Chaos, Solitons and Fractals 81 (2015) 527–533

Contents lists available at ScienceDirect

Chaos, Solitons and Fractals

Nonlinear Science, and Nonequilibrium and Complex Phenomena

journal homepage: www.elsevier.com/locate/chaos

Exploring the applications of fractional calculus: Hierarchically built semiflexible polymers

Florian Fürstenberg, Maxim Dolgushev*, Alexander Blumen

Theoretical Polymer Physics, University of Freiburg, Hermann-Herder-Str. 3, Freiburg, D-79104, Germany

ARTICLE INFO

Article history:
Available online 26 July 2015

Keywords:
Anomalous diffusion
Fractals
Polymers
Hyperbranched
Semiflexible

ABSTRACT

In this article we study, through extensions of the generalized Gaussian scheme, the dynamics of semiflexible treelike polymers under the influence of external forces acting on particular (say, charged) monomers. Semiflexibility is introduced following our previous work (Dolgushev and Blumen, 2009 [15]), a procedure which allows one to study treelike structures with arbitrary stiffness and branching. Exemplarily, we illustrate the procedure using linear chains and hyperbranched polymers modeled through Vicsek fractals, and obtain in every case the monomer displacement averaged over the structure. Anomalous behavior manifests itself in the intermediate time region, where the different fractal architectures show distinct scaling behaviors. These behaviors are due to the power law behavior of the spectral density and lead, for arbitrary pulling forces, based on causality and the linear superposition principle, to fractional calculus expressions, in accordance to former phenomenological fractional laws in polymer physics.

1. Introduction

One of the milestones of polymer science is the relationship between structure and dynamics. A major role in this aspect plays the polymer architecture, which can be taken into account using the generalized Gaussian structures' (GGS) formalism [1,2]. Now, for several classes of polymers the role of their topology on the dynamics in external fields has been studied using the standard GGS formalism. This classes include stars and dendritic polymers [3], scale-free polymer networks [4,5], hyperbranched polymers modeled by Vicsek fractals [6,7], Sierpinski gaskets [8], and also multihierarchical fractals [9]. In this respect regular fractal structures are of much interest since their dynamical properties may display scaling. From a practical point of view several types of hierarchically built, regular structures allow one to study their dynamics to a large extent analytically [6–8].

However, the standard GGS formalism neglects some important polymer features, such as the excluded volume and the hydrodynamic interactions; moreover, in the standard GGS approach the semiflexibility of polymer strands is not accounted for. Now, semiflexibility is particularly important when macromolecules of biological interest, such as DNA [10] or actin networks [11] are investigated, which possess a significant degree of stiffness [12–14]. Recently, we presented ways of taking such stiffness into account through an extension of the GGS-model for semiflexible treelike polymers (STP) [15]. In fact, the new model is quite general: It allows to treat treelike structures, in which at each single junction the functionality (number of nearest neighbors) and the degree of semiflexibility can vary. Clearly, the presence of such additional parameters renders the STP theory more complex than the standard GGS method. Nonetheless, as we showed recently in treating regular fractal structures, the STP framework still allows to handle semianalytically very large structures, which otherwise would not be accessible to a brute-force diagonalization procedure [16].

* Corresponding author. Tel.: +497612035903.
E-mail address: dolgushev@physik.uni-freiburg.de (M. Dolgushev).

