The Exchange Kinetics of Macromolecules Adsorbed on a Solid Surface: A Theoretical Investigation

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ABSTRACT: The exchange kinetics of macromolecules (e.g. polymers or proteins) desorbing from a solid surface is investigated using a theoretical model which accounts for both transport-controlled and detachment-controlled kinetics in a unified manner. In the transport-controlled regime, the decay has an effectively stretched-exponential behavior with an exponent that could vary anywhere from 0 to 1. The theoretical predictions agree well with the results from dynamic Monte Carlo simulations. The solution presented here will be valuable for interpreting exchange-kinetics experiments and can be used to obtain both the attachment rate and the detachment rate unambiguously.

I. Introduction

Adsorption of macromolecules (polymers, proteins) onto a solid surface plays an important role in a variety of applications, including chromatography, paint and coating, and biomedical material design, and therefore, has attracted considerable research efforts. Apart from the complicated surface processes one may encounter in the case of adsorption/desorption of macromolecules (e.g. conformational relaxation of polymers on the surface), the adsorption/desorption kinetics of macromolecules shares a physical picture similar to the case of small molecules adsorbed at interfaces (i.e. air–liquid or liquid–liquid). They both can be influenced or controlled by the transport of the materials to the adsorbing surface. This question has been explored theoretically as early as in 1946 by Ward and Tordai,[1] and has continued to receive considerable attention[2,3] even now.[4] Most of the theoretical work so far has focused on adsorption kinetics or desorption kinetics and has considered the influence of the transport step on such kinetics. Unfortunately, the theoretical model has no analytical solutions under these situations. Even the qualitative understanding of the interplay between the transport process and surface process is not very clear. As a result, measurements of adsorption kinetics or desorption kinetics have not been able to provide much quantitative results about adsorption and desorption rates of polymers at surfaces.

Recently, measurements of exchange kinetics have received considerable attention for polymers adsorbed on a surface.[5–10] In these experiments, polymers are first allowed to adsorb onto the surface while in equilibrium with their bulk solution. Then the bulk solution is replaced by another solution which contains a different polymer, or a similar polymer, but with certain labels that will allow one to trace the polymer.[5,6] The subsequent exchange of polymers and the resulting decay of the amount of originally adsorbed polymers, $\Gamma(t)$, can then be monitored by an appropriate detection method. Such experiments can probe the desorption of polymers from the surface. It has been reported that the decay of $\Gamma(t)$ monitored by such exchange-kinetics methods can be either diffusion-controlled or detachment-controlled.[6,7] The former shows a stretched-exponential decay, while the latter shows a simple-exponential decay. However, there have been no theoretical investigations (of such exchange kinetics) which consider the interplay between the surface detachment process and the transport processes. All the experimental data are analyzed by extracting the apparent decay rate from such measurements and by simply treating the extracted rate as the desorption rate. This rate apparently has contributions from both the transport step and surface detachment step.

We present here a simple model which is constructed on the basis of the physical picture of exchange kinetics we describe and which is also supported by our Monte Carlo simulation of the desorption of homopolymer chains from a solid surface. The model employed has been used earlier to study the adsorption and desorption kinetics under the influence of transport.[1–4] When one applied this simple model to exchange kinetics, under an ideal situation (i.e., the replacing molecules in the bulk are thermodynamically equivalent to those adsorbed on the surface), a simple analytical solution is obtained for the decay of the amount of the originally adsorbed molecules. This greatly simplifies the analysis of the data obtained in the experimental measurement of the exchange kinetics, and thus it will be possible to obtain both the attachment and the detachment rates of macromolecules on the surface from such studies.

