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To cite this article: L L Fan and L Liu 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **369** 012017

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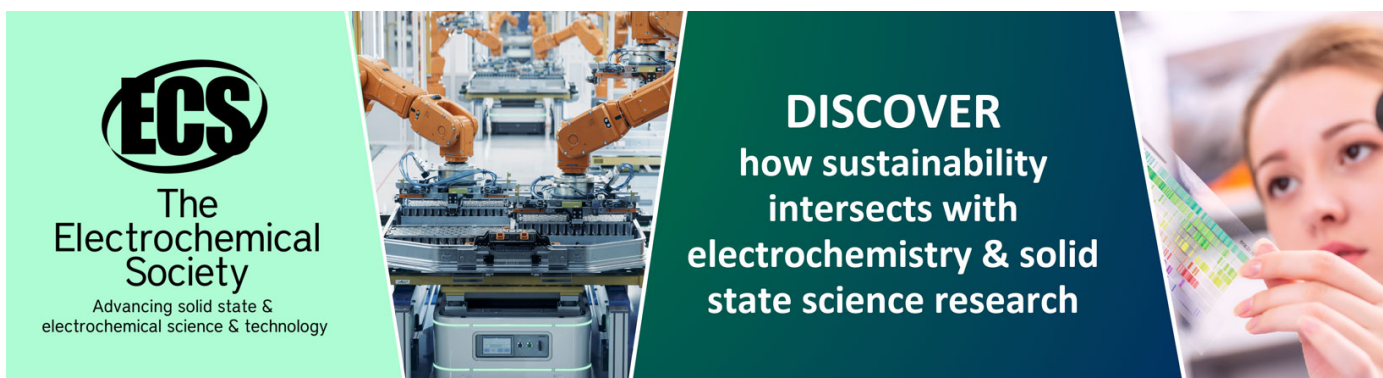
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Coarse grain simulations of linear polymer melts for chain lengths near the reptation transition

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Abstract. Melts of linear polymers differing in the lengths of the chains have been studied by coarse graining simulations. Each polymer is represented by a branched string of soft blobs, and uncrossability constraints are added to prevent chain crossings. Their dynamical and rheological properties are discussed by comparisons to assess the impact of the chain length on the bulk properties without using extrapolation techniques. A satisfactory quantitative agreement with experiments is observed for the diffusion coefficients and zero-shear viscosities of the linear polymers. The power-law relation between viscosity and molecular mass is indicative of the transition regime between Rouse and reptation dynamics.

1. Introduction

As the third branch of scientific study, computer simulations have become more and more prominent with advancements in modern computing technologies. They offer increased control over system parameters in comparison to experiments, access to measures sometimes inaccessible in experiments and a platform to test theoretical predictions[1, 2, 3]. At first sight, it is tempting to perform a polymer simulation where all chemical structures are included in an effort to capture as accurately as possible the interaction details[4, 5]. However, the fact is that polymers exhibit clear time and length scaling for dynamical behaviors. A direct prediction of the large scale dynamics and rheology from such a detailed method would require a huge computational effort that would be costly in terms of computation time. To reduce the computer consumption for the simulation of polymeric systems, coarse-graining approaches may be applied for the study of rheological responses in such systems [6, 7, 8].

The basic concept in coarse graining is to represent a group of atoms or monomers as a larger group unit that neglects the atomistic details within the unit. By this means, the replaced realistic parts will interact with each other as new repeated coarse grained particles. The coarse grain level is depending on the concern of the properties of interest. The less details are needed, the more monomer units could be assembled into a particle. According to this, particle-based simulations can be performed on different scales. In coarse-grained molecular simulations, one particle represents the center of mass of a few atoms. Accordingly a polymer chain will be substituted by string of hard spheres that with sufficient repulsive potential at short distance to prevent chain crossings [9, 10, 11, 12]. In order to reach even larger time and length scales, one coarse-grained particle may lump together many more atoms, such as every 20 monomeric units can be replaced with a mesoscopic entity, which is called ‘blob’. This leads to the soft interactions



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of the blobs that they are able to pass through each other easily[13, 14, 15, 16]. To prevent the unrealistic crossing, the additional restrictions have to be implemented in the entangled polymer system. Due to the generic nature of polymer, most of their chemical differences are not distinguished in large length scales. This naturally inspires us to develop a super coarse graining model that only keep track of the dynamics of the center of mass of the entire chain. Consequently, each polymer chain is sketched into a single particle that interacts with other coarse grained particles under the action of soft conservative energy and dominate entanglement effects[17, 18, 19]. Of course the structure of particle based program does not depend on the level of coarse graining, it in general follows the same loop: in the box with periodic boundary conditions, forces on the particles are calculated at a certain time, positions and velocities are updated to the next time step, and with the new velocities and positions, new forces are evaluated, etcetera.

