Analytical model for the dynamics of semiflexible dendritic polymers

Florian Fürstenberg, a) Maxim Dolgushev, and Alexander Blumen

Theoretical Polymer Physics, University of Freiburg, Hermann-Heider-Str. 3, D-79104 Freiburg, Germany

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We study the dynamics of semiflexible dendritic polymers following the method of Dolgushev and Blumen [J. Chem. Phys. 131, 044905 (2009)]. The scheme allows to formulate in analytical form the corresponding Langevin equations. We determine the eigenvalues by first block-diagonalizing the problem, which allows to treat even very large dendritic objects. A basic ingredient of the procedure is the observation that a set of eigenmodes in the semiflexible case is similar to that chosen by Cai and Chen [Macromolecules 30, 5104 (1997)] for fully flexible dendritic structures. Varying the flexibility of the macromolecules allows us to better understand their mechanical loss moduli $G''(\omega)$ based on their eigenvalue spectra. We present the $G''(\omega)$ for a series of stiffness parameters and for different functionalities of the branching points. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.3703757]

I. INTRODUCTION

Recently, much progress has been achieved in including semiflexibility into Rouse-type approaches, the latter being typical for completely flexible bead and spring models. Now, the usual Rouse-type models are Gaussian and generalized Gaussian schemes (GGS) allow to qualitatively understand, in a rigorous analytic-mathematical way, many static and dynamic properties of flexible, complex polymer structures. Evidently, GGS disregard the excluded volume, the finite extensibility of the bonds, and the angular restrictions present in macromolecules; the challenge is thus to include in the GGS some of these aspects, while keeping the overall procedure still mathematically manageable.

In this direction the inclusion of semiflexibility into the GGS has met with success, first for polymer chains and then, more recently, for arbitrary treelike structures. The basic idea here is to take semiflexibility into account through restrictions on the orientations of neighboring bonds. Here a problem arises, which, however, turns out to be readily dealt with: By introducing conditions on the orientations of neighboring bonds it turns out that other than nearest-neighbor bonds are in turn restricted in their orientations. However, this does not lead to an uncontrolled increase in the number of parameters: As we have shown, both the assumptions of freely rotating segments as well as independent maximal entropy considerations lead to the same relations between the parameters involved; the problem is fully determined by knowing the restrictions on the nearest-neighbor bonds alone.

Introducing semiflexibility into the GGS has its price, however; this consists in the appearance of additional terms in the dynamical matrix (DM) as compared to the fully flexible situation. In the picture of Refs. 1 and 2 the non-vanishing elements include, besides the diagonal terms and terms related to neighboring beads, also terms corresponding to next-nearest neighbor beads. This may appear somewhat problematic in the mathematical-analytical sense, by possibly limiting the number of structures for which the eigenvalues of the corresponding Laplacian can be determined by simpler methods than a brute-force, numerical diagonalization of the complete dynamical matrix, the latter being restricted to not-too-large objects.

Remarkably, however, highly symmetrical structures such as dendritic molecules (for simplicity we will focus here on the topology of dendrimers) turn out to have complete sets of eigenvectors whose structure is practically identical in the totally flexible and in semiflexible cases. We first discovered this feature based on numerical investigations. Then, by noticing particular relations between the eigenvalues and also symmetries in their degeneracies and after convincing ourselves (based on a large number of special cases and by evaluating numerically for given stiffness parameters the eigenvalues of all $f = 3$ dendrimers up to generation $g = 10$ and testwise for $f = 4$ and $f = 5$ dendrimers) that this feature is always fulfilled, we also succeeded in proving it analytically, in general form. This proof is one of the central results of this paper; to show it requires, however, a careful, somewhat formal development. Of course, the methods used here may be applicable to other polymer structures, fact which may pave the way for general mathematical-analytical studies of semiflexible behavior in macromolecules.

The paper is structured as follows: in Sec. II we first recall ways to take the semiflexibility of treelike polymers into account and then in Sec. III we display the elements of the dynamical matrix needed to model semiflexible dendritic molecules (SD). In Sec. IV we recall that a hierarchical procedure leads for fully flexible dendritic molecules (FD) to a particular, complete set of eigenvectors. As we proceed to show in Sec. V, the symmetries of this FD eigenvector set carry over also to SD; we use this knowledge to formulate a highly compact set of equations for the determination of the eigenvalues of SD of arbitrary functionality $f$ and generation $g$. In Sec. VI we discuss the resulting eigenvalue spectra for different stiffness parameters: As an application we also report the

a)florian.fuerstenberg@physik.uni-freiburg.de.
loss moduli obtained using these spectra. Section VII closes with our conclusions, whereas the proof that all eigenvalues obtained in this way are physically reasonable (i.e., real) is relegated to the Appendix.

II. THE MODEL

In this section we recall the model\(^2\) for semiflexible treelike polymers (STPs), on which this work is based. The STP-model allows to account for the semiflexibility in the GGS.\(^5\) The latter extends the Rouse model for linear polymer chains to arbitrary architectures, where the polymer structures are represented by beads located at \(r_i\) (\(i = 1, \ldots, N\)) connected by springs (bonds), say \(d_{ab} = r_i - r_j\). In the simplest case the potential \(V_{\text{GGS}}\) between the GGS beads is purely harmonic, so that it is diagonal in the bonds’ variables,

\[
V_{\text{GGS}}(d_{ab}) = \frac{K}{2} \sum_{a,b} d_{ab}^2. \tag{1}
\]

