Chain Dimensions and Fluctuations in Random Elastomeric Networks. 1. Phantom Gaussian Networks in the Undeformed State

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ABSTRACT: A matrix method is used to study the fluctuations of junctions and points along the chains in an undeformed phantom Gaussian network having the topology of a symmetrically grown tree. The fluctuations of the mean-square distances between any two points along the chain, or any two ϕ-functional junctions, which are separated by several ϕ-functional junctions, are calculated analytically. The basic results obtained in this paper will be used in subsequent papers to study the effect of deformation on fluctuations in elastomeric networks and the neutron scattering from undeformed and deformed networks.

Introduction

The statistical mechanics of random networks is most suitably described in terms of the phantom network model. The mathematical structure of the model was first outlined in detail by James[1] and James and Guth.[2] It is based on assumptions describing the transformations of junction points, or cross-links, under macroscopic deformation. The mean positions of the junctions transform affinely while their instantaneous fluctuations are independent of macroscopic deformation. Junctions are joined by Gaussian chains which may pass freely through one another as they undergo rapid fluctuations according to the kinetic characteristics of polymeric media.

The theory of James and Guth has subsequently been reinterpreted and improved by various authors.[3-8] Reference to these papers in the order cited provides a complete survey of the development of the theory of phantom networks. The theory developed especially by Graessley,[5,6] Flory,[7] and Pearson[8] leads to the evaluation of various molecular dimensions. In the concise but elegant paper by Pearson,[8] the mean-square fluctuations of points along the chain contour are described as a function of network topology. Additionally, cross-correlations among fluctuations of two different points on a chain are determined. These developments direct attention, for the first time, to smaller length scales than the end-to-end chain dimensions in a network. In view of recent progress in experimental techniques, it now seems possible to determine directly the configurational properties of chains of networks at the submolecular level.[8,9] The implications of the findings of Pearson for phantom networks are therefore of significant importance. However, to out knowledge, the mathematical details of his treatment of phantom networks have not appeared in the literature.

In the present study, we therefore attempt to give the details of calculations that lead to the results obtained by Pearson and to generalize the problem to the case when two points are separated by several junctions. An exposition of the subject in full detail seems to be timely due to increasing interest in polymeric networks.[10] In the following paper,[11] we also consider fluctuations of the chain contour in affine as well as real networks. Consideration of transformations of various microscopic dimensions with macroscopic strain, for the phantom, affine, and the real network models, leads to results that may now directly be checked by experiments.

Review of the Theory of Phantom Networks

In this section we briefly review the mathematical features of the phantom network theory, using the notation of Flory[7] and Pearson.[8] The reader is referred to these papers for details not covered in the present treatment. The network is assumed to consist of chains and junctions which can move freely through one another. Each chain is assumed to be Gaussian with the distribution $W(r)$ of the end-to-end vector $\mathbf{r}$ given as

$$W(r) = \left(\frac{3}{2\pi\langle r^2\rangle_0}\right)^{3/2} \exp(-3r^2/2\langle r^2\rangle_0) \qquad (1)$$

Here, $\langle r^2\rangle_0$ is the mean-squared end-to-end distance of chains in the bulk unperturbed state. Angular brackets denote averaging over all chains of the network.

Due to the phantomlike nature of chains and junctions, there are no intermolecular contributions, and the configuration partition function Z_N for the network may be expressed as the product of configuration functions for its individual chains[2]

$$Z_N = C\prod_{i<j}\exp(-3r_{ij}^2/2\langle r_{ij}^2\rangle_0) \qquad (2)$$

where C is a constant factor and the product includes all pairs of i,j junctions connected by a chain. Equation 2 can be written as

$$Z_N = C\exp(-\tfrac{1}{2}\sum_i\sum_j\gamma_{ij}^*|\mathbf{R}_i - \mathbf{R}_j|^2) \qquad (3)$$

where $\mathbf{R}_i$ and $\mathbf{R}_j$ are position vectors of junctions i and j, $r_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$, and $\gamma_{ij}^* = 3/2\langle r_{ij}^2\rangle_0$ if junctions i and j are connected by a chain and $\gamma_{ij}^* = 0$ otherwise. Equation 3 can be rewritten in the more convenient form

$$Z_N = C\exp(-\sum_i\sum_j\gamma_{ij}\mathbf{R}_i\cdot\mathbf{R}_j) \equiv C\exp(-\{\mathbf{R}\}^T\boldsymbol{\Gamma}\{\mathbf{R}\}) \qquad (4)$$

where

$$\gamma_{ij} = -\gamma_{ij}^* \qquad \text{if} \quad i \neq j$$
$$\gamma_{ii} = \sum_j\gamma_{ij}^* = \sum_j\gamma_{ji}^* \qquad (5)$$

and $\{\mathbf{R}\} = \{\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_\mu\}$ is the column vector formed by position vectors of all μ junctions. The superscript T is the transpose, $\boldsymbol{\Gamma}$ is the symmetric square matrix comprising the elements γ_{ij}, and a dot between vectors indicates the scalar product.

According to the theory, the μ junctions of the network are comprised of a set $\{\sigma\}$ of fixed junctions μ_σ in number and a set $\{\tau\}$ of μ_τ free junctions that fluctuate about a mean position. The latter set is the subject of the present study. The partition function of the network due to the fluctuating junctions is expressed as

$$Z_{N\tau} = C \exp[-\{\Delta \mathbf{R}_\tau\}^T \Gamma_\tau \{\Delta \mathbf{R}_\tau\}] \quad (6)$$

Here, the index τ indicates that the quantities of interest are for the fluctuating junctions, and

$$\{\Delta R_\tau\} = \{\mathbf{R}_{1\tau} - \bar{\mathbf{R}}_{1\tau}, \mathbf{R}_{2\tau} - \bar{\mathbf{R}}_{2\tau}, ..., \mathbf{R}_{\mu_\tau\tau} - \bar{\mathbf{R}}_{\mu_\tau\tau}\} \quad (7)$$

The bar superposed on the vectors in eq 7, and also in what follows, denotes the time average.

The product of the fluctuations of two junctions i and j averaged over the network may be obtained from eq 6 as

$$\langle \Delta \mathbf{R}_i \cdot \Delta \mathbf{R}_j \rangle = \frac{\int \Delta \mathbf{R}_i \cdot \Delta \mathbf{R}_j \exp[-\{\Delta \mathbf{R}_\tau\}^T \Gamma_\tau \{\Delta \mathbf{R}_\tau\}] \, d\{\Delta \mathbf{R}_\tau\}}{\int \exp[-\{\Delta \mathbf{R}_\tau\}^T \Gamma_\tau \{\Delta \mathbf{R}_\tau\}] \, d\{\Delta \mathbf{R}_\tau\}} = -\frac{\partial}{\partial \gamma_{ij}} \ln Z_\tau \quad (8)$$

where

$$d\{\Delta \mathbf{R}_\tau\} \equiv d\Delta \mathbf{R}_{1\tau} \, d\Delta \mathbf{R}_{2\tau} \, ... \, d\Delta \mathbf{R}_{\mu_\tau\tau} \quad (9)$$

and

$$Z_\tau = \int \exp[-\{\Delta \mathbf{R}_\tau\}^T \Gamma_\tau \{\Delta \mathbf{R}_\tau\}] \, d\{\Delta \mathbf{R}_\tau\} = \left(\frac{\pi^{\mu_\tau}}{\det \Gamma_\tau}\right)^{3/2} \quad (10)$$

Use of eq 10 in eq 8 leads to

$$\langle \Delta \mathbf{R}_i \cdot \Delta \mathbf{R}_j \rangle = \frac{3}{2} \frac{\partial}{\partial \gamma_{ij}} \ln |\det \Gamma_\tau| = \frac{3}{2} (\Gamma_\tau^{-1})_{ij} \quad (11)$$

where $(\Gamma_\tau^{-1})_{ij}$ is the ijth element of the inverse of Γ_τ. Equation 11 holds for all ij pairs of junctions joined directly by a chain as well as those separated by more than one chain.

