TU Clausthal

Studying Soft Interfaces with Shear Waves: Principles and Applications of the Quartz Crystal Microbalance (QCM-D)

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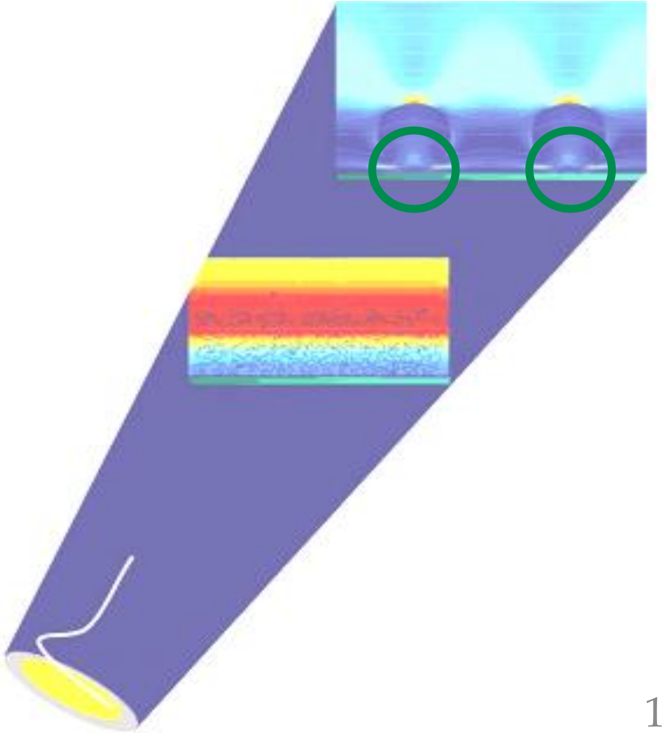
Johannsmann, D.; Leppin, C.; Langhoff, A.,
Studying Soft Interfaces with Shear Waves:
Principles and Applications of the Quartz Crystal Microbalance (QCM).
Sensors ***2021, 21, 3490.***

https://www.pc.tu-clausthal.de/en/research/qcm-modelling/



Acknowledgements
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- Clausthal Group
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- Andreas Böttcher: Hardware
- Philipp Sievers: Software

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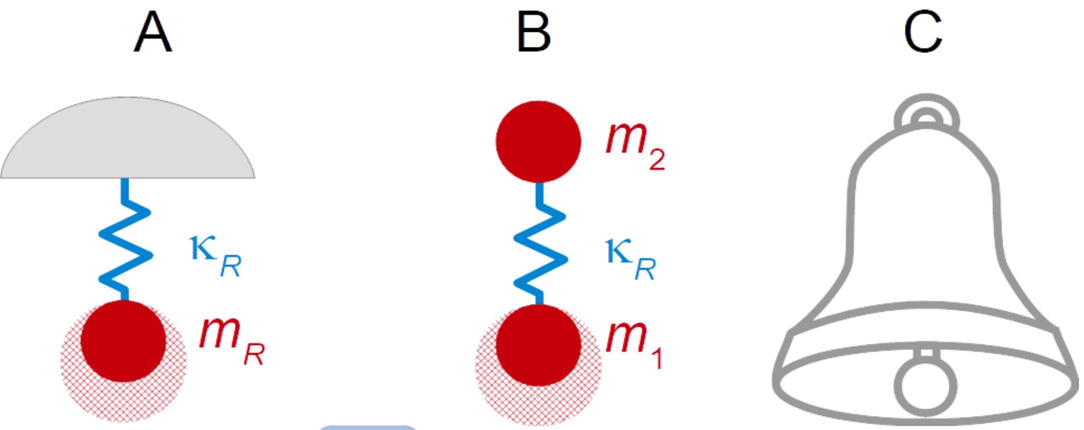
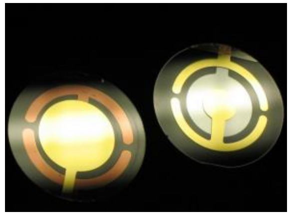
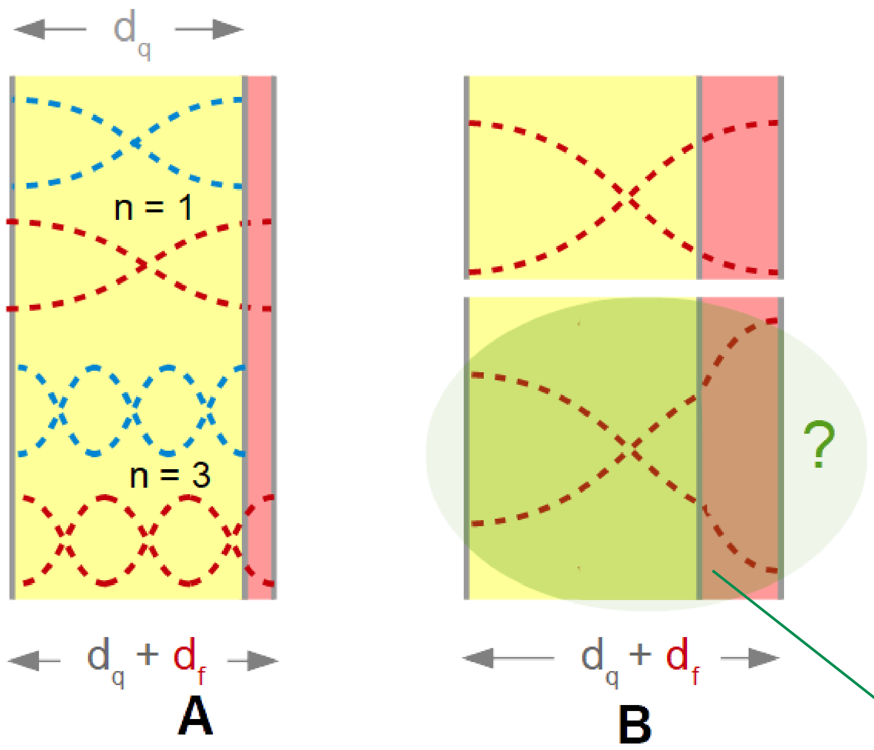


$$\omega_0 \approx (\kappa_R/m_R)^{1/2}$$

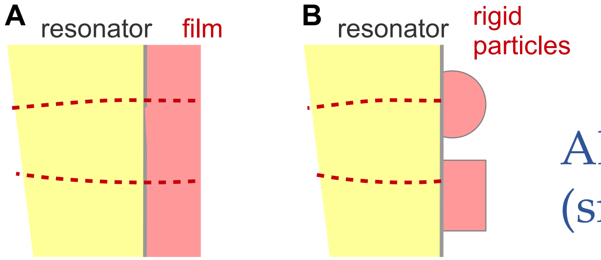




$$\frac{\Delta f}{f_{ref}} = -\frac{m_f}{m_q}$$

$$\Delta f = -\frac{2nf_0^2}{Z_q} m_f$$

Sauerbrey 1959



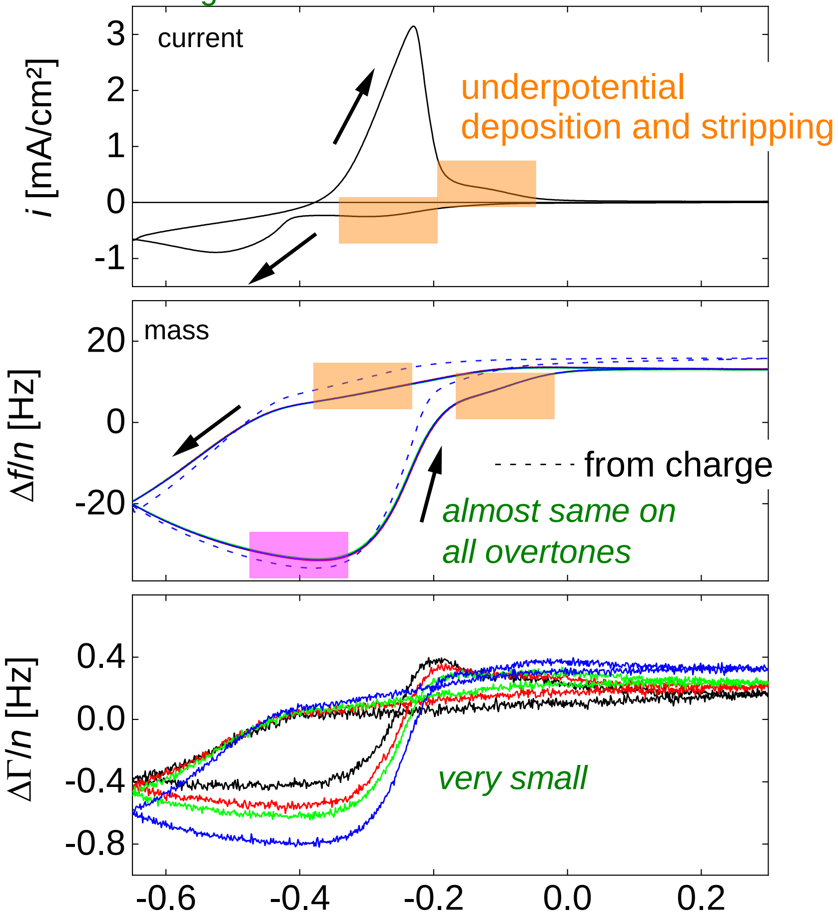
Also applies to (small) particles

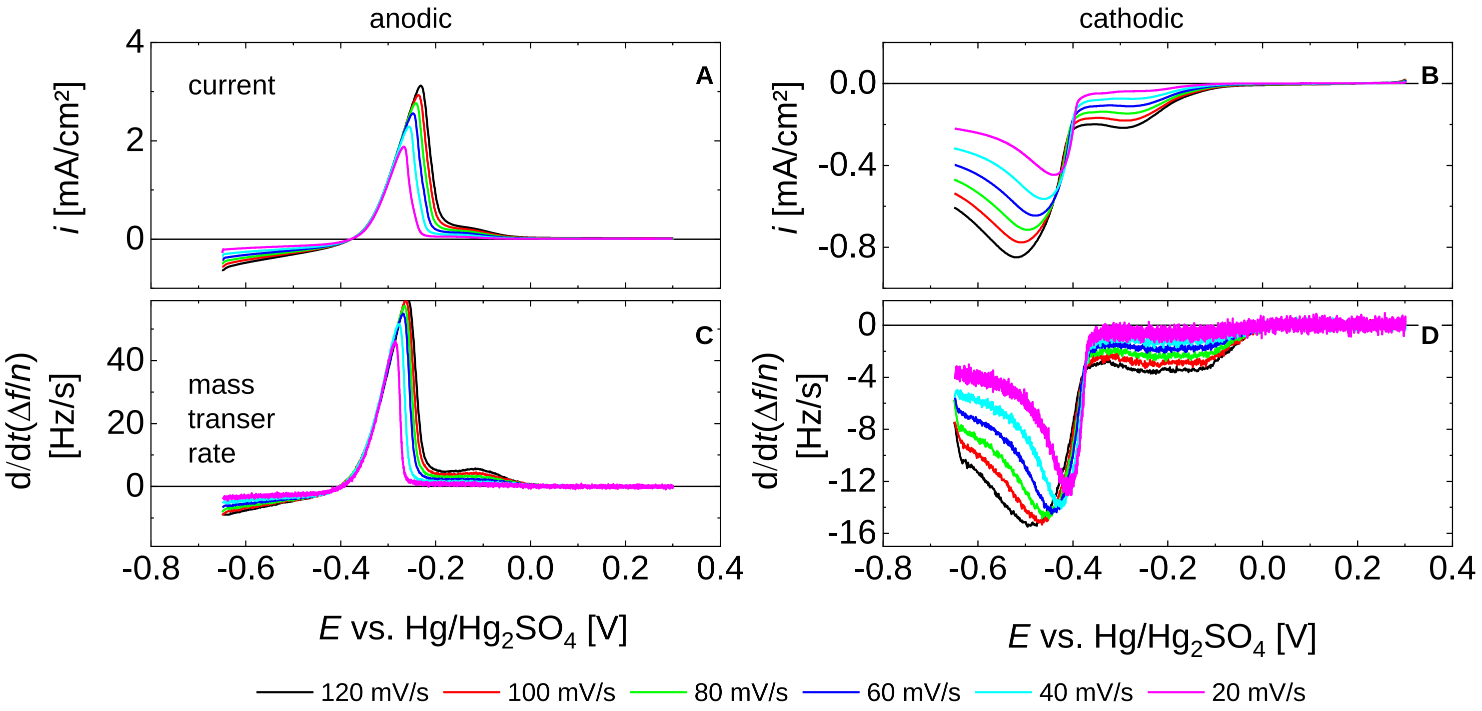
The QCM as a Gravimetric Sensor

Gravimetry not outdated
An example: Electrochemical QCM

current and mass-transfer rate are similar
… but not strictly the same

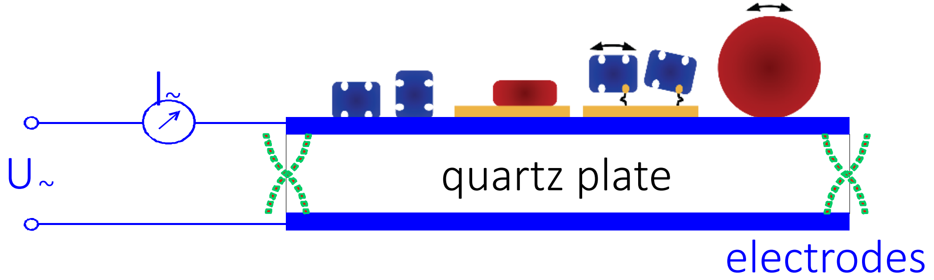
copper electrodeposition / stripping:
non-gravimetric effects weak





