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Determination of an atomic-scale frictional force law through quartz-crystal microbalance measurements

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A method is proposed for interpreting the results of recent quartz microbalance measurements of shear friction, based on a model in which the friction is assumed to be proportional to a power of the velocity of the adsorbed film relative to the microbalance. The amplitude dependence of the quality factor Q of this model for the microbalance is shown to depend critically on the exponent of the velocity in the force law, allowing one to infer this exponent from experiment.

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 has led to the emergence of a new field involving friction studies at nanometer length scales (nanotribology). Atomic force microscopes[1] have been utilized to study friction, adhesion, and lubrication for surface contacts as small as a single atom,[2–4] and have also been configured for nanoindentation experiments capable of nN force resolution and depth resolution to hundredths of a nanometer.[5] Surface force apparatus have meanwhile been modified to allow studies of the shear forces between two crystalline mica surfaces, either in direct contact or separated by molecularly thin liquids.[6–8] Another recently developed technique involves the use of a quartz-crystal microbalance to measure sliding friction levels of molecularly thin adsorbed films.[9–11] Quartz-crystal microbalances have found wide use over the years for precise mass measurements in engineering applications and in surface science.[12] Because of the wide availability of microbalances and the ease with which friction studies using them can be studied by molecular dynamical simulations (in fact, Robbins is already doing simulations of this experiment[13]), this possibility of using it for studies of friction at the atomic scale is thus of great interest. The purpose of this paper is to develop a technique for determining the precise dependence of the frictional shear force between the microbalance and the film on velocity and other parameters characterizing the adsorbed film.

A quartz-crystal microbalance consists of a single crystal of quartz which oscillates in transverse shear motion with a quality factor Q near 10^5. The driving force (supplied by an external oscillator circuit) typically has constant magnitude and is periodic with frequency $f=4-10$ MHz, the series resonant frequency of the oscillator. A metal electrode is deposited onto each major face of the crystal which, for well-controlled experiments, can be prepared in ultrahigh vacuum (UHV) (Ref. 9) and characterized *in situ* with Auger electron spectroscopy or scanning tunneling microscopy (STM).

Adsorption of monolayer films onto the microbalance electrodes produces shifts in both the frequency and quality factor (Q) of the vibration. Frequency shifts are due to the increased system inertia, while shifts in the quality factor are due to frictional shear forces exerted on the surfaces by the adsorbed film. Interfacial friction coefficients η_2 and characteristic film slip times τ are deduced from the shifts in the inverse quality factor $[\delta(Q^{-1})]$ and frequency using the relations[11]

$$\delta(Q^{-1})=4\pi\tau\delta f \ , \quad \eta_2=\rho_2/\tau \ , \tag{1}$$

where ρ_2 is the mass per unit area of the adsorbed film. Since this relationship is derived using a linear (in velocity) friction law, it is not expected to be valid for nonlinear laws.

Quartz microbalance measurements have been carried out for monolayers and bilayers of rare gas and simple molecular liquids and solids adsorbed on atomically smooth and atomically rough substrates.[9] The experimentally observed $\delta(Q^{-1})$'s for liquid films are relatively insensitive to substrate morphology, but are observed to decrease as the amplitude of vibration of the crystal oscillator is increased. Solid films are observed to be quite sensitive to details of substrate structure, with friction coefficients for certain solid layers on smooth surfaces being so low that they actually decouple from the oscillatory motion of the microbalance. This decoupling has prevented studies of their amplitude dependencies.

The above results were interpreted within the context of a linear friction model, whereby the frictional force was assumed to be directly proportional to the (average) sliding speed of the layer.[11] While facilitating the calculations, this assumption is in fact not rooted in physical observation. Indeed, the amplitude dependency of the liquid film slip times suggests that a nonlinear law may well hold for these systems. In the remainder of this paper, we present a model which demonstrates how the amplitude and frequency dependencies of experimentally measured quality factor and frequency shifts can be analyzed so as to provide information on the actual form of the frictional force law.

