Internal and interfacial friction in the dynamics of soft/solid interfaces

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We analyze theoretically the effect of friction on quartz crystal microbalance (QCM) measurements that probe soft (viscoelastic) films and biomolecular layers adsorbed from aqueous solutions. While water provides a natural environment for biomolecules, an interface with unknown rheological properties forms between the adsorbed soft molecular layer and the quartz substrate in the latter case. We investigate therefore the dynamics of soft films adsorbed onto a solid quartz surface within a continuum mechanics approach using both the Maxwell and the Voight/Kelvin models of viscoelasticity and their combination. The rigorous expressions derived for the acoustic response of a quartz crystal oscillator, accounting for both interfacial (sliding) friction and internal friction (viscosity), demonstrate that the QCM can be used as a sensor for quantitative characterization of friction effects as well as for “in situ” measurements of mechanical properties of adsorbed biomolecular films.

I. INTRODUCTION

A universal slip law for a moving interface between a solid and a fluid experiencing shear stress, has been demonstrated recently for cases when the no-slip condition breaks down. Experimentally, this situation can be addressed with a piezoelectric (quartz) plate, which oscillates in thickness-shear mode while in contact with a fluid medium. Traditionally, such quartz crystal oscillators have been utilized as a microbalance (QCM) for weighing a negligible amount of adsorbed mass in vacuum or in a gaseous environment. Current applications of the QCM in a vacuum or gas phase range from nanotribolgy experiments on thin films of solidified gases to sensor measurements of viscoelastic properties of thin films deposited onto the quartz crystal surface. In recent liquid phase experiments the QCM technique has been adopted as a biosensor for measuring the properties of adsorbed polymer- and biomolecular films. However, a finite amount of slippage arising from a weak coupling between film and oscillating substrate can change both the resonance frequency \( f \) and the quality factor \( Q \) of the oscillator and renormalize the results of measurements. Therefore, understanding the role of sliding friction in liquid QCM experiments is of key importance.

An extensive review of the theory of sliding friction and the quartz crystal microbalance method can be found in the recent book by Persson.

For a quantitative characterization of slippage effects it is convenient to use the ratio between the shift \( \Delta f \) of the QCM resonance frequency and the inverse quality factor \( \Delta (Q^{-1}) \). This measure was introduced in the QCM literature by Krim and Widom as a “slip time” \( \tau \),

\[
\tau = \frac{\Delta (Q^{-1})}{4 \pi |\Delta f|}.
\]

In the following we prefer to refer to the dissipation factor \( D \equiv Q^{-1} \) rather than to the inverse quality factor of the oscillator. The shifts \( \Delta D \) and \( \Delta f \) can be measured simultaneously in QCM experiments; one always finds \( \Delta D \) to be positive while the resonance frequency shift \( \Delta f \) is negative since mass loading lowers the oscillator resonance frequency compared to the unloaded state in vacuum.

According to the results of Krim’s group, a partial decoupling of the overlayer should occur when \( 2 \pi f \tau \geq 0.5 \). Typically, a quartz crystal oscillates with frequency \( f \sim 10 \, \text{MHz} \) and therefore decoupling starts when \( \tau \geq \tau_c \simeq 10^{-8} \, \text{s} \). For instance, in QCM experiments with thin water films \( \Delta f \sim 1 - 10 \, \text{Hz} \), \( \Delta D \sim 10^{-7} - 10^{-6} \) and hence \( \tau \sim 10^{-9} - 10^{-7} \, \text{s} \), which is quite close to \( \tau_c \). It follows that a relatively low decoupling threshold can lead to noticeable interfacial friction effects even in the case of molecularly thin films.

In the nanotribology QCM-experiments of Krim and collaborators, where they studied films of solidified gases, condensed onto a solid substrate, the interfacial friction coefficient \( \gamma_f \) for a thin rigid film was found to be inversely proportional to the slip time and proportional to the surface mass density \( m_f = \rho_f h_f \) of the film,

\[
\gamma_f = m_f / \tau.
\]

This result can also be viewed as the definition of the slip time \( \tau \), which is the characteristic time it takes for the film velocity to decrease by a factor \( 1/e \). However, for soft interfaces Eqs. (2) becomes invalid because of additional viscous dissipation of energy in the material.

In this article we analyze theoretically the QCM response, accounting for both viscosity and interfacial friction effects, and derive how the sliding friction coefficient is related to the values of \( \Delta f \) and \( \Delta D \), which can be measured. Throughout the paper we use the term “soft” to characterize properties which are opposite to “rigid”, i.e., the viscoelasticity of the material.

