Stick-Slip Mechanisms at the Nanoscale

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When two surfaces slide past each other, energy is mainly dissipated by stick-slip events. Macroscopic stick-slip is usually explained by asperities that come in and out of contact. Herein, we probe stick-slip at the nanoscale at interfaces and polymer coated interfaces by pulling single polymers covalently attached to an AFM cantilever tip laterally over solid substrates in liquid environment. We find two different stick mechanisms, namely desorption stick (DS) and cooperative stick (CS). While DS-slip resembles the velocity dependence of macroscopic stick-slip, CS-slip shows an increase in friction with velocity. For various reasons we anticipate that both stick mechanisms are necessary for a molecular understanding of stick-slip at the interface and interphase.

Keywords: Atomic Force Microscopy, Desorption Stick, Friction Mechanism, Single Molecule Force Spectroscopy, Nanotribology, Stick-Slip

Introduction

The earliest theories of friction between macroscopic solid bodies were developed by da Vinci, Amontons, and Coulomb stating that friction force depends linearly on normal force, but is independent of pulling velocity and contact area. Since then, it became more and more evident that friction is ultimately coupled to energy dissipation and that a distinction between static (sticking) and dynamic (sliding) friction has to be made (1). Such a transition between sticking and sliding (slip) is known as an underlying mechanism for friction caused by two objects moving past each other. Prominent examples are music from bowed instruments, the squeaking sound of chalk on a blackboard and the behavior of seismically active faults with periods of rapid slip causing earthquakes (2–4). Usually stick-slip is described by asperities coming in and out of contact, leading to local pressure fluctuations of Pa to GPa within microseconds (5). A descriptive explanation is that the static friction has to be overcome by an uphill motion along an asperity slope for a sliding motion to start (6, 7).

Recently, we developed an AFM-based system to measure the nanoscale friction of polymers at the liquid-solid interface (8). This study revealed two different stick mechanisms for poly(glutamic acid) and polystyrene based polymers, namely desorption stick (DS) and cooperative stick (CS) (Fig. 1). In DS the polymer is laterally (in 2 dimensions) confined on the substrate. In order to move the polymer across the surface, a significant force has to be overcome and desorption (into the third dimension) is favored compared to lateral movement for large parts of the friction experiment. The $F_z - x$ curve shows a decreasing force with increasing lateral extension (Fig. 1a). This is expected for geometrical reasons, as the angle between the polymer backbone and the substrate changes with the lateral distance moved Eq. (1). For a detailed explanation, see below (theoretical description of friction motifs).

In the case of CS the polymer is confined to 3 dimensions and stretched up to a point where the bonds between substrate and polymer break and the polymer detaches (Fig. 1b). The part of the polymer in between the AFM cantilever tip and the substrate is elastically stretched, similar to the worm-like chain increase in force (9, 10). Strong directional bonds, in particular hydrogen bonds, lead to such a behavior (11, 12).

Herein, we show further evidence for these two stick mechanisms at interfaces and investigate how they affect stick-slip. Finally, we compare the two different stick-slip mechanisms with macroscopic stick-slip.

Experimental Section

Polymers

Poly(styrene-b-propylene sulfide) (PS, $M_n = 1.26$ MDa, $M_w = 1.34$ MDa, PDI: 1.06), poly(isoprene-b-propylene sulfide) (PI,
versus 99.9%, Sigma-Aldrich) × \( \times \) \( \times \) were synthesized by sequential living \( \cdot \) 140 kDa, \( \cdot \) 1.75) and poly(sodium-4 styrene sulfonate) (PSS) with = 454 kDa, PDI = 15 and 11 mm 18 8.4). dsDNA was solvated in borate buffer for the covalent coupling of polymers were obtained by using solid substrates such as PTFE. A clear single polymer event (plateau of constant force) and a narrow detachment length distribution are required to confirm good functionalization quality (Supplemental Material: Fig. S1 and Table S1).

### Attachment of Polymers to AFM Cantilevers

The polymers were covalently attached to an AFM cantilever tip (silicon nitride, MLCT from Bruker AXS, USA) with the following protocol.

