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► **To cite this version:**

Thierry Charitat, Jean-François Joanny. Solid-like friction of a polymer chain. *European Physical Journal E: Soft matter and biological physics*, 2000, 3 (4), pp.369-376. 10.1007/s101890070007. hal-03433750

**HAL Id: hal-03433750**

**<https://hal.science/hal-03433750>**

Submitted on 17 Nov 2021

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# Solid like friction of a polymer chain

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(November 18, 2018)

## Abstract

We propose a simple friction model for isolated polymer chains on a solid substrate. The chains are pulled at constant velocity by one end, the other end can be trapped on the solid substrate on localised sites. We focus on the energy dissipation due to the traps. This simple model leads to non trivial friction laws, depending on the velocity and the distance between traps. Some refinements of the model such as the effect of thermal fluctuations are also reported.

61.41.+e: polymer, elastomer, and plastics.

68.45.-v: solid-fluid interfaces

81.40.Pq: friction, lubrication, and wear.

83.10.Nn: Polymer dynamics.

submitted to *Eur. Phys. J. E*

Friction phenomena occur at the interface between two media under relative motion. Their understanding is crucial for many technological applications and raises many fundamental questions. This is one of the oldest problems in physics but there is still a relatively poor understanding of the microscopic mechanisms of friction.

Dry solid friction is the older known form of friction, first introduced by da Vinci and Amontons. The dry friction laws give the friction force in terms of the load and the static and dynamic friction coefficients  $\mu_s$  and  $\mu_d$ . A first surprising result is that the friction coefficients do not depend of the contact area. The first microscopic model of Amontons's law [1,2] appeared in the middle of this century and shows the importance of the interface roughness. The dynamic friction coefficient depends only very weakly on the sliding velocity  $u$  [3–6], and in practice, the friction force reaches a constant value at vanishing velocity. There is still a poor understanding of dry friction, both from the theoretical and the experimental points of view, in part due to the difficulties to control the interfacial properties [3].

Fluid friction can be studied within the framework of hydrodynamics and is better understood. For a solid moving in a newtonian fluid, the friction law involves the viscosity of the fluid  $\eta$ , its density  $\rho$ , its size  $R$  and the velocity  $u$ . The dimensionless Reynolds number  $Re = \frac{\rho u R}{\eta}$  gives the ratio between the inertial and viscous forces. A simple scaling argument leads to the force acting on the solid as:  $f \sim \eta R u g(Re)$ , where  $g$  is a function of the Reynolds number. At low velocities, ie low Reynolds numbers, the friction force must be independent of the density  $\rho$ , and thus is proportional to  $\eta R u$ , (Stokes friction). At high Reynolds number, the viscous stresses are negligible and  $f \sim \eta R u Re \sim \rho R^2 u^2$ .

The friction between two polymeric media is a subject of major interest for many practical applications (lubrication, adhesion, extrusion, wetting). Polymeric systems also allow to work on well controlled surfaces and several microscopic parameters that can influence friction can be varied, such as a chain grafting density, chain lengths, chain affinity ... On the other hand, the complexity of the dynamic of the interfacial chains leads to a large variety of frictional behaviors: gel [7–9] or melt friction, slip transition [10–12] and stick-slip [13,14].

In a recent paper [15], Subbotin *et al* proposed a model describing the friction of confined polymers melt. In their model, the energy dissipation is simply due to the high friction of monomer anchored on the surface and the effect of loops and bridges on the friction law were precisely studied. In this paper, we present a simple friction model for a single polymer chain on a solid surface, focusing mainly on the microscopic mechanism of energy dissipation. We consider a polymer chain in a solvent, pulled by one of its extremities ( $s=N$  where  $s$  is the monomer number) at a constant velocity  $u$  (figure 1). The other extremity ( $s=0$ ) can be trapped on the surface by localised defects. Our aim is to calculate the dissipated energy due to the traps. This extremely simple and naive model gives a non trivial behavior of the friction force which is similar to solid friction in the sense that it may not vanish in the limit of small velocities. It could be also possible to test this behavior by micromanipulation of isolated polymer chains in a solvent with an atomic force microscope. Finally, it could be a possible way to introduce an energy dissipation in molecular motor models [16].

We first present the one chain problem on a linear and periodic array of traps. In this first part, we simply assume that the trapped monomer is leaving the trap when the tension reaches a critical value  $\tau$ . In the second part, we show how thermal fluctuations can induce the desorption of this monomer trapped in a potential barrier.

In a first approximation, the dynamics of a polymer chain can be described by the well-known Rouse model [17], which neglects hydrodynamic interactions. The polymer chain is represented as a set of  $N$  beads at position  $z$  connected by springs with entropic rigidity  $k = \frac{k_B T}{a^2}$ , where  $a$  is the monomer size. Each monomer behaves as a solid particle with a friction coefficient  $\zeta$  proportional to the solvent viscosity  $\eta$ ,  $\zeta \simeq \eta a$ . The Rouse equation which describes the dynamics of the chain is written (in one dimension) as:

$$\zeta \frac{\partial z(s, t)}{\partial t} = k \frac{\partial^2}{\partial s^2} z(s, t) + f(t) \quad (1)$$

where  $z(s, t)$  is the position of monomer  $s$  at time  $t$  and  $f(t)$  is a Langevin random force. The slowest relaxation mode of the chain has a characteristic time (the Rouse time)  $T_R = \frac{\zeta N^2}{k}$ . As it ignores hydrodynamic interactions, the Rouse model does not give a good description of polymers in dilute solutions. Nevertheless, the Rouse description is conceptually important and we choose it as a starting point to describe our results on polymer friction. In appendix A we show how it is possible to take into account hydrodynamic interactions within the framework of the Zimm model. This complication does not change qualitatively the behavior of the friction force. Our results are obtained for gaussian chains in a  $\Theta$  solvent. They can easily be generalised to polymer in a good solvent, but for a sake of clarity we do not show the results in the present paper.

