EQCM · 6-HOUR SHORT COURSE

MODULE 1

Fundamentals

From quartz crystal to the electrochemical interface

§ 1.1 Introduction and motivation

This course follows the EQCM technique from its piezoelectric roots to modern dissipation monitoring — connecting nanogram mass changes at an electrode to the underlying electrochemistry.

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Quartz (SiO_2) — the heart of every QCM device.

What is a QCM? — three-block teaser

A verbal hook before any equation: piezoelectric crystal → resonant oscillation → nanogram mass tracking.

Natural clear quartz (SiO_2) — macro morphology and Si–O lattice.

1

Piezoelectric heart

The sensing element is a thin slice of single-crystal α-quartz with metal electrodes patterned on each face — its lack of inversion symmetry is what makes it piezoelectric.

2

Resonant oscillation

An AC voltage applied across the electrodes drives the crystal into a thickness-shear mode at its natural resonant frequency f_0 (typically 5–10 MHz).

3

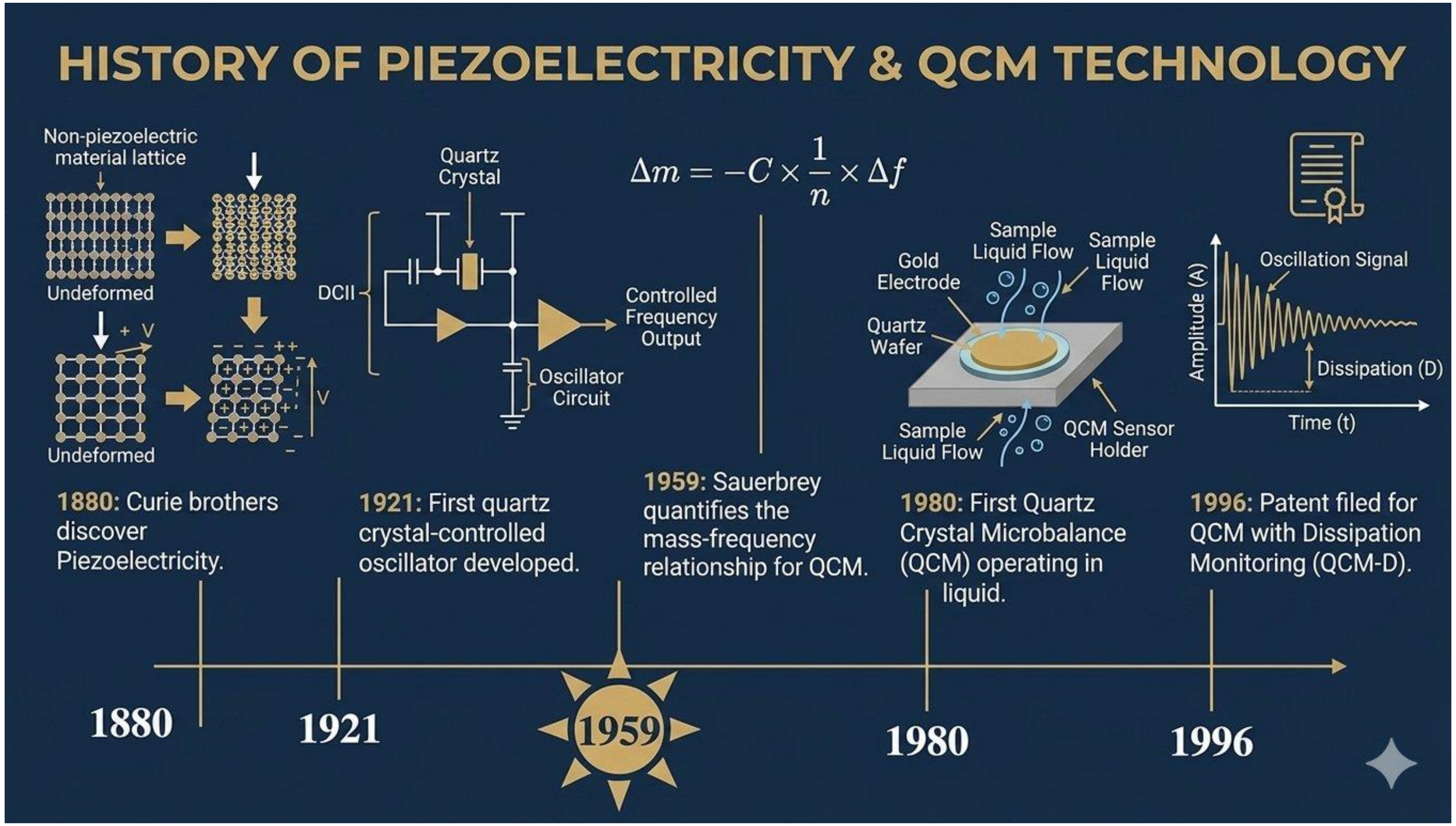
Nanogram mass tracking

When material adds to the surface, f_0 shifts down. The shift Δf is linear in the added mass — sensitive to ng cm^{-2}, in real time.

Image: clear-quartz reference · cf. Deakin & Buttry, Anal. Chem. 1989, 61, 1147A

A short history of piezoelectricity & QCM

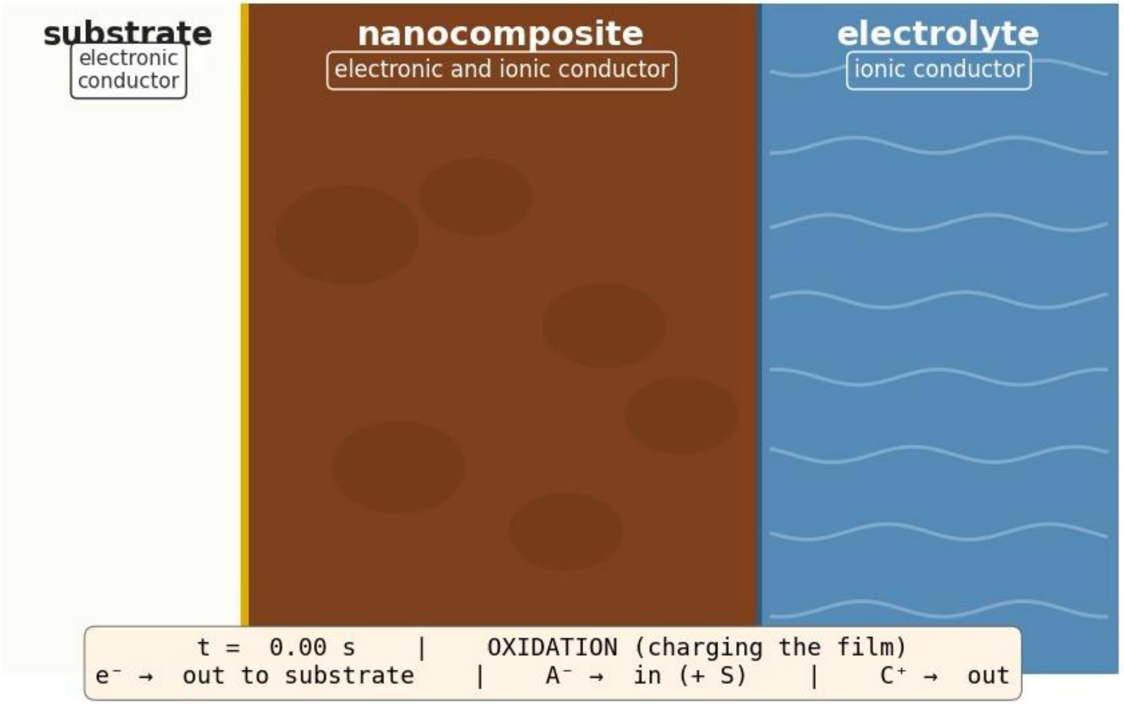
From the Curie brothers' discovery to dissipation monitoring — 100+ years to a routine electrochemical tool.



Take-away — Sauerbrey (1959) made QCM *quantitative*; operation in liquid (1980s) made it *electrochemical*; dissipation (1996) made it *viscoelastic*.

What questions does EQCM answer?

*Electrochemistry tells you **charge**. EQCM tells you **what the charge is doing**.*

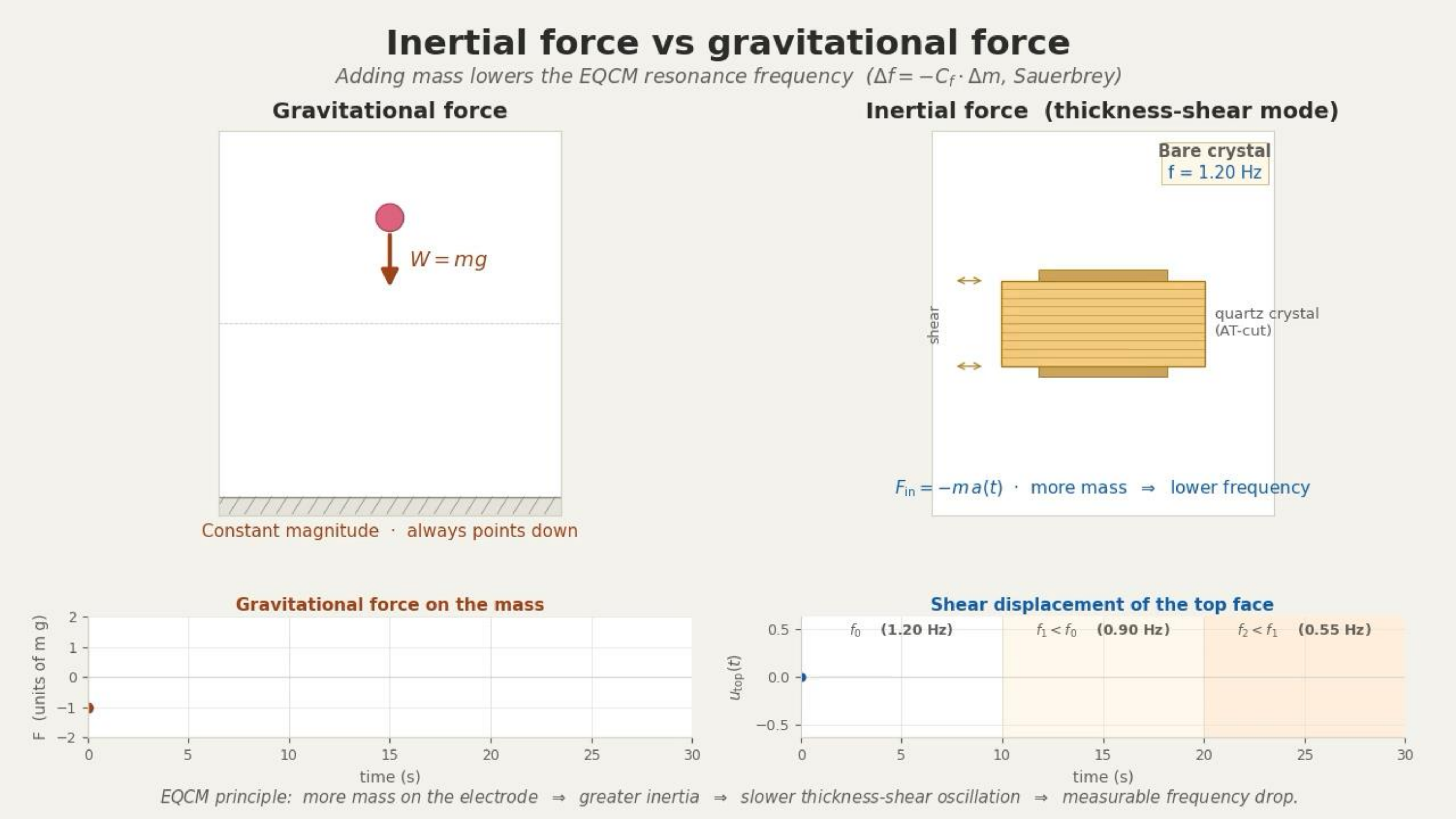


Three-region picture of the electrified film: e^- exchange at the substrate, A^- / C^+ / solvent (S) flux at the film | electrolyte boundary.

Typical EQCM questions

- **Deposition / dissolution**
  is the current 100 % faradaic?
- **Ion vs solvent transfer**
  what crosses the film, and how much?
- **SEI & passivation**
  when does the layer start to grow?
- **Adsorption (bio, organic)**
  surface coverage in real time.
- **Corrosion**
  rate from mass loss, not just current.
- **Viscoelastic films**
  soft vs rigid behaviour (with EQCM-D).

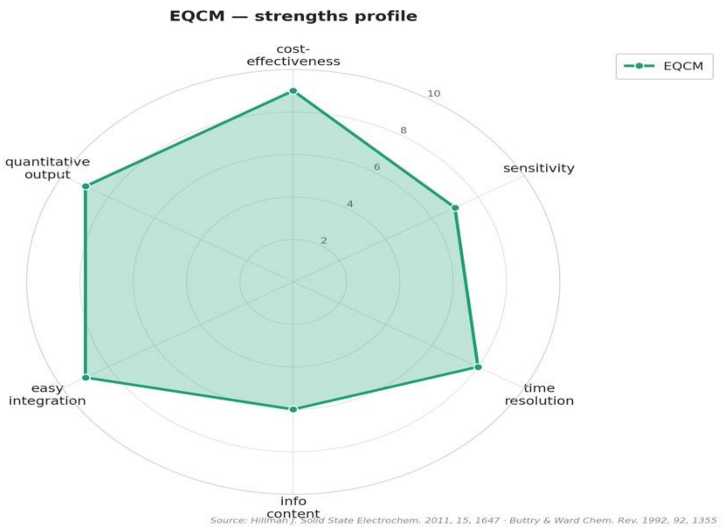
What is de difference between a gravitational an inertial microbalance?