Consider an oscillating surface with a mass m sitting on top of it, representing the film. (Since the liquid film thicknesses considered here are infinitesimal compared to typical bulk viscous penetration depths,[14] it is not unreasonable to treat the liquid, as well as the solid films, as

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rigid objects for the purpose of our calculations.) The force of sliding friction between the surface and the film (or viscous force if the film is a liquid) is taken to have the form

$$F=-\gamma|v|^n \mathrm{sgn}(v)\ , \tag{2}$$

where γ is a constant and v is the velocity of the film relative to the oscillating surface. This law encompasses the case of velocity-independent friction (for $n=0$), and also the ordinary interfacial viscous behavior (i.e., Darcy's law) for $n=1$ and higher power laws. The equation of motion for the film can then be written as

$$m\dot{v}_2=-\gamma|v_2-v_1|^n \mathrm{sgn}(v_2-v_1)\ , \tag{3}$$

where v_2 is the velocity of the film, $v_1=\omega A\sin(\omega t)$ is the velocity of the vibrating surface of the microbalance, A is its amplitude of vibration, and $\omega=2\pi f$. Equation (3) is expected to be valid for slip distances large compared to a lattice constant.

(Although it appears as if the assumed force law might not account for the case in which adsorbed layer does not slip, since the force vanishes for zero sliding velocity, this does not appear to be a problem. If $n=0$ the force does not vanish for vanishing relative sliding velocity, and while there could still be some ambiguity for the case of zero velocity of relative sliding, this can be resolved by using a model in which the force is given by $(2/\pi)F_0\tan^{-1}[(v_2-v_1)/\delta]$, where δ can be made as small as we wish. (For very small values of n as well, we must make a similar correction.) As for the $n>0$ cases, although there is always some slippage, in the limit as γ becomes large or ω approaches zero, v_2 becomes nearly equal to v_1. For example, consider the $n=1$ case, which can be solved exactly, $m\dot{v}_2=-\gamma(v_2-v_1)$, with $v_1=v_0\cos(\omega t)$. The solution is

$$v_2=(\omega^2m^2+\gamma^2)^{-1}[\gamma^2v_0\cos(\omega t)+\gamma m v_0\omega\sin(\omega t)]\ .$$

It is easily seen that as either γ approaches ∞ or ω approaches zero, v_2 approaches $v_0\cos(\omega t)$, implying that in these limits, the film does move with the quartz microbalance to a good approximation.)

Equation (3) can be rewritten in terms of the relative velocity $v=v_2-v_1$ as

$$\dot{v}=-\Gamma|v|^n \mathrm{sgn}(v)+A\omega^2\cos(\omega t)\ , \tag{4}$$

where $\Gamma=\gamma/m$. If Eq. (4) is then rewritten in time units of $T=2\pi/\omega$, it becomes

$$\dot{v}'=-\Gamma'|v'|^n \mathrm{sgn}(v')+(2\pi)^2A\cos(2\pi t')\ , \tag{5}$$

where $t'=t/T$, $v'=vT$, and $\Gamma'=\gamma/T^{n-2}$. Equation (5) can furthermore be rewritten in terms of variables scaled by the length scale $l=(\Gamma')^{-1/(n-1)}$, to yield

$$\dot{v}''=-|v''|^n \mathrm{sgn}(v'')+(2\pi)^2A'\cos(2\pi t')\ , \tag{6}$$

where $v''=v'/l$ and $A'=A/l$. In terms of these rescaled variables, the shift in inverse Q of the oscillator can then be written as

$$\delta(Q^{-1})=(\omega A)^{-2}\int_0^T dt\, fv=(2\pi A')^{-2}\int_0^1 dt'v''^{n+1}\ . \tag{7}$$

