End-Tethered Polymer Chains under AFM Tips: Compression and Escape in Theta Solvents

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We study the problem of an isolated end-grafted polymer chain confined under a finite-sized flat obstacle in a Θ solvent. For obstacles that are not too large this chain can undergo an escape transition where part of the chain remains trapped and the remainder escapes from under the obstacle. The spinodals of this system are influenced by the presence of a three-body term. We also study the problem of a chain under a tilted obstacle. We show that in this case there are two different escape possibilities. The system can then undergo the following series of transitions $C \to E \to C \to E$ as the chain is compressed, where C = confined and E = escaped.

Introduction

The deformation of single polymer chains is a classical problem in polymer science.[1−4] Polymer deformation can be induced by hydrodynamic flow, but in the majority of practical cases, the deformation occurs by interaction of a chain or chains with a surface. For a collection of chains end-grafted to a surface, i.e., a polymer brush,[5,6] the crowding of the chains at the surface causes chain stretching. In the case of polymer adsorption, the attraction of chains for a surface causes polymer compression.[7] Both of these situations have important applications in colloidal stabilisation.[8] In recent years it has become possible to observe and control the deformation of individual polymer chains. There are two methods of doing this. One can use a large biological molecule such as DNA which is capable of being stained and viewed directly in an optical microscope.[9−11] The chain can then be distorted using either a flow field or a magnetic or optical trap. The second method involves using an atomic force microscope to stretch individual chains.[12,13] AFM tips can also be used to squash an individual chain. This possibility recently inspired a study on how polymer chains behave when squashed by finite-size obstacles.[14−16] Although the

behavior of polymers compressed by infinite obstacles is well-understood it turns out that compression under a finite obstacle produces a series of surprises. One of these is that at a critical compression the chain partially escapes from under the obstacle. This escape transition has been studied previously for polymers in good solvents.[14−16] It is important to examine the role of solvent quality in this system. In this paper we study the case of a theta (Θ) solvent, where the binary interactions between monomers vanish. The previous studies have focused on the case of flat perfectly aligned obstacles[14,15] or on curved obstacles.[16] A flat obstacle is the simplest possible geometry to analyze, and in practice it is possible to make such an obstacle by polishing an AFM tip. However, in any real experiment the AFM tip and the grafting surface will not be aligned exactly parallel, and moreover, the tip cannot be exactly centered over the grafting point. It is thus important to consider misalignment of the compressing surfaces. We do this here and show that this misalignment, rather than being just a technical matter, can lead to some novel physics. In particular in the misaligned system there can be distinct left and right escapes with confined situations in between.

Squashing with a Finite-Sized, Flat Disk

We consider a chain with monomer size a and degree of polymerization N. In a Θ solvent such a chain has a natural size $aN^{1/2}$, where here and throughout the remainder of the paper we have ignored unimportant numerical prefactors. The compression of such a chain between two parallel plates separated by a distance H involves a free-energy penalty (in units of $k_B T$)

$$F_{confined} = Na^2/H^2 \qquad (1)$$

This free energy can be derived in a simple way[4] by using a collisional argument. Under compression, only those monomers at the plate walls can see the effect of the plates. The remaining monomers undergo an unrestricted random walk. Each collision with the walls costs of order $k_B T$ entropy, since the chain must reverse direction at the wall. Between collisions, the chains traverse a distance of order H which must equal $an^{1/2}$, where n is the number of monomer used. By counting monomers, we find there

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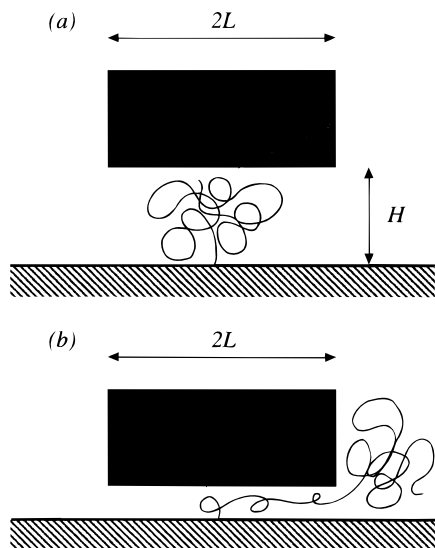**Figure 1.** (a) Compression of a chain under a disk of radius L, with surface separation H. In this state, the chain is imprisoned under the obstacle. (b) At stronger compressions, the free energy of the system is lowered by the chain forming a tether under the obstacle and partially escaping. Complete escape is not possible because the chain is grafted permanently to the lower surface.

are Na^2/H^2 collisions, thus leading to eq 1. Since the free-energy penalty for confinement increases as H^{-2}, the energy penalty can become many $k_B T$ even for moderate confinement.

