Dynamics of semiflexible treelike polymeric networks

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We study the dynamics of general treelike networks, which are semiflexible due to restrictions on the orientations of their bonds. For this we extend the generalized Gaussian structure model, in which the dynamics obeys Langevin equations coupled through a dynamical matrix. We succeed in formulating analytically this matrix for arbitrary treelike networks and stiffness coefficients. This allows the straightforward determination of dynamical characteristics relevant to mechanical and dielectric relaxation. We show that our approach also follows from the maximum entropy principle; this principle was previously implemented for linear polymers and we extend it here to arbitrary treelike architectures. © 2009 American Institute of Physics.

I. INTRODUCTION

The last decades are marked by the synthesis of greatly diversified branched polymers. The theory of flexible polymeric networks has also made serious advances using generalized Gaussian structures (GGS). Here we introduce stiffness concepts into the GGS model, focusing on the dynamics of treelike networks; these are networks (mathematically: graphs) without loops (cycles).

The simplest nontrivial example of a connected graph is the chain. Now, behind the idea of modeling chain polymers as simple (i.e., flexible) random walks is the assumption of Flory of the compensation in the melt of the intrachain and the interchain excluded-volume forces. However recent research shows that this idealization of the chain is an oversimplification. In fact, the justification of Flory’s idea—the extended plateau in the Kratky plot—is possibly due to the screening of the chain’s stiffness and thickness.

Classical models for semiflexible polymers fall into two main groups, being either discrete or continuous. The continuous variants are often based on the Kratky–Porod (worm-like chain) model, in which the chains are represented through smooth (everywhere at least once differentiable) curves. Such restrictions render the modeling of branched polymers quite difficult, given that the branching points introduce discontinuities in the derivatives. Because of this we prefer to work in a discrete scheme, such as the beads and springs model.

Bixon and Zwanzig pioneered the study of the dynamics of semiflexible chains in a discrete picture. Their model was subsequently extended to branched structures, such as star polymers, dendrimers, Cayley trees, and randomly branched polymers. More recently the BZ model was extended to the study of the dynamics of melts of chains and of the dynamics of proteins, for a summary of results see Ref. We note, however, that many of these works also include hydrodynamical interactions; this leads to systems of Langevin equations with rather complex dynamical matrices, which therefore allow only a numerical treatment. Following another course—staying within the Rouse scheme—we have recently determined analytically the dynamical matrices of semiflexible stars and dendrimers. Here we extend this approach and obtain the dynamical matrices of treelike networks of arbitrary topology.

The structure of this paper is as follows. In Sec. II we describe the model. In Sec. III we derive analytic expressions for the dynamical matrices corresponding to given treelike networks. Then in Sec. IV we evaluate as an example the mechanical relaxation moduli for semiflexible dendrimers built from star polymers. Furthermore, we show in Sec. V that our expressions can also be obtained based on the maximum entropy approach, previously applied to polymer chains only. The article ends with our conclusions.

II. THE MODEL

We start by recalling some basic ideas underlying the model of GGS, and its properties when applied to treelike networks. Then we extend the model by adding semiflexibility.

A GGS represents the extension of the classical Rouse model, developed for linear polymer chains, to systems of arbitrary topology. The structure is modeled as a network consisting of N beads connected by springs. The objects of our consideration are treelike networks, so that the number of springs is equal to \((N-1)\). With each spring is associated one bond, say \(a\), which connects two beads, say \(n\) and \(m\), so that the corresponding bond vector is related to the position vectors of the beads through

\[ \mathbf{d}_a = \mathbf{r}_n - \mathbf{r}_m = \sum_i B_{ai} \mathbf{r}_i. \]  

(1)

The matrix \( \mathbf{B}=(B_{ai}) \) displays the connections between the beads. Now, \( \mathbf{B} \) is simply related to the incidence matrix \( \mathbf{G} \) of graph theory, \( \mathbf{B}^T \) being the transposed matrix of \( \mathbf{G} \), hence \( \mathbf{B} = \mathbf{G}^T \) and \( \mathbf{G} = \mathbf{B}^T \). Thus Eq. (1) can be expressed as:

\[ \mathbf{d}_a = \mathbf{G} \mathbf{r}_n - \mathbf{G} \mathbf{r}_m = \sum_i \mathbf{G} B_{ai} \mathbf{r}_i. \]
\[ d_a = \sum_i (G^T)_{ia} r_i. \]  

We remark that for each bond \( a \) directed from bead \( m \) to bead \( n \) the \( N \times (N-1) \) matrix \( G=(g_{mn}) \) has as nonzero entries only \( g_{ma}=-1 \) and \( g_{nm}=1 \).

In the basic GGS formalism the potential energy \( V_R \) is purely harmonic. Expressed in the bond variables, \( V_R \) is diagonal,

\[ V_R(\{d_a\}) = \frac{K}{2} \sum_a d_a^2. \]

In Eq. (3) all bonds have been taken to be equal, with spring constant \( K=3k_BT/l^2 \), where \( l^2 \) is the mean-square length of each bond and \( k_BT \) is the Boltzmann constant. Using the relation between the bond and the bead variables, Eq. (2), we obtain,

\[ V_R(\{r_i\}) = \frac{K}{2} \sum_{ij} (G G^T)_{ij} r_i r_j, \]

which by setting

\[ A^R = GG^T \]

leads to

\[ V_R(\{r_i\}) = \frac{K}{2} \sum_{ij} A^R_{ij} r_i r_j. \]

