Derivation of the shear compliance of thin films on quartz resonators from comparison of the frequency shifts on different harmonics: A perturbation analysis

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Viscoelastic effects contribute to the shift in resonance frequency of quartz crystal resonators induced by deposition of thin films on the resonator surface. In turn, the mechanical stiffness of the film can be experimentally determined from a comparison of the resonance shifts on different harmonics. When the film is much thinner than the wavelength of shear sound, a series expansion of the viscoelastic effects to third order in film thickness leads to rather simple equations. When plotting the normalized frequency shift $\delta f/f$ versus the square of the overtone order $n^2$ one finds a linear relationship, where the slope is determined by the film’s elastic compliance. When the same analysis is carried out on the resonance bandwidths rather than the frequency shifts the viscous compliance is obtained. The effects of asymmetric coatings, electrodes, and liquid media are discussed. © 2001 American Institute of Physics. [DOI: 10.1063/1.1358317]

I. INTRODUCTION

Quartz crystal resonators have been used extensively to monitor the physical properties of thin layers on their surfaces. In commercial applications, film thickness determination usually is the main interest. For a thin film the frequency shift is a function of the mass alone; its acoustic properties may be ignored. In this approximation the well-known Sauerbrey equation holds, stating that the frequency shift is proportional to the deposited mass.

The determination of the shear compliance of a film from shifts of the resonance frequency has recently been addressed by a number of workers. The viscoelastic parameters are derived from a comparison of the frequency shifts on different overtones. “Overtone quartzes” with polished, planar surfaces are employed for these measurements. Generally speaking, viscoelastic effects are negligible whenever the film thickness is much less than the wavelength of sound. In this case the film is essentially located in an antinode of the standing shear wave. Since the film does not experience shear, the frequency shift is independent of the film’s elastic properties. If, on the other hand, the film thickness is comparable to one quarter of the wavelength of sound, the elastic effects are rather dramatic. The film itself then forms a resonator. The “film resonance” couples to the quartz crystal resonance and a rather complicated picture emerges.

The frequency shift is described by transcendental equations which can only be solved numerically. There is a rather interesting regime in between the Sauerbrey limit and the film resonance, where the viscoelastic effects are small but still significant. In this regime a perturbation analysis may be carried out and a rather simple scheme for determining the shear compliance emerges.

In terms of algebraic complexity, the easiest case is given by two identical films on both sides of the quartz plate. We provide the derivation for this case in full detail (Sec. III). Asymmetric situations with a film on just one side of the quartz are of more practical interest. The extension to this case is straightforward, although the equations become clumsier. A geometry with two films situated one above the other is interesting for two reasons: First, the analysis can serve to elucidate the role of the electrodes whose finite elasticity affects the results in some cases. Second, if a film is sandwiched between the quartz and the second layer, this film’s stiffness can be derived even if the film is very thin because the film has been moved away from the antinode of the standing wave by the addition of the cover layer. The article concludes with some remarks on films immersed in a liquid. This configuration is of some importance in the context of biosensors. Adsorbed films may be swollen in the ambient liquid, which results not only in an increased apparent thickness, but also in a softening of the layer.

II. EQUIVALENT CIRCUITS

The analysis starts out from the Mason equivalent circuit depicted in Fig. 1. The transformer represents piezoelectric coupling. The ratio $\Phi$ is given by $\Phi = S e'_{2\theta} d_q$ with $S$ the active surface area, $e'_{2\theta} = 9.65 \times 10^{-2}$ C m$^{-2}$ the relevant piezoelectric coefficient, and $d_q$ the thickness of the resonator. Note that acoustic impedances are normalized to unit area, whereas electric impedances are not. The acoustic impedance $Z_q$ of AT-cut quartz is $Z_{q} = 8.8 \times 10^{6}$ kg m$^{-2}$ s$^{-1}$. $k_q = \omega v_q$ is the wave number of transverse sound, with $v_q = 3325$ m s$^{-1}$ the speed of sound. $d_q$ is the resonator thickness. $C_0 = e_0 S/d_q$ is the electric capacitance with $e = 4.54$ the relative dielectric permittivity. The loads on either side are represented as single elements $Z_{t}$ and $Z_{b\ell}$. These impedances may have a complicated frequency dependence.
Note that the Mason circuit assumes a one-dimensional model, that is, laterally infinite piezoelectric plates. Stevens and Tierstein have provided a three-dimensional (3D) analytical calculation for the resonance frequencies of plane-convex quartz plates without films.\textsuperscript{11} We are not aware of a 3D analytical treatment of quartz plates covered with a film. Presumably, one will have to resort to a numerical finite element analysis.\textsuperscript{12}

If one is interested in sensoric applications rather than frequency control, a load has to be included in the model. The load could be a film, a liquid, a tip touching the surface, or any other object interacting with the oscillating quartz. Here we are concerned with stratified layers and layer systems coated onto the quartz surfaces. The loads are represented by generalized impedances, $Z_{fr}(\omega)$ and $Z_{bk}(\omega)$, on the front and the back side of the plate. Note that these elements are not to be understood as simple-valued quantities in the “lumped-element” sense.\textsuperscript{13} Their frequency dependence may be arbitrarily complex. $Z_{fr}$ and $Z_{bk}$ are defined as the ratio of stress, $\sigma$, and lateral velocity, $dudt$ (u the displacement), at the quartz surface. This ratio can be calculated either from application of the Kirchhoff rules to equivalent circuits like the one shown in Fig. 1\textsuperscript{14} or from a multilayer matrix formalism based on reflectivities as it is known from optics.\textsuperscript{5,15}

With given loads, $Z_{fr}(\omega)$ and $Z_{bk}(\omega)$, the circuit is fully specified and the electrical impedance, $Z_{el}$, across the electrical port can be straightforwardly calculated. Note, however, that the impedance itself is of minor interest in the context of sensor applications. Rather, one determines the resonance frequencies where the amplitude of motion and the current through the electrodes become large. The resonance condition is given by $Z_{el}(\omega)=0$. While frequencies can be easily measured with a relative accuracy down to $\Delta f/f \approx 10^{-7}$, the impedance can routinely only be determined with an accuracy of about 1%.

