Stretching an adsorbed polymer globule

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Using molecular dynamic simulation, we study the stretching of an adsorbed homopolymer in a poor solvent with one end held at a distance z_e from the substrate. We measure the vertical force f on the end of the chain as a function of the extension z_e and the substrate interaction energy w. The force reaches a plateau value at large extensions. In the strong adsorption limit, we show that the plateau value increases linearly in w in good agreement with a theoretical model. In the weak adsorption limit, a polymer globule with a layered structure is formed and elastically deformed when stretched. In both cases a simple theoretical model permits us to predict the relation between the necessary force to fully detach the polymer and its critical extension.

With the new development of single molecule experiments, the nanomanipulation of individual polymer chains and biological macromolecules is becoming a very important subject in order to understand their mechanical properties and characterize the intermolecular interactions. Forces on the scale of the pico-newton have been measured with imposed deformation on the scale of the nanometer with atomic force microscope (AFM) [1] or optical tweezers [2]. Experiments with AFM have been conducted with different kinds of biological molecules such as DNA [2], Titin [4] and more recently Myosin [5]. Although experiments on a flexible polymer are more difficult to conduct due to its small persistence length, there have been several recent studies in both good and poor solvent conditions [6,7]. They show that a stretching experiment can give insight on the determination of different mechanisms of adsorption and on the intermolecular forces inside the macromolecule. On the theoretical side, the stretching of chains in a poor solvent has been studied by Halperin *et al.* [8] who predicted that at weak extensions the spherical globule deforms into an ellipse and that for a finite stretching force there exists a sharp first order unwinding transition between a globule and a chain. Numerical and theoretical studies have confirmed this scenario and have shown that there exists a coexistence state between a globule and a stretched chain [9–16]. As shown in [14] the critical value of the force saturates toward a finite value when the polymerization index N goes to infinity. In the presence of an adsorbing substrate force-extension relations have been obtained theoretically for an ideal Gaussian chain [17], for a polyelectrolyte in good solvent [18] and for a polymer chain in a good solvent [19]. More recently, experimental results have been obtained for a stretched polymer chain in a poor solvent adsorbed on a substrate [7]. In this Brief Report, we consider the problem of an adsorbed polymer globule in a poor solvent with one end fixed at a distance z_e perpendicular to the adsorbing substrate. The substrate is characterized by an homogeneous interaction energy w with the polymer. We mainly investigate the effect of strong adhesion w, however we also perform simulations for intermediate adsorption

for which the onset of poor solvent effect are present. We do not investigate here the weak adsorption regime for which most of the chain can evaporate from the substrate. Simulation results for the retracting force on the fixed end as a function of z_e and w are compared with an analytical model. As we stretch the polymer, we observe that the force rises until it reaches a plateau value which depends on w.

We use a molecular dynamics simulation technique where the equations of motion are integrated with the Verlet algorithm and the temperature fixed with a Nosé-Hoover thermostat [20]. The interactions between monomers consist of two parts: $V(r) = V_1(r) + V_2(r)$ (r is the distance between two monomers). $V_1(r) = a(r - d_0)^2 + b(r - d_0)^4$ is the valence interaction between nearest-neighbors (NN) monomers and $V_2(r) = 4\epsilon((\sigma/r)^{12} - (\sigma/r)^6)$ the Lennard-Jones interaction between non-NN monomers which englobes the poor solvent effect. Here for simplicity surface tension effects do not depend on the polymer configuration, although this dependence can be taken into account as done in [21], using many body forces. Finally, we simulate the presence of the atomically flat substrate by adding an attractive interaction between the wall and the monomers: $V_w(z) = w((\sigma_a/z)^9 - (\sigma_a/z)^3)$, where z is the distance to the wall. In the following we take $\epsilon = \sigma = d_0 = 1$, $a = 3000$, and $b = 10000$. The energies and distances are, respectively, expressed in units of ϵ and σ and the time step is $\Delta t = 10^{-3}$. For the present study we take $k_b T = 0.8$ so that the simulated polymer is under poor solvent conditions and still above the freezing temperature [21]. We simulate a polymer adsorbed on the substrate with one end fixed at a distance z_e from the wall (Fig. 1). In a first run, starting from a free adsorbed globule, a constant force (usually $f = 10$) is applied to the end of the chain until it reaches the value z_e. A second run, of roughly 10^6 molecular dynamics (MD) steps with z_e fixed, ensures thermal equilibrium. Finally, during a third run of 10^7 MD steps, different quantities like the time-averaged force on the end of the chain f, the density and energy profiles are recorded. As shown in Fig. 1, the adsorbed globule has a semispherical shape due to the effect of the poor solvent.
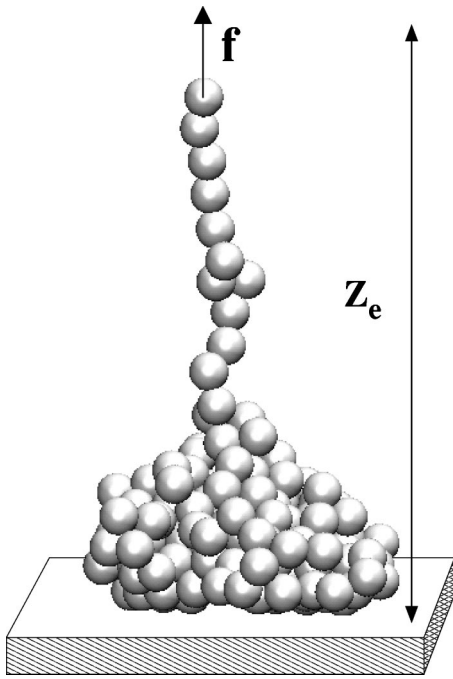
FIG. 1. Snapshot of the polymer adsorbed on the surface with a fixed end. (Simulation at $w=4$, $T=0.8$, $N=100$, and $z_e=15$.)

