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# An elementary molecular-statistical basis for the Mooney and Rivlin–Saunders theories of rubber elasticity

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## Abstract

By relaxing the assumption that the end-to-end vectors of molecules transform as macroscopic material line elements, we arrive at a generalization of the molecular-statistical theory of rubber elasticity. This generalization includes as special cases continuum-mechanical theories proposed by Mooney and by Rivlin and Saunders as improvements upon the classical neo-Hookean theory. © 2002 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

The goal of the molecular-statistical theory of rubber elasticity is to deliver, on the basis of microscopic considerations, a macroscopic constitutive relation  $\psi = \hat{\psi}(\mathbf{F})$  determining the free-energy density  $\psi$  as a function of the deformation gradient  $\mathbf{F}$ . The earliest efforts in this direction were those of Flory (1944), Flory and Rehner (1943), Guth and Mark (1934), James and Guth (1943), James (1947), Kuhn (1936, 1938), Kuhn and Grün (1946), Wall (1942a, b, 1943), and Treloar (1943a, b), each of whom obtained the neo-Hookean free-energy density

$$\hat{\psi}(\mathbf{F}) = \frac{1}{2}\mu(|\mathbf{F}|^2 - 3), \quad (1.1)$$

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involving a shear modulus  $\mu$  proportional to the product  $k_B\theta$  of the Boltzmann constant  $k_B$  with the absolute temperature  $\theta$ .<sup>1</sup> Tacit in the derivation of Eq. (1.1) is the premise of incompressibility, as embodied by the constraint  $\det \mathbf{F} = 1$ .

Subsequent to the development of the neo-Hookean theory, Treloar (1944) performed a series of experiments designed to test its validity. For uniaxial compression, predictions based on Eq. (1.1) agree well with the measurements taken over a wide range of strains. However, for simple extension and pure shear, Eq. (1.1) yields predictions that depart appreciably from the measurements—even at small strains. Two major difficulties are apparent. First, at sufficiently large strains the stress response curves for simple extension and pure shear grow sharply and exhibit an upward curvature, reflecting an increased resistance as molecules become more elongated. In contrast, the neo-Hookean theory yields response curves with linear growth. This discrepancy arises from the assumption, fundamental to the theory, that molecules adopt only coil-like configurations with end-to-end separations that are small in comparison to their fully extended lengths.<sup>2</sup> The second, more significant, disagreement between theory and experiment occurs for intermediate levels of strain—that is, for extension ratios and shear strains ranging between 1.5 and 4.0. In this regime, the theory both overestimates the stresses and fails to capture the upward curvatures of the relevant response curves.

Roughly concurrent with these advances in molecular theory and experiment, Rivlin (1948a, b) developed a continuum-mechanical theory for rubber elasticity. While the molecular-statistical theory rests on microphysical assumptions concerning the properties of polymeric molecules and networks, the continuum-mechanical theory hinges on macrophysical assumptions of invariance and symmetry. When combined with the constraint of incompressibility, these continuum-level assumptions require that the free-energy density take the form

$$\psi = \tilde{\psi}(I_1(\mathbf{B}), I_2(\mathbf{B})), \quad (1.2)$$

where  $\mathbf{B} = \mathbf{F}\mathbf{F}^T$  denotes the left Cauchy–Green tensor and the strain invariants  $I_1$  and  $I_2$  are defined by

$$I_1(\mathbf{B}) = \text{tr } \mathbf{B} \quad \text{and} \quad I_2(\mathbf{B}) = \frac{1}{2}((I_1(\mathbf{B}))^2 - I_1(\mathbf{B}^2)). \quad (1.3)$$

A special case of Eq. (1.2) is the Mooney (1940) free-energy density

$$\hat{\psi}(\mathbf{F}) = \frac{1}{2}\mu(\alpha I_1(\mathbf{B}) + (1 - \alpha)I_2(\mathbf{B}) - 3), \quad (1.4)$$

with  $\alpha$  a dimensionless material parameter taking values on the interval  $[0, 1]$  and  $\mu$ , as before, the constant shear modulus. This relation is the most general form of Eq.

<sup>1</sup> The exact features of the factor of proportionality determining  $\mu$  vary. In Kuhn's (1936, 1938) theory, this factor is simply the number  $\nu$  of molecules per unit volume—so that  $\mu = \nu k_B \theta$ . In the alternate formulation of James and Guth (1943),  $\nu$  is replaced by the cycle-rank  $\xi$ , which reckons the number of independent circuits in the network. For a network free of imperfections,  $\xi = (1 - 2/\phi)\nu$ , with  $\phi \geq 3$  the number of polymer chains emanating from each network junction; thus, for a tetrafunctional network, the theory of James and Guth (1943) predicts a shear modulus equal to one-half that given by the theory of Kuhn (1936, 1938).

