A Diffused-Constraint Theory for the Elasticity of Amorphous Polymer Networks. 1. Fundamentals and Stress–Strain Isotherms in Elongation

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ABSTRACT: The theory proposed is an extension of the constrained-junction theory of Flory and Erman and the subsequent constrained-chain theory of Erman and Monnerie. As in these earlier theories, the elastic free energy ΔA_{el} is calculated as the sum $\Delta A_{el} = \Delta A_{ph} + \Delta A_c$, where ΔA_{ph} is the contribution for a phantom network, and the additional term ΔA_c is due to the effects of constraints on fluctuations. Instead of allowing the constraints to affect the fluctuations of only the junctions or the centers of mass of the network chains, however, the constraints are now applied continuously along the chains. The results of illustrative calculations on this "diffused-constraint" model are compared with the corresponding results from the earlier theories.

Introduction

The primary aim of the molecular theories of rubberlike elasticity is to provide an equation of state which expresses the elastic force as a function of the thermodynamic parameters of the system (such as extent of deformation, temperature, and degree of network swelling) and its molecular parameters (such as the number of network chains, their mean-square dimensions, the functionality of the cross links, and chain topology).[1–7] Two major theories in this area are the "affine" (in which the junctions move linearly with the macroscopic deformation) and the "phantom" (in which junction fluctuations cause significant departures from affineness). They represent limiting behavior in that the constraints on junction fluctuations are at a maximum in the affine theory and at a minimum in the phantom theory. Experimental data generally lie between these two limits, which has prompted a considerable amount of additional work in which the junctions are constrained in different ways, to obtain better agreement between theory and experiment.[1–7]

The first attempt along these lines was to place the effects of the constraints entirely at the junction points themselves in what is called the "constrained-junction" theory of Flory and Erman.[3,5,8] Comparing the results of this theory with experiment provided estimates of the degrees of constraint and thus of the magnitudes of the junction fluctuations. Experimental values of these magnitudes have been obtained by neutron spin–echo measurements[9–11] and found, however, to be significantly larger than those indicated by the constrained-junction theory. This suggested that it would be more realistic to move some of the effects of the constraints from the cross-links to other parts of the network chains. This was done by having the constraints affect fluctuations of the centers of mass of the chains, in the "constrained-chain" approach by Erman and Monnerie.[12]

This type of network model can be made even more realistic by applying the constraints *continuously* along the chains, and the treatment of such a "diffused-constraint" model is the purpose of the present investigation. The development proceeds by placing this approach into context by first describing the classic affine and phantom models and the subsequent constrained-junction and constrained-chain models. The diffused-constraint model is then described and treated to obtain the most general expression for the elastic free energy. It is then applied to the calculation of stress–strain isotherms in elongation, and the results are compared with those from some of the earlier theories.

Evolution of Some of the Molecular Theories

The Affine Model. The simplest theory of rubberlike elasticity was developed by Kuhn[13–15] and improved by Treloar.[2,16] It is based on the assumption that an elastomeric network consists of ν freely-jointed Gaussian chains and that the mean-square end-to-end vector $\langle r^2 \rangle_0$ of the network chains in the undeformed state is the same as that of the un-cross-linked free chains. It is also assumed that there is no change in volume on deformation and that the network junctions displace affinely with macroscopic deformation. The intermolecular interactions of chains are neglected. This so-called affine model of a polymer network leads to the following equation for the elastic energy ΔA_{el}:

$$\Delta A_{el} = \frac{1}{2}\nu kT(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) \qquad (1)$$

Here, λ_x, λ_y, and λ_z are the components of the deformation tensor λ, defined as the ratios of the final length of the sample L_t to the initial length $L_{t,0}$ in the reference state (state of network formation) in the $t = x, y,$ and z directions, respectively, k is the Boltzmann constant, and T is the absolute temperature. A more rigorous statistical mechanical analysis by Flory has shown that eq 1 should contain an additional logarithmic term, $-\mu kT \ln(V/V_0)$, where μ is the number of junctions, V is

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the volume of the network, and V_0 is the volume of the network at the state of formation.

The force f under uniaxial tension in direction z is obtained from the thermodynamic expression

$$f = \left(\frac{\partial \Delta A_{el}}{\partial L}\right)_{T,V} = L_0^{-1}\left(\frac{\partial \Delta A_{el}}{\partial \lambda_z}\right)_{T,V} \quad (2)$$

where $\lambda = \lambda_z = L_z/L_{z,0}$. Because the volume of the sample is constant during deformation, the x and y components of the deformation tensor are $\lambda_x = \lambda_y = \lambda^{-1/2} \cdot (V/V_0)^{1/2}$. Performing the differentiation in eq 2 leads to the elastic equation of state

$$f = \left(\frac{\nu kT}{L_0}\right)[\lambda - (V/V_0)/\lambda^2] \quad (3)$$

It is useful to introduce the elongation α, related to the deformation tensor λ by the equations

$$\lambda_z = \left(\frac{V}{V_0}\right)^{1/3}\alpha = \left(\frac{v_{2c}}{v_2}\right)^{1/3}\alpha$$

$$\lambda_x = \lambda_y = \left(\frac{V}{V_0}\right)^{1/3}\alpha^{-1/2} = \left(\frac{v_{2c}}{v_2}\right)^{1/3}\alpha^{-1/2} \quad (4)$$

Here, v_2 and v_{2c} are volume fractions of the polymer in the network in the final state and the reference state, respectively. It is also convenient to define the reduced elastic force (modulus) as

$$[f^*] = \frac{f v_2^{1/3}}{A_d(\alpha - \alpha^{-2})} \quad (5)$$

where A_d is the cross-sectional area of the sample in the dry state. The reduced force for the affine network model calculated from eqs 3–5 is

$$[f^*]_{aff} = \frac{\nu kT v_{2c}^{2/3}}{V_d} \quad (6)$$

where V_d is the volume of the sample in the dry state ($v_{2c} = V_d/V_0$) and is independent of the elongation α.

