

## Experimental observation of interfacial slippage at the boundary of molecularly thin films with gold substrates

E. T. Watts, J. Krim, and A. Widom

*Department of Physics, Northeastern University, Boston, Massachusetts 02115*

(Received 18 August 1989)

Physisorbed monolayers and multilayers adsorbed on the surface electrodes of a resonating quartz microbalance produce shifts in both the frequency and amplitude of the oscillator. The shift in frequency results from mass loading and the shift in amplitude results from film dissipation effects. We have measured these shifts for molecularly thin nitrogen and krypton films and observe levels of film dissipation which cannot be adequately accounted for within the context of the "no-slip" boundary condition of hydrodynamics. The data provide strong evidence that the excess dissipation arises from slippage at the film substrate interface since the film thicknesses studied are negligible compared to the viscous penetration depths of the respective materials.

### I. INTRODUCTION

Consider the manner in which rain droplets form on a vertical window. One might easily conclude that there is no slippage at the water-glass interface. This so-called "no-slip" boundary condition has been utilized in continuum hydrodynamics for well over a century to successfully describe a wide range of experimental situations. Nonetheless, there exists neither a rigorous theoretical proof nor even a compelling theoretical argument which requires this to be so. The topic has attracted the likes of Maxwell,<sup>1</sup> Helmholtz,<sup>2</sup> and Thompson,<sup>3</sup> who have variously argued for and against the validity of the no-slip boundary condition. One hundred and thirty years have passed, and the topic of fluid flow and slip near solid boundaries is still rousing interest.<sup>4</sup> The resistance to sliding of molecularly thin films confined between two shearing planes has recently been measured with a modified surface-force apparatus,<sup>5-7</sup> but no explicit slippage at the liquid-plane interface was reported. Computer simulations have, however, raised into question the applicability of the no-slip condition for a contact line separating two immiscible fluids.<sup>8</sup>

Our purpose here is to report measurements of slipping at the interface of physisorbed monolayers with gold substrates. The method that we use is closely analogous to that originally employed by Helmholtz.<sup>2</sup> Helmholtz noted that if a solid boundary shakes back and forth, then film slippage can be experimentally probed by the inertial reaction forces. His experimental apparatus consisted of a torsional oscillator in the form of a "bifilarly" supported hollow sphere which he filled with water. By comparing the damping effects of water on glass to that on "gilt" glass, Helmholtz concluded that the water slipped more easily on gold than on glass, and that the slip length was approximately 0.2 cm wide. (Consider fluid flow through a tube with slippage occurring at the fluid-solid interface. The slip length  $\lambda$  is measured perpendicular to the wall, and represents the increase in tube radius necessary for an equal volume of flow to occur in a system governed by the no-slip condition.) This result was refuted nearly 30

years later in a paper read by Thompson,<sup>3</sup> which concluded that the slip region, if it existed at all, was at least ten times smaller than that deduced by Helmholtz.

Our measurements of the damping effects of molecularly thin nitrogen and krypton films have been carried out with a quartz-crystal oscillator vibrating in the transverse-shear mode. We observe damping which is in excess of that expected for films governed by the conventional no-slip boundary condition. Our data provide strong evidence that the excess damping is due to slippage at the film-substrate interface, and that the slip length is orders of magnitude less than that originally reported by Helmholtz.

### II. ACOUSTIC IMPEDANCE OF AN ADSORBED LAYER

Each face of a quartz-crystal oscillator acts as a planar surface in transverse-shear motion (Fig. 1). A reaction force is produced if a film is adsorbed on the two surfaces which are translating back and forth, or if the oscillator is exposed to a three-dimensional gas. Such reaction forces are conventionally described in terms of an acoustic impedance,  $Z(\omega)$ .

A planar surface which is driven by a periodic driving force  $F(\omega) = F_0 e^{i\omega t}$  in a direction parallel to the plane has velocity  $v(\omega) = v_0 e^{i\omega t}$ . The ratio  $Z_m = F_0/v_0$  is termed the "mechanical impedance." The acoustic im-

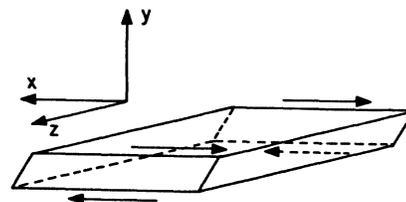


FIG. 1. Transverse-shear mode of oscillation. Adsorption occurs on the surfaces parallel to the  $x$ - $z$  plane, which move antiparallel to one another.

