

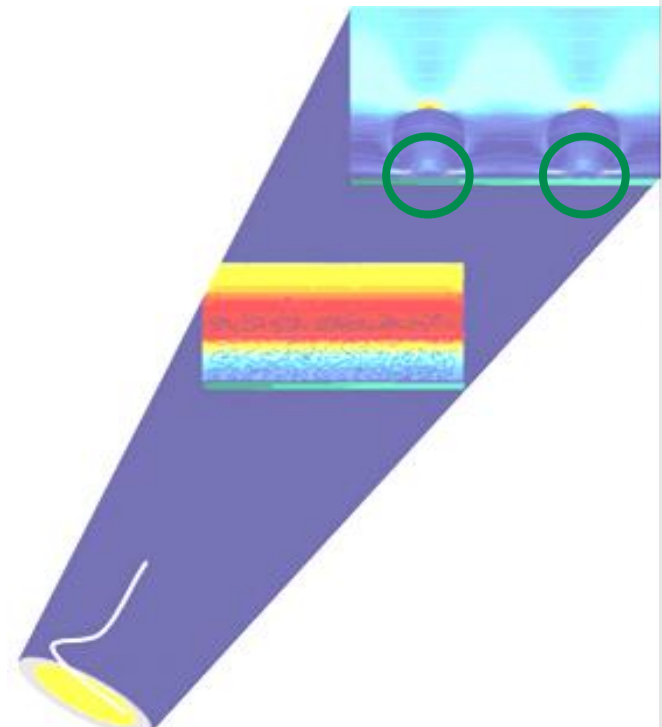
Is Partial Slip Under Transverse Oscillatory Loading a Transient Event?

Frederick Meyer,¹ Daniel Forchheimer,² Arne Langhoff,¹ Diethelm Johannsmann*¹

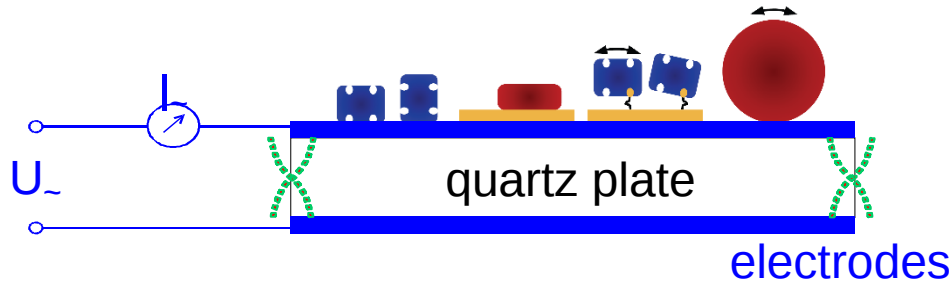
¹ Institute of Physical Chemistry, TU Clausthal, Germany

² Intermodulation Products AB, Sweden

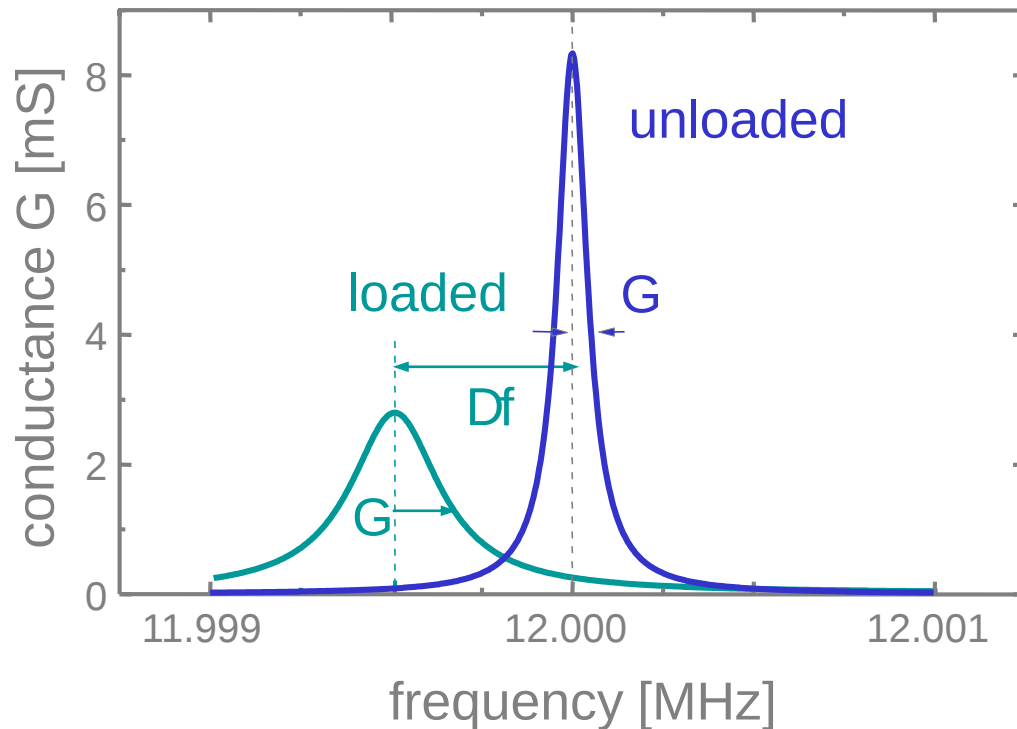
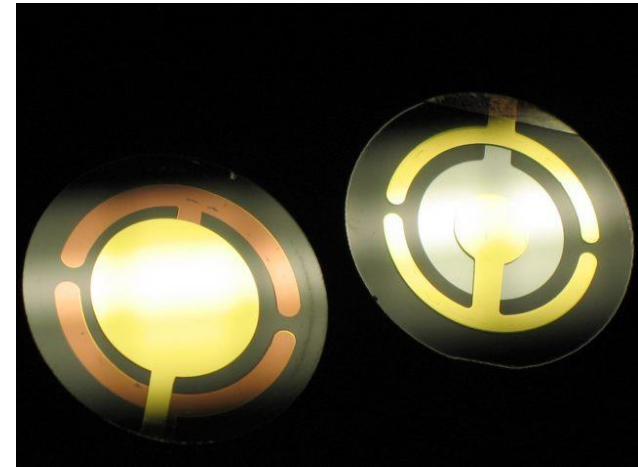
- High-frequency nonlinear contact mechanics
 - Intermodulation products
 - Sudden impacts
 - Crystallization
-
- High-frequency micromechanics:
*Sylvia Hanke, Rebekka König, Judith Petri,
Jana Vlachová, Frederick Meyer*
 - Intermodulation: *Daniel Forchheimer*
 - QCM work in general: *Arne Langhoff*



The 2nd-Generation Quartz Crystal Microbalance



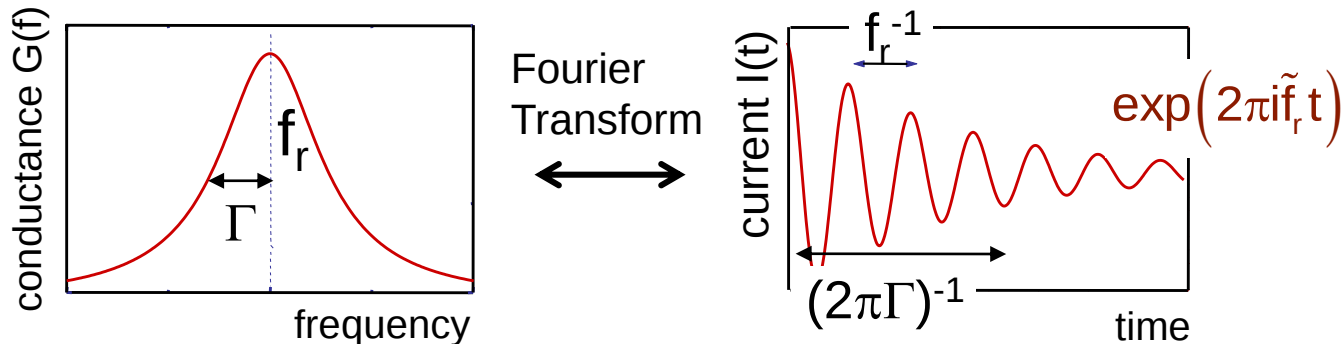
$f = f_{\text{res}}$: large amplitude of motion
 $\Rightarrow$ large current



