

The Detachment of a Polymer Chain from a Weakly Adsorbing Surface Using an AFM Tip

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Received August 26, 1998. In Final Form: March 11, 1999

Atomic force microscopy has been used to investigate the detachment of single polymer chains from surfaces and to measure the picoNewton forces required to extend the chain orthogonal to the surface. Such recent experiments show that the force–extension profiles provide interesting signatures which might be related to the progressive detachment of the chain from a surface. Using equilibrium scaling analysis, activation kinetics, and exactly solvable partition functions we predict force versus extension profiles for various extension rates. We also show how variation in the extension rate can distinguish heterogeneous monomer–surface contacts. The qualitative features that we predict, such as sawtooth force profiles with detachment forces which decrease with extension, maximal yielding forces at high extension rates, and featureless force profiles at large extension, are also seen in experiment.

I. Introduction

The statics and dynamics of single polymer chains at surfaces have received considerable attention in recent years. Much of this has been spurred by new experimental techniques such as atomic force microscopy (AFM)^{1–4} and optical/magnetic tweezers⁵ which allow one to manipulate single polymer chains. Some of these studies measure the force required to detach a chain from an adsorbing surface, and, in many of these, the force versus extension profile exhibits sharp discontinuities which have been interpreted in terms of unadsorbed loops of the chain. A number of different single-chain systems have been studied: methylated dextran,⁴ end-adsorbed polystyrene,² poly(dimethylsiloxane) (PDMS),^{1,6} a polyacrylamide copolymer chain,³ and a telechelic poly(ethylene oxide) (PEO) having chemically modified chain ends.⁷ Scaling analysis and self-consistent field theory have been used to explain the force profile for pull-off of polyelectrolyte chains;^{3,8} however, these theoretical treatments focused on large extensions and did not detail the features of loop detachment at shorter extensions, nor did these studies investigate the effect of different rates of extension.

In this paper we predict force–extension profiles for pulling an isolated polymer from a weakly adsorbing surface with different rates of pulling or extension. Our theoretical predictions are made using the simplest model: an ideal or Gaussian chain of N statistical monomers of size a where a fraction of the monomers is pinned to the uniformly adsorbing surface with a contact energy $\epsilon k_B T$. These monomer–surface contacts separate

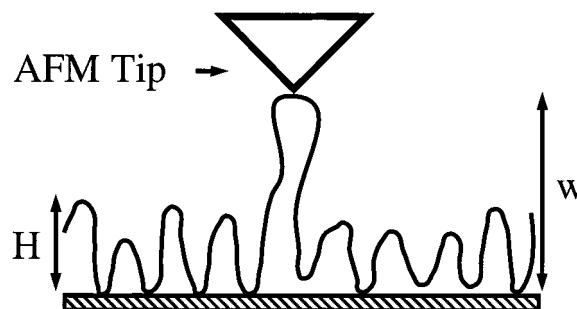


Figure 1. Schematic illustration of the “grabbing” and pulling of a loop, referred to as a pulled tether, of a weakly adsorbed chain on a surface. The pulled tether is elevated a distance $w > H$ above the adsorbing surface where H is the equilibrium height of the adsorbed layer. We consider cases where the pulling rate is very different from the rate of disassociation/association of the surface–monomer contacts.

the adsorbed chain into a series of loops and tails. We consider “grabbing” a loop or tail and extending this pulled tether a distance w orthogonal to the adsorbing surface as shown in Figure 1, while simultaneously measuring the force needed to extend the pulled tether.

In order to rip the chain from the surface, a sequence of surface-pinned monomers must be detached from the surface. Let’s first focus upon a single monomer–surface contact and consider the pulled tether as simply a “handle” by which we apply a tension to this surface-bound monomer. An energy path of detachment is $U(z)$ where U is a particular monomer–surface potential energy and z is a distance between monomer and surface. Without specifying an exact form of this potential, we can make general statements using features of the potential such as barrier height, Δ_0 , barrier width, δ_0 , and well depth, ϵ .⁹ First, a surface-bound monomer corresponds to residence in the well or minimum of the potential energy. For

(9) We have not included potential-dependent results in this paper as our aims are to point out generalized predictions that may be seen experimentally on a number of systems. However, one can simply follow the generalized treatment, extending to higher orders in force if needed, by adopting a specific surface–monomer potential energy function, $U(z)$. Alternatively, one might adopt a simple generalized form, for example, a simple cubic potential of the form $U(z) = A(z - z_0)^3 + B(z - z_0)^2$ with $A < 0$ and $B > 0$.

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detachment to occur, the system must overcome the potential barrier, Δ_0 , and it does so at a rate $\omega_0 = \omega \exp(-\Delta_0/k_B T)$ where ω is a characteristic frequency. Second, an applied tension, f , on the surface-bound monomer will alter the energy pathway according to $U(z) - fz$, effectively lowering the barrier from Δ_0 to Δ and facilitating detachment of the monomer from the surface. The tension on the surface-bound monomer is the tension of the pulled tether of n statistical monomers and is measured as the force on the AFM cantilever displaced a distance w from the surface.

