Network Models and their Dynamics: Probes of Topological Structure

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Summary: In this work we focus on the mechanical relaxation of macromolecules. Based on linear response theory, this relaxation is in general related to the set of eigenmodes and eigenfunctions of the system. Of particular importance are situations which lead to scaling in the time and frequency domains. Thus the relaxation of star polymers, of dendrimers and of hyperbranched structures does not display scaling. On the other hand, one expects that the relaxation of fractals, as in fact that of linear chains, does scale. Here we numerically analyse the behavior of networks modelled through finite Sierpinski-type lattices, for which we have previously established that in the Rouse picture the mechanical relaxation scales in frequency and in time. As we show here, in the Zimm model based on the preaveraged Oseen-tensor, the picture changes drastically; taking the hydrodynamic interactions into account leads to relaxation forms which do not scale.

Keywords: fractals; mechanical relaxation; polymer networks; polymer dynamics; scaling

Introduction

In this work we analyze possibilities of unveiling the topological structure of macromolecular systems based on their dynamical relaxation. As is by now well known, the information provided by macroscopically accessible relaxation forms is rather restricted. This is due both to the fact that structural details show up only in limited, intermediate regions, as well as to the fact that usual dynamical tests access only partial information about the substances under investigation. Exemplarily, performing macroscopic mechanical measurements (such as determining the mechanical moduli) highlights the eigenvalues, but not the eigenfunctions of the corresponding Langevin equations [1-4]. The same holds also for dielectric and for magnetic relaxation techniques [5,6]. To obtain additional information about the structure one has to go to more microscopical investigations, such as micromanipulations techniques, methods which are nowadays under strong development [7-10]. Such techniques allow to move small parts of the polymer with the help of optical tweezers or of attached magnetic beads; furthermore one can

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monitor the local displacements through fluorescence and magnetic resonance techniques. As we have pointed out [6,11,12] the theoretical modelling of such features not only involves the eigenvalues, but also the knowledge of the corresponding eigenfunctions.

Due to space limitations, we will focus in this paper on the question of *scaling*, namely on whether the relaxation forms display power law behaviors over large time (or equivalently, frequency) domains. We recall that in general scaling is a basic ingredient in the theoretic studies of polymers [13]; scaling is also reflected in the mathematical description of polymer dynamics, such as phenomenological approaches based on fractional calculus [14-16]. For this reason, we will confront some usual scaling situations (well-known from the study of *linear* macromolecules) to results for more general, regular lattices, such as deterministic fractals [17,18], which are characterized by strict dilation symmetry. Thus the dynamics of large, regular Sierpinski-type lattices, when described in a Rouse framework, were found to scale [17], and the corresponding parameters were found to depend on the spectral dimension of the lattices involved [17-20]. The approach of Refs. [17] and [18] was based on the extension of the Rouse-model [21] to so-called Generalized Gaussian Structures, GGS [22,23], models in which the beads are connected to each other via springs, not necessarily in a linear fashion [22-25]. Distinct from these findings, the relaxation patterns of star polymers, of dendrimers and of hyperbranched structures calculated using the GGS-framework do not scale [11,12,26,27]. The same statement holds for the relaxation forms of more generalized structures, such as networks built from complex subunits, or of dynamically created random structures, such as Small-World-Networks (SWN) [28-31]. We remark, however, that such networks lead to complex structured relaxation forms, which are in many cases characteristic for the underlying topology.

It is interesting that even for deterministic fractals scaling is not always obeyed. As we proceed to show, evaluating the relaxation in the usual Zimm scheme [32] – in which the hydrodynamic interactions (HI) are accounted for based on the preaveraged Oseen tensor [1,2,32,33] – leads to departures from scaling. The ensuing behavior depends in a very sensitive way on the HI-parameters. We will support these assertions by evaluating the storage modulus of Sierpinski-type gaskets both in the Rouse-GGS-scheme and also (while extending it by introducing the HI), in the Zimm-GGS-scheme.