Now consider a finite-sized parallel disk, of radius L, larger than the natural size of the chain, $L > aN^{1/2}$, but smaller than the fully elongated dimension of the chain, $L < aN$ (Figure 1a). For weak compressions, the chain does not see the edge of the disk and behaves as if it were compressed under an infinite plate. However, at intermediate separations, where the compression energy is fairly large, the overall energy can be minimized by the chain forming an umbilical tether from the grafting point to the edge of the disk, at distance L. The remaining monomers escape from under the obstacle (Figure 1b). The escaped portion of the chain is unconfined and suffers no free-energy penalty. However, those monomers within the tether suffer not only compression energy but also a stretching penalty. The stretching energy for a tether of m monomers is given by the standard Gaussian penalty:

$$F_{\text{stretch}} = L^2/(ma^2) \tag{2}$$

and the confinement penalty for the tether is ma^2/H^2. Thus, the free energy of an escaped conformation in units of $k_B T$ is

$$F_{\text{escaped}} = L^2/(ma^2) + ma^2/H^2 \tag{3}$$

The number of monomers in the tether is found as that which minimizes the energy (eq 3): $m = HL/a^2$ and $F_{\text{escaped}} = 2L/H$. The state of the chain (i.e., confined or escaped) at any given compression is determined as the state with the lower free energy: if $F_{\text{escaped}} < F_{\text{confined}}$ or $2L/H < Na^2/H^2$, then the chain adopts an escaped conformation. The separation at which the chain first escapes occurs at

$$H^* = Na^2/(2L) \tag{4}$$

Associated with this transition between confined and escaped states there is sometimes an energy barrier. This energy barrier is caused by the energy needed to stretch

the tether. It is equal to the energy needed to form a tether of length L from N monomers, i.e., $L^2/(Na^2)$. For very strong compressions, this barrier can disappear. This is because as the chain is compressed the three-body interactions between monomers cause a swelling of the chain in the lateral direction. Eventually this swelling becomes so great that the chain radius, R, is larger than the disk radius, L, and the chain can see the edge of the disk without needing to stretch. The chain radius under compression can be found by balancing a stretching force against the three-body force. This gives a free energy

$$F = R^2/(Na^2) + a^6(N/V)^3 V \tag{5}$$

where $V = R^2 H$ is the volume occupied by the chain. Minimizing this over R yields a chain radius

$$R = aN^{2/3}(a/H)^{1/3} \tag{6}$$

Setting $R = L$ gives the condition at which the energy barrier disappears. This is

$$H^+ = aN^2(a/L)^3 \tag{7}$$

A similar energy barrier can occur when we decompress an escaped chain. In order for an escaped chain to become imprisoned, it must remove all the monomers from the outside of the compressing disk to the inside. This involves an intermediate state which consists of the same tether of N monomers discussed above. At very weak compressions, this energy barrier disappears because the number of monomers outside the disk falls to zero. This number, $N - m$, was calculated above, so that setting $m = N$ gives the following condition for the energy barrier to vanish:

$$H^- = Na^2/L \tag{8}$$

It is simple to show that the chain makes a sudden jump in radius upon undergoing the transition at $H = H^*$. Thus, in the language of phase transitions, this represents a first-order transition. Ordinarily there is an energy barrier to be overcome to undergo the escape or imprisonment transition at $H = H^*$. For very strong compressions $H < H^+$ or for strong decompressions $H > H^-$, this energy barrier disappears and the system becomes absolutely unstable to the instability. These two values of H are the spinodals for the system.

