Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Crossland, A. H. and Van Der Hoff, B. M. E.(1976) 'Cylindrical Approximation of Constrained Chain Model for Rubber Elasticity. I. Constant Volume Deformations', Journal of Macromolecular Science, Part A, 10: 5, 825 — 853

To link to this Article: DOI: 10.1080/00222337608061221

URL: http://dx.doi.org/10.1080/00222337608061221

J. MACROMOL. SCI.–CHEM., A10(5), pp. 825-853 (1976)

Cylindrical Approximation of Constrained Chain Model for Rubber Elasticity. I. Constant Volume Deformations

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ABSTRACT

This paper reports a new model for rubber elasticity based on the geometric constraints imposed on a network chain and the chain segments by the crosslinks at each end. Through consideration of these constraints, the number of conformations available to a network chain can be calculated directly assuming the chain is on a lattice. By simplifying the model and by assuming affine deformation, the rigorous equations for the conformational entropy are reduced to an analytic expression for the strain-energy function. From this function, equations describing extension, compression and pure shear are derived. The model is tested against literature data for natural rubber and polybutadiene and is found to reproduce quantitatively all the salient features of the experimental

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stress-strain curves in the three modes of deformation. It is shown that the decrease in the Gaussian modulus with extension, often characterized by the C_2 term in the Mooney-Rivlin theory, arises naturally from the conformational entropy of a network chain, and special effects such as structure, topology, etc., need not be invoked to explain this phenomenon. The theory also predicts the near-constant modulus of extended highly swollen gels, an effect often considered as verification of Gaussian theory.

INTRODUCTION

There have been many attempts to describe the mechanics of elastomers using statistical thermodynamics. The most generally accepted formulation is the one based on the Gaussian distribution and has been derived in different ways by several authors [1-6]. Although there is disagreement in the method of derivation, there is general agreement on the final result, all theories predicting the same dependence of stress on strain. This Gaussian theory, however, agrees rather poorly with experiment and the rationalization of this deviation has dominated the literature for over two decades. Attempts to explain the observed departures from theory in terms of intramolecular energy effects, orientationally active short chains, excluded volume effects, entanglements and structuring in the network have been reviewed by Dusek and Prins [7]. These authors observe that the attempted corrections fall into two categories, those which predict only a small correction to the Gaussian theory and those explanations which are incomplete or qualitative. They conclude, "There is at the moment no quantitative theory to account for the behavior . . . ". Since none of the theories can account for all of the salient features of elastic stress-strain behavior, there is a real need for new interpretations. As Flory states [8], "A truly original viewpoint is needed and novel methods probably as well".

In this paper, a new model for a single network chain is presented which leads to new methods for calculating conformational chain entropies. Because a network chain is fixed at both ends by cross-links, the geometry of the system imposes constraints which invalidate the "random walk" assumption implicit in the Gaussian theories. In contrast, the new model utilizes these constraints as a basis for deriving a strain-energy function which is used to predict the stress-strain properties of both dry and swollen rubbers in the constant volume deformations of extension, compression, and pure shear.

THEORY

Model of the Network Chain

Consider a network chain of contour length, C, composed of n segments, each of molecular weight M_s and of length ℓ_s. The endpoints of the chain, which are connected into the network by crosslinks, are separated by distance L. For constant volume deformations, it can be assumed that the fluctuations of the endpoints are not a function of strain. The endpoints then can be considered as being fixed at their average position in space. This is consistent with the work of Hermans [9] and Flory [10], in whose theories the term accounting for endpoint fluctuation disappears for constant volume deformations. With the endpoints fixed, then all the segments of the chain are confined within a prolate ellipsoid as is shown in Fig. 1. This ellipsoid represents the total volume in which there exists a probability of finding a segment of the chain. It should be noted that the volumes available to neighbouring chains overlap to a considerable degree.

Just as the entire chain is constrained within a specific volume, each segment of the chain is confined within its own unique volume element. These volume elements are defined by the volumes of the spherical segments described when the chain is alternately pulled tight from opposite directions as is illustrated in Fig. 2. Furthermore, the sizes of these volume elements are a strong function of the end-to-end distance of the chain. Increasing the end-to-end distance reduces the volume available per segment, as can be seen by comparing Figs. 2a and 2b.

This model illustrates the strong similarity which exists between the compression of an ideal gas and the extension of an elastomer.

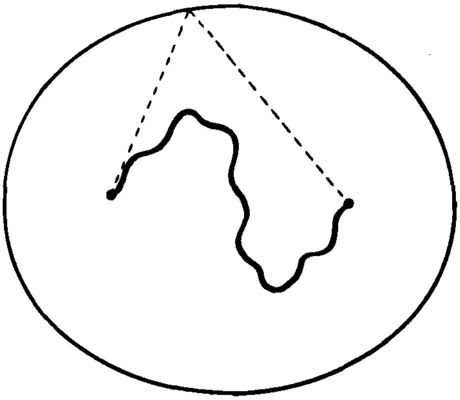

FIG. 1. Network chain constrained within a prolate ellipsoid.

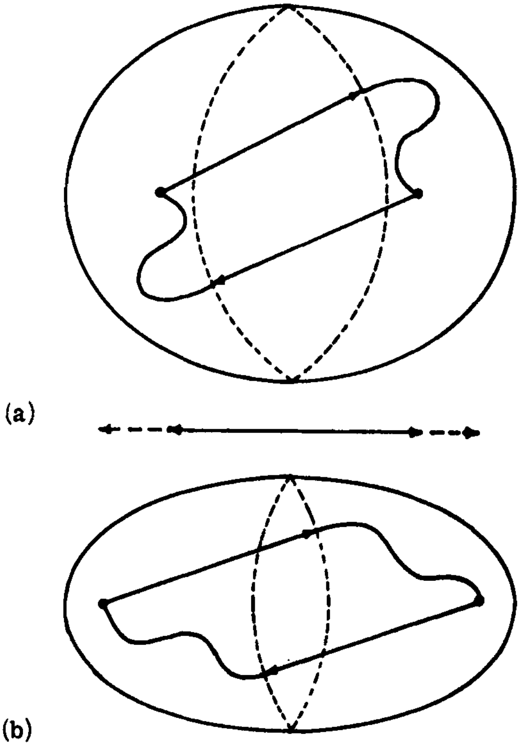

FIG. 2. Loss in available volume per segment as chain endpoints are extended: (a) undeformed chain; (b) extended chain.

Since under moderate deformation elastomers are largely incompressible, the loss in volume available per segment, as illustrated in Fig. 2, is performed with essentially no change in interatomic distances and hence, no change in interatomic forces. These are exactly the conditions assumed in the compression of an ideal gas, a loss in volume with no change in interparticle energy. It is reasonable to expect then, that the equation relating the loss in entropy of a chain segment during elongation may have a resemblance to the ideal gas law.

Conformational Entropies

The calculation of the number of conformations available to a specific network chain with end-to-end distance L must be performed while maintaining the criteria of constrained volume and connected segments. A standard technique for this type of calculation is to place the chain on a lattice. Here, the lattice co-ordination number is taken for convenience to be $z_0 + 1$. Then, for a random chain of n links, with one end fixed at a lattice point, the number of possible configurations Ω, is given by

$$\Omega = z_0^{n-1} \tag{1}$$

where z_0 represents the number of alternatives available for each successive random step. Since a real network chain is constrained by inviolate surfaces, its number of alternatives at each successive step z, must be less than z_0. The value of z for each link of the constrained chain can be calculated from considerations of the model just developed.

