Surface Instabilities of Monodisperse and Densely Grafted Polymer Brushes

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Surface effects on polymer brushes are of increasing interest, since recent experimental progress has nourished the hope that functional surfaces could facilitate the creation of novel materials, affecting almost every facet of modern life.[1–3] The creation of switchable brushes which react on variations of the external conditions are of particular interest in applications as diverse as textile industry, environmental technology or biotechnology.[4,5] At the same time, novel experimental techniques have allowed to create polymer brushes of very high grafting densities, reaching a chain stretch of 0.7 of maximum chain length.[6] The properties of brushes at low grafting densities are well described by self-consistent field (SCF) approaches[7,8] and scaling arguments.[9] Systems of high grafting densities have been simulated in rather recent studies, in which strong deviations of the density profiles from SCF predictions have been reported.[10–12] These were, at least partially, related to the finite extensibility of the chains.[11,13,14]

Modifications of brush properties, for instance due to polydispersity effects, have been studied essentially for moderate grafting densities within the framework of SCF approaches.[15] Already Dan et al.[16] and Skvortsov et al.[17] have found a sensitive behavior of the end-monomer distribution with respect to relatively small polydispersity effects using SCF methods. Altogether, existing SCF models were found to be less than satisfactory to describe polydisperse systems, even at low grafting densities.[18] In this work, we show that polymer brushes at high grafting densities display a highly selective behavior even with respect to changes of the size of the end-monomers (functionalized end-group), and we discuss implications for the grafting-from technique and the creation of functionalized surfaces.

Langevin molecular dynamics simulations were carried out using the simulation package LAMMPS[19] with a coarse-grained bead-spring chain model and a FENE bond potential to account for the finite extensibility.[20] The interaction was modeled as a short-range Lennard-Jones (LJ) potential, cut at its minimum to simulate a good solvent. Throughout the paper, LJ units are used. For a detailed description of the simulation parameters we shall refer to our earlier work.[11,21] The chains were end-grafted onto a planar substrate, forming a Cartesian pattern with periodic boundary conditions in lateral directions. The repulsive short-range potential of the substrate was recessed below the grafting plane by a little amount (0.858 LJ-units) to eliminate its effect on the first bond stretch. The grafting density in most of our simulations was $\sigma = 0.46$ (chains per unit area). A single bead was of unit size, and the average bond-length was 0.97, so that a grafting density of $\sigma \approx 1$ would deliver a close packing of monomers and fully stretched chains.[21] At $\sigma = 0.46$, the average chain stretch was reaching almost 0.7 of the maximum contour length, comparable with the stretch reached experimentally by Devaux et al.[6]

Figure 1 displays vertical density profiles and their (negative) gradients at different grafting densities, in arbitrary units, but to scale. The simulation results show that only at low grafting densities, the parabolic shape of the profile, as predicted by standard SCF theory for good solvent,[8] is approximately realized (solid diamonds). Its negative gradient is therefore increasing roughly linearly until the surface of the brush is reached (blank diamonds). At high grafting densities, finite extensibility of the chain creates a boxlike shape (solid squares) of the density profile,[12–14] and its negative gradient (blank squares) exhibits a narrow and highly pronounced peak near the surface of the brush. Since this density gradient corresponds to an osmotic pressure that the monomer is exposed to, the chain ends which reside inside this region experience a strong force pulling them up.[22]

The significance of this high-gradient zone is easily demonstrated once polydispersity is introduced into the brush, by embedding a single chain of modified length into the array of "standard" chains of $N = 64$, which form a brush of 8×8 chains at high grafting density $\sigma = 0.46$. Such densities were recently achieved experimentally by Devaux et al. using a grafting-from technique.[6] Figure 2 displays the average vertical bond force which is pulling at the embedded chain, as a function of the average vertical monomer coordinates. For comparison, the curve corresponding to "standard" chains is plotted as well (circles, compare also with ref 11 and references therein for a discussion of end-monomer tension in monodisperse brushes). A chain with a single extra monomer (solid squares) is stretched out significantly further and exhibits enhanced bond forces. Note that the average height of the chain end (i.e., the average height of monomer 65, $\approx$47 LJ-units) is elevated about 4 bond-lengths above the end of the normal chain (monomer 64, $\approx$43). With longer chains, this trend is continued, but a saturation is quickly reached at chain sizes around $N \approx 70$ monomers (see inset in Figure 2). Even more striking is the behavior of shorter chains: The removal of just a single monomer leads to a collapse of