Our paper is organised as follows. In the first section, we consider the interaction between one chain and a linear array of traps along the direction of the velocity, ignoring any thermal fluctuations. The traps are pointlike on the surface and the chain end point remains trapped as long as the chain tension is smaller than a critical value  $\tau$  which is the maximum force that can be exerted on the chain end by the trap. We first discuss the single trap problem and then a periodic one-dimensional array of traps with a period  $d$ . In appendix D we relate this model to the more realistic problem where the surface has a finite density of traps  $n$  per unit area. Complete calculations can be performed within the Rouse model; in the main text of the paper, we rather give simple scaling arguments postponing the detailed calculations in an appendix. Section II is devoted to the effect of thermal fluctuations. We describe each trap more realistically as a potential well and we estimate the escape probability of the trapped chain end when the tension increases. This amounts to calculating an effective critical tension with which the results of the previous section can be used. Following reference [18], we describe the release of the chain end as a Kramer process and we use a self-consistent force approximation. The last section summarises our results and discusses some possible extensions.

## I. POLYMER CHAIN INTERACTING WITH TRAPS

### A. The one trap problem.

We study a Gaussian polymer chain interacting with one trap on a solid surface. For simplicity, we consider the chain as two-dimensional and lying in the surface with a Gaussian conformation (at rest). The end point of the chain  $s = N$  moves at a velocity  $u$ . When the chain is free (not trapped), its average conformation can be obtained from the Rouse equation 1. The average position  $z_{free}(s, t)$  of monomer  $s$  at time  $t$  is

$$z_{free}(s, t) = \frac{1}{2} \frac{\zeta u}{k} s^2 = \frac{1}{2} u T_R \left( \frac{s}{N} \right)^2 \quad (2)$$

The tension of the chain at monomer  $s$  is given by the friction force on the chain end section containing  $s$  monomers  $\tau_{ch}(s, t) = k \frac{\partial z_{free}(s, t)}{\partial s} = \zeta u s$ . The tension on the free end of the chain vanishes, and the external force applied to pull the chain is  $N\zeta u = \frac{k}{N} u T_R$ . This can be viewed either as the friction force on the  $N$  monomers, or as the elastic tension of  $N$  springs in series extended over a distance  $u T_R$ . In the absence of trapping, the energy dissipated per unit time by the solvent viscosity is simply  $\frac{d\mathcal{E}_d}{dt} = N\zeta u^2$ .

When the end monomer ( $s=0$ ) gets trapped, the chain is progressively elongated by the motion of the pulled end ( $s=N$ ). The tension applied on the trapped monomer increases until it reaches the critical value  $\tau$ . The trapped chain end is then released and the chain contracts back to its free conformation.

The Rouse equation for the trapped chain allows the calculation of the chain tension (appendix A) :

$$\tau_{ch}(s, t) = k \frac{u T_R}{N} \left[ \frac{t}{T_R} + \frac{s}{N} + \frac{2}{\pi^2} \sum_{n=1}^{+\infty} \frac{1}{n^2} \left( 1 - \exp\left(-n^2 \pi^2 \frac{t}{T_R}\right) \right) \cos\left(\pi \frac{n}{N} (s - N)\right) \right] \quad (3)$$

The tensions on the trapped end ( $\tau_{tr}(t) = \tau_{ch}(s=0, t)$ ) and on the pulled end ( $\tau_{ch}(s=N, t)$ ) are plotted on figure 2. At short time after the trapping ( $t \ll T_R$ ), the tension on the pulled end remains constant (equal to the viscous friction force  $N\zeta u$ ), and the tension on the trapped monomer increases as  $\tau_{tr} \sim \zeta N u \left(\frac{t}{T_R}\right)^{1/2}$ . At larger times, ( $t \gg T_R$ ), the tension is uniform along the chain and both tensions increase as  $\zeta N u \frac{t}{T_R}$ . After the sticking time  $t_s$ , the tension  $\tau_{tr}$  becomes equal to the critical value  $\tau$ .

The characteristic velocity of the problem is obtained by comparing the friction force on the chain  $\zeta N u$  to the maximum force  $\tau$  that can be exerted by the trap  $u_c = \frac{\tau}{N\zeta} = \frac{N\tau}{k T_R}$ .

If  $u \ll u_c$ , the viscous force on the chain is smaller than  $\tau$ . When the trapped end is released from the trap, the whole chain is stretched with a constant tension and its extension is  $L = \frac{N\tau}{k}$ . The tension acting on the first monomer at time  $t$  is  $\tau_{tr}(t) \simeq \frac{k}{N} u t$  and the sticking time  $t_s$  is given by :

$$t_s = \frac{u_c}{u} T_R \quad (u \ll u_c \Leftrightarrow t_s \gg T_R)$$

The work performed to extend the chain is  $\frac{N\tau^2}{2k}$ . After the release of the trapped end, the elastic energy stored in the chain  $W_d = \frac{N\tau^2}{2k}$  is dissipated by a viscous process. This argument is essentially identical to the classical argument of Lake and Thomas [19] which has been used to study the adhesive properties of polymers by de Gennes [20,21].

If  $u \gg u_c$ , the viscous force on the chain is larger than  $\tau$ , and only a small part of the chain involving  $s_0(t) \sim \sqrt{\frac{k}{\zeta} t}$  monomers is elongated when the release of the trapped end occurs. It contributes to the tension on the trapped monomer as  $\tau_{tr}(t) \simeq \frac{k}{s_0(t)} u t$  and the sticking time  $t_s$  is now given by :

$$t_s = \left( \frac{\sqrt{\pi} u_c}{2 u} \right)^2 T_R = \frac{\pi \tau^2}{4 k u^2 \zeta}$$

where the numerical prefactor is obtained from the detailed calculations of the appendix. The force acting on the pulled monomer remains constant and equal to  $N\zeta u$  during the trapping with a good approximation. After the release of the trapped end, the tension of the pulled monomer is calculated in appendix B and is given by (B4). The extra energy dissipated due to the trapping is of the order of the elastic energy stored during the trapping in the deformed part of the chain  $W_d = s_0(t_s)\frac{\tau^2}{k} = N\frac{\tau^2}{k}\frac{u_c}{u}$ . More complete calculations confirming these scaling law can be done using the Rouse model. They are presented in appendices A and B. After the release of the anchored monomer, the chain relaxes to the steady state, and its elastic energy is dissipated. The total dissipated energy is

$$W_d = N\zeta u^2 t + \frac{4}{3\pi^{1/2}} N\zeta u^2 t_s \left(\frac{t_s}{T_R}\right)^{1/2} \quad (4)$$

