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Analysis of Experiments on Nematic Elastomers

G. C. Verwey and M. Warner*

Cavendish Laboratory, University of Cambridge, Madingley Road,
Cambridge CB3 0HE, England

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ABSTRACT: Nematic elastomers display the elasticity of conventional solids, liquid crystals, and entirely new effects due to the influence of strain in altering the ordering direction. We point out the most direct ways in which experiment can confront the molecular theories of temperature-induced shape changes and instabilities in the nematic director induced by large elastic strains. Experiments on nematic monodomain elastomers are examined critically, and suggestions for future experiments are made.

I. Introduction

In this paper we discuss how the unusual phenomena displayed by nematic elastomers can be critically evaluated and used to confront theoretical models. It turns out that there are models with no parameters in them, complicated predictions depending only on one, measured, quantity with correlations existing between various observable effects. We analyze in turn the situations most directly encountered: spontaneous deformations, strains imposed at temperatures lower than that of formation, and new nematic transitions in response to applied strains.

Liquid crystal polymers differ from their simple rod counterparts in that orientational order leads to a molecular shape change. Depending on the molecular coupling, this can be an elongation or flattening of the chain backbone. Conventional elastomers (composed of isotropic chains) derive their rigidity from the resistance of the component chains to imposed shape change. It is thus understandable that the behavior of nematic elastomers depends critically on the intrinsic anisotropy of their constituent chains. The fundamental measure of this anisotropy is $l_\parallel/l_\perp$, the ratio of the step lengths parallel and perpendicular to the director (the ordering direction). These step lengths reflect the mean-square chain dimensions respectively parallel and perpendicular to the director:

$$\langle R_\parallel^{\,2}\rangle = \frac{1}{3}l_\parallel L \tag{1}$$

$$\langle R_\perp^{\,2}\rangle = \frac{1}{3}l_\perp L \tag{2}$$

where L is the total arc length of the chain. These dimensions can be measured by scattering neutrons from labeled chains.

A practical complication is often that the elastomers may have been formed at a very different temperature from the current conditions and hence at formation had a different anisotropy ratio $l_\parallel/l_\perp$ from its current value. In this paper we analyze the connections between (i) observable chain anisotropy, (ii) spontaneous macroscopic strains on entering the isotropic state or on cooling to a state of higher nematic order, and (iii) the critical strains imposed in order to induce rotational transitions in the nematic director of the elastomer.

A further complication is that, without preparation prior to cross-linking, nematic elastomers will be polydomain. Neighboring domains undoubtedly interact elastically as they are strained. The underlying structure of nematic rubber elasticity is complex enough without this added ingredient. We limit our proposal for analysis to monodomain samples prepared by magnetic fields imposed prior to cross-linking. In an accompanying paper, we discuss multistep cross-linking schemes.

II. Analysis of Experiments

Since order parameter changes are large and since rubber elastic effects involve large strains, continuum models are inadequate. We must therefore compare with molecular theories. All those available[1,2] are essentially simple generalizations of ordinary Gaussian theory for conventional elastomers. The free energy per network strand becomes

$$F = \frac{1}{2}k_\mathrm{B}T\left(\lambda^2\frac{l_\parallel^{\,0}}{l_\parallel} + \frac{2}{\lambda}\frac{l_\perp^{\,0}}{l_\perp} + \ln\left(\frac{\det \mathbf{l}}{\det \mathbf{l}^0}\right)\right) \tag{3}$$

where superscript zero denotes the formation conditions and λ is the elongation (>1) or contraction (<1) factor along the ordering direction (there is a shrinkage/extension $1/\sqrt{\lambda}$ in the perpendicular directions so that volume is unchanged).

Spontaneous Shape Change. The natural shape change is always that minimizing the free energy (eq 3):

$$\lambda_\mathrm{m}^{\;3} = \frac{l_\parallel}{l_\perp}\frac{l_\perp^{\,0}}{l_\parallel^{\,0}} \tag{4}$$

An example is formation in the nematic state followed by heating to the isotropic state ($l_\parallel = l_\perp = l$, say), whence one predicts:

$$\lambda_\mathrm{iso} = (l_\perp^{\,0}/l_\parallel^{\,0})^{1/3} \tag{5}$$

a contraction. On cooling back to the original state, there must be the reverse change of $1/\lambda_\mathrm{iso} = (l_\parallel^{\,0}/l_\perp^{\,0})^{1/3}$, an elongation, λ_m say. Guo *et al.*[3] observe an elongation of $\lambda_\mathrm{m} = 1.05$ on cooling from the isotropic state just above the transition back to cross-linking conditions, $T_\mathrm{ni}^{\,+} = 393\ \mathrm{K} \rightarrow T_\mathrm{xl} = 391\ \mathrm{K}$. This shape change was reversible and persists even when samples are maintained for a prolonged period in the isotropic state.