We consider a polymer composed of $N=100$ monomers for which we perform a set of force-extension measurements for a broad range of values of w ($2<w<80$) and for z_e varying between 3 and z_e^c, the critical value at which the polymer fully detaches from the substrate. For all w, we observe that the force rises as we increase z_e and saturates to a force plateau value f_p for the large z_e values. This is illustrated in the inset of Fig. 2, where a full force-extension curve is plotted. It is then possible to plot f_p as a function of w (Fig. 2). We observe that in the strong adsorption regime, the dependance of the plateau in w is linear. For weaker w values, the poor solvent effects become prominent and the relation between f_p and w deviates from linearity.

In Fig. 3, we present a force-extension diagram in the regime of strong adsorption ($w=60$) that presents pronounced oscillations. For these large values of w, the unstretched part of the polymer is fully squashed on the sub-
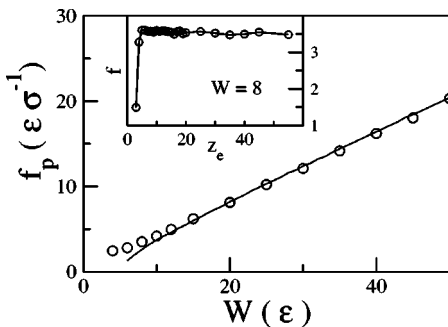

FIG. 2. Graph of f_p as a function of w for $T=0.8$. Circles are simulation results of the plateau value. The line corresponds to the theoretical prediction obtained by minimizing F with respect to N_c. The inset is a force-extension diagram for $w=8$.
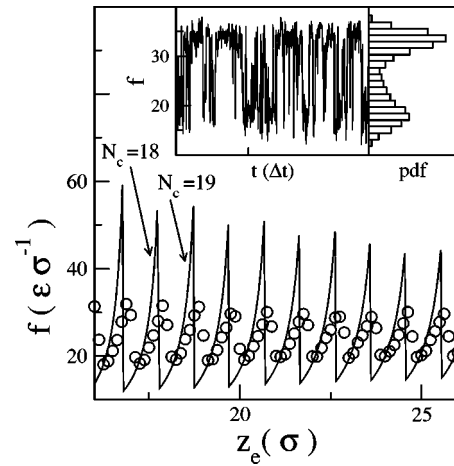

FIG. 3. Force-extension diagram in the strong adsorption limit for $T=0.8$ and $w=60$. Circles are simulation results and the line is the theoretical prediction presented below. Inset: $z_e=18$, time variation of the force together with its associated probability density function illustrating the dynamical coexistence between the two states with $N_c=18$ and $N_c=19$ monomers.

