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Alternative off-lattice model with continuous backbone mass for polymers

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We present an alternative model for polymers with flexible one-dimensional rod chains as backbone. This model is able to simulate polymers consisting of large monomer units that cannot be described by a bead spring model with satisfying results. In spite of using large coarse grained units no bond crossing can occur because of a continuous excluded volume along the backbone. Our model provides an effective way to describe anisotropic monomers with respect to their mass and their nonbonded interactions. The rods interact with confocal force fields. The geometric shape of the chemically realistic monomers is conserved by using ellipsoids which represents the interaction volume as building units for the coarse grained model of the monomers. Static and dynamic properties of linear polymer melts are investigated using a parametrization for the bisphenol-A-polycarbonate. We give evidence that our model is able to reproduce the expected scaling behavior of static and dynamic properties of polymer melts. Moreover, we are able to study the reptation behavior in a computationally efficient way.
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I. INTRODUCTION

The interest in the physics of polymers was pushed by the need of new materials in all fields of everyday life. Prominent examples for this are plastic bags made out of polyethylene or compact discs which mainly consist of bisphenol-A-polycarbonate (BPA-PC). The properties of these materials were investigated by experiments and for some a theory has been established. Nevertheless computer simulations can give a more detailed picture in this context.

Polymers can be modeled for computational purposes in a variety of ways; for a recent review see Binder [1]. Depending on the kind of question and the degree of abstraction, one has the basic choice between a model on a lattice or in continuous space. The bond fluctuation model [2] is one of the prominent representatives for a polymer model on the lattice. The main advantage of this type of models is the computational efficiency due to the restricted configuration space. With increasing computer power it was possible to stay closer to reality by simulating polymers by continuum models. Two widely used models of this class are the bead spring [3] and the united atom model [4]. In both models monomers or parts of them are considered to be represented by spherical force fields. In the united atom model the CH_2 groups are modeled by a spherical force field and the bonded interactions by harmonic forces. In this more atomistic model the anisotropic intermolecular potential functions of polyatomic molecules are constructed using spherical force fields. As an effect the inner degrees of freedom of the molecules like the stiff bonds between the units must also be taken into account. As the Newton equations have to be integrated such molecular-dynamics simulations are restricted to small time scales.

Other models have been developed in order to adapt an aspherical model to a molecule's geometry, i.e., the Kushick and Berne model [5] and the Gay and Berne model [6]. They consider ellipsoids as a model for molecules and calculate the forces between two interacting ellipsoids as a function of the overlap volume. As far as we know these models have not been used to study flexible polymers and have not been linked together to form a linear chain with a continuous backbone mass.

Our approach is an off-lattice model aiming at the diversity of the single polymers and simplifying the reconstruction of the correlation between monomer structure and polymer properties, which is difficult to deal with using the other models. Our model improves the simulation of polymers in two ways: (1) For the first time the geometry of the monomers enters into a model of polymers. In our model we construct the monomers of the polymer using ellipsoids that represent the interaction volume. In this volume we assumed the existence of a confocal force field which resembles the scaling behavior of realistic force fields. In contrast to ellipsoidal force fields this field reduces to a sphere with increasing distance to the generating point. (2) With our model it is possible to simulate polymer chains by a continuous flexible one dimensional mass. The masses of the atoms are combined to one unit and not concentrated in the center of mass like in a bead spring model but replaced by a one-dimensional axis. This is an important improvement even if the mass of the building units is not asymmetric as the geometry requires.

For a linear polymer this means that the masses of the atoms are smeared out over the backbone and no longer distributed on points as, for example, in the united atom model. The basic idea is that, taking all conformations of the represented monomer part into account and summing them into one unit, the resulting mass density is not isotropic and zero

