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Theory of Elasticity of Polymer Networks. 3

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ABSTRACT: The theory of elasticity of polymer networks is reformulated with greater generality and improved concision. In particular, the domains of constraint that, due to entanglements and steric requirements of real polymer chains, impede fluctuations of the junctions are introduced in a way that admits of a more rapid attenuation of these constraints than affine transformation of them with strain would allow. Illustrative calculations are presented on the contribution of the constraints to the stress in uniaxial deformation as a function of the extension ratio and the degree of dilation. The calculated reduced force is decidedly nonlinear with the reciprocal of the extension ratio.

Introduction

The elastic free energy of a polymer network that exhibits high elasticity can be expressed as the sum of two terms.[1-3] One represents the elastic free energy ΔA_{ph} of the hypothetical phantom network that is topologically identical with the real one. The other, ΔA_c, is due to the constraints arising from the material properties of real chains densely interspersed in the random network. Thus,

$$\Delta A_{el} = \Delta A_{ph} + \Delta A_c \quad (1)$$

A phantom network is, by definition,[4] one in which the physical effects of the chains between junctions are confined exclusively to the forces they exert on the pairs of junctions to which each is attached. Neither the space-filling characteristics of real chains nor the structural integrity that precludes transection of one chain by another is considered to be operative in the phantom network. The forces delivered to the junctions by the chains originate in the configurational-statistical characteristics of the chains as expressed, for example, in the distribution $W(\mathbf{r})$ of end-to-end vectors $\mathbf{r}$ for chains free of constraints. For chains of the lengths that are usual in representative elastomeric networks, $W(\mathbf{r})$ is Gaussian in good approximation.[5-7] The elastic free energy of a phantom network of Gaussian chains is given rigorously by[4,8]

$$\Delta A_{ph} = (1/2)\xi kT(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \quad (2)$$

where λ_1, λ_2, and λ_3 are principal extension ratios relative to the isotropic state of reference in which the chains assume random configurations corresponding to those of unperturbed, free chains, k is the Boltzmann constant, and ξ is the cycle rank of the network, or the number of independent circuits it contains.[4] With ξ thus defined, eq 2 holds for phantom networks of any functionality and irrespective of their structural imperfections.

In typical polymer networks that exhibit high elasticity the space pervaded by one chain is shared with many others and their associated junctions.[1,4] The degree of interpenetration is high. For illustration, consider the

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region of space demarcated, approximately, by the junctions that are topological first neighbors to a given junction, i.e., by the junctions at the remote ends of the chains emanating from the chosen junction.[9] As many as 50–100 other junctions may occur within this region. Most of them will be connected to the central junction only via pathways consisting of many consecutive chains. Thus, the preponderance of the junctions in the neighborhood of a given junction are not closely related to it in the topological pattern of the network.

Extensive interpenetration of different portions of the network that are topologically remote implies a maze of entanglements in which chains and junctions are inextricably involved. Gross separation of a given junction from its spatial neighbors is therefore precluded regardless of the strain. Entanglements of different parts of the network structure confer coherence not present in a hypothetical phantom network comprising chains that neither preempt space nor obstruct transection by one another.

Parenthetically, it should be noted that we employ the term "entanglement" to denote diffuse interspersion of chains and junctions in ways that render them inseparable. This view contrasts with the more conventional one of discrete entanglements consisting of well-defined loops of one chain about another. These latter are supposed to act effectively as cross-linkages between the specific chains thus intertwined. Objections to discrete entanglements as the principal manifestations of the mutual constraints involving interspersed portions of the network have been pointed out previously.[3,10] Further arguments and evidence against them as significant contributors to the elastic response of polymeric networks are presented in the following paper.[11]

The junctions in a phantom network of Gaussian chains undergo large fluctuations. Their mean-square magnitude $\langle(\Delta R)^2\rangle$ is $(3/8)\langle r^2\rangle_0$ in a tetrafunctional phantom network.[1,4] Thus, fluctuations of junctions, if uninhibited by the constraints aforementioned, would carry them well beyond their nearest spatial neighbors. Fluctuations of this magnitude must be impeded by the profusion of entanglements (diffuse, nonspecific; see above) in a real network. They are hindered also by the steric requirements of surrounding chains. Displacement of a junction requires alterations of the configurations of the chains joined to it, and accommodation of these changes is contingent on coordinated rearrangement of other portions of the network sharing the same region of space. This is necessitated by the dual conditions of dense occupancy of space and avoidance of steric overlaps, with both of which the assembly must comply.

The number of configurations accessible to the real network obviously is greatly reduced by the integrity of the network chains that confers permanency on the mutual entanglement of diverse portions of the network, and also by the steric requirements of real chains. This reduction is inconsequential in the undeformed network in the state of its formation from unperturbed, randomly configured chains. As will be apparent from consideration of an ensemble of such networks, the process of random interlinking of chains entails no change in entropy or free energy attributable to the network and the constraints it imposes. The impedence of the fluctuations depends on the strain, however, and this fact is of foremost importance. Whereas fluctuations of junctions (and other parts) of a Gaussian phantom network are independent of the strain,[4,8] the constraints on configurations in a real network render them strain-dependent. Restrictions on fluctuations, therefore, contribute to the elastic free energy in states of strain, and hence to the stress,[1,4] as was first pointed out by Ronca and Allegra.[12]

The network junctions are the entities most vulnerable to the effects of diffuse entanglements and of steric constraints, inasmuch as each of them is the nexus for the φ chains attached to it, the functionality φ being three or greater. Hence, the constraints on fluctuations in the network may be taken into account, presumably in good approximation, on the assumption that they are incident exclusively on junctions.[1] Constraints directly affecting network chains may be subsumed in the restrictions imposed on junctions in the formal treatment.

