Chain dimensions and fluctuations in elastomeric networks in which the junctions alternate regularly in their functionality

Aris Skliros, James E. Mark, and Andrzej Kloczkowski
1Department of Biochemistry, Biophysics, and Molecular Biology and L. H. Baker Center for Bioinformatics and Biological Statistics, Iowa State University, Ames, Iowa 50011-0320, USA
2Department of Chemistry, Polymer Research Center, University of Cincinnati, Cincinnati, Ohio 45221-0172, USA

(Received 17 October 2008; accepted 3 December 2008; published online 11 February 2009)

A matrix method is used to determine fluctuations of junctions and points along the polymer chains making up a phantom Gaussian network that has the topology of an infinite, symmetrically grown tree. The functionalities of the junctions alternates between $\phi_1$ and $\phi_2$, such that one end of each network chain has functionality $\phi_1$, while the opposite end has functionality $\phi_2$. Quantities calculated include fluctuations of $\phi_1$-functional and $\phi_2$-functional junctions, and fluctuations of points along network chains, as well as correlations of these fluctuations. This was done for points and junctions along any path in the network, where these points and junctions were separated by no junctions or several junctions. Fluctuations have also been calculated for the distances between points and junctions. The present results represent significant generalizations of earlier work in this area [Kloczkowski et al., Macromolecules 22, 1423 (1989)]. These generalizations and extensions should be very useful in a number of contexts, such as interpreting small-angle neutron scattering results on labeled paths in polymer networks, or fluctuations of loops in the Gaussian network model of proteins. © 2009 American Institute of Physics. [DOI: 10.1063/1.3063115]

I. INTRODUCTION

The simplest statistical mechanical model of random elastomeric polymer networks is based on the idea of “phantom” networks. The theory of such networks was first proposed 60 years ago by James and Guth. The polymer network is assumed to consist of chains connected at junctions (or cross-links), and these chains are Gaussian (i.e., the distribution function of the end-to-end distances of the chains is Gaussian). It was assumed that the chains have no excluded volume, and they can pass freely through one another (making them phantomlike) as they fluctuate around their mean positions. Additionally it was assumed that mean positions of junctions transform affinely with the macroscopic strain, while instantaneous fluctuations are independent of the macroscopic deformation.

The theory of such phantom networks has been further refined and improved by many authors. The studies by these authors led to the evaluation of various physical properties, such as molecular dimensions of the chains, their scattering characteristics, and the elastomeric properties of the networks in various deformations. In one important example, Pearson calculated mean-square fluctuations of points along the network chains and correlated these results with topological characteristics of the networks. This study also reported calculations of cross correlations of fluctuations for two different points on a chain, which enabled computations of the neutron scattering from labeled (deuterated) chains in a network. Kloczkowski et al. extended these computations to points of the network separated by junctions, improving some very early results by Ullman. These newer results enabled one to compute small-angle neutron scattering from labeled paths containing cross-links within an elastomeric network and associated predictions involving Kratky plots agreed well with experiment. Also, results originally derived for unimodal elastomers (in which all network chains have the same length) were further extended to regular bimodal networks with treelike topology. In the regular bimodal network each junction is connected with a constant number $\phi_2$ of short chains and a constant number $\phi_L$ of long chains, so that the functionality of the network ($\phi=\phi_2+\phi_L$) is invariant. Erman and Mark later generalized these results to elastomers with trimodal distributions of network chain lengths. The present paper extends previous work to novel networks that have unimodal distributions of chain lengths, but bimodal distributions of junction functionality. The investigation will focus on infinite and regular tree-like networks having alternating functionality, i.e., each chain of the network has functionality $\phi_1$ on one end, while its opposite end has functionality $\phi_2$. The polymer networks of this type can be synthesized by a proper choice of the monomer and end-linking agents. The structure of this report paper is (i) review of earlier results for simple unimodal networks, (ii) presentation of the new results computed for networks with alternating functionalities, and (iii) discussion of possible applications of these results in polymer science and in molecular biology.

130, 064905-1 © 2009 American Institute of Physics
A. Theory of the phantom networks

The theory presented elsewhere\textsuperscript{10} will now be briefly described. Each chain in the network is assumed to have the Gaussian distribution of the end-to-end vector $r$

$$W(r) = \left(\frac{3}{2\pi(r^2)_0}\right)^{3/2} \exp\left(-\frac{3r^2}{2(r^2)_0}\right).$$

(1)

The quantity $\langle r^2 \rangle_0$ is the mean-square end-to-end distance for the chains as unperturbed by excluded volume effects. The angular bracket denotes ensemble averaging over all chains in the network. The partition function is given by the product of configuration functions for the individual chains in the network since the phantomlike nature of the model means that there are no interactions between chains, except for their connections at the cross-links. Thus,

$$Z_N = C \prod_{i<j} \exp(-3r_{ij}^2/2(r_{ij}^2)_0).$$

(2)

Here $C$ is a constant, and the product includes all pairs $i$, $j$ of junctions connected directly by a chain, i.e., $\langle r_{ij}^2 \rangle_0 = \langle r^2 \rangle_0$. Equation (2) can be rewritten as

$$Z_N = C \exp\left(-\frac{1}{2} \sum_i \sum_j \gamma_{ij}^\ast (\frac{1}{2}R_i^2 + \frac{1}{2}R_j^2 - R_i \cdot R_j)\right),$$

(3)

where $R_i$ and $R_j$ denote position vectors of junctions $i$ and $j$

\begin{equation}
\gamma_{ij}^\ast = \begin{cases} 
\frac{3}{2(r_{ij}^2)_0} & \text{if junctions } i, j \text{ are connected by a chain} \\
0 & \text{otherwise.}
\end{cases}
\end{equation}

(4)

Equation (4) can be rewritten in the form

$$Z_N = C \exp\left(-\sum_i \sum_j \gamma_{ij}^\ast (\frac{1}{2}R_i^2 + \frac{1}{2}R_j^2 - R_i \cdot R_j)\right)$$

$$= C \exp\left(-\langle R \rangle^T T\langle R \rangle\right),$$

(5)

where $\langle R \rangle = \text{col}(R_1, R_2, \ldots, R_n)$ denotes a column vector containing position vectors of all $\mu$ junctions in the network, $T$ designates its transpose, and $T$ is the symmetric square matrix with elements $\gamma_{ij}$ defined as

$$\gamma_{ij} = -\gamma_{ji}, \quad i \neq j,$$

$$\gamma_{ii} = \sum_j \gamma_{ij} = \sum_i \gamma_{ij}^\ast.$$

(6)

The phantom network theory assumes that all the junctions in the network can be divided into two categories: fixed junctions located on the surface of the elastomer that do not fluctuate, and free junctions located within it that fluctuate around their mean positions. The partition function related to these freely-fluctuating junctions (denoted by the subscript $\tau$) is given by
network model of protein and based on the assumption of composed of chains of equal length.

The phantom network theory has been very successful in polymer science, where it forms a basis for rubberlike elasticity theory, and more sophisticated theories of rubberlike elasticity that extend it by considering excluded volume effects and entanglement constraints. It became also extremely successful in biology reformulated as the Gaussian network model of protein23 and based on the assumption of functionality

\[
\frac{Z_N}{N^z} = C \exp[-\{\Delta R_i, \Delta R_j\}]^T (\Delta R_i, \Delta R_j).
\]

Here \(\{\Delta R_i, \Delta R_j\}\) denotes the column vector of instantaneous fluctuations of all free junctions,

\[
\{\Delta R_i, \Delta R_j\} = \text{col}\{R_{i1}, R_{i2}, \ldots, R_{i\mu}, R_{j1}, R_{j2}, \ldots, R_{j\mu}\}.
\]

The bars above the vectors in Eq. (8) stand for the time average. To simplify the notation we will omit the subscript \(\tau\) referring to free junctions in the subsequent equations. The time average of the product of the fluctuations of two junctions \(i, j\) can be computed from Eq. (7) as follows:

\[
\langle \Delta R_i, \Delta R_j \rangle = \frac{\int \Delta R_i, \Delta R_j \exp[-\{\Delta R\}^T (\Delta R)]d\{\Delta R\}}{\int \exp[-\{\Delta R\}^T (\Delta R)]d\{\Delta R\}} = -\frac{\partial}{\partial \gamma_{ij}} \ln Z,
\]

where

\[
d\{\Delta R\} = d\Delta R_i d\Delta R_j d\Delta R_{i2} \cdots d\Delta R_{i\mu}
\]

and

\[
Z = \int \exp[-\{\Delta R\}^T (\Delta R)]d\{\Delta R\} = \left(\frac{\pi^{\nu}}{\text{det} \Gamma}\right)^{3/2}.
\]

