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_f'. This surprising result is a consequence of the fact that the film is "clamped" 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).[1] Biological applications have recently gained much in importance.[2] Historically, the strong dissipation was a problem for the operation of the QCM in liquids.[3] However, it was soon recognized that the dissipation contains valuable information about the system under study, as well.[4,5] 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.).[7] 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[8]

$$\frac{\delta f^*}{f} = \frac{\delta f + i\delta\Gamma}{f} \cong$$
$$-\frac{m_f}{m_q} + \left(\frac{m_f}{m_q}\right)^2 - \left(\frac{m_f}{m_q}\right)^3 - \frac{1}{3}(n\pi)^2\left(\frac{m_f}{m_q}\right)^3\left(\frac{J_f(\omega)Z_q^{\,2}}{\rho_f} - 1\right)$$
$$(1)$$

where δf^* is the complex frequency shift, δf is the frequency shift, $\delta\Gamma$ is the shift of half-band-half-width, f is the frequency, $Z_q = 8.8 \times 10^6$ kg m^{-2} s^{-1} is the acoustic impedance of the quartz plate, m_f is the areal mass density of the film, $m_q = Z_q/(2f_0)$ is the areal mass density of the quartz plate, n is the overtone order, J_f is the film's complex

viscoelastic compliance, and ρ_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_f', 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 film shears 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 clamps 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.[9] 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 "dissipation", $D = 2\Gamma/f$) versus the negative frequency shift, eliminating time as a variable.[10]

We investigate a simple case: the thin viscoelastic film in a Newtonian liquid. It turns out that the additional

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dissipation induced by the film is, under certain simplifying assumptions, proportional to the film's compliance, J_f'.

Calculation

We start out from the equation

$$\frac{\delta f^*}{f_0} = \frac{\delta f + i\delta\Gamma}{f_0} \cong \frac{i}{\pi Z_q}Z_{load} \cong \frac{i}{\pi Z_q}\frac{\sigma}{\partial u/\partial t} \qquad (2)$$

where Z_{load} is the impedance of the load, f_0 is the fundamental resonance frequency of the quartz, σ is the shear stress, and $\partial u/\partial t$ is the lateral speed at the quartz surface.

Z_{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_{load}, is the perturbation parameter. For large loads (and thick films, in particular), more complicated equations apply.[8]

For a viscoelastic film in a liquid, Z_{load} is given by[8]

$$Z_{load} = iZ_f\frac{Z_f\tan(k_fd_f) - iZ_{liq}}{Z_f + iZ_{liq}\tan(k_fd_f)} \qquad (3)$$

where Z_f and Z_{liq} are the acoustic impedance of the film and the liquid, respectively, k_f is the wavenumber of shear sound inside the film, and d_f is the film thickness. Z_f and Z_{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_f. 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

$$Z_{load} \approx Z_{liq} + iZ_fd_fk_f\left(1 - \frac{Z_{liq}^2}{Z_f^2}\right) \qquad (4)$$

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 $Z_{load} = Z_{liq}$. Referencing the measurement to the bare quartz in liquid, one therefore obtains

$$\frac{\delta f^*}{f_0} = \frac{\delta f + i\delta\Gamma}{f_0} \approx \frac{i}{\pi Z_q}(Z_{load} - Z_{liq}) =$$

$$\frac{-1}{\pi Z_q}Z_fk_fd_f\left(1 - \frac{Z_{liq}^2}{Z_f^2}\right) \qquad (5)$$

Using the relations $Z_f = \rho_f v_f$ (v_f is the speed of sound) and $k_f = \omega/v_f$, this amounts to

$$\frac{\delta f^*}{f_0} = \frac{\delta f + i\delta\Gamma}{f_0} = \frac{-1}{\pi Z_q}2\pi nf_0m_f\left(1 - \frac{Z_{liq}^2}{Z_f^2}\right) \qquad (6)$$

Apart from the term in brackets, eq 6 is equivalent to the Sauerbrey equation. Note that the mass, m_f, 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,[8] the viscoelastic factor enters *linearly* ($\propto m_f$) in a liquid environment. In air, the film surface is stress free, while it is "clamped" by the liquid here.

