Gravimetric sensors
“Quartz Crystal Microbalance” (QCM)

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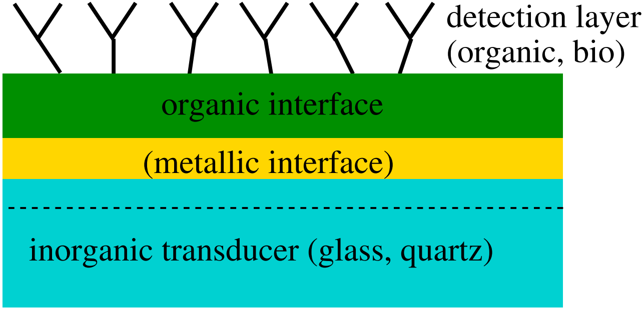
Direct detection (bio)sensors

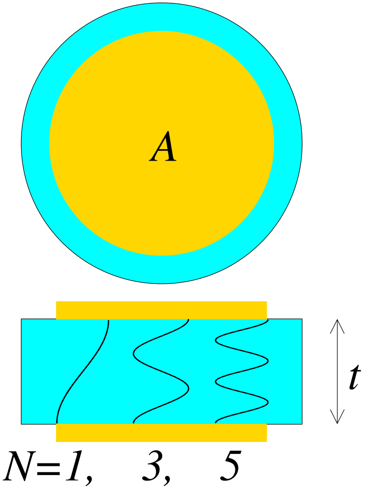
- No sample preparation: continuous monitoring + time resolution (kinetic)
- Surface immobilization of receptor molecules: multiple measurement steps are possible
- **Sensitivity** defined by mass to physical measurement conversion efficiency
- **Selectivity** defined by affinity of the surface functionalization to the targeted compound, rejecting unwanted interference (antibody)
- Improved signal to noise ratio by using evanescent wave (rejects bulk noise and keep only close-to-surface signal)
- **Detection limit** determined by system noise level (detection limit=noise/sensitivity) = complete system (electronics, fluidics ...)



Quartz crystal resonator basics

Examples of direction detection sensors:
Surface Plasmon Resonance, (optical) waveguide sensors, vibrating cantilever, electrochemical enzyme sensors

- **Quartz crystal resonator**: piezoelectric substrate confining an acoustic wave
- Boundary conditions: half-wavelength confined between parallel (plano-plano) or curved (plano-convex) sides of a quartz plate
- **Odd** overtones are confined in the same boundary conditions
- Resonance frequency determined by plate thickness and shear wave velocity: 3340 m/s in AT-cut quartz (temperature compensated)
- Application: $f = 5$ MHz requires $t = \lambda/2 = c/(2f) = 334\ \mu$m



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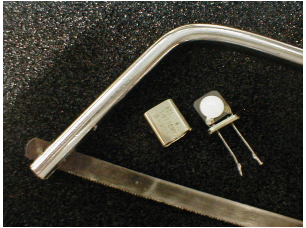
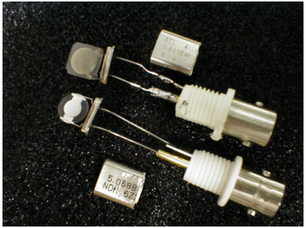
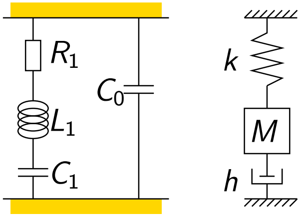




Butterworth-Van Dyke electromechanical model

- Butterworth-VanDyke model [1] [2] [3] : RLC series branch represents damped spring-mass ("motional branch")
- Electrodes separated by a dielectric define a parallel capacitance

Mechanical	Electrical
$M\ddot{x} + h\dot{x} + kx = F$	$L_1\ddot{q} + R_1\dot{q} + q/C_1 = U$
h (damping)	R_1 (resistance)
M (mass)	L_1 (inductance)
k (stiffness)	$1/C_1$ (capacitance)
x (displacement)	q (electrical charge)
$\dot{x}$ (velocity)	$i = dq/dt$ (current)
$Q = \frac{1}{h}\sqrt{kM}$	$Q = \frac{1}{R}\sqrt{\frac{L}{C}}$
$\omega_0 = \sqrt{\frac{k}{M}}$	$\omega_0 = \frac{1}{\sqrt{L_1 C_1}}$



[1] S. Butterworth, *On electrically-maintained vibrations*, Proc. Phys. Soc. (London), **27** 410–424 (1914)
[2] K.S. Van Dyke *The electric network equivalent of a piezoelectric resonator*, Phys. Rev **25** (6) 895 (1925)
[3] D.W. Dye, *The piezo-electric quartz resonator and its equivalent electrical circuit*, Proc. Phys. Soc. (London) **38** (1) 399 (1925)

