

On dissipation of quartz crystal microbalance as a mechanical spectroscopy tool

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Abstract. We report on theoretical analysis of dissipative effects in quartz crystal resonator applications to the dynamics of complex biological fluids and soft polymer films. As a mechanical spectroscopy tool, the quartz resonator can probe the storage and loss moduli $\mu(\omega)$ of a thin material sample in small amplitude oscillations where polymers exhibit linear viscoelasticity. We show how viscosity (internal friction) and slippage (interfacial friction) of the sample affect the acoustical characteristics of the quartz resonator. With respect to biosensor's application, we present rigorous expressions for the resonant frequency and damping of the quartz crystal which allow to quantify friction effects and even distinguish between them in resonator measurements performing on various frequencies. Possible application of the results in electronic nose and electronic tongue sensors is discussed.

1. Introduction

Usually acoustic transducers (e.g., piezoelectric crystal oscillators) are used in biosensors to monitor the small mass deposited onto the crystal surface, including the binding of biological molecules [1–6]. In piezoelectric oscillators, changes of the surface mass are proportional to the shift of the crystal resonant frequency Δf (principle of quartz microbalance). Also, quartz crystal microbalance (QCM) can naturally be considered as a mechanical spectroscopy tool which determines the viscoelastic material properties by probing samples in small amplitude oscillations at prescribed frequency ω . Several groups reported on the application of quartz crystal resonators to the viscoelastic characterization of thin organic films at a frequency range from a few Hz to about 100 MHz (see for review paper [3] and refs. in it). These experiments are of particular interest since the viscoelastic moduli of thin layer sample can sufficiently differ from the corresponding bulk magnitude.

Viscoelasticity is a common feature of complex biological fluids and in polymer rheology. A limiting case is that of highly viscous fluids – amorphous solids and glasses. Polymers exhibit linear viscoelasticity if both deformations and deformation rates are small [4–6] which holds in QCM dynamic measurements. 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. Recently, it was demonstrated [7] that in principle QCM is able to detect and resolve between these two types of viscoelastic materials by performing dynamical measurements on different frequencies. It was shown [7], that one can expect a straight line if $\Delta f(\omega)$ is plotted vs. ω^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 μ of the material. (The viscosity η_M of the Maxwell

fluid film can then be deduced directly from the measured values of ΔD or τ_0 if the film thickness is known.)

Recent applications of quartz crystal microbalance (QCM) as a sensor element for the electronic nose (Fig. 1) and electronic tongue (Fig. 2) bring up the fundamental question of how internal friction (effects of viscosity) and interfacial friction (slippage) can affect the QCM resonance frequency shift Δf and, hence, the mass sensitivity. In cases where the adlayer exhibits a viscoelastic behavior, both internal and interfacial friction may contribute to energy dissipation. Depending on the situation, the former or the latter type of friction may dominate. We suggest a dynamic “slip/no-slip” test that can be applied to QCM spectroscopy in thin films of adsorbed molecules. The test is based on our theoretical finding that the peak in the dissipation factor depends on the frequency while the peak value of dissipation factor caused by sliding friction is frequency independent. We also demonstrate that the combined action of these two mechanisms may cause the variation of the shift in the dissipation factor ΔD of quartz oscillator – a nonmonotonic function of adlayer parameters, which can vary in experiments. We also discuss our results in view of possible electronic nose and electronic tongue applications of QCM.

