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Abstract:

Nanoscale silica-silica contacts were recently found to exhibit logarithmic ageing for times ranging from 0.1 s to 100 s, consistent with macroscopic rate and state friction laws and several other ageing processes. Nanoscale ageing in this system is attributed to progressive formation of interfacial siloxane bonds between surface silanol groups. However, understanding or even data for contact behavior at ageing times < 0.1 s, before the onset of logarithmic ageing, is limited. Using a combination of atomic force microscopy experiments and kinetic Monte Carlo simulations, we find that ageing is nearly linear with ageing time at short time scales between ~ 5 and 90 ms. We demonstrate that ageing at these times requires the existence a particular range of reaction energy barriers for interfacial bonding. Specifically, linear ageing behavior consistent with experiments requires a narrow peak close to the upper bound of this range of barriers. These new insights into the reaction kinetics of interfacial bonding in nanoscale ageing advance the development of physically-based rate and state friction laws for nanoscale contacts.

Main text:

Phenomenological rate and state friction (RSF) laws [1–7] are widely used to describe the frictional behavior of rocks [1,7–12] and other materials [8,13–15]. An important aspect of RSF laws is the evolution effect, whereby the state of contacts evolves with contact time or slip [1,5]. One manifestation of the evolution effect is ageing, wherein static friction increases

with the time of quasi-stationary contact. Ageing has been observed for contact times ranging from 0.1 to 10^5 s [1,3,7,16]. Two classes of ageing mechanisms have been proposed: a temporal increase of real contact area (to which friction is proportional [17,18]), due to plastic creep [19], and interfacial chemical bond formation [20], resulting in an increase of friction without a change in real contact area.

To understand the physical basis of RSF laws, Li et al. performed slide-hold-slide (SHS) experiments for single-asperity hydroxylized silica-silica nanocontacts using atomic force microscopy (AFM) [21] whereby the sliding AFM tip was abruptly stopped and held stationary for a given hold time, then sliding resumed. A logarithmic increase of the friction drop ΔF (the difference between the maximum static friction after holding and the kinetic friction after sliding resumes) for hold times of 0.1 to 100 s occurred, the same dependence as for macroscale ageing [1,3,7,16]. Li et al. [21] proposed that ageing was due to interfacial chemical bond formation. First-principles calculations and kinetic Monte Carlo (kMC) simulations showed that ageing involves covalent interfacial siloxane (Si-O-Si) bonds forming [22] between interacting hydroxyl groups on opposing silica surfaces. This condensation reaction is an activated process whose barrier depends on the local atomic configuration. A distribution of barriers is expected due to the heterogeneity of the amorphous surfaces. The simulations showed that the logarithmic increase of static friction with hold time arose from the distribution of energy barriers [22-24], as expected from a recent general analysis of activated systems with such distributions [24]. These and other studies [26–28] provide asperity-level understanding of interfacial chemical bond-induced (ICBI) friction.

Deviation from logarithmic aging at shorter time scales was observed in these kMC simulations (see Fig. 4 in [22]). This implies that ageing may not be logarithmic for hold times less than ~ 0.1 s in experiments. Short time ageing should be sensitive to the initial barrier distribution. Thus, examining short time ageing can provide insight into this distribution, which is otherwise difficult to measure.

We conducted AFM experiments on short-time ageing behavior of oxidized Si AFM tips and Si(001) wafers; wafers were Piranha-treated to promote hydroxylation. Experimental procedures including sample preparations, probe characterizations and calibration details are presented elsewhere [27].We measured friction drop vs. log of effective contact time (hold time plus the time of stick on reloading prior to slip). Fig. 1 shows a representative example. Above 1 s, the friction drop follows a logarithmic trend. At shorter times, the trend deviates from logarithmic, similar to previous simulations [22,24].

