

# Free-energy density functions for nematic elastomers

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## Abstract

The recently proposed neo-classical theory for nematic elastomers is a molecular-statistical generalization of classical Gaussian network theory. The resulting free-energy density predicts the phenomenon of soft elasticity—the ability of elastomers to undergo large deformations with zero force and energy cost. The theory, however, suffers from several drawbacks: (i) extreme non-uniqueness as zero applied force corresponds to infinitely many possible deformations, (ii) insufficient moduli to model observed experimental behavior, and (iii) physically, a small, but non-zero, force must be applied. Here we propose an alternative continuum model for nematic elastomers that removes these drawbacks. Motivated by the molecular-statistical theory, we identify microstructural degrees of freedom as well as two independent strain tensors (the overall macroscopic strain plus a relative strain that indicates how the deformation of the elastomeric microstructure deviates from the macroscopic deformation) and propose expressions for the free energy as a function of the three quantities. The resulting theory provides a self-consistent bridge that connects neo-classical theory to continuum microstructural theories as well as to the classical theory of anisotropic nonlinearly elastic solids.

**Keywords:** A. Nematic elasticity; B. Polymeric material; B. Anisotropic material; B. Finite strain; B. Constitutive behavior

## 1 Introduction

Elastomers formed by cross-linking liquid-crystalline polymers can exhibit unusual properties due to the coupling of mobile mesogenic units to an elastic network. Nematic elastomers, for example, have been shown to display phase transitions, spontaneous shape changes, response to external fields, and formation of striped domains. But perhaps the most novel and interesting property is *soft elasticity*: the ability of the material to undergo large deformations under very small applied forces.<sup>1</sup> First predicted by Golubovic and Lubensky (1989) for gels, soft elasticity in nematic elastomers has been experimentally observed by Küpfer and Finkelmann (1994). Also, Verwey, Warner and Terentjev (1996) attributed the striped domain patterns observed by Kundler and Finkelmann (1995) to soft elasticity.

Warner, Gelling and Vilgis (1988), Warner and Wang (1991), and Bladon, Terentjev and Warner (1994) developed a simple but non-linear theory for nematic elastomers by extending the classical Gaussian network theory of rubber elasticity to allow for anisotropic distributions of the end-to-end vector. The resulting theory, which they called

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<sup>1</sup>Warner and Terentjev (1996) and Brand and Finkelmann (1998) give extensive reviews of nematic elastomers.

*neo-classical rubber elasticity*, models successfully many of the properties of nematic elastomers, including soft elasticity. According to this theory, soft elasticity arises from an invariance of the free-energy density made possible by the particular manner in which the microscopic degrees of freedom associated with the mesogenic units couple with the macroscopic degrees of freedom associated with the network. Indeed, this special and unusual invariance allows for a continuous spectrum of non-trivial minimizers (Olmsted, 1994). Consequently the neo-classical theory predicts that a nematic elastomer may assume infinitely-many stable equilibrium configurations with zero force and energy cost. Striped configurations have thus been interpreted as consisting of domains where the degrees of freedom takes values corresponding to one of the multiple energy minimizers (Verwey, Warner and Terentjev, 1996).

The neo-classical theory, however, has several drawbacks. Firstly, a continuous spectrum of non-trivial minimizers leads to a massive degree of non-uniqueness as infinitely many states are energetically equivalent. In particular, numerical methods would need some type of adscititious selection criterion. Conti, DeSimone and Dolzmann (2002a) have already discussed this point in the context of striping. To select a solution in their numerical investigations of stretched nematic-elastomeric sheets, these authors have added to the neo-classical free-energy density function an ad hoc perturbation term. Secondly, the single modulus that results from the neo-classical theory is inadequate for the behavior observed in some experiments (Mao, Warner, Terentjev and Ball, 1998). Finally, actual materials are only *semi-soft*: to induce deformation, a nonzero, albeit small, force must be applied.

Several further modifications to the neo-classical theory have been proposed. These include multi-stage cross-linking effects (Verwey and Warner, 1995), non-uniform deformations (Terentjev, Warner and Verwey, 1996), compositional fluctuations (Verwey, Warner and Terentjev, 1996; Verwey and Warner, 1997a), cross-linking by rigid-rod linkers (Verwey and Warner, 1997b), and finite extensibility effects (Mao, Warner, Terentjev and Ball, 1998). Some of these modifications do result in semi-softness rather than perfect softness and have been used to study striping (Conti, DeSimone and Dolzmann, 2002b), but there is still no complete agreement with experiment.

Our goal in this work is to develop governing equations for nematic elastomers subject to large strains that avoid the drawbacks of those arising from the neo-classical theory. We pursue however an alternative point of view in which we present a phenomenological, continuum treatment of nematic elastomers, independent of any particular microscopic model. Because we rely on additional kinematic degrees of freedom to represent the polymer microstructure, our approach is similar in spirit to the early continuum microstructural theories of solids developed by Mindlin (1964) and Toupin (1964). But just as Rivlin's (1948) development of the general theory of finite elasticity was motivated by the classical isotropic network theory of rubber elasticity, our developments are also closely motivated by the anisotropic neo-classical network theory of nematic elasticity. Importantly, the molecular-statistical theory suggests the relevant microstructural kinematic degrees of freedom as well as two non-linear strain tensors: the usual Cauchy–Green tensor that describes the overall macroscopic strain, plus a relative strain tensor that indicates how the deformation of the elastomeric microstructure deviates from the macroscopic deformation.

When a mathematical model exhibits a lack of uniqueness, the underlying cause may be an incompleteness of the model. We interpret the extreme non-uniqueness arising in the neo-classical theory of nematic elastomers as due to an incomplete constitutive theory—one that fails to take into account both strain measures mentioned above. Thus we propose a generic free-energy density function for a nematic elastomer that depends on both strain measures. We then use invariance arguments to restrict the form of possible

constitutive relations. In general, that function permits semi-soft solutions. If, however, we neglect dependence on the Cauchy–Green strain tensor, so that the free-energy density function depends only on the relative strain tensor, the resulting specialization includes the neo-classical free-energy density function as a special case. Most importantly, any free-energy density function of this kind possesses the same invariance properties as the neo-classical free-energy density function and, therefore, exhibits perfect softness (Carlson, Fried and Sellers, 2003). In particular, we thus view the neo-classical free-energy density function as incomplete and suggest that a dependence on the Cauchy–Green strain tensor is needed to regularize the energy. Indeed, this additional dependence makes it possible to break the special invariance arising from a dependence only on the relative strain tensor.

On the other hand, if the microstructure is constrained to deform materially, so that it stretches and rotates with the macroscopic continuum, then the relative strain tensor reduces to the identity tensor and our general free-energy density function reduces to that of a non-linear anisotropic elastic solid (Ericksen and Rivlin, 1954). Our work thus provides a self-consistent bridge that connects the neo-classical theory to continuum microstructural theories as well as to the classical theory of anisotropic nonlinearly elastic solids. It also justifies the ad hoc selection criteria of Conti, DeSimone and Dolzmann (2002a), which in our context corresponds to the simplest consistent generalization of the neo-classical theory. We believe that this approach will be fruitful in modeling the novel properties of elastomers that exhibit various liquid crystalline phases.

Because the neo-classical theory provides motivation for our formulation of the phenomenological theory, we first review it briefly and show how softness arises as a consequence of the special invariance inherent to the theory. We then turn to the formulation of a general continuum theory. In so doing, we follow standard ideas on non-linear continuum mechanics with microstructure. Nematic elastomers may sustain very large strains, so it is important to make a clear distinction between the reference and deformed configurations (Ogden, 1997). In this regard, we pay careful attention the formulation of the kinematics, balance laws, and constitutive relations. Consistency with the neo-classical statistical theory guides us in the choice of possible constitutive relations. In particular, we propose a simple expression for the free-energy density function of a nematic elastomer, discuss two mechanical tests to measure the elastic moduli, and show that the only possible truly soft deformations for a material described by such a response function are trivial rigid-body rotations.

