

# Software Package QTZ

## Handbook and Help-File

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#### Remarks:

- The help file in some cases does not display graphics (including some equations) properly. Please refer to the pdf-file in order to see them.
- We have recently implemented the impedance analyzer SA250B from Saunders. This analyzer is a card, not a separate instrument. Some remarks on the impedance analyzer do not apply to the card. (in {curly brackets}).

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## General

- Quartz Crystals
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- Why Impedance Analysis?
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- Why the Half-Band-Half (HBH) Width?
- Ring-Down
- Quartz Resonators are Acoustic Reflectometers

## Quartz Crystals

Quartz crystals are grown at a volume of about 3000 tons annually (a quarter of the amount of silicon grown per year, as of 1997). Quartz crystal resonators are highly precise and at the same time very economic clocks. For a review on the use of quartz crystals for time and frequency control see the tutorial by [J.R. Vig](#)

Advantages of quartz crystals for use as clocks are:

- They are weakly piezoelectric. Acoustic vibrations can easily be excited electrically. The *weak* piezoelectric coupling actually is an advantage for frequency control: The electrical boundary conditions do not affect the resonance properties very much.
- They are easy to handle. They are hard but not brittle. They do not dissolve in any of the common solvents.
- They have extremely low intrinsic acoustic losses. Q-factors of  $10^5$  are easily achieved.
- Importantly, there are **temperature-compensated cuts**, that is, cuts where the resonance frequency to first order does not depend on temperature. Most popular is the AT-cut. These cuts do not exist for silicon, which would otherwise be a strong competitor to quartz for timing applications. (Excitation could be achieved with other means like piezoelectric films sputtered onto to the resonator surface.)

Here are some disadvantages:

- Temperature compensation only works only at a single temperature (room temperature in case of the AT-cut). For other temperatures, the experimental requirements on temperature control can be rather severe.
- They only go to about 500 °C in temperature. Above that temperature,  $\beta$ -quartz forms.  $\beta$ -quartz is non piezo-electric. Even below the transition point, twinning occurs. People work on high temperature replacements for quartz, where candidate materials are Langasit (LGS) and GaPO<sub>4</sub>.
- It is not so easy to miniaturize them. The ratio of lateral dimension and thickness must be larger than 30, otherwise there is no good thickness shear mode. Small blanks are fragile.
- It is not so easy to structure them laterally. Structuring is possible with liquid etching (fast but not precise) or ion milling (precise but slow). While it would be nice to have an array of – lets say – 10 x 10 quartzes monolithically integrated into one chip, this seems tough in terms of microfabrication.

- Quartz plates cannot be monolithically integrated into a silicon chip (a potential advantage of Si-resonators)

## Oscillator Circuits

The easy way to build a clock with a quartz crystal is to place it into the feed-back loop of an operational amplifier. The amplifier then starts oscillating at the resonance frequency. This is a rather cheap device (~ 1 USD total for some mass products) but not the preferred way for advanced sensing. The drawbacks are

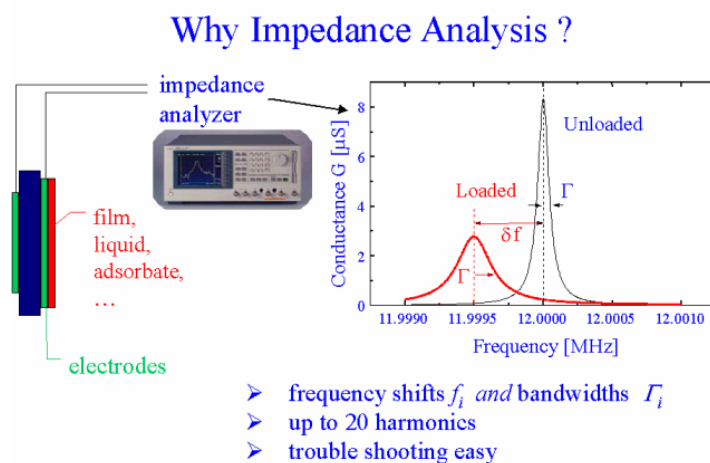
- The dissipated energy is not easily measurable. There is a commercial oscillator circuit from [Maxtek](#) (“PLO10”) which can measure dissipation as well.
- Oscillators only work on one harmonic.
- The exact frequency of oscillation depends on the details of the driving electronics. It is usually not at the maximum of the conductance curve (which we consider the acoustic resonance frequency, also called the “series resonant frequency”). Importantly, the oscillation frequency may depend on the Q-factor, that is, it may shift when the dissipation changes. (Also see the [Butterworth-van-Dyke equivalent circuit](#)).

Advantages of oscillator circuits are:

- They can be cheap.
- They can be very stable. If one goes for stability only, oscillator circuits are the best. The competing techniques ([impedance analysis](#) and [ring down](#)) in one way or another turn the quartz on and off periodically. This affects the temperature and induces subtle effects of internal relaxation. With impedance analysis and ring-down, the repeatability is somewhere in the range of 0.1 Hz. With oscillator circuits, one can do better.

## Why Impedance Analysis?

Impedance analysis is conceptually simple. It relies on the spectra of the electrical conductance. When the frequency of excitation matches the acoustic resonance frequency, the amplitude of oscillation becomes large. At the same time the current through the electrodes (that is, the conductance) becomes large, as well. Measuring the conductance around the resonance frequency, one obtains a *resonance curve*. All one needs to do is fit the theoretical resonance curve (the “Lorentz curve”) to the data and extract the resonance frequency and the bandwidth from the fit.



The advantages are

- Frequency *as well as* **bandwidth** are obtained.
- Other parameters (like the **amplitude of the resonance**, related to the total mass, and the **offset of the susceptance**, related to the parallel capacitance  $C_0$  and the dielectric environment of the resonator) are measured, as well. However, the accuracy obtained for these values is much less than the accuracy in frequency measurements.
- One can measure on many resonances (up to 25 in air, up to 10 in liquids) and thereby vary the wavelength of shear sound.
- Trouble shooting is easy. Not all resonances look nice. Some are contaminated by **anharmonic side bands** (especially on high harmonics). With impedance analysis, you *know*. You can discard the resonance or keep it but maintain a little question mark in the back of your head. You can save yourself a lot of time by tossing bad crystals to the waste bin right away.
- Last but not least: impedance analyzers have come down in price substantially. Impedance analysis has become a routine inspection tool in quartz crystal manufacturing. This market has grown and so has the competition for good and cheap instruments.

## Measure Frequencies!

Having read all the praise of impedance analysis, the reader might think that impedance analysis can provide all parameters of the **Tiersten equivalent circuit** (and there are quite a number of them....). Yes, it can, in principle, but only in principle. Why not in practice? It is really not so easy to measure an electrical impedance accurately. Accurately meaning: better than 1%. (Look into specs sheets of your multimeter...) An accuracy 1% is lousy for the quartz crystal microbalance (QCM). For the QCM anyone who does not do better than 10 ppm of relative accuracy in frequency determination hides his face. And this accuracy is needed. One cannot derive anything meaningful from a frequency measurement which is not accurate to 10 ppm. That's the point. It is easy to measure frequencies and everything else is more difficult. One can try, for sure. Start with a careful **calibration**, first of all. But you will see: it is a much different game. The strength of the QCM is in its tremendous accuracy in frequency determination.

## Why the half-band-half (HBH) width?

The community is uses different terms to quantify the dissipative interaction of a quartz crystal with its environment, which are

- The Half-Band-Full-Width ("HBFW",  $2\Gamma$ )
- The Half-Band-Half-Width ("HBH Width",  $\Gamma$ )
- The Quality-Factor (Q-factor,  $Q = \text{frequency} / \text{HBFW} = f/(2\Gamma)$ )
- The Dissipation ( $D = Q^{-1} = 2\Gamma / f$ )
- The Resistance

All of these can be displayed in the Graphics Panel. Half-band-full-width, half-band-half-width, Q-factor, and dissipation are simply related to each other. The Graphics Panel has the conversion implemented.

The resistance is a different matter. The resistance in this context is the inverse of the peak conductance,  $G_{\text{max}}$ . It is related to the bandwidth, but is *not* always strictly proportional to the bandwidth. Actually, one might hope that the ratio of the

two contains information as well. Unfortunately, this ratio turns out to behave quite erratic in practice (see "[Measure frequencies](#)").

This software uses the half-band-half width (HBHW, termed  $\Gamma$  here). Here is why: One can define a complex resonance frequency  $f^* = f + i\Gamma$ . If you Fourier transform the resonance curve, you find a decaying sine wave

$$\begin{aligned} u(t) &= u_0 \exp[i\omega t] \exp[-2\pi\Gamma t] \\ &= u_0 \exp[i2\pi(f + i\Gamma)t] \end{aligned}$$

The quantity  $\Gamma$  in this equation turns out to be the HBH width. In the same way, you can define a complex frequency shift  $\delta f^* = \delta f + i\delta\Gamma$ . Importantly, the "[generalized Sauerbrey equation](#)"

$$\frac{\delta f^*}{f_0} = \frac{\delta f + i\delta\Gamma}{f_0} \approx \frac{i}{\pi} \frac{Z^*}{Z_q} = \frac{i}{\pi Z_q} \frac{\sigma}{\partial u / \partial t}$$

holds for the complex frequency shift  $\delta f^*$ , where  $Z^*$  is the ratio of stress,  $\sigma$ , and lateral velocity at the quartz surface,  $\partial u / \partial t$  (see generalized Sauerbrey-equation for the definition of the other variables). It is a single complex equation, dealing with both the elastic and the dissipative interactions of the quartz with its environment. Frequency shift and dissipation can be conveniently described in one and the same set of equations, if the HBH width is used. The HBH width is the natural unit for dissipation. For instance, the HBHW and the negative frequency shift are the same if the quartz is in contact with a Newtonian liquid.

See: B.A. Auld: *Acoustic Fields and Waves in Solids*. Wiley, N.Y., Vol II, Ch 12, 1973.

## Ring-Down

Conventional impedance analysis works in the frequency domain: The exciting signal is a sine wave, the frequency of which is swept across the resonance. One can measure in the time domain as well. In this case, one excites the oscillation at the resonance frequency, turns the exciting signal off, and then watches the decay of the oscillation in the quiet period. The analogous procedure is known as "free induction decay" in nuclear magnetic resonance. As long as linear response holds (and that is a good assumption) the free decay is the Fourier transform of a resonance curve and contains the exact same information. The advantages of the ring-down technique are

- It's fast. It can, in principle, be repeated with an acquisition rate equal to the bandwidth of the resonance (easily 100 Hz, as least in liquids)
- It provides a "snapshot". If the properties of the resonator change more quickly than the sweep time of the impedance analyzer, the shape of the resonance turns funny and one cannot do anything about it. With ring-down, one has the full information in every single decay. The decays only last for a few milliseconds.
- Ring-down is better than impedance analysis when nonlinearities are present. These nonlinearities may originate from the quartz plates (if the drive level is too high) or from the sample (most likely in contact mechanics experiments). With ring down one has the complete real-time motion on the screen. If it is not a perfect sine wave: one sees it. One can search for overtones with a Fast Fourier Transform. More importantly: in the presence of nonlinearities the resonance frequency and the decay rate depend on the instantaneous amplitude. The

amplitude continuously decreases during ring-down and the frequency changes over time. This phenomenon is also called "chirp". The decay rate ( $2\pi\Gamma$ ) may change with amplitude, as well. One can explicitly derive a nonlinear spring constant and a nonlinear drag coefficient from the chirp and the nonlinear decay rate (Berg et al., Rev. Sci. Instrum. 74, 118, 2002, Phys. Rev. Lett 91, 145505, 2003).

Ring-down is implemented in QCM-D instrument by g-sense.

## Quartz Crystals are Acoustic Reflectometers

With impedance analysis one gains not only one frequency shift, but many and the bandwidths as well. What is this used for?

Let's first go back to the time-honored **Sauerbrey equation**:

$$\frac{\delta f}{f} \approx -\frac{m_f}{m_q} = -\frac{2f_0}{Z_q} m_f$$

where  $\delta f$  is the frequency shift,  $f$  the frequency,  $m_f$  the areal mass density of the film,  $m_q$  the areal mass density of the quartz,  $f_0$  the frequency of the fundamental, and  $Z_q$  the acoustic impedance of AT-cut quartz. The fractional decrease in frequency  $\delta f/f$  is equal to the fractional increase in mass (as long as  $m_f \ll m_q$ ). The second part of the equation expresses the mass of the quartz,  $m_q$ , as the acoustic impedance,  $Z_q$ , divided by twice the frequency of the fundamental,  $f_0$ . On the fundamental we have a standing wave with antinodes at the quartz surface. The thickness of the quartz,  $d_q$ , is  $\lambda/2$  with  $\lambda$  the wavelength of sound. We have  $\lambda = v / f_0 = (G/\rho)^{1/2} / f_0$  with  $v$  the speed of sound and  $G$  the shear modulus. This leads to  $m_q = \rho d_q = 1/2 (G \rho)^{1/2} / f_0$ . Remembering that  $Z_q = \rho v = (G \rho)^{1/2}$  yields the second part of the above equation.

But there is different way to look at this. There is a shear wave approaching the quartz–film interface. Without a film, the wave would be reflected with a reflection amplitude of  $r = 1$ . But there is a film. Part of the wave is reflected at the quartz–film interface and part of it enters the film. This wave is reflected at the film–air interface and comes back a little later, interferes with the wave which has not entered the film and creates a phase shift  $\phi$  for the total reflected wave. The coefficient of reflectivity of the total wave is not unity, it is  $\exp(i \phi)$ . How does this affect the resonance frequency? Well: the phase acquired during one round-trip through the acoustic cavity (a fancy word for the crystal) must be an integer multiple of  $2\pi$ . That's the "resonance condition". Therefore, the fractional shift in frequency must be the same as the fractional shift in phase picked up at the quartz–film interface, that is:

$$\frac{\delta f}{f} = -\frac{\phi}{2\pi}$$

Why is this better than the Sauerbrey equation? Because we are no longer assuming that there is a single film on the quartz surface. There could be anything there (a liquid, for instance, or a multilayer system).

In a second step we assume that the phase shift is small. We can then Taylor-expand  $r = \exp(i\phi)$  as  $r \approx 1 + i\phi$  and write

$$\frac{\delta f}{f} \approx -\frac{\text{Im}(r-1)}{2\pi}$$

Why this transformation? Because it can be readily generalized to the complex frequency shift  $\delta f^* = \delta f + i\delta\Gamma$ :

$$\frac{\delta f^*}{f} = \frac{\delta f + i\delta\Gamma}{f} \approx \frac{i(r-1)}{2\pi}$$

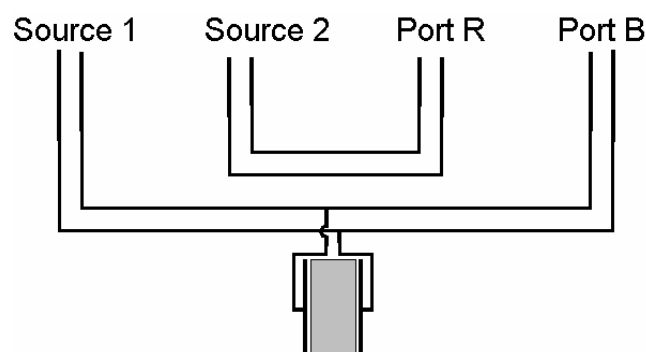
This equation shows that the quartz crystal really has turned into an acoustic reflectometer! The acoustic reflectivity can be calculated just as in the Fresnel formalism for multilayer optics, where the acoustic impedance takes the role of the refractive index.

## Getting Started

- Connect Quartz Plate to Impedance Analyzer
- Setup Communication
- Select a Harmonic
- Search the Resonance
- Measure and Display Results
- Save Results

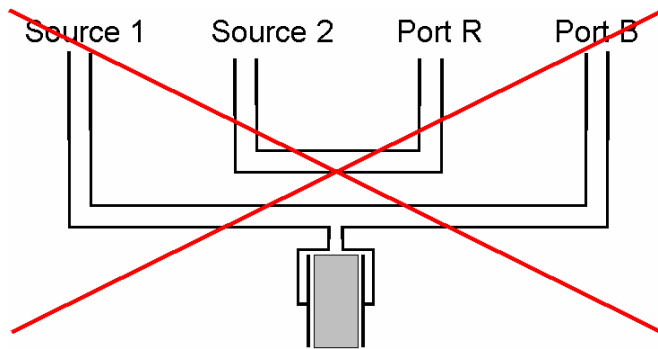
## Connect Quartz Plate to Impedance Analyzer

There are different ways to connect the quartz electrically. This is the easy way to connect the crystal to the *E5100 impedance analyzer*.



Some analyzers do not have two exits for the source. In this case use a power splitter on source 1

It is essential that the quartz connects the signal line and the ground. It should not be part of the signal line (as depicted below). In this configuration, the front electrode is not grounded.

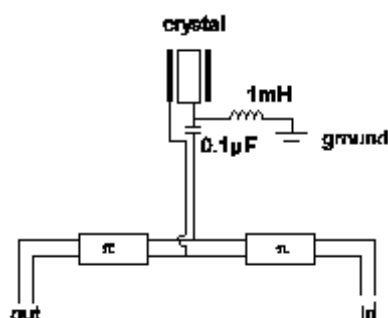


There are two better (but more complicated) ways to connect the crystal:

- Use an impedance test kit (which basically is a directional coupler). The impedance in this case is inferred from the parameter “S<sub>11</sub>”. Please refer to the literature for details. This is the preferred way, if you really care about calibration of the electrical impedance. Accurate calibration is not very important for the determination of frequency and bandwidth.