We will show that under certain conditions, the dissipation factor \( \Delta D \) can have a maximum as a function of the viscosity as well as of the sliding friction of the QCM-probed material. We derive the exact expressions for the maximal dissipation shift. The general analysis presented here is valid for arbitrary layer thickness. Sliding friction of ultrathin films, adsorbed from a gaseous (or liquid) phase, emerges as a special limiting case.
From a practical point of view, one of the particularly important topics treated here is concerned with liquid and biosensor QCM applications. Here the oscillator, with its adsorbed biomolecular layer, operates in a bulk viscous liquid (water), which provides a natural environment for *in situ* measurements. We have modeled this system as a layered soft (viscoelastic) material covered by a bulk Newtonian liquid. Linear viscoelasticity of different biological interfaces has been analyzed for both Maxwell and Kelvin/Voight schemes and their combination.

**FIG. 1.** Schematic depiction of a quartz crystal oscillator (microbalance) loaded on one side by a layered medium. Layer I could, e.g., be a thin biomolecular layer, layer II could be, e.g., bulk water.

**II. DAMPING OF A QUARTZ OSCILLATOR BY SLIPPING SOFT MATERIAL.**

Let us consider a quartz crystal microbalance (QCM), oscillating in thickness-shear mode and on one side covered by a soft adsorbed layer (as depicted schematically in Fig. 1). We describe the motion of the QCM as the forced vibration of a damped oscillator driven by periodic force.

When mass is deposited onto the crystal surface, the resonance frequency changes. For a small amount of mass or a molecularly thin film rigidly attached to the QCM surface, the shift of resonance frequency $\Delta f$ is proportional to the density $\rho$ and thickness $h$ of the overlayer, while there is no dissipation shift $\Delta D$. When the oscillator operates in a bulk liquid environment, both $\Delta f$ and $\Delta D$ are finite and depend on the density $\rho$ and the viscosity $\eta$ of the liquid. Classic results are Kanazawa and Gordon's resonance frequency shift of a QCM immersed in a bulk liquid:

$$\Delta f \approx -\frac{1}{2\pi m_q} \sqrt{\frac{\rho \eta \omega}{2}},$$

and Stockbridge's result for the QCM dissipation shift

$$\Delta D \approx \frac{1}{m_q} \sqrt{\frac{2\rho \eta}{\omega}}.$$
decoupling of the overlayer from the substrate. Effects of slippage can easily be included in the equation of motion for the oscillator. Following the damped oscillator model of Ref. 3, we may express the shift of resonance frequency and dissipation factor in the presence of slippage as

$$\Delta f \approx -Im\left(\frac{\tilde{Z}}{2\pi \gamma S(1 + \gamma \tilde{Z})}\right)$$

(8)

$$\Delta D \approx Re\left(\frac{\tilde{Z}}{\pi \alpha m_q(1 + \gamma \tilde{Z})}\right),$$

(9)

where as already mentioned $\gamma = 1/\gamma_S$.

Following the approach of Krim's group 3, we introduce the characteristic slip time $\tau_S$ as the ratio between the shift of the dissipation factor and the change in resonance frequency change,

$$\tau_s = -\frac{\Delta D}{4\pi \Delta f}. \tag{10}$$

Proceeding by means of an analogy, we define another ratio with dimension of time,

$$\tau_0 = -\frac{\Delta D}{4\pi \Delta f}. \tag{11}$$

in order to characterize the temporal QCM response when no-slip boundary conditions apply. Defined in this way, the characteristic time $\tau_0$ can be attributed solely to the effects of internal friction (viscosity) on the damping of the QCM, i.e., $\Delta D$ is proportional to the resistive term $\tilde{Z}$ in the acoustic “no-slip” impedance $\tilde{Z}$.

Using Eqs. (8)-(11), we may express the slippage coefficient $\lambda$ and the interfacial friction coefficient $\gamma$ as functions of $\tau_S$ and $\tau_0$. One finds

$$\gamma = \frac{\omega \tau_0 - \omega \tau_S}{2\pi \Delta f m_q}, \tag{12}$$

and

$$\gamma_S = 2\pi \Delta f m_q \frac{1}{\omega \tau_0 - \omega \tau_S}. \tag{13}$$

Let us consider a viscoelastic medium of finite thickness $h$ in contact with the quartz oscillator (Fig. 1). It is known, that the acoustic response of the oscillator strongly depends on the overlayer thickness. “Thin” or “thick” films refers to the film thickness being smaller or greater than the inverse values of the decay constant $\alpha$ and propagation constant $k$ of the acoustic waves propagating in the coated quartz plate.