Here \(K = 3 k_B T l^2\) denotes the spring constant, \(l^2\) is the mean-square length of each bond, \(k_B\) is the Boltzmann constant, and the sum runs over all bonds. Hence, from Eq. (1) follows\(^2\) that any two distinct bonds, say \(a\) and \(b\) (\(a \neq b\)), are uncorrelated, \(\langle d_{ab} \cdot d_{ab} \rangle_{\text{GGS}} = 0\), where the average is taken with respect to the Boltzmann distribution \(\exp(-V_{\text{GGS}}/k_B T)\). However, in reality the orientation of neighboring bonds is not arbitrary. As shown in Ref. 2, one may account for it by using the generalized potential

\[
V_{\text{STP}}(d_{ab}) = \frac{K}{2} \sum_{a,b} W_{ab} d_{ab} \cdot d_{ab}, \tag{2}
\]

which leads to non-zero correlations, \(\langle d_{ab} \cdot d_{ab} \rangle_{\text{STP}} = l^2(W^{-1})_{ab}\), where the average is taken with respect to the Boltzmann distribution, \(\exp(-V_{\text{STP}}/k_B T)\). Now, the matrix \(W\) turns out to be sparse under the following physically plausible conditions:\(^2\) (1) The average bond lengths are fixed \(\langle d_{ab} \cdot d_{ab} \rangle = l^2\). (2) Adjacent bonds, say \(a\) and \(b\), fulfill \(\langle d_{ab} \cdot d_{ab} \rangle = \pm l^2 q_i\), where \(q_i\) denotes the stiffness parameter related to bead \(i\) which is common to both \(a\) and \(b\), and the sign is plus for head-to-tail orientations of \(a\) and \(b\) and minus otherwise. (3) For non-adjacent bonds \(a\) and \(c\), connected through the minimal path \((b_1, \ldots, b_k)\) one has \(\langle d_{ac} \cdot d_{ac} \rangle = \langle d_{ab_1} \cdot d_{ab_1} \rangle \cdot \langle d_{b_1 \cdot b_2} \rangle \cdots \langle d_{b_{k-1} \cdot b_k} \rangle l^{-2(k-1)}\) (the freely rotating condition). The explicit form of the elements of \(W\), which follow from these conditions, is given in Refs. 1 and 2; the same expressions follow from the maximum entropy principle.\(^2\)

The matrix \(W\) is fundamental in describing the dynamics of STP. One may see this by recalling the Langevin equations for the beads’ positions \(r_i = \{x_i, y_i, z_i\}\).\(^4,5\) The Langevin equation, say for the \(x\)-component of the position vector \(r_i\), is given by\(^2\),\(^4,5\)

\[
\zeta \frac{\partial}{\partial t} x_i(t) + \frac{\partial}{\partial x_i} V_{\text{STP}}(\{r_k\}) = f_i(t). \tag{3}
\]

Here \(f_i\) is the \(x\)-component of the usual Gaussian force acting on the \(i\)th bead, for which \(\langle f_i(t) \rangle = 0\) and \(\langle f_i(t) f_j(t') \rangle = 2 k_B T \zeta \delta_{ij} \delta(t - t')\) hold. The transformation from the bonds’ to the positions’ variables, \(d_{ij} = r_i - r_j\), can be written in terms of the incidence matrix \(G\) (Ref. 15)

\[
d_{ij} = \sum_k (G^T)_{ik} r_k. \tag{4}
\]

Substitution of Eq. (4) into Eq. (2) gives

\[
V_{\text{STP}}(\{r_i\}) = \frac{K}{2} \sum_{k,a} (G G S)^T_{ki} r_k \cdot r_a. \tag{5}
\]

This allows to introduce the matrix \(A_{\text{STP}} = G G S^T\). Thus, from Eqs. (3) and (5) it follows:

\[
t_0 \frac{\partial}{\partial t} x_i(t) + \sum_{j=1}^N A_{ij}^{\text{STP}} x_j(t) = f_i(t)/K, \quad \forall i, \tag{6}
\]

where we introduce \(t_0 = \zeta/k_B\). The set of Langevin equations, Eq. (6), can be solved by diagonalizing the matrix \(A_{\text{STP}}\). Now, the elements of \(A_{\text{STP}}\) are known in closed form.\(^2\) To visualize the situation we display in Fig. 1 the neighborhood of a bead \(i\) of a treelike network, where we denote the nearest neighbors (NN) of the \(i\)th bead by \(i_k\) (one index) and the next-nearest neighbors (NNN) of \(i\) (NN of \(i_k\) but \(i\)) by \(i_{k+}\) (two indices). For these elements of \(A_{\text{STP}}\) read:

\[
A_{ii}^{\text{STP}} = \frac{f_i}{1 - (f_i - 1)q_i} + \sum_{i_k} \frac{(f_{i_{k+}} - 1)q_{i_{k+}}}{1 - (f_{i_{k+}} - 1)q_{i_{k+}}}, \tag{7}
\]

\[
A_{ii}^{\text{STP}} = -\frac{1 - (f_i - 1)(f_{i_{k+}} - 1)q_{i_{k+}}}{(1 - (f_i - 1)q_i)(1 - (f_{i_{k+}} - 1)q_{i_{k+}})}, \tag{8}
\]

FIG. 1. Nearest- and next-nearest neighborhood of a bead \(i\) of a treelike network. Here we denote one nearest neighbor of \(i\) by \(i_k\) and one of its next-nearest neighbors by \(i_{k+}\).
and
\[ A^\text{STP}_{iik} = \frac{q_i}{1 - (f_i - 2)q_i - (f_i - 1)q_i'}. \]

whereas all other elements of \( A^\text{STP} \) vanish. In Eqs. (7)–(9) the functionalities and stiffness parameters of the junctions \( i \) and \( i_k \) are \( f_i \) and \( f_{i_k} \) and \( q_i \) and \( q_{i_k} \), respectively.