In an AFM experiment, we control the rate of extension of the tether, \dot{w} , measured in units of statistical monomer size, a . Thus, we are applying an increasing tension to the surface-bound monomer according to the prevailing force law of the pulled tether. We characterize the rate of extension according to the activation kinetics of detachment. A very fast rate of extension is one where the surface-bound monomer has insufficient time to escape the barrier to detachment, even though the barrier is being continually tension-reduced. In this limit, detachment occurs instantaneously at a large extensional force which reduces the barrier to zero. This yielding force, f_{yield} , is the maximum force sustainable to the monomer–surface contact, and no detachment force can exceed this value. On the other hand, a very slow extension provides ample time for the surface-bound monomer to escape the contact without appreciable tension reduction of the barrier. We show that in these two limits the force profiles (i.e., force versus extension curves) are dramatically different. Fast extensions provide a saw-tooth pattern which details each monomer–surface detachment, while the slow extension provides a flat force profile and provides no signature of the detachments. Intermediate extension rates, where detachment occurs with escape over a tension-reduced barrier, provide an interesting combination of these two patterns: a saw-tooth force profile at short extension which diminishes into a characterless force at larger extensions. Our predicted force profiles recover the features of AFM profiles found from different single chain systems.

Our description is organized in the following manner. In the next section we use scaling analysis to describe an equilibrium adsorbed chain and the force required to pull the chain slowly from the surface. In section III, we consider extension rates which are sufficiently fast that we can probe individual detachments of monomer from the surface, but slow enough that these detachments are activated events, i.e., they proceed with a nonzero, tension-reduced activation barrier. We construct profiles for chains which are homogeneously pinned to the surface, as well as chains which are pinned to the surface with different energies and characterized by the relative rates of monomer–surface detachment and tether pulling. In section IV, we briefly describe the rate-independent force profiles for very fast extension where the detachment is an instantaneous yielding process, rather than an activation process. In conclusion, we summarize and propose extensions to both theoretical and experimental work.

II. Slow Extension of a Weakly Adsorbed Chain

The unadsorbed monomers form a series of loops and tails, or an adsorbing layer, of height H . This equilibrium height can be determined from scaling analysis and the chain's free energy,¹⁰

$$F \cong k_B T \frac{Na^2}{H^2} - \epsilon k_B T N \frac{a}{H} \quad (1)$$

The first term is the energy penalty associated with the reduction in conformational entropy upon confinement of the chain from solution, where it is of size $R_g \sim aN^{1/2}$, to an adsorbed layer of average height H . The second term represents the favorable contact energy resulting from Na/H monomer–surface contacts. The equilibrium height of the adsorbed ideal chain is that which minimizes the chain energy and is $H \cong 2(a/\epsilon)$ and is independent of (large) chain length. As the surface energy decreases, there are fewer monomer–surface contacts, larger loops and trains, and the adsorbed height increases. A lower limit of attractive surface energy for chain adsorption requires that $H < R_g \sim aN^{1/2}$, or $\epsilon > N^{-1/2}$.

When the extension of a pulled tether occurs at a sufficiently slow rate such that the monomer–surface contacts can detach and reform many times over the time scale of the pulling experiment, the force measured provides only averaged information about the strength of the surface–monomer contacts and not about the detachment process itself. In terms of each monomer–surface contact, the rate of application of tension is so slow that the monomer is able to escape the natural barrier, Δ_0 , without the aid of the barrier-reducing tension. In this case, contacts can be lost and reformed many times over an incremental increase in extension or applied force, and the chain/surface can be described wholly in equilibrium terms using scaling analysis. The free energy (in units of $k_B T$) of an adsorbed chain with a tether of n monomers, extended a distance w from the adsorbing surface is

$$F(n) \cong \frac{(N-n)a^2}{H^2} - \epsilon(N-n)\left(\frac{a}{H}\right) + \frac{w^2}{na^2} \quad (2)$$

where the last term is the stretching penalty associated with extending a Gaussian loop of n monomers to distance w where the height of the adsorbed train is independent of the pulled loop and remains $H \sim 2a/\epsilon$. The rapid reformation of monomer–surface contacts effectively exchanges monomers across contact or adsorption points, and the number of monomers in the extended loop, n , may increase to reduce the stretching penalty of the extended loop. Minimization of the energy yields $F \cong \epsilon(w/a) - N\epsilon^2/4$ and an extensional force, $f_{\text{slow}} = \partial F/\partial w \sim \epsilon k_B T/a$, which is constant throughout the slow pulling process. Thus, for very slow extension of the tether, the force will be constant, much like pulling a chain through a viscous medium, and will not signature the loss of individual monomer–surface contacts.