The \( N \times N \) matrix \( A^R=(A^R_{ij}) \) is the Rouse connectivity matrix. Its elements can be easily calculated.\(^{29}\) \( A^R_{ij}=(G G^T)_{ij} \) is the inner product of the rows \( i \) and \( j \) of \( G \). If \( i \neq j \), then these rows have a nonzero entry in the same column \( a \) if and only if there is an edge \( a \) joining beads \( i \) and \( j \). In this case, the two nonzero entries are \( +1 \) and \( -1 \), so that \( A^R_{ij}=(G G^T)_{ij}=-1 \). Similarly, \( A^R_{ii}=(G G^T)_{ii} \) is the inner product of the row \( i \) with itself, and, since the number of \( +1 \) or \( -1 \) entries in the \( i \)-th row is equal to the functionality \( f_i \) of the \( i \)-th bead, one has \( A^R_{ii}=f_i \).

The Rouse dynamics of the GGS is given by the following set of Langevin equations of motion:

\[ \frac{\partial}{\partial t} r_i(t) + \sum_{j=1}^N A^R_{ij} r_j(t) = f_i(t). \]

Here the first term is the friction force with friction coefficient \( \zeta \); the second term represents the harmonic force \((\partial/\partial r_i) V_R(\{r_i\}) \) obtained from the potential Eq. (6); \( f_i(t) \) is the stochastic Gaussian force acting on the \( i \)-th bead, for which \((f_i(t)=0 \text{ and } \langle f_i(t) f_j(t') \rangle = 2k_BT \zeta \delta_{ij} \delta_{\alpha\beta} \delta(t-t') \) hold (\( \alpha \) and \( \beta \) denote the \( x \), \( y \), and \( z \) directions).

Now we are at a point where we can introduce semiflexibility. Let us begin by remarking that under the potential given by Eq. (3) the equilibrium bond-bond correlations \( \langle d_a \cdot d_b \rangle_R \) [evaluated with respect to the Boltzmann distribution exp\((-V_R/k_BT)\)] vanish. Semiflexibility is now accounted for through geometrical restrictions on the bonds’ orientations. Inspired by Refs. 18 and 22 we do it through a generalization of Eq. (3),

\[ V_{BG}([d_a]) = \frac{K}{2} \sum_{a,b} W_{ab} d_a \cdot d_b. \]

The average values of \( d_a \cdot d_b \) with respect to the Boltzmann distribution exp\((-V_{BG}/k_BT)\) are readily computed under the assumption that the \( \{d_a\} \) are Gaussian,

\[ \langle d_a \cdot d_b \rangle = \langle \hat{f} (W^{-1})_{ab} \rangle. \]

Hence the knowledge of all \( \langle d_a \cdot d_b \rangle \) is sufficient in order to determine \( W \) through a matrix inversion. As we proceed to show, physically plausible, traditional\(^{18-22}\) choices of the \( \langle d_a \cdot d_b \rangle \) lead to particularly interesting, sparse matrices \( W \).

Thus we set for the mean-squared lengths,

\[ \langle d_a \cdot d_a \rangle = \langle \hat{f} \rangle, \]

and for adjacent bonds \( a \) and \( b \) (connected, say, by the \( i \)-th bead),

\[ \langle d_{ai} \cdot d_{bi} \rangle = \pm \langle \hat{f} \rangle f_i, \]

where the parameter \( f_i \) reflects the stiffness of the junction. We envisage the bonds to be directed, so that the plus sign holds for a head to tail arrangement and the minus sign in the other cases. For nonadjacent bonds \( a \) and \( c \) we take in the spirit of the freely rotating chain model,

\[ \langle d_{ai} \cdot d_{ci} \rangle = (\langle d_{ai} \cdot d_{bi} \rangle \langle d_{bi} \cdot d_{ci} \rangle \cdots \langle d_{bi} \cdot d_{ci} \rangle)^{f_i-2}, \]

where \((b_1, b_2, \ldots, b_{k-1}, b_k)\) denotes the shortest path that connects \( a \) with \( c \). Notice that this path is unique because we focus on treelike networks.

Note that the stiffness parameter \( f_i \) in Eq. (11) is associated with the bead \( i \); by this we assume equal average values for all bond pairs connected by this bead. In the limit \( f_i \to 0 \) for all \( i \), all averages involving different bonds vanish and the potential Eq. (8) takes the simple diagonal form, Eq. (3), which corresponds to a flexible polymer. In the opposite limit, an upper bound for \( f_i \) follows from the fact that the sum of the cosines of the angles between all pairs of bonds adjacent to a bead of functionality \( f_i \) is bounded\(^{30}\) by \( \Sigma_a \cos \theta_{ab} \leq f_i/2 \). Thus if all the averages of Eq. (12) are equal, one obtains \( f_i \leq 1/(f_i-1) \). We note that the exact equality for all \( \theta_{ab}=\theta \) (without averaging), i.e., \( \cos \theta = 1/(f_i - 1) \), is realizable in three dimensions only for functionalities \( f_i \leq 4 \). For higher functionalities this limit is attainable only on the average, i.e., for \( \langle d_{ai} \cdot d_{bi} \rangle \).