pedance is equal to the mechanical impedance per unit area,  $Z(\omega) = Z_m(\omega)/A$ , where  $A$  is the surface area in contact with the film or fluid which gives rise to the impedance. Acoustic impedance is generally expressed as  $Z(\omega) = R(\omega) - iX(\omega)$ , where the resistive term  $R(\omega)$  is proportional to average energy dissipation and the reactive term  $X(\omega)$  is associated with the inertia of the oscillator. Stockbridge<sup>9</sup> has solved for the shifts in frequency and the quality factor  $Q$  of a quartz-crystal oscillator in terms of the acoustic impedance  $Z$  to which it is exposed. For film adsorption on, or fluid exposure to, *both sides* of the crystal,

$$\delta \left[ \frac{1}{Q} \right] = \frac{4R}{\omega \rho_q t_q}, \quad \delta \omega = \frac{2X}{\rho_q t_q}, \quad (1)$$

where  $\rho_q$  and  $t_q$  are the density of quartz and the thickness of the quartz crystal, respectively, (Exposure to one side only will produce shifts which are one-half as large.)

In the following sections,  $Z_3^*$  and  $Z_3$  will denote the acoustic impedance of a bulk three-dimensional fluid including, and not including, viscoelastic effects, respectively. Similarly, the notation  $Z_2$  will represent the acoustic impedance of a two-dimensional film governed by the no-slip condition and  $Z_2^*$  will represent the acoustic impedance of a film which exhibits interfacial slippage. The term  $Z(\omega)$  represents the acoustic impedance at the surface of the quartz crystal due to the combined effects of all film and fluid phases which are present.

The acoustic impedance at frequency  $f = \omega/2\pi$  of a three-dimensional fluid with mass density  $\rho_3$  and bulk viscosity  $\eta_3$  is well established:<sup>10</sup>

$$Z_3 = R_3 - iX_3 = (1-i)\sqrt{\pi\eta_3\rho_3f} \quad (2)$$

Equation (2) inadequately describes the impedance of a gas at low pressure, where the time required for particles to relax to the equilibrium state after a collision with the oscillator is commensurate with the period of oscillation. The full expressions for the real and imaginary components of the acoustic impedance  $Z_3^* = R_3^* - iX_3^*$  in this "viscoelastic" regime are given by<sup>9</sup>

$$R_3^* = \sqrt{\pi\rho_3\eta_3f} \times \left\{ \frac{\omega\tau_r}{1+(\omega\tau_r)^2} \left[ \left( 1 + \frac{1}{(\omega\tau_r)^2} \right)^{1/2} + 1 \right] \right\}^{1/2}, \quad (3a)$$

$$X_3^* = \sqrt{\pi\rho_3\eta_3f} \times \left\{ \frac{\omega\tau_r}{1+(\omega\tau_r)^2} \left[ \left( 1 + \frac{1}{(\omega\tau_r)^2} \right)^{1/2} - 1 \right] \right\}^{1/2}. \quad (3b)$$

The time  $\tau_r$  is that which is required for the excess momentum of a fluid particle to fall to  $1/e$  of its initial value after a collision with the plane. It is generally written as  $N\tau_c$ , where  $N$  is an integer and  $\tau_c$  is the average time between collisions in the gas phase.

The acoustic impedance of a fluid film of thickness  $d$ , mass density  $\rho_3$ , and bulk viscosity  $\eta_3$  (assuming no gas is present and that the no-slip boundary condition is applicable) has been derived in various treatises on fluid mechanics<sup>10</sup> and via transmission-line theory:<sup>11</sup>

$$Z_2 = -\eta_3 k \tan(kd), \quad k^2 = (i\omega\rho_3/\eta_3). \quad (4)$$

If the adsorbed film is sufficiently thin so as to satisfy the condition  $|kd| \ll 1$ , the acoustic impedance becomes entirely reactive and directly proportional to the mass per unit area of the film,  $\rho_2$ :

$$Z_2 = -iX_2 = -i\omega\rho_2 d = -i\omega\rho_2 \quad \text{for } |kd| \ll 1. \quad (5)$$

Since frequency shifts are directly proportional to the reactive component of the acoustic impedance [Eq. (1)], it is evident from Eq. (5) that the shift in frequency is directly proportional to mass adsorbed (in the thin-film regime) and thus the term "microbalance" is applicable.

In practice, most adsorbed films coexist with bulk-vapor phases whose effects cannot be ignored. The full expression for the acoustic impedance of a film coexisting with a three-dimensional vapor (assuming the no-slip boundary condition is applicable) is given by<sup>11</sup>

$$Z(\omega) = Z_3^f \tanh(\Psi + \gamma d), \quad (6)$$

where  $Z_3^f = (1-i)\sqrt{\pi\eta_{3f}\rho_{3f}f}$  is the acoustic impedance of the bulk material of which the film is composed,  $Z_3^v = (1-i)\sqrt{\pi\eta_{3v}\rho_{3v}f}$  is the acoustic impedance of the vapor,  $\gamma = (1-i)/\delta$  is the propagation constant,  $\delta = \sqrt{2\eta_{3f}/\rho_{3f}\omega}$  is the film penetration depth, and  $\tanh(\Psi) = Z_3^v/Z_3^f$ . ( $\eta_{3v}$  and  $\rho_{3v}$  correspond to the bulk density and viscosity of the vapor;  $\eta_{3f}$  and  $\rho_{3f}$  to the bulk density and viscosity of the material of which the film is composed.) If the adsorbed form is sufficiently thin so as to satisfy the condition  $|kd| \ll 1$ , Eq. (6) simplifies to

$$Z(\omega) = -i\omega\rho_2 [1 - (Z_3^v/Z_3^f)^2] + Z_3^v \quad \text{for } |kd| \ll 1. \quad (7a)$$