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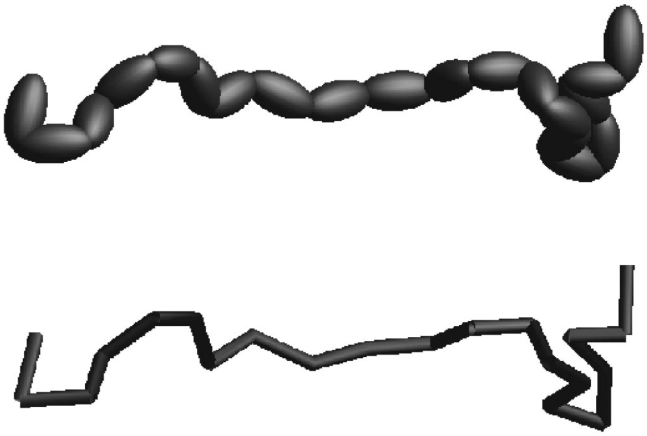

FIG. 1. Linear polymer chain modeled with the continuous backbone mass model.

dimensional. The construction of a linear polymer chain by our model is shown in Fig. 1. In the lower part the backbone of a linear polymer is shown while the upper part shows the interaction volume of the polymer chain in our model.

We apply our model to BPA-PC. In our investigations we use a parametrization for this polymer at 800 K, see Table I. We show that our model is able to reproduce the expected behavior of polymers. This is the topic of the following investigations dealing with the static and the dynamic properties of linear polymer chains.

II. CONTINUOUS BACKBONE MASS MODEL

The continuous backbone mass model in some sense interpolates between the united atom model and the bead spring model. On the one hand, it tries to stay as close as possible to the chemical realistic structure as does the united atom model, but on the other hand it integrates out all the inner degrees of freedom in the same way as the bead spring model in order to be computationally efficient. In contrast to these two models it uses *nonspherical* force fields for the nonbonded interaction. The main idea of this approach with a more general form of the force field is to generalize the united atom model in such a way that larger atom groups are combined into one construction unit, but the possible anisotropy of these groups is still taken into account. The reasoning is that the topology of the monomer has a strong influence on the physical properties. The simplest anisotropic geometrical object one can think of is an ellipsoid of rotational symmetric form and thus it is considered as the interaction volume of the chemical sequences in our model.

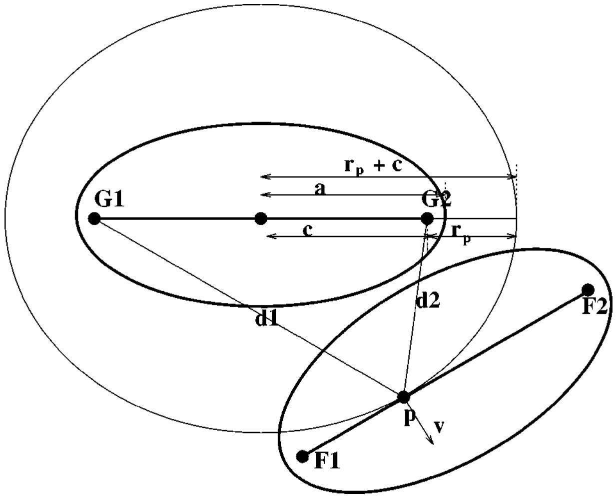

FIG. 2. Interaction with a confocal force field.

As one wants the force field to degenerate into a sphere with increasing distance, we use a confocal force field inside this interaction volume:

$$\mathcal{H}_{\text{inter}}=V_{\text{abs}}\left(\frac{d_1^{(p)}+d_2^{(p)}}{2}-c\right), \tag{1}$$

where $d_1^{(p)}$ and $d_2^{(p)}$ denote the distance of the point $\mathbf{p}$ to the focal points of the ellipsoid and V_{abs} is the absolute potential. In the case of the BPA-PC we take only a repulsive part,

$$V_{\text{abs}}(r)=r^{-6}, \tag{2}$$

into account because from quantum chemical calculations the attractive part proves to be negligible. The calculation of the distances is illustrated in Fig. 2.

The mass of the building units is distributed between the focal points of the ellipsoids, in the hard core region of the confocal potential. Because of this we perform the crossover from a zero-dimensional simulation, i.e., using point masses, of flexible polymers to a one-dimensional simulation. This also has the effect that no bond crossing can occur and thus prevents unphysical effects. These one-dimensional rods are assumed to be homogeneous. The calculation of the force of such a rod in a confocal force field leads to an elliptic integral. For this reason we use a Gaussian integration for the

TABLE I. Parameters of the continuous backbone mass model.

