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Stick-Slip Control in Nanoscale Boundary Lubrication by Surface Wettability

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We study the effect of atomic-scale surface-lubricant interactions on nanoscale boundary-lubricated friction by considering two example surfaces—hydrophilic mica and hydrophobic graphene—confining thin layers of water in molecular dynamics simulations. We observe stick-slip dynamics for thin water films confined by mica sheets, involving periodic breaking-reforming transitions of atomic-scale capillary water bridges formed around the potassium ions of mica. However, only smooth sliding without stick-slip events is observed for water confined by graphene, as well as for thicker water layers confined by mica. Thus, our results illustrate how atomic-scale details affect the wettability of the confining surfaces and consequently control the presence or absence of stick-slip dynamics in nanoscale friction.

Understanding friction plays a central role in technological applications and phenomena in diverse fields ranging from micromechanical devices to bioengineering [1] and to earthquakes [2]. Given the continuing miniaturization of mechanical devices towards the nanoscale [3], improved understanding of friction and wear could help in reducing energy consumption, improving reliability, and extending service life. Indeed, an important part of their design process consists of trying to minimize friction and to eliminate stick-slip dynamics [4].

Stick-slip control in lubricated friction is of particular importance given the vast number of applications where lubricants are used to reduce the detrimental effects of friction and wear [5]. Examples of mechanisms behind the emergence of stick-slip in boundary-lubricated systems have been numerically demonstrated to include repeated crystallization and shear melting of the thin lubricant film [6], interlayer slips within the ordered solidlike lubricant film, or wall slips at the wall-film interface [7]. Most of the numerical studies of stick slip in boundary lubrication have focused on coarse-grained or simplified or idealized models [6,8,9], not explicitly considering the atomic-scale interactions occurring in real systems. On a coarse-grained scale, a useful classification of the lubricant-surface interactions is given by the wettability of the confining surfaces by the lubricant, with systems displaying a larger contact angle or lower wetting generally exhibiting lower friction. Other approaches to friction control include, e.g., applying mechanical oscillations [10,11]. While the effect of wetting on lubricated friction has been studied experimentally in macroscopic [12–15] and nanoscale [16] systems and modeled using phenomenological finite-element models [17] and simplified molecular dynamics (MD) simulations of nanopatterned surfaces [18,19], less is known about the underlying atomic-scale processes and mechanisms responsible for the presence or absence of stick slip.

Given the large surface-to-volume ratio in boundary lubrication, the nature of the interaction between the lubricant and the confining surfaces originating from their atomic composition should play a crucial role. Thus, we study the interaction of a thin water layer (thickness $h$ around 0.5 nm unless stated otherwise) in MD simulations using full atomic models of two experimentally relevant confining surfaces with different wetting characteristics: crystalline mica, a hydrophilic substrate that strongly adsorbs water [20], and graphene, a hydrophobic surface interacting weakly with water [21]; see Fig. 1. We observe stick-slip dynamics for thin water layers confined by mica: each unit cell of mica contains two K$^+$ ions, interacting strongly with the water oxygens via Coulomb interactions, leading to the formation of atomic-scale capillary bridges next to the K$^+$ ions, connecting the two mica surfaces in the stick state. These bridges break during the subsequent slip event and reform during the next stick phase, a process that is also visible as the breaking and reforming of interfacial hydrogen bonds between water and mica. This mechanism is different from both the crystallization-shear melting transitions [6] and interlayer or lubricant-surface slips [7] observed before in simplified models. In contrast, water films confined by hydrophobic graphene, as well as thicker water layers confined by mica, exhibit fundamentally different dynamics with no stick slip.

To model the confined water film, we consider systems ranging from 200 to 1200 SPC/Fw water molecules [22]. We consider 2M1-muscovite mica with the formula $\text{KAl}_2\text{(Al}_{10}\text{Si}_3\text{)}\text{O}_{10}(\text{OH})_2$, with the force field parameters from Ref. [23]. One mica surface consists of $10 \times 6$ unit cells and has linear dimensions of $L_x = 52.07 \, \text{Å}$ and $L_y = 54.036 \, \text{Å}$; see Fig. 1. To create site disorder, mimicking a real mica surface with a random distribution of potassium ions on it, one K$^+$ ion of the pair in each unit cell is removed and subsequently placed on the bottom part of

