

QTM: A Software Package for the Analysis of QCM-Data

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0 Preface

QTM implements various sets of equations for the analysis of shifts of frequency and bandwidth ($\Delta f(n)$ and $\Delta \Gamma(n)$ with n the overtone order), acquired with a quartz crystal microbalance (QCM). Mostly, QTM derives the thickness and the softness of the layer under study. The term QCM in this text is synonymous to QCM(D), where the latter stands for “QCM with Dissipation monitoring”. A QCM(D) is any instrument, which acquires frequency and bandwidth on a number of different overtones. The shift in “bandwidth”, $\Delta \Gamma$ [Hz], carries information largely equivalent to the information contained in the shift of the “dissipation factor” ΔD [10^{-6}].

This manual describes version 2.0.0.0 of QTM. QTM has grown in a research environment and is less than perfect. Feedback is appreciated. QTM is freeware.

For an introduction of the background see the Ref. 1 (an open-access publication).

For the sake of readability, this manual is on the brief side, leaving some features of QTM without a mention. Hopefully, these features are self-explaining.

Numerous people have contributed to QTM. A specific mention goes to Ilya Reviakine and Arne Langhoff. Philipp Sievers has recently overhauled QTM from the software side.

Clausthal, May 2021

Diethelm Johannsmann

1 Overall Organization

To get started, save all files associated to QTM into a folder of your choice. There is no installer. Click QTM.exe to launch QTM.

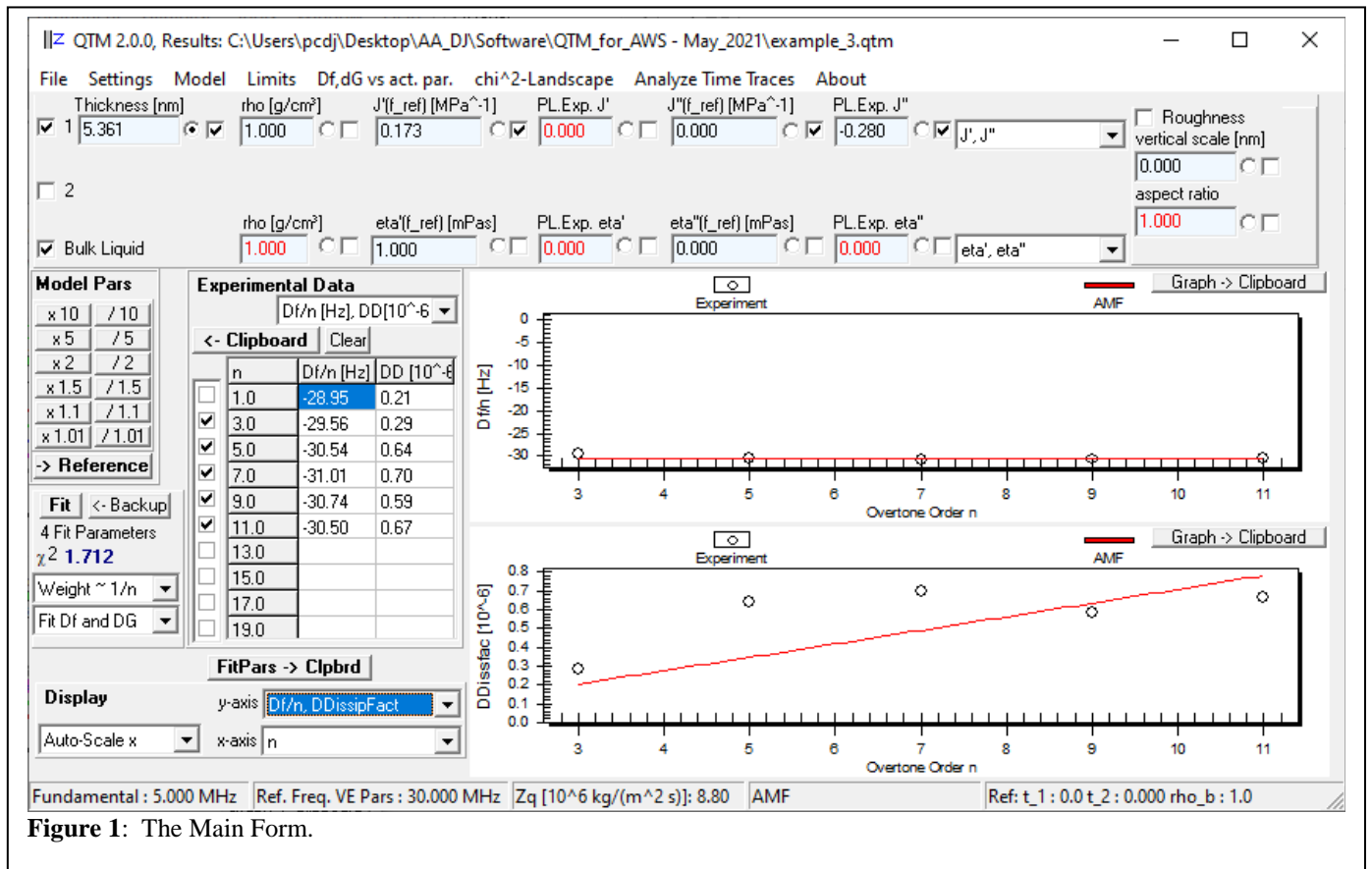
On start-up, QTM reads-in certain status information from the file QTM.ini. QTM saves work in files with the extensions .qtm and .qtd. Both are ASCII files. While you work, QTM saves all steps into TmpQTM.qtm (and TmpQTM.qtd in case you analyze entire files). This information is transferred to the file of your choice when you save. *.qtm contains control variables as well experimental frequency shifts, fit parameters, and the frequency shifts predicted by the fit for one single data set. *.qtm has the structure of an configuration file (also: “ini-file”). One can guess the meanings of the variables to some extent. *.qtd contains data and fit parameters for a time trace of data sets.

Experimental data can be edited into the table on the left-hand side in the Main Form. They can also be imported from the clipboard with the button <- Clipboard. One would typically collect the data (in the format shown in the Main Form) in Excel, load this set into the clipboard with CtrlC, and then click <- Clipboard in QTM.

Notation: The shifts of frequency and half bandwidth are called Δf and $\Delta \Gamma$. Dissipative processes are quantified by the half-bandwidth, here. Γ is related to the “dissipation factor” by the relation $D = Q^{-1} = 2\Gamma/f_r$. Δf and $\Delta \Gamma$ can be collected in a complex frequency shift $\tilde{\Delta f} = \Delta f + i\Delta \Gamma = \Delta f + if_{res}\Delta D/2$ (The tilde denotes a complex variable.) Δf , $\Delta \Gamma$, and ΔD are called Df, DG and DD in QTM.

Results can be exported as follows:

- *Fits -> Clipboard* saves data and fitted data to the clipboard.
- *Fit-Pars -> Clipboard* saves the fit parameters to the clipboard.
- *Graph -> Clipboard* saves the graph to the clipboard.



Most of the time, the user tries to find model parameters, which make the model (predictions shown as a red line the Main Form) agree with experimental data. It is advised to not jump to a fit right away, but to rather play around with parameters by hand and see, what a meaningful set of parameters might be. In order to do that, make a certain parameter “active” by checking the *round* button next to it. Once a parameters is active, it can be increased or decreased with the buttons “×5”, “/5” etc. on the left-hand side of the Main Form. Parameters can also be edited in the respective field.

2 Background

2.1 Viscoelastic layer systems, the acoustic multilayer formalism (AMF)

There is an established formalism to calculate the periodic stress at a resonators surface caused by planar layer systems.^{2,3,4,5} QTM calls this algorithm the “acoustic multilayer formalism” (AMF). The AMF is adapted from an analogous set of equations in optics (the Fresnel equations). Each layer supports two plane waves (propagating upwards and downwards), the amplitudes of which are fixed by the boundary conditions. For two layers in a liquid, the results can still be expressed in analytical form in one line (Eq. 8).