The model employed[1-3] subjects each junction to a domain of constraint due to entanglements and to steric requirements of the junction and its associated chains. In the undistorted network, the domain of constraint is spherical. The probability of a fluctuation of the junction from the center of its domain of constraint must decrease with the magnitude of the fluctuation owing to increased obstructions by entanglements and to the necessity of accommodating more drastic relocations of the subtended chains the greater the displacement. The exact form of the probability distribution for these fluctuations is unimportant.[2] It is conveniently taken to be Gaussian.[1]

The centers of the domains must be distributed with respect to the mean positions of the junctions in the phantom network in the manner required to preserve the distribution $W(\mathbf{r})$ for unperturbed chains in the undeformed network (e.g., under the conditions prevailing at its formation). If the network is formed under random, isotropic conditions, as is usual, the theory must comply with this requirement.

Both the mean positions of the domains of constraints and the shapes of the domains were originally assumed[1] to transform affinely (i.e., linearly) with the macroscopic strain. Adoption of this condition is virtually mandatory for the locations of the centers of the domains. It does not necessarily apply to the shapes of the domains. In comparing theory with experiment, it readily became apparent[1,3,13] that the constraints appear to relax somewhat more rapidly with strain than the assumption of affine deformation of the domains under strain, including swelling, would allow. The modification originally suggested to remedy this minor disparity between theory and experiment is found to be flawed when reexamined in detail (see below).

In the present paper we recast the previous theory in a form amenable to the improved refinement here introduced. A consolidated version of the theory is presented that clarifies the consequences of the main assumptions. For full details the reader is referred to the original paper.[1]

Distribution Functions in Strained Networks

Let the set of vectors $\{\bar{\mathbf{R}}\}$ define the locations of the mean positions of the network junctions, in the given macroscopic state of strain, when all constraints due to the material properties of the chains are suppressed; i.e., the $\{\bar{\mathbf{R}}\}$ locate the mean positions of junctions in the phantom network.[4] The point A in Figure 1 marks this mean position of a given junction. Its actual instantaneous position is represented by D located at $\Delta\mathbf{R}$ from A. As James and Guth[8] showed, the fluctuations $\{\Delta\mathbf{R}\}$ of the junctions about their mean positions are independent of the strain for a phantom network of Gaussian chains. The configuration function applicable to these fluctuations is[4,8]

$$Z_\mu = \text{const} \times \exp(-\{\Delta\mathbf{R}\}^{\mathrm{T}}\boldsymbol{\Gamma}_\mu\{\Delta\mathbf{R}\}) \qquad (3)$$

where $\boldsymbol{\Gamma}_\mu$ is the matrix that details the connectivity of the network comprising μ junctions (exclusive of junctions

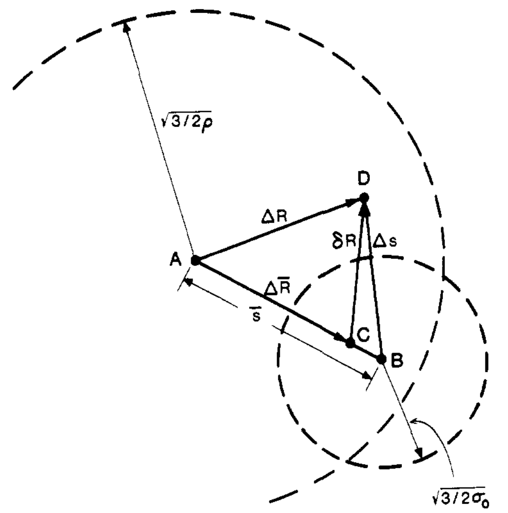

Figure 1. Diagramatic representation of the model. The point A denotes the mean position of the given junction in the phantom network. The outer dashed circle shown in part characterizes the range of fluctuations of the junction in the phantom network, the radius of the circle being equal to $\langle(\Delta R)^2\rangle^{1/2} = (3/2\rho)^{1/2}$. The point B marks the center of the domain of constraint shown by the smaller dashed circle of radius $\langle(\Delta s)^2\rangle^{1/2} = (3/2\sigma_0)^{1/2}$ in the undeformed state. Its center is displaced from A by the vector $\bar{\mathbf{s}}$. The mean position of the given junction under the combined influences of the (phantom) network and the constraints is located at C displaced by $\Delta\bar{\mathbf{R}}$ from A. The instantaneous position of the junction is at D located at $\Delta\mathbf{R}$ from A, at $\Delta\mathbf{s}$ from B, and at $\delta\mathbf{R}$ from C. Distortion of the domain of constraint under strain is not represented in the diagram.

considered to be fixed according to the scheme of James and Guth[8]). Since $\boldsymbol{\Gamma}_\mu$ is symmetric, the quadratic form in eq 3 may be reduced to a sum of squares in the "normal coordinates" specified by the eigenvectors of $\boldsymbol{\Gamma}_\mu$. The configuration function may thus be expressed, in principle, as a product of Gaussians, each a function of one of these coordinates.