II. Theoretical Model

The physical situation of interest consists of a surface which has an adsorbed layer of polymer chains with a surface coverage of Γ_0 (in mass per unit area) at time t = 0. These polymer chains are labeled by suitable means (e.g. isotopic label or fluorescence label), which allow one to distinguish these polymers from those in the bulk that have no labels. The label itself does not influence the thermodynamic properties of the chains as far as adsorption is concerned. As time elapses, the labeled chains will exchange with those unlabeled in the bulk. The system is otherwise in a thermodynamic equilibrium state if one does not differentiate between

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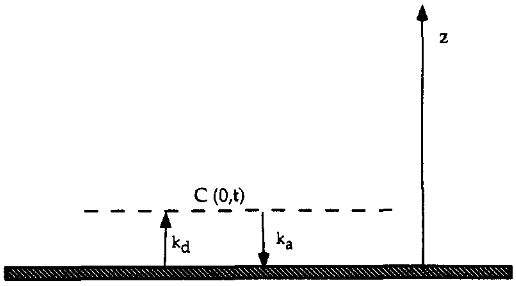

Figure 1. Schematic drawing of the exchange kinetics under consideration.

the labeled and unlabeled chains. We call the kinetics thus measured by monitoring the decay of the amount of the labeled chains on the surface, $\Gamma(t)$, as "exchange kinetics under an ideal situation". In a real experiment, the replacing chains in the bulk quite often will be different from those originally adsorbed on the surface. That difference will complicate the problem further. As a first step, we only focus on the exchange kinetics under the above-defined ideal situation.

The geometry of the system under consideration is depicted in Figure 1. The bulk solution extends infinitely along the positive z-direction, with the origin at the flat adsorbing surface. We use k_a and k_d to denote the attachment and detachment rates of polymers onto and from the adsorbing surface. These rates may have a complicated dependence on the surface coverage. We call k_a and k_d the *attachment* and *detachment* rates, respectively, rather than by the commonly used terms, "adsorption" and "desorption" rates, in order to differtiate them from the rates measured in adsorption/desorption kinetics. In the latter situation, the rates measured contain the combined effects of both the transport process and the surface process. The kinetic equation for the labeled chains then follows:

$$\frac{d\Gamma(t)}{dt} = -k_d\Gamma(t) + k_a(\Gamma_s)\, C(z,t)|_{z=0} \tag{1}$$

Here $C(z,t)$ is the concentration of the labeled chains at time t along the z-direction, and $C(z,t)|_{z=0}$ is the concentration near the surface region. Note k_a has the dimension of length/time, while k_d has the dimension of time^{-1}. We write k_a explicitly as a function of Γ_s, the total surface coverage that counts both the labeled and unlabeled chains on the surface, since k_a is expected to be strongly dependent on the total surface coverage. In comparison, k_d is not expected to be strongly dependent, but may be weakly dependent on the surface coverage in most situations.

Before proceeding with the problem, we would like to show that the above equation naturally leads to an attachment rate which is consistent with the Langmuir adsorption kinetics when the adsorption isotherm follows the Langmuir equation. When the adsorption is reversible and equilibrium is reached between bulk solution and the surface layer, then $d\Gamma/dt$ becomes zero and one has

$$k_d\Gamma^{eq} = k_a C^{eq} \tag{2}$$

The Langmuir adsorption isotherm is of the form

$$\frac{\Gamma}{\Gamma_{max}} = \frac{AC}{1+AC} \tag{3}$$

in which A is a constant. Rearranging the above and assuming k_d is not a function of Γ, one arrives at

$$k_a = k_d A(\Gamma_{max} - \Gamma) \tag{4}$$

This attachment rate is exactly what is commonly used when one speaks of Langmuir adsorption kinetics. The attachment rate is a decreasing function of the surface coverage.

Nevertheless, no assumption concerning the form of the adsorption isotherm is needed in our theoretical model about the exchange kinetics. The only assumption we need is the time independence of k_a and k_d in eq 1. In the case of exchange kinetics under the ideal situation, the total surface coverage is constant. Therefore, the assumption that k_a and k_d are independent of time can be justified. This is also the reason why we can separate the kinetic equations for the labeled and unlabeled chains. The bulk concentration of the labeled chains, $C(z,t)$, obeys the following mass-transport equation:

$$D\frac{\partial^2 C(z,t)}{\partial^2 z} = \frac{\partial C(z,t)}{\partial t} \tag{5}$$

in which D can be a function of distance [through its possible dependence on $C(z,t)$], but we shall assume that it is a constant. At time $t = 0$, $C(z,0) = 0$, since all the labeled chains are on the surface initially. The second boundary condition that is needed to determine $C(z,t)$ uniquely is

$$\frac{d\Gamma(t)}{dt} = D\frac{\partial C(z,t)}{\partial z}\bigg|_{z=0} \tag{6}$$

dictated by the conservation of mass.