A special case of Eqs. (7)–(9) is the fully flexible network, for which all \( q_i \) and \( q_{i_k} \) vanish. In this limiting case \( A^\text{STP}_{ii} \rightarrow f_i \), \( A^\text{STP}_{iik} \rightarrow -1 \), and \( A^\text{STP}_{iik} \rightarrow 0 \), by which one recovers the normal GGS Laplacian matrix \( A^{\text{GGS}} \). \( A^{\text{GGS}} \) has less non-vanishing terms than the general \( A^\text{STP} \) and is thus simpler, given that the only non-vanishing terms of \( A^{\text{GGS}} \) are of the form \( A^{\text{GGS}}_{ii} \) and \( A^{\text{GGS}}_{iik} \):

\[ A^{\text{GGS}}_{ii} = f_i, \]
\[ A^{\text{GGS}}_{ij} = \begin{cases} -1 & \text{if } i \text{ and } j \text{ are NN}, \\ 0 & \text{else}. \end{cases} \]

Now, the eigenvalues \( \{\lambda_k\} \) of \( A^\text{STP} \) are fundamental for determining the relaxation patterns of polymeric structures. Thus, the mechanical response function is the so-called complex shear modulus \( G'(\omega) = G'(\omega) + iG''(\omega) \), where \( G'(\omega) \) and \( G''(\omega) \) are the storage and loss moduli, respectively. Dividing them by \( v_k R \) one is led to reduced variables, which can be calculated also for STP based on the eigenvalue spectrum \( \{\lambda_k\} \) only. One has namely,

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

and

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

In Eqs. (12) and (13) the sum runs over the non-vanishing eigenvalues \( \{\lambda_k\} \) of the matrix \( A^\text{STP} \).

III. ANALYSIS OF \( A^\text{STP} \) FOR SD

The scheme presented in Sec. II allows one to treat different treelike structures with arbitrary topologies, even for arbitrary choices of the stiffness values of particular junctions. This was demonstrated in former works, where homogeneous and heterogeneous structures were investigated, such as linear chains and stars and SD. For this one has to determine all the eigenvalues \( \{\lambda_k\} \) of the particular \( A^\text{STP} \), a requirement which can be met in general only by a fully numerical diagonalization of the matrix \( A^\text{STP} \), which then limits the number of beads \( N \) that can be taken into account to a few thousand. For theoretical reasons and in order to find out universal features of the polymeric structures investigated, it is desirable to have results for much larger \( N \) values, so that at least part of the diagonalization procedure should be performed analytically, say by block-diagonalizing \( A^\text{STP} \) for particular structures. Interestingly, also SD allow a block-diagonalization of their \( A^\text{STP} \), as we show in detail in Sec. V.

In Fig. 2 we recall the topology of dendrimers: The construction starts with a central bead to which \( f \) beads (in Fig. 2, \( f = 3 \)) are attached, thus creating a dendrimer of generation \( g = 1 \). The procedure can be continued: To each of the peripheral beads one then attaches \((f-1)\) new beads, obtaining a dendrimer of generation \( g = 2 \). The procedure is then iterated up to generation \( g \). Fig. 2 displays the dendrimer of generation \( g = 3 \). In the GGS the beads of Fig. 2 are connected by infinitely extensible springs, whose orientations are uncorrelated. The situation described by the GGS is certainly not that of dendrimers in the narrow sense, whose monomers are connected by quite stiff, covalent bonds, with relatively well-defined orientations. To realistically describe such objects one has to put up with strong local restrictions, and such semiflexible schemes as considered here cannot do them full justice. Our semiflexible scheme is better justified in treating dendritic polymers with linear spacers between their branching points, such as given in Ref. 21. For these polymers the topological picture given in Fig. 2 also holds when coarse-graining each spacer into a bond.

We now turn to the consideration of SD. For these all internal beads have functionality \( f \), whereas the peripheral beads have unit functionality. In the following we assume a homogeneous situation, in which the stiffness value \( q \) of all the junctions is the same. Based on the general results for \( A^\text{STP} \), Eqs. (7)–(9), it is now a simple matter to write down the elements of the matrix \( A^\text{SD} = (A^\text{STP})^g \) for SD. In this way one can envisage four different situations for the diagonal elements \( A^\text{SD}_{ii} \), which we also depict in Fig. 3:
FIG. 3. Schematic drawing of the non-vanishing matrix elements of $A^{SD}$. Here the peripheral beads are indicated by full circles and the inner beads (not drawn) are located at the branching points. The open circles denote the beads for which the diagonal elements take particular $\mu$-values; the wavy lines indicate the non-diagonal terms as interactions: $v_1$ and $v_2$ for NN, $\rho$ for NNN beads.

1. If $i$ is a peripheral bead then $f_i = 1$. Furthermore, $i$ is then connected via a single neighbor with functionality $f$ to the SD. Thus, from Eq. (7) the value of $A^{SD}_{ii}$ follows (we denote it by $\mu_1$)

$$\mu_1 \equiv 1 + \frac{(f - 1)q^2}{1 - (f - 2)q - (f - 1)q^2}. \quad (14)$$

2. In a $g = 1$ dendrimer the central bead $c$ has as neighbors only peripheral beads. From Eq. (7) $A^{SD}_{ic}$ equals then, in similar fashion

$$\mu_2 \equiv \frac{f}{1 - (f - 1)q}. \quad (15)$$

3. For dendrimers with $g > 1$, a bead $j$ in the neighborhood of a peripheral bead has $(f - 1)$ peripheral beads as neighbors and one additional neighbor with functionality $f$. Again, based on Eq. (7), $A^{SD}_{jj}$ equals

$$\mu_3 \equiv \frac{f}{1 - (f - 1)q} + \frac{(f - 1)q^2}{1 - (f - 2)q - (f - 1)q^2}. \quad (16)$$