Reduction of the quadratic form in eq 3 in the manner indicated obviously is impracticable. In order to avoid the awkwardness of conducting the analysis in terms of unreduced functions for the network as a whole, we adopt the device of ostensibly identifying $\Delta\mathbf{R}$ for a typical junction with one of the normal (vector) coordinates. The distribution function for this coordinate, represented as the vector $\Delta\mathbf{R}$, is

$$\mathcal{R}(\Delta\mathbf{R}) = (\rho/\pi)^{3/2}\exp[-\rho(\Delta R)^2] \tag{4}$$

where

$$\rho = 3/2\langle(\Delta R)^2\rangle \tag{5}$$

The configuration function Z_μ is then the product of Gaussians like eq 4, one for each normal coordinate, or for each junction. Inasmuch as the entanglement constraints incident on the various junctions are considered below to be identical, it will be apparent that this procedure can be employed without error.

Although the magnitude of ρ is not required, we note in passing that the Gaussian parameter governing the fluctuations of a given junction in the absence of any specification of other fluctuations in the phantum network is[1,4]

$$\rho_1 = 3\varphi(\varphi - 2)/2(\varphi - 1)\langle r^2\rangle_0 \tag{6}$$

where φ is the functionality of the junctions and $\langle r^2\rangle_0$ is the mean-square length of a free chain. Thus, for a tetrafunctional phantom network the numerical factor in eq 6 is four. It would be incorrect, however, to identify ρ with ρ_1; the former parameter should represent normal modes of the network as a whole and not the fluctuation of one junction in the absence of other constraints.

The sphere of radius equal to the root-mean-square dispersion $\langle(\Delta R)^2\rangle^{1/2}$ of the junction fluctuations in the phantom network is represented by the large dashed circle in Figure 1. Let the constraints incident on junction i due to entanglements with neighboring chains and to steric requirements of real chains be centered at point B located at $\bar{\mathbf{s}}_i$ from the mean position of that junction in the corresponding phantom network. The mean range of these constraints is represented by the smaller dashed circle in Figure 1. Under the combined influences of the network junctions and the constraints, the mean position of junction i is located at point C displaced by $\Delta\bar{\mathbf{R}}_i$ from A. The displacements of the instantaneous position D of the junction from B and from C are denoted by vectors $\Delta\mathbf{s}_i$ and $\delta\mathbf{R}_i$, respectively; see Figure 1.

The set of vectors $\{\bar{\mathbf{s}}\}$ locating the centers of the domains of constraint relative to the mean positions of the corresponding junctions in the phantom network will be determined in due course from the requirement that the distribution $\mathcal{R}(\Delta\mathbf{R})$ must be unaffected by the constraints under the conditions prevailing at formation of the network from a system of random chains in unperturbed configurations.[14] The state of reference ordinarily is so defined as to match these conditions.

Let $\mathcal{S}(\Delta\mathbf{s})$ represent the distribution of the fluctuations $\{\Delta\mathbf{s}\}$ of the junctions from the centers of their respective domains of constraint that would obtain if the junctions were subject only to these constraints, i.e., if network forces due to the action of each chain on the junctions to which it is attached were somehow suspended. The form of the distribution $\mathcal{S}(\Delta\mathbf{s})$ is of little importance.[1,2] It is conveniently taken to be Gaussian; i.e., we express it by

$$\mathcal{S}(\Delta\mathbf{s}) = \pi^{-3/2}(\det\sigma_\lambda)^{1/2}\exp[-(\Delta\mathbf{s})^{\mathrm{T}}\sigma_\lambda(\Delta\mathbf{s})] \tag{7}$$

where σ_λ is the "stiffness" tensor governing the Gaussian distribution, generally ellipsoidal, at the strain defined by the tensor λ comprising the macroscopic extension ratios.

This domain of constraint for the undeformed network is depicted by the smaller dashed circle of radius $\langle(\Delta s)^2\rangle^{1/2}$ in Figure 1. The dependence of σ_λ on λ is postponed for later consideration.

Inasmuch as the primary distributions above are Gaussian, all other distributions derived from them must likewise be Gaussian.[1] They may be resolved therefore into component distributions along principal axes of the strain, and all equations can be rendered in scalar form. Replacing $\Delta\mathbf{R}$ by ΔX and $\Delta\mathbf{s}$ by Δx, we thus obtain

$$\mathcal{R}(\Delta X) = (\rho/\pi)^{1/2}\exp[-\rho(\Delta X)^2] \tag{4$'$}$$

$$\langle(\Delta X)^2\rangle = 1/2\rho \tag{5$'$}$$

$$\mathcal{S}(\Delta x) = (\sigma_{\lambda_x}/\pi)^{1/2}\exp[-\sigma_{\lambda_x}(\Delta x)^2] \tag{7$'$}$$

where σ_{λ_x} is the x component of σ_λ; it depends specifically on λ_x in a manner to be discussed later. The notation is simplified below by replacing λ_x with λ and σ_{λ_x} with σ_λ.

The a priori probability of a displacement $\Delta\mathbf{R}_i$ of junction i in the real network from its mean position in the corresponding phantom network is given by the product of eq 4 and 7, with $\Delta\mathbf{s}_i$ in the latter equation appropriately replaced by $\Delta\mathbf{R}_i - \bar{\mathbf{s}}_i$. The normalized result that follows from eq 4$'$ and 7$'$ for the X coordinate is expressed by

$$\mathcal{P}(\delta X_i) = [(\rho + \sigma_\lambda)/\pi]^{1/2}\exp[-(\rho + \sigma_\lambda)(\delta X_i)^2] \tag{8}$$

where (see Figure 1)

$$\delta X_i = \Delta X_i - \Delta \bar{X}_i \tag{9}$$

with $\Delta \bar{X}_i$ given by

$$\Delta \bar{X}_i = (1 + \rho/\sigma_\lambda)^{-1}\bar{x}_i \tag{10}$$

It will be apparent that $\Delta \bar{X}_i$ measures the displacement of the mean position of junction i in the real network from its mean position in the phantom network, this displacement being due to the constraints imposed by the surroundings when the system is subject to a strain denoted by the principal extension ratio $\lambda = \lambda_x$. The displaced mean position is represented by point C in Figure 1. According to eq 10, the displacement of the mean position of junction i due to the constraints incident on it is proportional to the vector $\bar{\mathbf{s}}_i$ (with components $\bar{x}_i$, $\bar{y}_i$, and $\bar{z}_i$) specifying the location of the center of the constraints. The a priori probability of a fluctuation δX_i measured therefrom (see Figure 1) is given by eq 8.