## 2 Neo-classical theory

### 2.1 Basic equations

A primary goal of the molecular-statistical theory of nematic elastomers is to derive a free-energy density function. Towards that goal, a standard assumption is that the free-energy density  $\psi$  decomposes into a sum of two terms of differing physical origin and form, viz.

$$\psi = \psi_e + \psi_n, \tag{2.1}$$

where  $\psi_e$  arises from the cross-linking of a polymer melt and represents the contribution due to an isothermal elastic deformation, and  $\psi_n$  is the contribution from mesogenic units that form the nematic phase. We discuss first the elastic contribution  $\psi_e$ .

Consider a nematic elastomer in two configurations: a reference configuration  $\mathcal{B}_*$  and

a deformed configuration  $\mathcal{B}$ .<sup>2</sup> The choice of the reference configuration is, of course, arbitrary, but a common choice is the configuration at the instant of cross-linking. We denote the macroscopic deformation gradient relating the two configurations by  $\mathbf{F}$  (that is,  $\mathcal{B}_*$  is mapped onto  $\mathcal{B}$  by a deformation  $\mathbf{y}$  with gradient  $\mathbf{F}$ ). In each configuration, the polymer consists of chains connected by cross-links. We denote by  $\mathbf{r}_*$  and  $\mathbf{r}$  the end-to-end vectors of a chain connecting two cross-links in the reference and deformed configurations. The neo-classical theory takes a simplified description of the polymer chains, a description that represents each chain solely by its end-to-end vector. The theory further assumes that the cross-links (and, thus, the end-to-end vectors) deform as material line elements, so that

$$\mathbf{r} = \mathbf{F}\mathbf{r}_*. \quad (2.2)$$

The polymer chains are mobile and may exist in many different conformations, so that a probability distribution describes the frequency of end-to-end vectors. Another basic assumption in the neo-classical theory is that this probability distribution  $p$  has the Gaussian form

$$p(\mathbf{r}; \mathbf{A}) = \frac{1}{\sqrt{8\pi^3 \det \mathbf{A}}} \exp\left(-\frac{1}{2}|\mathbf{A}^{-\frac{1}{2}}\mathbf{r}|^2\right) \quad (2.3)$$

where  $\mathbf{A}$ , the average of the tensorial second moment of the end-to-end vectors in the deformed configuration, viz.

$$\mathbf{A} = \int_{\mathcal{E}} p(\mathbf{r}; \mathbf{A}) \mathbf{r} \otimes \mathbf{r} \, dv(\mathbf{r}) = \langle \mathbf{r} \otimes \mathbf{r} \rangle, \quad (2.4)$$

represents the chain shape in the deformed configuration. Here,  $\mathcal{E}$  denotes three-dimensional space.

The assumed Gaussian form (2.3) of the probability distribution can be motivated by considering the polymer chains as being composed of freely jointed segments with a bias. By the central-limit theorem, the probability density for the distribution of end-to-end vectors approaches a Gaussian as the number of chain segments approaches infinity. For long, but finite, chain lengths that are not overly stretched, the probability density can be expected to be approximately Gaussian.

Importantly, (2.3) allows for both isotropic and anisotropic distributions of end-to-end vectors. For example, an isotropic distribution in the deformed configuration corresponds to the special case  $\mathbf{A} = \frac{1}{3}\langle |\mathbf{r}|^2 \rangle \mathbf{I}$ . More generally,  $\mathbf{A}$  is a symmetric and positive-definite tensor that allows for isotropy, uniaxiality, or biaxiality according to its number of distinct eigenvalues.

A further basic assumption is that the change  $\psi_e$  of the free-energy density due to an isothermal, elastic deformation has the purely entropic form

$$\psi_e = -nk_B\theta \int_{\mathcal{E}} p(\mathbf{r}_*; \mathbf{A}_*) \log\left(\frac{p(\mathbf{F}\mathbf{r}_*; \mathbf{A}) \det \mathbf{F}}{p(\mathbf{r}_*; \mathbf{A}_*)}\right) dv(\mathbf{r}_*), \quad (2.5)$$

with  $n$  the number-density of cross-links,  $k_B$  Boltzmann's constant, and  $\theta$  the absolute temperature. We emphasize that this quenched average is performed with respect to the referential probability

$$p(\mathbf{r}_*; \mathbf{A}_*) = \frac{1}{\sqrt{8\pi^3 \det \mathbf{A}_*}} \exp\left(-\frac{1}{2}|\mathbf{A}_*^{-\frac{1}{2}}\mathbf{r}_*|^2\right), \quad (2.6)$$

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<sup>2</sup>When necessary, we use a subscripted asterisk to distinguish quantities associated with the reference configuration from those associated with the deformed configuration.

where  $\mathbf{A}_*$  describes the chain shape in the reference configuration. Substitution of (2.2) and (2.3) into (2.5) and integrating yields

$$\psi_e = \frac{1}{2}nk_B\theta(\text{tr}(\mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top) - \log\det(\mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top) - 3). \quad (2.7)$$

For incompressible materials,  $\det\mathbf{F} = 1$ , so that (2.7) reduces to

$$\psi_e = \frac{1}{2}nk_B\theta(\text{tr}(\mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top) - \log\det(\mathbf{A}^{-1}\mathbf{A}_*) - 3). \quad (2.8)$$

The right side of (2.8) is the neo-classical free-energy density function derived by Bladon, Terentjev and Warner (1994). Interestingly, this expression depends on the alignment of end-to-end vectors in both the deformed and reference configurations. Moreover, it depends on  $\mathbf{F}$ ,  $\mathbf{A}$ , and  $\mathbf{A}_*$  through the unusual combination  $\mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top$ —a combination that we identify in section 4 as a *non-linear relative strain tensor*.

If both distributions in the reference and deformed configurations are isotropic with  $\mathbf{A}_* = \mathbf{A} = \frac{1}{3}\langle|\mathbf{r}|^2\rangle\mathbf{I}$ , then the elastic contribution to the free-energy density reduces to the classical expression

$$\psi_e = \frac{1}{2}nk_B\theta(\text{tr}(\mathbf{F}\mathbf{F}^\top) - 3) \quad (2.9)$$

for rubber elasticity, with  $\mathbf{F}\mathbf{F}^\top$  the left Cauchy–Green strain tensor.

While the elastic deformation provides the entropic contribution to the free-energy density, the nematic interactions provide the energetic contribution  $\psi_n$ . In the neo-classical theory, this contribution is assumed to have the form

$$\psi_n = \hat{\psi}_n(\mathbf{Q}), \quad (2.10)$$

where  $\mathbf{Q}$  is the classical traceless nematic order-tensor. This contribution is rotationally invariant and consequently depends only on scalar invariants of  $\mathbf{Q}$ , viz.

$$\psi_n = \hat{\psi}_n(\text{tr}\mathbf{Q}^2, \text{tr}\mathbf{Q}^3). \quad (2.11)$$

Consistent with the normalization of  $\psi_e$ , the nematic contribution  $\psi_n$  can be normalized so that it vanishes in the reference configuration:

$$\hat{\psi}_n(\text{tr}\mathbf{Q}_*^2, \text{tr}\mathbf{Q}_*^3) = 0, \quad \text{with} \quad \hat{\psi}_n(\text{tr}\mathbf{Q}^2, \text{tr}\mathbf{Q}^3) \geq 0. \quad (2.12)$$

To obtain a closed theory, the statistical model presumes further a functional relation between  $\mathbf{A}$  and  $\mathbf{Q}$ , so that the free-energy density reduces to a function of  $\mathbf{F}$  and  $\mathbf{Q}$ . The actual form of the closure relation strongly depends on the choice of the molecular model. For example, Bladon, Warner and Terentjev (1994) calculated this contribution for a melt consisting of freely-jointed chains of Maier–Saupe rods. A common approximation, however, is to assume that the eigenvalues of  $\mathbf{Q}$  (and those of  $\mathbf{A}$ ) are constant, so that the eigenvectors can only rotate. In this case, the nematic contribution is constant and can be neglected relative to the elastic contribution (Warner, 1999).

## 2.2 Soft elasticity

An important difference between the general neo-classical free-energy density function (2.8) and its isotropic specialization (2.9) is that (2.8) possesses a continuous spectrum of non-trivial minimizers. The following modification of Olmsted’s (1994) argument illustrates how those minimizers occur.

