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Modeling of QCM Data

Diethelm Johannsmann
Institute of Physical Chemistry, Clausthal University of Technology
johannsmann@pc.tu-clausthal.de
www.pc.tu-clausthal.de

Chapter numbers refer to the document
http://home.tu-clausthal.de/~pcdj/QCM_Modeling_Tutorial.pdf

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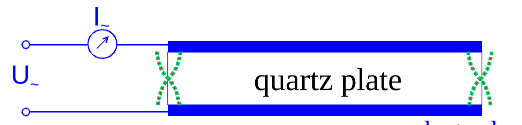
Some remarks on BAW resonators



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

$\Rightarrow$ large current

- exceptionally high Q
- *weakly* piezoelectric, piezoelectricity is convenient for detection, *but unessential for acoustic modeling*
- thickness shear mode, "TSM" resonators
  - shear displacement
  - *k*-vector ⊥ surface
  - width à thickness

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Some remarks on BAW resonators (2)

- The term "QCM" is used here for all BAW resonators (including, for instance, non-gravimetric $GaPO_4$ or LGS sensors[1])
- Theory below works best for planar, optically polished crystals on intermediate overtone orders ($n = 5 – 11$)
- Some of the theory applies to shear horizontal SAW devices in a very similar way.[2] The reflection coefficient of acoustic shear waves enters.
- Noise level for resonators exposed to the environment is ~ $\delta f/f \sim 10^{-7}$ (not as good as clocks)
- QCM is very simple
  ⇒ can be easily combined with other surface-analytical techniques (electrochemical cyclovoltammetry, SPR, AFM, …)

1 H. Fritze, H.L. Tuller, *Appl. Phys. Lett.* **78**, 976 (2001).
2 F. Martin, M.I. Newton, G. McHale, Ka.A. Melzak, E. Gizeli, *Biosensors and Bioelectr.* **19,** 627 (2004).
Y.V. Gulyaev, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **45,** 935 (1998).

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Probing soft matter with ultrasonic shear sound

- Inertia is about 10^6 times stronger than in conventional rheology
- Polymers: Time-Temperature Superposition (TTS)
  The QCM probes the samples under conditions equivalent to about −50°C (TTS does *not* hold for colloidal dispersions[2])
- The wavelength of shear sound enters the picture
  ⇒ evanescent shear waves, `surface specificity`

[1] J.D. Ferry, "*Viscoelastic Properties of Polymers*", Wiley, New York 1980.
[2] R. Lionberger, W.B. Russel, *J. Rheol.* **38**, 1885 (1994).
G. Fritz, W. Pechhold, N. Willenbacher, N.J. Wagner, *J. Rheol.* **47**, 303 (2003).
N.J. Wagner, *J. Coll. Interf. Sci.* **161**, 169 (1993).

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Assumptions of the standard model

- resonator is a planar, laterally infinite disk
- deformation is a plane wave, wave vector k perpendicular to the surface
- linear acoustics (stress proportional to strain)
- experimentalist measures the complex electric admittance $Y(\omega) = 1/Z(\omega)$

Not covered in the standard model
- energy trapping
- dielectric effects / piezoelectric stiffening (ground the front electrode well)
- roughness, heterogeneities
- compressional waves
- anharmonicity / nonlinearities
- spurious modes
- effects of temperature and static stress

Standard Model
H.L. Bandey, S.J. Martin, R.W. Cernosek, A.R. Hillman, *Anal. Chem.* **71**, 2205 (1999).
S.J. Martin, H.L. Bandey, R.W. Cernosek, A.R. Hillman, M.J. Brown, *Anal. Chem.* **72**, 141 (2000).
M.V. Voinova, M. Rodahl, M Jonson, B. Kasemo, Physica Scripta **59**, 391 (1999).
D. Johannsmann, *Macromol. Chem. Phys.* **200**, 501 (1999)
J. Kankare, *Langmuir* **18**, 7092 (2002).

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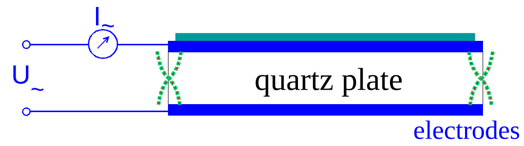
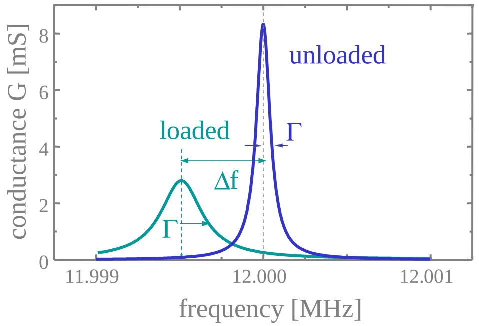
TU Clausthal — Impedance analysis



f = f_{res} : large amplitude of motion

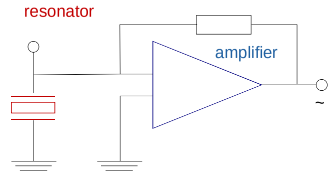
⇒ large current

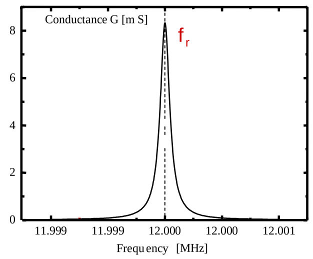


- shift of frequency (Δf) *and* of bandwidth ($\Delta\Gamma$)
- many overtones (5 – 15)

R. Beck, U. Pittermann, K.G. Weil, *Ber. Bunsen-Ges. Phys. Chem.* **92**, 1363 (1988).
The frequency-modulation approach put forward by
L. Bruschi, G. Delfitto, and G. Mistura (*Rev. Sci. Instr.* **70**, 153 (1999))
in essence is a very fast version of impedance analysis.

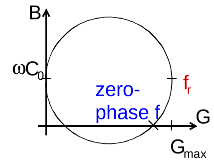
TU Clausthal — Oscillator circuits





advantages:
- low noise
- low cost

disadvantages:
- usually one harmonic only
- usually no bandwidth

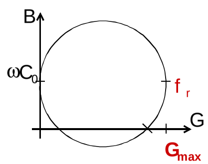


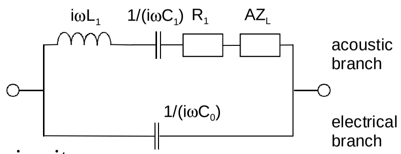
Oscillators often do not operate on the series resonance frequency, f_r, but rather on some other frequency (such as the zero phase frequency).

When ωC_0 or G_{max} change, this frequency changes, although f_r itself is unchanged
⇒ artifacts

See, e.g., P. Horowitz and W. Hill, *The Art of Electronics*, Cambridge University Press, New York, 1989.

TU Clausthal — Oscillator circuits with resistance monitoring





$R_1 = G_{max}^{-1}$ is monitored by some advanced circuits

The Butterworth-von-Dyke (BvD) circuit predicts[1]

$$R_1 = \frac{d_q^2}{8Ae_{26}^2} Z_q n\pi \frac{2\Gamma}{f}$$

d_q : thickness of the crystal, A: effective area

e_{26}=9.65×10^{-2} C/m^2: piezoelectric stress coefficient

Z_q = 8.8×10^{6}kg/(m^{2}s) : acoustic impedance of AT-cut quartz, *n*: overtone order

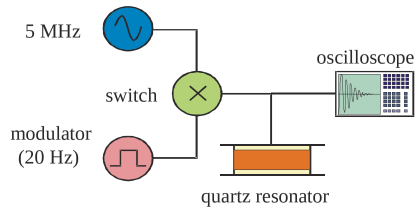
Impedance analysis tells: R_1 / Γ varies (although it shouldn't...)

⇒ R_1 is not the best measure of dissipative processes on the crystal surface[2]

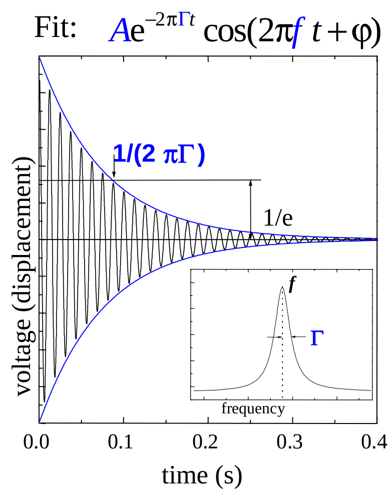
1 See eq. 12.21 in QCM_Modeling_Tutorial.pdf
2 See sect. 2 in QCM_Modeling_Tutorial.pdf

A. Arnau, T. Sogorb, Y. Jimenez, *Rev. Sci. Instr.* **73**, 2724 (2002).
C. Chagnard, P. Gilbert, A.N. Watkins, T. Beeler, D.W. Paul, *Sensors and Actuators B – Chemical* **32**, 129 (1996).

TU Clausthal — Ring down



Fit: $Ae^{-2\pi\Gamma t}\cos(2\pi f\, t+\varphi)$



Implemented by Q-sense (“QCM-D“)

“*D*” stands for dissipation

$D = Q^{-1} = 2\Gamma/f$

M. Rodahl, B. Kasemo, *Rev. Sci. Instr.* **67**, 3238 (1996).
K. Sittel, P.E. Rouse, E.D. Bailey, *J. Appl. Phys.* **25**, 1312 (1954).

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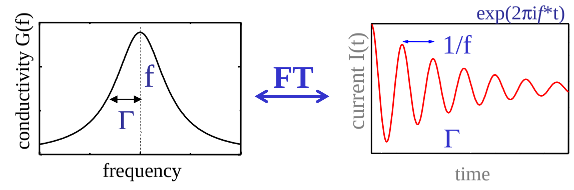
Complex resonance frequency

complex
resonance frequency
$f^* = f + i\Gamma$



Complex resonance curve[1]

$$\frac{u(f)}{F(f)} \propto \frac{1}{f_r^2 - f^2 + 2i\Gamma f} \approx \frac{1}{(f_r + i\Gamma)^2 - f^2} = \frac{1}{\tilde{f}_r^2 - f^2}$$

OK, if $\Gamma \ll f$ (always true for the QCM)

Complex frequency shift $\Delta\tilde{f} = \Delta f + i\Delta\Gamma$

`Reduces the number of equations used below by a factor of 2`

[1] See Chapter 2 in QCM_Modeling_Tutorial.pdf

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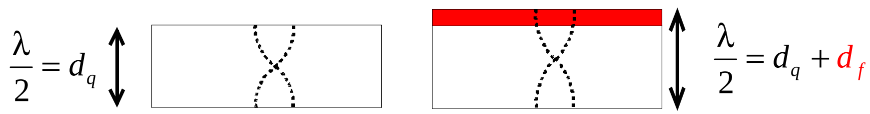
Microweighing: quartz crystal microbalance (QCM)



Sauerbrey equation

$$\Delta f = -\frac{2n f^2}{Z_q}\Delta m$$

Δf : frequency shift
Δm: mass per unit area
Z_q : acoustic impedance of quartz
n: overtone order

application: film thickness monitor

C. Lu, A. W. Czanderna (edts.), *Applications of Piezoelectric Quartz Crystal Microbalances*, Elsevier, Amsterdam 1984.
A. Arnau, (edt.), *Piezoelectric Transducers and Applications*, Springer, Heidelberg 2004.
J.W. Grate, *Chem. Rev.* **100**, 2627 (2000).
G. Sauerbrey, *Z. Phys.* **155**, 206 (1959).
M.D. Ward, D.A. Buttry, *Science* **249**, 1000 (1990).

