Memory and Lattice Constraints in Rubber Elasticity

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ABSTRACT: A molecular model of a network of Gaussian coils is proposed as a basis for a theory of rubber elasticity. Polymer chains are locked in the network, each chain in a unique topology in the manner described by the phantom-network model. The deformation of the chains and the retractive force exerted by stretched chains are controlled by a potential function composed of two parts: a "memory" potential, which tends to return the chain to its conformation at the time of cross-linking, and a "lattice" potential, which forces the chain to follow the macroscopic deformation. The potentials are taken to be harmonic, and all chain properties are calculated from the partition function. The model is unique in that (a) it accounts for a modulus which can be greater than that found by either the phantom-network or the fixed-junction model, (b) it is qualitatively in accord with memory effects found in networks cross-linked in the anisotropic state, and (c) it accounts for molecular deformations which can be less or greater than that predicted by the phantom-network model depending on the parameters of the potential energy function.

I. Introduction

The mechanical behavior of elastomers to first order can be understood as arising from the partial uncoiling of flexible polymer chains connected in an infinite network. While it has been relatively easy to design a molecular theory based on ghostlike chains that easily pass through each other,[1-3] it has been more difficult to design a theory which takes into account the effects of chain entanglement in the network.[3-8] Numerous trials have been offered with varying degrees of success. Here we put forth another suggestion that is simple enough in structure to permit straightforward calculation, yet sufficiently detailed to take into account some of the complexities inherent in a real rubbery material.

Recent experiments on carefully designed elastomeric networks provide useful background information on which a new theoretical model of rubber can be tested. Most of these are measurements are force vs. extension.[9] One important class of these is the study of networks that are cross-linked in an anisotropic condition.[10] These experiments demonstrate unambiguously that a rubbery network "remembers" the conditions under which cross-linking took place. The network memory plays a prominent role in the design of our model.[11] The results on anisotropic networks cannot be explained by the restricted fluctuation theory of Flory[5] and Erman and Flory,[6] though the author has recently heard of a variation of the Flory–Erman analysis designed for this problem.[12]

Small-angle neutron scattering experiments have been applied to the measurement of chain dimensions in stretched rubbers. The results do not fit the phantom-network or restricted-fluctuation models, and we have interpreted this as evidence that chain deformation does not necessarily follow changes in shape of the macroscopic material.

Many of the force-elongation studies fit the Flory–Erman restricted-fluctuation model well, but some rubbers have moduli that are too large[13,14] to be accounted for by the phantom network, fixed-junction network, or any interpolation based on partially suppressed fluctuations. The experiments on high-modulus rubbers, neutron scattering, and anisotropic rubbers provide a basis in fact for a modified theoretical approach to rubber elasticity.

Some researchers have questioned the reliability of the neutron-scattering experiments and the validity of the interpretation of the studies on high-modulus rubbers. The reader should bear in mind that what we have taken as fact is not universally accepted.

† Much of this work was performed while the author was a member of the Research Staff of the Ford Motor Co.

II. The Network and the Partition Function

Consider a sample of rubber composed of N polymer chains, each chain containing n segments. These segments have the properties of Kuhn statistical elements, and the polymer chains follow Gaussian random flight statistics. Each Kuhn element contains a few monomer units. The random-flight statistics apply in the absence of network constraints.

The network is formed by joining terminal segments of all the chains in permanent cross-link junctions, φ chains at each junction with $\varphi \geq 3$. The mean square end-to-end distance of the chains averaged over the ensemble is unchanged by cross-linking.

The individual polymer chains are constrained by the network after cross-linking. The end-to-end vector of a given chain, $\mathbf{R}$ is at a minimum potential energy when $\mathbf{R} = \mathbf{R}_c$ and $\mathbf{R}_c$ is, in general, not zero.

The constraints on chain i, for example, differ from those on chain j, so that $\mathbf{R}_c$ takes on different values for chains i and j. For this reason, the mean properties of a single polymer chain designated by an overhead bar differ from the ensemble average designated by broken brackets. Note that $\bar{\mathbf{R}}$ for a single chain is nonzero, while $\langle \mathbf{R} \rangle$ for the ensemble is zero by symmetry as is $\langle \bar{\mathbf{R}} \rangle$.

A. Network Cross-Linked in the Undeformed State. A sample containing N chains is cross-linked in the absence of an external stress. The system is isotropic. Before cross-linking, the probability that the end-to-end vector of a chain equals $\mathbf{R}$ is given by

$$P(\mathbf{R}) = (a/\pi)^{3/2} \exp[-a\mathbf{R}^2] \tag{1a}$$

$$\langle \mathbf{R}^2 \rangle = \overline{\mathbf{R}^2} = 3/2a \tag{1b}$$

The equivalence of $\overline{\mathbf{R}^2}$ for any chain and $\langle \mathbf{R}^2 \rangle$ for the ensemble was the same before cross-linking, owing to the freedom of motion of the polymer chains.

