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Polymer−Surface Interactions in Bridging Escape and Localization Transitions

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ABSTRACT: We consider conformational transitions of the coil to flower type that occur for polymer chains attached to a surface. We use a slit geometry to impose a confinement force on an end-grafted Gaussian chain and account for the effects of the interaction of the chain with the surfaces. In the repulsion mode, that is, when the adsorption parameter $c < 0$, a classical first-order escape transition is found, which is significantly modified near the critical condition ($c \approx 0$). When $c = 0$, the surface is "invisible" and no conformational transitions takes place. In the adsorption mode (one surface remains $c \leq 0$ but the other one $c > 0$), a bridging transition appears when the surfaces are still far apart. In addition, we discuss positional transitions that may occur when one surface is homogeneous and near critical ($c \approx 0$) and the other surface is heterogeneous, that is, having patches with different affinity for the chains. In this case it is feasible that the chain assumes flowerlike conformations without physically escaping from the confined region. An AFM with a polymer probe can be used to characterize polymer−surface interactions and corresponding surface heterogeneity.

Introduction

The investigation of conformational properties of individual macromolecules in polymer physics has a long history. Many of the results proved to be essential in the understanding of polymeric matter and are now textbook examples. The random coil, a swollen coil, a collapsed globule or torus, polymers in helix conformations, and fully extended chains are a few well-known examples.[1,2]

Recently there has been a renewed interest in the study of conformational transitions on the level of single chains that occur upon manipulating single (macro)molecules. These nanoexperiments can be performed, for example, by an atomic force microscope (AFM).[3−13] One can envision various systems for which a conformational transition exists.

A classical system in which a conformational transition takes place is depicted in Figure 1. One considers a chain grafted with one of its ends to the center of a disk with radius L. The chain assumes a coil configuration with radius R. Then, a second surface is introduced. The disk is pushed onto this surface such that a local slit geometry is generated, and the chain is squeezed. At a critical separation H^* the chain suddenly assumes a very different, heterogeneous conformation (see Figure 1B). It forms a strongly stretched stem from the grafting point to the edge of the cylinder, such that the remainder of the chain can be in a much less deformed crown. This conformation may be referred to as a flower, and the transition is known as the escape transition.[14−23] In this case the confinement generates an unfavorable (potential) field felt by all the segments when the chain is inside the slit and only by a part of the segments when it is in the flower conformation. The fact that the confinement can be represented by a potential field has been suggested by Sevick and Williams[19] in the context of the classical escape transition. Independent from this group and in the same year, a similar conclusion was reached by Skvortsov and coworkers[24] studying the adsorption to flower transition of a end-grafted long minority chain escaping from a brush.

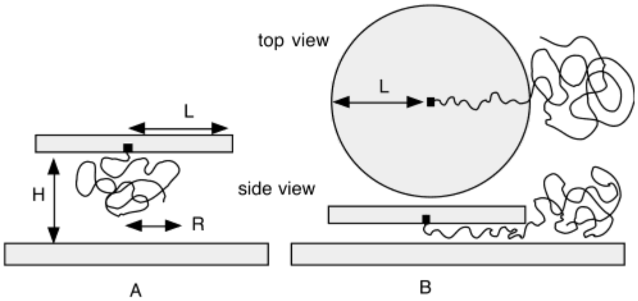

Figure 1. The classical escape transition. An end-grafted chain is squeezed between two (repulsive) surfaces. (A) On the left the chain is in a mushroom configuration. (B) On the right the chain partially escaped from the confinement. The radius of the disk L, the separation H, and the radius of gyration of the chain, R, are indicated. Both the side view and the top view are given for the chain in a flower conformation.

These conformational transitions can be analyzed conveniently by using the ideal chain model. In such a model one can write the partition function without the need to make any further approximations. Exact partition functions that feature phase transitions are rather unique in the field of statistical physics. In the fortuitous case of exact solutions, it is possible to analyze a phase transition in extremely large detail, that is, in the thermodynamic limit of infinitely large chain lengths, but for finite lengths as well. From this detailed analysis, a very transparent physical picture emerges. It can be shown that all these systems have very similar physical characteristics. Indeed, it proves possible to use the close analogy between the systems and "translate" known results from one system to all other cases.

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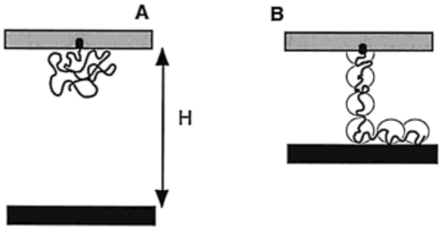

Figure 2. Schematic representation of the case when a chain grafted with one end on a surface with nonadsorbing properties ($c \leq 0$) is placed at some distance from an adsorbing surface (dark shading). (a) The chain remains as a mushroom. (b) The chain is in a flower configuration where a strongly stretched stem is formed such that the remainder of the chain can adsorb onto the surface. The spheres are blobs used in a scaling analysis.

In more detail, the strategy is based on the fact that the chains typically choose only between two populations of conformations. There is the set of homogeneous conformations, that is, the unperturbed or confined coil, and there is the set of inhomogeneous conformations. This last set of conformations are of a flowerlike structure. Part of the chain is strongly stretched, and the remainder is in the coil or pancake state. Intermediate conformations are effectively not available to the chains. As a consequence, the chain can only jumplike go from one set of conformations to the other. This is the reason that these conformational transitions are of the first-order type (in the thermodynamic limit of infinite chain length). The jumplike nature of the conformational transitions also implies that there exists an energy barrier associated with such transition. The reason for the existence of a barrier is also transparent. In all cases the chain has to invest stretching entropy in order to generate a stem before it can benefit from having a crown.

It is a challenge to try to observe conformational transitions in real experiments. In principle, such experiments are feasible by using an atomic force microscope (AFM). However, in an AFM experiment designed to capture, for example, the escape transition, one may encounter many problems. For example, it is difficult to approach the grafted chain “head on”. Also, on the length scale of the polymer chain, it is difficult to control the necessary ideal geometry. For this reason several alternative scenarios were considered such as a tilted cylinder or confinements with variable passage sizes.[16] Then, multiple transitions were envisioned, and the situation is more complex.

Obviously, for the classical escape transition it is important that the surfaces strongly repel the chains. This means that the enthalpic interactions of segments to the surface should be small enough such that unfavorable conformational entropy effects will dominate. If this is not the case, that is, when the chains are not repelled strongly by the surface, one must expect that the escape transition is modified. Indeed, it is necessary to understand the possible effects of polymer−surface interactions in order to be able to understand the possible outcomes of AFM experiments. The effect of polymer−surface interactions is the common theme in the systems that are visited in this paper.