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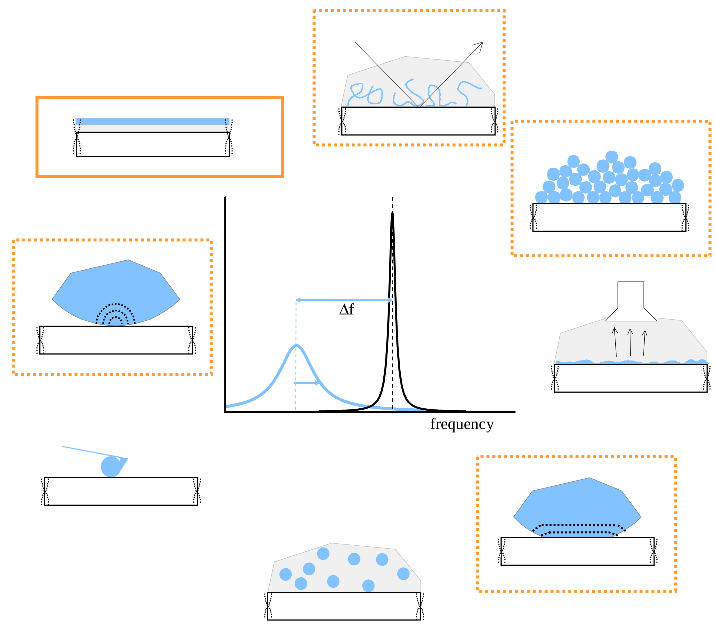
QCM as a dynamical probe



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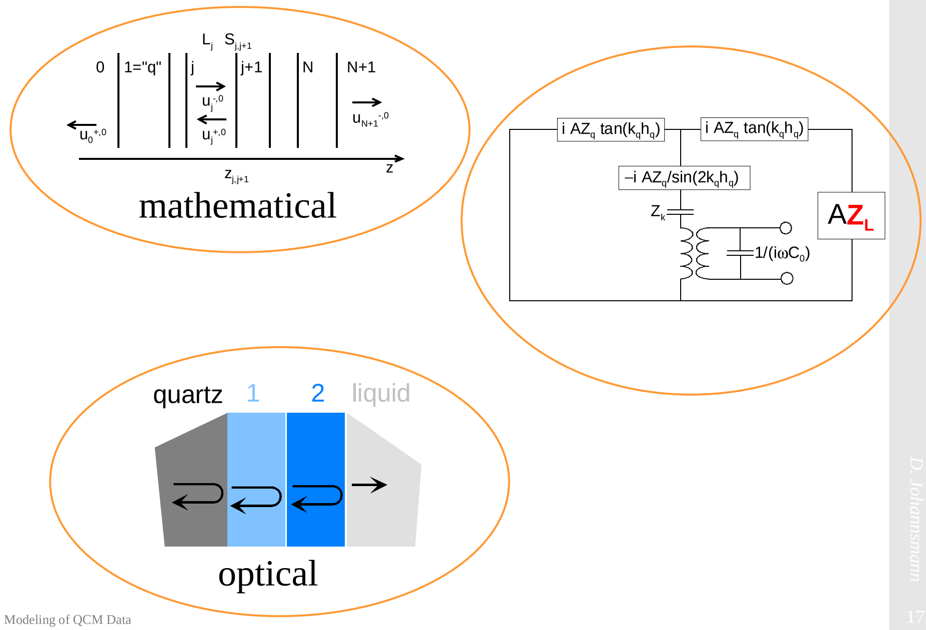
Ways of modeling layer systems



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Mathematical description

- N layers, supporting two waves traveling to the right ($u_j^{-,0}$) and to the left ($u_j^{+,0}$) each
- wave equation holds

$$u_j^- = u_j^{-,0} \exp(-i k_j z)$$

$$u_j^+ = u_j^{+,0} \exp(-i k_j z)$$

$$k_j = \frac{\omega}{c_j} = \omega\sqrt{\frac{\rho_j}{G_j}} = \omega\frac{\rho_j}{Z_j}$$

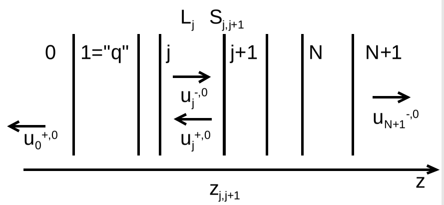
k : wavenumber,

$c=\sqrt{\frac{G}{\rho}}$: speed of sound

ρ: density

G : shear modulus

$Z=\rho c=\sqrt{\rho G}$ acoustic impedance (materials property)



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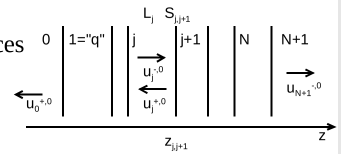
Mathematical description (2)

- Stress and displacement continuous at N+1 interfaces



$$u_j^+(z_{j,j+1}) + u_j^-(z_{j,j+1}) = u_{j+1}^+(z_{j,j+1}) + u_{j+1}^-(z_{j,j+1})$$

$$u_j^+(z_{j,j+1}) + u_j^-(z_{j,j+1}) = u_{j+1}^+(z_{j,j+1}) + u_{j+1}^-(z_{j,j+1})$$

$\Rightarrow$ homogenous linear system of 2N+2 equations for 2N+1 amplitudes

For example

$$\begin{bmatrix} -1 & 1 & 1 & 0 \\ 0 & \tilde{Z}_q & -\tilde{Z}_q & 0 \\ 0 & \exp(i\tilde{k}_q d_q) & \exp(-i\tilde{k}_q d_q) & -1 \\ 0 & \tilde{Z}_q \exp(i\tilde{k}_q d_q) & -\tilde{Z}_q \exp(-i\tilde{k}_q d_q) & 0 \end{bmatrix} \begin{bmatrix} u_0^{+,0} \\ u_q^{+,0} \\ u_q^{-,0} \\ u_2^{-,0} \end{bmatrix} = 0$$

Set the determinant to zero .... and find the resonance frequency

`- intransparent`

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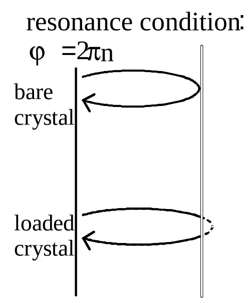
Optical picture



- resonance condition: phase acquired in one round trip is a multiple of 2π
- non-trivial reflectivity at the crystal – sample interface ("$r_{q,2}$") will change resonance frequency

(a) what is $r_{q,2}$?

(b) what is the relation between $r_{q,2}$ and Δf ?

Reflectivity

At an interface, the coefficients of reflection and transmission for the various waves *serve to satisfy the boundary conditions*

displacement(I): $u_a^{+,0} + u_a^{-,0} = u_b^{-,0}$

stress (II):
$$G_a \frac{d\left[u_a^{+,0} + u_a^{-,0}\right]}{dz} = G_b \frac{d u_b^{-,0}}{dz}$$
$$G_a i k_a \left[u_a^{+,0} - u_a^{-,0}\right] = G_b i k_b u_b^{-,0}$$
$$Z_a \left[u_a^{+,0} - u_a^{-,0}\right] = Z_b u_b^{-,0}$$

$$\Rightarrow \quad r_{a,b} = \frac{u_a^{+,0}}{u_a^{-,0}} = \frac{Z_a - Z_b}{Z_a + Z_b}$$

multilayers: iterative formalism[1]

[1] see section 5

R.M.A. Azzam, N.M. Bashara, *"Ellipsometry and Polarized Light"*, Elsevier, Amsterdam 1987.

M . Salomaki, K. Loikas, J. Kankare, *Anal. Chem.* **75**, 5895 (2003).

Z and *n*

$$r_{a,b} = \frac{u_a^{+,0}}{u_a^{-,0}} = \frac{Z_a - Z_b}{Z_a + Z_b}$$

This equation is reminiscent of the reflectivity of optical waves

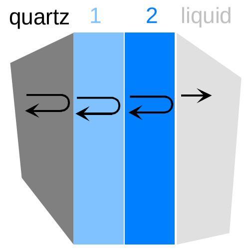
$$r_{a,b,opt} = \frac{n_a - n_b}{n_a + n_b}$$

The acoustic impedance plays the role of an refractive index

`Differences between acoustics and optics`

- in optics, n governs reflectivity *and* the speed of light (because the relative magnetic permeability is always close to one) in acoustics, Z governs the reflectivity only (because the density, ρ, varies)
- strictly speaking, n is not an optical impedance, but rather the inverse ratio of the optical impedance of the medium and vacuum
- no acoustic polarizations and angles of incidence (here)
- n varies by few percent, Z varies easily by a factor of 10

Δf and $r_{q,2}$



$$\frac{\Delta\tilde{f}}{\tilde{f}_f} \approx \frac{i}{2\pi}\left(1 - r_{q,2}\right)$$

- f_f :frequency of the fundamental
- proof in ch. 5
- holds in the complex sense $\frac{\Delta f + i\Delta\Gamma}{\tilde{f}_f} \approx \frac{i}{2\pi}\left(1 - r_{q,2}\right)$
- only holds for $r_{q,2} \approx 1$ (small-load approximation)

`QCM is an acoustic shear wave reflectometer`

True ultrasonic shear wave reflectometers provide equivalent information

I. Alig et al. (1997) Rev Scient Inst 68:1536

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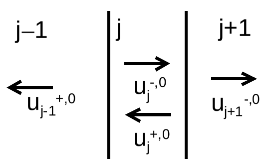
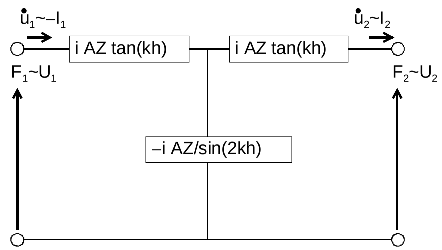
Electrical picture

Equivalent circuits map viscoelastic layers onto sets of discrete circuit elements[1]





[1]: section 11
R.N. Thurston, in C. Truesdell (edt.) *"Mechanics of Solids"*, vol. 4, chap. 36, p. 257, Springer, Heidelberg 1984.