Experiments were conducted under a range of conditions, with relative humidity values between $26.0 \pm 0.1\%$ and $80.0 \pm 0.1\%$, and applied load between 31 ± 3 nN and 819 ± 80 nN, and using more than 10 probes. In all cases, the lower limit of the logarithmic trend is between 0.1 and 1 s. Measurements at higher time resolution are consistent (Fig. S9).

Furthermore, the friction drop varies approximately linearly with effective contact time at short times. A typical example is shown in Fig. 1 (upper left inset), where the friction drop

increases approximately linearly from 5 to 90 ms contact time. A linear dependence of ageing on time has not been reported previously for nanoscale contacts.

To further explore the physics of linear ageing at short contact times, we conducted kMC simulations of interfacial siloxane bond formation. Our kMC model, originally presented in [22], simulates the time evolution of the number of interfacial chemical bonds. Each reaction site (from a 2D grid representing the interface) is initially assigned an energy barrier for bond formation randomly chosen from a given barrier distribution. Reaction sites with lower barriers are more likely to form interfacial bonds first. As the hold time increases, the number of bonds successively increases. In all simulations, we use a bond formation attempt frequency of 10^{13} Hz and a temperature of 300 K.

Both the number of bonds (Fig. 2(a)) and the energy barrier of the sites that react (Fig. 2(c)) increase logarithmically with time at longer contact times. For simulations over short contact times (Figs. 2(b) and (d)), the barriers for reactions within the 5-90 ms time window lie between 0.6-0.8 eV (Fig. 2(d)). This implies, within a given time window, there is an effective range of barriers for sites that contribute to contact ageing, and sites with barriers outside this range will not affect the ageing behavior. Note that the opposite argument does not hold true: an energy barrier within the range 0.6-0.8 eV can also affect the ageing outside the time window of 5-90 ms (see Fig. 2(d)).

Linearity at short contact times is not obtained in these simulations (Figs. 2(b)). We thus determine the key barrier distribution features required to obtain linear ageing at short contact times. To do this, we constructed an artificial barrier distribution, where the initial (t = 0, where t is the contact ageing time) distribution is decomposed into three parts: low, middle, and high barriers. Middle barriers lie within the range of effective energy barriers from $E_{b,mid}$ to $E_{b,mid} + E_{b,range}$ which we found were relevant for time scales from 5-90 ms (0.6-0.8 eV) (Fig. 3 (a)). Low ($E_{b,low}$) and high ($E_{b,high}$) barriers are described by two δ distributions, and the middle ($E_{b,mid}$ to $E_{b,mid} + E_{b,range}$) barriers are described by a uniform distribution. By tuning the peak values of $E_{b,low}$ and $E_{b,high}$, we observed that ageing for contact times between 5-90 ms is inded independent of $E_{b,low}$ or $E_{b,high}$, as long as these two values are outside of the range of effective barriers. If $E_{b,low}$ or $E_{b,high}$ cross over a boundary of the range of effect barriers, the low and high distribution affect the shape of the ageing curve (see Supplemental Material section SM 3). We now set $E_{b,low} = 0.4$ eV and $E_{b,high} = 0.95$ eV, and focus on understanding how the middle barriers impact linear ageing for contact times between 5 and 90 ms. Examples with three different parameter sets are shown in Fig. 3 (b).

We further vary the features of middle barriers ($E_{b,mid}$ and $E_{b,range}$) in the simulations to qualitatively and quantitatively match the experimental data. Here, "qualitative" means we maximize the linearity of the ageing curves within the first 5-90 ms of the simulations. Linearity is assessed using a Pearson correlation coefficient between simulated ageing curves and a straight line (using linearly interpolated values at evenly spaced contact times between 5-90 ms). A curve with high linearity can have a finite intercept when linearly extrapolated to 0 s, and does not have to pass through the origin. "Quantitative" means that the relative amount of ageing (e.g., the friction drop normalized by the kinetic friction force) obtained by simulations matches experimental results. We assume that the friction drop for a given contact time is proportional to the number of bonds formed during that time, and that it scales linearly with the tip-sample contact area [24,26]. At long contact times, the friction drop saturates once nearly all sites have reacted; this saturation value is determined by the number of possible reactions sites, i.e., the contact area. In optimizing the quantitative agreement, we require two quantities match experimental values: 1) the normalized number of bonds for contact between 5-90 ms. Here, relative values of these two quantities normalized by the total number of available reaction sites initially, not absolute values, will be compared with experimental observations. This is motivated the AFM's inability to measure the true contact area. Thus, a relative comparison permits a meaningful comparison. These criteria are further explained below.

