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Polymer Melt near a Solid Surface: A Molecular Dynamics Study of Chain Conformations and Desorption Dynamics

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ABSTRACT: We examine the static and dynamic properties of polymer chains in a melt in the presence of a solid surface. A molecular dynamics simulation is carried out using a coarse-grained bead−spring model of polymer chains. Both attractive and repulsive interactions between surface and monomers are examined. Static conformations are characterized in terms of trains of attached monomers and detached loops and tails. We compare these conformations to a random walk model. Chain desorption rates are measured in order to calculate characteristic desorption times. We distinguish between chains which desorb rapidly after arriving at the surface and chains which reach a relaxed state at the surface and then desorb at a constant rate. A kinetic model is developed as a means to predict desorption rates and late time chain conformations.

I. Introduction

The static and dynamic properties of polymers at solid surfaces play an important role in a host of applications such as thin films[1] or polymer-based composites. For instance, the addition of clay or glass filler particles to elastomers has long been known to enhance their mechanical properties. To investigate the microscopic reasons underlying this macroscopic behavior, it is of interest to understand in detail the conformation and dynamics of polymer chains close to a solid surface. This behavior has been investigated in the past by several authors, with particular emphasis on the modifications in dynamics induced by the surface (for reviews, see e.g., refs 2 and 3). Such studies are, to a large extent, motivated by experimental studies on the glass transition in thin polymer films.

In addition to the study of polymer melts near flat walls, recent interest has developed in the direction of studying nanoparticles embedded in a polymer matrix. This is related to the increasing importance of nanocomposites in which the filler particles may have dimensions comparable to that of the polymer chains.[4] Several simulation studies have appeared recently in which static and dynamic properties of model nanocomposites were investigated.[5−9] Much of the interest was directed to the layering effects around the particles and modification of local chain dynamics, which are quite similar to those observed in thin films.

In this article we present results from molecular dynamics simulations of a model polymer melt in the vicinity of a flat wall. We use a standard model and focus on two aspects that have not been investigated in previous work. First, we discuss the conformations of single chains adsorbed to the surface using the notions of trains, loops, and tails that are usually discussed for chains adsorbed from a solution. Second, we discuss the exchange dynamics between a chain adsorbed to the surface and the melt. We expect that the characteristic time associated with such desorption may play an important role in the mechanical properties of a filled elastomer.

Previous studies that have examined the adsorption and desorption kinetics through Monte Carlo and molecular dynamics simulations[10−16] as well as experimental work,[22] have mainly considered polymers in solution, where the attraction between surface and polymer is not masked by the surrounding molecules, or examined the buildup of an adsorbed polymer film in equilibrium with a dilute solution. Our aim here is quite different since the melt is in equilibrium near the surface, implying that the excluded volume should be screened between monomers. To our knowledge, only one study[17] has examined in some detail the chain conformations in this situation using Monte Carlo simulations of a lattice model.

II. Simulation Details

Molecular dynamics (MD) simulations are performed on a standard[19] “Lennard−Jones + FENE” model using the parallelized LAMMPS code.[20] All nonbonded interactions between monomers are of the form

$$U_{ij}^{LJ} = \begin{cases} 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}] & r_{ij} \le 2.5\sigma \\ 0, & r_{ij} > 2.5\sigma \end{cases} \tag{1}$$

In the following, $\epsilon = 1$ and $\sigma = 1$ are taken as units of energy and length, respectively. Bonds between monomers are represented by the FENE (finite extensibility nonlinear elastic) potential

$$U_{ij}^{FENE} = \begin{cases} 0.5kR_0^{\,2}\ln[1 - (r_{ij}/R_0)^2], & r_{ij} \le R_0 \\ \infty, & r_{ij} > R_0 \end{cases} \tag{2}$$

where $R_0 = 1.5\sigma$ and $k = 30\epsilon/\sigma^2$. This is a coarse-grained representation of a polymer chain which does not capture certain features, such as chain stiffness. However, this simplification is useful in order to examine behavior up to large chain lengths.

A smooth surface with no atomic structure is used. Interactions between monomers and the surface are represented by a Lennard−Jones potential where r_{ij} is the distance between

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Table 1. Parameters for All Systems Including N, M, $L/2$, and R_G in the Bulk

N	M	$L/2$	R_G
10	640	11	1.45
20	320	11	2.19
50	128	11	3.32
100	128	13	5.19

the monomer and the surface. For the surface–monomer interactions (sm) we choose $\sigma_{sm} = \sigma$ and $\epsilon_{sm} = 2\epsilon$. A cutoff length of $2.5\sigma_{sm}$ is used for an attractive surface, and a cutoff of $2^{1/6}\sigma_{sm}$ is used for a repulsive surface. The system has surfaces at the upper and lower boundaries, $z = \pm L/2$, and is periodic in the remaining directions.

A time step of $\Delta t = 0.006$ is used (the monomer mass being taken as unity, times are in units of $(m\sigma^2/\epsilon)^{1/2}$.

All systems are first equilibrated at constant NPT with $P = T = 1$. In this stage the walls are held at constant position and the box size is allowed to fluctuate in the periodic x and y directions. The average volume during this equilibration is then used for equilibration at constant NVT. Following this, a production run at constant NVT is performed with $T = 1$ maintained by rescaling the velocities every 100 time steps. We use this procedure to ensure that systems have the same density in the bulk. Both the equilibration and production run last several bulk chain relaxation times. We study systems of chains ranging in length from $N = 10$ to 100 with at least $M = 128$ chains in each system. The slab half-length $L/2$ (i.e., the distance from either wall to the box center) is chosen to be greater than the radius of gyration, so that chains do not form bridges between the two surfaces. A summary of system parameters is given in Table 1.

III. Static Properties

Monomer Density Profiles. To characterize the organization of the polymer melt near the surface, we first plot the monomer density as a function of distance from the surface, $\rho(d)$, in Figure 1. This profile is essentially independent of the molecular weight N. In this coarse-grained model the profile may change in the limit $N = 1$ to slightly lower the density near the surface, since the bonded monomers have a shorter equilibrium length than that of a Lennard–Jones interaction. For attractive surfaces there is a very sharp peak representing the layer of monomers closest to the surface. The peak occurs near the minimum of the interaction potential, $2^{1/6}\sigma$. Diminishing density oscillations persist for about three layers. It is well known that even a repulsive surface induces strong ordering. However, the size of the peaks in $\rho(d)$ is less than that for attractive surfaces.