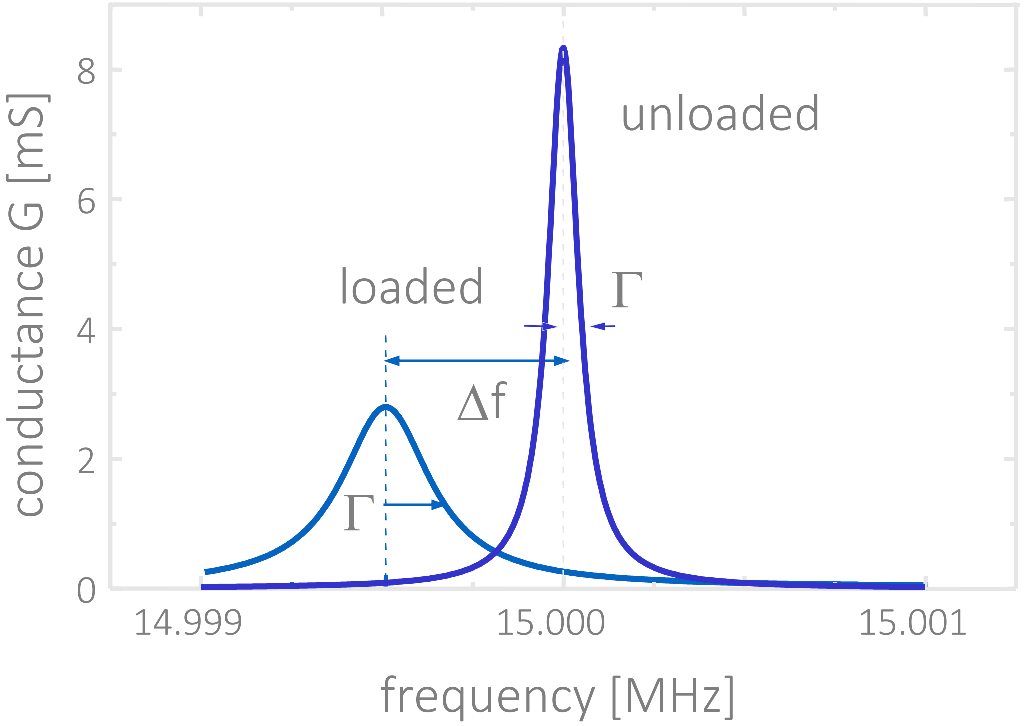
data from Christian Leppin

Beyond Gravimetry: the QCM-D



$f = f_{res}$: large amplitude of motion

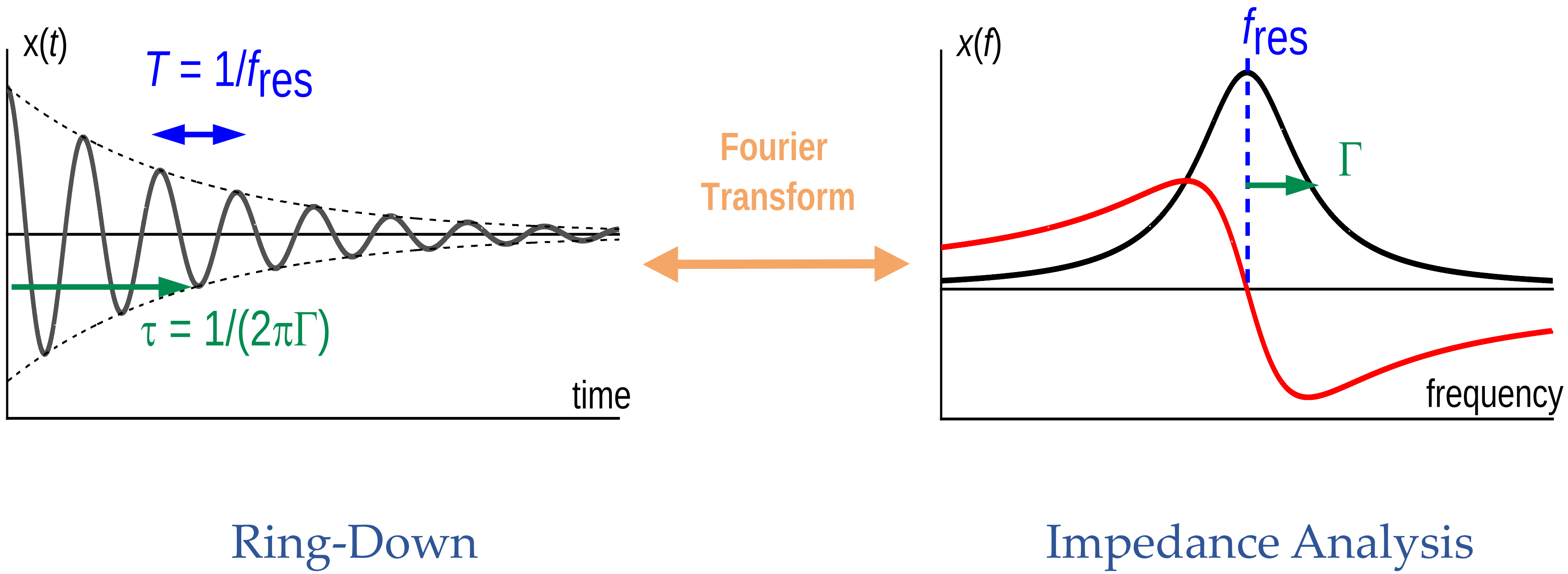
⇒ large current



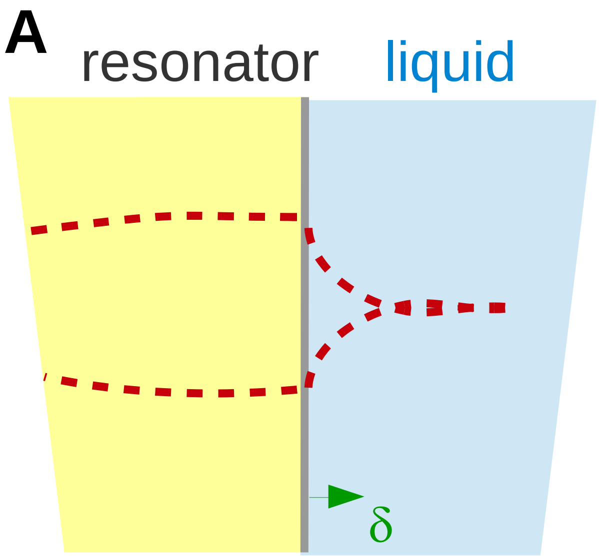
- Shifts in frequency and bandwidth: Δf, $\Delta\Gamma$
  Γ: half-band half width
  $\Delta\Gamma = \Delta D\, f_{res}/2$
  ΔD: shift in dissipation factor, $D = Q^{-1}$

- Many overtones (5, 15, 25, 35, 45, 55, 65 MHz)
  $\Delta f(n)$, $\Delta\Gamma(n)$

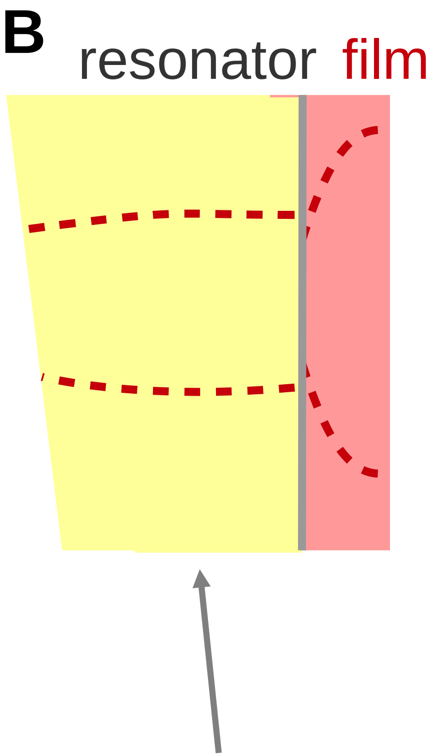
Impedance Analysis and Ring-Down are Equivalent



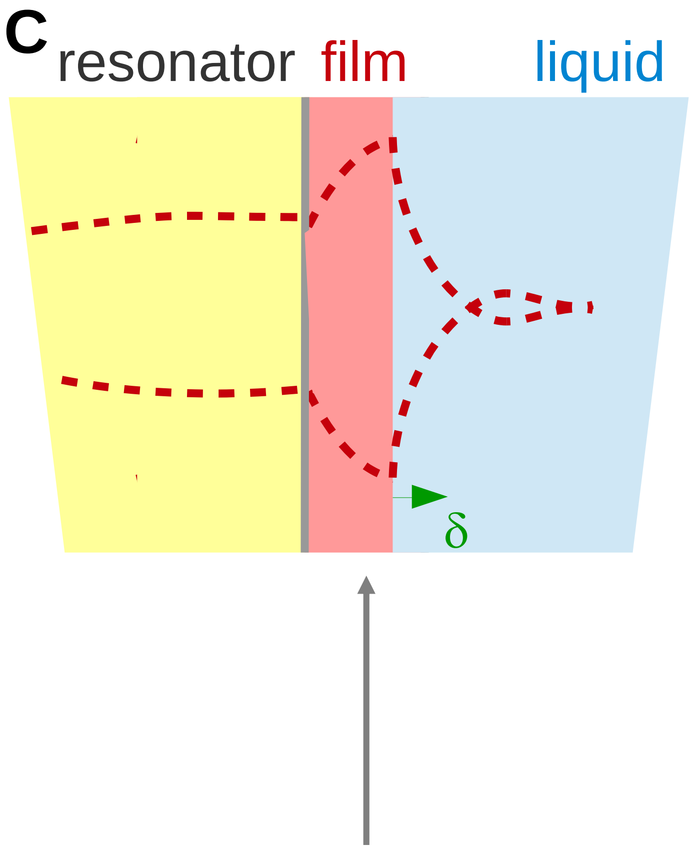
Three Important Cases



$$\frac{\Delta f + i\Delta\Gamma}{f_0} = \frac{i}{\pi Z_q}\sqrt{i\omega\varrho\tilde{\eta}}$$



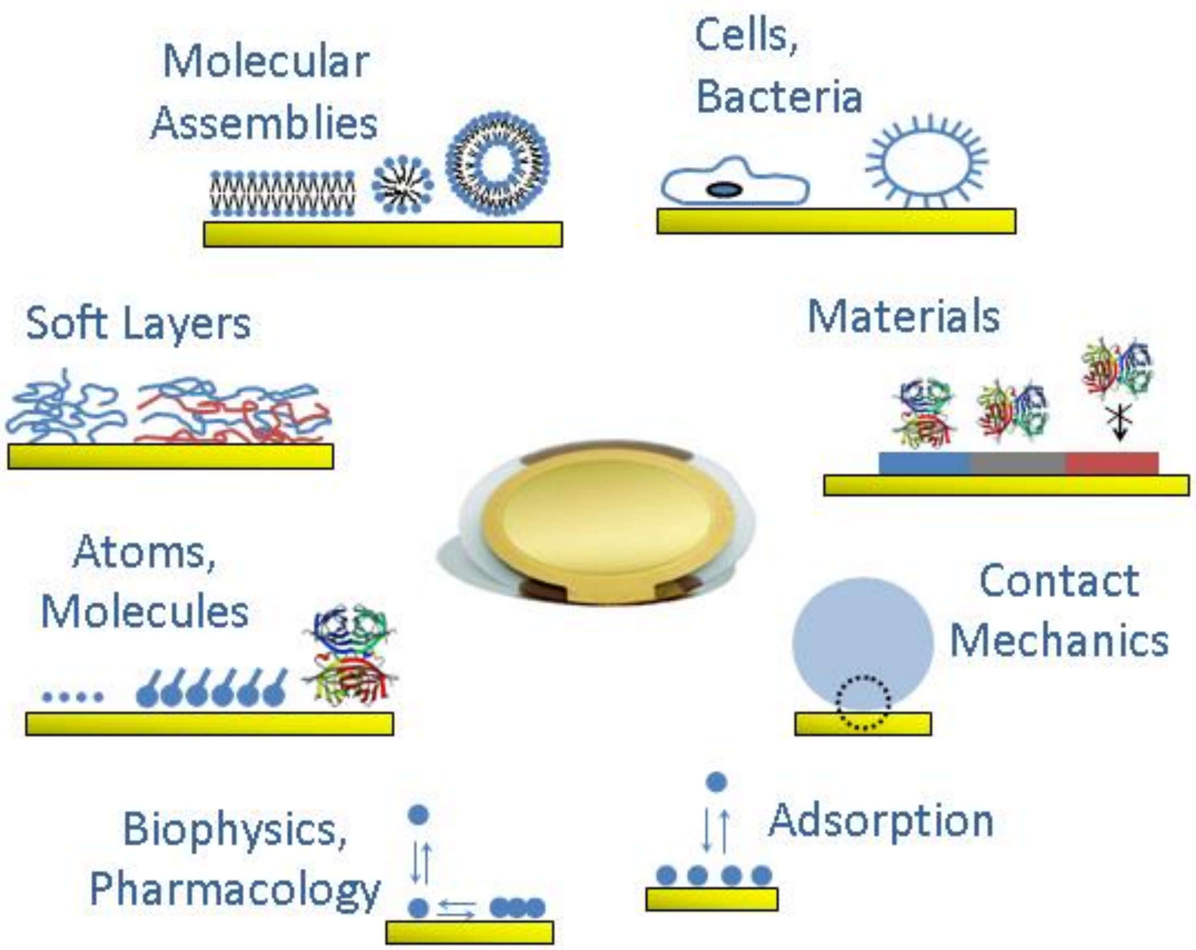
$$\frac{\Delta f + i\Delta\Gamma}{f_0} = \frac{i}{\pi Z_q} i\tilde{Z}_f \tan\left(\tilde{k}_f d_f\right)$$



$$\frac{\Delta f + i\Delta\Gamma}{f_0} = \frac{-\tilde{Z}_f}{\pi Z_q}\cdot\frac{\tilde{Z}_f \tan\left(\tilde{k}_f d_f\right) - i\tilde{Z}_{bulk}}{\tilde{Z}_f + i\tilde{Z}_{bulk}\tan\left(\tilde{k}_f d_f\right)}$$