The matrix \( W \) defines the potential energy in the bond representation. However, the system of Langevin equations requires that the potential energy be written in position variables. The corresponding matrix is easily obtained by inserting Eq. (2) into Eq. (8).

\[ A^{BG} = GWG^T. \]

### III. THE STRUCTURE OF THE MATRICES \( W \) AND \( A^{BG} \)

In this section we discuss the analytic structure of the matrices \( W \) and \( A^{BG} \). As we proceed to show, under the assumptions Eqs. (10)–(12) the matrix \( W \) takes a particularly simple, sparse form.
A. The matrix $W$

To render the proof simple we first denote the matrix introduced for treelike networks through Eqs. (9)–(12) by $V$. We then present the elements of the matrix $W$ and show that indeed $VV=1$, from which $V=W^{-1}$ follows. We now claim that the matrix $W=(w_{xy})$ is built from the elements $\{w_{xy}\}$ with the following properties:

1. All nondiagonal elements belonging to nonadjacent bonds, say $x$ and $y$, vanish,

$$w_{xy}=w_{yx}=0.$$ (14)

2. Nondiagonal elements corresponding to adjacent bonds, say $a$ and $b$, which hence have a bead, say $i$, in common, depend on its functionality $f_i$ and on the stiffness parameter $t_i$, see Eq. (11).

$$w_{ab}=w_{ba}=\pm \frac{t_i}{(f_i-1)t_i^2 + (f_i-2)t_i - 1}. $$ (15)

In Eq. (15) the plus sign holds for head to tail configurations and the minus sign otherwise. Since $0 \leq t_i \leq 1/(f_i-1)$ the expression $t_i/[ (f_i-1)t_i^2 + (f_i-2)t_i - 1]$ is always negative.

3. Each diagonal element corresponding to a particular bond, say to $b$, depends on its end beads, say $i$ and $j$, and hence on $f_i$ and $f_j$ and on $t_i$ and $t_j$. One has, namely,

$$w_{bb}=1 - \frac{(f_i-1)t_i^2}{(f_i-1)t_i^2 + (f_i-2)t_i - 1} - \frac{(f_j-1)t_j^2}{(f_j-1)t_j^2 + (f_j-2)t_j - 1}. $$ (16)

The diagonal elements $w_{bb}$ are always positive, since $0 \leq t_{ij} \leq 1/(f_{ij}-1)$. A special case of Eq. (16) is obeyed for a peripheral bond $b$ for which, say, $f_i=1$. In this case the term in Eq. (16) depending on $f_i$ vanishes and $w_{bb}$ turns out to depend only on the parameters of bead $j$.

We now turn to the multiplication of $V=(v_{xy})$ by $W=(w_{xy})$, set $VV=K$ and show that $K$ is the unit matrix, i.e., that $K=1$. Now each element of $K=(k_{ab})$, say $k_{ab}$, is associated with two bonds $a$ and $b$. $K$ divides our proof into two cases, depending on whether $b$ is a nonperipheral or a peripheral bond, see Fig. 1. In each case we first calculate the elements of $K$ associated with the nearest neighbors of $b$ and then we display all the other elements, always keeping in mind the sparsity of $K$, i.e., Eq. (14).

We start with a nonperipheral bond $b$ of a treelike network. Let $b$ begin at bead $i$ and end at bead $j$, see Fig. 1(a). Bead $i$ connects the vector $d_i$, with $(f_i-1)$ vectors $\{d_{i_a}\}$ and bead $j$ connects it with $(f_j-1)$ vectors $\{d_{j_b}\}$. As before, the stiffness parameters are taken to be $\pm t_i$ and $\pm t_j$.

For the $K$ element associated with the bonds $a_i \in \{a_i\}$ and $b$ we have,

$$\frac{f_i}{n=1} v_{c_{na}a_b} w_{a_b} + v_{c_{nb}b_b} w_{b_b} + \sum_{m=1}^{f_j} v_{c_{mb}w_{c_{mb}}} = 0. $$ (17)

In Eq. (17) we already took into account that the elements $\{w_{xy}\}$ corresponding to nonadjacent bonds vanish. Following Eqs. (10)–(12) the elements $\{v_{xy}\}$ are:

$$v_{a,\rho_a} = v_{b,\rho_b} = \pm t_i (\text{for } n \neq s), $$ (18)

$$v_{a,\rho_s} = 1, $$ (19)

and

$$v_{c_{na}a_b} = v_{c_{nb}b_b} = \pm t_i (\pm t_j), $$ (20)

the plus or minus sign being as discussed above. After inserting $\{w_{xy}\}$ and $\{v_{xy}\}$ from Eqs. (15), (16), and (18)–(20) into Eq. (17) we obtain

$$k_{a,b} = 0. $$ (21)

The same holds, evidently, for the $k_{c,b}$ elements, in which $c \in \{c_m\}$ are nearest neighbors of $b$,

$$k_{c,b} = \sum_{n=1}^{f_j} v_{c_{na}a_b} w_{a_b} + v_{c_{nb}b_b} w_{b_b} + \sum_{m=1}^{f_j} v_{c_{mb}w_{c_{mb}}} = 0. $$ (22)

Analogously, the diagonal element $k_{bb}$ is given by
\[ k_{bb} = \sum_{n=1}^{f_r-1} v_{ba_n} w_{a_n b} + v_{bb} w_{bb} + \sum_{m=1}^{f_r-1} v_{bc_m} w_{c_m b} = 1. \]  

(23)

If the bond \( b \) is peripheral, see Fig. 1(b), i.e., connected only through the bead \( i \) to the \((f_r-1)\) bonds \( \{a_n\} \), we find as variants of Eqs. (17) and (23),

\[ k_{ab} = \sum_{n=1}^{f_r-1} v_{a_n b} w_{a_n b} + v_{ab} w_{bb} = 0 \]  

(24)

and

\[ k_{bb} = \sum_{n=1}^{f_r-1} v_{ba_n} w_{a_n b} + v_{bb} w_{bb} = 1. \]  

(25)

All other elements of \( K \) associated with \( b \) and with a bond, say \( x \), nonadjacent to it, can be evaluated as follows. The shortest path, which connects \( x \) with \( b \) contains a bond, say \( y \), which is adjacent to \( b \), \( y \in \{a_n, c_m\} \). Then from Eq. (12) we have

\[ k_{ab} = v_{xy} k_{yb}, \]  

(26)

and since \( k_{yb} = 0 \) we also obtain that \( k_{ab} = 0 \).

