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Modified Chain Displacement Function for Gaussian Networks

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ABSTRACT

The probability that a polymeric chain reaches from one crosslink junction to a second is given by the probability that the chain's end-to-end vector is equal in magnitude and direction to the junction-to-junction vector. In calculating this probability, conventional Gaussian theories assume independent probabilities in the three coordinate directions. This assumption of independent probabilities means that the conventional Gaussian chain displacement function cannot refer to a specified direction as is required. In this paper, the directional probability is re-introduced into the Gaussian chain displacement function which leads to a novel strain-energy function. This strain-energy function is shown to be in quantitative agreement with reversible deformation data in extension and in pure shear. No additional parameters are introduced into the new function which allows the independent determination of both the crosslink density and the "front factor" (the ratio of the mean-square end-to-end distances of free and crosslinked chains).

INTRODUCTION

The Gaussian, or statistical, theory of rubber elasticity has been derived in a number of ways by a number of authors, and these derivations are discussed in standard texts.[1-3]. For constant volume deformations, these theories predict the same form for the strain-energy function for an elastomeric network.

$$W = G(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) \quad (1)$$

where W is the strain-energy, λ_i is the strain ratio in the i -th direction and G is a constant, or modulus. The differences among the various derivations of Eq. (1) arise from the different techniques of generating network averages which lead to different interpretations of the parameter G . This area is still one of considerable controversy and no attempt will be made to resolve it here.

For reversible, uniaxial deformation, Eq. (1) predicts,

$$\frac{1}{2} f / (\lambda - \lambda^{-2}) = G = \text{constant} \quad (2)$$

when f is the engineering stress or stress per unit of unstrained cross section and λ is the strain ratio in the direction of stress. Experiments have shown, however, that in simple tension, G is not independent of strain. Its value initially decreases with increasing elongation until at high strains its value increases rapidly. The rapid increase in G at high strains is usually attributed to finite extensibility. The decrease in G at low to moderate extensions has not found such a ready interpretation. Mark [4], in his review, concludes that this phenomenon is still not understood and its elucidation remains as one of the major problems in rubber-like elasticity. More recently, Crossland and van der Hoff [5] concluded that the decrease in G in extension is an inherent property of the chain displacement function, and, special topological or structural effects need not be introduced to account for this decrease. This conclusion was supported by the success of a strain-energy function based on a non-Gaussian displacement function in describing a wide variety of reversible deformations. Unfortunately, the complexity of the non-Gaussian displacement function required that the simplified three-chain network approach [6] be used.

Two major points can be taken from the above discussion. First, non-Gaussian chain displacement functions can be successful in representing experimental data. Secondly, the network calculations of the conventional, statistical theories affect only the interpretation of

the modulus G and do not introduce strain-dependent terms. Together, these observations suggest that the failure of the statistical theories to agree with observation probably lies at the level of the chain displacement function. It is the purpose of this letter to critically re-examine the Gaussian chain displacement function and propose an amended form.

THEORY

Consider a crosslinked network of ν chains. Although the cross-link junctions may fluctuate about their average positions, the distribution of the junction-to-junction vectors, \underline{r}_j , will remain unchanged by these fluctuations. Hence, the vulcanization process predetermines the initial distribution of the \underline{r}_j . It is assumed that the cross-link junctions are distributed randomly throughout space which means that there is an equal probability of finding a particular \underline{r}_j oriented in any direction and that the initial junction-to-junction distances, r_j , are distributed in a Gaussian manner about some average value, \bar{r}_j , i. e.,

$$d\nu = 4\beta_j^3 \pi^{-1/2} \nu r_j^2 \exp \{-\beta_j^2 r_j^2\} dr_j \tag{3}$$

where

$$\beta_j^2 = 3/2 \bar{r}_j^2 \tag{4}$$

The problem now is to calculate the probability that a network chain stretches from one specified junction to a second specified junction. If the origin of a coordinate system is placed at one junction, then, according to Flory [3], the problem becomes that of determining the probability that the chain's end-to-end vector reaches from the origin to the second specified junction. The second junction is represented mathematically by a small volume element, $\delta V = dx dy dz$. This probability can also be described as the probability that the network chain end-to-end vector \underline{r} coincides with the junction-to-junction vector or $P(\underline{r} = \underline{r}_j)$. In generating this probability, it is generally assumed that the probabilities in the three coordinate directions, $P(x)$, $P(y)$, and $P(z)$, are independent of one another, and the required probability may be found by taking the product of the separate Gaussian probabilities. The resulting expression depends only on the magnitude of \underline{r} and not on its direction. While the assumption

