Elasticity Theory. 6. Molecular Theory of the Mooney–Rivlin Equation and Beyond

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ABSTRACT: A theory of high elasticity based on the calculation of the distribution function of the gyration tensor for an elastic body is developed through terms that go one beyond the Mooney–Rivlin equation. There is but one free parameter in the theory to this order. The potential for bonded interactions is treated in the harmonic approximation, and the nonbonded interactions are handled by expressing the free energy density as a function of the segment density fluctuations. As is well-known, the Mooney–Rivlin C_1 term arises from the attractive entropic forces in the network. The C_2 and higher terms result from nonbonded interactions. Not considered explicitly here are the effects of finite chain extensibility or crystallization.

Introduction

The stress–strain behavior of highly elastic materials has been the subject of numerous theoretical investigations spanning more than 50 years. A fundamental theory of elastomers is made difficult by the fact that they are covalently bonded random networks containing something on the order of Avogadro's number of atoms, and so require a respectably detailed statistical mechanical study of their many-body interactions. Many of the earlier, and even some of the later, theories have avoided the many-body problem by decoupling the structural elements (chains) at an early stage of the calculations. The price that is paid for this approximation is the introduction of unknown parameters that can only be evaluated from experiment. One might hope to improve upon this situation by directly addressing the coupling between the chains and then following the consequences of this to the end.

A good theory of elasticity must address the following observations: (1) experimental data in uniaxial extension follow the Mooney–Rivlin equation if the extension ratio is not too large,[1] (2) in biaxial extension (uniaxial compression) the Mooney–Rivlin stress–strain relation is inadquate,[2,3] (3) the magnitude of the coefficient C_2 decreases with swelling,[4] and (4) the Frenkel–Flory–Rehner theory of swelling is inaccurate.[5]

The Mooney–Rivlin free-energy density is given by the expression

$$A/V = C_1(\lambda_1^2 + \lambda_2^2 + \lambda_3^2) + C_2(1/\lambda_1^2 + 1/\lambda_2^2 + 1/\lambda_3^2) \quad (1)$$

The author remarked some time ago[6] that the C_1 term, which arises from the attractive interactions, increases with increasing λ_α. Since the C_2 term increases with *decreasing* λ_α, it must be due to a repulsive interaction. The 1972 attempt to quantify C_2 is here superseded by a refined argument that introduces some new physical insight into the means by which the nonbonded interactions differ in cross-linked and un-cross-linked polymers.

It is useful to make a comment about the magnitude of the difference between the free energy of an elastomer and the same un-cross-linked linear polymer. Given the limitations of thermochemical data, polyethylene will be used as the base polymer. The increment in the standard-state free energy per CH_2 group in the liquid *n*-alkanes relative to the gas phase is about −0.7 kcal/mol, or about $-1.2kT$ per methylene group at room temperature.[7] The magnitude of the C_1 term is approximately νkT, where ν is the number of polymer chains. The elastic free energy is no more than about 1% of the total free energy of a typical elastomer. Suppose that one were to attempt a very complete description of the elastomer, with a through analysis of intermolecular correlations in the liquid-like state. The level of precision required to get the elastic part right would be on the order of one part in ten thousand. Even if one had a respectably good theory of the segmental correlations in polymers, the elastic part would require unprecedented accuracy in the correlation functions. Clearly, the theory of elasticity is, in essence, a *perturbation* theory with the un-cross-linked polymer forming the reference state. If Z_c and Z_u represent the partition functions for cross-linked and un-cross-linked polymers, this argument suggests that one write

$$Z_c = Z_u(Z_c/Z_u) \quad (2)$$

and treat Z_c/Z_u by a perturbation scheme. This approach will be taken here.

The ratio in eq 2 is formulated with potentials in the next section, and the physical quantity to be calculated, the distribution function of the gyration tensor, is discussed. A crucial argument is given there to justify the assertion that the nonbonded interactions are different in the cross-linked and un-cross-linked materials. Also introduced in that section is an expedient model to treat this difference in the statistical mechanical weighting of the potential in cross-linked and un-cross-linked systems.

The third section addresses the detailed calculations. The density fluctuations are handled in the form of a series in the Fourier components, the second term of which gives the C_2 term, and the third gives a C_3 term. Two parameters are required as substitutes for detailed evaluations of integrals over a reduced, dimensionless configuration space. The condition that the unstrained state is the state of maximal probability removes one parameter, and the value of the other can be closely specified.

The paper closes with some remarks about the possibilities for improving the potential energy. Should entanglements be considered, and how are they likely to affect the results? How might finite chain extensibility be incorporated into the theory? Is it possible to handle filled elastomers with this method for calculating the stress–strain relation?

Formulation

The theory to be presented follows the traditional methods of classical statistical mehcanics. The emphasis is on true potentials, which are then approximated so as

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to formulate a problem that can actually be solved. The reason for doing so is that the basic technique is powerful, and it will accommodate the next generation of improved potentials. The system considered is a covalently bonded (connected) random network that is possibly swollen with a diluent maintained at a fixed chemical potential.

The configuration integral for the elastomer with fixed constraints, which includes the locations of cross-links on the chains and entanglements, will be denoted by Z_c. (The momenta integrate trivially for a classical system, so the same symbol is used for the configuration integral as for the partition function in eq 2.) As is well-known,[8,9] one must average the logarithm of Z_c over all constraints for systems with frozen-in disorder. This average will be saved for the last in the expectation that the geometric average of Z_c will reduce to an arithmetic average of the argument in $Z_c = \exp(-A_c/kT)$, where A_c is the Helmholtz free energy and kT has its usual meaning. The configuration integral for the identical high molecular weight polymer, in solution with the diluent at the same volume fraction as the swollen elastomer, is Z_u. The identity

$$Z_c = Z_u(Z_c/Z_u) \tag{2}$$

gives $A_c = A_u + A_{el}$, where $A_{el} = -kT \ln (Z_c/Z_u)$. Assume that A_u is given by the standard-state free energy for polymer and solvent plus the Flory–Huggins mixing terms. It remains to calculate Z_c/Z_u.

The total potential energy of the systems (c and u) consists of separable contributions from bonded interactions and from nonbonded interactions, denoted by $V(b;X,x)$ and $V(\bar{b};X,x)$, respectively. Both depend upon polymer coordinates, X, and solvent coordinates, x. We assume for simplicity that systems c and u contain the same total number of atoms. (There is abundant experimental evidence[5] to show that the precise chemical structure of cross-links is not important to the thermodynamic properties under consideration.) Define the $3 \times (N + n_1)$ matrix $Y = [X, x]$, where N is the number of polymer segments and n_1 is the number of solvent molecules. Each column of this matrix consists of the x, y, and z coordinates of a segment or solvent molecule. The origin of coordinates is chosen as the center of mass of the system; i.e., $\sum_i y_i^\alpha = 0$ (throughout, Greek indices will range over spatial dimensionality or other small set, and roman indices will range over the numbers of units).

Define the (3×3) gyration tensor[10,11] S by

$$S = (N + n_1)^{-1} YY' \tag{3}$$

and let dS be the volume element associated with S. The transpose of a matrix or vector is denoted by the prime symbol. The distribution of S that will give an elastic equation of state is

$$P(S) = Z_c(S)/Z_u(S) = \frac{\int \exp\left\{-\frac{1}{kT}[V_c(\bar{b};X,x) + V_c(b;X,x)]\right\} \mathrm{d}X\, \mathrm{d}x/\mathrm{d}S}{\int \exp\left\{-\frac{1}{kT}[V_u(\bar{b};X,x) + V_u(b;X,x)]\right\} \mathrm{d}X\, \mathrm{d}x/\mathrm{d}S} \tag{4}$$

since the elastic free energy is

$$A_{el}(S) = -kT \ln P(S) \tag{5}$$

The value of S that maximizes $P(S)$ and minimizes $A_{el}(S)$ is $S°$; it is the solution of $\partial P(S)/\partial S|_{S=S°} = 0$. Thus

$$\Delta A_{el} = A_{el}(S) - A_{el}(S°) = -kT \ln [P(S)/P(S°)] \tag{6}$$

The deformation gradient tensor λ is defined by the equation

$$S = \lambda S° \lambda' \tag{7}$$

which follows directly from the fact that S and $S°$ are second-rank tensors. This definition of strain is macroscopic and therefore differs from the definition in continuum mechanics.[12] There is an advantage to defining λ by eq 7. This advantage relates to (i) the ambiguity involved in applying continuum definitions to an atomic or molecular system and (ii) the difficulty, if not impossibility (because of fluctuations) of measuring a microscopically defined continuum variable. The macroscopic λ in eq 7 can be measured with a ruler without addition assumptions about isotropy or homogeneity.

If identification of S with continuum distributions is required, one may define

$$S = \int \mathbf{rr}\, \mathrm{d}r \Big/ \int \mathrm{d}r \tag{8}$$

where $\mathbf{rr}$ is the dyadic (outer) product of the coordinates $\mathbf{r}$ of a point in the continuum, and $\mathrm{d}r$ is the volume element $\mathrm{d}x\mathrm{d}y\mathrm{d}z$. On the molecular side, we will assume that

$$S = (N + n_1)^{-1}YY' = N^{-1}XX' = \mu^{-1}X_\mu X_\mu' = \nu^{-1}X_\nu X_\nu' \tag{9}$$

to within terms that are comparable to the dimensions of a single molecule. The sums implicit in the matrix products are over segments plus solvent molecules, over segments only, over cross-links only, and over centers of mass of chains only, respectively. No perceptible error will be involved in these various versions of S provided they are used consistently in Z_c/Z_u and provided the S that is calculated is a truly macroscopic quantity.