The cantilevers were chemically cleaned and activated in oxygen plasma. Amino-functionalized cantilever tip surfaces for the covalent coupling of polymers were obtained by using Vectabond reagent (Axxora, Germany). The aminated cantilevers were immersed in a PEG (appropriate mixture of the bifunctional and the monofunctional linker, Rapp-Polymere, Germany) solution in dry chloroform (CHCl\(_3\), > 99.9%, Sigma-Aldrich) in order to provide coupling sites (heterobifunctional linker with NHS or maleimide reaction side) and a passivation (monofunctional with methoxy termination). For PS, PI, and PSPI a polymer solution (about 1 mg·ml\(^{-1}\) in CHCl\(_3\)) was used for an overnight coupling of the respective polymer. The functionalized cantilevers were rinsed and stored in CHCl\(_3\) until use in an experiment. For PGA and PLL a polymer solution (max. 10 mg·ml\(^{-1}\) in 50 mM borate buffer, pH = 8.0) was used. The cantilever tip was incubated for 90 minutes followed by rinsing in Tris buffer (10 mM, pH = 8.4). dsDNA was solvated in borate buffer with tris(2-carboxyethyl)phosphine (TCEP, Thermo Scientific) to reduce disulfide bonds. The cantilevers, which were coupled with DNA, were stored in PBS. Before the AFM measurement they were incubated for 1 h in 7M urea at 50°C to obtain single-stranded DNA (ssDNS). The bifunctional PEG was mixed with the monofunctional PEG using a ratio that provides just very few binding sites for the polymers. Thus, the attachment of just a few, ideally a single polymer was obtained. The quality of the functionalization was controlled before and after PEM experiments using solid substrates such as PTFE. Poly(tetrafluorethylene) (PTFE) samples of 1.5 mm thickness were purchased from GM GmbH, Germany. Self-assembled monolayers (SAMs) of defined hydrophobicity were prepared by keeping the gold-coated glass slides (CrNi: 29 nm, Au: 129 nm) for 12 h in 2 mM 1-dodecanethiol solved in ethanol (13, 14). Muscovite mica slides (11 × 11 mm\(^2\), KAl\(_2\)(OH,F)\(_2\)AlSi\(_3\)O\(_{10}\)(OH\(_2\)), Plano GmbH, Germany) were cleaved using a tape to gain an atomically flat and clean substrate. Tape residues were cleaned by immersing in acetone and drying with a gentle nitrogen stream prior to use.

Oxygen- and hydrogen-terminated diamonds were fabricated by electron beam lithography and exposure to oxygen or hydrogen plasma as given in (8, 15, 16). Si wafers were cleaned in an acidic bath consisting of deionized H\(_2\)O (54 mL), H\(_2\)O\(_2\) (84 mL), and H\(_2\)SO\(_4\) (198 mL) for 15 min at 80°C. Then, the substrate was rinsed with deionized H\(_2\)O and dried in a dry nitrogen flow.

Polyelectrolyte multilayers (PEMs) were deposited on Si wafers by the layer-by-layer technique (17) using poly(dimethyl ammonium chloride) (PDADMAC) with 135 kDa (PDI = 1.75) and poly(sodium-4 styrene sulphonate) (PSS) with 70 kDa (PDI = 2.5) after deposition of a 750 kDa initial poly(ethylene imine) (PEI) layer (18). The integer numbers correspond to PEMs with PDADMAC as outermost layer, while others have PSS as outer layer. Zeta potential measurements demonstrate that the net charge of the surface changes after each monolayer adsorption step (19–21).

For all substrates the root mean square (RMS) roughness was determined as published previously (8, 22): For PTFE the roughness was 7.6 nm, for the SAM 3.3 nm, 0.2 nm for Mica, 0.3 nm for the diamond substrates, and 0.09 nm for Si and 2.2 nm for the PEMs. Although the roughness of the different surfaces varies between 0.09 nm and 7.6 nm, we showed in an earlier publication that this does not affect the behavior of single polymer adhesion (23) and is, therefore, not sufficient to explain the different friction motifs. The same holds true for the zeta potential (15, 18), which is discussed in Balzer et al. (18).
Contact-Angle Measurements

A home-built goniometer equipped with a charge-coupled device (CCD) camera was used to determine the static contact angles. The contact angles of a 1.5 μL H₂O drop were determined using the drop analysis plugin (24, 25) for Java-based freeware ImageJ. For a detailed description of the analysis process please see Stalder et al. (24). In short, a polynomial was fit to the edge of the droplet. Then, a tangent was fit to this polynomial where the sample and the edge met to determine the enclosed angle. These static contact angles were measured at room temperature at least five times at different positions of the sample immediately after placing the droplet. The errors correspond to the standard deviation (see Table 1).