In stepping from the i-th to the (i + 1)th segment, the following criterion must be observed: the step must originate within the i-th volume element and terminate within the (i + 1)th volume element. With this in mind, consider the cross sections of the volume elements of the i-th and the (i + 1)th chain segments as is shown in Fig. 3.

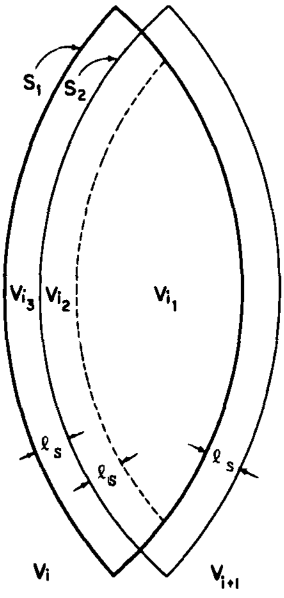

FIG. 3. Cross sections of i-th and (i + 1)th segment volume elements.

The i-th volume element V_i can be divided into three subelements based on the degree of constraint imposed on the number of available alternatives in these locations. These subelements are designated V_{i_1}, V_{i_2}, V_{i_3} in Fig. 3.

If the i-th segment lies in the volume subelement denoted in Fig. 3 by V_{i_1}, it can step one segment length ℓ_s in any direction and still remain in the volume element of the (i + 1)th segment. In this case, z would have the value of the random chain, z_0. If the i-th segment happens to lie on the surface denoted by S_1, z must have the value of unity because there exists only one possibility for the next step to fall within V_{i+1}, namely a step directly normal to S_1. Another possibility is that the i-th segment is found on the surface S_2. In this case, z would have the value of approximately $z_0/2$ because effectively one half the volume surrounding this lattice point is available for the next step. The value of z for the volume subelements designated V_{i_2} and V_{i_3} can be taken as the averages of the values at their surfaces.

For V_{i_2}:

$$z = 1/2[(z_0/2) + z_0] = 3z_0/4 \tag{2}$$

For V_{i_3}:

$$z = 1/2[1 + (z_0/2)] = (1/2) + (z_0/4) \tag{3}$$

The overall average value of z for the step from the i-th to the (i + 1)th segment is the volume average of the values of z for each subelement.

$$\bar{z}_i = z_0\left[\frac{V_{i_1}}{V_i} + \frac{3V_{i_2}}{4V_i}\right] + \left(\frac{1}{2} + \frac{z_0}{4}\right)\frac{V_{i_3}}{V_i} \tag{4}$$

By using Eq. (4), a value of z can be assigned to each step for the n links of the network chain and the total number of configurations can be computed from

$$\Omega = \prod_{i=1}^{n} \bar{z}_i \qquad (5)$$

and the conformational entropy change upon deformation follows directly from Boltzmann's Law

$$\Delta S = k \ln (\Omega / \Omega_0)$$

$$= k \sum_{i=1}^{n} \ln (\bar{z}_i / \bar{z}_{i_0}) \qquad (6)$$

Here Ω_0 and $\bar{z}_{i_0}$ are the values determined at some initial end-to-end distance L_0.

It should be noted that this method of calculation does not exclude those impossible conformations where two segments of the same chain occupy the same lattice point. The principal effect of these excluded conformations is to extend the initial end-to-end distance. This effect is not a serious limitation to the method presented here, because the initial end-to-end distances are determined empirically, as will be shown later.

It would seem that by using Eqs. (4), (5) and (6) in combination with classical network theories, there exists a straightforward route to the mathematical description of the mechanical behavior of elastomers. This method, which is fraught with mathematical difficulties, will be the subject of a subsequent publication. The remainder of this paper is devoted to the reduction of the constrained chain model to analytical expressions through simplification of the model.

Approximation for Calculating Conformations

The convenience of a single analytical formula may sometimes outweigh the loss in rigour when an expression, calculable only by numerical methods, is simplified by approximation. The first approximation required is a simpler expression for $\bar{z}_i$ as given by Eq. (4). This parameter is a function of the volume available to the i-th segment and as such, is also a function of both the end-to-end distance of the chain and the extension ratio of the bulk material. A simple relationship is required to represent $\bar{z}_i$ over the practical range of strain ratios.

The required relationship was determined by inspection. Values of the ratio z_i/z_{i_0} were plotted versus the ratio V_i/V_{i_0}. The resulting curves were convex, commencing at the origin and terminating at the point (1,1). The simplest function which reproduces this behavior is given by

$$\bar{z}_i/\bar{z}_{i_0} = (V_i/V_{i_0})^{1/\gamma} \tag{7}$$

An example of the degree of fit is given in Fig. 4. The values of $\bar{z}_i$ were calculated from Eq. (4) for a typical segment of a chain of 36 segments, each of unit length. The value of z_0 was taken to be 5 and the initial end-to-end distance to be 6. Choosing the contour length to be the square of the initial end-to-end distance makes the chain Gaussian, a basis which is used for want of an alternative. The value for z_0 is in the range found experimentally [11] in solution thermodynamics. However, it was found that changing z_0 by several multiples did not significantly affect the results. Of interest is the fact that over practically the entire range of V_i/V_{i_0}, $\bar{z}_i/z_{i_0}$ can be well represented by the function given by Eq. (7). In Fig. 4, the curve is drawn with

$$\gamma = 14$$

From Eq. (7), the entropy change for the i-th segment upon deformation is given by

$$\begin{aligned} \Delta S_i &= k \ \ln \ (V_i/V_{i_0})^{1/\gamma} \\ &= (k/\gamma) \ \ln \ (V_i/V_{i_0}) \end{aligned} \tag{8}$$

This last expression differs from the ideal gas law only by the factor $1/\gamma$. This similarity, between Eq. (8) and the ideal gas law, is to be expected owing to the similarity between the compression of an ideal gas and the effect of extension on a segment of an elastomeric chain, as was pointed out previously.

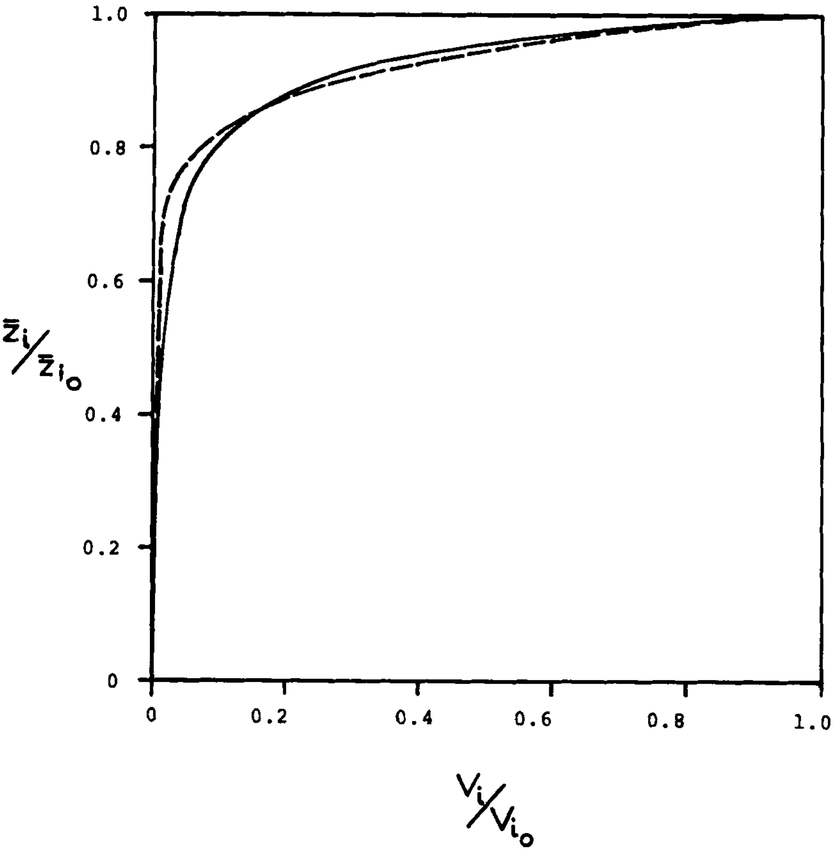

FIG. 4. Normalized number of alternatives versus segment volume for a typical segment of a Gaussian chain of 36 segments: (——) exact calculation, Eq. (4) (- -) approximation, Eq. (7).

