Dynamics of semiflexible recursive small-world polymer networks

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One of the fundamental issues in polymer physics is to reveal the relation between the structures of macromolecules and their various properties. In this report, we study the dynamical properties of a family of deterministically growing semiflexible treelike polymer networks, which are built in an iterative method. From the analysis of the corresponding dynamical matrix we derive the solution for its eigenvalues and their multiplicities, making use of a combined numerical and analytical approach. The eigenvalue spectra allow us to investigate the mechanical relaxation forms in depth for different values of the stiffness parameter. We observe that the dynamics of semiflexible networks is sensitive to the stiffness parameter. Our work paves a way to explore the structures of the highly symmetric polymers and provides a comprehensive understanding of the role of semiflexibility for the regular treelike networks which possess a small-world feature.

As a rapid developing discipline, polymer science has attracted much attention in the past few years, since it provides a powerful tool to study the macromolecules with various structures¹,². Currently, an important issue within the field of polymer science is to unveil how the underlying architecture of macromolecules affects their dynamic behaviors. Among various models, the Generalized Gaussian Scheme (GGS)³, which extends the well-known Rouse model⁴, has provided useful insights into many static and dynamic properties of the polymers. In particular, it has been successfully applied to a large variety of flexible polymer structures, such as dendrimers⁵, mesh-like polymers⁶,⁷, fractals⁸–¹⁰, dendritic¹¹,¹², regular hyperbranched structures¹³,¹⁴, scale-free¹⁵,¹⁶ and small-world¹⁷,¹⁸ networks, and so on. All these examples are important representatives of different classes of hyperbranched macromolecules, which possess macroscopically distinguishable behavior. Experimentally, topological features of the materials are evident, despite the averaging, smoothing out character inherent due to the structural disorder or polydispersity in the relaxation measurements¹⁹. While the GGS approach provides a basic means for the relation of the structure to the physical properties of polymers, it neglects some realistic features such as excluded volume and polymer stiffness, which are very important especially for biological macromolecules (proteins, DNA, etc.)²⁰–²².

While for analytic theories the inclusion of the excluded volume remains to be a hard task, recently, there have been a considerable number of theoretical investigations on the dynamic properties of semiflexible polymers²³–²⁹. Extending pioneering works for linear chains²⁰,²¹ and stars²², it was put forward as a framework for the arbitrary semiflexible treelike polymers (STP)²⁴, for the complex semiflexible loop polymers²⁵, and so on. In the theoretical approaches the semiflexibility was introduced by restricting the orientations of the bonds, which can be monitored through the related stiffness parameters²⁶–²⁸. Under such additional restrictions, it turns out that these approaches provide a more realistic description of semiflexible polymers²⁹. However, the price one has to pay for it is an increase of the complexity for an analytical solution of the problem. Indeed, the dynamical matrix of the semiflexible polymers, which couples the set of equations of motion, contains more non-vanishing elements than that of the fully-flexible polymers. Nevertheless, also in this case, based on the numerical and analytical methods, one can determine the spectra of the dynamical matrix, which allows one to study the dynamic properties of semiflexible polymers³³,³⁴.

The main purpose of this article is to uncover the dynamic properties of the regular treelike polymer networks in the framework of the STP model³⁴. For this, we investigate in the STP framework the mechanical relaxation properties for a family of recursive treelike polymer networks which display a small-world behavior³⁵. We first analyze the structure of the corresponding dynamical matrix and derive and analyze its spectra. Based on them we investigate for large polymer structures the mechanical loss moduli [G'(ω)], which allows one to observe the dynamical behavior of polymeric systems at different scales³,³⁶,³⁷. By comparing the [G'(ω)] of the flexible
polymer networks with that of the corresponding semiflexible ones, we observe that the stiffness parameter has dramatic influence on the dynamic properties of the polymers, especially in the high-frequency domain. Here, the STP framework allows us to carry on an in-depth analysis of the interplay between the structure and the dynamics of the polymer system. In particular, following the scheme of Refs. 33, 34, we show that the eigenmodes of the fully-flexible recursive treelike polymers keep their structures also in case when one introduces semiflexibility. This allows us to obtain analytic expressions for at least half of the corresponding eigenvalue spectra as a function of the stiffness parameter. It turns out that introducing semiflexibility leads to a reduction of the degeneracy of the spectra.

The report is structured as follows: Section Results introduces the construction of the recursive networks, whose dynamics is studied in the STP-framework. Here we also analyze the corresponding dynamical matrices, their eigenvectors and eigenvalue spectra, which allow us to calculate and to discuss the mechanical relaxation loss moduli $G'(\omega)$ for the polymer networks. Section Discussion summarizes our main results and conclusions. Finally, section Methods recalls briefly the tools which use in the report, namely, the STP-model and the eigenmodes of the fully-flexible recursive treelike polymers.

**Results**

**Network construction.** We start by introducing a model for a class of treelike networks with exponential growth, which are constructed in a deterministic iterative way. We denote by $U_g$ ($g \geq 0$) the deterministic treelike networks after $g$ iterations. Then the networks can be generated as follows. Initially ($g = 0$), $U_0$ consists of an isolated node, called the central node. For $g = 1$, $f(f$ is a natural integer) new nodes are generated connecting the central node to form $U_1$. For $g \geq 1$, $U_g$ is obtained from $U_{g-1}$ by adding $f$ new nodes to each existing node in $U_{g-1}$. Fig. 1 illustrates schematically the construction process of a network for the particular case of $f = 3$ for the first several iterations.