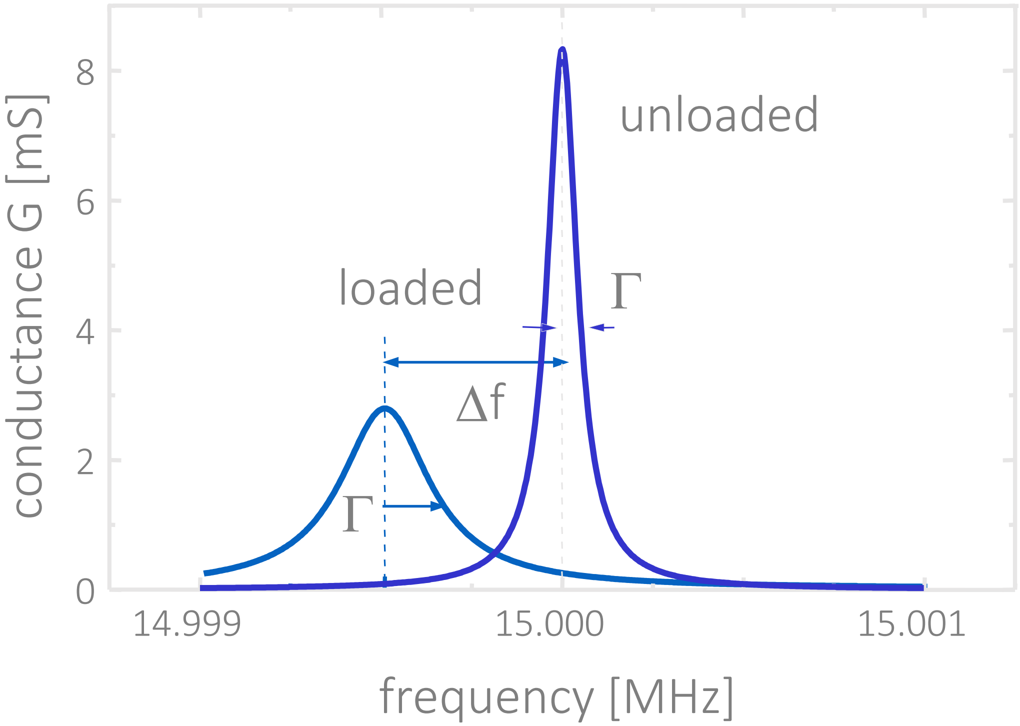
“ ~ “: complex variable

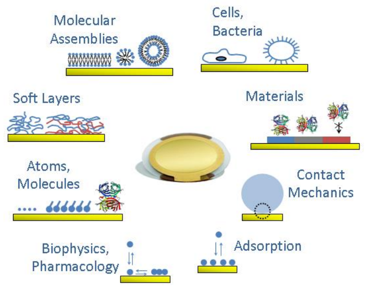
Structured Samples



???

The Small-Load Approximation





$$\frac{\Delta\tilde{f}}{f_0} = \frac{\Delta f + i\Delta\Gamma}{f_0} \approx \frac{i}{\pi Z_q}\tilde{Z}_L = \frac{i}{\pi Z_q}\frac{\hat{\sigma}}{\hat{v}}$$

$\tilde{Z}_L = \frac{\hat{\sigma}}{\hat{v}}$ "load impedance",

can be **area - averaged** $\tilde{Z}_L \rightarrow \left\langle \tilde{Z}_L \right\rangle_{area}$

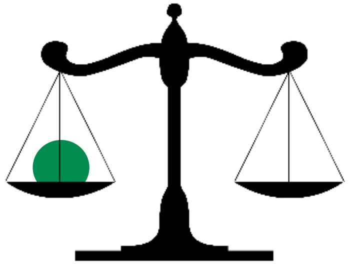
$\hat{\sigma}$ stress

$\hat{v}$ velocity

^: complex amplitude ($\sigma(t) = \hat{\sigma}\exp(i\omega t)$)

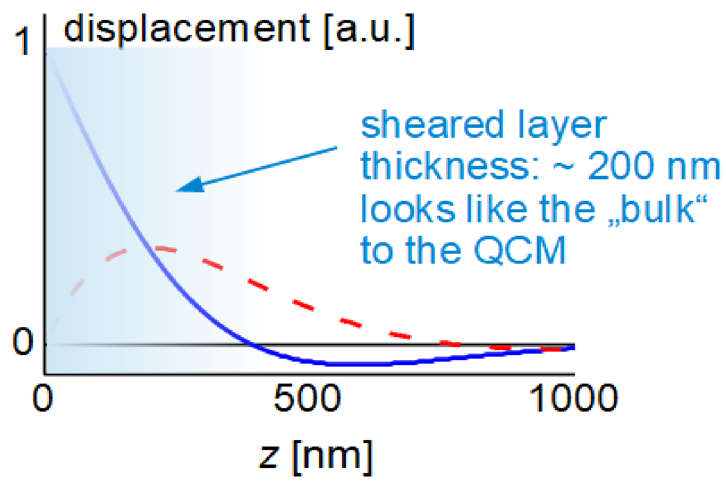
QCM: The Quartz Crystal Micro *Stress*-Balance

- periodic stress,
- in-phase and out-of-phase component determined separately



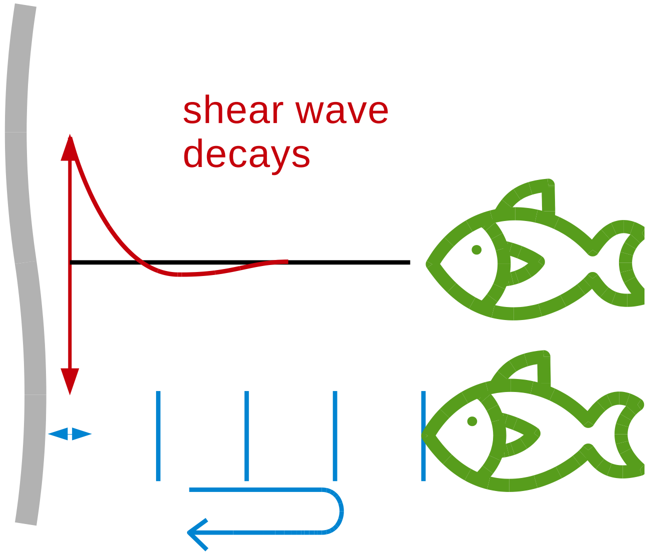
Semi-Infinite Liquids

- finite depth of penetration $\delta = (2\eta/(\rho\omega))^{1/2} \approx 200$ nm
  → QCM is **surface specific**
  unless… compressional waves are reflected somewhere. Avoid a geometry, where the opposite cell wall is parallel to the sensor surface.



- the load impedance is equal to the liquid's shear-wave impedance $\tilde{Z}_L = \tilde{Z}_{bulk} = \sqrt{\rho \tilde{G}} = = \sqrt{\rho i \omega \tilde{\eta}}$
  → Gordon-Kanazawa

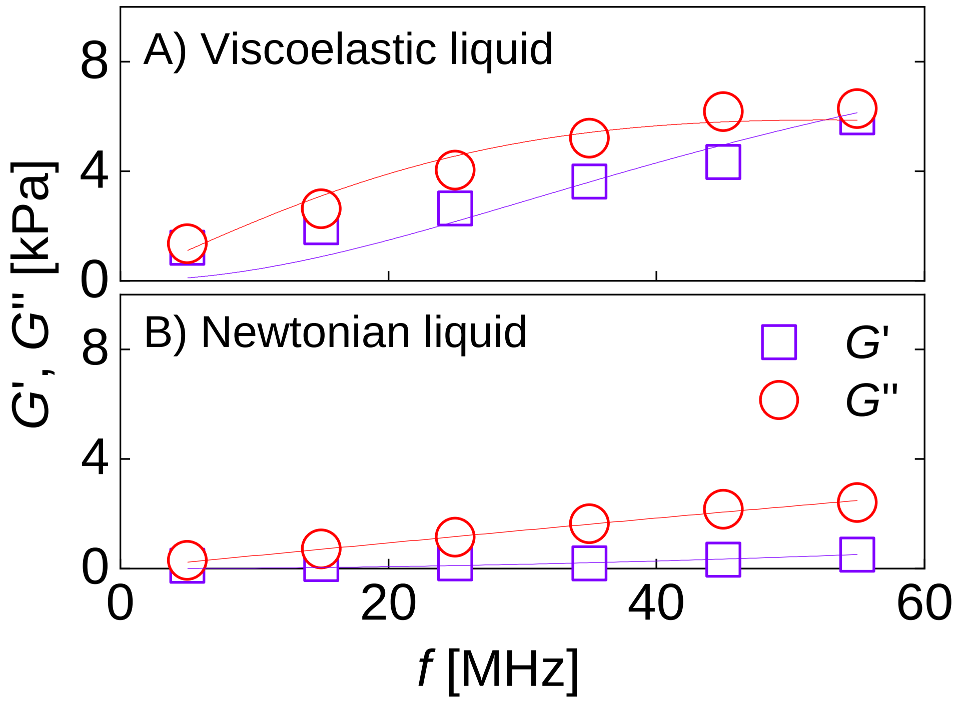
$$\frac{\Delta f + i\Delta\Gamma}{f_0} = \frac{i}{\pi Z_q}\tilde{Z}_{bulk} = \frac{-1+i}{\sqrt{2}}\frac{1}{\pi Z_q}\sqrt{\omega\varrho(\eta' - i\eta'')}$$

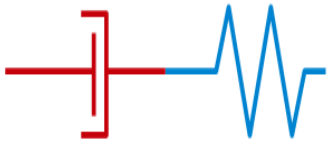


$$\varrho\eta' = \frac{G''}{\omega} = -\frac{\pi Z_q^2}{f_{res}}\frac{1}{2}\frac{\Delta f\,\Delta\Gamma}{f_0^2}$$

$$\varrho\eta'' = \frac{G'}{\omega} = \frac{\pi Z_q^2}{f_{res}}\frac{\left(\Delta\Gamma^2 - \Delta f^2\right)}{f_0^2}$$

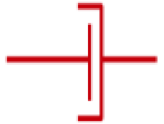
Viscoelastic Semi-Infinite Liquids





$$i\omega(\eta' - i\eta'') = G' + iG'' = G_\infty / (1 - i\omega\tau)$$

τ : relaxation time

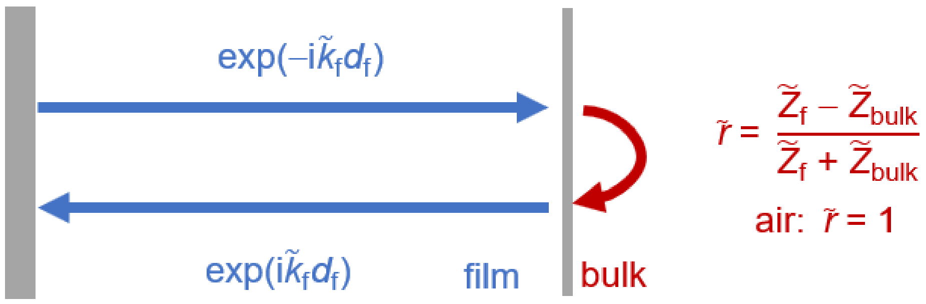


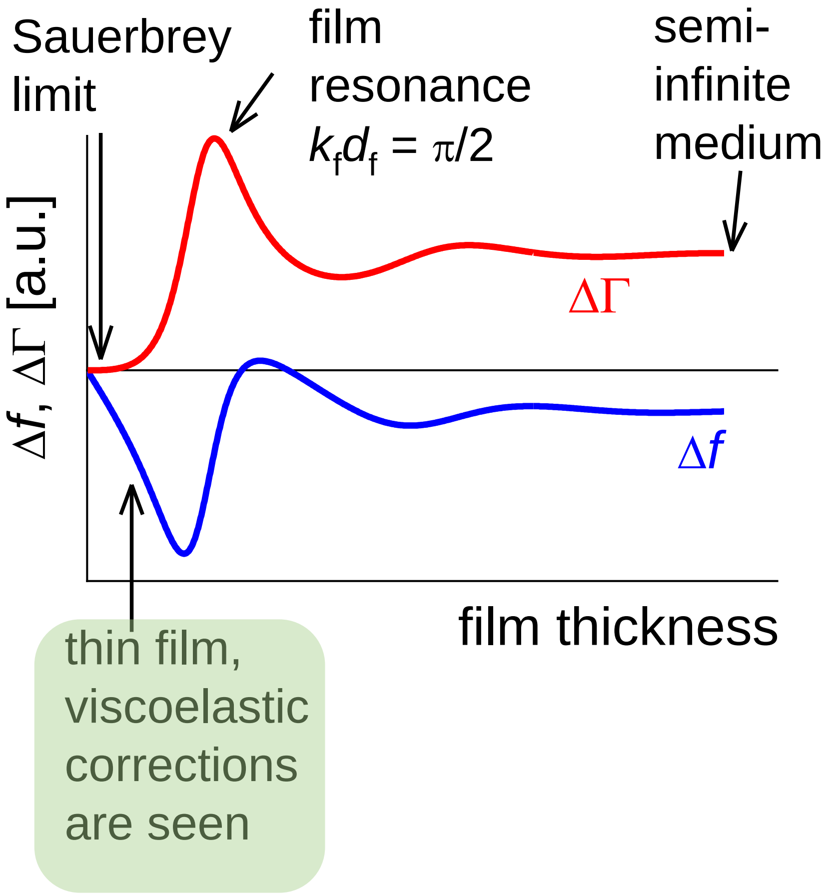
Hartl, J.; Peschel, A.; Johannsmann, D.; Garidel, P. Characterizing protein-protein-interaction in high-concentration monoclonal antibody systems with the quartz crystal microbalance.
Phys. Chem. Chem. Phys. 2017, *19*, 32698

