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Damping of a crystal oscillator by an adsorbed monolayer and its relation to interfacial viscosity

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The acoustic impedance of a monolayer adsorbed on the surface of a resonating quartz microbalance produces a shift in both the frequency and vibrational amplitude of the oscillator. The relation between acoustic impedance and fluctuations in film momentum is rigorously derived via the fluctuation-dissipation theorem within the context of two-dimensional fluid mechanics. The calculations reveal that the film-substrate interfacial viscosity can be deduced from measurements of acoustic impedance.

I. INTRODUCTION

Interfacial viscosity at a film-substrate boundary is a subject which at present is highly undeveloped. Measurements of this property would provide valuable information relevant to a variety of topics, including fractal and dendritic film growth,[1] bulk fluid flow and slip near solid boundaries,[2] phase transitions in adsorbed films,[3] and the study of adsorbed monolayers on liquid surfaces.[4] The problem of how to measure interfacial viscosity in a quantitative manner has remained long unsolved. In the following we will show how this property can be deduced from the impedance which an adsorbed film presents to the surface electrodes of an oscillating quartz microbalance.

It is well established that the frequency shift of a quartz crystal microbalance provides a measure of the adsorbed mass on its surface.[5] For thin, rigidly adhering films on transverse-shear-mode crystals, there is a linear relation between the frequency shift δf and the mass of the adsorbed film m_f,

$$\frac{\delta f}{f} = -\frac{m_f}{M_q}, \tag{1}$$

f is the resonant frequency and M_q is the mass of the quartz oscillator. The assumption that an adsorbed monolayer film is rigidly attached to the motion of the quartz crystal is an excellent one. Even so, a small degree of "slippage" must in principle occur on account of the oscillatory nature of the substrate. If the slippage can be detected, the interfacial viscosity can be deduced. Previous experimental efforts to measure "surface viscosities" of adsorbed monolayers[4] have encountered major difficulties involving the separation of the interfacial viscosity, or "substrate drag" contribution, from the "in-layer" two-dimensional shear viscosity. Such difficulties do not arise for films adsorbed on transverse-shear-mode oscillators since the adsorbed film itself does not undergo shear.

A complete treatment of the problem requires a theoretical computation of the dynamic acoustical impedance that the film presents to the transverse shear mode of the oscillator. Such calculations have been carried out previously for three-dimensional fluids[6] and thick adsorbed films.[7] In these calculations the impedance was derived from the Navier-Stokes relation assuming no slippage occurs at the substrate surface. Such an approach is inadequate for adsorbed monolayers where the fluid mechanics require a two-dimensional treatment.

In the following we will employ two-dimensional film fluid mechanics to explore the acoustic impedance presented by an adsorbed film to an oscillating quartz microbalance. We will show how the interfacial viscosity can be deduced from measurements of acoustic impedance and relate these results to characteristic decay times for film momentum fluctuations, as presented in a recent publication.[8]

II. FLUID-DYNAMIC MODEL OF TWO-DIMENSIONAL FILM FLOW

The equation of motion for two-dimensional film flow can be written in terms of a gradient in the two-dimensional spreading pressure ϕ and a viscous force $\beta \mathbf{v}_f$ which is directly proportional to the surface velocity $\mathbf{v}_f$ of the adsorbed film,[9]

$$m_f(d\mathbf{v}_f/dt) = -A_f \operatorname{grad}\phi - \beta \mathbf{v}_f \ . \tag{2a}$$

Dividing by the film area A_f one obtains

$$\rho_2(d\mathbf{v}_f/dt) = -\operatorname{grad}\phi - \eta_2 \mathbf{v}_f \ , \tag{2b}$$

where η_2 is the interfacial viscosity and ρ_2 is the mass per unit area of the adsorbed film.

Equation (2b) has widespread application to two-phase fluid films and flows exhibiting fractal behavior. In such cases it is commonly assumed that a balance exists between the viscous forces and pressure forces so that

$$\operatorname{grad}\phi = -\eta_2 \mathbf{v}_f \ . \tag{3}$$

Equation (3) is known as Darcy's law, describing the constant velocity flows observed at the boundaries separating two adsorbed film phases.[1]

Equation (2b) is also applicable to the case which we consider here, a single-phase adsorbed film. Neglecting boundary effects, Eq. (2b) implies

$$\int dA\,\rho_2(d\mathbf{v}_f/dt)=-\int dA\,\eta_2\mathbf{v}_f\ . \tag{4}$$

In the following sections we will consider how η_2 can be probed via the acoustic impedance which the film presents to a resonating quartz oscillator. Our central result will be

$$\eta_2=\frac{\rho_2}{\tau}\ , \tag{5}$$

where the "slip time" τ is a relaxation time associated with film-momentum fluctuations. It will be instructional to first describe the shear impedance which a bulk fluid presents to a resonating surface.