By combining Eqs. (9)–(11) the following formula is obtained:

\[
\langle \Delta R_i, \Delta R_j \rangle = \frac{3}{2} \frac{\partial}{\partial \gamma_{ij}} \ln |\text{det} \Gamma| = \frac{3}{2} (\Gamma^{-1})_{ij}.
\]

Hence, the mean-square fluctuations of the distance \(r_{ij} = |R_i - R_j|\) between junctions \(i\) and \(j\) can be computed from the formula for its square,

\[
\langle (\Delta r_{ij})^2 \rangle_0 = \langle (\Delta R_i - \Delta R_j)^2 \rangle = \frac{3}{2} [(\Gamma^{-1})_{ii} + (\Gamma^{-1})_{jj} - 2(\Gamma^{-1})_{ij}]^2.
\]

The phantom network theory has been very successful in polymer science, where it forms a basis for rubberlike elasticity theory, and more sophisticated theories of rubberlike elasticity that extend it by considering excluded volume effects and entanglement constraints. It became also extremely successful in biology reformulated as the Gaussian network model of protein23 and based on the assumption of..
\[
\langle (\Delta r_{ij})^2 \rangle = \frac{2}{\phi(\phi - 2)(d + 1)} (\phi - 1)^{d+1} - 1 - (r_{ij}^2)_{0}
\]  
(17)

since \( (r_{ij}^2)_{0} = (d + 1)(r_{ij})_{0} \), where \( (r_{ij}^2)_{0} \) is the mean-square end-to-end distance for unperturbed chains joining \( \phi \)-functional junctions. One should note that in a special case when \( d = 0 \) both Eqs. (16) and (17) reduce to Eqs. (14) and (15), respectively.

Also solved here is the more general problem of fluctuations of points along the chains in the network and correlations of fluctuations among such points. It was assumed that each chain between two \( \phi \) functional junctions is composed of \( n \) Gaussian segments connected by bifunctional junctions to form a chain, as shown in Fig. 2.

As a result, the diagonal elements \( \gamma_{ii} \) of the connectivity matrix (neglecting the constant factor \( 3/2(r_{ij}^2)_{0} \)) are \( \phi \) if the index \( i \) corresponds to the \( \phi \) functional junction, and two for the bifunctional junction. The off-diagonal elements \( \gamma_{ij} \) are \( -1 \) if \( i \) and \( j \) are directly connected by a chain segment, and zero otherwise. The recursion relations between the elements of the inverse matrix \( I^{-1} \) can also be derived. For the infinite number of tiers in the treelike network the solution of the problem has the following form:

\[
\begin{bmatrix}
\langle (\Delta R_i^2) \rangle & \langle \Delta R_i \cdot \Delta R_j \rangle \\
\langle \Delta R_i \cdot \Delta R_j \rangle & \langle (\Delta R_j^2) \rangle 
\end{bmatrix} = (r_{ij}^2)_{0}
\begin{bmatrix}
\frac{\phi - 1}{\phi(\phi - 2)} + \zeta(1 - \zeta)(\phi - 2) \\
1 + \zeta(\phi - 2) \left[ (\phi - 1) - \theta(\phi - 2) \right] \\
\frac{1}{\phi(\phi - 2)(\phi - 1)^d}
\end{bmatrix}
\begin{bmatrix}
\frac{\phi - 1}{\phi(\phi - 2)}(\phi - 2)(\phi - 1)^d \\
\frac{\phi - 1}{\phi(\phi - 2)} + \frac{\theta(1 - \theta)(\phi - 2)}{\phi}
\end{bmatrix}
\]

(18)

Here \( \zeta = (i - 1)/n \) and \( \theta = (j - 1)/n \) are fractional distances of sites \( i \) and \( j \) from nearest \( \phi \)-functional junctions on their left side (as shown in Fig. 3) with \( 0 < \zeta, \theta < 1 \), and \( d \) is the number of \( \phi \)-functional junctions between sites \( i \) and \( j \). If point \( j \) is on the left side of point \( i \) then \( \zeta \) and \( \theta \) in Eq. (18) have to be interchanged. The above formula is also valid when \( i \) and \( j \) belong to the same chain (\( d = 0 \)).

Fluctuations \( \langle (\Delta r_{ij})^2 \rangle \) of the distance \( r_{ij} \) are then

\[
\langle (\Delta r_{ij})^2 \rangle = \left[ \frac{2(\phi - 1)}{\phi(\phi - 2)} \right] - \left[ \frac{1 - 1}{(\phi - 1)^d} \right] + \frac{\phi - 2}{\phi} \zeta(1 - \zeta) + \theta(1 - \theta) - \zeta + \theta - 2\zeta \theta (\phi - 1)^d \\
+ \frac{\phi - 1}{\phi(\phi - 2)} \left[ \frac{1}{(\phi - 1)^d} \right] + \frac{\theta(1 - \theta)(\phi - 2)}{\phi(\phi - 2)} \left[ \frac{1}{(\phi - 1)^d} \right] (r_{ij}^2)_{0},
\]

(19)

where \( \eta \) is the contour distance between points \( i \) and \( j \) along the path. It is defined as \( \eta = d + \theta - \zeta \) if point \( i \) is on the left side of point \( j \), or \( \eta = d + \zeta - \theta \) if point \( i \) is on the right side of point \( j \). If points \( i \) and \( j \) are on the same chain (\( d = 0 \)), then

\[
\langle (\Delta r_{ij})^2 \rangle = \left[ \frac{\eta - (\phi - 2)}{\phi} \eta^2 \right] (r_{ij}^2)_{0}
\]

(20)

with \( \eta = |\theta - \zeta| \).

B. Treelike networks with alternating functionalities

Presented here are the analytical results for the James–Guth theory of phantom Gaussian networks applied to the infinite treelike network with alternating functionalities. All chains in the network are assumed to have the same length. Figure 4 shows a sketch of such a network with alternating functionality, in this case composed of four tiers.

The first tier is composed of the single central chain connecting junctions 1 and 2. The second tier in the sketch contains junctions 3–7, the third tier contains junctions 8–19, and finally the fourth tier is composed of junctions 20–49.

Generally, the number of junctions of the first tier is \( N_1 = 2 \), with one having the functionality \( \phi_1 \) and the other having functionality \( \phi_2 \). The second tier has \( N_2 = 1(\phi_1 - 1) + 1(\phi_2 - 1) \) junctions. The third tier has \( N_3 = 1(\phi_1 - 1)(\phi_2 - 1) + 1(\phi_2 - 1)(\phi_1 - 1) \). Likewise the \( r \)th tier contains \( N_r \) junctions, where

\[
N_r = \left\{ \begin{array}{ll}
(\phi_1 - 1)^{r/2}(\phi_2 - 1)^{(r - 2)/2} + (\phi_2 - 1)^{r/2}(\phi_1 - 1)^{(r - 2)/2} & \text{for even } r \\
(\phi_1 - 1)^{(r - 1)/2}(\phi_2 - 1)^{(r - 1)/2} + (\phi_2 - 1)^{(r - 1)/2}(\phi_1 - 1)^{(r - 1)/2} & \text{for odd } r
\end{array} \right.
\]

(21)

The graph representing the network has vertices corresponding to junctions and edges corresponding to the branches of the tree. Such a graph can be represented by the Laplacian matrix (frequently called the valency adjacency, or Kirchhoff matrix). It has the form
Equation (22) shows the Kirchhoff matrix for the first three tiers of the graph shown in Fig. 4. The off-diagonal elements \( (i,j) \) of the matrix are \(-1\) if vertices \( i \) and \( j \) are directly linked, and 0 otherwise, and the diagonal elements \((i,i)\) denote the functionality of the \( i \)th node. The factor \( \gamma = 3/2(r^2)\) ensures that the matrices \( \Gamma \) in Eqs. (22), (12), and (13) are identical.