Film in Air

$$\tilde{Z}_L = \tilde{Z}_f \frac{\hat{v}_{\rightarrow} - \hat{v}_{\leftarrow}}{\hat{v}_{\rightarrow} + \hat{v}_{\leftarrow}} = \tilde{Z}_f \frac{1 - \frac{\hat{v}_{\leftarrow}}{\hat{v}_{\rightarrow}}}{1 + \frac{\hat{v}_{\leftarrow}}{\hat{v}_{\rightarrow}}} = \tilde{Z}_f \frac{1 - \tilde{r}_S}{1 + \tilde{r}_S}$$

$$\frac{\Delta f + i\Delta\Gamma}{f_0} = \frac{i}{\pi Z_q} i\tilde{Z}_f \tan\left(\tilde{k}_f d_f\right)$$





Thin Film in Air

$$\frac{\Delta f + i\Delta\Gamma}{f_0} \approx -\frac{\omega m_f}{\pi Z_q}\left[1 + \frac{(n\pi)^2}{3}\left(\frac{\tilde{J}_f}{\rho_f}Z_q^2 - 1\right)\left(\frac{m_f}{m_q}\right)^2\right]$$

- prefactor: gravimetric
- second term in square brackets: viscoelastic correction

  $\propto m_f^2$ because film shears under its own inertia,
  viscoelastic effects only seen if $d_f > 100$ nm

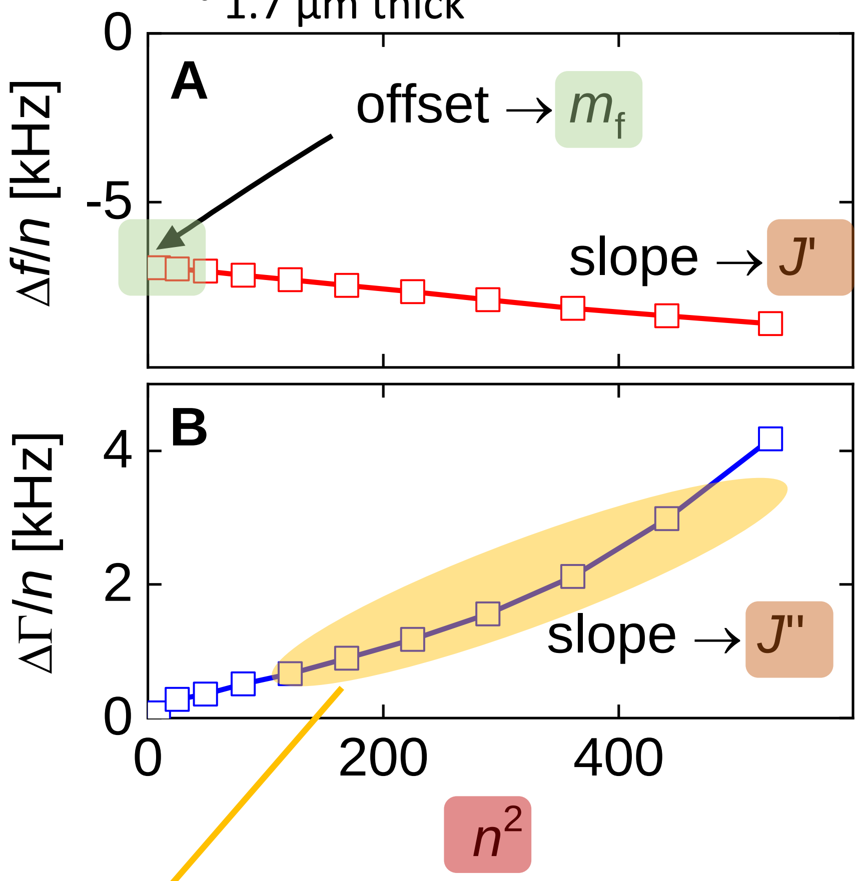
  $\propto n^2$

  depends on $\tilde{J}_f = J' - iJ''$: viscoelastic compliance

  $\tilde{J}_f = (\tilde{G}_f)^{-1} = (G' + iG'')^{-1}$, $\tilde{G}$: shear modulus

The non-trivial samples are the **soft** samples

spin-cast film of polyisopropylene, ~ 1.7 µm thick



why curved?

$$G' = \frac{J'}{J'^2 + J''^2}, \quad G'' = \frac{J''}{J'^2 + J''^2}$$

Domack, A.; Johannsmann, D.,
Plastification during sorption of polymeric thin films: A quartz resonator study.
Journal of Applied Physics **1996, 80, (5), 2599.**

Viscoelastic Dispersion

Soft samples: **stress relaxation** on the time scale of f_{res}^{-1}
$\rightarrow \tilde{J}_f = \tilde{J}_f(\omega)$

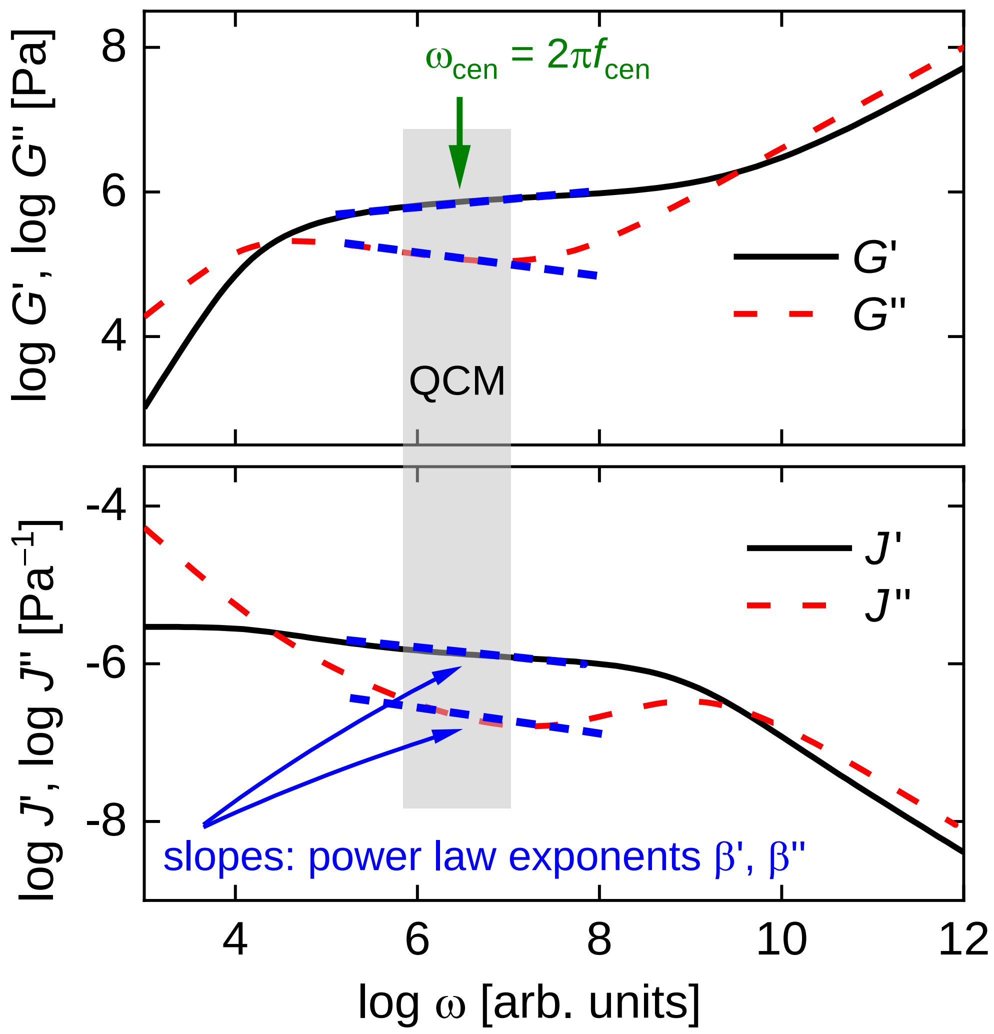
Viscoelastic spectra are smooth.

In the frequency range covered by the QCM, they can be approximated by **power laws**.

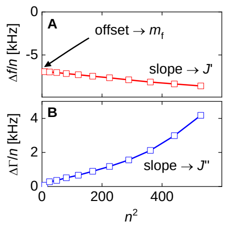
$$J_f'(f) \approx J_f'(f_{cen}) \left(\frac{f}{f_{cen}}\right)^{\beta'}$$

$$J_f''(f) \approx J_f''(f_{cen}) \left(\frac{f}{f_{cen}}\right)^{\beta''}$$

The 5 fit parameters are d_f, $J_f'(f_{cen})$, $J_f''(f_{cen})$, β', β''

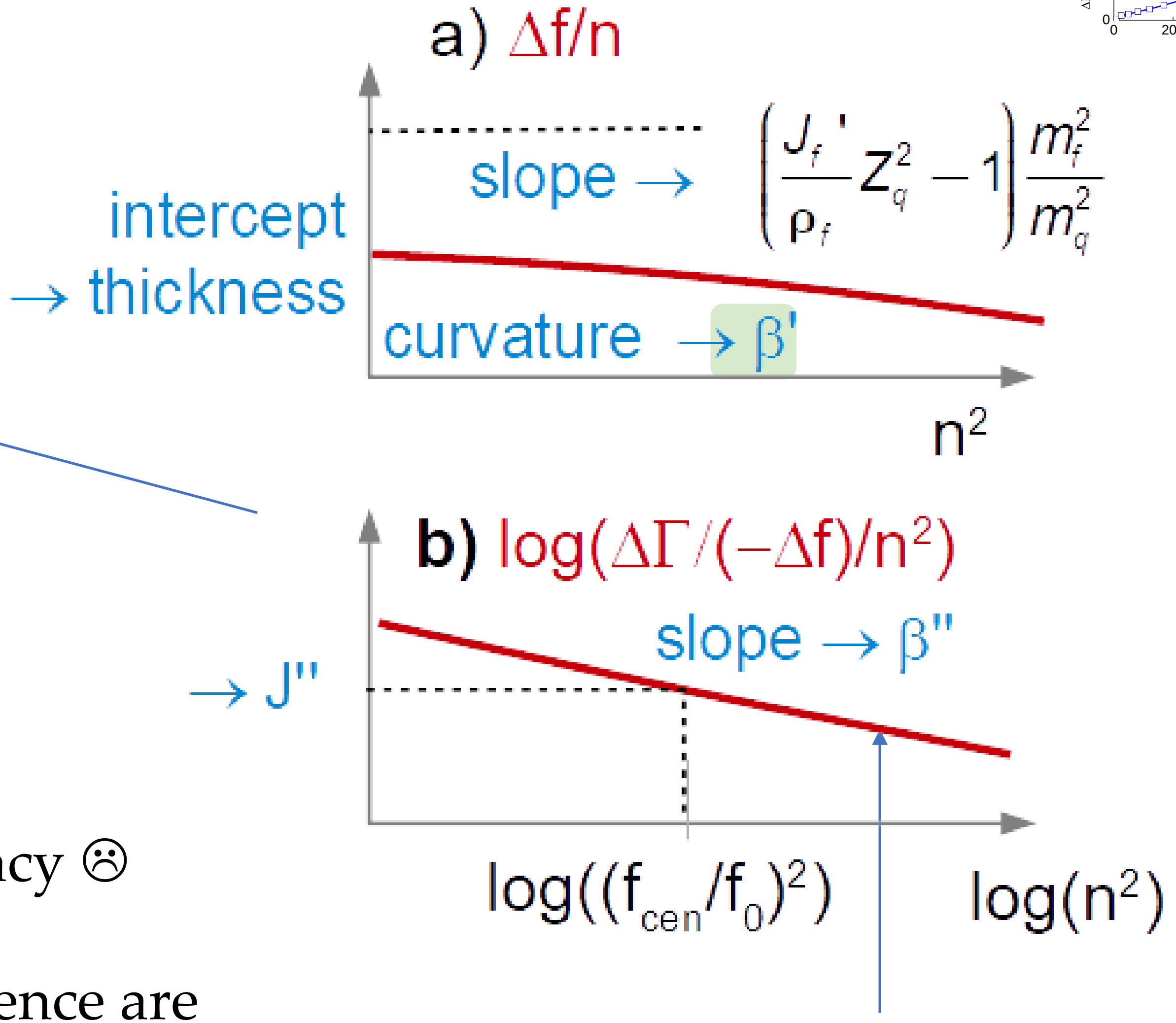


$\Delta\Gamma/(-\Delta f)$



$$\frac{\Delta f + i\Delta\Gamma}{f_0} \approx -\frac{\omega m_f}{\pi Z_q}\left[1 + \frac{(n\pi)^2}{3}\left(\frac{\tilde{J}_f}{\rho_f} Z_q^2 - 1\right)\left(\frac{m_f}{m_q}\right)^2\right]$$

$$\frac{\Delta\Gamma}{-\Delta f} \approx \frac{(n\pi)^2}{3}\left(\frac{J''_f(\omega)}{\rho_f} Z_q^2\right)\left(\frac{m_f}{m_q}\right)^2$$



$\beta' \leftarrow$ curvature in $\Delta f/n$ vs n,
often not determined with sufficient accuracy ☹

The 4 fit parameters determined with confidence are
d_f, $J_f'(f_{cen})$, $J_f''(f_{cen})$, ~~β'~~, β''

$$J_f''(f) \approx J_f''(f_{cen})\left(\frac{f}{f_{cen}}\right)^{\beta''}$$

Thin Film in Liquid *(different from film in air)*

$$\frac{\Delta f + i\Delta\Gamma}{f_0} = -\frac{\omega m_f}{\pi Z_q}\left[1 - \frac{\tilde{J}_f(\omega)}{\rho_f}\, i\omega\rho_{bulk}\eta_{bulk}\right]$$

$$\frac{\Delta f}{n} + i\frac{\Delta\Gamma}{n} \approx -\frac{2f_0^2}{Z_q} m_f \left[1 - n\left(J_f'(\omega) - iJ_f''(\omega)\right)\left(2\pi i\, f_0 \frac{\rho_{bulk}}{\rho_f}\eta_{bulk}\right)\right]$$

