"Electrochemical Quartz Crystal Microbalance"

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Tutorials EQCM

SESSION I: Fundamentals and experimental implementation

SESSION II: Exploitation for study of real systems

4.1 Materials (RH)

4.2 Phenomena (HP & RH)

- 4.2.1 Adsorption / desorption (RH)
- 4.2.2 UPD (RH)
- 4.2.3 (Bulk) deposition /dissolution (HP)
- 4.2.4 Molecular recognition (HP)
- 4.2.5 Complexation (RH)
- 4.2.6 Ion exchange (HP)
- 4.2.7 Wetting / solvation (RH)
- 4.2.8 Viscoelasticity (RH)
- 4.2.9 Stress& mechanical motion (RH)

5. Questions and further information (HP & RH)

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Characterization of electrochemical interfaces is ...

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Characterization of electroactive film materials is …

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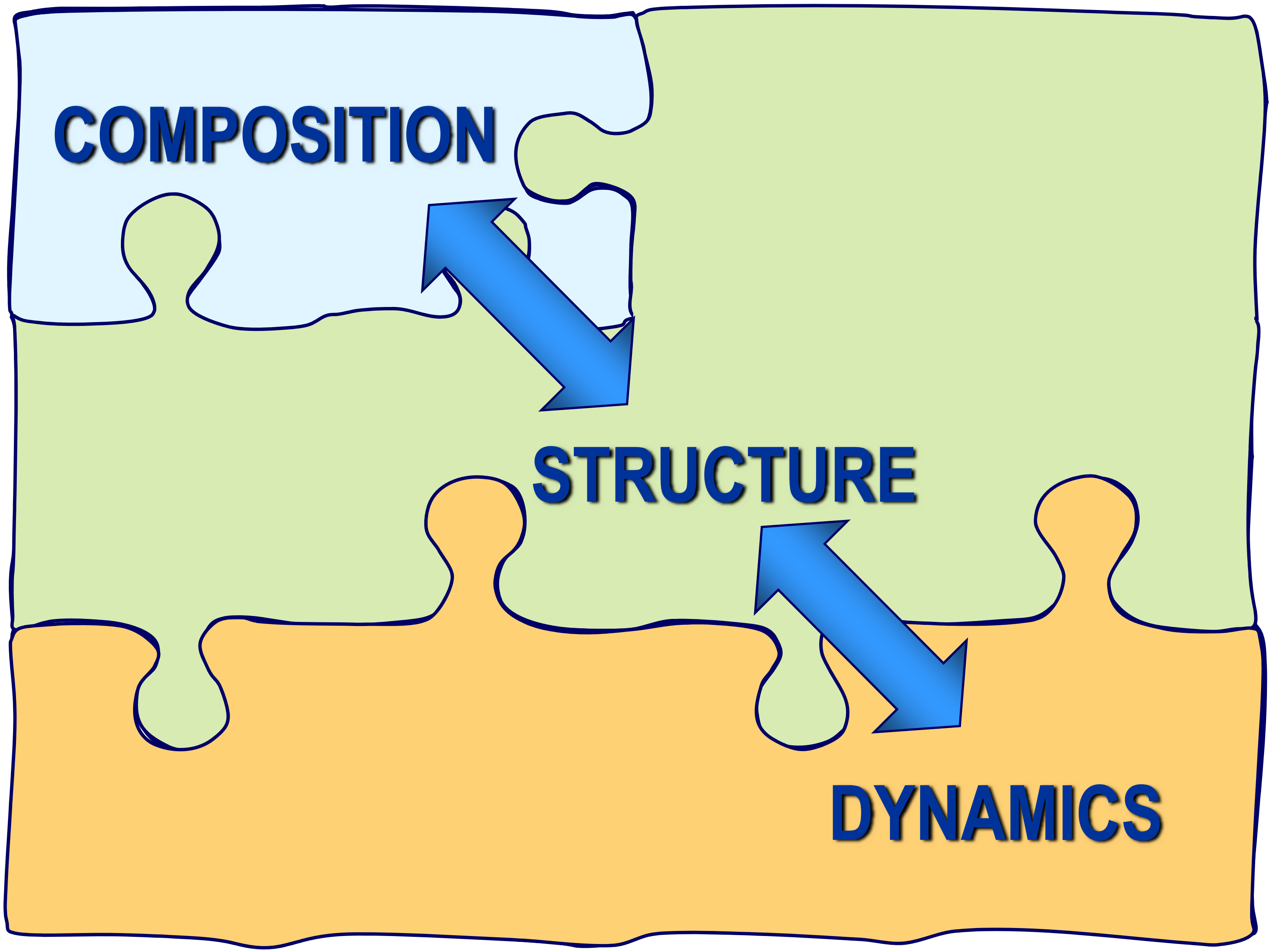
INFORMATION → UNDERSTANDING

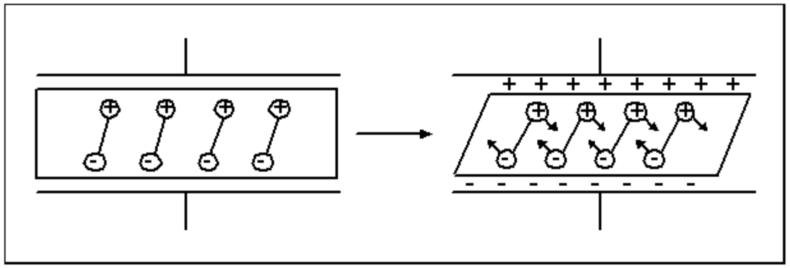


2. Methodology of measurements (H. Perrot)

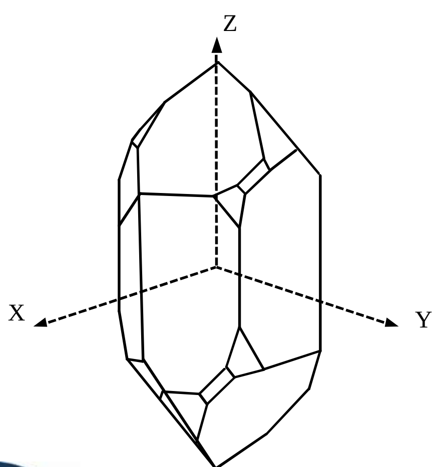
2.1 Basic concepts

► **Piezoelectric effect: direct or reverse**

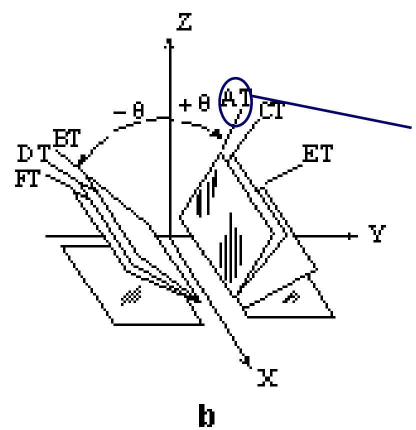
pressure → charge
charge → distortion



► **Piezoelectric crystals: quartz, $GaPO_4$, …**



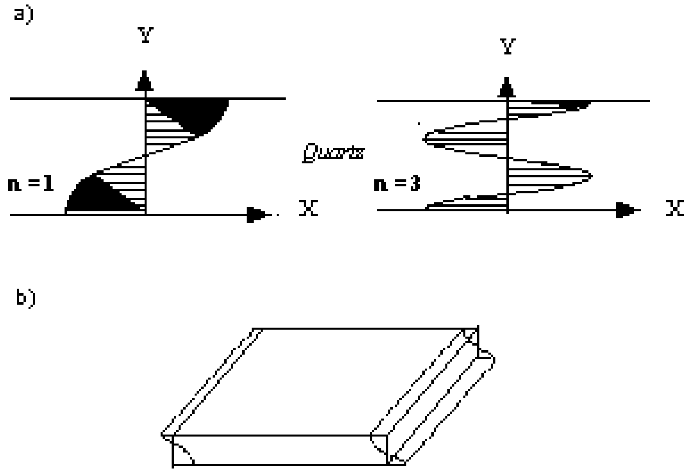
crystallographic representation



AT-cut, single rotation

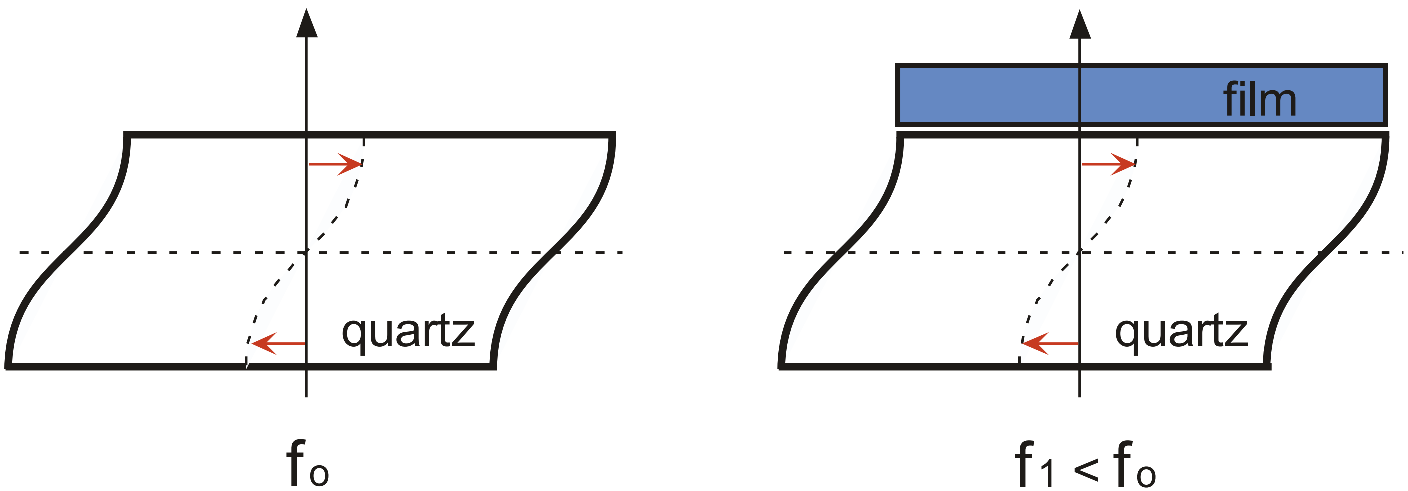
Classical quartz: AT cut 35' 12"

► Wave propagation of the u.s.



