Supporting Information

# Viscoelastic Modelling with Interfacial slip of a Protein Monolayer Electrode-Adsorbed on an Acoustic Wave Biosensor

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**1. Estimation of unloaded frequency**

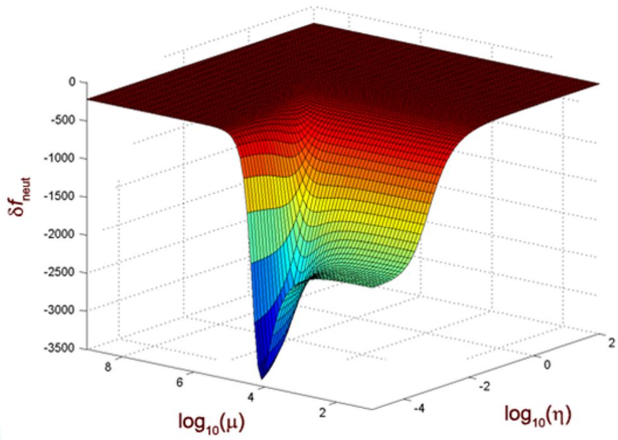
An estimate of the unloaded frequency of the device $f_0$ is required to calculate the expected frequency shift from Eq. 3. As mentioned above, this was not recorded in the original experiments. However, an estimate of $f_0$ can be obtained from the aqueous buffer assumption. Since each run was started in the buffer, the only initial frequency available is that for a device already loaded with buffer, such that $f_{obs}=f_0+\Delta f_{liq}$, where $f_{obs}$ is observed experimentally and $\Delta f_{liq}$ can be determined from Eq. 2. Therefore, from the observed initial frequencies and the assumption that the buffer has the properties of water, the fundamental frequency $f_0$ is given by

$$
\begin{aligned}
f_0 &= f_{obs} - \left[ \frac{-f_0}{\pi Z_q} \mathrm{Im}(Z_L) \right] \\
&= f_{obs} + \frac{f_0}{\pi Z_q} \mathrm{Im}\left( (1+j)\sqrt{\frac{2\pi f_0 \eta \rho}{2}} \right) \quad \text{(S1)} \\
&= f_{obs} + \frac{f_0^{3/2}}{Z_q}\sqrt{\frac{\eta\rho}{\pi}}
\end{aligned}
$$

Eq. S1 was solved numerically using the `fsolve` function in Octave 3.0.1, to obtain $f_0$.

## 2. Error analysis for the viscoelastic response

We test a wide range of stiffness and viscosity values observe the behavior of the neutravidin layer, varying the shear modulus between $\mu_f = 10 \rightarrow 10^9$ g·cm$^{-1}$·s$^{-2}$ and $\eta_f = 10^{-5} \rightarrow 10^2$ g·cm$^{-1}$·s$^{-1}$. For reference, $\mu_{\mathrm{quartz}} = 2.9\times10^{11}$ g·cm$^{-1}$·s$^{-2}$, $\mu_{\mathrm{gold}} = 50\times10^{11}$ and $\eta_{\mathrm{water}} = 10^{-2}$ g·cm$^{-1}$·s$^{-1}$. Fig. S1 shows surface plots of the absolute errors between the estimated and experimental values for typical experimental values, for the ranges of $\mu_f$ and $\eta_f$.



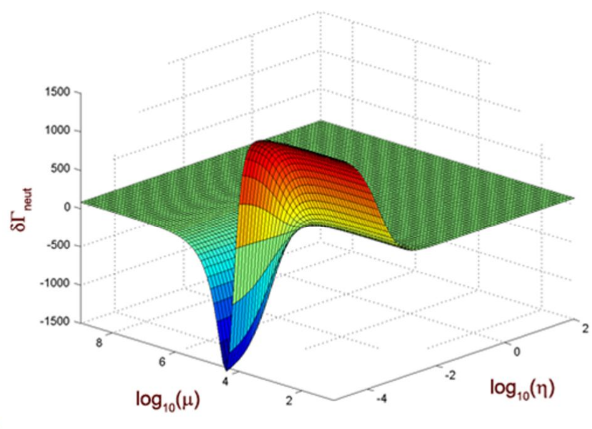




Figure S1. Absolute error between the model results for a) frequency and b) bandwidth, calculated with $\rho_{\mathrm{NAv}}$=0.875 g·cm$^{-3}$ and thickness 4.2 nm, and experimental results for run 12, $\Delta f$=-180.9 Hz and $\Delta\Gamma$=28.8 Hz. The spacing between the logarithmic values used in this analysis was $\log_{10}\Delta$=0.1.