EQCM among in situ electrochemical techniques

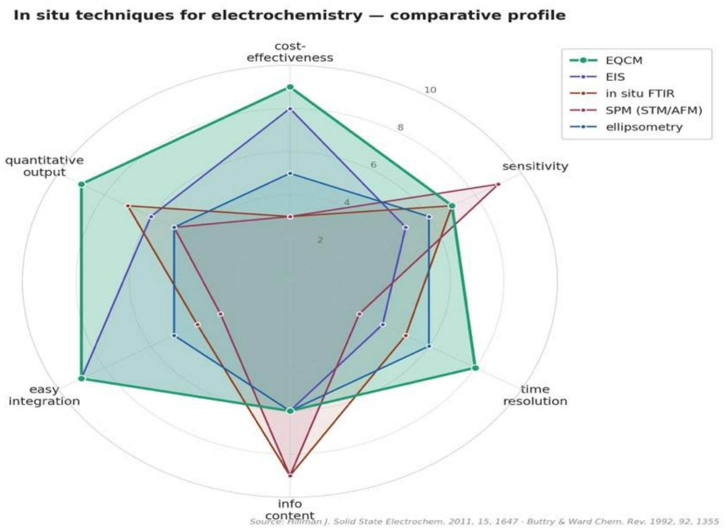
Three lenses on the same set of axes — what does EQCM bring, and what does dissipation add on top?

EQCM — strengths profile



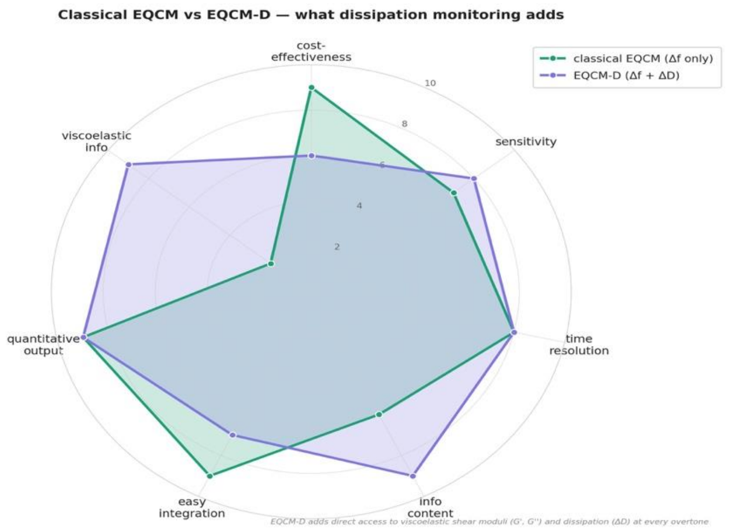
High on cost, time-resolution, easy integration & quantitative output.

vs. EIS, FTIR, SPM, ellipsometry



Each technique covers a different region — EQCM and EIS overlap strongly.

Classical EQCM vs EQCM-D



Adding ΔD opens viscoelastic info content with a small cost penalty.

EQCM’s unique selling points

Quantitative
known sensitivity factor C_f

Affordable
low-cost crystals & electronics

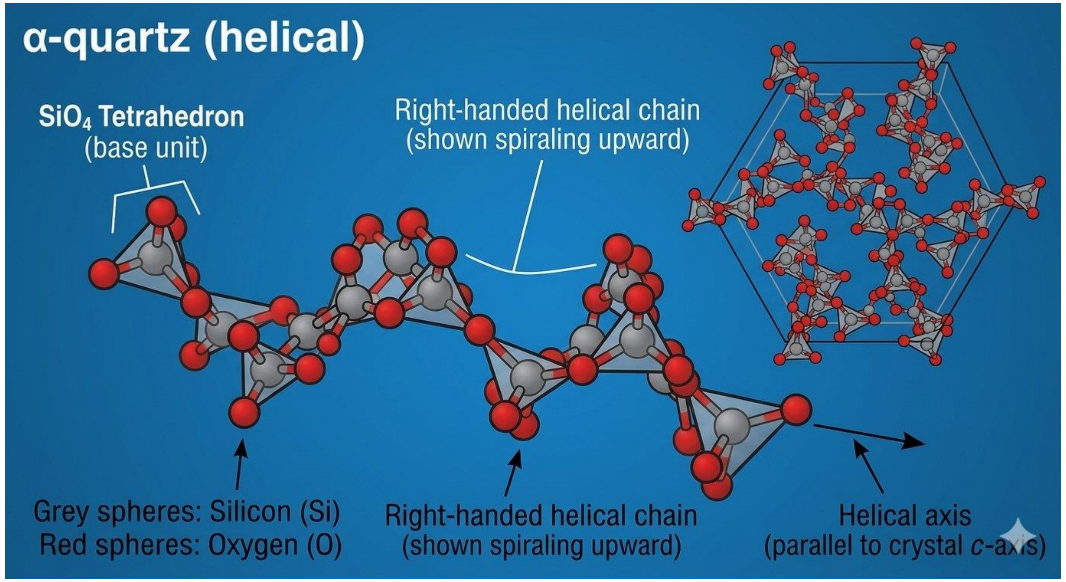
Real-time
ms-scale frequency tracking

Compatible
drops into most EC cells

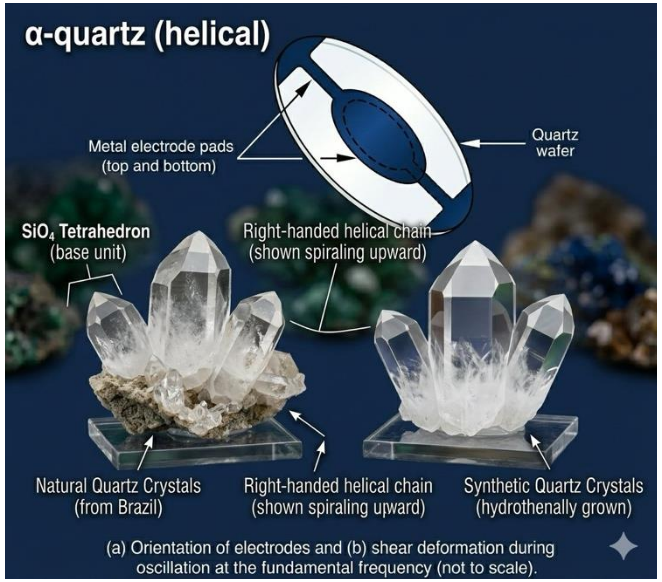
Adapted from Hillman, J. Solid State Electrochem. 2011, 15, 1647 · Buttry & Ward, Chem. Rev. 1992, 92, 1355

Quartz crystal — structure and importance

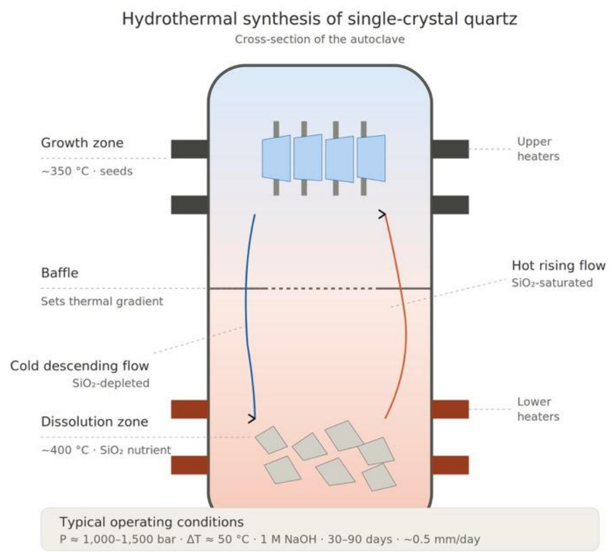
Why quartz? SiO_4 tetrahedra wound into helical chains break inversion symmetry → piezoelectricity, with low loss and machinable cuts.



α-quartz: SiO_4 tetrahedra in right-handed helical chains along the c-axis.



Natural (Brazil) and synthetic (hydrothermal) crystals — wafers cut from these.



Hydrothermal autoclave: source of low-defect, QCM-grade quartz.

No inversion symmetry

→ piezoelectric coupling

Low acoustic loss

→ $Q > 10^5$ in air

Zero-T-coeff cuts

→ stable f_0 near 25 °C

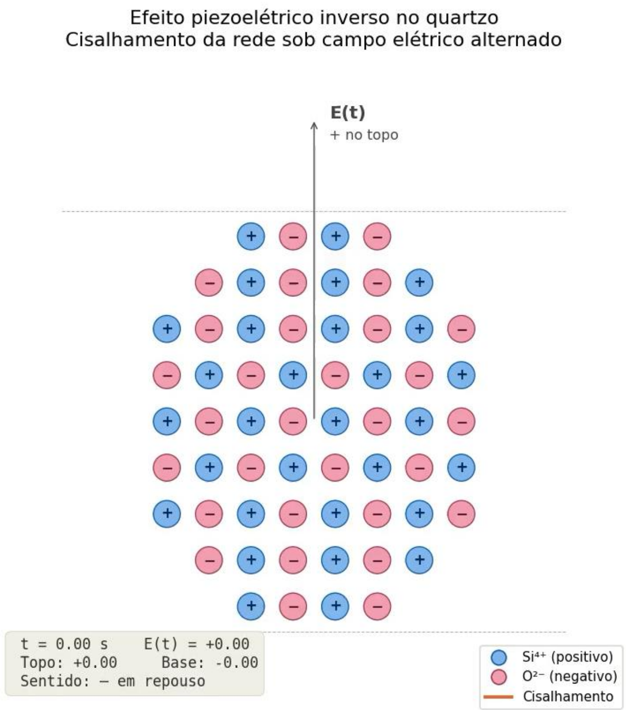
Abundant & machinable

→ low cost, reproducible

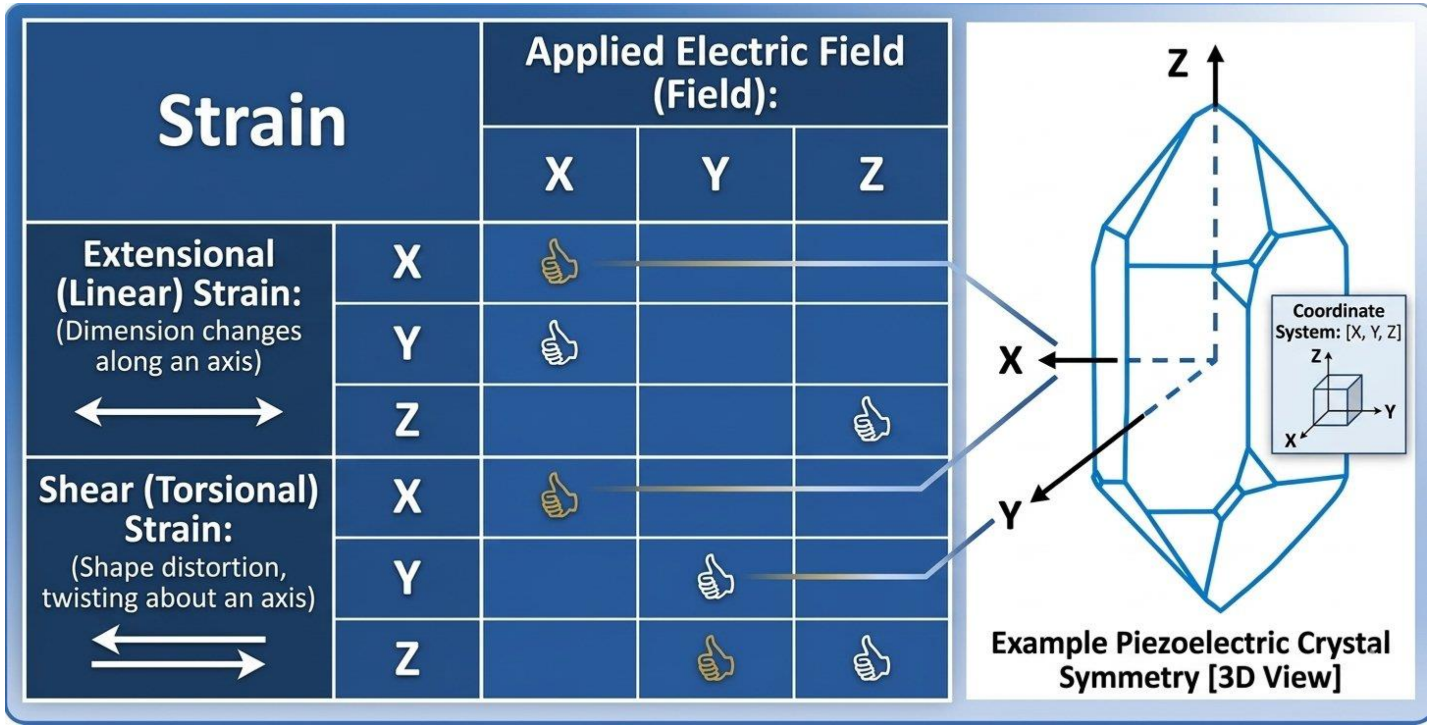
Crystal structure: standard textbook · synthesis: Iwasaki & Iwasaki, J. Cryst. Growth 2002

Direct & converse piezoelectric effects

Direct: *stress → polarization (sensors).* ***Converse:*** *field → strain (the QCM uses this side of the coin).*



Converse effect — applied E(t) shears the lattice (Si^{4+} vs O^{2-} displacement).

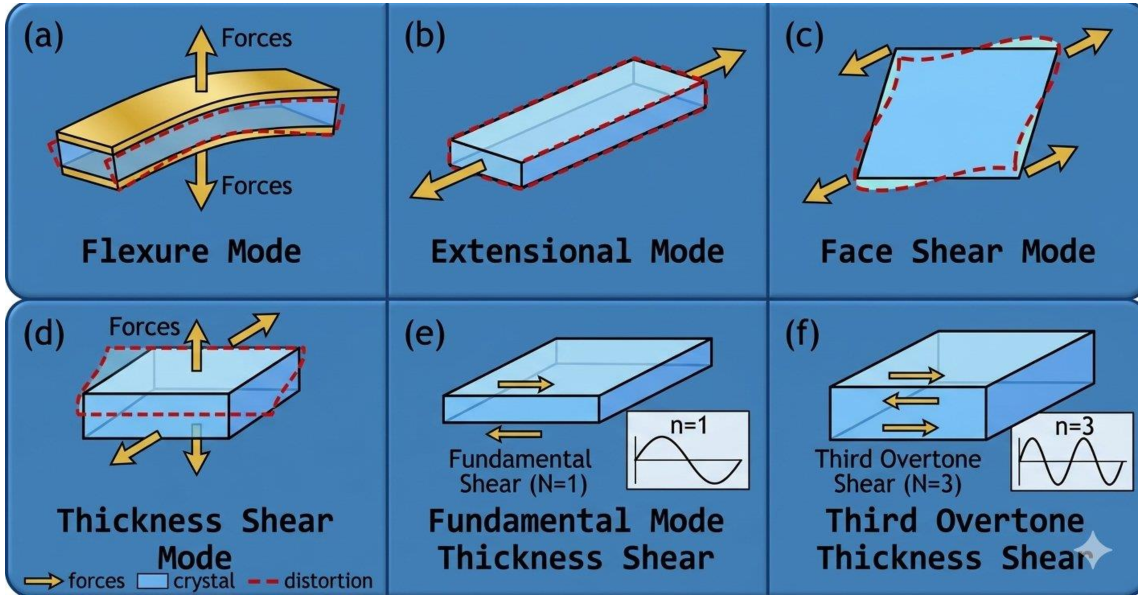


Symmetry of α-quartz allows specific (E, strain) couplings — thickness shear is the one we want.

