Atomic-Scale Origins of Friction[†]

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The fundamental origins of friction, an important physical phenomenon in light of both its everyday familiarity and its enormous economic impact, have been discussed and debated for at least 300 years, with very little resolved. Recent experimental investigations at atomic length and/or time scales are shedding new light on the manner in which mechanical energy is converted to thermal energy, i.e., heat.

I. Introduction

Proper attention to tribology could by most recent estimates lead to economic savings of 1.3% to 1.6% of the GNP,[1] more than $100,000,000,000 annually in the United States alone. Given such economic impact and everyday familiarity, one would think that physicists would have long ago established the atomic origins of friction. The topic has in fact been debated for over 300 years, but until recently there has been little progress.[2] One reason for the slow progress is that friction occurs at a buried interface which is difficult to probe experimentally during the sliding process. A second reason is that an ideal investigation of the atomic origins of friction involves characterization of the sliding interface both at atomic length scales ($\approx 10^{-9}$ nm) *and* atomic time scales ($\approx 10^{-12}-10^{-9}$ s).

Since fundamental experimental investigations of friction are ideally carried out at atomic time and/or length scales, their link to macroscopically observed phenomena must still be explored. When macroscopic solid surfaces touch each other, the contact between them occurs predominantly at the summits of the surface roughness. Because each of these contacts areas is small, perhaps only a few atoms in extent, the mechanics of such small contact zones must be considered in order to understand the system's overall behavior.[3] Characterization of the nature of contacting asperities is thus an area of high research activity within the tribological community. Employing established technologies, such as ultrahigh vacuum, for the preparation of crystalline samples, nanotribologists have meanwhile gathered information in situations where the nature of the contacting surfaces is already known. And they have collectively measured friction forces per unit true contact area which span 12 orders of magnitude, all in cases where no wear occurred at the sliding interface![4]

II. The Microscopic Origins of Macroscopic Friction

Friction is believed to arise from the adhesive forces between two surfaces in contact and the ploughing of harder asperities on the softer surface.[5] It is thus clear that the study of friction inevitably involves two inextricably entangled subissues: the roughness of the two surfaces in contact, and the fundamental interfacial mechanisms for conversion of mechanical energy to thermal energy. In the absence of wear and plastic deformation, friction is largely attributable to interfacial effects.[6] How does such "interfacial" friction originate at the atomic scale, and how might it manifest itself at the macroscopic level?

Interfacial friction has frequently been modeled at the atomic level by calculating the energy needed to overcome the intermolecular forces between two surfaces as one surface is slightly raised and then slid across the other.[7] Friction is defined within this context as the fraction of the energy which is "lost" (i.e., converted to heat) each time the surfaces move across some characteristic distance of atomic dimension. Israelachvili, for example, has employed this model (assuming a 10% energy "loss" per 0.1 nm) to obtain a value of 5×10^7 N/m² for the force per unit true contact area required to maintain sliding in single crystal mica surfaces separated by molecularly thin layers of cyclohexane and found good agreement with experiment.[8] Zhong and Tomanek[9] have estimated the frictional force for Pd/graphite based on *ab initio* total energy calculations and found agreement with atomic force microscopy (AFM) results by assuming that 100% of the energy used in "lifting" the Pd to potential heights was "lost" upon return to the lower potential energy sites. Such theories do not attempt to describe the mechanisms by which energy is dissipated and thus cannot reveal the atomic origins of such friction. They do however set an upper limit to the maximum shear stress which should be observed experimentally, typically 10^9-10^{10} N/m².

The essential question is of course how to calculate the fraction of the energy which is *not* converted to heat. In order to address this, a dissipative mechanism must be assumed. Two mechanisms have been investigated, one involving electronic excitations[10] and the other involving the excitation of atomic lattice vibrations (phonons). The contributions to the friction force attributable to these interfacial mechanisms can be written as separate components to good approximation, $F_f = F_{ph} + F_{eh}$. The two mechanisms have received a good deal of attention through the theoretical and computational works of Persson, Robbins, and Sokoloff.[11]

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At the atomic scale, the friction force exhibits a dependence on both sliding speed v_c and area, with the "force law" expressed as

$$F_f = F_{ph} + F_{eh} = \eta v_c A_c; \; \eta = \frac{\rho_2}{\tau} \qquad (1)$$

η is the shear stress per unit velocity, ρ_2 is the mass per unit area of the sliding object, and τ is a characteristic "slip time", which corresponds to the time for the moving object's speed to fall to $1/e$ of its original value, assuming it is stopped by frictional forces alone. At the macroscopic scale, Amontons' force law $F_f = \mu F_N$ is routinely used to describe friction, where μ is the ratio of the friction force F_f to the load or force normal to the interface F_N. The law has an entirely different form from the microscopic eq 1 in that μ is independent of the apparent contact area A, the loading force, and the sliding speed v.