Viscous losses are accounted for in the calculation via complex wave numbers, $k$. The complex frequency which solves the equation $Z_{el}(\omega)=0$ is to be understood in the sense that the imaginary part is the half-band half-width of the resonance. Without further assumptions, the resonance frequencies of the Mason circuit can be found with a numerical search of the zeros of the imaginary part of the electrical impedance $Z_{el}$ [see Fig. 1(a)]. The quartz blank is assumed to be covered with a 100 nm film of density $\rho = 10^{3}$ kg/m$^3$. The shear moduli $G$ are indicated in the figure. For high harmonics, the data approach a straight line, whose slope $S_n'$ contains the information on elasticity. The upward curvature on low harmonics is caused by the piezoelectric stiffening $Z_{el}$ (see Fig. 1). Neglecting $Z_{fr}$, one can calculate the slope $S_n'$ by a perturbation analysis.

![FIG. 1. The Mason equivalent circuit. Part (b) shows the circuit without the electrical capacitance and the element $Z_{fr}$ accounting for piezoelectric stiffening. The resonance condition used in the calculations is $Z_{fr}=0$.](image)

![FIG. 2. An explicit representation of a resonator loaded with a single film. Multilayers can be modeled by multiple sets of circuit elements such as shown on the right-hand side.](image)

![FIG. 3. Calculations of normalized frequency shifts $\delta f/f$ versus $n^2$ (n the overtone order) obtained by numerically searching the zeros of the imaginary part of the electrical impedance $Z_{el}$ [see Fig. 1(a)]. The Quartz blank is assumed to be covered with a 100 nm film of density $\rho = 10^{3}$ kg/m$^3$. The shear moduli $G$ are indicated in the figure. For high harmonics, the data approach a straight line, whose slope $S_n'$ contains the information on elasticity. The upward curvature on low harmonics is caused by the piezoelectric stiffening $Z_{el}$ (see Fig. 1). Neglecting $Z_{fr}$, one can calculate the slope $S_n'$ by a perturbation analysis.](image)
order, \( n^2 \). [For the generalized impedance, \( Z_q(\omega) \), of a single film see Eq. (6) below.] For high harmonics, the dependence of \( \delta f/\omega \) on \( n^2 \) approaches a linear relationship. The slope of this line, \( S_n \), contains the elastic compliance \( J'_f \). At low harmonics one finds a systematic positive deviation from the linear relationship. It is caused by piezoelectric stiffening as given by the term \( k_qd_q \). At low harmonics one finds a systematic positive deviation from the linear relationship. It is caused by piezoelectric stiffening as discussed above. This amounts so far just excluded harmonics lower than \( n=7 \) from the analysis of experimental data. A correction scheme seems possible as well.

At high harmonics, one also finds a slight deviation from the linear relationship. The linear relationship is the consequence of a series expansion of the load to third order in film thickness (see below). As the ratio between the film thickness and the wavelength of sound increases, this expansion becomes invalid. Also not contained in the calculation displayed in Fig. 3 is a possible dependence of the shear modulus \( G \) on frequency \( \omega \) (‘‘viscoelastic dispersion’’). Especially for polymers, the shear modulus is a function of frequency. In the MHz range, \( G \) smoothly increases with frequency with a power law exponent between 0 and 1/2. While one might be tempted to experimentally derive the dispersion \( G(\omega) \) from the nonlinearity in plots of \( \delta f/\omega \) versus \( n^2 \), this is dangerous because of the other sources of nonlinearity. However, viscoelastic dispersion can be straightforwardly included into the Mason circuit via the corresponding nontrivial frequency dependence of the wave number \( k \). The Mason circuit accounts for all other sources of nonlinearity as well. A numerical search of the zeros of \( Z_{\delta}\omega \) of the Mason circuit should therefore be employed whenever nonlinearities in the plot of \( \delta f/\omega \) versus \( n^2 \) are expected or observed.

The formalism can straightforwardly be extended to derive the viscoelastic compliance from the shifts in bandwidth. One plots the normalized shift of half-band half-width \( \delta f/\omega \) versus \( n^2 \) and reads the viscoelastic compliance \( J'_f \) from the slope of this line, \( S_n \)

### III. TWO IDENTICAL FILMS ON BOTH SURFACES

We now turn to the calculation of the impedance across the electrical port \( Z_{el} \). In the following we neglect the electrical capacitance \( C_0 \) since it does not affect the position of the series resonance frequency (which we term ‘‘resonance frequency’’). Also, we neglect the impedance \( Z_k \) accounting for piezoelectric stiffening as discussed above. This amounts to considering a mechanical impedance \( Z_m \) rather than \( Z_q \) as indicated in Fig. 1(b). We first discuss the symmetric situation with \( Z_{bk}=Z_{fk} \). From Fig. 1(b) one reads the condition

\[
0 = Z_m = \frac{iZ_q}{\sin(k_qd_q)} + \left[ iZ_q \tan\left( \frac{k_qd_q}{2} \right) + Z_{fk} \right]^{-1} \sin(k_qd_q) \tan\left( \frac{k_qd_q}{2} \right) + Z_{bk} \right]^{-1}
\]

\[
= -iZ_q \frac{1 + \tan^2\left( \frac{k_qd_q}{2} \right)}{2 \tan\left( \frac{k_qd_q}{2} \right) + Z_{fk}} + Z_{bf}
\]

\[
= -iZ_q \frac{1 + \tan^2\left( \frac{k_qd_q}{2} \right)}{2 \tan\left( \frac{k_qd_q}{2} \right) + Z_{bk}} + Z_{bf},
\]

where we have used the relation \( 1/\sin(2\chi) = [1 + \tan^2(\chi)]/[2 \tan(\chi)] \) in the second line. \( d_q \) is the thickness of the quartz plate and \( k_q \) is the wave number. \( Z_{fr} = 8.8 \times 10^6 \text{kg m}^{-2} \text{s}^{-1} \) is the acoustic impedance of AT-cut quartz. Note that \( Z_q \) is not a generalized impedance like \( Z_{fr} \) and \( Z_{bk} \) but a material constant.

