Electronic Contributions to Sliding Friction

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ABSTRACT We have measured the force required to slide argon monolayers on Ag(111) and Xe(111) surfaces, as well as the force required to slide xenon monolayers and bilayers along Ag(111) surfaces. Our experimental results allow estimation of the proportion of energy losses associated with the motion of electrons to that associated with excitation of atomic lattice vibrations.

1. Introduction

Friction is considered a "simple" force in much of the popular literature, [1] a notion reinforced by the fact that in a typical scientific or engineering education, the topic is treated within the first few weeks of an introductory physics course and then rarely revisited. In reality, frictional forces are far from simple. Although discussions of the fundamental mechanisms for frictional energy losses have been ongoing for at least 300 years, there has been very little resolved.[2] With the advent of new experimental 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 or time scales (nanotribology[3] ) has evolved, [4] allowing frictional dissipative mechanisms to be probed for the first time.[5]

The friction between two macroscopic solid objects in relative motion is generally discussed within the context of "Amontons' law",

$$F_f = \mu N$$  \hspace{1cm} (1)
which defines the friction coefficient $\mu$ as the ratio of the frictional force $F_f$ to the load or force normal to the interface $N$. The law is counterintuitive in that $\mu$ is independent of the apparent contact area $A$, the loading force, and the sliding speed $v$. At the atomic scale, the friction force does in fact exhibit a dependence on both sliding speed $v_c$ and area, with the “force law” expressed as

$$F_f = \eta v_c A_c; \quad \eta = \frac{\rho_2}{\tau}. \quad (2)$$

$\eta$ 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”, corresponding 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.

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 $N$, [6] while the instantaneous sliding speed of microscopic contact points (while sliding) is unlikely to be equal to the sliding speed of a macroscopic object, i.e. $v_c \gg v$. The sliding is believed to be nonuniform at atomic scales, exciting in the process atomic lattice vibrations (phonons), whose lifetimes may range from picoseconds to nanoseconds. Electronic contributions to the energy dissipation (attributed to conduction electron scattering from surface impurities) have also been suggested as significant contributors to frictional energy losses, if conducting interfaces are involved.[7] The slip time $\tau$ is therefore written in terms of separate phonon $\tau_{ph}$ and electron-hole $\tau_{eh}$ contributions according to

$$\frac{1}{\tau} = \left( \frac{1}{\tau_{ph}} + \frac{1}{\tau_{eh}} \right). \quad (3)$$

Definitive proof of electronic contributions to friction is of great interest, since to date the vast majority of fundamental theoretical treatments of friction have considered phonon contributions only.[2] A variety of practical applications become possible, moreover, in cases where electronic contributions dominate. For example, in the
case of adsorbed films or particles on metal substrates, the atoms could be dragged along the surface via electronic friction forces arising from an electrical current.

We describe here two experimental measurements which allow estimates of the relative contributions of electronic and phononic dissipation mechanisms to be made for the systems involved. The first involves comparative studies of monolayer slip times for Ar/Ag(111) and Ar/Xe/Ag(111), and the second involves comparative studies of bilayer and monolayer slip times for incommensurate solid films of Xe/Ag(111).

2. Experimental Details

The Quartz Crystal Microbalance (QCM) has been used for decades for microweighing purposes, [8] and was adapted for friction measurements in 1986-88 by Krim and Widom.[9] A QCM consists of a single crystal of quartz which oscillates in transverse shear motion with a quality factor $Q$ near $10^5$. Adsorption onto the microbalance produces shifts in both the frequency $f_0$ and the quality factor $Q$, which are indicative of the degree to which the adsorbate is able to track the oscillatory motion of the underlying substrate. Characteristic slip times $\tau$, and friction coefficients (i.e. shear stresses per unit velocity) $\eta$, are determined via the relations:[9]

$$\delta(Q^{-1}) = 4\pi\tau \delta f_0 \quad \eta = \frac{\rho_2}{\tau}$$

(4)

where $\rho_2$ is the mass per unit area of the adsorbate. We note that a sliding speed is required to report shear stresses for QCM measurements since the apparatus operates at a time scale sufficiently short so as to be able to resolve the velocity dependence of the friction force. [10]

Data were recorded for adsorption onto the surface of silver film electrodes which were electron-beam evaporated in situ and in ultrahigh vacuum conditions onto overtone polished quartz crystals ($f_0 = 8$ MHz). The evaporation was carried out with 99.999% pure Ag at a deposition rate of 0.05-0.1 nm/s. Samples were then transferred
within the vacuum system to a gas adsorption chamber where adsorption measurements were performed at 77.4K.

