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Chemical Origins of Frictional Ageing

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Although the basic laws of friction are simple enough to be taught in elementary physics classes and although friction has been widely studied for centuries, in the current state of knowledge it is still not possible to predict a friction force from fundamental principles. One of the highly debated topics in this field is the origin of static friction. For most macroscopic contacts between two solids, static friction will increase logarithmically with time, which phenomenon is referred to as ageing of the interface. One known reason for the logarithmic growth of static friction is the deformation creep in plastic contacts. However, this mechanism cannot explain frictional ageing observed in the absence of roughness and plasticity. Here, we discover molecular mechanisms that can lead to logarithmic increase of friction based purely on interfacial chemistry. Predictions of our model are consistent with published experimental data on friction of silica.

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Static friction between two solids is widely observed in nature [1-3]. Static friction increases while the surfaces are held together. This so-called frictional ageing is usually logarithmic with time [4-7]. It is generally accepted that ageing can be described by the rate and state friction law [8-10] which is a phenomenological law developed based on empirical observations. One well-established explanation of ageing is that the real contact area between surfaces grows with time due to plastic deformation and creep [1, 7, 11-12]. Although the friction force is independent of the nominal contact area in rough macroscopic contacts, it does depend on the real area of contacting asperities and therefore growth of the real contact area will lead to an increase in friction. Another hypothesis that has been also postulated in the literature is that frictional ageing can be controlled by interfacial chemistry, and more specifically, by increase of contact strength per unit area [13]. Experimental support for this hypothesis includes a measured dependence of static friction on humidity [14] and an observation of ageing of silica at normal loads that are too low to induce creep [15]. However, the physical origin of ageing in such experiments remains a mystery. One argument that puts in doubt the explanation in terms of interfacial chemistry is that it is unknown whether and how chemical bonding across the interface could lead to a logarithmic strengthening as a function of time.

Here, we discover a new mechanism of interface bonding by which friction can increase with time based purely on surface chemistry. Building on our discovery of interaction between surface reaction sites, we propose a new type of interfacial reaction kinetics where reaction proceeds logarithmically with time. We choose a specific case of silica because frictional ageing of this materials is relevant for a number of fields, including Earthquake studies in geophysics [14] and wafer bonding in semiconductor science [16]. Hypothetically, three kinds of mechanisms could lead to ageing of hydrophilic silica in humid environments in the absence of deformation creep [17]. These are formation of hydrogen bond network, meniscus condensation, and covalent bonding between hydroxylated silica surfaces. The latter mechanism involves formation of a siloxane bridge across the interface. For single asperity contacts, both meniscus condensation and hydrogen bonding take place on the time scales of at most 10^{-2} seconds [18-20]. Therefore these mechanisms cannot explain experimentally observed ageing over the period of hundreds of seconds or longer [7, 15]. Here, we demonstrate that in the absence of deformation creep, covalent bonding alone can lead to logarithmic ageing in silica contacts over experimentally relevant time scales. Although covalent bonding between silica surfaces has been extensively studied in literature [16-17, 21], contributions from the siloxane bonds to friction had been challenging to quantify because of the difficulty in directly monitoring the formation of these bonds during experiments. To demonstrate the mechanism of logarithmic ageing, we carry out atomistic simulations of siloxane bond formation on both amorphous silica and quartz interfaces. For these two cases we perform molecular dynamics (MD) simulations using

reactive force field (ReaxFF) [22] and density functional theory (DFT) calculations [23-24], respectively.

We have conducted simulations with both amorphous silica surfaces and quartz (001) surfaces. For simulation of amorphous silica, we used the Reaxff force field [22], which is implemented in LAMMPS. Amorphous sample is prepared from a random structure (2592 Si atoms and 5184 O atoms with the density of amorphous silica) by heating it up to 5000K and then equilibrating it for 30 ns. Amorphization of the sample has been confirmed by calculating the pair distribution function. The system is then cooled down to 300K in 20 ns and it is equilibrated for 10 ns before creating free surfaces. Surfaces are created by removing periodic boundary conditions in the direction normal to the surface. Reactions are studied on the top surface while the bottom surface (i.e., a 10Å-thick layer) is frozen, which means that atoms within that region are not allowed to relax. The surface is then relaxed at 300K for 15ns using a velocity-rescaling algorithm every 50ps. The dimension of the surface is 5nm × 5nm. After a surface has been prepared, we place water molecules on it and we allow the system to react and form hydroxyl groups. Due to these reactions, each surface is terminated with about one hundred hydroxyl groups, which corresponds to the surface density of 4 groups/nm². This density is consistent with experimental observations [25]. Interface is created by bringing two surfaces toward each other in displacement-controlled indentation simulations. The contact pressure is calculated as the sum of the total forces on atoms in the frozen layer of a sample divided by the nominal contact area of 25 nm². Calculations of reaction energies for siloxane formation from two hydroxyl groups is carried out at the pressure of ~2 GPa, which is in the same range as typical pressures in AFM experiments [15].