The mean-square fluctuation of the distance $r_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$ between junctions i and j is

$$\langle (\Delta r_{ij})^2 \rangle = \langle (\Delta \mathbf{R}_i - \Delta \mathbf{R}_j)^2 \rangle = \langle (\Delta R_i)^2 \rangle + \langle (\Delta R_j)^2 \rangle - 2 \langle \Delta \mathbf{R}_i \cdot \Delta \mathbf{R}_j \rangle = \tfrac{3}{2}[(\Gamma_\tau^{-1})_{ii} + (\Gamma_\tau^{-1})_{jj} - 2(\Gamma_\tau^{-1})_{ij}] \quad (12)$$

The summary given in the preceding paragraphs for fluctuations in a phantom network is essentially the one given by Pearson.[8] For a further quantitative description of fluctuations in terms of network topology, the explicit form of Γ and its inverse must be prescribed.

The Matrix Γ and Its Inverse

Interest in the present study is centered around the set $\{\tau\}$ of free junctions only. We therefore drop the use of the subscript τ in Γ and $\mathbf{R}$ in what follows for the sake of brevity.

The matrix Γ is known as the Kirchhoff or valency-adjacency matrix[4] in graph theory. Its form depends on the topological structure and connectivity of the network. In the present study, following Flory and Pearson, we consider only networks that have a treelike structure and are symmetrically grown about a central chain. For simplicity, all network chains are assumed to be of equal contour length. An example of the tetrafunctional symmetrically grown network is shown in Figure 1. The network grows symmetrically from the central chain defined by the junctions 1 and 2. These two junctions constitute the first tier of junctions, and the second tier is

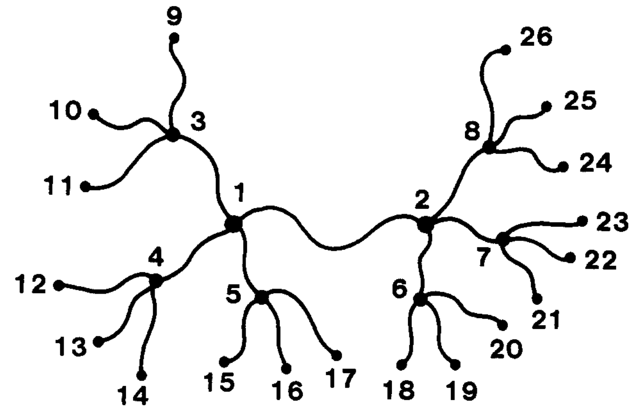

Figure 1. First three tiers of the symmetrically grown tetrafunctional ($\phi = 4$) network with a treelike structure. The junctions in subsequent tiers are numbered counterclockwise.

made up of the six junctions numbered from 3 to 8. The third tier consists of the remaining 18 junctions, labeled from 9 to 26. The network is assumed to grow in this way where the junctions in a given tier are numbered counterclockwise as shown. By assumption, no loops exist in a symmetrically grown network of the form shown in Figure 1. The matrix Γ for this tetrafunctional network is obtained according to eq 5 as eq 13, where $\gamma = 3/2\langle r^2 \rangle_0$

$$\Gamma = \gamma \left[\begin{array}{cc|cccccc|cccccccccccccccccc}
4 & -1 & -1 & -1 & -1 &&&&&&&&&&&&&&&&&&&&& \\
-1 & 4 &&&& -1 & -1 & -1 &&&&&&&&&&&&&&&&&& \\ \hline
-1 && 4 &&&&&& -1 & -1 & -1 &&&&&&&&&&&&&&& \\
-1 &&& 4 &&&&&&&& -1 & -1 & -1 &&&&&&&&&&&& \\
-1 &&&& 4 &&&&&&&&&& -1 & -1 & -1 &&&&&&&&& \\
& -1 &&&& 4 &&&&&&&&&&&& -1 & -1 & -1 &&&&&& \\
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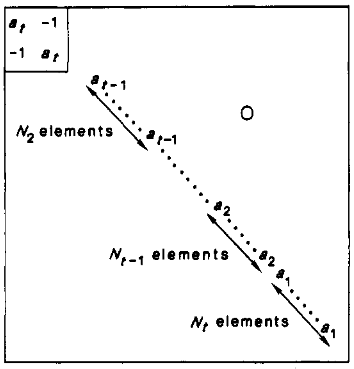
\end{array}\right] \quad (13)$$

and only the nonzero entries are indicated. The matrix is partitioned into submatrices for easy reference and grows toward the right and downward as the size of the network increases. The highly regular form of Γ follows from the numbering scheme shown in Figure 1. Thus the ith row or column is associated with the ith junction. The generalization of Γ to a network of junction functionality ϕ is straightforward; each element along the diagonal equates to ϕ, and there are ϕ off-diagonal -1's in each row or column, with exception of the last tier, where -1 occurs only once. The tth diagonal square submatrix is associated with junctions of the tth tier. Since there are $N_t = 2(\phi - 1)^{t-1}$ junctions in the tth tier, the tth diagonal square submatrix is of order $N_t \times N_t$. For a given junction in the tth tier, a -1 to the left of the diagonal corresponds to connection to a junction in the $(t - 1)$th tier and $\phi - 1$ subsequent -1's to connection with $\phi - 1$ junctions in the $(t + 1)$st tier.

The matrix Γ may be diagonalized as follows: (1) Divide the last N_t rows by ϕ and add to the preceding N_{t-1} rows such that the −1's on the right of the diagonal vanish. This changes the diagonal elements of the $(t-1)$st tier to $\phi - (\phi - 1)/\phi$. (2) Divide the N_{t-1} rows of the $(t-1)$st tier by $\phi - (\phi - 1)/\phi$ and add to the preceding N_{t-2} rows such that the −1's on the right of the diagonal vanish. This changes the diagonal elements of the $(t-2)$nd tier into

$$\phi - (\phi - 1)/[\phi - (\phi - 1)/\phi]$$

Continuation of this elimination process eventually leads to a matrix whose diagonal elements a_n are ordered as in eq 14. All off-diagonal elements in the upper right part



(14)

of the matrix are zeros with exception of the Γ_{12} element, which is equal to −1. Indexing the a's by starting from the lower right corner as shown in eq 14 has the advantage of concise representation as will be obvious below. According to the procedure described above, the recurrence relations for a_i are

$$a_1 = \phi$$

$$a_n = \phi - (\phi - 1)/a_{n-1} \tag{15}$$

and the solution of eq 15 is

$$a_n = [(\phi - 1)^{n+1} - 1]/[(\phi - 1)^n - 1] \tag{16}$$

In the limit when the number of tiers goes to infinity

$$\lim_{n\to\infty} a_n = \phi - 1 \tag{17}$$

The determinant of Γ for a finite system of t tiers is

$$\det(\Gamma) = \gamma^N (a_t^2 - 1) a_{t-1}^{N_2} a_{t-2}^{N_3} \ldots a_2^{N_{t-1}} a_1^{N_t} \tag{18}$$

where

$$N = \sum_{\nu=1}^{t} N_\nu = 2\frac{(\phi - 1)^t - 1}{\phi - 2} \tag{19}$$

The inverse of Γ may now be obtained according to the relation $(\Gamma^{-1})_{ij} = (\text{adjoint } \Gamma_{ij})/\det(\Gamma)$.

Fluctuations of Two Junctions Joined by a Single Chain. The first four elements of Γ^{-1} follow from eq 11 and the evaluation of Γ^{-1} as

$$\begin{bmatrix} \langle(\Delta R_1)^2\rangle & \langle\Delta \mathbf{R}_1\cdot\Delta \mathbf{R}_2\rangle \\ \langle\Delta \mathbf{R}_1\cdot\Delta \mathbf{R}_2\rangle & \langle(\Delta R_2)^2\rangle \end{bmatrix} = \frac{3}{2}\begin{bmatrix} (\Gamma^{-1})_{11} & (\Gamma^{-1})_{12} \\ (\Gamma^{-1})_{21} & (\Gamma^{-1})_{22} \end{bmatrix} = \frac{3}{2\gamma}\begin{bmatrix} \dfrac{a_t}{a_t^2 - 1} & \dfrac{1}{a_t^2 - 1} \\ \dfrac{1}{a_t^2 - 1} & \dfrac{a_t}{a_t^2 - 1} \end{bmatrix} \tag{20}$$

