QCMD-Analyze GUI User Guide

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Kazi Sadman

Shull Research Group

Northwestern University, Evanston, IL- 60208

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Running QCMDAnalyze.m will launch the program for analyzing data from QCM-D instruments to extract the fixed frequency rheological properties (shear modulus, $\rho|G_3^*|$, and phase angle ϕ) of a thin film or a bulk medium in contact with the crystal. This code uses the power-law analysis developed by Shull et al., which is a more realistic description of materials than the commonly used Voigt model.[6] The detailed approach was outlined by DeNolf et al. and Martin et al.[1, 2] This approach to solving QCM-D data is more accurate and robust than those analysis provided with commercial instruments because it uses minimal fit parameters, makes the fewest assumptions, uses MATLAB's powerful numerical solvers, and provides physical insight into the experiment and material parameters. Additionally, this analysis also provides checks and balances for accurate viscoelastic analysis of polymer films whose properties can span from glasses to soft gels in air or immersed in liquids, and also viscous polymer solutions. This file provides a guide on how to use the analysis, import data, and export results. Publication quality plots can be generated directly form this GUI.

Note: It is recommended to review this guide in its entirety before using the QCM-D analysis.

1 License Agreement

This code is protected by the open source GNU General Public License v3.0, which lets the user do almost anything with the project, except to distribute closed source versions. Closed source versions cannot be created without the author's consent.

2 Citation

This code is identified by the DOI: 10.5281/zenodo.1482780. If this code is used for publications, then it needs to be cited appropriately. Additionally, the analysis developed in references [1, 2, 6] should be cited.

3 Example files

Three example data files are provided.
1) The QCM-D response from pure water (Bulk limit)
2) A hydrogel equilibrating and then swelling in water (Thin film in water)
3) A PMMA film in air at room temperature (Thin film in air)

4 Buttons

Load QCM-D Data: This button opens a file selection window for you to navigate to your data. Your data should be in the format shown in the example files, where the appropriate referencing for the shifts is already done manually using the absolute frequencies. The program assumes you have referenced your shifts manually with respect to the bare crystal frequencies in air if your film is in air, or to the bare crystal frequencies in water if your film is in water. For a bulk measurement of a viscous liquid, the reference is the bare crystal in air. The code will read only excel files with the extension .xlsx. If you have a .xls file, simply changing the extension to .xlsx should make things work. Note the dissipation factor (ΔD_n) is used in the data, but a conversion is made to represent this as $\Delta\Gamma_n$ using Eq. 1.

$$\Delta\Gamma_n = \frac{\Delta D_n f_n}{2} \tag{1}$$

Bulk Calculation: If a bulk viscous liquid is being measured, then load the data and click this button. A

pop-up figure will appear with your solutions. Here you can use the 'Bulk water' file as an example to see the properties of water at different harmonics. The bulkcalc_Callback function near the end of the main code is called, and you can make changes to the plots here according to your needs.

Plot QCM Data: This file will plot the solutions for films in water or films in air. Make sure the correct radio button is selected for your situation. Note dp is written in mg/m^2 which is approximately the film thickness in nanometers if a density of $1g/cm^3$ is assumed. Likewise the $\rho|G_3^*|$ is the complex shear modulus at 15 MHz (harmonic, n=3). This quantity is $\approx 10^5 Pa - g/cm^3$ for water, and $\approx 3 * 10^9$ for polymer glasses. The phase angle ϕ is 90 for a Newtonian liquid like water, and $\approx 1^o$ for an elastic solid like a polymer glass. We define $|G_3^*|$ as usual:

$$G_3^* = |G_3^*| \exp(i\phi)$$

$$G_3' = |G_3^*| \cos(\phi)$$

$$G_3'' = |G_3^*| \sin(\phi)$$

$$\phi = \arctan(G''/G')$$

Calculation: Select which calculation to use for plotting the predicted shifts, as well as which plots are exported when 'Viscoelastic Plots' and 'Thickness Plots' are clicked. Note that for a 3:5,5 calculation, Δf_3, Δf_5 and $\Delta\Gamma_5$ are used to solve for mechanical properties. In this case, $\Delta\Gamma_3$ is used as a consistency check– the predicted value for this parameter should be fairly close to the experimentally determined one. In a 3:5,3 calculation, $\Delta\Gamma_5$ is used as the consistency check. NOTE: when 'Plot QCM Data' is clicked both the 3:5,3 and 3:5,5 calculations are done, and both solutions are displayed. Selecting one of the calculations here only selects which predicted shifts and viscoelastic plots are shown and exported. Ideally and in most cases, both the solutions should yield very similar answers. Only exceptions arise if the film is too thin and very close to the Sauerbrey limit, then the 3:5,5 calculation is more reliable. Similarly, if the film is too thick and $\Delta\Gamma_5$ is approaching 10,000 Hz, then the 3:5,3 calculation is more reliable. Refer to Figure 1 to understand the approximate thickness ranges needed for accurate viscoelastic analysis with the third and fifth harmonics. Generally, the 3:5,5 calculation is robust for most experiments.

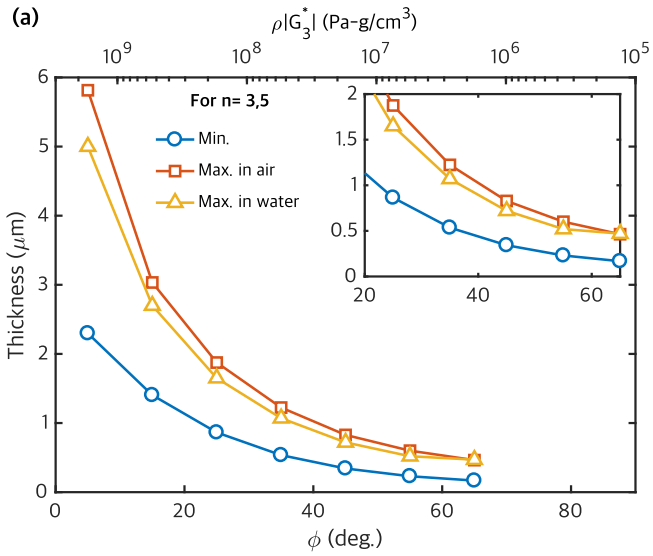

Figure 1: Approximate thickness ranges that apply for a film with a particular shear modulus. Stiffer films (high modulus/low phase angle) require a thicker film to provide sufficient deviation from the Sauerbrey limit for accurate viscoelastic analysis. This plot was recreated from *Anal. Chem. 2018, 90, 4079−4088.*[6]

Viscoelastic plots: This button will show you the viscoelastic plots outside the main GUI. The export_callback near the end of the main code is used to make these plots. You can change the way things are plotted here to customize for your publication needs. Only results for the 3:5,5 calculation are shown.

Thickness plots: This button will show you the d/λ_n and also the predicted shifts from your solutions. In this analysis, we exclusively only use the 3:5,5 calculation, therefore we have $\Delta\Gamma_3$ as a free parameter for a consistency check. If the code solved correctly, then $\Delta f_3, \Delta f_5$ and $\Delta\Gamma_5$ (3:5,5) should all have the experimental shifts and predicted shifts match exactly. The difference in the experimental and predicted value of $\Delta\Gamma_3$ should be as small as possible. In most real cases a small discrepancy in the predicted and experimental value is acceptable. Here, the thicknessplots_Callback near the end of the main code is called to make the plots. You can customize the output according to your needs. $\rho\delta_n$ is the shear wave decay length at the n^{th} harmonic. Here, the unites of g/m^2 provides the decay length in micron if a density of $1g/cm^3$ is assumed. The parameter $\rho d/(\rho d)_{sn}$ is the percent deviation from the Sauerbrey limit based on the solved thickness, shear modulus and phase angle.

Refresh: Relaunches the GUI and clears the memory. Useful if an error is encountered, or if you just want a clean new window.

Data range to solve: By default we solve every point. However, if the data set is large then it is desirable to solve only a portion of the data with larger intervals. For example, inputting 100:5:500 into the edit text boxes will solve every fifth point between the 100th and 500th data points.

Save plots: If this button is checked, then publication quality vector figures are exported into the working directory when 'Viscoelastic Plots' and 'Thickness Plots' are clicked.

Export Data: This button outputs a tab-delimited text file into the working directory with all the relevant values. This is useful if you want to do your own plotting outside MATLAB.