- Shifts in frequency and bandwidth: Δf , $\Delta \Gamma$
- many overtones $\Delta f(n)$, $\Delta \Gamma(n)$
- dependence on amplitude $\Delta f(n, u_0)$, $\Delta \Gamma(n, u_0)$
- Higher harmonics
- Intermodulation products

Small Load Approximation

Complex Resonance Frequency $\tilde{f}_r = f_r + i\Gamma$



Small-load approximation

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

$$Z_L = \frac{\hat{\sigma}}{\hat{v}} \text{ "load impedance"}$$

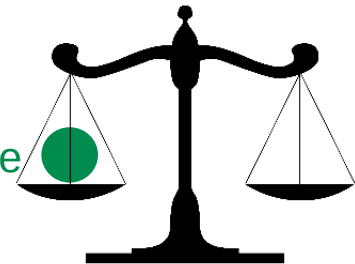
$\hat{\sigma}$ stress

$\hat{v}$ velocity

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

QCM: The Quartz Crystal
Micro *Stress*-Balance

periodic stress,
in-phase, out-of-phase



Mason, W.P., *Piezoelectric Crystals and their Applications to Ultrasonics* 1948

Pechhold, W *Acustica* 1959, 9, 48

Johannsmann, D., *The Quartz Crystal Microbalance in Soft Matter Research*, Springer 2014

Analogous equations exist in atomic force microscopy, valid **if** the perturbations are small

Small Load Approximation

Sauerbrey

$$\frac{\Delta \tilde{f}}{f_0} = \frac{i}{\pi Z_q} \frac{\text{inertial stress}}{\text{velocity}} = \frac{i}{\pi Z_q} \frac{i\omega \hat{v} \Delta m}{\hat{v}}$$

$$\Rightarrow \frac{\Delta f}{f} \approx - \frac{\Delta m}{m_q} \quad \Leftarrow \begin{cases} \Delta m : \text{Mass per unit area of film} \\ m_q = Z_q / (2f_0) : \text{Mass per unit area of crystal} \end{cases}$$

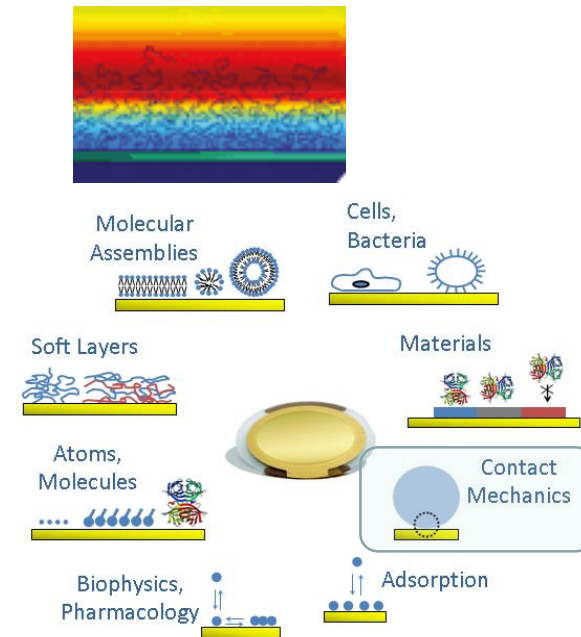


Stress might go back to **viscous drag**, **elastic forces** ...
acoustic multilayers, interfackal high-frequency rheology

The stress can be averaged over **area**:

$$\frac{\Delta \tilde{f}}{f_0} = \frac{i}{\pi Z_q} \frac{\langle \hat{\sigma} \rangle_{\text{area}}}{\hat{v}}$$

Discrete objects: $\langle \hat{\sigma} \rangle_{\text{area}} = \frac{N}{A} \hat{F}$ with $\hat{F}$ the periodic force

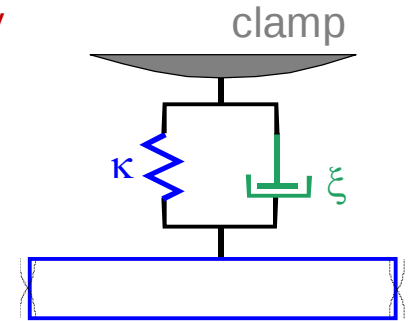
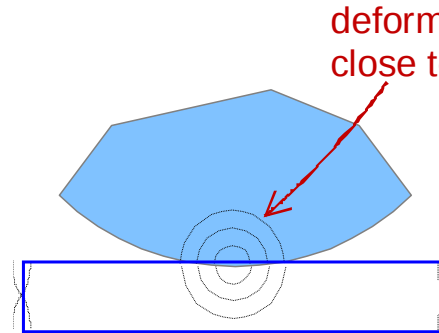
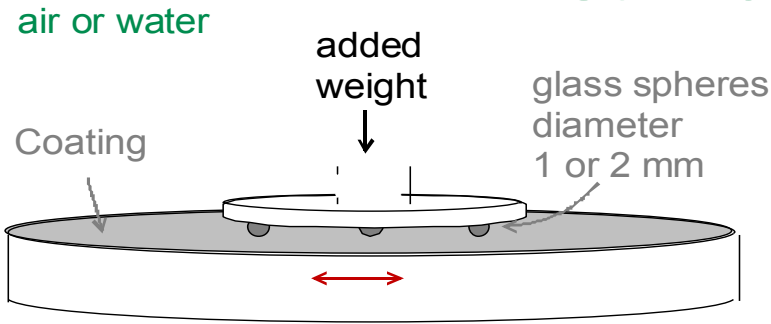


The force can be averaged over **time**:

$$\frac{\Delta \tilde{f}}{f_0} = \frac{i}{\pi Z_q} \frac{N}{A} \frac{2 \langle F(t) \exp(i\omega t) \rangle_{\text{time}}}{\hat{v}}$$

QCM covers **nonlinear** force-displacement relations

Stiffness of Sphere-Plate Contacts



soft link, heavy sphere

$$\rightarrow \tilde{\omega}_p \ll \omega$$

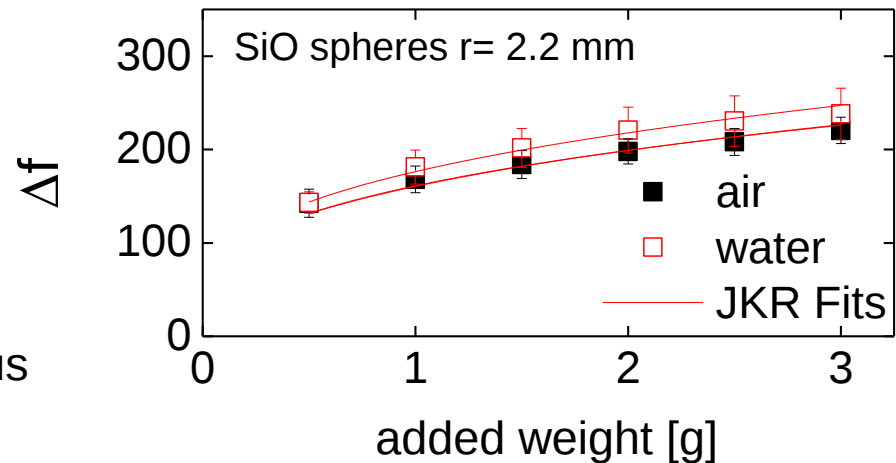
$$\frac{\Delta f}{f_0} = \frac{N}{A\pi Z_q \omega} \tilde{\kappa}$$

Elastic Load

Hertz-Mindlin: $\kappa = 2G^* a$

a : contact radius

$$\frac{1}{G^*} = \frac{1-2\nu_1}{4G_1} + \frac{1-2\nu_2}{4G_2} : \text{effective modulus}$$

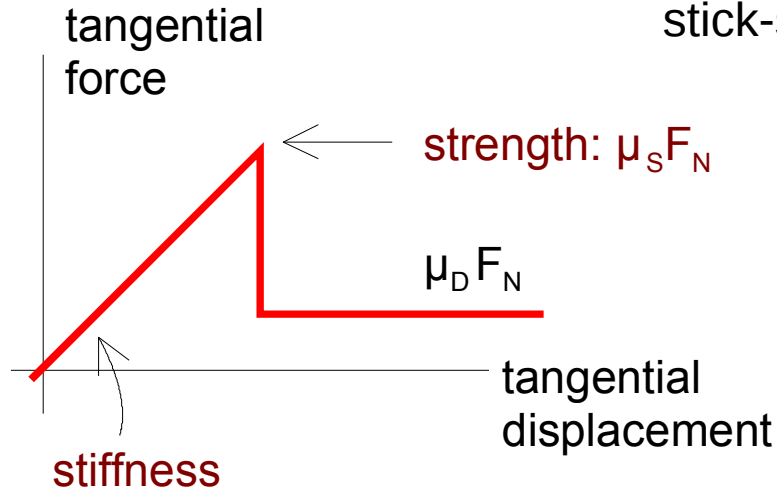


Vlachová, J.; König, R.; Johannsmann, D.
Beilstein J. Nanotechnol. **2015**, *6*, 845.