Numerical solution of Eq. (6), illustrated in Fig. 1, shows that $\delta(Q^{-1})$ has a peak at some value of the scaled amplitude A', so long as n is not equal to 1. For $n>1$ the force of friction will increase with increasing amplitude, reducing the slippage. This is illustrated in Fig. 2, where v_2 is plotted as a function of v_1 for both $n=0.1$ and 3, for A' less than and greater than the peak amplitude. After a short transient, the film settles into regular periodic (i.e., nonchaotic motion). From these figures it is apparent that v'' will be much less than v_1'' whenever $n>1$ and A' is to the right of the $\delta(Q^{-1})$ versus A' peak, or $n<1$ and A' is to the left of this peak. Since v_1 is of the order of ωA, then $\dot{v}''$ is small compared to ω^2A. For this case we therefore expect that in the asymptotic large amplitude limit [i.e., on the high amplitude side of the $\delta(Q^{-1})$ versus A' peak], we can neglect $\dot{v}''$ in Eq. (5). We then obtain $v''^n\approx(2\pi)^2A'\cos(2\pi t')$ and hence

$$Q^{-1}\approx A^{-(1-1/n)}\ , \tag{8}$$

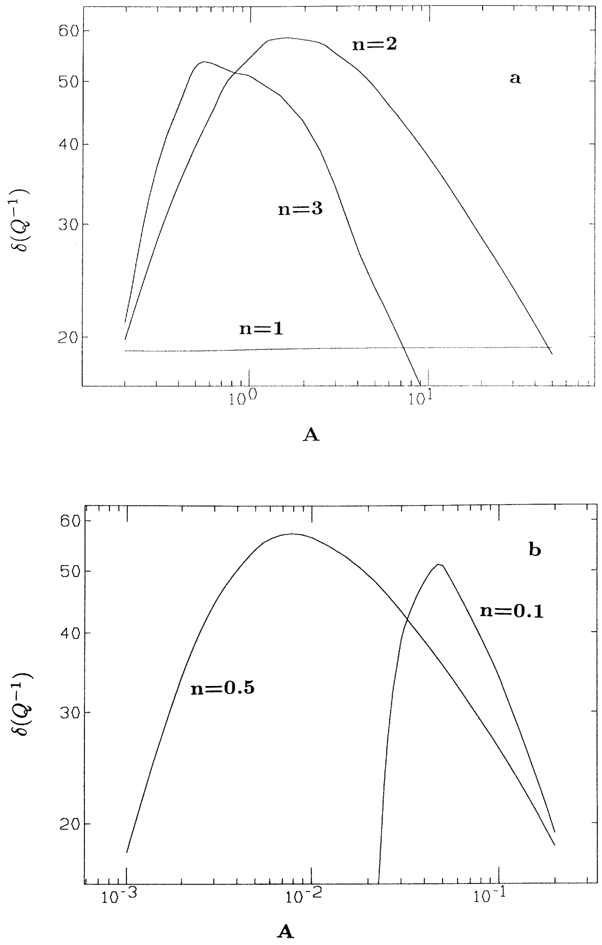

FIG. 1. The shift in the inverse $Q[\delta(Q^{-1})]$ is plotted on a log-log scale as a function of the amplitude in dimensionless units (a) for $n=1$, 2, and 3, and (b), for $n=0.1$ and 0.5.

implying that $\delta(Q^{-1})$ will always fall to zero as a power smaller than 1. This relationship can be used to determine n.

Because of the peak in the plot of $\delta(Q^{-1})$ versus A', if we observe in an experiment that $\delta(Q^{-1})$ decreases as some parameter (e.g., the pressure) is changed for fixed amplitude A, this might imply either a smaller or larger friction parameter γ, depending on which side of the peak the measurements were recorded, and on whether n is greater than or less than 1. In order to determine whether n is greater than or less than 1, the amplitude dependence of the frequency shift must be examined. On the basis of the calculations shown in Fig. 2, if n is greater than 1, it should increase (i.e., there should be less slippage) as the amplitude increases. The reverse is true if n is less than 1.

Then, for example, if $n > 1$ and we know that we are on the right of the peak and $\delta(Q^{-1})$ is observed to decrease as a certain parameter is changed for fixed amplitude and frequency, the peak location must have moved to lower amplitude, implying that l has decreased. From the definition of l under Eq. (4), we determine that γ must have increased. If n were less than 1, the reverse would be true. It appears as if microbalance measurements made to date have been done on the high amplitude side of the peak since $\delta(Q^{-1})$ decreases as A increases,[9] associated with very slight increases in the frequency shift. (Unfortunately, the data in that experiment were not precise enough to determine the precise value of n, but further experiments are planned with a goal of extracting the value of n.)

