Polymers Grafted onto Strongly Adsorbing Surfaces in Poor Solvents: Stretching, Fission, Phase Separation, and Globular Micelles in 2D

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(Received 8 June 1998)

Using both analytic theory and computer simulation we study the stretching along the surface of a strongly adsorbed polymer chain. In marked contrast to the case of nonadsorbed chains we show that the polymer does not undergo a Rayleigh instability. Instead it deforms steadily into a lens shape. Our results have dramatic consequences for submonolayer films formed from grafted chains. We show that strongly adsorbed chains do not form "octopus" or pinned micelles. Instead they fuse into compact islands, which in the limit of high grafting density can form a continuous network. [S0031-9007(99)08783-9]

PACS numbers: 61.41.+e

The subject of polymers grafted to surfaces has received considerable attention during the past decade [1]. Grafting has enabled studies of polymeric distortion and presents a number of novel problems. On the experimental front grafting of polymers is now reasonably straightforward and the development of techniques, such as atomic force microscopy, has allowed the direct study of polymerically grafted surfaces and single polymer chains on the scale of a few angstroms. Grafted polymers have a number of practical applications in colloidal stabilization, diblock copolymer microphases, drug delivery, and surface coatings. Much of the attention, both experimental and theoretical, has focused on the case of polymers in good solvents, where the chains are swollen. Considerably less attention has been placed upon the case of poor solvents. In poor solvents, such as air, isolated chains want to avoid contact with the solvent. An isolated chain in 3D in a bad solvent thus forms a roughly spherical globule of radius $R \sim aN^{1/3}$, where a is the monomer size and N is the number of monomers. The stretching of such chains was studied originally by Halperin and Zhulina [2] who argued that at weak extensions the globule deforms into an ellipse and then into a cylinder. At a critical extension the polymer undergoes a sharp first-order transition into a "ball and chain" configuration. This transition is a manifestation of the Rayleigh instability for a liquid cylinder [3,4]; i.e., the polymer can decrease its surface energy by breaking into a ball and a thin filament. This instability has consequences for chains grafted to nonadsorbing surfaces in a poor solvent. In this case the chains fuse to form "octopus" surface micelles or pinned micelles [5–10] which consist of a central core globule connected by several thin tethers to the surface. However, whenever the surface is strongly adsorbing we find that a very different picture emerges.

For strong surface adsorption an isolated chain forms a flat pancake of radius $R \sim aN^{1/2}$ and height a, effectively trapping the chain in 2D. Our aim is to examine the stretching deformation of this 2D system and to show that it is very different from the 3D case. In particular there is no sharp shape transition as a function of chain stretching and the chain remains more or less uniform in shape. We use four approaches to show this. One is analytic theory, one is numerical, and the other two are computer simulations. We then show how this novel chain deformation affects the interaction of two grafted chains [11]. In the strongly adsorbed case we show that there are no octopus micelles—the chains can fuse, but only to form globular micelles with no corona. This has dramatic consequences for strongly adsorbed monolayer films, which we predict should be much more uniform than their weakly adsorbed counterparts.

We begin by considering the stretching of a single chain in the x direction along the surface, with the end-to-end distance specified as $d = 2w$. The stretching involves two free energy penalties. One is the creation of an extra interface between the polymer and the solvent. This can be quantified by a line energy which is equal to the perimeter of the drop multiplied by the line tension Λ. In general $\Lambda = \lambda kT/a$, where λ is a constant of order unity. The second term is the deformation entropy of the polymer chain. We will show later that this is small except for strong deformations, so we ignore it in our initial calculation. The initial problem is then to calculate the shape which minimizes the perimeter of our globule for constant stretching distance d. Let the equation of one interface of the drop be $y(x)$. The perimeter of the drop is then $P = 4\int_0^w dx\sqrt{1 + (dy/dx)^2}$. Introducing a Lagrange multiplier $1/\rho$ to account for the fixed area of the drop leads us to minimize the functional

$$F = \int_0^w dx\sqrt{1 + (dy/dx)^2} - \rho^{-1}y\,. \qquad (1)$$

Taking the functional derivative yields a differential equation for the drop shape, $\rho(d/dx)[y'(1 + y'^2)^{-1/2}] = -1$ subject to the boundary conditions $y' = 0$ at $x = 0$ and $y = 0$ at $x = w$, where the prime means d/dx. The

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boundary condition $y = 0$ is the natural one—it says that the top half of the globule meets the bottom half at a point. Integrating yields the solution $[y + (\rho^2 - w^2)^{1/2}]^2 + x^2 = \rho^2$, i.e., a part of a circle with center $(0, -(\rho^2 - w^2)^{1/2})$ and radius ρ. The globule is thus lens shaped. We can test this by carrying out a numerical brute force minimization of the perimeter at constant area [Fig. 1(a)] for a given stretching distance. This does indeed yield a lens shape. This should be contrasted to the result for 3D [Fig. 1(b)] which exhibits a Rayleigh instability.