The acoustic multilayer formalism (AMF) calculates the periodic stress at the resonator surface and derives the complex frequency shift from the relation $\Delta\tilde{f}/f_0 = i/(\pi Z_q)\tilde{Z}_L$, where \tilde{Z}_L (the ratio of stress to velocity) is the load impedance. The latter relation is the small-load approximation. See the glossary in section 7 for the meaning of the other variables.

2.2 Limitations

- Flexural motion of the plate is not covered.

QTM is based on the parallel-plate model and assumes that the resonator undergoes a pure thickness-shear motion.

- Piezoelectric stiffening is not covered.
- Structured samples are not covered.
- QTM allows for two discrete layers, at most. Viscoelastic profiles are not covered.

In principle, viscoelastic profiles (for instance produced by a polymer brush) may be treated using the acoustic multilayer formalism, expanded to many layers. However, there is a rather easy way to predict Δf and $\Delta\Gamma$ for such situation, solving the underlying partial differential equation. Sample code is contained in “VE_Profile_Solve_ODE.py”. This Python program solves the wave equation for continuous profiles $\{G'(z), G''(z), \rho(z)\}$ and derives the shifts of frequency and bandwidth from the solution (section 4.6.3 in Ref. 1).

2.3 Roughness

QTM implements shallow, small-scale roughness following Ref. 6 and Eq. 14. More technically, the shear-wave impedance of the liquid is replaced by what is called $Z_{liq,eff}$ in Eq. 14. The results obtained with these equations must be treated with some care because of the assumptions made.

2.4 Perturbation analysis

Some short-comings inherent to the small-load approximation (SLA) are removed by the perturbation analysis (Box 2 in Ref. 1). However, the perturbation analysis only covers thin films. It fails at the film resonance. Whether the sample is thin enough to be modeled by perturbation analysis, can be checked by displaying the AMF results for the same set of

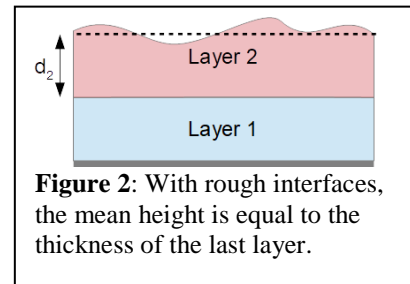


Figure 2: With rough interfaces, the mean height is equal to the thickness of the last layer.

parameters. If the AMF result shows a film resonance, the perturbation analysis is not applicable. The applicability can also be tested by comparing the 3rd-order result to the 5th-order result. The 5th-order result is always more accurate than the 3rd-order result, but if the two differ substantially, the 7th-order result would still produce a difference. If the 3rd-order result and the 5th-order result agree, one is safe.

In order to capture the film resonance and still avoid the approximations inherent to the SLA, one may numerically solve the generalized Lu-Lewis equation (Eq. 40 in Ref. 1). Python code doing this is provided in the file `Solve_Generalized_Lu_Lewis.py`.

The perturbation analysis is needed for stiff films in air. For layer systems in liquids, the changes may be ignored. For stiff films in air, the acoustic impedance of the electrode (!) must be known in order to properly derive the film's softness.

3 A Tour Through QTM

3.1 The Main Form

The Main Form has already been discussed to some extent in section 1. A few further comments:

- QTM has input verification. An input is only accepted after the user hits *Return*.
- Shifts of frequency and bandwidth are always to be understood as shifts with respect to some reference state. The reference state is edited in the *Settings* Form. The user may also turn some state into the reference state by clicking -> *Reference* in the Main Form.
- There are parameters entering the analysis unrelated to the sample. These are the frequency of the fundamental, f_0 , the shear-wave impedance of AT-cut quartz, Z_q , and the parameter f_{cen} from Eq. 2. The values are edited in the *Settings* Form.
- It is helpful to activate limits on the parameters in the *Limits* Form. QTM offers default limits, when the user clicks *Defaults* in the Limits Form. If limits are active, the respective fields in Main Form have light blue background. Otherwise, the background is white. If a certain parameter is at the limit or beyond the limit, the number turns red.

3.2 Fitting

Once a set of reasonable system parameters has been found, the quality of the model can be improved by a fit, that is, by a χ^2 -minimization. χ^2 is a measure of the goodness of a fit, defined as

$$\chi^2 = \frac{1}{2n_{ovt} - n_{fitpar}} \sum_n w_n \left[\left(\frac{\Delta f_n - \Delta f_{n,fit}}{\delta f} \right)^2 + \left(\frac{\Delta \Gamma_n - \Delta \Gamma_{n,fit}}{\delta f} \right)^2 \right] \quad \text{Eq. 1}$$

n_{ovt} is the number of overtones included in the analysis. n_{fitpar} is the number of fit parameters. The factor of 2 before n_{ovt} occurs because every overtone contributes two data points (Δf and $\Delta \Gamma$). If only Δf or only $\Delta \Gamma$ are used for fitting (box above “Fit with” button), the factor of 2 is replaced by 1.

δf is the statistical uncertainty on Δf and $\Delta \Gamma$ on the fundamental. The uncertainty is about the same on f and Γ , hence only one parameter. QTM's default value is $\delta f = 1$ Hz. This value can be changed by double-clicking onto the χ^2 symbol. δf only affects the value of χ^2 , not the fit parameters, which minimize χ^2 . If δf was estimated correctly and if χ^2 is of the order of unity, the quality of the fit is as good as it can be. χ^2 then is governed by statistical noise. *More often than not, systematic errors govern χ^2 .*

That leaves the question of how the statistical weight in Eq. 1, w_n , should depend on overtone order. If statistical noise dominates, the weights should be proportional to $1/n^2$ because the noise on Δf and $\Delta \Gamma$ is roughly proportional to the overtone order n . However, the errors may be systematic rather than statistic. For that reason, QTM also allows for statistical weights proportional to n^{-1} and n^0 . The Clausthal group mostly uses a weight proportional to n^{-1} .

A few more comments:

- When a fit goes wrong, the fit parameters often go to values far outside the reasonable range. Recover the previous state with <- *Backup*.
- Parameters are turned into fit parameters by checking the squares next to them. QTM allows for a maximum of 6 fit parameters.
- A typical choice for the fit parameters for a film in a liquid can be d_f , J' , J'' , and β' (see the remarks around Figure 4).
- Thickness, d , and density, ρ , cannot be active for fitting at the same time. d and ρ cannot be determined independently.
- The density of the bulk and the viscosity of the bulk cannot be fit parameters at the same time, because the QCM only determines the viscosity-density product.
- The confidence limits can be estimated with a procedure implemented the Form *chi² Landscape*. QTM varies the parameter of interest in a certain range and does a fit, adjusting the remaining fit parameters, only. The values of χ^2 resulting from these reduced fits is displayed versus the value of the respective parameter (Figure 3). This graph has a minimum at the value, where the first fit had converged. (After all, the fit undertaken from the Main Form had searched just that minimum.) Depending on how unique this result is, the χ^2 values increase more or less steeply to the left and right of the optimum. What, exactly, the confidence limits are (given a χ^2 landscape as shown in Figure 3) depends on the details (see, for instance, in en.wikipedia.org/wiki/Confidence_interval).