We show that inhomogeneously stretched polymers also occur due to a competition of stretching of the chain and obtaining favorable energetic interactions with an adsorbing surface (see Figure 2). Here again there is a transition from the coil, where the chain has no surface contacts, to the flower, where the chain has many contacts with the surface. This transition occurs when two surfaces are still very far from each other: one surface is as in the escape problem, repulsive ($c \leq 0$); the other one is strongly attractive ($c > 0$). Then, a stem can develop between the starting point of the chain on the nonadsorbing surface and the adsorbing surface. Since this stem can be considered as a bridge between two surfaces, this transition will be referred to as a bridging transition. Such bridging conformations were also considered in the model of detachment of single macromolecules from interfaces.[25−30]

The critical adsorption condition, that is, $c = 0$, on both surfaces is in between the escape and bridging regimes. When the surface is critical, the peculiar situation occurs that the chain does not “see” the surface. When the chain is confined in the slit with critical walls, the entropic conformational restrictions due to the confinement are compensated by weak attractive interactions, and then the confinement force is absent. In this case there is no conformational transition.

This special case then leads us to the study of conformational transitions that occur when an end-grafted chain is pressed against an energetically heterogeneous surfaces. We will show that in this case the chain can undergo positional transitions. Upon confinement the chain jumps from a region of low surface affinity (at close proximity to the grafting point) with many (but not all) of its segments to a patch with higher surface affinity (that is placed further away from the grafting point). These localization transitions may possibly be picked up by an AFM experiment as well, where the force changes jumplike as soon as the chain chooses a new position.

The remainder of this paper is as follows. First, we present the well-known Edwards equation and its exact solution for the bridging problem. This result is used to justify the two-state approach. We then discuss the influence of the adsorption energy on the escape transition and pay some attention to the critical adsorption case. In the second part of the paper we consider the scenario of a grafted chain confined by two large surfaces. One surface onto which the chain is grafted is homogeneously repulsive or critical ($c \leq 0$), and the other one is energetically heterogeneous. We show that in such a system localization transitions are possible. In the concluding section we discuss how the various systems can be investigated by the AFM technique.

Preliminaries

There is a well-known analogy between the trajectory of a diffusing particle and a conformation of an ideal chain. Both problems can accurately be represented by the appropriate diffusion equation. In the field of polymer physics this equation is known as the Edwards equation:[31]

$$\frac{\partial G(\vec{r}, N)}{\partial N} = \frac{b^2}{6}\nabla_r^{\,2} G(\vec{r}, N) - u(\vec{r})\, G(\vec{r}, N) \qquad (1)$$

In this equation b is the unit length (Kuhn segment) and $G(\vec{r}, N)$ is the end-point distribution of the Nth segment. Finally, $u(\vec{r})$ is the dimensionless external potential (expressed in units of k_BT), which may be of the self-consistent type.

For a particular problem this diffusion equation should be complemented by an initial condition and boundary conditions. The initial condition specifies the coordinate of the first segment, and the boundary condition defines the properties of the system at the boundaries. In this paper we consider the case in which there is a solid boundary. It is customary to use the de Gennes boundary condition:[2]

$$\frac{\hat{n}\cdot\nabla_{\mathrm{r}}G(\vec{r},\,N)}{G(\vec{r},\,N)} = -c \tag{2}$$

where $\hat{n}$ is the unit vector normal to the surface and c is the polymer−surface interaction parameter. It is necessary to explain the physical interpretation of the adsorption parameter c. When $c < 0$, the function G drops near the surface. This must indicate that the polymer avoids the surface; that is, the surface is repulsive. Alternatively, when $c > 0$, the surface attracts the polymers. At the point where $c = 0$, which is often referred to as the critical or adsorption−desorption threshold point, the surface is indifferent for the polymer. Inspection of eq 2 shows that the quantity $1/c$ has the dimension length, and $1/c$ may be identified as an extrapolation length.

At this point it is instructive to realize that the c parameter is an effective interaction parameter. It includes both the enthalpic contributions of the polymer−surface contacts and the entropic restrictions of the chain near the boundary.

The free energy of the chain is given by $F = -k_{\mathrm{B}}T \ln Q$, where the partition function Q is found from integration over the end-point distribution $G(\vec{r},\,N)$. From the free energy all other relevant properties follow, including changes in the chain structure, force−separation diagrams, and other characteristics of the phase transition.

The Bridging Transition

In this section we study the conformational properties of a chain that is placed at some distance from an adsorbing surface. Let us start to assume that it is possible to fix a chain with one of its ends at the position H above such surface as shown in Figure 2. Indeed, the bottom surface is characterized by a positive adsorption parameter, that is, $c > 0$. The top surface will be chosen to be repulsive for the chain. This effectively allows the chain to assume a coillike configuration near the top surface (see Figure 2a). The justification of this is given below in eq 5. The chain can also choose to form a flowerlike conformation. This flower is composed of a stem from the grafting point to the surface, and then the remainder of the segments can profit from the adsorption energy and forms a pancake (see Figure 2b).

Ideally one would like a method that is rigorous, which does not preassume specific properties of the system. Indeed, this is possible, and the natural starting point is the diffusion equation (1) complemented by the boundary condition (2). According to the plan described above, we introduce $z_0 = H$ as the starting point for the chain, and the corresponding end-point distribution $G(z,1;z_0) = \delta(z - z_0)$, where in the notation $G(z,N;z_0)$ the coordinate z_0 is added to show that all walks have started at this point.

The exact solution of this problem is known in the literature.[32,33] The end-point distribution that is the solution of the diffusion equation is most conveniently expressed in reduced variables, $Z = z/2R$, $Z_0 = z_0/2R$, and $C = cR$ (where R is the radius of gyration of the chain):

$$G(Z;Z) = \frac{1}{2R}\{\exp[-(Z - Z_0)^2] - \exp[-(Z + Z_0)^2]\} + \frac{\exp[-(Z + Z_0)^2]}{\pi R}[1 + \sqrt{\pi}CY(Z + Z_0 - C)] \tag{3}$$

where $Y(x) = \exp(x^2)\,\mathrm{erfc}(x)$ (erfc is the complementary error function). When $|x| \ll 1$ we have $Y(x) \approx 1 - 2x/\sqrt{\pi}$, when $x \gg 1$ the asymptote is $Y(x) \approx 1/\sqrt{\pi}x$, and in the other limit $x \ll -1$ we have $Y(x) \approx 2\exp(x^2)$.