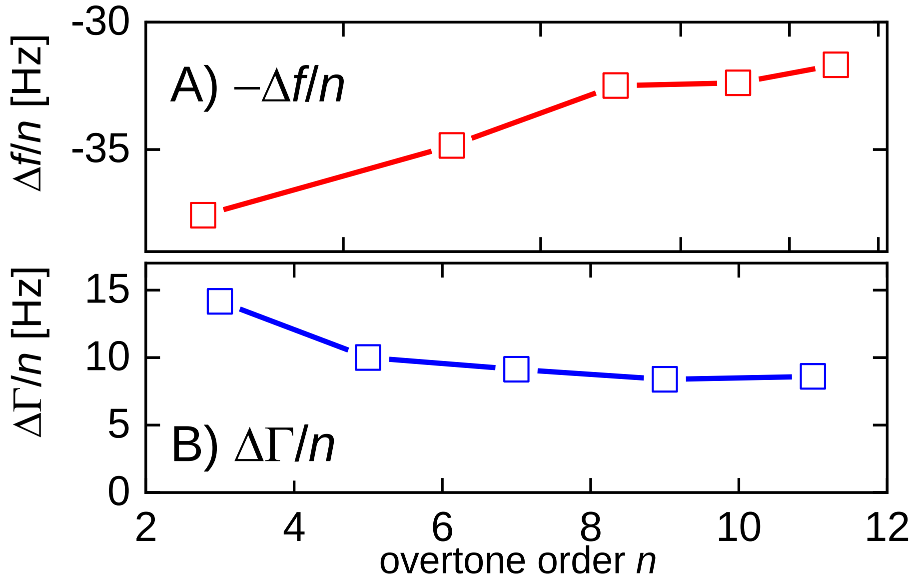
prefactor: gravimetric

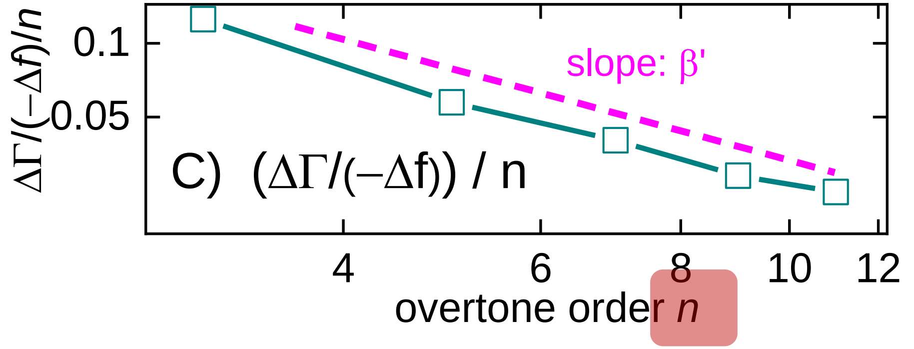
second term in square brackets: viscoelastic correction

- $\propto \eta_{bulk}$ because film shears under the stress exerted by the bulk

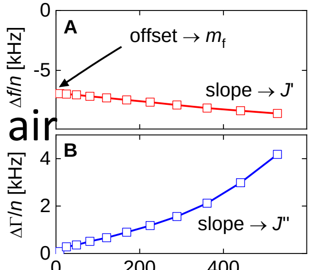
viscoelastic effects seen even for protein monolayers

- $\propto n$
- is negative (*lowers* the apparent mass, „missing mass effect“)

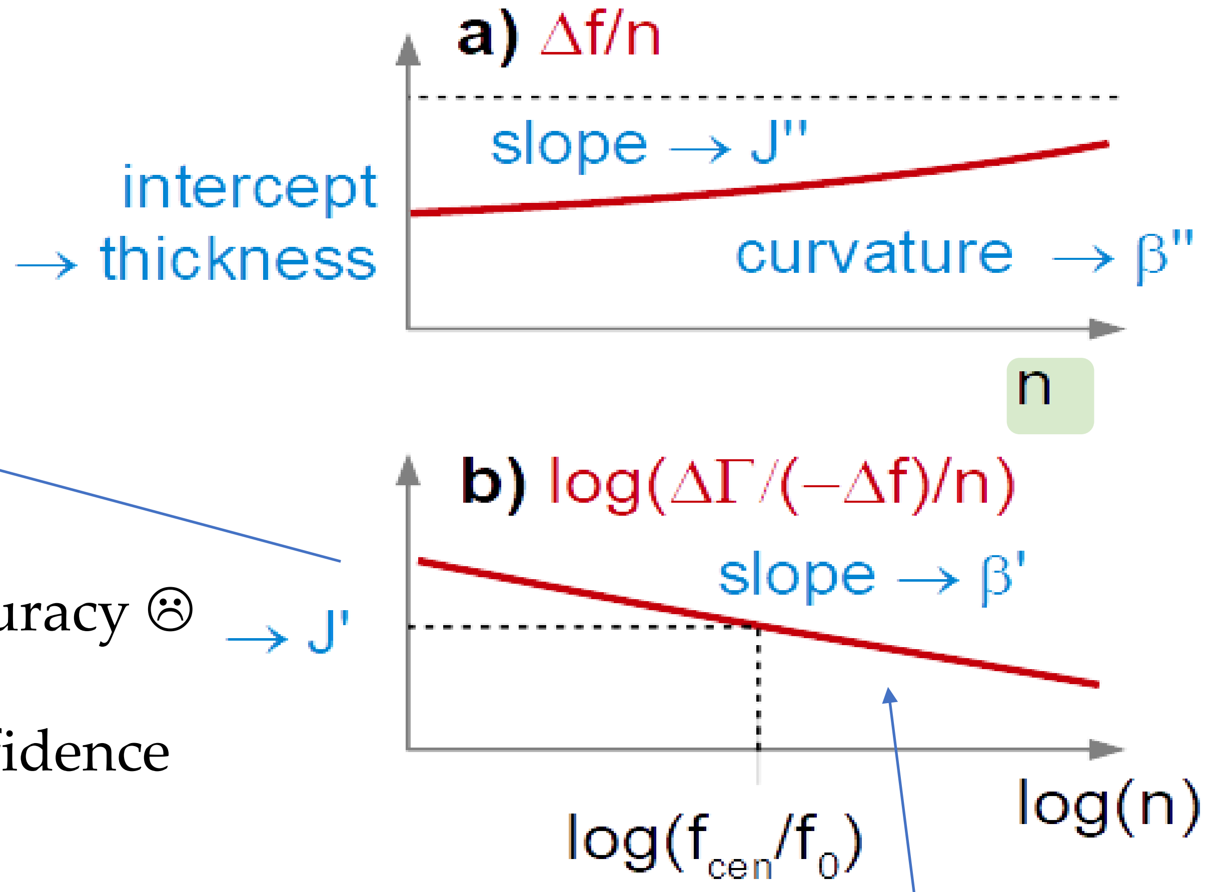




film in air



$\Delta\Gamma/(-\Delta f)$



$$\frac{\Delta\Gamma}{-\Delta f} \approx n\, J_f'(\omega)\, 2\pi f_0 \eta_{bulk}$$

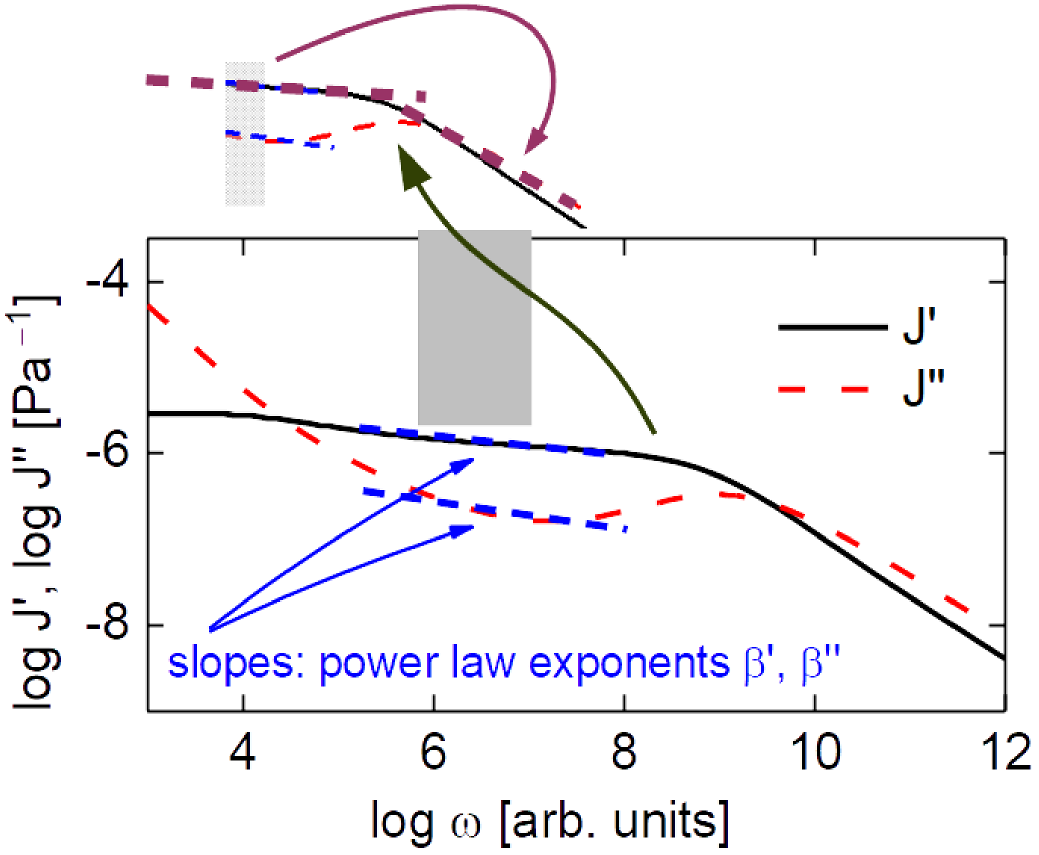
β'' ← curvature in $\Delta f/n$ vs n,
often not determined with sufficient accuracy ☹

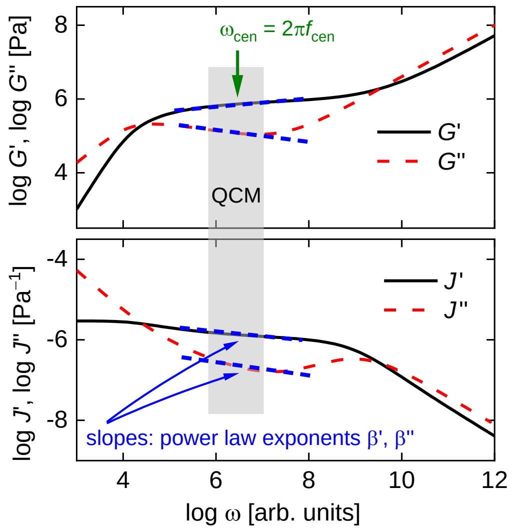
The 4 fit parameters determined with confidence are d_f, $J_f'(f_{cen})$, $J_f''(f_{cen})$, β', ~~β''~~

Note the differences between the film in air and the film in a liquid.

$$J_f'(f) \approx J_f'(f_{cen}) \left(\frac{f}{f_{cen}}\right)^{\beta'}$$

Interpretation of β′





In this example, a decrease in β′ (to more negative values) is indicative of a decreased rate of relaxation.
This argument requires an assumption on the function $\tilde{J}(\omega)$

Polymer Brushes, Samples with Viscoelastic Profiles

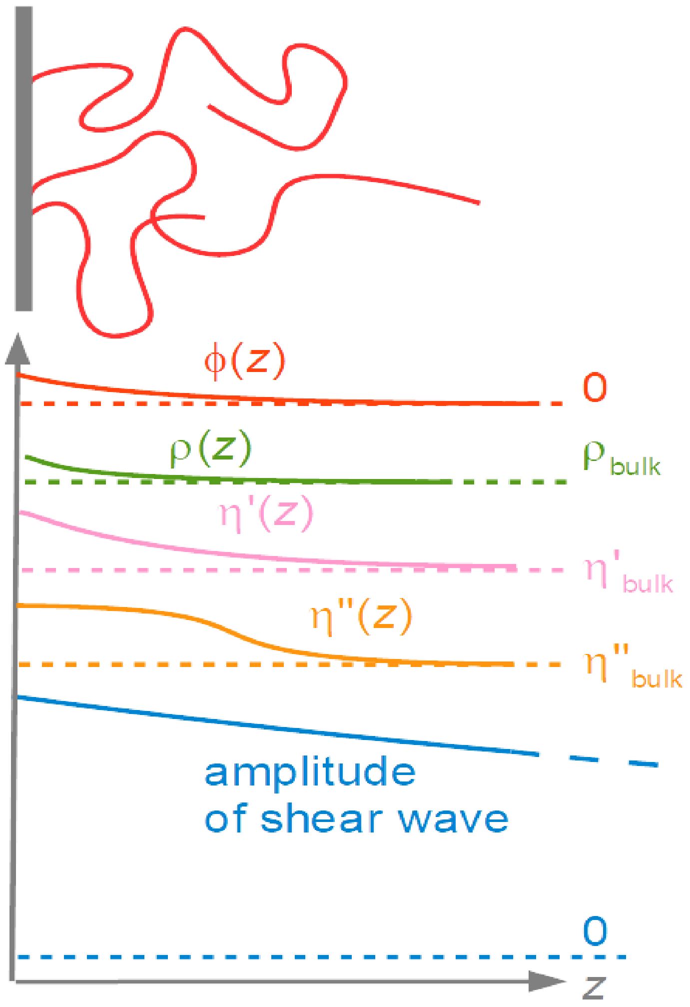
$m_f \rightarrow m_{app}$

$J'_f \rightarrow J'_{app}$

$$\tilde{m}_{app}(n) = \frac{Z_q}{2nf_0^2}\Delta\tilde{f}(n) \approx \int_0^\infty \varrho_{bulk}\left[\frac{\varrho(z)}{\varrho_{bulk}} - \frac{\eta_{bulk}}{\tilde{\eta}(n,z)}\right]dz$$

$$J_{app}'(n) = \frac{\Delta\Gamma}{-\Delta f}\frac{1}{\omega\eta_{bulk}} \approx \frac{\int_0^\infty J'(z)\varrho(z)\,dz}{\int_0^\infty\left(1-\omega\eta_{bulk}J''(z)\right)\varrho(z)\,dz}$$

