Nano-scale brushes: How to build a smart surface coating

Holger Merlitz,¹ ² Gui-Li He,³ Chen-Xu Wu,¹ and Jens-Uwe Sommer²

¹Department of Physics and ITPA, Xiamen University, Xiamen 361005, P.R. China
²Leibniz-Institut für Polymerforschung Dresden, 01069 Dresden, Germany
³Institut für Theoretische Physik II, Heinrich-Heine-Universität Düsseldorf, 40225 Düsseldorf, Germany

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Via computer simulations, we demonstrate how a densely grafted layer of polymers, a brush, could be turned into an efficient switch through chemical modification of some of its end-monomers. In this way, a surface coating with reversibly switchable properties can be constructed. We analyze the fundamental physical principle behind its function, a recently discovered surface instability, and demonstrate that the combination of a high grafting density, an inflated end-group size and a high degree of monodispersity are conditions for an optimal functionality of the switch.

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The creation of functional materials with extreme properties has become a key issue of modern nanotechnology. Countless potential fields of application have been spotted, including adhesives which stick on any surface, superhydrophobic coatings or anti-friction coatings, to cite just a few of them. Functional surfaces which are also able to adapt to their environment through a reversible switching mechanism are leading another step further. A polymer brush, i.e. a coating made of polymers which are densely grafted with one end onto a substrate, is regarded a good candidate for such a high-tech coating. Current approaches suggest the use of mixed brushes, one component of which would consist of hydrophilic and the second of hydrophobic polymers. A change of the solvent would then flip up the respective compatible layer while hiding the incompatible one. The reversible switching of such a mixed polymer brush was first observed in experiment by Sidorenko and analyzed in detail by Minko and Lemieux. Motornov et al. have recently applied this technology to modify the surface of colloids in order to create stimuli-responsive (“smart”) nanoparticles.

This article is going to present another approach and offering, through off-lattice computer simulations, a proof of principle for the reversible switching of homopolymer brushes (i.e. brushes consisting of only one polymer species), grafted at high density and featuring a modified end-monomer. Such high density brushes have recently been successfully created in the laboratory of Devaux et al. using a specially modified grafted-from technique. A systematic theoretical investigation of these high density brushes is presently a matter of intense research activities.

Perhaps the most striking feature of a high density brush is its sharp drop of monomer density near the surface, fundamentally different from the parabolic density profiles commonly found in low density brushes. This box-like profile has been predicted by modified SCF theories and was also obtained in early computer simulations. Most recently, refined theoretical models and computer simulations have delivered a considerable progress in terms of a quantitative understanding of polymer brushes at high grafting densities.

In our simulations, the polymers were created as a coarse-grained bead-spring model without explicit twist or bending potential, i.e. the bonds were freely rotating and freely jointed within the restrictions of excluded volume interactions. The “spring” was a finite extensible nonlinear elastic (FENE) potential. The beads represent spherical Kuhn monomers which interact via a shifted Lennard-Jones (LJ) potential

\[ U(r) = 4\epsilon \left( \frac{d}{r} \right)^{12} - \frac{d}{r} \left( \frac{d}{r_c} \right)^{6} - \frac{d}{r} \left( \frac{d}{r_c} \right)^{12} + \frac{d}{r} \left( \frac{d}{r_c} \right)^{6} , \]

where \( d \) stands for the bead size and \( \epsilon \) defines the potential depth. The parameter \( r_c \) is the cutoff distance: When cutting at the potential minimum, \( r_c = r_{\text{min}} = 2^{1/6}d \), the attractive tail of the pair interaction is removed and the chain monomers display an athermal behavior. A longer cutoff distance, however, retains the attraction, and now the pair interaction is exhibiting a temperature dependence which enters through the excluded volume interaction. For the monomer-monomer interaction, the potential was cut at \( r_{\text{min}} \), but all interactions involving the modified end-groups were cut at \( r_c = 2r_{\text{min}} \) to account for a temperature dependent solvent quality.

