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Non-equilibrium dynamics of single polymer adsorption to solid surfaces

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Abstract

The adsorption of polymers to surfaces is crucial for understanding many fundamental processes in nature. Recent experimental studies indicate that the adsorption dynamics is dominated by non-equilibrium effects. We investigate the adsorption of a single polymer of length N to a planar solid surface in the absence of hydrodynamic interactions. We find that for weak adsorption energies the adsorption timescales $\sim N^{(1+2\nu)/(1+\nu)}$, where ν is the Flory exponent for the polymer. We argue that in this regime the single chain adsorption is closely related to a field-driven polymer translocation through narrow pores. Surprisingly, for high adsorption energies the adsorption time becomes longer, as it scales as $\sim N^{1+\nu}$, which is explained by strong stretching of the unadsorbed part of the polymer close to the adsorbing surface. These two dynamic regimes are separated by an energy scale that is characterized by non-equilibrium contributions during the adsorption process.

(Some figures in this article are in colour only in the electronic version)

Polymer adsorption is a fundamental phenomenon that controls many natural processes [1]. The adsorption of the polymeric molecules to different surfaces and interfaces is important for adhesion, colloidal stabilization, development of composite materials and coatings, for cell adhesion and communication and for protein–DNA interactions [1, 2]. The importance of polymer adsorption has motivated extensive experimental and theoretical investigations to try and understand the underlying mechanisms. As a result, the equilibrium properties of adsorbed polymers are now well-understood [3]. However, many experimental studies [4], supported by theoretical ones [5–7], indicate that non-equilibrium behaviour is increasingly important in polymer adsorption dynamics.

One key parameter in polymeric adsorption is the height of the free energy barrier that monomers have to overcome in order to bind to the surface. If the barrier is high, one commonly calls the adsorption process chemisorption, while in the absence of a significant barrier it is called physisorption. A

further characterization of physisorption involves the strength of the binding interaction between each monomer and the surface. If this interaction is of the order of $k_B T$, the process is called weak physisorption, while one speaks of strong physisorption in the case of interactions of about $10k_B T$ or more, as for instance typically encountered for hydrogen bonding.

In chemisorption, the high barrier faced by monomers attaching to the surface slows down the adsorption process; this allows the adsorbed part of the polymer chain to partially relax in effectively equilibrium conformations, giving rise to the formation of large loops via the accelerated zipping mechanism [7, 8]. The absence of a significant barrier makes non-equilibrium effects even more important in physisorption [4, 7]. It is not clear what mechanisms drive the polymer adsorption away from equilibrium in this regime [7]. One of the possible contributions is the interaction between neighbouring polymer molecules that can significantly slow

down the overall dynamics. This source of deviation from equilibrium is commonly eliminated by considering the adsorption dynamics of single polymers [7, 9–12].

The adsorption of single macromolecules for weak polymer–surface interactions has been investigated by a combination of analytical and computational methods [7, 9–14]. Monte Carlo simulations with the bond fluctuation model revealed significant deviations from equilibrium dynamics [9, 10]. The adsorption time was reported to scale as $\sim N^{1.57 \pm 0.07}$ for self-avoiding polymers, while the exponent is equal to 1.50 ± 0.04 when the excluded volume interactions are neglected. Computer simulations and an approximate theory were also used to investigate irreversible adsorption of tethered chains [13, 14]. These investigations assumed that during the adsorption the polymer molecule has three parts: a segment of already bound monomers, a stretched linear part (‘stem’) and the remaining part (‘flower’) which is not affected by the force of adsorption. This theoretical model yields an adsorption time scaling as $\sim N^\alpha$ with $\alpha = 1 + \nu \approx 1.59$. Here ν is the Flory exponent for the polymer, and $\nu \approx 0.588$ in three dimensions. Simultaneously, in the Monte Carlo simulations a smaller value of α , namely ≈ 1.51 , has been observed [14], but it was argued that finite-size effects were responsible for this discrepancy. The stem–flower model was originally proposed by Brochard-Wyart [15] for polymer chains under strong flows (under constant and very large flow velocity). It has a clear physical picture that allows one to obtain specific predictions for the dynamical properties. However, the growth velocity of the adsorbed polymer has been shown to be not large [13, 14], not constant, and in time it even decays to zero; hence the validity of the stem–flower model to adsorption in all situations is questionable. Thus, despite many attempts, mechanisms of single polymer binding to surfaces are still not well-understood. In this paper we present theoretical arguments supported by simulation data that clarify several non-equilibrium features of single polymer adsorption.