In the limiting case of an ultrathin film (h$\alpha \ll 1$, $hk \ll 1$), acoustic shear waves can propagate through the adsorbed film without dissipation. Such a layer has a Sauervrey solid-like response, for which

$$\Delta f' = -f_0 \frac{m_f}{m_q}, \quad \Delta D = 0,$$

and where $m_f = \rho h_f$ is the mass per unit area of the film. Substitution of $\Delta f'$ and $\Delta D$ in Eq. (13) gives the coefficient of interfacial friction. For a molecularly thin overlayer one finds

$$\gamma_S = m_f/\tau_S,$$

which reproduces the result of Krim and Widom 3. For slipping soft material of arbitrary thickness, one must take into account both interfacial friction and viscosity and use Eqs. (8)-(13).

An analysis of the general expressions (8), (9) and (11) allows the dissipation factor $\Delta D(\lambda)$ to be expressed as a function of slippage as

$$\Delta D(\lambda) = \frac{1}{\pi f m_q (1 + \lambda \tilde{Z}^2 + \tilde{Z'}^2 + 2\lambda \tilde{Z})}. \tag{14}$$

From Eq. (14) it follows that the dissipation shift is a nonmonotonic function of slippage $\lambda$, which peaks for a critical value $\lambda^*$. If we take the limit $\tilde{Z} = 0$ corresponding to a rigid thin film, the maximal dissipation is

$$\Delta D(\lambda^*) = -\frac{\Delta f'}{f}. \tag{15}$$

The dissipation is maximal in this case ($\omega \tau_0 = 0$) when the condition

$$\omega \tau_S = 1$$

is satisfied, a criterion for sliding thin rigid films first found by Krim and Widom 3.

The condition (15) is readily understandable. For a non-dissipative medium, the damping of the oscillator is proportional to the inertial contribution $\Delta f' f \sim m_f$ associated with the slippage of the added mass pushed along the quartz surface. A rigid thin film will give rise to maximal dissipation when the sliding friction reaches the value

$$\gamma^* = m_f \cdot \omega. \tag{16}$$

or equivalently when the slippage coefficient is

$$\lambda^* = 1/(m_f \cdot \omega). \tag{17}$$

This maximum value of the dissipation factor is

$$\Delta D(\lambda^*) = m_f/m_q. \tag{18}$$

The lower the surface mass density is, the larger is the slippage coefficient $\lambda^*$ for which the dissipation factor is maximal, and the smaller is this maximal value (Fig. 2). An important consequence of the result (15) is that the maximum value of the dissipation factor is frequency independent. Therefore, one may consider the presence of such a frequency independent maximum as a test of whether slippage occurs in dynamic QCM measurements;
if the dissipation peak remains constant when the oscillation frequency $\omega$ is varied, the peak can be attributed to sliding friction.

![Graph showing dissipation factor $\Delta D$ vs. $\lambda \omega m_f$](image)

**FIG. 2.** Sketch of typical nonmonotonic dependence of the dissipation factor $\Delta D$ on the dimensionless slippage coefficient $\lambda \omega m_f$ for a thin, rigid film adsorbed onto the quartz plate. The calculation was done for film thickness $h_f = 1\mu m$ and film mass density $\rho_f = 1\text{ g/cm}^3$.

Experimentally, the sliding friction is an external parameter which can be changed, e.g., by varying pressure or temperature. Maxima in the dissipation have been observed experimentally for solid molecularly thin films sliding along a quartz surface oscillating in gaseous environments. The maxima appeared when the condition $\omega \tau_s = 1$ was met. In these experiments, the effect of interfacial friction on the QCM damping was obvious from the fact that viscous losses are negligible both in a gas and in rigid molecularly thin films. However, in experiments with soft films, the dissipation factor can reach a maximum as temperature or pressure is varied, since these affect the internal friction (shear viscosity) of the material. When slippage is absent (or negligibly small), viscoelastic effects dominate and the dissipation maximum becomes frequency dependent (see Section 3C).

In case of sliding thin viscoelastic overlayers, internal friction (viscosity) leads to additional but small contributions to the QCM damping since $\Delta \tilde{D} \neq 0$. As a result the position of the dissipation maximum is only slightly shifted. On the contrary, the viscosity of soft materials of finite thickness will significantly influence the damping and produce a “viscous”-type dissipation peak. In order to separate these effects, we study below the no-slip limiting case — when the interfacial slippage vanishes — for the viscoelastic film dynamics.

### III. ACOUSTIC IMPEDANCE OF A QCM LOADED BY A VISCOELASTIC LAYER

Viscoelasticity is a common feature of complex fluids and in polymer rheology. A limiting case is that of highly viscous fluids - amorphous solids and glasses. Polymers exhibit linear viscoelasticity. Both deformations and deformation rates are small. In the linear viscoelastic regime, there is proportionality between stored energy and strain and between strain rate and dissipated energy. The most well known mathematical formulations of linear viscoelasticity are the Maxwell model of relaxation in highly viscous fluids and the Kelvin/Voight model of viscoelastic solids.

