since the number of ϕ-functional junctions which separates two points is $d = \lambda - 1$. In the case of (A34) when point i is on the right side of point j, ζ and θ in eq A44 are interchanged. In the infinite network all junctions are equivalent, point i does not have to belong to the first tier, and eq 44 is valid for any two points of the network. Equation A44 gives the nondiagonal elements of eq 52.

References and Notes

(1) James, H. M. *J. Chem. Phys.* **1947**, *15*, 651.
(2) James, H. M.; Guth, E. *J. Chem. Phys.* **1947**, *15*, 669.
(3) Duiser, J. A.; Staverman, A. J. In *Physics of Non-Crystalline Solids*; Prins, J. A., Ed.; North-Holland Publ.: Amsterdam.
(4) Eichinger, B. E. *Macromolecules* **1972**, *5*, 496.
(5) Graessley, W. W. *Macromolecules* **1975**, *8*, 186.
(6) Graessley, W. W. *Macromolecules* **1975**, *8*, 865.
(7) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1976**, *351*, 351.
(8) Pearson, D. S. *Macromolecules* **1977**, *10*, 696.
(9) Ullman, R. *Macromolecules* **1986**, *19*, 1748.
(10) Mark, J. E.; Erman, B. *Rubberlike Elasticity. A Molecular Primer*; Wiley Interscience: New York, 1988.
(11) Erman, B.; Kloczkowski, A.; Mark, J. E. *Macromolecules*, following paper in this issue.
(12) Vilgis, T.; Boué, F. *Polymer* **1986**, *27*, 1156.

Chain Dimensions and Fluctuations in Random Elastomeric Networks. 2. Dependence of Chain Dimensions and Fluctuations on Macroscopic Strain

B. Erman*

School of Engineering, Bogazici University, Bebek 80815, Istanbul, Turkey

A. Kloczkowski and J. E. Mark

Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, Ohio 45221.

Received April 8, 1988; Revised Manuscript Received August 8, 1988

ABSTRACT: The fluctuations of points along a network polymer chain are studied by using a geometrical approach. Specifically, the effects of macroscopic strain on these fluctuations and on the chain dimensions are analyzed. According to the present treatment, fluctuations $\langle(\Delta r_{ij})^2\rangle$ of the distance between two points i and j on a chain in a phantom network are strain dependent. The results are generalized to affine and real networks described by the constrained junction theory of Flory. The properties of phantom, affine, and real networks are compared in detail.

Introduction

In the preceding paper[1] the matrix method was used to calculate chain dimensions and fluctuations in phantom networks. This method is very powerful and enables one to calculate the fluctuations of any point along the chain and the mean-square fluctuations of the distance between any two points of the network which may be separated by several junctions. Its only disadvantage is mathematical complexity.

In the present paper an alternative method is proposed which is based on simple geometrical considerations and an assumption of independence of fluctuations. The main advantage of this approach is its simplicity, although this treatment is limited only to points which belong to the same chain. Points which are separated by one or more (ϕ-functional) junctions cannot be treated by this method. Additionally, information about the fluctuations of junctions and fluctuations of the end-to-end vectors which is provided by the matrix method is needed. The preceding paper[1] focused on the fluctuations in an undeformed phantom network. Here we analyze the effect of macroscopic strain on these fluctuations and on chain dimensions in phantom, affine, and real networks.

In the first known paper devoted to the properties of a network at a length scale smaller than the end-to-end chain dimension, Pearson[2] assumed that the vector $\mathbf{r}_{ij}$ which joins two points i and j on the chain at a given instant is

$$\mathbf{r}_{ij} = \bar{\mathbf{r}}_{ij} + \Delta\mathbf{r}_{ij} \tag{1}$$

where $\bar{\mathbf{r}}_{ij}$ is the mean separation between points i and j and $\Delta\mathbf{r}_{ij}$ represents the instantaneous fluctuation of this distance. He assumed that the mean separation $\bar{\mathbf{r}}_{ij}$ transforms affinely in the strained state, that is

$$\bar{\mathbf{r}}_{ij} = \lambda\bar{\mathbf{r}}_{ij,0} \tag{2}$$

while the fluctuations $\Delta\mathbf{r}_{ij}$ are independent of the applied strain. The independence of the fluctuations $\Delta\mathbf{r}_{ij}$ follows rigorously from the treatment of James,[3] where points along the chains are considered as junctions in the primary configuration function of the network. In the present calculations, we consider only the multifunctional points as junctions. This leads, as shown below, to an alternative interpretation of the phantom network according to which the mean-square fluctuations $\langle(\Delta r_{ij})^2\rangle$ depend on the macroscopic strain although the mean-square fluctuations of the end-to-end vector $\langle(\Delta r)^2\rangle$ are strain independent.

The results are generalized to affine networks and to real networks described by the constrained junction theory of Flory.[4] This then permits detailed comparisons among phantom, affine, and real polymer networks.

Dependence of Chain Dimensions and Fluctuations on Macroscopic Deformation

With the insight gained in the preceding paper on fluctuations in a phantom network,[1] we can now analyze their dependence on macroscopic deformation. This is done here for phantom and affine networks and for real networks described by the constrained junction model.[4] Throughout the derivations, we confine attention to time averages for a single chain in the network as well as to ensemble averages. The former is emphasized in the interest of possibility extending the present treatment to viscoelastic phenomena in elastomeric networks.

0024-9297/89/2222-1432$01.50/0

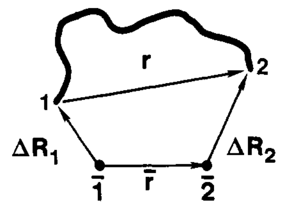

Figure 1. Instantaneous configuration of a chain in a phantom network. Points 1 and 2 denote ends of the chain at the given instant and $\bar{1}$ and $\bar{2}$ their mean time-averaged positions. Vectors $\mathbf{r}$ and $\bar{\mathbf{r}}$ are instantaneous and time-averaged end-to-end vectors, respectively, and $\Delta\mathbf{R}_1$ and $\Delta\mathbf{R}_2$ are instantaneous fluctuations of points 1 and 2 from their mean positions.