The dependence of the location of the peak in the $\delta(Q^{-1})$ versus ω curve for fixed A on Γ will now be studied using the same scaling arguments as used above in Eq. (6) to determine the dependence of the location of the peak in the $\delta(Q^{-1})$ versus A curve for fixed ω on Γ. The value of the amplitude at which the peak occurs (A_0) can be written as $A_0 = lA'_0$ where A'_0 is the value of the amplitude at which the peak occurs in scaled variables. Then, substituting the expression above Eq. (6) for the dependence of l on ω and Γ in this expression and solving for ω, we obtain for ω_0 the value of ω at which the peak

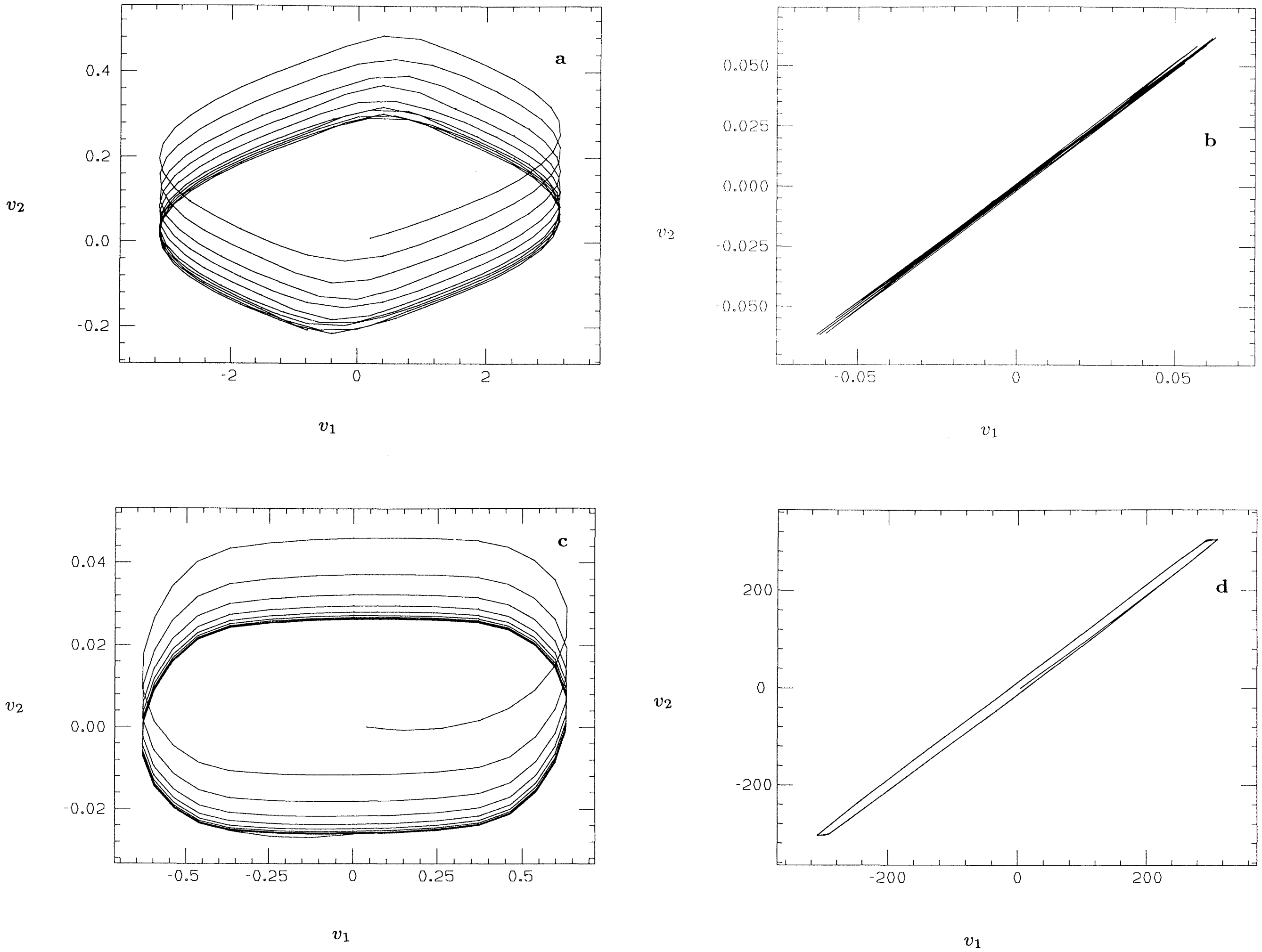

FIG. 2. The film velocity v_2 is shown as a function of the substrate velocity v_1 for (a) $n = 0.1$ and $A' = 0.5$, (b) $n = 0.1$ and $A' = 0.01$, (c) $n = 3$ and $A' = 0.1$, and (d) $n = 3$ and $A' = 50.0$.

in the $\delta(Q^{-1})$ versus ω curve occurs:

$$\omega_0=(A_0'/A_0)^{(n-1)/(n-2)}\Gamma^{-(n-1)} . \tag{9}$$

Thus, for $n>2$, the peak moves to smaller ω as Γ increases, and for $n<2$, it moves to larger ω. Hence, for $n>2$, it makes no difference whether we study the velocity dependence of $\delta(Q^{-1})$ by varying ω or A, but for n between 1 and 2 there is a difference.

We have developed a framework for extracting information about the strength and velocity dependence of the frictional force acting on a film adsorbed on a quartz-crystal microbalance. The method involves measurements of the amplitude and frequency dependencies of shifts in the inverse Q and the frequency due to the presence of the film, and avoids any assumption of a linear friction law. The technique proposed in this paper will allow one to obtain precise information about kinetic friction at the microscopic scale.

