Semisoft elastic response of nematic elastomers to complex deformations

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We consider a relaxed semisoft elastomer with its director oriented along the z axis that is first subjected to a large stretch in the x direction then to a slight x-z shear. We give a general argument that in any theory including director rotation, at the onset and end of the director rotation induced by these large stretches, there will be kinks in the stress-large strain curve (forming a stress-strain plateau) and zeros in the x-z shear modulus (C_5) associated with small shears imposed on top of the stretches. We then find the analytical forms of the C_5-strain curves for a particular model of semisoftness (arising from compositional fluctuations) and show that it, together with the known stress-strain curve, provides the basis for a strong test of this theory. Finally, we consider the scope for other semisoft models and show that the compositional fluctuations model in fact yielded a generic form, that is, it is the most general quadratic free energy that does not explicitly include a final state direction other than the director. By introducing such additional directions, a large range of alternative models could be developed.

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I. INTRODUCTION

The theory of ideal nematic elastomers [1,2] predicts that certain deformations will not cost energy; they will be "soft" [3,4]. These soft deformations are understood as a consequence of the existence of an isotropic reference state [5]: if there exists an isotropic state and the elastomer is cooled inducing an isotropic-nematic ordering, the material will deform by extending along the nematic director. The selection of an axis for the director breaks the symmetry of the isotropic state, so there are many other equivalent nematic states, each with a different deformation relative to the isotropic state. Provided the director is mobile, deformations that map between these equivalent nematic states must be soft. These symmetry arguments and limitations of their applicability are explored at length in [2].

The nematic elastomers realized in laboratories are not ideal and do not exhibit perfect soft elasticity. Instead a "stress-strain plateau" is observed [6]—if a nematic elastomer is prepared with its director along the z axis and is then stretched along the perpendicular x axis (the first step shown in Fig. 1), the stress-strain curve is seen to have three segments. The first and third have high elastic moduli and correspond to stretch before and after director rotation, while the middle section, corresponding to the period during director rotation, has a much lower, but still finite, elastic modulus. To compare, the ideal theory predicts that director rotation should start as soon as the sample is stretched, so the first region should not be observed, and that while director rotation continues the elastic modulus should be zero, not just small.

One theoretical approach to semisoft elastomers, developed by Warner and Terentjev, has been to construct microscopic models based on Gaussian entropic chains coupled to a nematic field [1,7]. These models result in free energies that depend on the Cauchy tensor describing the deformation of the final state relative to the formation state, and the nematic director in both of these states. One way to include semisoftness in this type of model is to take into account that different polymer strands in the network couple to the nematic order with different strengths, so that deformations that are soft for some strands are not soft for other strands [7]. This model, known as the compositional fluctuations model, only contains three (separately measurable) constants, an overall energy scale, μ, the average anisotropy of the Gaussian distribution of network chains, r, and a degree of nonideality, α. Despite so few constants, it is valid to large deformations and has successfully described [8] the stresses and singular director rotations observed in real elastomers, even at very large deformations (see Figs. 2 and 3).

If one is only interested in the mechanical properties of semisoft elastomers one can integrate out the final state nem-

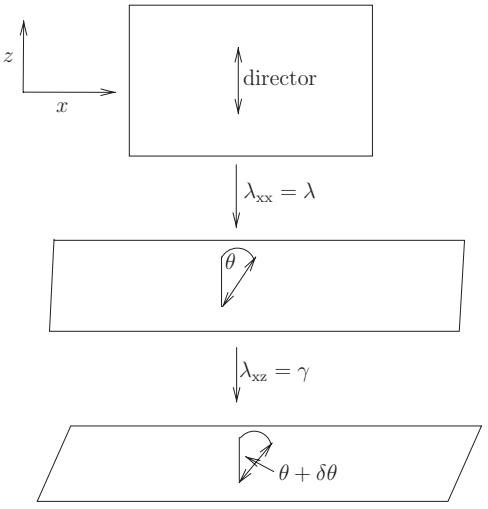

FIG. 1. A two step experiment in which the sample is prepared with the director along the z axis, then a stretch $\lambda_{xx}=\lambda$ is imposed [which may lead to director rotation (shown) and sympathetic shears (not shown)], then a small $\lambda_{xz}=\gamma$ shear is imposed at constant stretch.

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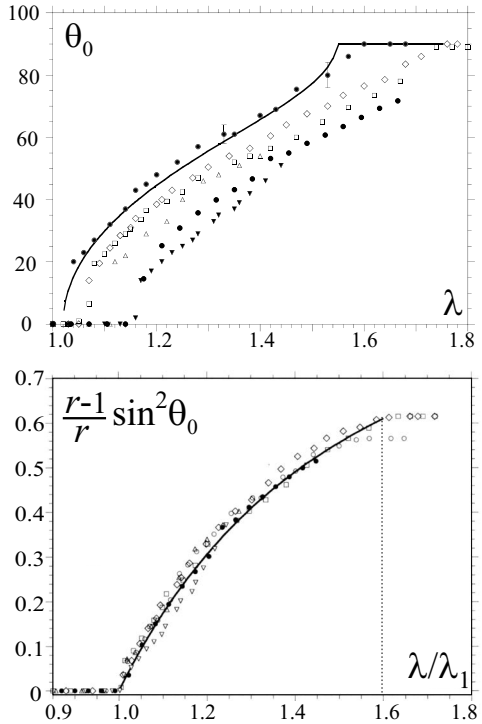

FIG. 2. Upper: Director rotation (θ_o) as a function of stretch (λ) for samples prepared by several different groups. The solid line is a theoretical curve [from Eq. (8)] fitted to the data for one sample. Lower: Plotting reduced rotation against reduced extension causes all the data sets to collapse onto one master curve. The solid line is the theoretical prediction derived from Eq. (8). Figure adapted from [2], see also [13] for the original analysis.

atic field to produce theories that only depend on the nematic field at formation and the strain. Conti *et al.* [9] applied this idea to the compositional fluctuations free energy to study the response of a thin film of semisoft elastomer stretched between rigid clamps. Ye *et al.* [10] have also used this fact to construct a phenomenological minimal model of the effective free energy, in this case using the Lagrangian strain tensor. Their approach elegantly captures the symmetry origins of semisoft behavior and predicts the vanishing shear modulus that this paper is concerned with. This paper addresses the microscopic model of semisoftness developed by Warner and Terentjev (complete with the final state nematic field) and is written in their notation. We both explore the model's predictions and provide phenomenological arguments that suggest a wide range of microscopic models would have produced the same predictions. In this sense, this paper contains elements of both the phenomenological and microscopic approaches to the subject.

