Operation of the Quartz Crystal Microbalance in Liquids: Derivation of the Elastic Compliance of a Film from the Ratio of Bandwidth Shift and Frequency Shift

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For a thin viscoelastic film deposited on a quartz crystal microbalance in a liquid environment, the change in dissipation induced by the presence of a film is proportional to the film’s elastic compliance, \( J' \). This surprising result is a consequence of the fact that the film is “damped” by a viscous fluid.

**Introduction**

The quartz crystal microbalance (QCM) is today routinely used in liquids. This development was first driven by electrochemical applications, namely, the electrochemical QCM (EQCM). Biological applications have recently gained much importance. Historically, the strong dissipation was a problem for the operation of the QCM in liquids. However, it was soon recognized that the dissipation contains valuable information about the system under study, as well. The group from Chalmers university, in particular, has much emphasized the value of dissipation for interface analysis. 6

Assuming a certain acoustic layer system, one can always predict the frequency shift and the bandwidth (the latter being proportional to dissipation). However, the inversion is often problematic. Depending on how many free parameters the model has, they cannot all be uniquely determined from the experimental data. There are some simple cases, where the formalism can be operated backward. For instance, the fractional complex frequency shift induced by a thin viscoelastic film in air is given by

\[
\frac{\Delta f^*}{f} = \frac{\Delta f + i \Delta \Gamma}{f} = -\frac{m_l}{m_q} + \left( \frac{m_q}{m_q} \right)^2 - \frac{1}{3} \left( \frac{m_l}{m_q} \right)^2 \left( \frac{\rho_f}{\rho_l} \right) \frac{Z_q^2}{q_f} - 1
\]

where \( \Delta f^* \) is the complex frequency shift, \( \Delta f \) is the frequency shift, \( \Delta \Gamma \) is the shift of half-band-half-width, \( f \) is the frequency, \( Z_q = 8.8 \times 10^9 \) kg m\(^{-2}\) s\(^{-1}\) is the acoustic impedance of the quartz plate, \( m_q \) is the areal mass density of the film, \( m_l = Z_q/(2f) \) is the areal mass density of the quartz plate, \( n \) is the overtone order, \( J \) is the film's complex viscoelastic compliance, and \( \rho_f \) is the film's density. Electrode effects have been neglected in eq 1. Plotting the fractional frequency shift \( \Delta f / f \) versus the square of overtone order, \( n^2 \), one can derive the compliance, \( J'/n \), from the slope. However, in practice this only works if the films are thicker than about 50 nm. Since the viscoelastic effects scale as the cube of the film’s mass, they are very difficult to observe for molecularly thin films. In air, the films shear under its own inertia. There is no clamp holding it from the other side. If the film is too thin, the forces of inertia are negligible and effects of internal shear vanish.

There is a second problem with the practical application of eq 1, which is the frequency dependence of the compliance (“dispersion”). In general, the dispersion is not known. Assuming that the frequency dependence is smooth (which is a good approximation for most polymers), one can use a power law with a certain guess for the exponent. Using this power law, one can use eq 1 to derive the compliance at a reference frequency. However, the outcome of this procedure depends on which exponent is chosen for the dispersion. While one might, in principle, attempt to fit the exponent from the experimental set of complex frequency shifts, this does not work in practice.

As we show below, this is different in liquids because the liquid damps the film from the other side. However, in liquids there is another problem, which is the issue of solvent uptake in the film: the mass is rarely known independently because there may be swelling of the film in the solvent. Hydrodynamically trapped solvent contributes to the mass of wet film. To eliminate the mass and focus on the film's intrinsic properties, one can consider the ratio of the half-band-half-width and the negative frequency shift. Both the frequency shift and shift in bandwidth are proportional to the film's mass in the thin-film limit. By considering the ratio of the two variables, one eliminates the mass. The ratio only depends on the intrinsic properties of the film under investigation. A similar concept is pursued in the D–f plot, where one plots the half-band-half-width (or, equivalently, the “dispersion”, \( D = 2f \Delta f \)) versus the negative frequency shift, eliminating time as a variable.

We investigate a simple case: the thin viscoelastic film in a Newtonian liquid. It turns out that the additional
dissipation induced by the film is, under certain simplifying assumptions, proportional to the film’s compliance, \( J \). 

**Calculation**

We start out from the equation

\[
\frac{\delta \Gamma}{f_0} = \frac{\delta f + i \delta \Omega}{f_0} = \frac{i}{\pi Z_q} Z_{\text{load}} \approx \frac{i}{\pi Z_q} \frac{\sigma}{iu \delta t} \tag{2}
\]

where \( Z_{\text{load}} \) is the impedance of the load, \( f_0 \) is the fundamental resonance frequency of the quartz, \( \sigma \) is the shear stress, and \( iu \delta t \) is the lateral speed at the quartz surface.

