Thermal friction enhancement in charged polymer brushes

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Abstract

We introduce a model for charged polymer brushes and we investigate its tribological response to changes in applied load, sliding velocity and temperature by means of molecular dynamics simulations. The proposed model exhibits different regimes of motion depending on temperature and sliding velocity. We find a remarkable increase...
of friction with temperature, which we attribute to the formation and rupture of transient bonds between individual polymers of opposite sliding layers, triggered by the out-of-plane thermal fluctuations of the polymers orientations. To highlight the effect of the molecular charges we compare these results with analogous simulations for the uncharged system. These findings are expected to be relevant to nanoscale rheology and tribology experiments of charged lubricated systems such as, e.g., confined zwitterionic polymeric brushes in a surface force apparatus.

Introduction

The possibility of controlling nano- and meso-scale friction and mechanical response in a variety of diverse physical systems has been investigated extensively in recent years.\textsuperscript{1–4} In particular, in confined geometries, friction is affected by temperature, usually exhibiting a regular “thermolubric” behavior, with friction decreasing as temperature increases at microscopic scales.\textsuperscript{5–9} The rationale for this standard behavior is random thermal fluctuations assisting the sliding interface in the negotiation of interlocking barriers, thus promoting advancement.

The reverse, namely friction increasing with temperature, is far less common, although it has been observed in specific situations.\textsuperscript{3,10–14} Certainly, inverted thermolubricity in poor heat-transfer conditions may promote instabilities in the frictional dynamics: the heat dissipated by friction itself can raise temperature, thus triggering a further increase in friction, eventually possibly leading to some kind of lockup, which cuts off this runaway condition.

Inverted thermolubricity was considered primarily as an ingredient for phenomenological models,\textsuperscript{15,16} but it was also investigated in atomic-scale friction within the most basic and fundamental model, namely the Prandtl-Tomlinson (PT) model,\textsuperscript{17} where it was shown that a peak in friction may arise in a range of temperatures corresponding to a transition from a multiple-slip regime (low $T$) to a single-slip regime (high $T$). However, that simple model fails to reproduce the observed features of the temperature and velocity dependence of friction,
and of the corresponding force traces measured via atomic-force microscopy (AFM).

Modeling via molecular dynamics (MD) simulations, as a sort of controlled computational “experiment”, has revealed to be extremely useful in investigating frictional processes of complex systems,\textsuperscript{18–20} possibly avoiding interpretative pitfalls arising from indirect or ex-situ characterization of contact surfaces.

In this work we investigate the possibility of an inverted thermal dependence of friction in “brushes” of polymers formed by charge-carrying units confined between surfaces in relative motion. We investigate if, and how, the thermal disordering and rearrangement of such brushes leads to an increase of friction, at least over suitable temperature ranges, especially those experimentally relevant.

Polymer brushes are flexible linear macromolecules which can be tethered to a surface with the aim of modifying its distinctive properties. These brushes can have neutral or charged terminations, depending on the specific surface features that are addressed.\textsuperscript{21} Applications involving polymer brushes include colloid stabilization, regulation in wetting and adhesion, and the formation of protective coatings, among many others.\textsuperscript{22–24} Even though a vast theoretical research on polymer brush lubrication has been carried out,\textsuperscript{25–27} there remain unanswered questions about the microscopic mechanisms of friction, especially under the influence of temperature, on surfaces decorated or covered with these complex molecules.

Here we develop a coarse-grained model to study friction between two pre-assembled polymer brushes.\textsuperscript{28–30} Our simulations demonstrate how the modification of the geometric rearrangement of locally charged (zwitterionic) molecular portions gives rise to different interlocking configurations at the sliding interface, leading to distinct frictional regimes, as a function of temperature.
Methods

The model

We propose a model inspired by surface force apparatus (SFA) experiments, with confined self-assembled vesicles formed by organic polymers composed of hydrophobic tails and hydrophilic heads consisting of short zwitterionic chains. The self-arranged vesicles can sit inside the SFA confined contact, as sketched in Fig. 1a: this arrangement provides a highly sensitive setup for the measurement of the frictional shear stress between well-characterized...
flat surfaces with molecular layers sticking out of them, in mutual shearing motion and under a controlled normal load. The solid surfaces and the visco-elastic deformability of the vesicles cooperate in generating an essentially atomically flat interface between the exposed surfaces of two contacting vesicles. This flat interface extends over the size of a vesicle, namely several micrometers across. All shearing occurs in this sliding interface, which is therefore responsible for all observed frictional forces.