Properties	Reduced units	Real units
Monomer mass, m	1	4.25×10^{-25} kg
Ellipsoid volume, V	715.27	715.27 Å^3
Ellipsoid large axis, a	7.35	7.35 Å
Ellipsoid short axis, b	4.82	4.82 Å
Bond length, l	11.1	11.1 Å
Bond angle, θ_0	110.56	110.56°
Spring constant (bond length), k_b	862.81	$8.63\times10^{25} N/(m\ \text{mol})$
Bending constant (bond angle), k_θ	26.5	$2.65\times10^{24} N/(m\ \text{mol})$
Simulation time step, Δt	0.001	2.06 fs

computation of this force. In order to form a linear chain the ellipsoids are connected at their focal points.

The parametrization of this model can be generalized to explicitly include side groups as well as branched polymers, which are linked to the backbone with harmonic potentials in order to have no influence on the moment of inertia of the rod chain.

The main ingredient of the simulation is the mass matrix of our rod chains. In order to construct it we must calculate first the Lagrangian of a single rod $\mathcal{L}_i = T_i - V_i$ with the kinetic energy T_i and the potential energy V_i. The subindex i marks the position of the rods in the chain. This one-dimensional homogeneous rod i has the length l_i starting at $\vec{a}_i$ and ending at $\vec{b}_i$. If we suppose that the rods all have the same mass m and that the velocity of the rod mass scales linearly with the position between the boundaries of the rod, the kinetic energy can be written as

$$T_i = \frac{1}{2}\int_0^{l_i} \frac{m}{l_i}\left(\frac{(l_i - x)\dot{\vec{a}}_i + x\dot{\vec{b}}_i}{l_i}\right)^2 dx = \frac{1}{6} m(\dot{\vec{a}}_i^2 + \dot{\vec{a}}_i\dot{\vec{b}}_i + \dot{\vec{b}}_i^2). \tag{3}$$

Adding the single terms of the rods building the chain we get the Lagrangian $\mathcal{L}$ of the whole rod chain. The equations of motion of the chain can be calculated from the Lagrange equations of the second kind. Since the equations of motion separate in each direction, we have only to solve three tridiagonal $(N+1)\times(N+1)$ matrices per chain, which consist of N rods per time step of the form

$$\mathbf{W}\ddot{\vec{x}} = \vec{F}, \tag{4}$$

$$\frac{m}{6}\begin{pmatrix} 2 & 1 & 0 & 0 & \dots \\ 1 & 4 & 1 & 0 & \dots \\ 0 & 1 & 4 & 1 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}\begin{pmatrix} \ddot{x}_0 \\ \ddot{x}_1 \\ \ddot{x}_2 \\ \vdots \end{pmatrix} = \begin{pmatrix} F_{10} \\ F_{11} + F_{21} \\ F_{22} + F_{32} \\ \vdots \end{pmatrix}, \tag{5}$$

with the force F_{ij} on the coordinate j of the flexible point i of the chain

$$F_{ij} = -\frac{\partial V_i}{\partial j} \tag{6}$$

and $\ddot{x}_i$ denoting the accelerations of the flexible points of the chain. The flexible points are the link points of the ellipsoids and the end points of the rod chain. The subindices mark the positions in the chain: 0 and $N+1$ are the end points of the chain and the numbers between them denotes the linking points of rods in the chain.

The bonded interactions between neighboring units are given by harmonic length and angle potentials:

$$\mathcal{H}_{bond} = \tfrac{1}{2} k (r - r_0)^2, \tag{7}$$

$$\mathcal{H}_{angle} = \tfrac{1}{2} k_\theta (\cos\theta - \cos\theta_0)^2 \tag{8}$$

with the bond lengths r and the bending angles θ. Here r_0 and θ_0 denote the mean values.