Thus each column of the matrix \( K \) contains only zeros, except for the diagonal element, which is unity. Therefore \( K \) is the unit matrix, fact which proves that \( W \) [as given by Eqs. (14)–(16)] is indeed the inverse of \( V \).

**B. The matrix \( A^{BZ} \)**

Now after determining \( W \) we are in the position to calculate the matrix \( A^{BZ} \). To evaluate the elements \( \{A^{BZ}_{ij}\} \) of the matrix \( A^{BZ} \) we use Eq. (13),

\[ A^{BZ}_{ij} = \sum_{ab} g_{ia} g_{jb} w_{ab}. \]  

(27)

The matrices \( G = (g_{ia}) \) and \( W = (w_{ab}) \) are quite sparse. Thus \( g_{ia} \) is nonzero only if bond \( a \) contains the bead \( i \) and \( w_{ab} \) is nonzero only if \( a \) is adjacent to \( b \) or if \( a \) equals \( b \). This leads also to many zeros in \( A^{BZ} \). Namely, nonvanishing elements \( A^{BZ}_{ij} \) can only be the diagonal elements and the elements corresponding to two beads \( i \) and \( j \), which are either neighbors or which have a common neighbor.

It is thus instructive to introduce a new notation, as given in Fig. 2. Starting from the bead \( i \) we denote its neighbors by \( i_k \) (one index) and the neighbors of \( i_k \) (with the exception of \( i \)) by \( i_{k_l} \) (two indices). The corresponding functionalities are \( f_i, f_{i_k}, \) and \( f_{i_{k_l}} \). We denote the bond between \( i \) and \( i_k \) by \( a_k \) and between \( i_k \) and \( i_{k_l} \) by \( a_{k_l} \). In this notation we have thus

\[ A^{BZ}_{ii} = \sum_{a_k} g_{ia_k} g_{ia} w_{a_k a}, \]  

(28)

and

\[ A^{BZ}_{ik} = \sum_{a_k} g_{ia_k} g_{ia} w_{a_k a} + \sum_{a_{k_l}} g_{ia_k} g_{ia_{k_l}} w_{a_k a_{k_l}}, \]  

(29)

and

\[ A^{BZ}_{ik} = \sum_{a_{k_l}} g_{ia_k} g_{ia_{k_l}} w_{a_k a_{k_l}}. \]  

(30)

That Eqs. (28)–(30) are correct is most readily seen by using Fig. 2 and keeping in mind the conditions on the \( g_{ia} \) and the \( w_{ab} \) listed below Eq. (27).

The nonzero elements of the incidence matrix \( G \) are either +1 or −1, the sign depending on the orientation of the bonds. The same holds also for the sign of the nonvanishing off-diagonal elements of the matrix \( W \), see Eq. (15). There are only four possibilities to orient two adjacent bonds. Going through all of them Eqs. (28)–(30) simplify to

\[ A^{BZ}_{ii} = \sum a_{a_k} [w_{a_k a}], \]  

(31)

\[ A^{BZ}_{ik} = -\sum a_{a_k} [w_{a_k a}], \]  

(32)

and

\[ A^{BZ}_{ik} = [w_{a_k a_{k_l}}]. \]  

(33)

After substituting the elements \( w_{ab} \) given by Eqs. (15) and (16) into Eqs. (31)–(33) we obtain

\[ A^{BZ}_{ij} = \frac{f_i}{1 - (f_i - 1) t_i} + \sum_{j_k} \frac{(f_i - 1) t_i^2}{(f_i - 1) t_i - (f_i - 1) t_{i_k}} \]  

(34)

and

\[ A^{BZ}_{ik} = -\frac{1 - (f_i - 1)(f_i - 1) t_i t_{i_k}}{(f_i - 1)(f_i - 1) t_i - (f_i - 1) t_{i_k}}, \]  

(35)

and

\[ A^{BZ}_{ik} = \frac{t_{i_k}}{1 - (f_i - 1) t_i - (f_i - 1) t_{i_k}^2}. \]  

(36)

As noticed before, Eqs. (34)–(36) are also correct when some of beads \( i, i_k \), or \( i_{k_l} \) are peripheral; in such a case, due to the
fact that the corresponding \((f-1)\) factor vanishes, the final expression simplifies.

In the flexible limit \(\{A_i^f \to 0\}\) we recover the elements of the usual Rouse connectivity matrix: \(A_{ii}^{BZ} \to f_i = A_{ii}^R\), \(A_{ij}^{BZ} \to -1 = A_{ij}^R\), and \(A_{ik}^{BZ} \to 0 = A_{ik}^R\).

