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Dynamics of Hyperbranched Polymers and Dendrimers: Theoretical Models

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Summary: Chemical reactions depend in many ways on the dynamics of the underlying reactants, and an important aspect is the distance covered by the reactants before the reaction act occurs. Hence, even diffusion-limited reactions between *point* particles in confined geometries and in low-dimensional systems display decay forms which are very different from those obtained from simple chemical kinetics. Clearly, even more complex decay forms hold for macromolecules, given their internal degrees of freedom. Here we discuss how the dynamics of macromolecules in solution relates to their topological structure and focus on the motion of macromolecular segments (monomers) under the influence of external fields. After a general survey of the method of generalized Gaussian structures (GGS) we recall the wealth of forms which are observed, depending on the topology and on the microscopic dynamics involved. Paradigmatic are the findings for the class of hyperbranched macromolecules; to these belong the dendrimers. While the dendrimers do not show a typical scaling behavior, as found, say, for linear chains, the situation is different for particular classes of regular hyperbranched polymers which are fractal. We end by discussing their pattern of motion in the GGS-Rouse-Zimm picture.

Keywords: dendrimers; fractals; hyperbranched macromolecules; reaction kinetics; scaling

Introduction

In chemical reactions an important aspect is the distance travelled by the reacting units before the reaction act occurs. In the absence of external fields, under isotropic and homogeneous conditions, an important quantity to this respect is the mean square displacement. In general the Einstein-relation holds, so that $\langle \mathbf{R}^2(t) \rangle$, the mean square displacement of a particle, is related in a

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straightforward way to its mean drift $\langle \mathbf{R}(t) \cdot \mathbf{F} \rangle$ in a constant external field **F**. For diffusion-limited reactions at first encounter, an even more important quantity is $S(t)$, the mean number of distinct sites visited by the reacting particle during the time t [1]. Now, many investigations have shown that the decay forms of even the simplest chemical reactions, say of the type

$$A + B \to B \tag{1}$$

may strongly differ from the simple exponential decay predicted by the classical kinetic reaction scheme of Eq. (1), see Ref. [1] for a review. Most of the decay forms turn out to be stretched exponentials [1]. With $\phi \neq 1$ and C, $\tilde{C}$ being constants, one has, say the concentration $\Phi(t)$ of A:

$$\Phi(t) = C \exp\left(-\tilde{C} t^{\phi}\right). \tag{2}$$

The reasons why Eq. (2) holds are manifold, and ϕ depends on the space in which the particles move, on the restrictions which they find on their way and on the local fields. Related to this is the fact that even for point-like particles, one finds [1] that $\langle \mathbf{R}(t) \cdot \mathbf{F} \rangle$ and $S(t)$ are not linear functions of t, obeying in general:

$$S(t) \sim t^{\beta} \text{ and } \langle \mathbf{R}(t) \cdot \mathbf{F} \rangle \sim t^{\gamma}, \text{ with } \beta \neq 1 \text{ and } \gamma \neq 1. \tag{3}$$

In general, the relation between $S(t)$ and $\Phi(t)$ is indirect [1]. The situation gets even more complex when one considers polymers, which have internal degrees of freedom. Here exact solutions are very scarce, an exception being, for instance, the trapping of the end monomer of a polymer diffusing along a linear chain [2].

We will hence restrict our task here to evaluate (as far as possible, analytically) the displacement of macromolecular segments under the influence of external fields. We note that recent observations on the microscopic level allow to monitor such motions: Thus parts of the polymer can be moved by optical tweezers or by attached magnetic beads; furthermore one can follow the local motions through fluorescence and magnetic resonance techniques [3-5].

The displacement of segments (monomers) under the influence of external fields provides valuable information on the macromolecule to which the monomers belong. In general, the motion is anomalous, in the sense of Eq. (3). Such a behavior will clearly influence the course of chemical reactions involving such macromolecules. Here we study this motion using Rouse-Zimm-type models and concentrate on hyperbranched structures [6,7]. In very general fashion, the dynamics of macromolecules is connected in approaches based on linear response to the eigenmodes and eigenfunctions of the system. We find that while for dendrimers the response functions do not scale [6,8,9], i.e. do not even depend algebraically, as a power law, on time or frequency [10,11], a different behavior arises for special classes of hyperbranched structures. As we will show, regular hyperbranched fractals (RHFs) do scale [7], in a way quite similar to the subdiffusive laws of Eq. (3), a feature well-known from the study of linear macromolecules.