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the sheet [24]. The graphene sheets have $L_x = 68.063 \, \text{Å}$ and $L_y = 36.841 \, \text{Å}$. The Lennard-Jones parameters for carbon are from Ref. [25]. The cutoff radius is $r_c = 10.0 \, \text{Å}$ for all potentials. Both sheets are parallel to the $xy$ plane with periodic boundary conditions along the $x$ and $y$ directions. Couette flow is generated by moving the top sheet at a constant velocity $V$, and the bottom sheet is constrained to move along the $x$ axis and is attached to a spring of stiffness $k$. The water molecules are confined by (b) two mica sheets (each of thickness of 8.34 Å) or (c) two monolayer graphene sheets. The color code of the atoms is water oxygen (red), water hydrogen (white), potassium (pink), silicon (yellow), aluminum (blue), mica oxygen (cyan), mica hydrogen (lime), and carbon (gray).

Simulation results for 256 water molecules confined by mica sheets for $P_\perp = 1 \, \text{atm}$ and $V = 0.1 \, \text{m/s}$ are shown in Fig. 2. The force per atom on the bottom sheet applied by the spring, $F_s/N_p$, exhibits characteristic stick-slip behavior [Fig. 2(a)]. Figure 2(b) shows the friction force per sheet atom on the bottom mica plate applied by the water and the top mica plate, $F_r/N_p$, exhibiting similar time dependence as the spring force, with superimposed high-frequency fluctuations due to the finite temperature. Figure 2(c) shows the position $Z$ of the center of mass of the top sheet in the $z$ direction. The center of the bottom mica sheet is fixed at $z = 4.16 \, \text{Å}$. During each slip event, $Z$ increases by roughly 10% [6]. Since the formation and breaking of interfacial chemical bonds is known to play a role in friction (see Ref. [29] for an example from rock friction), we show also the time dependence of the number of hydrogen bonds (i.e., the number of water hydrogens closer than 3 Å from the bottom mica surface) between water and the bottom mica surface in Fig. 2(d): bonds break as the system evolves from stick to the slip state.

For comparison, we also performed MD simulations of water confined by hydrophobic graphene sheets. We varied the number of water molecules from 200 to 1200, the
normal loads from $P_{\perp} = 1$ to 10 atm, and the driving
velocities from $V = 0.01$ to 0.1 m/s. Figure 2(c) shows the
spring force from simulations of 200 water molecules,
$P_{\perp} = 1$ atm, and $V = 0.1$ m/s; similar results are obtained
for other $P_{\perp}$ and $V$ values. We observe a small increase
of friction with $V$ for both mica and graphene; see the
Supplemental Material [30] and Refs. [31,32] for exper-
imental results on mica-confined systems with sliding
velocities significantly lower than those reachable in our
MD simulations. Our simulations thus demonstrate that
the stick-slip behavior does not arise for thin water films
confined by graphene. Instead, continuous, smooth sliding
with the maximum friction force well below that obtained
for mica is observed for all parameter values considered.
We also note that the same applies to the mixed system with
one graphene and one mica surface: slip is localized at the
hydrophobic graphene-water interface, and no stick-slip is
observed.

This difference between the two kinds of surfaces may
be explained by the relatively strong interaction of the
potassium ions on the mica surfaces with the oxygen atoms
of the water molecules via Coulomb interactions. Thus, the
ions could act as “freezing nuclei,” with the water mole-
cules gathering around them to form nanoscale capillary
water bridges [33,34], connecting the top and bottom
surfaces within the stick phase. As the system starts to
slip, these bridges would break. The interaction of carbon
atoms with oxygen is much weaker, and we expect that no
capillary bridges are formed between graphene sheets,
explaining the absence of stick-slip dynamics in that case.

To verify this hypothesis, we calculate the density
distributions $\rho(x, y)$ of water oxygens in the contact layer
relative to the bottom surfaces. Figure 3(a) shows $\rho(x, y)$
for a water film confined by mica sheets when the system
sticks [$t = 1$ ns in Fig. 2(a)]. Peaks in $\rho(x, y)$ are located at
the K$^+$ ions. Figure 3(b) presents the corresponding $\rho(x, y)$
graph during the first slip state when $t = 5$ ns [cf. again
Fig. 2(a)]: the peaks of $\rho(x, y)$ become smaller and broader.
Finally, Fig. 3(c) shows $\rho(x, y)$ for the subsequent stick
state at $t = 7$ ns [Fig. 2(a)], where we again observe that
the peaks are as high and narrow as those of the previous
stick state.

