Summary

Advanced Wave Sensors is a company that designs, develops, and manufactures ultrasensitive sensing systems based on the quartz crystal microbalance with dissipation (QCMD) measurement technology.

The basics: Quartz Resonators

At the core of the QCMD technology is a piezoelectric resonator, typically made of quartz (Figure 1), that is excited to oscillate at its resonance frequency in the thickness-shear mode by applying an alternating current through the electrodes deposited on its surface (Figure 2).

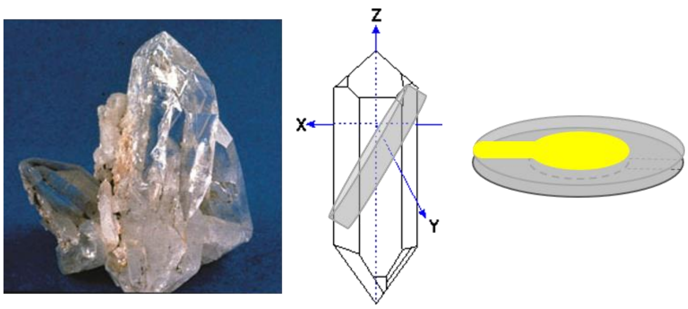

Figure 1. *At the heart of QCMD is a resonator (right) made of a piezoelectric material such as quartz (left), cut at a certain angle relative to the crystallographic axis (middle). Electrodes deposited on the sensor surface are shown in yellow.*

With the resonator oscillating in the thickness-shear mode, its two surfaces move in the opposite directions, as indicated by the arrows in Figure 2. The wavelength of the shear wave, λ, is therefore twice the thickness of the sensor, $\lambda = 2d$. Because $\lambda f = c$, where $c = \sqrt{\frac{G_q}{\rho_q}}$, is the speed of shear sound in the material and f is the frequency, the resonance frequency of such a resonator is given by $f_n = \frac{nc}{2d} = \frac{n}{2d}\sqrt{\frac{G_q}{\rho_q}}$, where G_q is the shear modulus of quartz, ρ_q is its density, and *n* is the (odd) overtone order. (The same expression may be derived formally by solving the equations describing the propagation of shear waves in elastic media subject to appropriate boundary conditions, as discussed in ref. 1. Plugging in 29×10^9 Pa for the shear modulus of AT quartz and 2650 kg/m^3 for the density, one obtains a frequency of ~ 5 MHz for a thickness of ~ 330 μm at the fundamental, where *n* = 1.

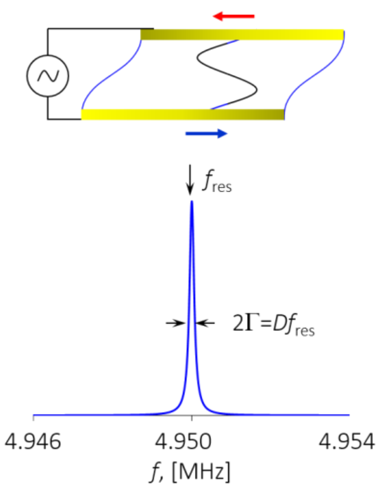

Figure 2. *Top:* A quartz resonator oscillating in a thickness-shear mode at the fundamental (*n* = 1, blue) and at the 3rd overtone (*n* = 3, black). The two surfaces move in the opposite directions, as indicated with the red and blue arrows. Gold electrodes are shown in yellow.

Bottom: Current peaks at the resonance frequency (in this case, *n* = 1 for a fundamental of ~ 5 MHz is shown). The resonance is characterized by a finite width 2Γ that is related to the dissipation *D* through the relationship $2\Gamma = Df_{res}$, where f_{res} is the resonance frequency on the given overtone.