4. Finally, bead $m$ may be well inside the dendrimer, in which case all its $f$ neighbors have the functionality $f$. Then from Eq. (7) $A^{SD}_{mm}$ equals

$$\mu_4 \equiv \frac{f}{1 - (f - 1)q} + \frac{f}{1 - (f - 2)q - (f - 1)q^2}. \quad (17)$$

We consider now the non-diagonal elements of $A^{SD}$ and depict these also in Fig. 3. For NN $A^{SD}_{ii}$ can take the following values:

1. If either $i$ or $i_2$ is a peripheral bead, we have from Eq. (8) that $A^{SD}_{ii_2}$ equals

$$v_1 \equiv -\frac{1}{1 - (f - 1)q}. \quad (18)$$

2. Otherwise, both beads have functionality $f$, so that $A^{SD}_{ii_2}$ turns out to be

$$v_2 \equiv -\frac{1 + (f - 1)q}{1 - (f - 1)q}. \quad (19)$$

Finally, one readily convinces oneself that each non-diagonal term $A^{SD}_{ii_2}$ requires that the bead $i_k$ intermediate between the beads $i$ and $i_2$ has functionality $f$, see Fig. 1. Thus, it follows from Eq. (9) that $A^{SD}_{ii_k}$ can take only one single value, namely,

$$\rho \equiv \frac{q}{1 - (f - 2)q - (f - 1)q^2}. \quad (20)$$

All other non-diagonal elements of the matrix $A^{SD}$ are zero.

IV. EIGENMODES OF FD

In this section we recall the structure of a particular, complete set of eigenmodes of the $A^{GGS}$-matrix for FD. For practical reasons we introduce here the notion of a subwedge. Subwedges are parts of the dendritic structure, as exemplarily depicted in Fig. 4; in fact their central bead (called root) has functionality $(f - 1)$. This distinguishes the subwedge from a dendritic structure, whose central bead (the core) has functionality $f$.

The procedure we will focus on was introduced in Ref. 26 and also used in other works, in which fully flexible dendritic subwedges and heterogeneous FD were analyzed. There it was possible, using a particular, complete set of eigenmodes $\mathbf{x}$ to block-diagonalize the linear system of equations corresponding to $A^{GGS}$. This simplified very much
the determination of the eigenvalues of $A^{GGS}$ together with their degeneracies.

As we will show in Sec. V, the same procedure holds also for the matrix $A^{SD}$. Furthermore, the advantage of the procedure is that it is very transparent: In it most of the eigenmodes have many vanishing entries, which facilitates an intuitive picture: Based on it one can readily see that the eigenmodes are linearly independent and one can easily determine the degeneracies of the related eigenvalues, as we proceed to show.

Starting point of the hierarchical procedure is the observation that one can choose the eigenvectors of a FD of generation $g$ in the following way: The first group consists of eigenvectors in which only peripheral beads (i.e., beads of the highest generation $g$) can move; in the second group only the peripheral beads and their nearest neighbors (generations $g$ and $(g-1)$) move, and so on. Finally, in group $(g+1)$, all beads of the FD, including the core of the FD move.

With this the hierarchical procedure is as follows: The eigenvectors of the first group are such that for them only two NNN peripheral beads move against each other, see Fig. 5, which depicts such an eigenmode. We denote its eigenvalue by $\lambda^{(1)}$. Now, for $f > 3$ such a motion can involve any two beads of a subwedge of generation $g = 2$. (Here Fig. 5 is slightly atypical, since for it $f = 3$.) Since each $g = 2$ subwedge has $(f-1)$ peripheral beads, this gives rise to $(f-2)$ different, linearly independent eigenmodes of the subwedge. Given that the number of $g = 2$ subwedges is $f(f-2)$, the first group of eigenvectors contains $f(f-2)(f-3)(f-2)$ elements. It follows that $\lambda^{(1)}$ is $f(f-1)(f-2)^2$-fold degenerate.

In the second group of eigenvectors two $g = 2$ subwedges move against each other, while all other beads are immobile, see Fig. 6. Because of symmetry, in each subwedge beads belonging to the same generation have the same amplitude; this amplitude is opposite to that of the beads of the same generation in the other subwedge. Here there appear two distinct eigenvalues, $\lambda^{(2)}_1$ and $\lambda^{(2)}_2$, which are, following a discussion similar to that above, $f(f-1)(f-2)^2$-fold degenerate.

Continuing the procedure, we reach the $g$th group of eigenvectors in which only peripheral beads of the FD are moving. Here all beads within the same generation have the same amplitude.

Finally, in the $(g+1)$th group, all beads (including the core of the FD) are moving. Hence the number of degrees of freedom is $(g+1)$, which leads to $(g+1)$ non-degenerate eigenvalues $\lambda^{(g+1)}_1, \ldots, \lambda^{(g+1)}_{g+1}$.

It is now a simple matter to verify that the set of these eigenmodes is complete: One has only to show that their number is equal to $N$, the number of beads of the FD. The number of these eigenmodes is

$$f(f-2) \sum_{i=1}^{g-1} i(f-1)^{g-1-i} + g(f-1) + (g+1)$$

$$= f(f-1)^{g-2} - \frac{g}{f-2},$$

where the right-hand-side of Eq. (21) equals $N$, the total number of beads of a FD of functionality $f$ and generation $g$. One verifies Eq. (21) readily, e.g., by noticing that the sum in it is the derivative of a finite geometrical series.