III. Intermediate Extension Rates of a Weakly Adsorbed Chain

At higher rates of extension, the system does not have ample time to trespass over the full detachment barrier. Detachment occurs as an “escape” over a tension-reduced barrier of height $\Delta(f)$, expressed generally to first order in tension as

$$\Delta(f) \approx \Delta_0 - \delta_0 f + O(f^2) \quad (3)$$

Each monomer detachment is a stochastic event that occurs after an averaged time, t , determined from

$$1 = \int_0^t dt \omega_0 \exp\left(\frac{\delta_0 f(t)}{k_B T}\right) \quad (4)$$

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For a Gaussian tether of n monomers, the force varies with extension, w , according to a simple linear force law, $f/k_B T = w/(na^2)$. The average extension at which the monomer–surface contact is lost is

$$\left(\frac{w}{a}\right)^{\text{det}} = n \left(\frac{a}{\delta_0}\right) \ln \left[\frac{w/a}{\omega_0} \frac{1}{n} \left(\frac{\delta_0}{a}\right) + 1 \right] \quad (5)$$

and the average detachment force is

$$\frac{f^{\text{det}}}{k_B T} = \left(\frac{1}{\delta_0}\right) \ln \left[\frac{w/a}{\omega_0} \frac{1}{n} \left(\frac{\delta_0}{a}\right) + 1 \right] \quad (6)$$

Upon detachment, the m monomers in the loop adjacent to the contact are added to the n monomers in the pulled tether and the force discontinuously decreases to

$$\frac{f}{k_B T} = \frac{(w/a)^{\text{det}}}{(m+n)a} \quad (7)$$

These expressions are valid for detachment forces between the equilibrium force needed to slowly detach the chain and the maximum force at which the barrier to detachment completely disappears, i.e., $f_{\text{slow}} < f^{\text{det}} < f_{\text{yield}}$.

A. Multiple Detachments from a Homogeneous Surface. We can generalize this description to the pulling-off of a chain adsorbed with multiple monomer–surface contacts. For simplicity, we assume that the chain is initially adsorbed onto the surface with contact points evenly spaced along the chain contour providing loops of fixed number of monomers n . We can assume n is simply the average loop size of the adsorbed chain: The average number of monomers per loop of an adsorbed chain of N monomers with Nal/H surface contacts is $n = H/a \cong 2/\epsilon$. Let k be an index which advances by one with each surface–monomer contact which is lost. Initially, $k = 1$, and the extension and force at the first detachment is given by eqs 5 and 6. For subsequent detachments, $k \geq 2$, the extension, $(w/a)_k^{\text{det}}$, is found from eq 4 and $w/a = (w/a)_{k-1}^{\text{det}} + wt/a$ to be

$$\left(\frac{w}{a}\right)_k^{\text{det}} = kn \left(\frac{a}{\delta_0}\right) \ln \left[\frac{y}{kna} + a_{k-1} \right] \quad (8)$$

with

$$a_k = \left(\frac{y}{kna} + a_{k-1}\right)^{k/k+1} \quad (9)$$

and $a_0 = 1$. We have introduced in the above equation the dimensionless parameter $y \equiv [(\dot{w}/a)/\omega_0](\delta_0/a)$. The ratio of barrier width to monomer size, (δ_0/a) , is constant and of order unity; consequently, y is the rate of extension relative to that of the detachment kinetics. Values of y range from zero, indicative of very slow pulling, to large positive numbers which indicate fast extension rates. Using eqs 8 and 9 and the assumption of Gaussian chains, we find the detachment force from

$$\frac{f_k^{\text{det}}}{k_B T} = \frac{(w/a)_k}{kna} \quad (10)$$

After detachment, this force is reduced discontinuously by a factor of $k/(k+1)$. Again, these expressions are valid for pulling forces between f_{slow} and f_{yield} . These correspond

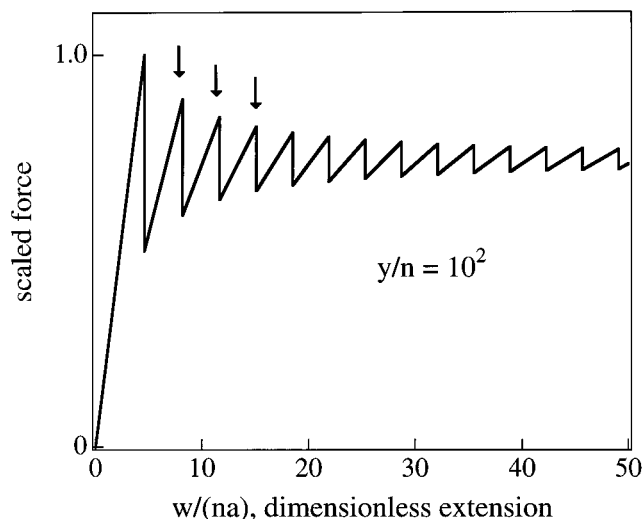


Figure 2. Scaled force, $f/f_{k=1}^{\text{det}}$, versus dimensionless extension, $w/(na)$, for the detachment of an adsorbed chain with equisized loops of n monomers with dimensionless pulling rate of $y/n = 100$. The discontinuities in the profile correspond to detachment of individual contact points which separate the pulled tether from an adjacent loop, and the maximum forces in each saw-tooth correspond to the detachment force, f_k^{det} . These contact points are lost or sacrificed according to an activated process with a tension-reduced barrier. The force required for detachment decreases with loss of successive contact points; i.e., pulling becomes easier with the removal of each contact point. Between the detachment of contact points, the force is linear with extension reflecting the Gaussian approximation. The slope or spring constant, $d f/d w$, is inversely proportional to the number of monomers in the pulled tether, and this diminishes with loss of successive contact points.

