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Diffusion and Exchange of Adsorbed Polymers Studied by Monte Carlo Simulations

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ABSTRACT: Monte Carlo simulations are performed of adsorbed polymers with various polymer lengths N and adsorption energies χ_s. Exchange times and the rates of lateral diffusion (along the surface) are investigated as a function of N and χ_s. Lateral diffusion is found to be a combination of reptation (diffusion of stored length along the chain) which is hardly affected by χ_s and dominates for longer polymers, and Rouse-like behavior (sideways movement), which is strongly affected by χ_s and dominates for shorter polymers. We relate the characteristic time for exchange of adsorbed polymers, as a function of polymer length N and adsorption energy χ_s, to the bulk diffusion coefficient at the surface density, to the polymer length and to the ratio of the surface and bulk densities. The differences of 2 and 3 orders in magnitude of the exchange times at fixed χ_s and N, respectively, can thus be reduced to factors of 4 and 2.

1. Introduction

Despite intense research effort on the adsorption of homopolymers in equilibrium, numerous questions remain concerning the kinetics of this adsorption.[1]

One of the first experiments on exchange of polymers was reported by Pefferkorn et al.,[2] who studied the exchange of radioactively labeled polystyrene; they found that the exchange time increases when less molecules where adsorbed. After those measurements, Frantz and Granick[3] measured the replacement of polystyrene (PS) by deuterated PS (dPS); dPS with a specific molecular mass is used to exchange PS with different molecular masses. In both measurements, the adsorption energy for the labeled PS is higher than that for the unlabeled PS. The exchange of polymers from the surface into a melt has been measured by Zheng et al.[4] They measured a smaller diffusion time of the polymers, which they attribute to extra friction between the surface and the polymer.

More attention has been given to the exchange between adsorbed polymers with different molecular weight or different adsorption energies at lower concentration.[5−8] Santore and co-workers[9,10] studied the self-exchange of polymers with and without a fluorescent label. They tested the effect of the fluorescent label on the adsorption and found it to be very small.

Dynamic Monte Carlo simulations for adsorbed polymers have been done for a single polymer on a surface,[11] and later for several, but short polymers.[12] In 1995, Wang et al.[13] published full Monte Carlo simulations for polymers with 85 bonds. A thorough analysis of the different time scales in the desorption and exchange kinetics was made by Takeuchi.[14]

The aim of the present paper is to theoretically analyze the diffusion of adsorbed polymers laterally along the surface, as well as the average time required for exchange of adsorbed polymers and those in solution. We focus on the scaling with respect to polymer length and adsorption energy. We restrict ourselves to the case of monodisperse, homogeneous polymer mixtures. To support our theoretical analysis, we use Monte Carlo simulations of a dynamical lattice polymer model; the same approach has been used before to study fractionation in quasi-binary polydisperse polymer mixtures,[15] and is described in detail by Van Heukelum and Barkema.[16]

The paper is organized as follows. Section 2 introduces the dynamics of a system in equilibrium. Section 3 describes the dynamical lattice polymer model used. This is followed by the results of the Monte Carlo simulations and the comparison with literature in section 4. Section 5 summarizes our results and conclusions.

2. Kinetic Behavior of Adsorbed Polymers

2.1. Polymer Diffusion. Polymers in a solvent are usually assumed to be in a regime where the instantaneous velocities are damped very quickly by the viscosity of the surrounding solvent. The mobility is governed by quasi-instantaneous fluctuations in the positions of segments of the polymers, and the diffusion of the polymers as a whole is well described by Brownian dynamics.

The regime where the polymers are neither mutually entangled nor restricted by their environment (for instance confined in a small volume), and where hydrodynamic interactions are absent, is known as the Rouse regime.[18,19] In this regime, the diffusion coefficient D of the polymers is linearly proportional to the inverse polymer length N^{-1}:

$$D = \frac{a}{N} \tag{1}$$

In solutions with a high polymer density, sideways movement of the polymers is blocked, and the remaining mechanism for mobility is reptation, i.e., movement of the polymer by means of the diffusion of stored length. As argued by De Gennes,[21] proven for one model,[22] and convincingly shown in computer simulations,[23−26] the