#### A. Highly viscous Maxwell fluids

Let us derive the acoustic impedance of a QCM covered by an overlayer of highly viscous material. A very viscous complex fluid responds initially to deformation in the same way as an elastic solid, but after the deformation stops the fluid relaxes. This relaxation processes can be characterized by the viscous relaxation time $\tau_M$, which is a measure of the time it takes for the remaining stress to be damped. Such viscoelastic behavior of the complex fluid can be characterized by the shear viscosity coefficient $\eta$ and the shear elasticity modulus $\mu$. The characteristic relaxation time $\tau_M$ is of the order of their ratio $\frac{\eta}{\mu}$.

$$\tau_M \sim \frac{\eta}{\mu}.$$ 

Viscoelastic properties of a complex fluid can be treated within the Maxwell model which represents a mechanical analogue of viscoelasticity via a dashpot (viscous newtonian element) and a spring (elastic hookian element), arranged in series (Fig. 3a). A Maxwell fluid subject to quartz crystal oscillations of frequency $\omega$ behaves as a newtonian viscous fluid with shear viscosity $\eta$ if $\tau_M \ll \omega^{-1}$. In this limit, the relation between the stress tensor $\sigma_{ik}$ and the strain tensor $u_{ik}$ is the same as for the ordinary newtonian fluid with $\sigma_{ik} = 2\omega \eta u_{ik}$. In the opposite case of large $\omega \gg \tau^{-1}$, the Maxwellian fluid responds to shear stress as a solid. The strain-stress relation $\sigma_{ik} = 2\mu u_{ik}$ describes the elasticity of a solid body.

![Basic models for the linear viscoelasticity of different materials. a) Maxwell fluid; b) Voight/Kelvin viscoelastic solid; c) and d) more complex rheological models of viscoelastic solids.](image)
The equation of motion for a maxwellian fluid, which includes both the limits of slow- and fast motion, is given by the expression

\[ 2\mu \frac{du_{ik}}{dt} = \frac{da_{ik}}{dt} + \sigma_{ik} \frac{1}{\tau_M}. \]  

(19)

Equation (19) assumes that the internal stress is exponentially damped on the characteristic time scale \( \tau_M \) after the applied stress is removed. Using Eq. (19), we find the stress-strain relation for maxwellian fluid to be of the form

\[ \sigma_{ik} = \frac{2\mu u_{ik}}{1 - i/\omega \tau_M}. \]  

(20)

which can be rewritten as

\[ \sigma_{ik} = 2\mu^* u_{ik}. \]  

(21)

Here \( \mu' \equiv \mu' + i\mu'' \) is the complex shear modulus of a Maxwell fluid. The real part (storage modulus) is

\[ \mu' = \frac{\eta^2 \omega^2 \mu}{\mu^2 + \omega^2 \eta^2}, \]  

(22)

while the imaginary part (loss modulus) is

\[ \mu'' = \frac{\omega \eta^2 \mu}{\mu^2 + \omega^2 \eta^2}. \]  

(23)

Using the strain-stress relation (21) and the conservation of momentum density,

\[ \frac{\partial \Pi_{ik}}{\partial x_k} = \frac{\partial}{\partial t} (\rho u_i), \]

we get a wave equation,

\[ \mu \frac{\partial^2 u_x(y,t)}{\partial y^2} = -\omega^2 u_x(y,t), \]  

(24)

for bulk shear waves propagating in the system. Here \( u_x(y,t) \) is the a component of the displacement vector (Fig. 1). Solving equation (24) with no-slip boundary conditions, we find the acoustic impedance of the maxwellian viscoelastic fluid overlayer of thickness \( h \) to be given by the expression

\[ \tilde{Z}_h = \frac{\xi \mu^*}{i \omega} \frac{1 - e^{2\xi h}}{1 + e^{2\xi h}}. \]  

(25)

Here \( \xi = \alpha + ik; \) \( \alpha \) is the decay constant and \( k \) is the propagation constant. These quantities are given by formulae

\[ \alpha_M = \frac{1}{\delta} \sqrt{1 + \chi_M^2 - \chi_M} \]  

(26)

\[ k_M = \frac{1}{\delta} \sqrt{1 + \chi_M^2 + \chi_M}. \]  

(27)

In Eqs. (26) and (27), the viscous wave penetration depth, \( \delta = (2\eta/\rho \omega)^{1/2} \) is the distance over which the amplitude falls off by a factor of \( e \), the viscoelastic ratio, \( \chi = \mu'/\mu^* \), is the ratio between real part (storage modulus) and the imaginary part (loss modulus) of the complex shear modulus. For Maxwell material

\[ \chi_M = \eta \omega / \mu. \]

Below we will characterize the material by the viscoelastic ratio \( \chi \) rather then by the relaxation time \( \tau_M \). These quantities are related, since \( \chi_M \approx \omega \tau_M \).