The difference in form between the microscopic and macroscopic friction laws is routinely rationalized by noting that the true area of contact $A_c \ll A$ between macroscopic objects is likely to be proportional to the loading force F_N,[12] while the instantaneous sliding speed of the microscopic contact points (while sliding) is unlikely to be equal to the sliding speed of the macroscopic object, i.e., $v_c \gg v$. Details of the nature of contacting asperities between macroscopic objects are thus necessary in order to bridge the gap between experiments carried out in situations where the precise nature of the contact is known ("nanotribology") and those where it is not.

III. Selected Experimental Results

As mentioned above, nanotribologists have have collectively measured friction forces per unit true contact area which span 12 orders of magnitude (10^{-2}—10^{10} N/m^2), in all cases without wear occurring at the sliding interface.[4] Here are three illustrative examples:

Diamond Tip/Diamond(111) and -(100). Germann *et al.*[13] employed an AFM in ultrahigh vacuum (UHV) conditions to study a clean diamond tip sliding at 2 nm/s on diamond(111) and -(100) substrates. The radius of the contact at zero applied load was estimated to be 2 nm. The friction force did not increase with load; thus the coefficient of friction as defined by Amontons' law was zero, indicating no increase in the contact area with applied load. The shear stress was nonetheless over 10^9 N/m^2, close to the theoretical upper limit of 100% conversion of potential energy gain to thermal energy, as discussed above.

Krypton/Au(111) Liquid and Solid Monolayers. This author and collaborators employed a quartz crystal microbalance (QCM) to study[14] monolayers of krypton adsorbed on Au(111) surfaces prepared in UHV, and observed shear stresses on the order of 0.5 N/m^2 for sliding speeds estimated to be on the order of 1 cm/s. The measurements were carried out at 77 K, where Kr first condenses as a liquid and then solidifies. We observed a peculiar result, in that the Kr films were "slipperier when dry": Friction forces for liquid films were about 5 times higher than those for solid films.

Xe/Ag(111) Solid Monolayers and Bilayers. Daly and this author employed a quartz microbalance to measure the force to slide one- and two-atom thick solid films of xenon along a crystalline silver surface[15] and observed shear stresses on the order of 10 N/m^2 for 1 cm/s sliding speeds. We observed a 27% increase in the friction for the two-atom thick film, whose lattice spacing and true area of contact were equal to that of the monolayer.

IV. Discussion

It is rather striking that friction forces per unit true contact area which span 12 orders of magnitude (10^{-2}–10^{10} N/m^2) have been reported in the literature, nine orders of magnitude being displayed by the three measurements listed in the previous section alone. For comparison, steel surfaces lubricated with MoS$_2$ films encounter friction forces per unit true contact area which are on the order of 10^7 N/m^2.[16] One thus might wonder what fraction of the "macroscopic" friction measured in the latter case is due to purely interfacial effects. This question clearly cannot be addressed until the exact nature of the contacting surfaces is known, *and* a thorough theory of interfacial friction is achieved. Since the experiments described in section III were all carried out in well-controlled circumstances, they allow for the possibility that such a theory might one day be obtained. Indeed, while current models of atomic-scale friction can more than account for a 9-order span, the details are far from certain.

Electronic friction arises from interfacial electronic interactions and is not expected to be substantially larger for a two-atom thick bilayer of xenon than a one-atom thick monolayer.[17] (One may eventually be able to deduce the thickness variation of electronic friction from surface resistivity measurements,[18] but at present no theory is accurate enough to yield a precise value.) Computational results meanwhile indicate that phonon-induced friction is significantly greater for a bilayer than a monolayer, perhaps by as much as 100%.[19] The Xe/Ag(111) measurement therefore allows the relative contributions of each mechanism to be gauged as a function of film thickness. As theoretical and simulational efforts become increasingly sophisticated in this area, the estimate will become far more precise. What is already clear, however, is that frictional energy dissipation in this system is concentrated to within a few atomic distances of the interface, a result which may be quite general.