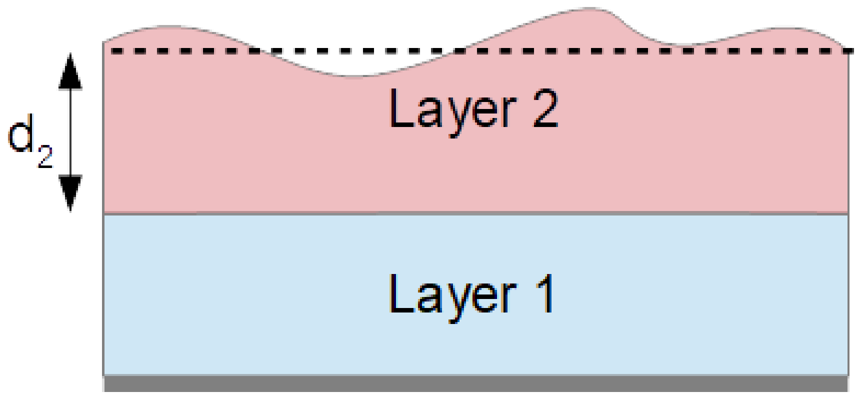
$$\approx \frac{\varrho_{bulk}}{m'_{app}}\int_0^\infty J'(z)\,dz$$



A word of caution: Interpretation is robust for thin layers. For thicker layers (> 100 nm), the acoustic waves have trouble distinguishing between a thick, dilute layer and thin, more compact layer. ☹

Small-Scale Roughness

$$\frac{\Delta f + i\Delta\Gamma}{f_0} = -\frac{1}{\pi Z_q}\omega\varrho h_r \frac{3\sqrt{\pi}}{2}\frac{h_r}{l_r} + \frac{i}{\pi Z_q}\sqrt{i\omega\varrho\eta}\left[1 - 2i\left(\frac{h_r}{\delta}\right)^2\right]$$



- h_r : vertical scale of roughness (must be << δ)
- l_r : lateral scale of roughness
- h_r/l_r: aspect ratio (must be << 1)

- in green: a gravimetric term (Sauerbrey-like, trapped mass), scales as h_r (as long as the aspect ratio is fixed)
- in orange: an effective bulk impedance of the liquid, change scales as h_r^2, affects Δf and $\Delta\Gamma$ in a similar way

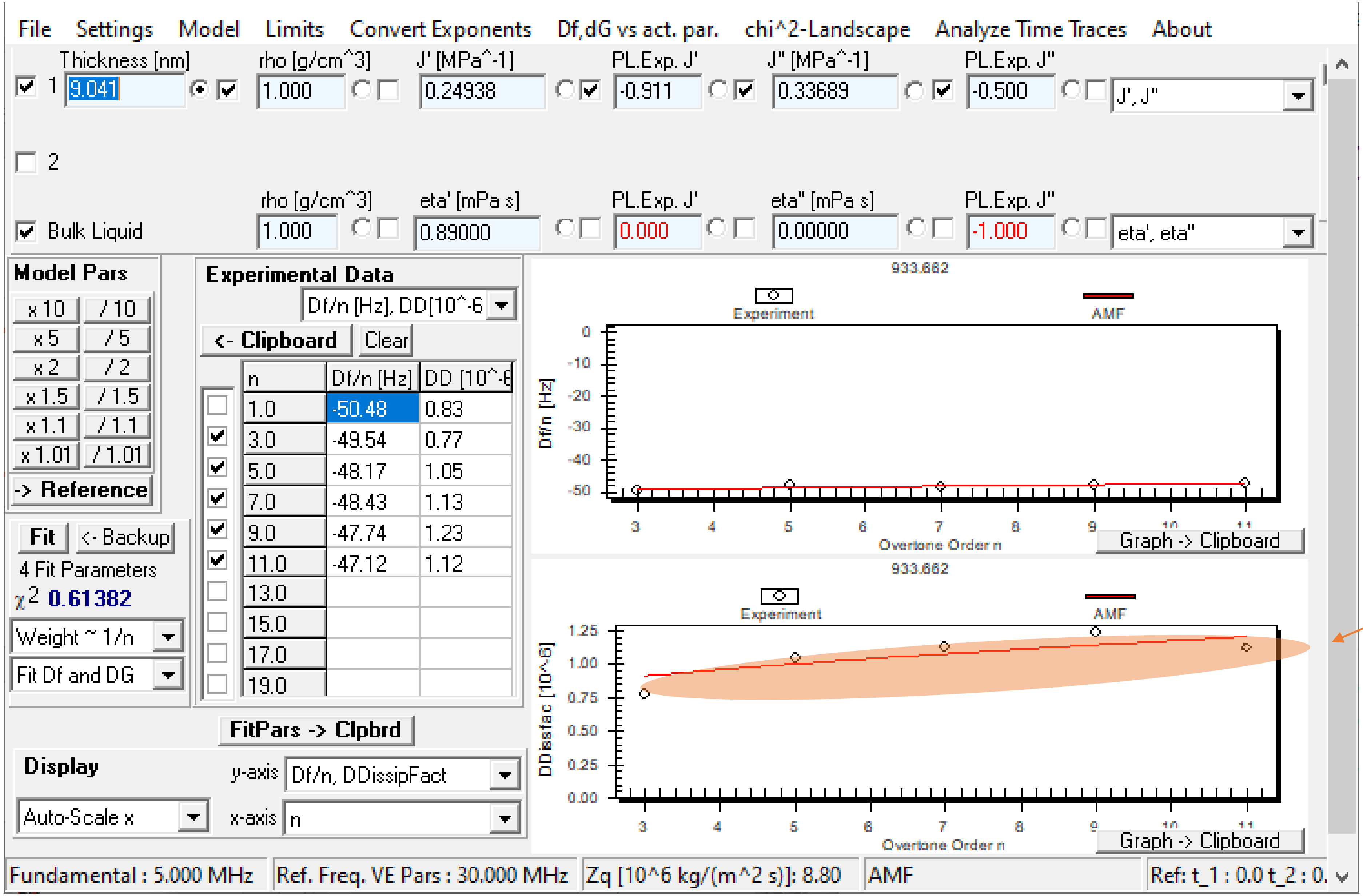
Small scale roughness affects Δf stronger than $\Delta\Gamma$.

Rechendorff, K.; Hovgaard, M.B.; Foss, M.; Besenbacher, F.
Influence of surface roughness on quartz crystal microbalance measurements in liquids. *J. Appl. Phys.* 2007, *101*

The Software Package QTM

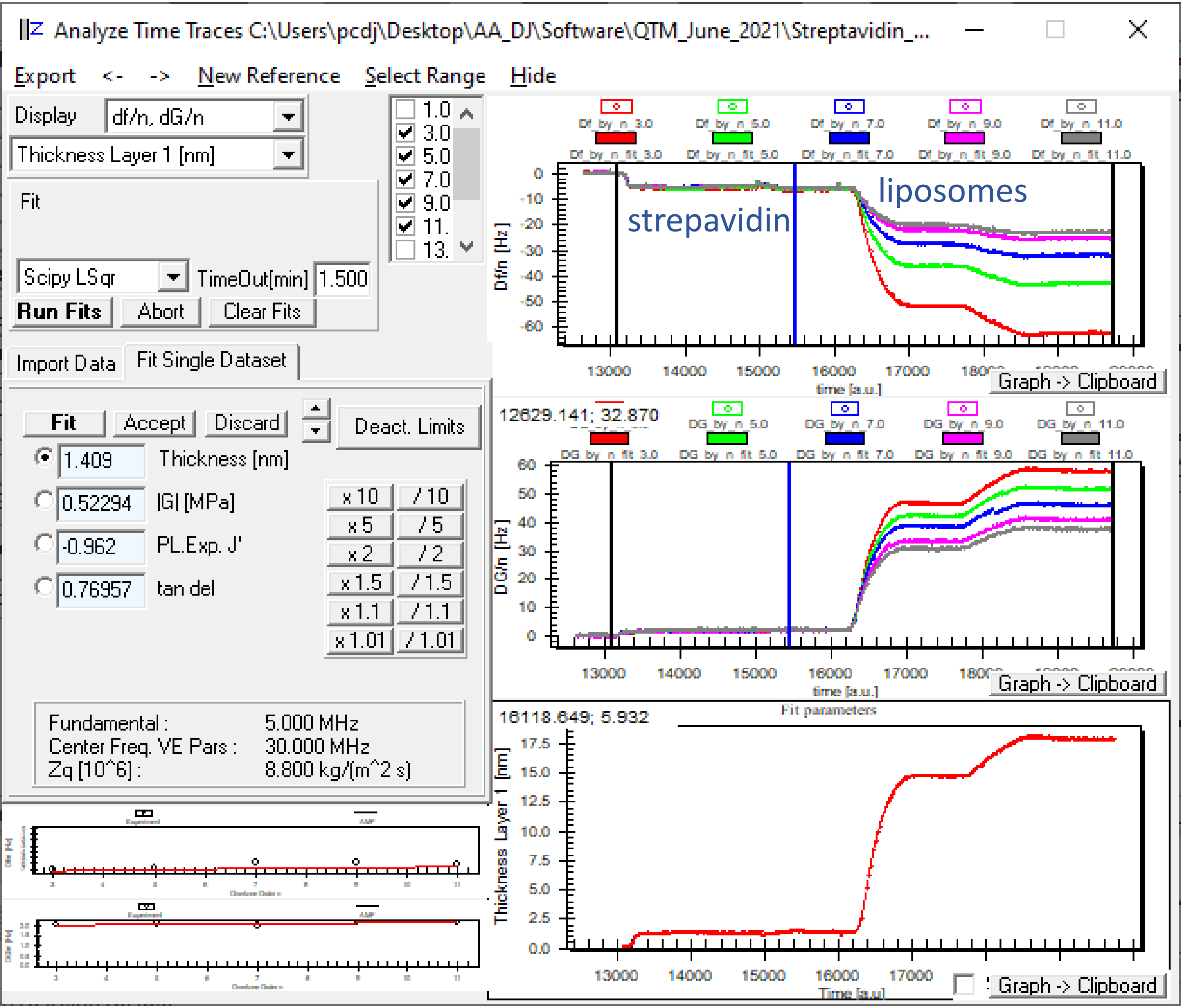
https://www.pc.tu-clausthal.de/en/research/qcm-modelling/

