

Switchable Friction Using Contacts of Stimulus-Responsive and Nonresponding Swollen Polymer Brushes

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Supporting Information

ABSTRACT: Stimulus-responsive (SR), solvated polymers can switch between an expanded state and a collapsed state via external stimuli. Using molecular dynamics simulations, I show that such SR polymers can be employed to control the frictional response between two opposing polymer brushes in relative sliding motion. By using a brush composed of SR polymers in contact with a nonresponding solvated polymer brush, the presence of capillaries and the overlap between molecules of the opposing brushes can be switched. When both brushes are solvated, a capillary is formed and polymers of the opposing brushes interdigitate. Interdigitation dominates friction upon shearing flat brush-bearing surfaces, while the breaking and formation of capillaries dominate friction in the low-velocity limit between rough brush-bearing surfaces. Thus, when either rough or flat polymer-bearing surfaces are sheared, friction between two swollen brushes can be high. In contrast, when the SR brush is collapsed, the solvent absorbs only in the brush that does not respond to the external stimulus. The latter circumvents the presence of capillaries and interdigitation of the brushes, which results in a low friction force upon shearing.



■ INTRODUCTION

Biological systems can strongly adapt their function and structure in response to small changes in the environment.^{1,2} This adaptation is often triggered by external stimuli, such as chemical composition, temperature, or light radiation. In recent years, there has been a rapid growth in interest in mimicking those biological systems in the development of smart functional materials. In particular, synthetic stimulus-responsive (SR) polymeric systems hold great potential³ and have resulted in systems that can possibly be used as artificial muscles,⁴ controlled drug delivery systems,⁵ and nanosensors.^{6,7}

Polymers expand in good solvents because of excluded volume and favorable polymer–solvent interactions. Such solvated polymers stretch upward to form a soft polymer brush when end-anchored at a high density to solid substrates.^{8,9} The swelling of polymer brushes can be controlled by the effective solvent quality; for poor solvents, the polymer brush will be collapsed.¹⁰ Hence, switching between the two states can be achieved by alternation of the effective solvent quality. This switching has been realized by directly replacing the solvent,¹⁰ by co-nonsolvency,^{11,12} by (UV) light,¹³ by changing the temperature¹⁴ or oxidation state,¹⁵ or by adjusting the pH of the solvent.¹⁶

Upon sliding two opposing, collapsed or swollen, polymer brushes in an (approximately) planar geometry, it was found that dissipation arises due to overlap of both brushes.¹⁷ In particular, molecular dynamics (MD) simulations, where it is straightforward to visualize the polymer chains, have exposed a strong correlation between friction and interdigitation.^{18,19}

Outside of the range of the linear response, the polymers show a shear-induced bending and extension that causes a reduction of the degree of interdigitation. On the basis of the latter, scaling laws that predict a sublinear friction–velocity relation have been derived.²⁰ This relation was found to agree with simulations²¹ and experiments.²² In fact, it was recently shown that as a direct consequence of this strong correlation between friction and interdigitation the friction between polyelectrolyte brushes can be tuned using a modulated electric field that reduces the overlap between the brushes.²³

In this article, I show, using MD simulations, that the kinetic friction coefficient between polymer brushes in relative sliding motion can be switched reversibly between high and low values by controlling interdigitation and capillary formation between opposing brushes. Such switching is achieved by using solvated systems that consist of a SR brush in contact with a brush that does not respond to the external stimulus. In one state, the SR brush is solvated and thus swollen. In this state, both brushes are interdigitated and connected via a capillary. Interdigitation mainly determines the friction force upon sliding of flat brush-covered surfaces,^{17–23} while the breakage and formation of capillaries dominate the dissipation between rough brush-bearing surfaces²⁴ in motion. Thus, in the state where both brushes are swollen, friction will be high upon shearing either flat or rough brush-bearing surfaces. In the other state, the SR

