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Competitive Adsorption Kinetics of End-Adsorbing Polymers

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ABSTRACT: The kinetics and equilibrium of adsorption of two competing species of end-adsorbing polymer chains are considered as a model system for study of competitive adsorption processes in commercially relevant colloidal stabilizers. Two typical situations are considered: invasion of an existing layer by shorter chains with a similar end group, and invasion by chains of the same length with a more strongly-adsorbing end group. It is shown that the short-chain invaders readily adsorb in the presence of an existing layer and lead to enhanced desorption of the original chains. Invading chains with stronger stickers are not effective in quickly displacing the original layer.

Introduction

In many applications involving stabilized colloids, the kinetics and equilibrium of competitive adsorption of two or more adsorbing polymeric stabilizers or surfactants are critical properties. The present work is concerned with competitive adsorption kinetics in a well-controlled model system to determine what phenomena may govern the replacement or washing off of one adsorbed polymer by another invading species.

The model system to be studied is that of end-adsorbed polymers forming a layer on the featureless surface of an ideal colloidal particle in solution. The adsorbing end group on the polymer is assumed to be small, structureless, and strongly adsorbing, with a binding energy Δ of several k_BT or more. The end group or "sticker" is assumed to adsorb to the surface at no specific sites and independently of other stickers already present (repulsive interactions between stickers on the surface will be briefly considered later).

The polymeric tails of such end-adsorbed polymers stretch away from the surface to form a "brush" if the coverage σ (number of chains per unit area) is sufficiently large.[1] This condition of large enough coverage is obtained in equilibrium for sufficiently strong binding energy Δ. Such brush structures are well characterized theoretically[1] if the brush thickness is somewhat smaller than the radius of the colloidal particle.

The model system avoids many complications which may be important for practical systems, including (1) entanglement effects, which arise if the adsorbing polymer has multiple adsorbing groups (including the case of a homopolymer for which each monomer is weakly attracted to the surface), (2) adsorbing groups with structure and/or interactions, *e.g.*, an incompatible copolymer tail used as the end group, (3) specific structuring of densely adsorbing short-chain molecules; i.e., surfactant condensed phases on the surface, and (4) micellization in solution of the adsorbing chains, which may complicate the adsorption and desorption processes.

Except for item 1, the model system considered in this paper is similar to those commonly used in many commercial applications in colloid stabilization.

In the basic physical situation of interest, a bare surface is exposed to a solution of adsorbing chains and a brush is formed by the successive adsorption of chains from the solution. This situation was studied by Ligoure and Leibler,[2] and we shall review their approach and results before extending their work to the problem of competitive adsorption. After a characteristic "construction time" τ_c, equilibrium obtains between the adsorbed brush and the solution. Beyond this time, chains exchange between the solution and the brush with a characteristic "exchange time" τ_{ex}. If the solution is then replaced with clean solvent, the brush desorbs in a "washing time" τ_w.

It is observed experimentally[3] that the washing time τ_w is much longer than the construction time τ_c. However, some observations indicate that if the solution is replaced with a solution of shorter chains with the same or a similar adsorbing end group, the original brush is readily displaced. We are thus interested in the kinetics governing the invasion and displacement of a brush by another end-adsorbing polymer, either added to or replacing the original solution.

1. Single-Species Kinetics

We review the results of ref 2 to set the stage for our analysis. A bare surface growing a brush from solution will have a final equilibrium governed by reversible exchange with that solution. The chains in the brush are stretched and crowded; the brush height and free energy per chain relative to a coil in dilute solution are known in the limit of strongly-stretched chains to be[1]

$$h = c_h N \sigma^{1/3}$$

$$f = c_f N \sigma^{2/3} \tag{1}$$

where $c_h = (12/\pi^2)^{1/3}$ and $c_f = {}^3/_2(\pi^2/12)^{1/3}$. The bound end group reduces the free energy by the binding energy Δ.

When a chain is bound it loses the translational entropy $k_BT \log c$ of a chain in solution with c chains per volume, retaining only the translational entropy $k_BT \log \sigma$ of a chain on the surface at coverage σ. Hence

$$f - \Delta + \log \sigma = \log c \tag{2}$$

is the equilibrium condition.

If the binding is strong ($\Delta \gg k_BT$) and the solution concentration not too low, we may say roughly that $f \approx \Delta$; hence in the final state of the adsorption kinetics, chains are strongly stretched. At an intermediate value of surface coverage on the approach to equilibrium, f is given by eq 1; at some early stage of the kinetics, $f \sim T$.

Beyond this stage, there is a substantial barrier to the approach of the adsorbing end of a chain to the surface. (Before this time, the growth kinetics is diffusion-limited.) The height of the barrier is the free energy cost f which

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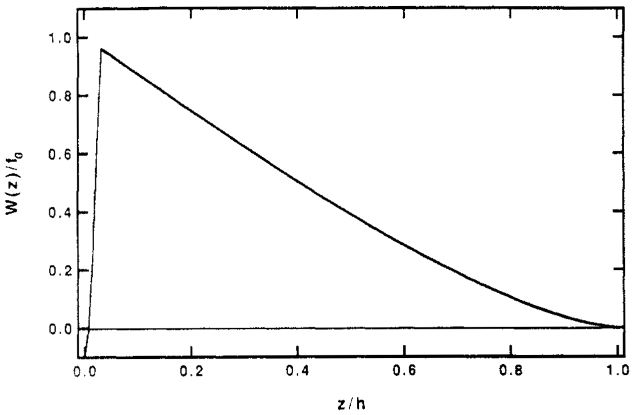

Figure 1. The potential barrier $W(z)$ of eq 3 is the work required to move the adsorbing end group to within z of the surface. (In this figure, the shape and depth of the adsorbing well are arbitrary; its range is in general much less than h.)

must be paid to stretch the chain and introduce it into the high monomer density of the brush, just before the sticker reaches the surface.

We may regard the distance z of the sticker from the surface as a reaction coordinate and write a potential $W(z)$ describing the work required to pull the sticker into the brush a distance z from the surface.[4] The characteristics of $W(z)$ are a long approach over a distance of the brush height h (typically hundreds of angstroms) to the surface with a large total work f followed by a steep drop of Δ into the bound state of the sticker over a distance of a few angstroms. For the case of a single adsorbing species $W(z)$ is given for z beyond the range of the sticker adsorption by

$$W(z) = \frac{2f}{\pi}[\cos^{-1}(z/h) - (z/h)(1-(z/h)^2)^{1/2}] \qquad (3)$$

and is displayed in Figure 1 (see Appendix). Here we are assuming that the end group is a small molecule and not a copolymer.