In all systems the density reaches the bulk value of $\rho \approx 0.925$, far from the surface. This is a validation of the procedure of equilibrating at NPT and then using the average volume for NVT.

From the density profile the notion of an attached monomer can be clearly defined. A monomer is considered to be attached if it is closer to the surface than the minimum after the first peak in $\rho(d)$ of the attractive surface. The minimum occurs at a distance of 1.65 from the attractive surface and 1.75 from the repulsive surface. Adsorbed chains may be divided into three components: trains which are contiguous series of attached monomers, loops, which are series of unattached monomers between two trains, and tails, which are series of unattached monomers extending to one end of the chain. To characterize the chain conformations we consider the number of attached monomers per chain, N_A, and the number of trains per chain, N_{tr}. These values serve as approximate measures of the degree of attachment of a chain to the surface. Other relevant properties are the lengths of trains, loops, and tails, l_{tr}, l_{loop}, and l_{tail}, respectively.

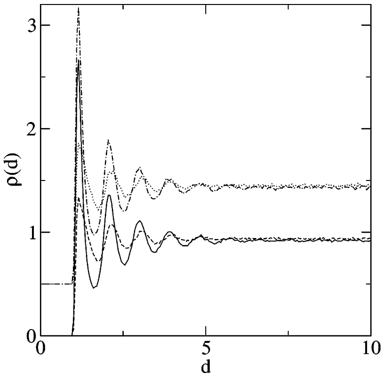

Figure 1. Parameters for all systems including N (chain length), M (number of chains), $L/2$ (slab half length), R_G (radius of gyration in the bulk).

Since chains are expected to be ideal at melt densities it is reasonable to compare the obtained results with a random walk model. We can make a further simplification by considering only the component of bond orientation normal to the surface. This reduces the problem to a one-dimensional random walk. Since all steps have the same length, the set of available positions is discretizable and an analytical solution can be derived. The wall is replaced by a penetrable plane following a procedure introduced by Silberberg.[18] This is justified since the ensemble of "penetrating" paths maps onto the ensemble of "reflected" paths. An attempt to compare numerical Monte Carlo results concerning train distributions with a one-dimensional random walk calculation was made by Bitsanis and ten Brinke.[17] However, their study involved only random walks starting on the surface and a continuous approximation to the random walk results that did not apply to our calculations for short chains. Here, we describe a model which yields a prediction for the number of trains per chain. The calculation is based on two simple formulas concerning random walks.[21] It should be noted, however, that the one-dimensional model does not provide information on attached train lengths. For this, we will turn to a three-dimensional random walk model.

Let us consider a one-dimensional random walk starting from the origin $z_i = 0$; the probability that up to and including the nth step the random walk returns to $z = 0$ exactly p times is given by (see ref 21 for a discussion)

$$z_n^{(p)} = \binom{n-p}{\frac{n}{2}} \frac{1}{2^{n-p}} \tag{3}$$

where n is even. Let us again consider a one-dimensional random walk starting from the origin $z_i = 0$; the probability for a first passage through $0 < a < n$ on the nth step is

$$f_n^{(a)} = \frac{a}{n} \binom{n}{\frac{n+a}{2}} \frac{1}{2^n} \tag{4}$$

Here, $a + n$ is even. Hence, a path of length n joining the origin and a site $a > 0$ has to go $(n + a)/2$ times up

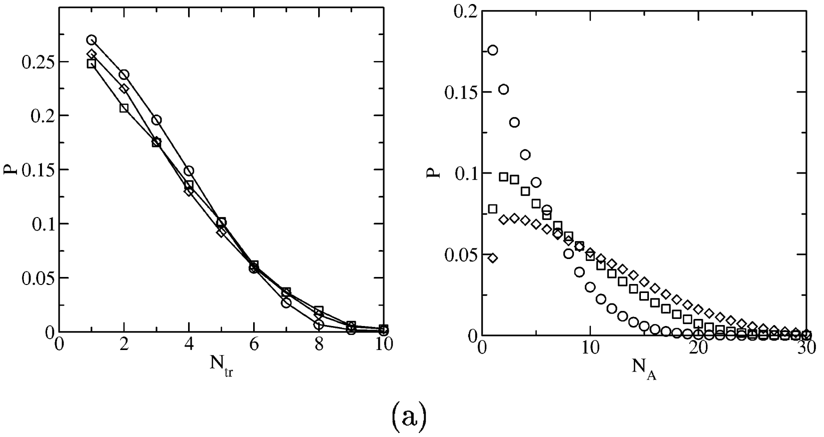

Figure 2. Comparison of simulation results and random walk model for (a) N_{tr} distribution by a 1D random walk model with $n = 16$ steps (circles) and MD simulation for $N = 50$ for attractive (squares) and repulsive (diamonds) surfaces, and (b) N_{A} distribution by 3D random walk (circles) and MD simulation with repulsive surface (squares) and attractive surface (diamonds), all with $N = 50$.

and $(n - a)/2$ times down, so the number of those paths is given by $\binom{n}{n+a/2} = \binom{n}{n-a/2}$. The factor a/n accounts for the first passage and is more difficult to derive.[21]

Now using eq 4 it is straightforward to find the number of paths of length n touching a plane at a distance $0 < a < n$ from their origin for the first time after r steps

$$\frac{a}{r}\binom{r}{\frac{r+a}{2}}2^{n-r}$$

We now calculate the number of attached paths: all possible one-dimensional random paths, starting from a given initial position z_i, having a length of n steps and touching at least once a plane at z_w (our wall). Let $a = z_w - z_i$, then the total number of attached paths, using eq 4 is given by

$$Z = 2^n + \sum_{a=1}^{n}\left[\sum_{r=a,\, a+2,\ldots}^{n} \frac{a}{r}\binom{r}{\frac{r+a}{2}}2^{n-r}\right] \tag{5}$$

The term 2^n accounts for the fact that all possible paths starting at the surface plane are attached. In the second sum the allowed values are $r = a + 2k$, $k = 0, 1, 2, \ldots$, as follows from the condition $a + n$ even in eq 4. In fact, once the surface is reached, the next contact can occur in a minimum of two steps and, in all cases, in an even number of steps. Now we can derive the probability that a random walk of length n, starting a positions away from the plane at z_w, has exactly t contacts with the plane. Using eqs 3 and 5 we have

$$p_{\mathrm{t}}^{(a)} = \sum_{r=a,\, a+2,\ldots}^{n-2(t-1)}\left(\frac{1}{Z}\frac{a}{r}\binom{r}{\frac{r+a}{2}}2^{n-r}z_{n-r}^{(t-1)}\right) \tag{6}$$