The above equations remain the same for the adsorption and desorption kinetics, but the boundary conditions are different. In the case of adsorption and desorption kinetics, the surface coverage becomes a function of time. Therefore, the equations have no analytical solution because of the nonlinearity of the second term in (1).

An analytical solution for $\Gamma(t)$ can be obtained using the Laplace transforms. The Appendix outlines the procedure. Although $\Gamma(t)$ depends on the three coefficients, k_a, k_d, and D, it is a function of only two parameters, since k_a, k_d, and D appear in the following combinations in the solution:

$$\alpha_1,\alpha_2 = \frac{k_a}{2D^{1/2}} \mp \left[\left(\frac{k_a}{2D^{1/2}}\right)^2 - k_d\right]^{1/2} \tag{7}$$

When $\alpha_1 \neq \alpha_2$, one gets

$$\frac{\Gamma(t)}{\Gamma_0} = \frac{1}{(\alpha_2 - \alpha_1)}[\alpha_2 f(\alpha_1 t^{1/2}) - \alpha_1 f(\alpha_2 t^{1/2})] \tag{8}$$

where

$$f(w) = \mathrm{erfc}(w)\exp(w^2) \tag{9}$$

in which erfc(w) is the complementary error function. When α_1 and α_2 are complex numbers, $\Gamma(t)$ is still a real function of t, because α_1 will be a complex conjugate of α_2 and $f(\alpha_2 t^{1/2})$ will be a complex conjugate of $f(\alpha_1 t^{1/2})$.

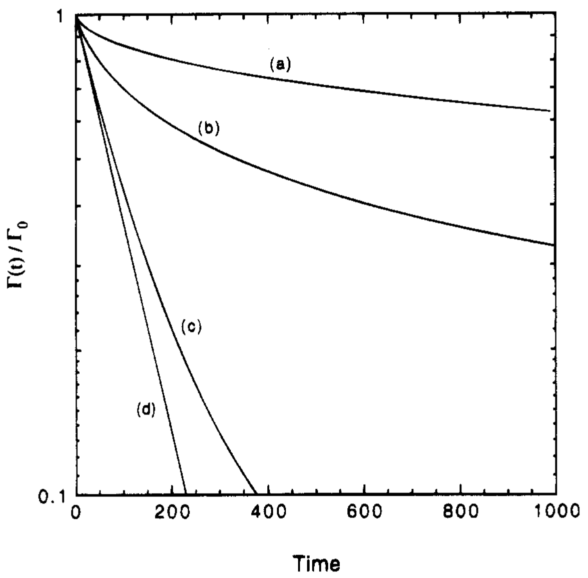

Figure 2. Sample calculations of $\Gamma(t)/\Gamma_0$ with $k_d = 0.01$ time^{-1}, $k_a = 0.02$ (length/time): (a) $D = 0.001$ length^2/time, $Q^2k_d/4D = 10$; (b) $D = 0.01$ length^2/time, $Q^2k_d/4D = 1$; (c) $D = 1.0$ length^2/time, $Q^2k_d/4D = 0.1$; (d) simple exponential decay function, $\exp(-k_dt)$.

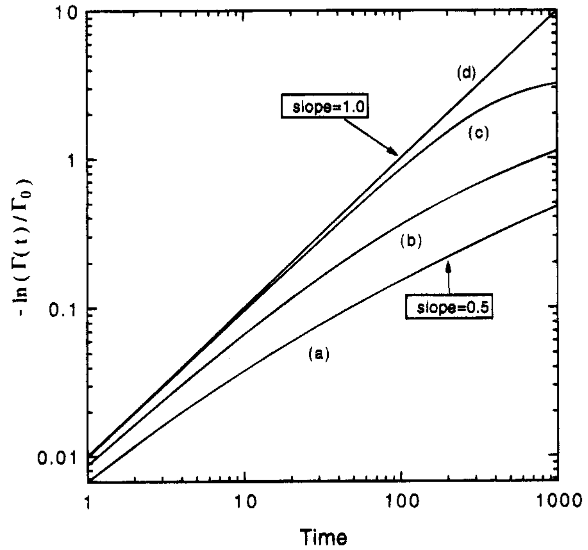

Figure 3. Data in Figure 2 replotted as $-\ln(\Gamma(t)/\Gamma_0)$ vs t.

