Orientational Order and Finite Strain in Nematic Elastomers

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Nematic elastomers exhibit large, spontaneous shape changes at the transition from the high-temperature isotropic phase to the low-temperature nematic phase. These finite deformations are studied here in the context of a nonlinear, properly invariant, variational theory that couples the orientational order and elastic deformation. The theory is based on the minimization of a free-energy functional that consists of two contributions: a nematic one due to the interaction of the mesogenic units and an elastic one arising from the stretching of the cross-linked polymer chains. Suitable choices for these two contributions allow for large, reversible, spontaneous shape changes in which the elastic deformation can affect the isotropic-nematic transition temperature. The change in transition temperature as well as the magnitude of the resulting spontaneous deformation are illustrated for various parameter values. The theory includes soft elasticity as a special case but is not restricted to it.

I. INTRODUCTION

Liquid-crystal elastomers are a new class of materials with unusual properties made possible by interactions between the elasticity of the polymer network chains and the orientational order of the mesogenic groups. For example, nematic elastomers exhibit phase transitions, spontaneous shape changes, response to external fields, and microstructures such as striped domains[1–6].

Unusual properties were first predicted by de Gennes[7], who also proposed a linear continuum theory in terms of the nematic order tensor of the mesogenic groups and the macroscopic, infinitesimal strain tensor. Importantly, de Gennes included contributions to the free-energy density that couple rotations of the mesogenic groups to the elastomeric network strain. Subsequently, Jarry & Monnerie[8] and Deloche & Samulski[9] explored extensions of de Gennes's ideas for the special case of stretched uniaxial specimens. Brand & Pleiner[10] further generalized de Gennes's work to include dynamics as well as external electric and magnetic fields.

Halperin[11] discussed the importance of sample history on the subsequent response of nematic gels. Noting that the free-energy should be minimized in the configuration occupied at the time of cross-linking, Halperin[11] reasoned that the alignment of the mesogenic groups in the configuration at the time of cross-linking is also energetically important. To account for this possibility, he proposed a contribution to the free-energy density that couples the change in the scalar uniaxial order parameter to the infinitesimal strain tensor.

In an alternative approach, Warner et al.[12] extended classical Gaussian network theory to allow for anisotropic distributions of the end-to-end vectors of the polymer chains and derived the contribution to the free-energy density due to elastic distortions of the network. Bladon et al.[13,14] further generalized this work to obtain a full three-dimensional tensorial expression that allows for isotropic, uniaxial, and biaxial phases. The resulting expression, called "neo-classical," is nonlinear, properly invariant, and depends on the deformation gradient and a symmetric and positive-definite tensorial measure of the polymer chain shape, called the step-length (or conformation) tensor. In accord with Halperin's ideas concerning the importance of the reference configuration, the free-energy density also depends explicitly on the corresponding measure of the polymer chain shape in the reference configuration. Bladon et al.[13,14] took the additional energetic contribution from the mesogenic elements to be that of the uncrosslinked melt and assumed a nonlinear function of the mesogenic order-tensor, such as the usual quartic Landau–de Gennes expansion. Their total free-energy density is thus a function of the referential and current polymer network shape as well as the alignment of the mesogenic groups, where these quantities are represented by the deformation gradient, the referential and current conformation tensors, and the current mesogenic order-tensor. For special molecular models, the conformation tensor has been related to the mesogenic order-tensor (e.g., Bladon et al.[15], Finkelmann et al.[16]), in which case the free-energy density reduces to a complicated function of the deformation gradient, and the referential and current mesogenic order tensors. In general, however, there is no simple relation that expresses the coupling between the conformation tensor of the polymer backbone and the nematic order tensor of the mesogenic groups.

One of the striking aspects of the neo-classical theory is that it predicts soft elasticity, i.e., deformations involving large strains but costing zero energy[20]. As support for soft deformations and the neo-classical model, Verwey, Warner & Terentjev[21] interpreted the observed formation of stripes as a consequence of soft elasticity, which has been further investigated by DeSimone & Dolzmann[22] and Conti et al.[23,24]. The recent experiments of Martinoty et al.[25], however, appear to contradict the assumptions of soft elasticity. They also find that the linear theory of Brand & Pleiner[10], which makes no appeal to soft elasticity, adequately describes the small-strain, low-frequency shear behavior of nematic elastomers.

Liquid-crystal elastomers, like classical isotropic elastomers, are able to undergo deformations involving substantial strains. A nonlinear theory is therefore needed to fully account for the interaction of the large strains with the orientation. While there is evidence of softness in some nematic elastomers, the experiments of Martinoty et al.[25] indicate a need for a nonlinear theory not restricted to soft elasticity.

As one step in this direction, Verwey & Warner[26] used the idea of compositional fluctuations to generalize the neo-classical expression. The resulting expression includes a small perturbation that eliminates the perfect softness of the neo-classical expression. Warner & Terentjev[17] generalized this expression to one that is quadratic in the deformation gradient.

Recently Carlson et al.[27] showed that a certain tensor that arises naturally in the neo-classical free-energy density and involves an unusual combination of deformation gradient and the referential and current conformation tensors can be interpreted as a nonlinear relative strain tensor that indicates how the deformation of the elastomeric microstructure deviates from the overall macroscopic deformation. This led Fried & Sellers[28] to propose an alternative class of free-energy densities based on simple invariance arguments and a dependence upon *two strain tensors*: (i) the usual left Cauchy–Green tensor that describes the overall macroscopic strain and (ii) the relative microstructural strain tensor.

The neo-classical expression then appears as a special case in which the free-energy density is independent of the overall macroscopic strain so that only the relative strain of the microstructure provides an energy penalty. Importantly, the class of free-energy densities proposed by Fried & Sellers[28] incorporates energetic penalties associated with both the overall macroscopic strain and the relative microstructural strain. For such free-energy densities, the only truly soft deformations are trivial rigid-body rotations. In addition, Fried & Sellers[28] took the conformation tensor as the order parameter and, thus, eliminated the need for an additional coupling relation. This approach to nematic elastomers provides a simple, nonlinear alternative that is not restricted to soft elasticity but certainly allows for it as a special case.

Our goal here is to study the interaction of orientational order with nonlinear elasticity in nematic elastomers as exemplified by spontaneous shape changes. These unusual states of finite strain occur at the transition from the high-temperature isotropic phase to the low-temperature uniaxial phase. They have been used to measure material parameters, and they are currently under investigation for possible applications. We follow a nonlinear variational approach based on minimizing an appropriate free-energy functional. In particular, we illustrate the finite spontaneous deformations of a monodomain specimen for two special cases of the free-energy density proposed by Fried & Sellers[28]. That free-energy density consists of nematic and elastic contributions that couple the nonlinear strain to the orientation. This coupling in particular allows for the observed shape changes.

The theory also predicts a dependence of the transition temperature on the elastic moduli. The elastic energy of the spontaneous deformation raises the energy well of the deformed configuration, thereby increasing the stability of the initial configuration and thus lowering the isotropic-nematic transition temperature. We illustrate the change in transition temperature as well as the magnitude of the resulting spontaneous deformation for the two different cases. The unusual effects studied here arise directly from the dependence of the energy on the relative strain tensor and, thus, can be attributed to the presence of microstructure.