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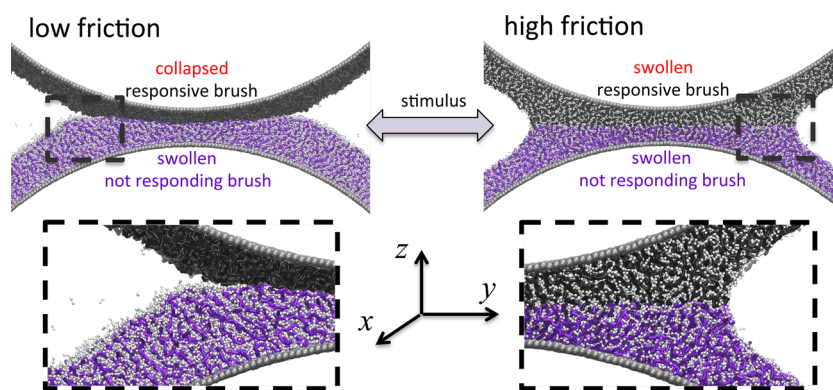


Figure 1. Principle of the friction switch explained via simulation snapshots. When the stimulus-responsive (SR) brush (black polymers) and the opposing nonresponding brush (purple polymers) are both swollen in solvent (gray dimers), the brushes interdigitate and a capillary is formed in the contact. Consequently, the friction is high. When the SR brush is in the collapsed state, the solvent maximizes the interaction with the brush that does not respond to the stimulus. Now, the opposing brushes do not interdigitate, and no capillary is formed. As a result, the friction for this system is low (snapshots are rendered using VMD³⁹). See Figure S1 of the Supporting Information for a more detailed picture of the change in interdigitation and density profiles for the parallel plate geometry.

brush is collapsed. The nonresponding brush will absorb the solvent, and there will be less interaction with the collapsed brush. As a result, the level of interdigitation of both brushes will be strongly reduced. Moreover, no capillary forms, and consequently, friction is low.

The method presented here is fundamentally different from those of earlier studies of friction control using SR polymeric systems. These studies considered either symmetric systems where opposing polymers are alike^{25,26} or single brushes or gels in contact with a rigid counter face.^{27,28} In such systems, the switching between brush states alters only the effect of dissipation mechanisms, and thus, the friction can be switched by only approximately 1 order of magnitude.^{25–28} In contrast, with my method of combining a SR brush in contact with a nonresponding brush, two important dissipation mechanisms, interdigitation and capillary hysteresis, can be switched on and off. This also results in strong changes in the dissipation caused by brush deformation. Consequently, friction can now be altered over almost 2 orders of magnitude, which significantly exceeds the results obtained previously.^{25–28} Comparable friction reductions are achieved using immiscible polymer brush systems.²⁹ However, in those systems, friction cannot be switched.

Asymmetric systems of SR brushes in contact with nonresponding polymeric systems have been studied extensively in the context of switchable adhesion.^{30,31} However, friction and adhesion are not necessarily related.^{32,33} In fact, it was recently shown that opposing polymer brushes moving in normal or transversal directions show a different mix of dissipation mechanisms and, thus, different friction–velocity relations.²⁴ Moreover, it was found experimentally that friction and adhesion can even anticorrelate for polymer brushes.³⁴ Thus, conclusions drawn from earlier adhesive studies of polymer brushes cannot be applied in predictions on the frictional response.

MODEL AND METHODS

The simulations are set up using a generic bead-spring model (the Kremer–Grest model³⁵). The Kremer–Grest model qualitatively reproduces the tribological response of end-anchored²⁹ and surface-adsorbed³⁶ polymers. Moreover, switching of surface properties³⁷ of SR polymers has also been qualitatively reproduced using the Kremer–Grest model. The interaction between consecutive beads is

modeled with the finitely extensible nonlinear elastic (FENE) potential, and all other interactions are described by the Lennard-Jones potential; therefore, the units of length and energy are given by σ and ϵ , respectively (typical values for ϵ of 30 meV and for σ of 0.5 nm³⁵). One bead represents roughly three to five monomers, such that the unit for the mass (m) is 10^{–22} kg and the unit of velocity (v) is 7 m/s. The equations of motion of all particles are solved with the velocity Verlet algorithm, as implemented in LAMMPS.³⁸