Computer simulations of polymer dynamics at the level of atoms or chain segments are being used by a number of groups to probe the above concepts. A complication inherent to these studies is the extremely slow dynamics of highly entangled polymers; this makes the simulations very computational intensive, even when using coarse-grained models. In this work, we present a mesoscopic coarse graining model for studying the entangled polymer system. The entanglement effect is accomplished by introducing the uncrossability constraint. The dynamical and rheological properties of linear chains are studied through the typical blob mean square displacements and stress autocorrelation function. A global overview of the TWENTANGLEMENT algorithm[14, 15], the simulation set-up and the applied analysis methods are provided in Section 2. The simulation results are presented and discussed in Section 3, where comparisons are implemented between linear polymers. Our main conclusions are summarized in Section 4.

2. Model and methods

We will apply the coarse-grained TWENTANGLEMENT model, to simulate linear polyethylene melts. Briefly, each coarse-grained particle or ‘blob’ represents a polymer fragment of 20 backbone carbon atoms plus attached hydrogen atoms.

2.1. Coarse-grain interactions

Because of the coarse-graining, the equation of motion of the position of the blobs can be described by the simple first order Langevin equation, which involves the conservative forces $\mathbf{F}^C$ derived from the potential of mean force Φ ,

$$\mathbf{F}_i^C = -\nabla_i \Phi \quad (1)$$

as well as the blob friction ξ and random forces $\mathbf{F}^R$ with the usual statistical properties,

$$d\mathbf{R}_i = -\frac{1}{\xi} \mathbf{F}_i^C dt + \mathbf{F}_i^R, \quad (2)$$

the fluctuation-dissipation theorem demands the relation between ξ and $\mathbf{F}^R$ given in Eq 3 as a condition for thermal equilibrium at the temperature of $T = 450$ K.

$$\langle \mathbf{F}_i^R(t) \rangle = 0, \langle \mathbf{F}_i^R(t) \mathbf{F}_j^R(0) \rangle = 6k_B T \xi \delta_{ij} \delta(t). \quad (3)$$

where k_B is the Boltzmann constant.

The potential of mean force can be approximately presented as a sum of three independent parts, ϕ^b , ϕ^θ and ϕ^{nb} , with the usual meaning of bonded potential, angular potential and non-bonded or van der Waals potential separately. Using microscopic simulations[7, 14] the distribution function P between bonded and non-bonded blobs can be determined. Hence, the potential of mean force can be obtained by taking minus $k_B T$ times the logarithm of measured distributions of blobs, i.e. $\Phi = -k_B T \ln P(\mathbf{R}^n)$.

2.2. Uncrossability

Because each blob represents a flexible collection of bonded atoms, the non-bonded repulsive interactions between blobs are much softer than those between atoms. The repulsions are, in fact, too weak to inhibit crossings of the coarse grained polymers and thus a key property determining the dynamics of polymer melts is lost upon coarse-graining. To prevent these unrealistic crossing events, Padding and Briels developed the TWENTANGLEMENT algorithm that uses elastic forces to contain and reverse bond crossings[14, 15]. In short: an ‘entanglement point’ $\mathbf{X}$ is introduced at the point where the bond between blobs i and $i + 1$ first crosses another bond. The binding energies ϕ^{bond} of these bonds are henceforth calculated using the contour length $L_{i,i+1}$ of the path from blob to blob via the entanglement point. The path between two consecutive blobs can collect multiple entanglement points by ‘crossing’ other paths, resulting in twisting paths of contour length

$$L_{i,i+1} = |\mathbf{R}_i - \mathbf{X}_1^{i,i+1}| + |\mathbf{X}_1^{i,i+1} - \mathbf{X}_2^{i,i+1}| + \dots + |\mathbf{X}_p^{i,i+1} - \mathbf{R}_{i+1}|, \quad (4)$$

running from one bead to the next via a sequence of p entanglement points. Beads may slide along an entanglement point, thereby causing the entanglement point to slip from one bond to the next. An entanglement point survives until the two involved bond paths disentangle, at which occasion the entanglement point is annihilated. The positions of the entanglement points are recalculated every time step by minimizing the elastic energy stored in the bonds, subject to fixed blob positions. The forces exerted by the entanglements on the blobs, by means of the bond energy $\phi^{\text{bond}}(L_{i,i+1})$, are included in the equation of motion of the blobs.

