Molecular Dynamics Simulations of the Force between a Polymer Brush and an AFM Tip

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A novel method to probe polymer-coated surfaces has recently been demonstrated by Overney *et al*.[1] Unlike the more established surface force apparatus technique,[2−4] in which two "macroscopic" surfaces are brought into contact, the new method utilizes an atomic force microscope (AFM) to measure the local properties of a polymer-coated surface through the use of a "microscopic" tip. Overney *et al*. applied this method to measure the response of polymers end grafted at one end to the surface, to both statically and dynamically applied forces, under various solvent conditions. Static force−displacement curves are much softer than those obtained using the surface force apparatus as the chains can partially avoid compression by escaping from the AFM tip, whose radius is of the order of the chain dimensions. Dynamic force−displacement curves allow direct measurement of the brush height, in addition to giving information on the viscoelastic properties of the system.

The interaction between a grafted layer, commonly referred to as a polymer brush, and the AFM tip is similar to that of a layer with a particle of finite size. A theoretical discussion of the latter situation has recently been presented by Subramanian *et al*.[5] Their treatment considered both the brush (high grafting density) and the mushroom (low grafting density) regimes. For solid brushes, in which the grafting points on the surface are immobile, they assumed that when the particle is pushed against the grafted chains, the chains undergo pure compression and do not splay. Under such an assumption, the force per unit area F/A of compression (force divided by the cross-sectional area of the compressing particle) does not depend on the radius of the compressing particle and is identical to F/A for a brush pressed by a flat (infinite radius) plate. In the mushroom regime, they allow the chains to deform and escape compression, and in this case Subramanian *et al*. find that the chains do splay to the side to avoid being compressed. We show below that in fact the chains readily splay to avoid compressions even in the brush regime.

In this communication, we calculate the interaction between a brush in a good solvent and an AFM tip using molecular dynamics simulations. Our purpose is to obtain the force−displacement curves for the penetration of such a tip into a brush as a function of the tip dimension and layer characteristics (chain length and grafting density). We also investigate the interaction between a brush and a tip onto which similar chains have been grafted. The interaction between a brush and an AFM tip can easily be simulated by a slight variation of the algorithms used to study forces between two surfaces bearing end-grafted polymer brushes.[6] To this end, the AFM tip is represented as an impenetrable surface, consisting of a long cylinder of radius r_{cyl}, with a spherical cap of radius r_{sph} ($\geq r_{cyl}$). When such a tip is moved into a brush, the surface of the tip starts interacting with the brush monomers. The magnitude of the interaction is determined from the distance of closest approach between the monomer and the tip (on either the spherical cap or the cylindrical part). The direction of the force on the monomer is normal to the tip surface and away from it. The response of the brush to compression by the tip is evaluated through the calculation of the total force exerted on the tip by the monomers of the brush. In the simulations whose results are given below, we assumed either a purely repulsive force between the monomers and the surface, as was done in earlier calculations of the interaction between brushes,[6] or one with an attractive short-range component.[7,8] Both of these forces gave qualitatively similar results.

The simulations started with an equilibrated brush containing $M = 200$ chains of length $N = 100$ and a tip far enough above that it was not in contact with the brush. The tip was then gradually pushed into the brush along a line normal to the grafting surface. After moving the tip to a prespecified distance from the grafting surface, the position of the tip was held fixed and the system reequilibrated. The monomers interacted with a purely repulsive Lennard-Jones 6−12 potential which is truncated at $r_c = 2^{1/6}\sigma$, where σ is the Lennard-Jones unit of length. Since only excluded volume interactions are included, this model represents a brush under good solvent conditions. Further details of the method can be found elsewhere.[6,9]

