Some Thoughts on the QCM that Might Eventually Get Turned into a Paper

Kenneth R. Shull and Diethelm Johannsmann

December 19, 2018

1 Relevant QCM Equations

One of the many great things about your book is that I don't need to feel the need to derive anything. It's already all out there. The aim of this section is to get all the equations you would need to develop a full solution all in one place. I'll eventually add a bit more to this, but I want to keep it reasonably concise, with clear definitions of everything but generally not worrying about approximations (apart from the SLA) or derivations.

The Lu-Lewis equation (Eq. 10.1.5 from ref. [1]) is

$$Z_q^* \tan\left(k_q^* d_q\right) = -Z_f^* \tan\left(k_f^* d_q\right) \tag{1}$$

The equation we actually solve numerically is Eq. 4.5.9 from ref. [1] :

$$\left[\frac{1}{iZ_q^* \tan\left(k_q^* d_q/2\right)} + \frac{1}{iZ_q^* \tan\left(k_q^* d_q/2\right) + Z_L^*}\right]^{-1} - \frac{iZ_q^*}{\sin\left(k_q^* d_q\right)} - \frac{\Phi^2}{i\omega C_0} = 0 \tag{2}$$

The complex complex load impedance is obtained from the impedance and complex wave number within each layer. The wave vector in each layer is evaluated at the complex resonant frequency, accounting for the loading of the crystal:

$$k_n^* d = \frac{2\pi \left(nf_1 + \Delta f_n^*\right) d\rho}{Z_n^*} \tag{3}$$

I haven't yet worked out all the algebra to convince myself that Eqs. 1 and 2 are actually the same equation (when the stiffening term in 2 is neglected), but I assume this works out to be the case. Also, how should we refer to the treatment based on the solution of Eq. 2? It doesn't seem that this is really due to Lu and Lewis.

I incorporated your solution to Eq. 2 in my own python code and regenerated your Fig. 1 in the paper I reviewed. The only thing I did which is a bit different is to assume a self consistent power law behavior for the rheology of the material, with a constant phase angle at all frequencies, equal to 90 degrees multiplied by the power law. So we have:

$$|G_n^*| = \left|G_{n_{ref}}\right| \left(n/n_{ref}\right)^{\phi/90} \tag{4}$$

Part of my motivation here is to convince the community is that Eq. 4 should ALWAYS be used in an appropriate way when analyzing rheological QCM data. I'm not sure if you agree or not, but I'll put some of my reasoning in this document and we can continue to iterate. In our group

we generally use $n_{ref} = 3$ for the reference harmonic. With this, I get a comparison of the full treatment (I refer to it as the Lu-Lewis or LL model) and the small load approximation (SLA) that looks very similar to what you have in your paper (see Figure 1). For all of my calculations I have used the following for the electrode properties, which I believe is the same as what you have used:

$$(d\rho)_{electrode} = 2.8\,\text{g}/\text{m}^2$$
$$(|G_3^*|\rho)_{electrode} = 3.0 \times 10^{11}\,\text{Pa} \cdot \text{g}/\text{cm}^3 \tag{5}$$
$$\phi_{electrode} = 0$$

For the film properties, I assume the following, which is closely related to what you used in your paper:

$$(d\rho)_{film} = 0.4\,\text{g}/\text{m}^2$$
$$(|G_3^*|\rho)_{film} = 5 \times 10^8\,\text{Pa} \cdot \text{g}/\text{cm}^3 \tag{6}$$
$$\phi_{film} = 11.3°$$

A comparison of results obtained from the small load approximation and the Lu-Lewis equation is shown below: I was really surprised from your paper to see this dramatic difference in the two treatments, which motivated me to make sure that the SLA was okay for what we are doing. It seems that we are indeed okay, but I really like the idea of getting a unifying treatment out there that includes both of our perspectives.
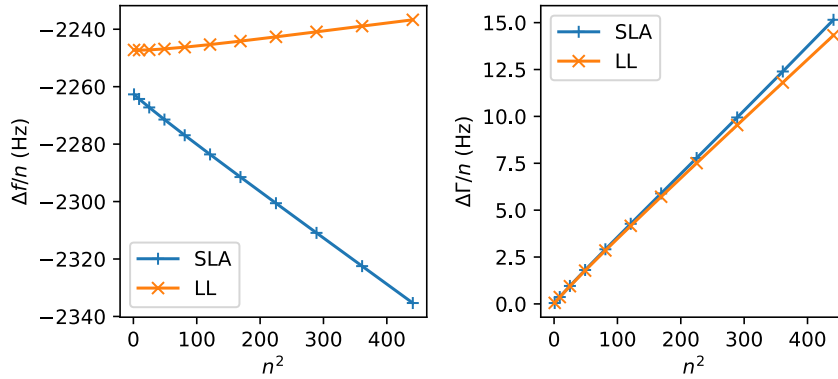

Figure 1: Comparison of the LL and SLA models for the electrode properties given in 5 and the film properties given in 6.

