The Atomic-scale Origins of Friction

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Abstract

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 random thermal motion, i.e. heat.

I. Introduction.

Financial losses in the U.S. resulting from ignorance of tribology amount to 6% of the GNP by one recent estimate [1], a whopping $420,000,000,000. Given such economic impact and everyday familiarity, one would think that physicists would have long ago established the origins of friction. The topic has in fact been debated for over 300 years [2], and little has been resolved. The situation as of 1992 was well summed up by J.A. Greenwood [3]:

"If some clever person would explain why friction exists, and is proportional to the (true) area of contact, our problem would be solved."

With the advent of new techniques capable of studying the force of friction
which results when a finite number of atoms is made to slide on a crystalline substrate, a new field involving investigations at atomic length and/or time scales, nanotribology, has evolved [4]. Employing established technologies, such as ultra-high vacuum, for the preparation of crystalline samples, nanotribologists are now able to gather information in situations where the nature of the contacting surfaces is known. And they have collectively unearthed the fact that even if tribologists are able to perfectly characterize a sliding interface (location and morphology of true contact, temperature, sliding speed, etc.), our ability to predict the friction which will occur at that interface is virtually nonexistent.

II. The Microscopic Origins of Macroscopic Friction

Friction is believed to arise from the adhesive forces between between two surfaces in contact, and the ploughing of softer asperities on the harder 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 at a buried interface, and the fundamental mechanisms for conversion of mechanical energy to random thermal motion. In many practical situations, for example machinery operation where the same two surfaces pass repeatedly over each other, a “wearless” situation is however achieved where the ploughing contributions are thought to become negligible. The friction in this case is largely attributable to interfacial effects [6]. How does such friction originate at the atomic scale, and how does it manifest itself at the macroscopic level?

Wearless friction has frequently been modelled by calculating the energy needed to overcome the intermolecular forces between two surfaces as one surface
is slightly raised and the 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 to obtain a value for the shear stress $s$ (the force per unit true contact area to maintain sliding) of $5 \times 10^7 \text{N/m}^2$, assuming a 10% energy “loss” per 0.1nm, in good agreement with experimental values obtained by the SFA for mica in air or separated by one molecular layer of cyclohexane. [8] Zhong and Tomanek [9] have estimated the frictional force for Pd/graphite based on \textit{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 physical origin of friction. They do however set an upper limit to the maximum shear stress which should be observed experimentally, typically $10^8\text{-}10^{10} \text{N/m}^2$.

The essential question is of course how to calculate the fraction of the energy which is \textit{not} converted to heat. In order to address this, a dissipative mechanism must be assumed. Two mechanisms have been investigated, one involving electronic excitations and the other involving phononic excitations. These mechanisms have received a good deal of recent attention through the theoretical and computational works of Persson, Robbins, and Sokoloff. [10]

At the atomic scale, the friction force exhibits a dependence on both sliding speed $v_c$ and area, with the “force law” expressed as
\[ F_f = \eta v_c A_c; \quad \eta = \frac{\rho_2}{\tau}. \]

\( \eta \) is the shear stress per unit velocity, \( \rho_2 \) is the mass per unit area of the sliding object and \( \tau \) 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. This is in direct contrast to Amontons' force law for macroscopic friction, \( F_f = \mu F_N \), which defines the friction coefficient \( \mu \) as the ratio of the friction force \( F_f \) to the load or force normal to the interface \( F_N \). The law is counterintuitive in the \( \mu \) is independent of the apparent contact area \( A \), the loading force, and the sliding speed \( v \).

The discrepancy 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 \( F_N \), \([11]\) 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. \( v_c \gg v \). The sliding is believed to be nonuniform at the atomic scale, exciting in the process atomic lattice vibrations (phonons), whose lifetimes may range from picoseconds to nanoseconds. Electronic contributions to the energy dissipation, attributed to the excitation of electronic motion, have also been suggested as significant contributors to frictional energy losses, if conducting interfaces are involved. \([12]\) The friction force is therefore written in terms of a separate phonon and electronic contribution, \( F_f = F_{ph} + F_{eh} \).
III. Selected Experimental Results

Nanotribologists are regularly surprised to discover that atomic-scale friction can be very different from what is observed at the macroscopic level. Here are three 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 2nm. 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 $10^8$ N/m$^2$, close to the theoretical upper limit of 100% conversion of potential energy gain to random thermal motion, 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 77K, 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 five times higher than for solid films.

Xe/Ag(111) solid monolayers and bilayers

C. 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/m² for 1 cm/s sliding speeds. Defying conventional wisdom that friction is proportional to true contact area, we observed a 27% increase in the friction for the two-atom thick film, whose lattice spacing and true area of contact was equal to that of the monolayer.

IV. Discussion

It is rather striking that the shear stresses mentioned above span more than nine orders of magnitude. Since the experiments were all carried out in well-controlled circumstances, they collectively provide crucial information on the fundamental origins of friction. Indeed, while current models of atomic-scale friction can more than account for a nine order span, the details are far from certain.

Electronic friction arises from interfacial electronic interactions, and is expected to be at most 5% greater for a two-atom thick bilayer of xenon than a one-atom thick monolayer. [16] In contrast, preliminary computational results indicate that phonon induced friction is significantly greater for a bilayer than a monolayer, perhaps by as much as 100%. [17] The Xe/Ag(111) measurement therefore allows the relative contributions of each mechanism to be gauged. Assuming the friction force associated with phonons (electrons) to be 100% (5%) greater for a bilayer than a monolayer, it can be shown that the experimentally observed 27% increase implies that electronic effects account for 77% of the dissipation. Assuming the phonon contribution to increase by a far more modest
33%, then electronic effects would account for 22% of the dissipation. As theoretical and simulative efforts become increasingly sophisticated in this area, the estimate will become far more precise. What is clear now however, is that frictional energy dissipation is concentrated to within a few atomic distances of the interface which is in motion.

Computer simulations of the slippage of Kr films on defect-free Au(111) have recently been carried out by Cieplak et al..[18] 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 modelled in a defect-free environment. [19] This difficulty is apparently overcome by the fact that the Kr films slide for such small distances that few defects are encountered. 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 for liquid Kr films than solid films (as are the phonon contributions). [20]

The AFM study of diamond/diamond(111) and the QCM study of Kr/Au(111) therefore provide two cases of solid-solid sliding in defect-free circumstances (In the former case, the tip is too small for defects to be present, and in the latter case the sliding distance is apparently too small for defects to
be important.), which are characterized by shear stresses differing by nine 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 (8nN), when the tip first makes contact. This corresponds to a $1.5 \times 10^9$ Pa normal adhesive force per unit area, which is virtually equal to that of Kρ/Au(111), $1.6 \times 10^9$ Pa. [21] This is consistent with recent SFA studies demonstrating that frictional forces are not related to the adhesive strength itself, to the adhesive reversibility. [22]

Sokoloff's extensive work on sliding of commensurate and incommensurate interfaces predicts a range of $10^{-5} - 10^6$ N/m² for the shear stress associated with interfaces in commensurate and incommensurate contact.[23] This demonstrates the wide range of values which can be attained based exclusively on the relative commensurability of the lattices. While the Kρ/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.[18] 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 $10 \text{m/s}$,[24] compared to the $1 \text{ cm/s}$ 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 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 for physisorbed systems.[25]

This brief calculation demonstrates several areas where experimental and/or theoretical investigations would be of great use. While nine 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 [26] 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.[27] [28]

As the price of energy rises, and the need to conserve both energy and raw materials becomes increasingly urgent, physicists’ rush to understand basic tribological processes can only be expected to accelerate.

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