The simulations were carried out using the open source LAMMPS molecular dynamics package. In this paper, the LJ system of units is used, with a monomer bead-size of \( d = 1 \), mass \( m = 1 \), and a potential depth of \( \epsilon = 1 \), which defines both energy and temperature units (using a Boltzmann constant \( k_B = 1 \)). The modified end-monomers were of different sizes as will be discussed below in the context of the simulation results. The equation of motion of any non-grafted monomer was given by the Langevin equation, in which a friction term was implemented as well as a random fluctuation term to create a diffusive motion at well defined temperature and to
FIG. 1: Surface switching: In good solvent, the modified end-monomers are “swimming” on top of the brush (left), in poor solvent, the corresponding chains are retreating (right). The 95% majority of unmodified chains are plotted transparent.

account for the implicit solvent. Further details about the simulation procedure are found in a previous publication [18].

For our simulations, $24 \times 24$ polymer chains, each of them with $N = 64$ monomers, were grafted in a Cartesian pattern onto a planar surface with a grafting density $\sigma = 0.46$ chains per unit area, yielding a high density brush with chains stretched to roughly 70% of their contour length, a value which has already been achieved in laboratory [8]. In both horizontal directions, the system had periodic boundaries to avoid any spurious finite size effects. The brush was assumed to be inside an athermal solvent, but a minority of 5% of the chains was chosen randomly and their end-monomers replaced with beads of different chemical properties. It was assumed that these end-groups were incompatible with the solvent, so that they would not mix with that solvent at low temperature. The 95% majority chains remained unmodified and shall be denoted as “normal” chains.

Figure 1 displays two snapshots, one of them taken at high temperature (left), and another one at low temperature (right). The modified end-monomers have got the diameter $d = 3$, trice the size of the standard monomers. The observed switching of the end-groups from above to below the brush surface is fully reversible and can be repeated as often as desired. Of course, whatever was facilitated via change of temperature in the simulation, could equally well being achieved through a change of solvent in the laboratory.

Figure 2 displays how the density distributions of the end-groups vary with the system temperature. At $T = 0.25$ (circles), they remain well below the brush surface as defined with the normal, i.e. unmodified chain ends (solid line). Around $T = 1$ (squares), the transition occurs, and at $T = 3.5$ the end-groups are well localized on top of the brush. The inset shows how the density profiles of the entire chains are affected. The normal chains are forming the box-like profile, characteristic for high density brushes, being almost flat inside and dropping steeply near the surface. At low temperature, the modified chains are collapsing into the brush, at high temperature, they become over-stretched and exhibit a density maximum at the brush surface.

The system is asking for a couple of conditions to be satisfied in order to make such a brush functional. Figure 3 displays the average heights and vertical rms-fluctuations (inset) of the chain-ends as a function of temperature and for three different end-group diameters. The dotted line corresponds to the unmodified “normal” chain-ends which are athermal and have got the standard diameter $d = 1$. It is clearly visible how the functional end-groups of size $d > 1$ penetrate the surface at a temperature $T \approx 1$ and stay on top of the brush at any higher temperature (squares and triangles). The end-group of size $d = 1$, however, does never switch (circles). The vertical rms-fluctuations (inset) exhibit a decrease of fluctuations for the inflated end-groups with increasing temperature. This is an interesting observation, since it implies that these groups stay pinned on top of the brush without significant vertical fluctuations, an important condition to make the surface modification fully functional. There is no such pinning effect with the modified group of size $d = 1$, which continues to diffuse all through the brush at any temperature (i.e. solvent quality).

Why is the size of the end-group of the essence? The explanation is based on the results found in recent studies on high-density polymer brushes [11, 22]. The box-like density profile of such a brush, as shown in Fig. 2 (inset, solid line), exhibits a sharp density drop within a narrow
FIG. 3: Importance of end-group size: Average height of the end-monomer as a function of temperature $T$ for different end-group diameters. The dotted line is the brush surface, defined as the average position of the unmodified end-monomer. The grafting density is $\sigma = 0.46$. Inset: The vertical rms fluctuations. Axes are scaled in Lennard-Jones units.

surface layer, and remains almost flat otherwise. Now it is important to recall that any density gradient is generating an osmotic pressure which is pushing the monomer towards the direction of lowest density. Consequently, a high density brush contains a zone, localized just below the surface, in which any monomer is exposed to a strong push upwards, while the osmotic pressure deep inside the brush remains insignificant. This is fundamentally different from the situation with low-density brushes, the vertical profiles of which are parabolic in good solvent \cite{12,13} and thus distributing the osmotic pressure all the way through the brush and lacking any steep density gradient near the surface. As was shown in \cite{11}, minority chains, when being slightly longer than the standard chain, or alternately end-modified with an inflated end-monomer, were being pulled all the way through the osmotic pressure zone and exhibited a stretching energy of roughly twice the amount measured at the normal (majority) chains. To the contrast, chains which were just a little shorter than average or which had got a reduced end-monomer size, tend to collapse into the brush with a diminishing probability to reach up to the surface. Intermediate states are strongly suppressed because of the large amount of free energy required to stretch the chain up to reach the osmotic pressure zone. In this way, polydispersity effects are amplified, creating a surface instability inside high density brushes.

