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Measurement of the friction of thin films by means of a quartz microbalance in the presence of a finite vapor pressure

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In recent years, the quartz-crystal microbalance technique (QCM) has been succesfully applied to the field of nanotribology. In this paper we examine the effect of a finite vapor pressure on the accuracy of thin-film friction measurements taken with a QCM by solving the Navier-Stokes equation of the combined system quartz-crystal-adsorbed film-bulk vapor. We also discuss the details of the calibration procedure of the QCM carried out at both room temperature and low temperature, and describe the data acquisition and analysis specific to tribological applications. Finally, we present some preliminary data of the friction of a Kr monolayer adsorbed on gold at low temperatures that show the sliding of the film.

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I. INTRODUCTION

The field of nanotribology, which studies the friction of nanoscale objects sliding on a surface, has developed considerably over the past few years.[1] Many experimental techniques have been successfully applied in this area: surface force apparatus[2], atomic force microscopy,[3] and quartz-crystal microbalance (QCM).[4]

Hereafter, we deal with the QCM technique, which was first employed to study the interfacial viscosity of thin films in equilibrium with a bulk vapor by Watts *et al*.[5] Several studies have already been published on the acoustic behavior of a quartz surrounded by a fluid.[6] In particular, Lea and Fozooni analyzed the response of a quartz immersed in a vapor and covered with a film locked to the substrate.[7] Krim and Widom investigated the same system, taking into account the possibility of interfacial slippage at the solid surface, and derived a formula for the friction of a thin film as measured by the QCM.[8] The analysis of the acoustic response of a quartz crystal immersed in a liquid incorporating interfacial slip was also studied.[9] In this paper we instead examine the effect of a finite vapor pressure on the accuracy of thin film friction measurements taken with a QCM by solving the Navier-Stokes equation of the combined system quartz crystal-adsorbed film-bulk vapor. Our results are identical with previously published analyses when the adsorbed film is locked to the substrate. However, they disagree with the formulas heuristically derived in the case of slippage of the film at the solid boundary when the effect of the vapor in equilibrium with the film cannot be neglected.

This paper is organized as follows. We first discuss the solution of the linearized Navier-Stokes equation, describing an adsorbed film in equilibrium with a bulk vapor, with a detailed discussion of the boundary conditions applied at the various interfaces. These results are then compared with the existing formulas. We then discuss a general data analysis procedure based on the formulas just derived, that allows a simultaneous determination of the thickness and of the interfacial friction of the adsorbed film from the key parameters of the quartz resonator. We have measured these quantities with a frequency-modulation technique. In Sec. III, we briefly present such a technique, focusing on the corrections that must be done on the measured quantities derived by a careful analysis of the circuit. As a check of the validity of our data acquisition and analysis procedure, we have decided to evaluate the vapor contribution in the absence of adsorption. The standard treatment of this contribution is that proposed by Stockbridge,[10] who introduced a phenomenological relaxation time which depends on the gas. The good agreement found between our results and those published in the literature is a guarantee of the reliability of our method. Finally, we present some preliminary data of the friction of a Kr monolayer adsorbed on gold at low temperatures that show sliding of the film.

II. ACOUSTICAL THEORY OF THE QUARTZ OSCILLATOR

A. Determination of the total acoustic impedance

Let us consider an AT-cut quartz plate, which is characterized by a shear motion of its two parallel faces. Its mechanical resonances have frequencies $f_{0,\mathrm{n}}$ equal to odd multiples of $c/2\mathrm{t}$, where $n=1,3\ldots$ is the order of the resonance, c is the speed of sound of the quartz shear mode, and t is the thickness of the plate.

