

Compression and Escape of a Star Polymer

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The problem of a polymer confined within a slit is a classic problem that is generally well understood.^{1,2} More recently, researchers have explored a related problem: a chain, end-tethered to a surface and compressed by an obstacle, e.g., the flat end of a cylinder, whose size is not much larger than the natural dimension of the chain.^{3–13} When compressed weakly, the chain does not “see” the edge of the compressing obstacle, it deforms uniformly, and the force that the chain imposes on the obstacle grows monotonically with compression. However, beyond a critical compression, the chain can reduce its energy by forming a stretched umbilical tether from the grafting point to the edge of the disk so that many of the monomers in the chain can “escape” from underneath the compressing obstacle. Upon such an escape, the compressive force decreases abruptly, signaling the reduction in the number of monomers trapped beneath the cylindrical obstacle. Depending upon the radius of the compressing cylinder relative to the natural size of the chain, there can be a significant energetic barrier to escape, arising from the extra energy that is needed to stretch the chain to the edge of the obstacle. In this case, the escape transition can be described as a first-order transition between “states” of a chain: imprisoned and escaped. This escape transition has been described using theory and computer simulation, but has not yet been shown experimentally. However, it should be possible to show this escape transition by compressing a surface-tethered chain with the polished tip of an atomic force microscope (AFM).

In this note we describe a more complicated and somewhat different problem: the compression of a star polymer of equisized arms whose center is fixed or tethered to the surface. Using a simple Flory approach, we show that multiple escape transitions occur and that imprisoned and escaped arms can coexist when the star polymer is compressed. We consider a star polymer of M arms where each arm is comprised of N statistical monomers, each of size a . The flat end of a cylinder of radius L is centered on the star center at a controlled distance H above the grafting surface. We refer to H as the compression distance: H is small when the system is strongly compressed and is large when the system is weakly compressed. We are interested in the escaped state of the star polymer as well as the force that the star polymer exerts on the cylinder when a given compression, H , is applied. In the simplest picture of an ideal chain, i.e., when there are no excluded volume interactions among the monomers in the chain, all arms of the star will escape simultaneously at a critical compression. This is because each arm of N monomers acts independently and the escape transition is identical to that of a single end-tethered chain of N monomers. However, when excluded volume interactions are included, then each arm will escape at a different com-

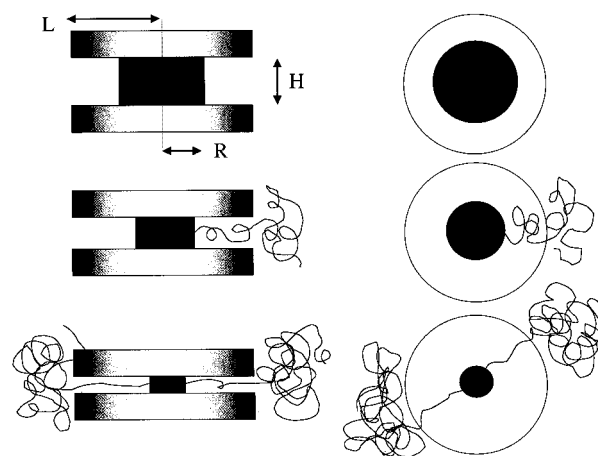


Figure 1. Schematic of a star polymer centrally tethered between the gap of size H between the faces of two cylinders of radius L . On the left is the side view while on the right is a top view for three different compressions, H . At weak compression (top), the arms of the star polymer are wholly confined between the cylinder faces and the radius of the confined polymer or nucleus (shown in dark) is R . Above the first critical compression (middle), one arm of the chain partially escapes, forming an umbilical tether reaching from the nucleus to the edge of the obstacle and an escaped plume. The size of the nucleus normally increases with compression; however, upon arm escape the nucleus radius decreases. A second critical compression or second arm escape is pictured at the bottom. Further compression will lead to additional escapes until all arms have escaped and the nucleus disappears.

pression. We can imagine $M + 1$ different “states” of the chain: (0) a fully confined state where all arms of the chain are underneath the obstacle; (1) a partially escaped star where one arm has escaped from underneath the obstacle and the others remain imprisoned; (2) a star with two of M arms have escaped, and so forth; as well as (M) a fully escaped state where all arms have escaped from beneath the obstacle. This is a simple compression problem where multiple escape transitions arise from the architecture of the chain. Unlike the escape of an end-tethered linear polymer, it is possible for escaped arms to coexist simultaneously with confined arms.

