Macromolecules **1997,** *30,* 4189−4195

Compositional Fluctuations and Semisoftness in Nematic Elastomers

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Received December 9, 1996; Revised Manuscript Received April 14, 1997⊗

ABSTRACT: Compositional fluctuations in the strands of a nematic network lead to variations in intrinsic anisotropy. We show that these fluctuations can have a large effect if the chains are persistent. We calculate the threshold to the semisoft striped state. This can be large (and the semisoft moduli large) even if the chain anisotropies are small. Softness is violated if the fluctuating chains are cross-linked in the nematic state. A case where smectogenic elements are incorporated into the network is given. The Landau free energy is derived and shown to have linear terms of semisoft systems. The nonstriped nematic elastomer instability experiments are re-examined in the light of our theoretical results.

I. Introduction

Ideal Gaussian nematic elastomers can deform at constant free energy; that is, no stress is required for certain shape changes.[1−3] This remarkable mechanical property, more characteristic of a liquid than a solid, has been termed soft elasticity. It can be shown to arise because the anisotropic distribution of nematic chain shapes in a network can be rotated without changing form and hence free energy, in response to a mechanical deformation. It is also predicted[4] that the threshold to a striped state found by Kundler and Finkelmann[5] should ideally occur at an extension $\lambda_1 = 1$, that is, immediately on the imposition of strain.

In practice, deformations are only semisoft. Where soft response would be expected, a small modulus is indeed observed,[6] much less than in the conventional regime for the same sample, but still significant. Electric fields should have no discernible mechanical effect on conventional elastomers because of the difference in energy scales set by elasticity ($\sim\mu$ the shear modulus) and fields E ($\sim{}^1/_2(\Delta\epsilon)\epsilon_0 E^2$ with $\Delta\epsilon$ the dielectric anisotropy). By contrast there should theoretically be a large soft response to electric fields.[7] Experimentally small but significant fields are required[8−10] to obtain a response that is thus evidently only semisoft.

In an accompanying paper[11] we calculated the effect on softness of rigid rod cross-links. Here we return to compositional fluctuations as a mechanism. Significant deviations from softness are obtained for *persistent* chains with compositional fluctuations, far beyond those expected[3] from uncorrelated A/B units along an A/B random copolymer. We shall also examine the effect of compounding two-step linking with persistence in fluctuations in anisotropy. In addition to a large stripe threshold, we also find linear terms in the Landau−de Gennes free energy and thus paranematic and even supercritical high-temperature behavior.

II. Models of Anisotropy Fluctuations for Semisoft Elasticity

The ideal nematic elastic free energy can be kept constant under soft distortions $\boldsymbol{\lambda}^{\text{soft}} = \mathbf{l}^{1/2}\mathbf{R}\mathbf{l}_0{}^{-1/2}$ where $\mathbf{R}$ is an arbitrary rotation, $\mathbf{l}_0$ is the shape tensor of a strand chain before and $\mathbf{l}$ that after deformation $\boldsymbol{\lambda}$. [$\mathbf{l}$ defines a Gaussian chain distribution $P(\mathbf{R})$ since it defines the second moment $\langle R_i R_j\rangle = {}^1/_3 l_{ij} L$ where $\mathbf{R}$ is the end to end vector and L the chain arc length. One can think here of the system being cross-linked in the same, nematic state that deformations are being carried out in, that is $\mathbf{l}_0$ reflects the current and formation anisotropy. If cross-linking was carried out in the isotropic state, the $\mathbf{l}$ at that moment would have been spherical. Cooling to the current, nematic state sees spontaneous distortions of both chains (and hence their distributions) and of the sample. Measuring $\boldsymbol{\lambda}$ now with respect to this relaxed state, we find also that the $\mathbf{l}_0$ entering the free energy and soft mode results in the current nematic form. To this extent we can assume that the system was cross-linked in the nematic state in this section, although in reality the isotropic state could have been the original formation state. Examples of this equivalence are discussed below.] In an earlier paper[3] we noted that if the shape tensor $\mathbf{l}^i$ varies in its anisotropy between chains i, then $\boldsymbol{\lambda}^{\text{soft}}$ can no longer be simultaneously soft for all chains. Even the best choice will meet with a small resistance from each chain individually, and overall, the system will offer a small modulus resisting shape change.

A variation in anisotropy arises[3] from fluctuations in the compositions of a chain overall, the two types of monomer in a random copolymer having different anisotropies. If the choice is random and the deviation from mean anisotropy just in proportion to the number fluctuations from the mean composition, the modulus is[3] very small $\sim 10^{-4}-10^{-8}\mu$ (the shear modulus for the elastomer in its isotropic state being $\mu = {}^3/_2 n_s k_B T$, with n_s the number density of strands in the network). The threshold λ_1 and the semisoft modulus for a striped nematic elastomer are far too small if this simple model for fluctuation-induced semisoftness is adopted. Reference 4 derives the free energy in terms of mean chain anisotropy $\langle r\rangle$ and $\langle {}^1/r\rangle$ where $r^i = l^i_{\|}/l^i_{\perp}$ is the shape anisotropy for the ith chain. Under conditions where the only cause of anisotropy is simple number fluctuations, the predicted threshold

$$\lambda_1 = \left[\frac{1 - 1/\langle r\rangle}{1 - \left\langle \dfrac{1}{r}\right\rangle}\right]^{1/3} \tag{1}$$

for such idealised copolymers is $\lambda_1 \approx 1.0001$.

Experimentally, λ_1 is in the range 1.02−1.15. By considering a chain persistence induced by the nematic mean field, even for ideally random copolymers, we find

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⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1997.

