

## Tribology Focus Topic

Room: 203 C - Session TR+AS+NS+SS-MoA

## Molecular Origins of Friction

**Moderator:** I. Szlufarska, University of Wisconsin-Madison, M. Müser, Saarland University, Germany

2:00pm **TR+AS+NS+SS-MoA1 Unraveling and Eliminating Dissipation Mechanisms in Polymer Brush Interfaces**, *M.H. Müser*, FZ Jülich, Germany **INVITED**

Surfaces covered with end-anchored polymers under good solvent conditions have excellent tribological properties. Friction between such surfaces is commonly attributed to the interdigitation of opposing polymer brushes. However, this conclusion tends to be based on idealized geometries neglecting capillaries or surface roughness. Using molecular dynamics simulations, we find that, depending on the direction of motion, dissipation due to capillary and shape hysteresis can contribute in a similar fashion as interdigitation. The two alternative mechanisms are even likely to become dominant at small sliding velocity. We also analyze how friction can be tuned through the solvent quality, thereby providing guidelines for the optimization of the investigated systems.

2:40pm **TR+AS+NS+SS-MoA3 Molecular Dynamics Simulations of Adhesion & Friction between Carbon-based Materials, Silicon, and Silicon Carbide**, *K.E. Ryan*, United States Naval Academy, *K. Vummaneni, J.D. Schall*, Oakland University, *J.A. Harrison*, United States Naval Academy

The nanoscale properties of two bodies in contact cannot be fully analyzed on an atomistic level using experimental methods or understood solely using continuum mechanics. Molecular dynamics (MD) simulations allow nanoscale behavior to be modeled by resolving the positions, velocities, and forces of discrete atoms in the system. Diamond has been of interest as both an object of scientific study and as an ideal material for applications such as, cutting tool coatings, waste water purifiers, chemical sensors, electronic devices, and micro- and nanoelectromechanical systems (M/NEMS) because of its unique electrical, mechanical, and tribological properties. Due to its high fracture strength and chemical robustness, it can withstand exposure to harsh environments and resist mechanical wear. It can be grown in nanocrystalline form with nearly equivalent mechanical performance to the crystalline form. Silicon, due to the ability to create atomically sharp tips, is frequently used in scanning probe microscopy. Recently, carbon implantation of preformed Si-tips has been used to improve wear properties. In this work, MD was used to simulate the nanoscale adhesion and tribological behavior between diamond, diamond-like carbon (DLC) surfaces and silicon, and silicon carbide tips. Work of adhesion values from the MD simulations with axisymmetric tips are compared to, and discussed within the context of, complementary AFM experiments where available, finite element simulations, and continuum mechanics-based analytical models. MD simulations show that the work of adhesion is sensitive to the identity of the contacting materials because they have inherent roughness differences. In addition, work of adhesion values obtained from continuum mechanics-based analytical models are consistently higher than values obtained using the atomic-force microscope, which are higher than the simulated values. A recently developed bond-order potential for C-, H-, and Si-containing systems was used to carry out these simulations. The novel aspects of this model will be discussed.

3:00pm **TR+AS+NS+SS-MoA4 Electronic Friction at the Atomic Scale: Conduction, Electrostatic and Magnetic Effects**, *Z. Fredricks, K.M. Stevens, J. Krim*, North Carolina State University

In the study of friction at the nanoscale, phononic, electrostatic, conduction electron and magnetic effects all contribute to the dissipation mechanisms [1,2]. Magnetic contributions are increasingly alluded to in current studies, but remain poorly characterized. We report here our observations magnetic friction for sliding adsorbed films on various magnetic films substrates in the presence and absence of an external field. Using a quartz crystal microbalance (QCM), we record the sliding friction of liquid monolayers of nitrogen, a diamagnetic material, as well as liquid oxygen, a paramagnetic material, on nickel alloy and graphene/nickel surfaces. In the prior literature, these systems have been reported to exhibit sensitivity to external fields. The work presented here compares and contrasts fundamental dissipation mechanisms in sliding adsorbed films [3] to studies performed by means of magnetic tip microscopy [1]. [1] I. Altfeder and J. Krim, *J. Appl. Phys.* (2012), [2] Highland et al., *PRL* (2006) [3] J. Krim, *Advances in Physics*, Vol. 61, Iss. 3, 155-323 (2012); Work supported by NSF DMR