Cylindrical Approximation of a Network Chain

In the second approximation required to achieve an analytical expression, the prolate ellipsoid of Fig. 1 is replaced by a cylinder of diameter D. Consider again the volume available to the i-th segment of the chain. If the chain is pulled tight along the axis

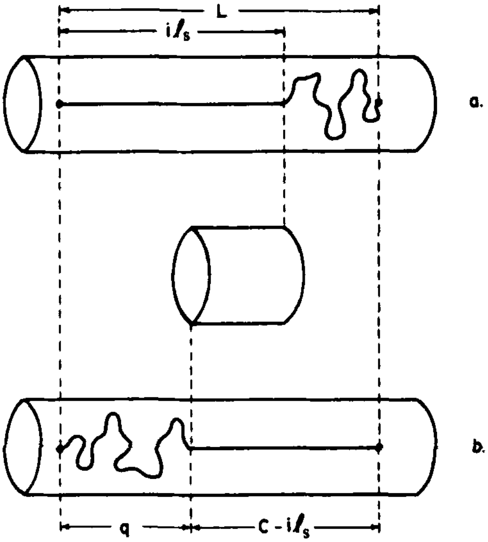

FIG. 5. Cylindrical model for approximate calculation of volume available for a segment.

joining the endpoints from the right, the i-th segment will lie at a distance $i\ell_s$ from the left-hand endpoint as is shown in Fig. 5a. Similarly, if the chain is pulled tight from the other end, as in Fig. 5b, the i-th segment will lie at a distance $q = L - (C - i\ell_s)$ from the left-hand endpoint. The volume available to the segment is then approximately (neglecting the curvature at each end)

$$V_i = (\pi/4)\,D^2\,(i\ell_s - q)$$

$$= (\pi/4)\,D^2\,(C - L) \tag{9}$$

It is obvious that the volumes available to segments of the chain close to the crosslink points will not be given by Eq. (9). For long chains, however, these end-effects will be relatively insignificant.

When the chain is deformed in the same ratio as the macroscopic dimensions (affine deformation), the strain ratio can be written

$$\lambda = L/L_0 \tag{10}$$

Also, because the volume of an elastomer remains essentially constant during deformation, the diameters of the cylinder after and before deformation are related by

$$D = D_0\,\lambda^{-1/2} \tag{11}$$

The ratio of the volume available to the i-th segment after and before deformation can then be calculated

$$\frac{V_i}{V_{i_0}} = \frac{(\pi/4)(D_0\,\lambda^{-1/2})^2(C - L_0)}{(\pi/4)D_0^2(C - L_0)}$$

$$= \frac{CL^{-1}L_0 - L_0}{C - L_0} \tag{12}$$

The ratio C/L_0, which is given by the maximum extensibility of the chain, is of special significance to this theory and will be designated henceforth by Λ. Equation (12) can now be written

$$V_i/V_{i_0} = (CL^{-1} - 1)/(\Lambda - 1) \tag{13}$$

Combining Eqs. (6), (7), and (13) yields the change in entropy for the chain upon deformation

$$\Delta S = k \sum_{i=1}^{n} \ln\,(V_i/V_{i_0})^{1/\gamma}$$

$$= \frac{nk}{\gamma}\ln\left(\frac{CL^{-1} - 1}{\Lambda - 1}\right) \tag{14}$$

The network response to a stress involves contributions not only from chains whose axes are oriented in the direction of stress, but in other directions as well. The change in entropy for an average chain in the network will be the average of the contributions in the three coordinate directions.

$$\Delta S = \frac{nk}{3\gamma}\left[\ln(CL_x^{-1} - 1) + \ln(CL_y^{-1} - 1) + \ln(Cl_z^{-1} - 1) - 3\ln(\Lambda - 1)\right] \quad (15)$$

This expression represents the stored entropy function for an average network chain in a constant volume deformation.

Average Initial Cross Section of a Network Chain

Before the stored entropy function can be related to experimental quantities, it is necessary to calculate the contribution of an average chain to the initial cross section of the bulk material. To calculate this quantity on a statistical basis without specific information about the chain is a fruitless, if not an impossible, task. Instead, the following approach has been adopted.

The true average contribution to the cross section must lie in between the maximum and minimum possible contributions and, hence, can be represented by a weighted average of the extremes.

If we assume the stress is acting in the X-direction, then the average number of times the chains in each of the three coordinate directions cross the arbitrary Y-Z plane must be found. The conformations giving the minimum number of crossings are illustrated in Fig. 6A. The chain on the X-axis crosses once, while the chains along the other axes cross twice. The average cross section of a single chain a, is given by the volume of the chain divided by its contour length.

$$a = M_c/\rho C \quad (16)$$

where ρ is the density of the polymer and M_c is the molecular weight of the chain between adjacent crosslinks. For the uncoiled chains in Fig. 6A, then, the contributions of the chains in the X and Y or Z directions are a and 2a, respectively.

At the other extreme, schematically represented in Fig. 6B, the chains are tightly packed into regular volumes, each of length L_0. In this conformation, these chains have a far greater contribution to the average cross section. The cross-sectional contribution along the X-axis A_x, is given by

$$A_x = M_c/\rho L_0 = M_c \Lambda/\rho C = \Lambda a \quad (17)$$

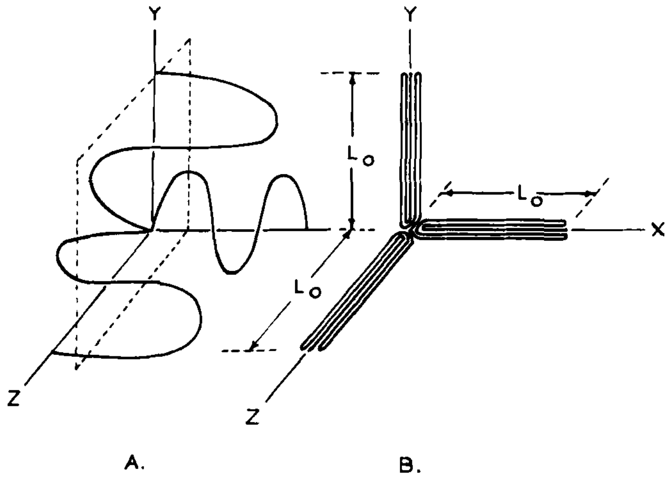

FIG. 6. Conformations of chains giving (A) minimum contributions and (B) maximum contribution to cross section.