Our aim is to describe qualitatively the compression of a star polymer and the expected multiple escape transitions. We consider the star polymer, when fully confined between the compressing obstacles of radius L , to form a nucleus of monomers of size R which is smaller than L , as shown in Figure 1. With weak compression, the radial extent of the star (or radius of the nucleus) increases so as to maintain a balance between the stretching energy of the arms and the excluded volume energy of the monomers. But at a critical compression, one arm can escape, forming a highly stretched radial tether, removing its monomers from the nucleus and distributing these between the tether and an escaped plume. As there are fewer monomers in the nucleus, its size, R , is reduced abruptly upon escape of the arm. Further compression will shuffle the monomers of this escaped arm from the nucleus and umbilical tether to the escaped plume. The radius of the nucleus will again increase with further

compression until, at a subsequent critical compression, another arm forms a radial tether and an escaped plume. These individual arm escapes happen repeatedly with further compression until all arms have partially escaped from underneath the obstacle. All partially escaped arms are identical, i.e., they have the same average distribution of monomers in nucleus, tether, and plume, irrespective of the compression at which their escape took place.

We can express the Helmholtz free energy of the star polymer and predict the force profile for squashing the star with a finite-sized cylindrical obstacle. We do this by writing down the minimal free energy of each of the $M + 1$ states, $F_j(H)$ where the subscript refers to the number of escaped arms, $0 < j < M$, and by assuming that the chain adopts the lowest free energy state. Herein, all energies are in units of $k_B T$. The compressive force profile is then $f(H) = -\partial F_j(H)/\partial H$, where j denotes the state with the lowest energy. Implicit to the energy equations which we use is the assumption that chain fluctuations occur within each state; however, we ignore the possibility that these fluctuations can lead to different states. This has been shown to be a reasonable assumption for the escape of end-tethered chains in the limit of large obstacle size, relative to the natural chain size.^{12,13}

The state energies are constructed from three contributions: excluded volume, stretching, and compression. The excluded volume contribution is cast in terms of binary interactions among monomers, written in the form $\omega c^2 V$ where ω is the binary interaction energy and c is the concentration of monomers in the volume V . The stretching contribution is taken to be Gaussian: $dx^2/(na^2)$ where d is the dimensionality of the stretching, i.e., $d = 1$ for a unidirectional stretched tether and $d = 2$ for stretching in two directions within the nucleus, and x is the distance stretched by the linear arm of n monomers. Finally, the compression energy of an n -monomer chain confined to a slit of width H is of the form na^2/H^2 . In this first approach to the problem, we make the simplifying assumption that the monomer density within the nucleus is homogeneous; that is, we neglect that the monomer density falls from the center to the edge of the nucleus. Each of these energy contributions, expressed for each arm, whether confined or escaped, yields the energy expressions for each state.

For a star with all arms confined, we have

$$F_0(H) = \frac{\omega(MN)^2}{R^2 H} + M \frac{2R^2}{Na^2} + M \frac{Na^2}{H^2} \quad (1)$$

where all MN monomers of the star are within the nucleus of volume $R^2 H$. The binary interactions promote large R but each arm of N monomers pays a radial stretching penalty which limits the size of the nucleus. To minimize free energy, the nucleus adopts a squared radial extent of $R^2 = Na\sqrt{\omega NH}$.

For a star with M_e arms partially escaped, we consider all partially escaped arms to have P monomers in the nucleus of radius R , Q monomers in the umbilical tether stretched unidirectionally from R to L , and the remaining $N - P - Q$ monomers in the escaped plume. The free energy is then

$$F_{M_e}(H) = \frac{\omega(MN - M_e(N - P))^2}{R^2 H} + (M - M_e) \frac{2R^2}{Na^2} + M_e \frac{R^2}{Pa^2} + M_e \frac{|L - R|^2}{Qa^2} + \left(M_e \frac{3Q}{a^2} \left(\frac{\omega a^2}{2|L - R|H} \right)^{2/3} \right) + (MN - M_e(N - P - Q))a^2/H^2 + \frac{5}{2} M_e \left(2^3 \left(\frac{w}{a^3} \right)^2 (N - P - Q) \right)^{1/5} \quad (2)$$