Because the load impedance \( Z_{fr} \) is much smaller than the impedance of the quartz \( Z_q \), resonances occur close to the poles of the tangent. We write the argument of the tangent as

\[
\frac{k_qd_q}{2} = n \frac{\pi}{2}(1 + \varepsilon), \quad n = 1, 3, 5, \ldots
\]

with \( \varepsilon = \varepsilon' + i\varepsilon'' \) a small complex number and \( n \) the overtone order. The resonances correspond to standing waves with antinodes at the quartz surface. For the fundamental, the wavelength is just twice the quartz thickness. Only odd harmonics are electrically excited because the total shear-induced polarization vanishes for symmetric strain patterns. For the resonance frequency \( \omega_r \), one has

\[
\omega_r = \omega_{n,u}(1 + \varepsilon) = nk_qv_q(1 + \varepsilon) = n \frac{\pi}{d_q} \sqrt{G_q/\rho_q}(1 + \varepsilon) = n \frac{\pi}{m_q} Z_q(1 + \varepsilon),
\]

with \( \omega_{n,u} \) the \( n \)th resonance frequency of the unloaded quartz, \( k_qv_q = 2\pi/k_qv_q = \pi/m_q \) the wave number of shear sound on the fundamental, \( G \) the shear modulus, \( \rho \) the density, \( m \) the mass per unit area, \( v = (G/\rho)^{1/2} \) the speed of sound, and \( Z = \rho v = (G/\rho)^{1/2} \) the acoustic impedance. The index \( q \) denotes the quartz. \( \varepsilon \) is equal to the normalized complex frequency shift \( \delta f/\omega = \delta f/\omega + i\delta \Gamma/\omega \), where \( \Gamma \) is the half-band half-width of the resonance.

Inserting \( \cot[n\pi/2(1 + \varepsilon)] = -\tan(n\pi\varepsilon/2) \) into Eq. (1) one derives the resonance condition

\[
0 = iZ_q \tan\left( \frac{n \pi}{2} \varepsilon \right) + Z_{fk}.
\]

The generalized impedance \( Z_{fk} \) is the ratio between the shear stress \( \sigma \) and the velocity \( du/dt \) at the quartz surface. One has

\[
Z_{fk} = \frac{\sigma}{du/dt} = G_f \frac{du/dz}{du/dt} = \frac{G_fk_f(u_+ - u_-)}{i\omega(u_+ + u_-)} = \sqrt{\rho_fG_f} \frac{1-r}{1+r} = Z_f \frac{1-r}{1+r},
\]
where \( z \) is the vertical coordinate, \( u_+ \) and \( u_- \) are the amplitudes of the waves traveling in the upward and the downward direction, \( r = u_- / u_+ \) is the reflection coefficient evaluated just above the quartz surface, and the index \( f \) denotes the medium in contact with the quartz surface. As Eq. (5) shows, the calculation of the generalized impedance amounts to a calculation of a reflection amplitude, which can be done analogously to the matrix formalism in optics.\(^8\) Alternatively, one could apply the Kirchhoff rules to equivalent circuits such as shown in Fig. 2.

We now assume that the load \( Z_u \) is given by a film with a thickness \( d_f \) and an acoustic impedance \( Z_{f} \). Here and in the following the index \( f \) denotes a film. With a perfectly reflecting film–air interface and a phase factor of \( \exp(i k_f d_f) \) between the film surface and the quartz–film interface one arrives at\(^9\)

\[
Z_u = \frac{1 - \exp(2 i k_f d_f)}{1 + \exp(2 i k_f d_f)} = i Z_f \tan(k_f d_f) = i Z_f \tan \left( n \pi (1 + \varepsilon) \frac{Z_q m_f}{m_q Z_f} \right),
\]

where Eq. (3) has been used for \( k_f = \omega / v_f \). The factor of 2 arises because we consider the following the index \( m \) which is a small number it can serve as a perturbation parameter. One can write \( \varepsilon = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \cdots \) and iteratively solve for the different perturbation orders.

Series expansion of the tangents in Eq. (8) to first order \( [\tan(x) \approx x] \) results in

\[
0 \approx \frac{n \pi}{2} \varepsilon + n \pi \mu (1 + \varepsilon).
\]

Solving for \( \varepsilon = \delta f / f \) one finds

\[
\varepsilon \approx - \frac{2 \mu}{1 + 2 \mu} \approx -2 \mu.
\]

Viscoelasticity has dropped out and the Sauerbrey equation\(^2\) was recovered. The factor of 2 arises because we consider films on both surfaces. In order to capture the viscoelastic effects one has to expand the tangent to third order. Using

\[
\tan(x) \approx x + \frac{x^3}{3}
\]

the resonance condition reads

\[
0 \approx n \frac{\pi}{2} \varepsilon + \frac{1}{3} \left( n \frac{\pi}{2} \varepsilon \right)^3 + n \pi \mu (1 + \varepsilon)
+ \frac{1}{2} (n \pi \mu)^3 \xi^2 (1 + \varepsilon)^3.
\]

Expanding Eq. (12) to first order in \( \varepsilon \) one finds

\[
0 \approx n \pi \mu + \frac{1}{3} (n \pi \mu)^3 \xi^2 + \varepsilon \left[ \frac{n \pi}{2} + n \pi \mu + (n \pi \mu)^3 \xi^2 \right].
\]

By solving Eq. (13) for \( \varepsilon \) and expanding the solution to third order in \( n \) and \( \mu \) we find the first order perturbation result

\[
\varepsilon_1 = - \left( n \pi \mu + \frac{1}{3} (n \pi \mu)^3 \xi^2 \right) \left[ \frac{n \pi}{2} + n \pi \mu + (n \pi \mu)^3 \xi^2 \right]
= -2 \mu + 4 \mu^2 - 8 \mu^3 - \frac{1}{2} (n \pi)^2 \mu^3 \xi^2.
\]