of independent probabilities is undoubtedly valid for free chains, it cannot be correct for network chains which required not only that $r = r_j$ but also that both vectors have the same orientation. In fact, taking the product of the separate probabilities simply gives the probability that \underline{r} has length r_j , i. e.,

$$\begin{aligned} P(r = r_j) &= P(x) \cdot P(y) \cdot P(z) \\ &= \beta_f^3 \pi^{-3/2} \exp \{ -\beta_f^2 r_j^2 \} \end{aligned} \quad (5)$$

where

$$\beta_f^2 = 3/2 \bar{r}_f^2 \quad (6)$$

and \bar{r}_f^2 is the mean squared end-to-end distance of the set of free chains.

Since the required probability, $P(\underline{r} = \underline{r}_j)$ is the probability of the equality of two vectors, it must be given by the product of two probabilities, the probability that \underline{r} has the same direction as \underline{r}_j and the probability that $r = r_j$. The probability that \underline{r} has the same direction as \underline{r}_j is given by the probability that the axis of the vector \underline{r} passes through the small element of area δA as opposed to some other location on the spherical surface of radius, r_j , as is shown in Fig. 1. The area element δA represents the cross-sectional area of the second specified crosslink junction. Since all orientations of \underline{r} are equally probable, this probability $P(\delta A)$ is simply the area δA divided by the area of the surface.

$$P(\delta A) = \delta A / 4\pi r_j^2 \quad (7)$$

Since the probability that $r = r_j$ has already been described in Eq. (5), then the chain displacement function is given by:

$$P(\underline{r} = \underline{r}_j) = P(\delta A) \cdot P(r = r_j) \quad (8)$$

$$= (\delta A \beta_f^3 / 4\pi^{5/2} r_j^2) \exp \{ -\beta_f^2 r_j^2 \} \quad (9)$$

If the network is now so deformed that \underline{r}_j assumes some new value, \underline{r}_k , then:

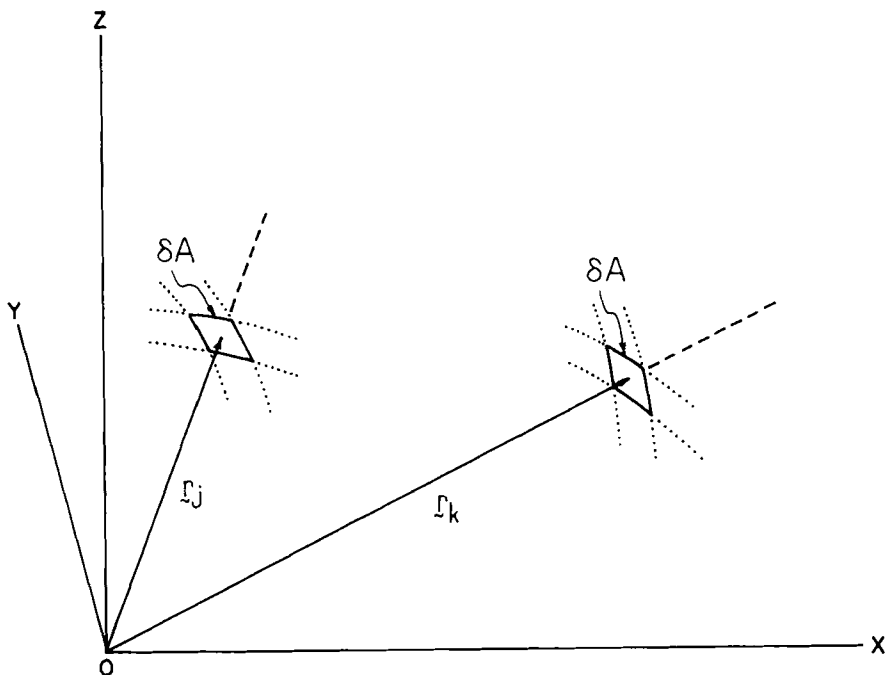


FIG. 1. Vectors \underline{r}_j and \underline{r}_k oriented in the direction of the area elements, δA .