3. Argon Monolayers on Ag(111) and Xe/Ag(111)

Monolayers and bilayers of xenon adsorbed on Ag(111) surfaces have been studied for well over a decade, resulting in a high degree of experimental precision and theoretical accuracy concerning the overall system parameters and the associated interaction potentials. [11] [12] [13] At 77.4 K, xenon condenses onto Ag(111) as an “uncompressed” solid monolayer with an atom-atom spacing of 0.452 nm, or 5.624 atoms/nm². The monolayer accommodates further atoms by compressing, until it reaches a spacing of 0.439 nm (5.97 atoms/nm²), that of the bulk solid. Further accommodation of atoms into the first layer then becomes increasingly difficult. Subsequent atoms which are unable to force their way into the first layer form a two-dimensional second layer gas phase [14] which ultimately solidifies into a layer whose spacing is equal to that of the “compressed” monolayer, 0.439 nm, thus forming the bilayer.

Figure 1 depicts frequency shift versus pressure data for Xe adsorption at 77.4 K. The verticality of the steps in the isotherm are indicative of large (∼100 nm) regions of substrate crystalline uniformity. Each step in the isotherm corresponds to the condensation of a monomolecular solid layer of Xe. Slip times recorded for argon monolayers condensed on top of the Xe monolayer and bilayer, as well as directly onto the Ag(111) are also listed in the Figure.

Under the assumption of a rigid substrate, the dependence of $\tau_{ph}$ on the substrate potential corrugation $c$ (the difference between the maximum and minimum of the potential energy along the surface in the direction of motion) follows the relation [15]

$$
\tau_{ph} \propto c^{-2}.
$$

(5)

Within this simple scenario, the slip time $\tau_{ph}$ for Ar/Ag(111) should be approximately $12^2$ times longer than that for Ar/Xe/Ag(111), since $c$ is estimated to increase by a factor of 12 when a Xe monolayer is present. [16] Slip times $\tau$ typical of Ar monolayers condensed at
77.4 K onto bare Ag (τ = 1.5 ns) are however observed to be shorter than those for Ar monolayers condensed onto Xe monolayers (τ= 4 ns) and Xe bilayers (τ ≈4 ns). This result implies that at least one of the assumptions underlying Eq.(5) is incorrect for the system under study: Electronic effects may in fact be the dominant dissipative mechanism rather than the phonon dissipative assumed by the model, or else the Xe/Ag(111) substrate is not sufficiently rigid to be modelled as such. We note that the slip times listed in Figure 1 were determined via Eq.(4) under the most trivial assumption that changes in quality factor upon Ar uptake are entirely attributable to slippage at the Ar-Xe interface. Treatments involving slippage at the Xe/Ag interface (characterized by τ = 2 – 3 ns) reduce the magnitude of the enhancement of the slippage.

![Graph](image)

**Figure 1.** Microbalance frequency shift versus residual gas pressure for xenon adsorbed on Ag(111) at 77.4 K
4. Xe Monolayers and Bilayers on Ag(111)

Electronic friction arises from interfacial electronic interactions, and is expected to be at most 5% greater for a two-atom thick bilayer than a one-atom thick monolayer. [17] 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%. [18] Measurement of the relative slip times of the xenon monolayer and bilayer themselves therefore should also allow the relative contributions of each mechanism to be gauged.

Figure 2 presents slip time $\tau$ versus coverage for the Xe adsorption data displayed in Figure 1, where one monolayer has been defined as 5.970 atoms/nm$^2$, the spacing of the compressed monolayer. [19] The trace exhibits a high degree of sensitivity to the phase of the adsorbed film, and in particular on whether significant levels of two-dimensional gas are present. Friction forces for solid monolayers and bilayers only are therefore compared only in regions where the two-dimensional gas was at a minimum, and the monolayer lattice spacing is equal to that of the bilayer.

![Figure 2. Slip time $\tau$ versus coverage (1 monolayer = 5.970 atoms/nm$^2$). The dotted box encloses the monolayer to bilayer regime which is re-displayed in Figure 3.](image-url)
The dotted box in Figure 2 encloses the monolayer to bilayer regime. These data are redisplayed in Figure 3 along with data recorded on two other silver film substrates. The lower portion of the Figure depicts the shear stress $s$, or the force per unit area which would be required to slide the films at a constant speed of 1 cm/s (the approximate speed at which the films are slipping). The friction force per unit area associated with the two-layer thick film, $15.1 \pm 0.5$ N/m$^2$, is 27% greater than that associated with sliding of the one-atom thick film, $11.9 \pm 0.4$ N/m$^2$. This level is well above the 5% maximum increase expected for energy dissipation by electronic processes alone, so phonon dissipative mechanisms must clearly be present.