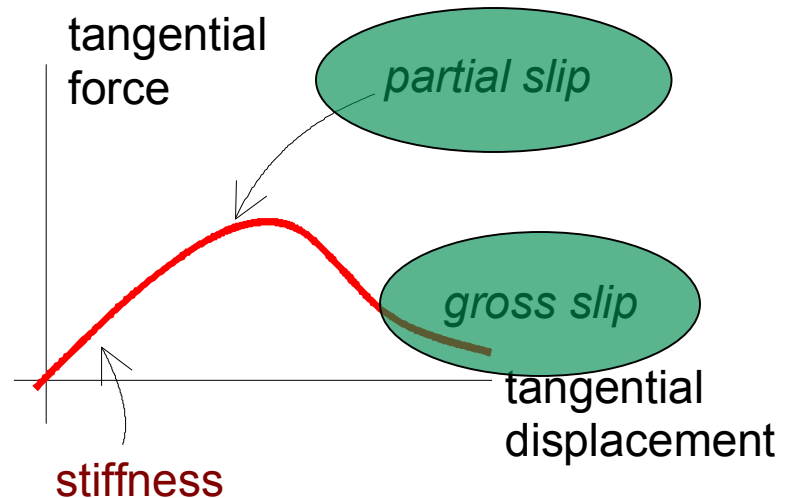
Contact Stiffness → Contact Strength

Coulomb friction

Quasi-static, force control:
stick-slip transition is an instability



Oscillatory motion, strain control:
⇒ Partial slip *not* an instability



Small Load Approximation

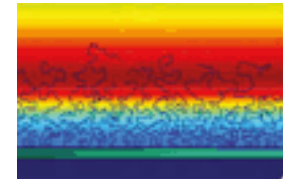
Sauerbrey

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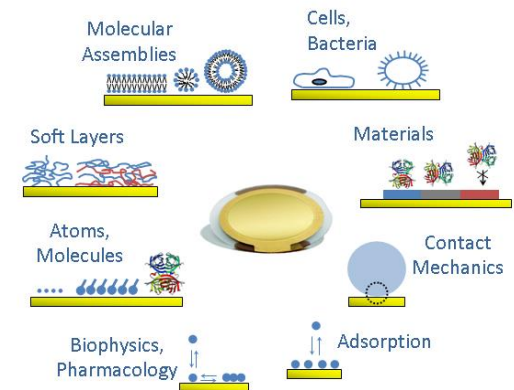


Stress might go back to **viscous drag**, **elastic forces** ...
acoustic multilayers, QTM
high-frequency polymer rheology



The stress can be averaged over **area**: $\frac{\Delta \tilde{f}}{f_0} = \frac{i}{\pi Z_q} \frac{\langle \hat{\sigma} \rangle_{\text{area}}}{\hat{v}}$

Discrete objects: $\langle \hat{\sigma} \rangle_{\text{area}} = \frac{N}{A} \hat{F}$ with $\hat{F}$ the periodic force



The force can be averaged over **time**: $\frac{\Delta \tilde{f}}{f_0} = \frac{i}{\pi Z_q} \frac{N}{A} \frac{2 \langle F(t) \exp(i\omega t) \rangle_{\text{time}}}{\hat{v}}$

QCM covers **nonlinear** force-displacement relations

The QCM and Nonlinear Response

The stress can be averaged over **time**: $\frac{\Delta \tilde{f}}{f_0} = \frac{i}{\pi Z_q} \frac{2 \langle \sigma(t) \exp(i\omega t) \rangle_{\text{time}}}{\hat{v}}$

Loads are small $\rightarrow$ **strain – control**

$$u \approx u_0 \cos(\omega t) \Rightarrow dt = \frac{1}{\omega} \frac{1}{\sqrt{1 - (u/u_0)^2}} du$$

Stress and force can be averaged over **displacement, u**

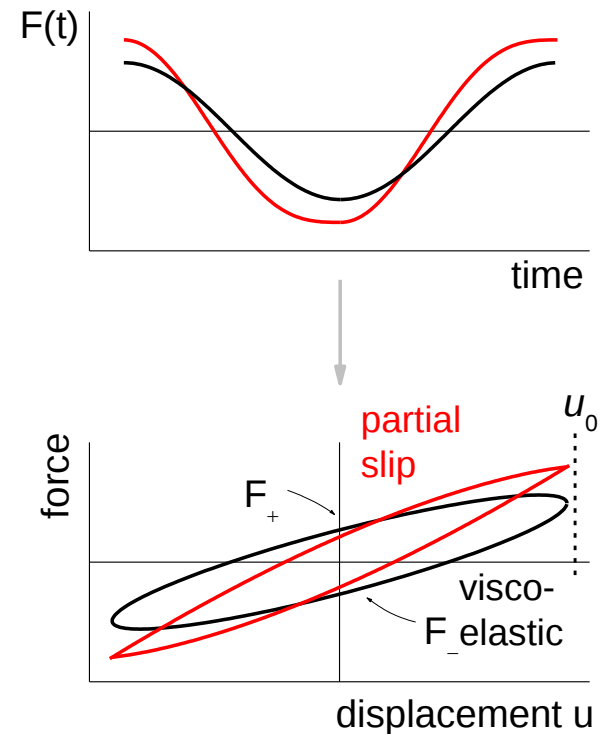
$$\Rightarrow \Delta f \sim \langle F(t) \cos(i\omega t) \rangle_{\text{time}}$$

$$= \left\langle \left(F_+(u, u_0, \omega) + F_-(u, u_0, \omega) \right) \frac{u/u_0}{\sqrt{1 - (u/u_0)^2}} \right\rangle_u$$

$$\Delta \Gamma \sim \langle F(t) \sin(i\omega t) \rangle_{\text{time}}$$

$$= \left\langle \left(F_+(u, u_0, \omega) - F_-(u, u_0, \omega) \right) \right\rangle_u$$

$\Delta f, \Delta \Gamma$ are weighted averages of friction loop
shape of friction loop uncertain