The ideal model for nematic elastomers predicts that, in the geometry of Fig. 1, the modulus for an infinitesimal *x-z* shear (the second stage the figure) should vanish. The fact that a finite shear modulus has been observed in small-strain rheological experiments [11] has raised questions about the interpretation of the materials observed in the laboratory as nonideal nematic elastomers [12], despite the clear experimental evidence for the large stress-strain plateau, the very close correspondence between the observed and predicted

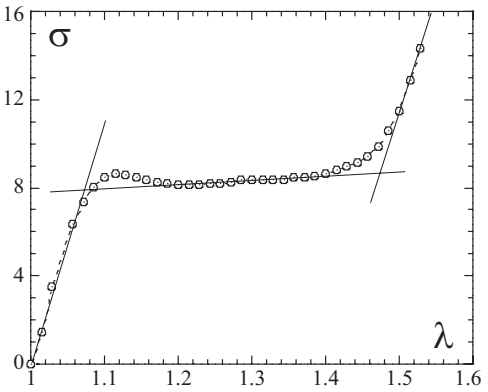

FIG. 3. Stress-strain data for an elastomer showing a threshold to a subsequent stress-strain plateau and then final classical behavior. The solid lines show the stress curves predicted by the compositional fluctuations model. (We thank S.M. Clarke for permission to reproduce this data.)

forms for the director rotation [8,13], and the systematic study [8] of the variation of the length of the stress plateau with anisotropy, *r*. In this paper, we are concerned with the small-strain rheological signal associated with each end of this important plateau seen in large strain experiments, attempting to resolve these questions.

Small-shear ($\lambda_{xz} \lesssim 10^{-4}$) mechanical experiments offer a much more limited route to exploring constitutive relations than large strain experiments ($\lambda_{xx} \lesssim 5$) which at the same time induce large (90°) rotations of nematic order upon which the new properties of nematic elastomers are predicated. Lubensky and Ye [10] have proposed that small-strain rheology could explore a wider range of the elastomer's response by small strains being imposed on top of the large, director rotation-inducing elongations that form the distinctive semisoft plateau. They predict, from nonlinear continuum elasticity, that the small strain shear modulus as a function of the (large) preimposed stretches will vanish at the onset and at the completion of director rotation. These are novel, most distinctive properties and hugely extend the scope of conventional experiments. We analyze these phenomena using the same (nonlinear, molecularly based, and frame independent) elasticity theory as was used to describe the original semisoft plateau and director rotation. Our approach is complementary to that of the original approach to the problem by Lubensky and Ye.

We demonstrate that the zeros in the shear modulus and the kinks in the stress-strain curve for the large strains will feature in any nonideal elastomer theory that incorporates director rotation. This intimate link between the stress plateau and the vanishing of the apparent shear modulus suggests that, since both the stress-strain plateau and director rotation have been so convincingly observed, the zeros in the shear modulus probably also exist although they have not yet been seen. Working on this premise, we calculate the full form of the apparent shear modulus as a function of preimposed strain. We find that it does indeed predict the zeros in the shear modulus. In addition, taken together with the stress-strain curve predicted by the model, there are enough model-specific features to test the model very rigorously.

Finally, we examine the scope for nonideal models of semisoftness other than that of the compositional fluctuation model. We show that, despite its initial derivation from the molecular mechanism of compositional fluctuations, the frame-independent elastic model is in fact the most general quadratic model that does not explicitly use directions other than the nematic director, so it is in fact very general. However, many other models can be made by including other directions in the final state. All these models will include the kinks in the stress-strain curve and the zeros in the shear modulus found in the compositional fluctuations model, but other details will be different. These models could be developed further if, in the future, the free energy of the type yielded by the compositional fluctuations model was not to fit experimental data.

II. GENERAL CONSEQUENCES OF DIRECTOR ROTATION

Consider a block of relaxed nematic elastomer that has its director oriented along the z axis. The block is stretched in the x direction by a factor of λ (see Fig. 1). The force needed to generate this strain suppresses any λ_{zx} shear by generating a restoring torque, but all other elements of the deformation tensor $\underline{\underline{\lambda}}$ are free to relax to whatever value minimizes the free energy of the elastomer. The director after deformation, $\hat{\mathbf{n}}$, must by symmetry lie in the x-z plane, so let the angle it makes with the z axis be θ. This setup is illustrated in the first step of Fig. 1 and is the geometry used in [6] and all subsequent experiments on director reorientation and "stripe domains" [2].

Any model of a nonideal elastomer will predict a free energy density for the elastomer as a function of the imposed stretch θ and all the other components of the deformation tensor:

$$F = F(\lambda, \theta, \lambda_{xz}, \dots). \tag{1}$$

The behavior of the elastomer will be given by minimizing F over all the variables except λ. We define F_θ to be the free energy after minimizing over all variables except λ and θ. Both before director rotation, and when θ is still very small, we can expand F_θ in powers of θ. Since nothing in the setup distinguishes $\pm x$ only even powers of θ can appear, giving

$$F_\theta = A(\lambda) + B(\lambda)\theta^2 + C(\lambda)\theta^4 + \cdots. \tag{2}$$

This is minimized by taking

$$\theta = \begin{cases} 0, & B \geqslant 0, \\ \pm\sqrt{-B/2C}, & B < 0. \end{cases} \tag{3}$$