To get a handle on how the Lu-Lewis results depend on the material properties, I fix the properties as defined in Eqs. 5 and 6, except for the magnitude of the film modulus, which is allowed to vary. This is what I obtain:
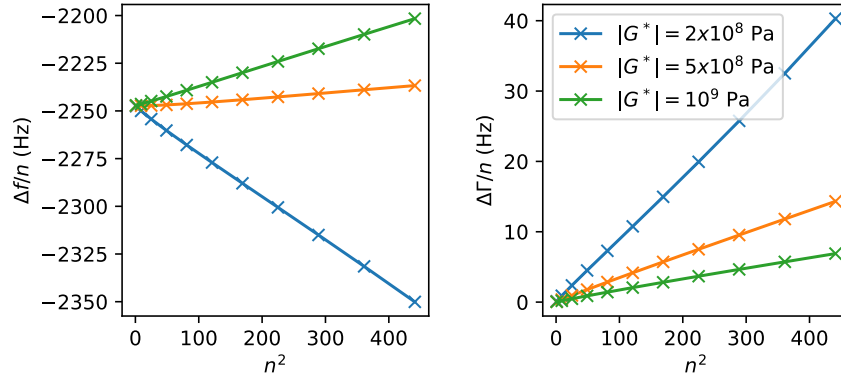
Figure 2: Result from the Lu-Lewis model for the parameters listed in Eqs. 5 and 6 varying the values of $\left| G_3^* \right|$ for the film as indicated (with $\rho_f = 1 \text{ g/cm}^3$).

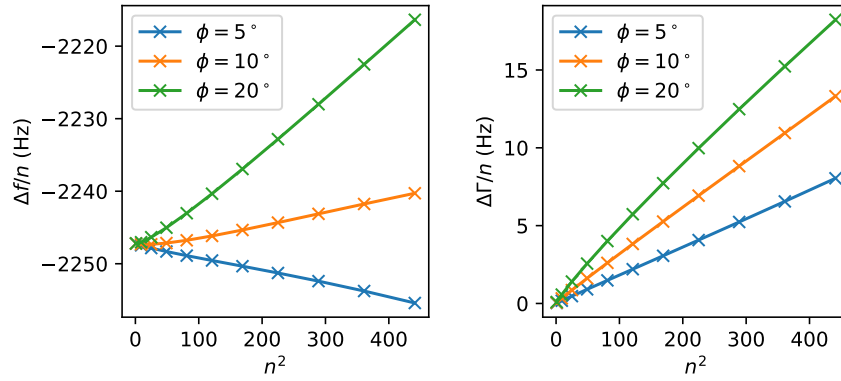Finally, if I fix everything but allow the phase angle to vary, this is what I obtain:

Figure 3: Result from the Lu-Lewis model for the parameters listed in Eqs. 5 and 6 varying the values of ϕ for the film as indicated.

2 Thicker films

Things look quite a bit different if we use thicker films. Suppose we use a 5 μm glassy polymer film, representative of some of our experiments. Here's the set of film properties:

$$
\begin{aligned}
(d\rho)_{film} &= 5 \text{ g/m}^2 \\
\left(\left| G_3^* \right| \rho \right)_{film} &= 10^9 \text{ Pa} \cdot \text{g/cm}^3 \\
\phi_{film} &= 1.5°
\end{aligned}
\tag{7}
$$

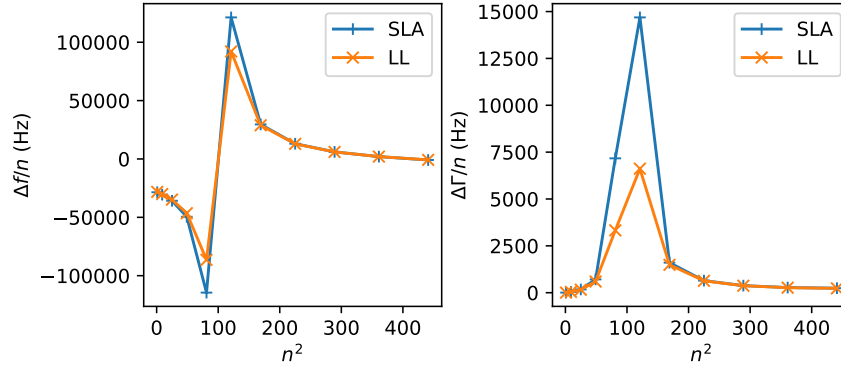Here's what the comparison of the LL and SLA models looks like in this case:

Figure 4: Comparison of the LL and SLA models for the electrode properties given in 5 and the film properties given in 7.

If we replot this as a function of linear *n* and just worry about the first few harmonics, it looks like the plot below.
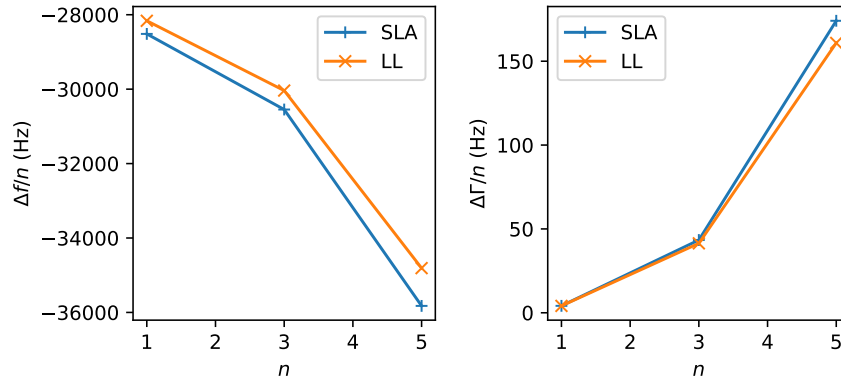

Figure 5: Comparison of the LL and SLA models for the electrode properties given in 5 and the film properties given in 7.

References

[1] Johannsmann, D. *The Quartz Crystal Microbalance in Soft Matter Research*. Soft and Biological Matter (Springer International Publishing, Cham, 2015). URL http://link.springer.com/10.1007/978-3-319-07836-6.