Investigating Wear Mechanisms of Alkylsilane Monolayers through Molecular Dynamics Simulation

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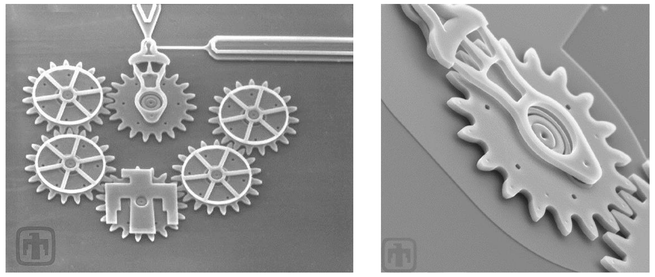
Motivation and Project Overview

Tribology involves the study of friction and wear of interacting surfaces as well as their lubrication, which refers to the methodology used to reduce or overcome these concerns. Understanding this behavior on the nanoscale is important for developing new technologies which overcome friction-induced wear. This becomes especially important as device components get smaller and the effect of these interactions becomes more prominent, such as in microelectromechanical and nanoelectromechanical systems (MEMS and NEMS).



MEMS devices from Sandia National Laboratories, www.mems.sandia.gov

Why simulation?
Experiments provide only a basic understanding of the mechanisms involved with nanoscale lubrication; molecular simulations help us to gain a deeper understanding of behavior at the nanoscale. In addition, simulation allows us to systematically introduce non-ideality into systems, which is essential for studying the mechanisms associated with friction-induced wear.

Why amorphous substrates?
Previous research[1,2] has shown that amorphous substrates more accurately represent the substrates used in laboratory studies of self-assembled monolayers, as a result of the preparation process. For this reason, it is important to study monolayers on amorphous substrates in order to more accurately predict their behavior in real-world devices and relate our results to those found experimentally .

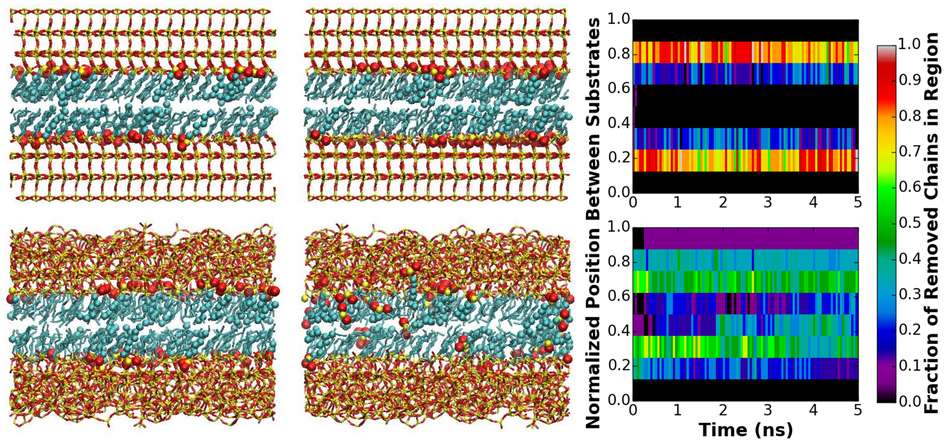
Why study wear?
Alkylsilane monolayers are known to degrade over time, whereby chains break off of the surface. In order for these monolayers to be used successfully as lubricants it is necessary to understand both how the degradation process is initiated as well as how it proceeds with time. Understanding this will yield enhanced insight into the key factors which affect long-term tribological stability.

Simulation Setup and Conditions

- Crystalline systems were assembled by attaching 100 hexylsilane chains to a beta-cristobalite silica substrate. Amorphous systems were assembled by attaching 100 hexylsilane chains to an amorphous silica substrate generated by the method described in [1].
- Substrates were mirrored and rotated 180° to obtain a dual monolayer system.
- Equilibration was performed for 1ns to allow systems to relax toward energetically favorable configurations.
- Compression of the two substrates was performed at a rate of 1m/s.
  - Snapshots were gathered at various separation distances in preparation for shearing.
- Three different separations were chosen for constant separation shearing at a velocity of 10m/s for 1ns.
- A specified fraction of chains was detached from each substrate at random and shearing was continued at velocity of 10m/s for 5ns.