We now return to eq 4 and integrate the solvent coordinates. This converts the true potentials into potentials of mean force $\bar{V}$, which we now proceed to approximate. The bonded potential[13,14] will be written as

$$\frac{1}{kT}\bar{V}(b;X) = \gamma\, \mathrm{tr}\, (XKX') \tag{10}$$

in the standard approximation introduced by James and Guth for elasticity[15] and by Rouse for viscoelasticity.[16] Here $\gamma = {}^3/_2\langle l^2\rangle_0$, where $\langle l^2\rangle_0$ is the mean square length of one statistical bond in a chain. The matrix K is a Kirchhoff matrix which describes the connectivity of the network (K_c) or the linear chains (K_u). In the latter case, K_u is a direct sum of matrices, one for each chain. The matrix K has as many zero eigenvalues as there are connected components in the molecular graph whose structure is codified by K.[11]

At this stage we might simply assert that the effect of the nonbonded interactions in the numerator and denominator will cancel in the equation

$$P(S) = \frac{\int \exp[-(1/kT)\bar{V}_c(\bar{b};X) - \gamma\, \mathrm{tr}\, (XK_cX')]\, \mathrm{d}X/\mathrm{d}S}{\int \exp[-(1/kT)\bar{V}_u(\bar{b};X) - \gamma\, \mathrm{tr}\, (XK_uX')]\, \mathrm{d}X/\mathrm{d}S} \tag{11}$$

that results from eq 4 upon integration over $\mathrm{d}x$ with use of eqs 9 and 10. If this is done we are left with a phantom network model, which will be shown to give the C_1 term only. Furthermore, we are left with a collapsed network upon solving for $S°$. The nonbonded interactions *must not be ignored* in eq 11. The difficult aspect of this part of the computation has been in seeing how $\bar{V}_c(\bar{b};X)$ and $\bar{V}_u(\bar{b};X)$ could give different, strain-dependent, contributions to $P(S)$. The following general argument suggests how this comes about.

It should first be remembered that one need not look for a large difference between $\bar{V}_c$ and $\bar{V}_u$. If there is only a small difference between these terms, perhaps amounting to no more thane about 0.1% of $\bar{V}_u$ according to the observations in the Introduction, one might have a contribution that is significant to elasticity.

It is somewhat easier to describe the argument by use of a mixture of time-average and ensemble-average language than to use either one alone. First consider a pair of chains that are interacting with one another in the cross-linked state. The constraints imposed by the network cross-links (and possibly entanglements as well) will ensure that the two chains remain in close proximity for the lifetime of the material. Those two chains (assumed distinguishable by labeling) in the un-cross-linked sample are not subject to such contraints. They will eventually diffuse away from one another, and the Poincaré recurrence time for them to reassociate is probably longer than the lifetime of the universe. The time-averaged configurations of the elastomer are not identical with those of the linear chain reference state, and therefore the ensemble average of the configurations differ as well.

Now one might ask the following: Upon averaging over all constraints, will it not be the case that any configuration of the labeled chains in the un-cross-linked material will be found in the cross-linked state, and therefore the above argument, while plausible for a given set of constraints, is vitiated upon stepping up to the large ensemble? The answer is no, because the average over the ensemble of constraints is, in effect, a geometrical average over these more widely separated configurations of the two object chains. In the un-cross-linked system the averaging is included as a part of a single configuration integral and is akin to an arithmetic average. The net effect of the two-state ensemble averaging is that one must expect the contributions to the numerator and denominator of eq 11 from the nonbonded interactions to be different in general, even though the monomer–monomer potential of mean force is identical in both. The constraints that operate in the network give a weighting to the nonbonded interactions that is different from that for the linear chain system.

There is another factor related to the randomness of network structure that is coupled to the potential for nonbonded interactions, and that is the variation in topology from domain to domain. Imagine that the elastomer is divided into cells of edge length b and that the connectivity of the chains within each cell is drawn as a molecular graph. There will be wide variations in the drawings from one cell to another owing to the randomness of the network structure if, say, the cells contain 10–1000 cross-links. These different structures have different numbers of circuits, and hence different effective attractive interactions. The attractive interactions exert compressive stresses on the material which, in turn, influence the density fluctuations. (That there are compressive stresses may be inferred from the known collapse of phantom networks.) Hence, one concludes that random network topology causes the density fluctuations in the elastomer to be larger than those in the linear chain reference system, contrary to the assertion of Ball and Edwards.[17,18] Stein and co-workers have obtained correlation lengths in elastomers ranging from 30 to 40 nm by Debye–Bueche analysis of light scattering data.[19,20] These results provide direct evidence for large density fluctuations of immense size, which corroborates the above discussion. The contention here is that the fluctuations have a topological origin and that they exist even if the cross-links are distributed uniformly throughout the material.

It is difficult to develop the theory directly along the lines of this argument. What is suggested is that the effects of constraints be imposed on the integrations, which would couple the bonded and nonbonded terms in a complicated way. One would likely get caught up in an exhausting exercise of generating local structures that would include cross-links and then doing integrals that would result in the evaluation of determinants of Kirchhoff matrices[14] for the local structures. It is not clear that this could be done without interjecting an uncontrolled approximation as to how the connections to the rest of the network would be treated.

Instead of this, an expedient approximation is now introduced. Let the range of the segment–segment potential be different in the two systems. Dimensional arguments, used in conjunction with the approximate nonbonded potential that is to be introduced, will justify the method. What is proposed is to replace the restriction on the range of integrations that the constraints impose with a restriction on the range of the potential for a pair of segments. This will introduce a parameter that will be eliminated on minimizing the free energy in the unstrained state.

The nonbonded interactions will be treated with a density fluctuation theory. In a proper theory of liquid structure this would be done by expressing the free energy density as a functional of the density.[21,22] Expansion about the mean density, with truncation at the quadratic term, would then involve calculation of direct correlation functions for all the interactions in the system, and prior to integrating over solvent coordinates these are solvent molecules,[23,24] polymer segments, and cross-links all interacting with one another. Despite recent progress in the application of this theory to polymer molecules, to use it in a perturbative scheme is not trivial. Besides, as is traditional in polymer theory, one might expect reasonable results to be obtained from a coarser description of the system. We therefore adopt Flory's technique of using macroscopic thermodynamics to describe the free energy density in mesoscopic domains that are inhabited by averaged configurations of solvent molecules and polymer segments.[25]

This approach to the nonbonded interactions entails the replacement

$$\bar{V}(\bar{b};X) \rightarrow \int a[\rho(\mathbf{r})]\,\mathrm{d}r \tag{12}$$

where the integral of the (Helmholtz) free energy density $a[\rho(\mathbf{r})]$ is taken over the volume of the system. The density $\rho(\mathbf{r})$ is an implicit function of the coordinates X through the standard equation

$$\rho(\mathbf{r}) = \sum_{j=1}^{N} \delta(\mathbf{r} - X_j) \tag{13}$$

where the X_j are the the coordinates of segment j. Now expand the free energy as a function[26] (not functional) of the density fluctuations about the mean density $\bar{\rho}$. This gives

$$\begin{aligned} \bar{V}(\bar{b};x) &\approx a(\bar{\rho})V + \frac{1}{2}a''(\bar{\rho})\int [\rho(\mathbf{r}) - \bar{\rho}]^2\,\mathrm{d}r \\ &= a(\bar{\rho})V - \frac{1}{2}a''(\bar{\rho})\bar{\rho}^2 V + \frac{1}{2}a''(\bar{\rho})\int [\rho(\mathbf{r})]^2\,\mathrm{d}r \end{aligned} \tag{14}$$

to terms of second order. The nature of the second-order derivative a'' will be discussed later. For now, it is noted that when eq 14 is substituted into eq 11, the first two constant terms of eq 14 cancel in numerator and denominator, and eq 11 becomes

$$P(S) = \frac{\int \exp[-(a''/2kT)\int [\rho_c(\mathbf{r})]^2\,\mathrm{d}r - \gamma\,\mathrm{tr}\,(XK_cX')]\,\mathrm{d}X/\mathrm{d}S}{\int \exp[-(a''/2kT)\int [\rho_u(\mathbf{r})]^2\,\mathrm{d}r - \gamma\,\mathrm{tr}\,(XK_uX')]\,\mathrm{d}X/\mathrm{d}S} \tag{15}$$

It is now important to come to an understanding of the coupling between polymer segment and solvent molecule density fluctuations and how this coupling influences the free energy density expansion once the solvent coordinates have been integrated out. To do this, return to eq 4 and make a substitution analogous to eq 12 to give

$$V(\bar{b};X,x) \rightarrow \int a[\rho_2(\mathbf{r}),\rho_1(\mathbf{r})]\,\mathrm{d}r$$

where $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ are the densities of solvent molecules and polymer segments, respectively. An expansion of $a[\rho_2(\mathbf{r}),\rho_1(\mathbf{r})]$ about $\overline{\rho_2}$ and $\overline{\rho_1}$ then gives the fluctuation term

$$^1/_2\int \{a_{11}[\rho_1(\mathbf{r}) - \overline{\rho_1}]^2 + 2a_{12}[\rho_1(\mathbf{r}) - \overline{\rho_1}][\rho_2(\mathbf{r}) - \overline{\rho_2}] + a_{22}[\rho_2(\mathbf{r}) - \rho_2]^2\}\,\mathrm{d}r \tag{16}$$

where $a_{11} = (\partial^2 a/\partial\rho_1{}^2)_{T,V,\rho_2}$, etc. To calculate with this complicated integral a simplification is in order. One might assert that the fluctuations are dominated by concentration fluctuations when a diluent is present, so that $\rho_1(\mathbf{r}) + \rho_2(\mathbf{r}) = \overline{\rho_1} + \overline{\rho_2}$. This unfortunately misses an important contribution from fluctuations in the overall segment density, which become dominant as $\bar{\rho}_1 \rightarrow 0$. In any event, this method eliminates the solvent coordinates from eq 16 so that one can proceed with an analysis of the polymer density alone. The price that one pays for assuming constant total density is that dry systems have to be treated separately from swollen ones.

What happens to this argument when working with the potential of mean force, as in eqs 12 and 14? The free energy density $a[\rho(\mathbf{r})]$ in eq 12 carries a "memory" of the solvent, and the segment density fluctuations are influenced by the now-averaged properties of the solvent. The volume elements within which the fluctuations occur are in contact with one another and eventually are in contact with a reservoir of solvent that is maintained at chemical potential μ_1. The segment density fluctuations take place at constant μ_1,[27] and a'' in eq 14 is

$$a''(\bar{\rho}) = (\partial^2 a/\partial\rho_2{}^2)_{T,V,\mu_1} \tag{17}$$

As is shown in Appendix A, eq 17 neatly solves the problem of the coupling of solvent and segment density fluctuations discussed above and gives a smooth transition between the swollen and dry states. Helfand and Tagami[27] used similar arguments to assess the influence of a diluent on the interphase between two polymers.