There is viscous resistance to the motion of the chain through the brush. This may be described within a Zimm model,[5] in which local correlation blobs of size $\xi(\phi)$ (here $\phi(z)$ is the local monomer concentration in the brush) along the chain move with a Stokes drag coefficient $6\pi\eta\xi$. The sum of viscous drag acting on the motion of the coordinate z is then the sum over blobs $\sum_i 6\pi\eta\xi_i = 6\pi\eta(h-z)$; hence the diffusion coefficient $D(z)$ is the inverse of the drag coefficient, or

$$D(z) = T/[6\pi\eta(h-z)] \qquad (4)$$

for chains with end group a distance z from the surface.

We may then write a Fokker–Planck equation[6] for the evolution of the distribution $P(z,t)$ of positions z of the end-groups:

$$\frac{dP}{dt} = -\frac{d}{dz}J(z) = \frac{d}{dz}\left[D(z)\left(\frac{dP}{dz} + P\frac{dW}{dz}\right)\right] \qquad (5)$$

If the barriers to adsorption or desorption from the brush are substantial, we may expect the evolution to be rate-limited; that is, the current $J(z)$ will be nearly constant in space and $P(z)$ will adopt a steady-state profile and change slowly without buildup of end groups at any location within the brush.[6] (By contrast, if the barriers are small, the kinetics will be diffusion-limited, and the evolution of $P(z,t)$ in space as well as time will be nontrivial.)

If we assume $J(z) = J$, we may solve the differential equation on $P(z)$ implied by J = const to obtain

$$J = \left(\int_0^h dz\,\frac{\exp[W(z)]}{D(z)}\right)^{-1} P(z)\exp[W(z)]\Big|_0^h \qquad (6)$$

We define $W(h) = 0$, so that the end-group potential at the surface takes the value $W(0) = f - \Delta$ and the maximum of the end-group potential is $W(z_{\max}) = f$. We expect the distance $z_{\max}$ from the end group to the surface when $W(z)$ is maximum to be a molecular length.

Now we imagine fixing (by injecting or removing chains as necessary) the concentration of chain end groups at the adsorbing surface and at the brush edge. If we fix $P(0) = \sigma$ and $P(h) = 0$, we are describing J_{out}, the current of chains escaping from the brush (backflow is prohibited, as chains are destroyed when they reach $z = h$). If we fix $P(0) = 0$ and $P(h) = c$, we are describing J_{in} (no escape is possible, since chains are destroyed when they reach the surface). In equilibrium, $J_{\text{in}} = J_{\text{out}}$, which we show below implies the equilibrium condition eq 2.

We now approximate the denominator of eq 6; it is clearly dominated by the region near $z_{\max}$, where $W(z)$ takes its maximum value $W(z_{\max})$. As pointed out by Halperin,[7] interesting consequences result from the extreme asymmetry of $W(z)$. We may summarize his arguments as follows. The integral in eq 6 is well approximated by $l\exp[W(z_{\max})]/D(z_{\max})$. Here l is the width of the region around $z_{\max}$ in which $W(z)$ is within k_BT of its maximum. This width l is much greater than the microscopic length $z_{\max}$, over which the potential $W(z)$ decreases sharply from $W(z_{\max})$ to the value $W(0)$ characterizing the bound state of the sticker, because $W(z)$ is slowly varying for z larger than $z_{\max}$. The work done to bring the polymer chain to the surface was done over a large distance, namely, the brush height h. A sensible approximation is then

$$\int_0^h dz\,\frac{\exp[W(z)]}{D(z)} \approx \frac{\exp[W(z_{\max})]}{D(z_{\max})\,W'(z_{\max})} \qquad (7)$$

where $W'(z_{\max})$ is the derivative of $W(z)$ at $z_{\max}$ in the direction of increasing z. That is, W' is the force required to pull the sticker from outside the brush to $z_{\max}$, just short of adsorption, and hold it there (see Appendix).

The approximation eq 7 leads to

$$J_{\text{in}} = c\exp[-f](DW')\big|_{z_{\max}}$$

$$J_{\text{out}} = \sigma\exp[-\Delta](DW')\big|_{z_{\max}} \qquad (8)$$

Setting $J_{\text{in}} = J_{\text{out}}$ indeed recovers the equilibrium condition eq 2.

The consequences of the asymmetry in $W(z)$ deserve several remarks. In the conventional language of Kramers rate theory,[6] the "rate-limiting step" in discussions of steady-current solutions to the Fokker–Planck equation (eq 5) amounts to the range of the reaction coordinate that dominates the integral in the denominator of the expression (eq 6) for the current. Typically the maxima of $W(z)$ are symmetric, so the rate-limiting step is crossing the region within k_BT of the maximum of the largest barrier.

In the present case, the rate-limiting step may be described as the process of first activating the sticker off of the surface and then its diffusion a sufficient distance away from the surface to be assured of drifting out of the brush in the comparatively small potential gradient $W'(z)$. The likelihood of return to the surface of a just-desorbed end is very great—it would be certain if the small derivative

W' were everywhere zero. As pointed out in ref 7, the quantity DW' may be interepreted as a "drift velocity" v_{drift}; W' is the force on the reaction coordinate (derivative of the work), and D is the mobility.

In the present case, the populations of adsorbed and just-desorbed stickers are essentially in equilibrium, with $P(z_{\max}) \approx \sigma \exp[-\Delta]$. This may be seen by putting a source of chains at $z = 0$ and a sink at $z = z_{\max}$; the resulting current J_{out} is larger than in eq 8 by the large factor $[W(z_{\max})/z_{\max}]/W'$.

Having determined the currents J_{out} and J_{in} in terms of the diffusion coefficient $D(z)$, the force W' on a sticker held near the surface, the coverage σ, and the bulk chain concentration c, we may write simple kinetic equations for the surface coverage as a function of time. Following Ligoure and Leibler, for a single species we write

$$\mathrm{d}\sigma/\mathrm{d}t = J_{\mathrm{in}} - J_{\mathrm{out}}$$

$$\mathrm{d}s/\mathrm{d}T = \exp[-f^{\mathrm{eq}}s^{2/3}] - s\exp[-f^{\mathrm{eq}}] \tag{9}$$

with the reduced coverage $s \equiv \sigma/\sigma^{\mathrm{eq}}$ and the reduced time $T \equiv t/\tau_0$, where $\tau_0 \equiv \eta N\sigma^{\mathrm{eq}}/c$. Here σ^{eq} and $f^{\mathrm{eq}} \equiv f(\sigma^{\mathrm{eq}})$ are the values that obtain in the final equilibrium state.