The Phantom Model. A different model of the polymer network, the so-called phantom network, was developed by James and Guth in the forties.[17–20] They assumed that the network chains are Gaussian and interact only at junction points. This means that chains may pass freely through one another, i.e., are "phantom", and thus excluded volume effects and chain entanglements are neglected. They also assumed that all junctions at the surface of the network are fixed and deform affinely with macroscopic deformation but that all inside junctions fluctuate around their mean positions. The fluctuations of polymer chains and junctions are independent of the deformation, while the mean positions of junctions or chain segments inside the network displace affinely with macroscopic deformation. According to the theory, the fluctuations $\langle(\Delta r)^2\rangle$ of the mean-square end-to-end vector in a unimodal network having a functionality ϕ and a treelike topology are[21,22]

$$\langle(\Delta r)^2\rangle = \frac{2}{\phi}\langle r^2\rangle_0 \quad (7)$$

The fluctuations of a network junction around its mean position $\langle(\Delta R)^2\rangle$ are characterized by[21,22]

$$\langle(\Delta R)^2\rangle = \frac{(\phi - 1)}{\phi(\phi - 2)}\langle r^2\rangle_0 \quad (8)$$

Similarly, the fluctuations $\langle(\Delta R_i)^2\rangle$ of the ith segment along a chain composed of n such segments around its mean position are[21,22]

$$\langle(\Delta R_i)^2\rangle = \left[\frac{\phi - 1}{\phi(\phi - 2)} + \left(1 - \frac{2}{\phi}\right)\theta(1 - \theta)\right]\langle r^2\rangle_0 \quad (9)$$

where

$$\theta = i/n \quad (10)$$

denotes the position of the ith segment along the chain as a fraction of the chain contour length between two junctions. In the special cases where $\theta = 0$ or $\theta = 1$, eq 9 reduces to eq 8.

The vector $\mathbf{r}_{ij}$ between two points i and j in the network is

$$\mathbf{r}_{ij} = \bar{\mathbf{r}}_{ij} + \Delta\mathbf{r}_{ij} \quad (11)$$

where $\Delta\mathbf{r}_{ij}$ is the instantaneous fluctuation of $\mathbf{r}_{ij}$ and $\bar{\mathbf{r}}_{ij}$ is its time average. Squaring both sides of the above equation and taking the ensemble average leads to

$$\langle r_{ij}^2\rangle = \langle \bar{r}_{ij}^2\rangle + \langle(\Delta r_{ij})^2\rangle \quad (12)$$

since instantaneous fluctuations and mean values are uncorrelated. If points i and j are two ends of a chain, then from eqs 7 and 12, it follows that

$$\langle \bar{r}^2\rangle = \left(1 - \frac{2}{\phi}\right)\langle r^2\rangle_0 \quad (13)$$

Because the mean positions of junctions transform affinely with macroscopic strain while the fluctuations are strain independent, we have

$$\mathbf{r}_{ij} = \boldsymbol{\lambda}\bar{\mathbf{r}}_{ij} + \Delta\mathbf{r}_{ij} \quad (14)$$

i.e.,

$$\langle r^2\rangle = \left[\left(1 - \frac{2}{\phi}\right)\frac{\lambda_x^2 + \lambda_y^2 + \lambda_z^2}{3} + \frac{2}{\phi}\right]\langle r^2\rangle_0 \quad (15)$$

The elastic free energy of the phantom network is

$$\Delta A_{ph} = \frac{1}{2}\left(1 - \frac{2}{\phi}\right)\nu kT(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) \quad (16)$$

which is very similar to eq 1 for the affine network. The only difference is that the so-called front factor ($\nu/2$ for the affine network) is replaced by $\xi/2$ for the phantom network model. The quantity

$$\xi = \left(1 - \frac{2}{\phi}\right)\nu \quad (17)$$

is the network cycle rank, i.e., the number of cuts required to reduce the network to an unconnected tree. For a perfect network without dangling chains and composed of μ junctions and ν chains

$$\mu = 2\nu/\phi \quad (18)$$

and

$$\xi = \nu - \mu \quad (19)$$

The reduced force for the phantom network model is[3]

$$[f^*]_{ph} = \frac{\left(1 - \frac{2}{\phi}\right)\nu kT v_{2c}^{2/3}}{V_d} \quad (20)$$

Thus, as was the case for the affine network (eq 6), the

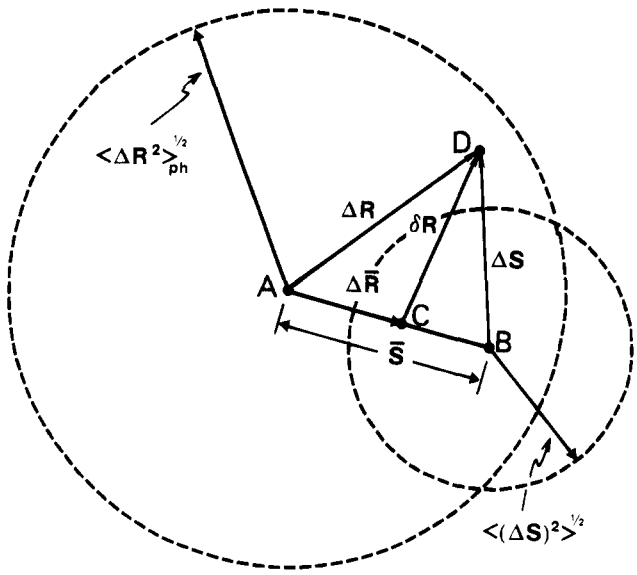

Figure 1. Schematic representation of the effect of constraints on the fluctuations of junctions in the Flory constrained-chain theory.[3] Point A is the mean position of a junction in a phantom network. Point B is the center of constraints. Under the combined action of the phantom network and the constraints, the junction now fluctuates around point C, and point D is its instantaneous position.

modulus is independent of elongation, with the only difference being the factor $(1 - 2/\phi)$.