<sup>2</sup> To remedy this problem, Treloar (1946) extended the neo-Hookean theory to account for non-Gaussian chain statistics.

(1.2) that, under conditions of simple shear, leads to a linear relation between the shear stress and the amount of shear. On setting  $\alpha = 1$  and noting that  $I_1(\mathbf{B}) = |\mathbf{F}|^2$ , Eq. (1.4) reduces to relation (1.1) obtained from the molecular-statistical theory.

For simple extensions in the intermediate range of strains, experiments performed by Rivlin and Saunders (1951) showed that predictions based on Eq. (1.4) improve markedly over those based on Eq. (1.1). However, for simple compression, Rivlin and Saunders (1951) found that Eq. (1.4) falls short, giving predictions that are inferior to those obtained from Eq. (1.1). Further, even when Eq. (1.4) yields predictions consistent with observations, a single value of  $\alpha$  is inadequate to fit the data acquired from tests performed in different experimental configurations.

In addition to simple extension and compression, Rivlin and Saunders (1951) performed a broad spectrum of very careful experiments and found that their observations were consistent with the generalization

$$\hat{\psi}(\mathbf{F}) = \frac{1}{2}\mu(\alpha I_1(\mathbf{B}) + (1 - \alpha)f(I_2(\mathbf{B})) - 3) \quad (1.5)$$

of Eq. (1.4) involving a function  $f$  consistent with the requirement that  $f''(I_2) < 0$  for all admissible values of  $I_2$ . We refer to Eq. (1.5) as the Rivlin–Saunders free-energy density.<sup>3</sup>

Our goal here is to provide a molecular-statistical theory leading to a class of free-energy densities which includes both Eqs. (1.4) and (1.5). To achieve this, we take the most elementary of possible approaches. We begin with a brief synopsis of the classical approach, making clear the assumptions needed to obtain the neo-Hookean theory. Subsequently, we relax just one of these assumptions—which concerns with the manner in which the end-to-end vectors of molecules transform under a macroscopic deformation. This relaxation leads to a broad class of free-energy densities with the general form (1.2) arising in Rivlin's (1948a, b) continuum-mechanical theory. Straightforward specializations then lead to the particular forms (1.4) and (1.5).

## 2. Neo-Hookean elasticity

From the atomistic perspective, rubber is an amorphous network of polymeric molecules cross-linked at various junctions. At the continuum level, each material point is viewed as consisting of such a network. Hereafter, we confine our attention to a single material point and denote by  $\mathbf{F}$  the deformation gradient at that point.

Within the framework of statistical mechanics, the neo-Hookean theory of rubber elasticity can be obtained as a consequence of the following assumptions:

<sup>3</sup> It is not our view that the Rivlin–Saunders free-energy density represents the culminating achievement of the theory of rubber elasticity. Indeed, in a recently published paper, Criscione et al. (2000) developed a framework that allows specific forms of the free-energy density to be determined with a degree of accuracy that improves upon that possible with the Rivlin–Saunders description.

- A<sub>1</sub>. Each molecule is a freely jointed chain consisting of an identically large number of monomer units.
- A<sub>2</sub>. The distance separating the ends of each molecule is always small in comparison with the fully extended length of the molecule.
- A<sub>3</sub>. Under a macroscopic deformation, the end-to-end vectors of molecules transform as macroscopic material line elements.
- A<sub>4</sub>. Interactions between molecules are negligible in comparison to those between the monomer units of single molecules.
- A<sub>5</sub>. The network is free of loose chain ends and other imperfections.