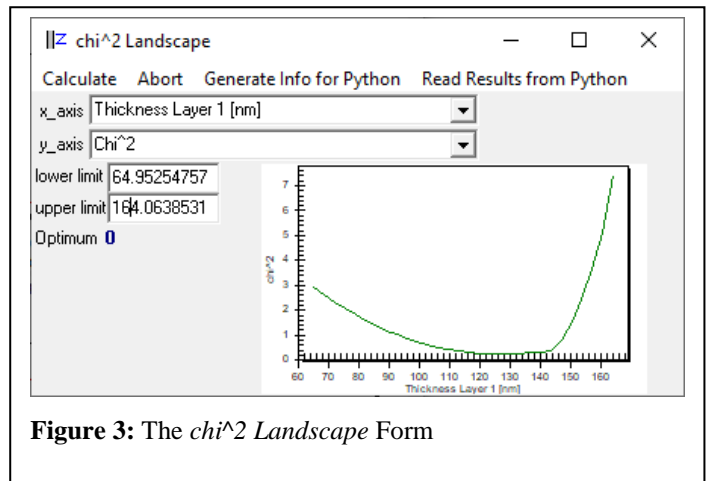


Figure 3: The *chi² Landscape* Form

3.3 Choice of parameters quantifying viscoelasticity

In rheology, a material's stiffness is usually described in terms of the shear modulus, \tilde{G} , where the tilde denotes a complex number. Sometimes, the viscosity, $\tilde{\eta} = \tilde{G}/(i\omega)$ is also used. For the QCM, it is often convenient to use the compliance, $\tilde{J} = 1/\tilde{G}$, rather than \tilde{G} or $\tilde{\eta}$. The reasons are discussed below Eq. 4. For easier interpretation, the QTM offers other sets of parameters, which are

- J' and J''
- G' and G''
- η' and η''
- G' and η'
- $|\tilde{J}|$ and $\tan \delta_L$
- $|\tilde{G}|$ and $\tan \delta_L$
- $|\tilde{\eta}|$ and $1/(\tan \delta_L)$

The user can choose between the different representations in the boxes on the right-hand side. When the representation is changed, QTM changes the values accordingly. Sometimes intricacies arise when a parameter becomes infinite after conversion. For instance, $\tan \delta_L$ is infinite if G'' is zero. When the choice of the viscoelastic parameters is changed, the limits for fitting are set to their default values (which depend on the choice).

Importantly, the viscoelastic parameters depend on frequency. This may create the impression that the problem was underdetermined because there are separate values of J' and J'' for every single overtone. However, the frequency dependence of J' and J'' usually is smooth. QTM assumes power laws of the form

$$J'(f) = J'_{cen}(f_{cen}) \left(\frac{f}{f_{cen}} \right)^{\beta'}$$

$$J''(\omega) = J''_{cen}(f_{cen}) \left(\frac{f}{f_{cen}} \right)^{\beta''}$$

Eq. 2

or, in case the modulus is used

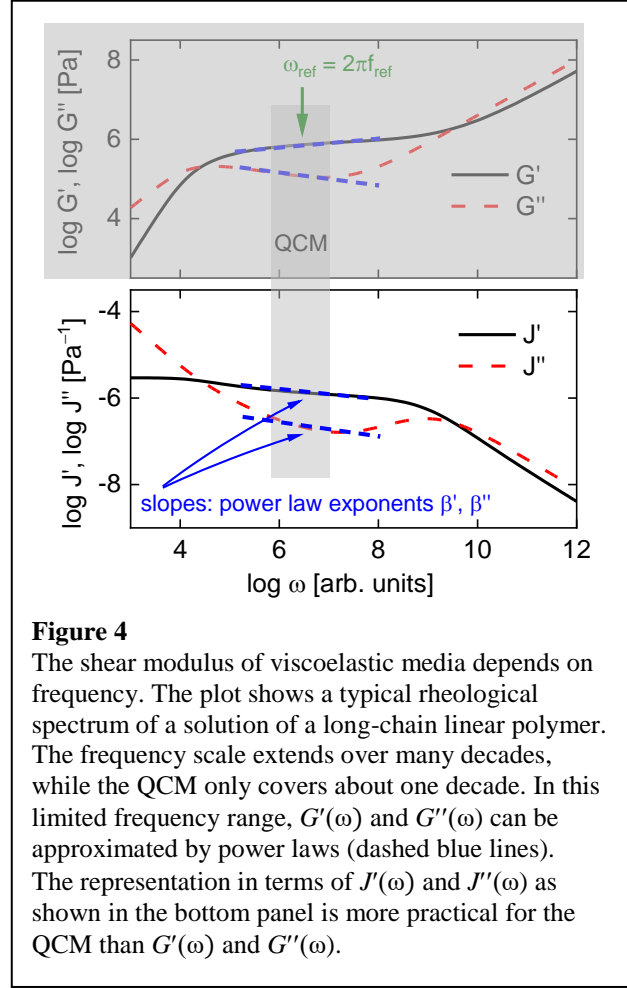
$$G'(f) = G'_{cen}(f_{cen}) \left(\frac{f}{f_{cen}} \right)^{\gamma'}$$

$$G''(\omega) = G''_{cen}(f_{cen}) \left(\frac{f}{f_{cen}} \right)^{\gamma''}$$

f_{cen} is a frequency in the center of the accessible range. Power laws may also apply to the viscosity. Power laws always apply to the real part and the imaginary part, never the absolute value or the loss tangent.

The Kramers-Kronig relations impose limits on the power-law exponents. For instance, one has $-2 < \beta' < 0$ and $-1 < \beta'' < 1$ for the power law exponents linked to J' and J'' . These limits are implemented as default limits in the Limits Form. There is a problem with power laws: A power law behavior in $J'(\omega)$ and $J''(\omega)$ does not translate to a power law after converting to $G'(\omega)$ and $G''(\omega)$ with the relations $G' = J'/|\tilde{\gamma}|^2$ and $G'' = J''/|\tilde{\gamma}|^2$. QTM has to make approximations, when converting between compliance and modulus.

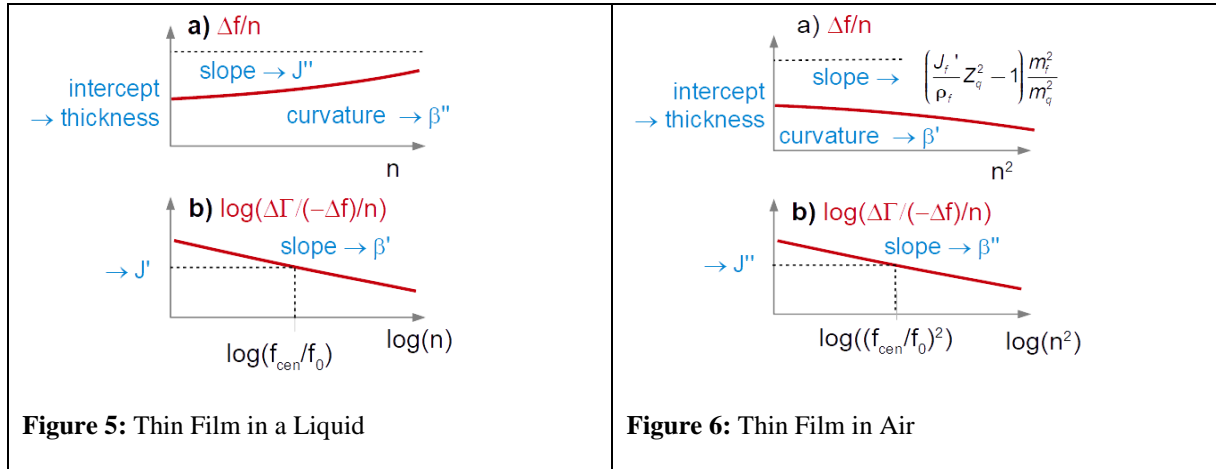
J' and J'' are the most suitable parameters because there are simple and intuitive relations between J' and J'' , on the one hand, and the data sets $\{\Delta f/n(n), \Delta \Gamma/n(n)\}$ on the other. Those relations pertain to *thin* films. There are two sets of such relations, one for the film in air, and one for the film in a liquid.