AFM Imaging

The MFP3D-SA AFM (Asylum Research, USA) was used with AC 240 TS cantilevers (Olympus, Japan) for intermittent-contact mode imaging (force constant of about 1.8 N·m⁻¹, resonance frequency of 70 kHz) at a scan rate of 0.5 Hz.

Single Polymer Friction Measurements

The AFM measurements were performed with a MFP3D-SA (Asylum Research, USA) and carried out at room temperature in a closed fluid cell. All measurements were performed in water or chloroform. We did not control the pH of the solution as the PEMs composed from strong electrolytes do not show a pH dependence. Additionally, it was shown that single polymer adhesion was not significantly dependent on pH (26, 27). Force-extension traces were taken at least at three different positions on the interface leading to at least 100 force-extension curves for each measurement. The sampling rate was set to 5 kHz. The traces were obtained from the deflection-piezopath signal (28, 29). The deflection is the difference signal between two segments of the photodiode and was converted in a force by determining the optical lever sensitivity (voltage/nm) and the spring constant (pN/nm). For the optical lever sensitivity the slope of the indentation part of the first five and the last five retraction curves was determined and averaged. Then the spring constant of each cantilever was calibrated in the respective medium after placing the droplet. The polymer was allowed to adsorb for 1 s. While retracting the AFM cantilever tip (1 μm·s⁻¹), the polymer successively desorbed from the surface. Prior to friction experiments the polymer was completely desorbed from the surface to check for the single polymer force sensor quality. If plateaus of constant force occurred, they were fitted with an s-curve to gain force and length distributions (see Supplemental Material: Table S1 and Fig. S1). Please note that we could not find any evidence for loop or tail formation of the adsorbed polymers. A succession of loops and trains should result in intermittent drops in desorption force and tails in a shortening of the detachment length. For all polymers a smooth plateau of constant force or rupture events were detected. For measuring single polymer friction, the polymer was not completely desorbed but only pulled up to a certain z-extension, Rₑ, where the polymer was still in contact with the surface. Then, the partly adsorbed single polymer was pulled laterally over the substrate, keeping z fixed (creep and drift effects from the z-piezo were in the order of 5 nm·s⁻¹, which is much less than the relevant distances presented here), enabling frictional forces to be investigated. The vertical cantilever deflection (Fᵥ) was used to calculate the lateral force Fₑ and friction force Fᵣ (see the following section). Direct measurement of Fₑ is not possible as the lateral force constant is more than two orders of magnitude larger than the vertical one and, therefore, insufficient to detect single polymer friction (33). Lateral pulling was performed perpendicular to the cantilever axis in order to use symmetric coupling of the force exerted by the polymer to the cantilever for forward and backward lateral motion (34).

Theoretical Description of the Friction Motifs

The decrease in Fₑ for DS can be described by:

\[ Fₑ = Fₑₐₜ · \cos (\phi) \quad (1) \]

The variables are defined in Fig. 2(a). For steady state, the angle \( \phi \) of the peptide for a fixed height is:

| Substrate | Polymer | Solvent | Static contact angle | Desorption | Friction | No. of curves |
|-----------|---------|---------|-----------------------|------------|----------|--------------|
| SAM       | PGA     | H₂O     | 96 (±3)°              | Plateau    | DS-slip  | 129          |
| PTFE      | PS      | H₂O     | 115 (±6)°             | Plateau    | DS       | 496          |
| PTFE      | PSPI    | H₂O     | 115 (±6)°             | Plateau    | DS       | 473          |
| PTFE      | PSPI    | CHCl₃   | 115 (±6)°             | Plateau    | slip     | 64           |
| PTFE      | PGA     | H₂O     | 115 (±6)°             | Plateau    | CS-slip  | 99           |
| HD        | PI      | H₂O     | 58 (±4)°              | Plateau    | slip, DS | 85           |
| HD        | DNA     | H₂O     | 58 (±4)°              | Plateau    | DS-slip  | 40           |
| OHD       | PSPI    | H₂O     | 84 (±4)°              | Plateau    | DS-slip (O- and H-term.) | 387 |
| Mica      | DNA     | H₂O     | below detection limit | Rupture events | CS-slip | 194          |
| Si        | PI      | H₂O     | 61 (±3)°              | Rupture events | DS, CS  | 43           |