Generalized Gaussian Structures and Relaxation

To focus our ideas on particular network structures we choose to perform our study based on the Rouse-Zimm approaches [1,2,21,32] and on their extension to GGS [22-25]. Now a GGS is a set of beads connected to each other by springs (with elasticity constant K) and subject to friction (with friction constant ζ). We denote the configuration of such a GGS by $\{\mathbf{R}_k(t)\}$, where $\mathbf{R}_k(t) = (R_{xk}(t), R_{yk}(t), R_{zk}(t)) = (X_k(t), Y_k(t), Z_k(t))$ is the position of the kth bead at time t. In Rouse-fashion the interbead potential energy $U(\{\mathbf{R}_k\})$ contains only harmonic terms, stemming from the pairs of monomers directly bound to each other:

$$U(\{\mathbf{R}_k\}) = \frac{K}{2} \sum_{\beta,m,n} R_{\beta n} A_{mn} R_{\beta n} . \tag{1}$$

In the sum on the right-hand-side (rhs) of Eq. (1) all bonds are taken to be equal, with spring constant $K = 3k_B T / l^2$ (where l is the average length of an isolated bond in thermal equilibrium); β runs over the components x, y and z, and the GGS is accounted for through the N x N matrix $\mathbf{A} = (A_{ij})$. This matrix (the so-called connectivity matrix, [22,24]) is symmetric: its diagonal element A_{ii} equals the number of bonds emanating from the ith bead, and its off-diagonal elements A_{ij} are either equal to -1 if i and j are connected by a bond, or zero otherwise. Moreover, as is usual in the Rouse-Zimm scheme, the x,y and z components decouple, so that one can focus on only one of them.

Turning now to the solvent we note that it causes, first, the damping given by ζ; furthermore it is the source of the HI between the beads. In Zimm-fashion one has for the magnitude of the HI between the ith and the jth bead:

$$\mathrm{H}_{ij} = \left(\delta_{ij} + \zeta_r \left\langle l / R_{ij} \right\rangle \left(1 - \delta_{ij}\right)\right). \tag{2}$$

Here δ_{ij} is Kronecker's delta and $R_{ij} = \left|\mathbf{R}_{ij}\right| = \left|\mathbf{R}_i - \mathbf{R}_j\right|$ is the distance between the centers of the beads i and j. The (dimensionless) damping factor ζ_r in Eq. (2) equals $\zeta/(6\pi\eta_0 l)$, where η_0 is the solvent's viscosity; ζ_r can also be formulated in terms of an effective radius a, so that $\zeta_r = a/l$. In numerical analyses one often sets $\zeta_r = 0.25$, a value which we will also adopt. A further simplification of Eq. (2) consists in assuming the distribution of interbead distances to be Gaussian; this leads to:

$$\left\langle R_{ij}^{-1}\right\rangle = \left(\frac{6}{\pi\left\langle R_{ij}^{2}\right\rangle}\right)^{1/2}. \tag{3}$$

We note that for general networks, such as fractals, given that the structures contain loops (and distinct from what holds for linear chains, star-polymers, dendrimers and general hyperbranched structures), the interbead distances $\sqrt{\left\langle R_{ij}^{2}\right\rangle}$ between nearest neighbors (ij) vary as a function of the location of the (ij)-pair in the network.

It remains to recall that in solution each bead experiences the presence of random forces, here denoted by $f_i(t)$, which (based on the fluctuation-dissipation theorem) are related to ζ. One usually assumes the $f_i(t)$ to be zero-centered, $\left\langle f_i(t)\right\rangle = 0$, and Gaussian; in this way $\left\langle f_i(t) f_j(t')\right\rangle = 2k_B T\zeta(\mathbf{H}^{-1})_{ij}\delta(t-t')$ holds, where $\mathbf{H}^{-1}$ is the inverse matrix to $\mathbf{H} = (H_{ij})$ [1]. The fact that the inverse of $\mathbf{H}$ exists is related to the stability problem of the Zimm scheme, see Refs. [11,12].