For the tightly packed chains on the other two axes, the cross sections are given by

$$A_y = A_z = L_0 A_x^{1/2} = L_0 \Lambda^{1/2} a^{1/2} \tag{18}$$

The true average contribution to the cross section will not be either of the two extremes, but somewhere in between, probably closer to the minimum for a low density, amorphous elastomer. For this reason, the true average contribution will be assumed to be the weighted average of the two extremes with the minimum weighted by a factor w. The average contributions to the cross sections are then given by

$$\begin{aligned} \overline{A}_x &= [1/(w+1)]\,(\Lambda a + wa) \\ &= [a/(w+1)]\,(\Lambda + w) \end{aligned} \tag{19}$$

$$\bar{A}_y = \bar{A}_z$$

$$= [1/(w + 1)]\ (L_0 \Lambda^{1/2} a^{1/2} + 2wa) \tag{20}$$

The overall average now becomes

$$\bar{A} = (\bar{A}_x + \bar{A}_y + \bar{A}_z)/3$$

$$= \left[\frac{a(\Lambda + w)}{w + 1} + \frac{2(L_0 \Lambda^{1/2} a^{1/2} + 2wa)}{w + 1} \right] /3 \tag{21}$$

which after substitution for a and simplification, becomes

$$\bar{A} = \frac{M_c(\Lambda + 5w + 2Ca^{-1/2} \Lambda^{-1/2})}{3\rho \Lambda L_0 (w + 1)} \tag{22}$$

If the chain has x monomer units, each of length ℓ_m, a structural parameter β, can be defined by

$$\beta = \ell_m a^{-1/2} = (\rho \ell_m^3 / M_m)^{1/2} \tag{23}$$

where M_m is the molecular weight of a monomer unit. For any particular elastomer, β can be evaluated from knowledge of the chemical composition and the bond angles and lengths in the polymer backbone. Equation (22) can now be rewritten into the desired form:

$$\bar{A} = \frac{M_c(\Lambda + 5w + 2\beta x \Lambda^{-1/2})}{(3\rho \Lambda L_0 (w + 1)} \tag{24}$$

Uniaxial Deformation

For an elastomer, the uniaxial deformations of extension or compression are essentially constant volume processes. Taking the X-axis as the direction of stress, then the strain ratios are related by

$$\lambda_y = \lambda_z = \lambda_x^{-1/2} \tag{25}$$

and since affine deformation has been assumed, the end-to-end distances of the chains are related by

$$L_y = L_z = L_0^{3/2} L_x^{-1/2} \tag{26}$$

The stored entropy function, Eq (15) can now be written in terms of L_x, which yields

$$\Delta S = \frac{nk}{3\gamma}\left[\ln(CL_x^{-1} - 1) + 2(CL_0^{-3/2} L_x^{1/2} - 1) - 3\ln(\Lambda - 1)\right] \tag{27}$$

and the tension along the X-axis is given by

$$f = -T \frac{\partial \Delta S}{\partial L_x} \tag{28}$$

$$= -\frac{nkT}{3\gamma}\left(- \frac{CL_x^{-2}}{CL_x^{-1} - 1} + \frac{CL_0^{-3/2} L_x^{-1/2}}{CL^{-3/2} L_x^{1/2} - 1}\right)$$

$$= \frac{n\Lambda kT}{3\gamma L_0}\left(\frac{1}{\Lambda\lambda - \lambda^2} - \frac{1}{\Lambda\lambda - \lambda^{1/2}}\right) \tag{29}$$

The stress per unit of undeformed cross section can be found by dividing Eq. (29) by Eq. (24)

$$\tau = f/\bar{A}$$

$$= \Xi\left[\frac{1}{\Lambda\lambda - \lambda^2} - \frac{1}{\Lambda\lambda - \lambda^{1/2}}\right] \tag{30}$$

where

$$\Xi = \frac{\rho(w + 1)\Lambda^2 RT}{\gamma M_s(\Lambda + 5w + 2x\beta\Lambda^{-1/2})} \tag{31}$$

The parameter Ξ, which is introduced for convenience of notation, contains no strain-dependent variables and is a constant for any particular vulcanizate. According to the constrained chain model, then, the stress-strain properties of any particular vulcanizate can be represented by only two empirical parameters: Λ and Ξ.

Pure Shear

For an incompressible elastomer subjected to pure shear by a stress acting along the X-axis, the strain ratios are related by

$$\lambda_y = \lambda_x^{-1}$$

$$\lambda_z = 1 \tag{32}$$

and again assuming affine deformation, the end-to-end distances are related by

$$L_y = L_0^2 L_x^{-1}$$

and

$$L_z = L_0 \tag{33}$$

For this mode of deformation, the stored entropy function can be written as

$$\Delta S = \frac{nk}{3\gamma}\left[\ln(CL_x^{-1} - 1) + \ln(CL_0^{-2} L_x - 1) - 2\ln(\Lambda - 1)\right] \tag{34}$$

and the tension in the X-direction is found by using Eq. (28).

$$f = -\frac{nkT}{3\gamma}\left(-\frac{CL_x^{-2}}{CL_x^{-1} - 1} + \frac{CL_0^{-2}}{CL_0^{-2}L_x - 1}\right)$$

$$= \frac{n\Lambda kT}{3\gamma L_0}\left(\frac{1}{\Lambda\lambda - \lambda^2} - \frac{1}{\Lambda\lambda - 1}\right) \tag{35}$$

The stress per unit of undeformed cross section is then given by

$$\tau = f/\overline{A}$$

$$= \Xi\left(\frac{1}{\Lambda\lambda - \lambda^2} - \frac{1}{\Lambda\lambda - 1}\right) \tag{36}$$

where all symbols retain their previous significance.

Uniaxial Deformation of Swollen Elastomers

For an elastomer, swollen to volume fraction of polymer v_2, the stress per unit of swollen undeformed cross section τ_s is determined simply by substituting the swollen equivalent of Λ

$$\Lambda_s = C/L_0 v_2^{-1/3} = \Lambda v_2^{1/3} \tag{37}$$

into Eqs. (30) and (31) and by accounting for the presence of solvent in the initial cross section.

$$\tau_s = \frac{f_s}{\overline{A}_s v_2^{-2/3}}$$

$$= \Xi_s\left(\frac{1}{\Lambda v_2^{1/3}\lambda - \lambda^2} - \frac{1}{\Lambda v_2^{1/3}\lambda - \lambda^{1/2}}\right) \tag{38}$$

where

$$\Xi_s = \frac{\rho(w + 1)\, v_2^{4/3} \Lambda^2 \; RT}{\gamma M_s(\Lambda v_2^{1/3} + 5w + 2x\beta\, \Lambda^{-1/2}\; v_2^{-1/6})} \tag{39}$$

In Eq. (38), λ represents the ratio of the extended swollen length to the initial swollen length.

In the Eqs. (30)-(39), the extension, compression, or shear properties of an elastomer are given by expressions with essentially four parameters. The first parameter, Λ, defines the ratio of the contour length to the initial end-to-end distance and, hence, establishes the maximum extensibility of the chain. The second parameter, x, which gives the number of monomer units, describes the size of the chain. The quantity γM_s, which can be treated as a single parameter, hereafter called ξ, reflects the flexibility of the chain. The fourth parameter is w, the weighting factor from the cross-sectional calculation, which effectively describes the packing of the chain. It is believed that the properties of a specific chain cannot be described with fewer parameters unless some assumption is made concerning the relationship between these parameters. For example, in the case of a Gaussian chain, the Λ, x, and M_s parameters are related by

$$\Lambda = C/L_0 = n\ell_s/n^{1/2}\,\ell_s = n^{1/2} = (xM_n/M_s)^{1/2} \tag{40}$$

No such relationship is assumed here because it leads to a loss of generality.

