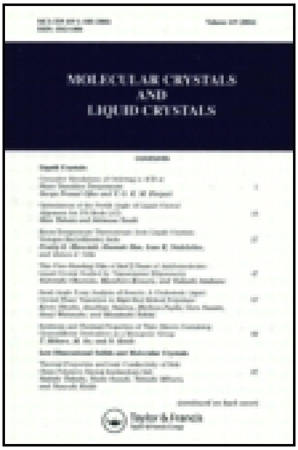

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Reorientation Dynamics of a Nematic Elastomer

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The relaxation back to the zero-field state of a nematic elastomer that has undergone a Frederiks transition, is investigated by a combination of the "neo-classical" theory of liquid crystal rubber elasticity and the simplest time evolution equations for a system described by two coupled, non-conserved order parameters (director and strain). Results are compatible with the recent experimental findings of Chang, Chien and Meyer *[Phys. Rev. E*, **56**, 595 (1997)]. In addition, it is predicted that the absence of a "semi-soft" elastic threshold changes the long-time decay of the effective refractive index of the medium from exponential to inverse power law.

Keywords: nematic rubbers; Frederiks transition: dynamics

INTRODUCTION

A liquid crystalline elastomer is a crosslinked polymer liquid crystal. It is also known as a solid liquid crystal or an anisotropic rubber. Because of the coupling between the nematic director and the polymer matrix, these materials exhibit a plethora of exotic phenomena: macroscopic sample shape changes on going from the isotropic to the nematic phase[1]; memory effects[2]; stress-induced molecular switching[3]; and strain-induced discontinuous director rotation[4], sometimes proceeding via an intermediate, non-uniform, 'stripe-domain' state[6]. For a review see Warner and Terentjev[7] and references therein.

One of the most important properties of liquid crystals (LCs), and the main reason why they are such popular components of display devices, is their ready orientability by external fields. In a typical elastomer, by contrast, the strong anchoring of the director to the polymer matrix as expressed by the elastic energy density $\mu = n_x k_B T \sim 10^5$ J/m^3, where n_x is the number of strands per unit volume, seems to imply that (unphysically large) electrical fields of strength $\sim 10^7 - 10^8$ V/m are required in order to effect director rotation. That is, in an elastomer it is easy to rotate the director by applying a strain, but much harder to induce a deformation by rotating the director.

However, very recently Meyer and co-workers succeeded in field-aligning a confined nematic elastomer gel (a homogeneous mixture of LC and very tenuous, i.e., weakly crosslinked, polymer)[8]. There are two important differences between this and the Frederiks transition in ordinary nematics: firstly, it is characterised by a threshold *field*, rather than voltage; secondly, relaxation on switching off the field can be non-exponential. They interpreted their results by assuming that the anisotropic polymer matrix is uniformly distributed throughout the LC, thereby producing a mean orienting effect equivalent to an effective internal field applied along the director. The scale of spatial variation of this internal field is then the required additional length. Subsequently, Terentjev and Warner have noted[9] that the existence of a threshold field can be explained very naturally in the context of the neo-classical theory of elastomers[7], as a consequence of the fact that, in a nematic elastomer, the director is anchored in *bulk* to the elastic network. It is therefore tempting to model relaxation from an externally-imposed orientation using the same formalism. This is what is attempted here. It will be seen that the dynamics of elastomers differs from that of conventional nematics in ways that should be amenable to experimental verification.

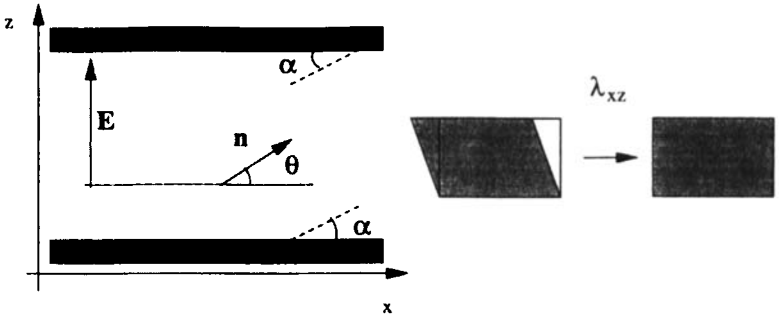

FIGURE 1: Experimental geometry considered: At $t = 0$, the nematic director **n** makes an angle θ_0 with the x-axis. On switching off the field **n**, parametrised by θ, relaxes towards the pretilt α induced by the bounding plates. The only allowed strain is λ_{xz}, which relaxes to zero.