After cross-linking, a particular chain is at a minimum potential at $\mathbf{R} = \mathbf{R}_c$, and this potential is taken to be quadratic in the displacement from the minimum.

$$V/kT = b(\mathbf{R} - \mathbf{R}_c)^2 \tag{2a}$$

The probability that the end-to-end vector is given by $\mathbf{R}$ is

$$P(\mathbf{R};\mathbf{R}_c) = (a/\pi)^{3/2} \exp[a\mathbf{R}^2] \exp[-b(\mathbf{R} - \mathbf{R}_c)^2]/Q(\mathbf{R}_c) \tag{2b}$$

where $Q(\mathbf{R}_c)$, the partition function, is obtained by inte-

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gration of the numerator in eq 2b.

$$Q(\mathbf{R}_c) = (a/(a+b))^{3/2} \exp[-(ab/(a+b))\mathbf{R}_c^2] \quad (2c)$$

The parameter b is a measure of the stiffness of the restoring potential, larger values of b corresponding to smaller fluctuations in chain length.

Upon stretching, the sample becomes anisotropic. It is much more convenient to work in cartesian coordinates, $\mathbf{R} = (X, Y, Z)$ and $\mathbf{R}_c = (X_c, Y_c, Z_c)$. Calculations will be followed through for the x component only; the y and z components are obtained in the same way.

A primary objective is to determine physical properties of the network as a function of deformation. If the x dimension is $L_x°$ before stretching and L_x after stretching, the deformation is defined by $\lambda_x = L_x/L_x°$. Since rubber does not change appreciably in volume upon distortion, $\lambda_x\lambda_y\lambda_z$ is set equal to unity. This assumption is convenient but not essential to the analysis.

Upon stretching, the potential breaks into two terms, a memory term and a lattice term.

$$V_x/kT = \underbrace{b_0(X - X_c)^2}_{\text{memory}} + \underbrace{b_1(X - \lambda_x X_c)^2}_{\text{lattice}} \quad (3)$$

The memory term is centered at the position of minimum potential energy at the moment of cross-linking. The lattice represents the network in the deformed state, and it is the lattice that deforms affinely with the macroscopic sample. The x component of the partition function is given by

$$Q(X_c;\lambda_x) = \int P(X;X_c) \exp[-V_x/kT]\, dX \quad (4a)$$

$$Q(X_c;\lambda_x) = (a/E(\lambda_x))^{1/2} \exp[-D(\lambda_x)X_c^2/E(\lambda_x)] \quad (4b)$$

$$D(\lambda_x) = a(b_0 + b_1\lambda_x^2) + b_0b_1(\lambda_x - 1)^2 \quad (4c)$$

$$E(\lambda_x) = a + b_0 + b_1 \quad (4d)$$

The change in free energy on stretching of a single chain is

$$\Delta A_1(X_c;\lambda_x) = -kT \ln [Q(X_c;\lambda_x)/Q(X_c;1)] \quad (5)$$

The number of chains at a minimum potential energy at $X = X_c$ is given by

$$N(X_c) = N(c/\pi)^{1/2} \exp[-cX_c^2] \quad (6a)$$

and the free energy change of the network (x component) is

$$\Delta A_x(\lambda_x) = \int N(X_c)\Delta A_1(X_c;\lambda_x)\, dX_c \quad (6b)$$

The result is

$$\Delta A_x(\lambda_x)/NkT = 0.5 \ln (E(\lambda_x)/E(1)) + \frac{1}{2c}\left[\frac{D(\lambda_x)}{E(\lambda_x)} - \frac{D(1)}{E(1)}\right] \quad (6c)$$

The retractive force exerted by the network in the presence of an external stress is given by $\partial(\Delta A)/\partial\lambda$. The constraint of constant volume must be imposed in performing this calculation. We defer this to a later section.

B. Network Cross-Linked in the Deformed State. The polymer of N chains is the same as above. However, before cross-linking, the material is deformed and frozen; the deformation is given by λ_x^c, λ_y^c, and λ_z^c. Cross-linking is carried out on the frozen system, after which the material is reheated and allowed to relax. In the relaxed state, the deformation is given by λ_x^r, λ_y^r, and λ_z^r.

The equations are only slightly more complicated than before. Here it is necessary to distinguish between events before and after orientation as well as before and after cross-linking.

$P(\mathbf{R})$ and $P(X)$ for the un-cross-linked polymer are obtained from eq 1a. A polymer chain in the network whose end-to-end vector equals $\mathbf{R}$ is at minimum potential energy $\mathbf{R}_0$ just before stretching and is at a minimum potential energy immediately after stretching when $\mathbf{R} = \mathbf{R}_c$. $X_c = \lambda_x X_0$. The x component of the potential energy at an arbitrary deformation λ_x is

$$V_x = b_0(X - \lambda_x^c X_0)^2 + b_1(X - \lambda_x X_0)^2 \quad (7)$$

The number of chains characterized by a minimum potential energy X_0 in the isotropic state is

$$N(X_0) = N(c/\pi)^{1/2} \exp[-cX_0^2] \quad (8)$$

The difference between cross-linking in the anisotropic state and in the isotropic undeformed polymer is seen in the difference between eq 3 and 7 and between eq 6a and 8. Note that the difference disappears if $\lambda_x^c = 1$.