Table 1. Overview of single polymer desorption and friction experiments; static contact angle, desorption behavior, type of mostly observed friction traces and number of evaluated friction traces.
Fig. 2. Modeling of DS. (a) Schematics of lateral pulling. Upon stick, the angle $\phi$ between polymer and the normal to the substrate increases until the lateral force $F_x$ equals the friction force $F_R$ and the polymer slides. $L_N$ denotes the adsorbed polymer length, $v_x$ the lateral pulling velocity, $R_z$ the fixed $z$-extension between AFM cantilever tip and substrate, and $F_{tan}$ the force acting along the polymer. (b) $F_z$ versus $x$ and $F_x$ versus $x$ curve for a PS on PTFE in H$_2$O. The decrease of $F_z$ prior to the slip event is fit with Eq. 4 (solid white line). (c) $F_z$ versus time for PSPI on OHD (H-terminated region) in H$_2$O ($z = 525$ nm, at $v_x = 0.52 \mu$m s$^{-1}$) showing a decrease of $F_z$ on forward (blue) lateral pulling motion and $F_z$ increase to the initial value after the end of the backward (black) lateral movement ($x = 0.51 \mu$m). During the dwell time of 1s $F_z$ stays constant (grey). (d) Dependence of friction force $F_R$ on pulling velocity $v_x$ for an adsorbed polymer length of $L_N$: 301 (black) and 447 (blue) for PSPI on HD in H$_2$O.

$$\tan \phi = R_x \cdot R_z^{-1}$$  \hspace{1cm} (2)

This results in:

$$F_z = F_{tan} \cdot \cos \left( \arctan \left( R_x \cdot R_z^{-1} \right) \right)$$  \hspace{1cm} (3)

The tangential force $F_{tan}$ acts along the polymer backbone and stays constant while the polymer is held in a stretched state between cantilever tip and surface. Fig. 2(b) shows this fit to a DS trace for PS on PTFE in H$_2$O. Steady state is reached at a lateral extension of around 2592 nm. Thus, the polymer angle $\phi$ can be calculated from $R_x = 2592$ nm and $R_z = 2679$ nm by Eq. (2) to be 44° and $R = 3728$ nm. The maximum desorption length from standard pulling experiments is $L = 3841$ nm.

It is possible that the anchor point does not lie exactly below the cantilever tip at the start of the slope. This is accounted for by an additional angle $\phi_0$ and the slightly modified version of Eq. (3):

$$F_z = F_{tan} \cdot \cos \left( \arctan \left( R_x \cdot R_z^{-1} \right) + \phi_0 \right)$$  \hspace{1cm} (4)

In Fig. 2(b) we obtain a typical value for $\phi_0$ of about 6° by fitting the data with Eq. (4) (white solid line).

The $F_x$ vs. $x$ curve can be calculated from the $F_z$ vs. $x$ plot using the relation:

$$F_x = F_z \cdot R_x \cdot R_z^{-1}$$  \hspace{1cm} (5)

All $F_x$ values corresponding to slip events are set to 0, while $F_x$ increases until it counterbalances the friction force $F_R$. Therefore, $F_R$ can be determined from the final plateau height $F_x$ (see Fig. 2b). Then, the polymer starts to slide and the $F_x$ value is again set to 0. The slope in $F_z$ does not result from hydrodynamic effects on the cantilever (8).

Results and Discussion

Desorption Stick versus Zipper Like Desorption

Single polymer friction is measured by desorbing an adsorbed polymer from the surface up to a certain $z$-extension, $R_z$. Then, the partly adsorbed single polymer is pulled laterally over the substrate. The various force components of the single polymer geometry when subject to lateral pulling are determined as depicted in Fig. 2(a). The observed decrease in $F_z$ with lateral pulling (Fig. 2b) could be caused by several molecular mechanisms. To exclude others than DS, we first in Fig. 2(c) show that the polymer stays at the lateral position. Here an example trace of PSPI on OHD (H-terminated region) in H$_2$O with a starting z-extension of 525 nm is shown. The maximum detachment length has been determined from standard pulling experiments to be 1191 nm. No detachment occurs within approximately 500 nm of lateral pulling. As the corresponding time trace of $F_z$ is symmetric, showing a negative slope on the forward (blue) and positive slope on the backward (black) lateral trace, the polymer does not follow the tip, but stays laterally at the same position.
This is further supported by a constant force during the dwell time of 1 s (grey).