### B. The many-traps problem.

We now consider a polymer pulled at a velocity  $u$  on a two dimensional surface with a density of traps  $n$ . We refer to appendix D for a discussion of the trapping probability that gives the mean distance  $d(u)$  between trapping events. The problem is then equivalent to a one dimensional array of traps along the velocity direction with an average density  $1/d(u)$ . For simplicity, we consider here a periodic lattice with a distance  $d(u)$  between traps. We then calculate the average friction force in a steady state as  $F_{fr} = \frac{W_d}{d}$  where  $W_d$  is the energy dissipated on each trap.

We first consider the limit of very low velocities  $u \ll u_c$ . When the chain is trapped on one defect and is just on the verge of detaching, the chain has a constant tension  $\tau$  and its size is  $L = \frac{N\tau}{k}$ . If this is smaller than the distance  $d$  between traps, the traps are independent and we can use the results of the previous section. The energy dissipated per trap is  $W_d \sim \frac{N\tau^2}{k}$  and the friction force is  $F_{fr} \sim \frac{N\tau^2}{kd}$ . If  $d \ll N\tau/k$ , the chain end gets trapped before the full relaxation of the tension. The number of monomers where the tension has relaxed increases as  $t^{1/2}$  and the position of the first monomer is given by  $z(t) \sim \frac{\tau t^{1/2}}{(\zeta k)^{1/2}}$ .

The chain gets trapped again when  $z(t) = d$  or after a time  $t_a \sim \frac{\pi\zeta kd^2}{4\tau^2}$ . The tension then becomes uniform along the chain over the Rouse time  $T_R$  and equal to  $\tau' = k(L - d)/N$ . The chain stretches then back to a uniform tension  $\tau$  over the time  $d/u$ . The dissipated energy per trap is  $W_d = \frac{N\tau^2}{2k} - \frac{N\tau'^2}{2k}$  and the friction force is  $F_{fr} \sim \tau$ .

This quasi-static description remains valid as long as  $d/u > T_R$ . If this is not the case, the tension does not have time to relax to the smaller value  $\tau'$  over the whole chain and remains equal to  $\tau$  (in fact slightly larger) on the pulled monomer. As long as the viscous force is small ( $u < u_c$ ) this tension balances the friction force and thus  $F_{fr} \sim \tau$ . In this case, the dissipated energy per trap is of the order of the elastic energy of a chain spanning the distance  $d$  i.e. containing  $s = kd/\tau$  monomers.

If the velocity  $u$  is larger than the critical value  $u_c$ , the total dissipation is dominated by the viscous forces. The defects are independent if  $t_s(u) \ll \frac{d}{u}$  i.e. if  $d > \frac{\tau^2}{k\zeta u}$ . In this case the dissipation is due to individual traps and the friction force is  $F_{fr} \sim \frac{\tau^3}{k\zeta u d} \sim \frac{N\tau^2}{kd} \frac{u_c}{u}$ . It decreases with the velocity. If  $d \ll \frac{\tau^2}{k\zeta u}$ , as above, the dissipated energy per trap is of the

order of the elastic energy of the chain section spanning the length  $d$  with a tension  $\tau$  and the friction force is  $F_{fr} = \tau$ .

All these results are summarized on figure 3 in a velocity-distance between traps  $(u, d)$  diagram.

## II. THERMAL FLUCTUATIONS.

In the previous section, we have considered point-like traps and we have ignored thermal fluctuations describing the chain statistics by the average position of each monomer. In a more realistic model, these two assumptions are relaxed. Each trap is an attractive potential well  $V(z - z_0)$  for the chain end with an extension  $b$  around the trap position  $z_0$  and a depth  $U_0$ . The maximum tension that can be exerted by the trap  $\tau$  is the slope of this potential at the inflection point  $z_1$ . We want to study here strong trapping and we only focus on the case where  $\frac{\tau b}{k_B T} \gg 1$ . This can be achieved for a reasonable tension if the size of the trap is larger than the monomer size  $a$  (typically a few times) but is much smaller than the chain size and the distance between traps  $d$ . A typical trapping potential is sketched on figure 4.a.

Thermal fluctuations have two effects; they can induce a new trapping of a chain end that has just escaped from the trap; they can also cause the release of the end monomer even if the tension is lower than the critical value  $\tau$ .

In references [22,23], Wittmer *et al* and Clement *et al* have shown that the readsorption of the chain can occur until the terminal monomer leaves the first Pincus blob of size  $\xi = k_B T / \tau_{tr}$ . The size of this Pincus blob in the strong trapping limit is smaller than the size of the trap  $b$  when the tension is equal to the critical tension. The retrapping effect can then be neglected.

The escape of a particle submitted to an external force from a potential well can be studied using Kramers rate theory. If the constant external force is  $\tau_{tr}$ , particle is submitted to the effective potential  $U(z) = V(z) - \tau_{tr}z$  (choosing the origin at the center of the trap). This potential has a minimum value at a position  $z_{min}$  corresponding to the equilibrium position of the particle and a maximum value at a position  $z_{max}$  ( $z_{min} < z_1 < z_{max}$ ). The escape time due to thermal fluctuations from the potential is the first passage time of the particle at the position  $z_{max}$ . Within Kramers rate theory [24], this is given by

$$t_e(\tau_{tr}) = t_1 \exp \left[ \frac{U(z_{max}) - U(z_{min})}{k_B T} \right] \quad (5)$$

where  $t_1$  is given by the curvature of the potential  $U(z)$  at the positions  $z_{min}$  and  $z_{max}$

$$t_1(\tau) = \frac{2\pi\zeta}{\left( -\frac{d^2U}{dz_{max}^2} \frac{d^2U}{dz_{min}^2} \right)^{1/2}} \quad (6)$$

Our aim here is to use these result to discuss the escape of the trapped end under the action of the time-dependent tension and to calculate the chain tension  $\tau_e$  when the trapped end escapes from the potential well. The results of the previous section can then be used with the effective critical tension  $\tau_e$  instead of  $\tau$ .