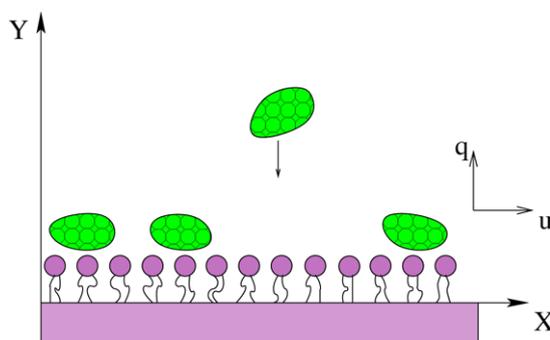


Fig. 1. Sketch of a molecular architecture of quartz crystal microbalance, a mass sensing element in electronic nose; a receptive surface is regarded as a molecularly thin layer of organic molecules (e.g., thiol SAM or Langmuir–Blodgett lipid film, covalently coupled to the QCM surface). Odorant compounds which are typically polar and hydrophobic molecules with molecular masses ~ 300 Da [1], are adsorbed from gaseous phase or vapour to the receptive layer on QCM surface. Right corner insertion depicts the geometry of acoustic waves (shear bulk waves) propagated in the system of AT-cut quartz plate; here q is the wave vector and u is the substrate boundary displacement.

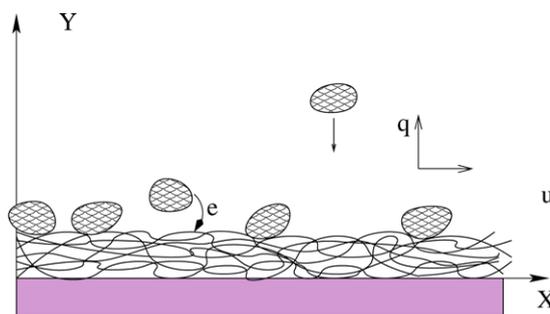


Fig. 2. Schematic depiction of QCM working in liquid phase – the quartz crystal microbalance as a mass detector in electronic tongue applications; the receptive surface can be, e.g., redox polymer matrix. In electrochemical (EQCM) measurements, such quartz microbalance was found [20] to monitor mass changes during the redox processes at interfaces.

2. The effects of slippage and viscous dissipation in QCM measurements

Figure 1 shows the sketch of QCM's architecture, a mass-sensing element of gas sensor (the so-called electronic nose) where the tested molecules from gas or vapour are adsorbed onto a chemically modified receptive surface of the quartz (spin-coating or electroactive polymers, self-assembled monolayers and lipid coating by Langmuir–Blodgett technique are selected examples of organic materials in electronic nose technology [8]). Here we will consider the receptive layer as a molecularly thin film rigidly attached to the quartz surface. For such film, the shift of resonance frequency Δf is proportional to the density ρ and thickness h of the overlayer [9], while the dissipation vanishes. A finite amount of slippage can arise either from incommensurate densities [10,11] or weak coupling between the layer of odorant molecules and the substrate and change both the resonance frequency f and the quality factor Q of oscillator (an extensive analysis of sliding friction in the low-density limit can be found in the recent book by Persson [11]).

For a quantitative characterization of slippage effects it is convenient to use the ratio of the inverse quality factor $\Delta(Q^{-1})$ to the shift Δf of the QCM resonance frequency. This value was introduced in the QCM community by Krim and Widom [12] as a “slip time”,

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

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 ΔD and Δf can be measured simultaneously in QCM experiments [1,2,13]; one always finds ΔD to be positive while the resonance frequency shift Δf is negative since mass loading lowers the oscillator resonance frequency (in comparison to its unloaded state in vacuum). According to the results of Krim's group [12], a partial decoupling of the overlayer should occur when $2\pi f\tau \geq 0.5$. Typically, a quartz crystal oscillates with frequency $f \sim 10$ MHz and therefore decoupling starts when $\tau \geq \tau_c \simeq 10^{-8}$ s. For instance, in QCM experiments with thin water films [13] $\Delta f \sim 1-10$ Hz, $\Delta D \sim 10^{-7}-10^{-6}$ and hence $\tau \sim 10^{-9}-10^{-7}$ s, which is quite close to τ_c . Thus, a relatively low decoupling threshold can lead to noticeable interfacial friction effects even in case of molecularly thin films. In nanotribological QCM-experiments of Krim and collaborators [14,15], the interfacial friction coefficient γ_f for thin rigid films 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. This result can also be viewed as the definition of the slip time τ , which is [12] the characteristic time it takes for the film velocity to decrease by a factor of $1/e$. However, for soft interfaces this result should be corrected because of additional viscous dissipation of energy in the material.

