Some remarks on BAW resonators

- quartz plate
- electrodes

\[ f = f_{\text{res}}; \text{ large amplitude of motion} \Rightarrow \text{large current} \]

- exceptionally high Q
- weakly piezoelectric, piezoelectricity is convenient for detection, \textit{but unessential for acoustic modeling}
- thickness shear mode, “TSM” resonators
  - shear displacement
  - \textit{k}-vector \perp surface
  - width \perp thickness
Some remarks on BAW resonators (2)

- The term “QCM” is used here for all BAW resonators (including, for instance, non-gravimetric GaPO4 or LGS sensors)
- 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.
- 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)
- The wavelength of shear sound enters the picture
  ⇒ evanescent shear waves, surface specificity

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

Contents
1. General
2. Detection Schemes
3. Complex Resonance Frequencies and Overview of Modeling
4. Mathematical Description
5. Optical Description
6. Electrical Description and the Small Load Approximation
7. Layer Systems
8. Perturbation Analysis
9. Software Package QTM
10. Contact Mechanics
11. Nonlinearities
12. Conclusions
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 \( \omega C_0 \) or \( G_{\text{max}} \) change, this frequency changes, although \( f_r \) itself is unchanged ⇒ artifacts


Modeling of QCM Data

Impedance analysis

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

\[ \frac{1}{\omega C_1} \] : acoustic branch
\[ \frac{1}{\omega C_0} \] : electrical branch

\( R_{\text{max}} = G_{\text{max}}^{-1} \) is monitored by some advanced circuits

The Butterworth-von-Dyke (BvD) circuit predicts

\[ R_i = \frac{d_i^2 Z_{\text{n}}}{8\pi e_{\text{eff}}} \frac{2\Gamma}{f} \]

\( d_i \): thickness of the crystal, A: effective area
\( e_{\text{eff}} = 9.65 \times 10^{-12} \text{ C/m}^2 \): piezoelectric stress coefficient
\( Z_{\text{n}} = 8.8 \times 10^8 \text{ kg/(m s)} \): acoustic impedance of AT-cut quartz, \( n \): overtone order

Impedance analysis tells: \( R_i / \Gamma \) varies (although it shouldn’t…)
⇒ \( R_i \) is not the best measure of dissipative processes on the crystal surface

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

Impedance analysis tells:

1/(2 \( \pi \Gamma \))

 Implemented by Q-sense ("QCM-D")

“D” stands for dissipation

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

Complex resonance frequency

\[ f^* = f + i \Gamma \]

Complex resonance curve

\[
\frac{u(f)}{F(f)} \propto \frac{1}{f^2 - f^2 + 2i\Gamma f} = \frac{1}{(f_c + i\Gamma)^2 - f^2}
\]

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

Complex frequency shift \( \Delta f = \Delta f^* + \Gamma \)

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

---

Microweighing: quartz crystal microbalance (QCM)

\[
\frac{\lambda}{2} = d_q, \quad \frac{\lambda}{2} = d_q + d_f
\]

Sauerbrey equation

\[
\Delta f = -\frac{2nf^2}{Z_q} \Delta m
\]

\( \Delta f \): frequency shift
\( \Delta m \): mass per unit area
\( Z_q \): acoustic impedance of quartz
\( n \): overtone order
application: film thickness monitor

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### Mathematical Description

- N layers, supporting two waves traveling to the right ($u_{j}^{-}$) and to the left ($u_{j}^{+}$) each
- wave equation holds
  \[ u_{j}^{-} = u_{j}^{+} \exp(-ik_{j}z) \]
  \[ u_{j}^{+} = u_{j}^{-} \exp(-ik_{j}z) \]

\[ k_{j} = \frac{\omega}{c_{j}} = \frac{\rho_{j}}{G_{j}} = \frac{\rho_{j}}{Z_{j}} \]

\[ - N \text{ layers, supporting two waves traveling to the right (} u_{j}^{-} \text{) and to the left (} u_{j}^{+} \text{) each} \]
\[ \text{wave equation holds} \]
\[ u_{j}^{-} = u_{j}^{+} \exp(-ik_{j}z) \]
\[ u_{j}^{+} = u_{j}^{-} \exp(-ik_{j}z) \]

\[ k_{j} = \frac{\omega}{c_{j}} = \frac{\rho_{j}}{G_{j}} = \frac{\rho_{j}}{Z_{j}} \]

\[ \rho: \text{density} \]
\[ G: \text{shear modulus} \]
\[ Z = \rho c = \sqrt{\rho G} \text{ acoustic impedance (materials property)} \]