The latter expression is the product of the probability to reach z_w in r steps for the first time and then have $t - 1$ more contacts within the $n - r$ steps left. Note that any path of length n having t contacts cannot start further than $n - 2(t - 1)$ step lengths from the wall. Normalizing by Z ensures that any attached path has a probability of 1 to have at least one contact. Now the total probability for an attached path to have exactly t contacts with the plane can easily be written using eq 7

$$p(t) = \sum_{a=0}^{n-2(t-1)} p_t^{(a)} \tag{7}$$

1. Comparison to 1D Random Walk. We are now able to compare the results from MD simulations to random walk predictions, as given by eq 7. The use of a one-dimensional model reproduces the chain behavior in a single direction, z, perpendicular to the wall. As the train length for a one-dimensional random walk is strictly zero steps, a single attachment point of the one-dimensional walk corresponds to a train for the three-dimensional chain (as steps in the x and y direction are not taken into account). Thus, eq 7 gives the probability distribution for N_{tr}, the number of trains per adsorbed chain. Still, the one-dimensional walk length n has to be chosen in accordance with the 3D studied chains containing N monomers. As successive steps in the random walk are uncorrelated, the step length in a random path corresponds to the product of the bond length l and the persistence length, l_{p}, of the 3D chain. Hence, the number of uncorrelated steps in the one dimension random walk has to satisfy $nll_{\mathrm{p}} = \langle z^2\rangle = {}^1\!/_3\,\langle R^2\rangle = {}^1\!/_3\,(N - 1)ll_{\mathrm{p}}$, where $\langle R^2\rangle$ is the end-to-end mean square distance of a bulk chain and is given by $\langle R^2\rangle = (N - 1)ll_{\mathrm{p}}$. For our model $l = 0.97$ and $l_{\mathrm{p}} = 1.32$.[19] Using this mapping we can compare the analytical prediction to the numerical result. The outcome of this comparison is shown in Figure 2a for the probability distribution function of N_{tr}. Very good agreement between the model and simulation is obtained.

2. 3D Random Walk. Other quantities characteristic of chain conformations, such as N_{A}, l_{tr}, l_{loop}, and l_{tail}, cannot be obtained from the calculation in one dimension. Therefore, we performed simple random walk simulations in three dimensions to compare the resulting statistics to those obtained in the simulation. No interaction was implemented between the surface and the random walk, and the surface was impenetrable. The step length for the random walk was chosen to be equal to the persistence length of the bulk chain as discussed above. The number of steps is equal to the number of bonds in the polymer ($N - 1$ for a polymer of N monomers). Thus, we have the same end-to-end mean

Table 2. Measured Mean Values for Adsorbed Chains in the Studied Systems[a]

	10*a*	10*r*	10*rw*	20*a*	20*r*	20*rw*	50*a*	50*r*	50*rw*	100*a*	100*r*	100*rw*
$\bar{N}_{\mathrm{A}}$	3.82	3.15	2.25	5.72	4.55	3.09	9.54	7.38	4.74	14.23	10.34	6.62
$\bar{N}_{\mathrm{tr}}$	1.53	1.60	1.49	2.05	2.14	1.99	3.05	3.12	3.00	4.59	4.46	4.16
$\bar{N}_{\mathrm{tail}}$	1.22	1.28	1.58	1.39	1.44	1.77	1.58	1.62	1.84	1.66	1.73	1.91
$\bar{l}_{\mathrm{tr}}$	2.28	1.90	1.44	2.65	2.16	1.52	2.97	2.40	1.57	3.18	2.56	1.59
$\bar{l}_{\mathrm{loop}}$	1.99	2.12	1.83	3.00	3.16	3.01	5.04	5.06	5.28	7.18	7.55	7.92
$\bar{l}_{\mathrm{tail}}$	4.03	4.11	3.42	7.83	7.89	7.16	19.0	19.5	17.99	35.9	36.4	35.3

[a] The labels in the first line give the chain length followed by *a* (attractive wall), *r* (repulsive wall), or *rw* (3D random walk simulation in continuum space).

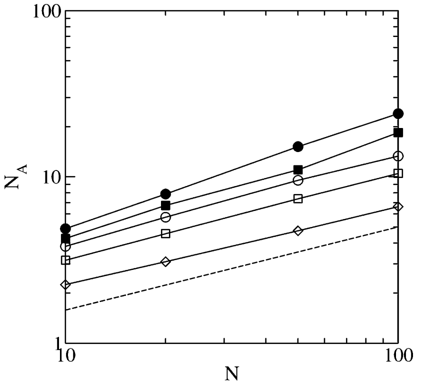

Figure 3. Attached monomers/chain N_A as a function of chain length N for attractive (circles) and repulsive (squares) surfaces. Open symbols are for overall averages, and filled symbols are averages over "relaxed" conformations only. Results of a 3D random walk are also shown (diamonds). Dashed line is $\sim N^{0.5}$.

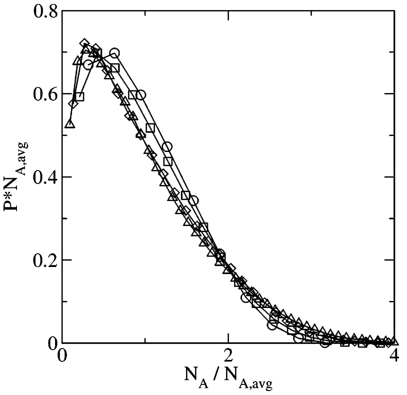

Figure 4. N_A distribution scaled by $\bar{N}_A$ for repulsive surface. $N = 10$ (circles), 20 (squares), 50 (diamonds), 100 (triangles).