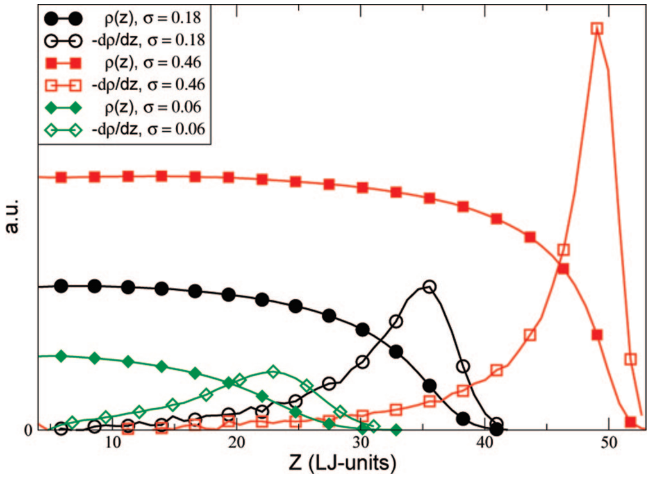

Figure 1. Vertical density profiles (solid symbols) and their (negative) gradients (blank symbols) at different grafting densities.

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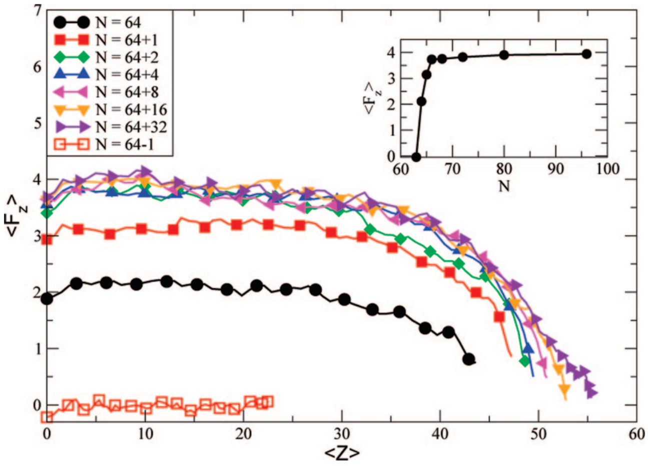

Figure 2. Average vertical bond forces acting on single chains of different lengths as a function of the vertical coordinate. The chains are embedded into a dens brush ($\sigma = 0.46$) of chain length $N = 64$. Inset: Bond forces averaged over $0 < Z < 20$ as a function of chain length.

the chain into the brush (blank squares in Figure 2) and its bond tension disappears entirely.

A similar behavior has already been predicted by Skvortsov et al.[17] in the framework of the classical (Gaussian) SCF model. They found the same transition from collapsed minority chains (of chain length $K < N$) to overstretched minority chains (of $K > N$). However, since the density profile was parabolic in this model, they found a smoother transition when compared to our simulations, which include the finite chain stretch and hence a much steeper monomer density gradient near the surface. A chain which is just marginally longer than N is able to extend all the way through the gradient zone and thereby picking up the entire amount of pull. At $K = 65$, the lateral average end-monomer fluctuation, $\langle R_{xy}{}^2\rangle^{1/2} = 3.6$ LJ-units, is reduced compared to the standard chain ($\langle R_{xy}{}^2\rangle^{1/2} = 6.2$ at $N = 64$). To the contrast, a slightly shorter chain is barely able to reach up into this narrow surface gradient and hence experiences a much lower pull than the average chain. Instead of stretching out just a little further to catch up with the average, the chain is collapsing into the brush. At chain lengths of $K = 63$, the lateral fluctuations of the endmonomers are larger compared to the $K = 65$ chain, but, with ($\langle R_{xy}{}^2\rangle^{1/2} = 3.8$, significantly smaller than the standard $N = 64$ chain.

The above observation provokes questions concerning effects of surface modifications at such high grafting densities. To investigate this further, two brushes were created as large arrays of 24 × 24 chains of length $N = 64$, again grafted at high density ($\sigma = 0.46$). In the first brush (denoted as brush 1), 5% of the chains (total number: 30) were selected randomly and their end monomers were replaced with beads of twice the standard size, i.e., $\sigma = 2$. We shall denote these modified chains as type 1 chains. The second brush (denoted as brush 2) had to undergo the same procedure, but here 5% of the end monomers were replaced with smaller beads ($\sigma = 0.5$) to create polymers which we shall denote as type 2 chains.

Figure 3 displays vertical density profiles, and Figure 4 the bond tensions of the various chain species. The differences between type 1 (squares) and type 2 chains (diamonds) are significant and confirm the results obtained above with polydisperse chains: Even the slightest modification near the brush surface can induce dramatical changes of the chain conformations. In our set up, the average bond tension of type 2 chains was reduced by a factor of 2 compared to standard chains. To the contrast, the type 1 chains with inflated end monomers were stretched beyond the average brush surface and exhibited about twice the average bond tension. Note that the average positions of type 1 and type 2 end monomers (maximum z-coordinates in Figure 4) differed by 10 LJ-units—a gap, 1 order of magnitude larger than the actual difference of chain lengths. This amplification effect could in principle be exploited to create functionalized brushes (see discussion below).