For calculations on quartz, we employ DFT simulations using VASP [23-24, 26] Projector Augmented Wave (PAW) method with 520 eV energy cut-off is used in our simulation. Wave function is expanded at Γ point during the relaxation. Convergence of energy with k points was tested and Γ point calculations were found to be sufficient. Relaxation is carried out until forces on all ions are lower than 0.01 eV/Å (0.016 nN). We perform simulations on quartz (001) surfaces with 3 × 3 supercell. Surface silicon atoms are terminated with geminal groups (two hydroxyl groups associated with one silicon atom) to obtain a complete passivation of the surface silicon atoms.

Surprisingly, we found that the rate of interfacial siloxane formation depends not only on the initial configurations of the silanol groups, but also on the history of reactions on the surrounding sites. This point is illustrated in Fig.1, where we plot a histogram of interaction energies I between pairs of neighboring reaction sites on amorphous silica interface. I is defined as the difference between reaction energies in the presence and in the absence of a siloxane bridge on a nearest-neighbor site. One key conclusion from Fig. 1 is that there is always a finite amount of interaction for all the pairs of reactions we have studied. Another important conclusion is that although this interaction energy is randomly distributed and the specific distribution may depend on the condition of the

surface, interaction energy is strongly biased towards positive values (see vertical dashed line in Fig. 1). This observation means that formation of an interfacial siloxane bonds increases the energy barrier to formation of siloxane bonds on neighboring sites, because change in reaction energy is proportional to the change in reaction barrier [27-28]. We have observed similar trends for quartz surfaces [20].

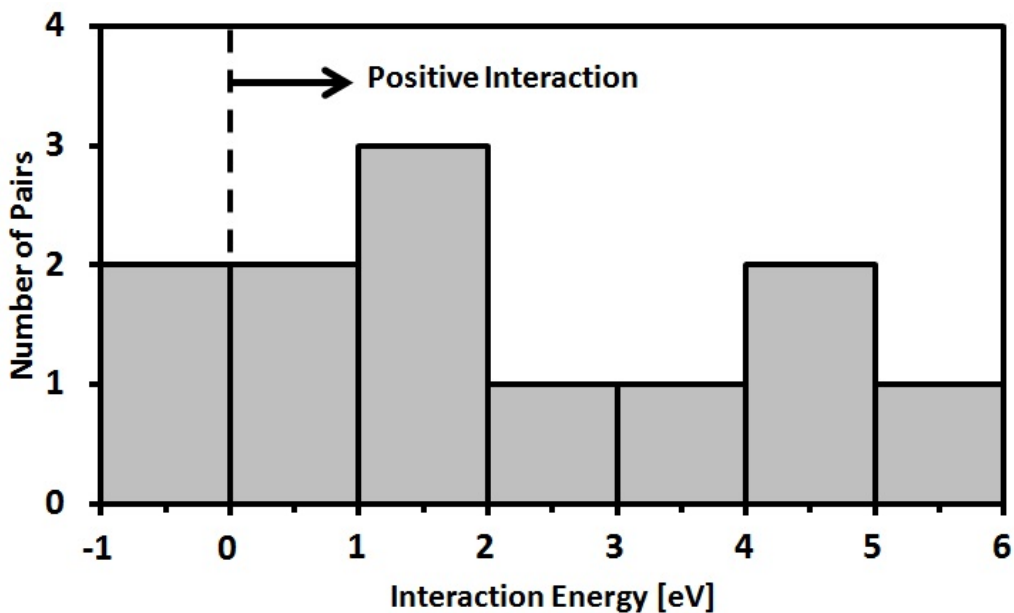


Figure 1. Distribution of interaction energies for distinct pairs of reaction sites on amorphous silica. The interaction energy is defined as the difference between reaction energies in the presence and in the absence of a neighboring siloxane bridge. Positive interaction means that formation of one siloxane bond increases energy barrier to form another siloxane bond on a neighboring site. This figure shows that (i) interaction is always finite and (ii) interaction is biased toward positive values.