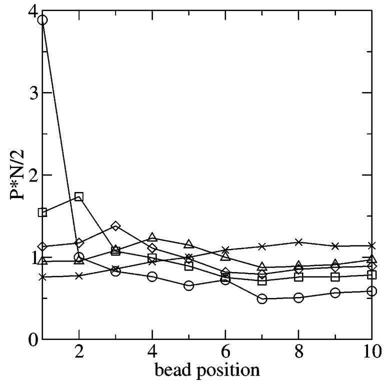

Figure 5. Attached monomer positions for attractive surface, $N = 50$ and $N_A = 1$ (circles), 2 (squares), 3 (diamonds), 4 (triangles), 8 (crosses).

square radius for the polymer and the random walk as $(N - 1)ll_p = \langle R^2 \rangle$. The results of this comparison are summarized in Table 2. As expected, the random walk model is in good agreement with the MD simulations for the distribution of N_{tr}. However, the distribution and the mean of N_A, the number of attached monomers per chain, differ significantly as shown in Figure 2b. N_A is in fact larger in the simulation than for a random walk. We associate this discrepancy with the known tendency of polymer chains to lie "flat" on a substrate, which has been observed in a number of simulations.[2] Since the FENE bond length is shorter than the equilibrium distance of the Lennard–Jones potential, longer trains allow for closer packing of monomers in the attached layer and are therefore favored.

For an ideal chain, at any given attached monomer the neighboring monomer along the chain has a characteristic probability of being in the attached layer as well. Simulation results show an exponential decay for the distribution of l_{tr}, in agreement with this explanation. The average train length converges with increasing N to values between 2.5 and 4 for both surfaces. The average loop length $\bar{l}_{\mathrm{loop}}$ does not appear to converge but rather increases as approximately $N^{0.5}$. As would be expected, $\bar{l}_{\mathrm{tail}}$ depends essentially linearly on N.

The dependence of N_A on N is shown in Figure 3. A power law dependence is clearly observed with an exponent of approximately 0.5. This exponent also agrees with the random walk model, although the actual value of N_A is larger for the simulations. This is consistent with our finding that the number of trains per chain is predicted by the random walk model but the length of these trains is greater than predicted. Surface–monomer attraction increases, N_A but does not alter the scaling with N. Also shown in Figure 3 are values for chains which have relaxed on the surface, as explained in the following section. The distributions $P(N_A)$, scaled by the mean $\bar{N}_A$, for a repulsive surface are shown in Figure 4. It appears that the distribution approaches a universal curve at large N.

We also examined the position of attached monomers along the chain (Figure 5). To do this we consider a set of chains with a given value of N_A and then measure the fraction of the attached monomers on these chains as a function of distance from chain end. This gives a distribution for attached monomer positions which is divided by $2/N$, the value of the uniform distribution if the attached monomers were randomly distributed.

The difference from a random distribution of attachments is most pronounced for $N_A = 1$, chains with only one attached monomer. Here, the probability that an attached monomer lies at a chain end is increased by a factor of 4 for $N = 50$. As one looks at chains with larger N_A, the most probable attachment location shifts (by one unit at a time) away from the chain end and decreases in magnitude. This is expected and indicates a greater chance that attached monomers are consecutive. A similar result is found for three-dimensional random walks, although the peaks are smaller.

IV. Dynamics

A. Measuring Desorption Dynamics. In this study we concentrate on the intrinsic dynamics of the population of adsorbed chains. This population is continually exchanging chains with the rest of the melt, and the characteristic time scale for renewing this population can be seen as a “lifetime” of the interfacial region. To characterize the transition of chains from adsorbed to desorbed conformations, we calculate correlation functions defined as

$$G(t) = \langle n_{\mathrm{ads}}(t)/n_{\mathrm{ads}}(0)\rangle \qquad (8)$$

in which $n_{\mathrm{ads}}(t)$ is the number of adsorbed chains at time t, in some set of “labeled” chains. In particular, we are interested in evolution of chains which are adsorbed on the surface at $t = 0$ or some subset of this group, for instance, all chains with $N_{\mathrm{A}} = i$ at $t = 0$. Here, two slightly different methods can be used.[13] In the first any labeled chain remains permanently labeled (as in the case of experiments where chains are labeled with, say, radioactive or fluorescent labels). This measure is a true correlation function in that it depends only on the correlation between chain conformation at $t = 0$ and at some later time t. Thus, a chain is considered “adsorbed” at a given time as long as $N_{\mathrm{A}} > 0$, although the chain may have desorbed from and readsorbed to the surface any number of times since $t = 0$. This measure has the advantage of being more closely related to experimental methods. However, it has the disadvantage that the form of $G(t)$ depends not only on desorption dynamics but also on adsorption and diffusion in the bulk. This unnecessarily complicates the interpretation of the results. Furthermore, at long times $G \rightarrow P_{\mathrm{ads}}$, where P_{ads} is the fraction of all chains in the system which are adsorbed on a surface. Thus, $G(t)$ is influenced by the finite size of the system at long times. This inhibits comparisons between systems of different sizes or different surface-to-volume ratios.

In the second method the label is removed from a chain as soon as it leaves the surface and it can no longer contribute to n_{ads}. Thus, $G(t)$ is a measure of the fraction of chains which have never left the surface over a period of time t. This measure, which describes only the desorption kinetics, is used here. It should be pointed out that $G(t)$ is a function of chain history, not just chain conformations at two instances separated by a given time interval. Therefore, chain conformations, as characterized by N_{A}, must be measured at frequent intervals to observe the first desorption. For accurate comparisons, the size of this interval must be the same for all systems. We measured N_{A} for all chains every four simulation time steps.

There is one more issue that must be considered in defining $G(t)$. Monomers undergo vibrational motion over short time and lengths scales before forces from bonds and neighboring monomers are felt. To accurately calculate dynamical properties it is necessary to average over this behavior. For instance, it is possible for a monomer which, over a longer time scale, lies in the attached layer to make several short excursions outside of this layer due to its vibrational motion. These events cannot properly be construed as detachment. We take a characteristic time to be the smallest Rouse relaxation time,[19] $\tau_{\mathrm{vib}} = \zeta b^2/3\pi^2 kT$, where ζ is the monomer friction coefficient whose value we take to be $\zeta \approx 20$ from ref 19 and $b \approx 1.28$ is the bond length so that $\tau_{\mathrm{vib}} = 1.1$. Therefore, we take the actual value of $N_{\mathrm{A}}(t)$ for a given chain to be the average of its instantaneous value between $t - \tau_{\mathrm{vib}}$ and t, rounded to the nearest integer.