These transitions and spinodals should be experimentally accessible as a distinctive force−compression profile. In the imprisoned state, the force, is

$$f_{\text{confined}} = -\frac{\partial F_{\text{confined}}}{\partial H} = 2Na^2/H^3 \tag{9}$$

whereas in the escaped state the force is

$$f_{\text{escaped}} = -\frac{\partial F_{\text{escaped}}}{\partial H} = 2L/H^2 \tag{10}$$

Figure 2 shows the force versus displacement profile for our chain between two parallel surfaces, where the tether point of the chain corresponds to the center of the disk of radius L. The dark line is the force profile predicted for chains adopting only stable conformations, as opposed to metastable ones, and is expected whenever the compressing force is increased slowly over the experiment. At the critical compression distance, H^*, the chain undergoes a transition to escape when compressed and to the confined or imprisoned state when decompressed. The ratio of forces is 2 at the critical compression. The dotted lines of Figure 2 represent the forces experienced in the
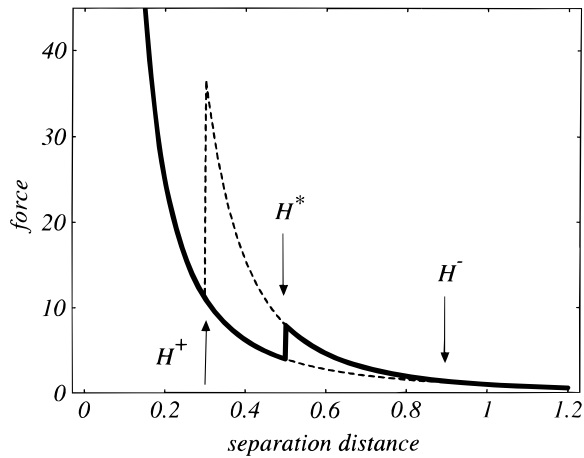
Figure 2. Force, in units of $kTL^3/(N^2a^4)$, versus separation distance, H, in units of Na^2/L, for a chain compressed by a disk of radius L in a Θ solvent. The full line is the force profile for the globally stable states, showing a discontinuity at the transition between escaped and trapped states at $H = H^*$. The dotted lines show the force profile for the metastable (locally stable) states. The trapped chain becomes supercompressed until the spinodal at $H = H^+$, and the escaped chain becomes super decompressed until the spinodal at $H = H^-$.

metastable states. The compression heights at which escape occurs from metastable and stable trapped states can be experimentally appreciable.

Squashing with a Finite-Sized, Step Disk: A Model of a Finite Wedge

As mentioned in the Introduction, in any real experiment it would be difficult to align the obstacle and the grafting surface to be exactly parallel or to exactly center the obstacle over the chain grafting point. It is thus necessary to consider the problem of a chain in a finite wedge. This problem is tractable but involves many mathematical complications which obscure the physics of the system. Here we examine a stepped system. This models a finite wedge and includes the essential physics of a wedge. The step model simplifies the analysis considerably, in the manner of the "monoblock" picture presented in the work of Brochard-Wyart et al.[17] In one direction the compressing object has a step. In the other (out of the page in Figure 3), it is infinite and planar. Figure 3 is a schematic of the geometrical parameters describing the step in this problem: D represents the height of the step and P and Q are the lengths from step to edge which are constrained by $Q + P = 2L$. The chain end is tethered directly underneath the step. Under compression, the chain has a number of choices. For weak compression, it will choose to lie entirely under the wide step. For stronger compressions it can escape. There are two choices for escape. It can escape to the left or to the right. The case of most interest occurs when $P < Q$. In this case, there is a competition between escape to the left, with a large compression penalty but a short tether, and escape to the right, with a weak compression penalty but a long tether.

Free-energy expressions for each characteristic conformation, i.e., the fully imprisoned state, and the small and large escaped states, are constructed from the compression and stretching energies (eqs 1, 2). We must account for the difference in compression energy under steps of height H and $H + D$ and the difference in stretching along the lateral dimension, where the polymer has to

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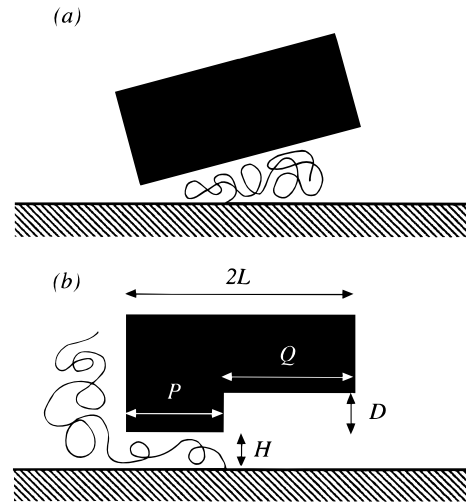