**B. Thin Maxwell-fluid overlayers**

Here we derive the shifts \( \Delta f \) and \( \Delta D \) characteristic of a Maxwell fluid thin film rigidly attached to the surface of a QCM oscillating in vacuum. By a series expansion in \( \hbar \alpha \ll 1 \) and \( \hbar k \ll 1 \), which is permissible in the special case of a thin overlayer, we find from (25) - (27) and from (4) and (5) that

\[ \Delta f \approx \frac{h \rho \omega}{2\pi m_q} \left( 1 + \frac{h^2 \rho \omega^2}{3\mu} \right) \]  

(28)

\[ \Delta D \approx \frac{2h^3 \rho^2 \omega}{(3m_q \eta)} \]  

(29)

It should be noted, that Eq. (29) has the same form as the dissipation factor for a thin pure viscous layer with constant shear viscosity coefficient \( \eta \).

From expression (28) we obtain for the equivalent mass \( m_M \) of the film

\[ m_M = m_f (1 + h^2 \rho \omega^2 / 3\mu) \]  

(30)

which differs from the actual mass \( m_f \) and depends on the shear elasticity \( \mu \) of the material. Our results (28) - (30) are in agreement with those of Johannsmann et al., who calculated and measured by QCM the equivalent mass of a viscoelastic Langmuir-Blodgett film. The characteristic “viscous” time \( \tau_0 \) for a thin Maxwell film is, therefore

\[ \tau_0 \approx (h^2 \rho)/(3\eta). \]  

(31)

Because \( \tau_0 \) is defined as the ratio between the experimentally measured values of \( \Delta D \) and \( \Delta f \), one can calculate from Eq. (31) the viscosity of a thin Maxwell film if the film mass density and thickness are known or measured separately (e.g., by neutron scattering or ellipsometry methods).

Let us now proceed with a comparison between the results for a Maxwell fluid with those for a thin viscoelastic solid film.

**C. Solid viscoelastic Voight/Kelvin overlayers**

In the Voight/Kelvin scheme (Fig. 3b) for describing viscoelastic solid materials, a complex viscoelastic shear
modulus, $\mu'_V \equiv \mu_V' + i \mu''_V$, is used. Its real part is the storage modulus
\[ \mu'_V = \mu, \] (32)
while the imaginary part is the loss modulus
\[ \mu''_V = \omega \eta. \] (33)

The dynamics of viscoelastic solids can also be characterized by the retardation time $\tau_V \sim \eta_V/\mu_V$ or by the viscoelastic ratio
\[ \chi_V = \frac{\mu}{\eta \omega}. \] (34)

The acoustic impedance of a quartz oscillator in the absence of slip is given by expression (35) where $\xi_V = \alpha_V + i \kappa_V$
\[ \alpha_V = \frac{1}{\delta} \sqrt{\frac{1 + \chi_V^2 - \chi_V}{1 + \chi_V^2}}, \quad k_V = \frac{1}{\delta} \sqrt{\frac{1 + \chi_V^2 + \chi_V}{1 + \chi_V^2}}, \quad \delta = \sqrt{\frac{2\eta}{\rho \omega}}. \] (36)

In the same manner as in the previous section, we find from (35) taken together with (33) and (36) that
\[ \Delta f \approx -\frac{1}{2\pi \omega} \frac{\rho \omega}{m_q} \left(1 + \frac{2h^2 \chi_V}{3\delta^2(1 + \chi_V^2)}\right) \] (37)
\[ \Delta D \approx \frac{2h^3 \rho \omega}{3\pi \omega} \frac{1}{\delta^2(1 + \chi_V^2)}, \quad \delta = \sqrt{\frac{2\eta}{\rho \omega}}. \] (38)

The characteristic time $\tau_0$ depends on frequency and viscoelastic moduli of the material. One finds
\[ \tau_0 \approx \frac{h^2 \rho \eta \omega^2}{3(\mu^2 + \eta^2 \omega^2)}. \]
We therefore obtain the equivalent mass of the Voight/Kelvin layer as
\[ m_V = m_f \left(1 + \frac{h^2 \mu \omega^2 \rho}{3(\mu^2 + \eta^2 \omega^2)}\right), \] (39)
which includes a correction of the true film mass density $m_f$ due to the viscoelasticity of the material.

Equations (38) and (39) together with $\tau_0$ allow us to calculate the viscoelastic parameters $\mu_V$ and $\eta_V$ from simultaneously measured values of $\Delta f$ and $\Delta D$ if it possible to control the film thickness $h$ independently.