Summarizing, the dynamics of $Y_i(t)$ is given by the Langevin equation [1]:

$$\zeta\frac{\partial Y_i(t)}{\partial t} = \sum_{j=1}^{N} H_{ij}\left(-\frac{\partial U(\{Y_k\})}{\partial Y_j} + f_j(t)\right), \tag{4}$$

or, in matrix form, by setting $\mathbf{Y} = (Y_1, Y_2, ..., Y_N)^T$ and $\mathbf{f} \equiv (f_1, ..., f_N)^T$, where T denotes the transposition:

$$\frac{\partial \mathbf{Y}(t)}{\partial \mathrm{t}} + \sigma\mathbf{H}\mathbf{A}\mathbf{Y}(t) = \frac{1}{\zeta}\mathbf{H}\mathbf{f}, \tag{5}$$

with $\sigma = K/\zeta$. The solution of Eq. (5) is readily obtained by diagonalizing the product $\mathbf{HA}$. This involves finding (in standard way) N linearly independent normalized eigenvectors $\mathbf{Q}_i$ of $\mathbf{HA}$, so that $\mathbf{HAQ}_i = \lambda_i\mathbf{Q}_i$. Setting $\mathbf{Q} \equiv (\mathbf{Q}_1, \mathbf{Q}_2, ..., \mathbf{Q}_N)$ one has $\mathbf{HAQ} = \mathbf{Q\Lambda}$, where $\mathbf{\Lambda}$ is the diagonal matrix whose elements are λ_i. Then

$$\mathbf{Q}^{-1}\mathbf{HAQ} = \mathbf{\Lambda} \tag{6}$$

holds, with $\mathbf{Q}^{-1}$ being the inverse of $\mathbf{Q}$.

If one is interested in the relaxation moduli, then only $\mathbf{\Lambda}$ matters. In fact the complex dynamic modulus $G^*(\omega)$ or, equivalently, the real component $G'(\omega)$ and its imaginary counterpart

$G''(\omega)$ (the storage and the loss moduli [3,4]), read for $\omega > 0$ (see also Eqs. 4.159 and 4.160 of Ref. [1]):

$$G'(\omega) = \nu k_B T \frac{1}{N} \sum_{i=2}^{N} \frac{(\omega / 2\sigma\lambda_i)^2}{1 + (\omega / 2\sigma\lambda_i)^2} \tag{7}$$

and

$$G''(\omega) = \nu k_B T \frac{1}{N} \sum_{i=2}^{N} \frac{\omega / 2\sigma\lambda_i}{1 + (\omega / 2\sigma\lambda_i)^2} . \tag{8}$$

In Eqs. (7) and (8) ν is the number of polymer segments (beads) per unit volume and the λ_i are the eigenvalues of the matrices of interest. Here we have assumed λ_1 to be the (nondegenerate) vanishing eigenvalue, $\lambda_1 = 0$. In the absence of HI one has formally **H** = **I,** where **I** is the identity matrix; hence one must diagonalize **A**. In the presence of HI the eigenvalues of interest are those of **HA**. In the next section we will, based on Eq. (7), numerically determine $G'(\omega)$ for a set of deterministic fractals, given that such structures are often used to model polymer networks [19,20,22,23,34-39].

Relaxation Forms of Dual Sierpinski Gaskets

As discussed in the previous section, in the presence of HI one needs first to diagonalize **A** in order to obtain, using Eqs. (2) and (3), the matrix **H**; diagonalizing **HA** consecutively leads to the eigenvalues required in Eqs. (7) and (8). In the absence of HI the eigenvalues of **A** are sufficient to determine $G'(\omega)$ and $G''(\omega)$ based on Eqs. (7) and (8).

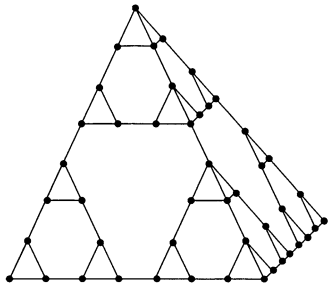

Figure 1. Dual Sierpinski gasket at the stage $N = 4^3$. Two faces of the object are visible, in perspective. The structure is displayed as being very regular, quite atypical for a GGS in solution.