Recently, disordered nematic elastomers have been studied by Uchida[29,30]. For simplicity, we consider here only homogeneous monodomain samples and neglect any contribution to the free energy arising from random disorder.

II. GENERAL THEORY

Here we briefly summarize the theory of Fried & Sellers[28]. As we are considering deformations involving finite strains, it is important to distinguish between quantities that refer to the undeformed, reference configuration from those that refer to the deformed, current configuration (cf., e.g., Ogden[31]). The kinematic state of the elastomer is described by the macroscopic deformation $\boldsymbol{\chi}$ and a symmetric, positive-definite, second-order conformation tensor $\boldsymbol{A}$, which provides a measure of the polymer chain shape in the current configuration. We denote by $\boldsymbol{A}_*$ the corresponding measure of the chain shape in the reference configuration. The deformation $\boldsymbol{\chi}$ maps the region $\mathcal{B}_*$ of 3-dimensional space occupied by the body in the reference configuration onto the region $\mathcal{B}$ of 3-dimensional space occupied by the body in the current configuration. The conformation tensor $\boldsymbol{A}$ is defined as the ensemble average of the tensorial second moment of the polymer end-to-end vectors $\boldsymbol{r}$: $\boldsymbol{A} = \langle \boldsymbol{r} \otimes \boldsymbol{r} \rangle$. $\boldsymbol{A}$ is clearly symmetric and positive-definite. Denote by $\boldsymbol{F} = \mathsf{Grad}\boldsymbol{\chi}$ the macroscopic deformation gradient. $\boldsymbol{F}$ maps an infinitesimal material line element $d\boldsymbol{x}_*$ in $\mathcal{B}_*$ into a line element $d\boldsymbol{x} = \boldsymbol{F} d\boldsymbol{x}_*$ in $\mathcal{B}$. As is standard, we assume that the elastomer is incompressible, which requires that $\mathsf{det}\boldsymbol{F} = 1$.

A basic postulate of the theory is that the free-energy density ψ is determined by the deformation gradient $\boldsymbol{F}$ and the conformation tensor $\boldsymbol{A}$:

$$\psi = \hat{\psi}(\boldsymbol{F}, \boldsymbol{A}; \boldsymbol{A}_*). \tag{1}$$

The dependence on the reference configuration is represented by the referential conformation $\boldsymbol{A}_*$ and is indicated explicitly. This assumed form expresses the view that $\boldsymbol{F}$ and $\boldsymbol{A}$ provide a consistent and complete description of network distortion and chain shape in the current configuration. For main-chain elastomers, this assumption appears to be quite reasonable. For side-chain elastomers where the mesogenic units are pendant to a flexible backbone, the side-chain order can be different from the backbone order[16]. Importantly, $\hat{\psi}$ cannot be arbitrary as it is subject to the invariance requirements imposed by material symmetry and objectivity. As shown by Fried & Sellers[28], these requirements are met if and only if there exists a reduced free-energy density function $\tilde{\psi}$ such that

$$\hat{\psi}(\boldsymbol{F}, \boldsymbol{A}; \boldsymbol{A}_*) = \tilde{\psi}(\boldsymbol{F}\boldsymbol{F}^\top, \boldsymbol{A}^{-1}\boldsymbol{F}\boldsymbol{A}_*\boldsymbol{F}^\top, \boldsymbol{A}). \tag{2}$$

The result (2) has an appealing interpretation. It allows for a dependence on the left Cauchy–Green strain tensor $\boldsymbol{F}\boldsymbol{F}^\top$, which, as in the theory of rubber elasticity, serves as a nonlinear measure of overall macroscopic strain. It also allows for a dependence on the quantity $\boldsymbol{A}^{-1}\boldsymbol{F}\boldsymbol{A}_*\boldsymbol{F}^\top$, which we can interpret as a *relative strain tensor* (Carlson et al.[27], Fried & Sellers[28]). Note that, in a composite medium with anisotropic *material* microstructure, the microstructure will stretch and rotate with the macroscopic continuum. If, in particular, the microstructure is described by a symmetric and positive-definite tensor, say $\boldsymbol{M}$, the tensor $\boldsymbol{F}\boldsymbol{M}\boldsymbol{F}^\top$ describes the deformation of the microstructure as it stretches and rotates with the continuum. A nematic elastomer differs from a composite in that its microstructure is *nonmaterial* in the sense that the kinematics of $\boldsymbol{A}$ are independent of the macroscopic deformation. The quantity $\boldsymbol{A}^{-1}\boldsymbol{F}\boldsymbol{A}_*\boldsymbol{F}^\top$ is a natural nonlinear measure of the deformation of the microstructure relative to the macroscopic continuum. Thus, (2) shows that the free-energy density depends upon two distinct strain tensors (the overall macroscopic strain and the relative microstructural strain) and the current conformation tensor.

A standard assumption for nematic elastomers is that the free-energy density consists of two parts differing in their physical origin and in their form:

$$\psi = \psi_{\rm el} + \psi_{\rm n}. \tag{3}$$

The part $\psi_{\rm el}$ is due to the entropic elastic deformation of the network and expresses the coupling of the nematic order with the stretching of the cross-linked polymer chains. The other part $\psi_{\rm n}$ arises from the interaction of the mesogens and determines the stability of the elastomer phase in the reference configuration.

For $\psi_{\rm el}$, Fried & Sellers[28] proposed a simple expression linear in the two strain tensors:

$$\begin{aligned}\psi_{\rm el} = \frac{\mu_1}{2}\mathsf{tr}(\boldsymbol{F}\boldsymbol{F}^\top - \boldsymbol{I}) + \frac{\mu_2}{2}\big\{\mathsf{tr}(\boldsymbol{A}^{-1}\boldsymbol{F}\boldsymbol{A}_*\boldsymbol{F}^\top - \boldsymbol{I}) \\ - \log\det(\boldsymbol{A}^{-1}\boldsymbol{F}\boldsymbol{A}_*\boldsymbol{F}^\top)\big\},\end{aligned} \tag{4}$$

where μ_1 and μ_2 are nonnegative elastic moduli. This free-energy density vanishes in the reference configuration when $\boldsymbol{F} = \boldsymbol{I}$ and $\boldsymbol{A} = \boldsymbol{A}_*$. The logarithmic term is needed to give a vanishing internal body force in the reference configuration. In the isotropic case, where $\boldsymbol{A} = \boldsymbol{A}_* \propto \boldsymbol{I}$, (4) reduces to the classical neo-Hookean expression of rubber elasticity, with shear modulus $\mu = \mu_1 + \mu_2$. Further, when μ_1 vanishes, (4) corresponds to the neo-classical expression derived by Bladon et al.[13,14] in their extension of Gaussian network theory. Thus the neo-classical expression is seen to be a special case where the free-energy density is independent of the overall macroscopic strain $\boldsymbol{F}\boldsymbol{F}^\top$. For this special case, there is no elastic energy penalty for material deformations where the microstructure (represented by $\boldsymbol{A}$) stretches and rotates with the macroscopic continuum. Such deformations have been called soft as there is no resistance to the deformation. A non-zero μ_1 provides an energy penalty for the material deformations, thereby eliminating perfect softness. Without the term involving the logarithm, (4) can be viewed as a special case of the generic free-energy density function (7.50) introduced by Warner & Terentjev[17].

