

## Basics of a Quartz Crystal Microbalance

### Introduction

This document provides an introduction to the quartz crystal microbalance (QCM) which is an instrument that allows a user to monitor small mass changes on an electrode. The reader is directed to the numerous reviews<sup>1</sup> and book chapters<sup>2</sup> for a more in-depth description concerning the theory and application of the QCM. A basic understanding of electrical components and concepts is assumed.

The two major points of this document are:

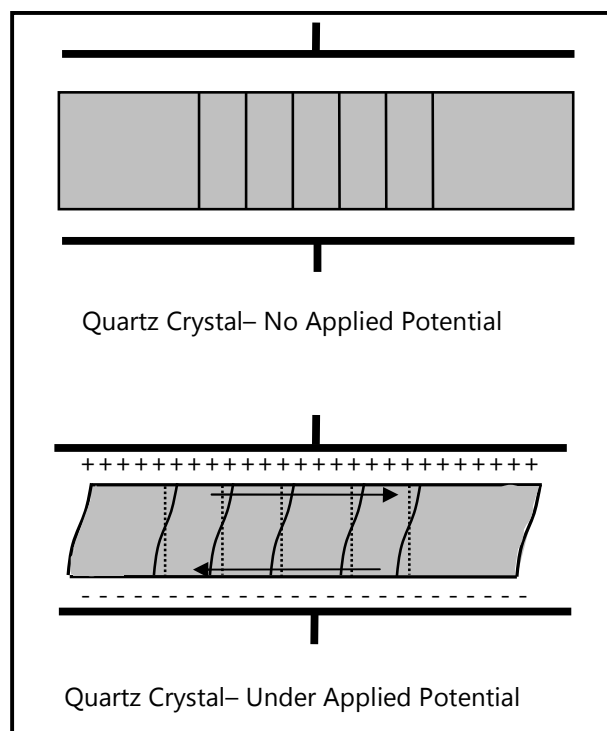
- Explanation of the Piezoelectric Effect
- Equivalent Circuit Models

### Explanation of the Piezoelectric Effect

The application of a mechanical strain to certain types of materials (mostly crystals) results in the generation of an electrical potential across that material. Conversely, the application of a potential to the same material results in a mechanical strain – a deformation. Removal of the potential allows the crystal to restore to its original orientation. The igniters on gas grills are a good example of everyday use of the piezoelectric effect. Depressing the button causes the spring-loaded hammer to strike a quartz crystal thereby producing a large potential that discharges across a gap to a metal wire igniting the gas.

Quartz is by far the most widely utilized material for the development of instruments containing oscillators partly due to historical reasons (the first crystals were harvested naturally) and partly due to its commercial availability (synthetically grown nowadays). There are many ways to cut quartz crystal and each cut has a different vibrational mode upon application of a potential.

The AT-cut has gained the most use in QCM applications due to its low temperature coefficient at room temperature. This means that small changes in temperature only result in small changes in frequency. It has a vibrational mode of thickness shear deformation as shown below in Figure 1.



**Figure 1. Graphical Representation of Thickness Shear Deformation.**

The application of an alternating potential (a sine wave in nearly all cases) to the crystal faces causes the crystal to oscillate. When the thickness of the crystal ( $t_q$ ) is twice the acoustical wavelength, a standing wave can be established where the inverse of the frequency of the applied potential is  $\frac{1}{2}$  of the period of the standing wave. This frequency is called the

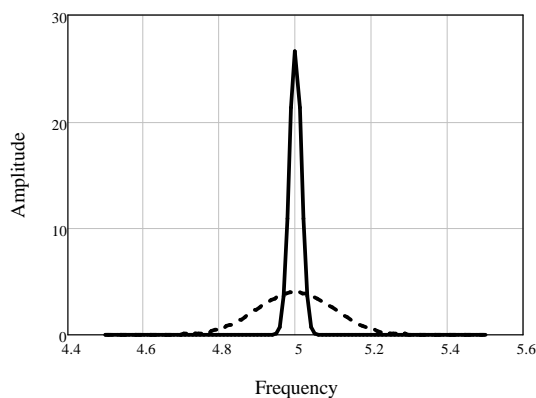
resonant frequency,  $f_0$ , and is given by the equation

$$f_0 = \sqrt{\frac{\mu_q}{\rho_q}} / 2t_q \quad (1)$$

where  $\mu_q$  is the shear modulus (a ratio of shear stress to shear strain),  $\rho_q$  is the density, and  $t_q$  is the crystal thickness. The amount of energy lost during oscillation at this frequency is at a minimum. The ratio of peak energy stored to energy lost per cycle is referred to as the quality factor,  $Q$  and is given by the equation

$$Q = \frac{f_c}{\Delta f_{FWHM}} \quad (2)$$

where  $f_c$  is the center frequency and  $\Delta f_{FWHM}$  is the full width at half max. This full width at half max is also called the bandwidth. For quartz crystals in air,  $Q$  can exceed 100,000 while in solution  $Q$  decreases to  $\sim 3000$ . This is because the crystal has been damped by the solution. This damping increases the amount of energy lost per cycle, decreasing  $Q$  as shown in Figure 2 below.