During binding to the surface the polymer molecule can be viewed as consisting of two segments: the adsorbed monomers and the block of free monomers not on the surface. Theoretical studies argue that adsorption (for weak interactions) can be viewed as a sequential zipping process [13, 14] in which the size of the adsorbed block increases by one monomer a time. This sequential mechanism suggests that the single polymer adsorption process is closely related to field-driven polymer translocation (detailed later in the text), which has been intensively studied in recent years [16, 22]. During field-driven translocation, the polymer molecule moves through a pore sequentially, decreasing the number of monomers on the *cis* side of the pore and sequentially increasing the number of monomers on the *trans* side of the pore. Theoretical studies of translocation based on the microscopic dynamics of the polymer [16, 17] showed that memory effects are crucial for understanding this process. The memory effects appear to be due to the finite time to dissipate away or replenish the local enhancement in the density of monomers at the pore. From these works on translocation, it is reasonable to expect that the same memory effects in the polymer should also play a role in the adsorption of single polymers to a surface.

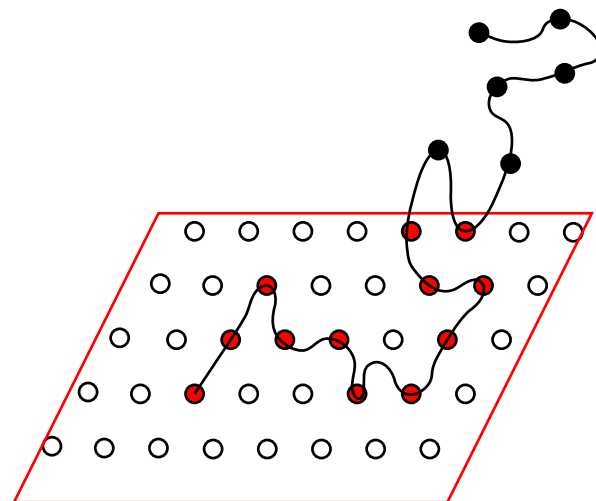


Figure 1. Schematic view of single polymer adsorption to a planar surface. Unfilled circles correspond to binding sites available for adsorption by monomers. Red filled circles describe the surface sites already occupied by the polymer. Black filled circles represent monomers that are not adsorbed on the surface yet.

Consider a single polymer molecule that is near a solid surface, which starts to adsorb to the surface as shown in figure 1. We assume that there are uniformly distributed binding sites on the surface, that the energy of adsorption per site is equal to ε , and that the distance between binding sites is the same as the size of each monomer. We then use a Monte Carlo based FCC-lattice polymer code in three dimensions for self-avoiding polymers, with the rigid flat surface placed at $z = 0$, and study the adsorption dynamics for a variety of polymer lengths and for different strengths of the adsorption energy, in the absence of hydrodynamic interactions. In this polymer model the individual monomers perform both reptation and ‘sideways’ movements [18] with each kind of movement attempted with frequency unity, which provides us with the definition of time. This model has been used before to simulate the diffusion and exchange of polymers in an equilibrated layer of adsorbed polymers [19]. Recently, we have used this code extensively to study polymer translocation under a variety of circumstances [16, 17, 20].

The process of adsorption involves a change in the free energy ΔF for the polymer: the polymer loses energy due to the attractive interaction between the surface and the monomers, and loses entropy as adsorption makes the polymer collapse into two dimensions from three. The value of the adsorption energy ε dictates the sign of ΔF , and thereby determines the fate of a partially adsorbed polymer. At high adsorption energies, the polymer will nearly completely adsorb since adsorption is energetically favoured, while at low adsorption energies it will desorb since desorption is entropically favoured. In between, there is a critical value ε^* at which a partially adsorbed polymer will both adsorb and desorb with equal probability, for which the entropy gain for desorption is exactly compensated by the energetic gain for adsorption.