Load impedance

- Electromechanical analogy maps mechanical (and acoustic) quantities onto electrical quantities
  force $F \leftrightarrow$ voltage U
  speed $\dot{u} \leftrightarrow$ current I
  mechanical impedance $Z_m = \frac{F}{\dot{u}} \leftrightarrow$ electrical impedance $Z_{el} = \frac{U}{I}$
- Force can be mormalized to area $A \Rightarrow \sigma = \frac{F}{A}$ (σ:stress)

The parameter $\frac{\sigma}{\dot{u}}$ can not be called "acoustic impedance" because the term is taken by $Z = \sqrt{\rho G}$

We call $Z_L = \frac{\sigma}{\dot{u}}$ "load impedance", "load", or "surface impedance"

`ZL is central to the physics of the QCM`

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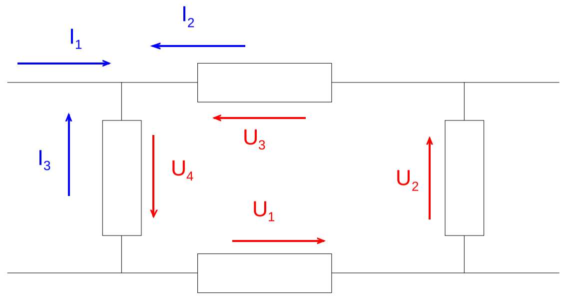
Kirchhoff rules

Once, one has a circuit with discrete elements, one can apply the Kirchhoff rules in order to calculate the input-output relations

(1) Sum of the currents entering a junction is zero
(2) Sum of the voltages in a loop is zero



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Mechanical Kirchhoff rules

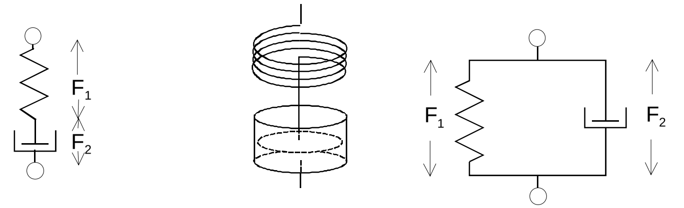
Watch out !
Mechanical Kirchhoff rules are the other way round
For two springs in series, the displacements (and the current) are additive, not the force

Polymer rheology:
Springs and dashpots are drawn as they are physically arranged
(→ different set of Kirchhoff rules)

mechanical Kirchhoff rules
$F_{tot}^{-1} = F_1^{-1} + F_2^{-1}$

physical situation

electrical Kirchhoff rules
$F_{tot}^{-1} = F_1^{-1} + F_2^{-1}$



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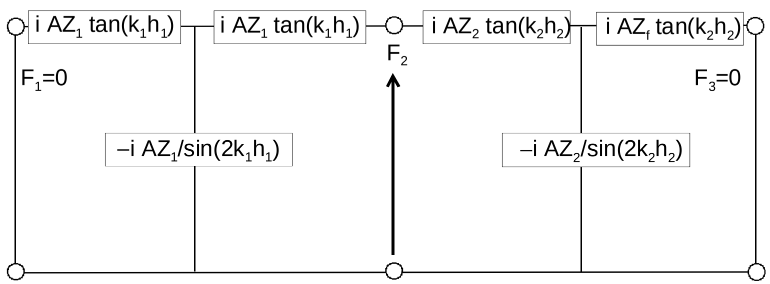
Layer systems



composite resonator with stress-free ports

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Piezoelectricity

Piezoelectricity is depicted as a tranformer

ϕ : "ratio of the number of loops"

$I_{el} = \phi \dot{u}$

$U_{el} = \frac{1}{\phi} F = \frac{1}{\phi} A\sigma$

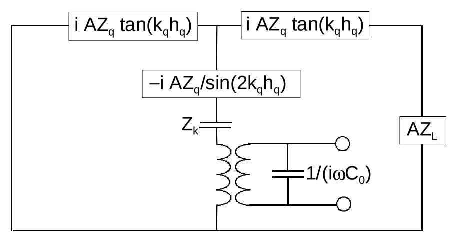
$Z_{el} = \frac{U_{el}}{I_{el}} = \frac{1}{\phi^2}\frac{A\sigma}{\dot{u}} = \frac{1}{\phi^2} Z_m$

$\phi = \frac{Ae_{26}}{d_q}$

d_q : Thickness of the crystal

e_{26} :piezoelectric stress coefficient $e_{26} = 9.65\times10^{-2}\,\mathrm{C/m^2}$ for AT-cut quartz

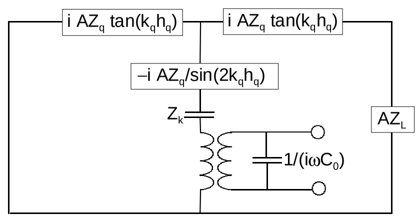
Z_k: accounts for piezoelectric stiffening (small effect)



Mason circuit

W.P. Mason, *"Piezoelectric Crystals and their Applications to Ultrasonics"*, Van Nostrand, Princeton 1948.
H.F. Tiersten, *J. Acoust. Soc. Amer.* **35**, 234 (1963).
J.F. Rosenbaum, *Bulk Acoustic Wave Theory and Devices*, Artech House 1988.
T. Nakamoto et al., *Jpn. J. Appl. Phys.* **29**, 963 (1990).
D. Johannsmann et al., *Phys. Rev. B* **46**, 7808 (1992).
H.L. Bandey, S.J. Martin, R.W. Cernosek, A.R. Hillman, *Anal. Chem.* **71**, 2205 (1999).

Benefits of the Mason circuit



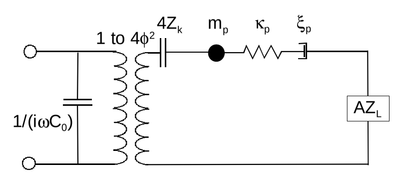
- easy to apply, once you believe it
  (predictive, not a cartoon !)
- rigorous treatment of piezoelecticity
- covers loads on *both* surfaces
- predicts the amplitude of oscillation
- predicts the resistance R_1 from the active area and the Q-factor

- close to resonances:
  some approximations yield the *Butterworth - van - Dyke (BvD) circuit*

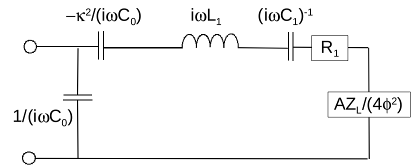
```
Mason circuit is safe ground for complicated situations
```


BvD circuit

mechanical



electrical



$$Z_k = \phi^2 \frac{1}{\mathrm{i}\omega C_0} = \left(\frac{Ae_{26}}{d_q}\right)^2 \frac{1}{\mathrm{i}\omega C_0}$$

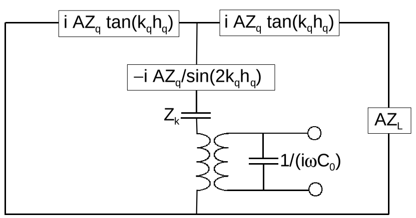
$$\kappa_p = \frac{AG_q}{d_q}\frac{(n\pi)^2}{2} = \kappa_{q,stat}\frac{(n\pi)^2}{2}$$

$$m_p = \frac{A\rho_q d_q}{2} = \frac{1}{2}Am_q$$

$$\xi_p = AZ_q \frac{n\pi}{2}\tan(\delta)$$

BvD circuit (also called 4-element circuit) is derived from Mason circuit in section 11
John Henderson, *Electronic Devices. Concepts and Applications*, Prentice Hall, NJ,(1991) p. 357.

Amplitude of oscillation



Determine the "current" (speed) through the element AZ_L, from the Kirchhoff rules
$\Rightarrow$ amplitude of oscillation, *a*:

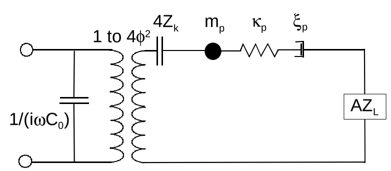
$$\frac{a}{QU_{el}} = \frac{4}{(n\pi)^2}d_{26} = \frac{1.25\ \text{pm}}{n^2\ \ \text{V}}$$

$d_{26} = 3.1\times10^{-12}$ m/V: piezoelectric strain coefficient

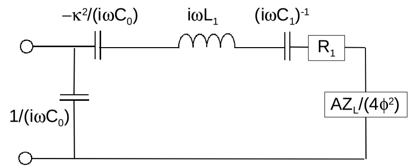
L.O. Heim, D. Johannsmann, J. Appl. Phys. **100**, 094505 (2006)

Active area

mechanical



electrical

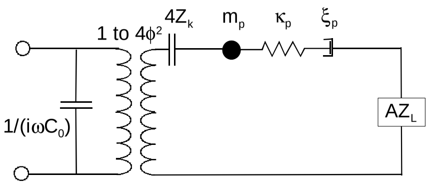


$$R_1 = \frac{1}{4\phi^2}\xi_p$$
$$= \frac{1}{4\phi^2}AZ_q\frac{n\pi}{2}\tan(\delta)$$
$$= \frac{d_q^2}{4A^2e_{26}^2}AZ_q\frac{n\pi}{2}\frac{1}{Q}$$
$$= \frac{c_q^2}{16\, f_f^2 A^2 G_q^2 d_{26}^2}AZ_q\frac{n\pi}{2}\frac{1}{Q}$$
$$= \frac{1}{32\, f_f^2 AZ_q d_{26}^2}n\pi\frac{1}{Q}$$

$$A = \frac{n\pi}{32\, f_f^2 AZ_q d_{26}^2}\frac{1}{QR_1}$$

L.O. Heim, D. Johannsmann, J. Appl. Phys. **100**, 094505 (2006)

TU Clausthal — Small-load approximation



$$\frac{\Delta\tilde{f}}{\tilde{f}_f} = \frac{i}{\pi Z_q} Z_L$$

Small-load approximation (SLA) (ch. 7)

f_f: frequency of the fundamental

For multilayers, the load can can be calculated from the optical multilayer formalism

For complex samples (sand piles, biological cells, foams, AFM tips, ...) one can write more generally

$$\frac{\Delta\tilde{f}}{\tilde{f}_f} = \frac{i}{\pi Z_q} \langle Z_L \rangle$$

where $\langle\ \rangle$ is the area average (potentially weighted with the amplitude distribution)

`The SLA is the link between the QCM and complex samples`

D. Johannsmann, K. Mathauer, G. Wegner, and W. Knoll, *Phys. Rev. B* **46**, 7808 (1992).
F. Eggers, Th. Funck, *J. Phys. E: Sci. Instrumen.* **20**, 523 (1987).