The Sauerbrey equation corresponds to the first term on the right-hand side. As anticipated, Eq. (14) contains a viscoelastic term scaling as the square of the overtone order, \( n^2 \). However, Eq. (14) is at variance with intuition: if a material is added to the quartz surface which has the exact same acoustical properties as the quartz plate (\( \xi = 1 \)) the viscoelastic effects must vanish. In terms of acoustics, this layer only increases the thickness of the quartz plate and the normalized frequency shift on all harmonics equals the fractional increase in thickness. On the other hand, viscoelastic effects would not disappear in this case if Eq. (14) was the full result. This inconsistency is caused by the fact that we have so far only considered terms linear in \( \varepsilon \), while the nontrivial viscoelastic effects appear in third order in \( n \) and \( \mu \). In order to consistently treat viscoelasticity, one has to proceed to a third order perturbation. One replaces \( \varepsilon \) by \( \varepsilon_1 + \varepsilon_2 \) in Eq. (12):

\[
0 \approx n \frac{\pi}{2} (\varepsilon_1 + \varepsilon_2) + \frac{1}{3} \left( n \frac{\pi}{2} (\varepsilon_1 + \varepsilon_2) \right)^3
+ n \pi \mu (1 + \varepsilon_1 + \varepsilon_2) + \frac{1}{2} (n \pi \mu)^3 \xi^2 (1 + \varepsilon_1 + \varepsilon_2)^3.
\]
$0 = n \pi \mu + \frac{1}{3} (n \pi \mu)^3 \xi^2 + \epsilon_1 \left( \frac{n \pi}{2} + n \pi \mu + (n \pi \mu)^3 \xi^2 \right) + \epsilon_1^2 (n \pi \mu)^3 \xi^2 + \epsilon_1^3 \left( \frac{n \pi}{24} + \frac{(n \pi \mu)^3}{3} \xi^2 \right) + \epsilon_2 \left[ \frac{n \pi}{2} + n \pi \mu + (n \pi \mu)^3 \xi^2 + \epsilon_1 (n \pi \mu)^3 \xi^2 \right] + \epsilon_2^2 \left( \frac{(n \pi)^3}{8} + (n \pi \mu)^3 \xi^2 \right) \right].$  \hfill (16)

Solving Eq. (16) for $\epsilon_2$ and expanding the result to third order in $n$ and $\mu$ yields

$$\epsilon_2 = -2 \mu + 4 \mu^2 - 8 \mu^3 - \frac{1}{2} (n \pi)^2 \mu^3 \xi^2 - \epsilon_1 + \epsilon_1^2 (n \pi)^2 \mu^3 \xi^2.$$  \hfill (17)

The sum $\epsilon_{2,\text{tot}}$ of $\epsilon_1$ and $\epsilon_2$ is

$$\epsilon_{2,\text{tot}} = \epsilon_1 + \epsilon_2 = -2 \mu + 4 \mu^2 - 8 \mu^3 - \frac{1}{2} (n \pi)^2 \mu^3 (\xi^2 - 1).$$  \hfill (19)

For the third order perturbation one goes back to Eq. (16), where one replaces $\epsilon_2$ by $\epsilon_3$ and $\epsilon_1$ by $\epsilon_{2,\text{tot}}$. Inserting $\epsilon_{2,\text{tot}}$ from Eq. (19) and again expanding to third order in $n$ and $\mu$ one finds

$$\epsilon_3 = 0.$$  \hfill (20)

The perturbation calculation breaks off at third order and $\epsilon_{2,\text{tot}}$ is the full result. Note that the viscoelastic effects now vanish if $\xi^2 = 1$, as is required from physical intuition. $\xi$ is related to the viscoelastic compliance by

$$\xi^2 = \frac{Z_q^2}{Z_f} = \frac{J_f}{J_q} = (J_f - i J_f^\prime) \frac{Z_q^2}{\rho_f^2},$$  \hfill (21)

where $J = I / G$ is the elastic compliance. When deriving the shear compliance one plots the normalized frequency shift $\delta f / \ell I f \ell (= \epsilon')$ and the normalized shift if half-band half-width $\delta I f / \ell I f \ell (= \epsilon'')$ versus the square of the overtone order $n^2$ and fits straight lines according to

$$\epsilon' = \frac{\delta f}{f} \approx A + S_n' n^2;$$  \hfill (22a)

$$\epsilon'' = \frac{\delta I f}{f} \approx S_n'' n^2.$$  \hfill (22b)

From the offset in the plot of the normalized frequency shifts, $A$, one obtains the film’s mass [cf. Eq. (19)]. From Eqs. (19) and (21) one reads that the film’s elastic compliance $J_f'$ is related to the slope in the plot of $\delta f / \ell I f \ell$. $S_n'$, by

$$J_f' = \frac{\rho_f}{Z_q^2} \left( 1 - \frac{3 S_n''}{2 \pi^2 \mu^3} \right).$$  \hfill (23a)

The viscous compliance $J_f''$ is given by

$$J_f'' = \frac{\rho_f}{Z_q^2} \left( \frac{3 S_n''}{2 \pi^2 \mu^3} \right).$$  \hfill (23b)

In the following we extend the above analysis to more complicated configurations. It turns out that the equations are much clumsier if, for instance, the loads on both sides are not equal. However, with the formal procedure established, one will not bother with algebraic complications and just perform the series expansions by programs capable of formal algebra like MATHEMATICA. The above steps can be formalized and more complicated geometries are easily covered by just replacing $Z_0$ and $Z_0^\prime$ with the appropriate functions.