During the growth process but far from completion, the desorption of chains is negligible because the adsorption barrier $f \sim N\sigma^{2/3}$ is still much less than the desorption barrier Δ. Then the second term of eq 9 may be dropped, and "quasilogarithmic" growth is obtained by Ligoure and Leibler. This suggests a characteristic time for construction of the brush

$$\tau_{\mathrm{c}} = \int \mathrm{d}t = \int_0^1 \mathrm{d}s\, \exp[f^{\mathrm{eq}}s^{2/3}] \approx \frac{3\exp[f^{\mathrm{eq}}]}{2f^{\mathrm{eq}}} \tag{10}$$

The sum over time intervals is dominated by the slowest growth rates near $s = 1$, but the contributions from smaller s lead to the factor $1/f^{\mathrm{eq}}$. Near the end of the growth process, J_{in} and J_{out} are comparable; an expansion about the final equilibrium leads to an exponential relaxation with the same time scale τ_{c}.

After equilibrium is reached, $J_{\mathrm{in}} = J_{\mathrm{out}} = \exp[-f^{\mathrm{eq}}]$. Now imagine tagging those chains on the surface and observing as they escape into solution and are replaced by chains from solution; the current of tagged chains is essentially J_{out}, and thus the characteristic exchange time is $\tau_{\mathrm{ex}} = \exp[-f^{\mathrm{eq}}]$. If we imagine replacing the solution of chains with clean solvent after final equilibrium is reached, again we expect the current of chains out of the brush will be $J_{\mathrm{out}} = \exp[-f^{\mathrm{eq}}]$, and the "washing time" for the brush to significantly desorb will be $\tau_{\mathrm{w}} = \tau_{\mathrm{ex}}$.

2. Competitive Adsorption

Having reviewed the results obtained using the approach of Ligoure and Leibler for the adsorption and desorption kinetics of a single species, we turn to the problem of competitive adsorption, or replacement of chains in a brush already grown by "invading" chains newly added to the solution. We may consider replacing the solution of adsorbing chains with a solution of invading chains, or we may just add the invaders to the solution. As in section 1, we shall not consider solutions so concentrated that they may osmotically compress the brush.[8] We shall consider two different types of invading chains as typical situations: first, shorter invading chains with the same adsorbing end group; and second, invading chains of the same length with a more strongly adsorbing end group.

Consider first the case of shorter invading chains. Because these chains are shorter, the barrier presented to them by the existing brush of long chains is considerably smaller than $f \approx \Delta$. Initially (before many short chains have adsorbed) we may estimate it from the work required to transfer a random-coil configuration of a short chain to the concentration $\phi(0) \sim \sigma^{2/3}$ near the surface; hence $f_{\mathrm{s}}^{(0)} \sim (N_{\mathrm{s}}/N_{\mathrm{l}})f$. If this barrier is smaller than $k_{\mathrm{B}}T$, the short-chain adsorption is initially diffusion-limited, until enough short chains adsorb that they form a barrier to further short chains; in any case, the construction time for the short-chain brush will be controlled by this short-chain barrier.

We may expect a construction time for the short chains given by eq 10 and equilibrium described by eqs 1 and 2, with $N = N_{\mathrm{s}}$. To compare the construction times for short and long chains with the same sticker, we solve the equilibrium equation eq (2) to leading order in logarithmic terms to find $\sigma_{\mathrm{s}} \approx (N_{\mathrm{l}}/N_{\mathrm{s}})^{3/2}\sigma_{\mathrm{l}}[1 - 3/(2f_{\mathrm{l}}) \log (N_{\mathrm{l}}/N_{\mathrm{s}})]^{3/2}$. Using this in eq 10 we find

$$\tau_{\mathrm{c}}^{(\mathrm{s})} \approx (N_{\mathrm{s}}/N_{\mathrm{l}})^{3/2}\tau_{\mathrm{c}}^{(\mathrm{l})} \tag{11}$$

Thus the short chains adsorb readily in the presence of the existing long-chain brush; i.e., they adsorb with a characteristic time much shorter than the growth times for the original brush. We may expect that the number of short chains adsorbed quickly reaches a value in equilibrium with the current number of long chains adsorbed, which will itself change only slowly. In other words, the adsorbed coverage of short chains will follow adiabatically the long-chain coverage.

If the addition of short chains into a brush of long chains increases the total height, as we shall see presently, we should expect to see an initial increase in the brush thickness before final equilibrium is reached. The thickness increases because the added short chains crowd the long chains and cause them to stretch more near the surface (see eq 14). The final brush height will be near that of a brush of short chains, as the long chains are either washed off or actively replaced by short chains.

In an intermediate state on the approach to equilibrium, there will be both long and short chains adsorbed, forming a "bimodal" brush, composed of chains of two different lengths. The properties of such a brush have been studied theoretically[9] and by simulation.[10] For present purposes, the following properties of bimodal brushes are important. The shorter chains form a more strongly stretched layer within the brush close to the surface, through which the long chains pass. The outer portion of the brush is predominantly occupied by long chains; the stretching in this region is more characteristic of a brush containing the long chains only.

The free energy to add a long chain to a bimodal brush is always greater than that required to add a short chain; for a bimodal brush with σ_{s} short chains (length N_{s}) and σ_{l} long chains (length N_{l}) per unit area, we have

$$f_{\mathrm{s}} = c_f N_{\mathrm{s}}\sigma^{2/3}$$

$$f_{\mathrm{l}} = c_f[N_{\mathrm{s}}\sigma^{2/3} + (N_{\mathrm{l}} - N_{\mathrm{s}})\sigma^{2/3}] \tag{12}$$

where $\sigma = \sigma_{\mathrm{s}} + \sigma_{\mathrm{l}}$ is the total coverage.

The height h_{s} of the short-chain layer determines the diffusion coefficient $D_{\mathrm{s}} = T/(6\pi\eta h_{\mathrm{s}})$ of a short chain with its end group approaching the surface and is given by

$$h_{\mathrm{s}} = c_h N_{\mathrm{s}}(\sigma^{2/3} - \sigma_{\mathrm{l}}^{2/3})^{1/2} \tag{13}$$

The total height h of the bimodal brush determines the diffusion coefficient $D_{\mathrm{l}} = T/(6\pi\eta h)$ of a long chain with its end group approaching the surface and is given by

$$h = c_h[N_s\sigma^{1/3} + (N_l - N_s)\sigma_l^{1/3}] \tag{14}$$

Finally, the force required to hold the end group of a short or long chain near the surface just short of adsorption (with the free end located at the edge of the short-chain layer or the brush edge respectively—see Appendix) is

$$W'_s = [2c_f(\sigma^{2/3} - \sigma_l^{2/3})]^{1/2}$$

$$W'_l = [2c_f]^{1/2}\sigma^{1/3} \tag{15}$$

Notice that the addition of short chains to a long-chain brush increases the tension considerably, while having a less dramatic effect of the total height of the brush. This means the drift velocity of an escaping long chain will be larger when short chains have adsorbed, because the force of the end group coordinate will be larger while the drag coefficient is much the same. This will lead to an increase in the current of escaping long chains, even if the activation factor $\exp[-\Delta]$ for the initial desorption event is unaffected by the presence of short chains.