Let

$$\bar{\mathbf{F}} = \mathbf{A}^{-\frac{1}{2}}\mathbf{F}\mathbf{A}_*^{\frac{1}{2}}. \quad (2.13)$$

Then, in terms of  $\bar{\mathbf{F}}$ , (2.8) becomes

$$\psi_e = \frac{1}{2}nk_B\theta(\text{tr}(\bar{\mathbf{F}}\bar{\mathbf{F}}^\top) - \log\det(\bar{\mathbf{F}}\bar{\mathbf{F}}^\top) - 3). \quad (2.14)$$

Provided that we can interpret  $\bar{\mathbf{F}}$  as a deformation gradient, (2.14) has the form of the free-energy density for an *isotropic material*. In that case, we can say that there are configurations  $\bar{\mathcal{B}}_*$  and  $\bar{\mathcal{B}}$  such that the elastomer is isotropic. Trivially, when  $\bar{\mathbf{F}} = \mathbf{R}$  with  $\mathbf{R}$  a rigid-body rotation ( $\mathbf{R}^\top\mathbf{R} = \mathbf{R}\mathbf{R}^\top = \mathbf{I}$ ,  $\det\mathbf{R} = 1$ ) (2.14) achieves a minimum value of  $\psi_e = 0$  (Carlson, Fried and Sellers, 2003). However, in terms of the actual deformation gradient  $\mathbf{F}$ , the expression  $\bar{\mathbf{F}} = \mathbf{R}$  is equivalent to

$$\mathbf{F} = \mathbf{A}^{\frac{1}{2}}\mathbf{R}\mathbf{A}_*^{-\frac{1}{2}}, \quad (2.15)$$

where, since  $\det\mathbf{F} = 1$ , we must have

$$\det(\mathbf{A}^{-1}\mathbf{A}_*) = 1. \quad (2.16)$$

Granted (2.15) and (2.16), it follows from (2.8) that  $\psi_e = 0$  regardless of the form of  $\mathbf{A}$ . The nematic contribution  $\psi_n$  to the free-energy density vanishes only for special choices of  $\mathbf{A}$ . In view of (2.11), the choice  $\mathbf{Q} = \mathbf{R}'^\top\mathbf{Q}_*\mathbf{R}'$  obtained by rotating the referential nematic order-tensor yields  $\psi_n = 0$ . Under such a rotation, we have  $\mathbf{A} = \mathbf{R}'^\top\mathbf{A}_*\mathbf{R}'$ . Thus, for  $(\mathbf{F}, \mathbf{A}, \mathbf{Q})$  belonging to the continuous spectrum of solutions

$$\mathbf{F} = \mathbf{A}^{\frac{1}{2}}\mathbf{R}\mathbf{A}_*^{-\frac{1}{2}}, \quad \mathbf{A} = \mathbf{R}'^\top\mathbf{A}_*\mathbf{R}', \quad \mathbf{Q} = \mathbf{R}'^\top\mathbf{Q}_*\mathbf{R}', \quad (2.17)$$

the total free-energy density is left invariant. Clearly,  $\det\bar{\mathbf{F}} = \det\mathbf{F} = 1$ , so that  $\bar{\mathbf{F}}$  is a kinematically possible deformation for an incompressible material. However, for nematic elastomers with an isotropic distribution in the reference and deformed configurations, these minimizers reduce to the trivial rigid-body rotations  $\mathbf{F} = \mathbf{R}$ .

Importantly, the above argument shows that the neo-classical theory implies the existence of two kinematically possible configurations  $\bar{\mathcal{B}}_*$  and  $\bar{\mathcal{B}}$  in which the elastomer can be modelled as isotropic (2.14). The deformation gradient from  $\bar{\mathcal{B}}_*$  to  $\bar{\mathcal{B}}$  is  $\mathbf{A}_*^{-1/2}$  and that from  $\bar{\mathcal{B}}$  to  $\bar{\mathcal{B}}_*$  is  $\mathbf{A}_*^{1/2}$ . Hence, the relationship between these configurations can be represented diagrammatically as

$$\begin{array}{ccc} \bar{\mathcal{B}}_* & \xrightarrow{\mathbf{F}} & \bar{\mathcal{B}} \\ \mathbf{A}_*^{-\frac{1}{2}} \downarrow & & \uparrow \mathbf{A}_*^{\frac{1}{2}} \\ \bar{\mathcal{B}}_* & \xrightarrow{\bar{\mathbf{F}} = \mathbf{R}} & \bar{\mathcal{B}} \end{array}$$

The consequence of such isotropic configurations for the neo-classical theory is that any rotation from  $\bar{\mathcal{B}}_*$  to  $\bar{\mathcal{B}}$ , which corresponds to (2.17)<sub>1</sub>, minimizes  $\psi_e$ . Consequently, the neo-classical theory always allows for non-trivial soft elasticity when there is an anisotropic distribution of end-to-end vectors in the reference configuration  $\bar{\mathcal{B}}_*$ .

### 3 General continuum theory

The neo-classical theory as summarized above assumes that the distribution of end-to-end vectors is Gaussian. We now turn to the development of a general non-linear continuum theory that makes no such restrictive assumptions on the microstructure.

### 3.1 Kinematics

As before, we consider an incompressible nematic elastomer in a given reference state that occupies a region  $\mathcal{B}_*$ . Consistent with a continuum view, we model the material as having (i) macroscopic degrees of freedom associated with network distortion and (ii) additional microscopic degrees of freedom associated with the polymer chain-shape. In particular, at each point  $\mathbf{x}$  of  $\mathcal{B}_*$ , we loosely envision a cross-linked network of polymeric molecules that include nematic mesogens as main-chain elements or as pendant side-groups. As suggested by the Gaussian probability density (2.3), we model this additional structure in the reference configuration by a symmetric and positive-definite tensor  $\mathbf{A}_*$  that describes the macroscopic chain shape in the reference state and may vary from point to point in  $\mathcal{B}_*$ .

The kinematical state of the nematic elastomer in the deformed configuration  $\mathcal{B}$  is thus described by two time- and space-dependent fields:

- $\mathbf{y}$ , the deformation from the reference region  $\mathcal{B}_*$  to the current configuration  $\mathcal{B}$ ; and
- $\mathbf{A}$ , a measure of the average chain shape of the polymer molecules in the current configuration.

We use Grad and Div to denote differentiation on  $\mathcal{B}_*$  and, in particular, write

$$\mathbf{F} = \text{Grad} \mathbf{y} \quad (3.1)$$

for the deformation gradient. Incompressibility of the medium requires that  $\det \mathbf{F} = 1$ . We require also that  $\mathbf{A}$  be symmetric and positive-definite.

### 3.2 Basic laws

We follow the now standard procedure for non-linear continuum theories, where balance laws are supplemented by a dissipation principle, a principle that in conjunction with invariance requirements is used to obtain restrictions on constitutive equations. We formulate these basic laws in the referential setting, using  $\mathcal{P}_*$  to designate an arbitrary regular part of referential region  $\mathcal{B}_*$  with boundary  $\partial \mathcal{P}_*$  oriented by a unit normal field  $\boldsymbol{\nu}_*$  directed outward from  $\mathcal{P}_*$ .

For simplicity, inertial effects are incorporated in the external body force densities.

#### 3.2.1 Balance of forces

We consider two types of force systems: one associated with the macroscopic degrees of freedom, the other associated with the additional microscopic degrees of freedom. To each system of forces there corresponds a distinct balance law.