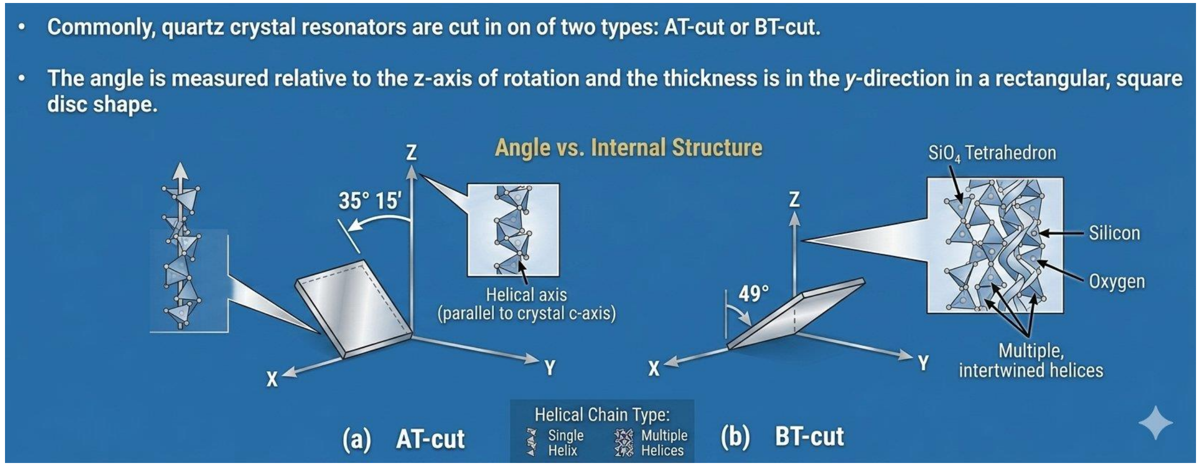
> **Take-away —** an AC field along the right axis produces an oscillating *shear strain* — the basis of the QCM.

Strain modes and the AT-cut

Of the modes available, thickness-shear is the one we want — and it is the AT-cut that selects it cleanly.



Six basic modes of motion — (e) fundamental & (f) third-overtone thickness-shear are the QCM working modes.



AT-cut (35°15') vs BT-cut (49°) — angle measured from the z-axis.

Why AT-cut for QCM?

- Pure thickness-shear at fundamental
- Zero temperature coefficient near 25 °C
- v_tr ≈ 3 340 m s^{-1} → N = v_tr / 2 ≈ 1.67 MHz·mm

Take-away — the AT-cut is the workhorse of QCM: pure shear, low temperature drift, well-known frequency constant.

Temperature dependence of f_0 — why AT wins

Bechmann curves show how cut angle controls the slope of Δf/f vs T near 25 °C — the AT-cut hits a flat sweet spot.

Bechmann curves — Δf/f vs T (schematic)

AT-cut 35° 15'

df/dT ≈ 0 near 25 °C — flat curve, ideal for room-T work.

AT-cut 35° 20'

small angle change → curve tilts up at high T.

BT-cut 49°

parabolic, large drift across 0–80 °C — used at higher T only.

(axes: T — horizontal, Δf/f — vertical, zero crosses near 25 °C)

What this means in practice

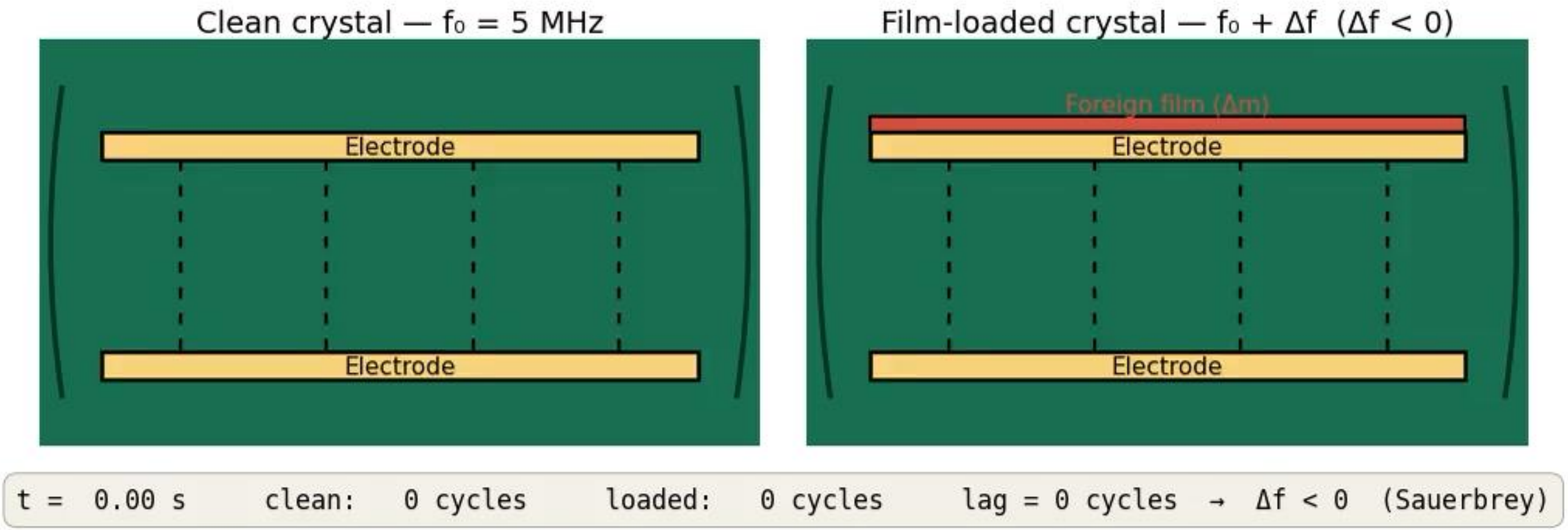
- **Sensitivity scale**
  1 °C drift on a 5 MHz crystal can shift f by tens of Hz — comparable to a sub-monolayer of metal.
- **Why AT for room-T work**
  near 25 °C, df/dT ≈ 0 → measurement uncertainty is dominated by mass, not temperature.
- **Operational rule**
  thermostat the cell to ±0.1 °C, especially in liquid where the entire crystal contacts the bath.

Take-away — AT-cut = small *df/dT* at room T, but you still need a thermostat to reach ng-cm^{-2} accuracy.

Bechmann's curves: Bechmann, Proc. IRE 1956, 44, 1600 · SAU1959 Fig. 10

The resonant condition — standing shear wave

Thickness equals λ/2 in the fundamental mode. The crystal acts as a half-wavelength resonator; loading it lengthens λ and lowers f.



Clean crystal (left) vs film-loaded (right) — same elapsed time, fewer cycles when loaded → Δf < 0 (Sauerbrey).

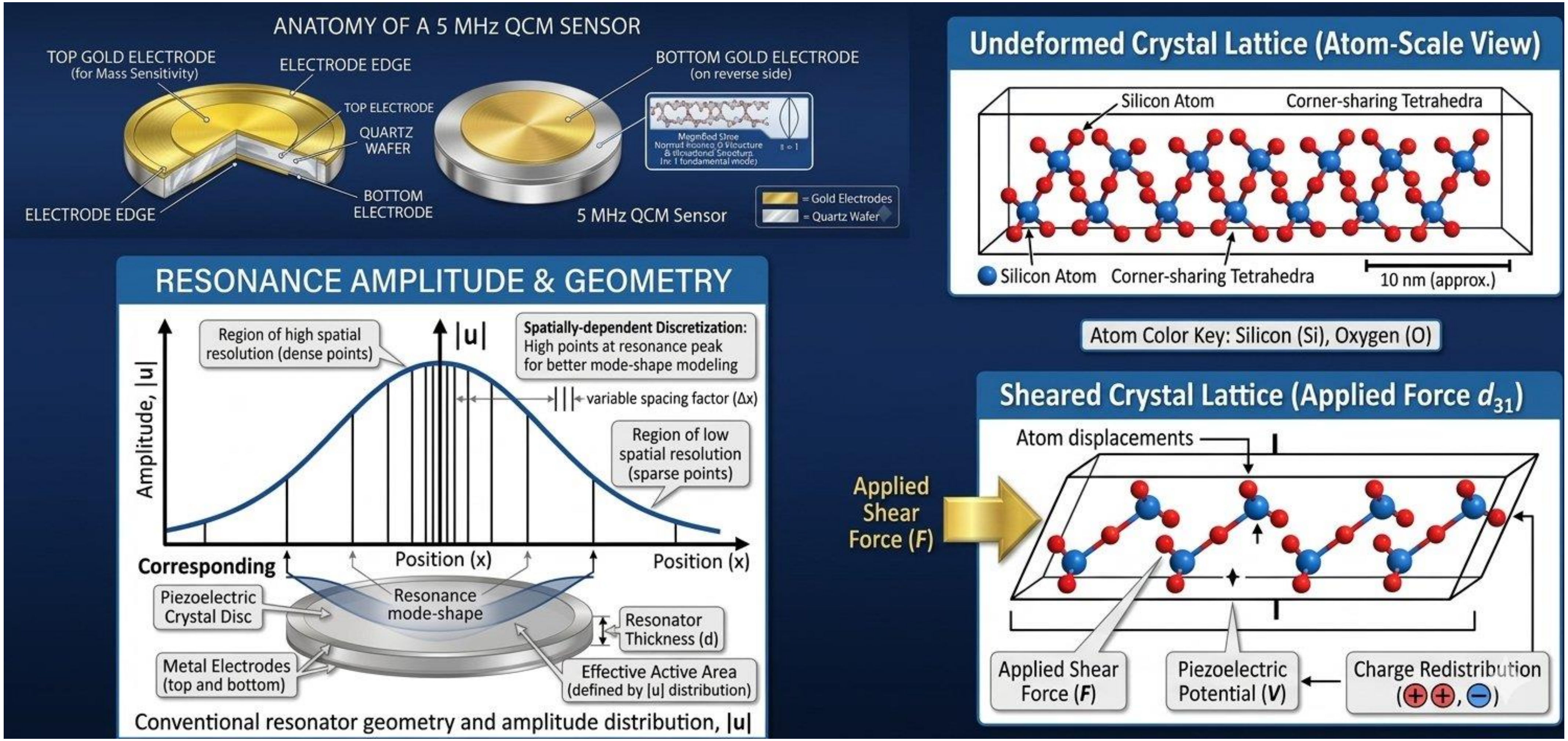
$$f_0 = v_{tr} / (2 \cdot t_q)$$

$v_{tr} \approx 3\,340\ m\ s^{-1}$ (AT-cut shear-wave speed) · $N = v_{tr} / 2 \approx 1.67$ MHz · mm (frequency constant)

Animation: course materials · cf. Buttry & Ward, Chem. Rev. 1992, Fig. 2 ·

Geometry — electrode placement & active area

The piezoactive zone is the overlap of the two electrodes. Lateral amplitude is ≈Gaussian — energy trapping confines vibration.



5 MHz QCM sensor — anatomy, mode-shape (Gaussian |u|), and atom-scale view of shear coupling.

Mechanical analogy — balance vs QCM

Classical balances measure weight (force of gravity); the QCM measures mass via inertia of an oscillator — independent of g.

Mass	Weight
Amount of matter of an object	Measure of the gravitational force exerted by earth on an object
Constant for any object anywhere in the universe.	Varies when the object is moving away from the surface of the earth.
It can be measured by the variation of an specific physical property of an object as a function of time	Measured with an equal arms balance.
Unit: grams	Unit: Newton (N). Force needed to accelerate 1 kg in 1m s^{-2}.

Reference: how mass differs from weight — operationally and dimensionally.

Pan balance

$P = m \cdot g$

Compares unknown to a reference mass — needs gravity. Unit: newton.

