Models for the Dynamics of Hyperbranched Macromolecules

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Summary: We focus on the motion of hyperbranched macromolecules in solution, paying particular attention to the relation between underlying topological structure and dynamics; we consider especially the mechanical moduli. Under the prominent representatives of hyperbranched polymers are both regular structures (such as the dendrimers) as well as disordered structures (such as irregular Cayley-trees). Evidently, batch-prepared hyperbranched macromolecules are closer to the latter. In order to theoretically determine their mechanical moduli we employ the method of generalized Gaussian structures (GGS), which allows us to study the situation including or excluding the hydrodynamic interactions (HI). Disordered hyperbranched structures display a complex dynamics; here we recall several analytical and numerical schemes for determining it and compare our theoretical results to the experimental data.

Keywords: Cayley-trees; dendrimers; fractals; hyperbranched macromolecules; scaling

Introduction

Much recent interest has developed around hyperbranched macromolecules [1,2], structures without loops and hence (topologically-speaking) tree-like. A well-known subclass of such tree-like molecules are, of course, the dendrimers [3,4], whose constitutive pattern is extremely regular. Evidently, the synthesis of perfectly regular dendrimers is by far more demanding than that of usual hyperbranched macromolecules, for which in batch reactions one accepts a certain polydispersity and also a high pattern diversity. Furthermore, besides the dendrimers, also other regular hyperbranched structures are possible; one such family is given by the regular hyperbranched fractals (RHF) [5,6].

In many applications not only the static but also the dynamical properties of macromolecules matter. Here we will focus on the dynamics of hyperbranched macromolecules, and particularly on their mechanical properties, given by the mechanical moduli $G'(\omega)$ and $G''(\omega)$. We will perform our analysis in the framework of generalized Gaussian structures (GGS), which are extensions of the Rouse- and Zimm-models to arbitrary topologies, see a recent review [7].

From the beginning we find typical differences in the response functions according to which structure we are considering. While for dendrimers the response functions do not scale [8–10], i.e. do not depend algebraically, as a power law, on time or frequency [11], a different behavior arises for special classes of hyperbranched structures. We recall that RHF do scale [5,6], in a way quite similar to the well-known behavior found for linear macromolecules. The advantage of focusing on RHF is that their eigenfrequencies can be readily computed to very high accuracy using recursion formulas. This fact dispenses us in the Rouse-picture from having to diagonalize very large matrices; in

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particular we are able to calculate for RHF the mechanical moduli $G'(\omega)$ and $G''(\omega)$ to high accuracy. In fact, even disordered systems are amenable to a semi-analytical treatment in the Rouse-picture [12,13].

Turning to the Zimm-model the general picture, even for hierarchically built fractals, changes; the introduction of the hydrodynamic interactions (HI) based on the preaveraged Oseen-tensor leads to relaxation patterns which in general do not scale. Thus no scaling is apparent for Sierpinski-type networks [14]; on the other hand, under HI RHF still scale very well [5,6,15]. Furthermore, the introduction of HI requires in practically all cases of relevance a by-far more extensive numerical treatment, for which numerical diagonalization procedures are required.

Generalized Gaussian Structures and Relaxation

To focus our ideas on particular polymer topologies we choose to perform our study based on the Rouse-Zimm approaches [16–21] and on their extension to generalized Gaussian structures GGS [7,22–24]. A GGS consists of beads subject to friction (with friction constant ζ), connected to each other by springs (with elasticity constant K). The configuration of a GGS is given by the set of position vectors $\{\mathbf{R}_k(t)\}$, 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 vector of the kth bead at time t. In the absence of external forces the potential energy $U(\{\mathbf{R}_k\})$ reads:

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

Here β runs over the components x, y, and z, and the GGS is taken into account through the $N \times N$ matrix $\mathbf{A} = (A_{ij})$. The matrix $\mathbf{A}$ is the so-called connectivity, adjacency or Laplace matrix [22,25,26], and 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. The interactions mediated by the solvent are taken into account through the HI-tensor (mobility matrix), $\mathbf{H} = (H_{ij})$ [17–19,27,28] between the ith and jth beads. In a simplified picture $\mathbf{H}_{ij}$ reads:

$$\mathbf{H}_{ij} = \left(\delta_{ij} + \alpha\left\langle R_{ij}^2\right\rangle^{-1/2}(1-\delta_{ij})\right)\mathbf{I} \equiv H_{ij}\mathbf{I}, \tag{2}$$

with δ_{ij} being the Kronecker-delta, $\alpha = \zeta_r l\sqrt{6/\pi}$ and $\zeta_r = \zeta/6\pi\eta_0 l$, where l is the average bond length, ζ the friction constant and η_0 the solvent's viscosity. As is usual in the Rouse-Zimm picture, the components of each bead experience the influence of random forces, here denoted by $f_i(t)$; these are taken to be zero-centered, i.e., $\langle f_i(t)\rangle = 0$ and Gaussian distributed.

Given that the motion of the different components X_i, Y_i or Z_i decouples, one may restrict oneself to either one of the components, say Y_i. Setting $\sigma = K/\zeta$, $\mathbf{Y} = (Y_1, Y_2, ..., Y_N)^T$ and $\mathbf{f} \equiv (f_1, f_2, ..., f_N)^T$, where T denotes the transposed vector, leads to the Langevin equation [7,21,24,29,30]:

$$\frac{\partial \mathbf{Y}(t)}{\partial t} + \sigma\mathbf{HAY}(t) = \frac{1}{\zeta}\mathbf{Hf}(t) \tag{3}$$

The solution of Eq. (3) 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 Λ is the diagonal matrix whose elements are λ_i. Then

$$\mathbf{Q}^{-1}\mathbf{HAQ} = \mathbf{\Lambda} \tag{4}$$

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

If one is interested in the relaxation moduli, then only Λ 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 [31,32]), read for $\omega > 0$ (see also Eqs. 4.159 and 4.160 of Ref. [18]):

$$G'(\omega) = \nu k_B T\frac{1}{N}\sum_{i=2}^{N}\frac{(\omega/2\sigma\lambda_i)^2}{1+(\omega/2\sigma\lambda_i)^2} \tag{5}$$

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and

$$G''(\omega) = \nu k_B T \frac{1}{N} \sum_{i=2}^{N} \frac{\omega/2\sigma\lambda_i}{1 + (\omega/2\sigma\lambda_i)^2} \qquad (6)$$

In Eqs. (5) and (6) ν is the number of polymer segments (beads) per unit volume, k_B is Boltzmann constant, 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 $\mathbf{H} = \mathbf{I}$, where $\mathbf{I}$ is the identity matrix; hence one must diagonalize $\mathbf{A}$. In the presence of HI the eigenvalues of interest are those of $\mathbf{HA}$. In the next section we will, based on Eqs. (5) and (6), numerically determine $G'(\omega)$ and $G''(\omega)$ for our hyperbranched structures under study.

Hyperbranched Structures: Dendrimers and Regular Hyperbranched Fractals

As is well-known, a most prominent subclass of hyperbranched macromolecules are the dendrimers [3,4,29,30], which we present on the left-hand side (lhs) of Fig. 1. Dendrimers start from a central core from which *f*-arms emerge. Now, at each new generation the ends of the arms get $(f-1)$ new arms attached to them. In the case of an ideal dendrimer structure the growth ends at the *g*th generation, and it is customary to consider the central core to be the zeroth generation. Viewed topologically, such dendrimers are chemical realizations of finite Cayley-trees.