For the macroscopic degrees of freedom, we introduce a deformational force system consisting of a *stress* tensor  $\mathbf{S}$  and an *external deformational body-force density*  $\mathbf{b}$ . The body-force density  $\mathbf{b}$  is assumed to include inertial forces. We impose the balance of deformational forces by requiring that

$$\int_{\partial \mathcal{P}_*} \mathbf{S} \boldsymbol{\nu}_* da + \int_{\mathcal{P}_*} \mathbf{b} dv = \mathbf{0} \quad (3.2)$$

for all  $\mathcal{P}_*$  and all time. Locally, this equivalent to the field equation

$$\text{Div} \mathbf{S} + \mathbf{b} = \mathbf{0}. \quad (3.3)$$

Due to the microscopic degrees of freedom, we introduce an additional force system consisting of *internal* and *external body-force densities*  $\mathbf{\Pi}$  and  $\mathbf{\Gamma}$ , and subject to its own balance law. Both  $\mathbf{\Pi}$  and  $\mathbf{\Gamma}$  are symmetric second-order-tensors. The external body-force density  $\mathbf{\Gamma}$  can arise, for example, from external electric or magnetic fields. We also assume that it includes inertial forces. We impose this additional balance of microstructural forces by requiring that<sup>3</sup>

$$\int_{\mathcal{P}_*} (\mathbf{\Pi} + \mathbf{\Gamma}) dv = \mathbf{0} \quad (3.4)$$

for all  $\mathcal{P}_*$  and all time. The local version of this balance is

$$\mathbf{\Pi} + \mathbf{\Gamma} = \mathbf{0}. \quad (3.5)$$

A precedent for introducing an additional force balance involving internal and external forces can be found in Ericksen's (1960, 1961) theory of anisotropic fluids. There the additional force balance arises from the additional rotational degrees of freedom introduced by the director.

### 3.2.2 Balance of moments

We ignore external couples by assuming that all moments are expressible as torques and impose moment balance by requiring that<sup>2</sup>

$$\int_{\partial\mathcal{P}_*} \mathbf{y} \times \mathbf{S}\boldsymbol{\nu}_* da + \int_{\mathcal{P}_*} (\mathbf{y} \times \mathbf{b} + 2\text{dual}(\mathbf{A}\mathbf{\Gamma})) da = \mathbf{0} \quad (3.6)$$

for all  $\mathcal{P}$  and all time. Here,  $\text{dual } \mathbf{M}$  is defined so that  $\frac{1}{2}(\mathbf{M} - \mathbf{M}^\top)\mathbf{v} = (\text{dual } \mathbf{M}) \times \mathbf{v}$  for all vectors  $\mathbf{v}$ . In view of the balances (3.3) and (3.5), the local version can be expressed as

$$\mathbf{S}\mathbf{F}^\top + \mathbf{A}\mathbf{\Pi} = (\mathbf{S}\mathbf{F}^\top + \mathbf{A}\mathbf{\Pi})^\top. \quad (3.7)$$

Since  $\det \mathbf{F} = 1$ , we can identify the first term of left side of (3.7) with the Cauchy stress-tensor  $\mathbf{T}$ , so that (3.7) shows that the Cauchy stress-tensor is not necessarily symmetric:

$$\mathbf{T} + \mathbf{A}\mathbf{\Pi} = (\mathbf{T} + \mathbf{A}\mathbf{\Pi})^\top. \quad (3.8)$$

This result is typical for continuum theories of materials with microstructure. In the absence of microstructure, the balance of moments reduces to the usual form  $\mathbf{T} = \mathbf{T}^\top$ , which states that the Cauchy stress-tensor is symmetric.

### 3.2.3 Dissipation

We consider a purely mechanical situation where the first and second laws combine to yield a principle of dissipation imbalance and impose that imbalance by requiring that,

<sup>3</sup>More generally, we might introduce a microstructural stress  $\boldsymbol{\Sigma}$ —a third-order-tensor. Under these circumstances, (3.5) would be replaced by  $\int_{\partial\mathcal{P}_*} \boldsymbol{\Sigma}\boldsymbol{\nu}_* da + \int_{\mathcal{P}_*} (\mathbf{\Pi} + \mathbf{\Gamma}) dv = \mathbf{0}$ .

<sup>2</sup>In keeping with Anderson, Carlson and Fried (1999), the torque  $\int_{\mathcal{P}_*} 2\text{dual}(\mathbf{A}\mathbf{\Pi}) dv$  induced by  $\mathbf{\Pi}$  is not accounted for in the moment balance (3.6) since this torque acts internally. In the presence of a microstructural stress, it would be necessary to include the associated moment in (3.6).

for each  $\mathcal{P}_*$ , the time-rate of the total free-energy of  $\mathcal{P}_*$  not exceed the power expended by the external forces acting on  $\mathcal{P}_*$ :<sup>3</sup>

$$\overline{\int_{\mathcal{P}_*} \dot{\psi} dv} \leq \int_{\partial\mathcal{P}_*} \mathbf{S}\boldsymbol{\nu}_* \cdot \dot{\mathbf{y}} da + \int_{\mathcal{P}_*} (\mathbf{b} \cdot \dot{\mathbf{y}} + \boldsymbol{\Gamma} \cdot \dot{\mathbf{A}}) dv \quad (3.9)$$

for all  $\mathcal{P}$  and all time. Locally, in view of (3.3) and (3.5), we obtain

$$\dot{\psi} - \mathbf{S} \cdot \dot{\mathbf{F}} + \boldsymbol{\Pi} \cdot \dot{\mathbf{A}} \leq 0. \quad (3.10)$$

This shows that changes in the polymer microstructure can contribute to the dissipation.

### 3.3 Constitutive theory

The above general laws must be supplemented by constitutive relations that specify the behavior of individual materials. To be at least consistent with the neo-classical theory, we must allow for a constitutive dependence on the deformation gradient  $\mathbf{F}$  and the microstructural variables  $\mathbf{A}$  and  $\mathbf{A}_*$ . Our point of view here is that the kinematics of the microstructure is completely represented by  $\mathbf{A}$ , so that there is no need for  $\mathbf{Q}$  and hence no need for an additional closure relation. For simplicity, we restrict our attention to a constitutive theory in which these are the only independent variables. Thus, we postulate:

$$\psi = \hat{\psi}(\mathbf{F}, \mathbf{A}, \mathbf{A}_*), \quad \mathbf{S} = \hat{\mathbf{S}}(\mathbf{F}, \mathbf{A}, \mathbf{A}_*) - p\mathbf{F}^{-\top}, \quad \text{and} \quad \boldsymbol{\Pi} = \hat{\boldsymbol{\Pi}}(\mathbf{F}, \mathbf{A}, \mathbf{A}_*), \quad (3.11)$$

where  $p$  is the constitutively indeterminate pressure arising from the constraint of incompressibility. This choice clearly includes as a special case the neo-classical elastic free energy expressed by (2.8). It allows for coexistent isotropic, uniaxial, and biaxial phases.

#### 3.3.1 Thermodynamic restrictions

Thermodynamics imposes restrictions on the constitutive assumptions (3.11). Employing the approach taken by Coleman and Noll (1963), we find that the dissipation imbalance (3.10) holds in all processes consistent with the constraint of incompressibility and the force and moment balances if and only if

$$\psi = \hat{\psi}(\mathbf{F}, \mathbf{A}, \mathbf{A}_*), \quad \mathbf{S} = \frac{\partial \hat{\psi}(\mathbf{F}, \mathbf{A}, \mathbf{A}_*)}{\partial \mathbf{F}} - p\mathbf{F}^{-\top}, \quad \text{and} \quad \boldsymbol{\Pi} = -\frac{\partial \hat{\psi}(\mathbf{F}, \mathbf{A}, \mathbf{A}_*)}{\partial \mathbf{A}}. \quad (3.12)$$

Thus, the free-energy density function  $\hat{\psi}$  serves as a potential for the constitutively determinate part of the stress  $\mathbf{S}$  as well as for the internal body-force density  $\boldsymbol{\Pi}$ . Further, from (3.12)<sub>3</sub>,  $\boldsymbol{\Pi}$  must be symmetric.

