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Energy functions for rubber from microscopic potentials

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The finite deformation theory of rubber and related materials is based on energy functions that describe the macroscopic response of these materials under deformation. Energy functions and elastic constants are here derived from a simple microscopic (ball-and-spring) model. Exact uniaxial force-extension relationships are given for Hooke's Law and for the thermodynamic entropy-based microscopic model using the Gaussian and the inverse Langevin statistical approximations. Methods are given for finding the energy functions as expansions of tensor invariants of deformation, with exact solutions for functions that can be expressed as expansions in even powers of the extension. Comparison with experiment shows good agreement with the neo-Hookean energy function and we show how this derives directly from the simple Gaussian statistical model with a small modification. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2723870]

I. INTRODUCTION

The microscopic theory of the elasticity of rubber and other elastomers is the statistical theory.[1] The molecules are considered to consist of links that rotate freely, and at equilibrium the molecules take up random-walk paths between pinning and cross-linking points. In this theory, the change in Helmholtz free energy A on extension is just given by the change in entropy. In the simple statistical theory, the probability distribution of separations r between pinning points is given by the Gaussian distribution. By considering the entropy of the network, in two early papers, Wall was able to derive macroscopic force-extension relationships from this microscopic model.[2] For an incompressible material under uniaxial stress. Wall obtained the force-extension relationship for a unit cube

$$F = \frac{dA}{d\lambda} = NkT\left(\lambda - \frac{1}{\lambda^2}\right), \qquad (1)$$

where λ is the extension and N is the number of chains per unit volume. The shape of Eq. (1) is considered to fit experimental data rather poorly.[3] Between $1\frac{1}{2} < \lambda < 4$, natural rubber is considerably softer and at higher extensions stiffens faster than this model predicts. While the stiffening at large extensions is adequately accounted for by the finite length of polymer chains[4–7] and by the crystallization that can occur at high extension,[1] the softening at the lower strains remains essentially unexplained.[3]

Experimental data are therefore fitted using phenomenological models, in which the free energy is expressed as a function of the invariants of the deformation tensor.[8] The simplest is the *neo-Hookean* function which is

$$A = C_{10}(\mathbf{I}_1 - 3) = C_{10}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3), \qquad (2)$$

and which may be deduced from the Gaussian statistical theory. It yields Eq. (1) directly. The *Mooney-Rivlin* function fits experimental data much better, and is[8,9]

$$A = C_{10}(\mathbf{I}_1 - 3) + C_{01}(\mathbf{I}_2 - 3) = C_{10}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + C_{01}(\lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2 - 3). \qquad (3)$$

Many more complicated functions have been proposed; for example, Yeoh and Fleming fit a large body of data with an energy function with four constants and with exponential and logarithmic functions of the invariants.[7]

It is difficult to relate the terms in a phenomenological model to the underlying molecular physics. While the C_{10} term in the Mooney-Rivlin function corresponds to the Gaussian statistical model, it is not clear what the physical origin of the C_{01} term might be. Indeed, even the statistical model does not correspond explicitly to properties of individual molecules. Wall and subsequent workers derived it from the network entropy, and Treloar has discussed the difficulty of considering the entropy, energy, and force in individual molecules.[1] In the case of crystalline materials, model solids (ball-and-spring models) have been very useful relating microscopic and macroscopic properties.[10,11] Realistic interatomic potentials are used and the internal energy can be written down as an explicit function of deformation. Then elastic constants are obtained by differentiation.[12] Some attempts have been made to set up a model solid for rubber by connecting the origin to a number of nearby points with springs. The difficulty with such models is to obtain isotropy, since the macroscopic behavior retains the symmetry of the microscopic unit cell. Wang and Guth[4] set up three- and four-spring models with cubic and tetrahedral symmetries. Arruda and Boyce used an eight-spring model, the eight {111} springs connecting a point at the center of the cube to the corners.[6] They used the inverse Langevin function for the Helmholtz free energy of a finite chain, instead of the Gaussian function, and they obtained an excellent fit to experimental force-extension data at high strains. However, the lengths of the {111} springs are given directly by the first invariant $\mathbf{I}_1$, and consequently their model cannot be used to test force laws that might in spherical symmetry yield other invariants in the free energy expression.

