ESCAPE TRANSITION OF A COMPRESSED POLYMER MUSHROOM UNDER GOOD SOLVENT CONDITIONS

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PACS 36.20.-r
PACS 36.20.Ey
PACS 82.45.+z

Abstract

The escape transition of a flexible polymer chain of chain length $N$, endgrafted at a hard wall and compressed by a piston of radius $R$, is studied by Monte Carlo simulation and by phenomenological arguments. In contrast to previous theories which have predicted a jump in the force $f$ at a critical value $H_{t}$ of the height $H$ of the piston above the wall, we find that the transition (which is sharp only for $N \to \infty$) is characterized by a flat region of $f$ in the $f$ vs $H$ isotherm, i.e. a jump in the height occurs at the transition from $H_{\text{esc,t}}$ to $H_{\text{imp,t}}$, with $(H_{\text{imp,t}} - H_{\text{esc,t}})/H_{\text{esc,t}} \approx 0.26$.

Deformation of polymers at interfaces by applied forces occurs in the context of colloid stabilization, biopolymers at cell membranes, interaction between polymers and AFM tips, etc.\textsuperscript{1,2}. Due to their flexibility, the polymer chains may undergo conformational transitions induced by such forces. Much recent interest has found the prediction\textsuperscript{3-7} that a polymer mushroom compressed by a cylindrical disk of radius $R$, that is much larger than the linear dimension $R_0$ of the undeformed polymer ($R_0 \sim aN^{\nu}$, $a$ being the segment length and $\nu \approx 0.59$) but much smaller than its linear extension $aN$, undergoes an "escape transition" (Fig. 1a,b). For $H \ll R_0$ but still exceeding some

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Fig1.png}
\caption{a) Schematic plot of a "mushroom" (i.e., a chain grafted with one end at a flat repulsive wall). The grafting site is indicated by a cross ($\times$). Linear dimensions $R_{gl}, R_{g2}$ of the coil are indicated. b) Compression of a mushroom by a piston of radius $R$ which has its lower surface at a distance $H$ from the grafting surface. The part of the chain that is underneath the piston forms a chain of $n_t$ blobs of diameter $H$. The force required to keep the piston at the distance $H$ is denoted by $f$. c) Top view of a compressed mushroom that is completely "imprisoned" underneath the piston of radius $R$. The chain configuration can be described as a self-avoiding two-dimensional random walk of $N'$ blobs of diameter $H$.}
\end{figure}
transition value $H_t$ the mushroom gets deformed into a quasi-two-dimensional ($d=2$) conformation, with a lateral gyration radius (note that $^8 \nu = 3/4$ in $d=2$), cf. (Fig.1c),

$$R_{\text{gll}} \sim (H/\alpha)^{1-3/(4\nu)} a N^{3/4}.$$  

(1)

Eq. 1 derives from the concept that the chain can be divided into $N'$ blobs with $N' = N/n_b$ where the number of monomers in a blob $n_b \sim (H/\alpha)^{1/\nu}$ since $^8,^9 H \sim a n_b^\nu$. The free energy of the chain then is $^3,^8 F_{\text{imp}} \sim k_B T N' \sim k_B T (a/H)^{1/\nu}$.

However, when $H$ gets even smaller, a transition to a partially escaped configuration of the chain may occur (Fig. 1b). Then only $n_b < N'$ blobs remain under the piston while the rest of the monomers are in one large blob outside. This transition is driven by the gain in configurational entropy due to the part of the chain that has "escaped". Subramanian et al.$^3$ estimate the free energy of this state as

$$F_{\text{esc}} \approx F_0 + F_{\text{str}} \sim k_B T \left[ n_t + (R/H)^{4} n_t^{-3} \right],$$