The partial derivative in (3.12)<sub>2</sub> indicates differentiation on the manifold determined by the constraint of incompressibility. It can be related to the standard partial derivative by introducing a smooth extension  $\bar{\psi}$  of  $\hat{\psi}$  without the constraint and eliminating the component parallel to  $\mathbf{F}^{-\top}$ , i.e.,

$$\frac{\partial \hat{\psi}(\mathbf{F}, \mathbf{A}, \mathbf{A}_*)}{\partial \mathbf{F}} = \left( \boldsymbol{\mathbb{I}} - \frac{1}{|\mathbf{F}^{-1}|^2} \mathbf{F}^{-\top} \otimes \mathbf{F}^{-\top} \right) \frac{\partial \bar{\psi}(\mathbf{F}, \mathbf{A}, \mathbf{A}_*)}{\partial \mathbf{F}}, \quad (3.13)$$

<sup>3</sup>By reasoning identical to that underlying the omission of internal torque from (3.6), the power  $\int_{\mathcal{P}_*} \boldsymbol{\Pi} \cdot \dot{\mathbf{A}} dv$  expended by the internal body-force density  $\boldsymbol{\Pi}$  is not included in (3.9). In the presence of microstructural stress, it would be necessary to include the corresponding associated power in (3.9).

where  $\mathbf{I}$  denotes the identity mapping from the space  $\text{Lin}$  of second-order tensors into itself,  $\mathbf{L} \otimes \mathbf{M}$  is the linear operator from  $\text{Lin}$  to  $\text{Lin}$  defined by  $(\mathbf{L} \otimes \mathbf{M})\mathbf{N} = (\mathbf{M} \cdot \mathbf{N})\mathbf{L}$ , and the second factor on the right side of (3.13) is the standard partial derivative evaluated on the constraint manifold.

### 3.3.2 Material Symmetry

Certain transformations of the reference configuration can leave the subsequent material response unchanged. The invariance arising from such material symmetry restricts the class of possible constitutive functions. As the free-energy density function serves as a potential for the other constitutive quantities, we need to consider only its invariance properties.

A rotation  $\mathbf{H}$  of the reference configuration leads to the transformations

$$\mathbf{F} \mapsto \mathbf{FH}, \quad \mathbf{A} \mapsto \mathbf{A}, \quad \mathbf{A}_* \mapsto \mathbf{H}^\top \mathbf{A}_* \mathbf{H}. \quad (3.14)$$

The only material anisotropy, however, is embodied by the microstructural variables  $\mathbf{A}$  and  $\mathbf{A}_*$ . Thus we require that all such rotations leave the subsequent response of the elastomer unchanged, i.e.,

$$\hat{\psi}(\mathbf{FH}, \mathbf{A}, \mathbf{H}^\top \mathbf{A}_* \mathbf{H}) = \hat{\psi}(\mathbf{F}, \mathbf{A}, \mathbf{A}_*) \quad \text{for all rotations } \mathbf{H}. \quad (3.15)$$

In conjunction with the polar-decomposition theorem, the material symmetry requirement (3.15) is met if and only if there exists a function  $\tilde{\psi}$  of  $\mathbf{FF}^\top$ ,  $\mathbf{A}$ , and  $\mathbf{FA}_*\mathbf{F}^\top$  such that

$$\hat{\psi}(\mathbf{F}, \mathbf{A}, \mathbf{A}_*) = \tilde{\psi}(\mathbf{FF}^\top, \mathbf{A}, \mathbf{FA}_*\mathbf{F}^\top). \quad (3.16)$$

### 3.3.3 Objectivity

Objectivity is the requirement that constitutive relations be invariant under superposed rigid motions. In this case, the relevant transformations are

$$\mathbf{F} \mapsto \mathbf{RF}, \quad \mathbf{A} \mapsto \mathbf{RAR}^\top, \quad \mathbf{A}_* \mapsto \mathbf{A}_*, \quad (3.17)$$

with  $\mathbf{R}$  a rotation. Thus we also require that  $\hat{\psi}$  satisfy the invariance

$$\hat{\psi}(\mathbf{RF}, \mathbf{RAR}^\top, \mathbf{A}_*) = \hat{\psi}(\mathbf{F}, \mathbf{A}, \mathbf{A}_*) \quad \text{for all rotations } \mathbf{R}. \quad (3.18)$$

Combining the requirements (3.16) and (3.18) of symmetry and objectivity shows that  $\tilde{\psi}$ , which we refer to as the *reduced free-energy density function* is isotropic in the sense that

$$\tilde{\psi}(\mathbf{RFF}^\top \mathbf{R}^\top, \mathbf{RAR}^\top, \mathbf{RFA}_*\mathbf{F}^\top \mathbf{R}^\top) = \tilde{\psi}(\mathbf{FF}^\top, \mathbf{A}, \mathbf{FA}_*\mathbf{F}^\top), \quad (3.19)$$

for all rotations  $\mathbf{R}$ .

### 3.3.4 Normalization

Without loss of generality, we assume that the free-energy density functions  $\hat{\psi}$  and  $\tilde{\psi}$  are normalized so that they vanish in the reference state (where  $\mathbf{F} = \mathbf{I}$  and  $\mathbf{A} = \mathbf{A}_*$ ), viz.

$$\hat{\psi}(\mathbf{I}, \mathbf{A}_*, \mathbf{A}_*) = \tilde{\psi}(\mathbf{I}, \mathbf{A}_*, \mathbf{A}_*) = 0. \quad (3.20)$$

### 3.4 Governing equations

Combining the local deformational force balance (3.3) and the relation (3.12)<sub>2</sub> for the deformational stress  $\mathbf{S}$ , we obtain the partial differential equation

$$\text{Div}\left(\frac{\partial\hat{\psi}(\mathbf{F}, \mathbf{A}, \mathbf{A}_*)}{\partial\mathbf{F}}\right) + \mathbf{b} = \mathbf{F}^{-\top}\text{Grad}p. \quad (3.21)$$

Similarly, combining the local microstructural force balance (3.5) and the relation (3.12)<sub>3</sub> for the internal force density  $\mathbf{\Pi}$ , we obtain the partial differential equation

$$\frac{\partial\hat{\psi}(\mathbf{F}, \mathbf{A}, \mathbf{A}_*)}{\partial\mathbf{A}} = \mathbf{\Gamma}. \quad (3.22)$$

Furthermore, a direct calculation shows that, granted the invariance postulate (3.18), the moment balance (3.7) holds. Thus, given a free-energy density function  $\hat{\psi}$  that satisfies the invariance conditions (3.16) and (3.19), equations (3.21) and (3.22) are the resulting governing equations for a nematic elastomer.

These equations can be also derived in an alternative way. For example, the governing equations (3.21) and (3.22) are the counterparts to the Euler–Lagrange equations that would arise from variations of the energy functional

$$\mathcal{E}(\mathbf{y}, \mathbf{A}) = \int_{\mathcal{B}_*} \hat{\psi}(\mathbf{F}, \mathbf{A}, \mathbf{A}_*) dv + \phi(\mathbf{y}, \mathbf{A}, \mathbf{A}_*), \quad (3.23)$$

with  $\phi$  being a joint potential that generates the equilibrium contributions to the external force densities  $\mathbf{b}$  and  $\mathbf{\Gamma}$  and any deformational traction distributed over  $\partial\mathcal{B}_*$ . Varying  $\mathbf{y}$  subject to the constraint  $\det\mathbf{F} = 1$  yields the equilibrium counterpart of (3.21), and varying  $\mathbf{A}$  yields the equilibrium counterpart of (3.22). Inertial terms can also be included by minimizing the action.

Although our constitutive framework does not account for viscous dissipation, that effect could be easily incorporated (Fried and Gurtin 1994; Fried 1996) to yield a dynamical theory that allows for the description of important non-equilibrium processes, such as stripe formation and evolution.

## 4 Relation to neo-classical theory

In the previous section we arrived at a rather general continuum theory for nematic elastomers in which the material response is determined by an isotropic reduced free-energy density function  $\tilde{\psi}$ . The question naturally arises as to what relation, if any, that theory has to the neo-classical theory.

Invariance due to material symmetry requires  $\tilde{\psi}$  be a function of the left Cauchy–Green strain tensor  $\mathbf{F}\mathbf{F}^\top$ . This is a common measure of strain in isotropic non-linear elasticity. If we interpret the deformation gradient  $\mathbf{F}$  as a macroscopic measure of the distortion of the network cross-links, then the left Cauchy–Green tensor provides a measure of the extensions of the network cross-links in the nematic elastomer.