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Treloar and Riding showed how to set up a truly isotropic model, by integrating over all spring orientations.[5] They studied the inverse Langevin function, the function that corrects the Gaussian statistical model for finite chain lengths. Treloar and Riding were only able to do the integration numerically, so that they did not obtain an explicit energy function that might be expanded in terms of the invariants. Indeed, for most spring functions, analytic integration does not appear to be possible. We show here how macroscopic properties (elastic constants and force-extension curves) may nevertheless be calculated analytically for various spring functions. Then we show how an energy function expressed in terms of the invariants may be obtained. Finally, we use our model to show that a correction to the simple Gaussian statistical model gives the best fit to the data.

II. THEORY

Homogeneous elastic deformation of a solid is described by a suitable deformation tensor such as the Lagrangian deformation tensor. For an isotropic solid, the elastic energy is invariant to rotation and therefore has to be a function of the tensor invariants under rotation such as the eigenvalues, the trace, and the determinant of the deformation tensor. For the three-dimensional homogeneous deformation $\mathbf{A}=\{\alpha_{ij}\}$, there are three fundamental invariants, which may be taken as the normal extensions, the eigenvalues of $\mathbf{A}$, which are the normal extensions λ_1, λ_2, λ_3, or any convenient combinations of them such as $\mathbf{i}_1=\mathrm{Tr}\,\mathbf{A}=\lambda_1+\lambda_2+\lambda_3$, $\mathbf{i}_2=\lambda_1\lambda_2+\lambda_2\lambda_3+\lambda_3\lambda_1$, and $\mathbf{i}_3=\mathrm{Det}\,\mathbf{A}=\lambda_1\lambda_2\lambda_3$; or $\mathbf{I}_1=\lambda_1^2+\lambda_2^2+\lambda_3^2$, $\mathbf{I}_2=\lambda_1^2\lambda_2^2+\lambda_2^2\lambda_3^2+\lambda_3^2\lambda_1^2$, and $\mathbf{I}_3=\lambda_1^2\lambda_2^2\lambda_3^2$. Then the stored elastic energy (here, the Helmholtz free energy A) may generally be expanded as a polynomial in the three invariants, for example,

$$
\begin{aligned}
A &= c_0^{pqr}\mathbf{i}_1^p\mathbf{i}_2^q\mathbf{i}_3^r,\\
A &= c_3^{pqr}(\mathbf{i}_1-3)^p(\mathbf{i}_2-3)^q(\mathbf{i}_3-1)^r, \qquad (4)\\
A &= C_0^{pqr}\mathbf{I}_1^p\mathbf{I}_2^q\mathbf{I}_3^r,
\end{aligned}
$$

or

$$A = C_3^{pqr}(\mathbf{I}_1-3)^p(\mathbf{I}_2-3)^q(\mathbf{I}_3-1)^r,$$

with summation over repeated indices. Our notation for the coefficients uses upper and lower cases and the subscript 3 or 0 to indicate the presence or absence of the constants in the terms in $\mathbf{i}$ or $\mathbf{I}$. Ogden,[8] for example, uses the fourth line of Eq. (1), and in this form expresses the neo-Hookean stored energy function as $C_3^{100}=\frac{1}{2}G$ (G is the shear modulus) and all other $C_3^{pqr}=0$. For incompressibility, $\mathbf{i}_3=\mathbf{I}_3=1$, $r=0$, and the superscripts reduce to pq. It is the coefficients C_3^{pqr}, etc., that are normally determined on the basis of theoretical analysis of isotropic continuous elastic media and empirical comparison with experiment rather than being derived from microscopic force laws.