As in non-linear elasticity, additional, higher-order terms involving the two strain tensors can be included in the elastic energy. Here we consider only the simple relation (4) with two elastic moduli. Warner & Terentjev[17] have presented an alternative argument for the elastic energy in which they add an additional contribution quadratic in $\boldsymbol{F}$ to the neo-classical elastic energy density.

For the nematic free-energy density $\psi_{\rm n}$, Fried & Sellers[28] proposed a Landau–de Gennes power-series expansion in terms of an order parameter. As order parameter, they chose the traceless part of the conformation tensor:

$$\boldsymbol{A}_0 = \boldsymbol{A} - \tfrac{1}{3}(\mathsf{tr}\boldsymbol{A})\boldsymbol{I}. \tag{5}$$

Invariance requires that $\psi_{\rm n}$ be an isotropic function, so that it reduces to a function of the two scalar invariants $\mathsf{tr}(\boldsymbol{A}_0^2)$ and $\mathsf{tr}(\boldsymbol{A}_0^3)$. A standard fourth-order polynomial expansion of $\psi_{\rm n}$ in terms of $\boldsymbol{A}_0$ is

$$\psi_{\rm n} = \frac{\alpha}{2}\left(\frac{T}{T_c} - 1\right)\mathsf{tr}(\boldsymbol{A}_0^2) + \frac{\beta}{3}\mathsf{tr}(\boldsymbol{A}_0^3) + \frac{\gamma}{4}(\mathsf{tr}\boldsymbol{A}_0^2)^2, \tag{6}$$

where α, β, and γ are material constants and T_c is a fixed temperature (typically slightly below the transition temperature). For simplicity, the only temperature dependence is through the first term.

In the absence of external fields, the governing equilibrium equations are the Euler–Lagrange equations associated with minimizing the total free-energy $\int_{\mathcal{B}_*}\tilde{\psi}\,dv$ in conjunction with representations (3), (4), and (6). The resulting equations allow for biaxial, uniaxial, and isotropic phases. In the sequel we assume uniaxial symmetry with variable degree of alignment, an assumption corresponding to common experimental situations.

III. UNIAXIAL SYMMETRY

We now focus on applications involving uniaxial symmetry. In so doing, we consider two models. The most basic of these has been used in studies on the effect of deformation on the striping instability (DeSimone & Dolzmann[22] and Conti et al.[23,24]). As this model may not accurately reflect the changes in the microstructure over a large range of temperatures, we also consider an alternative model where the nematic elastomer is treated as a freely-jointed chain (e.g., Finkelmann et al.[16]).

A. Basic model

DeSimone & Dolzmann[22] and Conti et al.[23,24] considered nematic elastomers subject to the constraint $\mathsf{det}\boldsymbol{A} = \mathsf{det}\boldsymbol{A}_*$. Essentially, this normalization imposes the requirement that the volume occupied by a generic polymer chain remains unchanged regardless of shape changes and, thus, embodies what might be considered a constraint of microstructural incompressibility. In this case, the last term in (4) vanishes. Further, when such a material has uniaxial symmetry in both the reference and deformed configurations, the conformation tensors can be expressed as

$$\left.\begin{aligned} \boldsymbol{A} &= a^{-1/3}(\boldsymbol{I} + (a-1)\boldsymbol{n}\otimes\boldsymbol{n}),\\ \boldsymbol{A}_* &= a_*^{-1/3}(\boldsymbol{I} + (a_*-1)\boldsymbol{n}_*\otimes\boldsymbol{n}_*),\end{aligned}\right\} \tag{7}$$

where a is scalar a measure of the uniaxial alignment in the current configuration and $\boldsymbol{n}$ is the uniaxial director. The quantities a and $\boldsymbol{n}$ appearing in $(7)_1$ satisfy $a > 0$ and $|\boldsymbol{n}| = 1$, with $a < 1$ being the oblate phase, $a > 1$ the prolate phase, and $a = 1$ the isotropic phase. The corresponding quantities evaluated in the reference configuration are denoted by a_* and $\boldsymbol{n}_*$. Note that the representations for $\boldsymbol{A}$ and $\boldsymbol{A}_*$ in (7) are normalized with $\mathsf{det}\boldsymbol{A} = \mathsf{det}\boldsymbol{A}_* = 1$. We also have

$$\left.\begin{aligned} \boldsymbol{A}^{-1} &= a^{1/3}\left(\boldsymbol{I} + (a^{-1}-1)\boldsymbol{n}\otimes\boldsymbol{n}\right),\\ \boldsymbol{A}_0 &= a^{-1/3}(a-1)(\boldsymbol{n}\otimes\boldsymbol{n} - \tfrac{1}{3}\boldsymbol{I}).\end{aligned}\right\} \tag{8}$$

Substitution into (4) and (6) yields the explicit relations valid for uniaxial phases

$$\begin{aligned} \psi_{\mathrm{el}} = \tfrac{1}{2}\mu_1\{|\boldsymbol{F}|^2 - 3\} + \tfrac{1}{2}\mu_2(a/a_*)^{1/3}\{|\boldsymbol{F}|^2 \\ + (a^{-1}-1)|\boldsymbol{F}^{\top}\boldsymbol{n}|^2 + (a_*-1)|\boldsymbol{F}\boldsymbol{n}_*|^2 \\ + (a_*-1)(a^{-1}-1)|\boldsymbol{n}\cdot\boldsymbol{F}\boldsymbol{n}_*|^2 - 3\} \end{aligned} \tag{9}$$

and

$$\psi_{\mathrm{n}} = \frac{(a-1)^2}{a^{2/3}}\left\{\frac{\alpha}{3}\left(\frac{T}{T_c} - 1\right) + \frac{2\beta(a-1)}{27a^{1/3}} + \frac{\gamma(a-1)^2}{9a^{2/3}}\right\}. \tag{10}$$

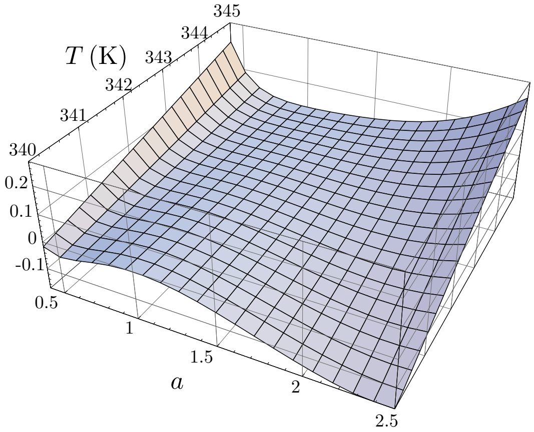

FIG. 1: The nematic contribution ψ_{n} to the free-energy density as a function of temperature T and order parameter a. At high temperatures, the free-energy density has a single minimum at the isotropic phase $a = 1$. At low temperatures, there are two relative minima with the absolute minimum at the prolate phase $a > 1$.