If there is a repulsion between adsorbing groups on the surface, i.e., a dependence of the binding energy on surface coverage, then the presence of additional short chains will reduce the barrier to desorption of the long chains, and the rate of escape of the long chains will be increased.

The currents and equations of motion for the coverages of long and short chains take forms analogous to eqs 8 and 9

$$\mathrm{d}\sigma_\alpha/\mathrm{d}t = J_{\mathrm{in}}^{\alpha} - J_{\mathrm{out}}^{\alpha}$$

$$J_{\mathrm{in}}^{\alpha} = c_\alpha \exp[-f_\alpha] D_\alpha W'_\alpha$$

$$J_{\mathrm{out}}^{\alpha} = \sigma_\alpha \exp[-\Delta] D_\alpha W'_\alpha \tag{16}$$

where $\alpha \in \{\mathrm{s,l}\}$ denotes short or long chains.

We take the initial equilibrium value of the long-chain coverage $\sigma_l^{(0)}$ as a scale for the coverage variables, defining $s_l = \sigma_l/\sigma_l^{(0)}$ and s_s similarly. Likewise, we adopt the same time rescaling as in section 1, $T = t/\tau_0$, with $\tau_0 = \eta N_l \sigma_l^{(0)}/c_l^{(0)}$. Then our equations of motion take the form

$$\frac{\mathrm{d}s_s}{\mathrm{d}t} = \left\{\frac{c_s}{c_l^{(0)}} \exp[-f_s] - s_s \exp[-f_l^{(0)}]\right\}\left\{\frac{N_l}{N_s}\right\}$$

$$\frac{\mathrm{d}s_l}{\mathrm{d}t} = \left\{\frac{c_l}{c_l^{(0)}} \exp[-f_l] - s_l \exp[-f_l^{(0)}]\right\}\times \left\{\frac{s^{1/3}}{[(N_s/N_l)s^{1/3} + (1 - N_s/N_l)s_l^{1/3}]}\right\} \tag{17}$$

where the first and second summands in each equation arise from J_{in} and J_{out}, respectively, and the second factors arise from $D_\alpha W'_\alpha$.

The equilibrium conditions are analogous to eq 2

$$\sigma_\alpha \exp[-\Delta] = c_\alpha \exp[-f_\alpha] \tag{18}$$

Upon dividing by the equilibrium condition $\sigma_l^{(0)} \exp[-\Delta] = c_l^{(0)} \exp[-f_l^{(0)}]$ describing the initial state to replace $\exp[-\Delta]$ in eq 18, we obtain

$$s_\alpha \exp[-f_l^{(0)}] = \frac{c_\alpha}{c_l^{(0)}} \exp[-f_\alpha] \tag{19}$$

When final equilibrium is reached, this equation holds, $J_{\mathrm{in}}^{\alpha} = J_{\mathrm{out}}^{\alpha}$, and the first factors in eq 17 vanish.

As eq 17 is somewhat complicated, we analyze their behavior with the simplifying assumptions (i) $N_s \ll N_l$ and (ii) $c_s \sim c_l^{(0)}$. We now proceed to describe the behavior of eq 17 under these conditions.

Because $D_s W'_s$ (the second factor in the first of eq 17) is N_l/N_s, the growth time of the short-chain brush in the presence of the existing long-chain brush is a factor of N_s/N_l smaller [unless c_s is greatly different from $c_l^{(0)}$]. Essentially, the equilibrium condition eq 18 means that the final equilibrium value $f_s^{(\mathrm{eq})}$ is nearly Δ, just as the initial value $f_l^{(0)}$ was close to Δ. The adsorbing short chains eventually see a barrier very similar to the original long-chain adsorption. The short-chain adsorption rate is faster by the factor N_l/N_s because the diffusion constant is larger for the short chains.

Since the growth time for the short-chain brush is so much shorter than for the long-chain brush, the adiabatic approximation

$$s_s \exp[-f_l^{(0)}] \approx \frac{c_s}{c_l^{(0)}} \exp[-f_s] \tag{20}$$

is well justified in the second of eq 17 for studying the desorption of the long chains. Likewise, the first of eq 17 with $s_l = 1$ ($\sigma_l = \sigma_l^{(0)}$) should describe the initial adsorption of the invading short chains.

We now focus on the desorption of the long chains. Under our assumptions i and ii above, the equilibrium value of σ_s is much greater than $\sigma_l^{(0)}$; we expect $f_l^{(0)} \approx f_s^{(\mathrm{eq})}$ as described above. Solving eq 20 to leading order in the logarithmic terms gives

$$\sigma_s \approx \sigma_s^{(\mathrm{eq})} \approx \sigma_l^{(0)}(N_l/N_s)^{3/2} \times [1 + (f_l^{(0)})^{-1} \log ((c_s/c_l^{(0)})(N_s/N_l)^{3/2})]^{3/2} \tag{21}$$

We approximate the appearances of σ and σ_s in the second of eq 17 using eq 21.

The adsorption of short chains increases the adsorption barrier f_l for long chains; equivalently, the equilibrium coverage of long chains is markedly decreased even if the concentration c_l of long chains in solution is unchanged [$c_l = c_l^{(0)}$]. After the short chains have equilibrated but before many long chains have desorbed, using eqs 12 and 21 we have to leading order in logarithmic corrections

$$f_l \approx f_l^{(0)}[1 + (f_l^{(0)})^{-1} \log ((c_s/c_l^{(0)})(N_s/N_l)^{3/2}) + s_l^{2/3}] \tag{22}$$

Using this in eq 17, it is evident that the adsorbing current of long chains is negligible immediately after the short chains have adsorbed. This persists until a new equilibrium condition is approached; again using the adiabatic approximation eq 21, we have from the equilibrium condition eq 19

$$s_l \approx \frac{c_l}{c_s}\left(\frac{N_l}{N_s}\right)^{3/2} \exp[-f_l^{(0)} s_l^{2/3}] \tag{23}$$

For large adsorption energy and hence $f_l^{(0)} \gg 1$, we have

$$s_l \sim [f_l^{(0)}]^{-3/2}[\log (c_l/c_s) + {}^3/_2 \log (N_l/N_s)]^{3/2} \tag{24}$$

(Here we have assumed that the term in brackets is positive, i.e., $c_l/c_s > (N_s/N_l)^{3/2}$.) The final equilibrium long-chain coverage is reduced by a factor of roughly $[f_l^{(0)}]^{-3/2}$ by the introduction of short chains even if $c_l = c_l^{(0)}$.