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 [7-10,12-15] and on their extension to generalized Gaussian structures GGS [16-18]. A GGS consists of beads subject to friction, connected to each other by springs. The configuration of GGS is given by the set of position vectors $\{\mathbf{R}_k\}$, 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. The potential energy $U(\{\mathbf{R}_k\})$ reads

$$U(\{\mathbf{R}_k\})=\frac{K}{2}\sum_{\beta,m,n} R_{\beta m}A_{mn}R_{\beta n}-\sum_{\beta,n}F_{\beta n}R_{\beta n}\,. \tag{4}$$

Here K is the spring constant, 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 [16,19,20], 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 such as the hydrodynamic interactions (HI) are taken into account through the HI-tensor (mobility matrix) [13-15,21,22] between the *i*th and *j*th beads. In a simplified picture $\mathbf{H}_{ij}$ reads:

$$\mathbf{H}_{ij} = \left(\delta_{ij} + \alpha < R_{ij}^2 >^{-1/2} \left(1 - \delta_{ij}\right)\right)\mathbf{I} \equiv H_{ij}\mathbf{I}, \tag{5}$$

with $\alpha = \zeta_r l \sqrt{6/\pi}$ 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.

We observe now that the motion of the different components X_i, Y_i, and Z_i decouples. Hence one may restrict oneself to either one of the components, say Y_i. Setting $\sigma = K/\zeta$ and $\mathbf{Y} = (Y_1, Y_2, ..., Y_N)^T$, $\mathbf{f} \equiv (f_1, f_2, ..., f_N)^T$ and $\mathbf{F} \equiv (F_1, F_2, ..., F_N)^T$, where T denotes the transposed vector, leads to the Langevin equation [8,9,18,23-25];

$$\frac{d\mathbf{Y}(t)}{dt} + \sigma \mathbf{HAY}(t) = \frac{1}{\zeta}\mathbf{H}[\mathbf{f}(t) + \mathbf{F}(t)], \tag{6}$$

where the matrix A is defined as after Eq. (4). Equation (6) has the following formal solution:

$$\mathbf{Y}(t) = \frac{1}{\zeta}\int_{-\infty}^{t} dt' \exp[-\sigma(t-t')]\mathbf{HA}]\mathbf{H}[\mathbf{f}(t') + \mathbf{F}(t')]. \tag{7}$$

To bring Eq. (7) to a more manageable form, one proceeds by diagonalizing the product **HA**, i.e. by determining *N* linearly independent normalized eigenvectors $\mathbf{Q}_i$ of **HA**, so that $\mathbf{HAQ}_i = \lambda_i \mathbf{Q}_i$. **HA** has only one vanishing eigenvalue, which we denote by λ_1. A further simplification of Eq. (7) arises when a constant external force **F** acts on a single monomer. Assuming now that this monomer is picked randomly, but once chosen *fixed* (quenched disorder), one obtains [8,9,16-18, 26,27] for the doubly averaged *Y(t)* (averaged both over the thermal fluctuations and over the positions of all the monomers in the GGS):

$$\langle\langle Y(t)\rangle\rangle = \frac{F\tilde{H}_{1,1}t}{N\zeta} + \frac{F}{\sigma N\zeta}\sum_{i=2}^{N}\frac{1-\exp(-\sigma\lambda_i t)}{\lambda_i}\tilde{H}_{ii}. \tag{8}$$

Here $\tilde{H}_{ii} = \sum_{k,l} Q^{-1}_{ik} H_{kl} Q_{li}$ and $\tilde{H}_{1,1}$ simplifies to $\tilde{H}_{1,1} = \sqrt{N}\sum_k Q^{-1}_{1k} H_{k1}$. In the Rouse case, where **H=I**, one has even that $\tilde{H}_{ii} = 1$.

Hyperbranched Structures: Dendrimers and Regular Hyperbranched Fractals

In previous work we have studied topologically distinct structures, ranging from star molecules to Sierpinski-type fractals and to networks composed of subunits [8,9,18,26-33]; here we restrict ourselves to hyperbranched macromolecules. Their study is, in general, much simplified, since they are (topologically-speaking) trees, i.e. they are devoid of loops. A most prominent subclass of hyperbranched macromolecules form the dendrimers; one dendrimer is depicted on the left side of Fig. 1. Dendrimers start from a central core from which f arms emerge. In Fig. 1 this central part is indicated by a dashed circle. 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 realisations of finite Cayley-trees. For $f=3$ the dendrimer consists of $N = 3\cdot(2^g-1)+1$ beads, and its number of bonds is $3\cdot(2^g-1)$.