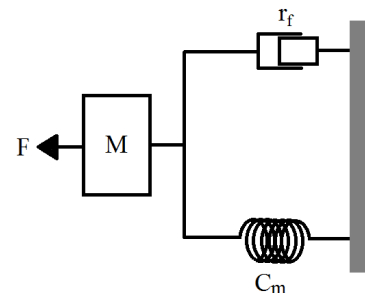


**Figure 2. Comparison of High Q and Low Q.**

### Equivalent Circuit Model

The mechanical model (Figure 3) of an electroacoustical system consists of a mass ( $M$ ), a compliance ( $C_m$ ), and a resistance ( $r_f$ ). The compliance represents energy stored during

oscillation and the resistance represents energy dissipation during oscillation.



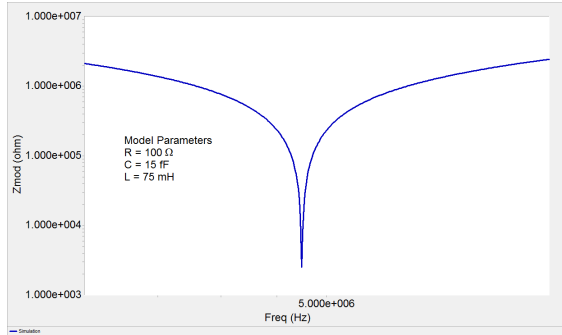
**Figure 3. Quartz Crystal Microbalance Equivalent Mechanical Model.**

The QCM mechanical model can be electrically modeled in several different ways. The easiest model to understand might be an RLC circuit as shown in Figure 4.



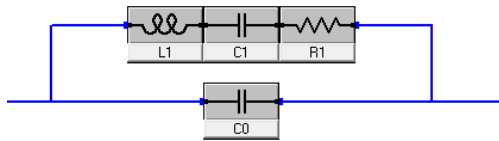
**Figure 4. RLC Circuit.**

Here  $R_1$  represents the energy dissipated during oscillation,  $C_1$  represents the energy stored during oscillation, and  $L_1$  represents the inertial component related to the displaced mass. At the resonant frequency,  $f_s$ , the impedance of the circuit is at a minimum and is equal in magnitude to  $R_1$  as shown in Figure 5.



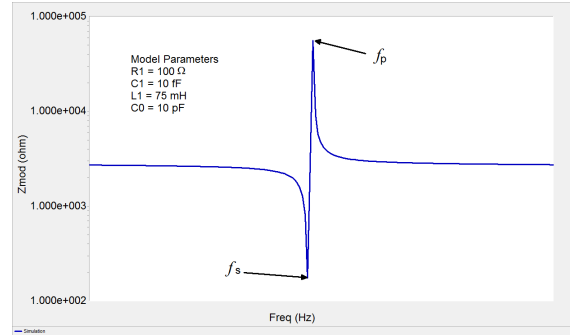
**Figure 5. Impedance Spectrum for a Series RLC Circuit.**

Making electrical contact to a quartz crystal is most easily done by addition of an electrode to each face of the crystal. These electrodes introduce an additional capacitance ( $C_0$ ) in parallel with the series RLC as shown in Figure 6. This circuit is commonly referred to as the Butterworth – van Dyke (BvD) model.



**Figure 6. Butterworth – van Dyke Equivalent Circuit Model.**

The circuit shown above now has two resonant frequencies,  $f_s$  and  $f_p$ , which stand for the series resonant frequency (as in the original RLC circuit) and the parallel resonant frequency, respectively. The impedance spectrum for the BvD model is shown below with a minimum at  $f_s$  and a maximum at  $f_p$ .



**Figure 7. Impedance Spectrum for the Butterworth – van Dyke Equivalent Circuit Model.**

Most commercial QCMs that rely upon a phase lock oscillator, manually cancel out  $C_0$ , and only report the series resonant frequency,  $f_s$  since  $f_s \sim f_0$  and  $f_s$  is obviously dependent upon  $L_1$ . The eQCM 10M reports both frequencies,  $f_s$  and  $f_p$ , and a relative impedance spectrum.

Since these two resonant frequencies are dependent upon  $L_1$ , mass changes on the surface of the electrode will result in frequency changes. When a deposited film is thin and rigid, the decrease in frequency can be directly correlated to the increase in mass using the Sauerbrey<sup>4</sup> equation.

$$\Delta f_s = -\frac{2f_0^2 mn}{(\mu_q \rho_q)^{1/2}} \quad (3)$$

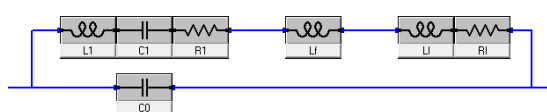
where  $f_0$  is the fundamental frequency of the crystal as defined in Equation (1),  $m$  is the mass added,  $n$  is the harmonic number (e.g.  $n = 1$  for a 5 MHz crystal driven at 5 MHz), and  $\mu_q$  and  $\rho_q$  are as defined above. Equation (3) can be reduced to

$$\Delta f = -C_f m \quad (4)$$

where  $C_f$  is the calibration constant. The calibration constant for a 5 MHz At-cut quartz crystal in air is  $56.6 \text{ Hz cm}^2 \mu\text{g}^{-1}$ .