It remains to specify the distribution $H(\bar{x})$ of mean relative positions of the centers of constraint. In view of eq 10 this distribution is directly related to the distribution $\Theta(\Delta\bar{X})$ of the relative displacements of the mean positions of junctions due to the constraints. The actual, or instantaneous, distribution of the components $\{\Delta X\}$ of the vectors $\{\Delta \mathbf{R}\}$ that locate the junction in the real network under strain λ relative to their mean positions in the phantom network is given by the convolution of $\mathcal{P}(\delta X)$ with $\Theta(\Delta\bar{X})$, i.e., by

$$\mathcal{R}_*(\Delta X) = \int \mathcal{P}(\delta X) \times \Theta(\Delta\bar{X})\, d\Delta\bar{X} \tag{11}$$

The symbol for this distribution is distinguished from $\mathcal{R}$ for the a priori probability function for the phantom network by the asterisk subscript. In the reference state $\mathcal{R}_*(\Delta X)$ must equate to $\mathcal{R}(\Delta X)$ as expressed by eq 4′, as was pointed out above. It follows that $\Theta(\Delta\bar{X})$ also must be Gaussian in this state. In view of eq 10, $H(\bar{x})$ must likewise be Gaussian in the state of reference.[1] In due course we adopt the plausible assumption that the centers of the steric constraints are affine (i.e., linear) in the macroscopic strain. Under this assumption, $H(\bar{x})$ will be required to remain Gaussian at all strains. For the present, we introduce the less drastic assumption that $H(\bar{x})$ remains Gaussian for all strains, without stipulating that its variance shall be affine in λ. It follows at once (see eq 10 and 11) that $\Theta(\Delta\bar{X})$ and $\mathcal{R}_*(\Delta X)$ must remain Gaussian for all strains.

Accordingly, we write

$$H(\bar{x}) = (\eta_\lambda/\pi)^{1/2} \exp(-\eta_\lambda \bar{x}^2) \tag{12}$$

Substitution of eq 10 in eq 12 yields

$$\Theta(\Delta\bar{X}) = (\eta_\lambda/\pi)^{1/2}(1 + \rho/\sigma_\lambda) \exp[-\eta_\lambda(1 + \rho/\sigma_\lambda)^2(\Delta\bar{X})^2] \tag{13}$$

with σ_λ dependent on λ in a manner yet to be specified.

Substitution of eq 8 and 13 in eq 11 and execution of the integration lead to

$$\mathcal{R}_*(\Delta X) = (\rho_{*\lambda}/\pi)^{1/2} \exp[-\rho_{*\lambda}(\Delta X)^2] \tag{14}$$

where

$$\rho_{*\lambda} = (\rho + \sigma_\lambda)^2/(\rho + \sigma_\lambda + \sigma_\lambda^2/\eta_\lambda) \tag{15}$$

which can be rearranged to

$$\rho/\rho_{*\lambda} = 1 + (\sigma_\lambda/\rho)[(\sigma_\lambda/\rho)(\rho\eta_\lambda^{-1} - 1) - 1]/(1 + \sigma_\lambda/\rho)^2 \tag{16}$$

Compliance with the requirement that the actual distribution $\mathcal{R}_*(\Delta X)$ in the state of reference must conform to $\mathcal{R}(\Delta X)$ for the phantom network dictates that

$$\eta_0^{-1} = \rho^{-1} + \sigma_0^{-1} \tag{17}$$

Replacement of $\rho\eta_\lambda^{-1}$ in eq 16 by

$$\rho/\eta_\lambda = (\eta_0/\eta_\lambda)(1 + \rho/\sigma_0) \tag{18}$$

which follows from eq 17, yields

$$\rho/\rho_{*\lambda} = 1 + \frac{(\sigma_\lambda/\rho)^2(\eta_0/\eta_\lambda - 1) + (\sigma_\lambda/\rho)[(\eta_0/\eta_\lambda)(\sigma_\lambda/\sigma_0) - 1]}{(1 + \sigma_\lambda/\rho)^2} \tag{19}$$

Convolution of $H(\bar{x})$ as given by eq 12 with $\mathcal{P}(\delta X)$ given by eq 8 yields the distribution $\mathcal{S}_*(\Delta x)$ of displacements Δx of junctions in the strained network from the centers of their domains of constraint. The result obtained after making the substitution $\delta X = \Delta X - \Delta\bar{X} = \Delta x + \bar{x}/(1 + \sigma_\lambda/\rho)$ is

$$\mathcal{S}_*(\Delta x) = (\sigma_{*\lambda}/\pi)^{1/2} \exp[-\sigma_{*\lambda}(\Delta x)^2] \tag{20}$$

where $\sigma_{*\lambda}$ is defined by

$$\sigma_\lambda/\sigma_{*\lambda} = [(\sigma_\lambda/\rho)^2 + \sigma_\lambda/\rho + \sigma_\lambda/\eta_\lambda]/(1 + \sigma_\lambda/\rho)^2 \tag{21}$$

or

$$\sigma_\lambda/\sigma_{*\lambda} = 1 + [(\sigma_\lambda/\rho)(\rho\eta_\lambda^{-1} - 1) - 1]/(1 + \sigma_\lambda/\rho)^2 \tag{22}$$