As seen in Fig. 1 (inset), the linear fit intersects the vertical axis at a finite friction drop. This means there is a sudden increase in friction drop at the very beginning (t < 5 ms) of ageing. Fig. 1 shows that the friction drop at t=5 ms lies between 100-300 nN. The maximum friction drop measured in experiments is approximately 5000 nN. Thus, the friction drop at t=5 ms is at most ~300/5000 = ~6% of the total ageing. Assuming linearity between friction drop and the number of bonds, the normalized number of bonds at t=5 ms contact time should also be less than 6%. For our second quantitative criterion, we also estimate from Fig. 1 that the relative increase in the number of bonds for t=5-90 ms should be less than 10%. This is obtained by taking the difference of the largest variance in the friction drop for t=5-90 ms in experiments, i.e., 600-100 = 500 nN, and dividing by the maximum measured friction drop (5000 nN). Note that ageing for contact time beyond 100 s are not measured experimentally; since there is no clear saturation at t = 100 s, the saturation value of friction drop must be higher than 5000 nN. Therefore, the two quantitative criteria, 6% and 10%, correspond to the upper limits of these ratios.

Note that the percentages of reaction sites with low, middle, and high barrier values affect the simulation results. However, the exact barriers in experiments are not known *a priori*. We set the percentage of reaction sites with barriers $E_{b,low}$ at 4%; these sites control the initial sudden increase in friction drop (t < 5 ms) in simulations. A value less than 6% meets the first quantitative criterion. We also set the percentage of reaction sites with middle ($E_{b,mid}$ to $E_{b,mid} + E_{b,range}$) barriers to be 30%. Simulation results with other percentages are similar, and the specific choice does not affect our qualitative conclusions (see SM 6). In the following simulations, we narrow the size of the parameter space, i.e., we only vary $E_{b,mid}$ and $E_{b,range}$ while satisfying the qualitative and quantitative criteria.

We first compare the qualitative simulation results with experimental data. In Fig. 4 (a), we report the Pearson correlation coefficient of ageing curves with a linear fit while varying $E_{b,mid}$ and $E_{b,range}$, ensuring that the barriers are always within the range of effective barriers (0.6-0.8 eV). The three markers correspond to the three different parameter sets, with the same markers used in Fig. 3 (b). There is a large variation in linearity depending on the specific parameters. Better linearity is obtained when either (1) for a given value of $E_{b,mid}$,

the largest possible range $E_{b,range}$ is used, or (2) for a given value of $E_{b,range}$, the largest possible $E_{b,mid}$ is used.

To analyze the shape of the aging curve, we define a normalized total reaction rate $k_{tot} = \frac{1}{N_{0,total}} \sum_{i=1}^{N} k_i$, where $k_i = A \exp(-E_{b,i}/k_B T)$ is the reaction rate of the *i*th reaction site, $E_{b,i}$ is the energy barrier of the *i*th reaction site, $N_{0,total}$ is the total number of available reaction sites initially, *N* is the number of reaction sites that have not formed interfacial bonds, *A* is the attempt frequency, k_B is Boltzmann's constant, and *T* is temperature. If interfacial bonding events can be described as Poisson processes, then on average, k_{tot} in the time period from *t* to $t + d\tau$ (assuming that a previous bond formed at *t*, and the next bond forms at $t + d\tau$) is proportional to $1/d\tau$ [29]. Also, the slope of the friction drop vs. contact time curve (i.e., the ageing curve) is by definition $d\Delta F/dt \propto -dN/dt$. Thus, k_{tot} is proportional to the slope of the ageing curve.