The essential steps of the perturbation calculation are

1. Expand the total impedance $Z_n$ to third order in $\mu$ [cf. Eq. (12)].
2. Expand the result from step (1) to first order in $\epsilon$ [cf. Eq. (13)].
3. Set the result from step (2) equal to zero and solve for $\epsilon$ to obtain the first order perturbation result $\epsilon_1$ [cf. Eq. (14)].
4. Expand $\epsilon_1$ to third order in $n$ and $\mu$ [cf. Eq. (14)].
5. Replace $\epsilon$ by $\epsilon_1 + \epsilon_2$ in step (1) [cf. Eq. (15)].
6. Expand the result from step (5) to first order in $\epsilon_2$ [cf. Eq. (16)].
7. Set the result from step (6) equal to zero and solve for $\epsilon_2$ [cf. Eq. (17)].
8. Expand $\epsilon_2$ to third order in $n$ and $\mu$. The second order perturbation result is $\epsilon_{2,\text{tot}} = \epsilon_1 + \epsilon_2$. [cf. Eqs. (18) and (19)].
9. Go back to step (5) and replace $\epsilon_2$ by $\epsilon_3$. Also replace $\epsilon_1$ by $\epsilon_{2,\text{tot}}$.
10. Repeat steps (6)–(9) incrementing the perturbation order until the calculation breaks off, that is, until the resulting $\epsilon_3$ is zero. This will usually happen at third order.

If one is interested in a more accurate calculation, one may replace all expansions to third order by expansions to fifth (or higher) order. The fifth order result for the symmetric situation (both surfaces covered with films of the same kind) is

$$\epsilon \approx -2 \mu + 4 \mu^2 - 8 \mu^3 + 16 \mu^4 - 32 \mu^5 + \frac{3}{2} (\pi n)^2 (- \mu^3 + 8 \mu^4 - 40 \mu^5) (\xi^2 - 1) + \frac{3}{10} (\pi n)^4 \mu^5 (- 2 \xi^4 + 5 \xi^2 - 3).$$  \hfill (24)

For a single film on just one surface (cf. Sec. IV) the fifth order result is

$$\epsilon \approx - \mu + \mu^2 - \mu^3 + \mu^4 - \mu^5 + \frac{3}{2} (\pi n)^2 (- \mu^3 + 4 \mu^4 - 10 \mu^2) (\xi^2 - 1) + \frac{3}{10} (\pi n)^4 \mu^5 (- 2 \xi^4 + 5 \xi^2 - 3).$$  \hfill (25)
By expanding all terms to an order higher than three, a non-linear dependence of \( e \) on \( n^2 \) can be captured. In general, it seems more reasonable to address this problem by numerical solution of the equation \( Z_m = 0 \). In this way piezoelectric stiffening and viscoelastic dispersion are covered as well.

IV. SINGLE FILM ON ONE SURFACE

The symmetric case was treated in full detail because it is arithmetically the most simple one. In practice, one will usually have to deal with just one film, that is, with an asymmetric situation. When the back side is not covered \( (Z_{bk} = 0) \), the total impedance cannot be simplified as in Eq. (1). However, the formalism works the same way. The resonance condition now is [cf. Eq. (4)]

\[
Z_{ft} \tan \left( \frac{n \pi e}{2} \right) - Z_{ft} \cot \left( \frac{n \pi e}{2} \right) - 2iZ_q = 0 \quad \Rightarrow \quad Z_{ft} - 2iZ_q \cot \left( \frac{n \pi e}{2} \right).
\] (26)

Inserting Eq. (6) for \( Z_{ft} \) and expanding to third order in \( n \) and \( \mu \) results in

\[
0 = \frac{n \pi e}{2} + \frac{\left( n \pi e \right)^3}{24} + \frac{n \pi \mu}{2} (1 + \varepsilon) + \frac{(n \pi)^2 \mu^2}{8} \varepsilon (1 + \varepsilon)^2 + \frac{(n \pi \mu)^3}{6} \xi^2.
\] (27)

Expanding to first order in \( \varepsilon \) yields [cf. Eq. (12)]

\[
0 = -\frac{n \pi \mu}{2} + \frac{\left( n \pi \mu \right)^3}{6} \xi^2 + \varepsilon \left( \frac{n \pi}{2} + \frac{n \pi \mu}{2} + \frac{(n \pi)^3 \mu^2}{8} + \frac{(n \pi \mu)^3}{2} \xi^2 \right).\] (28)

Solving Eq. (28) for \( \varepsilon \) and expanding the result to third order in \( n \) and \( \mu \) yields

\[
\varepsilon_1 = -\mu + \mu^2 - \mu^3 - (n \pi)^2 \mu^3 \left( \frac{\xi^2}{3} - \frac{1}{4} \right).
\] (29)

Replacing \( \varepsilon \) by \( \varepsilon_1 + \varepsilon_2 \) in Eq. (27), expanding to first order \( \varepsilon_2 \), and solving for \( \varepsilon_2 \) yields

\[
\varepsilon_2 = -\mu + \mu^2 - \mu^3 + \frac{(n \pi)^2 \mu^3}{4} \frac{\mu + \mu^3 (\xi^2 + 1)}{3} \xi^2 + \varepsilon_1 ((n \pi)^2 \mu^3 - 1) + \varepsilon_1 \left( -\frac{(n \pi)^2 \mu^3}{4} \right) \left( \mu + \mu^3 (\xi^2 + 1) \right) + \varepsilon_1 \frac{(n \pi)^2}{6} [1 - \mu + 4 \mu^2 + 4 \mu^3 (\xi^2 - 1)].
\] (30)

Inserting Eq. (29) into Eq. (30) and expanding the result to third order in \( n \) and \( \mu \) yields

\[
\varepsilon_2 = \frac{1}{12} (n \pi)^2 \mu^3
\] (31)

and

\[
\varepsilon_{2,\text{tot}} = -\mu + \mu^2 - \mu^3 - \frac{1}{3} (n \pi)^2 \mu^3 (\xi^2 - 1).
\] (32)

Again, the perturbation calculation breaks off at third order \( (\varepsilon_3 = 0) \) and Eq. (32) is the full result.

