Cospectral polymers: Differentiation via semiflexibility

Maxim Dolgushev, a Ganna Berezovska, and Alexander Blumen
Theoretical Polymer Physics, University of Freiburg, Hermann-Herder-Str. 3, Freiburg D-79104, Germany

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We consider polymer structures which are known in the mathematical literature as “cospectral.” Their graphs have (in spite of the different architectures) exactly the same Laplacian spectra. Now, these spectra determine in Gaussian (Rouse-type) approaches many static as well as dynamical polymer characteristics. Hence, in such approaches for cospectral graphs many mesoscopic quantities are predicted to be indistinguishable. Here we show that the introduction of semiflexibility into the generalized Gaussian structure scheme leads to different spectra and hence to distinct macroscopic patterns. Moreover, particular semiflexible situations allow us to distinguish well between cospectral structures. We confirm our theoretical results through Monte Carlo simulations. © 2010 American Institute of Physics. [doi:10.1063/1.3505147]

I. INTRODUCTION

The problem of the cospectrality of different graphs (the fact that topologically distinct structures have exactly the same Laplace spectrum) has encountered a lot of interest in the mathematical and chemical literature. For macromolecular structures this feature is very important since, in the framework of the Rouse-model and its extensions, it implies for cospectral polymers that their main static and dynamical properties (such as the radius of gyration and the mechanical relaxation moduli) are indistinguishable.

The problem is, of course, to be seen in a major perspective, namely, whether it is possible to determine through macroscopic and mesoscopic measurements the underlying microscopic topology of polymer structures. In fact, there are cases in which the spectra of two structures are different but, even then, the structures can hardly be distinguished through their macroscopic properties; as clear examples one may mention fractal networks which (although possessing different microscopic structures, such as ones that follow the patterns of Sierpinski gaskets and of dual Sierpinski gaskets) still show a scaling behavior in large part determined solely through their spectral dimension.

In this work we will focus on cospectral polymers and analyze their properties in the framework of the generalized Gaussian systems (GGS) and their extensions. As a result we will show that the simplest nontrivial pair of cospectral graphs does lead to different spectra when one introduces semiflexibility into the GGS. In fact, as we proceed to show, this allows for some of the microscopic quantities of the graphs (such as their gyration radius) to be quite different.

The paper is structured as follows. In the next section we introduce the problem of cospectrality and discuss physical quantities directly related to the spectral distribution. In Sec. III we recall Gaussian-based models used to depict flexible and semiflexible polymers and discuss results based on them in Sec. IV. In Sec. V we present the simulation model, whose results are given in Sec. VI. Finally, the article ends in Sec. VII with our conclusions.

II. THE PROBLEM OF COSPECTRALITY AND RELEVANT QUANTITIES

Many physical problems pertaining to complex structures depend strongly on their topology. In a mathematical framework the structures can be represented as graphs, i.e., by nodes (vertices) connected by edges. The connections between the vertices are reflected in the Laplacian (connectivity) matrix \( A = (A_{ij}) \). Each diagonal element, say \( A_{ii} \), gives the number of bonds \( f_i \) incident with the \( i \)th vertex (i.e. its functionality), \( A_{ii} = f_i \). Furthermore, if two vertices (say, \( i \) and \( j \)) are connected then one has \( A_{ij} = A_{ji} = -1 \), otherwise one has \( A_{ij} = A_{ji} = 0 \).

It turns out that the eigenvalue spectrum \( \{ \lambda_k \} \) of \( A \) is fundamental for many properties characterizing such structures. The knowledge of the spectrum allows to determine for (classical) random walks the mean probability of being (still or again) at the initial node and provides for quantum walks a lower bound for this probability (for some systems even the exact value). The spectrum of \( A \) is related to luminescence depolarization, to the molecular energy levels in Hückel’s theory, to the mean survival probability for coherently moving excitons in the presence of traps, as well as to the static and dynamical properties of flexible polymers (such as the mechanical and the dielectric relaxation).

An important statical feature of polymers is their gyration radius \( R_g \). It is connected in a straightforward way to the viscosity and can be determined through light- and small-angle neutron scattering experiments. In the GGS framework the average square gyration radius of a flexible polymer is related to the nonvanishing eigenvalues \( \{ \lambda_k \} \) of \( A \) through

\[ R_g^2 = \langle r^2 \rangle \approx \sum_{\lambda_k > 0} \frac{\lambda_k^2}{N} \]

Electronic mail: dolgushev@physik.uni-freiburg.de.
\[ \langle R^2 \rangle = \frac{l^2}{N} \sum_{k=2}^{N} \frac{1}{\lambda_k}, \tag{1}\]

where \(l^2\) is the mean-squared length of each bond and \(N\) is the number of beads in the polymer.

