Crossover from Rouse to Reptation Dynamics: A Molecular-Dynamics Simulation

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We present the results of an extensive molecular-dynamics simulation of a dense polymer system. We show for the first time that simulations are able to cover the whole regime from pure Rouse dynamics to reptation dynamics and give strong evidence of the latter. The mean square displacements clearly exhibit a $t^{1/4}$ power law. A mode analysis shows that the high-frequency modes follow the Rouse relaxation while those at lower frequency display reptation relaxation. Both quantities give the same entanglement length.

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The physics of polymeric liquids is one of the fascinating and challenging problems of modern condensed-matter physics.[1] Because of the topological interactions, melts of linear polymers display a rich and unusual viscoelastic behavior.[2] Though experiments have been very important in elucidating many of the properties of these complex systems, they are unable to investigate the microscopic origin of this behavior directly. For this reason, computer simulations of the motion of highly entangled polymers can play an important role in understanding these complex systems. Here we present results of the first large-scale molecular-dynamics simulation of a melt of linear polymers which covers the range from the short-chain, nonentangled regime (Rouse) to the highly entangled regime (reptation).

The dynamics of polymeric melts is typically discussed in terms of the Rouse and reptation model.[2] For short chains, the surrounding monomers cause a stochastic motion of an individual monomer. This motion is constrained by the connections of the monomer along the chain, leading to standard Rouse behavior. Although there are some questions about the short-time behavior, this theory describes the systems very well.[3-8] The longest relaxation time $\tau_N \sim N^2$, where N is the number of bonds, while the diffusion constant $D \sim N^{-1}$ and viscosity $\eta \sim N$. Experimentally, for $N > N_e$, the entanglement length, this dependence changes to $D \sim N^{-2}$ and $\eta \sim N^{3.4}$.[8] This is usually explained by the reptation model of Edwards[9] and de Gennes.[10] Physically, reptation means that chains on a length scale larger than $d_T \sim N_e^{1/2}$ (the diameter of a chain of N_e bonds) move predominantly along their own contour. The chain has a Rouse-type relaxation up to a time $\tau_e \sim N_e^2$, after which one has a Rouse relaxation along the coarse-grained path of a chain with bonds, consisting of N_e monomers each. Since this is a one-dimensional diffusion along a random-walk path, the chain needs a time $\tau_{\text{rep}} \sim (N/N_e)N^2$ to leave the original tube. Consequently, one gets $\eta \sim N^3$.[11] This model has been very successful in the description of qualitative aspects of the dynamics of melts. Though the $\eta \sim N^{3.4}$ behavior was interpreted as a short-chain effect, it persists for chains of more than 1000 N_e.[12,13] Microscopically, this *Ansatz* leads to a power-law regime in the mean square displacement $g_1(t)$ of the monomers of the form $g_1 \sim t^{1/2}$, $t < \tau_e$; $g_1 \sim t^{1/4}$, $t < \tau_N$; $g_1 \sim t^{1/2}$, $t < \tau_{\text{rep}}$.[2,10] Finally for $t > \tau_{\text{rep}}$, $g_1 \sim t$. The $t^{1/4}$ behavior is a direct consequence of the reptation concept. However, until now it has not been seen directly![3-7,14,15] Consequently the validity of the concept has been questioned and alternative approaches have been discussed.[16]

It is clear that computer simulations should be capable of yielding insight into the microscopic mechanism of the dynamics of such systems.[17] However, up to now all attempts have failed to see the expected signature of reptation in $g_1(t)$.[3-6,15] What became evident from these studies was that it would be extremely difficult to see the anticipated effects and that the static screening length certainly is much smaller than the entanglement length. One recent investigation, in particular, of long chains on the cubic lattice ($N = 800$) (Ref. 15) cast considerable doubt on the general validity of the reptation concept. However, Monte Carlo simulations on a lattice have one serious disadvantage.[18] In order to have a high acceptance of the moves, the density ρ has to be relatively small ($\rho = 0.5$ in Ref. 15). Thus the chains have to be very long in order to mimic a melt of long polymers. An alternative approach is to do continuum simulations of off-lattice chains at a higher density. Here we present such a calculation using a molecular-dynamics method where the monomers are very weakly coupled to a frictional background and to a heat bath.[19,20]

