

# A Polymer End-Tethered to a Potential Stripe: A Simple Example of an Escape Transition

E. M. Sevick and D. R. M. Williams\*

Research School of Chemistry and Research School of Physical Sciences,  
Australian National University, Canberra, ACT 0200, Australia

Received April 16, 1999; Revised Manuscript Received July 23, 1999

**ABSTRACT:** We study the problem of a single ideal polymer chain tethered to a surface at the midpoint of a repulsive potential stripe. If the potential is very weak, the chain remains unperturbed. However, as the potential is increased, the chain conformation undergoes a sudden change. The chain forms a tether to the edge of the stripe and moves most of the monomers off to the region of lower potential. This is a simple example of an escape transition previously discussed for compression of polymer chains. We show how these two systems are analogous and clear up some controversy regarding the exact form of the force versus height curve for the compressive system.

## I. Introduction

The deformation of polymer chains by externally applied forces is one of the most fundamental topics in polymer science. One example, the compression of an ideal polymer chain lodged between two infinite plates, is a classical problem which is well-understood.<sup>1,2</sup> The ideal chain resists compression in the slit because confinement reduces the chain's entropy. The free energy penalty for compression of a chain of  $N$  monomers of size  $a$  sandwiched between plates separated by a distance  $H$  is  $F \propto kTNa^2/H^2$  in the regime of moderate compression  $a \ll H \ll N^{1/2}a$ .<sup>1,2</sup> Recently a different compression problem was tackled. This is the problem of a chain tethered by one end to a surface and compressed by an obstacle, the flat end of a cylinder of radius  $R$  (Figure 1a).<sup>3–12</sup> A novel transition was predicted to occur in this system. At weak compressions the chain remains wholly under the obstacle: we refer to this completely confined chain as imprisoned. However, at a certain critical compression the chain partially escapes from underneath the obstacle by forming a stretched tether from the grafting site to the edge of the obstacle. The remainder of the chain sits outside the obstacle and avoids compression: the chain has escaped. This escape transition was predicted to be first-order; i.e., at the critical compression, quantities such as the chain size and compressive force undergo finite jumps. This transition can only occur when the obstacle size  $R$  is larger than the natural chain size  $aN^{1/2}$  but still smaller than the fully extended chain length  $Na$ . One likely place in which this transition might be seen is in atomic force microscopy experiments on single polymer chains, which are now fairly commonplace. The existence of this transition and some of the details have been confirmed by several Monte Carlo simulations.<sup>8–12</sup> Another place where escape might occur is in emulsion polymerization, where a polymer can be confined inside an oily drop, but where compression might cause escape.

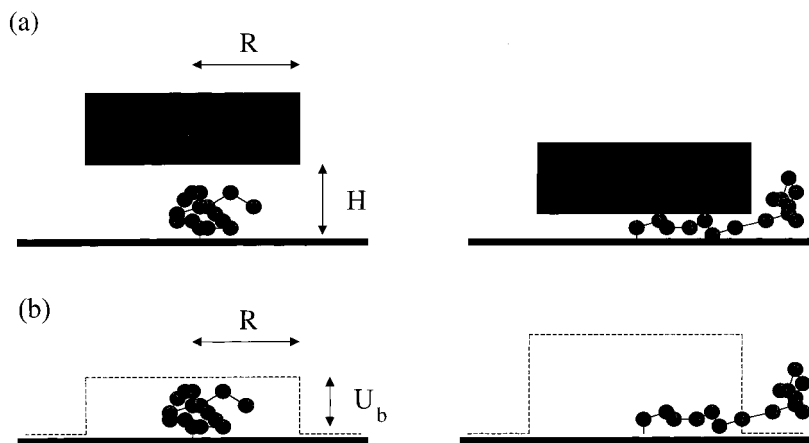
In this paper, another escape problem is presented which contains the same essential physics of the escape transition, but permits a simpler analysis. We consider a chain which is end-tethered to the center of a repulsive

potential stripe (Figure 1b). Any monomer that resides within the stripe, i.e., between  $-R$  and  $R$  from the tether point, is penalized an energy,  $U_b$ , while monomers located outside of the stripe suffer no potential energy penalty. If the energy per monomer,  $U_b$ , is small, the chain will remain confined to the potential stripe; in analogy to the compression problem, we say that the chain is imprisoned. However if  $U_b$  is made sufficiently large, the chain will form a tether, stretched to the edge of the potential stripe such that the remaining monomers will be deposited outside of the stripe. Similar to a highly compressed system, the chain has escaped.