Figure 1 shows the force−displacement curves obtained for grafted layers for two values of the surface coverage, $\rho_a\sigma^2 = 0.1$ and 0.07, compressed by tips of various combinations of the radii r_{cyl} and r_{sph}. These two values of ρ_a are in the brush regime in which the height h scales as $h \sim N\rho_a^{1/3}$.[7] Also shown are the results for a flat plate pushed against a polymer brush and for two brushes pushed against each other, with $M = 50$ chains attached to each surface. The force F is normalized by the area A of contact. For the simulations with the tip, this area equals that of the spherical cap. The distance D between the grafting surface of the brush and the opposing surface (either the spherical cap or the flat plate) is normalized by N (which is proportional to the brush height) and the number of grafted surfaces n_s in the system. For the bare plate and tip, $n_s = 1$, while for two surfaces coated with end-grafted chains, $n_s = 2$. From the results in Figure 1a, one can make the following observations: (a) In the brush regime, the force between two surfaces coated with end-grafted polymers is nearly identical with that between a bare and an end-grafted surface, when the displacement is normalized by the separation at which the repulsion first appears. Although not shown in the figure for the sake of clarity, results for systems with $N = 50$ at the same surface coverage also collapse onto the same curve. (b) When the brush is compressed by tips of small radius ($r_{cyl} \lesssim 10\sigma$ in the case), the force−displacement curves collapse onto one curve. The chains that are in contact with a small-radius tip avoid compression by moving away from the tip, so that the resistance to compression increases very slowly. This result is in contrast to the assumption of Subramanian

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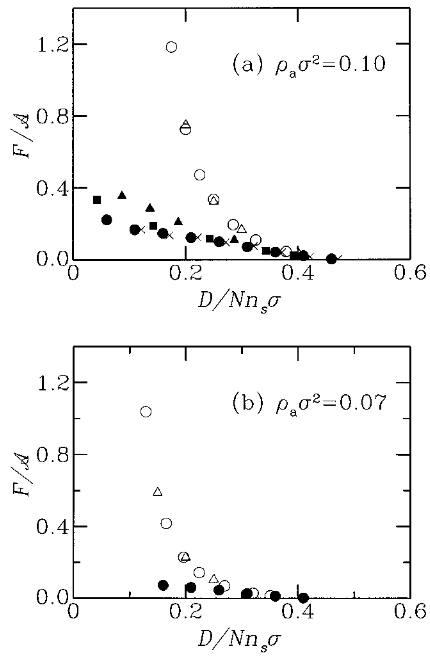

Figure 1. Force−displacement curves for a brush with grafting density (a) $\rho_a = 0.1\sigma^{-2}$ and (b) $0.07\sigma^{-2}$ for chain length $N = 100$, compressed by an identical brush (○), an infinite, bare surface (△), and an AFM tip. The radii (r_{cyl}/σ, r_{sph}/σ) of the tip are (7, 10) (×), (10, 14) (●), (14, 20) (■), and (16, 100) (▲). The distance D between the surfaces is scaled by the chain length N and the number of surfaces bearing end-grafted polymer, n_s.

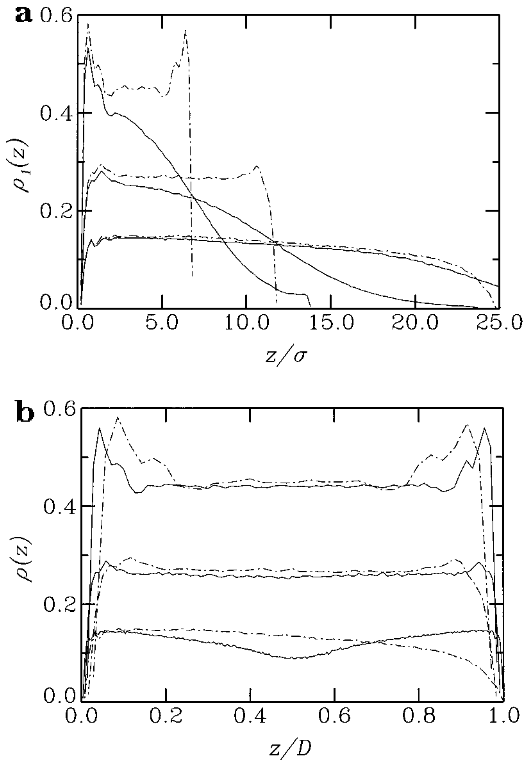

Figure 2. (a) Monomer density $\rho_1(z)$ of a brush as a function of the distance z from its grafting surface, when the brush is compressed by an another identical brush (solid curve) or by an infinite, bare surface (dashed curve). The grafting density of the brush is $\rho_a\sigma^2 = 0.03$. The plots shown correspond to distances $D = 49.8\sigma$, 24.0σ, and 14.0σ between the grafting surfaces of the two brushes and to distances $D = 24.8\sigma$, 12.0σ, and 7.0σ between the grafting surface of the brush and the bare surface. The highest density plots correspond to the smallest values of D. (b) Total density profile $\rho(z)$ in the space between the two surfaces for the situations described above as a function of z/D. Note that for a brush being compressed by a flat surface, $\rho(z) = \rho_1(z)$.

