

Supplementary Figure 1 Dip in the tip surface separation. A dip in the tip-surface separation is observed after velocity inversion in the symmetric system for both the (PMMA-PMMA) experiments (a) and the simulations (b). The dip in the tip-surface separation occurs approximately in the center of the linear regime of the transient response in the friction force, in which the polymers readjust their alignment. In addition the solvent is slightly depleted in the center of the contact during that stage of velocity inversion. The tics have the same spacing as the data in Fig. 1(c) and (d) of the main text. For the experiments the absolute height change in the dip minimum was 70 nm (approximately 4% of the total equilibrium separation by two swollen brush heights) and occurred after a sliding distance of approximately 1000 nm. For the simulations the absolute height change in the dip minimum was 2  $\sigma$  and occurred at a sliding distance of approximately 30  $\sigma$ .



**Supplementary Figure 2 Transient response after velocity inversion asymmetric system.** The measured (a) and simulated (b) force traces for the asymmetric system. The experimental force traces are flattened after the transient response.



Supplementary Figure 3 Transient response after velocity inversion symmetric system. The simulated transient response in the friction force after velocity inversion (blue curve in (a), (b) and (c), sliding velocity =  $0.01\sigma/\tau$ , sliding distance =  $85\sigma$ , normal load  $F_n = 500\varepsilon/\sigma$ ) plotted in the same graph with (red curves) (a) the average velocity v of the solvent, (b) the average tilting angle  $\theta$  of the polymers and (c) the difference in height h of the visco-elastic pile-up between the front and the back of the contact. The snapshots in (c) reveal that the overall shape at the point marked by the triangle has not yet converged to the shape of the solvent velocity can be superimposed with the friction force from velocity reversal up to the point marked by a circle. This is also the moment, at which the polymers start to switch noticeably from one to the opposite orientation. Both, friction and tilting angle are almost linear functions of the sliding distance up to the point marked by a triangle, as can be seen in (b). Finally, the overall shape relaxes between the points marked by the triangle and the diamond, as shown (c).



**Supplementary Figure 4 The two cylinder geometry.** To study conformal sliding and asperity collisions we set up two parallel cylinders.



**Supplementary Figure 5 The friction forces for the symmetric and asymmetric system in long term measurements.** The symmetric system consists out of two PNIPAM brushes. The asymmetric system consists of a PNIPAM brush (colloid) on a PMMA brush-covered surface. The brushes are fully solvated. The friction reduction remains approximately two orders of magnitude. Over 4 hours, the force for the symmetric system slowly decreases. We believe this is due to wear: The chain pullout decreases the grafting density and reduces the friction forces. The friction force for the asymmetric system slowly increases. We believe this is due to the slow evaporation of acetophenone from the PMMA brush.



Supplementary Figure 6 Wear of the brushes. The change in tip surface separation after increasing the scan size from 30  $\mu$ m to 50  $\mu$ m for the symmetric PNIPAM-PNIPAM system (blue curve) and the asymmetric PNIPAM-PMMA system (red curve). Before the increase in scan size, we measured over the 30  $\mu$ m x 30  $\mu$ m area for more than 4 hours (at a scan rate of 1 Hz and normal load of 35 nN).



Supplementary Figure 7 Typical wear-scars after long-term sliding a symmetric contact. AFM image (a) and microscope image (b) of wear scars in the PNIPAM brush after long term friction measurements. We measured over the 30  $\mu$ m x 30  $\mu$ m area for more than 4 hours and consecutively for 2 hours over the 60  $\mu$ m x 60  $\mu$ m area (scan rate 1 Hz and normal load 35 nN).



Supplementary Figure 8 FTIR of the PMMA brushes. Fourier transform infrared spectroscopy (FTIR) of PMMA brushes, wavenumbers  $(cm^{-1})$ : 3050-2990 (CH stretching vibration), 1730 C=O (double bond stretching vibration), 1450 (CH3 and CH2 deformation vibration), 1260-1040 (C-O-C single bond stretching vibration), 880-960 (C-O-C single bond deformation vibration). At 1730 cm<sup>-1</sup> the characteristic stretching vibration peak of the C=O group is apparent.



**Supplementary Figure 9 FTIR spectra of PNIPAM brushes**. FTIR of PNIPAM brushes, wavenumbers (cm<sup>-1</sup>) 3289 (N-H symmetric and asymmetric stretching vibration), 3078, 2971, 2933, 2874 (asymmetric and symmetric C-H stretching vibration in -CH2-), 1635 (C=O stretching vibration), 1535 (amide II), 1458, C-H asymmetric bending deformations, 1386, C-H symmetric bending deformations, 1366-1170 C-N asymmetric stretching vibrations. At 1635 and 1535 cm<sup>-1</sup> the characteristic stretching vibration peaks of the amide group are apparent.