The eigenvalues \(\{\lambda_k\}\) are also relevant for many dynamical features.\(^{12}\) For example, in mechanical relaxation experiments one usually looks at the response of polymeric materials to applied harmonic strain fields and measures the complex shear modulus \(G'(\omega) = G''(\omega) + iG''(\omega)\). Dividing the \(G'(\omega)\) and \(G''(\omega)\) by \(\nu k_B T\) (where \(\nu\) is the number of beads per unit volume, \(k_B\) is the Boltzmann constant, and \(T\) is the temperature) renders them dimensionless. For the reduced variables \([G'(\omega)]\) and \([G''(\omega)]\) one has in the GGS picture,\(^{12}\) which applies for instance to dilute polymer solutions

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

and

\[ G''(\omega) = G''(\omega)/\nu k_B T = \frac{1}{N} \sum_{k=2}^{N} \frac{\omega \tau_0/2\lambda_k}{1 + (\omega \tau_0/2\lambda_k)^2}. \tag{3}\]

In Eqs. (2) and (3) \(\tau_0\) is the largest finite relaxation time (rotational relaxation time)\(^{23}\) of the system.

For fractal polymers, the spectral density \(\rho(\lambda)\) obeys the relation \(\rho(\lambda) \sim \lambda^{(d_s-2)/2}\), where \(d_s\) is the spectral dimension of the fractal. For \(d_s < 2\) the gyration radius scales as \(\langle R^2 \rangle \sim N(d_s-2)/d_s\), where \(N\) is the number of monomers in the fractal (see, e.g., Ref. 10) and the mechanical relaxation moduli \(G'(\omega)\) and \(G''(\omega)\) scale as \(\omega^{d_s/2}\) (see, e.g., Ref. 14). It is hence evident that fractal objects with the same spectral dimension \(d_s\) (such as the Sierpinski and the dual Sierpinski gaskets), albeit having different spectra, can be hardly distinguished through the experimental determination of \(\langle R^2 \rangle\) or of \(G'(\omega)\) and \(G''(\omega)\).

The situation is even worse in the case when two different structures have identical relaxation spectra. Such structures are called cospectral and it is known that for large \(N\) almost all trees (graphs without loops) have cospectral partners\(^{20}\) (cited after Ref. 4). In Fig. 1 we display the smallest cospectral pair of trees, which consist of \(N = 11\) beads each.\(^{13}\) From the evidence presented above it is clear that within the GGS model the above-mentioned experiments (determination of \(R_s\), relaxation measurements) would not be able to distinguish flexible polymers belonging to one or to the other topological form of the pair. As we proceed to show, the situation changes when we restrict the flexibility of the bonds. Such a reduction in flexibility can be due to intrinsic constraints concerning adjacent bonds or simply follow from other spatial limitations, such as the excluded volume conditions to which the monomers forming the structure are submitted. In order to take flexibility restrictions into account we will use our recent extension of semiflexible chain approaches\(^{27,28}\) to semiflexible treelike structures.\(^{15}\)

Hence we show in the following that focusing on the pair of graphs of Fig. 1 and including semiflexibility leads to different eigenvalue spectra of the members of the cospectral pair.

III. THEORETICAL MODELS

A. Flexible polymers

The GGS framework extends the Rouse model for polymer chains\(^7\) to arbitrary polymer structures.\(^{10,12}\) The polymer structure is represented by beads located at the positions \(r_i\) (\(i = 1, \ldots, N\), connected by springs (bonds); if two beads, say \(i\) and \(j\), are connected, we denote the corresponding bond, say \(a\), through \(d_a = r_i - r_j\). The potential energy of the structure is taken to be harmonic and hence

\[ V_{\text{GGS}}(d_a) = \frac{K}{2} \sum_a d_a^2 \tag{4}\]

holds. Here \(K = 3k_B T/l^2\) 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. A more usual representation of the potential \(V_{\text{GGS}}\) uses the position description. The transformation from the bonds’ to the positions’ variables can be formulated in terms of the incidence matrix \(G\).\(^{17}\) Now, the elements of \(G = (G_{ij})\) are \(G_{ia} = -1\) and \(G_{ia} = 1\), when bond \(a\) connects the beads \(i\) and \(j\); the elements \(G_{ja}\) and \(G_{ia}\) are zero otherwise. One has

\[ d_a = \sum_k (G^T)_{ik} r_k, \tag{5}\]

where \(G^T\) is transposed to \(G\). As can be readily verified, the product \(GG^T\) is equal to the Laplacian matrix, \((A_{kn}) = A = GG^T\).\(^{17}\) Therefore, using the position variables, the potential, Eq. (4), takes the more familiar form

\[ V_{\text{GGS}}(r_i) = \frac{K}{2} \sum_{k,n} A_{kn} r_k \cdot r_n. \tag{6}\]

The dynamics of the GGS obeys a set of Langevin equations which are given (say for the \(x\)-component of the position vector \(r_i = \{x_i, y_i, z_i\}\)) by\(^{12}\)}
TABLE I. Eigenvalues \(\{\lambda_i\}\) of the connectivity matrix \(A\) for the two distinct graphs given in Fig. 1; the eigenvalues are arranged in ascending order.