III. MODEL SOLID FOR RUBBER

In the valence force-field method,[10] a crystal lattice is treated as a ball-and-spring problem. Vectors $\mathbf{s}_i$ are written down for all the atoms, indexed i, related to an atom at the origin by an n-body potential. Under the Lagrangian deformation $\mathbf{A}$, these vectors become $\mathbf{s}'=\mathbf{A}\cdot\mathbf{s}$, and the terms in the elastic energy are

$$
\begin{aligned}
U_i &= f_i(\mathbf{s}_i'\cdot\mathbf{s}_i'),\\
U_{ij} &= g_{ij}(\mathbf{s}_i'\cdot\mathbf{s}_j'),
\end{aligned}
\qquad (5)
$$

for two-body and three-body potentials, respectively, and using internal energy U or Helmholtz free energy A as appropriate for each physical model. Conventional isothermal elastic constants c_{IJ}, c_{IJK}, etc., are obtained by differentiating the elastic energy with respect to Lagrangian strain.[12] We have shown elsewhere how to obtain the Lagrangian elastic constants by differentiating with respect to the elements of the deformation matrix and converting.[13] However, in this paper we require only the differentials with respect to the deformation, the deformation elastic constants, which we denote $c_{IJ\cdots}^d$ in Voigt notation or $c_{ijkl\cdots}^d$ in tensor notation. That is, we are interested in the normal stress and the nth-order deformation elastic constants given by

$$
\begin{aligned}
\sigma_1 &= \left.\frac{\partial U}{\partial\alpha_{11}}\right|_{\mathbf{A}=\mathbf{I}} = \left.\frac{\partial U}{\partial\lambda_1}\right|_{\mathbf{A}=\mathbf{I}},\\
c_{IJ} = c_{IJ}^d = c_{ijkl}^d &= \left.\frac{\partial^2 U}{\partial\alpha_{ij}\partial\alpha_{kl}}\right|_{\mathbf{A}=\mathbf{I}}, \qquad (6)\\
c_{IJK\cdots}^d = c_{ijklmn\cdots}^d &= \left.\frac{\partial^n U}{\partial\alpha_{ij}\partial\alpha_{kl}\partial\alpha_{mn}\cdots}\right|_{\mathbf{A}=\mathbf{I}}.
\end{aligned}
$$

Strictly, for the normal stress and the elastic constants to have the correct units of pressure, A must be the elastic energy density per unit mass and corrections should be made for the density and the lattice constant,[12,13] but here we take these correction factors to be unity. We will also be interested in the force-extension relationships for uniaxial tension in a principal direction under the constraint that the material is incompressible. These are obtained in the usual way. For uniaxial tension or compression in the z direction, incompressibility is imposed using

$$\lambda_1 = \lambda_2 = \frac{1}{\sqrt{\lambda_3}} \qquad (7)$$

(the extension λ is then equal to λ_3) and

$$F = \frac{dU}{d\lambda_3}. \qquad (8)$$

For crystals, the vectors $\mathbf{s}_i$ are simply the interatomic bonds, obtained from the known crystallography, and the potentials used are approximations to the true n-body interatomic potentials. For our simple model of isotropic elastomers, the microscopic springs are the lengths of free polymer chain between pinning points and the potentials are two body. They are not interatomic potentials but arise from thermodynamic considerations. Because the material is isotropic, the vectors $\mathbf{s}_i$ can have no preferred directions. They will not have a unique length or a unique spring constant. We model this, following Treloar and Riding,[5] by connecting the "atom" at the origin to the entire sphere at unit radius, with an infinite number of elementary springs which contribute amounts dU to the potential. Then the total elastic stored energy function is found by integrating over the sphere. In spherical polar coordinates, the vector $\mathbf{s}$ is $(\cos\theta\sin\varphi, \sin\theta\sin\varphi, \cos\varphi)$, and the total elastic energy is

$$U = \int_0^{2\pi}\int_0^{\pi} f(\mathbf{s}'\cdot\mathbf{s}')\sin\varphi\, d\varphi\, d\theta. \tag{9}$$