This problem has two different motivations. First, it has recently become possible to make chemically striped surfaces with a stripe width of the same order as the effective size of a polymer chain.<sup>13–15</sup> Polymers grafted to such stripes should show the kind of transition considered here. Second, the escape transition in a striped potential is directly analogous to escape in the compression problem. Unlike the compression problem,<sup>7</sup> the partition function of a chain tethered in a striped potential can be evaluated exactly in some limits and very simply in most other cases. This is important because there have been several recent attempts to describe the escape transition in the compression problem in terms of coexistence of two phases or states. According to this, the compressive force, like the coexistence pressure, would be constant through the transition from one state (imprisoned) to another (escaped). We show in this paper that this is incorrect in the experiment where the height is the independent variable and the force is measured.

This paper is organized as follows: In the next section we describe the escape of an end-tethered chain from a potential stripe using a mean-field approach. While illustrative, this coarse-grained approach does not detail the escape transition to the extent expected in, for example, computer simulation. Thus, in section III we present a simple model consisting of a single monomer tethered to the midpoint of the stripe by an expandable spring. This model possesses a simple partition function from which thermodynamic properties such as free energy and, by analogy with the compression problem, force can be unambiguously calculated. In section IV we construct the partition function for a finite-sized exten-

\* Corresponding author. E-mail: drw110@rsphy9.anu.edu.au.



**Figure 1.** The analogy between the escape by compression and the escape from a repulsive potential stripe. In panel a the chain is compressed by a finite obstacle. At weak compressions or large slit width  $H$  (left), the chain is imprisoned, while at stronger compressions (right) it escapes. In panel b the chain is tethered to the center of a potential stripe. For a small potential,  $U_b$  (left), all monomers reside in the repulsive potential, i.e., the chain is imprisoned, while for a larger potential (right), the chain escapes.

sible chain of many monomers end-tethered to the potential stripe. From this partition function, we show that the compressive force profile (force versus slit width) has characteristics distinctly different from that expected from a pressure profile (pressure versus volume) in two-phase coexistence. In the transition region, our force profiles display a maximum rather than a flat force profile, which one might anticipate from analogy with say, gas–liquid coexistence. This is discussed in some detail in section V, where we examine the case of experiments conducted with force as the independent variable. Throughout this paper we make the simplification that the problem is one-dimensional. Thus only the trajectory in the  $x$  direction is considered and the problem becomes that of a chain tethered to a potential bump.

## II. Mean-Field Description

Similar to the compressive escape problem, a mean-field analytic calculation can provide a first description of the system. When the chain is entirely confined to the potential stripe, or it is in an imprisoned state, its Helmholtz free energy is simply given by  $F_{\text{imp}} = NU_b$ . In the escaped state the chain can form a tether of  $p$  monomers with the remaining  $(N - p)$  monomers escaped outside of the potential stripe. The free energy of this state consists of two terms: a stretching penalty for the tether,  $\alpha kTR^2/(pa^2)$ , and the energy of the tether,  $pU_b$ . Here  $\alpha$  is a numerical constant. The average number of monomers in the tether,  $p$ , is that which minimizes the chain's free energy, i.e.,  $p = \sqrt{\alpha}(R/a)\sqrt{kTU_b}$ , and the free energy of the escaped state is thus  $F_{\text{esc}} = 2\sqrt{\alpha}(R/a)\sqrt{U_b}kT$ . Neglecting fluctuations, which lead to an exchange of states, we say that the state, imprisoned or escaped, of lower free energy prevails. The critical potential at which the transition between states occurs occurs when  $F_{\text{imp}} = F_{\text{esc}}$ , or

$$U_b^* = 4\alpha kTR^2/(N^2 a^2) \quad (1)$$

One obvious signature for the transition is a discontinuous change in slope of the free energy curve. Below the transition the free energy is proportional to  $U_b$ , whereas above the transition it grows only as  $U_b^{1/2}$ . For a sharp transition, we require the potential thickness,  $R$ , to be several times the natural size of the chain,  $R_0$