$$P(\underline{r} = \underline{r}_k) = (\delta A \beta_f^3 / 4\pi^{5/2} r_k^2) \exp \{-\beta_f^2 r_k^2\} \tag{10}$$

Since the value of δA does not change with strain, the entropy change for the chain ΔS_c caused by this deformation is given by:

$$\begin{aligned} \Delta S_c &= k \ln \{P(\underline{r} = \underline{r}_k) / P(\underline{r} = \underline{r}_j)\} \\ &= k \ln \{r_j^2 r_k^{-2} \exp [-\beta_f^2 (r_k^2 - r_j^2)]\} \\ &= -k \{\ln(r_k^2 / r_j^2) + \beta_f^2 (r_k^2 - r_j^2)\} \end{aligned} \tag{11}$$

If the usual assumption of affine deformation is made and since no preferential orientation of the \underline{r}_j exists, then [1, 2]

$$r_k^2 = (1/3) (\lambda_x^2 + \lambda_y^2 + \lambda_z^2) r_j^2 \quad (12)$$

and

$$\Delta S_c = -k \{ \ln [(1/3)(\lambda_x^2 + \lambda_y^2 + \lambda_z^2)] + (1/3)\beta_f^2 (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) r_j^2 \} \quad (13)$$

It should be noted that ΔS_c depends only on the length of r_j and not on its direction. Hence, in order to determine the change in entropy for the whole network (ΔS_N), ΔS_c should be summed over the distribution of chain lengths, given by Eq. (3).

$$\Delta S_N = \int_0^\infty \Delta S_c (4\nu\beta_j^3 \pi^{-1/2} r_j^2 \exp\{-\beta_j^2 r_j^2\}) dr_j \quad (14)$$

The integrals involved in evaluating Eq. (14) are of the form:

$$\int_0^\infty x^2 \exp\{-ax^2\} dx = \pi^{1/2}/4a^{3/2} \quad (15)$$

$$\int_0^\infty x^4 \exp\{-ax^2\} dx = 3\pi^{1/2}/8a^{5/2} \quad (16)$$

where x is the variable of integration and a is constant. Integrating and substituting in Eqs. (4) and (6) yields,

$$\Delta S_N = -\frac{1}{2}R\nu \{ \bar{r}_j^2 \bar{r}_f^{-2} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) + 2 \ln [(1/3) (\lambda_x^2 + \lambda_y^2 + \lambda_z^2)] \} \quad (17)$$

which in turn leads to the strain-energy function:

$$\begin{aligned} W &= -T \Delta S_N \\ &= \Xi_1 (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) + \Xi_2 \ln (1/3) (\lambda_x^2 + \lambda_y^2 + \lambda_z^2) \end{aligned} \quad (18)$$

where

$$\begin{aligned} \Xi_1 &= \frac{1}{2} \nu RT \bar{r}_j^2 / \bar{r}_f^2 \\ \Xi_2 &= \nu RT \end{aligned} \tag{19}$$

$$\Xi_2 / 2 \Xi_1 = \bar{r}_f^2 / \bar{r}_j^2 \tag{20}$$

In uniaxial deformation along the x-axis, let $\lambda = \lambda_x$, then

$$\lambda_y = \lambda_z = \lambda^{-1/2} \tag{21}$$

and Eq. (18) becomes:

$$W = \Xi_1 (\lambda^2 + 2\lambda^{-1} - 3) + \Xi_2 \ln (\lambda^2 + 2\lambda^{-1}) - \Xi_2 \ln 3 \tag{22}$$

The engineering stress is given by

$$\begin{aligned} f &= dW/d\lambda \\ &= 2 \Xi_1 (\lambda - \lambda^{-2}) + 2 \Xi_2 (\lambda - \lambda^{-2}) / (\lambda^2 + 2\lambda^{-1}) \\ &= 2 (\lambda - \lambda^{-2}) [\Xi_1 + \Xi_2 / (\lambda^2 + 2\lambda^{-1})] \end{aligned} \tag{23}$$

Equation (23) predicts that a plot of G , as defined by Eq. (2) against $(\lambda^2 + 2\lambda^{-1})^{-1}$, should produce a straight line with slope Ξ_2 and zero intercept Ξ_1 .