<table>
<thead>
<tr>
<th>(\lambda_i)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N)</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td>(\xi)</td>
<td>0.144</td>
<td>0.454</td>
<td>0.623</td>
<td>0.691</td>
<td>1.011</td>
<td>2.364</td>
<td>3.344</td>
<td>4.210</td>
<td>5.347</td>
<td>3.480</td>
<td>5.347</td>
</tr>
</tbody>
</table>

\[
\xi^2 \frac{\partial^2 x_i(t)}{\partial t^2} + \xi \sum_{j=1}^N A_{ij} x_j(t) = f_i(t),
\]

and similarly for \(y_j(t)\) and \(z_j(t)\). Here \(f_i\) is the \(x\) component of the usual Gaussian force acting on the \(i\)th bead, for which \(\langle f_i(t) f_i(t') \rangle = 2k_BT \xi \delta_i \delta(t-t')\) hold. After inserting Eq. (6) into Eq. (7) we obtain

\[
\xi^2 \frac{\partial^2 x_i(t)}{\partial t^2} + \kappa \sum_{j=1}^N A_{ij} x_j(t) = f_i(t).
\]

The usual procedure of solving Eq. (8) requires the diagonalization of the matrix \(A\), by which the corresponding eigenvalues \(\{\lambda_i\}\) follow. In this framework the spectrum both of structure 1 and of structure 2 of Fig. 1 is as in Table I.

**B. Semiflexible treelike polymers**

We now show that taking into account a more realistic situation, in which the structures 1 and 2 are semiflexible, leads to eigenvalue spectra which are not necessarily identical. Given that both structures are treelike, we can make use of our recent model \(^{13}\) for semiflexible treelike polymers (STP), in which semiflexibility is introduced via restrictions on the bonds’ orientations. For this we fix the mean bond length, \((d_a, d_b) = \tilde{f}\), and take for adjacent bonds (say, \(a\) and \(b\)) that their average orientations obey \((d_a, d_b) = (-1)^s \tilde{f} f_i\), see Ref. 15 for details. In particular, for the expression \((d_a, d_b) = (-1)^s \tilde{f} f_i\), the parameter \(s\) equals 0 for a head to tail configuration of the oriented bonds \(a\) and \(b\) and is 1 otherwise; the parameter \(f_i\) (we assume \(f_i \neq 0\)) reflects the stiffness of the junction \(i\) and is bounded from above by \(f_i < 1/(f_j-1)\). \(^{20}\)

Now, as discussed in Ref. 15, one is led, either by the maximum entropy principle or through a generalization of the freely rotating chain picture, to the following form of the potential for a semiflexible treelike polymer:

\[
V_{\text{STP}}(\{\mathbf{r}_i\}) = \frac{K}{2} \sum_{a,b} W_{ab} d_a \cdot d_b,
\]

where the \(W_{ab}\) and hence the matrix \(W= \{W_{ab}\}\) is known in analytical closed form. Thus the elements \(W_{xy}\) are as follows.

For nonadjacent bonds, say \(a\) and \(c\), the corresponding elements vanish, \(^{15}\)

\[
W_{ac} = W_{ca} = 0.
\]

For adjacent bonds, say \(a\) and \(b\), which hence have a bead, say \(i\), in common, one has \(^{15}\)

\[
W_{ab} = W_{ba} = (-1)^s \frac{f_i}{(f_j-1)^2 + (f_j-2)t_i - 1}.
\]

where \(t_i\) is the stiffness degree and \(f_j\) is the functionality of the \(i\)th bead; here again we have \(s=0\) for head to tail configurations and \(s=1\) otherwise. The diagonal element of \(W\) corresponding to bond \(b\), which connects the beads \(i\) and \(j\), is

\[
W_{bb} = 1 - \frac{(f_i-1) t_i^2}{(f_j-1)^2 + (f_j-2)t_i - 1} - \frac{(f_j-1) t_j^2}{(f_j-1)^2 + (f_j-2)t_j - 1},
\]

with the corresponding \((t_i, f_i)\) and \((t_j, f_j)\) parameters. Finally, we note that in the limit where all \(t_i\) tend to zero one is led to \(W_{ab} = W_{ba} = 0\) and to \(W_{bb} = 1\), and one recovers thus the potential for flexible treelike polymers as given in Eq. (4).