2.3. Analysis methods

The dynamics of polymers in the melt will be quantified by the diffusion coefficient, as extracted from the mean square displacement

$$D(t) = \frac{1}{6t} \langle |\mathbf{R}_i^{\text{cm}}(t) - \mathbf{R}_i^{\text{cm}}(0)|^2 \rangle, \quad (5)$$

with $\mathbf{R}_i^{\text{cm}}(t)$ the center of mass position of the i^{th} polymer at time t , and the pointy brackets denoting an average over all reference times and molecules.

Stress relaxation moduli are calculated from equilibrium simulations by means of the auto correlation

$$G(t) = \frac{V}{6k_B T} \sum_{\alpha\beta} \langle \sigma_{\alpha\beta}(t) \sigma_{\alpha\beta}(0) \rangle, \quad (6)$$

where the sum runs over the six off-diagonal elements and the stress tensor is given by

$$\sigma_{\alpha\beta} = -\frac{1}{V} \sum_{\langle i,j \rangle} (Y_{i,\alpha} - Y_{j,\alpha}) f_{ij,\beta}. \quad (7)$$

Here $Y_{i,\alpha}$ denotes the α -component of the position $\mathbf{Y}_i$ of the i^{th} entity – either a blob or an entanglement point – in the box of volume V , $f_{ij,\beta}$ is the β -component of the force exerted on this entity by entity j , and the sum runs over all entity pairs[15].

3. Results and discussions

In this section the dynamical and rheological properties of melts of polymers will be studied through comparisons. We note that advances in hardware and software have made it possible to simulate the linear polymers over considerably longer time scales than in previous TWENTANGLEMENT studies[15]. This has now made possible a direct evaluation of the dynamical properties of the longer chains, without resorting to the procedure of estimation.

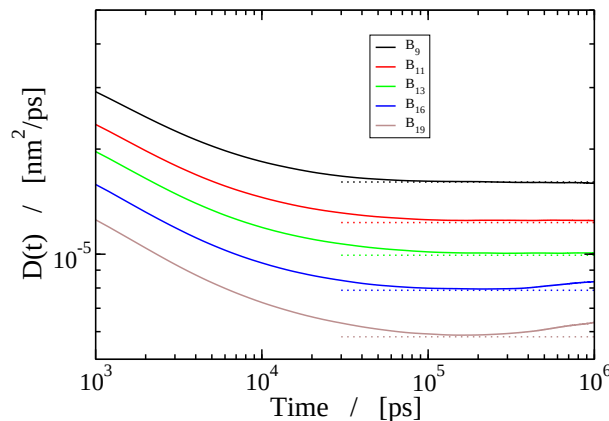


Figure 1. Time-dependent diffusion coefficients for linear polymers of various lengths, as extracted from the mean squared displacement of the polymer center of mass.

3.1. Diffusion

From theory and experimental observations it is known that the diffusion coefficient in a melt of linear polymers decays with increasing molecular mass M , with $D \propto M^{-1}$ for short polymers in the Rouse regime and $D \propto M^{-2}$ for long polymers in the reptation regime[20, 21, 22]. Figure 1 shows the time-dependent center-of-mass diffusion coefficients as extracted from the simulations by Equation 5. After a transient decay on the nanosecond time scale, the functions are seen to reach a plateau value that defines the long time diffusion coefficient D . For the longest chain, which does not reach a clear plateau, D is approximated by the minimum value of the $D(t)$ curve. The terminal diffusion coefficients are plotted in Figure 2 against the molecular weight, showing a satisfactory quantitative agreement with the experimental data by Pearson *et al.*[23]. Fitting the data with a power law yields an exponent of -1.27, indicating that the chains

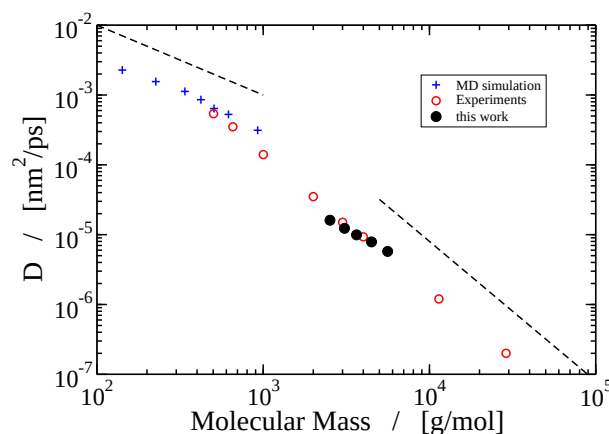


Figure 2. Long time diffusion coefficients of linear polymers as a function of molecular mass. The black dots are the results of this study, the red circles represent experimental data from Pearson *et al.*[23], and the blue pluses show molecular dynamics simulation results obtained by Mondello *et al.*[24, 25]. The dashed lines illustrate the slopes expected for the Rouse regime (left, $D \propto M^{-1}$) and the reptation regime (right, $D \propto M^{-2}$).