Consider a partially adsorbed polymer of length N , with m monomers (counting from one end) completely adsorbed

Table 1. The critical desorption rate $v^* = \exp[-\varepsilon^*/(k_B T)]$ as a function of polymer length N .

N	v^*
100	0.405
120	0.395
140	0.392
160	0.38
200	0.365
400	0.36
800	0.342

on the surface while the rest ($N - m$) of the monomers are moving freely (off the surface). If one assumes that the adsorbed part of the polymer takes the form of a self-avoiding random walk on the two-dimensional adsorbing plane, then the partition function of this polymer is given by $Z = [A_2 \mu_2^m m^{\gamma_1^{(2D)}-1}] [A_3 \mu_3^{(N-m)} (N-m)^{\gamma_1^{(3D)}-1}]$. Here, $\gamma_1^{(2D)} = 49/32$ and $\gamma_1^{(3D)} \approx 1.16$ are two universal scaling exponents [21], and A_2 , A_3 , μ_2 and μ_3 are model-dependent quantities. For this partially adsorbed polymer $\frac{\partial \Delta F(\varepsilon)}{\partial m}$ can be estimated as $\frac{\partial \Delta F(\varepsilon)}{\partial m} \simeq -\varepsilon + k_B T \ln(\mu_3/\mu_2) + 1/N$ corrections. Equating $\frac{\partial \Delta F(\varepsilon)}{\partial m}$ to zero then yields the critical adsorption energy $\varepsilon^* \simeq k_B T \ln(\mu_3/\mu_2)$ in the limit of $N \rightarrow \infty$. Note that this expression is only an estimate, since in the adsorbed state not all monomers of the polymer adhere to the surface; moreover, as has been demonstrated in [13], the adsorbed part of the polymer takes a very compact conformation—much more compact than a self-avoiding walk in two dimensions. Nevertheless, $\frac{\partial \Delta F(\varepsilon^*)}{\partial m} = 0$ shows that ε^* is of the order of $k_B T$.

For our model we determine ε^* in the following manner. We start with a polymer of length N with $N/2$ monomers from one end constrained to the surface (i.e. constrained to $z = 1$) without an adsorption energy, while the remaining $N/2$ monomers are free, and equilibrate the polymer under this constraint (the free $N/2$ monomers encounter the surface only as a planar obstacle). At time $t = 0$, an adsorption energy ε is introduced, and simultaneously the constraint is lifted. We repeat this exercise for polymer lengths ranging from $N = 100$ to 800 , while tuning the suppression of the desorption rate by a factor of $v \equiv \exp[-\varepsilon/(k_B T)]$, until, on average, the adsorbed part of the polymer neither grows nor shrinks. The results for the critical values v^* for several polymer lengths are summarized in table 1; from this table we conclude that $v^* \approx 0.34 \pm 0.01$ for our model, and thus that $\varepsilon^*/(k_B T) = 1.08 \pm 0.03$. Since we use $\varepsilon \geq 2k_B T$, our polymers always adsorb, and any reference to high or low adsorption energies will henceforth refer to $\varepsilon > \varepsilon^*$.

The specific manner in which we simulate surface adsorption is as follows. We take a polymer of length $(N + n^*)$ with n^* monomers from one end constrained to $z = 1$ without an adsorption energy (a process we term ‘grafting’ for later reference), and equilibrate the rest of the polymer in $z > 0$, i.e. during the equilibration process the N free monomers encounter the surface only as a planar obstacle. We index the monomers consecutively along the chain, starting with $i = -n^*$ for the grafted end. The free end is thus indexed by $i = N$, and the last grafted monomer corresponds to $i = 0$. At $t = 0$

we switch on the attractive interaction between the monomers and the surface, and simultaneously lift the constraint. The dynamics of the polymer for $t > 0$ is then governed by, in addition to self-avoiding polymer dynamics, the fact that the ratio of probability of a monomer (including the grafted monomers) jumping from $z = 1$ to 2 and that of a monomer jumping from $z = 2$ to 1 is given by the Boltzmann ratio $\exp[-\varepsilon/(k_B T)]$. Throughout this paper we choose $n^* = 30$; since we use adsorption energies higher than or equal to $2k_B T$, this implies that the probability for the entire polymer to detach from the surface is practically zero. It should be noted also that the specific value of n^* does not affect the adsorption dynamics as long as $n^* \ll N$.