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diffusion coefficient D of very long and highly entangled polymers scales with polymer length N as

$$D = \frac{b}{N^2} \tag{2}$$

This scaling was first proposed for bulk polymers, but it also applies to adsorbed polymers.[27]

In the simulations reported in this work, the combination of polymer lengths and densities is such that there is always some, but never complete, entanglement. Consequently, the diffusive behavior can be characterized by a combination of Rouse and reptation dynamics. Combining eqs 1 and 2 in a way that yields the correct limits, one can obtain the relation between the diffusion coefficient D and polymer length N at constant polymer density ρ which is given by

$$\frac{1}{D_d N} = \left(\frac{1}{a} + \frac{N}{b}\right) \tag{3}$$

where d is the dimensionality of the space in which the polymer diffuses − three in the bulk and two along the surface. The parameter a is expected to decrease with increasing polymer density ρ, in contrast to the parameter b. Below (above) the crossover molecular weight $N^* = (b/a)$, the movement is dominated by Rouse (reptation) dynamics, respectively. Furthermore, this crossover depends on the polymer density. Fluctuations in the polymer length give rise to an increase in the diffusion coefficient by a factor of $1 + O(N^{-1/2})$, which for relatively short polymers is not negligible.[20,24] These finite-length effects are not accounted for in eq 3.

The computer simulations feature a (density dependent) combination of Rouse and repton moves. Most experimental situations are better described by a combination of the Zimm model, which takes into account hydrodynamics of the fluid and yields $D = aN^{-0.5}$. If Rouse dynamics is replaced by hydrodynamics, eq 3 will change to

$$\frac{1}{D_d N^{0.5}} = \left(\frac{1}{a} + \frac{N^{1.5}}{b}\right)$$

In most articles to date, the relation between the diffusion coefficient and the polymer size is more or less captured by a powerlaw dependence, i.e., $D = cN^{-x}$. For instance, Sukhishvili et al.[28] measured the diffusion of poly(ethylene glycol) on a modified silica surface at low polymer densities. In a double-logarithmic plot, they fitted the bulk and surface diffusion coefficients as a function of polymer length to powerlaws, $D \sim N^{-1/2}$ and $D \sim N^{-3/2}$, respectively. Many experimental and simulation results are well fitted with such powerlaws, but the value of the exponent x is not universal. We prefer to use eq 3 instead of the more commonly used powerlaw description, as the former has the advantage that the expected limits for high and low density are recovered.

2.2. Exchange between the Solution and Adsorbed Layer. In equilibrium, there is a continuous exchange of polymers in the bulk and those adsorbed on the surface. We are interested in the typical time scale for this exchange, as a function of molecular parameters, such as the polymer length N and the adsorption energy χ_s. This time scale can be identified by measuring the distribution $h(t)$ of residence times t between the moment the polymer touches the surface and leaves it again. Such a histogram is expected to follow an exponential decay

$$h(t) = h(0)\exp(-t/\tau_{\mathrm{exch}}) \tag{4}$$

in which τ_{exch} is the characteristic exchange time.

We relate this characteristic time to the time $\tau_{b\to s}$ in which (i) one polymer molecule diffuses from the bulk to the surface and (ii) another molecule diffuses back ($\tau_{s\to b}$) as expressed by the following equation:

$$\tau_{\mathrm{exch}} = \tau_{b\to s} + \tau_{s\to b} \tag{5}$$

The equilibrium polymer density near the attractive surface is higher than that in the bulk. The layer of increased density will typically have a thickness equal to the radius of gyration R_g, which scales with polymer length; either as $R_g \sim N^{1/2}$ for a Θ-solvent or when the density is high, or as $\sim N^{3/5}$ for a dilute polymer in a good solvent. Outside this layer, in which the polymers feel the surface, the polymer solution is assumed to have a constant bulk density ρ_b. The time $\tau_{b\to s}$ required for a polymer in the bulk to diffuse through a layer of increased density to the surface is given by

$$\tau_{b\to s} = \frac{{R_g}^2}{D_3} \tag{6}$$

where D_3 is the bulk diffusion coefficient at the density in the adsorbed layer.

In equilibrium the number of adsorbing and desorbing polymers per unit time should by definition be the same, i.e.

$$\frac{\rho_b}{\tau_{b\to s}} = \frac{\rho_s}{\tau_{s\to b}} \tag{7}$$

in which ρ_s is the polymer density at the surface and $\tau_{s\to b}$ the time required for an adsorbed polymer to move from the surface to the bulk.