In a pure shear deformation, where x is the largest principal strain axis, let $\lambda = \lambda_x$; then

$$\begin{aligned} \lambda_y &= \lambda_x^{-1} \\ \lambda_z &= 1 \end{aligned} \tag{24}$$

and Eq. (18) becomes

$$W = \Xi_1 (\lambda^2 + \lambda^{-2} - 2) + \Xi_2 \ln (\lambda^2 + \lambda^{-2} + 1) - \Xi_2 \ln 3 \tag{25}$$

and the engineering stress along the largest principal strain axis becomes

$$\begin{aligned}
 f &= dW/d\lambda \\
 &= 2 \Xi_1 (\lambda - \lambda^{-3}) + [2 \Xi_2 (\lambda - \lambda^{-3}) / (\lambda^2 + \lambda^{-2} + 1)] \\
 &= 2(\lambda - \lambda^{-3}) [\Xi_1 + \Xi_2 (\lambda^2 + \lambda^{-2} + 1)^{-1}] \quad (26)
 \end{aligned}$$

Equation (26) predicts that in pure shear a plot of $\frac{1}{2}f/(\lambda - \lambda^{-3})$ as a function of $(\lambda^2 + \lambda^{-2} + 1)^{-1}$ should produce a straight line with slope Ξ_2 and zero intercept Ξ_1 . It should be noted that both the Gaussian and the two-constant Mooney-Rivlin function [1] predict that $\frac{1}{2}f/(\lambda - \lambda^{-3})$ is independent of λ .

DISCUSSION

Since the above theory has a Gaussian basis, it can only be expected to apply to networks with long, highly flexible chains. The polybutadiene extension data of van der Hoff and Buckler [7] do not exhibit finite extensibility effects until quite high elongations and, since polybutadiene is highly flexible, these data should provide a good first test of the theory. When these data are plotted in the manner suggested by Eq. (23), as is shown in Fig. 2, reasonably straight lines result up to extensions of about $\lambda = 3.5$, or $(\lambda^2 + 2\lambda^{-1})^{-1} = 0.078$, when slight negative deviations from theory start to appear. This would seem to be the limit for the applicability of the Gaussian approximation in this case. The positive deviations which appear at even higher extensions are attributed to finite extensibility.

The molecular interpretations of Ξ_1 and Ξ_2 allow the quantities ν and \bar{r}_f^2/\bar{r}_j^2 to be calculated from the stress/strain data, and these values are reported in Table 1. The values of ν so found, are compared with values estimated from the quantity of crosslinking agent added [7] and from the zero intercept ($2C_1$) on a Mooney-Rivlin plot [7]. Neither set of estimates from stress-strain analysis agree with the chemical estimates. But, agreement is not expected because of the high efficiencies attributed to free radical cure systems at low concentrations. The estimates calculated from the present theory do, however, reflect better the trend in the initial moduli or stiffnesses of the vulcanizates.

A comparison of the chain displacement function for the network chain, $P(\underline{r} = \underline{r}_j)$ given by Eq. (9), with the equivalent expression generally assumed for a free chain, denoted here by $P(r = r_j)$ and