V. EIGENMODES OF SD

In this section we show that the hierarchical procedure introduced in Sec. IV is also applicable to SD. This reduces drastically the computation effort for the determination of the eigenvalues of $A^{SD}$ and highlights fundamental features of the SD dynamics.
Here it pays to stop and understand why the procedure of Sec. IV works for FD: In these the interactions $A_{ij}^{GGS}$ involve only NN-beads, see Eq. (11). Now, the linear homogeneous equations to be fulfilled read:

$$
\tau_0 \dot{x}_i + \sum_{j=1}^{N} A_{ij} x_j = 0, \quad \forall i, \quad (22)
$$

where $A$ stand for $A^{GGS}$ now.

The choice of eigenmodes in Sec. IV is, given Eq. (11), fully compatible with Eq. (22): The bead $k$ connecting the two subwedges moving in opposite directions is at rest ($x_k = 0$), since from its NN two move in opposite directions with the same amplitude (by which their terms in Eq. (22) cancel each other) and the other NN are at rest. Moreover, having $x_k = 0$ is (because in $A^{GGS}$ only NN-interactions are active) sufficient to allow all the beads outside the two moving subwedges to be at rest.

However, here we investigate SD and for them the interactions extend to NNN-beads, see Eqs. (14)–(20) and Fig. 3. This fact may let one doubt whether the procedure highlighted in Sec. IV is still applicable, particularly since in Eq. (22) the values of the non-diagonal $A_{ij}^{SD}$ are not anymore equal to ($-1$), but differ among themselves. A careful consideration of, say, Figs. 5–7 reveals that also here the choice of eigenmodes in Sec. IV is compatible with Eq. (22), in which $A$ now stands for $A^{SD}$. As before, the bead $k$ connecting the two subwedges moving in opposite directions is at rest ($x_k = 0$): Due to the very high symmetry of the dendritic structure, the contributions to the sum for $x_k$ of Eq. (22) of the moving NN and NNN of bead $k$ cancel each other. The same happens also for the NN of $k$ which are at rest: The contributions to their respective sums in Eq. (22) of the moving NN of $k$ also cancel. This is now sufficient to allow all the beads outside the two moving subwedges to be at rest.

We now focus on the hierarchical procedure and number the amplitudes of the beads in a moving branch of the SD generationwise from the periphery towards the core. In this way we follow the different groups of eigenmodes. To readily derive the equations which follow we found it helpful to use Fig. 3 together with, say, Figs. 5–7.

We recall that in the first group of eigenmodes two NNN peripheral beads are moving oppositely to each other, see Fig. 5. This means that $x_2 = x_3 = \cdots = x_{g+1} = 0$. For bead $1$ the diagonal element is $\mu_1$ and it interacts with the other moving bead via $\rho$. For this group of eigenmodes the set, Eq. (22), reduces to one equation of motion, namely to

$$
-\tau_0 \dot{x}_1 = \mu_1 x_1 - \rho x_1 = (\mu_1 - \rho) x_1. \quad (23)
$$

One can readily verify that the eigenvalue $\lambda^{(1)} = \mu_1 - \rho$ related to this motion equals $l/(1 + q)$ when the time is measured in units of $\tau_0$.

The second group of eigenvectors is characterized by $x_3 = \cdots = x_{g+1} = 0$ (we assume that $g \geq 2$). With help of Fig. 6 together with Fig. 3 one determines now readily that $x_1$ and $x_2$ must obey the following system of equations of motion:

$$
\begin{align*}
-\tau_0 \dot{x}_1 &= \mu_1 x_1 + v_1 x_2 + (f - 2) \rho x_1 \\
-\tau_0 \dot{x}_2 &= \mu_3 x_2 + (f - 1) v_1 x_1 - \rho x_2. \quad (24)
\end{align*}
$$

Determining the eigenvalues of this system of equations is, in standard fashion, equivalent to solving the eigenvalue problem of its coefficient matrix, i.e.,

$$
A_2 = \begin{pmatrix}
\mu_1 + (f - 2) \rho & v_1 \\
(f - 1)v_1 & \mu_3 + (f - 2) \rho \\
(f - 1)^2 \rho & (f - 1)v_2 \\
(f - 1)^2 \rho & (f - 1)^2 \rho
\end{pmatrix}. \quad (25)
$$

From a mathematical point of view one may wonder whether the eigenvalues of $A_2$ are real (the physical problem admits only real eigenvalues). This is indeed the case and we will prove this fact in general form (also for the following matrices) in the Appendix.

Considering now the third and the fourth groups of eigenvectors (assuming $g \geq 3$ and $g \geq 4$, respectively) one is led to the following matrices:

$$
A_3 = \begin{pmatrix}
\mu_1 + (f - 2) \rho & v_1 & \rho \\
(f - 1)v_1 & \mu_3 + (f - 2) \rho & v_2 \\
(f - 1)^2 \rho & (f - 1)v_2 & \mu_4 - \rho
\end{pmatrix}. \quad (26)
$$

$$
A_4 = \begin{pmatrix}
\mu_1 + (f - 2) \rho & v_1 & \rho & 0 \\
(f - 1)v_1 & \mu_3 + (f - 2) \rho & v_2 & \rho \\
(f - 1)^2 \rho & (f - 1)v_2 & \mu_4 + (f - 2) \rho & v_2 \\
0 & (f - 1)^2 \rho & (f - 1)^2 \rho & \mu_4 - \rho
\end{pmatrix}. \quad (27)
$$

The matrix for the fifth and for higher groups of eigenvectors, in which two subwedges move against each other, can be given in general form. The matrix $A_n$ is a $n \times n$ matrix ($n = 5, \ldots, g$) and it reads

FIG. 7. Example of a movement corresponding to the third group of eigenmodes: two subwedges of third generation move against each other.
Until now, the core of the SD was immobile. Finally, in the \((g + 1)\)th group of eigenvectors the core is also mobile. Moreover, now all beads can move and all beads within the same generation move in the same manner. We follow now the corresponding system of equations as a function of the increasing size of the SD.