Let us define the matrix \(\tilde{A} = (\tilde{A}_{ij})\) through

\[
\tilde{A} = G W G^T.
\]

In the case of vanishing stiffness values, \(t_i \to 0\), the matrix \(W\) is the identity matrix, \(W = 1\), and \(\tilde{A}\) turns into the usual connectivity matrix \(A = GG^T\) of the GGS. The substitution of Eq. (5) into Eq. (9), while taking Eq. (13) into account, leads to

\[
V_{\text{STP}}(\{\mathbf{r}_i\}) = \frac{K}{2} \sum_{k,n} \tilde{A}_{kn} r_k \cdot r_n,
\]

and to the following set of Langevin equations, say, for the \(x\)-component of the position vector \(\mathbf{r}_i = (x_i, y_i, z_i)\):

\[
\xi \frac{\partial^2 x_i(t)}{\partial t^2} + \kappa \sum_{j=1}^N A_{ij} x_j(t) = f_i(t).
\]

Hence, also for STP, the eigenvalue spectrum, now of the matrix \(\tilde{A}\), is fundamental. In the Appendix we prove that the gyration radius of STP is also given by Eq. (1), as was the case for flexible polymers, described through the GGS picture. The proof that the structure of the mechanical relaxation moduli, Eqs. (2) and (3), stays unchanged when going from flexible polymers to STP was already presented in Ref. 30. Thus we can continue to use for STP Eqs. (1)–(3), in which the \(\{\lambda_k\}\) have to be replaced by \(\{\tilde{\lambda}_k\}\), the nonvanishing eigenvalues of \(\tilde{A}\). The \(\{\tilde{\lambda}_k\}\), however, as we will show in the next section, differ, in general, for the structures 1 and 2, and hence can lead to differences in the measurable quantities discussed in Sec. II.

**IV. THEORETICAL RESULTS**

We hence focus on the polymeric structures depicted on Fig. 1 and we restrict locally their flexibility. Now, the junctions affected have as functionalities either 2, 3, or 4, and we thus associate to them the stiffness parameters \(t, q, p\), respectively. A first choice of parameters lets \(q\) and \(p\) depend on \(t\); we set, namely, \(q=t/2\) and \(p=r/3\). This choice ensures that the two limiting cases of very flexible and of quite stiff junctions are simultaneously satisfied for all three junction.
types involved. If \( t=0 \) then one has automatically \( q=0 \) and \( p=0 \); on the other hand, for \( t \to 1 \) one also has \( q \to 1/2 \) and \( p \to 1/3 \), the maximal possible values allowed for these parameters.

To present the results clearly, we plot in Fig. 2 the corresponding relaxation spectra in a large \( t \)-range, starting at \( t=0 \) and increasing \( t \) toward unity. Given that in this \( t \)-range several eigenvalues change their value considerably, we have chosen to display them in a logarithmic scale; this implies, however, that the eigenvalue \( \lambda_1=0 \), which is unaffected by any stiffness consideration, cannot be shown. In Fig. 2 are thus visible only the remaining ten eigenvalues, two of which are degenerate for \( t=0 \) (see Table 1), a degeneracy lifted for \( t>0 \). In the figure the results for structure 1 are indicated through black, continuous lines and those for structure 2 through red, dashed lines. One can thus note that for \( t \neq 0 \) differences appear between the eigenvalues of structure 1 and of structure 2. A careful analysis shows that in general (apart from \( \lambda_1=0 \)) only the two eigenvalues \( \lambda_5 \) and \( \lambda_6 \) stay the same for the two structures and that they equal \( \lambda_5^{\text{Str1}}=\lambda_5^{\text{Str2}}=1/(1+q) \) and \( \lambda_6^{\text{Str1}}=\lambda_6^{\text{Str2}}=1/(1+p) \), analytical expressions which we obtained using the MATHEMATICA7 package.

We hence do indeed find that under realistic conditions, such as semiflexible situations, the spectra of structure 1 and of structure 2 are different. Now it is of interest to know whether these differences are due solely to our choice of parameters and in how far the differences in the spectra allow to uniquely characterize through macroscopic experiments the structures under investigation. For this we use the possibilities inherent in the STP model used,\(^\text{15}\) which allow to vary in a very free manner the stiffness values of each type of junction (in fact, one can do this even locally, for each junction, see Ref. 16). We now investigate changes from the parameter choice \((t,q,p)\)\((t/2,t/3)\) which led to Fig. 2.

Let us thus look at the influence of the tripartite junctions, for which \( f=3 \), and start by rendering them very flexible by setting \( q=0 \), so that we have \((t,q,p)\)\((t,0,t/3)\). The corresponding spectra are displayed in Fig. 3. We again remark that for all \( t>0 \) the spectrum for structure 1 differs from that of structure 2 and that only \( \lambda_5 \) and \( \lambda_6 \) are the same for both structures. Since here we consider \( q=0 \), the eigenvalue \( \lambda_5=1/(1+q) \) differs from the case displayed on Fig. 2, being now \( \lambda_5^{\text{Str1}}=1 \). Meanwhile, the eigenvalue \( \lambda_6=1/(1+p) \) stays the same as before, because we again have, as in Fig. 2, \( p=t/3 \). We notice, furthermore, that under the choice \( q=0 \) the difference between the lower lying eigenvalues for the two structures gets larger, a fact which will influence the experimental observables, as we show below. On the other hand, the differences in the higher lying eigenvalues are smaller than in Fig. 2.