The first three terms are simply the excluded volume and stretching contributions associated with monomers residing in the nucleus. These arise from the N monomers of each of the imprisoned arms and the P monomers from the partially escaped arms. The fourth term is the unidirectional stretching of the Q -tether. The fifth term is the combination of the excluded volume interactions and lateral stretching of each tether or $\omega Q^2/(|L - R|HT) + T^2/(Qa^2)$, where the volume of the Q -tether is assumed to be that of a rectangular cube of length $L - R$, height H , and thickness T which is taken as that which minimizes the energy of the entire star, i.e., $T = Q(\omega a^2/2|L - R|H)^{1/3}$. The sixth term is the compression energy associated with the fully confined arms of N monomers and the $P + Q$ monomers of the escaped arms. The last term is the combined stretching and binary interaction energies associated with the $m = N - P - Q$ monomers of each arm which has escaped. This term is simply $\omega m^2/R_0^3 + 3R_0^2/(ma^2)$ for each plume, where the size of the escaped plume, R_0 , is taken to be that which minimizes the energy of the entire star molecule. The distribution of monomers in the escaped arms, P and Q , and the radial extent of the imprisoned arms, R , adopt values which minimize eq 2.

Finally, for a star with all arms partially escaped, there is no nucleus and each arm is comprised of a Q -tether stretched a distance L and an escaped plume of $N - Q$ monomers. The free energy is thus

$$F_M(H) = M \left(\frac{3Q}{a^2} \left(\frac{\omega a^2}{2LH} \right)^{2/3} \right) + \frac{L^2}{Qa^2} + \frac{Qa^2}{H^2} + \frac{5}{2} \left(2^3 \left(\frac{w}{a^3} \right)^2 (N - Q) \right)^{1/5} \quad (3)$$

The first term is the combined binary interaction and lateral stretching energy of the Q -tethers and the second term is the radial stretching of the tethers from the center of the cylinder to its edge. The third term is the compression energy of the Q monomers beneath the cylinder. The last term is the energy of the escaped portion, cast similarly to that of eq 2. The number of monomers within the tether, Q , will assume a value which minimizes eq 3. Implicit to eqs 1–3 is the assumption that individual tethers and escaped plumes do not interact with monomers in other tethers and plumes and that the arms “feel” one another only through interchain interactions which occur in the nucleus.

It is convenient to recast the distances L , R , and H in terms of the ideal size $R_g \approx \sqrt{Na}$ of an arm of the star, i.e., $l = L/(\sqrt{Na})$, $r = R/(\sqrt{Na})$, and $h = H/(\sqrt{Na})$, and to express the number of monomers in the tether and plume as fractions of arm length, i.e., $p = P/N$ and $q = Q/N$. Letting $\psi = \sqrt{N\omega}/a^3$ quantify the excluded

volume energy, eqs 1–3 become

$$F_0(h) = \frac{\psi M^2}{r^2 h} + 2Mr^2 + MH^2 \quad (4)$$

$$F_{M_c}(h) = \frac{\psi(M_c + pM_e)^2}{r^2 h} + 2M_c r^2 + \frac{M_e r^2}{p} + M_e \frac{|l-r|^2}{q} + 3M_e q \left(\frac{\psi}{2|l-r|h} \right)^{2/3} + \frac{M_c + (p+q)M_e}{h^2} + M_e \frac{5}{2} (2^3 \psi^2 (1-p-q))^{1/5} \quad (5)$$

$$F_M(h) = M \left(3q \left(\frac{\psi}{2lh} \right)^{2/3} + \frac{l^2}{q} + \frac{q}{h^2} + \frac{5}{2} (2^3 \psi^2 (1-q))^{1/5} \right) \quad (6)$$

The values p , q , and r which minimize the free energy are found either analytically or numerically using a quasi-Newton minimization routine.¹⁴ When using the numerical method, it is important to check that the values are global rather than local minima. We do this by evaluating the free energies for thousands of randomly chosen values of p , q , and r and comparing those values with the energy found numerically.

We have minimized each of the state energies, eqs 4–6, with respect to the size of the nucleus, umbilical tether, and escaped plume; the values of these quantities which are associated with the minimal energy state provide a “first picture” of the state of the star polymer throughout the compression process. Figure 2 is the fraction of MN monomers of a 3-armed star distributed in the nucleus, umbilical tether, and escaped plume as a function of dimensionless compression, $H/(\sqrt{Na})$. Each discontinuity in the distribution is associated with the escape of an arm of the star polymer. The first arm escapes at $H \approx 0.223R_g$ as noted by the decrease in the fraction of monomers in the nucleus from $p = 1$ and the sudden appearance of monomers in the umbilical tether and escaped plume. Subsequent escapes occur at smaller compressions $0.19R_g$ and $0.05R_g$, where all arms have escaped and there are no confined arms beneath the cylinder. Between escape transitions, the number of monomers in the nucleus does not change significantly with compression. However, the monomers in the umbilical tether are continuously fed to the escaped plume with compression: i.e., the tether becomes more stretched with compression. The dribbling of monomers from the tethers to the escaped plumes becomes more significant with each subsequent escape transition. Figure 3 gives the size of the nucleus, or radial extent of the confined arms, as a function of compression for the same three-armed star polymer. With each escape transition, the radius of the nucleus decreases discontinuously in accord with the loss of monomers associated with an escape of an arm. Between transitions the nucleus size increases with compression as one would expect for a roughly constant number of monomers which suffer binary excluded volume interactions.