Integration over the coordinates of the free end leads to the partition function, which is a function of the coordinate of the starting point and the adsorption parameter $Q(Z_0,C)$:

$$Q(Z_0,C) = 1 + \exp(-(Z_0)^2)[Y(Z_0 - C) - Y(Z_0)] \tag{4}$$

This partition function is easily split into one due to the coil and one that can be attributed to a flower state $Q = Q_{\mathrm{coil}} + Q_{\mathrm{flower}}$, where

$$Q_{\mathrm{coil}}(Z_0,C) = \mathrm{erf}(Z_0) \approx 1 \tag{5}$$

and

$$Q_{\mathrm{flower}}(Z_0,C) = \exp(-(Z_0)^2)Y(Z_0 - C) \tag{6}$$

The free energy $F = -\ln Q$ of each branch is found from eqs 5 and 6. (Here and below we normalize the free energy to $k_{\mathrm{B}}T$.) The branches intersect when $C^* = 2Z_0$, or in natural variables the bridging transition is expected to occur at a distance proportional to the chain length:

$$H^* = cN/6 \tag{7}$$

Here and below all lengths are normalized to the segment size b. So, instead of H/b we write H and instead of cb we use c.

It is of interest to illustrate that it is possible to arrive at the result of eq 7 by making use of the two-state approximation. For this we need to understand the free energy difference between the coil, which is homogeneously adsorbed on the adsorbing surface, and the completely detached coil.

The free energy of the chain that is homogeneously adsorbed is found by inserting the starting point of the chain to be exactly at the boundary of the adsorbing surface ($H = 0$) in eq 6. The partition function for this case reduces to $Y(-C)$. When $C > 1$, we recover the known result, which in natural variables can be expressed as $Q(c,N) = 2\exp(c^2N/6)$. The free energy of adsorption is thus given by

$$F_{\mathrm{ads}} = -Nc^2/6 \tag{8}$$

The arguments to obtain the relevant characteristics for the bridging transition in this system are now straightforward. Let us first assume that the flower has a stem with m segments and calculate the free energy for this case. Then we can optimize the free energy with respect to this number m.

The free energy of the flower with a particular m has two terms. The first one is due to the stretching of the

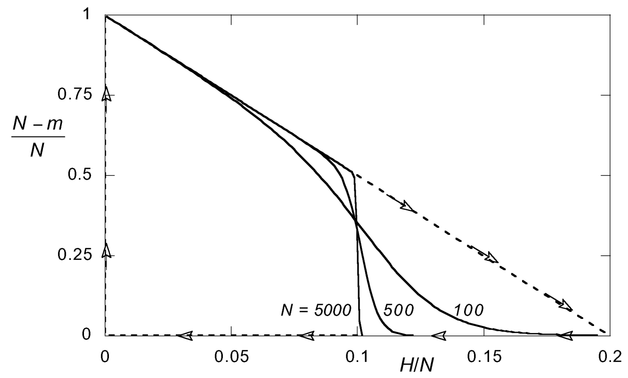

Figure 3. Average fraction of segments in the pancake for an ideal chain of N segments with one end fixed at a distance H from an adsorbing surface with adsorption interaction parameter $c = 0.6$. The value of the chain length is indicated. The dashed lines with arrows are the possible hysteresis loops in the limit of infinite chain length ($N \to \infty$).

stem, and the second one is due to the favorable interactions with the surface:

$$F_{\text{flower}}(m) = F_{\text{stem}}(m) + F_{\text{ads}}(m) = 3H^2/2m - (N - m)c^2/6 \quad (9)$$

Here the coil state is taken as the reference for the free energy. Optimization of the free energy of the flower with respect of m gives the expected number of segments in the stem

$$m = 3H/c \quad (10)$$

The transition point is now found by equating the optimized free energy of the flower, that is, $F_{\text{flower}} = Hc - Nc^2/6$, with the free energy of the coil. The result shows that the length of the stem at the transition point is proportional to the length of the chain in accordance with eq 7.

Combining eqs 10 and 7 shows that at the transition point the number of segments in the stem is exactly equal to the number of segments in the crown, that is, $m^* = N/2$.

The average fraction of segments in the pancake $(N - m)/N$ is presented as a function of the ratio H/N for various values of the chain length in Figure 3. The results were obtained from the analysis of the exact partition function. In the limit of infinite chain length the curves are very simple. The number of segments in the pancake (and thus also the number of segments in the stem) is a linear function of the separation up to the transition point. At the transition point, $m = (N - m) = N/2$. For larger separation there are no contacts. These results show that the two-state approximation is very good in the limit of long chains. For finite chain length, the transition becomes more gradual. Only in the limit of infinite chain length is the bridging transition a first-order one. The number of polymer segments in contact with the surface, n_s, is proportional to the number of segments in the pancake $(N - m)$, $n_s = (N - m)c$. The gain in adsorption energy is proportional to n_s. Therefore, we expect at the transition to have a jump in the enthalpy of the system.

The dashed lines in Figure 3 are the possible hysteresis effects for the infinite chain length case. The ends of the hysteresis loops are spinodal points. Between the binodal and spinodal lines there may be conformational states of the polymer that are metastable and only live for a finite amount of time. For example, it is possible that the coil is stable but that still a flower is present, although from a free energy perspective this is unfavorable (that is, $H > H^*$). Alternatively, it is possible that the coil conformation is found even when the flower is most favorable (that is, $H < H^*$). The presence of a metastable region finds its origin in the fact that there is an energy barrier that needs to be crossed before the most stable conformation is found. At the spinodal points, the energy barrier between the metastable and stable conformation is lost, and the system can move without any problems to the stable conformation. For very long chains the two spinodal points are $H^{**}/N \approx 0$ and $H^{**}/N = cN/3 = 2H^*/N$.

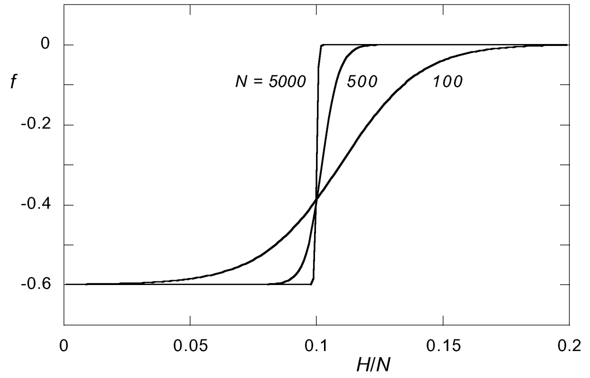

Figure 4. Force acting on the chain end as a function of the distance of the end to the adsorbing surface for various values of the chain length N as indicated. The adsorption parameter has the value $c = 0.6$.

