Macromol. Symp. **2004**, *217*, 267-272

Polymer Chain Dynamics Predicted by n-Renormalized Rouse Models: Numerical Studies

Margarita Kroutieva,[*1] *Nail Fatkullin,*[1] *Rainer Kimmich*[2]

[1] Department of molecular physics, Kazan State University, Kremlevskaya 18, Kazan, Russia
E-mail: margarita.kroutieva@ksu.ru
[2] Universität Ulm, Sektion Kernresonanzspektroskopie, 89069 Ulm, Germany

Summary: Features of the renormalized and twice renormalized Rouse models were examined numerically. Based on numerical evaluations of the generalized Langevin equation in renormalization approaches, nonexponential normal mode autocorrelation functions were derived, that can be described over two orders of magnitude by stretched exponential functions. The mode number dependence of the stretching parameter was evaluated. The consequences of the nonexponential correlation functions on dynamical properties are discussed. As a basis for predictions for the behavior of diffusion and spin-lattice relaxation dispersion, the time dependence of the mean-squared segment displacement and of the autocorrelation function of the segment tangential vector, respectively, were obtained taking into account finite chain lengths.

Keywords: generalized Langevin equation; relaxation; renormalized Rouse model; segment diffusion; theory

Introduction

The elucidation of dynamical properties of entangled polymer melts is the main challenge of statistical physics of macromolecules. The term "chain entanglement" in general represents the topological constraints and the excluded-volume effect of a matrix consisting of polymer chains longer than the critical length (L_c). The general task to be solved in context with entangled polymer dynamics is how to reduce the multi-chain entanglement problem to a tractable formalism.

Essentially there are two different approaches under discussion in the current literature. In the reptation (tube) model the entanglement effect is intuitively thought to result in a fictitious tube in which the tagged chain is confined on a time scale shorter than the "disengagement time" (τ_d) [1]. Besides the phenomenological reptation theory an alternative, microscopic approach for the treatment of entangled polymer melts was proposed [2]. It is based on the approximate solution of

DOI: 10.1002/masy.200451321

the generalized Langevin equation (GLE) of motion for the n-th Kuhn segment,

$$\zeta_0\left[\frac{\partial\vec{r}_n(t)}{\partial t}+\int_0^t\sum_m\Gamma_{nm}(t-\tau)\frac{\partial\vec{r}_m(\tau)}{\partial\tau}d\tau\right]=\frac{3k_B\mathrm{T}}{b^2}\frac{\partial^2\vec{r}_n}{\partial n^2}+\vec{F}_n^Q(t), \tag{1}$$

by using the Zwanzig-Mori projection operator technique. ζ_0 is the "bare" friction coefficient of a Kuhn segment, k_B is the Boltzmann constant, T is the absolute temperature, b is the Kuhn segment length, and $\vec{F}_n^Q(t)$ is the "projected" stochastic force acting on the Kuhn segment number n at time t. The quantity $\Gamma_{nm}(t)$ denotes the memory matrix which describes projected dynamical correlations of the fluctuating part of intermolecular forces acting on the segments with numbers n and m at the times 0 and t. These forces alone are the actual cause of entanglement effects in polymer systems.

The memory matrix term qualitatively reflects two most important consequences of the entanglement effect on chain dynamics. Polymer chains cannot cross each other. Firstly, this leads to motional correlations increasing with the number of neighboring chains during some time interval. That is, friction *increases with time*. This effect is accounted for by the time integral in Eq. 1. Secondly, the friction phenomenon becomes *nonlocal*: Motions of segment m induce a friction force acting on segment n. The dependence of the memory matrix on the numbers of two segments, n and m, takes this qualitatively into account. There is a number of fundamental insoluble problems of general character connected with this picture (see detailed discussions in [3] and especially in review [8]). That is, explicit expressions for the memory matrix cannot be derived in an exact and systematic way.

Renormalized Rouse models adopt the superposition approximation for reducing three particle correlation functions, that are hidden in the spelt-out definition of the memory matrix. A special kind of approximation named after Ref. [2] "renormalization" is used. The essence of the renormalization is the following. The memory matrix contains variables, the time dependence of which is determined by the so-called *"projected"* dynamics in contrast to the *real* dynamics relevant for experiments. The first renormalization, referred to simply as "Renormalized Rouse Model" (RRM), is nothing more than approximating the unknown projected dynamics by the dynamics expected in the frame of the ordinary Rouse Model valid in the absence of any memory term. The second renormalization, producing the "Twice Renormalized Rouse Model" (TRRM), is the approximation of the projected dynamics by the dynamics predicted by the RRM. The "nfold-Renormalized Rouse Model" is analogously defined by the use of the *(n-1)*-fold-Renormalized Rouse Model as an approach for the projected dynamics.