Inasmuch as all the distribution functions governing the network behavior are Gaussian, analysis may be carried out separately in each coordinate direction. In the following, only the x component is treated. For brevity the x component of the extension ratio is simply written as λ.

The Phantom Network. The instantaneous configuration of a typical chain in a phantom network is shown in Figure 1. Points 1 and 2 denote the ends of the chain at the given instant and $\bar{\mathbf{r}}$ is the time-averaged end-to-end vector. (Time averages are designated by an overbar and pertain to a single chain. Ensemble averages are denoted by angular brackets.) Here $\Delta\mathbf{R}_1$ and $\Delta\mathbf{R}_2$ are the instantaneous fluctuations of the points 1 and 2 from their mean positions $\bar{1}$ and $\bar{2}$, respectively, and $\mathbf{r}$ is the instantaneous end-to-end vector. Squaring both sides of the equation

$$\mathbf{r} - \bar{\mathbf{r}} = \Delta\mathbf{R}_2 - \Delta\mathbf{R}_1 \quad \text{or} \quad x - \bar{x} = \Delta X_2 - \Delta X_1 \tag{3}$$

and taking the time average leads to

$$\overline{x^2} = \bar{x}^2 + 2(\overline{\Delta X_1^2} - \overline{\Delta X_1 \Delta X_2}) \tag{4}$$

since $\overline{\Delta X_1^2} = \overline{\Delta X_2^2}$. The symbols in eq 3 denote the x components of the corresponding vectorial quantities given in the preceding line. The time average of fluctuations in a phantom network of uniform structure is identical with the ensemble average. Use of the known relations[1,2]

$$\overline{(\Delta R_1)^2} = \frac{\phi - 1}{\phi(\phi - 2)}\langle r^2\rangle_0 \tag{5}$$

$$\overline{\Delta\mathbf{R}_1\cdot\Delta\mathbf{R}_2} = \frac{1}{\phi(\phi - 2)}\langle r^2\rangle_0 \tag{6}$$

in eq 4 leads to

$$\overline{x^2} = \bar{x}^2 + (2/\phi)\langle x^2\rangle_0 \tag{7}$$

where the subscript zero denotes the state of reference and $\overline{r_0^2} = \langle r^2\rangle_0$. Taking the ensemble average and using the relations $\langle\overline{x^2}\rangle = \overline{\langle x^2\rangle} = \langle x^2\rangle$ that hold at equilibrium, one obtains the well-known result[1,5]

$$\langle x^2\rangle = [(1 - 2/\phi)\lambda^2 + 2/\phi]\langle x^2\rangle_0 \tag{8}$$

In calculations leading to eq 8, the two relations[6]

$$\langle\bar{r}^2\rangle_0 = (1 - 2/\phi)\langle r^2\rangle_0$$

$$\langle(\Delta r)^2\rangle = (2/\phi)\langle r^2\rangle_0 \tag{9}$$

are used, together with the fact that the mean vectors transform affinely with macroscopic deformation:

$$\langle\bar{x}^2\rangle = \lambda^2\langle\bar{x}^2\rangle_0 = \lambda^2(1 - (2/\phi))\langle x^2\rangle_0 \tag{10}$$

In Figure 2, the position of a point i on the chain is defined in terms of various vectors as shown. The point is at a fractional distance ζ from junction 1. This means that the ratio of the chain length from junction 1 to point i to the total contour length of the chain between junction 1 and 2 is ζ. The vector $\Delta\mathbf{S}_i$ (see Figure 2) describes the fluctuation of point i from its temporary position (when $\Delta\mathbf{R}_1$, $\Delta\mathbf{R}_2$, and $\bar{\mathbf{r}}$ are fixed). These fluctuations are uncorrelated with the fluctuations of the junctions

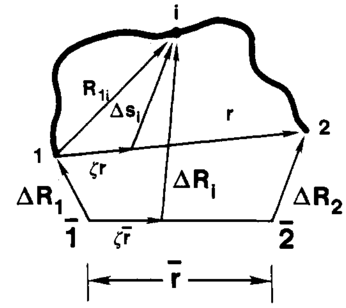

Figure 2. Position of a point i on the chain in a given instant defined in terms of two vectors $\Delta\mathbf{S}_i$ and $\Delta\mathbf{R}_i$, which join the fractions ζ of the end-to-end vectors $\mathbf{r}$ and $\bar{\mathbf{r}}$, respectively, with point i, and also in terms of vector $\mathbf{R}_{1i}$, which joins junction 1 with point i.

$$\overline{\Delta\mathbf{S}_i\cdot\Delta\mathbf{R}_1} = \overline{\Delta\mathbf{S}_i}\cdot\overline{\Delta\mathbf{R}_1} = 0$$

$$\overline{\Delta\mathbf{S}_i\cdot\Delta\mathbf{R}_2} = \overline{\Delta\mathbf{S}_i}\cdot\overline{\Delta\mathbf{R}_2} = 0 \tag{11}$$

and since $\overline{\Delta\mathbf{S}_i} = 0$ (from the definition of the fluctuations) we have

$$\overline{\Delta\mathbf{S}_i\cdot\bar{r}} = \overline{\Delta\mathbf{S}_i}\cdot\bar{\mathbf{r}} = 0 \tag{12}$$

in the undeformed as well as in the deformed state.

