

Simulation of Polymers Using the Ellipsoidal Model

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Abstract. We present a recently developed model for polymer simulation, the ellipsoidal model. The geometric shape of the chemically realistic monomers is conserved by using ellipsoids as building units for the coarse grained model of the monomers. Static and dynamical properties are investigated using a parameterization for the Bisphenol-A-Polycarbonate. Our advantage employing this model is, that smaller chain lengths can be used to investigate physical properties than with other models. One also can reinsert the chemically realistic chain after a simulation to investigate properties of the atomistic scale.

1 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 out 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. Depending on the kind of question and the degree of abstraction, one has the basic choice between a lattice model and a model in continuum. If one wants to stay as close as possible to the chemically realistic chain it may be of advantage to remain in real space. The approach to the computational modeling we have undertaken is to retain as much as possible of the chemically realistic chain and still stay computationally efficient. The goal is to examine the correlation between the chemical structure and the physical properties which is very time consuming at atomistic scale.

2 Model and Methods

We consider the interaction volume of chemical sequences to be of rotational symmetric ellipsoidal form. These ellipsoids are then connected at their focal

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points to form a chain. The interaction volume is taken as a con-focal force field and its hard core region, the connection between the focal points, is chosen to represent the mass of the building unit, which is assumed to be homogeneous. Thus in the ellipsoidal model linear polymers are simulated by rod chains which on the one hand give a realistic excluded volume region along the backbone of the chain and on the other hand are closer to the geometric form of the chemical sequence in contrast to a bead in e.g. united-atom model see M. Bishop et. al. (1979). The bonded interactions between neighboring units are harmonic angle and torsion potentials. For details see K.M. Zimmer and D.W. Heermann (1995). In this paper we present data obtained by molecular dynamics simulations. To estimate the force on the rods, we use a 10 point Gauss integration. At each time step we solve the equations of motion for a rod chain, which leads to a tridiagonal matrix.

3 Parameterization of BPA-PC

In this investigation we focus on the simulation of BPA-PC. We use the parameterization of K.M. Zimmer et. al. (1996) in which each repeating unit is mapped to one ellipsoid. We identify the focal points of the modeling ellipsoids with the center of mass of the backbone atoms of the carbonate-groups. Thus the lengths of the ellipsoids are about $l \approx 11 \text{ \AA}$. This potential of the chemically detailed monomer shows us that in the case of polycarbonate the strength of the attractive part of the potential is very small. Thus we set the absolute value of the intermolecular potential to be a r^{-6} potential. The intra-chain parameters are optimized for each temperature, using lengths and angles distributions received from quantum chemical calculations as input.

4 Static Properties

First we want to present some data and considerations concerning the statics of a BPA-PC melt within the ellipsoidal model. We did compute the single chain structure factor, as described in P. G. de Gennes (1979). This structure function

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

of the individual chains provides a test on which length scale the self-avoiding interaction is screened. The index $|\mathbf{q}|$ indicates the spherical average over \mathbf{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 $\xi(\rho) < 2\pi/q < \langle R^2 \rangle^{1/2}$, whereby ρ is the density of the polymer melt. Fitting straight lines with the slope of $1/\nu = 1.695$ and 2 to the data in fig. 1 we find a crossing of the two regimes at $q = 0.225 \text{ \AA}^{-1}$.

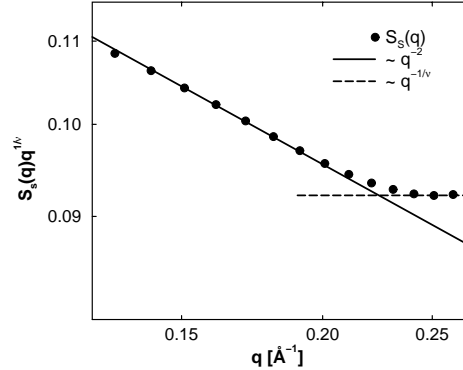


Fig. 1. Single chain structure factor for chains with length $N = 30$ at $\rho = 1.374\text{g/cm}^3$ and $T = 800\text{ K}$

This gives a screening length $\xi(\rho = 1.374\text{g/cm}^3) \approx 27.9\text{ \AA}$. Since our average monomer length is about 11 \AA , the inter-molecular interaction is screened out at a distance of about 2.5 monomer lengths.

