

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

ELIOT FRIED

Department of Theoretical and Applied Mechanics
University of Illinois at Urbana-Champaign
Urbana, IL 61801-2935, USA
e-fried@uiuc.edu

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 as improvements upon the classical neo-Hookean theory by Mooney and by Rivlin and Saunders.

1. Introduction

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

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

involving a shear modulus μ proportional to the product $k_B\theta$ of the Boltzmann constant k_B with the absolute temperature θ .[†] Tacit in the derivation of (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, Treolar (1944) performed a series of experiments designed to test its validity. For uniaxial compression, predictions based on (1.1) agree well with the measurements taken over a wide range of strains. However, for simple extension and pure shear, (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,

[†] The exact features of the factor of proportionality determining μ vary. In Kuhn's (1936, 1938) theory, this factor is simply the number ν of molecules per unit volume—so that $\mu = \nu k_B\theta$. In the alternate formulation of James & Guth (1943), ν is replaced by the cycle-rank ξ , 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 & Guth (1943) predicts a shear modulus equal to one-half that given by the theory of Kuhn (1936, 1938).

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.[‡] 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 (1948) 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 (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 α a dimensionless material parameter taking values on the interval $[0, 1]$ and μ , as before, the constant shear modulus. This relation is the most general form of (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 $I_1(\mathbf{B}) = |\mathbf{F}|^2$, (1.4) reduces to the relation (1.1) obtained from the molecular-statistical theory.

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

In addition to simple extension and compression, Rivlin & 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 (1.4) in which f is a decreasing function of I_2 . We refer to (1.5) as the Rivlin-Saunders free-energy density.

[‡] To remedy this problem, Treolar (1946) extended the neo-Hookean theory to account for non-Gaussian chain-statistics.

Our goal here is to provide a molecular-statistical theory leading to a class of free-energy densities which includes both (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 (1948) 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:

- A₁. Each molecule is a freely-jointed chain consisting of an identically large number of monomer units.
- A₂. The distance separating the ends of each molecule is always small in comparison the fully-extended length of the molecule.
- A₃. Under a macroscopic deformation, the end-to-end vectors of molecules transform as macroscopic material line elements.
- A₄. Interactions between molecules are negligible in comparison to those between the monomer units of single molecules.
- A₅. The network is free of loose chain-ends and other imperfections.

Assumption A₁ 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 ℓ of a molecule comprised by 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). The distribution function for the end-to-end vector \mathbf{r} of a molecule then admits the explicit representation

$$\frac{1}{(2\pi)^3} \int_{\mathcal{E}} \frac{\sin(|\mathbf{r}||\boldsymbol{\omega}|)}{|\mathbf{r}||\boldsymbol{\omega}|} \left(\frac{\sin(\ell|\boldsymbol{\omega}|)}{\ell|\boldsymbol{\omega}|} \right)^n dv(\boldsymbol{\omega}), \quad (2.1)$$

where \mathcal{E} denotes three-dimensional Euclidean space. Moreover, provided that n is sufficiently large, (2.1) reduces to the Gaussian distribution

$$p(|\mathbf{r}|; \ell) = \left(\frac{3}{2\pi\ell^2} \right)^{\frac{3}{2}} \exp\left(-\frac{3|\mathbf{r}|^2}{2\ell^2} \right). \quad (2.2)$$

The necessity of assumption A_2 becomes apparent on inspection of (2.2), which delivers a nonvanishing probability for the physically untenable situation where the end-to-end separation $|\mathbf{r}|$ equals or exceeds the fully-extended chain-length νl . Hence, granted A_2 , the Gaussian (2.2) serves as a valid distribution.

Assumption A_3 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_3 requires that

$$\mathbf{r} \mapsto \mathbf{F}\mathbf{r}. \quad (2.3)$$

In view of (2.3), the ratio

$$\zeta(\mathbf{F}, \mathbf{r}; \ell) = \frac{p(|\mathbf{F}\mathbf{r}|; \ell) \det \mathbf{F}}{p(|\mathbf{r}|; \ell)} \quad (2.4)$$

determines the conditional probability that a molecule with undistorted end-to-end vector \mathbf{r} has distorted end-to-end vector $\mathbf{F}\mathbf{r}$. Here, we follow Wall & 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 require that $\det \mathbf{F} > 0$.