APPLICATION OF THEORY TO EXPERIMENT

Uniaxial Deformation

The extension data of Mullins (12) were chosen to establish the parameters in the model for three reasons. First, the experimental stress-strain relationships of elastomers in extension have unique characteristics which make the selection of the parameters easier. Secondly, in the material used by Mullins, natural rubber + dicumyl peroxide (DCP), quantitative relationships between the amount of crosslinking agent present and the number of crosslinks formed are generally assumed [13-15]. Finally, the experimental data cover the full range of extension to rupture and it can be determined if the model is specific to a limited range of strain or generally applicable.

The theoretical relationship, Eq. (30), was fitted to the data by optimizing the Λ and Ξ parameters to give the best least-squares fit for each vulcanizate. After some experience had been gained with the model, it was found that initial estimates of Λ could be obtained from the position of the minimum in the experimental Mooney-Rivlin plot.

A Mooney-Rivlin plot is a method of presenting uniaxial deformation data in which the Gaussian modulus

$$G_u = \tau/(\lambda - \lambda^{-2}) \tag{41}$$

is plotted versus λ^{-1}. Mullins' extension data and the fitted theoretical curves are presented in this manner in Fig. 7. The agreement between theory and experiment is excellent, the new model representing a large improvement over the Gaussian theory which predicts a horizontal straight line on this type of plot. The single formula, Eq. (30), predicts not only the decrease in the Gaussian modulus at low to moderate strains, but also the rapid increase at high extensions. It can now be seen that the decrease in the Gaussian modulus with extension, frequently characterized by the second invariant of the Mooney-Rivlin theory, arises naturally from the conformational entropy of a network chain and special effects such as topology, order, entanglement, etc. need not be invoked to explain this phenomenon.

At the highest crosslink density, the fit of theory to experiment is not as good. This effect, anticipated in the theoretical section, is attributed to the larger relative significance of end-effects in short chains.

To compare theoretical values of the number of monomer units per chain x, with estimates based on the concentration of DCP, it is necessary to establish the parameters ξ and w for natural rubber. Since this was done through an optimization procedure involving use of other sets of results besides the extension data of Mullins, the results of that procedure, $\xi = 160$ and $w = 2$ will be utilized now and justified later. With the parameters Λ and Ξ established for each vulcanizate from the stress-strain curve fitting, values of x were calculated from Eq. (31). Chemical estimates of the number of monomer units per chain x_c, were obtained by using Eq. (42):

$$x_c = \frac{1}{2}\left(\frac{\text{moles of monomer units}}{\text{moles of DCP}}\right) \tag{42}$$

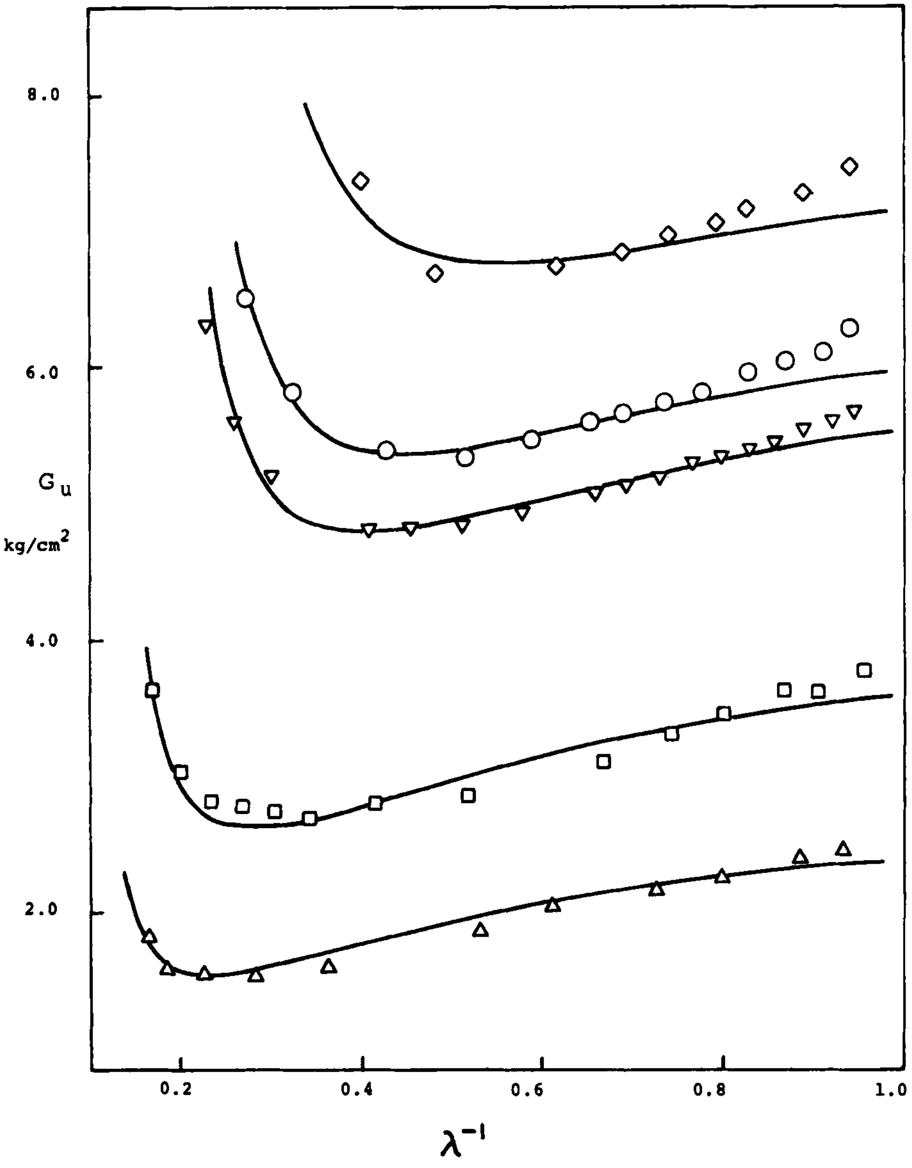

FIG. 7. Mullins' extension data [12] for natural rubber and fitted theoretical curves from Eq. (30): (△) $\Lambda = 9.19$, $\Xi = 315.4$ kg/cm^2; (□) $\Lambda = 7.80$, $\Xi = 330.3$ kg/cm^2; (▽) $\Lambda = 5.70$, $\Xi = 243.1$ kg/cm^2; (○) $\Lambda = 5.25$, $\Xi = 215.2$ kg/cm^2; (◇) $\Lambda = 4.50$, $\Xi = 174.8$ kg/cm^2.