Let us consider first the relation (see Figure 2)

$$\Delta\mathbf{R}_1 + \mathbf{r} = \bar{\mathbf{r}} + \Delta\mathbf{R}_2 \tag{13}$$

Squaring both sides of it and averaging over time we obtain

$$\overline{\Delta\mathbf{R}_1\cdot\mathbf{r}} = \tfrac{1}{2}[\bar{r}^2 - \overline{r^2}] \tag{14}$$

since

$$\overline{\Delta\mathbf{R}_1\cdot\bar{r}} = \overline{\Delta\mathbf{R}_1}\cdot\bar{\mathbf{r}} = \overline{\Delta\mathbf{R}_2}\cdot\bar{\mathbf{r}} = \overline{\Delta\mathbf{R}_2\cdot\bar{r}} = 0 \tag{15}$$

and $\overline{(\Delta\mathbf{R}_1)^2} = \overline{(\Delta\mathbf{R}_2)^2}$ and $\overline{\Delta\mathbf{R}_1} = \overline{\Delta\mathbf{R}_2} = 0$. The condition $\overline{\Delta\mathbf{R}_1} = 0$ (or $\overline{\Delta\mathbf{S}_i} = 0$) does not require the fluctuations to be isotropic, although usually it is assumed that the probabilities of fluctuation of a junction from its mean position in any direction are the same in the undeformed as well as in the deformed networks.[5] The fluctuations of ellipsoidal symmetry also fulfill these conditions. Now we use another relation (see Figure 2):

$$\Delta\mathbf{R}_i = \Delta\mathbf{R}_1 + \mathbf{R}_{1i} - \zeta\bar{\mathbf{r}} \tag{16}$$

The vector $\Delta\mathbf{R}_i$ describes the effective fluctuation of a point i from its mean position which is due to the fluctuation of junctions $\Delta\mathbf{R}_1$ and $\Delta\mathbf{R}_2$ and the fluctuation $\Delta\mathbf{S}_i$ of the chain itself when $\Delta\mathbf{R}_1$ and $\Delta\mathbf{R}_2$ are kept fixed. Here $\mathbf{R}_{1i}$ is a vector joining junction 1 with point i at the given instant.

Squaring both sides of eq 16 and averaging over time we obtain

$$\overline{(\Delta\mathbf{R}_i)^2} = \overline{\mathbf{R}_{1i}^2} + \overline{(\Delta\mathbf{R}_1)^2} + \zeta^2\bar{r}^2 - 2\zeta\bar{\mathbf{r}}\cdot\overline{\Delta\mathbf{R}_1} + 2\zeta\overline{\mathbf{r}\cdot\Delta\mathbf{R}_1} + 2\,\overline{\Delta\mathbf{S}_i\cdot\Delta\mathbf{R}_1} - 2\zeta^2\bar{r}^2 - 2\zeta\bar{\mathbf{r}}\cdot\overline{\Delta\mathbf{S}_i} \tag{17}$$

because (see Figure 2)

$$\mathbf{R}_{1i} = \zeta\mathbf{r} + \Delta\mathbf{S}_i \tag{18}$$

Using eq 11, 12, 14, and 15 and assuming that the known formula for the freely jointed chain

$$\overline{R_{1i}^2} = \zeta\overline{r^2} \tag{19}$$

holds in the deformed as well as the undeformed state, we finally obtain

$$\overline{(\Delta R_i)^2} = \overline{(\Delta R_1)^2} + \zeta(1 - \zeta)\bar{r}^2 \tag{20}$$

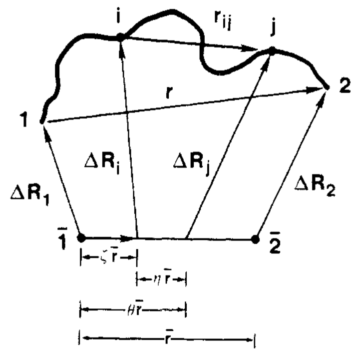

Figure 3. Two points i and j on the chain whose fractional distances from junction 1 are ζ and θ, respectively. The fluctuations of points i and j around their mean positions $\zeta\bar{\mathbf{r}}$ and $\theta\bar{\mathbf{r}}$ are $\Delta\mathbf{R}_i$ and $\Delta\mathbf{R}_j$, and the fluctuation of the junctions are $\Delta\mathbf{R}_1$ and $\Delta\mathbf{R}_2$.

The formula for the time averages for the x component $\overline{(\Delta X_i)^2}$ of $\overline{(\Delta R_i)^2}$ in the deformed state can be written as

$$\overline{(\Delta X_i)^2} = \overline{(\Delta X_1)^2} + \zeta(1-\zeta)\lambda^2\bar{x}^2_0 \qquad (21)$$

or by using eqs 9–10 as

$$\overline{(\Delta X_i)^2} = \left[\zeta(1-\zeta)\left(1-\frac{2}{\phi}\right)\lambda^2 + \frac{\phi-1}{\phi(\phi-2)}\right]\overline{x^2_0} \qquad (22)$$

The ensemble average is obtained from eq 22 as

$$\langle(\Delta X_i)^2\rangle = \left[\zeta(1-\zeta)\left(1-\frac{2}{\phi}\right)\lambda^2 + \frac{\phi-1}{\phi(\phi-2)}\right]\langle x^2\rangle_0 \qquad (23)$$

In the undeformed state eq 23 gives us the same result as obtained earlier by using the matrix method.[1,2] It points out the important fact that the fluctuations of points along the chain depend on macroscopic deformation, in contrast to those of the junction points (ζ = 0 or 1).

In Figure 3, positions of two points i and j on the chain are shown together with various vectorial quantities. The fractional distances of points i and j from junction 1 are ζ and θ, respectively. The fractional distance between the two points is $\eta = |\zeta - \theta|$.