As a third way of choosing our parameters we let the junctions with functionalities 2 and 4 be very flexible (setting \( t=0 \) and \( p=0 \)) and concentrate the semiflexible behavior on the tripartite junctions, by varying \( q \) in a range from \( q=0 \) up to values quite near \( q=1/2 \). The parameter choice is hence \((t,q,p)\)\((0,q,0)\), situation just complementary to the previous choice, leading to Fig. 3. In Fig. 4 we display the spectra, which for \( q \neq 0 \) again turn out to be different for structures 1 and 2; the largest differences are found for the eigenvalues \( \lambda_7, \lambda_{10} \), and \( \lambda_{11} \).

Now, based on the STP-theory and on the computed spectra, we turn to the determination of the behavior of experimental observables. We start with the averaged square radius of gyration, \( \langle R_g^2 \rangle \), which can be calculated, following

![Fig. 2. Relaxation spectra \( [\lambda_k] \) of structures 1 and 2 of Fig. 1, for different values of the stiffness parameter \( t \), where we set \( q=t/2 \) and \( p=t/3 \), see the text for details.](image1)

![Fig. 3. Relaxation spectra \( [\lambda_k] \) of structures 1 and 2 of Fig. 1, for different values of the stiffness parameter \( t \), where we set \( q=0 \) and \( p=t/3 \), see the text for details.](image2)

![Fig. 4. Relaxation spectra \( [\lambda_k] \) of structures 1 and 2 of Fig. 1, for different values of the stiffness parameter \( q \), where we set \( t=0 \) and \( p=0 \), see the text for details.](image3)
the argument of Sec. III, according to Eq. (1). The results for $\langle R_g^2 \rangle / l^2$ (F is here constant) are given in Fig. 5 for structure 1 (continuous lines) and for structure 2 (dashed lines) for the three choices of parameters, $(t, t/2, t/3)$ in black, $(t, 0, t/3)$ in blue, and $(0, q, 0)$ in green. All lines have the point $t=q=0$ in common, which corresponds to the parameter choice $(0,0,0)$, i.e., to a fully flexible situation. Remarkably, it is only for this parameter choice that the values of $\langle R_g^2 \rangle$ for both structures are identical.

A closer analysis of the data of Fig. 5 reveals, moreover, that not all parameter choices are best suited to differentiate between the two structures. Evidently, the differences get larger for larger $t$ and/or larger $q$ values. In addition, the role played by the lower eigenvalues turns out to be very important; the largest differences are found for the parameter choice $(t,0,0)\,$, given in blue in Fig. 5; as remarked before, for it the difference in the low lying $\lambda$-values is largest.

Another remarkable aspect concerns the ordering of the curves for the parameter choices involved; whereas for $(t, t/2, t/3)$ and $(t, 0, t/3)$ the $\langle R_g^2 \rangle$-values for structure 1 lie above those for structure 2, the opposite is true for the choice $(0, q, 0)$; for it the $\langle R_g^2 \rangle$-values are larger for structure 2 than for structure 1, as is indeed obvious from Fig. 5. The reason for this behavior is again to be traced back to the spectra, see Figs. 2–4, where $\lambda_2$ (the smallest nonvanishing eigenvalue) obeys the inequality $\lambda_{2}^{\text{Str1}} < \lambda_{2}^{\text{Str2}}$ for the $(t, t/2, t/3)$ and the $(t, 0, t/3)$ parameters and the inequality $\lambda_{2}^{\text{Str2}} < \lambda_{2}^{\text{Str1}}$ for the $(0, q, 0)$ parameter choice.

We now turn to considering dynamical relaxation and focus on $\langle G^2(\omega) \rangle$, since from our experience $^{15,16,30}$ its form is affected most by changes in the spectra. We also choose the semiflexibility parameters according to the pattern $(t,0,t/3)$, for which the low-lying eigenvalues for the two structures differ clearly. In order to exemplify the results we present in Fig. 6 $\langle G^2(\omega) \rangle$ computed for the value $t=0.9$. Here we expect larger deviations in the lower frequency range. Indeed, Fig. 6 shows in the range of small frequencies a small, but qualitative difference between the curves for structures 1 and 2. Thus the black curve (structure 1) displays at frequencies around $\omega \tau_0=0.1$ an almost linear behavior, whereas the red dashed line (structure 2) maintains its convex form.

Similar changes are also to be found for the other choices of parameters, but their magnitude is smaller than what is found in Fig. 6. We conclude that for experimental purposes the radius of gyration is more adequate than relaxation measurements in helping to differentiate between the two semiflexible structures under investigation. For this we have also tested other cospectral structures, based on McKay’s procedure $^{26}$ which allows to obtain arbitrary large cospectral pairs. Also in these cases (where $N$ varied between $N=17$ and $N=143$) we found that the radius of gyration is the more adequate quantity to monitor. On the other hand, the structures of each pair of cospectral graphs obtained in this way are very similar, so that for them the difference in $\langle R_g^2 \rangle$ is in the percent range.