What is the origin of the interaction between neighboring siloxane bonds? Generally, there could be three types of physical phenomena responsible for the interactions: (i) Direct interaction between the silanol groups, which includes electrostatic interaction, hydrogen bonding, *etc.*; (ii) Indirect interaction due to charge transfer between the two reaction sites; (iii) Elastic interaction through the surrounding bulk silica. Indirect interaction due to charge transfer can be excluded because the electron density calculated around a reaction site is the same regardless of whether there is a siloxane bond on a neighboring site or not. We test the remaining two hypotheses by carrying out the following simulations on quartz. We pick two pairs of reaction sites on quartz surface – one in a parallel and one in an antiparallel configuration, as shown in Figs. 2a and 2b, respectively. The corresponding interaction energies are defined as I_a and I_b . We calculate $\Delta I = I_a - I_b$ as a function of the interfacial separation. For the test of our hypothesis we choose the interfacial separation for which ΔI is 0.483 eV, which is on the same order as

typical interaction energy I for quartz. To determine if ΔI arises from direct electrostatic interaction, we calculate ΔI for isolated siloxane bridges without the surrounding bulk (Figs. 2c and 2d). We confirmed that electron densities around isolated siloxane groups are the same as around siloxane bridges between silica surfaces. We find that ΔI for isolated bridges is 0.003 eV, which means that direct electrostatic interactions cannot account for the calculated interactions between siloxane bridges across silica interface. To verify that ΔI arises primarily from elastic deformation of the bulk, we calculate this energy using a force field that has explicit terms for bond bending and stretching [29]. We find that contributions to ΔI from elastic deformation of O-Si-O bond angles is 0.482 eV, which is within 0.2% of ΔI calculated in ab initio calculations of silica interface. This difference increases to 12.3% for other indentation depths. Based on the quantitative agreement between elastic energy stored in bond angles and ΔI calculated for the entire system, we conclude that interaction between interfacial siloxane bridges is mediated by deformation of tetrahedra in the silica structure. Figure 3 shows a chain of tetrahedra that connect two reaction sites and for which the changes of elastic energy were found to be significantly larger than for other tetrahedra. It is important to point out that although we considered a specific reaction where a siloxane bridge is formed by two hydroxyl groups from the opposite surfaces, this elastic interaction mechanism is universal and is expected to be active in other siloxane-forming reactions on silica, such as the ones discussed by Vigil *et. al.*[17].

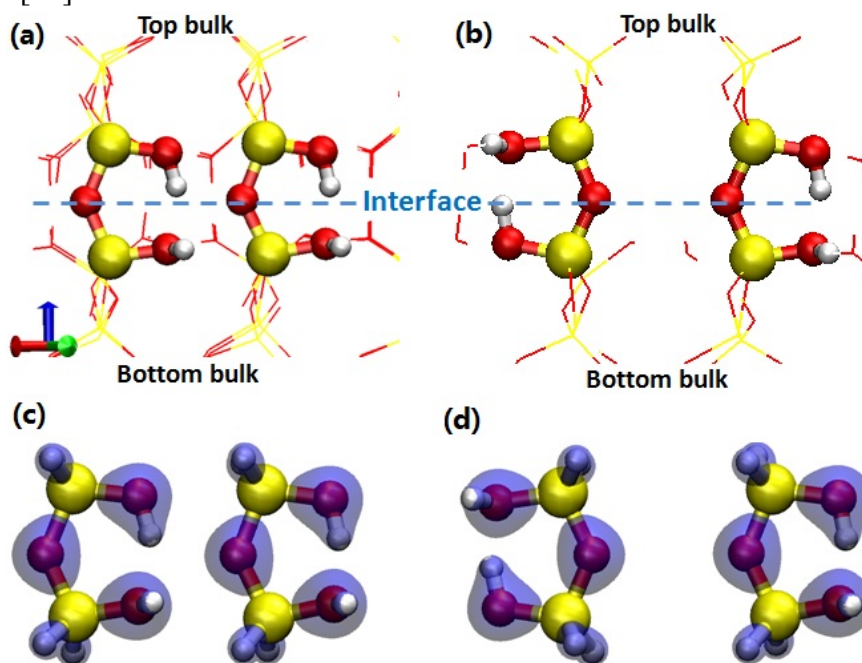


Figure 2. Atom configuration of the two pairs of reaction sites we have selected on quartz for verification of interaction mechanism. (a) “parallel” configuration; (b) “anti-parallel” configuration; (c) “parallel” configuration as isolated groups; (d) “anti-parallel” configuration as isolated groups. Yellow, red and white atoms correspond to Si, O, and H, respectively. Shaded areas around atoms in (c) and (d) mark electron densities associated with each atom. Blue line in

the centre of (a) and (b) represents the position where the interface is. Visualizations are made using the VMD [30] software.