The inverse matrix \( \Gamma^{-1} \) enables calculation of mean-square fluctuations and cross correlations of instantaneous fluctuations of junctions in the network from Eq. (12). This follows the procedure presented elsewhere,\(^{10}\) which uses a variant of Gaussian elimination. The matrix \( \Gamma \) in Eq. (22) has a special structure reflecting the treelike structure of the graph and the method of labeling the nodes shown in Fig. 4, where one starts from the first tier in the center and moves upward to higher tiers, numbering each of them. The same method of labeling nodes in the treelike network was used in a previous study.\(^{10}\) Because of this, the structure of the matrix \( \Gamma \) resembles the same matrix (the simpler case when all junctions have the same functionality \( \phi \)) described in detail earlier.\(^{10}\) Similarly, as was done earlier, the matrix \( \Gamma \) can be partitioned into submatrices corresponding to consecutive tiers of the tree. This partitioning is illustrated by the lines placed into Eq. (22). The square submatrix corresponding to the first tier has size \( 2 \times 2 \), is located at the upper-left side of the diagonal and has the general form \([\phi_1^{-1}, \phi_2^{-1}]\). The square submatrix corresponding to the second tier has size \((\phi_1 + \phi_2-2) \times (\phi_1 + \phi_2-2)\) and contains \(\phi_1-1\) occurrences of \(\phi_2\) and \(\phi_2-1\) occurrences of \(\phi_1\) along the diagonal. All off-diagonal elements of this square submatrix are zero. The square submatrix corresponding to the third tier has size \(2(\phi_1-1)(\phi_2-1) \times 2(\phi_1-1)(\phi_2-1)\) and contains the same number \((\phi_1-1)(\phi_2-1)\) of \(\phi_1\) entries and \(\phi_2\) entries along the diagonal, and all zeros off-diagonal. Generally for the \(t\)th tier the size of the square submatrix is \(N_t \times N_t\), where \(N_t\) is given by Eq. (21). For \(t\)-odd, the first diagonal elements are always \(\phi_1\) whereas the last elements are always \(\phi_2\). For \(t\)-even, we have the opposite order that is that the first diagonal elements are always \(\phi_2\), whereas the last elements are \(\phi_1\). Let us assume that the number of tiers is even, without a loss of generality. The matrix \( \Gamma \) is diagonalized by using the same method of Gaussian elimination as done elsewhere.\(^{10}\) All rows of \( \Gamma \) containing the element \(\phi_1\) on the diagonal of the square submatrix corresponding to the \(t\)th tier are first divided by \(\phi_1\). Similarly, all rows of \( \Gamma \) containing \(\phi_2\) on the diagonal of the square submatrix corresponding to the \(t\)th tier respectively are divided by \(\phi_2\). These rows are added to the preceding \(N_{t-1}\) rows of \( \Gamma \) containing the square submatrix corresponding to the \((t-1)\)st tier to eliminate all the \(-1\) entries on the right of the diagonal. This changes the diagonal elements of the \((t-1)\)st square submatrix: the elements \(\phi_1\) are changed to \(\phi_1 - [(\phi_1-1)/\phi_2]\), and elements \(\phi_2\) are changed to \(\phi_2 - [(\phi_2-1)/\phi_1]\). The same process is repeated to eliminate all the \(-1\) elements on the right of the diagonal in rows containing the square submatrix corresponding to the \((t-2)\)nd tier. The elements \(\phi_1\) on the diagonal of this square submatrix of size \(N_{t-2} \times N_{t-2}\) will change to
The sizes of the square submatrices corresponding to tiers\( \equiv 2 \) are shown in lower left corners. All off-diagonal elements in the upper right part of the matrix are zeros, except the (1,2)nd element which equals \(-1\). The diagonal elements of the matrix that originally had values \( \phi_1 \) now have the values \( a_i \). Here, the subscript \( i \) refers to the corresponding tier in the reverse order (i.e., the 1-st tier has index \( t \), and the last tier \( t \) has index 1), and the diagonal elements that originally had values \( \phi_2 \) are now \( b_i \). The elements \( a_i \) and \( b_i \) satisfy the recurrence relations

\[ a_1 = \phi_1, \]
\[ b_1 = \phi_2, \]
\[ a_k = \phi_1 - \frac{\phi_1 - 1}{b_{k-1}}, \]
\[ b_k = \phi_2 - \frac{\phi_2 - 1}{a_{k-1}}. \]

As the number of tiers of the network goes to infinity \( (t \rightarrow \infty) \), the solutions of these recurrence equations converge to \( \alpha = \lim_{t \rightarrow \infty} a_i \) and \( \beta = \lim_{t \rightarrow \infty} b_i \) that satisfy the set of equations

\[ \alpha = \phi_1 - \frac{\phi_1 - 1}{\beta}, \]
\[ \beta = \phi_2 - \frac{\phi_2 - 1}{\alpha}, \]

and are

\[ \alpha = \frac{\phi_1}{\phi_2}(\phi_2 - 1), \]
\[ \beta = \frac{\phi_2}{\phi_1}(\phi_1 - 1). \]
The mean-square fluctuations of the distance between junctions $i$ and $j$ connected by a chain,

$$
\begin{bmatrix}
    \langle (\Delta R_i)^2 \rangle & \langle \Delta R_i \cdot \Delta R_j \rangle \\
    \langle \Delta R_i \cdot \Delta R_j \rangle & \langle (\Delta R_j)^2 \rangle
\end{bmatrix}
= \frac{3}{2} \begin{bmatrix}
    (\Gamma^{-1})_{11} & (\Gamma^{-1})_{12} \\
    (\Gamma^{-1})_{12} & (\Gamma^{-1})_{22}
\end{bmatrix}
= \frac{3\beta}{2\gamma(\phi_i \phi_2 - \phi_1 - \phi_2)} \begin{bmatrix}
    \phi_2 (\phi_1 - 1) & 1 \\
    1 & \phi_1 (\phi_2 - 1)
\end{bmatrix}.

(28)

The mean-square fluctuations of the distance between junctions $i$ and $j$ joined by a chain computed from Eq. (13) are

$$
\langle (\Delta r_{ij})^2 \rangle_0 = \frac{3}{2\gamma(\phi_1 \phi_2 - \phi_1 - \phi_2)} \frac{\phi_2 (\phi_1 - 1)}{\phi_1} \frac{\phi_1 (\phi_2 - 1)}{\phi_2}.
$$

(29)

If both ends of chains have the same functionality $\phi_1 = \phi_2 = \phi$, then Eqs. (28) and (29) reduce to Eqs. (14) and (15), respectively, as expected.

C. Fluctuations of two junctions separated by several chains

In the case of two junctions separated by several chains there are three possibilities. Both of two junctions may have the same functionality $\phi_1$, both may have functionality $\phi_2$, and finally one junction may have functionality $\phi_1$ and the other has functionality $\phi_2$. Each of these three cases gives different results, although the final equations are quite similar. A method of Gaussian elimination of off-diagonal elements of the matrix analogous to that used earlier is used. The details of the derivations for infinite tree-like networks with alternating functionalities are given in Appendix A. Fluctuations of junctions are expressed by formulas similar to those in Eq. (27), i.e., if a given junction has functionality $\phi_1$ its mean-square fluctuations are $3\beta/[2\gamma(\alpha\beta-1)]$, while if its functionality is $\phi_2$, the mean-square fluctuations are $3\alpha/[2\gamma(\alpha\beta-1)]$. The similarity between these results and earlier results given by Eq. (27) arises from the fact that for an infinite network with treelike topology, all junctions of the same functionality are equivalent and each of them can be chosen as a central one. The intermediate junctions separating two junctions under consideration influence only the correlations between their instantaneous fluctuations. The intermediate junctions have either $\phi_1$ or $\phi_2$ functionality and each of these two classes of junctions gives a different contribution to the fluctuational cross correlations. It is assumed that there are $d=d_1+d_2$ intermediate junctions separating the two junctions, with $d_1$ of them having functionality $\phi_1$ and $d_2$ having functionality $\phi_2$. It can be shown (see Appendix A) that correlations of fluctuations of two junctions are given by $3/[2\gamma(\alpha\beta-1)]\xi^{d_1}\xi^{d_2}$. The final results can be summarized as follows:

1. Both junctions have functionality $\phi_1$

In this case it is obtained $d_1 = d_2 - 1$ and

$$
\begin{bmatrix}
    \langle (\Delta R_i)^2 \rangle & \langle \Delta R_i \cdot \Delta R_j \rangle \\
    \langle \Delta R_i \cdot \Delta R_j \rangle & \langle (\Delta R_j)^2 \rangle
\end{bmatrix}
= \frac{2\phi_2}{\phi_1 (\phi_1 \phi_2 - \phi_1 - \phi_2)} \left[ (\phi_1 - 1) - \frac{1}{(\phi_2 - 1)^d_1 (\phi_1 - 1)^d_1} \right].
$$

(30)

The mean-square fluctuations of the distance between junctions $i$ and $j$ are

$$
\langle (\Delta r_{ij})^2 \rangle_0 = \langle r_{ij}^2 \rangle_0 \frac{\phi_2}{\phi_1 (\phi_1 \phi_2 - \phi_1 - \phi_2)} \left[ (\phi_1 - 1) - \frac{1}{(\phi_2 - 1)^d_1 (\phi_1 - 1)^d_1} \right].
$$

(31)
2. Both junctions have functionality $\phi_2$

In this case $d_2=d_1-1$ and

$$
\begin{bmatrix}
\langle (\Delta R_i)^2 \rangle & \langle \Delta R_i \cdot \Delta R_j \rangle \\
\langle \Delta R_j \cdot \Delta R_i \rangle & \langle (\Delta R_j)^2 \rangle
\end{bmatrix} = \frac{3}{2\gamma(\phi_1\phi_2-\phi_1-\phi_2)}
\begin{bmatrix}
\phi_1(\phi_2-1) & \phi_1 \\
\phi_2 & \phi_2(\phi_2-1)^{d_2}(\phi_1-1)^{d_1}
\end{bmatrix}.
\tag{32}
$$