The structure of the matrix \(A^{BZ}\) is special, in that the sum of all the elements of any row (or, for that matter, any column) vanishes. It follows that one eigenvalue, say \(\lambda_1\), vanishes, \(\lambda_1 = 0\). The corresponding eigenvector is \((1,1,\ldots,1)\) and describes the translation of the whole polymer.

The nonvanishing eigenvalues of \(A^{BZ}\), namely, \(\{\lambda_2,\lambda_3,\ldots,\lambda_N\}\), are sufficient to determine many of the dynamical properties of GGS. Here we consider mechanical relaxation. For this one focuses on the response function of the harmonic strain, which is the complex shear modulus \(G'(\omega)\). Its real \(G'(\omega)\) and imaginary \(G''(\omega)\) parts are given by:

\[
G'(\omega) = \frac{v k_B T}{N} \sum_{k=2}^{N} \frac{(\omega \tau_0/2\lambda_k)^2}{1 + (\omega \tau_0/2\lambda_k)^2}
\]

and

\[
G''(\omega) = \frac{v k_B T}{N} \sum_{k=2}^{N} \frac{\omega \tau_0/2\lambda_k}{1 + (\omega \tau_0/2\lambda_k)^2},
\]

where we set \(\tau_0 = \zeta/K\), \(\zeta\) and \(K\) being as in Eq. (7). Here it is practical to use the reduced variables denoted by \([G'(\omega)]\) and \([G''(\omega)]\) and defined through

\[
[G'(\omega)] = \frac{1}{N} \sum_{k=2}^{N} \frac{(\omega \tau_0/2\lambda_k)^2}{1 + (\omega \tau_0/2\lambda_k)^2}
\]

and

\[
[G''(\omega)] = \frac{1}{N} \sum_{k=2}^{N} \frac{\omega \tau_0/2\lambda_k}{1 + (\omega \tau_0/2\lambda_k)^2}.
\]

FIG. 3. Dendrimer of generation \(g=2\) built from star polymers of functionality \(f=3\) with arm length \(n=2\).

In order to exemplify the procedure we focus here on dendrimers whose building blocks are stars (DS), see Fig. 3, which presents such a structure at generation \(g=2\) for stars with arm length \(n=2\) and functionality \(f=3\). A DS is hence a hyperbranched polymer created from a normal dendrimer by replacing its monomers by star molecules of the same functionality \(f\) and having \(n\) bonds in each arm. Thus the length of the spacers is \(2n\). To fix the ideas we focus on the functionality \(f=3\). We consider a homogeneous case, so that all beads of functionality \(f=3\) have the same stiffness parameter \(q\), with \(q \in (0,1/2)\), and all beads of functionality \(f=2\) have the stiffness parameter \(t\), with \(t \in (0,1)\). We then construct the matrix \(A^{BZ}\) using Eqs. (34)–(36). Based on it we determine its eigenvalues \(\{\lambda_k\}\) and evaluate the reduced moduli, Eqs. (39) and (40). We focus on the intermediate region of frequencies, which is most influenced by the particular structure of the network.

IV. DENDRIMERS BUILT FROM STAR POLYMERS

In order to exemplify the procedure we focus here on dendrimers whose building blocks are stars (DS), see Fig. 3, which presents such a structure at generation \(g=2\) for stars with arm length \(n=2\) and functionality \(f=3\). A DS is hence a hyperbranched polymer created from a normal dendrimer by replacing its monomers by star molecules of the same functionality \(f\) and having \(n\) bonds in each arm. Thus the length of the spacers is \(2n\). To fix the ideas we focus on the functionality \(f=3\). We consider a homogeneous case, so that all beads of functionality \(f=3\) have the same stiffness parameter \(q\), with \(q \in (0,1/2)\), and all beads of functionality \(f=2\) have the stiffness parameter \(t\), with \(t \in (0,1)\). We then construct the matrix \(A^{BZ}\) using Eqs. (34)–(36). Based on it we determine its eigenvalues \(\{\lambda_k\}\) and evaluate the reduced moduli, Eqs. (39) and (40). We focus on the intermediate region of frequencies, which is most influenced by the particular structure of the network.

Figure 4 displays the reduced loss and storage moduli for DS for different \(n\), i.e., for different spacer lengths. The stiffness parameters are taken to be \(t=0.5\) and \(q=0.3\). We start with the case of a simple dendrimer; then no scaling laws are evident in the double logarithmic plots of \([G'(\omega)]\) and \([G''(\omega)]\). Semiflexibility is apparent in \([G'(\omega)]\), where a local minimum can be seen in the region of the
maximum.\textsuperscript{21,22,27} For larger \( n \), i.e., for longer spacers, the chainlike local parts of the network lead to an incipient scaling, as was previously observed in the case of flexible DS.\textsuperscript{33,34} Typically, for stiff linear chains \([G'(\omega)]\) scales as \(\omega^{1/4}\textsuperscript{13,35}\) here we obtain a best fit to the numerical curves using the power law \(\omega^{0.29}\).\textsuperscript{29} We view the small deviation (having 0.29 instead of 0.25) as being due to the finite site of the spacers, to the rest flexibility (the stiffness parameter is \( t =0.5 \)) and to the influence of the branching points.