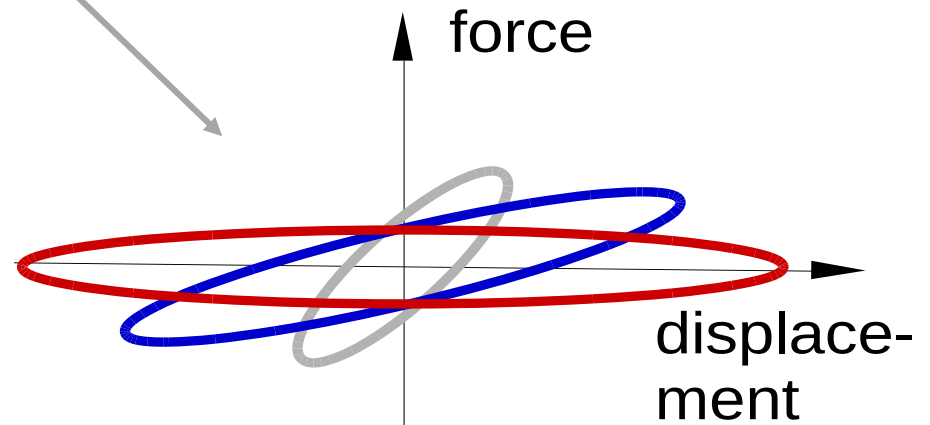
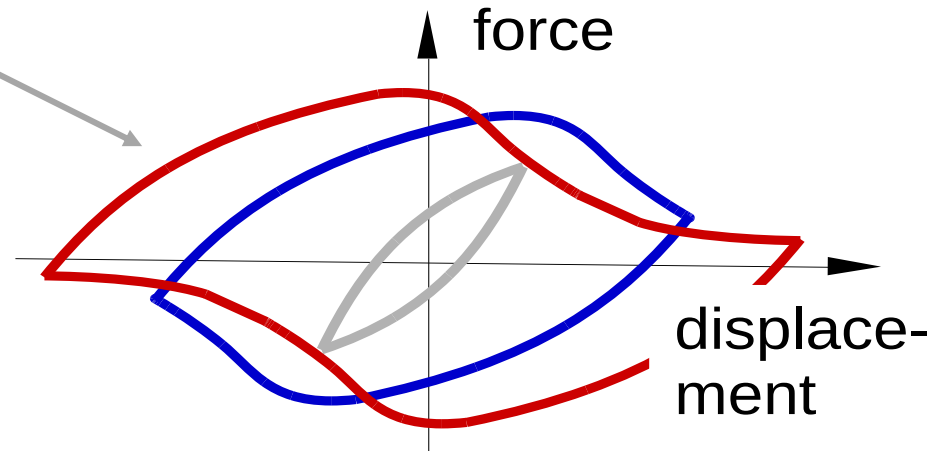


Shape of Friction Loop?

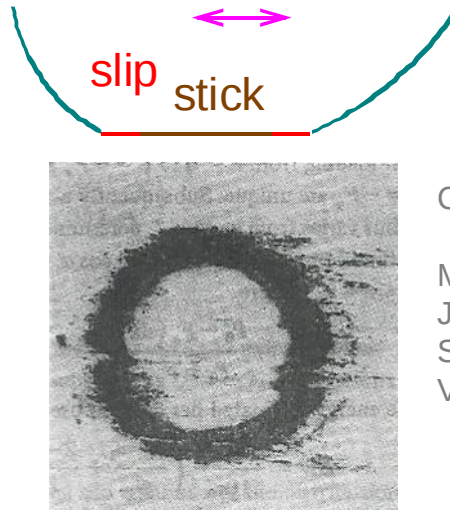
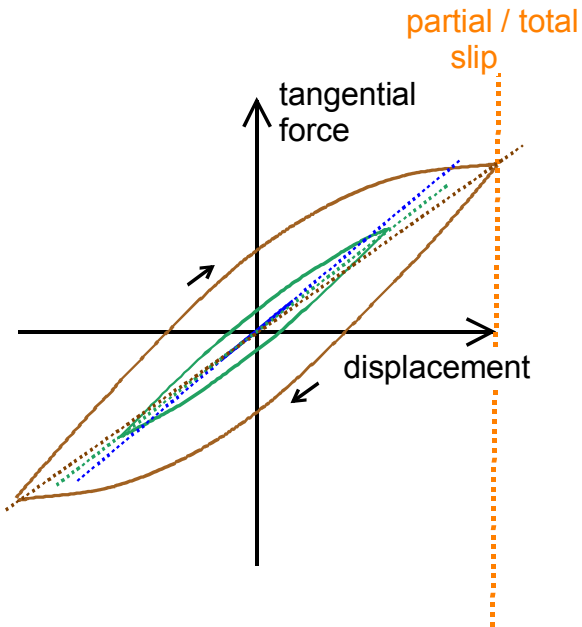
Data fit to Mindlin model

They might also be explained by a temperature-induced softening of the contact

This question can be answered with 3rd harmonic generation



Partial Slip

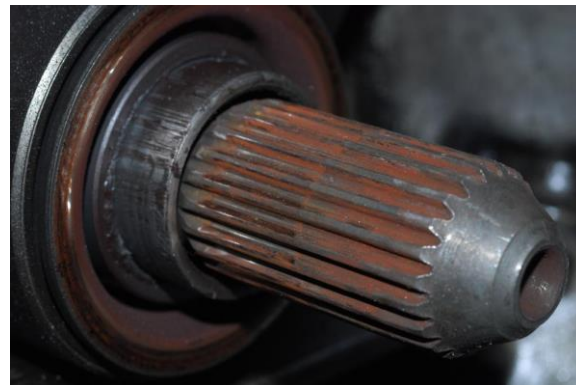


Cattaneo, C.,
Rendiconti dell' Accademia Nazionale dei Lincei **1938**
Mindlin, R.D.; Deresiewicz H.: *J. Appl. Mech.* **1953**
Johnson, K. L., *Contact Mechanics* **1985**
Savkoor, A. R. Tech. University Delft, **1987**
Varenberg, M.; Etsion, I.; Halperin, G.,
Tribology Letters **2005**

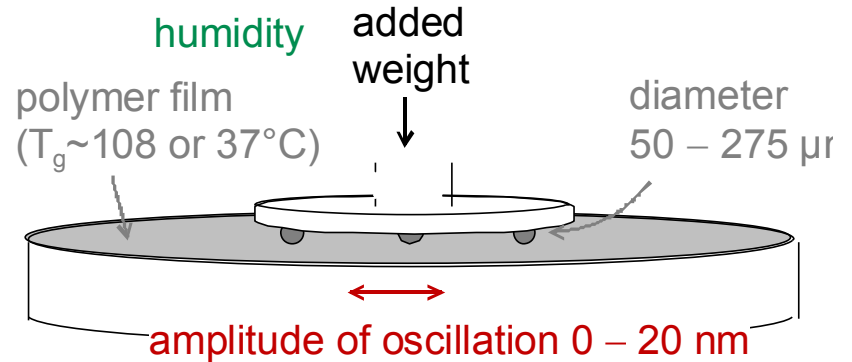
When transient: $\Rightarrow$ Transition state between stick and slip, mixed lubrication, ...

When slow: $\Rightarrow$ Contact aging, compaction, soil mechanics, granular media, ...

When oscillatory: $\Rightarrow$ **Fretting wear**



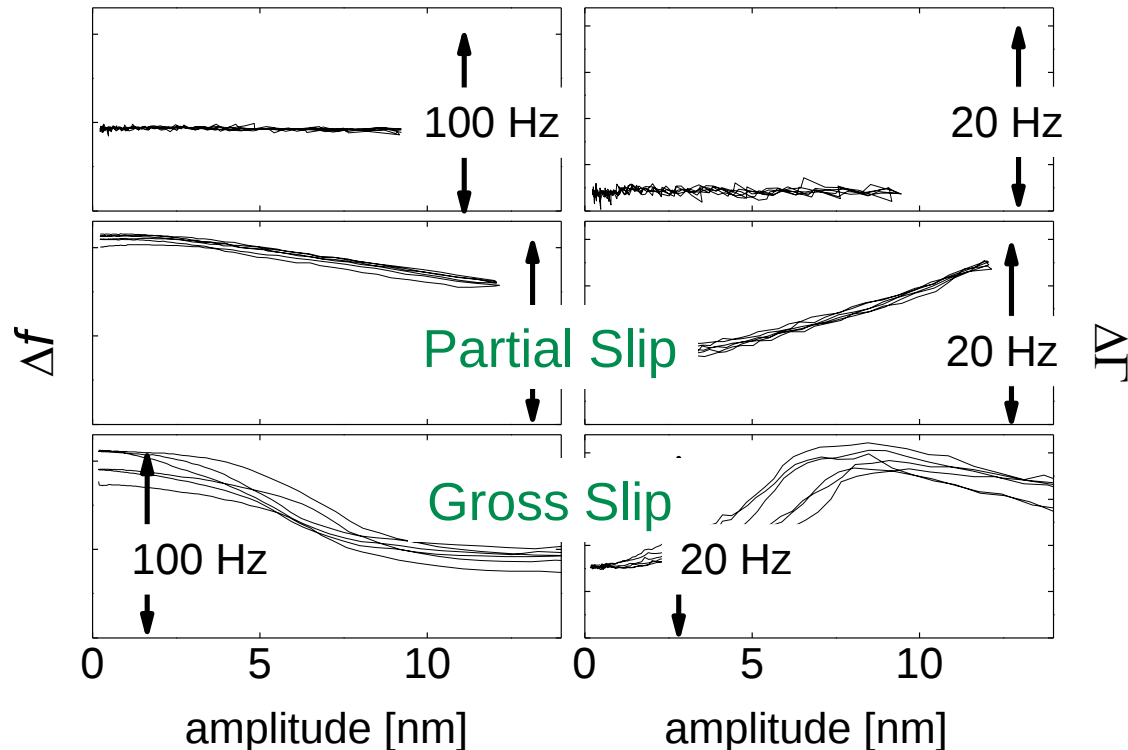
Partial Slip and Gross Slip



Small spheres ($d = 50 \mu\text{m}$)
soft substrate ($T_g \sim 37^\circ\text{C}$)