The way how the *n*-fold-Renormalized Rouse Model is formulated resembles iterative algorithms for the derivation of approximate solutions of a known equation. However, there is a significant difference. Actually the *n*-fold renormalization is a way for the determination of an underdetermined equation rather than an algorithm for finding approximate solutions. The iterative repetition of the renormalization procedure does not necessarily lead to solutions approaching reality more and more.

The mathematical analysis of the memory matrix [8] for a melt of infinitely long polymer chains shows that a qualitative transition of the memory matrix properties arises after the third renormalization step. There will be no longer any time regime in which the normal mode dynamics approaches Markovian behavior. Therefore, n=3 is a mathematically and physically distinct limit beyond which further renormalizations diverge from reality. Regarding the general scaling predictions of *n*-fold renormalizations for the self-diffusion coefficient, $D_{nRR} \propto \frac{b^2}{\tau_s \psi^n} N^{-\left(\frac{n+2}{2}\right)}$, and for the terminal relaxation time, $\tau_1^{nRR} \propto \tau_s \psi^n N^{\frac{n+4}{2}}$, in comparison to experimental data also suggests, that n=3 provides a reasonable approach.

In our previous paper [3] the dynamical properties of the RRM and TRRM were already investigated in the Markovian approximation resulting in exponential decays of the normal mode autocorrelation functions. The main objective of the present study is to investigate the dynamical properties of *n*-times renormalized Rouse theories numerically.

Results

The numerical mode autocorrelation functions derived from the GLE with the aid of renormalization approaches are nonexponential for intermediate mode numbers ($1<p<<N$) as shown in Figure 1. The autocorrelation functions can be approximated over two orders of magnitude in the range $C_p(t)/C_p(0) \geq 0.01$ by stretched exponential functions:

$$C_p(t) = C_p(0) exp\left[-\left(t/\tau_p^*\right)^{\beta_p}\right]. \qquad (2)$$

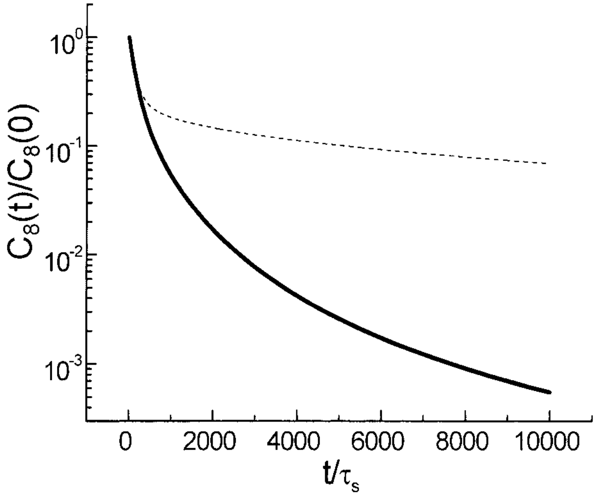

Figure 1. Normal mode autocorrelation function for p=8 of polymer chains consisting of N=100 segments. The entanglement parameter is assumed to be ψ =1. The curves refer to the renormalized (RRM, solid line) and to the twice renormalized Rouse (TRRM, dash line) models.

The fitting parameters β_p and τ_p^* depend on the mode number, the chain length, and the entanglement parameter ψ, which is proportional to the initial norm of the memory matrix and can be expressed in principle by microscopic parameters of the system [2, 3, 6, 8]. In the TRRM, β_p and τ_p^* differ from those found for the RRM. The parameter τ_p^* can be expressed by the normal mode relaxation time τ_p and the stretching parameter β_p. The stretching parameter β_p shows a minimum as a function of the normal mode number p, and approaches unity for decreasing p (see Figure 2).

The minimum values of the stretching parameter are 0.26 and 0.67 for the TRRM and RRM, respectively (p=8, N =100, ψ =1). These values correspond to a nonexponentiality of the autocorrelation functions predicted for the TRRM stronger than for the RRM (Figure 1). Qualitatively the same behavior of the stretching parameter was found in computer simulations reported in Refs [4,5].

The nonexponentiality of the normal mode autocorrelation functions and the finite length of the polymer chains lead to slower dynamics than expected for the asymptotical Markovian approximation for infinitely long chain lengths $N \to \infty$.