\( Z_{\text{load}} \) is the ratio of stress and speed at the quartz surface; it is not a material constant. Equation 2 is the first-order approximation in a perturbation analysis, where the load, \( Z_{\text{load}} \), is the perturbation parameter. For large loads (and thick films, in particular), more complicated equations apply.

For a viscoelastic film in a liquid, \( Z_{\text{load}} \) is given by

\[
Z_{\text{load}} = iZ_l \tan(k_d d_l) - iZ_{\text{liq}} \left( \frac{1}{Z_l} + iZ_{\text{liq}} \tan(k_d d_l) \right) \tag{3}
\]

where \( Z_l \) and \( Z_{\text{liq}} \) are the acoustic impedance of the film and the liquid, respectively, \( k_d \) is the wavenumber of shear sound inside the film, and \( d_l \) is the film thickness. \( Z_l \) and \( Z_{\text{liq}} \) are material properties. In the following, we confine ourselves to thin films, that is, we perform a Taylor expansion of eq 3 to first order in \( d_l \). A thin film in this context is a film which is much thinner than the escape depth of the shear wave. In principle, the escape depth may be changed by the presence of the film. However, it will always increase because the film is more rigid than the liquid. Thus such a change will never result in a situation where the thin-film condition is violated due to this change. The result of the Taylor expansion is

\[
Z_{\text{load}} \approx Z_{\text{liq}} + iZ_l d_l k_s \left( 1 - \frac{Z_{\text{liq}}^2}{Z_l^2} \right)^{1/2} \tag{4}
\]

The frequency shift is usually determined with respect to a reference state, where the quartz is already immersed in liquid. When the film is absent, one has \( Z_{\text{load}} = Z_{\text{liq}} \). Referencing the measurement to the bare quartz in liquid, one therefore obtains

\[
\frac{\delta \Gamma}{f_0} = \frac{\delta f + i \delta \Omega}{f_0} \approx \frac{i}{\pi Z_q} (Z_{\text{load}} - Z_{\text{liq}}) = -\frac{1}{\pi Z_q} Z_l k_s d_l \left( 1 - \frac{Z_{\text{liq}}^2}{Z_l^2} \right) \tag{5}
\]

Using the relations \( Z_l = \rho_v \nu_l \) (\( \nu_l \) is the speed of sound) and \( k_s = \omega / \nu_l \), this amounts to

\[
\frac{\delta \Gamma}{f_0} = \frac{\delta f + i \delta \Omega}{f_0} = -\frac{1}{\pi Z_q} 2 \pi n f \rho_v \nu_l \left( 1 - \frac{Z_{\text{liq}}^2}{Z_l^2} \right) \tag{6}
\]

Apart from the term in brackets, eq 6 is equivalent to the Sauerbrey equation. Note that the mass, \( m_s \), includes hydrodynamically trapped liquid. We are at this point not concerned with the question of what the “Sauerbrey mass” is. The term in brackets is a viscoelastic correction. As opposed to films in air or a vacuum, where the viscoelastic correction scales as the third power of mass, the viscoelastic factor enters linearly (\( \sim m_s \)) in a liquid environment. In air, the film surface is stress free, while it is “damped” by the liquid here.

As such, eq 6 is of limited practical use because the mass, \( m_s \), is usually not known independently. Since the frequency shift contains the product of the mass and the real part of the term in brackets, the two effects cannot be disentangled. Note, however, that the mass can be eliminated by considering the ratio of the shift in half-band-half-width, \( \delta \Omega \), and the negative frequency shift, \( -\delta f \). One has

\[
\frac{\delta \Gamma}{-\delta f} = \frac{-\text{Im}(1 - Z_{\text{liq}}^2/Z_l^2)}{\text{Re}(1 - Z_{\text{liq}}^2/Z_l^2)} \tag{7}
\]

In the following, we assume that the liquid is Newtonian with a density \( \rho_{\text{liq}} \) and a viscosity \( \eta \). The acoustic impedance then is

\[
Z_{\text{liq}} = \sqrt{\nu_0 \rho_{\text{liq}}} \tag{8}
\]

For the film, we use

\[
Z_f = \sqrt{\nu_0 G_f} = \sqrt{\rho_f J} \tag{9}
\]

where \( \rho_f \) is the film density, \( G_f \) is the shear modulus, and \( J = G_f/\nu_f = J''/J' \) is the compliance. Inserting eqs 8 and 9 into eq 7, we find

\[
\frac{\delta \Gamma}{-\delta f} = \frac{-\text{Im}(1 - \nu_0 \rho_{\text{liq}} J'/\rho_f)}{\text{Re}(1 - \nu_0 \rho_{\text{liq}} J'/\rho_f)} = \frac{\nu_0 \rho_{\text{liq}} J'}{\rho_f - \nu_0 \rho_{\text{liq}} J''} \tag{10}
\]