When $\alpha_1 = \alpha_2 = \alpha$,

$$\frac{\Gamma(t)}{\Gamma_0} = \frac{1}{\pi^{1/2}}[2\,\alpha\, t^{1/2} + \pi^{1/2} f(\alpha t^{1/2})\,(1 - 2\alpha^2 t)] \quad (10)$$

In Figure 2, we present several sample calculations for $\Gamma(t)/\Gamma_0$ when $k_d = 0.01$ (time^{-1}) and $k_a = 0.02$ (length/time) are kept constant and the diffusion coefficient, D, is varied from 0.001 to 1 (length^2/time). Curve b ($D = 0.01$) corresponds to $\alpha_1 = \alpha_2$. It can be seen from the figure that when the diffusion coefficient becomes progressively smaller, the decay deviates more and more from the simple-exponential function. In Figure 3, the same data are replotted using $-\ln(\Gamma(t)/\Gamma_0)$ vs t on a log–log plot. The dependence of $\Gamma(t)$ on t is not strictly a stretched-exponential function, but for a limited range of t, it often can be approximated by a stretched-exponential function. For example, curve a in Figure 3 exhibits a straight line with a slope of 0.5 for t that spans from 200 to 2000, 2 orders of magnitude in time.

Whether $\Gamma(t)$ is closer to a simple-exponential decay function or to a stretched-exponential decay depends on the relative magnitudes of $(k_a/2D^{1/2})^2$ and k_d. Note that these two variables have the same dimensions. It is easy to show that when diffusion is fast, so that $(k_a/2D^{1/2})^2 \ll k_d$, (8) reduces to

$$\Gamma(t) = \Gamma_0 \exp(-k_d t) \quad (11)$$

as one would expect when the rate of detachment controls the decay.

On the other hand, when k_d is small compared to $(k_a/2D^{1/2})^2$, one has

$$\alpha_1 \approx k_d D^{1/2}/k_a + ... \quad (12)$$

$$\alpha_2 \approx k_a/D^{1/2} - k_d D^{1/2}/k_a \quad (13)$$

as well as the inequality

$$\alpha_2 \gg \alpha_1 \quad (14)$$

Therefore, $\Gamma(t)$ can be approximated by

$$\Gamma(t) \approx \Gamma_0 f(\alpha_1 t^{1/2}) \quad (15)$$

This approximation, however, will not be valid as $t \to 0$. Nevertheless, since we are interested only in estimating the time of decay, we can use this approximation. The function $f(w)$ decays to $(1/e)$ at approximately $w = 1.25$. Thus if one defines τ_{off} as the time needed for $\Gamma(t)$ to decay to $1/e$, then one has the following approximation:

$$\tau_{\text{off}} \approx 1.56 k_a^{\,2}/(k_d^{\,2} D) \quad (16)$$

This approximation is only held when $\alpha_2 \gg \alpha_1$.

The above discussions have shown that the relative magnitudes of $k_a^2/(4D)$ and k_d determine whether the decay will be detachment-controlled or transport-controlled. The role of D is easy to understand. When D is small, $k_a^2/(4D)$ will be large and, therefore, the decay will be transport-controlled, or vice versa. However, the role of k_d seems to be counter to physical intuition. If one keeps $k_a^2/(4D)$ constant and decreases k_d, the decay will become transport-controlled rather than detachment-controlled. This counter-intuition is due to the fact that k_a is strongly dependent on k_d, as shown by (2):

$$k_a = k_d \Gamma^{\text{eq}}/C^{\text{eq}} = k_d Q \quad (17)$$

where Q is a quantity which does not vary significantly when k_d is varied. Using the above relationship, the inequality which determines the decay to be more detachment-controlled becomes

$$Q^2 k_d/4D \ll 1 \quad (18)$$

Now the role of k_d is consistent with physical intuition. When k_d becomes smaller, the above inequality will be satisfied. Therefore, the decay will be more detachment-controlled.