In accordance with Pearson's treatment,[2] points i and j refer to the ends of two Gaussian subchains dividing the entire chain. Thus the vector $\mathbf{r}_{ij}$ shown in Figure 3 locates the beginning and end of a Gaussian subchain. For further calculations, a relationship between $\overline{r_{ij}^2}$ and $\overline{r^2}$ in the deformed state is needed. Here we make the assumption that the relation

$$\overline{r_{ij}^2} = \eta\overline{r^2} \qquad (24)$$

holds both in the deformed and the undeformed states for subchains separated by $\eta = |i-j|/n$ Gaussian subchains. This assumption is essentially a consequence of the equality

$$\overline{r_{ij}^2}_0/\overline{r^2_0} = \overline{r_{ij}^2}/\overline{r^2}$$

which may plausibly be expected to approximate the behavior of chains in deformed phantom networks. Squaring both sides (see Figure 3) of the expression

$$\mathbf{r}_{ij} = \eta\bar{\mathbf{r}} + \Delta\mathbf{R}_j - \Delta\mathbf{R}_i \qquad (25)$$

and using eq 24, we obtain

$$\overline{\Delta\mathbf{R}_i\cdot\Delta\mathbf{R}_j} = \tfrac{1}{2}[\overline{(\Delta R_i)^2} + \overline{(\Delta R_j)^2} + \eta^2\bar{r}^2 - \eta\overline{r^2}] \qquad (26)$$

because

$$\overline{\Delta\mathbf{R}_i\cdot\bar{\mathbf{r}}} = \overline{\Delta\mathbf{R}_i}\cdot\bar{\mathbf{r}} = \overline{\Delta\mathbf{R}_j\cdot\bar{r}} = \overline{\Delta\mathbf{R}_j}\cdot\bar{r} = 0 \qquad (27)$$

since $\overline{\Delta\mathbf{R}_i} = \overline{\Delta\mathbf{R}_j} = 0$ from the definition of the fluctuations. By using the relation

$$\Delta\mathbf{R}_i = \Delta\mathbf{R}_1 + \zeta\mathbf{r} + \Delta\mathbf{S}_i - \zeta\bar{\mathbf{r}} \qquad (28)$$

after time averaging we have

$$\overline{\Delta\mathbf{R}_i} = \overline{\Delta\mathbf{R}_1} + \overline{\Delta\mathbf{S}_i} \qquad (29)$$

so that eq 27 is a direct consequence of eq 12 and 15. Using the result obtained earlier (eq 20) for fluctuations $\overline{(\Delta R_i)^2}$ and $\overline{(\Delta R_j)^2}$ of points i and j along the chain, the cross-correlation $\overline{\Delta\mathbf{R}_i\cdot\Delta\mathbf{R}_j}$ becomes

$$\overline{\Delta\mathbf{R}_i\cdot\Delta\mathbf{R}_j} = \overline{(\Delta R_1)^2} + \tfrac{1}{2}[\zeta(1-\zeta) + \theta(1-\theta) + \eta^2]\bar{r}^2 - \tfrac{1}{2}\eta\overline{r^2} \qquad (30)$$

since $\overline{(\Delta R_1)^2} = \overline{(\Delta R_2)^2}$.

Equation 30 can be written differently, as

$$\overline{\Delta\mathbf{R}_i\cdot\Delta\mathbf{R}_j} = \overline{(\Delta R_1)^2} + \tfrac{1}{2}[\zeta(1-\zeta) + \theta(1-\theta) + \eta^2 - \eta]\bar{r}^2 - \frac{\eta}{2}[\overline{r^2} - \bar{r}^2] = \overline{(\Delta R_1)^2} + [\min(\zeta,\theta) - \zeta\theta]\bar{r}^2 - \frac{\eta}{2}[\overline{r^2} - \bar{r}^2] \qquad (31)$$

because of the definition of the minimum function

$$\min(\zeta,\theta) = \frac{\zeta + \theta - |\zeta - \theta|}{2} = \frac{\zeta + \theta - \eta}{2} \qquad (32)$$

Equation 31 has been derived by using the matrix method in the preceding paper.[1] Since the fluctuations of the end-to-end distance

$$\overline{(\Delta r)^2} = \overline{r^2} - \bar{r}^2 = \frac{2}{\phi}\overline{r^2_0} \qquad (33)$$

as well as fluctuations of junctions $\overline{(\Delta R_1)^2}$ are strain independent, eqs 9 and 10 give the result

$$\overline{\Delta X_i\Delta X_j} = \left\{[\min(\zeta,\theta) - \zeta\theta]\left(1-\frac{2}{\phi}\right)\lambda^2 + \frac{\phi-1}{\phi(\phi-2)} - \frac{\eta}{\phi}\right\}\overline{x^2_0} \qquad (34)$$

The ensemble average of eq 34 gives

$$\langle\Delta X_i\Delta X_j\rangle = \left([\min(\zeta,\theta) - \zeta\theta](1-2/\phi)\lambda^2 + \frac{\phi-1}{\phi(\phi-2)} - \eta/\phi\right)\langle x^2\rangle_0 \qquad (35)$$

Using the formula[1,2]

$$\langle(\Delta r_{ij})^2\rangle = \langle(\Delta\mathbf{R}_i - \Delta\mathbf{R}_j)^2\rangle = \langle(\Delta R_i)^2\rangle + \langle(\Delta R_j)^2\rangle - 2\langle\Delta\mathbf{R}_i\cdot\Delta\mathbf{R}_j\rangle \qquad (36)$$

and eq 23 and 35, the expression for $\langle(\Delta x_{ij})^2\rangle$ is obtained as

$$\langle(\Delta x_{ij})^2\rangle = \eta\langle x^2\rangle - \eta^2\langle\bar{x}^2\rangle = [\eta(1-\eta)(1-2/\phi)\lambda^2 + 2\eta/\phi]\langle x^2\rangle_0 \qquad (37)$$

Equation 37 indicates that fluctuations of chain dimensions, $\langle(\Delta r_{ij})^2\rangle$, depend on λ. This result differs from that obtained by Pearson[2] due to the different assumptions made concerning the strain dependence of fluctuations of chain points.