Figure 3. Geometry for the chain compressed under a wedge (a) and under our step approximation to a wedge (b). In both cases, two distinct types of escape are possible: escape to the left through the narrow passage (shown in b) and escape to the right through the wide passage.
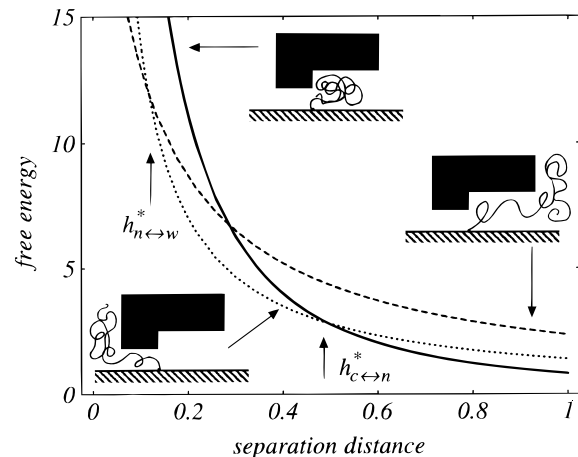

Figure 4. Free energy, F, in units of $kTNa^2/L^2$ versus separation distance, h, for confined (full line), narrow escape (dotted line), and wide escape (dashed line) for the step geometry with $d = 0.1$ and $\epsilon = 0.3$. The confined to narrow escape transition occurs at $h = h^*_{c \leftrightarrow n}$ and the narrow to wide escape occurs at $h = h^*_{n \leftrightarrow w}$.

stretch distances P and Q. The energy in units of $k_B T$ of a polymer compressed by a step disk is given by

$$F_{confined} = Na^2/(D + H)^2 \tag{11}$$

where we have assumed that all N of the chain's monomers are preferentially located underneath the larger gap as monomers under the more narrow gap would be more energetically penalized. This assumption (that partitioning of monomers between the large and small gaps is absent) is reasonable for $D > H$, where there is a significant difference in compression energy per monomer between confinement in the narrow and large gaps. However our free-energy expression (eq 11) is also valid in the limit $D \ll H$, since in that limit the confinement energy is the same under both steps. Thus expression 11 can be considered as universal.

If escape occurs through the narrow gap, the free energy of the escaped state can be calculated using the results for the flat plate for the previous section (eq 3) by the transformation $L \rightarrow P$. The number of monomers in the
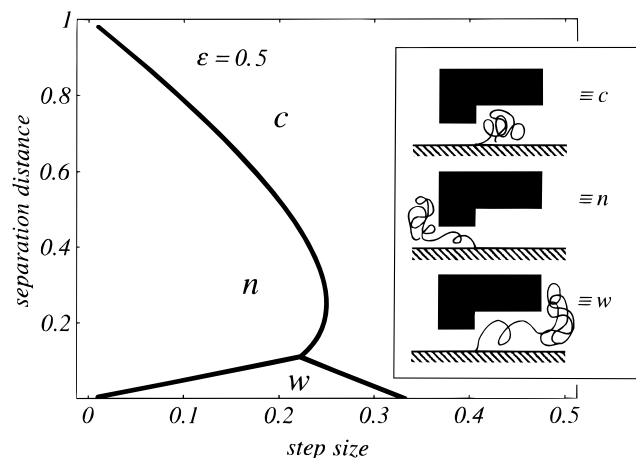
Figure 5. Separation distance, h, versus step size, d, phase diagram for a tethered chain underneath a step at fixed offset, $\epsilon = 0.5$. The three regions of the phase diagram are shown in the insets: c = confined; n = narrow escaped; and w = wide escaped. Note that for fixed d near 0.23 by steadily decreasing h we can go through transitions from an imprisoned state to a narrow escape to imprisoned and finally to a wide escape; i.e., the phase diagram is re-entrant.
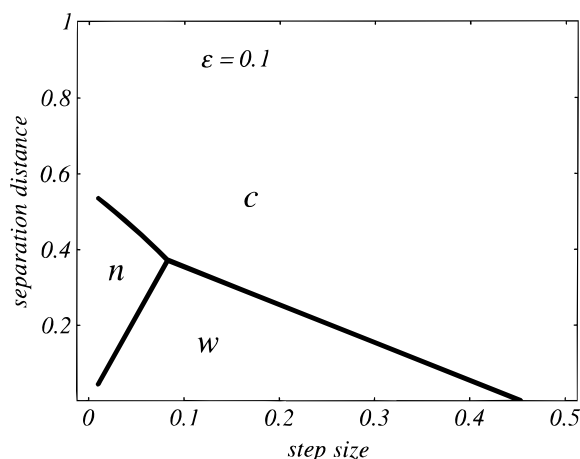