Turning to the structures of Fig. 1, we are able to demonstrate that the efficiency of the radius of gyration in differentiating between structures is not depending on our underlying STP-model, but is also evident from Monte Carlo simulations. These numerical findings add weight to our conclusions, as we proceed to show.

V. SIMULATION MODEL

We perform our Monte Carlo simulations using the three-dimensional bond fluctuation model (BFM). $^{31,32}$ In the BFM each bead of a coarse-grained polymer is represented by a cube made of eight lattice sites and excluded volume restrictions are imposed by requiring that each lattice site belongs to one bead at most. In terms of the unit cell distance the length of the bonds is allowed to take only the values 2, $\sqrt{5}$, $\sqrt{6}$, 3, and $\sqrt{10}$. Altogether, the three-dimensional BFM allows 108 different bond vectors and 87 different angles between them. The complete set of allowed bond vectors follows from the set{ $(2,0,0),(2,1,0),(2,1,1),(2,2,1),(3,0,0),(3,1,0)$} by applying to it all the operations of the cubic point group.

In a local step a randomly chosen bead attempts to move randomly to one of the six nearest neighbor sites. The attempt is rejected if at least one of the sites of the elementary cube in the new position is already occupied or if the restrictions on the bonds’ lengths are violated. Given the BFM restrictions, such moves conserve the topology of the object and do not let polymer segments cross each other. The schematic representation of the polymer in the BFM and some of the allowed moves are sketched in Fig. 7.
We use the Metropolis algorithm\textsuperscript{33} to determine the transition probability \( w \),
\[
  w = \min \left[ 1, \exp \left( -\frac{\Delta U}{k_BT} \right) \right],
\]
for accepting a local move which is allowed by the excluded volume and the bond length constrains, but which involves
an energy change of \( \Delta U \). As we assume good solvent conditions, we do not take further energetic restrictions into account.
One Monte Carlo step (MCS) is achieved when in average each bead has attempted one local step.

To evaluate the energy difference \( \Delta U \) in energy for each attempted step involves only the junction (say \( i \)) which is moving and its nearest neighbors; hence only pairs of bonds, one of which at least is attached to \( i \), have to be accounted for. Thus
\[
  \frac{\Delta U}{k_BT} = -\sum_{[a,b]} (1)^s \cos \theta_{ab} \leq \frac{f_i}{2},
\]
In Eq. (17) the sum \([\cdots]\) runs over all the distinct pairs \((a,b)\) of bond vectors, each involving the \( i \)th bead and \( \theta_{ab} \) are the angles between the bond vectors \( a \) and \( b \). In the same way as in Sec. III, the parameter \( s \) can only take the values 0 and 1, where for bond vectors in a head to tail configuration \( s=0 \), and \( s=1 \) holds otherwise.

In the present simulations we assume that in the limit of stiff polymers the bonds tend to distribute symmetrically around each junction point \( i \). This is a particular assumption, which follows the theoretical ideas of Sec. III. In general, simulations allow, of course, to introduce for each pair of bonds particular restrictions on the bonds’ orientations. To be in line with the theoretical developments we hence assume that the bending potential \( U_i \), associated with the junction \( i \) is
\[
  \frac{U_i}{k_BT} = B_i (1 - \cos \theta). \tag{19}
\]
Now, for \( B_i = B \) Eq. (19) is one of the classical potential forms used in simulating semiflexible chains.\textsuperscript{34,35} To close our remarks about \( U_i \), we note that assuming as limiting cases symmetrical bead arrangements around each junction point is not problematic, since the maximal value of \( f_i \) both for structure 1 and for structure 2 is four; now, in three-dimensions, \( d=3 \), for \( f_i \leq 4 \) bead arrangements of maximal symmetry lead, as noted in Ref. 30, to the equality in Eq. (17). Only for \( f_i > 4 \) care must be exercised in \( d=3 \); in general, one is then forced to resort to non-symmetric bond arrangements\textsuperscript{30} in order to attain the maximal value of the average given in Eq. (17).

Following Eq. (18), the difference \( \Delta U \) in energy for each attempted step involves only the junction (say \( i \)) which is moving and its nearest neighbors; hence only pairs of bonds, one of which at least is attached to \( i \), have to be accounted for. Thus
\[
  \frac{\Delta U}{k_BT} = -\sum_{[a,b]} (1)^s B_j (\cos \theta_{ab}^{\text{new}} - \cos \theta_{ab}^{\text{old}}), \tag{20}
\]
where the sum \([\cdots]\) goes over all pairs of adjacent \((a,b)\) bond vectors, at least one of which involves \( i \). In Eq. (20) \( j \) denotes the site common to \( a \) and \( b \) and \( \theta_{ab}^{\text{new}} \) \((\theta_{ab}^{\text{old}})\) are the new (old) angles.