A minimal model for simulating the frictional properties of this interface must include at least the exposed polar heads of the polymers sticking out from the vesicle, as sketched in Fig. 1b. We simulate these heads in a united-atom style as a string of 5 point-like particles. From the interface point of view, the rest of the molecules, namely the glycerol group and the long alkyl tails have the role of providing a directed support to the heads, and transmitting the load and shear forces acted by the SFA setup. In a coarse-grained representation of the hydrophobic inner part of the vesicle, we model this part of the system by parallel rigid layers, one for each contacting vesicle: we name them SUP and SUB layers. The lateral arrangement of molecules in these two layer is modeled using triangular lattices whose periodicity $a/2 = 0.41$ nm sets the equilibrium intermolecular spacing (see Fig. 1d). This spacing $a$ is the characteristic distance between neighboring molecules, matched to the typical areal number density of these vesicle-forming polymers, namely $1.72$ molecules/nm$^2$. To prevent trivial and unrealistic perfect-commensuration effects, we impose a relative angle of rotation $\phi$ between the layers’ crystalline directions (opposite rotations by $\pm \phi/2$ for each layer). The value of $\phi = 19.65^\circ$ and the numbers of lattice repetitions in the rigid layers are adapted in order to fit a supercell periodic in the horizontal $xy$ plane accommodating both lattices, as detailed in the Supplementary Information (SI). We represent the experimental mesoscopic interface within a rectangular simulation supercell with dimensions $l_x = 8.32$ nm and $l_y = 14.41$ nm. The supercell contains 206 molecules in each layer, and 4 times as many atoms in each of the SUP and SUB rigid layers.

The link between the zwitterionic molecular part and the rigid layers is provided by the
NP1 and NP2 units of each molecule, that represent the non-polar tails as a pair of point-like particles. Each of these pairs of bonded atoms remains “planted” in one (out of four) of the lattice nodes in either the SUP or the SUB layer. The intralayer-molecule interaction results in keeping these nonpolar sections aligned close to vertical and to regularly spaced, while allowing for a limited degree of elastic deformability, see Fig. 1b and c.

The SUB-layer particles (magenta particles in Fig. 1c) are kept fully frozen. Those in the SUP layer (purple particles in Fig. 1c and d) are constrained to form an identical, yet misaligned, rigid layer, allowed to translate in the three directions.

Each embedded macromolecule consists therefore in a chain of seven particles, as depicted in Fig. 1b. It starts with a cation (CA, red particle), followed by three uncharged residues (R1-R3, grey), by an anion (AN, blue), and by two uncharged particles, NP1 (green) and NP2 (cyan). Inspired by the dipalmitoylphosphatidylcholine molecule, we set the masses (in a.m.u.) of the molecular beads to 60 for CA, 15 for R1–R3, 80 for AN, and 50 for NP1 and NP2. The CA and AN beads carry an associated charge of $q=0.25$ and $-q$ respectively in elementary-charge units, while all other beads are neutral. For comparison, we also consider a fully uncharged version of the model, with $q=0$ for all beads. Successive atoms in each chain are connected by elastic springs representing both the stretching and the angular degrees of freedom. All equilibrium angles are 180°, except for the NP2-NP1-AN angle, which we set to 111°, representative of a sp$^3$ skeleton oxygen, attempting to keep the polar heads tilted away from vertical.\textsuperscript{38}

The intramolecular harmonic interactions follow the standard expression

$$U_{\text{bond}}(r) = \frac{1}{2}k_{\text{bond}} \left( r - r_0 \right)^2$$

for linear springs, and

$$U_{\text{angle}}(\theta) = \frac{1}{2}k_{\text{angle}} \left( \theta - \theta_0 \right)^2$$

for angular springs. Table 1 lists the parameters adopted for both kinds of intramolecular
Table 1: Intramolecular interaction parameters for the bonded interactions. All interactions not listed here involve non-bonded atoms and are of the Morse type, Eq. (1).