For a SD of generation one there are only two kind of beads, the peripheral beads and the core itself. Thus, we have the following equations of motions:

\[
\begin{aligned}
-\tau_0 \dot{x}_1 &= \mu_1 x_1 + v_1 x_2 + (f - 1)\rho x_1 \\
-\tau_0 \dot{x}_2 &= \mu_2 x_2 + f x_1,
\end{aligned}
\]  

(29)

for which the corresponding matrix is

\[
B_1 = \begin{pmatrix}
\mu_1 + (f - 1)\rho & v_1 \\
f v_1 & \mu_2
\end{pmatrix}.
\]

(30)

In the same way, the matrices of SD of generations two and three are

\[
B_2 = \begin{pmatrix}
\mu_1 + (f - 2)\rho & v_1 & \rho \\
(f - 1)v_1 & \mu_3 + (f - 2)\rho & v_2 \\
f (f - 1)\rho & f v_2 & \mu_4
\end{pmatrix},
\]

(31)

and

\[
B_3 = \begin{pmatrix}
\mu_1 + (f - 2)\rho & v_1 & \rho & 0 \\
(f - 1)v_1 & \mu_3 + (f - 2)\rho & v_2 & \rho \\
(f - 1)\rho & (f - 1)v_2 & \mu_4 + (f - 1)\rho & v_2 \\
0 & f (f - 1)\rho & f v_2 & \mu_4
\end{pmatrix}.
\]

(32)

The matrices for \(g \geq 4\) can be expressed in a general way. One has namely for \(B_n\) \((n = 4, \ldots, g)\), where \(B_n\) is a \((n + 1) \times (n + 1)\) matrix:

\[
B_n = \begin{pmatrix}
\mu_1 + (f - 2)\rho & v_1 & \rho & 0 & \cdots & 0 \\
(f - 1)v_1 & \mu_3 + (f - 2)\rho & v_2 & \rho & 0 & \cdots \\
(f - 1)\rho & (f - 1)v_2 & \mu_4 + (f - 2)\rho & v_2 & \rho & 0 & \cdots \\
0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
\cdots & 0 & (f - 1)\rho & (f - 1)v_2 & \mu_4 + (f - 2)\rho & v_2 & \rho \\
\cdots & 0 & (f - 1)\rho & (f - 1)v_2 & \mu_4 + (f - 1)\rho & v_2 & \rho \\
0 & \cdots & 0 & f (f - 1)\rho & f v_2 & \mu_4 & \mu_4
\end{pmatrix}.
\]

(33)
Here one should recall that $B_g$ is the $(g + 1) \times (g + 1)$ matrix which determines the eigenfrequencies of the $(g + 1)$th group of eigenvectors.

Due to the inclusion of the core, $B_n$ differs structurally from $A_n$ mainly by the appearance of a new row and a new column; one may also notice that the core possesses $f$ NN in the next generation instead of the $(f - 1)$ NN for the root of a subwedge.

Equations (23)–(33) include the FD in the fully flexible limit $q \to 0$. In particular, in this limit $\rho = 0$ holds and the matrices given by Eqs. (25)–(33) get to be tridiagonal. In this case the eigenvalue problem can be reformulated in terms of recurrent trigonometric or hyperbolic relations, see Refs. 9 and 26.

The system of the $A$ and $B$ matrices is extremely valuable in determining the eigenvalues of $A^{SD}$. We recall (as just pointed out in Sec. IV) that a dendritic structure of functionality $f$ and generation $g$ is composed of $N = [f(f - 1)^g - 2f(f - 2)]$ beads. Thus, $N$ grows exponentially with $g$, fact which quickly limits any attempts to numerically diagonalize the corresponding $A^{SD}$-matrix. Now, using the procedure of Sec. IV we succeeded here to block-diagonalize $A^{SD}$ in terms of $(g + 1)$ distinct sparse matrices of maximal size $(g + 1)$. In this way we can, for arbitrary $f$ and $g$, evaluate very precisely the eigenvalues of $A^{SD}$. Furthermore, as discussed in Sec. IV, the degeneracies of the eigenvalues are also known exactly.

Another advantage of the procedure appears when studying a series of SD with growing generation. One realizes readily that in going from generation $g$ to generation $(g + 1)$ only the eigenvalues of two new matrices, namely of $A_{g+1}$ and $B_{g+1}$, have to be determined, since the matrices $A_1, \ldots, A_g$ stay unchanged.

VI. DISCUSSION

The procedure established in Sec. V allows us now to determine the eigenvalue spectrum of very large SD. Here we study SD of generation $g = 10$ with functionality $f = 3$ and $f = 4$. Based on their spectra we evaluate then, using Eq. (13), the reduced loss moduli $[G''(\omega)]$ related to mechanical relaxation. Here we focus only on $[G''(\omega)]$, given that the loss moduli display a richer structure than the storage moduli.16

In Fig. 8 we present the eigenvalue spectra for SD of generation $g = 10$ as a function of the stiffness parameter $q$. Each curve shows the eigenvalues in ascending order. Given that the difference between the smallest and the largest eigenvalue is huge, we found it convenient to plot the spectra in semilogarithmic scales. The upper part of Fig. 8 displays the situation for $f = 3$, the lower part for $f = 4$, and $q$ is as indicated in the figure.

The first observation is, in both cases, the broadening of the spectra with increasing $q$: With growing stiffness the largest eigenvalues increase, whereas the smallest eigenvalues decrease.