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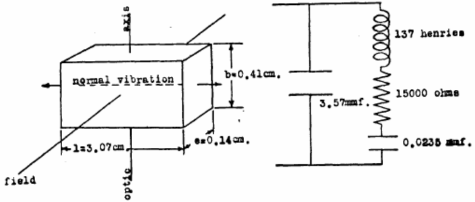

Fig. 4—Resonator N_2 and Its Equivalent Network for Normal Fundamental Mode

[1] S. Butterworth, *On electrically-maintained vibrations*, Proc. Phys. Soc. (London), **27** 410–424 (1914)
[2] K.S. Van Dyke *The electric network equivalent of a piezoelectric resonator*, Phys. Rev **25** (6) 895 (1925)
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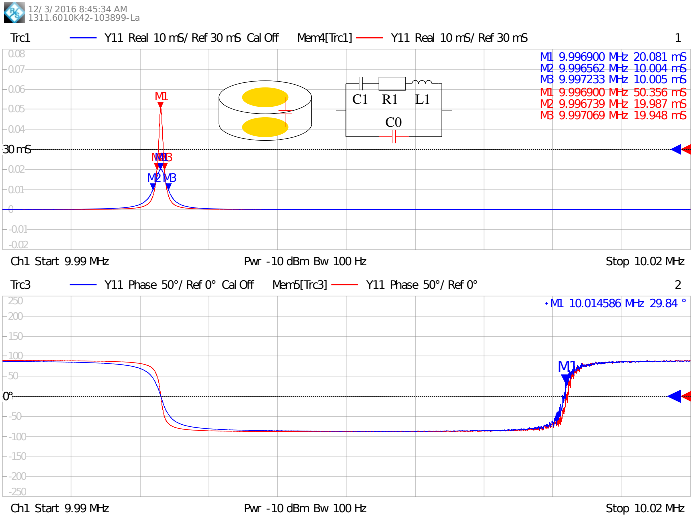
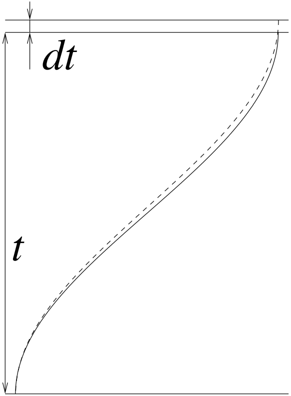


Antiresonance: new concept introduced by the parallel capacitance

QCM sensitivity [4]

- QCM is claimed to detect "mass" bound to the sensor surface
- Definition of the sensitivity: $S = \frac{df}{f_0} \cdot \frac{A}{dm}$
- Allows for comparing a wide range of acoustic transducers, from kHz to GHz and nanometric to macroscopic
- Sauerbrey (1959) : $\frac{dt}{t} = \frac{df}{f} = \frac{d\lambda}{\lambda} \Rightarrow S = \frac{df}{f} \cdot \frac{A}{A\rho dt} = \frac{df}{f} \frac{f}{\rho df \cdot t} = \frac{1}{\rho \cdot t}$



t: QCM thickness, $\rho = 2.643$ g.cm^{-3}: quartz density, $dm = A \cdot \rho \cdot dt$: adsorbed mass over area A

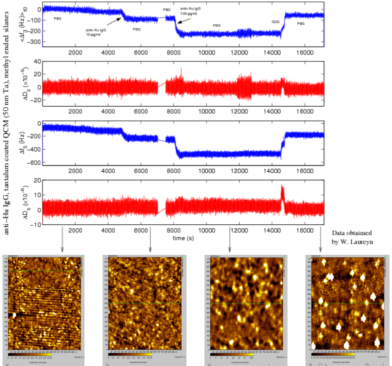
Assumption: perturbation ($dt \ll t$) of a layer with same properties than quartz ($\rho_L = \rho$)

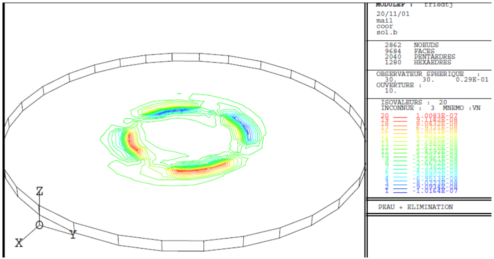
Numerical application: 5 MHz QCM exhibits $S = 11$ cm^2/g

[4] G. Sauerbrey, *Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung*, Zeitschrift für Physik A Hadrons and Nuclei, **155** (2), 206–222 (1959)