The governing Euler–Lagrange equations become:

$$\left.\begin{aligned} \mathsf{Div}\left(\frac{\partial\psi}{\partial\boldsymbol{F}}\right) &= \boldsymbol{F}^{\top}\mathsf{Grad}p,\\ (\boldsymbol{I} - \boldsymbol{n}\otimes\boldsymbol{n})\frac{\partial\psi}{\partial\boldsymbol{n}} &= \boldsymbol{0},\\ \frac{\partial\psi}{\partial a} &= 0,\end{aligned}\right\} \tag{11}$$

in conjunction with representations (9) and (10). The Lagrange multiplier p in the mechanical force-balance $(11)_1$ arises from the constraint $\mathsf{det}\boldsymbol{F} = 1$ of macroscopic incompressibility. In particular, we can identify the Piola stress as $\boldsymbol{S} = -p\boldsymbol{I} + \partial\psi/\partial\boldsymbol{F}$. Further, the projection operator $\boldsymbol{I} - \boldsymbol{n}\otimes\boldsymbol{n}$ in the director equation $(11)_2$ arises from the director constraint $|\boldsymbol{n}| = 1$. The last equation $(11)_3$ arises from variations in the parameter a.

B. Freely-jointed chain

We now consider an alternative model that allows for microscopic volume changes. For a freely-jointed chain, Finkelmann et al.[16] relate the conformation tensor $\boldsymbol{A}$ to the classical order tensor $\boldsymbol{S}$ of the mesogens. In particular, for mesogens with length normalized to unity,

$$\boldsymbol{A} = \boldsymbol{I} + 3\boldsymbol{S}. \tag{12}$$

And in the uniaxial case[33], $\boldsymbol{S} = S(\boldsymbol{n}\otimes\boldsymbol{n} - \tfrac{1}{3}\boldsymbol{I})$, with $S = \langle P_2(\cos\theta)\rangle$.

Since $\boldsymbol{S}$ is traceless, (12) implies the constraint $\mathsf{tr}\boldsymbol{A} =$

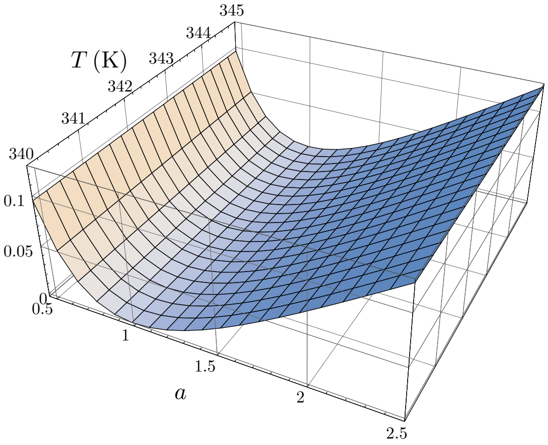

FIG. 2: The elastic contribution ψ_e to the free-energy density, due to the spontaneous elastic deformation as a function of temperature and order parameter. Here, $\mu_1 = \mu_2 =$ constant, so that explicit temperature dependence is absent. The minimum is at the isotropic reference configuration $a = a_* = 1$.

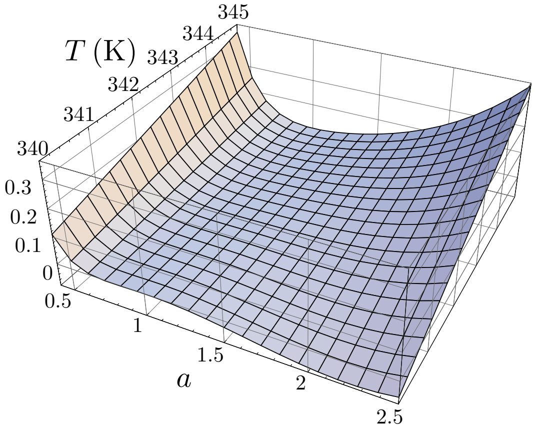

FIG. 3: The total free-energy density ψ as a function of temperature T and order parameter a for the basic model. For the assumed parameter values, the nematic contribution dominates the elastic contribution except in the vicinity of the transition temperature.

3. Furthermore, we have the results:

$$\left.\begin{aligned} \boldsymbol{A} &= (1-S)\boldsymbol{I} + 3S\boldsymbol{n}\otimes\boldsymbol{n}, \\ \boldsymbol{A}_0 &= 3\boldsymbol{S}, \\ \boldsymbol{A}^{-1} &= (1-S)^{-1}(\boldsymbol{I} - 3S(1+2S)^{-1}\boldsymbol{n}\otimes\boldsymbol{n}), \\ \det\boldsymbol{A} &= (1-S)^2(1+2S). \end{aligned}\right\} \qquad (13)$$

Analogous results relate $\boldsymbol{A}_*$ to the order tensor $\boldsymbol{S}_* = S_*(\boldsymbol{n}_*\otimes\boldsymbol{n}_* - \frac{1}{3}\boldsymbol{I})$ in the reference configuration. Importantly, $\det\boldsymbol{A}_*$ is equal to $(1-S_*)^2(1+2S_*)$ and, thus, generally differs from $\det\boldsymbol{A} = (1-S)^2(1+2S)$.

In particular, the relation (12) allows one to replace the dependence of the free energy on $\boldsymbol{A}$ by $\boldsymbol{S}$. The two contributions to the free-energy density take the form:

$$\psi_\mathrm{n} = S^2\left\{3\alpha\left(\frac{T}{T_c} - 1\right) + 2\beta S + 9\gamma S^2\right\}, \qquad (14)$$

and

$$\begin{aligned} \psi_\mathrm{el} = \tfrac{1}{2}\mu_1\big\{|\boldsymbol{F}|^2 - 3\big\} + \frac{\mu_2(1-S_*)}{2(1-S)}\bigg\{&|\boldsymbol{F}|^2 \\ &- \frac{3S}{1+2S}|\boldsymbol{F}^\top\boldsymbol{n}|^2 + \frac{3S_*}{1-S_*}|\boldsymbol{F}\boldsymbol{n}_*|^2 \\ &- \frac{9SS_*}{(1-S_*)(1+2S)}|\boldsymbol{n}\cdot\boldsymbol{F}\boldsymbol{n}_*|^2 - 3\bigg\} \\ &- \tfrac{1}{2}\mu_2\log\frac{(1-S_*)^2(1+2S_*)}{(1-S)^2(1+2S)}. \qquad (15) \end{aligned}$$

In this case, the governing Euler–Lagrange equations are $(11)_{1,2}$ and

$$\frac{\partial\psi}{\partial S} = 0, \qquad (16)$$

in conjunction with (14) and (15).

Pereira & Warner[19] and Warner & Terentjev[17] discuss in detail how the material parameters appearing above can be related to experiments on the specific heats, the order parameter curve, and the phase transition temperature.