Eq. 3

For the film in a liquid the relation is

$$\frac{\Delta f}{n} + i \frac{\Delta \Gamma}{n} \approx \frac{-2nf_0^2}{Z_q} m_f \left[1 - n \left(2\pi f_0 \frac{\rho_{bulk}}{\rho_f} \eta_{bulk} \right) J_f - i J_f \right] \quad \text{Eq. 4}$$



It is instructive to analyze the ratio $\Delta\Gamma/(-\Delta f)$. For the thin film in a liquid, the ratio is linked to J'_f as

$$\frac{\Delta\Gamma}{-\Delta f} \approx 2\pi n f_0 \eta_{bulk} J'_f \quad \text{Eq. 5}$$

For the thin film in air, one has

$$\frac{\Delta f}{n} + i \frac{\Delta \Gamma}{n} \approx \frac{-2nf_0^2}{Z_q} m_f \left[1 + \frac{n\pi^2}{3} \left(\frac{J_f' - iJ_f''}{\rho_f} Z_q^2 - 1 \right) \left(\frac{m_f}{m_q} \right)^2 \right] \quad \text{Eq. 6}$$

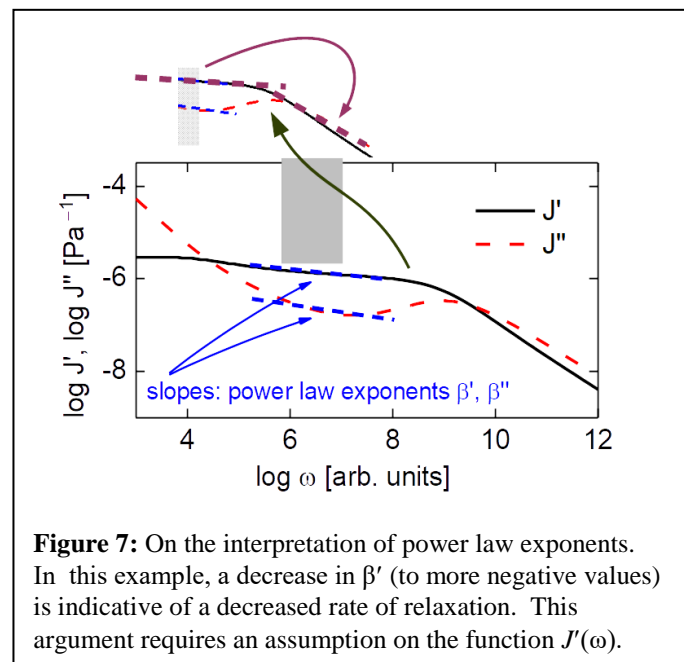
and

$$\frac{\Delta\Gamma}{-\Delta f} \approx \frac{n\pi^2}{3} \left(\frac{J_f''}{\rho_f} Z_q^2 \right) \left(\frac{m_f}{m_q} \right)^2 \quad \text{Eq. 7}$$

Both in air and in liquid, J' and J'' appear in the numerator of the viscoelastic correction. The trivial case (Sauerbrey behavior) corresponds to $J'=J''=0$.

The following paragraph explains the matter in prose for the film in a liquid. Similar arguments apply the film in air (Figure 6, the roles of J' and J'' are interchanged). Assume a single film in a bulk liquid. This problem has a total of 5 unknowns, which are d_f , $J'(f_{cen})$, $J''(f_{cen})$, β' , and β'' . 4 out of these 5 parameters can be inferred from plots as shown in Figure 5. The correspondences are:

- the thickness is proportional to the intercept with the y-axis.
- J'' is proportional to the slope.
- J' is proportional to the ratio $\Delta\Gamma/(-\Delta f)$, see Eq. 5.
- β' is about equal to the slope in a log-log plot shown in Figure 5b.



The parameter β'' is linked to the curvature of the line in Figure 5a. Unfortunately, this curvature cannot usually be determined with confidence from the experimental data. For that reason, β'' often remains uncertain.

The parameter β' is linked to the rates of relaxation. Figure 7 shows an example. In this case, β' is close to zero on the rubber plateau and decreases, when the rubber plateau moves to the left. This is just one example. The interpretation of changes in β' requires an assumption on the shape of the curve $J(\omega)$.

3.4 Time traces

Data from entire files are handled in the Form *Analyze Time Traces* (Figure 8). In a first step, import the data from a file. Make sure to have selected the correct format of the input (box next to "Format of input". One may skip lines. QTM handles a maximum of 10 000 lines, but it is advisable to work with smaller numbers for the sake of speed.

One may hide data points, data sets, or ranges of data.

One may select a new reference state.

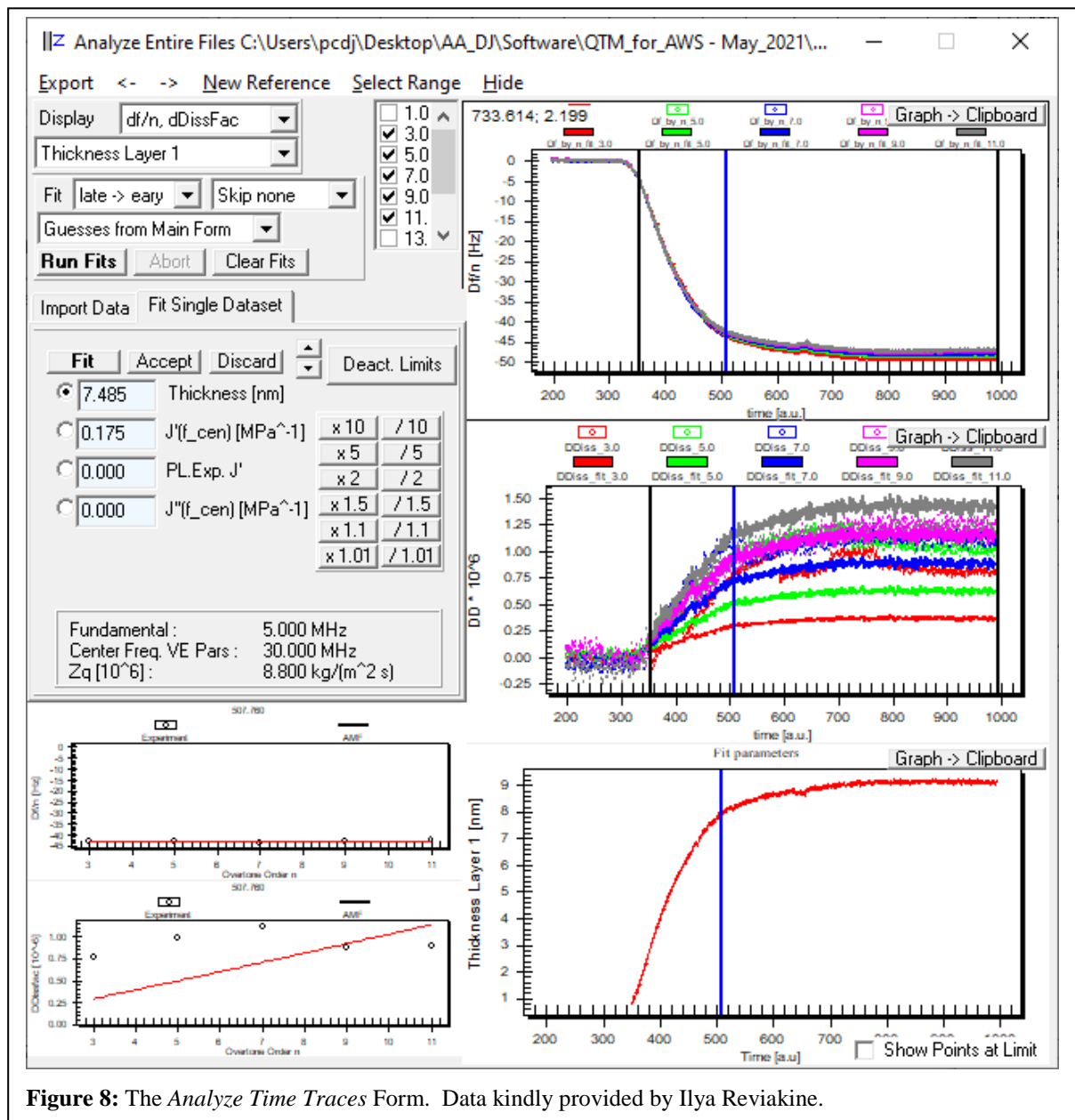


Figure 8: The *Analyze Time Traces* Form. Data kindly provided by Ilya Reviakine.