The neo-classical free energy expression (2.8) suggests, however, the quantity

$$\mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top \quad (4.1)$$

as a strain measure. In fact, this quantity is a *relative strain*. Note that  $\mathbf{F}\mathbf{A}_*\mathbf{F}^\top$  represents the manner by which  $\mathbf{A}_*$  would transform if the microstructure were to deform materially. Thus the quantity  $\mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top$  describes how the distortion of the polymer

chain shape deviates from the overall macroscopic strain  $\mathbf{F}\mathbf{F}^\top$  of the sample. In the case where the microstructure deforms materially, (4.1) reduces to the identity tensor, and the macroscopic deformation  $\mathbf{y}$  provides complete information on the deformation.

In accord with continuum microstructural theories where the kinematic state can change independently through translational and microstructural degrees of freedom, we view  $\mathbf{F}\mathbf{F}^\top$  as an appropriate strain measure for the translational degrees of freedom and  $\mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top$  as an *independent strain measure* for the relative distortion of the microstructural degrees of freedom. Thus the total state of strain is expressed by two strain measures: one for the macroscopic degrees of freedom, the other for the microscopic degrees of freedom.

With no loss of generality, we can express the free-energy density as a function  $\check{\psi}$  of the two strain tensors and the current microstructure:

$$\hat{\psi}(\mathbf{F}, \mathbf{A}, \mathbf{A}_*) = \check{\psi}(\mathbf{F}\mathbf{F}^\top, \mathbf{A}, \mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top). \quad (4.2)$$

Invariance also requires that  $\check{\psi}$  be an isotropic function, viz.

$$\check{\psi}(\mathbf{R}\mathbf{F}\mathbf{F}^\top\mathbf{R}^\top, \mathbf{R}\mathbf{A}\mathbf{R}^\top, \mathbf{R}\mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top\mathbf{R}^\top) = \check{\psi}(\mathbf{F}\mathbf{F}^\top, \mathbf{A}, \mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top) \quad (4.3)$$

for all rotations  $\mathbf{R}$ .

The expression (4.2) makes clear the connection between our theory and the neo-classical theory. Specifically, we can view the neo-classical expression (2.8) for the free-energy density as a special case of our (4.2), a case in which the free-energy density is independent of the left Cauchy–Green strain tensor and depends on the relative strain tensor (4.1) linearly through its first scalar-invariant and also through the logarithm of its third scalar-invariant.

A simple example serves to show that the left Cauchy–Green strain tensor  $\mathbf{F}\mathbf{F}^\top$  is insufficient to characterize the strain of a nematic elastomer. Suppose that an external field changes the orientation of the nematic mesogens but does not change the shape of the material. In this case,  $\mathbf{F}\mathbf{F}^\top = \mathbf{I}$ , but  $\mathbf{A} = \mathbf{R}\mathbf{A}_*\mathbf{R}^\top$  where  $\mathbf{R}$  is the rotation; while the left Cauchy–Green tensor reduces to the identity tensor, the relative strain (4.1) does not.

Just as the left Cauchy–Green tensor is not the only possible measure of strain in non-linear elasticity, (4.1) is not the only possible measure of relative strain in nematic elasticity. Some equivalent relative strain measures are

$$\mathbf{A}^{-1/2}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top\mathbf{A}^{-1/2}, \quad \mathbf{F}\mathbf{A}_*\mathbf{F}^\top\mathbf{A}^{-1}, \quad \mathbf{A}_*\mathbf{F}^\top\mathbf{A}^{-1}\mathbf{F}. \quad (4.4)$$

The choice of which one to use is dictated by taste and/or convenience.

In the special case where the microstructure deforms materially, so that the relative strain tensor (4.1) is the identity tensor, it follows from (4.1) that  $\mathbf{A} = \mathbf{F}\mathbf{A}_*\mathbf{F}^\top$ . Thus, by (4.2)

$$\psi = \check{\psi}(\mathbf{F}\mathbf{F}^\top, \mathbf{F}\mathbf{A}_*\mathbf{F}^\top, \mathbf{I}). \quad (4.5)$$

Since  $\mathbf{A}_*$  is fixed by the choice of reference configuration, (4.5) is a constitutive relation for the free-energy density of a non-linear anisotropic elastic solid where the  $\mathbf{A}_*$  contains the fixed anisotropy of the reference configuration (Ericksen and Rivlin, 1954).

The idea of a relative strain measure goes back at least to the works of Mindlin (1964) and Toupin (1964) on elastic solids with director  $\mathbf{d}$ . They introduced the quantity

$$\mathbf{F}^\top(\mathbf{d} - \mathbf{F}\mathbf{d}_*) \quad (4.6)$$

to describe the relative deviation of the director from the macroscopic deformation of the solid. This quantity vanishes when the director deforms as a material line element. They then postulated an energy as function of the total strain, the relative strain and the director. The relative strain measure (4.1) is a tensorial analog of (4.6), the choice of which is guided by molecular-statistical Gaussian network theory.

## 5 Special constitutive assumptions

To obtain explicit constitutive relations, additional assumptions need to be made. We follow the molecular-statistical theory and assume that, as in (2.1), the free-energy density  $\psi$  consists of separate elastic and nematic contributions  $\psi_e$  and  $\psi_n$ . One possibility is to express  $\psi_e$  and  $\psi_n$  in terms of the scalar invariants of the independent variables and then use the Cayley–Hamilton theorem to obtain the most general polynomial expression. As  $\psi$  must be an isotropic function of three tensorial quantities, this procedure would lead to coefficients too numerous to be practical. Here we follow a simpler approach in an attempt to obtain practical expressions that capture the essential qualitative features. For example, one could consider the special case where the elastic contribution  $\psi_e$  to the free-energy density decouples in each variable and is linear in each strain tensor. Such an expression however would lead to a non-vanishing internal body-force in the reference configuration. Again taking our cue from the statistical theory, we add a “correction” to give a vanishing internal body-force and postulate that

$$\psi_e = \frac{1}{2}\mu(\text{tr}(\mathbf{F}\mathbf{F}^\top) - 3) + \frac{1}{2}\beta(\text{tr}(\mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top) - \log\det(\mathbf{A}^{-1}\mathbf{A}_*) - 3). \quad (5.1)$$

The expression (5.1) is consistent with the normalization condition (3.20). We can identify  $\mu$  with the usual shear modulus and  $\beta$  as a modulus associated with the contribution of the distortion of the polymer chains relative to the overall macroscopic deformation. Comparison with the neo-classical expression (2.8) shows that (5.1) reduces to (2.8) when  $\mu = 0$  and  $\beta = nk_B\theta$ . The expression (5.1) can be viewed as a generalization of the classical neo-Hookean expression arising in the theory of isotropic rubber elasticity to nematic rubber elasticity. In their study of stretched nematic-elastomeric sheets, Conti, DeSimone and Dolzmann (2002a) use (5.1) with  $\mu$  small relative to  $\beta$ . We, however, make no assumption on the relative magnitudes of these moduli.

For the nematic contribution  $\psi_n$ , a fourth-order Landau expansion in terms of the scalar invariants of  $\mathbf{A}$  and  $\mathbf{A}_*$  captures thermally-induced phase transitions. In particular, an expansion in the traceless component  $\mathbf{A} = \mathbf{A} - \frac{1}{3}(\text{tr}\mathbf{A})\mathbf{I}$  of  $\mathbf{A}$  provides a simple description (Fried and Sellers, 2003):

$$\psi_n = \frac{1}{2}\alpha_1\text{tr}(\mathbf{A}^2 - \mathbf{A}_*^2) + \frac{1}{3}\alpha_2\text{tr}(\mathbf{A}^3 - \mathbf{A}_*^3) + \frac{1}{4}\alpha_3((\text{tr}\mathbf{A}^2)^2 - (\text{tr}\mathbf{A}_*^2)^2), \quad (5.2)$$

where the coefficients  $\alpha_i$  may depend on the absolute temperature  $\theta$  and where  $\mathbf{A}_* = \mathbf{A}_* - \frac{1}{3}(\text{tr}\mathbf{A}_*)\mathbf{I}$ . The referential quantity  $\mathbf{A}_*$  appears explicitly in the nematic free-energy density in order to satisfy the normalization condition (3.20). The expression (5.2) might seem to be at odds with the material symmetry requirement (3.16). Note, however, that (3.16) allows for dependence upon the invariants of  $\mathbf{F}\mathbf{A}_*\mathbf{F}^\top(\mathbf{F}\mathbf{F}^\top)^{-1} = \mathbf{F}\mathbf{A}_*\mathbf{F}^{-1}$  and, further, that

$$\left. \begin{aligned} \text{tr}(\mathbf{F}\mathbf{A}_*\mathbf{F}^{-1}) &= \text{tr}(\mathbf{A}_*), \\ \text{tr}((\mathbf{F}\mathbf{A}_*\mathbf{F}^{-1})^2) &= \text{tr}(\mathbf{A}_*^2), \\ \text{tr}((\mathbf{F}\mathbf{A}_*\mathbf{F}^{-1})^3) &= \text{tr}(\mathbf{A}_*^3). \end{aligned} \right\} \quad (5.3)$$

Thus, (5.2) is consistent with the requirements (3.16) and (3.19) of material symmetry and objectivity.