According to the construction algorithm of $U_g$, it is easy to see that at each iteration $g_i$ ($g_i \geq 1$) the number of newly generated nodes is $L(g_i) = f(f + 1)^{g_i - 1}$. Thus, the network order (i.e., the total number of nodes), $N_g$, at iteration $g$ leads to

$$N_g = \sum_{g_i = 0}^g L(g_i) = (f + 1)^g.$$

The corresponding number of edges (bonds) at iteration $g$ is $N_g - 1$, which holds for all treelike networks.

This class of networks displays typical features of macromolecules in the polymer science. Their cumulative degree distribution $P_{cum}(k)$, defined as the probability that the degree of a uniformly chosen node is greater than or equal to $k$, decays exponentially with $k$ as $P_{cum}(k) = (f + 1)^{-k}$. The average path length (APL), which represents the mean of the shortest distance between two nodes over all node pairs, increases logarithmically with the network size. The diameter, defined as the maximum length of the shortest path between two nodes over all node pairs, also grows logarithmically with the network order.

The features of the APL and of the diameter indicate that this class of polymer networks shows small-world behavior. In addition, the degree correlations of the networks depend on the functionality $f$. The network is uncorrelated for $f = 3$. And the network is assortative and disassortative when the functionality $f$ is in the interval $[1, 2]$ and $[4, \infty)$, respectively.

After introducing the topological characteristics of the polymer networks, next we will investigate the dynamical properties on them, which is the primary topic of the present report.

**Dynamics of semiflexible $U_g$.** We start with a summary of the main formulas concerning the dynamics of semiflexible $U_g$; the details of the STP-model used here are provided in section Methods.

In the STP-framework, the semiflexibility is modeled through the complementary interactions between the next-nearest neighboring beads. In particular, one introduces the so-called stiffness parameters, which are related to the pairs of adjacent bonds. Exemplarily, the stiffness parameter $q$, of bead $i$ which connects bonds $I_i$ and $I_0$ is defined as $q = \pm \left(I_i / I_0 \right)^q$, where $\langle \ldots \rangle$ denotes an average. $\hat{f}$ is the mean-square length of each bond, and the sign depends on the orientation of bonds. We note also that the beads of functionality $f_0 = 1$ do not connect any pair of bonds, so that no stiffness parameters are associated with them, see section Methods for details.

The dynamics of the polymer networks is described by a set of Langevin equations, i.e., say, for the $x$-component of the position vector $r_i = \{x, y, z\}$ one has:

$$\tau_0 \frac{\partial}{\partial t} x_i(t) + \sum_{j=1}^{N} A^{\text{STP}}_{i} x_j(t) = \hat{f}_i(t) / K, \quad \forall i.$$

Here $\tau_0 = \zeta / K$, $\zeta$ is the friction constant, $K$ is the spring constant (see also equation (45) in Methods). Moreover, $\hat{f}_i(t)$ is the $x$-component of the usual fluctuating Gaussian force acting on the $i$th bead, for which $\langle \hat{f}_i(t) \rangle = 0$ and $\langle \hat{f}_i(t) \hat{f}_j(t') \rangle = 2k_B T \delta(t - t') \delta_{ij}$ hold.

The interaction between the beads is described through the dynamical matrix $A^{\text{STP}} = \left( A^{\text{STP}}_{i j} \right)$, whose entries are known in closed form.

Here it is worthwhile to introduce a notation to present the situation of the bead sites, see Fig. 2. Starting from an arbitrary bead $i$ in the structure, we denote its neighbors by $i_1$, and the neighbors of $i_1$ by $i_2$. The corresponding functionalities of beads $i$ and $i_1$ are $f_i$ and $f_1$, respectively, while the corresponding stiffness parameter of junctions $i$ and $i_2$ are $q_i$ and $q_1$, respectively. For these all the non-vanishing elements of the matrix $A^{\text{STP}}$ are given by:

$$A^{\text{STP}}_{i i} = \frac{f_i}{1 - (f_i - 1) q_i} + \sum_{i_1} \frac{(f_{i_1} - 1) q_i^2}{1 - (f_{i_1} - 2) q_i^2 - (f_i - 1) q_i}.$$

and

$$A^{\text{STP}}_{i_1 i} = -\frac{1 - (f_{i_1} - 1) q_i q_{i_1}}{(1 - f_i q_i) (1 - (f_i - 1) q_i)},$$

whereas all other elements of $A^{\text{STP}}$ vanish.

Based on the structure of $A^{\text{STP}}$, equation (3) ~ (5), it is a simple matter to determine all elements of the matrix $A^{\text{STP}}$ for $U_g$. For simplicity, we assume that all beads of the same functionality $f_i$ in the semiflexible polymer $U_g$ have the same stiffness parameter $q_i$.
We assume that the stiffness parameter $q_i$ of the inner bead $i$ which has functionality $f_i > 1$ is taken to be $q_i = \frac{q}{f_i - 1}$, where $q$ is a real number between 0 and 1.

Now, we can categorize the diagonal elements into two different situations:

1. If $i$ is a peripheral bead then $f_i = 1$. It is connected by a single neighbor $i_k$ of functionality $f_{i_k}$ to the rest of the $U_g$. Thus, according to equation (3) the value of $\left(A_{g}^{\text{STP}}\right)_{ii}$ follows:

$$\left(A_{g}^{\text{STP}}\right)_{ii} = 1 + \frac{q^2}{\left(f_i - 1 + q\right)(1 - q)}.$$  \hspace{1cm} (6)

2. Otherwise, the bead $i$ has functionality $f_i > 1$, hence the value of $\left(A_{g}^{\text{STP}}\right)_{ii}$ turns out to be:

$$\left(A_{g}^{\text{STP}}\right)_{ii} = \frac{f_i}{1 - q} + \sum_{i_k \in A_i^{(g)}} \frac{q^2}{\left(f_i - 1 + q\right)(1 - q)},$$  \hspace{1cm} (7)

where the set $A_i^{(g)}$ contains only the neighbor beads $\{i_k\}$ of bead $i$, which have functionality $f_{i_k} > 1$ in the $g$th generation.