The integrated equations of motion are

$$\ddot{\mathbf{r}}_i = -\nabla \textstyle\sum_{j \neq i} U_{ij} - \Gamma \dot{\mathbf{r}}_i + \mathbf{W}_i(t). \tag{1}$$

The interaction potential U_{ij} is purely repulsive (Lennard-Jones) between all monomers with a strong attractive interaction between neighbors along the chain[19] and $\mathbf{W}_i$ is a Gaussian white-noise source. The time unit is $\tau = \sigma(m/\epsilon)^{1/2}$ in standard Lennard-Jones units in which

σ is the unit of length, m is the mass of a monomer, and ϵ is the unit of energy. Here we choose $\Gamma = 0.5\tau^{-1}$ and set $\sigma = m = \epsilon = 1$. Besides Γ the other parameters were the same as in Ref. 19. For short times ($t \ll \Gamma^{-1}$) the motion of a monomer is ballisticlike in a standard molecular dynamics, while for long times the motion is diffusive. For a single chain this reproduces Rouse-type dynamics. Simulations were carried out for a density $\rho\sigma^3 = 0.85$, a temperature $T/\epsilon = 1.0$, and a time step $\Delta t = 0.006\tau$. We monitored the maximum separation between monomers along the chain to assure that no bond cuts occurred. With $\mathbf{r}_1$ and $\mathbf{r}_N$ being the positions of the two ends of the chain, we found that

$$\langle R^2(N)\rangle = \langle (\mathbf{r}_1 - \mathbf{r}_N)^2\rangle = \langle l^2\rangle c_\infty N, \tag{2}$$

with average bond length $\langle l^2\rangle = 0.940$, and a persistence length $l_p = \sqrt{c_\infty} \approx 1.34$. Systems studied had M chains with N monomers per chain, for $M/N = \frac{25}{10}, \frac{30}{20}, \frac{16}{50}, \frac{20}{75}, \frac{20}{100}$, and $\frac{20}{150}$. After equilibration we ran the systems for up to 15×10^6 time steps. These times allowed all chains to move at least $2\langle R_G^2\rangle$. Figure 1 shows a plot of $\langle R^2\rangle$ and the mean squared radius of gyration $\langle R_G^2\rangle$. Thus, our chains consist of up to more than 100 persistence lengths and should be able to cover the crossover to the entangled regime.

The importance of strong fluctuations of the outer monomers was already seen for chains in a straight tube.[5,21] To confine ourselves to the "most entangled monomers" we calculated the mean square displacements of the five innermost monomers as a function of time. A detailed description of the properties of the chains, especially with respect to the position of the monomers along the chain, is in preparation.[22] The function

$$g_1(t) = \frac{1}{5}\sum_{i=N/2-2}^{N/2+2} \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2\rangle \tag{3}$$

was evaluated typically out to about $\frac{1}{3}$ of the total run time, averaging over all chains and at least 500 starting states. Since the introduced random force causes an overall diffusion of the whole system, this is subtracted from the motion of the chains. D was then calculated from the extrapolation of the motion of the center of mass of the chains. Figure 2 gives our results for $g_1(t)$ for chains of length $N \geq 30$ and D for $N = 10$ to 150. The plot of D shows that the data deviate from Rouse behavior ($6DN \sim \text{const}$) for $N \gtrsim 30$. As has been seen experimentally,[23] we even find a stronger than N^{-2} decrease of D, which is known to be a crossover effect due to the strongly enhanced mobility of the chain ends. Using[2]

$$D(N) = \tfrac{4}{15} D_{\text{Rouse}}(N) N_e/N, \tag{4}$$

where D_{Rouse} is the expected diffusion constant due to the Rouse model, we find $N_e \approx 110$ for the largest chain of $N = 150$. However, it is well known that the real entanglement length cannot be determined accurately from the diffusion constant. For homopolymeric melts, the bare diffusion constant typically gives values for N_e which are about twice as large as the N_e from the plateau modulus of the viscosity.[23,24] Also, we are still in the crossover regime where the slope for $D(N)$ is somewhat steeper than the expected N^{-2}. Therefore, we believe that this estimation of N_e is too large, as shown below where we find that N_e is actually smaller than about 50 monomers for our model.