A. Hooke's law

Hooke's law potential is given by

$$f = k(\sqrt{\mathbf{s}'\cdot\mathbf{s}'} - 1)^2 \tag{10}$$

and the integral over the sphere of Eq. (9) does not appear to be possible. However, from the elementary spring $\mathbf{s}$ we may obtain the elementary contributions to stress, elastic constants, and force. With the deformation matrix diagonalized as appropriate for an isotropic solid,

$$\mathbf{s}' = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}\cdot\mathbf{s}, \tag{11}$$

we have, for example,

$$dc_{11} = k\frac{\partial^2}{\partial\lambda_1^2}\{\sqrt{\lambda_1\cos^2\theta\sin^2\varphi + \lambda_2\sin^2\theta\sin^2\varphi + \lambda_3\cos^2\varphi} - 1\}^2 \sin\varphi\, d\theta\, d\varphi\big|_{\mathbf{A}=\mathbf{I}} = 2k\cos^4\theta\sin^5\varphi\, d\theta\, d\varphi, \tag{12}$$

and this is readily integrated over the sphere to give $c_{11} = 8\pi/5$. The other elastic constants are obtained in the same way. Introducing incompressibility, Young's modulus at zero strain is $Y_{\text{inc}} = \frac{3}{2}(c_{11} - c_{12}) = 8\pi/5$. In what follows, the elastic constants are normalized using $k = 5/8\pi$ to give unity stiffness, $Y_{\text{inc}} = 1$, under incompressibility in simple extension at zero strain ($\lambda = 1$).

The force-extension relationship is obtained similarly. Under the assumption of incompressibility and with uniaxial extension in the z direction, there is no functional dependence on θ and the integral over θ just gives a multiplying factor of 2π. The force due to an elemental spring is

$$\begin{aligned} dF &= \frac{dU_{\text{inc}}}{d\lambda} = 2\pi k\frac{d}{d\lambda}\sin\varphi\left(\sqrt{\frac{\sin^2\varphi}{\lambda} + \lambda^2\cos^2\varphi} - 1\right)^2 d\varphi \\ &= \frac{2\lambda^3 - 1 + (2\lambda^3 + 1)\cos 2\varphi\sin\varphi}{2\sqrt{2}\lambda^{3/2}\sqrt{\lambda^3 + 1 + (\lambda^3 - 1)\cos 2\varphi}} \\ &\quad\times\left(\frac{\sqrt{2}\sqrt{\lambda^3 + 1 + (\lambda^3 - 1)\cos 2\varphi}}{\sqrt{\lambda}} - 2\right)d\varphi, \end{aligned} \tag{13}$$

and the total force is

$$\begin{aligned} F &= \int_{\varphi=0}^{\pi} dF = \frac{2\pi k}{3\lambda^{5/2}(\lambda^3 - 1)^2}\lambda^2(4(\lambda^3 - 1)^3 \\ &\quad - 3\lambda^3(2\lambda^6 - \lambda^3 - 1) + 3\lambda^{5/2}(4\lambda^3 - 1) \\ &\quad \times\sqrt{(\lambda^3 - 1)}\tanh^{-1}\sqrt{1 - \lambda^{-3}}). \end{aligned} \tag{14}$$

This function is plotted in Fig. 1 (with $k = 5/8\pi$ to normalize to unity stiffness at $\lambda_3 = 1$) and we see that it reproduces the expected behavior of the model. In particular, it stiffens with extension while springs are rotating to align with the extension, giving limiting Hooke's law behavior at large extension with an increased stiffness of 5/3. Of course, it does not agree well with experiment. The data points in Fig. 1 are those cited by Mooney[9] from Gerke[15] and Hencky,[16] and they show a monotonic decrease in stiffness with extension. We have fitted the data with Mooney's two-parameter expression,[9]

$$F = \tfrac{1}{2}G(1 + \lambda)(1 - \lambda^{-3}) + \tfrac{1}{2}H(1 - \lambda)(1 - \lambda^{-3}), \tag{15}$$

with G and H as free fitting parameters and normalized by the slope of the fits at $\lambda = 1$. The fits to the Gerke data (omitting the two points at highest extension) and the Hencky data are not identical (both are shown), nor are they identical to the fits Mooney gave,[9] but the two data sets agree very well after normalization. The root mean square residuals are 0.036 (Hencky) and 0.043 (Gerke).