Equation 10 still is exact to first order in \( d_f \). Further simplifying assumptions can be made with regard to the right-hand side. First, the densities in soft-matter experiments usually are similar. Assuming \( \rho_f \approx \rho_{\text{liq}} \) yields

\[
\frac{\delta \Gamma}{-\delta f} \approx \frac{\nu_0 J'}{1 - \nu_0 J''} \tag{11}
\]

Second, most films of interest are substantially more rigid than the ambient liquid. Even films which are statically soft will often appear rigid at MHz frequencies. The denominator in eq 11 can be rewritten as \( 1 - \nu_0 J'/\nu_f liq \) with \( J''/\nu_f liq = (\nu_0)^{-1} \) being the viscous compliance of the liquid. The elastic compliance of the liquid is infinite. If the film is much more rigid than the liquid, the denominator is equal to unity and one has

\[
\frac{\delta \Gamma}{-\delta f} \approx \nu_0 J' = 2 \pi n f \rho_v \nu_l J' \tag{12}
\]

Equation 12 is the central result. By plotting \( \delta \Gamma/\delta f \) versus overtone order \( n \), one can obtain the film’s elastic compliance \( J' \) from the slope. Both \( \delta f \) and \( \delta \Omega \) increase linearly with film thickness. Therefore eq 12 can be applied to very thin films. This contrasts to eq 1, where the effects of finite elasticity only induce measurable effects for films thicker than about 50 nm, because they are proportional to the third power of thickness.

The detailed calculation shows that the requirement of the film being much thinner than the escape depth indeed needs to be taken seriously. When calculating shifts and
The total thickness, $d_{tot}$, of the quartz immersed in water and air were measured using a Network analyzer E5100A (Agilent Technologies, USA) for the compliance of a polymer film in both air and water. The transition region and the application of eq 15 becomes important when considering the ratio \( \frac{d}{d_0} \), which is much less than the wavelength of sound, an arbitrary number of films can be placed one above the other as well, and one can write

\[
\frac{\delta f^*}{f_0} = -\frac{1}{\pi Z_q} \left\{ \sum_{q=1}^{m} Z_q k_q d_q \left( 1 - \frac{Z_{liq}^2}{Z_q^2} \right) \right\} \tag{13}
\]

where the indices 1 and 2 stand for the first and the second film. Equation 13 can be independently derived by Taylor-expanding eq 39 from ref 8 to first order in \( d_1 \) and \( d_2 \). As long as the total thickness, \( d_{tot} \), is much less than the wavelength of sound, an arbitrary number of films can be considered and one can write

\[
\frac{\delta f^*}{f_0} = -\frac{1}{\pi Z_q} \int_{d_0}^{d_{tot}} Z_q(z) k_q(z) \left( 1 - \frac{Z_{liq}^2}{Z_q^2(z)} \right) dz \tag{14}
\]

where the dimensionless variables \( \rho(z) \) and \( \rho_{liq} \) were used in the fourth line. Again considering the ratio \( \delta f/\delta f^* \) and using \( J(z) = j^* (z) - j (z) \), one finds

\[
\frac{\delta f}{f} = -\rho \frac{Z_q}{Z_{liq}} \int_{d_0}^{d_{tot}} \left( 1 - \frac{Z_{liq}^2}{Z_q^2(z)} \right) dz \tag{15}
\]

If the film has a sharp outer edge, the denominator is about the thickness of the layer and the ratio \( \delta f/\delta f^* \) is indeed proportional to the average \( j \). If, on the other hand, there is a smooth range of transition, then the approximation leading to eq 12 (\( \delta f^*/\delta f \approx 1 \)) is not valid in the transition region and the application of eq 15 becomes more complicated.

**Experiment**

We test the above relation 12 by determining the compliance of a polymer film in both air and water. The measurements were performed with 5 MHz gold-coated AT cut quartz crystals (Moxtek, Torrance, CA) and a Network analyzer E5100A (Agilent Technologies, USA) at room temperature. Before a polymer film was coated onto the quartz, the resonance frequencies and bandwidths of the quartz immersed in water and air were measured as the reference state. Polyisobutylene (PIB) with a molecular weight of \( M_w = 1.1 \times 10^6 \) g/mol and a polydispersity index of \( M_w/M_n \sim 1.29 \) was purchased from Polymer Laboratories, Frankfurt, Germany. The density of PIB is 0.92 g cm\(^{-3}\). The polymer films were spun-coated onto the quartz from a PIB-toluene solution. The quartz with the PIB film was dried in a vacuum for 2 h at room temperature in order to remove residual solvent. The optical thickness of PIB film was determined as \( ~280 \) nm by ellipsometry (Ellipsometer ELX-02C, DRE, Ratzberg, Germany). The shifts of the resonance frequency and half-band-half-width of the quartz with PIB film were then measured in air and water.