- Use a  $\pi$ -network. This is the preferred way if you worry about piezoelectric stiffening. The  $\pi$ -network provides a certain amount of electrical separation between the crystal and the network analyzer. That reduces the influence of the electrical circuit on the crystal's behavior. The standard way of testing crystals is based on a  $\pi$ -network (IEC-444). The problem is: with the  $\pi$ -network, the crystal surface is not usually grounded. You have to provide some extra elements for grounding (which interferes with the calibration to a small extent).

We use a  $\pi$ -network in when we measure with the SA250B network analyzer. The connection in this case looks like this



There is an LC-circuit between the test fixture (the  $\pi$ -network) and the crystal in order to ground it. Make the cable between the test fixture and the crystal as short as possible.

Possibly, load a certain “state” of the impedance analyzer (including a previously acquired calibration) from a floppy disk in the impedance analyzer. (Applies to the E5100 only, start with the SAVE/RECALL button).

After electrical connection is made, **search for resonances** with the impedance analyzer. Adjust **center and span** from the front panel of the impedance analyzer until you see a resonance on the screen.

Note: Center and Span from the impedance analyzer will be overwritten from the software, once the computer takes over. What you have entered from the front panel of the impedance analyzer does not affect the flow of the program.



## Setup Communication

The software is usually shipped in the demonstration mode. In order to make it active for measurement, the type of analyzer ("Analyzer") in the Control Panel must be changed from "Demo Version" to whatever analyzer is present. You may be prompted for the registration key, when you change this setting. {Also, make sure that the interface board is set correctly. A third thing which can go wrong is the GPIB address}. When these three settings are correct, you should be able to change the number of points (for instance). When you click "test communication" the software should respond with the product and version number of the impedance analyzer.

If you get funny results, turn the impedance analyzer off and on again. The impedance analyzer may have been in some awkward state, where it does not respond properly.

## Select a Harmonic

This step assumes that you have correctly **connected the quartz** plate to the impedance analyzer and that the **communication** works. Before you can start a measurement you need to tell the software where to search for resonances. This is done in the Harmonics Panel. You can have up to 25 harmonics active. Make a harmonic active by clicking its checkbox on the right hand side of the panel. Now the software wants to know the reference frequency, the reference HBH width, the center, and the span. You can, in principle, input these manually from the Harmonics Panel. More convenient is the **Search Panel**.

## Search the Resonance

The Search Panel allows you do change center and span until you have the resonance of interest nicely on the screen. Click "Acquire" in order to see the conductance spectrum. You can input a new center and a new span manually. Or you can increase the span as indicated on the buttons (should be self-explaining). Typically, you will in a first step enter the frequency where you expect the resonance (let's say 5 MHz) as the center manually. But you don't find the resonance, because it is never exactly where you expect it. In a second step, you increase the span by a factor of 2. You still don't see it. You increase it again. And again. And there it is. But now the span is rather large. You have the resonance of interest as well as a number of **anharmonic side bands** on the screen. In the next step, you move the center of the screen so that the resonance of interest is in the center. There is an easy way to do this: click onto the graph. The mouse has to be *on* a data point. The arrow turns into a hand when this is the case. The resonance of interest then is in the center. Keep decreasing the span until you have single nice peak. Then click "Acquire + Fit". Does the fit look nice? If yes, click "Accept as Reference" The software will use these values in the future as the **reference state** for this harmonic. **Center and span** are always updated when you leave the Search Panel. The reference values are only updated when you click "Accept as Reference"

You should repeat this process for a few harmonics. Try high ones ( $n = 35$ , for instance). See how many resonances look nice. Also play around with the **number of points**, the **system bandwidth** (the "number of averages", in case you have the SA250B), and the **drive level** (to be set in the Control Panel). Minimize the time needed for reliable data acquisition. If the data acquisition rate is high, there is a dependence of the derived resonance frequency on the speed of data acquisition. There are two options: (a) reduce the speed (b) perform **two sweeps in upward and downward direction** and calculate the arithmetic average of the derived fit parameters as a "second best" approximation to the true parameters.

Don't worry if a resonance appears **asymmetric**. This is indicative of improper **calibration**. By and large, calibration is uncritical because all you are after, are frequencies and bandwidths. The fit takes care of improper calibration to a large extent.

## Measure and Display Results

If you have **connected the resonator**, selected a harmonic and **searched** the resonances of interest, you can start a measurement. Click "Start" in the Main Panel. What is the noise level? In air you should easily reach less than 1 Hz. In water, it is a little higher because the bandwidth has increased. The frequency may drift in case you do not **control the temperature** or if there a **stresses in the mount**, which still relax.

You can convert the data in various ways. For instance, you may want to normalize the frequency shifts by the overtone order,  $n$ , if you anticipate the **Sauerbrey equation** to hold. If it holds,  $\delta f/n$  is the same on all harmonics. Or you might want to normalize frequency shift and HBH width by  $n^{1/2}$  in case you anticipate to measure a **viscosity**. If the sample is a Newtonian liquid,  $\delta f/n^{1/2}$  is the same on all harmonics.

The **HBH width** can be converted to other common units like the Q-factor or the dissipation.

Maximum conductance, phase, and offsets are only displayed if you have checked "**Save Amplitudes, Phases and Offsets**" in the Control Panel. They are of minor importance.

If you wish to export the converted data, you can do so by placing the mouse on the graph, clicking the right mouse button, and selecting the **export dialog**. The same dialog allows you to export the graphs.

You can convert frequency shift to a **Sauerbrey mass** and the complex frequency to a **viscosity** in the Graphics Panel without resorting to the **Modeling Panel**. For more advanced ways of treating the data (like deriving a viscous compliance of the film) you have to use the Modeling Panel. See **Display** for more options on how to display or convert fit parameters.

## Save Results

If you are only interested in the frequencies and HBH widths, you find these in the file with extension ".fre". The current filename is displayed in the graphics panel. See "**Filenames and Formats**" for the format and for the names of the files containing the data.

## Select Harmonics

- **Reference Frequency and Reference Bandwidth**
- **Center and Span**
- **Include Harmonic in Measurement**
- **Spans and Fitting Ranges**
- **Opening the Search Panel**

## – Profiles

### Reference Frequency and Reference Bandwidth

The importance of the reference frequency and the reference HBH width cannot be over-emphasized. The frequency shifts are outright meaningless without the correct reference values.

Internally, the reference frequencies and bandwidths are saved in the qtz.ini file. They can be saved and loaded to/from files with the extension “.ref” from the **Harmonics Panel**. The files contain two lines with 25 columns each. The two lines contain the reference frequencies and the reference HBH widths. The 25 columns correspond to the 25 harmonics.

The first line (header) in the files with extension “.fre” also contains the reference frequencies.

You can change the reference state from the graphics panel as well. Click onto “new reference state”.

### Center and Span

When a measurement is initiated, the window of the impedance analyzer is adjusted according to the parameters “center” and “span”. If these parameters are not correct, the resonance of interest will not be found. Center and Span for every harmonic are shown in the **Harmonics Panel**.

QTZ keeps track of the centers and spans during the measurements. Anytime a measurement has been performed, the new value for center is equal to the resonance frequency as determined by fitting a resonance curve to the conductance curve. The new span is equal to the product of the old half-band-half (HBH) width and a number called “**span factor**”. (Exceptions: when clicking “Take Data with Fit” in the Search Panel, center and span remain unchanged. Center and Span are *not updated* if the boxes “**Keep Centers Fixed**” or “**Keep Spans Fixed**” in the Control Panel are checked.)

Center and Span can be set manually in the Search Resonances Panel. {Setting them from the front panel of the impedance analyzer remains without effect for the flow of measurement.} The program sets center and span prior to data acquisition according to its own internal settings (saved in qtz.ini). Center and Span can be saved and loaded to/from files with the extension “.csp” from the Harmonics Panel. The files contain two lines with 25 columns each, where the first line contains the centers and the second line contains the spans. The 25 columns correspond to the 25 harmonics. The software does not know, whether these centers and span correspond to channel A or channel B. When you load them, it assigns them to the channel indicated on the upper left of the Harmonics Panel.

Center and Span must not be confused with the **reference frequency** and the reference HBH width. While the latter are determined on the bare quartz and are not changed during the flow of the program, center and span are constantly updated. Center and Span are *not updated* if the boxes “**Keep Centers Fixed**” or “**Keep Spans Fixed**” in the Control Panel are checked.

Center and Span can be either edited manually or be increased or decreased with the respective buttons in the Search Panel. All changes are saved and will be used for the next measurement on this harmonic.

Center can also be set by clicking onto a data point in the graph (cursor must assume the shape of a hand).

Center and span can get lost if the **Lorentz fit** fails. In this case you have to interrupt the measurement, go to the Search Panel, and find them again. Also see "**Abandon Harmonic when Fit Fails**".

## Include Harmonic in Measurement

One of the benefits of impedance analysis is that you can compare results obtained on the different harmonics. You can include up to 25 different harmonics. A harmonic is included into the measurement by checking the box "**Include in Measmnt.**" on the right hand side in the Harmonics Panel.

## Spans and Fitting Ranges

Before a measurement can be initiated, **center and span** must be set. That leaves the question: what should the software pick for center and span? For the center it picks the last resonance frequency as determined with the **Lorentz fit** on the respective harmonic (unless the box "Keep Centers Fixed" in the Control Panel is clicked). For the span the software uses the product of the previous HBH width and a factor which is called "span factor". A typical value is 8. The span factor can be viewed and changed from the Spans and Fitting Ranges Panel to be reached from the Harmonics Panel.

Usually, you want to limit the range of data included into the fit to frequencies close to the resonance. Away from the resonance, electrical imperfections show up. The software **guesses** the resonance frequency and the bandwidth. The fitting range is based on this guess. Usually it is centered at the resonance frequency and extends to higher and to lower frequency by the estimated HBH width *times* a certain factor. A typical value is 2. This factor can be set in the Spans and Fitting Ranges Panel. The fitting range may be chosen as asymmetric, that is, two different factors may apply on the high frequency and the low frequency side. This may be useful when the data are contaminated by **anharmonic side bands**, which are often located to the right of the main resonance. In this case one would choose a narrow range for fitting to the right of the resonance and a somewhat larger range to the left. The fitting ranges can be viewed and changed from the Spans and Fitting Ranges Panel to be reached from the Harmonics Panel.

## Opening the Search Panel

The Search Panel is opened from the Harmonics Panel by clicking one of the buttons on the left hand side. Typically, you use the Search Panel to determine the **center, the span**, and the **reference values**.

## Profiles

The conductance spectrum allows to judge whether a given harmonic is a "good one". Some quartz blanks are better than others. In order to keep a record of the quality of a resonator, one may save the conductance spectra and display them together on a common graph. The conductance spectra are saved from the Search Panel. The filename of the spectra is the default filename + 4 digits indicating the counter and the extension ".spc" (example: "test0002.spc" for spectrum no. 2 from the experiment "test").

The conductance spectra can be collected in a single graph in the Profiles Panel. It is reached from the Harmonics Panel. When the Profiles Panel is opened, the software displays the selected conductance spectra together. The spectra are identified by their counter (as given in the filename). You can either display all spectra with a counter between a minimum and a maximum integer or you can input a list of integers separated by commas and display the spectra with counters as given in the list. The software re-scales the spectra vertically so that they look similar

on the screen. It also offsets them vertically by a value specified in the field "gap". The y-scale is in arbitrary units. The x-scale is in "fractional frequency shift"  $\delta f/f$ . If you wish to have the same fractional span for all spectra, you can set a default fractional span in the Search Panel and set the "Fractional Span for Profile".

Set the span large enough. It is the purpose of the Profile option to see the **anharmonic side bands** (also called "spurious modes"), not to perform fits on the resonance of interest. The anharmonic side bands should be well separated from the main resonance.

## Search Panel

The Search Panel allows you to find:

- **center and span** of a given harmonic (to be selected in the Harmonics Panel)
- **reference** frequency and reference half-band-half-width of a given harmonic

Enter the Search Resonances Panel from the Harmonics Panel.

The conductance spectra can be saved. This is mostly used for assessing whether a given resonance is "good enough". It is recommended to collect the conductance spectra of a resonator in the Profile Panel and print this sheet for future reference. These spectra should have a span sufficiently large to show the anharmonic side bands. The Profile Panel uses the fractional frequency shift as the x-axis. One can input a fractional span (typical: 0.002) and use this same fractional span on all spectra to be saved for the profile.

There is a "Movie Mode" which continuously saves conductance spectra without fitting. This is mostly used for complicated spectra which contain some qualitative information but are not easily fitted with resonance curves. (The software may crash when fits fail too badly.) Upon clicking the "Take Movie" button the software keeps measuring conductance spectra and saves them in separate files. Center and span remain unchanged for the entire movie. The software automatically increments the counter (filename of the spectra has 4 digits for the counter). You can either just show the movie, or show the movie and fit resonance curves at the same time. With this "Reanalysis" you don't risk interrupting a running experiment when a fit fails. Whenever a file is saved, the software records the filename and the time when the spectrum was taken in a file with extension **".mov"**.

You can set a guess value for the phase (see **Asymmetric Resonances and the Phase** for details).

## Measurement

- **Measurement**
- **Display Results**
- **Filenames and Formats**

## Measurement

A measurement on a single resonance is usually done from the **Search Panel**. For a continuous measurement (potentially on many harmonics), click the "Start" button in the Main Panel.

## Display Results

There are two levels of displaying the results. The "raw data" are the shifts of frequency and bandwidth,  $\delta f$  and  $\delta \Gamma$ . These raw data are saved into a file, where the filename is the default filename plus the extension **".fre"**. The Graphics Panel shows

these raw data. For the **HBH width**, the Graphics Panel allows for the conversion to other common units like the Q-factor or the dissipation.

The software also allows to display frequencies and HBH-widths normalized to overtone order,  $n$ , or to the square root of the overtone order,  $n^{1/2}$ . Normalizing to  $n$  is the natural display in the **Sauerbrey limit**, normalizing to  $n^{1/2}$  is the natural display for a **semi-infinite (Newtonian) liquid**, where "natural display" means that the different harmonics should show the same values when rescaled in this way.

The Graphics Panel goes beyond the display of "raw data" in two ways: Firstly, it allows to convert the frequencies to Sauerbrey masses according to

$$\frac{\delta f}{f} \approx -\frac{m_f}{m_q} = -\frac{2f_0}{Z_q} m_f \quad (1)$$

where  $m_f$  and  $m_q$  are the areal mass density of the film and the quartz, respectively,  $f_0$  is the frequency of the fundamental and  $Z_q = 8.8 \cdot 10^6 \text{ kg m}^{-2} \text{ s}^{-1}$  is the acoustic impedance of AT-cut quartz. This conversion can be done without resorting to any kind of modeling. It needs the frequency of the fundamental,  $f_0$ , which is shown (and can be changed) at the bottom of the Graphics Panel. One can also convert the Sauerbrey mass to a "Sauerbrey thickness" (in nm). For this conversion, the density of the film is needed (shown at the bottom of the Graphics Panel).

A second kind of conversion is the calculation of a complex viscosity  $\eta = \eta' - i \eta''$  from  $\delta f$  and  $\delta \Gamma$  according to

$$\frac{\delta f + i \delta \Gamma}{f_0} = \frac{i}{\pi} \frac{Z}{Z_q} = \frac{i}{\pi} \frac{\sqrt{\rho G}}{Z_q} = \frac{i}{\pi} \frac{\sqrt{i \omega \eta \rho}}{Z_q} = \frac{i}{\pi} \frac{\sqrt{i \omega \rho (\eta' - i \eta'')}}{Z_q} \quad (2a)$$

or

$$\frac{(\delta f^2 - \delta \Gamma^2) + 2i \delta f \delta \Gamma}{f_0^2} = \frac{-\omega \rho (i \eta' + \eta'')}{\pi^2 Z_q^2} \quad (2b)$$

where  $\rho$  is the density of the liquid and  $G = G' + iG''$  is the shear modulus. This conversion requires the density,  $\rho$ , and the frequency of the fundamental,  $f_0$ , as input parameters (shown and edited at the bottom of the Graphics Panel).

More specifically, the Graphics Panel allows to display the following data:

*Upper panel:*

- Frequency Shift (default)
- Frequency Shift /  $n$  (different harmonics superimpose in Sauerbrey limit)
- Frequency Shift /  $\text{Sqrt}(n)$  (different harmonics superimpose for Newtonian liquid)
- Frequency /  $n$  (usually not same for all harmonics, decreases with overtone order)
- **Maximum Conductance** ( $G_{\text{max}}$ , the radius of the circle in the polar diagram)
- **Normalized Amplitude**
- **Parallel Capacitance  $C_0$**
- **Phase**



- Real Part of Viscosity  $\eta'$  (calculated by the eq. 2, uses density of the liquid and fundamental frequency as shown at the bottom of the Graphics Panel)
- Fractional Frequency Shift  $\delta f/f$  (different harmonics superimpose in Sauerbrey limit)
- Sauerbrey Mass (calculated by the Sauerbrey equation)
- Sauerbrey Thickness (calculated by the Sauerbrey equation, uses density of the film as displayed at the bottom of the panel)
- Modulus of G  $|\omega\eta| = \omega(\eta'^2 + \eta''^2)^{1/2}$
- $\chi^2$  of the fit

*Lower panel:*

- HBH Width,  $\Gamma$  (default)
- HBHW Shift,  $\delta\Gamma$
- HBHW Shift /  $n$ , (harmonics superimpose for Sauerbrey limit in liquids, see third order perturbation eq. 5)
- HBHW Shift /  $\sqrt{n}$  (harmonics superimpose for Newtonian liquid)
- Q-Factor ( $f/(2\Gamma)$ )
- Dissipation ( $Q^{-1}$ )
- Resistance R
- Imag. Part of Viscosity  $\eta''$  (calculated by eq. 2, uses density of the liquid as displayed at the bottom of the panel)
- Offset Conductance
- Offset Susceptance
- Temperature Set Point
- Temperature Upper Sensor
- Temperature Lower Sensor
- Drive Level
- $z$  (contact mechanics only)
- Fract. HBHW Shift  $d\Gamma / f$
- Loss tangent  $\tan\delta = G''/G' = J''/J' = \eta'/\eta''$
- HBH Width /  $\sqrt{n}$

There is a Checkbox which allows to displays the guess values rather than the fit results. This is of use for trouble shooting and in case the resonances are contaminated by **anharmonic side bands**.