As depicted in Figure 1, two cylinders with a radius R of 100 σ that each have 464 polymers grafted onto them with a grafting density α of 2.5 times the critical grafting density α_c [$=1(\pi R_{\text{gr}}^2)$] for brush formation^{8,9} are set up. Each polymer consists of 30 beads ($R_{\text{gr}} = 3.7\sigma$; test runs using 100 beads showed qualitatively the same results). The brush is undersaturated with solvent as in experiments where the solvent is in equilibrium with the gas phase and condenses into the brush. During switching between the different states, the total amount of solvent is kept constant. The simulations are performed in the NVT ensemble (temperature $T = 0.6\epsilon/k_B$) via a Langevin thermostat on the wall atoms alone. The thermostat is applied only in the direction perpendicular to the direction of motion such that there is no measurable interference of the thermostat with the (hydro)dynamics of the system.⁴⁰ Unless stated differently, all parameters were chosen like they were in ref 24.

Figure 1 shows snapshots of the simulation cell for two different states (swollen or collapsed) of a SR brush. To model bad and good solvent conditions, the forces between the polymer and solvent are set to zero for distances beyond the potential minimum ($r \geq 2^{1/6}\sigma$) and $r \geq 2.5\sigma$, respectively. The interaction between the polymers of opposing polymer brushes is made purely repulsive ($r \geq 2^{1/6}\sigma$); the interaction between nonconnected solvent monomers is slightly attractive ($\epsilon = 0.5$; $\sigma = 1$; $r_{\text{cut}} = 2.5\sigma$), and the interaction between the solvent and polymers is attractive ($\epsilon = 1.2$; $\sigma = 1$; $r_{\text{cut}} = 2.5\sigma$). In the system shown on the left in Figure 1, the SR brush is collapsed and the solvent maximizes the interaction with the brush that does not respond to the stimulus. There is no capillary, and the opposing brushes do not interdigitate. In the system shown on the right in Figure 1, the SR brush is swollen and the solvent now connects both brushes. There is a capillary, and the opposing brushes interdigitate.

To compare the tribological responses of the two different systems, the cylinders are forced to slide in two directions (x and y). Sliding in the x -direction is comparable to sliding in a conformal geometry, so that dissipation is mainly determined by overlap of opposing brushes.²⁰ With sliding in the y -direction, I mimic asperity collisions, where the dissipation is composed of a mix of dissipation mechanisms.²⁴ Next to steady state interdigitation, now also transient interdigitation,⁴¹ shape hysteresis,⁴² and breakage and formation of capillaries⁴³ contribute to the dissipated energy. For sliding parallel to

the x -direction, the normal load is kept constant in accordance with most experimental systems. For sliding parallel to the y -direction, the height is kept constant to mimic engineering systems in which asperity collisions can induce large fluctuations in pressure.

RESULTS AND DISCUSSION

Figure 2 shows the friction force upon sliding ($v = 0.02\sigma/\tau$) in the x -direction while the stimulus responsive brush switches

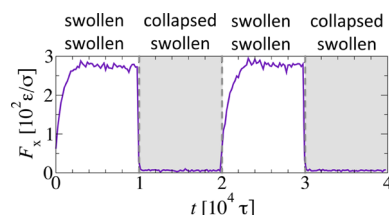


Figure 2. Friction force upon sliding the two cylinders parallel to the x -axis at a velocity v of $0.02\sigma/\tau$ and a constant normal load F_N of $500\epsilon/\sigma$, while switching between the swollen and collapsed states of the stimulus-responsive (SR) brush. The times of switching are denoted by the gray dashed lines.