QCM — inertial mass

$\Delta f \propto \Delta m$

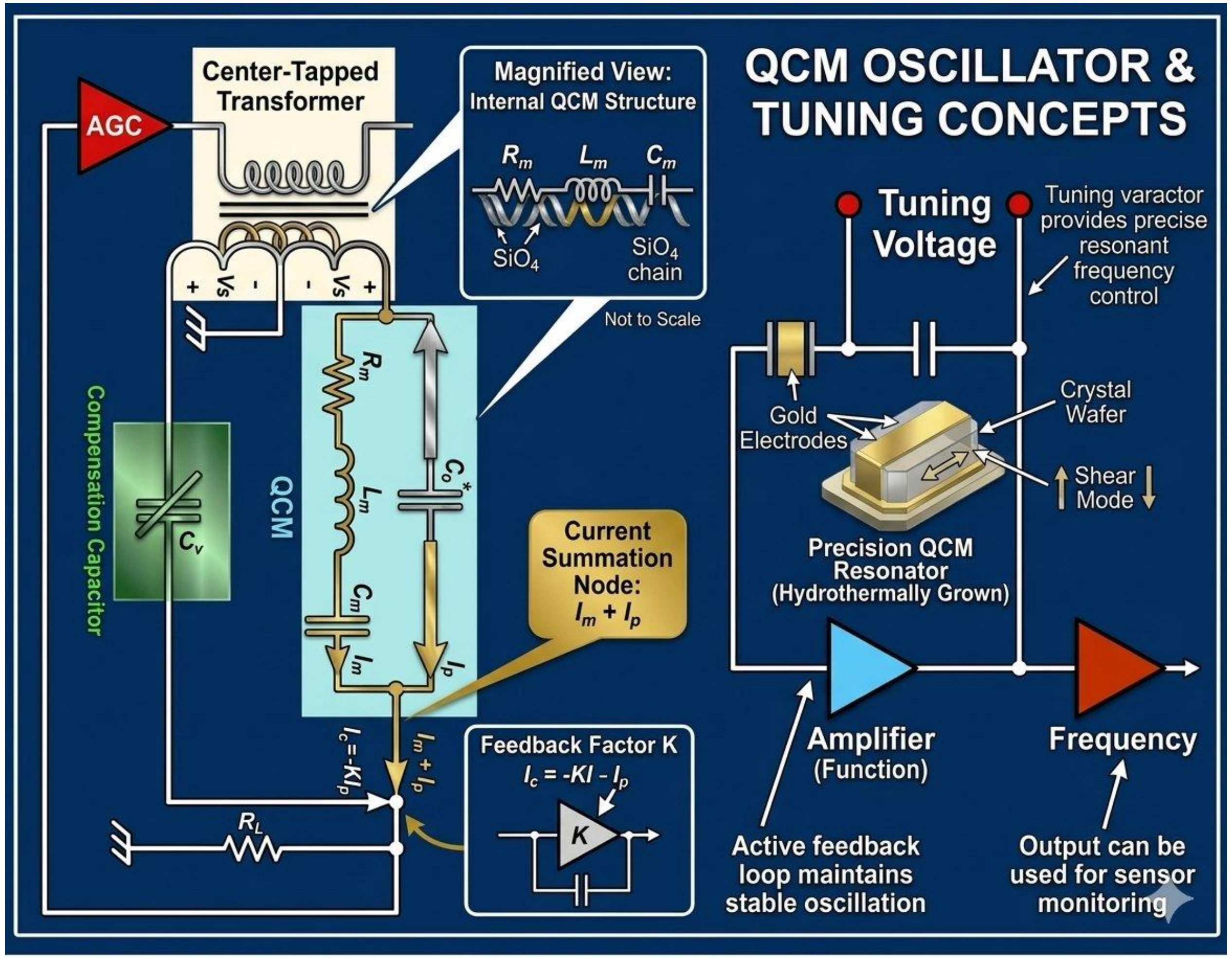
Mass shifts the inertia of the oscillator — works in any gravitational field.

Take-away — the QCM is an *inertial* balance: it would still work in space. The Sauerbrey constant Cf hides the mechanics behind $\Delta f = -C_f \cdot \Delta m/A$.

Both are quantitative — but only one stays calibrated when you change planet, lab, or solvent density. ***QCM ✓***

Oscillator circuit — how we drive the crystal

The crystal sits in the feedback loop of an active oscillator. The loop locks onto the series-resonance frequency; a counter reads f at ~1 Hz / 0.1 s.



Pierce-Miller-style oscillator: quartz + amplifier + tuning + counter.

Reading the diagram

- **Crystal as BVD network**
  R_m, L_m, C_m (motional branch) ‖ C_0* (static capacitance)
- **Active feedback loop**
  amplifier compensates losses → sustained oscillation at series resonance.
- **Compensation capacitor C_v**
  cancels parallel C_0* so the loop locks onto the motional branch only.
- **Tuning varactor**
  fine-tunes the resonant frequency (precise voltage-controlled offset).
- **Output**
  frequency counter → typical resolution ≈ 1 Hz in 0.1 s gate.

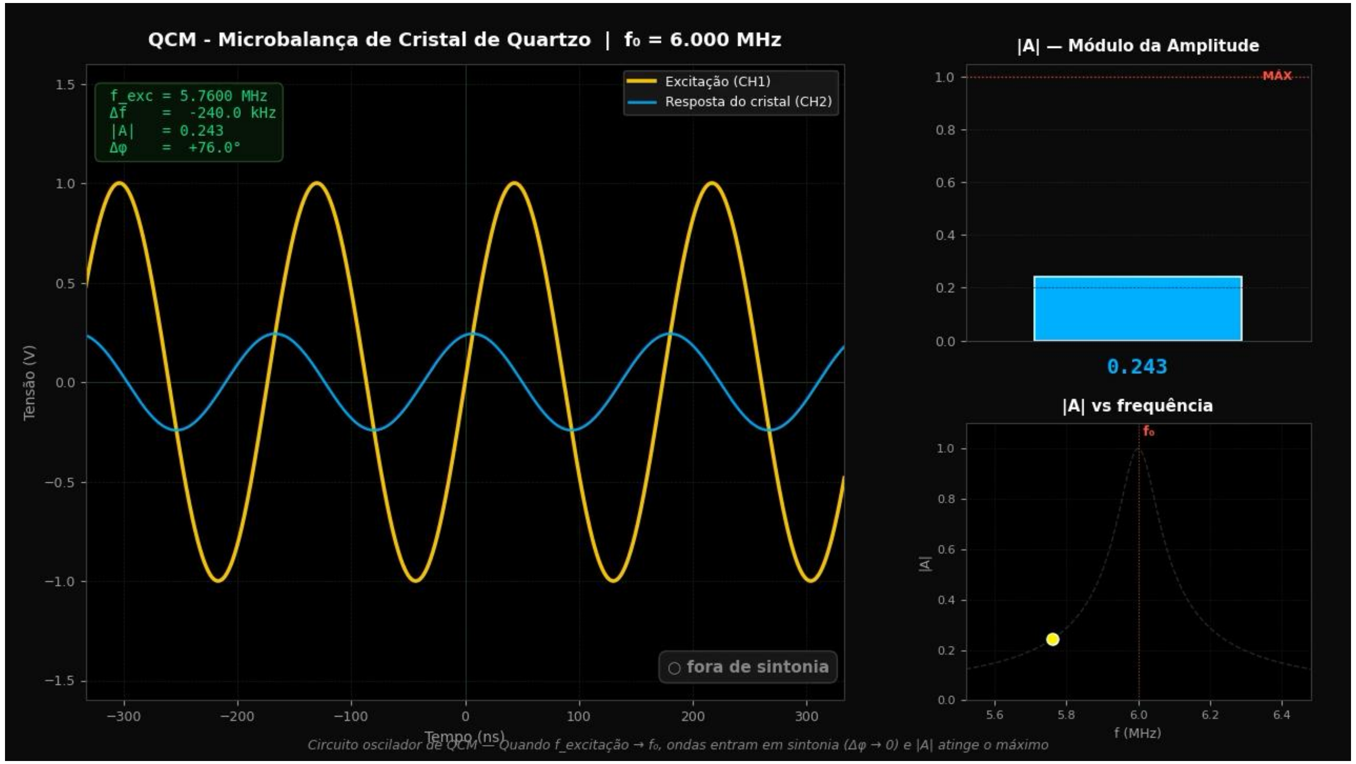
Resonance and standing waves — recap

Brief reminder before mass loading: nodes, antinodes, harmonics, and quality factor Q.

1
Standing wave
A wave reflected between two boundaries forms nodes (zero amplitude) and antinodes (maximum amplitude). The crystal thickness selects which wavelengths are allowed.

2
Resonance & overtones
Allowed frequencies: f_n = n·v_tr/(2·t_q), n = 1, 3, 5 … Only odd harmonics are piezoelectrically active (symmetry argument).

3
Quality factor Q
Q = (energy stored) / (energy lost per cycle) ≈ f_res / FWHM. Free 5 MHz crystal in air: $Q > 10^5$. In water: Q drops to ~3×10^3.



Excitação (CH1) vs resposta do cristal (CH2). Quando f_exc → f_0, |A| atinge o máximo e Δφ → 0.

Take-away Resonance gives us narrow lines (high Q) — and Δf measured against a high-Q line is what makes nanogram sensitivity possible.

Mass loading on the crystal — concept

A rigid film extends the resonator: longer acoustic wavelength → lower frequency.

Composite resonator

Bare crystal (t_q, ρ_q): $f_0 = v_{tr} / (2 \cdot t_q)$
+ rigid film (t_f, ρ_f) moving in phase:
$\lambda \uparrow \;\rightarrow\; f \downarrow \;\rightarrow\; \Delta f < 0$

Key assumptions for Sauerbrey to hold

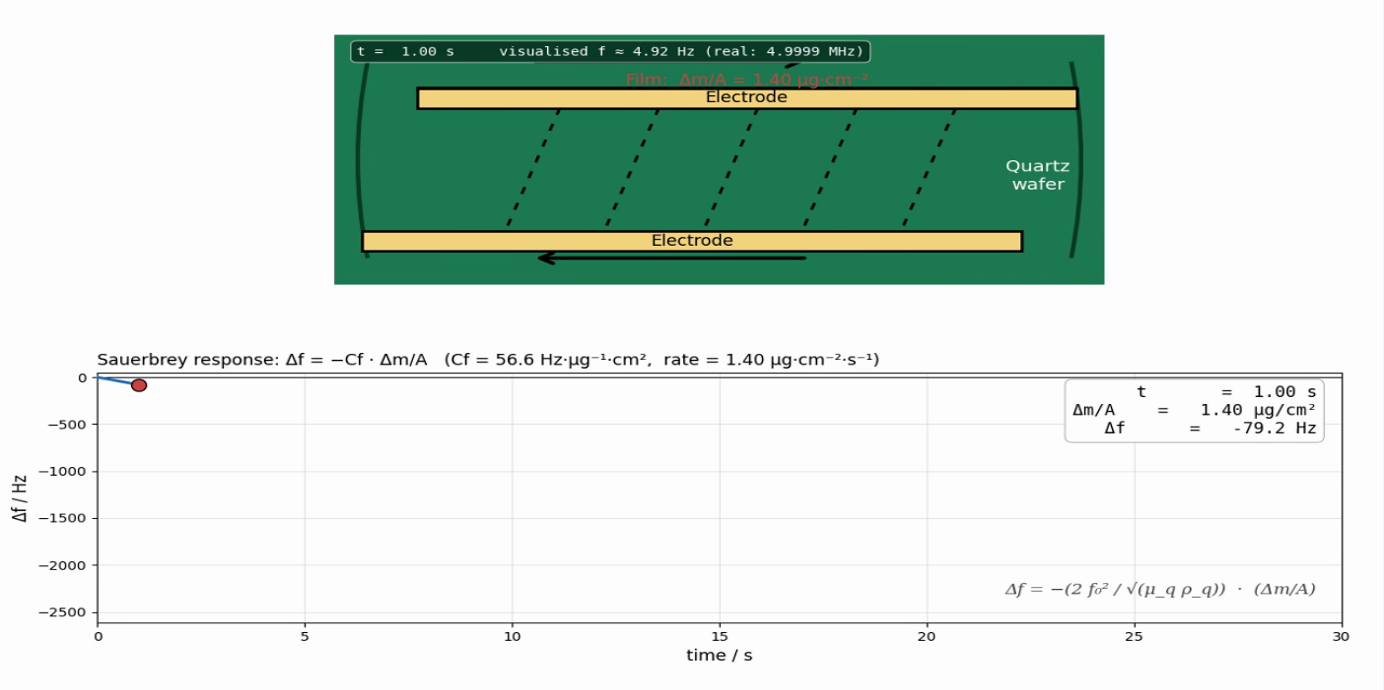
Rigid film — no internal damping; ρ_f and μ_f match the crystal's acoustic impedance well enough.

No-slip interface — the film moves synchronously with the gold electrode (no decoupling).

Thin layer — added mass < 2 % of the active crystal mass (≈ 9 µg cm^{-2} for a 5 MHz AT-cut).

Uniform deposit — mass spread evenly over the piezoactive area.

Thickness-shear mode (TSM) + Δf curve



Mass deposits onto the electrode (Δm/A = 1.40 µg cm^{-2} s^{-1}). Δf follows Sauerbrey linearly with time.

Take-away The added mass behaves as an inertial extension of the quartz disc — the shear wave 'sees' ($t_q + t_f$). This is the core idea of Sauerbrey.

Animation: course materials · cf. BW1992 Fig. 2 (p. 1357)

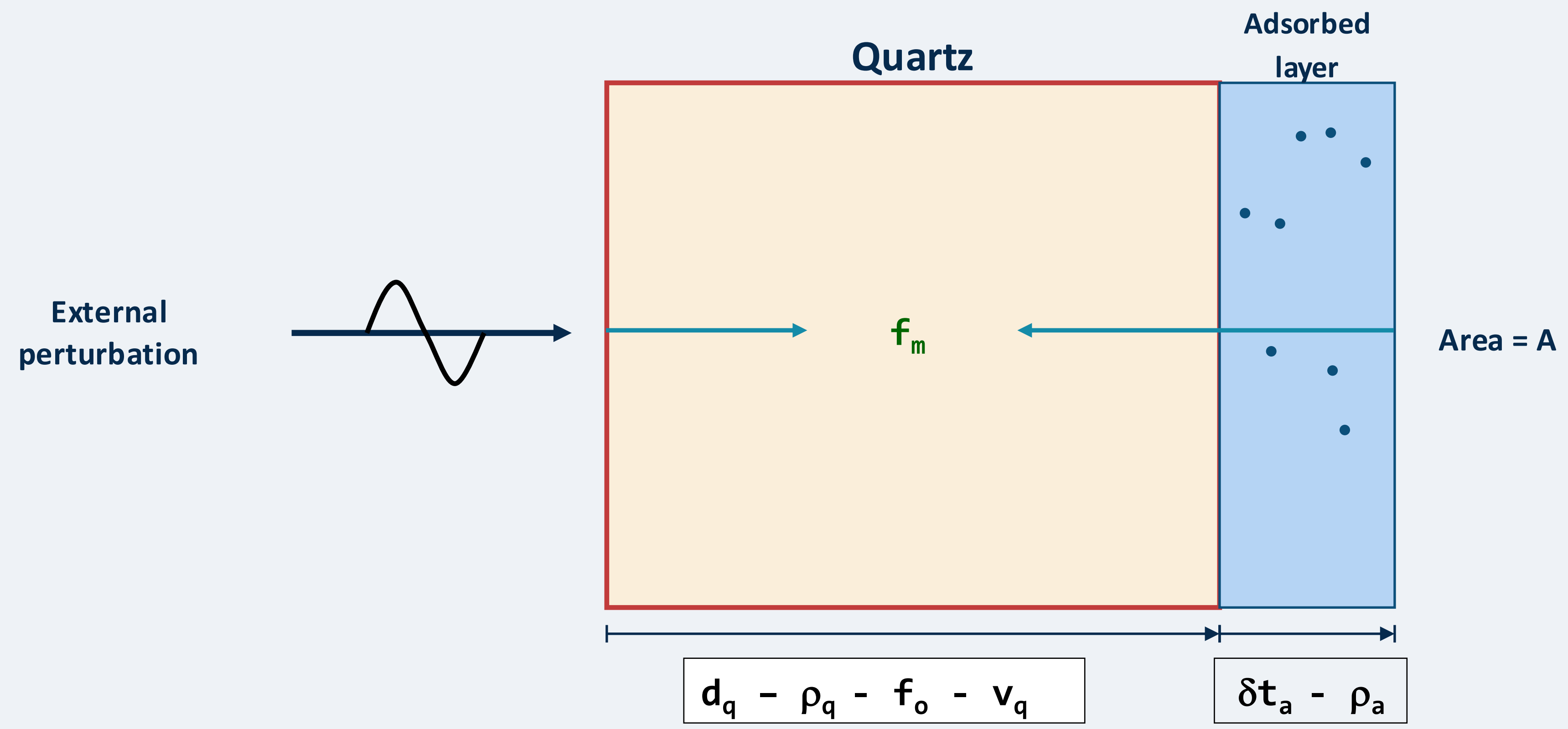
QUARTZ CRYSTAL MICROBALANCE

Derivation of the **Sauerbrey Equation**

From fundamental relations to mass sensitivity at 6 MHz

1. The Physical System

A quartz disk under shear oscillation, with a thin adsorbed layer on its surface



Variables: f_m measured frequency · f_0 fundamental frequency · t_q, ρ_q quartz thickness and density

v_q, μ_q shear wave velocity and modulus · δt_a, ρ_a adsorbed layer thickness and density · A active area