The partition function for the single chain is

$$Q(X_c;\lambda_x,\lambda_x^c) = (a/E(\lambda_x))^{1/2} \exp[-D_c(\lambda_x)X_0^2/E(\lambda_x)] \quad (9a)$$

$$D_c(\lambda_x) = a(b_0(\lambda_x^c)^2 + b_1\lambda_x^2) + b_0b_1(\lambda_x - \lambda_x^c)^2 \quad (9b)$$

$E(\lambda_x)$ is given as before in eq 4d. The free energy of deformation is normally calculated with respect to the relaxed sample, which is, in general, anisotropic.

$$\Delta A_x(\lambda_x,\lambda_x^c)/NkT = 0.5 \ln [E(\lambda_x)/E(\lambda_x^r)] + \frac{1}{2c}\left[\frac{D_c(\lambda_x)}{E(\lambda_x)} - \frac{D_c(\lambda_x^r)}{E(\lambda_x^r)}\right] \quad (10)$$

The deformation in the relaxed state, λ_x^r, is found by setting the retractive force equal to zero.

C. Molecular Dimensions and Network Parameters. The probabilty that the x component of the end-to-end distance of a chain in the network is equal to X is given by

$$W(X;X_c,\lambda_x) = P(X) \exp[-V_x/kT]/Q(X_c,\lambda_x) \quad (11)$$

For convenience we consider chains cross-linked in the undeformed condition only. The mean values of the moments are given by

$$\overline{X^p} = \int X^p W(X;X_c,\lambda_x)\, dX \quad (12)$$

It follows that

$$\bar{X} = \frac{b_0 + b_1\lambda_x}{E(\lambda_x)} X_c \quad (13a)$$

$$\overline{X^2} = \bar{X}^2 + 0.5/E(\lambda_x) \quad (13b)$$

and the mean square fluctuation in X, δ_x, becomes

$$\delta_x^2 = 0.5/E(\delta_X) \quad (13c)$$

The mean square fluctuation is believed to be a sensitive function of chain deformation and in our model very much dependent on the steepness of the potential energy function. We assume that in the undeformed state

$$\langle\delta_x^2\rangle = A_f\langle X^2\rangle \quad (14)$$

In a phantom network A_f has been shown to be equal to $2/\varphi$. In real networks it is much less, but still dependent on network functionality. The lattice-restoring constant b_1 is taken to be a function of deformation, but a and b_0 are not. In the undeformed state, b_1 is designated as $b_1°$. The assumption made earlier that $\langle X^2\rangle$ is unchanged by cross-linking yields

$$\frac{1}{a} = \frac{1}{a + b_0 + b_1^\circ} + \frac{1}{c}\left(\frac{b_0 + b_1^\circ}{a + b_0 + b_1^\circ}\right)^2 \quad (15)$$

Equations 14 and 15 taken together give

$$(b_0 + b_1^\circ)/a = (1 - A_f)/A_f \quad (16a)$$

$$c/a = 1 - A_f \quad (16b)$$

In the undeformed state the relative importance of the memory and lattice potentials is described by a parameter α according to which

$$b_1^\circ/a = \alpha(1 - A_f)/A_f \quad (17a)$$

$$b_0/a = (1 - \alpha)(1 - A_f)/A_f \quad (17b)$$

The dependence of b_1 on deformation can be written symbolically as

$$b_1 = b_1^\circ \psi(\lambda) \quad (18)$$

There are three factors that are clearly important in the function $\psi(\lambda)$. First of all, it is normalized to unity at $\lambda = 1$. Second, the junction points are redistributed when the sample is stretched, and inasmuch as the junctions are foci of entanglement constraints $\psi(\lambda)$ should vary as λ^{-2}, a suggestion previously made by Ronca and Allegra[4] and Flory.[5] Third, the space-filling property of other molecules and elastic constraints of other chains impart a limit on fluctuations that is independent of deformation. Accordingly we hypothesize that $\psi(\lambda)$ takes the form

$$\psi(\lambda) = K + (1 - K)/\lambda^2 \quad (19)$$

This form is consistent with the above considerations but is certainly not unique.