The Affine Network. The end points of chains in an affine network are assumed to be fixed. Points along the chain contour fluctuate in time, subject only to the constancy of the end-to-end vector. Otherwise, the configurational rearrangements of the chain contour are not affected by the neighboring chains. In this sense, the chain contour behaves "phantom-like". All effects of surrounding chains are included in the condition that chain end points

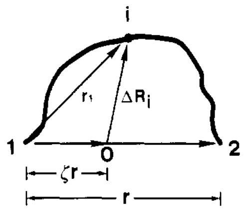

Figure 4. Fluctuation $\Delta\mathbf{R}_i$ of a point i whose fractional distance from junction 1 is ζ around the mean position $\zeta\mathbf{r}$ in an affine network.

should be fixed. Whether or not fixing the end points totally accounts for intermolecular effects is a continuing controversy, to be resolved only by testing the affine network assumption with the results of carefully performed experiments.

It is intuitively evident that an affine network is equivalent to a phantom network with infinite junction functionality. In this section we derive conclusions based on this statement. These conclusions on the fluctuations of points on an affine network chain are rederived more rigorously in the next section.

In the limit when $\phi \rightarrow \infty$, the expression for $\langle(\Delta X_1)^2\rangle$ in eq 5 becomes zero and eq 22 reads, for an affine network, as

$$\overline{(\Delta X_i)_{\mathrm{af}}{}^2} = \zeta(1-\zeta)\lambda^2\overline{x^2{}_0} \tag{38}$$

The ensemble average becomes

$$\langle(\Delta X_i)^2\rangle_{\mathrm{af}} = \zeta(1-\zeta)\lambda^2\langle x^2\rangle_0 \tag{39}$$

where the subscript af denotes affine. The cross correlation of fluctuations of points i and j is obtained from eq 35 in the limit $\phi \rightarrow \infty$ as

$$\langle\Delta X_i \Delta X_j\rangle_{\mathrm{af}} = [\min(\zeta,\theta) - \zeta\theta]\lambda^2\langle x^2\rangle_0 \tag{40}$$

and fluctuations $\langle(\Delta x_{ij})^2\rangle$ are obtained from eq 37 as

$$\langle(\Delta x_{ij})^2\rangle_{\mathrm{af}} = \eta(1-\eta)\lambda^2\langle x^2\rangle_0 \tag{41}$$

Figure 4 shows fluctuations of the chain in the affine network.

Real Networks. A real network is described as one that exhibits behavior between the phantom and the affine models. Such behavior is described theoretically by the constrained junction theory of Flory.[4] According to this model, all intermolecular interactions are assumed to affect the fluctuations of junctions, with no direct constraining effect on points along the chain. The extent of the fluctuations are measured by the κ parameter. For the phantom network $\kappa = 0$ and fluctuations of junctions are independent of macroscopic deformation. For $\kappa = \infty$, the network is affine and the junctions are frozen. The basic question that will be answered in this section is how are the fluctuations $\langle(\Delta R_i)^2\rangle$, $\langle\Delta\mathbf{R}_i\cdot\Delta\mathbf{R}_j\rangle$, and $\langle(\Delta r_{ij})^2\rangle$ affected by changing κ?

The instantaneous configuration of a chain between junctions 1 and 2 is shown in Figure 5. Here $\bar{\mathbf{r}}_{\mathrm{ph}}$ is the mean end-to-end vector obtained in the phantom network and $\bar{\mathbf{r}}$ denotes the same vector in the real network. The difference between $\bar{\mathbf{r}}_{\mathrm{ph}}$ and $\bar{\mathbf{r}}$ is due to the action of constraints that displace junctions 1 and 2 by $\Delta\bar{\mathbf{R}}_1$ and $\Delta\bar{\mathbf{R}}_2$, respectively. The vectors $\delta\mathbf{R}_1$ and $\delta\mathbf{R}_2$ represent the instantaneous fluctuations of points 1 and 2, respectively, from their mean locations in the real network. Here $\mathbf{r}$ is the instantaneous end-to-end vector for the chain and $\delta\mathbf{R}_i$ is the instantaneous fluctuation of point i in the real network from its mean position.

The time average $\overline{(\delta R_i)^2}$ may be written by using the analogy with the procedure for the phantom network,

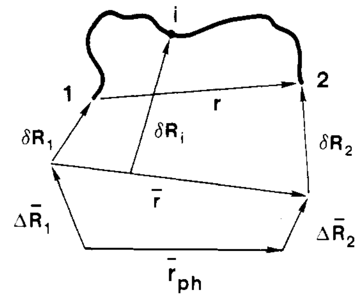

Figure 5. Instantaneous configuration of a chain in a real network. The vectors $\bar{\mathbf{r}}$ and $\bar{\mathbf{r}}_{\mathrm{ph}}$ denote mean end-to-end vectors for real network and phantom network, respectively. The vectors $\Delta\bar{\mathbf{R}}_1$ and $\Delta\bar{\mathbf{R}}_2$ show the displacement of junctions 1 and 2 from their phantom to real positions due to the action of the constraints, and vectors $\delta\mathbf{R}_1$, $\delta\mathbf{R}_2$, and$\delta\mathbf{R}_i$ show the instantaneous fluctuations of junctions 1 and 2 and point i on the chain from their mean positions in a real network.