From expression (38) it follows that if during the experiment the shear elasticity is constant but the viscosity varies, the dissipation factor as a function of shear viscosity $\eta$ will have a maximum when $\eta^* = \mu/\omega$ (or $\chi_V = 1$, respectively) (Fig. 4). And vice versa, in experiments with constant viscosity but varying shear elasticity $\mu$, the resonance frequency shift will have a maximum for $\mu^* = \eta \omega$ ($\chi_V = 1$) (Fig. 5). The maximum value of the dissipation factor
\[ \Delta D(\eta^*) = \frac{h^3 \rho^2 \omega^2}{3m_q \mu} \]
depends on the vibration frequency $\omega$ squared. Since the dissipation peak due to sliding friction was found to be frequency independent, this strong frequency dependence of $\Delta D(\eta^*)$ can be used as a test to see if slippage is absent in QCM “viscoelastic” thin film measurements. Note that the “viscous” peak value $\Delta D(\eta^*)$ is weaker by a factor $h^2 \rho \omega^2/\mu$ than the peak value $\Delta D(\chi^*)$ of Eq. (38).

It should be noted, that the frequency behavior of the QCM characteristics in the linear viscoelasticity region, viz. $\Delta f(\omega)$, can also test for the type of material - either viscoelastic fluid or viscoelastic solid. This is because from our results (38) and (39) for $\Delta f_M$ and $\Delta f_V$, it follows that we expect a straight line if $\Delta f(\omega)$ is plotted vs. $\omega^2$ for the case of a Maxwell fluid and a deviation from a straight line for other types of viscoelastic materials. In the case of Maxwell fluid, the slope of the straight line gives the elastic modulus $\mu$ of the material. (The viscosity $\eta_M$ of the Maxwell fluid film can then be deduced directly from the measured values of $\Delta D$ or $\tau_0$ if the film thickness is known.)

FIG. 4. Calculated dissipation factor $\Delta D$ of a quartz crystal microbalance (QCM) covered with a thin film of a Voight/Kelvin viscoelastic solid as a function of its inverse viscoelastic ratio $\chi^* = \eta \omega/\mu; h_1 = 1 \mu m, \omega = 2\pi \cdot 10 MHz, \mu = 10^{15} dyne/cm^2, \rho = 1 g/cm^3.
Due to an adsorbed viscoelastic solid thin film; \( h_1 \) is typical for biological QCM experiments while \( \Delta h_{1,2} \) refer to the second layer, \( \eta_1 \) and \( \rho_1 \) denote the viscosity and density of the water solution, \( \mu_{1,2} \), \( \alpha_{1,2} \) and \( k_{1,2} \) are given by Eqs. (32), (33), (36) and (37) for Maxwell layers or by Eqs. (32) - (35) for Voight/Kelvin layers, respectively. The acoustic response \( \Delta f \) can be calculated using the general results (5) and (6) together with (11) and (12), where \( \tilde{Z}_b \) has to be substituted for \( Z \).

In the next section we analyse formulae (11) - (14) in the limiting case of a thin viscoelastic overlayer rigidly attached to the quartz plate and loaded by water bulk solution on top.

V. APPARENT “DISAPPEARANCE” OF THE EQUIVALENT FILM MASS IN LIQUID QCM MEASUREMENTS.

As shown in Section III, the viscosity and elasticity of the tested material affect the measured equivalent mass \( m_{eq} \) of the film, which therefore differs from the “true” film mass \( m_f \). When the system operates in a solution, acoustic shear waves penetrate through the thin overlayer and interact with the bulk viscous medium on its top. Let us analyse how the viscosity of the solution (index “2”) changes the dissipation and resonance frequency shift of the QCM covered by a viscoelastic (index “1”) and how it influences its equivalent mass.

First, we restrict our attention to the special case of a pure viscous overlayer. By a series expansion valid for the thin film limit \( h/\delta \ll 1 \), we find that the shift in resonance frequency when the QCM oscillates in bulk water is a function of the mechanical properties of the overlayer, \( \rho_1 \) and \( \eta_1 \), which enter to linear order in the (small) film thickness:

\[
\Delta \tilde{f} \approx \frac{1}{2\pi m_q} \left\{ \frac{\eta_2}{\delta_2} h_1 \rho_1 \omega - 2 \left( \frac{\eta_2}{\delta_2} \right)^2 \frac{h_1}{\eta_1} \right\},
\]