In reference [18], two approximations (so-called adiabatic and self-consistent force approximation) are proposed to discuss the escape of a particle from a potential well under

the action of a non constant force. We have checked that both lead to very similar results. For a sake of clarity, we present here the simpler self-consistent force approximation. In this approximation, the tension is obtained self-consistently by calculating the escape time from equation 5 and 6 for a tension  $\tau_{tr}$  increasing with time and by imposing that  $\tau_e = \tau_{tr}(t_e)$ .

In the limit of small velocities  $u \ll u_c$ , the chain tension at the end point increases as  $\tau_{tr} = \frac{kut}{N}$ . The self-consistency equation for the effective critical tension can then be written as :

$$\frac{N\tau_e}{ku} = t_1 \exp [\{U(z_{max}) - U(z_{min})\} / k_B T] \quad (7)$$

where the potential is calculated with the tension  $\tau_e$ . If the velocity is very small, the critical tension  $\tau_e$  is very small and the escape time can be expanded in powers of the tension. For a vanishing tension, the escape time is  $t_e^0 = t_1 \exp(U_0/k_B T)$  where  $t_1 \sim \zeta b/\tau$  (assuming that the potential has only one energy scale  $U_0 \sim \tau b$  and one length scale  $b \sim z_1$ ). The effective critical tension is then :

$$\tau_e = \frac{kut_e^0}{N} \frac{1}{1 + \alpha(\tau b/k_B T)(t_e^0/t_s(u))} \quad (8)$$

where  $t_s(u)$  is the sticking time introduced in the previous section and  $\alpha$  a numerical constant. This result is valid as long as the thermal escape time is small enough  $t_e^0 \ll \frac{k_B T}{\tau b} t_s(u)$  leading to  $\frac{u}{u_c} \ll \frac{u_1}{u_c} \sim (Na/b)^2 \exp -(U_0/k_B T)$ .

We assume for simplicity that the thermal escape time is larger than the Rouse time of the whole chain. The tension is thus uniform along the whole chain when the escape from the trap arises; the velocity  $u_1$  is then smaller than  $u_c$ . In this limit of vanishing velocities, if the traps are independents, the friction force is  $F_{fr} = \frac{N\tau_e^2}{2kd}$  and vanishes as  $u^2$ . If the escape time is smaller than the Rouse time only a fraction of the chain containing  $s \sim (kt_e^0/\zeta)^{1/2}$  monomers is stretched. The critical tension is  $\tau_e = (k\zeta t_e^0)^{1/2} u$  and the friction force is  $F_{fr} = \frac{s\tau_e^2}{2kd}$ ; it also vanishes as  $u^2$ .

If the velocity is larger than  $u_1$ , the effective tension increases between a value of order  $k_B T/b$  and  $\tau$ . The variation of the effective critical tension explicitly depends on the shape of the potential and cannot be expressed in simple analytical form. A simple expression can only be given if the velocity is large enough. In this case, the two positions  $z_{max}$  and  $z_{min}$  are close to the potential inflection point  $z_1$ . One can then expand the potential around  $z = z_1$

$$U(z) = U_1 + (\tau - \tau_e)(z - z_1) - \frac{1}{3}\gamma\tau z_1 \left(\frac{z - z_1}{z_1}\right)^3 \quad (9)$$

where  $\gamma$  is a number of order one. The effective tension can be calculated from this expansion :

$$\tau_e = \tau \left(1 - \frac{1}{\beta^{2/3}} \log^{2/3} \left(t_s(u) \frac{\tau_e}{\tau} \left(1 - \frac{\tau_e}{\tau}\right)^{1/2} / t_1^0\right)\right) \quad (10)$$

where we define the dimensionless number  $\beta = (4\tau z_1)/(3k_B T\gamma^{1/2})$  and the microscopic time  $t_1^0 = (\zeta z_1)/(2\gamma^{1/2}\tau)$ . This expansion is valid if  $\beta$  is larger than  $\log(t_s/t_1)$ . Qualitatively



the effective tension is equal to the maximal force exerted by the potential if the sticking time  $t_s$  is smaller than a time of the order of the thermal escape time. The effective tension increases smoothly (with a logarithmic dependence in  $u$ ) between  $k_B T/b$  and  $\tau$ . At first order we can use the power law found in the previous section in the framework of the zero temperature theory.

A similar calculation can be made at larger velocities  $u \gg u_c$ . If the thermal escape time is larger than the Rouse time, the effective critical tension is close to  $\tau$  and a law similar to eq. 10 is found (only the argument of the logarithm is slightly different). One can thus also use the zero temperature result for the friction force.

Finally, if the traps are not independent one should compare the thermal escape time to the sticking time that, in this case, is of order  $d/u$ . The escape of the trap is dominated by thermal fluctuations if the thermal escape time is smaller.

### III. CONCLUDING REMARKS

In this paper, we have studied a very specific model for the friction of a polymer chain on a solid surface. We have considered a two-dimensional gaussian polymer chain interacting with traps on a solid substrate. All the dissipation in this model is due to viscous friction in the solvent surrounding the chain and there is no dissipation associated to the substrate. Our main result is that, neglecting thermal fluctuations, the traps exert a finite friction force on the chain that does not vanish when the velocity goes to zero. This friction force originates in the elastic energy stored in the chain which is then dissipated by viscous friction in the liquid. At higher velocity the friction force decreases with the velocity due to the fact that the portion of chain that is stretched gets smaller. If thermal fluctuations are taken into account, the friction force formally vanishes at zero velocity. Nevertheless, for most practical cases the traps are strong enough and the effect of thermal fluctuations will appear only at infinitely small velocities. However, a very weak logarithmic dependence of the friction force on the velocity still remains, due to the fact that the trapping cross section depends logarithmically on the velocity.

