Dynamics of pulled desorption with effects of excluded-volume interaction: The p-Laplacian diffusion equation and its exact solution

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received 30 May 2011; accepted in final form 5 July 2011
published online 4 August 2011

PACS 82.35.Gh – Polymers on surfaces; adhesion
PACS 62.25.-g – Mechanical properties of nanoscale systems
PACS 82.37.-j – Single molecule kinetics

Abstract – We analyze the dynamics of desorption of a polymer molecule which is pulled at one of its ends with force \( f \), trying to desorb it. We assume a monomer to desorb when the pulling force on it exceeds a critical value \( f_c \). We formulate an equation for the average position of the \( n \)-th monomer, which takes into account excluded-volume interaction through the blob-picture of a polymer under external constraints. The approach leads to a diffusion equation with a \( p \)-Laplacian for the propagation of stretching along the chain. This has to be solved subject to a moving boundary condition. Interestingly, within this approach, the problem can be solved exactly in the trumpet, stem-flower and stem regimes. In the trumpet regime, we get \( \tau = \tau_0 n_d^2 \), where \( n_d \) is the number of monomers that have desorbed at the time \( \tau \). \( \tau_0 \) is known only numerically, but for \( f \) close to \( f_c \), it is found to be \( \tau_0 \sim f_c / (f^{2/3} - f_c^{2/3}) \). If one used simple Rouse dynamics, this result would change to \( \tau \sim f_c n_d^2 / (f - f_c) \). In the other regimes too, one can find exact solution, and interestingly, in all regimes \( \tau \sim n_d^2 \).

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Introduction. – Single-molecule experiments, in which one exerts an external force on a long-chain molecule have become ubiquitous [1]. These experiments provide very interesting information on the structure and dynamics of long-chain molecules. Mechanical force can be used to unzip the double-stranded DNA, emulating the action of enzymes that mechanically force the two strands apart during the process of replication [2]. Force has also been used to desorb a molecule adsorbed on a surface [3,4]. Motivated by the experiments, the statistical mechanics of an adsorbed polymer molecule, at one end of which a force is acting trying to desorb it has been extensively studied [5–7]. Parallel to these are statistical mechanics of DNA unzipping by force [8]. In spite of a large amount of activity on the equilibrium statistical mechanics of these systems, there have been only few studies of the dynamics. The earliest study of the dynamics of such a system seems to be that of Sebastian [9], who investigated the Rouse dynamics of a long-chain molecule pulled out from a potential well. It was found that the escape of the polymer from the well happened if the pulling force \( f \) exceeded a critical value \( f_c \) and that the time needed for escape of \( n_d \) monomers scaled as \( n_d^2 / (f - f_c) \). Similar results were obtained by Marenduzo et al. who did simulations [10]. There have also been simulations of the desorption of a pulled polymer [11]. However, there has not been any analytic theory of the dynamics of this process, with excluded-volume interactions included. In this letter, we develop such a theory based on the equations originally formulated by Brochard-Wyart et al. [12]. The approach leads to a diffusion type of equation for the propagation of stretching along the polymer. As it accounts for excluded-volume interactions, the equation is non-linear and in the mathematics literature it is referred to as diffusion equation with \( p \)-Laplacian [13]. In the case of pulled desorption, one has to solve this non-linear equation with a moving boundary condition. Interestingly, an exact solution can be found for this problem for all the limits of interest. In the trumpet regime, the time for desorption of \( n_d \) monomers \( \tau \) scales as \( f_c n_d^2 / (f^{2/3} - f_c^{2/3}) \), very similar to what was found for the much simpler model of escape from a well by
pulling [14]. If one adopted Rouse dynamics, this would change to $\tau \sim f_c n_n^2/(f-f_c)$. Surprisingly, in the other regimes too, time scales exactly in the same fashion as in the trumpet regime, though the dependence on the forces is changed.