III. Uniaxial Deformation

The free energy of deformation of a network cross-linked in the anisotropic state is the sum of three terms similar to those of eq 10. If the deformation is uniaxial, $\lambda_x = \lambda$, $\lambda_x^r = \lambda^r$, $\lambda_x^c = \lambda^c$, $\lambda_y = \lambda_z = \lambda^{-1/2}$, etc. If the parameters of eq 17–19 are inserted, the expression for ΔA becomes

$$\Delta A/NkT = 0.5 \ln\left[\frac{E(\lambda)}{E(\lambda^r)}\right] + \ln\left[\frac{E(\lambda^{-1/2})}{E((\lambda^r)^{-1/2})}\right] + 0.5\left[\frac{D_c(\lambda)}{E(\lambda)} - \frac{D(\lambda^r)}{E(\lambda^r)}\right] + \frac{D_c(\lambda^{-1/2})}{E(\lambda^{-1/2})} - \frac{D_c((\lambda^r)^{-1/2})}{E((\lambda^r)^{-1/2})} \quad (20a)$$

$$E(\lambda) = A_f + (1 - A_f)(1 - \alpha + \alpha\psi(\lambda)) \quad (20b)$$

$$D_c(\lambda) = (1 - \alpha)\lambda_c^2 + \alpha\lambda^2\psi(\lambda) + \frac{\alpha(1 - \alpha)(1 - A_f)}{A_f}(\lambda - \lambda_c)^2\psi(\lambda) \quad (20c)$$

The equations simplify in the important special situation in which cross-linking is performed in the isotropic conditions. In that case, λ_r, λ_c, $D_c(\lambda_r)$, and $E(\lambda_r)$ are all equal to one.

An important qualitative result of eq 20c is that small values of A_f, which correspond to small fluctuations in chain geometry, lead to large values in the free energy of deformation as well as high values of the modulus. This relation between fluctuations and free energy change disappears if there is no memory term, i.e., $\alpha = 1$.

The retractive force is obtained by differentiation of eq 20a with respect to λ. The result is

$$f/NkT = 0.5[E'(\lambda)/E(\lambda) - E'(\lambda^{-1/2})/(\lambda^{3/2}E(\lambda^{-1/2}))] + 0.5[(D_c(\lambda)/E(\lambda))' - (D_c(\lambda^{-1/2})/E(\lambda^{-1/2}))'/\lambda^{3/2}] \quad (21)$$

The functions $E'(\lambda)$ and $D_c'(\lambda)$ are directly calculable from eq 19, 20b, and 20c. If $\psi(\lambda)$ and α equal one, the free energy change on stretching and retractive force become

$$\Delta A/NkT = 0.5(\lambda^2 + 2/\lambda - 3) \quad (22a)$$

$$f/NkT = \lambda - \lambda^{-2} \quad (22b)$$

In this limit, the magnitude of the fluctuations characterized by A_f does not influence either the free energy change or the force. This is a significant difference from earlier theories.

IV. Numerical Results

A small number of calculated results based on this model are presented in tables and figures to follow. In order to keep the quantity of material under control, and to exhibit the properties of the model as well, we have chosen to fix one of the parameters. The quantity K in eq 19 is set equal to 0.2 in all computations.

A. Chain Dimensions. Chain dimensions in a rubber change upon deformation, owing to the changes in positions occupied by the cross-link junctions. The quantities of interest are those that can be measured, which are projections of the radius of gyration of labeled polymer chains in the plane perpendicular to the direction of an incident neutron beam in a scattering experiment.

In uniaxial deformation, projections of the radius of gyration perpendicular and parallel to the stretching direction are obtainable from experiment. These quantitites, which are designated $R_\perp$ and $R_\parallel$, respectively, are given, for a system cross-linked in the isotropic condition, by

$$R_\perp^2 = 0.5R_g^{\circ 2}[1 + \langle Y^2\rangle/\langle Y^{\circ 2}\rangle] \quad (23a)$$

$$R_\parallel^2 = 0.5R_g^{\circ 2}[1 + \langle X^2\rangle/\langle X^{\circ 2}\rangle] \quad (23b)$$

R_g° is the radius of gyration in the undeformed state, and the x direction is, as above, the stretching direction. Expressing the results in terms of the parameters A_f and α leads to

$$\langle X^2\rangle/\langle X^{\circ 2}\rangle = \frac{A_f}{E(\lambda)} + \frac{(1 - A_f)(1 - \alpha + \alpha\lambda\psi(\lambda))^2}{E^2(\lambda)} \quad (24a)$$

$\langle Y^2\rangle/\langle Y^{\circ 2}\rangle$ is obtained from eq 24a by substitution of $\lambda^{-1/2}$ for λ. Note that if $\psi(\lambda) = 1$, $A_f = 2/\varphi$, and $\alpha = 1$, one finds

$$\langle X^2\rangle/\langle X^{\circ 2}\rangle = \lambda^2[1 - (2/\varphi)] + 2/\varphi \quad (24b)$$

which agrees with the calculation of the phantom network.

If $\psi(\lambda) = 1$, $A_f = 0$, and $\alpha = 1$, the result is

$$\langle X^2\rangle/\langle X^{\circ 2}\rangle = \lambda^2 \quad (24c)$$

in accord with the prediction of the fixed-junction model.

