Quantitative Study of Polymer Dynamics Through Hierarchical Multi-scale Dynamic Simulations

Vagelis A. Harmandaris and Kurt Kremer

Max-Planck-Institut für Polymerforschung,
Ackermannweg 10, 55128 Mainz, Germany

(Dated: September 9, 2008)

Abstract

The long time dynamics of polymeric materials has been extensively studied in the past through various experimental techniques and computer simulations. While computer simulations typically treat generic, simplified models, experiments deal with specific chemistries. In this letter we present a hierarchical approach that combines atomistic and coarse-grained simulations to quantitatively study polymer dynamics. As an example we predict diffusion coefficients of atactic polystyrene melts of molecular weights relevant to polymer processing (up to 50kDa) without any adjustable parameter and compare the results to experiment.

PACS numbers: 36.20-y, 61.25.H-, 83.10Rs
Introduction. The dynamics of polymers is a prototypical soft matter problem and has attracted considerable experimental and theoretical attention for many years \([1, 2, 3, 4]\). For the two limiting cases of short, but already fully flexible polymer chains in a melt, and very long, fully entangled chains well established (scaling) theories, namely the Rouse and reptation theory, exist and have been tested in detail by experiments and computer simulations of highly idealized models \([1, 5, 6, 7]\). However most of these approaches provide either a semi quantitative link between theory and experiment in the sense that scaling relations are verified, or quantitative information for short chains with simple chemical structure, like PE. What is still missing is a direct quantitative link between chemical structure and measurable quantities like diffusion constants or viscosities, especially for high molecular weight entangled systems. In addition the crossover regime from Rouse like to reptation like behavior, which for example for polystyrene (PS) covers a range of molecular weights from about \(M \approx 1\)kDa to \(M \approx 100\)kDa, is still under discussion. In this regime it is also not clear, to what extent universal theories describe the properties and to what extent chemical details surface strongly, which makes the applicability of a general analytic theory virtually impossible. This is a situation, where well tailored computer simulation can be of significant help.

On the microscopic level detailed atomistic molecular dynamics (MD) simulations allow quantitative predictions of the dynamics of simple polymers with rather low molecular weight \([6]\). However, due to the broad spectrum of characteristic lengths and times involved in polymeric systems, it is not feasible to apply them to systems of more complex chemical structure or of high molecular weight.

On the mesoscopic level coarse-grained (CG) molecular dynamics and Monte Carlo simulations have proven to be very efficient means to study the dynamics of long, entangled simple model polymer systems \([5, 7]\). In a similar way, structure-based CG models have been employed to study the dynamics of specific polymer melts. There groups of chemically connected atoms are lumped into ‘superatoms’. Effective, coarse-grained interaction potentials are obtained by averaging over microscopic details of the underlying atomistic models. The direct link to the chemistry is maintained through the choice of appropriate superatoms and the resulting set of structurally defined CG bonded and non-bonded temperature dependent effective potentials (more precisely free energies) \([5, 8, 9]\). By doing that structural properties of polymeric systems are described quite well. However CG simulations cannot be used for a direct quantitative study of dynamics because the intrinsic time scale of the CG model is not the same as that of the underlying chemical system.
One reason is the use of (softer) effective CG potentials, which results in a significantly reduced effective friction between the beads compared to the original monomers. To overcome this limitation the ratio between the CG time and chemically realistic time scale has to be derived from either experiments or atomistic simulations [8, 9]. However a direct comparison of the resulting dynamics to experiment and the extension to long, entangled chains are still missing.

In this letter we extend this approach and present a hierarchical methodology that combines dynamic simulations, on different length and time scales. This approach allows us to predict through CG simulations, not only qualitatively, but also quantitatively, the dynamics of polymer systems of molecular weight relevant to polymer processing without any adjustable parameter. As an example the whole methodology is applied in atactic polystyrene at T=463K, which has been extensively studied in the past through experiments (see for example [2, 10] and references within and simulations [8, 9]). The chosen temperature is a typical process for PS.

**Simulation Methodology.** In order to derive a time scaling factor $S$ between different models we match the mean square displacements of the monomers in amplitude and slope. The latter is important, since the motion characteristics of the different models coincides only above a characteristic length scale. A three level ansatz is needed in order to also capture the effect of the chain length dependent melt density onto the scaling factor.