We now turn to another class of hyperbranched polymers, namely to regular hyperbranched fractals (RHF), which we also present in Fig. 1. Our study is motivated by the search of scaling [10,11]; we recall that such RHFs (generalized Vicsek fractals) [7] 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 in Fig. 1 by a dashed 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 on its right side 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 fractal [7]. Embedded in the 2d-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 $\bar{d}_f = 2\bar{d}_r$. Furthermore, in many dynamical features, such as $\langle\langle Y(t)\rangle\rangle$, the spectral dimension $\tilde{d}$ enters; for general RHF one has [7] $\tilde{d} = 2\ln(f+1)/\ln(3f+3)$.

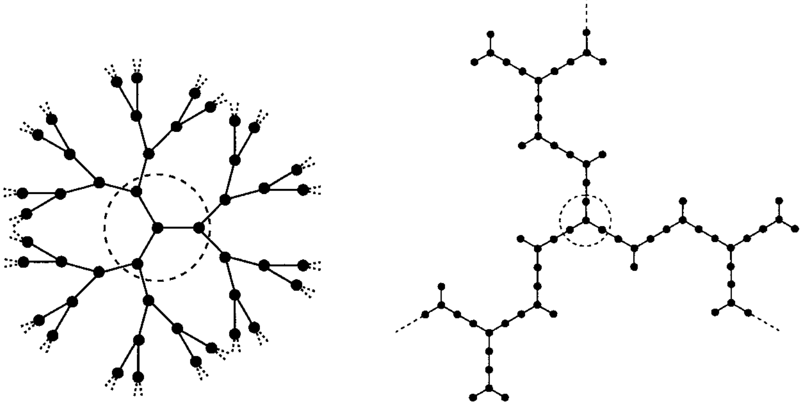

Figure 1. Left: Dendrimer with functionality $f = 3$ at the fourth generation, $g = 4$. Right: Regular hyperbranched fractal (RHF) with $f = 3$ at generation $g = 3$.

For the possible chemical realization of RHFs we note from Fig. 1 that RHFs are built from structural entities whose valence c equals 1,2 and f, entities which we denote by M_1, M_2 and M_f, respectively. One has a large variety of M_f entities at one's disposal, such as the building blocks of polycarbosilanes [34] or copolyesters [35]. For $f = 3$, condensed triarylamines are interesting candidates; they have been synthesized as bridged molecules [36] and exist in a polymer phase [37]. A fact to be remarked, see Fig. 1, is that chemical compounds corresponding to RHFs with small f, say $f = 3$, do not suffer for large g from the extreme overcrowding found in dendrimers.

Drift Patterns

As shown above, the evaluation of $\langle\langle Y(t)\rangle\rangle$, Eq. (8), requires the knowledge of the eigenvectors and eigenvalues of the matrices **A**, **HA** and $\mathbf{Q}^{-1}\mathbf{HQ}$. In the presence of HI one needs first to diagonalize **A** in order to obtain the $\langle R_{ij}^2\rangle$, needed in Eq. (5) for **H**; the diagonalization of **HA** leads then to the eigenvalues required in order to compute $\langle\langle Y(t)\rangle\rangle$ based on Eq. (8). In the absence of HI (Rouse case), it is sufficient to know all the eigenvalues of **A**. For dendrimers and for RHFs the evaluation of the eigenvalues of **A** is a simple matter, since one can avoid the direct numerical diagonalization of **A** by making use of analytical recurrence relations, see Refs. [7,24,33] for a review. For **HA**, on the other hand, direct diagonalization and inversion procedures [38-40] are necessary, which imply (because of restricted computer time and memory) an upper limit of roughly 5.000 segments for the polymers to be treated.

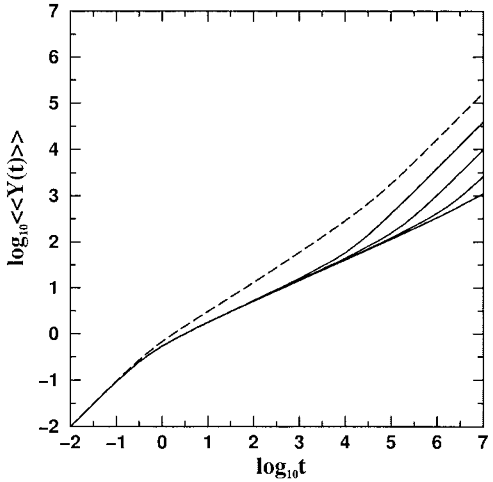

Figure 2. The averaged monomer displacement $\langle\langle Y(t)\rangle\rangle$ under an external force. Displayed are in doubly-logarithmic scales to basis 10 and in dimensionless units both t and the normalized $\langle\langle Y(t)\rangle\rangle$, see text for details

