

Calculated Behaviors and Interplays of Harmonic Resonances in the QCM

Kay Keiji Kanazawa
 Department of Chemical Engineering
 Stauffer III, 381 North-South Mall
 Stanford University
 Stanford, CA 94305-5025
 Tel: (650)723-7891
 Email:
 kanazawa@chemeng.stanford.edu

Measurement of the behavior of the odd overtones of the fundamental resonant frequency of a quartz crystal microbalance (QCM) is receiving increasing attention. For overlayers which are non-dispersive such as Newtonian liquids or elastic solids, these overtones provide additional measurements to serve to verify the measurements taken at the fundamental frequency. These are being used, for example, in the QCM-D instrument commercially available from Q-Sense. Similar measurements are also available using impedance analysis techniques on the quartz resonator. For each separate resonance, the changes in the resonant frequency and the resonator losses are determined and compared to existing models. We present here an analytical study of those changes focused however, not on each separate resonance, but on the interplay of the various resonances. To our knowledge, such a study has not been available to date.

The analysis is based on the electromechanical model from which the values of the equivalent circuit parameters used to describe crystal resonances are calculated under various conditions of loading. These values are the resonant frequency itself, along with the inductance, series capacitance, and resistance of that equivalent circuit. This is studied as a function of the load on the QCM. This loading varies as the acoustic thickness of the deposited overlayer changes. In the simplest case, this situation occurs when a layer of fixed mechanical properties increases in thickness. This takes place under conditions of uniform deposition. Another situation occurs when the layer is of fixed thickness, but the shear modulus of the film varies. In the case of the formation of a gel layer for example, this shear modulus would be

thought to decrease. The decreased modulus gives rise to an increasing acoustic thickness. For utility to the user, these equivalent circuit changes are plotted either as a function of the thickness of the deposit or as a function of the shear modulus.

For the case of the softening film, where the shear modulus is presumed to vary for a film of fixed thickness, we plot the inverse of the square root of the modulus along the abscissa. At $x=0$, the stiffness (or modulus) is infinite and with increasing x , the modulus decreases. The resonant frequencies of all the resonances up to the seventh harmonic reveals some very interesting behavior. The most striking is the appearance of resonances at even harmonics. Thus for a 5 MHz crystal, resonances can be seen to occur in the neighborhood of 10, 20 and 30 MHz. The absence of the even harmonics for unloaded crystals is a result of the symmetry of the system. When loaded only on one face however, the symmetry is broken and it is not surprising then that even harmonics will occur. While evidence for this same behavior is still seen in the case where the modulus is fixed, but the thickness varies, it is not quite so clear. Another characteristic of interest that can be seen in both sets of curves are the crossing of the resonances. For one specific case, the resonance which is near 15 MHz for thin films decreases in frequency to approach 5 MHz at some thickness value. As it approaches 5 MHz, the resonance which was near 5 MHz for thin films suddenly decreases in frequency. This behavior is very reminiscent of that of coupled oscillators where the oscillation frequencies approach one another.

We show the behaviors of the inductance, series capacitance and resistance with increasing acoustic thickness. All of these variables undergo extremely large changes, even with the presumption of an elastic film. Time permitting, we will discuss the changes in these behaviors as the film properties include a film viscosity.