(2)

where $F_0 = k_B T n_t$ would be the free energy of a two-dimensional chain of blobs having its natural size $(R_0 \sim H n_t^{3/4})$, while $F_{\text{str}}$, is the free energy cost of stretching this chain up to the radius $R$, namely $^{10} F_{\text{str}} = k_B T (R/R_0)^4$. Minimizing $F_{\text{esc}}$ with respect to $n_t$ then yields the simple result $^8 F_{\text{esc}} \sim k_B T (R/H)$. Subramanian et al.$^{3-6}$ then locate a first order transition at $H = H_t$ between these states by equating $F_{\text{esc}} = F_{\text{imp}}$, which yields $H_t/a \sim (aN/R)^{\nu/(1-\nu)}$, and is accompanied by a jump in the force $f = -(\partial F/\partial H)_T$ at the transition.

While it is clear that this escape transition can become sharp only for $N \to \infty$, but will be somewhat rounded for finite $N$, the very existence of this transition for good solvent conditions has been called into question recently. It was argued that this transition may only occur for bad and Theta solvent conditions, while then a critical temperature $T_c$ is reached, analogous to the critical temperature of polymers in dilute solution in bad solvents, so that for $T > T_c$ (in the good solvent regime) this transition is completely eliminated by statistical fluctuations.

We have studied this problem by Monte Carlo simulation of an off-lattice bead spring model which has been previously proven valuable for chains both in the bulk and near surfaces.$^{11-13}$ In this model coarse-grained effective bonds are represented by springs described by the finitely extensible nonlinear elastic (FENE) potential,

$$U_{\text{FENE}} = -\frac{K}{2} r^2 \ln \left[ 1 - (l_l - l_0)^2 / R^2 \right], \quad \text{if } l_{\text{min}} < l < l_{\text{max}},$$

(3)

with $l$ being the bond length, $R = l_{\text{max}} - l_0$, and $l_0$, $l_{\text{max}}$, $l_{\text{min}} = 2l_0 - l_{\text{max}}$ being the equilibrium value of the bond length and its maximum or minimum extension, respectively. As before,$^{11-13}$ parameters were chosen such that $l_{\text{max}} = 1$ as the unit of length and $l_0 = 0.7$, $K = 40$ (in units of $k_B T$).

The non-bonded interactions between beads are described by the Morse potential,

$$U_M(r) = -\varepsilon \left\{ \exp[-2\alpha(r - r_{\text{min}})] - 2\exp[-\alpha(r - r_{\text{min}})] \right\},$$

(4)

where $r$ is the distance between beads, and the parameters are chosen as $r_{\text{min}} = 0.8, \varepsilon = 1$, and $\alpha = 24$. Due to the large value of $\alpha$, $U_M(r)$ decays to zero very rapidly for $r > r_{\text{min}}$, and is completely negligible for $r > 1$ already. These choices of parameters allow the use of a very fast link-cell algorithm. Choosing a temperature $k_B T = 1.0$, we are in the good solvent regime of the model, well above its $\theta$-temperature ($k_B \theta \approx 0.62^{10}$).

The impenetrable surface plane is at $z = 0$, so the beads can only be located in the halfspace $(x,y,z > 0)$, the grafted end being at the coordinate origin. The center of the hard cylindrical piston is always at the line $x = y = 0$, exactly above the grafted end, and the height of the piston $H$ above the surface and its radius $R$ are the parameters which are varied in our simulations as well as the chain length (choosing $N = 128, 256, 512, 768, 1024$ and $1280$, respectively).

Clearly, the choice of the piston center exactly above the grafted end is somewhat special, but arguments have been presented$^9$ that the escape transition persists also for off-centered piston positions. The most symmetric case studied here should thus be taken as a generic example only.

As a simulation technique, we choose a combination of configurational bias methods$^{14}$ and simple random hopping moves$^{11}$ for generating well-equilibrated initial states, and a combination of random hopping moves and two- and three-dimensional pivot moves$^{15}$ for the Monte Carlo averaging. Technical details about these (rather involved)
algorithms, which allow the study of much longer chain lengths rather than when one uses the simple random hopping algorithm only\textsuperscript{11,12}, will be presented elsewhere\textsuperscript{10}.