After the short chains have reached the limited equilibrium with the initial coverage of long chains—when $s_l = 1$ and $s \approx s_s \approx (N_l/N_s)^{3/2}$—the second factor in the second of eq 17 is approximately $(N_l/N_s)^{1/2}$. This enhancement in the desorption rate of long chains arises from the increase

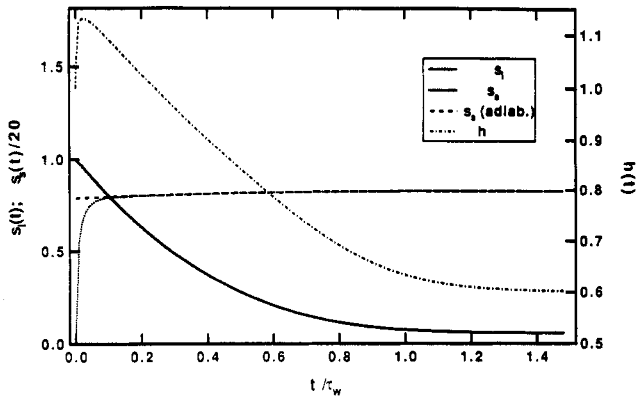

Figure 2. Results from the full equations of motion, eq 17, for s_l and s_s are compared to numerical integration of the adiabatic approximation, eqs 20 and 25, for parameter values $f_l^{(0)} = 8$, $N_l/N_s = 10$, $c_s = c_l^{(0)}$, and $c_l = 0.01c_l^{(0)}$.

in tension W'_l brought about by the presence of short chains. Using eq 21 the equation of motion for s_l becomes

$$\frac{ds_l}{dt} \approx \left\{\frac{c_l}{c_s}\left(\frac{N_l}{N_s}\right)^{3/2} \exp[-f_l^{(0)} s_l^{2/3}] - s_l\right\} \frac{(N_l/N_s)^{1/2} \exp[-f_l^{(0)}]}{[(N_s/N_l)^{1/2} + s_l^{1/3}]} \tag{25}$$

The approximations in eq 25 reflect both the adiabatic approximation eq 20 and the approximate solutions of eq 20 leading to eqs 21 and 22. One may make only the adiabatic approximation by solving numerically eq 20 for the adiabatic value of s_s and the second of eq 17 for the time dependence of s_l.

In Figure 2, results from the full equations of motion, eq 17, for s_l and s_s are compared to numerical integration of the adiabatic approximation, eqs 20 and 25, for parameter values $f_l^{(0)} = 8$, $N_l/N_s = 10$, $c_s = c_l^{(0)}$, and $c_l = 0.01c_l^{(0)}$. Except for the short-time behavior, the approximation is evidently quite good. Numerical results in Figures 3–7 were obtained within the adiabatic approximation.

Also displayed in Figure 2 is the time dependence of the total brush height $h(t)$. Notice that the brush height overshoots its initial value by a substantial amount before decreasing to the final equilibrium value. This happens because the rapid adsorption of short chains before many long chains have desorbed does increase somewhat the brush height (see eq 14).

The final brush height is of course given by eq 14 with the equilibrium coverages. If the long chains are removed from the solution and we use the rough approximation $f_{eq} \approx \Delta$ to describe the initial and final equilibria of long and short chains, respectively, then the final height $h(\infty)$ will be given by $h(\infty) \approx h(0)(N_s/N_l)^{1/2}$.[11]

The washing time in the presence of short chains is described by the off-current term only (or we may consider the case $c_l = 0$); if s_l is not yet as small as $(N_l/N_s)^{-3/2}$, we have

$$ds_l/dt \approx -s_l^{2/3} \exp[-f_l^{(0)}](N_l/N_s)^{1/2} \tag{26}$$

which has solution

$$s_l \approx (1 - t/\bar{\tau}_w)^3$$

$$\bar{\tau}_w = \frac{1}{3}\left(\frac{N_s}{N_l}\right)^{1/2} \exp[f_l^{(0)}] \tag{27}$$

This new "washing time" $\bar{\tau}_w$ is smaller than the single-species desorption result by a factor $(N_s/N_l)^{1/2}$.

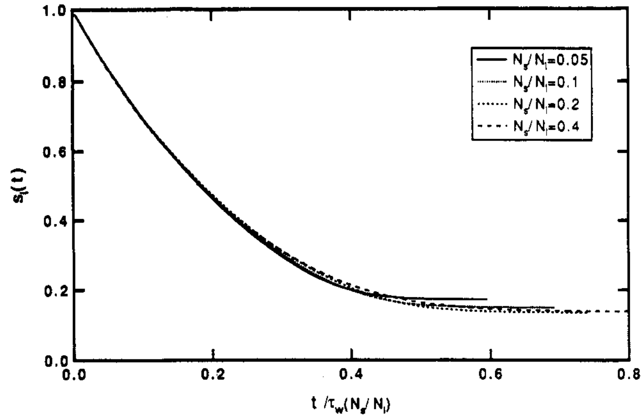

Figure 3. Dependence of $s_l(t)$ (with adiabatic approximation eq 25) on the ratio N_s/N_l. Here t is plotted in units of $\bar{\tau}_w$ for parameter values $c_s = c_l = c_l^{(0)}$, $f_l^{(0)} = 20$, and $N_s/N_l = 0.05, 0.1, 0.2$, and 0.4.

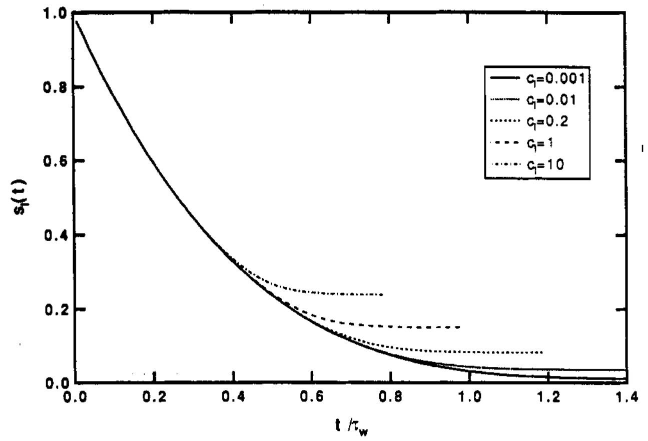

Figure 4. Dependence of $s_l(t)$ on the value of c_l, with t plotted in units of $\bar{\tau}_w$. Parameter values are as in Figure 3, $c_s = c_l^{(0)}$, $f_l^{(0)} = 20$, and $N_s/N_l = 0.1$; $c_l/c_l^{(0)}$ takes the values 0.001, 0.01, 0.1, 1, and 10.