Detailed all atom simulations, using a model in which hydrogens and carbons are treated explicitly [11], have been performed for rather short PS chains ($M=1\text{kDa}$, $T=463\text{K}$, only 10 repeat units) at the experimental density of $0.925\text{gr/cm}^3$. Only for such small chains reliable data for the mean square displacement of the monomers can be obtained with all-atom MD simulations. To somewhat overcome this problem united atom (UA) models are frequently employed; here we are using the TraPPE one [12]. There hydrogens are lumped together with carbons, defining new $\text{CH}_x$ types of united atoms. For UA simulations it is usually assumed that the time scale does not in a detectable way deviate from all atom simulations, because hydrogens are very small and the ”coarse-graining” of the UA models is of the order of hydrogen-carbon bond which is only about 1 Å. However this assumption, which in many cases (for example UA models for PE, PB, PI) works reasonably well, fails to work for the UA-TraPPE PS model; i.e. it predicts for PS a much faster dynamics. This is most probably, due to the too low dihedral barriers or due the missing electrostatic interactions but does not affect the overall conformations [9]. Various systems, with molecular weight from $1\text{kDa}$ to $10\text{kDa}$ ($T=463\text{K}$), have been studied by this method. Beyond that CG models are used, which however do not reproduce the motion patterns down to length scales
FIG. 1: Coarse-graining mapping scheme of PS: one monomer is mapped to two different CG beads ($\sigma_A = 4.1\text{Å}, m_A = 27\text{amu}$ and $\sigma_B = 5.2\text{Å}, m_B = 77\text{amu}$) [9].

of the order of one or two monomers.

Thus we adopt the following strategy. First UA and CG simulations are performed, for molecular weights between 1 and 10kDa in order to obtain the time scaling factor $S_{UA-CG}(M)$. Then the UA results are calibrated by all atom simulations, however for much shorter times only, resulting in an additional scaling factor $S_{AA-UA}(M)$. With $S(M) = S_{AA-UA}(M) \cdot S_{UA-CG}(M)[\text{sec}/\tau]$ we calibrate the time scale to determine long chain polymer diffusion constants and compare these to experiment.

The molecular dynamics package GROMACS [13] was used to perform all the atomistic (AA and UA) MD simulations. Initial well-equilibrated atomistic polymer melts are obtained by back-mapping CG melts [9]. All simulations have been performed at constant temperature and volume ($NVT$ ensemble) at experimental densities [14]. The overall simulation time of the production runs ranged from 50 ns to 300 ns depending on the molecular weight.

CG MD simulations have been performed using a CG model for PS in which one PS monomer is mapped onto two effective coarse grained beads, i.e. a 2:1 model [9] (see Figure 1). CG bead “A” corresponds to the CH$_2$ of a PS monomer plus the half mass of each of the two neighboring CH groups along the chain backbone, whereas CG bead “B” is the phenyl ring. This model does not lose too many structural details in comparison to all atom systems, while still being very efficient compared to atomistic simulations. Various monodisperse atactic PS melts, with molecular weight from 1kDa up to 50kDa have been studied with CG MD simulations. Note that the characteristic molecular weight $M_e$ for the formation of entanglements for atactic PS is about 15kDa (at $T=463K$) [10]. All CG systems have been originally generated by a combination of Monte Carlo and MD simulations following the procedure by Auhl et al. [9, 15]. CG MD simulations are performed in dimensionless LJ units using $m_A$ to scale all masses, $\sigma_{AV} = (\sigma_A + ...
to scale all lengths and $\epsilon = kT$ to scale all energies. In order to control the temperature in the system we use a Langevin thermostat with friction coefficient $\Gamma = 1.0 \tau^{-1}$. All coarse-grained MD simulations are performed using the ESPResSo package [16] with a time step $\Delta \tau = 0.01 \tau$, with $\tau = \sqrt{m_A \sigma_{AV}^2 / \epsilon}$. MD simulations ran for times between $1 \times 10^4 \tau$ and $3 \times 10^6 \tau$ depending upon the system size.