Real Networks as Intermediate Cases

Constrained-Junction Theory. A real network exhibits properties that fall between those of the affine and phantom model, and theories have been constructed to take this into account,[3,5,8,23] an example being the constrained-junction theory. They are based on the idea that in real networks, excluded-volume interactions and chain entanglements affect the elastic behavior of the network chains. A parameter which measures the effect of the constraints thus introduced is the degree of chain interpenetration in the network. It is defined as the average number of spatially-neighboring junctions within the domain of fluctuations of a given junction in the network:

$$\Gamma = \frac{4\pi}{3}\langle r^2 \rangle_0^{3/2} \frac{\mu}{V_0} \tag{21}$$

In the constrained-junction network model, a given junction is assumed to be under the joint action of the phantom network and the constraint domains, as shown schematically in Figure 1. Point A locates the mean position of the junction in the phantom nework. The large dashed circle of radius $\langle (\Delta R)^2 \rangle_{ph}^{1/2}$ represents the fluctuation domain of the junction in the phantom network, and the smaller circle of radius $\langle (\Delta s)^2 \rangle_0^{1/2}$ represents the domain size of the constraint centered at point B. Point C is the mean position of the junction under the joint action of the phantom network and the constraint, and point D denotes the instantaneous location of the junction, subject to fluctuations ΔR, Δs, and δR from points A, B, and C, respectively. A quantitative measure of the constraint is given by the ratio

$$\kappa = \frac{\langle (\Delta R)^2 \rangle_{ph}}{\langle (\Delta s)^2 \rangle_0} \tag{22}$$

where the phantom limit corresponds to $\kappa = 0$, and the affine limit to $\kappa = \infty$. Flory and Erman[3,5,8] assumed also that the parameter κ is proportional to the average number Γ of junctions in the domain occupied by the chain, given by eq 21.

The elastic free energy of the network in the constrained-junction theory is the sum of the free energy of the phantom network ΔA_{ph} (given by eq 16) and the constraint free energy ΔA_c:

$$\Delta A_{el} = \Delta A_{ph} + \Delta A_c \tag{23}$$

The free energy from the constraints is given in terms of the components of the principal extension ratios:

$$\Delta A_c = \frac{1}{2}\mu kT \sum_t [B_t + D_t - \ln(B_t + 1) - \ln(D_t + 1)], \qquad t = x, y, z \tag{24}$$

where

$$B_t = \frac{\kappa^2(\lambda_t^2 - 1)}{(\lambda_t^2 + \kappa)^2} \tag{25}$$

and

$$D_t = \frac{\lambda_t^2 B_t}{\kappa} \tag{26}$$

The reduced force $[f^*]$ in uniaxial deformation from this constrained-junction theory is given by

$$[f^*] = [f^*]_{ph}\left[1 + \frac{2}{\phi - 2}\frac{[\alpha K(\lambda_1^2) - \alpha^{-2}K(\lambda_2^2)]}{\alpha - \alpha^{-2}}\right] \tag{27}$$

Here, $\lambda_1 = \lambda$, $\lambda_2 = \lambda^{-1/2}$, and $[f^*]_{ph}$ is the phantom modulus given by eq 20. The function $K(\lambda^2)$ is defined as

$$K(\lambda^2) = \frac{B\dot{B}}{B+1} + \frac{D\dot{D}}{D+1} \tag{28}$$

with $B(\lambda^2)$ and $D(\lambda^2)$ given by eqs 25 and 26. Finally,

$$\dot{B} \equiv \frac{\partial B}{\partial \lambda^2} = B\left[\frac{1}{\lambda^2 - 1} - \frac{2}{\lambda^2 + \kappa}\right] \tag{29}$$

and

$$\dot{D} \equiv \frac{\partial D}{\partial \lambda^2} = \frac{1}{\kappa}(\lambda^2 \dot{B} + B) \tag{30}$$

The reduced force $[f^*]$ in the constrained-junction theory always lies between the modulus of the affine network $[f^*]_{aff}$ (given by eq 6) and the modulus of the phantom network $[f^*]_{ph}$ (given by eq 20), irrespective of the elongation. In the limit $\kappa = 0$, eq 27 gives the phantom modulus, while in the limit $\kappa = \infty$, one obtains the affine modulus.

Vilgis and Erman[24] recently put this theory into context by proving that the free energy of constraints in the constrained-junction theory has the same functional form as in the replica model.

Constrained-Chain Theory. Recently, Erman and Monnerie[12] extended the idea of constraints affecting fluctuations in real networks,[3,5,8,23] but with their effects on the centers of masses of the chains (instead of at their junctions). Figure 2 shows a phantom chain used in the analysis. Although fluctuations of a given point i on a chain around its mean position $\langle (\Delta R_i)^2 \rangle$ do not depend on the deformation of the network, its fluctuations around the center of mass of the $\langle (\Delta G_i)^2 \rangle$ chain are deformation dependent. This is due to the fact that

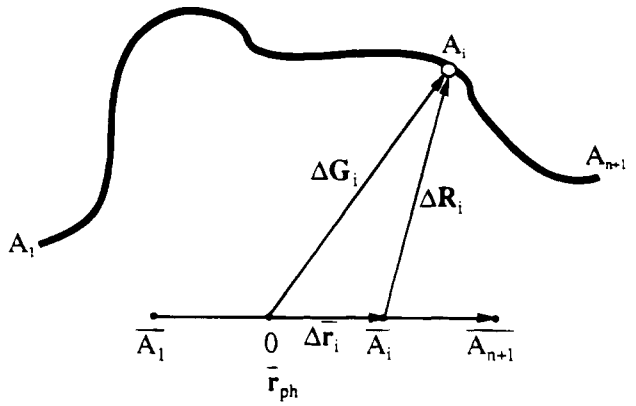

Figure 2. A position of point i along the chain relative to the mean position of the center of mass of the chain.[12] The vector $\Delta\mathbf{R}_i$ shows the instantaneous fluctuations of point i from its mean position, and the vector $\Delta\mathbf{G}_i$ shows the instantaneous fluctuations from the center of mass of the chain.