to bounds on the dimensionless pulling rates of $\exp(\epsilon/k_B T) - 1 < y/n < \exp(\Delta_0/k_B T)$.

Figure 2 is the predicted force profile constructed from eqs 8–10 for the pull-off of a chain of equisized loops where the rate of pulling is $y/n = 100$ and $\delta_0/a \equiv 1$. It is important to recognize that this profile is constructed from a sequence of detachment events, each detachment being described in terms of its average or expected lifetime. An experimental force profile, in contrast, is comprised of stochastic detachment events: as such it would retain the discontinuous forces, but the magnitude of both force and extension at detachment will vary from the averaged values of our predictions. Figure 2 shows that the average detachment force decreases with successive loss of monomer–surface contacts, or $f_k^{\text{det}} > f_{k+1}^{\text{det}}$. This general decrease in consecutive detachment forces becomes more pronounced at higher pulling speeds. The spring constant, or slope ($d f/d w$) between detachments, diminishes discontinuously with the loss of adjacent contacts because of the increase in the number of monomers in the pulled tether. This decrease in spring constant is most dramatic with the loss of the first few surface contacts with the force attaining a constant value plateau at large extension of the pulled tether. Clearly, our simplistic assumption of a Gaussian pulled tether can be replaced by an inextensible Langevin tether, or other nonlinear spring model. This would result in replacement of the linear force profiles between detachment points with a pulling force which grows more strongly with extension and an increase in the detachment force, according to eq 4. Irrespective of the particular model, the tether becomes increasingly compliant with the increase in the number of monomers in the tether that occurs with each lost contact and the detachment force is discontinuous. Our predictions, constructed from averaged detachment events and pulled

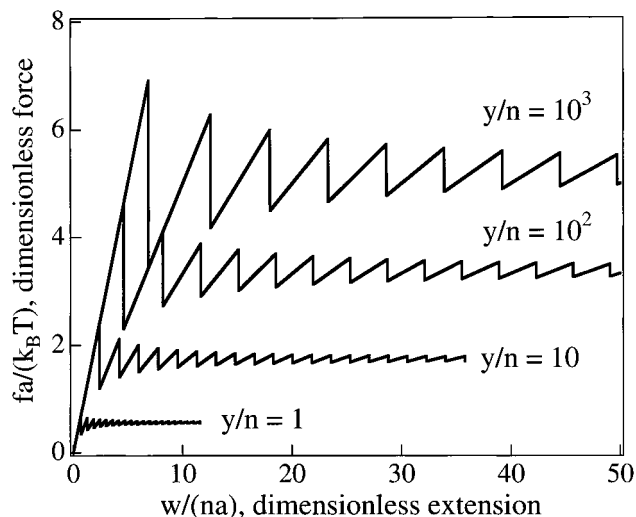


Figure 3. Dimensionless force, $fa/(k_B T)$, versus dimensionless extension, $w/(na)$, for the detachment of an adsorbed chain with equisized loops of n monomers with dimensionless pulling rates $y/n = 1, 10, 10^2, 10^3$. Note that as the pulling rate increases, the force increases and larger extensions are required to detach each monomer–surface contact. Moreover, with larger pulling rates, the consecutive detachment forces decrease with each contact lost. The pulling rates are not sufficiently large that tension on the contact reaches the yielding force, f_{yield} .

tethers which are Gaussian, nevertheless capture features of experimentally obtained force profiles. Senden et al.¹ observed experimentally similar force profiles for a PDMS chain adsorbed to a silica surface, as did Rief et al.⁴ using methylated dextran adsorbed to a chemically modified gold surface. They found that the spring constant decreases with consecutive discontinuities and that the maximum forces in the saw-tooth profiles diminish with extension, ending in a force which is constant over larger extension.

Figure 3 shows the effect of extension rate upon the average force profile for a chain of equisized loops. With increased rate of extension, the detachment forces increase from $f_{\text{slow}} = \epsilon k_B T/a$, the equilibrium value, to f_{yield} , which we have arbitrarily chosen to be larger than the forces at these extension rates. Moreover, each k th detachment occurs at larger extensions when the rate of pulling is increased.