Fig. 2 presents typical data for the relation between the force exerted by the polymer on the piston (measured from the z-component of the virial tensor\textsuperscript{11,13}) and the height, for a number of choices of \( R \) and \( N \) (we consider only choices \( R \gg l_0N^* \), of course). We can recognize clearly that the \( f \) vs. \( H \) relation exhibits two branches: for large \( H \) there is a branch that increases rather steeply with decreasing \( H \), corresponding to imprisoned chains, then there is a transition region resembling a "van der Waals loop", and again a (somewhat less steep) increase with decreasing \( H \) sets in - this latter branch corresponds to escaped chains. This assignment of different states belonging to these branches can be made very directly either by inspection of the chain configurations or by recording the radial monomer density distribution \( \rho(r) \), where \( r = \sqrt{x^2 + y^2} \), \( x, y, z \) being the coordinates of a monomer (Fig. 3).

![Figure 2](image1.png)

**Fig. 2.** Normalized force \( f_{\text{imp}}/kBT \) plotted vs. distance \( H \), for several choices of \( N \) and \( R \), as indicated in the figure. The ratio \( (H_{\text{imp}} - H_{\text{esc}})/H_{\text{esc}} \) is given in brackets in the legend for each set. \( H_{\text{esc}} \) and \( H_{\text{imp}} \) are measured as the left and right side of the transition region, marked by the horizontal section, drawn according to the Maxwell rule, for each set.

![Figure 3](image2.png)

**Fig. 3.** Radial density distribution function \( \rho(r) \) of the monomers in a compressed mushroom for the choice \( R = 60 \) and \( N = 512 \). Several values of \( H \) are included, as shown in the figure.

One sees that in the "imprisoned" state of a chain the distribution rises fast to a maximum at a distance \( r_{\text{max}} \ll R \), and then it decreases steadily until at \( r \approx 6r_{\text{max}} \) it is essentially zero. Decreasing \( H \) first leads to a slight shift of \( r_{\text{max}} \) to larger values, but then the shape of \( \rho(r) \) changes qualitatively: it becomes much broader, and a side peak at \( r > R \) develops. These distributions correspond to the flat part of the isotherm in Fig. 2. Finally \( \rho(r < R) \) is completely flat, and for \( r > R \) a single pronounced maximum occurs: this form of the distribution is typical for the "escaped" chains.
Actually the loops in the transition region in Fig. 2 have metastable and unstable parts, in analogy to the loops at the liquid-gas transition. In fact, increasing the simulation time substantially the extent of the metastable branches gets somewhat smaller. Thus the equilibrium behavior is estimated by a Maxwell construction (horizontal straight lines in Fig. 2).

Figs. 2, 3 hence constitute a clear proof that an escape transition (although somewhat rounded) does exist in the good solvent regime, contrary to recent claims\textsuperscript{7} (the latter work has considered too short chains, \( N \leq 100 \), and hence failed to detect it). A more detailed analysis\textsuperscript{16} shows that the transition does become sharp in the limit where \( N \to \infty \) and \( R/l_0 N^\nu \to \infty \): i. e., the radius of the piston must increase more strongly than the unperturbed radius of the mushroom (but must be much less than the linear chain length \( l_0 N \), of course, because otherwise there is no more any chance for an escaped state of the chain).