Before embarking on the detailed calculation of eq 15, it may prove beneficial to discuss this problem more correctly in density functional terms. In place of eq 14 one should write

$$\bar{V}(\bar{b};X) \approx a(\bar{\rho})V + {}^1/_2\int\int [\rho(\mathbf{r}') - \bar{\rho}]C(\mathbf{r}',\mathbf{r}'') \times [\rho(\mathbf{r}'') - \bar{\rho}]\,\mathrm{d}r'\,\mathrm{d}r''$$

where $C(\mathbf{r}',\mathbf{r}'')$ is the direct correlation function, which carries a subscript u or c for the reference system or the elastomer, respectively. A first approximation to $C(\mathbf{r}',\mathbf{r}'')$ is provided by the mean-spherical model, in which $C(\mathbf{r}',\mathbf{r}'') \rightarrow u(\mathbf{r}' - \mathbf{r}'')$, where $u(\mathbf{r}' - \mathbf{r}'')$ is the potential of mean force acting between the segments at $\mathbf{r}'$ and $\mathbf{r}''$. On introducing a Flory–Krigbaum–Fixman[25,26] potential in the form of a Gaussian with a strength deriving from a free energy density expanded at constant solvent chemical potential, one arrives at a theory that gives results that are essentially identical with those to be obtained from the simpler theory embodied in eq 14. The essence of the physics of the many-body problem of high elasticity is contained in eq 15, and there is no immediate need to consider higher approximations.

Evaluation

Choose the origin of coordinates to coincide with the center of mass of the two systems; the gyration tensor S is given by eq 9 for both. Now consider the segment density $\rho(\mathbf{r})$. Let the center of mass (CM) of chain j (a chain is attached to a cross-link on at least one end so that it is a part of the connected gel molecule) be located at $\mathbf{r}_j$. The contribution to the segment density at $\mathbf{r}$ from a chain at $\mathbf{r}'$ is $\rho_S(\mathbf{r} - \mathbf{r}')$, and the total segment density is

$$\rho(\mathbf{r}) = \int \rho_S(\mathbf{r} - \mathbf{r}')\rho_C(\mathbf{r}')\,\mathrm{d}r' \tag{18}$$

where $\rho_C(\mathbf{r}')$ is the density of chain CM in volume element $\mathrm{d}r'$ located at $\mathbf{r}'$. Define the Fourier components of the density functions by

$$\hat{\rho}(\mathbf{k}) = \int \rho(\mathbf{r})\exp(i\mathbf{k}\cdot\mathbf{r})\,\mathrm{d}r \tag{19}$$

With use of eq 13 for the chain CM term, it follows that

$$\hat{\rho}_C(\mathbf{k}) = \sum_{j=1}^{\nu}\exp(-i\mathbf{k}\cdot\mathbf{r}_j) = \sum_{j=1}^{\nu}\exp(-ik_\alpha x_j{}^\alpha) \tag{20}$$

for a fixed set of $\mathbf{r}_j$. The last form makes use of the summation convention on Cartesian indices. The convolution theorem then gives

$$\hat{\rho}(\mathbf{k}) = \hat{\rho}_S(\mathbf{k})\hat{\rho}_C(\mathbf{k}) = \hat{\rho}_S(\mathbf{k})\sum_j \exp(-ik_\alpha x_j{}^\alpha) \tag{21}$$

where now the $x_j{}^\alpha$ comprise the jth column of X_ν. Furthermore, we have

$$\int [\rho(\mathbf{r})]^2\,\mathrm{d}r = \frac{1}{(2\pi)^3}\int \hat{\rho}(\mathbf{k})\hat{\rho}(-\mathbf{k})\,\mathrm{d}k \tag{22}$$

The segment density about the CM of a chain will be taken from Debye and Bueche[28] (see also ref 14). The Fourier version of their distribution is

$$\hat{\rho}_S(\mathbf{k}) = \sum_{p=1}^{n}\exp[-(^1/_3 - u + u^2)\langle s^2\rangle_0 k^2] \tag{23}$$

for a chain of n segments, where $u = p/n$ and $\langle s^2\rangle_0 = n\langle l^2\rangle_0/6$ is the radius of gyration of the chain. The cross-links alter the term $(^1/_3 - u + u^2)$ in eq 23 through their perturbing effects on the Kirchhoff matrix elements that reflect the connections between the chain and the rest of the network. As mentioned earlier, a direct calculation of these elements is tedious in the extreme if one tries to calculate a refinement to $(^1/_3 - u + u^2)$. All these messy calculations will be swept into an approximation to eq 23 in the form

$$\hat{\rho}_S(\mathbf{k}) = n\exp(-ak^2/2) \tag{24}$$

where a = constant × $\langle s^2\rangle_0$, and the constant for the cross-linked system will be smaller than that for the un-cross-linked system.

Now return to eq 21 and expand the exponential to get

$$\sum_j \exp(-ik_\alpha x_j{}^\alpha) = \nu\Big[1 - \frac{1}{2}k_\alpha k_\beta S^{\alpha\beta} + \frac{i}{3!}k_\alpha k_\beta k_\gamma S^{\alpha\beta\gamma} + \frac{1}{4!}k_\alpha k_\beta k_\gamma k_\delta S^{\alpha\beta\gamma\delta} + \dots\Big] \quad (25)$$

where

$$S^{\alpha\dots\sigma} = \nu^{-1}\sum_{j=1}^{\nu} x_j{}^\alpha \dots x_j{}^\sigma \quad (26)$$

The term $k_\alpha \sum x_j{}^\alpha$ vanishes by choice of the origin of coordinates. The $S^{\alpha\dots\sigma}$ are geometrical "invariants" that characterize the macroscopic size and shape of the system. Note that the $S^{\alpha\beta}$ are the components of the gyration tensor and that these are fixed in the overall integration in eq 15.

The $S^{\alpha\dots\sigma}$ are macroscopic quantities, and this means that the dominant contributions to the **k**-space integral in eq 22 arise from small **k**. To keep the integral convergent, factor $\exp(-{}^1/{}_2 k_\alpha k_\beta S^{\alpha\beta})$ from eq 25 to get

$$\sum_j \exp(-k_\alpha x_j{}^\alpha) = \nu \exp(-{}^1/{}_2 k_\alpha k_\beta S^{\alpha\beta}) F(\mathbf{k}) \quad (27a)$$

where

$$F(\mathbf{k}) = 1 + \frac{i}{3!}k_\alpha k_\beta k_\gamma S^{\alpha\beta\gamma} + \frac{1}{4!}k_\alpha k_\beta k_\gamma k_\delta (S^{\alpha\beta\gamma\beta} - 3S^{\alpha\beta}S^{\gamma\delta}) + \dots \quad (27b)$$

to terms of $O(k^4)$. Upon inserting eqs 21 and 27 into eq 22, one obtains

$$\int [\rho(\mathbf{r})]^2\,\mathrm{d}r = \frac{\nu^2}{(2\pi)^3}\int [\hat{\rho}_\mathrm{S}(\mathbf{k})]^2 \times \exp(-k_\alpha k_\beta S^{\alpha\beta}) F(\mathbf{k}) F(-\mathbf{k})\,\mathrm{d}k \quad (28)$$

Now set $S = RS_\mathrm{d}R'$, where $S_\mathrm{d} = \mathrm{diag}\,(S_1,S_2,S_3)$ is the matrix of principal components of S, and R is a rotation matrix. The effect of this transformation can be absorbed into **k** by the replacement $\mathbf{k} \to \mathbf{k}R$, and since the Jacobian of this transformation is unity, eq 28 becomes

$$\int [\rho(\mathbf{r})]^2\,\mathrm{d}r = \frac{\nu^2}{(2\pi)^3}\int [\hat{\rho}_\mathrm{S}(\mathbf{k})]^2 \times \exp(-\sum_\alpha S_\alpha k_\alpha{}^2) F(\mathbf{k}) F(-\mathbf{k})\,\mathrm{d}k \quad (29)$$

since $\hat{\rho}_\mathrm{S}(\mathbf{k})$ is invariant to the rotation R. The series $F(\mathbf{k})$ is now understood to be evaluated in the frame that diagonalizes S.

Use of eqs 24 and 27b in eq 29 gives

$$\int [\rho(\mathbf{r})]^2\,\mathrm{d}r = \frac{N^2}{(2\pi)^3}\int \exp[-\sum (S_\alpha + a)k_\alpha{}^2] \times \Big[1 + \frac{1}{12}k_\alpha k_\beta k_\gamma k_\delta S_\mathrm{d}{}^{\alpha\beta\gamma\delta} - \frac{1}{4}(\sum S_\alpha k_\alpha{}^2)^2 + \dots\Big]\,\mathrm{d}k \quad (30)$$

where $N = \nu n$ is the total number of polymer segments as before and the subscript d on $S_\mathrm{d}{}^{\alpha\beta\gamma\delta}$ serves as a reminder that this tensor is evaluated in the frame that diagonalizes S. This series in eq 30 is very slowly convergent, as we will see, but at least it is susceptible to term-by-term integration. That will be enough to determine the functional form of the deformation-dependent terms that emerge from it.