Another class of hyperbranched polymers are the regular hyperbranched fractals (RHF) [5,6], which we present on the right-hand side (rhs) of Fig. 1. Our study is motivated by the search of scaling [11,20]; we recall that such RHFs (generalized Vicsek fractals) [5,6] obey scaling. For the construction we take again $f = 3$. Fig. 1 shows schematically the structure at generation $g = 3$. Iteratively, one starts from the RHF at $g = 1$, indicated on the rhs of Fig. 1 by a circle. To this object one attaches through 3 bonds, in star-wise fashion, 3 identical copies of itself, obtaining the RHF at $g = 2$, which consists of 16 beads. The iterative procedure is now obvious; Fig. 1 presents the finite RHF for $f = 3$ and $g = 3$. The regular pattern of Fig. 1 can be readily generalized to arbitrary *f*. It turns out that all these objects are fractals [5,6]: Embedded in the 2*d*-Euclidean space, such a RHF has a fractal dimension $\bar{d}_r$ of $\bar{d}_r = \ln(f+1)/\ln 3$. This differs from the fractal dimension corresponding to the mass of the RHF in solution, $\bar{d}_f$, by a factor of two, so that

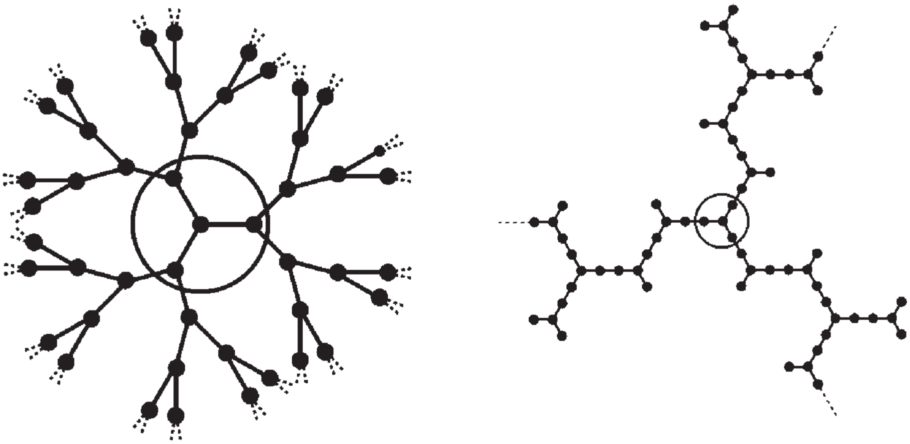

Figure 1.
Left: Ideal dendrimer with $f = 3$ at the fourth generation; the circle shows the first generation of the dendrimer. Right: Regular hyperbranched fractal with functionality $f = 3$ at generation $g = 3$; the circle indicates the first generation of the RHF.

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$\overline{d}_f = 2\overline{d}_r$. Furthermore, in many dynamical features, the spectral dimension $\tilde{d}$ enters; for general RHF one has [5,6] $\tilde{d} = 2\ln(f+1)/\ln(3f+3)$.

Let us continue by considering the relaxation forms which are obtained for dendrimers and for RHF. As shown above, the evaluation of $G'(\omega)$ and of $G''(\omega)$, Eqs. (5) and (6), requires the knowledge of the eigenvalues of the matrices $\mathbf{A}$, $\mathbf{HA}$ and $\mathbf{Q}^{-1}\mathbf{HQ}$. In the presence of HI one needs first to diagonalize $\mathbf{A}$ in order to obtain the $\langle R_{ij}^2 \rangle$ needed in Eq. (2) for $\mathbf{H}$; the diagonalization of $\mathbf{HA}$ leads then to the values required in order to compute $G'(\omega)$ and of $G''(\omega)$ based on Eqs. (5) and (6). In the absence of HI (Rouse case), it is sufficient to know all the eigenvalues of $\mathbf{A}$. For dendrimers and for RHF the evaluation of the eigenvalues of $\mathbf{A}$ is a simple matter, since one can avoid the direct numerical diagonalization of $\mathbf{A}$ by making use of analytical, recurrence relations, see Refs. [5,6,8,29] for a review. For $\mathbf{HA}$, on the other hand, direct diagonalization and inversion procedures [33–35] are necessary, which imply (because of restricted computer time and memory) an upper limit of roughly 5000.