Some experiments show that the detachment forces may sometimes increase with extension rather than decrease^{1,2} as shown in our predictions of equisized loops. In some instances both decreases and increases in the detachment forces have been observed.^{7,11} This could be attributed to the stochastic nature of the detachment event or to the likelihood of loops with different sizes. Experimentally, it would be difficult to distinguish whether the size and breadth of a “tooth” is attributable to loop size or to the stochastic nature of the detachment. We can envision an experiment where the adsorbed chain is comprised of surface “sticky” monomers at known intervals. In this case, an ensemble of AFM force profiles for the ripping-off of the chain might be used to discriminate loop size in the stochastic, irreversible process. On the computational side, one might construct a stochastic simulation that mimics the stochastic barrier escape to detachment. In this work, we are limited to predicting individual detachment events as averaged events. However, we can show that our description, cast for loops of different sizes, predicts discontinuous forces at detachments and that these

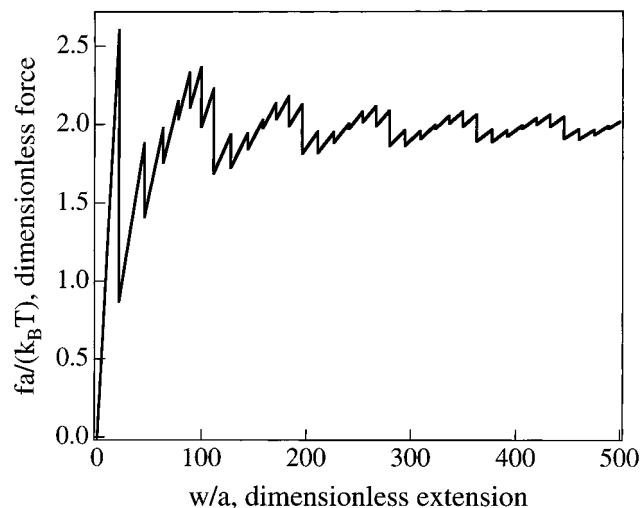


Figure 4. Dimensionless force, $fa/(k_B T)$, versus dimensionless extension, w/a , for the detachment of a chain having unequal loop sizes with a dimensionless pulling rate of $y=100$. We have ordered the loop sizes in the following way. The first loop has 2 monomers and each consecutive loop size is double that of the previous loop until the loop size is 32. Loops following an $n = 32$ loop are $1/2$ the size of the previous loop until the loop size reaches 2. The loop sizes thus both increase and decrease according to $m(k) = rm(k-1)$ where $m(k)$ is the number of monomers in the k th loop and $r = 2$ and $1/2$. As a result of this geometric series of loop sizes, the detachment forces of consecutive monomer–surface contacts both increase and decrease in accord with the size of the tether, $\sum_{k=1}^K m(k)$, relative to the adjacent loop, $m(K+1)$. Detail in the force profile is more apparent at small extensions when the spring constant, d^2w/dx^2 , and detachment forces are large. However, at larger extension, both spring constant and detachment force diminish and may become indiscernible from experimental noise.

detachment forces both increase and decrease with successive detachments, Figure 4.

B. Multiple Detachment from a Heterogeneous Surface. An obvious extension is to consider chains having a distribution of surface–monomer contacts with differing energy pathways to detachment. These different contacts can be categorized by the rate at which these contacts are lost under tension. At any given extension rate, y , the monomer–surface contacts can be separated into two categories: *weak* contacts which disassociate and reform many times within the time scale of the pulling and *strong* contacts which are “static” during the pulling and which disassociate via a tension-reduced activation barrier. Strong surface–monomer contacts define the loops and, as shown above, loss of these strong surface–monomer contacts results in discontinuities in the force–extension profiles. The effect of weak, labile contacts is to alter the force profile between discontinuities which mark the loss of strong contacts.

We can predict the force profile between discontinuous detachment forces from the exact solution to the partition function of an ideal tether¹² of m monomers with one end fixed on the surface (strong contact) and with the opposite end located at w and on the AFM tip. The analytic method which we use has been applied to different problems and is explained in detail in various texts. Here we provide briefly the governing equation and appropriate boundary/initial conditions for the propagator of an ideal chain which provides analytic solutions to the force profiles. We apply this method in two situations: (1) where the surface–monomer attraction is a contact potential at the grafting

(11) Haupt, B. J.; Senden, T. J., unpublished work.

(12) de Gennes, P. G. *Rep. Prog. Phys.* **1969**, *32*, 187.

plane, and (2) where the contact potential is also operative at the AFM tip, allowing for weak adsorption onto both grafting and pulling surfaces.

