On the Dynamics and Disentanglement in Thin and Two-Dimensional Polymer Films

H. Meyer, T. Kreer, A. Cavallo, J. P. Wittmer and J. Baschnagel

1 Institut Charles Sadron, 6 rue Boussingault, 67083 Strasbourg, France

Abstract

We present results from molecular dynamics simulations of strictly two-dimensional (2D) polymer melts and thin polymer films in a slit geometry of thickness of the order of the radius of gyration. We find that the dynamics of the 2D melt is qualitatively different from that of the films. The 2D monomer mean-square displacement shows a $t^{8/15}$ power law at intermediate times instead of the $t^{1/2}$ law expected from Rouse theory for nonentangled chains. In films of finite thickness, chain entanglements may occur. The impact of confinement on the entanglement length $N_e$ has been analyzed by a primitive path analysis. The analysis reveals that $N_e$ increases strongly with decreasing film thickness.

1 INTRODUCTION

Thin polymer films are in the focus of current research not only due to their technological importance, but also because their properties can differ substantially from those of the bulk [1]. For example, polymers in the bulk melt are considered ideal Gaussian chains [2]. Since the extensions of a Gaussian chain in different spatial directions are uncoupled, Silberberg [3] hypothesized that polymer conformations remain unperturbed in the direction parallel to the film surface. In perpendicular direction, however, conformations may be perturbed because chains are folded back into the film at the surface. This reflection thus leads to an increase of the self-density, and one may expect that, for ultrathin films, this increase could also alter chain conformations and dynamics in direction parallel to the surface.

The impact of this increased self-density on chain entanglements was discussed in Ref. [4] and recent experiments support the idea that the effective entanglement density decreases with film thickness [5]. On the other hand, in strictly two dimensions chains do not overlap so that there are no entanglements. The properties of two-dimensional (2D) melts have recently been discussed theoretically [6]. Interestingly, the theory suggests that the intuitive expectation—if entanglements are absent, the Rouse model [2] should apply—is not true. Chain relaxation in 2D is predicted to be faster than Rouse dynamics.

In this paper, we present results on polymer conformation and dynamics in thin films at high temperature (i.e., far above the glass transition; the dynamics close to the glass transition is discussed e.g. in Refs. [7, 8]). For films of finite thickness, we exemplify the impact of confinement on the entanglement length for one chain length, $N = 256$. For strictly 2D films, we present data for a broader range of chain lengths, which provide evidence for monomer dynamics faster than expected from Rouse theory, in accord with the predictions of Ref. [6].
2 SIMULATION MODEL

The results presented in this article are obtained with a flexible, purely repulsive bead-spring model. The model is derived from a coarse-grained model for polyvinylalcohol (cgpva) [9] which has been employed to study polymer crystallization [10]. It is characterized by two potentials: a harmonic bond potential and a nonbonded potential of Lennard-Jones (LJ) type. The parameters of the bond potential are adjusted so that the ratio of bond length $\ell_0$ to monomer diameter $\sigma_0$ is approximately the same as in the standard Kremer-Grest model (i.e., $\ell_0 = 0.97\sigma_0$) [11]. While the Kremer-Grest model utilizes a 12-6 LJ potential to describe nonbonded interactions, our nonbonded potential has a softer repulsive part. It is given by

$$U_{\text{cgpva}}(r) = \epsilon_{\text{cgpva}} \left[ \left( \frac{\sigma_0}{r} \right)^9 - \left( \frac{\sigma_0}{r} \right)^6 \right],$$

where $\epsilon_{\text{cgpva}} = 1.511 k_B T$ and the monomer diameter $\sigma_0$ is related to the standard LJ $\sigma$ by $\sigma_0 = 0.89\sigma$. Equation (2.1) is truncated in the minimum ($r_{\text{cut}} = 1.02\sigma$) and shifted to zero in order to obtain purely repulsive nonbonded interactions. In the following we report all data in LJ units: lengths are given in units of $\sigma$, temperature in units of $\epsilon/k_B$ (energy $\epsilon = 1$ and Boltzmann’s constant $k_B = 1$), and time in units of $\tau = \sqrt{\alpha^2 m/\epsilon}$ (mass $m = 1$).

We perform molecular dynamics simulations in the canonical ensemble with a Langevin thermostat (friction constant $\Gamma = 0.5$) at temperature $T = 1$ and monomer density $\rho = 1.2$. (In terms of $\sigma_0$ this density corresponds to $0.84\sigma_0^{-3}$, the typical melt density of the Kremer-Grest model [11].) The equations of motion are integrated by the velocity-Verlet algorithm with an integration time step of 0.01.