Detection limit

- the smallest quantity that can be detected using the sensor
- e.g. 3σ with σ the measurement fluctuation (noise)
- includes all sources of noise: electronics, fluidics, digitization
- detection limit=noise/sensitivity
- long term drift=low noise correlated noise: baseline stabilization prior to running a measurement (double layer stabilization, temperature stabilization)
- Typical resolution: 1 Hz at 5 MHz=0.2 ppm $\Rightarrow \frac{dm}{A} = 18$ ng/cm^2
- Protein film: $\rho_{protein} = 1.4$ g/cm^3 and 5 nm thick $\Rightarrow$ 700 ng/cm^2
- $\Rightarrow$2.5% surface coverage by proteins can be detected with QCM





- J.-M Friedt, K. H. Choi, L. Francis and A. Campitelli, *Simultaneous Atomic Force Microscope and Quartz Crystal Microbalance measurements: interactions and displacement field of a QCM*, Japanese J. Appl. Phys., **41** (6A), 2002, 3974-3977

Displacement and acceleration

- $\vec{F} = m \cdot \vec{a}$
- static displacement: $A_0 = C \times V = 2$ pm/V since $C = 1.4 \cdot 10^{-12}$ m/V
- dynamic displacement[5] if $Q = 1000$: $A = A_0 \times Q = 2$ nm/V
- $x = A\sin(\omega t) \Rightarrow v = A \cdot \omega(\omega t) \Rightarrow |\vec{a}| \leq A \cdot \omega^2$
- $f = 5$ MHz: $|a| = 2 \cdot 10^{-9} \times (2\pi \times 5 \cdot 10^6) = 2 \cdot 10^6$ m/s^2

Excellent gravimetric sensitivity linked to the huge acceleration on the sensor surface

[5] J.-M Friedt, K. H. Choi, L. Francis, A. Campitelli, *Simultaneous Atomic Force Microscope and Quartz Crystal Microbalance measurements: interactions and displacement field of a QCM*, Jap. J. of Appl. Phys. **41** (6A) pp.3974-3977 (2002)

Dissipation measurement (QCM-D)

- Frequency related to "mass" (acoustic wave confinement boundary condition variation)
- Dissipation $= Q^{-1}$ related to viscous losses
- Viscous losses related to the conformation of the molecules
- B. Kasemo in Göteborg: creation of Q-Sense [6] (using aliasing !)

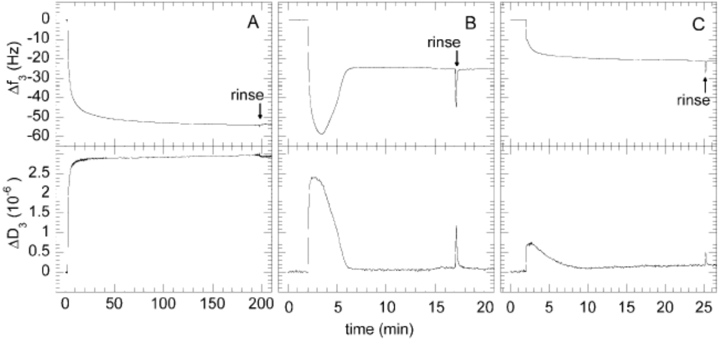


FIGURE 1 QCM-D responses for the deposition of different lipid mixtures on SiO_2 in the presence of 2 mM EDTA. Changes in frequency and dissipation at 15 MHz (*upper* and *lower panels*, respectively). (*A*) DOPC/DOPS (molar ratio increase 1:1), example of formation of an SVL. (*B*) DOPC/DOPS (4:1), example of SLB formation (case 1) triggered at an elevated critical vesicular coverage. (*C*) DOTAP, example of SLB formation (case 2) triggered at low vesicular coverage. Lipid exposure starts at 2 min; rinses with EDTA-containing buffer (*arrows*).

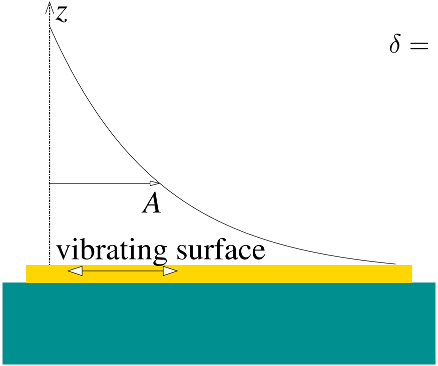
Biophysical Journal 85(5) 3035–3047

R. Richter & al, *Pathways of Lipid Vesicle Deposition on Solid Surfaces: A Combined QCM-D and AFM Study*, Bio. J. **85** 3035–3047 (2003)

[6] M. Rodahl, F. Höök, A. Krozer, P. Brzezinski, B. Kasemo, *Quartz crystal microbalance setup for frequency and Q-factor measurements in gaseous and liquid environments*, Rev. Sci. Instrum. **66** (7) 3924–3930 (1995)

