Nanotribology of a Kr Monolayer: A Quartz-Crystal Microbalance Study of Atomic-Scale Friction

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(Received 15 October 1990)

A quartz-crystal microbalance has been utilized to probe sliding-friction effects in Kr monolayers undergoing solidification on Au and Ag surfaces. Solid layers are observed to be far more sensitive to surface morphology than liquids. The behavior of liquid layers is consistent with a frictional force whose magnitude is a nonlinear function of the sliding velocity.

The topic of interfacial sliding and atomic-scale friction has experienced a major burst in activity since 1987, much of which has developed quite independently and spontaneously.[1-12] First-principles calculations have been reported for the friction which arises from slippage at solid-solid interfaces[1,2] and molecular-dynamics simulations have been carried out for slippage at fluid-fluid, fluid-solid, and solid-solid interfaces and contact points.[3-5] Experimental developments include modifications of the surface force apparatus to probe the sliding friction of surfaces separated by molecularly thin fluids,[6,7] and the discovery that slippage effects in molecularly thin adsorbed films can be probed by means of a quartz-crystal microbalance[8-10] (QCM). Friction at a tip-substrate contact point has also been measured, by monitoring the resistance to sliding experienced by the tip of an atomic force microscope.[11] This emerging area of physics is well described by the term "nanotribology," or the study of friction at nanometer length scales.

Progress in nanotribology is essential to all areas of friction, since macroscopically observed friction is known to depend dramatically on the local chemical and atomic details of the surfaces in contact, and also on whether monolayers or submonolayers of adsorbents are present on these surfaces.[13] We present here a QCM investigation of basic nanotribological properties of Kr monolayers adsorbed on Au and Ag surfaces.

Our QCM consists of a single crystal of quartz (AT cut) which oscillates in transverse shear motion with a quality factor Q near 10^5. It is mounted horizontally within a vacuum chamber which is plunged directly into a liquid-nitrogen bath. As Kr gas is admitted to the chamber, adsorption occurs under *equilibrium* conditions onto Au or Ag electrodes which are evaporated onto the major surfaces of the QCM. At 77.4 K, Kr condenses as a uniform film which is one or two monolayers thick (for pressures remaining below the bulk condensation point), depending on the uniformity of the substrate.[14] At 77.4 K, the first monolayer generally condenses as a liquid, but solidifies as the pressure is increased.[15]

The adsorbed film produces shifts in both the frequency (f) and amplitude of vibration, which are simultaneously recorded as a function of pressure. Gas-phase

corrections are performed, and then a characteristic film slip time (τ) is obtained from the relation[8]

$$\delta(Q^{-1}) = 4\pi\tau\delta f, \tag{1}$$

where the film-substrate frictional force is assumed to be directly proportional to the sliding speed (Stokes's law). (An *in situ* calibration is carried out with a gas which does not condense at 77.4 K, allowing conversion of amplitude shifts into quality-factor shifts.[9]) τ corresponds to the time for an object's speed to fall to $1/e$ of its original value, assuming that it has been pushed at constant speed and then released, allowing frictional forces to bring it to a stop. Our "object" of interest is a film which is adsorbed on an oscillatory substrate. In this case τ represents an average over all film particles, and substantial decoupling effects occur when the slip time exceeds the period of oscillation. Partial decoupling effects should also be quite evident for values of $\omega\tau = 2\pi f\tau \geq 0.5$, where the percent of film mass which effectively couples to the oscillation is 80% or less. The value of τ deduced from Eq. (1) can be of the correct magnitude even if Stokes's law is not applicable, but will, however, be dependent on sliding velocity.[10]

Experiments were carried out on "smooth" and "rough" Au and Ag substrates, whose surface areas were determined by means of nitrogen-adsorption measurements. The systems Kr/Au and Kr/Ag exhibited no differences in sliding behavior so long as the interface morphologies were comparable. This is consistent with the fact that the van der Waals force (the only "normal force" present) which binds a Kr atom to a Au surface is within 10% of that of a Ag surface[16] ($\approx 2\times10^{-5}$ dyn).