Figure 6. Separation distance, h, versus step size, d, diagram with $\epsilon = 0.1$. The regions are labeled as in Figure 5. Note that in this diagram there is no re-entrant transition.

tether is $m = HP/a^2$ and the free energy is

$$F_{escaped}^{narrow} = 2P/H \qquad (12)$$

Similarly, we can calculate the number of monomers in the tether for escape to the right, $m = Q(D + H)/a^2$. The free energy is

$$F_{escaped}^{wide} = 2Q/(H + D) \qquad (13)$$

We now need to compare the free energies of the three states (eqs 11−13). We will investigate these states as a function of the geometry of the object and the object distance from the grafting surface, using the dimensionless separation distance $h \equiv HL/(Na^2)$ and dimensionless step size $d \equiv DL/(Na^2)$. We need one other variable, ϵ, which controls the relative length of each step, so that $P = L(1 - \epsilon)$, $Q = L(1 + \epsilon)$, and $-1 < \epsilon < 1$. ϵ measures the displacement of the grafting point from the center of the obstacle and is thus referred to as the "offset."

Figure 4 shows a characteristic plot of the free energy for different states of the tethered chain as a function of compression or scaled height h, for $d = 0.10$ and $\epsilon = 0.3$. The actual state of the tethered chain at any compression,
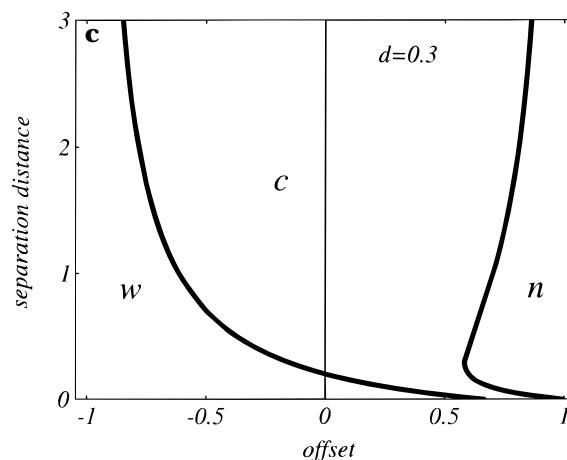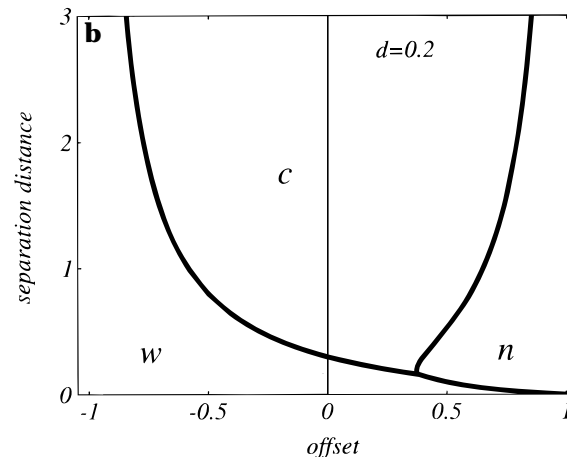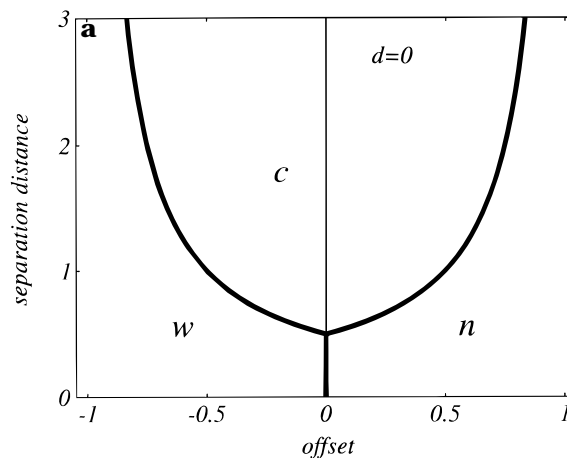