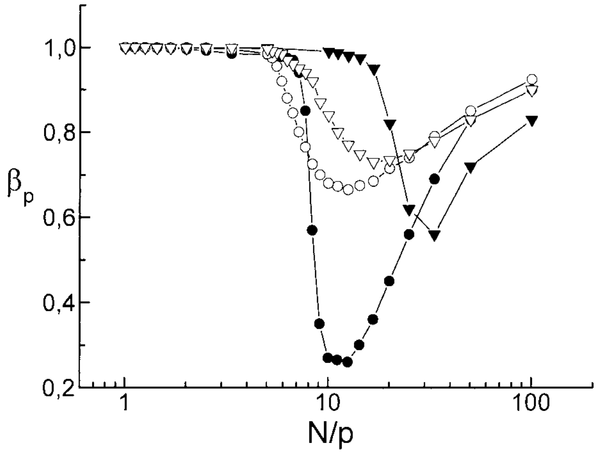

Figure 2. Mode number dependence of the stretching-parameter β_p for the RRM and TRRM for different entanglement parameters: ψ = 0.4 (hollow triangles), ψ = 1 (hollow circles) for RRM and ψ = 0.1 (filled triangles), ψ = 1 (filled circles) for TRRM. The number of Kuhn segments was assumed to be N=100.

The time dependence of the mean-squared segment displacement following from the TRRM is plotted in Figure 3. As a consequence of the finite chain length and the nonexponential autocorrelation functions, the slope at short times becomes asymptotically flatter. The autocorrelation function of the segment tangential vector is plotted in Figure 4 versus time. This function determines spin-lattice relaxation [6,7]. It is also influenced by the finite length and the nonexponential behavior of the normal mode autocorrelation functions.

We anticipate that numerical results for the three times renormalized Rouse Model (ThRRM) which can be formulated as it was described in the introduction will show similar tendencies. The autocorrelation functions are expected to be more strongly nonexponential, and the dynamics is slowed down relative to the corresponding Markovian approximation.

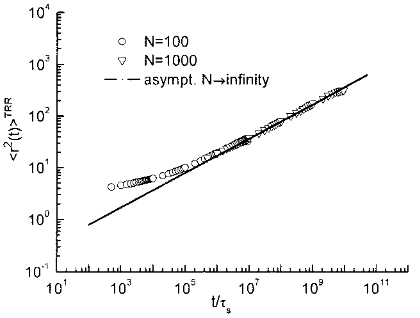

Figure 3. Mean-squared segment displacement for polymer chains of different lengths (N=100 and N=1000) and for an entanglement parameter ψ=1 according to the TRRM. The solid line represents the Markovian approximation $N \to \infty$.

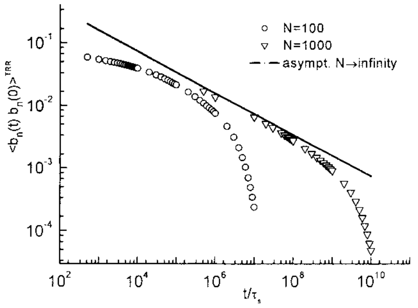

Figure 4. Autocorrelation function of the tangential vector of segments for different chain lengths (N=100 and N=1000). The entanglement parameter is ψ=1. The data have been calculated for the TRRM and are compared with the Markovian approximation (solid line).

Conclusions

The generalized Langevin equation was evaluated numerically using renormalization approaches. According to the RRM and TRRM, the normal mode autocorrelation function decays nonexponentially for intermediate mode numbers and can be approximated by stretched exponential functions. The mode number dependence of the stretching parameter is in accordance with computer simulation results [4,5]. Compared with the Markovian approximation for infinitely long chains, $N \to \infty$, chain dynamics is slowed down by the nonexponentiality of the autocorrelation functions and the finite length of the polymers.

This work was supported by the Volkswagen-Stiftung (1/74602), RFBR (02-03-32921 and 03-03-06209) and CRDF BRHE.

[1] Doi M, Edwards S.F., "*The Theory of Polymer Dynamics*", Clarendon, Oxford **1986**
[2] Schweizer K.S., *J. Chem. Phys.* **1989**, *91*, 5802
[3] N.F.Fatkullin, R.Kimmich, M.Kroutieva, *JETP* **2000**, *91*, No 1, 150
[4] Shaffer J.S., *J. Chem. Phys.* **1995**, *103*, 761
[5] Padding J.T. and Briels W.J., *J. Chem. Phys.* **2002**, *117*, 925
[6] Fatkullin N. and Kimmich R., *J. Chem. Phys.* **1994**, *101*, 822
[7] Fatkullin N., Kimmich R. and Weber H.W., *Phys. Rev. E* **1993**, *47*, 4600
[8] Kimmich R and Fatkullin N., Polymer chain dynamics and NMR, *Advan. Polym. Sci.* **2004**, *170*, p.5.