V. FILMS ON ELECTRODES

In practice, the film(s) of interest will usually be deposited on an electrode, the elastic properties of which may not be ignored. Note, however, that the oscillation may be excited across an air gap, if all effects of electrodes are to be eliminated.\(^{19,20}\) The impedance of a two-layer system is\(^{21}\)

\[
Z_{\text{f}} = i Z_f \tan (k_d f) + Z_e \tan (k_d f) \quad \Rightarrow \quad \frac{Z_{\text{f}}}{Z_e} = \tan ((k_d f) Z_{\text{f}}).\] (33)

The indices \( e \) and \( f \) denote the electrode and the film, respectively. A special situation, where the film of interest actually is the middle layer and the top layer is deposited to enhance the viscoelastic effects, was covered in-depth in Ref. 20 and is not further discussed here. In the following we assume that the electrodes are thin as well. All series expansions are performed to third order in the combined powers of the dimensionless mass of the electrode, \( \mu_e = m_e / \mu_q \), and of the film, \( \mu_f \), that is, the third order term contains terms of the form \( \mu_e^3, \mu_f^3, \mu_e^2 \mu_f, \) and \( \mu_f^2 \), but not, for instance, terms of the form \( \mu_e^2 \mu_f \).

For the symmetric situation one has \( Z_{bk} = Z_{ft} \). Inserting Eq. (33) for \( Z_{ft} \) in Eq. (4) and performing the same expansions as before yields

\[
0 = n \pi \mu (\mu_e + \mu_f) + \frac{\left( n \pi (\mu_e + \mu_f) \right)^3}{3} \xi_e^2 + \frac{\left( n \pi \mu_f \right)^3}{3} (\xi_f^2 - \xi_e^2) + \varepsilon \left( \frac{n \pi}{2} + n \pi (\mu_e + \mu_f) \right) [n \pi (\mu_e + \mu_f)]^3 (\xi_f^2 - \xi_e^2) + \frac{(n \pi \mu_f)^3}{3} (\xi_f^2 - \xi_e^2).
\] (34)

The perturbation calculation again terminates at second order and the full result is

\[
\varepsilon_{2,\text{tot}} = -2 (\mu_e + \mu_f) + 4 (\mu_e + \mu_f)^2 - 8 (\mu_e + \mu_f)^3 - \frac{1}{3} (n \pi)^2 [(\mu_e + \mu_f)^3 (\xi_e^2 - 1) + \mu_f^3 (\xi_f^2 - \xi_e^2)].
\] (35)

For one film and electrodes on both sides (the situation most commonly encountered in practice) one has

\[
\varepsilon_{2,\text{tot}} = -2 \mu_e + 4 \mu_e^3 - 8 \mu_e - \mu_f (1 - 4 \mu_e + 12 \mu_e^2) + \mu_f (3 - 6 \mu_e - 6 \mu_e^2) + \mu_f^3 (1 - 6 \mu_e) - \mu_f^3 (\xi_f^2 - \xi_e^2) + \mu_f^3 (\mu_e + \mu_f)^3 (\xi_e^2 - 1) + \mu_f^3 (\xi_f^2 - \xi_e^2).
\] (36)

The reference frequency in the above cases was assumed to be the frequency of the quartz plate without electrodes. In practice, the reference frequency is usually measured with electrodes. In order to account for this change of reference
we first derive a quantity \( e_{\text{ref}} \) from Eqs. (35) and (36) by setting \( \mu_f \) to zero. The new normalized frequency shifts \( e^* \) are subsequently obtained by a series expansion of \( (e - e_{\text{ref}})/(1 + e_{\text{ref}}) \) to third order in \( n \) and \( \mu \). The result for the symmetric situation (two-layer system on both sides) is

\[
e^* = -2 \mu_f (1 - 2 \mu_e + 4 \mu_e^2) + 4 \mu_f^2 (1 - 4 \mu_e) - 8 \mu_f^3
- (n \pi)^2 (\mu_e \mu_f^2 + 2 \mu_e^2 \mu_f) (\xi_f^2 - 1) + \frac{\mu_f^3}{3} (\xi_f^2 - 1)^2.
\]

(37)

For a single film and electrodes on both sides the result is

\[
e^* = -\mu_f (1 - 2 \mu_e + 4 \mu_e^2) + 4 \mu_f^2 (1 - 4 \mu_e) - \mu_f^3
- (n \pi)^2 (\mu_e \mu_f^2 + 2 \mu_e^2 \mu_f) (\xi_f^2 - 1) + \frac{\mu_f^3}{3} (\xi_f^2 - 1).
\]

(38)

Note that the first term in square brackets, related to the mechanical properties of the electrodes, may outweigh the effect of the film’s elasticity if the film is thinner than the electrode. This effect was discussed in detail in Ref. 20. Table I summarizes the results for the different configurations.

Clearly, taking the effect of the electrodes properly into account requires the knowledge of the acoustic impedance of the electrode material and the electrode thickness. For the common materials, the acoustic impedance can be obtained from the literature. Gold, silver, copper, and aluminum have acoustic impedances of \( 23.2 \times 10^6 \), \( 16.7 \times 10^6 \), \( 20.3 \times 10^6 \), \( 8.22 \times 10^6 \), and \( 8.86 \times 10^6 \) kg m\(^{-2}\)s\(^{-1}\), respectively. The electrode thickness, on the other hand, is more difficult to obtain. One can, in principle, derive some information from a plot of the normalized reference frequencies \( f/n^2 \) versus \( n^2 \) but the accuracy of this procedure is poor. The thickness may also be measured with thickness sensors monitoring the evaporation procedure, but again, the accuracy of these data usually is unsatisfactory. Therefore it is desirable to make the error introduced by the electrodes small. This can be achieved by choosing an electrode material with an acoustic impedance similar to the acoustic impedance of AT-cut quartz. The material of choice is