between the swollen and collapsed states. The normal load is kept constant at $F_N = 500\epsilon/\sigma$. When the SR brush is in the swollen state, the friction is approximately 60 times higher than when the brush is in the collapsed state. Just after the polymer–solvent interactions are switched to create the swollen SR brush (gray dashed lines), the force relaxes approximately exponentially to the steady state force. Analysis of the binary interaction count [determined via the radial distribution function between the two different polymers, integrated between zero and the interaction cutoff, $\int_0^{r_{\text{cut}}} \rho_{12}(r) dr$] shows that both brushes interdigitate almost immediately after switching [within 100τ , where τ is the unit of time; for comparison, the relaxation time of the radius of gyration of solvated polymers with the surfaces not in contact (τ_0) is 15044τ]. Analysis of the snapshots shows that the exponential transient response (with a relaxation time of $\sim 2000\tau$) results from the tilting of the polymers toward the equilibrium angle⁴⁴ after the brushes have interdigitated. Figure 2 also shows that the force exhibits a slight overshoot before reaching the steady state friction force. This overshoot resembles the stress overshoot that is observed at the initiation of a shear thinning, entangled polymeric system.⁴⁵ For my setup, the overshoot seems to correlate with the solvent density in the interpenetration zone. The solvent, which was initially depleted from the collapsed brush, now re-enters via the contact zone and finally finds its equilibrium density distribution (with a relaxation time of $\sim 5000\tau$). During the stress overshoot, the polymer:solvent density ratio in the interpenetration zone is still higher than the polymer:solvent density ratio upon steady state sliding, which results in a temporarily higher shear stress.

Friction force F_x versus velocity v for the two SR brush states is shown in Figure 3 (purple circles for the swollen SR brush state and gray squares for the collapsed SR brush state). Below the characteristic relaxation time of interdigitation, all energy barriers for the polymers can be overcome by temperature.²⁰ That is why at the lowest velocities F_x scales linearly with the velocity for both systems. At these velocities, the friction differs by a factor of 65. Because of the change in the effective radius of the collapsed brush and the change in the elastic response, the contact area changes by a factor 1.24. Thus, the effect of the change in contact area is expected to be of little importance

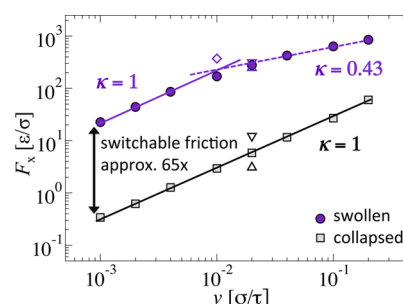


Figure 3. Friction force F_x versus velocity v for sliding of the two cylinders in parallel to the x -axis at a constant normal load. The purple circles give F_x values for the system in which the SR brush is swollen ($F_N = 500\epsilon/\sigma$), and the gray squares give F_x values for the system in which the SR brush is collapsed ($F_N = 500\epsilon/\sigma$). The upward and downward triangles denote the friction force obtained for lower ($F_N = 250\epsilon/\sigma$) and higher ($F_N = 1000\epsilon/\sigma$) normal loads, respectively. The diamond denotes the friction between two collapsed brushes ($F_N = 500\epsilon/\sigma$).

with respect to the friction reduction. On the other hand, the degree of interdigitation (binary interaction count) is 263% higher for the swollen state than for the collapsed state, which shows that the degree of interdigitation strongly effects the friction forces. For the collapsed SR brush, I find a linear response for all tested velocities. For the swollen SR brush, the friction crosses over into a sublinear power law scaling $F_x \sim v^\kappa$, where $\kappa = 0.43$. The observed exponent is lower than the value of $0.57^{20,24}$ or 0.54^{21} that is generally observed for sliding interdigitated opposing polymer brushes. This lower exponent is caused by the increase in height between the cylinders that is induced by the first normal stress, which is created due to shear alignment of the polymers outside the linear response.⁴⁵ This increase in height results in a change in the shear rate that is different from simulations performed at a constant distance.^{20–24} In fact, normalizing the velocity by the average height between the cylinders in the contact area results in an effective exponent κ of 0.55. For the swollen and collapsed states, the friction is expected to continue to decrease with velocity, because below a Weissenberg number (W) of 1 there are no, for the friction force relevant, energy barriers in the system that cannot be overcome by temperature.²⁰ The diamond symbol in Figure 3 denotes the friction force upon sliding two collapsed brushes in contact. Because of the absence of a lubricating solvent, high friction is expected. However, the friction is only slightly higher than the friction upon sliding the two swollen brushes (purple circles). A possible reason for the relatively low friction force might be the smaller contact area at the interface between the dry brushes.