$= aN^{1/2}$ , so that thermal fluctuations are unimportant. Let us set  $R = BR_0$  where  $B$  is larger than 1. The critical potential for escape is then  $U_b^* = 4\alpha B^2 kTN^{-1}$ . Note that this escape potential is very small due to the factor  $N$ . For large  $N$  it can be very much less than  $kT$ . This shows that escape can occur even for very weak potentials. What is important in this problem is not the energy per monomer,  $U_b$ , but the energy of all the monomers  $NU_b$ . A similar situation exists in the classic problem of polymer adsorption, where the energy per monomer is small but the total energy is very large.

We note one interesting point about this transition. At the critical potential it is easy to show that the number of monomers in the tether is equal to the number of monomers in the escaped part, i.e.,  $p = N/2$ , and that the stretching free energy and the change in potential energy are equal. A similar thing happens in the case of the compression problem.

## III. A Monomer on a Spring, End-Tethered to a Potential Stripe

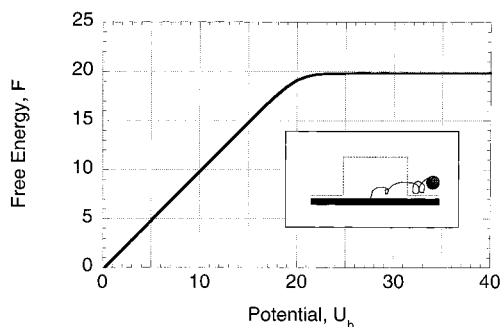
Although the mean-field calculation is useful in understanding the escape transition in a striped potential, it does not go beyond the calculations previously presented for compressive systems. To do this we need to examine the full statistical mechanics of the escaping system. In this section we do this with the very simplest case, that of one monomer, tethered to the origin by a spring of energy  $wx^2$ . The partition function for this system is

$$Z = \int_{-\infty}^{\infty} dx \exp(-\beta(wx^2 + U(x))) = 2 \int_0^R dx \exp(-\beta(wx^2 + U_b)) + 2 \int_R^{\infty} \exp(-\beta wx^2) \quad (2)$$

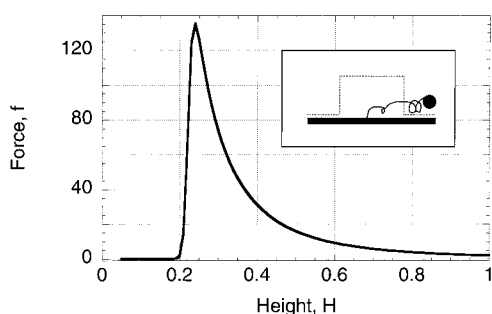
where  $\beta \equiv 1/(kT)$ . This can be evaluated as

$$Z = \sqrt{\pi/(\beta w)}(1 + \text{erf}(R\sqrt{\beta w})(\exp(-\beta U_b) - 1)) \quad (3)$$

where erf is the error function. From this partition function, all of the thermodynamic properties of the monomer-spring system can be derived. In particular, we can obtain the Helmholtz free energy  $F = -kT \ln Z$ , given in Figure 2. In all the computations we set the monomer size  $a$  equal to 1. At small  $U_b$  the monomer is imprisoned in the potential stripe and the free energy



**Figure 2.** The free energy,  $F$ , versus a stripe potential,  $U_b$ , for the one-monomer spring, end-tethered in potential stripe. The parameters used here are  $kT = 1$ , spring constant  $w = 2.0$ , and potential stripe thickness  $R = 3.0$ . For small potentials the free energy grows linearly with the potential until a critical potential of  $U_b \approx 20$  is reached. Beyond this critical repulsive potential, the spring is stretched across  $R = 3.0$  and the monomer resides outside of the repulsive potential strip. The single-monomer chain has escaped.



**Figure 3.** The force,  $f$ , versus compression,  $H$ , for the one-monomer spring, end-tethered underneath an obstacle. The parameters are the same as in Figure 2. With compression, the force increases until  $H \approx 0.25$ , where the force drops to zero, signaling the escape of the single monomer from underneath the obstacle.

is simply proportional to  $U_b$ . However, at a critical  $U_b$  the single monomer escapes from the stripe and the system free energy is attributable to the spring energy only. Thus the free energy is constant for  $U_b$  greater than the critical escape potential. For a realistic many-monomer system, a stretched tether will contain monomers and, above the critical potential, the free energy will depend on  $U_b$ . We will show this in the following section.