Assumption A<sub>1</sub> implies that the orientations of contiguous monomers are uncorrelated—that is, that the average angle between any pair of adjacent monomer units vanishes. As a consequence of this, the ensemble averaged end-to-end length  $\ell$  of a molecule comprising  $n$  monomer units of length  $l$  is given by  $\ell = \sqrt{n}l$  (which, for  $n$  sufficiently large, is much smaller than the molecular length  $nl$ ). Moreover, the Fourier transform of the distribution function for the end-to-end vector  $\mathbf{r}$  of such a molecule assumes the explicit form

$$\left( \frac{\sin(l|\boldsymbol{\kappa}|)}{l|\boldsymbol{\kappa}|} \right)^n \quad (2.1)$$

and the distribution function itself is given in terms of the inverse Fourier transform

$$\frac{1}{8\pi^3} \int_{\mathcal{E}} \exp(-i\mathbf{r} \cdot \boldsymbol{\kappa}) \left( \frac{\sin(l|\boldsymbol{\kappa}|)}{l|\boldsymbol{\kappa}|} \right)^n d\nu(\boldsymbol{\kappa}), \quad (2.2)$$

where  $\mathcal{E}$  denotes three-dimensional Euclidean space. Provided that  $n$  is sufficiently large, Eq. (2.2) reduces to the Gaussian distribution

$$p(|\mathbf{r}|; \ell) = \left( \frac{3}{2\pi\ell^2} \right)^{3/2} \exp\left( -\frac{3|\mathbf{r}|^2}{2\ell^2} \right). \quad (2.3)$$

The necessity of assumption A<sub>2</sub> becomes apparent on inspection of Eq. (2.3), which delivers a non-vanishing probability for the physically untenable situation where the end-to-end separation  $|\mathbf{r}|$  equals or exceeds the fully extended molecular length  $nl$ . Hence, granted A<sub>2</sub>, the Gaussian (2.3) serves as a valid distribution.

Assumption A<sub>3</sub> requires that the network deform homogeneously with the deformation gradient  $\mathbf{F}$ . More specifically, writing  $\mathbf{r}$  for the end-to-end vector of a generic molecule belonging to the network at the point in question, assumption A<sub>3</sub> requires that

$$\mathbf{r} \mapsto \mathbf{F}\mathbf{r}. \quad (2.4)$$

In view of Eq. (2.4), the ratio

$$\zeta(\mathbf{F}, \mathbf{r}; \ell) = \frac{p(|\mathbf{F}\mathbf{r}|; \ell) \det \mathbf{F}}{p(|\mathbf{r}|; \ell)} \quad (2.5)$$

determines the conditional probability that the undistorted end-to-end vector of the molecule is  $\mathbf{F}\mathbf{r}$  instead of  $\mathbf{r}$ . Here, we adopt the approach of Wall and Flory (1951),

who, to account for the dispersion of network junctions, allow for local volume changes. Thus, instead of imposing the constraint  $\det \mathbf{F} = 1$  as a universal requirement, we merely insist that  $\det \mathbf{F} > 0$ .

Granted Eq. (2.5), the deformation-induced entropy of a molecule with undistorted end-to-end vector  $\mathbf{r}$  is given by

$$k_B \log \zeta(\mathbf{F}, \mathbf{r}; \ell) \quad (2.6)$$

with  $k_B$  the Boltzmann constant.

Assumption  $A_4$  requires that the (macroscopic) free-energy density must be purely entropic. Granted that the network contains  $\nu$  molecules per unit volume, assumption  $A_5$  implies that all molecules are equally active in the deformation. Thus, bearing in mind Eq. (2.6), the free-energy density is given by

$$\hat{\psi}(\mathbf{F}) = -\mu \int_{\mathcal{E}} p(|\mathbf{r}|; \ell) \log \zeta(\mathbf{F}, \mathbf{r}; \ell) dv(\mathbf{r}), \quad (2.7)$$

where the shear modulus  $\mu$  is determined in terms of the Boltzmann constant  $k_B$  and the absolute temperature  $\theta$  by

$$\mu = \nu k_B \theta. \quad (2.8)$$

We note that, since  $\zeta(\mathbf{Q}, \mathbf{r}; \ell) = 1$  for any rotation  $\mathbf{Q}$ , the free-energy density (2.7) complies automatically with the normalization  $\hat{\psi}(\mathbf{Q}) = 0$ .