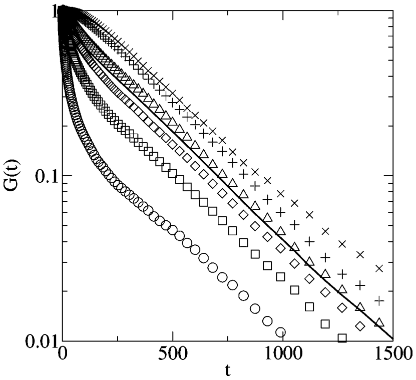

Figure 6. Decay of $G(t)$ for $N_{\mathrm{A}} = 1$ (circles), 2 (squares), 3 (diamonds), 4 (triangles), 6 (pluses), 8 (crosses) and for all adsorbed chains (solid line). Results are for $N = 10$ and an attractive surface.

B. Decay Rates and Desorption Times. To gain insight into the desorption process we consider a representative case and examine the form of $G(t)$ when it is broken down according to the value of N_{A} at $t = 0$. Figure 6 shows the evolution of $G(t)$ for a system of chain length $N = 10$ at an attractive wall. The behavior of $G(t)$ for the entire set of adsorbed chains consists of a short transient period, where desorption is rapid, followed by exponential decay. The length of the transient period is related to the equilibration time of adsorbed chains. This point is more evident when one considers the form of $G(t)$ for chains which have a given value of N_{A} at $t = 0$. For $N_{\mathrm{A}}(0) = 1$, the transient period is much larger and most of the chains desorb before the onset of exponential decay. The transient period shrinks with increasing $N_{\mathrm{A}}(0)$. At around $N_{\mathrm{A}}(0) = 4$, the form of $G(t)$ is exponential essentially from $t = 0$. At larger $N_{\mathrm{A}}(0)$, the opposite behavior is observed, $G(t)$ decays more slowly at early times before the exponential regime.

The existence of a transient and an exponential regime is explained as follows. A key factor in the behavior of polymers at surfaces is that the molecules have many possible adsorbed conformations. By contrast, in a Lennard–Jones fluid ($N = 1$) there is basically only one “adsorbed state” and $G(t)$ is entirely exponential. Exponential decay implies that molecules desorb at a given rate regardless of the amount of time they have been on the surface. Thus, in the exponential regime, the average conformation of an adsorbed molecule at a given time is statistically equivalent to the average conformation at any other time. Such chains are “fully relaxed” on the surface. However, in the transient regime the rate of desorption is time varying. This implies that the average conformation of adsorbed molecules evolves the longer they remain on the surface. Chains which have recently arrived on the surface, or are about to leave it, have a conformation with $N_{\mathrm{A}} \approx 1$. In Figure 7 we plot the evolution of $\bar{N}_{\mathrm{A}}$ with the amount of time a chain has been adsorbed to the surface, t_{ads}. (Note the different definition, $t_{\mathrm{ads}} = 0$ is the moment when a chain first arrives at the surface. By contrast, in calculating $G(t)$, any adsorbed chain conformation can be taken as $t = 0$.) After a sufficiently long time the set of chains which are still adsorbed has a constant value of $\bar{N}_{\mathrm{A}}$. In other words, these chains have no memory of their initial state $N_{\mathrm{A}}(0)$ and their *average* conformation

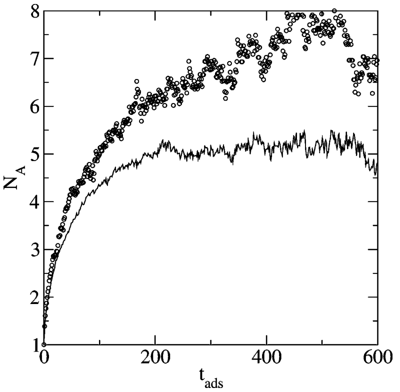

Figure 7. Average number of attachments as a function of time adsorbed to an attractive surface for $N = 10$ (solid line) and 50 (circles).

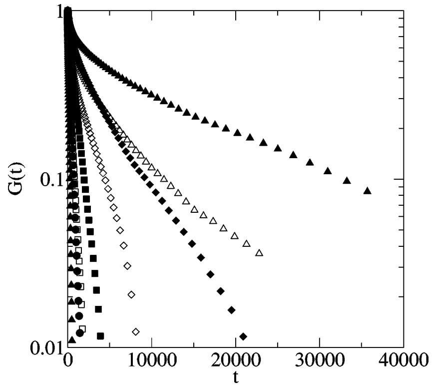

Figure 8. Decay of $G(t)$ at repulsive and attractive surfaces for $N = 10$ (circles), 20 (squares), 50 (diamonds), and 100 (triangles). Open symbols are for repulsive surfaces, and filled symbols are for attractive surfaces.

does not change. However, the size of this set is constantly decreasing as more chains desorb.

On the basis of this behavior one can (roughly) divide adsorbed chains into two categories. The shape of $G(t)$ demonstrates that a single characteristic desorption time cannot describe the behavior of all adsorbed chains. Chains which spend a long time on the surface migrate toward states of larger N_A and "diffuse" around a certain $\bar{N}_A$ before desorbing. We label these "slow" chains. The initial fast decay of $G(t)$ represents mainly chains that have only been on the surface a short time; they have few attached monomers and are able to desorb quickly. This population of "rapid" chains is frequently renewed on a time scale shorter than the average adsorption lifetime, but in order to see the dynamics of *all* adsorbed chains, one has to wait much longer. At large t_{ads} chains continue to desorb from the surface but the average conformation of the remaining adsorbed chains (as characterized by $P(N_A)$ and $\bar{N}_A$, for instance) does not change. This is compatible with a constant desorption rate and the exponential behavior of $G(t)$.

Results for $G(t)$ (for all adsorbed chains) at various N and for both attractive and repulsive surfaces are shown in Figure 8. The desorption time increases with N and also with attraction. Due to screening effects in the melt, the attractive part of the monomer−surface interaction is not expected to inhibit desorption as significantly as in solution. The slightly slower dynamics seen here are most likely due to the higher density peak in the adsorbed layer for an attractive surface. A crossover to exponential decay at late times is observed for all N.

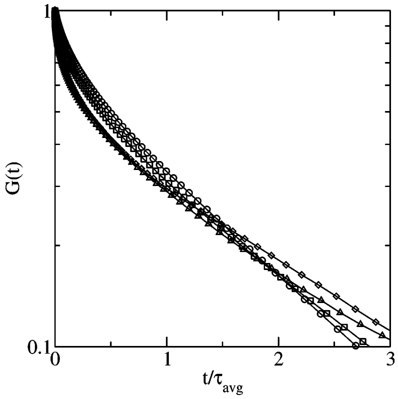

Figure 9. Decay $G(t)$ for a repulsive surface with time rescaled by τ_{avg} for $N = 10$ (circles), 20 (squares), 50 (diamonds), and 100 (triangles).