An adsorption experiment (BSA), data from Ilya Reviakine

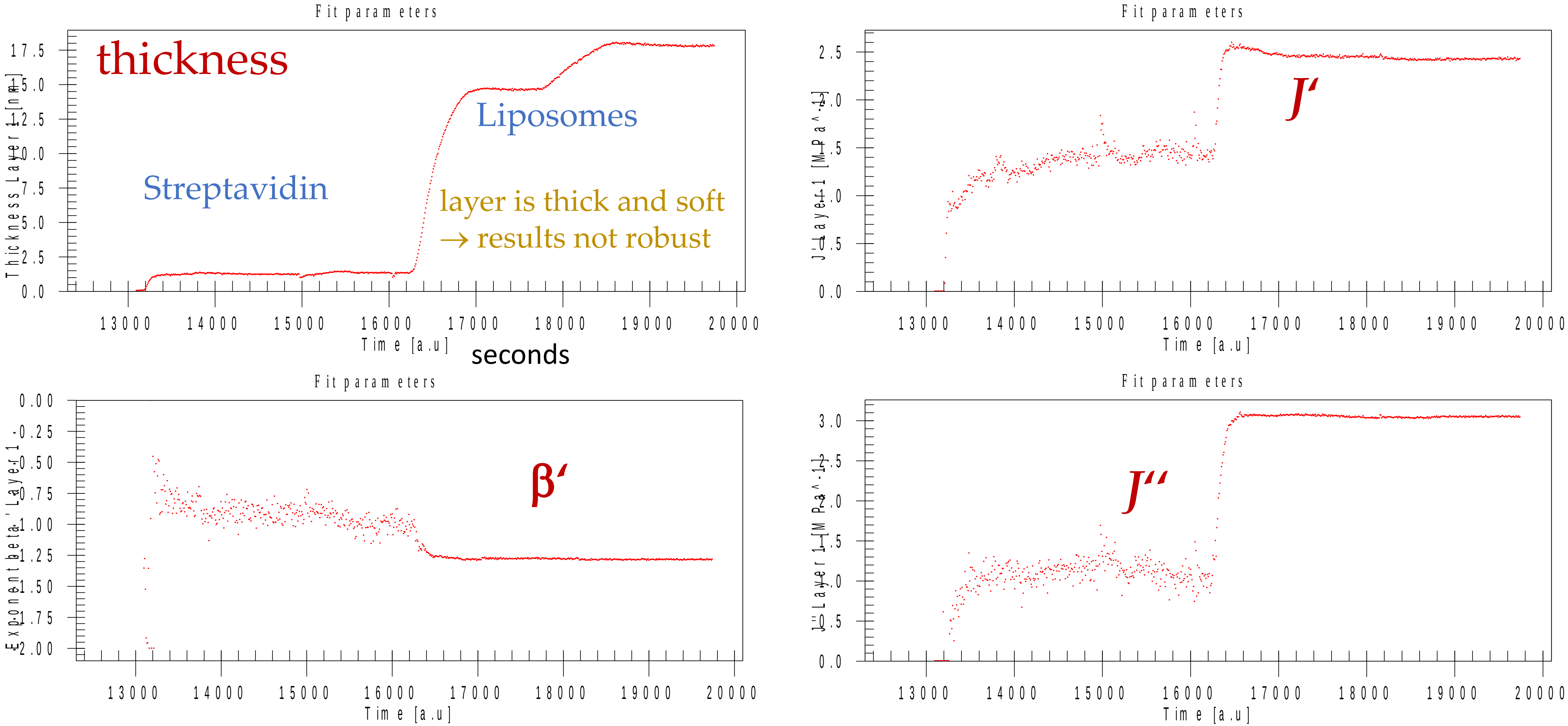


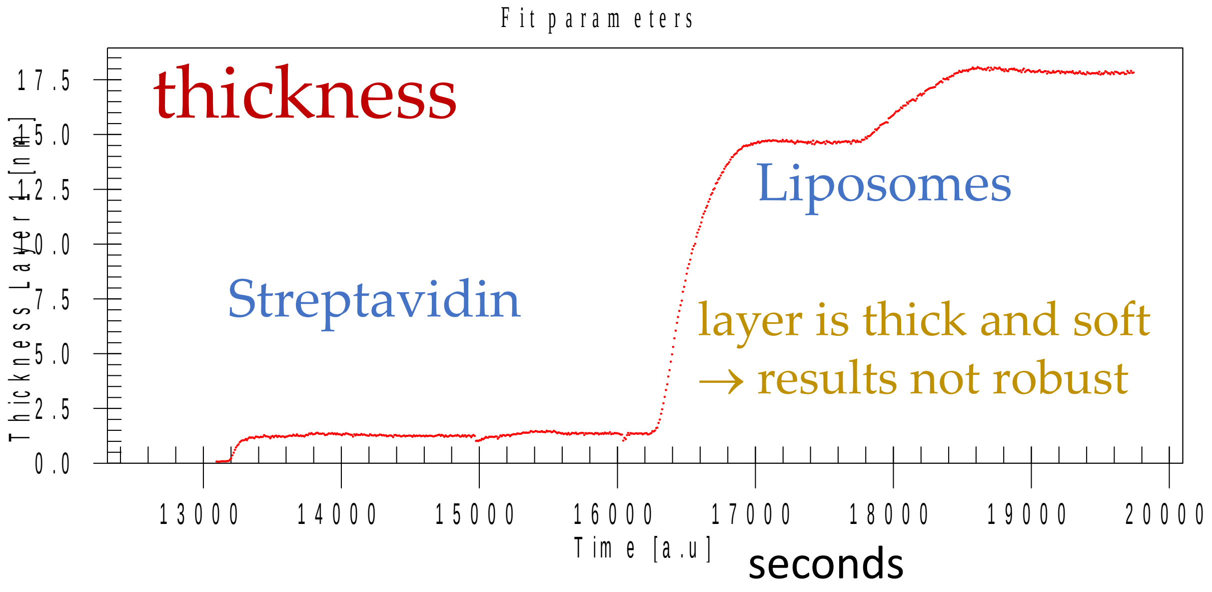
Those deviations are similar over the entire experiment. (this is not „noise“ in the narrow sense)

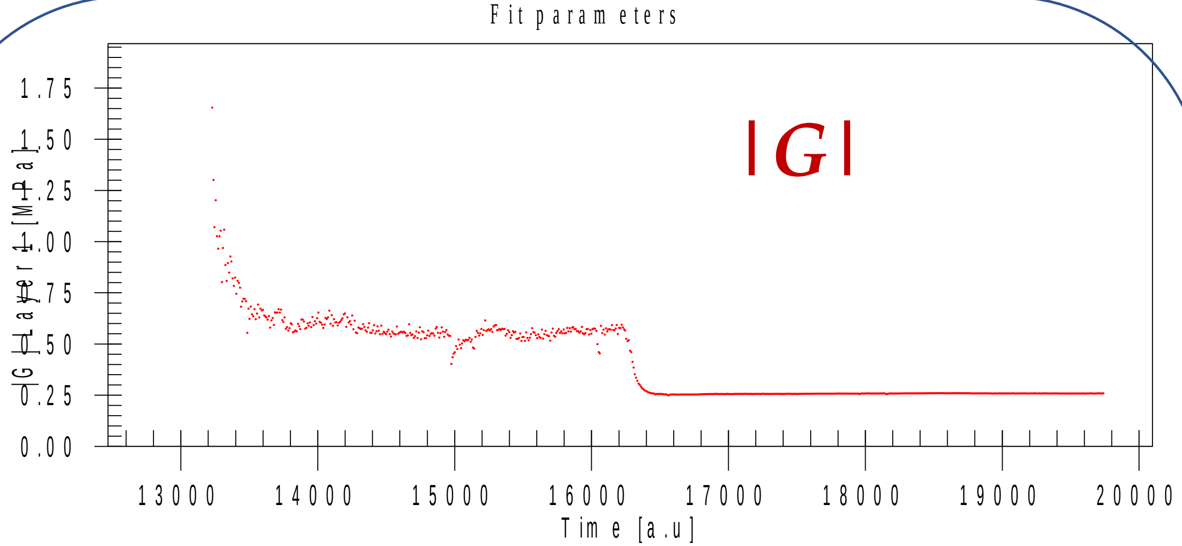
Streptavidin + Liposomes

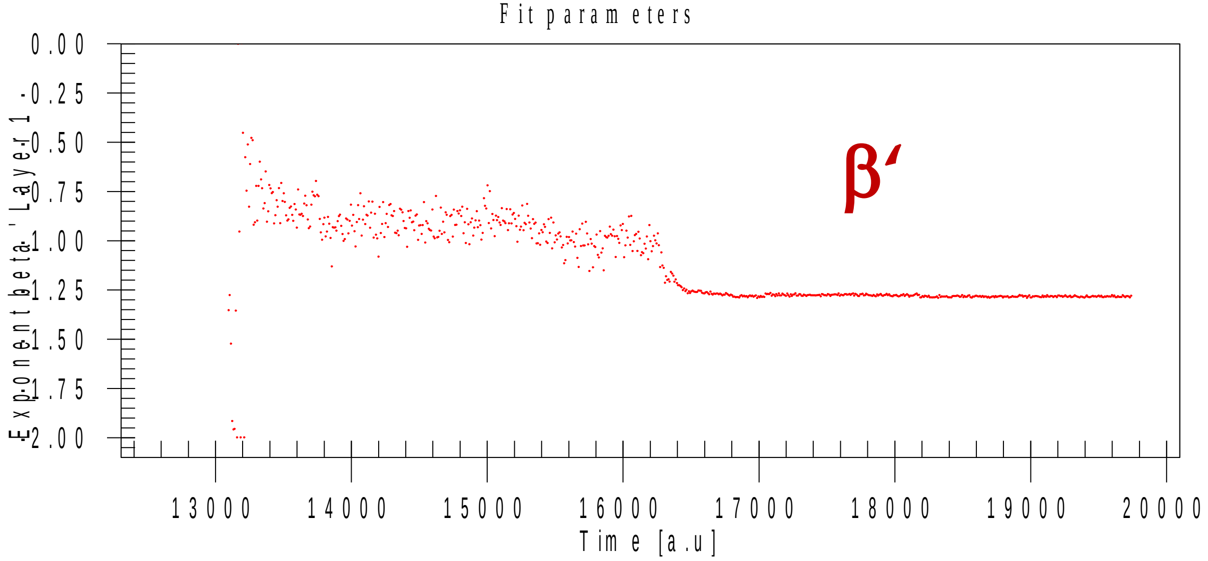


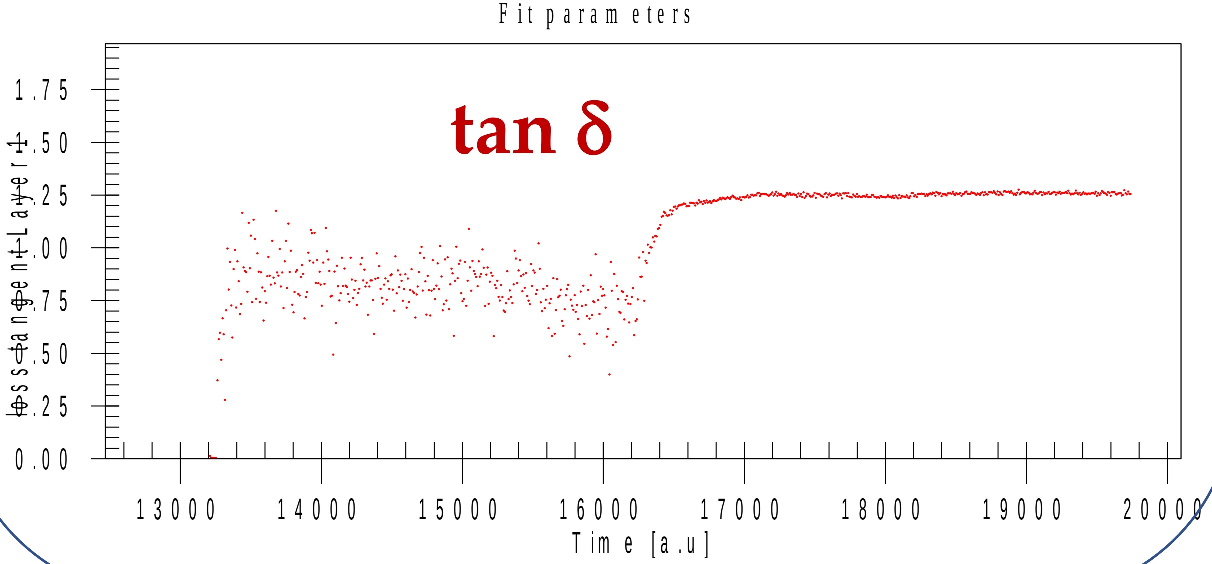
First streptavidin,
then liposomes,
data from Ilya Reviakine


Fit parameters
thickness
Liposomes
Streptavidin
layer is thick and soft
→ results not robust
Time [a.u]
seconds
Fit parameters
J‘
Time [a.u]
Fit parameters
β‘
Time [a.u]
Fit parameters
J‘‘
Time [a.u]