strate and forms a bidimensional (2D) globule. These oscillations are due to the discrete character of the chain and the peaks correspond to the transfer of a monomer from the globule to the chain. As we increase z_e, f increases rapidly until the next monomer can escape from the 2D globule. The stretching tension is then released, and f diminishes abruptly. As we still increase z_e this process repeats as long as there are enough monomers adsorbed. N_c being the number of monomers in the chain, we furthermore observe a dynamical coexistence between states with N_c and N_c+1 monomers in the chain. This is illustrated in the inset of Fig. 3 where we plot the dynamical variation of f together with its associated probability density function. For a fixed value of $z_e=18$, the system can be in two different states with $N_c=18$ and $N_c=19$. As a consequence the distribution function of f is bimodal. For smaller values of w the morphology of the adsorbed polymer is qualitatively different. As shown in Fig. 1, in the weak adsorption regime the polymer forms a 3D globule partially wetting the substrate. As we will discuss below, the top of the globule which is in contact with the chain is elastically deformed. As a consequence, the necessary force to extract a monomer varies continuously and the oscillations in the force-extension curve almost disappear (inset of Fig. 2).

We present a phenomenological model in order to understand the different results reported above. We assume that the fixed force and fixed z ensembles are equivalent. This is in principles valid, only in the thermodynamic limit. We therefore assume that the system is big enough to have small fluctuations. As shown in Fig. 1, the globule-chain system can be described as a stretched chain in coexistence with an adsorbed globule. There are two main contributions to the free energy F of the system: the free energy of the stretched chain F_c and the free energy of the adsorbed globule F_g. Let N_g and N_c be, respectively, the number of monomers in the adsorbed globule and in the chain, so that $N=N_c+N_g$. The major contribution to F_c comes from the reduction of the fluctuations of the stretched chain [22]

$$F_c = -N_c k_b T \log \left(4\pi \frac{k_b T}{f d_0} \sinh(f d_0/k_b T) \right) + f z_e, \quad (1)$$

where the potential energy of the chain is neglected. The dominant part of F_g comes from the interaction energy of the monomers with the substrate and the interaction between the monomers. We can neglect here the entropic contribution to F_g [23]. In the regime of strong adsorption, the interaction between monomers within the 2D squashed globule can be neglected relative to the substrate interaction. For large w values we have $F_g = -N_g w_{min}$ where w_{min} is the substrate potential minimum ($w_{min} \simeq 0.38 w$). We write the total free energy $F = F_c + F_g$, where z_e is fixed and f is an implicit function of z_e and N_c. Here z_e is given by the nonlinear Langevin relation [22]:

$$z_e = N_c d_0 \left[\coth \left(\frac{f d_0}{k_b T} \right) - \frac{k_b T}{f d_0} \right]. \quad (2)$$

We express the free energy F as a function of the unknown N_c by inverting numerically Eq. (2) for f. We then minimize numerically the free energy F with respect to N_c by keeping w and z_e fixed. For a large value of z_e, we substitute in Eq. (2) the obtained value of N_c to get the plateau force f_p. The simulated f_p values presented in Fig. 2 are in good agreement with our theoretical model for large w. In the high w limit and for $T=0$, we expect f_p to scale linearly with w so that $z_e = N_c d_0$. In this case the entropic contribution can be neglected relative to the free energy of the globule energy so that $f_p \propto 0.38 w$ in relative good agreement with the simulations ($f_p \propto 0.40 w$ for $T=0.8$). In the weak adsorption limit, the model underestimates f_p since the interaction between the monomers has not been included in F_g. In this case one should add to F_g monomer-monomer interactions of the wetting globule together with surface tension corrections. The surface tension correction gives a contribution of the order of $\gamma(N-N_c)^{2/3}$ to F_g, where γ is a phenomenological surface tension parameters. This contribution plays only a minor role. We find by performing the same minimization as above that there is a very slight decrease of the plateau value as z_e increased, this is also confirmed by our MD simulation. A good agreement between simulation and theory is also found for the extension-curve of Fig. 3 obtained for various values of z_e using the same procedure as above. The smoothing out of the peaks is due to the dynamical coexistence between states with N_c and N_c+1 monomers in the chain. This dynamical coexistence is induced by the thermal fluctuations and gives rise to important time variations of f.