- Thickness Shear Moder (TSM)
- Bulk Acoustic Wave (BAW)
- Resonant condition
- n: overtone number

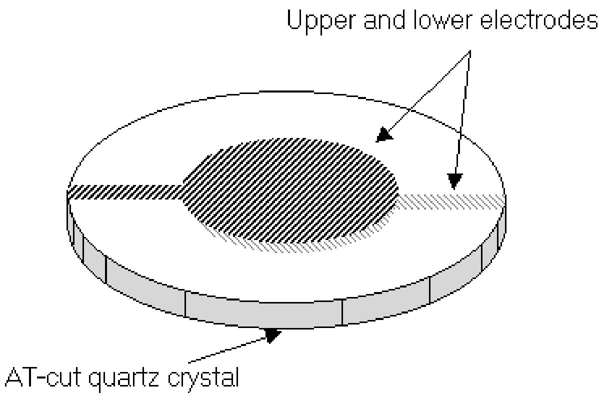
► Resonant frequency change (basic interpretation)



New frequency f_1 depends on the mass of the film

2.2 Instrumentation based on quartz resonators

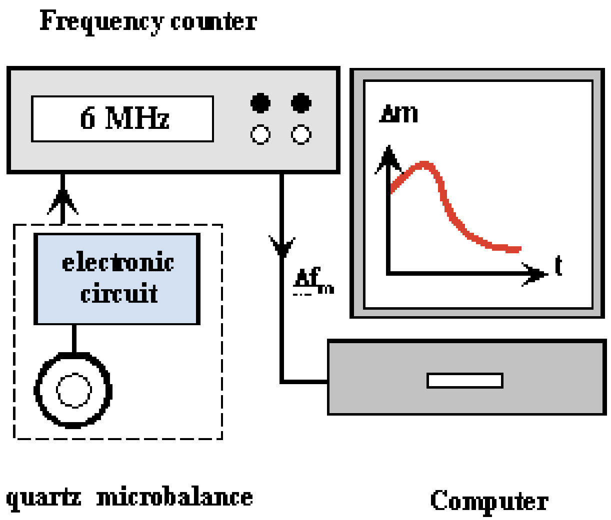
2.2.1 Active mode or classical QCM



Quartz resonator (6 MHz)

$e_q = 275\ \mu m$
$e_{gold} = 0.2\ \mu m$
Cr underlayer

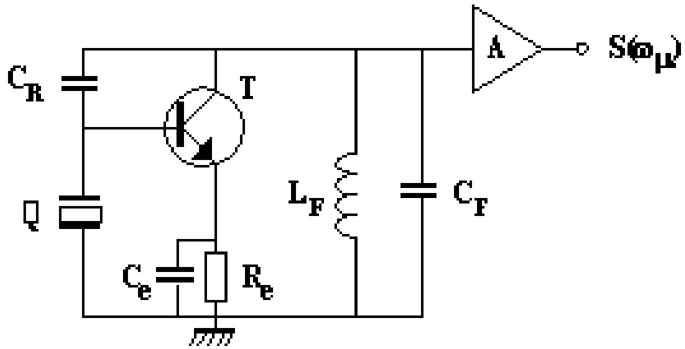
Quartz holder



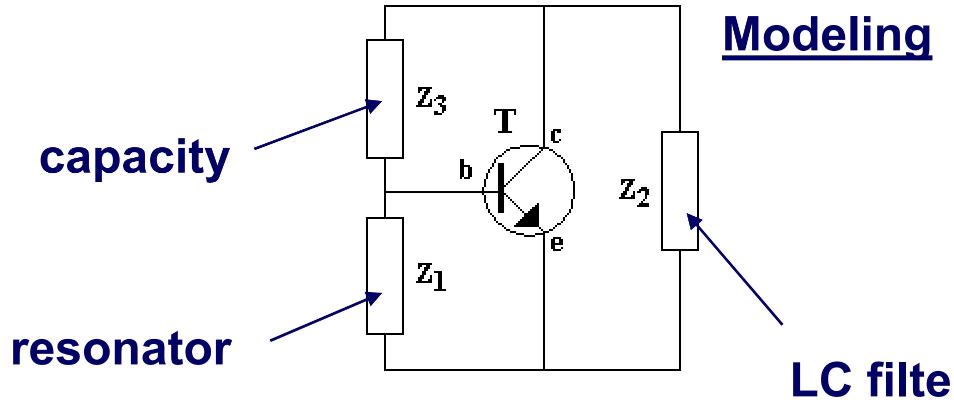
Complete experimental set-up

- ▶ **Condition of Barkhausen (or oscillation): phase shift: 0° and gain > 1**

Example: **Miller configuration**



Modeling

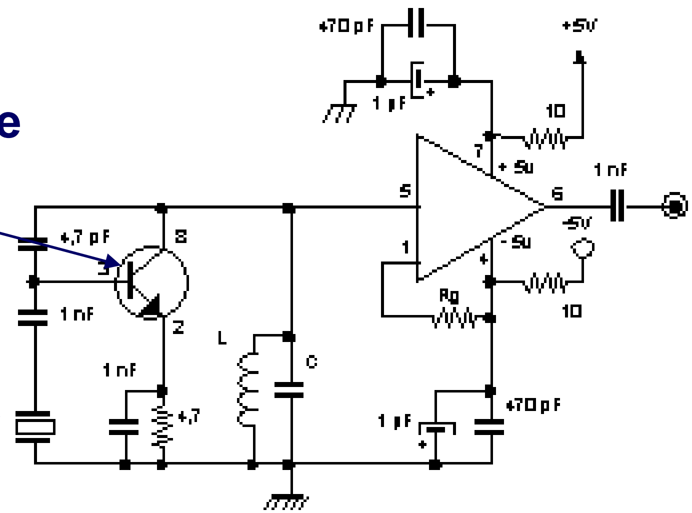


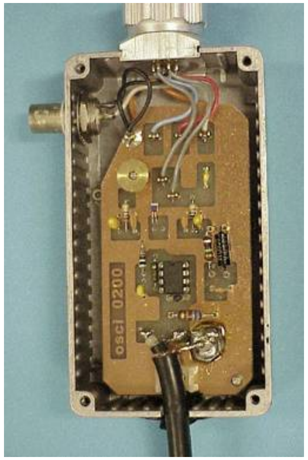
$$\mathrm{Re}[Y_2Y_3 + Y_1Y_3 + Y_1Y_2] = 0$$

- ▶ **Schematic representation with the different values given previously**

OPA 660:
large frequency range
high gain

resonator

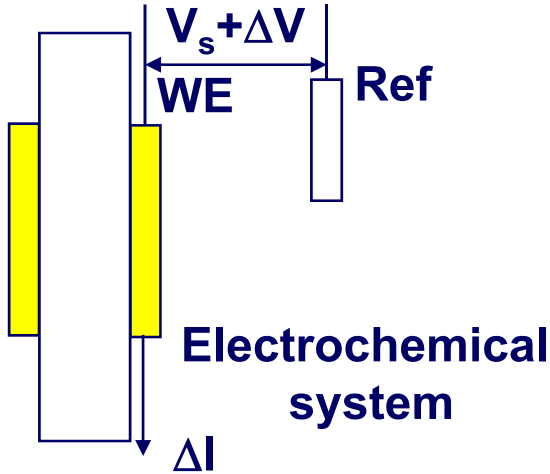




2.2.2 Passive mode or electroacoustic measurements

► **Principle of measurement**

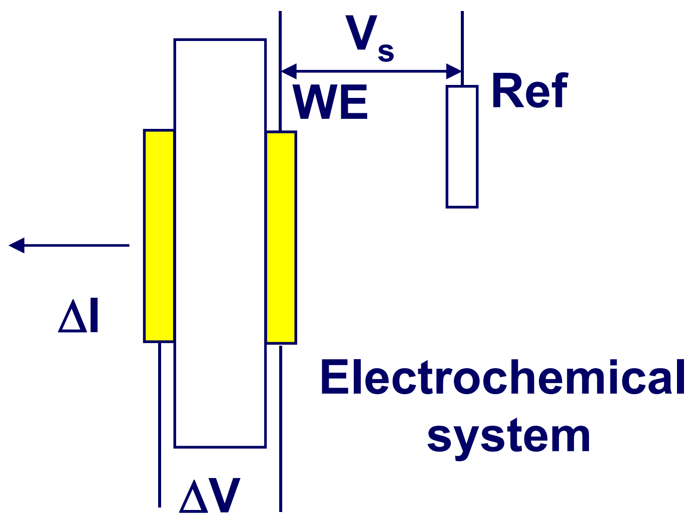
1. **Electrochemical impedance**



$$FRA \Rightarrow Z_{exp}^{electrochemical} = \frac{\Delta V}{\Delta I}$$

f : from 1 mHz to 100kHz

2. **Electroacoustic impedance**



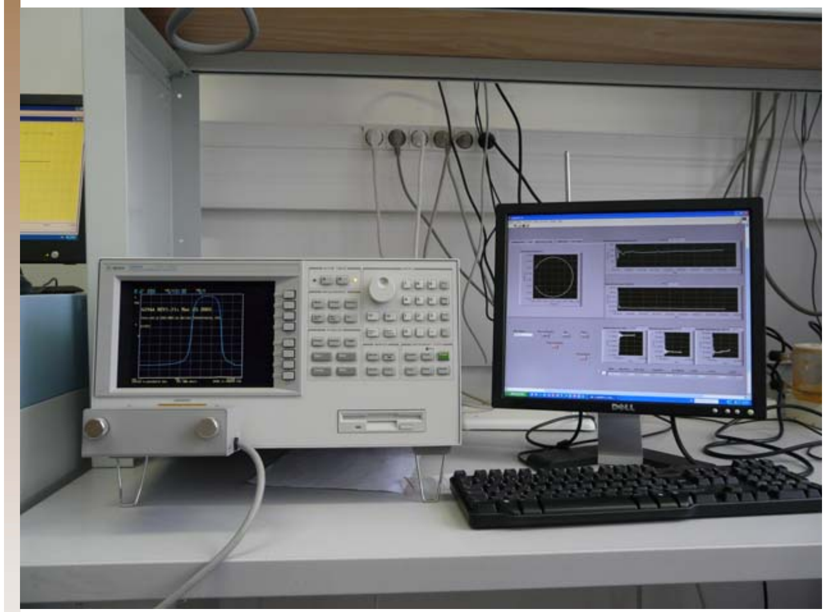
Network analyzer

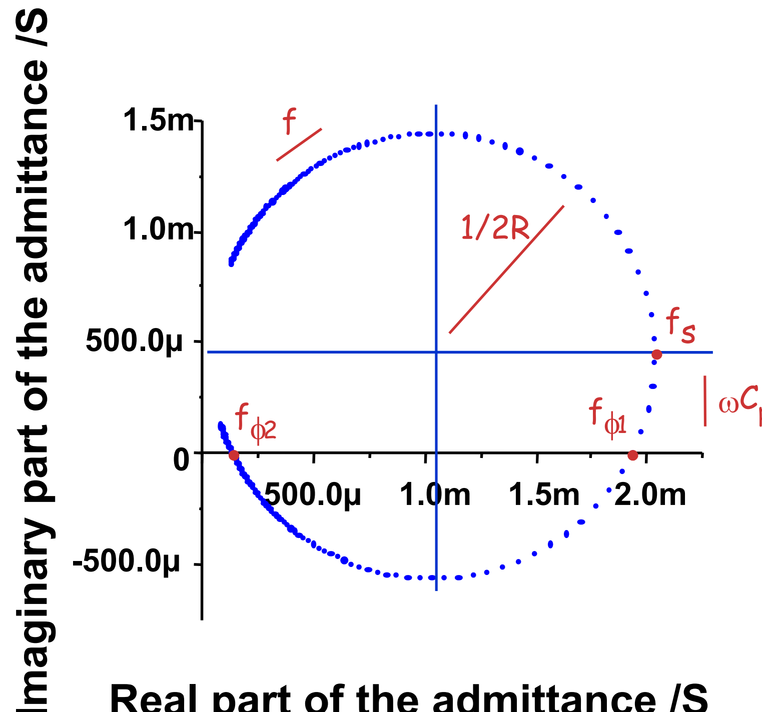
$$\Rightarrow Y_{exp}^{electroacoustic} = \frac{\Delta I}{\Delta V}$$

f: few MHz

► How to do the electroacoustic measurements

Different apparatus can be used: HP 4194A, Agilent 4294A, Solartron 1260…





Two key parameters can be extracted directly: R and f_s close to f_m

Fast estimation and more accurate values available by fitting

2.2.3 Sensitivity of the quartz resonators

► **First equation for the gravimetric sensor**

$$\Delta f_m = -2.26\ 10^{-6}\ \frac{f_n^2}{n}\frac{\Delta m}{A} = -k_S^{th}\Delta m$$

Sauerbrey equation (1959):

- Valid for small mass changes (Δm<10% of the total mass of the quartz)
- Valid for purely elastic material as quartz or equivalent

Theoretical sensitivity:

At 6 MHz: 1 Hz is equivalent to few ng, it is less than one monolayer of adsorbed oxygen on the electrode surface!