THEORY

The Free Energy

Let us consider the standard 'splay' geometry for the Frederiks transition: a macroscopically uniform sample of nematic elastomer is sandwiched between two aligning plates inducing a (typically small) pretilt α. Further assume that, when an electric field is applied perpendicular to the plane of the cell, the director **n** rotates in the xz-plane and is parametrised by the angle θ that it makes with the x-axis, which is a function of the coordinate z only (see figure 1). It is also useful to define the angle by which reorientation occurs, $\omega = \theta - \alpha$. A form of the strain tensor that satisfies the requirements of mechanical compatibility and incompressibility[9], for fixed layer thickness, is:

$$\lambda = \begin{pmatrix} 1 & 0 & \lambda_{xz} \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \qquad (1)$$

i.e., we only allow simple shears parallel to the plates. In this paper we shall only consider spatially homogeneous strains and tilts, for which the neo-classical free energy density (FED) of a semi-soft nematic rubber is[7, 9],

$$f = \frac{1}{2}\mu \mathrm{Tr}\left[\ell_0 \lambda^T \ell^{-1} \lambda\right] + \frac{1}{2}\mu A \left[\sin(\theta - \alpha) - \lambda_{xz} \cos\theta \cos\alpha\right]^2, \qquad (2)$$

where ℓ is the persistence length tensor describing the chain shape (the subscript 0 referring to the state prior to the deformation), and A is the semi-soft parameter. In its principal axes frame, ℓ can be written as:

$$\ell = \begin{pmatrix} \ell_{\parallel} & 0 & 0 \\ 0 & \ell_{\perp} & 0 \\ 0 & 0 & \ell_{\perp} \end{pmatrix} = \ell_{\perp} \begin{pmatrix} r & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \qquad (3)$$

where $r = \ell_{\parallel}/\ell_{\perp}$ is the chain anisotropy (ratio of principal chain step lengths). If the director $\mathbf{n}$ is rotated by Ω in the xz-plane, then $\ell(\Omega) = R^T(\Omega)\ell R(\Omega)$, $R(\Omega)$ being the appropriate rotation matrix. Finally, the semi-soft elasticity coefficient A subsumes all the (microscopic) sources of inhomogeneity (fluctuations in the composition, or the length, of strands between crosslinks, impurities, ...) that act as barriers to rotation[6]. When $A = 0$ (soft elasticity), there exist deformations which cost no energy; typically, $A \ll 1$. Since we are only concerned with relaxation upon removal of the external field, the same does not appear in the FED; instead it just creates the initial conditions for θ and λ_{xz}.

Using eqs. (2) and (3), the reduced FED becomes

$$\begin{aligned} \frac{2f}{\mu} &= 3 + \frac{(r-1)^2}{r}\sin^2(\theta - \alpha) \\ &+ \frac{r-1}{r}\lambda_{xz}\sin(\theta-\alpha)\left[(r+1)\cos(\theta+\alpha) - (r-1)\cos(\theta-\alpha)\right] \\ &+ \frac{\lambda_{xz}^2}{r}\left[1 + (r-1)\sin^2\alpha\right]\left[1 + (r-1)\sin^2\theta\right] \\ &+ A\left[\sin(\theta-\alpha) - \lambda_{xz}\cos\theta\,\cos\alpha\right]^2. \end{aligned} \qquad (4)$$

The Evolution Equations

The simplest possible dynamical *Ansatz* is to equate the rate of change of the relevant variables (two non-conserved order parameters) to the gradient of the FED:

$$\frac{\partial\theta}{\partial t} = -\Gamma_\theta \frac{\partial(2f/\mu)}{\partial\theta}, \qquad (5)$$

$$\frac{\partial\lambda_{xz}}{\partial t} = -\Gamma_\lambda \frac{\partial(2f/\mu)}{\partial\lambda_{xz}}, \qquad (6)$$

where Γ_θ, Γ_λ are, respectively, the director and strain 'mobilities': $\Gamma_\theta = \mu/(2\gamma_1)$, with γ_1 the LC viscosity. The model is purely dissipative, i.e., it does not include any coupling to hydrodynamic variables (only sound waves, as the elastomer is a solid). Still, this is not a drastic simplification: the speed of sound in an elastomer being of the order of m/s, any sound waves will traverse a typical experimental sample (a few centimeters in size) in $\sim 10^{-2}$ s, much less than the duration of a reorientation experiment ($\sim 10^{2}$[8]). Moreover, we are neglecting solvent diffusion and related effects.