Douglas *et al.*[7] have reported observing stretched-exponential decays of Γ in their experiments and have interpreted the stretched-exponential behavior as due to the "diffusion-controlled" decay. However, there is an important difference between their interpretation and ours. The diffusion process they have discussed is the diffusion of the chains through the *adsorbed polymer layer* (or the "adlayer" in their terminology). The diffusion process we have discussed above is the diffu-

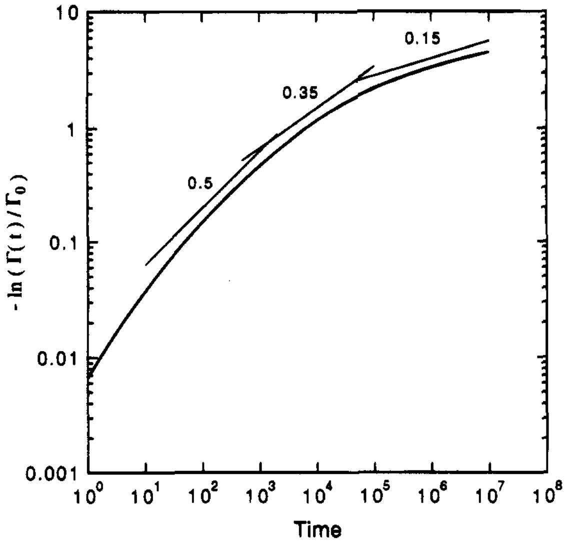

Figure 4. Replot of curve (a) in Figure 3 over a wider range of t. The three short lines indicate three different slopes β (with the values specified by the numbers above the lines).

sion of the detached chains in the bulk, away from the surface layer. On the first sight, it may not appear that the diffusion in the bulk solution can exert such a significant influence on the overall decay measured in the exchange kinetics, since the overall decay reported in the experiments in refs 7 and 8 is on the order of hours, whereas diffusion in the bulk typically takes only several minutes. But what is different about exchange kinetics is the strong tendency of the detached chains to be readsorbed if they cannot be transported away relatively fast. Therefore, it is the coupling between the readsorption and diffusion in the bulk that causes the overall decay in the exchange kinetics to slow down significantly. Douglas *et al.* have overlooked this aspect, and therefore, in order to explain the slow diffusion that is on the order of hours, they invoke the idea of sluggish diffusion through the adsorbed polymer layers.

The above model proposed for the exchange kinetics can readily explain the experimental results reported by Douglas *et al.* without any additional assumptions. In particular, we focus on the results reported in Figures 3 and 4 of ref 7 where stretched-exponential decays with an exponent less than 0.5 are observed. According to our model, one can observe a stretched-exponential decay ($\exp(-t^{\beta})$) with an exponent β, that could lie anywhere between 0 and 1. To illustrate this, we have replotted curve a in our Figure 3 over a much wider range of t (spanning a total of 7 orders of magnitude) in Figure 4. The three short lines in the figure indicate three different slopes, i.e., three different β's. Experimental measurements rarely probe decays over a range of t spanning 7 orders of magnitudes. The typical range of time covered in the experiments reported by Douglas *et al.* is about 2 orders of magnitude. One can see from our Figure 4 that if the range of observation is from $t = 10^3$ to $t = 10^5$ [during which $\Gamma(t)/\Gamma_0$ varies from about 0.5 to 0.04], the observed exponent will be approximately 0.3. It is also apparent from this figure that the smaller the initial measured values of $\Gamma(t)/\Gamma_0$ are (i.e. the further along the tail the monitored decay lies), the smaller the observed β will be. This trend can be easily seen in the results reported in Figures 3 and 4 of ref 7.

Recently, we have carried out dynamic Monte Carlo simulations of desorption of homopolymers from a solid surface and have observed similar stretched-exponential decays. In fact, it is these results that make one appreciate the role of diffusion in the *bulk* in causing the stretched-exponential decay of Γ. Below we present the dynamic Monte Carlo simulation results which support the above theoretical model for the exchange kinetics.

III. Comparison with Dynamic Monte Carlo Simulation

We have performed dynamic Monte Carlo simulations to investigate the dynamical properties of adsorbed homopolymers on a flat surface. Part of the study has been reported in a previous publication,[11] but for a better understanding of the results, the details of the simulation models are reported here again.