The large variation in linearity observed in Fig. 4 (a) can be explained in terms of k_{tot} as follows. The value of k_{tot} decreases with contact time because the number of sites still able to react to interfacial bonds decreases with contact time. Since k_i increases exponentially with decreasing E_i , the magnitude of decrease in k_{tot} is larger when the reaction site with lower energy barrier reacts. Also, higher k_{tot} means that the time period for forming the same number of bonds is shorter than for a lower k_{tot} . Therefore, when there is a higher concentration of lower barrier sites at the interface, not only there will be more bonds forming at shorter times, but the value of k_{tot} (or the slope of the ageing curves) will decrease much faster with contact time, resulting in larger deviations from linearity. The simulation results support the above explanations (see SM 4).

To test for quantitative agreement with experimental results for appropriate parameters, in Figs. 4(b) and (c) we show how the number of bonds at 5 ms and the increase in the number of bonds during t=5-90 ms depend on $E_{b,mid}$ and $E_{b,range}$. Here, the number of bonds is normalized by $N_{0,total}$. Fig. 4(b) shows that as $E_{b,mid}$ and $E_{b,range}$ decrease, the number of bonds at 5 ms increases. Also in Fig. 4(c), a relatively small increase in the number of bonds can be achieved with a narrow barrier distribution (small $E_{b,range}$) centered either at low $E_{b,mid}$ (close to 0.6 eV) or at high $E_{b,mid}$ (close to 0.8 eV). These results can also be explained in terms of the total reaction rate. Specifically, when $E_{b,mid}$ is smaller and $E_{b,range}$ is narrower, there are more sites with low barriers, the total reaction rate increases, and more bonds form within shorter times. When most of the bonds with barriers between $E_{b,mid}$ and $E_{b,mid} + E_{b,range}$ form before 5 ms, there will be little increase in the number of bonds during the subsequent 5-90 ms time interval, as manifested in the left bottom region of the plot in Fig. 4(c). In the right bottom region of the same plots, almost no bonds can form before 5 ms, but due to the high barriers and low total reaction rate, the increase in number of bonds is also small during 5-90 ms time interval.

By combining our qualitative and quantitative criteria for matching simulation results with experiments, we can narrow down the parameter space (Fig. 4 (d)). Cases that meet the following criteria are considered to be a good match with experiment (marked as brown in

Fig. 4 (d)): (1) the Pearson correlation coefficient must be larger than 0.98; (2) the normalized number of bonds at 5 ms must be smaller than 6%; and (3) the increase in the normalized number of bonds must be smaller than 10%. Other cases are labelled in white in the same figure. From this, the region of possible parameters lies in the right bottom corner of the figure, where the barriers have a relatively narrow distribution close to 0.8 eV (upper bound of the range of effective barriers). This is within the range of siloxane bond formation from a previous DFT study [22]. Provided this condition is satisfied, a highly linear ageing trend that matches experiments is obtained.

Based on our previous theoretical work [22], we also provide an analytical explanation of how the properties of the middle barrier distribution affect the linearity of the ageing curve, and show that a narrow middle distribution is consistent with simulation and experiments. More details are in the SM 8 and 9.