Finally, we note that there is an important difference between our findings in Figs. 2, 3 and the theory of Subramanian et al.\textsuperscript{3\textendash}6: the latter predicts that the transition is characterized by a jump in \( f \) at \( H_t \), while Fig. 2 suggests instead a flat region of \( H \) (from \( H_{\text{esc},t} \) to \( H_{\text{imp},t} \) at some "critical" strength \( f_i \) of the force): i. e. one observes (for \( N \to \infty \)) a jump when one plots \( H \) vs. \( f \) but not the other way round. The reason for this discrepancy is in fact very simple: \( H \) is an extensive thermodynamic variable, while the force \( f \{f = -(\partial F/\partial H)_T\} \) is the conjugate intensive variable. We have an analogy with the liquid-gas transition (\( H \) corresponds to the volume \( V \), \( f \) to the pressure \( p \)) where it is the Gibbs potential \( G(T, p) = f(T, V) + pV \), which is equal in both phases at the transition pressure \( p_{\text{coes}}(T) \), while for \( V \) one has a jump from \( V_{\text{liq}} \) to \( V_{\text{gas}} \). We have to use a similar Legendre transform here, \( G(T, f) = F(T, H) + fH \). Writing \( F_{\text{esc}} = c' R/H \) and \( F_{\text{imp}} = c k_B T a/N(\alpha/H)^{1/v} \), we obtain\textsuperscript{17}

\[
G_{\text{esc}}(T, f) = F_{\text{esc}}(T, H) + fH = 2(c' k_B T)^{1/2} f^{1/2} 
\]

\[
G_{\text{imp}}(T, f) = \nu^{1/(1+v)}(1 + 1/\nu)(c k_B T a^{1/v})^{1/(1+v)} f^{1/(1+v)},
\]

Now the transition is located from \( G_{\text{esc}}(T, f_1) = G_{\text{imp}}(T, f_1) \) at

\[
a f_1 / k_B T = \left[\nu^{1/(1+v)}(1 + 1/\nu)/2 \right]^{2(1+v)/(\nu-1)} \left( c' R/a \right)^{(1+v)/(1-v)} / (c N)^{2v/(1-v)},
\]

and the associated values of the height, \( H_{\text{esc},t} \) and \( H_{\text{imp},t} \) which limit the region where the escaped state (\( H < H_{\text{esc},t} \)) or the imprisoned state (\( H > H_{\text{imp},t} \)) represent the thermal equilibrium are

\[
H_{\text{esc},t} / a = \left( 1 + \nu/2 \right) \nu^{1/v} \left( c N a / c' R \right)^{\nu/(1-v)}, \quad H_{\text{imp},t} / a = \left( 1 + \nu/2 \right) \nu^{1/v} \left( c N a / c' R \right)^{\nu/(1-v)}. 
\]

Using \( \nu \approx 0.59 \), one finds \( (H_{\text{imp},t} - H_{\text{esc},t}) / H_{\text{esc},t} \approx 0.26 \), which is indeed compatible with our data (Fig. 2). A more detailed analysis\textsuperscript{16} shows that the predicted variation of the transition height with \( N^\nu/(1-v) \approx N^{1.44} \) also can be verified.

In summary, we have presented the first evidence from simulations that when compressing a polymer mushroom by a cylindrical piston under good solvent conditions one will encounter an escape transition, as predicted recently\textsuperscript{3\textendash}6. Although for finite \( N \) inevitably a rounding of the transition takes place, clear signals of the transition can both be recorded from the force vs. height isotherm (Fig. 2) and from the bimodal character of the radial monomer density distribution (Fig. 3). However, in thermal equilibrium there is no jump of the force at the transition height, instead there is a regime of constant force for \( H_{\text{esc},t} < H < H_{\text{imp},t} \). Of course, it is conceivable to follow the loops containing metastable and unstable pure escaped (imprisoned) states inside this "forbidden" region, as our simulation shows. We expect that these remarks could be relevant for observations of interactions between chains and atomic force microscope (AFM) tips.

This work was supported in part by the Deutsche Forschungsgemeinschaft (DFG) under grant No 436BUL113/92 and by the Bulgarian National Science Foundation under grant X-640/1997.
9. By the symbol $\sim$ we mean that prefactors of order unity are suppressed.
17. For the sake of completeness, we allow constants of order unity, $c, c'$ here.