Elements of Γ^{-1} corresponding to fluctuations of junctions other than junctions 1 and 2, joined by a chain, are more complicated. However, in the limit when the number of tiers goes to infinity, all these elements go to the same limits, and eq 20 can be written for any pair i,j of two junctions joined by a chain as

$$\begin{bmatrix} \langle(\Delta R_i)^2\rangle & \langle\Delta \mathbf{R}_i\cdot\Delta \mathbf{R}_j\rangle \\ \langle\Delta \mathbf{R}_i\cdot\Delta \mathbf{R}_j\rangle & \langle(\Delta R_j)^2\rangle \end{bmatrix} = \frac{3}{2\gamma}\begin{bmatrix} \dfrac{\phi - 1}{\phi(\phi - 2)} & \dfrac{1}{\phi(\phi - 2)} \\ \dfrac{1}{\phi(\phi - 2)} & \dfrac{\phi - 1}{\phi(\phi - 2)} \end{bmatrix} \tag{21}$$

The mean-squared fluctuation $\langle(\Delta r_{12})^2\rangle$ in the distance between junctions 1 and 2, given by eq 12, is

$$\langle(\Delta r_{12})^2\rangle = \frac{3}{2\gamma}\left[\frac{2(a_t - 1)}{a_t^2 - 1}\right] = \frac{3}{2\gamma}\,\frac{2(\phi - 1)^t - 2}{(\phi - 1)^{t+1} + (\phi - 1)^t - 2} \tag{22}$$

In the limit when $t \to \infty$, eq 22 reduces, for any pair i,j joined by a chain, to

$$\langle(\Delta r_{ij})^2\rangle = \frac{3}{2\gamma}\,\frac{2}{\phi} = \frac{2}{\phi}\langle r_{ij}^2\rangle_0 \tag{23}$$

Fluctuations of Two Junctions Separated by Several Chains. In the case when two junctions m and n are separated by d other junctions, the average fluctuations are, for $t \to \infty$

$$\begin{bmatrix} \langle(\Delta R_m^2)\rangle & \langle\Delta \mathbf{R}_m\cdot\Delta \mathbf{R}_n\rangle \\ \langle\Delta \mathbf{R}_m\cdot\Delta \mathbf{R}_n\rangle & \langle(\Delta R_n^2)\rangle \end{bmatrix} = \frac{3}{2}\begin{bmatrix} (\Gamma^{-1})_{mm} & (\Gamma^{-1})_{mn} \\ (\Gamma^{-1})_{nm} & (\Gamma^{-1})_{nn} \end{bmatrix} = \frac{3}{2\gamma}\begin{bmatrix} \dfrac{\phi - 1}{\phi(\phi - 2)} & \dfrac{1}{\phi(\phi - 2)(\phi - 1)^d} \\ \dfrac{1}{\phi(\phi - 2)(\phi - 1)^d} & \dfrac{\phi - 1}{\phi(\phi - 2)} \end{bmatrix} \tag{24}$$

The derivation of eq 24 is shown in the Appendix. When junctions m and n are separated by one chain only, $d = 0$ and the fluctuations given by eq 24 reduce to those given by eq 21.

The mean-squared fluctuations of the distance r_{mn} are

$$\langle(\Delta r_{mn})^2\rangle = \langle(\Delta \mathbf{R}_m - \Delta \mathbf{R}_n)^2\rangle = \frac{2}{\phi(\phi - 2)(d + 1)}\,\frac{(\phi - 1)^{d+1} - 1}{(\phi - 1)^d}\langle r_{mn}^2\rangle_0 \tag{25}$$

since $\langle r_{mn}^2\rangle_0 = (d + 1)\langle r_{12}^2\rangle_0 = (3/2\gamma)(d + 1)$. In the limit as $d \to \infty$, we have

$$\lim_{d\to\infty} \langle(\Delta r_{mn})^2\rangle = \frac{2(\phi - 1)}{\phi(\phi - 2)}\langle r_{12}^2\rangle_0 \tag{26}$$

When $d = 0$, eq 25 reduces to eq 23.

Equation 26 may be written, with the help of eq 23, as

$$\frac{\langle(\Delta r_{mn})^2\rangle_{d=\infty}}{\langle(\Delta r_{mn})^2\rangle_{d=0}} = \frac{(\phi - 1)}{(\phi - 2)} \tag{27}$$

The relative value of the fluctuations $\langle(\Delta r_{mn})^2\rangle$ measured with respect to the distance $\langle r_{mn}^2\rangle_0$ decreases, in the limit $d \to \infty$, as d^{-1}, but the absolute value of the fluctuations increases by the factor $(\phi - 1)/(\phi - 2)$. The role of intermediate junctions is specially important in the scattering of neutrons in the long-wavelength region, which will be considered in a subsequent paper.

Fluctuations of Points along a Chain. The previous approach may be generalized to obtain fluctuations of any two points i and j on a network chain. We assume that all chains consist of n equal length segments and of $n - 1$ junctions with functionality 2 which separate the segments as shown in Figure 2. In this figure, a two-tiered network is shown with $n = 4$. In labeling the junctions the same convention is used as before, modified by the ne-

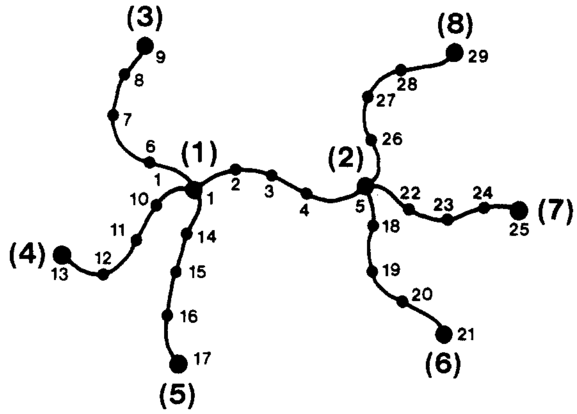
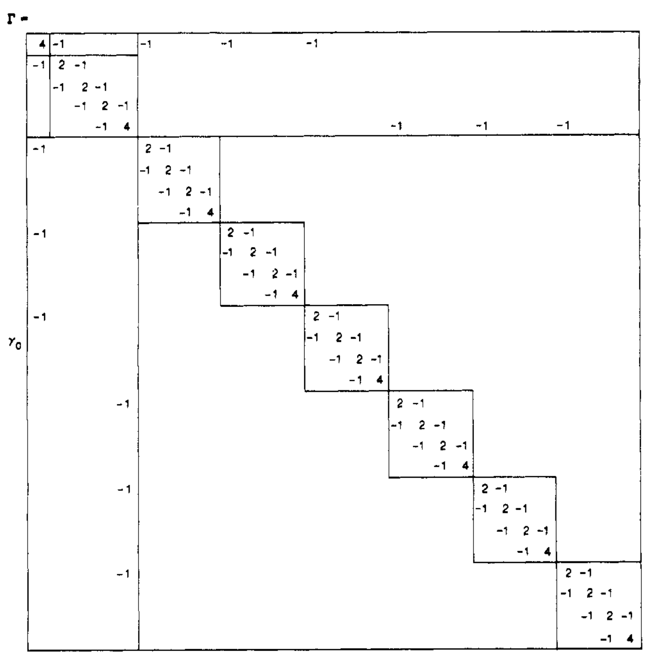


Figure 2. Tetrafunctional network with additional 2-functional junctions which separate each chain into $n = 4$ segments of equal length. The new method of labeling junctions for the first two tiers is shown. Numbers in parenthesis correspond to the previous method of numbering the ϕ-functional junctions in Figure 1. The relation between new number m' of the ϕ-functional junction and the old number m is $m' = n(m - 1) + 1$.

cessity of counting 2-functional junctions. The pattern of labeling is self-explanatory as is seen from the figure. The valency adjacency matrix for the network of Figure 2 may be written as eq 28. The matrix $\mathbf{\Gamma}$ of eq 28 is partitioned



(28)

into two square submatrices belonging to tiers 1 and 2. A 4-functional junction labeled as m in Figure 1 is now labeled by m' in Figure 2; it is represented by an entry of 4 at the $m'm'$ position on the diagonal, where

$$m' = n(m - 1) + 1 \qquad (29)$$

The entires of 2 along the diagonal refer to the 2-functional junctions. The matrix may be generalized to the case of ϕ-functional junctions separated by $n - 1$ 2-functional junctions. In this case, the matrix will contain a ϕ on the diagonal elements $\Gamma_{\nu\nu}$ where ν is given by eq 29. The remaining elements of the diagonal will contain a 2 corresponding to 2-functional junctions. Nondiagonal elements ij of $\mathbf{\Gamma}$ contain a -1 if junctions i and j are directly connected. Otherwise they are zero. In rows (columns) containing a ϕ, -1 occurs ϕ times if the ϕ-functional junctions does not belong to the last tier. For a ϕ-functional junction belonging to the last tier, there is a single -1 in the row (column). In general, the dimension of the square submatrix corresponding to the tth tier is $N'_t \times N'_t$, where

$$N'_t = 2(\phi - 1)^{t-1}n = N_t n \qquad (30)$$

In each of these submatrices we can isolate sub-submatrices of order $n \times n$, corresponding to a given ϕ-functional junction within a given tier. Each of these sub-submatrices has the form

$$\mathbf{A}_n = \underbrace{\begin{bmatrix} 2 & -1 & & & & & \\ -1 & 2 & -1 & & & & \\ & -1 & 2 & -1 & & & \\ & & \ddots & \ddots & \ddots & & \\ & & & -1 & 2 & -1 & \\ & & & & -1 & 2 & -1 \\ & & & & & -1 & \phi \end{bmatrix}}_{n - 1 \text{ times}} \qquad (31)$$