Repulsive walls are placed in the $xz$-plane at $y = 0$ and $y = D$ by introducing a short-range monomer-wall interaction: we choose $U_{\text{nw}}(y) = 2U_{\text{cgpva}}(y)$ if $y < r_{\text{cut}}$ and $D - y < r_{\text{cut}}$. For strictly two-dimensional (2D) films a wall distance of $D = 1.9$ was chosen. This distance is so small that the monomers only vibrate perpendicular to the film plane with a maximum amplitude of $\pm 0.22$ [12]. For the 2D melt, simulations were also performed with the Kremer-Grest model as a “control experiment”. The results reported in the next section are the same for both models.

3 DYNAMICS IN STRICTLY TWO-DIMENSIONAL FILMS

In a 2D melt, chains cannot overlap; they must stay separated from each other. These segregated chains have an irregular shape [6] which is determined by (binary) contacts with other chains. Recent theoretical work suggests that the perimeter $L$ of 2D chains is not proportional to the radius of gyration $R_g$ (this would be the case if the chains were disk-like objects). Rather it is predicted that $L \sim N^{5/8}$, whereas $R_g \sim N^{1/2}$ [6]. Recent simulation results support this prediction [13].

The theory of Ref. [6] considers a chain as sequence of self-similar subchains containing $s$ monomers ($1 \ll s \leq N$). So one expects the radius of gyration and the perimeter of the subchains to scale with $s$ as $R_g(s) \sim s^{1/2}$ and $L(s) \sim s^{5/8}$. These conformational features have an impact on the dynamics. Reference [6] suggests that the subchain relaxation is controlled by friction at chain boundary and predicts that the corresponding relaxation time $\tau(s)$ scales with $s$ as $\tau(s) \sim s^{15/8}$ ($1 \ll s \leq N$).

We can test this prediction by analyzing the mean-square displacement (MSD) of the innermost monomer of a chain, $g_1(t)$. For displacements inside the volume pervaded by a chain, the distance covered by a monomer in time $t$ should be proportional to $R_g(s)$. Thus, we expect to find $g_1(t) \sim R_g^2(s) \sim s \sim t^{8/15}$, instead of the Rouse prediction $g_1(t) \sim t^{1/2}$ [2]. Figure [1] shows
that this prediction agrees well with the simulation. Moreover, the right panel of Fig. 1 reveals that the simulated \( g_i(t) \) is sufficiently precise to distinguish between \( t^{8/15} \) and \( t^{1/2} \)—albeit the exponents are numerically very close—and that Rouse behavior may be ruled out.

In addition to that, we find that also the center of mass exhibits a power-law regime where \( g_{cm}(t) \sim t^{0.87} \) before free diffusion sets in. This power law, however, is not yet understood.

### 4 Chain Conformations and Entanglements in Thin Films

In this section we present simulation results for polymer films having a thickness \( h (= D - \sigma_0) \) that exceeds the monomer diameter sufficiently so that chains can overlap. All films contain 48 chains of length \( N = 256 \). They were prepared by slow compression of bulk configurations followed by long equilibration at constant \( h \) (equilibration time \( > 3 \times 10^5 \); the end-to-end vector autocorrelation function decays to 0.1 in \( \tau_{ee} \approx 1.5 \times 10^5 \)). In the following, we first discuss the dependence of the chain size on film thickness. This analysis will suggest that finite-\( h \) effects become prominent for \( D = 4, 8, 16 \) (\( R_g^{\text{bulk}} = 7.5 \)). Accordingly, we focus on these film thicknesses in our subsequent discussion of polymer dynamics.

#### 4.1 Thickness dependence of the chain size

Figure 2 shows the components of the radius of gyration parallel \( (R_g^x) \) and perpendicular \( (R_g^y) \) to the wall as a function of film thickness \( h \). For \( h > R_g^{\text{bulk}} \) we find that the parallel component remains very close to the bulk value, \( i.e. R_g^x = R_g^{\text{bulk}}^2 / 3 \), whereas the perpendicular component decreases strongly. This behavior agrees well with results from other simulations [14, 15] and experiments (measuring \( R_g^x \)) [16]. It may be interpreted, to first approximation, as an evidence
for ideal chain behavior in sufficiently thick polymer films. The term “ideal behavior” means that chain conformations are random-walk like [2]. Since the dimensions of a random walk in $x$, $y$, and $z$ directions are uncoupled, Silberberg suggested that in polymer films only the chain extension perpendicular to the film surface is depressed below its bulk value by the finite film thickness, whereas the parallel component remains unaltered (“Silberberg hypothesis”) [3].