Substitution into (3.12) leads to

$$\mathbf{S} = -p\mathbf{F}^{-\top} + \left( \mathbb{I} - \frac{1}{|\mathbf{F}^{-1}|^2} \mathbf{F}^{-\top} \otimes \mathbf{F}^{-\top} \right) (\mu\mathbf{F} + \beta\mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*) \quad (5.4)$$

for the stress tensor and

$$\begin{aligned} \mathbb{I} &= \frac{1}{2}\beta(\mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top - \mathbf{I})\mathbf{A}^{-1} - \alpha_1(\mathbf{A} - \frac{1}{3}(\text{tr}\mathbf{A})\mathbf{I}) \\ &\quad - \alpha_2(\mathbf{A}^2 - \frac{1}{3}(\text{tr}\mathbf{A}^2)\mathbf{I}) - \alpha_3(\text{tr}\mathbf{A}^2 - \frac{1}{3}(\text{tr}\mathbf{A})^2)(\mathbf{A} - \frac{1}{3}(\text{tr}\mathbf{A})\mathbf{I}). \end{aligned} \quad (5.5)$$

for the internal body-force density. Note that  $\mathbb{I}$  vanishes in the reference configuration when  $\mathbf{F} = \mathbf{I}$  and  $\mathbf{A} = \mathbf{A}_*$ :

$$\begin{aligned} \mathbb{I} &= -\alpha_1(\mathbf{A}_* - \frac{1}{3}(\text{tr}\mathbf{A}_*)\mathbf{I}) - \alpha_2(\mathbf{A}_*^2 - \frac{1}{3}(\text{tr}\mathbf{A}_*^2)\mathbf{I}) \\ &\quad - \alpha_3(\text{tr}\mathbf{A}_*^2 - \frac{1}{3}(\text{tr}\mathbf{A}_*)^2)(\mathbf{A}_* - \frac{1}{3}(\text{tr}\mathbf{A}_*)\mathbf{I}) = \mathbf{0}. \end{aligned} \quad (5.6)$$

This equation determines the possible  $\mathbf{A}_*$  and allows for isotropic, uniaxial, and biaxial symmetry.

In terms of the Cauchy stress, (5.4) becomes

$$\mathbf{T} = -p\mathbf{I} + \left( \mathbb{I} - \frac{1}{|\mathbf{F}^{-1}|^2} \mathbf{F}^{-\top} \otimes \mathbf{F}^{-\top} \right) (\mu\mathbf{F}\mathbf{F}^\top + \beta\mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top). \quad (5.7)$$

Thus the special choice (5.1) of the elastic contribution to the free-energy density yields a Cauchy stress-tensor linear in the orthogonal projections of  $\mathbf{F}\mathbf{F}^\top$  and  $\mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top$  and an internal body-force density linear in  $\mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top$ . In particular, when the measure  $\mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top$  of relative strain reduces to the identity, (5.7) reduces to the neo-Hookean expression for the Cauchy stress-tensor.

Importantly, the sole soft solutions corresponding to (5.1) are trivial rigid-body rotations. We choose a stable equilibrium configuration as the reference configuration. In this case,  $\mathbf{A}_*$  is a critical point of  $\psi_n$ . In the absence of external forces and torques, the force-free deformations are solutions of

$$\mathbf{T} = -p\mathbf{I}, \quad \mathbb{I} = \mathbf{0}, \quad (5.8)$$

and are the trivial rigid-body rotations

$$\mathbf{F} = \mathbf{R}, \quad \mathbf{A} = \mathbf{R}\mathbf{A}_*\mathbf{R}^\top, \quad (5.9)$$

where  $\mathbf{R}$  is an arbitrary rotation. Thus the non-uniqueness in the force-free strain has been eliminated to within trivial rigid-body rotations.

It is well-known that the neo-Hookean model, while adequate for many purposes, fails to capture the full range of observed phenomena in conventional rubber. The need for models which more closely match experimental observations led Mooney (1940) and Rivlin (1948) to propose phenomenologically-based constitutive relations that give the free-energy density as a function of the first and second principal invariants

$$I_1(\mathbf{F}\mathbf{F}^\top) = \text{tr}(\mathbf{F}\mathbf{F}^\top) \quad \text{and} \quad I_2(\mathbf{F}\mathbf{F}^\top) = \frac{1}{2}((\text{tr}(\mathbf{F}\mathbf{F}^\top))^2 - \text{tr}(\mathbf{F}\mathbf{F}^\top)^2) \quad (5.10)$$

of the left Cauchy–Green strain. The simplest such relation, due to Mooney (1940), is linear in  $I_1(\mathbf{F}\mathbf{F}^\top)$  and  $I_2(\mathbf{F}\mathbf{F}^\top)$ . In accord with this approach, we suggest

$$\begin{aligned} \psi_e &= \frac{1}{2}\mu(\lambda_1 I_1(\mathbf{F}\mathbf{F}^\top) + (1 - \lambda_1)I_2(\mathbf{F}\mathbf{F}^\top) - 3) + \frac{1}{2}\beta(\lambda_2 I_1(\mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top) \\ &\quad + (1 - \lambda_2)I_2(\mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top) - (2 - \lambda_2)\log\det(\mathbf{A}^{-1}\mathbf{A}_*) - 3), \end{aligned} \quad (5.11)$$

with  $0 \leq \lambda_1 \leq 1$  and  $0 \leq \lambda_2 \leq 1$ , as a counterpart of Mooney's (1940) expression appropriate for nematic elastomers. Again, the sole soft deformations corresponding to (5.11) are the trivial rigid-body rotations (5.9).

The two simple expressions (5.1) and (5.11) illustrate how the left Cauchy–Green strain tensor serves to regularize the neo-classical energy. Clearly more general expressions involving, for example, coupling of the two strain tensors can be generated. The need, however, for such generality and the resulting mathematical complexity is a question for experiment.

## 6 Examples

We now discuss two mechanical tests that make it possible to determine the elastic moduli  $\mu$  and  $\beta$  in the free-energy density function (5.1). We consider a monodomain specimen cross-linked with uniaxial chain shape described by the referential conformation tensor

$$\mathbf{A}_* = A_{*\perp} \mathbf{I} + (A_{*\parallel} - A_{*\perp}) \mathbf{n}_* \otimes \mathbf{n}_*. \quad (6.1)$$

Further, we restrict our attention to situations where the material remains uniaxial, so that

$$\mathbf{A} = A_{\perp} \mathbf{I} + (A_{\parallel} - A_{\perp}) \mathbf{n} \otimes \mathbf{n}, \quad (6.2)$$

with  $\mathbf{n}$  the current director. Throughout our discussion, we assume that the material parameters  $A_{\perp}$  and  $A_{\parallel}$  are known, having been determined by other (e.g., optical) means.

### 6.1 Imposed stretch

Consider a sheet-like specimen subjected to an imposed stretch in directions perpendicular to its thinnest dimension. Depending upon the ratio  $A_{\parallel}/A_{\perp}$  and the angle between  $\mathbf{n}$  and the direction of the stretch, instabilities involving rotations of the director can occur (Verwey, Warner and Terentjev, 1996). Provided that  $A_{\parallel}/A_{\perp} > 1$ , the stretch in the direction  $\mathbf{n}_*$  is stable. If  $A_{\parallel}/A_{\perp} < 1$ , then the stretch in the direction orthogonal to  $\mathbf{n}_*$  is stable. For simplicity we assume that  $A_{\parallel}/A_{\perp} > 1$  and that the direction of stretch is parallel to  $\mathbf{n}_*$ , so that  $\mathbf{A} = \mathbf{A}_*$  and the deformation gradient is given by

$$\mathbf{F} = \lambda^{-\frac{1}{2}} \mathbf{I} + (\lambda - \lambda^{-\frac{1}{2}}) \mathbf{n}_* \otimes \mathbf{n}_*, \quad (6.3)$$

with  $\lambda$  the stretch in the direction parallel to the director.