For the nitrogen and krypton films discussed here, the acoustic mismatch factor  $1 - (Z_3^v/Z_3^f)^2 \approx 0.9998$ , so that Eq. (7a) can be even further simplified:

$$Z(\omega) = -i\omega\rho_2 + Z_3^v \quad \text{for } |kd| \ll 1. \quad (7b)$$

To take into account potential slippage at the interface, we use an approach first introduced by Lamb in 1879.<sup>12</sup> A "coefficient of sliding friction"  $\eta_2$  or equivalently a slip length  $\lambda$ , is defined by the relation

$$\eta_2 = \frac{\eta_3}{\lambda}. \quad (8)$$

The coefficient of sliding friction, referred to more recently as the "interfacial viscosity,"<sup>13</sup> has the same units as acoustic impedance and is entirely dissipative in nature. Infinite  $\eta_2$  implies that an infinite force is required to slide the film along the surface, and so implies that the no-slip boundary condition is applicable. Zero interfacial viscosity implies that the film is free to slide along the surface with no energy dissipation whatsoever (as does superfluid helium), so that the quartz oscillator would detect no film at all, i.e.,  $Z = 0$ . The impedance of the film under the no-slip condition, therefore, adds in parallel to that of the interfacial viscosity:

$$\frac{1}{Z_2^*} = \frac{1}{\eta_2} + \frac{1}{Z_2}. \quad (9)$$

The expressions for  $Z_2$  and  $\eta_2$  given by Eqs. (4) and (8) can be substituted into Eq. (9) to yield the acoustic impedance of a film which exhibits interfacial slippage:

$$Z_2^* = \frac{-\eta_3 k \tan(kd)}{1 - \lambda k \tan(kd)} \quad (10)$$

If the adsorbed film is sufficiently thin so as to satisfy the condition  $|kd| \ll 1$  (i.e., its thickness is negligible compared to the penetration depth), then Eq. (10) reduces to

$$Z_2^* = \frac{-i\omega\rho_2}{1 - i\omega\tau}, \quad \tau = (\lambda\rho_3 d / \eta_3) = \frac{\rho_2}{\eta_2} \quad \text{for } |kd| \ll 1. \quad (11)$$

The quantity  $\tau$  is a characteristic slip time previously discussed by Krim and Widom in great detail from a microscopic viewpoint.<sup>13</sup> The slip time characterizes the decay of total film momentum with respect to the substrate. The term "slippage" should therefore be treated with great caution, since not all particles are "slipping" (or "hopping") in the same direction. Nonzero slip time implies only that more particles are slipping or hopping in one direction than the other, with respect to the substrate motion.

The slip time  $\tau$  can be determined experimentally by noting that the resistive and reactive components of  $Z_2^*$  in Eq. (11) are given by

$$R_2^* = \frac{\rho_2 \omega^2 \tau}{1 + \omega^2 \tau^2}, \quad X_2^* = \frac{\rho_2 \omega}{1 + \omega^2 \tau^2} \quad (12)$$

Taking the ratio  $R_2^* / X_2^* = \omega\tau$ , therefore, allows a direct determination of the slip time.

### III. EXPERIMENTAL DETAILS

We determined the acoustic impedance of the molecularly thin films studied here by recording vapor-pressure isotherms at room temperature and at 77.4 K. The resistive and reactive components of the acoustic impedance were deduced from direct measurements of the frequency and amplitude shifts of a quartz-crystal microbalance. Descriptions of the apparatus and technique are given elsewhere,<sup>9,14</sup> and are summarized here. The microbalance crystals for these studies were polished 7.4 MHz AT-cut quartz which had quality factors near  $10^5$ . The adsorption substrates were gold electrodes deposited on the planar faces of the crystal. We produced the electrodes by evaporation of 99.999%-pure Au at  $5 \times 10^{-8}$  Torr onto the faces of the quartz blanks. During the plating process the crystals were radiantly heated by the evaporation boat to temperatures over 200°C. This procedure produces a mosaic structure with a (111) fiber texture, as determined by electron microscopy and x-ray diffraction.<sup>15</sup>