It follows from eq 16 that

$$\sigma_\lambda/\sigma_{*\lambda} - 1 = (\sigma_\lambda/\rho)^{-1}(\rho/\rho_{*\lambda} - 1) \tag{23}$$

Hence, from eq 19 one obtains

$$\sigma_\lambda/\sigma_{*\lambda} = 1 + \frac{(\sigma_\lambda/\rho)(\eta_0/\eta_\lambda - 1) + (\eta_0/\eta_\lambda)(\sigma_\lambda/\sigma_0) - 1}{(1 + \sigma_\lambda/\rho)^2} \tag{24}$$

Contribution to the Elastic Free Energy from Constraints on Fluctuations

The contribution ΔA_c to the elastic free energy from the steric constraints comprises two terms due, respectively, to (i) distortion of the fluctuations of junctions from the distribution $\mathcal{R}(\Delta\mathbf{R})$ in the phantom network to $\mathcal{R}_*(\Delta\mathbf{R})$ in the real network, and (ii) alteration of the distribution of displacements $\Delta\mathbf{s}$ of the junctions about the centers of the constraints considered to be incident on them from $\mathcal{R}(\Delta\mathbf{s})$ to $\mathcal{R}_*(\Delta\mathbf{s})$. The partition function associated with the former contribution, expressed for one dimension, is

$$\Omega_{\Delta X} = \mu!\prod_j \omega_j^{\mu_j}/\mu_j! = \prod_j (\omega_j\mu/\mu_j)^{\mu_j} \tag{25}$$

where μ is the total number of junctions, μ_j is the number of them located at ΔX_j to $\Delta X_j + \delta(\Delta X_j)$ from their mean positions in the phantom network, and ω_j is the a priori probability of a displacement in this range. Since

$$\omega_j = \mathcal{R}(\Delta X_j)\delta(\Delta X_j)$$

and

$$\mu_j/\mu = \mathcal{R}_*(\Delta X_j)\delta(\Delta X_j)$$

it follows from eq 4′ and 14 that

$$\ln \Omega_{\Delta X} = (\mu/2) \ln (\rho/\rho_{*\lambda_x}) - (\rho - \rho_{*\lambda_x})\sum \mu_j(\Delta X_j)^2 = (\mu/2)[\ln (\rho/\rho_{*\lambda_x}) - (\rho/\rho_{*\lambda_x} - 1)] \tag{26}$$

Summing over the principal axes $t = x, y, z$, one obtains for the total contribution from this source to the reduced elastic free energy[1]

$$(kT)^{-1}\Delta A_{\Delta\mathbf{R}} = (\mu/2)\sum_t [B_t - \ln (B_t + 1)] \tag{27}$$

where

$$B_t = \rho/\rho_{*\lambda_t} - 1 \tag{28}$$

Treatment of the distortion of the distribution of vectors $\Delta\mathbf{s}$ using eq 7′ and 20 similarly yields

$$\ln \Omega_{\Delta X} = (\mu/2)[\ln(\sigma_{\lambda_x}/\sigma_{*\lambda_x}) - (\sigma_{\lambda_x}/\sigma_{*\lambda_x} - 1)] \tag{29}$$

and (see eq 23)

$$(kT)^{-1}\Delta A_{\Delta s} = (\mu/2)\sum_t [g_t B_t - \ln(g_t B_t + 1)] \tag{30}$$

where

$$g_t = \rho/\sigma_{\lambda_t} \tag{31}$$

Combination of eq 27 and 30 gives

$$(kT)^{-1}\Delta A_c = (\mu/2)\sum_t \{(1 + g_t)B_t - \ln[(B_t + 1)(g_t B_t + 1)]\} \tag{32}$$

for the reduced elastic free energy due to the constraints. Substitution of ΔA_c together with ΔA_{ph} according to eq 2 into eq 1 gives the total elastic free energy.

Relationship of Stress to Strain

Principal components of the stress are given by[1]

$$\tau_t = 2V^{-1}\lambda_t^2(\partial\Delta A_{el}/\partial\lambda_t^2) \tag{33}$$

The contribution of the constraints follows as

$$\tau_{c;t} = 2V^{-1}\lambda_t^2\dot{A}_{c;t} \tag{34}$$

where

$$\dot{A}_{c;t} \equiv \partial\Delta A_c/\partial\lambda_t^2 \tag{35}$$

It follows from eq 32 that

$$\dot{A}_{c;t} = (\mu/2)kTK(\lambda_t^2) \tag{36}$$

where

$$K(\lambda^2) = B[\dot{B}(B + 1)^{-1} + g(\dot{g}B + g\dot{B})(gB + 1)^{-1}] \tag{37}$$

$$\dot{B} \equiv \partial B/\partial\lambda^2 \tag{38}$$

$$\dot{g} \equiv \partial g/\partial\lambda^2 \tag{39}$$

the subscript t identifying the principal axis being omitted.