To compare eq 12 to the perturbation approach applicable in air, we plot the normalized frequency shift \( \delta f/\delta f^* \) of PIB-coated quartz obtained in air versus the square of the overtone order, \( n^2 \), as shown in Figure 1. The detailed calculation shows that electrode effects have to be included in the analysis. Equation 1 has to be replaced by

\[
\frac{\delta f}{f} = -\mu_t (1 - 2 \mu_e + 4 \mu_e^2) + \mu_t^2 (1 - 4 \mu_e) - \mu_t^3 - \frac{n w}{3} \left( \frac{\mu_t^2 + 2 \mu_e \mu_t}{\mu_t^2 + \mu_e^2} \right) \left( \frac{z_{liq}^2}{z_{liq}^2} - 1 \right) \tag{16}
\]

where the dimensionless variables \( \mu_t = m/m_o, \mu_e = m/E \) (the suffix e denotes the electrode), \( z_{liq}^2 = Z_{liq}^2 z_{liq}^2 = 1 \), and \( z_{liq}^2 = Z_{liq}^2 = 1 \). The densities of PIB and gold are 0.92 and 19.3 g cm\(^{-3}\), respectively. By linear fitting, \( \mu_t \) and \( S_n \) are obtained as \( 2.97 \times 10^{-4} \) and 7.07 \( 10^{-8} \), respectively. Note that the harmonics lower than \( n = 7 \) are excluded from the fit because they are affected by piezoelectric stiffening. The thickness of the PIB film...
is calculated as 284 nm based on the density of 0.92 g cm$^{-3}$, which agrees well with the optical thickness of 280 nm, determined by ellipsometry.

For the calculation of the film’s elastic compliance, $J_f'$, one needs the thickness of gold electrodes. The manufacturer quotes a thickness of 320 ± 20 nm. Using values of 300 and 340 nm, the elastic compliance of PIB film, $J_f'$, is calculated as 5.8 and 10 GPa$^{-1}$, respectively. Unfortunately, the thickness of the electrode enters the calculation rather sensitively. A thickness error of 7% shifts the derived value of $J_f'$ by a factor of 2. Generally speaking, the use of aluminum electrodes, where $e_e$ ~ 1, is preferable for the measurements of compliance in the dry. The effects of electrodes are much less severe in liquids. By referencing the measurement to the quartz without film in liquid, the electrode effect is canceled out.

Figure 1 also demonstrates the limits posed on the analysis by a possible frequency dependence of $J(\omega)$. Clearly, the data are systematically different from a straight line. Apart from viscoelastic dispersion, higher order terms in the perturbation analysis are a second source for nonlinearity in this plot. We confine ourselves to fitting without considering viscoelastic dispersion, for simplicity.

Figure 2 shows the plot of $\delta\Gamma/\delta f$ versus overtone order $n$ of the same film immersed in water. Figure 2 contains fewer harmonics than Figure 1 because the increased dissipation induced by the liquid creates an overlap of the central harmonics with the anharmonic sidebands. This effect is particularly strong on high harmonics, some of which have to be discarded. The line is the fit of eq 12 through the origin, where the slope is $B = 0.154$. Using $f_0 = 5$ MHz and $\eta = 10^{-3}$ Pa s, one finds a value $J_f' \sim 5$ GPa$^{-1}$. In panel b, we show $J_f'$ calculated from $J_f' = \delta\Gamma/(-\delta f)(\omega \eta)^{-1}$ with $\omega = 2\pi f_0$ and the ratio of $\delta\Gamma$ and $-\delta f$ for all harmonics, separately. The derived $J_f'$ is in the same range for all harmonics. One should not attribute a significance to the increase of $J_f'$ with frequency. This frequency dependence is caused by the fact that this film is already in a range where the thin-film limit is questionable. The induced error tends to artificially increase $J_f'$ on high harmonics. The value of 5 GPa$^{-1}$ is close to the result obtained in the dry. While the data show more scatter than the data in Figure 1, the problem of unknown electrode thickness is avoided in liquids. Also, the measurement in liquid can be carried out on much thinner films.

**Conclusion**

The shift of dissipation of a QCM operating in liquid induced by a thin film is proportional to the film’s elastic compliance, $J_f'$. By considering the ratio of the half-band-half-width and the negative frequency shift, one can obtain the elastic properties of the coating. The experiment gave consistent results for a polymer sample studied in the dry and in the liquid. The measurement in liquid can be applied to arbitrarily thin films and does not suffer from electrode effects. This result should have much significance in sensing of biological adsorbates.

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