C. Relation between the two models

The two models are based on different constitutive assumptions, so that they can imply different behavior, for example $\det\boldsymbol{A} \neq \det\boldsymbol{A}_*$ for the freely-jointed chain. However, by (15), it follows that for the model based on the freely-jointed chain, $\det\boldsymbol{A} = \det\boldsymbol{A}_* + O(S^2 - S_*^2)$ when $S \sim S_*$. Thus, if the order parameter S in the current configuration differs only slightly from that S_* in the reference configuration, the constraint $\det\boldsymbol{A} = \det\boldsymbol{A}_*$ underlying the basic model is met. Furthermore, by (7), it follows that for the model based on microscopic incompressibility, $\operatorname{tr}\boldsymbol{A} \to 3$ as $a \to 1$, which is consistent with $(15)_1$ for all S. Thus we see that the freely-jointed model and the basic model become consistent in the case of weak deviations between the alignment S and its referential counterpart S_*. In this limit, the two models then show similar behavior.

IV. EXAMPLE: SPONTANEOUS SHAPE CHANGES

Nematic elastomers are known to exhibit spontaneous shape changes at the transition from the high-temperature isotropic phase to the low-temperature nematic phase. These states of large strain can be easily modeled with the above variational theory. Here, we

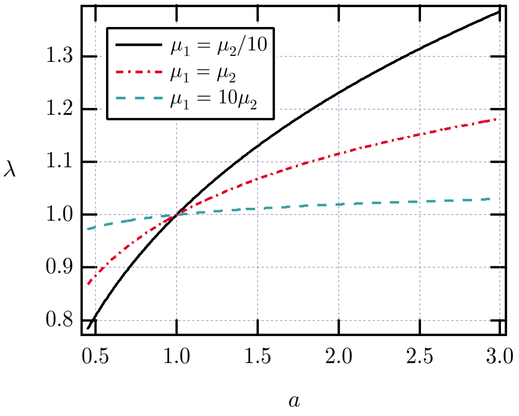

FIG. 4: The spontaneous stretch λ as a function of the order parameter a from (21). The largest strains occur when $\mu_2 \gg \mu_1$. For $\mu_2 \ll \mu_1$, the free-energy density approximates that of a neo-Hookean material, so that the spontaneous shape changes become less significant.

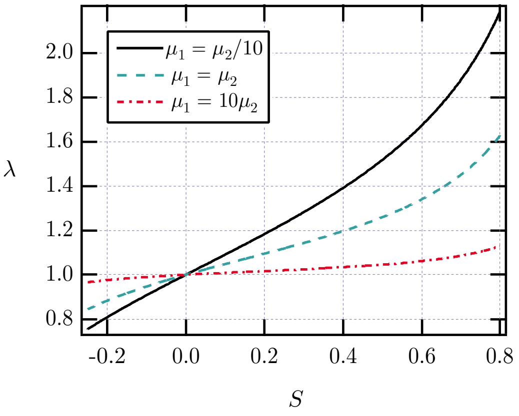

FIG. 5: The spontaneous stretch λ as a function of the order parameter S from (22). Again, the largest strains occur when $\mu_2 \gg \mu_1$.

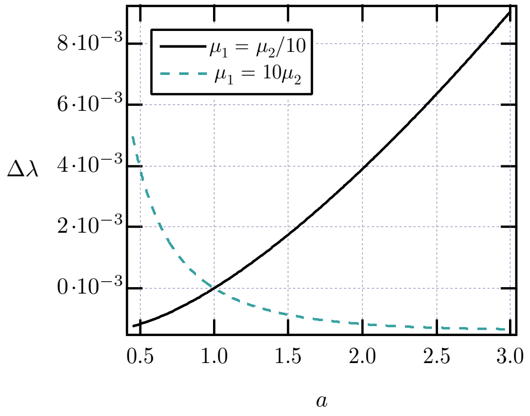

FIG. 6: The relative stretch $\Delta\lambda = (\lambda - \lambda_{\text{approx}})/\lambda$ as given by (21) and the asymptotic formulas (23). When the ratio of the elastic moduli is small, the expansions provide an excellent approximation.

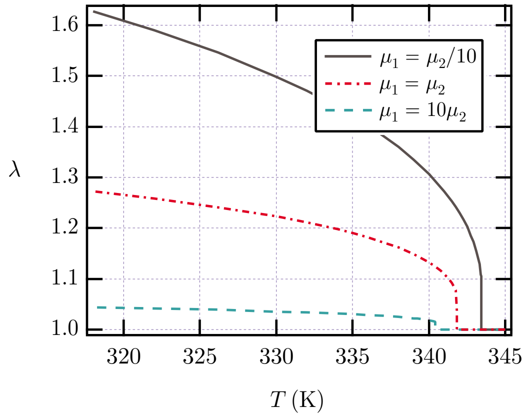

FIG. 7: The spontaneous stretch λ as a function of temperature T for the basic model. For fixed ψ_{n}, increasing the ratio μ_2/μ_1 increases the transition temperature.

consider a nematic elastomer sample initially in the high-temperature isotropic phase. In terms of the order parameters, we have $a_* = 1$ and $\boldsymbol{A}_* = \boldsymbol{I}$ for the basic model or $S_* = 0$ and $\boldsymbol{S}_* = \boldsymbol{0}$ for the freely-jointed chain model. We further assume that the temperature of the reference configuration is sufficiently above the transition point so that the reference configuration is stable with $a = a_* = 1$ ($S = S_* = 0$) the absolute minimum of the free-energy density. We further assume that, as the temperature is lowered, the elastomer transforms to the prolate uniaxial phase—so that $a > 1$ ($S > 0$), which requires $\beta < 0$. In this case, the sample extends without rotation in the direction of the director and contracts in the direction orthogonal to the director. Let $\lambda > 0$ be the stretch in the direction of the director $\boldsymbol{n}$ (which, in the present discussion, equals $\boldsymbol{n}_*$). The deformation gradient of the spontaneous shape change becomes

$$\boldsymbol{F} = \lambda^{-1/2}\boldsymbol{I} + (\lambda - \lambda^{-1/2})\boldsymbol{n}_*\otimes\boldsymbol{n}_*. \tag{17}$$

Substituting (17) in (9), we obtain

$$\psi_{\text{el}} = \tfrac{1}{2}(\mu_1 + \mu_2 a^{-2/3})\lambda^2 + (\mu_1 + \mu_2 a^{1/3})\lambda^{-1} - \tfrac{3}{2}(\mu_1 + \mu_2) \tag{18}$$

for the basic model and

$$\psi_{\text{el}} = \frac{1}{2}\left(\mu_1 + \frac{\mu_2}{1+2S}\right)\lambda^2 + \left(\mu_1 + \frac{\mu_2}{1-S}\right)\lambda^{-1} - \frac{3}{2}(\mu_1 + \mu_2) + \frac{\mu_2}{2}\log\left\{(1+2S)(1-S)^2\right\} \tag{19}$$

for the freely-jointed chain model.