Interests:
- in-situ measurement
- high mass sensitivity
- fast response

► Theoretical mass sensitivity

f_m/MHz	e/µm	k_S^{th} / Hz g^{-1} cm^{-2}	Gain / 6 MHz
6 fundamental mode	278	8.14 10^7	-
9 fundamental mode	185	18.31 10^7	X2.25
27 (9 MHz 3rd overtone)	185	54.95 10^7	X6.75
27 fundamental mode	62	164.85 10^7	X20.25

In term of direct mass:

f_m/MHz	k_S^{th} / Hz g^{-1} cm^{-2}	Δm/ng cm^{-2} if Δf_m=1 Hz	Δm/ng if Δf_m=1 Hz (A=0.2 cm^2)
6 fundamental mode	8.14 10^7	12.28	2.457
9 fundamental mode	18.31 10^7	5.46	1.092
27 (9 MHz 3rd overtone)	54.95 10^7	1.82	0.364

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► Calibration with copper

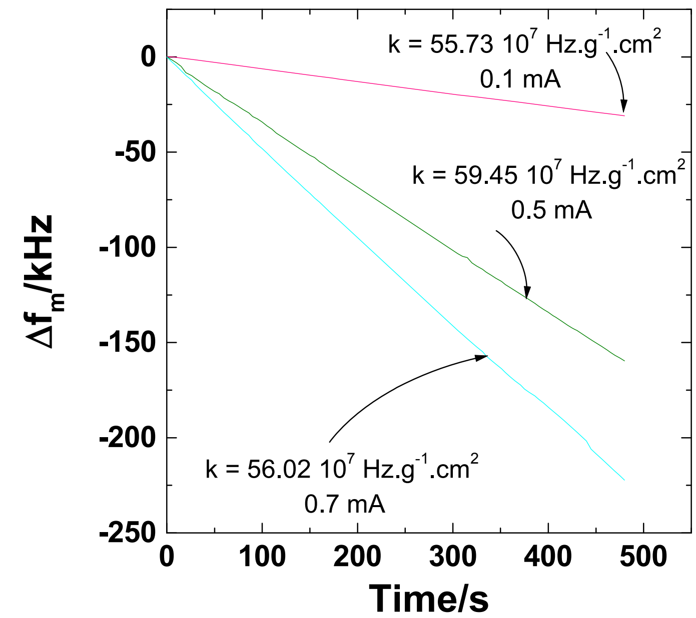
Electrodeposition under controlled current:

$$Cu^{2+} + 2e^{-} \rightarrow Cu$$

- microbalance frequency shift: Δf_m

- mass change from the Faraday law: Δm_F

$$k_S^{exp} = \frac{\Delta f_m}{\Delta m_F}$$



Frequency/MHz	Δm/ng if Δf_m=1 Hz (A=0.2 cm²)	
	Experimental/pg	Theoretical/pg
6	2670	2454
9	1226	1093
27(3)	350	364

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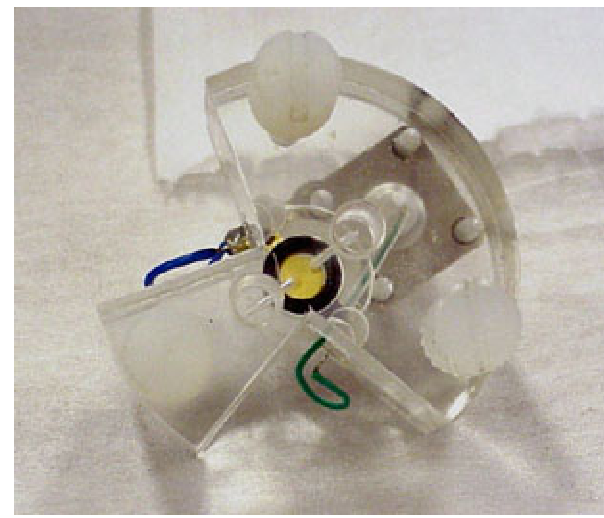
2.3 Other acoustic wave devices

► **Overview of different microbalances**

2 — 6 — 9 — 27 → Frequency MHz

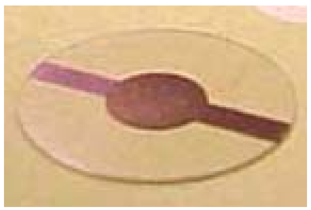
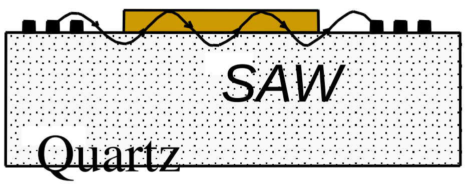
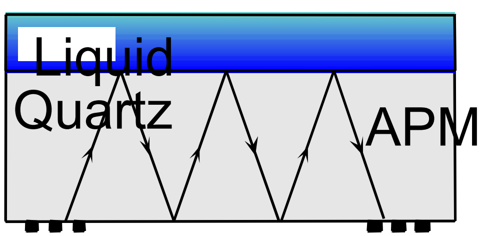


Material reactivity

Electro-chemistry

Biosensors

► Other acoustic wave devices

Device	Mass sensitivity	Mass for 1Hz
	$-2.26\ 10^{-6}\ f_0^2$	6 MHz: 12 ng cm^{-2}
	$-2.26\ 10^{-6}\ f_0^2$	200 MHz: 10 pg cm^{-2}
	$-10\ f_0$	104 MHz: 1 ng cm^{-2}