The open upward and downward triangles in Figure 3 show the friction force for half and twice the default load, respectively. The friction force is almost independent of the normal load for the system with the swollen SR brush (purple symbols). The capillary that is formed between the two swollen brushes creates an adhesive contact between the two surfaces. For adhering surfaces, the friction is proportional to the molecular (thermodynamic) contact area,⁴⁶ which does not change so strongly upon variation of the normal load. There is no capillary for the system with a collapsed SR brush (gray symbols). Therefore, friction now increases more strongly with the normal load than for the system with the swollen SR brush. The latter indicates that the decrease in friction depends on the normal load. When $F_N = 1000\epsilon/\sigma$, the system shows a

switching of friction by a factor 26, while when $F_N = 250\epsilon/\sigma$, the friction changes by a factor 80.

Part of the decrease in friction arises from a decrease in the level of overlap of polymers on the opposing surfaces, and part of it is due to elimination of the capillary. To study the effect of switching interdigitation alone, I set up simulations using the parallel plate geometry (see the Supporting Information). The interaction energies of the two different geometries are related via the generalized version of the Derjaguin approximation.⁴⁷ The simulations using the parallel plate geometry are performed at a degree of compression comparable to that of the simulations in the cylinder geometry. Because there is no capillary, the decrease in friction is less pronounced (factor of 15 at the lowest velocities). Surprisingly, the change in the degree of interdigitation is also less pronounced. The latter implies that the presence of a capillary strongly enhanced the effect of interdigitation.

So far, I have discussed the switching of friction between brush-covered surfaces in a conformal geometry. However, all realistic engineering surfaces have roughness on many length scales,⁴⁸ and touching surfaces only make contact on a very small fraction of the apparent contact area. When two rough surfaces are forced to slide, small asperities bump into each other, causing large fluctuations in stress. By moving the cylinders in the y -direction, I intend to mimic the sliding of rough brush-covered surfaces in contact. During the asperity collisions that occur upon sliding in the y -direction, alternative dissipation mechanisms, such as capillary and shape hysteresis, can come into play.²⁴ Figure 4 shows work W per asperity

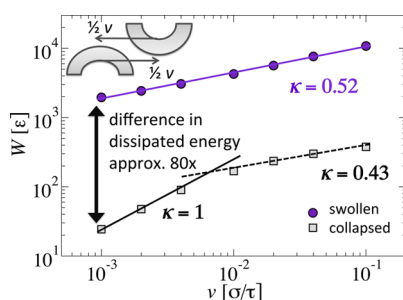


Figure 4. Work W per asperity collision vs velocity v for sliding the two cylinders in y at a constant distance. The purple circles give W values for the system in which the SR brush is swollen, and the gray squares give W values for the system in which the SR brush is collapsed.

collision upon moving the polymer brushes in the y -direction. The height between the surfaces was chosen such that the normal load at equilibrium was the same for both systems ($F_N = 500\epsilon/\sigma$). When both the SR brush and the nonresponding brush are swollen (purple circles), the work versus velocity shows a power law dependency of $W \sim v^\kappa$, where $\kappa = 0.52$. As discussed in more detail in ref 24, the total dissipation is composed of a mix of dissipation mechanisms that are all intertwined. The latter results in a power law dependency in which the exponent depends on the relative contribution of the different dissipation mechanisms. In contrast, when the SR brush is collapsed, the contributions of two dissipation mechanisms (i.e., interdigitation and capillary hysteresis) are strongly reduced. The residual dissipation is due to shape hysteresis and solvent flow. The work versus velocity for the system with a collapsed SR brush (gray squares) shows at high

velocities an apparent power law scaling with an effective exponent (κ) of 0.43. At the lowest velocities, the work versus velocity shows a linear response ($W \sim v$). The higher exponent for the collapsed SR brush implies that the effect of the SR brush collapse on the switching of friction becomes increasingly stronger at lower velocities. This effect will proceed until velocities at which the system with the swollen SR brush shows a linear response are reached. Because of the breakage and formation of capillaries, the latter will occur only at extremely low velocities.