We may well ask how small N_s may be taken with $\bar{\tau}_w$ still given by eq 25. First, we must have $W'_l h_s > 1$, which ensures that the increased tension acts over a distance such that $W(z)$ decreases by k_BT. If we combine eq 13 for h_s and eq 15 for W'_l with the equilibrium estimate eq 21 for σ_s, we find $W'_l h_s \sim f_l^{(0)}$, which is certainly larger than unity. Next, we must ensure that σ_s is not too large, so that our model of a solvated brush is valid. Again using the rough equilibrium estimate eq 21, we have $N_s\sigma_s^{2/3} \sim \Delta$; we want $\sigma_s \ll 1$ (in units of chains per microscopic length squared), so we must have $(N_s/\Delta)^{3/2} \gg 1$ (N_s in Kuhn steps, say, and Δ in units of k_BT). For $\Delta = 10$, our results may apply to short chains with $N_s > 50$ or so.

To test the dependence of the washing time $\bar{\tau}_w$ and the final equilibrium value of s_l on various parameters, eq 25 has been integrated numerically. Figure 3 shows the behavior of $s_l(t)$ with t given in units of $\bar{\tau}_w$ for parameter values $c_s = c_l = c_l^{(0)}$, $f_l^{(0)} = 20$, and the ratio $N_s/N_l = 0.05$, 0.1, 0.2, and 0.4. Evidently the characteristic decay time of $s_l(t)$ is well described by $\bar{\tau}_w(N_s/N_l)$ as given in eq 27.

Figure 4 shows the effect of varying c_l, for parameter values as above with $N_s/N_l = 0.1$; $c_l/c_l^{(0)}$ takes on the values 0.001, 0.01, 0.1, 1, and 10. The initial decay of $s_l(t)$ is clearly independent of c_l, but the final equilibrium value depends on c_l. In Figure 5, the final equilibrium value $s_l(\infty)^{2/3}$ is plotted against log (c_l); linear behavior consistent with eq 24 is obtained.

The dependence of $s_l(t)$ on c_s is shown in Figure 6 for parameter values as above, with $c_l/c_l^{(0)} = 1$ and $c_s/c_l^{(0)} = 0.001, 0.01, 0.2, 1$, and 10. The characteristic decay time

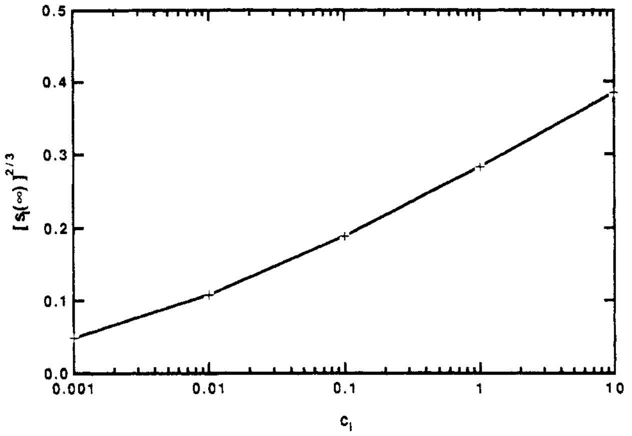

Figure 5. Final equilibrium value $s_l(\infty)^{2/3}$ from Figure 4 plotted against log (c_l); linear behavior consistent with eq 24 is obtained.

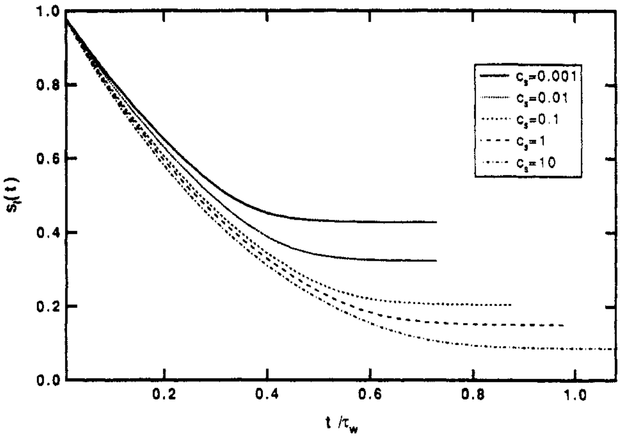

Figure 6. Dependence of $s_l(t)$ on c_s for parameter values $f_l^{(0)} = 20$, $N_s/N_l = 0.1$, and $c_l/c_l^{(0)} = 1$; $c_s/c_l^{(0)}$ takes the values 0.001, 0.01, 0.2, 1, and 10. The characteristic decay time depends very weakly on log (c_s) (neglected in the approximations leading to eq 27).

depends very weakly on log (c_s) (neglected in the approximations used above). The final equilibrium value $s_l(\infty)^{2/3}$ is displayed against log (c_s) in Figure 7; the linear decrease is consistent with eq 24.

If s_l becomes as small as $(N_l/N_s)^{-3/2}$, which occurs if $\Delta > N_l/N_s$ or c_l is small enough, then the factor representing $D_l W'_l$ becomes approximately N_l/N_s. At this point, the brush height is nearly that of the short-chain brush, and the diffusion constant of the exiting long chains is enhanced by a factor $(N_l/N_s)^{1/2}$. Then the equation describing the desorption of the long chains becomes

$$\mathrm{d}s_l/\mathrm{d}t \approx -\exp[-f_l^{(0)}](N_l/N_s) \qquad (28)$$

and the decay of s_l becomes exponential with a characteristic time $\tau_w = (N_s/N_l)\exp[f_l^{(0)}]$.

3. Stronger Adsorption and Discussion

We now turn our attention to another possible strategy for displacing the original brush, namely, replacing the original solution with or adding to it a solution of chains of the same length with a more strongly adsorbing end group. (This approach obviously will not lead to a shorter brush, though there may be other reasons for wanting to displace the original chains.)