Shear wave penetration depth

- Newtonian fluid: constant stress-strain relation defines the viscosity
- Fluids characterized by dynamic (shear) viscosity η: dragged by the shear wave
- Exponentially decaying displacement [7] with depth ($\neq$ propagative pressure wave)
- $A(z) = A(0)\exp(-z/\delta)$ with $\delta = \sqrt{\frac{\eta}{\rho\omega}}$
- Considering the dynamic viscosity of water $\eta = 1$ cP, and $\rho = 1$ g.cm^{-3}, then

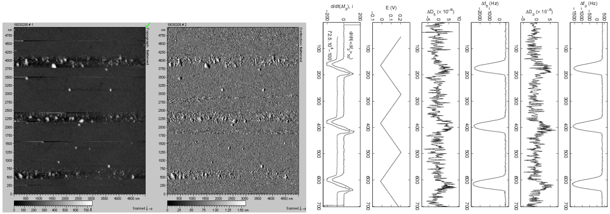


$$\delta = \sqrt{\frac{10^{-2}}{2\pi \times 5 \cdot 10^{6}}} \text{ cm} = 180 \text{ nm}$$

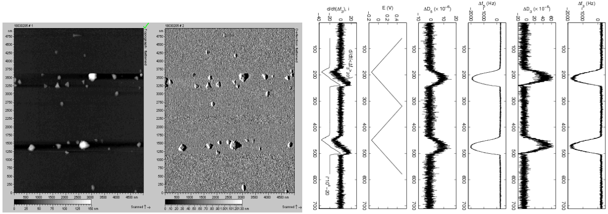
[7] K.K Kanazawa & J.G. Gordon, *The oscillation frequency of a quartz resonator in contact with liquid*, Analytica Chimica Acta **175** 99–105 (1985)

Measurement examples: electrochemical deposition

- Reversible thin film deposition controlled electrically
- Examples: $Cu \leftrightarrow Cu^{2+} + 2e^{-}$ or $Ag \leftrightarrow Ag^{+} + e^{-}$



Ag

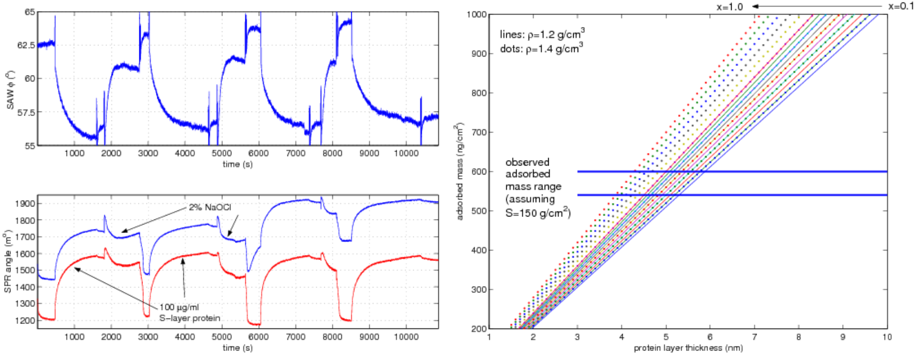


Cu

Rigid layer $\Rightarrow \Delta f_n / n \propto \Delta m_{layer}$ (low damping)
Viscous layer $\Rightarrow \Delta f_n / \sqrt{n} \propto \{\Delta m_{liquid}, \Delta m_{layer}\}$ (high damping)

Measurement examples: globular proteins

- surface chemistry: hydrophobic thiol on gold
- S-layer protein forms a crystal on a hydrophobic surface (reversible)
- little/no variation of the quality factory (damping)
- simultaneous optical measurement: thickness and density of the layer

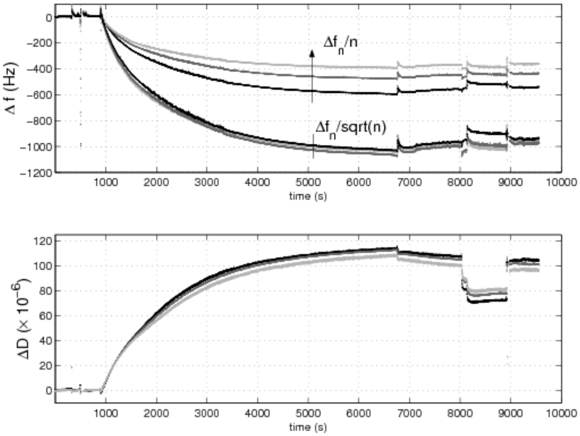


Globular proteins ∼ thin **rigid** film: valid approximations for both acoustic (mass effect) and optics ⇒ conditions applied during BIAcore's radiolabelling calibration [8]