et al.[5] (c) As the tip radius increases, it becomes increasingly difficult for the chains to escape compression by moving away from the tip. This results in a crossover toward the case of compression by a flat plate, as observed for $r_{cyl} = 16\sigma$. This value of tip dimension is significantly larger than the mean separation between chains on the grafting surface, which is approximately $d \simeq 3.2\sigma$ for $\rho_a\sigma^2 = 0.10$. Simulations with a very large tip ($r_{cyl} = 21\sigma$) show that F/A steadily approaches that for a flat plate.

Force−displacement curves for brushes at a somewhat lower grafting density, $\rho_a = 0.07\sigma^{-2}$, are presented in Figure 1b. As in Figure 1a, results are shown for a polymer brush compressed by another polymer brush or by a flat plate. Not surprisingly, as ρ_a decreases, the force−displacement curve for a small-radius tip increases even more slowly with compression compared to that for a flat surface (coated or not).

In the AFM experiment of Overney *et al.*[1] there were only a few chains directly under the tip. Our simulation results for small-radii tips ($r_{cyl} \lesssim 10\sigma$) are therefore closest to the experimental situation studied in ref 1. We disagree with their conclusion that the force−displacement curve for an AFM tip is comparable for small compression to that for a second flat surface. We believe the problem arises in matching two different sets of experiments, a difficulty which does not arise in the simulations.

The similarity between the force−displacement curve for two brushes and that of a brush against a bare surface can be understood heuristically from the similarity of the total monomer density distribution in the two cases. Figure 2a shows the monomer density $\rho_1(z)$ for chains grafted to one surface for the brush compressed by another brush (solid curve) and for a brush compressed by a flat plate (broken curve). The plots display $\rho_1(z)$ for three values of the separation D between the plates. Obviously $\rho_1(z)$ for the two systems are very different. However, the *total* density $\rho(z)$ as a function of the normalized coordinate z/D (Figure 2b) of the two systems is very similar, especially at the higher values of compression. This similarity in the density distribution leads to a corresponding similarity in the pressure (repulsive force between the confining surfaces), even though there is considerable interpenetration of monomers from the two opposing surfaces when both surfaces are coated with end-grafted polymer. This result clearly demonstrates that from the force profile alone, one cannot determine the amount of polymer interpenetration. The layering near the surface for small D arises from the finite volume of the monomers and does not depend on whether or not the polymers are end grafted to the surface.

In order to demonstrate that the chains do indeed escape the tip, we show in Figure 3 the local monomer number density $\rho(z,r)$ as a function of the distance z from the grafting surface, for three values of the lateral distance r from the point on the tip that is closest to the grafting surface. The plot is for $\rho_a = 0.1\sigma^{-2}$, $N = 100$, $r_{cyl} = 10\sigma$, and $r_{sph} = 14\sigma$. The distance between the tip and the grafting surface of the brush is 11σ, much less than the brush height, which is about 50σ.[7] The monomer density for the region under the tip ($r < r_{cyl}$) drops off to zero at the surface of the tip, while for larger values of r, it extends further out. One can see that although the tip penetrates significantly into the