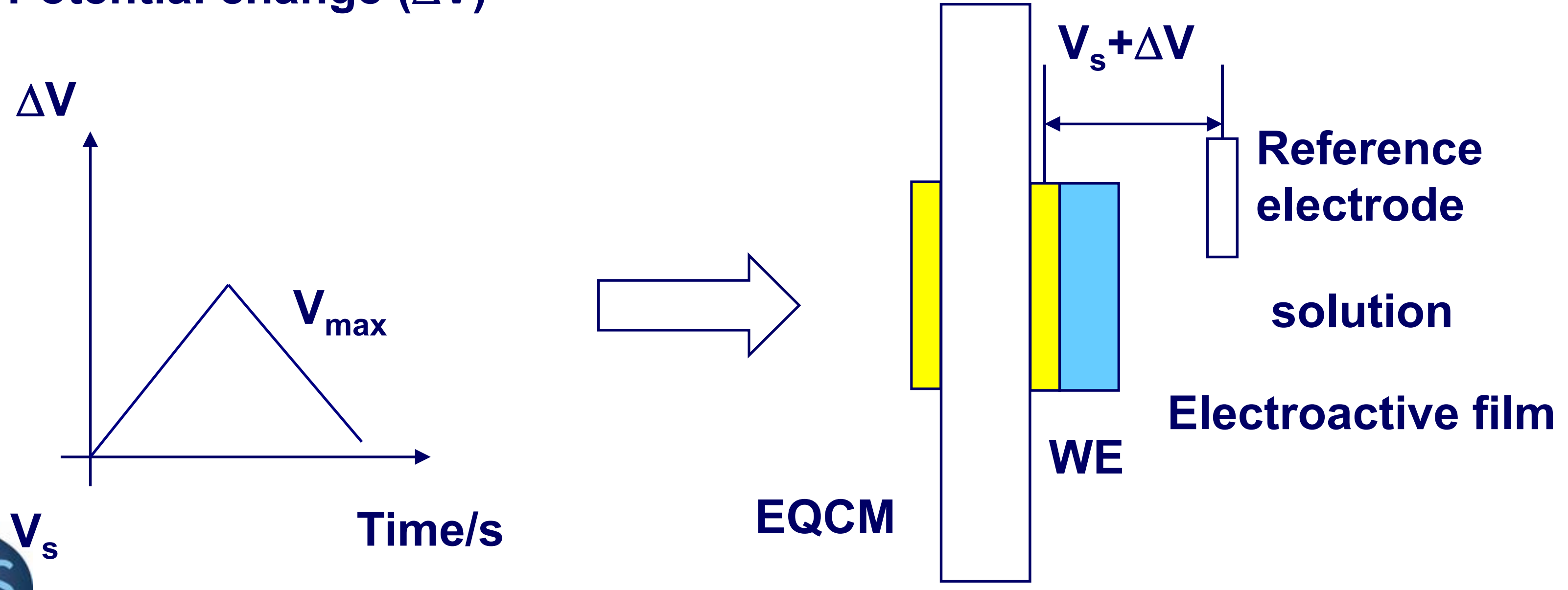
2.4 Electrochemical coupling techniques

2.4.1 Cyclic electrogravimetry

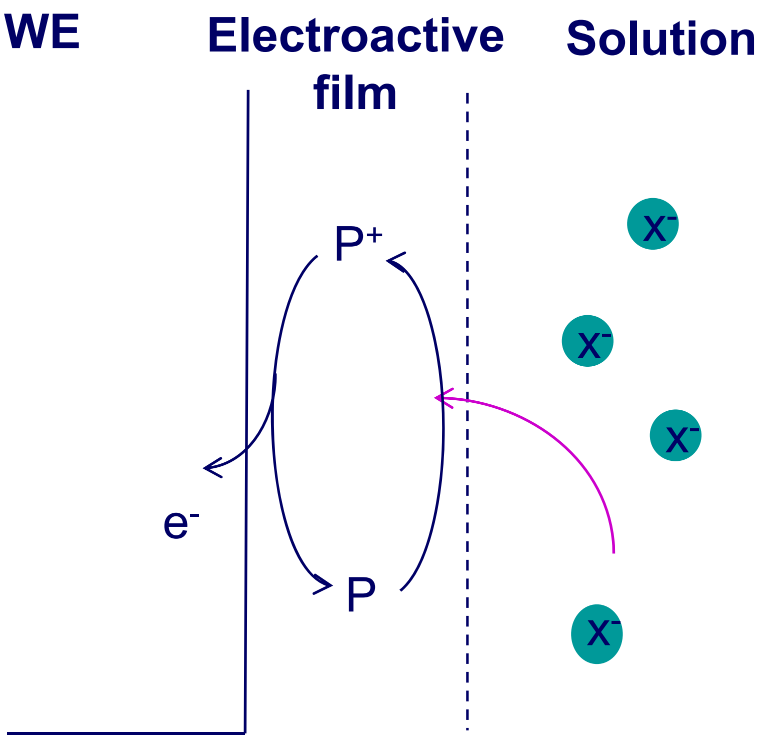
▶ **Electroactive film on the QCM**

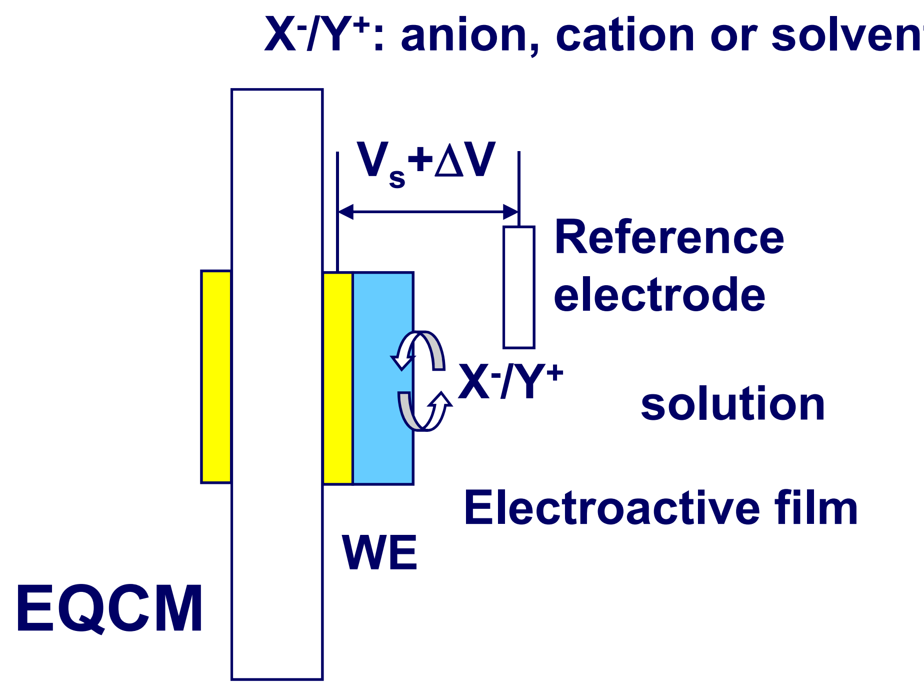
$$\left\{\left[P^{n+}.nX^-\right]\ \alpha\ \left[Y^+X^-\right]\ \beta\ \left[H_2O\right]\right\}_p + \nu e^- \Leftrightarrow \left\{\left[P^{(n-\nu)+}.(n-\nu)X^-\right]\ (\alpha-\delta)\ \left[Y^+X^-\right]\ (\beta-\varepsilon)H_2O\right\}_p + \delta Y_s^+ + (\delta+\nu)X_s^- + \varepsilon\left[H_2O\right]_s$$

▶ **Potential change (ΔV)**



► Current response and mass response





Motion of electrons and ions due to the film electroactivity

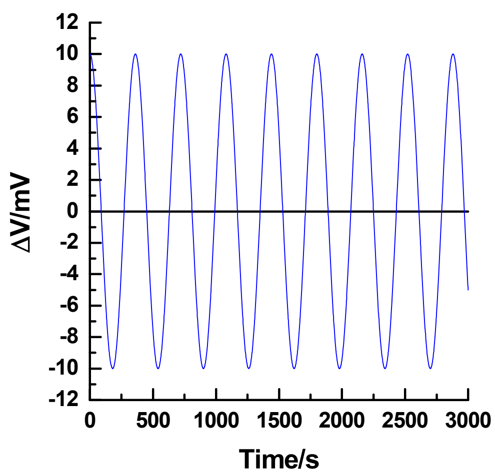
- **Current response: i=k(V)**
- **Mass response: m=k'(V)**

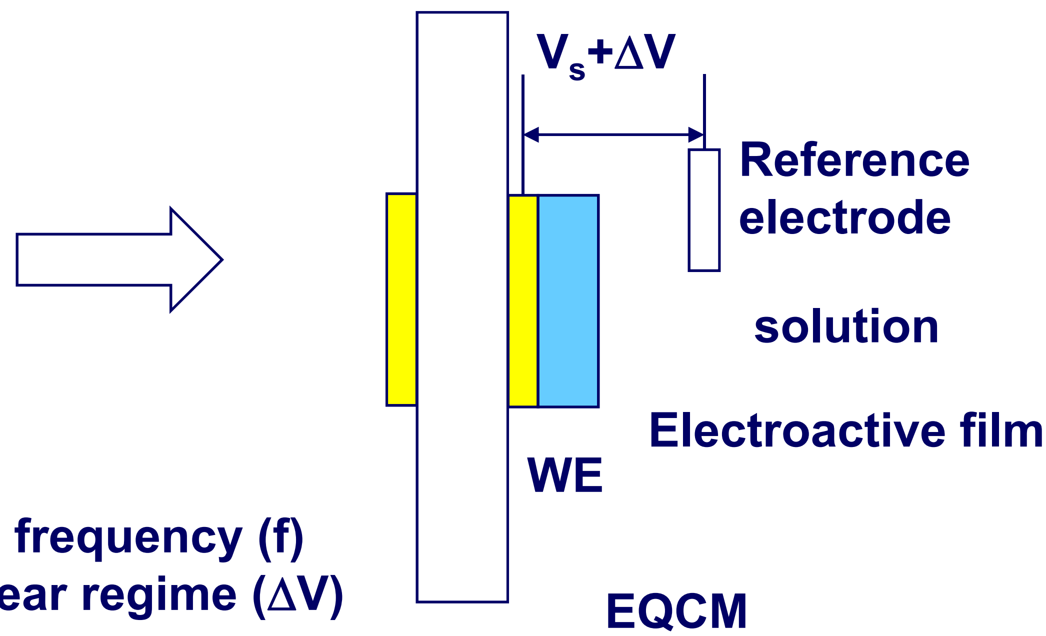
2.4.2 *ac*-electrogravimetry

► Electroactive film on the QCM

$$\left\{\left[P^{n+}.nX^{-}\right]\ \alpha\ \left[Y^{+}X^{-}\right]\ \beta\ \left[H_2O\right]\right\}_p + \nu e^{-} \Leftrightarrow \left\{\left[P^{(n-\nu)+}.(n-\nu)X^{-}\right]\ (\alpha-\delta)\ \left[Y^{+}X^{-}\right]\ (\beta-\varepsilon)H_2O\right\}_p + \delta Y_s^{+} + (\delta+\nu)X_s^{-} + \varepsilon\left[H_2O\right]_s$$

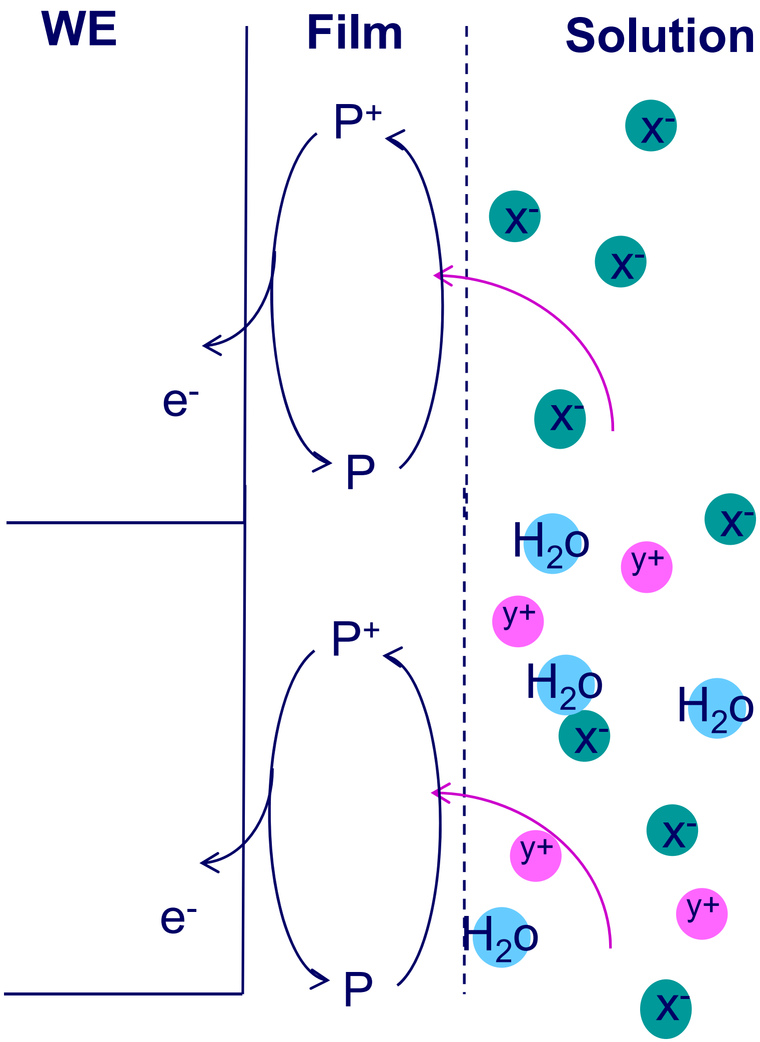
► Potential modulation

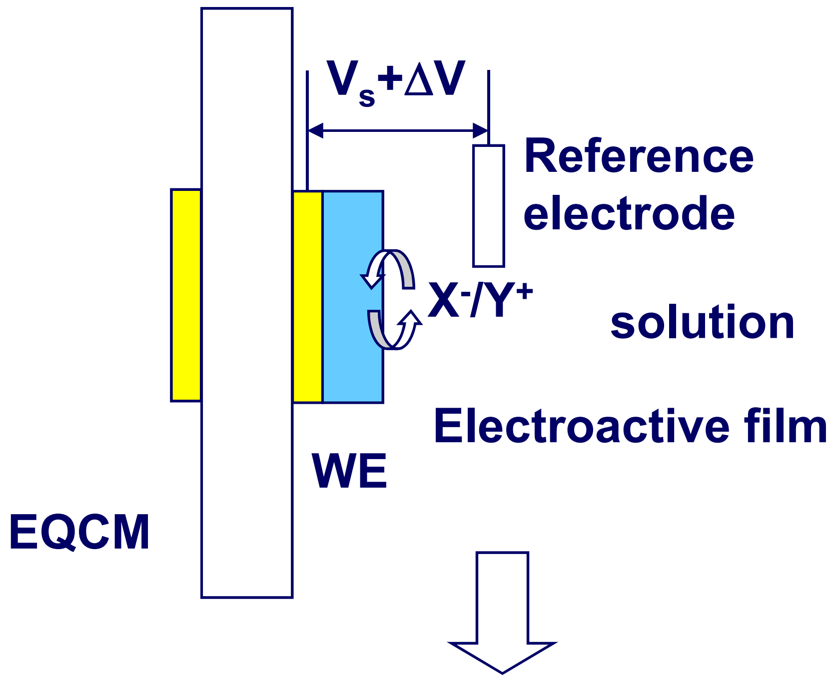


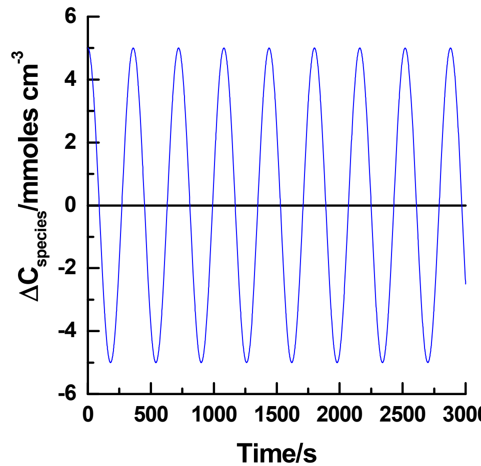


- Potential modulation at a given frequency (f)
- Small amplitude to keep the linear regime (ΔV)
- Under equilibrium (V_s)