For a macroscopic sample consisting of a statistical ensemble of independent chains, the static friction coefficient is proportional to the average number of trapped chains. Furthermore, our model gives an interesting result concerning the dependence of this coefficient with the sample history. During a friction experiment at velocity  $u$ , the average fraction of trapped chains is given by  $f \sim \frac{t_s(u)u}{d}$ . For  $u \ll u_c$  this fraction is constant and equal to  $f_0 \sim \frac{N\tau}{kd}$ . For  $u \gg u_c$  it decreases with the velocity as  $f_u \sim \frac{N\tau}{kd} \frac{u_c}{u}$ . In this case, if the motion is stopped fast enough, the static friction coefficient is lower than  $f_0$  and increases with time until it reaches  $f_0$ .

Our model may look very simplistic, but we believe that many of the assumptions made here do not have a strong influence on the main results although they may change the quantitative value of the friction force. For example, we have assumed that only the last monomer of the chain (the chain end that is not pulled) interacts with the traps. It is easily checked that identical results are obtained (within a factor 2) if any monomer not too close to the chain end interact with the traps. We have explicitly performed the Rouse calculations in this case, they are slightly more complicated and we do not present them in this paper. Another extension that we would like to make in the future is the case where

several monomers of the same chain interact with the traps. There is of course a possibility that at the same time several monomers are trapped; this then leads to correlated release (cascades). We believe however that the same qualitative results would be obtained and that the friction force would remain finite at low velocities. We also have assumed a periodic array of traps. A more realistic approach would be to introduce disorder both in the positions of the traps and in the distance between traps. A weak disorder is clearly not important. If the traps are independent, then the averaging of the dissipation is straightforward. If the average distance between traps is small, the tension of the end monomer remains roughly constant as the tension fluctuations due to the trappings do not propagate to the pulled monomer. Disorder could play an important role if it introduces strong fluctuations (such as rare trapping events with a strong critical tension). It would then be interesting to study the fluctuations in the friction force.

A last limitation is that we have only studied the stationary friction state. Transient effects are obviously very important and must be studied independently.

It is also important to discuss the orders of magnitude of the predicted effects. Our more quantitative discussion of the release from the trap clearly shows that the solid-like friction can only be observed if the energy barrier is large  $\tau b/k_B T \gg 1$  otherwise the whole escape process is thermally activated and there is no solid friction. This could be achieved for example with a trap size of the order of a few monomer sizes  $b \sim 10a$  and  $\tau b/k_B T \sim 10$ . The critical velocity for a chain of 1000 monomers is then of the order of  $0.1\text{mm/s}$  i.e. in the accessible range for atomic force microscopy. One must however notice that the chain tensions can then be rather large and that it is not clear that the chain elasticity remains gaussian. This would of course change the quantitative value of the friction force but not the qualitative physics.

In the future, we would like to use our very simple model to study the solid friction of a polymer gel moving on a solid substrate in order to give a quantitative interpretation of the recent experiments of Gong and Osada [8]

## APPENDIX A: TRAPPED CHAIN.

It is convenient to perform all calculations using the Laplace transformation, defined by :

$$\tilde{z}(s, p) = \int_0^{+\infty} z(s, t) e^{-pt} dt \quad (\text{A1})$$

For the trapped chain, the following Rouse equation has to be solved:

$$\zeta (p\tilde{z}(s, p) - z_{free}) = k \frac{\partial^2}{\partial s^2} \tilde{z}(s, p) \quad (\text{A2})$$

with the boundary conditions :

$$\begin{aligned} \tilde{z}(s = 0, p) &= 0 \\ \tilde{z}(s = N, p) &= \frac{u}{p^2} \end{aligned} \quad (\text{A3})$$

The solution of this equation is given by:

$$\begin{aligned} \tilde{z}_d(s, p) &= \frac{u}{p^2} \left[ 1 + \frac{1}{2} p T_R \left( \frac{s}{N} \right)^2 + \frac{\sinh \sqrt{T_R p} \frac{(s-N)}{N}}{\sinh \sqrt{T_R p}} \right] \\ z_d(s, t) &= u T_R \left[ \frac{t}{T_R} \frac{s}{N} + \frac{1}{2} \left( \frac{s}{N} \right)^2 + \frac{2}{\pi^3} \sum_{n=1}^{+\infty} \frac{(-1)^n}{n^3} \left( 1 - e^{-n^2 \pi^2 \frac{t}{T_R}} \right) \sin \left( \pi \frac{n}{N} (s - N) \right) \right] \end{aligned} \quad (\text{A4})$$

and the tension along the chain is given by:

$$\tau_{ch}(s, t) = k \frac{u T_R}{N} \left[ \frac{t}{T_R} + \frac{s}{N} + \frac{2}{\pi^2} \sum_{n=1}^{+\infty} \frac{1}{n^2} \left( 1 - e^{-n^2 \pi^2 \frac{t}{T_R}} \right) \cos \left( \pi \frac{n}{N} (s - N) \right) \right] \quad (\text{A5})$$

At large time  $t \gg T_R$ , the tension on the trapped monomer behaves as :

$$\tau_{tr}(s = 0, t) \simeq \frac{k}{N} u t \quad (\text{A6})$$

which corresponds to the tension of  $N$  springs under the extension  $ut$ .

For short times  $t \ll T_R$ , the tension on the trapped monomer behaves as :

$$\tau_{tr}(s = 0, t) = \frac{2}{\sqrt{\pi}} \frac{k}{N} u T_R \sqrt{\frac{t}{T_R}} \quad (\text{A7})$$

As given in the main text, the sticking time is obtained when this tension is equal to the critical value  $\tau$ .