Substituting eqs 6 and 7 in eq 5 leads to:

$$\tau_{\mathrm{exch}} = \tau_{b\to s} + \tau_{s\to b} = \left(1 + \frac{\rho_s}{\rho_b}\right)\frac{{R_g}^2}{D_3} \tag{8}$$

R_g, D_3, and ρ_s/ρ_b take into account the effect of polymer length on the exchange rate; ρ_s/ρ_b and, to lesser degree, also D_3 take into account the effect of the adsorption energy. The scaling of the exchange time with N will satisfy $N^2/a + N^3/b$, because ${R_g}^2 \sim N$ and $D_3^{-1} = N/a + N^2/b$.

3. Monte Carlo Simulation for the Kinetics of Adsorbed Polymers

3.1. Monte Carlo Algorithm. In these simulations, a lattice polymer model is used. A polymer with N bonds is described as a self-avoiding walk on a face-centered-cubic (FCC) lattice, with the exception that monomers which are adjacent in the chain may occupy the same lattice site. The set of lattice sites occupied by the polymer is called the *tube*, and the difference between N and the length of the tube is called *stored length*. Monomers belonging to different polymers are never allowed to reside on the same lattice site.

The polymers diffuse by two different kinds of Monte Carlo mechanisms. The first mechanism is that of reptation along a chain: if for a given monomer one of

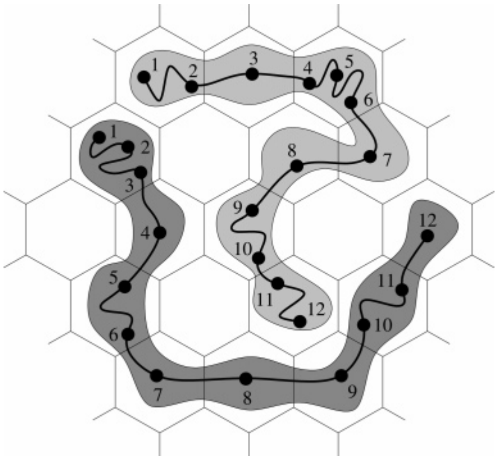

Figure 1. Illustration of the two-dimensional version of the lattice polymer model. In the upper polymer, interior monomers 2, 4, 6, 9, 10, and 11 can either diffuse along the tube, or move sideways; monomer 7 can join either 6 or 8; the end monomers 1 and 12 can move to any vacant nearest-neighbor site. In the lower polymer, interior monomers 3, 5, 6, 10, and 11 can either diffuse along the tube, or move sideways; monomer 1 can move to any vacant nearest-neighbor site, and monomer 12 can join its neighbor 11. All other monomers are not mobile.

its adjacent monomers is located on the same lattice site, while its other adjacent monomer is located on a nearest-neighbor lattice site, it can move to that lattice site. A contracted end monomer, on the same lattice site as its neighbor in the chain, can move to a randomly chosen neighboring lattice site, and an extended end monomer can move to the lattice site that contains its neighbor in the chain. Throughout this article, we will call these kind of moves repton moves.

The second mechanism in our simulations corresponds to sideways movement of the polymer. If any monomer in the interior of the chain occupies the same lattice site as one of its neighbors (but not the other), it can move to any empty lattice site, as long as it does not get separated by more than one lattice spacing from the monomers adjacent along the chain. Also the reverse is allowed: if the two adjacent monomers occupy sites which are nearest-neighbors of each other, the monomer inbetween can join either of the two.

The allowed moves are illustrated in Figure 1. By introducing repton moves in this way, the scaling of the diffusion constant with polymer length N in the long-polymer limit is correct; this is in contrast to the so-called slithering snake method,[29] which yields a diffusion constant for reptation which practically does not depend on N.[30]

If in equilibrium all allowed configurations would be equally likely, the density of stored length would be low, and the dynamics slow. Without excluded-volume effects, polymers would then have a stored length density of about $^1/_{12}$, since the coordination number of the FCC lattice is 12. We stimulate the presence of stored length by an entropic contribution of ln(4) per unit of stored length, thereby raising the density of stored length to around $^1/_4$. As a consequence, the rate at which an extended end monomer is contracting is four times higher than the rate of the reverse process, i.e., moving away from its adjacent neighbor in a specific direction. Similar relations hold for sideways moves of interior monomers.