In this case, the brush at any stage consists of chains with identical polymeric parts; hence the free energy per chain f for either type and the total brush height h are given by the monodisperse brush results, eq 1, with $\sigma = \sigma_s + \sigma_w$ (σ_s and σ_w are the coverages of the strongly and weakly adsorbing chains, with adsorption energies $\Delta_s > \Delta_w$, respectively).

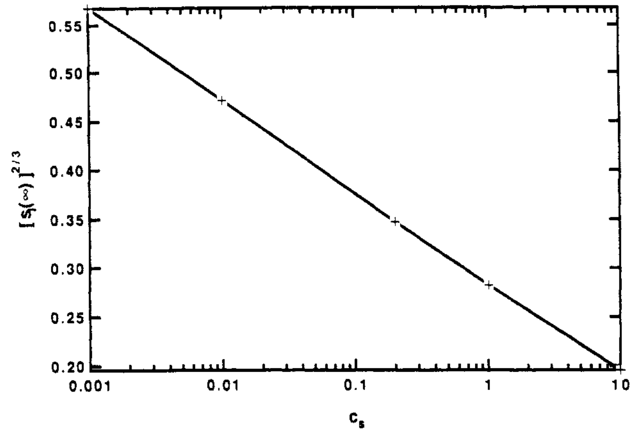

Figure 7. Final equilibrium value $s_l(\infty)^{2/3}$ from Figure 6 plotted against log (c_s); the linear decrease is consistent with eq 24.

The equations describing the adsorption equilibrium are the obvious generalizations of eq 2, namely

$$f - \Delta_\alpha + \log \sigma_\alpha = \log c_\alpha \qquad (29)$$

where now $\alpha \in \{s,w\}$.

Evidently, since $\Delta_s > \Delta_w$ we may expect $\sigma_s > \sigma_w$ in final equilibrium; strongly adsorbing chains will drive off weakly adsorbing chains in equilibrium even if the bulk concentrations c_s and c_w are comparable. In the extreme case $\Delta_s \gg \Delta_w$, we expect $f \approx c_f N \sigma_s^{2/3} \approx \Delta_s$, so that the equilibrium coverage of weakly-adsorbing chains is exponentially small, $\sigma_s \sim c_s \exp[-(\Delta_s - \Delta_w)]$.

Consider now the kinetic route to this final equilibrium. In contrast to the case of invading short chains, invading chains of the same length face exactly the same barrier to adsorption $\exp[-f]$ as the last weakly-adsorbing chains to arrive. Hence the characteristic time for the strongly-adsorbing chains to reach equilibrium with the existing brush is just the exchange time τ_{ex} of that brush.

Once they reach the surface, the strongly-adsorbing chains adsorb readily; the total coverage σ increases, and so does the barrier $\exp[-f]$ to adsorption of either species. The on-current $J_{on}{}^w$ of weakly-adsorbing chains becomes negligible when the barrier grows by a few $k_B T$, and the weak adsorbers start to come off. The current $J_{out}{}^w$ is still given by an equation like eq 16

$$J_{out}{}^w = \sigma_w \exp[-\Delta_w] D_w W'_w$$

The tension W' in the end of an adsorbed or just-desorbed chain of either type and the diffusion coefficient D for both types of chain with adsorbing end near to the surface are both given by the single-species results, eqs 3 and 4

$$W' = [2c_f]^{1/2} \sigma^{1/3}$$

$$D = T/(6\pi\eta h) \qquad (30)$$

Now note that, in contrast to the case of invading short chains, the drift velocity $v_{drift} = DW'$ is independent of σ—just as in the single-species kinetics of ref 2 summarized in section 1. The increased tension and the reduced diffusion constant due to the presence of more strongly adsorbing chains have canceling effects. The washing time τ_w for the weakly-adsorbing chains is unaffected by the invading strongly-adsorbing chains.[12]

In summary, we have considered two scenarios of competitive adsorption onto a surface from solution of strongly end-adsorbing polymer chains. We have neglected some possibly important complications, including micellization of the chains in solution, multiple adsorbing groups per chain, structure of the adsorbing group (e.g., an insoluble copolymer arm), and interaction of adsorbing groups themselves or competition for adsorption sites. With these simplifying assumptions, we have written kinetic equations for the surface coverage of two competing species of end-adsorbing chains in two illustrative cases: first, the invasion of an existing brush by shorter chains with the same adsorbing group, and second, the invasion of a brush by more strongly adsorbing chains of the same length.

In the case of shorter invading chains, the evolution of the surface coverages after the short chains are introduced may be described as follows. The short chains see a much smaller barrier to adsorption than the original long chains and thus adsorb readily, forming a bimodal brush in a time comparable to the growth time of a short-chain brush. The coverage of short chains then responds adiabatically to the long-chain coverage. The original long chains themselves desorb from the surface and do so at a rate which is $(N_l/N_s)^{1/2}$ times faster than the time for such a brush to desorb into clean solvent. The increased desorption rate is not due to a change in the activation barrier $\exp[-\Delta]$ for the end group to leave the surface. Rather, it results from an increase in the drift velocity of a just-desorbed chain, because the crowded short chains lead to higher tension in chains near the surface and hence a larger force driving the chains outward.

More strongly adsorbing invading chains do not accelerate the desorption of the original brush. In this case, the invading chains see the same barrier to adsorption as the original weakly adsorbing chains; the strong adsorbers begin to appear on the surface in a time comparable to the exchange time of the original brush. Furthermore, once some coverage of strongly-adsorbing chains is present, the desorption rate of weak adsorbers is not increased beyond its value for desorption into clean solvent. The effects of increased tension due to the crowding by the additional strongly-adsorbed chains is canceled by the increased drag on weak adsorbers as they drift out of the brush, so that the drift velocity of a weak adsorber exiting the brush is unchanged.

Acknowledgment. I thank Ludwik Leibler and Tom Witten for helpful conversations, Avi Halperin for lively discussions on the rate-limiting step in end-adsorbed polymer desorption, and Daniel Ou-Yang for stimulating this work with discussions of his experiments prior to publication.

Appendix

The potential $W(z)$ is the work required to pull the end group of a chain from outside the brush up to a distance z from the surface. In the process, work is done against the brush osmotic pressure and the "entropic springs" of the chain.

In the case of a monodisperse brush and a single adsorbing species, the form of $W(z)$ is easily obtained. The work $W(z)$ is the integral $\int_h^z \mathrm{d}z'\, F(z')$ over the displacement z' of the end group of the force $F(z')$ required to hold the end group at z'. This force $F(z')$ is equal and opposite to the tension in the chain at the end group. The tension at the nth monomer of a chain with adsorbing end at z' is $\mathrm{d}z/\mathrm{d}n(n;z')$; hence the total work may be written

$$W(z) = \int_z^h \mathrm{d}z' \frac{\mathrm{d}z}{\mathrm{d}n}(0;z') \qquad (31)$$

where $n = 0$ refers to the adsorbing end of the chain.