Consider a pulled tether chain of m monomers with ends fixed at \mathbf{r} and \mathbf{r}' and denote the normalized weighting function of such a chain by $G_m(\mathbf{r}, \mathbf{r}')$. If m is sufficiently large and if G_m varies slowly on the atomic scale, then G_m will satisfy

$$\frac{\partial G_m(\mathbf{r}, \mathbf{r}')}{\partial m} - \frac{a^2}{6} \nabla_{\mathbf{r}}^2 G_m(\mathbf{r}, \mathbf{r}') = 0 \quad (11)$$

together with an initial boundary condition $G_0(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$, indicating that a tether of zero size must begin and end at the same location. The potential at the adsorbing surface is attractive and short-ranged, of the order of a monomer size a , and gives rise to another boundary condition

$$\hat{\mathbf{n}} \cdot \nabla G_m \Big|_{\text{surface}} = -\frac{1}{D} \quad (12)$$

where $\hat{\mathbf{n}}$ is the outward normal from the adsorbing surface, and D is an adsorption length.¹² Here $D > 0$ corresponds to adsorption, and the strength of the adsorption increases as D approaches 0. This boundary condition corresponds to the prescription of an attractive force $k_B T/D$ that the surface exerts on the contacting monomers. From a solution of eq 11 and boundary conditions, an expression for G_m results, which can then be used to determine the force, $-f$, required to maintain the pulled tether at a distance $r = w$ from the surface:

$$-f(w)/k_B T = \frac{1}{G_N(w)} \frac{\partial G_N(w)}{\partial w} \quad (13)$$

In the first case we consider an ideal tether, doubly end tethered to the grafting surface (at $\mathbf{r} = 0$) and to the pulling surface or AFM tip (at $\mathbf{r}' = w\mathbf{e}_z$), where monomer-surface contacts can form on the grafting surface only and loops are not formed on the AFM tip. The result for G can be written in the form:¹³⁻¹⁵

$$G(w) = \frac{1}{\sqrt{\pi} R_g} \exp\left(-\frac{w^2}{4R_g^2}\right) \left(1 + \sqrt{\pi} \frac{R_g}{D} Y\left(\frac{w}{2R_g} - \frac{R_g}{D}\right)\right) \quad (14)$$

where $R_g^2 = a^2 m/6$ is the radius of gyration of the Gaussian tether in bulk solution, $Y(x) = \exp(x^2) \text{erfc}(x)$, and $\text{erfc}(x)$ is the complementary error function. The force, $-f$, exerted by the chain on the two surfaces is then given by

$$\frac{-f}{k_B T} = \frac{1}{D} + \frac{w}{2R_g^2 \left(1 + \sqrt{\pi} \frac{R_g}{D} Y\left(\frac{w}{2R_g} - \frac{R_g}{D}\right)\right)} \quad (15)$$

For small separations, the force is $f(k_B T) \sim 1/D$; i.e., the same force required to pull a long untethered chain adsorbed to the surface. When $w \gg R_g^2/D$, then the force is $f(k_B T) \sim w/(2R_g^2)$ and the springlike behavior of a nonadsorbing tether is recovered. Figure 5 shows the crossover between the constant force and the spring force for two values of the adsorption strength.

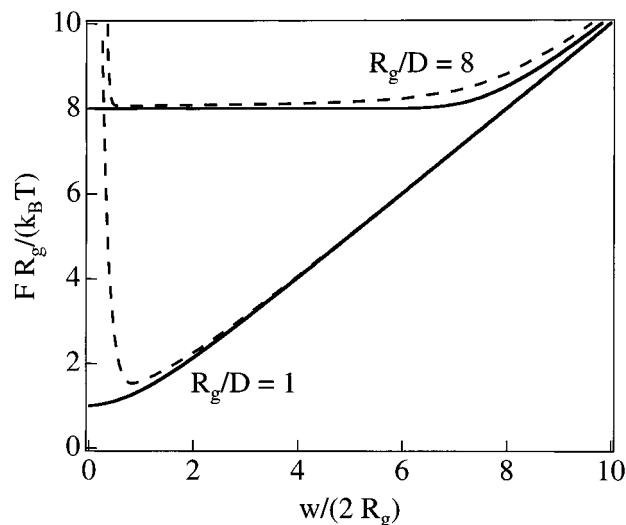


Figure 5. Dimensionless force, $fR_g/k_B T$ vs dimensionless extension, $w/(2R_g)$ where $R_g = a\sqrt{N}/\sqrt{6}$, predicted from solution of exact partition function for an ideal doubly end tethered chain which (1) adsorbs weakly onto the grafting surface (bold lines), and (2) adsorbs weakly onto both grafting and AFM surfaces (dashed lines). The strength of the adsorption energy is characterized by R_g/D , set to $R_g/D = 1$ and to $R_g/D = 8$ (a stronger interaction). Note that at large extension, the pulling force is similar to that of an ideal, noninteracting chain. However, at smaller extensions, $w \approx D$, the weak interactions result in a force which is almost constant and independent of extension, but larger than that found for nonadsorbing surfaces.