We use a simulation volume of \( 200 \times 200 \times 200 \) lattice units and implement periodic boundary conditions in the \( x, y, \) and \( z \) directions. We start to store the conformations (in intervals of 1000 MCS each) after letting the polymer equilibrate for \( 5 \times 10^5 \) MCS. The presented simulation data are averaged over the \( 5 \times 10^5 \) realizations thus obtained.

VI. SIMULATION RESULTS

Simulations using the BFM-method presented in the previous section allow now an independent check of the possibility to distinguish experimentally between semiflexible cospectrinal structures. Given our results in Sec. IV, we focus on the mean-square radius of gyration \( \langle R_g^2 \rangle \). Now, we can tune the semiflexible behavior at each junction through the parameters \( B_i \) of Eq. (18). To be close to the different models studied in Sec. IV, we will take either the \( B_i \) to be constant for all junctions or we will set some \( B_i \) for particular junctions to be zero, depending on their functionality.

The mean-square radius of gyration divided by \( \langle R_g^2 \rangle \), namely, \( \langle R_g^2 \rangle / \langle l_b^2 \rangle \), both evaluated as described above through the BFM, is presented in Fig. 8. In the figure the results for structure 1 are denoted by open circles and those for structure 2 by filled triangles. Using in each case the \( 5 \times 10^5 \) realizations involved, the relative standard error is around \( 1.05 \times 10^{-4} \) for \( \langle R_g^2 \rangle \) and around \( 0.4 \times 10^{-4} \) for \( \langle l_b^2 \rangle \) giving a total relative standard error of around \( 1.5 \times 10^{-4} \) on \( \langle R_g^2 / l_b^2 \rangle \), well below the size of the symbols used. As is evident, depending on the \( B_i \)-parameters used, the results fall into three groups, which we color-coded. Black stands for the cases in which the parameters \( B_i \) are the same for all junctions, blue denotes the cases in which we set \( B_i = 0 \) only for trifunctional
concerned, short ranged excluded volume effects can hardly differ; what interests us here is their qualitative agreement.

The first thing to note is that for full flexibility (all junctions having $B_i=0$) the results for structures 1 and 2 are indistinguishable. While this is not for surprise for the analytical GGS model, it is very noteworthy here, since in the BFM-simulations excluded volume constrains are explicitly taken into account. We conclude that in what the value of $\langle R_{2g}^2 \rangle$ is concerned, short ranged excluded volume effects can hardly be seen.

Turning now to the role of the angular restrictions we find, similarly to the STP-model, that the $\langle R_{2g}^2 \rangle/\langle t_{2f}^2 \rangle$-values are larger for structure 1 than for structure 2 when all $B_i$ are taken to be equal. The same holds in the case when only the trifunctional junctions are allowed to be totally flexible. On the other hand, varying the parameters $t$, $q$ and $p$ in the STP-model or varying the $B_i$ in BFM-simulations is not the same thing, and thus the results of Figs. 5 and 8 differ; what interests us here is their qualitative agreement.

The gyration radius reflects how the mass points are positioned relatively to each other and is defined by $25$

$\langle R_C \rangle = \frac{1}{N} \sum_{i=1}^{N} (\mathbf{r}_i - \mathbf{R}_C)^2$, \hspace{1cm} (A1)

where $\mathbf{R}_C$ is the position of the center of mass

$\mathbf{R}_C = \frac{1}{N} \sum_{i=1}^{N} \mathbf{r}_i$. \hspace{1cm} (A2)

We note that a careful study$^8$ allows to reformulate Eq. (A1) based on the $G$-matrix

VII. CONCLUSIONS

We devoted this article to examining possibilities of differentiating between branched polymers whose structures follow that of cospectral graphs. While indeed, in the frame-work of generalized Gaussian structures, such polymers will show the same relaxation spectra and will be thus indistinguishable when monitored through usual macroscopic and mesoscopic means, we were able to demonstrate that introducing more realistic aspects into the picture, such as the semiflexibility of junction points, leads to different spectra even for the simplest pair of cospectral graphs. Furthermore, static quantities, such as the averaged square radius of gyration, are well suited to distinguish between such cospectral structures. We have demonstrated these facts using both the analytical STP approach$^{15}$ and also independent Monte Carlo simulations, employing the BFM.$^{32}$ It follows that measurements can be devised that may indeed differentiate macroscopically between the cospectral structures. We note that a rather straightforward means to change the persistence length of single stranded DNA involves changing the ionic strength, see, e.g., Ref. 36. In order to apply our model to such situations would require, however, (because of the relatively long range of the electrostatic interaction) an appropriate extension.

Our mathematical-analytical treatment was rendered possible through the extension of the GGS-approach to semiflexible situations, as presented in Ref. 15. As it turned out here, for purposes of differentiation, it would be best to have different stiffness conditions at junctions of different type, as we have demonstrated here by letting the trifunctional junctions behave differently from the rest. This, of course, does not yet exhaust the possibilities offered by the STP-approach, since the theory allows to treat even situations in which each junction behaves independently of the others,$^{16}$ a feature which might turn out to be of relevance in future studies. We hope that our findings will be helpful in experimental studies on hyperbranched polymers, especially on structures which are cospectral.