Granted (2.4), the deformation-induced entropy of a molecule with undistorted end-to-end vector is given by

$$k_B \log \zeta(\mathbf{F}, \mathbf{r}; \ell), \quad (2.5)$$

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 ν molecules per unit volume, assumption A_5 implies that all molecules are equally active in the deformation. Hence, the free-energy density is given by

$$\hat{\psi}(\mathbf{F}) = -\mu \int_{\mathcal{V}} p(|\mathbf{r}|; \ell) \log \zeta(\mathbf{F}, \mathbf{r}; \ell) dv(\mathbf{r}), \quad (2.6)$$

where the shear modulus μ is determined in terms of the Boltzmann constant k_B and the absolute temperature θ by

$$\mu = \nu k_B \theta. \quad (2.7)$$

We note that, since $\zeta(\mathbf{Q}, \mathbf{r}; \ell) = 1$ for any rotation \mathbf{Q} , the free-energy density (2.6) complies automatically with the normalization $\hat{\psi}(\mathbf{Q}) = 0$.

To evaluate the integral on the right-hand side of (2.6), we first expand the logarithmic factor in the integrand and use the fact that $p(\cdot; \ell)$ is a distribution to obtain

$$\hat{\psi}(\mathbf{F}) = \frac{1}{2}\mu \left(\frac{3}{\ell^2} \int_{\mathcal{V}} p(|\mathbf{r}|; \ell) (|\mathbf{F}\mathbf{r}|^2 - |\mathbf{r}|^2) dv(\mathbf{r}) - 2 \log \det \mathbf{F} \right). \quad (2.8)$$

Next, applying Theorem A.2 of the Appendix to the integral term in (2.8), recalling once again that $I_1(\mathbf{B}) = |\mathbf{F}|^2$, and defining the third strain-invariant

$$I_3(\mathbf{B}) = \det \mathbf{B}, \quad (2.9)$$

we arrive at the neo-Hookean free-energy density

$$\hat{\psi}(\mathbf{F}) = \frac{1}{2}\mu(I_1(\mathbf{B}) - \log I_3(\mathbf{B}) - 3) \quad (2.10)$$

for compressible rubber. The classical neo-Hookean expression (1.1) for incompressible rubber follows from (2.10) 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} .

If we continue to invoke assumptions A_1 , A_2 , and A_4 , the distribution function (2.1) and its Gaussian approximation (2.2) remain unchanged. However, when \mathbf{r} transforms to $\mathbf{K}(\mathbf{F})\mathbf{r}$, the relevant conditional probability is no longer (2.4), but, rather, is $\zeta(\mathbf{K}(\mathbf{F}), \mathbf{r}; \ell)$. The expression (2.6) for the free-energy density is, therefore, replaced by

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

and, bearing in mind (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 (2.10). The inequality (3.2) ensures that the logarithmic term in (3.5) is well-defined, while the 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 (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 Q_1 and Q_2 and observe that, under their combined influence, $F \mapsto Q_1 F Q_2$. Consistent with this observation, we require that any mapping K entering into a rule of the form (3.1) obey

$$K(Q_1 F Q_2) = Q_1 K(F) Q_2 \quad (3.6)$$

for all rotations Q_1 and Q_2 . A standard argument then shows that K satisfies this functional requirement if and only if it admits the representation

$$K(F) = \kappa_1(\iota(B))F + \kappa_2(\iota(B))F^* + \kappa_3(\iota(B))BF, \quad (3.7)$$

with

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

the adjugate of F and $\iota(B) = (I_1(B), I_2(B), I_3(B))$ the list of deformation invariants. The inequality (3.2) imposes a non-trivial restriction on the coefficients κ_1 , κ_2 , and κ_3 ; further, to ensure that (3.3) holds, κ_1 , κ_2 , and κ_3 must be consistent with $\kappa_1(\iota(1)) + \kappa_2(\iota(1)) + \kappa_3(\iota(1)) = 1$.