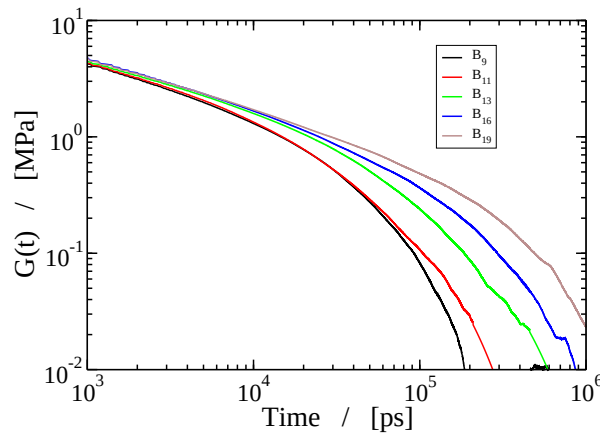


Figure 3. Block-averaged stress relaxation moduli for five melts of linear polymers of various chain lengths.

under investigation are in the transition region between the Rouse and reptation regimes. In comparison with the experimental data, the simulated transition occurs at a higher molecular mass and over a wider mass range; we suspect that this is a consequence of the softness of the coarse-grained system, in which the beads are less strongly confined by their neighbours and the uncrossable bonds than are the atoms in an experimental melt.

Both Figure 1 and Figure 2 suggest that the simulations with the largest linears have not yet reached the terminal diffusion coefficients. Besides this, the diffusion coefficient may have an additional regime between Rouse and reptation as suggested by Harmandaris *et al.*[20].

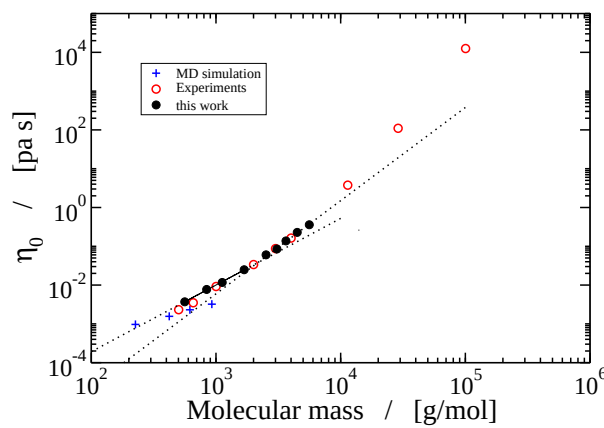


Figure 4. Zero shear viscosities of melts of linear polymers as a function of the molecular mass. The black dots are the results of this study, the red circles represent experimental data from Pearson *et al.*[23], and the blue pluses show simulation results obtained by Mondello *et al.*[24] using molecular dynamics. The dashed lines highlight the experimental scaling laws at low mass ($\eta \propto M^{1.8}$) and high mass ($\eta \propto M^{3.5}$).

3.2. Stress relaxation moduli

Stress relaxation moduli for five linear polymers are collected in Figure 3. The curves almost coalesce for short time and fan out for large time, with the longer polymers relaxing more slowly than the shorter ones. The resulting viscosities at vanishing shear rate are plotted in Figure 4, supplemented with the zero-shear viscosities of three shorter chains, down to B₂. The results indicate that the simulations are in the transition regime between Rouse and reptation dynamics. The power of 1.71 ± 0.05 extracted from the first four points is appreciably lower than the power of 2.4 ± 0.2 extracted from the next four points, confirming that the simulated melts are in the transition regime. Comparison with the experimental viscosities of Pearson *et al.*[23] reveals a good quantitative agreement. The location and width of the transition regime of the simulated melts appear to agree with those of the experimental melts.

4. Conclusions

The diffusive and rheological properties of linear polyethylene polymers of various lengths have been studied by computer simulations using the highly coarse-grained TWENTANGLEMENT technique. Comparing the simulated linear polymers, highlights the impact of the chain length on the dynamical properties of the melt. By calculating the autocorrelation function of the chains, it is found that the longer arm has a slower relaxation decay. Comparison with the experimental viscosities gives good quantitative agreement and a regime for chains lies between the Rouse and reptation is investigated and confirmed from the scaling exponents. In future work, longer chains and new topologies of polymer will be investigated by this model.

Acknowledgments

Authors acknowledge the financial support of National Natural Science Foundation of China(Grant:21704010) and Natural Science Foundation of Liaoning Province(Grant:2015010217-301).

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