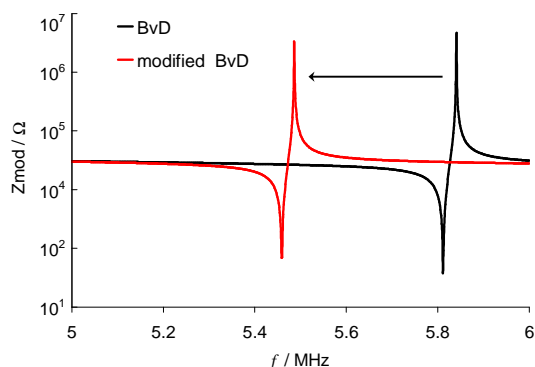
The majority of electrochemical experiments will correspond to a low-loading case, allowing you to directly correlate changes in frequency with changes in mass using the Sauerbrey equation (4).

Once a film has been deposited and the quartz crystal is immersed in a liquid, the BvD model can be modified as shown below to include coupling to the liquid.



**Figure 8. Equivalent Circuit Model for a Quartz Crystal Immersed in a Liquid**

Three new components account for the mass loading of the film,  $L_f$ , and the liquid loading (based on  $\eta_L$  and  $\rho_L$ ),  $L_l$  and  $R_l$ . Both new mass loadings  $L_f$  and  $L_l$  have the effect of reducing the frequency as indicated with the black arrow in the chart below. The original BvD model (black curve) shows resonance approximately 300 kHz higher than the modified BvD model (red curve). Notice that the shapes of the resonance curves are identical despite the addition of the film and liquid loading.



**Figure 9. Comparison of BvD and Modified BvD Models.**

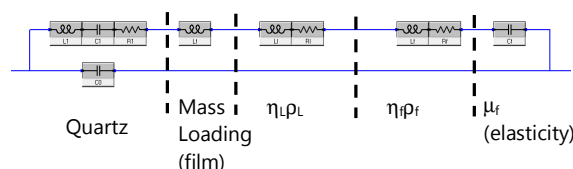
Knowing the liquid's viscosity and density allows one to calculate<sup>3</sup> the expected frequency decrease upon immersing the crystal in that liquid using the equation

$$\Delta f = -f_a^{3/2} \left( \frac{\eta_L \rho_L}{\pi \mu_q \rho_q} \right)^{1/2} \quad (5)$$

where  $f_a$  is the frequency of the crystal in air,  $\eta_L$  is the viscosity of the liquid,  $\rho_L$  is the density of the liquid,  $\mu_q$  is the shear modulus of the quartz crystal, and  $\rho_q$  is the density of the quartz crystal.

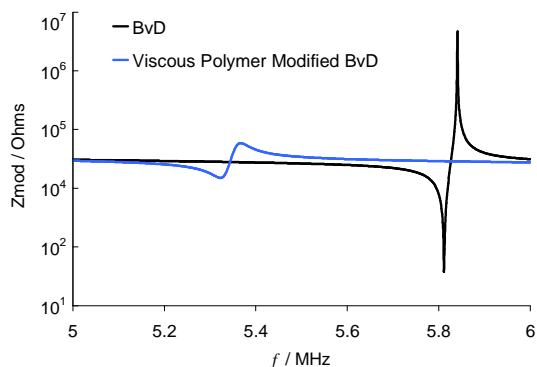
For example, upon immersing the crystal in pure water, a frequency decrease of approximately 800 Hz is expected.

Equation (4) holds as long as the film is assumed to be thin and rigid. When the film is no longer acoustically thin or is not rigid the BvD model can be modified further as shown below.



**Figure 10. One Possible Equivalent Circuit Model for a Quartz Crystal Coated with a Polymer Film and Immersed in a Liquid**

Two new features have been added – Film Loading ( $\eta_f \rho_f$ ) and Elasticity ( $\mu_f$ ). A viscoelastic polymer will influence the resonant frequencies based on the film's viscosity ( $\eta_f$ ), density ( $\rho_f$ ) and elasticity ( $\mu_f$ ). If the polymer is rigid or  $\eta_f \rho_f$  does not change during the experiment, there will be no change in peak shape and contributions from  $\eta_f \rho_f$  can be ignored. In cases where  $\eta_f \rho_f$  does change during the experiment, the frequency, magnitude and shape of the peak will also change as shown in Figure 11.



**Figure 11. Comparison of BvD and Viscous Polymer Modified BvD Models.**

Another way to visualize if  $\eta_f \rho_f$  is changing during an experiment is to look at the reduced quality factor,  $Q_R$  as a function of time.

$$Q_R = \frac{(f_s + f_p)/2}{(f_p - f_s)} \quad (6)$$

Changes in  $Q_R$  correspond to changing  $\eta_f \rho_f$ . Quantifying changes in  $\eta_f \rho_f$  is challenging mathematically and will not be explored further here. The reader is directed to the literature<sup>5</sup> for additional information at this time.

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