Since before any strain was applied $\theta=0$, the sample must start with $B \geqslant 0$. When the director rotates, θ becomes nonzero, and so B must become negative. Thus, at the onset of director rotation, B must pass through $B=0$ and, if this happens at a threshold $\lambda=\lambda_1$, the B generically behaves as $B \sim \lambda_1 - \lambda$. We thus expect θ to grow as $\theta \propto \sqrt{-B} \propto \pm\sqrt{\lambda-\lambda_1}$. We can calculate the gradient of the stress-strain curve (the apparent extension modulus at high strains) on either side of this point as the second derivative of the minimized free energy with respect to λ:

$$\frac{d^2F}{d\lambda^2} = \begin{cases} A'', & B = 0^+ \\ A'' - B'^2/2C, & B = 0^-, \end{cases} \tag{4}$$

where the prime indicates derivative with respect to λ. Since C is positive definite (to ensure the theory gives finite values for θ) the stress-strain curve has a discontinuous reduction in gradient at the onset of rotation, which reflects the start of a stress-strain plateau.

The onset of rotation occurs when the quadratic term in the free energy vanishes ($B=0$) making F_θ quartic to leading order in θ. In nematic elastomers the director couples to the elastomer network, that is changes in the director cause deformations of the elastomer and vice versa. As θ is adjusted slightly to explore this quartic well, there is an accompanying deformation, $\underline{\underline{\lambda}}$. The only component of $\underline{\underline{\lambda}}$ that can reflect the sign of θ is the λ_{xz} shear component. Since F_θ is quartic in θ, the energy cost of imposing such a shear will also be quartic in λ_{xz}, so the corresponding shear modulus disappears at this point.

Because nematic order is of quadrupolar symmetry, F_θ must be π periodic in θ and is in fact more properly expressed as a power series in $\sin 2\theta$. At the end of director rotation $\theta = \pm\pi/2$ so $\sin 2\theta$ is again vanishing and F can again be truncated at fourth order. This means that the cessation of director rotation can be described as the reverse of the onset director rotation, so the transition is again accompanied by a vanishing apparent shear modulus (for x-z shear) and a discontinuity (this time an increase) in the gradient of the stress-strain curve marking the end of the plateau.

III. SEMISOFT RESPONSE OF THE COMPOSITIONAL FLUCTUATIONS MODEL

A model of semisoftness based on compositional fluctuations takes the underlying ideal nematic rubber free energy [1] and adds [7] to it a nonideal part (α) to yield a frame-independent free energy density

$$F = \frac{1}{2}\mu\,\mathrm{Tr}(\underline{\underline{\ell}}_o \cdot \underline{\underline{\lambda}}^T \cdot \underline{\underline{\ell}}^{-1} \cdot \underline{\underline{\lambda}}) + \frac{1}{2}\mu\alpha\,\mathrm{Tr}[(\underline{\underline{\delta}} - \hat{\mathbf{n}}_o\hat{\mathbf{n}}_o) \cdot \underline{\underline{\lambda}}^T \cdot \hat{\mathbf{n}}\hat{\mathbf{n}} \cdot \underline{\underline{\lambda}}], \tag{5}$$

where $\hat{\mathbf{n}}$ is the final state director and $\hat{\mathbf{n}}_o$ is the initial director, $\underline{\underline{\ell}}$ is derived from $\hat{\mathbf{n}}$ as $\underline{\underline{\ell}} = \underline{\underline{\delta}} + (r-1)\hat{\mathbf{n}}\hat{\mathbf{n}}$ and, as before, μ, r, and α are scalar constants of the elastomer. The compositional fluctuations derivation considers a set of entropic chains each with a Gaussian distributed spanning vector $\mathbf{R}$ with anisotropic second moment $\langle \mathbf{RR} \rangle \propto \underline{\underline{\delta}} + (\tilde{r}-1)\hat{\mathbf{n}}\hat{\mathbf{n}}$, where $\hat{\mathbf{n}}$, the direction of nematic order, is the same for all chains, but the measure of shape anisotropy $\tilde{r}$ is not. The model gives simple microscopic interpretations of the quantities in the free energy. The overall energy scale, μ, is given by nk_bT, where n is the number of cross links between chains. The measure of nonideality, α, is given by $\langle \frac{1}{\tilde{r}} \rangle - \frac{1}{\langle \tilde{r} \rangle}$, r is the average shape anisotropy of the chains ($r = \langle \tilde{r} \rangle$) and $\underline{\underline{\ell}}$ is the second moment tensor of the spanning vector for a chain with average anisotropy.

The ultimate aim of this section is to calculate the apparent shear modulus for an infinitesimal shear $\lambda_{xz} = \gamma$ imposed

after a large preimposed stretch $\lambda_{xx}=\lambda$ (using the geometry of Fig. 1). However, before calculating this modulus, we recap the sympathetic shears and director rotations caused by imposing a stretch of λ perpendicular to the director predicted by the model and present some of the experimental data confirming these predictions. For this discussion we introduce a more precise notation. The initial stretch, $\lambda_{xx}=\lambda$, will cause the tensor deformation $\underline{\underline{\lambda}}_i$ and will cause the director to rotate to an angle θ_o with the z axis. The small shear imposed after the initial stretch will be described by the tensor $\underline{\underline{\lambda}}_2=\underline{\underline{\delta}}+\gamma\hat{\mathbf{x}}\hat{\mathbf{z}}$, and the associated change in the director angle will be $\delta\theta$. Therefore, the total tensor deformation is given by $\underline{\underline{\lambda}}=\underline{\underline{\lambda}}_2\cdot\underline{\underline{\lambda}}_i$, and the final angle between the director and the z axis is given by $\theta_o+\delta\theta$.