### Mathematical Description (2)

- Stress and displacement continuous at $N+1$ interfaces
  \[ u_{j}^{-}(z_{j+1}) + u_{j}^{+}(z_{j+1}) = u_{j+1}^{-}(z_{j+1}) + u_{j+1}^{+}(z_{j+1}) \]

\[ u_{j}^{-}(z_{j+1}) + u_{j}^{+}(z_{j+1}) = u_{j+1}^{-}(z_{j+1}) + u_{j+1}^{+}(z_{j+1}) \]

\[ \Rightarrow \text{homogenous linear system of } 2N+2 \text{ equations for } 2N+1 \text{ amplitudes} \]

For example

\[ \begin{pmatrix} -1 & 1 & 1 & 0 \\ 0 & \tilde{Z}_{q} & -\tilde{Z}_{q} & 0 \\ 0 & \exp(i\tilde{k}_{q}d_{q}) & \exp(-i\tilde{k}_{q}d_{q}) & -1 \\ 0 & \tilde{Z}_{q} \exp(i\tilde{k}_{q}d_{q}) & -\tilde{Z}_{q} \exp(-i\tilde{k}_{q}d_{q}) & 0 \end{pmatrix} = 0 \]

Set the determinant to zero .... and find the resonance frequency - intransparent
Optical picture

- resonance condition: phase acquired in one round trip is a multiple of $2\pi$
- non-trivial reflectivity at the crystal–sample interface

($"r_{n2}"$) will change resonance frequency

(a) what is $r_{n2}$?
(b) what is the relation between $r_{n2}$ and $\Delta f$?

Reflectivity

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

displacement(I):
$$u_{s}^{r,0} + u_{s}^{t,0} = u_{b}^{0}$$

stress (II):
$$G_i \frac{d[ u_{s}^{r,0} + u_{s}^{t,0} ]} {dz} = G_k \frac{d[ u_{b}^{r,0} ]} {dz}$$
$$G_i ik_s [ u_{s}^{r,0} - u_{s}^{t,0} ] = G_k ik_b u_{b}^{r,0}$$
$$Z_s [ u_{s}^{r,0} - u_{s}^{t,0} ] = Z_b u_{b}^{r,0}$$

$$r_{s,b} = \frac{u_{s}^{r,0}} {u_{s}^{t,0}} = \frac{Z_s - Z_b} {Z_s + Z_b}$$

multilayers: iterative formalism\(^1\)

1 see section 5

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, $\rho$, 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
\[ \frac{\Delta f}{f_i} = \frac{i}{2\pi} (1 - r_{q,2}) \]

- frequency of the fundamental
- proof in ch. 5
- holds in the complex sense \( \frac{\Delta f + \Delta f}{f_i} = \frac{i}{2\pi} (1 - r_{q,2}) \)
- 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


Electrical picture

Equivalent circuits map viscoelastic layers onto sets of discrete circuit elements:

- Electromechanical analogy maps mechanical (and acoustic) quantities onto electrical quantities
  - force \( F \) ↔ voltage \( U \)
  - speed \( \dot{u} \) ↔ current \( I \)

- Force can be normalized to area \( A \) ⇒ \( \sigma = \frac{F}{A} \) (\( \sigma \): 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"

\( Z_L \) is central to the physics of the QCM
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

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)