As a second step we consider the non-diagonal nearest-neighbor (NN) elements of $A_{g}^{\text{STP}}$. There are also two distinct cases:

1. If either $i$ or $i_k$ is a peripheral bead. From equation (40) the value of $\left(A_{g}^{\text{STP}}\right)_{ik}$ leads to:

$$\left(A_{g}^{\text{STP}}\right)_{ik} = \frac{1}{1 - q}.$$  \hspace{1cm} (8)

2. Otherwise, both two beads have functionality $f_i > 1$ and $f_{i_k} > 1$, so that $\left(A_{g}^{\text{STP}}\right)_{ik}$ turns out to be:

$$\left(A_{g}^{\text{STP}}\right)_{ik} = -\frac{1 + q}{1 - q}.$$  \hspace{1cm} (9)

Finally, we have to determine the next nearest-neighbor (NNN) elements of $\left(A_{g}^{\text{STP}}\right)_{ik}$. These elements depend only on the bead $i_k$ of functionality $f_{i_k}^{(g)}$ lying between the beads $i$ and $i_k$. From equation (41), the $\left(A_{g}^{\text{STP}}\right)_{ik}$ can take only one single value, which is

$$\left(A_{g}^{\text{STP}}\right)_{ik} = \frac{q}{\left(f_{i_k}^{(g)} - 1 + q\right)(1 - q)}.$$  \hspace{1cm} (10)

All other non-diagonal elements of the matrix $A_{g}^{\text{STP}}$ vanish.

According to the construction of $U_g$ and the elements of $A_{g}^{\text{STP}}$ discussed above, it is easy to observe that the matrix $A_{g}^{\text{STP}}$ has the following block form:

$$A_{g}^{\text{STP}} = \begin{pmatrix}
L_g & B_g & B_g & \ldots & B_g \\
B_g^T & D_g & C_g & \ldots & C_g \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
B_g^T & C_g & C_g & \ldots & D_g \\
& & & & (f + 1) \times (f + 1)
\end{pmatrix},$$  \hspace{1cm} (11)

where each block is a $(f + 1)^{f - 1} \times (f + 1)^{f - 1}$ matrix. Here $L_g$ represents the $(f + 1)^{f - 1}$ inner beads. $C_g$ and $D_g$ correspond to the $\left(1 + f\right)^{f - 1}$ peripheral beads. $B_g$ describes the interaction between them.

Furthermore, to bead $i$, at each subsequent iteration, $f$ new beads will be linked. Hence, the degree of bead $i$ in the generation $g$ evolves as:

$$f_i^{(g)} = f_i^{(g-1)} + f.$$  \hspace{1cm} (12)

Thus, in the generation $g$, all the inner beads have functionalities larger than one. Therefore, from equation (7) all the diagonal elements of $A_{g}^{\text{STP}}$ have functionalities $f_i^{(g)}$.
elements of matrix $I_g$ are:

$$ (I_g)_{ii} = \frac{\hat{f}_g^{(2)}}{1-q} + \sum_{i\in A_1^g} \left( \frac{\hat{f}_g^{(2)} - 1+q}{(1-q)} \right), $$

and the NN elements of matrix $I_g$ are:

$$ (I_g)_{ii} = -\frac{1+q}{1-q}. $$

Moreover, the NNN elements of $I_g$ are determined as:

$$ (I_g)_{ii} = \frac{q}{\left( \frac{\hat{f}_g^{(2)} - 1+q}{(1-q)} \right)}. $$

All other non-diagonal elements of the matrix $I_g$ vanish.

Now, as can be inferred from the $U_g$ construction, the structure of the matrix $B_g$ takes the form:

$$ B_g = \begin{pmatrix}
B_g^{(1)} & B_g^{(2)} & \ldots & B_g^{(f)} \\
B_g^{(3)} & B_g^{(4)} & 0 & 0 \\
B_g^{(5)} & 0 & B_g^{(4)} & 0 \\
\vdots & \vdots & \vdots & \vdots \\
B_g^{(3)} & 0 & 0 & \ldots & B_g^{(4)}
\end{pmatrix}, $$

where each block is a $(f+1)^{r-2} \times (f+1)^{r-2}$ matrix. The component matrices $B_g^{(2)}$, $B_g^{(4)}$, and $B_g^{(4)}$ are diagonal matrices. The matrix $B_g^{(1)}$ obeys similar relations as matrix $B_C$.

Furthermore, in equation (11) the block $C_g$ represents the NNN interaction among the peripheral beads of the network. Therefore, its elements are given by equation (10). Moreover, $C_g$ is a diagonal matrix. The main diagonal entries of $C_g$ are given by:

$$ (C_g)_{ii} = \frac{q}{(gf+1+q)(1-q)}, $$

and by:

$$ (C_g)_{ii} = \frac{q}{((g+j+1)f+q)(1-q)}, $$

where $(1+f)^{-2} < i \leq (1+f)^{-1}$ and $2 \leq j \leq g$.

Finally, let us consider the blocks $D_g$, which are also diagonal matrices. According to equation (6) and the bead degree, the main diagonal entries of $D_g$ can be expressed as:

$$ (D_g)_{ii} = 1 + \frac{q^2}{(gf+1+q)(1-q)}, $$

and

$$ (D_g)_{ii} = 1 + \frac{q^2}{((g+j+1)f+q)(1-q)}, $$

where $(1+f)^{-2} < i \leq (1+f)^{-1}$ and $2 \leq j \leq g$.