The force needed to keep the chain at position H can be found from $f = -(\partial F/\partial H)$. When the chain is in the coil state, that is, $H > H^*$, the force to maintain this distance is typically very small, especially when $H^* > R$. The result for the flower conformation is extremely simple:

$$f = -c \quad (11)$$

This means that the force is attractive and constant, that is, independent of the distance H. All these results are in full accordance with the exact analysis in the limit of long chains and not too small values of the field c, that is, when $c > 1/\sqrt{N}$.

In Figure 4 the force−distance curves are presented for the bridging transition, for several values of the degree of polymerization N. Here again we generated exact (ideal chain) results from the evaluation of the partition function, including all possible conformations. In line with eq 11, the force is constant and negative when a bridge is formed and is zero without the bridge. The transition is sharp for long chains and relatively more gradual for shorter chains.

It is of interest to analyze the bridging transitions from a “blob” perspective, for example at the transition point. In a one k_BT per blob Ansatz it follows that the adsorbed chain with free energy $F_{\text{ads}} = Nc^2/6$ has $Nc^2/6$ blobs. The number of segments in a chain is N, and thus, there are $6/c^2$ segments in a blob. The size of the adsorption blob ξ_{ads} is apparently equal to $\xi_{\text{ads}} = 1/c$. The blob size in the stem is given by the ratio of the height and the number of blobs $\xi_{\text{stem}} = H/F$, which is simply the inverse of the force, $\xi_{\text{stem}} = -1/f$. Therefore, the blobs in the stem are equal in size to the blobs in the adsorbed layer.

It is instructive to reflect on the basis of the two-state approximation. We started with the exact partition function as given in eq 4, wherein all possible chain conformations were taken into account. From the analysis of this exact solution it follows that the bridging transition is first-order. The reason for this can also be extracted from the exact results. It turns out that there exists a barrier between the coil and flower states. The origin of the barrier is that the chain has to form a stem that crosses from one surface to the other which is very long compared to the radius of gyration of the chain. In other words, it has to stretch significantly before the chain can know about the presence of a favorable state near the surface. The barrier is thus of pure entropic origin. We will return to the consequences of having a barrier in the system in the discussion section. The barrier is the reason for the relative importance of two sets of conformations, the coil and the flower, and the practical absence of intermediate conformations. In the thermodynamic limit, the weight of these intermediate conformations will be zero.

The Escape Transition

In this section we discuss a closely related problem of the escape transition. As explained in the Introduction, it is possible to characterize the escape transition to be the result of the presence of a barrier.

The system that features the classical escape transition is schematically shown in Figure 1 and qualitatively discussed above and extensively in the literature.[14−23] Of interest for the present discussion is to consider how the escape transition is modified by a finite affinity of the polymer segments for the surface. In particular, we account for arbitrary but still repulsive interactions, that is, $0 < -c < \infty$.

For the confined polymer we use the results of the exact theory for the ideal chain confined within a slit with separation H. For this problem an exact expression for the free energy of confinement was obtained in the literature[34] as the result of a solution of the diffusion eq 1 with boundary conditions of eq 2 at $z = 0$ and $z = H$. According to ref 34, in the strong confinement limit, $R/H \ll 1$, the free energy of confinement assumes the form

$$F_{\text{conf}} = \frac{\alpha^2 \tilde{N}}{\tilde{H}^2} \tag{12}$$

where $\tilde{N} = R^2 = N/6$, $\tilde{H} = H/2$, and α is the root of the equation

$$\alpha \tan \alpha = \lambda \tag{13}$$

Here, $\lambda = -\tilde{H}c$ is the scaled interaction parameter.

Constructing and optimizing the free energy of the stretched and escaped chain (which will further referred to as a flower) is straightforward and similar to that in the bridging problem. The result is

$$F_{\text{flow}} = \frac{\alpha L}{\tilde{H}} \tag{14}$$

and for the transition point we obtain

$$\tilde{H}^* = \alpha \frac{\tilde{N}}{L} \tag{15}$$

To obtain the direct results, we need to express from eq 13 α as a function of λ and to substitute this expression in eqs 14 and 15. This can be done numerically. One can also use the asymptotic expansion for $\alpha(\lambda)$ at small and at large values of λ. When the system is still far from critical, that is, $\lambda \gg 1$, we have $\alpha(\lambda) = \pi/(2(1 + \lambda^{-1}))$, and when the system is close to critical, that is, $\lambda \ll 1$, the result is $\alpha(\lambda) = \sqrt{\lambda}$.

Let us first take the system far from critical. In this regime the free energies of confined and flower chains are given by

$$F_{\text{conf}} \cong \frac{\pi^2}{4} \frac{\tilde{N}}{(\tilde{H} + \xi)^2} \tag{16}$$

$$F_{\text{fl}} \cong \frac{\pi}{2} \frac{L}{\tilde{H} + \xi} \tag{17}$$

respectively, where $\xi = -1/c$ denotes the extrapolation length in the case of repulsive interactions.

The condition for the escape transition is

$$\tilde{H}^* = \frac{\pi}{2}\tilde{N}/L - \xi \tag{18}$$

This result approaches the classical escape equations in the infinite repulsion case, where $\xi \to 0$. Equations 16 and 17 thus tell us that the effect of finite c value is simply a renormalization of the width of the slit, $\tilde{H}_{\text{eff}} = \tilde{H} + \xi$.

Much closer to the critical interaction, that is, when $\lambda \gg 1$, the free energies of the two basic states, the confined coil and the flower, reduce to

$$F_{\text{conf}} \cong \frac{\tilde{N}}{\tilde{H}\xi} \tag{19}$$

$$F_{\text{fl}} \cong \frac{L}{\sqrt{\tilde{H}\xi}} \tag{20}$$

respectively. The escape transition takes place at

$$\tilde{H}^* = \frac{1}{\xi}\left(\frac{\tilde{N}}{L}\right)^2 \tag{21}$$

From eq 21 we conclude that when $-c < L^2/N^2$, the chain can be completely compressed up to the monomer length, before the escape transition will occur. For this reason, the near-critical conditions are of less importance for escape transitions. Also, we should expect that when H is small, the density of polymer segments in the gap is relatively high and the Gaussian approximation becomes less valid. In principle, one should then account for the excluded-volume effects.[18]

In Monte Carlo simulations on the escape transition by Milchev[17] and Jimenez,[35] results were obtained for finite chain length. In the simulations the transition remains smooth (small chains), but the results were consistent with a first-order transition in the thermodynamic limit.[15] The scaling arguments mentioned above for Gaussian chains in the context of the bridging transition may be extended to estimate the effect of excluded volume on the escape transition as was done in the literature.[16,21]

In Figure 5 the escape transition phase diagrams, calculated in the original coordinates H vs N/L, are given for several values of the repulsive interaction parameter c. The results were generated by the rigorous