[8] J.-M Friedt, L. Francis, G. Reekmans, R. De Palma, A. Campitelli and U.B. Sleytr, *Simultaneous surface acoustic wave and surface plasmon resonance measurements: electrodeposition and biological interactions monitoring*, J. of Appl. Phys., **95** (4), 2004, 1677-1680

Measurement examples: fibrillar proteins

- Globular proteins (S-layer, IgG, IgE, BSA ...) are short and spread on the surface (5-10 nm) as a rigid layer
- Fibrillar proteins (collagen, fibrinogen) extend deep in the buffer solution, equivalent to a thick layer full of solvent $\Rightarrow$ strong contribution of **viscosity**

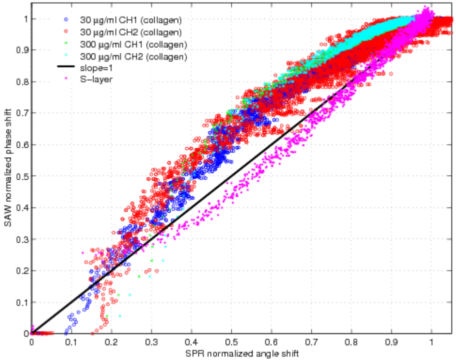


- rigid interaction: $\Delta f_N \propto N$
- viscous interaction: $\Delta f_N \propto \sqrt{N}$
- Large damping variation and $\Delta f_N / N$ scaling as $\sqrt{N}$ as opposed to constant: signatures of viscous interactions

30 μg/ml collagen

Measurement conclusions

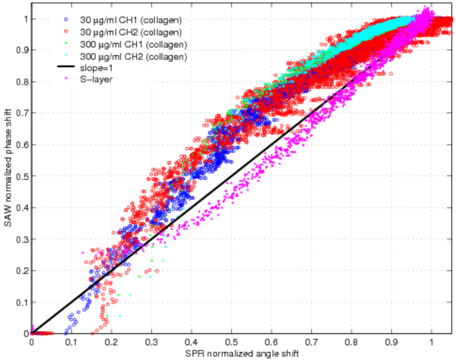
⇒ optics **underestimates** the adsorbed mass (lower optical index than expected)



Analyte (bulk concentration, μg/ml)	surface density (ng/cm^2)	d (nm) SAW/SPR	x (%) SAW/SPR	$\Delta f_n/\sqrt{n}$ (Hz) QCM	$\Delta f_n/n$ (Hz) QCM	ΔD ($\times 10^{-6}$) QCM
Cu		2 − 12	?	?-1000	NO	50
S-layer	560±20	4.7 ± 0.7	75 ± 15	NO	45=900	3-5
CTAB	135±15	1.0 ± 0.1	100	NO	8=160	0.2-0.5
collagen (30μg/ml)	1750±150	16.0 ± 3.0	25 ± 15	1000	NO	100
collagen (300μg/ml)	2100±200	19.0 ± 3.0	35 ± 10	1200	NO	>120
fibrinogen (46μg/ml)	750±100	6.0 ± 1.5	50 ± 10	110±5	55±5≃ 1110	4-10
fibrinogen (460μg/ml)	1500±500	13.0 ± 2.0	50 ± 10	NO	100=1700	8-10

Measurement conclusions

⇒ acoustics **overestimates** the adsorbed mass (bound solvent to the organic layer)



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Sensitivity mapping & packaging

Scanning Electrochemical Microscope mapping of a QCM gravimetric sensitivity [9]

2546 • ANALYTICAL CHEMISTRY, VOL. 64, NO. 21, NOVEMBER 1, 1992

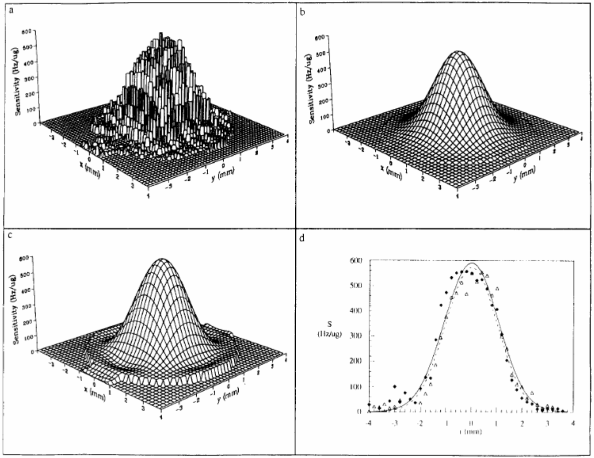


Figure 7. Determination of the sensitivity distribution $S(r,\theta)$ for the 5-MHz AT-cut plano-convex quartz crystal microbalance in 20 mM $CuSO_4$ solution: (a) raw data, (b) Gaussian curve-fit, (c) smoothed data (R_{corr} = 0.975), and (d) line plot (Δ, - - -) parallel (x = 0) and (♦, —) perpendicular (y = 0) to upper electrode tabs with the Gaussian curve-fit ($R_{corr,x=0}$ = 0.969, $R_{corr,y=0}$ = 0.974).