S0024-9297(96)01801-3 CCC: $14.00

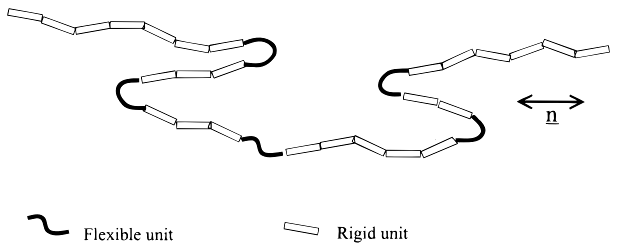


Figure 1. $N - n$ rods of length a can only reverse direction along **n** at the spacers. They form substrands that make up a random walk of $(n + 1)$ steps of average length $Na/(n + 1)$. In the perpendicular direction the walk is as that of an N-step aligned random walk.

greatly enhanced fluctuations in shape and thus a discrepancy between $1/\langle r\rangle$ and $\langle 1/r\rangle$ sufficient to give large values of λ_1.

A. Effectively Rodlike Substrands of Equal Lengths. The crudest model of persistent effects is to consider a copolymer of two species: (i) rods of length a which align with the nematic field and (ii) flexible units which allow the next substrand, composed of consecutive rods, to reverse along the director. The chain is now partially persistent since the direction of one rod along the director is the same as those to which it is directly attached. Reversals are only possible at flexibles which thus define the beginning and end of a substrand of connected rods (see Figure 1).

The strand as a whole, as far as its parallel dimension is concerned, is a random walk but with larger step lengths parallel than perpendicular to the ordering direction. The difference between the random walks in the two directions depends on the number of flexibles present, and it is the fluctuations in this that determine the degree of semisoftness. We shall explore various models of these fluctuations, but first it is interesting to speculate how persistence might arise in real chains and how this might correspond to our models. Side chain polymer liquid crystals typically have one pendant rod per monomer. These rods are bulky, and their packing possibly demands that the backbone stretch out when the side chains are nematically ordered. This explains how side chain polymers can have backbones with such high anisotropies r and hence apparent order, Q, despite being mostly rather flexible. A monomer lacking a pendant rod does not feel this constraint, and this section of the chain can be more isotropic. If one were to have a random copolymer where some monomers had, for example, differently pendant rods (e.g. a perpendicular rather than parallel connector, making such monomers more typically smectogenic), then such monomers would not only offer themselves as a point for reversal of chain direction but also represent a region of flattened (oblate $Q < 0$) chain backbone (see Figure 2). The rods of our model are the regions of backbone that are stretched out and aligned. We are of course only interested in the chain backbone statistics since these are the elastically active components and not the details of the side chain ordering.

The individual rods are not completely aligned and thus execute an unrestricted random walk perpendicular to **n**. Let there be $(N - n)$ rods between cross-links and n flexible units. The perpendicular dimension is

$$\langle R_\perp{}^2\rangle = \frac{1}{3}Na^2(1 - Q) \equiv \frac{1}{3}l_\perp Na \qquad (2)$$

Thus $l_\perp = a(1 - Q)$ where the $(1 - Q)$ factor represents the mean square projection of the rods perpendicular to **n** (see Figure 2).

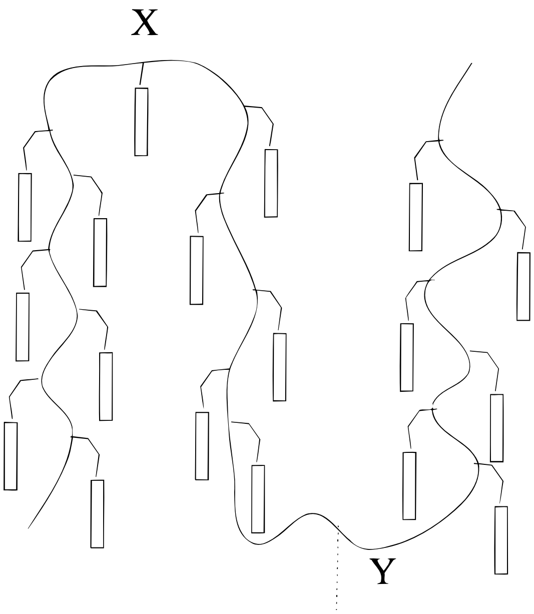


Figure 2. The high density of attachment of pendant rods in a side chain polymer liquid crystal could possibly make an inherently flexible backbone rather anisotropic. Rods that are perpendicularly pendant (X), or monomers with their rods missing (Y), offer possibilities for chain reversal.

Assuming the n flexible units to be equally spaced, there are $(n + 1)$ substrands of length $Na/(n + 1)$ executing a random walk along **n**, thus

$$\langle R_\parallel{}^2\rangle = \frac{1}{3}(n + 1)\left(\frac{Na}{n + 1}\right)^2 (1 + 2Q) \equiv \frac{1}{3}l_\parallel Na \qquad (3)$$

$$l_\parallel = \frac{N}{n + 1}a(1 + 2Q) \qquad (4)$$

If the number of flexibles fluctuates, then $l_\parallel$ but not $l_\perp$ will vary and hence

$$\langle r\rangle = \frac{1 + 2Q}{1 - Q}\left\langle\frac{N}{n + 1}\right\rangle \qquad (5)$$

$$\left\langle\frac{1}{r}\right\rangle = \frac{1 - Q}{1 + 2Q}\left\langle\frac{n + 1}{N}\right\rangle \qquad (6)$$

If the rods and flexibles are chosen randomly, then there will be a mean number of rods in a chain $\langle n\rangle$, with $\langle n\rangle/N = \chi$, and with approximately Poissonian fluctuations in n: $p(n) = \mathrm{e}^{-\langle n\rangle}\,\langle n\rangle^n/n!$. In that event the averages required in (5) and (6) can be exactly evaluated and give $\langle r\rangle = r/\chi$ and $\langle 1/r\rangle = (1/r)(\chi + 1/N)$ where we denote $(1 + 2Q)/(1 - Q) = r$, the shape anisotropy if we had a freely jointed chain with order Q. Thus the stripe threshold is

$$\lambda_1 = \left[\frac{1}{1 - \dfrac{1}{N(r - \chi)}}\right]^{1/3} \qquad (7)$$

Even for a high fraction $\chi = 0.3$ of flexibles and low link order $Q = 0.3$ ($r \approx 2.3$), we still get modest thresholds, $\lambda_1 \approx 1.02$.