| harmonic bonds |  |  |
|----------------|-----------------|-----------------|
| particle 1 | particle 2 | $k_{\text{bond}}$ (N·m$^{-1}$) | $r_0$ (nm) |
| CA | R1 | 480 | 0.16 |
| R1 | R2 |  |  |
| R2 | R3 |  |  |
| R3 | AN |  |  |
| AN | NP1 |  |  |
| NP1 | NP2 | 0.67 |  |

| harmonic angular interactions |  |  |
|-------------------------------|-----------------|-----------------|
| particle 1 | particle 2 | particle 3 | $k_{\text{angle}}$ (eV·rad$^{-2}$) | $\theta_0$ (degree) |
| CA | R1 | R2 | 20 | 180 |
| R1 | R2 | R3 |  |  |
| R2 | R3 | AN |  |  |
| R3 | AN | NP1 |  |  |
| AN | NP1 | NP2 | 2 | 111 |

For the non-bonded pairwise particle-particle interactions we adopt a Morse potential

$$V_{\text{Morse}}(r) = D_0 \left[ e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)} \right]$$

with a standard shift and a linear term added so that both potential energy and force drop to zero at a cutoff distance $R_c$, see SI. The stiffness parameter $\alpha = 15$ nm$^{-1}$ and the cutoff distance $R_c = 1$ nm are the same for all interaction pairs. The values of the potential well depth $D_0$ and equilibrium spacing $r_0$ are listed in Table 2. Note that, while all non-bonded beads interact pairwise through Morse terms, as an exception, cross-layer interactions are restricted to the polar heads of the molecules (CA, R1-R3 and AN spheres in Fig. 1), with
Table 2: Values for the Morse-interactions parameters between pairs of particles.

| particle 1         | particle 2         | $D_0$ (eV) | $r_0$ (nm) | $r_0$ (nm) |
|--------------------|--------------------|------------|------------|------------|
| default            | 0.010              | 0.41       | 0.41       | 0.82       |
| SUP                | NP1/2 (SUP layer)  | 5.0        |            |            |
| SUP                | NP1/2 (SUB layer)  | 0.0        |            |            |
| SUB                | NP1/2 (SUB layer)  | 5.0        |            |            |
| SUB                | NP1/2 (SUP layer)  | 0.0        |            |            |
| SUB                | SUP                | 0.0        |            |            |
| NP1 (SUP layer)    | NP1 (SUP layer)    | 5.0        |            |            |
| NP1 (SUP layer)    | NP1 (SUB layer)    | 0.0        |            |            |
| NP1 (SUB layer)    | NP1 (SUB layer)    | 5.0        |            |            |
| NP2 (SUP layer)    | NP2 (SUP layer)    | 5.0        |            |            |
| NP2 (SUP layer)    | NP2 (SUB layer)    | 0.0        |            |            |
| NP2 (SUB layer)    | NP2 (SUB layer)    | 5.0        |            |            |

spurious cross-layer terms removed by the $D_0 = 0$ values in Table 2.

Within the cutoff radius, Coulombic pairwise interactions are computed directly in real space, while outside that distance interactions are evaluated in reciprocal space. For the reciprocal space, a particle-particle particle-mesh solver (PPPM) \cite{PPPM1,PPPM2} is used with an accuracy of $10^{-4}$ eV·nm$^{-1}$; further details are presented in the SI.

**Simulations**

We adopt LAMMPS\cite{LAMMPS} as the simulation platform for integrating the equations of motion

$$m_i \ddot{r}_{iu} = F_{iu} - \gamma_{iu} m_i \dot{r}_{iu} + \xi_{iu}.$$  \hspace{1cm} (1)

In addition to the conservative forces $F_{iu}$ explicitly provided by the force fields described in the previous section, we need to model interactions with a solvent which we keep implicit, and do not include in the simulation. The solvent is simulated by a Langevin thermostat with
a damping rate $\gamma_{iu}$ applied to all particles forming the molecules and Gaussian random forces $\xi_{iu}$.\(^{42}\) This thermostat is set to act only along the coordinates $u = y, z$, in order to prevent any spurious thermostat-originated frictional damping along the most relevant sliding direction $u = x$.\(^{43,44}\) Figure S1 of the SI illustrates the robustness of the friction simulated in our model against the precise value of $\gamma_{iy} = \gamma_{iz} = \gamma$ adopted. Eventually, we select a value $\gamma = 1 \text{ ps}^{-1}$ for all simulations.