Granted that K takes the form given in (3.7), a series of tedious calculations give expressions (too lengthy to reproduce here) for $|K(F)|^2$ and $\det K(F)$ in terms of $I_1(B)$, $I_2(B)$, and $I_3(B)$. Consistent with our expectations concerning invariance and symmetry, (3.5) then determines the free-energy density as a function of the invariant list $\iota(B)$. Since the aforementioned expressions for $|K(F)|^2$ and $\det K(F)$ include implicit dependencies on $\iota(B)$ through the coefficients κ_1 , κ_2 , and κ_3 , (3.5) and (3.7) allow a broad variety of free-energy densities.

4. Free-energy densities as volume-weighted combinations

Suppose that, for each $i = 1, 2, \dots, m$, K_i obeys $\det K_i(F) > 0$, $K_i(Q) = Q$ for all rotations Q , and $K_i(Q_1 F Q_2) = Q_1 K_i(F) Q_2$ for all rotations Q_1 and Q_2 .[†] 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 $\alpha_i \nu$ molecules per unit volume transform according to $r \mapsto K_i(F)r$, a transparent extension of the argument leading to (3.5) leads to the further generalization

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

of the neo-Hookean expression (2.10).

[†] Thus, in particular, each K_i admits a representation of the form (3.7).

5. Mooney elasticity

We consider (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 . While the first of (5.1) is simply the conventional rule $\mathbf{r} \mapsto \mathbf{F}\mathbf{r}$ corresponding to assumption A_3 and, thus, demands that end-to-end vectors transform as material line elements, the second of (5.1) gives rise to a rule, $\mathbf{r} \mapsto \mathbf{F}^*\mathbf{r}$, which requires that end-to-end vectors transform as vectors normal to material surface elements.

Writing $\alpha = \alpha_1$, inserting (5.1) in (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 (2.9) 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 with the neo-Hookean case, the classical Mooney expression (1.4) for incompressible rubber follows from (5.3) on stipulating that the deformation gradient comply with the constraint $\det \mathbf{F} = 1$.

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 κ obeys $\kappa(3) = 1$, so that $\mathbf{K}_2(\mathbf{Q}) = \mathbf{Q}$. Then, defining f through

$$f(I_2) = \kappa^2(I_2)I_2 - \frac{3}{2}\log \kappa(I_2) \quad (6.2)$$

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

$$\hat{\psi}(\mathbf{F}) = \frac{1}{2}\mu(\alpha I_1(\mathbf{B}) + (1 - \alpha)f(I_2(\mathbf{B})) - (2 - \alpha)\log \det \mathbf{F} - 3) \quad (6.3)$$

for compressible rubber. As for neo-Hookean and Mooney elasticity, the Rivlin-Saunders expression (1.5) for incompressible rubber follows from (6.3) on stipulating that the deformation gradient comply with the constraint $\det \mathbf{F} = 1$.

From (6.2), the empirical inequality $f'(I_2) < 0$ suggested by the data of Rivlin and Saunders (1951) holds provided that

$$\left(\frac{3}{2} - 2\kappa(I_2)I_2\right)\kappa'(I_2) > \kappa^2(I_2). \quad (6.4)$$

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 material surface elements. To obtain the Rivlin–Saunders free-energy density, the relevant end-to-end vectors reorient as material surface elements but are scaled by a factor depending on the state of strain.

Assumption A_3 is analogous to the Born rule for crystalline solids (Born, 1915), 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, 1994, 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.

It is important to recognize the limitations, as embodied in assumptions A_1 , A_2 , A_4 , and A_5 , inherent to our approach. Of these, the most significant is associated with assumptions A_1 and A_2 , which 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 would account, in the manner of Treloar (1946), for non-Gaussian chain statistics.

A. Appendix

Lemma A.1. *Let Γ 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 Λ the spectral resolution of Σ .

Proof. Since Γ has positive determinant, we use the polar decomposition theorem to express Γ 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 Σ as $\Omega\Lambda\Omega^\top$, with Λ the spectral resolution of Σ and Ω rotations. 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 $\sigma = \Omega^T \mathbf{r}$ while bearing in mind that Ω 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 Γ 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 (2.2). 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 (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 Λ the spectral resolution of $\sqrt{\Gamma^T \Gamma}$. 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 Λ and σ in terms of the spectral basis $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$, we infer that

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

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 result

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

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

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