2. Fundamental Relations

Three independent relations from acoustics and geometry combine into the resonance condition

Starting relations

Half-wavelength resonance:

$$t_q = \frac{1}{2}\,\lambda_q$$

Crystal mass:

$$t_q A\,\rho_q = m_q$$

Acoustic shear velocity:

$$v_q = \frac{\mu_q}{\rho_q}$$

Result

Fundamental frequency

$$f_0 = \frac{v_q}{2\,t_q} = \frac{\lambda_q}{\lambda_q}$$

Physical meaning

The crystal resonates when its thickness equals half a shear wavelength. f_0 is fixed by material properties (μ_q ρ_q) and geometry (t_q).

3. Perturbation by Adsorption

Differentiating the resonance condition with v_q held constant

Differentiate : $f_0 = \frac{v_q}{2\, t_q}$

$$\frac{df}{f_0} = - \frac{dt}{t_q}$$

An adsorbed layer adds effective thickness:

the layer behaves as a quartz extension

→ dt = δt_a

Required hypothesis

Acoustically rigid layer

The adsorbed thickness is much smaller than the quartz thickness:

Typically: $\delta t \sim 1\%\ t_q$

Otherwise viscoelastic effects dominate and the simple linear relation breaks down.

$$df = -\frac{2\, f_o^2}{\sqrt{(\mu_q\, \rho_q)}\, A}\, dm$$

4. Chain of Substitutions

From the linear relation to mass — three substitutions

1 **Substitute** $f_0 = \frac{v_q}{2\, t_q}$

$$\frac{df}{f_0} = -\frac{2\, f_0}{v_q}\, dt$$

2 **Substitute** $v_q = \sqrt{\frac{\mu_q}{\rho_q}}$ **and** $\mathrm{dt} = \frac{dm}{A\, \rho_q}$ **:**

$$\frac{df}{f_0} = -\frac{2\, f_0}{\sqrt{\frac{\mu_q}{\rho_q}}} \frac{dm}{A\, \rho_q}$$

3 **Multiply both sides by f_0 → Sauerbrey equation:**

Δf is directly proportional to Δm

Negative sign: added mass lowers the resonance frequency.

SAUERBREY EQUATION

$$\mathrm{df} = -\frac{2\, f_0^2}{\sqrt{\frac{\mu_q}{\rho_q}}} \frac{dm}{A\, \rho_q} = -\frac{2\, f_0^2}{\sqrt{\mu_q\, \rho_q}} \frac{dm}{A}$$

Compact form:

$$\Delta f = -K\, \Delta m \ where\ K = \frac{2\, f_0^2}{A\sqrt{\mu_q\, \rho_q}}$$

where K is the Sauerbrey constant

5. Numerical Application — 6 MHz AT-cut crystal

Plug in material constants and compute the sensitivity

AT-cut quartz constants

Fundamental Frequency: $f_0 = 6$ MHz $= 6 \times 10^6$ Hz

Shear modulus: $\mu_q = 2{,}947 \times 10^{11}$ g·cm^{-1}·s^{-2}

Quartz density: $\rho_q = 2{,}648$ g·cm^{-3}

Numerator: $2\, f_0^2 = 7.2 \times 10^{13}$ Hz^2

Denominator: $\sqrt{(\mu_q \cdot \rho_q)} = 8.834 \times 10^5$ g·cm^{-2}·s^{-1}

Sauerbrey constant

$$\Delta f = -K\, \Delta m \text{ where } K = \frac{2\, f_0^2}{A\sqrt{\mu_q\, \rho_q}}$$

$$\mathbf{K \equiv\ 0.0815\ \ Hz{\cdot}cm^2{\cdot}ng^{-1}}$$

Practical sensitivity

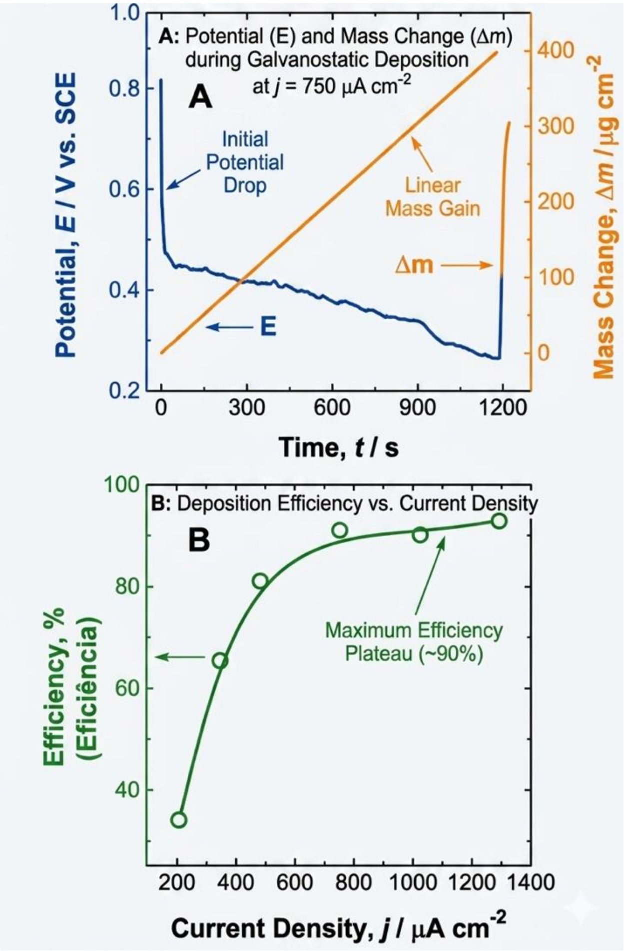
1 ng·cm^{-2} → Δf ≈ −0.082 Hz

1 Hz drop ≡ 12.3 ng·cm^{-2} adsorbed

Sub-monolayer mass detection on a few cm²: that is why QCM is used for adsorption, biosensing and thin-film monitoring.

Worked example — galvanostatic deposition

From a constant-current pulse: read mass directly from Δf, compare with Faraday, get the efficiency.



$$[PtCl_6]^{2-} + 4e^- \longrightarrow Pt_{(s)} + 6Cl^-$$

Step-by-step calculation

Setup

5 MHz AT-cut crystal: C_f = 56.6 Hz·cm²·μg⁻¹. Galvanostatic step j = 750 μA cm⁻², duration Δt = 1200 s.

1. Charge passed

$q = j \cdot \Delta t$

$q = 0.88\ \mathrm{C\ cm^{-2}}$

2. Faraday mass (theory)

$\Delta m_F = q \cdot M / (z\ F)$

for z=4, M=195,08 mol/g: $\Delta m_f \approx 444\ \mu g\ cm^{-2}$

3. Measured mass from Δf

$\Delta m_S = -\Delta f / C_f$

with $\Delta f \approx -22.6$ kHz: $\Delta m_S \approx 400\ \mu g\ cm^{-2}$

4. Current efficiency

$\eta = \Delta m_S / \Delta m_F$

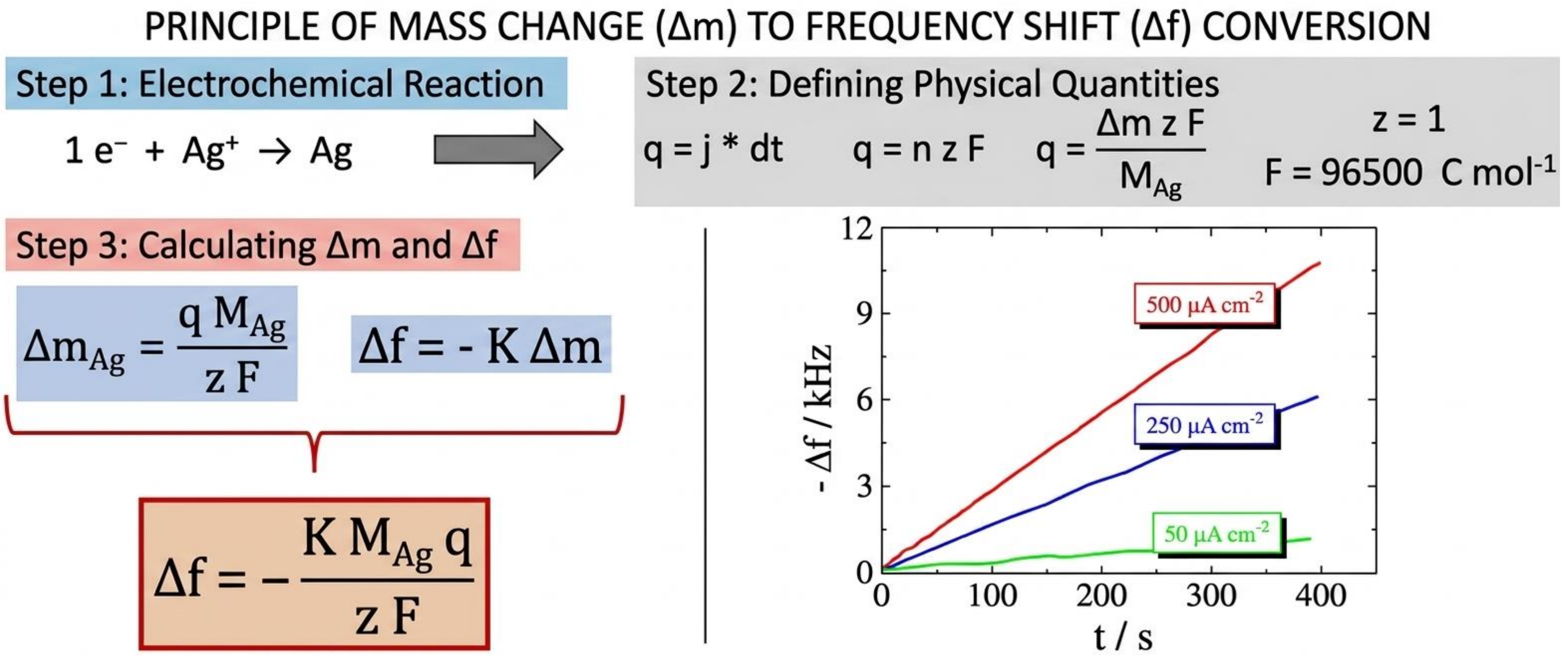
$\eta \approx 90\ \%$ (plateau region)

Take-away Efficiency rises with current density and saturates near 90 % — the missing 10 % is dendritic loss / parasitic reactions, not a Sauerbrey failure.

Data: deposition curves & η(j) · Format adapted from QN2000 Fig. 5

Sensitivity factor — theoretical vs experimental

C_f is constant only on paper. Experimentally the local sensitivity k(r) is bell-shaped: calibrate!



Take-away Always calibrate; electrodeposit a known amount of Ag or Cu, fit Δf vs q, and use the slope as your experimental C_f. The theoretical 56.6 Hz·cm²·μg⁻¹ is an upper bound.