To evaluate the integral on the right-hand side of Eq. (2.7), we first use Eqs. (2.5) and (2.3), and use the fact that  $p(\cdot; \ell)$  is a distribution and expand the logarithmic factor in the integrand to obtain

$$\hat{\psi}(\mathbf{F}) = \frac{1}{2} \mu \left( \frac{3}{\ell^2} \int_{\mathcal{E}} p(|\mathbf{r}|; \ell) (|\mathbf{F}\mathbf{r}|^2 - |\mathbf{r}|^2) dv(\mathbf{r}) - 2 \log \det \mathbf{F} \right). \quad (2.9)$$

Next, applying Theorem A.2 of the appendix to the integral term in Eq. (2.9), recalling once again that  $I_1(\mathbf{B}) = |\mathbf{F}|^2$ , and defining the third strain invariant

$$I_3(\mathbf{B}) = \det \mathbf{B}, \quad (2.10)$$

we arrive at the neo-Hookean free-energy density

$$\hat{\psi}(\mathbf{F}) = \frac{1}{2} \mu (I_1(\mathbf{B}) - \log I_3(\mathbf{B}) - 3) \quad (2.11)$$

for compressible rubber. The classical neo-Hookean expression (1.1) for incompressible rubber follows from Eq. (2.11) on stipulating that the deformation gradient satisfy the constraint  $\det \mathbf{F} = 1$ .

### 3. Departures from neo-Hookean elasticity

We now relax assumption  $A_3$  by supposing that the end-to-end vector  $\mathbf{r}$  of a generic molecule transforms according to

$$\mathbf{r} \mapsto \mathbf{K}(\mathbf{F})\mathbf{r}, \quad (3.1)$$

where  $\mathbf{K}$  obeys

$$\det \mathbf{K}(\mathbf{F}) > 0 \quad (3.2)$$

for all  $\mathbf{F}$  with  $\det \mathbf{F} > 0$ , and

$$\mathbf{K}(\mathbf{Q}) = \mathbf{Q} \quad (3.3)$$

for all rotations  $\mathbf{Q}$ . We observe that the conventional choice  $\mathbf{K}(\mathbf{F}) = \mathbf{F}$  satisfies both Eqs. (3.2) and (3.3).

If we continue to invoke assumptions  $A_1$ ,  $A_2$ , and  $A_4$ , the distribution function (2.2) and its Gaussian approximation (2.3) remain unchanged. However, when  $\mathbf{r}$  transforms to  $\mathbf{K}(\mathbf{F})\mathbf{r}$ , the relevant conditional probability is no longer Eq. (2.5), but, rather, is  $\zeta(\mathbf{K}(\mathbf{F}), \mathbf{r}; \ell)$ . Then, granting assumption  $A_5$ , Eq. (2.7) is replaced by

$$\hat{\psi}(\mathbf{F}) = -\mu \int_{\mathcal{E}} p(|\mathbf{r}|; \ell) \log \zeta(\mathbf{K}(\mathbf{F}), \mathbf{r}; \ell) dv(\mathbf{r}) \quad (3.4)$$

and, bearing in mind Eq. (3.2), we may apply Theorem A.2 of the appendix to obtain the generalization

$$\hat{\psi}(\mathbf{F}) = \frac{1}{2} \mu (|\mathbf{K}(\mathbf{F})|^2 - 2 \log \det \mathbf{K}(\mathbf{F}) - 3) \quad (3.5)$$

of the neo-Hookean expression (2.11). Inequality (3.2) ensures that the logarithmic term in Eq. (3.5) is well defined, while relation (3.3) guarantees that the free-energy density is normalized as in the neo-Hookean case considered above.

Without further restrictions on the mapping  $\mathbf{K}$ , the right-hand side of Eq. (3.5) may, in general, yield an expression inconsistent with the invariance and symmetry requirements imposed in conventional continuum-mechanical descriptions of rubber elasticity. To formulate such restrictions, we examine the invariance and symmetry properties of the conventional choice  $\mathbf{r} \mapsto \mathbf{F}\mathbf{r}$ . Specifically, we consider changes of observer and reference configuration characterized, respectively, by arbitrary rotations  $\mathbf{Q}_1$  and  $\mathbf{Q}_2$  and observe that, under their combined influence,  $\mathbf{F} \mapsto \mathbf{Q}_1 \mathbf{F} \mathbf{Q}_2$ . Consistent with this observation, we require that any mapping  $\mathbf{K}$  entering into a rule of the form (3.1) obey

$$\mathbf{K}(\mathbf{Q}_1 \mathbf{F} \mathbf{Q}_2) = \mathbf{Q}_1 \mathbf{K}(\mathbf{F}) \mathbf{Q}_2 \quad (3.6)$$

for all rotations  $\mathbf{Q}_1$  and  $\mathbf{Q}_2$ . A standard argument (Truesdell and Noll, 1965) then shows that  $\mathbf{K}$  satisfies this functional requirement if and only if it admits the representation