Sauerbrey mass and viscosity are the model parameters most users are primarily interested in. They can be displayed in the Graphics Panel without resorting to complicated **Modeling**. One can do more. The Modeling Panel implements an acoustic multilayer algorithm, allowing for the determination of layer parameters other than the Sauerbrey mass or the viscosity (such as the viscous compliance of a film).

## Filenames and Formats

The first line in all files ("header") contains a description of what the respective columns contains. In some cases, it is the reference frequency or the reference bandwidth of the respective harmonic (files with extension .fre, .fge, .amp, .off, chi, mas, vis).

Generally speaking, one can **export** any kind of data from the Graphics Panel with a right mouse click onto the Graph (-> Export Dialog). This includes derived or converted quantities, which are not saved otherwise, and the image itself.

During a continuous measurement (initiated with "Start", Main Panel) Frequency shifts and shifts in HBH width are automatically saved into a file with the "Default Filename" and the extension ".fre". If the measurement was conducted on the second quartz, the filename is the Default Filename + "\_B.fre". When a **reference quartz** is present, corrected values (the difference of the two values) are saved in a file with the Default Filename + "\_c.fre".

Measurements in the Search Panel are not automatically saved. They can be saved with the Save Button. The save button appends the respective *differences* with regard to the reference values to the file with extension .fre.

In case the option "Save Guess Values" in the Control Panel is clicked, there are additional files with extension ".fge" (and possibly "\_B.fge" for Channel B as well as "\_c.fge" for the corrected values). They contain the values guessed by the software prior to the fit.

*Format:* The 1st column in the file with extension ".fre" contains the time *in minutes*. The 2nd and the 3rd column contain  $\delta f$  and  $\delta \Gamma$  of harmonic number 1. Columns 4 and 5 contain  $\delta f$  and  $\delta \Gamma$  of the 2nd harmonic, and so on. At the end of each line there are 5 more numbers which are the temperature set point, the temperature reading from the upper sensor, the temperature reading from the lower sensor, the drive level, and the distance "z" (for contact mechanics experiments). Evidently, the temperatures are only meaningful if a temperature control is used.

The first line (header line) provides the reference values. This line will show as the column label (or the caption) after you import the file to Origin or Excel.

QTZ saves *shifts* of frequencies and bandwidths, not the values themselves.

There are other kinds of raw data, which are of less interest. These are

- The maximum conductance (**G\_max**) and the phase  $\varphi$
- The offset of the conductance (**G\_off**) and the susceptance (**B\_off**)

The ratio of maximum **conductance G\_max** and HBH width,  $\Gamma$ , has a meaning in the context of the **Butterworth-van-Dyke equivalent circuit**. It can be converted to an effective total mass of the resonator.

The **offset of the susceptance** is related to the electrical capacitance  $C_0$  and therefore has a meaning, as well.

The maximum conductance, **G\_max**, and phase,  $\varphi$ , are saved into a file with extension ".amp" (and possibly "\_B.amp" for Channel B) *if the field "Save Amplitudes, Phases and Offsets"* in the Control Panel is checked. *Format:* The 1st column contains the time in minutes, the following 2 x 25 columns contain the maximum conductance **G\_max** and the phase  $\varphi$  of the 25 harmonics. At the end of each line there are 5 more numbers which are the temperature set point, the temperature reading from the upper sensor, the temperature reading from the lower sensor, the drive level, and the distance "z".



The offsets are saved into a file with extension ".off" (and possibly "\_B.off" for Channel B) *if the field Save Amplitudes, Phases and Offsets* in the Control Panel is checked. The 1st column contains the time in minutes, the following 2 x 25 columns contain the offsets G\_off and B\_off of the 25 harmonics. At the end of each line there are 5 more numbers which are the temperature set point, the temperature reading from the upper sensor, the temperature reading from the lower sensor, the drive level, and the distance "z".

When the field "Save Amplitudes, Phases and Offsets" in the Control Panel is checked, the software also generates file with extension ".chi" (and possibly "\_B.chi" for Channel B) containing the  $\chi^2$  of the fits. The first column contains the time. The 2nd and the 3rd column contain the  $\chi^2$  value and a zero for the 1st harmonic. Columns 4 and 5 contain the mass and a zero for the 2nd harmonic, and so on. At the end of each line there are 5 more numbers which are the temperature set point, the temperature reading from the upper sensor, the temperature reading from the lower sensor, the drive level, and the distance "z".

The **Sauerbrey mass** and the **viscosity** can be calculated and saved from the Graphics Panel. When clicking ("Save Mass as...") the software creates a file with extension ".mas" (possibly "\_B.mas" for Channel B or "\_c.mas" for the corrected values). The first column contains the time. The 2nd and the 3rd column contain the Sauerbrey mass (in SI units) and a zero for the 1st harmonic. Columns 4 and 5 contain the mass and a zero for the 2nd harmonic, and so on. At the end of each line there are 5 more numbers which are the temperature set point, the temperature reading from the upper sensor, the temperature reading from the lower sensor, the drive level, and the distance "z".

When clicking ("Save Viscosity as...") the software creates a file with extension ".vis" (possibly "\_B.vis" for Channel B or "\_c.vis" for the corrected values). The first column contains the time. The 2nd and the 3rd column contain the real and the imaginary part of the viscosity of harmonic number 1. Columns 4 and 5 contain the real and the imaginary part of the viscosity for the 2nd harmonic, and so on. At the end of each line there are 5 more numbers which are the temperature set point, the temperature reading from the upper sensor, the temperature reading from the lower sensor, the drive level, and the distance "z".

*Neither the mass nor the viscosity are automatically saved during data acquisition.*

Comments are saved in a file with extension ".cmt".

Conductance spectra are saved in files with extension ".spc" (Search Panel). The filename contains four digits encoding the counter (for instance "test0003.spc").

Raw data from **Fast Mode** are saved in files with extension ".fmd". The columns are:

- 1: Time in Seconds (!)
- 2: Frequency Shift
- 3: Shift in HBH width
- 4: Susceptance B
- 5: Conductance G
6. Center Frequency
7. Bandwidth in the Reference State

Results from modeling are saved in files with extension ".mod". The assignment of the columns depends on what parameters were selected for fitting. The header contains an assignment of the columns to the variables.

Acoustic layer systems (as displayed in the modeling panel) are displayed in files with extension ".las".

There are files for internal use with extensions “.spa” and “.swp”.

## Various Options

- Default Filename
- Comment, Save Settings
- Time, Reset Clock
- Number of Resonators, Reference Quartz
- Number of Points
- Drive Level
- System Bandwidth
- Time Delay
- Interface Board
- Impedance Analyzer
- GPIB-Address
- Disregard Imaginary Parts in Lorentz Fits
- Keeps Spans Fixed, Keep Centers Fixed
- Compensate For Drift, Sequence of Overtone Orders
- Use Derivative in Polar Plot for Guess Values
- Abandon Harmonic When Fit Fails
- Adjust Window of Analyzer to Resonance
- Sweep Both Directions
- Temperature Dependent Reference Frequencies
- Save Amplitudes, Phases, and Offsets
- Save Guess Values
- Polar Plot

## Status Information

The flow of the program is determined by status variables. All of these are save in the file QTZ.ini. The file QTZ.ini can be edited. Some of the variable names are self-explaining and you can alter the values by editing them in qtz.ini.

You may want to save status information if many users share the instrument. This can with the Export button in the Control Panel. Hans and Franz, for instance, would export the status information to files named "Hans.ini" and "Franz.ini". Whenever they their start to work, they “Import” their status with the respective button in the Control Panel. This action writes the contents of “Hans.ini” to “QTZ.ini”. QTZ always talks to QTZ.ini.

*Rescue action in case of software malfunction:*

There is a file “factory\_settings.ini”. This status is loaded when you click “Factory S.” in the Control Panel. In case the system is in some weird state, where it does not even want to start, rename the file “factory\_settings.ini” to “QTZ.ini”. The software will then start in a safe mode.

## Default Filename

There is a default filename associated with each experiment. QTZ uses this filename together with various extensions in order to record the results of the measurements. It may also add the two characters “\_B” if the respective data apply to channel B, two characters “\_c” if the respective data were obtained on channel A but corrected with the data from channel B. Also, it appends of numerals (like “0001” if it numbers spectra of the conductance (extension “.spc”).

When you click “New” in the graphics panel, the Default Filename will be “..\Data\Datax”, where “..” stands for the current working directory, and “x” stands for some numeral. It is “1” if data the file “..\Data\Data1” does not exist yet, otherwise it’s “..\Data\Data2” (or “..\Data\Data451” depending on how often “New” was clicked before). When you click “Save as...” in the Graphics Panel, the filename you choose turns into the new Default Filename.

There is a source of confusion when you have multiple channels active and open a file connected to Channel B (“test\_B.fre”) or the corrected values (“test\_c.fre”). The software then thinks that test\_B is the new default filename and starts creating files with the name “test\_B\_B.fre” and “test\_B\_c.fre”. *Open the file corresponding to channel A.* The data for Channel B will automatically pop up when you select channel B on the upper right of the Graphics Panel.

## Comments

You can input a comment into the field named “Comment” in the Graphics Panel. When you hit Return this comment is save into a file with the default file name and the extension “.cmt”. All comments are appended to the end of the file.

If the field “Save Continuously” is checked, the comment is saved together with the time whenever one cycle of measurements (on all harmonics) is finished. Typical comments would be “lamp on” or “lamp off”. In this way one can record certain information with a time tag.

When the button “Write Status into Comment file” in the Graphics Panel is clicked, the software appends the entire contents of the file “QTZ.ini” to the file with extension “.cmt”.

## Time, Reset Clock

The time is displayed in **minutes** (exception: fast mode). You can reset the clock from the Graphics Panel. You can also define  $t = 0$  to be some time in the past. That you would do if you continue an experiment which (talking of the sample) has started some time ago.

The software accounts for a change of date (at midnight). If you start the software after it has not been used for a while, the current “time” often is rather large. This occurs because the  $t = 0$  is the time when the Reset Clock button was last pushed.

The time corresponding to  $t=0$  changes when you open an existing file. The software extracts the  $t=0$  value from the header line of this file and uses it for further measurements. When you Reset the clock, the header line of the file is changed accordingly.

You can also choose  $t=0$  by clicking into the graph (“New  $t=0$ ”).

## Number of Resonators, Reference Channel

You normally measure with a single resonator connected to the impedance analyzer. However, you may want to have a reference quartz close to the sample which experiences the same drifts of temperature (or viscosity) as the quartz covered

with your sample. The software allows for simultaneous measurement on two resonators.

Set the number of resonators from the Control Panel.

If you have a SA250B impedance analyzer, just connect the reference channel to the "B OUT" and the "B IN" plugs on the card. If you have an E5100A, you need to split the output from RF OUT 1 into two (a normal "T" connector is fine) and insert directional couplers before the resonators. The signal from the second resonator then goes to Channel B on the E5100. (Channel B is optional, you might not have it).

If "#B is Reference" in the Control Panel is checked, then channel B considered to be the reference resonator. The software generates a file with extension "\_c.fre" containing the frequency shifts from resonator 1 minus the frequency shifts from resonator 2 as well as the differences in the HBH widths.

## Number of Points

The impedance analyzers usually allows for a selection of a number of measurement points. A typical value is 201. If speed is a concern, 101 or even 51 points also do a good job with regards to the fit results, although the data traces do not look as nice.

Set the number of points from the Control Panel.

You may want to use a large number of data points in case you are searching resonances and don't quite know where to search. In order to be able to have a large span and a good resolution at the same time (so you don't miss narrow resonances), you need to increase the number of points.

## Drive Level

The issue of the drive level (to be set in the Control Panel) is somewhat tricky for quartz crystals. On the one hand, you want it to be as high as possible because a large signal on the receiver of the impedance analyzer increases its sensitivity. (You can overload the receiver, though. Insert an attenuator in this case.) On the other hand, the frequency of quartz resonators depends on the drive level. It has mostly to do with dissipation of heat. That's why one should not use drive levels higher than 0 dBm (~220 mV) in air.

In liquids the situation is different. Because there is good thermal contact to a heat sink, the drive level can be higher here. Check for effects of heat from the **Drive Level Dependence Panel**.

The unit for the drive level is dBm, where 0 dBm is 1 mW of power. Convert to Volts with the equation  $\text{Power} = \text{Voltage}_2^2 / Z_{el}$  with  $Z_{el}$  the impedance of the cable (50 Ohms for BNC cables). 0 dBm corresponds to about 220 mV.

When thermal effects are present, you usually see the quality of the fit decrease. As the impedance analyzer sweeps the frequency, the resonator properties change. This is a disadvantage of the use of impedance analyzers. It can be circumvented to some extent with the ring-down technique.

## System Bandwidth

The "System Bandwidth" (to be set in the Control Panel) of the impedance analyzer adjusts the trade-off between speed and accuracy. When the bandwidth is high you get lousy data at a marvelous speed and vice versa. The same is achieved with the "Number of averages" in case you have an SA250B analyzer.

But unfortunately that is not all.... At high speeds there is a systematic error due to the fact that the sweep usually proceeds from low to high frequencies. Crudely

speaking, the situation is the following: When the nominal frequency of the source changes, the crystal needs a certain time to adjust to the new situation. This time is the inverse system bandwidth (or something close). As a consequence, there is a delay between what the nominal frequency and the actual frequency. The delay leads to a shift in the apparent resonance frequency. You can check by reversing the sweep direction.

## Time Delay

When measurements extend over many days, you may want to have intervals between data points, so that the files don't become very large. Large files are awkward to handle with Origin or Excel. This can be done by choosing a non-zero time delay in the Graphics Panel. The time delay causes a break in the measurement every time a measurement cycle (an all harmonics) has been completed.

You may want to have a variable time delay (for instance, no delay, when you start, followed by a longer delay after 1 hour). This can be achieved from the Programmable Delay Panel (to be reached from the Graphics Panel).

## Interface Board

{At this point, the software can deal with two different GPIB-boards which are the Keithley 488.2 board and the National Instruments 488.2 PCI GPIB board. The Keithley board has been tested really well. It is the recommended solution if the choice is still open. The NI 488.2 PCI GPIB board has also worked, but testing has been less extensive. } The 250B does not have an interface board

## Impedance Analyzer

The software is able to communicate with a number of different impedance analyzers which are

- 8712ET (Agilent)
- 4195A (Agilent)
- E5100A (Agilent) (recommended, well adapted to the needs)
- 4396A (Agilent)
- 4395A (Agilent)
- R3753BH (Advantest)
- 4916A (Agilent)
- SA250B (Saunders) (cheaper than the E5100)

Certain restrictions apply with regard to certain options. There should be a message when you try to do something which this specific analyzer cannot do.

The software has been tested most thoroughly for the E5100A from Agilent.

## GPIB-Address

{In order to communicate, the interface board and the impedance analyzer need to have a common understanding of what the analyzer's address (an integer between 0 and 20) is. The address can either be set from the impedance analyzer or from computer (Control Panel). It doesn't matter, as long as a consensus is reached.}

## Disregard Imaginary Parts in Lorentz Fits

This outdated option is not recommended. You can, if you want to, confine the Lorentz fits to the real part of the admittance curve (the conductance  $G$ ). However, you only lose accuracy, that's all.

## Keeps Spans Fixed, Keep Centers Fixed

Usually, the software keeps updating the center and span according to the previous result from the Lorentz fit. In principle, that's necessary in order to keep track of what is going on. The danger is: if a fit goes wrong then the software searches the resonance at the wrong spot next time it tries to measure it. Depending on how bad it is, this resonance is lost. See [Abandon Harmonic when Fit Fails](#) for further measures dealing with this situation.

In case you anticipate that the bandwidth will remain about the same over the entire duration of the experiment (for instance, because the experiment is carried out on thin films in air) then you may consider to just keep the span fixed. This is safer. If you also anticipate that the frequency only moves by less than half of the current span, you may consider leaving the center fixed, as well. Both options can lead to serious errors though, if the center and/or span in fact are variable.

## Compensate For Drift, Sequence of Overtone Orders

When you compare the frequency shifts on different harmonics (for instance in order to derive a viscous modulus) and the sample changes its properties *with time* then there is a problem because the data from the higher harmonics are acquired at a later time than the data on the lower harmonics. What might appear as a dependence on overtone order in reality is a dependence on time. If the drift is sufficiently smooth and linear, you can circumvent the problem by always reversing the order of measurement after each cycle of measurement on all harmonics. This is what the button "Compensate for Drift" in the Control Panel does. If this option is active the software does each measurement twice: once increasing the overtone order and once decreasing the overtone order. It calculates arithmetic means of the frequency shifts and bandwidths and uses these means for further analysis.

## Use Derivative in Polar Plot for Guess Values

This option deals with asymmetric resonances. See ["How the software guesses values used in the Lorentz fit"](#) for details. *It is recommended to check this option.*

## Abandon Harmonic When Fit Fails

When a fit fails that does not necessarily make the program crash. But it may. Now the problem is: when a fit failed once, the center and the span will be wrong next time. If the resonance is still somewhere close by, the situation will recover. If not... the fit will fail again... and again... and again... and at some point the program *will* crash. That's not good for measurements running over night. Therefore, there is an option to abandon a harmonic altogether when the fit fails once (to be found in the Control Panel.) This option is recommended when the instrument is running on its own.