The model. — We think of a polymer of $N$ monomers, with excluded-volume interactions. The unadsorbed molecule would have a Flory radius $R_F \sim a^{N\nu}$, where $a$ is the size of a monomer. We shall label the monomer position along the contour length of the monomers with $n$ which varies from $-N$ to $0$. It is convenient to imagine this as a continuous variable. The solid surface on which the polymer is adsorbed is located at $x=0$ and at the time $t=0$, one starts pulling on the end with $n=0$ with a force $f$ in the positive $x$-direction. If the force on the monomer at the surface exceeds a critical value $f_c$ then the monomer is assumed to desorb. A simple view of the desorbed part of the molecule is in terms of the blob-picture introduced by Pincus [15–17] and used by Brochard-Wyart et al. [12,18–20] and Sakaue [21] to study the dynamics of pulled polymers. In this section, we shall discuss what has been referred to as the trumpet regime [20]. The other regimes are discussed later on. Let us denote the average position of the $n$-th monomer in the direction of pulling by $x(n,t)$. As a result of pulling, the end at $n=0$ desorbs and starts moving as more and more monomers desorb. The desorbed part of the polymer may be imagined to consist of blobs of (varying) size $R_b$ stretched out in the $x$-direction (see fig. 1). Denoting by $\Delta n_b$ the number of blobs of size $R_b$, we can write

$$x(n,t) = \sum b R_b \Delta n_b,$$  \hspace{1cm} (1)

where the sum in eq. (1) is over all the blobs to the left of the $n$-th monomer. Let us say that $\Delta n_b$ blobs contain $\Delta n$ monomers in total. As a blob of size $R_b$ contains $(R_b/a)^{1/\nu}$ monomers, where $\nu$ is the Flory exponent, $\Delta n$ and $\Delta n_b$ are related through $\Delta n_b = \Delta n/(R_b/a)^{1/\nu}$. Hence $x(n,t) = a^{1/\nu} \sum b R_b^{1-1/\nu} \Delta n$. The size of a blob is related to the force by $R_b = k_B T/f$, where $k_B T$ represents the thermal energy. Thus $x(n,t) = a \int_{n_d(t)}^{x} \frac{dn'}{k_B T} e^{(a/n')^{1/\nu} - 1}$, where $-n_d(t)$ labels the last monomer that is desorbed at the time $t$. On differentiating this with respect to $n$, we get

$$\frac{\partial x(n)}{\partial n} = a \left( \frac{af(n)}{k_B T} \right)^{(1-\nu)/\nu}. \hspace{1cm} (2)$$

This is the equation that we shall use in our analysis and is contained in the paper by Brochard-Wyart et al. [12]. Using this we wish to calculate the average time of desorption of $n$-th monomer. We now calculate the frictional force acting on the portion of the chain in the interval $(x,x+\Delta x)$. Denoting the viscosity of the medium by $\eta$, a blob of size $R_b$ would experience a frictional force $\eta \nu R_b$ where $\nu$ is the velocity with which the blob is moving. Hence the total force experienced by that region would be $\eta \nu \sum b \Delta x$. Hence the net force acting on the $n$-th monomer is $f - \eta \int_n^{b} \frac{\partial x(n',t)}{\partial t} dn'$. Using this in eq. (2), we get the equation that describes the building-up of tension along the chain on the right-hand side of the wall [12]:

$$\frac{\partial x(n)}{\partial n} = a \left( \frac{af(n)}{k_B T} \right)^{(1-\nu)/\nu}. \hspace{1cm} (3)$$

In eq. (3), $-n_d(t) < n < 0$ where $n$ denotes any particular monomer on the desorbed part of the polymer. It may be noted that in the Rouse model, the analogue of eq. (2) would be linear in the force and may be obtained by putting $\nu = 1/2$. Further, each monomer experiences a force $\eta v$ (free-draining regime). Hence in the Rouse case, instead of eq. (3) we have

$$\frac{\partial x}{\partial n} = a \left[ \frac{a}{k_B T} \left( f - \int_n^0 \eta v \frac{\partial x(n,t)}{\partial t} dn \right) \right]^{(1-\nu)/\nu}. \hspace{1cm} (4)$$

The diffusion equation with $p$-Laplacian. — It is convenient to use dimensionless variables (a tile on top of the variable indicates that it is dimensionless) $\xi = x/\xi$, $\tilde{n} = n/g$, $t = t/\tau_b$ with $\xi = k_B T/f$, $g = (\xi/a)^{1/\nu}$, and $\tau_b = \eta \xi^3/k_B T$. This leads to

$$\tilde{\partial} \tilde{x} \tilde{n} = \left[ \left( 1 - \int_{\tilde{n}}^{0} \tilde{\partial} \tilde{x} \tilde{t} \tilde{n} \tilde{t} \right)^{(1-\nu)/\nu} \right]. \hspace{1cm} (5)$$