## **Supplementary Notes**

To put ourselves into a position in which we can rightfully compare experiment and simulation, we tried to match dimensionless numbers as well as possible rather than to make selected parameters identical. The rational is that dimensionless numbers predominantly determine responses in fluid mechanics. Unfortunately, one can essentially only dispose of two parameters in the experiments, i.e, the degree of polymerization P, and the grafting density  $\alpha$ , once a specific chemistry is identified. We chose them such that the Weissenberg number W, i.e, the product of shear rate  $\gamma$  and the characteristic relaxation time  $\tau$  would be of similar order of magnitude. We also tried to keep the geometry, charaterized by the ratio of brush height and radius of curvature, similar. A third parameter is the swelling ratio, which is the swollen brush height normalized by the dry brush height. In the experimental system, the ratio of swollen and unswollen brush is a little greater than three. In the simulations, the swelling ratio is approximately 2.6. The detailed rational for the choices of grafting densities and chain lengths can be summarized as follows: Firstly, experiments are done at much smaller velocities and much smaller shear rates  $\gamma$  than the simulations. They deviate by approximately four decades. Thus, in order to roughly match the Weissenberg number Wbetween simulation and experiment, we needed to set up experimental systems with correlation times exceeding those of the in-silico brushes by a similar factor. This could be achieved by using large degrees of polymerization. To make a crude estimate, we pursue as follows: Polymer brushes have a spectrum of relaxation times<sup>1</sup>. For interdigitation, the relevant relaxation time and thus W scales as  $\gamma(\eta(k_{\rm B}T)^{-1})P^{2.31}(\alpha_{\rm g}/d)^{0.31}$ , where  $\eta$  is the solvent viscosity, T is the temperature, P is the degree of polymerization,  $\alpha_g$  is the grafting density, and d is the distance between the chains<sup>2</sup>. Thus, we can calculate the ratio  $W_{exp}/W_{sim} = 0.21$ . Even if our calculations are off by one decade, we would argue that we targeted the Weissenberg sufficiently well, as we see no qualitatively different results in the simulations

when changing shear rates by one decade in either direction. Secondly, we tried to keep the geometric ratio  $R/L_0$  (R is tip radius and  $L_0$  is the swollen brush height) constant. For the experiments and simulations described in the main text, we had  $R/L_0 = 6$  and  $R/L_0 = 5$ , respectively. In addition, all fluids are low viscosity solvents. Thus, the solvents should always respond reasonably fast to changes and the polymers be much slower.

One parameter that turned out different between simulations and experiments is the Tabor coefficient,  $\mu_{T}$ , which is a dimensionless measure for how long-ranged interactions are. Specifically, we associate a short-range interaction (or in the language of Hertzian contact mechanics a JKR-like contact) with the experimental systems, in particular for the symmetric contacts. Therefore, we found a weaker increase of the friction force on the normal load in the experiments than in the simulations. Yet, the differences between JKR and DMT like contacts are relatively subtle, i.e., prefactors and exponents describing displacement-load curves differ by no more than O(30%). This is why one can expect that exponents differ for laboratory and in-silico brushes, but trends will be similar.

## **Supplementary Methods**

The experimental data is averaged over 70-150 force traces, symmetrized and small residual oscillations (due to interference of the laser-light) are filtered out by fitting and subtracting a cosine with a separation- dependent phase-shift. Moreover, the first 100 force traces are discarded. In the simulations, 5 force traces were needed to equilibrate the system.

We discussed in the main text, that for the symmetric system both the simulated and the measured transient response after velocity-inversion can be fitted with an empirical shape function that consists of an exponential relaxation, a linear regime and an exponential relaxation to the steady state force. The 3 different regimes are connected via a Heaviside function  $\theta(x)$ , where  $\theta(x < 0) = 0$ ,  $\theta(x > 0) = 1$  and  $\theta(x = 0) = 0.5$ . This results in the following fit-function:

$$F = -F_{ss} \exp(-x/\lambda_1) \theta(X_1 - x) + (Ax + B) \theta(x - X_1) \theta(X_2 - x) + F_{ss}(1 - C\exp(-x/\lambda_2) \theta(x - X_2)),$$

in which  $F_{ss}$  is the steady state force, x is the sliding distance,  $\lambda_1$  and  $\lambda_2$  are the first and second relaxation distance resp., A sets the slope of the linear regime, B the crossing with the y-axis for the linear regime, C the decay of the final exponential relaxation and  $X_1$  and  $X_2$  are the distances at which we link regime 1 to 2 and 2 to 3 resp.. By normalizing the measured or simulated force by  $F_{ss}$  and the sliding distance by, e.g.  $\lambda_1$ , we are left with 6 fitting parameters. By imposing that at  $X_1$  and  $X_2$  the function and its derivative should be continuous, we can eliminate 4 more parameters, such that 2 independent fitting parameters remain. At the highest simulation velocities ( $\nu > 0.01\sigma/\tau$ ) not all data perfectly matched the shape function. For these datasets an extra fitting parameter is introduced by replacing the function for the initial relaxation by  $-F_{ss} + D(1 - \exp(-x/\lambda_1))$ , such that the final value of the initial relaxation can be different from 0.

## **Supplementary References**

1. de Beer, S. and Müser, M. H. Alternative dissipation mechanisms and the effect of the solvent in friction between polymer brushes on rough surfaces, *Soft Matter* **9**, 7234-7241 (2013).

2. Spirin, L., Galuschko, A., Kreer, T., Johner, A., Baschnagel, J. and Binder, K., Polymerbrush lubrication in the limit of strong compression, *Eur. Phys. J.* E **33**, 307-311 (2010).