III. ACOUSTIC IMPEDANCE OF A THREE-DIMENSIONAL FLUID

The acoustic impedance of a three-dimensional viscous fluid to shear-mode oscillations of a planar surface has received extensive treatment within the realm of ultrasonics. In this section we will summarize the major points in order to draw later analogy with the two-dimensional case.

Oscillations of a planar surface ca be related to the oscillations of a mass M_m suspended from some fixed support by a spring having compliance C_m and subjected to some light damping force $R_m v$, which is proportional to the velocity v.[10] If a periodic force $F=F_0\cos(\omega t)$ is applied to the mass, the latter experiences forced oscillations of that frequency and the equation of motion is

$$F_0\cos(\sigma t)=M_m\frac{d^2x}{dt^2}+R_m\frac{dx}{dt}+\frac{x}{C_m}\ . \tag{6}$$

Under steady conditions the velocity at a given time will be

$$v=\frac{F}{R_m-i(\omega M_m-1/\omega C_m)}\ , \tag{7}$$

and the velocity amplitude is given by

$$v_0=\frac{F_0}{[R_m^2+(\omega M_m-1/\omega C_m)^2]^{1/2}}\ . \tag{8}$$

Equations (6)–(8) are identical in form with those which represent an electric circuit composed of a resistance R, a capacitance C, and an inductance L in series with an alternating emf V. The ratio

$$Z_m=F/v \tag{9}$$

is consequently termed the "mechanical impedance," and may be written as

$$Z_m=R_m-iX_m\ . \tag{10}$$

It can be shown that the "mechanical resistance" R_m is proportional to average energy dissipation per unit time $\dot{E}$,

$$R_m\propto\dot{E}\ . \tag{11}$$

The mechanical reactance

$$X_m=(\omega M_m-1/\omega C_m) \tag{12}$$

is associated with the inertia of the oscillator. The "mechanical Q factor" is analogous to the electrical Q factor

$$Q_m=\frac{\omega M_m}{R_m},\quad Q_e=\frac{\omega L}{R}\ . \tag{13}$$

It is within this framework that shear oscillations of a planar surface in contact with a viscous fluid (gas or liquid) are generally studied.[11] For a plane oscillating in the x direction with velocity $v_0\cos(\omega t)$, the motion of the surrounding fluid obeys the classical Navier-Stokes relation

$$\rho_3\frac{\partial v_x}{\partial t}=\eta_3\frac{\partial^2 v_x}{\partial z^2}\ , \tag{14}$$

where ρ_3 is the three-dimensional mass density of the fluid and η_3 is the bulk fluid viscosity. The mechanical impedance of the fluid to shear oscillations is generally expressed as $Z_m=Z_3A$, where Z_3 is the mechanical impedance per unit area, or "acoustical shear impedance," and A is the surface area in contact with the fluid. The solution to Eq. (4) yields the classical shear impedance of the fluid,

$$Z_3=R_3-iX_3=(1-i)\sqrt{\pi f\rho_3\eta_3}\ , \tag{15}$$

where f is the frequency of oscillation. The average energy dissipated by the fluid per unit time is

$$\dot{E}=\tfrac{1}{2}v_0^2AR_3\ . \tag{16}$$

Equation (15) is inadequate to describe the actual impedance of a gas at low pressure. After gas molecules collide with the oscillating surface, they may rebound with a nonequilibrium component of translational momentum P_x^*. Such molecules can only relax to the equilibrium state by collision with other gas molecules, and this process takes time. If the time taken is commensurate with the period of oscillation, then the gas exhibits a finite unrelaxed shear modulus and behaves as a viscoelastic fluid. This situation is treated phenomenologically by replacing the viscosity η_3 with a complex quantity η_3^* defined by

$$\eta_3^*=\eta_3\left[\frac{1}{1-i\omega\tau_r}\right]\ , \tag{17}$$

where τ_r is the time for the excess particle momentum to relax to $1/e$ of its initial equilibrium value. Substitution of Eq. (17) into the equation of motion for the fluid results in modified expressions for the acoustic impedance of the viscoelastic gas,

