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Molecular dynamics (MD) simulations for polymers

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Abstract. We review some recent MD simulations for polymer melts. For the melt chains of up to six entanglement lengths are taken into account. The data strongly support the reptation picture.

1. Introduction

In recent years computer simulations have become increasingly important and valuable for the investigation of polymeric systems [1-3]. For polymers especially, detailed analytical theories can often only be worked out for ideal systems, which are not available for experiments. This often makes a direct comparison rather difficult. Here computer simulations can play an important role in bridging the gap between experiment and analytical theory.

2. Polymer melt

Because of the extremely slow relaxation in polymer systems there is no possibility of performing a simulation for the dynamics of, for example, a melt with chemical details [4,5]. The models have to be as idealized as possible. For our purpose this means one has to take the excluded volume and the non-crossability of the chains into account. For a molecular dynamics simulation, where one essentially integrates Newton's equations of motion, one has to optimize the potential parameters for the above requirements together with an as large as possible integration time step. The interaction potential then was taken to be [3]

$$U^0(r) = \begin{cases} 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6 + \frac{1}{4}] & r \leq 2^{1/6}\sigma \\ 0 & r > 2^{1/6}\sigma \end{cases} \quad (1)$$

for the monomer-monomer potential, with ϵ, σ being the standard Lennard-Jones parameters. For the nearest neighbours along the chain an attractive (FENE) potential

$$U^{\text{bond}}(r) = \begin{cases} 0.5R_0^2 k \ln[1 - (r/R_0)^2] & r \leq R_0 \\ \infty & r > R_0 \end{cases} \quad (2)$$

was added. The parameters were set to $k = 30\epsilon/\sigma^2$, $R_0 = 1.5\sigma$, $k_B T = 1.0\epsilon$ and the density to $\rho = 0.85\sigma^{-3}$. The integration timestep $\Delta t = 0.006\tau$. The samples

investigated contained chain lengths N between $N = 5$ and $N = 400$ and 20 chains (10 for $N = 400$). To check finite-size effects, one sample of $M = 100$ chains of length $N = 200$ was investigated.

To investigate the dynamics of polymer melts extremely long runs are necessary. Thus a stabilization of the integration procedure is needed. This was done by solving Newton's equation of motion with a very weak coupling of the particles to a friction and a heat bath [4, 6]. The friction and the heat bath are coupled via the fluctuation dissipation theorem. The programs were optimized following the layered linked cluster method [7].

For short chains, one typically observes the classical Rouse behaviour. Once the chains significantly exceed the entanglement length N_e , a dramatic slowing down occurs [8, 9]. The diffusion constant $D(N)$ changes from $D \sim 1/N$ to $D \sim 1/N^2$. Within the reptation picture, the chain is assumed to move on a scale of distances larger than $\Delta r^2 \sim \langle R^2(N_e) \rangle$, the diameter of a chain of length N_e and times larger than $\tau_e \sim N_e^2$ along its own contour. Thus the Rouse-like mean square displacement of the monomers $g(t)\alpha t^{1/2}$ should cross over to $g(t)\alpha t^{1/4}$. Figure 1 shows this for inner monomers. From this we get $N_e \approx 35$ and $\tau_e \approx 1800\tau$. Combining all the various ways to analyse the data, we find strong evidence for the reptation picture.

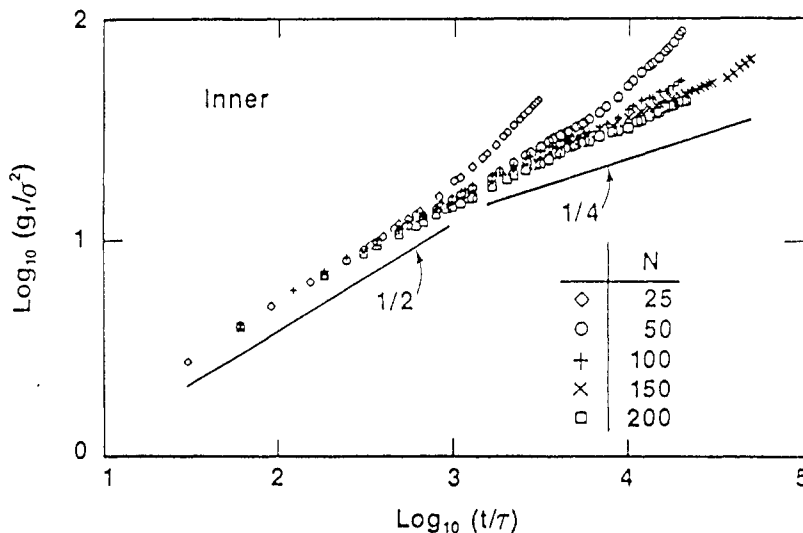


Figure 1. Mean square displacement $g_1(t)$ against t/τ averaged over the inner 5 monomers for five values of N ; the minimal slope reached is about 0.27.