At a certain frequency f^*, its behavior in vacuum can be described by a complex acoustical impedance

$$Z_0 \equiv R_0 - jX_0 = R_0 - j\pi nAZ_q \frac{f^* - f_{0,n}}{f_0,n}, \tag{1}$$

where A is the area of one electrode, $Z_q = 8.862 \times 10^5$ g/cm^2 sec is the quartz acoustic impedance, and the dissipative term R_0, which accounts for all the losses in the plate, is related to the quality factor Q_0 via

$$\frac{1}{Q_0} = \frac{2R_0}{\pi nAZ_q}. \tag{2}$$

When the quartz plate is immersed in a fluid, its impedance will change because of the adsorption of a film onto the quartz surfaces and the viscous coupling with the surrounding vapor. The global contribution per unit area can be expressed in terms of a complex impedance $Z_{sfv}=R_{sfv}\text{-}X_{sfv}$, in series with Z_0. If both faces of the quartz plate are exposed to the fluid, the total dissipative and inertial terms become, R_0+2AR_{sfv} and $X_0+2AX_{sfv,}$ respectively. The quality factor will then decrease by an amount $\Delta(1/Q)$ equal to

$$\Delta\frac{1}{Q}\equiv\frac{1}{Q}-\frac{1}{Q_0}=\frac{4R_{sfv}}{\pi nZ_q}, \tag{3}$$

and the resonance frequency f will also be diminished by

$$\Delta f\equiv f-f_{0,n}=-2X_{sfv}\frac{f_{0,n}}{\pi nZ_q}. \tag{4}$$

The exact shifts will obviously depend on the explicit forms of R_{sfv} and X_{sfv}. In order to determine them, we apply the linearized Navier-Stokes equation to the combined system quartz crystal-adsorbed film-bulk vapor. Let d be the thickness of the adsorbed film and ρ_f and η_f its bulk mass density and viscosity, respectively, while η_v and ρ_v represent the viscosity and density of the bulk vapor. If we assume, as is customary, that the transverse velocity field depends only on the vertical distance z from the electrode surface, the general stationary solutions to the Navier-Stokes equations in the vapor and film regions are

$$\begin{aligned} v_f(z)&=Ae^{-(1-j)z/\lambda_f}+Be^{+(1-j)z/\lambda_f}, \quad 0<z<d,\\ v_v(z)&=Ce^{-(1-j)z/\lambda_v}+De^{+(1-j)z/\lambda_v} \quad d<z, \end{aligned} \tag{5}$$

where the quantities A–D are integration constants and $\lambda_{f,v}=\sqrt{\eta_{f,v}/\pi f\rho_{f,v}}$ are the viscous penetration depths in the film and vapor phases, respectively.

The four constants can be univocally determined by imposing the following boundary conditions on the velocity fields v_f and v_v: (a) $v_v=0$, very far from the film; (b) $v_v=v_f$ at the film-vapor interface (i.e., no slippage at this boundary); (c) at this interface, the force exerted by the vapor on the film must be equal to that caused by the film on the vapor, that is $\eta_v(dv_v/dz)_{z=d}=-\eta_f(dv_f/dz)_{z=d}$; and (d) we assume, in general, that there may be slippage at the solid-film interface. Because of this, there will be a frictional force F_{sf} at this boundary. As the last condition, we then impose that the force F_{sf} must be equal and opposite to that due to the film, that is $F_{sf}=+\eta_f(dv_f/dz)_{z=0}$. Finally, we make the plausible assumption that F_{sf} depends linearly on the relative velocity between the quartz plate and the film.

$$F_{sf}=-\eta_2[v_0-v_f(0)], \tag{6}$$

where η_2 is called the coefficient of the sliding friction or interfacial viscosity. This condition is consistent with recent QCM studies of the velocity dependence of η_2.[11]

The velocity profile in the film region can then be easily calculated to be

$$v_f(z)=v_0\frac{e^{-(1-j)z/\lambda_f}+\alpha e^{-(1-j)(2d-z)/\lambda_f}}{[1+\alpha e^{-2(1-j)d/\lambda_f}]+\dfrac{Z_f}{\eta_2}[1-\alpha e^{-2(1-j)d/\lambda_f}]}, \tag{7}$$

where $Z_f=(1-j)\sqrt{\pi f\eta_f\rho_f}$ is the complex acoustic impedance of a bulk system with the same density and viscosity as those of the adsorbed film, and $\alpha=(\mathcal{Z}_f-\mathcal{Z}_v)/(Z_f+Z_v)$, $Z_v\equiv R_v-jX_v=(1-j)\sqrt{\pi f\eta_v\rho_v}$ being the impedance of the bulk vapor, represents the acoustic mismatch between film and vapor.