In this case, the number of extended springs is  $s_0(t) \sim N \sqrt{\frac{t}{T_R}}$ .

## APPENDIX B: DETACHMENT

After the detachment of the trapped monomer, the chain relaxes to the steady state, and its elastic energy is dissipated. The Rouse equation becomes:

$$\zeta (p\tilde{z}(s, p) - z_d(s)) = k \frac{\partial^2}{\partial s^2} \tilde{z}(s, p) \quad (\text{B1})$$

where  $z_d(s) \simeq uT_R \left[ \frac{1}{2} \left( \frac{s}{N} \right)^2 + \frac{t_s}{T_R} - 4 \frac{t_s}{T_R} i^2 \text{erfc} \left( \frac{1}{2} \sqrt{\frac{T_R s}{t_s N}} \right) \right]$  ( $i^n \text{erfc}(x)$  is a repeated integral of the error function defined in [26]) gives the conformation of the chain at the time where the chain detaches from the trap. The boundary conditions are:

$$\begin{aligned} \frac{\partial \tilde{z}}{\partial s}(s=0, p) &= 0 \\ \tilde{z}(s=N, p) &= uT_R \left( \frac{1}{2} + \frac{t_s}{T_R} \right) \frac{1}{p} + \frac{u}{p^2} \end{aligned} \quad (\text{B2})$$

The solution of (B1) is given by:

$$\tilde{z}(s, p) = Au_+(s, p) + Bu_-(s, p) \frac{1}{2N} \sqrt{\frac{T_R}{p}} \left( u_-(s, p) \int_0^s z_d(s') e^{\sqrt{pT_R} \frac{s'}{N}} ds' - u_+(s, p) \int_0^s z_d(s') e^{-\sqrt{pT_R} \frac{s'}{N}} ds' \right) \quad (\text{B3})$$

where  $u_{\pm} = e^{\pm \sqrt{pT_R} \frac{s}{N}}$ ,  $A$  and  $B$  are two constants determined by (B2). The first boundary condition gives  $A = B = \frac{\alpha}{2}$ . In the limit of large times, the second condition gives  $\alpha \simeq \frac{\tilde{z}(N)}{\cosh(\sqrt{pT_R})}$ . At large times, the tension on the pulled monomer is given by:

$$\begin{aligned} \tilde{\tau}_d(N, p) &\simeq N\zeta \frac{u}{p} + 8i^3 \text{erfc}(0) N\zeta u \sqrt{\frac{t_s}{T_R}} t_s \\ \tau_d(N, t) &\simeq N\zeta u + 8i^3 \text{erfc}(0) N\zeta u \sqrt{\frac{t_s}{T_R}} t_s \delta(t) \end{aligned} \quad (\text{B4})$$

By integrating this tension over time one finds the dissipated energy given in the main text (equation 4).

### APPENDIX C: HYDRODYNAMIC INTERACTIONS.

The calculations presented in the main text of this paper have been made using the Rouse dynamics for the polymer chains on the solid surface. This ignores two effects : the direct friction of the chains on the solid surface and the hydrodynamic interactions between monomers. The hydrodynamic interactions close to a surface are difficult to calculate explicitly. However if we remain at a scaling level, it is sufficient to introduce the local stretching blobs [27]. If the local tension of the chain is  $\tau_{ch}$ , the local blob has a size  $\xi_t \sim k_B T / \tau_{ch}$  and contains  $g_t \sim (\xi_t/a)^2$  monomers. The friction force on a blob is  $6\pi\eta\xi_t$  and the hydrodynamic interactions are screened at the scale of the blob so that the dynamics of the chain of blobs can be studied using the Rouse model; the total friction is the sum of the frictions over all the blobs. As in the Rouse model, a free chain pulled by one end with a velocity  $u$  has on average a trumpet like shape studied in details by Brochard and her coworkers [28]. The Zimm equation of motion is obtained by writing a force balance on the blobs

$$k \frac{\partial^2 z}{\partial s^2} = 6\pi\eta u \frac{\partial z}{\partial s} \quad (C1)$$

The average position of monomer  $s$  is then

$$z_{free}(s) = \left( \frac{k_B T}{6\pi\eta u} \right)^{1/2} \left[ \exp\left(\frac{6\pi\eta u s}{k}\right) - 1 \right] \quad (C2)$$

The force balance on a section of chain containing  $s$  monomers close to the free end point is obtained by integration of the equation of motion  $k \frac{\partial z}{\partial s} = 6\pi\eta u z$ . Note that the tension increases very rapidly from the free end point and that the nonlinear elasticity certainly becomes relevant. We do not discuss this effect here and refer to reference [28].

For a chain trapped by one end on the surface, the sticking time does not depend on the dynamical model at low velocities (if it is larger than the characteristic relaxation time of the chain which is the Rouse time of the chain of blobs)  $t_s = N\tau/(uk)$ . The dissipated energy is still the elastic energy of a chain with uniform tension  $\tau$ .

At high velocities, the sticking time is obtained by a scaling argument similar to that used in the Rouse model. When the end point escapes from the trap after a time  $t_s$ , a chain section of  $s(t_s)$  monomers is stretched with a tension  $\tau$ . The characteristic relaxation time of this chain section is the Rouse time of the corresponding chain of blobs  $t_s = \frac{6\pi\eta s^2 \tau}{k^2}$ . Using the integrated equation of motion, we find the sticking time  $t_s = \frac{\tau}{6\pi\eta u^2}$ . It has the same dependence on the velocity as in the Rouse model but a different dependence on the tension which is due to the fact that one must now consider the chain as a Rouse chain of Pincus blobs and not of monomers.

The crossover velocity is obtained by comparing the low and high velocity results  $u_c = \frac{k}{6\pi\eta N}$  and the energy dissipated on a trap at high velocity is the elastic energy of a chain section containing  $s(t_s)$  monomers:  $W_d = \frac{\tau^2}{6\pi\eta u}$ . Here also we find the same dependence on velocity but a different tension dependence if we compare to the Rouse model.