B. The Gaussian thermodynamic force function

The true thermodynamic molecular potential is derived by many authors from the properties of the random walk in three dimensions.[1,17] From the Gaussian distribution of expectation distances between two points separated by a number of steps N, the free energy for a single molecule is readily shown to be

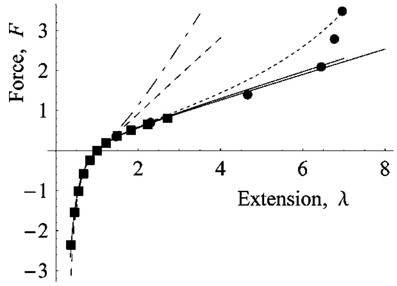

FIG. 1. Force-extension plots for the microscopic Hooke's law model of Eq. (14) (chain-dotted curve), for the molecular thermodynamic model of Eq. (18) (broken curve), and for the inverse Langevin function of Eq. (21) (dotted curve). The data from Gerke and Hencky (Refs. 9, 15, and 16) are shown for comparison with fits to Mooney's expression, Eq. (15) (solid curves). All plots are normalized to unity gradient at $\lambda = 1$.

$$A = kT\left(-\ln r + \tfrac{1}{2}r^2\right) \tag{16}$$

for a separation of pinning points (cross-links, or chain ends) of r. A may be differentiated as in Eq. (12) and integrated over the sphere to yield the normalized elastic constants. The force law for a single polymer chain or elemental spring, as in Eq. (8), is

$$dF = C\frac{d}{d\lambda_3}\left(-\ln\sqrt{\mathbf{s}'\cdot\mathbf{s}'} + \frac{1}{2}\mathbf{s}'\cdot\mathbf{s}'\right)\sin\varphi d\theta d\varphi. \tag{17}$$

With incompressibility, and integrating as in Eqs. (8) and (9) for extension in the z direction, the force is

$$F = \frac{2\pi C}{\lambda^2(\lambda^3-1)} \times\left(-2 + 3\lambda + 4\lambda^3 + 6\lambda^4 - 2\lambda^6\frac{9\lambda^4\tanh^{-1}\sqrt{1-\lambda^3}}{\sqrt{1-\lambda^3}}\right). \tag{18}$$

For Young's modulus of unity at $\lambda_3=1$, we have $C=5/8\pi$, and then the stiffness goes to 5/6 at large extensions. The force is plotted in Fig. 1 with this value of C. The fit to the data is little better than Hooke's law fit.

C. Potentials written as expansions in even powers of spring length: The inverse Langevin function

For most spring functions $f(\mathbf{s}')$ the integral of Eq. (9) is not soluble, and so an expression for A as a polynomial expansion in terms of the invariants in the form of Eq. (1) cannot be directly obtained. However, spring functions that can be expanded in integer powers of $\mathbf{s}'\cdot\mathbf{s}'$ (even powers of spring length) do give a polynomial expansion for A. We may solve the integrals

$$\frac{3}{4\pi}\int_{\text{sphere}}\mathbf{s}'\cdot\mathbf{s}'\sin\varphi d\theta d\varphi = \lambda_1^2+\lambda_2^2+\lambda_3^2 = \mathbf{I}_1,$$

$$\frac{15}{4\pi}\int_{\text{sphere}}(\mathbf{s}'\cdot\mathbf{s}')^2\sin\varphi d\theta d\varphi = 3\mathbf{I}_1^2 - 4\mathbf{I}_2, \tag{19}$$

$$\frac{35}{4\pi}\int_{\text{sphere}}(\mathbf{s}'\cdot\mathbf{s}')^3\sin\varphi d\theta d\varphi = 5\mathbf{I}_1^3 + 12\mathbf{I}_1\mathbf{I}_2 - 8\mathbf{I}_3,$$

etc.

Unfortunately the number of terms on the right increases faster than the number of equations, so we cannot invert these relationships to find out what terms in the expansion of the spring function correspond to each term in the invariants. We have only, from the first equation, that C_0^{100} and C_3^{100} correspond to the term in $\mathbf{s}'\cdot\mathbf{s}'$.