## Adjust Window of Analyzer to Resonance

Usually, the software deals flexibly to a situation, where it does not find a resonance anywhere in the frequency window of the measurement. It looks whether the maximum of  $G$  is on the right or the left edge and moves the window of the measurement, accordingly. At the same time, it doubles the span. Most of the time, this works and the resonance will eventually be found. However, when there is no



resonance, this behavior may also induce a software crash. Therefore this process can be switched off by *not* ticking the option "Adjust Window of Analyzer to Resonance" in the Control Panel.

## Sweep Both Directions

When the sweeps are performed very fast, there is a systematic error in the determination of the resonance frequency because the sweeps always occurs in the same direction (usually upward). In case you want to perform fast sweeps and still get rid of this error you can perform sweeps in both directions. This of course doubles the time for data acquisition. The software will do the sweep and the fit twice (once with an upward sweep and once with a downward sweep) and use the arithmetic average of all fit parameters for further analysis.

## Temperature Dependent Reference Frequencies

*This option is not implemented in some of the versions.*

When you perform measurements as a function of temperature, a reference quartz is warmly recommended. Without a reference crystal one can still calibrate the frequency dependence of the reference frequencies and use the temperature (as measured with a sensor somewhere close to the quartz) in order to account for temperature effects. This requires a calibration of temperature-frequency coupling, which is done in from the Temperature Panel (to be reached from the menu item Measure in the Main Panel).

Temperature-Frequency coupling is usually well described by cubic polynomials. The coefficients of these polynomials are determined in the Temperature-Frequency-Coupling Panel (to be reached from the Harmonics Panel). The software uses the fit function

$$f_{res}(T) = f_{res}(T_{infl}) + a(T - T_{infl}) + c(T - T_{infl})^3$$

where the fit parameters are shown in red. The fit parameters are collected in the Temperature-Frequency-Coupling Panel. They can be changed manually but would usually be determined by fitting. This done in the panel "Fit Cubic Polynomials to Temperature Frequency C." which can again be reached from the panel Temperature-Frequency-Coupling. One can either do a least-square fit or change parameters by hand (or with the spin buttons) until an agreement between data and fit is found.

## Save Amplitudes, Phases, and Offsets

The Lorentz fit has six fit parameters in total, which are the frequency,  $f_{res}$ , the HBH width,  $\Gamma$ , the maximum conductance,  $G_{max}$ , the phase,  $\phi$ , the offset of the conductance,  $G_{off}$ , and the offset of the susceptance,  $B_{off}$ . In most cases, only the frequency and the bandwidth are of practical interest. However, you can save the other parameters as well. See [Filenames and Formats](#) for the file structure. The maximum conductance, the phase, and the offsets are only saved if the option "Save Amplitudes, Phases, and Offsets" in the Control Panel has been checked.

You can also allow for sloped offsets ("Allow for Sloped Offsets in Fits") in the control panel. Evidently, this increases the quality of the fits. On the other hand, it seems a little dangerous to have too many fit parameters.

## Save Guess Values

The software needs **guess values** in order to start the Levenberg-Marquardt fit on the resonance curves. The guess values can be saved in files with extension **".fge"** (and possibly **"\_B.fge"** for Channel B as well as **"\_c.fge"** for the corrected values).. Using the guess values rather than the fitted parameters for further analysis makes sense for very high harmonics. Here, the anharmonic sidebands may have merged with the main resonance to the extent that they cannot be disentangled from the main resonance. The conductance spectrum shows a sharp increase below the resonance of interest and a gradual decrease above (the latter being a superposition of many anharmonic side bands.) The initial sharp increase is rather well captured by the guess value for the resonance frequency (at least the shifts, there is ambiguity about the value itself).

## Polar Plot

When this option is clicked, the graphs showing the resonance show *B* versus *G* rather than *B* and *G* versus frequency. One should see a circle. If the **calibration** is correct, the peak of the resonance is at 3 o'clock.

## Modeling

- Generalized Impedances
- Tiersten Equivalent Circuit
- Butterworth-van-Dyke Equivalent Circuit
- Generalized Sauerbrey Equation
- Calculation of Generalized Impedances by the Matrix Formalism
- Semi-Infinite Liquid (Viscoelastic) Medium
- Viscoelastic Film in Air
- Viscoelastic Film in Liquid
- Two Viscoelastic Films in Air (Electrodes)
- Two Viscoelastic Films in Liquid (Electrodes)
- Thin Film (Sauerbrey) Limit
- 3rd Order Perturbation
- Piezoelectric Stiffening
- Viscoelastic Dispersion
- Slip
- Point Contacts
- Modeling Panel
- D-f Plots
- Interpretation of the Amplitude of a Resonance
- Interpretation of the Offset of the Susceptance

## Generalized Impedances

The impedance is an animal with many faces. Let's first consider the elastic collision between two pin balls in one dimension. Both energy and momentum must be conserved. Defining the "reflection coefficient" as the speed of ball 1 after the



collision divided by the initial speed, (ball 2 initially at rest) one finds:

$$r = \frac{m_1 - m_2}{m_1 + m_2}$$

where  $m$  is the mass and "1" is the incoming particle. The impedance in this case is the mass or, equivalently, the ratio of momentum and speed or, equivalently,  $E / (2 p^2)$  with  $E$  the energy and  $p$  the momentum.

For wave waves at interfaces, both energy flux and momentum flux are conserved at the interface. The impedance in this case is the ratio of the momentum flux density and the speed, or equivalently,  $E / (2 p^2)$  with  $E$  the energy flux density and  $p$  the momentum flux density. One has

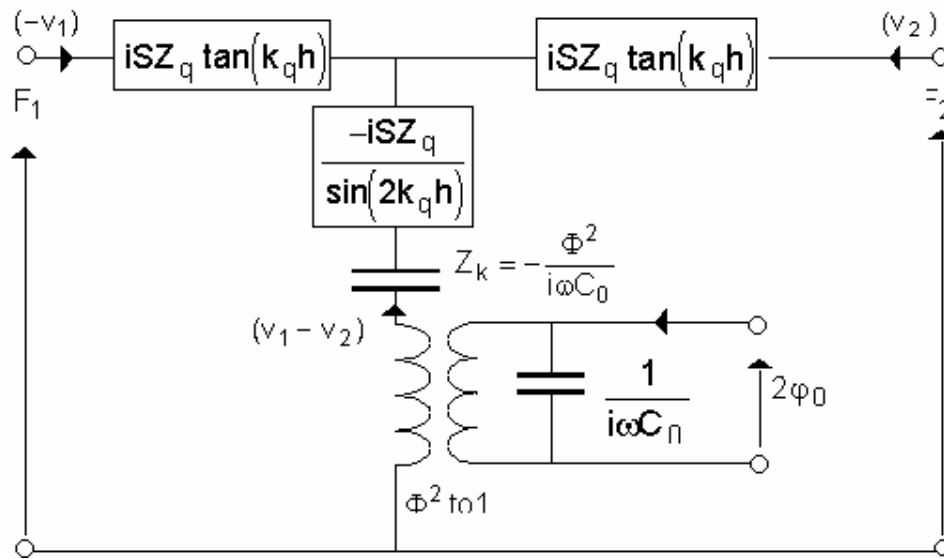
$$r = \frac{Z_1 - Z_2}{Z_1 + Z_2}$$

For optics, the impedance of a medium is proportional to its refractive index  $n$ . In electrical cables, it is the  $(L/C)^{(1/2)}$  where  $L$  is the self-inductance per unit length and  $C$  is the capacitance per unit length. In acoustics, the impedance is  $Z_{ac} = (G\rho)^{(1/2)}$  where  $G$  is the modulus and  $\rho$  is the density. Given that the speed of sound,  $v$ , is  $(G/\rho)^{(1/2)}$ , one can also write  $Z_{ac} = \rho v$ .

In all of these cases, the impedance can also be written as a ratio between "momentum flux" and "speed". For optics, the ratio comes down to  $D/H$ , with  $D$  the dielectric displacement and  $H$  the magnetic inductance. In electrical circuits, it is the ratio of voltage and current, in acoustics, it's the ratio of stress and speed (speed being the time derivative of displacement, *not* the speed of sound). For acoustics, there is a subtlety: the impedance may or may not be normalized to area. As long as plane waves are considered, one should normalize the impedance to area. For finite objects (like a quartz plate), one may keep the lateral size as a pre-factor. This is how it is done in the **Tiersten equivalent circuit**. For the purpose of distinction, the latter quantity can be called "mechanical impedance". The mechanical impedance is the product of the acoustic impedance and the active area. *Mechanical* impedances are the elements of the equivalent circuits, such as the Tiersten equivalent circuit or the **Butterworth-van-Dyke equivalent circuit**. The lateral size of the quartz plate does matter when calculating the current through the electrodes, that is, transforming from the acoustic to the electrical branch.

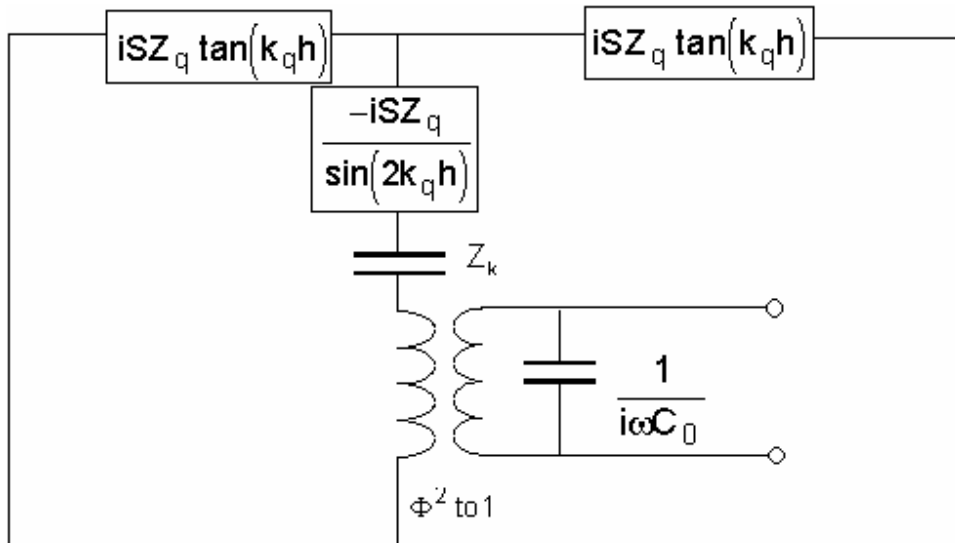
## Tiersten Equivalent Circuit

Equivalent circuits are graphic representations for the equations governing the propagation of waves in layered media. The equations are recovered from the equivalent circuits in the form of the Kirchhoff-rules. The equivalent circuit of a piezoelectric plate of infinite lateral extension has been derived by Tiersten. For a tutorial see: R.N. Thurston, in C. Truesdell (edt.) "*Mechanics of Solids*", vol. 4, chap. 36, p. 257, Springer-Verlag, Heidelberg 1984. In its most general form, the plate is a transducer: The equivalent circuit is given by

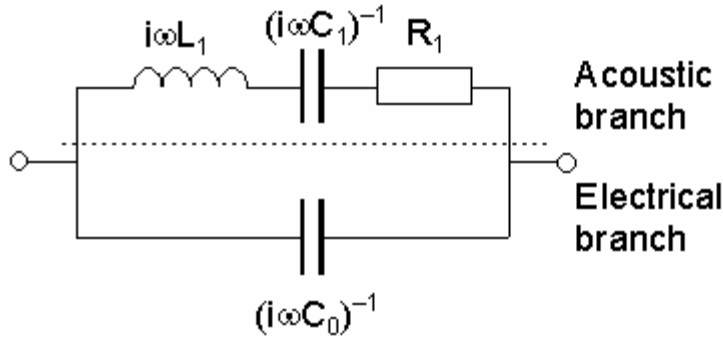


Here  $Z_q$  is the acoustic impedance of at-cut quartz,  $S$  is the active area,  $k_q$  is the wave number,  $h$  is half of the thickness of the plate, and  $C_0$  is the parallel capacitance. The piezo effect is visualized as a transducer with  $\Phi = S e'_{26} / d_q$  ( $e'_{26} = 9.65 \cdot 10^{-2} \text{ C m}^{-2}$  the piezoelectric coefficient and  $d_q$  the thickness of the resonator).  $Z_k$  accounts for piezoelectric stiffening. The ports on the left and the right correspond to the two faces of the plate. The electrical port is in the lower right.

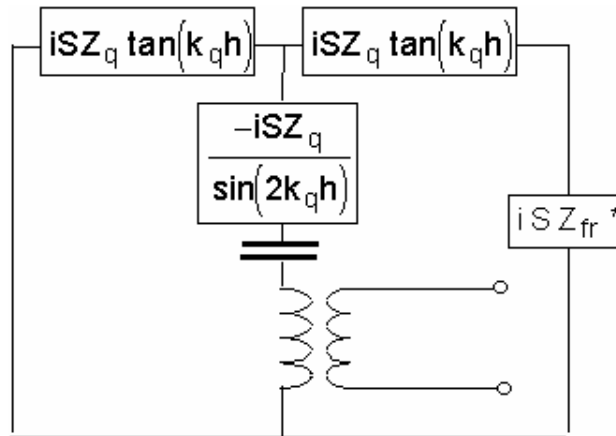
In the absence of external forces and loads, the above circuit can be closed on the left and the right hand side, resulting in



Close to resonances, this circuit can be simplified to the **Butterworth-van-Dyke equivalent circuit** [see R.N. Thurston, in C. Truesdell (edt.) "Mechanics of Solids", vol. 4, chap. 36, p. 257, Springer-Verlag, Heidelberg 1984]:

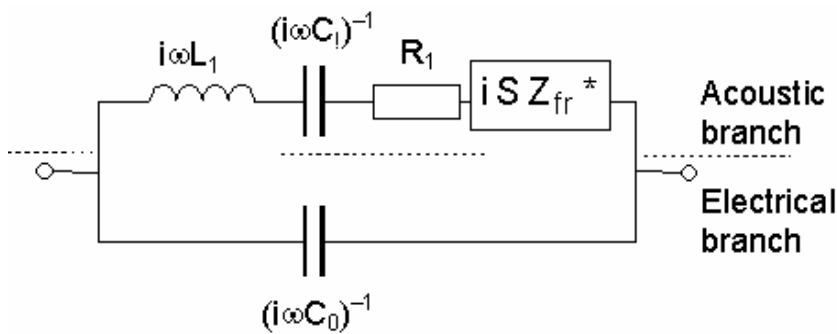


An external load on one surface is accounted for by writing:

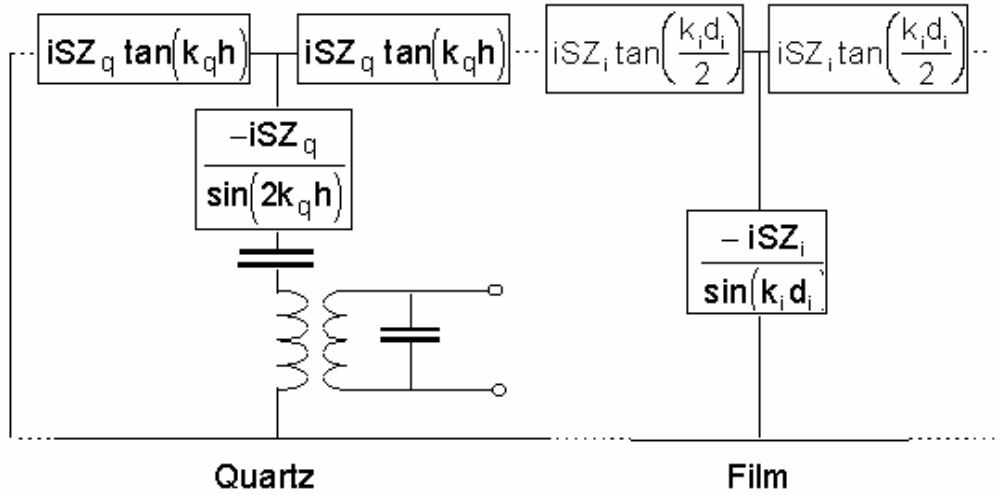


where the effect of the added layers is modeled by a generalized impedance  $Z^* = \sigma / (\partial u / \partial t)$  with  $\sigma$  the stress and  $u$  the displacement. Loads on the back side (left hand side) are treated analogously by inserting an element of the form  $(i S Z_{bk})$  into the line on the left hand side.