Figure 4 is the force profile, $-\partial F/\partial H$ vs $H/(\sqrt{Na})$ for the same $M = 3$ -armed star where $L/(\sqrt{Na})$ and $\psi = 20$, calculated from the minimum of the state energies, eqs 4–6. Again, each discontinuous drop in the compressive force marks the escape of a single arm. Although we do not picture it here, with smaller cylindrical radius and binary interaction term, it is

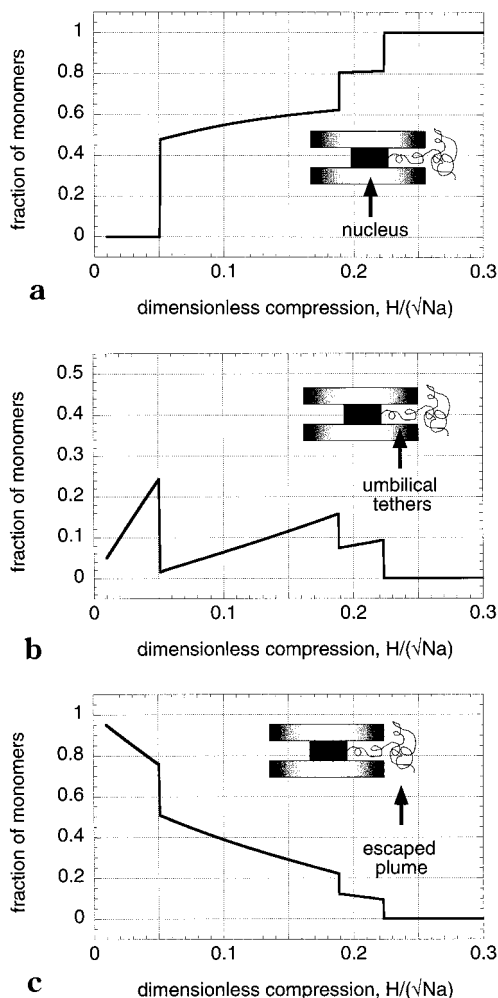


Figure 2. Fraction of monomers of a three-armed star distributed in (a) the nucleus, (b) the umbilical tether, and (c) the escaped plume, as a function of dimensionless compression, H/\sqrt{Na} . The radius of the compressing cylinder is $L/(\sqrt{Na}) = 5$ and $\psi = 20$.

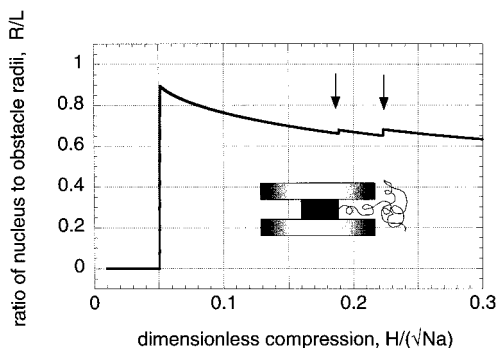


Figure 3. Scaled radial extent, R/L , of the confined arms of a three-armed star vs dimensionless compression, $H/(\sqrt{Na})$, as per Figure 2. The arrows indicate the escape of the first arm at $H = 0.223R_g$ and a second arm at $H = 0.19R_g$.

possible to construct equilibrium force profiles which contain fewer discernible escape transitions than arm number, indicating that arms may escape at or nearly at the same compression. Indeed, in the limit of $\omega = 0$ where binary interactions are absent and the arms of the chain are ideal, all arms will escape at the identical compression. Likewise, we have also constructed equilibrium profiles for larger cylindrical radii and we find that as expected the escape transitions occur at much larger compressions (smaller H). For very large cylindri-