Differentiating eq. (5) gives $\tilde{\partial}^2 \tilde{x} \tilde{n} = \frac{1-\nu}{\nu} \frac{\partial \tilde{x} \tilde{n}}{\partial \tilde{n}} \frac{\partial \tilde{x} \tilde{n}}{\partial \tilde{t}}$. We shall put $\nu = 3/5$ and the equation becomes

$$\tilde{\partial}^2 \tilde{x} \tilde{n} = 2 \frac{\partial \tilde{x} \tilde{n}}{\partial \tilde{t}} \frac{\partial \tilde{x} \tilde{n}}{\partial \tilde{n}}. \hspace{1cm} (6)$$

Putting $\tilde{n} = 0$ in eq. (5) leads to

$$\left( \frac{\partial \tilde{x} \tilde{n}}{\partial \tilde{n}} \right)_{\tilde{n}=0} = 1. \hspace{1cm} (7)$$

48006-p2
Further, at the monomer that is in the process of desorbing, the force has to have the critical value, which we denote by \( \tilde{f}_c \). Therefore, at the desorbing end, the boundary condition would be

\[
\left( \frac{\partial \tilde{x}}{\partial \tilde{n}} \right)_{\tilde{n} = -\tilde{n}_d(t)} = \tilde{f}_c^{(1-\nu)/\nu}.
\]  
(8)

In terms of dimensioned variables, \( \tilde{f}_c = f_c/fT \). That is, it is the ratio of the critical force to the actual force exerted, and in order to have desorption, \( \tilde{f}_c < 1 \). The initial condition has all the monomers adsorbed. Thus

\[
\tilde{x}(\tilde{n}, 0) = 0.
\]  
(9)

Equation (6) is a diffusion equation with a \( p \)-Laplacian, where \( \frac{\partial \tilde{x}}{\partial \tilde{n}} \) is small —this means that the tension spreads rapidly in regions where there is little tension\(^1\).

In the case of Rouse dynamics, eq. (4) would lead to the diffusion equation \( \frac{\partial \tilde{c}}{\partial t} = \kappa_0 T \tilde{c}^{2/3} \). Thus with, or without the excluded-volume interaction, the stretching of the polymer obeys a diffusion equation, and not a wave equation for which the disturbances propagate as pulses. Therefore, any movement of tension along the chain is diffusive. It is interesting to note that excluded-volume interaction speeds up the diffusive motion (see ref. [19]).

### The solution

As time passes, the polymer desorbs. We shall look for solutions of the form \( \tilde{x}(\tilde{n}, \tilde{t}) = \tilde{f}^* \tilde{n} \tilde{h}(\tilde{u}) \), \( \tilde{n} = \frac{\tilde{n} + \tilde{n}_d(t)}{\tilde{n}_0} \) and \( \tilde{n}_d(t) = \tilde{v}_d t^\alpha \). We take \( \tilde{v}_d \) to be a constant, to be determined. We need to choose values for the unknowns \( \alpha, \beta, \gamma \) and \( \tilde{v}_d \). The boundary condition at the free end now reads

\[
\left( \frac{\partial \tilde{x}}{\partial \tilde{n}} \right)_{\tilde{n} = 0} = \tilde{f}_c^{\beta - \beta} \tilde{h}'(\tilde{v}_d) = 1,
\]  
(10)

which can be satisfied by putting \( \gamma = \beta \) and imposing the condition

\[
\tilde{h}'(\tilde{v}_d) = 1.
\]  
(11)

Putting the form \( \tilde{x}(\tilde{n}, \tilde{t}) = \tilde{f}^* \tilde{n} \tilde{h}(\tilde{u}) \) into eq. (6) leads to an equation for \( \tilde{h}(\tilde{u}) \) that has only the variable \( \tilde{u} \) in it if we choose \( \alpha = \beta = 1/2 \). The resultant equation is

\[
3\tilde{h}''(\tilde{u}) + \sqrt{\tilde{h}'(\tilde{u})}((\tilde{u} - \tilde{v}_d)\tilde{h}'(\tilde{u}) - \tilde{h}(\tilde{u})) = 0.
\]  
(12)

In addition, the conditions (8) and (9) give

\[
\tilde{h}'(0) = \tilde{f}_c^{2/3},
\]  
(13)

and

\[
\tilde{h}(0) = 0.
\]  
(14)

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\(^1\)An equation of the form \( \frac{\partial \tilde{c}}{\partial t} = D \frac{\partial^2 \tilde{c}}{\partial \tilde{x}^2} - \frac{\partial \tilde{c}}{\partial \tilde{x}} \) is known as a diffusion equation with \( p \)-Laplacian. This has a diffusion coefficient proportional to \( \tilde{c}^{-p} \) (see ref. [19]).