For uniaxial deformations it is convenient to define the strain by the axial elongation α at the prevailing volume V, which may differ from the volume V^0 in the reference state. Then the principal extensions λ_t relative to the state of reference are

$$\lambda_1 = \alpha(V/V^0)^{1/3}$$
$$\lambda_2 = \lambda_3 = \alpha^{-1/2}(V/V^0)^{1/3} \tag{40}$$

The contribution of the constraints to the tension f is given by

$$\begin{aligned} f_c &= L^{-1}(\partial\Delta A/\partial\alpha)_V \\ &= (L^0)^{-1}(V/V^0)^{-1/3}\sum_t \dot{A}_{c;t}\partial\lambda_t^2/\partial\alpha \\ &= (\mu kT/L^0)(V/V^0)^{1/3}[\alpha K(\lambda_1^2) - \alpha^{-2}K(\lambda_2^2)] \end{aligned} \tag{41}$$

Recalling that the tension for a phantom network under uniaxial deformation is

$$f_{ph} = (\xi kT/L^0)(V/V^0)^{1/3}(\alpha - \alpha^{-2}) \tag{42}$$

we obtain

$$f_c/f_{ph} = (\mu/\xi)[\alpha K(\lambda_1^2) - \alpha^{-2}K(\lambda_2^2)](\alpha - \alpha^{-2})^{-1} \tag{43}$$

For a perfect tetrafunctional network $\mu/\xi = 1$.

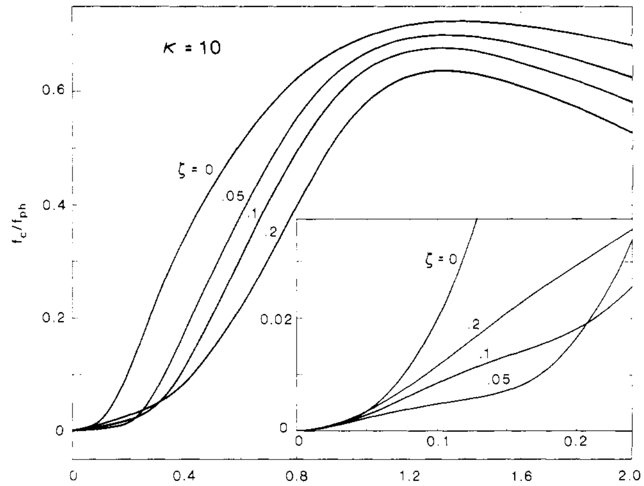

Figure 2. Ratio of the tensile force f_c due to constraints on junction fluctuations to the force f_{ph} for the corresponding phantom network plotted against the reciprocal of the extension ratio α. The curves have been calculated for $\kappa = 10$ and the values of ζ indicated. The inset shows peculiarities of the functional dependence in the range of high extension (small α^{-1}) on an enlarged scale. Calculations are for a perfect tetrafunctional network with $\mu/\xi = 1$ in the absence of diluent ($V/V^0 = 1$).

Effect of Deformation on the Domains of Constraint

Implementation of the relationships derived above requires specification of the dependences of η_λ/η_0 and σ_λ/σ_0 on λ. The former ratios for the three principal axes characterize the dispersion of the centers of the domains of constraint under strain; the latter ratios characterize the alteration in the size and shape of the domains.

That the centers of the domains of steric constraints should be affine in the macroscopic strain seems inescapable. Hence, as hinted earlier, we let

$$\eta_\lambda/\eta_0 = \lambda^{-2} \tag{44}$$

for each principal axis.

The dependence of σ_λ on λ is more problematical. Previously,[1-3] we have taken the deformation of the domains of constraint likewise to be affine in the strain. On this basis $\sigma_\lambda/\sigma_0 = \lambda^{-2}$. It was recognized from inspection of experimental results, however, that the constraints appear to be attenuated more rapidly with strain, or with volume dilation by swelling, than this relation stipulates. Inhomogeneities in structure and topology could cause distension of the domains with strain to exceed calculations based on affine deformation of them. The relation

$$\sigma_\lambda/\sigma_0 = \lambda^{-p} \tag{45}$$

with $p > 2$ was offered as a possible alternative[1] to the equation above. Calculations were presented for $p = 3$ and 4 as well as for $p = 2$.[1,13] Use of eq 45 with $p \neq 2$, in conjunction with eq 44 leads to a free energy ΔA_c which does not vanish as $(\sigma_0/\rho) \to 0$,[15] as may readily be shown.

As an alternative means of modifying the dependence of σ_λ on λ, we express the variance $1/\sigma_\lambda$ of the steric constraints as a series in powers of λ commencing with λ^2; i.e., we let

$$1/\sigma_\lambda = \lambda^2/\sigma_1 + \lambda^3/\sigma_2 + ... \tag{46}$$

Then

$$1/\sigma_0 = 1/\sigma_1 + 1/\sigma_2 + ... \tag{47}$$

Truncation at the cubic term gives

$$\sigma_0/\sigma_\lambda = \lambda^2[1 + \kappa\zeta(\lambda - 1)] \tag{48}$$

where

$$\kappa = \sigma_0/\rho$$
$$\zeta = \rho/\sigma_2 \quad (49)$$

The definition of κ corresponds to that given previously;[1] departures from affine transformation of the a priori probability function are introduced through the parameter ζ. In the limit of vanishing constraints, i.e., as $\kappa \to 0$, the deformations of the domains of constraint must be affine. It follows that $\kappa\zeta = (\sigma_0/\sigma_2) \to 0$ and $(\sigma_0/\sigma_\lambda) \to \lambda^2$ in this limit. Substitution of this result in eq 19 gives $B = 0$ according to eq 28. Hence, ΔA_c vanishes and the anomaly of the previous formulation using eq 45 is circumvented. The obvious requirement that the network must conform to phantom behavior in the limit is then fulfilled. In the opposite limit where fluctuations are suppressed by taking $\kappa = \infty$ and $\zeta = 0$, the elastic free energy converges to the expression for affine transformation of junctions, as was found previously.[1]