B. Random Walks of Fluctuating Effective Step Lengths. The problem with the above model is that there are much more potent contributions to the fluctuations that distinguish between $1/\langle r\rangle$ and $\langle 1/r\rangle$ and hence provide a substantial λ_1. We have assumed that the flexibles are equally spaced. If they are chosen at random, the substrands they create will be of varying

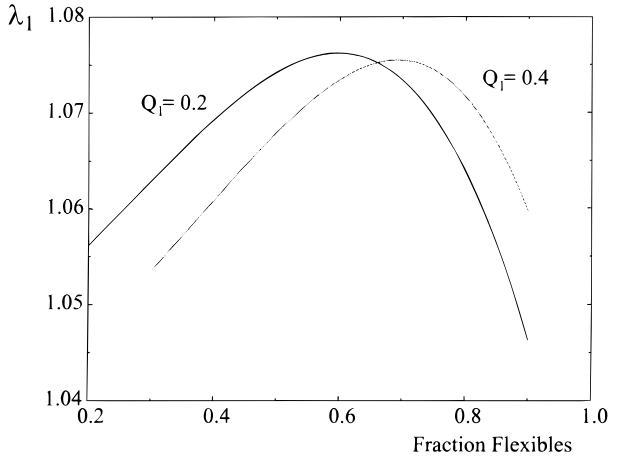


Figure 3. Threshold λ_1 for chains randomly composed of rods with restricted jointing and of flexible units allowing reversal along the director. The probability of finding a linker has been chosen to give a mean chain length of $\langle N\rangle$, in this case $\langle N\rangle = 20$.

length $a_i = n_i a$ where the ith substrand has n_i nonreversing links of length a. With the same assumptions about the random walks parallel and perpendicular to the director as before, we have

$$\langle R_\perp{}^2\rangle = \frac{1}{3}[\sum_i n_i a^2(1 - Q_1) + \sum_i a^2(1 - Q_2)] \equiv \frac{1}{3} l_\perp Na \tag{8}$$

$$l_\perp = a\,[(1 - Q_1)\sum_i n_i + (1 - Q_2)\sum_i]/N \tag{9}$$

and

$$\langle R_\parallel{}^2\rangle = \frac{1}{3}[\sum_i (n_i a)^2(1 + 2Q_1) + \sum_i a^2(1 + 2Q_2)] \equiv \frac{1}{3} l_\parallel Na \tag{10}$$

$$l_\parallel = a\,[(1 + 2Q_1)\sum_i n_i{}^2 + (1 + 2Q_2)\sum_i]/N \tag{11}$$

where $N = \sum_i n_i + \sum_i$ is the total number of elementary rods and flexibles and is extracted from both $\langle R_\perp{}^2\rangle$ and $\langle R_\parallel{}^2\rangle$ as it is proportional to the total chain arc length. In the parallel direction we have in effect a random walk of substrands i of fluctuating step length $n_i a$. Since $\langle R^2\rangle$ for a random walk depends on the square of its step lengths, we have the $\sum_i n_i{}^2$ factor.

The flexibles and cross-linker sites are selected randomly during polymerization, the selection of the former dictating the individual substrand lengths $n_i a$, the latter the arc length Na of a complete strand. We must average over such events. Additionally we have put in the order Q_1 of the rods and Q_2 of the flexibles (while somewhat arbitrarily assigning rods and flexibles the same length a).

The simulation of chain assembly is shown in Figure 3 where λ_1 is plotted against the mean fraction of flexibles, χ. The flexibles have order parameter $Q_2 = 0$. This generates a λ_1 in the range $\sim$1.04−1.08 for 5% cross-link density, that is $\langle N\rangle = 20$.

As the fraction of flexibles increases, $\langle r\rangle$ diminishes and λ_1 increases since $\langle 1/r\rangle$ approaches 1 more rapidly than $\langle r\rangle$ does. Eventually λ_1 diminishes at higher volume fraction of flexibles because the more potent fluctuation mechanism is destroyed.

There are circumstances when λ_1 can be very much higher, particularly if the sign of the coupling and hence the order parameter of the different types of monomers differs. As an illustration, Figure 4, $Q_1 = 0.4$ and $Q_2 = -0.3$ have been chosen. The backbone rods are modestly ordered, and the flexibles are oblate; that is, they contribute in a flattened way to overall chain shape. Thus as λ increases, $\langle r\rangle \to 1^+$ and $\langle 1/r\rangle \to 1^-$, the latter approaching 1 more rapidly and thus explaining the divergence in threshold λ_1.

Our purpose has not been to model a particular type of chain in detail but to demonstrate that fluctuations in composition can go toward explaining the observed values of λ_1 in the range 1.02−1.15. This can be achieved even if the mean anisotropy is quite small.

III. Multistage Cross-Linking of Compositionally Fluctuating Systems

A multiple-stage cross-linking process in which any of the cross-linking stages are in the nematic phase will be affected by compositional fluctuations. The free energy per strand is calculated in refs 11 and 12 for pointlike cross-links:

$$F = \frac{1}{2}k_\mathrm{B}T\,[\langle \mathrm{Tr}\mathbf{A}\boldsymbol{\lambda}^T\mathbf{l}^{-1}\boldsymbol{\lambda}\rangle + \ln(\det[\mathbf{l}/a])] \tag{12}$$

where $\mathbf{A} = (1 - \alpha)\mathbf{l}_0 + \alpha\boldsymbol{\lambda}_f{}^{-1}\mathbf{l}_\mathrm{f}\boldsymbol{\lambda}_\mathrm{f}{}^{-1T}$ with $(1 - \alpha)$ the