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[Fig. 2: (Colour on-line) (a) Plot of \( \tilde{x}(\tilde{n}, \tilde{t}) \) against \( -\tilde{n} \) for different values of \( \tilde{t} \). (b) \( \tilde{v}_d \) against \( \tilde{f}_c \). The full curve is the result of numerical calculations while the dashed curve is the result of using eq. (15).]

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Equation (12) has to be solved subject to the initial conditions of (13) and eq. (14). Further, the value of \( \tilde{v}_d \) is uniquely determined by the condition of eq. (11). The numerically obtained \( \tilde{x}(\tilde{n}, \tilde{t}) \) is plotted against \( -\tilde{n} \) for different values of \( \tilde{t} \) in fig. 2. One can calculate the position of the pulled end of the polymer as a function of time, to get \( \tilde{x}(0, \tilde{t}) = \sqrt{t} \tilde{h}(\tilde{v}_d) \). In fig. 2 we give a plot of \( \tilde{v}_d \) against the dimensionless force \( \tilde{f}_c \). We now analyze the behavior of \( \tilde{v}_d \) in the region where the pulling force exceeds the critical force only by a small amount. That is, \( \tilde{f}_c \sim 1 \). In this case \( \tilde{v}_d \ll 1 \) and one can do a perturbation analysis of eq. (12). We put \( \tilde{h}(\tilde{u}) = h_0(\tilde{u}) + \tilde{v}_d h_1(\tilde{u}) + \tilde{v}_d^2 h_2(\tilde{u}) \). Our aim is to evaluate \( h'(\tilde{v}_d) \) up to terms quadratic in \( \tilde{v}_d \). This can be achieved by evaluating \( h_1(\tilde{u}) \) correct up to \( \tilde{u}^{-1} \). Doing this we find that \( h_0(\tilde{u}) = \tilde{f}_c^{2/3} \tilde{u}, h_1(\tilde{u}) = f_c \tilde{u}^2 / 6 \) and \( h_2(\tilde{u}) = 0 \). Using these to evaluate \( h'(\tilde{v}_d) \) gives \( h'(\tilde{v}_d) = \tilde{f}_c^{2/3} + \tilde{f}_c^2 \tilde{v}_d^2 / 3 \). This can be used to solve eq. (11) to get

\[
\tilde{v}_d = \sqrt{\frac{3(1 - \tilde{f}_c^{2/3})}{\tilde{f}_c}}.
\]  
(15)

Thus \( \tilde{n}_d \), the number of monomers that have desorbed at the time \( \tilde{t} \) is given by

\[
\tilde{n}_d = \tilde{v}_d \tilde{t}^{1/2}.
\]  
(16)

Defining \( \tau_0 = \frac{\tau^* (\alpha f_c/k_B T)}{3(\alpha f_c/k_B T)^{2/3} - (\alpha f_c/k_B T)^{2/3} + (\alpha f_c/k_B T)^{2/3}} \) with \( \tau^* = \eta a^3 / k_B T \), this becomes \( \tau = \tau_0 n_d^2 \) in terms of dimensioned variables, for \( f \) close to \( \tilde{f}_c \). The case of Rouse dynamics was discussed in [14]. The result is (written in the notations of this paper)

\[
\tau = f_c n_d^2 / (2 \zeta (f - f_c))
\]  
(17)

for \( f \) close to \( f_c \), where \( \zeta = k_B T / \eta a^3 \). This is very similar to the result with excluded-volume interaction, except that the dependence on the force is different in the two cases. The result \( \tau \sim n_d^2 \) is in agreement with results of simulation, which found the total time of desorption of the molecule to be proportional to \( N^2 \) [11]. The above results show that as the force increases, excluded volume decelerates the desorption. This is a result of the nonlinear stretching of the molecule with excluded volume, leading to an effective friction dependent on the pulling force.