In order to calculate the inverse of the matrix $\mathbf{\Gamma}$, we use the method employed above for the system without 2-functional junctions. Accordingly, the -1's in the upper (lower) half of the matrix $\mathbf{\Gamma}$ have to be eliminated, following which the determinant equates to the product of the terms along the diagonal. We start from the rows of the last submatrix of $\mathbf{\Gamma}$ corresponding to the last tier of a symmetrically grown tree. The tth submatrix contains $\mathbf{A}_n$ matrices which appear $N_t = 2(\phi - 1)^{t-1}$ times. Diagonalizing an $\mathbf{A}_n$ matrix leads to

$$\begin{bmatrix} \frac{n\phi - (n-1)}{(n-1)\phi - (n-2)} & & & & 0 \\ & \ddots & & & \\ & & \frac{3\phi - 2}{2\phi - 1} & & \\ & & & \frac{2\phi - 1}{\phi} & \\ & & & & \phi \end{bmatrix} \qquad (32)$$

The product of the elements on the diagonal of the matrix given by eq 32 is equal to

$$n\phi - (n - 1) \qquad (33)$$

In diagonalizing the elements of the tth tier, we change the elements of the $(t - 1)$th tier from $a_1 = \phi$ to

$$a_2 = \phi - \frac{(\phi - 1)[(n - 1)a_1 - (n - 2)]}{na_1 - (n - 1)} \qquad (34)$$

or in general

$$a_k = \phi - \frac{(\phi - 1)[(n - 1)a_{k-1} - (n - 2)]}{na_{k-1} - (n - 1)} \qquad (35)$$

The determinant of the matrix $\mathbf{\Gamma}$ of a finite system of t tiers is given by the product

$$\det(\Gamma) = \gamma_0^N[na_1 - (n - 1)]^{N_t} \times [na_2 - (n - 1)]^{N_{t-1}} \ldots [na_{t-1} - (n - 1)]^{2(\phi-1)} \times \{na_t^2 - 2a_t(n - 1) + (n - 2)\} \qquad (36)$$

The last term in eq 36 results from the first tier. Here $N = 2n[(\phi - 1)^t - 1]/(\phi - 2)$ and $\gamma_0 = 3/2\langle r_1^2\rangle_0$ where $\langle r_1^2\rangle_0$ is the mean-square end-to-end distance for a single segment.

The solution of the recurrence formula given by eq 34 and 35 is

$$a_k = \frac{n[(\phi - 1)^k - (\phi - 1)] + (\phi - 2)[(\phi - 1)^k + 1]}{n[(\phi - 1)^k - (\phi - 1)] + (\phi - 2)} \qquad (37)$$

In the special limit when the number of tiers goes to infinity

$$\lim_{k\to\infty} a_k = \frac{n + \phi - 2}{n} \tag{38}$$

In the case when $n = 1$, i.e., there are no 2-functional junctions between ϕ-functional ones, we recover eq 16 from eq 37 and eq 17 from eq 38.

To calculate the elements of the inverse matrix $\mathbf{\Gamma}^{-1}$ corresponding to the first tier we have to calculate determinants which are formed by crossing out the ith row and the jth column of the first submatrix of $\mathbf{\Gamma}$ corresponding to the first tier of the tree. The (i–i)th minor D_{ii} obtained by crossing out ith row and column is a product of two determinants

$$D_{ii} = \gamma_0^{N-1} \det (\mathbf{A}_{i-1}) \det (\mathbf{A}_{n+1-i}) \tag{39}$$

where $\mathbf{A}_n$ is given by eq 31, with

$$\det (\mathbf{A}_n) = na_t - (n - 1) \tag{40}$$

In view of eq 40, eq 39 results in

$$D_{ii} = \gamma_0^{N-1}[(i - 1)a_t - (i - 2)][(n + 1 - i)a_t - (n - i)] \tag{41}$$

Carrying out the operations for the calculation of the (i–j)th minor D_{ij} leads to

$$D_{ij} = \gamma_0^{N-1} \det (\mathbf{A}_{\min(i-1,j-1)}) \det (\mathbf{A}_{n+1-\max(i,j)}) (-1)^{|i-j|} = (-1)^{i+j}[(\min (i,j) - 1)a_t - (\min (i,j) - 2)][(n + 1 - \max(i,j))a_t - (n - \max(i,j))] \tag{42}$$

where max (i,j) and min (i,j) are the maximum and minimum functions, respectively.

From eq 41, 42, and 36, the four elements of the inverse of $\mathbf{\Gamma}$ corresponding to the first tier are obtained as

$$(\mathbf{\Gamma}^{-1})_{ii} = \gamma_0^{-1}\frac{[a_t(i - 1) - (i - 2)][a_t(n + 1 - i) - (n - i)]}{na_t^2 - 2a_t(n - 1) + (n - 2)}$$

$$(\mathbf{\Gamma}^{-1})_{ij} = \gamma_0^{-1}[a_t(\min (i,j) - 1) - (\min (i,j) - 2)]\frac{[a_t(n + 1 - \max (i,j)) - (n - \max (i,j))]}{na_t^2 - 2a_t(n - 1) + (n - 2)}$$

$$(\mathbf{\Gamma}^{-1})_{ji} = \gamma_0^{-1}[a_t(\min (i,j) - 1) - (\min (i,j) - 2)]\frac{[a_t(n + 1 - \max (i,j)) - (n - \max (i,j))]}{na_t^2 - 2a_t(n - 1) + (n - 2)}$$

$$(\mathbf{\Gamma}^{-1})_{jj} = \gamma_0^{-1}\frac{[a_t(j - 1) - (j - 2)][a_t(n + 1 - j) - (n - j)]}{na_t^2 - 2a_t(n - 1) + (n - 2)} \tag{43}$$

The positions of 2-functional junctions i and j may be expressed as fractions of the length of the chain between ϕ-functional junctions as

$$\zeta = \frac{i - 1}{n} \qquad 0 \le \zeta \le 1$$

$$\theta = \frac{j - 1}{n} \qquad 0 \le \theta \le 1 \tag{44}$$

In the limit as the number of tiers goes to infinity, eq 43 reduces to eq 45, with

$$\begin{bmatrix} \langle \Delta R_i^2 \rangle & \langle \Delta\mathbf{R}_i\cdot\Delta\mathbf{R}_j \rangle \\ \langle \Delta\mathbf{R}_i\cdot\Delta\mathbf{R}_j \rangle & \langle \Delta R_j^2 \rangle \end{bmatrix} = \frac{3n}{2\gamma_0} \times \begin{bmatrix} \frac{\phi - 1}{\phi(\phi - 2)} + \frac{\zeta(1 - \zeta)(\phi - 2)}{\phi} & \frac{\phi - 1}{\phi(\phi - 2)} + \frac{(\phi - 2)[\min (\zeta, \theta) - \zeta\theta] - \eta}{\phi} \\ \frac{\phi - 1}{\phi(\phi - 2)} + \frac{(\phi - 2)[\min (\zeta, \theta) - \zeta\theta] - \eta}{\phi} & \frac{\phi - 1}{\phi(\phi - 2)} + \frac{\theta(1 - \theta)(\phi - 2)}{\phi} \end{bmatrix} \tag{45}$$

$$\eta = |\zeta - \theta| \tag{46}$$

and

$$\gamma_0 = 3/2\langle r_1^2 \rangle_0 \tag{47}$$

where $\langle r_1^2 \rangle_0$ is the mean-squared end-to-end distance for a single segment, related to the mean-squared end-to-end distance of a network chain by

$$\langle r^2 \rangle_0 = n\langle r_1^2 \rangle_0 \tag{48}$$

so that

$$\gamma = \frac{3}{2\langle r^2 \rangle_0} = \gamma_0/n$$

The min (ζ,θ) function appearing in eq 45 may also be written as

$$\min (\zeta,\theta) = (\zeta + \theta - |\zeta - \theta|)/2 \tag{49}$$

as was done by Pearson,[8] although there were misprints in his formulas for nondiagonal elements.