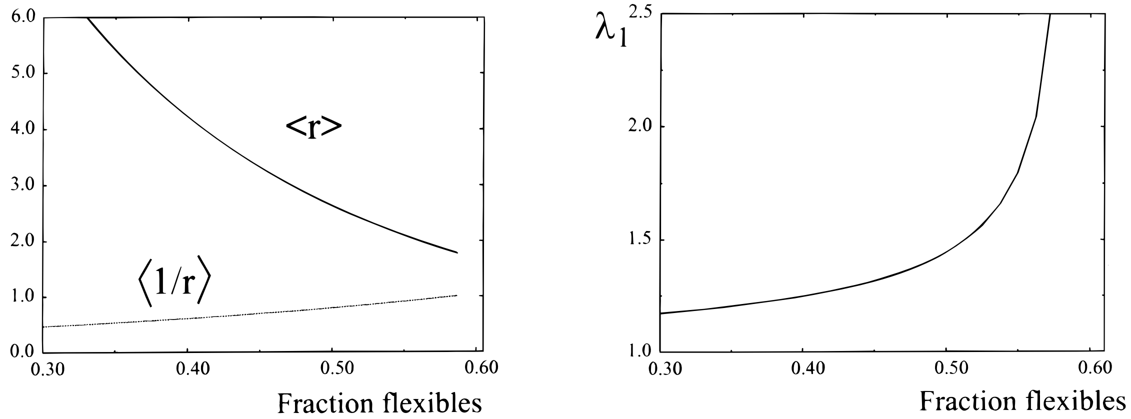


Figure 4. Mean anisotropy $\langle r\rangle$ and mean inverse anisotropy $\langle 1/r\rangle$, and the threshold λ_1 for chains randomly composed of rods with restricted jointing and of flexible units allowing reversal along the director. The probability of a flexible, χ, determines both the mean shape $\langle r\rangle$ (since flexibles are oblate, $Q_2 = -0.3$) and the fluctuations in shape (governing λ_1) through the fluctuations in the spacing between flexibles along the chain. The probability of finding a linker has been chosen to give a mean chain length of $\langle N\rangle$, here $\langle N\rangle = 20$.

fraction of first stage strands (of shape tensor $\mathbf{l}_0$) and α the second stage fraction (with shape and deformation at this stage of $\mathbf{l}_f$ and $\boldsymbol{\lambda}_f$, respectively). The current shape is given by $\mathbf{l}$. The generalization to several stages is trivial[12]

$$\frac{2F}{k_B T} = \left(\mathrm{Tr}[\mathbf{A}\boldsymbol{\lambda}^T\mathbf{l}^{-1}\boldsymbol{\lambda}] + \ln\left[\frac{\det \mathbf{l}}{a^3}\right]\right) \tag{13}$$

where the tensor $\mathbf{A}$ is given by

$$\mathbf{A} = \sum_\alpha \frac{N_\alpha}{N_t} (\boldsymbol{\lambda}_\alpha^T \mathbf{l}_\alpha{}^{-1} \boldsymbol{\lambda}_\alpha)^{-1} \tag{14}$$

However because of compositional fluctuations, both tensors $\mathbf{A}$ and $\mathbf{l}$ may vary from strand to strand. The strain imposed at the various formation states means that most strands are distorted away from their equilibrium state. We must still look for a relaxing deformation, $\boldsymbol{\lambda}_r$, which minimises the free energy over all strands. Taking the case where the cross-linking conditions have uniaxial symmetry, for example a sample cross-linked first in the isotropic state and then uniaxially stretched and further cross-linked in either the quasi-isotropic or nematic state, we find[19] on evaluating the free energy (12) with $\boldsymbol{\lambda}$ set equal to $\boldsymbol{\lambda}_r$

$$f = \frac{1}{2} n_s k_B T \left[\left\langle \frac{A_\parallel}{l_\parallel} \right\rangle \lambda_r{}^2 + \left\langle \frac{A_\perp}{l_\perp} \right\rangle \frac{2}{\lambda_r}\right] \tag{15}$$

where n_s is the number density of network strands. Thus we find on minimizing over $\boldsymbol{\lambda}_r$

$$\lambda_r = \left(\frac{\left\langle \dfrac{A_\parallel}{l_\parallel} \right\rangle}{\left\langle \dfrac{A_\perp}{l_\perp} \right\rangle}\right)^{1/3} \tag{16}$$

Measuring $\boldsymbol{\lambda}$ from its relaxed value (as one would do in an experiment), $\boldsymbol{\lambda}_{\text{total}} = \boldsymbol{\lambda}\boldsymbol{\lambda}_r$, one can write the free energy as

$$f = \frac{1}{2} n_s k_B T \langle \mathrm{Tr}[\mathbf{l}^* \boldsymbol{\lambda}^T \mathbf{l}^{-1} \boldsymbol{\lambda}] \rangle \tag{17}$$

where $l^* = \boldsymbol{\lambda}_r \mathbf{A} \boldsymbol{\lambda}^T{}_r$. This can fluctuate from strand to strand but does so differently from $\mathbf{l}_r$, the persistence length tensor for the relaxed sample. The director (and hence the current $\mathbf{l}$) may be rotated by an angle θ from its orientation in the relaxed state by the imposition of further deformation $\boldsymbol{\lambda}$.

The hardening can still be determined by averaging over strands and minimizing the free energy. Using the following convenient shorthand

$$r_{\parallel\parallel} = \left\langle \frac{A_\parallel}{l_\parallel} \right\rangle \qquad r_{\parallel\perp} = \left\langle \frac{A_\parallel}{l_\perp} \right\rangle$$
$$r_{\perp\parallel} = \left\langle \frac{A_\perp}{l_\parallel} \right\rangle \qquad r_{\perp\perp} = \left\langle \frac{A_\perp}{l_\perp} \right\rangle \tag{18}$$

we can express $\lambda_r = (r_{\parallel\parallel}/r_{\perp\perp})^{1/3}$ and hence

$$l_\parallel^* = A_\parallel \left(\frac{r_{\parallel\parallel}}{r_{\perp\perp}}\right)^{2/3}$$

$$l_\perp^* = A_\perp \left(\frac{r_{\parallel\parallel}}{r_{\perp\perp}}\right)^{-1/3} \tag{19}$$

These are fluctuating quantities and will appear as averages with elements of l in the free energy (17) and then (20).