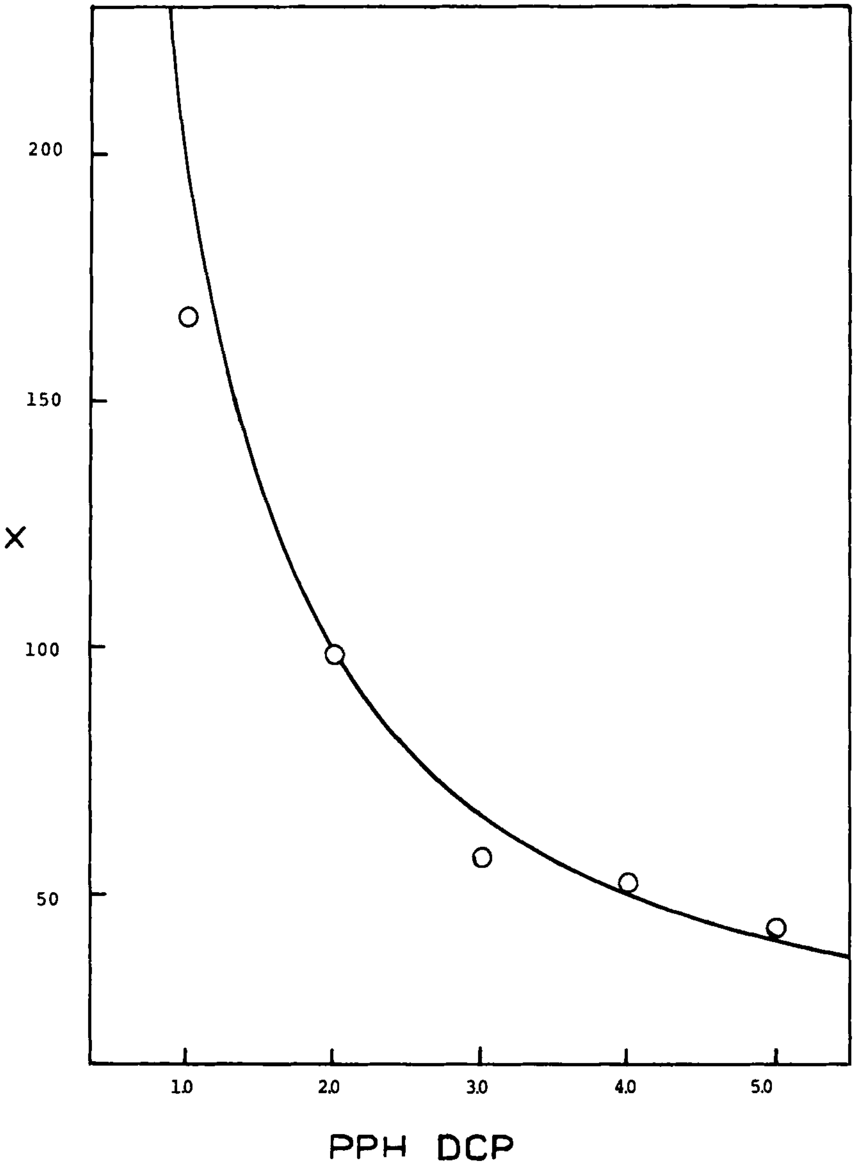

FIG. 8. Monomer units per chain as a function of DCP concentration for Mullins' extension data [12]: (——) chemical estimate, Eq. (42); (○) from extension data, Eq. (31).

The resulting values of x and x_c are plotted together in Fig. 8. Again the agreement is good, the average deviation being less than 9%.

To illustrate that the constrained chain model is applicable to more than one type of elastomer, Eq. (30) was fitted to the data of van der Hoff and Buckler [16] for polybutadiene networks in extension. The extremely high degree of fit for these data, shown in Fig. 9,

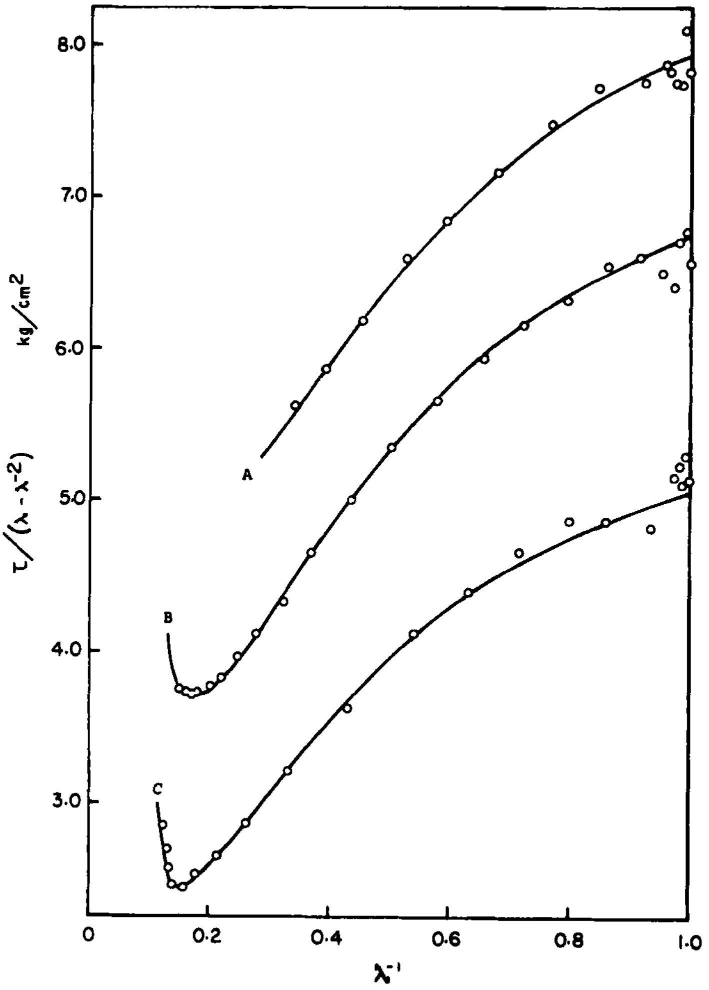

FIG. 9. Data of van der Hoff and Buckler [16] for polybutadiene networks in extension and fitted curves from Eq. (30): (A) $\Lambda = 9.5$, $\Xi = 1145.5$ kg/cm^2; (B) $\Lambda = 11.8$, $\Xi = 1571.5$ kg/cm^2; (C) $\Lambda = 13.7$, $\Xi = 1625.5$ kg/cm^2.

is probably due to both the large values of Λ, which minimize the end-effects, and the experimental technique, which minimizes viscoelastic effects.

Uniaxial deformation can be either extension or compression and Eq. (30) should apply in both cases. In Fig. 10, Eq. (30) is fitted to Ang's data [17] for DCP-cured natural rubber in compression. Because the compression curves are relatively featureless, there is no method for finding an initial estimate of Λ from the experimental data. Therefore, in this case, Λ values were assigned by interpolation of the experimental values of the initial modulus of Mullins' extension data. The values $\xi = 160$ and $w = 2$ were used as before, and the values of x were adjusted to give the fit. As with the extension data, the fit at low degrees of crosslinking is excellent. The single formula, Eq. (30), which reproduced the complex behavior of the extension curves, also describes the relatively constant moduli in compression. Because it seems unlikely that the introduction of extra crosslinks could drastically affect the shapes of the curves, the deviations which occur at high crosslink densities are attributed to experimental scatter in this instance.

Pure Shear

If Eq. (15) truly represents a strain-energy function, it should serve to describe behavior in more than one type of deformation. In Fig. 11, experimental values of the Gaussian modulus in pure shear,

$$G_{ps} = \tau/(\lambda - \lambda^{-3}) \tag{43}$$

and the fitted theoretical curve from Eq. (36) are plotted versus strain ratio. The experimental data are from Treloar [18]. Again, the fit is excellent, the theoretical curve quantitatively reproducing all the features of the experimental curve.

The material used for this experiment was from a sulfur-cured natural rubber network and the parameters used to fit the data are not necessarily comparable with those of a peroxide-cured network. The wandering of sulfur crosslinks during deformation may give this type of material a larger extensibility than a network crosslinked to the same degree with peroxide. This larger extensibility may result in an artificially large value of Λ. In this case, however, the movement of crosslink points does not seem to affect the results. Assuming the same values of ξ and w as used previously, the number of monomer units per chain was found to be 84, which is the value expected for a peroxide-cured network with the same initial modulus.