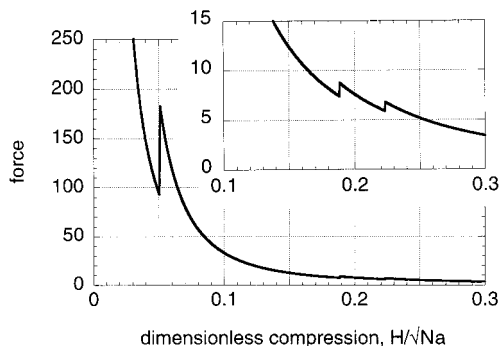


Figure 4. Compressive force, f , in units of $k_B T L^3 / (N a^2)$, vs dimensionless compression, $H / (\sqrt{N} a)$, as per Figure 2. Note that to achieve escape of the last arm, a large compression force must be applied and that escape of the first few arms occurs at lower compressive forces, on the order of piconewtons.

cal radii escape occurs at compression distances on the order of a statistical monomer size—which is experimentally not discernible. That is, for large $L \gg R_g$, escape does not take place. For $L = 5R_g$ (Figures 2–4), the last arm escapes at $H \approx 0.05R_g$. Depending upon the arm length of the star, this separation can also correspond to a monomer size and may not be experimentally accessible. The free energy equations are not appropriate at this length scale and the result cannot be interpreted in terms of arm escape.

Before closing, we relate these predictions to some practicalities of possible AFM experiments. First, it is important to emphasize that these predictions are for chains at equilibrium where thermal fluctuations which lead to escape or retraction of an arm have been ignored. Several simulations which construct the average compressive force of an ensemble of finite-sized chains at fixed compression show that fluctuations between states will “blur” the transition.^{10,11,13} That is, the equilibrium force profile will not be discontinuous as shown here and in other mean-field treatments. However, an exact calculation of a finite-sized chain’s partition function shows unambiguously that the escape transition occurs, it is marked by a maximum and minimum in the force profile, and that this transition becomes more sharp as the size of the chain increases.^{13,15} Furthermore, Langevin simulation of the dynamics of finite-sized chains shows, not surprisingly, that the compressive force changes abruptly upon escape or retraction.¹⁶ Thus, in theory, the escape transition should be evident in experiment. However, what about the practicality of the experiment? It is important to emphasize that the geometry which we have imposed in this paper is experimentally inconvenient. That is, it is difficult to center an AFM tip exactly over the fixed center of a star and to maintain parallelism between the grafting surface and tip surface. However, as demonstrated in a previous paper, escape transitions are still predicted to occur in such nonaligned geometries although it is considerably more difficult to predict at what compression escape will first occur.⁶ Escape transitions are predicted to be absent when the compressing surface is not flat but curved, as in a spherical tip.⁵ We have not considered surface roughness; however, one might reasonably argue that surfaces be smooth on the length scale of a few statistical monomers. Thus, we might anticipate that in practice, the AFM tip be polished flat. Finally, the magnitude of our predicted compressive forces are on the order of or $1/\sqrt{N}(L/(\sqrt{N}a))^3$ or β/\sqrt{N} pN since kT/a is roughly a piconewton. These magni-

tudes are comparable to the range of forces accessible in AFM experiments. As shown in Figure 4, changes in the forces due to arm escape are also of this order.

In summary, we have shown with this simple treatment that polymer architecture can result in multiple escape transitions. These transitions are characterized by a sharp decrease in the measured force with compression and correspond to the partial escape of arms of a center-tethered star polymer. At any given compression, partially escaped arms coexist simultaneously with confined arms. In this first approach, the simplest of descriptions is used; that is, a simple Flory description is used and we assume a homogeneous monomer distribution within the nucleus. This last assumption is contrary to what one might expect for star molecules. These assumptions can be lifted and the numerical approach used here still employed. For example, we can alternatively employ an approximate scaling approach or “blobology” instead of the Flory approach, as has been done in the simpler end-tethered squashing problem.^{3,4} However the adoption of blobology would not change the qualitative results as can be demonstrated by redoing the end-tethered problem in Subramanian et al.^{3,4} using the Flory approach. We acknowledge that by using the size R of the nucleus as a minimization variable (rather than performing a functional minimization to find the density distribution which in turn provides R) we imprecisely predict the size of the nucleus, R . However, as long as the radius of the compressing cylinders is sufficiently large, i.e., we choose $L > R$, then the inarguable qualitative results will remain the same: compression will result in multiple escapes and with each partial escape of an arm, the nucleus will decrease with size. It is possible to construct more rigorous descriptions of this problem, as for example in the evaluation of partition functions or stochastic evaluation using Monte Carlo simulation. However, these should give roughly similar results to those presented here, with the exception that each transition will be less sharp, particularly as the ratio of chain to obstacle size decreases.^{12,13}

References and Notes

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