The oscillator circuitry is designed to drive the crystal with a constant amplitude at its series-resonant frequency, i.e.,  $F(t) = F_0 \cos(\omega_0 t)$ . The amplitude of vibration of a damped oscillator driven at its own resonant frequency by a constant driving force is given by<sup>16</sup>

$$A(\omega_0) = \frac{F_0/M}{R\omega_0} = \frac{1}{M\omega_0} \frac{F_0}{R} \quad (13)$$

where  $M$  is the total effective mass of the oscillator. Our experiments are carried out in a regime satisfying the condition  $m_{\text{film}} \ll M_{\text{bare}}$ , where  $M_{\text{bare}}$  is the mass of the microbalance with no adsorbed film and  $m_{\text{film}}$  is the mass of the adsorbed film. In this regime, there is a linear relationship between the change in frequency— $\delta\omega$ —and  $m_{\text{film}}$ :

$$\frac{\delta\omega}{\omega_0} = - \frac{m_{\text{film}}}{M_{\text{bare}}} \quad (14)$$

Equation (14) implies that  $\delta\omega \ll \omega_0$  in our experimental regime, and so, to good approximation, we can utilize Eq. (13) in a simpler form:

$$A = K \frac{F_0}{R} \quad (15)$$

where  $K$  is a constant.

Before transferring the crystal to our cryostat for gas-adsorption studies, we operated it as a microbalance in the metal-deposition chamber in order to verify the validity of Eq. (15). (No change in amplitude is expected for thin deposits of gold since slippage of a solid-gold film on a solid-gold substrate is expected to be minimal). The crystal was then set in narrow channels which were machined into the ends of the 0.1-in.-diam oxygen-free high-conductance copper rods of a vacuum feedthrough, and were connected to exterior oscillator circuitry. The crystal was exposed to air for approximately 30 min during this mounting procedure. The crystal was mounted horizontally in a high-vacuum ( $1 \times 10^{-8}$  Torr) chamber which could be directly submerged into a liquid-nitrogen bath. The very large temperature coefficient of approximately 100 Hz/K at 77.4 K combined with a typical frequency stability of a few parts in  $10^9$  would allow changes in frequency due to heating to be detected. No such heating effects were, however, observed.

Helium gas was introduced to the chamber at 77.4 K to further check the applicability of the assumptions underlying Eq. (15) and to calibrate the *in situ* response of the crystal to a bulk vapor with known acoustic impedance. The response of the microbalance to thin films of nitrogen or krypton was then recorded.

### IV. EXPERIMENTAL RESULTS

A thin solid-gold film deposited on a solid-gold electrode should exhibit minimal slippage as the surface oscillates. The frequency shift associated with the deposited mass should therefore be accompanied by no significant shift in amplitude of vibration, so long as the deposited film remains thin. Figure 2 shows a plot of the change in inverse amplitude of the oscillator circuit [proportional to change in dissipation according to Eq. (15)] versus frequency shift of the microbalance as approximately ten layers of gold are deposited. As expected,  $\delta(1/A) = 0$  within the experimental resolution. This also demonstrates that frequency shifts of the oscillator circuitry produce no spurious accompanying amplitude shifts.

We next carried out measurements on helium gas at 77.4 K. Figure 3 shows a plot of  $\delta(1/A)$  versus the real

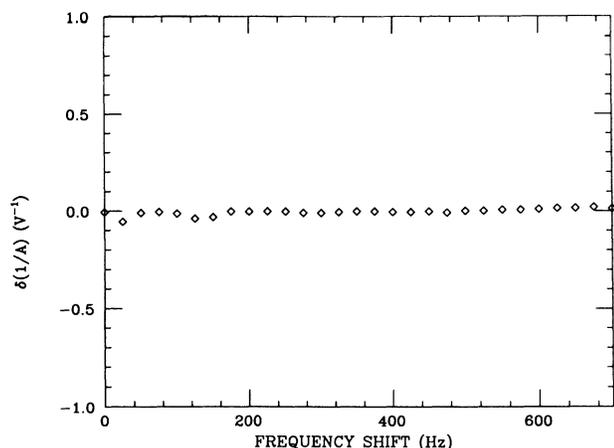


FIG. 2. The amplitude of the quartz crystal remains constant (no energy dissipation) for gold deposition onto the crystal electrodes. The frequency shift corresponds to an added mass of about ten layers of gold.

component of acoustic impedance of helium gas. The acoustic impedance is determined from Eq. (3a) utilizing the known density and viscosity of helium gas at 77.4 K. Figure 3 shows that the circuit response to the acoustic impedance to which the crystal is exposed is linear. We use the slope of this linear response to provide an *in situ*, quantitative calibration of the system. The response of the system was also studied for nitrogen-gas exposure at room temperature. The slope of this response was within 15% of that measured at 77.4 K and remained linear up to 2.2 g/cm<sup>2</sup> s, the highest impedance studied. Changes in inverse amplitude observed for krypton and nitrogen adsorption at 77.4 K were converted to actual units of impedance employing the slope of the helium-gas calibration shown in Fig. 3.