Finally, the aforementioned results could be explained by DS or by a zipper mechanism, where the polymer is peeled from the substrates without any mobility of the chain (35, 36). The zipper mechanism can be seen as a sequential breaking of bonds at the point where the polymer leaves the surface. DS can be viewed as pulling the polymer out of the potential of the surface, which corresponds to transfer of the last part of the chain to infinity into solution. DS and zipper mechanism can be distinguished by their velocity dependence. For a zipper mechanism bonds are broken successively, leading to a velocity (force loading rate) dependence. Fig. 2(d) shows that this is not the case.

**Occurrence of Slip, Desorption Stick, and Cooperative Stick**

We have determined single polymer friction on 10 different polymer-substrate-solvent combinations to cover charged and uncharged polymers and substrates as well as good and poor solvents. For example traces, see Fig. S2. The probability of all these combinations of slip, DS, and CS is shown in Fig. 3. We observe the following general trends: Hydrophobic polymers (PS, PSPI, PI) on hydrophobic substrates in poor solvent show mainly DS (solid blue). At the same time, hydrophobic polymers on hydrophobic substrates in good solvent show mainly CS-slip (solid black). By contrast, charged polymers (PGA, ssDNA) on charged substrates in good solvent show mainly CS-slip while charged polymers on hydrophobic substrates show mixed behavior.

In our experiments the block copolymer PSPI and the linear polymer PS reveal both the same qualitative behavior. Thus, we conclude that the block structure of the polymer is not decisive for the frictional behavior.

**Relation Between Desorption and Stick-Slip Motives**

Our results present a complex interplay of DS, CS, and slip for single polymers at the solid-liquid interface. In Table 1 we show which of the combinations prevail for all 10 polymer-substrate-solvent combinations. We observe that the two main motifs are DS-slip and CS-slip. On hydrophobic substrates we observe mainly DS-slip, on hydrophilic substrates CS-slip. Rupture events in standard desorption experiments are strongly correlated to CS in lateral pulling experiments. This points toward a mechanism that is largely independent of pulling angle φ.

**Velocity Dependence of DS-slip and CS-slip**

Fig. 4(a) shows the lateral pulling for one of the investigated model systems, namely PGA, being pulled across a hydrophobic self-assembled monolayer of methyl terminated alkanthiols on gold (SAM) in H2O with a velocity of v = 0.42 μm·s−1 and a fixed z-extension of Rz = 240 nm. First, the polymer slides across the surface with a constant plateau force Fz. The lateral force component Fr depends on the lateral force component Fz, which counterbalances the friction force Fn, is undetectably small. At approximately x = 0.4 μm, the polymer sticks to the substrate. During the following decrease in Fz (0.4 μm–0.7 μm, orange area), that is, DS, the lateral force Fz increases. The static friction coefficient is high enough to favor desorption over sliding. At 0.7 μm Fz jumps back to its initial value, that is, the polymer relaxes to a conformation similar to the original one. This scenario is repeated in a periodic manner (here twice) until the polymer detaches from the surface (at around 1.3 μm). A five and ten times higher lateral pulling velocity (Fig. 4b) results in a higher frequency but lower amplitude (Fz) of the stick-slip motion. Fz is about 43 pN for 0.42 μm·s−1 and 19 pN for 4.20 μm·s−1. The stick-slip sequence is not dominated by the structure of the substrate as consecutive traces along the same line taken at 0.42 μm·s−1 show different slip-CS sequences in each Fz versus the x curve (Fig. 4c). Fig. 4(d) depicts the frequency of DS for all traces and velocities.

