{4}[D_1 + 2D_2]$. The D_2 term has a tendency to repel the director from the principal extension diagonal of shear, imposed in the geometry $\boldsymbol{D}$, the effect being reversed when one interchanges prolate and oblate backbone chain anisotropy ($r > 1$ and $r < 1$, the sign of D_2 reversing on this exchange). This explains the ± signs above being associated with D_2. The variation of r with temperature is the underlying origin of the change in elastic response. Theoretically, the nematic-isotropic transition must be weakly first order. Significant pretransitional effects and the influence of quenched disorder are expected, and one needs to determine r and the nematic order parameter $Q(T)$ experimentally. Figure 2(b) shows such a dependence in our elastomer.

Experimental measurements.—Full details of the sample preparation and experimental protocol will be given in a later paper, where we shall also illustrate the universality of the observed effect by studying a set of widely differing materials. Monodomain nematics of side-chain siloxane liquid crystalline elastomers with mesogenic vinyl-terminated benzoic methyl esters and divinyl alkyl quinone crosslinkers (5% density) were prepared following the procedure of Finkelmann *et al.* [10] of crosslinking under uniaxial aligning stress. The orientational order parameter $Q(T)$, measured by x-ray scattering, and the model parameter $r(T)$, independently measured from thermal expansion [11], are shown in Fig. 2(b). The glass transition and clearing transition temperatures were determined by DSC to be approximately 0 and 90 °C, respectively. Dynamic mechanical measurements were made on a TA Instruments DMTA at DERA, Farnborough, in single-shear mode. The sample dimensions were $7 \times 7 \times 0.4$ mm. The amplitude of the applied deformation was 10 μm, that is at a strain of 2.5% what we checked was well in the linear regime. Data were collected over the frequency range 0.1 to 100 Hz in displacement ($\boldsymbol{D}$) and vorticity ($\boldsymbol{V}$) geometries, using exactly the same sample placed in the shear field in different orientations.

Figure 3(a) presents the temperature dependence of the dynamic storage modulus when the director was oriented in the displacement and vorticity directions at frequencies of 0.5, 5, and 50 Hz. In the log-rolling, $\boldsymbol{V}$ case (solid lines, with data symbols suppressed), the modulus shows an expected simple fall with rising temperature, due the high-temperature tail of the glass transition, with no other features. In contrast, when the director is in the displacement $\boldsymbol{D}$ direction, there is a pronounced reduction in modulus relative to that in the vorticity direction. This behavior is in excellent agreement with the predictions of the model discussed above. The remarkable dip disappears at $T_{\rm ni}$, for all frequencies, when the moduli in the two geometries become nearly equivalent ($2C_4$ and $2C_5$, respectively). Taking the ratio, G'_D/G'_V for the two geometries, reduces the dependence on the underlying rubber dynamics (contained in μ) and focuses on the effects of director relaxation. Plotting this ratio for a range of frequencies, Fig. 3(b), we find a remarkable superposition of the critical

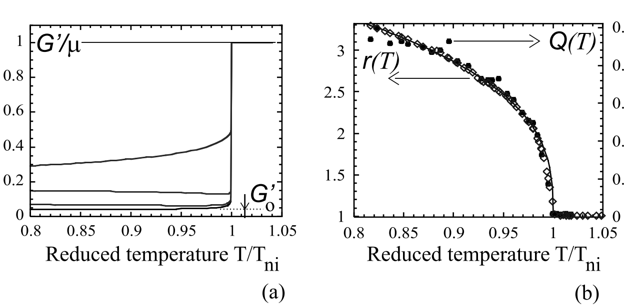

FIG. 2. (a) Theoretical plot of storage modulus, G'_D (in units of μ), for the given $Q(T)$ data and frequencies, $\omega\tau = 0.1$, 0.5, 2, and 20 (increasing curves). The modulus approaches the semisoft constant G'_0 at zero frequency. (b) Experimentally measured effective anisotropy, $r(T)$ (diamonds), and nematic order parameter, $Q(T)$ (bullets). The behavior near $T_{\rm ni}$ closely follows the relation $r = 1 + 4.5Q$.