$$R_3^*=\sqrt{\pi f\rho_3\eta_3}\left\{\frac{\omega\tau_r}{1+(\omega\tau_r)^2}\left[\left[1+\frac{1}{(\omega\tau_r)^2}\right]+1\right]\right\}^{1/2}\ , \tag{18}$$

$$X_3^* = \sqrt{\pi f \rho_3 \eta_3} \left\{ \frac{\omega\tau_r}{1+(\omega\tau_r)^2} \left[\left[1+\frac{1}{(\omega\tau_r)^2} \right]^{1/2} - 1 \right] \right\}^{1/2} . \tag{19}$$

Equations (18) and (19), derived by Stockbridge,[12] are essentially identical to those derived earlier by Herzfeld and Litovitz[13] for liquids with a complex shear modulus.

It is useful to take the ratio R_3^*/X_3^* which may be thought of as a "dissipation per unit mass." For small $\omega\tau_r \ll 1$ this ratio reduces to

$$\frac{R_3^*}{X_3^*} = 1+\omega\tau_r \ . \tag{20}$$

The term $\omega\tau_r$ may therefore be interpreted as the "excess dissipation per unit mass" arising on account of momentum-relaxation effects.

IV. ACOUSTIC IMPEDANCE OF AN ADSORBED FILM

A. General considerations

We now consider the case of a film adsorbed on a planar surface oscillating in the x direction with velocity $v_0\cos(\omega t)$. The classical shear impedance presented by the film is denoted

$$Z_2 = R_2 - iX_2 = 0 - i\omega\rho_2 \ . \tag{21}$$

That $R_2 = 0$ implies the film is rigidly attached to the surface and dissipates no energy. The reactive term $X_2 = \omega\rho_2$ is obtained in analogy with Eq. (12), remembering that $Z_m = Z_2 A$.

The case of a rigidly attached film is in fact an approximation to the true physical situation. Consider a film adsorbed on a substrate which is moving at constant velocity. If the substrate suddenly stops, the velocity (and therefore momentum) of the film will fall exponentially to zero. The time constant τ for this exponential decay will depend on the friction between the film and the substrate, and may be thought of as a characteristic "slip time," i.e., a characteristic length of time that the film slips before stopping. Equation (21) will therefore be an adequate approximation only if the period of oscillation remains much longer than τ. When τ becomes comparable to the period of oscillation, film slippage will start to become observable. To convince oneself that this is indeed the case, one need only think of a tablecloth being snapped out from underneath a table setting. We write, in analogy with Eqn. (20), an expression which reflects momentum relaxation effects, yet yields the classical result for $\tau = 0$,

$$\frac{R_2^*}{X_2^*} = \omega\tau \ . \tag{22}$$

In the following we will rigorously derive this rather phenomenological result which relates film momentum fluctuations τ to film dissipation R_2^*. The fluctuation-dissipation theorem[14] has not, to our knowledge, been applied to acoustic impedance in the standard literature. We take this opportunity to derive the results in completely quantum-mechanical form.

B. Quantum-mechanical derivation

Consider once more a film which is adsorbed on a planar substrate which is oscillating back and forth in the x direction with velocity $v_x = v_0\cos(\omega t)$. What will be (to lowest-order perturbation theory) the rate at which the "shaking" heats up the film? This heating rate is equal in magnitude to $\dot{E}$, the rate at which the film dissipates energy. The quantum-mechanical expression for the heating rate yields a rigorous expression for the real part of the acoustic impedance. A dispersion relation can then be employed to obtain both the resistive and reactive parts of the full impedance.

Let H represent the Hamiltonian for the film when the substrate is *not* shaking back and forth. The film is then described by the quantum states

$$H|n\rangle = E_n|n\rangle \ . \tag{23}$$

When the substrate moves at velocity v_x the film Hamiltonian reads

$$\mathcal{H} = H - v_x P_x \ . \tag{24}$$

To lowest-order perturbation theory, Eq. (24) implies transitions at a rate

$$W^+(i \mapsto f) = \left[\frac{\pi v_0^2}{2\hbar^2} \right] |\langle f|P_x|i\rangle|^2 \delta(\omega - (E_f - E_i)/\hbar) \ , \tag{25}$$

which increase the film energy, and transitions at a rate

$$W^-(i \mapsto f) = \left[\frac{\pi v_0^2}{2\hbar^2} \right] |\langle f|P_x|i\rangle|^2 \delta(\omega + (E_f - E_i/\hbar) \ , \tag{26}$$

which decrease the film energy. Because the film is in an initial state with probability

$$p_i = \exp(F - E_i)/k_B T \ , \tag{27}$$

there will be an averaged heating rate in the film of

$$\dot{E} = \sum_i p_i \sum_f (E_f - E_i)[W^+(i \mapsto f) - W^-(i \mapsto f)] \ . \tag{28}$$