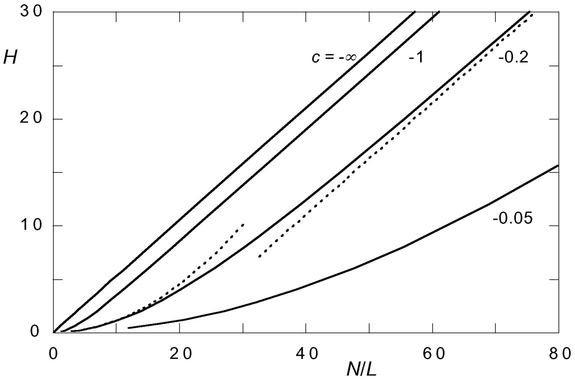

Figure 5. Escape transition H vs N/L phase diagrams for the ideal chain between two repulsive surfaces at various values for the interaction parameter $-c$ as indicated. The dotted lines are asymptotes given by eqs 18 and 21.

equations (solid lines), wherein α was evaluated numerically from eq 13. The dotted lines are asymptotes for small and large values for λ. The crossover from the near critical behavior to the strongly repulsive regime takes place at $H^* = \xi = -1/c$. The escape transition at given c value occurs when the separation distance H becomes less than the value of $H^*(c, N/L)$, indicated by the corresponding solid line.

The force needed to confine the chain and the flower can be calculated by $f = -\partial F/\partial H = -{}^{1}/_{2}\partial F/\partial \tilde{H}$. For $c < 0$ the force is always repulsive and decreases with separation. The force $f(H)$ is, however, different in the confined and flower states. Far from critical we have

$$f_{\mathrm{conf}} \cong \frac{\pi^2}{4}\frac{\tilde{N}}{(\tilde{H}+\xi)^3} \tag{22}$$

$$f_{\mathrm{fl}} \cong \frac{\pi}{4}\frac{L}{(\tilde{H}+\xi)^2} \tag{23}$$

for the confined coil and the flower, respectively. Again, we recover the known results that the force jumps in the transition point from one $f(H)$ dependence to the other. The force-jump value is equal to $\Delta f = L^3/(\pi\tilde{N}^2)$. Note that this jump is not a function of the value of the interaction parameter.

However, when c is small, we have significant deviations that become very pronounced when H is of order $\xi = -1/c$. For this regime we have

$$f_{\mathrm{conf}} \cong \frac{1}{2\xi}\frac{\tilde{N}}{\tilde{H}^2} \tag{24}$$

$$f_{\mathrm{fl}} \cong \frac{1}{4}\frac{L}{\xi^{1/2}\tilde{H}^{3/2}} \tag{25}$$

for the confined and the flower states, respectively. In this regime the jump in the force at the transition point equals $\Delta f \approx \xi L^4/(4\tilde{N}^3)$. Interestingly, the jump in the force is, in the critical region, a function of c; it increases upon the approach toward critical. As $\xi < N^2/L^2$ (to have an escape transition), Δf cannot diverge. The value of the jump in the force thus cannot exceed $\Delta f = {}^{1}/_{4}L^2/\tilde{N}$.

In Figure 6 we show the force as a function of the separation for several values of the (repulsive) interaction parameter. In this case we used the two-state approximations to generate the curves. In the fully repulsive case $-c \rightarrow \infty$ the classical result is found. Upon decreasing the distance H between the surfaces the force increases strongly. At the transition point H^* the force jumps to a lower value. After the jump, the repulsion of the flower leads to a further increase in the force. When c is made less negative, that is, when the surface affinity approaches the critical value, the force remains lower and the jump occurs at lower values of H. As expected, the magnitude of the jump depends on c when it occurs at low values of H.

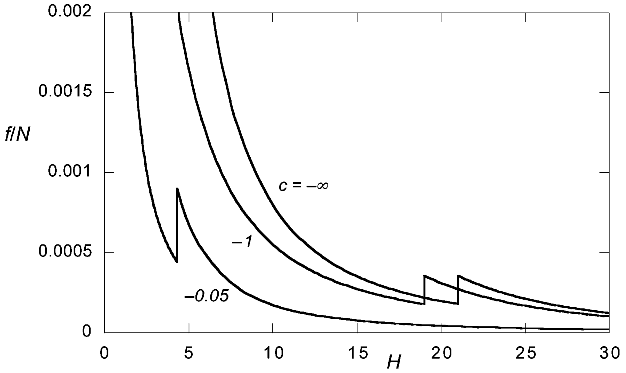

Figure 6. Normalized force vs separation for a chain between repulsive surfaces at various values of the repulsive interaction parameter c as indicated. For all three curves $N/L = 40$.

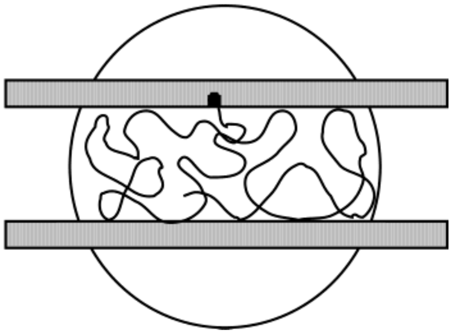

Figure 7. Schematic representation of the case when a chain grafted with one end on a surface with critical adsorption energy is placed at some distance from another critical surface (same intermediate gray shading). The sphere is a blob used in a scaling consideration.

The results of Figure 6 show a sharp transition in the force at the transition point. As was shown for the force in the case of the bridging transition (see Figure 3), the jumps in the force become less abrupt when fluctuations and finite chain lengths are taken into account. In this case more smooth van der Waals loops will be found. These loops indicate an instability in the system in this sense that for a fixed force it is possible that there is a jumpwise variation of H.[19]

Now it is of interest to consider the limit of critical adsorption energy, that is, $c = 0$, separately. It is quite obvious from the above that in this case the force to squeeze the chain is zero and that there is no escape transition. We can rationalize this by the fact that the chain, physically confined by the two surfaces, does not “see” the surfaces from a free energy perspective. Its free energy is equal to that of the reference, that is, the unperturbed Gaussian coil. It is as if the boundary condition is mirrorlike.

In Figure 7 a schematic representation is given to illustrate the case that both surfaces are critical. Indeed, in this case there is just a single blob, because the surface is not felt by the chain in a free energy sense. The sphere drawn in Figure 7 is present in the $x-y$

plane and is larger than the separation H between the surfaces.

Heterogeneous Surfaces

The cases studied above may have experimental counterparts. As mentioned already, an AFM tip may be used to be the top substrate. One needs to worry of course about the geometry and the fact that the polymer chain that is end-attached to the tip should not stick to the tip−surface. In an alternative experiment one can glue a colloid particle onto the tip. This particle can, on its turn, have a long end-grafted chain attached to it. In this case, the geometry is already better controlled, and in principle the particle surface can be chosen such that the chain does not have an affinity for it. An AFM experiment with a polymer probe may thus be used to examine the polymer−surface interactions, that is, to characterize the surface with respect to its interactions with the polymer chain.