In the striped potential problem, there is no physical force. However, by setting the confining potential equal to  $U_b = kT a^2 / H^2$ , where  $H$  is the slit width between surface and obstacle, we can map our striped potential problem onto the compressive problem. This allows us to write the free energy as a function of  $H$ , and hence to obtain the force  $f = -\partial F / \partial H$ . With this mapping, we predict a force profile,  $f$  versus  $H$ , which has a sharp drop near the expected transition (Figure 3). The force falls to zero at strong compression, or small  $H$ , simply because the single monomer is outside of the obstacle: there are no monomers confined underneath the obstacle imposing a force upon the obstacle. It is important to note that this calculation is an “exact” one, albeit for the simplest of model systems. We have followed strictly the rules of statistical mechanics: evaluate  $Z$ , find the Helmholtz free energy  $F = -kT \ln Z$ , and then calculate  $f = -\partial F / \partial H$ . No artificial constructions are needed and statistical mechanics gives us the answer to the problem directly.

One important point should be noted. In mapping from the compression problem to the potential problem we have replaced a purely entropic free energy term by a purely enthalpic potential term. This mapping is only approximate, but from the point of view of equilibrium thermodynamics, it does not matter what the origin of the terms in the free energy are, all that matters is the free energy.

In fact, as one referee has pointed out, the case of a single monomer under compression can be solved exactly; i.e., we can evaluate the partition function. When this is done, we see no sharp escape transition, merely a smooth crossover. We will not do this calculation here, but only mention that this occurs mainly because only one monomer is involved and there is no monomer in the tether. This means that this is a very special case and one which is not relevant to the general case where there are many monomers. In some sense the results for a single monomer are spurious, because once the monomer has escaped, the tether suffers no compression penalty.

#### IV. A Long Chain End-Tethered to a Potential Stripe

The one-monomer problem is both simple and artificial and cannot be expected to capture all of the physics of a chain tethered in a repulsive potential stripe. The above calculation can be extended to two or more monomers, but only at the expense of great algebraic complexity. Instead, we take a different approach. We describe the polymer as a random walk on in one dimension. The trajectory of an  $N$ -monomer chain consists of  $N$  unidirectional steps of size  $\pm 1$ , starting from an origin which is the midpoint of the striped potential of width  $2R$ . The partition function of this finitely extensible chain is then

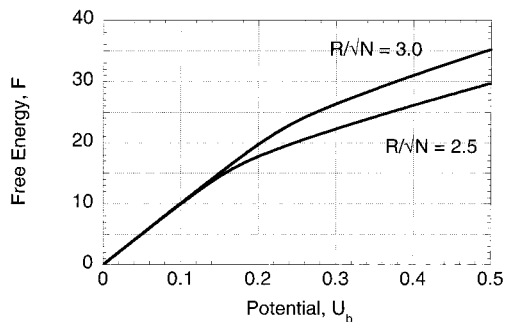
$$Z = \sum_{\text{all trajectories, } i} \exp(-\beta U_i) \quad (4)$$

where  $U_i$  is the energy of  $i$ th trajectory, equal to the sum of the energy felt by each of the  $N$  monomers. The partition function can be simplified by introducing a function  $Q_N(n, R)$ , which is the number of unbiased random walks of length  $N$  which have exactly  $n$  monomers in the region  $|x| \leq R$ . Each of these walks represents a chain of energy  $nU_b$ , so that the partition function can be recast as

$$Z = \sum_{n=0}^N Q_N(n, R) \exp(-\beta n U_b) \quad (5)$$

where the sum is over  $n$ , the number of monomers within the striped potential. This partition function permits direct evaluation of the free energy as well as the compressive force for the isomorphic compression problem.