Medium size spheres (140 μm)
soft substrate ($T_g \sim 37^\circ\text{C}$)

Large spheres (275 μm)
hard substrate ($T_g \sim 108^\circ\text{C}$)



Partial Slip $\Rightarrow$ Nonlinear Stress-Strain Relations

Quantitative models for the force-displacement relation exist
(but: quasi-static)

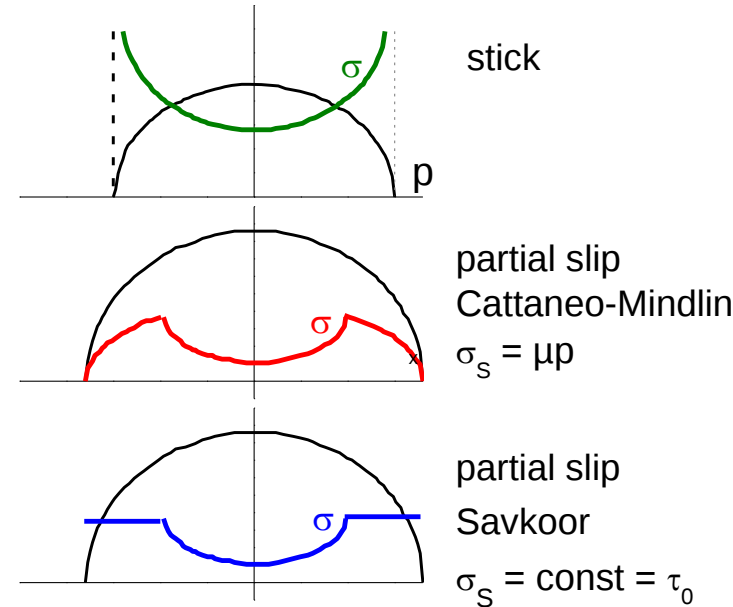
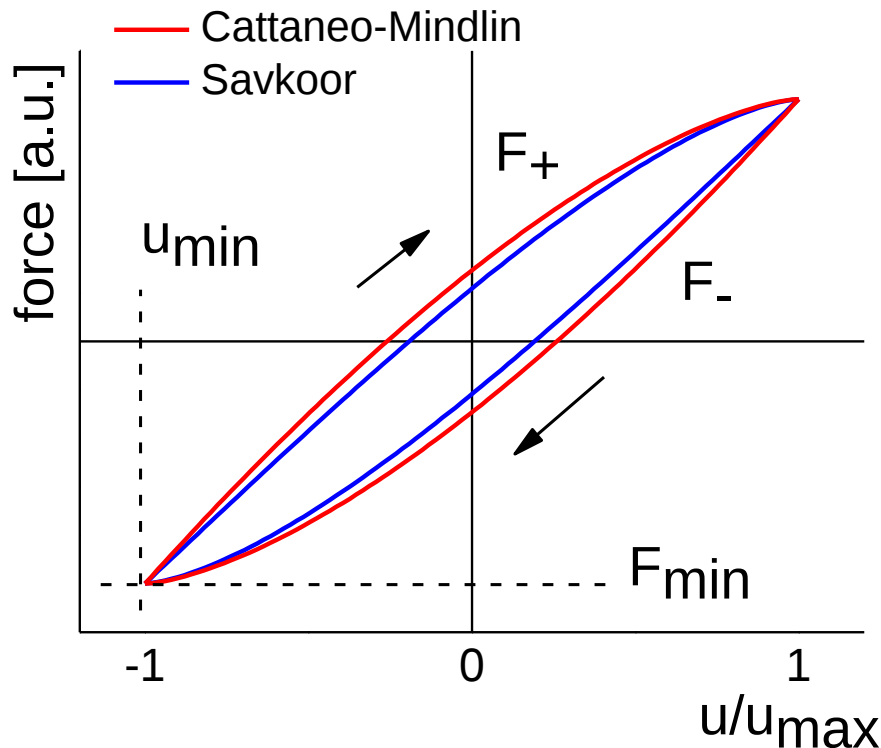
Stress in sliding zone follows Coulomb ($\sigma_s = \mu p$)

Cattaneo, C., *Rendiconti dell' Accademia Nazionale dei Lincei* **1938**

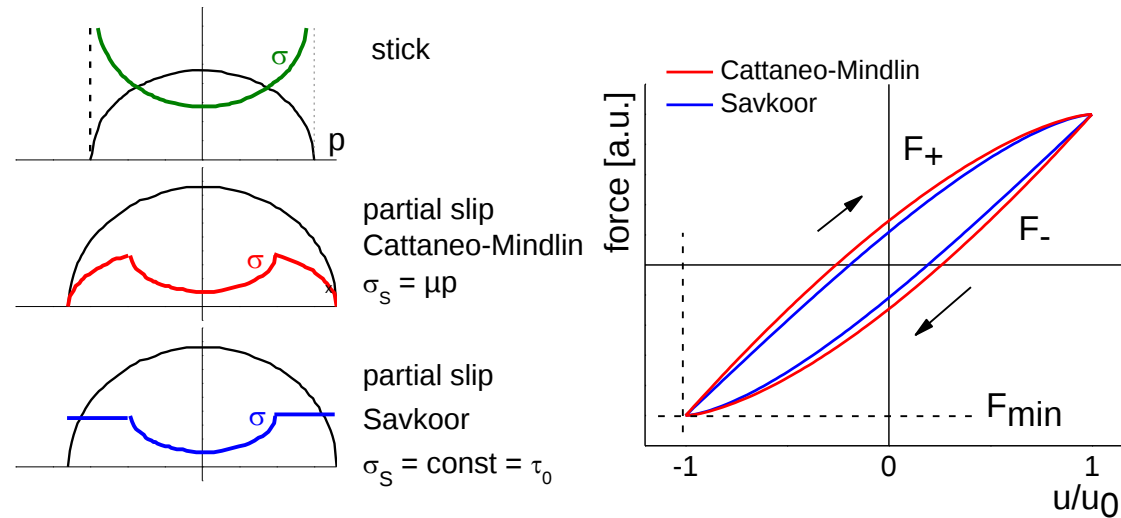
Mindlin, R.D.; Deresiewicz H.: *J. Appl. Mech.* **1953**

Stress in sliding zone constant ($\sigma_s = \text{const.}$)