The results of our numerical evaluations for $\langle\langle Y(t)\rangle\rangle$ are presented in Fig. 2 for RHFs with $f=3$. We set $\sigma=1$ and $F/\zeta=1$. The calculations in the Rouse case (given by continuous curves) are for the systems $N = 4^4, 4^5, 4^6$, and 4^7 from above. For the system with $N = 4^6$ we have also performed calculations under HI-conditions, taking $\zeta_r = 0.25$; the results are given through a dashed curve. Note that in Fig. 2 the scales are doubly logarithmic. Clearly evident from the figure is that at long times one reaches a linear domain, $\langle\langle Y(t)\rangle\rangle \simeq F\tilde{H}_{11}t/(N\zeta)$, see Eq. (8). Because of the N dependence of $\langle\langle Y(t)\rangle\rangle$, in Fig. 2 the curves belonging to RHFs of different sizes are shifted with respect to each other. On the other hand, for very short times all of the curves merge; this is the domain where $\langle\langle Y(t)\rangle\rangle = Ft/\zeta$. In the logarithmic scales of Fig. 2 these two domains appear as straight lines with slope 1. Now, as often stressed [6-9,17,18,29-31], the intermediate domain is that which is typical for the polymer considered. In Fig. 2 the intermediate domain appears as a straight line, whose slope γ is less than unity. This demonstrates nicely that $\langle\langle Y(t)\rangle\rangle$ scales, i.e. obeys Eq. (3), with $\gamma \simeq 0.45 \simeq 1 - \tilde{d}/2$ in the absence and $\gamma \simeq 0.64$ in the presence of HI. This finding is remarkable, especially when compared to other fractal structures, such as the Sierpinski-gaskets. There one finds that scaling is obeyed in the Rouse case (no HI), but not in the Zimm case (with HI) [30]. We hence expect that diffusion-limited reactions involving RHFs might lead to decay laws obeying Eq. (2).

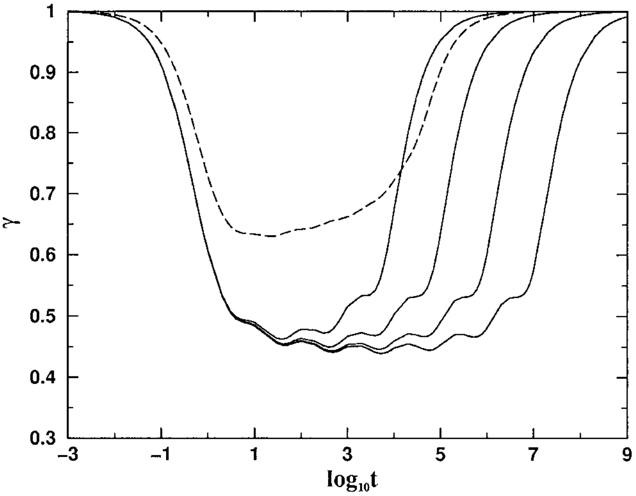

Figure 3. The slope γ (derivative) of Fig. 2, see text for details.

In order to render the scaling analysis more quantitive, we plot in Fig. 3 the derivative of the curves of Fig. 2; for forms obeying Eq. (3) the derivative would equal γ. In both cases (with and without HI) the intermediate domains show very broad minima; superimposed on these is a waviness due to the hierarchical structure of the particular RHF.

We stop to note that dendrimers behave differently in the intermediate range; neither in the presence nor in the absence of HI do dendrimers show scaling. What one observes (see Refs. [8,9,18] for details) is a somewhat logarithmic dependency, when one plots $\langle\langle Y(t)\rangle\rangle$ in double logarithmic scales. The reason for this is to be found in the exponential growth of the dendrimer in each generation, an aspect which gets mirrored in its dynamics. It follows that the observables discussed in this paper, but also more macroscopically-minded quantities, such as the mechanical moduli, can differentiate well between dendrimers and RHFs.

Summary

In this paper we have concentrated on regular hyperbranched fractals (RHFs), a class of polymers whose dynamical properties obey scaling; these objects have well-determined fractal and spectral dimensions. Using the GGS-formalism we have calculated the displacement of RHF-type macromolecules in solution, where we have also taken the influence of hydrodynamic interactions into account. The general picture that emerges is that RHF-type macromolecules do obey scaling, fact with differentiates them from the dendrimers. RHFs are also prime candidates for future studies of diffusion-limited reactions involving macromolecules with complex topology. We do hope that substances with RHF-architecture will be soon synthesized, thus allowing for their experimental investigation.

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