As shown in the bottom panel of Figure 2, the current running through the resonator peaks at the resonance frequency. The peak has a finite width, characterized by a finite bandwidth, half-width at half-maximum (HWHM) Γ, that describes losses during the oscillations. It is directly related to the dissipation D through the relationship $2\Gamma_n = D_n f_n$ where f_n is the resonance frequency at the n^{th} overtone, and to the quality factor $Q_n = \frac{f_n}{2\Gamma_n} = \frac{1}{D_n}$. Quartz resonators are useful in electronics as time and frequency control elements because their quality factors are very large. For a 5 MHz sensor, the values of the quality factor in air easily reach ~10^5 at room temperature. The resonance peaks are very sharp, and the value of the resonance frequency can be determined with ppm accuracy.

How does AWSensors QCMD work

The proprietary electronics used in AWSensors QCMD instruments implements impedance analysis.[2] Shortly, the complex electrical admittance of a resonator $Y(f)$ is measured at several frequencies f around the resonance. To determine the resonance parameters, f_{res} and D, the measured admittances are fit with a phase-shifted Lorentzian

$$Y(f) = G(f) + iB(f) = e^{i\phi}\frac{iG_{max}\Gamma}{f_{res}-f-i\Gamma} + G_{off} + iB_{off}.$$

Electrical admittance can be expressed as a complex number, with the real part, the conductance $G(f)$ and the imaginary part, the susceptance $B(f)$. When plotted as a function of frequency, $G(f)$ gives the familiar resonance peak shape that reflects the oscillation amplitude of the resonator, while $B(f)$ its phase. When plotted against each other, the plot appears as an ellipse (Figure 3). The parameters G_{off} and B_{off} describe the translation of the ellipse in the $B(f) - G(f)$plane, while ϕ describes its rotation. These parameters account for the imperfections of the electrical connections between the resonator and the acquisition electronics not accounted by the calibration and isolate the resonance parameters, f_{res} and Γ, from the influence of the calibration errors. G_{max} is the maximum value of conductance at the resonance. Further discussion can be found in ref. 1.

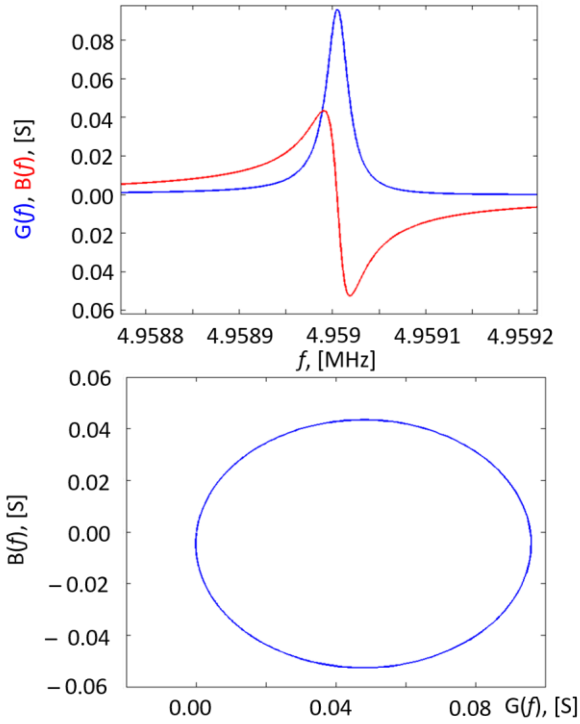

Figure 3: *Top:* Real (blue) and imaginary (red) parts of the electrical admittance of a 5 MHz quartz resonator in air plotted as a function of frequency.

Bottom: imaginary part of the admittance plotted vs. the real part appears as an ellipse.

Comparison with other acquisition methods

Currently, only one other acquisition method provides both frequency and dissipation of the resonator directly: the ring-down method implemented by Q-Sense.[3] The resonance parameters are obtained by analyzing the decay of the oscillations of a resonator that is switched off shortly after excitation. Mathematically, ring-down and impedance analysis methods are related by a simple Fourier transform: the data plotted in the top part of Figure 3 as a function of frequency give a decaying oscillatory function when transformed into the time domain. Further details can be found in ref. 4 and 5.