The fluctuations of the mean-square distance $\langle (\Delta r_{ij})^2 \rangle$ between points i and j is obtained by using eq 12 and 45 as

$$\langle (\Delta r_{ij})^2 \rangle = \frac{3}{2\gamma}\left[\eta - \frac{(\phi - 2)}{\phi}\eta^2\right] \tag{50}$$

Inasmuch as η is independent of the absolute position of i and j relative to the ϕ-functional cross-links, $\langle (\Delta r_{ij})^2 \rangle$ depends only on the length of the sequence between points i and j. For finite number of tiers, when a_t is given by eq 37, the mean-square fluctuations in $\mathbf{r}_{ij}$ become

$$\langle (\Delta r_{ij})^2 \rangle = \frac{3}{2\gamma}\left[\eta - \eta^2 \frac{n(\phi - 1)^t(\phi - 2)}{(\phi - 1)^t n\phi - 2n(\phi - 1) + 2(\phi - 2)}\right] \tag{51}$$

It is seen from eq 51 that only the quadratic term in η is t-dependent.

Fluctuations of Two Points on Chains Separated by Several ϕ-Functional Junctions. The results of the previous section may be generalized to the case where 2-functional junctions are separated by several ϕ-functional junctions. Figure 3 depicts two points i and j separated by three 4-functional junctions, for example. The positions of junctions i and j (in units of the length of the chain between ϕ-functional junctions) with respect to the nearest ϕ-functional junction from the left are ζ and θ ($0 \le \zeta, \theta < 1$). The i,j elements of the inverse matrix of $\mathbf{\Gamma}$ for two points i and j separated by d ϕ-functional junctions leads, in the limit $t \to \infty$, to eq 52, if point i is on the left side of point j.

$$\begin{bmatrix} \langle (\Delta R_i)^2 \rangle & \langle \Delta\mathbf{R}_i\cdot\Delta\mathbf{R}_j \rangle \\ \langle \Delta\mathbf{R}_i\cdot\Delta\mathbf{R}_j \rangle & \langle (\Delta R_j)^2 \rangle \end{bmatrix} = \frac{3}{2\gamma} \times \begin{bmatrix} \frac{\phi - 1}{\phi(\phi - 2)} + \frac{\zeta(1 - \zeta)(\phi - 2)}{\phi} & \frac{[1 + \zeta(\phi - 2)][(\phi - 1) - \theta(\phi - 2)]}{\phi(\phi - 2)(\phi - 1)^d} \\ \frac{[1 + \zeta(\phi - 2)][(\phi - 1) - \theta(\phi - 2)]}{\phi(\phi - 2)(\phi - 1)^d} & \frac{\phi - 1}{\phi(\phi - 2)} + \frac{\theta(1 - \theta)(\phi - 2)}{\phi} \end{bmatrix} \tag{52}$$

If point i is on the right side of point j, then j and ζ in the nondiagonal elements of eq 52 have to be interchanged. The derivation of eq 52 is shown in the

Figure 3. Two points i and j of the network separated by $d = 3$ ϕ-functional junctions (where $\phi = 4$). The position of points i and j are measured with respect to the nearest ϕ-functional junction from the left in units of the length of the chain contour between ϕ-functional junctions.

Appendix. The mean-square fluctuation in r_{ij} is obtained from eq 52 as

$$\langle(\Delta r_{ij})^2\rangle = \frac{3}{2\gamma}\left\{\frac{2(\phi-1)}{\phi(\phi-2)}\left[1-\frac{1}{(\phi-1)^d}\right] + \frac{\phi-2}{\phi}\left[\zeta(1-\zeta)+\theta(1-\theta)-\frac{\zeta+\theta-2\theta\zeta}{(\phi-1)^d}\right] + \frac{\eta-d}{(\phi-1)^d}\right\} \quad (53)$$

where the distance between i and j is now

$$\eta = d + \theta - \zeta \quad \text{if point } i \text{ is on the left side of point } j$$
$$\eta = d + \zeta - \theta \quad \text{if point } i \text{ is on the right side of point } j \quad (54)$$

In the special case when $d = 0$, eq 53 reduces to eq 50. When $\zeta = 0$ and $\theta = 1$, eq 53 leads to eq 25.

The important difference between the expressions given by eq 50 and eq 53 is that when the points i and j are not separated by a ϕ-functional junction, $\langle(\Delta r_{ij})^2\rangle$ depends only on the relative distance between i and j, whereas the specific locations of i and j on the chains are required when they are separated by ϕ-functional junctions. This position dependence does not vanish even when $d \to \infty$. In this limit, eq 53 gives

$$\lim_{d\to\infty}\langle(\Delta r_{ij})^2\rangle = \frac{3}{2\gamma}\left\{\frac{2(\phi-1)}{\phi(\phi-2)} + \frac{(\phi-2)}{\phi}[\zeta(1-\zeta)+\theta(1-\theta)]\right\} \quad (55)$$

Discussion

The present paper forms a base for subsequent papers in which the effect of deformation on fluctuations in elastomeric networks (phantom and real) and scattering of neutrons from networks will be studied.

By using a matrix approach and developing the recurrence method to find the inverse of the matrix Γ, we were able to calculate the fluctuations of position of any junction and any point along the chain, as well as to calculate the fluctuations of the mean-square distance between any two points in the network.

These two points can be separated by several ϕ-functional junctions. In the special case when there are no ϕ-functional junctions which separate two points we recover the results obtained earlier by Pearson.[8]

The ϕ-functional junctions which separate two points of the network have an important effect on its long-wavelength scattering of neutrons. In most neutron scattering experiments on networks, some deuterated chains are cross-linked with other nondeuterated chains to form a network. In such a case one measures the scattering form factor $S(\mathbf{k})$ of a single labeled path progressing through the network via numerous meshes.[12]

The scattering law obtained by Pearson[8] corresponds to the different type of experiment where the labeled (deuterated) chain is end-linked with nonlabeled chains, so one measures the form factor $S(\mathbf{k})$ from a single mesh.

The small-angle neutron scattering from random elastomeric networks will be studied by us in another paper.

The present paper deals with chain dimensions and fluctuations in the undeformed phantom networks. In the following paper[11] we study the effect of deformation on chain dimensions and fluctuations in the affine, phantom, and real networks.

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Appendix

We first derive eq 24 for fluctuations of ϕ-functional junctions and then eq 52 for fluctuations of two points of the network separated by ϕ-functional junctions.

The position of a junction within the network can be described by one number i when the convention like that used in Figure 1 is applied or by two numbers (λ,μ). The first number λ labels the tier to which junction i belongs and μ is the number of junction within a given tier where the counterclockwise convention is used.

$$1 \le \mu \le 2(\phi-1)^{\lambda-1} \quad (A1)$$

The number i of the junction is then (see Figure 1)

$$i = 2\frac{(\phi-1)^{\lambda-1}-1}{\phi-2} + \mu \quad (A2)$$

For example, the junction with $i = 12$ in Figure 1 has ($\lambda = 3$, $\mu = 4$). To calculate the elements of the inverse matrix Γ^{-1} we use the formula

$$(\Gamma^{-1})_{ij} = (\text{adjoint } \Gamma_{ij})/\det \Gamma \quad (A3)$$

First we calculate minor D_{ii} which is formed by crossing-out the ith row and the ith column of Γ where $i = (\lambda, \mu)$. Using the previously described method of elimination of -1's on the right of the diagonal we obtain

$$D_{ii} = \gamma^{N-1}(a_1^{N_t}a_2^{N_{t-1}} \ldots a_{t-\lambda}^{N_{\lambda+1}}) \times (a_{t-\lambda+1}^{N_\lambda-1}a_{t-\lambda+2}^{N_{\lambda-1}-1} \ldots a_{t-1}^{N_2-1}) \times [a^*_{t-\lambda+2}a^*_{t-\lambda+3} \ldots a^*_{t-1}(a_t a^*_t - 1)] \quad (A4)$$

where

$$N_k = 2(\phi-1)^{k-1} \quad (A5)$$

and N is given by eq 19.