From microscopic experiments, there has been a longstanding controversy as to whether reptation describes the chain motion or not [10–13]. To understand this, we have to map the model monomers onto chemical monomers. The characteristic length here is *not* the persistence length, but the entanglement length N_e or entanglement molecular mass M_e respectively. To check this a plot of $D(N)$ divided by the extrapolated Rouse diffusion constant $D_{\text{Rouse}}(N)$ against N/N_e or M/M_e should give a universal curve for all systems. Figure 2 shows this for our data, for polyethylene (PE) [14] and for polystyrene (PS) [15]. It shows excellent agreement between PE and our data, while there are deviations for PS. This raises some questions about the validity

of universality in this crossover region. Since PS has a small side group, while PE does not, we think the agreement with PE is more significant than the deviations with PS. (Fitting the data to PS would just shift N_e .) This mapping makes it possible to predict length and time scales, using the persistence lengths and monomeric friction coefficients. With τ_e being the time, when the deviations from Rouse are becoming significant we find for PDMS at 373 K, $\tau_e = 10^{-7}$ s while for PTHF at $T = 418$ K, $\tau_e = 3.2 \times 10^{-9}$ s and for PEP at 500 K we get $\tau_e = 10^{-8}$ s. Considering a maximal time resolution of $\Delta t \leq 10^{-8}$ s, for the old neutron spin echo instrument in Grenoble, it is clear that deviations from Rouse were seen for PTHF [11], but not for PDMS [12]. Recently they were also found for PEP [13] using a new instrument with a resolution of 4×10^{-8} s.

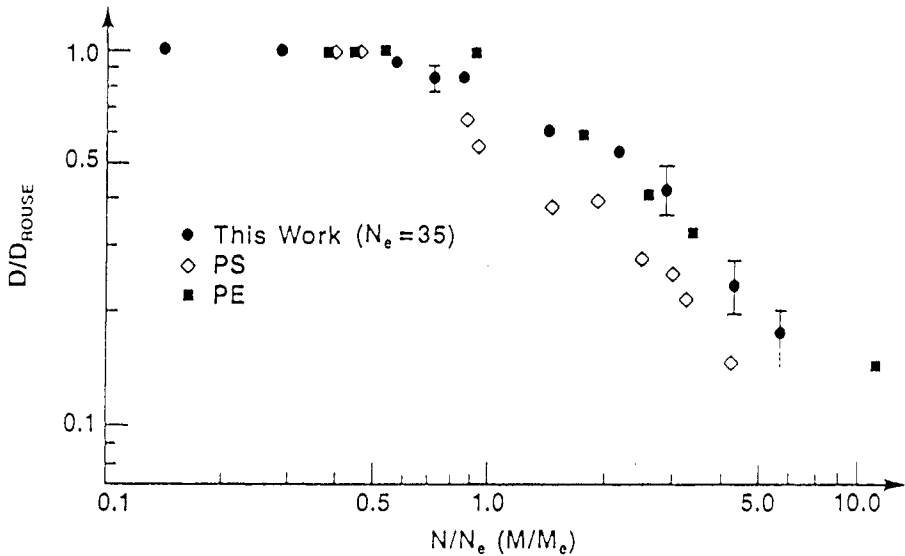


Figure 2. Diffusion data for PS [25] and PE [24] compared with the simulation results [4].

3. Conclusions

In this paper we very shortly reviewed some recent work on the dynamics of polymer systems. We showed that simulations can successfully bridge the gap between theory and experiment. We have been able to predict time and length scales explicitly, where theory only gives general relationships. For the polymer melt already within the crossover regime there are indications that support the reptation model. The mapping onto chemical polymers was able to resolve a longstanding controversy between neutron spin echo experiments.

On the basis of the above discussed examples, we think we were in a good position to investigate more complicated and/or other important problems of polymer physics. Investigations on the hydrodynamic properties of polymers in solution are currently underway [16]. There, besides the q^{-3} power law for the dynamic scattering function, we also directly observed the $t^{2/3}$ power law for the mean square displacements of

the monomers. The more complicated the systems under consideration become, the more difficult it will be to provide both well controlled experiments and a thorough analytical theory. With increasing computer power, simulations will become more and more important.

Acknowledgments

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