In this paper we show that our model is able to reproduce the expected behavior of polymer melts concerning some static and dynamic properties. In this investigation we use a parametrization for BPA-PC obtained from quantum chemical calculations [7]. Table I gives an example for a parametrization at 800 K. In this parametrization one ellipsoid represents one monomer. The data is obtained by molecular-dynamics simulation. Time integration was done by a velocity Verlet algorithm. We simulate the polymers at high temperatures to avoid the effect of the slowing down of the motion below the glass temperature according to the Vogel-Fulcher law. This will have no effect on the structure of the simulated polymer because no bond can break and the vibrations of the bonded interactions will be held at an acceptable limit by the choice of an appropriate time step. To compute the force on the rods within the confocal force fields, we use a 10-point Gauss integration. To investigate the properties of our model we perform simulations at different chain lengths and different densities. The different densities are related to different volume fractions Φ. We calculate the volume fraction Φ as ratio of the volume where according to the given kinetic energy no monomer can be the total system volume.

A. Static properties

First we present some data and considerations concerning the static properties of a linear polymer melt within our model. We first validate that our model is able to reproduce the scaling laws of the Rouse model within the range in which they are good approximations. The Rouse model describes the polymer as a random chain of points. Two regimes can be found concerning the polymer statics: At short distances the polymer is a self-avoiding random walk as the excluded volume effect prevents the monomers from being in the same place at the same time. At long distances the polymer chain is a pure random walk since in a melt the interactions have no effect beyond a certain screening length. For example, the end-to-end distance $R = \vec{r_N} - \vec{r_1}$ of a chain consisting of N monomers obeys the scaling law $\langle R^2 \rangle \propto N^{2\nu}$ with the universal exponent ν. In the case of the simple random walk $\nu = 0.5$ and for the self-avoiding random walk $\nu \approx 0.59$.

In order to prove that this behavior of polymers is also seen in our model we compute the single chain structure factor $S_s(q)$,

$$S_s(q) = \left\langle \frac{1}{N}\left|\sum_{j=1}^{N} e^{i\vec{q}\cdot\vec{r}_j}\right|^2 \right\rangle_{|\vec{q}|}, \tag{9}$$

and estimate the screening length ξ. The index $|\vec{q}|$ indicates the spherical average over $\vec{q}$ vectors of the same absolute value. One expects good solvent properties $S_s(q) \sim q^{-2}$ on length scales $\langle l \rangle < 2\pi/q < \xi(\rho)$ and random walk behavior $S_s(q) \sim q^{-1/\nu}$ for $\xi(\rho) < 2\pi/q < \langle R^2 \rangle^{1/2}$, where ρ is the density of the polymer melt and $\nu = 0.59$ as expected by the self-avoiding random walk [8].

In Fig. 3 we show that our model reproduces the expected behavior. It displays the single chain structure factor for a volume faction of $\Phi = 0.6$ and a chain lengths of 30. We averaged over 200 configurations that were written out every 60 000 molecular-dynamics steps. Fitting straight lines with a slope $1/\nu = 1.695$, respectively, 2 to the data in Fig. 3 we find a crossover between the two regimes at q

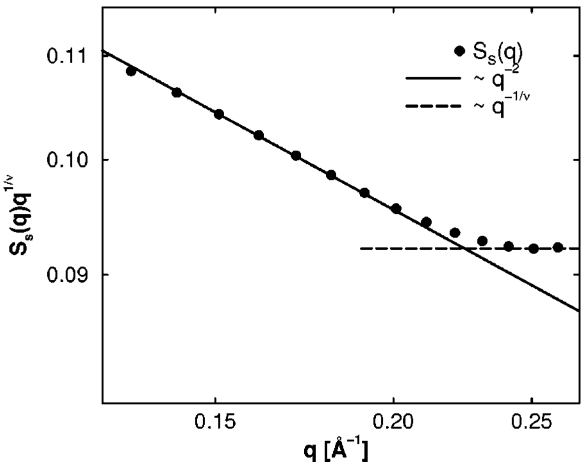

FIG. 3. Single chain structure factor for chains with length $N=30$ at $\Phi=0.60$ and $T=800$ K.

$=0.225$ Å^{-1}. This yields a screening length $\xi(\rho=1.374\ \mathrm{g/cm}^3)\approx 27.9$ Å. Since our average monomer length is about 11.1 Å, the intermolecular interaction is screened out at a distance of about 2.5 monomer lengths at a volume fraction $\Phi=0.60$.