Indeed, when it proves possible to recognize by a polymer probe technique the difference between repulsive surfaces, attractive surfaces, and surfaces that have a critical adsorption energy for the probe chain, we may try to make the next step.

Surfaces of practical interest typically are not homogeneous. For example, the surfaces may be rough or have patches that are chemically different from other regions on the surface. Surface inhomogeneities that occur on length scales that are small as compared to the persistence length of the polymer chains are most likely not very important. One can argue that the chain then feels some average interaction. However, on some larger length scale the effects of variations in surface affinity may be very large. In an AFM experiment it is possible to scan along the surface in the $x-y$ plane, and thus, the polymer probe may be used to examine heterogeneity effects. In the following we consider a system in which one of the surfaces is inhomogeneous at least on the length scale of the radius of gyration of the chains.

Localization Transition

We consider the case that the chain is grafted on the top surface and assume that this surface is close to critical ($c \approx 0$). In contrast to the systems discussed above, it is not important that this surface is limited in size. We can assume that it is large enough so that the chains cannot physically escape from it. It is important however that the top surface is energetically homogeneous. Let us start by considering the case in which the surface that is to be probed (i.e., the bottom surface) is repulsive for the chain and that there are patches on the surface where the surface is more repulsive, characterized by an adsorption parameter c_1, and other patches where the interaction is near critical, that is, the surface has a surface affinity given by c_2: $c_1 < c_2 \approx 0$. One can envision that when the polymer chain is positioned over a patch with high repulsion (c_1), it is unhappy and wants to escape to the region with less repulsion. The position of the polymer probe is characterized by the shortest distance L to the patch with energy c_2. Again, we express L in units of the segment size b. A graphical representation is given in Figure 8. Let us consider that this chain is compressed. Anticipating the escape of the chain from patch number 1 to number 2, we can again balance the free energies for the two states: the first one is the confined coil above region 1, and the other is the flower composed of a stem with length L and a crown in region 2.

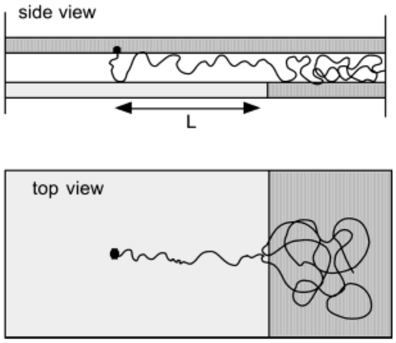

Figure 8. Illustration of a flower grown laterally after a part of the chain jumped to a region where the interaction with the surface is less repulsive. The top surface is critical, and the light shading on the bottom surface indicates a region with high repulsion. The distance L between the grafting point and the start of the less repulsive surface patch is indicated. Both a side view and a top view are given of the flower conformation.

The free energy of the chain that is compressed and resides completely above a repulsive region with $\alpha_1 = \alpha(\lambda_1)$ is given by $F_{\mathrm{comp}} \approx \alpha_1^2\tilde{N}/H^2$. (This formula is similar to eq 12, but differs in H due to the fact that, for the asymmetric two-surface problem with one surface critical, the free energy is given by the same equation as for the symmetrical problem, but with a double separation.) We assume again a flower that grows laterally into the less repulsive region with $\alpha_2 = \alpha(\lambda_2)$. Constructing and optimizing the free energy of this flower, one easily obtains

$$F_{\mathrm{fl}} \approx \frac{L}{H}\sqrt{{\alpha_1}^2 - {\alpha_2}^2} + \frac{{\alpha_2}^2\tilde{N}}{H^2} \tag{26}$$

and this gives the following equation for the transition point:

$$H^* \approx \frac{\tilde{N}}{L}\sqrt{{\alpha_1}^2 - {\alpha_2}^2} \tag{27}$$

which reduces to the result of eq 15 for the escape transition when $\alpha_2 = 0$ ($c_2 = 0$). These results were expected, of course, because the region of critical adsorption energy is seen by the chain as completely unconstrained region of space.

If an end-grafted chain is pressed against the inhomogeneous surface with patches of different surface affinity, it can undergo multiple positional transitions. We trust that the analogy of the positional transitions with the multiple transitions discussed by Guffond et al.[16] is clear to the reader. To give an example, let us consider a situation which is shown in Figure 9.

Referring to Figure 9, we consider that a chain is pressed against the repulsive surface with less repulsive "islands", that is, regions with different affinity. Depending on the separation, on the distances L_1 and L_2 (see Figure 9) from the grafting point to islands 1 and 2, and on the affinities of these islands, the chain would prefer either to stay confined in the unfavorable region with $\alpha_0 = \alpha(\lambda_0)$ or to escape into the less repulsive region $\alpha_1 = \alpha(\lambda_1)$, thus forming a flower 1, or even to form a flower 2 with a longer stem, but with a more happy crown within island 2 of the lowest repulsive affinity $\alpha_2 = \alpha(\lambda_2)$.

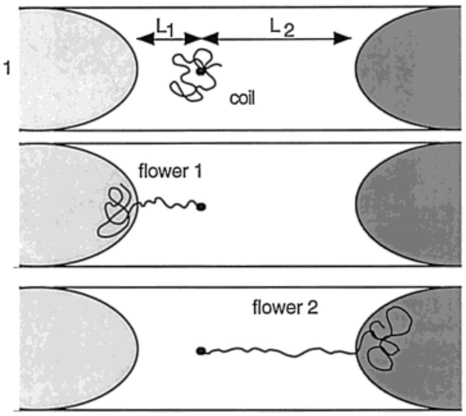

Figure 9. Top views of a chain, which is pressed against an inhomogeneous surface. More dark shadings on this surface indicate less repulsive regions. The top surface (not shown) is assumed critical. Three possibilities for the chain are given. Top: the chain is in the coil conformation in region 0. Middle: the chain formed a flower (number 1) with a short stem of length L_1 and with a crown in the nearest less repulsive island. Bottom: the chain formed a flower (number 2) with a longer stem but with the crown in the island of the lowest repulsive affinity.