The mean-square fluctuations of the distance between junctions $i$ and $j$ are

$$
\langle (\Delta r_{ij})^2 \rangle_0 = \langle r^2 \rangle_0 \frac{2\phi_1}{\phi_2(\phi_1\phi_2-\phi_1-\phi_2)} \left[ (\phi_2-1) - \frac{1}{(\phi_2-1)^{d_2}(\phi_1-1)^{d_1}} \right].
\tag{33}
$$

3. The first junction (i) has functionality $\phi_1$ and the second one (j) functionality $\phi_2$

In this case $d_1=d_2$ and

$$
\begin{bmatrix}
\langle (\Delta R_i)^2 \rangle & \langle \Delta R_i \cdot \Delta R_j \rangle \\
\langle \Delta R_j \cdot \Delta R_i \rangle & \langle (\Delta R_j)^2 \rangle
\end{bmatrix} = \frac{3}{2\gamma(\phi_1\phi_2-\phi_1-\phi_2)}
\begin{bmatrix}
\phi_2(\phi_1-1) & 1 \\
\phi_1 & \phi_1(\phi_2-1)
\end{bmatrix}.
\tag{34}
$$

The mean-square fluctuations of the distance between junctions $i$ and $j$ are then

$$
\langle (\Delta r_{ij})^2 \rangle_0 = \langle r^2 \rangle_0 \frac{1}{(\phi_1\phi_2-\phi_1-\phi_2)} \left[ \phi_2(\phi_1-1) + \phi_1(\phi_2-1) \right] - \frac{2}{(\phi_2-1)^{d_2}(\phi_1-1)^{d_1}}.
\tag{35}
$$

If the first junction $i$ has functionality $\phi_2$ and the second junction $j$ has functionality $\phi_1$ then the diagonal elements in Eq. (34) should be interchanged.

If both ends of chains have the same functionality $\phi_1=\phi_2=\phi$ Eqs. (30), (32), and (34) reduce to Eq. (16), and Eqs. (31), (33), and (35) reduce to Eq. (17).

D. Fluctuations of points along a chain

To study fluctuations of points along the chain the earlier method is followed, and it is assumed that all chains consist of equal length segments, and there are $n-1$ junctions of functionality 2 connecting these segments. Figure 4 illustrates this approach, and the method of numbering all junctions for a treelike network with alternating multifunctional functionalities composed of two tiers.

The Kirchhoff matrix corresponding to the graph in Fig. 5 is shown in Eq. (36), and its diagonal elements correspond to the functionality of a given node in the network. Two larger square submatrices corresponding to the first two tiers of the network and smaller square subsubmatrices of size $n\times n$ corresponding to individual chains have been indicated.
A Gaussian elimination method is used again. Assume that the number of tiers of the network is even so the entry in the lowest right corner of the matrix is \(1\). The diagonalization of the lowest diagonal subsubmatrix corresponding to a chain leads to

\[
\begin{align*}
\phi_1 & = \frac{n \phi_1 - (n - 1)}{(n - 1) \phi_1 - (n - 2)} \\
\frac{3 \phi - 2}{2 \phi_1 - 1} & = \frac{2 \phi_1 - 1}{\phi_1} \\
\end{align*}
\]

where all elements of the subsubmatrix above the diagonal are zeros. During the process of diagonalization of the elements of the \(t\)-tier we change the elements of the preceding \((t - 1)\)st tier from \(a_1 = \phi_1\) and \(b_1 = \phi_2\) to

\[
\begin{align*}
a_2 & = \phi_1 - \frac{(\phi_1 - 1)[(n - 1)b_1 - (n - 2)]}{nb_1 - (n - 1)}, \\
b_2 & = \phi_2 - \frac{(\phi_2 - 1)[(n - 1)a_1 - (n - 2)]}{na_1 - (n - 1)}, \\
\end{align*}
\]

or more generally to

\[
\begin{align*}
a_k & = \phi_1 - \frac{(\phi_1 - 1)[(n - 1)b_{k-1} - (n - 2)]}{nb_{k-1} - (n - 1)}, \\
b_k & = \phi_2 - \frac{(\phi_2 - 1)[(n - 1)a_{k-1} - (n - 2)]}{na_{k-1} - (n - 1)}. \\
\end{align*}
\]

For infinite networks the solutions of these recurrence equations converge to \(\alpha = \lim_{t \to \infty} a_t\) and \(\beta = \lim_{t \to \infty} b_t\), which satisfy the set of equations

\[
\begin{align*}
\alpha & = \phi_1 - \frac{(\phi_1 - 1)[(n - 1)\beta - (n - 2)]}{n\beta - (n - 1)}, \\
\beta & = \phi_2 - \frac{(\phi_2 - 1)[(n - 1)\alpha - (n - 2)]}{n\alpha - (n - 1)}. \\
\end{align*}
\]

Equations (40) can be rewritten as
The positions of two-functional junctions $i$ and $j$ can be expressed as the fraction of the chain between $\phi_1$-functional and $\phi_2$-functional junctions, counted from the closest $\phi_1$-functional junction to the point $i$ or $j$. Thus,

$$\zeta = \frac{i - 1}{n},$$

$$\theta = \frac{j - 1}{n}.\quad(46)$$

The convention that fractional distances of points along the chain are counted from the closest $\phi_1$-functional junction is very important for the final results, and should be remembered. Introducing this notation and using Eq. (42) leads to

$$\begin{bmatrix}
\langle (\Delta R)^2 \rangle \\
\langle \Delta R_1 \Delta R_2 \rangle
\end{bmatrix} = \frac{3n}{2\gamma_0} \begin{bmatrix}
\frac{\phi_2(\phi_1 - 1)}{\phi_1(\phi_2 - \phi_1)} & \frac{\zeta(1 - \zeta)(\phi_1 - 1) + \zeta(\phi_2 - 1)}{\phi_1} \\
\frac{\phi_1(\phi_2 - \phi_1)}{\phi_1(\phi_2 - \phi_1)} & \frac{\phi_1(\phi_2 - 1)}{\phi_1(\phi_2 - \phi_1)} + (\phi_1 - \phi_2) \frac{\min(\zeta, \theta) - \zeta\theta + \max(\zeta, \theta)}{\phi_2}
\end{bmatrix}.$$

It should be noted that for $\phi_1 = \phi_2 = \phi$ and $d = 0$ one obtains the earlier results, specifically those given by Eq. (18). Also, for $\zeta = 0$ and $\theta = 1$ one recovers the results in Eq. (28), as could be expected, since
\[
\frac{\phi_2(\phi_1 - 1)}{\phi_1(\phi_1 \phi_2 - \phi_1 - \phi_2)} + \frac{\phi_1 - \phi_2}{\phi_1 \phi_2} = \frac{\phi_1(\phi_2 - 1)}{\phi_2(\phi_1 \phi_2 - \phi_1 - \phi_2)}.
\]

(48)

and

\[
\frac{\phi_2(\phi_1 - 1)}{\phi_1(\phi_1 \phi_2 - \phi_1 - \phi_2)} + \frac{1}{\phi_1} = \frac{1}{\phi_1 \phi_2}.
\]

(49)

The fluctuations of the mean-square distance \(\langle (\Delta r_{ij})^2 \rangle_0\) between points \(i\) and \(j\) on the chain computed from Eq. (13) are

\[
\langle (\Delta r_{ij})^2 \rangle_0 = \langle (\Delta r)^2 \rangle_0 \left[ \eta - \eta^2 \frac{\phi_1 \phi_2 - \phi_1 - \phi_2}{\phi_1 \phi_2} \right],
\]

(50)

where the fractional distance \(\eta\) between points \(i\) and \(j\) is

\[
\eta = |\zeta - \theta| = \zeta + \theta - 2 \min(\zeta, \theta).
\]

(51)

For \(\phi_1 = \phi_2 = \phi\) Eq. (51) reduces to Eq. (20), and for \(\eta = 1\) one recovers the result given by Eq. (29). If the fractional distances are measured not from the \(\phi_1\)-functional junctions, but from \(\phi_2\)-functional ones, then the quantities \(\zeta\) and \(\theta\) in Eq. (47) must be replaced by \(1 - \zeta\) and \(1 - \theta\), respectively.

E. Fluctuations of two points on chains separated by several \(\phi_1\), \(\phi_2\) functional junctions

It is straightforward to generalize results from the last two sections to the case where two-functional junctions are separated by several \(\phi_1\) and \(\phi_2\) functional junctions. Figure 5 shows an example of two points \(i\) and \(j\) separated by three-functional and four-functional junctions.