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[1] G. Binning, C. F. Quante, and C. Gerber, Phys. Rev. Lett. **56**, 630 (1986); J. B. Pethica, *ibid.* **57**, 3235 (1986).

[2] C. Mathew Mate, C. M. McClelland, R. Erlandsson, and S. Chiang, Phys. Rev. Lett. **59**, 1942 (1987).

[3] R. Erlandsson, G. Hadziioannou, C. M. Mate, G. M. McClelland, and S. Chiang, J. Chin. Phys. **89**, 5190 (1988).

[4] G. Neubauer, S. R. Cohen, G. McClelland, D. Horne, and C. M. Mate, Rev. Sci. Instrum. (to be published).

[5] N. A. Burnham, D. D. Dominguez, R. L. Mowery, and R. J. Colton, Phys. Rev. Lett. **64**, 1931 (1990); U. Landman, W. D. Luetke, N. A. Burnham, and R. J. Colton, Science **248**, 454 (1990); N. A. Burnham and R. J. Colton, J. Vac. Sci. Technol. A 7, 2906 (1990).

[6] J. N. Israelachvili, P. M. McGuiggan, and A. M. Homola, Science **240**, 189 (1988).

[7] J. Van Alsten and S. Granick, Phys. Rev. Lett. **61**, 2570 (1988).

[8] M. Hirano, K. Shinjo, R. Kaneko, and Y. Murata, Phys. Rev. Lett. **67**, 2642 (1991).

[9] J. Krim, R. Chiarello, and D. H. Solina, Phys. Rev. Lett. **66**, 181 (1991).

[10] E. T. Watts, J. Krim, and A. Widom, Phys. Rev. B **41**, 3466 (1990).

[11] J. Krim and A. Widom, Phys. Rev. B **38**, 12 184 (1988).

[12] C. Liu and A. W. Czanderna, *Applications of Piezoelectric Quartz Microbalances* (Elsevier, New York, 1984).

[13] M. O. Robbins (unpublished).

[14] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Addison-Wesley, Reading, MA, 1959), p. 89.