Piezoelectricity

Piezoelectricity is depicted as a transformer: "ratio of the number of loops"

\[ I_{in} = \frac{U_1}{\phi} = A \sigma \]

\[ U_{in} = \frac{I_{in}}{Z_{in}} = \frac{A \sigma}{\phi^2} = \frac{1}{\phi^2} Z_{in} \]

Φ: Thickness of the crystal
\( \varepsilon_{33} \): piezoelectric stress coefficient \( \varepsilon_{33} = 9.65 \times 10^{-12} \text{C/m}^2 \) for AT-cut quartz

\( Z_{in} \): accounts for piezoelectric stiffening (small effect)

Mason circuit

Benefits of the Mason circuit

- Easy to apply, once you believe it (predictive, not a cartoon!)
- Rigorous treatment of piezoelectricity
- Covers loads on both surfaces
- Predicts the amplitude of oscillation
- Predicts the resistance $R_i$ 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

Amplitude of oscillation

Determine the "current" (speed) through the element $A Z_L$, from the Kirchhoff rules
\[ \frac{a}{QU_i} = \frac{4}{(n \pi)^2} d_{33} = \frac{1.25 \ \text{pm}}{n^2 \ \text{V}} \]
\[ d_{33} = 3.1 \times 10^{-12} \ \text{m/V}; \text{piezoelectric strain coefficient} \]

Active area

\[ R_i = \frac{1}{4 \phi} \varepsilon \]
\[ = \frac{1}{4 \phi} A Z_n \frac{n \pi}{2} \tan(\delta) \]
\[ = \frac{d_{33}^2}{4 A e_{33}^2} A Z_n \frac{n \pi}{2} \frac{1}{Q} \]
\[ = \frac{c_{33}^2}{16 f_j A e_{33}^2} A Z_n n \pi \frac{1}{2} \frac{1}{Q} \]
\[ = \frac{1}{32 f_j A Z_n d_{33}^2} A Z_n n \pi \frac{1}{2} \frac{1}{Q} \]
\[ A = \frac{n \pi}{32 f_j A Z_n d_{33}^2} \frac{1}{QR_i} \]
Small-load approximation

$\frac{N}{f_i} = \frac{i}{\pi Z_q}$

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

$f_i$: frequency of the fundamental

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

For complex samples (sand piles, biological cells, foams, AFM tips, ...)

one can write more generally

$\frac{N}{f_i} = \frac{i}{\pi Z_q} \langle Z_L \rangle$

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

The SLA is the link between the QCM and complex samples

Semi-infinite medium

$\frac{N}{f_i} = \frac{i}{\pi Z_q} Z_L$

$Z_L = Z_{eq} = \sqrt{\sqrt{\rho \omega \eta}}$ = $\frac{1}{2} f_i \sqrt{\frac{\eta}{\rho \omega}}$

$\frac{N}{f_i} = \frac{1}{2} f_i \frac{i-1}{\sqrt{2}} \sqrt{\frac{\eta}{\rho \omega}}$

Newtonian liquid (purely viscous, viscosity $\eta$ independent of frequency)

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

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

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

  water, 5 MHz $\delta = 250$ nm

QCM is surface specific

Non-Newtonian liquids

$\frac{N}{f_i} = \frac{1}{2} \sqrt{\rho \omega \eta} \sqrt{\Delta \Gamma}$

$\eta = \frac{\pi Z_q f_i \sqrt{\Delta \Gamma}}{\rho_{eq}}$

$\eta = \frac{1}{2} \rho_{eq} \frac{(\Delta \Gamma^2 - \Delta f^2)}{f_i^2}$

- $\Delta \Gamma \leq \Delta \Gamma$
- $\sqrt{\eta}$ scaling breaks down because $\eta$ 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 $\eta'$ (can't be, 2nd law of thermodynamics)
- Experiments fail for very viscous polymers ($\eta > 50$ cps)

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 Kanazawa-Gordon result.
W.P. Mason, J. Colloid Sci. 3, 147 (1948). This reference contains a similar equation in the context of torsional resonators.
Roughness