Table 1. Parameters for Systems to Study the Effect of Molecular Weight

name variable	systems					
number of bonds	10	15	25	50	80	100
number of polymers	640	864	800	400	1024	1600
width of the box	40	45	50	50	80	100
height of the box	50	80	100	100	160	200

This dynamics lends itself extremely well for efficient computer simulations. Specifically, we use a technique known as multispin coding. For a general introduction into multispin coding we refer to Newman and Barkema,[17] while the application of multispin coding to this lattice polymer model is discussed in detail by Van Heukelum and Barkema.[16] Implemented in this way, a fast workstation can perform close to a billion elementary repton moves per second, thus enabling simulations with millions of monomers over a time scale of millions of moves per monomer. In practice, this means that we can perform simulations which are 10−100 times longer (or larger) then performed before.[13,30]

In the simulations presented in this work, the simulation box is periodic in two directions, but in the third direction there are two hard walls. One of these two walls is inert (but impenetrable), while the polymer has specific interactions with the other wall. Specifically, the energy is lowered by a binding energy of χ_s per site next to the wall which is visited by a polymer. The consequence of this binding energy is that the rate of vacating a site near the sticky wall is reduced by a factor of $\exp(-\chi_s/(k_B T))$, where k_B is Boltzmann's constant and T the temperature. Note that the energy is insensitive to whether a site is occupied by one or by multiple monomers.

3.2. Parameters Used in the Simulations. The simulations for exchange and diffusion are always started from an equilibrated configuration. The time given to equilibrate is chosen such that even the longest residing polymer can at least exchange twice from the surface to the solution and vice versa. We verified that after this equilibration the amount of adsorbed polymers and the polymer density profile perpendicular to the surface are stable. These two latter requirements are fulfilled on a much shorter time scale than the exchange of the polymer: the amount of segments in the first layer is already constant on a scale of 1% of the exchange time and gradients in the polymer density are evened out after 25% of the exchange time.

The focus of our research is to study the effect of molecular weight on the rate of exchange, and the surface diffusion of adsorbed polymers. The systems used in the simulations are listed in Table 1. In the simulations, the adsorption energy gain per site χ_s was kept constant at 0.8 $k_B T$ or at 1.6 $k_B T$ and the overall polymer volume fraction was $\rho = 0.08$, as can be deduced from Table 1. This volume fraction is around the overlap concentration, for the small polymers just below and for the large polymers just above their overlap concentration.

Besides the role of molecular weight, we investigated the role of the adsorption energy per monomer. This was done for polymers with $N = 80$ bonds; the size of the box was as listed in Table 1.

We define one unit of time in our simulation such that all monomers have statistically attempted to move once in both directions along the chain, while statistically 10% of the monomers have attempted sideways moves.

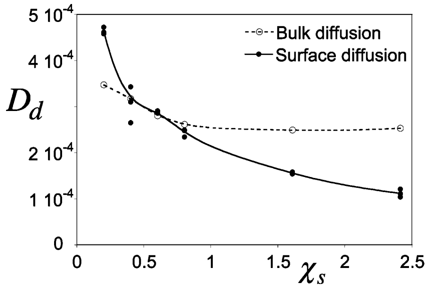

Figure 2. Surface and bulk diffusion coefficient as a function of adsorption energy χ_s for $N = 80$. The diffusion coefficient in the bulk is measured at a density close to ρ_s. The density ρ_s which corresponds to a specific adsorption energy χ_s is denoted in Table 2.

Table 2. Density at the Surface ρ_s Which Corresponds to the Adsorption Energy χ_s

χ_s	ρ_s
0.2	0.02
0.4	0.07
0.6	0.21
0.8	0.37
1.6	0.73
2.4	0.88

To give an impression on the amount of moves: the calculations for the surface diffusion take in general 6×10^5 time steps for polymers with $N = 80$ and $\chi_s = 1.6\ k_BT$, while the calculations of the exchange time take 40 times longer. Shorter times suffice for weaker adsorption energies and/or shorter polymers.