Applying the same approximations and transformations which lead to the Butterworth-van-Dyke circuit, one arrives at



If the load is a system of films, one can use the following circuit



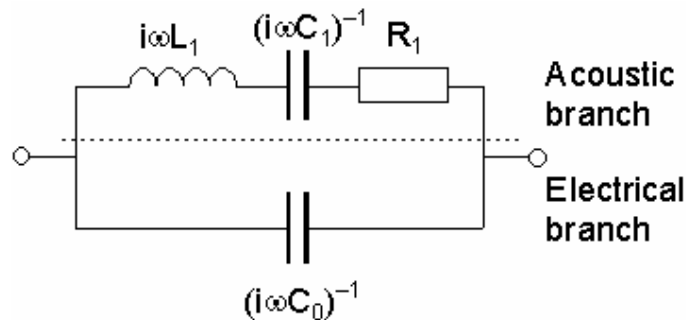
Alternatively, one can write

$$Z^* = \frac{\sigma}{\partial u / \partial t} = \frac{G(\partial u / \partial z)}{\partial u / \partial t} = \frac{Gik(u_+ - u_-)}{i\omega(u_+ + u_-)} = \sqrt{\rho G} \frac{1-r}{1+r} = Z \frac{1-r}{1+r}$$

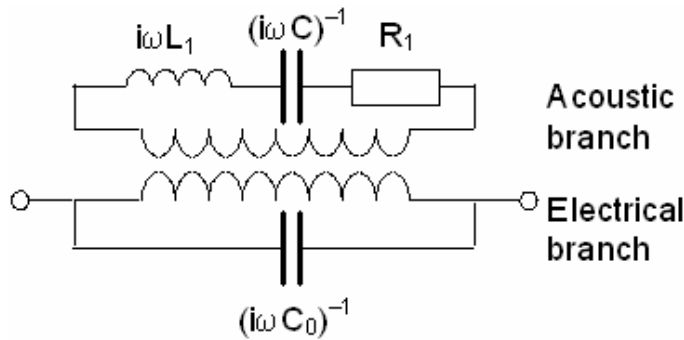
where  $Z$  is the acoustic impedance above the quartz surface and  $r$  is the reflection coefficient evaluated above the quartz surface. Note that  $Z^*$  depends on the geometry, it is not a material property.

## The Butterworth-van-Dyke Equivalent Circuit

The Tiersten circuit is the conceptual basis for analysis. In practice it is impossible to determine its parameters from measurements. Therefore, one might as well simplify it to obtain a circuit, where all parameters have a meaning in terms of experiments. This is the Butterworth-van-Dyke circuit:



Above all quantities are electric. Below is a slightly modified circuit, showing the conversion between electric and mechanical impedances as a transformer:



The transformer converts mechanical and electrical quantities in the following way:

$$I_{el} = \Phi \partial u / \partial t$$

$$U_{el} = \frac{1}{\Phi} S \sigma = \frac{1}{\Phi} F$$

$$Z_{el} = \frac{1}{\Phi^2} Z_{mech}$$

$$\Phi = S e_{26}' / d_q$$

Here  $S$  is the active area,  $\sigma$  is the stress,  $F$  is a force, and  $e_{26}' = 9.65 \cdot 10^{-2} \text{ C m}^{-2}$  is a piezoelectric coefficient. With the above circuit, one can maintain the parameters  $C_1$ ,  $L_1$ , and  $R_1$  as a mechanical capacitance, inductance, and resistance, respectively. The following relations hold for the parameters:

$L_1$  m goes to  $2 m_q$

$C_1$  m goes to  $1/4$  of this

$$L_{1,m} = \frac{m_q}{2} = \frac{d_q A_{el}}{2} = \frac{Z_q A_{el}}{4 f_0}$$

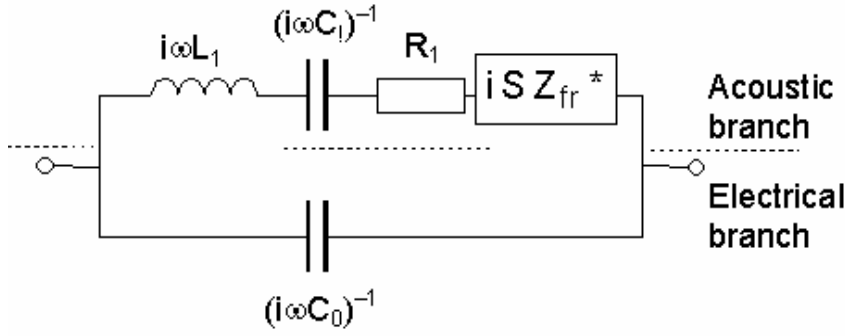
$$C_{1,m} = \frac{2}{n^2 \pi^2} \frac{d_q}{A_{el} G_q}$$

$$R_{1,m} = \frac{1}{Q} \sqrt{\frac{L_{1,m}}{C_{1,m}}}$$

$$\sqrt{\frac{L_{1,m}}{C_{1,m}}} = \frac{n\pi}{4} S Z_q$$

$$\frac{1}{\sqrt{L_{1,m} C_{1,m}}} = \omega_{res} \approx 2\pi n f_0$$

A load can be accounted for by introducing an additional element into the circuit in the following way:



The resonance condition for this circuit leads to the generalized Sauerbrey equation. Note that this is again the fully electrical circuit.  $Z_{fr}^*$  needs to be multiplied with  $S/\Phi^2$  to convert to an electrical impedance.

## The Generalized Sauerbrey Equation

From the extended Butterworth-van-Dyke equivalent circuit, one arrives at the following approximation:

$$\frac{\delta f}{f_0} \approx \frac{i}{\pi} \frac{Z^*}{Z_q} = \frac{i}{\pi Z_q} \frac{\sigma}{\dot{u}}$$

This equation can serve as the starting point for calculations of the frequency shift. It is not limited to layer systems.

The above equation is an approximation in so far as all nonlinear terms in the Tiersten circuit have been linearized ( $\tan(x) \sim x$ , whenever a tangent occurs).

## Calculation of Generalized Impedances, Matrix Formalism

For the generalized impedance, the following equation holds:

$$Z^* = \frac{\sigma}{\partial u / \partial t} = \frac{G(\partial u / \partial z)}{\partial u / \partial t} = \frac{Gik(u_+ - u_-)}{i\omega(u_+ + u_-)} = \sqrt{\rho G} \frac{1-r}{1+r} = Z \frac{1-r}{1+r}$$

where  $Z$  is the acoustic impedance of the medium just above the quartz surface and  $r$  is the reflection coefficient evaluated above the quartz surface. Quartz crystals are acoustic reflectometers. (Note that the quantity " $r$ " here is evaluated *above* the quartz surface. This differs from the definition in "[Quartz crystals are acoustic reflectometers](#)".)

The calculation of  $Z^*$  (the *load*) comes down to a calculation of acoustic reflectivities. This is done in analogy to the calculation of optical reflectivities in multilayered media, where the acoustic impedance of a medium takes the role of the refractive index. This software uses the matrix formalism. The reflectivity above the quartz surface is calculated as the ratio of the waves traveling into the backward direction ( $u_-$ ) and in the forward direction ( $u_+$ ):  $r = u_- / u_+$ . The amplitudes are calculated as

$$\begin{pmatrix} u_+(1) \\ u_-(1) \end{pmatrix} = \hat{L}_1 \cdot \hat{S}_{12} \cdot \hat{L}_2 \cdot \hat{S}_{23} \cdot \dots \cdot \hat{S}_{N-1,n} \cdot \hat{L}_N \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

where  $L$  and  $S$  are matrices transforming the amplitudes. At the very end of the layer

system, there is no reflected wave. The transmitted wave has been normalized to unity.  $L$  describes the propagation across a layer. One has

$$\hat{L}_i = \begin{pmatrix} \exp(ik_i d_i) & 0 \\ 0 & \exp(-ik_i d_i) \end{pmatrix}$$

where  $k$  is the wave vector and  $d$  is the thickness.  $S_{i-1,i}$  takes care of reflection at interfaces. One has

$$\hat{S}_{i-1,i} = \frac{1}{2} \begin{pmatrix} 1 + Z_{i-1}/Z_i & 1 - Z_{i-1}/Z_i \\ 1 - Z_{i-1}/Z_i & 1 + Z_{i-1}/Z_i \end{pmatrix}$$

where  $Z$  is the acoustic impedance,  $(\rho G)^{1/2}$ , of the respective medium. Here the layers have been labeled 1..N such that "N" is the outermost layer. In the literature one also finds another definition, where "1" is the outermost layer.

### Semi-Infinite Liquid (Viscoelastic Medium)

For a semi-infinite medium, the application of the generalized Sauerbrey equation is particularly simple. The generalized impedance  $Z^*$  is the acoustic impedance of the liquid  $Z$ . Using  $Z = (\rho G)^{1/2}$ ,  $G = i \omega \eta$ , and  $\eta = \eta' - i \eta''$  one arrives at

$$\frac{\delta f + i \delta \Gamma}{f_0} = \frac{i Z}{\pi Z_q} = \frac{i \sqrt{\rho G}}{\pi Z_q} = \frac{i \sqrt{i \omega \eta \rho}}{\pi Z_q} = \frac{i \sqrt{i \omega \rho (\eta' - i \eta'')}}{Z_q}$$

$$\frac{(\delta f^2 - \delta \Gamma^2) + 2i \delta f \delta \Gamma}{f_0^2} = \frac{-\omega \rho (i \eta' + \eta'')}{\pi^2 Z_q^2}$$

### Viscoelastic Film in Air

For a single film in air the matrix formalism yields

$$Z^* = Z_f \frac{1 - \exp(2ik_f d_f)}{1 + \exp(2ik_f d_f)} \approx i Z_f \tan(k_f d_f)$$

$Z_f$  is the acoustic impedance of the film,  $k_f$  is the wave number, and  $d_f$  is the thickness.

The pole of the tangent is the "film resonance". At the film resonance, the dissipation becomes large and the frequency shift changes sign. The frequency shift may be positive above the resonance. Often the film resonance is smeared out, so that the shift does not really turn positive. Still one finds an asymmetric pattern, characteristic of resonance phenomena.

At the pole of the tangent the load becomes large and the generalized Sauerbrey equation no longer holds. The above equation becomes inadequate. There is not a single resonance, but a coexistence of two resonances. The two resonances correspond to a symmetric (lower frequency) and an antisymmetric (higher frequency) motion of film and quartz. As the thickness increases, the symmetric

mode disappears, while the antisymmetric mode grows in strength (Martin et al., *Anal. Chem.* **2000**, 72, 141)

## Viscoelastic Film in Liquid

For a single film in a semi-infinite medium (liquid) the matrix formalism yields

$$Z_{\text{fl}} = i Z_f \frac{Z_f \tan(k_f d_f) - i Z_l}{Z_f + i Z_l \tan(k_f d_f)}$$

The indices *f* and *l* denote the film and the liquid, respectively. *Z* is the acoustic impedance, *k* is the wave number, and *d* is the thickness. At the pole of the tangent one has a "film resonance".

## Two Viscoelastic Films in Air (Electrodes)

For two films in air the matrix formalism yields

$$Z_{\text{ff}} = i \frac{Z_f \tan(k_f d_f) + Z_e \tan(k_e d_e)}{1 - Z_f / Z_e \tan(k_f d_f) \tan(k_e d_e)}$$

The indices *e* and *f* denote the electrode (the lower film, in general) and the film, respectively. *Z* is the acoustic impedance, *k* is the wave number, and *d* is the thickness. Electrode effects can be noticeable.

## Two Viscoelastic Films in Liquid (Electrodes)

For two films in a semi-infinite medium (liquid) the matrix formalism yields

$$Z_{\text{ff}} = i Z_e \frac{Z_f (Z_e \tan(k_e d_e) + Z_f \tan(k_f d_f)) + i Z_l (Z_e \tan(k_f d_f) \tan(k_e d_e) - Z_f)}{Z_f (Z_e - Z_f \tan(k_f d_f) \tan(k_e d_e)) + i Z_l (Z_e \tan(k_f d_f) + Z_f \tan(k_e d_e))}$$

The indices *e*, *f*, and *l* denote the electrode (the lower film, in general) the film, and the liquid, respectively. *Z* is the acoustic impedance, *k* is the wave number, and *d* is the thickness. Electrode effects can be noticeable.

## Thin Film (Sauerbrey Limit)

For thin films, one may apply Taylor expansions to all equations relating the frequency shift to properties of the film. The crudest approximation is given by  $\tan(x) \sim x$ , where ever a  $\tan$  occurs. In this limit the time honored Sauerbrey equation is recovered:

$$\frac{\delta f}{f} \approx -\frac{m_f}{m_q} = -\frac{2f_0}{Z_q} m_f$$

It holds in air and in liquid (provided that the reference frequencies are taken in presence of the liquid).

In liquids the Sauerbrey equation often yields masses which are larger than expected. This is caused by entrapped liquid. The combination of surface plasmon resonance measurements with the QCM can help to find out about the degree of swelling of a film in liquid.



### Third Order Perturbation

Expanding all nonlinear terms in the model to first order leads to rather simple form, the Sauerbrey equation. In this limit, all information on viscoelasticity is lost. The information on viscoelasticity is recovered by Taylor expanding all terms to third order ( $\tan(x) \sim x + 1/3 x^3$ ). However, since the Tiersten circuit also contains such terms, a perturbation analysis must be carried out (J. Appl. Phys. **89**, 6356 (2001)).

The equations below all treat situations, where one has two films in a liquid. The following abbreviations are used:

$$\begin{aligned}\mu_e &= \frac{m_e}{m_q}, \mu_f = \frac{m_f}{m_q} \\ \xi_e &= \frac{Z_q}{Z_e}, \xi_e^2 = J_e \frac{Z_q}{\rho_e} \\ \xi_f &= \frac{Z_q}{Z_f}, \xi_f^2 = J_f \frac{Z_q}{\rho_f} \\ \xi_l &= \frac{Z_l}{Z_q \sqrt{2\pi n i}} = \frac{\sqrt{f_0 \rho_l \eta_l}}{Z_q}\end{aligned}\quad (1)$$

$\mu$  and  $\xi_l$  are *small*. They serve as perturbation parameters. The indices *e* and *f* denote the electrode (the first layer, in general) and the film (the second layer), respectively.

The exact equations depend on the state of reference. In case the reference frequencies were taken with the electrodes and the liquid present, one has

$$\begin{aligned}\frac{\delta f^*}{f} &= -\mu_f (1 - 2\mu_e + 4\mu_e^2) + \mu_f^2 (1 - 4\mu_e) - \mu_f^3 \\ &\quad + 2i n \pi \mu_f \xi_l^2 (\xi_f^2 - 1) - (n\pi)^{\frac{3}{2}} \xi_l (1-i) (2\mu_e \mu_f (\xi_e^2 - 1) + \mu_f^2 (\xi_f^2 - 1)) \\ &\quad - (n\pi)^2 \left( (\mu_e \mu_f^2 + \mu_e^2 \mu_f) (\xi_e^2 - 1) + \frac{\mu_f^3}{3} (\xi_f^2 - 1) \right)\end{aligned}\quad (2)$$

If the reference frequency was taken in the dry state, one has

$$\begin{aligned}\frac{\delta f^*}{f} &= -\frac{(1-i) \xi_l}{\sqrt{n\pi}} (1 + 4\mu_e^2 - \mu_f + \mu_f^2 + 2\mu_e (2\mu_f - 1)) \\ &\quad - 2\mu_e + 4\mu_e^2 - 8\mu_e^3 - \mu_f (1 - 4\mu_e + 12\mu_e^2) + \mu_f^2 (1 - 6\mu_e) - \mu_f^3 \\ &\quad - \sqrt{n\pi} \xi_l^3 \frac{2}{3} (1+i) \\ &\quad + 2i n \pi \xi_l^2 (\mu_f (\xi_f^2 - 1) + \mu_e (\xi_e^2 - 1)) \\ &\quad - (n\pi)^{\frac{3}{2}} (1-i) \xi_l ((2\mu_e \mu_f + \mu_e^2) (\xi_e^2 - 1) + \mu_f^2 (\xi_f^2 - 1)) \\ &\quad - \frac{(n\pi)^2}{3} ((2\mu_e^3 + 3\mu_e \mu_f^2 + 3\mu_e^2 \mu_f) (\xi_e^2 - 1) + \mu_f^3 (\xi_f^2 - 1))\end{aligned}\quad (3)$$

If the reference frequency was taken in the dry state with no electrode, one has

$$\begin{aligned}
\frac{\delta f^*}{f} = & -\frac{\xi_l (1-i) \left( 1 + 4\mu_e^2 - \mu_f + \mu_f^2 + 8\mu_f \mu_e^2 + 2\mu_e (\mu_f + \mu_f^2) + 8\mu_e^3 \right)}{\sqrt{n\pi}} \\
& -\mu_f (1 - 2\mu_e + 4\mu_e^2) + \mu_f^2 (1 - 4\mu_e) - \mu_f^3 \\
& -\frac{2\sqrt{n\pi}(1+i)}{3} \xi_l^3 \\
& + 2in\pi \xi_l^2 \left( (\mu_f + 2\mu_e \mu_f) (\xi_f^2 - 1) + (2\mu_e^2 + \mu_e) (\xi_e^2 - 1) \right) \\
& + (n\pi)^{\frac{3}{2}} \xi_l (1-i) \left( (-2\mu_e \mu_f - 4\mu_f - \mu_e^2 - 8\mu_e^3) (\xi_e^2 - 1) - \mu_f^2 (1 + 2\mu_e) (\xi_f^2 - 1) \right) \\
& -\frac{(n\pi)^2}{3} \left( (3\mu_e \mu_f^2 + 3\mu_e^2 \mu_f) (\xi_e^2 - 1) + \mu_f^3 (\xi_f^2 - 1) \right) \\
& -\frac{4(n\pi)^{\frac{5}{2}}(1+i)}{9} \xi_l^3 \mu_e^3 (\xi_e^2 - 1)
\end{aligned} \tag{4}$$

The simplest case, where the reference frequency was taken in presence of the electrode and the liquid deserves further consideration. If electrode effects can be ignored (either because they are thin or because aluminum electrodes are used) the perturbation equations are further simplified to give

$$\begin{aligned}
\frac{\delta f^*}{f} = & -\mu_f + \mu_f^2 - \mu_f^3 + 2in\pi \mu_f \xi_l^2 (\xi_f^2 - 1) - (n\pi)^{\frac{3}{2}} \xi_l (1-i) \mu_f^2 (\xi_f^2 - 1) \\
& - (n\pi)^2 \frac{\mu_f^3}{3} (\xi_f^2 - 1) \\
\approx & -\mu_f \left( 1 - 2in\pi \mu_f \xi_l^2 (\xi_f^2 - 1) \right) \\
\approx & -\mu_f \left( 1 - \frac{Z_l^2}{Z_f^2} \right)
\end{aligned} \tag{5}$$

In the second line only terms linear in  $\mu$  were retained. Importantly, viscoelastic effects now appear in *first order* in  $\mu$ . This compares to the case in air, where viscoelastic effects occur in third order in  $\mu$ . Viscoelastic effects are much easier to observe in liquids, because the liquid exerts shear onto the layer. In air the layer of interest only shears due to its own inertia. Viscoelastic effects *can* be discriminated from pure mass loading (which evidently is also proportional to the mass) via the dependence on overtone order.