In Fig. 5 we show how the reduced loss and storage moduli of the DS are influenced by changes in the stiffness parameter \( t \) of the spacers. Here we keep \( q \) and \( n \) fixed by taking \( q=0.3 \) and \( n=6 \). In Fig. 5 the presence of the spacers manifests itself (as in the previous Fig. 4) by an emerging scaling law in the intermediate region. In the scaling range the slope decreases with growing stiffness from \( \omega=0.46 \) for flexible spacers (\( t=0.00 \)) to \( \omega=0.28 \) for rather stiff spacers (\( t=0.75 \)); these exponents are close to the values for flexible linear chains (given by \( \omega^{0.25} \)) and for stiff linear chains (given by \( \omega^{0.18} \)), respectively. At low frequencies the scaling regions terminate in a small shoulder, which is due to the influence of the branching points.

V. INTRODUCING STIFFNESS BASED ON THE MAXIMUM ENTROPY PRINCIPLE

A fruitful alternative method for taking semiflexibility into account is based on the maximum entropy principle (MEP).\textsuperscript{36} MEP was applied to linear chains by Winkler, Reineker and Harnau (WRH), first in a discrete\textsuperscript{28} and then in a continuous picture.\textsuperscript{16} Subsequent work has shown\textsuperscript{37} that the results obtained by MEP for chains in the continuous framework match the Lagowski–Noolandi–Nickel findings,\textsuperscript{17,38} reproducing earlier work by Bawendi and Freed.\textsuperscript{15} The equations of motion of the continuous WRH model\textsuperscript{16} are similar to even earlier results by Gotlib and Svetlov.\textsuperscript{14} In this paragraph we show for arbitrary, discrete treelike networks that the MEP concept leads to the BZ model.

We start by recalling the basic ideas of MEP, see Refs. 28 and 36. The procedure leads to a distribution function for a system of mass points under microscopic constraints. The basic quantity here is the entropy \( S \), which in a mechanical context is given by

\[
S = -k_B \int \psi([d]) \ln \psi([d]) d^{3(N-1)}[d],
\]

where the \([d]\) denote all the components of the segment vectors that build the considered network, \( k_B \) is the Boltzmann constant, \( \psi([d]) \) is the distribution function, \( (N-1) \) is the number of bonds, and \( 3(N-1) \) is the number of degrees of freedom. Since the entropy at equilibrium and under the given constraints is maximal, the distribution function can be obtained based on the variation of the Lagrange function constructed from the entropy \( S \) under the constraint of normalization,

\[
\int \psi([d]) d^{3(N-1)}[d] = 1,
\]

of restriction on the length of each bond,

\[
\langle d_i^2 \rangle = \int d_i^2 \psi([d]) d^{3(N-1)}[d] = \phi_{ii},
\]

and under additional constraints on adjacent bonds,

\[
\langle d_i \cdot d_j \rangle = \int (d_i \cdot d_j) \psi([d]) d^{3(N-1)}[d] = \phi_{ij}.
\]

On the other hand, given that the coupling of non-nearest bonds is a function of the nearest-bond couplings, no independent constraints are introduced on nonadjacent bonds. Corresponding to each constraint of the form of Eqs. (43) and (44) we have Lagrangian multipliers \( u_{aa} \) and \( u_{ab} \). The Lagrange function is therefore,

\[
\mathcal{L} = -\int \psi([d]) \left( \ln \psi([d]) + \sum_{(a,c)} u_{ac} d_i \cdot d_j \right) d^{3(N-1)}[d],
\]

where \( c \) is either \( a \) or a nearest neighbor to \( a \). One should note that in our MEP approach the Lagrangian multipliers corresponding to nonadjacent bonds are exactly zero. The constraints of Eq. (44) are symmetric, \( \phi_{ab} = \phi_{ba} \), and therefore the matrix \( U \) is also symmetric. From the variation of the Lagrange function one obtains as distribution function,
\[
\psi(d) = \frac{1}{Z} \exp \left( - \sum_{(a,c)} u_{ac} d_a \cdot d_c \right).
\]

Here \( Z \) is the partition function,

\[
Z = \int \exp \left( - \sum_{(a,c)} u_{ac} d_a \cdot d_c \right) \delta^{(N-1)}(d),
\]

in agreement with the normalization condition, Eq. (42). The multipliers can be obtained from the expectation values \( \phi_{aa} \) and \( \phi_{ab} \), Eqs. (43) and (44), which follow from differentiating Eq. (47) with respect to \( u_{aa} \) or to \( u_{ab} \),

\[
\langle d_a^2 \rangle = \phi_{aa} = - \frac{\partial \ln Z}{\partial u_{aa}}
\]

and

\[
\langle d_a \cdot d_b \rangle = \phi_{ab} = - \frac{\partial \ln Z}{\partial u_{ab}}.
\]

The partition function \( Z \) has the form of a Gaussian integral (47) and is thus readily evaluated,

\[
Z = \pi^{3M/2} (\det U)^{-3/2},
\]

where the matrix \( U \) is the symmetric matrix constructed from the Lagrangian multipliers \( u_{ab} \). Inserting Eq. (50) into Eqs. (48) and (49) gives

\[
\langle d_a \cdot d_c \rangle = \frac{3}{2} \frac{\partial \ln Z}{\partial u_{ac}} = \frac{3}{2} (U^{-1})_{ac},
\]

where \( c \) is either \( a \) or a nearest neighbor to \( a \).

Note that in the MEP method constraints are introduced only on the mean-square length of the bonds and on pairs of adjacent bonds, Eqs. (48) and (49), respectively. Using Eqs. (10) and (11) for these constraints relate Eq. (51) to Eq. (9) through

\[
\frac{3}{2} (U^{-1})_{ab} = l^2 (W^{-1})_{ab},
\]

where \( b \) is either equal to \( a \) or is a nearest neighbor of \( a \). Hence Eq. (52) holds for \( a = b \) and for adjacent \((a,b)\) pairs. We recall that in our MEP picture the constraints on nonadjacent bond pairs are not independent conditions, so that the corresponding elements of \( U \) vanish.