| Table I. (a) Relations between the slopes \( S'_n \) in a plot of \( \delta f/f \) vs \( n^2 \) and the elastic compliance \( J'_e \) of the film. (b) Relations between the slopes \( S''_n \) in a plot of \( \delta f'/f' \) vs \( n^2 \) and the viscous compliance \( J'_v \) of the film. The dark areas signify the film of interest and the hatched areas are the electrodes. In the lower two lines, the measurements are referenced to frequencies in the presence of electrodes, that is, the quantities \( e^* \) from the text have been used. The parameter \( \mu \) is related to the thickness of the respective layer \( d \) by the relation \( \mu = 2d \rho_f/Z_e \). For thin films the parameter \( \mu_i \) is determined with fair accuracy from experiment as \( \mu = \delta d/f \). For the electrodes it has to be determined independently. The parameter \( \xi_e = Z_e/\rho_e \) is 2.67, 1.92, 2.34, and 0.94 for gold, silver, copper, and aluminum, respectively. Its (small) imaginary part may be determined from measurements on bare quartzes. | |
|---|---|---|---|
| Config. | Eq. | Slope of \( \delta f/f \) vs. \( n^2 \), \( S'_n \) | Elastic Compliance \( J'_e \) |
| 19 | \(-\frac{2}{3} \pi^2 \mu' \left( \text{Re}(\xi'_e) - 1 \right)\) | \(\frac{\rho_f}{Z'_e} \left( 1 - S'_n \frac{3}{2\pi^2 \mu'} \right)\) |
| 32 | \(-\frac{1}{3} \pi^2 \mu' \left( \text{Re}(\xi'_e) - 1 \right)\) | \(\frac{\rho_f}{Z'_e} \left( 1 - S'_n \frac{3}{\pi^2 \mu'} \right)\) |
| 37 | \(-2\pi^2 \left( (\mu_i \mu_f' + \mu'_e \mu_f) \left( \text{Re}(\xi'_e) - 1 \right) + \frac{\mu_f'}{3} \left( \text{Re}(\xi'_e) - 1 \right) \right)\) | \(\frac{\rho_f}{Z'_e} \left( 1 - S'_n \frac{3}{2\pi \mu'_{fe}} - 3 \frac{\mu_e + \mu'_e}{\mu_f + \mu'_f} \text{Re}(\xi'_e) - 1 \right)\) |
| 38 | \(-\pi^2 \left( (\mu_i \mu_f' + \mu'_e \mu_f) \left( \text{Re}(\xi'_e) - 1 \right) + \frac{\mu_f'}{3} \left( \text{Re}(\xi'_e) - 1 \right) \right)\) | \(\frac{\rho_f}{Z'_e} \left( 1 - S'_n \frac{3}{\pi \mu'_{fe}} - 3 \frac{\mu_e + \mu'_e}{\mu_f + \mu'_f} \text{Re}(\xi'_e) - 1 \right)\) |

<table>
<thead>
<tr>
<th>Config.</th>
<th>Eq.</th>
<th>Slope of ( \delta f'/f' ) vs. ( n^2 ), ( S''_n )</th>
<th>Viscous Compliance ( J'_v )</th>
</tr>
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<tbody>
<tr>
<td>19</td>
<td>(-\frac{2}{3} \pi^2 \mu' \text{Im}(\xi'_e))</td>
<td>(\frac{\rho_f}{Z'_e} S''_n \frac{3}{2\pi^2 \mu'})</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>(-\frac{1}{3} \pi^2 \mu' \text{Im}(\xi'_e))</td>
<td>(\frac{\rho_f}{Z'_e} S''_n \frac{3}{\pi^2 \mu'})</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>(-2\pi^2 \left( (\mu_i \mu_f' + \mu'_e \mu_f) \text{Im}(\xi'_e) + \frac{\mu_f'}{3} \text{Im}(\xi'_e) \right))</td>
<td>(\frac{\rho_f}{Z'_e} \left( 1 - S''<em>n \frac{3}{2\pi \mu'</em>{fe}} - 3 \frac{\mu_e + \mu'_e}{\mu_f + \mu'_f} \text{Im}(\xi'_e) \right))</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>(-\pi^2 \left( (\mu_i \mu_f' + \mu'_e \mu_f) \text{Im}(\xi'_e) + \frac{\mu_f'}{3} \text{Im}(\xi'_e) \right))</td>
<td>(\frac{\rho_f}{Z'_e} \left( 1 - S''<em>n \frac{3}{\pi \mu'</em>{fe}} - 3 \frac{\mu_e + \mu'_e}{\mu_f + \mu'_f} \text{Im}(\xi'_e) \right))</td>
<td></td>
</tr>
</tbody>
</table>
An example illustrates the order of magnitude of the electrode effect. If one has a 5 MHz quartz plate with a 100 nm polymer film (density $\rho = 10^3$ kg m$^{-3}$, shear modulus $G = 10^5$ Pa) on top of a 100 nm gold electrode ($\rho_e = 19.3 \times 10^3$ kg m$^{-3}$), acoustic impedance $Z_e = 23.7 \times 10^6$ kg m$^{-2}$ s$^{-1}$, where there is a gold electrode on the back side as well) the effect of the electrode [the term $(\mu_e \mu_f^2 + \mu_f^2 \mu_e)(\xi_f^2 - 1)$ in Eq. (38)] amounts to about $-130\%$ of the term related to the film [the term $\mu_f^2/3(\xi_f^2 - 1)$ in Eq. (38)]. For aluminum, on the other hand, the electrode effect is only $0.5\%$ of the effect of the film.

VI. FILMS IN LIQUIDS

For films immersed in liquids the situation is somewhat more complicated. However, the dynamic properties of polymeric adsorbates in a liquid environment (such as human blood) might be of a high relevance for biosensing applications. For instance, the liquid may swell the adsorbate, thereby increasing the acoustic thickness. In addition, the solvent penetrating into the film will act as a plasticizer, thereby softening the adsorbate. A certain fluidity is required for many kinds of biological activity, which may be going on inside the layer. Probing a layer’s softness therefore potentially is of great benefit in biological applications.

The presence of liquid entails experimental subtleties, some of which we mention in passing. The quartz plate must remain stress free. The solvent viscosity should be known and remain constant. Because the wavelength of shear sound in water at 5 MHz is well below 1 $\mu$m, “thin” adsorbates must be only a few nanometers thick. Surface roughness will trap solvent, which then appears as part of the film. Finally, slight flexural contributions to the mode of motion may generate longitudinal sound, which spoils the measurement. The latter effect can be checked upon with ideal Newtonian liquids, which should induce a frequency shift equal to the induced shift in the half-band half-width. If this relation is found not to be true, this particular quartz plate must be discarded.