Savkoor, A. R. Tech. University Delft, 1987



Partial Slip $\Rightarrow$ Nonlinear Stress-Strain Relations



Cattaneo-Mindlin

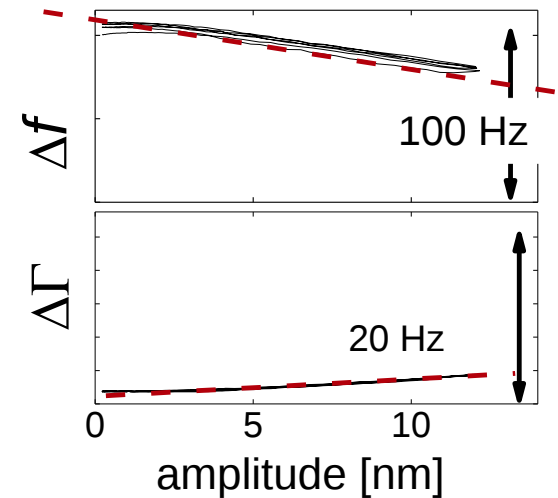
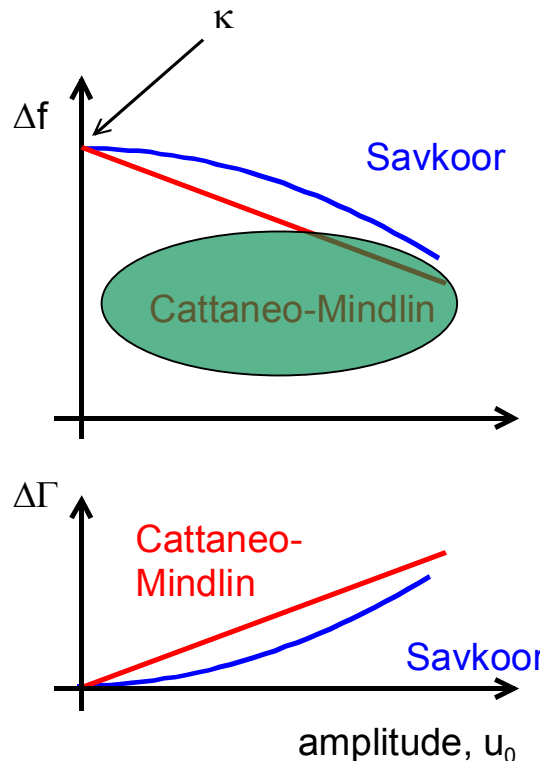
$$\Delta f(u_0) \approx \frac{N}{A 2n\pi^2 Z_q} \kappa \left(1 - \frac{\kappa}{3\mu F_N} u_0 \right)$$

$$\Delta \Gamma(u_0) \approx \frac{N}{A 2n\pi^2 Z_q} \kappa \frac{4}{9\pi} \frac{\kappa}{\mu F_N} u_0$$

Savkoor

$$\Delta f(u_0) \approx \frac{N}{A 2n\pi^2 Z_q} \kappa \left(1 - \frac{5}{8} \left(\frac{\kappa u_0}{4\tau_0 a^2} \right)^2 \right)$$

$$\Delta \Gamma(u_0) \approx \frac{N}{A 2n\pi^2 Z_q} \kappa \frac{8}{6\pi} \left(\frac{\kappa u_0}{2\tau_0 a^2} \right)^2$$



Also: Leopoldes, J.; Jia, X.,
PRL 2010

Multifrequency Lockin Analysis

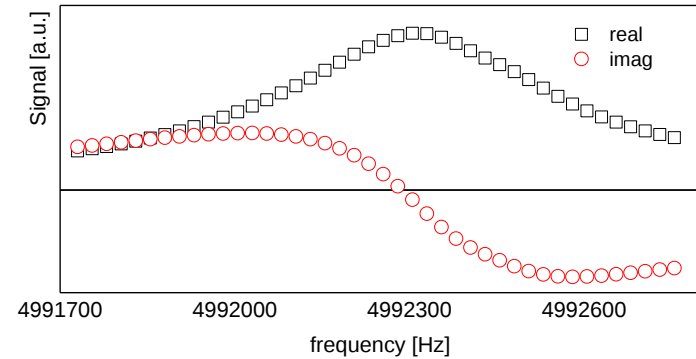
Intermodulation Products AB, Sweden

A) Frequency combs

A fast (milliseconds) way to probe resonances

42 freqs, fit Lorentzians $\rightarrow \Delta f, \Delta \Gamma$

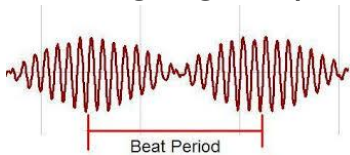
(no calibration required)



B) Intermodulation products

Excite with 2 frequencies

$\rightarrow$ beating signal (fast amplitude ramps)

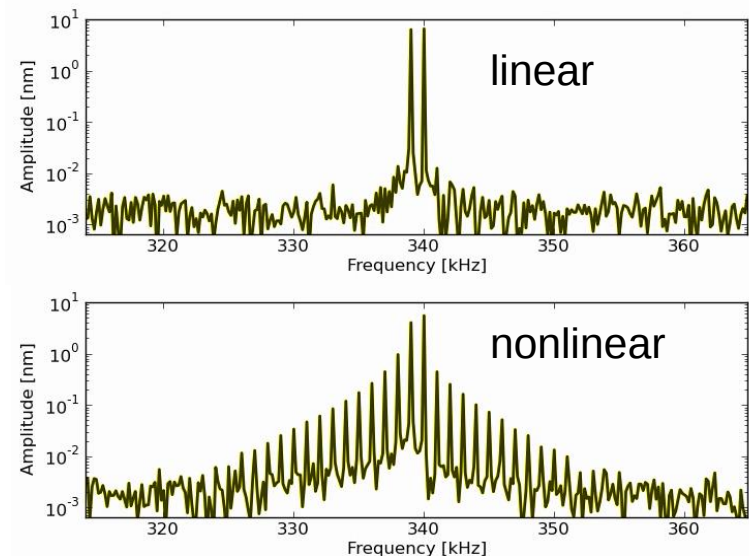


Nonlinearities $\rightarrow$ signals at $f = 2f_1 - f_2$ and $2f_2 - f_1$

- Fast
- Signal resonantly enhanced, response function well understood

C. Hutter *et al.* Phys. Rev. Lett. **2010**, 104, 050801

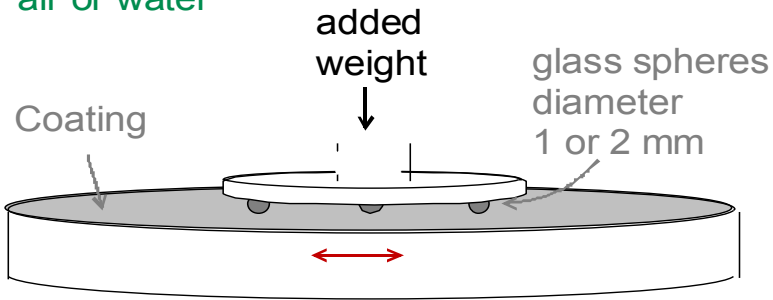
- Calibration issues



C) 2nd and 3rd Harmonic Generation

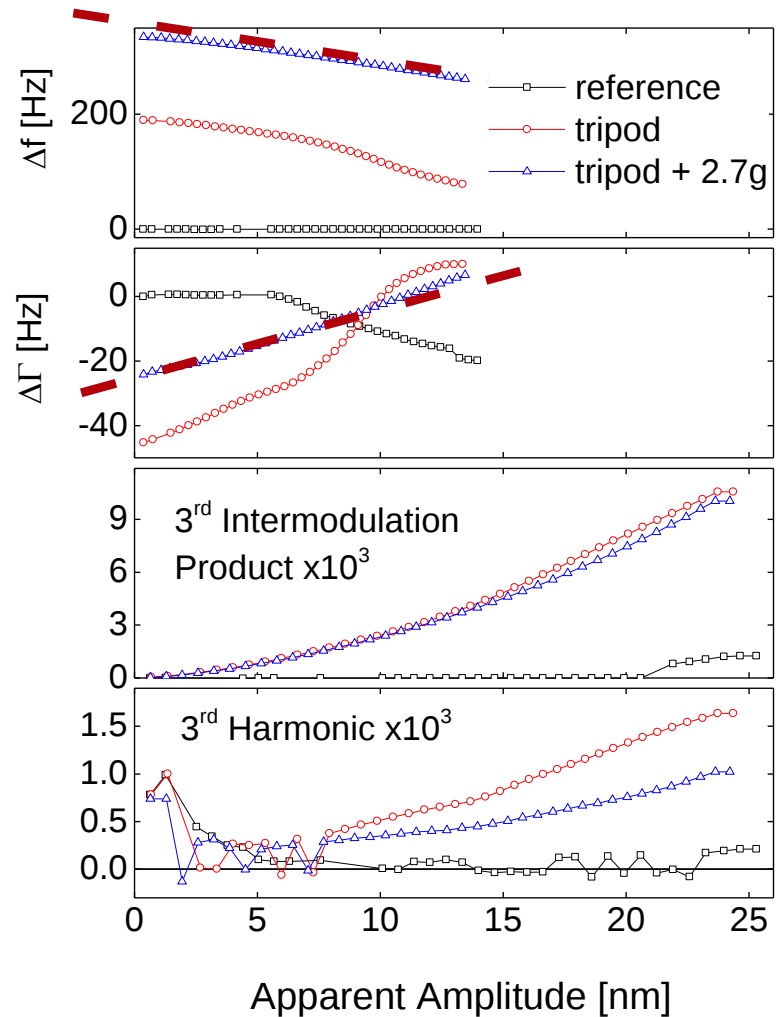
- Excite at f , probe at $2f, 3f$, etc... (also: determine background)
- Signal *not* resonantly enhanced
- Probes MHz dynamics