As was done earlier, \(10\) the convention that fractional distances are measured from the closest multifunctional junction on the left of a given point, as shown in Fig. 5, is used. In addition to this, it is important to note that we make the convention that point \(j\) is always located on the right side with respect to the point \(i\) that is assumed to be located in the first tier. For infinite treelike network we can always set the system of reference according to this convention. As already described \(10\) point \(j\) can be described by three numbers (\(\lambda, \mu, \nu\)). The first number from the left corresponds to the tier the point belongs to, the second number labels the chain within the tier, and the third number gives the position of the point along the chain. Also, \(1 \leq \nu \leq n + 1\).

This gives rise to four possibilities:

(1) The closest multifunctional junctions on the left of both points \(i\) and \(j\) are \(\phi_1\)-functional, and the conventions are those given in Fig. 4. The values \(\lambda\) for the point \(j\) are always odd; \(d_1 = d_2 = (\lambda - 1)/2\).

\[
\frac{\langle (\Delta R_{ij})^2 \rangle}{\langle \Delta R \cdot \Delta R \rangle} = \frac{3n}{2 \gamma_0} \left[ \frac{\phi_2(\phi_1 - 1)}{\phi_1(\phi_1 \phi_2 - \phi_1 - \phi_2)} + \frac{\phi_1 - \phi_2}{\phi_1 \phi_2} + \frac{\phi_1(\phi_2 - 1)}{\phi_2(\phi_1 \phi_2 - \phi_1 - \phi_2)} \right].
\]

(52)

with \(\zeta\) and \(\theta\) (0 \(\leq \zeta\), \(\theta\) \(\leq 1\)) being fractions of the length of the chain for points \(i\) and \(j\), respectively, from the closest multifunctional junction on the left (Fig. 6).

(2) The closest multifunctional junction on the left of point \(i\) is \(\phi_1\)-functional and on the left of point \(j\) is \(\phi_2\)-functional. The convention shown in Fig. 4 is used. Points \(i\) and \(j\) are then separated by \(d = d_1 + d_2\) intermediate junctions, with \(d_1\) of them having functionality \(\phi_1\) and \(d_2\) having functionality \(\phi_2\). For this case \(\lambda\) for the point \(j\) is always even.

We have \(d_1 = (\lambda - 2)/2\), \(d_2 = \lambda/2\); and \(d_1 = d_2 - 1\).

\[
\frac{\langle (\Delta R_{ij})^2 \rangle}{\langle \Delta R \cdot \Delta R \rangle} = \frac{3n}{2 \gamma_0} \left[ \frac{\phi_2(\phi_1 - 1)}{\phi_1(\phi_1 \phi_2 - \phi_1 - \phi_2)} + \frac{\phi_1 - \phi_2}{\phi_1 \phi_2} + \frac{\phi_1(\phi_2 - 1)}{\phi_2(\phi_1 \phi_2 - \phi_1 - \phi_2)} \right].
\]

(53)

with \(\zeta\) and \(\theta\) (0 \(\leq \zeta\), \(\theta\) \(\leq 1\)) being fractional distances of points \(i\) and \(j\) from the closest multifunctional junctions on their left.
(3) The closest multifunctional junctions on the left of both points \( i \) and \( j \) are \( \phi_2 \)-functional. We have \( d_1 = d_2 = (\lambda - 1)/2 \). For this case \( \phi_1 \) and \( \phi_2 \) in Eq. (52) are switched.

\[
\left[ \begin{array}{c}
\langle (|\Delta R_{ij}|^2) angle \\
\langle \Delta R_{ij}, \Delta R'_{ij} \rangle
\end{array} \right] = \frac{3n}{2\eta} \times \\
\left[ \begin{array}{c}
\phi_1 (d_2 - 1) + \frac{\zeta (1 - \zeta)}{\phi_1 (d_1 - 1)} \\
\phi_2 (d_1 - 1) + \frac{\zeta (1 - \zeta)}{\phi_2 (d_2 - 1)} + \zeta (\phi_2 - \phi_1)
\end{array} \right]
\]

\[
\left[ \begin{array}{c}
\langle \phi_1 \phi_2 - \phi_1 - \phi_2 \rangle \\
\phi_1 \phi_2
\end{array} \right] = \frac{3n}{2\eta} \times \\
\left[ \begin{array}{c}
\phi_1 (d_2 - 1) + \frac{\zeta (1 - \zeta)}{\phi_1 (d_1 - 1)} \\
\phi_2 (d_1 - 1) + \frac{\zeta (1 - \zeta)}{\phi_2 (d_2 - 1)} + \zeta (\phi_2 - \phi_1)
\end{array} \right]
\]

\[
\left[ \begin{array}{c}
\langle \phi_1 \phi_2 - \phi_1 - \phi_2 \rangle \\
\phi_1 \phi_2
\end{array} \right] = \frac{3n}{2\eta} \times \\
\left[ \begin{array}{c}
\phi_1 (d_2 - 1) + \frac{\zeta (1 - \zeta)}{\phi_1 (d_1 - 1)} \\
\phi_2 (d_1 - 1) + \frac{\zeta (1 - \zeta)}{\phi_2 (d_2 - 1)} + \zeta (\phi_2 - \phi_1)
\end{array} \right]
\]

with \( \zeta \) and \( \theta (0 \leq \zeta, \theta \leq 1) \) being fractional distances of points \( i \) and \( j \) from the closest multifunctional junctions on their left.

The closest multifunctional junctions on the left of point \( i \) is \( \phi_2 \)-functional and on the left of point \( j \) is \( \phi_1 \) functional. We have \( d_2 = (\lambda - 2)/2, d_1 = \lambda/2 \). For this case \( \phi_1 \) and \( \phi_2 \) in Eq. (53) are switched.

\[
\left[ \begin{array}{c}
\langle (|\Delta R_{ij}|^2) \rangle \\
\langle \Delta R_{ij}, \Delta R'_{ij} \rangle
\end{array} \right] = \frac{3n}{2\eta} \times \\
\left[ \begin{array}{c}
\phi_1 (d_2 - 1) + \frac{\zeta (1 - \zeta)}{\phi_1 (d_1 - 1)} \\
\phi_2 (d_1 - 1) + \frac{\zeta (1 - \zeta)}{\phi_2 (d_2 - 1)} + \zeta (\phi_2 - \phi_1)
\end{array} \right]
\]

\[
\left[ \begin{array}{c}
\langle \phi_1 \phi_2 - \phi_1 - \phi_2 \rangle \\
\phi_1 \phi_2
\end{array} \right] = \frac{3n}{2\eta} \times \\
\left[ \begin{array}{c}
\phi_1 (d_2 - 1) + \frac{\zeta (1 - \zeta)}{\phi_1 (d_1 - 1)} \\
\phi_2 (d_1 - 1) + \frac{\zeta (1 - \zeta)}{\phi_2 (d_2 - 1)} + \zeta (\phi_2 - \phi_1)
\end{array} \right]
\]

\[
\left[ \begin{array}{c}
\langle \phi_1 \phi_2 - \phi_1 - \phi_2 \rangle \\
\phi_1 \phi_2
\end{array} \right] = \frac{3n}{2\eta} \times \\
\left[ \begin{array}{c}
\phi_1 (d_2 - 1) + \frac{\zeta (1 - \zeta)}{\phi_1 (d_1 - 1)} \\
\phi_2 (d_1 - 1) + \frac{\zeta (1 - \zeta)}{\phi_2 (d_2 - 1)} + \zeta (\phi_2 - \phi_1)
\end{array} \right]
\]

where \( \zeta \) and \( \theta (0 \leq \zeta, \theta \leq 1) \) are fractions of the length of the chain for points \( i \) and \( j \), respectively, from the closest multifunctional junction on their left (Fig. 6).

II. DISCUSSION

This study has resulted in the formulation of a model of polymer networks with alternating functionalities and obtained analytical solutions for an infinite network having a treelike topology and composed of phantom Gaussian chains. The ability to compute mean-square fluctuations of junctions and points along the chains, and correlations between instantaneous fluctuations of two points or junctions, even those separated by other intermediate junctions was made possible. This study has also resulted in the computations of mean-square fluctuations of the distance between any two points (or junctions) in such networks.

The preparation of networks with alternating junction functionalities is being planned.25 One promising approach would be the azide-alkyne reactions that have already been used to prepare model networks.26 These elastomers would be studied in a variety of ways. With regard to experiments, we would study the long-wavelength scattering of neutrons from deuterated paths in networks with alternating functionalities. The elastomeric properties of such networks would also be studied, and theoretical predictions with experimental data obtained by mechanical deformations and equilibrium swelling would be compared. With regard to additional theoretical work, the effects of constraints, due to excluded volume effects, on the elastomeric properties of these materials would be studied.