As such, eq 6 is of limited practical use because the mass, m_f, 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, $\delta\Gamma$, and the negative frequency shift, $-\delta f$. One has

$$\frac{\delta\Gamma}{-\delta f} = \frac{-\text{Im}(1 - Z_{liq}^2/Z_f^2)}{\text{Re}(1 - Z_{liq}^2/Z_f^2)} \qquad (7)$$

In the following, we assume that the liquid is Newtonian with a density ρ_{liq} and a viscosity η. The acoustic impedance then is

$$Z_{liq} = \sqrt{i\omega\rho_{liq}\eta} \qquad (8)$$

For the film, we use

$$Z_f = \sqrt{\rho_f G_f} = \sqrt{\rho_f/J_f} \qquad (9)$$

where ρ_f is the film density, G_f is the shear modulus, and $J_f = G_f^{-1} = J_f' - iJ_f''$ is the compliance. Inserting eqs 8 and 9 into eq 7, we find

$$\frac{\delta\Gamma}{-\delta f} = \frac{-\text{Im}(1 - i\omega\rho_{liq}\eta J_f/\rho_f)}{\text{Re}(1 - i\omega\rho_{liq}\eta J_f/\rho_f)}$$

$$= \frac{\omega\rho_{liq}\eta J_f'}{\rho_f - \omega\rho_{liq}\eta J_f''} \qquad (10)$$

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 $\rho_f \approx \rho_{liq}$ yields

$$\frac{\delta\Gamma}{-\delta f} \approx \frac{\omega\eta J_f'}{1 - \omega\eta J_f''} \qquad (11)$$

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 $1 - J_f''/J_{liq}''$ with $J_{liq}'' = (\omega\eta)^{-1}$ 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

$$\frac{\delta\Gamma}{-\delta f} \approx \eta\omega J_f' = 2\pi nf_0\eta J_f' \qquad (12)$$

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_f' from the slope. Both δf and $\delta\Gamma$ 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

bandwidths from eqs 2 and 3 and backing out the elastic compliance J from these simulated data, one finds deviations with a thickness in the range of 10 nm already. The details depend on the properties of the film. The deviation is highest on the high harmonics. This caveat should be kept in mind.

Finally, we discuss films where the acoustic properties of the film vary along the vertical coordinate, z. This would be a typical situation for polymer layer adsorbed from an analyte solution. These films are often dilute with density gradients along the vertical axis. While one would wish to state that the QCM determines the "average" J of the adsorbate, a word of caution is necessary.

Because eq 5 is linear in thickness, it holds for two films placed one above the other as well,

$$\frac{\delta f^*}{f_0} = \frac{-1}{\pi Z_q}\left\{ Z_{f1}k_{f1}d_{f1}\left(1 - \frac{Z_{liq}^2}{Z_{f1}^2}\right) + Z_{f2}k_{f2}d_{f2}\left(1 - \frac{Z_{liq}^2}{Z_{f2}^2}\right)\right\} \quad (13)$$

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_{f1} and d_{f2}. 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

$$\frac{\delta f^*}{f_0} = \frac{-1}{\pi Z_q}\sum_{i=1}^{m} Z_{fi}k_{fi}d_{fi}\left(1 - \frac{Z_{liq}^2}{Z_{fi}^2}\right)$$

$$\approx \frac{-1}{\pi Z_q}\int_0^{d_{tot}} Z_f(z)k_f(z)\left(1 - \frac{Z_{liq}^2}{Z_f^2(z)}\right)dz$$

$$= \frac{-1}{\pi Z_q}2\pi n f_0 \int_0^{d_{tot}} \rho_f(z)\left(1 - \frac{i\omega\eta\rho_{liq}}{\rho_f(z)G_f(z)}\right)dz$$

$$\approx \frac{-2nf_0\rho}{Z_q}\int_0^{d_{tot}}[1 - i\omega\eta J_f(z)]\,dz \quad (14)$$

where $\rho_f(z) \sim \rho_{liq} \sim \rho$ was used in the fourth line. Again considering the ratio $\delta\Gamma/(-\delta f)$ and using $J_f(z) = J_f'(z) - iJ_f''(z)$, one finds

$$\frac{\delta\Gamma}{-\delta f} = \frac{\omega\eta\int_0^{d_{tot}} J_f'(z)\,dz}{\int_0^{d_{tot}}[1 - J_f''(z)\omega\eta]\,dz} \quad (15)$$