$$\Delta\mathbf{G}_i = \Delta\mathbf{R}_i + \Delta\bar{\mathbf{r}}_i \tag{31}$$

where $\Delta\bar{\mathbf{r}}_i$ is the vector from the mean position of the center of mass of the chain to the mean position of the point i in the phantom network. Since mean positions deform affinely, we have

$$\Delta\bar{\mathbf{r}}_i = (\theta - 1/2)\lambda\bar{\mathbf{r}}_0 \tag{32}$$

where $0 \le \theta \le 1$ is the fractional position of the point i on the chain defined by eq 10, and $\bar{\mathbf{r}}_0$ is the chain's mean end-to-end vector in the undeformed state. Inserting eq 32 into eq 31, squaring, and averaging over all points along the chain leads to the following expression for the x-component of the fluctuations of the center of mass of the chain:

$$\langle(\Delta X_G)^2\rangle = \frac{1 + (\lambda_x^2 - 1)\Phi}{4(1 - 2/\phi)}\langle x^2\rangle_0 \tag{33}$$

with the parameter Φ given by

$$\Phi = \left(1 - \frac{2}{\phi}\right)^2\left(\frac{1}{3} + \frac{2}{3n}\right) \tag{34}$$

where n is the number of segments per chain.

The elastic free energy in the constrained-chain theory is given by the same two terms in eq 23, where the phantom network contribution is described by eq 16 and the contribution due to constraints on chains is[12]

$$\Delta A_c = \frac{1}{2}\nu kT \sum_{t=x,y,z} [B_t + D_t - \ln(B_t + 1) - \ln(D_t + 1)] \tag{35}$$

The quantities B_t and D_t are defined as

$$B_t = \frac{h\kappa_G(1 - \Phi)(\lambda_t^2 - 1)}{(\lambda_t^2 + h)^2} \tag{36}$$

and

$$D_t = \frac{\lambda^2 B_t}{h} \tag{37}$$

where the parameter h is a function of the macroscopic deformation tensor λ:

$$h(\lambda_t) = \kappa_G[1 + (\lambda_t^2 - 1)\Phi] \tag{38}$$

The parameter κ_G is a measure of the strength of the constraints affecting the fluctuations of the center of mass of the chain in the phantom network and is defined similarly to the parameter κ (eq 22) in the constrained-junction theory. Specifically,

$$\kappa_G = \frac{\langle(\Delta R_G)^2\rangle_0}{\langle(\Delta s_G)^2\rangle_0} \tag{39}$$

where $\langle(\Delta R_G)^2\rangle_0$ are fluctuations of the center of mass of the chain in the undeformed phantom network:

$$\langle(\Delta R_G)^2\rangle_0 = \frac{\langle r^2\rangle_0}{4(1 - 2/\phi)} \tag{40}$$

The quantity $\langle(\Delta s_G)^2\rangle_0$ denotes the domain size of the constraint affecting fluctuations of the center of mass of the chain in the phantom network and is similar to $\langle(\Delta s)^2\rangle_0$ in the constrained-junction theory, as shown in Figure 1. [If the constraints, on the average, are distributed uniformly inside the network, then one may asume that $\langle(\Delta s_G)^2\rangle_0 = \langle(\Delta s)^2\rangle_0$.]

The constrained-chain theory of Erman and Monnerie leads to the following expression for the reduced force (modulus) in uniaxial deformation:

$$[f^*] = [f^*]_{ph}\left[1 + \frac{\phi}{\phi - 2}\frac{[\alpha K(\lambda_1^2) - \alpha^{-2}K(\lambda_2^2)]}{\alpha - \alpha^{-2}}\right] \tag{41}$$

where $\lambda_1 = \lambda$, $\lambda_2 = \lambda^{-1/2}$, and $[f^*]_{ph}$ is the phantom modulus given by eq 20. The function $K(\lambda^2)$ is defined by eq 28, with $B(\lambda^2)$ and $D(\lambda^2)$ given by eqs 36 and 37. Also,

$$\dot{B} \equiv \frac{\partial B}{\partial\lambda^2} = B\left[\frac{1}{\lambda^2 - 1} - \frac{2}{\lambda^2 + h} + \frac{\kappa_G\Phi(\lambda^2 - h)}{h(\lambda^2 + h)}\right] \tag{42}$$

and

$$\dot{D} \equiv \frac{\partial D}{\partial\lambda^2} = B\left(\frac{1}{h} - \frac{\kappa_G\Phi\lambda^2}{h^2}\right) + \frac{\lambda^2\dot{B}}{h} \tag{43}$$

where $h(\lambda)$ is defined by eq 38.

In the limit $\kappa_G = 0$, the free energy in the constrained-chain theory reduces to the elastic free energy of the phantom network. It is similar to the constrained-junction theory in this regard. However, in the limit $\kappa_G = \infty$ the elastic free energy in the constrained-chain model exceeds the free energy of the affine network, which is the limiting value for the constrained-junction model. Thus, the reduced force in the constrained-chain model converges to the phantom modulus (given by eq 20) in the limit $\kappa_G = 0$, but for sufficiently large values of κ_G exceeds the affine modulus given by eq 6.