For each simulation we prepare an initial configuration by executing a sufficiently long “running in” simulation starting from the initial state shown in Fig. 1c, letting the dynamics evolve with the appropriate load, temperature and fixed sliding velocity of the SUP layer, until a steady state is reached. In the appropriate steady-state configuration, we attach a pulling stage to the SUP layer (yellow sphere in Fig. 1c), through a spring of stiffness $k = 1 \text{ eV} \cdot \text{nm}^{-2} \approx 0.16 \text{ N} \cdot \text{m}^{-1}$, equivalent to a shear stress per unit elongation $k/(\text{supercell area}) = 1.34 \times 10^9 \text{ MPa} \cdot \text{m}^{-1}$. We carry out the simulations with the stage advancing at constant speed in the $x$ direction: $x_{\text{stage}} = v_{\text{stage}} t$. A default $v_{\text{stage}} = 5 \text{ m} \cdot \text{s}^{-1}$, in the range of a typical MD approach, is adopted, but we explore other velocities too. In each simulation, the total advancement of the stage amounts to 100 nm. We obtain the instantaneous shear stress from the spring elongation. We start averaging this shear stress when the system enters a steady sliding state, until the end of the simulation. This corresponds to discard an initial transient of 20–25 nm, until at least the first slip event takes place.

We report the averaged shear stress with vertical bars reflecting the root mean squared fluctuations observed along the corresponding friction trace. Large bars indicate stick-slip dynamics, while small bars originate from smooth sliding.

We apply relatively moderate values of loads ($L$) in the 0–20 MPa range, relevant for SFA experiments on organic brushes.
Figure 2: (a) The nonmonotonic variation of the frictional shear stress and (b) the distance between the rigid layers as a function of temperature for charged and uncharged systems. $v_{\text{stage}} = 5 \text{ m s}^{-1}$, $L = 10 \text{ MPa}$. (c-f) Shear traces for the pointed temperatures in panel (a). Symbols in (c-f) refer to the snapshots in Fig. 3.

Results

Figure 2a displays the frictional shear stress as a function of temperature. Consider first the green symbols, reporting the simulations of the default model, the one involving nonzero charges. At low temperature, a smooth sliding regime (Fig. 2c) characterized by extremely small friction is observed. In the smooth-sliding regime the two layers remain substantially flat and well ordered due to the Coulombic interactions between cations and anions in the same layer (see Figs. 3a and 4a): chains of opposite layers do not entangle, and they slide on top of each other encountering a quite small corrugation, due to the discommensuration associated to the mutual angular misalignment. Starting from approximately $T \geq 200 \text{K}$, stick-slip dynamics sets in, see Fig. 2d, and friction increases substantially. As temperature is raised, thermal fluctuations promote out-of-plane chain movements leading to transient interlocking (see Figs. 3b and 4b). The cationic chain head reaching through the opposite
An important parameter of a tribological contact is the critical velocity $v_c$ above which intermittent stick-slip dynamics tends to disappear. In our simulations, we can observe this disappearance as a function of $v_{stage}$ at $T = 150$ K in Fig. 6. With the adopted model param-
Figure 4: (a, b) Top views of the snapshots of Fig. 3a (150 K) and 3b (300 K), including a horizontal slice from the sliding plane in between the chains to immediately above the rigid SUP layer. This slice is the unshaded part of the side views (c) and (d). Black dashed circles highlight SUB chains intersecting the SUP-chains cation plane. The end cation of each of those SUB chains, feels a relatively strong Coulomb interaction with two top-chain anions, generating interlocking spots responsible for stick.

eters, our simulations show clear stick-slip dynamics for \( v_{\text{stage}} < 3 \, \text{m} \cdot \text{s}^{-1} \) and smooth sliding for \( v_{\text{stage}} > 6 \, \text{m} \cdot \text{s}^{-1} \). The model predicts therefore a critical velocity \( \approx 5 \, \text{m} \cdot \text{s}^{-1} \). However \( v_c \) can change by several orders of magnitude depending on system parameters. For example at \( T = 50 \, \text{K} \) (see dot-dashed line in Fig. 6a) the critical velocity is extremely small, and simulations capable to observe stick slip would be far too long. It is therefore unfeasible to evaluate \( v_c \) systematically through simulations. Experimentally, in Ref. 46 this critical velocity is reported for SFA experiments involving squalane films. In those experiments, an increase of \( v_c \) with increasing temperature was observed: that result is compatible with the outcome of the present model.