As we increase the value of z_e, we assume that the polymer fully detaches from the substrate when $N_c=N$. Using the relation between f, z_e and N_c given in Eq. (2), we obtain the relation between the force f and the critical extension z_e^c at which the polymer detaches from the substrate. We plot in Fig. 4 the theoretical curve $f(z_e^c)$ and the simulation results for different values of w and different system sizes. Here again a good agreement is found between theory and simulation for the large w values. The agreement is slightly less satisfactory for weaker w values. In this case, we observe that the detachment occurs suddenly when a finite number of
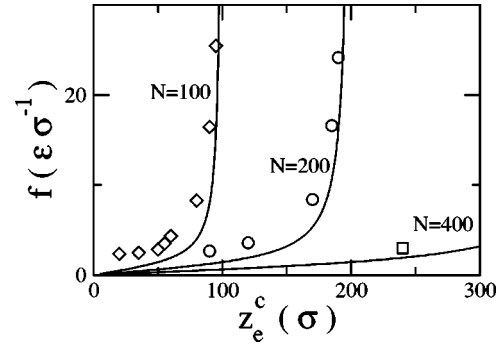
FIG. 4. Force at the detachment point z_e^c for different values of w and N. Diamonds: $N=100$, $w=3,4,6,8,10,20,40,60$ from left to right. Circles: $N=200$, $w=4,8,10,20,40$. Square: $N=400$, $w=4$. Full lines are theoretical predictions.

monomers are still adsorbed on the substrate ($N_c < N$). This is analogous to the first-order unwinding transition observed on a globule under tension and discussed in the Introduction.

We finally investigate the globule structure in the regime of weak adsorption in order to quantify its elastic deformation upon stretching. We represent in Fig. 5 the monomer density $\rho(z)$ and energy $E(z)$ profiles along z for different values of z_e. The density $\rho(z)$ presents decaying density oscillations similar to the one observed for a liquid in the presence of a solid substrate [24]. The presence of the density oscillations are due to the poor solvent effect. We have checked that in the good solvent case there are no density oscillations. As shown in Fig. 5 (top) the overall shape of the density profile in the globule is invariant, up to a normalization factor, as we stretch the chain. The layered structure can therefore co-exist with the stretched chain. As the monomers are extracted, the globule shape remains qualitatively the same, independent of the size and of the tension as long as the number of monomer in the globule is large enough. In Fig. 5 (bottom), we plot the energy density profiles $E(z)$ where $E(z)$ is the sum of the valence and of the Lennard-Jones interaction energies. We can see from $E(z)$ plotted for different values of z_e that there exist three different regions. In the first region ($z < 3$) mostly corresponding to the first
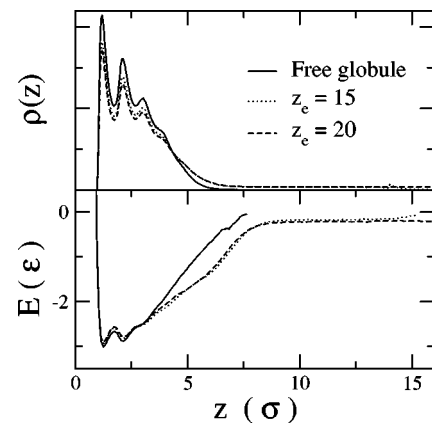
FIG. 5. (Top) $N=100$, density profiles $\rho(z)$ showing layering for a free globule and globules with $z_e=15$ and 20 ($w=8$). (Bottom) Energy profiles $E(z)$ for the same parameters.

adsorbed layers, the energy is independent of z_e. This is consistent with the above discussion on the negligible globule shape variation upon stretching. A second region, roughly comprised between $z=3$ and $z=8$, is formed between the globule and the chain. In this matching region the top of the globule is elastically deformed and pushed up by the tension. The overall vertical mechanical equilibrium is ensured by the elevation of the top of the globule. The small difference in the energy profiles computed for $z_e=15$ and $z_e=20$ in the second region also demonstrates that the elastic deformation is independent of the stretched chain length. Finally the third region ($z>8$), corresponds to the stretched chain with a very small potential energy, confirming our main theoretical hypothesis.

The picture we have presented above holds also for larger value of N. Simulations which are not presented here have shown that f_p depends only weakly in N and finally saturates. To summarize, our simulations have shown that there is a plateau value for the force that depends on the substrate interaction w. In the strong adsorption limit the unstretched part of the polymer forms a 2D globule. A dynamical coexistence between states with N_c and N_c+1 monomers in the chain has been observed. For weaker w values the adsorbed polymer forms a 3D globule wetting the substrate and elastically deformed upon stretching. A simple theoretical model of the force extension relation is presented and leads to a good agreement with simulation results. The influence of the chain persistance length, of the temperature and of finite size effects will be presented elsewhere. We hope that this work will motivate new experiments on the stretching of long molecules and biomolecules. The weak adsorption regime will be investigated elsewhere.

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