X^-/Y^+: anion, cation or solvent

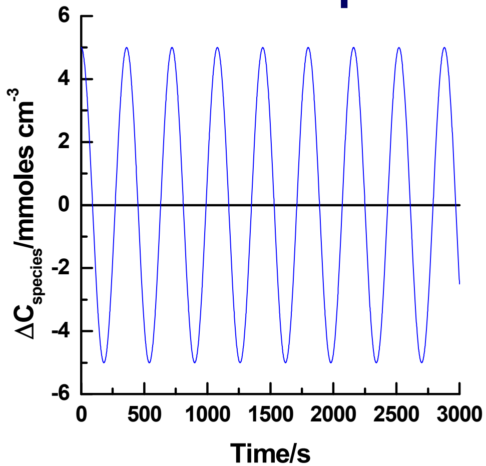




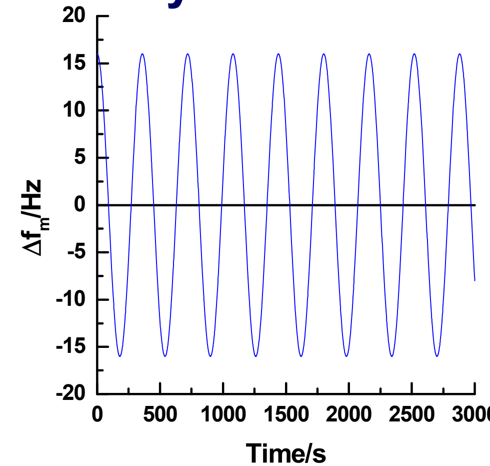


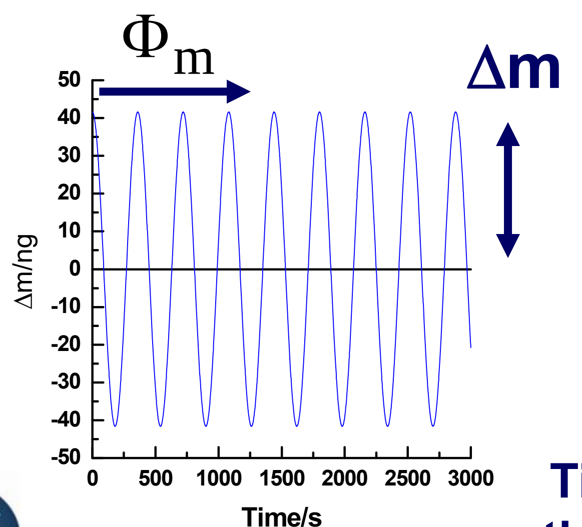
▶ Film mass changes: Δm

Equivalent to a change of the film density



EQCM





Gravimetric regime

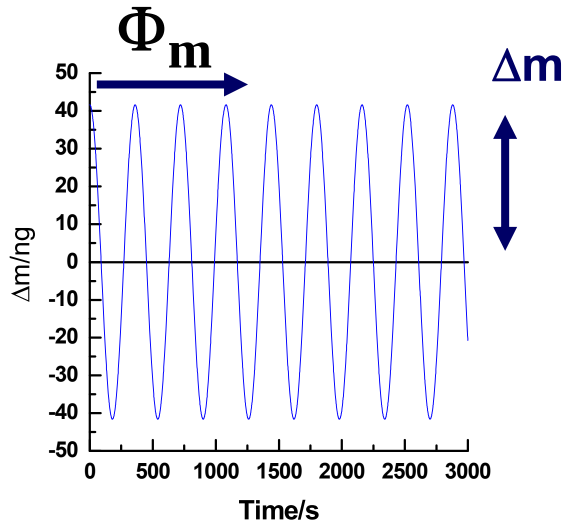
Sauerbrey equation:

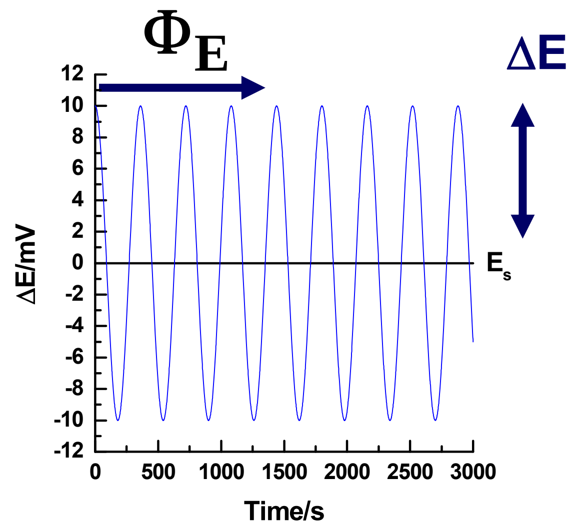
$$\Delta m = -\frac{\Delta f_m}{k_s}$$

Time response of the film mass (Δm)

Mass response

Potential modulation





Frequency Response Analyzer (FRA):

$$\frac{\Delta m}{\Delta E} = \frac{|\Delta m|}{|\Delta E|} e^{j(\Phi_m - \Phi_E)}$$

At a given frequency modulation

$$(\omega = 2 \times \pi \times f)$$

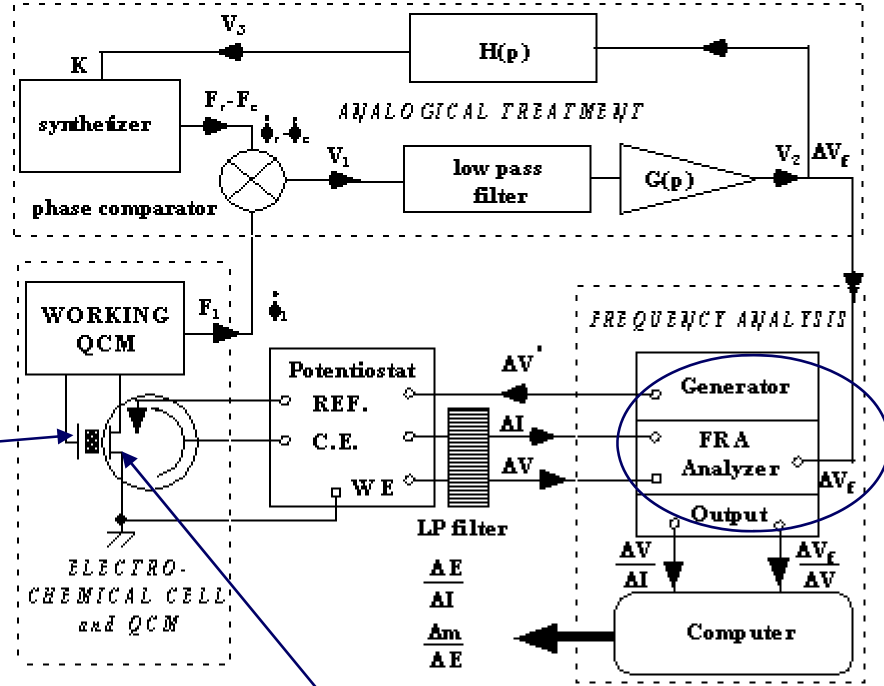
Interests:

- linear regime (models)
- frequency dependent: kinetic information
- possibility of electrochemical coupling
- ionic identification
- non charged species detected