Note that dependence of the viscoelastic parameters  $\xi_f$  and  $\xi_l$  on  $n$  (via their frequency dependence was dropped in the above equations. One really should write:

$$\begin{aligned}
\frac{\delta f^*}{f} \approx & -\mu_f \left( 1 - 2in\pi \mu_f \xi_l^2(n) (\xi_f^2(n) - 1) \right) \\
\approx & -\mu_f \left( 1 - \frac{Z_l^2(n)}{Z_f^2(n)} \right)
\end{aligned} \tag{6}$$

In the last line, the frequency shift was expressed as the mass times a "contrast function". Since the equation is linear in  $z$ , it also holds in an integral sense:

$$\frac{\delta f^*}{f} \approx - \int_0^{\infty} \rho(z) \left( 1 - \frac{Z_t^2}{Z_f^2(z)} \right) dz \approx - \rho \int_0^{\infty} \left( \frac{G_f(z) - G_t}{G_f(z)} \right) dz \quad (7)$$

The term in brackets is the acoustic contrast function. Since the shear modulus of a polymer solution is much higher than the shear modulus of the solvent, the acoustic contrast easily saturates (comes close to unity). The contrast function in optics is similar to the contrast function above, where the shear modulus,  $G$ , is replaced by the dielectric constant,  $\epsilon$ . Importantly, the contrast does not easily saturate in optics. In this respect, optics and acoustics work much differently (see Combined SPR and QCM measurements).

*We have recently implemented 5-th order perturbation. It is basically the same as 3rd order perturbation, with the difference that all Taylor expansions are carried to 5th order.*

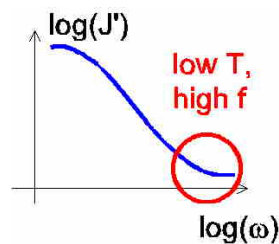
## Piezoelectric Stiffening

The perturbation analysis neglects the element  $Z_k$  in the Tiersten circuit. This element accounts for piezoelectric stiffening. The shear modulus of a piezoelectric material depends on whether or not the shear-induced surface polarization is compensated by a current through the electrodes. If not, the material is stiffer than in the presence of electrodes. For higher harmonics, there is a polarization in the antinodes inside the quartz which is inaccessible to the current through the electrodes. The term  $Z_k$  therefore depends on overtone order: it scales as  $1/n$ . For this reason, the perturbation analysis works less well on low harmonics.

## Viscoelastic Dispersion

It is important to keep in mind that the viscoelastic properties of any given medium usually depend on frequency. The higher the frequency, the higher  $G'$ . For the loss modulus, the frequency dependence may increase or decrease with frequency. For polymers in the MHz range, it usually decreases.

Importantly, the frequency dependence is smooth. Viscoelastic spectra are usually displayed on a logarithmic scale spanning many decades in frequency. The QCM, on the other hand, only operates on one decade.



In such a narrow frequency range, one may approximate the frequency dependence by a power law of the form

$$G'_f(\omega) \approx G'_f(\omega_{ref}) \left( \frac{\omega}{\omega_{ref}} \right)^{\beta}$$

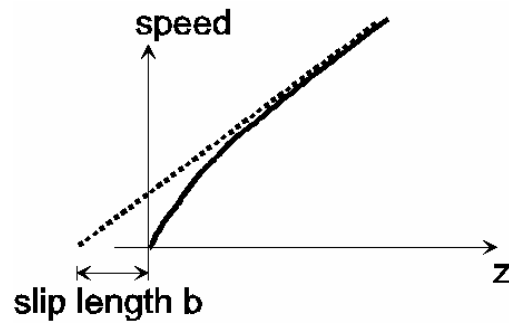
where the exponent,  $\beta$ , is termed "dispersion parameter". An analogous equation

holds for  $G''$  (and for the compliances  $J'$  and  $J''$ ). Based on what is known about soft films,  $\beta$  should be positive and less than 1 for  $G'$ . For  $J'$  it should be negative and larger than -1. For  $J''$  it will also usually be negative.

Due to dispersion, a plot of  $\delta f/f$  versus  $n^2$  (films in air) does *not* yield a straight line, although the perturbation theory predicts an  $n^2$  dependence. Dispersion is not the only reason, why there may be curvature in this plot. The perturbation analysis leading to this kind of display was carried out to third order in  $\mu$  ( $\mu$  the mass of the film divided by the mass of the quartz). At this level of approximation, the viscoelastic parameters enter the equations linearly. Carrying the approximation to higher orders would also introduce a curvature in  $\delta f/f$  vs.  $n^2$ . This problem can be solved by numerically searching for the zeros of the Tiersten circuit with load (which can be done). This still leaves the problem of flexural modes and other imperfections related to the finite lateral width of the quartz plate. For this reason, the dispersion parameter should usually *not* be a fit parameter in the modeling.

## Slip

Slip at the quartz surface can be introduced into the model by using the equations for a film in a liquid, where the “film” is a liquid layer with reduced viscosity. Inside this layer, the shear gradient is increased, leading to the following flow profile:



In the above graph, the slope is proportional to  $\eta(z)^{-1}$ . The slip length,  $b_{slip}$ , is defined by

$$b_{slip} = d_{slip} \left[ \frac{\eta_{\infty}}{\eta_{layer}} - 1 \right] = \int_0^{\infty} \left[ \frac{\eta_{\infty}}{\eta(z)} - 1 \right] dz$$

where  $\eta$  is the viscosity and  $d_{slip}$  is the thickness of the layer with reduced viscosity. In the above graph, slip is not produced by a discrete layer, but rather by a region where the viscosity varies continuously.

In quantitative terms, one starts from perturbation theory for a film in liquid:

$$\begin{aligned} \frac{\delta f^*}{f} &= -\mu + \mu^2 - \mu^3 + 2i n \pi \mu \xi_l^2 (\xi^2 - 1) - (1-i) (n \pi)^{\frac{3}{2}} \mu^2 \xi_l (\xi^2 - 1) - \frac{1}{3} (n \pi)^2 \mu^3 (\xi^2 - 1) \\ &= -\mu + \mu^2 - \mu^3 + (\xi^2 - 1) \left[ 2i n \pi \mu \xi_l^2 - (1-i) (n \pi)^{\frac{3}{2}} \mu^2 \xi_l - \frac{1}{3} (n \pi)^2 \mu^3 \right] \end{aligned}$$

with

$$\mu = \frac{m_{slip}}{m_q} = \frac{\rho_{slip} d_{slip} 2f_0}{Z_q}$$

$$\xi_i = \frac{Z_{sq}}{Z_q} \frac{1}{\sqrt{2\pi n i}} = \frac{\sqrt{\rho_{sq} \eta_{sq} f_0}}{Z_q}$$

$$\xi = \frac{Z_q}{Z_{slip}}$$

Using these relations, one finds to first order in  $\mu$ :

$$\begin{aligned} \frac{\delta f^*}{f} &= -\mu + 2i n \pi \mu \xi_i^2 (\xi^2 - 1) \\ &= \mu \left[ -1 + 2i n \pi \xi_i^2 (\xi^2 - 1) \right] \\ &= \mu \left[ -1 + \frac{i \omega \eta_{sq} \rho}{Z_q} \left( \frac{Z_q}{i \omega \eta_{slip} \rho} - 1 \right) \right] \\ &\approx \mu \left[ -1 + \frac{i \omega \eta_{sq} \rho}{Z_q} \left( \frac{Z_q}{i \omega \eta_{slip} \rho} \right) \right] \\ &= \mu \left[ -1 + \frac{\eta_{sq}}{\eta_{slip}} \right] \\ &= \rho b_{slip} \end{aligned}$$

To the experimenter slip looks like a negative Sauerbrey mass. Higher order terms lead to a dependence on overtone order. Conversely, a dependence on overtone order may be used to infer not only the slip length  $b_{slip}$ , but also information about the profile of  $\eta(z)$  (for instance the thickness of the slip layer  $d_{slip}$  if a box model is assumed).

## Point Contacts

From the extended Butterworth-van-Dyke equivalent circuit, one arrives at the approximation:

$$\frac{\delta f^*}{f} \approx \frac{i}{\pi} \frac{Z^*}{Z_q} \approx \frac{i}{\pi Z_q} \frac{\sigma}{\omega}$$

The application of this equation is not limited to layered systems. For a sphere touching the quartz with a contact radius  $r_c \ll \lambda$ , ( $\lambda$  the wavelength of sound), one can write

$$Z^* = \frac{r_c^2}{r_e^2} \frac{\sigma}{\omega}$$

where  $r_e$  is the electrode radius (i.e. the radius of the active area). For spherical waves emanating from the point of contact, the impedance can be approximated by

[Laschitsch et al., J. Appl. Phys. **85**, 3759 (1999).]

$$Z^* = \frac{K r_c}{r_e^2} \frac{\sigma}{i \omega} (1 + i k r_c)$$

The frequency shift is *positive* and proportional to the radius of contact, the bandwidth scales as  $r_c^2$ . (S. Berg et al. *J. App. Phys.* **92**, 6905, (2002)).

## Modeling Panel

The theory outlined above is the basis for model calculations implemented in the Modeling panel. Let's first recall the assumptions underlying the model:

- All layers are laterally homogeneous.
- The quartz plate has infinite lateral extension. The model is one-dimensional in the sense that it only knows waves traveling *along* the surface normal.
- There is no coupling between the shear waves and compressional waves (for instance caused by the finite extension of the quartz plate or by surface roughness).
- There is no coupling between the thickness shear resonance and the anharmonic sidebands.
- Linear response holds: all stresses are proportional to strain, the linear viscoelastic parameter completely specify a material's mechanical behavior.
- Piezoelectric stiffening is ignored.

In the upper section of the modeling panel the user defines the "acoustic system". The "system" may contain up to two layers plus an ambient medium on both sides of the quartz. Each layer is specified by

- Thickness,  $d$  [nm]
- Density  $\rho$  [g/cm<sup>3</sup>]
- Elastic shear compliance  $J'$  at 10 times the fundamental [GigaPascal<sup>-1</sup>]  
( $10 f_0$  is the "reference frequency")
- Dispersion parameter for  $J'$ ,  $\beta'$   
("Power Law Exponent", typical values:  $-0.5 < \beta' < 0$ )
- Viscous shear compliance  $J''$  at 10 times the fundamental [GigaPascal<sup>-1</sup>]  
( $10 f_0$  is the "reference frequency")
- Dispersion parameter for  $J''$ ,  $\beta''$   
("Power Law Exponent", typical values:  $-1 < \beta'' < 0$ )

For the ambient medium there is no thickness. Also, the viscoelasticity is stated in terms of the viscosity,  $\eta$ . Viscosity is related to the complex compliance,  $J$ , via the relation  $J^{-1} = i \omega \eta$ . Note that  $\eta = \eta' - i \eta''$  (as opposed to  $\eta' + i \eta''$ , which would result in negative values for  $\eta''$ ). Also  $J = J' - i J''$ . (But  $G = G' + i G''$ ).

Layer systems can be saved and loaded from files with the extension ".las".

The *reference state* is important edit the reference state in the respective panel.

Only one parameter can be the "active parameter" (round "radio" button). The active parameter can be changed quickly with the buttons on the right hand side. For instance, if the active parameter is the film thickness and the user clicks the button "x 1.1" the software multiplies the film thickness by 1.1 every time the button is

clicked and updates the predicted frequency shifts and HBH widths (blue lines in the bottom graphs).

Up to six parameters can be selected as fit parameters. Technically, the software could handle more parameters, but in practice it is hard to see how more than six parameters should be extracted from the data in a meaningful way. Selection of the fit parameters is done by checking the square checkboxes. *It is not advised to select the dispersion parameters (power law exponents) as fit parameters.*

At this point, three different sets of equations are implemented. The first one ("Generalized Impedance") calculates the generalized impedance,  $Z^*$ , for the front and the back side with the matrix formalism and uses these impedances in the generalized Sauerbrey equation. The second mode and the third mode apply the perturbation analysis in 3<sup>rd</sup> and 5<sup>th</sup> order.

*The perturbation analysis is only applicable to thin films.* It is the preferred mode of analysis when the focus is on the viscoelastic properties of the films. In this case the perturbation analysis is more accurate than the "Generalized Impedance" mode because nonlinearities in the Tiersten circuit are taken care of. Generally speaking, the shortcomings of the "Generalized Impedance" mode are less severe when all materials involved are much softer than the quartz plate.

The fit parameters are displayed in a separate window. This window has an option to Reanalyze the data from an entire file. In this way you can obtain plots of – let's say – the viscous compliance versus time.

## D-f Plots

With regard to the physical properties of a system evolving with time (for instance an adsorbate growing in thickness) it can be instructive to eliminate time as a variable and plot the HBH half width (proportional to the dissipation, D) versus the frequency shift ("D-f plot"). This plot eliminates the kinetics. Regardless of the kinetics one can make predictions on how the dissipation should scale with frequency shift. In air, the dissipation should scale as the cube of film thickness, that is, the cube of the negative frequency shift. In water, the dissipation should scale linearly with frequency shift, if one has a thin, homogeneous film, the viscoelastic properties of which do not vary with time. A D-f plot can be produced from the graphics panel by choosing the frequency shift as the x-axis in the lower plot. There also is a D-f-Plot Panel to be opened from the Modeling Panel.

## Interpretation of the Amplitude of a Resonance

The focus of interest in the context of quartz crystal resonators usually is on the frequency and the half-band-half-width. However, the **Butterworth-van-Dyke equivalent circuit** has *three* parameters, which are the inductance  $L_1$ , the resistance  $R_1$ , and the capacitance  $C_1$ . The third parameter is related to the amplitude of the resonance. We define the amplitude as the ratio of peak resistance ( $1/G_{\max} - 1$ ) and the bandwidth. Based on the Tiersten equivalent circuit, one has the following relations

$$\begin{aligned}
\frac{1}{G_{\max}} &= R(fres) = \frac{1}{\Phi^2} \operatorname{Re}(Z_{\text{mech}}) \\
&\approx \frac{S}{\Phi^2} \operatorname{Re} \left( i Z_q 2 \cot \left( \frac{k d_q}{2} \right) \right) \\
&\approx \frac{S}{\Phi^2} \operatorname{Re} \left( -i Z_q 2 \tan \left( \frac{(k' + i k'') d_q}{2} - \frac{n\pi}{2} \right) \right) \\
&\approx \frac{S}{\Phi^2} \operatorname{Re} \left( -i Z_q 2 \tan \left( \frac{k' (\sqrt{1 - i \tan \delta}) d_q}{2} - \frac{n\pi}{2} \right) \right) \\
&\approx \frac{S}{\Phi^2} \operatorname{Re} \left( -i Z_q 2 i \tanh \left( \frac{n\pi}{2} \frac{\delta}{2} \right) \right) \\
&\approx \frac{S}{\Phi^2} Z_q \pi n \frac{\delta}{2} \\
&= \frac{S}{\Phi^2} Z_q \pi n \frac{1}{2Q}
\end{aligned}$$

Here  $S$  is the active area and  $\Phi = S \epsilon_{26} / d_q$  transforms from mechanical to electrical quantities (see the BvD circuit). Following this line of reasoning one can define a normalized amplitude according to:

$$\begin{aligned}
Z_q' &= \frac{\Phi^2}{S} \frac{1}{G_{\max}} \frac{2Q}{n\pi} = \frac{S \epsilon_{26}^2}{d_q^2 G_{\max}} \frac{2Q}{n\pi} = \frac{\pi r_{26}^2 \epsilon_{26}^2}{d_q^2} \frac{4f_0^2}{v_q^2} \frac{1}{G_{\max}} \frac{2Q}{n\pi} \\
Z_{\text{norm}} &= \frac{Z_q'}{Z_q}
\end{aligned}$$

We have first defined a quantity  $Z_q'$ , which should be equal to  $Z_q$  according to the above argument. The normalized amplitude is just the ratio of  $Z_q'$  and  $Z_q$ .

## Interpretation of the Offset of the Susceptance

According to the Butterworth-van-Dyke equivalent circuit the susceptance far away from the resonance is given by

$$B_{\text{off}} = -\frac{1}{2\pi f C_0}$$

where  $C_0 = S \epsilon_0 \epsilon / d_q$ , is the electric ("parallel") capacitance. This capacitance may depend on the dielectric environment and contain physical information.

## Fast Mode

With full frequency sweeps, the time for data acquisition per data point typically is 0.5 seconds or more and it is difficult to go any faster. However, there is a way around this limitation (sacrificing some accuracy). In the "Fast Mode" the impedance analyzer measures the conductance,  $G$ , and the susceptance,  $B$ , at a single frequency on the center of the resonance. It can do so with a data acquisition rate of about 25 Hz (Agilent E5100). From the shifts of  $G$  and  $B$  the software estimates shifts in  $f$  and  $\Gamma$ .