Assuming that the specimen is stress-free on its remaining sides, (5.4) reduces to

$$\mathbf{S} = (\mu + \beta) (\lambda - \lambda^{-2}) \mathbf{n}_* \otimes \mathbf{n}_*, \quad (6.4)$$

or, equivalently, (5.7) gives

$$\mathbf{T} = (\mu + \beta) (\lambda^2 - \lambda^{-1}) \mathbf{n}_* \otimes \mathbf{n}_*. \quad (6.5)$$

Thus we obtain the sum of the elastic moduli in terms of the imposed stretch  $\lambda$  and either of the stresses  $S_{\parallel}$  or  $T_{\parallel}$  in the direction of stretch:

$$\mu + \beta = \frac{S_{\parallel}}{(\lambda - \lambda^{-2})} = \frac{T_{\parallel}}{(\lambda^2 - \lambda^{-1})}. \quad (6.6)$$

## 6.2 Spontaneous deformations

We now consider shape changes induced by heating or cooling. We assume that the director does not rotate and that only  $A_\perp$  and  $A_\parallel$  change with the temperature, so that

$$\mathbf{A} = A_\perp \mathbf{I} + (A_\parallel - A_\perp) \mathbf{n}_* \otimes \mathbf{n}_* \quad (6.7)$$

The deformation gradient then has the form

$$\mathbf{F} = \ell^{-\frac{1}{2}} \mathbf{I} + (\ell - \ell^{-\frac{1}{2}}) \mathbf{n}_* \otimes \mathbf{n}_*, \quad (6.8)$$

with  $\ell$  the stretch associated with the thermal expansion or contraction in the direction of the director. We further assume that the temperature variations that induce the spontaneous deformation do not significantly affect  $\mu$  and  $\beta$ . Minimization of the energy (5.1) with respect to  $\ell$  yields

$$\ell^3 = \frac{\frac{\mu}{\beta} + \frac{A_{*\perp}}{A_\perp}}{\frac{\mu}{\beta} + \frac{A_{*\parallel}}{A_\parallel}} \quad (6.9)$$

Importantly, the spontaneous stretch  $\ell$  depends on the ratio of the elastic moduli  $\mu$  and  $\beta$ . For the neo-classical free-energy function (2.8), the expression (6.9) determining  $\ell$  reduces to  $\ell^3 = A_{*\perp} A_\parallel / A_\perp A_{*\parallel}$ , which is independent of  $\beta$ .

Solving (6.9) for the moduli yields

$$\frac{\mu}{\beta} = \frac{1}{\ell^3 - 1} \left( \frac{A_{*\perp}}{A_\perp} - \frac{A_{*\parallel}}{\ell^3 A_\parallel} \right) \quad (6.10)$$

In particular, when the sample is cooled to the isotropic state where  $A_\parallel = A_\perp = A$ , we obtain

$$\frac{\mu}{\beta} = \frac{\ell^3 A_{*\parallel} - A_{*\perp}}{A(1 - \ell^3)}. \quad (6.11)$$

In general, the relations (6.6) and (6.10) comprise a linear system of two equations in two unknowns. This system determines  $\mu$  and  $\beta$  uniquely in terms of  $\lambda$ ,  $\ell$ ,  $A_{*\perp}$ ,  $A_{*\parallel}$ ,  $A_\perp$ , and  $A_\parallel$ .

If, as would seem reasonable, we require that the moduli  $\mu$  and  $\beta$  be positive, then it follows from (6.10) that the spontaneous stretch  $\ell$  must satisfy either

$$\frac{A_{*\perp} A_\parallel}{A_{*\parallel} A_\perp} \leq \ell^3 \leq 1 \quad \text{or} \quad 1 \leq \ell^3 \leq \frac{A_{*\perp} A_\parallel}{A_{*\parallel} A_\perp}. \quad (6.12)$$

## 7 Discussion

We have presented a continuum model for nematic elastomers where a tensor  $\mathbf{A}$  models additional microstructural degrees of freedom associated with polymer-chain shape. The theory is internally consistent with no need for a relation coupling  $\mathbf{A}$  to the traceless nematic order-tensor  $\mathbf{Q}$ . Motivated by the statistical theory, we identify  $\mathbf{A}$  as the average of the second moment of the end-to-end vectors of the polymer chains. The neo-classical molecular-statistical theory further motivates us to introduce two independent strain measures: the left Cauchy–Green tensor  $\mathbf{F}\mathbf{F}^\top$ , which measures the overall macroscopic strain of the elastomer, and the relative strain tensor  $\mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top$ , which

measures the deformation of the polymer chains relative to the overall deformation. In our view, constitutive relations should be functions of both strain measures. We find that a constitutive theory developed in accord with this precept eliminates the degeneracy of the neo-classical theory.

In addition to the neo-classical expression, various non-linear expressions for the elastic contribution to the free-energy density have already been proposed. These include that used by Conti, DeSimone and Dolzmann (2002a) in their numerical scheme. Also, based on several microscopic mechanisms, Verwey and Warner (1997a,b) replaced  $\mathbf{A}^{-1}$  in (2.8) with a uniaxial perturbation to obtain a free-energy density function with an additional contribution, which was given by Terentjev (1999) as

$$\psi_e = \frac{1}{2}nk_B\theta(\text{tr}(\mathbf{A}^{-1}\mathbf{F}\mathbf{A}_*\mathbf{F}^\top) - \log\det(\mathbf{A}^{-1}\mathbf{A}_*)) + \epsilon|\mathbf{n} - \mathbf{n}_* + (\mathbf{F}^\top\mathbf{n}) \times (\mathbf{n} - \mathbf{n}_*)|^2 - 3), \quad (7.1)$$

where  $\mathbf{n}$  is the unit director representing the axis of uniaxial alignment. When  $\epsilon$  is small but nonzero, the additional terms break the degenerate symmetry of the neo-classical expression.

Additionally, Olmsted (1994) suggested an elastic free-energy density function constructed from

$$\text{tr}(\mathbf{A}^{-n}(\mathbf{F}\mathbf{A}_*\mathbf{F}^\top)^m) \quad (7.2)$$

with  $m$  and  $n$  arbitrary. In proposing the above, Olmsted claimed that an additional explicit dependence on  $\mathbf{F}\mathbf{F}^\top$  is excluded by invariance. As we have shown, however, invariance due to material symmetry and objectivity does not exclude such a dependence. And we view the unusual invariance exhibited by (2.8) as degenerate. Not only does an expansion such as (7.2) fail to account properly for the idea of relative strain as suggested by the statistical theory, but it also excludes the overall macroscopic strain—a quantity we view as fundamental.

In an alternative approach, Uchida and Onuki (1999) proposed

$$\psi_e = \frac{1}{2}nk_B\theta\text{tr}(\mathbf{F}^\top\mathbf{F} - \delta\mathbf{F}^\top\mathbf{Q}\mathbf{F}) \quad (7.3)$$

with  $\mathbf{Q}$  the traceless nematic order-tensor and  $\delta$  an additional material parameter. Here the choice of variables is different, and there is no need for an additional closure relation. The expression (7.3) takes into account the overall macroscopic strain expressed by the right Cauchy-Green strain tensor  $\mathbf{F}^\top\mathbf{F}$ , but fails to incorporate the relative strain of the microstructure implied by the statistical theory.

In the mechanics of deformable media, force arises from strain. Our approach here has been to identify potentially important strain measures and to develop constitutive relations as functions of those measures. For nematic elastomers, two strain measures arise naturally. Both of these measures seem to be important in the mechanical description of these novel materials.

## Acknowledgments

This work was supported by the National Science Foundation and the Department of Energy.

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