$$\mathbf{K}(\mathbf{F}) = \kappa_1(\iota(\mathbf{B}))\mathbf{F} + \kappa_2(\iota(\mathbf{B}))\mathbf{F}^* + \kappa_3(\iota(\mathbf{B}))\mathbf{B}\mathbf{F} \quad (3.7)$$

with

$$\mathbf{F}^* = (\det \mathbf{F})\mathbf{F}^{-\top} \quad (3.8)$$

the adjugate of  $\mathbf{F}$  and  $\iota(\mathbf{B}) = (I_1(\mathbf{B}), I_2(\mathbf{B}), I_3(\mathbf{B}))$  the list of deformation invariants. Inequality (3.2) imposes a non-trivial restriction on the coefficients  $\kappa_1$ ,  $\kappa_2$ , and  $\kappa_3$ ; further, to ensure that Eq. (3.3) holds,  $\kappa_1$ ,  $\kappa_2$ , and  $\kappa_3$  must be consistent with  $\kappa_1(\iota(\mathbf{1})) + \kappa_2(\iota(\mathbf{1})) + \kappa_3(\iota(\mathbf{1})) = 1$ .

Granted that  $\mathbf{K}$  takes the form given in Eq. (3.7), a series of tedious calculations give expressions (too lengthy to reproduce here) for  $|\mathbf{K}(\mathbf{F})|^2$  and  $\det \mathbf{K}(\mathbf{F})$  in terms of  $I_1(\mathbf{B})$ ,  $I_2(\mathbf{B})$ , and  $I_3(\mathbf{B})$ . Consistent with our expectations concerning invariance and symmetry, Eq. (3.5) then determines the free-energy density as a function of the invariant list  $\iota(\mathbf{B})$ . Since the aforementioned expressions for  $|\mathbf{K}(\mathbf{F})|^2$  and  $\det \mathbf{K}(\mathbf{F})$  include implicit dependencies on  $\iota(\mathbf{B})$  through the coefficients  $\kappa_1$ ,  $\kappa_2$ , and  $\kappa_3$ , Eqs. (3.5) and (3.7) encompass a broad variety of free-energy densities.

#### 4. Free-energy densities as volume-weighted combinations

Suppose that, for each  $i = 1, 2, \dots, m$ ,  $\mathbf{K}_i$  obeys  $\det \mathbf{K}_i(\mathbf{F}) > 0$ ,  $\mathbf{K}_i(\mathbf{Q}) = \mathbf{Q}$  for all rotations  $\mathbf{Q}$ , and  $\mathbf{K}_i(\mathbf{Q}_1 \mathbf{F} \mathbf{Q}_2) = \mathbf{Q}_1 \mathbf{K}_i(\mathbf{F}) \mathbf{Q}_2$  for all rotations  $\mathbf{Q}_1$  and  $\mathbf{Q}_2$ .<sup>4</sup> Further, let  $\alpha_1, \alpha_2, \dots, \alpha_m$  be numbers consistent with the constraints

$$0 \leq \alpha_i \leq 1, \quad i = 1, 2, \dots, m, \quad \text{and} \quad \sum_{i=1}^m \alpha_i = 1. \quad (4.1)$$

Then, assuming that, for each  $i = 1, 2, \dots, m$ , the end-to-end vectors of  $\alpha_i v$  molecules per unit volume transform according to  $\mathbf{r} \mapsto \mathbf{K}_i(\mathbf{F})\mathbf{r}$ , a transparent extension of the argument leading to Eq. (3.5) leads to the further generalization

$$\hat{\psi}(\mathbf{F}) = \frac{1}{2} \mu \left( \sum_{i=1}^m \alpha_i |\mathbf{K}_i(\mathbf{F})|^2 - 2 \log \prod_{i=1}^m (\det \mathbf{K}_i(\mathbf{F}))^{\alpha_i} - 3 \right) \quad (4.2)$$

of the neo-Hookean expression (2.11).