Based on the structure of dynamical matrix $A_{STP}^g$ discussed above, in the next subsection, we will determine the eigenvalue spectra of this matrix.

**Eigenvalue spectra of $A_{STP}^g$.** In order to study the dynamical properties of the semiflexible polymer $U_g$, we will use the results of the previous subsections. In particular, the solution of the set of equations (2) requires diagonalization of $A_{STP}^g$. For several highly symmetric structures, such as dendrimers and Vicsek fractals, the set of eigenvalues can be obtained with the help of the similarity between the eigenvectors’ structure of the fully flexible polymer and that of the corresponding semiflexible case, fact which also is of judicious use in case of $U_g$-networks. We develop our study of the eigenvalues of the semi-flexible polymers in three steps: First, in Methods we recall the spectra distribution of the fully flexible case; here we discuss the features of the corresponding eigenvectors and show that these features are also applicable to the semiflexible $U_g$ polymers – we use a combined analytical and numerical approach to derive their eigenvalues.

Let $v$ denote the eigenvector, whose corresponding eigenvalue is $\lambda$. $v$ can be expressed as

$$ v = \begin{pmatrix}
v_1 \\
v_2 \\
v_3 \\
\vdots \\
v_{f+1}
\end{pmatrix}, $$

where all $v_i$ of the vector $v$ have same sizes. For fully-flexible $U_g$ (see Methods), we distinguish between the following two cases:

In the first case, the vector $v$ satisfies following relations:

$$ v_1 = 0, $$

$$ v_2 + v_3 + \ldots + v_{f+1} = 0. $$

Based on the above two expressions of the eigenvectors, one can readily observe that, in this case, only beads of highest generation can move, while their ascendants(inner beads) are immobile, see Fig. 3. Moreover, the sum of the amplitudes associated with the $f$ mobile descendants, which are generated by arbitrary bead in the $(g-1)$th generation, vanishes.

In the second case, the vector $v$ satisfies following relation:

$$ v_2 = v_3 = v_4 = \ldots = v_{f+1}. $$

In this case, all of the $f$ mobile descendants generated by the same bead in the $(g-1)$th generation have the same amplitude, see Fig. 4.

We make a brief summary by noticing that for $U_g$ the eigenmotions of beads can be categorized into two groups: (i) Motions involving immobile inner beads. (ii) Motions involving mobile inner beads. As we proceed to show, this finding allows us to readily study the spectrum of the dynamical matrix in the corresponding semiflexible $U_g$ polymers.

First we show that $U_g$ have similar structure of eigenvectors in the fully-flexible and in semiflexible cases, i.e. we consider the following eigenvalue problem:

$$ A_{STP}^g v = \lambda v, $$

where $A_{STP}^g$ is the dynamical matrix of $U_g$. Based on equation (11), equation (25) can be expressed as

$$ \begin{pmatrix}
I_g & B_g^{(2)} & B_g^{(4)} & \ldots & B_g^{(f)} \\
B_g^{(3)} & D_g & C_g & \ldots & C_g \\
B_g^{(5)} & \ldots & \ldots & \ldots & C_g \\
\vdots & \vdots & \vdots & \vdots & \vdots \\
B_g^{(3)} & \ldots & \ldots & \ldots & D_g
\end{pmatrix} \begin{pmatrix}
v_1 \\
v_2 \\
v_3 \\
\vdots \\
v_{f+1}
\end{pmatrix} = \lambda \begin{pmatrix}
v_1 \\
v_2 \\
v_3 \\
\vdots \\
v_{f+1}
\end{pmatrix}, $$

where vectors $v_i (1 \leq i \leq f+1)$ are components of $v$. Equation (26) leads to the following equations:
corresponds to the eigenvalue set (24). Then equation (27) can be reduced to

\[
\begin{align*}
&\begin{cases} 
L_g v_1 + B_g v_2 + \cdots + B_g v_{f+1} = \lambda v_1 \\
B_g^T v_1 + D_g v_2 + \cdots + C_g v_{f+1} = \lambda v_2 \\
\vdots \\
B_g^T v_1 + C_g v_2 + \cdots + D_g v_{f+1} = \lambda v_{f+1} 
\end{cases} \\
\text{where the inner beads are immobile, the eigenvector } v \text{ satisfies equations (22) and (23). Then the system (27) can be reduced to}
\end{align*}
\]

\[
\begin{align*}
&\begin{cases} 
(D_g - C_g) v_2 = \lambda v_2 \\
(D_g - C_g) v_3 = \lambda v_3 \\
\vdots \\
(D_g - C_g) v_f = \lambda v_f 
\end{cases}
\end{align*}
\]

(28)

Let $E_g = D_g - C_g$ be the matrix that have the same size of $D_g$ and $C_g$, then $E_g$ is also a diagonal matrix. The system (28) defines an eigenvalue problem which is corresponding to the following matrix:

\[
AN_g = \begin{pmatrix} E_g & 0 & 0 & \cdots & 0 \\
0 & E_g & 0 & \cdots & 0 \\
0 & 0 & E_g & \cdots & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
0 & 0 & 0 & \cdots & E_g 
\end{pmatrix} (f-1) \times (f-1)
\]

(29)

Obviously, each eigenvalue of matrix $E_g$ is also an eigenvalue of matrix $AN_g$ with multiplicity $f-1$. As a real and diagonal matrix, $E_g$ has exactly $(f + 1)^{-1}$ eigenvalues and the eigenvalues of matrix $E_g$ is equivalent to the main diagonal entries of matrix $E_g$.