The friction switch, presented herein, should work in a manner independent of the interaction between the polymers of the opposing brushes. The solvent will create an effectively repulsive force between the polymers of the swollen brush and keep in the low-friction state the collapsed SR and swollen nonresponding brush from interdigitating or forming a capillary. That is why the method presented here shows a larger change in friction than for switching of friction using dry hydrophilic and hydrophobic brushes,⁴⁹ where interdigitation and the presence of capillaries are not switched on and off. The results presented here imply that, when the friction is strongly determined by interdigitation and capillary hysteresis, having a single brush in contact with a bare surface will result in less friction than having a contact of two opposing brushes. On the other hand, for systems in which interdigitation is not the main cause of a strong interfacial interaction and dissipation,^{50,51} the method presented here will work less well.

Preliminary friction force microscopy results of an ongoing study of sliding a poly(*N*-isopropylacrylamide) (PNIPAM) brush-covered tip on a poly[oligo(ethylene glycol) methyl ether methacrylate] (POEGMA) brush-covered surface completely immersed in water qualitatively confirm the results presented here. Specifically, above the lower critical solution temperature (LCST) of PNIPAM, the measured friction forces are a factor of approximately 5–10 lower than the LCST of PNIPAM. The switching in friction is weaker in the experiments compared to the simulations presented here, which can be expected. The effect of the normal load has not yet been studied experimentally and will strongly affect the relative change in friction (see Figure 3). Moreover, the Hertzian contact geometry, as created in typical AFM setups, is different from the geometry studied in this work. A different geometry will result in a different mix of dissipation mechanisms,²⁴ and thus, the effect of the decrease in the level of interdigitation will be different, too. Furthermore, the difference in the contact angle of water on PNIPAM measured above and below the LCST is $\sim 40^\circ$ measured in air or even $\sim 0^\circ$ for air bubbles in water.⁵² The simulations presented here were performed with purely repulsive or attractive interactions between polymers and solvent that translate into more extreme changes in the contact angle. Test simulations using more moderate changes in the interactions between the polymer and solvent (ϵ_{ps}) show a switching of friction that is lower and thus closer to the experimental observations.

Besides switching of friction using stimulus-responsive polymeric systems, other methods of controlling friction have been developed. Friction due to instabilities (stick–slip motion) can be controlled by mechanical oscillations, as was shown for macroscopic engineering surfaces⁵³ and atomically flat surfaces.⁵⁴ Between elastic membranes and rigid counter faces, friction can be altered by introducing wrinkles.⁵⁵ Friction between metal surfaces and an AFM tip can be controlled electrochemically via surface oxidation⁵⁶ or surface reconstruc-

tion.⁵⁷ All these methods are developed to control friction between solid surfaces in relative sliding motion. The friction forces in such systems are generally stronger than for solvated polymer brushes. Thus, because the method presented here acts in a different friction regime, it is complementary to the methods developed to control friction between solid surfaces. Moreover, solid surfaces in relative sliding motion often show wear, which might alter the control of friction over time. An advantage of using stimulus-responsive polymer brushes is that the brushes also form a protective layer that circumvents wear of the solid surface underneath the brush. Damage of the brush itself due to chain pull-out^{58,59} at the anchor points can be strongly reduced by the employment of a protective layer onto the anchoring points of the polymers.⁶⁰

SUMMARY AND CONCLUSIONS

In summary, I have shown using MD simulations that the friction between two opposing polymer brushes in relative sliding motion can be controlled by using an asymmetric contact that consists of a stimulus response (SR) brush and a swollen brush that does not respond to the external stimulus. In the simulations, the responsiveness of the SR brush was modeled via a direct change in the polymer–solvent interactions. Experimentally, switching between the swollen and collapsed state can be realized, e.g., by changing the temperature or oxidation state, via cononsolvency, or by adjusting the pH of the solvent. For the cases discussed here, both brushes interdigitate and form a capillary when the SR brush is swollen. Interdigitation is the main cause of friction upon shearing two flat brush-covered surfaces, while the breakage and formation of capillaries dominate the dissipation for rough brush-covered surfaces. Thus, when both brushes are swollen, friction for both flat and rough brush-covered surfaces is high. On the other hand, when the SR brush is collapsed, the solvent absorbs in only the nonresponding brush and keeps both brushes from interdigitating. Moreover, there is no capillary formed in the contact. Consequently, the friction between the collapsed and swollen brush, on either flat or rough surfaces, is very low.

ASSOCIATED CONTENT

Supporting Information

Switching in friction for the parallel plate geometry. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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