The more general expression of the total acoustic impedance seen by the quartz Z_{sfv} is, by definition, equal to

$$Z_{sfv}\equiv\frac{F}{v_0}=-\frac{F_{sf}}{v_0}, \tag{8}$$

where we have exploited the fact that, in equilibrium, the driving force F must be equilibrated by the friction force F_{sf}.

From the previous three equations, it can be easily derived that the total quartz-film-vapor acoustic impedance is

$$Z_{sfv}=Z_f\frac{1-\alpha e^{-2(1-j)d/\lambda_f}}{[1+\alpha e^{-2(1-j)d/\lambda_f}]+\dfrac{Z_f}{\eta_2}[1-\alpha e^{-2(1-j)d/\lambda_f}]}. \tag{9}$$

As a check of the validity of the general expression [Eq. (9)], let us consider a few particular cases. First, we assume that there is no slippage at the solid-fluid interface, i.e., $\eta_2=\infty$. This implies that

$$Z_{sfv}=Z_f\frac{1-\alpha e^{-2(1-j)d/\lambda_f}}{1+\alpha e^{-2(1-j)d/\lambda_f}}\equiv Z_{fv}, \tag{10}$$

where the symbol Z_{fv} emphasizes that in this case the formula represents the contribution due to both film and vapor. This result coincides with that found by Lea and Fozooni, assuming the no-slip boundary condition.[7]

As another possibility, we consider the case when there is again no slippage at the solid boundary but also no vapor, i.e., $\eta_2=\infty$ and $\rho_v=0$. This implies that $Z_v=0$ and thus $\alpha=+1$. Equation (9) then becomes

$$Z_{sfv}=Z_f\frac{1-e^{-2(1-j)d/\lambda_f}}{1+e^{-2(1-j)d/\lambda_f}}\equiv Z_{fd}, \tag{11}$$

where the symbol Z_{fd} indicates that this corresponds to the acoustic impedance of a film of thickness d.

Finally, we assume that there is no adsorbed film but only vapor. Thus $\eta_2=\infty$ and $d=0$, and the total impedance reduces to

$$Z_{sfv}=Z_f\frac{1-\alpha}{1+\alpha}\equiv Z_v \tag{12}$$

as expected.

With these particular expressions, the reciprocal of Z_{sfv} can be easily rewritten as

$$\frac{1}{Z_{sfv}}=\frac{1}{Z_{fv}}+\frac{1}{\eta_2}, \tag{13}$$

which says that the total acoustic impedance Z_{sfv} of the combined system substrate-film-vapor can be considered as the parallel between the film-vapor impedance Z_{fv} and the impedance η_2 due to the slippage of the film at the solid boundary.

B. Determination of the interfacial viscosity

Formula (13) means that it is possible, at least in principle, to measure the friction force of a film adsorbed on a solid surface with a quartz microbalance. As such, it is a matter of course that the film-vapor contribution Z_{fv} must be determined very accurately.

Let us now analyze the term Z_{fd} given by Eq. (11). First of all, in the great majority of quartz microbalance applications, the adsorbed film thickness d is much smaller than the viscous penetration depth λ_f. For instance, for an Ar liquid film at 84 K, $\lambda_f=45$ nm even at a frequency of 30 MHz. Needless to say, this latter condition is even more satisfied if one is interested in the friction of an atomically thin film. This fact means that the acoustic impedance of the film can be simplified as

$$Z_{fd}\simeq -j\omega\rho_f d, \tag{14}$$

where $\omega=2\pi f$, a result already found in previous studies.[5,7]

Furthermore, in most applications, the condition $Z_v \ll Z_f$ is also well satisfied. For example, for the same Ar liquid film considered above, $Z_v=0.009\ Z_f$. As a consequence, the impedance Z_{fv} can be very well approximated by the sum

$$Z_{fv}\simeq Z_v+Z_{fd}, \tag{15}$$

where we have neglected terms of order $(Z_v/Z_f)^2$ and $(d/\lambda_f)^2$, and higher.