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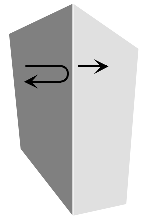
Contents

TU Clausthal — Semi-infinite medium

Semi-infinite medium



$$\frac{\Delta\tilde{f}}{\tilde{f}_f} = \frac{i}{\pi Z_q} Z_L$$

$$Z_L = Z_{liq} = \sqrt{i\rho\omega\eta} = \frac{1+i}{\sqrt{2}} f_f \sqrt{n}\sqrt{\rho\eta}$$

$$\frac{\Delta\tilde{f}}{\tilde{f}_f} = \frac{1}{\pi Z_q}\frac{i-1}{\sqrt{2}} f_f \sqrt{n}\sqrt{\rho\eta}$$

Newtonian liquid (purely viscous, viscosity η independent of frequency)

- $-\Delta f = \Delta\Gamma$
- $\Delta f \propto \sqrt{n}$

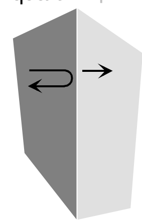
Watch-out: complex sample are often non-Newtonian in the MHz regime

- Wave penetrates exponentially to a depth $\delta = \sqrt{\frac{2\eta}{\rho\omega}}$

  water, 5 MHz $\delta = 250$ nm

`QCM is surface specific`

TU Clausthal — Non-Newtonian liquids



$$\frac{\Delta\tilde{f}}{\tilde{f}_f} = \frac{1}{\pi Z_q}\frac{i-1}{\sqrt{2}} f_f \sqrt{n}\sqrt{\rho\eta} = \frac{1}{\pi Z_q}\frac{i-1}{\sqrt{2}} f_f \sqrt{n}\sqrt{\rho(\eta' - i\eta'')}$$

$$\eta' = -\frac{\pi Z_q^2 f}{\rho_{liq}}\frac{\Delta f \Delta\Gamma}{f_f^2}$$

$$\eta'' = \frac{1}{2}\frac{\pi Z_q^2 f}{\rho_{liq}}\frac{(\Delta\Gamma^2 - \Delta f^2)}{f_f^2}$$

- $-\Delta f \leq \Delta\Gamma$
- $\sqrt{n}$ scaling breaks down because η depends on frequency

`This model does not cover roughness, slip, and compressional waves`

other caveats:

- Experimental values are usually off from the literature values by ~ 10% (usually on the high side)
- Experiments often yield negative η'' (can't be, 2nd law of thermodynamics)
- Experiments fail for very viscous polymers (η > 50 cps)

K.K. Kanazawa, J.G. Gordon II, *Anal. Chim. Acta* **99**, 175 (1985).
A.P. Borovikov, *Instruments and Experimental Techniques*,, **19**, 223 (1976). This reference misses a factor of 2 in eqs. 1, 2, and 3. Otherwise, Borovikov's result is the same Kananazawa-Gordon result.
W.P. Mason, *J. Colloid Sci.* **3**, 147 (1948). This reference contains a similar equation in the context of torsional resonators.

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Torsional Resonators for Measurements of Viscosity

Complicated geometry: empirical calibration

Lower frequency (100 kHz)

⇒ penetration depth ↗

⇒ measured viscosity more practically relevant

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Roughness

L. Daikhin et al. Anal. Chem. 74, 554 (2002).

Small scale roughness, Gaussian distribution

Account for roughness by using a liquid with an effective acoustic impedance of

$$Z_{liq} \approx \sqrt{\frac{\rho_{liq}\omega\eta}{2}}\left[\left(1+2\frac{h_r^2}{\delta^2}\right)+i\left(1+3\sqrt{\pi}\frac{h_r^2}{l_r\delta}-2\frac{h_r^2}{\delta^2}\right)\right]$$

h_r : vertical scale of roughness (rms)

l_r: lateral correlation length

```
Roughness leads to a trapped layer of liquid as well
as an excess dissipation
```

L. Daikhin, E. Gileadi, G. Katz, V. Tsionsky, M. Urbakh, *Anal. Chem.* **74**, 554 (2002).
S.J. Martin, G.C. Frye, A.J. Ricco, *Anal. Chem.* **65**, 2910 (1993).

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Sheet contact model

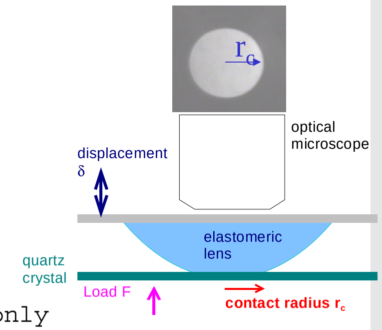
$$\frac{\Delta f}{f_f}=\frac{i}{\pi Z_q}K_A\frac{A_c}{A}Z_L$$

A_c : contact area

A: effective area of the crystal

K_A: weight factor

(takes care of amplitude distribution)




```
Using a small contact area is the only
way to do Interfacial viscoelastic spectroscopy
on polymers with the QCM.
Otherwise the frequency shift is too large.
```

Ultrasonic reflectometry is an alternative[2]

C.M. Flanigan, M. Desai, K.R.Shull, *Langmuir* **16**, 9825, (2000).
K.R. Shull, *Materials Science and Engineering* R **36**, 1 (2002).
A.M. König, M. Düwel, M. Kunze, B. Du, D. Johannsmann, *Langmuir* **22**, 229 (2006).
M. Kunze, K.R. Shull, D. Johannsmann, *Langmuir* **22**, 169 (2006).
[2] I. Alig I, D. Lellinger J. Sulimma, S. Tadjbakhsch, *Rev. Scient. Instr.* **68**, 1536 (1997).

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Complex fluids

$$\frac{\Delta\tilde{f}}{\tilde{f}_f}=\frac{i}{\pi Z_q}\langle Z_L\rangle=\frac{i}{\pi Z_q}\left\langle\frac{\sigma}{\dot{u}}\right\rangle$$

Task: calculate $\left\langle\frac{\sigma}{\dot{u}}\right\rangle$

- *Nematic liquid crystals* : Detailed investigations based on reflectometry[1]
- *Colloidal dispersions* : Need computational fluid dynamics to predict the average stress. Work has been done on colloidal dispersions in contact with torsional resonators (~ 100 kHz)[2]

```
The issue needs more attention. Small dispersed
particles are of much practical relevance
```

[1] Nematic liquid crystals:
F. Kiry, P. Martinoty, *Journ. Phys. (Paris)* **38**, 153 (1977).
P. Martinoty, S. Candau, *Mol. Cryst. Liq. Cryst.* **14**, 243 (1971).
H. Muramatsu, F. Iwasaki, *Mol. Cryst. Liq. Cryst.* **258**, 153 (1995).
A. Domack, D. Johannsmann, *Appl. Phys. Lett.* **80**, 4750 (2002),
J.P. de Gennes, J. Prost, *The Physics of Liquid Crystals*, Oxford University Press, Oxford, 1993, ch. 5.2.2
[2] Colloidal Dispersions
J. Bell, T. Köhler, D. Woermann, *Ber. Bunsenges. Phys. Chem.* **101**, 879 (1997).
R. Lionberger, W.B. Russel, *J. Rheol.* **38**, 1885 (1994).
G. Fritz, W. Pechhold, N. Willenbacher, N.J. Wagner, *J. Rheol.* **47**, 303 (2003).
N.J. Wagner, *J. Coll. Interf. Sci.* **161**, 169 (1993).

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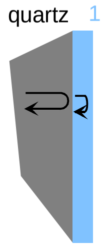
Sauerbrey film



$$\frac{\Delta\tilde{f}}{\tilde{f}_f} = \frac{i}{\pi Z_q} Z_L$$

Thin film: $Z_L = \frac{\sigma}{\dot{u}} = \frac{-m_f\,\omega^2 u^0}{i\,\omega u^0} = i\omega m_f$

m_f : areal mass density of the film

u^0 :amplitude of displacement at crystal – sample

$$\frac{\Delta\tilde{f}}{\tilde{f}_f} = \frac{\Delta f + i\Delta\Gamma}{\tilde{f}_f} = \frac{-\omega m_f}{\pi Z_q} = \frac{-2f}{Z_q} m_f = \frac{-2nf_f}{Z_q} m_f$$

- fractional frequency film $\Delta f/f$ same on all harmonics
- $\Delta f \propto n$ ("Sauerbrey scaling")
- no increase in bandwidth
- holds for rough films in an average sense

G. Sauerbrey, *Z. Phys.* **155**, 206 (1959).

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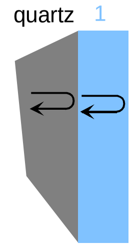
Viscoelastic films



$$\sigma = -G_f \frac{\partial u}{\partial z} = -G_f \cdot (-i k_f)\left(u_f^{-,0} - u_f^{+,0}\right)$$
$$= i G_f \frac{\omega}{c_f}\left(u_f^{-,0} - u_f^{+,0}\right)$$
$$= i\omega Z_f \left(u_f^{-,0} - u_f^{+,0}\right)$$

$$\frac{\Delta\tilde{f}}{f_f} = \frac{i}{\pi Z_q} \frac{i\omega Z_f\left(u_f^{-,0} - u_f^{+,0}\right)}{i\omega\left(u_f^{-,0} + u_f^{+,0}\right)} = \frac{i}{\pi Z_q} Z_f \frac{1-\exp(-2 i k_f d_f)}{1+\exp(-2 i k_f d_f)}$$

$$= \frac{i}{\pi Z_q} Z_f \frac{\exp(i k_f d_f) - \exp(-i k_f d_f)}{\exp(i k_f d_f) + \exp(i k_f d_f)}$$

$$\frac{\Delta\tilde{f}}{f_f} == \frac{-1}{\pi Z_q} Z_f \tan(k_f d_f)$$

C.S. Lu, O. Lewis, *J. Appl. Phys.* **43**, 4385 (1972).
D. Johannsmann, K. Mathauer, G. Wegner, and W. Knoll, *Phys. Rev. B* **46**, 7808 (1992).
V.E. Granstaff, S.J. Martin, *J. Appl. Phys.* **75**, 1319 (1994).