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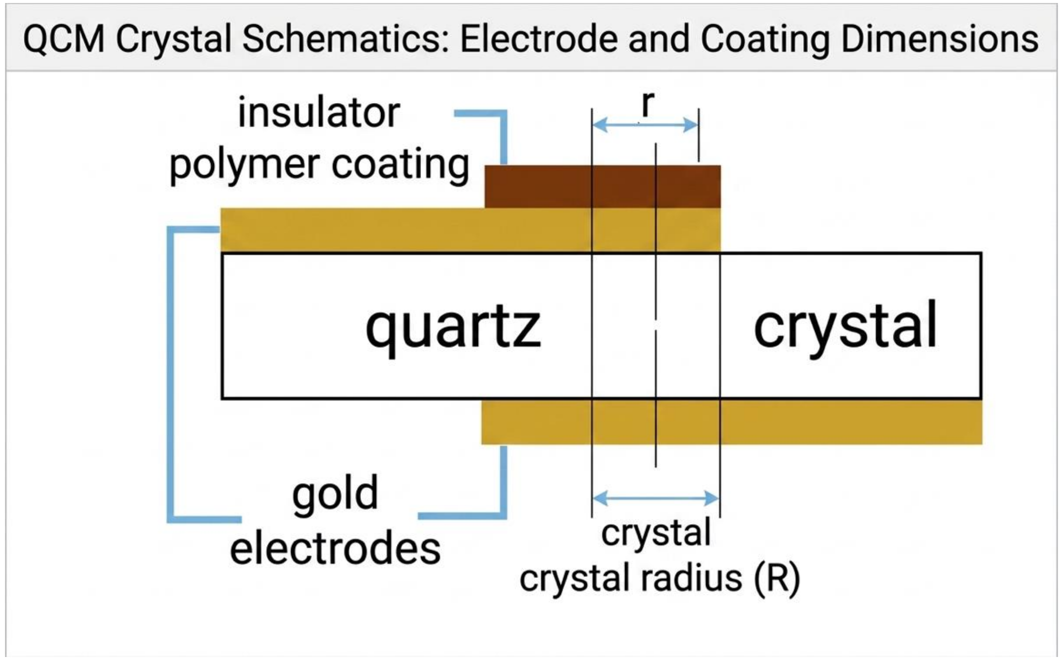

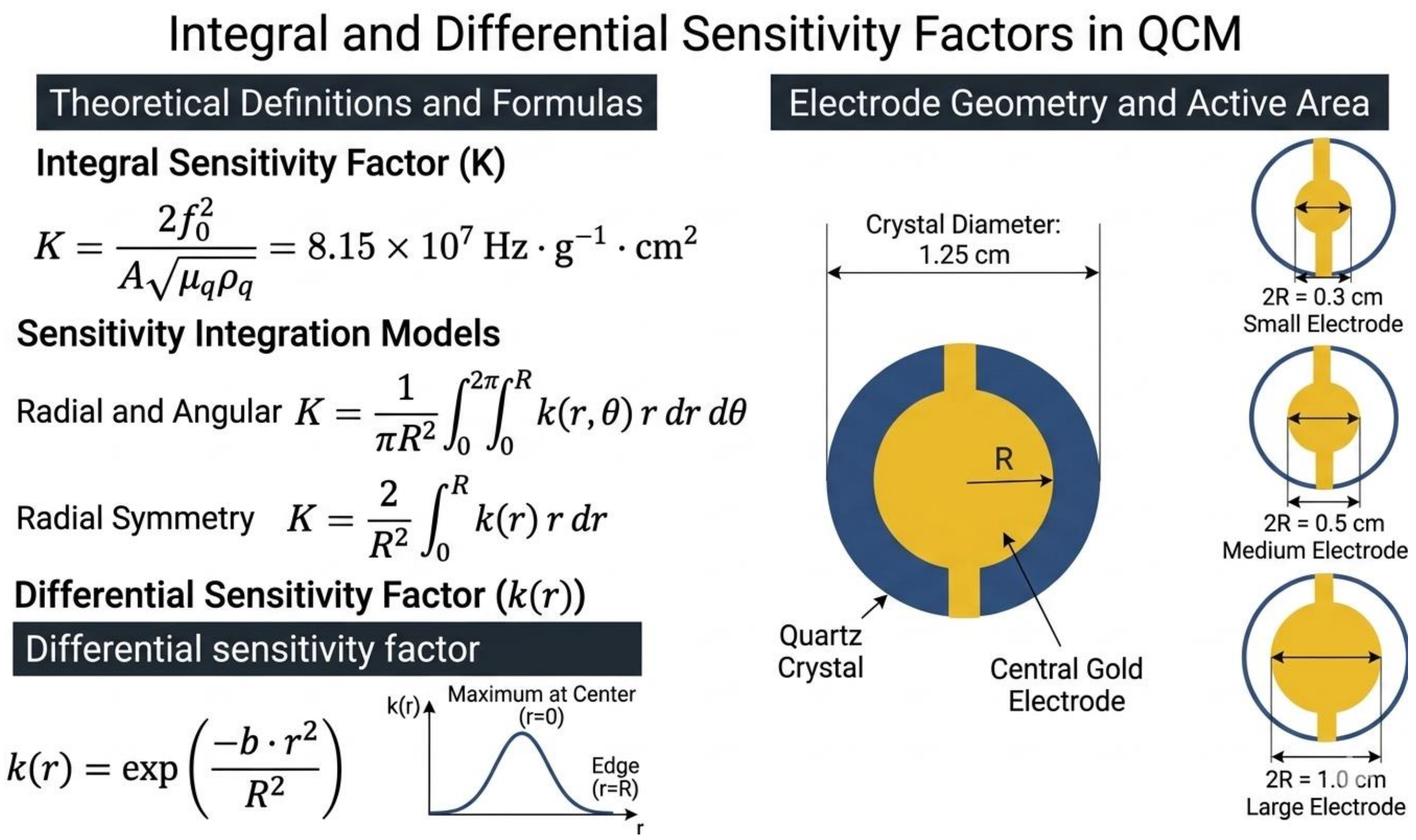

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Sensitivity model & data: QN2000 Tabela 1 (p. 667) · BW1992 Fig. 10 (p. 1367)

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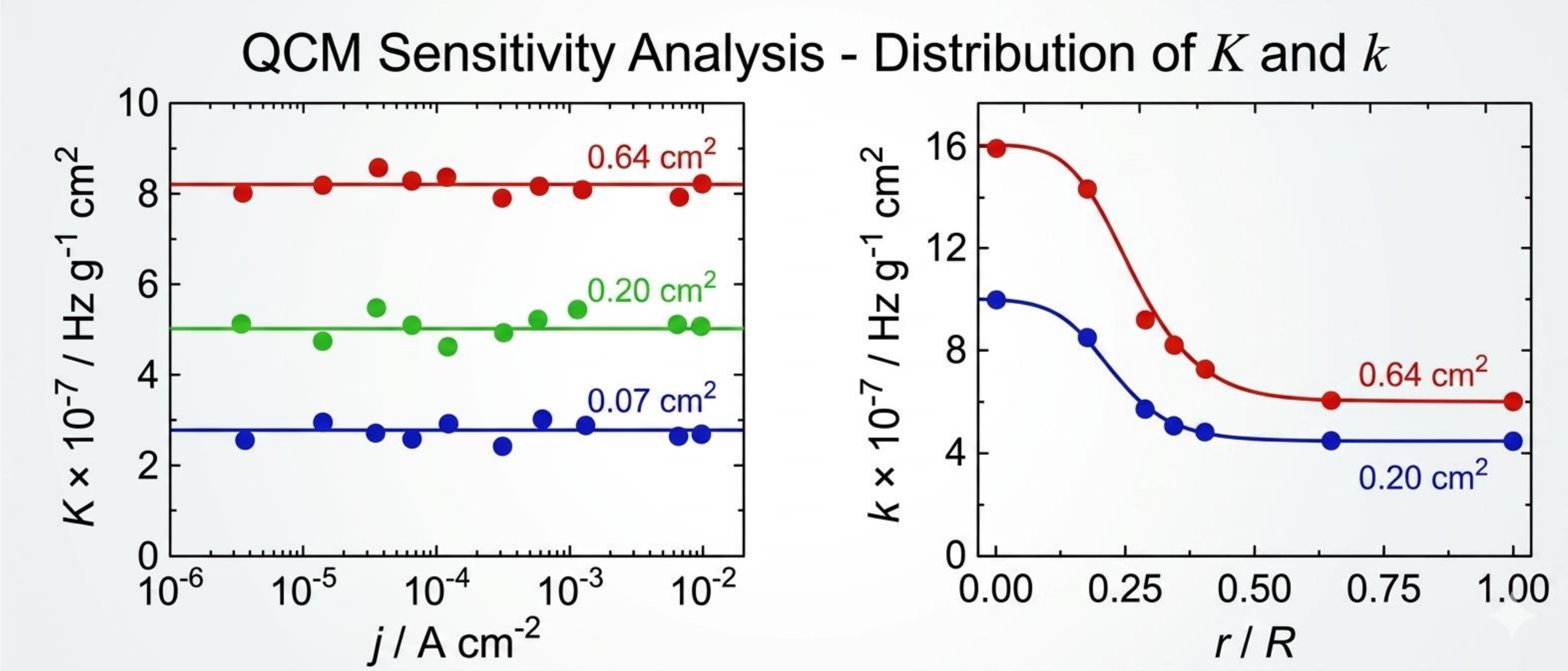

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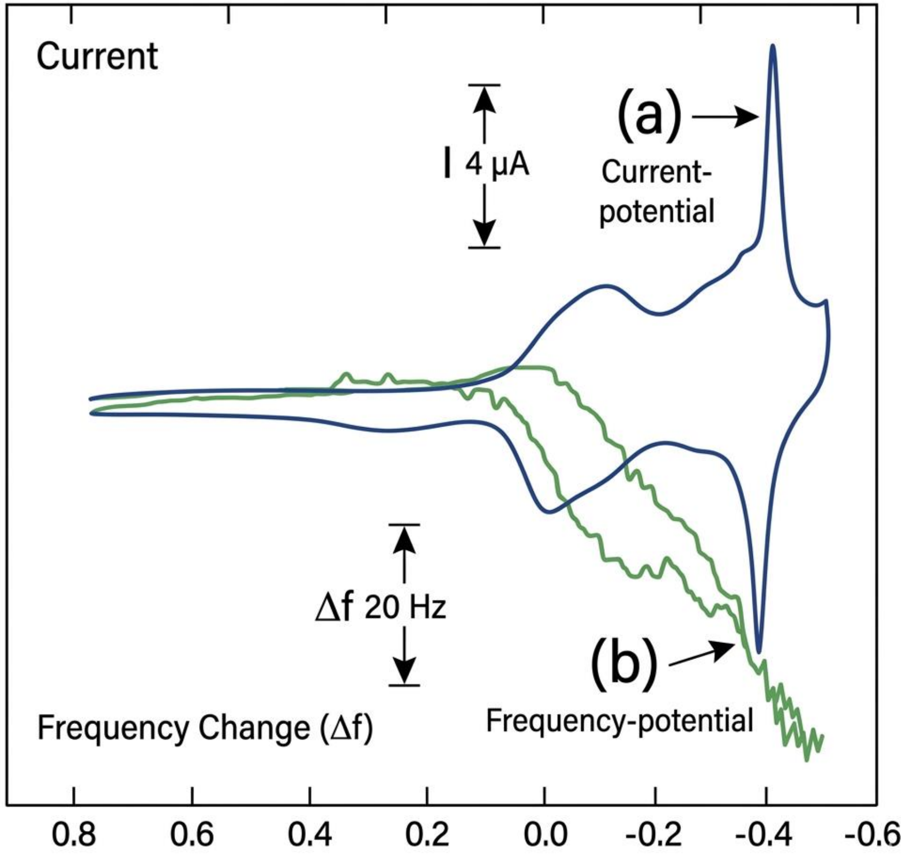
Underpotential deposition (UPD) — textbook EQCM result

Pb on Au from 0.1 M $HClO_4$ — current + Δf in one sweep tell the monolayer story.



Current-Potential and Frequency-Potential Curves for Pb Stripping in the Absence of PbC

Reading the simultaneous traces

(a) Current-potential curve

Two distinct stripping peaks (≈ −0.2 V and ≈ −0.4 V) — UPD layer detaches in two electrochemically resolved steps before bulk Pb stripping.

(b) Frequency-potential curve

Δf rises stepwise as Pb leaves the surface. Each Δf step pairs with a current peak — confirming each peak is a real mass-loss event, not capacitive.

Monolayer calibration

Hexagonal close-packed Pb on Au(111): expected mass ≈ 320 ng cm^{-2}, Δf ≈ 18 Hz at 5 MHz. Measured Δf ≈ 20 Hz → consistent with full UPD monolayer.

Take-away UPD on Au is the canonical proof that EQCM resolves sub-monolayer mass changes in real time — and pairs them unambiguously with the responsible faradaic current.

Limitations of Sauerbrey — when does it fail?

Four classes of perturbation can break the linear Δf ↔ Δm relation. Recognise them before quoting a mass.

1. **Rigid-film assumption**
   Soft polymers, hydrogels, swollen films: internal damping decouples top layers from the crystal. Symptom: $|\Delta f|$ smaller than mass implies, and $\Delta D \neq 0$.

2. **Thin-layer limit ($\Delta m < 2\ \%\ m_q$)**
   Thick deposits add their own resonance; $v_{tr,film} \neq v_{tr,quartz}$. Look for non-linear Δf-vs-q and overtone-dependent Δf/n.

3. **Uniform deposit**
   Localised corrosion or dendritic deposition concentrates mass off-centre. Because k(r) is peaked, weighting depends on where mass lands.

4. **Vacuum/air operation**
   Immersion in liquid adds the Kanazawa baseline: $\Delta f_K = -\sqrt{f_0^3\ \eta_L\ \rho_L / \pi\ \mu_q\ \rho_q}$. Subtract before reading mass — covered in § 1.4.

Take-away Smart practice: report Δf for several overtones, check overtone-normalised Δf/n consistency, and watch ΔD if you have it. When any of these flag a problem — re-think before computing mass.

Failure modes compiled from BW1992 §II.D · ARH2011 — 'Complications and opportunities'

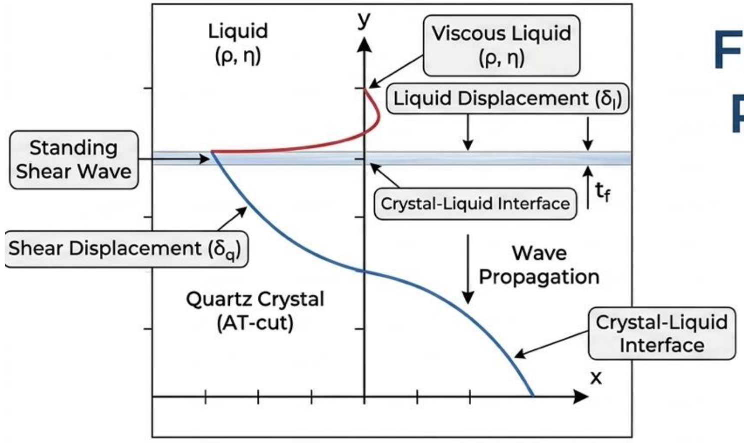
What happens when we immerse the crystal?

1 **Old wisdom (pre-1985)**
'A liquid will damp the resonance to extinction.' For decades QCM was considered a vacuum/gas-phase technique only.

2 **Reality (Bruckenstein 1985, Kanazawa 1985)**
In water the crystal still oscillates. Q drops from ~10^5 to ~3×10^3 — losses rise, but the resonance survives.

3 **Typical baseline shift**
Air → water at 5 MHz: $\Delta f_0 \approx -800$ to -3000 Hz, depending on geometry and wetting. Reproducible to a few Hz once thermally equilibrated.

4 **Damped shear wave penetrates the liquid**
Decay length δ_L = √(η_L / (π · ρ_L · f_0)) ≈ 250 nm in water at 5 MHz. The crystal probes only the first few hundred nanometres.