The results of the calculations for $G'(\omega)$ are presented in double-logarithmic scales in Fig. 2 for dendrimers with $f = 3$ and with $g = 8$; they are based on Eq. (5) where we also set $\sigma = 1$. Displayed are the results both for the Rouse and for the Zimm case under HI-conditions, taking $\zeta_r = 0.25$. The results clearly show in the intermediate domain that no scaling is visible, i.e., that the curves cannot be approximated by straight lines. As discussed in Ref. [21] the curves, however, can be well approximated in the double logarithmic scales of Fig. 2 by logarithmic forms. The situation is different for the RHF, as we have discussed in Refs. [5,6]. Both in the presence and in the absence of HI, for RHF the relaxation forms $G'(\omega)$ and $G''(\omega)$ do scale in the intermediate domain. This means that the curves are practically linear in the double logarithmic scales chosen. Lack of space does not allow us to display them here and we refer the interested reader to the original publications [5,6].

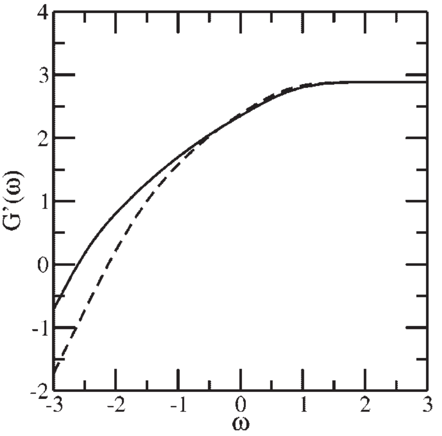

Figure 2.
Normalized storage modulus $G'(\omega)$ for a dendrimer with $f = 3$ and $g = 8$, evaluated according to Eq. (5) for the Rouse case (full line) and for Zimm model (dotted lines) with $\zeta_r = 0.25$. The scales are double-logarithmic to basis 10.

What is now the experimental situation? As stressed above the synthesis both of dendrimers and of perfect RHF is quite complex, so that in many cases in applications one is satisfied with the hyperbranched structures obtained from batch reactions, in which one efficiently inhibits the formation of loops. Evidently, the macromolecules obtained in this way are polydisperse and have a rather disordered structure. We are thus forced to turn now to the question of theoretically handling disorder, which we will discuss in the next chapter.

Disordered Hyperbranched Structures

To fix the ideas it is now very appropriate to turn to the experimental situation for an acetylated hyperbranched polyglycerol, see Fig. 3. The experimental results are given in Fig. 4, where both $G'(\omega)$ and $G''(\omega)$ are plotted. The hyperbranched polyglycerol was synthesized according to a method developed by Mülhaupt et al. [36–38]. Polyglycerols were obtained as transparent, highly viscous liquids whose rheological properties depend, besides on the branching structure, to a large extent on the number of hyxdroxyl groups per molecule.

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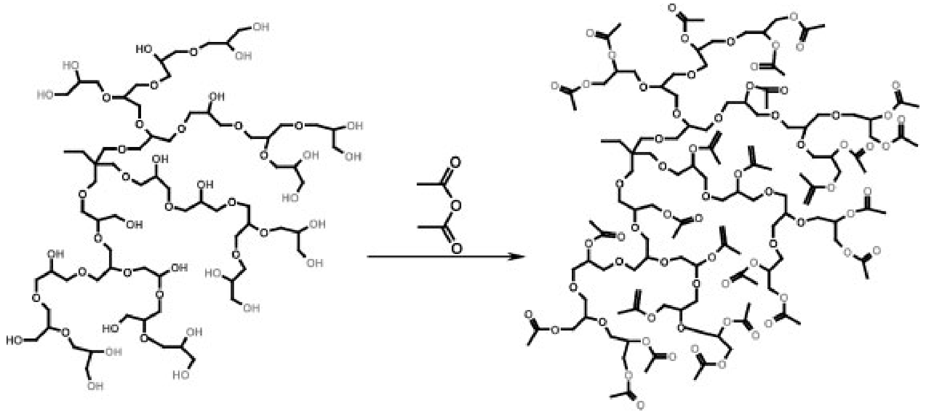