In previous work [17,18] we have used the fact that the determination of the eigenvalues of **A** can be performed iteratively for dual Sierpinski-gaskets [40]; this allowed us to show that in the Rouse-picture the corresponding $G'(\omega)$ and $G''(\omega)$ scale over many orders of magnitude in time and frequency [17,18]. This finding prompts us to focus here on the same family of fractals, while also incorporating HI into the picture.

The Sierpinski gasket variant whose mechanical relaxation we analyze is displayed in Fig. 1. One can construct it by starting from the well-known Sierpinski-gasket in 3*d*, and connecting the *center* of each small tetrahedron via springs to the centers of its neighboring tetrahedra. These centers play then the role of the beads of the usual GGS. The construction may be viewed as being the dual of the Sierpinski gasket; note that the dual fractal has as coordination number 4 instead of 6, the coordination number of the original gasket. However, the dual structure has the same fractal and spectral dimensions as the 3*d* gasket, namely

$$\bar{d} = \frac{\ln 4}{\ln 2} = 2, \tag{9}$$

and

$$\tilde{d} = 2\frac{\ln 4}{\ln 6} = 1.54741.... \tag{10}$$

In Fig. 1 we show the dual lattice at the stage $N = 4^3$. Given that we are not in the position to diagonalize analytically **HA**, we employ to this end both for **HA** and for **A** numerical methods; the eigenvalues of **A** obtained through recurrence procedures [17,18,40] are then used as a benchmark for the numerical approach. As standard routines from computational linear algebra we followed [41,42] to diagonalize and [43] to invert matrices with dimensions up to $N = 4^6$. In this way we need in-core storage for two $N \times N$ matrices and auxiliary storage for $N(N+1)/2$ matrix elements; this sets the limit for the sizes of numerically treatable systems. We then use the obtained eigenvalues to evaluate via Eq. (7) $G'(\omega)$ for several fractals with different *N*.

Our results, both for the Rouse and for the Zimm model, are presented in Fig. 2. The dotted lines give the results of the Rouse-model, whereas the solid lines correspond to the Zimm-model. The sizes of the finite fractals which we use range from $N = 4^3$ to $N = 4^6$ beads. The figure displays $G'(\omega)$ in dimensionless units, where we have set $\sigma = 1$ and $\nu k_B T / N = 1$. Clearly evident from the figure (and rather uninteresting) is in both cases the limiting, connectivity-independent

behaviour at very small and very high ω; for $\omega << 1$ one has $G'(\omega) \sim \omega^2$ and for $\omega >> 1$ one finds $G'(\omega) \sim \omega^0$. One may note that the structure-dependent features are to be found in the frequency domain intermediate between these two limiting behaviours.

We start our discussion by considering first the Rouse-model, in the absence of HI $(\zeta_r \equiv 0)$. As can be inferred from the dotted lines of Fig. 2, we find a quite nice scaling behavior for $N = 4^6$ in the intermediate domain. We also note that by going from $N = 4^3$ to $N = 4^6$ the slope in this domain changes from 0.840 to 0.769. The last value can be compared to the theoretically expected $\tilde{d}/2 = 0.7737$.

The situation differs, however, in the presence of HI. In Fig. 2 we set $\zeta_r = 0.25$ for the interaction parameter of the Zimm-model. As dominant qualitative change from the dotted lines to the solid lines we find, first, that under HI the intermediate domain gets smaller; this finding parallels the situation encountered for $G'(\omega)$ of finite dendrimers in the Rouse- and in the Zimm-GGS pictures [11,23]. The most important aspect of the solid lines of Fig. 2, however, is that in the intermediate frequency domain scaling has practically disappeared.