Wang et al.[12] took a similar approach to examine the desorption of polymers in dilute solution from a flat surface. They report a power law dependence of the desorption time on N which is equivalent to the behavior of the relaxation time of the first Rouse mode. They also report a much smaller transient period for $G(t)$. The longer period reported here is most likely due to screening of the surface attraction by the melt, which prolongs the relaxation time of an adsorbed chain.

To compare the effect of chain length and monomer−surface interaction on the dynamics it is useful to define a desorption time. A typical approach would be to obtain a time τ_{exp} by fitting the late time desorption to $G(t) \approx \exp(-t/\tau_{exp})$. This measure is characteristic of chains which are fully relaxed on the surface and have a "maximal" number of attachments. However, as we discussed, the population of adsorbed chains can be split into two groups: rapid and slow chains. Then τ_{exp} is relevant only for slow chains. It does not reflect desorption time scales for the rapid chains or the ratio of rapid to slow chains in the system. Intuitively, one expects these properties to also depend on chain length and surface−monomer interactions. For instance, at low N chains are likely to relax more quickly on the surface and thus have a smaller percentage of rapid chains than at high N. To obtain a measure which is characteristic of the desorption of all adsorbed chains, we measure the average adsorbed lifetime

$$\tau_{avg} = \int_0^\infty G \, dt \tag{9}$$

Since chains that stay on the surface for a short time are frequently renewed, their contribution to this measure is significant relative to the contribution from long time adsorbed chains.

We now consider more closely the effect of varying N on desorption dynamics. Two issues must be considered: the effect on the shape of $G(t)$ and the effect on the time scale τ_{avg}. To examine the first point we replot $G(t)$ for a repulsive wall scaled by τ_{avg} in Figure 9 (the result is similar for the attractive wall). The integral of each curve is thus equal to 1. This allows one to compare the qualitative nature of desorption at different N. If $G(t)$ is purely exponential, then there are essentially no rapid chains; all molecules become fully relaxed on the surface before desorbing. (Remember that the relative terms "rapid" and "slow" are used only to compare chains within a given system. Certainly "slow" short

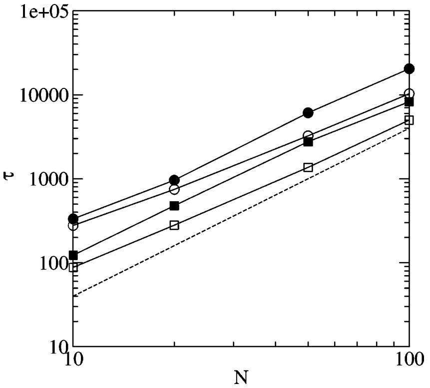

Figure 10. Desorption times for a wall as a function of N for repulsive (squares) and attractive (circles) surfaces. Open symbols are for τ_{avg}, and filled symbols are for τ_{exp}. Dashed line is $\sim N^2$.

chains may desorb more quickly than “rapid” long chains.) By rescaling it is possible to see how the importance of rapid chains depends on N. At low N the $G(t)$ has an early crossover to the exponential regime. The transient regime grows with increasing N, but in comparing the $N = 50$ and 100 cases it appears that G converges to a universal curve at large N. As N increases, one would expect the transient period to increase because it takes longer for chains to fully relax on the surface. One might assume this would be true for all N, but it appears that above $N \approx 50$ the behavior may be universal. This conclusion needs to be confirmed for larger N. If it is true, the implication is that the relaxation time of an adsorbed chain (which determines the crossover in $G(t)$) is proportional to the desorption time scale, independent of N. Recall that a convergence at large N was also found for the static conformation distribution (Figure 4).

In Figure 10 we plot the dependence of the two desorption time measures on N. If a power law description of these results is attempted, the exponents are systematically smaller than 2 (in the range 1.5−2) for the chain length investigated. This is somewhat surprising. Naively, one may expect that desorption from the surface will take place essentially through diffusive motion. Thus, in an average sense it could be expected that τ_{avg} will be related to the time needed for an adsorbed chain to diffuse a distance on the order of R_G away from the surface, $\tau_{avg} \approx R_G^2/D$. Since $R_G \approx N^{1/2}$, $D \approx N$ in the Rouse regime, and $D \approx N^2$ in the reptation regime this predicts

$$\tau_{avg} \sim \begin{cases} N^2, & N < N_e \\ N^3, & N > N_e \end{cases} \tag{10}$$

Our results are clearly not compatible with this simple description. This is particularly true in the large N regime since the entanglement length of MD bead−spring chains has been estimated to be $N_e \approx 34$.[19] Our results do not display a stronger N dependence for $N > N_e$.

C. Microscopic Kinetics of Adsorption/Desorption. The behavior observed for $G(t)$ is, in fact, reminiscent of what would be expected from a description in which each adsorbed chain is described as a point moving along the one-dimensional ‘reaction coordinate’ N_A ($0 < N_A < N$). If we assume that this ‘coordinate’ is undergoing simple diffusive dynamics, we may schematically write for the number of chains attached by N_A monomers at time t $F(N_A, t)$

$$\frac{\partial F(N_A, t)}{\partial t} = \frac{1}{\tau}\left[\frac{\partial^2}{\partial {N_A}^2} F(N_A, t)\right] \tag{11}$$

where τ is a transition time.

The boundary conditions are as follows. At $N_A = N$, the flux is zero

$$\frac{\partial F(N, t)}{\partial N_A} = 0 \tag{12}$$

As $N_A \to 0$, we have an adsorbing boundary condition since a chain that reaches this state is forever removed from the tagged population. Hence

$$F(0, t) = 0 \tag{13}$$

Within such a description the function $F(N_A, t)$, starting from any initial condition $F(N_A, 0)$, will evolve rapidly toward an essentially factorized distribution

$$F(n, t) \approx P_1(n) \exp(-t/\tau_1) \tag{14}$$

where $P_1(n)$ and $1/\tau_1$ are the first eigenfunction and eigenvalue of the diffusion problem, yielding

$$P_1(n) = \frac{\pi}{2N} \sin\left(\frac{\pi}{2} n/N\right) \tag{15}$$

$$\tau_1 = (2N/\pi)^2 \tau \tag{16}$$

Hence, if we consider the normalized distribution of N_A in the limit of long adsorption times, the average number of attached monomers in this limit is proportional to and the long time relaxation takes place on a

$$\bar{N}_A = \int_0^N nP(n)\, \mathrm{d}n = \frac{2}{\pi} N \tag{17}$$

time scale that scales such as N^2.