Equation 30 is now integrated term by term to obtain

$$\int [\rho(\mathbf{r})]^2\,\mathrm{d}r = \frac{N^2}{(4\pi)^{2/3}|S + a\mathbf{1}|^{1/2}}\Big[1 + \frac{1}{16}\sum_\alpha \frac{S_\mathrm{d}{}^{\alpha\alpha\alpha\alpha}}{(S_\alpha + a)^2} + \frac{1}{8}\sum_{\alpha<\beta}\frac{S_\mathrm{d}{}^{\alpha\alpha\beta\beta}}{(S_\alpha + a)(S_\beta + a)} - \frac{3}{16}\sum_\alpha \frac{S_\alpha{}^2}{(S_\alpha + a)^2} - \frac{1}{8}\sum_{\alpha<\beta}\frac{S_\alpha S_\beta}{(S_\alpha + a)(S_\beta + a)} + \dots\Big] \quad (31)$$

which are the only terms (to the order given) that survive the **k**-space integrations. Write the determinant $|S + a\mathbf{1}|$ as

$$|S + a\mathbf{1}| = |S|\Big[1 + a\Big(\frac{1}{S_1} + \frac{1}{S_2} + \frac{1}{S_3}\Big) + \frac{a^2(S_1 + S_2 + S_3) + a^3}{|S|}\Big]$$

so that the series expansion

$$|S + a\mathbf{1}|^{-1/2} = |S|^{-1/2}\Big\{1 - \frac{1}{2}\Big(\frac{1}{S_1} + \frac{1}{S_2} + \frac{1}{S_3}\Big) + \frac{3a^2}{8}\Big[\Big(\frac{1}{S_1{}^2} + \frac{1}{S_2{}^2} + \frac{1}{S_3{}^2}\Big) + \frac{2}{3|S|}(S_1 + S_2 + S_3)\Big] + \dots\Big\}$$

in powers of a may be carried out. The other terms in eq 31 are likewise expanded in powers of a/S_α. We now need to inspect the nature of terms that result from the use of eq 31 and eq 15.

The structure of the Kirchhoff matrices for the bonded interactions in the cross-linked and un-cross-linked systems makes it convenient to discuss the former in terms of the fixed positions of cross-links and the latter in terms of fixed positions of the CM of the molecules. This minor inconsistency could be remedied by integrating both numerator and denominator in eq 15 over the positions of the chain segments for the bonded terms alone with molecular centers fixed. (This integration must be carried out before combining the bonded and nonbonded terms, since the development between eqs 18 and 24 averaged over the chain segment coordinates.) The term tr $(XK_\mathrm{u}X')$ in the denominator is simply replaced by an uninteresting constant when integrated. The corresponding term in the numerator becomes tr $(X_\nu K_\mathrm{c}{}^* X_\nu{}')$ when integrated over midchain segments with fixed cross-links, where $K_\mathrm{c}{}^*$ is the Kirchhoff matrix for the reduced network.[29] This is just the matrix used by James and Guth, as we have shown. The matrix is more complicated if the CM of the chains are held fixed.

Now make a polar decomposition of the configuration spaces for the remaining coordinates. (The discussion here is limited to the numerator in eq 15. Similar considerations apply to the denominator.) This gives

$$X_\nu = R(\nu S_\mathrm{d})^{1/2} V \quad (32)$$

where the $3 \times \nu$ matrix V satisfies $VV' = 1_3$ and $VJ' = 0$, where $J = (1, 1, \dots, 1)$ is a row of ones (the latter condition fixes the origin of X_ν). The rotation R has been absorbed into the **k**-space integration in proceeding from eq 28 to eq 29, and for present purposes $X_\nu = (\nu S_\mathrm{d})^{1/2} V$. Consider the tensor $S_d^{\alpha\alpha\beta\beta}$ in eq 31; it is given by

$$\begin{aligned} S_d^{\alpha\alpha\beta\beta} &= \nu^{-1}(\nu S_\alpha)(\nu S_\beta)\sum_i v_i^\alpha v_i^\alpha v_i^\beta v_i^\beta \\ &= S_\alpha S_\beta[\nu \sum_i v_i^\alpha v_i^\alpha v_i^\beta v_i^\beta] \end{aligned} \tag{33}$$

If the exponential function in which this term appears is expanded, the integration to be done is

$$\int_{VV'=1}(\sum_i v_i^\alpha v_i^\alpha v_i^\beta v_i^\beta) \operatorname{etr}(-\nu\gamma^* S V K_c^* V)\, \mathrm{d}V$$

where $\gamma^* = {}^3/_2 \langle r^2\rangle_0$. To actually carry out the integral requires that one transform to a frame that diagonalizes K_c^*, but then the $\sum_i v_i^\alpha v_i^\alpha v_i^\beta v_i^\beta$ terms inherit components from the transformation matrix. Since the structure of K_c^* for the random system is highly complicated, it seems that the integral is very difficult to estimate. At the very least, the form of eq 33 makes it plausible that

$$S^{\alpha\alpha\beta\beta}/(S_\alpha + a)(S_\beta + a) = (1 + a/S_\alpha)^{-1}(1 + a/S_\beta)^{-1}[\nu \sum_i v_i^\alpha v_i^\alpha v_i^\beta v_i^\beta]$$

can be $O(\nu^b)$, where $b > 0$. (Remember that $\sum_i v_i^\alpha v_i^\alpha = 1$; the quadruple sum consists of the diagonal components in $(\sum_i v_i^\alpha v_i^\alpha)(\sum_i v_i^\beta v_i^\beta) = 1$. The average off-diagonal component is bound to be much smaller than the average diagonal component.)

Before collecting terms in eq 31, an observation that will simplify the equation is in order. Let us examine the term $S_d^{\alpha\alpha\alpha\alpha}/S_\alpha^2 = A_\alpha$. When this is integrated over $\mathrm{d}X/\mathrm{d}S$ with (for the elastomer) or without (for the linear chain reference system) the term for the bonded potential, there results a dimensionless number. If we take the elastic body to have spherical or cubical symmetry in the unstrained state, and the same for the linear chain system, then the three components of A_α must be equal. Using this principle allows one to write

$$\int [\rho(\mathbf{r})]^2\, \mathrm{d}r = \frac{N^2}{(4\pi)^{3/2}|S|^{1/2}}\left\{B_1 - B_2 a\left(\frac{1}{S_1} + \frac{1}{S_2} + \frac{1}{S_3}\right) + B_3 a^2\left(\frac{1}{S_1^{\,2}} + \frac{1}{S_2^{\,2}} + \frac{1}{S_3^{\,2}}\right) + \frac{B_4 a^2}{|S|}(S_1 + S_2 + S_3) + \ldots\right\} \tag{34}$$

where the B_i are constants that derive from the "shape tensors" $S^{\alpha\alpha\beta\beta\ldots\sigma\sigma}/S_\alpha S_\beta \ldots S_\sigma$.

Unfortunately, the B_i are enormously difficult to calculate, as discussed above. The theory, at this stage of the development, is little more than an analysis of the functional form of the terms that can emerge from a series expansion of the density fluctuation integral, and on that account it is less than completely satisfactory.

I believe that this problem is inherent in the theory of elasticity and will be very difficult to overcome. The reason for this belief is this: One must begin a discussion of a molecular system with inter- and intramolecular potentials and use these to deduce macroscopic properties. The local liquid-like structure of the elastomer, as manifest in a radial distribution function $g(r)$, is coupled into the three-dimensional network structure at distances where $g(r)$ for normal liquids has reached its asymptotic value of unity. The fact that experimental results depart from the classical Gaussian theory predictions is evidence that there is a coupling between liquid-like structure and the network connectivity. The propagation of forces throughout the entire network cannot help but couple together the local potential with the attractive entropic force that encompasses macroscopic dimensions. In a crystal or small-molecule liquid the forces are transmitted between near-neighbor atoms or molecules; in an elastomer there is that contribution, but there is also a transmission of forces between topological neighbors that are far removed from one another. The perturbing effects of the topological interactions on the local interactions is inherently small, but they pervade the macroscopic sample.

The $\langle r^2\rangle_0/S_\alpha$ are the only dimensionless parameters available to describe this coupling. The only intrinsic network characteristics that convert $\langle r^2\rangle_0/S_\alpha$ into intensive variables are the κ_α, the smallest nonzero eigenvalues of the Kirchhoff matrix.[30] The only intensive deformation-dependent parameters in the elasticity problem are $\langle r^2\rangle_0/\kappa_\alpha S_\alpha$. The series presentation of $\int [\rho(\mathbf{r})]^2\, \mathrm{d}r$ has shown what powers of these parameters are to be found.

A few words of explanation regarding the shape tensors are in order here. The elastic body, in this treatment, is unconstrained by a container. The fluctuations in shape that it undergoes, for fixed gyration tensor S, include twists and bends and all the other deformations that an elastic material might be subjected to by the application of forces. These various deformation modes are influenced by the topology of the network, and hence the average values of the shape tensors are different for the elastomer and for the linear chain reference system. However, these tensors also exist for the reference system.

We will apply eq 34 to both numerator and denominator in eq 15. Before doing this, it should be noted that the deformation-dependent terms in eq 34 provide some insight into the elastic properties of the un-cross-linked system. One sees in that equation the emergence of a stress–strain relation of the same form as the Mooney–Rivlin equation, with a C_1 constant varying as $(a^2/V^2)f(\nu)$. This is an entanglement contributions varying as the square of $\langle r^2\rangle_0$ (proportional to the number of contacts between two chains) and inversely as the square of the volume (the concentration effect). A complete theory along these lines might lead to an explanation of the Langley trapping factor.[31] More will be said about this term in the Discussion.

The contribution from the bonded interactions now must be included in the numberator of eq 15. In Appendix B it is shown that these terms contribute

$$\gamma^* \operatorname{tr}(XK_c^*X') = \nu\gamma^* \operatorname{tr}(S_d V K_c^* V') \sim \nu\gamma^*\kappa_1(S_1 + S_2 + S_3) \tag{35}$$

to the free energy in the asymptotic limit of large ν, to within terms that are inconsequential for thermodynamics. Equations 34 and 35 may now be assembled to give

$$A_{el}(S) = \nu k T\gamma^*\kappa_1(S_1 + S_2 + S_3) + \frac{a''N^2}{|S|^{1/2}}\left\{[(B_2a)_u - (B_2a)_c]\left(\frac{1}{S_1} + \frac{1}{S_2} + \frac{1}{S_3}\right) - [(B_3a^2)_u - (B_3a^2)_c]\left(\frac{1}{S_1^{\,2}} + \frac{1}{S_2^{\,2}} + \frac{1}{S_3^{\,2}}\right) + \ldots\right\} \tag{36}$$

where the subscripts u and c apply to the quantities in parentheses. By the discussion following eqs 11 and 23, the constant terms $(B_2a)_u - (B_2a)_c$ and $(B_3a^2)_u - (B_3a^2)_c$ are both positive. Terms that are only dependent on the volume, i.e., $|S|^{1/2}$, have been dropped from eq 34 since they may be adsorbed into A_u.