Computer simulations of the slippage of Kr films on defect-free Au(111) have been carried out by Cieplak *et al.*[20] Their simulation was based on the assumption that the energy is dissipated by phonons in the film, and it provided a very acceptable description of the experimental data reported for Kr/Au(111).[14] The agreement is surprising for a number of reasons. The first is that a defect concentration of even one part in 10^7 should have raised the experimental friction levels beyond that modeled in a defect-free environment.[21] The agreement is also surprising in that electronic contributions to friction have been completely neglected. This issue is most likely resolved by the fact that a small increase in the substrate potential corrugation utilized in the phonon model could easily mask the electronic contributions. This is true even in the region of the solid−liquid phase transition, since electronic contributions to friction might easily be greater

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for liquid Kr films than for solid films (as are the phonon contributions).[22]

The AFM study of diamond/diamond(111) and the QCM study of Kr/Au(111) provide cases of solid−solid sliding in well-controlled experimental situations which are characterized by shear stresses differing by 9 orders of magnitude. Let us now examine the factors which may play a role in this enormous difference:

Discrepancies in the values due to differing adhesive strengths can be ruled out. The diamond/diamond(111) adhesive interaction can be estimated from the value of the negative load (8 nN), when the tip first makes contact. This corresponds to a 1.5×10^9 Pa normal adhesive force per unit area, which is virtually equal to that of Kr/Au(111), 1.6×10^9 Pa. (The latter value was obtained by assuming van der Waals interactions at the Kr/Au(111) surface and assuming the Kr to be positioned at a location where attractive "adhesive" forces are balanced by hard-core repulsive forces.) This is consistent with recent SFA studies demonstrating that frictional forces are not related to the adhesive strength itself, but to the adhesive reversibility.[23]

Another potential explanation for the large difference in shear stress when comparing diamond to Kr is that the very low corrugation of the Au(111) surface allows the Kr to thermally migrate over the surface, while the same would not be true of diamond. This does not appear to be consistent with experimental observation, however, since friction levels are not markedly higher for Kr film coverages (such as the complete monolayer which covers mm² in area) where thermal migration is greatly inhibited.

Sokoloff's extensive work on sliding of commensurate and incommensurate interfaces predicts a range of 10^{-5}−10^8 N/m² for the shear stress associated with interfaces in commensurate and incommensurate contact.[24] This demonstrates the wide range of values which can be attained based exclusively on the relative commensurability of the lattices. While the Kr/Au system is a clear case of incommensurate contact, the atomic-scale asperity of the diamond AFM tip is far more comparable to a commensurate system. Other factors however could also account for the difference in shear stress. For example,

the corrugation of the Au surface potential is much smoother than the insulating diamond surface due to its electronic nature. This easily accounts for a factor of 10^3 in the difference in shear stresses.[20] Both phonon and electron theories of friction predict the shear stress to be directly proportional to sliding velocity. The sliding velocity of the AFM tip (i.e., the slip portion of the slip−stick motions which are observed) is not known, since it is faster than present AFM electronics can resolve. It might easily be on the order of 10 m/s,[25] compared to the 1 cm/s estimated for Kr/Au. This would account for another factor of $\approx 10^3$. A remaining issue involves electronic interactions: A Kr film is clearly physisorbed on Au. It is reasonable to assume that the diamond−diamond interaction is closer to a physisorbed system than to a chemisorbed system since the adhesive strength is comparable to that of Kr/Au and also since the atoms at the end of the tip do not become detached. Nonetheless, the chemical nature of the diamond tip−diamond surface interaction is poorly characterized. Shear stresses for chemisorbed systems are typically 3 orders of magnitude higher than those for physisorbed systems.[26]

This brief calculation demonstrates several areas where experimental and/or theoretical investigations would be of great use. While 9 orders of magnitude in shear stress can be accounted for in a very gross manner, details are enormously lacking. Experimental and theoretical studies of the phononic and electronic contributions to friction would be of great assistance, as well as more precise experimental information on the sliding speed of the interface when it is actually moving. Very long slip times of the physisorbed films at very low coverages[27] meanwhile remain completely unexplained by any model. Further theoretical work on "friction-free" (more precisely phonon-friction-free) sliding would also be of great interest.[28,29]

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