Consider now the eigenvalue $\lambda^{(1)}$ (here we use the notation of Sec. IV), which follows from Eq. (23), $\lambda^{(1)} = 1/(1 + q)$. This eigenvalue has the highest degeneracy and is situated in the intermediate part of the spectra. As one readily sees from Fig. 8, with growing $f$ the region of this eigenvalue in the spectrum is growing. The reason is that its degeneracy is growing with $f$. Indeed, using the results of Sec. IV, we obtain that for large $g$ the eigenvalue $\lambda^{(1)}$ occupies approximately the $[(f - 2)^2/(f - 1)^2]$th part of the spectrum, which part is equal to $1/4 = 0.25$ for $f = 3$ and to $4/9 \approx 0.44$ for $f = 4$. For less degenerate eigenvalues the situation is less dramatic: For large $g$, the eigenvalue $\lambda^{(i)}$ (again using the notation of Sec. IV, $i < g$, $j = 1, \ldots, i$) occupies approximately the $[(f - 2)^2/(f - 1)^{i+1}]$th part of the spectrum. This corresponds for each of the $\lambda^{(1)}_1$, $\lambda^{(1)}_2$, and $\lambda^{(1)}_3$ eigenvalues to $1/8 \approx 0.125$ and $1/16 = 0.0625$ for $f = 3$ and to $4/27 \approx 0.148$ and $4/81 \approx 0.0494$ for $f = 4$, respectively.

Now, with these eigenvalues and based on Eq. (13) we are able to calculate the reduced loss moduli $[G''(\omega)]$. As a function of $q$ we show in Fig. 9 $[G''(\omega)]$ for SD with $g = 10$. The upper and lower parts of Fig. 9 display the findings for $f = 3$ and for $f = 4$, respectively. Here one should recall the universal behavior of such $[G''(\omega)]$-curves: One always has at small frequencies $[G''(\omega)] \sim \omega$, whereas for large frequencies $[G''(\omega)] \sim \omega^{-1}$ holds.5 Hence, the particular structure of the SD is recognizable only in the intermediate $\omega$-region. As an example, the regions of small and large frequencies are clearly evident in Fig. 9. Moreover, from Fig. 9 one sees that the $[G''(\omega)]$ do not scale in the intermediate region, i.e., in double-logarithmic plots they are not nearly straight lines for
FIG. 9. Reduced loss moduli \([G''(\omega)]\) for dendritic polymers of functionality \(f = 3\) (upper part) or \(f = 4\) (lower part), based on the spectra of Fig. 8.

SD; scaling behavior is, on the other hand, the rule for linear chains and for fractals.\(^{28-31}\) In fact, for FD the corresponding curves in the region of intermediate frequencies can be approximated through logarithmic forms.\(^8\) The broadening of the spectra with growing \(q\), as discussed above, manifests itself through a broadening of the \([G''(\omega)]\)-shapes. This feature was observed earlier in the study of a whole series of semiflexible polymers.\(^1\)

In both parts of Fig. 9 the \([G''(\omega)]\) widen more towards the domain of large frequencies. Furthermore, with growing \(q\), the \([G''(\omega)]\)-curves start displaying a local minimum. The reason for it can be traced back to the eigenvalues, as given in Fig. 8. Namely, in Fig. 8 one observes at the right of the \(\lambda^{(1)}\) range a clear step in both spectra, whose height increases with \(q\). In each case this leads to a (pseudo)-gap in the eigenvalue spectrum for intermediate frequencies and to a local minimum of \([G''(\omega)]\) in the same region.\(^{16,22,23}\) Moreover, there appear differences in the \([G''(\omega)]\), depending on the functionality. Namely, for quite stiff SD the heights of the local maxima depend on \(f\); while for \(f = 3\) the two maxima of \([G''(\omega)]\) have approximately the same height, for \(f = 4\) the left maximum of \([G''(\omega)]\) is somewhat higher than the right one. Finally, the left side of \([G''(\omega)]\) is more bent for \(f = 3\) than for \(f = 4\). This is due to the fact that \(\lambda^{(1)}\) plays a more important role for \(f = 4\) than for \(f = 3\), which means that a single eigenvalue increasingly dominates the behavior of \([G''(\omega)]\), pushing it towards a simpler, Lorentzian form.

VII. CONCLUSION

The work presented here is devoted to the study of the dynamics of semiflexible dendritic structures. Here we have taken the local stiffness into account through correlations between bonds, modeled via a freely rotating chain assumption, which is equivalent to a maximum entropy condition.\(^1,2\) This leads to a set of Langevin equations for the beads’ dynamics. The eigenvalue spectrum of the resulting dynamical matrix (DM) is crucial and in many cases sufficient for determining fundamental physical quantities such as the mechanical relaxation moduli.\(^1\) Based on the symmetry of dendritic structures, we succeeded here in the effective block-diagonalization of the DM \(A^{SD}\), by which the determination of the spectra of SD of arbitrary generation \(g\) and functionality \(f\) becomes particularly easy. The key feature in this procedure turns out to be the structure of the corresponding eigenvectors. As we proved, despite the fact that \(A^{SD}\) has a more complex form than \(A^{GGS}\) for FD (in \(A^{SD}\) additional terms related to NNN interactions appear and the dependence on the stiffness parameter \(q\) leads to differences in the microscopic interactions), the eigenvectors of both matrices are similar. Through this procedure the reduction in the effort required to determine the eigenvalues is enormous: While in the conventional way one has to diagonalize a matrix whose size grows exponentially with the generation \(g\) of the SD, here the matrices which have to be diagonalized are of size \((g + 1) \times (g + 1)\) at most. Thus, considering a SD which has so many beads as the number of atoms in the earth is not a big problem anymore. Moreover, the diagonalization procedure allows us to look into the structure of the spectrum and to focus on the role of the highly degenerate eigenvalues. This helps us to understand the shape of the mechanical relaxation forms for SD as a function of their functionality and stiffness.