Typically, one first picks a representative data set and finds a good set of system parameters from the Main Form. One then selects a range of data to be fitted. There is a choice with regard to the guesses, from which the fit starts. The guess may be the result from the fit of the one data set, which was analyzed in detail. The guess may also be the result from the previous fit. The former method may go wrong when the properties of sample vary strongly over time and the data set analyzed first is not actually representative for the entire range of data. The latter method goes wrong when one fit fails. After one fit has failed, all following fits also fail because of the poor values for the guess. If the latter option is chosen, it is sometimes helpful to proceed from late to early times because the sample slowly varies in its properties at the end of the experiment.

3.5 More details

- Thickness versus mass per unit area

On a fundamental level, the QCM cannot independently determine the thickness and the density of a layer. Only the product of the two (the mass per unit area) enters the equations of the AMF. QTM nevertheless displays the thickness because the density often is known with good accuracy and because many users are more familiar with the unit nm than with the unit $\mu\text{g}/\text{cm}^2$. (If the density is $1\text{ g}/\text{cm}^3$, $1\text{ }\mu\text{g}/\text{cm}^2$ correspond to a thickness of 10 nm.) Again, the derived thickness depends on the chosen density.

QTM uses the term "mass" for "mass per unit area". The unit is $\mu\text{g}/\text{cm}^2$. QTM displays the mass per unit area, after the user double-clicks onto the field showing the layer thickness.

- Discard data from the fundamental

For a number of (poorly understood) reasons, the frequency shift measured on the fundamental often does not match the expectations well and the data from the fundamental might just as well be discarded. Depending on the experimental conditions, data from the 3rd overtone and/or the 13th overtone can be problematic as well.

4 Fits using Python

QTM in its stand-alone version minimizes χ^2 with the Simplex algorithm. The Simplex algorithm has difficulties with 4 and more fit parameters when the starting values are far away from a good match.

In order to do better, you may delegate the χ^2 -minimization to an external Python program. The filename is PyQTM.py, contained in the folder PyQTM. When option Python "Python Module Operational" in the Settings panel is checked, QTM gives you a choice between the Simplex method and the SciPy LeastSquares method. A new menu item appears on the main menu, also dealing with Python. (This menu item should not be needed, usually.)

SciPy's LeastSquares module uses the "Trust Region Reflective algorithm". It says on the web that this was a „generally robust method“. We can confirm that.

QTM can only do this, if Python is installed and if the file PyQTM.py is linked to Python as the program opening it by default. (It will not work, if PyQTM.py by default is opened with Spyder. There may be problems, if the path is set incorrectly.) Once the ShellExecute command starts Python, PyQTM does whatever it has been asked to do by the information contained in QPY.qpy. When finished, it writes the results into other files. Once the time stamp on these files changes, QTM reads this information in. While running, Python beeps occasionally to let you know, that it is still alive and well.

In the Python file, you see the source code. You might start from PyQTM.py and expand, following your own ideas.

Sometimes, the ShellExecute command, which calls the Python program, does not work properly. In this case, one may let QTM call the Python program (for instance from the Time Traces Form), let QTM crash, and then execute the Python program from Spyder. QTM writes the information needed by Python program into the file QPY.qpy. PyQTM.py can run, using these directives, regardless of whether it was called from QTM or from Spyder.

5 Strengths and Limitations of QTM

- While OTM allows for up to 6 fit parameters and up to 2 layers, the uniqueness of the fit results may be in question, if the number of fit parameters is too large.
- Robust results are obtained for thin films. If immersed in a liquid, the film must be much stiffer than the liquid to let the results be unique.
- If the choice of the viscoelastic parameters is either $\{J', J''\}$ or $\{|J|, \tan \delta\}$, one out of the two power law exponents can be obtained with confidence. In liquids, this exponent is β' (pertaining to J'). In air, it is β'' (pertaining to J''). If the modulus or the viscosity is used, neither of the two power law exponents can be trusted because the errors in the two exponents are correlated.
- For stiff films in air, be aware of the short-comings of the AMF. Check, whether the perturbation analysis gives different results.

6 Underlying Equations

6.1 Acoustic multilayer formalism

The Acoustic Multilayer Formalism is the canonical model of the QCM in contact with viscoelastic layers. The community agrees on these equations. (Others use other variables, but not other equations.)

QTM allows for a maximum of two layers. The AMF result for a system of two layers embedded in a liquid still fits into one line:

$$\frac{\Delta \tilde{f}}{f_0} = \frac{-\tilde{Z}_e \tilde{Z}_f \left(\tilde{Z}_e \tan(\tilde{k}_e d_e) + \tilde{Z}_f \tan(\tilde{k}_f d_f) \right) + i\tilde{Z}_{liq} \left(\tilde{Z}_e \tan(\tilde{k}_f d_f) \tan(\tilde{k}_e d_e) - \tilde{Z}_f \right)}{\pi \tilde{Z}_q \tilde{Z}_f \left(\tilde{Z}_e - \tilde{Z}_f \tan(\tilde{k}_f d_f) \tan(\tilde{k}_e d_e) \right) + i\tilde{Z}_{liq} \left(\tilde{Z}_e \tan(\tilde{k}_f d_f) + \tilde{Z}_f \tan(\tilde{k}_e d_e) \right)} \quad \text{Eq. 8}$$

Eq. 8 can be a fit function in Excel. The Excel solver should produce the same fits as QTM. If the interface to the bulk liquid displays small-scale roughness, QTM replaces \tilde{Z}_{liq} in Eq. 8 by $\tilde{Z}_{liq,eff}$ from Eq. 14.

For a *single layer in air*, Eq. 8 simplifies to

$$\frac{\Delta \tilde{f}}{f_0} = \frac{-1}{\pi \tilde{Z}_q} \tilde{Z}_f \tan(\tilde{k}_f d_f) \quad \text{Eq. 9}$$

Taylor expansion of Eq. 9 to 1st order in film thickness, d_f , yields the Sauerbrey result. There is a twist with regard to the Taylor expansion to 3rd order in d_f . This expansion reveals finite-compliance effects in the thin-film limit. Taylor expansion of Eq. 9 to 3rd order in film thickness yields

$$\frac{\Delta \tilde{f}}{f_0} = \frac{-\omega m_f}{\pi Z_q} \left(1 + \frac{(n\pi)^3}{3} \frac{\tilde{J}_f}{\rho_f} Z_q^2 \frac{m_f^2}{m_q^2} \right) = -\frac{1}{f_0} C \rho_f d_f \left(1 + \frac{(n\pi)^3}{3} \frac{\tilde{J}_f}{\rho_f} Z_q^2 \frac{m_f^2}{m_q^2} \right) \quad \text{Eq. 10}$$

In step 2 the mass-sensitivity constant, C , was introduced. One may remember that for 5 MHz crystals and a density of $\rho_f = 1 \text{ g/cm}^3$, a film thickness of 1 nm corresponds to a frequency shift of 5.7 Hz (meaning $C\rho_f = 5.7 \text{ Hz/nm}$). The viscoelastic correction is the second term in the brackets.

However, the perturbation analysis substantially modifies this result to

$$\frac{\Delta \tilde{f}}{f_0} = \frac{-\omega m_f}{\pi Z_q} \left(1 + \frac{(n\pi)^3}{3} \left(\frac{\tilde{J}_f}{\rho_f} Z_q^2 - 1 \right) \frac{m_f^2}{m_q^2} \right) \quad \text{Eq. 11}$$

If the film's stiffness is comparable to the stiffness of the crystal (if $\tilde{Z}_f \approx Z_q$), the difference is substantial. If $\Delta f(n)$ is naively analyzed with Eq. 10, one may find negative values for G' or J' .