A. Response to finite elongation perpendicular to the initial director

The compositional fluctuations model of semisoftness predicts that the response of an elastomer to a finite elongation perpendicular to the initial director will be one of three possibilities depending on the amount of elongation. The full forms for the deformation responses ($\underline{\underline{\lambda}}_i$) and director rotations that result from applying the stretch $\lambda_{xx}=\lambda$, which are stated below, were derived in [14] and are discussed in [2]. Introducing the threshold strain

$$\lambda_1=\left(\frac{r-1}{r-1-\alpha r}\right)^{1/3}, \tag{6}$$

if $\lambda\leqslant\lambda_1$ the director does not rotate, ($\theta_o=0$) and the deformation tensor ($\underline{\underline{\lambda}}_i$) is simply that expected from a classical rubber:

$$\underline{\underline{\lambda}}_i=\begin{pmatrix}\lambda & 0 & 0\\ 0 & 1/\sqrt{\lambda} & 0\\ 0 & 0 & 1/\sqrt{\lambda}\end{pmatrix}. \tag{7}$$

If $\lambda_1\leqslant\lambda\leqslant\sqrt{r}\lambda_1$ then the director starts to rotate and the deformation tensor includes sympathetic λ_{xz} shears:

$$\sin^2\theta_o=\frac{r(\lambda^2-\lambda_1^2)}{(r-1)\lambda^2},\quad \underline{\underline{\lambda}}_i=\begin{pmatrix}\lambda & 0 & \lambda_{xz}\\ 0 & 1/\sqrt{\lambda_1} & 0\\ 0 & 0 & \sqrt{\lambda_1}/\lambda\end{pmatrix}. \tag{8}$$

See Fig. 2 for a comparison of this prediction for $\theta_o(\lambda)$ with experimental data. The shear is

$$\lambda_{xz}^2=\frac{(\lambda^2-\lambda_1^2)(r\lambda_1^2-\lambda^2)}{r\lambda^2\lambda_1^3}. \tag{9}$$

If $\sqrt{r}\lambda_1\leqslant\lambda$ then the director rotation is complete ($\theta_o=\pi/2$) and the elastomer once again deforms as a classical rubber would:

$$\underline{\underline{\lambda}}_i=\begin{pmatrix}\lambda & 0 & 0\\ 0 & r^{1/4}/\sqrt{\lambda} & 0\\ 0 & 0 & 1/(r^{1/4}\sqrt{\lambda})\end{pmatrix}. \tag{10}$$

The deformation gradient tensor must have $\det(\underline{\underline{\lambda}})=1$, so that the deformations are at constant density since the shear moduli governing shape change are about 10^{-4} times smaller than the bulk modulus governing volume change.

The model also predicts that the stress-strain curve for the elastomer should have different gradients in these three regions, with a much lower gradient in the middle region forming a stress plateau (see [2]). This stress prediction is confirmed over a huge range of strains; typical data is shown in Fig. 3. Since the model predicts all three stress gradients and also the position of the two kinks in the curve (five quantities) in terms of three underlying constants, it is already highly nontrivial. These five quantities and the form of the director rotation have already been shown to match the model predictions by several groups [6,13,15].

B. Semisoft response to small shears compounded with large strains

Using the geometry described in Fig. 1, we wish to calculate the apparent shear modulus for the final infinitesimal shear (C_5) as a function of the arbitrary finite stretch λ imposed during the first stage of the experiment. If after applying the initial stretch λ, causing an initial deformation $\underline{\underline{\lambda}}_i$ and the director to make an angle θ_o with the z axis, we then impose an additional infinitesimal shear $\underline{\underline{\lambda}}_2=\underline{\underline{\delta}}+\gamma\hat{\mathbf{x}}\hat{\mathbf{z}}$, which causes θ_o to change to $\theta_o+\delta\theta$, then, since both perturbations are small, we can expand the resulting free energy in powers of $\delta\theta$ and γ,

$$F=D\gamma^2+E\delta\theta^2+G\delta\theta\gamma. \tag{11}$$

There are no linear terms in this expansion because there is no spontaneous shear or director rotation. Minimizing this energy with respect to $\delta\theta$ gives $\delta\theta=-G\gamma/2E$. Putting this value back into F we can read off the apparent shear modulus C_5 as twice the coefficient of the quadratic term in γ,

$$C_5=2\left(D-\frac{G^2}{4E}\right). \tag{12}$$

In order to calculate C_5, we must evaluate Eq. (5) at a total deformation $\underline{\underline{\lambda}}=\underline{\underline{\lambda}}_2\cdot\underline{\underline{\lambda}}_i$ and director angle $\theta=\theta_o+\delta\theta$, expand the result to second order in γ and $\delta\theta$, and then read off the coefficients (D, G, and E) we need for Eq. (12). Since the $\underline{\underline{\lambda}}_i$ are large deformations, we must compound rather than add the two consecutive deformations (multiply the tensors). In the first region (below the strain threshold—$\lambda\leqslant\lambda_1$), we have

$$F=\frac{\mu}{2\lambda}\left\{(\lambda^3+\gamma^2 r)\left[1+\left(\frac{1}{r}-1\right)\sin^2\theta\right]+\alpha\lambda^3\sin^2\theta+2\gamma r\left(\frac{1}{r}-1\right)\sin\theta\cos\theta+r\left[1+\cos^2\theta\left(\frac{1}{r}-1\right)\right]+1\right\}. \tag{13}$$

Expanding this out around $\theta=0$ we can read off the coefficients we need for C_5 as

$$D = \frac{\mu r}{2\lambda},$$

$$E = \frac{\mu}{2\lambda}\left[\lambda^3\left(\frac{1}{r} - 1 + \alpha\right) - 1 + r\right],$$

$$G = \frac{\mu}{\lambda}(1 - r). \tag{14}$$

Substituting these expressions into Eq. (12) gives the apparent shear modulus before the semisoft threshold,

$$C_5(\lambda) = \frac{\mu r}{\lambda}\left(\frac{\lambda^3 - \lambda_1^3}{\lambda^3 - r\lambda_1^3}\right). \tag{15}$$