Figure 3.
Chemical structure of an acetylated hyperbranched polyglycerol.

To eliminate the influence of sticky sites the samples were acetylated. After this modification step, the polymers have as chemical structure the one given on the rhs of Fig. 3.

The polymer sample under investigation had an averaged molecular weight of $M_w = 52000$ g/mol and a polydispersity index of $M_w/M_n = 1{,}4$. The degree of branching of the molecules (which corresponds to the number of linear, branched and terminal monomers incorporated into the polymer) amounted to 0.5. Further details of the molecular characterization of this and other polymers of a series of acetylated and non-acetylated hyperbranched polyglycerols will be given in a forthcoming publication [39]. The rheological oscillatory measurements were performed on an universal dynamical spectrometer UDS200 of Paar-Physica company. The result is a master curve at the reference temperature $T_{ref} = 10°C$, made up of individual isotherms, which have been measured in the temperature range from $-20\,°C$ to $30\,°C$. Temperatures higher than $30\,°C$ could not be realized due to diminishing torque values, while temperatures smaller than $-10\,°C$ (a value already close to the samples' glass transition temperature of $T_g = -\ 23\,°C$) lead to transducers overload. Nevertheless, using the time-temperature superposition principle, the resulting master curves can be brought to span almost 5 decades.

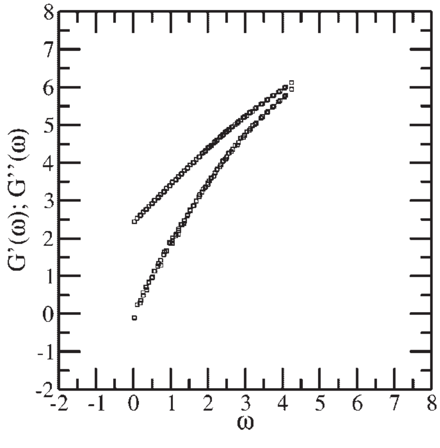

Figure 4.
Experimentally determined relaxation moduli for an acetylated hyperbranched polyglycerol at the reference temperature $T_{ref} = 10\,°C$. The scales are double-logarithmic to basis 10. The moduli are given in Pa, and the frequency ω in rad/s.

As is evident from Fig. 4, the patterns of $G'(\omega)$ and of $G''(\omega)$ turn out to lie between the patterns found for RHF (which show perfect scaling in the intermediate domain) and the forms for dendrimers (with their quasi-logarithmic shapes). For the analysis of the relaxation forms of Fig. 4 we have to leave the topologically very regular dendrimers and RHF and turn to disordered structures.

In order to treat disorder several theoretical approaches [12,13] have been suggested; these can be pursued quite far, before numerical means have to be used.

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The basic idea is to view disordered hyperbranched polymers as being defective dendrimers. In one of these approaches [13] one lets the functionality of each site vary randomly. Fundamental is now the so-called degree distribution p_k, which denotes the probability that an arbitrary vertex is connected to exactly k other vertices. Now in scale-free networks [13,40,41] p_k follows a power law, i.e. $p_k \sim k^{-\gamma}$. We stop to note that scale-free networks differ from the classical random graphs [42], for which the distribution p_k is Poissonian, and also from the small-world-networks [43,44]. As was shown in Ref. [13], the eigenvalue spectrum for scale-free hyperbranched macromolecules can be obtained (based on recursion relations) through the solution of non-linear differential equations; the spectrum is neither purely RHF, nor does it follow the form found for dendrimers.