Substitution of eq 44 and 48 into eq 19 yields (see eq 28)

$$B = (\lambda - 1)(1 + \lambda - \zeta\lambda^2)/(1 + g)^2 \quad (50)$$

where (see eq 31 and 48)

$$g = (\kappa\sigma_\lambda/\sigma_0)^{-1} = \lambda^2[\kappa^{-1} + \zeta(\lambda - 1)] \quad (51)$$

Also

$$\dot{B}/B = [2\lambda(\lambda - 1)]^{-1} + (1 - 2\zeta\lambda)[2\lambda(1 + \lambda - \zeta\lambda^2)]^{-1} - 2\dot{g}(1 + g)^{-1} \quad (52)$$

$$\dot{g} = g\lambda^{-2} + (\zeta/2)\lambda = \kappa^{-1} - \zeta(1 - 3\lambda/2) \quad (53)$$

Numerical Calculations

Specification of κ and ζ enables one to calculate B, g, $\dot{B}$, and $\dot{g}$ according to eq 50, 51, 52, and 53, respectively, as functions of λ. Substitution of these quantities in eq 37 gives $K(\lambda^2)$, the function required for calculation of the stress according to eq 34 and 36. Similarly, the relative contribution f_c/f_{ph} of entanglement and steric constraints to the tension in uniaxial deformation may be calculated as a function of the linear extension ratio α and the dilation V/V^0 through use of eq 40, 37, and 43. Results of calculations of f_c/f_{ph} for $\kappa = 10$ are shown in Figure 2 as functions of α^{-1} for the several values of ζ indicated. All calculations were carried out for a perfect tetrafunctional network for which $\mu/\xi = 1$ in eq 43. Increase of ζ causes f_c/f_{ph} to decrease more precipitously with extension α in the range $\alpha^{-1} < 1$ (i.e., $\alpha > 1$). As found previously,[1] this ratio that measures the departure from phantom network behavior reaches a maximum in the range of small compressions ($\alpha^{-1} > 1$) and then decreases gradually with further compression, i.e., with further increase in α^{-1}. The rate of this gradual decrease increases with ζ.

Corresponding calculations for $\kappa = 5$ are shown in Figure 3. Similar features are exhibited. As in Figure 2, the height of the maximum is decreased slightly by increase in ζ. The calculated decrease in f_c/f_{ph} with decrease in α^{-1} in the extension range $\alpha^{-1} < 1$ is by no means linear as the Mooney–Rivlin formulation would require, and substantial errors may arise from its use to determine the intercept according to accepted practice.

The effect of dilation is shown in Figure 4 for $\kappa = 10$ with $\zeta = 0$ (dashed curves) and with $\zeta = 0.10$ (solid curves). The magnitude of f_c/f_{ph} decreases with the dilation ratio V/V^0 indicated for each curve. The curves remain sigmoidal for

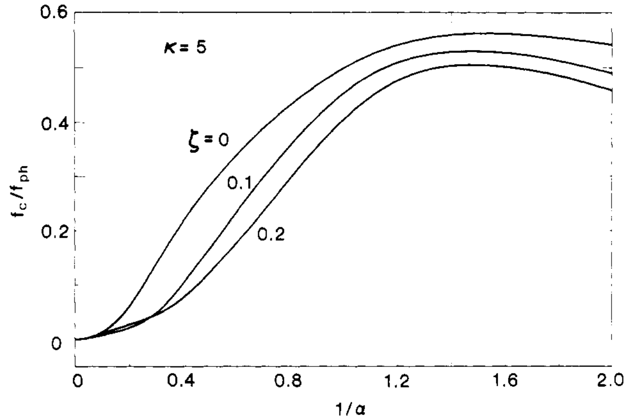

Figure 3. Calculations corresponding to those in Figure 2 with $\kappa = 5$.

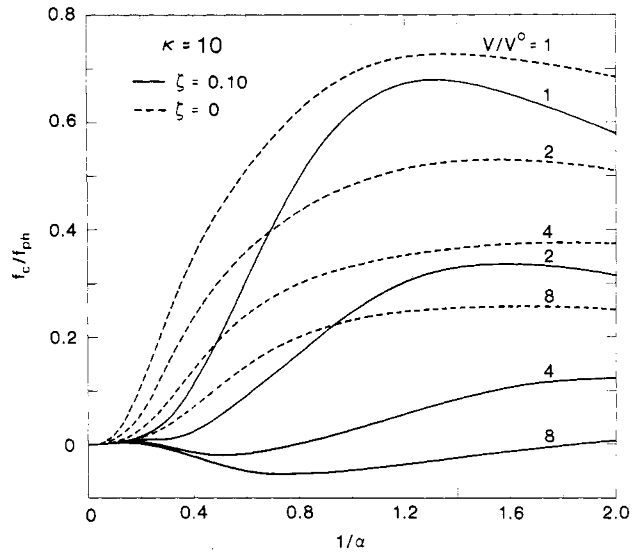

Figure 4. Effect of dilution, denoted by V/V^0, on f_c/f_{ph} for $\kappa = 10$. Dashed and solid curves are for $\zeta = 0$ and 0.10, respectively. The curves for $V/V^0 = 1$ correspond to those in Figure 2.