Small scale roughness, Gaussian distribution

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

\[ Z_{\text{eff}} = \left( \frac{\rho \omega}{2} \right) \left( \frac{1 + 3 \frac{h^2}{\delta^2}}{1 + \frac{h^2}{\delta^2}} \right) \]

\( h \): vertical scale of roughness (rms)
\( \delta \): lateral correlation length

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

Complex fluids

\[ \frac{\Delta f}{f_1} = \frac{i}{\pi Z_{\text{q}}} A Z_{\text{q}} \]

Task: calculate \( \left\langle \sigma^2 \right\rangle / \mu \)

- Nematic liquid crystals: Detailed investigations based on reflectometry
- 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)

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

1 Nematic liquid crystals:

2 Colloidal Dispersions

Sheet contact model

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


Torsional Resonators for Measurements of Viscosity

Complicated geometry: empirical calibration
Lower frequency (100 kHz)
\[ \Rightarrow \text{penetration depth} \]
\[ \Rightarrow \text{measured viscosity more practically relevant} \]
Sauerbrey film

\[
\frac{\Delta f}{f_i} = \frac{i}{\pi Z_q} \Delta f
\]

Thin film: \( Z_q = \frac{\sigma}{iu} = \frac{-m_j \omega^2 u^0}{i \omega u^0} = i \omega m_j \)

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

Viscoelastic films

\[
\sigma = -G_i \frac{\partial u}{\partial z} = -G_i \left( -i k d \right) \left( u_i^{+} - u_i^{-} \right) = i G_i \frac{\omega}{c_i} \left( u_i^{+} - u_i^{-} \right) = i \omega Z_i \left( u_i^{+} - u_i^{-} \right)
\]

\[
\frac{\Delta f}{f_i} = \frac{-i \omega Z_i \left( u_i^{+} - u_i^{-} \right)}{\pi Z_q} = \frac{i}{\pi Z_q} Z_i \left[ 1 - \exp(-2i k d_i) \right] = \frac{1}{\pi Z_q} Z_i \left[ 1 + \exp(-2i k d_i) \right]
\]

\[
\frac{\Delta f}{f_i} = \frac{-1}{\pi Z_q} Z_i \tan(k_i d_i)
\]

- right on the film resonance, the small-load approximation does not apply, the rigorous solution look like this
- higher order resonances \( (3/2 \pi, 5/2 \pi, ...) \) have been rarely observed
- only two parameters can be determined independently. Good choice: \( m_j, Z_q \)

\[
\frac{\Delta f}{f_i} = -\frac{1}{\pi Z_q} Z_i \tan(k_i d_i) \left( \frac{Z_i}{Z_q} \tan \left( \frac{\omega}{c_i} d_i \right) \right) = -\frac{Z_i}{Z_q} \tan \left( \frac{\omega}{c_i} \sqrt{\frac{G_i}{d_i}} \right)
\]

\[
\frac{\Delta f}{f_i} = -\frac{Z_i}{Z_q} \tan \left( \frac{\omega}{c_i} \rho_i d_i \right) = -Z_i \frac{\omega}{Z_q} \tan \left( \frac{\omega}{Z_q} m_i \right)
\]
The thin-film limit

\[ \Delta \tilde{f} = \frac{-1}{\pi \nu} \tan(k_d d_i) = \frac{-1}{\pi \nu} \left( k_d d_i + \frac{1}{3}(k_d d_i)^3 \right) \]

\[ = \frac{-1}{\pi \nu} \left( k_d d_i \left( 1 + \frac{1}{3} \omega^2 \rho \frac{m^2}{G_i} \right) \right) \]

\[ = \frac{-1}{\omega \nu} \left( 1 + \frac{1}{3} \omega^2 \frac{m}{\rho \pi} \right) \]

- additive viscoelastic correction
- correction proportional to compliance \( J \)
- \( \Delta \tilde{f} \sim \) Sauerbrey term + a term depending on \( J \) (elastic compliance)