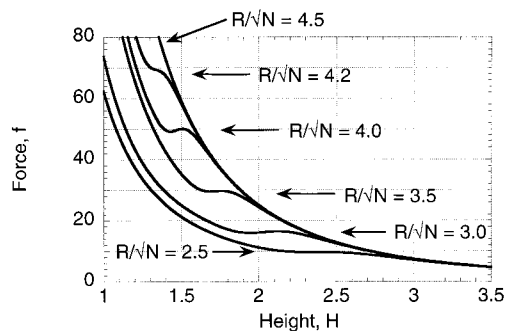
The problem is to evaluate the function  $Q_N$ . Here we take two approaches: exact (full) enumeration and stochastic (partial) enumeration. If we were able to generate each random walk configuration of  $N$  steps, we could exactly partition the count and construct the function  $Q_N$ . However, there are  $2^N$  configurations available to an  $N$  monomer chain; so for a chain of  $N = 25$  monomers there are nearly 34 million random walks. Each of these can be enumerated on a computer and an exact count of  $Q_N$  can be generated. However, for



**Figure 4.** The Helmholtz free energy,  $F$ , versus the potential,  $U_b$ , for the case of an  $N = 100$  monomer chain tethered to the midpoint of potential stripes of range (or half-thickness)  $R/\sqrt{N} = 3.0$  and  $R/\sqrt{N} = 2.5$ . Here  $kT$  is unity. The energy was evaluated directly from the partition function using  $10^8$  one-dimensional random walks to obtain  $Q_N$ . At small repulsive potential, the free energy is a linear with  $U_b$ , indicating that the chain is trapped. At higher potentials the chain escapes and the free energy increases more weakly with  $U_b$ .

larger  $N$ , such a direct and complete enumeration is not possible. In that case, we evaluate  $Q_N$  stochastically. We do this by randomly generating many random walks, say  $10^8$  chains, a mere  $1/10^{24}$  of all possible  $N = 100$  chains, and partition these into  $Q_N$ . While this does not provide an exact  $Q_N$ , we can show that a stochastic generation of  $1/30$  of all possible random walks of  $N = 25$  provides a  $Q_N$  which is indistinguishable from that constructed from exact/full enumeration. For  $N = 100$ , where we are unable to generate this fraction of walks, we have been able to show that the character of the free energy and force profiles are unchanged near the transition region and at weak compression. Only in the region of high compression, or low  $H$ , where the unbiased random walks become rare, do the profiles change with the number of random walks generated.

Once we have the function  $Q_N$ , either exactly or stochastically, we can evaluate the partition function,  $Z$ , and hence  $F$  and the force,  $f = -\partial F/\partial H$ . Figure 4 provides the free energy versus potential,  $U_b$ , for an  $N = 100$  chain for two different potential ranges,  $R$ . Like the single monomer-spring model, the free energy is proportional to  $U_b$  at small potentials, indicating that all monomers of the chain are imprisoned within the potential stripe. Above a critical  $U_b$ , monomers escape and the free energy is less sensitive to the magnitude of the potential, as there are fewer monomers residing within the stripe. Figure 5 provides the force,  $f$ , versus slit separation,  $H$ , for  $N = 100$  inextensible chains, where  $H$  is again related to the stripe potential according to  $U_b = kT a^2/H^2$ . Force curves are presented for various obstacle radii, spanning 2.5–4.5 times the natural size of the chain. At weak compressions, the chain is fully imprisoned underneath the obstacle and the force is independent of the size of the obstacle. At very strong compression, after escape takes place, the magnitude of the force profile depends on the number of monomers in the tether,  $p$ . Escape from larger obstacles requires longer tethers, more monomers underneath the obstacle, and hence higher compressive force. The transition between the imprisoned and escaped portions of the force profile is marked by a maximum in the force curve. The maximum becomes more marked with an increase in obstacle size, occurring at stronger compressions (lower  $H$ ) and higher compressive force. It is important to emphasize that these force curves were generated from partition functions and are



**Figure 5.** The force,  $f$ , versus compression,  $H$ , obtained as described in Figure 4 with the variable mapping  $U_b = kT/H^2$ . Various different potential ranges  $R$  are shown. At weak compression ( $H > 3.0$ ), all obstacles exert the same force on the chain, which has all of its monomers trapped. With further compression, the chains partially escape from the smaller obstacles, first, and escape from progressively larger obstacles at higher compressions. The escape transition is marked by a departure from the obstacle-independent (weak compression) curve with an S-shaped force profile, which exhibits a local maximum in the force. This local maximum is particularly evident for obstacles which are 3–4 times the natural size of the chain. Once escaped, the larger obstacles require a larger compressive force, as there are more monomers in the stretched tether.