In conclusion, for nanoscale silica-silica contacts, ageing follows an approximately linear trend with contact times below ca. 0.90 ms, then transitions to a logarithmic dependence. kMC simulations demonstrated that ageing at short times is determined by interfacial reaction kinetics. Specifically, ageing within the contact time period 5 to 90 ms is related to bond formation events at reaction sites with barriers ranging from ca. 0.6 to 0.8 eV. Sites with barriers outside this range have no effect on ageing for contact times between 5 to 90 ms. By comparing experimental and simulation results, we further narrowed down the parameter space, showing that the barrier distribution should be relatively narrow and close to the upper bound of effective barriers (0.8 eV) to produce linear ageing behavior matching experiments. By providing these new physical insights into non-logarithmic dependence of ageing at short contact times, we further establish the chemical bond mechanism for nanoscale ageing, and provide a stronger foundation for physically-based RSF models for nanoscale asperity contacts.



Fig. 1: Friction drop vs. effective contact time. Relative humidity = 80%, applied normal load = 284 nN, temperature T = 297 K, loading point velocity 1.53 µm/s, and adhesion undetermined. Upper left inset: data points from an effective contact time of ca. 5 ms to 0.11 s, with a linear time scale. The friction drop increases linearly with effective contact time from ca. 5 to 90 ms. The best-fit line is the red solid line in the inset. Results for contact times of 1, 10, and 100 s fall on a best-fit line, which is the purple solid line in the main plot, extended by a purple dashed line. Data points for a contact time of 0.1 s are clearly above this extrapolated line. The lower limit of the logarithmic trend is between 0.1 and 1 s. The lower right inset shows one lateral force vs. lateral displacement curve for a 0.07 s hold time, and the friction drop. Hold times are varied randomly to exclude systematic errors.



Fig. 2: kMC simulations of number of bonds and energy barrier as a function of contact time. [(a) and (b)] Time evolution of the normalized number of interfacial bonds plotted on logarithmic (full range) and linear (early times) time scales. The number of bonds is normalized by the total number of available reaction sites before ageing occurs. [(c) and (d)] Energy barrier for sites that form bonds at a given point in time as a function of time for Gaussian and uniform barrier distributions. The Gaussian distribution has a mean value of 0.8 eV with a standard deviation of 0.2 eV; the uniform distribution has a lower bound of 0.2 eV with a range of 1.2 eV. Dashed lines in (d) indicate the range of effective barriers within 5-90 ms.



Fig. 3: Artificial energy barrier distribution and kMC simulation results with different parameter sets. (a) Schematic plot of artificial barrier distribution. The barriers are decomposed into three parts. Low () and high () barriers are described by a δ distribution, and middle (to) barriers are described by a uniform distribution. In our simulation, we set the percentage of reaction sites with low, middle, and = 0.4 eV, and high barriers to be 4%, 30%, and 66%, respectively. We use = 0.95 eV. are two free parameters in the model. (b) Time evolution of and interfacial number of bonds normalized by within 5-90 ms, with different values of . In (b), we show every 10th data points of the simulations for clarity. and



Fig. 4: Qualitative and quantitative evaluation of ageing curves with various sets of parameters. In all plots, different values of and are considered. (a) Linearity of ageing curves are quantified by Pearson correlation coefficient (higher coefficient means higher linearity). The three markers in this plot correspond to the three parameter sets used in Fig. 3(b) as denoted by the symbol used. (b) Number of bonds normalized by at 5 ms. (c) Increase in the normalized number of bonds during 5-90 ms. (d) Possible parameter space of middle barrier distribution shown in brown, and the impossible region shown in white. The possible region is selected when all the three criteria (both qualitative and quantitative) are met, i.e., Pearson correlation coefficient > 0.98, normalized number of bonds at 5 ms < 6%, and increase in the normalized number of bonds < 10%. Simulation results here are averaged over 10 simulations with different random seeds.

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Author contributions: K. T. prepared the probes and substrates, designed and performed experiments, obtained and analyzed the data, established analytical models and proposed explanations. Z. L. designed and performed simulations, and analyzed and proposed explanations for simulation results. Y. L. designed and performed primary simulations. R. W. C. oversaw the experiments with additional guidance from D. L. G. I. S. oversaw the simulations. K. T. and Z. L. wrote the manuscript with input from all coauthors.