A thermodynamic treatment that takes into account the finite length of the polymer chains has been given by James and Guth[14] and subsequent authors (see Treloar[3]). It yields the force on a molecule which has n links of length l as a function of the separation r of its ends as

$$F = \frac{kT}{l}L^{-1}\left(\frac{r}{nl}\right), \tag{20}$$

where L^{-1} is the inverse Langevin function, with the series expansion

$$L^{-1}(x) = 3x + \frac{9}{5}x^3 + \frac{297}{175}x^5 + \frac{1539}{785}x^7 + \dots . \tag{21}$$

This can be integrated for the energy, giving even powers only of $\mathbf{s}'\cdot\mathbf{s}'$. Then since the integrals of Eq. (19) can be evaluated, so can the integral of Eq. (9). Elastic constants and the force-extension function are obtained explicitly using Eqs. (6)–(8). The resulting force-extension plot is shown in Fig. 1. The fit to the data is poor; in particular, the onset of stiffening at large extensions is much too slow.

IV. COEFFICIENTS OF INVARIANTS

Since the integral of the energy function of Eq. (9) for A is not generally possible, we require another method for finding the coefficients C^{pqr} or c^{pqr} for polynomial expansions of U or A in terms of the invariants of the deformation tensor. The elastic constants may be used for this, since we have seen that they may be found using Eqs. (6) and (12) even when the integral of Eq. (9) is not possible. Elastic constants may also be tabulated for the invariants and their functions, e.g., for $\mathbf{I}_1^p\mathbf{I}_2^q\mathbf{I}_3^r$. Then we may write a matrix equation relating an elastic constant vector $\mathbf{E}=(\sigma_1, c_{11}, c_{12}, c_{111}\dots)$ for the energy function, a vector consisting of the invariant coefficients $\mathbf{C}=(C_3^{000}, C_3^{100}, C_3^{010}, C_3^{001}, C_3^{011}, \dots)$, and a matrix $\mathbf{X}$ compiled from the elastic constants of each function of the invariants, such that

$$\mathbf{E} = \mathbf{X}\cdot\mathbf{C},$$

$$\mathbf{X}^T\cdot\mathbf{E} = \mathbf{X}^T\cdot\mathbf{X}\cdot\mathbf{C}, \tag{22}$$

$$\mathbf{C} = (\mathbf{X}^T\cdot\mathbf{X})^{-1}\cdot\mathbf{X}^T\cdot\mathbf{E}.$$

We use this expression for $\mathbf{C}$ to obtain the coefficients of the invariants when the elastic constants are known. Note that the matrix $\mathbf{X}$ is not necessarily square. We calculate elastic constants up to some order of our choice, giving m rows in $\mathbf{X}$, and we choose some number n of the C^{pqr}, corresponding to n columns of $\mathbf{X}$. If $m=n$ then Eq. (22) is exact, while if $m>n$ then Eq. (22) is overdetermined and the solution is a multivariate linear regression best estimate of $\mathbf{C}$. The matrix $\mathbf{V}=\mathbf{X}^{\mathbf{T}}\cdot\mathbf{X}$ is square, and for a solution of Eq. (22) to exist it is necessary that $\det\mathbf{V}$ is not zero. This will occur if the columns of $\mathbf{X}$ are not linearly independent. Then we require to find the null space of $\mathbf{X}$, the list of vectors $\mathbf{u}$ such that $\mathbf{X}\cdot\mathbf{u}=0$. We may read this as indicating that the contribution of some C_{pqr} to the elastic constants $\mathbf{E}$ is the same as the contribution of some linear combinations of other C_{pqr}, and we delete the corresponding column of $\mathbf{X}$ and row of $\mathbf{C}$.

If we are interested only in finding the coefficients C_{pq} for an expansion assuming incompressibility, we may use instead of the elastic constants a series of points along the force-extension curve, calculated for the energy function and for each term $\mathbf{I}_1^p\mathbf{I}_2^q$.