Given this setup, *on average* we expect the monomers to be adsorbed on the surface in a sequential zipping manner: on average monomer $n_1 (> 0)$ will be adsorbed on the surface (i.e. attain $z = 1$) for the first time earlier than monomer $n_2 > n_1$. For future reference, at any time t for any configuration of the adsorbing polymer we can identify the monomer with the highest index $n(t)$, which has $z = 1$, to be called the ‘active monomer’. This definition divides the entire polymer into two segments: (i) a part consisting of monomers $i \leq n(t)$, largely adsorbed to the surface, and (ii) another part consisting of monomers $i > n(t)$ that behave as a polymer of length $[N - n(t)]$ tethered on the surface at the location of the active monomer.

In light of $n(t)$ as defined in the above paragraph, it is important to note that our setup involving the initial grafting of the polymer—albeit simplified—does capture the adsorption dynamics in a real situation. In reality, a long polymer does not adsorb starting from one end; almost always it starts to adsorb somewhere in the middle. Imagine, for a polymer of length N , a situation when the monomer with index n_0 (somewhere in the middle of the polymer), is the first one to adsorb. By definition, this monomer immediately divides the polymer into two separate ‘sub-polymers’—of lengths n_0 and $(N - n_0)$, respectively. If $\varepsilon > \varepsilon^*$, then (on average) these two sub-polymers will start being adsorbed independently (in stating this, we disregard the steric interactions between them) *from their common end*: one from monomer n_0 towards monomer 1, and the other from monomer n_0 towards N . The adsorption dynamics for a polymer in a real situation—at least in the scaling sense, which is the main focus of this paper—is the same as that of the polymer in our setup (which starts to adsorb from one end). Our setup—similar to the existing ones [13, 14]—therefore is purely a choice of convenience to study the adsorption dynamics in a real situation.

Returning to our setup, if adsorption were a sequential zipping process for every single realization, then the adsorption dynamics can be described solely by the active monomer index $n(t)$ as a function of time, and the dynamics of adsorption can be mapped exactly on to that of field-driven translocation. More precisely, in polymer translocation driven by a potential difference ΔV across the pore, when a monomer crosses from the *cis* (*trans*) to the *trans* (*cis*) side, the length of the polymer segment on the *cis* side reduces (increases) by one monomer with an energy gain (penalty) of magnitude $q\Delta V$, where q is the charge of one monomer. Similarly, (a) if the active

monomer happens to detach from the surface (with an energetic penalty ε) then the length of part (ii) of the polymer increases by roughly one monomer; (b) alternatively, if the index of the active monomer increases by one (with an energy gain of ε), then the length of part (ii) of the polymer decreases by one monomer. In reference [16], based on memory effects in polymer dynamics, two of us showed that the total number of translocated monomers at time t increases as a power-law $\sim t^{(1+\nu)/(1+2\nu)}$ at *weak* fields; recently, this has been confirmed by different polymer models [22, 23]. This implies that if the adsorption process were a sequential zipping process for every single realization for our setup, $n(t)$ would scale $\sim t^{(1+\nu)/(1+2\nu)}$. Based on this result—although in a real situation adsorption is a sequential zipping *only on average, and not for every single realization*—on average we expect $n(t)$ to increase in time t also as $\sim t^{(1+\nu)/(1+2\nu)}$ for our setup, i.e. the adsorption timescales as $\sim N^{(1+2\nu)/(1+\nu)}$, when the adsorption energies are not very high. We demonstrate this in the paragraphs below.