Introducing the spectral functions

$$S^+(\omega) = \sum_i \sum_f p_i |\langle f|P_x|i\rangle|^2 \delta(\omega - (E_f - E_i)/\hbar) \ , \tag{29}$$

$$S^-(\omega) = \sum_i \sum_f p_i |\langle f|P_x|i\rangle|^2 \delta(\omega + (E_f - E_i)/\hbar) \ , \tag{30}$$

Eqs. (28)–(30) read as

$$\dot{E} = \left[\frac{\pi v_0^2}{2\hbar} \right] \omega[S^+(\omega) - S^-(\omega)] \ . \tag{31}$$

Equations (27), (29), and (30) imply that the transition rates for film cooling are smaller than the transition rates for film heating by precisely the Boltzman factor

$$S^-(\omega) = e^{-(\hbar\omega/k_B T)} S^+(\omega) \ . \tag{32}$$

Introducing the symmetric spectral function

$$S(\omega)=\tfrac{1}{2}[S^{+}(\omega)+S^{-}(\omega)] \ , \tag{33}$$

Eqs. (31)–(33) imply an average heating rate of

$$\dot{E}=\left[\frac{\pi v_0^2}{\hbar}\right]\omega S(\omega)\tanh\left[\frac{\hbar\omega}{2k_BT}\right] . \tag{34}$$

From the viewpoint of acoustic resistance

$$R_2^*(\omega)=\mathrm{Re}Z_2^*(\omega+i0^+) \ , \tag{35}$$

the heating rate for velocity amplitude v_0 of the substrate, and adsorbed film area A is given by Eq. (16),

$$\dot{E}=\tfrac{1}{2}AR_2^*(\omega)v_0^2 \ . \tag{36}$$

By comparing the macroscopic Eq. (36) for the heating rate to the microscopic Eq. (34), one finds the Callen-Welton-Kuba fluctuation-dissipation theorem for acoustic resistance in completely quantum-mechanical form,

$$AR_2^*(\omega)=\left[\frac{2\pi}{\hbar}\right]\omega\tanh\left[\frac{\hbar\omega}{2k_BT}\right]S\omega) \ . \tag{37}$$

To relate $S(\omega)$ to momentum fluctuations in the film when the substrate is *not* oscillating, one may proceed in the following manner. From Eq. (29),

$$\int_{-\infty}^{+\infty}S^{+}(\omega)e^{-i\omega t}d\omega = \sum_i\sum_f p_i|\langle f|P_x|i\rangle|^2 e^{-i(E_f-E_i)t/\hbar} \ , \tag{38}$$

$$\int_{-\infty}^{+\infty}S^{+}(\omega)e^{-i\omega t}d\omega = \sum_i\sum_f p_i\langle i|P_x(t)|f\rangle\langle f|P_x(0)|i\rangle \ , \tag{39}$$

$$\int_{-\infty}^{+\infty}S^{+}(\omega)e^{-i\omega t}d\omega=\langle P_x(t)P_x(0)\rangle \ . \tag{40}$$

Similarly,

$$\int_{-\infty}^{-\infty}S^{-}(\omega)e^{-i\omega t}d\omega=\langle P_x(0)P_x(t)\rangle \ . \tag{41}$$

Equations (33), (37), (40), and (41) yield the Kubo formula for acoustic resistance in completely quantum-mechanical form,

$$AR_2^*(\omega)=\left[\frac{1}{2\hbar}\right]\tanh\left[\frac{\hbar\omega}{2k_BT}\right] \times\omega\int_{-\infty}^{+\infty}dt\,\cos(\omega t)\langle P_x(0)P_x(t) + P_x(t)P_x(0)\rangle \ . \tag{42}$$