http://dx.doi.org/10.1016/j.chaos.2015.07.006
0960-0779/

Nowadays, new techniques allow to manipulate particular sites of polymers, say by letting such sites be dragged by external pulling forces [11,17]. It is thus of interest to analyze theoretically the impact of external fields on the polymers' dynamics. To be more specific, here we study the dynamics of semiflexble Vicsek fractals (VF) under such external forces, by employing a Langevin approach based on the STP-method [15]. A basic quantity is then the average over the structure (structural average, SA) of the mean monomer displacement $\langle\langle y(t)\rangle\rangle$ as a function of time. As we proceed to show, in the STP-framework the $\langle\langle y(t)\rangle\rangle$ obeys an equation formally very similar to that found in the GGS model, the difference residing in the different eigenvalues obtained in the presence or absence of stiffness. This allows us to study the $\langle\langle y(t)\rangle\rangle$ of semiflexible VF by using the reduced diagonalization scheme of Ref. [16]. As we proceed to show, the displacements of the VF monomers are sensitive to the inclusion of local stiffness constraints, especially for short times. However, the particular character of the subdiffusive behavior remains unchanged. This result differs from the behavior of linear chains, for which similar local constraints lead to a new, additional subdiffusive scale for short times.

The paper is structured as follows: Section 2 is devoted to the theoretical model; in it we display the necessary extensions of the GGS to include stiffness and we discuss the role of the external fields. In Section 3 we briefly recall structural and spectral properties of VF. In Section 4 we study the dynamics of VF. In each case we display the numerically evaluated $\langle\langle y(t)\rangle\rangle$ and discuss the findings in the presence of stiffness. The paper ends with our conclusions.

2. The model

Both the GGS [1] and the STP model [15] are based on the classical bead-and-spring picture [18]. We will use $\{\mathbf{r}_k\}$ to denote the centers of the N beads and $\{\mathbf{d}_a\}$ for the $N-1$ bonds (springs), so that e.g. $\mathbf{d}_a = \mathbf{r}_n - \mathbf{r}_m$ is the bond connecting n and m. Following [15,19–23], semiflexibility is introduced based on the potential

$$V_{\mathrm{STP}}(\{\mathbf{d}_a\}) = \frac{K}{2}\sum_{a,b} W_{ab}\,\mathbf{d}_a\cdot\mathbf{d}_b. \tag{1}$$

Here the sum runs over all bonds a and b. The spring constant is $K = 3k_BT/l^2$, while k_B and T denote the Boltzmann constant and the temperature, respectively, while l^2 is the bond mean-square length, which is taken to be identical for all bonds. For trees the bonds $\{\mathbf{d}_a\}$ are independent of each other. Assuming them to be Gaussian distributed implies for the averages $\langle\mathbf{d}_a\cdot\mathbf{d}_b\rangle$ that [15]

$$\langle\mathbf{d}_a\cdot\mathbf{d}_b\rangle = l^2(\mathbf{W}^{-1})_{ab}, \tag{2}$$

so that the matrix $\mathbf{W} = (W_{ab})$ is known when all the values $\{\langle\mathbf{d}_a\cdot\mathbf{d}_b\rangle\}$ are known. Now following the traditional assumptions [15,19–23] the average square length of all bonds is taken to be constant, say $\langle\mathbf{d}_a^2\rangle = l^2$, and for two adjacent bonds, say $\mathbf{d}_a$ and $\mathbf{d}_b$, one requires that

$$\langle\mathbf{d}_a\cdot\mathbf{d}_b\rangle = \pm l^2 q_i \tag{3}$$

is obeyed, where the plus sign holds for a head-to-tail orientation of the bonds and the minus sign otherwise. In Eq. (3) q_i is the stiffness parameter related to site i, common to the bonds $\mathbf{d}_a$ and $\mathbf{d}_b$. Further relations between nonadjacent bonds follow readily from a maximum entropy principle and turn out to be consistent with the picture of freely-rotating segments [15]. Thus, any two non-adjacent bonds, say $\mathbf{d}_a$ and $\mathbf{d}_c$, fulfill the condition

$$\langle\mathbf{d}_a\cdot\mathbf{d}_c\rangle = \langle\mathbf{d}_a\cdot\mathbf{d}_{b_1}\rangle\langle\mathbf{d}_{b_1}\cdot\mathbf{d}_{b_2}\rangle\cdots\langle\mathbf{d}_{b_k}\cdot\mathbf{d}_c\rangle l^{-2k}, \tag{4}$$

where $(b_1,\ldots,b_k)$ is the unique path connecting a and c.