The calculation in the second region of the semisoft plateau ($\lambda_1 \leqslant \lambda \leqslant \sqrt{r}\lambda_1$) is more involved because of the more complicated deformations. Substituting the appropriate form for $\underline{\underline{\lambda}}_i$ [Eq. (8)] into the free energy, we find an F that is valid for arbitrary θ:

$$F = \frac{\mu}{2\lambda}\left\{\sin^2\theta(1-r)\left[\frac{\lambda^3}{r\lambda_1^3} + \left(\sqrt{\lambda}\lambda_{xz} + \gamma\sqrt{\frac{\lambda_1}{\lambda}}\right)^2\right] + \lambda^3 + \frac{\lambda}{\lambda_1} + r\left(\sqrt{\lambda}\lambda_{xz} + \gamma\sqrt{\frac{\lambda_1}{\lambda}}\right)^2 + [r + (1-r)\cos^2\theta]\frac{\lambda_1}{\lambda} + 2(1-r)\sin\theta\cos\theta\sqrt{\frac{\lambda_1}{\lambda}}\left(\sqrt{\lambda}\lambda_{xz} + \gamma\sqrt{\frac{\lambda_1}{\lambda}}\right)\right\}. \tag{16}$$

Expanding out about θ_o, we can extract the coefficients to calculate C_5:

$$\frac{2\lambda D}{\mu} = \sin^2\theta_o(1-r)\frac{\lambda_1}{\lambda} + r\frac{\lambda_1}{\lambda},$$

$$\frac{2\lambda E}{\mu} = \cos 2\theta_o(1-r)\left(\frac{\lambda^3}{\lambda_1^3 r} + \lambda\lambda_{xz}^2 - \frac{\lambda_1}{\lambda}\right) - 2\sin 2\theta_o(1-r)\sqrt{\lambda_1}\lambda_{xz},$$

$$\frac{2\lambda G}{\mu} = 2\sin 2\theta_o(1-r)\sqrt{\lambda_1}\lambda_{xz} + 2\cos 2\theta_o(1-r)\frac{\lambda_1}{\lambda}. \tag{17}$$

Calculating C_5 is now simply a matter of using Eqs. (8) and (9) to replace θ_o and λ_{xz} by λ in these expressions then compiling the expressions into C_5 using Eq. (12). The details of this manipulation can be found in the Appendix; the result is

$$C_5 = \frac{4\mu r[\beta^2(1+r) - \beta^4 - r]}{\lambda\beta^3(r-1)^2}, \tag{18}$$

where $\beta = \lambda/\lambda_1$.

In the region after the semisoft plateau, when the director rotation is complete ($\lambda > \sqrt{r}\lambda_1$), substituting the appropriate $\underline{\underline{\lambda}}_i$ [Eq. (10)] into the free energy gives

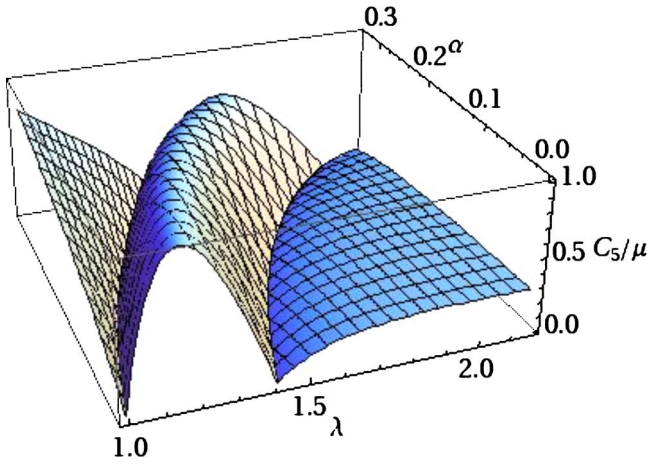

FIG. 4. (Color online) C_5 vs λ and α calculated with the chain anisotropy parameter $r=2$.

$$F = \frac{\mu}{2\lambda}\left[(\lambda^3 + \gamma^2\sqrt{r})\left(1 - \frac{r-1}{r}\sin^2\theta\right) + \alpha\lambda^3\sin^2\theta - \gamma\sqrt{r}\frac{r-1}{r}\sin 2\theta + \sqrt{r}\left(1 - \frac{r-1}{r}\cos^2\theta\right) + 1\right]. \tag{19}$$

Expanding this about $\theta = \pi/2$ gives the coefficients

$$D = \frac{\mu}{2\sqrt{r}\lambda},$$

$$E = \frac{\mu}{2\sqrt{r}\lambda}\left[\frac{\lambda^3}{\sqrt{r}}\left(1 - \frac{1}{r} - \alpha\right) + 1 - r\right],$$

$$G = \frac{\mu}{\sqrt{r}\lambda}(1-r), \tag{20}$$

which, when substituted into Eq. (12) give

$$C_5 = \frac{\mu}{\sqrt{r}\lambda}\left(\frac{\lambda^3 - r^{3/2}\lambda_1^3}{\lambda^3 - \sqrt{r}\lambda_1^3}\right). \tag{21}$$

The full graph of the apparent shear modulus (C_5) variation with λ and the strength of semisoftness α is shown in Fig. 4. A slice through this graph at constant α is shown in Fig. 5. The graphs clearly show kinks in C_5 along the zeros at the beginning and end of director rotation. Differentiating the form for $C_5(\lambda)$, it is straightforward to show that at the first kink $C_5 \propto |\lambda - \lambda_1|$ and at the second kink $C_5 \propto |\lambda - \sqrt{r}\lambda_1|$. The constants of proportionality in these relations are different on each side of each kink. This explicit form reproduces the expected zeros at the onset and end of director rotation. However, the full functional form is model-specific, so features such as the peak value, the ratio of the gradients on either side of the zero, and the position of the peak can all be used to test particular models.

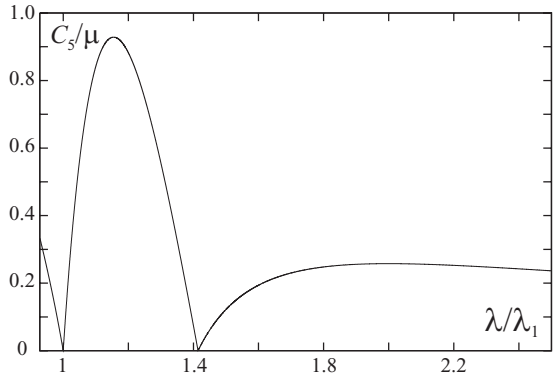

FIG. 5. C_5 vs reduced extension (λ/λ_1) calculated with the chain anisotropy parameter $r=2$ and $\alpha=0.1$.