- strongest sensitivity at center of electrode
- sensitivity vanishes on the surrounding of the resonator
- the higher the overtone, the better the energy confinement over the electrode
- O-ring around the sensor will **not** impact the acoustic wave

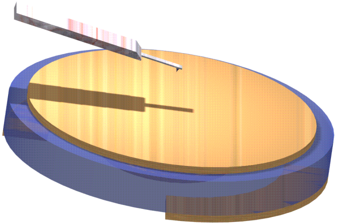
[9] A.C. Hillier & M.D Ward, *Scanning electrochemical mass sensitivity mapping of the quartz crystal microbalance in liquid media*, Anal. Chem. **64** (21) 2539–2554 (1992)

Beyond the bulk acoustic resonator: FBAR

- $S = \frac{df}{f} \cdot \frac{A}{dm} = \frac{1}{\rho \cdot t} \Rightarrow \frac{df}{f} = \frac{dm}{\rho \cdot A \cdot t} = \frac{dm}{m}$ with m the mass of the resonator
- increasing S requires shrinking m and hence t
- thin Film Bulk Acoustic Resonator: replace bulk acoustic resonator with piezoelectric film on a membrane
- **but** rising S associated with rising f_0 ...
- ... and oscillator noise rises with f_0, degrading the detection limit
- $\Rightarrow$ is the detection limit improved on a FBAR architecture ?

Challenge of generating shear wave on a thin piezoelectric film deposited using a vapor method (C-axis normal to the growth plane)

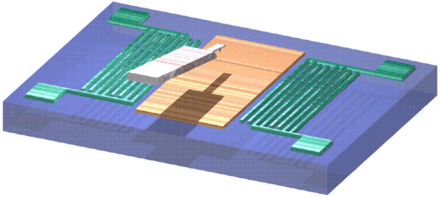
Beyond the bulk acoustic resonator: SAW



- Another strategy for reducing the mass of the vibrating element: confine the acoustic wave to the surface
- **SAW**: Surface Acoustic Wave devices
- Rayleigh wave boundary conditions only met at the free surface ...
- ... but Rayleigh waves exhibit out-of-plane component radiating as pressure waves in fluids.
- Shear wave can be confined on a surface if a **slow** guiding layer is deposited on the surface (cf optical fiber)
- Love-mode SAW devices exhibit high sensitivity and compatibility with liquid media
- Love mode SAW sensors extensively used as bio-sensors.

Example: N-isopropyl acrylamide (N-IPAAM) is a polymer whose conformation (hydrophilic v.s hydrophobic) changes with temperature

Beyond the bulk acoustic resonator: SAW



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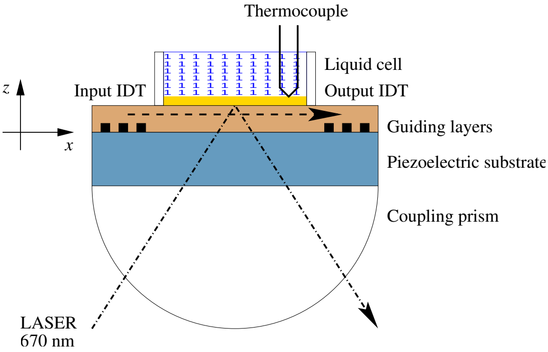
Measurement example

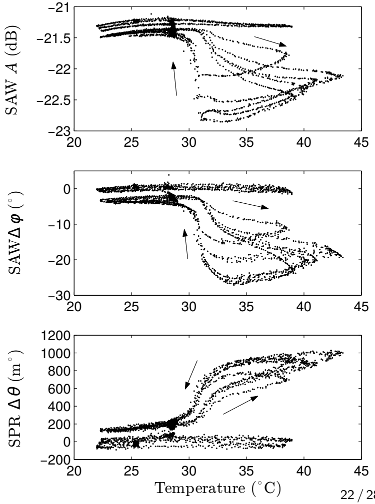
- From SAW: phase and **magnitude** measurements
- From SPR: optical thickness

→ exploit the viscous dissipation of the propagating acoustic wave

NIPAAM (N-isopropyl acrylamide)



Notice this is *very* difficult to reproduce with QCM (bottom side of sensor in contact with prism)