Figures 1–3 depict the nematic contribution ψ_{n}, the elastic contribution ψ_{el} and total free-energy density ψ for this special case of the basic model. At high temperatures ψ_{n} has a single minimum at the isotropic phase

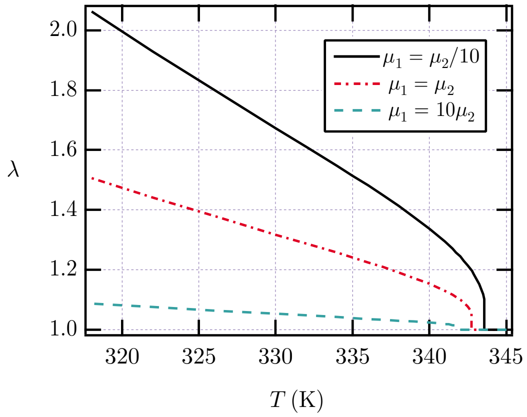

FIG. 8: The spontaneous stretch λ as a function of temperature for the freely-jointed chain model. In contrast to the basic model, the stretch is asymptotically linear as the temperature decreases. The larger strains are due to the nonvanishing of the logarithmic term in the elastic energy (15). Further, the shift in transition temperature as well as the jump in λ is less for the freely-jointed chain model.

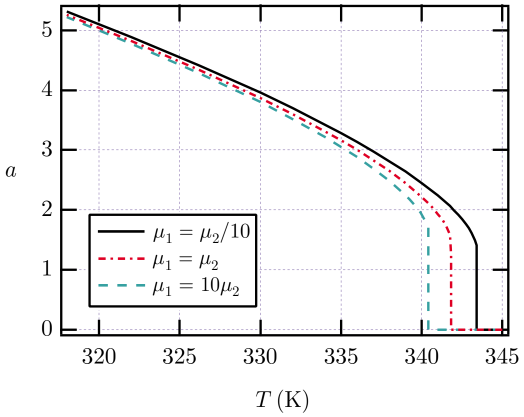

FIG. 9: The order parameter a as a function of temperature for the basic model. The elastic moduli have little effect on the jump in a at the transition temperature. Also a tends to a value independent of the ratio of the elastic moduli as the temperature decreases.

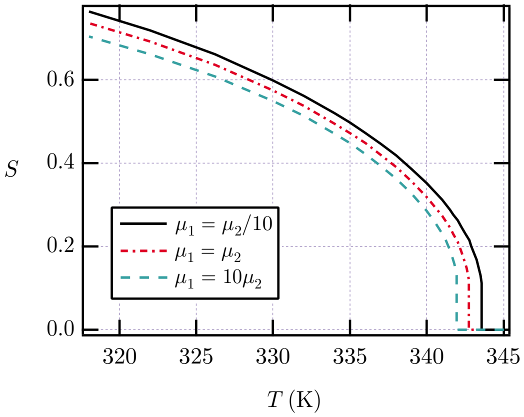

FIG. 10: The order parameter S as a function of temperature for the freely-jointed chain model. In contrast to the basic model, S does not tend to a value independent of the ratio of the elastic moduli as the temperature decreases.

$a = 1$. At sufficiently low temperatures ψ_{n} has two relative minima corresponding to the prolate and oblate phases. For the assumed parameter values[34], the prolate phase $a > 1$ has lower energy. In the absence of any deformation, the stable phase would correspond to the absolute minimum of ψ_{n}. Figure 2 shows that the elastic contribution ψ_{el} has a single minimum at the reference configuration, here taken to be the isotropic phase[35]. The effect of ψ_{el} here is therefore to penalize changes from the isotropic phase. A shape change due to the phase transition may consequently increase the total free-energy density, which can alter the location and relative depths of the energy wells. In particular, the transition temperature can be altered. The more ψ_{n} dominates ψ_{el}, however, the smaller is the effect on the transition temperature.

We further assume that the elastomer is subjected only to the hydrostatic pressure (with Cauchy stress tensor $-p\boldsymbol{I}$), which requires that

$$\frac{\partial \psi}{\partial \lambda} = 0. \tag{20}$$

Consequently the mechanical force balance $(11)_1$ is automatically satisfied. Solving (20) for λ yields

$$\lambda^3 = \frac{\mu_1 + \mu_2 a^{1/3}}{\mu_1 + \mu_2 a^{-2/3}} \tag{21}$$

for the basic model and

$$\lambda^3 = \frac{\mu_1 + \mu_2 (1 - S)^{-1}}{\mu_1 + \mu_2 (1 + 2S)^{-1}} \tag{22}$$

for the the freely-jointed chain model, which shows that the spontaneous stretch is coupled to the elastic moduli and the order parameter. In view of (21), the spontaneous stretch λ is nontrivial only if the coupling term in the elastic free-energy density is nonzero ($\mu_2 \neq 0$) and the phase changes ($a \neq 1$ or $S \neq 0$).

Figures 4 and 5 illustrate the spontaneous stretch λ for various values of the ratio μ_1/μ_2 for the two models. In both cases, the stretch λ is very sensitive to this ratio. When $\mu_1 \gg \mu_2$, λ remains close to 1, so that the shape change is small. In this case, the free-energy density differs little from that of a neo-Hookean material (for which a spontaneous shape change is impossible). On the other hand, when $\mu_2 \gg \mu_1$, the stretch λ can reach 1.6 or more for highly aligned elastomers in the prolate phase. It is the presence of the term involving μ_2 that allows for the spontaneous shape change. The larger μ_2 is relative to μ_1, the larger the spontaneous stretch at the transition.

These two asymptotic cases can be of practical interest. For example, when $\mu_2 \ll \mu_1$, the elastomer is weakly nematic and the elastic free energy deviates slightly from that of an isotropic neo-Hookean material. Alternatively, soft elasticity implies that $\mu_1 \ll \mu_2$. The result (21) can be easily approximated in these two limiting cases.

$$\left.\begin{aligned} \lambda^3 &= a + a^{2/3}(1-a)\frac{\mu_1}{\mu_2} + o\left(\frac{\mu_1}{\mu_2}\right); \\ \lambda^3 &= 1 + a^{1/3}(1-a^{-1})\frac{\mu_2}{\mu_1} + o\left(\frac{\mu_2}{\mu_1}\right). \end{aligned}\right\} \qquad (23)$$

Figure 6 shows that the expressions (23) provide very good approximations to the stretch when the appropriate ratio of the moduli μ_1 and μ_2 is small.