Handles: This allows access into MATLAB's handle structure where all the data is stored internally. After you have solved for solutions, click this button and MATLAB will open the workspace in debugging mode. Here, there will be a new variable called "Handles" in the workspace. If you double click this, then the

internal data structure is revealed. For example, the variable phiout{1} stores all the phase angles from the 3:5:3 calculation, and phiout{2} stores all ϕ from the 3:5,5 calculation. Likewise, the variable d5out stores d/λ_5. To leave the handle structure, click "Quit Debugging" in the main MATLAB window. More information on d/λ_n can be found in *Anal. Chem. 2018, 90, 4079−4088.*[6] Here, d is the film thickness and λ_n is the wavelength of the shear wave at the n^{th} harmonic.

$$\lambda_n = \frac{1}{f_n}\left[\frac{|G_n^*|}{\rho}\right]^{1/2}\frac{1}{cos(\phi)} \tag{2}$$

Verify Solutions: If the experiment was done correctly with the right reference state, and if the film was of good quality, then the solver will converge to a solution for ϕ, $d\rho$, and $\rho|G_3^*|$. Verifying solutions will confirm the solver converged properly to a solution. In this case, the solver exitflag is a positive value. Any 'solution' with a negative exitflag value should be discarded. This exitflag value is also exported in the text file output. For more information of the solver exitflag, visit MathWorks here. *Note: one should always perform a sanity check for the values expected for the mechanical properties of the subject material based on physical intuition. Solver convergence is a necessary criteria to believe the data, but not the only criteria. Make sure to have selected the correct film environment, and that your predicted shifts after solving match.*

5 General notes

1) The code is good at finding missing values in the imported data. However, there is a chance data import may fail if there are too many missing data points, or if the data columns are of varying lengths. Data may have to be manually cleaned before importing if an error is encountered.
2) The GUI has zoom, grab and data cursor functionality enabled. You can select the data cursor, and then click on individual points for the exact values.
3) Often, if the shifts do not solve (maybe because your film is too thin), then the calculation will return non-sense for modulus and ϕ. For example, all the ϕ will be 90, which is the upper bound on the numerical solver. However, even if the code does not solve because the film is too thin, the $d\rho$ value is reliable.
4) Refer to Figure 2 to gain intuition on how ϕ and $\rho|G_n^*|$ are roughly correlated. Refer to Figure 1 to understand the approximate thickness ranges needed for accurate viscoelastic analysis. In general, the stiffer the material, the thicker it has to be for being in the optimal viscoelastic regime. Polymer glasses such as poly(styrene) or poly(methylmethacrylate) need $\approx 5\mu m$ films, while polymer gels/complexes need $\approx 1\mu m$ films. The maximum $\Delta\Gamma_n$ that is trustworthy is $\approx 10,000$ Hz.
5) The code is written in MATLAB 2018b. Version specific errors may occur, especially if you are on a much older version. Generally, 2015a and up should work fine.
6) A good crystal with a reliable response should have absolute $\Gamma < 100$ Hz for the measured harmonics.
7) We plot $d\rho$ in mg/m^2, which is the areal mass of the film. Here, if one assumes the film is $\approx 1g/cm^3$ then 1000 mg/m^2 is $\approx 1\mu m$.
8) Bug reporting should be done under issues on the main GitHub page under Issues.
9) To learn the kinds of experiments which can be performed using the QCM, the reader is referred to several publications.[3, 7, 5, 4, 8]
10) Films should be as smooth and homogeneous as possible.
11) For high temperature experiments, the bare crystal frequencies at all appropriate temperatures needs to be used as the reference.

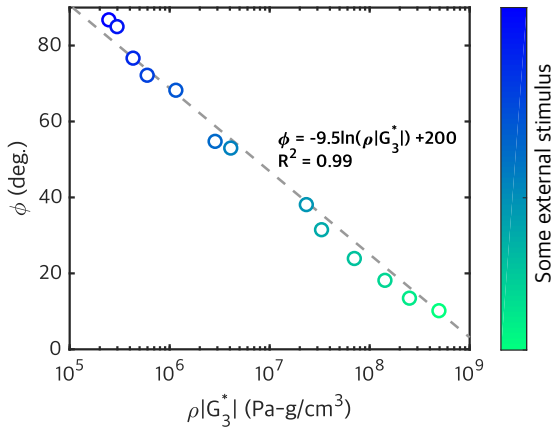

Figure 2: The phase angle and the shear modulus are correlated approximately according to the relationship shown for mechanical properties calculated in the megahertz regime. This plot was recreated from *Anal. Chem. 2018, 90, 4079−4088.*[6] Refer to *Macromolecules 2017, 50, 23, 9417-9426* for the experimental details.[5]

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