Defining

$$k_BTA\rho_2G(t)=\tfrac{1}{2}\langle P_x(0)P_x(t)+P_x(t)P_x(0)\rangle \tag{43}$$

as the quantum-mechanical correlation function of momentum fluctuations for a film with mass density ρ_2, Eq. (42) can be written as

$$R_2^*(\omega)=k_BT\left[\frac{2\rho_2}{\hbar}\right]\omega\tanh\left[\frac{\hbar\omega}{2k_BT}\right]\int_0^{\infty}dt\,\cos(\omega t)G(t) \ , \tag{44}$$

which is the rigorously exact microscopic expression for acoustic resistance of an adsorbed film. In the classical limit $\hbar\omega \ll k_BT$, it is sufficiently accurate to write Eq. (44) in the form

$$R_2^*(\omega)=\rho_2\omega^2\int_0^{\infty}dt\,\cos(\omega t)G(t) \ . \tag{45}$$

Both the reactive and resistive components of the acoustic impedance may be obtained by expressing the impedance in terms of a complex frequency ζ, and then taking the limit of real frequency ω,

$$Z_2^*(\zeta)=Z_2^*(\omega+i0^+)=R_2^*(\omega)-iX_2^*(\omega) \ . \tag{46}$$

The complete acoustic impedance obeys the Kubo formula

$$Z_2^*(\zeta)=(i\zeta\rho_2)\int_0^{\infty}e^{i\zeta t}dG(t) \ , \tag{47}$$

and is determined by the acoustic resistance via the dispersion relation

$$Z_2^*(\zeta)=-i(2\zeta/\pi)\int_0^{\infty}\frac{R_2^*(\omega)}{(\omega^2-\zeta^2)}d\omega \ . \tag{48}$$

The correlation function $G(t)$ is directly proportional to the excess film momentum and therefore is directly proportional to $\int dA\, v_f$. Employing Eq. (4) and the normalization $G(0)=1$, we may write

$$\rho_2\,dG_D(t)/dt=-\eta_2G_D(t) \ , \tag{49}$$

or equivalently an exponential decay

$$G_D(t)=e^{-t/\tau} \tag{50}$$

with the correlation time $\tau=\rho_2/\eta_2$, thus confirming Eq. (5). Substitution of Eq. (50) into Eq. (47) allows the acoustic impedance to be expressed in terms of film momentum fluctuations,

$$Z_2^*(\omega+i0^+)=\frac{-i\rho_2\omega}{1-i\omega\tau} \ . \tag{51}$$

The resistive and reactive components of Z_2^* are

$$R_2^*=\frac{\rho_2\omega^2\tau}{1+\omega^2\tau^2} \ , \tag{52}$$

$$X_2^*=\frac{\rho_2\omega}{1+\omega^2\tau^2} \ . \tag{53}$$

The ratio $R_2^*/X_2^*=\omega\tau$ confirms our phenomenological result, Eq. (22).

V. DAMPING OF A QUARTZ MICROBALANCE

In this section we discuss how the acoustic impedance is measured via the frequency and amplitude shifts of a quartz crystal microbalance. The resistive and reactive components of the acoustic impedance of an adsorbed film [Eqs. (52) and (53)] are plotted in Fig. 1 as functions of $\omega\tau$. The upper diagram shows $X_2^*/X_2=X_2^*/\rho_2\omega$, a ratio indicative of the mass sensitivity of the oscillator. Essentially all of the mass of the film is detected for $\omega\tau<0.1$, where X_2^*/X_2 is quite close to unity. This is referred to as the "motionally narrowed regime." As $\omega\tau$ increases beyond 0.1, the mass sensitivity drops precipitously. The oscillator is no longer useful as a microbalance in this regime, as the film is no longer able to track the motion of the substrate.

The dissipative term R_2^*/X_2 is plotted in the lower portion of Fig. 1. This term is nearly equal to $\omega\tau$ in the motionally narrowed regime and reaches a maximum at $\omega\tau=1$. As $\omega\tau$ further increases the dissipation decreases. This latter result indicates that the film is no longer shaking and, as a result, does not dissipate energy. In order to measure both mass adsorption and dissipation effects, data must therefore be recorded in the motionally narrowed regime, $\omega\tau<0.1$.