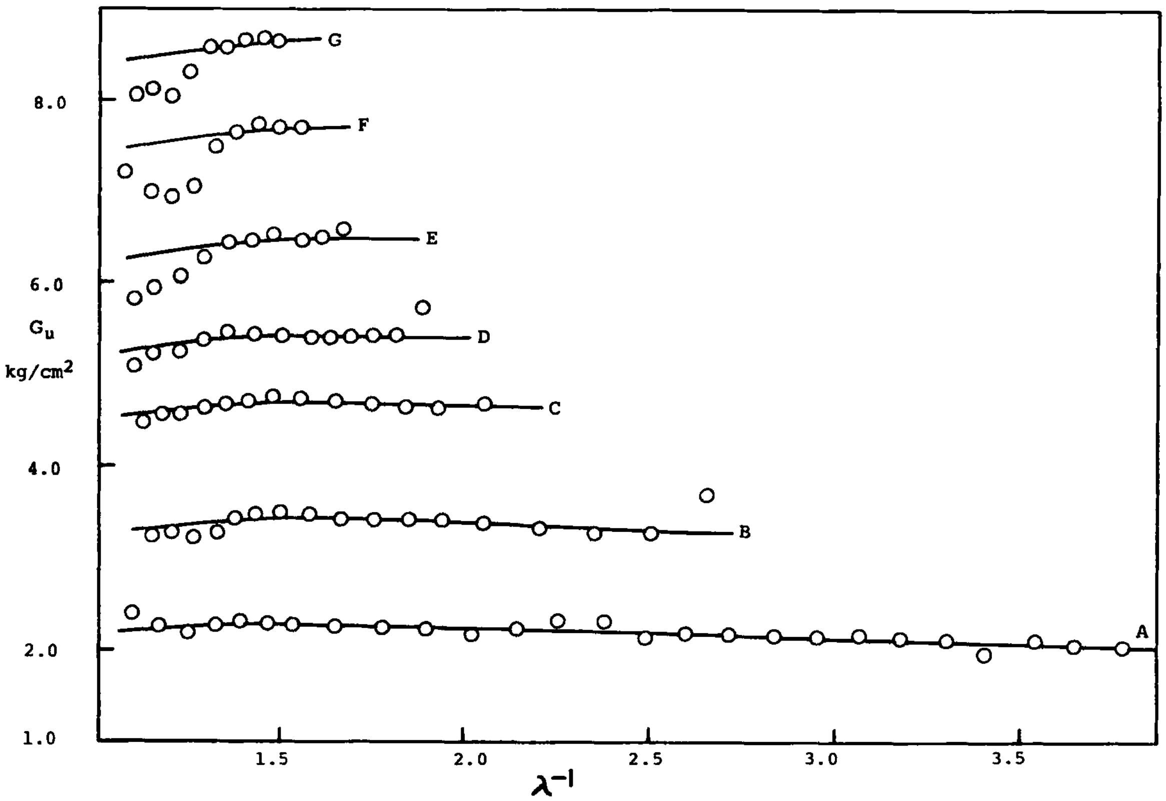

FIG. 10. Ang's compression data [17] for natural rubber and fitted theoretical curves from Eq. (30): (A) $\Lambda = 9.30$, $x = 185$; (B) $\Lambda = 8.16$, $x = 111$; (C) $\Lambda = 6.70$, $x = 74$; (D) $\Lambda = 5.93$, $x = 62$; (E) $\Lambda = 4.93$, $x = 51$; (F) $\Lambda = 4.30$, $x = 42$; (G) $\Lambda = 3.63$, $x = 39$.

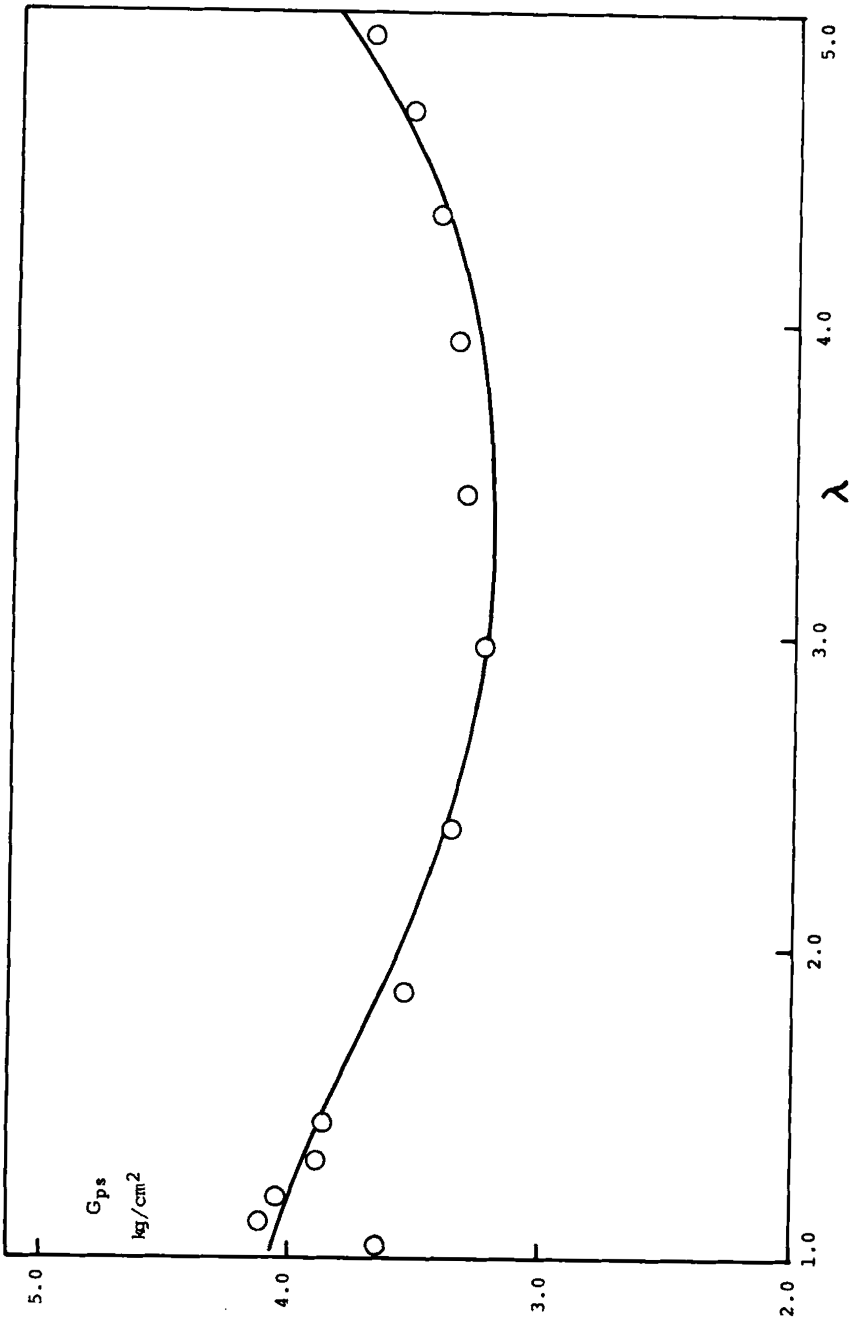

FIG. 11. Treloar's pure shear data [18] for natural rubber and fitted theoretical curve from Eq. (36), $\Lambda = 7.231$, $x = 84$.