Connection with SANS Experiments. Mitchell *et al.*[4] measured the chain anisotropy for the same system as above and found

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$$R_\parallel{}^0/R_\perp{}^0 \equiv (l_\parallel{}^0/l_\perp{}^0)^{1/2} = 1.1 \qquad (6)$$

Microscopic theory predicts from this the spontaneous distortion

$$\lambda_\mathrm{m} = (l_\parallel{}^0/l_\perp{}^0)^{1/3} \equiv (R_\perp{}^0/R_\perp{}^0)^{2/3} = 1.06 \qquad (7)$$

agreeing well with the mechanical measurement $\lambda_\mathrm{m}{}^\mathrm{obs} = 1.05$ of ref 3.

Experiments Conducted at Temperatures Lower Than Formation. One can cross-link at $T_\mathrm{xl} \sim T_\mathrm{ni}$ (as has just been described) and then cool down to lower temperatures to conduct experiments, for instance,[5] $T = T_\mathrm{xl} = 391\ \mathrm{K} \rightarrow T_\mathrm{expt} = 323\ \mathrm{K}$ (with $T_\mathrm{g} = 303$ K). There will be a further spontaneous shape change, λ_m, given by eq 4, where this time $l_\parallel$ and $l_\perp$ refer to a more anisotropic state rather than to the isotropic state of the first example given. Experiments are then carried out by imposing (or measuring) coaxial strains λ relative to this new state:

$$\lambda' = \lambda\lambda_\mathrm{m} \qquad (8)$$

where λ' is the total strain relative to the original state. Inserting λ' into F (eq 3), one obtains:

$$2F/k_\mathrm{B}T = \left(\frac{l_\perp^0 l_\perp^{0\,2}}{l_\parallel l_\perp{}^2}\right)^{1/3}\left[\lambda^2 + \frac{2}{\lambda}\right] + \ln(...) \qquad (9)$$

which corresponds to a shift $(...)^{1/3}$ in the energy scale. Otherwise, eq 9 resembles the free energy of a conventional elastomer. It is as if the elastomer is *apparently* formed at the current condition, so long as one uses strains based on the current relaxed state, rather than the original state.

New Transitions in Nematic Elastomers. An interesting experiment to perform on an elastomer in its nematic state (either at its formation temperature or another) is to apply strains with principal axes not coincident with the nematic order. The director can then respond by rotating. One is then probing a solid with mobile anisotropy.

The generalization of eq 9 to where strains are not imposed purely along the director is

$$2F/k_\mathrm{B}T = \mathrm{Tr}\{\mathbf{l}\cdot\boldsymbol{\lambda}^\mathrm{T}\cdot\mathbf{l}'^{-1}\boldsymbol{\lambda}\} + \ln(...) \qquad (10)$$

where the scale $(...)^{1/3}$ has, for simplicity, been suppressed and λ is measured with respect to the relaxed state at this temperature, with $l_\parallel$ and $l_\perp$ currently the diagonal elements of the shape tensor $\mathbf{l}$ before any imposed λ. The shape tensor $\mathbf{l}'$ characterizes the chain anisotropy (including its direction) after the imposition of λ.

At low temperatures where nematic order is strong and presumably little perturbed in *magnitude* by elastic effects, the order after imposing λ is as before, but with the director now rotated by θ. Correspondingly the current shape tensor is the original one rotated by θ to a new principal frame: $\mathbf{l}' = \hat{\mathbf{R}}_\theta{}^\mathrm{T}\mathbf{l}\hat{\mathbf{R}}_\theta$. A concrete example is that of imposed extension by a factor of λ along x with the initial director along z (here the principal axes of distortion and nematic order are aligned, but their largest eigenvalues correspond to different directions). A full analysis[6,7] of eq 10 shows that the director remains along z until a critical strain λ_c is reached, $\lambda_\mathrm{c} = (l_\parallel/l_\perp)^{1/3}$, whereupon it rotates discontinuously by $\theta = \pi/2$ about y to be along x. This λ prediction locating the instability is in terms of the extension relative to the current relaxed state and relates to the anisotropy $l_\parallel/l_\perp$ of this state. One can either measure the anisotropy using scattering or rely on a further consequence of the model, namely, that the spontaneous change in shape between the isotropic and current state is $(l_\parallel/l_\perp)^{1/3}$. Thus the λ imposed along x to induce the instability is predicted to be numerically equal to the spontaneous z distortion associated with the transition from the isotropic state to the current state, that is, $\lambda_\mathrm{c} = \lambda_\mathrm{m}$.