The absolute error in Fig. S1 above is given by $\delta_{\mathrm{abs}} = (\Delta_{\mathrm{calc}} - \Delta_{\mathrm{exp}})$, so a value of $\delta_{\mathrm{abs}}$ close to zero is a good prediction of the observed data well. The viscoelastic model is successful at predicting the $\Delta\Gamma$

response in dissipation, with the smallest error being on the order of $\delta\Gamma = 0.06$ for $\mu_f = 4\times10^4$ g·cm$^{-1}$·s$^{-2}$ and $\eta_f = 0.002$ g·cm$^{-1}$·s$^{-1}$. However, the minimum error in the frequency is $\delta f = -224$ Hz, so the maximum predicted $\Delta f$ is -44 Hz. This corresponds to the Sauerbrey wavelength extension for a layer with the given density and thickness, Eq. 1. The monolayer is acoustically very thin at 4.2 nm, so the response is limited by the acoustic energy stored in the thin film.

Another possible explanation is due to errors in the estimate of surface coverage or density of neutravidin. Full surface coverage of neutravidin is approximately 7 pmol·cm$^{-2}$, which would result in less hydration than was used in the estimate. The viscoelastic model can fit the data, but only for $c_{surf} \geq 7$ pmol·cm$^2$, which is quite a bit higher than close packing. With a density 0.87 g·cm$^{-3}$ for full coverage neutravidin monolayer, the maximum gravimetric response is -51.9 Hz. Even if we assume 10 molecular layers of water as a rigidly-bound hydration layer,[15] this yields a gravimetric shift of -106 Hz, somewhat more than half the measured result. The effect of introducing viscoelasticity to this layer, with $\rho_{\text{NAv-full}} = 0.8$ g·cm$^{-3}$ and $h_{\text{NAv-hydrated}} = 7.5$ nm, was tested for the same system as in Figure 5. As above, the model predicts $\Delta\Gamma$ fairly well ($\delta\Gamma_{\text{min}} = 0.1$). However, the best prediction for $\Delta f$ is -107 Hz, which is the gravimetric limit.

Table S1. Model estimates of viscoelasticity and interfacial slip for film relaxation time $\omega\tau = 0.3$. The units of $\mu_{NAv}$ are $g \cdot cm^{-1} \cdot s^{-2}$, for $\eta_{NAv}$, $g \cdot cm^{-1} \cdot s^{-1}$, and for $s$, $cm^2 \cdot s \cdot g^{-1}$. ([a]no solution found for $\omega\tau = 0.3$, so $\omega\tau = 0.22$ was used)

| | $\Delta f$ /Hz | $\Delta R$ /Ω | $\log(\eta_{NAv})$ | $\log(\mu_{NAv})$ | $s_0$ ($\times 10^{-5}$) |
|---|---|---|---|---|---|
| n1 | -175 | 1.38 | -1.90 | 6.36 | 6.96 |
| n2 | -170 | 0.99 | -1.73 | 6.53 | 6.63 |
| n6 | -162 | 1.73 | -2.04 | 6.23 | 6.25 |
| n7 | -214 | 1.82 | -2.16[a] | 6.26 | 9.10 |
| n8 | -188 | 0.78 | -1.63[a] | 5.27 | 9.65 |
| n9 | -182 | 1.77 | -2.05 | 6.22 | 7.57 |
| n10 | -197 | 1.69 | -2.13[a] | 6.29 | 7.95 |
| n11 | -205 | 2.12 | -2.25[a] | 6.16 | 8.54 |
| n12 | -173 | 1.82 | -2.06 | 6.21 | 7.02 |
| n13 | -178 | 1.67 | -2.02 | 6.24 | 7.30 |
| n14 | -181 | 1.86 | -2.07 | 6.19 | 7.57 |
| n15 | -164 | 1.54 | -1.99 | 6.28 | 6.34 |
| n16 | -208 | 2.30 | -2.14 | 6.14 | 8.96 |
| n17 | -189 | 1.61 | -2.09[a] | 6.31 | 7.83 |
| n18 | -157 | 1.48 | -1.99 | 6.27 | 5.85 |
| n19 | -165 | 3.40 | -2.38 | 5.89 | 7.06 |
| n20 | -179 | 1.15 | -1.84 | 6.43 | 7.19 |
| n21 | -174 | 1.25 | -1.87 | 6.40 | 6.94 |
| n22 | -170 | 2.46 | -2.23 | 6.05 | 6.58 |
| n23 | -218 | 2.44 | -2.18 | 6.10 | 9.66 |
| n24 | -178 | 0.79 | -1.70[a] | 5.19 | 9.33 |
| n25 | -197 | 2.60 | -2.34[a] | 6.07 | 8.18 |
| n26 | -176 | 1.47 | -1.95 | 6.32 | 7.11 |
| n27 | -187 | 2.40 | -2.20 | 6.07 | 7.65 |
| | | Mean | -2.0±0.2 | 6.1±0.3 | 8±1 |