1. Discrete Model/Transition Times. Obviously the above picture, treating N_A as a continuous variable, is oversimplified. However, it is interesting to discuss the dynamics in terms of the (discrete) ‘reaction coordinate’ N_A and defining transition rates between the ‘states’ with different values of N_A. A transition time between two neighboring (on the N_A axis) adsorption states is defined as the average time that a chain stays in the initial state before migrating to the final state (for instance, $\tau_{i\to i+1}$ a change from $N_A = i$ to $N_A = i + 1$). One can alternatively speak in terms of a transition rate $k_{i\to i\pm 1}$, which is the inverse of the respective transition time.

The transition times are measured as follows. We consider a set of chains all in states $N_A = i$ and measure the rate at which they leave this state without counting chains which later enter $N_A = i$ from neighboring states. If $R(i, t)$ is the number of chains remaining in state I, then

$$\frac{\partial R(i, t)}{\partial t} = -\left({\tau_{i\to i+1}}^{-1} + {\tau_{i\to i-1}}^{-1}\right) R(i, t) \tag{18}$$

The total residence time in state i is given by $\tau_i^{-1} = \tau^{-1}_{i\to i+1} + \tau^{-1}_{i\to i-1}$. The fractions of chains which, upon leaving state i, move to state $i + 1$ or to state $i - 1$ are

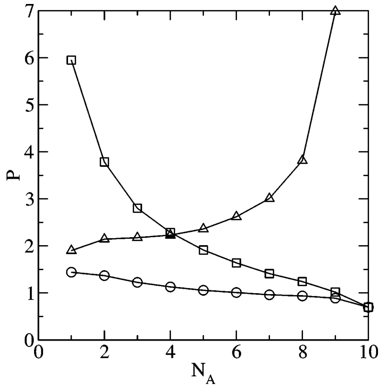

Figure 11. Overall residence times (circles) and transition times $\tau_{i\to i-1}$ (squares) and $\tau_{i\to i+1}$ (triangles) for $N_A = i$. Values are calculated using only chains which have been attached for at least a time of 100. For a repulsive surface and $N = 10$.

labeled f_+ and f_- respectively. They are related to the transition times by

$$f_+\tau_{i\to i+1} = f_-\tau_{i\to i-1} \tag{19}$$

The transition times are calculated using these two equations, the measured residence times, and $f_\pm$ of all chains in state i.

A typical range of transition times is shown in Figure 11. The values were calculated using only chains which had been adsorbed for $t_{ads} > 100$ for reasons explained below. Residence times in highly adsorbed states are shorter and become essentially constant as $N_A \to N$. This does not imply that detachment of an individual monomer becomes faster. Rather, it can be explained by the fact that strongly adsorbed chains inevitably have many monomers near the adsorbed layer and thus have more chances to exchange attached and detached monomers per unit of time. Thus, a particular transition time depends not only on N_A but also strongly on the detailed chain conformation, including the number of trains, tails, and position of chain center of mass. As the number of trains of a chain is not simply related to N_A, its influence on transition times is difficult to extract. One can argue that if a chain is strongly adsorbed it has, *on average,* the mean number of trains for the specific system, so its residence times are expected to be constant *on average*, a hypothesis supported by the measures.

The overall distribution of the number of attached monomers per chain, N_A, has been shown to agree with the distribution predicted by an ensemble of random walks (representing ideal chains in the melt) in the vicinity of the surface. In a time evolving system this distribution represents a set of chains which have been adsorbed to the surface for varying lengths of time. We now consider the properties of the distribution $P(N_A, t_{ads})$, that is, the distribution for the subset of adsorbed chains which have been continuously attached to the surface for a time of exactly t_{ads}. Clearly, for $t_{ads} = 0$, when a given chain has just arrived on the surface, it is attached by exactly one monomer and P is a delta function at $N_A = 1$. At late times $G(t)$ undergoes exponential decay. Thus, we expect that a stationary distribution is reached as $t_{ads} \to \infty$. This indeed occurs in our simulations, as can be seen for the case of a repulsive wall with $N = 10$.

We note here that we necessarily make a simplification in describing adsorbed configurations by one parameter, N_A. A more complete description would also include the location of the attached monomers along the chain backbone as well the position of the unattached portions of the chain with respect to the surface. If a chain conformation is sufficiently described, then its evolution should depend only on its current state. However, in our simplified approach we cannot rule out the possibility that a chain's evolution will also depend on its history. For instance, chains with $N_A = 1$ which have just arrived on the surface may have a different average behavior from chains with $N_A = 1$ which have been attached for a long time. This would imply that there are other differences between the configurations not described by N_A.

2. Late Time $P(N_A, t)$. Now we may consider any set of adsorbed chains and ask how its distribution $P(N_A, t_{ads})$ evolves in time. At any time t_{ads} we are only interested in members of the original set which have *never* left the surface. In absolute terms, this is a set whose size decreases to zero over time. It is useful to distinguish here between absolute and normalized terms. We start by labeling some finite number of chains which have *just* arrived on the surface. Then we define $X(t_{ads})$ as the number of chains which have remained continuously attached at time t_{ads}. The distribution $P(N_A)$ is normalized, so that $\sum_{N_A=1}^{N} P(N_A, t_{ads}) = 1$. We define the related value $F(N_A, t_{ads}) = P(N_A, t_{ads})X(t_{ads})$ which is the actual number of chains in the set with N_A attached monomers. It follows that

$$\sum_{N_A=1}^{N} F(N_A, t_{ads}) = X(t_{ads}) \tag{20}$$

The transition times describe the rate of change of the absolute numbers of chains. A master equation can be written as

$$\frac{\partial F(i, t)}{\partial t} = -({\tau^{-1}}_{i\to i+1} + {\tau^{-1}}_{i\to i-1})\,F(i, t) + {\tau^{-1}}_{i\to i+1}\,F(i+1, t) + {\tau^{-1}}_{i\to i-1}F(i-1, t) \tag{21}$$

The solution of this equation approaches a factorized distribution where only the total number of chains X decreases in time, $F(N_A, t_{ads}) = P(N_A)X(t_{ads})$ at late times. This is related to the exponential decay of $G(t)$ by $X(t) \approx e^{-t/\tau_{exp}}$.