We have arrived at the elastic equation of state

$$A_{el}(S) = D_1(S_1 + S_2 + S_3) + D_2\left[\left(\frac{1}{S_1} + \frac{1}{S_2} + \frac{1}{S_3}\right) - b'\left(\frac{1}{S_1^{\,2}} + \frac{1}{S_2^{\,2}} + \frac{1}{S_3^{\,2}}\right)\right] \tag{37a}$$

where

$$D_1 = 3\nu kT\kappa_1/2\langle r^2\rangle_0 \tag{37b}$$

and

$$D_2 = \frac{cV_2^{\,2}/|S|^{1/2}}{\beta\phi_2^{\,2} + \bar{V}_1\phi_1/kT(1-\phi_1\chi')} \tag{37c}$$

with use of Appendix A. Here b' and c are the two free parameters of the theory. The quantity $V_2 = N\bar{V}_2$ is the volume of the elastomer evaluated at the mean density, which is independent of S. This is a subtle point that will be important shortly.

The components of S are independent variables. The unstrained state is the state of minimum free energy, as determined by solution of the three equations

$$(\partial A/\partial S_\alpha)_{T,n_1} = (\partial A_{\text{el}}/\partial S_\alpha)_{T,n_1} + (\partial A_{\text{u}}/\partial S_\alpha)_{T,n_1} = 0 \tag{38a}$$

It is assumed that, at equilibrium, A_{u} is a function of volume alone. This gives

$$(\partial A_{\text{el}}/\partial S_\alpha)_{T,n_1} - pV/2S_\alpha = 0 \tag{38b}$$

where p is the hydrostatic pressure on the reference system. This may be taken as small as one likes, so that the unstrained state $S_\alpha = S_\alpha{}^\circ$ is determined by

$$(\partial A_{\text{el}}/\partial S_\alpha)_{T,n_1} = D_1 - D_2{}^\circ\left(\frac{1}{(S_\alpha{}^\circ)^2} - \frac{2b'}{(S_\alpha{}^\circ)^3}\right) - \frac{1}{2}\frac{D_2{}^\circ}{S_\alpha{}^\circ}\times \left[\left(\frac{1}{S_1{}^\circ} + \frac{1}{S_2{}^\circ} + \frac{1}{S_3{}^\circ}\right) - b'\left(\frac{1}{(S_1{}^\circ)^2} + \frac{1}{(S_2{}^\circ)^2} + \frac{1}{(S_3{}^\circ)^2}\right)\right] = 0 \tag{39}$$

The last term of this equation arises from the derivative of $|S|^{-1/2}$ in eq 37c. That is the only term in eq 37c that is variable; the remaining terms are essentially parameters of the potential, and they are independent of strain. In the unstrained state, $D_2 = D_2{}^\circ$.

It is clear from eq 39 that $S_1{}^\circ = S_2{}^\circ = S_3{}^\circ$, which is a consequence of choosing the elastic body to be such that the smallest eigenvalue of the Kirchhoff–James–Guth matrix is triply degenerate. Equation 39 reduces to

$$D_1 = D_2{}^\circ\left(\frac{5/2}{(S_\alpha{}^\circ)^2} - \frac{7b'/2}{(S_\alpha{}^\circ)^3}\right) = 0, \qquad \alpha = 1, 2, 3 \tag{40}$$

If the values of b' and c were known, this equation could be solved to give the volume of the unstrained elastomer. Instead, eq 40 is used to evaluate $D_2{}^\circ$. Henceforth, attention is restricted to systems that are cured in the bulk, for which the denominator in eq 37c is simply β_2, the compressibility of the elastomer in the unstrained state. Furthermore, only the stress–strain relation is developed here. Swollen systems or systems cured in the presence of a diluent will be considered elsewhere.

Equation 40 gives

$$D_2{}^\circ = \frac{2D_1(S_\alpha{}^\circ)^2}{5 - 7b'/S_\alpha{}^\circ}$$

we also have $S_\alpha = \lambda_\alpha{}^2 S_\alpha{}^\circ$ from eq 7. Substituting these expressions into eq 37a gives

$$A_{\text{el}} = D_1 S_\alpha{}^\circ\left\{(\lambda_1{}^2 + \lambda_2{}^2 + \lambda_3{}^2) + \frac{2|\lambda|^{-1}}{5-7b}\times \left[\left(\frac{1}{\lambda_1{}^2} + \frac{1}{\lambda_2{}^2} + \frac{1}{\lambda_3{}^2}\right) - b\left(\frac{1}{\lambda_1{}^4} + \frac{1}{\lambda_2{}^4} + \frac{1}{\lambda_3{}^4}\right)\right]\right\} \tag{41}$$

where $b = b'/S_\alpha{}^\circ$. The determinant $|\lambda|$ arises from the dependence of D_2 on $|S|^{1/2}$.

Because the S_α are independent, so are the λ_α. For now we will take $|\lambda| = 1$ on the basis of experimental evidence. (It should be possible to calculate the volume for the system in any state of strain by minimizing A with respect to $|\lambda|$. Here is another problem that is reserved for future developments.)

The principal stresses are given by[12]

$$\sigma_\alpha = (2/V)\lambda_\alpha{}^2(\partial A_{\text{el}}/\partial\lambda_\alpha{}^2)_T$$

and the stress difference is

$$\sigma_1 - \sigma_2 = \frac{2D_1S_\alpha{}^\circ}{V}\left\{\lambda_1{}^2 - \lambda_2{}^2 - \frac{2}{5-7b}\left[\left(\frac{1}{\lambda_1{}^2} - \frac{1}{\lambda_2{}^2}\right) - 2b\left(\frac{1}{\lambda_1{}^4} - \frac{1}{\lambda_2{}^4}\right)\right]\right\} \tag{42}$$

Let $\lambda = \lambda_1 = 1/\lambda_2{}^2$ to get

$$\frac{\sigma_1 - \sigma_2}{\lambda^2 - 1/\lambda} = [f] = \frac{2D_1S_\alpha{}^\circ}{V(5-7b)}[(5-11b) + 2/\lambda - 4b/\lambda^3] \tag{43a}$$

or

$$[f] = 2C_1 + 2C_2/\lambda - 2C_3/\lambda^3 \tag{43b}$$

where

$$C_1 = (D_1S_\alpha{}^\circ/V)\left(\frac{5-11b}{5-7b}\right) \tag{43c}$$

$$C_2/C_1 = 2/(5-11b) \tag{43d}$$

and

$$C_3/C_1 = 4b/(5-11b) \tag{43e}$$

The next-to-last equation allows the undetermined parameter b to be evaluated from the oft-measured[1] ratio C_2/C_1 as

$$b = 5/11 - 2C_1/11C_2 \tag{44}$$

The conditions $C_1 > 0$ and $b > 0$ translate into $b < 5/11$ and $C_2/C_1 > 2/5$, respectively. The requirement that $b > 0$ follows from eq 36 and agrees with the experimental finding[3] that the reduced force, $[f]$, has negative curvature as a function of $1/\lambda$.

Equations 43 lead to the conclusion that the reduced force is maximal at $\lambda^{-1} = \lambda_{\text{m}}{}^{-1} = 1/(6b)^{1/2}$. If the extremum can be located accurately from experiments, this relation provides a means to evaluate the parameter b. Note that if $\lambda_{\text{m}}{}^{-1} < 1$, we must have $b > 1/6$.

Discussion

The elastic equation of state given by eqs 43 depends upon a single arbitrary parameter b. The quantity D_1 appearing in eq 43 depends upon the structure of the network as detailed in eq 37b. The smallest nonzero eigenvalue of the Kirchhoff matrix, κ_1, that appears in that equation is not subject to arbitrary specification. At the very least, one should be able to calculate κ_1 and hence D_1 with the use of computer simulations that model polymer network formation.[30]

If one chooses to terminate the power series development of the nonbonded interactions with the term that varies as $1/S_\alpha$, i.e., the C_2 term, the theory would then entail no arbitrary parameters. Inclusion of the next higher order term in the series is based on a desire to provide a better fit to experimental data in the uniaxial compression region.

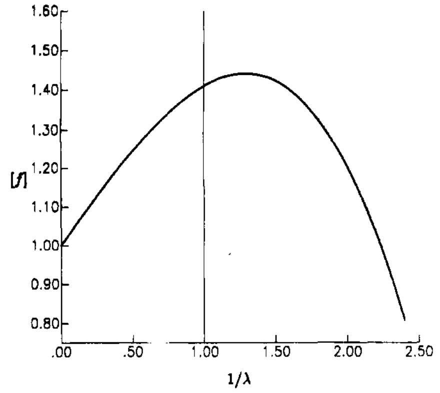

Figure 1. Mooney plot of the normalized reduced force [f] vs $1/\lambda$ as calculated from eqs 43 with $b = 0.1$.

Desultory efforts to devise an empirical function of a single parameter to provide an even better fit in the compression region have not yet been successful. The functions

$$D_2\left(\frac{1}{S_1} + \frac{1}{S_2} + \frac{1}{S_3}\right) \exp\left[-b'\left(\frac{1}{S_1} + \frac{1}{S_2} + \frac{1}{S_3}\right)\right]$$

and

$$\frac{D_2\left(\frac{1}{S_1} + \frac{1}{S_2} + \frac{1}{S_3}\right)}{1 + b'\left(\frac{1}{S_1} + \frac{1}{S_2} + \frac{1}{S_3}\right)}$$

have been explored as replacements for the D_2 term in eq 37a, but they seem not to offer a distinct advantage over the latter.