If the film has a sharp outer edge, the denominator is about the thickness of the layer and the ratio $\delta\Gamma/(-\delta f)$ 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 ($J_f'' \ll J_{liq}''$) 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 (Maxtek, 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
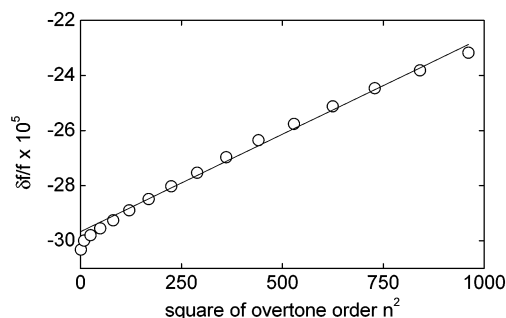
Figure 1. Normalized frequency shifts $\delta f/f$ vs the square of the overtone order, n^2, for a 280 nm polyisobutylene film in air. The straight line is a linear fit, where the first three data points have been excluded from the fit because they are affected by piezoelectric stiffening. The elastic compliance of the film, J_f', is extracted from the slope S_n' of the linear fit by eq 18.

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 PSS, Mainz, Germany. The density of PIB is 0.92 g cm^{-3}. The polymer films were spin-cast 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, Ratzeburg, 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 $\delta f/f$ 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[8]

$$\frac{\delta f^*}{f} = -\mu_f(1 - 2\mu_e + 4\mu_e^2) + \mu_f^2(1 - 4\mu_e) - \mu_f^3 -$$
$$(n\pi)^2\left((\mu_e\mu_f^2 + \mu_e^2\mu_f)(\xi_e^2 - 1) + \frac{\mu_f^3}{3}(\xi_f^2 - 1)\right) \quad (16)$$

where the dimensionless variables $\mu_f = m_f/m_q$, $\mu_e = m_e/m_q$ (the suffix e denotes the electrode), $\xi_f^2 = Z_q^2/Z_f^2 = J_f Z_q^2/\rho_f$, and $\xi_e^2 = Z_q^2/Z_e^2 = J_e Z_q^2/\rho_f$ have been introduced. Writing[8]

$$\frac{\delta f}{f} \approx -A + S_n'n^2 \quad (17)$$

one can infer the elastic compliance, J_f', from the slope as

$$J_f' = \frac{\rho_f}{Z_q^2}\left(1 - S_n'\frac{3}{\pi^2\mu_f^3} - 3\left(\frac{\mu_e}{\mu_f} + \frac{\mu_e^2}{\mu_f^2}\right)(Re(\xi_e^2) - 1)\right) \quad (18)$$

The parameter A in eq 17 collects all terms independent of n. One has $A \approx \mu_f$. The normalized areal mass density of the film, μ_f, is inferred from the offset of the $\delta f/f$ versus n^2 plot. For the electrodes, the thickness as quoted by the manufacturers is used in order to derive μ_e. The parameter $\xi_e = Z_q/Z_e$ is $\xi_e = 0.38$ (derived from $Z_q = 8.8 \times 10^6$ kg m^{-2} s^{-1} and $Z_{gold} = 23.2 \times 10^6$ kg m^{-2} s^{-1}). The densities of PIB and gold are 0.92 and 19.3 g cm^{-3}, respectively. By linear fitting, μ_f and S_n' are obtained as 2.97×10^{-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.[7] 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' by a factor of 2. Generally speaking, the use of aluminum electrodes, where $\xi_e \sim 1$, 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 $\omega = 2\pi n f_0$ 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
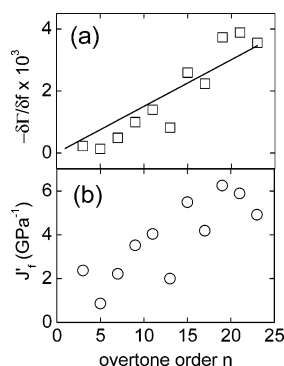
Figure 2. (a) Plot of the half-band-half-width shift vs the negative frequency shift for a 280 nm polyisobutylene film immersed in water. The reference state is the bare quartz in water. (b) Direct calculation of J_f' using $J_f' = \delta\Gamma/(-\delta f)(\omega\eta)^{-1}$, $\omega = 2\pi n f_0$ ($f_0 = 5$ MHz), and $\eta = 10^{-3}$ Pa s.

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'. 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.