Experimental stress–strain isotherms for dry and swollen networks can be well represented by the theoretical curves from the constrained-chain model.[12]

The Present Theory, with Diffused Constraints

The present theory extends the results of the Erman–Monnerie theory[12] by letting the constraints affect fluctuations of all points along the chains, including network junctions. This idea of diffusing the constraints so as to include fluctuations of all such points along phantom chains was introduced recently by Erman.[25]

Figure 3 shows a network chain composed of n freely-jointed bonds. Points A_0 and A_n denote the instantaneous positions of junctions, and points $\bar{A}_0$ and $\bar{A}_n$ their mean positions in the phantom network. Vectors $\Delta\mathbf{R}_0$ and $\Delta\mathbf{R}_n$ denote instantaneous junction fluctuations,

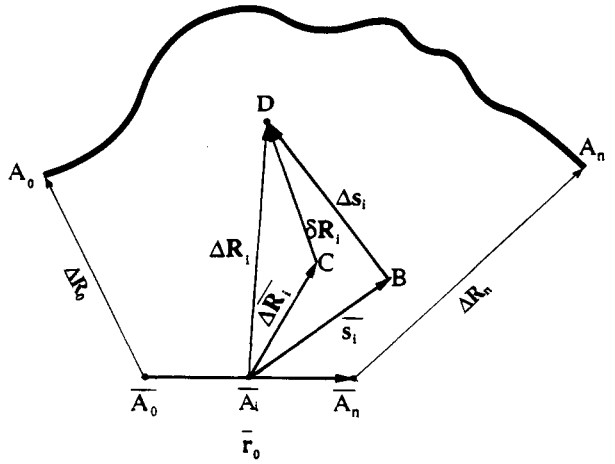

Figure 3. Effect of the center of constraints located at point B on the fluctuations of point i along the chain.[12] The detailed description of various symbols is provided in the text.

and $\Delta\mathbf{R}_i$ is the fluctuation of the point i of the chain from its mean position $\bar{A}_i$, located at $(i/n)\lambda\bar{\mathbf{r}}_0 = \theta\lambda\bar{\mathbf{r}}_0$ from the point A_0. The quantity $\bar{\mathbf{r}}_0$ is the chain's mean end-to-end vector in the undeformed state, and $0 \le \theta \le 1$ is the fraction of the contour length of the chain from the junction A_0 to point i. Point B located at the distance $\bar{\mathbf{s}}_i$ from $\bar{A}_i$ represents the center of entanglement constraints, and point D is the instantaneous position of the point i in the real network under the combined action of the phantom network and the constraints. Point C is the new mean position of point i in the real network, around which i fluctuates under the joint effect of the phantom network and the constraints.

The probability of the fluctuation $\Delta\mathbf{R}_i$ of the point i from its mean position in the phantom network is[14]

$$P(\Delta\mathbf{R}_i) = C \exp\left[-\frac{\gamma}{\frac{\phi-1}{\phi(\phi-2)} + \left(1-\frac{2}{\phi}\right)\theta(1-\theta)}(\Delta\mathbf{R}_i)^2\right] \tag{44}$$

with

$$\gamma = \frac{3}{2\langle r^2\rangle_0} \tag{45}$$

where C is the normalization constant.

If point i of the chain is under the joint action of the phantom network and the constraints, then following the treatment of Flory,[3,5,8] the joint probability of having point i at $\delta\mathbf{R}_i$ in the real network is

$$P(\delta\mathbf{R}_i) = C\,P(\Delta\mathbf{s})\,P(\Delta\mathbf{R}_i) \tag{46}$$

Here, $P(\Delta\mathbf{s})$ is the distribution of constraints, which was assumed by Flory to be Gaussian and affine under deformation

$$P(\Delta\mathbf{s}) = \left(\frac{\det\boldsymbol{\sigma}_\lambda}{\pi^3}\right)^{1/2} \exp[-\Delta\mathbf{s}^{\mathrm{T}}\boldsymbol{\sigma}_\lambda\Delta\mathbf{s}] \tag{47}$$

The tensor $\boldsymbol{\sigma}_\lambda$ is defined as

$$\boldsymbol{\sigma}_\lambda = \sigma_0(\lambda\lambda^{\mathrm{T}})^{-1} \tag{48}$$

where $1/\sigma_0$ is proportional to the mean-square range of entanglement constraints in the undeformed state. The distribution $P(\Delta\mathbf{s})$ is independent of the position of the center of constraints, if on average the constraints are uniformly distributed inside the network. Under this assumption the parameter σ_0 is the same for all points i along the chain and is the same as in the constrained-junction theory.[3,5,8] The constant C in eq 46 guarantees the proper normalization of $P(\delta\mathbf{R}_i)$:

$$\int P(\delta\mathbf{R}_i)\,\mathrm{d}(\delta\mathbf{R}_i) = 1 \tag{49}$$

The probability of fluctuations of point i along the chain from its mean position in phantom network $\bar{A}_i$ in the presence of constraints $P^*(\Delta\mathbf{R}_i)$ is given by the convolution

$$P^*(\Delta\mathbf{R}_i) = P(\delta\mathbf{R}_i)^* \,\Theta(\Delta\bar{\mathbf{R}}) \tag{50}$$

where $\Theta(\Delta\bar{\mathbf{R}})$ is a Gaussian distribution independent of deformation.

Following Flory's arguments, it may be shown that the distribution $P^*(\Delta X_i)$ for the x-component of the point i on the chain in the real network in the presence of constraints is

$$P^*(\Delta X_i) = C \exp\left[-\frac{\alpha'}{1+\frac{\kappa^2(\lambda_x^2-1)}{(\lambda_x^2+\kappa)^2}}(\Delta X_i)^2\right] \tag{51}$$

with

$$\alpha' = \frac{\gamma}{\frac{\phi-1}{\phi(\phi-2)} + \left(1-\frac{2}{\phi}\right)\theta(1-\theta)} \tag{52}$$

where $\theta = i/n$ is the fractional distance of point i on the chain from A_0. The equations for the y- and z-components are similar.