► Complete system

3. Δf_m

2. { - WE: ΔI
- QCM: Δm



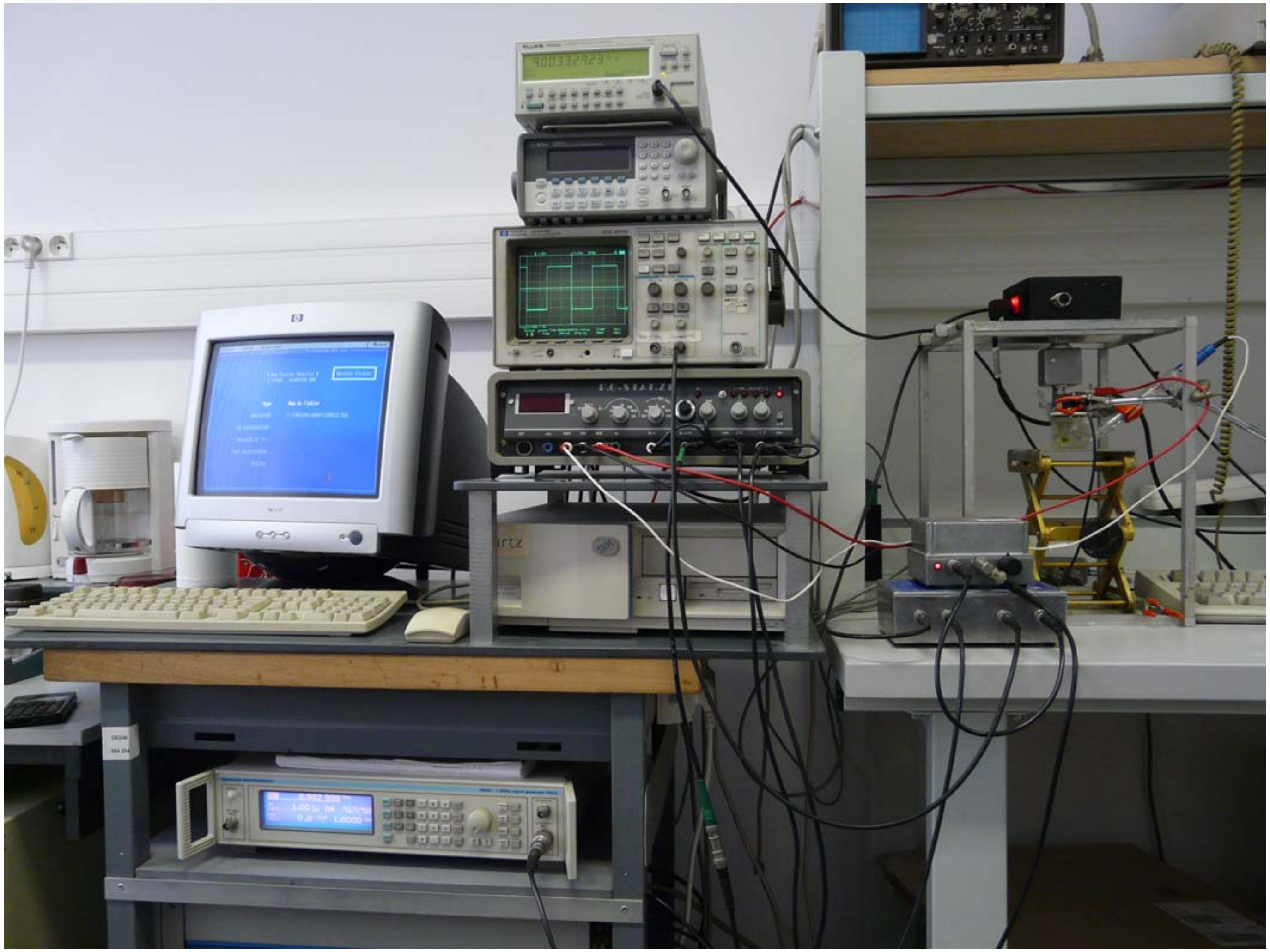
4. ΔV_f

5. FRA
Solartron 1254
with 4 channels!!

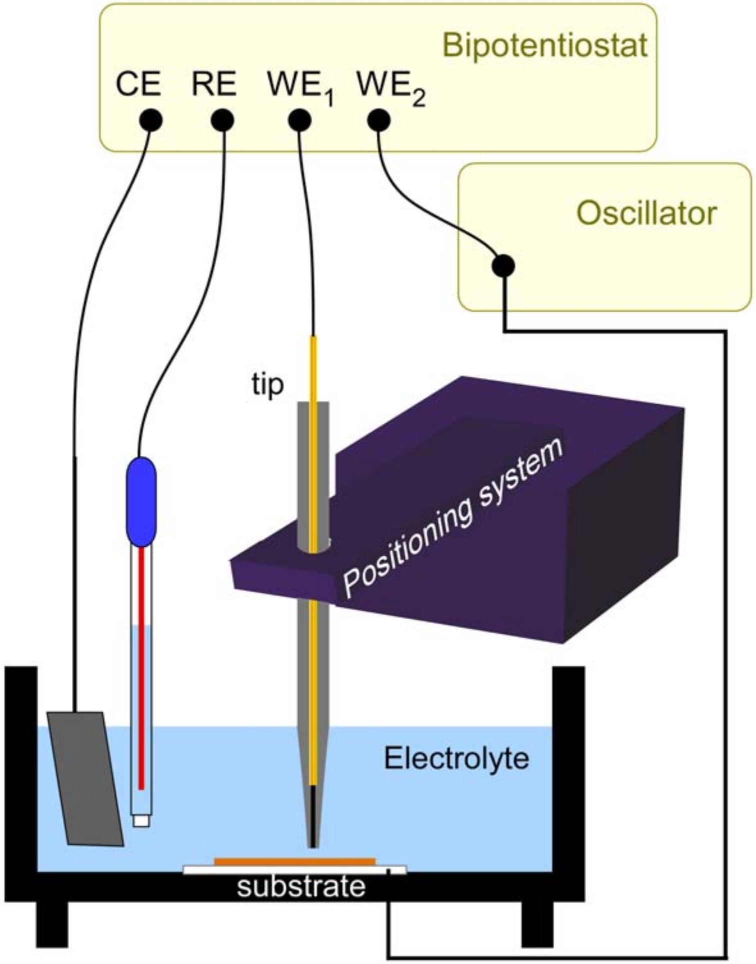
1. Sine wave perturbation: ΔV

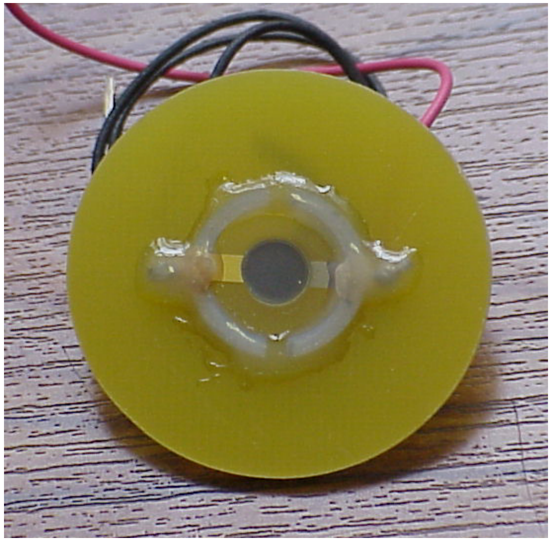
Final TF wished: $\dfrac{\Delta E}{\Delta I}$ and $\dfrac{\Delta m}{\Delta E}$

► Experimental set up



2.4.3 SECM and microbalance





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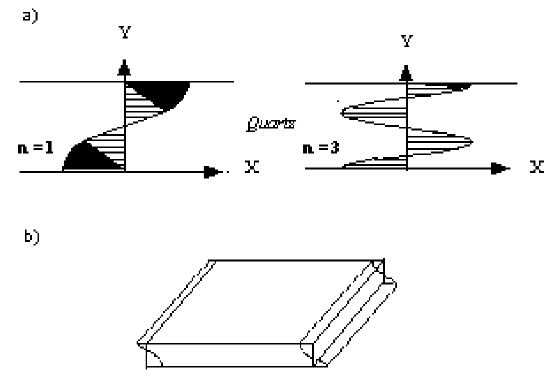
3. Data interpretation, limitations, modelling (HP and ARH)

3.1. Response factors

► **Mass**



Resonant condition: $e = \dfrac{n\lambda_n}{2}$

where e is the film thickness and λ_n is the wave length

First relation: $\lambda_n = v\dfrac{1}{f_n}$ where v is the u.s. speed and f_n

Second relation: $e = \dfrac{m}{A\rho}$ where m is the mass of the quartz, A the active surface and ρ, the quartz density.

Thus, by combining theses equations, it leads to: $f_n = \dfrac{nvA\rho}{2m}$

For an increase of mass Δm: $\Delta f_n + f_n = \dfrac{nvA\rho}{2(m+\Delta m)} = \dfrac{nvA\rho}{2m(1+\dfrac{\Delta m}{m})}$

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If Δm is small compared with m then: $\Delta f_n + f_n = \frac{nvA\rho}{2m}(1 - \frac{\Delta m}{m})$

(Taylor exp ansion)

According to the definition of f_n : $\Delta f_n = \frac{nvA\rho}{2m}(1 - \frac{\Delta m}{m}) - \frac{nvA\rho}{2m}$

and after simplification: $\Delta f_n = -\frac{nvA\rho}{2m^2}\Delta m$

As $m = \frac{nvA\rho}{2f_n}$, it comes: $\Delta f_n = -\frac{2}{v\rho}\frac{f_n{}^2}{n}\frac{\Delta m}{A}$

Sauerbrey equation: $$\boxed{\Delta f_n = -2.26\ 10^{-6}\frac{f_n{}^2}{n}\frac{\Delta m}{A}}$$

-Valid for small mass changes (Δm<10% of the total mass of the quartz)
-Valid for material purely elastic as quartz crystal or equivalent
-Valid for an infinite and uniform film

► Viscosity and density (Kanazawa and Gordon)

$$\Delta f_m = -f_n^{-\frac{3}{2}}\left(\frac{\rho_l \eta_l}{\pi \mu_q \rho_q}\right)^{\frac{1}{2}}$$

where μ_q is the quartz stiffness, ρ_q the quartz density, ρ_l the solution density and η_l the solution viscosity.

In means, at 6 MHz, the frequency shift between air and water is around 2kHz

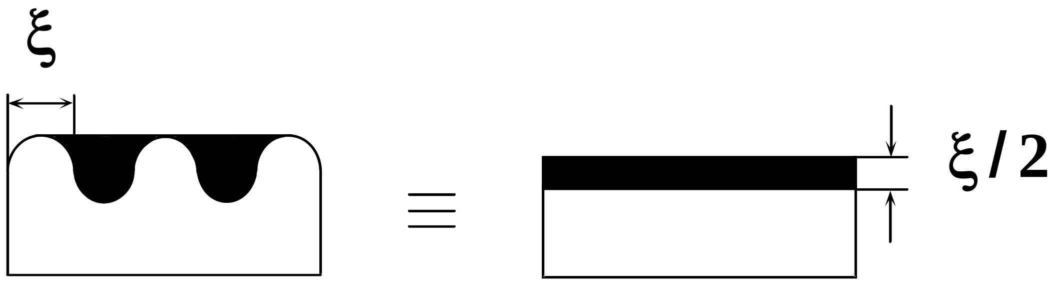
► Combining mass effect and liquid effect (Martin)

$$\Delta f_m \cong -\frac{2f_n^2}{N\sqrt{\bar{c}_{66}\rho_q}}\left[\rho_f h_f + \left(\frac{\rho_l \eta_l}{4\pi f_n}\right)^{\frac{1}{2}}\right]$$

mass

viscosityxdensity

► Roughness effect (Schumacher)



Roughness surface $\equiv$ **Rigid liquid film**

Rigid mass: $\Delta m_l = \frac{\rho_l \xi}{2}$

$$\Delta f_m = \frac{-2 f_n^{\,2} \Delta m_l}{(\mu_q \rho_q)^{1/2}}$$

► Effect of the liquid conductivity (Hager)

$$\Delta f_m = -k_1 \Delta(\rho_l \eta_l)^{1/2} + f(\Delta \varepsilon_l)$$

where

- k_1 is a numeric constant

- ρ_l is the liquid density

- η_l is the liquid density

and $f(\Delta \varepsilon_l)$ is a function of the dielectric constant

- ► **Viscoelastic films (Mason, Martin…)**

$f_m = f(\rho_f, h_f, G', G'')$ where ρ_f is the film density, h_f the film thickness and G', G" the viscoelastic parameters of the film.