Watch out! Perturbation correction needed, strong electrode effects

- \( \Delta \tilde{f} \propto J \) (viscous compliance)

\[ J' = \frac{3 \rho \nu Z_f}{8 f_i} \frac{1}{m_f^3} \frac{1}{\pi} \Delta \tilde{f} \] use high \( f_i \) or high \( n \) in order to gain sensitivity

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

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

\( \Rightarrow G' \) depends on frequency unless \( \omega \) is small

\( \omega \ll \frac{\mu}{\eta} \) relaxation rate

in this limit on typically has \( G' \ll G'' \)

Usually: \( G(\alpha) \) a monotonously increasing function of \( \omega \)

Also: Kramers-Kronig relations

Film in liquid

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...)

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Usually: \( G(\alpha) \) a monotonously increasing function of \( \omega \)

Also: Kramers-Kronig relations

Fluffy layers

\[ \Delta f_f = \frac{-\omega m_i}{\pi Z_{liq}} \left( 1 - \frac{Z_{liq}^2}{Z_i^2} \right) \]

Because this relation is linear in mass, \( m_i \), it also holds in an integral sense:

\[ \int \Delta f_f \, dz = \int \frac{-\omega m_i Z_{liq}}{\pi Z_i^2} \left( Z_i^2(z) - Z_{liq}^2 \right) \rho(z) \, dz \approx \int \frac{-\omega m_i Z_{liq}}{\pi Z_i^2} \left( G_i(z) - G_{liq} \right) \rho_i \, dz \]

\([...]:\) contrast generating function

Sauerbrey thickness

- Sauerbrey thickness in liquids always contains contribution from the solvent

A viscoelastic term \( \left( 1 - \frac{Z_i^2}{Z_{liq}^2} \right) \) 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?)

Comparision of acoustic and optical thickness

\[ \frac{\Delta f_f}{f_f} = \frac{\rho \omega}{\pi Z_{liq}} \int \frac{G_i(z) - G_{liq}}{G_i(z)} \, dz \]

Surface plasmon resonance spectroscopy

\[ \Delta (\sin \theta) = \frac{2 \pi}{n_i \lambda} \left( \frac{\varepsilon_i \varepsilon_m}{\varepsilon_i + \varepsilon_m} \right) \frac{1}{\sqrt{\varepsilon_i \varepsilon_m}} \int \frac{G_i(z) - G_{liq}}{G_i(z)} \, dz \]

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

Acoustic contrast \( \propto 1 \) even for dilute layers

⇒ Acoustic thickness \( \propto \) geometrical thickness

Optical contrast \( \propto \) concentration

⇒ Optical thickness \( \propto \) adsorbed amount

Acoustic thickness \( \propto \) degree of swelling

Optical thickness \( \propto \) adsorbed amount

(solves the "missing mass problem")

QCM data alone cannot yield the degree of swelling
To first order in slip length, slip looks like a negative Sauerbrey mass:

\[
\Delta \Gamma = -\frac{\Delta f}{f_i} = -\frac{\Im \left( 1 - \frac{Z_{\text{in}}^2}{Z_i^2} \right)}{\Re \left( 1 - \frac{Z_{\text{in}}^2}{Z_i^2} \right)} = \omega \eta J_i,
\]

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

**Electrodes**

Two Viscoelastic Films in Air

\[
\frac{\Delta f}{f_i} = - \frac{1}{\pi Z_i} \frac{Z_i \tan (k_i d_i) + Z_s \tan (k_s d_s)}{1 - Z_{\text{in}}/Z_i \tan (k_i d_i) \tan (k_s d_s)}
\]

Two Viscoelastic Films in Liquid

\[
\frac{\Delta f}{f_i} = \frac{-Z_s Z_i \left( Z_s \tan (k_s d_s) + Z_i \tan (k_i d_i) \right) + i Z_{\text{in}} \left( Z_s \tan (k_i d_i) \tan (k_s d_s) - Z_i \right)}{\pi Z_i Z_s \left( Z_s - Z_i \tan (k_i d_i) \tan (k_s d_s) \right) + i Z_{\text{in}} \left( Z_s \tan (k_i d_i) + Z_i \tan (k_s d_s) \right)}
\]