The parameter κ in eq 51 is now a point i dependent function (because of the θ dependence), since

$$\kappa(\theta) = \frac{\sigma_0}{\alpha'} = \frac{\sigma_0}{\gamma}\left[\frac{\phi-1}{\phi(\phi-2)} + \left(1-\frac{2}{\phi}\right)\theta(1-\theta)\right] \tag{53}$$

Following the arguments used by Flory in the constrained-junction theory, the elastic free energy of the constraints affecting fluctuations of the ith segment of network chains is

$$\Delta A_c(\theta) = \frac{1}{2}\nu kT \sum_{t=x,y,z} [B_t(\theta) + D_t(\theta) - \ln[B_t(\theta)+1] - \ln[D_t(\theta)+1]] \tag{54}$$

with

$$B_t(\theta) = \frac{\kappa^2(\theta)(\lambda_t^2-1)}{[\lambda_t^2+\kappa(\theta)]^2} \tag{55}$$

and

$$D_t(\theta) = \frac{B_t(\theta)\lambda_t^2}{\kappa(\theta)} \tag{56}$$

where the parameter $\kappa(\theta)$ is defined by eq 53. Because the constraints are affecting fluctuations of all points along the chain, the free elastic energy of constraints must be averaged over all segments of the chain. This gives

$$\Delta A_c = \frac{1}{2}\nu kT \sum_{t=x,y,z} \int_0^1 W(\theta)[B_t(\theta) + D_t(\theta) - \ln[B_t(\theta)+1] - \ln[D_t(\theta)+1]]\,\mathrm{d}\theta \tag{57}$$

where $W(\theta)$ is the distribution of constraints among

different points along the chain. If this distribution is uniform, then $W(\theta) = 1$ inside the integrand of eq 57. In the case when constraints are assumed to affect only fluctuations of junctions (as in the constrained-junction theory), θ is limited to $\theta = 0$ or $\theta = 1$ only.

The distribution $W(\theta)$ in eq 57 is

$$W(\theta) = \delta(\theta) + \delta(\theta - 1) \tag{58}$$

where δ denotes the Dirac δ-function. Additionally, because each junction is shared by ϕ chains, ν in eq 57 should be replaced by $2\nu/\phi = \mu$ and one recovers the elastic free energy of constraints in the constrained-junction theory.[3,5,8] On the other hand, if constraints are assumed to affect the fluctuations of the midpoints of the chains only

$$W(\theta) = \delta(\theta - 1/2) \tag{59}$$

and one recovers an expression equivalent (but not identical) to the elastic free energy of constraints in the Erman–Monnerie theory.[12] We should note that the present theory does not reduce identically to the constrained-chain theory, because it characterized the deformation-dependent fluctuations of the centers of mass of the chains and not the deformation-independent fluctuations of the midpoints of the chains.

It is useful to relate the parameter $\kappa(\theta)$ to the parameter κ_F (defined by eq 22) in the Flory constrained-junction theory:

$$\kappa_F = \frac{\sigma_0}{\gamma}\frac{\phi - 1}{\phi(\phi - 2)} \tag{60}$$

where γ is defined by eq 45. The result is

$$\kappa(\theta) = \kappa_F\left[1 + \frac{(\phi - 2)^2\theta(1 - \theta)}{\phi - 1}\right] \tag{61}$$

It should be noted that the parameter κ_G in the constrained-chain theory can also be expressed in terms of κ_F:

$$\kappa_G = \frac{\sigma_0}{\gamma}\frac{1}{4(1 - 2/\phi)} = \kappa_F\frac{\phi^2}{4(\phi - 1)} \tag{62}$$

One should also note that $\kappa_G = \kappa(\theta = 1/2)$.

The reduced force (modulus) in the present theory becomes

$$[f^*] = [f^*]_{ph}\left[1 + \frac{\phi}{\phi - 2}\int_0^1 \frac{[\alpha K(\lambda_1^2) - \alpha^{-2}K(\lambda_2^2)]}{\alpha - \alpha^{-2}}\,d\theta\right] \tag{63}$$

where the phantom modulus $[f^*]_{ph}$ is given by eq 20, $\lambda_1 = \lambda$, and $\lambda_2 = \lambda^{-1/2}$. The function $K(\lambda^2)$ is defined by eq 28, with B and D given by eqs 55 and 56, and $\tilde{B}$ and $\tilde{D}$ given by eqs 29 and 30 [with κ replaced by $\kappa(\theta)$]. It is also assumed that the constraints are distributed uniformly among different points along the chain and that $W(\theta) = 1$.

Illustrative Numerical Calculations for Stress–Strain Isotherms in Elongation

In these illustrative numerical calculations, the modulus $[f^*]$ was calculated as a function of inverse elongation α^{-1} for dry networks ($v_2 = 1$). It was normalized by $\nu kTv_{2c}^{2/3}/V_d$, so the affine modulus (eq 6) in the figures corresponds to $[f^*] = 1$, and the phantom modulus given by eq 20 corresponds to $[f^*] = (1 - 2/\phi)$. The numerical integration over θ in eq 63 was performed using 10-point Gaussian quadrature. The results of the present theory were compared with results of the Flory constrained-junction theory[3,5,8] and the Erman–Monnerie constrained-chain theory.[12] Because each of these theories uses a differently defined parameter κ, the calculations were performed for the same value of the parameter κ_F, which was defined by Flory as a ratio of the mean-square fluctuations of junctions to the mean-square range of constraints, and is given by eq 60. This means that for a given value of κ_F, the parameter κ_G in the Erman–Monnerie constrained-chain theory was calculated from eq 62. To show the effect of the substitution of κ_F by κ_G in the Erman–Monnerie constrained-chain theory, curves are also shown for the Erman–Monnerie theory with κ_G equal to κ_F. These curves were plotted using dashed lines in order to distinguish them from other (solid-line) curves obtained for the same value of κ_F. Figure 4 shows the results obtained for a small value of the parameter κ_F, namely $\kappa_F = 0.5$. All theories give results very close to the phantom network limit $[f^*] = (1 - 2/\phi)$. The Flory constrained-junction theory shows the smallest deviation from the phantom limit $[f^*] = (1 - 2/\phi)$, i.e., $[f^*] = 1/2$ for the tetrafunctional network ($\phi = 4$). The largest values of the modulus are obtained for the present theory (marked "New" on the plot), but the difference between the present theory and the Erman–Monnerie theory is small. The calculations performed for the Erman–Monnerie theory for $\kappa_G = 0.5$ (dashed line) give lower values of the modulus than do the same calculations for $\kappa_F = 0.5$. In the limit of high extensions α, all theories converge to the phantom limit $[f^*] = (1 - 2/\phi)$. It can be also shown that in the limit $\kappa_F = 0$, they all give the constant modulus $[f^*] = (1 - 2/\phi)$ (phantom modulus) irrespective of elongation.