As it was shown in Ref. [15], based on Eqs. (2)–(4) the matrix $\mathbf{W}$ can be expressed for treelike structures analytically. Transforming the bond variables $\{\mathbf{d}_a\}$ to bead variables $\{\mathbf{r}_k\}$ one obtains the potential energy of a STP [15]

$$V_{\mathrm{STP}}(\{\mathbf{r}_i\}) = \frac{K}{2}\sum_{i,j=1}^{N} A_{ij}^{\mathrm{STP}}\mathbf{r}_i\cdot\mathbf{r}_j, \tag{5}$$

where the elements of the matrix $\mathbf{A}^{\mathrm{STP}} = (A_{ij}^{\mathrm{STP}})$ are as follows [15]:

$$A_{ii}^{\mathrm{STP}} = \frac{f_i}{1-(f_i-1)q_i} + \sum_{i_k}\frac{(f_{i_k}-1)q_{i_k}^2}{1-(f_{i_k}-2)q_{i_k}-(f_{i_k}-1)q_{i_k}^2}, \tag{6}$$

$$A_{ii_k}^{\mathrm{STP}} = -\frac{1-(f_i-1)(f_{i_k}-1)q_iq_{i_k}}{(1-(f_i-1)q_i)(1-(f_{i_k}-1)q_{i_k})}, \tag{7}$$

and

$$A_{ii_{ks}}^{\mathrm{STP}} = \frac{q_{i_k}}{1-(f_{i_k}-2)q_{i_k}-(f_{i_k}-1)q_{i_k}^2}. \tag{8}$$

In Eqs. (6)–(8) i_k denotes a nearest neighbor of bead i and i_{ks} denotes a next-nearest neighbor of bead i, which is connected to i through the bead i_k. Moreover, q_j stands for the stiffness degree and f_j for the functionality (number of nearest neighbors) of bead j.

Now, the dynamics of STP is given by the following set of Langevin equations:

$$\zeta\dot{\mathbf{r}}_n(t) + \frac{\partial}{\partial\mathbf{r}_n}V_{\mathrm{STP}}(\{\mathbf{r}_i(t)\}) = \tilde{\mathbf{f}}_n(t) + \mathbf{F}_n^p(t), \quad \text{for } n = 1,\ldots,N. \tag{9}$$

Here ζ is the friction coefficient, $V_{\mathrm{STP}}(\{\mathbf{r}_i\})$ is given by Eq. (5), and $\tilde{\mathbf{f}}_n(t)$ is the random force (thermal noise) acting on the nth bead; the distribution of $\{\tilde{\mathbf{f}}_n(t)\}$ is taken to be Gaussian with $\langle\tilde{\mathbf{f}}_n(t)\rangle = 0$ and $\langle\tilde{f}_{\alpha n}(t)\tilde{f}_{\beta m}(t')\rangle = 2k_BT\zeta\,\delta_{\alpha\beta}\delta_{nm}\delta(t-t')$. In this way Eq. (9) fulfills the requirements of the fluctuation-dissipation-theorem, where the pulling forces $\mathbf{F}_n^p(t)$ are in principle arbitrary and are assumed to act on a particular bead (say the kth) only. To fix the ideas, $\mathbf{F}_n^p(t)$ is switched on at time $t = 0$ and is oriented along the y-axis. Hence

$$\mathbf{F}_n^p(t) = \delta_{nk}F_0\theta(t)\mathbf{e}_y, \tag{10}$$

where F_0 is the magnitude of $\mathbf{F}_n^p(t)$ and $\mathbf{e}_y$ is the unit vector in the y-direction. With it the y-components of the Langevin set, Eq. (9), read:

$$\zeta\dot{y}_n(t) + K\sum_{m=1}^{N} A_{nm}^{\mathrm{STP}}y_m(t) = \tilde{f}_{yn}(t) + \delta_{nk}F_0\theta(t), \quad \text{for } n = 1,\ldots,N, \tag{11}$$