References:

- [1] J. H. Dieterich, J. Geophys. Res. 77, 3690 (1972).
- [2] J. H. Dieterich, Pure Appl. Geophys. **116**, 790 (1978).
- [3] J. H. Dieterich, J. Geophys. Res. 84, 2161 (1979).
- [4] J. H. Dieterich, J. Geophys. Res. Solid Earth 84, 2169 (1979).
- [5] A. Ruina, J. Geophys. Res. Solid Earth 88, 10359 (1983).
- [6] A. L. Ruina, Friction Laws and Instabilities: A Quasistatic Analysis of Some Dry Frictional Behavior, Doctoral dissertation, Brown University, 1982.
- [7] C. Marone, Annu. Rev. Earth Planet. Sci. 26, 643 (1998).
- [8] F. Heslot, T. Baumberger, B. Perrin, B. Caroli, and C. Caroli, Phys. Rev. E 49, 4973 (1994).
- [9] J. R. Rice, Pure Appl. Geophys. PAGEOPH 121, 443 (1983).
- [10] T. E. Tullis and J. D. Weeks, in Frict. Faulting (Springer, 1987), pp. 383–414.
- [11] J. R. Rice and A. L. Ruina, J. Appl. Mech. 50, 343 (1983).
- [12] J. H. Dieterich, Mech. Behav. Crustal Rocks 24, 103 (1981).
- [13] A. D. Corwin and M. P. de Boer, Microelectromechanical Syst. J. 18, 250 (2009).
- [14] A. D. Corwin and M. P. de Boer, Phys. Rev. B 81, 174109 (2010).
- [15] S. S. Shroff, N. Ansari, W. Robert Ashurst, and M. P. de Boer, J. Appl. Phys. 116, 244902 (2014).
- [16] P. Berthoud, T. Baumberger, C. G'sell, and J.-M. Hiver, Phys. Rev. B 59, 14313 (1999).
- [17] F. P. Bowden and D. Tabor, Proc. R. Soc. Lond. A. Math. Phys. Sci. 391 (1939).
- [18] I. Szlufarska, M. Chandross, and R. W. Carpick, J. Phys. D. Appl. Phys. 41, 123001 (2008).
- [19] J. H. Dieterich and B. D. Kilgore, Pure Appl. Geophys. PAGEOPH 143, 283 (1994).
- [20] G. Vigil, Z. Xu, S. Steinberg, and J. Israelachvili, J. Colloid Interface Sci. 165, 367 (1994).
- [21] Q. Li, T. E. Tullis, D. Goldsby, and R. W. Carpick, Nature 480, 233 (2011).
- [22] Y. Liu and I. Szlufarska, Phys. Rev. Lett. 109, 186102 (2012).
- [23] A. Li, Y. Liu, and I. Szlufarska, Tribol. Lett. 56, 481 (2014).
- [24] Z. Li and I. Szlufarska, Phys. Rev. Mater. 2, 063602 (2018).
- [25] A. Amir, Y. Oreg, and Y. Imry, Proc. Natl. Acad. Sci. 109, 1850 (2012).
- [26] K. Tian, N. N. Gosvami, D. L. Goldsby, Y. Liu, I. Szlufarska, and R. W. Carpick, Phys. Rev. Lett. 118, 076103 (2017).
- [27] K. Tian, D. L. Goldsby, and R. W. Carpick, Phys. Rev. Lett. **120**, 186101 (2018).

- [28] K. Tian, N. N. Gosvami, D. L. Goldsby, and R. W. Carpick, J. Phys. Chem. B 122, 991 (2018).
- [29] D. T. Gillespie, J. Comput. Phys. 22, 403 (1976).
- [30] See Supplemental Material [url] for more experimental and simulation results, derivations of analytical models, and detailed discussions, which includes Refs. [22][23][28][31]
- [31] K. Pearson, Proc. R. Soc. London 58, 240 (1895).