The calculation of the diffusion is done by measuring the center of mass displacement as a function of time. For the measurements of the diffusion of the polymer along the surface, we monitor frequently whether the polymer is still residing at the surface. The squared displacement $r^2(\Delta t)$ over a time interval of length $\Delta t = t' - t$ is only averaged over those polymers which have been touching the surface all the time from times t to t'.

4. Results and Discussion

4.1. Diffusion over the Surface. The Monte Carlo simulations are designed to reproduce Rouse and reptation dynamics, qualitatively capturing the proper scaling with polymer length. They are therefore also suited to study dynamical properties. The first topic of investigation is the rate of diffusion along the surface.

First we compare the bulk diffusion coefficient D_3 to the surface diffusion coefficient D_2 for polymers with different adsorption energies and constant length $N = 80$. For comparison, we determined in simulations of a bulk system without surfaces the bulk diffusion coefficient D_3 as a function of density ρ_s. We also performed simulations with the surface and measured the surface diffusion coefficient D_2, as well as the density ρ_s near the surface in these simulations. The measured densities near the surface for different adsorption energies are presented in Table 2. The results are shown in Figure 2.

With increasing density, the bulk diffusion coefficient D_3 decreases, saturating at a density of $\rho_s \approx 0.3$. For the polymer length $N = 80$ studied here, this density corresponds to an adsorption energy of $\chi_s \approx 0.8\ k_BT$. Experiments on semidilute solutions[32] yielded a decrease of more than 2 orders of magnitude, with D scaling as $\rho^{-1.75}$; the decrease in our simulations is much smaller and does not show powerlaw behavior.

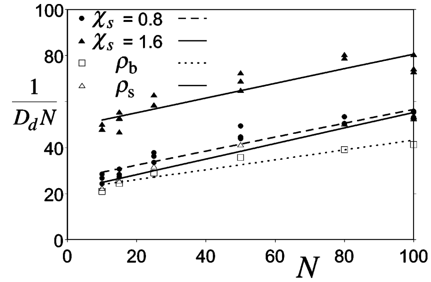

Figure 3. Surface and bulk diffusion coefficient as a function of polymer length N. The closed symbols represent the surface diffusion D_2 for $\chi_s = 0.8$ and $1.6\ k_BT$ and the open symbols the diffusion in the bulk D_3. The bulk diffusion D_3 is measured at the bulk density ρ_b and at a density ρ_s close to the surface density for χ_s of $1.6\ k_BT$.

Table 3. Linear Regression on the Lines in Figure 3

kind of diffusion	adsorption energy/density	intercept $1/a$	slope $1/b$	R^2	N^*
bulk diffusion	ρ_b	22	0.21	0.92	100
bulk diffusion	ρ_s	22	0.34	0.96	63
surface diffusion	$0.8\ k_BT$	26	0.30	0.91	87
surface diffusion	$1.6\ k_BT$	49	0.32	0.86	153

At low adsorption energies, the density dependence of D_2 and D_3 is the same; at adsorption energies larger than $1\ k_BT$, the surface diffusion decreases more than the corresponding bulk diffusion. This can be due to the activated nature of the Rouse diffusion along the surface, or to the decrease in stored length which slows down reptation, or both. At the lowest adsorption energy the polymer readily leaves the surface, and the time it resides on the surface is short. This means that most polymers do not stay on the surface long enough to travel over a distance equal to their own length and, therefore, the measurements of the diffusion is likely biased.

The surface diffusion is plot in Figure 3 as a function of polymer length for two different adsorption energies. For comparison, the bulk diffusion is shown not only at the bulk density of $\rho_b = 0.08$, (i.e., the total density in the systems, see Table 1), but also at the surface density, for polymers with $\chi_s = 1.6\ k_BT$. The diffusion is linearized according to eq 3, to identify separately the contributions from Rouse and reptation dynamics.