At the same time, the overlayer contribution to the dissipation factor is very small and appears only to second order in \( h/\delta \ll 1 \),

\[
\Delta \tilde{D} \approx \Delta D_0 \left\{ 1 - \frac{2\pi h_1^2 \rho_1 \omega}{\eta_1} \left( \frac{\eta_2}{\eta_1 \rho_1} - 1 \right) \right\},
\]

where

\[
\Delta D_0 = 2f_0 \left( \frac{\eta_2 \rho_2}{\pi f \rho_1 C_{06}} \right)^{1/2}.
\]

is Stockbridge’s result for the dissipation of a QCM in a purely viscous bulk liquid. We conclude from (14) that the equivalent film mass of a purely viscous layer, \( m \approx m_f (1 - (\eta_2 \rho_2)/(\eta_1 \rho_1)) \), is obviously equal to zero if \( \eta_2 \rho_2 = \eta_1 \rho_1 \).
For a QCM probing a thin layer of a Maxwell material \((h\alpha \ll 1, h\kappa \ll 1)\) in a bulk solution, we find that the resonance frequency shift and equivalent mass take the same form as for a purely viscous film. However, the dissipation in a Maxwell fluid includes a term linearly dependent on the film thickness, which appears due to the finite elasticity \(\mu_1\) of the material:

\[
\Delta \tilde{D} \approx \frac{1}{\pi fm_q} \left\{ \frac{\eta_2}{\delta_2} + 2 \left( \frac{\eta_2}{\rho_2} \right)^2 \frac{h_1 \omega}{\mu_1} \right\}. \tag{47}
\]

Finally, we obtain in a similar way the response of a QCM covered by a thin Voight/Kelvin overlayer when the system operates in a liquid:

\[
\Delta \tilde{D} \approx \frac{1}{\pi fm_q} \left\{ \frac{\eta_2}{\delta_2} + h_1 \rho_1 \omega - 2 \left( \frac{\eta_2}{\rho_2} \right)^2 \frac{h_1 \omega^2 \eta_1}{\mu_1^2 + \omega^2 \eta_1^2} \right\}. \tag{48}
\]

\[
\Delta \tilde{f} \approx -\frac{1}{2\pi m_q} \left\{ \frac{\eta_2}{\delta_2} + h_1 \rho_1 \omega - 2 \left( \frac{\eta_2}{\rho_2} \right)^2 \frac{h_1 \omega^2 \eta_1}{\mu_1^2 + \omega^2 \eta_1^2} \right\}. \tag{49}
\]

When \(\eta_\omega \ll \mu\), viscoelastic solid and viscoelastic fluid films dissipate the same amount of energy. In the opposite case of \(\eta_\omega \gg \mu\), a viscoelastic solid film will dissipate much less energy than will a Maxwell fluid film.

The equivalent mass of a viscoelastic solid film

\[m_V \approx m_f \left(1 - \frac{\eta_2 \rho_2 \omega^2 \eta_1}{\rho_1 (\mu_1^2 + \omega^2 \eta_1^2)}\right)
\]

equals zero when \(\eta = \eta_0\), where

\[\eta_0 = \eta_2 \rho_2 \left\{ \frac{1}{\delta_2} + 1 - \frac{1}{\mu_1 \rho_1 \eta_1} \frac{2 \mu_1 \rho_1}{\omega \eta_2 \rho_2} \right\}.
\]

When the viscosity of the top layer vanishes, \(\eta_2 = 0\), viscoelastic corrections to the equivalent mass appear only in higher order corrections in the film thickness (see sections 3B and 3C).

A simple analysis of expressions [18] and [19] reveals nonmonotonic behavior of the dissipation factor \(\Delta D(\mu, \eta)\) and the resonance frequency shift \(\Delta f(\mu, \eta)\). The dissipation factor will reach a maximum when \(\mu^* = \eta_\omega\) if the viscosity is constant. In the same way, the resonance frequency has a minimum as a function of viscosity when \(\eta^* = \mu/\omega\) (Fig. 6). This circumstance must be taken into account in QCM adsorption experiments if viscoelastic parameters and the layer thickness can vary simultaneously during adsorption from the liquid phase.

It should be mentioned, that the QCM characteristics in the case of a Maxwell fluid are monotonic functions of film viscoelasticity, decreasing with \(\mu\) and \(\eta\), respectively.

\[
\text{FIG. 6. Relative resonance frequency shift } \delta f \text{ due to a thin viscoelastic solid overlayer as a function of its viscoelastic ratio } \chi = \mu/\eta_\omega. \text{ QCM operates in a bulk aqueous solution; } \delta f = (|\Delta f - \Delta f_0|)/\Delta f_{\text{Sauerbrey}}, \text{ where } \Delta f_0 = -\eta/2\pi m_q \delta, \Delta f_{\text{Sauerbrey}} = -h_\omega/2\pi m_q.
\]

VI. DISCUSSION: SOFT MATTER AND BIOSENSOR APPLICATIONS OF QCM

One of the current challenges is to apply the QCM technique to probing biological materials in solution: polymers and complex fluids, which are dominated by viscous effects. Typically adsorbed from a liquid phase, they form soft biological interfaces of multilayer architecture at the solid substrate. Recently it has been reported that mechanical properties of (bio)polymer and amphiphilic self-assembled films, adsorbed films of proteins, enzymes, membrane microspheres (vesicles) and even living cells can be investigated by using quartz crystal microbalance (QCM) technique in bulk aqueous solution. It seems crucial that an adequate physical model is chosen for a quantitative interpretation of such QCM measurements to be possible. In addition, biosensor applications of the quartz crystal microbalance (QCM) technique are faces with the need to control the interfacial friction, when the probed biopolymer material can slip relative to the quartz surface during its oscillatory motion. The slip of the adjacent layer, affecting the resonance frequency shift \(\Delta f\) and dissipation factor \(\Delta D\) of the oscillator arises from the weak coupling between film and substrate.