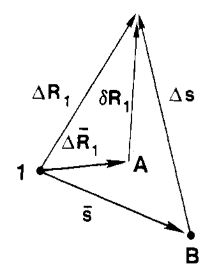

Figure 6. Effect of constraints on the mean position and fluctuation of a junction in the real network. Point 1 and $\Delta\mathbf{R}_1$ represent the mean position of the junction and the fluctuation from this position in the phantom network, respectively. Due to the action of the center of constraint B located at the distance $\mathbf{s}$ from phantom center the mean position of junction in the real network is shifted to point A located at distance $\Delta\bar{\mathbf{R}}_1$ from the phantom center. The instantaneous fluctuation of the junction from the real center is represented by $\delta\mathbf{R}_1$.

according to which variable ΔX_1 in eq 21 must be changed into δX_1. Thus

$$\overline{(\delta X_i)^2} = \overline{(\delta X_1)^2} + \zeta(1-\zeta)\bar{x}^2 \tag{42}$$

where

$$\bar{x} = \bar{x}_{\mathrm{ph}} + \Delta\bar{X}_2 - \Delta\bar{X}_1 \tag{43}$$

as is seen from Figure 5. According to the theory[4]

$$\Delta\bar{X}_1 = \frac{\kappa\lambda}{\lambda^2+\kappa}\bar{s}_{1x,0} \qquad \Delta\bar{X}_2 = \frac{\kappa\lambda}{\lambda^2+\kappa}\bar{s}_{2x,0} \tag{44}$$

where $\bar{s}_{1x,0}$ and $\bar{s}_{2x,0}$ are the x components of the vectors from the mean phantom locations of the respective junctions to the centers of constraints operating on each junction. The geometry around a junction is shown in further detail in Figure 6. Point 1 denotes the mean position of the junction in the phantom network. Its fluctuation in the phantom network is represented by $\Delta\mathbf{R}_1$. Point B represents the center of constraints operating on the junction; it is at a distance $\mathbf{s}$ from the phantom center. The instantaneous position of the junction is at a distance $\Delta\mathbf{s}$ from point B. Under the combined action of the network connectivity and constraints, the actual mean position of the junction will be at point A. The instantaneous fluctuation of the junction from point A is represented by the vector $\delta\mathbf{R}_1$.

The ensemble average of eq 42 reads as

$$\langle(\delta X_i)^2\rangle = \frac{\lambda^2}{\lambda^2+\kappa}\,\frac{\phi-1}{\phi(\phi-2)}\langle x^2\rangle_0 + \zeta(1-\zeta)\langle\bar{x}^2\rangle \tag{45}$$

where the ensemble average of $(\delta X_1)^2$ has been substituted from the constrained junction theory.[4] The average $\langle\bar{x}^2\rangle$

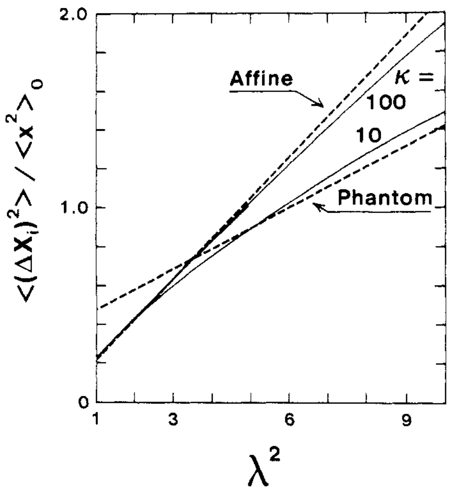

Figure 7. Ratio of the mean-square fluctuations of the point i whose fractional distance from the junction is $\zeta = 0.3$ to the mean-square fluctuations of the end-to-end distance in the undeformed state $\langle (\Delta X_i)^2 \rangle / \langle x^2 \rangle_0$ as a function of the square of extention ratio λ^2. The dashed straight lines represent results for affine and phantom models and full lines for real networks with $\kappa = 10$ and 100.

cannot be determined from the theory since the cross-correlations of the vectors $\Delta\bar{\mathbf{R}}_1$ and $\Delta\bar{\mathbf{R}}_2$ are not known. Thus an assumption is required for obtaining $\langle \bar{x}^2 \rangle$. Since $\bar{\mathbf{r}}_{ph}$ is uncorrelated with $\Delta\bar{\mathbf{R}}_1$ and $\Delta\bar{\mathbf{R}}_2$ due to the random effect of constraints, we obtain from eq 43

$$\langle \bar{x}^2 \rangle = \langle \bar{x}^2{}_{ph} \rangle + \langle (\Delta\bar{X}_2 - \Delta\bar{X}_1)^2 \rangle \quad (46)$$

or from eq 44

$$\langle \bar{x}^2 \rangle = \langle \bar{x}^2{}_{ph} \rangle + \left(\frac{\kappa\lambda}{\lambda^2 + \kappa} \right)^2 \langle (\Delta\bar{s}_{x,0})^2 \rangle \quad (47)$$

where

$$\langle (\Delta\bar{s}_{x,0})^2 \rangle = \langle (\bar{s}_{2x,0} - \bar{s}_{1x,0})^2 \rangle \quad (48)$$

For the phantom network, the second term on the right-hand side of eq 47 vanishes and we recover $\langle \bar{x}^2 \rangle = \langle \bar{x}^2 \rangle_{ph}$ as expected. For the affine limit, eq 47 is satisfied identically, if

$$\langle (\Delta\bar{s}_{x,0})^2 \rangle_{af} = \langle \bar{x}^2 \rangle_0 - \langle \bar{x}^2 \rangle_{ph,0} \quad (49)$$

However, in the affine limit $\langle \bar{x}^2 \rangle_0$ equates to the mean-squared end-to-end chain dimension $\langle x^2 \rangle_0$. Inasmuch as the end-to-end chain dimensions are expected to be the same in the phantom and the affine networks in the undistorted state,[4] eq 49 may also be written as

$$\langle (\Delta\bar{s}_{x,0})^2 \rangle_{af} = \langle x^2 \rangle_{ph,0} - \langle \bar{x}^2 \rangle_{ph,0} = \frac{2}{\phi} \langle x^2 \rangle_0 \quad (50)$$

where eq 9 is used in obtaining the second line. Equation 50 represents a condition on the spatial dispersion $\langle (\Delta\bar{s}_{x,0})^2 \rangle_{af}$ of constraint centers in the affine limit so that chain dimensions are identical in the reference states of the phantom and affine network models.