*Time Mapping.*— The problem of time scales can be discussed in terms of local (monomeric) friction coefficients. For both the Rouse as well as the reptation model the local motion is governed by a scalar friction coefficient $\zeta$, so that the melt viscosity $\eta \propto \zeta$ and the chain diffusion constant $D(N) \propto \zeta^{-1}$. For the modeling of the polymer melt this bead friction depends on the specific representation of the polymer. The softer CG potentials result in a significantly reduced effective friction coefficient, $\zeta^{CG}$, between beads compared to the friction coefficient in the united atom description, $\zeta^{UA}$, and the all atom description, $\zeta^{AA}$, respectively. As a consequence the time in the dynamic CG simulations does not correspond to the real time of the polymeric system and has to be properly scaled. In most cases the differences between all atom and united atom simulations are much smaller then the typical error bars of a simulation. For the TraPPE-UA PS model however this is not the case. Though in general a disadvantage, for PS this makes it possible to obtain a proper scaling by employing the AA-UA-CG hierarchy. Thus the time scaling parameter, which is the ratio of the effective bead frictions in the atomistic and the CG description, is given by

$$S(M) \equiv \frac{\zeta^{AA}}{\zeta^{CG}} = S_{AA-UA}(M) \cdot S_{UA-CG}(M)$$

Because the local energy landscape is quite complex and fluctuating it is not possible to give a well founded analytical prediction of $S$. Therefore, $S$ should be obtained using data taken either from atomistic simulations, as done here, or directly from experiment.

To determine $S$ we match mean square displacements (MSD) of chain beads over a considerable time, where both amplitude and shape coincide. First we examine the time mapping of the CG data based on the UA MD simulations. Figure 2 shows the mean square displacements averaged over all beads $i$ of the CG model and the correspondingly analyzed UA model (circles), $g_1(t) = \langle (r_i(t) - r_i(0))^2 \rangle_i$ from UA MD and CG MD simulations for a specific PS melt (1kDa, $T=463K$). The scaling factor, $S_{UA-CG}$, in order to match the two curves on top of each other in the long time regime, gives $S_{UA-CG}(M=1kDa)= 3.1 ps/\tau$. With this scaling factor both curves coincide above a distance of about 10 Å and a corresponding time of about 200 ps. Below that distance and time the coarse graining results in a different shape of the curve, illustrating that a mere crossing
FIG. 2: Time scaling of the CG simulations using UA data and of the UA simulations using atomistic data for a PS melt ($M=1kDa$, $T=463K$), based on the motion of the polymer beads.

of the curves is not sufficient to determine $S$. Note also that $S_{UA-CG}$ is the same if the mapping is based on a quantity describing the orientational dynamics (for example the end-to-end vector autocorrelation function) of the PS chains [17].

In general $S_{UA-CG}$ depends on molecular weight and density, which depends on $M$ (chain end free volume effect), as shown in Figure 3 (circles) for the systems studied by both UA MD and CG MD simulations. As we can see $S_{UA-CG}$ varies in the short length regime (up to about 50 monomers), ranging from 3.1ps/$\tau$ to about 6.0ps/$\tau$, and then it remains constant. This is in phase with the observed change in density, which varies from 0.925g/cm$^3$ for 1kDa to about 0.97g/cm$^3$ for the 10kDa and higher molecular weight melts (see Figure 2) [14]. At high molecular weights (above 10kDa) the change in the polymer dynamics is entirely due to the increase of the molecular weight. On the other hand, in the short length regime the density effect is very important. The latter one is not being described accurately in the CG model, resulting into a dependence of $S$ on the density (and on the molecular length).

The important result of Figure 3 is that a single value for the time scaling parameter $S$ is appropriate to describe the dynamics of long polymer chains. However the UA model itself includes some minor coarse graining and in the case of the TraPPE-UA PS model predicts faster dynamics than the all-atom simulations. Thus we have to follow a same procedure as above, however now for the two models exhibiting atomistic detail. A typical example is shown in Figure 2 (squares). Though qualitatively similar, there is a remarkable quantitative difference. As Figure 2 displays the two sets of data perfectly match from a distance above about 3Å, this is for significantly smaller length scales than before, of the order of the size of a benzene ring ($R_G$ is shown with arrow). For the present case of Figure 2 we arrive at $S_{AA-UA}(M=1kDa)=35$, resulting
FIG. 3: Time mapping of the CG simulations of the PS melts using UA and AA data, and density as a function of $M$ ($T=463K$).