For the two limiting cases exhibited in (23), the relevant ratio of μ_1 and μ_2 can be related to measurable parameters. Assuming that $a \neq 1$ for the basic model, we obtain

$$\left.\begin{aligned} \frac{\mu_1}{\mu_2} &\approx \frac{\lambda^3 - a}{a^{2/3}(1-a)}, & \frac{\mu_1}{\mu_2} &\ll 1; \\ \frac{\mu_2}{\mu_1} &\approx \frac{\lambda^3 - 1}{a^{1/3}(1-a^{-1})}, & \frac{\mu_1}{\mu_2} &\gg 1. \end{aligned}\right\} \qquad (24)$$

Similar relations can also be obtained from (22) in terms of the order parameter S for the freely-jointed chain:

$$\left.\begin{aligned} \frac{\mu_1}{\mu_2} &\approx \frac{\lambda^3(S-1)+1+2S}{3S(1+2S)}, & \frac{\mu_1}{\mu_2} &\ll 1; \\ \frac{\mu_2}{\mu_1} &\approx \frac{\lambda^3 - 1}{(1-S)^{-1} - (1+2S)^{-1}}, & \frac{\mu_1}{\mu_2} &\gg 1. \end{aligned}\right\} \qquad (25)$$

As the elastic moduli must be non-negative, the theory places restrictions on possible stretches λ and order parameters. Consider, for example, $(24)_1$. For $\lambda > 1$, $(24)_1$ requires that $\lambda < a^{1/3}$ in the prolate phase $a > 1$. However, for $0 < \lambda < 1$, $(24)_1$ requires $\lambda > a^{1/3}$ in the oblate phase $a < 1$. Similar restrictions follow from $(24)_2$. It is not yet clear if either of the limiting cases leading to (23) and (24) can be expected in general.

It is easily seen that the Euler–Lagrange equation $(11)_2$ is automatically satisfied with the deformation gradient $\boldsymbol{F}$ is as given in (17) and when $\boldsymbol{n} = \boldsymbol{n}_*$. The only equation remaining to be solved is $(11)_3$ or (16), which provides an additional relation involving the appropriate order parameter and the stretch λ. In conjunction with (21), the spontaneous stretch can then be determined as a function of the temperature T. Numerical solutions of the full equations for various parameters are given in Figures 7 through 10, which illustrate the different responses of the two models for different ratios of elastic moduli.

V. DISCUSSION

The original linear theory of de Gennes[7] allowed for spontaneous strains but that was restricted to infinitesimal strains. Observed strains, however, can be 200% or more. To adequately describe such large strains, a properly invariant nonlinear theory is needed.

The variational theory proposed here provides a consistent, nonlinear description of the mechanical interaction of deformation and orientation in nematic elastomers. It presumes the existence of a free-energy density depending on the deformation gradient and the conformation tensor. Proposed constitutive expressions for the nematic and elastic contributions to the free-energy density capture well the phase changes as well as the large, spontaneous shape changes observed in nematic elastomers. The theory also predicts an effect of the deformation on the transition temperature. As the theory involves only the deformation gradient and the conformation tensor, no additional closure relation is needed, although a closure relation can be introduced when available for special cases such as the freely-jointed chain. The theory is, furthermore, not restricted to soft elasticity, although soft

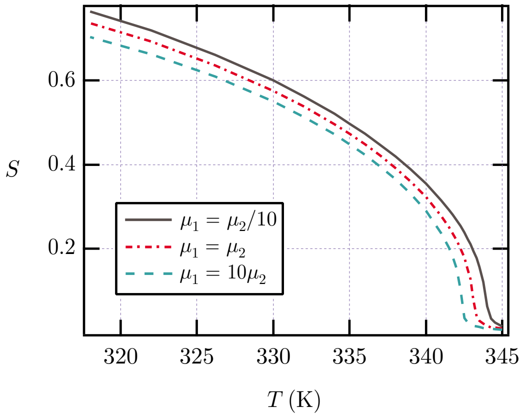

FIG. 11: The order parameter S as a function of temperature for the freely-jointed chain model. A smooth transition is obtained by including a linear term in the free-energy density.

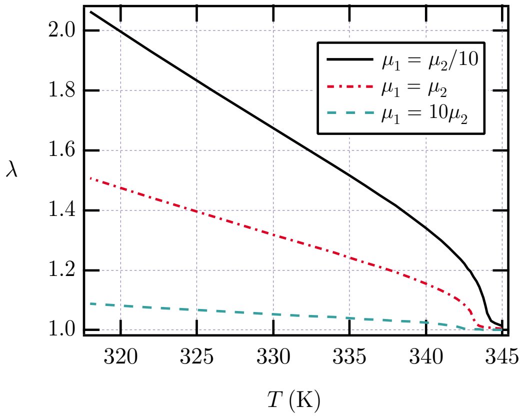

FIG. 12: The spontaneous stretch λ as a function of temperature T for the freely-jointed chain model. A smooth transition is obtained by including a linear term in the free-energy density.

elasticity is included as a special case ($\mu_1 = 0$). Additional higher-order terms in the strain tensors can also be systematically included, though for simplicity we have not done so here.

Of key importance in the theory is the elastic modulus μ_2, which arises from the presence of microstructure. Both spontaneous deformations and a shift in the transition temperature occur only when μ_2 is nonzero. In particular, the ratio of the two elastic moduli determines the extent of the spontaneous deformation. The greater μ_2 is in comparison to μ_1 the larger is the spontaneous strain as well as the shift in transition temperature. The presence of microstructure that can deform independently of the overall macroscopic deformation therefore induces the unusual properties of nematic elastomers.

The theory predicts sharp transitions with jumps in the spontaneous stretch and order parameter. Experimental data indicate however that the actual transitions are smooth. Such discrepancies led Pereira & Warner[19] to suggest that the elastomer behaves as if it were under effective external fields, which are however internal in origin. This motivated them to include a term linear in S in the energy, as would be expected if an external field were present. They also suggested that the additional contribution to the elastic energy ψ_{el} proposed by Verwey & Warner[26] would give rise to such a linear term. As shown by Pereira & Warner[19], however, this extra linear term vanishes for the case where the elastomer is crosslinked in the isotropic state, which is the problem studied here.

Alternatively, Selinger et al.[32] attribute the smooth transition to heterogeneities arising from quenched disorder. The considered a Gaussian distribution of transition temperatures and obtained a good fit to the data over a large range of temperatures. Further, the presence of heterogeneities would imply spatial gradients in the order parameters, which may also contribute to the free energy and affect the sharpness of the transition. At this point, the exact cause of the smooth transitions is unclear. Experimentally, additional contributions to the free energy appear be important and could arise from various effects. Figures 11 and 12 illustrate the effect of including a small, ad hoc linear term for the freely-jointed chain model. Clearly the effect of such a term is to smooth the transition. A similar result holds for the basic model.

For main-chain elastomers, the chain elements composing the backbone are the mesogenic units. Thus the order of the backbone is determined by the order of the mesogenic units. For side-chain elastomers, the mesogenic units are typically rods pendant to a flexible backbone, so that the relation between the backbone order and the order in the mesogenic side-chain units is unknown. This is one of the difficulties with the interpretation of data for side-chain elastomers. If the birefringence is determined mainly by the polarisable side chains, then measurements of the birefringence would only provide the order of the side-chain units. The conformation tensor $\boldsymbol{A}$ is a measure, however, of the backbone order. Our theory is based on $\boldsymbol{A}$ as the measure of the microstructure, and hence neglects this complication. Finkelmann et al.[16] addressed this problem by assuming a linear relation between the two measures of order. Assuming that μ_2 was the only modulus in the elastic energy (neo-classical model), they inverted (22) to obtain the backbone order as a function of the measured spontaneous stretch. Comparison to birefringence measurements supported the linear assumption for this special model. The effect of a more general model of the elastic energy with additional moduli was not discussed. As we have shown, however, the ratio of the moduli can significantly affect the spontaneous stretch and could be important in the interpretation of the data.