The first observation in Figure 3 is that $1/D_dN$ increases with N, showing that reptation occurs and plays a role. Furthermore, the difference between surface diffusion and the corresponding bulk diffusion is largest for an adsorption energy of $1.6\ k_BT$ per site. This difference is mainly caused by the offset of the curves, i.e., the Rouse dynamics, see eq 3. The bulk diffusion at the relatively high density ρ_s is comparable to the surface diffusion with $\chi_s = 0.8\ k_BT$, as was the case in Figure 2. In Figure 3, straight lines are drawn; the parameters belonging to those lines are presented in Table 3. There are, however, clearly significant deviations from those lines. We attribute this to the fact that the scaling of D with N both in the Rouse and reptation regime holds for very long polymers; the multiplicative correction of the order of $1 + N^{-1/2}$ is larger for small N.[20,24]

Although the linear fits are far from perfect, some general features can be deduced from Table 3. The intercept with the vertical axis increases with increasing

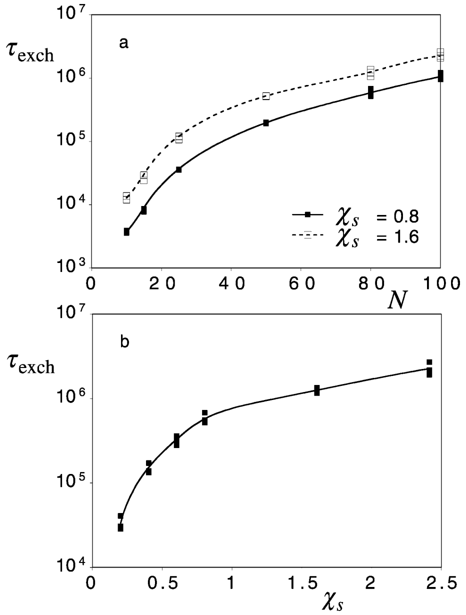

Figure 4. The characteristic exchange time τ_{exch} (a) as a function of the polymer length N for $\chi_s = 0.8$ and 1.6 k_BT and (b) as a function of the adsorption energy χ_s for $N = 80$. Both figures are in semilog scale; the lines are guides to the eye.

adsorption energy. This is partly because sideways movement along the surface is hindered by the increasing polymer density, and partly due to the increased activation energy. The slopes of the lines for different adsorption energies are comparable. This indicates that the reptation is hardly influenced by the density.

As a consequence of these general features, there is a crossover polymer length N^*, below which Rouse dynamics dominates. In most of our simulations, the polymer length N was smaller than N^*, yet also for these small polymers the effect of reptation can be seen. The exact value of N^* depends on parameters in the model and is therefore not a generic feature. At small N, the points in Figure 3 deviate from the straight line. As discussed above, this is probably due to effects of small polymer lengths.

4.2. Exchange Time of a Polymer. Not only does the polymer diffuse over the surface, it can also diffuse back into the solution, its place being taken by another polymer which thus adsorbs. The number of polymers which stay continuously adsorbed over a time interval with length Δt decays exponentially, with a decay time τ_{exch}, see eq 4. To determine this exchange time τ_{exch} for different systems, we fitted the data to

$$\tau = \frac{-\delta t}{\ln\dfrac{n_{ads}(t + \delta t)}{n_{ads}(t)}} \tag{9}$$

in which we averaged over the initial times t. The exchange time is expected to depend on N, χ_s, and ρ_b. (The last parameter has not been varied.)

In Figure 4, the exchange time τ_{exch} is plotted as a function of polymer length N (Figure 4a) and as a function of the adsorption energy χ_s (Figure 4b). The exchange time τ_{exch} increases with increasing polymer length, as well as with increasing adsorption energy χ_s. For the different lengths, τ_{exch} varies over 3 decades. For the different χ_s, τ_{exch} varies over close to 2 decades.

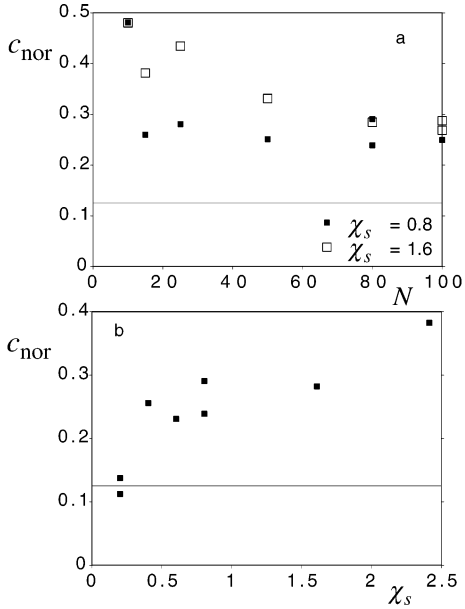

Figure 5. Normalized-exchange-time constant c_{nor} (a) as a function of the polymer length N for $\chi_s = 0.8$ and 1.6 k_BT and (b) as a function of the adsorption energy χ_s for $N = 80$. The horizontal straight line is placed at $c_{\text{nor}} = 0.125$.