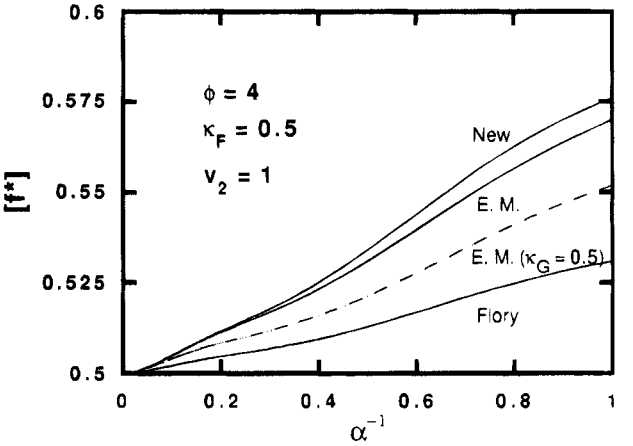

Figure 4. Modulus $[f^*]$ normalized by $\nu kTv_{2c}^{2/3}/V_d$ shown as a function of the inverse elongation α^{-1}. The results in this figure and the following ones are for a dry network ($v_2 = 1$) with tetrafunctional cross-links ($\phi = 4$) and pertain to the Flory theory, the Erman–Monnerie theory (E.M.), and the present theory ("New"). The results in this particular figure were calculated for $\kappa_F = 0.5$ and additionally for $\kappa_G = 0.5$ for the E.M. theory (dashed line).

Figure 5 shows the same relationships for a larger value of the parameter κ_F (specifically, $\kappa_F = 2$). The results are very similar to those in Figure 4. All theories give values of the modulus larger than those for $\kappa_F = 0.5$, and the deviations from the phantom limit increase, as could be expected.

Results for an even larger value of κ_F, namely 5, are shown in Figure 6. The structure of the plots is very similar to those in Figures 4 and 5. The increase of κ_F increases all moduli, and the modulus in the present (new) theory does exceed the affine limit $[f^*] = 1$ at small elongations ($\alpha \approx 1$).

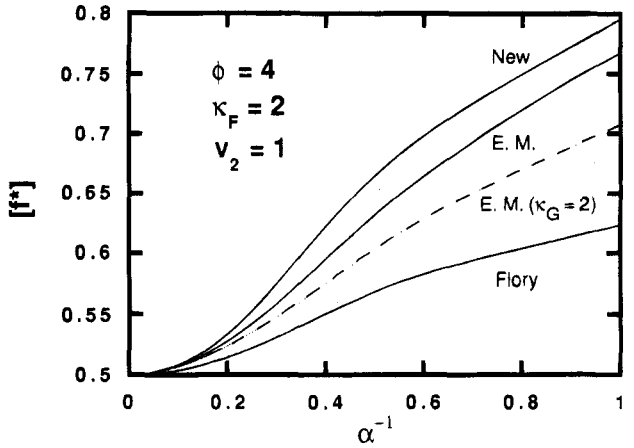

Figure 5. Values of the modulus for $\kappa_F = 2$, and additionally for $\kappa_G = 2$ for the Erman–Monnerie theory (dashed line).

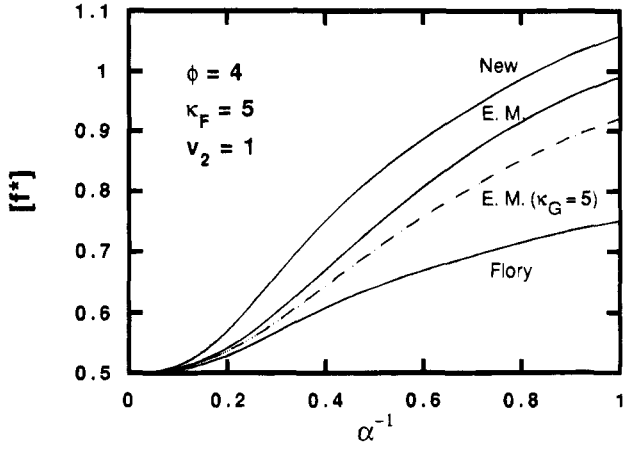

Figure 6. Values of the modulus for $\kappa_F = 5$, and additionally for $\kappa_G = 5$ for the Erman–Monnerie theory (dashed line).