The coefficients a_k are uneffected by crossing-out the ith row and the ith column and satisfy the recurrence formula (eq 15) with solution given by eq 16. The coefficients a^*_k which are effected satisfy the recurrence relations

$$a^*_{t-\lambda+2} = \phi - \frac{(\phi-2)}{a_{t-\lambda+1}} = a_{t-\lambda+2} + 1/a_{t-\lambda+1} \quad (A6)$$

and

$$a^*_{k+1} = \phi - \frac{(\phi-2)}{a_k} - \frac{1}{a^*_k} = a_{k+1} + \frac{1}{a_k} - \frac{1}{a^*_k} \quad (A7)$$

for $t - \lambda + 2 \le k \le t - 1$. Using eq 11, 18, and A3, we obtain

$$\langle(\Delta R_i)^2\rangle = \frac{3}{2\gamma}\frac{(a^*_t a_t - 1)a^*_{t-1}a^*_{t-2} \ldots a^*_{t-\lambda+2}}{(a_t^2-1)a_{t-1}a_{t-2} \ldots a_{t-\lambda+2}a_{t-\lambda+1}} \quad (A8)$$

In the limit where the number of tiers is going to infinity

$$a_k = a = \phi - 1 \tag{A9}$$

becomes k independent and eq A7 can be written as

$$a^*_k - \frac{1}{a} = a - \frac{1}{a^*_{k-1}} \tag{A10}$$

Because of eq A10 and A6, we have

$$\left(a^*_t - \frac{1}{a}\right)a^*_{t-1}a^*_{t-2} \dots a^*_{t-\lambda+2} = a^{\lambda-3}\left(a^*_{t-\lambda+2} - \frac{1}{a}\right) = a^{\lambda-2} \tag{A11}$$

and eq A8 becomes

$$\langle(\Delta R_i)^2\rangle = \frac{3}{2\gamma}\frac{a}{a^2-1} = \frac{3}{2\gamma}\frac{\phi-1}{\phi(\phi-2)} \tag{A12}$$

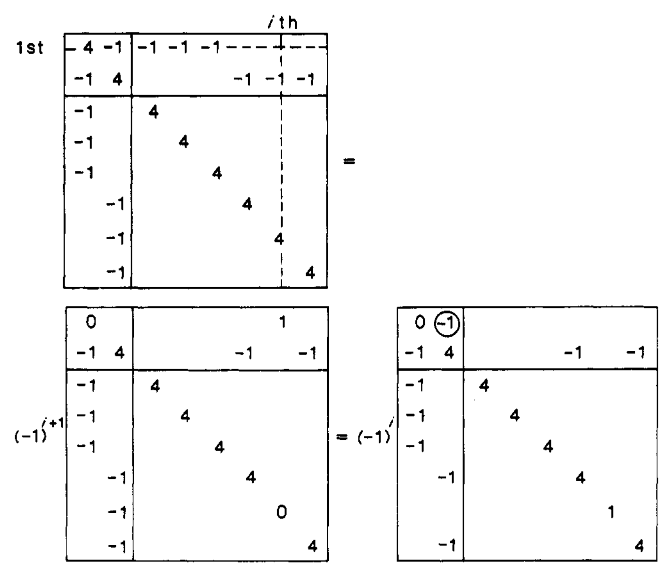
The fluctuations of junction i are the same as fluctuations of junction 1 in the first tier given by diagonal elements of eq 21.

We have proven rigorously an intuitive fact that in an infinite network with treelike topology all junctions are equivalent and each of them can be chosen as a central one. We will use this to calculate the correlations between fluctuations of the first junction in Figure 1 and the ith one, where $i = (\lambda, \mu)$. The number d of ϕ-functional junctions which separate junction number 1 from junction number i is

$$d = \lambda - 2 \quad \text{if} \quad 1 \le \mu \le (\phi - 1)^{\lambda-1}$$

$$d = \lambda - 1 \quad \text{if} \quad (\phi-1)^{\lambda-1} + 1 \le \mu \le 2(\phi-1)^{\lambda-1} \tag{A13}$$

Now we have to calculate the minor D_{1i} which is formed by crossing-out the first row and the ith column of Γ. An example of such a minor is shown below



(A14)

Crossing out the first row and the ith column is equivalent to setting all elements in this row and column to zero with the exception of the element at their intersection which is set to 1. There is additionally the sign factor $(-1)^{i+1}$. Then we interchange the first row with the ith one and this changes only the sign of determinant. Generally the determinant obtained in this way differs from that of Γ only slightly. Instead of ϕ it has 1 as the $(i$–$i)$th element and 0 (or −1 if junction i is directly connected with junction 1) as the (1–1)st element. In the first row −1 appears ϕ times (or only once if i belongs to the last tier) at the same positions as in the ith row of Γ. By using the method of elimination of nonzero elements on the right of the diagonal, we easily see the following. In the diagonal submatrix corresponding to the λth tier, all diagonal elements become $a_{t-\lambda+1}$ with the exception of the $(i$–$i)$th element which is equal to 1. In the diagonal submatrix corresponding to the $(\lambda - 1)$st tier, all diagonal elements become $a_{t-\lambda+2}$ except one which is $a^*_{t-\lambda+2}$ and is given by eq A6. This element during the diagonalization procedure effects one diagonal element $a^*_{t-\lambda+3}$ in the $(\lambda - 2)$nd tier and finally we obtain the recurrence relation A7 for these effected coefficients.

The (2–2)nd diagonal element becomes a_t if $1 \le \mu \le (\phi - 1)^{\lambda-1}$ or a^*_t if $(\phi - 1)^{\lambda-1} + 1 \le \mu \le 2(\phi - 1)^{\lambda-1}$. The most crucial element in the diagonalization procedure is the first −1 [circled in (A14)] in the first row at the position corresponding to the $(\lambda - 1)$st tier. The remaining $(\phi - 1)$ −1's in the first row which correspond to the $(\lambda + 1)$st tier can be eliminated easily. We note that when the row containing $a^*_{t-\lambda+2}$ is divided by $a^*_{t-\lambda+2}$ and added to the first row, this −1 is eliminated but $-1/a^*_{t-\lambda+2}$ appears in the first row at the position corresponding to the $(\lambda - 2)$nd tier. If we divide the row containing $a^*_{t-\lambda+3}$ by $(a^*_{t-\lambda+2}a^*_{t-\lambda+3})$ and add it to the first row, we eliminate $-1/a^*_{t-\lambda+2}$ but $-1/(a^*_{t-\lambda+2}a^*_{t-\lambda+3})$ appears in the first row at the position corresponding to the $(\lambda - 3)$rd tier. The continuation of this process leads finally to

$$-1/(a^*_{t-\lambda+2}a^*_{t-\lambda+3} \dots a^*_{t-1}) \tag{A15}$$

in the first or the second position in the first row, which corresponds to the first tier. If $1 \le \mu \le (\phi - 1)^{\lambda-1}$ then term A15 becomes the (1–1)st element of the minor and

$$D_{1i} = \gamma^{N-1}(-1)^{i+1}(a_1^{N_t}a_2^{N_{t-1}} \dots a_{t-\lambda}^{N_{\lambda+1}}) \times (a_{t-\lambda+1}^{N_\lambda - 1}a_{t-\lambda+2}^{N_{\lambda-1}-1} \dots a_{t-1}^{N_2-1}a_t) \tag{A16}$$

If $(\phi - 1)^{\lambda-1} + 1 \le \mu \le 2(\phi - 1)^{\lambda-1}$, then term A15 becomes the (1–2)nd element of the minor and

$$D_{1i} = \gamma^{N-1}(-1)^{i+1}(a_1^{N_t}a_2^{N_{t-1}} \dots a_{t-\lambda}^{N_{\lambda+1}}) \times (a_{t-\lambda+1}^{N_\lambda-1}a_{t-\lambda+2}^{N_{\lambda-1}-1} \dots a_{t-1}^{N_2-1}) \tag{A17}$$

Using eq 11, 18, and A3 we obtain

$$\langle \Delta\mathbf{R}_1 \cdot \Delta\mathbf{R}_i \rangle = \frac{3}{2\gamma}\frac{a_t^m}{(a_t^2 - 1)a_{t-1}a_{t-2} \dots a_{t-\lambda+2}a_{t-\lambda+1}} \tag{A18}$$