The shearing stationary wave in quartz crystal and its propagation into a liquid

Frequency Diminution Produced by a Liquid

$$\Delta f = -\sqrt{\frac{f_0^3 \cdot \eta_L \cdot \rho_L}{\pi \cdot \mu_q \cdot \rho_q}}$$

Formula Key:

- Δf: Frequency Change
- f_0: Resonance Frequency
- η_L, ρ_L: Liquid Viscosity and Density
- μ_q, ρ_q: Quartz Shear Modulus and Density

Take-away The crystal in liquid is not 'dead' — it just rings against a viscous boundary layer. That boundary layer is what produces the Kanazawa shift, which we quantify in the next slide.

KG1985 Fig. 2 (p. 102) · BW1992 Fig. 8 (p. 1363) · Bruckenstein & Shay 1985

The Kanazawa-Gordon equation

A single equation captures the immersion baseline — and exposes Δf as a viscosity probe.

K A N A Z A W A – G O R D O N (1 9 8 5)

$$\Delta f = -\sqrt{\left(f_0^{3} \cdot \eta_L \cdot \rho_L / (\pi \cdot \mu_q \cdot \rho_q) \right)}$$

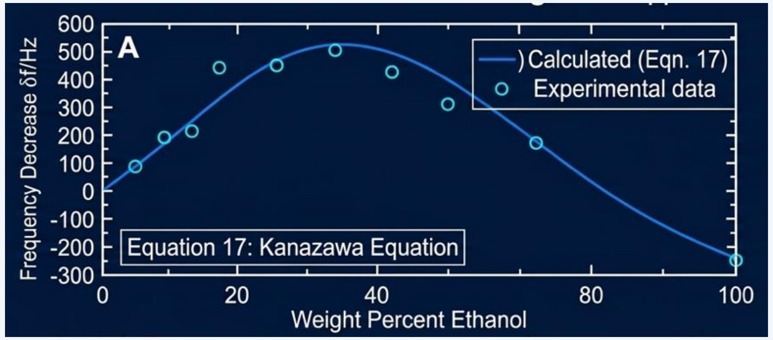
Derivation outline

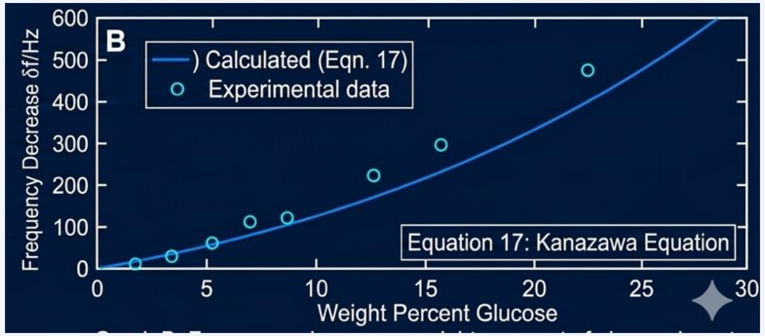
1. Couple a standing shear wave in quartz to a semi-infinite Newtonian fluid.
2. The fluid velocity decays as $\exp(-y/\delta_L)$ with $\delta_L = \sqrt{\eta_L / (\pi \rho_L f_0)}$.
3. Effective mass of the viscous boundary layer = $\rho_L \cdot \delta_L / 2$.
4. Substitute into the Sauerbrey form → $\Delta f \propto \sqrt{\eta_L \rho_L}$.

Worked numerical example — water at 25 °C

$\eta_L = 0.89$ cP, $\rho_L = 1.00$ g cm^{-3}; $\mu_q = 2.947 \times 10^{11}$ dyn cm^{-2}, $\rho_q = 2.648$ g cm^{-3}.
→ $\Delta f_K \approx -710$ Hz at $f_0 = 5$ MHz; ≈ -1400 Hz at $f_0 = 10$ MHz.

Kanazawa's original data — Δf vs % ethanol & % glucose





Ethanol shows non-monotonic Δf because the product η·ρ peaks near 40 wt% — a striking pedagogical case.

Take-away Δf in liquid scales with $\sqrt{\eta_L \rho_L}$. The same quartz can therefore be used as a viscosity sensor — and the immersion baseline must be subtracted before reading any surface mass.

Mass changes are still measurable in liquid

Kanazawa = baseline. Sauerbrey = perturbation on top of it. That is why EQCM works in electrochemistry.

Two contributions superimpose

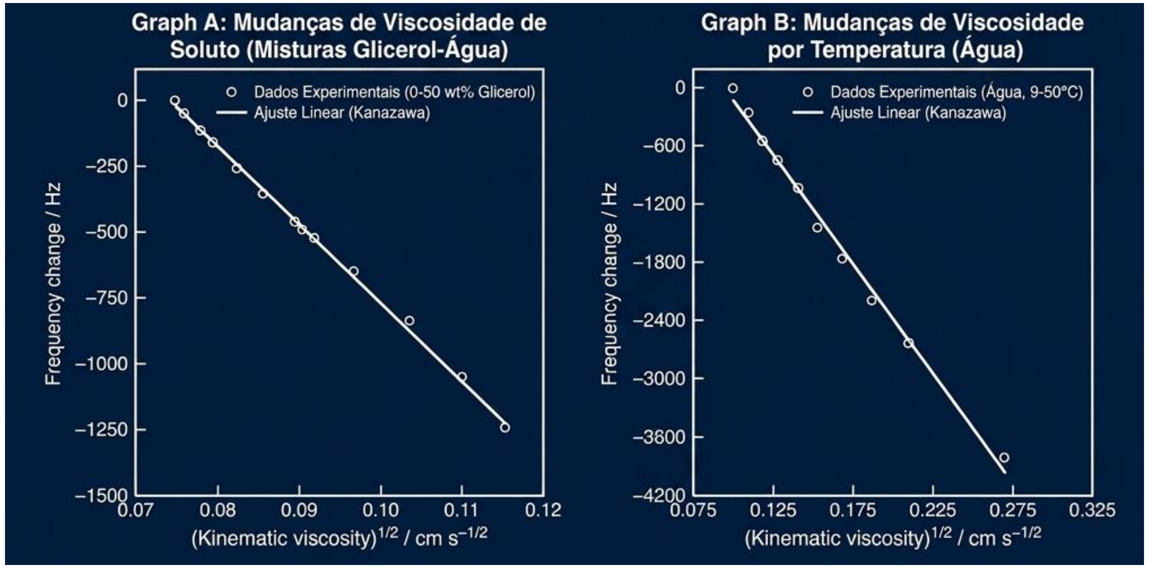
$$\Delta f_{\text{total}} = \Delta f_{\text{Sauerbrey}} + \Delta f_{\text{Kanazawa}}$$

- **Δf_Kanazawa** is a constant baseline as long as η_L and ρ_L don't change.
- **Δf_Sauerbrey** carries the electrochemistry — surface mass changes still obey $\Delta f_S = -C_f \cdot (\Delta m/A)$.
- **Validity:** the deposit must be rigid, thin (< 2 % m_q), and uniform — i.e. the same Sauerbrey hypotheses as in air.

Practical recipe in an electrochemical experiment

1. Immerse in the electrolyte at open circuit → record steady Δf_Kanazawa.
2. Re-zero the frequency reading; this becomes the new electrochemical baseline.
3. Start the potential program. All subsequent Δf is read as Sauerbrey mass — provided η_L, ρ_L, T are constant.

Δf is linear in √(kinematic viscosity)



Take-away Treat the immersion baseline as a one-time zero. Once it's subtracted, every Δf you record during the experiment converts to surface mass via Sauerbrey — same equation, same calibration.

What else can shift the frequency?

Beyond mass and Kanazawa, five more perturbations modulate Δf. Each will be addressed in turn.

1 Liquid viscosity / density

Kanazawa baseline. $\Delta f \propto \sqrt{\eta_L \cdot \rho_L}$. Already covered.

2 Viscoelastic film properties

Soft polymer films store and dissipate energy. Δf alone is ambiguous → need ΔD (covered in slide 27).

3 Mechanical stress in rigid films

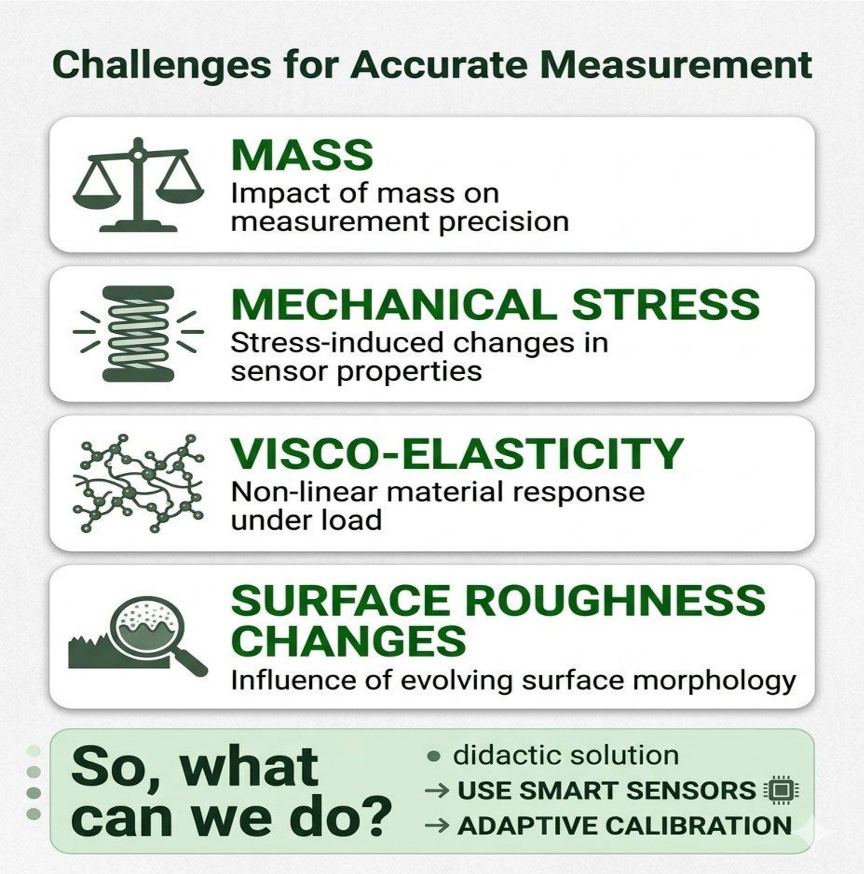
Pd-H, electrochromic oxides, electroformed metals: lattice strain alters the resonant frequency directly.

4 Surface roughness (trapped fluid)

Pores, fissures and dendritic deposits trap liquid that moves rigidly with the surface → apparent extra mass.

5 Interfacial slip

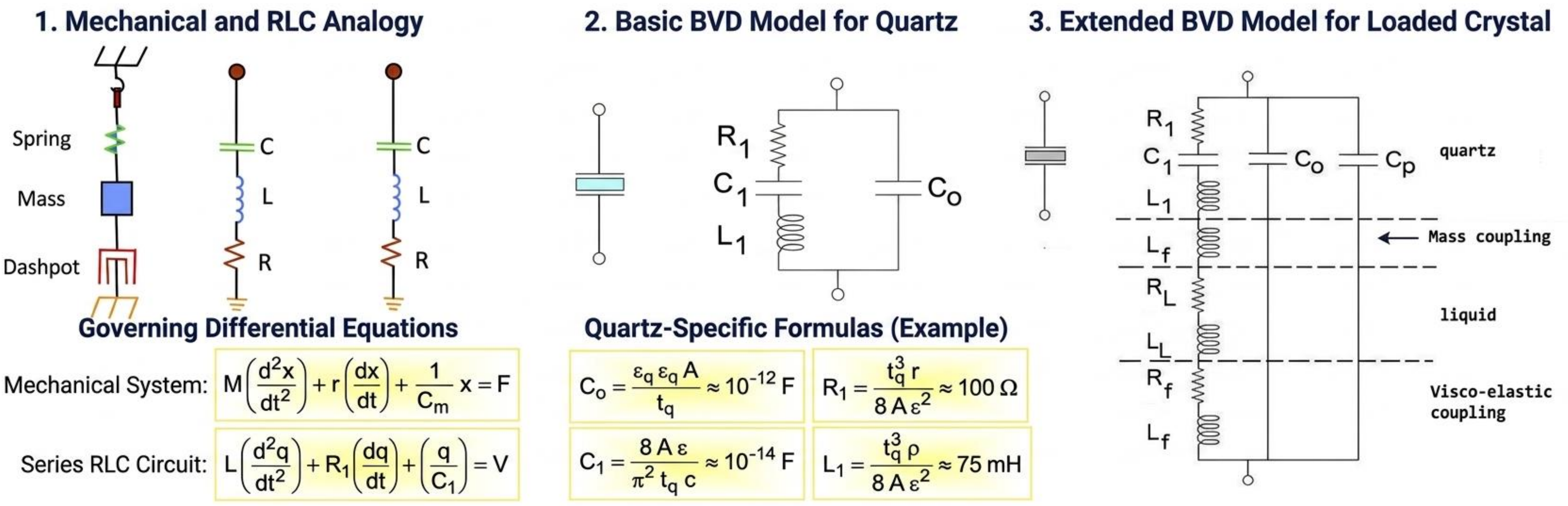
Hydrophobic / non-wetted surfaces can decouple from the quartz oscillation: $|\Delta f|$ smaller than Sauerbrey predicts.



Take-away Δf alone cannot distinguish between mass, viscosity, stress, roughness or slip. Modern practice combines ΔD, overtone-dependence checks, and an equivalent-circuit fit (next slides).

Equivalent circuit — Butterworth–Van Dyke (BVD) and its analogies

Replace the loaded resonator by a circuit. Each component has a physical meaning — and the loaded crystal just adds elements.



Take-away BVD turns the quartz into a familiar RLC network. Mass appears as inductance, loss as resistance, elasticity as capacitance. Fitting an admittance spectrum recovers all four electrical components — and via them, the physics.

Admittance spectra — G(f) and B(f) around resonance

Bandwidth ($f_2 - f_1$) tells you dissipation; peak G_max tells you loss; both decrease as the crystal is loaded.