3:40pm **TR+AS+NS+SS-MoA6 Chemical Origins of Interfacial Friction: Insights from Atomistic Simulations**, *I. Szlufarska, K. Huang*, University of Wisconsin-Madison, *Y. Liu*, Massachusetts Institute of Technology **INVITED**

While interfacial chemistry plays a critical role in frictional response of materials, understanding chemical changes that occur in sliding mechanical contacts has been challenging. Experimentally, the difficulty lies in the limited ability to characterize contacts *in situ* and typically chemical characterization of interfaces is carried out before or after sliding. Modeling and simulations can provide powerful insights into the chemistry of frictional contacts, however models that possess a high level of chemical fidelity are often limited to small system sizes and short simulation time scales. Here, we overcome this limitation by bringing together complementary simulation methods that range from *ab initio* calculations based on the density functional theory (DFT), large scale molecular dynamics (MD) simulations with reactive empirical potentials, and the kinetic Monte Carlo (kMC) technique. In this talk we will discuss examples of how these methodologies have been used to identify chemical origins of friction. One example is the discovery of mechanisms that underlie aging of silica in aqueous environments, which is of interest for multiple phenomena ranging from wafer bonding to shallow tectonic earthquakes. We have demonstrated that in the absence of deformation creep, aging of silica takes place by formation of interfacial siloxane bridges. We have discovered a new mechanism for interaction between these bridges and have shown that this interaction is critical to explain experimentally observed logarithmic dependence of aging on time. In addition, we will discuss our newly developed theory that enables efficient and accurate calculations of friction at solid/liquid interfaces directly from MD simulations and that overcomes the typical time scale limitations of standard MD simulations. This theory has been validated for multiple types of surfaces and liquids and it can be used for design of chemical interfaces for applications in aqueous environments, such as nano- and micro-fluidics.

4:20pm **TR+AS+NS+SS-MoA8 The Relationship Between Molecular Contact Thermodynamics and Surface Contact Mechanics**, *N. Nikogeorgos, C.A. Hunter, G.J. Leggett*, University of Sheffield, UK

The atomic force microscope (AFM) has been used widely to study nanoscale tribological phenomena, but a unified model for the mechanics of the tip-sample interaction is lacking. Experimental data show that nanoscale friction depends strongly on interfacial chemistry, but these correlations are not explained adequately by existing models. Here we report measurements of interactions between hydrogen bond-forming molecules adsorbed onto solid surfaces and AFM tips. By making measurements in liquid mixtures, we demonstrate a quantitative correlation between the surface shear strength in a nanoscale contact and the free energy of solution-phase hydrogen bonding interactions, uniting classical contact mechanics with equilibrium thermodynamics. We demonstrate that the thermodynamics of intermolecular interactions may be determined quantitatively from nanoscale friction measurements. It has been found that the contact mechanics are best modeled by treating the friction force as the sum of a load-dependent term (attributed to "molecular plowing") and an area-dependent term attributed to shearing (adhesion). The relative contributions of plowing and shearing are determined by the coefficient of friction,  $\mu$ , and the surface shear strength  $\tau$ . The transition from adhesion- to load-determined friction is controlled by the solvation state of the surface: solvated surfaces represent a limiting case in which the shear term approaches zero, and the friction-load relationship is linear, while in other circumstances, the friction-load relationship is non-linear and consistent with Derjaguin-Muller-Toporov (DMT) mechanics. A striking correlation has been observed between the concentration-dependence of the association constant ( $K_a$ ) for the formation of 1:1 hydrogen-bonded complexes and the pull-off force  $F_a$  and surface shear strength  $\tau$  for the same molecules when one partner is immobilized by attachment to an AFM probe and the other is adsorbed to a surface. Analysis of the concentration-dependence of  $F_a$  and  $\tau$  enables the prediction of  $K_a$  with remarkably high precision, indicating that for these hydrogen bonding systems, the tip-sample adhesion is dominated by the H-bond thermodynamics. For hydrocarbon surfaces, we have found that friction-load relationships are also fitted by DMT mechanics, and experimentally determined works of adhesion correlate closely with predictions from Lifshitz theory. For polymer brushes, a broader range of behavior is observed, but this may also be understood if the contact mechanics are modeled by treating the friction force as the sum of a load-dependent term and an area-dependent term attributed to shearing.