For the compressed chain we have $F_{\text{comp}} \approx \alpha_0^2\tilde{N}/H^2$, while for the each flower indexed by $i = 1, 2$, $F_{\text{fl}} \approx (L_i/H)(\alpha_0^2 - \alpha_i^2)^{1/2} + \alpha_i^2\tilde{N}/H^2$. Comparing the free energies of these three states and choosing as the actual state of the chain the state of lowest free energy, we can construct phase diagrams for the situation of Figure 9. Examples of such phase diagrams are given in Figure 10. In both cases we assume infinite repulsive surface under the grafting point $-c_0 = \infty$ ($\alpha_0 = \pi/2$) and the critical affinity for island 2, $c_2 = 0$ ($\alpha_2 = 0$). The affinity of island 1 is assumed somewhat intermediate (being less repulsive in the case of Figure 10b than in the case of Figure 10a). The phase diagrams are plotted in coordinates of the scaled separation $h = H(L_1 + L_2)/\tilde{N}$ vs $x = L_1/(L_1 + L_2)$. Lines represent binodals for the transitions: $x = (\alpha_0^2 - \alpha_1^2)^{1/2}/h$ (confined → flower 1), $1 - x = (\alpha_0^2 - \alpha_2^2)^{1/2}/h$ (confined → flower 2), and $x = [(\alpha_0^2 - \alpha_2^2)^{1/2} + (\alpha_0^2 - \alpha_1^2)/h]/[(\alpha_0^2 - \alpha_1^2)^{1/2} + (\alpha_0^2 - \alpha_2^2)^{1/2}]$ (flower 1 → flower 2). As can be seen in Figure 10, different transition scenarios are possible in the course of chain compression. Apart from the single transitions from confined state to each flower a sequence of transitions, that is, confined → flower 1 → flower 2 is possible at some combinations of distances L_1 and L_2.

For the particular choice of the parameters the meeting point of the three binodals is $x' \approx 2(\zeta_1/\pi)^{1/2}$; $h' \approx \pi/2 + (\pi\zeta_1)^{1/2}$ when $\lambda \gg 1$ and $x' \approx (1 - 1/(\pi\zeta_1))/2$; $h' \approx \pi - 1/\zeta_1$ when $\lambda \ll 1$, where $\zeta_1 = \xi_1(L_1 + L_2)/\tilde{N}$ is the scaled interaction length for island 1. The second interesting point in the phase diagram, x'', is the lowest value of x, at which the double transition is possible. This value is zero, if $\zeta_1 < 2/\pi$, and equals $x'' \approx {}^1/_2 - 1/(\pi\zeta_1)$ in the case of less repulsive surface of island 1. Obviously, the double transition is possible, when the relative distance from the grafting point to the island number 1, $x = L_1/(L_1 + L_2)$, satisfies the inequality $x'' < x < x'$.

Using the expressions for the free energies and eq 13, the equations for the force in all the states can be derived. The force for the case that the chain is completely confined is given by

$$\frac{f_{\text{conf}}}{\tilde{N}} = \frac{2\alpha_0^{\,2}}{H^3}(1 - \Lambda_0) \tag{28}$$

where $\Lambda_0 = \lambda_0/(\alpha_0^2 + \lambda_0^2 + \lambda_0)$. The force when the chain is in the conformational flower state of type i:

$$\frac{f^{(i)}_{\text{flower}}}{\tilde{N}} = \frac{2\alpha_i^{\,2}}{H^3}(1 - \Lambda_i) + \frac{L_i\sqrt{\alpha_0^{\,2} - \alpha_i^{\,2}}}{\tilde{N}H^2}\left(1 - \frac{\Lambda_0\alpha_0^{\,2} - \Lambda_i\alpha_i^{\,2}}{\alpha_0^{\,2} - \alpha_i^{\,2}}\right) \tag{29}$$

Hence, the force−separation profiles can be calculated numerically. Examples of such profiles, corresponding to the movements along the dotted lines in Figure 10b, are shown in Figure 11. When moving along the right dotted line in Figure 10b, only one transition compressed → flower 2 takes place and appears at about $H = 39$ in the natural units (Figure 11). The second profile in Figure 10b (which corresponds to the left dotted line) has two jumps in the force in the course of the chain compression. These jumps are due to the transitions confined → flower 1 and flower 1 → flower 2. It is obvious that in the general case of richer surface map with many islands of different surface affinity the force−separation profiles would be more complicated, reflecting multiple positional transitions. It is also clear that the shape of such profiles would depend on the position of the chain grafting point relative to the position of patches on the surface map.

Bridging Transition in Attractive Mode

In the second problem we consider the attractive case. More specifically, we consider that the top surface is

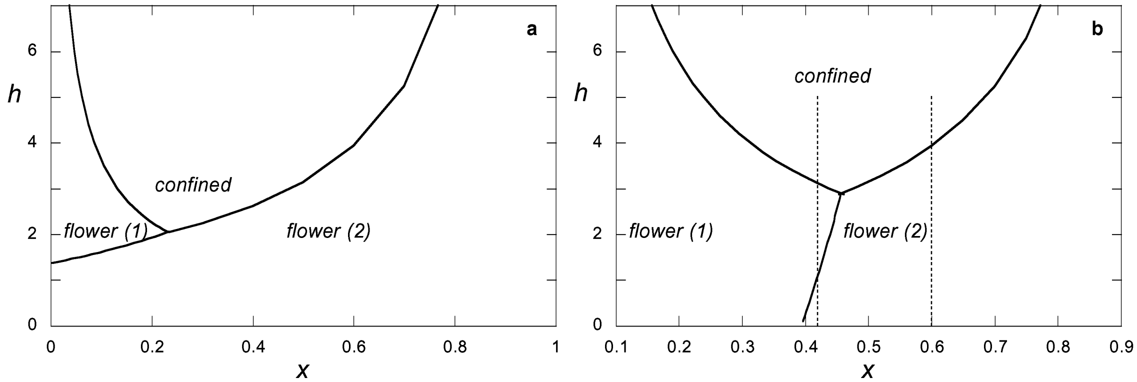

Figure 10. Scaled separation $h = H(L_1 + L_2)/\tilde{N}$ vs $x = L_1/(L_1 + L_2)$ phase diagrams for a chain compressed against an inhomogeneous surface. Parameters: $c_0 = -\infty$; $c_2 = 0$; (a) $c_1 = -10(L_1 + L_2)/\tilde{N}$, (b) $c_1 = -0.333(L_1 + L_2)/\tilde{N}$. The dotted lines are cuts through the phase diagram for which the force curves will be presented in Figure 11.