The conformation of the chain being pulled in when some $N' < N$ of the monomers have been pulled into the brush is identical to the conformation of the last N' monomers of the most-stretched chain in the brush (with its free end at $z = h$). The remaining $N - N'$ monomers of the chain being pulled in form a random unstretched coil beyond $z = h$; the tension is zero at and beyond the N'th monomer.

Using the methods developed in ref 13, we use the analogy between the chain conformation $z(n)$ in the self-consistent potential $w\phi(z)$ (w is an interaction parameter and $\phi(z)$ is the monomer density) and the Newtonian mechanics of a falling body in one dimension to compute $\mathrm{d}z/\mathrm{d}n(0;z')$.

The equation of motion $\mathrm{d}^2z(n)/\mathrm{d}n^2 = w\, \mathrm{d}\phi(z(n))/\mathrm{d}z$ implies a conservation of "energy"

$$E = {}^1/_2(\mathrm{d}z/\mathrm{d}n)^2 - w\phi(z) \qquad (32)$$

Together with the vanishing of the chain tension at the N'th monomer at $z = h$, where $\phi(h) = 0$, we have

$$\frac{1}{2}\left(\frac{\mathrm{d}z}{\mathrm{d}n}\right)^2 = w\phi(z) = \frac{f}{N}(1 - (z/h)^2) \qquad (33)$$

where the second equality is a basic result from ref 13.

So we have

$$W(z) = (2f/N)^{1/2}\int_z^h \mathrm{d}z'\,(1 - (z'/h)^2)^{1/2}$$

$$= \frac{2f}{\pi}[\cos^{-1}(z/h) - (z/h)(1 - (z/h)^2)^{1/2}] \qquad (34)$$

Here eq 1 for f and h has been used to simplify the prefactor. Note that $W(0) = f$, the work to introduce a new chain into the brush. The function $W(z)/f$ is displayed in Figure 1.

Now we consider the process of pulling a short chain into a bimodal brush. The short chain enters the brush in several stages. To determine the conformation adopted by the short chain, recall that the tension at its free end, or in any monomers beyond the brush edge, must vanish. We therefore seek among the conformations of chains in the brush to find fragments of conformations with a given number of monomers and no tension on the free end.

First, before the entire short chain has been pulled into the brush, the $N' < N_s$ monomers inside the brush have a conformation identical to the last N' monomers of the most-stretched long chain. Next, when the entire short chain has been pulled into the brush and its free end is at some $z < h$, the short chain has a conformation identical to the last N_s monomers of a long chain with free end at the same $z < h$. This situation persists as the adsorbing end of the short chain is pulled into the inner region $z < h_s$, where the only free ends present belong to adsorbed short chains.

When the free end of the short chain approaches $z = h_s$, the conformation is the last N_s monomers of the least-stretched long chain. The last $N_l - N_s$ monomers of this chain are unstretched and form a random coil just outside h_s; the first N_s monomers of this least-stretched long chain have the same conformation as the most-stretched short chain. As the adsorbing end of the invading chain is pulled the rest of the way to the surface, with N' monomers pulled inside h_s, its conformation is that of the $N_s - N'$th through the N'th monomer of the last-stretched long chain and a random coil of $N_s - N'$ monomers beyond h_s. When the adsorbing group reaches the surface, $N' \rightarrow N_s$, and the chain conformation is that of the first N_s monomers of the least-stretched long chain—which is exactly the same as the conformation of the most-stretched short chain.

From the discussion surrounding eq 7 in the main text, we see that only the chain conformation just at the point of adsorption/desorption is required to determine the "drift velocity" entering the expressions of eq 8 for the currents J_{in} and J_{out}. From the description just given of the adsorption process, we see that the relevant configurations are the most-stretched configurations, for chains of either species.

We recall that the drift velocity v is the product of the chain diffusion coefficient D (discussed in section 1) and the force on the end-group coordinate $\mathrm{d}W/\mathrm{d}z$, which is equal to the chain tension $\mathrm{d}z/\mathrm{d}n$ at the adsorbing end. The chain tension for the most-stretched long and short chains in a bimodal brush can be calculated from the conservation of "energy" analogous to eq 33. We need the value of $w\phi(z)$ only at $z = 0$, $z = h$, and $z = z_0$, where z_0 is the boundary of the inner region of the bimodal brush where the short-chain free ends reside.

At the brush edge $w\phi(h) = 0$, and using eqs 7–9 from ref 9, we easily obtain

$$\begin{aligned} w\phi(0) &= c_f\sigma^{2/3} \\ w\phi(z_0) &= c_f{\sigma_{\mathrm{l}}}^{2/3} \end{aligned} \qquad (35)$$

Then the tension at the adsorbing end for short and long chains just at the point of adsorption/desorption is

$$\begin{aligned} \mathrm{d}z/\mathrm{d}n &= [2(w\phi(0) - w\phi(z_0))]^{1/2}, \quad \text{short} \\ &= [2w\phi(0)]^{1/2}, \quad \text{long} \end{aligned} \qquad (36)$$

from which eq 15 follows immediately.

References and Notes

(1) For a recent review, see: Milner, S. T. *Science* **1991**, *251*, 905 and references therein.

(2) Ligoure, C.; Leibler, L. *J. Phys. (Paris)* **1990**, *51*, 1313.

(3) Ou-Yang, H. D., to be published.

(4) This potential $W(z)$ is *not* the parabolic potential felt by a monomer at a distance z from the surface (see Appendix).

(5) See: Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, 1986; Section 4.2.

(6) See: van Kampen, N. G. *Stochastic Processes in Physics and Chemistry*; North-Holland: Amsterdam, The Netherlands, 1987; Chapter VIII.

(7) Halperin, A. *Europhys. Lett.* **1989**, *8*, 351. Halperin, A. *Macromolecules* **1989**, *22*, 2403.

(8) de Gennes, P.-G. *Macromolecules* **1980**, *13*, 1069.

(9) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1989**, *22*, 853.

(10) Chakrabarti, A.; Toral, R. *Macromolecules* **1990**, *23*, 2016.

(11) If the aim in practice were to destabilize a colloidal suspension, N_s/N_l could be chosen small enough to make the resulting layer too short to stabilize the particles.

(12) Of course, as discussed in section 2, if the adsorbing groups repel each other on the surface, then the binding energy is effectively lowered, and the washing time will be reduced.

(13) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610.