air or water

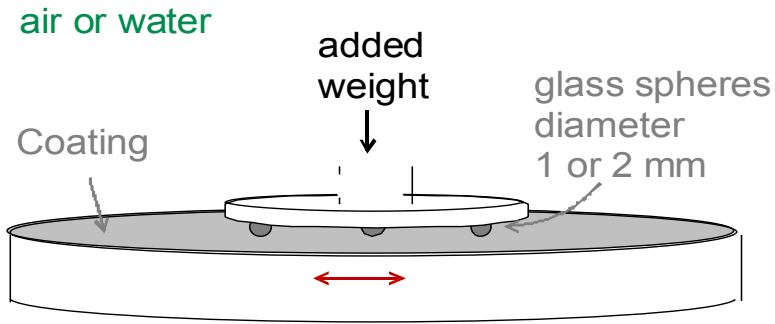


- Mindlin model works here (does not always work)
- There *is* a 3rd harmonic signal
- There *is* a weak 2nd harmonic signal (normal forces involved)
- Here: 5 MHz (fundamental mode) results are different on overtones
- Strong intermodulation products

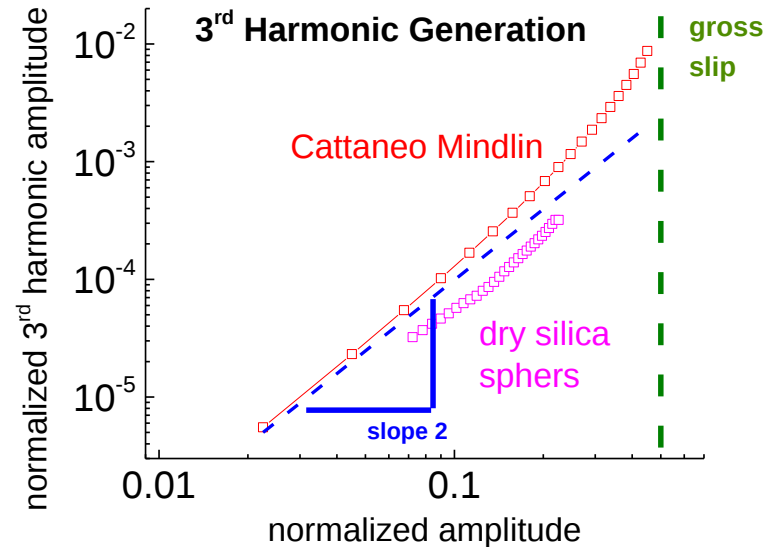
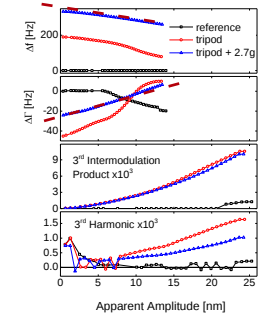
Partial Slip



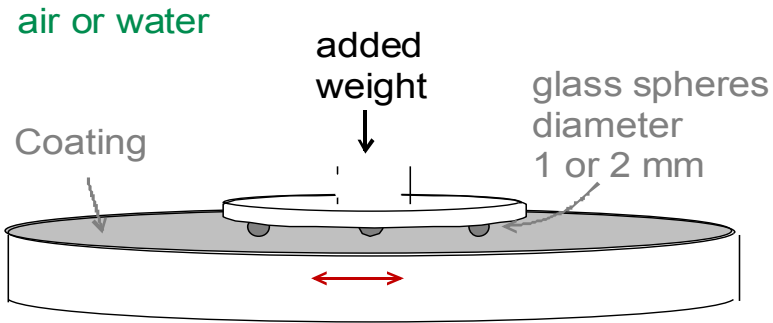
Partial Slip



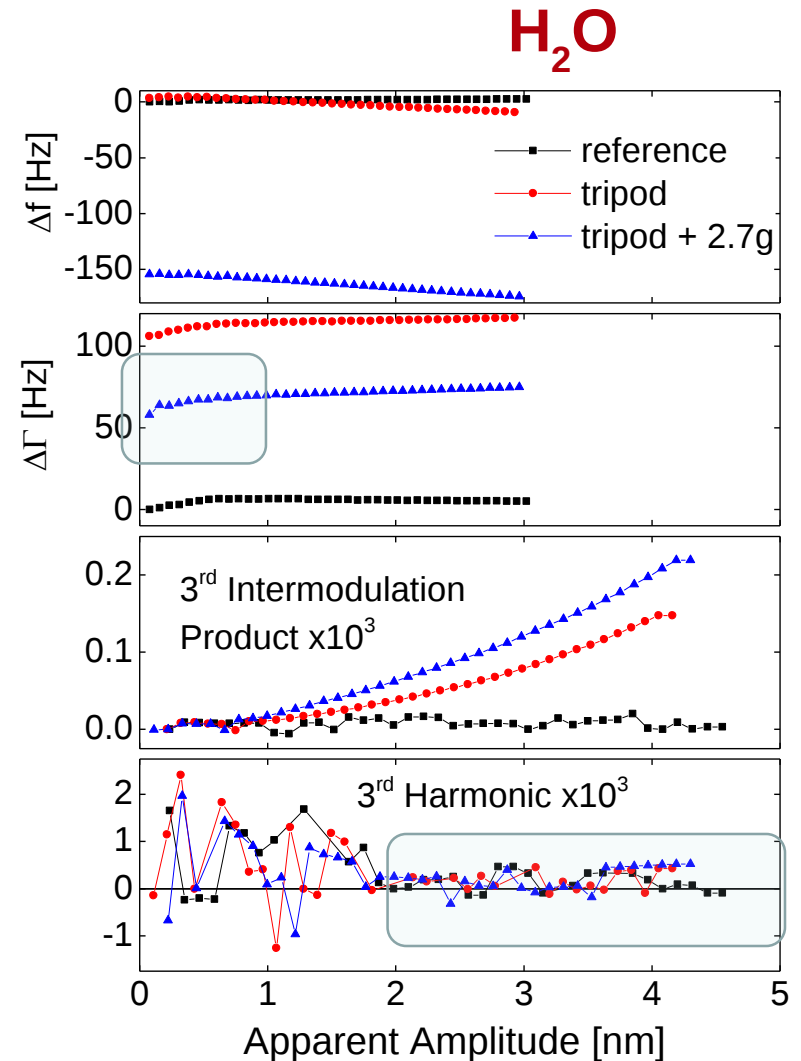
- Mindlin model works here (does not always work)
- Red: Mindin-Theory
- Calibration issues
- Partial slip is at least partially transient