Based on equations (17)-(20), the main diagonal entries of matrix $E_g$ can be easily evaluated:

\[
(E_g)_{11} = (D_g)_{11} - (C_g)_{11} = 1 - \frac{q}{g^f - 1 + q}
\]

(30)

and

\[
(E_g)_{ii} = (D_g)_{ii} - (C_g)_{ii} = 1 - \frac{q}{(g^{-j+1})f + q},
\]

(31)

where $(1 + f)^{-2} < i \leq (1 + f)^{-1}$ and $2 \leq j \leq g$. From equation (30) and (31), there are $g$ distinct eigenvalues of matrix $E_g$, namely,

\[
\lambda_1 = 1 - \frac{q}{g^f - 1 + q},
\]

(32)

whose multiplicity is 1 in the matrix $E_g$ and $f-1$ in the matrix $A_g^{STP}$, and

\[
\lambda_2 = 1 - \frac{q}{(g^{-j+1})f + q},
\]

(33)

where $2 \leq j \leq g$. The multiplicity of this eigenvalue is $(f + 1)^{-1}$ in the matrix $E_g$ while in the matrix $A_g^{STP}$ its multiplicity is

\[
M_j = (f + 1)^{-2} f (f-1)
\]

(34)

We now calculate the total number $N_g$ of eigenvalues for the group that the inner beads are immobile

\[
N_g = f - 1 + \sum_{i=2}^{g} (f-1) f (f+1)^{-2} = (f-1) (f+1)^{-1}.
\]

(35)

A special case of equation (32) and (33) is the fully flexible case, for which $q$ vanish. We observe that in this case $\lambda_1 \rightarrow 1$ and $\lambda_2 \rightarrow 1$, which corresponds to the eigenvalue set $FE_1$ of the fully flexible case.

When the inner beads are mobile, the eigenvector $v$ satisfies equation (24). Then equation (27) can be reduced to

\[
\begin{align*}
&\begin{cases} 
L_g v_1 + f B_g v_2 = \lambda v_1 \\
B_g^T v_1 + (D_g + (f-1) C_g) v_2 = \lambda v_2 
\end{cases}
\end{align*}
\]

(36)

which is equivalent to determining the eigenvalues of the following matrix:

\[
AS_g = \begin{pmatrix} L_g & f B_g \\
B_g^T & D_g + (f-1) C_g 
\end{pmatrix}
\]

(37)

in which each block is a $(f + 1)^{-1} \times (f + 1)^{-1}$ matrix and $AS_g$ is a $2(f + 1)^{-1} \times 2(f + 1)^{-1}$ matrix. The diagonalization of matrices $AS_g$ can be performed numerically. As discussed in previous subsection, $L_g$ and $B_g$ are sparse matrices, while $D_g$ and $C_g$ are diagonal matrices, that is to say, the matrix $AS_g$ is considerably sparse, which is of great help to the diagonalization procedure.

In summary, the total number of eigenvalues corresponding to the group that inner beads are mobile is:

\[
N_g = 2(f + 1)^{-1}.
\]

(38)

By summing those from group (i), equation (35), and, from group (ii), equation (38), we have

\[
N_g + N_l = (f-1)(f+1)^{-1} + 2(f+1)^{-1} = (f+1)^{-1} \equiv N_{39}.
\]

(39)

which indicates that we have found the all eigenvalues of $U_g$.

In order to demonstrate the influence of stiffness, we plot in Fig. 5 and Fig. 6 the distribution of the eigenvalue spectra for $U_g$. The left part and the right part of Fig. 5 display the eigenvalues in ascending order for $U_g$ of $f = 3$ and of $f = 4$, respectively. From Fig. 5, it is easy to notice that with the increase of the stiffness parameter $g$, the large eigenvalues of the dynamical matrix grow, while the small ones decrease. By comparing the left part and the right part of Fig. 6, we observe that the number of distinct eigenvalues in the semiflexible $U_g$ is higher than for its flexible counterparts. In case of $U_g$, the reason for this phenomenon lies in the the dynamical matrix, which has more non-vanishing elements for semiflexible $U_g$.

Another feature which becomes apparent in both parts of Fig. 5 is that the eigenvalue $\lambda_g = \frac{f}{f+q}$, which is located in the in-between part of the spectra, has the highest multiplicity. As the stiffness parameter $g$ decreases from 1 to 0, $\lambda_g$ increases gradually and approaches 1 (Note that in the corresponding fully flexible network, this eigenvalue equals 1 for any functionality). From equation (34) we know that the multiplicity of $\lambda_g$ is $(f + 1)^{-1}(f-1)$, which is increasing with functionality $f$ and generation $g$. For $U_g$ of any $g$, $\lambda_g$ occupies exactly $[f(f-1)/(f+1)^2]$ parts of the whole spectrum. For example, $\lambda_g$ takes 3/8 part for $f = 3$ and 12/25 part for $f = 4$, respectively. As we will show, these differences of spectra between the two types of polymer networks $U_g$ will lead to different dynamic behaviors.

To conclude this part, it turns out that the determination of eigenvalues discussed here is based on a judicious use of the typical bead motions in the highly symmetric polymers. This approach can provide analytical expressions of a large part of the spectra and their multiplicities in the semiflexible polymer network with arbitrary functionality and generation. Instead of the traditional brute-force numerical diagonalization of the complete dynamical matrix, this approach considerably reduces the computational complexity of the eigenvalue problem and may pave the way for exploring other semiflexible polymers with complex topology, especially for symmetric architectures.