This formula implies that Eq. (13) can be rewritten as

$$\frac{1}{Z_{sfv}}=\frac{1}{Z_v+Z_{fd}}+\frac{1}{\eta_2}. \tag{16}$$

In other words, the contribution due to the interfacial viscosity is in parallel with the series of the vapor and of the film impedances. If we solve this equation in terms of R_{sfv} and X_{sfv} we obtain

$$\frac{X_{sfv}}{R_{sfv}^2+X_{sfv}^2}=\frac{\omega\rho_f d+X_v}{R_v^2+(\omega\rho_f d+X_v)^2} \tag{17}$$

and

$$\frac{R_{sfv}}{R_{sfv}^2+X_{sfv}^2}=\frac{R_v}{R_v^2+(\omega\rho_f d+X_v)^2}+\frac{1}{\eta_2}. \tag{18}$$

The first equation yields the film thickness d as

$$d=\frac{1}{2\omega\rho_f}\left[R_{sfv}^2+X_{sfv}^2+\sqrt{(R_{sfv}^2+X_{sfv}^2)^2-4R_v^2X_{sfv}^2}\right]-\frac{X_v}{\omega\rho_f}, \tag{19}$$

which can be substituted in the second equation in order to calculate the interfacial viscosity η_2.

Finally, the slip time τ_s, which represents the time required for the adsorbed film speed to decay to $1/e$ of its initial value after the oscillating substrate has been put to rest in the absence of a bulk vapor, can be calculated from the ratio[8]

$$\tau_s=\frac{\rho_f d}{\eta_2}. \tag{20}$$

These conclusions are in contrast with the formulas introduced heuristically by other authors,[5] according to which the vapor impedance is in series with the parallel of the film impedance and the interfacial viscosity, i.e.,

$$Z_{sfv}^{*}=Z_v+Z_{fd}\eta_2/(Z_{fd}+\eta_2). \tag{21}$$

In the limit of very low vapor density, the two approaches yield identical results. In the presence of a vapor, the slip time determined from the equivalent circuit of impedance Z_{sfv}^{*} is usually larger than that deduced from formula (16). As an example, for Kr vapor pressures below 1 Torr, the two approaches yield essentially the same results, while for pressures above 10 Torr this discrepancy can be as high as 15% or more, depending on the amount of sliding observed.

C. Determination of the vapor contribution

The quantities R_{sfv} and X_{sfv} in the previous equation can be obtained by the measured amplitude and frequency shifts of the quartz oscillator through Eqs. (3) and (4). Thus, in order to determine η_2, it is necessary to evaluate the vapor contribution accurately.

At high pressure, the vapor impedance has the well established expression $R_v=X_v=\sqrt{\pi f\eta_v\rho_v}$. At low pressure, the vapor behaves as a viscoelastic fluid, and starts to deviate from the behavior predicted by the high pressure impedance. Stockbridge proposed[10] that the viscosity of the vapor can be phenomenologically expressed as $\eta_v/(1+j\omega\tau_v)$, where τ_v is a characteristic relaxation time. According to this approach, the corrected vapor impedance becomes

$$Z_v=R_v-jX_v=\sqrt{\pi f\eta_v\rho_v}\,[F(\omega\tau_v)-jG(\omega\tau_v)], \tag{22}$$

where F and G are two scaling functions equal to[10]

$$F(\omega\tau_v)=\sqrt{\frac{\sqrt{1+\omega^2\tau_v^2}+\omega\tau_v}{1+\omega^2\tau_v^2}},$$

$$G(\omega\tau_v)=\sqrt{\frac{\sqrt{1+\omega^2\tau_v^2}-\omega\tau_v}{1+\omega^2\tau_v^2}}. \tag{23}$$

Besides this viscous coupling, there is an hydrostatic effect due to the compression of the quartz faces which causes an increase of the shear frequency. For an AT-cut plate, this contribution has been determined to be equal to[10]

$$\frac{\Delta f_{\text{hydro}}}{f} = +[(18.35-0.015)T]\times 10^{-10}P \equiv h_p P, \qquad (24)$$

where the pressure P is in units of Torr and the temperature T is in K.

The overall frequency shift caused by immersing an AT quartz plate in a vapor is therefore given by

$$\Delta f = \Delta f_{\text{hydro}} + \Delta f_{\text{viscous}} = h_p f P - \frac{2f}{nZ_q} G(2\pi f \tau_v)\sqrt{f\eta_v \rho_v/\pi}, \qquad (25)$$

which can be rewritten as

$$y \equiv \frac{\Delta f}{f} + \frac{2}{nZ_q} G(2\pi f \tau_v)\sqrt{f\eta_v k_v P/\pi} = h_p P, \qquad (26)$$

where we have used the fact that at low pressure the gas is ideal, i.e., $\rho_v = k_v P$. If we plot the scaled quantity y as a function of the vapor pressure P, the data should lie on a straight line passing through the origin and with slope equal to h_p.