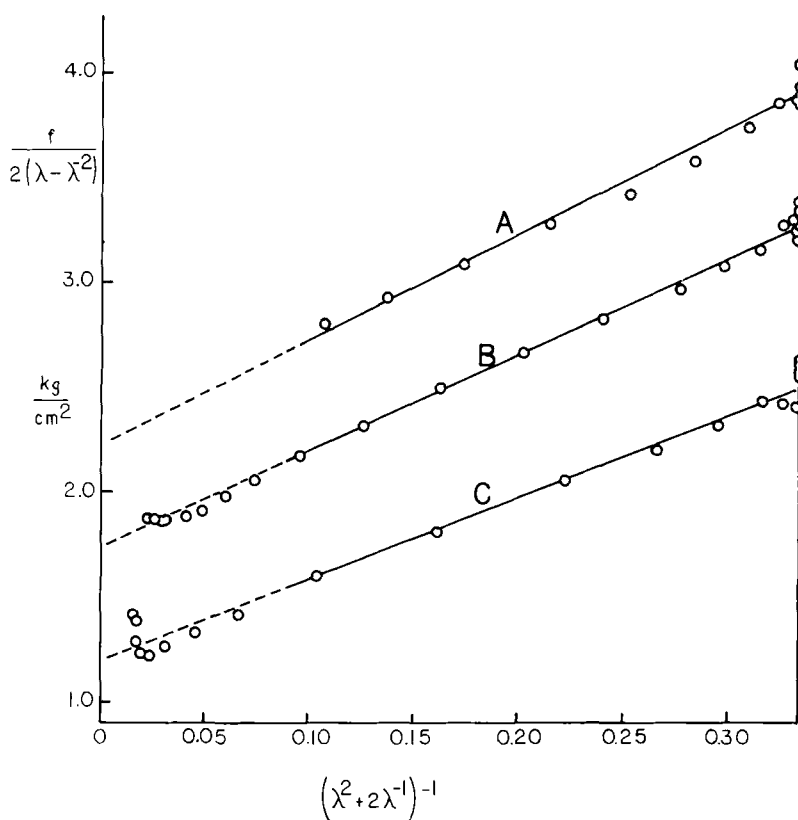


FIG. 2. Reversible, polybutadiene extension data of van der Hoff and Buckler [7], plotted according to Eq. (23) with fitted theoretical lines.

given by Eq. (5), shows that $P(\underline{r} = \underline{r}_j)$ decreases more rapidly with r_j than does $P(r = r_j)$. This means that the introduction of a crosslink onto the end of a free chain will cause the end-to-end distance of the chain to retract. Thus, it is predicted that for normal vulcanization processes, which take place in finite time intervals, the mean squared junction-to-junction distance, \bar{r}_j^2 , will be less than the mean squared end-to-end distance of the equivalent set of free chains, \bar{r}_f^2 . This prediction is supported by the values of the ratio, \bar{r}_f^2/\bar{r}_j^2 , listed in

TABLE 1. Summary of Parameters Obtained from Curve-Fitting Polybutadiene Extension Data (Fig. 2) and Comparison with Values Obtained by Other Techniques

Sample	Ξ_1 (kg/cm ²)	Ξ_2 (kg/cm ²)	$\bar{r}_f^2 / \bar{r}_j^2$	Ξ_2 / RT	ν (mole/liter)	
					Chem. est. ^a	$2C_1 / RT^a$
A	2.23	5.02	1.13	0.199	0.229	0.153
B	1.72	4.70	1.37	0.186	0.078	0.106
C	1.14	4.18	1.84	0.166	0.032	0.066

^aData of van der Hoff and Buckler [7].

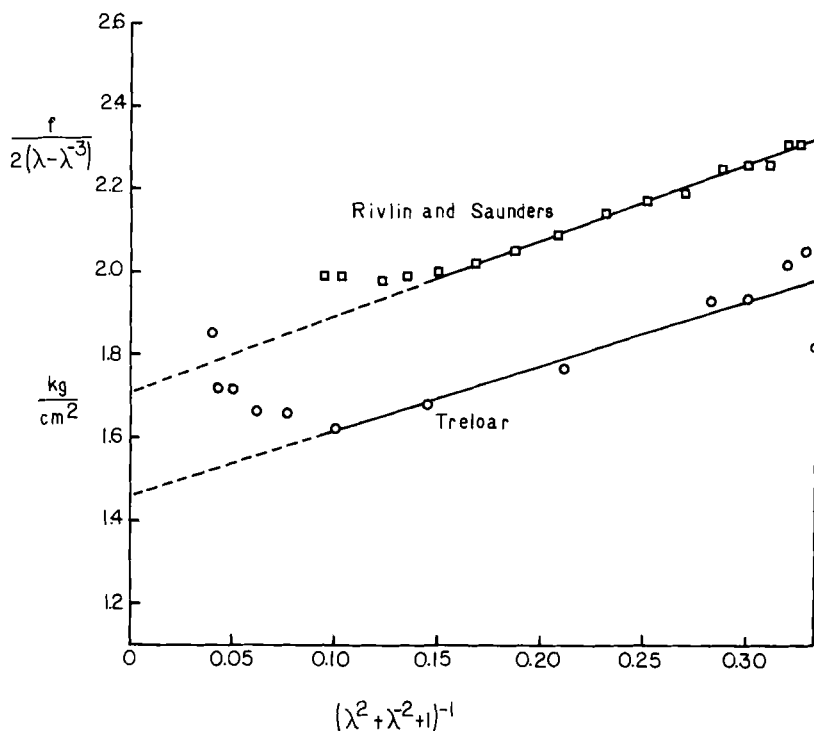


FIG. 3. Reversible, pure shear data of Rivlin and Saunders [8] and Treloar [9] for sulfur-cured natural rubber vulcanizates plotted according to Eq. (26) and fitted with theoretical lines.