## APPENDIX D: TRAPPING CROSS SECTION

In this appendix, we study the trapping cross section for the free chain end by the potential well of a trap on the surface. We focus on the undisturbed part of chain end of size  $\delta r$ . At very low velocity  $u \ll u_0 = R/T_R$  ( $T_R$  is the Rouse time) and  $\delta r$  is the chain radius  $R$ . At higher velocity the chain is stretched by the hydrodynamic friction and  $\delta r$  is equal to the local stretching blob size ( $\delta r \sim u^{-1/3}$ ). If we take the origin at the center of the first blob containing the free chain end, the surface monomer concentration at a distance  $r$  is :

$$c(r) \sim \delta r^{-2} \exp -(r/\delta r)^2 \quad (\text{D1})$$

The trap acts as an absorbing site and we consider that the chain end gets trapped when it diffuses to the surface of the trap of radius  $b$  (figure 1). If the trap is at a distance  $r$  from the average position of the end point, the concentration gradient close to the trap is  $c(r)/b$ . The total flux of end point towards the trap is thus given by :

$$q = 2\pi b D c(r)/b \quad (\text{D2})$$

The relevant diffusion constant  $D$  is equal to the Rouse diffusion constant of the whole chain  $D = k_B T / (N\zeta)$  at very low velocity and to the Rouse diffusion coefficient of the stretching blob  $D = k_B T / (s\zeta)$  ( $s$  is the number of monomers in the blob) at high velocity. Note that in two dimensions there are logarithmic corrections to this result as there is no stationary diffusion state. If the impact parameter (the minimum distance between the trap and the average chain end position) is  $c$  and if the distance is minimum at time  $t = 0$  the distance  $r$  varies with time as  $r^2 = c^2 + u^2 t^2$ . The probability  $p(c)$  that the chain with an impact parameter  $c$  gets trapped is obtained by integration over time of the flux  $q$ ,  $p(c) \sim \frac{u_0}{u} \exp -(c/R)^2$ . This probability is of course smaller than one. The trapping probability is thus equal to one if  $c < R \log^{1/2}(u_0/u)$  and decays as a gaussian for larger values of  $c$ . The trapping cross section (a length in two dimensions) is obtained by integration over the impact parameter

$$\sigma \sim R \log^{1/2}(u_0/u) \quad (\text{D3})$$

At higher velocity  $u > u_0$ , the trapping probability is always smaller than 1 and one can integrate the flux  $q$  to find the trapping probability and then the cross-section. One must however take into account that  $\delta r$  is now the size of the stretching blob and that the diffusion constant is not the diffusion constant of the whole chain but the one of a chain of size  $\delta r$ . The result is

$$\sigma \sim \left( \frac{a^2 k_B T}{\zeta u} \right)^{1/3} \quad (\text{D4})$$

The average distance between trapping events can then be calculated from the surface density of traps  $n$ ,  $d = 1/\sigma n$ .

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## Figures caption

- **Figure 1:** Polymer chain pulled at constant velocity  $u$  on a periodic 2D lattice of traps.
- **Figure 2:** Force (normalised by  $N\zeta u$ ) applied on the trapped monomer ( $s=0$ , black) and on the pulled one ( $s=N$ , grey) versus time (normalised by  $T_R$ ), according to equation 3.
- **Figure 3:** Friction force in a  $(u, d)$  diagram for the many traps problem at zero temperature.
- **Figure 4:** Trapping potential a)  $V(z)$  and b)  $U(z) = V(z) - \tau_{tr}z$ .



FIGURES

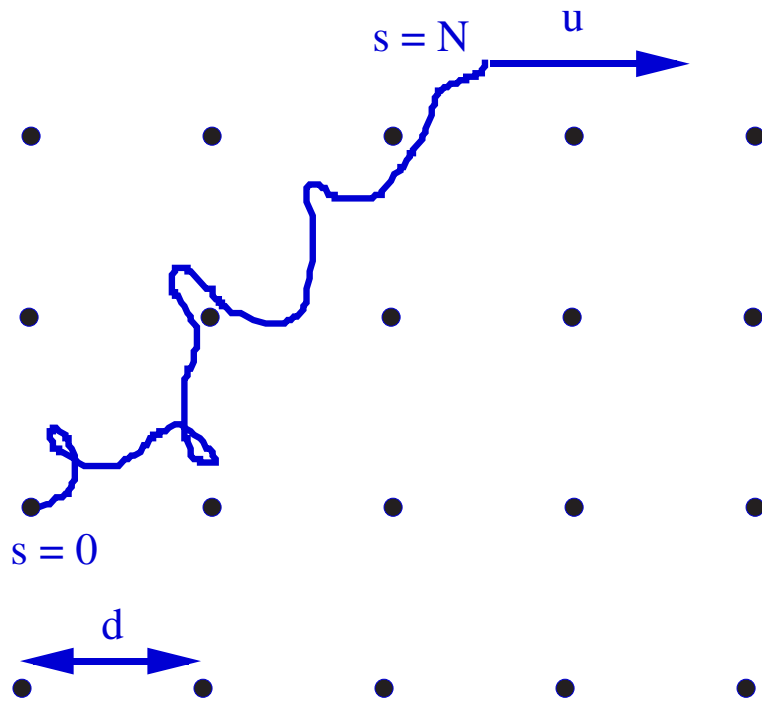


FIG. 1.