5 Dynamical Properties

The examination of various mean-square displacements leads to an understanding of the dynamical behavior. For this we define two different displacements: the mean-square displacement of the monomers in the center of the chains

$$g_1(t) \equiv \left\langle [\mathbf{r}_{N/2}(t) - \mathbf{r}_{N/2}(0)]^2 \right\rangle, \quad (2)$$

and the mean-square displacement of the center of mass of the chains,

$$g_3(t) \equiv \left\langle [\mathbf{r}_{\text{CM}}(t) - \mathbf{r}_{\text{CM}}(0)]^2 \right\rangle. \quad (3)$$

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

$$D = \lim_{t \rightarrow \infty} \frac{g_3}{6t}. \quad (4)$$

According to the reptation theory one would expect a crossover from $\sim N^{-1}$ to a $\sim N^{-2}$ regime (M. Doi and S.F. Edwards (1987)). Our data in fig. 2 show a crossover from a Rouse to a reptation regime which is consistent with the reptation theory. During the last years evidence for the reptation model was given by simulations, e.g. K. Kremer and G.S. Grest (1990) and W. Paul (1991). The study of the late time behavior of the mean-square

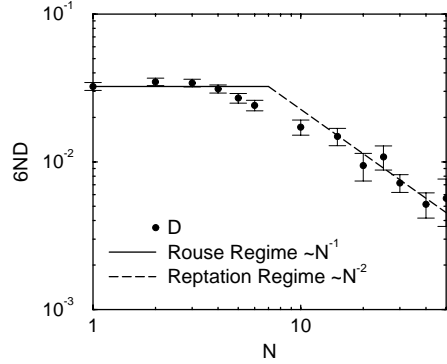


Fig. 2. Diffusion constants at $T = 800$ K and $\rho = 1.374\text{g/cm}^3$

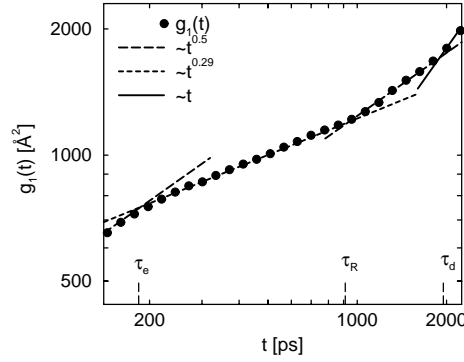


Fig. 3. $g_1(t)$ at $T = 1000$ K, $\rho = 0.687\text{g/cm}^3$, chain length $N = 40$

displacement $g_1(t)$ leads to the several crossovers predicted by the reptation theory, M. Doi and S.F. Edwards (1987). $g_1(t)$ shows Rouse behavior $\sim t^{1/2}$ at times $t < \tau_e = N_e^2/W$. At larger times $t > \tau_e$ the motion is restricted to a movement along a tube surrounding the chain. 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 $t = \tau_N = N^3/N_e W$ we have fully relaxed tube constraints and $g_1(t) \sim t$. Fig. 3 shows this predicted behavior of $g_1(t)$ very clearly in all of these four regimes. Only 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 W. Paul (1991) (≈ 0.3). The reason for this deviation from the theoretical value is the influence by crossover effects due to the fact that our chain lengths are only six times the entanglement

length. Nevertheless it is interesting that we can see the predicted behavior in all of the four regimes with chains not longer than 40 monomers whereas simulations using the bond fluctuation model need to perform systems with 5 times larger chain lengths (up to $N = 200$). In spite of using long chain segments we still have a continuous chain, thus no bond crossing is possible. So we are able to take advantage of scaling laws and examine rather long effective chain lengths. Looking at 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 density of $\rho = 0.68\text{g/cm}^3$ yields a square tube diameter $d_T^2 \approx 745\text{\AA}^2$. Thus we have $d_T \approx 27$ \AA.

6 Conclusions

We have presented data obtained by molecular-dynamics simulations of the ellipsoidal model using a parameterization for Bisphenol-A-polycarbonate (BPA-PC). Some static and dynamical properties of BPA-PC were investigated. We estimate a screening length $\xi(\rho = 1.374\text{g/cm}^3)$ of ≈ 27.9 \AA. For the entanglement length we get $N_e \approx 77$ \AA. Looking at the mean-square displacements of inner monomers we could identify directly the four regimes of different dynamics according to the reptation model, even with rather short chain lengths. With our model it is possible to see effects at moderate chain lengths which can usually only be investigated at very large chain lengths.

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