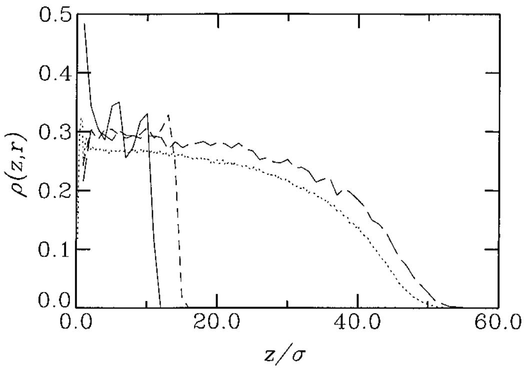

Figure 3. Local monomer density $\rho(z,r)$ as a function of z for $r = 1\sigma$ (solid curve), 10σ (short dashed curve), and 15σ (long dashed curve). z is the distance from the grafting surface of the brush and r is the lateral distance from the center of the tip. The plot is for $N = 100$, $\rho_a\sigma^2 = 0.1$, $r_{cyl} = 10\sigma$, and $r_{sph} = 14\sigma$. The distance of closest approach between the spherical cap and the grafting surface is 11σ. Also shown for comparison is the density profile $\rho(z)$ for an identical isolated brush (dotted curve).

brush, the local density has not increased in the region under the tip, retaining a plateau value of about $0.3\sigma^{-3}$, except very close to the grafting surface immediately under the tip center. This plateau value is only slightly higher than the plateau value of about $0.26\sigma^{-3}$ for a single brush at the same value of ρ_a. The density profile at $r = 15\sigma$ is very similar to the density profile $\rho(z)$ of an identical isolated brush (the dotted curve in Figure 3), though somewhat higher. While for larger r, the profile should be identical to the isolated brush profile, we do not observe this due to the finite size of the simulation cell in the lateral dimensions (44.7σ for the case shown in Figure 3). The chains under the tip spread out on the surface, and reorient themselves in such a way that they avoid the region underneath the tip. Thus rather than a significant increase in the local density under the tip, there is a slight increase in density in the vicinity of the tip.

We have also simulated a system in which chains of the same length as in the brush are grafted onto the compressing surface of the tip. The grafting density is taken to be identical to that of the brush. To our knowledge, this situation has not been studied experimentally; however, grafting of chains on the surface of the tip should be technically feasible.[10] Figure 4 shows the force−displacement curve for such system, together with the curves for the same brush, compressed by a bare tip of identical radius and by another brush. The chains are length $N = 100$ and the grafting density $\rho_a = 0.1\sigma^{-2}$. The tip radius $r_{cyl} = 10\sigma$. The force exerted by the brush on the tip also includes the interaction between the monomers belonging to the brush and those belonging to the tip. Covering the tip with chains clearly gives a much steeper force−displacement curve compared to a bare tip penetrating a brush. This differs from the case of a flat plate compressing the brush, which gives the same force−displacement curve as when the flat plate is covered with chains. Even so, resistance

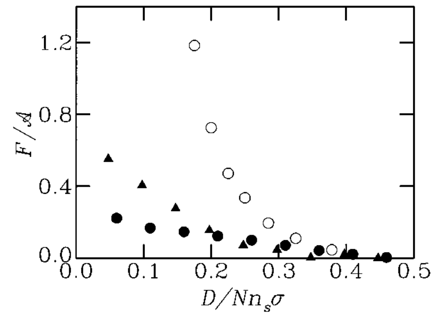

Figure 4. Force−displacement curves for a brush with grafting density $\rho_a = 0.1\sigma^{-2}$ and chain length $N = 100$, compressed by an identical brush (○), a bare tip of radius $r_{cyl} = 10\sigma$ (●), and a tip of the same radius coated with end-grafted chains of length $N = 100$ at the same grafting density (▲).

(per unit area) to penetration remains much weaker than the resistance to compression by another brush (or a flat plate). Analysis of the local monomer density shows that chains from both surfaces again avoid compression by reorienting themselves.

In conclusion, we have calculated the force−displacement curves for the penetration of a finite area surface (that represents an AFM tip) into an end-grafted polymer layer in the brush regime. When the tip area is small, the force per unit area of the compressing object is much smaller than when the brush is compressed by an infinite plate or another identical brush. This is because the chains can escape compression by lateral motion, even when the grafted layer is in the brush regime. As the tip dimensions are increased, the force−displacement curve crosses over as expected to that for an infinite surface area. However, this crossover occurs when the tip area is significantly larger than the area per chain head in the brush. We also found that covering the finite area tip with chains increases the repulsion compared to the repulsion of a bare tip. The resulting force−displacement curve is still significantly softer than compression by an infinite area plate or another brush.

References and Notes

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