Simulations were performed using the LAMMPS[3] molecular dynamics package under the following conditions:
- Force field parameters obtained from the Optimized Potentials for Liquid Simulations all-atom (OPLS-AA) force field
- Temperature controlled at 298K using a Nose-Hoover thermostat with atom integration in the NVT ensemble
- Electrostatic interactions were computed using the particle-particle, particle-mesh algorithm (PPPM)

Results

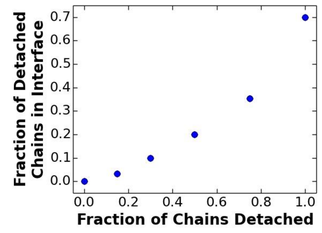


Simulation snapshots of hexylsilane monolayer systems before (left) and after (middle) 5ns of shearing at 10m/s for crystalline (top) and amorphous (bottom) substrates. Heat maps (right) show the locations of the centers of mass of detached chains during shearing. Silicon is yellow, oxygen is red, carbon is blue. Detached chains are shown as spheres. Hydrogens are not shown for clarity.

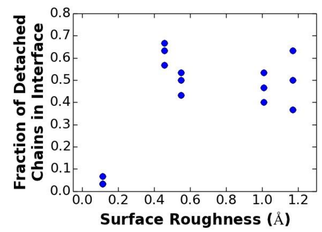
Free-Chain Mobility

A free chain is considered to be mobile if at any point in time during shearing its center of mass is within 2Å of the centerline between the monolayers.

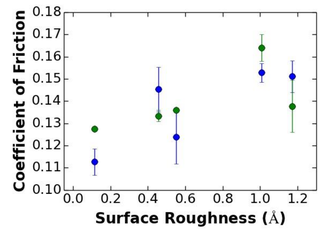
The plot to the right shows the free-chain mobility of systems as a function of the number of detached chains. All systems were constructed using crystalline substrates. As more chains are detached from the substrate, free-chain mobility greatly increases and activity at the interface becomes more noticeable, suggesting a reduction in monolayer stability .



The plot to the right shows free-chain mobility as a function of surface roughness when 15% of chains were attached from each system. The crystalline system (roughness≅0.1Å) displayed very little movement among detached chains. However, in the amorphous systems there was a significant degree of free-chain mobility. This suggests that surface roughness and substrate structure may play an integral role in the wear process of the alkylsilane monolayers.



The plot to the right shows coefficient of friction of monolayers with varying surface roughnesses, without (blue) and with (green) 15% of chains detached from the substrate. It is found that the amorphous systems yield higher coefficients of friction than the crystalline systems. Also, in most cases, the coefficient of friction increased after 15% of chains were detached from the substrate.



Conclusions

- In crystalline substrates, free-chain mobility is correlated with the fraction of broken chains
- Amorphous systems have a higher degree of free-chain mobility compared to crystalline systems, which we attribute to increased surface roughness
- Systems with amorphous substrates have higher coefficients of friction, suggesting an inclination toward increased wear under all conditions

Future Work

- Systematic detachment of chains based on bond distances
- Investigate the influence of chain length on free-chain mobility
- Further investigate the impact of the fraction of detached chains on amorphous substrates

Acknowledgements

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References

[1] Black, J., Iacovella, C., Cummings, P., & McCabe, C. (In preparation).
[2] Chandross, M., Webb, E., Stevens, M., Grest, G., & Garofalini, S. *Physical Review Letters*, vol. 93, 2004.
[3] Plimpton, S., *Journal of Computational Physics*, vol. 117, 1995.