Acknowledgments

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[34] The parameters used here are those used by Warner & Terentjev[17], p. 18, and Pereira & Warner[19].

[35] Here, (21) has been used to reduce ψ_{el} to a function of a and T.

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1035	Kasimov, A. R., and D. S. Stewart	On the dynamics of self-sustained one-dimensional detonations: A numerical study in the shock-attached frame—*Physics of Fluids* (submitted)	Nov. 2003
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1037	Fried, E., and M. E. Gurtin	The unifying nature of the configurational force balance—*Mechanics of Material Forces* (P. Steinmann and G. A. Maugin, eds.), in press (2003)	Dec. 2003
1038	Panat, R., K. J. Hsia, and J. W. Oldham	Rumpling instability in thermal barrier systems under isothermal conditions in vacuum—*Philosophical Magazine*, in press (2004)	Dec. 2003
1039	Cermelli, P., E. Fried, and M. E. Gurtin	Sharp-interface nematic–isotropic phase transitions without flow—*Archive for Rational Mechanics and Analysis* **174**, 151–178 (2004)	Dec. 2003
1040	Yoo, S., and D. S. Stewart	A hybrid level-set method in two and three dimensions for modeling detonation and combustion problems in complex geometries—*Combustion Theory and Modeling* (submitted)	Feb. 2004
1041	Dienberg, C. E., S. E. Ott-Monsivais, J. L. Ranchero, A. A. Rzeszutko, and C. L. Winter	Proceedings of the Fifth Annual Research Conference in Mechanics (April 2003), TAM Department, UIUC (E. N. Brown, ed.)	Feb. 2004
1042	Kasimov, A. R., and D. S. Stewart	Asymptotic theory of ignition and failure of self-sustained detonations—*Journal of Fluid Mechanics* (submitted)	Feb. 2004
1043	Kasimov, A. R., and D. S. Stewart	Theory of direct initiation of gaseous detonations and comparison with experiment—*Proceedings of the Combustion Institute* (submitted)	Mar. 2004
1044	Panat, R., K. J. Hsia, and D. G. Cahill	Evolution of surface waviness in thin films via volume and surface diffusion—*Journal of Applied Physics* (submitted)	Mar. 2004
1045	Riahi, D. N.	Steady and oscillatory flow in a mushy layer—*Current Topics in Crystal Growth Research*, in press (2004)	Mar. 2004
1046	Riahi, D. N.	Modeling flows in protein crystal growth—*Current Topics in Crystal Growth Research*, in press (2004)	Mar. 2004
1047	Bagchi, P., and S. Balachandar	Response of the wake of an isolated particle to isotropic turbulent cross-flow—*Journal of Fluid Mechanics* (submitted)	Mar. 2004

List of Recent TAM Reports (cont'd)

No.	*Authors*	*Title*	*Date*
1048	Brown, E. N., S. R. White, and N. R. Sottos	Fatigue crack propagation in microcapsule toughened epoxy—*Journal of Materials Science* (submitted)	Apr. 2004
1049	Zeng, L., S. Balachandar, and P. Fischer	Wall-induced forces on a rigid sphere at finite Reynolds number—*Journal of Fluid Mechanics* (submitted)	May 2004
1050	Dolbow, J., E. Fried, and H. Ji	A numerical strategy for investigating the kinetic response of stimulus-responsive hydrogels—*Journal of the Mechanics and Physics of Solids* (submitted)	June 2004
1051	Riahi, D. N.	Effect of permeability on steady flow in a dendrite layer—*Journal of Porous Media*, in press (2004)	July 2004
1052	Cermelli, P., E. Fried, and M. E. Gurtin	Transport relations for surface integrals arising in the formulation of balance laws for evolving fluid interfaces—*Journal of Fluid Mechanics* (submitted)	Sept. 2004
1053	Stewart, D. S., and A. R. Kasimov	Theory of detonation with an embedded sonic locus—*SIAM Journal on Applied Mathematics* (submitted)	Oct. 2004
1054	Stewart, D. S., K. C. Tang, S. Yoo, M. Q. Brewster, and I. R. Kuznetsov	Multi-scale modeling of solid rocket motors: Time integration methods from computational aerodynamics applied to stable quasi-steady motor burning—*Proceedings of the 43rd AIAA Aerospace Sciences Meeting and Exhibit* (January 2005), Paper AIAA-2005-0357 (2005)	Oct. 2004
1055	Ji, H., H. Mourad, E. Fried, and J. Dolbow	Kinetics of thermally induced swelling of hydrogels—*International Journal of Solids and Structures* (submitted)	Dec. 2004
1056	Fulton, J. M., S. Hussain, J. H. Lai, M. E. Ly, S. A. McGough, G. M. Miller, R. Oats, L. A. Shipton, P. K. Shreeman, D. S. Widrevitz, and E. A. Zimmermann	Final reports: Mechanics of complex materials, Summer 2004 (K. M. Hill and J. W. Phillips, eds.)	Dec. 2004
1057	Hill, K. M., G. Gioia, and D. R. Amaravadi	Radial segregation patterns in rotating granular mixtures: Waviness selection—*Physical Review Letters* **93**, 224301 (2004)	Dec. 2004
1058	Riahi, D. N.	Nonlinear oscillatory convection in rotating mushy layers—*Journal of Fluid Mechanics* (submitted)	Dec. 2004
1059	Okhuysen, B. S., and D. N. Riahi	On buoyant convection in binary solidification—*Journal of Fluid Mechanics* (submitted)	Jan. 2005
1060	Brown, E. N., S. R. White, and N. R. Sottos	Retardation and repair of fatigue cracks in a microcapsule toughened epoxy composite—Part I: Manual infiltration—*Composites Science and Technology* (submitted)	Jan. 2005
1061	Brown, E. N., S. R. White, and N. R. Sottos	Retardation and repair of fatigue cracks in a microcapsule toughened epoxy composite—Part II: *In situ* self-healing—*Composites Science and Technology* (submitted)	Jan. 2005
1062	Berfield, T. A., R. J. Ong, D. A. Payne, and N. R. Sottos	Residual stress effects on piezoelectric response of sol-gel derived PZT thin films—*Journal of Applied Physics* (submitted)	Apr. 2005
1063	Anderson, D. M., P. Cermelli, E. Fried, M. E. Gurtin, and G. B. McFadden	General dynamical sharp-interface conditions for phase transformations in viscous heat-conducting fluids—*Journal of Fluid Mechanics* (submitted)	Apr. 2005
1064	Fried, E., and M. E. Gurtin	Second-gradient fluids: A theory for incompressible flows at small length scales—*Journal of Fluid Mechanics* (submitted)	Apr. 2005
1065	Gioia, G., and F. A. Bombardelli	Localized turbulent flows on scouring granular beds—*Physical Review Letters*, in press (2005)	May 2005
1066	Fried, E., and S. Sellers	Orientational order and finite strain in nematic elastomers—*Journal of Chemical Physics*, in press (2005)	May 2005