In order to set up the Fast Mode, one must first acquire a resonance curve. It is done automatically when the form is opened. One can change center and span with buttons similar to the ones in the Search Panel. After you click "Start" the software determines  $G$  and  $B$  at the center frequency and again performs fits. For this second type of fits, the parameters  $G_{\max}$ ,  $\text{phase}$ ,  $G_{\text{off}}$ , and  $B_{\text{off}}$  are not fit parameters.



The values from the calibration step are used and kept fixed. The only active fit parameters are the frequency and the HBH width. Since there are only two measured numbers ( $G$  and  $B$  at one single frequency) the "fit" really amounts to solving an implicit nonlinear equation (predicting  $G$  and  $B$  from  $\delta f$  and  $\delta \Gamma$ ). Note that this procedure assumes that the other input parameters to the fit are constant. We have seen artifacts in the Fast Mode, caused by fluctuation electric fields in the environment of the crystal.

Because updating the graphics takes time, the software only displays data once in a while. The interval is specified in the field "Number of Samples" on the right hand side.

The amount of data acquired in the fast mode can be overwhelming. Consider a time delay between the slices of data (to be set with in the "Time Delay" field).

It may be of interest whether the system under investigation responds to changes in drive level (that is, amplitude of lateral displacement). This can be investigated with the button "Modulate Amplitude". The software will go back and forth between an upper level and a lower level (both in dBm) with a period to be specified in the Period field.

## Temperature Control

It is highly recommended to run the instrument in an environment with temperature control. Usually, a constant temperature is good enough. There also is a temperature control unit which can be addressed from the software and can perform arbitrary ramps and steps.

The control unit is based on PID logics. Its function is governed by the parameters "PROP", "INT" and "DIFF1" and "DIFF2". These can be set in the Temperature Configuration Panel. Please refer to the manual of the control unit for a detailed description. Here are some rules of thumb:

If you have overshooting, decrease PROP (make the response to a deviation from the set point less strong) and increase INT (make the system slower). If the system is too slow, go the other way. Be careful with the parameters DIFF1 and DIFF2. Don't decrease the response time (Temperature Configuration Panel) to below 350 ms. The control unit talks to the PC via a slow serial interface. If the response time is less than 350 ms, essential bits of the communication can get lost.

The performance of the cell with regard to accuracy, stability, and speed of temperature jumps depends on the cell design. Generally speaking, it is difficult to perform fast jumps because the quartz is not well connected thermally to its environment. *Slow* ramps can be done well.

The Temperature Control Panel is reached from the Main Panel via the menu item Measure -> Temperature Control. The software allows for three different types of programmed temperature cycles

- (a) Set a certain fixed temperature (upper right).
- (b) Perform temperature sweeps (lower right). The sweeps may or may not be reversed. They can be repeated.
- (c) Perform a temperature program as indicated in the sub panel "Temperature Program". Each line in the window corresponds to ramp, where the three entries correspond to the initial temperature, the final temperature, and the duration of the sweep. If the initial and the final temperature are the same, the temperature remains constant for this period of time.

When the user hits "Start" the software initiates the temperature program. After all lines have been executed, the temperature remains at the final temperature of the last line. A temperature program may be interrupted (for instance to do some manipulation with the sample.) When the button "Resume" is clicked the software determines what the current temperature should be, based on the current time, the time when the program was initiated, and the program as given in the window. That is: an interruption does not stop the clock of the temperature program.

The Control unit has two sensors. Usually, sensor 1 (upper connector on the control unit) is close to the heating elements and sensor 2 (bottom connector) is close to the sample. The feed back logics uses sensor 1. One can interchange the sensors but it is not recommended.

Consider the use of temperature dependent reference frequencies for experiments with variable temperature.

## Drive Level Dependence

The resonance frequency depends on the drive level. Most of this effect is caused by temperature. At high drive levels, the energy dissipated in the quartz plate is significant and heats the quartz, shifting the frequency via temperature-frequency-coupling. There is a panel to check for drive level dependence. You can either define a series of drive levels, or define a series of drive level ramps.

## Combined SPR and QCM Measurements

The QCM and SPR spectroscopy are common techniques for measuring film thicknesses in the range a few monomolecular layers. Both techniques are based on the reflection of a wave at the substrate–film interface and share common principles. The existence of standing waves in the layer system defines a resonance condition (frequency or coupling angle), the shift of which is used to probe film thickness during growth.

Provided that the layer is much thinner than the wavelength of light, the shift of the plasmon coupling angle is to first order in film thickness given by

$$\frac{n\omega}{c} \Delta(\sin \theta_c) = \Delta k_x \approx \frac{\omega}{c} \frac{2\pi}{\lambda} \left( \frac{\epsilon_m \epsilon_a}{\epsilon_m + \epsilon_a} \right)^2 \frac{1}{\sqrt{-\epsilon_m \epsilon_a (\epsilon_a - \epsilon_m)}} \frac{(\epsilon_f - \epsilon_a)(\epsilon_f - \epsilon_m)}{\epsilon_f} d_f \quad (1)$$

with  $n$  the refractive index of the ambient medium,  $\theta_c$  the coupling angle,  $\epsilon$  the dielectric constant,  $d_f$  the film thickness, and  $\lambda$  the wavelength. The indices "a", "f", and "m" denote the ambient medium, the film, and the metal substrate, respectively. Eq. 1 can be generalized to account for continuous refractive index profiles, for example created by a dilute adsorbate:

$$\Delta(\sin \theta_c) \approx \frac{2\pi}{n\lambda} \left( \frac{\epsilon_m \epsilon_a}{\epsilon_m + \epsilon_a} \right)^2 \frac{1}{\sqrt{-\epsilon_m \epsilon_a (\epsilon_a - \epsilon_m)}} \int_0^\infty \frac{(\epsilon_f(z) - \epsilon_a)(\epsilon_f(z) - \epsilon_m)}{\epsilon_f(z)} dz \quad (2)$$

where the integral is termed the "ellipsometric moment". This is the quantity determined in any technique based on optical reflectometry, including ellipsometry and SPR spectroscopy. When working with metal surfaces, one can further assume that  $\epsilon_f(z) - \epsilon_m \approx \epsilon_a - \epsilon_m$  and pull this quantity out of the integral, leading to

$$\Delta(\sin \theta_c) \approx \frac{2\pi}{n\lambda} \left( \frac{\epsilon_m \epsilon_a}{\epsilon_m + \epsilon_a} \right)^2 \frac{1}{\sqrt{-\epsilon_m \epsilon_a}} \int_0^\infty \frac{\epsilon_f(z) - \epsilon_a}{\epsilon_f(z)} dz \quad (3)$$

We define the “optical thickness”  $d_{opt}$  as the thickness of an equivalent compact layer generating the same shift of the surface plasmon as the film under study. One has

$$d_{opt} = \Delta(\sin \theta_c) \left[ \frac{\varepsilon_{dry} - \varepsilon_a}{\varepsilon_{dry}} \right]^{-1} \left( \frac{2\pi}{n\lambda} \left( \frac{\varepsilon_m \varepsilon_a}{\varepsilon_m + \varepsilon_a} \right)^2 \frac{1}{\sqrt{-\varepsilon_m \varepsilon_a}} \right)^{-1} \quad (4)$$

where  $\varepsilon_{dry}$  is the dielectric constant of the adsorbate in its dry state. The term in square brackets is a weight function describing how strongly a film of a given thickness and refractive index affects the coupling angle.

Similar equations hold for quartz crystal resonators. In the long-wavelength-limit ( $d_f \ll \lambda$ ) one has

$$\begin{aligned} \frac{\delta f^*}{f} &= -\frac{m_f}{m_q} \left[ 1 - \left( \frac{Z_q^2}{Z_f^2} - 1 \right) \frac{Z_a^2}{Z_q^2} \right] \\ &\approx -\frac{m_f}{m_q} \left[ 1 - \frac{Z_a^2}{Z_f^2} \right] = -\frac{m_f}{m_q} \left[ \frac{Z_f^2 - Z_a^2}{Z_f^2} \right] \end{aligned} \quad (5)$$

For convenience, eq. 5 is again derived in the appendix. The quantity  $\delta f^*$  is the complex frequency shift  $\delta f + i \delta \Gamma$ , where  $f$  is the frequency and  $\Gamma$  is the half-band half-width.  $m_f$  and  $m_q$  are the mass per unit area of the film and the quartz plate, respectively. One has the relation  $m_q = Z_q / (2f_0)$  with  $f_0$  the fundamental frequency.  $Z_a$ ,  $Z_f$ , and  $Z_q$  are the acoustic impedances of the ambient medium (the liquid), the film, and the quartz, respectively. One has  $Z_q = 8.8 \cdot 10^6 \text{ kg m}^{-2} \text{ s}^{-1}$ . The acoustic impedance is given by  $Z = (\rho G)^{1/2}$  with  $\rho$  the density and  $G$  the shear modulus. The second line makes use of the relation  $Z_q \gg Z_f$ , which is true for soft adsorbates. In soft matter experiments,  $G$  varies much stronger than  $\rho$ . The acoustic impedance is to large extent governed by the material's shear modulus. For liquids one has  $G = i\omega\eta$  with  $\eta = \eta' - i\eta''$  the viscosity. The acoustic impedance is the acoustic analog of the refractive index,  $Z^2$  is the analog of the dielectric constant. Because eq. 5 is linear in mass, it also holds in an integral sense:

$$\frac{\delta f^*}{f} \approx -\frac{1}{m_q} \int_0^\infty \left[ \frac{Z_f^2(z) - Z_a^2}{Z_f^2(z)} \right] \rho(z) dz \approx -\frac{\rho}{m_q} \int_0^\infty \left[ \frac{G_f(z) - G_a}{G_f(z)} \right] dz \quad (6)$$

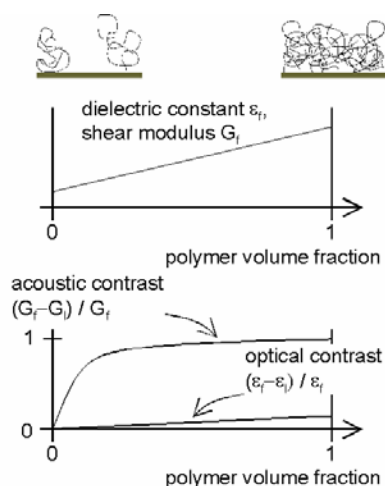
The integral could be called “acoustic moment”. We define the acoustic thickness  $d_{ac}$  as the thickness of a hypothetical compact layer ( $G_f \gg G_a$ ) inducing the same frequency shift as the layer of interest:

$$d_{ac} = -\frac{\delta f^* m_q}{f \rho} \quad (7)$$

Eq. 7 is the Sauerbrey equation. The acoustic thickness is the Sauerbrey mass divided by the density.

Comparing eqs. 4 and 7 and one might assume that the information contained in surface plasmon resonances and quartz crystal resonances should be essentially the same. However, this is very often not the case. Firstly, the contrast in acoustics is usually much larger than in optics. While refractive indices generally vary in the

range of some percent, shear moduli may easily increase over orders of magnitude even for rather dilute adsorbates. In optics the weight function (square brackets in eq. 4 and 6) is smaller than unity and roughly proportional to the concentration. Therefore, the plasmon shift is approximately proportional to the *adsorbed amount*. In acoustics, on the contrary, the weight function (square brackets in eq. 6) easily saturates even for dilute adsorbates. The acoustic thickness reaches the *geometric thickness* at rather low coverage and does not increase further upon densification of the film by prolonged adsorption. More pictorially speaking, if the adsorbate drags some solvent along in its shear movement, the trapped solvent appears as a part of the film.



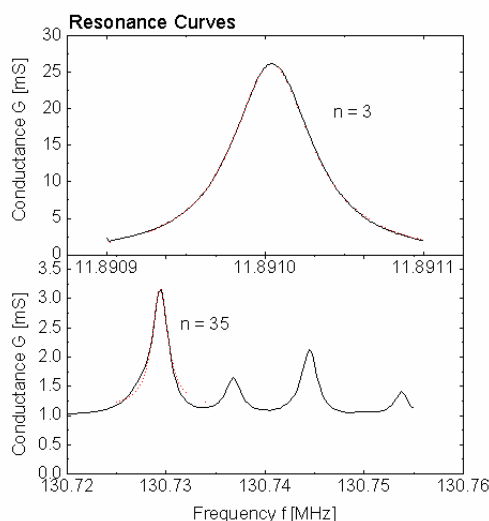
Swelling therefore effectively increases the acoustic thickness, while it affects the optical thickness to a much lesser degree.

[1] See, for example. W. Knoll, in: *Handbook of Optical Properties*, R. E. Hummel, P. Wißmann (eds.) Vol II, 373 (1997).

## Pitfalls, Tips, and Tricks

- Anharmonic Side Bands
- Wrong Frequencies when Speed of Measurement is Too High
- Compressional Waves, Cuvette Resonances
- Ground the Front Electrode
- Reasons for "Bad Resonances"
- Energy Trapping
- Electrode-Less Excitation
- Consider Aluminum Electrodes (Z-Match)
- Export Graphics
- Temperature-Frequency Coupling
- Design Issues for the Holder
- Calibration of Impedance Analyzer
- Time is not properly displayed in graphics panel
- Tips on Cleaning and Handling

## Anharmonic Side Bands



Unfortunately, the pure thickness shear modes are not the only modes which are excited electrically. There are other modes, containing nodal lines across the surface of the quartz. See the [tutorial by Vig](#) for a good explanation and a graphical representation of the mode structure. These anharmonic side bands may interfere with the measurement in two ways. If they overlap with the main resonance, the main resonance cannot be fitted with a resonance curve. Even if they do not overlap much, there may be coupling between the main resonance and anharmonic side bands. This coupling affects frequency and bandwidth of the main resonance and therefore introduces artifacts.

## Wrong Frequencies when Speed of Measurement is Too High

Compare the inverse **system bandwidth** to the sweep time. If the inverse system is not less than the sweep time divided by the number of points then there is a problem. Check by reversing the **sweep direction** (Search Panel). In case the resonance frequencies are much different for sweeping the frequency up and sweeping down, the system bandwidth should be decreased. Alternatively, consider use of the option "Sweep both Directions" (Control Panel).

## Compressional Waves, Cuvette Resonances

Ideally, the quartz crystal should be a thickness shear resonator. That is not always true. There are flexural contributions to the mode structure, which may emit compressional waves. You can check with an ultrasonic microphone. If the opposing cuvette wall is parallel to the quartz plate, standing waves (cuvette resonances) may occur, which have a strong influence onto the frequency and the bandwidth. One can check for cuvette modes by varying the temperature (and thereby the speed of sound).

One can fight cuvette resonances by

- tilting the opposing cuvette wall with respect to the quartz
- placing an irregularly shaped object ("spoiler") in-between the crystal and the opposing wall.

## Ground the Front Electrode

If the front electrode is in contact with the liquid and all kinds of funny electrochemical processes can occur if it is not grounded. Also, the dielectric

properties of the medium affect the results of the measurement via piezoelectric stiffening. This only applies to experiments in liquids. Check which of the pins of the holder is connector to the outer lead of the BNC connector. This pin is connected to the ground. Place the quartz in the holder such that the front electrode connects to this pin. If the front electrode is not grounded, you still see nice resonances, but the frequency keeps drifting around erratically.

## Reasons for Bad Resonances

- Insufficient **energy trapping**
- **Stress in the holder**
- An "old quartz". Quartz plates which have seen many cycles of cleaning deteriorate
- Scratches, defects
- Small wedge distortions, imperfect parallelism of the two surfaces
- Laterally inhomogeneous sample

## Energy Trapping

Usually, the oscillation is confined to the center the quartz plate in order to minimize the effects of the holder onto the resonance. The trick is to make the quartz thicker in the center than at the rim. This procedure is called "energy trapping". Using plane-convex plates or beveled wafers is one solution. "Overtone quartzes" usually just employ keyhole-shaped electrodes. The amplitude of oscillation is large at the center and decreases exponentially towards the rim. For sensing purposes, one often employs keyhole shaped back electrodes and conventional electrodes covering the entire plate on the front because one wants to avoid lateral heterogeneity at the sensing interface. The thicker the keyhole-shaped electrode on the back, the better the energy trapping. The efficiency of energy trapping increases with overtone order due to the decreasing wavelength of sound. What matters for energy trapping is the ratio of the thickness of the back electrode and the wavelength of sound.

Energy trapping is one cause of flexural contributions to the mode of oscillation, where the latter may launch compressional waves into the liquid.

In air, energy trapping is not strictly necessary. One can place the quartz on a flat surface. It is supported by dust grains and asperities, which are so small that they hardly affect the resonance. One cannot, however, clamp a wire to the resonator without severely disturbing the resonance. In the absence of energy trapping the electrical excitation has to occur across an air gap.

## Electrode-Less Excitation

In case one wants to avoid electrodes (either because of the adverse consequences of energy trapping or because they interfere with the **measurements of a shear compliance**) one can eliminate them. The quartz can also oscillate in an electrical field applied externally. The peak conductance is small but measurable. One just places the quartz plate onto the metal plate (bottom electrode). It is supported by small asperities and dust grains, which hardly affect the resonance. The upper electrode (a second metal plate) must be close to the quartz without pushing onto it.

## Consider Aluminum Electrodes (Z-Match)

In case one is interested in the determination of a shear compliance, the electrodes have undesirable effects. They do enter the calculation (see **third order perturbation**). If the electrode thickness is not known with good accuracy, large systematic errors result. There is, however, one electrode material which is acoustically very similar to AT-cut quartz, which is aluminum. Its acoustic impedance is  $Z_{al} = 8.22 \cdot 10^6 \text{ kg m}^{-2} \text{ s}^{-1}$  (to be compared to the impedance of AT-cut quartz of  $Z_q = 8.8 \cdot 10^6 \text{ kg m}^{-2} \text{ s}^{-1}$ ). Aluminum is acoustically very similar to AT-cut quartz, aluminum electrodes have little effect on the derived shear compliance of the film.