The simulations are carried out on a cubic lattice of size 50^3, with periodic boundary conditions applied in the x- and y-directions. The $z = 0$ layer is the impenetrable adsorbing surface, and the layer at $z = 49$ is a noninteracting hard wall. The chains are modeled as self-avoiding walks on the lattice, and only attractive segment/surface interactions, with $\epsilon_s = 1.0k_BT$, are applied with the Metropolis rule[12] whenever a segment is in the $z = 1$ layer (in direct contact with the adsorbing surface). The simulation starts with an appropriate number of chains in the box, so that when the system reaches equilibrium, the concentration in the bulk, C^{eq}, is maintained at a nearly constant level (i.e. 0.027 ± 0.004) for each chain length (in the other work, we have used ϕ^b to denote this bulk concentration, but here we want to be consistent with the previous theoretical section). Only the extended Verdier–Stockmayer[12] relaxation method is employed for generating subsequent dynamic trajectories after the system is equilibrated by a combination of reptation and the extended Verdier–Stockmayer relaxation. Some of the other details, such as how to determine the equilibrium bulk concentration, can be found in ref 13.

A chain is defined as adsorbed whenever there is at least one segment of that chain in direct contact with the adsorbing wall. These chains are reversibly adsorbed on the surface, and they constantly exchange with the chains in the bulk. To monitor the dynamics of the exchange, we define the following correlation function:

$$G(t) = \langle N_s(t)/N_s(0) \rangle \tag{19}$$

Here, $N_s(0)$ and $N_s(t)$ are the number of "labeled" chains adsorbed on the surface at times 0 and t, respectively. We distinguish the initially adsorbed chains from the rest (those in the bulk at time $t = 0$) by "labeling" the former. Two different correlation functions are extracted from the trajectory. In one, as soon as a labeled chain leaves the surface, it is no longer considered as labeled. Thus its subsequent return to the surface does not contribute to $N_s(t)$. The correlation function thus obtained, denoted by $G_c(t)$, describes only the *detachment* of the adsorbed chains from the surface. In the other, the label is retained regardless of whether that chain has left the surface, and the subsequent return of that chain to the surface contributes to the count of $N_s(t)$. The latter "labeling" method is closer, or equivalent, to the "labeling" method adopted in experiments, since in a real experiment the label is always permanently attached. The correlation function thus obtained, denoted by $G_{nc}(t)$, is the one that we have discussed in the above theoretical section, the decay of $\Gamma(t)$ in exchange kinetics under the ideal situation.

We have examined decay of both $G_c(t)$ and $G_{nc}(t)$ for the chain length in the range 5–85. For all the chain

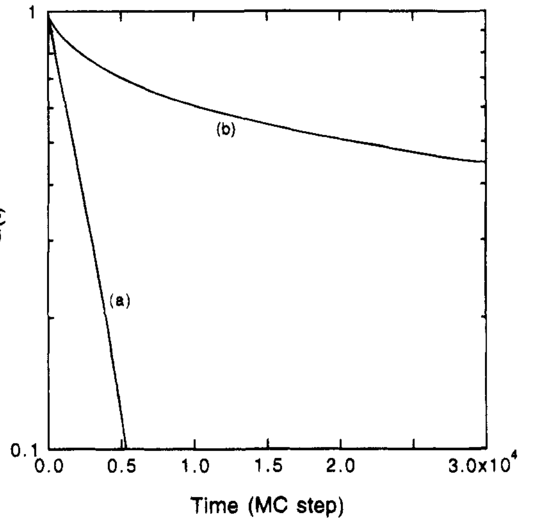

Figure 5. (a) $G_c(t)$ and (b) $G_{nc}(t)$ determined from the simulations for chain length, $l = 10$.