- ► **Criteria to validate the gravimetric regime**

1. Complementary techniques: electrochemistry, ellipsometry…
2. Electroacoustic measurements: approach by measuring f_s and R

Case	Parameters	Exp. data	Interpretation
Rigid layer (Sauerbrey)	ρ_s (mass density)	Δf_s; $\Delta R=0$	$\Delta f_s \uparrow \rightarrow \downarrow \rho_s$
Newtonian medium	ρ_l, η_l	Δf_s or ΔR	$\Delta f_s \uparrow \rightarrow \downarrow \sqrt{\rho_l \eta_l}$ or $\Delta R \uparrow \rightarrow \uparrow \sqrt{\rho_l \eta_l}$
Viscoelastic layers	ρ_f, h_f, G', G''	Complete spectrum	See RH contribution

Piezoelectric Transducers and Appli., A. Arnau Ed., Springer 2008

Gravimetric application

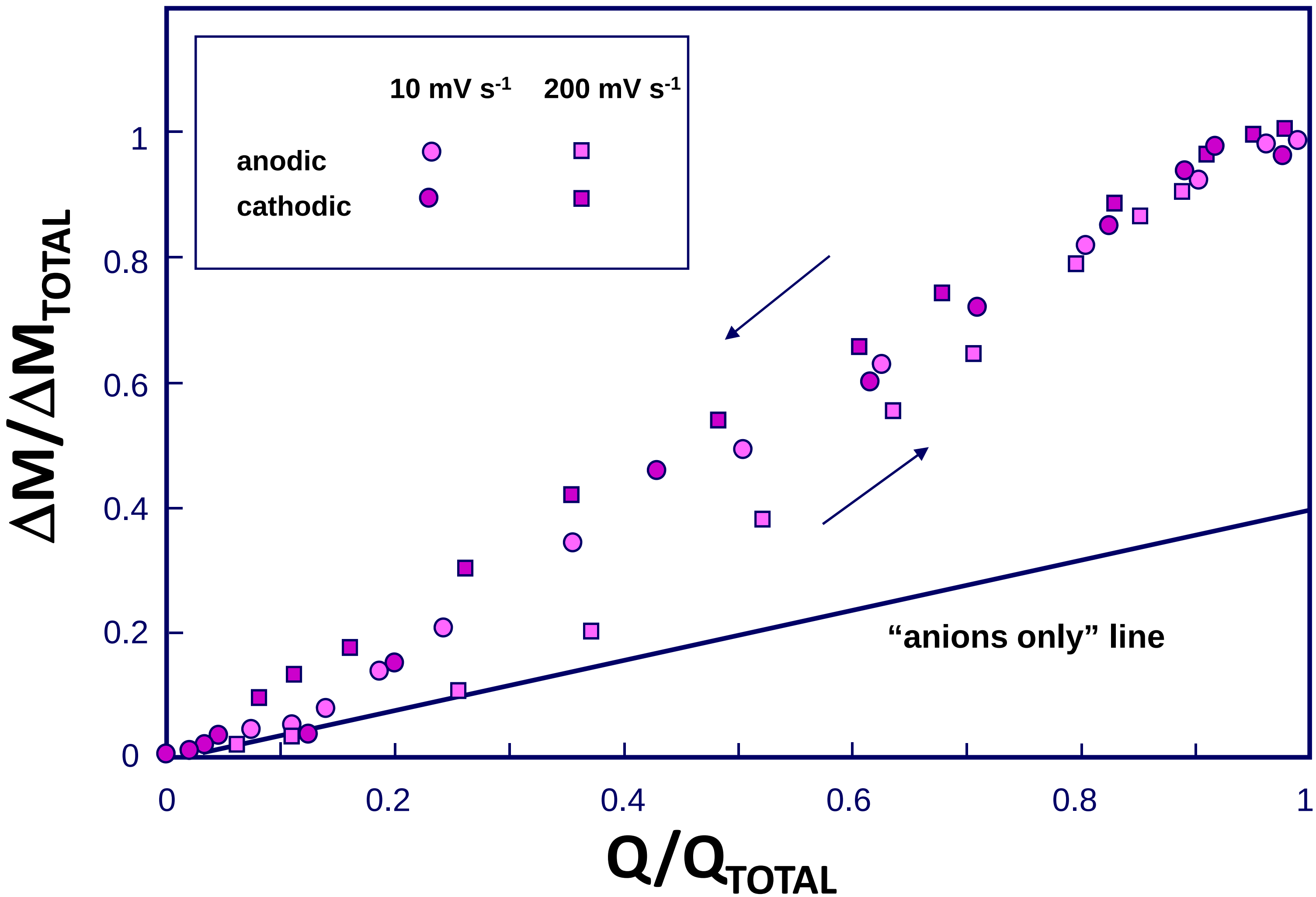
Processes involved

- **Electron transfer**
  - Q, but not Δm
- **Coupled counter ion transfer (for films)**
  - electroneutrality constraint
    - Q, but not Δm
- **Solvent transfer for films**
  - activity constraint
    - not Q, but Δm
- **Structural change**
  - triggered by charge and/or volume effects
  - e.g. polymer relaxation
    - directly, neither Q nor Δm
    - indirectly, possibly Δm
- **Co-ion ("salt") transfer**
  - activity constraint (permselective at low concentration)
    - not Q, but Δm

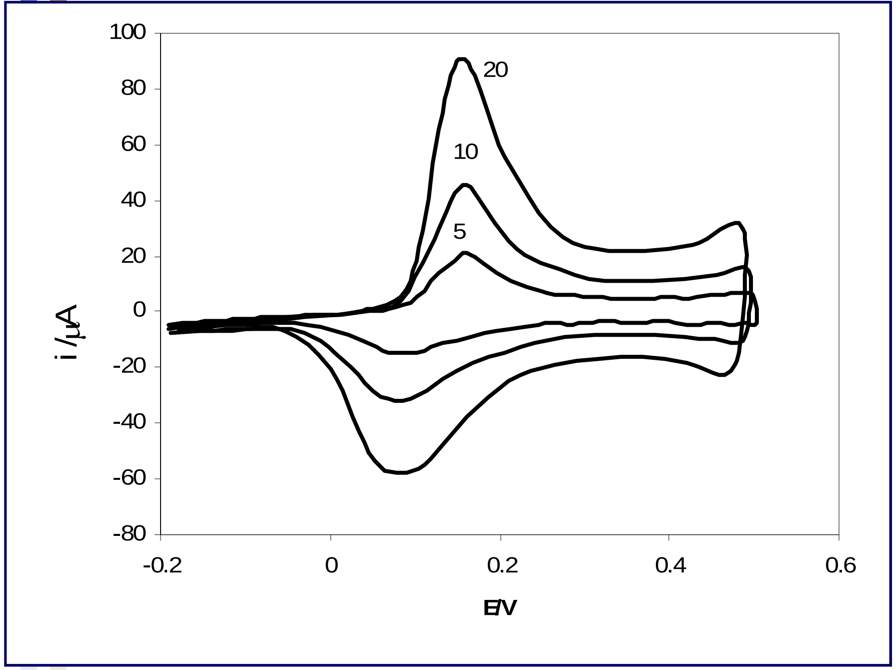
Diagnostic: mass change vs charge plot

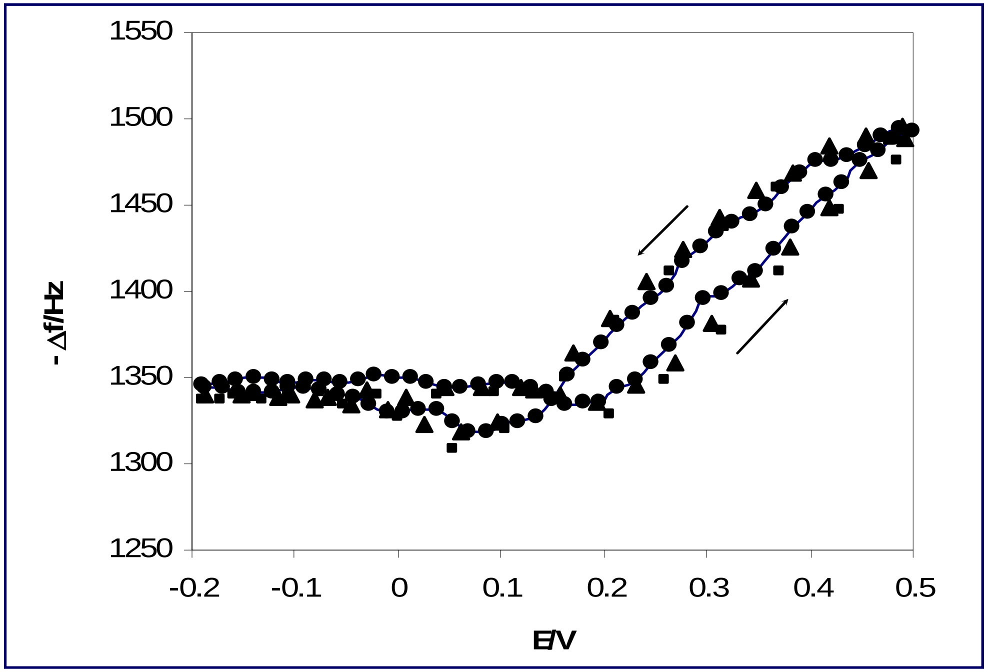
- **Qualitatively**
  - sign of slope indicates ion charge
  - zero slope signals "neutral" (solvent, salt)
- **Quantitatively**
  - value of slope indicates molar mass
  - seldom clearly resolved
    - "weighted" average of several species
- **Solvent transfer**
  - thermodynamically to be expected
  - may be minor or major
  - may be bound or free
    - QCM provides no direct insight
    - timescale (e.g. voltammetric scan rate) may resolve?

PVF REDOX SWITCHING: kinetic permselectivity



Polyaniline redox-driven ion and solvent transfer





Polyaniline / 1 M $HClO_4$

scan rate, v / mV s^{-1}: 5 (•), 10 (▲), 20 (◆).

Acoustically thin film:

Γ = 35 nmol cm^{-2}

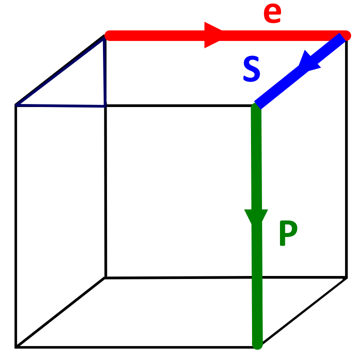
Visualizing mechanistic possibilities

- Identify different types of elementary step
  - assign each to a coordinate (dimension)
  - coupled processes require only one dimension
    - coupled electron / counter ion transfer
  - each coordinate associated with a characteristic timescale
    - characteristic dependence on E, T, pH, c, ...
- Apply principle of "scheme-of-squares"
  - extend to required number of elementary steps, i.e .dimensions
    - e/A^- & S ⇨ 2D
    - e/A^- & C^+A^- ⇨ 2D
      - e/A^- & S & P ⇨ 3D
      - e/A^- & S & C^+A^- ⇨ 3D
        - e/A^- & S & C^+A^- & P ⇨ 4D
- Identify pathways
  - recognize mechanistic diversity

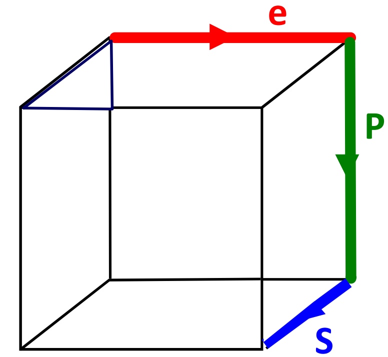
Mechanistic possibilities for oxidation

- High overpotential

Electron/ion transfer first



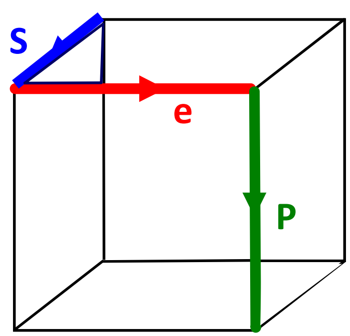
ECC'