Data are presented here for one smooth Au surface and two rough Ag surfaces. The smooth surface was prepared by thermal evaporation of 650 Å of 99.999% pure Au at 0.5 Å/s in 10^{-9} torr vacuum onto a 5-MHz overtone-polished quartz crystal[17] held at room temperature. This procedure minimized the root-mean-square roughness as determined by x-ray reflectivity[18] and also the surface area, which was close to that of a geometrically flat plane. The sample was transferred within the vacuum system to the Kr adsorption chamber and, after recording of the adsorption data, was examined in air
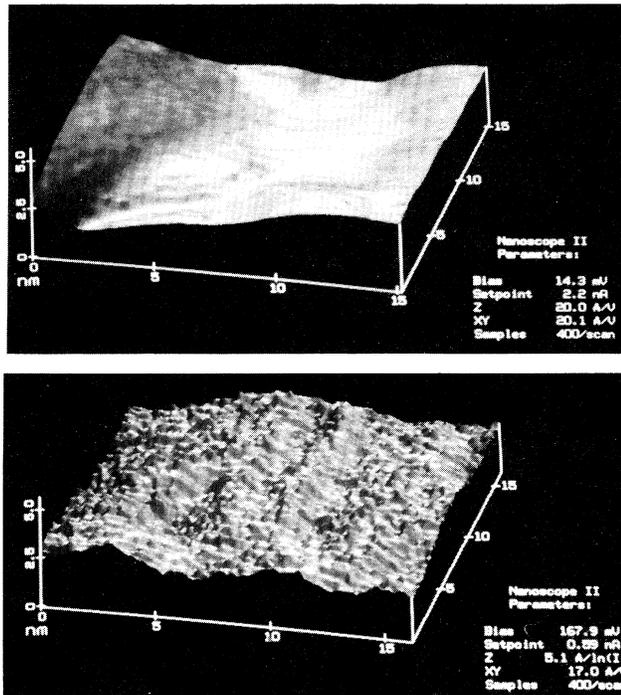
FIG. 1. STM images for the "smooth" Au (top) and "rough" Ag (Ref. 22) (bottom) substrates utilized for these studies. Each is the surface of a film which has been evaporated onto the surface of a quartz oscillator which translates back and forth along the horizontal axis with amplitude of vibration ≈ 1 nm.

FIG. 2. Kr adsorption data at 77.4 K on "smooth" Au (squares), and "rough" Ag substrates (crosses and circles) (see text).

with a scanning tunneling microscope (STM). A "rolling hill" topology was observed (Fig. 1), consistent with previous reports of samples prepared in this manner.[19] This surface, although relatively flat and chemically pure, should not be termed Au(111) [a weak (111) fiber texture is, however, expected to be present[20]].

The rough Ag surfaces were 8- and 5-MHz commerical quartz crystals, with respective surface areas 1.5 and 3.5 times that of a geometrically flat plane. Thes surfaces were indicated by liquid-nitrogen-adsorption measurements[21] and analysis of STM data[22] to be self-affine fractals with local fractal dimension $D = 2.3 \pm 0.1$. Figure 1 shows an STM image of one such sample.[22]

Figure 2 shows adsorption data for the three samples along with the value of $\omega\tau$ determined by means of Eq. (1). Frequency shifts are directly proportional to the mass of the film which effectively couples to the motion. [The frequency shifts of the 8-MHz crystal have been divided by a factor of $(\frac{8}{5})^2 = 2.56$ in order to allow direct comparison with the data recorded on the 5-MHz samples.] Shifts in inverse quality factor are directly proportional to the energy dissipated on account of the presence

of the film. The gas-phase contribution is shown by the dash-dotted line in the quality-factor-shift data, and is negligible in the frequency-shift data.

Data for the smooth Au surface are represented by squares in Fig. 2. Frequency shifts of 10.4 and 12.5 Hz (labeled "liquid monolayer" and "solid monolayer") correspond to film coverages where the monolayer spacings are equal to the spacing in the bulk liquid (0.066 atoms/Å^2) and solid (0.078 atoms/Å^2), respectively. The sudden rise in the frequency data near 1.45 torr is characteristic of a liquid-solid transition occurring within the film. A peak in the dissipation data is centered on this transition and presumably due to the density fluctuations or regions of two-phase coexistence associated with the transition and not to actual changes in the slippage behavior of the film. A second peak is observed near 1.6 torr, consistent with the presence of another phase transition occurring within the solid monolayer. We are unable to identify this apparent transition. Given the morphology of the substrate and the fact that similar dissipation peaks occur in many of the rough surfaces, it seems unlikely to be due to a commensurate-incommensurate transition. Dissipation peaks above 1.7 torr are associated with further layer and bulk condensation. The dissipation attributed to the phase transitions makes it difficult to isolate that portion which is due to slippage. Nonetheless, we have chosen to study the phase-transition region in order to directly compare the solid and liquid slippage behavior. Despite the complications of the phase transitions, it is apparent that the solid phase exhibits more slippage on the smooth Au substrate

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than does the liquid phase since substantial film decoupling effects are observed in solid-film regime (> 1.45 torr) which are not present in the liquid-film regime. These are evidenced by decreases in the magnitude of the frequency shift as the pressure exceeds 1.45 torr, along with values of $\omega\tau$ which surpass 0.5.

The rough silver samples (crosses and circles in Fig. 2) exhibit greater frequency shifts because monolayer coverings of these higher-surface-area substrates require more particles. Evidence for the presence of phase transitions has been smeared away in the frequency data, presumably on account of substrate heterogeneity. In addition, the frequency-shift data exhibit no evidence for decoupling, consistent with the fact that the values of $\omega\tau$ remain for the most part well below 0.1. The 1.5 rough-Ag dissipation data (crosses) is distinctive in that a discontinuity is observed at 0.55 torr close to where liquid monolayer completion occurs in the smooth Au sample. Also present are remnants of the dissipation peaks which occurred at 1.45 and 1.6 torr in the smooth-Au data. In stark contrast to the data for the smooth Au substrate, the slip time steadily decreases as the pressure increases.