The velocity dependence of the CS-slip is shown in Fig. 4(e, f) for PGA on a patterned mono-crystalline diamond with oxygen and hydrogen termination (OHD). The OHD pattern can be confirmed by friction force microscopy as shown in Balzer et al. (8). While in the H-terminated section, PGA results in a constant plateau force Fz during lateral pulling, that is, a slip event with undetectably low friction force, O-termination shows sticking of the polymer to the substrate. Fig. 4(e, f) show CS, where the polymer is stretched up to a point where the bonds between substrate and polymer break and the polymer detaches. A clear velocity dependence is observed, which is opposite to DS. For CS the force increases with velocity. As successive
Fig. 4. Velocity dependence of single polymer stick-slip. (a) Vertical force ($F_z$) and lateral force ($F_x$) versus lateral extension ($x$) of PGA on SAM in H$_2$O. (b) $F_z$ versus $x$ with $v_x$ of 0.42 μm·s$^{-1}$, 2.02 μm·s$^{-1}$ and 4.20 μm·s$^{-1}$. (c) Consecutive $F_z$ versus $x$ curves along the same line with a lateral velocity of 0.42 μm·s$^{-1}$. DS events are indicated by dashed white lines. The curves are vertically offset by 100 pN in (b) and (c). (d) Frequency of DS events versus lateral pulling velocity $v_x$. Each data point represents a single trace. (e) PGA on OHD in H$_2$O with $v_x = 0.36$ μm·s$^{-1}$ and CS on O-terminated region. (f) PGA on OHD in H$_2$O with $v_x = 3.31$ μm·s$^{-1}$ and CS on O-terminated region. The crossing of the O/H boundary is indicated in the lateral pulling trace by a vertical black line and the bond breaking energy is highlighted in grey.

CS-slip events are rare, the velocity dependent frequency cannot be determined. Further examples for lateral pulling curves on hydrophilic substrates such as Si and mica showing either DS-slip and CS-slip are given in Fig. S3 and are quantified in Fig. 3.

Comparison to Macroscopic Stick-Slip

In macroscopic stick-slip the frequency increases with velocity and up to a critical pulling velocity the friction force decreases. Above this critical velocity pure sliding is observed (37). In these macroscopic experiments an inhomogeneous surface is required, being either chemically or topographically structured (e.g., a violin bow or an earthquake vault). This is similar to what we observe for DS-slip events. Fig. 4(d) shows that the frequency increases with velocity, although DS itself is not a velocity dependent process. In addition, the amplitude of the friction force decreases with velocity (Fig. 4b). Also similar to macroscopic stick-slip, the spatial stick-slip frequency of PGA on SAM does not resemble the SAM structure. We observe different stick-slip patterns for consecutive traces with one and the same polymer on the same surface along the same line (Fig. 4c). Therefore, we can exclude that the periodicity of stick-slip directly reflects the surface pattern, consistent with macroscopic stick-slip.

A significant difference compared to the macroscopic explanation for stick-slip is the origin of DS-slip. The common view for macroscopic bodies is that surface defects and asperities lead to interlock and cause stick (5). In DS polymer solvability and chemical substrate termination dominate the friction behavior, while topography has a marginal effect on DS (8).

The origin of macroscopic stick-slip would better fit CS-slip. For CS strong directional bonds (in analogy to asperities) keep the polymer confined in three dimensions and cause the polymer to be elastically stretched in between the tip and the substrate. The directional bonds are mainly HBs. Their breaking and reforming depends on velocity and can be seen as underlying mechanism for CS.

A recent theory by Serr et al. (12) allows the determination of the friction coefficient per HB from the energy dissipated during lateral pulling. The area indicated in Fig. 4(e, f)
provides a bond breaking energy of \( E_{0.36} = 3.12 \cdot 10^{-19} \) N\( \cdot \)m and \( E_{3.31} = 6.69 \cdot 10^{-18} \) N\( \cdot \)m for velocities of 0.36 \( \mu \)m\( \cdot \)s\(^{-1}\) and 3.31 \( \mu \)m\( \cdot \)s\(^{-1}\), respectively. Assuming an energy of 5 k\( \beta \)T per HB (12) and having determined that the adsorbed polymer part is at maximum 131 nm with a monomer length of 0.37 nm (38), the number of HBs that are broken can be estimated to 0.04 HBs/monomer (14 HBs/polymer) for 0.36 \( \mu \)m\( \cdot \)s\(^{-1}\) and 0.9 HBs/monomer (323 HBs/polymer) for 3.31 \( \mu \)m\( \cdot \)s\(^{-1}\). The difference in HB number leads to different friction coefficients per HB, namely \( \gamma_{0.36HB} = 9.3 \cdot 10^{-8} \) kg\( \cdot \)s\(^{-1}\) and \( \gamma_{3.31HB} = 7.7 \cdot 10^{-8} \) kg\( \cdot \)s\(^{-1}\).

Following Erbas et al. (11), who derive a steady-state friction coefficient from the Fokker-Planck equation in the presence of an external force in a corrugated periodic potential, our data requires a cooperativity factor of \( m = 3 \). The cooperativity factor specifies how many HBs are broken collectively. Interestingly, the strength of HBs as well as their cooperativity decreases with higher velocity, as expected from macroscopic stick-slip. Unclear is why so many more HBs are formed at higher velocity or why the energy per HB should be higher at higher velocity.