#### 5. Mooney elasticity

We consider Eq. (4.2) with  $m = 2$  and select the particular forms

$$\mathbf{K}_1(\mathbf{F}) = \mathbf{F} \quad \text{and} \quad \mathbf{K}_2(\mathbf{F}) = \mathbf{F}^* \quad (5.1)$$

for  $\mathbf{K}_1$  and  $\mathbf{K}_2$ . A direct calculation shows that  $\det \mathbf{K}_2(\mathbf{F}) > 0$  and  $\mathbf{K}_2(\mathbf{Q}) = \mathbf{Q}$  for all rotations  $\mathbf{Q}$ . While the first of Eq. (5.1) is simply the conventional rule  $\mathbf{r} \mapsto \mathbf{F}\mathbf{r}$  corresponding to assumption A<sub>3</sub> and, thus, demands that end-to-end vectors transform as material line elements, the second of Eq. (5.1) gives rise to a rule,  $\mathbf{r} \mapsto \mathbf{F}^*\mathbf{r}$ , which follows on assuming that all vectors  $\mathbf{s}$  orthogonal to  $\mathbf{r}$  transform according to  $\mathbf{s} \mapsto \mathbf{F}\mathbf{s}$  and, thus, requires that end-to-end vectors transform as vectors normal to material surface elements.

Writing  $\alpha = \alpha_1$ , inserting Eq. (5.1) in Eq. (4.2), and using the identities

$$\det \mathbf{F}^* = (\det \mathbf{F})^2 \quad \text{and} \quad |\mathbf{F}^*|^2 = \frac{|\mathbf{F}^{-\top}|^2}{(\det \mathbf{F}^{-\top})^2} = \frac{I_1(\mathbf{B}^{-1})}{I_3(\mathbf{B}^{-1})} = I_2(\mathbf{B}) \quad (5.2)$$

along with the definitions (1.3) and (2.10) of the strain invariants  $I_1$ ,  $I_2$ , and  $I_3$ , we obtain the Mooney free-energy density

$$\hat{\psi}(\mathbf{F}) = \frac{1}{2} \mu (\alpha I_1(\mathbf{B}) + (1 - \alpha) I_2(\mathbf{B}) - (2 - \alpha) \log I_3(\mathbf{B}) - 3) \quad (5.3)$$

for compressible rubber. As in the neo-Hookean case, the conventional Mooney expression (1.4) for incompressible rubber follows from Eq. (5.3) on stipulating that the deformation gradient comply with the constraint  $\det \mathbf{F} = 1$ .

<sup>4</sup> Thus, in particular, each  $\mathbf{K}_i$  admits a representation of the form (3.7).

## 6. Rivlin–Saunders elasticity

We replace the second of the rules (5.1) by

$$\mathbf{K}_2(\mathbf{F}) = \kappa(I_2(\mathbf{B}))\mathbf{F}^*, \quad (6.1)$$

where, consistent with the requirements that  $\det \mathbf{K}_2(\mathbf{F}) > 0$  and  $\mathbf{K}_2(\mathbf{Q})$ ,  $\kappa$  obeys

$$\kappa(I_2) > 0 \quad (6.2)$$

for all admissible values of  $I_2$  and

$$\kappa(3) = 1. \quad (6.3)$$

Then, defining  $f$  through

$$f(I_2) = I_2 \kappa^2(I_2) - \frac{3}{2} \log \kappa(I_2) \quad (6.4)$$

and proceeding as above, we obtain the Rivlin–Saunders free-energy density

$$\hat{\psi}(\mathbf{F}) = \frac{1}{2} \mu (\alpha I_1(\mathbf{B}) + (1 - \alpha) f(I_2(\mathbf{B}))) - (2 - \alpha) \log I_3(\mathbf{B}) - 3 \quad (6.5)$$

for compressible rubber. As in neo-Hookean and Mooney elasticity, the Rivlin–Saunders expression (1.5) for incompressible rubber follows from Eq. (6.5) on stipulating that the deformation gradient comply with the constraint  $\det \mathbf{F} = 1$ .

Given an expression for  $\kappa$ , Eq. (6.4) determines  $f$  uniquely. However, given an expression for  $f$ , Eq. (6.4) is a transcendental equation that may possess multiple solutions or even be insoluble. From Eq. (6.2),  $f$  as defined by Eq. (6.4) is consistent. The empirical inequality  $f''(I_2) < 0$  suggested by the data of Rivlin and Saunders (1951) holds for all admissible values of  $I_2$  provided that  $\kappa$  obeys

$$\kappa(I_2) \kappa''(I_2) > \frac{4}{3} (\kappa^3(I_2) \kappa(I_2) \kappa'(I_2) + I_2 \kappa^2(I_2) \kappa'(I_2) + \kappa^3(I_2)) + (\kappa'(I_2))^2 \quad (6.6)$$

for all admissible values of  $I_2$ .