A normalized plot of the reduced force against the reciprocal of the extension ratio is shown in Figure 1 for an arbitrarily selected value of $b = 0.1$. On the face of it the equation fails miserably in the region $1/\lambda > 2.0$. Experiments in the biaxial stretch region reveal that the reduced force is nearly constant when $1/\lambda > 1$. In fact, eq 43b predicts that the reduced forced will become negative for sufficiently small λ, which is clearly nonsense. This problem could be circumvented by adding yet another parameter and a term that goes as $1/\lambda^5$ with a positive sign. I have chosen to resist the introduction of another parameter, in the belief that to do so would tend to cloud what is likely to be an important issue in the region of high compression, and that is limited chain extensibility. It is well-known from the work of Mark and co-workers[32] that limited chain extensibility in the region of uniaxial extension eventually becomes important and causes the reduced force to swing upward. One must expect that a similar behavior will occur on the biaxial stretch side and that limited chain extensibility is likely to be an extremely important feature of rubber elasticity in the region where $1/\lambda > 1.6$. In fact, recent results of Xu and Mark[3] show that the reduced force has an extremum near $1/\lambda = 1.2$ and that the curve then levels off at larger values of $1/\lambda$.

The constraint that b be greater than zero translates in the discussion following eq 44 into the ratio $C_2/C_1 > 2/5$ for systems cured in the bulk (a discussion of the solvent dependence of C_2 follows). Perusal of a review[1] of data shows that $C_2/C_1 > 0.4$ for approximately 90% of the elastomeric systems that were considered in 1975. A more thorough analysis of the literature will be undertaken in the future. Suffice it to say at this time that a three-term equation of state seems to be reasonably well consistent with experimental data with some notable exceptions that merit further consideration.

The dependence of the non-Gaussian terms on the quality of the solvent as conveyed through eq 37c enables one to make some definite predictions about the solvent dependence of C_2 and C_3. The term involving the χ parameter in eq 37c dominates the factor involving the compressibility for all but the smallest amounts of adsorbed solvent. Everything else being equal, the equation predicts that the smaller is χ, the larger are the values of the C_2 and C_3 terms. For a given interaction parameter, these coefficients decrease with increasing concentration of diluent. All this seems to be in, at least, qualitative accord with observations.[4,33]

The treatment of the nonbonded interactions which is offered here suggests that it is possible to obtain a contribution to the C_1 term from density fluctuations. The last explicit term in eq 34 is of the form

$$C_1 = \text{const} \times \beta_2^{-1} V^{-1/3} \langle r^2 \rangle_0^{\,2} (\lambda_1^{\,2} + \lambda_2^{\,2} + \lambda_3^{\,2}) \quad (45)$$

for a polymer melt, where the constant should depend only upon the state of the system at the time of cure and not upon any material parameters. A measurement of the temperature coefficient of the apparent value of C_1 for an un-cross-linked high molecular weight polymer in the plateau region should give a stress temperature coefficient of sign opposite to that for the cross-linked system, since for the cross-linked system $C_1 \propto 1/\langle r^2 \rangle_0$, whereas for the un-cross-linked system $C_1 \propto (\langle r^2 \rangle_0)^2$. Whether or not such measurements could be made in some sense of equilibrium as required by this thermodynamic analysis remains to be seen.

Obvious opportunities exist for improving this treatment of nonbonded interactions, among these being a more comprehensive analysis of the density fluctuation correlations. The incorporation of a contribution from "entanglements" through terms similar to those in eq 45 has presented itself. Whether or not it is necessary to include this term in an equilibrium theory can only be judged after careful analysis (via computations) of the relation between the smallest eignevalue term and measured stress–strain isotherms.

The calculation of modified configuration integrals, such as might be required to otbain single-chain statistics or to incorporate higher order terms in the potential for non-Gaussian effects, is apt to pose technical difficulties. Further developments in mathematical techniques may be required to address some of these additional interesting problems. The structure of the theory is such that it enables one to formulate a potential energy function for even a difficult system, such as a filled elastomer, in a coherent and logical fashion.

A final, somewhat unrelated, comment on the Valanis–Landel[34] hypothesis might be of interest. We have seen that the elastic free energy must be a symmetric function of the $\lambda_\alpha^{\,2}$. If the function that describes this free energy can be expanded in a *convergent* power series in the $\lambda_\alpha^{\,2}$ and if the volume is consistent ($\lambda_1\lambda_2\lambda_3 = 1$), then the free energy will *appear* to be separable when viewed as the power series, even though the original function might not be separable. Examples of such functions are provided by those mentioned earlier in this section.

Conclusion

A theory of rubber elasticity has been presented in which both bonded and nonbonded interactions are considered. The bonded interactions are treated by means of techniques borrowed from multivariate statistics,[35] and this gives the dominant contribution to the C_1 term of Mooney–Rivlin phenomenological theory. The nonbonded interactions are analyzed by means of an expansion of the density fluctuations in powers of $\langle r^2\rangle_0/S_\alpha$. It is suggested that a three-term series expansion yields an equation that can be compared with experimental data and the single parameter evaluated either from the location of the extremum in the reduced force curve or from the measured ratio of C_2/C_1. The coefficients of the non-Gaussian terms are shown to depend upon the presence and quality of a diluent, which modifies the magnitude of the density fluctuations. The fluctuations differ in the network and the corresponding solution of linear chains by virtue of the constraints imposed by the polymer network which act to restrict the range of the intermolecular potential. The form of the solvent dependence of the C_2 term is similar to that recently advocated by Deloche and Samulski.[36] Comparisons with other theories, as discussed by Gottlieb and Gaylord,[37] should be attempted. We are currently undertaking further analysis of the equations presented here.

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Appendix A. Variance of the Segment Density Fluctuations[27]

The derivative $(\partial^2 a/\partial\rho_2^2)_{T,V,\mu_3}$ will be obtained here. Consider the first derivative; since it is taken at constant volume, the volumes in both the free energy density and the segment density cancel to give

$$(\partial a/\partial\rho_2)_{T,V,\mu_1} = (\partial A/\partial n_2)_{T,V,\mu_1} \qquad \text{(A1)}$$

where n_2 is the number of polymer segments in the volume V. Now, since

$$\mathrm{d}A = \mu_1\,\mathrm{d}n_1 + \mu_2\,\mathrm{d}n_2 - P\,\mathrm{d}V - S\,\mathrm{d}T \qquad \text{(A2)}$$

one has

$$\begin{aligned}(\partial A/\partial n_2)_{T,V,\mu_1} &= \mu_2 + \mu_1(\partial n_1/\partial n_2)_{T,V,\mu_1} \\ &= \mu_2 - \mu_1\frac{(\partial\mu_1/\partial n_2)_{T,V,n_1}}{(\partial\mu_1/\partial n_1)_{T,V,n_2}} \qquad \text{(A3)}\end{aligned}$$

with the second verison arising from the rule for implicit differentiation. An interchange of the order of differentiation in the numerator of the second term in eq A3 gives

$$(\partial A/\partial n_2)_{T,V,\mu_1} = \mu_2 - \mu_1\frac{(\partial\mu_2/\partial n_1)_{T,V,n_2}}{(\partial\mu_1/\partial n_1)_{T,V,n_2}}$$

or

$$(\partial a/\partial\rho_2)_{T,V,\mu_1} = \mu_2 - 1/(\partial\ln\mu_1/\partial\mu_2)_{T,V,n_2} \qquad \text{(A4)}$$

The second term is now seen to contribute nothing to the second derivative taken at constant μ_1.

We now proceed to calculate

$$(\partial^2 a/\partial\rho_2^2)_{T,V,\mu_1} = V(\partial\mu_2/\partial n_2)_{T,V,\mu_1}$$

obtained with the use of eq A4. The derivative on the right is given by

$$\begin{aligned}(\partial\mu_2/\partial n_2)_{T,V,\mu_1} &= (\partial\mu_2/\partial n_2)_{T,V,n_1} + \\ &\qquad (\partial\mu_2/\partial n_1)_{T,V,n_2}(\partial n_1/\partial n_2)_{T,V,\mu_1} \\ &= \mu_{2,2}^{V} - \mu_{2,1}^{V}(\mu_{1,2}^{V}/\mu_{1,1}^{V}) \qquad \text{(A5)}\end{aligned}$$

where $\mu_{2,2}^{V} = (\partial\mu_2/\partial n_2)_{T,V,n_1}$, etc., and where use has again been made of the rule leading to eq A3.

The derivatives at constant volume are conveniently converted into constant-pressure derivatives at this stage. We have

$$(\partial\mu_\alpha/\partial n_\sigma)_{T,V,n_\gamma} = (\partial\mu_\alpha/\partial n_\sigma)_{T,P,n_\gamma} + \bar{V}_\alpha(\partial P/\partial n_\sigma)_{T,V,n_\gamma} \qquad \text{(A6)}$$

where α, σ, and γ ($\sigma \neq \gamma$) take the values (1, 2). The partial molecular (or segmental) volume of component α is $\bar{V}_\alpha = (\partial\mu_\alpha/\partial P)_{T,n_1,n_2}$. The last term in eq A6 simplifies on use of

$$(\partial P/\partial n_\sigma)_{T,V,n_\gamma} = -\frac{(\partial V/\partial n_\sigma)_{T,P,n_\gamma}}{(\partial V/\partial P)_{T,n_1,n_2}} = \frac{\bar{V}_\sigma}{V\beta}$$

where $\beta = -(\partial\ln V/\partial P)_{T,n_1,n_2}$ is the compressibility of the system. This finally gives

$$\mu_{\alpha,\sigma}^{V} = \mu_{\alpha,\sigma}^{P} + \bar{V}_\alpha\bar{V}_\sigma/V\beta \qquad \text{(A7)}$$

where $\mu_{\alpha,\sigma}^{P} = (\partial\mu_\alpha/\partial n_\sigma)_{T,P,n_\gamma}$. Use of eq A7 in eq A5 yields the cumbersome, but exact, equation

$$\begin{aligned}&(\partial^2 a/\partial\rho_2^2)_{T,V,\mu_1} \\ &\quad = \frac{[\mu_{2,2}^{P}\mu_{1,1}^{P} - (\mu_{1,2}^{P})^2]V\beta + \bar{V}_2^{\,2}\mu_{1,1}^{P} + \bar{V}_1^{\,2}\mu_{2,2}^{P} - 2\bar{V}_1\bar{V}_2\mu_{1,2}^{P}}{\beta\mu_{1,1}^{P} + \bar{V}_1^{\,2}/V} \\ &\quad = \frac{\bar{V}_2^{\,2}\mu_{1,1}^{P} + \bar{V}_1^{\,2}\mu_{2,2}^{P} - 2\bar{V}_1\bar{V}_2\mu_{1,2}^{P}}{\beta\mu_{1,1}^{P} + \bar{V}_1^{\,2}/V} \qquad \text{(A8)}\end{aligned}$$