Key frequencies on the spectrum

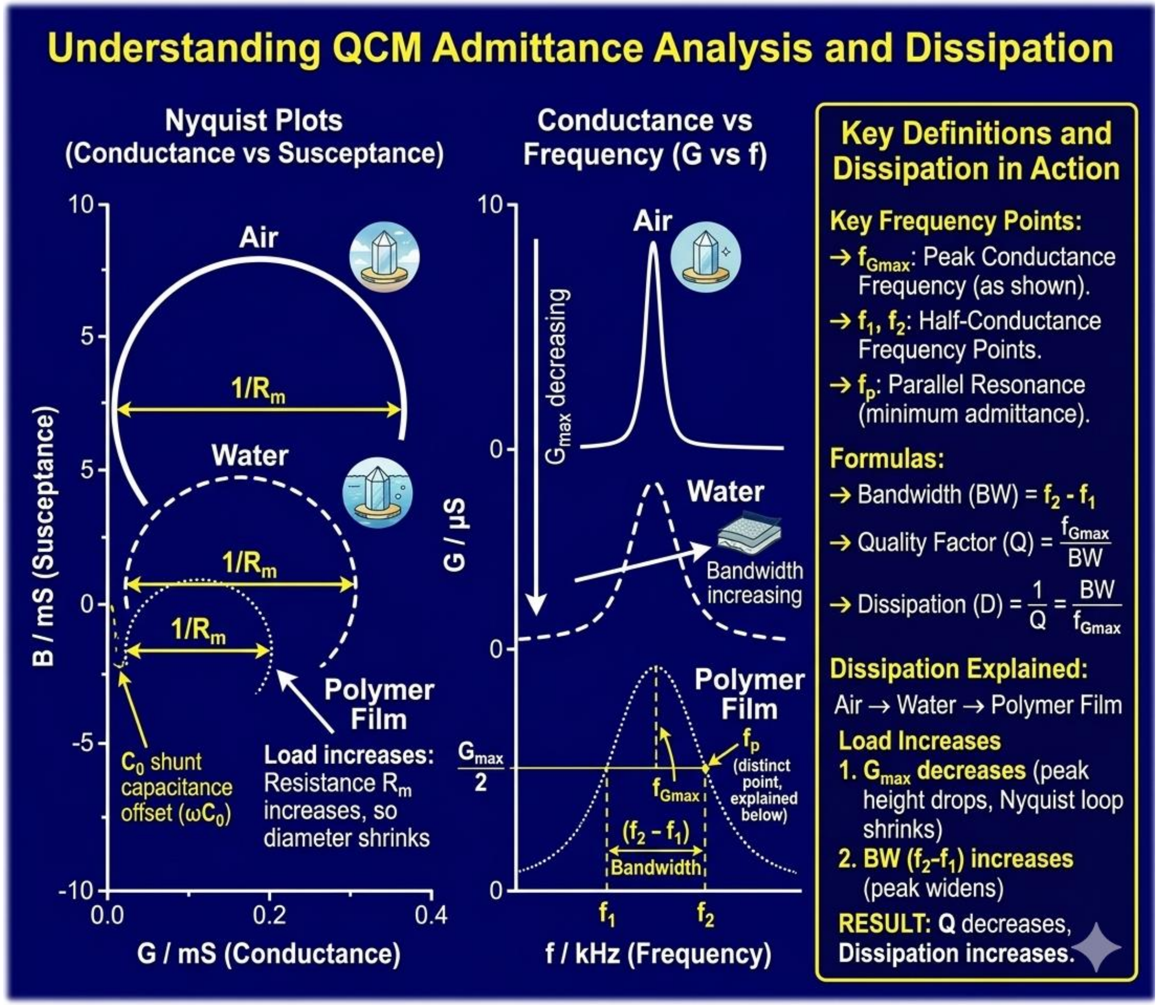
- **f_{Gmax}** peak conductance — close to series resonance f_s.
- **f_1, f_2** half-conductance points; $BW = f_2 - f_1$.
- **f_p** parallel resonance — minimum admittance.

Formulas at a glance

Bandwidth: $BW = f_2 - f_1$

Quality factor: $Q = f_{Gmax} / BW$

Dissipation: $D = 1 / Q = BW / f_{Gmax}$



Air → water → polymer film

As the load increases, G_max drops (Nyquist loop shrinks) and BW grows (peak widens). Q decreases ⇒ dissipation rises.

Take-away G(f) and B(f) give you mass AND loss in one measurement. Δf tracks the peak position; ΔBW tracks dissipation. EQCM-D (D-monitoring) is built on exactly this.

QN2000 Figs. 15, 17 (p. 675) · BW1992 Fig. 7 (p. 1362)

Viscoelasticity — when films are not rigid

Polymer and hydrogel films store and dissipate energy. Δf alone is not enough — ΔD recovers the missing physics.

Complex shear modulus G*

$$G^* = G' + j\,G''$$

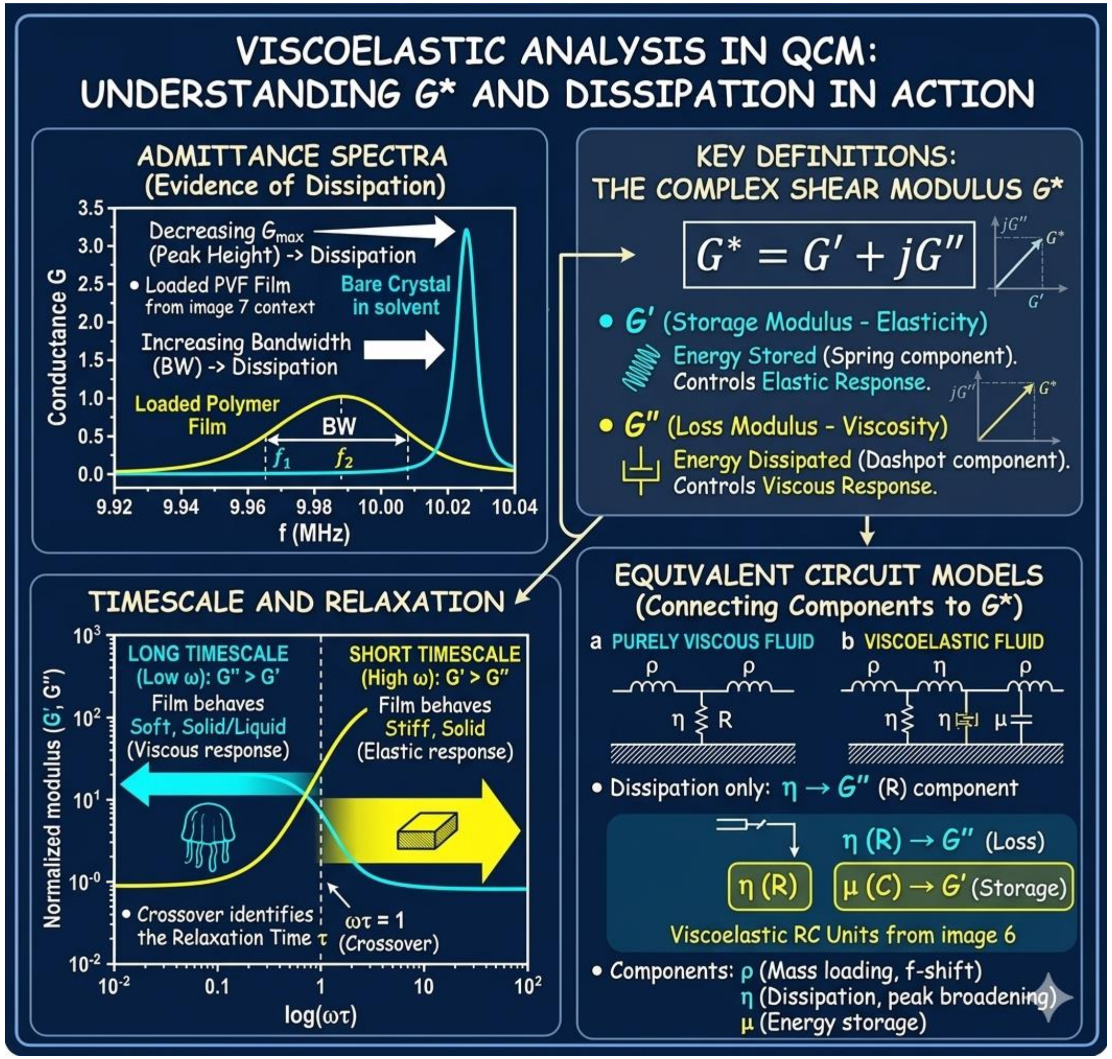
G′ storage modulus → elastic (spring) response; **G″** loss modulus → viscous (dashpot) response.

Timescale and relaxation

- **Long timescale** $\omega\tau \ll 1$ → G″ > G′, film flows like a viscous liquid.
- **Short timescale** $\omega\tau \gg 1$ → G′ > G″, film behaves as an elastic solid.
- **Crossover** $\omega\tau = 1$ identifies the polymer's relaxation time τ.

Practical consequence — measure ΔD too (EQCM-D)

For a rigid film ΔD ≈ 0; for a soft film ΔD ≠ 0 and grows with thickness. Reporting both Δf and ΔD removes the Δm ambiguity.



Take-away Closing thought for Module 1 — Δf, ΔD and admittance spectra together turn the QCM from a 'mass balance' into a true mechanical-impedance probe. Module 2 (instrumentation) will show how to record them in practice.

BW1992 Fig. 9 (p. 1364) · ARH2011 Fig. 5 · Easley et al. J. Polym. Sci. 2022

Group exercise — Cu deposition calculation

Work in groups of 3-4. ~10 minutes. Compute, sanity-check, decide whether Sauerbrey is valid.

Given — experimental dataset

Crystal	5 MHz AT-cut, active area $A = 0.20\ cm^2$
Sensitivity factor	$C\_f = 56.6\ Hz \cdot \mu g^{-1} \cdot cm^2$
Electrolyte	$0.10\ mol\ L^{-1}\ CuSO_4$ in $0.50\ mol\ L^{-1}\ H_2SO_4$
Cathodic current	$i = 100\ \mu A$ (constant)
Pulse duration	$\Delta t = 300\ s$
Measured Δf	$\Delta f = -\ 1860\ Hz$

Your tasks

i. **Sauerbrey mass.** Compute $\Delta m_S = -\Delta f \cdot A / C_f$.

ii. **Faraday mass.** Compute $\Delta m_F = i \cdot \Delta t \cdot M\_Cu / (z \cdot F)$ with $M\_Cu = 63.55\ g\ mol^{-1}$, $z = 2$.

iii. **Current efficiency.** $\eta = \Delta m_S / \Delta m_F$. Is it consistent with literature for $Cu^{2+} \rightarrow Cu$ in H_2SO_4?

iv. **Validity check.** Is Sauerbrey applicable here? Justify using thin-layer, rigid-film, and uniform-deposit criteria.

SOLUTION (reveal after group work)

i. Sauerbrey mass

$$\Delta m_S = -\Delta f \cdot A / C\_f = (1860 \cdot 0.20) / 56.6$$

$$\Delta m_S \approx 6.57\ \mu g$$

ii. Faraday mass

$$\Delta m_F = i \cdot \Delta t \cdot M\_Cu / (z \cdot F) = (100\times10^{-6} \cdot 300 \cdot 63.55) / (2 \cdot 96485)$$

$$\Delta m_F \approx 9.88\ \mu g$$

iii. Current efficiency

$$\eta = \Delta m_S / \Delta m_F = 6.57 / 9.88$$

$$\eta \approx 66\ \%$$

iv. Validity $\Delta m/A \approx 33\ \mu g\ cm^{-2} < 2\ \%$ of m_q ($\approx 9\ mg\ cm^{-2}$) → thin-layer OK. Cu is metallic and rigid → no viscoelastic losses. Sauerbrey valid; the missing 34 % is parasitic H_2 evolution + dendritic loss.

Take-away Real measurements rarely give $\eta = 100\ \%$. Sauerbrey gives you the deposited mass; Faraday gives you the charge. Their ratio is the current efficiency — a direct, quantitative diagnostic of the electrode reaction.

Adapted from QN2000 Fig. 5 (p. 668) — Cu/Pt deposition examples

When does Sauerbrey fail? — open discussion

For each case below, decide: Sauerbrey OK, or use full impedance / ΔD? Identify the dominant complication.

a **Au oxide monolayer in H_2SO_4** — OK

Thin, rigid, uniform 2-D layer (~ a few atomic layers). $\Delta m <$ 100 ng cm^{-2}. Textbook Sauerbrey case — used as a standard cleanliness check.

b **Thick polypyrrole in aq. $LiClO_4$** — FAILS

Viscoelastic, solvated, swelling/shrinking with redox state. Δf and ΔD are both significant. Needs full impedance analysis and a viscoelastic film model.

c **Pd film during H absorption** — FAILS

H insertion induces large lattice strain → mechanical stress contribution to Δf. Apparent mass is wrong by orders of magnitude. Cheek & O'Grady 1990.

d **Hydrogel-modified electrode** — FAILS

Hugely viscoelastic and water-rich. Sauerbrey under-estimates the wet mass. EQCM-D required to separate mass from coupled solvent and chain dynamics.

e **Localised pitting corrosion of Ni** — FAILS

Non-uniform mass loss concentrated at pits. Local k(r) weighting dominates → Δf is geometry-biased and cannot be converted to a true mass per area.

Take-away Three failure modes recur: viscoelasticity (b, d), mechanical stress (c), and non-uniform mass distribution (e). When in doubt — measure ΔD and check overtone-dependence before quoting any mass.

Module 1 — takeaway

Three points to remember. And a glimpse of what Module 2 brings to the bench.

1 What EQCM is

Piezoelectric resonator + electrochemistry.

Mass resolution down to ~1 ng cm^{-2} in real time, in liquid, while controlling potential — the only technique that does all three at once.

2 Sauerbrey — and its limits

$\Delta f = -C_f \cdot (\Delta m / A)$

valid when the deposit is thin (< 2 % m_q), rigid, and uniform. Calibrate experimentally with Ag or Cu — don't rely on the theoretical 56.6 $Hz \cdot cm^2 \cdot \mu g^{-1}$.

3 Beyond Sauerbrey

In liquid → add the Kanazawa baseline.

Soft / wet films → measure ΔD too; fit admittance spectra with an extended BVD circuit. Δf alone hides viscoelasticity and stress.

NEXT
MODULE 2

Instrumentation and practice

- Real EQCM cells, holders, gaskets, electrical contacts
- Oscillators, frequency counters, admittance analysers
- Surface preparation and cleaning protocols
- EQCM-D and viscoelastic data reduction
- Live demo — a galvanostatic Cu deposition in our cell, from setup to mass calculation

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