## 7. Discussion

Within our framework, the Mooney and Rivlin–Saunders free-energy densities arise similarly—by allowing some fraction of the molecular end-to-end vectors to transform in a manner other than as material line elements. To obtain the Mooney free-energy density, the relevant end-to-end vectors transform as vectors normal to material surface elements. To obtain the Rivlin–Saunders free-energy density, the relevant end-to-end vectors reorient as vectors normal to material surface elements but are scaled by a factor that depends on the local state of strain through the second strain invariant  $I_2$ . The breakdown of the neo-Hookean theory in the intermediate range of strains is commonly attributed to junction constraints associated with chain entanglements (Flory, 1976; Ronca and Allegra, 1975). In view of our results, it is tempting to speculate that chain entanglements may result in the formation of surface-like elements.

Assumption  $A_3$  is analogous to the Born rule for crystalline solids (Born, 1915), a rule which dictates that lattice vectors deform as material line elements. While the Born rule is reliable for monatomic crystals that admit descriptions as Bravais lattices,



it often fails for other kinds of crystals (Ericksen, 1984, 1997; Zanzotto, 1992). One might therefore expect that, for a material with a molecular structure as complex as that of rubber, the Born-like hypothesis  $A_3$  would prove to be of limited applicability. As such, we see no physical basis for dismissing the more general class of transformation rules considered here—including the particular choice leading to the Rivlin–Saunders free-energy density.

A precedent for a transformation rule of the form (3.1) exists in the rheology literature. In molecular-statistical theories for polymer solutions, the analog of the conventional transformation rule (2.4) is the requirement that the end-to-end vector  $\mathbf{r}$  of a generic molecule evolve according to the equation  $\dot{\mathbf{r}} - \mathbf{W}\mathbf{r} = \mathbf{D}\mathbf{r}$  (Lodge, 1968; Yamamoto, 1956), where  $\mathbf{D}$  and  $\mathbf{W}$  denote the symmetric and antisymmetric components of the macroscopic velocity gradient and a superposed acute accent represents the partial time derivative. This assumption delivers the upper-convected Maxwell fluid. A generalized evolution equation of the form  $\dot{\mathbf{r}} - \mathbf{W}\mathbf{r} = \mathbf{G}(\mathbf{D}, \mathbf{r})\mathbf{r}$ , with  $\mathbf{G}$  a symmetric and isotropic function of  $\mathbf{D}$  and  $\mathbf{r}$ , was considered by Phan Thien and Tanner (1977). When  $\mathbf{G}$  is independent of  $\mathbf{r}$  and linear in  $\mathbf{D}$ , the equation of Phan Thien and Tanner (1977) specializes to the linear bead-spring equation of Gordon and Schowalter (1972), a equation that delivers the full spectrum of rheological theories delimited by the lower- and upper-convected Maxwell fluids.

It is important to recognize the limitations, as embodied by assumptions  $A_1$ ,  $A_2$ ,  $A_4$ , and  $A_5$ , inherent to our approach. Assumptions  $A_1$  and  $A_2$  confine the validity of the theory to situations in which the end-to-end separations are always much smaller than the fully extended molecular length. In view of this observation, it would be unreasonable to use a free-energy density arising from our framework—including the Rivlin–Saunders expression—in a situation involving strains in excess of those in the intermediate range. A more general theory might account, in the manner of Treloar (1946), for non-Gaussian chain statistics. Furthermore, intermolecular interactions that may have non-negligible internal-energy density are excluded by assumption  $A_4$ , while potentially important influences associated with defects are precluded by assumption  $A_5$ .

## 8. Uncited References

Heinrich and Kaliske, 1997; James and Guth (1941); James and Guth (1944); Kuhn (1934)

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## Appendix

**Lemma A.1.** Let  $\Gamma$  be a tensor with positive determinant and suppose that the integral

$$\Phi(\Gamma) = \int_{\mathcal{E}} \phi(|\mathbf{r}|, |\Gamma \mathbf{r}|) dv(\mathbf{r}) \quad (\text{A.1})$$

exists. Then

$$\Phi(\Gamma) = \Phi(\Sigma) = \Phi(\Lambda) \quad (\text{A.2})$$

with  $\Sigma = \sqrt{\Gamma^\top \Gamma}$  and  $\Lambda$  the spectral resolution of  $\Sigma$ .