Figure 2 shows that Silberberg’s hypothesis, albeit approximately valid for $h > R_{g,\text{bulk}}$, becomes violated on decreasing $h$ below $R_{g,\text{bulk}}$: we find that $R_{g,x} > R_{g,\text{bulk}}$. This systematic trend of chain swelling suggests that the screening of intrachain excluded volume interactions, responsible for ideal chain behavior [17], progressively diminishes with decreasing $h$. Qualitatively, this deviation from ideal behavior may be rationalized as follows [14, 15]. Screening of intrachain excluded volume interactions in the bulk is caused by strong chain overlap. Since the monomer density $\rho_c$ resulting from the $N$ monomers of the chain in its pervaded volume ($\sim R_{g,\text{bulk}}^3$) is very small ($\rho_c = N/R_{g,\text{bulk}}^3 \sim N^{-1/2}$), a chain must have $N^{1/2}$ contacts with other chains to maintain the constant melt density $\rho$. Thus, a condition for strong chain overlap is $\rho_c/\rho = N/(\rho R_{g,\text{bulk}}^3) \ll 1$. When confining the melt to thicknesses $h \leq R_{g,\text{bulk}}$, $\rho_c$ changes: $\rho_c(h) = N/h R_{g,\text{bulk}}^2$. Thus, with decreasing film thickness it becomes progressively more difficult to fulfill the condition $\rho_c/\rho \ll 1$.

The impact of this reduced overlap on chain conformations in ultrathin polymer films has recently been worked out by Semenov and Johner [6]. Their theory predicts strong deviations from ideal behavior. For the parallel component of the end-to-end distance, $R_{e,\parallel}^2(h, N)$ ($= R_{e,x}^2 + R_{e,z}^2$), the result reads

$$R_{e,\parallel}^2(h, N) \approx N b_e^2 \left[ 1 + f(h) \frac{4}{b_e^2} \ln N \right], \quad f(h) = \frac{1}{4\pi \rho h},$$

(4.1)

where $b_e$ is (taken to be) the statistical segment length of the bulk.

Figure 2 tests this prediction. It depicts a scaling of $R_{e,x}(h)$ according to Eq. (4.1) for two data sets, the results obtained for the present bead-spring model and the results published in Ref. [15] for the bond-fluctuation lattice model. Within the statistical uncertainties the
Fig. 3. Primitive paths determined by the algorithm of Ref. [18]. View along the normal of the film; laterally, periodic boundary conditions apply. Left: $D = 16 \approx 2R_g$, center: $D = 8 \approx R_g$, right: $D = 4 \approx 0.5R_g$. For the thinner films, the entanglement network is not percolating any more.

simulation results for both (microscopically very distinct) models agree with one another and with the theoretical prediction of Eq. (4.1).

4.2 Impact of film thickness on the entanglement density

The right panel of Fig. 1 compares $g_i(t)$ in 2D with that for films of finite thickness (in the latter case, $g_i(t)$ is measured parallel to the walls). While monomer motion is faster than Rouse dynamics in 2D, we find a slowing down of the MSD at intermediate times for finite film thickness, which increases with increasing $h$. We speculate that this systematic trend towards slower monomer motion is attributed to an increase of the entanglement density when the film thickness approaches bulk-like values.

To test this idea we performed a primitive path analysis (PPA) via the algorithm proposed in Ref. [5, 18]. This algorithm consists in contracting the bonds of each chain while fixing the chain ends and preserving the excluded volume only between monomers of different chains. The resulting network of primitive paths is shown in Fig. 3 for three choices of $D$. From the statistics of the primitive path network one can directly deduce the entanglement length $N_e$ due to interchain entanglements [18]. We performed this analysis for at least 5 configurations for each film thickness. Considerable fluctuations were found which are probably due to the small number of chains in the simulation box. However, we checked that these fluctuations are not due to finite size effects: Doubling of the box size for a given configuration leaves the results obtained from the PPA almost unchanged.