Extension of Swollen Elastomers

The final and most critical test of the new theory is in the prediction of the extension properties of vulcanizates swollen to various degrees. Mullins' data [12] were used for the same reasons as mentioned previously. Mullins reports extension data for both the dry rubber and its gel swollen to four concentrations of solvent. The severity of this test can be appreciated when it is considered that once the values of w, Λ, x, and ξ are established for the dry rubber, four other sets of data must be predicted simultaneously without any adjustable parameters.

For the dry rubber, the curve was fitted by assigning x the value x_c, calculated from the amount of crosslinking agent by Eq. (42), on assigning Λ the value dictated by the minimum in the Mooney-Rivlin curve, setting $w = 2$ as before, and adjusting ξ to give the fit. With these data, ξ was found to be 150, which is reasonably close to the value 160 used previously. Once these values had been established, the theoretical curves for the swollen systems were calculated by using Eq. (38).

The experimental data and the theoretical curves for both dry and swollen gels are given in Fig. 12. The agreement between theory and experiment is reasonably good. Of significant interest is the fact that at high degrees of swelling, the rate of decrease of the modulus with extension is very small. This near constancy of the modulus was once taken as verification of the Gaussian theory. This phenomenon can now be seen to be a special case within the framework of the theory presented here.

Not only are the slopes of the experimental curves well reproduced, but also the absolute value of the moduli. This is particularly gratifying because the moduli are a strong function of the Ξ_s parameter and, hence, of the method used to calculate the contribution of the average chain to the initial cross section. The agreement between theory and experiment is a strong validation of the methodology adopted.

The only significant deviation of experiment from theory occurs at large extensions of the highly swollen gels. This deviation is principally attributed to the failure of the approximation $(V_i/V_{i_0})^{1/\gamma}$ to represent z_i/z_{i_0} at high degrees of strain (and hence small values of V_i/V_{i_0}) as can be seen in Fig. 4.

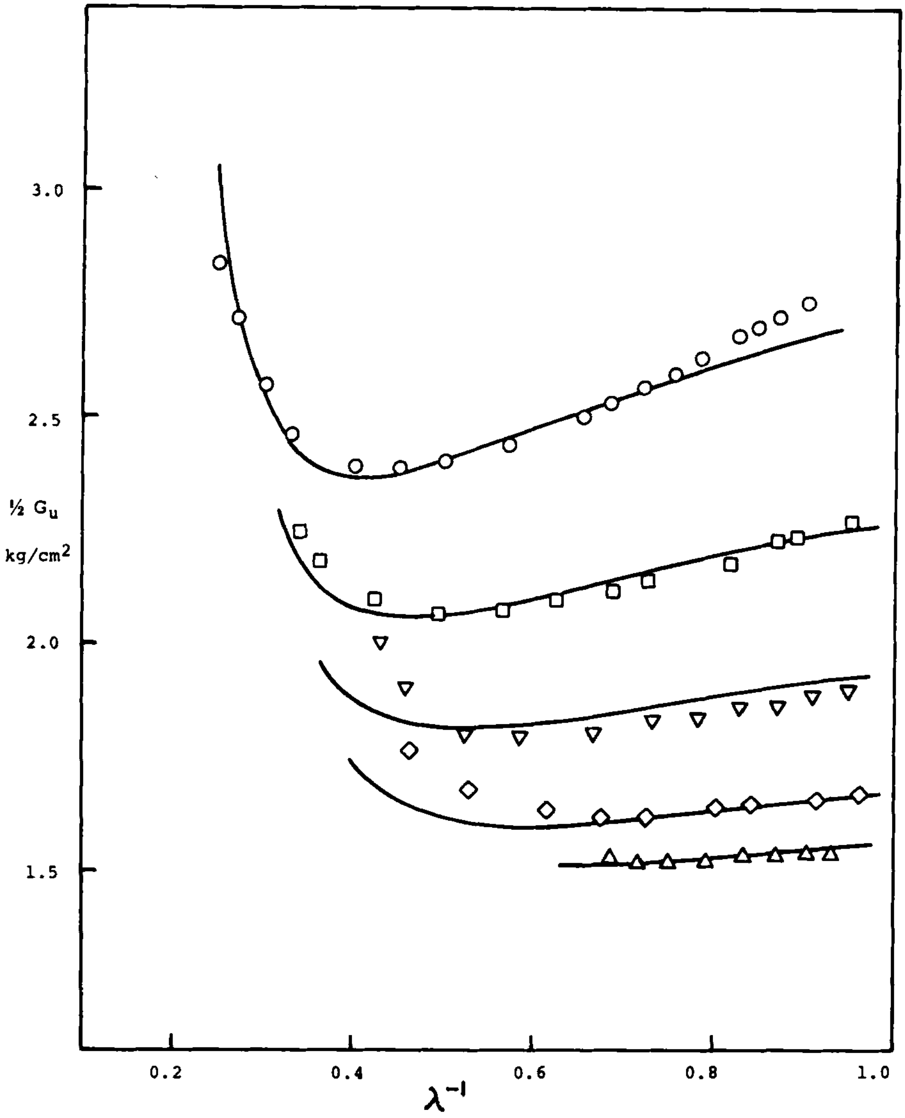

FIG. 12. Mullins' extension data [12] for a natural rubber vulcanizate swollen to various degrees and fitted theoretical curves from Eq. (39), $\Lambda = 5.248$, $x = 66$, $\xi = 150$: (○) $v_2 = 1.0$; (□) $v_2 = 0.753$; (▽) $v_2 = 0.585$; (◇) $v_2 = 0.455$; (△) $v_2 = 0.407$.

Justification of Model Parameters

Now that all the sets of data used to test the model have been presented, the method used to establish the parameters in the model can be discussed. The following procedure was used.

An arbitrary value was selected for w and then the value of ξ which gave the smallest average deviation of x from x_c in Fig. 8 was determined. Using these values of w and ξ, the degree of fit of Eq. (38) to the swollen stress-strain data was then assessed. This process was repeated for a number of values of w. The effect of changing the weight factor was manifested in a number of ways. First, and most important, was the effect on ξ. For example, if w was assigned the value of unity, ξ would be 107. However, using such small values for w and ξ would worsen the fit of x to x_c in Fig. 8. In the other direction, increasing the value of w would increase ξ, but the fit of theory to the extension data for swollen gels would deteriorate. The value of $w = 2$ gives an excellent fit to both sets of data.

This discussion points out a limitation of the data presented here. Neither of the parameters ξ or w are susceptible to direct observation under the condition of constant volume deformation. This limitation will be removed in Part II of this series, where nonconstant volume deformations are considered. It will be shown that the flexibility parameter ξ, can be determined directly from experimental data and the value so obtained for natural rubber completely corroborates the value obtained in this paper by optimization.

CONCLUSIONS

Any theory, no matter how cleverly conceived or rigorously derived, must, in the final analysis, be tested in the harsh light of experiment evidence. In the present case, this has been done with a fair degree of rigor, and no contradictions to the proposed theory have been found. The quantitative agreement between theory and experiment in the wide variety of strains illustrated here is the strongest possible validation of the novel concepts contained in the constrained chain model. It is concluded that the theory presented here forms a strong link between the visible, observed mechanical properties and the invisible microstructure of elastomeric networks.

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Accepted by editor June 1, 1975
Received for publication September 16, 1975