Now, in the Appendix we succeed in showing that for treelike networks the elements of \( U^{-1} \) for nonadjacent pairs of bonds can be related, as in Eq. (52), to the corresponding elements of \( W^{-1} \) given by Eq. (12). Hence Eq. (52) holds for all bond pairs. Therefore,

\[
\frac{3}{2} l^{-1} = l^2 W^{-1},
\]

from which

\[
U = \frac{3}{2l^2} W
\]

follows.

Equation (54) establishes, of course, that the two approaches (MEP and BZ) are very similar. For treelike networks, under the conditions just outlined, the MEP is operationally equivalent to the freely rotating chain assumption of Eq. (12). From \( U \) we can perform the bond to position transformation, Eq. (2), in order to obtain the \( A \)-forms needed for the Langevin equation,

\[
A^{\text{MEP}} = \frac{2l^2}{3} GUG^T = A^{\text{BZ}}.
\]

Thus using the MEP for semiflexible treelike networks we obtain the same set of Langevin equations as in the BZ-model. From a physical point of view the MEP is more transparent, because it doesn’t require any constraints on pairs of nonadjacent bonds, such as Eq. (12). From a technical point of view, however, it is more difficult to implement it, because Eq. (52) provides at first only an incomplete knowledge of the matrix \( U^{-1} \), and its completion requires to perform additional steps, as discussed in the Appendix.

Finally, we recall that we focused on semiflexible treelike networks, for which the procedures presented could account for all the constraints. In the presence of loops there arise additional constraints, requiring an extension of the approach. Here the MEP may turn out to be helpful.

VI. CONCLUSIONS

In this paper we studied the dynamics of semiflexible treelike networks. Extending the GGS model by taking into account the geometrical restrictions on the bonds’ orientations we succeeded in obtaining in general form the GGS potential energy both in the bond and in the position variables. The analytical structure of the corresponding matrix \( A^{\text{BZ}} \) leads to a full system of Langevin equations, which describe the dynamics of the treelike structure under consideration. Our expressions are very general, since we are able to take different restrictions at each junction (connection or branching point) into account. The results obtained allow one to consider not only treelike branched structures of any given complexity, but also to treat heterogeneous polymers with different stiffness parameters. Starting with a rather homogeneous case, we exemplified our procedure by considering the mechanical relaxation of dendrimers built from stars, in which two types of junctions (with \( f = 2 \) and with \( f = 3 \)) with distinct stiffness parameters (\( t \) and \( q \)) are present.

In addition, to stress the universality of our results, we derived them in an alternative way using the maximum entropy principle. We find it very significant that the same picture arises from both approaches, another sign of universality in the theory of polymer networks.

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APPENDIX: THE ELEMENTS OF THE U^{-1} MATRIX CORRESPONDING TO PAIRS OF NONADJACENT BONDS

In this Appendix we show that in treelike networks for each pair of nonadjacent bonds, say \( d \) and \( e \), the relation

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\frac{3}{2} l^{-1} = l^2 W^{-1},
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Equation (54) establishes, of course, that the two approaches (MEP and BZ) are very similar. For treelike networks, under the conditions just outlined, the MEP is operationally equivalent to the freely rotating chain assumption of Eq. (12). From \( U \) we can perform the bond to position transformation, Eq. (2), in order to obtain the \( A \)-forms needed for the Langevin equation,
\[ \frac{1}{2} (U^{-1})_{de} = I^2(W^{-1})_{de} \]  
(A1)

holds.

For the purposes of the proof we denote by \((d,a_2,\ldots,a_{n-1},e)\) the (unique) shortest path of bonds between \(d\) and \(e\) and also set \(d=a_1\) and \(e=a_n\). We thus have as path \((a_1,\ldots,a_n)\) with \(n \geq 3\) and assign to the corresponding vertices (beads) the numbers from 0 to \(n\), see Fig. 6. From each vertex \(i\) one can grow a subtree \(S_i\); the whole structure builds the tree \(T\). Because \(T\) does not have any loops, any pair of bonds corresponding to different subtrees \(S_i\) and \(S_j\) is nonadjacent.

We start by considering the matrix \(P\), which follows from the matrix \(U\) of \(T\) by a convenient permutation \(\Pi\) of the \(u_{ij}\) elements,

\[ P = \Pi U \Pi^{-1}. \]  
(A2)

In this way the columns and the rows of \(U\) are permuted in a symmetric way. Explicitly, we place the \(a_1,\ldots,a_n\) in the upper left corner, see Eq. (A3),

\[ P = \begin{pmatrix}
  u_{a_1a_1} & u_{a_1a_2} & 0 & \cdots & 0 & x_{a_1}^T \\
  u_{a_2a_1} & u_{a_2a_2} & u_{a_2a_3} & \cdots & 0 & x_{a_2}^T \\
  \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
  0 & 0 & \cdots & u_{a_{n-1}a_{n-2}} & u_{a_{n-1}a_{n-1}} & x_{a_{n-1}}^T \\
  0 & 0 & \cdots & 0 & u_{a_{n-2}a_{n-1}} & x_{a_{n-2}}^T \\
  x_{a_1} & x_{a_2} & \cdots & x_{a_{n-1}} & x_{a_n} & S
\end{pmatrix}. \]  
(A3)

