

Studies of the Nanotribology of Interfacial Water

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Motivation—The behavior of water near surfaces is critical to a wide range of important processes, such as protein folding, the stability of colloid suspensions, enzyme activity, swelling in clays and “stiction” in microelectromechanical systems (MEMS). The nanometer-scale ordering of water near hydrophilic (water-loving) surfaces has been studied extensively using a variety of techniques. The results indicate that a change in intermolecular bonding often occurs, resulting in an increase in molecular ordering. Although thin water films on these surfaces normally don’t form solid ice at room temperature, our studies suggest that they do possess properties distinctly different from those of the bulk liquid. An example, involving the viscosity of interfacial water, is presented here.*

Accomplishment—We have used the unique, Sandia-developed Interfacial Force Microscope (IFM), a quantitative and mechanically-stable scanning force-probe technique, to study the viscous properties of adventitious water confined between a tip and substrate, both hydrophilic. The relative humidity (RH) was varied, and measurements of both normal and lateral forces imposed on the tip were recorded as it slowly approached the substrate. The lateral force, or friction force, was measured by modulating the tip position laterally and obtaining the force signal by synchronous detection. We observed a friction force prior to tip/substrate contact, indicating that the interfacial water had a significant level of viscosity, which opposes tip motion. Figure 1 shows the results for a lateral modulation of ~ 25 Å at a frequency of 100 Hz under a RH of 20%. The red curve shows the normal or adhesive force. The sudden negative jump in force at a relative separation of ~ 42 Å indicates contact between the water coatings on tip and substrate,

giving rise to an attractive meniscus force. This force increases until the two surfaces make contact, then rapidly turns repulsive (positive). A small viscous-friction force is observed due to the meniscus. At ~ 23 Å, however, the friction force begins a rapid rise, indicating contact between the interfacial water layers. A model fit to this rise, based on a formula derived by P. J. Feibelman (1114), yields a value for the viscosity of the interfacial water a million times greater than that reported for bulk water and implies a significant level of water ordering near the two surfaces. Approximately this same value has been found for four samples differing in substrate material and surface functionalization. In contrast, if the two surfaces are functionalized with hydrophobic (water-hating) monolayers, as shown in Fig. 2, there is no indication of a viscous interfacial layer and the after-contact friction is very low (these monolayers are excellent lubricants). However, the reasons for the friction decrease after the peak at ~ 19 Å has not yet been fully explained.

Significance—These measurements are the first to show clearly the remarkable tribology of interfacial water. They motivate an expansion of efforts to determine the root cause of the behavior and its implications in many areas where it may have dramatic consequences, e.g., in controlling the flow characteristics of water desalination membranes. Recent IFM developments have resulted in greater sensitivity and simplified operation. One envisioned application of the new capability is the quantitative measurement of friction and drive-train forces at various locations in complex MEMS devices, opening a smooth path to device qualification and facilitating the diagnosis of root causes in a failure-analysis setting. *[Phys. Rev. Lett. **96**, 177803 (2006)].

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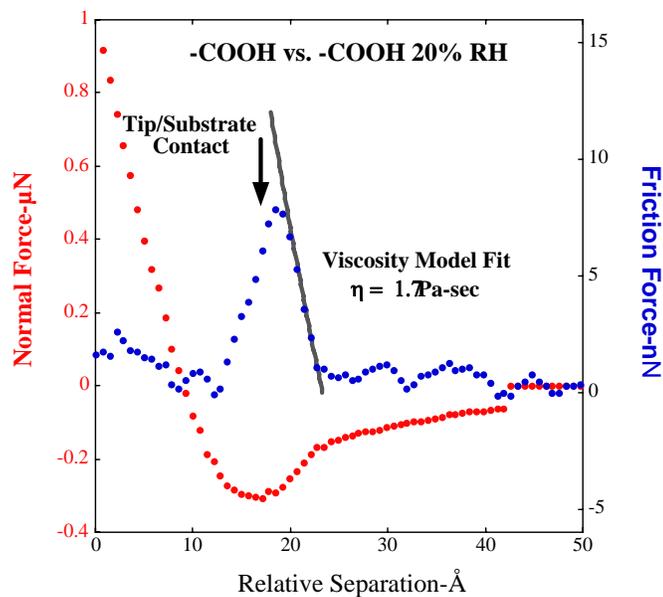


Figure 1. Normal (red) and viscous-friction forces (blue) plotted against relative interfacial separation for an Au tip and substrate functionalized by hydrophilic monolayers having carboxylic acid end groups under a 20% relative humidity. The solid line is a model fit according to the Feibelman formula. The model fit results in an interfacial water viscosity of 1.7 Pa-sec. This value is approximately one million times larger than that reported for bulk water. The significant level of the adhesive interaction is indicative of the hydrogen bonding capabilities of the acid end groups.

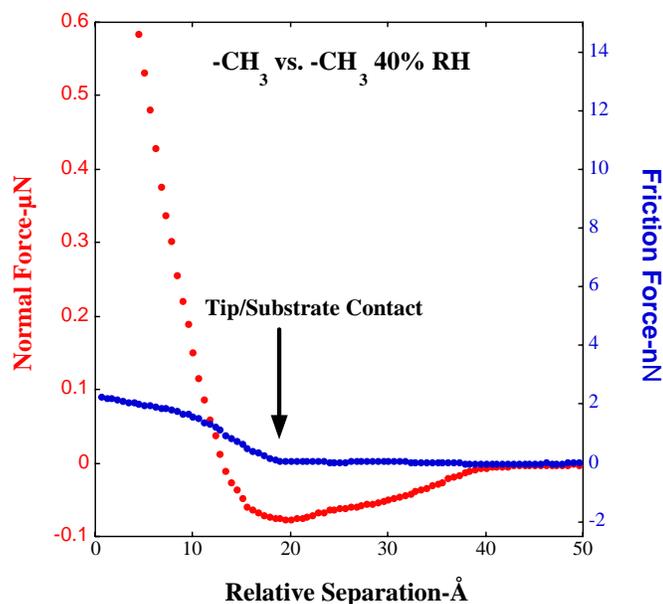


Figure 2. If the monolayers are terminated by hydrophobic (water hating) methyl groups, the friction is very low (even if the data is taken at 40% RH) and is appreciable only after the two surfaces have come into mechanical contact. Notice also, that the adhesive interaction, judged by the maximum negative normal force, is considerably less for the $-\text{COOH}/-\text{COOH}$ interaction of Fig. 1 due to the lack of chemical bonding in the $-\text{CH}_3/-\text{CH}_3$ case.