Coming back to Fig. 2a, as temperature increases to \( T \approx 600 \, \text{K} \) friction increases less and less until it peaks near 800 K. The transient bonds are numerous and relatively short-lived. The energy of each one of such bonds can be estimated (neglecting the small Morse contributions) by the difference in Coulomb attraction of a cation placed in between two adjacent anions of the opposite layer (distance \( \approx 0.41 \, \text{nm} \)) and placed in its flat-layer config-
Figure 5: (a) The percentile hooking fraction $h$ as a function of the stage displacement correlated with the frictional shear stress for the same simulation as in Fig. 2d. (b) The total potential energy $U$ for the same simulation.
Figure 6: Stick slip to smooth sliding transition as a function of velocity. (a) The frictional shear stress as a function of the sliding velocity, charged system, \( L = 10 \) MPa. (b-e) Shear traces for the pointed velocities in panel (a) at 150 K. Dashed line: fit of \( T = 150 \) K and \( v_{\text{stage}} > 6 \) m s\(^{-1}\). Dot-dashed line: fit of the \( T = 50 \) K, including all points.

uration (distance \( \approx 0.51 \) nm), which gives \( \approx 85 \) meV. This transient bond energy is close to the thermal energy \( k_B T \approx 86 \) meV for \( T \approx 1000 \) K, precisely in the temperature region of the observed friction peak. For even higher \( T > 1000 \) K these bonds are destabilized and eventually friction decreases. In order to analyze the effect of the molecular charges on friction, we run analogous simulations for the uncharged system, reported as red curves in Fig. 2.

Remarkably, across the temperature range from \( T = 0 \) K to \( T = 550 \) K, friction is significantly larger than for the charged system. The reason for this difference is that, even at 0 K, both molecular layers are significantly disordered due to the lack of long-range interactions. The chain-orientation disorder leads to a tilt-angle disorder too, and to a significant corrugation of the two mutually sliding layers of molecular heads (CA). This corrugation is reflected also in the consistently larger average SUP-SUB distance, shown in Fig. 2b, compared to the charged case. Due to this extra corrugation, the hooked fraction of the uncharged system
Figure 7: (a,c) The frictional shear stress and (b,d) the average distance between the rigid layers as a function of load $L$, with $v_{\text{stage}} = 5 \, \text{m}\cdot\text{s}^{-1}$.

remains significant, even down to low temperature.

The shear traces for the uncharged system (Fig. 2e,f) exhibit stick slip of smaller amplitude than for the charged system. As illustrated in Fig. 3d,e and in the SI movies, this is due to the uncharged brushes showing a larger density of protruding chains ready to interlock before the slip event has exhausted the energy stored in the pulling spring (Fig. 3f). For $T > 300$ K thermal fluctuations start to undermine the weaker Morse-type bonds of the protruding chains leading to a progressive decrease in friction.

So far, the applied load $L$ was fixed to 10 MPa. To explore how $L$ affects the discussed phenomenology, we perform friction load cycles between 0 and 20 MPa and then back to 0 reported in Fig. 7. The outcome of these simulations indicates that the shear stress does not change significantly upon loading, despite the chain-layer compression visible in Fig. 7b,d. Additionally, the unloading data retrace those of the loading simulations, with no visible hysteresis. For this reason, each point in Fig. 7 is obtained as an average over both loading
and unloading traces for that given load. The frictional shear traces for different loads are reported in Figs. S2 and S3 of the SI. The traces of the charged system, Fig. S2, show that the critical velocity remains practically unchanged for all the investigated loads at $T \simeq 150$ K. Given such a weak friction dependence on load, it is essentially meaningless to define a friction coefficient for this model. The uncharged system exhibits a marginally significant friction increase with load.