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48006-p3
Larger forces: the stem and the stem-flower regimes. –

The stem regime ($f > f_c > k_BT/a$). In this case, the molecule is stretched to the maximum extent, and would form what has been referred to as the stem [18]. The desorbed part has $n_s(t)$ monomers and a length of $a n_s(t)$. As a result, it obeys $\eta a^2 n_s(t) \dot n_s(t) = f - f_c$. Introducing the dimensionless variables $\dot \bar n_s(t) = n_s(t)$, $\dot f = (af/k_BT)$, $\bar f_c = a f_c/k_BT$, and $\bar f = (k_BT/\eta a^2)$, this may be solved to get $\dot \bar n_s(t) = \sqrt{2(f-f_c)/\bar f}$, showing that in this case too, the desorption time scales like $n_s^2$.

The stem-flower regime ($f_c < k_BT/a < f$) [18] (see fig. 1). The length of the stem region at any time can be found using the results of previous section, if one remembers that at one end of the stem there is a pulling force $f$ and the other end has $k_BT/a$. Therefore, the stem consists of $\dot n_s(t) = \sqrt{2(f-f_c)/\bar f}$ monomers. The dynamics of the flower part is easily analyzed using the p-Laplacian equation. In terms of $\bar x = x/a$, it reads

$$\frac{\partial^2 \bar x}{\partial t^2} = \frac{1}{2} \left( \frac{\partial}{\partial \bar x} \left( \frac{1}{\bar x} \frac{\partial \bar x}{\partial \bar x} \right) \right),$$

and has to be solved subject to the conditions $(\bar \alpha_{\bar n})_{\bar n = n_s(t)} = 1$, $(\bar \alpha_{\bar n})_{\bar n = 0} = \bar f_c^{2/3}$ and $\bar x(\bar n, 0) = 0$. As earlier, putting $\bar x(\bar n, t) = \sqrt{t} h(u)$, $u = (\bar n + \bar n_s(t))/\sqrt{t}$, and $\bar n_s(t) = v_s \sqrt{t}$, leads exactly to eq. (12), but with the conditions $h(0) = 0$, $h'(0) = \bar f_c^{2/3}$ and $h''(v_s - \alpha) = 1$, where $\alpha = \sqrt{2(f-f_c)/\bar f}$. The procedure of solution is just the same as earlier and the result is that $\tau \propto n_s^2$, the proportionality constant being known only numerically.

Finally, we discuss the value of $f_c$ which depends on the adsorption regime. For the weak adsorption regime de Gennes and Pincus [22] have shown that the adsorption chain can be seen as a string of adsorption blobs with the size of each blob $D \propto a (\epsilon - \epsilon_c)^{-\nu/\phi}$, where $\phi$ is the crossover exponent. The dimensionless adhesion energy $\epsilon = \epsilon_c/k_BT$ and $\epsilon_c$ is the critical adsorption energy (if $\epsilon < \epsilon_c$, then there is no adsorption). The critical force results from the condition that the size of the Pincus blob is equal to that of the adsorption blob, which leads to $f_c = k_BT(\epsilon - \epsilon_c)^{\nu/\phi}/a$. In the opposite limit of the strong adsorption we have $f_c = \epsilon/a > \epsilon_c/k_BT/a$.

Summary and conclusions. – We have analyzed the dynamics of desorption of an adsorbed polymer as a result of pulling at one of its ends with a force $f$. Our analysis takes into account the non-linear stretching of the polymer, which is due to the excluded-volume interactions. The resultant p-Laplacian diffusion equation has to be solved subject to a moving boundary condition. Interestingly, exact solutions can be found in all regimes of interest. In the trumpet regime we find that the time $\tau$ required to desorb $n_s$ monomers is given exactly by $\tau = \tau_0 n_s^2$ with $\tau_0 = (\eta a^2/k_BT)(a/f_c/3k_BT)\sqrt{(k_BT f_c/a)^{2/3} - (k_BT f_c/a)^{2/3}}$, for $f$ close to $f_c$. For the simple Rouse model, this gets modified to $\tau = f_c n_s^2/(2\zeta(f-f_c))$. In the stem and stem-flower regime too, time has a quadratic dependence on the number of desorbed monomers, though force dependence is different.

We are indebted to A. Milchev for useful discussions. This investigation has been supported by the Deutsche Forschungsgemeinschaft (DFG) Grant No. SFB 625/B4. KLS thanks the Max Planck Institute for Polymer Research in Mainz, Germany for hospitality during his visit to the Institute. KLS has financial support through the J. C. Bose fellowship program of Department of Science and Technology, Government of India.

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