Table 1. Parameters Extracted from the Simulation[a]

l	C^{eq}	k_d (time^{-1})	D (length^2/time)	Γ^{eq}	k_a (length/time)
5	0.023	2.5×10^{-3}	0.03	0.33	3.6×10^{-2}
10	0.031	4.1×10^{-4}	0.013	0.62	8.2×10^{-3}
20	0.027	6.8×10^{-5}	0.0057	0.83	2.1×10^{-3}
50	0.026	5.6×10^{-6}	0.0020	1.04	2.2×10^{-4}
85	0.023	2.3×10^{-6}	0.0011	1.18	1.2×10^{-2}

[a] The time is in Monte Carlo steps, and the length is in lattice unit length. l denotes the number of beads in the chain.

lengths examined, $G_c(t)$ exhibits an unequivocally simple-exponential decay, while $G_{nc}(t)$ decays much slower than $G_c(t)$, and often it exhibits stretched-exponential behavior. It is these results that have led us to investigate the exchange kinetics theoretically. Figure 5 presents an example of the difference between $G_c(t)$ and $G_{nc}(t)$ for one of the chain lengths examined.

In order to compare the results from the simulation with the theoretical predictions in the above sections, we need to determine k_d, k_a, and D independently from the simulation. $G_c(t)$ provides k_d directly. Since the chains in the simulations are reversibly adsorbed on the surface, k_a can be related to k_d through (2). Therefore, we only need to evaluate Γ^{eq} and C^{eq} from the simulations in order to obtain k_a, and that can be easily done.[14] The diffusion coefficient, D, of the chains in the bulk is evaluated by monitoring the displacement of the average center of mass of the chains as a function of Monte Carlo step in the simulation. Table 1 summarizes the coefficients determined in the simulations for several chain lengths.

From the simulations, D is found to have a power-law dependence on the chain length with an exponent of 1.21, which is what one expects for a Rouse chain with excluded-volume interactions (we have examined a total of eight different chain lengths). The coefficient k_d is found to have a power-law dependence on the chain length as well, with an exponent of ~2.5. This result has been discussed in a previous publication.[11] The physical meaning of the attachment rate k_a is not well-understood. Nevertheless, we found k_a also has a power-law dependence on the chain length but with an exponent of ~2.0. Apparently, this k_a is quite different from the rate of conformational relaxation when a homopolymer is brought into contact with an adsorbing wall, as examined by Shaffer.[14] In the latter case, it has been reported to have a power-law dependence with an exponent of ~1.5.

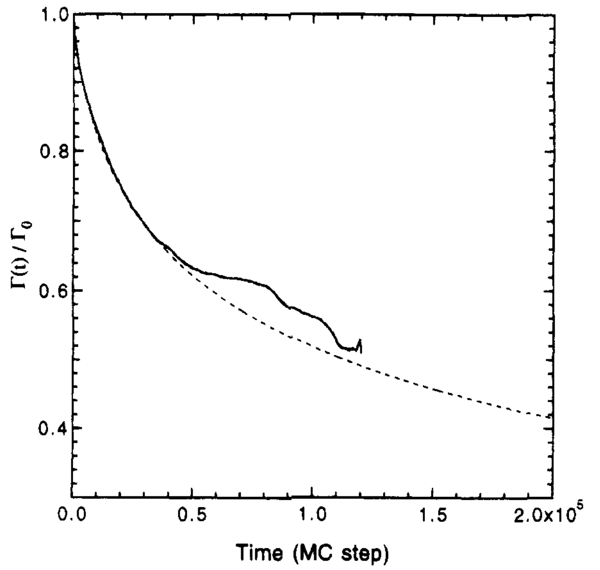

Figure 6. Solid line: $G_{nc}(t)$ determined from the simulation for $l = 20$. Dashed line: Calculated according to (8) using parameters tabulated in Table 1 for $l = 20$.

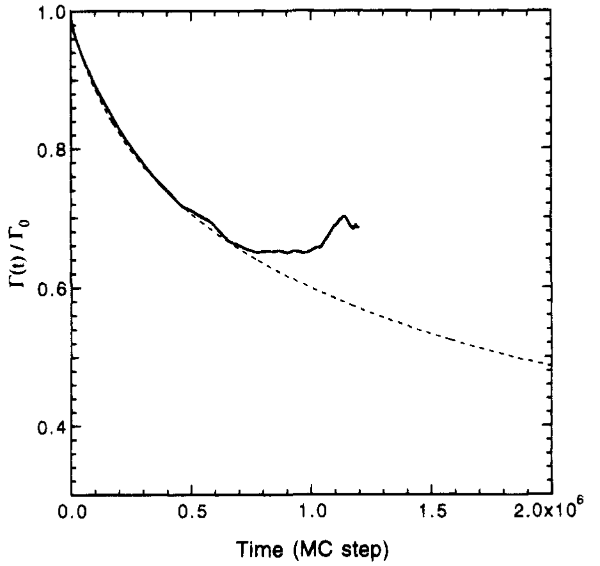

Figure 7. Solid line: $G_{nc}(t)$ determined from the simulation for $l = 85$. Dashed line: Calculated according to (8) using parameters tabulated in Table 1 for $l = 85$.