**Mechanical relaxation.** The eigenvalue spectrum $[\lambda_g]$ of $A_g^{STP}$ plays a fundamental role in the static and dynamic properties of
polymers. In this report we focus on the mechanical relaxation, which is represented by the complex shear modulus
\[ G' (\omega) = G'(\omega) + iG''(\omega), \] (40)
where its real part \( G'(\omega) \) and imaginary part \( G''(\omega) \) are the storage modulus and the loss modulus respectively. The dimensionless storage \([G'(\omega)]\) and loss \([G''(\omega)]\) moduli are given by
\[ [G'(\omega)] = \frac{G'(\omega)}{v k_B T} = \frac{1}{N} \sum_{k=2}^{N} \frac{(\omega \tau_0 / 2 \lambda_k)^2}{1 + (\omega \tau_0 / 2 \lambda_k)^2}, \] (41)
and
\[ [G''(\omega)] = \frac{G''(\omega)}{v k_B T} = \frac{1}{N} \sum_{k=2}^{N} \frac{\omega \tau_0 / 2 \lambda_k}{1 + (\omega \tau_0 / 2 \lambda_k)^2}, \] (42)
where \( \tau_0 \) is as in in equation (2) and the \{\lambda_k\} are the nonvanishing eigenvalues of the matrix \( A_k^{\text{STP}} \).

Based on the eigenvalues discussed in the previous subsection, we calculate the reduced loss moduli \([G''(\omega)]\) of \( U_g \). In the left part and the right part of Fig. 7, we display in double logarithmic scales the \([G'(\omega)]\) of \( U_g \) of \( f = 3 \) and \( f = 4 \), respectively, for different values of the stiffness parameter \( q \). Here we keep the generation fixed by taking \( g = 6 \) and vary the stiffness parameter by increasing \( q \) from the pure Rouse (fully-flexible) case, \( q = 0 \), to the semiflexible case \( q = 0.888 \).

From Fig. 7, it is easy to observe that in both Rouse case and semiflexible case, for very low frequencies \( \omega \), we have \([G'(\omega)] \sim \omega^4\); and that for very high frequencies \( \omega \), we have \([G'(\omega)] \sim \omega^{-1}\). Note that these well-known universal scaling laws hold for nearly all finite polymer networks. Hence, the particular structure of a polymer leaves its significant fingerprints in the intermediate region. Here, in the double-logarithmic scale, nearly no straight lines are observable in the intermediate region of \([G'(\omega)]\), which means that it appears a nonscaling behavior in this region. In Fig. 7, we can infer from the curve, that differences in the stiffness parameter \( q \) affect the intermediate behavior of \([G'(\omega)]\) dramatically.

As it is shown in Fig. 7, the \([G'(\omega)]\)-curves show a major peak in the intermediate region. With increasing stiffness parameter \( q \), the \([G'(\omega)]\) curve starts to bend downwards in the in-between region. The semiflexibility is reflected in the \([G'(\omega)]\) through a local minimum and a second minor peak appearing at intermediate frequencies. The reason for this fact lies in the unique spectra distribution of the polymer network. In Fig. 5, we can see that there is a clear gap in each spectrum near the value 1.0. In the left part of Fig. 5, for \( q = 0.333 \), the largest eigenvalue smaller than 1.0 is \( \lambda \sim 0.9808 \), and the smallest eigenvalue greater than 1.0 is \( \lambda \sim 5.1127 \), thus this gap is about 4.1319, while it is equal to 7.489 for \( q = 0.666 \) and to 20.947 for \( q = 0.888 \), respectively. Hence, the gap in the spectra depends strongly on \( q \), growing with \( q \) dramatically. Moreover, with increasing stiffness parameter \( q \), the \([G'(\omega)]\) curves get wider especially in the high frequency region, which is also observed before in a series of semiflexible polymer networks. The explanation for this phenomenon lies in the broadening of the eigenvalue spectra with growing stiffness parameter \( q \).
In order to have a deeper understanding of \(G_0(v)\) curves, in Fig. 8 we plot the derivative \(a(v) = \frac{d \log(G'(\omega))}{d \log(\omega/2)}\) for the \([G'(\omega)]\) curves of Fig. 7 as a function of \(\log(\omega/2)\) in a simple logarithmic scale. As we can see from Fig. 8, the value of \(a(v)\) starts to decrease from 1.0 in the low frequency domain and falls down around \(\omega/2 < 1\). In the intermediate region, the value again goes up rapidly and then it descends to the value \(-1.0\) in the high frequency. From the left part of Fig. 8, we can see that there are 3 intersection points between the straight line \(a(v) = 0\) and the \(a(v)\) curve for the \(q = 0.729\), which indicates that a local minimum of the \([G_0(v)]\) can be observed when \(q = 0.729\). Moreover, the intersection points between these two curves shift to higher \(v\)-region with growing stiffness parameter, which means that, in the \([G'(\omega)]\), the local minimum and the second minor peak shift to the high frequency region with increasing \(q\). This feature is also apparent from Fig. 7.

We conclude that the mechanical relaxation functions show that the networks \(U_g\) belong to the class of polymeric structures whose dynamics does not scale in the intermediate frequency (or time) domain. Such a non-scaling behavior show other well-known structures, namely dendrimers and some structurally disordered SFNs (SDSFNs)\(^{12,15,27,33,41}\). Nevertheless, their relaxation dynamics differs from that of the \(U_g\) especially for the semiflexible case. Namely, the \([G'(\omega)]\) of semiflexible dendrimers show a considerable broadening towards both low and high frequencies\(^{33}\), whereas for \(U_g\) the curves in the low-frequency domain display only little differences. Hence the relaxation at the large scales is for the \(U_g\) networks less affected by stiffness than for dendrimers. In comparison to SDSFNs\(^{41}\), inclusion of stiffness leads for several SDSFNs to a local minimum in \([G'(\omega)]\) which, however, considerably less pronounced than by \(U_g\). This is also obvious from the inspection of the corresponding local slopes, which for SDSFNs do not show big jumps as in Fig. 8\(^{41}\).