Figure 4 shows the frequency and amplitude data for nitrogen-film adsorption at 77.4 K. The data are recorded in a regime satisfying  $|kd| \ll 1$ , and so according to Eqs. (1) and (7b) the frequency shift is due to the sum of

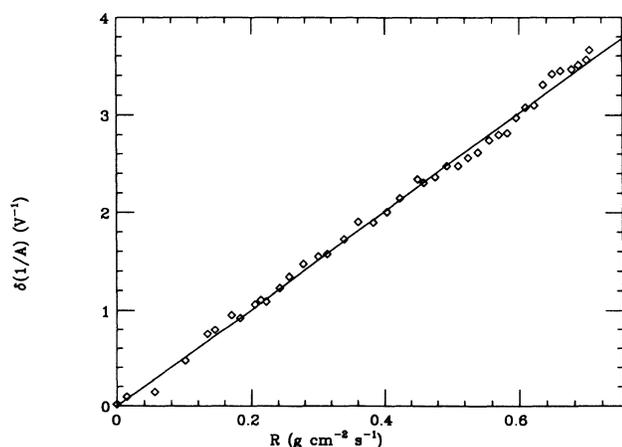


FIG. 3. The change in  $(1/A)$  due to helium-gas pressure is plotted vs the calculated acoustic resistance ( $R$ ) ( $\eta_3 = 82.8 \mu\text{P}$ ;  $N = 10$ ). The solid line shows the fit to the data, allowing quantitative calibration of the measurements.

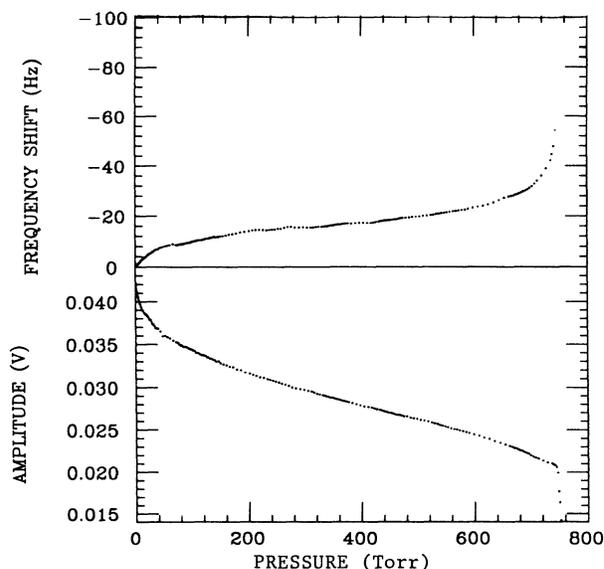


FIG. 4. Raw data for nitrogen adsorption on gold. The frequency shift is proportional to adsorbed mass. The shift in amplitude results from energy dissipation.

the imaginary components of the film ( $\omega\rho_2$ ) and vapor ( $X_3^*$ ) impedances. The contribution of the vapor phase is small compared to that of the film. Once subtracted, the film thickness can be determined according to Eq. (5) or Eq. (12). It is apparent that the frequency shift (and therefore the film thickness) diverges as the pressure approaches saturation from below. This indicates that the film thickness remains uniform up to at least 50 Å, consistent with complete wetting of the gold substrate by the liquid-nitrogen film. Such behavior is typical of simple molecular films adsorbing on gold substrates at temperatures above their respective triple points.<sup>17</sup> Pfeifer *et al.* have very recently utilized similar nitrogen-adsorption data on evaporated silver films as evidence that the surface of the silver is self-affine or fractal at microscopic length scales.<sup>18</sup> We have analyzed the data of Fig. 4 in terms of monolayer film coverages and also according to the manner prescribed by Pfeifer *et al.* and observe no evidence suggesting surface roughness or fractal behavior in any of the gold substrates utilized for these studies.<sup>19</sup>

Figure 5 shows the experimental data of Fig. 4, plotted as  $R$  versus liquid-nitrogen film thickness. The values of impedance  $R$  have been obtained from the shifts in inverse amplitude according to the helium-gas calibration described above. For comparison, we also plot the predicted value of  $R$  according to Eq. (6) (dots) and Eq. (3a) (dashes), utilizing the experimentally measured pressure and film thicknesses. The coincidence of the theoretical curves indicates the validity of the assumption  $|kd| \ll 1$  for the range of film thicknesses studied. Equation (7), therefore, adequately describes the system in this film-thickness regime. The theoretical curves depict the resistive component of the acoustic impedance, and both curves fall far short of the experimentally observed value. It is apparent that more energy dissipation is occurring than can be accounted for within the context of a no-slip boundary condition.