In the absence of slippage, the shifts in QCM resonance frequency and in the dissipation factor for a one side coverage, can be calculated as follows [12]

$$\Delta\tilde{f} = -Im\left(\frac{\tilde{Z}}{2\pi m_q}\right) = \frac{\tilde{Z}''}{2\pi m_q} \quad (2)$$

and

$$\Delta\tilde{D} = Re\left(\frac{\tilde{Z}}{\pi f m_q}\right) = \frac{\tilde{Z}'}{\pi f m_q}, \quad (3)$$

where $\tilde{Z} = \tilde{Z}' + i\tilde{Z}''$ is the acoustic impedance of QCM. Here we indicate acoustic characteristics determined in the absence of slippage (no-slip boundary conditions) by a tilde sign ($\tilde{}$) over the appropriate symbol. The effect of a potential slip can arise from a weak coupling of the adlayer and the oscillating substrate. In this case the no-slip boundary condition breaks down and a finite difference between velocity of the quartz surface \dot{q}_0 and velocity v_0 of the adjacent layer at the interface (index 0) appears leading to an interfacial friction force, F_s , where

$$F_s = \gamma_s(\dot{q}_0 - v_0). \quad (4)$$

Here γ_s is the proportionality coefficient characterizing sliding friction, which is a constant in the low shear rate approximation. Slippage can also be characterized by a slippage coefficient λ which is simply the inverse of the sliding friction coefficient, $\lambda = \gamma_s^{-1}$. The no-slip condition corresponds to $\lambda \rightarrow 0$, while the opposite limit $\lambda \rightarrow \infty$ gives infinite slippage and complete decoupling of the overlayer from the substrate. Effects of slippage can easily be included in Δf and ΔD as follows:

$$\Delta f \approx -Im\left(\frac{\tilde{Z}}{2\pi m_q(1 + \lambda\tilde{Z})}\right), \quad (5)$$

$$\Delta D \approx Re\left(\frac{\tilde{Z}}{\pi f m_q(1 + \lambda\tilde{Z})}\right), \quad (6)$$

where, as it has already been mentioned, $\lambda = 1/\gamma_s$, $m_q = h_q\rho_q$ is the quartz plate surface mass.

Since both slip and viscosity can contribute to the QCM damping, the problem of how to distinguish between these two dissipative factors is of key importance. Let us now consider a viscoelastic thin film of tested molecules in contact with the quartz oscillator ("thin" or "thick" films refers to the film thickness being smaller or greater than the inverse values of the decay constant α and propagation constant k of the bulk acoustic waves propagating in the coated quartz plate [16,17]). Following the approach developed by us earlier [17,18], we have calculated the acoustic impedance \tilde{Z} for viscoelastic thin layer when the QCM oscillates in a gaseous phase. By using (2) and (3) we then found

$$\Delta\tilde{f} \approx -\frac{h\rho\omega}{2\pi m_q} \left\{ 1 + \frac{h^2}{3} \frac{\rho\omega^2 G'}{G'^2 + G''^2} \right\}, \quad (7)$$

$$\Delta\tilde{D} \approx \frac{h^3 \rho^2 \omega^3}{3\pi f m_q} \frac{G''}{G'^2 + G''^2}, \quad (8)$$

where $G'(\omega)$ and $G''(\omega)$ are the storage and loss moduli of the viscoelastic adlayer of the thickness h and density ρ , respectively. In analogy with (1), let us introduce for general case of slipping viscoelastic material, the characteristic time τ as the ratio of the shift of the measured dissipation factor to the change in resonance frequency change:

$$\tau_s = -\frac{\Delta D}{4\pi\Delta f}, \quad (9)$$

where Δf and ΔD are experimentally measured values. In order to characterize the temporal QCM response when no-slip boundary conditions apply, we define another characteristic value