As for the velocity dependence, in the stick slip regime it is also expected to be very mild. Indeed, Fig. S4 shows essentially no dependence, as long as the dynamics is stick slip. The charged system at $T = 150$ K reaches smooth sliding for $v_{\text{stage}} > 6 \text{ m/s}^{-1}$. The resulting friction linear increase, practically invisible in Fig. S4, is clear in Fig. 6a. Likewise, the smooth-sliding dynamics at 50 K also produces velocity-linear friction over all simulated velocities. In contrast, the uncharged system has stick slip dynamics at all simulated temperatures resulting in velocity-independent friction.

Figure 5 and analogous plots for different dynamical conditions exhibit clear signs of correlation between the hooking fraction $h$ and the frictional shear stress. We expect that $h$ should also correlate with the total potential energy $U$. Specifically, we expect a decrease in total potential energy as the number of hooked stick points increases. This anticorrelation is illustrated in Fig. S5 of the SI for the uncharged system at $T = 0$ K. However, at $T = 300$ K, the total potential energy is extremely noisy due to thermal fluctuations, see Fig. 5, and these anticorrelations are hard to detect visually.

Figure S6 of the SI illustrates these correlations with scatter plots for the charged (S6a) and uncharged (S6b) models at $T = 300$ K, related to the traces of Fig. 2d,f. These scatter plots provide qualitative hints of these correlations. For a quantitative evaluation of these correlations, we calculate the Pearson correlation coefficient

$$
\rho_{U,h} = \frac{\sum U_t h_t - i\bar{U}\bar{h}}{\sqrt{(\sum U_t^2 - i\bar{U}^2)(\sum h_t^2 - i\bar{h}^2)}},
$$

(2)
Figure 8: Correlation coefficient $\rho_{Uh}$ between hooked fraction and total potential energy, Eq. (2), for the charged and uncharged systems at $v_{\text{stage}} = 5 \text{ m s}^{-1}$ as a function of (a) the applied load and (b) the temperature. As in smooth sliding $h \equiv 0$, $\rho_{Uh}$ is defined for stick-slip dynamics only.

and report it as a function of load and temperature in Fig. 8. $\rho_{Uh}$ is systematically negative, confirming the expected anticorrelation. At $T = 300 \text{ K}$ the uncharged model exhibits more negative anticorrelation compared to the charged model at all the investigated loads (Fig. 8a). As a function of temperature, so far the charged and uncharged models behave quite differently. The charged model has null $h$ at low temperature (smooth sliding), and therefore $\rho_{Uh}$ is undefined. As stick slip develops, $\rho_{Uh}$ becomes more and more negative. In contrast, the uncharged system exhibits stick slip down to zero temperature with the correspondingly largely negative $\rho_{Uh}$. As temperature is raised, these correlations approach zero and correspondingly friction decreases (Fig. 2a).

Discussion and conclusions

In this work we have introduced and studied a model that offers a microscopic implementation for friction mediated by thermally-activated formation and rupture of interfacial contacts, a subject which so far was explored by means of phenomenologic theory.$^{12,48–55}$ This kind
of theory has found wide application in describing friction and wear in dry and lubricated contacts over a wide range of lengths, and revealed the origin of new, unexpected phenomena such as non-Amonton’s variation of friction force with normal load, and nonmonotonic dependence of friction on sliding speed and temperature. The microscopic model proposed here advances understanding mechanisms underlying the phenomenological theory and offers new pathways for the rational control of frictional response.

The main outcome of this model consists in a remarkable increase in friction with temperature. Depending on the operating conditions, sliding can occur with stick slip or smooth advancement. The high-friction stick state results from the interlocking of polymer chains promoted by thermal fluctuations. In the proposed model, Coulombic interactions between the polymeric brushes enhance the inter-polymer interactions, favoring flat and ordered layers and smooth sliding at low temperature. We can imagine different types of inter-polymer interactions, for example hydrogen bonding or solvent-mediated couplings, that could support a similar kind of low-temperature ordering. Thermally-activated interlocking is therefore likely to account for thermally-enhanced friction also in more general contexts, as for example in the experiments of Ref. 46.

Charged brushes are promising systems for the control of friction by externally-applied electric fields. The change in the orientation of the molecular dipoles due to the field may affect interlocking and, therefore, friction.\textsuperscript{56} We hope that this model stimulates further experiments in this and other directions.