It is important to note that during adsorption for our setup, a monomer with index $[n(t) + n_1]$ may get adsorbed by the surface before any of the in between monomers (with indices $n(t) + 1, \dots, n(t) + n_1 - 1$) do. For such an event, the adsorbed part of the polymer is said to form a ‘loop’ of length n_1 between monomers with indices $n(t)$ and $[n(t) + n_1]$; in fact, it is precisely such ‘loop formations’ that prevent adsorption—unlike translocation, for which the first passage of the monomers through the pore takes place strictly sequentially—from being a sequential zipping process for every single realization. Consequently, the traditional way to follow the progress of adsorption for our setup is to track the average total number of adsorbed monomers $s(t)$ at time t , so that $s(\tau_{\text{ad}}) \sim N$ would define the adsorption time τ_{ad} . However, since $s(t)$ for any single realization will saturate at a value $\sim O(N)$, care needs to be taken in measuring $s(t)$, otherwise saturation effects might affect the numerical determination of the true exponent. In order to avoid saturation effects, we define t_n as the average time, and s_n as the average number of adsorbed monomers when the n th monomer attains $z = 1$ for the first time, with the condition that no monomer with index $>n$ has ever attained $z = 1$. Since t_n is defined only until $n = N$, this method ensures that s_n never saturates.

Indeed, we find that adsorption of the individual monomers is *not* a sequential process for every single realization precisely because of the loop formations as discussed above paragraph; however, as shown in figure 2, s_n does scale linearly with n , confirming that adsorption on average is indeed a sequential zipping process. This property ensures that the exponent we get for s_n as a function of t_n is the same as the one that one would get from tracking $s(t)$ as a function of t . A remarkable feature of figure 2 is the collapse of all s_n versus n curves on a single master curve: it shows that the proportion of monomers in the loops within the adsorbed part of the polymer, given by $(n - s_n)$, is independent of ε , a feature that we will return to shortly.

In figure 3(a) we present the data for weak interactions with the surface, i.e. when the adsorption energy is not too high ($\varepsilon \leq 5$), for which we do obtain the exponent $(1+\nu)/(1+2\nu)$, corresponding to $\tau_{\text{ad}} \sim N^{(1+2\nu)/(1+\nu)}$. Additionally, the data

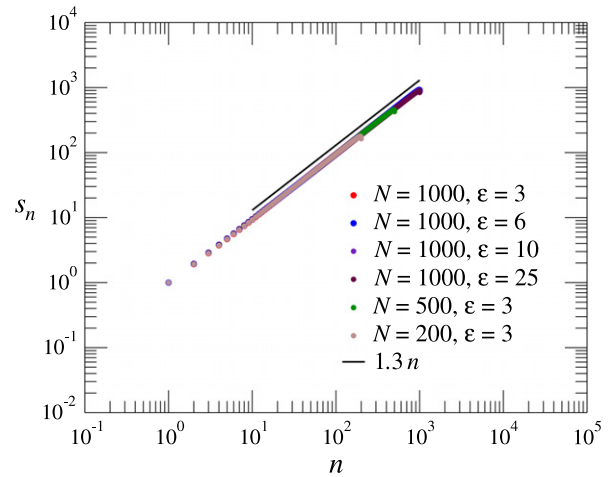


Figure 2. Scaling of s_n as a function of n , for several values of N and ε ; all curves collapse on a single master curve, corresponding to the scaling $s_n \sim n$, represented by the solid black line.

exhibit energy-dependence (see the inset, and also figure 3(c)), demonstrating that for $\varepsilon \leq 5$ the higher adsorption energy also yields faster adsorption, like higher field means shorter (field-driven) translocation time at weak fields [16]. The situation changes for stronger interactions ($\varepsilon > 5$): in figure 3(b), we register a slowly decreasing slope in the t_n - s_n log-log plot with increasing adhesion energy; eventually for the virtually irreversible adhesion process $\varepsilon = 25$, we recover an exponent $1/(1+\nu)$, i.e. $\tau_{\text{ad}} \sim N^{1+\nu}$, in agreement with [9, 10, 13, 14]. For these values of ε , τ_{ad} is independent of ε .