IV. MODELS OF SEMISOFTNESS

In this section we consider the scope for models of semisoftness other than the compositional fluctuations model. We first show that, despite its initial derivation, the compositional fluctuations free energy is in fact the most general quadratic free energy that only manifestly contains one direction in both the initial and final states. We then show how recovering the ideal model amounts to assuming that there is an isotropic reference state. Finally, we consider the scope for other models that contain more directions and are not quadratic in the deformation tensor.

A. Generality of the compositional fluctuations form of the semisoft free energy density

The compositional fluctuations model of semisoftness breaks ideality by introducing a distribution of coupling strengths between the polymer backbone chains and the nematic mean field. Since there are other ways (for instance, by introducing aligned rigid-rod crosslinks), one could imagine breaking ideality, the success of this particular model in describing experimental data raises a question—is it simply the case that compositional fluctuations are the dominant cause of nonideality or is there an underlying reason why, whatever the microscopic cause of nonideality, the same or similar form of the semisoft free energy results? To address this question, we consider a sample of nonideal nematic elastomer that is subject to a deformation $\Lambda_{ij} \equiv \partial R_i / \partial x_j$ that takes it from a reference state ($\mathbf{x}$) to a target state ($\mathbf{R}$). Here we use $\underline{\underline{\Lambda}}$ rather than $\underline{\underline{\lambda}}$ because we reserve $\underline{\underline{\lambda}}$ for deformations from relaxed states, and this reference state may not be relaxed. If it is not relaxed, there will be a spontaneous relaxing deformation, $\underline{\underline{\Lambda}}_r$, to a relaxed state. Functions of $\underline{\underline{\Lambda}}$ can be recast in terms of deformations from the relaxed state ($\underline{\underline{\lambda}}$) by substituting

$$\underline{\underline{\Lambda}} = \underline{\underline{\lambda}} \cdot \underline{\underline{\Lambda}}_r. \tag{22}$$

The first subscript on Λ_{ij} (i) is clearly a target state subscript and should only be contracted with subscripts from other target state variables. The second (j) is a reference state subscript which must be contracted only with reference state subscripts if rotational invariance is to be observed. Therefore, the most general free energy we can write down that is quadratic in Λ is of the form

$$F = \sum_{i,j} \mathrm{Tr}(\underline{\underline{A}}_i \cdot \underline{\underline{\Lambda}}^T \cdot \underline{\underline{B}}_j \cdot \underline{\underline{\Lambda}}), \tag{23}$$

where the matrices $\underline{\underline{A}}_i$ are constructed out of reference state vectors and scalars, while the matrices $\underline{\underline{B}}_j$ are constructed out of target state scalars and vectors. If we assume that the reference state is characterized by a single direction $\hat{\mathbf{n}}_0$ and the final state by a single direction $\hat{\mathbf{n}}$ (so both states are uniaxial), this becomes

$$F = \mathrm{Tr}(H\underline{\underline{\Lambda}}^T\underline{\underline{\Lambda}} + J\hat{\mathbf{n}}_o\hat{\mathbf{n}}_o\underline{\underline{\Lambda}}^T\underline{\underline{\Lambda}} + K\hat{\mathbf{n}}_o\hat{\mathbf{n}}_o\underline{\underline{\Lambda}}^T\hat{\mathbf{n}}\hat{\mathbf{n}}\underline{\underline{\Lambda}} + L\underline{\underline{\Lambda}}^T\hat{\mathbf{n}}\hat{\mathbf{n}}\underline{\underline{\Lambda}}). \tag{24}$$

In general, this free energy will not be relaxed and will undergo a spontaneous deformation to a relaxed state. The relaxing deformation, $\underline{\underline{\Lambda}}_r$, must also be volume-preserving so it must have a determinant of 1. For the resulting free energy not to have any soft deformations, this spontaneous deformation must not break the uniaxial symmetry of the reference state. If it were to break this symmetry, there would be other equivalent deformations that break the same symmetry differently, leading to multiple relaxed states and soft deformations mapping between them. Experimentally, the spontaneous distortions of monodomain elastomers on changing conditions are always along the original director. Therefore, $\hat{\mathbf{n}}$ must be equal to $\hat{\mathbf{n}}_o$ and $\underline{\underline{\Lambda}}_r$ must be of the form

$$\underline{\underline{\Lambda}}_r = a\left[\underline{\underline{\delta}} + \left(\frac{1}{a^3} - 1\right)\hat{\mathbf{n}}_o\hat{\mathbf{n}}_o\right], \tag{25}$$

where a is a constant to be determined. Substituting this deformation into Eq. (24) and taking the trace gives

$$F = a^2\left(2H + \frac{H+J+K+L}{a^6}\right). \tag{26}$$

Minimizing this with respect to a we obtain the preferred value:

$$a^6 = \frac{H+J+K+L}{H}. \tag{27}$$

We can now recast the original free energy in terms of deformations away from the relaxed state, $\underline{\underline{\lambda}}$, by substituting $\underline{\underline{\Lambda}} = \underline{\underline{\lambda}} \cdot \underline{\underline{\Lambda}}_r$, giving

$$F = a^2\,\mathrm{Tr}\left[H\underline{\underline{\lambda}}^T\underline{\underline{\lambda}} + L\underline{\underline{\lambda}}^T\hat{\mathbf{n}}\hat{\mathbf{n}}\underline{\underline{\lambda}} + \left(\frac{J+H}{a^6} - H\right)\hat{\mathbf{n}}_o\hat{\mathbf{n}}_o\underline{\underline{\lambda}}^T\underline{\underline{\lambda}} + \left(\frac{K+L}{a^6} - L\right)\hat{\mathbf{n}}_o\hat{\mathbf{n}}_o\underline{\underline{\lambda}}^T\hat{\mathbf{n}}\hat{\mathbf{n}}\underline{\underline{\lambda}}\right]. \tag{28}$$