B. Dynamic properties

The dynamics of polymers is as intriguing as ever. Whether the investigation of the dynamics is made by experiment or computer simulation, surprising new insight is found. Since the work of de Gennes [8] it was tried to find the phenomenon of reptation in polymer melts. Experimental evidence [9] and computer simulation [10,11] gave reason to believe that the reptation model is indeed valid. Previous simulation models needed very long chains concerning the number of units to reach the reptation regime, lattice models [12] as well as off-lattice models [13]. Our model shows the predicted dynamic behavior in the mean-square displacement of the chains already at 40 repeating units at a volume fraction of $\Phi=0.32$.

One advantage of a computer simulation on the monomer scale is that the positions of the monomers and their time developments are known. Thus direct insight into the dynamic behavior of polymer systems is given by the examination of various mean-square displacements. For this we define, as usual, three different displacements: the mean-square displacement of the monomers in the center of the chains,

$$g_1(t)\equiv\langle[\vec{r}_{N/2}(t)-\vec{r}_{N/2}(0)]^2\rangle, \tag{10}$$

the corresponding quantity relative to the center of mass of the chains,

$$g_2(t)\equiv\langle[\vec{r}_{N/2}(t)-\vec{R}_{\mathrm{COM}}(t)-\vec{r}_{N/2}+\vec{R}_{\mathrm{COM}}(0)]^2\rangle, \tag{11}$$

and the mean-square displacement of the center of mass of the chains (COM),

$$g_3(t)\equiv\langle[\vec{r}_{\mathrm{COM}}(t)-\vec{r}_{\mathrm{COM}}(0)]^2\rangle. \tag{12}$$

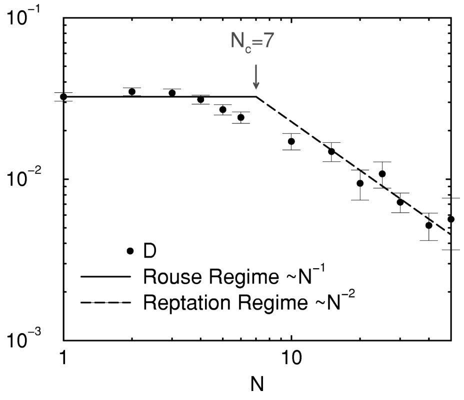

FIG. 4. Diffusion constants at $T=800$ K and $\Phi=0.60$.

The crossover from Rouse behavior to reptation dynamics can be easily shown by the investigation of the diffusion constant D,

$$D=\lim_{t\to\infty}\frac{g_3}{6t}. \tag{13}$$

According to the reptation theory one would expect a crossover from $\sim N^{-1}$ to a $\sim N^{-2}$ regime [14]. Our data in Fig. 4 for a density of $\Phi=0.60$ show a crossover from a Rouse to a reptation regime that is consistent with the reptation theory. The entanglement length N_e is twice the chain length N_c where this crossover occurs, $N_e=2N_c$. Using this correlation we find $N_e=4\pm1$ at this density. This is an interesting result due to the fact that for studies of long-scale dynamics by computer simulations a rather small entanglement length is needed since the long-scale dynamics is determined by the ratio N/N_e which in consequence must be very large. Thus we need not to simulate very long chains at the density of $\Phi=0.60$ to get an ratio of N/N_e of approximately 7, which is in the present simulations in polymer physics a common value [15].

The study of the late time behavior of the mean-square displacement $g_1(t)$ leads to the several crossovers predicted by the reptation theory [14]. At short time scales $g_1(t)$ is effected by excluded volume interactions and follows the behavior $g_1(t)=\langle l^2\rangle(Wt)^{1/[1+1/(2\nu)]}$, where $\nu=0.59$ as we have to deal with a self-avoiding chain. Here W denotes a displacement rate. At larger time scales Rouse behavior $\sim t^{1/2}$ occurs at times $\tau_R<t<\tau_e=N_e^2/W$. Here τ_R is called the Rouse time and τ_e the entanglement time. At larger times $t>\tau_e$ the motion is restricted to a movement along a tube surrounding the chain. Therefore the diffusion of the monomers is a random walk on the tube of the polymer, which is again a random walk. Therefore the exponents predicted for this region are only half of the Rouse values $g_1(t)\sim t^{1/4}$. This prediction is valid only for times $t<\tau_R=N^2/W$ (Rouse time). For later times we expect $g_1(t)\sim t^{1/2}$, while starting at $t=\tau_N=N^3/N_eW$ we have fully relaxed tube constraints and $g_1(t)\sim t$. Figure 5 shows this predicted behavior of $g_1(t)$ very clearly in all of these four regimes. It displays $g_1(t)$ for a chain lengths of 40 repeating units at a volume fraction of $\Phi=0.30$. This simulation was performed over 4 000 000 molecular-dynamics steps and took 12 days on a Sun Ultra Sparc Two. The solid points are calculated averaging ap-