The area of the globule is $A = 2w^2 f(q)$, where $f(q) \equiv q^{-2}\sin^{-1}(q) - (q^{-2} - 1)^{1/2}$ and $q \equiv w/\rho$ $(0 < q < 1)$. q describes the flatness of the lens: a small q indicates a very flat lens with the drop shape being very close to a rectangle. The area must be equal to the area of the undistorted drop πR_0^2, giving one equation. The perimeter is $P = 4w\sin^{-1}(q)q^{-1}$. These equations can be written in a form which gives the perimeter and stretching distance $2w$ parametrically in terms of q.

$$w = R_0\sqrt{\frac{\pi}{2f(q)}}\,P = 4R_0 q^{-1}\sqrt{\frac{\pi}{2f(q)}}\,\sin^{-1}(q)\,. \qquad (2)$$

In the limit of weak stretching $(w - R_0 \ll R_0)$ this becomes $P = 2\pi R_0 + \pi R_0^{-1}(w - R_0)^2$ while for strong stretching $w \gg R_0$ we obtain $P = 4w$, i.e., the result for a long rectangle. The corresponding force laws $F = \frac{1}{2}\Lambda dP/dw$ are interesting. For weak stretching we obtain linear response $F = \Lambda\pi R_0^{-1}(w - R_0)$. However, for strong stretching we obtain $F = 2\Lambda$ (i.e., a constant). The crossover between these two regimes occurs at $w \approx 2.5R_0$. This implies that beyond a critical force of $F_{\mathrm{crit}} = 2\Lambda$ the line tension cannot resist the applied force and the globule stretches indefinitely. However, in this regime, where w is significantly larger than R_0, the entropy of chain deformation becomes important. This provides a free energy penalty of $U \approx kT/(Na^2)(4w^2) = 4kT/(\pi R_0^2)w^2$ and a force of $F = 4kT/(\pi R_0^2)w$. Hence there are two force regimes. For weak stretching $w < 2.5R_0$, the line tension dominates the response to the force and the response is linear. At stronger stretching $w > 2.5R_0$, the entropic force comes into play. At these extensions dF/dw is dominated by the entropic part and the line tension provides a constant background. The slope of the force curves, dw/dF, is very different in the two regimes. The ratio of the slopes for weak and strong stretching is $\approx \lambda^{-1}(4/\pi^2)a/R_0 \ll 1$. Thus the slope is much smaller initially. Note that the force contributed by the line tension is still very high, even in the regime where the entropic part dominates dF/dw. Indeed it is not until $w = \lambda\pi R_0^2/2a = \lambda Na/2$ that the entropic stretching begins to dominate the free energy. In this regime the chain is stretched to its full extension and our assumption of a Hookean restoring force breaks down.

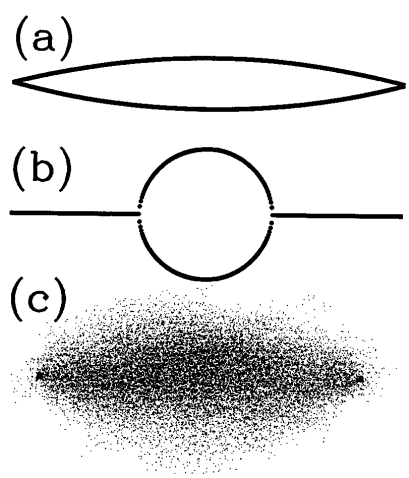

FIG. 1. The shape of a polymer droplet stretched a fixed distance. In (a) is the 2D result of a numerical minimization of the perimeter of the droplet at constant area. In (b) is a cross section of the 3D result of minimization of the area at fixed volume. Note that in this case a Rayleigh instability occurs and the droplet takes the shape of a sphere connected to the tether points by two cylinders of zero radius. In (c) we show the result of Monte Carlo simulation for a 200 monomer chain, stretched a distance of 50 units. After equilibrium was reached the system was run for 10^7 Monte Carlo steps per monomer and 100 images of the chain were plotted. This yields an average shape close to the zero temperature lens shape in (a) but with some thermal rounding.