Most important, these new results may have significant impact on the well-known elastic network models of proteins23,27,28 and the characterization of other biological structures. Elastic network models originated from the phantom network models of polymers in general, by a direct application of Eq. (12) to the contact matrices corresponding to biological structures. They represent a simplified form of normal mode analysis, where the details of intermolecular potentials are neglected. Also, it is assumed that all interactions between residues (or atoms, depending on the coarse-grained model) both bonded and nonbonded are springlike with a universal spring constant. Our present results enable us to predict large-scale motions of loops in macromolecular structures, even if the detailed coordinates of these loops are missing in the structures deposited in the PDB. Since large loops are usually highly mobile the exact coordinates of the corresponding atoms are frequently unavailable in the published PDB files. Our theory may help to overcome this problem by allowing us to compute the fluctuational dynamics of residues in the loop from the coordinates of multifunctional junctions to which the loops are attached at the ends. Results we obtain for protein loops will be presented in a subsequent paper.
ACKNOWLEDGMENTS

It is a pleasure to acknowledge the financial support provided by the National Institutes of Health through Grant Nos. 1R01GM081680, 1R01GM072014, and 1R01GM073095. Also, J.E.M. wishes to acknowledge financial support provided by the National Science Foundation through Grant No. DMR-083454 (Polymers Program, Division of Materials Research).

APPENDIX A: FLUCTUATIONS OF TWO JUNCTIONS SEPARATED BY SEVERAL $\phi_1$, $\phi_2$ functional junctions

First we calculate minors corresponding to diagonal elements of the matrix. Let us assume that the number of tiers is even, i.e.,
\[ a_1 = \phi_1, \]
\[ b_1 = \phi_2, \]
\[ a_2 = \phi_1 - \frac{\phi_1-1}{b_1}, \]
\[ b_2 = \phi_2 - \frac{\phi_2-1}{a_1}, \ldots. \]

We assume that the diagonal element of the matrix for which we compute the minor is $a_{r-\lambda+1}$. Then we have
\[ b_{r-\lambda+2}^* = \phi_2 - \frac{\phi_2-1}{a_{r-\lambda+1}} = b_{r-\lambda+2} + \frac{1}{a_{r-\lambda+1}}, \]
\[ a_{r-\lambda+3}^* = \phi_1 - \frac{\phi_1-1}{b_{r-\lambda+2}} = a_{r-\lambda+3} + \frac{1}{b_{r-\lambda+2}} - b_{r-\lambda+2}^*, \]
and generally for $t-\lambda+1 \leq k \leq t$, $a_k^* = a_k + (1/b_{k-1}) - (1/b_{k-1})^t$, and $b_k = b_k + (1/a_{k-1}) - (1/a_{k-1})$.

(I) To calculate the determinant $D_{ii}$ corresponding to a junction with functionality $\phi_1$ at the $\lambda$th tier, where $\lambda$ is an even number we observe that
\[ D_{ii} = \gamma^{N-1}a_1^{N_1}b_1^{N_0} \cdots \]
\[ = \frac{N_0}{a_{r-\lambda}} b_{r-\lambda-1} a_{r-\lambda+1} a_{r-\lambda+2} \cdots a_{r-\lambda+1} \times a_{r-\lambda+2} a_{r-\lambda+3} \cdots a_{r-1} \]
\[ D = \gamma a_1^{N_1} b_1^{N_0} \cdots a_{r-1}^{N_{r-1}} b_{r-1}^{N_{r-2}} (a/b_i-1), \]
\[ D_{ii} = \frac{1}{\gamma b_{r-\lambda+1} a_{r-\lambda+2} \cdots a_{r-1} (a/b_i-1)}, \]
\[ (a/b_i-1) a_{r-1}^* b_{r-2}^* \cdots b_{r-\lambda+3} a_{r-\lambda+2}^* \]
\[ = \alpha \left( \beta - \frac{1}{a_{r-1}} \right) a_{r-1}^* b_{r-2}^* \cdots b_{r-\lambda+3} a_{r-\lambda+2}^* \]
\[ = \beta^{(\lambda-1)/2} \alpha^{(\lambda-1)/2} (a/b_i-1) = \frac{\beta}{\alpha} \frac{1}{\alpha-1}. \]

Hence, $D_{ii} = \frac{\alpha^{(\lambda+1)/2} \beta^{(\lambda-1)/2}}{\alpha^{(\lambda-1)/2} \beta^{(\lambda-1)/2}} (a/b_i-1) = \frac{\alpha}{\alpha-1}$.

Therefore, if $\lambda$ is odd and if the functionality of the junction is $\phi_2$, then the mean-square fluctuations are $[3a/2 \gamma (a/b_i-1)]$.

(II) To calculate the determinant $D_{ii}$ corresponding to a junction with functionality $\phi_2$ at the $\lambda$th tier, where $\lambda$ is an even number we observe that
\[ D_{ii} = \gamma^{N-1}a_1^{N_1}b_1^{N_0} \cdots a_{r-\lambda-1} b_{r-\lambda-1} a_{r-\lambda+1} b_{r-\lambda+1} \cdots a_{r-1} b_{r-1} \]
\[ D = \gamma a_1^{N_1} b_1^{N_0} \cdots a_{r-1}^{N_{r-1}} b_{r-1}^{N_{r-2}} (a/b_i-1), \]
\[ D_{ii} = \frac{1}{\gamma b_{r-\lambda+1} a_{r-\lambda+2} \cdots a_{r-1} (a/b_i-1)}, \]
\[ (a/b_i-1) a_{r-1}^* b_{r-2}^* \cdots b_{r-\lambda+3} a_{r-\lambda+2}^* \]
\[ = \alpha \left( \beta - \frac{1}{a_{r-1}} \right) a_{r-1}^* b_{r-2}^* \cdots b_{r-\lambda+3} a_{r-\lambda+2}^* \]
\[ = \beta^{(\lambda-1)/2} \alpha^{(\lambda-1)/2} (a/b_i-1) = \frac{\beta}{\alpha} \frac{1}{\alpha-1}. \]

Hence, $D_{ii} = \frac{\alpha^{(\lambda+1)/2} \beta^{(\lambda-1)/2}}{\alpha^{(\lambda-1)/2} \beta^{(\lambda-1)/2}} (a/b_i-1) = \frac{\beta}{\alpha} \frac{1}{\alpha-1}$.

(III) To calculate the determinant $D_{ii}$ corresponding to a junction with functionality $\phi_1$ at the $\lambda$th tier, where $\lambda$ is an odd number we observe that
\[ D_{ii} = \frac{1}{\gamma b_{r-\lambda+1} a_{r-\lambda+2} \cdots a_{r-1} (a/b_i-1)}, \]
\[ (a/b_i-1) a_{r-1}^* b_{r-2}^* \cdots b_{r-\lambda+3} a_{r-\lambda+2}^* \]
\[ = \alpha \left( \beta - \frac{1}{a_{r-1}} \right) a_{r-1}^* b_{r-2}^* \cdots b_{r-\lambda+3} a_{r-\lambda+2}^* \]
\[ = \beta^{(\lambda-1)/2} \alpha^{(\lambda-1)/2} (a/b_i-1) = \frac{\beta}{\alpha} \frac{1}{\alpha-1}. \]
Hence, if \( \lambda \) is odd and if the functionality of the junction is \( \phi_1 \) then the mean-square fluctuations are \( 3\beta/2\gamma(\alpha\beta-1) \).

\[ D_{ij} = \frac{1}{D} \frac{1}{a^{ij} \beta^i(\alpha\beta-1)} \]  

(A6)

In the case where \( \lambda \) is even, the same procedure is followed as in the case where \( \lambda \) is odd, and the (1,2) element becomes \( -1/a_{i-1}^* b_{r-2}^* \cdots a_{i-\lambda+3}^* b_{i-\lambda+2}^* \). Thus the minor \( D_{ij} \) is

\[ D_{ij} = \frac{1}{D} \frac{1}{a^{ij} \beta^i(\alpha\beta-1)} \]

(A7)

Since \( d_2=\lambda/2 \), \( d_1=(\lambda-2)/2 \) we have

\[ D_{ij} = \frac{1}{D} \frac{1}{a^{ij} \beta^i(\alpha\beta-1)} \]

(A8)

\[ \frac{3}{2} \gamma(\phi_1 \phi_2 - \phi_1 \phi_2) \phi_1 (\phi_2 - 1)^{-2} (\phi_1 - 1)^{2d_i} \]

(ii) Since junction \( i \) has functionality \( \phi_2 \) and belongs to the first tier, \( i=2 \). We consider again the cases where \( \lambda \) is odd and even. When \( \lambda \) is odd the (2,2) element of the matrix becomes \(-1/a_{i-1}^* b_{i-2}^* \cdots a_{i-\lambda+2}^* \). Then we have

\[ D_{ij} = \frac{1}{D} \frac{1}{a^{ij} \beta^i(\alpha\beta-1)} \]