Although the Fig. 2 data provide strong evidence that the slip time deduced from Eq. (1) is of the correct order of magnitude (decoupling effects are indeed observed for $\omega\tau > 0.5$), they do not provide insight concerning the applicability of Stokes's law itself. This can be checked by investigating whether or not the slip time is dependent on oscillator velocity. (No such dependence is present if Stokes's law is applicable.[10]) Figure 3 shows a log-log plot of slip time versus substrate velocity amplitude for 3.5 rough Ag, recorded close to the liquid monolayer completion point. The slip time is clearly dependent on the substrate velocity (indicating a nonlinear friction
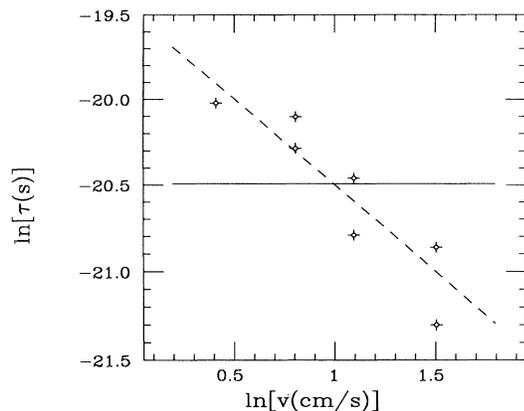
law), and the slope of the data is consistent with a value of -1. We observe similar behavior for all film coverages on the rough Ag substrates and also for the liquid-film regime (below 1.45 torr) on the smooth Au substrate. Numerical methods based on nonlinear friction laws will be utilized in the future to deduce quantitative film sliding speeds and slip lengths. Sliding velocity amplitudes and slip lengths are evidently higher for the solid film on smooth Au, but the nature of the friction law remains unknown. It is far more difficult to obtain quantitative information for this system on account of the film decoupling effects.

Figure 4 displays interfacial viscosity data for the three surfaces discussed here. The interfacial viscosity, $\eta = \rho/\tau$, where ρ is the mass per unit area of the film,[9] is the force per unit area necessary to slide the film along the surface at a constant speed of 1 cm/s. Interfacial viscosity data are qualitatively similar for all three substrates in the low-pressure regime where liquid films are present. In addition, the values of η are close in magnitude for 1.5 rough Ag and smooth Au, ≈ 40 dyn/cm^2 per cm/s, or 6×10^{-14} dyn/atom per cm/s at liquid monolayer completion. The "coefficient of friction" for these systems is quite small, 3×10^{-9}, indicative of the fact that perpendicular loading forces are virtually nonexistent.

Sliding behavior for solid (or perhaps "solidlike" in the case of the rough Ag substrates) films is far more sensitive to details of interface morphology. Solid films slide more easily on smooth Au than do liquid films, while the reverse is true for the 1.5 rough Ag substrate.

FIG 3. Logarithm of slip time vs logarithm of estimated substrate velocity amplitude for Kr on the 3.5 rough Ag sample. The solid line denotes the slope expected for a linear friction law (Stokes's law). The dashed line denotes a slope of -1.
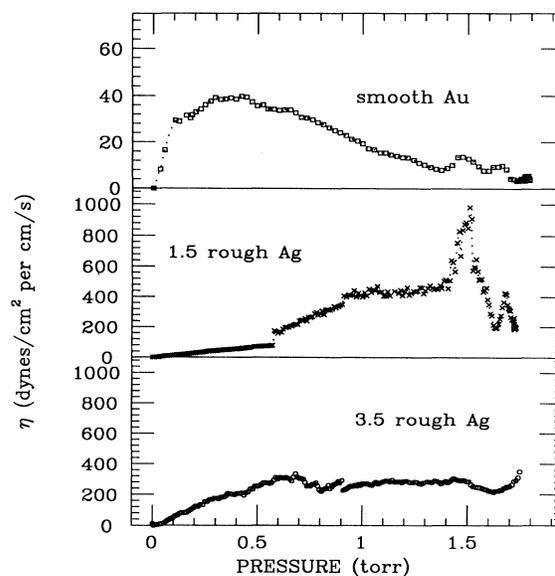
FIG. 4. Interfacial viscosity as a function of pressure for Kr adsorption on smooth Au and rough Ag substrates.

The peaks (or oscillations) observed at 1.45 and 1.6 torr are assumed to be due to the occurrence of phase transitions. Disregarding these, $\eta \approx 5$ dyn/cm^2 per cm/s for the solid film on smooth Au. This value falls intermediate between Sokoloff's calculated values for commensurate (10^9 dyn/cm^2) and incommensurate (10^{-4} dyn/cm^2) planar interfaces sliding at 1 cm/s.[1]

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