Table 1. In a hypothetical, instantaneous vulcanization process, there would be no time for crosslink junction retraction and \bar{r}_f^2 would equal \bar{r}_j^2 . The decrease in the ratio \bar{r}_f^2/\bar{r}_j^2 with increasing crosslink density, as reported in Table 1 is to be expected for two reasons. First, at higher concentrations of crosslinking reagents, the cure proceeds faster allowing less time for crosslink retraction. Secondly, at high crosslink densities, a substantial number of crosslinks are formed after the "gel point" has been reached. After the "gel point", the retraction of new crosslinks becomes restricted by the integrity of the network and the ratio \bar{r}_f^2/\bar{r}_j^2 should tend towards fractional values.

Another test of the theory is presented in Fig. 3, where two sets

TABLE 2. Summary of Parameters Obtained from Curve-Fitting Natural Rubber Pure Shear Data (Fig. 3)

Data source	$\bar{\epsilon}_1$ (kg/cm ²)	$\bar{\epsilon}_2$ (kg/cm ²)	ν (mole/liter)	\bar{r}_f^2/\bar{r}_j^2
Rivlin and Saunders [8]	1.71	1.85	0.073	0.54
Treloar [9]	1.46	1.57	0.062	0.54

of reversible pure shear data for sulfur-cured natural rubber are plotted according to the manner suggested by Eq. (26). These data agree well with the fitted theoretical lines up to the point when finite extensibility effects are evident. The parameters obtained from the curve-fitting procedure are listed in Table 2. Again the estimates of ν are proportional to the initial moduli. Unfortunately, for these data, there are no independent estimates of the crosslink density. The fractional values of \bar{r}_f^2/\bar{r}_j^2 found by this analysis must reflect the high initial molecular weight of natural rubber. A high initial molecular weight would result in a "gel point" very early in the vulcanization process and the large proportion of crosslinks added subsequently would drive the values \bar{r}_f^2/\bar{r}_j^2 below unity to the fractional values found here. The value of \bar{r}_f^2/\bar{r}_j^2 for Treloar's data should be larger than for the other set of data. The identity between the values obtained from the curve fitting is attributed to the fact that the data come from different sources and are not part of a continuous series of vulcanizates prepared under similar conditions.

In conclusion, the conventional Gaussian chain displacement function is criticized because it fails to account for the probability that the chain end-to-end vector lies in the direction of the junction-to-junction vector. Incorporation of this probability into the chain displacement function leads to a new Gaussian strain-energy function which quantitatively describes reversible deformation data in two modes for two different elastomers. The new strain energy function does not contain any parameters which were not inherent in the original function. But, it does permit the calculation of the front factor, \bar{r}_f^2/\bar{r}_j^2 , independently from the calculation of the crosslink density.

REFERENCES

- [1] L. R. G. Treloar, The Physics of Rubber Elasticity, 3rd Ed., Oxford Univ. Press, London, 1975, Chap. 4.

- [2] P. Meares, Polymers, Structure and Bulk Properties, Van Nostrand, London, 1965, Chap. 7.
- [3] P. J. Flory, Principles of Polymer Chemistry, Cornell Univ. Press, Ithaca, N. Y., 1953, pp. 402-409, 464-470.
- [4] J. E. Mark, Rubber Chem. Technol., 48, 495 (1975).
- [5] A. H. Crossland and B. M. E. van der Hoff, J. Macromol. Sci.-Chem., A10, 825 (1976).
- [6] L. R. G. Treloar, The Physics of Rubber Elasticity, 3rd Ed., Oxford Univ. Press, London, 1975.
- [7] B. M. E. van der Hoff and E. J. Buckler, J. Macromol. Sci.-Chem., A1, 747 (1967).
- [8] R. S. Rivlin and D. W. Saunders, Phil. Trans. Roy. Soc., A243, 251 (1951).
- [9] L. R. G. Treloar, Trans. Faraday Soc., 40, 59 (1944).

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