In the absence of further information on the structure of constraints in the real networks, we replace $\langle (\Delta\bar{s}_{x,0})^2 \rangle$ in eq 47 by $\langle (\Delta\bar{s}_{x,0})^2 \rangle_{af}$ from eq 50. With this approximation, eq 45 may be written

$$\langle (\delta X_i)^2 \rangle = \left\{ \frac{\lambda^2}{\lambda^2 + \kappa} \frac{\phi - 1}{\phi(\phi - 2)} + \zeta(1 - \zeta) \left[(1 - 2/\phi)\lambda^2 + \left(\frac{\kappa\lambda}{\lambda^2 + \kappa} \right)^2 \frac{2}{\phi} \right] \right\} \langle x^2 \rangle_0 \quad (51)$$

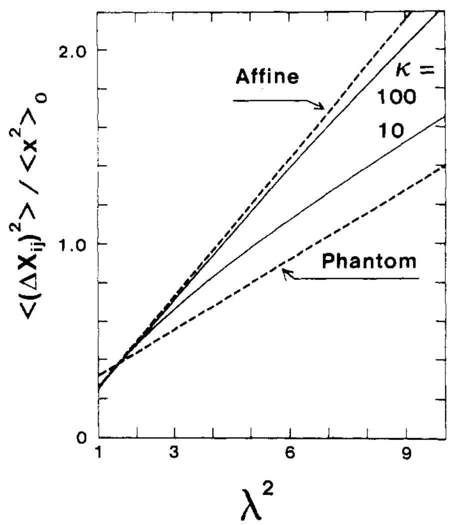

Figure 8. Ratio of the mean-square fluctuations of the distance $\mathbf{r}_{ij}$ between points i and j whose fractional distances from one junction are $\zeta = 0.3$ and $\theta = 0.7$, respectively, to the mean-square fluctuations of the end-to-end distance in the undeformed state $\langle (\Delta x_{ij})^2 \rangle / \langle x^2 \rangle_0$ as a function of the square of the extension ratio λ^2. The dashed straight lines represent results for affine and phantom models and the full lines for real networks with $\kappa = 10$ and 100.

Equation 51 reduces to eq 23 when $\kappa = 0$, and to eq 38 when $\kappa = \infty$.

By comparing Figures 3 and 5, the averages for $\delta X_i \delta X_j$ for the real network may be written by modifying the expression given by eq 35. Thus, for the real network

$$\overline{\delta X_i \delta X_j} = \overline{(\delta X_1)^2} + [\min(\zeta,\theta) - \zeta\theta]\bar{x}^2 - (\eta/2)[\overline{x^2} - \bar{x}^2] \quad (52)$$

The ensemble average is

$$\langle \delta X_i \delta X_j \rangle = \langle (\delta X_1)^2 \rangle + [\min(\zeta,\theta) - \zeta\theta] \langle \bar{x}^2 \rangle - (\eta/2)[\langle \overline{x^2} \rangle - \langle \bar{x}^2 \rangle] \quad (53)$$

The expression for $\langle x^2 \rangle$ has been given previously[7] as

$$\langle x^2 \rangle = [\lambda^2(1 - 2/\phi) + (2/\phi)(1 + B)] \langle x^2 \rangle_0 \quad (54)$$

where[4]

$$B = \kappa^2(\lambda^2 - 1)(\lambda^2 + \kappa)^{-2} \quad (55)$$

Substituting eq 54 and 47 into eq 53 leads to

$$\langle \delta X_i \delta X_j \rangle = \left\{ \frac{\lambda^2}{\lambda^2 + \kappa} \frac{\phi - 1}{\phi(\phi - 2)} + [\min(\zeta,\theta) - \zeta\theta] \left[(1 - 2/\phi)\lambda^2 + \frac{2}{\phi} \left(\frac{\kappa\lambda}{\lambda^2 + \kappa} \right)^2 \right] - (\eta/\phi) \left[1 + B - \left(\frac{\kappa\lambda}{\lambda^2 + \kappa} \right)^2 \right] \right\} \langle x^2 \rangle_0 \quad (56)$$

Equation 56 reduces to the corresponding expression for the phantom and affine networks when $\kappa = 0$ and ∞, respectively.

Finally, the expression for the average $\langle (\delta x_{ij})^2 \rangle$ may be written as

$$\langle (\delta x_{ij})^2 \rangle = \eta \langle x^2 \rangle - \eta^2 \langle \bar{x}^2 \rangle = \left[\eta(1 - \eta)(1 - 2/\phi)\lambda^2 + (2/\phi)(1 + B)\eta - \left(\frac{\kappa\lambda}{\lambda^2 + \kappa} \right)^2 (2/\phi)\eta^2 \right] \langle x^2 \rangle_0 \quad (57)$$

Comparison of Results for Phantom, Affine, and Constrained Junction Models

The mean-square fluctuations $\langle (\Delta X_i)^2 \rangle$ for a phantom, affine, and a real network are given by eq 23, 39, and 50, respectively. Results of calculations from these equations are compared in Figure 7 for $\zeta = 0.3$, $\phi = 4$, and $\kappa = 10$ and 100. The fluctuations represented by the ratio $\langle(\Delta X_i)^2\rangle/\langle x^2\rangle_0$ along the ordinate are linear in λ^2 for the affine and the phantom models. Results for these two are shown with dashed curves. It is interesting to note that the two lines intersect around $\lambda^2 = 3.5$, due to the strain dependence of the fluctuations of point i in the phantom network. At low values of λ, the fluctuations in the phantom network are larger than those in the affine network due to the freedom of the junction points. However, as λ is increased the affine behavior results in larger fluctuations, as seen in Figure 7. The fluctuations in the real network are very close to the affine limit at low values of λ for $\kappa = 10$ and 100. Phantomlike behavior at low λ is obtained only when κ is less than unity. At higher extensions the curve for $\kappa = 10$ is substantially closer to the phantom result. Similarly, the one with $\kappa = 100$ is close to the affine limit.