A comparison of the different exchange times requires the radius of gyration R_g; see eq 8. It can be written as a function of N[33]

$$R_g = \frac{lN^{1/2}}{\sqrt{6}} \tag{10}$$

in which l is the persistence length (one lattice spacing in our simulations), and N the effective polymer length, i.e., polymer length divided by the persistence length. Due to the presence of stored length in our polymers, the effective polymer length is around $3N/4$; see section 3. At the high densities in the bulk and at the surfaces, R_g scales as $N^{1/2}$; we are not in the dilute regime where R_g would scale as $N^{3/5}$. Combining this with eq 8, the measured τ_{exch} can be normalized to the constant c_{nor}

$$c_{\text{nor}} \equiv \frac{\tau_{\text{exch}} D_3}{N\left(1 + \dfrac{\rho_s}{\rho_b}\right)} \approx 0.125 \tag{11}$$

Figure 5 shows the normalized exchange time. The increase in exchange time τ_{exch} with increasing polymer length, almost 3 orders of magnitude difference, becomes smaller than a factor of 2 in c_{nor}, for adsorption energies of 0.8 k_BT and 1.6 k_BT. The effect of normalization on the exchange time as a function of the adsorption energy is less spectacular, but still there is a decrease in the difference from more than a factor of 100 to less than a factor of 4.

In eqs 8 and 11 we used the "measured" diffusion coefficients; alternatively, we could have used the relation $\tau_{\text{exch}} = N^2/a + N^3/b$, but then we would have been plagued by finite-length corrections as much as we were in describing the diffusion coefficient.

The measured normalized exchange times in Figure 5 are above the expected value of 0.125, indicated by a line. One reason for the deviation might be an underestimation of the distance over which the polymer feels the adsorbed polymers: if instead of R_g the end-to-end distance $R_e \approx R_g/\sqrt{6}$ is used, the value of 0.125 would become 0.75. The point at $N = 10$ and $\chi_s = 0.8\ k_{\mathrm{B}}T$ is an outlier, probably due to the low adsorbed amount and the resulting large scattering in ρ_s.

For the different adsorption energies, the range of measurements of c_{nor} has narrowed significantly for the less extreme cases; see Figure 5b. Apparently, the essential features of the exchange time have been captured by the use of both D_3 and the ratio of the densities.

For different polymer lengths, the dominant part of the normalization comes from the length-dependence of the bulk diffusion coefficient. If in eq 11 we would use the diffusion constant at the (low) bulk concentration instead of at the surface density, the dominant part of the normalization at constant adsorption energy would still be captured; the normalization at constant polymer length would then be lost, however.

5. Conclusions

We have shown that our dynamical Monte Carlo simulations of adsorbed polymers can reach long times. To a first approximation, the surface diffusion can be explained as a combination of Rouse dynamics and reptation. The separation in these two mechanisms gives extra information on their relative importance. The results show that the Rouse dynamics is strongly affected by the adsorption energy and the accompanying higher density, while the reptation is not.

The exchange time for polymers as a function of polymer length is mainly determined by their diffusion coefficient in the bulk; see Figure 5a. Using the bulk diffusion coefficient at a density comparable to that in the layer next to the surface gives better results than using the diffusion coefficient at bulk density. However, the differences are small. At the same adsorption energy, the density near the surface is influenced by N, but also this effect is small.

The dependence of the exchange time on the adsorption energy is not as well captured by the normalization, i.e., eq 11, as the effect of the polymer length.

For moderate adsorption energies, the exchange time is explained by the diffusion at the density in the adsorbed layer and linearly related to the ratio of the density at the adsorbed layer over the density in the bulk; see Figure 5b. We had less success in explaining the results for very low and high adsorption energies. As suggested by Zheng et al.[4] and Wang et al.,[13] that would probably require one to take into consideration details of the conformation of the adsorbed polymer, such as the number of "trains" and the average length of these; we only used the density in the first layer, which is related to the total number of contacts.

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