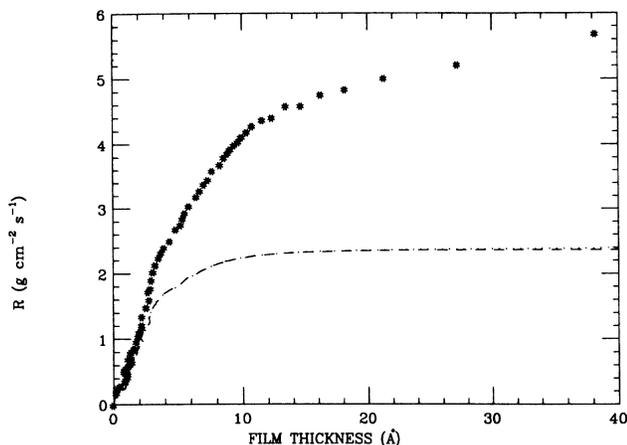


FIG. 5. The measured acoustic resistance for the adsorption of nitrogen (\*) is plotted as a function of film thickness ( $\rho_3=0.806 \text{ g/cm}^3$ ). The theoretical resistance (assuming the no-slip boundary condition) is shown due to (a) gas pressure ( $\eta_3=53.7 \mu\text{P}$ ), Eq. (3a) (dashed line), and (b) gas pressure plus the liquid-adsorbed film (dotted line), Eq. (6), utilizing the experimentally measured pressure and film thickness.

Interfacial slippage is a potential source of energy dissipation. The amount of energy dissipation is characterized by the slip time,  $\tau$ . As mentioned above, the slip time provides an indication of the average time required for the particles to track the continuously changing direction of crystal motion. Assuming that the excess dissipation observed in Fig. 5 is due to interfacial slippage, one can deduce a slip time from Eq. (12). This is plotted in Fig. 6 as a function of total film thickness, starting with a thickness corresponding to that of a monolayer. The asterisks represent the same data as shown in Fig. 5. Subsequent measurements (squares) were taken after exposing the same gold surface to air for 27 h. The result of this air exposure is to allow physisorption of contaminants (primarily hydrocarbons) to the gold surface.<sup>15</sup> The nitrogen isotherm recorded after this air exposure exhibits

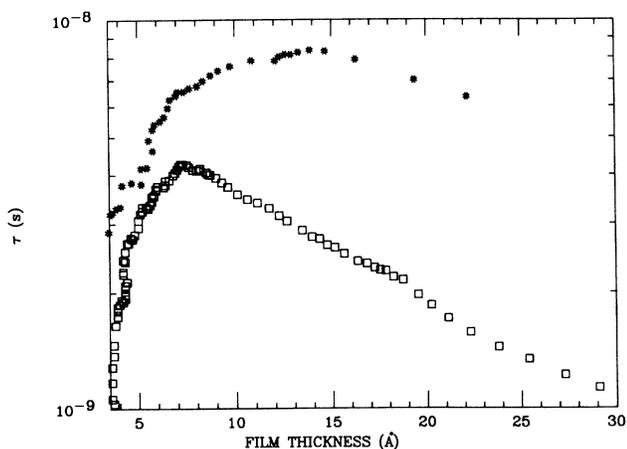


FIG. 6. Slip time as a function of film thickness beginning at 1 monolayer. The slip time for adsorption on fresh gold (asterisks) is always longer than that for adsorption on gold which has been exposed to air for 27 h (squares).

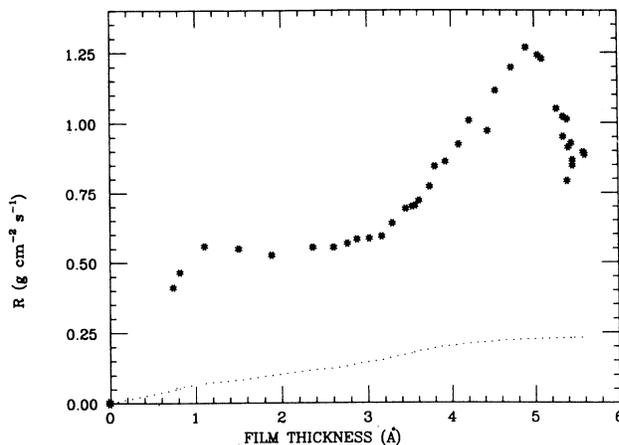


FIG. 7. The measured acoustic resistance of krypton adsorbed on gold (\*) as a function of film thickness ( $\rho_3=2.5 \text{ g/cm}^3$ ). The theoretically expected value (assuming the no-slip condition) is shown by the dotted line (Kr gas  $\eta_3=70.6 \mu\text{P}$ ).

no increase in monolayer step height within experimental resolution. This indicates that the surface area has not significantly increased. The intuitive hypothesis, which is substantiated by the measurements, is that the adsorbed contaminants should help pin the film and reduce the amount of slipping. The slip times on the surface which has been exposed to air are indeed shorter.