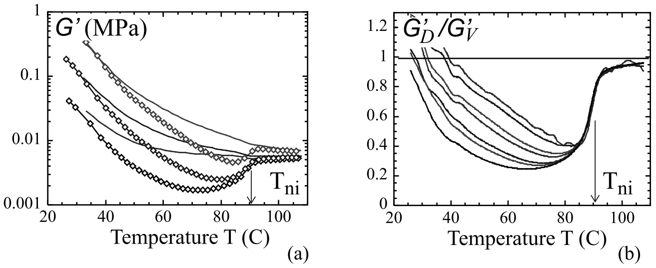

FIG. 3. (a) Temperature variation of storage modulus G'_D, at frequencies of 0.5, 5, and 50 Hz (increasing pairs of curves). Each pair of curves shows the data for $\boldsymbol{D}$ geometry by symbols and the corresponding $\boldsymbol{V}$ data by solid lines. (b) The ratio of moduli in the two geometries at various frequencies, 0.1, 0.5, 1, 5, 10, 50, and 100 Hz (increasing curves, shown by solid lines with data symbols suppressed for clarity). The ratio approaches unity in the isotropic phase, but shows a pronounced universal drop in the critical region below $T_{\rm ni}$.

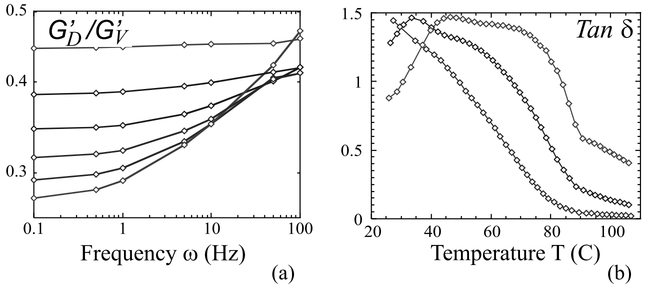

FIG. 4. (a) Frequency variation of storage moduli ratio, taken at different temperatures below T_{ni}: 76, 78, 80, 82, 84, and 86 °C (increasing curves). (b) The phase angle (loss factor) $\tan\delta$, at several frequencies: 0.5, 5, and 50 Hz (increasing curves), showing the dramatic increase in mechanical loss in the whole range of the nematic phase.

behavior near T_{ni} (the remaining rise at lower temperatures is due to the incomplete cancellation of glass-transition effects).

Figure 4(a) presents the frequency dependence of the storage moduli ratio G'_D/G'_V. The main change in the reduced modulus occurs over the region 10–50 Hz. The characteristic frequency ω_0, theoretically calculated as $1/\tau = D_1/\gamma$, could be a function of temperature through its dependence on nematic order parameter. This dependence for the coupling constant D_1 is explicit in the molecular model, but also on symmetry grounds the proportionality $D_1 \propto Q^2$ is expected. Usually the rotational viscosity γ is also $\propto Q^2$ [9,12]. Without extending the frequency range to significantly higher values, we could not unambiguously discern the temperature dependence from Fig. 4(a); we can conclude only that the characteristic frequency ω_0 remains constant or increases with temperature increasing towards T_{ni}.

We can now estimate the characteristic values. Because of the uncertainty arising from only a limited experimentally accessible frequency range and the tail of the glass transition, we view the value of $\omega_0 \sim 10$ Hz, used here as only an estimate. Far from the nematic-isotropic transition temperature T_{ni} we can take $r \sim 3$, Fig. 2(b). The coupling constant D_1 is, then, $\approx 4\mu \sim 20$ kPa, Fig. 3(a). Everything depends on the rotational viscous coefficient γ, which takes different values in different environments: small molecules, polymers, and elastomers. Taking a typical value in ordinary nematic liquid crystals $\gamma \sim 0.1$ Pa · s [9], we would obtain a rather short time scale $\tau \sim 10^{-6}$ s. The rotational viscosity of the *same* side-chain nematic polymer was measured in [13], confirming that the director mobility is altered by long polymer backbones, reaching $\gamma \sim 10$ Pa · s at low temperatures. Our result for characteristic frequency ω_0 means that the effective viscosity for the crosslinked elastomer has to be much higher, $\gamma \geq 10^3$ Pa · s. Such a dramatic increase is evidence of the further retarding effect of cross linking chains into the rubbery network.

In Fig. 4(b) one also finds the temperature dependence of the loss factor, the phase angle $\tan\delta = G''/G'$ at frequencies of 0.5, 5, and 50 Hz. It is clear from this plot that the values of $\tan\delta$ are extremely large over an extensive temperature window between the glass transition and the nematic clearing temperature. This highlights the large mechanical loss that arises from the internal director rotation. Since this very high mechanical loss is pronounced at all frequencies and is a sensitive function of temperature, one envisages great potential in acoustic and damping applications of nematic elastomers. We note that earlier studies of polydomain [14] and monodomain [15] elastomers found no nematic effects and instead concentrated on smectic phases.

To summarize, we have predicted a qualitatively new dynamic mechanical softening of nematic elastomers, which is due to the internal director relaxation. We studied the effect experimentally and confirmed the predicted universal decrease in the storage modulus. The mechanical relaxation of nematic elastomers is dramatically different from that in ordinary polymers and rubbers.

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