(A9)

\[ \frac{3}{2} \gamma(\phi_1 \phi_2 - \phi_1 \phi_2) \phi_1 (\phi_2 - 1)^{-2} (\phi_1 - 1)^{2d_i} \]

When \( \lambda \) is even, the (2,1) element of the matrix becomes \(-1/b_{i-1}^* a_{i-2}^* \cdots a_{i-\lambda+2}^* \). Then the ratio \( D_{ij}/D \) is

\[ D_{ij} = \frac{1}{D} \frac{1}{a^{ij} \beta^i(\alpha\beta-1)} \]

(A10)

\[ \frac{3}{2} \gamma(\phi_1 \phi_2 - \phi_1 \phi_2) \phi_1 (\phi_2 - 1)^{-2} (\phi_1 - 1)^{2d_i} \]

(iv) When \( \lambda \) is odd the (1,2) element of the matrix becomes \(-1/a_{i-1}^* b_{i-2}^* \cdots a_{i-\lambda+2}^* \). Then we have

\[ D_{ij} = \frac{1}{D} \frac{1}{a^{ij} \beta^i(\alpha\beta-1)} \]

(D12)
\[ \frac{D_{ij}}{D} = \frac{1}{a^{(\lambda-1)/2}b^{(\lambda-1)/2}(\alpha\beta - 1)}. \]  

In this case, \( d_1 = d_2 = (\lambda - 1)/2 \) thus

\[ \frac{D_{ij}}{D} = \frac{1}{a^{(\lambda-2)/2}b^{(\lambda-2)/2}(\alpha\beta - 1)}. \]  

When \( \lambda \) is even, the (1,1) element of the matrix becomes 
\(-1/b^{\ast}_{1-2}a^{\ast}_{2-2} \cdots a^{\ast}_{n-2+2}. \) Then we have

\[ \frac{D_{ij}}{D} = \frac{1}{a^{(\lambda-3)/2}b^{(\lambda-3)/2}(\alpha\beta - 1)}. \]  

In this case \( d_1 = d_2 = (\lambda - 2)/2 \) and we have

\[ \frac{D_{ij}}{D} = \frac{1}{a^{(\lambda-4)/2}b^{(\lambda-4)/2}(\alpha\beta - 1)}. \]  

Since Eqs. (A16) and (A17) give the same result we conclude that the mean-square fluctuations between these two points are

\[ \frac{3}{2} \gamma (\phi_1 \phi_2 - \phi_1 - \phi_2) (\phi_2 - 1)^{d_2}(\phi_1 - 1)^{d_1}. \]  

**APPENDIX B: CALCULATION OF THE ELEMENTS \( \Gamma_{ij}^{-1} \) of the inverse of matrix \( \Gamma \)**

In order to calculate the elements \( \Gamma_{ij}^{-1} \) of the inverse of matrix \( \Gamma \), we first compute the determinant of matrix \( \Gamma \),

\[ \text{det}(\Gamma) = \gamma_0^n [na_i - (n - 1)]^{\nu} [nb_i - (n - 1)]^{\varphi} \cdots [na_{i-1} - (n - 1)]^{\nu} [nb_{i-1} - (n - 1)]^{\varphi} \times [(n + 1 - i)b_i - (n - i)]. \]  

For the diagonal elements of matrix \( \Gamma \) we find their minors which are given by the following formula:

\[ D_{ii} = \gamma_0^{n-1} [(na_i - (n - 1)]^{\nu} [nb_i - (n - 1)]^{\varphi} \cdots [na_{i-1} - (n - 1)]^{\nu} [nb_{i-1} - (n - 1)]^{\varphi} [(i - 1)a_i - (i - 2)] \times [(n + 1 - i)b_i - (n - i)]. \]  

To calculate the diagonal elements of the inverse matrix corresponding to the first tier we divide Eq. (B2) by Eq. (B1) which gives

\[ \Gamma_{ii}^{-1} = \gamma_0 [i(i - 1)a_i - (i - 2)] [(n + 1 - i)b_i - (n - i)], \]  

Similarly the minor corresponding to the \((i, j)\) element in the first tier is

\[ D_{ij} = \text{det}(A_{\min(i-1,j-1)})\text{det}(A_{n+1-\max(i,j)}) \]  

which leads to

\[ \Gamma_{ij}^{-1} = \gamma_0^{n-1} [(i(i - 1)a_i - (i - 2)] [(n + 1 - i)b_i - (n - i)], \]  

**APPENDIX C: FLUCTUATIONS OF TWO POINTS OF A CHAIN SEPARATED BY SEVERAL \( \phi \), \( \varphi \) functional junctions**

The determinant of the matrix is given by the formula

\[ \text{det}(\Gamma) = \gamma_0^n [na_i - (n - 1)]^{\nu} [nb_i - (n - 1)]^{\varphi} \cdots [na_{i-1} - (n - 1)]^{\nu} [nb_{i-1} - (n - 1)]^{\varphi} \times [(a_i + b_i) + (n - 2)]. \]  

The point \( j \) can be described by three numbers \((\lambda, \mu, \nu) \). The first number from the left corresponds to the tier to which the point belongs, the second number labels the chain within the tier, and the third number \( \nu \) gives the position within the chain, \( 1 \leq \nu \leq n+1 \).

We have four different possibilities. The reader should refer to the matrices in Eqs. (36) and (37) for their convenience. We consider all possibilities: (1) The closest multifunctional junctions on the left of point \( i \) is \( \phi_1 \)-functional and on the left of point \( j \) is \( \phi_2 \)-functional. The convention shown in Fig. 4 is used. Points \( i \) and \( j \) are then separated by \( d = d_1 + d_2 \) intermediate junctions, with \( d_1 \) of them having function-

\[ \phi_1, \phi_2 \] and \( d_2 \) having functionality \( \phi_2 \). In this case, the \( \lambda \) of \( j \) is always even. We use the convention that point \( j \) is always to the right of point \( i \), thus making it to the right of the first tier, \( \lambda = 2 \).

\[ d_1 = d_2 = \frac{\lambda}{2}, \]  

The product of diagonal elements in the diagonal submatrix corresponding to the \( \lambda \)th tier gives

\[ [na_{i-\lambda+1} - (n - 1)]^{\nu} [(n - \nu) (n - \nu + 1)a_{i-\lambda+1} - (n - 1)]^{\nu} \times \gamma_0 [n(n - 2)]^{\nu} [n(n - 2)]^{\nu}. \]  

This will be proved below. As was found earlier, the submatrix corresponding to the \( \lambda \)th tier contains a number of submatrices equal to the number of \( \phi_1 \) and \( \phi_2 \) functional junctions of this tier. Each of these latter submatrices represents the connectivity of the points in each chain on the tier.
Therefore, the value of \( b_{j}^{*} \) at the \( n \)th row after the inverse Gaussian elimination is obtained. The next step is applying the inverse Gaussian elimination to the submatrix in the \( (\lambda -1) \)th tier corresponding to the chain in which the element \( b_{\lambda-1}^{*} \) occurs. Then the row of \( b_{\lambda-2}^{*} \) (designated the \( r \)th row) multiplied by \( 1/(v-1) \) is added to the \( r \)th row. A \( -1/(v-1)b_{\lambda-2}^{*} \) appears in the \( (i, \sigma -1) \) element. Then the \( (\sigma -1) \)th row multiplied by \( 1/(v-1)(2b_{\lambda-2}^{*} - (n-2)) \) is added to the \( \sigma \)th row. A \( -1/(v-1)(2b_{\lambda-2}^{*} - (n-2)) \) appears in the \( (i, \sigma -2) \) element. Continuing the procedure it is finally obtained a \(-1/(v-1)(nb_{\lambda-2}^{*} - (n-1))\) in the \( (i, \sigma -3) \) element. We then add the \( (\sigma -1) \)th row on the \( \sigma \)th row multiplied by \( 1/(v-1)(nb_{\lambda-2}^{*} - (n-1))\) to the \( \sigma \)th row. Then, on the \( \sigma \)th row above \( a_{\sigma -1}^{*} \) a \(-1/(v-1)(nb_{\lambda-2}^{*} - (n-1)) \) is obtained. Continuing the procedure a \(-1/(v-1)(nb_{\lambda-2}^{*} - (n-1)) \) on the \( \sigma \)th row above the \( b_{\sigma}^{*} \) element is finally obtained. The determinant of the first submatrix corresponding to the first tier is

\[
B[i - 1, a_i - (i - 2)] = \frac{1}{(v-1)(nb_{\lambda-2}^{*} - (n-1)) \cdots (na_{i-1}^{*} - (n-1))}.
\]

Hence,

\[
D_{ij} = \gamma_{i-1}^{(i-1)}[(i-1)a_i - (i-2)][(n-1)\lambda_{i-1} - (n-v)] - \gamma_{i-2}^{(i-1)}[(i-1)a_i - (i-2)][(n-1)\lambda_{i-1} - (n-v)]
\]

\[
\times [nb_{\lambda-2}^{*} - (n-1)]^{3}[na_{i-1}^{*} - (n-1)]^{3}[nb_{\lambda-2}^{*} - (n-1)]^{3}[na_{i-1}^{*} - (n-1)]^{3}.
\]

Therefore,

\[
\frac{D_{ij}}{D} = \gamma_{i-1}^{(i-1)}[(i-1)a_i - (i-2)][(n-1)\lambda_{i-1} - (n-v)] - \gamma_{i-2}^{(i-1)}[(i-1)a_i - (i-2)][(n-1)\lambda_{i-1} - (n-v)]
\]

\[
\times [nb_{\lambda-2}^{*} - (n-1)]^{3}[na_{i-1}^{*} - (n-1)]^{3}[nb_{\lambda-2}^{*} - (n-1)]^{3}[na_{i-1}^{*} - (n-1)]^{3}.
\]
Applying the same procedure as before, it is concluded that on the
in Ref. 10.