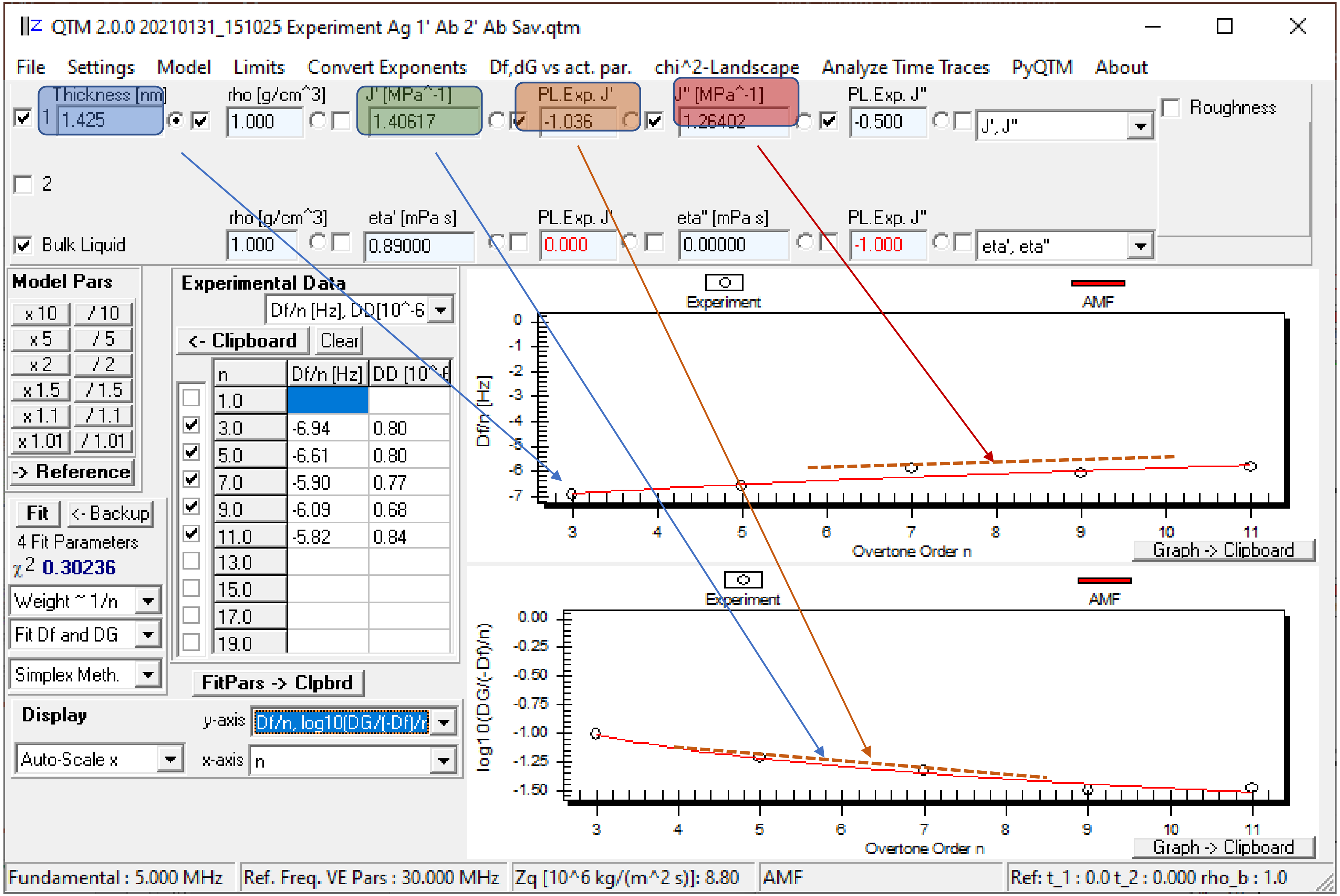


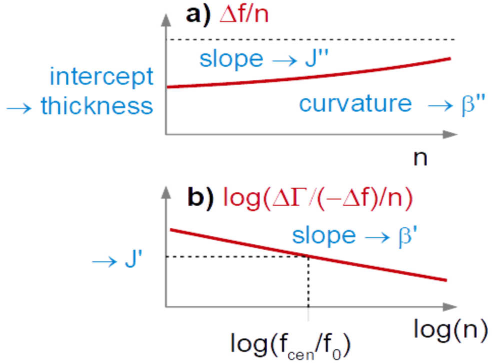




Viscoelastic parameters converted to |G| and tan δ_L

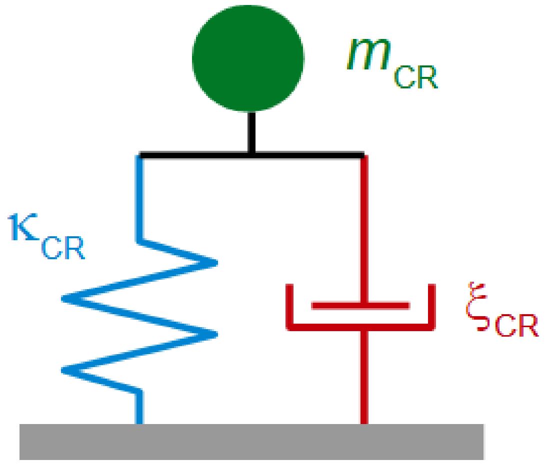
Streptavidin

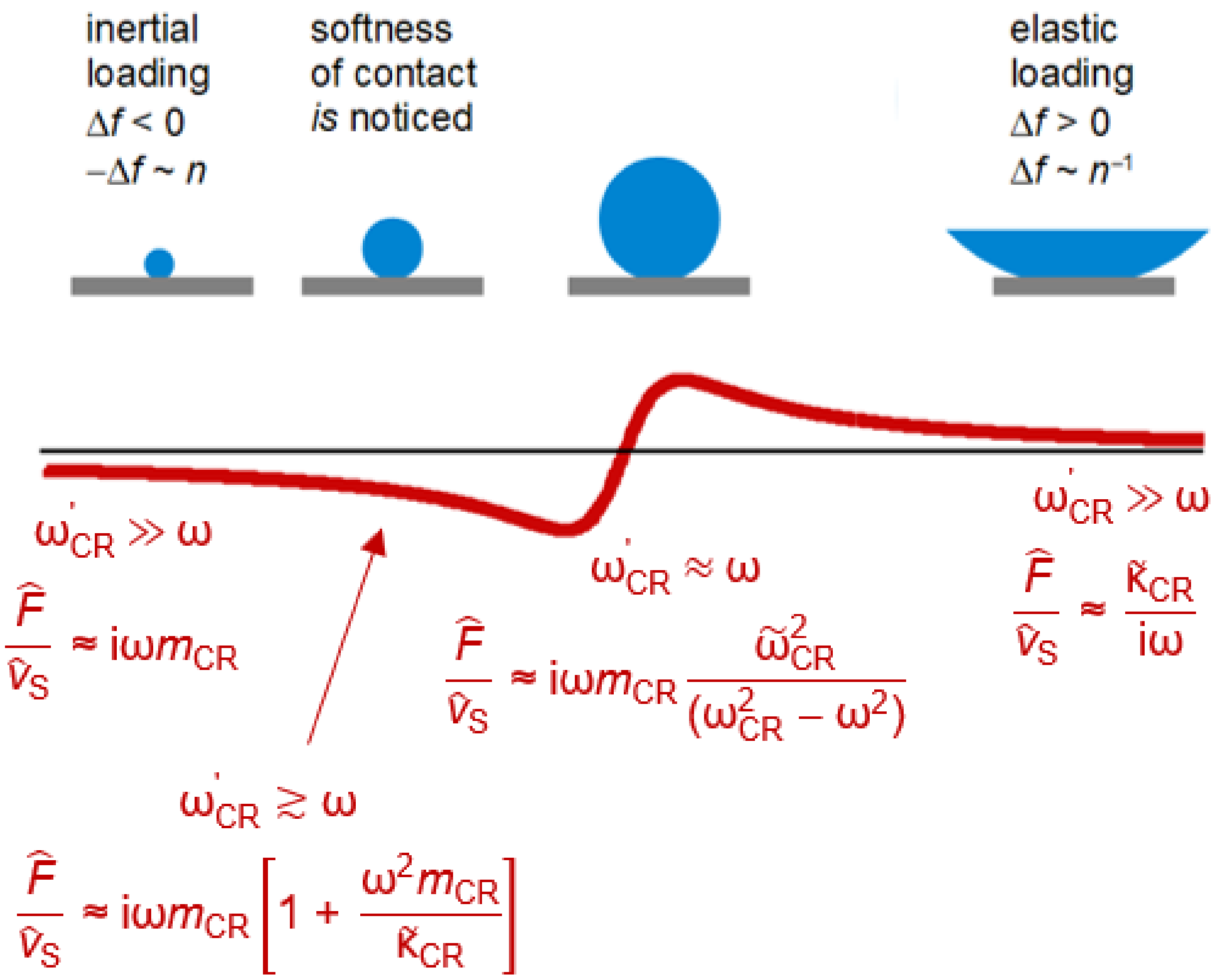




Particles, Coupled Resonances, Δf can be > 0

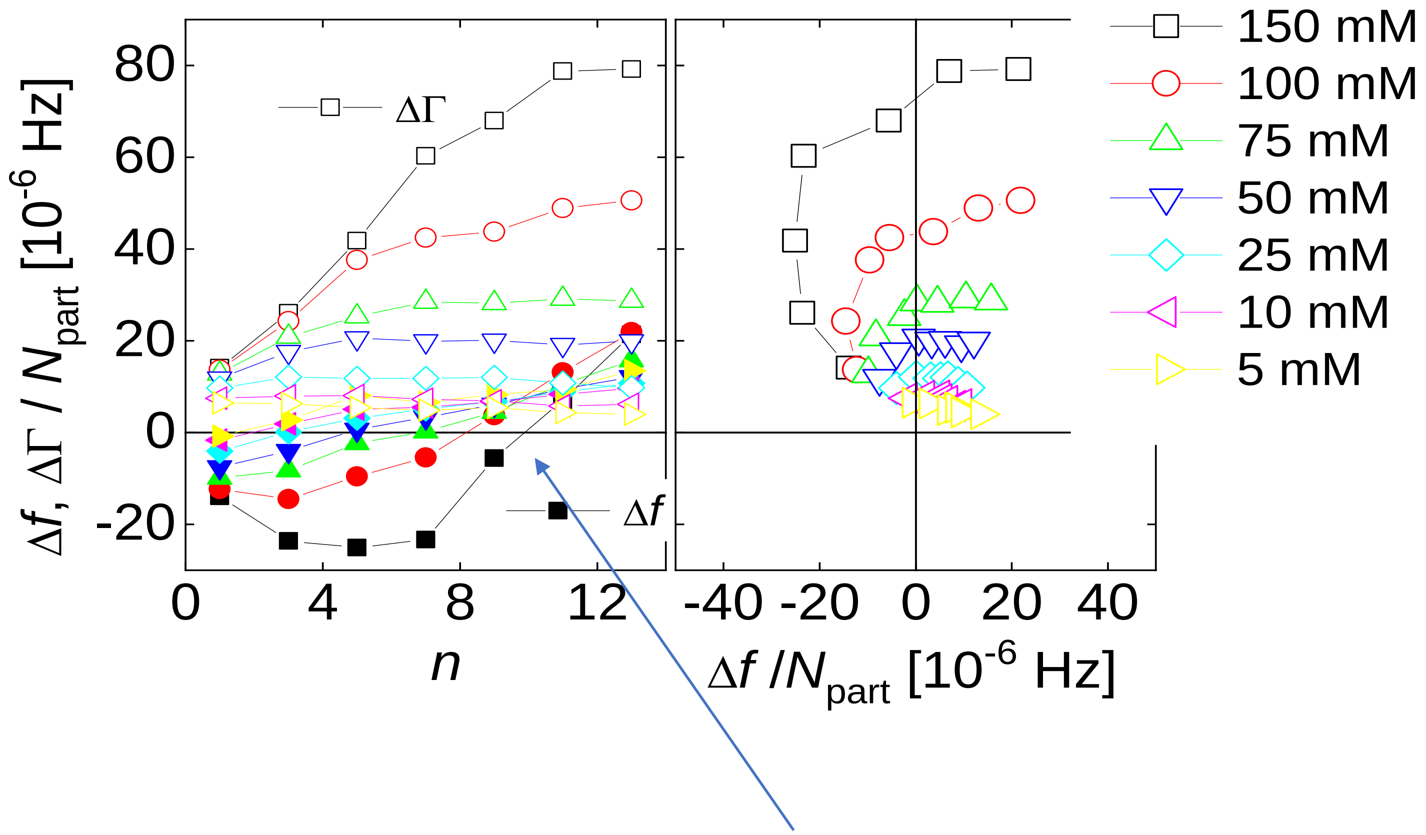
$$\frac{\Delta f + i\Delta\Gamma}{f_0} = -\frac{n_P}{A_{eff}}\frac{\omega m_{CR}}{\pi Z_q}\left[\frac{\tilde{\omega}_{CR}^2}{\tilde{\omega}_{CR}^2 - \omega^2}\right]$$

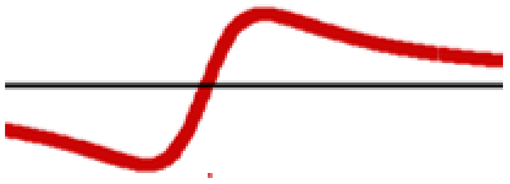




Coupled Resonances, $\Delta f > 0$

Shifts of frequency and bandwidth caused by the deposition of micron-sized silica spheres. The polar diagram on the right displays spirals, characteristic for the coupled resonance.
The ion strength as indicated in the legend tunes the stiffness of the contact, where large ion strength leads to stiff contacts.





Olsson, A.L.J.; van der Mei, H.C.; Johannsmann, D.; Busscher, H.J.; Sharma, P.K.
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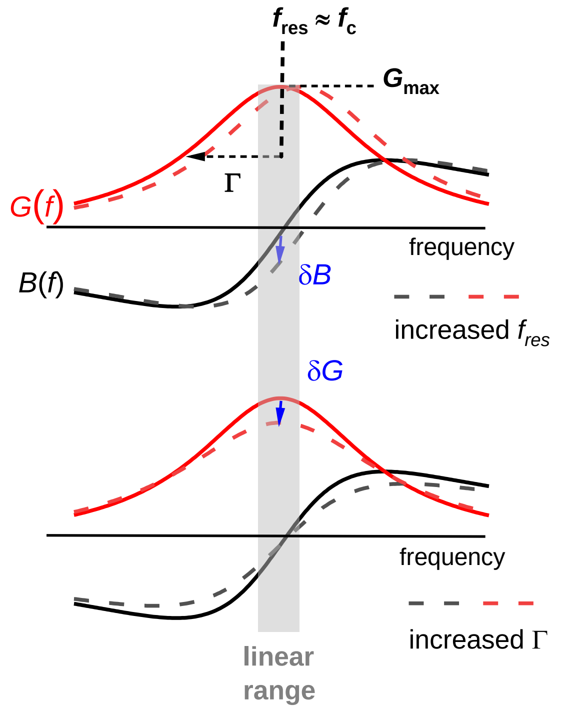
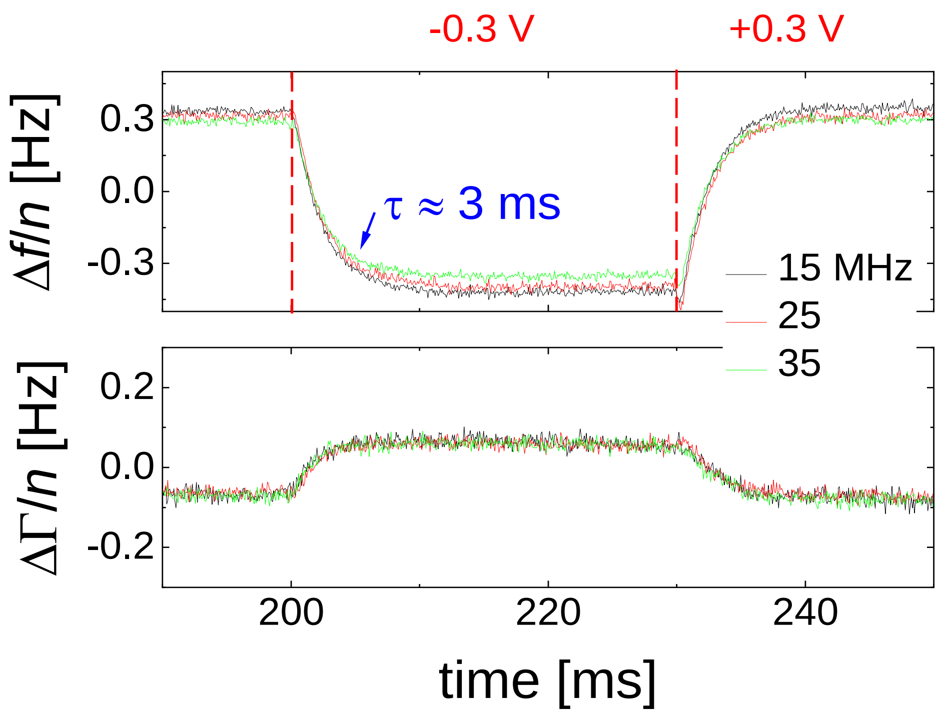
Anal. Chem. 2012, *84*, 4504

Fast Measurements with the Fixed-Frequency-Drive Mode Application to the Electrochemical QCM (EQCM)





In this experiment, accumulation and averaging reduced the noise to a few mHz. This is the "**modulation QCM**"

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- Pax, M.; Rieger, J.; Eibl, R.H.; Thielemann, C.; Johannsmann, D. Measurements of fast fluctuations of viscoelastic properties with the quartz crystal microbalance. *Analyst* 2005, *130*, 1474–1477
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Conclusions

- The QCM-D gives access to thickness **and** softness
- It differentiates between **elastic** and **viscous** softness
- It can even do **viscoelastic spectroscopy** (“high frequency rheology”)
    - It can do so to some extent (one out of two **power-law exponents**)
- It’s an active field of research