**Proof.** Since  $\Gamma$  has positive determinant, we use the polar decomposition theorem to express  $\Gamma$  as  $\Theta \Sigma$ , with  $\Sigma = \sqrt{\Gamma^\top \Gamma}$  symmetric and positive definite and  $\Theta = \Gamma \Sigma^{-1}$  a rotation. Then,  $|\Gamma \mathbf{r}| = |\Sigma \mathbf{r}|$  and it follows that  $\Phi(\Gamma) = \Phi(\Sigma)$ . Next, since  $\Sigma = \sqrt{\Gamma^\top \Gamma}$  is symmetric and positive definite, we use the spectral decomposition theorem to express  $\Sigma$  as  $\Omega \Lambda \Omega^\top$ , with  $\Lambda$  the spectral resolution of  $\Sigma$  and  $\Omega$  a rotation. Then,  $|\Sigma \mathbf{r}| = |\Lambda \Omega^\top \mathbf{r}|$  and it follows that

$$\Phi(\Gamma) = \int_{\mathcal{E}} \phi(|\mathbf{r}|, |\Lambda \Omega^\top \mathbf{r}|) dv(\mathbf{r}). \quad (\text{A.3})$$

Thus, introducing  $\sigma = \Omega^\top \mathbf{r}$  while bearing in mind that  $\Omega$  is a rotation, we apply the change of variables theorem for integration over  $\mathcal{E}$  to obtain

$$\Phi(\Gamma) = \Phi(\Sigma) = \int_{\mathcal{E}} \phi(|\sigma|, |\Lambda \sigma|) dv(\sigma) = \Phi(\Lambda), \quad (\text{A.4})$$

which completes the proof.  $\square$

**Theorem A.2.** Let  $\Gamma$  be a tensor with positive determinant and define  $\phi(\cdot, \cdot; \ell)$  by

$$\phi(|\mathbf{r}|, |\Gamma \mathbf{r}|; \ell) = p(|\mathbf{r}|; \ell) |\Gamma \mathbf{r}|^2 \quad (\text{A.5})$$

with  $p(\cdot; \ell)$  the Gaussian distribution introduced in Eq. (2.3). Then,

$$\int_{\mathcal{E}} \phi(|\mathbf{r}|, |\Gamma \mathbf{r}|; \ell) dv(\mathbf{r}) = \frac{\ell^2 |\Gamma|^2}{3}. \quad (\text{A.6})$$

**Proof.** For  $\phi(\cdot, \cdot; \ell)$  as defined in Eq. (A.5), Lemma A.1 implies that

$$\int_{\mathcal{E}} \phi(|\mathbf{r}|, |\Gamma \mathbf{r}|; \ell) dv(\mathbf{r}) = \int_{\mathcal{E}} \phi(|\sigma|, |\Lambda \sigma|; \ell) dv(\sigma) \quad (\text{A.7})$$

with  $\Lambda$  the spectral resolution of  $\sqrt{\Gamma^\top \Gamma}$ . Thus, using the representations

$$\Lambda = \sum_{i=1}^3 \lambda_i \mathbf{e}_i \otimes \mathbf{e}_i \quad \text{and} \quad \sigma = \sum_{i=1}^3 \sigma_i \mathbf{e}_i \quad (\text{A.8})$$

for  $\Lambda$  and  $\sigma$  in terms of the spectral basis  $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ , we infer that

$$\int_{\mathcal{E}} \phi(|\mathbf{r}|, |\Gamma \mathbf{r}|; \ell) dv(\mathbf{r}) = \left( \frac{3}{2\pi\ell^2} \right)^{3/2} \sum_{i=1}^3 \int_{\mathbb{R}^3} \lambda_i^2 \sigma_i^2 \prod_{j=1}^3 \exp\left(-\frac{3\sigma_j^2}{2\ell^2}\right) d\sigma_1 d\sigma_2 d\sigma_3 \quad (\text{A.9})$$

and, drawing on the integral identities

$$\int_{\mathbb{R}} \exp(-a^2 x^2) dx = \frac{\sqrt{\pi}}{a} \quad \text{and} \quad \int_{\mathbb{R}} x^2 \exp(-a^2 x^2) dx = \frac{\sqrt{\pi}}{2a^3} \quad (\text{A.10})$$

we arrive at the result

$$\int_{\mathcal{E}} \phi(|\mathbf{r}|, |\mathbf{F}\mathbf{r}|; \ell) dv(\mathbf{r}) = \frac{\ell^2}{3} \sum_{i=1}^3 \lambda_i^2 \quad (\text{A.11})$$

which, since  $\sum_{i=1}^3 \lambda_i^2 = |\mathbf{A}|^2 = |\mathbf{F}|^2$ , completes the proof.  $\square$

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