For a *single layer in a liquid* Eq. 8 simplifies to

$$\frac{\Delta \tilde{f}}{f_0} = \frac{-\tilde{Z}_f}{\pi Z_q} \frac{\tilde{Z}_f \tan(\tilde{k}_f d_f) - i \tilde{Z}_{liq}}{\tilde{Z}_f + i \tilde{Z}_{liq} \tan(\tilde{k}_f d_f)} \quad \text{Eq. 12}$$

Taylor expansion of 1st order in the mass per unit area yields

$$\Delta \tilde{f} = -\frac{2f_0 f}{Z_q} m_f \left(1 - \frac{\tilde{Z}_{liq}^2}{\tilde{Z}_f^2} \right) = -\frac{2f_0 f}{Z_q} m_f \left(1 - \frac{\tilde{J}_f}{\rho_f} \tilde{Z}_{liq}^2 \right) \quad \text{Eq. 13}$$

Even for very thin films, this equation is different from the Sauerbrey equation. The term in brackets is sometimes associated with the “missing mass effect”. For films in liquids, finite compliance lowers the apparent mass, if determined with the Sauerbrey equation.

6.2 Roughness

Shallow roughness on small scales is modeled as:

$$\begin{aligned} \frac{\Delta f}{f_0} &= \frac{-Z_{liq,eff}''}{\pi Z_q} \approx \frac{-1}{\pi Z_q} \sqrt{\frac{\rho_{liq} \omega \eta_{liq}}{2}} \left(1 + 3\sqrt{\pi} \frac{h_r^2}{l_r \delta} - 2 \frac{h_r^2}{\delta^2} \right) \\ \frac{\Delta \Gamma}{f_0} &= \frac{Z_{liq,eff}'}{\pi Z_q} \approx \frac{1}{\pi Z_q} \sqrt{\frac{\rho_{liq} \omega \eta_{liq}}{2}} \left(1 + 2 \frac{h_r^2}{\delta^2} \right) \end{aligned} \quad \text{Eq. 14}$$

QTM assigns the effective shear-wave impedance to the bulk medium. In this way, roughness can be part of the acoustic multilayer formalism.

Eq. 14 is formulated for Newtonian bulk media.. For these, the wavenumber in the bulk is given as $\tilde{k}_{liq} = (1 - i)/\delta$. Should the bulk be viscoelastic, Eq. 14 is replaced by

$$\frac{\Delta \tilde{f}}{f_0} = \frac{i}{\pi Z_q} \tilde{Z}_{liq,eff} \approx \frac{i}{\pi Z_q} \left[\sqrt{\frac{\rho_{liq} \omega \tilde{\eta}_{liq}}{2}} \left(1 + h_r^2 \tilde{k}_{liq}^2 \right) + i \omega \rho_{bulk} \frac{3}{2} \sqrt{\pi} \frac{h_r}{l_r} h_r \right] \quad \text{Eq. 15}$$

6.3 Perturbation analysis

The equations can be abbreviated by the use of the following variables:

Reduced mass: $\mu_e = m_e/m_q$, $\mu_f = m_f/m_q$

Reduced shear-wave impedance

$$\zeta_e(\omega) = \frac{Z_q^2}{\tilde{Z}_e^2(\omega)} - 1, \quad \zeta_f(\omega) = \frac{Z_q^2}{\tilde{Z}_f^2(\omega)} - 1, \quad \xi_{liq}(\omega) = \frac{\tilde{Z}_{liq}(\omega)}{Z_q} \quad \text{Eq. 16}$$

Index e : first layer (“electrode”)

Index f : second layer (“film”)

Index liq : bulk medium (“liquid”)

For brevity, the reduced shear-wave impedance was written without the tilde.

6.3.1 Semi-infinite liquid

$$\begin{aligned} \text{SLA result: } \frac{\Delta \tilde{f}}{f_0} &= \frac{i}{\pi Z_q} \tilde{Z}_{liq} \\ \text{3rd order: } \frac{\Delta \tilde{f}}{f_{ref}} &= \frac{i}{n\pi} \left(\xi_{liq} + \frac{1}{3} \xi_{liq}^3 \right) \\ \text{5th order: } \frac{\Delta \tilde{f}}{f_{ref}} &= \frac{i}{n\pi} \left(\xi_{liq} + \frac{1}{3} \xi_{liq}^3 + \frac{1}{5} \xi_{liq}^5 \right) \end{aligned} \quad \text{Eq. 17}$$

6.3.2 Viscoelastic film in air

$$\begin{aligned} \text{SLA result: } \frac{\Delta \tilde{f}}{f_0} &= \frac{-\tilde{Z}_f}{\pi Z_q} \tan(\tilde{k}_f d_f) \\ \text{3rd order: } \frac{\Delta \tilde{f}}{f_{ref}} &= -\mu_f + \mu_f^2 - \left(1 + \frac{1}{3} (n\pi)^2 \zeta_f \right) \mu_f^3 \\ \text{5th order: } \frac{\Delta \tilde{f}}{f_{ref}} &= -\mu_f + \mu_f^2 - \left(1 + \frac{(n\pi)^2}{3} \zeta_f \right) \mu_f^3 + \left(1 + \frac{4(n\pi)^2}{3} \zeta_f \right) \mu_f^4 \\ &\quad - \left(1 + \frac{10(n\pi)^2}{3} \zeta_f + \frac{(n\pi)^4}{15} (1 - 2\zeta_f) \zeta_f \right) \mu_f^5 \end{aligned} \quad \text{Eq. 18}$$

6.3.3 Viscoelastic film in liquid

$$\text{SLA result: } \frac{\Delta \tilde{f}}{f_0} = \frac{-1}{\pi Z_q} \frac{\tilde{Z}_f \tan(\tilde{k}_f d_f) - i \tilde{Z}_{liq}}{\tilde{Z}_f + i \tilde{Z}_{liq} \tan(\tilde{k}_f d_f)} \quad \text{Eq. 19}$$

3rd order:

$$\begin{aligned} \frac{\Delta \tilde{f}}{f_{ref}} = & \frac{i}{n\pi} \left(\xi_{liq} + \frac{1}{3} \xi_{liq}^3 \right) - \left(1 + \frac{i \xi_{liq}}{n\pi} - \zeta_f \xi_{liq}^2 \right) \mu_f \\ & + \left(1 + \left(\frac{i}{n\pi} + i n \pi \zeta_f \right) \xi_{liq} \right) \mu_f^2 - \left(1 + \frac{(n\pi)^2}{3} \zeta_f \right) \mu_f^3 \end{aligned}$$

5th order

$$\begin{aligned} \frac{\Delta \tilde{f}}{f_{ref}} = & \frac{i \xi_{liq}}{n\pi} + \frac{i \xi_{liq}^3}{3n\pi} + \frac{i \xi_{liq}^5}{5n\pi} + \left(-1 - \frac{i \xi_{liq}}{n\pi} + \zeta_f \xi_{liq}^2 + \frac{(-5i + 15i \zeta_f) \xi_{liq}^3}{15n\pi} + \zeta_f \xi_{liq}^4 \right) \mu_f + \\ & \left(1 + \left(\frac{i}{n\pi} + i n \pi \zeta_f \right) \xi_{liq} - 4 \zeta_f \xi_{liq}^2 + \frac{(5i - 45i \zeta_f)}{15n\pi} + \frac{(15i \pi^2 \zeta_f - 15i \pi^2 \zeta_f^2)}{15n\pi} \xi_{liq}^3 \right) \mu_f^2 + \\ & \left(-1 - \frac{1}{3} n^2 \pi^2 \zeta_f + \left(-\frac{i}{n\pi} - 4i n \pi \zeta_f \right) \xi_{liq} + \left(10 \zeta_f + \frac{n^2 (-10 \pi^3 \zeta_f + 20 \zeta_f^2)}{15\pi} \right) \xi_{liq}^2 \right) \mu_f^3 + \\ & \left(1 - \frac{4}{3} n^2 \pi^2 \zeta_f + \left(\frac{i}{n\pi} + 10i n \pi \zeta_f + \frac{n^3 (-5 \pi^4 \zeta_f + 10 \pi^4 \zeta_f^2)}{15\pi} \right) \xi_{liq} \right) \mu_f^4 + \\ & \left(-1 - \frac{10}{3} n^2 \pi^2 \zeta_f - \frac{1}{15} n^4 \pi^4 \zeta_f (-1 + 2 \zeta_f) \right) \mu_f^5 \end{aligned}$$