Figures 6 and 7 present the calculations according to (8) with the parameters tabulated in Table 1, along with the $G_{nc}(t)$ determined in the simulations for $l = 20$ and $l = 85$. The simulations were carried out with a finite lattice length along the z-direction. Thus the later part of the decay from the simulation deviates upward from the theoretical predictions since the theory assumes an infinite extension along the z-directions. The agreement between the theoretical predictions and the Monte Carlo simulation results down to $\Gamma(t)/\Gamma_0 \sim 2/3$ is very good. A test of the theoretical predictions at smaller $\Gamma(t)/\Gamma_0$ would require a larger simulation box. Figures 6 and 7 confirm that the physical picture adopted by us and the theoretical predictions obtained in the above sections are correct and that it is the transport process in the bulk that affects the decay of the exchange kinetics.

The Monte Carlo simulation results reported here are limited to only one surface/segment interaction energy, $\chi_s = 1.0k_BT$, and although this may limit what one can infer about the detachment kinetics, the physical picture we have proposed above, specifically the relationship between the detachment kinetics and exchange kinetics remains valid under more general situations. In the simulations reported here, all the $G_{nc}(t)$ studied are transport-controlled. This is of course due to the limited range of the physical situation we have investigated. However, we do not expect any fundamental change in the physical picture of the exchange kinetics presented above even if the surface/segment interaction is much higher than we have presently investigated. When the surface/segment interaction is very high, $G_{nc}(t)$ merely becomes detachment-controlled, and our solution already covers this limit.

We close our discussion with a few brief general comments. The kinetics of adsorption and desorption have been recognized to be important for a number of years, and the general theoretical formalism used is not different from the physical picture employed here. However, adsorption problems do not admit analytical solutions except in highly simplified cases since the surface coverage varies with time (and, often, in a complicated or unknown manner). In contrast, the equations for the exchange-kinetics experiments of the type addressed in the present paper can be solved analytically when k_a and k_d remain constant, and such exchange-kinetics experiments can be used to determine *detachment* and *attachment* rate constants. Perhaps a combination of adsorption-kinetics, desorption-kinetics, and exchange-kinetics experiments may assist one in developing a comprehensive picture of the dynamics of polymer adsorption and desorption.

We are presently carrying out additional dynamic Monte Carlo simulations to investigate exchange kinetics when the replacing chains are different from those initially residing on the surface. These simulations will be valuable for interpreting experiments in which the replacing chains differ from the initially adsorbed chains.

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Appendix

Applying a Laplace transform to (5), one has

$$D\frac{\partial^2 \bar{C}(z,P)}{\partial z^2} = P\bar{C}(z,P) \qquad (20)$$

$\bar{C}(z,P)$ is the Laplace transform of $C(z,t)$, and $C(z,t)$ is zero at time $t = 0$. The solution of the above equation has to be finite along the positive z-direction, thus

$$\bar{C}(z,P) = A(P)\exp(-(P/D)^{1/2}z) \qquad (21)$$

where $A(P)$ is an undetermined coefficient, which is a function of P, but not a function of z. The second boundary condition in (6) gives

$$A(P) = -\frac{P\bar{\Gamma}(P) - \Gamma_0}{(PD)^{1/2}} \qquad (22)$$

Applying a Laplace transform to (1) and substituting the above-determined $C(z,P)$, one obtains

$$\bar{\Gamma}(P) = \Gamma_0\frac{(PD)^{1/2} + k_a}{P((PD)^{1/2} + k_a) + k_d(PD)^{1/2}} \qquad (23)$$

One can obtain $\Gamma(t)/\Gamma_0$ easily from (23) by applying an inverse Laplace transform.

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