Both equations use small-load approximation

---

1 section 8.3.4
G. McHale, M. I. Newton, J. Appl. Phys. 95, 373 (2004) and references therein
Failure of the small-load approximation

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

\[
\frac{\Delta f}{f_0} = \frac{d_i}{d_q} = -\frac{m_i}{m_q}
\]

However the SLA results is

\[
\frac{\Delta f}{f_0} = \frac{-nZ_m}{\pi Z_q} \tan \left( \frac{\omega}{Z_i} m_l \right) - \frac{m_i}{m_q}
\]

Perturbation analysis

Small-load-approximation

\[
\frac{\Delta f}{f_i} = \frac{1}{\pi Z_i} \frac{Z_i}{Z_f} \frac{Z_f}{Z_q}
\]

was linearized on the left-hand-side in \( \Delta f \)!

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

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

\[
\tan \left( \frac{\Delta f}{f_i} \right) = \frac{1}{Z_i} \frac{Z_f}{Z_q}
\]

Taylor expand both sides in \( \Delta f \), and solve iteratively (ch. 9)

- Thin viscoelastic film:

\[
\frac{\Delta f}{f_i} = \frac{2 f_m m_l}{Z_q} \left( 1 + \frac{1}{3} \frac{Z_i}{Z_f} \left( \frac{m_l}{m_q} \right)^2 \right) m_i m_q \frac{Z_m}{Z_f} \frac{1}{Z_f} \frac{Z_f}{Z_q}
\]

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, quantitative 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, neither \( G \) nor \( J \) are determined well.

\[
\eta G = \frac{1}{m} \left( J^*(\omega) + J^*(\omega) \right)
\]

\[
\eta G = \frac{1}{m} \left( J^*(\omega) + J^*(\omega) \right)
\]
Modeling of QCM Data

D. Johannsmann

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9. Software Package QTM
10. Contact Mechanics
11. Nonlinearities
12. Conclusions

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

Quartz crystals as micromechanical probes

\[ \Delta f = \Delta f' + i \Delta \Gamma \]

\[ \Delta f' = \frac{i}{\pi Z_q} - \frac{i}{\pi Z_q} \frac{\sigma}{\bar{u}} \]

\[ Z_L: \text{ load impedance} \]
\[ \sigma: \text{ stress} \]
\[ \bar{u}: \text{ speed} \]

\[
\begin{align*}
Z_c &= \frac{\sigma}{\bar{u}} \\
Z_L &= \frac{L}{\bar{u}} \\
\end{align*}
\]
Discrete loads

**loads**

- **mass**
  \[ Z_L = N \frac{-\omega^2 m u_0}{i\omega u_0} = N i\omega m \]

- **spring**
  \[ Z_L = N \frac{K}{i\omega} \]

- **dashpot**
  \[ Z_L = N \xi \]

\( N \): number density

**contact mechanics**

- **mass**
  \[ m \]

- **spring**
  \[ \kappa \]

- **dashpot**
  \[ \xi \]

**Point contact model**

\[ \Delta f \propto \frac{1}{\omega} \]

- **flourocarbon-flourocarbon**

- **fluorocarbon**

- **piezo travel [µm]**

- **Hertz-Mindlin model: stress concentration at tip**

  \[ \kappa = K \alpha \approx F q \]  

  \( K \): modulus

  \( q \): radiation of sound

  + interfacial friction,
  + coupling to other modes of oscillation

  \[ \Delta f \propto \frac{1}{\omega} \]

- **loading with a (complex) spring**

  \[ \frac{\Delta f}{f_i} = \frac{i}{\pi Z_N} \frac{1}{i\omega} \left( \kappa_s(\omega) + i\omega \xi_s(\omega) \right) \]

  \( \kappa_s(\omega) = 2\pi^2 Z_N A \frac{\Delta f}{f_i} \)