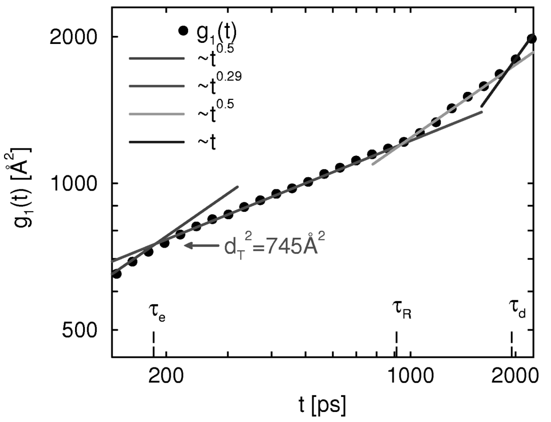

FIG. 5. $g_1(t)$ at $T=1000$ K, $\Phi=0.32$, and chain length $N=40$.

proximately 1000 data points of $g_1(t)$ with a spacing of 4000 molecular-dynamics steps to obtain points with equidistant spacings on a logarithmic length scale to illuminate the different regimes. The theoretical $t^{1/4}$ law is not fully reached but displays an exponent of approximately 0.29. It coincides with the result presented in [11] (≈ 0.3). The reason for this deviation from the theoretical value could be the influence of crossover effects due to the fact that our reptation regime is only a half-decade long. So we have here no random walk along the tube of the chain. Or it might be that another theory describes the dynamics of polymer chains in that regime. Several theoretical approaches have been developed on this topic in recent years, such as an analysis in the mode coupling theory that predicts a value of 9/32 [16]. With this value our results are in better agreement, but the chain length used here is still too short to state definite conclusions regarding the validity of the theory.

It is interesting that we can see the predicted behavior in all of four regimes with chains not longer than 40 monomers at a volume fraction of $\Phi=0.3$ whereas simulations with the bond fluctuation model have to calculate four times larger chain lengths (up to $N=200$) at a volume fraction of $\Phi=0.5$ [17]. If we have a look at the effective chain length [11]

$$\tilde{N} \equiv N[\langle l^2\rangle^{3/2}\Phi]^{1/(3\nu-1)} \tag{14}$$

with the bond length l, the number of flexible points N of the chain, and the volume fraction Φ, we see that the bond length enters into this equation via $\approx l^{3.9}$. This investigation demonstrates an advantage of our model that in spite of using anisotropic chain segments our model is still able to reach time scales where entanglement effects influence the dynamics of the chains. So we are able to take advantage of these scaling laws and examine rather long effective chain lengths. This encouraged us to pursue the studies presented in the following section. Considering the mean-square displacements of the inner monomers of the chains one is able to determine the tube diameter d_T. Its square is of the order of the value of the mean-square displacement g_1 at the entanglement time τ_e. Our data for chains with chain length $N=40$ at a mean temperature $T=1000$ K and a volume fraction of $\Phi=0.32$ yield a square tube diameter $d_T^2 \approx 745$ Å^2. Thus we have $d_T \approx 27$ Å. If we have a look at the tube diameter of polyethylene, which has a tube diameter of about 23 Å [1] we find that our value is comparable to the tube diameter of other polymers and may be in good agreement with experimental values to be found for BPA-PC.