Much more insight into the behavior of the chains is given by the direct analysis of $g_1(t)$. Figure 2 shows that for short chains no deviation from Rouse behavior is seen (to study early time deviations from Rouse behavior[3] we shall analyze shorter times[22]). For $N \geq 50$ at a time $\tau_e \approx 1700\tau$ and a distance $d^2 \approx 21$, we find strong

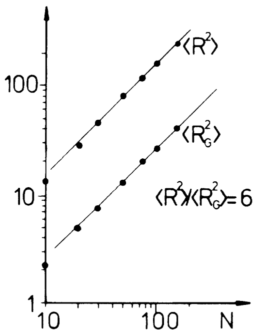

FIG. 1. Mean square end-to-end distance $\langle R^2(N)\rangle$ and radius of gyration $\langle R_G^2(N)\rangle$ vs N for $10 \leq N \leq 150$. The lines give the expected slope of 1.

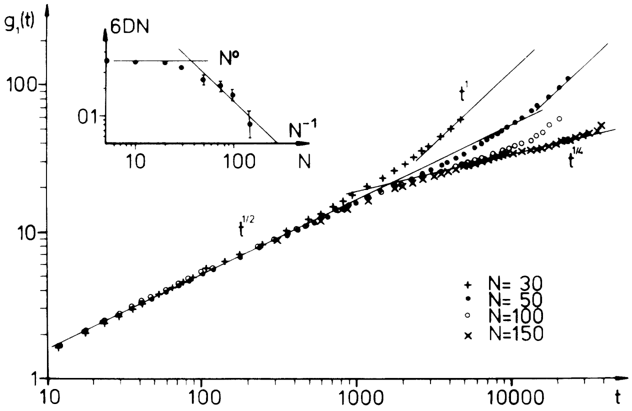

FIG. 2. Mean square displacement $g_1(t)$ vs t/τ. Inset: Diffusion constant $6DN$ vs N. D was obtained from the diffusion, $6D = \lim_{t\to\infty} \langle [r_{\text{c.m.}}(t) - r_{\text{c.m.}}(0)]^2\rangle$, of the entire chain with

$$\mathbf{r}_{\text{c.m.}} = N^{-1}\sum_{i=1}^{N} \mathbf{r}_i.$$

The time is given in units of τ.

deviations from the Rouse $t^{1/2}$ behavior. One sees a crossover from a weak dip ($N=50$) to a clear $t^{1/4}$ behavior ($N=150$) for $g_1(t)$, as expected by reptation. It is important to note that these values are *independent* of chain length, meaning that the internal monomers do not feel their chain ends. If we assume a Rouse model for the motion of the monomers up to a time τ_e, $g_1(\tau_e)$ should give $g_1(\tau_e) \cong 2\langle R_G^2(N_e)\rangle$. With $d^2 = g_1(\tau_e) = 21$ and a persistence length of 1.34, $N_e \cong 35$. This is more than 20 persistence lengths for the present model. It should be noted that the average over all monomers of the chains for $g_1(t)$ does not display a clean $t^{1/4}$ behavior because of the very mobile ends. As expected, the estimates of N_e from g_1 and from D give somewhat different answers.

To check the validity of the data as well as the equilibration we calculated the Rouse modes given by

$$\mathbf{X}_p(t) = \frac{1}{N}\left[\sum_{i=1}^{N} \mathbf{r}_i(t)\cos\left(\frac{p\pi(i-1)}{N-1}\right)\right] - \frac{1}{2N}[\mathbf{r}_1(t) + \mathbf{r}_N(t)]. \quad (5)$$