The viscous coupling due to the presence of the vapor also causes a decrease in the quartz resonance amplitude A. The variation of $1/A$ can be associated to the variation in $1/Q$ and therefore, via Eq. (3), to

$$\Delta\frac{1}{A} = k_A \Delta\frac{1}{Q} = \frac{4k_A}{\pi n Z_q} R_v = K_A \sqrt{\pi f \eta_v \rho_v} F(2\pi f \tau_v), \qquad (27)$$

where K_A is a proportionality constant which must be determined experimentally.

III. EXPERIMENTAL SETUP

To measure the friction of atomically thin adsorbed films, we have mounted the quartz resonator in a double-wall copper cell to reduce thermal gradients. The entire setup was attached to the cold flange of an homemade liquid nitrogen cryostat. The maximum temperature difference between the top and bottom parts inside the inner copper cell was estimated to be less than 1 μK. The temperature stability was better than 1 mK. For further details about the cryogenics, see Ref. 12.

Close to resonance, the behavior of an AT quartz crystal can be accurately described by an equivalent circuit given by the parallel of a static capacitance C_0 with the series formed by the motional capacitance C_q, the motional inductance L_q, and a resistance R_q that determines the intrinsic Q factor of the crystal[13] (see Fig. 1). If R_q is small, the crystal exhibits a series resonance at

$$f_s = \frac{1}{2\pi}\frac{1}{\sqrt{L_q C_q}}$$

and a parallel resonance at

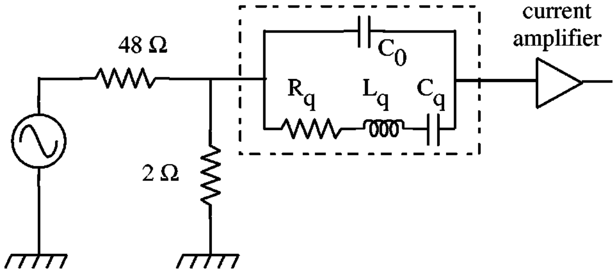

FIG. 1. Schematic diagram of the electric connection of the quartz crystal. The dashes enclose the equivalent circuit of an AT-cut quartz crystal.

$$f_p = \frac{1}{2\pi}\frac{1}{\sqrt{L_q C_p}},$$

where

$$C_p = \frac{C_0 C_q}{C_0 + C_q}$$

and

$$f_p - f_s \simeq \frac{f_s C_q}{2C_0}.$$

For the crystals employed in this study, such a difference amounted to about 11 KHz at the fundamental mode and to $\simeq$ 4 KHz at the third overtone.

To drive the QCM to its mechanical resonance, we have used a frequency modulation (FM) technique.[14] Such a technique locks the radio frequency generator onto a frequency $f_{\max}$ ($f_{\min}$) corresponding to the maximum (minimum) transmitted power through the quartz plate. It has been extensively applied in recent years to the study of the adsorption of light cryogenic gases on alkali metals[15] thanks to its wide flexibility and its easy control of the key parameters of the QCM. For example, one can easily choose which quartz resonance to follow: the series resonance f_s, that is very close to the locking frequency $f_{\max}$, or the parallel one f_p very near $f_{\min}$. Furthermore, the simplicity of the circuit (see Fig. 1) allows an accurate determination of f_s (f_p) from the measured values $f_{\max}$ ($f_{\min}$); see below. Another useful advantage of this FM technique is the possibility of working with any quartz resonance mode, fundamental or overtone. Finally, it is also possible to vary the rf power applied to the quartz crystal in a controlled way by simply changing the output power of the generator.