thus unambiguous. Errors associated with a stochastic (partial) evaluation of  $Q_N$  are minimal. We have shown that the  $R = 2.5, 3.0$ , and  $3.5$  force profiles are unchanged when the number of unbiased random walks used to generate  $Q_N$  are reduced from 100 to 15 million. There are some changes to the force curves for the larger radii obstacles ( $R = 4.2$  and  $4.5$ ) at strong compression, and these variations are not correlated with the number of random walks generated. This occurs as an escaped chain with only a few  $p$  tether monomers within  $R$  of the tether point and the remaining monomers located outside of the  $R$  is rarely sampled in our unbiased generation of random walks. Nevertheless, the character of the curves, namely the maximum, does not change.

## V. Force as the Independent Variable

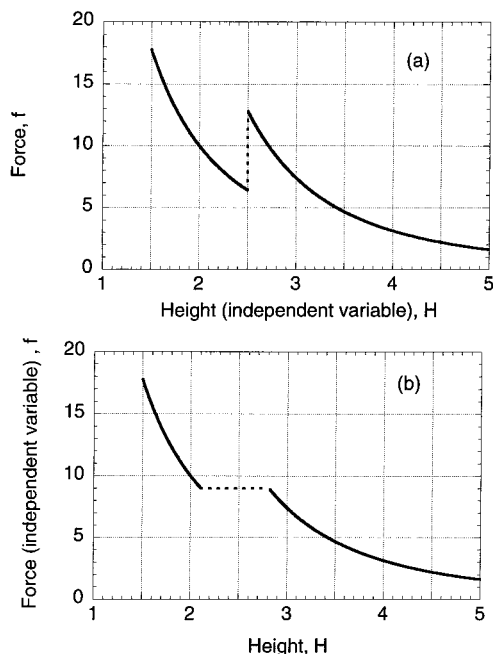
Our motivation for studying this system has been to examine a real experimentally feasible system (a polymer tethered to a stripe), and to clear up some issues surrounding the more complicated compressive system. In particular, by choosing  $U_b = kT a^2/H^2$  we can map one problem onto the other. This is particularly important as there is some confusion concerning the escape transition in compressive systems. The original predictions<sup>3–6</sup> of this transition were based upon simple mean-field calculations, and most of the conclusions have been confirmed by more recent Monte Carlo simulations.<sup>8–12</sup> However, Monte Carlo simulations of this system suffer from a major drawback, common to all first-order transition problems. This is the fact that we have a system with two states, “imprisoned” and “escaped”, with a barrier between them. This energetic barrier is attributed to the stretching free energy of the tether. An imprisoned chain needs to stretch beyond the obstacle to see that escape is favorable, and this can cost a large amount of free energy. This means that the system often becomes trapped in one of the two states. Thus, Metropolis-based Monte Carlo simulations, where successive configurations are made by attempted moves on only one or a few monomers, must be run over very many configurations in order to see the transition.

Inevitably, in an attempt to speed up the collection of data, parameters are chosen such that the barrier is small. This of course leads to a significant washing out of the transition and, in particular, to a removal of any jumps in the force curve. This has led several authors to state in preprints that there are no jumps in the force versus compression curves. In particular there have been attempts to draw an analogy between the escaping system and a system with coexisting phases, the most usual one being the liquid–gas coexistence of a fluid in a closed container. The conclusions from this kind of analogy have led to the prediction of a flat region of the force versus compression curve, i.e., near the transition the force is independent of compression. In particular, even when the Monte Carlo data show a maximum in the force curve, there have been attempts to apply a Maxwell construction to the data and to give a flat force curve.

This is not what is predicted by the early theories, nor is it what is seen in exact calculations of the compression problem<sup>7</sup> or in the potential problem studied here. What has been done here and in recent work by Ennis et al.<sup>7</sup> is to examine the problem from the point of view of classical statistical mechanics, which gives a unique prescription for finding the correct answer. We calculate the partition function,  $Z$ , at fixed  $H$ , find the Helmholtz free energy  $F = -kT \ln Z$ , and then calculate the force  $f = -\partial F/\partial H$ . This procedure does give, correctly, a maximum in the force versus height curves, and no spurious Maxwell constructions are needed.