Figure 7. Three separation distance, h versus offset, ϵ, phase diagrams for different values of the step size, d. In (a) we have $d = 0$ (i.e., no step) and the diagram is symmetrical about $\epsilon = 0$. The chain undergoes a transition from a confined to an escaped state. In (b) $d = 0.2$, and we thus have a step and the phase diagram is no longer symmetrical. In (c) $d = 0.3$ and re-entrant transitions are possible.

h, corresponds to the state of lowest free energy. Consequently, from Figure 4, we predict that, as the chain is compressed, $h \rightarrow 0$, the chain is initially in the confined state until $h^*_{c \leftrightarrow n}$, where the chain escapes through the narrow passage. Then at $h^*_{n \leftrightarrow w}$, the chain escapes through the wide passage. The chain passes from trapped to narrow escape to wide escape, the intermediate narrow escape being preferable at moderate compressions as the chain suffers less of a stretching over the distance $0.7L$ than the stretching over $1.3L$, which is necessary for wide escape. However, as the chain is compressed further, the compression penalty of the tether under the region of
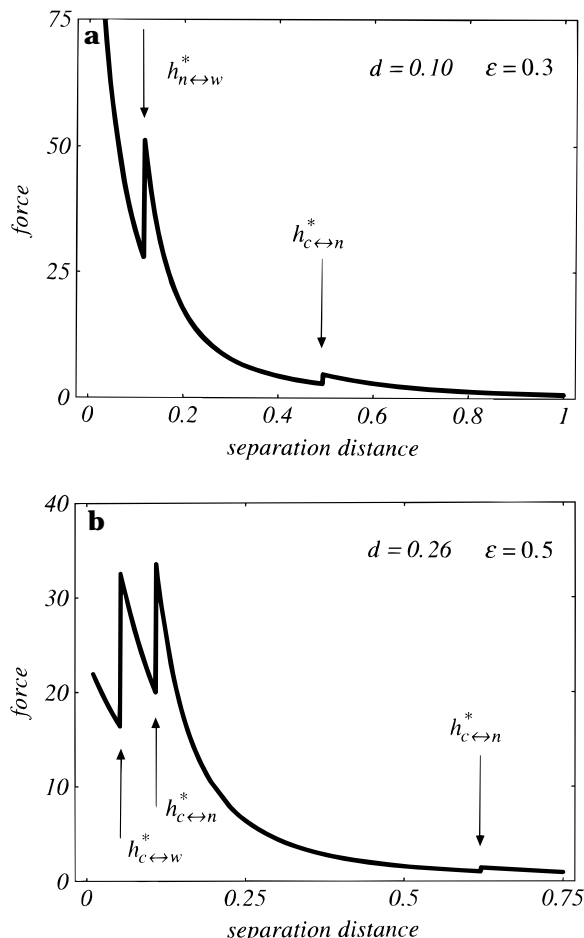
Figure 8. Two force (in units of $kTL^3/(N^2a^4)$) compression profiles for a chain compressed by a step. In (a) we have $d = 0.1$ and $\epsilon = 0.3$. In (b) $d = 0.26$ and $\epsilon = 0.5$. The transitions between the confined, c, narrow escaped, n, and wide escaped, w, states are shown by the arrows.

height h is greater than the difference in stretching energies and the chain escapes through to the wider passage of height, $h + d$, to reduce the total free energy.

The critical compression at which the tethered chain adopts a different state, $h^*_{i\leftrightarrow j}$, is found from the intersection of the lowest free energy curves, $F_i = F_j$. Three different critical compressions occur: $h^*_{c\leftrightarrow n}$ represents the compression distance for the transition of a confined chain to one that has escaped through the narrow portion of the wedge; $h^*_{c\leftrightarrow w}$ represents the transition compression from compressed to escape through the wider section of the wedge; and $h^*_{n\leftrightarrow w}$ represents the compression transition from narrow escape to wide escape. The expressions for the compression transitions are expressed in the geometrical parameters ϵ and d as

$$h^*_{c\leftrightarrow n} = \frac{1}{4(1 - \epsilon)}(1 \pm \sqrt{1 - 8d(1 - \epsilon)}) - d \quad (14)$$

$$h^*_{c\leftrightarrow w} = \frac{1}{2(1 + \epsilon)} - d \quad (15)$$

$$h^*_{n\leftrightarrow w} = \frac{1}{2\epsilon}(1 - \epsilon)d \quad (16)$$

These transition lines coupled with the condition of lowest free-energy yield the phase diagram for the system (Figure 5). Since we have three parameters in our system h, d, and ϵ, it is convenient to draw two kinds of phase diagrams. In the first kind we plot h versus d for fixed