A clear trend emerges from Fig. 3. While for $D = 2R_g^{\text{bulk}}$ the entanglement length, $N_e = 72 \pm 6$, is only slightly larger than the bulk value ($N_e = 68 \pm 6$), smaller film thicknesses lead to strong disentanglement: $N_e = 90 \pm 8$ for $D = R_g^{\text{bulk}}$ and $N_e = 135 \pm 10$ for $D = R_g^{\text{bulk}}/2$ [20]. The thinnest film may be considered as practically disentangled. This conclusion is supported, on the one hand, by the snapshot of Fig. 3—the primitive path mesh does not percolate—and, on the other hand, by the MSD which shows no slowing down with respect to Rouse dynamics.
5 CONCLUSION

The presented simulation results show that 2D polymer melts display monomer dynamics that is faster than expected from Rouse theory. We find no indication of a reptation-like slowing down, even not for \( N = 1024 \) which shows the signature of reptation dynamics in the bulk. With increasing film thickness, however, the effect of entanglements on the dynamics becomes gradually visible. This implies that \( N_e \) is altered by spatial confinement; in ultrathin films it increases with decreasing \( h \). The primitive path analysis of Ref. [18]—determining interchain entanglements—allows to quantify the extent of disentanglement with respect to the bulk.

An issue for future studies is the role of intrachain entanglements. The model underlying the analysis of Ref. [5] assumes that the total entanglement density remains constant. While the number of interchain entanglements is supposed to decrease with film thickness, the number of intrachain entanglements should increase. The PPA algorithm can be modified such that intrachain entanglements are conserved beyond a certain chemical distance [19]. Preliminary tests suggest that when preserving intrachain entanglements beyond 64 monomers, almost no difference is found. When decreasing this distance to 16 neighboring monomers, the entanglement lengths are smaller than the values reported here, and the effect appears to be stronger in thin film. However, we presently feel that the inclusion of intrachain entanglements cannot compensate the loss of interchain entanglements discussed above. We thus suggest that the total entanglement density decreases. A more detailed analysis of this problem is underway.

We thank A. Johner and K. Binder for numerous helpful discussions. We are indebted to the DFG (KR 2854/1-2), the Université Louis Pasteur, the IUF, and the ESF STIPOMAT programme for financial support. A generous grant of computer time by the IDRIS (Orsay) is also gratefully acknowledged.

References

[1] S. Granick et al., J. Poly. Sci. B: Polymer Physics 41, 2755 (2003).
[2] M. Rubinstein and R. H. Colby, Polymer Physics (Oxford University Press, Oxford, 2003).
[3] A. J. Silberberg, Colloid Interface Sci. 90, 86 (1982).
[4] H. R. Brown and T. P. Russell, Macromolecules 29, 798 (1996).
[5] L. Si et al., Phys. Rev. Lett. 94, 127801 (2005).
[6] A. N. Semenov and A. Johner, Eur. Phys. J. E 12, 469 (2003).
[7] J. Baschnagel and F. Varnik, J. Phys.: Condens. Matter 17, R851 (2005).
[8] S. Peter, H. Meyer, and J. Baschnagel, J. Polym. Sci. B, in press (2006).
[9] H. Meyer and F. Müller-Plathe, J. Chem. Phys. 115, 7807 (2001).
[10] H. Meyer and F. Müller-Plathe, Macromolecules 35, 1241 (2002).
[11] K. Kremer and G. S. Grest, J. Chem. Phys. 92, 5057 (1990).
[12] The energy cost for two polymers to cross each other is \( E_x \approx 70 k_B T \) if \( D = 1.9 \). By contrast, we found a maximum energy of \( E_c \approx 8 k_B T \) for the closest approach between two monomers in the simulation.
Since \( E_c \ll E_x \), no chain crossings were observed; the film with \( D = 1.9 \) may be considered as “strictly” two-dimensional.
[13] A. Cavallo, M. Müller, and K. Binder, Europhys. Lett. 61, 214 (2003).
[14] M. Müller, J. Chem. Phys. 116, 9930 (2002).
[15] A. Cavallo et al., J. Phys.: Condensed Matter 17, S1697 (2005).
[16] R. L. Jones et al., Nature 400, 147 (1999).
[17] J. P. Wittmer et al., Phys. Rev. Lett. 93, 147801 (2004).
[18] R. Everaers et al., Science 303, 823 (2004).
[19] S. K. Sukumaran, et al., J. Polym. Sci. B 43, 917 (2005).
[20] We feel that our results should not be interpreted in the sense that the criterion for an increase of \( N_e \) is necessarily \( h < R_g^{\text{bulk}} \). It may be that it rather requires \( h \) to become smaller than the tube diameter \( d_t^{\text{bulk}} \). A test of this hypothesis necessitates simulations of larger \( N \) because the two scales, \( d_t^{\text{bulk}} \) and \( R_g^{\text{bulk}} \), are not well separated for the studied chain length \( N = 256 \).
Time ($\tau$)

MSD $g_0 t^{1/2}$

- 2D
- $R_g/2$
- $R_g$
- $2R_g$
- bulk