Stockbridge[9] has solved for the shifts in frequency and Q of a quartz crystal microbalance in terms of the acoustic impedance Z^* presented to an oscillating planar surface. For film adsorption on, or fluid exposure to *one side only,*

$$\delta\left[\frac{1}{Q}\right]=\frac{2R^*}{\omega\rho_q t_q}\ , \tag{54a}$$

$$\delta\omega=\frac{X^*}{\rho_q t_q}\ , \tag{54b}$$

where ρ_q and t_q are the density of quartz and the thickness of the quartz crystal, respectively. For film or fluid exposure *on both sides,*

$$\delta\left[\frac{1}{Q}\right]=2\left[\frac{2R^*}{\omega\rho_q t_q}\right]\ , \tag{55a}$$

$$\delta\omega=2\left[\frac{X^*}{\rho_q t_q}\right]\ . \tag{55b}$$

Dividing Eq. (55a) by Eq. (55b),

$$\frac{\delta(1/Q)}{\delta\omega}=\left[\frac{2R^*}{\omega\rho_q t_q}\right]\Big/\left[\frac{X^*}{\rho_q t_q}\right]=\frac{2R^*}{\omega X^*}=2\tau\ , \tag{56a}$$

$$\delta\left[\frac{1}{Q}\right]=2\tau\delta\omega\ . \tag{56b}$$

Equation (56b) is the primary result of our earlier work.[4] Simultaneous measurement of quality factor and frequency shift will therefore allow determination of τ. The interfacial viscosity η_2 is obtained from Eq. (5), where ρ_2 is the mass per unit area of the films as determined by Eq. (1),

$$\frac{\delta f}{f}=-\frac{m_f}{M_q}=-\frac{\rho_2}{\rho_q t_q}\ . \tag{57}$$

Equation (57) corresponds to film adsorption on one side only. When adsorption occurs on both sides of the crystal, the term on the far right must be multiplied by a factor of 2.

As a final note, we describe a situation which is typical for these types of measurements. A quarts crystal whose resonant frequency is 8 MHz and which is driven by a conventional Pierce oscillator circuit[15] is typically stable to ±0.1 Hz for a period of several hours to several days. Changes in dissipation $\delta(1/Q)\geq 1\times10^{-8}$ are easily detectable. A monolayer of krypton ($\rho_2\approx 105$ ng/cm^2) adsorbed on both sides of the crystal will produce a frequency shift of 30 Hz ($\delta\omega=188.4$ rad/sec). We employ Eq. (56b) to predict the minimum slip time which will be observable,[16]

$$\tau_{\min}=\frac{\delta(1/Q)_{\min}}{2\delta\omega}=\frac{1\times10^{-8}}{2(188.4\,\mathrm{sec}^{-1})}=2.6\times10^{-11}\,\mathrm{sec}\ . \tag{58}$$

Our work has in fact been inspired by experimental observations of the damping of quartz oscillators by physi sorbed monolayers.[3] Krypton monolayers adsorbed on gold at 77 K exhibit slip times on the order of 1×10^{-9} sec, the exact time depending on the manner in which the substrate is prepared. Equation (5) allows us to deduce an interfacial viscosity near 100 g/s cm^2, or "surface poise" per unit area. The complete experimental details will be published in a future work.

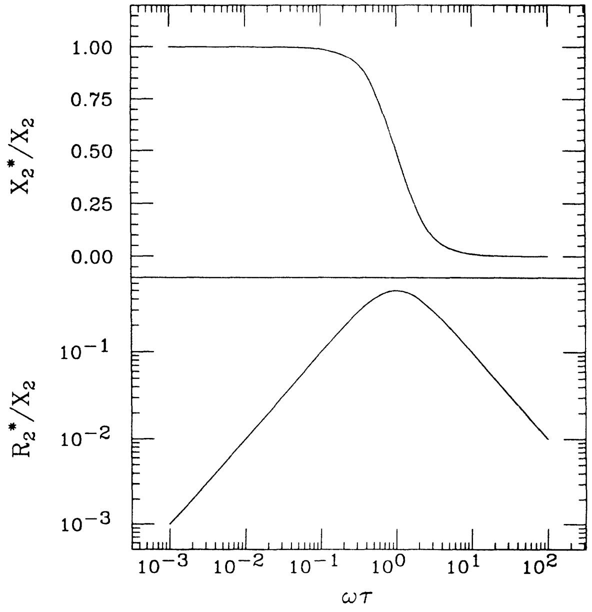

FIG. 1. Acoustic impedance of an adsorbed film. The reactive component X_2^*/X_2 is indicative of mass sensitivity. The resistive component R_2^*/X_2 is proportional to energy dissipation. All quantities are unitless.

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[16] We have been conservative in making this estimate. The actual minimum will depend on overall crystal stability.