The term in brackets vanishes by virtue of the conditions for stability of a homogeneous phase.[38]

The Gibbs free energy of a small volume element is given by the Flory–Huggins expression

$$G = G^\circ + kTn_1(\ln\phi_1 + B\phi_2) \qquad \text{(A9)}$$

where G° is the standard-state free energy of the system, ϕ_α is the volume fraction of component α, and

$$B = \sum_{l=0}^{\infty} B_l\phi_2^{\,l}$$

is a phenomenological representation of noncombinatorial contributions to the free energy. From eq A9 one finds

$$\mu_1 = \mu_1^\circ + kT[\ln\phi_1 + \phi_2 + \chi\phi_2^{\,2}]$$

and

$$\mu_2 = \mu_2^\circ + kT(\bar{V}_2/\bar{V}_1)[-\phi_1 + \psi\phi_1^{\,2}]$$

where

$$\chi = \sum_{l=0}^{\infty}(l+1)(B_l - B_{l+1})\phi_2^{\,l} = \sum_{l=0}^{\infty}\chi_l\phi_2^{\,l}$$

and

$$\psi = \sum_{l=0}^{\infty}(l+1)B_l\phi_2^{\,l} = (B - \phi_2\chi)/\phi_1$$

These give

$$\begin{aligned}\mu_{1,1}^{P} &= (kT\phi_2^{\,2}/n_1)(1 - \phi_1\chi') \\ \mu_{2,2}^{P} &= (kT\bar{V}_2\phi_1\phi_2/\bar{V}_1 n_2)(1 - \phi_1\chi') \qquad \text{(A10)}\end{aligned}$$

and

$$\mu_{1,2}^{P} = \mu_{2,1}^{P} = -kT(\phi_2^{\,2}/n_2)(1 - \phi_1\chi')$$

where

$$\chi' = \sum_{l=0}^{\infty} (l + 2)\chi_l \phi_2^{\,l}$$

Upon inserting eqs A10 into A8, one finds

$$(\partial^2 a/\partial \rho_2^{\,2})_{T,V,\mu_1} = \frac{\bar{V}_2^{\,2}}{\beta\phi_2^{\,2} + \bar{V}_1\phi_1/kT(1 - \phi_1\chi')} \quad \text{(A11)}$$

A satisfactory approximation for the compressibility of the solution is

$$\beta = \phi_1\beta_1 + \phi_2\beta_2 \quad \text{(A12)}$$

In the absence of diluent, eq A11 with the use of eq A12 reduces to

$$(\partial^2 a/\partial \rho_2^{\,2})_{T,V,\mu_1} = \bar{V}_2^{\,2}/\beta_2$$

as it should for a pure phase.

Appendix B. Asymptotic Distribution Function of the Gyration Tensor

At the level of approximation discussed here, the bonded and nonbonded parts of the potential are decoupled and analyzed separately. This requires an analysis of the distribution function of the gyration tensor for the "phantom" network in the domain where $-kT \ln P(S) = O(N)$, which condition stems from the requirement that the free energy by an extensive quantity.

The leading term of the asymptotics of the multivariate distribution function[35] has been determined to be

$$P(S) \sim \exp[-\gamma N(\kappa_1 S_1 + \kappa_2 S_2 + \kappa_3 S_3)] \quad \text{(B1)}$$

where only the exponential terms (that contribute to the thermodynamics of the macroscopic system) are given here. In applying this to rubber elasticity, we want to specialize eq B1 to ellipsoids of revolution and to elastic bodies that have cubic or spherical symmetry in the unstrained state, for which the three smallest nonzero eigenvalues κ_1, κ_2, and κ_3 of the Kirchhoff matrix are triply degenerate. (We have demonstrated this degeneracy for cubic symmetry by means of computations on large network stimulations.[30]) Thus, eq B1 specializes to

$$P_0(S) \sim \exp[-\gamma N\kappa_1(S_\parallel + 2S_\perp)] \quad \text{(B2)}$$

where $P_0(S)$ is the distribution function for the phantom network. Although this could be written in terms of the radius of gyration $s^2 = S_\parallel + 2S_\perp$, present purposes favor explicit identification of the components of s^2.

In addition to the leading term expressed as eq B1, the next term in the asymptotic series is also known. It is a very complex function of the eigenvalues of K.

We now need to answer the question: Can other terms in the asymptotic series contribute to $P(S)$ for the macroscopic system? The answer is no, as will now be demonstrated.

In previous work[11] we have shown that

$$P_0(S) \propto \int \operatorname{etr}(ikhSh') \prod_{\alpha=1}^{3} D(k_\alpha)\, \mathrm{d}k_\alpha \prod_{\alpha<\beta} |k_\alpha - k_\beta|\, \mathrm{d}h \quad \text{(B3)}$$

where dh is the volume element of the Lie group $h \in SO(3)$, and

$$D(k_\alpha) = \prod_{l=1}^{N-1} (\gamma N\kappa_l + ik_\alpha)^{-1/2}$$

The transpose of h is h' and $hh' = h'h = 1$. Constant terms and terms depending on S that do not contribute to the thermodynamics are omitted from eq B3.

Let us consider $\operatorname{etr}(ikhSh') = \exp[i \operatorname{tr}(khSh')]$ for the case $S = \operatorname{diag}(S_\perp, S_\perp, S_\parallel)$. We have

$$\begin{aligned}
\operatorname{tr}(khSh') &= \sum_{\alpha=1}^{3} k_\alpha \sum_{\beta=1}^{3} h_{\alpha\beta}^{\,2} S_\beta \\
&= \sum_{\alpha} k_\alpha[(h_{\alpha1}^{\,2} + h_{\alpha2}^{\,2})S_\perp + h_{\alpha3}^{\,2}S_\parallel] \\
&= (k_1 + k_2 + k_3)S_\perp + (S_\parallel - S_\perp)\sum_{\alpha} k_\alpha h_{\alpha3}^{\,2} \\
&= k_1 S_\parallel + (k_2 + k_3)S_\perp + \Delta_2 h_{23}^{\,2} + \Delta_3 h_{33}^{\,2}
\end{aligned}$$

where the last two lines follow from the orthogonality of h and where $\Delta\alpha = (S_\parallel - S_\perp)(k_\alpha - k_1)$. Choose a parameterization of h to be given by a sequence of rotations through angles α, β, and γ about the z, x, and z axes to give

$$\operatorname{tr}(khSh') = k_1 S_\parallel + (k_2 + k_3)S_\perp + \Delta_2 \sin^2\beta \cos^2\gamma + \Delta_3 \cos^2\beta \quad \text{(B4)}$$

The integral over h now becomes

$$\int \operatorname{etr}(ikhSh')\, \mathrm{d}h = 2\pi \exp[ik_1 S_\parallel + i(k_2 + k_3)S_\perp + \mathcal{J}(\Delta_2,\Delta_3)]$$

where

$$\exp[\mathcal{J}(\Delta_2,\Delta_3)] = \int \exp[i\Delta_2 \sin^2\beta \cos^2\gamma + i\Delta_2 \cos^2\beta] \sin\beta\, \mathrm{d}\beta\, \mathrm{d}\gamma \quad \text{(B5)}$$

At this stage it is convenient to anticipate the steepest descents calculation of $P(S)$ and concomitantly to recall eq B1. The integral over the k_α in eq B3 is dominated by the pole of $D(k_\alpha)$ at $k_\alpha = i\gamma N\kappa_1$ nearest the origin. This is the term, with details yet to be worked out, that gives

$$\exp[ik_1 S_\parallel + i(k_1 + k_2)S_\perp] \rightarrow \exp[-\gamma N\kappa_1(S_\parallel + 2S_\perp)] \quad \text{(B6)}$$

Now, $S_\alpha = O(N^{2/3})$ for the macroscopic elastomer, and conjecture, verified by computations,[30] gives $\kappa_1 = O(N^{-2/3})$. The argument on the right-hand side of (B6) is therefore of $O(N)$.

Now, suppose that $\mathcal{J}(\Delta_2,\Delta_3)$ in eq B5 is commensurate with N. This could happen if $k_\alpha - k_1 = O(N^{1/3})$, and prior to further analysis one must entertain this possibility. In this case, at least one of the $\Delta_\alpha = O(N)$, and approximations to the integral in eq B5 for large arguments are permitted. It is not hard to show that the properties of h and the invariant measure on h are sufficient to establish that $\mathcal{J}(\Delta_2,\Delta_3)$ is symmetric in Δ_2 and Δ_3. (Alternatively, a direct series expansion and term-by-term integration will show the same.) Both Δ_2 and Δ_3 are large if one of them is large by virtue of this symmetry, and k_2 and k_3 are interchangeable in eq B3. First let $k_\alpha - k_1 = ix_\alpha$ and then perform the integration over γ in eq B5 to give

$$\exp[\mathcal{J}(\Delta_2',\Delta_3')] \propto \int_0^{\pi} \sin\beta\, \mathrm{d}\beta \exp\left[-\frac{1}{2}\Delta_2' \sin^2\beta - \Delta_3' \cos^2\beta\right] I_0\left[\frac{1}{2}\Delta_2' \sin^2\beta\right] \quad \text{(B7)}$$

where constants (i.e., 2π) are omitted and where $\Delta_\alpha' = (S_\parallel - S_\perp)x_\alpha$. The function $I_0(\bullet)$ is the modified Bessel function.