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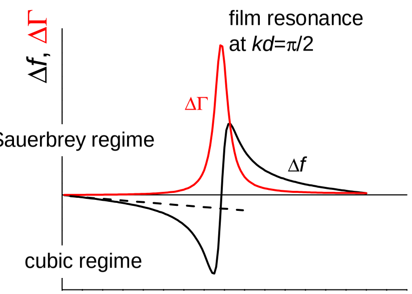
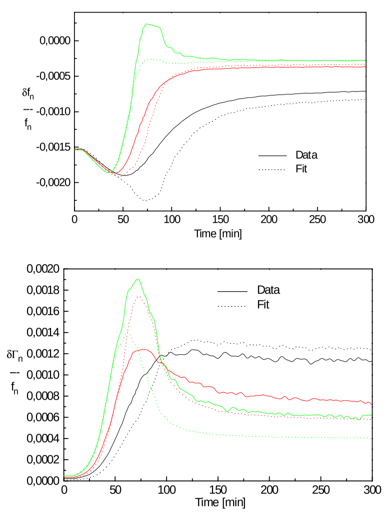
Film resonance



$k\,d = 2\pi n\, f_f\, (\rho/G)^{1/2}\, d$

swelling



Δf and $\Delta\Gamma$ of a polymer during swelling in solvent vaper

A. Domack, D. Johannsmann J. Appl. Phys. 80, 2599 (1996)

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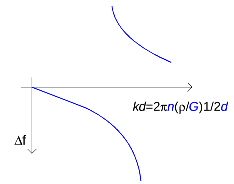
Film resonance (2)

- right on the film resonance, the small-load approximation does not apply, the rigorous solution look like this



- higher order resonances (kd = 3/2π, 5/2π, ...) have been rarely observed

- only two parameters can be determined independently. Good choice: m_f , Z_f

$$\frac{\Delta\tilde{f}}{f_f} = \frac{-1}{\pi Z_q} Z_f \tan(k_f d_f) \frac{-Z_f}{\pi Z_q} \tan\left(\frac{\omega}{c_f} d_f\right) = \frac{-Z_f}{\pi Z_q} \tan\left(\frac{\omega\sqrt{\rho_f}}{\sqrt{G_f}} d_f\right)$$

$$= \frac{-Z_f}{\pi Z_q} \tan\left(\frac{\omega}{Z_f} \rho_f d_f\right) = \frac{-Z_f}{\pi Z_q} \tan\left(\frac{\omega}{Z_f} m_f\right)$$

S.J. Martin, H.L. Bandey, R.W. Cernosek, A.R. Hillman, M.J. Brown, *Anal. Chem.* **72**, 141 (2000).

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Thin-film limit

$$\frac{\Delta\tilde{f}}{f_f} = \frac{-1}{\pi Z_q} Z_f \tan(k_f d_f) \approx \frac{-1}{\pi Z_q} Z_f \left(k_f d_f + \frac{1}{3}(k_f d_f)^3\right)$$

$$= \frac{-1}{\pi Z_q} Z_f k_f d_f \left(1 + \frac{1}{3}\omega^2 \frac{\rho_f}{G_f}\frac{m_f^2}{\rho_f^2}\right) = \frac{-1}{\pi Z_q}\omega m_f \left(1 + \frac{1}{3} J_f \frac{Z_q^2}{\rho_f}\left(\frac{m_f}{m_q} n\pi\right)^2\right)$$

$$= \frac{-1}{\pi Z_q}\omega m_f \left(1 + \frac{1}{3}\frac{Z_q^2}{Z_f^2}\left(\frac{m_f}{m_q} n\pi\right)^2\right)$$

- *additive* viscoelastic correction
- correction proportional to compliance J
- Δf ~ Sauerbrey term + a term depending on J' (elastic compliance)
  Watch out! Perturbation correction needed, strong electrode effects
- $\Delta\Gamma \propto J''$ (viscous compliance)

$J'' = \frac{3}{8}\frac{\rho_f Z_q}{f_f^4}\frac{1}{m_f^3}\frac{1}{n^3\pi^2}\Delta\Gamma$, use high f_f or high n in order to gain sensitivity

Modeling of QCM Data

D. Johannsmann, K. Mathauer, G. Wegner, and W. Knoll, *Phys. Rev. B* **46**, 7808 (1992).

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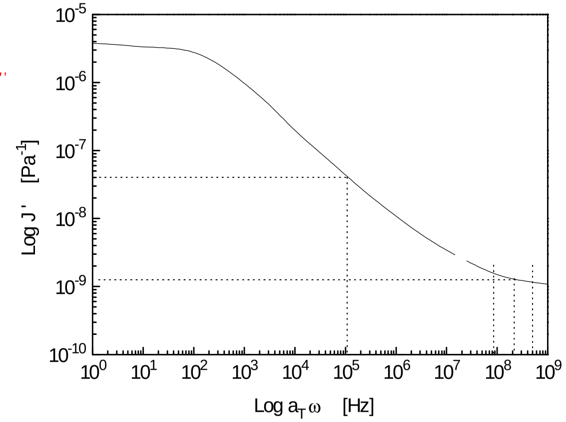
Viscoelastic dispersion

- J' and J'' depend on frequency
- typically, the dependence on frequency is smooth
- fair approximation over a frequency range of a decade: power laws

$$J'(f) \approx J_0'(f_{ref})\left(\frac{f}{f_{ref}}\right)^{\beta'}$$

$$J''(f) \approx J_0''(f_{ref})\left(\frac{f}{f_{ref}}\right)^{\beta''}$$



Modeling of QCM Data

J.D. Ferry, L. D. Grandine, E. R. Fitzgerald, J. Appl. Phys. 24(7), 911 (1953).

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Voigt-based modeling

A very simple model of rheology[1] says

$G(\omega) = \mu + i\omega\eta$

But! That model has infinite stiffness at $\omega \to \infty$

(and the QCM operates at high frequency...)

Much better

$G(\omega) = \mu + \left(\frac{1}{i\omega\eta} + \frac{1}{\mu_2}\right)^{-1}$ (3 elements, "Voigt-Kelvin-Model")

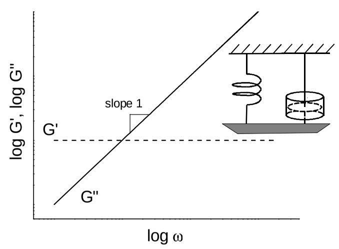
$\Rightarrow$ G' depends on frequency unless ω is small

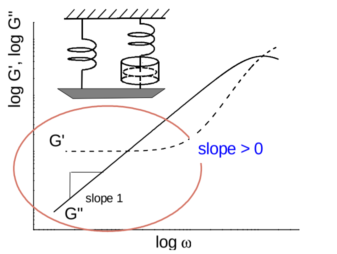
$\omega \ll \frac{\mu_2}{\eta}$, μ_2/η: relaxation rate"

in this limit on typically has $G'' \ll G'$

Usually: $G'(\omega)$ a monotonously increasing function of ω

Also: Kramers-Kronig relations





Modeling of QCM Data

[1]M.V. Voinova, M. Rodahl, M. Jonson, B. Kasemo, Physica Scripta **59**, 391 (1999).

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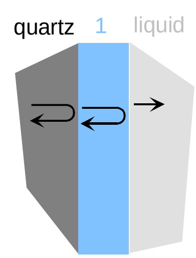
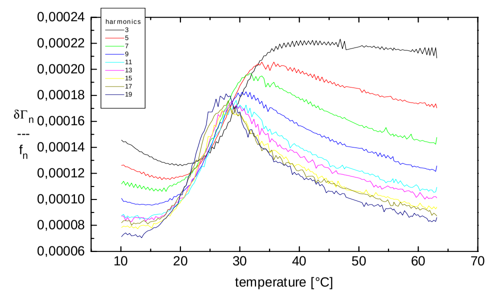
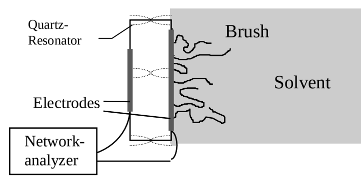
Film in liquid

$$\frac{\Delta\tilde{f}}{f_f} = \frac{-Z_f}{\pi Z_q}\frac{Z_f \tan(k_f d_f) - i Z_{liq}}{Z_f + i Z_{liq}\tan(k_f d_f)}$$



- film resonance
- Voigt model is equivalent





Modeling of QCM Data

A. Domack, O. Prucker, J. Rühe, D. Johannsmann, *Phys. Rev. E* **56**, 680 (1997).

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Viscoelastic effects in liquids

$$\frac{\Delta\tilde{f}}{f_f} \approx \frac{i}{\pi Z_q}\left[Z_{liq} + i\omega m_f\left(1-\frac{Z_{liq}^2}{Z_f^2}\right)\right]$$

Use the crystal inserted in the liquid as the reference state

$$\Rightarrow \frac{\Delta\tilde{f}}{f_f} \approx \frac{-\omega m_f}{\pi Z_q}\left(1-\frac{Z_{liq}^2}{Z_f^2}\right)$$

$\left(1-\frac{Z_{liq}^2}{Z_f^2}\right)$ is a viscoelastic correction, which even enters for very thin films (linear in m_f).

This happens because the film is clamped by the liquid on the outer side.

(Films in air shear under their own inertia, which leads to a smaller shear strain)

`The viscoelastic correction reduces the apparent mass ("Sauerbrey mass") whenever the film is very soft.`

`This effect is unrelated to the increase of mass induced by swelling in the liquid phase.`

D. Johannsmann, *Macromol. Chem. Phys.* **200**, 501 (1999), eq. 13.
M.V. Voinova, M. Jonson, B. Kasemo, *Biosens. Bioelectr.* **17**, 835 (2002).
J. Kankare, *Langmuir* **18**, 7092 (2002).

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Fluffy layers

$$\frac{\Delta\tilde{f}}{f_f} \approx \frac{-\omega m_f}{\pi Z_q}\left(1-\frac{Z_{liq}^2}{Z_f^2}\right)$$

Because this relation is linear in mass, m_f, it also holds in an integral sense:

$$\frac{\Delta\tilde{f}}{f_f} \approx -\frac{-\omega}{\pi Z_q}\int_0^\infty\left[\frac{Z_f^2(z)-Z_{liq}^2}{Z_f^2(z)}\right]\rho(z)\,dz \approx -\frac{\rho\omega}{\pi Z_q}\int_0^\infty\left[\frac{G_f(z)-G_{liq}}{G_f(z)}\right]dz$$

[...] : contrast generating function

A. Laschitsch, B. Menges, D. Johannsmann, *Appl. Phys. Lett.* **77**, 2252 (2000).

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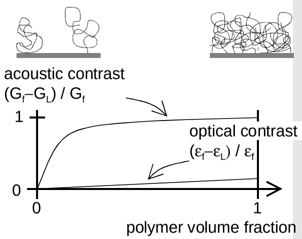
Comparison of acoustic and optical thickness

$$\frac{\Delta\tilde{f}}{f_f} \approx -\frac{\rho\omega}{\pi Z_q}\int_0^\infty\left[\frac{G_f(z)-G_{liq}}{G_f(z)}\right]dz$$

Surface plasmon resonance spectroscopy

$$\Delta(\sin\theta_c) \approx \frac{2\pi}{n_r\lambda}\left(\frac{\varepsilon_q\varepsilon_{liq}}{\varepsilon_q+\varepsilon_{liq}}\right)^2\frac{1}{\sqrt{-\varepsilon_q\varepsilon_{liq}}}\int_0^\infty\left[\frac{\varepsilon_f(z)-\varepsilon_{liq}}{\varepsilon_f(z)}\right]dz$$



same?