6.3.4 Two viscoelastic films in air

SLA-Result:

$$\frac{\Delta \tilde{f}}{f_0} = \frac{-1}{\pi Z_q} \frac{\tilde{Z}_f \tan(\tilde{k}_f d_f) + \tilde{Z}_e \tan(\tilde{k}_e d_e)}{1 - \tilde{Z}_f / \tilde{Z}_e \tan(\tilde{k}_f d_f) \tan(\tilde{k}_e d_e)} \quad \text{Eq. 20}$$

3rd order:

$$\begin{aligned} \frac{\Delta \tilde{f}}{f_{ref}} = & -\mu_e + \mu_e^2 - \left(1 + \frac{(n\pi)^2}{3} \zeta_e \right) \mu_e^3 - \left(1 - 2\mu_e + 3 \left(1 + \frac{(n\pi)^2}{3} \zeta_e \right) \mu_e^2 \right) \mu_f \\ & + \left(1 - 3 \left(1 + \frac{(n\pi)^2}{3} \zeta_e \right) \mu_e \right) \mu_f^2 - \left(1 + \frac{(n\pi)^2}{3} \zeta_f \right) \mu_f^3 \end{aligned} \quad \text{Eq. 21}$$

5th order:

$$\begin{aligned}
\frac{\Delta \tilde{f}}{f_{ref}} = & -\mu_e + \mu_e^2 + \left(-1 - \frac{1}{3}n^2\pi^2\zeta_e\right)\mu_e^3 + \left(1 + \frac{4}{3}n^2\pi^2\zeta_e\right)\mu_e^4 + \\
& \left(-1 - \frac{10}{3}n^2\pi^2\zeta_e - \frac{1}{15}n^4\pi^4\zeta_e(-1+2\zeta_e)\right)\mu_e^5 + \\
& \left(-1+2\zeta_e + (-3-n^2\pi^2\zeta_e)\mu_e^2 + \left(4+\frac{16}{3}n^2\pi^2\zeta_e\right)\mu_e^3 + \left(-5-\frac{50}{3}n^2\pi^2\zeta_e - \frac{1}{3}n^4\pi^4\zeta_e(-1+2\zeta_e)\right)\mu_e^4\right)\mu_f + \\
& \left(1+(-3-n^2\pi^2\zeta_e)\mu_e + (6+8n^2\pi^2\zeta_e)\mu_e^2 + \left(-10-\frac{100}{3}n^2\pi^2\zeta_e - \frac{2}{3}n^4\pi^4\zeta_e(-1+2\zeta_e)\right)\mu_e^3\right)\mu_f^2 + \\
& \left(-1-\frac{1}{3}n^2\pi^2\zeta_f + \left(4+\frac{4}{3}n^2\pi^2(3\zeta_e+\zeta_f)\right)\mu_e + \left(-10-\frac{1}{3}n^4\pi^4\zeta_e(-2+3\zeta_e+\zeta_f)\right) - \frac{10}{3}n^2\pi^2(9\zeta_e+\zeta_f)\mu_e^2\right)\mu_f^3 + \\
& \left(1+\frac{4}{3}n^2\pi^2\zeta_f + \left(-5-\frac{1}{3}n^4\pi^4\zeta_e(-1+2\zeta_f) - \frac{10}{3}n^2\pi^2(3\zeta_e+2\zeta_f)\right)\mu_e\right)\mu_f^4 + \\
& \left(-1-\frac{10}{3}n^2\pi^2\zeta_f - \frac{1}{15}n^4\pi^4\zeta_f(-1+2\zeta_f)\right)\mu_f^5
\end{aligned}$$

Eq. 22

6.3.5 Two viscoelastic films in a liquid

SLA-Result:

$$\frac{\Delta \tilde{f}}{f_0} = \frac{-Z_e \tilde{Z}_f \left(\tilde{Z}_e \tan(\tilde{k}_e d_e) + \tilde{Z}_f \tan(\tilde{k}_f d_f) \right) + i \tilde{Z}_{liq} \left(\tilde{Z}_e \tan(\tilde{k}_f d_f) \tan(\tilde{k}_e d_e) - \tilde{Z}_f \right)}{\pi Z_q \tilde{Z}_f \left(\tilde{Z}_e - \tilde{Z}_f \tan(\tilde{k}_f d_f) \tan(\tilde{k}_e d_e) \right) + i \tilde{Z}_{liq} \left(\tilde{Z}_e \tan(\tilde{k}_f d_f) + \tilde{Z}_f \tan(\tilde{k}_e d_e) \right)}$$

Eq. 23

3rd order:

$$\begin{aligned}
\frac{\Delta \tilde{f}}{f_{ref}} = & \frac{i}{n\pi} \left(\xi_{liq} + \frac{1}{3} \xi_{liq}^3 \right) - \left(1 + \frac{i}{n\pi} \xi_{liq} - \zeta_e \xi_{liq}^2 \right) \mu_e + \left(1 + \left(\frac{i}{n\pi} + i n \pi \zeta_e \right) \xi_{liq} \right) \mu_e^2 \\
& - \left(1 + \frac{1}{3} (n\pi)^2 \zeta_e \right) \mu_e^3 \\
& - \left(1 + \frac{i}{n\pi} \xi_{liq} - \zeta_f \xi_{liq}^2 - 2 \left(1 + \left(\frac{i}{n\pi} + i n \pi \zeta_e \right) \xi_{liq} \right) \mu_e + 3 \left(1 + \frac{1}{3} (n\pi)^2 \zeta_e \right) \mu_e^2 \right) \mu_f \\
& + \left(1 + \left(\frac{i}{n\pi} + i n \pi \zeta_f \right) \xi_e - 3 \left(1 + \frac{1}{3} (n\pi)^2 \zeta_e \right) \mu_e \right) \mu_f^2 \\
& - \left(1 + \frac{1}{3} (n\pi)^2 \zeta_f \right) \mu_f^3
\end{aligned}$$

Eq. 24

5th order:

$$\begin{aligned}
\frac{\Delta \tilde{f}}{f_{ref}} = & \frac{i \xi_{liq}}{n\pi} + \frac{i \xi_{liq}^3}{3n\pi} + \frac{i \xi_{liq}^5}{5n\pi} + \left(-1 - \frac{i \xi_{liq}}{n\pi} + \zeta_e \xi_{liq}^2 + \frac{(-5i + 15i \zeta_e) \xi_{liq}^3}{15n\pi} + \zeta_e \xi_{liq}^4 \right) \mu_f + \\
& \left(1 + \left(\frac{i}{n\pi} + i n \pi \zeta_e \right) \xi_{liq} - 4 \zeta_e \xi_{liq}^2 + \left(\frac{5i - 45i \zeta_e}{15n\pi} + \frac{n(15i \pi^2 \zeta_e - 15i \pi^2 \zeta_e^2)}{15n\pi} \right) \xi_{liq}^3 \right) \mu_e^2 + \\
& \left(-1 - \frac{1}{3} n^2 \pi^2 \zeta_e + \left(-\frac{i}{n\pi} - 4i n \pi \zeta_e \right) \xi_{liq} + \left(10 \zeta_e + \frac{n^2(-10\pi^3 \zeta_e + 20\pi^3 \zeta_e^2)}{15\pi} \right) \xi_{liq}^2 \right) \mu_e^3 + \\
& \left(1 - \frac{4}{3} n^2 \pi^2 \zeta_e + \left(\frac{i}{n\pi} + 10i n \pi \zeta_e + \frac{1}{3} i n^3 \pi^3 \zeta_e (-1 + 2\zeta_e) \right) \xi_{liq} \right) \mu_e^4 + \\
& \left(-1 - \frac{10}{3} n^2 \pi^2 \zeta_e - \frac{1}{15} n^4 \pi^4 \zeta_e (-1 + 2\zeta_e) \right) \mu_f^5 + \\
& \left(-1 - \frac{i \xi_{liq}}{n\pi} + \zeta_f \xi_{liq}^2 + \frac{(-5i + 15i \zeta_f) \xi_{liq}^3}{15n\pi} + \zeta_f \xi_{liq}^4 + \right. \\
& \quad \left(2 + \left(\frac{2i}{n\pi} + 2i n \pi \zeta_e \right) \xi_{liq} + \frac{(-90\pi \zeta_e - 30\pi \zeta_f) \xi_{liq}^2}{15\pi} + \left(\frac{10i - 60i \zeta_e - 30i \zeta_f}{15n\pi} - 2i n \pi \zeta_e (-1 + \zeta_f) \right) \xi_{liq}^3 \right) \mu_e + \\
& \quad \left. \left(-3n^2 \pi^2 \zeta_e + \left(-\frac{3i}{n\pi} - 12i n \pi \zeta_e \right) \xi_{liq} + \left(\frac{n^2(45\pi^3 \zeta_e^2 + 15\pi^2 \zeta_e (-2 + \zeta_f))}{15\pi} + \frac{405\pi \zeta_e + 45\zeta_f}{15\pi} \right) \xi_{liq}^2 \right) \mu_e^2 + \right. \\
& \quad \left. \left(4 + \frac{16}{3} n^2 \pi^2 \zeta_e + \left(\frac{4i}{n\pi} + 40i n \pi \zeta_e + \frac{4}{3} i n^3 \pi^3 \zeta_e (-1 + 2\zeta_e) \right) \xi_{liq} \right) \mu_e^3 + \left(-5 - \frac{50}{3} n^2 \pi^2 \zeta_e - \frac{1}{3} n^4 \pi^4 \zeta_e (-1 + 2\zeta_e) \right) \mu_e^4 \right) \mu_f + \\
& \left(1 + \left(-\frac{i}{n\pi} + i n \pi \zeta_f \right) \xi_{liq} - 4 \zeta_f \xi_{liq}^2 + \left(\frac{5i - 45i \zeta_f}{15n\pi} + \frac{n(15i \pi^2 \zeta_f - 15i \pi^2 \zeta_f^2)}{15\pi} \right) \xi_{liq}^3 + \right. \\
& \quad \left(-3 - n^2 \pi^2 \zeta_e + \left(-\frac{3i}{n\pi} - 3i n \pi \zeta_e (3\zeta_e + \zeta_f) \right) \xi_{liq} + 2n^2 \pi^2 \zeta_e (-1 + 2\zeta_f) + \frac{270\pi \zeta_e + 180\zeta_f}{15\pi} \right) \xi_{liq}^2 \right) \mu_e + \\
& \quad \left(6 + 8n^2 \pi^2 \zeta_e + \left(\frac{6i}{n\pi} + i n^3 \pi^3 \zeta_e (-2 + 3\zeta_e + \zeta_f) + \frac{n(810i \pi^2 \zeta_e + 90i \pi^2 \zeta_f^2)}{15\pi} \right) \xi_{liq} \right) \mu_e^2 + \\
& \quad \left(-10 + \frac{100}{3} n^2 \pi^2 \zeta_e + \frac{2}{3} n^4 \pi^4 \zeta_e (-1 + 2\zeta_e) \right) \mu_e^3 \right) \mu_f^2 + \\
& \left(-1 - \frac{1}{3} n^2 \pi^2 \zeta_f + \left(-\frac{i}{n\pi} - 4i n \pi \zeta_f \right) \xi_{liq} + \left(10 \zeta_f + \frac{n^2(-10\pi^3 \zeta_f + 20\pi^3 \zeta_f^2)}{15\pi} \right) \xi_{liq}^2 + \right. \\
& \quad \left(1 - \frac{4}{3} n^2 \pi^2 (3\zeta_e + \zeta_f) + \left(\frac{4i}{n\pi} + \frac{4}{3} i n^3 \pi^3 \zeta_e (-1 + 2\zeta_f) + 8i n \pi (3\zeta_e + 2\zeta_f) \right) \xi_{liq} \right) \mu_e + \\
& \quad \left. \left(-10 + \frac{1}{3} n^4 \pi^4 \zeta_e (-2 + 3\zeta_e + 2\zeta_f) - \frac{10}{3} n^2 \pi^2 (9\zeta_e + \zeta_f) \right) \mu_e^2 \right) \mu_f^3 + \\
& \left(1 + \frac{4}{3} n^2 \pi^2 \zeta_f + \left(\frac{i}{n\pi} + 10i n \pi \zeta_f + \frac{n^2(-5i n \pi^4 \zeta_f + 10\pi^4 \zeta_f^2)}{15\pi} \right) \xi_{liq} + \left(5 - \frac{1}{3} n^4 \pi^4 \zeta_e (-1 + 2\zeta_f) - \frac{10}{3} n^2 \pi^2 (3\zeta_e + 2\zeta_f) \right) \mu_e \right) \mu_e^4 + \\
& \left(1 - \frac{10}{3} n^2 \pi^2 \zeta_f - \frac{1}{15} n^4 \pi^4 (-1 + 2\zeta_f) \right) \mu_f^5
\end{aligned}$$

Eq. 25

7 Glossary

Variable	Definition	Comment
C	Mass-sensitivity constant	Eq. 10
d	Thickness of a layer	
D	Dissipation factor	$D = 1/Q = 2\Gamma/f_r$
f	Frequency	
\tilde{f}	Complex resonance frequency	$\tilde{f} = f_r + i\Gamma$
f_r	Resonance frequency	also: “series resonance frequency”
f_0	Resonance frequency at the fundamental	
\tilde{G}	Shear modulus	
h_r	Vertical scale of roughness	Eq. 14, “ h ” for “height”
h_r/l_r	Aspect ratio	Eq. 14, “ l ” for “lateral”
\tilde{J}	Shear compliance	
\tilde{k}	wave number	
m	Mass per unit area	
n	Overtone order	
q	As an index: quartz resonator	
ref	As an index: reference state of a crystal in the absence of a load	
\tilde{Z}	Shear-wave impedance	$\tilde{Z} = \rho\tilde{c} = (\rho\tilde{G})^{1/2}$
\tilde{Z}_L	Load impedance	
Z_q	Acoustic shear-wave impedance of AT-cut quartz	$Z_q = 8.8 \cdot 10^6 \text{ kg m}^{-2} \text{ s}^{-1}$
β', β''	Power law exponents for J' and J''	Eq. 2, (“PL exp” in QTM)
Γ	Imaginary part of a resonance frequency, Half-band half width	
δ	Penetration depth of a shear wave	Newtonian liquids: $\delta = (2\eta_{liq}/(\rho_{liq}\omega))^{1/2}$
δ_L	Loss angle	$\tan \delta_L = G''/G' = J''/J'$ often called δ in rheology
Δ	As a prefix: A shift induced by the sample	
$\tilde{\eta}$	Viscosity	$\tilde{\eta} = \tilde{G}/(i\omega)$
μ	Non-dimensional mass	Eq. 16
ξ_{liq}	Non-dimensional shear-wave impedance of the bulk liquid	Eq. 16
ζ	Non-dimensional inverse square shear-wave impedance	Eq. 16

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