The surprising aspect of two different scaling regimes for s_n versus t_n , as shown in figures 3(a) and (b), is that *for long enough polymers adsorption is faster for low ε -values than for high ε -values*. This is demonstrated in figure 3(c). In fact, figure 3(c) leaves one wondering whether the slowdown of adsorption is due to phenomena at the adsorbing surface that are different for strong adsorption energies and weak adsorption energies. For example, for high ε -values it has been shown in [13] that the adsorbed part of the polymer takes a very compact form. Based on the result of [13], it may be argued that since for high ε -values the individual monomers are essentially irreversibly adsorbed, the polymer needs to form systematically bigger loops to access available surface sites for adsorption, a phenomenology that is absent for low ε -values; and as a result adsorption is slower for high ε -values than for low ε -values. Such a possibility is, however, ruled out by the collapse of the data over a very wide range of ε values in figure 2: it shows that on average the fraction of monomers in the loops (given by $(n - s_n)$) has no dependence on ε ; i.e. steric hindrance due to the adsorbed part of the polymer does not cause the slowdown of adsorption at high ε -values. Instead, as explained quantitatively below, the physics of the slowdown of adsorption at larger ε -values is explained by the lack of availability of not-yet-adsorbed monomers near the surface.

For high adsorption energies the monomers that were close to the surface at $t = 0$ initially get quickly and effectively irreversibly adsorbed, while the monomers that are far away from the surface at $t = 0$ cannot respond to this fast change

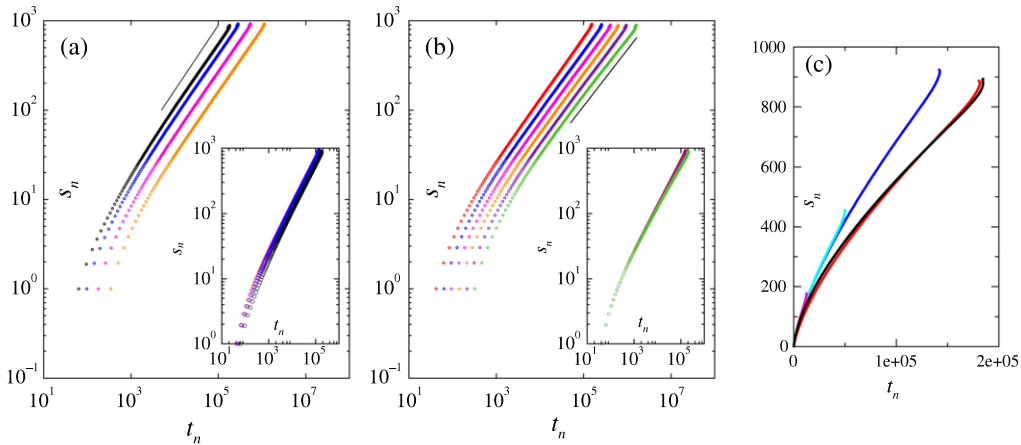


Figure 3. (a) Weak adsorption data for $N = 1000$ (from left to right) $\varepsilon = 2$ (black), $\varepsilon = 3$ (blue), $\varepsilon = 4$ (magenta) and $\varepsilon = 5$ (orange): the data are progressively separated by a factor of 2 along the x -axis for clarity. The original data are shown in the inset in the same colour scheme. The solid (black) line corresponds to an exponent $(1 + \nu)/(1 + 2\nu) \simeq 0.73$. (b) Strong adsorption data for $N = 1000$ (from left to right) $\varepsilon = 6$ (red), $\varepsilon = 7$ (blue), $\varepsilon = 8$ (magenta), $\varepsilon = 9$ (orange), $\varepsilon = 10$ (brown) and $\varepsilon = 25$ (green): the data are progressively separated by a factor of 1.5 along the x -axis for clarity. The original data are shown in the inset in the same colour scheme. The solid (black) line corresponds to an exponent $1/(1 + \nu) \simeq 0.63$. Data correspond to an average over $\simeq 400\,000$ realizations for each value of N and ε . (c) Comparison of adsorption speed at several energies and N -values: $N = 1000$, $\varepsilon = 2$ (red), $N = 1000$, $\varepsilon = 3$ (blue), $N = 500$, $\varepsilon = 3$ (cyan), $N = 200$, $\varepsilon = 3$ (magenta), and $N = 1000$, $\varepsilon = 10$ (black). Note that adsorption is slower for $\varepsilon = 10$ than for $\varepsilon = 3$.