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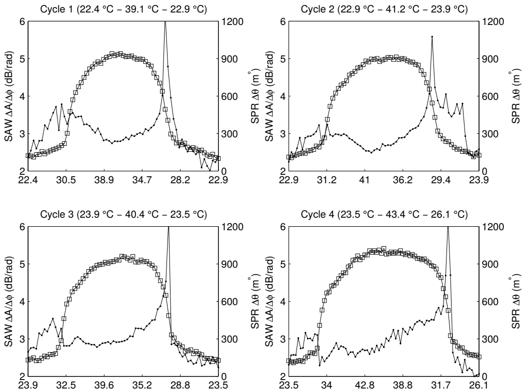
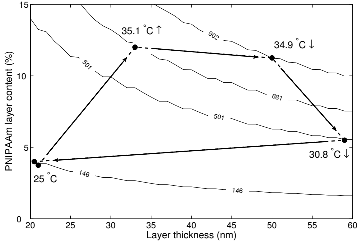
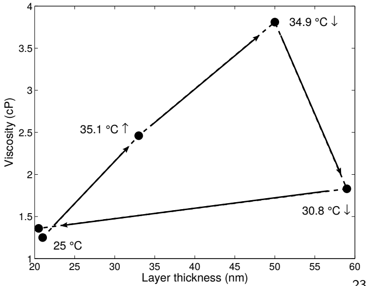


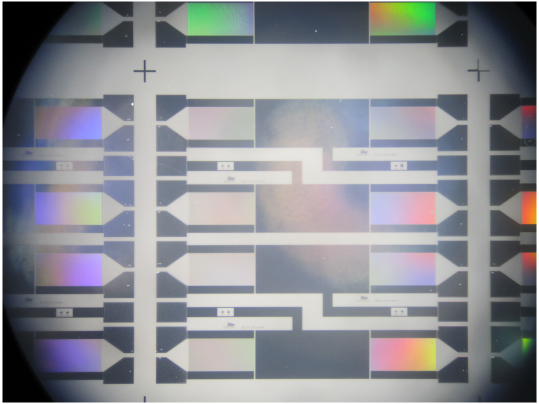
L. Francis, J.-M. Friedt, C. Zhou, P. Bertrand *In situ evaluation of density, viscosity and thickness of adsorbed soft layers by combined surface acoustic wave and surface plasmon resonance*, Anal. Chem. 2006; **78** (12) (2006), pp. 4200-4209

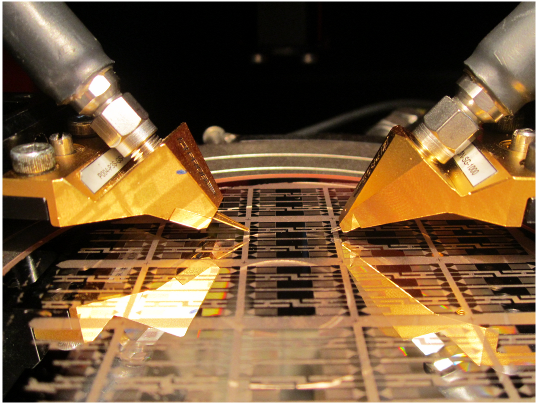




Device characterization

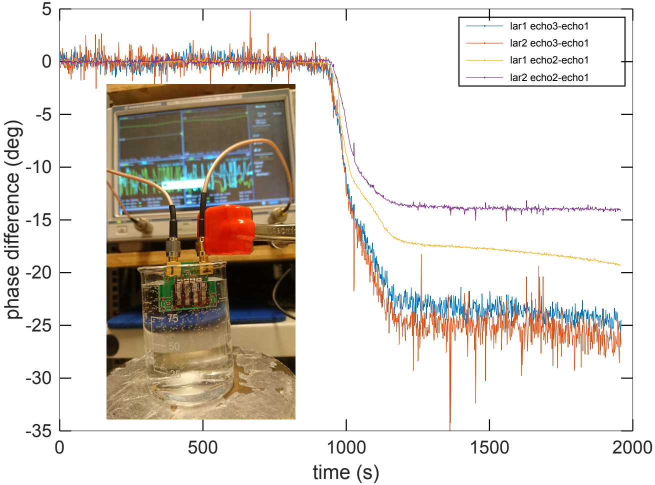
- Typical frequency: 150 MHz
- Acoustic wave velocity: shear wave on quartz 5060 m/s
- $\lambda = c/f = 33\ \mu$m
- two-electrodes separated by a 50% gap: 8 μm-wide electodes
- fluidic confinement challenge: water over the electrodes induces a capacitive short circuit $\Rightarrow$ wall with wavelength width over the acoustic path to confine the liquid





Ongoing project

Lithium tantalate substrate: high permittivity ($\varepsilon_r \simeq 40$) substrate propagating a shear wave $\Rightarrow$ no need for fluidic confinement !