RESULTS AND DISCUSSION

Equations (5) and (6) are non-linear ordinary differential equations, and can only be solved numerically. However, it is instructive to study their asymptotic behaviour, when $\theta \sim \alpha$ and $\lambda_{xz} \sim 0$. In this regime they can be linearised:

$$\frac{d}{dt}\begin{pmatrix} \omega \\ \lambda_{xz} \end{pmatrix} = -\underline{\underline{M}} \cdot \begin{pmatrix} \omega \\ \lambda_{xz} \end{pmatrix}, \qquad (7)$$

where $\underline{\underline{M}}$ is the matrix of first derivatives of the right-hand sides of equations (5) and (6) with respect to θ and λ_{xz}, evaluated at $\theta = \alpha$, $\lambda_{xz} = 0$. It is straightforwardly obtained but rather cumbersome, so we do not present it here. *If* α (pretilt) *and* A (semi-softness) *do not vanish simultaneously*, then $\underline{\underline{M}}$ can be diagonalised, yielding

$$\omega(t) = A_\theta e^{-\nu_1 t} + B_\theta e^{-\nu_2 t}, \qquad (8)$$

$$\lambda_{xz}(t) = A_\lambda e^{-\nu_1 t} + B_\lambda e^{-\nu_2 t}, \qquad (9)$$

where ν_i are the eigenvalues of $\underline{\underline{M}}$, and A_θ, B_θ, A_λ, B_λ are constants

Γ_θ	ν_1	ν_2
1.0	2.0125	0.0379671
10.0	6.12382	0.159025
0.1	1.63217	0.00586099

TABLE I: Eigenvalues of $\underline{\underline{M}}$ for $r = 1.44$, $A = 0.1$, $\alpha = 3°$, $\Gamma_\lambda = 1$.

determined by the initial conditions. In all cases investigated one of the eigenvalues is much smaller than the other (see Table I), therefore the long-time behaviour is essentially purely exponential and governed by the smaller eigenvalue.

If, on the other hand, $\alpha = A = 0$, then $\underline{\underline{M}}$ is singular (i.e., at least one eigenvalue vanishes), hence the behaviour of $\omega(t)$ and $\lambda_{xz}(t)$ is determined by terms beyond linear order, which implies power-law, rather than exponential, decay. It is nevertheless possible to extract some analytical results in the limit where the strain is a much faster variable than the director, i.e., for $\Gamma_\lambda/\Gamma_\theta \gg 1$. Minimisation of f^* with respect to λ_{xz} and substitution of the resulting $\lambda^*_{xz} = \lambda^*_{xz}(\theta)$ yields, after expansion to $\mathcal{O}(\theta^4)$,

$$\frac{1}{\mu} f^*_{asymp}(\theta) = \frac{3}{2} + \frac{1}{2}(r-1)^2\theta^4 + \mathcal{O}(\theta^6), \tag{10}$$

wherewith equation (5) is readily integrated to give

$$\theta(t) = \left[8(r-1)^2\Gamma_\theta t + \theta_0^{-2}\right]^{-1/2} \overset{(t\to\infty)}{\sim} t^{-1/2}, \tag{11}$$

with $\theta_0 \equiv \theta(t = 0)$. As might intuitively be expected, a *semi-soft* medium relaxes exponentially, while a planar-aligned *soft* medium exhibits slower, algebraic (power-law) relaxation. Notice that a non-zero tilt ($\alpha \neq 0$) has the same effect as $A \neq 0$, i.e., the elastomer behaves as semi-soft. We thus expect most elastomers to be 'semi-soft' in practice, although very slow decays are possible if $A \ll 1$ and $\alpha \sim 0$.