Finally, through this study we have demonstrated that the knowledge of the analytical structure of the DM in the presence of stiffness\(^2\) helps to advance in the investigation of semiflexible polymers.

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APPENDIX: PROOF THAT THE EIGENVALUES OF THE \(A\) AND \(B\) MATRICES OF SEC. V ARE ALL REAL

Here we consider the \(A\)-matrices, Eqs. (25)–(28), and the \(B\)-matrices, Eqs. (30)–(33), and demonstrate that all their eigenvalues are real. As is well-known, real and symmetric matrices have only real eigenvalues. Now, for non-trivial \(f (f > 2)\) the \(A\) and \(B\) matrices are not symmetric. Nonetheless, we will show that each of them is similar to a real and symmetric matrix. We recall here that two matrices, say \(A\) and \(\tilde{A}\), are similar if there exists a non-singular matrix \(D\) such that

\[
\tilde{A} = D^{-1}AD.
\] (A1)
Similar matrices have the same eigenvalues, with the same multiplicities.\(^{32}\)

We start with the group of \(A\)-matrices, namely, with \(A_1, A_3, A_4, \) and \(A_n\), Eqs. (25)–(28). As can be readily inferred by inspection, their non-vanishing, non-diagonal elements obey:

\[
A_{i+1,i} = (f-1) A_{i,i+1}, \quad (A2)
\]

\[
A_{i+2,i} = (f-1)^2 A_{i,i+2}, \quad (A3)
\]

whereas all other non-diagonal elements vanish.

Let the dimension of the \(A\)-matrix under consideration be \(m\). We take now for \(D\) the diagonal, \((m \times m)\)-matrix with elements

\[
D_{ii} = (f-1)^{i/2}. \quad (A4)
\]

Evidently, \(D\) is not singular. Its inverse, \(D^{-1}\), is also diagonal, with elements

\[
(D^{-1})_{jj} = (f-1)^{-j/2}. \quad (A5)
\]

Because of the diagonal structure of \(D\) and \(D^{-1}\), the transformation based on Eq. (A1) is particularly simple. One has

\[
\tilde{A}_{ij} = (D^{-1})_{ii} D_{jj} A_{ij} \quad (A6)
\]

and then

\[
\tilde{A}_{i+1,i} = (f-1)^{-1/2} A_{i+1,i} = (f-1)^{1/2} A_{i,i+1} = \tilde{A}_{i,i+1}, \quad (A7)
\]

and

\[
\tilde{A}_{i+2,i} = (f-1)^{-1} A_{i+2,i} = (f-1) A_{i,i+2} = \tilde{A}_{i,i+2}, \quad (A8)
\]

whereas all other non-diagonal elements vanish. We infer that the matrix \(\tilde{A}\), which is similar to \(A\), is symmetric and real.

We turn now to the group of \(B\)-matrices, namely to \(B_1, B_2, B_3, \) and \(B_n\), Eqs. (30)–(33). Each of them can be seen as being a \((m+1) \times (m+1)\)-matrix. The situation here is slightly different from that of the \(A\)-matrices: The non-diagonal elements inside the upper-left \((m \times m)\)-submatrix again fulfill

\[
B_{i+1,i} = (f-1) B_{i,i+1} \quad \text{for } i = 1, \ldots, m-1 \quad (A9)
\]

and

\[
B_{i+2,i} = (f-1)^2 B_{i,i+2} \quad \text{for } i = 1, \ldots, m-2 \quad (A10)
\]

whereas the last two pairs of non-vanishing elements obey

\[
B_{m+1,m} = f B_{m,m+1} \quad (A11)
\]

and

\[
B_{m+1,m-1} = f(f-1) B_{m-1,m+1}. \quad (A12)
\]

As transformation matrix \(\hat{D}\) we again use a diagonal \((m+1) \times (m+1)\)-matrix. Its elements are now

\[
\hat{D}_{ii} = \begin{cases} 
(f-1)^{i/2} & \text{for } i = 1, \ldots, m \\
(f-1)^{m/2} & \text{for } i = m+1 . \end{cases} \quad (A13)
\]

\(\hat{D}^{-1}\) is then also diagonal, with elements

\[
(\hat{D}^{-1})_{jj} = \begin{cases} 
(f-1)^{-j/2} & \text{for } j = 1, \ldots, m \\
(f-1)^{-m/2} & \text{for } j = m+1 . \end{cases} \quad (A14)
\]

Consider now the matrix \(\tilde{B} = \hat{D}^{-1} B \hat{D}\). We first infer that its upper-left \((m \times m)\)-submatrix is symmetrical, because the transformation \(\hat{D}\) acts on the respective elements in the same way as given in Eqs. (A7) and (A8). Thus, there remain only two pairs of non-vanishing elements to be considered. We find

\[
\tilde{B}_{m+1,m} = f^{-1/2} B_{m+1,m} = f^{1/2} B_{m,m+1} = \tilde{B}_{m,m+1} \quad (A15)
\]

and

\[
\tilde{B}_{m+1,m-1} = f^{-1/2}(f-1)^{-1/2} B_{m+1,m-1} \nonumber
\]

\[
= f^{1/2} B_{m-1,m-1} = \tilde{B}_{m-1,m+1} . \quad (A16)
\]

The last two equations complete the proof that the matrix \(\tilde{B}\), which is similar to \(B\), is indeed real and symmetric.