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Supporting Information Available

See the Supplementary Information for: details of the chain arrangement, supercell geometry and inter-molecular interactions; the average shear stress as a function of the damping parameter $\gamma$ (Fig. S1); the definition of the hooking fraction $h$; the frictional shear traces of the charged (Fig. S2) and uncharged (Fig. S3) systems for the load dependence of Fig. 7a and c; shear stress and SUP-SUB distance dependence on sliding velocity for charged and uncharged systems (Fig. S4); correlation of the hooking fraction, shear stress and total potential energy for the uncharged system at $T=0$ K (Fig. S5); scatter plots illustrating the anticorrelation between the total potential energy and the hooking fraction that determine the $T=300$ K points in Fig. 8b for charged and uncharged systems (Fig. S6); technical details about 4 short supporting movies illustrating the MD simulations corresponding to the last 30 nm of the stage’s displacement in the shear traces of Figure 2c-f.

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Graphical TOC Entry
Supporting Information for

Thermal friction enhancement in charged polymer brushes

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Supercell geometry

Intending to arrange periodically two arrays of molecules according to triangular lattices we introduce primitive vectors

\[
a_1 = a (\cos(\phi/2), \sin(\phi/2)) \quad a_2 = a (\cos(\pi/3 + \phi/2), \sin(\pi/3 + \phi/2)) \tag{S1}
\]

\[
b_1 = a (\cos(-\phi/2), \sin(-\phi/2)) \quad b_2 = a (\cos(\pi/3 - \phi/2), \sin(\pi/3 - \phi/2)) \tag{S2}
\]

with spacing \(a = 0.82\) nm, and rotated by \(\phi/2\) in opposite directions.

We need a common periodicity and therefore, a matching lattice vector

\[
m_1 a_1 + m_2 a_2 = m_2 b_1 + m_1 b_2 \tag{S3}
\]

with integers \(m_1\) and \(m_2\). This evaluation of this common lattice vector is a special case of the theory described in Ref. 1.

We find that a reasonably-sized supercell is obtained with \(m_1 = 13\) and \(m_2 = 7\). We solve, e.g., the \(y\) component of Eq. (S3):

\[
m_1 \sin(\phi/2) + m_2 \sin(\pi/3 + \phi/2) = m_1 \sin(\pi/3 - \phi/2) - m_2 \sin(\phi/2). \tag{S4}
\]

We obtain

\[
\phi = 2 \arctan \left( \frac{\sqrt{3}}{10} \right) \simeq 19.65286^\circ. \tag{S5}
\]

With the adopted geometry both rotated lattices have lattice points along \(x\) and \(y\). To determine them we solve the null components of the equations

\[
n_1 a_1 + n_2 a_2 = (l_x, 0) \tag{S6}
\]

\[
n'_1 a_1 + n'_2 a_2 = (0, l_y), \tag{S7}
\]
obtaining \( n_1 = 11, n_2 = -2, n'_1 = -7 \) and \( n'_2 = 20 \). The remaining components of the equations provide

\[
l_x = a [n_1 \cos(\phi/2) + n_2 \cos(\phi/2 + \pi/3)] \simeq 8.32 \text{ nm} \tag{S8}
\]

\[
l_y = a [n'_1 \sin(\phi/2) + n'_2 \sin(\phi/2 + \pi/3)] \simeq 14.41 \text{ nm}. \tag{S9}
\]

Alternatively, the opposite corner \((l_x, l_y)\) of a rectangular supercell with a corner at the origin \((0, 0)\) is obtained as \((l_x, l_y) = 4a_1 + 18a_2\).

**Cutoff of the two-body potential**

For the non-bonded pairwise particle-particle interactions we adopt a Morse potential with a standard shift and a linear term added as follows:

\[
V(r) = \begin{cases} 
V_{\text{Morse}}(r) - V_{\text{Morse}}(R_c) - (r - R_c) \frac{dV_{\text{Morse}}}{dr} \bigg|_{r=R_c}, & r < R_c \\
0, & r \geq R_c 
\end{cases} \tag{S10}
\]

so that the truncated potential vanishes smoothly at \( R_c \).