**Discussion**

In summary, we presented a systematic theoretical investigation of the dynamic properties of a family of growing semiflexible treelike polymer networks in the framework of STP. The main goal of this article is to explore the impact of various polymer structures and of the different degrees of stiffness \(q\), on the dynamic behavior of the polymer networks. To achieve this goal, we analyzed the dynamical matrix for the polymer networks and characterized their spectra. We succeeded to obtain a large part of the spectra analytically.

Based on the eigenvalue spectra, we have investigated the mechanical relaxation forms for the semiflexible polymer networks. In the in-between region, \([G'(\omega)]\) curve shows a nonscaling behavior, while in the very low and very high frequency, it shows \(\omega^{-1}\) and \(\omega^{1}\) behaviors respectively. Moreover, it turns out that the relaxation behavior is very sensitive to the stiffness. Indeed, with the increasing stiffness parameter \(q\), the \([G'(\omega)]\) curves get broader especially in the high frequency domain (showing that the stiffness is very important at the local scales) and they start to show a local minimum and another minor peak in the in-between region. Such a distinct qualitative
behavior is observed when the stiffness parameter $q$ gets higher than 0.729 (for $f = 3$), as it follows from the analysis of the derivative for the $[G'(o)]$. These observations show that the considered networks $U_{x}$ belong to the same class as the well-known, extensively synthesized$^{40}$ dendrimers. As we have found, however, the semiflexibility allows one to distinguish the groups) and with monomers consisting of both active and inactive with hypermonomers (monomers with high number of functional groups) and with monomers consisting of both active and inactive groups$^{42}$, will pave the way to the compounds with the properties of $U_{x}$. Finally, it is expected that the methods presented here can be extended to other classes of large semiflexible polymer networks.

**Methods**

**Modelling Semiflexibility.** The polymer structure is modeled as a network, which consists of $N$ beads located at $r_{i}(i = 1 \cdots N)$ connected by springs (bonds)

$$I_{x} = r_{i} - r_{j}.$$  

(43)

We can express the transformation (43) from the bond to the positions’ variables by the incidence matrix $G^{x}$.

$$I_{x} = \sum_{a} G^{x}_{a} r_{a}.$$  

(44)

Here the $G^{x}$ is the transposed matrix to $G$; the matrix $G = (G_{ab})$ has nonzero entries only $G_{aa} = -1$ and $G_{ab} = 1$, where the bond $a$ starts in bead $j$ and ends in bead $i$.

For the fully flexible polymers, the potential energy between beads is purely harmonic, so that it is diagonal in the bonds,

$$V_{p}(I_{x}) = \frac{K}{2} \sum_{a} W_{a} I_{a}^{2},$$  

(45)

Here the sum runs over all the bonds that build up the polymer. In equation (45), the spring constant $K$ equals $3k_{B}T$ if $k_{B}$ denotes the Boltzmann constant, $T$ is the temperature, and $F$ is the mean-square bond length (all bonds are of the same mean-square length). From equation (45) it follows that in the GGS picture the equilibrium bond-bond correlations $(I_{a}, I_{b})$ are evaluated with respect to the Boltzmann distribution exp($-V_{p}/k_{B}T$) vanishes$^{24}$. However, for semiflexible polymers, the bonds are correlated, i.e. their orientations are not arbitrary. In order to account for this feature, as discussed in Ref. 24, one may extend equation (45) and use the generalized potential energy $V_{c}$:

$$V_{c}(I_{x}) = \frac{K}{2} \sum_{a} W_{a} I_{a}^{2}.$$  

(46)

Under the assumption that $I_{x}$ follow normal distribution, the average of $(I_{a}, I_{b})$ with respect to the Boltzmann distribution is

$$\langle I_{a}, I_{b} \rangle = F(W^{-1})_{ab}.$$  

(47)

In this way one has the relation between the potential energy and the mean scalar products of bonds. For the latter the following traditional$^{25-26}$ conditions are taken: First, the mean-squared length

$$\langle I_{a}, I_{a} \rangle = F.$$  

(48)

For adjacent bonds $I_{a}$ and $I_{b}$ which are connected by the bead $i$ one has

$$\langle I_{a}, I_{b} \rangle = \pm F q_{i}.$$  

(49)

Here the parameter $q_{i}$ reflects the stiffness degree of the bond $i$: the plus or minus sign of $q_{i}$ depends on the connection of bonds $I_{a}$ and $I_{b}$, e.g. the plus sign holds for a bead to tail arrangement whereas the minus sign appears in the other cases. In a three-dimensional space $q_{i}$ is restricted by $q_{i} < 1/(f_{i} - 1)$, where $f_{i}$ is the functionality of the bead$^{26}$. Another limit $q_{i} = 0$ leads to a fully-flexible model. For non-adjacent bonds $I_{a}$ and $I_{b}$, one has as in the freely rotating chain model,

$$\langle I_{a}, I_{b} \rangle = \langle I_{a}, I_{b} \rangle \langle I_{b}, I_{c} \rangle \cdots \langle I_{m}, I_{n} \rangle F^{-2k}.$$  

(50)

Here $(a, b, c, \ldots, m, n)$ denotes the unique, shortest path from bond $I_{a}$ to bond $I_{b}$.