No! The acoustic contrast saturates, whereas the optical contrast doesn't.

Acoustic contrast ~ 1 even for dilute layers

⇒ Acoustic thickness ~ geometrical thickness

Optical contrast ∝ concentration

⇒ Optical thickness ~ adsorbed amount

$\frac{\texttt{Acoustic thickness}}{\texttt{Optical thickness}}$ `~ degree of swelling`

(solves the "missing mass problem")

`QCM data alone cannot yield the degree of swelling`

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Sauerbrey thickness

- Sauerbrey thickness in liquids *always* contains contribution from the solvent

- A viscoelastic term $\left(1-Z_q^2/Z_{liq}^2\right)$ is usually recognized because it entails
  (a) a dependence on overtone order and
  (b) an increase in $\Delta\Gamma$
  Conversely, if the Sauerbrey mass is the same on all overtones and if $\Delta\Gamma$ is small, then the viscoelastic correction is small, as well

- Other techniques have similar problems (e.g. SPR: refractive index?)

D-f ratio

$$\frac{\Delta \tilde{f}}{f_f} \approx \frac{-\omega m_f}{\pi Z_q}\left(1-\frac{Z_{liq}^2}{Z_f^2}\right)$$

$$\Rightarrow$$

$$\frac{\Delta\Gamma}{-\Delta f} = \frac{-\mathrm{Im}\left(1-Z_{liq}^2/Z_f^2\right)}{\mathrm{Re}\left(1-Z_{liq}^2/Z_f^2\right)} \approx \omega \eta J_f'$$

Film's mass eliminated by considering $\frac{\Delta\Gamma}{-\Delta f}$

B. Du, D. Johannsmann, *Langmuir* **20**, 2809 (2004).

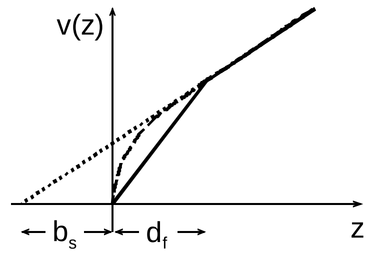
Slip

$$b_s = \left[\frac{\eta_{liq}}{\eta_f}-1\right] d_f$$

$$b_s = \int_0^\infty \left[\frac{\eta_{liq}}{\eta(z)}-1\right] dz$$

$$\frac{\Delta f}{f_f} = -\frac{2f}{Z_q}\rho_{liq} b_s$$

To first order in slip length, slip looks like a negative Sauerbrey mass[1]



[1] section 8.3.4
G. McHale, M.I. Newton, *J. Appl. Phys.* **95**, 373 (2004) and references therein

Electrodes

Two Viscoelastic Films in Air

$$\frac{\Delta \tilde{f}}{f_f} = \frac{-1}{\pi Z_q}\frac{Z_f \tan(k_f d_f) + Z_e \tan(k_e d_e)}{1 - Z_f / Z_e \tan(k_f d_f)\tan(k_e d_e)}$$

Two Viscoelastic Films in Liquid

$$\frac{\Delta \tilde{f}}{f_f} = \frac{-Z_e}{\pi Z_q}\frac{Z_f\left(Z_e \tan(k_e d_e) + Z_f \tan(k_f d_f)\right) + iZ_{liq}\left(Z_e \tan(k_f d_f)\tan(k_e d_e) - Z_f\right)}{Z_f\left(Z_e - Z_f \tan(k_f d_f)\tan(k_e d_e)\right) + iZ_{liq}\left(Z_e \tan(k_f d_f) + Z_f \tan(k_e d_e)\right)}$$

Both equations use small-load approximation

D. Johannsmann, *Macromol. Chem. Phys.* **200**, 501 (1999)

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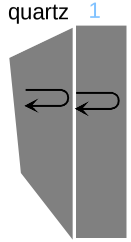
Failure of the small-load approximation



Consider a film with the exact same properties as AT-cut quartz

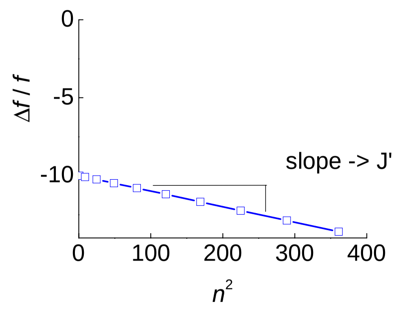
$$\Rightarrow \frac{\Delta f}{f_0} \equiv -\frac{d_f}{d_q} \equiv -\frac{m_f}{m_q}$$

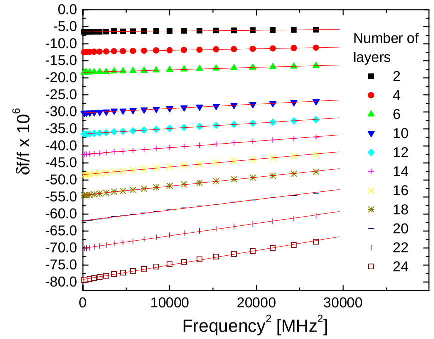
However the SLA results is

$$\frac{\Delta \tilde{f}}{f_0} = \frac{-nZ_f}{\pi Z_q}\tan\left(\frac{\omega}{Z_f}m_f\right) \neq -\frac{m_f}{m_q}$$

SLA can yield a negative apparent compliance

$$\frac{\Delta f}{f_f} = \frac{-1}{\pi Z_q}\omega m_f\left(1+\frac{1}{3}J_f\frac{Z_q^2}{\rho_f}\left(\frac{m_f}{m_q}n\pi\right)^2\right)$$





Negative *J´* ?

O. Wolff, E. Seydel, D. Johannsmann, Faraday Disc. **107**, 91 (1997)

Perturbation analysis

Small-load-approximation: $\frac{\Delta \tilde{f}}{\tilde{f}_f} = \frac{i}{\pi Z_q}\frac{Z_L}{\tilde{Z}_q}$

was linearized on the left-hand-side in Δf !

Fine, as long as right-hand-side is linearized in film thickness, as well (Sauerbrey).

Otherwise, there is an incosistency

Choices

(a) numerically search zero's of Mason circuit

(b) find successive approximations to the SLA

If the back of the crystal is unlaoded and piezoelectric stiffening is neglected, the Mason circuit leads to

$$\tan\left(\pi\frac{\Delta \tilde{f}}{\tilde{f}_f}\right) = i\frac{Z_L}{\tilde{Z}_q}$$

Taylor expand both sides in Δf, and solve iteratively (ch. 9)

....

Thin viscoelastic film:

$$\frac{\Delta \tilde{f}}{f_f} = -\frac{2\tilde{f}_0}{Z_q}m_f\left(1+\frac{1}{3}\left(\frac{Z_q^2}{Z_f^2}-1\right)\left(\frac{m_f}{m_q}\pi n\right)^2\right) \approx -\frac{2\tilde{f}_0}{Z_q}m_f\left(1+\frac{1}{3}\left(J\frac{Z_q^2}{\rho_f}-1\right)\left(\frac{m_f}{m_q}\pi n\right)^2\right)$$

D. Johannsmann, *J. Appl. Phys.* **89**, 6356 (2001).

Iterative solution (2)

For the equations, see ch. 9 and the QTZ-handbook (available from the author)

- Perturbation indispensible for viscoelastic analysis in air
  In liquids, effects not quite as severe

- The combined effects of electrodes and perturbation strongly shift
  the derived values for J' in air ⇒ independent knowledge of electrode thickness needed

- In air, J'' is determined with good reliability

- In liquids , J'' is determined with good reliability

- With regard to the other parameters, quanitative derivation of model parameters is difficult
  (too many free parameter, don't omit frequency dependence of $J'(\omega)$ and $J''(\omega)$)

- Because G and J are related in complicated way,
  neigher G' nor G'' are determined well.

$$G'(\omega) = \mathrm{Re}\left(\frac{1}{J(\omega)}\right) = \frac{J'(\omega)}{J'^2(\omega)+J''^2(\omega)}$$

$$G''(\omega) = \mathrm{Im}\left(\frac{1}{J(\omega)}\right) = \frac{J''(\omega)}{J'^2(\omega)+J''^2(\omega)}$$

$$\eta'(\omega) = \frac{1}{\omega}G''(\omega) = \frac{1}{\omega}\frac{J''(\omega)}{J'^2(\omega)+J''^2(\omega)}$$

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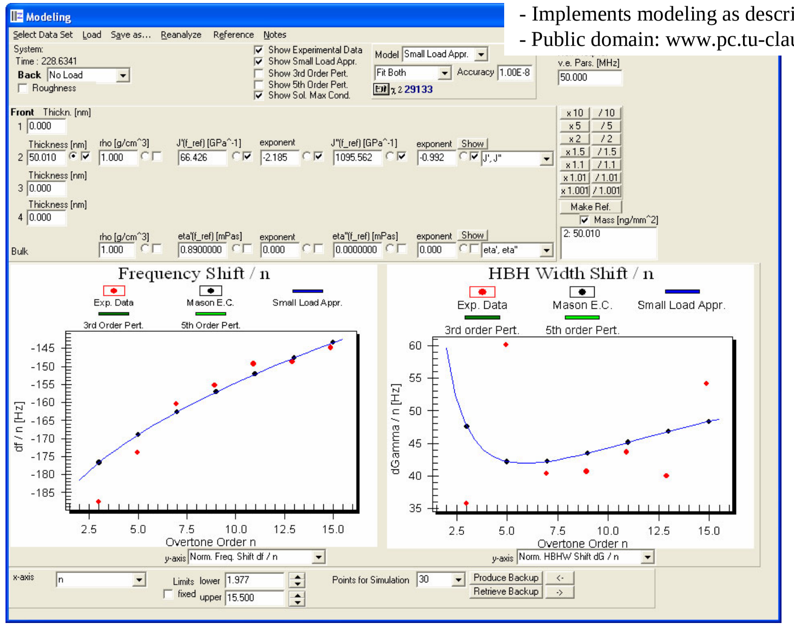
Software package QTM