As the chains are Gaussian, these are eigenmodes of the chains and cross correlations turned out to be zero within our error bars. The amplitudes $\langle \mathbf{X}_p(0)\cdot\mathbf{X}_p(0)\rangle$ vary as p^{-2} as required for an ideal melt chain. Together with Fig. 1 this gives a very sensitive check on the equilibrium of the system.[25] Of special importance is the behavior of the autocorrelation function $\langle \mathbf{X}_p(t)\cdot\mathbf{X}_p(0)\rangle$. For $N/p < N_e$, the longest relaxation time for mode p is $\tau_p \sim (N/p)^2$, while for $N > N_e$ we expect $\tau_p \sim (N/p)^3$ if reptation holds. Figure 3 shows the relaxation time τ_p vs N/p, which should give a universal curve. The data almost perfectly define a common curve with a clear crossover from $\tau_p \sim (N/p)^2$ to $\tau_p \sim (N/p)^3$ for $N_e = N/p \approx 35 \pm 5$. This is also displayed in the inset. Thus the internal modes define a value of $\tau_e \approx 1800\tau$ and $N_e \approx 35$ which are exactly the same τ_e and N_e as from g_1. It should be noted that neither experiment nor simulation has shown this behavior before.

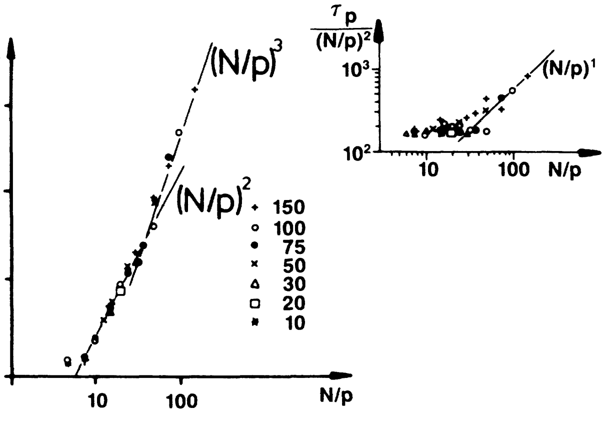

FIG. 3. Relaxation time of the various modes for $10 \le N \le 150$ vs N/p. Inset: $\tau_p(p/N)^2$ vs N/p. The time τ_p was obtained as the inverse relaxation rate. After an initial drop all the data ($N/p \gtrsim 10$) showed a single exponential decay, defining τ_p. Note that the time here is given in terms of the integration time step, $\Delta t = 0.006\tau$. This gives the crossover at about $\tau_e = 1800\tau$.

We can also check how the results for the diffusion are influenced by the free ends. This could be done by comparing the bead friction ζ calculated from the modes with that calculated from the Rouse limit of D. The relaxation rate of the modes in the Rouse limit[12] (plateau of inset in Fig. 3) is given by $\tau_p = (N/p)^2\zeta l^2/3\pi^2 k_B T$ which gives $\zeta_{\text{modes}} \approx (30 \pm 3)\tau^{-1}$. From the diffusion constant $D = k_B T/N\zeta$, one gets $\zeta_D \approx (15 \pm 3)\tau^{-1}$. This factor of 2 was also found for polystyrene.[26]

To further compare our results with experiments, we need to map our monomers onto chemical species. Here we will do this for two examples, namely polydimethylsiloxane (PDMS) at room temperature and polystyrene (PS) at about 210 °C. Usually the persistence lengths are compared. However, this is not the proper way to proceed since one knows that N_e is not only a function of density, but also a function of temperature and pressure. Instead, we map the entanglement lengths by comparing N_e measured from the plateau modulus to that found from the Rouse modes. Since the increase in relaxation time of the modes produces the plateau modulus, we think this is the natural choice. Thus, $N_e = 35$ corresponds to $M_e = 18\,000$ (PS) and 9000 (PDMS), which means that our longest chains are equivalent to molecular weights of about 77 000 (PS) and 38 000 (PDMS), respectively. With[8,27] $l\sqrt{c_\infty} = 6$ Å (PDMS) and 7 Å (PS) and molecular weights of 104 (PS) and 72 (PDMS), this gives, with $d_T^2 = 0.8\langle R^2(N_e)\rangle^2$, tube diameters of $d_T \approx 82$ Å (PS) and $d_T \approx 60$ Å (PDMS).[2,28]

These data can be also used to calculate the distance where an onset of the $t^{1/4}$ regime should be seen. As our data show, the onset of the $t^{1/4}$ regime is given by $d^2 = 2\langle R_G^2(N_e)\rangle$. Again using the above data and $R^2/R_G^2 = 6$, one finds $d = 39$ Å (PDMS) and 53 Å (PS). Since the early neutron spin-echo experiments did not label the inner part of a chain,[3] it is clear why they did not observe the $t^{1/4}$ regime, although they studied PDMS up to $M_w = 60\,000$. The averaging over all monomers strongly smeared out the effect of reptation, which then was beyond the resolution of the experiment. But by use of a triblock copolymer with a labeled center, especially for PDMS, it should be possible to verify the predicted value of 39 Å for the onset of the $t^{1/4}$ regime. Such an experiment has yet to be performed.