However, this does not entirely settle the matter, since in principle there are two possible experiments that can be conducted. In one scenario, which we refer to as experiment A, the height of the obstacle is controlled and the force or other quantities are measured; i.e., the height is the independent variable. Alternatively in experiment B, a fixed force is applied, and the other quantities, including  $H$ , are measured: in this experiment, force is the independent variable. Case B is in fact the case of most importance to some AFM experiments, where it is usual to fix the force rather than the displacement. In all cases studied thus far, by mean-field theory, partition function methods, and Monte Carlo simulation, case A is used. In this case the Helmholtz free energy,  $F = U - TS$ , is the appropriate thermodynamic potential, and a maximum in the force curve is both predicted and seen in simulation and from the partition function. Case B clearly is different, since a maximum in the force curve corresponds to a multivalued function when seen with force as the independent variable. In case B, the appropriate potential is the Gibbs free energy,  $G$ , which is given by  $G = F + Hf$ . Now, of course, for most of the force curve both potentials give the same answer for the force versus  $H$  relation, since  $f = -\partial F/\partial H$  and  $0 = \partial G/\partial H = \partial F/\partial H + f$ . However, near the transition this cannot be the case.

What happens here can best be resolved by considering the specific example of the escape under compression using the mean-field approach. The Gibbs free energy of the imprisoned state is  $G_{\text{imp}} = kTNa^2/H^2 + fH$ . With  $f$  fixed this needs to be minimized over  $H$ , to give  $H_{\text{imp}} = (2NkTa^2/f)^{1/3}$  and a Gibbs free energy of  $G_{\text{imp}} = 3(NkTa^2 f^2/4)^{1/3}$ . In the escaped state the Gibbs free energy is  $G_{\text{esc}} = pkTa^2/H^2 + kTR^2/(pa^2) + fH$ , where we have set the parameter  $\alpha$  equal to 1. This needs to be minimized over the number of trapped monomers,  $p$ ,



**Figure 6.** The force versus compression curve obtained in the mean field approximation under two different conditions: (a) where height is the independent variable and (b) where force is the independent variable. The full lines are the predicted force vs compression curves in each case, while the dotted lines are used as guides to emphasize the jump in the measured quantities, either force in part a or height in part b. This coarse grained mean-field treatment was accomplished with  $kT = 1$ ,  $a = 1$ ,  $N = 100$ , and  $R = 20$ .

and the height,  $H$ , giving  $p = HR/a^2$  and  $H_{\text{esc}} = (2RkT/f)^{1/2}$ . The final form of the Gibbs free energy when escape takes place is then  $G_{\text{esc}} = (8fRkT)^{1/2}$ . Under conditions of fixed given force, the system wants to minimize the Gibbs free energy. The imprisoned and escaped configurations have different dependencies on  $f$ ; i.e., they grow as  $f^{2/3}$  and  $f^{1/2}$ , respectively. Thus, as the force is increased, we expect a jump from imprisoned to escaped. This occurs when  $G_{\text{esc}} = G_{\text{imp}}$ , i.e., at a critical force of

$$f^* \approx kT \frac{R^3}{N^2 a^4} \quad (6)$$

Here the numerical factor refactors have not been included, as they have been approximated in the free energy contributions. When this critical force is reached, the system suddenly jumps from imprisoned to escaped. This results in a sudden decrease in the height, which can easily be calculated to be

$$\delta H = \frac{9}{64} Na^2 R^{-1} \quad (7)$$

This jump could be a considerable fraction of the initial chain radius.

We can use these results and the earlier results with  $H$  as the independent variable to plot  $f$  versus  $H$  curves for the two cases (Figure 6). Note that the force versus height curve shows a sudden jump in the case where force is the independent variable (Figure 6b). There is no flat region in the curve, and no coexistence. The analogy between this system and the liquid–gas system is false. This is basically because in the liquid–gas system coexistence arises from cooperative effects—the system can place some atoms in a gas phase and some

in the liquid phase to lower the total free energy. In the escape system the chain is either imprisoned or escaped, and it makes no sense to put some of the chains in one state while the remainder are in another. Essentially, the system chooses which state has the lowest free energy and puts all the chains there. This result is modified somewhat by thermal fluctuations, where states of high energy can be populated,<sup>7</sup> but this is different from coexistence.