Quartz Resonators as Sensors

The resonance parameters, f_{res} and *D*, are extremely sensitive to what happens at the sensor surface. The most common case to consider is that of a thin, stiff film, on top of the resonator shown in Figure 4. In this case, the shear wave extends into the film unperturbed, making the whole resonator effectively thicker. Therefore, the resonance frequency is reduced. Günter Sauerbrey[6] showed that in this case, the change in the resonance frequency Δf is proportional to the change in the mass of the resonator, Δm, i.e., the mass of the film:

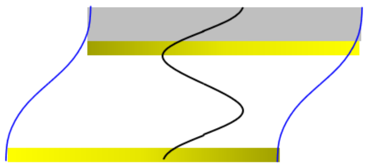

Figure 4: The principle behind microgravimetry.

$\frac{\Delta f}{n} = \frac{f_{film} - f_{bare}}{n} = -C\Delta m = -C\rho h$, where f_{film} and f_{bare} are resonance frequencies with and without the film, respectively; ρ is film density and h is its thickness. *C* is the Sauerbrey constant given by $\frac{2f_1^2}{\sqrt{G_q \rho_q}}$. For an f_1 of 5 MHz, *C* is 0.057 Hz·cm^2/ng. The users may be more familiar with the inverse, 1/*C*, quoted in the literature: ~ 18 ng/(cm^2·Hz). A quartz resonator thus became a (mass) sensor, and the name “microbalance” comes from its ability to accurately measure the mass of thin, rigid films deposited on the surfaces of quartz resonators in vacuum or in liquid down to submolecular dimensions. Interesting applications of QCMD to atomic sub-molecular films are reviewed in ref. 7.

Figure 5: A resonator in viscous liquid of density ρ_{liq} and viscosity η_{liq}.

The Sauerbrey relationship works the same way with the resonator immersed in liquid as it does in vacuum or air, as long as the film is homogeneous and smooth. That is to say, the changes in the resonance frequency and dissipation, Δf and ΔD, are not affected by the presence of the liquid. But the resonance parameters themselves, f_{res} and *D*, are. As shown in Figure 5, in the case of a resonator immersed in liquid, the acoustic wave emanating from the surface decays, withdrawing the energy from the resonator that is dissipated in the liquid through viscous damping.

In that case, $\Delta f_n = -\Delta\Gamma_n = -\frac{1}{2}\Delta D_n f_n = -C\sqrt{\frac{n\rho_{liq}\eta_{liq}}{4\pi f_n}}$, where the frequency and dissipation changes are between the resonator immersed in liquid and in the dry state. This expression is usually referred to as the Kanazawa-Gordon[8] relationship, although it appears earlier, e.g., in the works by Mason.[9] The key things to note here are that shifts in frequency and bandwidth are equal and opposite, and scale with the square root of the overtone order *n*. In practice, QCMD is not a very good viscometer because the decay length of the shear elastic waves in liquid, $\delta = \sqrt{\frac{\eta}{\pi f \rho}}$ is of the order of a few hundred nanometers at the most. While this makes QCMD attractive as sensing technology because it confers surface sensitivity, the measurements of viscosity at these lengthscales are heavily affected by surface roughness, contamination, and other surface-dependent effects. Note, that the expression for the penetration depth can be generalized to complex viscosities for viscoelastic films and non-Newtonian fluids.

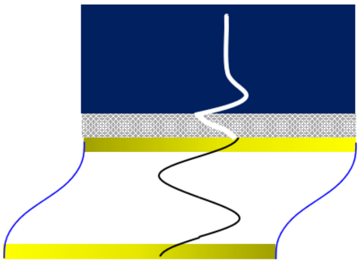

Figure 6: Viscoelastic film in liquid is described by a complex frequency-dependent shear elastic modulus G'(f) + iG"(f).