Non-specific binding of proteins from powder milk ($\simeq 500\ \mu$g/ml)

Conclusion

- The quartz crystal resonator: much more than a "microbalance"
- direct detection system for probing thin film properties, including mass (density$\times$ thickness) and viscosity
- Readily accessible substrates (cf. electronics quartz resonators) for experimenting
- Opportunity to use radiofrequency electronics design skills
- Ability to measure sub-100 ng.cm^{-2} masses: even used on satellites to assess outgassing [10] [11] ! Applicability to practical point of care biosensors? [12]

TODO

- Experiment by yourself[13]: `jmfriedt.free.fr/QCM_BUP.pdf`
- Tuning fork for gas sensing: QEPAS (Quartz Enhanced Photo-Acoustic Spectroscopy)

[10] R. Naumann, W. Moore, D. Nisen, W. Russell & P. Tashbar, *Quartz crystal microbalance contamination monitors on Skylab: A quick look analysis* (1973)

[11] B.E. Wood *& al.*, *Review of Midcourse Space Experiment (MSX) satellite quartz crystal microbalance contamination results after 7 years in space*, Proc. 9th Intl Symp. on Materials in a Space Environment (2003)

[12] T. Leïchlé, L. Nicu & T. Alava, *MEMS Biosensors and COVID-19: Missed Opportunity*

[13] J.-M. Friedt, *Introduction à la microbalance à quartz : aspects théoriques et expérimentaux*, Bulletin de l'Union des Physiciens n.852 (March 2003), pp.429-440

RLC model

Consider a circuit with $L = 1.5$ mH, $C = 0.5$ pF and $R = 50\ \Omega$.

1. What is the theoretical resonance frequency of this circuit? [14]
2. What is the theoretical quality factor of this circuit? [14]
3. Plot the impedance (real and imaginary part) of this circuit in a range from 0.9 to 1.1 times the resonance frequency.
4. Plot the admittance (real and imaginary part) of this circuit in a range from 0.9 to 1.1 times the resonance frequency.
5. What is the physical meaning of the imaginary part of the admittance in the low frequency region?
6. What is the meaning of the magnitude of the impedance at resonance frequency?
7. What is the imaginary part of the impedance at resonance frequency?
8. Plot the magnitude of the scattering coefficient of this circuit. The admittance and scattering coefficient of a one-port device are related by

   $$S = \frac{1 - Z_0 \times Y}{1 + Z_0 \times Y}$$

   with $Z_0 = 50\ \Omega$ the reference impedance.
9. Plot the magnitude of the scattering coefficient of this circuit, replacing $R = 50\ \Omega$ with $R = 150\ \Omega$. Compare with the previous chart and interpret.

[14] J. Vig, *Quartz crystal resonators and oscillators – A tutorial*, 2000 at https://www.am1.us/wp-content/uploads/Documents/U11625_VIG-TUTORIAL.pdf

BvD model

1. A practical surface acoustic wave transducer is fabricated by patterning electrodes on a piezoelectric substrate. This structure creates a capacitance in parallel to the RLC circuit: the resulting circuit is called the Buttworth-Van Dyke model, with a static capacitance C_0 in parallel to RLC. Repeat the numerical simulations (3, 4) of the previous slide with $C_0 = 200$ pF.
2. How does the angle of the admittance compare between RLC and Butterworth-Van Dyke?
3. How does the piezoelectric electromechanical coupling coefficient relate to C_0 and C? [15]
4. Two measurements of SEAS10 resonators sold by SENSeOR as temperature sensors have been collected on a network analyzer and are available at `http://jmfriedt.org/seas10w2.s1p` and `http://jmfriedt.org/seas10z2.s1p`. The standard format for such datasets is the Touchstone format with `snp` extension (`s1p` for a measurement in reflection, `s2p` for a measurement in transmission).
   - Find the format of this file and by reading the header analyze its content.
   - Plot the magnitude of the reflection coefficient from each file. Reading Touchstone files in GNU/Octave is easily achieved using `dlmread()` and skipping the five first lines, or with `gnuplot` whose imaginary part notation is `{0,1}` so that a complex number is written as `re*{1,0}+im*{0,1}`.
   - What is the difference between the W and Z files? Which one is most appropriate to characterize the sensor properties?
5. From the data collected, what is the quality factor of the resonance? The sensor is made of two resonances in parallel, so that two quality factors must be provided for each sensor.
6. The operator has mistakenly forgotten to calibrate the instrument before characterizing the instrument, and provides the datasets at `http://jmfriedt.org/seas10w2uncal.s1p` and `http://jmfriedt.org/seas10z2uncal.s1p`. Repeat the previous analysis and comment.

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[15] J. Vig, *Quartz crystal resonators and oscillators – A tutorial*, 2000 at `https://www.am1.us/wp-content/uploads/Documents/U11625_VIG-TUTORIAL.pdf`