4:40pm **TR+AS+NS+SS-MoA9 Friction of a Thermally Activated Ensemble of Nanocontacts**, *P.V. Antonov, J.W.M. Frenken*, Leiden University, Netherlands

We report the first stages of an experiment to lower dry, unlubricated friction by use of a tailor-made nanostructure. In previous studies, we have demonstrated that random thermal fluctuations change the familiar, atomic stick-slip motion of the tip of a friction force microscope (FFM) into a thermal drifting motion, when these fluctuations are strong enough with respect to the barriers in the energy landscape. Based on a two-mass-two-spring model of an FFM [1], we know that these excitations are concentrated in the last nanometers of the tip, because of its extremely small mass and its flexibility. To achieve similar behavior in a macroscopic contact with an area well beyond that of the very specific tip-surface geometry of an FFM, we have shaped one of the two, macroscopic contacting surfaces in the form of a micro-fabricated array of Si nanopillars, each with a well-defined spring coefficient, equal to that of a standard FFM tip. This pattern can be regarded as a large multitude of FFM-like tips, each one exhibiting the thermal fluctuation motion that we identified as a lubricating effect in an FFM. Since the density of these asperities is high, the forces on each individual asperity are always low enough to keep its deformations completely elastic. We expect that each of the tip-like pillars will fluctuate independently under the load of a ball-shaped AFM tip and as a result of this, it should be possible to translate the entire, multi-asperity contact by an extremely low lateral force. This approach should lead not only to low friction, but also to a characteristic, strong dependence of the sliding motion and the friction force on temperature and on sliding velocity. We will also explore how the thermal fluctuation behavior changes as a function of the dynamic properties of the individual nanopillars and how it evolves when we scale up the total number of asperities that are simultaneously in contact.

[1] S.Yu. Krylov, J.W.M. Frenken, *Phys. Rev. B* **80**, 235435 (2009).

5:00pm **TR+AS+NS+SS-MoA10 Nanoprobng of Friction and Charge Transport Properties of Vanadium Dioxide under the Metal-Insulator Transition**, *J.H. Kim*, KAIST, Republic of Korea, *D. Fu, K. Wang, J. Wu*, University of California, Berkeley, *J.Y. Park*, KAIST, Republic of Korea

The nanomechanical and electrical properties of vanadium dioxide ( $\text{VO}_2$ ) thin films across thermal-driven phase transitions were investigated using ultra-high vacuum atomic force microscopy.  $\text{VO}_2$  thin films were deposited on an n-type, heavily-doped silicon wafer by pulsed laser deposition. X-ray diffraction revealed textured polycrystalline structures in the monoclinic phase with preferential orientations in the (100) and (120) planes. Friction and conductance mapping were obtained as a function of temperature across the metal-insulator transition. When below the transition temperature, the friction decreased, whereas the friction increased markedly when above the transition temperature. This peculiar result can be attributed to the combined effects of thermally-activated tip sliding, associated with phonon at the insulating phase, and electronic contributions in the metallic phase.

5:20pm **TR+AS+NS+SS-MoA11 Non-Uniform Friction-Area Dependency for Antimony Oxide Surfaces Sliding on Graphite**, *M.Z. Baykara*, Bilkent University, Turkey, *C. Ritter*, Humboldt Universität zu Berlin, Germany, *B. Stegemann*, HTW Berlin – University of Applied Sciences, Germany, *M. Heyde*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *K. Rademann*, Humboldt Universität zu Berlin, Germany, *J. Schroers, U.D. Schwarz*, Yale University

We present frictional measurements involving controlled lateral manipulation of antimony nanoparticles on graphite featuring atomically smooth particle-substrate interfaces via tapping- and contact-mode atomic force microscopy. As expected from earlier studies, the power required for lateral manipulation as well as the frictional forces recorded during the manipulation events exhibit a linear dependence on contact area over a wide size range from 2000 nm<sup>2</sup> to 120,000 nm<sup>2</sup>. However, we observe a significant and abrupt increase in frictional force and dissipated power per contact area at a value of about 20,000 nm<sup>2</sup>, coinciding with a phase transition from amorphous to crystalline within the antimony particles. Our results suggest that variations in the structural arrangement and stoichiometry of antimony oxide at the interface between the particles and the substrate may be responsible for the observed effect.

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