in the polymer's configuration near the surface. As a result, during the adsorption process the polymer adopts a stretched configuration close to the surface, while far away from the surface the polymer remains largely in its $t = 0$ coiled shape: this is the stem–flower picture of Brochard-Wyart [15]. (It is precisely this stem–flower shape that invalidates the physics behind the exponent $(1 + \nu)/(1 + 2\nu)$, seen at low adsorption energies. The number $(1 + 2\nu)$ in the denominator is derived from the Rouse exponent, and the number $(1 + \nu)$ in the numerator assumes that during adsorption the polymer's size scales as $\sim [N - n(t)]^\nu$; both fail at the stem (of the stem–flower model), which is highly stretched.) In fact, the occurrence of ν in the exponent $1/(1 + \nu)$ at high adhesion energies stems from the polymer's size-scaling N^ν at $t = 0$, as we argue next. Let us denote, by $z(t)$, the distance that the stem extends in real space from the surface at time t . The total number of monomers in the flower at time t —still largely in the same coil shape as at $t = 0$ —is $Q(t) \sim N - z(t)^{1/\nu}$. In such a configuration, the flower would lose monomers through the stem to the surface, and the rate of loss of monomers is proportional to the gradient of monomeric density along the stem, $\sim 1/z(t)$. The solution of the differential equation $\dot{Q}(t) \sim 1/z(t)$ yields $z(t) \sim t^{\nu/(1+\nu)}$. Since all the monomers that were present within a distance $z(t)$ at $t = 0$ —apart from the few within the stem at $z(t)$ —are adsorbed by time t , the total number of adsorbed monomers at time t scales as $s(t) \sim z(t)^{1/\nu} \sim t^{1/(1+\nu)}$. Note that in this qualitative derivation there is no dependence on the adsorption energy (except that it needs to be high!), as observed in the inset of figure 3(b). When hydrodynamic interactions are included, following the physics of field-driven translocation [16] we expect the adsorption time to scale $\sim N^{(1+\nu)/(3\nu)}$ for not too high adhesion energies; however, at present we do not understand how cooperative motions of the monomers in the presence of hydrodynamics would affect the exponent at high adhesion energies.

An increase in the energy of adsorption allows one to cross-over from weak to strong regimes of physisorption, both characterized by different exponents. The remaining question is what determines the energy scale ε_c that separates these two regimes. This can be understood if we return to $\Delta F \simeq -\varepsilon + k_B T \ln(\mu_3/\mu_2)$, wherein the first term lowers the free energy due to favourable adsorption to the attractive surface, while the second term increases the free energy because of entropy reduction by going from three dimensions to a more constrained two-dimensional surface. It is reasonable to suggest that two dynamic regimes of adsorption are separated when the free energy gain per monomer is comparable with thermal energy, i.e. $|\Delta F| \simeq k_B T$. Our estimates for critical adsorption yield $\mu_3/\mu_2 \approx 3$, which leads to $\varepsilon_c \simeq 2$. Our simulations show that $\varepsilon_c \approx 5$, suggesting deviations from (equilibrium) free energy concepts in (non-equilibrium) surface adhesion process. As shown in figure 3(c), the adsorption proceeds faster for lower adsorption energies, with the most optimal adsorption speed at ε close to ε_c . Since these types of energies are typical for protein–DNA interactions [2], one can suggest that this might be a mechanism by which biological adhesion processes are controlled.

To conclude, using computer simulations and theoretical arguments we studied single polymer adsorption to solid surfaces in the absence of hydrodynamic interactions. Our analysis shows that the adhesion process is non-equilibrium. Details of the adsorption process depend on the strength of adsorption energies: for weak (polymer–surface) interactions the dynamics is determined by memory effects as in field-driven polymer translocation, while for strong interactions adsorption is limited by stretching of the unadsorbed part of the polymer. It is argued that the adsorption process is most optimal at low interaction energies, and this might be the mechanism by which biological surface adhesion processes are controlled.

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