

## Signatures For Newtonian Fluids On Smooth QCM's

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### INTRODUCTION

An increasing number of applications for the quartz crystal microbalance (QCM) involves its use in liquid media. For modeling, the liquid is most often treated as Newtonian, having a constant viscosity and no elastic energy storage over the frequency range of interest. There are occasions in which the experimental measurements such as frequency change and resistance change upon immersion of the QCM from air to liquid are at variance with the model predictions. These discrepancies have been attributed to non-Newtonian fluid behavior or rough surfaces. We describe here two different combinations of experimental observables whose value can serve as signatures, or indicators of immersion into a Newtonian fluid.

### CALCULATIONS

The theoretical underpinnings for this study are all contained in the early paper by S.J. Martin, V.E. Granstaff and G.C. Frye(1) which we refer to as MGF.

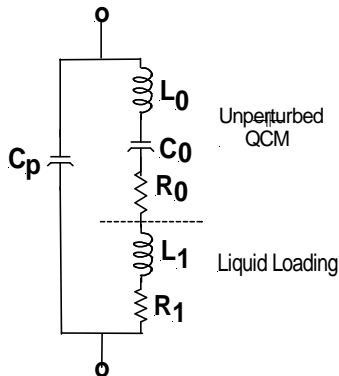


Figure 1. The modified BvD Circuit of MGF.

An important concept they developed was that the effects of the liquid are described by additional circuit elements which are independent of the elements describing the quartz. They obtained explicit expressions for all of these elements in terms of the physical parameters of the quartz and liquid. Using those expressions, we have calculated relations describing the changes in frequency and resistance upon immersion as follows:

$$\Delta f = -\sqrt{N} f_{1U}^{3/2} \sqrt{\frac{\rho_L \eta_L}{\rho_Q \bar{c}_{66}}} \quad (1)$$

$$\Delta R = \frac{\pi \bar{c}_{66} h_Q}{8e_{26}^2 A} \sqrt{\frac{N}{f_{1U}}} \sqrt{\frac{\rho_L \eta_L}{\pi \rho_Q \bar{c}_{66}}} \quad (2)$$

$N$  is the harmonic number,  $f_{1U}$  is the fundamental resonant frequency of the unloaded crystal,  $\rho_L$  and  $\eta_L$  are the density and viscosity of the liquid,  $\rho_Q$  is the quartz density,  $\bar{c}_{66}$  the piezoelectrically stiffened quartz shear modulus,  $h_Q$  is the quartz thickness,  $e_{26}$  is the piezoelectric constant, and  $A$  is the effective electrode area. From these, we show that the ratio of  $\Delta f/\Delta R$  which we call the signature  $S_1$ , yields a number independent of the liquid parameters and of the harmonic number. It does depend on the area. But recognizing that the dissipation  $D=\omega L_Q/(R_0+R_1)$ , then the dissipation change  $\Delta D$  upon immersion can be calculated. If we take  $S_2=\Delta f/N\Delta D$ , we find that this comes to the very simple value of  $f_{1U}/2$ ! This is independent of area. For a 5 MHz Maxtek crystal, we find that  $S_1=2.03$  and  $S_2=2.5 \times 10^6$ . We find support of these values by obtaining the value of these ratios using the complete electromechanical theory.

### RESULTS

We have compared these predictions to an initial limited set of water-glycerol solutions. Using the Maxtek RQCM we measured  $\Delta f$  and  $\Delta R$ , as shown in the table below:

Table 1. Values of  $S_1$

Pct Glycerol	$S_1$
0	1.997
15	1.956
30	1.960
50	1.860
75	2.70

The values are all very close to the model value of 2.03. The discrepancies at the higher glycerol concentration are probably due to measurement inaccuracy resulting from the small current in the crystal resulting from the extremely high resistance.

Comparative measurements using the QCM-D instrument was possible only for the zero and 15% glycerol solution due to difficulties in introducing the more viscous solutions into the cell. These results are shown below:

Table 2. Values of  $S_2 \times 10^{-6}$  at various harmonics

Pct Gly	N=1	N=3	N=5	N=7
0	2.04	2.43	2.41	2.33
15	2.26	2.57	2.54	2.65

The values are in reasonably good agreement, with perhaps the exception of the fundamental. We have frequently had problems with obtaining reliable data at the fundamental frequency. It was satisfying that the relation holds over the harmonic range.

### SUMMARY

Expressions for two combinations of experimental measurables were obtained from the MGF theory. These combinations called  $S_1$  and  $S_2$  are predicted to yield values which are independent of harmonic number and of liquid parameters. These model values are predicated on a Newtonian liquid and a smooth surface. Failure of either of these would be expected to yield values quite different from the model calculations.

REFERENCE 1. S.J. Martin, V.E. Granstaff and G.C. Frye, Anal. Chem. **63**, 2272 (1991)

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