- Implements modeling as described above
- Public domain: www.pc.tu-clausthal.de



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Quartz crystals as micromechanical probes

$$\Delta\tilde{f} = \Delta f + i\Delta\Gamma$$

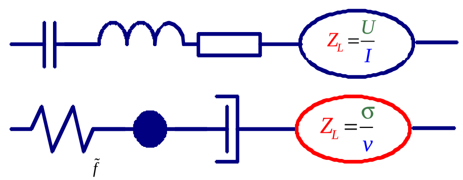
$$\frac{\Delta\tilde{f}}{f_f} \approx \frac{i}{\pi Z_q} Z_L = \frac{i}{\pi Z_q}\frac{\sigma}{\dot{u}}$$

Z_L: load impedance

σ: stress

$\dot{u}$: speed

electro-mechanical analogy



crystal load impedance

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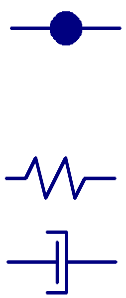
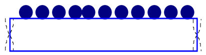
Discrete loads

loads

mass  $Z_L = N\frac{-\omega^2 m\, u_0}{i\omega\, u_0} = N\, i\omega m$

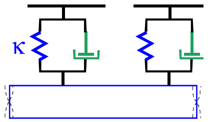
spring $Z_L = N\frac{\kappa}{i\omega}$

dashpot $Z_L = N\xi$



quartz crystal microbalance

contact mechanics



N : number density

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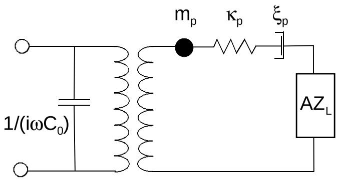
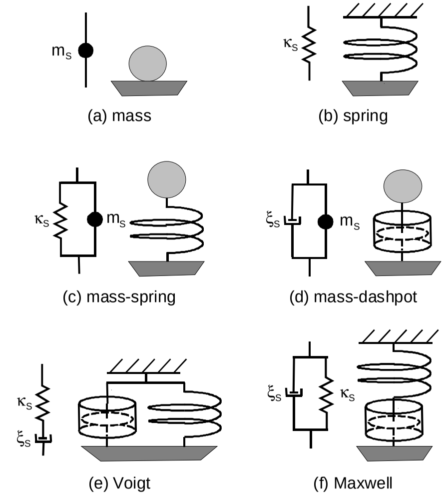
Discrete loads





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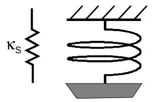
Loading with a (complex) spring

$$\frac{\Delta f}{f_f} \approx \frac{i}{\pi Z_q}\frac{\sigma}{\dot{u}} = \frac{i}{\pi Z_q}\frac{N_S}{A}\frac{\kappa_S u_0}{i\omega u_0} = \frac{1}{\pi Z_q}\frac{N_S}{A}\frac{\kappa_S}{\omega}$$



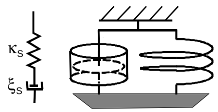
(b) spring

Complex Extension (Voigt coupling)

$$\frac{\Delta\tilde{f}}{f_f} = \frac{N_S}{\pi Z A_q}\frac{1}{\omega}\left(\kappa_S(\omega) + i\omega\xi_S(\omega)\right)$$

$$\kappa_S(\omega) = 2\pi^2 Z_q n\frac{A}{N_S}\Delta f(\omega)$$

$$\xi_S(\omega) = \frac{\pi Z_q}{f_f}\frac{A}{N_S}\Delta\Gamma(\omega)$$



(e) Voigt

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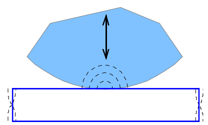
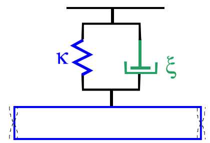
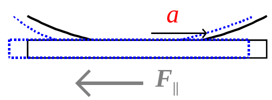
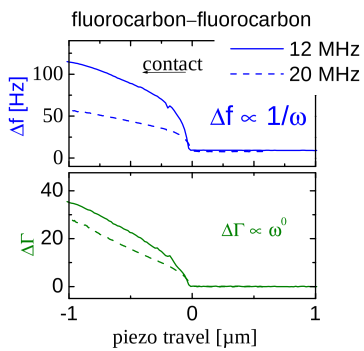
Point contact model









$$\frac{\Delta f^*}{f_f} = \frac{i}{\pi Z_q}\left(\frac{\kappa}{i\omega} + \xi\right)$$

Hertz-Mindlin model: stress concentration at tip

$\kappa = Ka \propto F^{1/3}$ (K: modulus)

ξ: radiation of sound: , $\xi \approx \kappa ka = Kk a^2$

+ interfacial friction,

+ coupling to other modes of oscillation

....

A. Laschitsch, D. Johannsmann, *J. Appl. Phys.* **85**, 3759 (1999)

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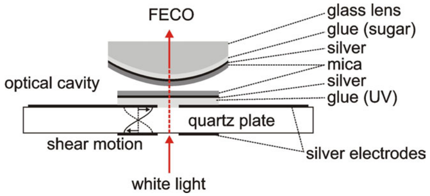
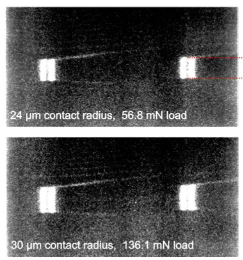
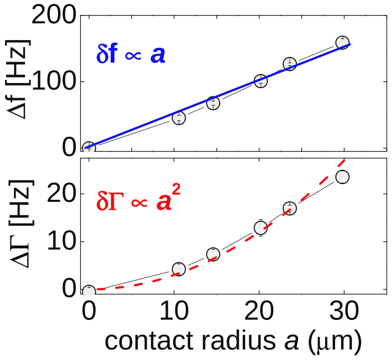
Test with surface forces apparatus

$$\frac{\Delta f^*}{f_f} = \frac{i}{\pi Z_q} \frac{K a}{i\omega} (1 + i k a)$$







S. Berg, D. Johannsmann, M. Ruths, *J. Appl. Phys.* **92**, 6905 (2002).

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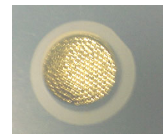
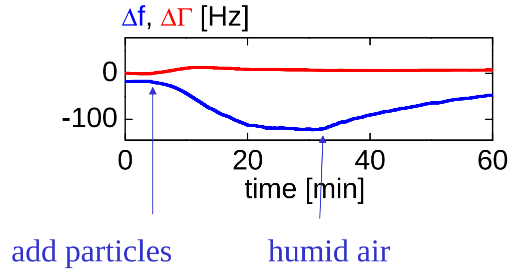
Capillary forces





J.N. D'Amour, J.J.R. Stålgren, K.K. Kanazawa, C.W. Frank, M. Rodahl, D. Johannsmann, *Phys. Rev. Lett.* **96**, 058301 (2006)

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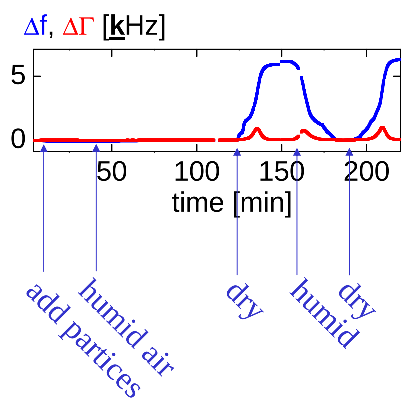
Hysteretic sandcastle effect



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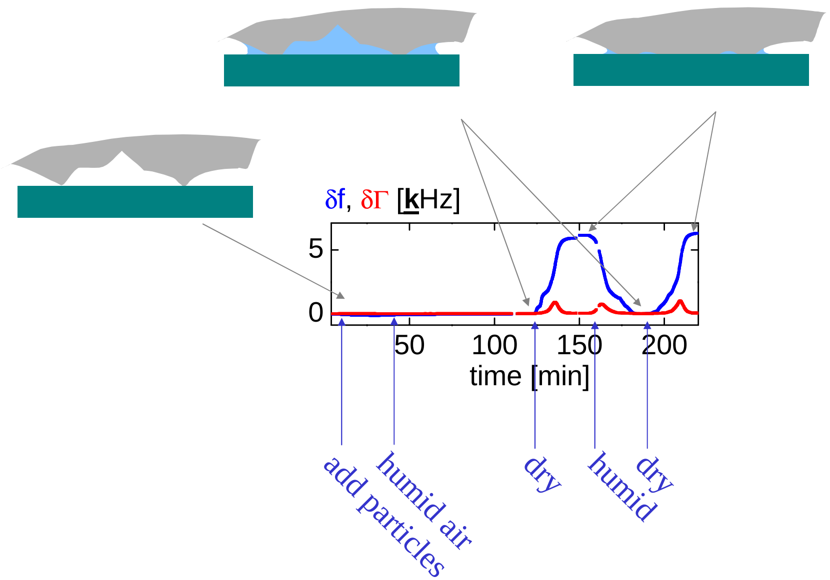
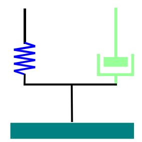
Capillary forces

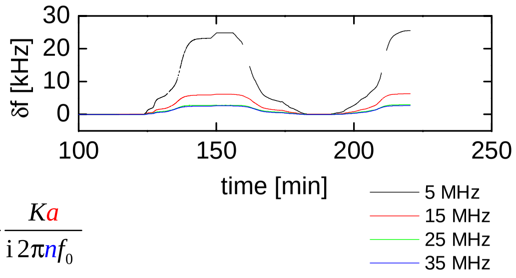


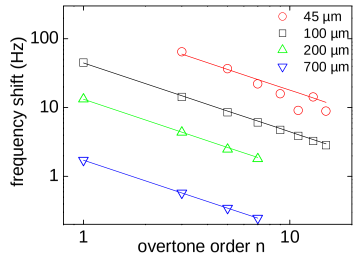
Inverse n-scaling

1/n scaling



$$\frac{\delta f^*}{f_0} = \frac{i}{\pi Z_q}\left(\frac{\kappa}{i\omega}+\xi\right) \approx \frac{i}{\pi Z_q}\frac{Ka}{i\,2\pi n f_0}$$



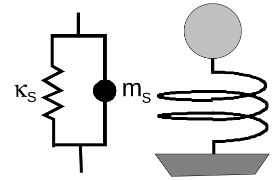


Loading with a spring and a mass

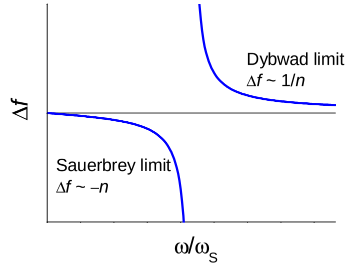
$$Z_L = \frac{N_S}{A}\left(Z_{mass}^{-1}+Z_{spring}^{-1}\right)^{-1} = \frac{N_S}{A}\left(\frac{1}{i\omega m_S}+\frac{i\omega}{\bar{\kappa}_S}\right)^{-1}$$

$$\omega_S = \sqrt{\frac{\bar{\kappa}_S}{m_S}}$$

$$\frac{\Delta \tilde{f}}{f_r} = -\frac{N_S}{A}\omega m \frac{1}{1-\frac{\omega^2}{\omega_S^2}}$$



(c) mass-spring



G.L. Dybwad, *J. Appl. Phys.* **58**, 2789 (1985).