The analysis just carried out is valid in the limit of zero temperature; i.e., it neglects the effect of thermal fluctuations on the overall shape of the chain. In order to see if our conclusions remain valid when thermal effects are introduced, we have carried out two different and totally independent Monte Carlo computer simulations of this system. These are both lattice based and use Hookean springs, a square lattice, local nearest-neighbor interactions, and the Metropolis algorithm. In both at most one monomer can occupy each lattice site. We show results here only for one simulation, which uses a Hookean spring energy between neighboring monomers of $\frac{1}{2}kr^2$ with $k = 0.6kT$ and a local bond energy between contacting monomers of $1kT$. The other simulation produces similar results. We have checked explicitly, by plotting the radius of gyration of the polymer as a function of temperature that our chain is below the θ point. In the simulation an initially unstretched collapsed chain, tethered at one end, is subjected to a force at the other end and then equilibrated. The force is then increased slightly and again the system is equilibrated. This process is then repeated. The simulations produce the droplet shapes and force the curve shown in Figs. 1(c) and 2. Both of these simulations confirm that the above picture of a more or less uniform lens-shaped droplet is correct, although naturally some thermal fluctuations are imposed on top of the overall shape. These fluctuations mean that at intermediate stretching the drop resembles a map of Japan. Figure 2 also shows clearly the two different stretching regimes. In the particular case of a 200 monomer chain the boundary between these regimes should lie at $d \approx 5R_0 = 5\sqrt{N/\pi} = 40$, in good agreement with the Monte Carlo data.

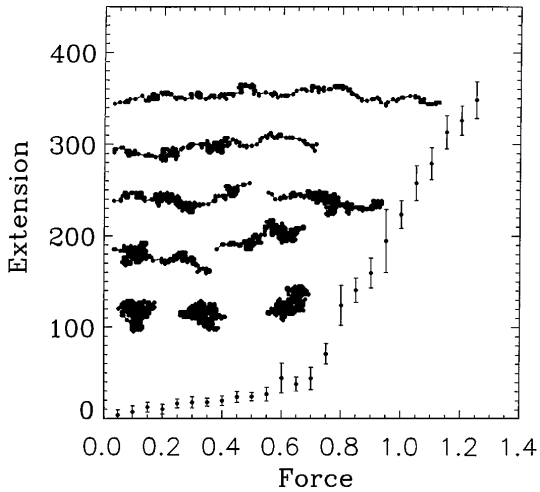

FIG. 2. The extension (in lattice constants a) versus force curve (in units of kTa^{-1}) for a 200 monomer chain from the Monte Carlo simulation. Note the two linear regimes, one at low force, dominated by line tension and the other at high force dominated by chain stretching. The images are snapshots of the chain at different extensions. Note that the chain often exhibits a blobby configuration; i.e., thermal fluctuations imposed upon the lens shape of Fig. 1(a) are important. For each force a total of 2.5×10^6 Monte Carlo steps per monomer were attempted.

Thus we have two main conclusions for the stretching of a single chain on a strongly adsorbing surface. The first is that the chain extends to take a fairly uniform shape; i.e., it does not undergo a ball-and-chain or Rayleigh instability. This is in marked contrast to the weakly adsorbing or 3D case. The second conclusion is that there are two force regimes, both with approximately linear response, but with no sudden jumps between them. Before we consider extensions and implications of these conclusions we discuss briefly the results of an earlier study of the problem [12]. Wittkop *et al.* have carried out a Monte Carlo simulation of this system using a fixed extension and have measured the force using a novel "jump attempt" method. They find that the polymer does undergo a Rayleigh instability, in marked contrast to our claim. We cannot say precisely why the four methods we have used disagree so strongly with the conclusion of their study. One of many possibilities is that the pictures generated in Ref. [12] are of chains which are not equilibrated. Indeed if we take a chain and apply a steadily increasing force but do not equilibrate the chain between force increments, we can readily get the polymer to form a ball and chain. This, however, is not the equilibrium shape. Another possibility is that in Ref. [12] an attractive potential with a range of three lattice sites is used. For a large number of monomers this should be equivalent to our contact-only model. However, in Ref. [12] 100 monomers are used and in that case a substantial fraction of the chain is influenced by each monomer. This "long range" effect might give rise to a Rayleigh instability for short chains.

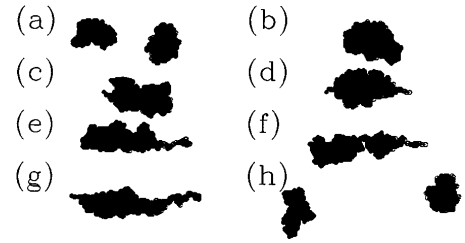

FIG. 3. Monte Carlo results for a pair of 500 monomer chains. The chains begin in (a) as roughly circular pancakes separated by a distance of 100. They are then brought together (solid points) at a fixed rate until they fuse at a distance of 30 (b). After further collision they are separated at the same fixed rate (empty circles) until at a distance of 120 they undergo fission (h).