Inspecting this form, we see that relaxation has reduced the number of unknown constants in the theory from four to three because we can write

$$F = a^2\,\mathrm{Tr}[H\underline{\underline{\lambda}}^T\underline{\underline{\lambda}} + L\underline{\underline{\lambda}}^T\hat{\mathbf{n}}\hat{\mathbf{n}}\underline{\underline{\lambda}} + M\hat{\mathbf{n}}_o\hat{\mathbf{n}}_o\underline{\underline{\lambda}}^T\underline{\underline{\lambda}} - (M+L)\hat{\mathbf{n}}_o\hat{\mathbf{n}}_o\underline{\underline{\lambda}}^T\hat{\mathbf{n}}\hat{\mathbf{n}}\underline{\underline{\lambda}}], \tag{29}$$

where $M=(J+H)/a^6-H$. The coefficients in this free energy can be rewritten without loss of generality as

$$a^2H = \frac{1}{2}\mu,$$

$$a^2L = \frac{1}{2}\mu\left(\alpha + \frac{1}{r} - 1\right),$$

$$a^2M = \frac{1}{2}\mu(r-1). \tag{30}$$

Substituting these forms into F, we recover the form of the free energy identical to the expression stemming from the compositional fluctuations model, Eq. (5). Since this derivation is not microscopic, it does not provide microscopic interpretations of the quantities in F, in particular the identification of r as the degree of anisotropy of the second moment of the chain shape distribution is not strictly justified. However, since this identification is exact for the ideal model (Gaussian chains all with the same anisotropic second moment), r is likely to retain a very similar meaning in any microscopic nonideal model that tends to the ideal model (as apposed to just the ideal free energy) in its $\alpha \to 0$ limit.

B. Recovering ideality

The above equations can easily be inverted to find α, r, and μ in terms of H, J, K, and L giving

$$\mu = 2(H+J+K+L)^{1/3}H^{2/3},$$

$$r = \frac{H+J}{H+J+K+L},$$

$$\alpha = \frac{L}{H} - \frac{K+L}{H+J}. \tag{31}$$

Interestingly, if $K=J=0$ then $\alpha=0$ and the ideal elastomer free energy is recovered. Inspecting the original form of the free energy, we see that this corresponds to the reference state being isotropic because the terms that depend on $\hat{\mathbf{n}}_o\hat{\mathbf{n}}_o$ have been set to zero. This is a manifestation of the Golubovic-Lubensky theorem [5] that an isotropic state leads to soft modes of deformation. In this case, the spontaneous deformation does break symmetry because it introduces a direction $\hat{\mathbf{n}}_o$ into an otherwise isotropic system. More generally, $\alpha=0$ if

$$\frac{J}{H} = \frac{K}{L}, \tag{32}$$

which is equivalent to demanding that F factorizes to the generic form

$$F = \mathrm{Tr}[(N\underline{\underline{\delta}} + P\hat{\mathbf{n}}_o\hat{\mathbf{n}}_o)\underline{\underline{\Lambda}}^T(R\underline{\underline{\delta}} + U\hat{\mathbf{n}}\hat{\mathbf{n}})\underline{\underline{\Lambda}}]. \tag{33}$$

This F also has an isotropic state which can be demonstrated by substituting $\underline{\underline{\Lambda}} = \underline{\underline{\lambda}}(N\underline{\underline{\delta}} + P\hat{\mathbf{n}}_o\hat{\mathbf{n}}_o)^{-1/2}$, giving

$$F = \mathrm{Tr}[\underline{\underline{\lambda}}^T(R\underline{\underline{\delta}} + U\hat{\mathbf{n}}\hat{\mathbf{n}})\underline{\underline{\lambda}}], \tag{34}$$

which has no $\hat{\mathbf{n}}_o$ dependence. This means that any directions that can be defined in the state obtained by applying $\underline{\underline{\Lambda}} = (N\underline{\underline{\delta}} + P\hat{\mathbf{n}}_o\hat{\mathbf{n}}_o)^{-1/2}$ do not enter into the free energy of deformations imposed from this state. Therefore, this state is in effect isotropic.

C. Route to semisoftness by introducing another direction

The above argument demonstrates that nonideal elastomer theories are made by destroying the existence of an isotropic state, in accordance with the Golubovic-Lubensky theorem. Further, it shows that if this is done simply by introducing a *single* direction, typically $\hat{\mathbf{n}}$, into the reference state one must end up with the generic model, Eq. (5), or remain with the ideal model. However, this does not mean that there are no other nonideal models; it only means that in order to find them we must introduce new directions into the theory or deviate from the quadratic form in Eq. (24) by introducing terms that depend on symmetry-allowed variants of $\underline{\underline{\Lambda}}$. We can introduce a direction straightforwardly by defining a new reference state direction $\mathbf{k}_o$ and a corresponding final state vector $\mathbf{k}$. The vector $\mathbf{k}$ can either be a free direction that we minimize over for a given deformation (like $\hat{\mathbf{n}}$) or can be defined as a final state vector derived from the initial state vector through variants of $\underline{\underline{\Lambda}}$ such as $\underline{\underline{\Lambda}}\mathbf{k}_o$ or $\underline{\underline{\Lambda}}^{-T}\mathbf{k}_o$. This last possibility is how a vector area expressed by a normal to the plane would be expected to transform, provided $\det \underline{\underline{\Lambda}} = 1$. This is discussed at length under the theory of smectic elastomers in Ref. [2] (2007 edition).

Having introduced a new direction into the problem, it becomes much harder to write down a general form for F because, not only do we have to consider cross terms between the two direction in both states, we can also define various scalars (such as $\hat{\mathbf{n}}\cdot\mathbf{k}$ and $\mathbf{k}\cdot\mathbf{k}$) the coefficients of which could be functions of $\underline{\underline{\Lambda}}$. Also allowing terms that are not quadratic in $\underline{\underline{\Lambda}}$ leads to even more possible terms. Since relaxation only removes one degree of freedom from a system, these considerations lead us to conclude that, by including such terms, a large number of alternative models could be constructed if physical phenomena were to be found that the above generic semisoft free energy cannot explain.