The above calculation does not consider monomer adsorption and loop formation on the pulling surface or AFM tip even though one end of the chain is effectively tethered to the AFM tip. Such a situation may be realizable in AFM experiments with special telechelic chains or ABC triblocks where A and C are short blocks which strongly adsorb onto the surface and tip, respectively, and B adsorbs weakly onto the grafting surface only. However, without such selectively synthesized chains, it is more likely that adsorption also occurs on the AFM tip surface as well. If the adsorbing boundary condition of the form of eq 12 is applied at both $z = 0$ and $z = w$, then we can construct profiles for a telechelic chain which weakly adsorbs onto both surface and tip. The analytic results are given in the appendix and are included in Figure 5. A comparison between the case of single and double adsorbing surfaces shows that the for doubly adsorbing surfaces (grafting surface + AFM tip) larger forces are required to increase the small separation between grafting and AFM tip surfaces. The only qualitatively new feature is the enhanced attraction between the surfaces at short range ($w \sim D$) due to additional bridging by the chain. Clearly, there is some artificiality in the ideal chain result, because the presence of excluded volume effects in real systems limits the depth of the attraction.¹⁶ At large separations, $w \gg R_g^2/D$, there is no difference in the separation forces of single and double adsorbing surfaces, because the chain is sufficiently stretched that the effect of both adsorbing surfaces can be neglected.

Such a system is envisaged in an ABABAB multiblock polymer having A blocks which may form strong surface-monomer contacts and B blocks which are limited to form loops of monomer which only weakly adsorb into surfaces. For sufficiently slow pulling rates, we could consider each B loop to be a weakly adsorbing end-tethered chain whose

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(16) Ingersent, K.; Klein, J.; Pincus, P. *Macromolecules* **1990**, *23*, 548.

force–extension profile is characterized by Figure 5, but where loss of A block–surface contacts provides the discontinuous saw-tooth profiles of the previous section. The pulled loop is discontinuously fed an AB block and further extension of the new BAB loop once again follows the force profile for a weakly adsorbing, but bigger, end-tethered chain.

IV. Fast Extension of an Adsorbed Chain

Consider now pulling rates that are very large such that the tension applied to the monomer–surface contact reduces the barrier height, Δ , to zero. This force is called the yielding force and, from eq 3, is $f_{\text{yield}} \approx \Delta_0/\delta_0$. At this tension, detachment is no longer an activated event and occurs instantaneously at f_{yield} which is determined by the exact monomer–surface potential. No force greater than f_{yield} can be maintained by an individual monomer–surface contact.

For a homogeneously adsorbed chain of equisized loops of n monomers, fast extension will lead to detachments where the first K detachments occur as barrierless, instantaneous events at force f_{yield} . The $k > K$ detachments occur with a tension-reduced activation barrier. As the rate of extension is increased, K increases, until all contacts are lost instantaneously at f_{yield} . These $k \leq K$ barrierless detachments are still marked by discontinuities in the force profile. The barrierless detachments occur at extension

$$\left(\frac{w}{a}\right)_{k \leq K}^{\text{det}} = kna \left(\frac{f_{\text{yield}}}{k_B T}\right) \quad (16)$$

and successive, activated detachments ($k > K$) at

$$\left(\frac{w}{a}\right)_k^{\text{det}} = kn \left(\frac{a}{\delta_0}\right) \ln \left[\frac{y}{kn} + \exp \left[\frac{\delta_0}{a} \frac{1}{kn} \left(\frac{w}{a}\right)_{k-1}^{\text{det}} \right] \right] \quad (17)$$

with $f_{k > K}^{\text{det}} < f_{\text{yield}}$ and given by the force law, eq 10. As the extension rate is increased further, detachments of higher order, i.e., larger K , along with the earlier detachments $k < K$, will occur instantaneously at $f_{k \leq K}^{\text{det}} = f_{\text{yield}}$. Thus, with fast extension, the force profile is independent of extension rate at low extensions. As the extension rate increases, this range of rate-independent extension grows, as shown in Figure 6.

V. Conclusion

Using a simple ideal chain model, we have used scaling analysis, activation kinetics, and exactly solvable partition functions to predict force profiles for the detachment of chains from adsorbing surfaces by pulling a loose tether from the surface. Although we do not include detail such as finite extensibility or monomer–monomer interactions, we are able to reconstruct much of the character of experimental AFM force–profiles. Our analysis considers cases where the time scale of equilibration of the monomer–surface contacts is both shorter and longer than the time scale of the pulling experiment and where surfaces provide either homogeneous or heterogeneous contacts. When the extension rate is slow, the monomer–surface contact has ample time to exchange monomers between the pulled tether and adjacent loop and the force is constant as the chain is being ripped slowly from the surface. However, if the extension rate is made faster and commensurate with the kinetic rate of detachment, then the magnitude of the pulling force details individual