Numerical values of $R_\parallel/R_g^\circ$ and $R_\perp/R_g^\circ$ are given for the fixed-junction and phantom networks and for our model in Tables I and II. Graphical representations are presented in Figures 1 and 2. For computational purposes, the phantom network is taken to be tetrafunctional. The phantom and fixed-junction results are[15,16]

phantom network

$$R_\parallel^2 = R_g^{\circ 2}[1 + 0.5(\lambda^2 - 1)(1 - (2/\varphi))] \quad (25a)$$

$$R_\perp^2 = R_g^{\circ 2}[1 + 0.5(\lambda^{-1} - 1)(1 - (2/\varphi))] \quad (25b)$$

fixed junctions

$$R_\parallel^2 = R_g^{\circ 2}[1 + 0.5(\lambda^2 - 1)] \quad (25c)$$

$$R_\perp^2 = R_g^{\circ 2}[1 + 0.5(\lambda^{-1} - 1)] \quad (25d)$$

Table I
$R_\parallel/R_g^\circ$ as a Function of Deformation

			memory-lattice model			
λ	phantom network	fixed junctions	$A_f = 0.05$, $\alpha = 0.7$	$A_f = 0.05$, $\alpha = 0.9$	$A_f = 0.2$, $\alpha = 0.7$	$A_f = 0.2$, $\alpha = 0.9$
1.1	1.0259	1.0512	1.0307	1.0408	1.0221	1.0291
1.2	1.0536	1.1045	1.0590	1.0810	1.0416	1.0563
1.3	1.0828	1.1597	1.0853	1.1205	1.0590	1.0816
1.5	1.1456	1.2748	1.1324	1.1971	1.0892	1.1279
1.7	1.2135	1.3946	1.1742	1.2709	1.1151	1.1700
2.0	1.3229	1.5811	1.2305	1.3777	1.1496	1.2287
2.5	1.5207	1.9039	1.3157	1.5497	1.2024	1.3221
3.0	1.7321	2.2361	1.3974	1.7198	1.2547	1.4162
4.0	2.1794	2.9155	1.5622	2.0641	1.3644	1.6149
5.0	2.6458	3.6056	1.7334	2.4178	1.4827	1.8284
7.0	3.6056	5.000	2.0937	3.1484	1.7401	2.2885

Table II
$R_\perp/R_g^\circ$ as a Function of Deformation

			memory-lattice model			
λ	phantom network	fixed junctions	$A_f = 0.05$, $\alpha = 0.7$	$A_f = 0.05$, $\alpha = 0.9$	$A_f = 0.2$, $\alpha = 0.7$	$A_f = 0.2$, $\alpha = 0.9$
1.1	0.9886	0.9770	0.9849	0.9809	0.9887	0.9857
1.2	0.9789	0.9574	0.9712	0.9641	0.9783	0.9728
1.3	0.9707	0.9405	0.9589	0.9494	0.9686	0.9611
1.5	0.9574	0.9129	0.9373	0.9245	0.9512	0.9407
1.7	0.9471	0.8911	0.9190	0.9043	0.9360	0.9234
2.0	0.9354	0.8660	0.8963	0.8802	0.8163	0.9018
2.5	0.9220	0.8367	0.8674	0.8509	0.8900	0.8742
3.0	0.9129	0.8165	0.8459	0.8300	0.8693	0.8534
4.0	0.9014	0.7906	0.8162	0.8023	0.8392	0.8243
5.0	0.8944	0.7746	0.7966	0.7847	0.8183	0.8048
7.0	0.8864	0.7559	0.7726	0.7637	0.7913	0.7804

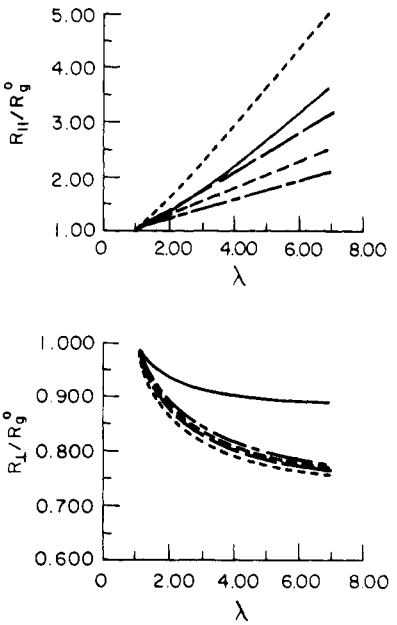

Figure 1. $R_\parallel$ and $R_\perp$ vs. λ: (---) fixed junctions; (—) phantom network; (–·–) $A_f = 0.05$, $\alpha = 0.7$; (– –) $A_f = 0.05$, $\alpha = 0.8$; (— —) $A_f = 0.05$, $\alpha = 0.9$. $\psi(\lambda) = 0.2 + 0.8\lambda^{-2}$.