Measurements of krypton adsorption at 77.4 K were also recorded on the same surface as that utilized for Fig. 5 and after the 52 h of air exposure. In this case, the maximum vapor pressure is 1.7 Torr, much less than the 760 Torr for the nitrogen adsorption. The film contribution therefore dominates the resistive component of the acoustic impedance. Data for krypton adsorption (asterisks) on the fresh gold surface are shown in Fig. 7. Uniform film thicknesses are now limited on account of incomplete wetting by the krypton, which is below its bulk triple point. Additional adsorption results in the formation of bulk clusters (not shown), which generally reduce film dissipation levels, apparently acting as pinning sites. The krypton-vapor contribution is shown by the dots. The dissipation rises and then levels off as the monolayer adsorbs (thickness near 3 Å). As the film thickens, the dissipation sharply increases in the range 3–5 Å. This may well be due to the relative ease with which an incomplete second layer might slip. As the thickness approaches that corresponding to completion of the second layer ( $\approx 6 \text{ Å}$ ), the dissipation sharply decreases.

Figure 8 compares the characteristic slip times for krypton adsorption before (asterisks) and after (squares) the extended air exposure. Again, the slip times are decreased for the more contaminated sample. The theoretical derivation of dissipation at an interface assumes the monolayer to be complete. Nonetheless, it is interesting to note that at submonolayer coverages the slip times are increased. This is entirely consistent with the notion that an incomplete layer is more free to slip on the surface.

## V. DISCUSSION

The measurements presented here have shown the no-slip boundary condition to be inadequate for our experi-

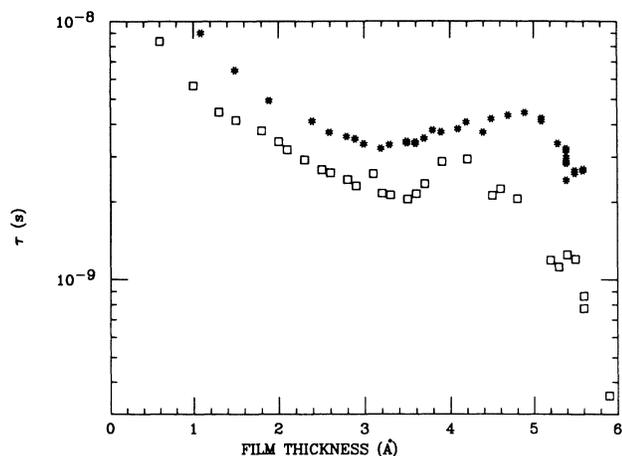


FIG. 8. The slip time for krypton plotted vs film thickness. As with nitrogen adsorption, slip time on the air-exposed surface (squares) is shorter than that on the fresh gold substrate (asterisks).

mental situation, and we believe the discrepancy can be explained by film-slippage effects. There are two possibilities as to where the slippage might occur: the substrate-film interface and the film-vapor interface. If slippage were occurring only at the film-vapor interface, then slip times for the nitrogen films on the two gold substrates should be comparable in the thicker-film regime where the substrate-film interface presumably has little effect. There is, however, no evidence that the two curves in Fig. 5 are converging at higher coverages. While this does not preclude the occurrence of slippage at the film-vapor interface, it does indicate that the dominant effect is at the substrate-film interface. The intuitively appealing result that the slip times are shorter on the air-exposed sample than on the fresh gold surface provides an additional indication that the slippage is dominated by the substrate-film interface.

The monolayer slip times observed for nitrogen and krypton on either of the two surfaces are quite close in overall magnitude. Krypton- and nitrogen-monolayer slip times on the fresh gold surface are close to  $3.5 \times 10^{-9}$  s, and close to  $2.5 \times 10^{-9}$  s on the air-exposed surface. This may be coincidental since the nitrogen films are liquid at 77 K and the krypton films are most likely to be solid. Further studies of the temperature dependence of adsorbed films will be required to clarify this point. The interfacial viscosity of the nitrogen monolayer ( $\rho_2 \approx 34.5$  ng/cm<sup>2</sup>) therefore ranges from [Eq. (11)] 10–14 g/s cm<sup>2</sup> or surface poise/cm<sup>2</sup>, while that of the krypton mono-