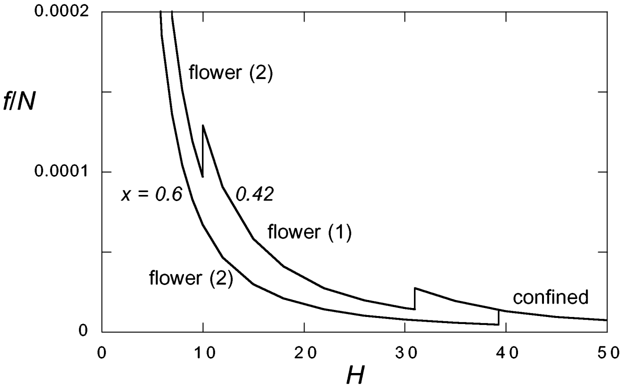

Figure 11. Force of confinement of a chain compressed on a heterogeneous surface along positional coordinates specified by the dashed lines in Figure 10b. The part of the curve corresponding to the fully confined chain and the flower conformations are indicated. Parameters: $c_0 = -10^8$; $c_2 = -10^{-8}$; $N/(L_1 + L_2) = 60$; $x = L_1/(L_1 + L_2)$ is indicated.

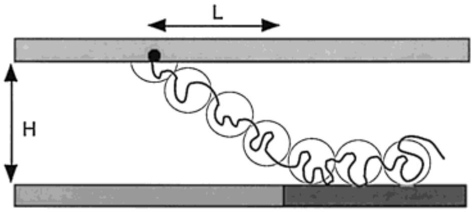

Figure 12. Illustration of a flower grown toward a region with high surface affinity (dark shading). The top surface as well as the remainder of the surface is critical (or repulsive). The distance H between the surfaces and the lateral displacement L between the grafting point and the position of the high affinity region are indicated. The spheres are blobs that are used in the scaling arguments.

nonadsorbing $c \leq 0$ and homogeneous. Again, we envision that the bottom surface has regions with low affinity and other regions with high affinity. Let the chain be positioned above a region with low affinity and L in the $x-y$ plane away from the grafting point. In this case the jump toward an attractive region and the string of stretching blobs is not formed vertically down, but under some angle (see Figure 12).

The natural consequence of a flower with a tilted stem is that the force is not normal to the surface but in the direction of the stem. The normal force is given by

$$f_{\mathrm{n}} = -cH/\sqrt{H^2 + L^2} \tag{30}$$

Like in the case of homogeneous adsorption-active surface, the force is attractive and independent of the chain length, but its magnitude now decreases with decreasing separation H. The binodal is of course shifted to smaller H values with increasing values of L. Especially when H^* is of the same order as L, we should expect to be able to have enough resolution to resolve these effects. In an AFM experiment one can systematically vary the value of L by placing the tip on different $x-y$ coordinates.

Discussion

Of course, there are several techniques to measure surface heterogeneity such as AFM and STM for relatively small length scales, a Brewster angle microscope for micrometer length scale, and for example contact angle measurements on a macroscopic scale. If one is interested in the relevant interactions of a particular macromolecule with a particular substrate, one is not necessarily interested in the inhomogeneities on the sub-nanometer scale or on the macroscopic scale. Instead, the surface irregularities on the polymer length scale are important. A polymer molecule has several parameters: there is the contour length, the radius of gyration, and the persistence length. It is not trivial to judge which of the surface irregularities are important for a particular polymer system and which ones are not. Applying the polymer chain of interest in an AFM experiment as a polymer probe and preparing the substrate such that this surface can be scanned in an AFM apparatus, a wealth of information can be generated, precisely relevant for the surface–polymer system of interest.

If long-range attraction is found, and when this force is constant upon decreasing the distance, we are in the adsorption regime. Alternatively, repulsion is picked up only when the chains are compressed with respect to their radius of gyration. Depending on the geometry, one can search for the escape transitions or in localization transitions as explained above. By scanning the surface in the $x-y$ plane, one can obtain the necessary relevant information on the heterogeneity of the surface.

The conformational transitions discussed above are analyzed only up to the level of the interaction force as a function of the separation between the surfaces. It is important to discuss an interesting analogy between the treated problems and corresponding problems in the literature. This analogy will help us to instantly obtain more results.

In eq 8 it was shown that the free energy of the adsorbed chain can be written as $F_{\mathrm{ads}} = \phi_{\mathrm{ads}}N$, where the proportionality constant in front of the degree of polymerization can be seen as the (external) potential due to an adsorbing field. Then, in the escape problem, it was possible to write the free energy of the confined chain in the same form. Referring to eq 12, we may write $F_{\mathrm{conf}} = \phi_{\mathrm{conf}}N$, where the proportionality constant ϕ_{conf} may be referred to as the (external) potential due to the confinement. Indeed, the similarities between the bridging and the escape transition can thus be traced to the common properties of the free energy of the perturbed chains: the free energy is found by $N\phi$. There are a number of other systems showing the same behavior. We may mention the rolling transition and the coil to flower transition in liquid–liquid transitions studied by Skvortsov and co-workers.[24,36−38] The analogy between these systems may be exploited because results obtained from one system may be translated directly to all others.

In the AFM-with-polymer-probe experiment it should be expected that the force–distance curve for the inward movement will differ from the outward movement of the surfaces. The first-order character of the conformational transitions are due to this. Of special interest are the dynamics of the crossings of barriers when the system slips into one of the metastable branches.[39,40] Indeed, conformational transitions may prove to be excellent testing grounds to investigate barrier crossing events. As for several of the systems discussed above, exact or nearly exact partition functions are available, and one can elaborate on theoretical prediction regarding the dynamics of these systems. Work along this line is in progress.

Conclusions

We have analyzed the conformational transitions that can occur for a polymer molecule grafted with one of its ends to a (repulsive or critical) surface and then pressed upon another surface. The conformational transitions that have been discovered in these systems have much of their physics in common. The analogy between the problems is traced back to the feature that the chain in the confined state has a free energy that scales proportional to the chain length N. Typically, there are two possible sets of conformations that the polymer can choose from. One set of conformations is characterized by a homogeneous shape of the molecule, that is, a coil. This state is chosen when the confinement is not strong. The other set of conformations is characterized by an inhomogeneous shape of the molecule, that is, the flower.

When the surfaces are repulsive for the chains, we can find the escape transition. It was shown that the main effect of finite polymer surface interaction is similar to a renormalization of the distance between the surfaces. The transition is seriously modified if the adsorption parameter $c < 1/H$, and the transition will vanish when the surface is critical $-c < L^2/N^2$. In the regime where $c > 0$ the bridging transition is found.

When the surface is overall repulsive, but when there exist discrete patches with near-critical adsorption energy, one can find again conformational transitions from a homogeneous coil to a flower. The flowers grow laterally along the surface in order to minimize the free energy of confinement.

We have speculated about the use of an AFM in which there is a polymer chain grafted either directly on the tip or onto a colloidal particle that is glued on the tip, to determine the polymer−surface interactions. Such experiments should be sensitive for relevant surface heterogeneity. Experiments of this type will give direct information on the way polymers interact with nonideal surfaces.

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