We continue by grouping together bonds corresponding to the subtrees \(S_0, S_1, \ldots, S_{n}\). By this we obtain that the lower right corner of \(P\) takes a block-diagonal form, \(S = \text{Diag}(S_0, S_1, \ldots, S_{n})\), where each square block \(S_i\) corresponds to the subtree \(S_i\). All the other elements of the matrix \(S\) equal zero because bonds corresponding to different subtrees are nonadjacent. The dimension of the matrix \(S\) is \((N-n-1)\). Furthermore, in Eq. (A3) the \(x_{a_i}\) are column vectors with \((N-n-1)\) elements and \(x_i^T\) their transposed row vectors. Each vector \(x_{a_i}\) contains nonzero elements only at positions, which correspond to the subtrees \(S_{i-1}\) and \(S_i\) because the bond \(a_i\) is, apart from \(a_{i-1}\) and \(a_{i+1}\), adjacent only to bonds in \(S_{i-1}\) and in \(S_i\). We stop to note that since \(U\) is a symmetric matrix, so is \(P\).

Now we proceed by showing that

\[ (P^{-1})_{a_ia_n} = \frac{(P^{-1})_{a_1a_2}(P^{-1})_{a_2a_n}}{(P^{-1})_{a_1a_n}}. \]  
(A4)

Given that under the cofactor method the elements of the inverse of \(P\) are

\[ (P^{-1})_{ij} = (-1)^{i+j}/M_{ij}(\det P)^{-1}, \]  
(A5)

it is hence sufficient to show that

\[ M_{a_ia_n} = \frac{M_{a_1a_2}M_{a_2a_n}}{M_{a_1a_n}}. \]  
(A6)

In Eq. (A6) \(M_{ij}\) is the minor of \(P\), which corresponds to the element \(u_{ij} = (P)_{ij}\) and since \(P\) is symmetric so are the \(M_{ij}\).

To calculate \(M_{a_ia_n}\) we use the relation

\[ \det(\tilde{A} \tilde{B}) = \det \tilde{D} \det(\tilde{A} - \tilde{B}^{-1} \tilde{C}), \]  
(A7)

where the matrices \(\tilde{A}\) and \(\tilde{B}\) are square matrices with nonzero determinant. Given that \(M_{a_ia_{i-1}} = M_{a_{i-1}a_i}\), we calculate the minor by deleting the first row and the \((n-1)\)th column of \(P\). Calculating the determinant according to Eq. (A7) we have

\[ M_{a_ia_{n-1}} = \det S \det(\tilde{A} - \tilde{B} S^{-1} \tilde{C}). \]  
(A8)

Here the matrix \(\tilde{A}\) is given by deleting the first row and the \((n-1)\)th column in the upper left \(n \times n\) block of \(P\) and has therefore a triangular form given by:

\[ \tilde{A} = \begin{pmatrix}
  u_{a_2a_1} & u_{a_2a_2} & u_{a_2a_3} & 0 & \cdots & 0 \\
  0 & u_{a_3a_2} & u_{a_3a_3} & u_{a_3a_4} & \cdots & \vdots \\
  \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
  0 & 0 & \cdots & u_{a_{n-1}a_{n-3}} & u_{a_{n-1}a_{n-4}} & 0 \\
  0 & 0 & \cdots & 0 & u_{a_{n-1}a_{n-2}} & u_{a_{n-1}a_{n-2}} \\
  0 & 0 & \cdots & 0 & 0 & u_{a_{n-1}a_{n-2}} \\
  0 & 0 & \cdots & 0 & 0 & 0
\end{pmatrix}. \]  
(A9)

The other matrices are as follows:

\[ \tilde{B} = \begin{pmatrix}
  x_{a_2}^T \\
  \vdots \\
  x_{a_n}^T
\end{pmatrix}, \]  
(A10)

\[ \tilde{C} = (x_{a_1}, x_{a_2}, \ldots, x_{a_{n-1}}), \]  
(A11)

and because of the block-diagonal structure of \(S\),

\[ S^{-1} = \text{Diag}(S_0^{-1}, S_1^{-1}, \ldots, S_{n-1}^{-1}). \]  
(A12)

For the calculation of the product \(\tilde{B} S^{-1} \tilde{C}\) we consider first the product \(x_{a_i}^T S^{-1} x_{a_j}\), evidently for \(i+j \leq n\). Now, for \(j \geq 2\),
holds. The proof is as follows. Both the column \( x_{ai} \) as well as \( S^{-1} x_{ai} \) have nonzero elements only at positions corresponding to the subtrees \( S_{i-1} \) and \( S_{i} \). The row \( x_{ai}^T \) has nonzero elements only at positions corresponding to the subtrees \( S_{i+1} \) and \( S_{i+2} \). Therefore if \( j \geq 2 \) the product \( x_{ai}^T S^{-1} x_{aj} \) vanishes. Transposing Eq. (A13) we obtain for \( j \geq 2 \),

\[
\frac{3}{2} (U^{-1})_{de} = (d_d \cdot d_d) \cdots (d_{a_{n-1}} \cdot d_{a_{j-1}}) f^{-2(n-2)}.
\]

(A22)

where use was made of Eq. (9).

Thus, under the above mentioned specifications, Eq. (A1) holds also for nonadjacent bonds.

\[\text{Eq. (A1) holds also for nonadjacent bonds.}\]