1. Simple Shear. Taking the case of the simple shear semisoft deformation appropriate to the stripe instability, one can write the free energy (17)[4] as

$$\begin{aligned}\frac{2f}{n_s k_B T} = {} & \lambda^2 \cos^2\theta \left\langle \frac{l_\perp^*}{l_\perp} \right\rangle + \lambda_{xx}{}^2 \cos^2\theta \left\langle \frac{l_\parallel^*}{l_\parallel} \right\rangle + \frac{1}{\lambda^2 \lambda_{xx}{}^2} \left\langle \frac{l_\perp^*}{l_\perp} \right\rangle + \\ & \delta^2 \sin^2\theta \left\langle \frac{l_\parallel^*}{l_\parallel} \right\rangle + \lambda^2 \sin^2\theta \left\langle \frac{l_\perp^*}{l_\parallel} \right\rangle + \lambda_{xx}{}^2 \sin^2\theta \left\langle \frac{l_\parallel^*}{l_\perp} \right\rangle + \\ & \delta^2 \cos^2\theta \left\langle \frac{l_\parallel^*}{l_\perp} \right\rangle + 2\delta\lambda_{xx} \sin\theta\cos\theta \left(\left\langle \frac{l_\parallel^*}{l_\parallel} \right\rangle + \left\langle \frac{l_\parallel^*}{l_\perp} \right\rangle\right)\end{aligned} \tag{20}$$

where $\delta \equiv \lambda_{zx}$ is the simple shear. This simplifies to give

$$\begin{aligned}\frac{2f}{n_s k_B T} = {} & r_{\perp\perp}{}^{1/3}\, r_{\parallel\parallel}{}^{1/6} \Bigg(\lambda^2 \cos^2\theta + \lambda_{xx}{}^2 \cos^2\theta + \frac{1}{\lambda^2 \lambda_{xx}{}^2} + \\ & \sin^2\theta\delta^2 + \lambda^2 \sin^2\theta \frac{r_{\perp\parallel}}{r_{\perp\perp}} + \lambda_{xx}{}^2 \sin^2\theta \frac{r_{\parallel\perp}}{r_{\parallel\parallel}} + \\ & \cos^2\theta\delta^2 \frac{r_{\parallel\perp}}{r_{\parallel\parallel}} + 2\sin\theta\cos\theta\delta\lambda_{xx}\left(\frac{r_{\parallel\perp}}{r_{\parallel\parallel}} - 1\right)\Bigg)\end{aligned} \tag{21}$$

This equation is now very similar to the semisoft shear free energy derived for the case of simple compositional fluctuations, with $r_{\parallel\perp}/r_{\parallel\parallel}$ taking the role of $\langle r \rangle$ and $r_{\perp\parallel}/r_{\perp\perp}$ taking that of $\langle 1/r \rangle$. The prefactor (21) merely alters the effective number of strands and hence the magnitude of the stress. Thus one expects similar behavior, with a threshold λ_1 for the onset of the semisoft deformation:

$$\lambda_1{}^3 = \frac{1 - \dfrac{r_{\parallel\parallel}}{r_{\parallel\perp}}}{1 - \dfrac{r_{\perp\parallel}}{r_{\perp\perp}}} \tag{22}$$

2. Discussion and Examples of Cross-Linking Histories. a. Network Cross-Linked in One Nematic Stage. For a once-cross-linked network $r_{\perp\perp} = r_{\parallel\parallel} = 1$, $r_{\parallel\perp} = \langle r \rangle$, and $r_{\perp\parallel} = \langle 1/r \rangle$, one recovers the expected expression (1) for λ_1.

b. Network Cross-Linked in Two Stages One of Which is in the Nematic State. Let us consider an example of a network which is cross-linked in two stages, the first in the isotropic state and the second in the nematic state, with N_1 cross-links in the isotropic state and N_2 cross-links in the nematic state and with a uniaxial deformation $\boldsymbol{\lambda}_f$ during the second stage. For simplicity let us assume that the persistence length tensors $\mathbf{l}$, although varying from chain to chain, are the same in both the second-stage cross-linking and in the experimental conditions. (This typically means the second-stage cross-linking temperature is also the temperature at which mechanical experiments are performed.) Thus $\mathbf{A} = a(N_1/N_t)\mathbf{I} + (N_2/N_t)\boldsymbol{\lambda}_f{}^{-1}\mathbf{l}_f\boldsymbol{\lambda}_f{}^{-1T}$ and $\mathbf{l} = \mathbf{l}_f$.

If we further assume that $l_\perp = a$, the step length in the isotropic state (and consequently the variation in the persistence length tensor arises only through variation in $l_\parallel$), we find

$$\lambda_1{}^3 = \frac{1 - \dfrac{1}{\langle r\rangle}\left[1 + \lambda_f{}^2\left(\langle r\rangle\left\langle\dfrac{1}{r}\right\rangle - 1\right)\Big/\left(\lambda_f{}^2 + \dfrac{N_2}{N_1}\langle r\rangle\right)\right]}{1 - \left\langle\dfrac{1}{r}\right\rangle} \qquad (23)$$

Thus the hardening is found to be similar to that for a network once cross-linked in the nematic state, when N_2 is large compared to N_1. Also λ_1 tends to 1 as N_2 tends to zero, recovering the fact that a network once cross-linked in the isotropic state must be soft by symmetry.

c. Network Cross-Linked in Multiple Stages in Non-Nematic States. We consider networks cross-linked (multiply) at high temperature where the order is only due to the imposed stretch and not to an intrinsically nematic state. This order is very small. We refer to these states as isotropic; paranematic would be a more accurate name for them. In this case **A** arises only from the deformations $\boldsymbol{\lambda}_\alpha$ at each cross-link stage, α, and this is the same for each chain. Therefore its components $A_\parallel$ and $A_\perp$ can be factored out of the averages, and one finds

$$r_{\perp\perp} = A_\perp\left\langle\frac{1}{l_\perp}\right\rangle = \frac{A_\perp}{A_\parallel}r_{\parallel\perp} \qquad (24)$$

$$r_{\perp\parallel} = A_\parallel\left\langle\frac{1}{l_\perp}\right\rangle = \frac{A_\perp}{A_\parallel}r_{\parallel\parallel}$$

Thus

$$\lambda_1 = 1 \qquad (25)$$

there is no hardening of soft deformations due to compositional fluctuations for networks prepared solely in the isotropic state by however many cross-linking steps and for whatever strain history.