The circuit we have employed was fed by a high-stability commercial generator, model HP8648B. The signal across the quartz was amplified by an homemade rf amplifier specially designed to guarantee an output proportional to the square of the input signal, a feature particular important for the subsequent data analysis. This stage was formed by an operational amplifier followed by a multiplier. The resistance of 2 Ω was chosen to guarantee a low input impedance. The remaining electronic components forming this circuit are described in detail elsewhere.[16] Most of the data presented here, unless stated otherwise, were taken with an excitation power of about 10 nW. At this power level, the measured resonant frequency typically drifted by less than 0.1 Hz overnight with a 6-MHz quartz plate. The corresponding lateral displacement of the gold electrodes amounted to about 20 Å.[17]

Because of the presence of the static capacitance C_0, the two main quantities measured in the experiment, namely the frequency $f_{\max}$ and the amplitude $V_{\max}$ of the maximum transmitted signal, differ slightly from the series resonance frequency f_s and amplitude V_s. More precisely, f_s is a bit larger than $f_{\max}$. In the assumption of $Q \gg 1$, the series resonance f_s can be determined from the $f_{\max}$ value via the formula

$$f_s = \frac{f_{\max}}{1 - \frac{1}{2M}\left(\sqrt{1+\frac{M^2}{Q^2}} - 1\right)}, \tag{28}$$

where M is a figure of merit defined as $M = f_s/(f_p - f_s)$.

As a check of the validity of this expression, we can consider the two limiting cases corresponding to a very narrow series resonance, i.e., $Q=\infty$, and to a parallel resonance well above the series one, i.e., $M=0$. In both these situations, the above formula yields $f_s = f_{\max}$, as expected. This correction is in general not negligible when the overall frequency decrease corresponding to the adsorption of a film is small, and thus in the present study the measurements of $f_{\max}$ were always converted to f_s.

Instead the measured amplitude of the maximum transmitted signal $A_{\max}$ is larger than that expected for a simple series resonance A_s. In the assumption of $Q \gg 1$, the measured quantity $A_{\max}$ has to be reduced by the adimensional factor:

$$A_s = A_{\max} \frac{2}{\sqrt{1+\frac{M^2}{Q^2}} + 1}. \tag{29}$$

Again, when $Q=\infty$ or $M=0, A_s = A_{\max}$, as expected.

IV. CALIBRATION

As a check of our data-acquisition and analysis procedure, we have decided to evaluate the vapor contributions described by formulas (25) and (27) by taking extensive measurements with He and Kr using various quartz plates with different resonance frequencies. This study was carried out at $T=30$ °C, where only the vapor affects the QCM behavior. The two gases were chosen because of their quite different atomic masses.

Figure 2 shows the room temperature results acquired with a quartz crystal excited at its third overtone shear mode corresponding to a frequency of 18 MHz. We point out that practically coincident curves have also been obtained at the fundamental frequency of 6 MHz and with other quartz plates of different fundamental frequency. The quantity y, according to Eq. 26, is equal to

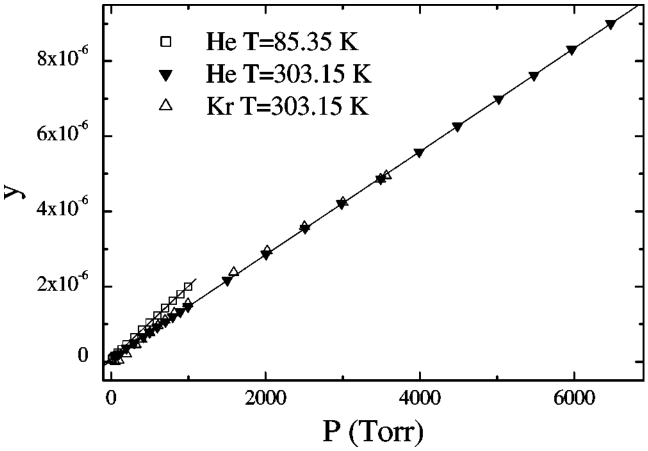

FIG. 2. Calibration of the QCM at room temperture and at low temperature. For further details, see the text.

$$y = \frac{f - f_0}{f} + \frac{2}{3}\frac{G(2\pi f \tau_v)}{Z_q}\sqrt{f \eta_v k_v P/\pi}, \tag{30}$$

where f_0 is the resonance frequency in vacuum and η_v is deduced from thermodynamical tables.