Here we proceed in a simpler manner. For this we create the underlying disordered hyperbranched structure by means of a Monte Carlo algorithm. During the procedure we distinguish between active and inert end-beads and let the functionality of each bead be maximally 3. We hence start from a star of four beads, the central bead having three active neighbors and hence having $f = 3$. Now, each active end-bead may get, randomly 0,1, or 2 beads attached to it, each of these three probabilities having a chance of 1/3. Furthermore, if in such a step no bead gets attached, the corresponding end-bead is turned into an inert one. Otherwise, one or two active beads, respectively, are attached to the old end-bead. We then continue the process by picking one of the still active beads at random, and by determining for it how many new beads (if any) get attached to it. We continue the process until it either stops before reaching 900 beads (then we discard the structure), or after having obtained a structure consisting of 900 beads, structure which we utilize in the following. Then we compute the eigenvalue spectrum according to the procedures discussed above and evaluate $G'(\omega)$ and $G''(\omega)$ according to Eqs. (5) and (6).

In Fig. 5 we display our numerical results (full lines), obtained by averaging over 10 such structures. The calculations where done for the Zimm case, with $\zeta_r = 0.25$. In the same Figure we have replotted, for comparison, the experimental data (squares). We find, indeed, a very good fit (the Rouse-model fits less well, due to its larger intermediate regime). Now, the intermediate regime is (as always for these problems) [7] the most important: The limiting cases of very low and very high frequencies are namely independent of the particular structure under study, being $G'(\omega) \sim \omega^{-2}$ and $G''(\omega) \sim \omega$ for very small ω and $G'(\omega) \sim \omega^0$ and $G''(\omega) \sim \omega^{-1}$ for very large ω. Fig. 5 also makes clear that the underlying structure is not a fractal; for fractals we would have clearer linear intermediate regimes both for $G'(\omega)$ and for $G''(\omega)$ and, furthermore, the two curves would be parallel to each other in a large ω-range. On the other hand, the deviations from linearity are much less evident in Fig. 5 than in the case of dendrimers. What remains to be seen is whether at even higher frequencies the experimental data will follow the theoretical curves of Fig. 5, which in this range can be viewed for the moment only as predictions.

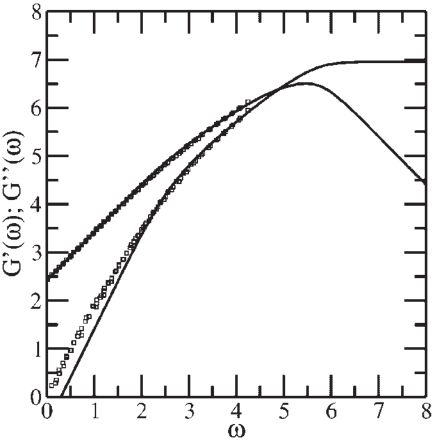

Figure 5.
Full lines: Relaxation moduli $G'(\omega)$ and $G''(\omega)$ obtained from 10 random hyper-branched structures with $N = 900$. The evaluation follows Eqs. (5) and (6) and was done for the Zimm model with $\zeta_r = 0.25$. Squares: Experimental data as in Fig. 4. The scales are double-logarithmic to basis 10.

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Conclusions

In this work we displayed dynamical features of several families of hyperbranched molecules. We have performed our calculations in the framework of GGS, which are the natural extension of the simple Rouse- and Zimm-models to complex networks. We focused on the relaxation moduli, which are experimentally well-accessible quantities. As also exemplified here, their measurement allows to get information on the internal structure of the substances investigated. Furthermore, we analyzed in a simple model the dynamics of random hyperbranched polyglycerols. The model leads a very reasonable agreement with the experimental data, reproducing the qualitative features of such hyperbranched macromolecules.

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