Comparison with existing experiment is unfortunately not straightforward. The preliminary experiment of Mitchell et al.[5] yields a rotational instability, the director jumping from z to x at $\lambda_\mathrm{c} = 1.13$, again in the elastomers cited above, but now at $T = 323$ K, about 70 K below the transition and cross-linking temperatures. The spontaneous distortion in going from the isotropic state to this was not reported. Earlier SANS scattering determinations of $(R_\parallel/R_\perp)^2 \equiv l_\parallel/l_\perp = 1.29$ relate to higher temperatures (~393 K) where the anisotropy is much less and cannot be compared with the lower temperature strain experiments. A value of 1.29 would give $\lambda_\mathrm{c} = 1.09$, certainly a lower bound than the actual λ_c value. Ideally in future experiments one should compare the measured λ_m and $(R_\parallel/R_\perp)^2$ to the instability strain λ_c observed at the same conditions.

Further complexity is available to experiment. Strains imposed at angles other than $\pi/2$ to the original director will lead to a gradual rotation followed at a λ_c, now less than λ_m, by an instability of the director. Examples are given in ref 7. In fact the curves of Mitchell *et al.*[5] qualitatively resemble those predicted for angles close to, but distinctly less than, $\pi/2$, a possibility noted by these authors.

We have discussed the instability of the z state at λ_c. Actually at a lower λ imposed along x we find the z and x states have equal energy. In rotating $\mathbf{l}$ from z to x to give $\mathbf{l}'$, we have in eq 10

$$\mathbf{l}' = \begin{pmatrix} l_\parallel & 0 \\ 0 & l_\perp \end{pmatrix} \rightarrow \begin{pmatrix} l_\perp & 0 \\ 0 & l_\parallel \end{pmatrix} \qquad (11)$$

(the y entries being unchanged and hence suppressed), and hence the free energies of the two states (on substitution in eq 10) are equal for

$$\lambda_\mathrm{thermo} = \lambda_\mathrm{m}\left[\frac{2}{1 + \lambda_\mathrm{m}{}^{3/2}}\right]^{1/3} \qquad (12)$$

thus locating the thermodynamic transition. The fact that this is less than the point λ_c where the state becomes unstable indicates that there is a region of hysteresis, the thermodynamic transition being roughly in between the bounds of stability. It can easily be shown[7] that (for strains applied at $\pi/2$) this interval is $(\sqrt{\lambda_\mathrm{m}}, \lambda_\mathrm{m})$. Mitchell *et al.*[5] allude to hysteresis, and further investigation would be revealing.

The above analysis assumes nematic order is merely rotated by imposition of noncoaxial strain; that is, $\mathbf{l}'$ is merely rotated from $\mathbf{l}$ at constant anisotropy. At higher temperatures, $T \sim T_\mathrm{ni}$, the nematic order is not rigid and may reduce in response to λ. Complex possibilities arise, and a range of predictions are made.[8] In reality the experiments of Mitchell *et al.*[5] most likely involve a reduction of the order parameter as well as a rotation and they should really be analyzed with this in mind.

For various imposed strains eq 10 yields no rise in the free energy at all, that is, deformation without imposed stress. This remarkable apparent liquefaction of a solid is another consequence of the mobile internal degree of freedom. Concrete examples are given in an accompanying paper.

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References and Notes

(1) Abramchuk, S. S.; Khokhlov, A. R. *Dokl. Akad. Nauk SSSR* **1988**, *297*, 385. [Translation: *Dokl., Phys. Chem.* **1988**.]

(2) Warner, M.; Gelling, K. P.; Vilgis, T. A. *J. Chem. Phys.* **1988**, *88*, 4008.

(3) Guo, W.; Davis, F. J.; Mitchell, G. R. *Phys. Lett. E*, to be published.

(4) Mitchell, G. R.; Davis, F. J.; Guo, W.; Cywinski, R. *Polymer* **1991**, *32*, 1347.

(5) Mitchell, G. R.; Davis, F. J.; Guo, W. *Phys. Rev. Lett.* **1993**, *71*, 2947.

(6) Bladon, P.; Terentjev, E. M.; Warner, M. *Phys. Rev. E (Rapid Commun.)* **1993**, *47*, 3838.

(7) Bladon, P.; Terentjev, E. M.; Warner, M. *J. Phys. II (Fr.)* **1994**, *4*, 75.

(8) Bladon, P.; Terentjev, E. M.; Warner, M. *Macromolecules* **1994**, *27*, 7067.

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