  \( \xi_s(\omega) = \frac{\pi Z_N A}{f_i} \Delta \Gamma(\omega) \)
Test with surface forces apparatus

\[ \frac{\Delta f}{f_i} = \frac{i K a}{\pi Z_i} (1 + i k a) \]

Capillary forces

\[ \Delta f, \Delta \Gamma \] [Hz]

Modeling of QCM Data

D. Johannsmann


Hysteretic sandcastle effect

Modeling of QCM Data

D. Johannsmann

Modeling of QCM Data

D. Johannsmann

Capillary forces

\[ \delta f, \delta \Gamma \] [kHz]

D. Johannsmann
In the context of QCM data modeling, we consider two scenarios: loading with a spring and a mass, and loading with a dashpot and a mass.

### Loading with a Spring and a Mass

The frequency shift due to loading is given by:

\[
\frac{\delta f}{f_0} = \frac{i}{\pi \kappa} \left( \frac{K_a}{i \omega} + \xi \right) = \frac{i}{\pi \kappa} \frac{K_a}{i \omega} + \xi
\]

where \( \kappa \) is the spring constant, \( K_a \) is a constant, and \( \xi \) is a damping term.

\[
\omega_N = \frac{1}{\sqrt{m_s k_0}}
\]

\[
\frac{\Delta f}{f_r} = -N_s \frac{\omega m}{A \omega} \left( \frac{1}{\omega - \omega_s} \right)
\]

### Loading with a Dashpot and a Mass

The frequency shift for this case is:

\[
Z_L = \frac{N_s}{A} \left( Z_{mass}^{-1} + Z_{dashpot}^{-1} \right) = \frac{N_s}{A} \left( \frac{1}{i \omega m_s} + \frac{1}{\xi} \right)^{-1}
\]

- \( \tau_s = \frac{m_s}{\xi} \) is the momentum relaxation time, slip time.
- \( Z_L = \frac{N_s}{A} i \omega m_s \left( \frac{1 - i \omega \tau_s}{1 + \omega^2 \tau_s^2} \right) \)
- \( \frac{\Delta f}{f_i} = \pi Z_s \left( \frac{1 - i \omega \tau_s}{1 + \omega^2 \tau_s^2} \right) \)
- \( \xi = \frac{\Delta \Gamma}{\omega (\Delta f)} \)
- Prediction: \( \Delta \Gamma \) scales as \( n \)

**Contents**

1. General
2. Detection Schemes
3. Complex Resonance Frequencies and Overview of Modeling
4. Mathematical Description
5. Optical Description
6. Electrical Description and the Small Load Approximation
7. Layer Systems
8. Perturbation Analysis
9. Software Package QTM
10. Contact Mechanics
11. **Nonlinearities**
12. Conclusions

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**Interfacial Friction**

- Shear motion
- Quartz resonator
- Gold/gold contact

**Graph:**
- Nominal distance vs. force
- Nonlinear force laws → anharmonic motion

**Equation:**
\[ \dot{\mathbf{x}} + \xi \dot{x} + kx + \text{nonlinear terms} = 0 \]

**Nonlinear forces:**
- Friction force
- Liquid-like friction
- Coulomb friction
- Sliding friction

**Modeling of QCM Data**

**Ring-down:**
- 5 MHz
- Oscilloscope
- Frequency
- Modulator (20 Hz)

**Graph:**
- Voltage vs. time
- Fit function
- Quality of fit decreased when contact was just established

**Chirp:**
- Fit on 10–50 slices separately
- Nonlinear resonator
Two-timing approximation

\[
\frac{\Delta f}{f_0} = \frac{2}{a} \frac{1}{\pi A \omega} \langle F(t) \cos(\omega t) \rangle
\]

\[
\frac{\Delta \Gamma}{f_0} = \frac{2}{a} \frac{1}{\pi A \omega} \langle F(t) \sin(\omega t) \rangle
\]

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

---

Mindlin partial slip

\[ \Delta = \omega \pi \Delta \Gamma \]

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

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

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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-fledged 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)