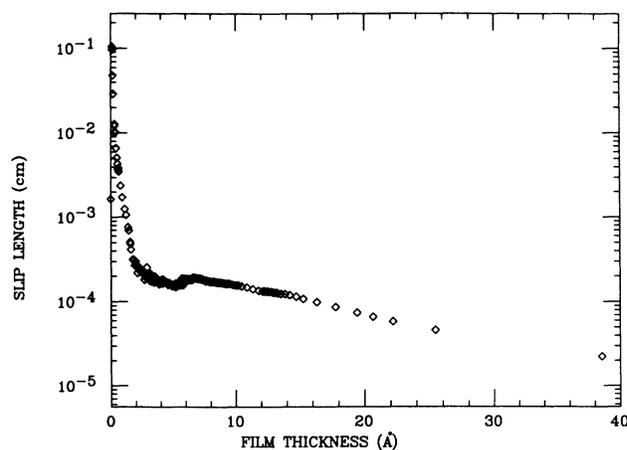


FIG. 9. Slip length for nitrogen adsorption on the fresh gold substrate as a function of film thickness.

layer ( $\rho_2 \approx 105$  ng/cm<sup>2</sup>) ranges from 30 to 42 surface poise/cm<sup>2</sup>.

The quantity  $\tau$  appears to be the best gauge of interfacial properties for the films which we have studied. Nonetheless, it is interesting to examine the slip length defined by Eq. (8) to compare our results with those of Helmholtz. The slip length of the nitrogen film adsorbed on fresh gold is plotted versus the film thickness in Fig. 9, assuming the film to have the same  $\eta_3$  as bulk liquid nitrogen. The small values which we observe are consistent with the findings of Whetham, and further limit the parameter's size. The fact that the slip length continues to decrease with increasing film thickness may well indicate a vanishingly small  $\lambda$  for macroscopic fluid dimensions. Therefore, although we have strong evidence for film slippage in thin films, the use of the no-slip boundary condition for the description of macroscopic fluid flow appears well justified. Finally, we emphasize that the levels of slippage which we have observed are not of sufficient magnitude to alter in any way the results of previous studies which have employed the quartz oscillator as a microbalance alone. We wish only to draw attention to the fact that in addition to microweighing, the quartz oscillator can be utilized as a probe of interfacial slippage effects.

#### ACKNOWLEDGMENTS

This work has been supported by the National Science Foundation (NSF) Low Temperature Physics Program Grant No. DMR-86-57211 (J.K. and E.T.W.)

<sup>1</sup>J. C. Maxwell, *Philos. Trans. R. Soc. London* **157**, 49 (1867).

<sup>2</sup>H. Helmholtz and X. Piotrowski, *Sitzungsber. Akad. Wiss.* **40**, (1860).

<sup>3</sup>W. C. Whetham (presented by J. J. Thompson), *Philos. Trans. R. Soc. London* **181**, 559 (1890).

<sup>4</sup>A. Khurana, *Phys. Today* **41**(5) 17 (1988).

<sup>5</sup>J. N. Israelachvili, *Acc. Chem. Res.* **20**, 415 (1987).

<sup>6</sup>J. N. Israelachvili, P. M. McGuiggan, and A. M. Homola, *Sci-*

*ence* **240**, 189 (1988).

<sup>7</sup>J. Van Alsten and S. Granick, *Phys. Rev. Lett.* **61**, 2570 (1988).

<sup>8</sup>J. Koplich, J. Banavar, and J. Willemsen, *Phys. Rev. Lett.* **60**, 1282 (1988); P. A. Thompson and M. O. Robbins, *Phys. Rev. Lett.* **63**, 766 (1989).

<sup>9</sup>C. D. Stockbridge, *Vacuum Microbalance Techniques* (Plenum, New York, 1966), Vol. 5.

<sup>10</sup>L. D. Landau and E. M. Lifshitz, *Fluid Mechanics*, Vol. 6 of

- Course of Theoretical Physics* (Pergamon, London, 1959), pp. 88–90.
- <sup>11</sup>M. J. Lea and P. Fozooni, *Ultrasonics* **23**, 133 (1985); *Phys Lett.* **109A**, 295 (1985).
- <sup>12</sup>Sir Horace Lamb, *Hydrodynamics*, 1st Am. Ed. (Cambridge University Press, Dover, New York, 1945), p. 586.
- <sup>13</sup>J. Krim and A. Widom, *Phys. Rev. B* **38**, 12 184 (1988).
- <sup>14</sup>J. Krim, Ph.D. thesis, University of Washington, 1984.
- <sup>15</sup>J. Krim, *Thin Solid Films* **137**, 297 (1986).
- <sup>16</sup>A. P. French, *Vibrations and Waves* (Norton, New York, 1971).
- <sup>17</sup>J. Krim, J. G. Dash, and J. Suzanne, *Phys. Rev. Lett.* **52**, 640 (1984).
- <sup>18</sup>P. Pfeifer, Y. J. Wu, M. W. Cole, and J. Krim, *Phys. Rev. Lett.* **62**, 1997 (1989).
- <sup>19</sup>E. T. Watts, Ph.D. thesis, Northeastern University, 1989.