This is an important result particularly as it applies to all soft deformations and can be seen as follows. Let us return to the free energy expression eq (17)

$$f = \frac{1}{2}n_s k_B T\ \mathrm{Tr}[\mathbf{l}^* \boldsymbol{\lambda}^T \mathbf{R}_\theta^T (\mathbf{l}_r)^{-1}\mathbf{R}_\theta \boldsymbol{\lambda}] \qquad (26)$$

The current shape tensor **l** is that in the relaxed state, $\mathbf{l}_r$, but rotated by θ, the rotations $\mathbf{R}_\theta$ being explicitly displayed in eq 26. If the network was cross-linked in the isotropic state, then in each stage of formation $l_\parallel = l_\perp = a$ and is the same for each chain. (Note that it could vary from chain to chain if, for example, different monomers had different lengths.) Thus for each chain $\mathbf{l}_i{}^{-1} = (1/a)\mathbf{I}$ and consequently

$$\mathbf{A} = a\sum_\alpha \frac{N_\alpha}{N_t}\boldsymbol{\lambda}_\alpha{}^{-1}\boldsymbol{\lambda}_\alpha{}^{T-1} \qquad (27)$$

and therefore

$$\mathbf{l}^* = a\boldsymbol{\lambda}_r \sum_\alpha\left(\frac{N_\alpha}{N_t}\boldsymbol{\lambda}_\alpha{}^{-1}\boldsymbol{\lambda}_\alpha{}^{T-1}\right)\boldsymbol{\lambda}_r{}^T \qquad (28)$$

Changes in a from chain to chain can be accounted for by absorbing them into the effective number of strands. Thus

$$n_{s\ \mathrm{eff}}(a) = n_s(a)\frac{a}{\langle a\rangle} \qquad (29)$$

and we can define a new **l***

$$\mathbf{l}^* = \langle a\rangle\boldsymbol{\lambda}_r \sum_\alpha\left(\frac{N_\alpha}{N_t}\boldsymbol{\lambda}_\alpha{}^{-1}\boldsymbol{\lambda}_\alpha{}^{T-1}\right)\boldsymbol{\lambda}_r{}^T \qquad (30)$$

The effective formation shape, l^*, is constant for all chains, and the minimum in free energy occurs when $\boldsymbol{\lambda} = \mathbf{I}$ because **l*** is chosen so as to measure $\boldsymbol{\lambda}$ from its relaxed value (see eqs 15 and 16). Consider a deformation $\boldsymbol{\lambda} = \mathbf{R}_\theta \mathbf{l}^{*1/2}\mathbf{R}_\theta^T\mathbf{R}_\phi\mathbf{l}^{*-1/2}$, where $\mathbf{R}_\phi$ is an additional, arbitrary rotation matrix. Note that when $\theta = \phi = 0$ this deformation $\boldsymbol{\lambda} = \mathbf{I}$. For general θ and ϕ, one finds the free energy

$$f = \frac{1}{2}n_{s\ \mathrm{eff}}k_B T\langle \mathrm{Tr}[\mathbf{l}^*(\mathbf{l}_r)^{-1}]\rangle \qquad (31)$$

which is independent of θ and ϕ; thus we see the energy is a constant equal to its value at $\boldsymbol{\lambda} = \mathbf{I}$ and there is no hardening of the soft deformations. This leads naturally to an experimental test, *if compositional fluctuations are the only hardening mechanism a sample cross-linked in two isotropic stages will be completely soft*. This is not true of the rigid rod mechanism discussed in the previous paper and is a means of distinguishing between the two causes of semisoftness.

IV. Effect on Nematic–Isotropic Phase Transition: Laudau–de Gennes Free Energy

Hardening due to compositional fluctuations will have an impact on the nematic–isotropic phase transition. It can be illustrated by examining the Laudau–de Gennes theory for a sample prepared in a single cross-linking stage. Taking a simple model, let us assume that the strands behave as freely jointed rods but with different coupling to the nematic field. Thus for each strand

$$l_\parallel = (1 + 2\tau Q)a \qquad (32)$$

$$l_\perp = (1 - \tau Q)a \qquad (33)$$

where τ varies from strand to strand because of the fluctuations in coupling to the nematic field of the strands' monomers.

The free energy averaged over strands is

$$\frac{2f}{n_s k_B T} = \left\langle\frac{l_\parallel^0}{l_\parallel}\right\rangle\lambda^2 + \left\langle\frac{l_\perp^0}{l_\perp}\right\rangle\frac{2}{\lambda} - \langle \ln\det[l_0 l^{-1}]\rangle \qquad (34)$$

($\lambda_{xx} = \lambda_{yy} = 1/\sqrt{\lambda}$ by symmetry). Minimizing over λ one finds the relaxed state

$$\lambda_r{}^3 = \frac{\left\langle\dfrac{l_\perp^0}{l_\perp}\right\rangle}{\left\langle\dfrac{l_\parallel^0}{l_\parallel}\right\rangle} \qquad (35)$$

and the free energy is

$$\frac{2f}{n_s k_B T} = 3\left\langle\frac{l_\parallel^0}{l_\parallel}\right\rangle^{1/3}\left\langle\frac{l_\perp^0}{l_\perp}\right\rangle^{2/3} - \langle \ln\det[\mathbf{l}_0\mathbf{l}^{-1}]\rangle \qquad (36)$$

We now expand in small powers of Q. Note that det $\mathbf{l}_0\mathbf{l}^{-1} = (\det \mathbf{l}_0)/(\det \mathbf{l})$ with $\det \mathbf{l} = (1 + 2\tau Q)(1 - \tau Q)^2 =$

$(1 + O(Q^2))$ and therefore contributes no terms of order Q. One finds at $O(Q)$

$$\frac{2f}{n_s k_B T} = 3\left(\langle l_{\|}^{0}\rangle\langle l_{\perp}^{0}\rangle^{2}\right)^{1/3}\left(1 - \frac{2}{3}\left(\langle\tau^{2}\rangle - \langle\tau\rangle^{2}\right)Q_0\left(\frac{2}{l_{\|}^{0}} + \frac{1}{l_{\perp}^{0}}\right)Q + O(Q^2)\right) \tag{37}$$

Thus we find a negative linear Q term in the free energy which has the same effect as a mechanical field stretching the sample parallel to the initial director orientation. The consequences of such a mechanical field have been studied.[13,14] They include a small residual order in the "isotropic" state (really a paranematic state) and changes in the phase transition. If the field is above the critical value, there will no longer be a discontinuous change in Q at a phase transition induced by lowering the temperature; that is, the system is in a supercritical paranematic state.