Experimentally, one measures by conoscopy the intensity of light transmitted through the cell, which is a function of the difference in optical path

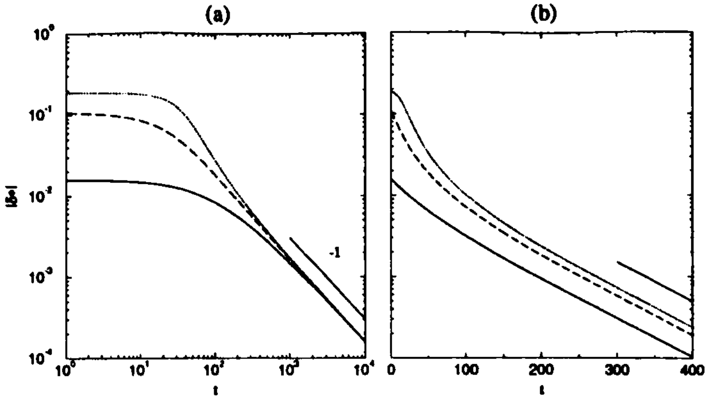

FIGURE 2: Reduced optical path difference δ^* *vs* time in (a) a soft elastomer ($A = 0$) and (b) a semi-soft elastomer, with fast strain ($\Gamma_\theta/\Gamma_\lambda = 0.1$) and no pretilt ($\alpha = 0$). $r = 1.44$ and $\theta_0 = 15°$ (solid lines), 45° (dashed), and 75°(dotted). (a) is a double logarithmic plot and (b) a linear-logarithmic plot; the short straight lines on the right of each graph give the predicted asymptotic slopes.

δ for ordinarily and extraordinarily polarised rays. For normal light incidence,

$$\delta = \frac{1}{\lambda}\int_0^d [n_{eff}(\alpha) - n_{eff}(\theta)]\, dz \sim \frac{1}{\lambda}\int_0^d \omega(z)^2\, dz, \tag{12}$$

where λ is the wavelength of light, d is the cell thickness, and $n_{eff}(\Theta)$ the effective refractive index ($\Theta = \alpha$ or θ). Figure 2 shows the behaviour of $\delta^* = \lambda\delta/d$ for soft and semi-soft elastomers, respectively, as obtained from the numerical solution of equations (5) and (6), as well as the asymptotic limits found analytically using equations (8) and (11) (time is in units of Γ_λ^{-1}). By contrast, for an ordinary nematic characterised by a single elastic constant K, $\omega(z)$ is a solution of the diffusion equation

$$\gamma_1 \frac{\partial \omega}{\partial t} = K \frac{\partial^2 \omega}{\partial z^2}, \tag{13}$$

whence

$$\delta \sim \exp\left(-\frac{2\pi^2 K}{\gamma_1 d^2} t\right), \tag{14}$$

i.e., it is always exponential, whereas the same is true of a semi-soft elastomer only at long times. However, the present theory is compatible with a decay experimentally indistinguishable from the pure exponential suggested by Meyer *et al.*'s results[8] if we use their values for γ_1 and K, and in addition make the reasonable choices $\mu \sim 10^3 - 10^4$ J/m^3, $A \sim 8 \times 10^{-2} - 8 \times 10^{-3}$, for which the crossover time into the exponential regime is $t_\times \sim 4$ seconds and the time constant $\tau \sim 50$ seconds.

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References

[1] J. Schätzle, W. Kaufhold and H. Finkelmann. *Makromol. Chem.*, **190**, 3269 (1989); G. R. Mitchell, M. Coulter, F.J. Davis and W. Guo, *J. Phys. II (Paris)*, **2**, 1121 (1992).
[2] C.H. Legge, F.J. Davis and G.R. Mitchell, *J. Phys. II (Paris)*, **1**, 1253 (1991).
[3] F.J. Davis and G.R. Mitchell, *Polymer Commun.*, **28**, 8 (1987).
[4] P. Bladon, E.M. Terentjev and M. Warner, *Phys. Rev. E*, **47**, R3838 (1993): *J. Phys. II (Paris)*, **4**, 75 (1994).
[5] G.R. Mitchell, F. J. Davis and W. Guo, *Phys. Rev. Lett.*, **71**, 2947 (1993): P. M. S. Roberts, G.R. Mitchell and F.J. Davis, *J. Phys. II (Paris)* **7**, 1337 (1997).
[6] I. Kundler and H. Finkelmann, *Makromol. Chem. Rapid Commun.*, **16**, 679 (1995): G. C. Verwey, M. Warner and H. Terentjev, *J. Phys. II (Paris)*, **6**, 1273 (1996): H. Finkelmann, I. Kundler, E.M. Terentjev and M. Warner, *J. Phys. II (Paris)*, **7**, 1059 (1997).
[7] M. Warner and E.M. Terentjev, *Prog. Polym. Sci.*, **21**, 853 (1996).
[8] C.-C. Chang, L.-C. Chien and R.B. Meyer, *Phys. Rev. E*, **56**, 595 (1997).
[9] E.M. Terentjev and M. Warner (unpublished).