**Long-range solver for Coulomb interactions**

The PPPM solver used for systems, such as ours, which are periodic in \( x \) and \( y \), but not in \( z \), requires an ad-hoc extension. The system is treated as if it were periodic in \( z \), but inserting an empty volume between the slabs and thus removing unphysical dipole inter-slab interactions. For the parameter setting the fraction of empty volume in between slab repetitions, we adopt the value 3.0 recommended by the developers of the simulation software LAMMPS.\(^2\)
Figure S1: The average shear stress as a function of the damping parameter $\gamma$ for the charged model. Simulations are carried out for $v_{\text{stage}} = 2.5 \text{ m}\cdot\text{s}^{-1}$, $T = 150 \text{ K}$, $L = 10 \text{ MPa}$. 
The hooking fraction $h$

In order to quantify the degree of interpenetration of the chains we introduce a “hooking fraction” $h$ as the fractional number of chains whose cation crosses the average level of cations of the opposite layer, like the highlighted chains in Fig. 4b,d of the main text. The definition for $h$ is the following:

$$h = \frac{1}{2} (h_{\text{SUP}} + h_{\text{SUB}}), \quad (S11)$$

where

$$h_{\text{SUB}} = \frac{1}{N_{\text{SUB}}} \sum_{j=1}^{N_{\text{SUB}}} \theta(z_{j}^{\text{CA}} - \bar{z}_{\text{SUP}}), \quad (S12)$$

$$h_{\text{SUP}} = \frac{1}{N_{\text{SUP}}} \sum_{i=1}^{N_{\text{SUP}}} \theta(\bar{z}_{\text{SUB}} - z_{i}^{\text{CA}}). \quad (S13)$$

Here $\theta()$ is the usual $\theta$ function, equal to one or zero according to the sign of its argument, and

$$\bar{z}_{\text{SUP}} = \frac{1}{N_{\text{SUP}}} \sum_{i=1}^{N_{\text{SUP}}} z_{i}^{\text{CA}}, \quad \bar{z}_{\text{SUB}} = \frac{1}{N_{\text{SUB}}} \sum_{j=1}^{N_{\text{SUB}}} z_{j}^{\text{CA}}. \quad (S14)$$

For example, the hooking fraction as a function of time is illustrated in Fig. 5a. $h$ clearly correlates with the stick-slip dynamics.
Figure S2: The frictional shear traces of the charged model obtained for stepwise increasing load $L$. Averages (including the load-decreasing traces – not shown) are reported in Fig. 7a of the main text. Simulation conditions: $v_{\text{stage}} = 5 \text{ m s}^{-1}$, (left) $T = 300 \text{ K}$ and (right) $T = 150 \text{ K}$. 
Figure S3: Same as Fig. S2 but for the uncharged model – Averages reported in Fig. 7c of the main text.
Figure S4: (a) The frictional shear stress and (b) the distance between the rigid layers as a function of the advancement velocity of the stage for the two indicated temperatures and for load $L = 10$ MPa.
Figure S5: (a) The percentile hooking fraction $h$ as a function of the stage displacement correlated with the frictional shear stress for the uncharged model at $T = 0$ K. (b) The total potential energy for the same simulation.
Figure S6: Scatter plot illustrating the correlation between the total potential energy and the hooked fraction for (a) charged system (b) uncharged system. Correlation coefficients for these data are reported in Figure 8b of the paper. $L = 10$ MPa and $T = 300$ K.
SI movies

Each of the SI movies reports the final 6 ns (i.e. the last 30 nm displacement) of a MD simulation. In simulation time, the frame rate is 1 frame every 20 ps. In running time, the frame rate is 10 frames per second. For clarity, like in Fig. 3 of the main text, the movies only include a 5 nm $y$-thick slice of the simulation cell (whose entire $y$-side is 14.41 nm).

Each movie contains one highlighted SUP particle to make the displacement of the rigid top layer more evident.

- **charged\_150K.mp4**: the last 6 ns of the MD simulation corresponding to the force trace shown in Figure 2c;

- **charged\_300K.mp4**: the last 6 ns of the MD simulation corresponding to the force trace shown in Figure 2d;

- **uncharged\_150K.mp4**: the last 6 ns of the MD simulation corresponding to the force trace shown in Figure 2e;

- **uncharged\_300K.mp4**: the last 6 ns of the MD simulation corresponding to the force trace shown in Figure 2f.

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