Assuming the friction force associated with phonons to be 100% greater for a bilayer than a monolayer, the experimental result would imply that electronic effects account for 77% of the dissipation for the monolayer. Assuming phonon friction to increase by a far more modest 33%, then electronic effects would account for 22% of the dissipation. As theoretical and simulational efforts become increasingly sophisticated in this area, the estimate will become far more precise.

![Figure 3](image.png)

**Figure 3.** Slip time $\tau$ and shear stress $s$ (the friction force per unit area) versus coverage for three different Ag(111) surfaces (from [19]).
5. Discussion

Our studies have demonstrated that simple scenarios involving either exclusively phononic or exclusively electronic dissipation mechanisms cannot account for experimental observation. Assuming that both phonon and electronic mechanisms are significant, the question remains as to whether both effects are prevalent in systems which exhibit much higher friction levels (Table 1, from[20]). For example, AFM measurements of solid-solid systems such as diamond/diamond(111)[21] are typically characterized by shear stresses on the order of $10^6$-$10^9$ N/m$^2$, compared to $\approx 10$ N/m$^2$ for the systems described here (despite the fact that the two systems exhibit similar adhesive strengths[20]). Have the phonon friction levels been so reduced for the physisorbed systems that electronic contributions have been revealed, or are the electronic contributions equally prevalent in higher-friction scenarios? In the latter case, such effects might be cited as possible explanations for the chemical sensitivity of AFM friction measurements.[22]

As other factors influencing the friction, particularly the interfacial commensurability of the two materials in contact and the actual sliding speed of the contacts, are progressively understood, the role of electronic friction in high friction systems (including macroscopic systems) will become increasingly known.

Acknowledgements

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TABLE 1. Shear stresses measured at solid-solid interfaces by various techniques, for selected experimental works (From [22]. $F_f$ is the force of friction, $A_c$ the area of interfacial contact, and $s = F_f/A_c$ the shear stress. AFM values are quoted for "jump to contact" (negative load) conditions.

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>$F_f(N)$</th>
<th>$A_c(m^2)$</th>
<th>$s(N/m^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mica/mica # [26]</td>
<td>0.07</td>
<td>$4 \times 10^{-9}$</td>
<td>$2.5 \times 10^7$</td>
</tr>
<tr>
<td>mica/mica # [27]</td>
<td>$10^{-4}$</td>
<td>$10^{-9}$</td>
<td>$10^5$</td>
</tr>
<tr>
<td>mica/lubricated mica # [28]</td>
<td>$\approx 10^{-9}$</td>
<td>$10^4 - 10^7$</td>
<td></td>
</tr>
<tr>
<td>mica/lubricated mica # [29]</td>
<td>$\approx 10^{-9}$</td>
<td>$2 \times 10^6$</td>
<td></td>
</tr>
<tr>
<td>W/a-C:H/Si(100) - [23]</td>
<td>$10^{-7}$</td>
<td>$6 \times 10^{-17}$</td>
<td>$1.6 \times 10^9$</td>
</tr>
<tr>
<td>diamond/diamond(111) + [21]</td>
<td>$3 \times 10^{-9}$</td>
<td>$4 \times 10^{-18}$</td>
<td>$1.3 \times 10^9$</td>
</tr>
<tr>
<td>lubricated Si(100) - [24]</td>
<td>$32 \times 10^{-9}$</td>
<td>$4 \times 10^{-18}$</td>
<td>$10^{10}$</td>
</tr>
<tr>
<td>C$_{60}$/island/NaCl(001) + [25]</td>
<td>$5 \times 10^{-9}$</td>
<td>$7 \times 10^{-15}$</td>
<td>$10^4 - 10^5$</td>
</tr>
<tr>
<td>Kr/Au(111) + [3]</td>
<td>$5 \times 10^{-6}$</td>
<td>$10^{-5}$</td>
<td>$5 \times 10^{-1}$</td>
</tr>
<tr>
<td>Kr/rough Ag - [3]</td>
<td>$5 \times 10^{-4}$</td>
<td>$10^{-5}$</td>
<td>$5 \times 10^1$</td>
</tr>
<tr>
<td>C$_2$H$_4$/Ag + [30]</td>
<td>$6 \times 10^{-6}$</td>
<td>$10^{-5}$</td>
<td>$6 \times 10^{-1}$</td>
</tr>
<tr>
<td>C$_2$H$_4$/lubricated Ag + [30]</td>
<td>$2 \times 10^{-7}$</td>
<td>$10^{-5}$</td>
<td>$2 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

**Macroscopic Methods**

| copper/lubricated copper + [31] | $6.7 \times 10^7$ |
| steel/Mo$_2$-coated steel # [32] | $2.5 \times 10^7$ |

- ambient environment + ultra-high vacuum environment # dry air or argon environment
REFERENCES


[18] M. Robbins, private communication