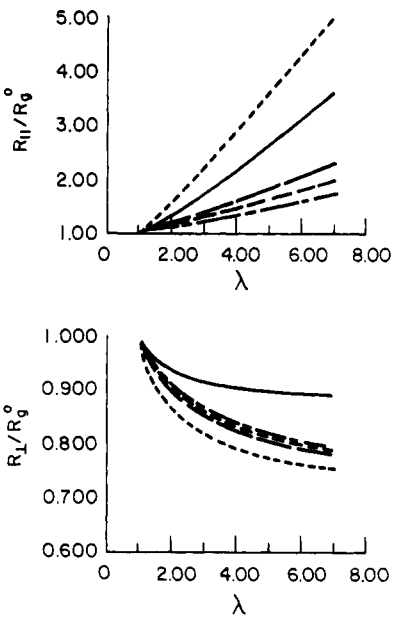

Figure 2. $R_\parallel$ and $R_\perp$ vs. λ: (---) fixed junctions; (—) phantom network; (–·–) $A_f = 0.2$, $\alpha = 0.7$; (– –) $A_f = 0.2$, $\alpha = 0.8$; (— —) $A_f = 0.2$, $\alpha = 0.9$. $\psi(\lambda) = 0.2 + 0.8\lambda^{-2}$.

From the tables and the figures certain general results are seen.

1. The changes of $R_\parallel$ and $R_\perp$ with λ are largest for the network with fixed junctions.

2. Increasing the stiffness (A_f) increases the variation of $R_\parallel$ and $R_\perp$ with λ.

3. A larger memory effect (smaller α) gives smaller variations of $R_\parallel$ and $R_\perp$ with λ.

4. When $R_\parallel$ and $R_\perp$ are compared with the prediction of the phantom network at constant values of α and A_f, $R_\parallel$ changes less than $R_\perp$. For example, if $\lambda = 2$, the phantom-network model predicts $R_\parallel/R_g^\circ = 1.3229$ and $R_\perp/R_g^\circ = 0.9354$. The model presented here at $\lambda = 2$, $A_f = 0.05$ and $\alpha = 0.7$ yields $R_\parallel/R_g^\circ = 1.2305$ and $R_\perp/R_g^\circ = 0.8963$. The same trend can be seen in Figures 1 and 2. This is a consequence of the decreasing stiffness with increasing elongation.

5. The variation of stiffness with elongation also changes the shape of the plots of $R_\parallel$ or $R_\perp$ vs. λ. This appears clearly in the plot of $R_\parallel/R_g^\circ$ in Figure 1.

B. Uniaxial Deformation Isotropic Network. The free energy change on deformation of a phantom network is

$$\Delta A/NKT = 0.5[(1 - (2/\varphi))][\lambda^2 + 2/\lambda - 3] \quad (26)$$

If the junctions are fixed in position, the calculated result

Table III
Change in Free Energy upon Uniaxial Extension and Compression[a]

λ	phantom network	A_f = 0.05, α = 0.9	A_f = 0.05, α = 0.7	A_f = 0.2, α = 0.9	A_f = 0.2, α = 0.7
0.3	0.939	3.125	4.443	1.683	1.696
0.4	0.540	1.838	2.690	0.9986	1.014
0.5	0.313	1.080	1.606	0.5861	0.5960
0.6	0.173	0.6048	0.9056	0.3259	0.3304
0.7	0.087	0.3043	0.4559	0.1624	0.1636
0.8	0.035	0.1229	0.1834	0.0648	0.0649
0.9	0.008	0.0283	0.0419	0.0147	0.0146
1	0.000	0.00	0.00	0.00	0.00
1.1	0.007	0.0245	0.0357	0.0125	0.0122
1.2	0.027	0.0924	0.1327	0.0463	0.0450
1.3	0.057	0.1966	0.2795	0.0975	0.0942
1.5	0.146	0.4951	0.6896	0.2407	0.2301
1.7	0.267	0.8927	1.220	0.4265	0.4041
2.0	0.500	1.642	2.190	0.7672	0.7196
2.5	1.013	3.239	4.190	1.469	1.363
3.0	1.667	5.233	6.626	2.321	2.138
4.0	3.375	10.38	12.81	4.447	4.068
5.0	5.600	17.09	20.79	7.136	6.510
7.0	11.571	35.28	42.42	14.23	12.97

[a] Results are expressed in units of NkT.

Table IV
Extension of Sample in Relaxed State (λ_r) as a Function of Sample Extension When Cross-Linked (λ_c)

λ_c	A_f = 0.05, α = 0.7	A_f = 0.05, α = 0.8	A_f = 0.05, α = 0.9	A_f = 0.2, α = 0.7	A_f = 0.2, α = 0.8	A_f = 0.2, α = 0.9
1.2	1.143	1.125	1.089	1.064	1.047	1.027
1.5	1.361	1.315	1.225	1.161	1.118	1.065
2.0	1.739	1.648	1.465	1.333	1.241	1.129
3.0	2.536	2.369	2.003	1.723	1.520	1.268
5.0	4.207	3.910	3.228	2.644	2.202	1.606
7.0	5.908	5.490	4.523	3.671	2.995	2.022

is obtained by eliminating the factor $1 - (2/\varphi)$ in eq 26. In Table III, free energy changes upon uniaxial deformation are given for the phantom network and in a few examples for our model. Higher stiffness (lower A_f) corresponds to a greater free energy change, and the memory effect increases the change in free energy considerably for the stiffer system. Higher values of A_f corresponding to lower stiffness of the network yield lower free energy changes.