The phenomenological relaxation time τ_v is instead expressed in terms of the room-temperature collision time of the corresponding gas τ_{col}, via the simple relation $\tau_v = k_\tau \tau_{\mathrm{col}}$, where the proportionality constant k_τ is chosen so that the resulting points lie on a straight line.

In the case of Fig. 2, k_τ is practically zero for helium and about 10 for krypton (i.e., $\tau_v \simeq 10^{-10}$ sec). The resulting points lie on a quite good straight line with slope equal to $(13.77 \pm 0.03) \times 10^{-10}$ Torr^{-1} determined by a least-square linear interpolation. This result agrees very well with the value of 13.80×10^{-10} Torr^{-1} deduced by Stockbridge's formula [Eq. (24)] for $T=30$ °C. A similar result was obtained for oxygen with a ''ring-down'' technique, in which the quartz crystal is driven to resonance by an oscillator that can be intermittently disconnected causing the crystal oscillation amplitude to decay exponentially.[18] The acoustic parameters of the crystal can then be derived from the analysis of the decay curve.

The same graph also shows the results obtained with helium at 85.35 K. At this temperature the helium adsorption contribution is still negligible. The scaled points also lie on a straight line of slope $(19.44 \pm 0.03) \times 10^{-10}$ Torr^{-1}, practically coincident with the value deduced from Eq. (24). We remark that also at this temperature the viscoelastic effects of helium are insignificant, that is the quantity y of the graph is calculated for $\tau_v = 0$.

Figure 3 reports the variation of the inverse of the quartz amplitude $\Delta(1/A) = (1/A) - 1/A_0$, A_0 being the amplitude in vacuum, as a function of the viscous resistance $R_v = \sqrt{\pi f \eta_v k_v P} F(2\pi f \tau_v)$. The value of τ_v is the same as that used in the corresponding curves of Fig. 2. According to Eq. (27), the experimental points should collapse on a straight line whose slope yields the proportionality constant of the QCM which cannot be determined *a priori*. A least-square linear interpolation of the data of Fig. 3 gives $K_A = 6.369 \pm 0.001$ sec/V g cm^2.

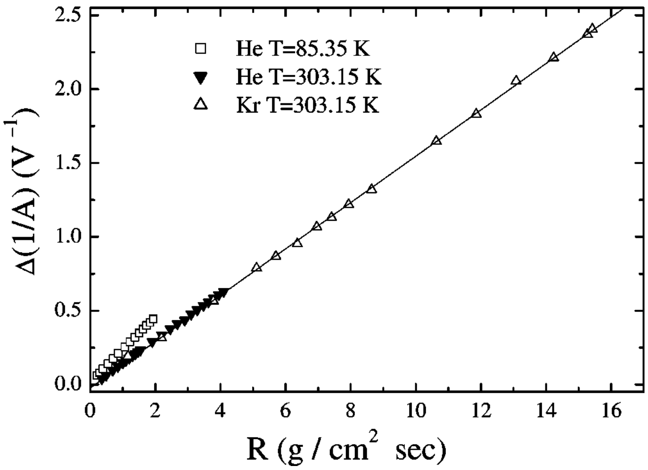

FIG. 3. Calibration of the QCM amplitude at room temperature and at low temperature. For further details, see the text.

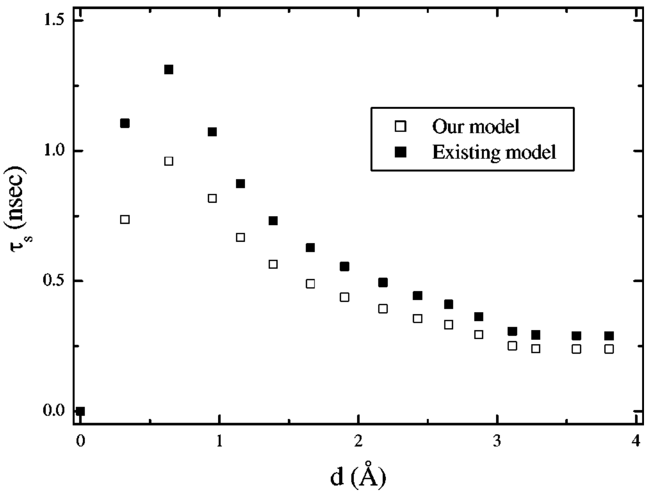

FIG. 4. Slip time of a Kr film adsorbed on gold at $T = 84.55$ K. For further details, see the text.