Although the above single chain results are of fundamental importance in understanding the deformation of polymers in 2D it is the case of two or more chains that is relevant in practical problems of grafted chains at surfaces. Indeed the original motivation of this work was to extend the octopus micelle problem to strongly adsorbing surfaces. To do this we need to examine the case of two tethered polymers separated by a distance X. If X is very large we expect that the two chains will form individual circular pancakes of radius R_0. However, at some smaller separation X_c the chains will want to fuse. Our aim here is to find when this occurs and the shape of the fused globule. The second question can be answered immediately. The fused globule will be lens shaped with the radius R_0 in Eq. (2) replaced by $R_2 = \sqrt{2}R_0$ and with $w = X/2$. We can show that at fusion the entropic free energy is negligible compared to the line energy. Thus to find the critical distance we need to equate the perimeter of the

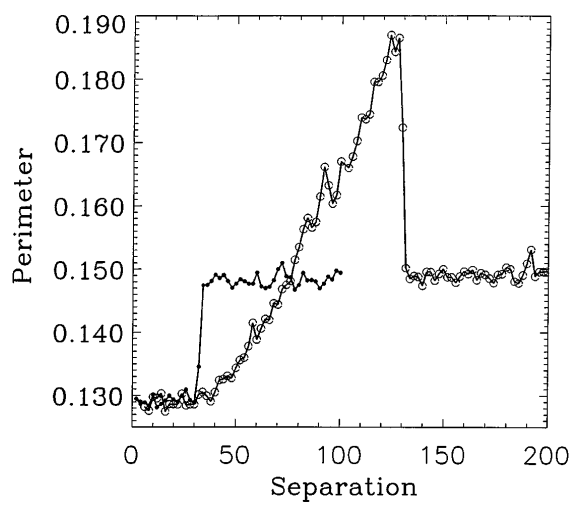

FIG. 4. The perimeter versus separation distance for the scenario shown in Fig. 3. Here the "perimeter" is defined as $p = (2 - n)/2$, where n is the number of nearest-neighbor contact per monomer. Very clear evidence of hysteresis can be seen.

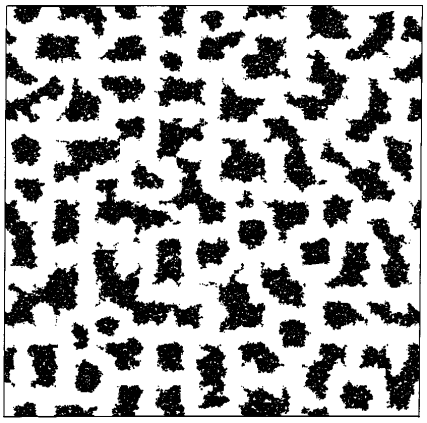

FIG. 5. Results from a Monte Carlo simulation of 400 polymer chains each of 200 monomers on a 500×500 lattice. This image is taken after 10^6 Monte Carlo steps per monomer. There is clear evidence for formation of globular surface micelles, but there are no octopus micelles, i.e., no long tethers. The dynamics of this system become very slow at long times so this picture is only an approximation of the "final" state of the system.

fused globule to the two perimeters of the individual pancakes. This yields a critical value of $q_c = 0.481$ or a critical distance of $X_c = 6.022R_0$; i.e., the chains fuse across several pancake radii. At this critical distance the aspect ratio of the lens is $2y(0)/2w = q^{-1} - (q^{-2} - 1)^{1/2} = 0.2566$. Note that X_c is the distance at which the free energies of the fused and separated states are equal. These two states are, however, separated by a very large energy barrier. Given a long enough waiting time the transition will occur at X_c. However, in practice the transition may occur well away from X_c, and the system will show substantial hysteresis. This can be seen in Monte Carlo simulations of a two-chain system (Figs. 3 and 4). Here the tethered ends are first placed far apart and then slowly moved together at a rate of two lattice sites per 10^6 attempted moves per monomer. The process is then reversed.

Finally we consider how a system of chains grafted to a surface behaves. In the 3D case or no or weak adsorption [5–10,13] what is found is a number of octopus or pinned micelles, with thin tethers connecting the micelle cores to the surface. In theory chains which are widely separated can fuse to form one micelle and hence the surface is very unevenly coated by chains. The 2D case of strong adsorption should be very different. We have shown that chains can fuse only when they are of order a six chain radii apart. When they do fuse they should not form tethers but should form more or less uniform globular micelles. This implies that a surface coated with such chains should have a much more uniform appearance than one coated by weakly adosrbing chains. This can be readily shown by Monte Carlo simulation (Fig. 5).

In conclusion we have shown that the deformation of a strongly adsorbed polymer chain in a poor solvent is very different from the weakly adsorbed case. In particular the 2D chain does not undergo a Rayleigh instability, and there are no sharp jumps in the force curve. However, many questions remain, especially the effect of hysteresis upon chain-chain interactions.

The authors thank Tim Senden for useful discussions. D. R. M. W. was supported by an ARC QEII and an ARC large grant.

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