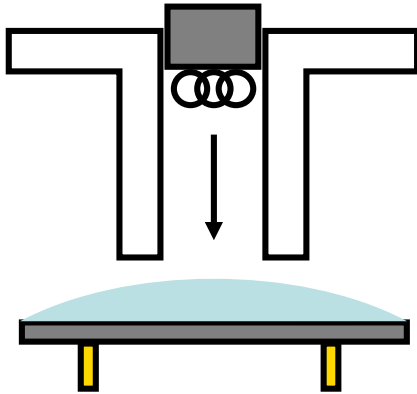
Partial Slip in Liquids



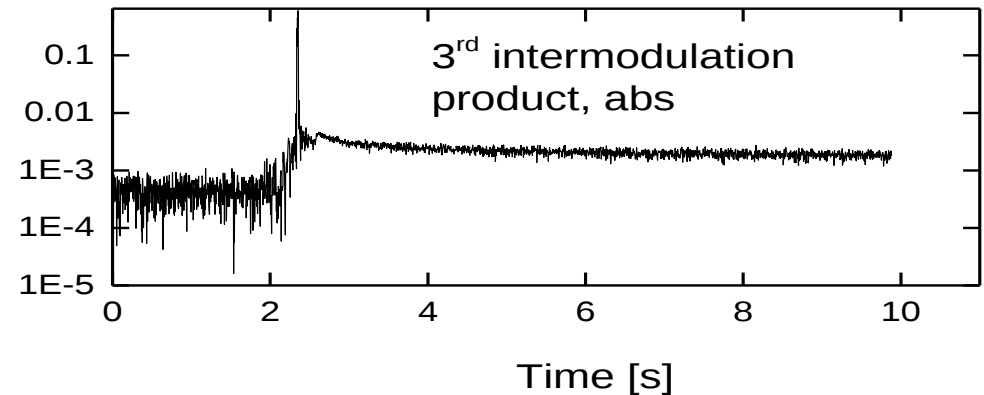
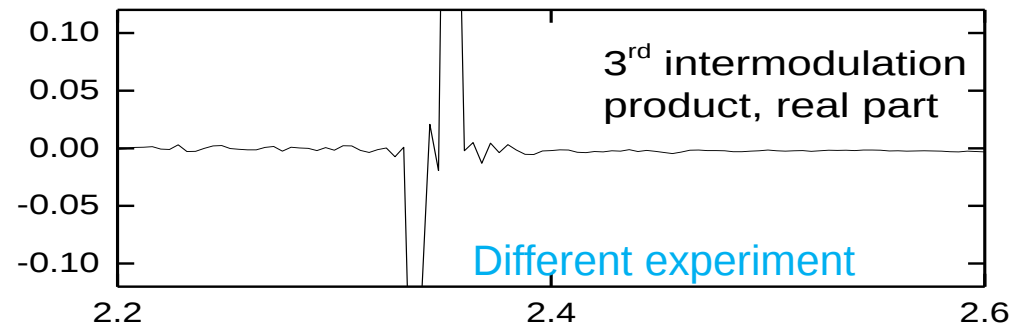
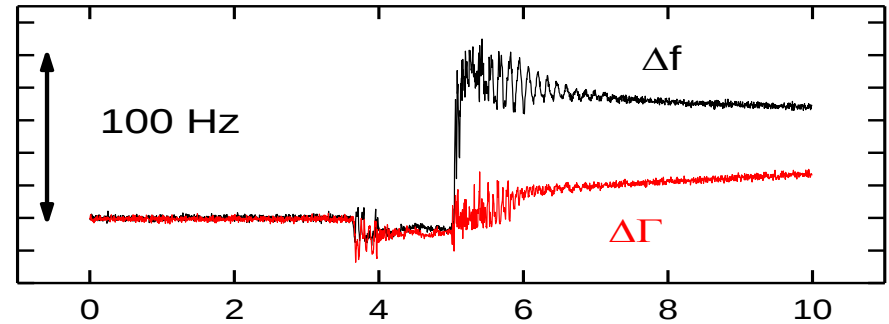
- Rich phenomenology at small amplitudes
- No 3rd harmonic generation
- Intermodulation products seen



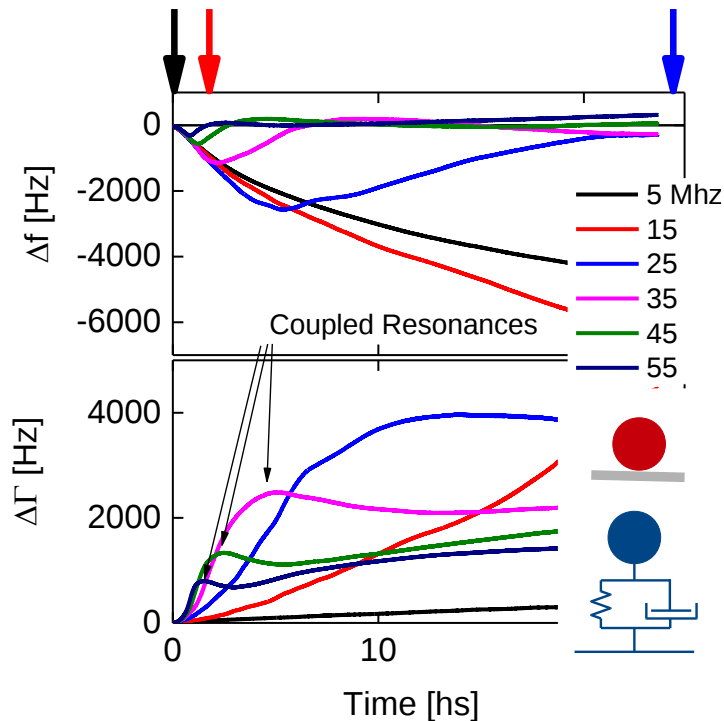
Sudden Impacts



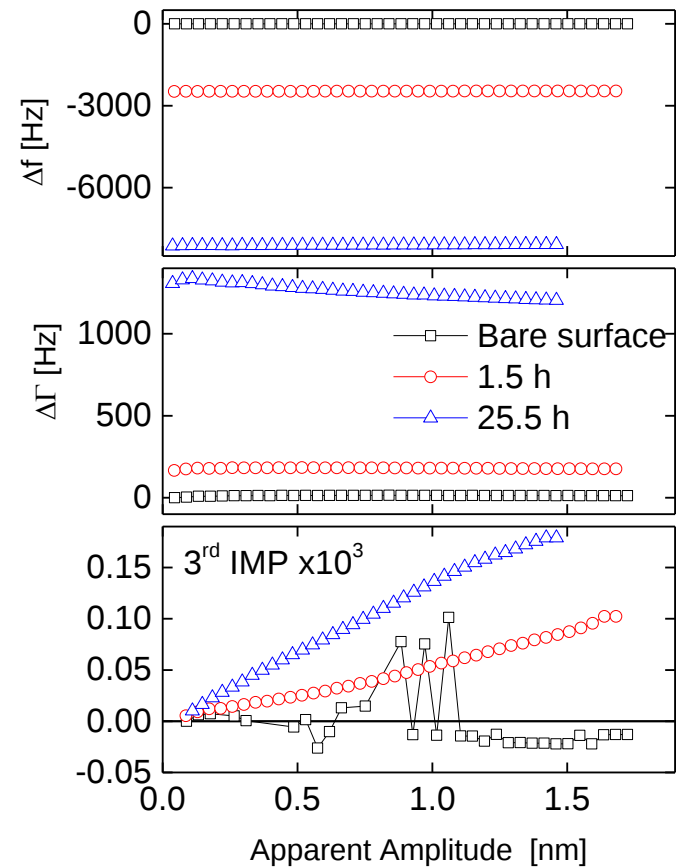
- Transient friction events accessible
- Nonlinearities only *at* impact



Crystallization



- $\text{CaCO}_3(\text{aq})$, $T = 23^\circ\text{C}$
thiolated gold surface, quiescent solution
initial supersaturation $S = 1.5$
- Conventional QCM: Coupled Resonances



Multifrequency Lockin Amplifier (separate experiment)

- $\Delta f(u)$, $\Delta \Gamma(u)$ do *not* fit Mindlin model
- no 3rd harmonic generation
- Intermodulation products seen

Conclusions

- Fast QCM measurements ($\Delta t = 4$ ms)
- 3rd harmonic generation: Partial slip *is* a transient event.
- Intermodulation products probe nonlinear mechanics.
- Impact of particles on QCM surface can be monitored.
Nonlinearities are most pronounced during first impact.
- CaCO_3 nanoparticles (crystals) formed as individual objects
Undergo rocking motion with nonlinear response.