Hence, after proceeding the same way as before it is obtained that

\[ n\alpha - (n - 1) = \frac{\phi_1(\phi_2 - 1)}{\phi_2}, \]

\[ n\beta - (n - 1) = \frac{\phi_2(\phi_1 - 1)}{\phi_1}, \]

\[ n\alpha \beta - (n - 1)(\alpha + \beta) + (n - 2) = \frac{\phi_1\phi_2 - \phi_1 - \phi_2}{n}, \]

\[ \frac{D_{ij}}{D} = -\frac{n\gamma_0^{-1}}{\phi_1} \left[ \frac{\zeta}{\phi_2} + 1 \right] \left[ \frac{(1 - \theta)(\phi_1\phi_2 - \phi_1 - \phi_2)}{\phi_2} + 1 \right]. \]

(\text{C4})

\[ \theta = \frac{\mu - 1}{n} \Rightarrow 0 \leq \theta \leq 1, \]

\[ \zeta = \frac{i - 1}{n} \Rightarrow 0 \leq \zeta \leq 1, \]

\[ \frac{D_{ij}}{D} = -\frac{n\gamma_0^{-1}}{\phi_1} \left[ \frac{\zeta}{\phi_2} + 1 \right] \left[ \frac{(1 - \theta)(\phi_1\phi_2 - \phi_1 - \phi_2)}{\phi_2} + 1 \right]. \]

(\text{C5})

In the case where \( \phi_1 = \phi_2 \), Eq. (C5) reduces to Eq. (A44) in the earlier study. 10

(2) The closest multifunctional junctions on the left of both points \( i \) and \( j \) are \( \phi_1 \)-functional. The convention shown in Fig.
4 is used again. The point \( i \) is considered to be on the first tier, thus having a \( \phi_1 \)-functional junction on its left by default.

We always assume that the point \( j \) is to the right of the first tier thus having

\[ 1 + \varphi_1^{(\lambda-1)/2} \varphi_2^{(\lambda-1)/2} \leq \mu \leq 2 \varphi_1^{(\lambda-1)/2} \varphi_2^{(\lambda-1)/2}, \]

\[ d_1 = d_2 = \frac{\lambda - 1}{2}. \]

The product of diagonal elements in the diagonal submatrix corresponding to the \( \lambda \)th tier is

\[ [na_{i-\lambda+1} - (n - 1)] \cdot [(n - 1)b_{i-\lambda+1}] = \left[ (n - 1) \right]^{\lambda - 1}. \]

(\text{C6})

Applying the same procedure as before, it is concluded that on the \( i \)th row above the \( b_{i-1}^* \) element there is

\[ -\frac{1}{(n - 1)(na_{i-\lambda+2} - (n - 1)) \cdot \cdots (na_{i-1} - (n - 1))}. \]

(\text{C7})

The determinant of the first submatrix corresponding to the first tier becomes

\[ B[(i - 1)a_i - (i - 2)] \]

where

\[ B = \frac{1}{(n - 1)(na_{i-\lambda+2} - (n - 1)) \cdot \cdots (na_{i-1} - (n - 1))}. \]

Hence, after proceeding the same way as before it is obtained that

\[ \frac{D_{ij}}{D} = -\frac{n\gamma_0^{-1}}{\phi_1} \left[ \frac{\zeta}{\phi_2} + 1 \right] \left[ \frac{(1 - \theta)(\phi_1\phi_2 - \phi_1 - \phi_2)}{\phi_2} + 1 \right]. \]

(\text{C8})

In the case where \( \phi_1 = \phi_2 \), Eq. (C8) reduces to Eq. (A44) in Ref. 10.

(3) The closest multifunctional junctions on the left of both points \( i \) and \( j \) are \( \phi_2 \)-functional. For this case we also have \( d_1 = d_2 = (\lambda - 1)/2. \) For this case the opposite convention of Fig. 4 is used, which means that all \( \phi_1 \) junctions are
switched with $\phi_2$ and vice versa. Furthermore the $\lambda$ of $j$ is always odd. We always assume that the point $j$ is always to the right of the first tier thus having:
\[ 1 + \varphi_1^{(\lambda - 1)/2} \varphi_2^{(\lambda - 1)/2} \leq \mu \equiv 2 \varphi_1^{(\lambda - 1)/2} \varphi_2^{(\lambda - 1)/2}. \]

The product of diagonal elements in the diagonal submatrix corresponding to the $\lambda$th tier is
\[
[n a_{\lambda - \lambda + 1} - (n - 1)]^{N_{\lambda} - 1}[(\nu - 1)[(n + \nu + 1) a_{\lambda - \lambda + 1} - (n - \nu)]],
\]
\[ - (n + \nu)]\times [n b_{\lambda - \lambda + 1} - (n - 1)]^{N_{\phi}}. \tag{C9} \]

Applying the same procedure as before it is concluded that on the $i$th row below the $b_i'$ element is
\[
\text{det} \left[ \sum_{i=0}^{N_{\lambda}} \frac{1}{\phi_1^{(\lambda - 1)/2} \phi_2^{(\lambda - 1)/2}} \right]
\]

In the case where $\phi_1 = \phi_2$, Eq. (C11) reduces to Eq. (A44) in Ref. 10.

(4) The closest multifunctional junctions on the left of point $i$ is $\phi_2$-functional and on the left of point $j$ is $\phi_1$-functional. For this case the opposite convention of Fig. 4 is used, which means that all $\phi_1$ junctions are switched with $\phi_2$ and vice versa. Furthermore the $\lambda$ of $j$ is always even. We assume that the point $j$ is always to the right of the first tier thus having
\[ 1 + \varphi_2^{(\lambda - 2)/2} \varphi_1^{(\lambda - 2)/2} \leq \mu \equiv \varphi_2^{(\lambda - 2)/2} \varphi_1^{(\lambda - 2)/2} + \varphi_2^{(\lambda - 2)/2} \varphi_1^{(\lambda - 2)/2}. \]

For this case
\[ d_2 = \frac{\lambda - 2}{2}, \quad d_1 = \frac{\lambda}{2}. \]

The product of diagonal elements in the diagonal submatrix corresponding to the $\lambda$th tier is
\[
\text{det} \left[ \sum_{i=0}^{N_{\lambda}} \frac{1}{\phi_1^{(\lambda - 1)/2} \phi_2^{(\lambda - 1)/2}} \right]
\]

In the case where $\phi_1 = \phi_2$, Eq. (C14) reduces to Eq. (A44) in Ref. 10.

\begin{align*}
\text{det} &\left[ (\nu - 1)(n a_{\lambda - \lambda + 2} - (n - 1)) \cdots (n b_{\lambda - 1} - (n - 1)) \right] \\
&= - (\nu - 1)(n a_{\lambda - \lambda + 2} - (n - 1)) \cdots (n b_{\lambda - 1} - (n - 1)). \tag{C10}
\end{align*}

The determinant of the first submatrix corresponding to the first tier is
\[
B[(i - 1)b_i - (i - 2)] \text{ where } B
\]
\[ = - (\nu - 1)(n a_{\lambda - \lambda + 2} - (n - 1)) \cdots (n b_{\lambda - 1} - (n - 1)). \]

Hence, after following the same steps as before it is obtained that
\[
\text{det} \left[ (\nu - 1)(n a_{\lambda - \lambda + 2} - (n - 1)) \cdots (n b_{\lambda - 1} - (n - 1)) \right] \\
&= - (\nu - 1)(n a_{\lambda - \lambda + 2} - (n - 1)) \cdots (n b_{\lambda - 1} - (n - 1)). \tag{C11}
\]

In the case where $\phi_1 = \phi_2$, Eq. (C11) reduces to Eq. (A44) in Ref. 10.