We point out that this standard calibration is not required. The resonance amplitude is proportional to the resonator quality factor through the relation

$$A = A_0 \frac{Q}{Q_0}, \tag{31}$$

where the index refers to quantities measured in vacuum. The total acoustic resonance can then be derived directly from

$$R_{sfv} = \frac{n\pi Z_q}{4} \frac{A_0}{Q_0} \Delta \frac{1}{A}, \tag{32}$$

without the need of a helium calibration, which may contaminate the surface. We have checked this procedure against the standard calibration, without finding any difference between the two.

From the analysis of the results plotted in Figs. 2 and 3 and of those acquired with the other quartz plates, also employing simple gases like N_2, Ar, and Xe, we can safely conclude that our method accurately measures the gas contribution. We point out that helium is the only gas we have investigated whose behavior can be accurately fitted by $\tau_v = 0$.

With this technique we have measured the friction of Kr films adsorbed on the gold electrodes of commercially made quartz crystals. After mounting, the crystals were typically outgassed to 70 °C for a couple of days, and flushed with high-purity Ar gas several times. The gold surface was then characterized by measuring vapor pressure adsorption isotherms of Ar and Kr at 84.55 K. Near liquid-vapor bulk coexistence, the Ar film thickness was found to diverge as a function of the chemical potential difference from coexistence with an exponent very close to $-1/3$, implying that the gold surface was flat and not rough.[12] Instead, the Kr curve did not show any stepwise features indicating a layer-by-layer growth but only a smooth continuous line, suggesting that the average size of the crystallites forming the evaporated polycrytalline gold electrodes was not very large. This result was not unexpected due to the limited baking procedures that our apparatus allowed us to do. In fact, adsorption curves indicating layer-by-layer growth have been measured only after a baking the quartz crystal at 350 °C for 12 h under ultrahigh vacuum conditions.[19]

Despite this, with our QCM setup we could observe sliding of Kr films condensed at low temperatures. Figure 4 shows a representative isothermal scan of the slip time τ_s of a film of Kr adsorbed on gold at $T = 84.55$ K as a function of its thickness d. At this temperature the saturated vapor pressure is near 9 Torr. The closed symbols are the data determined according to formulas (16)–(20), while the open ones are evaluated using expression (21) for the total impedance. For this system, the discrepancy between the two methods amounts to less than 15%, as already mentioned. Slip times of the order of nanoseconds were also reported by Krim and co-workers for Kr films adsorbed on gold surfaces of various qualities at $T = 77.4$ K.[5,20] More precisely, on fresh gold surfaces they found slip times as high as 3.5 nsec, while on the air-exposed surface $\tau_s \leqslant 2.5$ nsec. The quantitative differences with respect to our results are likely due to the poorer quality of the gold surface we have employed.

The times reported on the graph have been calculated assuming a relaxation time τ_v of the bulk vapor equal to zero. Certainly this is an oversimplification, because τ_v is not negligible, as our room-temperature calibration data clearly show. On the other hand, we do not know how to extrapolate this phenomenological time to low temperatures in a reliable way, nor are we aware of any procedure to measure it directly at low temperatures. The assumption of $\tau_v = 0$ in our analysis implies that the slip times in Fig. 4 represent a lower bound to the correct case.

V. CONCLUSIONS

We have examined the acoustic theory of a film adsorbed on an oscillating quartz crystal in the presence of a bulk vapor with the Navier-Stokes equation. By allowing the possibility of sliding of the film at the solid surface, we have derived a procedure that permits an accurate and simultaneous measurement of the film thickness and of the interfacial viscosity η_2 or slip time τ_s from the quartz resonator parameters. Given the usually very small values of τ_s, this determination requires a very precise evaluation of the vapor contribution. With our apparatus we have successfully tested the existing model originally proposed by Stockbridge to account for it. The experimental data have been obtained using a frequency-modulation technique. The data acquisition and analysis have been described in some detail. Finally, we have measured the slip time of a monolayer of Kr on gold, and found a value of the order of nanoseconds, slightly smaller than the values measured by Krim and co-workers on more uniform surfaces.

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