**Comparison to Polymer Coated Substrates**

In order to reduce energy dissipation, substrates are often equipped with a lubricating polymer coating (39). In particular with polyelectrolytes low friction coefficients of 0.006–0.0001 can be achieved (40–43). The main reason for this lubrication is likely the steric repulsive interaction between polymers from opposing layers (40, 42, 44–47).

In order to observe single polymer friction traces on polymer coated substrates we use polyelectrolyte multilayers with a well-defined composition and thickness.

**Fig. 5** depicts a PEM substrate, (PSS/PDADMAC)\(_{14}\) prepared in 0.1 M NaCl, with a thickness of 89 (± 4) nm in H\(_2\)O, determined by AFM imaging of the scratch area (18). The roughness and swelling behavior of those PEMs in H\(_2\)O has been studied in ref. (22). Fig. 5 (b, c) show that the distinction of many motifs might be challenging and can give only approximate values of motif transition points for the lateral extension \( x \). Therefore the following quantification has to be interpreted with care and the future will have to see many more experiments.

We perform lateral pulling with PLL in H\(_2\)O on both PEM coated and scratched areas. Fig. 5(b) represents a DS event until about 200 nm of lateral extension \( x \) with a detachment of a polymer segment. A plateau of constant force \( F_z \) with a desorption event at 250 nm follows. Then, a sudden increase in force is observed, which hints towards a stretching event, before the last polymer detaches and the force drops down to 0 at 285 nm. Here, we can speculate about CS being a result of the interaction of the AFM cantilever tip bound polymer with the Si substrate or some PSS, PDADMAC or PEI (initial layer) residues, which can be seen in the scratch area in Fig. 5(a).

Fig. 5(c) shows a much more complex \( F_z \) versus \( x \) curve. Here the Si substrate is completely covered by the PSS/PDADMAC double layers. At first DS appears until about 80 nm of lateral extension and the polymer desorbs from the PEM layer. Then, the last adsorbed polymer segment reveals CS until 180 nm. After relaxation the polymer slips over the PEM until 245 nm.
After another CS event a final DS process occurs, starting at 270 nm over the next 80 nm. Finally, the polymer detaches from the substrate at about 350 nm. The $F_x$ versus $x$ curves taken on (PSS/PDADMAC)$_{14}$ show many DS (60% of the friction events), but mostly CS (80%) as described in detail in Fig. 5(d).

Fig. 5(d) illustrates the frequency of the respective friction events for PEMs with 14 and 14.5 double layers of PSS/PDADMAC, prepared in 0.1 M NaCl. The samples show a high amount of CS event independent of the charge of the final PEM layer. By contrast, for the scratched PEM area, we find a higher amount of the slip motif.

In case of positively charged pulling polymer (PLL) and positively charged outermost polyelectrolyte layer (14 bilayers) the DS type is significantly present while for opposite charges no DS could be detected (PLL and 14.5 bilayers). This could be explained by stronger repulsion in the first case and net attraction in the second case. CS is always pronounced. This hints toward interdigitation being largely independent of electrostatic interaction.

**Conclusion**

We have determined the stick-slip mechanisms for 10 different polymer-substrate-solvent combinations. Hydrophobic polymers on hydrophobic substrates in poor solvent show mainly DS. At the same time, hydrophobic polymers on hydrophobic substrates in good solvent show mainly slip. By contrast, charged polymers on charged substrates in good solvent show slip and CS, while charged polymers on hydrophobic substrates show mixed behavior. The velocity dependence of the amplitude and periodicity of DS-slip resembles many properties of macroscopic stick-slip, likely making this an important molecular mechanism also in macroscopic systems. On the other hand, CS matches our current picture of macroscopic stick-slip, because CS is likely caused by the breaking and reforming of hydrogen bonds (in analogy to asperities). We, therefore, anticipate that both mechanisms are necessary for a thorough molecular understanding of macroscopic stick-slip. Our mechanistic insights might guide the design of low friction polymer coatings and polymer based lubricants. In addition, the presented single molecule data represents a broad test set for MD-Simulations.

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**Supplemental Material**

Supplemental data for this article can be accessed on the publisher's website.

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