The limit of strong coupling of the layer to the solid surface corresponds to the widely used “no-slip” boundary condition. Experimentally, this boundary condition applies to thin solid films evaporated onto the quartz surface. Among biomaterials, the no-slip conditions can easily be realized for Langmuir-Blodgett films, which can be extremely strongly coupled to the solid substrate.

The usage of QCM for biological and biomedical purposes brings out the problem of accounting for the complex rheology of the biological interface formed by the adsorbed biomolecular films. In some special cases or
for particular type of shear deformations, the linear viscoelasticity of polymers can be treated within either the Maxwell or the Voigt/Kelvin schemes. The results of the Voigt/Kelvin model can readily be applied to quartz crystal acoustic measurements of adsorbed proteins, which conserve their shape during adsorption and do not flow under shear deformation as well as to polymer films far from the glass transition region. The Maxwell fluid scheme is appropriate for polymer solutions that are pure liquids (at low shear rates) and polymers in the amorphous state and in the vicinity of the polymer liquid-glass transition. Viscoelastic materials with more complex rheology (e.g., cells, membranes, liquid crystal polymers etc.) can be described by a combination of these two basic viscoelastic schemes. Two such schemes are illustrated in Figs. 3c and 3d. They can be analysed in a similar as we have done here way by substitution of the corresponding expressions for the complex shear modulus $\mu^*$ in the general results (22) - (27) and then in (8) - (11). For instance, the complex shear modulus for the material described by scheme of Fig. 3d, is given by the expression

$$
\mu^* = \frac{\mu_1 + i\omega\eta_b}{\omega\eta_1\mu_1} + \frac{1}{\mu_2 + i\omega\eta_2}.
$$

(50)

Such a model well describes, e.g., the viscoelasticity of the lyotropic lamellar phase (the so-called “onion phase”) which organizes itself into multilamellar vesicles which are closed-packed and fill up the space.

It is convenient to describe the frequency behavior of a complex viscous medium exhibiting a spectrum of relaxation times in terms of the three-parameter model $\eta^* = \eta/(1 + i\omega\tau)^b$ of the complex viscosity suggested by Reed, Kanazawa and Kaufman. In this model, $\eta$ is the viscosity of the liquid, $b$ is a characteristic exponent related to the distribution of relaxation times $\tau$. In the same manner, we can introduce in our model a complex shear modulus of the form

$$
\mu^* = \mu/(1 - i/\omega\tau)^b
$$

which is a generalization for the case of a relaxation time distribution characterized by the exponent $b$. In particular, the Maxwell fluid corresponds to the value $b = 1$.

In summary, recent results show that in cases where the adsorbed material forms a soft interface to the quartz crystal microbalance (QCM), both internal and interfacial friction mechanisms may contribute to energy dissipation. The combined action of these mechanisms may cause the variation of the shift $\Delta D$ in the dissipation factor to be a nonmonotonic function of material parameters, which can be varied in an experiment. Depending on the system, one or the other type of friction may dominate. We have suggested here a dynamic “slip/no-slip” test that can be applied to QCM measurements with thin adsorbed films. The test is based on the frequency dependence of a peak in the dissipation factor. We have shown that the peak value of $\Delta D$ caused by sliding friction is frequency independent while the viscoelastic peak is strongly dependent on frequency.

Besides being able to understand the role of interfacial friction, an important problem for the application of the QCM technique to biosensing remains. How can the device recognize what type of material is being probed except by detection of an “anonymous” deposited mass? In this article we suggest that analysing the frequency behavior of QCM characteristics as one of possible test what material is layered over the quartz surface.

Another way is a direct biochemical modification of QCM surface for selective binding of tested biological molecules. Recently, an immunosensing system based on antigen-coated QCM has been reported elsewhere. It has been shown that QCM results were in agreement with those of enzyme linked immunosorbent assay (ELISA). Perhaps the successful road to QCM usage as a biosensor device, is to combine both of dynamic measurements and immunology treatment directions.

Presented here rigorous formulae for experimentally measured $\Delta f$ and $\Delta D$ values, make it possible to investigate viscoelastic contribution in a wide range of biomolecular materials and can be useful for the correct interpretation of biologically oriented QCM experiments.

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