The retractive force exerted by a uniaxially stretched phantom or fixed-junction network is given by

$$f = CNkT(\lambda - \lambda^{-2}) \qquad (27)$$

where $C = 1 - (2/\varphi)$ for the phantom model and 1.0 for a network with fixed junctions. For convenience, a reduced force $[f^*]$ is defined equal to $f/(NkT(\lambda - \lambda^{-2}))$. Plots of $[f^*]$ vs. λ for our model emphasize how it differs from the others. Examples of the results are shown in Figures 3 and 4. From these figures, the general properties of the force-deformation relationship as a function of model parameters is clear.

1. Increasing stiffness (small A_f) corresponds to an increased retractive force provided that α is not equal to unity.

2. The memory effect increases the retractive force slightly.

3. A softening of the rubber relative to the phantom network is seen as the sample is stretched, though this softening is slightly reversed at high deformation owing to the memory potential.

C. Uniaxial Deformation on Systems Cross-Linked in the Anisotropic State. If the system is allowed to relax after cross-linking in the anisotropic state, the network remains anisotropic. The extension in the relaxed state is found by setting the retractive force equal to zero. Some calculated results of this effect are presented in Table IV. Decreases in A_f and α yield greater anisotropy after relaxation. The variation of retractive force with extension for systems cross-linked at $\lambda_c = 3$ for different

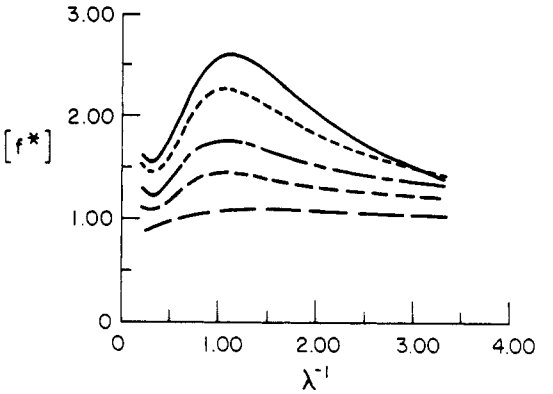

Figure 3. Reduced force, $[f^*]$, vs. λ^{-1}: (—) A_f = 0.05, α = 0.7; (---) A_f = 0.05, α = 0.8; (–·–) A_f = 0.05, α = 0.9; (– –) A_f = 0.05, α = 0.95; (— —) A_f = 0.05, α = 1. $\psi(\lambda) = 0.2 + 0.8\lambda^{-2}$.

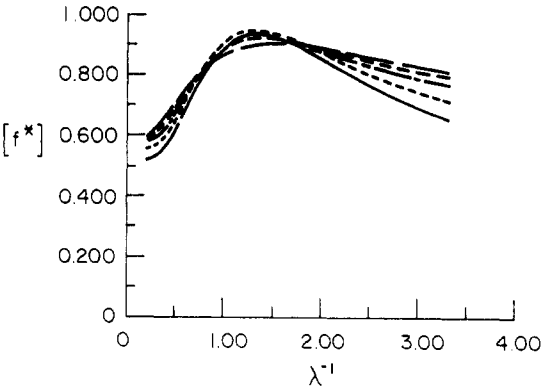

Figure 4. Reduced force, $[f^*]$, vs. λ^{-1}: (—) A_f = 0.2, α = 0.7; (---) A_f = 0.2, α = 0.8; (–·–) A_f = 0.2, α = 0.9; (– –) A_f = 0.2, α = 0.95; (— —) A_f = 0.2, α = 1. $\psi(\lambda) = 0.2 + 0.8\lambda^{-2}$.

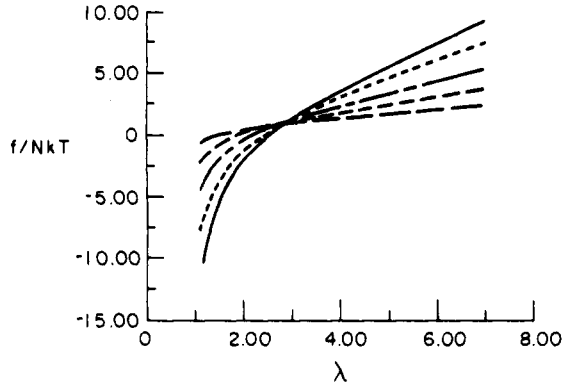

Figure 5. Force vs. deformation for a network cross-linked in the uniaxially stretched state; $\lambda_c = 3$, $\alpha = 0.7$: (—) $A_f = 0.05$; (---) $A_f = 0.065$; (–·–) $A_f = 0.1$; (– –) $A_f = 0.16$; (— —) $A_f = 0.3$. $\psi(\lambda) = 0.2 + 0.8\lambda^{-2}$.