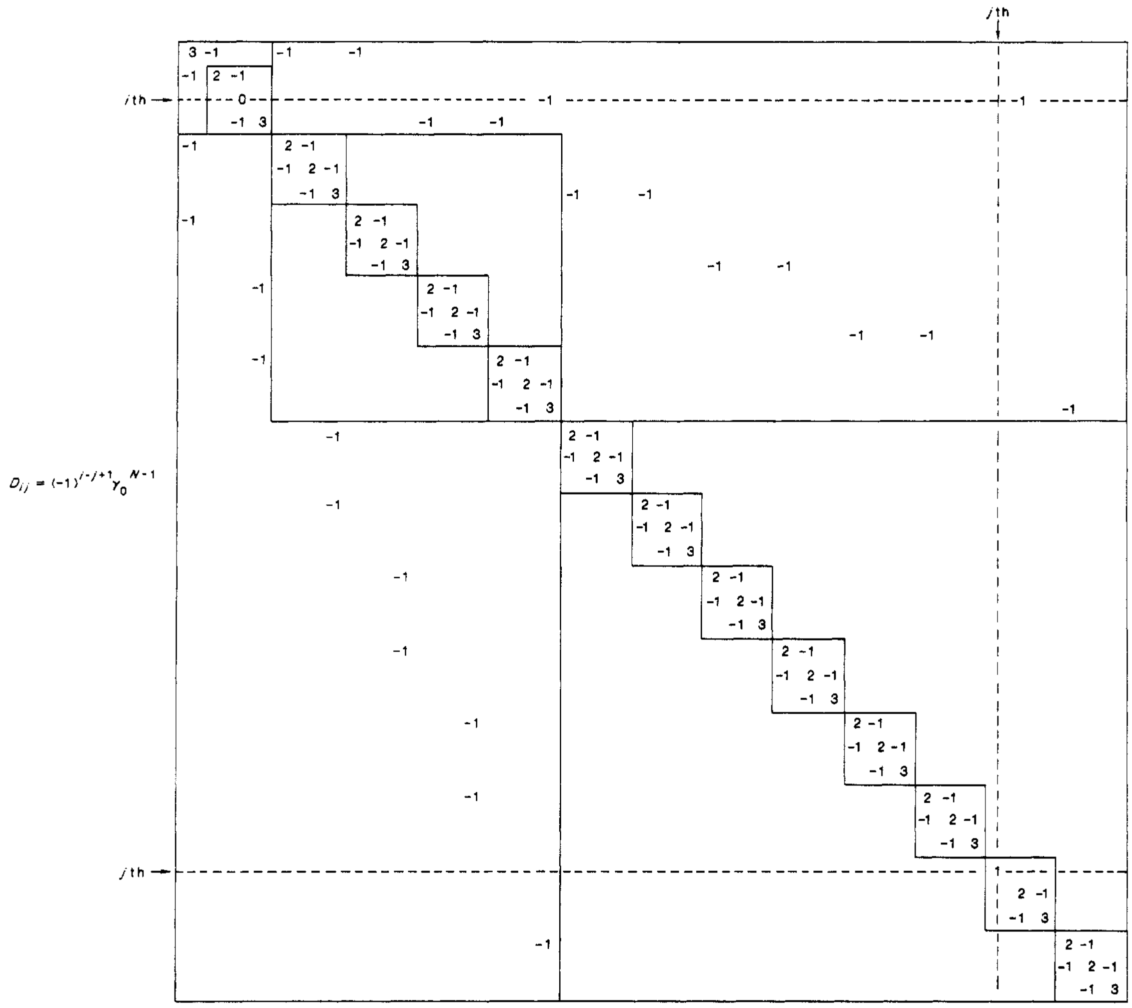
with m equal 1 or 0. In the limit where the number of tiers t goes to infinity, because of (A9) we have

$$\langle \Delta\mathbf{R}_1 \cdot \Delta\mathbf{R}_i \rangle = \frac{3}{2\gamma}\frac{1}{\phi(\phi-2)(\phi-1)^{\lambda-1-m}} = \frac{3}{2\gamma}\frac{1}{\phi(\phi-2)(\phi-1)^d} \tag{A19}$$

where d is the number of junctions separating junctions 1 and i. Because for an infinite network all junctions are equivalent and each can be picked up as number 1, eq A19 gives nondiagonal elements in eq 24.

The derivation of eq 52 is similar to the derivation of eq 24. The position of point i within the network can be described by one number i when a labeling method like that used in Figure 2 is applied or alternatively it can be described by three numbers (λ, μ, ν). The first number λ labels the tier to which point i belongs, the second number μ labels the chain within the given tier, and inequality (A1) is satisfied. The third number ν describes the position of the point i within a given chain

$$1 \le \nu \le n + 1 \tag{A20}$$



(A23)

Here $n - 1$ is the number of 2-functional junctions between ϕ-functional ones, so that each chain is divided into n segments of equal length. We use the convention that for $\lambda > 1$, ν has to be greated than 1; i.e., although we count points within a given chain starting from the junction of the $(\lambda - 1)$st tier, this point does not belong to the λth tier. Equation A20 is equivalent to

$$0 \leq \zeta \leq 1 \tag{A21}$$

where ζ is defined by eq 44. The relation between the number i and (λ, μ, ν) is

$$i = 2n \frac{(\phi - 1)^{\lambda-1} - 1}{(\phi - 1)} + (\mu - 2)n + \nu \tag{A22}$$

for $\lambda > 1$ or $i = \nu$ for $\lambda = 1$. For example point number $i = 16$ in Figure 2 has ($\lambda = 2$, $\mu = 3$, $\nu = 4$) and the point with the number $i = 30$ would have ($\lambda = 3$, $\mu = 1$, $\nu = 2$). As previously, one can prove rigorously that in the limit $t \rightarrow \infty$, i.e., for an infinite network, all ϕ-functional junctions become equivalent and fluctuations of any point within the network whose fractional distance from the nearest ϕ-functional junction is ζ are the same as fluctuations of a point with fractional distance ζ within the first tier. Because of this the diagonal elements in eq 52 are the same as diagonal elements in eq 45. To calculate the nondiagonal elements in eq 52, we use the same method we used earlier. For simplicity we assume that point i belongs to the first tier and $i = (\lambda = 1, \mu = 1, \nu = i)$ while point j is $j = (\lambda, \mu, \nu)$. We calculate the minor D_{ij} which is formed by crossing-out the ith row and the jth column of $\boldsymbol{\Gamma}$. An example of matrix $\boldsymbol{\Gamma}$ is given by eq 28. Performing the same operations as in (A14) the minor D_{ij} becomes $(-1)^{i+j+1}$ times the determinant formed from $\boldsymbol{\Gamma}$ in the following way. All elements of the jth row and the jth column are set to zero with exception of the $(j-j)$th element which is set to 1. The ith row is the same as the jth row of $\boldsymbol{\Gamma}$, only its $(i-i)$th element is changed to zero. An example is given in eq 23. We use the method described earlier of diagonalization of (A23) through elimination of -1's on the right of the diagonal. The product of diagonal elements in the diagonal submatrix corresponding to the λth tier gives

$$[na_{t-\lambda+1} - (n-1)]^{N_\lambda - 1}\{(\nu - 1)[(n - \nu + 1)a_{t-\lambda+1} - (n - \nu)]\} \tag{A24}$$

where

$$N_\lambda = 2n(\phi - 1)^{\lambda-1} \tag{A25}$$

and $a_{t-\lambda+1}$ is given by recurrence formula 35 with the solution given by eq 37. The last term in (A24) is due to the diagonal sub-submatrix containing the $(j-j)$th element. The product of diagonal elements in the diagonal submatrix corresponding to the $(\lambda - 1)$st tier is

$$[na_{t-\lambda+2} - (n-1)]^{N_{\lambda-1}-1}[na^*_{t-\lambda+2} - (n-1)] \tag{A26}$$

where $a^*_{t-\lambda+2}$, instead of eq 35, is given by

$$a^*_{t-\lambda+2} = \phi - (\phi - 2)\frac{[a_{t-\lambda+1}(n-1) - (n-2)]}{[na_{t-\lambda+1} - (n-1)]} - \frac{\nu - 2}{\nu - 1} \tag{A27}$$

The product of diagonal elements in the diagonal submatrix corresponding to the $(\lambda - 2)$nd tier becomes

$$[na_{t-\lambda+3} - (n-1)]^{N_{\lambda-2}-1}[na^*_{t-\lambda+3} - (n-1)] \tag{A28}$$

where

$$a^*_{t-\lambda+3} = \phi - (\phi - 2)\frac{[a_{t-\lambda+2}(n-1) - (n-2)]}{[na_{t-\lambda+2} - (n-1)]} - \frac{[a^*_{t-\lambda+2}(n-1) - (n-2)]}{[na^*_{t-\lambda+2} - (n-1)]} \quad \text{(A29)}$$

etc., up to the second tier. The new coefficients a^*_k effected by crossing out the ith row and the jth column satisfy generally the recurrence relation

$$a^*_{k+1} = \phi - (\phi - 2)\frac{[a_k(n-1) - (n-2)]}{[na_k - (n-1)]} - \frac{[a^*_k(n-1) - (n-2)]}{[na^*_k - (n-1)]} \quad \text{(A30)}$$

for $t - \lambda + 2 \le k \le t - 1$.