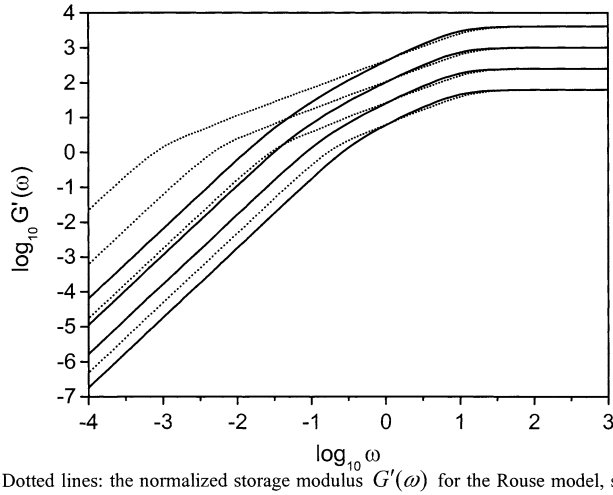

Figure 2. Dotted lines: the normalized storage modulus $G'(\omega)$ for the Rouse model, shown in double-logarithmic scale and in dimensionless units for $N = 4^3, 4^4, 4^5$, and 4^6 from below; the evaluation follows Eq. (7), see text for details. Full lines: ditto, for the Zimm model, with $\zeta_r = 0.25$.

To render this aspect even more clear we plot in Fig. 3 the quantity $\alpha' = d\ln G'(\omega)/d\ln\omega$, i.e. the derivative of the solid lines (i.e. the slopes of the Zimm-curves) of Fig. 2. Immediately apparent are for very small and for very large ω the limiting, theoretically expected values for the slope α', namely 2 and 0. If one had scaling in the intermediate range of the solid lines, one would expect to see an intermediate plateau in the curves of Fig. 3. This is clearly not the case; we find in the intermediate domain a quite mild cross-over behavior. The cross-over range has a width which depends on N; for $N = 4^6$ we find that the slope extends from values above 0.8 to values below 1.4. Hence, depending on N and also on ζ_r (calculations not presented here, to be discussed elsewhere [44]), the apparent fractal dimension (if one likes to call it so) covers quite a large range. In Refs. [19] and [20] it was suggested, based on an effective medium approach, that the slope should equal $\bar{d}/d$ in the dilute regime considered here. From our numerical calculations we do not find indications that the value $\bar{d}/d \simeq 0.667$ (where we used $\bar{d} = 2$ and $d = 3$) mirrors the findings well.

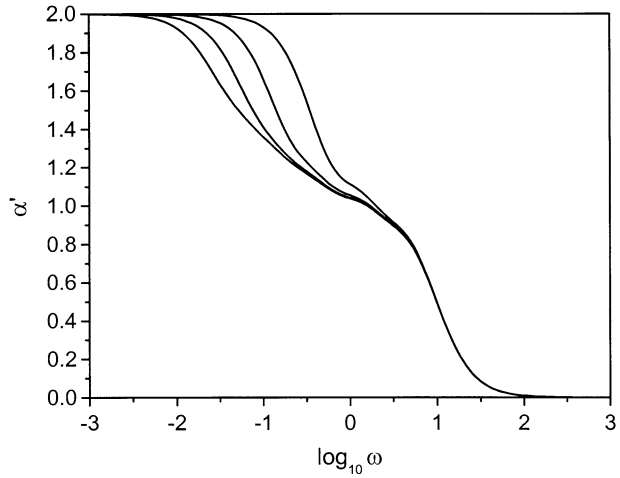

Figure 3. Local slopes α' of the $G'(\omega)$ of the Zimm-model, as displayed in Fig. 2. Plotted is $\alpha' = d\ln G'(\omega)/d\ln\omega$ as a function of ω. The parameters are $\zeta_r = 0.25$ and $N = 4^3, 4^4, 4^5$ and 4^6 (from right to left).

Conclusions

In this article we have analysed, based on finite, dual Sierpinski-gaskets in $3d$, the scaling behavior of $G'(\omega)$ in the presence and absence of HI. To keep the discussion as simple as possible we have concentrated on Generalized Gaussian Structures (GGS), and on the extension of the Rouse- and the Zimm-approaches [21,32] to them. In the absence of HI we found that $G'(\omega)$ scales very nicely in the intermediate frequency domain. This scaling, however, gets lost when introducing HI via the Zimm-formalism, based on the preaveraged Oseen-tensor. Moreover, we found that the shape of $G'(\omega)$ is very sensitive to the magnitude of ζ_r and to N, the number of monomers which make up the finite fractal considered.

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