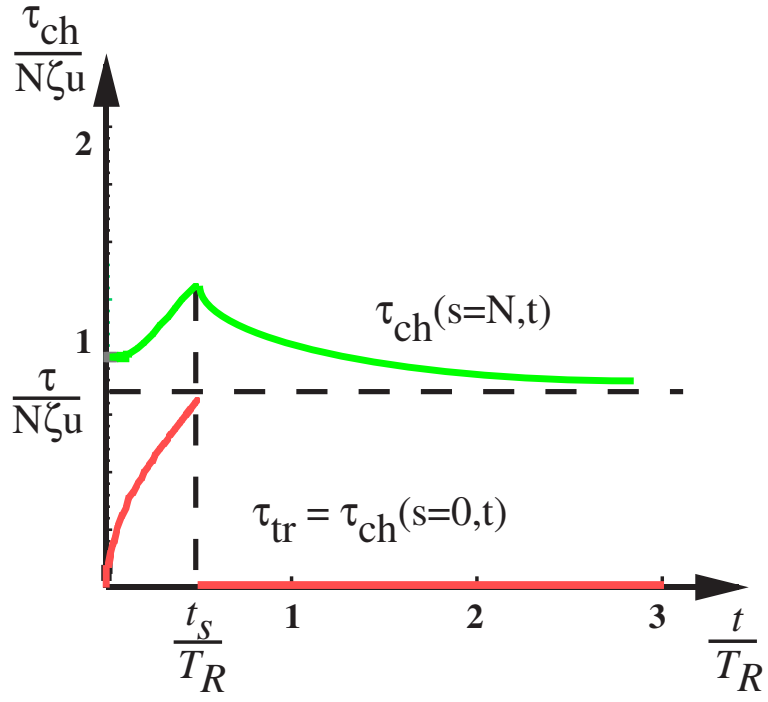


FIG. 2.

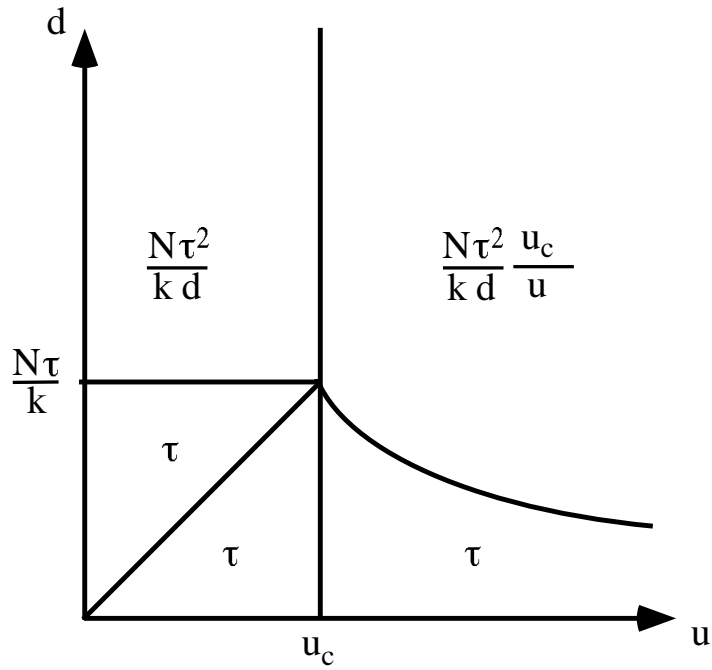


FIG. 3.

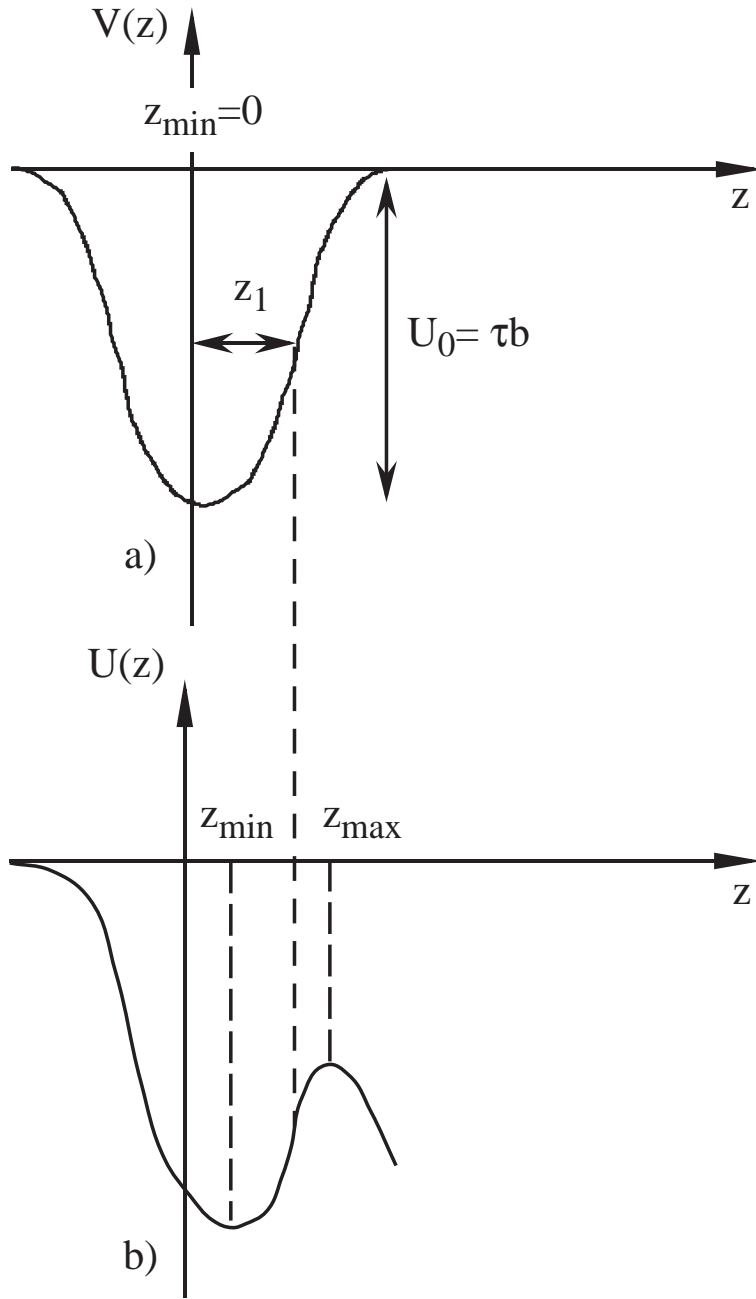


FIG. 4.