## Export Graphics

The content of any Graphics Panel can be exported with the right mouse button and the export dialog.

## Temperature-Frequency Coupling

In case you find unexpected variations of the frequency with no corresponding signature in the bandwidth, check for temperature. Actually, one advantage connected to the measurement of bandwidth is given by the fact that bandwidth is less susceptible to temperature changes than frequency. The coefficient for **temperature frequency coupling** depends on the crystal cut. It can only be minimized for one harmonic at a time (via the angle of the cut). In air, it is often difficult to keep the temperature of the quartz constant because the thermal coupling of the quartz can only occur across the rim. In liquids, thermal control is less of a problem. Consider temperature-dependent reference frequencies.

## Design Issues for the Holder

Building a holder for measurements in liquids is not easy.

- Avoid stress
- Avoid leaks
- Consider larger quartz plates (1 inch); energy trapping is easier for larger quartzes.
- If you find an influence of the holder on the frequency, consider using a thicker keyhole shaped back electrode (energy trapping).
- Things become easier if one electrode reaches around the side (see the quartz plates supplied by [MaxTek](#)). Then both cables can connect from the back of the quartz plate.
- Consider electrically conducting O-rings for sealing.
- Mount the quartz plates a day before you start the measurement.

## Calibration of Impedance Analyzer

By and large, a calibration of the impedance analyzer is not necessary as long as all the user needs is the resonance frequency and the bandwidth. However, without calibration the resonances often appear asymmetric or even inverted. Please refer to the manual of the impedance analyzer with regard to details of calibration procedure. Typically, calibration involves connecting an "open", a "short", and a "load" (50 Ohm resistor) to the cable instead of the quartz. Calibration information can often be save and retrieved (so that you don't have to repeat it every time you turn on the instrument). The software deals with improper calibration with the phase and the offsets.



## Time is not properly displayed in graphics panel

The Graphics software can only deal with numbers up to a certain limited precision. When the time is very large (months) then there is problem. Reset the clock.

## Tips on Cleaning and Handling

Here is a copy from the site of Stanford Research Instruments  
<ftp://ftp.thinksrs.com/PDFs/Manuals/QCM100m.pdf>

(a good site, we purchase equipment from them)

### Crystal Handling

- Keep the crystals in a clean environment. When not in use, store them in their original box and wrapper.
- Avoid scratching the center part of the crystal.
- Always rinse with deionized water, or another appropriate pure liquid, before drying the crystal.
- Always use a flow of dry, oil-free, non-reactive gas (e.g. nitrogen) to blow-dry the crystal. It is better to chase liquid off the crystal than to evaporate it on the crystal.
- Hold the sensor crystal with a pair of tweezers. Using bare fingers will contaminate the crystal. Hold it on the outer edge outside the electrode area to prevent scratches. The tweezers should be blunt ended with smooth gripping surfaces and preferably made of soft plastic material.
- Before starting a surface cleaning, ensure that the crystal material will not be damaged by the chemicals. Perform a test run on a discarded or practice crystal whenever possible.

### Cleaning

...

The most appropriate cleaning method depends on the sample system, the interaction of the sample with the crystal surface, and the properties of the Sensor Crystal itself.

Note: Before starting a surface cleaning, ensure that the crystal material will not be damaged by the chemicals. Perform a practice test on a discarded crystal whenever possible. *Avoid basic (high pH) cleaners since they will etch the quartz surface.* Several proven cleaning procedures follow. Proper crystal handling procedures must be used throughout any cleaning process.

### *General Purpose*

For general purpose applications such as electrochemistry and liquid or viscoelastic film studies, it is usually sufficient to sonicate the crystals in a solution of non-basic detergent in deionized water. Immediately rinse liberally with deionized water and dry in a gentle flow of nitrogen gas.

### *Hydrocarbon contaminants*

UV/ozone treatment<sup>21</sup> is a powerful tool for removing hydrocarbon impurities which have been adsorbed from the ambient air. This method does not affect the quartz surface, it is low cost and is very efficient. It is often used for crystals used in high vacuum environments.

### *Biomaterials (lipids, proteins and similar biomolecules)*

Start by treating the crystal in a UV/ozone chamber for 10 minutes, then immerse it into a 1:1:5 solution of hydrogen peroxide (30%), ammonia (25%) and deionized water heated to a temperature of about 75°C for 5 minutes<sup>22</sup>. Immediately rinse liberally with deionized water



and dry in a gentle flow of nitrogen gas. Immediately before measurement, treat the crystal with UV/ozone for 10 minutes.

#### *Lipid vesicles on SiO<sub>2</sub> surfaces*

Treat the crystal in a UV/ozone chamber for 10 minutes, then immerse it into water with 2% of sodium dodecyl sulfate (SDS) at room temperature for 30 minutes<sup>23</sup>. Rinse generously with deionized water and blow dry with nitrogen gas. Immediately before measurement, treat the crystal with UV/ozone for 10 minutes.

#### *Polystyrene removal*

To clean polystyrene (PS) off a crystal, immerse the crystal into a 1:1 solution of hexane and deionized water and treat it in an ultrasonic bath for 1 minute. Rinse thoroughly with deionized water and blow dry with nitrogen gas.

#### Crystal rinsing

Rinse sensor crystals with deionized or distilled water or another appropriate pure liquid. In order to prevent recontamination follow these two steps:

1. Hold the crystal with a pair of tweezers from below to prevent washing contaminants from the tweezers onto the crystal. This is generally most critical in biological applications.
2. Chase the liquid off the crystal with a flow of nitrogen gas. Liquid remaining on the edge of the crystal can be wicked off with a clean, lint-free cloth.

#### Head Cleaning

It is not uncommon for crystals to break and for chemicals to enter the crystal cavity. In either case, it is very important to act fast and rinse the crystal cavity, the POGO™ contacts and the POGO contact sockets to remove any traces of solution that might lead to corrosion. Even though the POGO contacts and sockets are gold coated, unrinsed chemicals can still lead to corrosion and permanent damage to the holder. This is especially true in electrochemical experiments where oxidizing acids are often part of the liquid solution.

Start by removing the crystal from the Crystal Holder and exposing the POGO pins. Putting your thumbnail under the POGO head pull firmly with your fingers to remove each contact pin from its socket. Rinse the pins and the sockets with deionized water to remove all traces of chemicals.

#### Tips for Operation in Liquids

To minimize measurement errors in liquid phase QCM experiments, the sample liquid should be prepared carefully. Changes in temperature or the properties of the solvent as well as air bubbles will affect the sensor signal.

For reproducible measurements, keep the following tips in mind.

- Degas the sample liquid
- The sample liquid should be degassed prior to measurement to avoid the formation of airbubbles on the surface of the crystal.
- Soak the crystal in the sample liquid overnight
- To minimize random fluctuations, it is best to immerse the crystal, mounted in its holder, in the sample solution several hours before the experiment is started.
- Wait for the temperature to stabilize
- To avoid the formation of air bubbles and reduce temperature related artifacts, the sample liquid should have approximately the same temperature as the measurement chamber's working temperature ( $\pm 2^{\circ}\text{C}$ ). Wait at least one hour for the temperature to

stabilize, before performing any accurate measurements, after a crystal is immersed in a liquid.

- Prepare your solutions carefully
- To avoid unwanted effects due to changes in the properties of the buffer liquid or solvent, solutions should be prepared carefully. Whenever possible, use purified samples at high concentration and dilute them in the appropriate buffer or solvent just before measurement. Use solvents or buffers from the same stock during one measurement.

## Frequently Asked Questions (FAQs)

- Why is the fundamental often "bad" ?
- When can I trust a resonance ?
- In a group of resonances the one with the lowest frequency has a small amplitude. Is this the resonance of interest ?
- Why does the theory often work better on higher harmonics ?
- Should I use a  $\pi$ -network?
- Why is normalized frequency  $f/n$  not the same on all harmonics?
- To what extent is it justified to assume linear response?
- What is the time life time of a crystal?
- Does the cell of QCM have to be on a table with vibration isolation?

## Why is the fundamental often bad?

The fundamental often looks nice if you look at the conductance spectra but behaves strangely, once the measurement has started. The reason is poor energy trapping. Energy trapping is less efficient on low harmonics. Quartzes designed for use on the fundamental often have a convex upper surface.

## When can I trust a resonance?

- It should be well separated from the anharmonic side bands.
- It should be both the largest harmonic in a group of harmonics and the one with the lowest frequency (see anharmonic side bands).
- It should be fitted well.
- Don't worry about asymmetry (caused by imperfect calibration, not a problem).

## In a group of resonances the one with the lowest frequency has a small amplitude. Is this the resonance of interest ?

That's basically not good news. This usually says that the two lowest resonances are coupled, and this can have all kinds of unpredictable consequences. If you wish to use these resonances somehow, consider selecting them *both* and see later what the results are. The general rule is: the lowest resonance in a group of resonance is the pure thickness shear mode, the other ones are the anharmonic side bands. But the pure thickness shear mode should also have the largest amplitude. If not, something is wrong.

## Why does the theory often work better on higher harmonics?

Firstly: yes, that is a fact. In practice, the highest harmonics which are still well separated from the anharmonic side bands yield the best results. There is more than one reason:

- Piezoelectric stiffening scales as  $1/n$  and becomes less important on high harmonics.
- The efficiency of energy trapping depends on the ratio of the electrode thickness and the wavelength of sound. Energy trapping therefore is more efficient on higher harmonics.
- Quartz plates are three dimensional bodies. In the oscillating state, there is shear strain in all directions. The theory assumes a laterally infinite plate with shear strain only present along the surface normal. This approximation becomes better on higher harmonics because the importance of in-plane shear decreases relative to the increasing shear strain along the vertical direction.

### Should I use a PI-network?

$\pi$ -networks are employed for highly precise characterization of quartz blanks according to the standard IEC 444. Here is the [unit from Agilent](#), also see the [Transat homepage](#). With a  $\pi$ -network one can gain additional accuracy by shielding the quartz from electrical disturbances. Without the  $\pi$ -network, the apparent resonance parameters slightly shift upon a change of the input impedance of the network analyzer. This effect is related to piezoelectric stiffening. Note, however, that the front electrode must be grounded by additional little circuitry when using  $\pi$ -networks in liquids.

### Why is normalized frequency $f/n$ not the same on all harmonics?

There are two reasons: The first one is **piezoelectric stiffening**. The second has to do with the stress gradients in the plane of the surface. The ideal picture assumes plane waves. This picture is good on high harmonics. On low harmonics one should really view the lateral amplitude distributions as a standing wave with a k-vector in the surface plane. The presence of this wave increases the resonance frequency. On high harmonics the normal component of the k-vector becomes much higher than the lateral component and the importance of this effect decreases.

### To what extent is it justified to assume linear response?

Usually this is a good assumption as long the **drive level** is not too high. In air, -5 dBm is safe. We have observed deviations from linearity (amplitude-dependent frequencies, occurrence of overtones) in contact mechanics experiments, where the surface was touched with a small stylus. Here the local stresses become high.

### What is the life time of a crystal?

They do degrade with time, but not quickly. We reuse them for about a year. Even small scratches are tolerable to some extent.

As time goes by, two things happen:

- The bandwidth increases
- The mode structure becomes less nice (See **Profiles Panel**)

### Does the cell of QCM have to be on a table with vibration isolation?

Not at all. The quartz oscillates at a MHz frequency. All disturbances from the building would be at a much lower frequency.

## Details

- Lorentz Fits
- How the software finds the guess values used in the Lorentz fit
- Asymmetric Resonances and the Phase

## Lorentz Fits

After the conductance spectra have been taken, the program fits a resonance curve ("Lorentz curve") to the spectra. Unless the button Disregard Imaginary Parts for Lorentz Fitting is checked, the program uses both the real part (conductance  $G$ ) and the imaginary part (susceptance,  $B$ ) of the complex admittance,  $Y$ , for fitting. The fit functions are

$$G_{fit} = G_{max} \left[ \frac{f^2 (2\Gamma)^2}{(f_0^2 - f^2)^2 + (2\Gamma)^2 f^2} \cos \varphi - \frac{(f_0^2 - f^2) f (2\Gamma)}{(f_0^2 - f^2)^2 + (2\Gamma)^2 f^2} \sin \varphi \right] + G_{off}$$

$$B_{fit} = G_{max} \left[ -\frac{(2\Gamma)^2 f}{(f_0^2 - f^2)^2 + (2\Gamma)^2 f^2} \sin \varphi - \frac{(f_0^2 - f^2) f (2\Gamma)}{(f_0^2 - f^2)^2 + (2\Gamma)^2 f^2} \cos \varphi \right] + B_{off}$$

All fit parameters are in red. The software performs a Levenberg-Marquardt fit, where the fit routine is from Numerical Recipes.

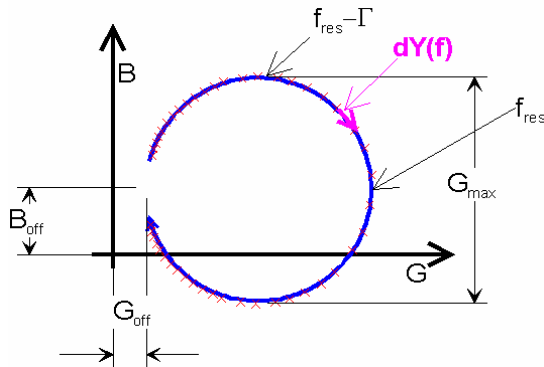
The shifts of frequency  $\delta f$  and shifts of HBH width  $\delta \Gamma$  are the most important fit parameters. The other fit parameters are mainly used to ensure a good fit quality. The offsets of the real part  $G_{off}$  should ideally be zero. The offset of the imaginary part  $B_{off}$  is related to the electrical capacitance across the electrodes.

The phase angle  $\varphi$  should ideally also be zero. One reason for it to become non-zero is a finite conductivity of the electrodes, which again may possibly be probed in this way. Usually, a non-zero phase angle is caused by **calibration** problems.

The maximum conductance  $G_{max}$  is about (but not strictly) inversely proportional to the bandwidth. It can be analyzed in terms of a total mass.

## How the software guesses the starting values used in the Lorentz fit

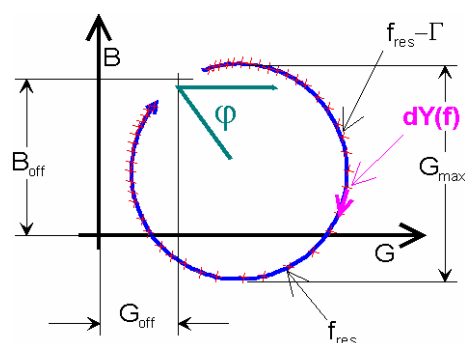
The following figure shows a "nice" symmetric Lorentz curve as you get it when all the settings are correct and you have performed proper calibration.



The resonance curve is a circle in the complex plane of the admittance  $Y = G + iB$ . At plus and minus infinity the admittance is about constant and equal to  $G_{off} + iB_{off}$ . Ideally,  $G_{off}$  is zero and  $B_{off}$  is equal to  $i\omega C_0$  with  $C_0$  the parallel capacity (see also the Butterworth-van-Dyke equivalent circuit). From such a curve

the parameters of the fit are easily guessed. In particular, the resonance frequency corresponds to the maximum of  $G$ .

So far so good. Often this is not what the resonance looks like. Often it looks like this:



This happens when the calibration was not done right. Or when one measures transmission rather than admittance. There are certain operations on curves in the complex plane which leave angles invariant and transform circles to circles. They are of the form  $z \rightarrow (A + Bz) / (C + Dz)$  with arbitrary complex numbers  $A$ ,  $B$ ,  $C$ , and  $D$ . Imperfect calibration and misinterpretation of a transmittance as an admittance amount to such a transformation. As long as one only cares about frequencies, this does not matter. The fit function given under Lorentz Fits perfectly accounts for the rotation by the angle  $\varphi$ . The frequency  $f_{res}$  and the HBH width  $\Gamma$  are still determined just fine.

The problem is: how to find proper guess values for the resonance frequency. The frequency where  $G$  is at its maximum is no longer a good starting point. The following trick works OK. Take the distance in the complex plane between two adjacent data points and plot the modulus of this distance ( $|dY|$ ) versus frequency. Pretend this was a resonance curve (it isn't...) and determine  $f_{res}$  and  $\Gamma$  from this curve. This is what happens when the option "Use Derivative in Polar Plot for Guess Values" in the Control Panel is checked.

## Asymmetric Resonances and the Phase

When **calibration** is imperfect the resonances appear asymmetric on the screen. As a consequence, the phase angle  $\varphi$  in the Lorentz fits is non-zero. This is no problem at all. The fitting takes care of the phase angle. You may want to have the option "**Use Derivative in Polar Plot for Guess Values**" in the Control Panel clicked. This option implements a routine for guessing the initial values for fitting, which takes asymmetry into account.

## About

This program was written by Diethelm Johannsmann, Institute of Physical Chemistry, TU-Clausthal ([www.pc.tu-clausthal.de](http://www.pc.tu-clausthal.de)), Germany.

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Numerous people have contributed with practical experience and suggestions. I gratefully acknowledge contributions by:

Steffen Berg, Charles Bouchard, Andreas Bund, Arno Domack, Binyang Du, Ilshat Gubaidullin, Alex Laschitsch, Jörn Lübber, Eike Lüthgens, Anne-Claire Saby-Dubreuil, Andreas Scheller, Zhehui Wang, Oliver Wolff, Katrin Wondraczek