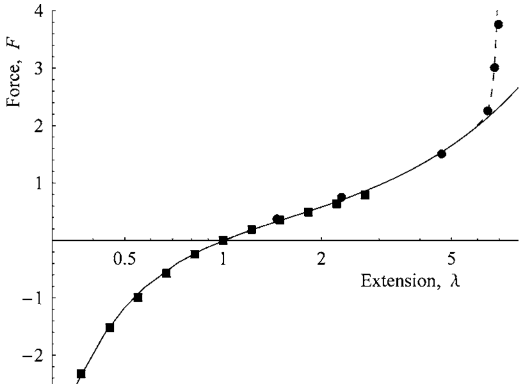

FIG. 2. The semilogarithmic force-extension plot for microscopic zero-unstrained-length Hooke's law model of the first line of Eq. (19). The data from Gerke (circles) and Hencky (squares) (Refs. 9, 15, and 16) are shown for comparison. All plots are normalized to unity gradient at $\lambda=1$. The curve $y=x/3+(x/6.8)^{40}$ is plotted (dotted curve) in the region of the two highest data points.

V. COMPARISON WITH EXPERIMENT

It is striking that the fits to experiment obtained with the Gaussian and inverse Langevin thermodynamic models are so poor (Fig. 1). Early authors pointed out the difficulty of attributing a stress-strain curve to the *individual* molecule. In 1938 Pelzer[18] noted that if the entropy of a single molecule may be taken as a function of a single coordinate only, the probability distribution of lengths is the simple Gaussian of the form $e^{-\beta^2x^2}$, rather than the three-dimensional form $r^2e^{-\beta^2x^2}$, the logarithmic terms in Eqs. (16) and (17) disappear and the behavior of the molecule is Hooke's law with a *zero* unstrained length. This is the energy function of the first line of our Eq. (19), and yields the neo-Hookean[8] or Wall[2] force law immediately. However, it was considered to be absurd that the molecules should be under tension when the bulk rubber is unstrained. Consequently, Pelzer and subsequent authors used the three-dimensional Gaussian distribution of the form $r^2e^{-\beta^2r^2}$. As Treloar[1] pointed out, while this permits the molecule to be unstrained when the bulk rubber is unstrained, it leads to the erroneous concept that the molecule is under a compressive force when held at less than its equilibrium length. Network analyses such as that of Wall[2] were therefore safer.

Yet the simple Gaussian model is just the first term of the inverse Langevin expansion, which would appear to give real and rigorous meaning to the entropy and stress-strain curve of a single molecule. Using the first line of Eq. (19) in our model, we recover the neo-Hookean equation and we fit it to the data of Hencky and Gerke.[9,15,16] Using the slope of the fits at $\lambda_3=1$ to normalize the data and the fits, as in Sec. III. The fits are shown in Fig. 2; they are, in fact, better than the fits of Fig. 1 to the Mooney expression, with root mean square residuals of 0.036 (Hencky) and 0.037 (Gerke).

In our model solid, there is no difficulty at all in the rubber molecules being under tension while the bulk material is unstrained. In the model, this can be represented by adding an incompressible or slightly compressible liquid to the model, with energy

$$U=\tfrac{1}{2}k_V(V-V_0)^2=\tfrac{1}{2}k_V(\lambda_1\lambda_2\lambda_3-1)^2,$$

with k_V large or going to infinity. In reality, that is exactly what the polymer chains are supposed to constitute, in between the pinning or cross-linking points. So our model predicts a small hydrostatic pressure in this liquid, which is physically acceptable.

Finally, we note that the inverse Langevin function of Fig. 1 stiffens much too slowly to account for the stiffening at high strain of the data. The limiting form of the neo-Hookean model at high strain is the straight line $y=x/3$. To this, we have found it necessary to add a term in a very high power of x, x^{40}, to fit the higher data points (dotted line in Fig. 2). We conclude that entirely different physics is at play here. The polymer chains must be long enough in the rubbers studied here that the inverse Langevin function is not sensibly different from the simple Gaussian theory, and the stiffening observed here must be due to some other phenomenon such as crystallization.

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