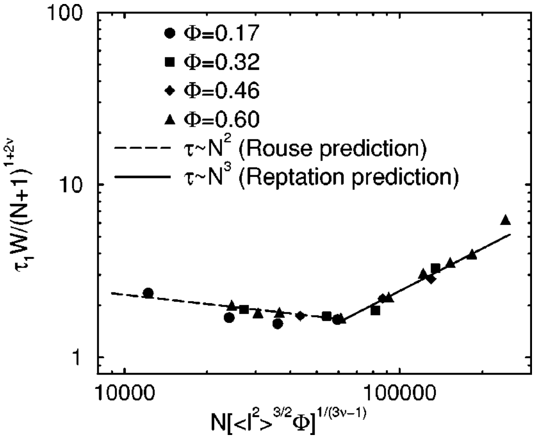

FIG. 6. Log-log plot of the scaled relaxation times $\tau_1 W/N^{1+2\nu}$ vs the scaled chain lengths $\tilde{N}$.

III. RELAXATION TIMES AND THEIR CROSSOVER SCALING ANALYSIS

The crossover from Rouse behavior to reptation dynamics can be investigated by the definition of the relaxation times τ_1, τ_2, and τ_3 from the intersection points of the curves of the several mean-square displacements as follows:

$$g_1(\tau_1) = \langle R_G^2\rangle, \tag{15}$$

$$g_2(\tau_2) = 2/3\langle R_G^2\rangle, \tag{16}$$

$$g_3(\tau_3) = g_2(\tau_3), \tag{17}$$

where R_G denotes the radius of gyration of the chain. We now introduce the effective chain length as given by Eq. (14), which leads to a crossover scaling law for the relaxation times τ [11],

$$\frac{W\tau}{N^{1-2\nu}} = \tilde{\tau}(\tilde{N}). \tag{18}$$

Figures 6, 7, and 8 show that our data are quite consistent with Eqs. (14) and (18). The data shown in the figures are obtained from simulations that were performed up until at least the diffusion time was reached to ensure that the errors are at an acceptable limit. Exceptions are two runs with chain lengths 40 and 50 at a volume fraction of $\Phi=0.60$, because even for the smaller of the two chains the reptation regime lasts for one decade and it would take twice the simulation time to reach the diffusion regime. The scattering of the data that is seen cannot be avoided by the currently available computer power and is known from the former investigations of the relaxation times by computer simulations. As there exist different relaxation times and, moreover, the problem of aging of polymer melts, which means that there exist relaxation times that are on a time scale that cannot be ne-

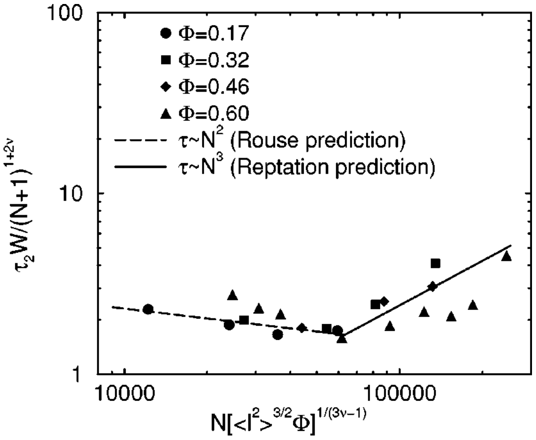

FIG. 7. Log-log plot of the scaled relaxation times $\tau_2 W/N^{1+2\nu}$ vs the scaled chain lengths $\tilde{N}$.

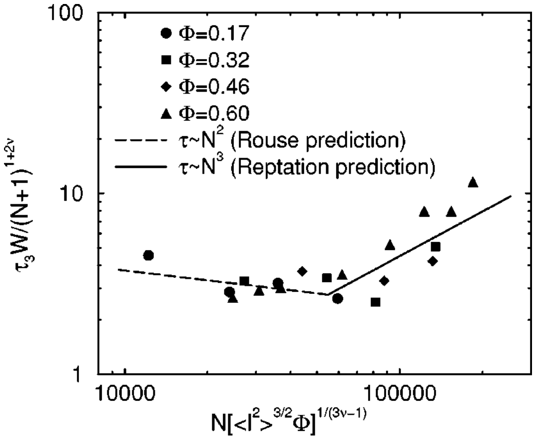

FIG. 8. Log-log plot of the scaled relaxation times $\tau_3 W/N^{1+2\nu}$ vs the scaled chain lengths $\tilde{N}$.

glected in computer simulation studies. Nevertheless, the symbols are smaller than the statistical errors of the measured values.