In the present system, the localization of the osmotic pressure zone is exploited to facilitate an effectively switching surface. At low temperature, the interaction of the poor solvent with the end-group generates an effective force which is pushing the chain-end below the surface. Alternately, one may discuss the effective size of that chain-end, which now represents a single attractive particle inside a melt of athermal monomers. At low temperature, its excluded volume remains below the monomer volume, and the modified chain therefore behaves the same way as the short minority chain discussed above: It stays in a collapsed state inside the brush (Fig. 4, lower chain). With increasing temperature, its excluded volume inside the melt is exceeding that of the athermal monomers and the chain, now effectively being marginally longer than average, is penetrating the osmotic pressure zone and stretched above the brush surface (Fig. 4, upper chain). If, however, the end-group is of equal size as the athermal monomers, then its excluded volume cannot exceed their volume at any finite temperature, and the switch cannot occur (circles in Fig. 3).

When considering the fact that the above discussed localization of the osmotic pressure occurs particularly at high grafting densities, then it is obvious that the observed switching of end-groups should be less effective at moderate grafting densities. Figure 5 contains a comparison of two brushes, one of them at high grafting density ($\sigma = 0.46$) and the second at moderate density ($\sigma = 0.2$) which corresponds to a chain stretch of roughly 45% of the contour length. The switch does still take place, though at a higher temperature $T \approx 2$ (diamonds) instead of $T \approx 1$ with the high density brush (squares). The rms-fluctuations (inset) however indicate that the end-groups now exhibit strong vertical fluctuations and do not stay pinned at the surface as they did at high grafting density. At moderate grafting densities, the vertical density gradient is much smoother and extends over a longer distance below the brush surface, and hence the

FIG. 4: Surface instability: Sketch of chain conformations with a modified end group in a high density brush. The box-like density profile creates a narrow zone of osmotic pressure near the surface, which, at high temperature, is pushing the end-group out of the brush (upper chain). At low temperature, the poor-solvent interaction with the end-group is compensating the osmotic pressure and the chain is collapsing (lower chain).
amplification of chain-end modifications and their effects on chain statistics is significantly reduced \[11\]. Such a brush at \(\sigma = 0.2\) could still be used to create a functional surface through end-group modification, but in that case the switch of the surface properties would be less pronounced than with high density brushes, due to the enhanced vertical mobility of the end-groups.

In summary, a homopolymer brush can be used to create a reversibly switchable surface through end-group modification. In order to achieve a highly efficient switch, a couple of conditions have to be satisfied. First, the brush density should be high, to generate a surface instability which amplifies the interactions of modified end-groups with the solvent. Then, the modified ends should remain the minority because it requires the unmodified majority chains to maintain a steep density gradient near the surface. As another condition, the modified end-groups have to be over-sized in order to push through the surface under good solvent (or high temperature) conditions and stay put without major vertical fluctuations. Finally, the present simulations were carried out under ideal conditions in the sense that a monodisperse environment of majority chains was assumed, which is not perfectly achievable under laboratory conditions. An increasing degree of polydispersity would lead to a diffusion of the osmotic pressure zone and thereby reduce the amplification of solvent interactions with the end-groups, similar to the behavior found at reduced grafting density in Fig. 5. Although a certain amount of polydispersity would be allowable without dramatically affecting its

function, further detailed studies are required to analyze how exactly the efficiency of switching would depend on the degree of polydispersity in the system.

Unlike traditional approaches to switchable surfaces via mixed polymer brushes, the modification of end-groups would be technically rather simple and appears highly flexible, since a huge variety of groups, including mixtures of them, could be attached to the chain ends and allow for the creation of truly “smart” surfaces.

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\* Electronic address: merlitz@gmx.de

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