Note that, if the cross-linking is in the isotropic phase, $Q_0 = 0$, there is no linear Q term. There will, however still be a Q^2 term generated. Returning to eq 36 and inserting $l_{\|}^{0} = l_{\perp}^{0} = a$ for a network cross-linked in the isotropic phase, one finds

$$\frac{2f}{n_s k_B T} = 3 + 3(\langle\tau^2\rangle - \langle\tau\rangle^2)Q^2 + O(Q^3) \tag{38}$$

These results are in contrast to the theory of Warner *et al.*[15] who show that, for a compositionally homogeneous nematic elastomer, one expects

$$f(Q) = -C_1 Q_0^{\,2} Q^2 + C_2 Q^4 + ... \tag{39}$$

i.e. $-Q^2$ and $+Q^4$ terms for an elastomer cross-linked in the nematic state and only $+Q^4$ terms for elastomers crosslinked in the isotropic phase. If, however, there are no compositional fluctuations, clearly the energy reverts to the result of Warner *et al.* Thus compositional fluctuations, even for networks formed in the isotropic state where there is no effect on softness, still destabilize (slightly) the nematic state and lower the nematic–isotropic phase transition temperature.

V. Nematic Transitions in Weakly Anisotropic Elastomers

We have largely been concerned with explaining how the threshold λ_1 for stripe development, that is for semisoft deformation, can be quite substantial, $\lambda_1 \approx 1.05-1.15$. These values can be obtained for systems with fairly high anisotropy $\langle r\rangle$ by examining compositional fluctuations and rigid rod crosslinks. There remains the problem that some experiments[16] in a geometry similar to that of Finkelmann apparently show sharp transitions from $\theta = 0$ to $\theta = \pi/2$ (where θ is the angle between the initial and current director orientations) without an intervening stripe region. These samples are cross-linked in a single step as monodomain nematic melts to form monodomain elastomers. The spontaneous distortions on heating to the isotropic phase are relatively small, indicating a small backbone shape anisotropy, $\langle r\rangle$. We now reanalyze this type of experiment in the low anisotropy, $\langle r\rangle \to 1$ limit.

Since there is only one cross-linking stage, in (17) we have $\mathbf{l}^*$ being simply the unrotated form of $\mathbf{l}$, that is, corresponding to the director $\mathbf{n}_0$ in the relaxed state, whereas $\mathbf{l}$ corresponds to an $\mathbf{n}$ which has been rotated by θ (see Figure 5).

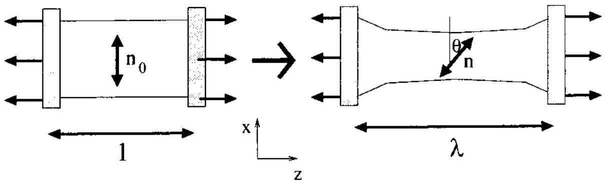


Figure 5. The experiment of Mitchell *et al.* and Finkelmann *et al.* The elastomer is clamped at its ends and stretched by a factor of λ perpendicular to the original director $\mathbf{n}_0$, thereby inducing it to rotate by an angle θ.

The free energy (17) for the $\theta = 0$, $\theta = \pi/2$ and the semisoft[4] states are

$$f_0 = \frac{1}{2}n_s k_B T\left(\lambda^2 + \frac{2}{\lambda}\right) \tag{40}$$

$$f_{\pi/2} = \frac{1}{2}n_s k_B T\left(\left\langle\frac{1}{r}\right\rangle\lambda^2 + \frac{2\sqrt{\langle r\rangle}}{\lambda}\right) \tag{41}$$

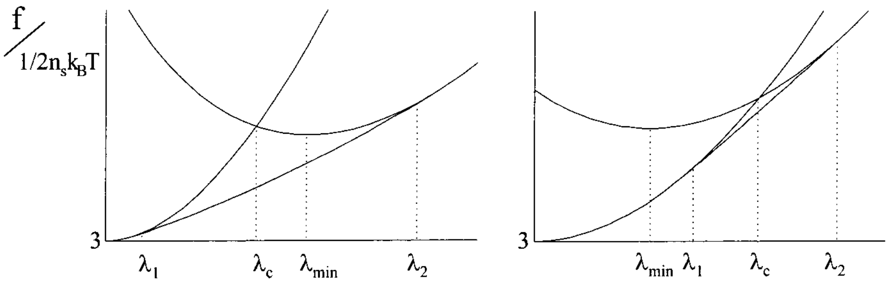
$$f_{ss} = \frac{1}{2}n_s k_B T\left(\lambda^2\left(1 - \frac{1}{\lambda_1^3}\right) + \frac{3}{\lambda_1}\right) \tag{42}$$

In the latter state the director rotates continuously from $\theta = 0$ to $\pi/2$ at relatively little energy but at the cost of some shearing. The clamps by which the sample is gripped forbid this in any gross sense, and stripes are the consequence.[4] The three energies are shown as a function of λ in Figure 6, with f_{ss} connecting the initial (f_0) and final ($f_{\pi/2}$) curves, that is spanning from $\lambda = \lambda_1$ to $\lambda = \lambda_2$.