in $S_{AA-CG}(M=1kDa)=110ps/\tau$. This together with computational efficiency of the TraPPE UA model allows us to determine the time scaling factor with its full chain length dependence (up to $M=10kDa$), as shown in Figure 3 (squares). Note the similar qualitative but the large quantitative difference between $S_{UA-CG}(M)$ and $S_{AA-CG}(M)$. Alternatively one can follow the observation, that the variation of $S$ follows approximately the changes in density rather than the molecular weight itself, even though this density change is due to the chain length variation. This is not surprising since, for polymers both density and monomeric friction coefficient vary with molecular weight because of the higher chain end free volume (free volume theory) and two melts with the same density would be expected to have the same friction coefficient [2]. Therefore by performing the time mapping for the short chain system but at the density of the longer chains one also can obtain a reliable estimate of $S_{AA-UA}$. If we follow this procedure the combined time mapping $S_{AA-CG}(M)$ varies between $\simeq 110ps/\tau$ (for the 1kDa system) and $\simeq 700ps/\tau$ for the high (10kDa and above) molecular weight (polymeric) regime. Here we follow the latter because of the extensive computational effort needed to obtain reliable data for MSDs of long all-atom PS chains. $S_{AA-CG}$ now can be applied to determine absolute diffusion constants in long chain PS melts, based on CG simulations.

**Self-Diffusion Coefficient of Polystyrene Melts.**— Following the hierarchical methodology described above, the dynamical and rheological properties of long entangled polymeric systems can be obtained from the CG dynamic simulations in real units. Here we focus on the self-diffusion coefficient, $D$, which can be calculated directly from the MSD of the chain center-of-mass by rescaling $\tau$ to sec by the above described procedure. Data for the self-diffusion coefficient of the CG PS melts, scaled with $S_{AA-CG}(M)$, as a function of the molecular weight (squares) are shown
FIG. 4: Self-diffusion coefficient of PS melts as a function of the molecular weight ($T=463K$).

in Figure 4 and are compared to experimental data (circles) [10]. Both simulation and experimental data are not corrected for the chain end free volume. The range of molecular weights (up to 50kDa) spans the regime from unentangled to entangled PS melts.

The results show a remarkable qualitative and quantitative agreement between the experimental and the simulated diffusion coefficients (see figure 4). This is of particular importance if we consider that results from the CG dynamic simulations are compared to experimental data, by using only detailed atomistic simulations for a few reference short-chain systems, without any adjustable parameter. The error bars in the AA-scaled CG data are mainly due to the high error bars in the underlying all-atom data. The larger deviation between the simulation and the experimental data in the short length regime is not surprising if we consider the effect of the (small) polydispersity of the experimental data ($I \approx 1.04$): in these short chains the presence of even only a small amount of PS oligomers acts like an effective dilution and can increase the free volume and the diffusion of the systems.

Note also that the entire regime of both simulation and experimental data can be fitted using a power-law dependence ($D \sim M^{-b}$) with a single exponent of about $b \approx 2.1 \pm 0.2$. For short chain polymer melts the Rouse model predicts $b=1$ while long entangled polymer melts the pure reptation theory predicts $b=2$ [1]. However the Rouse model neglects the molecular weight dependence of the density and and thus of the friction coefficient. In order to eliminate this effect a correction can be made for $D$ as it is often done in the analysis of experiments; this will be a part of a future work [17].

It is of interest to estimate the time scales involved in the dynamics of the PS systems studied
here: the diffusion coefficient of the higher molecular weight PS melts (50kDa) is of the order of about $10^{-11}\ cm^2/sec$. This results into a relaxation time of the whole chain - decorrelation of the end-to-end vector $\tau_d$ (according to reptation theory $\tau_d = \frac{<R^2>}{3\pi^2 D}$) of about 6.0ms, many orders of magnitude longer that what can be modeled with atomistic molecular dynamic simulations in such systems.

In conclusion we present a hierarchical simulation approach that combines dynamic simulations on different length and time scales. A mapping over a small range of molecular lengths, using atomistic and united-atom simulation data, shows that the time mapping parameter $S$ varies as a function of chain length induced by different melt densities. The asymptotic plateau value of $S$ can be used for scaling the CG dynamic results of longer polymeric chains, where it is not possible to have reliable atomistic data at all.