In the case where the film on top of the resonator surface is thin but not rigid, the shear acoustic wave gets attenuated in the material of the film. The motion of the film material is no longer in-phase with the resonator, and some of the energy is dissipated in the film due to viscous effects (Figure 6). Solution of wave equations for this case lead to an expression for the frequency and dissipation shifts in terms of the mass of the film and its complex shear elastic modulus $G'(f) + iG"(f)$, where G' and $G"$ are the frequency-dependent shear storage and loss moduli, respectively. For thin films, the model predicts that the frequency shift due to a viscoelastic film is always smaller than that due to a rigid film of the same thickness, and that the ratio of dissipation to frequency is independent of the thickness of the film. Further discussion can be found in refs. 1 and 4, and more recent approaches to robust fitting of QCMD data for thin, homogeneous, viscoelastic films are discussed in ref. 10.

QCMD as a force sensor

The simple geometric constructions and the corresponding solutions of the shear wave propagation equations described above work well for simple cases, such as thin films or infinite liquids, but a more powerful way of thinking about QCMD is as a *force sensor* (Figure 7). Approaching the resonator as a force sensor can explain phenomena such as positive frequency shifts (negative apparent

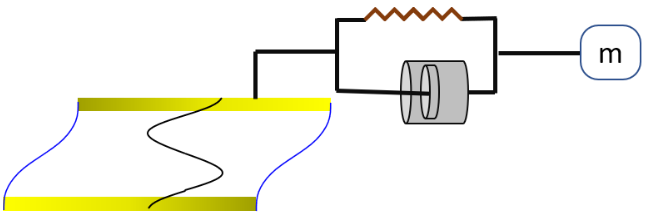

Figure 7: QCMD can be thought of sensing a force applied to the surface of a resonator. Applied force can be thought of as a mass m coupled to the resonator surface through a spring with a constant k (brown) and a dashpot that describes dissipative losses (in the simplest case, viscosity, i2πfη, grey).

mass) and serve as a robust basis for deriving quantitative models of resonator interfaces with complex lateral structures.

The origin of the applied force may vary. In the case of a Sauerbrey film, the force originates from a small mass rigidly coupled to the surface of the resonator (large *k*, small *m*, no dashpot). Because there are no dissipative forces, the coupled mass (the film) and the resonator behave as one rigid body; the mass moves in-phase with the resonator, as shown in Figure 4.

For large *k* and *m*, the frequency shift may become positive. The cross-over between the negative and the positive frequency shifts depends on the value of *k* and on the dissipation. It therefore occurs at different frequencies for different values of these parameters. These phenomena were elegantly investigated in a series of papers by Olsson et al.[11] and have applications to the studies of bacterial and eukaryotic cell adhesion at surfaces: QCMD turns out to be sensitive to the forces the cells exert at the resonator surface.[12,13]

In the case of laterally heterogeneous films in liquids (Figure 8), the forces exerted at the oscillating resonator surface are hydrodynamic. In these cases, the analysis of the QCMD data allows the determination of shapes and sizes of molecules, molecular assemblies, or particles, adhering to the resonator surface. Effective media approximation based on intrinsic viscosity and discrete modelling approaches applicable to such systems are discussed in refs. 14 and 15.

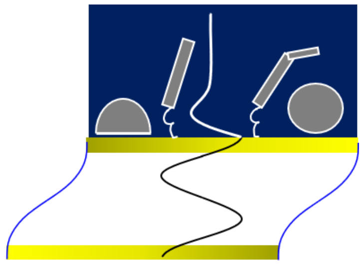

Figure 8: Analysis of hydrodynamic effects yields shapes and sizes of the adhering molecules or molecular assemblies.

Unique features of AWSensors' products

QCMD is a versatile technology for label-free, real-time analysis of the liquid/solid or gas/solid interfaces capable of providing quantitative information about the amount of material, elastic properties, topology, and conformation of molecular assemblies. AWSensors has developed unique QCMD instrumentation consisting of data acquisition electronics, software, resonators, and fluid handling. Our implementation allows data collection at rates of up to 250 points per second on 7 overtones with a sensitivity of 0.6 ng/cm^2 with the classical 5 MHz sensors. AWSensors pioneered the commercial development of the high-fundamental frequency (HFF) resonators[16] offering further improvements in sensitivity. We offer very competitive prices, flexibility, and seamless integration of fluidics and electrochemistry.

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