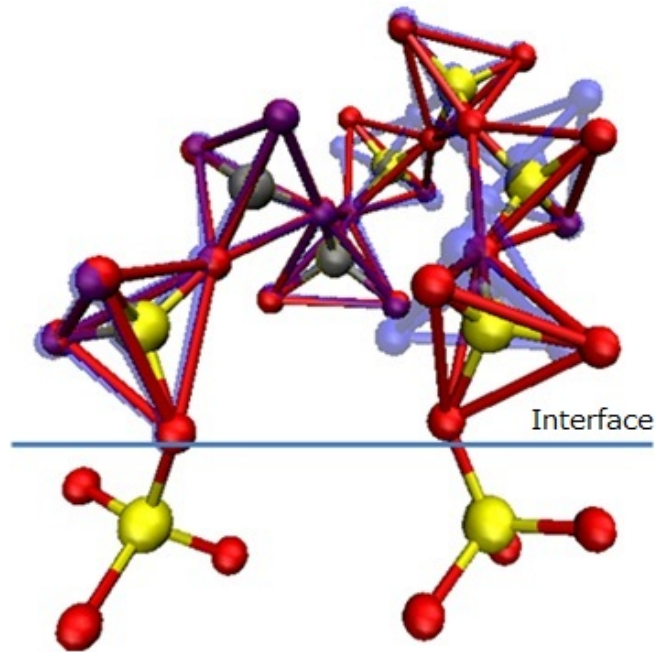


Figure 3. Chain of silica tetrahedra with large contributions to elastic energy from bending of O-Si-O bonds. Changes in elastic energy have been induced by formation of the second (right) siloxane bridge in the presence of the first (left) siloxane bridge. Yellow and red atoms correspond to Si and O, respectively. Shaded blue atoms represent positions of atoms in the same tetrahedra before formation of the second (right) siloxane bridge. Hydrogen atoms are removed from the picture for visualization purposes.

A critical question that remains to be addressed is whether formation of siloxane bridges can lead to a logarithmic strengthening of the interface with time. It is known that for materials with direct bonding, friction is proportional to the number of strong bonds that form across the interface [17, 31-33]. Consequently, to explain logarithmic ageing, one needs to demonstrate that the concentration of interfacial siloxane bridges increases logarithmically with time. A hint comes from an early work of Prandtl [11], who showed that if friction is controlled by elastic instabilities, friction force will decrease logarithmically with time as a result of elastic relaxation of the interface. By treating interfacial chemical reactions as relaxation events and following a similar analytical derivation to that of Prandtl, one can show that formation of siloxane bridges will follow a logarithmic reaction rate [20]. This explanation is, however, far from complete because the key assumption of the derivation is that reaction energy barriers for different sites are uniformly distributed.

There are multiple phenomena that can control the distribution of energy barriers for interfacial reactions. One possibility is that the energy barrier associated with a

reaction site may depend on the atomic pressure acting on that site. Consequently, the energy barriers associated with the reaction sites that are in direct contact with the counter-surface will be determined by the distribution of atomic pressures [32, 34] (red lines in Figs. 4a). Another possibility is that the reaction barrier may be influenced by the geometry of the reaction complex. Specifically, if the energy barrier is assumed to be linear with the distance between two reacting silanol groups in the plane of the interface, then distribution of energy barriers is linear (red lines in Figs. 4b). Real interfaces can be controlled by a combination of physical phenomena. Indeed, the distribution of energy barriers calculated from MD simulation on an amorphous silica surface [red line in Fig.4c] is more complex than the isolated pressure and geometry distributions, but still non-uniform.