Where $\langle r\rangle$ is appreciable, the semisoft transition region (λ_1, $\lambda_2 = \lambda_1\sqrt{\langle r\rangle}$) is reasonably wide (see Figure 6a). This seems to be the case in the Finkelmann materials[5,6,17] and is corroborated by the large spontaneous thermal expansion at the $n-i$ transition: $\lambda_{\text{spont}} \approx \langle r\rangle^{1/3} \approx 1.5$. When the anisotropy is small, $\langle r\rangle \to 1^+$ and equally $\langle 1/r\rangle$ tends to 1^-, then we have seen that λ_1 can be large. Then $\lambda_2 = \lambda_1\sqrt{\langle r\rangle}$ will be close to λ_1 and the interval of the transition rather narrow. The situation is qualitatively different (see Figure 6b). The minimum of the $f_{\pi/2}(\lambda)$ curve, $\lambda_{\min}$, is inside the crossing deformation λ_c. The energy benefit from descending from f_0 or $f_{\pi/2}$ to f_{ss} is small. It is unlikely, however, that the energy of the clamped region and the stripe walls is sufficient to overwhelm this energy benefit and thereby suppress stripe formation altogether. The energy available can be assessed from taking its value at $\lambda = \lambda_c$

$$f_0(\lambda_c) - f_{ss}(\lambda_c) = \frac{1}{2}n_s k_B T\frac{1}{\lambda_1} \times \left[\left(\frac{1}{\langle r\rangle}\right)^{1/3}\left(\frac{2}{\sqrt{\langle r\rangle}+1}\right)^{2/3}\left(1 + \sqrt{\langle r\rangle}\left(\sqrt{\langle r\rangle} + 1\right)\right) - 3\right] \approx \frac{1}{2}n_s k_B T\,\frac{\epsilon}{\lambda_1}$$

when $\langle r\rangle$ is close to 1, $\langle r\rangle = 1 + \epsilon$. This analysis uses $\lambda_1^{\,3} = (1 - 1/\langle r\rangle)/(1 - \langle 1/r\rangle)$ and $\lambda_c^{\,3} = \lambda_1^{\,3}\ 2\langle r\rangle/(\sqrt{\langle r\rangle} + 1)$. Thus weak anisotropy could give a "transition" at a reasonably high value of $\lambda \approx \lambda_1$. The narrowness of the stripe interval might give the appearance of a fairly sharp transition between $\theta = 0$ and $\theta = \pi/2$ with an apparent drop of order in the sample during the transition. The latter would come from regions at $\pm\theta$ mis-



(a) (b)

Figure 6. Semisoft free energies for large (a) and small (b) anisotropy; $\langle r\rangle \gg 1$ and $\langle r\rangle \approx 1$ respectively.

Table 1. Cross-Linking Conditions under Which Compositional Fluctuations Affect λ_1 at $O(1/N)$ and Hence Harden the Soft Deformations of a Nematic Elastomer[a]

	nematic	isotropic
single stage	yes	no
multistage	yes	no

[a] The differences between this table and the equivalent one for the effect of rigid cross-links will indicate the experiments decisive in discriminating between the two causes of semisoftness.

aligned with the axis at either $\theta = 0$ or $\pi/2$ about which one would naturally measure order.

It is not clear whether this speculation addresses the lack of stripes and relatively high threshold observed in the weakly anisotropic elastomers of Mitchell *et al.*[16] The nonstriped explanation previously advanced[18] (when predicting such effects) was that shear (and hence softness) was suppressed altogether by the clamps. One then makes the transition from $\theta = 0 \rightarrow \pi/2$ either when the energies cross at λ_c or a higher $\lambda = \lambda_{\rm spont}$ where the $f_{\theta=0}$ energy becomes locally unstable with respect to rotations. At the time these predictions were made, semisoftness had not been anticipated and the minimum of $f_{\theta=\pi/2}(\lambda)$ was expected to be at $f = 3$. The soft trajectory between $\theta = 0$ and $\pi/2$ is absolutely flat at $f = 3$ (zero energy cost). The transition from the $f_{\theta=0}$ to the $f_{\theta=\pi/2}$ branch at $\lambda \geq \lambda_c$ is thus qualitatively as in Figure 6a, that is, to a region of negative slope, $df/d\lambda < 0$, and thus further spontaneous distortion along the extension direction (in effect negative stress and thus buckling in strips). This current picture of a transition to a region of positive $df_{\theta=\pi/2}/d\lambda$ avoids these possible difficulties. A further observation that would help decide between these various possibilities would be precise details of the hysteresis that accompanies the transitions of the Mitchell type.

VI. Conclusions

We have shown that compositional fluctuations along with persistence in chains can lead to quite large thresholds, λ_1, to a striped semisoft state when an elastomer is extended perpendicular to its original director. Multistage cross-linking is shown to have a further effect on λ_1. The creation of semisoftness, that is, of a small energy associated with what would otherwise be deformation without cost, leads not only to a threshold but also to a low but finite modulus. Our predictions should be tested against both thresholds and moduli.

One requires not only that strands fluctuate in their anisotropy, but also that these variations permanently record fluctuations in anisotropy to the network. It is thus required that additionally the linkage, single or multistage, be performed in the nematic state. This is summarized in Table 1.

There are qualitative differences between this table and that for rigid rod cross-linkers.[11] These differences are the clue to which experiments are vital to discerning whether rigid rod cross-links or compositional fluctuations dominate the semisoftness. In the former case it is rather multistage linkage, whether nematic or isotropic, that determines whether semisoftness is obtained.

We have also speculated on why more weakly anisotropic networks do not display stripe transitions. Finally we have obtained linear terms in the Landau–de Gennes free energy for semisoft elastomers, that is, the apparent field that is acting on such systems even when they are relaxed.

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(19) We have taken for the relaxation a uniaxial incompressible form

$$\lambda_r = \begin{pmatrix} \lambda_r & 0 & 0 \\ 0 & \dfrac{1}{\sqrt{\lambda_r}} & 0 \\ 0 & 0 & \dfrac{1}{\sqrt{\lambda_r}} \end{pmatrix}$$

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