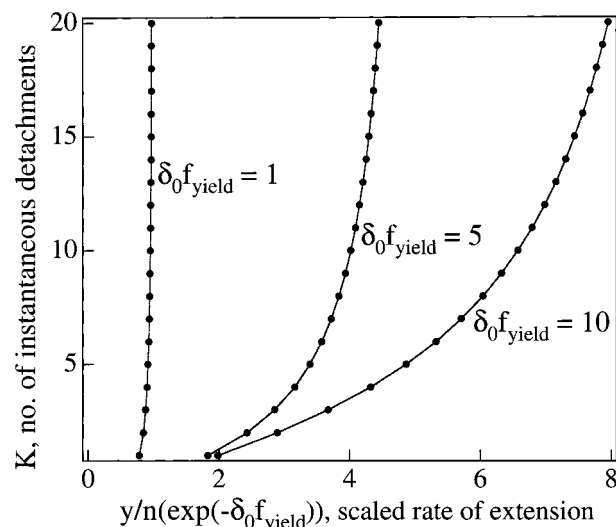


Figure 6. The number of instantaneous detachments, K , versus the scaled extension rate, $y/n \exp(-\delta_0 f_{\text{yield}})$, for surfaces with yielding forces $\delta_0 f_{\text{yield}} = 1, 5, \text{ and } 10$. At any given extension rate and yielding force, the first K detachments occur instantaneously at an applied force equal to f_{yield} , while subsequent detachments occur as activated events with detachment forces less than f_{yield} . For any given surface, as the extension rate is increased, a larger number of detachments occur instantaneously at f_{yield} .

detachments of monomers from the surface. We have shown that the force profile will be discontinuous, marking an individual detachment and that, on average, the magnitude of the detachment force decreases with successive detachments. As the extension rate is increased, the magnitude of the detachment force increases and larger extensions are required for detachment. At very large extension rates, the applied force is sufficiently large to reduce the barrier to detachment to zero and the detachment occurs instantaneously at a yielding force, f_{yield} , which characterizes the monomer–surface contact. At these large extension rates, the force profile is saw-tooth shaped with detachment forces that are equal for successive detachment events and independent of extension rate. We have also shown that a heterogeneous surface with different monomer–surface contact energies will still display discontinuous force profiles: strong contacts will give rise to the discontinuous detachment forces while the dissociation/reassociation of weaker contacts will alter the force–extension curve between these discontinuous detachments. Moreover, by increasing the extension rate so that it is comparable with the kinetics of weak contact detachment, we may also probe discontinuous detachment events of both weak and strong contacts.

Our results suggest additional experiments where the extension rate of the chain, or probe tip velocity, is varied and the chain is comprised of surface “sticky” monomers spaced at known intervals along the chain backbone, or the adsorbing surface is atomistically patterned. Stochastic simulations are required to construct predictions which are comparable with individual AFM force profiles. Detail such as monomer–monomer interactions, solvency, and inextensibility would be appropriately included in these stochastic simulations. However, in this paper, our predictions are limited to average detachment events; that is, we construct force profiles as a sequence of detachment events whose lifetime is averaged. Despite our simplistic assumption of Gaussian chains, we are able to predict general trends seen in AFM experiments.

Acknowledgment. The authors thank Dr. Tim Senden of the Research School of Physical Sciences and Engineering at ANU for inspiring this work and for his discussions, as well as an anonymous reviewer for noting an error in the manuscript.

Appendix

The solution to eq 11 subject to the initial condition and the boundary condition, eq 12, at $z = 0$ and $z = w$ can be deduced from known results for the equivalent heat equation,¹⁷ which have more recently been applied to ideal polymers.^{18–20} Specializing to the case of interest, when the ends of the chain are at $z = 0$ and $z = w$, we obtain

$$G(0, w) = \frac{2}{w} \sum_{m=1}^{\infty} \exp\left(-\frac{4R_g^2 \alpha_m^2}{w^2}\right) (-1)^{m-1} \frac{\alpha_m^2}{\alpha_m^2 + \lambda^2 + \lambda}$$

where $\lambda = -w/(2D)$ and α_m is given by the m th root with non-negative real part

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$$\alpha_m = \arctan\left(\frac{\lambda}{\alpha_m}\right) + \frac{(m-1)\pi}{2}$$

Note that α_1 is purely imaginary for $D > 0$ (i.e., an adsorbing surface), and α_2 is purely imaginary for $w > 2D$.

The force on the chain can then be found from $-f/(k_B T) = (\partial G/\partial w)/G$, where

$$\frac{\partial G}{\partial w} = \frac{2}{w^2} \sum_{m=1}^{\infty} \exp\left(-\frac{4R_g^2 \alpha_m^2}{w^2}\right) \frac{(-1)^{m-1} \alpha_m^2}{(\alpha_m^2 + \lambda^2 + \lambda)^2} \left(-\alpha_m^2 - 3\lambda^2 + \frac{8R_g^2 \alpha_m^2 (\alpha_m^2 + \lambda^2)}{w^2} - \frac{2\alpha_m^2 \lambda}{\alpha_m^2 + \lambda^2 + \lambda} \right)$$

Some care is required in evaluating these expressions for large values of w because convergence is slow and there is a significant cancellation between the terms for $m = 1$ and $m = 2$.

LA981112V

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