Using the method described above we can semidiagonalize almost the entire matrix in (A23) except the first submatrix corresponding to the first tier. The only term which is left outside this submatrix is one -1 in the ith row on the left of the $(i-j)$th element. The remaining -1's on the right can be eliminated easily. The -1 on the left is either on $(j-1)$st position or more to the left if point i is directly connected with the ϕ-functional junction from the $(\lambda - 1)$st tier [as in (A23)]. We will consider the more general case when -1 is on the $(j-1)$st position. The case when point j is directly connected with junction from the $(\lambda - 1)$st tier corresponds to $\nu = 2$. Dividing by 2 the $(j-1)$st row and adding to the ith one we get rid of -1 on the $j-1$ position in the ith row but instead we have $-^1/_2$ on the $(j-2)$nd position. Multiplying the $(j-2)$nd row of the partially diagonalized matrix ($^3/_2$ is now its $(j-2, j-2)$nd element) by $-^1/_3$ and adding to the ith one we obtain $-^1/_3$ as its $(j-3)$rd elements, and finally we obtain $-1/(\nu - 2)$ as its $(j - \nu + 2)$nd element. The $(j - \nu + 2, j - \nu + 2)$nd element of the partially diagonalized matrix is $(\nu - 1)/(\nu - 2)$ and when we multiply the $(j - \nu + 2)$nd row by $1/(\nu - 1)$ and add to the ith row we now obtain $-1/(\nu - 1)$ in the ith row at the position which correspond to the $(\lambda - 1)$st tier. The diagonal element of the partially diagonalized matrix at the same position is $a^*_{t-\lambda+2}$. Multiplying the row containing $a^*_{t-\lambda+2}$ by $1/[a^*_{t-\lambda+2}(\nu - 1)]$ and adding it to the ith row, we obtain $-1/[a^*_{t-\lambda+2}(\nu - 1)]$ at the position shifted by 1 to the left. The diagonal element at this position is

$$(2a^*_{t-\lambda+2} - 1)/a^*_{t-\lambda+2} \quad \text{(A31)}$$

Continuing the process we obtain

$$-1/\{[na^*_{t-\lambda+2} - (n-1)](\nu - 1)\} \quad \text{(A32)}$$

in the ith row at the position corresponding to the $(\lambda - 2)$nd tier. The continuation of this procedure leads finally to

$$B = -1/\{[na^*_{t-1} - (n-1)] \ldots [na^*_{t-\lambda+2} - (n-1)](\nu - 1)\} \quad \text{(A33)}$$

appearing in the ith row at the position corresponding to the first tier. If

$$1 \le \mu \le (\phi - 1)^{\lambda-1} \quad \text{(A34)}$$

then B appears in the ith row at the first position, while if

$$(\phi - 1)^{\lambda-1} + 1 \le \mu \le 2(\phi - 1)^{\lambda-1} \quad \text{(A35)}$$

then B appears in the ith row at $(n + 1)$st position. Both cases are illustrated below, where the first submatrix corresponding to the first tier is shown.

$$\begin{array}{r} \\ \\ \\ \\ i\text{th} \rightarrow \\ \\ \\ (n+1)\text{th} \rightarrow \end{array}\begin{vmatrix} a^*_t & -1 & & & & & & \\ -1 & 2 & -1 & & & & & \\ & -1 & 2 & -1 & & & & \\ & & -1 & 2 & -1 & & & \\ B & & & & 0 & & & \\ & & & & -1 & 2 & -1 & \\ & & & & & -1 & 2 & -1 \\ & & & & & & -1 & a_t \end{vmatrix}$$

$$\begin{vmatrix} a_t & -1 & & & & & & \\ -1 & 2 & -1 & & & & & \\ & -1 & 2 & -1 & & & & \\ & & -1 & 2 & -1 & & & \\ & & & & 0 & & & B \\ & & & & -1 & 2 & -1 & \\ & & & & & -1 & 2 & -1 \\ & & & & & & -1 & a^*_t \end{vmatrix}\begin{array}{l} \\ \\ \\ \\ \leftarrow i\text{th} \\ \\ \\ \leftarrow (n+1)\text{th} \end{array} \quad \text{(A36)}$$

The diagonalization of (A36) in the case of (A34) gives the value of determinant of (A36) which equals

$$B[(n + 1 - i)a_t - (n - i)] \quad \text{(A37)}$$

while in the case of (A35) the determinant of (A36) becomes

$$B[(i-1)a_t - (i-2)] \quad \text{(A38)}$$

In the first case

$$D_{ij} = \gamma_0^{N-1}(-1)^{i+j}\{[na_1 - (n-1)]^{N_t} \ldots [na_{t-\lambda} - (n-1)]^{N_{\lambda+1}}\}\{[na_{t-\lambda+1} - (n-1)]^{N_\lambda - 1} \ldots [na_{t-1} - (n-1)]^{N_2 - 1}\}[(n - \nu + 1)a_{t-\lambda+1} - (n - \nu)] \times [(n + 1 - i)a_t - (n - i)] \quad \text{(A39)}$$

and in the second case

$$D_{ij} = \gamma_0^{N-1}(-1)^{i+j}\{[na_1 - (n-1)]^{N_t} \ldots [na_{t-\lambda} - (n-1)]^{N_{\lambda+1}}\}\{[na_{t-\lambda+1} - (n-1)]^{N_\lambda - 1} \ldots [na_{t-1} - (n-1)]^{N_2 - 1}\}[(n - \nu + 1)a_{t-\lambda+1} - (n - \nu)] \times [(i-1)a_t - (i-2)] \quad \text{(A40)}$$

From eq 20, 36, and A3

$$\langle \Delta\mathbf{R}_i \cdot \Delta\mathbf{R}_j \rangle = (3/2\gamma_0)[(n - \nu + 1)a_{t-\lambda+1} - (n - \nu)] \times [\alpha a_t - (\alpha - 1)]/\{[na_t^2 - 2a_t(n-1) + (n-2)] \times [na_{t-1} - (n-1)] \ldots [na_{t-\lambda+1} - (n-1)]\} \quad \text{(A41)}$$

where $\alpha = (n + 1 - i)/n$ or $\alpha = (i - 1)/n$.

In the limit $t \to \infty$ for an infinite network

$$a_k = \frac{n + \phi - 2}{n} \quad \text{(A42)}$$

becomes k independent and

$$\langle \Delta\mathbf{R}_i \cdot \Delta\mathbf{R}_j \rangle = \frac{3}{2\gamma}\frac{[1 + (\phi - 2)(1 - \beta)][1 + \alpha(\phi - 2)]}{\phi(\phi - 2)(\phi - 1)^{\lambda-1}} \quad \text{(A43)}$$

Here $\beta = (\nu - 1)/n$ and $\gamma = \gamma_0/n$. We should note that in the case of (A34) point j is on the left side of i, while in the case of (A35) point j is on the right side of i. Since we use the convention shown in Figure 3 and we measure the fractional distance of the point from the nearest junction on the left in the case (A34), $\theta = 1 - \beta$ and $\zeta = 1 - \alpha$, while in the case of (A35) $\zeta = \alpha$ and $\theta = \beta$. In the case of (A35) when point i is on the left side of point j:

$$\langle \Delta\mathbf{R}_i \cdot \Delta\mathbf{R}_j \rangle = \frac{3}{2\gamma}\frac{[1 + (\phi - 2)\zeta][(\phi - 1) - \theta(\phi - 2)]}{\phi(\phi - 2)(\phi - 1)^d} \quad \text{(A44)}$$

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.

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

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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.

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