$$\tau_0 = -\frac{\Delta \tilde{D}}{4\pi\Delta \tilde{f}}. \quad (10)$$

Defined in this way, the characteristic time τ_0 can be attributed solely to the effects of internal friction (viscosity) on damping of the QCM, i.e., $\Delta \tilde{D}$ is proportional to the resistive term $Re(Z)$ in the acoustic “no-slip” impedance \tilde{Z} . Using Eqs (5)–(10), one can find the slippage coefficient λ or the interfacial friction coefficient γ_s , from experimentally measured τ_s value

$$\lambda \approx \frac{\omega\tau_0 - \omega\tau_s}{2\pi\Delta \tilde{f}m_q}, \quad (11)$$

where τ_0 is given by (10) with $\Delta \tilde{f}$ and $\Delta \tilde{D}$ deduced from (7) and (8), respectively. In the limit 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 Sauerbrey solid-like response [9], for which $\Delta \tilde{f} = -f_0 \cdot m_f/m_q$, $\Delta \tilde{D} = 0$, where $m_f = \rho h$ is the surface mass (i.e., mass per unit area) of the film; in this case the coefficient of interfacial friction $\gamma_{s0} = m_f/\tau_s$, which reproduces the result of researchers in [12,14,15]. In general situation of slipping viscoelastic adlayer, the QCM characteristics are given by Eqs (5), (6) together with (7), (8). Using the general expressions (5), (6), the dissipation factor $\Delta D(\lambda)$ as a function of slippage $\Delta D(\lambda)$ is

$$\Delta D(\lambda) \approx \frac{1}{\pi f m_q} \frac{\tilde{Z}' + \lambda(\tilde{Z}'^2 + \tilde{Z}''^2)}{1 + \lambda^2(\tilde{Z}'^2 + \tilde{Z}''^2) + 2\lambda\tilde{Z}'}. \quad (12)$$

From Eq. (12) it follows that the dissipation shift peaks for a critical value of slippage coefficient λ^* . If we take the limit $\tilde{Z}' = 0$ corresponding to a rigid thin film, the maximal dissipation is

$$\Delta D(\lambda^*) = -\frac{\Delta \tilde{f}}{f}. \quad (13)$$

The condition (13) is readily understandable. For a non-dissipative medium, damping of the oscillator is proportional to the inertial contribution $\Delta \tilde{f}/f \sim m_f$ 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

$$\gamma^* = m_f \cdot \omega, \quad (14)$$

or equivalently when the slippage coefficient is $\lambda^* = 1/(m_f \cdot \omega)$. This maximum value of the dissipation factor is

$$\Delta D(\lambda^*) = m_f/m_q. \quad (15)$$

The lower the surface mass density is, the larger is the slippage coefficient λ^* (for which the dissipation factor is maximal) and the smaller is this maximal value. 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 frequency independent maximum as a test of whether slippage occurs in dynamic QCM measurements; if the dissipation peak remains constant when the oscillation frequency ω is varied, the peak can be attributed to sliding friction.

Experimentally, the sliding friction is an external parameter which can be changed, e.g., by varying pressure or temperature. Maxima in the dissipation has been observed experimentally [14,15] for solid molecularly thin films sliding along a quartz surface, which oscillates in gaseous environments. The maxima appeared when the condition $\omega\tau = 1$ 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 non-rigid films, the dissipation factor can reach a maximum as temperature or pressure is varied, since these affect the internal friction (viscosity) of the material. In case of sliding thin viscoelastic overlayers, internal friction leads to additional although 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. To the contrary, the viscosity of soft materials of finite thickness will significantly influence the damping and can produce a “viscous” dissipation peak.