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APPENDIX: GYRATION RADIUS OF SEMIFLEXIBLE TREELIKE POLYMERS

The gyration radius reflects how the mass points are positioned relatively to each other and is defined by$^{25}$

$\langle R_{2g}^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} (\mathbf{r}_i - \mathbf{R}_C)^2$, \hspace{1cm} (A1)

where $\mathbf{R}_C$ is the position of the center of mass

$\mathbf{R}_C = \frac{1}{N} \sum_{i=1}^{N} \mathbf{r}_i$. \hspace{1cm} (A2)
\[
\langle R^2_Q \rangle = \frac{1}{N^2} \sum_{a,b=1}^{N} ((G^T G)^{-1})_{ab} \langle d_a \cdot d_b \rangle.
\]  
(A3)

Now, the evaluation of the average \( \langle d_a \cdot d_b \rangle \) with respect to the Boltzmann distribution, \( \exp(-V_{STP}/k_BT) \), where \( V_{STP} \) is given by Eq. (9), and under the assumption that the \( \{d_a\} \) are Gaussian-distributed gives
\[
\langle d_a \cdot d_b \rangle = \hat{f}^2(W^{-1})_{ab}.
\]  
(A4)

Using the previous equation and the symmetry of \( W^{-1} \) we obtain
\[
\langle R^2_Q \rangle = \frac{\hat{f}^2}{N^2} \sum_{a,b=1}^{N} ((G^T G)^{-1})_{ab} \langle W^{-1} \rangle_{ba}
\]
\[= \frac{\hat{f}^2}{N^2} \sum_{a=1}^{N-1} ((W G G^T)^{-1})_{aa} = \frac{\hat{f}^2}{N} \text{Tr}[(W G G^T)^{-1}].
\]  
(A5)

Since \( \text{Tr}[(W G G^T)^{-1}] = \text{Tr}[(G^T G W)^{-1}] \) the gyration radius is given by
\[
\langle R^2_Q \rangle = \frac{\hat{f}^2}{N} \sum_{a=1}^{N-1} \frac{1}{\lambda_a},
\]  
(A6)

where \( \{\lambda_a\} \) are the eigenvalues of the matrix \( G^T G W \).

Now, the eigenvalue spectrum \( \{\lambda_a\} \) of \( G^T G W \) coincides with the set of the nonvanishing eigenvalues \( \{\bar{\lambda}_a\} \) of \( \bar{A} = G W G^T \). This fact was used previously for semiflexible star polymers, 37 but it is worth rederiving in general. In order to do this we follow the method described on p. 19 of Ref. 17.

Let us consider a graph with \( m \) edges and \( n \) vertices. Corresponding to this graph, the incidence matrix \( G \) has \( m \) columns and \( n \) rows. Let us introduce the following square, \((n+m) \times (n+m)\) matrices:
\[
M_1 = \begin{pmatrix} -\lambda I_n & GW \\ 0 & I_m \end{pmatrix}
\]
(A7)

and
\[
M_2 = \begin{pmatrix} I_n & -GW \\ G^T & -\lambda I_m \end{pmatrix}.
\]  
(A8)

In Eqs. (A7) and (A8) \( I_k \) denotes the identity matrix of dimension \( k \times k \) and \( 0 \) denotes the zero matrix. The product of the matrices (A7) and (A8) gives
\[
M_1 M_2 = \begin{pmatrix} GWG^T - \lambda I_n & 0 \\ G^T & -\lambda I_m \end{pmatrix}
\]  
(A9)

and
\[
M_2 M_1 = \begin{pmatrix} -\lambda I_n & 0 \\ -AG^T & G^TGW - \lambda I_m \end{pmatrix}.
\]  
(A10)

Now, both \( M_1 \) and \( M_2 \) are square matrices and thus \( \det(M_1 M_2) = \det(M_2 M_1) \) holds. Based on Eqs. (A9) and (A10) we deduce that
\[
(-\lambda)^m \det(GWG^T - \lambda I_n) = (-\lambda)^n \det(G^T GW - \lambda I_m).
\]  
(A11)

Equation (A11) relates the characteristic polynomials of the matrices \( G^T GW \) and \( GWG^T \). For treelike structures one has \( n = m + 1 \) and thus
\[
\det(GWG^T - \lambda I_n) = -\lambda \det(G^T GW - \lambda I_{n-1}).
\]  
(A12)

It follows that the eigenvalue spectrum of the matrix \( GWG^T = \bar{A} \) consists of the full spectrum of the matrix \( G^T GW \) and of one additional eigenvalue equal to zero. Thus Eq. (A6) is identical to Eq. (1), in which the nonvanishing \( \{\bar{\lambda}_a\} \) are replaced by the nonvanishing \( \{\lambda_a\} \), the eigenvalues of \( \bar{A} \).