To gain more insight into the nucleation and breaking of
the capillary bridges between the surfaces, we calculate the
density profiles $\rho(z)$ of water oxygens across the gap.
When the system is slipping [Fig. 3(d)], $\rho(z)$ exhibits
two separate peaks, consistent with breaking of the capil-
ary bridges. In the stick state [Fig. 3(e)], $\rho(z)$ exhibits
multiple peaks spanning the gap. This can be understood
as the water molecules forming nanoscale capillary
bridges between the two mica surfaces. In contrast to this
behavior, the density distributions $\rho(x, y)$ of the water film
consisting of 200 water molecules confined by graphene
sheets in Fig. 4 show that water clusters to form a single,
relatively large dropletlike structure between the two
graphene sheets, without any apparent signature of
breaking-reforming transitions. The corresponding density
profiles $\rho(z)$ (Supplemental Material [30]) are similar to
previous observations in equilibrium graphene-confined
systems [35].

Thus, when the two mica surfaces are very close
together, the thin confined water film loses its fluidity,
and the bulk flow properties of water play little or no role in friction. However, they may be recovered by increasing the thickness of the water layer [36], with the conditions approaching those of hydrodynamic lubrication. To this end, we performed MD simulations with four different, larger thicknesses of the water layer: \( h = 1.77, 2.03, 2.29, \) and 2.56 nm, corresponding to 1536, 1792, 2048, and 2304 water molecules, respectively. For these thicker water films, the stick-slip dynamics disappears. Instead, smooth sliding dynamics is observed, which at a first glance looks similar to that in the graphene-confined system. However, subtle differences can still be observed between the two surfaces. Zooming in to the spring force time series (e.g., the one shown in Fig. 2(e)) reveals periodic oscillations corresponding to the eigenfrequency of the spring-bottom plate mass (\( M \)) system \( f = 1/(2\pi)\sqrt{k/M}. \) For both surfaces, the varying amplitudes of these oscillations at each period [blue circles in Figs. 5(a) and 5(b)] form sequences of time-ordered observations \( X(n) \), which can be well described by an autoregressive model \( X(n + 1) = aX(n) + W(n) \) (or equivalently, the Ornstein-Uhlenbeck process \( X(n + 1) - X(n) = -(1 - a)X(n) + W \), with \( W \) white noise originating from the interaction with the fluctuating lubricant and \( a \) a model parameter, both extracted using the \( R \) package [37]. For water confined by graphene, we find \( a \approx 0.8 \) and \( \delta W \approx 0.1 \text{ pN} \) for all conditions considered, while we find \( a \approx 0.1 \) and \( \delta W \approx 0.3 \text{ pN} \) for thick water films (\( h \geq 1.77 \text{ nm} \)) confined by mica. Accordingly, the autocorrelation function (ACF) of \( X(n) \) for mica decays more rapidly to zero than its counterpart for graphene. In both cases, the ACFs computed from the simulation data agree with those of the corresponding autoregressive model [see Figs. 5(c) and 5(d)]. The observation that \( \delta W \) does not significantly depend on \( h \) for \( h \geq 1.77 \text{ nm} \) indicates that the screened mica-water interaction has a subnanometer range, resulting essentially in a surface effect of the fluctuations of the water layer. Also, the stronger interaction of mica with the fluctuating lubricant (as compared to that of graphene) results in a factor of 3 greater \( \delta W \) [see also Figs. 5(e) and 5(f)].

In summary, the presence or absence of breaking-reforming transitions of local capillary bridges in the water film, controlled by the atomic structure and the ensuing wettability (hydrophilic mica vs hydrophobic graphene) of the confining surfaces, plays a crucial role in whether stick-slip dynamics is observed or not. For mica, the decisive role of the K\(^+\) ions in the formation of the nanoscale capillary bridges suggests that the microscopic details behind stick-slip dynamics should in general depend on the atomic structure of the system, and it would be interesting to perform similar studies for other confining surfaces with different surface-lubricant interactions. Nevertheless, we expect our main observations to be rather general and to open up interesting possibilities in controlling nanoscale boundary-lubricated friction by tuning the wettability of the confining surfaces.

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