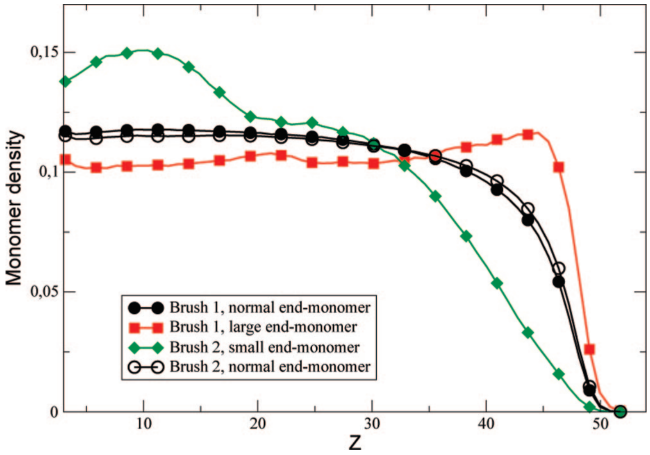

Figure 3. Properties of chains with modified end-monomers: Vertical density profiles.

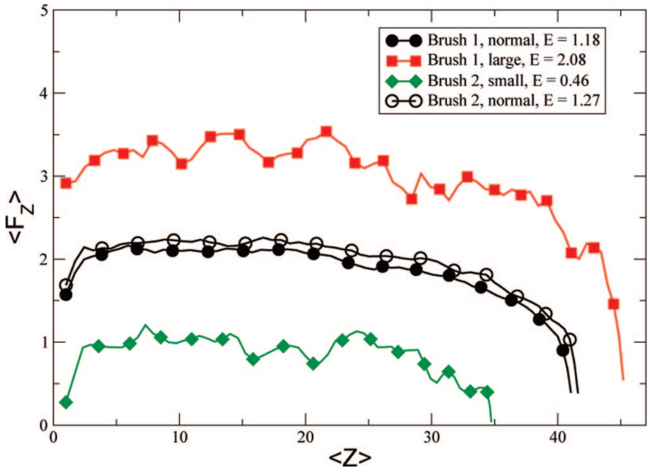

Figure 4. Properties of chains with modified end-monomers: Forces pulling on monomers in vertical direction. E denotes the free energy of stretching per monomer (LJ-units).

An interesting detail shall be pointed out: The modification of 5% of chain ends did not leave the remaining 95% of chains unaffected. They were stretched out a little further in brush 2 with type 2 chains (blank circles) when compared to brush 1 of type 1 chains (solid circles). The excess free energy of the chains (relative to the free and relaxed conformation) can be computed as the integral over the vertical bond tension,[11] i.e. the area below the curves in Figure 4. These free energies are easily found (in LJ-units per monomer) to be $E_1 = 2.08 \pm 5\%$ (type 1 chains), $E_2 = 0.46 \pm 5\%$ (type 2 chains), $E_{01} = 1.18 \pm 1\%$ (standard chains inside brush 1) and $E_{02} = 1.27 \pm 1\%$ (standard chains inside brush 2). The total free energy of brush 1 is therefore $0.05E_1 + 0.95E_{01} = 1.23$, and brush 2 yields $0.05E_2 + 0.95E_{02} = 1.22$, which are identical within the total error of about 1%. This implies that, despite of dramatic differences in the free energies of the modified chains, the total free energies of both systems remained invariant, because the deviations caused by modified chains were counter balanced by the majority of unmodified chains of the system.

In summary, we have observed that the surface of a monodisperse brush exhibits an instability which amplifies minor perturbations like chain length or end monomer size of single chains. The amplification factor (i.e., the change of the average vertical positions of the end monomers divided by the difference of chain lengths) was significant and did amount to roughly a factor of 10 (Figure 4). The origin of this instability is the high density gradient of the brush near its surface (Figure 1). Although the effects discussed here refer to brushes at high grafting densities ($\sigma = 0.46$), they did also show up at moderate densities around $\sigma \approx 0.2$ (though with less impressive amplification factors, data not shown), a result of the qualitative deviation of the brush profile from the parabolic SCF approximation.

It is interesting to think about implications of this instability for technical applications. First, it is obvious that grafting-from techniques, used to grow these high density brushes, might be suffering an additional degree of polydispersity: Single chains which are just marginally shorter than the average are collapsing and subsequently unable to reach up to the surface again, so that any further accessibility to chemical modifications remains prohibited. Hence it would be interesting to investigate the degree of polydispersity of the grafting-from technique as a function of grafting density in computer simulations. Second, a modification of the brush surface by adding functional groups would lead to much stronger effects at high grafting densities when compared to low densities. After the attachment of such a group, the modified chain can be expected to stay outside the brush surface and to remain functional over a much larger portion of time as compared with similar situations at lower grafting densities. On the other hand, any chemical modification which would shorten the chain length would cause this chain to collapse into the brush and to escape from any further interaction with the brush environment.

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