**Conditions of equations (48) – (50), the potential energy $V_{c}(I_{x})$ of equation (4) has an analytic-closed form$^{24}$. In order to get the $V_{c}$, the frame of bonds, we substitute equation (44) into equation (49), leading to

$$V_{c}(r_{i}) = \frac{K}{2} \sum_{a} A_{a}^{TP} r_{a} r_{a}$$  

(51)

where $A_{a}^{TP}$ is the so-called dynamical matrix and is given by $A_{a}^{TP} = GGW^{T}$. Based on equation (51), one can readily write down the equation of motions (2), where the structure of $A_{a}^{TP}$ is presented in equations (5)–(5).

**Spectra of flexible polymer networks** $U_{p}$. According to the construction of $U_{p}$, the dynamical matrix $A_{a}^{x}$ of fully-flexible $U_{x}$ is the connectivity matrix and is given by$^{26}$

$$A_{a}^{x} = \begin{pmatrix} A_{a}^{GGS} + f I_{a} & -I_{a} & -I_{a} & \cdots & -I_{a} \\ -I_{a} & -I_{a} & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -I_{a} & 0 & 0 & \cdots & -I_{a} \end{pmatrix}.$$  

(52)

whose characteristic polynomial satisfies following recursive relation$^{26}$

$$Q_{x}(\lambda) = (\lambda - f)(\lambda - f)^{T} - \frac{\lambda - f}{\lambda - 1}.$$  

(53)

We use notation $FE_{x}$ to represent the eigenvalues set of matrix $A_{a}^{GGS}$. Note that the polymer networks have $(f + 1)!$ nodes, which indicated that there are $(f + 1)!$ eigenvalues in the set $FE_{x}$. Based on the recursive relation of the characteristic polynomial $Q(\lambda)$, $FE_{x}$ can be divided into two subset $FE_{1}$ and $FE_{2}$. That is to say, $FE_{x} = FE_{1} \cup FE_{2}$, where $FE_{1}$ contains eigenvalue 1 with multiplicity $(f - 1)(f + 1)^{-1}$.

Thus, $FE_{1} = \{1, 1.1, \ldots, 1.1\}$

(54)

$FE_{2}$ consists the remaining $(2f + 1)!^{-1}$ eigenvalues which are determined by the following equation$^{26}$

$$\lambda - f = \frac{\lambda - 1}{\lambda - 1},$$  

(55)

where $\lambda_{f}^{-1}$ is an arbitrary eigenvalue in the set $FE_{2}$. Note that equation (55) have two roots for each $\lambda_{f}^{-1}$. Thus, each eigenvalue in $FE_{2}$ generates two new eigenvalues in $FE_{2}$. And the $FE_{2}$ set can be fully determined by recursively applying above two equations.

Similarly to the eigenvalues, the eigenvectors of $A_{a}^{GGS}$ can be determined from those of $A_{a}^{GGS}^{T}$. Let $v$ denote the eigenvector, whose corresponding eigenvalue is $\lambda$. $v$ can be expressed as

$$v = \begin{pmatrix} v_{1} \\ v_{2} \\ \vdots \\ v_{f + 1} \end{pmatrix},$$  

(56)

where all $v_{i}$ of the vector $v$ have same sizes. We can solve equation $$(\lambda^{T} - A_{a}^{GGS})v = 0$$  

to determine the vector $v$. We distinguish two cases: $\lambda \in FE_{1}$ and $\lambda \in FE_{2}$, which will be addressed as follows.

For the first case of $\lambda \in FE_{1}$, where all $\lambda = 0$, the equation $$(\lambda^{T} - A_{a}^{GGS})v = 0$$  

(57)

leads to the following equations:

$$v_{1} = 0$$  

(58)

$$v_{2} + v_{3} + \cdots + v_{f + 1} = 0.$$

For the second case of $\lambda \in FE_{2}$, we can have following relations:

$$[(\lambda - f)I_{a} - A_{a}^{GGS}]v_{1} + v_{2} + \cdots + v_{f + 1} = 0,$$

(59)

$$v_{1} + (\lambda - f)v_{1} = 0 \quad (2 \leq i \leq f + 1).$$  

(60)

Resolving equations (59) and (60) to find

$$(\lambda - f - \frac{1}{\lambda - 1})I_{a} - A_{a}^{GGS} v_{1} = 0,$$

(61)

$$v_{1} = -\frac{1}{\lambda - 1}v_{1} \quad (2 \leq i \leq f + 1),$$  

(62)

which shows that all the $v_{i}(2 \leq i \leq f + 1)$ have same values and are uniquely determined by the $v_{1}$, Equation (61) together with equation (55) indicates that $v_{1}$ is an eigenvector of matrix $A_{a}^{GGS}$ associated with the eigenvalue $\lambda - f - \frac{1}{\lambda - 1}$ determined.
by $\Delta^{-1}$. Thus, eigenvector $\nu$ can be expressed as

$$
\nu = \begin{pmatrix}
\nu_1 \\
\nu_2 \\
\nu_3 \\
\vdots \\
\nu_{l+1}
\end{pmatrix} = \begin{pmatrix}
\nu_1 \\
-\frac{1}{z-1} \nu_1 \\
-\frac{1}{z-1} \nu_1 \\
\vdots \\
-\frac{1}{z-1} \nu_1
\end{pmatrix},
$$

which implies that $\nu$ satisfies the following relation:

$$
\nu_2 = \nu_3 = \cdots = \nu_{l+1}. \tag{64}
$$

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**Author contributions**

Y.Q., M.D. and E.Z.Z. designed the research, performed the research, and wrote the manuscript.

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