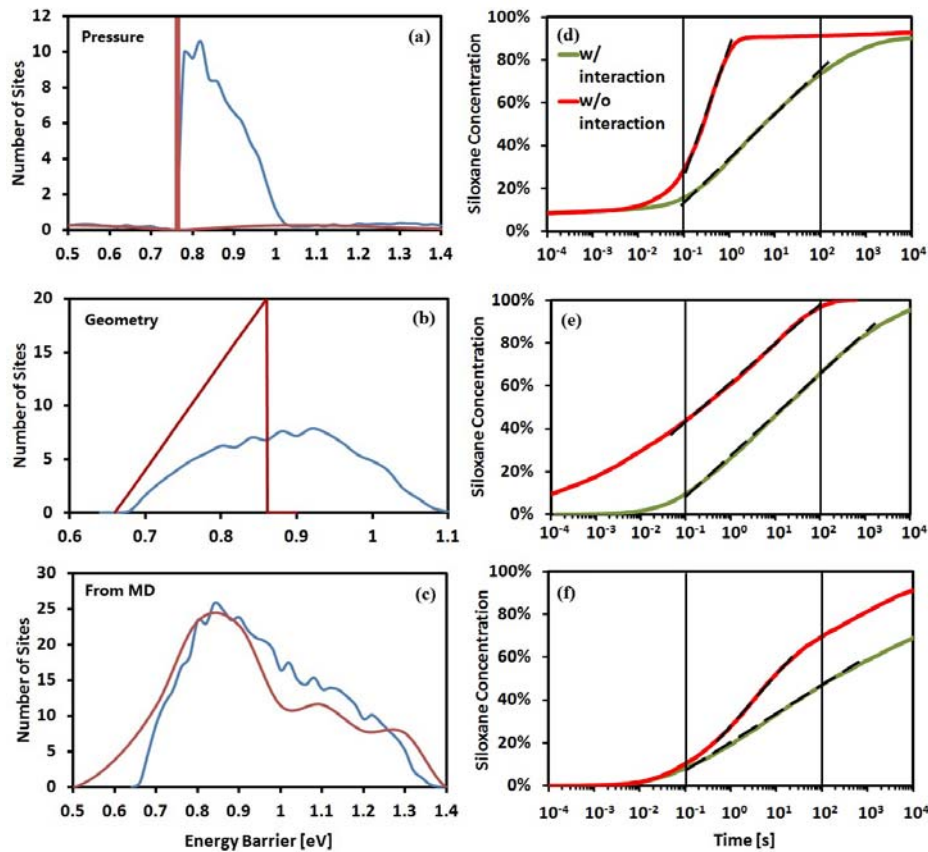


Figure 4. Distributions of reaction barriers (left column) and the corresponding reaction rate curves (right column). Shown are reaction barriers that are controlled by (a and d) pressure, (b and e) geometry, and (c and f) calculated directly from MD simulations. Red and blue lines correspond to cases without and with interactions, respectively. In (b) 20% of atoms (which are assumed to interact with the opposite surface) were assigned barriers according to the pressure distribution and the remaining atoms were assigned a constant energy barrier. Variations between different sets of kMC simulations are comparable to the thickness of the line. Black vertical lines in d-f refer to the time interval in AFM single contact friction experiment [15]. As stated in the main text, the siloxane concentration shown here is proportional to the magnitude of static friction.

We now demonstrate that the newly discovered interactions among reaction sites on silica lead to an extended regime of logarithmic growth of interfacial strength as a function of time. Toward this goal, we have carried out kinetic Monte Carlo (kMC) simulations both in the absence and in the presence of the interaction between neighboring sites. As shown in Figs. 4 d-f, each distribution leads to a period of time during which concentration of siloxanes depends logarithmically on time. This concentration saturates and approaches a constant value at longer time scales – a feature that had been also observed in laboratory experiments on ageing [35]. For all distributions considered here, adding interactions leads to a significant increase in the range of logarithmic growth (Figs. 4 d-f). The effect of interactions on the evolution of siloxane concentration can be understood by examining energy barriers for reactions that actually took place in a system with interaction. If we plot the *final* distributions of these barriers (blue lines in Figs.4 a-c) and compare them to the corresponding *initial* distributions (red lines in Figs.4 a-c), the *final* distributions are broader and their shapes are closer to a uniform distribution. Interaction broadens the distribution of reaction barriers of the sites that have not yet reacted and in turn leads to an extended logarithmic reaction regime in time. Finally, it is worth asking whether our results are consistent with published experimental data on frictional ageing of silica. A particularly useful comparison can be made to single asperity studies on silica [15], since these measurements exclude the effects of surface roughness. In their studies Li *et al.*[15] observed a (5-6)-fold increase of static friction over three decades of time (vertical black lines in Figs. 4 d-f). We find that within the range of physically justifiable parameters [20], it is possible to find a set that leads to at least five-fold increase of static friction over at least three decades of time. This parameter set was chosen to plot data in Figs. 4 d-f.

In conclusion, we have discovered that the presence of the interactions, combined with a pre-existing distribution of reaction energy barriers, leads to a logarithmic increase of interfacial strength as a function of time in the absence of plastic deformation. Using kMC simulations we find that generally the stronger the interaction is or the larger the width of the initial distribution, the longer the regime of logarithmic reaction rate. The discovered effect of energy barrier distribution on reaction rate could be generalized to all interfaces if reactions were to occur on the time scales that span the experimental measurement.

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