## VI. Summary

In this paper we have discussed the escape transition which occurs when a polymer is tethered to a potential stripe. This is a system which is of some experimental interest due to recent advances in making patterned surfaces on the appropriate lengthscale, of order 1000 Å. The reader should, however, note that our study is a very simplified version of the real experimental systems. Often these involve grooved or rough surfaces and often the chains are only weakly adsorbed so that not all the monomers feel the potential. Apart from being a possible experimental system, the case of a polymer on a potential stripe is a simple example of an escape transition, which previously has been discussed for the compression problem. The potential problem has the advantage of containing the essential physics of the more complicated system, but in a much simpler form, allowing some exact analysis. This has enabled us to clear up some of the controversy and confusion that has surrounded the computer simulation of this system. We note finally that the problem of a polymer in a potential contains a lot of rich and interesting physics, some of which has been discussed recently.<sup>16,17</sup>

In this paper we have concentrated on the case of a polymer confined in one-dimension by a potential. A referee has pointed out three other cases where escape either does or might occur. One is in emulsion polymerization, where a polymer can be confined inside an oily drop, but where compression might cause escape. Another is the familiar case of a bidisperse polymer brush, where a small number of longer chains can escape from the main section of the brush and lie outside it.<sup>18</sup> A third is in the case of colloids, which are often

coated with polymers in order to stabilize the system. In this case only the average distance between particles is kept constant, since the density of particles is fixed. There is the possibility in this case of a phase separation occurring due to the escape transition, in particular due to the negative slope in the force versus height curves seen in parts of Figure 5. A precise calculation of this is beyond the scope of this paper, but it does suggest an interesting effect—namely, that grafted polymers can cause an effective attraction between colloidal particles.

**Acknowledgment.** D.R.M.W. acknowledges support from an ARC QEII. The authors thank Dr. Andrei Milchev for suggesting the striped potential problem several years ago. He is also thanked for providing preprints<sup>11,12</sup> prior to publication.

## References and Notes

- (1) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, 1979.
- (2) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: New York, 1986.
- (3) Subramanian, G.; Williams, D. R. M.; Pincus, P. A. *Europhys. Lett.* **1995**, *29*, 285.
- (4) Subramanian, G.; Williams, D. R. M.; Pincus, P. A. *Macromolecules* **1996**, *29*, 4045.
- (5) Williams, D. R. M.; MacKintosh, F. C. *J. Phys. 2* **1995**, *9*, 1417.
- (6) Guffond, M. C.; Williams, D. R. M.; Sevick, E. M. *Langmuir* **1997**, *21*, 5691.
- (7) Ennis, J. P.; Sevick, E. M.; Williams, D. R. M. Preprint.
- (8) Jimenez, J.; Rajagopalan, R. *Langmuir* **1998**, *14*, 2598.
- (9) Jimenez, J.; Rajagopalan, R. *Eur. Phys. J. B* **1998**, *5*, 237.
- (10) Arteca, G. C. *Int. J. Quant. Chem.* **1997**, *65*, 219.
- (11) Milchev, A.; Yamakov, V.; Binder, K. Preprint.
- (12) Milchev, A.; Yamakov, V.; Binder, K. Preprint.
- (13) Heier, J.; Kramer, E. J.; Walheim, S.; Krausch, G. *Macromolecules* **1997**, *30*, 6610.
- (14) Rockford, L.; Liu, Y.; Mansky, P.; Russell, T. P.; Yoon, M.; Mochrie, S. G. *J. Phys. Rev. Lett.* **1999**, *82*, 2602.
- (15) Pereira, G. G.; Williams, D. R. M. *Phys. Rev. Lett.* **1998**, *80*, 2849.
- (16) Sommer, J. U.; Blumen, A. *Phys. Rev. Lett.* **1997**, *79*, 439.
- (17) Sommer, J. U.; Blumen, A. *J. Chem. Phys.* **1996**, *105*, 6008.
- (18) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1989**, *22*, 853.

MA990589Q