A very simple example would be introducing a new direction $\mathbf{k}_o$ that is initially aligned with $\hat{\mathbf{n}}_o$ but, unlike $\hat{\mathbf{n}}$, transforms under the deformation $\underline{\underline{\Lambda}}$ as $\mathbf{k} = \underline{\underline{\Lambda}}^{-T}\mathbf{k}_o$. One possible relaxed free energy (because it is relaxed, we use $\underline{\underline{\lambda}}$ rather than $\underline{\underline{\Lambda}}$) constructed using this direction is

$$F = \frac{1}{2}\mu\,\mathrm{Tr}(\underline{\underline{\ell}}_o\cdot\underline{\underline{\lambda}}^T\cdot\underline{\underline{\ell}}^{-1}\cdot\underline{\underline{\lambda}}) - \alpha\left(\frac{\hat{\mathbf{n}}\cdot\lambda^{-T}\mathbf{k}_o}{|\underline{\underline{\lambda}}^{-T}\mathbf{k}_o|}\right), \tag{35}$$

which has a simple physical interpretation—the elastomer is semisoft because it contains regions of a weakly ordered Smectic A phase. For weak smectic order there would be a small energy penalty for rotating the director away from the current layer normal, $\hat{\mathbf{k}} \propto \lambda^{-T}\mathbf{k}_o$. Thus, the semisoft term in Eq. (35) is effectively $-\alpha(\hat{\mathbf{n}}\cdot\hat{\mathbf{k}})^2$.

Kundler and Finkelmann have observed (using x rays) embryonic regions of smectic order in macroscopically nematic elastomers and have termed such specimens cybotatctic nematic elastomers [8]. However, it has been observed in such systems with smectic fluctuations that the semisoft

behavior—that is, the precise form of the director rotation (from 0 to 90°, along with singular edges), the correlation between the length of the semisoft plateau and the magnitude of spontaneous thermal distortions, and the variation of semisoftness (and hence the initial threshold) with degree of smectic ordering—was well described [8] by the generic model.

V. CONCLUSIONS

We have shown that any theory including director rotation will lead to zeros in the apparent shear modulus (C_5) and kinks in the stress-strain curve (forming a stress-strain plateau) at the onset and end of director rotation. We have calculated this modulus as a function of preimposed strain for a particular model of semisoftness, and shown it does predict these zeros, but also predicts other features which could form the basis of further experimental tests. Finally, we have shown that this form of the semisoft free energy (derived from considering compositional fluctuations) is the most general quadratic nonideal free energy that can exist without explicitly including physical directions other than the nematic director in the final state. This suggests that the model is more general than its microscopic origin might suggest, which may explain its success to date in fitting various experimental data.

APPENDIX: ALGEBRAIC MANIPULATIONS BETWEEN EQS. (17) and (18)

Introducing $\beta=\lambda/\lambda_1$, we see immediately that substituting the expression for $\sin\theta_o$ [Eq. (8)] into the expression for C gives

$$\frac{2\lambda C}{\mu}=\frac{r}{\beta^3}. \tag{A1}$$

The expressions for E and F are more complicated, so it is worth considering them one part at a time. First we calculate $\sin 2\theta$ and $\cos 2\theta$:

$$\sin 2\theta = 2\sin\theta\sqrt{1-\sin^2\theta} \tag{A2}$$

$$=\frac{2\sqrt{r}}{r-1}\sqrt{\left(1-\frac{1}{\beta^2}\right)\left(\frac{r}{\beta^2}-1\right)} \tag{A3}$$

and

$$\cos 2\theta = 1-2\sin^2\theta = 1-\frac{2r}{r-1}\left(1-\frac{1}{\beta^2}\right). \tag{A4}$$

Second, we reexpress λ_{xz} as

$$\lambda_{xz}^2=\frac{1}{r\lambda\beta}(\beta^2-1)(r-\beta^2). \tag{A5}$$

We can now calculate two larger expressions needed for G:

$$2\sin 2\theta(1-r)\sqrt{\lambda_1}\lambda_{xz}=-\frac{4}{\beta^3}(\beta^2-1)(r-\beta^2) \tag{A6}$$

and

$$\frac{\lambda_1}{\lambda}2\cos 2\theta(1-r)=\frac{2+2r}{\beta}-\frac{4r}{\beta^3}. \tag{A7}$$

Adding these two expressions to find G, we get

$$\frac{2\lambda G}{\mu}=4\beta-2\frac{r+1}{\beta}. \tag{A8}$$

To find E we need to first compute one more fragment:

$$\cos 2\theta(1-r)\left(\frac{\beta^3}{r}+\lambda\lambda_{xz}^2\right)$$
$$=\frac{1}{r}\left(1+r-\frac{2r}{\beta^2}\right)\left(\beta^3+\frac{1}{\beta}(\beta^2-1)(r-\beta^2)\right), \tag{A9}$$

which multiplies out to give

$$=\beta\left(2+\frac{1}{r}+r\right)-\frac{3}{\beta}(r+1)+\frac{2r}{\beta^3}. \tag{A10}$$

Substituting these results for the three fragments back into Eq. (17), we see that

$$\frac{2\lambda E}{\mu}=\beta\left(r+\frac{1}{r}-2\right). \tag{A11}$$

We can now substitute these expressions for E, C, and G into Eq. (12) to find C_5,

$$C_5=\frac{\mu}{\lambda}\left(\frac{r}{\beta^3}-\frac{(2\beta^2-r-1)^2}{\beta^3\left(r+\frac{1}{r}-2\right)}\right), \tag{A12}$$

which simplifies to

$$C_5=\frac{4\mu}{\lambda\beta^3}\left(\frac{\beta^2(1+r)-\beta^4-r}{r+\frac{1}{r}-2}\right), \tag{A13}$$

the result stated in the paper.

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