These scaling plots of the relaxation times show the crossover from a Rouse to a reptation regime, which is consistent with the reptation theory [8,14]. From this we can obtain another value of N_e. We get $N_e = 9 \pm 3$ for a volume fraction of $\Phi = 0.60$ and a mean bond length of 11.1 Å. This value is higher than the former that we obtained from the crossover in the behavior of the diffusion exponents. Note that we estimated these values form log-log plots. Hence the error bars are quite large.

IV. CONCLUSIONS

In this paper we presented the continuous backbone mass model for polymers and data obtained by molecular-dynamics simulations using a parametrization for bisphenol-A-polycarbonate. The dynamics of a flexible polymer model consisting of one-dimensional rods is investigated. We focus on the static and dynamic properties for a wide range of densities (from $\Phi = 0.17$ to $\Phi = 0.60$) and chain lengths ($N = 1$ to 50). Concerning the statics we found the typical crossover predicted from the Rouse model and estimate a screening length of about 2.5 monomer lengths. We investigate the dynamics of the polymer system analyzing several mean-square displacements. Performing a scaling analysis for several relaxation times we were able to give evidence for the crossover from Rouse to reptation dynamics. Looking at the mean-square displacements of inner monomers we could identify directly the four regimes of different dynamics according to the reptation model.

We showed that with rotational ellipsoids polymers consisting of larger anisotropic monomers can be modeled successfully and with computational efficiently. The use of a one-dimensional hard core region prevents bond crossing. With a bead-spring model large monomers must be constructed out of spheres with volumes larger than the interaction volume estimated by quantum chemical calculations to prevent bond crossing. Recently a model for BPA-PC using the bead-spring model has been published that uses two large beads per monomer [18]. This will enlarge the number of chain units by a factor of 2 and will take 23 times more computer time to pass the Rouse time before the dynamic regimes [15] are entered.

[1] K. Binder, *Monte Carlo and Molecular Dynamics Simulations in Polymer Science* (Oxford University Press, Oxford, 1995).
[2] J. Baschnagel *et al.*, J. Chem. Phys. **95**, 6014 (1991).
[3] M. Bishop, M. H. Kalos, and H. L. Frisch, J. Chem. Phys. **70**, 1299 (1979).
[4] J. P. Ryckaert and A. Bellemanns, Chem. Phys. Lett. **30**, 123 (1975).
[5] J. Kushnick and B. J. Berne, J. Chem. Phys. **64**, 1362 (1976).
[6] J. G. Gay and B. J. Berne, J. Chem. Phys. **74**, 3316 (1981).
[7] K. M. Zimmer, A. Linke, and D. W. Heermann, Macromol. Theory Simul. **5**, 1065 (1996).
[8] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, London, 1979).
[9] D. Richter *et al.*, Phys. Rev. Lett. **64**, 1389 (1990).
[10] K. Kremer, G. S. Grest, and I. Carmesin, Phys. Rev. Lett. **61**, 566 (1988).
[11] W. Paul, K. Binder, D. W. Heermann, and K. Kremer, J. Chem. Phys. **95**, 7726 (1991).
[12] J. Sklonick, R. Yaris, and A. Kolinski, J. Chem. Phys. **88**, 1407 (1998).
[13] K. Kremer and G. S. Grest, J. Chem. Phys. **92**, 5057 (1990).
[14] M. Doi and S. F. Edwards, *Theory of Polymer Dynamics* (Wiley, New York, 1987).
[15] B. Dünnweg, G. S. Grest, and K. Kremer, in *Volumes in Mathematics and its Applications*, edited by S. Whittington (Springer-Verlag, Heidelberg, 1998), Vol. 102, p. 159.
[16] K. Schweizer, J. Chem. Phys. **91**, 5802 (1989).
[17] W. Paul, K. Binder, D. W. Heermann, and K. Kremer, J. Phys. II **1**, 37 (1991).
[18] W. Tschoep *et al.*, Acta Polym. **49**, 61 (1998).