Loading with a dahpot and a mass

$$Z_L = \frac{N_S}{A}\left(Z_{mass}^{-1}+Z_{dashpot}^{-1}\right)^{-1} = \frac{N_S}{A}\left(\frac{1}{i\omega m_S}+\frac{1}{\bar{\xi}_S}\right)^{-1}$$

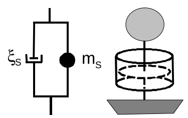
$$\tau_S = \frac{m_S}{\bar{\xi}_S}$$ momentum relaxation time, slip time

$$Z_L = \frac{N_S}{A} i\omega m_S \left(\frac{1-i\omega\tau_S}{1+\omega^2\tau_S^2}\right)$$

$$\frac{\Delta f}{f_f} = \frac{-N_S \omega m_S}{\pi Z_q}\frac{1-i\omega\tau_S}{1+\omega^2\tau_S^2}$$

$$\tau_S = \frac{1}{\omega}\frac{\Delta\Gamma}{(-\Delta f)}$$

Prediction: $\frac{\Delta\Gamma}{(-\Delta f)}$ scales as n



(d) mass-dashpot

J. Krim, D. H. Solina, R. Chiarello, *Phys. Rev. Lett.* **66**, 181 (1991).
E. T. Watts, J. Krim, A. Widom, *Phys. Rev. B* **41**, 3466 (1990).

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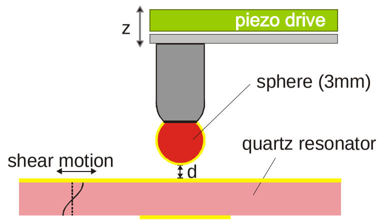
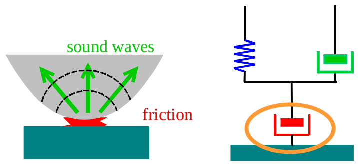
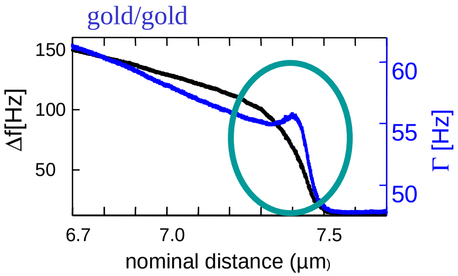
Interfacial Friction







S. Berg, T. Prellberg, D. Johannsmann, *Rev. Sci. Instr.* 74, 118 (2003).
S. Berg, D. Johannsmann, *Phys. Rev. Lett.* **91**, 145505 (2003).

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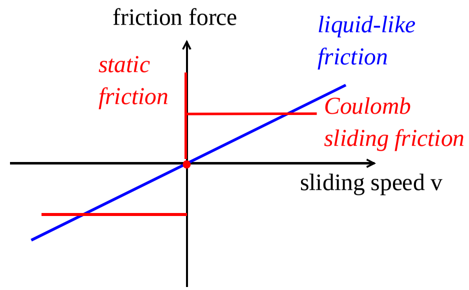
Nonlinear force laws → anharmonic motion

$$m\ddot{x} + \xi\dot{x} + \kappa x + \textit{nonlinear terms} = 0$$



Nonlinearities: harmonic oscillation *not expected*

⇒ search for nonlinearities

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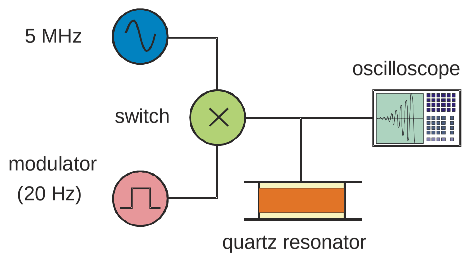
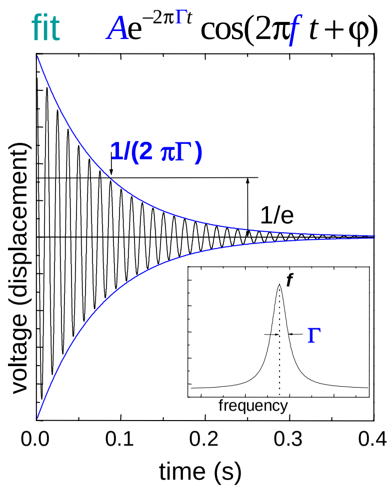
Ring-down





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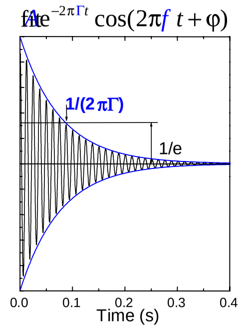
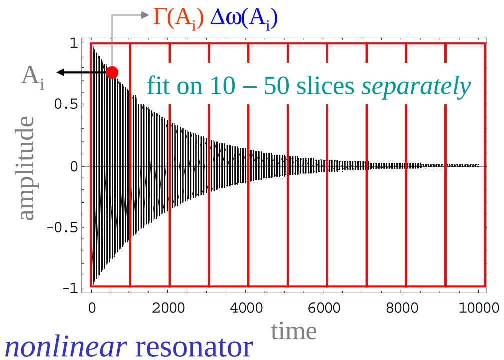
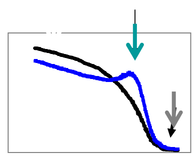
Chirp

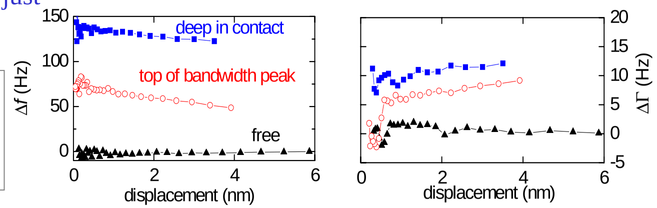




⇒ *nonlinear* resonator

quality of fit decreased when contact was just established





Two-timing approximation

$$\frac{\Delta f}{f_f} = \frac{2}{a}\frac{1}{\pi A Z_q}\frac{1}{\omega}\left\langle F(t)\cos(\omega t)\right\rangle$$

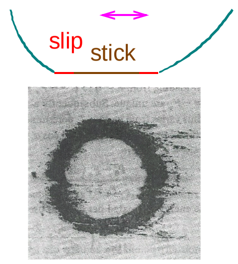
$$\frac{\Delta\Gamma}{f_f} = \frac{2}{a}\frac{1}{\pi A Z_q}\frac{1}{\omega}\left\langle F(t)\sin(\omega t)\right\rangle$$

The QCM probes in-phase and out-of-phase components of the force F(t) (like a lock-in amplifier)

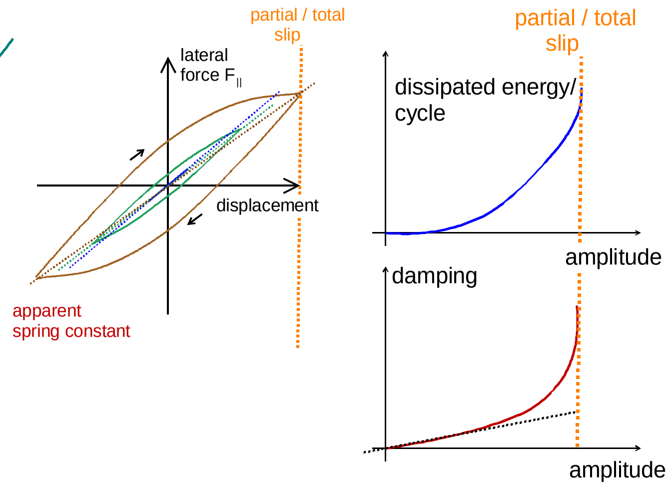
S. Strogatz: *Nonlinear Dynamics and Chaos*, chapter 7.6, Addison-Wesley 1996.
S. Berg, T. Prellberg, D. Johannsmann, *Rev. Sci. Instr.* **74**, 118 (2003).
F.J. Giessibl, *Appl. Phys. Lett.* **78**, 123 (2001).

Mindlin partial slip

microslip model

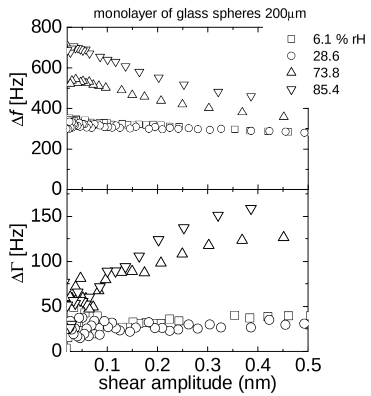


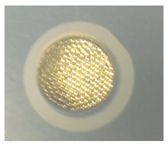
continuous stick-to-slip transition



R.D. Mindlin, H. Deresiewicz *J. Appl. Mech.* **20,** 327 (1953)

Mindlin partial slip





Compatible with partial slip

Contact Mechanics with the QCM
- High frequency
- Non-destructive
- Sensitive to nonlinearities via the amplitude dependence of Δf and $\Delta\Gamma$!

Binyang Du

Contents

What the QCM can do

- Provide the mass per unit area of a thin film
- Provide the complex MHz viscosity of a semi-infinite medium (polymers require small contact area)
- Provide $J''(\omega)$ of a film in air
- Provide $J'(\omega)$ of a film in liquid
- Provide more viscoelastic data based on full-fledged modeling
- Provide the strength of sphere-plate contacts
- Provide the stress speed-ratio (“load impedance”) of complex samples

Challenges

- complex samples, high frequency fluid dynamics
- understand contact mechanics in liquid media (“rupture event scanning”)
- understand dielectric effects
- full-flegded finite element modeling of the resonator (mode patterns, anharmonic side bands, energy trapping, compressional waves)
- increase the sensitivity
- combine QCM with other instruments (SPR, electrochemistry, AFM)