Thus, by using the correct transition times as input to eq 21, it should be possible to find a stationary solution for $P(N_A)$ which matches the true distribution for fully relaxed chains (those which have been adsorbed for long times) in our simulation. To verify this we first measured $\tau_{i\pm1}$ from all transitions occurring in the simulation and used these values as parameters in eq 21. We then solve the equation with an initial condition in which F is large for $N_A = 1$ and zero elsewhere. (Other initial conditions give the same result.) The solution is carried out until $P(N_A)$ reaches a stationary form. However, the result does not agree with the actual late time distribution (Figure 12). The disagreement is evidence that these transition times do not accurately reflect the behavior of fully relaxed chains. As a second approach we computed new values of $\tau_{i\pm1}$ counting only the transitions of chains which had been attached for $t_{ads} > 100 \approx \tau_{avg}$. This time the solution agrees with the actual late time distribution.

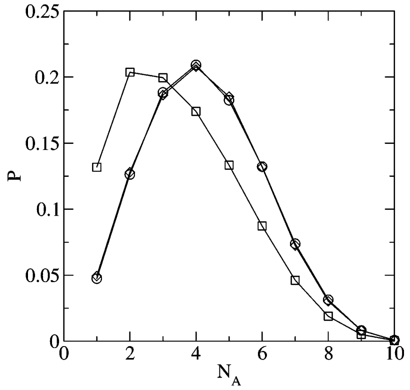

Figure 12. Distribution of N_A for chains in the limit of long attachment times. The actual late time distribution (circles) is compared with stationary solutions of $P(N_A)$ from eq 21 using $\tau_{i\pm1}$ calculated for all transitions (triangles) and calculated for transitions only of chains which have been attached for $t_{ads} >$ 100 (squares). For a repulsive surface and $N = 10$.

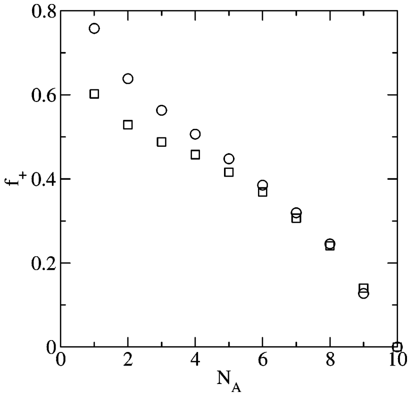

Figure 13. Fraction of chains in state $N_A = i$ which undergo a transition to state $N_A = i + 1$ rather than $N_A = i - 1$. Squares are values for all chains. Circles are for chains which have been attached for at least a time of 100. For a repulsive wall and $N = 10$.

This difference implies that chain behavior depends not only on N_A but also on the chain history. Chains which have been attached only a short time are not statistically equivalent to chains which have been attached a long time but have the same number of attached monomers. To clarify the difference in behavior, we plot the percentage of transitions which increase (rather than decrease) N_A in Figure 13. At high N_A the two curves converge, most chains in state i evolve to $i + 1$ rather than $i - 1$ regardless of how long the chain has been attached to the surface. This is expected since only a limited variety of such conformations are possible. However, for chains with few attachments (low N_A), chain history is important in predicting the chain's behavior. Chains which have only been attached for a short time are more likely to desorb than chains which have been attached a long time. We propose one possible explanation for this behavior. Chain adsorption and desorption should be more likely to occur at chain ends. Thus, a chain with $N_A = 1$ which has recently arrived on the surface tends to be attached near a chain end and can desorb easily. Chains which have spent a longer time on the surface may have attached monomers anywhere along the chain background. Even when such chains have only one attached monomer there is a greater probability that this monomer is near the center of the chain and is unlikely to immediately desorb.

We now consider chain conformations in the limit of long adsorption times. As chains remain on the surface for an increasing amount of time, their conformation distribution reaches a steady shape as discussed above. This distribution is related to the transition times and has a peak near where $\tau_{i\to i+1} = \tau_{i\to i-1}$. A typical distribution $P(N_A)$ at late times is shown in Figure 12, and the late time value of $\bar{N}_A$ is shown as a function of N in Figure 3. It scales as $\bar{N}_{A,late} \approx N^{0.59}$, approximately similar to the scaling of $\bar{N}_A$. This late time conformation should be related to the desorption rate in the exponential region of $G(t)$. In the simple diffusion model described above one would expect a desorption time scaling as $N_{A,\ late}{}^2$. This is not rigorously correct as the desorption and adsorption time display a dependence on N_A. However, the general idea remains and yields an expected desorption time that will depend on N more weakly than N^2, as observed in the simulations.

V. Conclusion

We examined static and dynamic properties of polymers in a melt in the presence of a flat surface. Static conformations were compared to predictions from a random walk model and found to be in good agreement for the number of trains per chain. The length of the trains is larger than in the random walk model, reflecting a tendency of chains to lie flat on the surface.

For dynamic properties we measured the evolution of chain conformations as described by a single parameter N_A, the number of "attached" monomers. The population of chains is shown to contain a portion of weakly adsorbed chains with rapid desorption dynamics and strongly adsorbed chains with slower desorption dynamics. The strongly adsorbed chains are responsible for a slow-down in dynamics near the surface. Slightly slower desorption is observed for an attractive surface; this is attributed to greater ordering in the adsorbed monomer layer. The desorption time is seen to scale slightly slower than N^2, even for chains that are in the reptation regime. A kinetic model for chain desorption was proposed to rationalize the behavior and conformation of strongly adsorbed chains. If a simple "diffusion" model in terms of the variable N_A was adopted, such a model would yield a desorption time scaling as N^2. Our results indicate a more complex behavior in that the behavior of chains depends not only on N_A but also on the length of time a chain has been attached to the surface. This suggests that to sufficiently describe the conformations at least one more parameter is needed, for instance, the distance of the chain center of mass from the surface.

This work traces the outline of a more complete study to be undertaken. The static characterization of a wider range of systems by the method presented here would permit extraction of general dependencies of the melt conformations on chain length and surface interaction that are questions of great interest from both a practical and a fundamental point of view. The bases of a detailed dynamic study gives the ingredients to further develop a more complete model capable of predicting the different time scales and behavior of adsorbed chains. The establishment of characteristic times also provides guidelines for precise studies of complex nonlinear dynamics dependent phenomena. In particular, the desorption time defined in this work can be used as a measure of the lifetime of the melt/solid interface and should be of importance when discussing the response of this interface to high-frequency oscillations.

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