For a two layer system immersed in a liquid the impedance $Z_{l1}$ is

$$Z_{l1} = \frac{Z_e Z_f \tan(k_e d_e) + Z_f \tan(k_d d_f)}{Z_e - Z_f \tan(k_e d_e) \tan(k_d d_f)} + i \frac{Z_e \tan(k_e d_e) \tan(k_d d_f) - Z_f}{Z_e - Z_f \tan(k_e d_e) \tan(k_d d_f)}.$$  

(39)

where the index $l$ denotes the liquid. Setting $\tan(k_e d_e) = 0$ one sees that in the absence of electrodes (or when using thin enough aluminum electrodes) the impedance is

$$Z_{l1} = iZ_e \frac{Z_f \tan(k_d d_f) - iZ_f}{Z_f + iZ_f \tan(k_d d_f)}.$$  

(40)

The presence of the liquid modifies the picture in two ways. First, viscous dissipation is not the only loss mechanism. Even if the ambient medium were purely elastic, energy would be radiated away from the quartz in the form of transverse sound waves. Therefore the imaginary unit “$i$” enters the equations explicitly. Second, the impedance $Z_f$ of the liquid strongly depends on frequency, that is, overtone order. For an ideal liquid, one has

$$0 = -\frac{\sqrt{n \pi}}{4} \xi_i(1 - i) + \frac{n \pi}{4} (2 \mu_e + \mu_f) - i \frac{(n \pi)^2}{2} \xi_f (\mu_e \xi_f^2 + \mu_f \xi_f^2) + \frac{(n \pi)^2}{4} \xi_i(1 - i)(\mu_e \xi_i^2 + 2 \mu_e \mu_f \xi_i^2 + \mu_f \xi_f^2)$$

$$+ \frac{(n \pi)^3}{12} [2 \mu_e \xi_f^2 + 3 \mu_e \mu_f (\mu_e + \mu_f) \xi_f^2 + \mu_f^3 \xi_f^2] + e \left[ \frac{n \pi}{4} (1 + 2 \mu_e + \mu_f) - i \frac{(n \pi)^2}{8} \xi_i (1 + 4 \mu_e \xi_i^2 + 4 \mu_f \xi_f^2) ight.$$  

$$+ \frac{(n \pi)^5}{8 \xi_i (1 - i)(\mu_f + 4 \mu_e \xi_i^2 + 8 \mu_e \mu_f \xi_i^2 + 4 \mu_f^2 \xi_f^2)} + \frac{(n \pi)^3}{16} [\mu_f^2 + 8 \mu_e \xi_i^2 + 12 \mu_e \mu_f (\mu_e + \mu_f) \xi_i^2 + 4 \mu_f^2 \xi_f^2] \right].$$  

(42)
We only provide the final result of the calculation, which is

$$e^* = -\mu_j (1 - 2\mu_e + 4\mu_i^2) + \mu_j^3 (1 - 4\mu_e) - \mu_j^3$$

$$+ 2i\pi \mu_j \xi_j^3 (\xi_j^2 - 1) - (n \pi)^{3/2} \xi_j (1 - i)$$

$$\times [2\mu_e \mu_j (\xi_j^2 - 1) + \mu_j^2 (\xi_j - 1)]$$

$$- (n \pi)^3 \left( \mu_e \mu_j^2 + \mu_j^3 \mu_j (\xi_j^2 - 1) - \frac{\mu_j^3}{3} (\xi_j^2 - 1) \right).$$

(43)

If the electrode effects can be neglected this results simplifies to

$$e^* = -\mu + \mu^2 - \mu^3 + 2i\pi \mu \xi_j^3 (\xi_j^2 - 1) - (1 - i)$$

$$\times (n \pi)^{3/2} \mu^2 \xi_j (\xi_j^2 - 1) - \frac{1}{2} (n \pi)^2 \mu^3 (\xi_j^2 - 1)$$

$$- \mu + \mu^2 - \mu^3 + (\xi_j^2 - 1) [2i\pi \mu \xi_j^3 - (1 - i)]$$

$$\times (n \pi)^{3/2} \mu^2 \xi_j - \frac{1}{2} (n \pi)^2 \mu^3].$$

(44)

Comparison with Eq. (32) (single film in air) shows that the term $n^2 \pi^2 \mu^3 / 3$ has been replaced by the term in square brackets in Eq. (44). When plotting $\delta f / f$ versus $n^2$ one no longer obtains a linear relationship. Interestingly, the new terms in the square brackets in Eq. (44) may actually increase the effects related to viscoelasticity. For a film with a thickness in the nanometer range, $\mu$ is of the order of $10^{-5}$, while $\xi_j$ is about $2 \times 10^{-4}$ for water in contact with a 5 MHz quartz. Depending on the film thickness, the first term in square brackets ($\approx n \mu \xi_j^3$) may be much larger than the last term ($\approx n^2 \mu^3$). This increase in sensitivity occurs because the film has been moved away from the antinode of the standing shear wave. Being placed at the foot of the transverse sound wave propagating into the liquid, it experiences a substantial amount of shear stress. As a consequence, the film’s shear compliance affects the frequency shift.

VII. CONCLUSIONS

The viscoelastic compliance of thin films deposited on quartz resonators can be inferred from comparison of the shifts in frequency and bandwidth on various overtones. While the full analysis requires the numerical solution of $Z_{el}(\omega) = 0$, considerable insight can be gained from approximate solutions. When plotting the normalized frequency shift $\delta f / f$ and the normalized shifts of half-band half-width $\delta \Gamma / f$ versus the square of the overtone order $n^2$ linear relationships for many cases of interest. The slopes contain the elastic and the viscous compliance $J'$ and $J''$.

The analysis also covers films in liquid environments, where the dependence of $\delta f / f$ and $\delta \Gamma / f$ on overtone order is more complicated. Probing film stiffness in liquids allows one to infer swelling and solvent induced plastification. This should be particularly useful in the context of bioanalytics.

ACKNOWLEDGMENTS

The author thanks Oliver Wolff for stimulating discussions.

17. Note that the approximation $Z_{el} \approx Z_q$ breaks down close to the film resonance. As a consequence the resonance frequencies do not go to infinity. Rather, one has to separate branches at frequencies above and below the resonance frequency of the bare quartz.