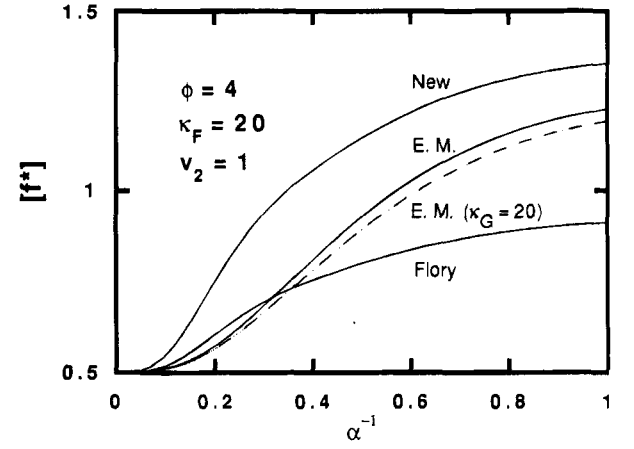

Figure 7. Values of the modulus for $\kappa_F = 20$, and additionally for $\kappa_G = 20$ for the Erman–Monnerie theory (dashed line).

Figure 7 shows plots obtained for $\kappa_F = 20$. A characteristic feature of this figure is that for larger elongations (smaller α^{-1}), the modulus calculated for the Flory constrained-junction theory exceeds that calculated for the Erman–Monnerie constrained-chain theory. It should be noted that the difference between the moduli of the Erman–Monnerie theory calculated for $\kappa_F = 20$ and $\kappa_G = 20$ decreases rapidly. Additionally, however, the differences between the results of the present theory and the Erman–Monnerie theory are much increased.

Results obtained for a very large value of the parameter κ_F (specifically 1000) are shown in Figure 8. The modulus for the constrained-junction model essentially

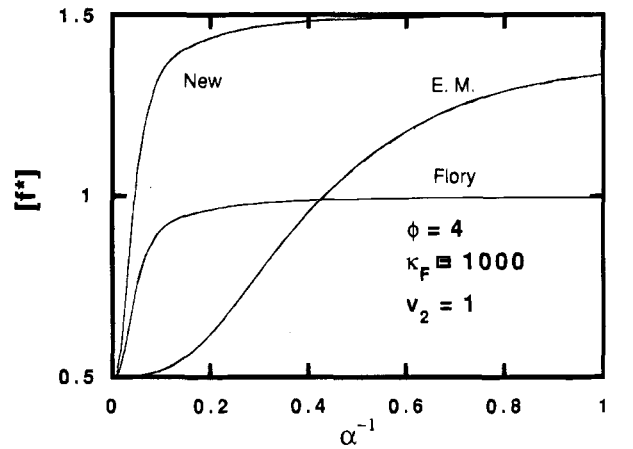

Figure 8. Values of the modulus for $\kappa_F = 1000$. The curve for the Erman–Monnerie theory calculated for $\kappa_G = 1000$ overlaps the curve obtained for $\kappa_F = 1000$.

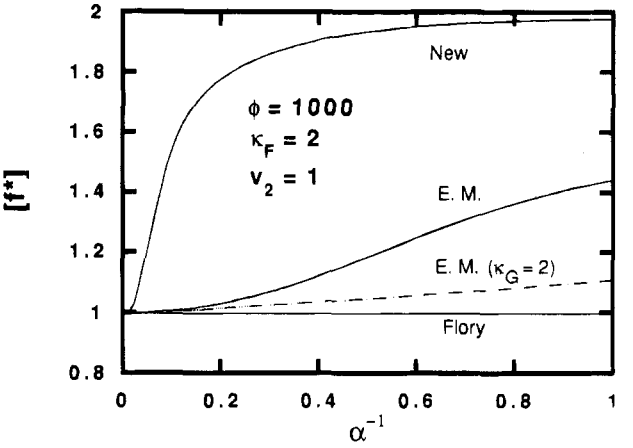

Figure 9. Values of the modulus for networks of very high functionality ($\phi = 1000$) and for $\kappa_F = 2$ and additionally for $\kappa_G = 2$ for the Erman–Monnerie theory (dashed line).

reaches the affine limit $[f^*] = 1$ for most elongations, except for $\alpha > 10$. The constrained-chain model gives practically the same value of the modulus for $\kappa_F = 1000$ and $\kappa_G = 1000$. One should also note that $[f^*]$ in the present theory reaches also the limiting value 1.5 for most of the elongation range. It can be shown analytically that the upper limit of the modulus in the present theory is $(2 - 2/\phi)$ (i.e., 1.5 for $\phi = 4$), whereas the Erman–Monnerie theory does not show such an upper limit.

The last figure shows similar plots but in the limit of very large functionality $\phi = 1000$, while the κ parameter was chosen to be rather small ($\kappa_F = 2$). In this limit, the constrained-junction theory shows the affine behavior $[f^*] = 1$, but the modulus in the present theory converges to $[f^*] \approx 2$ for small elongations. This is a direct consequence of the more general limit $[f^*] = (2 - 2/\phi)$. The modulus in the Erman–Monnerie theory[12] does not show the existence of such a limit.

The fitting of the constrained-junction theory to experimental data usually gave relatively large values of the parameter κ (κ_F in our notation), corresponding almost to the affine limit. Because the interpretation of the experimental results by this theory was not satisfactory in this regard, Flory and Erman attempted to improve it by introducing the additional parameter ζ.[26] The additional modifications leading to the Erman–Monnerie constrained-chain model had the significant advantage of having only a single parameter

κ_G and the fact that its values obtained by fitting theory to experimental data were now relatively small.

Since the shapes of the $[f^*]$ vs. α^{-1} curves for the present theory and those for the Erman–Monnerie constrained-chain and Flory constrained-junction models are very similar, it can be anticipated that the present theory will fit experimental data at least as well as these other theories. It will presumably, however, give more realistic values of the constraint parameters and associated fluctuation magnitudes suitable for comparisons with neutron scattering results. In fact, good representations should be attainable for values of the parameter κ_F even lower than κ_G in the Erman–Monnerie theory. It can be anticipated that the values of κ_F obtained by comparisons with theory should be of the order of unity. Such detailed comparisons between theory and experiment are in the process of being carried out.

The theory can also, of course, be extended to other properties. A related treatment of birefringence, for example, has been carried out and is described elsewhere.[27]

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