Clearly the integrand in eq B7 has its maximum value near $\beta = \pi/2$. Since Δ_2' is large by assumption, one may approximate $I_0(\bullet)$ by its asymptotic expansion. Equation

B7 becomes

$$\exp[\mathcal{J}(\Delta_2',\Delta_3')] \sim \int_0^\pi \mathrm{d}\beta \frac{\exp(-\Delta_3' \cos^2 \beta)}{(2\pi\Delta_2')^{1/2}}[1 + O(1/\Delta_2')]$$

and this integrates to

$$\exp[\mathcal{J}(\Delta_2',\Delta_3')] \sim \frac{\exp(-\Delta_3'/2)I_0(\Delta_3'/2)}{(2\pi\Delta_2')^{1/2}}$$

But, $\Delta_3' = O(N)$ by assumption, and again the asymptotic expansion of $I_0(\bullet)$ is allowed. This gives

$$\exp[\mathcal{J}(\Delta_2',\Delta_3')] \sim \frac{1}{(\Delta_2'\Delta_3')^{1/2}}$$

which contradicts the assumption that $\mathcal{J}(\Delta_2',\Delta_3') = O(N)$. This proves that $\mathcal{J}(\Delta_2',\Delta_3')$ cannot contribute to the thermodynamics of a macroscopic system.

[The situation with individual molecules is quite different. For the linear chain, for example, $\kappa_1 = O(N^{-2})$, $S = O(N)$ for the most interesting range of S, and thus $\gamma N(\kappa_2 S_1 + \kappa_2 S_2 + \kappa_3 S_3) = O(1)$. In this case $\mathcal{J}(\Delta_2',\Delta_3')$ supplies important terms of $O(1)$ and gives rise to non-Gaussian contributions to the distribution function. We have performed numerical quadratures of eq B3 for linear and circular molecules[39] and have made an evaluation of the integral for these cases.]

It will now be shown that a steepest descents evaluation of eq B3 gives an equivalent, in the logarithmic sense, asymptotic result to that obtained by the more accurate, but also more difficult, analysis. Write

$$P(S) \sim \int \exp[F(S,k)] \prod \mathrm{d}k_\alpha$$

where

$$F(S,k) = ik_1 S_\parallel + i(k_2 + k_3)S_\perp + \mathcal{J}(\Delta_2,\Delta_3) - {}^1/_2\sum_\alpha \sum_l \ln(\gamma N\kappa_l + ik_\alpha) + \sum_{\alpha<\beta} \ln|k_\alpha - k_\beta| \quad \text{(B8)}$$

The extremum of $F(S,k)$, should one exist, is given by the solution of the equations $\partial F/\partial k_\alpha = 0$. These equations are

$$\begin{aligned} iS_\parallel - (S_\parallel - S_\perp)(\mathcal{J}_2 + \mathcal{J}_3) - ig_1 + \frac{1}{k_1 - k_2} + \frac{1}{k_1 - k_3} &= 0 \\ iS_\perp + (S_\parallel - S_\perp)\mathcal{J}_2 - ig_2 - \frac{1}{k_1 - k_2} + \frac{1}{k_2 - k_3} &= 0 \quad \text{(B9)} \\ iS_\perp + (S_\parallel - S_\perp)\mathcal{J}_3 - ig_3 - \frac{1}{k_1 - k_3} - \frac{1}{k_2 - k_3} &= 0 \end{aligned}$$

where $\mathcal{J}_\alpha = \partial\mathcal{J}/\partial\Delta_\alpha$ and where

$$g_\alpha = \frac{1}{2}\sum_l \frac{1}{\gamma N\kappa_l + ik_\alpha} \quad \text{(B10)}$$

From this set one derives three simpler equations:

$$s^2 = S_\parallel + 2S_\perp = g_1 + g_2 + g_3 \quad \text{(B11)}$$

$$ik_1 S_\parallel + i(k_2 + k_3)S_\perp + \Delta_2\mathcal{J}_2 + \Delta_3\mathcal{J}_3 = i(g_1 k_1 + g_2 k_2 + g_3 k_3) - 3 \quad \text{(B12)}$$

and

$$-(S_\parallel - S_\perp)(\mathcal{J}_2 - \mathcal{J}_3) + i(g_2 - g_3) = 2/(k_2 - k_3) + 1/(k_1 - k_3) - 1/(k_1 - k_2) \quad \text{(B13)}$$

Now, for any spectrum of eigenvalues κ_l, the solution of the real eq B11 requires the k_α to be pure imaginary. Furthermore, since all the $S_\alpha = O(N^{2/3})$, and owing to the symmetry of eqs B9 together with eq B11, the g_α must be of $O(N^{2/3})$. Since $\gamma N\kappa_l = O(N^{1/3})$ for small l, the $g_\alpha = O(N^{2/3})$ only if at least one term in eq B10 is $O(N^{2/3})$, which means that $ik_\alpha = -\gamma N\kappa_j + t_\alpha$, with $t_\alpha = O(N^{-2/3})$, for some j. The asymptotics will be dominated by the smallest possible κ_j, and all that remains for us to decide is how many of these smallest eigenvalue terms we need to retain in eq B10.

Owing to the complexity of the algebraic eqs B9, it is crucial to view the asymptotics in the broadest sense. To do this, return to the alternative rendition of the multivariate integral that we are interested in estimating, which is

$$\int_{VV'=1} \mathrm{etr}\,(-\gamma NSV\kappa V')\,\mathrm{d}V$$

where V is a $3 \times (N-1)$ matrix representation of a Stiefel manifold. The eigenvalues of S are ordered $S_1 \geq S_2 \geq S_3$, and those of κ ordered $0 < \kappa_1 \leq \kappa_2 \leq \kappa_3 \leq ... \leq \kappa_{N-1}$. The integrand is maximal at $V = V_0 = [\mathbf{1}, 0]$, where $\mathbf{1}$ is the 3×3 identity, and so the integral is dominated by contributions from V in the vicinity of V_0. Thus κ_1, κ_2, and κ_3 control the asymptotics. For the networks under consideration, $\kappa_1 = \kappa_2 = \kappa_3$ by the assumed isotropy and isometry in the unstrained state, and therefore only one threefold degenerate eigenvalue is critical in eq B10.

[The small eigenvalues of the Kirchhoff matrix are related to Debye-like modes of motion of the elastomer. These long-wavelength excitations have effective force constants, i.e., eigenvalues, that are proportional to

$$\sum_{\alpha=1}^{3} \sin^2(j_\alpha/m), \quad j_\alpha \ll m$$

where $m \propto N^{1/3}$. The smallest eigenvalues are threefold degenerate as each of j_α in turn take the value unity while the other two are zero. Thus $\kappa_1 = \kappa_2 = \kappa_3 \propto 1/m^2 = O(N^{-2/3})$. Debye[40] made no use of crystal structure in deriving the ν^2 law; he used the equations for an elastic continuum. All macroscopic elastic bodies have a Debye density of states for sufficiently long wavelength excitations. Whether these "states" are manifested as vibrations or relaxations depends only on the magnitude of the dissipation relative to inertia.]

Given $ik_\alpha = -\gamma N\kappa_1 + t_\alpha$ as a trial solution to eqs B9–B13, let us estimate the g_α in eq B10. We have

$$g_\alpha = 3/2t_\alpha + \frac{1}{2}\sum_{l=2}^{M} \frac{\omega_l}{\gamma N(\kappa_l - \kappa_1) + t_\alpha} \quad \text{(B14)}$$

where the sum is over all distinct eigenvalues $\kappa_l > \kappa_1$ with degeneracy ω_l, there being M distinct eigenvalues. By assumption, $t_\alpha = O(N^{-2/3})$, and by the paragraph above, $\kappa_l - \kappa_1 \geq O(N^{-2/3})$. Thus t_α is negligible in the sum. Furthermore

$$\langle s^2\rangle_0 = \langle l^2\rangle_0 \frac{1}{N}\sum_{l=1}^{M} \frac{\omega_l}{\kappa_l} \quad \text{(B15)}$$

is the mean square radius of gyration for the phantom network.[14] The shift by κ_1 in the denominator in eq B14 does not cause the sum therein to differ drastically from that in eq B15, and therefore

$$g_\alpha = 3/2t_\alpha + O(\langle s^2\rangle_0)$$

Now recall that phantom networks collapse. This is, $\langle s^2\rangle_0$

$\ll O(N^{2/3})$, so that

$$g_\alpha = 3/2t_\alpha \tag{B16}$$

is a very good approximation. [The differences between networks and independent chains need to be stressed once more. The arguments leading to eq B16 do not hold for single chains. In fact, $t_\alpha = O(N^{-1})$ and $\gamma N(\kappa_l - \kappa_1) = O(N^{-1})$ for small l, so that t_α is not negligible in this case. Furthermore, $\langle s^2 \rangle_0 = O(N)$, and so the sum in eq B15 must be retained.]

The eqs B11–B13 now reduce to

$$S_\parallel + 2S_\perp = (3/2)(1/t_1 + 1/t_2 + 1/t_3) \tag{B17}$$

$$t_1 S_\parallel + (t_2 + t_3)S_\perp + i(S_\parallel - S_\perp)[(t_1 - t_2)\mathcal{J}_2 + (t_1 - t_3)\mathcal{J}_3] + 3 = 0 \tag{B18}$$

$$-i(S_\parallel - S_\perp)(\mathcal{J}_2 - \mathcal{J}_3) - (3/2)(t_2 - t_3) + 2/(t_2 - t_3) + 1/(t_1 - t_3) - 1/(t_1 - t_2) = 0 \tag{B19}$$

Both sides of eq B17 are $O(N^{2/3})$, each term on the left-hand side of eq B18 is $O(1)$, and the large terms in eq B19 are the last three on the left. Happily, one need not actually solve these equations, since eq B18 asserts, together with the argument following eq B7, that $t_1 S_\parallel + (t_2 + t_3)S_\perp$ is at most $O(1)$. This term contributes a thermodynamically insignificant constant to the distribution $P(S)$. We finally have

$$P_0(S) \sim \exp[-\gamma N \kappa_1 (S_\parallel + 2S_\perp)] \tag{B20}$$

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