ϵ and in the second we plot h versus ϵ for fixed d. In Figure 5 we see a typical example of the diagram for a tether offest of $\epsilon = 0.5$. For large $d \approx 0.4$ the system is always in the confined state no matter what the compression. For smaller step sizes, $d = 0.3$, the system undergoes a transition from the confined state to escape through the wide step. For smaller d still, we get a complicated re-entrant behavior where the chain is first confined, then escapes through the narrow step, is then confined again, and finally escapes through the wide slit. At still smaller step sizes, $d = 0.1$, compression results in a transition from a confined state to escape through the narrow step and finally escape through the wide step. We note that the re-entrant behavior is not universal and depends on ϵ. For $\epsilon = 0.1$ (Figure 6), we do not see re-entrant behavior and the phase diagram is slightly simpler. Indeed, by solving eqs 14–16 simultaneously it is possible to show that re-entrance occurs only in the range

$$\frac{\epsilon}{(1 + \epsilon)^2} < d < \frac{1}{8(1 - \epsilon)} \quad (17)$$

This range is only nonzero for $\epsilon > 1/3$ so that for $\epsilon < 1/3$ there is no re-entrance.

In Figure 7, we see examples of the h versus offest, ϵ, phase diagrams for fixed values of the step size d. For $d = 0$ (Figure 7a), we have a symmetrical phase diagram with transitions from confined to escaped states as the system is compressed. Naturally the critical height $h^* = 1/(2(1 - |\epsilon|))$ gets larger as $\epsilon \to 1$ and the tether is placed very close to the edge of the obstacle. For $d = 0.2$, the phase diagram is no longer symmetrical (Figure 7b) and escape via the wide step becomes favored. For $d = 0.3$ (Figure 7c), re-entrant transitions are possible for $\epsilon \approx 0.6$.

It is also of interest to examine the force versus compression curves for this system, since these can be directly measured using an atomic force microscope. In the confined, narrow escape, and wide escape situations these are respectively

$$f_{confined} = 2\frac{L^3}{N^2 a^4}(d + h)^{-3} \quad (18)$$

$$f^{narrow}_{esc} = 2\frac{L^3}{N^2 a^4}(1 - \epsilon)h^{-2} \quad (19)$$

$$f^{wide}_{esc} = 2\frac{L^3}{N^2 a^4}(1 + \epsilon)(d + h)^{-2} \quad (20)$$

As in the simple case of no step, at the critical compressions the force will show a discontinuous change. Sample force curves are shown in Figure 8.

Conclusion

In this paper we have discussed the compression of a chain in a Θ solvent by a finite-sized obstacle or disk. As in the previous studies[14-16] for the case of a good solvent, we find an escape transition from a confined or imprisoned state to an escaped state. For the Θ solvent case, the critical compression distance is $Na^2/(2L)$, which is approximately the ratio of the unperturbed chain size squared to the disk diameter. The system shows regions of metastability where there are two minima in the free energy, one escaped and one imprisoned. The limits of these regions of metastability are given by the two spinodals. These spinodals are governed in one case by the chain swelling via three-body interactions and in the other case by the finite number of monomers in a chain.

The Θ solvent problem yields similar behavior to the good solvent case, suggesting that the escape transitions studied previously may well be a fairly universal phenomenon.

In the second part of this paper, we have studied the confinement of a chain under a finite wedge. This is an experimentally important problem since in practice the two confining surfaces will not be parallel. In this system, which we have approximated by a stepped surface, there are two escape transitions possible and a relatively complicated phase diagram. This complexity arises from the competition between the three possible chain states. For the stepped system, there are also metastable states. The calculations for these states follow that for the simpler no-step system and we will not discuss them here.

There are at least two ways of investigating the transitions we have predicted here. The simplest is to perform a computer simulation. This would enable the full phase diagram for the system to be mapped out.

Experimentally the most straightforward experiment is to use a polished AFM tip and measure the force profile. The main prediction of this paper is that the force profile will show discontinuities as the chain escapes from under the tip. In the case of a poorly aligned tip, more than one discontinuity will be present.