Furthermore the multi-scale nature of the proposed scheme, combined with a proper back-mapping procedure [8, 9, 18], allows to study time scales ranging from a few fs up to ms by MD simulations and to compare directly to experimental data without any adjustable parameter. The accuracy of the CG dynamical predictions, compared to experimental data, of course depends on the accuracy of the underlying microscopic (atomistic) model with which the CG “raw” data are scaled. This opens up the way for developing simulation methodologies that can be used for quantitative studies of the dynamics and the rheology of complex systems within the $M$ regime relevant to the polymer processing. The proposed approach can be directly extended to other polymer chemistries by properly choosing a structure-based CG model, which reproduces structural properties for length scales of about 0.5-1 nm and larger. Furthermore it can be used for the study such different systems as non-equilibrium polymer melts, polymers at temperatures near to $T_g$, or polymer/solid interfacial systems.

One the other hand, and despite the success of the proposed methodology, still a number of issues remain. For example, for multi-component systems or polymers in solution, the nature of the friction might not allow a renormalization in time with a single quantity. For such systems molecular dynamics simulations could be used for the calculation of the entire friction matrix, which can be then involved in the equations of motion on an even more coarse level, as for example in the level of the primitive paths [19] or through the GENERIC formalism [20].

Acknowledgments. — Very fruitful discussions with Nico van der Vegt, Dirk Reith and Burkhard Dünweg are greatly appreciated.
[1] M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics* (Claredon Press, Oxford, England, 1986).
[2] J.D. Ferry, *Viscoelastic Properties of Polymers* (John Wiley and Sons, New York, 1980).
[3] *Monte Carlo and Molecular Dynamics Simulations in Polymer Science* edited by K. Binder, (Oxford University Press, New York, 1995).
[4] T. Mcleish, Adv. Phys. 51, 1379 (2002).
[5] K. Kremer, in *Proceedings of the International School of Solid State Physics - 34th Course: Computer Simulations in Condensed Matter: from Materials to Chemical Biology* ed. by K. Binder, K. and G. Ciccoti (Erice, 2006).
[6] V.A. Harmandaris and V. Mavrantzas, Molecular Dynamic Simulations of Polymers in *Simulation Methods for Polymers*, ed. by D.N. Theodorou and M. Kotelyanski (Marcel Dekker, 2004); V. Harmandaris et al., Macromolecules, 36, 1376 (2003).
[7] J. Baschnagel et al., Adv. Polym. Sc. 152, 41 (2000).
[8] W. Tschöp et al., Acta Polym. 49, 61, (1998); S.O. Nielsen, G. Srinivas, and M. Klein, J. Chem. Phys. 123, 124907 (2005); V.A. Harmandaris et al., Macromolecules 39, 6708 (2006); B. Hess et al., Soft Matter 2, 409, (2006); J. Padding and W.J. Briels, J. Chem. Phys. 117, 925 (2002); W. Paul and N. Pistoor, Macromolecules 27, 1249 (1994).
[9] V.A. Harmandaris et al., Macrom. Chem. and Phys. 208, 2109 (2007); V.A. Harmandaris et al., Macromolecules 40, 7026 (2007).
[10] T.P. Lodge, Phys. Rev. Lett. 83, 3218 (1999); M. Antonietti, K.J. Fölsch, and H. Sillescu, Makromol. Chem. 188, 2317 (1987); O. Urakawa et al., Macromolecules 37, 1558 (2004); C. Liu, J., He, E. van Ruymbeke, R. Keunings, and C. Baily, Polymer 47, 4461 (2006).
[11] F. Müller-Plathe Macromolecules 29, 4782 (1996).
[12] C.D. Wick, M.G. Martin, and J.I. Siepmann, J. Phys. Chem. B 104, 8008 (2000).
[13] H.J.C. Berendsen, D. van der Spoel, and R. van Drunen, Comp. Phys. Comm. 91, 43 (1995).
[14] P. Zoller and D.J. Walsh, *Standard Pressure-Volume-Temperature Data for Polymers* (Technomic, Lancaster, 1995).
[15] R. Auhl et al., J. Chem. Phys. 119, 12718 (2003).
[16] A. Arnold et al., Comp. Phys. Comm 174, 704 (2006).
[17] V.A. Harmandaris and K. Kremer, in preparation.
[18] C. Peter, L. Delle Site, and K. Kremer, Soft Matter 4, 859 (2008).

[19] R. Evereaers et al., Science 303, 823 (2004); S.K. Sukumaran et al., J. Polym. Sci. Polym. Phys. 43, 917 (2005).

[20] H. Öttinger, Beyond Equilibrium Thermodynamics (John wiley & Sons, New Jersey, 2005).