To conclude, we present a simulation which is able to cover the crossover from Rouse to reptation. The data compare extremely well with results obtained by viscosity and diffusion-constant measurements interpreted by the reptation model. This is the first case where the microscopic polymer dynamics is shown with the reptation model. A final proof, however, would be the identification of the motion of the monomers along the primitive path.[22]

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[1] For an overview, see e.g., P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca, NY, 1979).

[2] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).

[3] D. Richter, A. Baumgärtner, K. Binder, B. Ewen, and J. B. Hayter, Phys. Rev. Lett. **47**, 109 (1981), and **48**, 1695 (1982).

[4] A. Baumgärtner and K. Binder, J. Chem. Phys. **75**, 2994 (1981).

[5] K. Kremer, Macromolecules **16**, 1632 (1982).

[6] M. Bishop, D. Ceperley, H. L. Frisch, and M. H. Kalos, J. Chem. Phys. **76**, 1557 (1982).

[7] A. Kolinski, J. Skolnick, and R. Yaris, J. Chem. Phys. **86**, 1567 (1987), and references therein.

[8] J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1980).

[9] S. F. Edwards, Proc. Phys. Soc. London **91**, 513 (1967).

[10] P. G. de Gennes, J. Chem. Phys. **55**, 572 (1971), and **72**, 4756 (1980).

[11] M. Doi and S. F. Edwards, J. Chem. Soc. Faraday Trans. 2 **74**, 1789, 1802, 1818 (1978).

[12] R. H. Colby, L. J. Fetters, and W. W. Graessley, Macromolecules **20**, 2226 (1987).

[13] M. Rubinstein, Phys. Rev. Lett. **59**, 1946 (1987). This paper considers chains in a straight tube and solves the dynamics of de Gennes's defects. The author shows that under certain conditions the 3.4 power law of the viscosity can remain for all chain lengths.

[14] A. Baumgärtner, Faraday Symp. Chem. Soc. **18**, 221 (1983). Here results of the first simulation which did not disagree with reptation were presented. However, no further analysis was given.

[15] A. Kolinski, J. Skolnick, and R. Yaris, J. Chem. Phys. **86**, 7164 (1987).

[16] J. Skolnick, R. Yaris, and A. Kolinski, J. Chem. Phys. **88**, 1407 (1988); J. Skolnick and R. Yaris, J. Chem. Phys. **88**, 1418 (1988), and references therein.

[17] Microscopic means on length scales of a statistical monomer and times much larger than the time for bond fluctuations of the chemical bonds.

[18] K. Kremer and K. Binder, Comput. Phys. Rep. (to be published).

[19] G. S. Grest and K. Kremer, Phys. Rev. A **33**, 3628 (1986).

[20] T. Schneider and E. Stoll, Phys. Rev. B **17**, 1302 (1978).

[21] K. Kremer and K. Binder, J. Chem. Phys. **81**, 6381 (1984).

[22] K. Kremer, G. S. Grest, and I. Carmesin, to be published.

[23] N. Watanabe and T. Katoka, Macromolecules **20**, 530 (1987); M. Antoniette, K. J. Fölsch, and H. Sillescu, Makromol. Chem. **188**, 2317 (1987).

[24] W. W. Graessley, to be published; see also W. Hess, Macromolecules **19**, 1395 (1986).

[25] I. Carmesin and K. Kremer, to be published.

[26] H. Sillescu, private communication.

[27] P. J. Flory, *Statistical Mechanics of Chain Molecules* (Intersience, New York, 1969).

[28] W. W. Gressley, J. Polym. Sci. Polym. Ed. **18**, 27 (1980).