Results of calculations for the fluctuations of the mean-square length $\langle(\Delta x_{ij})^2\rangle/\langle x^2\rangle_0$ of a portion of a chain between points i ($\zeta = 0.3$) and j ($\theta = 0.7$) are presented in Figure 8. Trends in the curves are similar to those shown in Figure 7.

Acknowledgment. It is a pleasure to acknowledge the financial support provided by the National Science Foundation through Grant DMR 84-15082 (Polymers Program, Division of Materials Research).

References and Notes

(1) Kloczkowski, A.; Mark, J. E.; Erman, B., preceding paper in this issue.
(2) Pearson, D. S. *Macromolecules* **1977**, *10*, 696.
(3) James, H. M. *J. Chem. Phys.* **1947**, *15*, 651.
(4) Flory, P. J. *J. Chem. Phys.* **1977**, *66*, 5720.
(5) Mark, J. E.; Erman, B. *Rubberlike Elasticity. A Molecular Primer*; Wiley-Interscience: New York, 1988.
(6) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1976**, *351*, 351.
(7) Erman, B.; Flory, P. J. *Macromolecules* **1983**, *16*, 1601.

Comparison of Experiment and the Proposed General Linear Viscoelastic Theory. 5. Zero Shear Viscosity of Polybutadiene over a Wide Molecular Weight Range

Y.-H. Lin

Exxon Chemical Company, Baytown Polymers Center, Baytown, Texas 77522.
Received January 27, 1988; Revised Manuscript Received August 22, 1988

ABSTRACT: The viscosity data of nearly monodisperse polybutadiene samples recently obtained by Graessley et al. over a wide molecular weight (MW) range have been analyzed in terms of the proposed general linear viscoelastic theory. The transition from the $\eta_0 \propto M^{3.4}$ region to the $\eta_0 \propto M^3$ region with increasing MW as predicted by the theory is supported by the experimental results. This supports the validity of the chain length fluctuation mechanism as incorporated into the general theory. Over more than 3 decades of MW above M_c, good agreement between theory and experiment is obtained. The present result of analysis is consistent with the previous conclusion that the tube renewal process is negligible in a monodisperse system. It is proposed that the approximate 35% higher values of the experimental results in the low MW region, $M_e < M < M_c$, related to the abnormal higher M_c/M_e ratio of polybutadiene. This seems to occur to polymers of high plateau modulus.

I. Introduction

In the molecular weight (MW) region, where most viscosity measurements for various polymers have been done, the zero shear viscosity η_0 varies with MW as $\eta_0 \propto M^{3.4}$.[1,2] The *pure* reptation model (originally proposed by de Gennes[3] and further developed by Doi and Edwards[4-7] into a constitutive equation) predicts $\eta_0 \propto M^3$. Models including the chain length fluctuation effect[8-10] have been proposed to account for the discrepancy. The chain length fluctuation relaxes the "tube" stress at chain ends and its effect theoretically becomes negligible at very high MWs. Thus, in the very high MW region, one would expect that $\eta_0 \propto M^{3.4}$ transits into $\eta_0 \propto M^3$. Whether this will occur is an important test to the chain length fluctuation mechanism.[8-11]

For this purpose, Graessley et al.[12] recently measured the melt viscosity of polybutadiene over a wide range of MW to as high as 1.65×10^7. The entanglement MW (M_e) of polybutadiene is relatively small compared to most other polymers. This helps reach the M/M_e region sufficiently high to see if the $\eta_0 \propto M^3$ asymptote indeed occurs. Theoretical estimation[8-10] indicates that M/M_e needs to be much larger than $\sim$100 to see the transition.

Graessley et al. analyzed their results in terms of Doi's equation[9]

$$\eta_0 = \text{const } M^3[1 - \mu(M_e/M)^{0.5}]^3 \qquad (1)$$

with $\mu = 1.7$ (an adjustable parameter) and $M_e = 1850$ (calculated by using $M_e = \rho RT/G_N$ with $G_N = 1.2 \times 10^7$ dyn/cm^2). The analysis suggested an asymptotic limit of $\eta_0/M^3 \approx 1 \times 10^{-9}$. On the other hand, using the viscosity–molecular weight ratio (η_0/M) for Rouse chains (value obtained in the MW region: $M < M_c$ and corrected to constant free volume), they obtained $\eta_0/M^3 = 6.4 \times 10^{-9}$ for pure reptation. They attributed the difference of the two η_0/M^3 values to the tube renewal process.

The validity of the tube renewal model,[13,14] which Graessley et al. have used to interpret the viscosity data of polybutadiene, was recently questioned on a theoretical ground.[15] Furthermore, extensive comparisons of the proposed general linear viscoelastic theory and the viscoelastic[10,16-18] and diffusional data[19] of (nearly) monodisperse polystyrene samples have consistently led us to reach a conclusion that the tube renewal process is negligible in a monodisperse sample.

Here the melt viscosity data obtained by Graessley et al. and by Roovers[12a-c] are compared with the proposed general linear viscoelastic theory.[10] The transition from the $\eta_0 \propto M^{3.4}$ region to the $\eta_0 \propto M^3$ region with increasing MW as predicted by the theory is in agreement with the

0024-9297/89/2222-1437$01.50/0