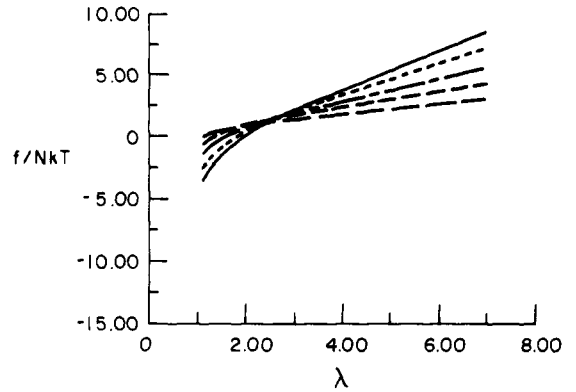

Figure 6. Force vs. deformation for a network cross-linked in the uniaxially stetched state; $\lambda_c = 3$, $\alpha = 0.9$: (—) $A_f = 0.05$; (---) $A_f = 0.065$; (–·–) $A_f = 0.1$; (– –) $A_f = 0.16$; (— —) $A_f = 0.3$. $\psi(\lambda) = 0.2 + 0.8\lambda^{-2}$.

values of α and A_f is shown in Figures 5 and 6. Note that the retractive force vanishes ($\lambda = \lambda_c$) when the sample is quite anisotropic.

V. Discussion

The model of rubber elasticity proposed here begins with a structure not unlike that of the phantom network. It differs from the phantom network in three important ways.

1. The macroscopic and molecular deformation are coupled through a potential function which depends on both the environmental effects of the lattice and the memory of conformation at cross-linking.

2. In a phantom-network, a fixed-junction-network, and the Flory–Erman models, the time-averaged vector connecting the ends of a polymer chain deforms affinely with the macroscopic sample. Here, the lattice deforms affinely, but, in general, the polymer chains do not. Chain deformation is calculated from the statistical mechanical probability.

3. The fluctuations in chain length are coupled to the potential function: the smaller the fluctuation, the stiffer the sample and the higher the modulus. The memory part of the potential plays a crucial role in achieving this effect.

In a qualitative sense, the model has several successes. It accounts, in a general way, for networks prepared in the deformed anisotropic state. The relationship of the potential function to the modulus allows for the possibility that the modulus is even greater than that predicted for the fixed-junction network. The theory is consistent with chain deformation substantially less than found for a phantom network, but whether deformation is greater or less than that of the phantom network depends on the stiffness of the lattice and the relative importance of the memory.

The model has some faults which are easy to recognize. First of all, the problem is analyzed as if it were sufficient to follow the end points of a polymer chain and ignore the intervening segments. In fact, the assumption is really somewhat more subtle. The influence of the intermediate segments is projected on to the behavior of the vector connecting the chain ends. We assert that for the purpose of calculation of equilibrium properties of the network this is a reasonable and useful procedure. Further progress in the theory may require retraction of that assumption.

In carrying out numerical calculations, it is assumed that the magnitude of the fluctuations varies with deformation in a particular way (eq 19). Stress–strain measurements are consistent with this formulation, but it is not strongly grounded in physical theory. It would be extremely useful to have a better analysis of how fluctuations depend on network deformation.

The model has more parameters than one would like, and it would be desirable to test it by performing a number of different experiments on the same material. It is relatively easy to fit a stress–uniaxial deformation study by adjusting the parameters. It would be very interesting to know whether the same parameters would also suffice for analysis of chain dimensions by neutron scattering, for example. The theory has to be in accord with experiment, and if different measurements on the same material are conducted, a more critical test of the model is possible.

References and Notes

(1) James, H. M. *J. Chem. Phys.* **1947**, *15*, 651.
(2) James, H. M.; Guth, E. *J. Chem. Phys.* **1947**, *15*, 669.
(3) Flory, P. J. *Proc. R. Soc. London, A:* **1976**, *A351*, 351.
(4) Ronca, G.; Allegra, G. *J. Chem. Phys.* **1975**, *63*, 4990.
(5) Flory, P. J. *J. Chem. Phys.* **1977**, *66*, 5720.
(6) Flory, P. J.; Erman, B. *Macromolecules* **1982**, *15*, 800.
(7) Deam, R. T.; Edwards, S. F. *Philos. Trans. R. Soc. London, A:* **1976**, *A280*, 27.
(8) Marrucci, G. *Macromolecules* **1981**, *14*, 434.
(9) A survey of much of this work is contained in Mark, J. E. *Adv. Polym. Sci.* **1982**, *44*, 1.
(10) See, for example, Hvidt, S.; Kramer, O.; Batsberg, W.; Ferry, J. D. *Macromolecules* **1980**, *13*, 933.
(11) Beltzung, M.; Picot, C.; Herz, J. *Macromolecules* **1984**, *17*, 663, provides a recent example of this type of investigation.
(12) This information was supplied to the author by one of the referees of the manuscript.
(13) Dossin, L. M.; Graessley, W. W. *Macromolecules* **1979**, *12*, 123.
(14) Pearson, D. S.; Graessley, W. W. *Macromolecules* **1980**, *13*, 1001.
(15) Pearson, D. S. *Macromolecules* **1977**, *10*, 696.
(16) Ullman, R. *J. Chem. Phys.* **1979**, *71*, 436.