From expression (8) it follows that if during an experiment the viscoelastic properties of adlayer vary, the dissipation factor reaches a maximum when $G' = G'' \equiv G$. Hence, the maximum value of the “viscous” dissipation factor $\Delta\tilde{D}_{\max} = h^3\rho^2\omega^2/3Gm_q$ depends on the vibration frequency ω , while the dissipation peak caused by sliding friction was found to be frequency independent. Note that the “viscous” peak value $\Delta\tilde{D}(\eta^*)$ is smaller by a factor $h^2\rho\omega^2/3G$ than the peak value $\Delta D(\lambda^*)$. When slippage is absent (or negligibly small), viscoelastic effects dominate and the dissipation maximum becomes frequency dependent.

Our result provides a method to quantify friction effects and even distinguish between them in QCM spectroscopy measurements performing on various frequencies.

3. Discussion: “missing mass” in electronic tongue QCM applications

Among artificial sensor systems, the arrays of electronic chemical sensors (electronic nose) working in gaseous environment and imitating the mammalian sense of smell [8] remain the primary instrumentation, although sensors operating in aqueous phase and having the same properties of electronic nose (the so-called electronic tongue) have been reported [19]. In many cases, electronic tongue which can be regarded as a wet chemical counterpart of the electronic nose [19–21]. Recently, the integration of electronic nose and electronic tongue into a multisensor device has been proposed to improve the quality analysis of liquid samples and related volatile components [19]. The simultaneous usage of these two types of sensors covered with the same sensitive substances (metalloporphyrins) has been utilized by authors [19] to optimize the sensor characteristics.

If the QCM is used as a mass sensor in electronic tongue applications, the density and viscosity of the solution affect the resonance frequency of the oscillator. The classical result of Gorgon and Kanazawa [22] for the shift of resonance frequency of QCM immersed into a bulk liquid is:

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

In the thin film limit, the conventional approach assumes that the total frequency shift Δf_{total} due to the bulk liquid and a thin overlayer should be a sum of their contributions, so the detected mass derived from Δf is given by the difference $\Delta f_{\text{total}} - \Delta f_L$.

Recently, however we reported a new interesting result, that for non-rigid materials in liquid QCM measurements the mass of the detected adlayer (the equivalent surface mass) differs from its “true mass” [7,18]. Since the equivalent surface mass M_s was found to be much smaller than the film surface mass $M = \rho \cdot h$, we called this phenomenon the “missing mass” effect [7].

Also, it was shown that when the QCM operates in a liquid phase, the resonance frequency shift was found to be [7]:

$$\Delta f_{\text{total}} \approx \Delta f_L - \frac{M\omega}{2\pi m_q} \left\{ 1 - \frac{2}{\rho} (\eta_L / \delta_L)^2 \frac{G''}{G'^2 + G''^2} \right\}, \quad (16)$$

where G' and G'' are the overlayer viscoelastic moduli, index “L” denotes liquid phase and δ_L is a viscous length of bulk newtonian liquid [7]. Hence, in contrast to the results obtained for a gaseous phase, in liquids even in the thin film approximation, a viscous correction of surface mass appears already in first order in the film thickness h :

$$M_s = M \left\{ 1 - \frac{\eta_L \rho_L \omega}{\rho} \frac{G''}{G'^2 + G''^2} \right\}. \quad (17)$$

This result can be useful for interpreting QCM data in electronic tongue and biosensor applications since the correct estimation of the mass derived from the QCM response can be a crucial step towards using the microbalance as a mass sensor in complex biological liquids where biomolecules adsorbed from the solution make a soft film on the receptive surface of oscillator [21]. In some situations, it would be useful to combine the voltammetric electronic tongue and QCM technique to relate the mass changes and charge transport phenomena in analytical chemistry applications and *in situ* electrochemical measurements. For example, it has been reported elsewhere [20] that if a coating layer is a redox active polymer, the QCM can monitor the mass changes which accompany the redox processes in receptive polymer matrix. In there, the relationship between the charge Q , a measure of the total number of electrons produced or consumed in redox reactions, and mass transport has been derived from the combined QCM and voltammetry data.

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