$\zeta = 0$. For $\zeta = 0.1$ a minimum appears for $V/V^0 > 0$. With increase in V/V^0 it is displaced toward larger α^{-1}, and f_c becomes negative in the vicinity of the minimum. At the highest dilation, f_c/f_{ph} is negative out to $\alpha^{-1} = 1$ and beyond. Thus, the reduced force $[f] = f/(V/V^0)^{1/3}(\alpha - \alpha^{-2})$ is predicted to increase with extension, in contrast to its behavior in undiluted systems. This prediction is confirmed by experiments on highly swollen networks, as the results treated in the following paper[11] show.

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(14) The present theory is not applicable as it stands to networks formed in states of strain such that the configurations of the chains are not random and not isotropically distributed.
(15) Calculations presented previously[1,13] for $p > 2$ are in error owing to omission of the terms of eq 19 and 24 that involve the quantity $(\eta_0/\eta_\lambda)(\sigma_\lambda/\sigma_0) - 1$. These terms vanish only when $(\sigma_0/\sigma_\lambda) = \eta_0/\eta_\lambda$. The omission does not seriously vitiate the calculations presented previously[1,13] for $\eta_0/\eta_\lambda = \lambda^2$ and $\sigma_0/\sigma_\lambda = \lambda^p$ with $p > 2$. This error is avoided in the present rendition. We are grateful to Dr. R. W. Brotzman and Professor B. E. Eichinger[16] for turning our attention to the omission of this term.
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Relationships between Stress, Strain, and Molecular Constitution of Polymer Networks. Comparison of Theory with Experiments

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ABSTRACT: The theory recast in the preceding paper accounts for the relationship of the equilibrium stress to strain for elastomeric networks within probable limits of experimental error throughout the range of deformation accessible to experiment, including biaxial extension, pure shear, and torsion as well as simple elongation and compression. Effects of dilation by swelling on the stress–strain relationship are well reproduced by the same set of parameters: the reduced force $[f^*_{ph}]$ for the equivalent phantom network, and κ and ζ that characterize the local constraints on fluctuations of junctions and their dependence on strain. Two of these three parameters appear to be related by $\kappa[f^*_{ph}]^{1/2}$ = const, as follows from the premise that κ should depend on the degree of interpenetration in the network. Values of $[f^*_{ph}]$ deduced from elastic and swelling measurements agree approximately with "chemically" determined reduced forces given by $\xi kT/V^0$. It follows that one of the parameters is determinable independently and that discrete ("trapped") entanglements do not contribute appreciably to the stress.

Introduction

Experimental results on (i) the relationship of stress to strain, (ii) the effect of dilation on the stress–strain relationship in simple extension, and (iii) the effect of the degree of cross-linking on the form of this relationship are examined in this paper according to the theory presented in the preceding one.[1] For the interpretation of (iii), we introduce the physically plausible postulate that the parameter κ should be proportional to the degree of interpenetration in the network.

Most of the experimental results treated below pertain to uniaxial deformations. They are presented in terms of the reduced force, or reduced nominal stress, defined by

$$[f^*] = f^*(V/V^0)^{-1/3}(\alpha - \alpha^{-2})^{-1} \quad (1)$$

where f^* is the tensile force per unit area measured in the reference state, V^0 is the volume in that state, V is the volume of the system at measurement, and α is the extension ratio relative to the length of the sample when isotropic at the same volume V. According to theory,[1,2]

$$[f^*] = [f^*_{ph}](1 + f_c/f_{ph}) \quad (2)$$

where f_c is the contribution to the force f from the constraints on fluctuations of junctions,[1,2] f_{ph} is the force that would be exerted by the equivalent phantom network at the same elongation, and $[f^*_{ph}]$ is the reduced force in the limit of high extension (and/or dilution) where f_c/f_{ph} vanishes. Thus, $[f^*_{ph}]$ is the reduced force for the equivalent phantom network.

According to theory,[2,3]

$$[f^*_{ph}] = \xi kT/V^0 \quad (3)$$

where ξ is the cycle rank of the network; see eq 42 of the preceding paper.[1] Implicit in identification of ξ with the value that follows directly from the chemical constitution of the network is the assumption that the effective degree of connectivity is not enhanced by discrete entanglements[1] of the kind often assumed to entwine one chain of the network specifically with another. Specific entanglements of this kind are to be distinguished from the diffuse entanglements addressed by the theory[1,2] under consideration. In the fourth section below, we examine the validity of eq 3 by comparing values of $[f^*_{ph}]$ deduced according to eq 2 from stress–strain–swelling measurements with those calculated from chemically determined "circuit densities" ξ/V^0.

Dependence of Stress on Strain

Stresses for uniaxial deformation covering a wide range of extension ratios α can be determined by combining measurements in simple extension with measurements on the inflation of a sheet of the rubber.[4–7] The latter experiments require measurement of the inflation pressure, of the radius of curvature at the pole of the inflated sheet, and of the linear deformation in the plane of the sheet and likewise at the pole. The strains may be expressed either as equibiaxial extensions or, preferably for purposes at hand, as uniaxial compressions. Measurements in compression and in elongation should be performed on samples from the same specimen of rubber.

Rivlin and Saunders[6] applied this procedure to vulcanized natural rubber. Their measurements in extension cover the range from $\alpha = 1.1$ to 3, and in compression from $\alpha = 0.85$ to 0.14, i.e., equibiaxial extensions from $\alpha_2 = \alpha_3 = 1.08$ to 2.6. Similar experiments were reported a few years ago by Pak and Flory[7] on networks of poly(dimethylsiloxane), PDMS, cross-linked using dicumyl peroxide at 165 °C. The experiments covered a fourfold range

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