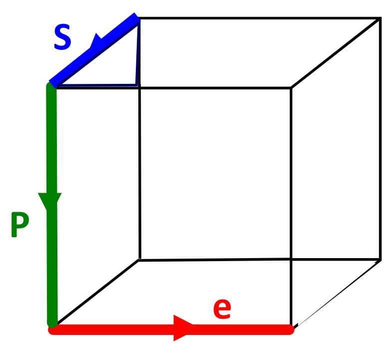
EC'C

- Low Overpotential

Solvent transfer first

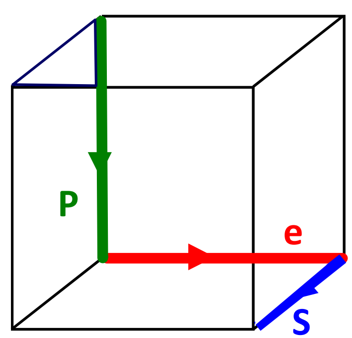


CEC'

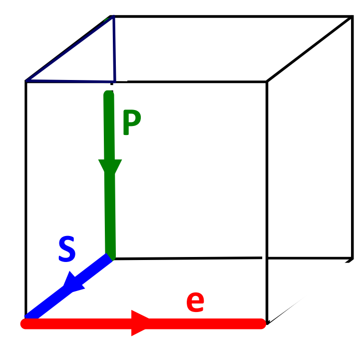


CC'E

Polymer reconfiguration first



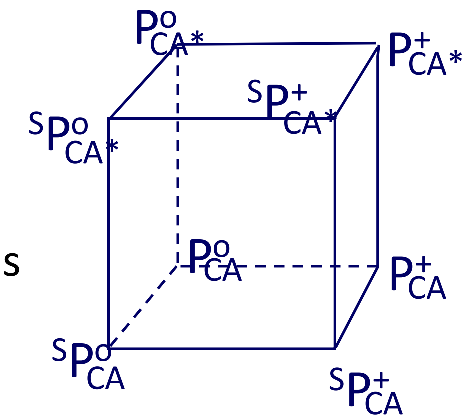
C'EC

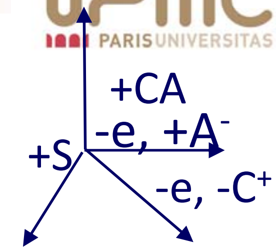


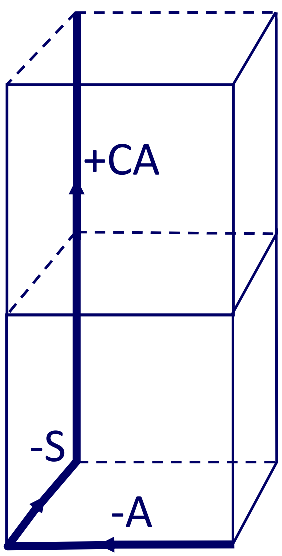
C'CE

Nomenclature

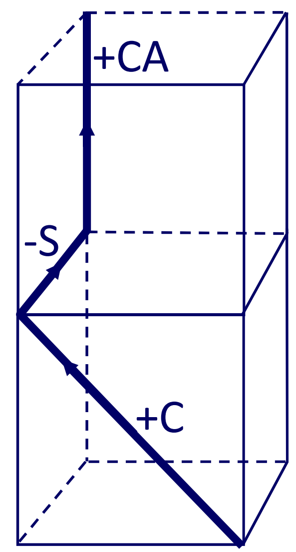
- Corners represent species
  - signal redox state, solvation, structure
- Edges represent processes
  - analogous process may link different species
  - consider absolute mass and mass change?







- Multiple similar elementary steps
  - fused cubes
- "Diagonal" transfers possible
  - represent coupling
  - energetically unlikely
  - require similar timescales

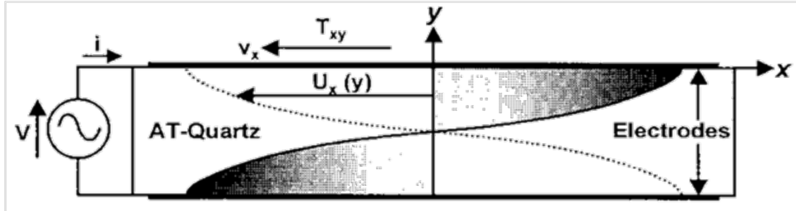


Electroacoustic approach

Resonator coupling to ambient medium

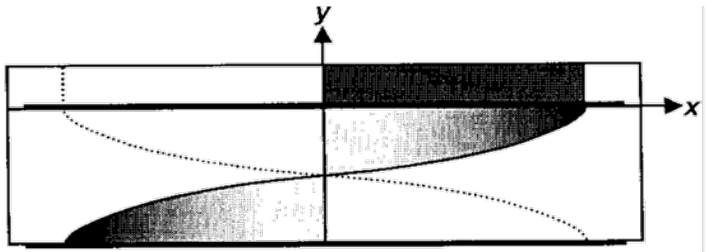
❑ Film motion

- Resonator induces motion at electrode surfaces



- Rigidly coupled films move synchronously with exciting electrode

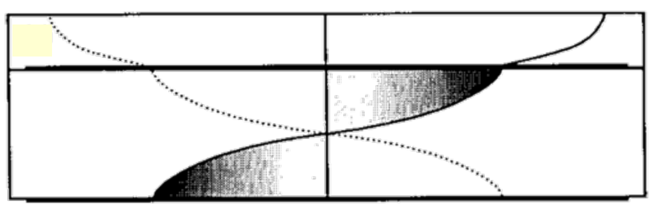
  ↳ *phase shift, ϕ = 0*



- Non-rigidly coupled films move non-synchronously with exciting electrode

  ↳ *acoustic deformation*

  ↳ *phase shift, ϕ > 0*



- Acoustic deformation changes with polymer loading

  ↳ *ϕ increases with film thickness*

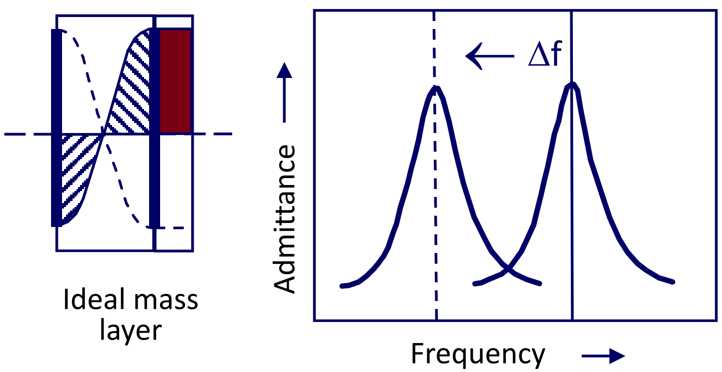
  ↳ *ϕ decreases with G*

  ↳ *film resonance when $\phi = \pi/2$*

Admittance spectra as a diagnostic tool

❑ Acoustically thin ("rigid") film

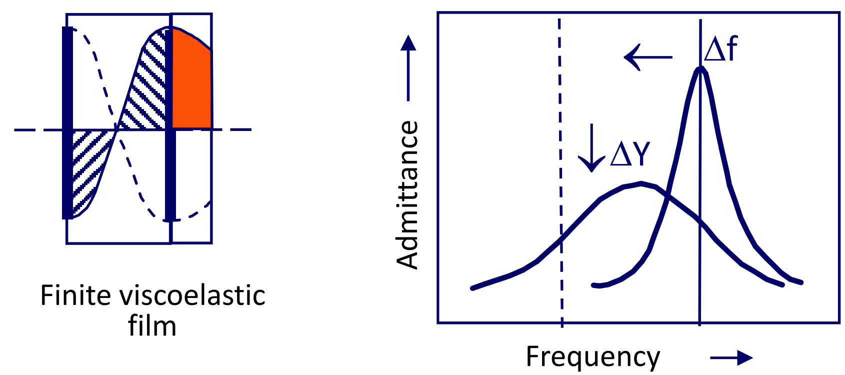
- no acoustic deformation



- energy storage, but no loss
- gravimetric probe of surface populations
  - ↳ film deposition
  - ↳ mobile species exchange
  - ↳ $\Delta f = -\left(\frac{2f_0^2}{\rho_q v_q}\right)\frac{\Delta m}{A}$ *gives* $\Delta\Gamma$

❑ Acoustically thick (viscoelastic) film

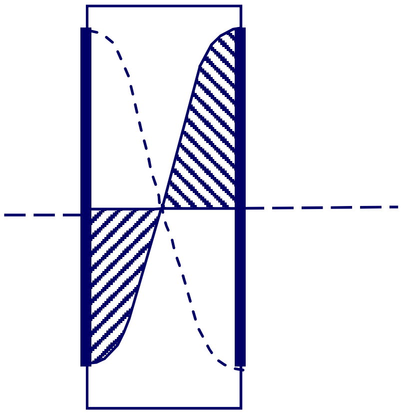
- acoustic deformation



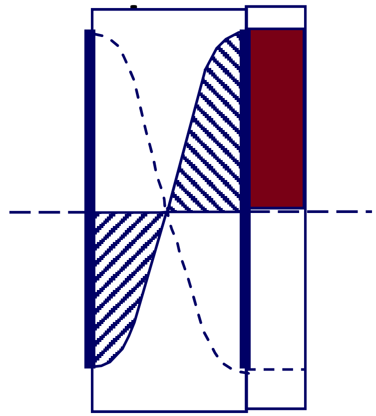
- energy storage and loss
- interfacial rheology probe
  - ↳ matrix dynamics
  - ↳ **Z** → **G** = G' + jG"

Building blocks for composite resonator

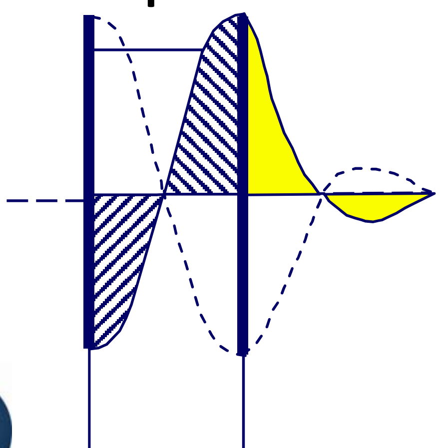
Unperturbed



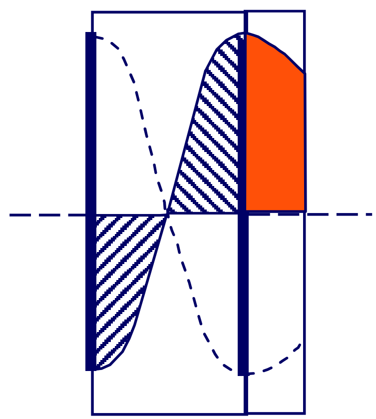
Ideal mass



Semi-infinite liquid

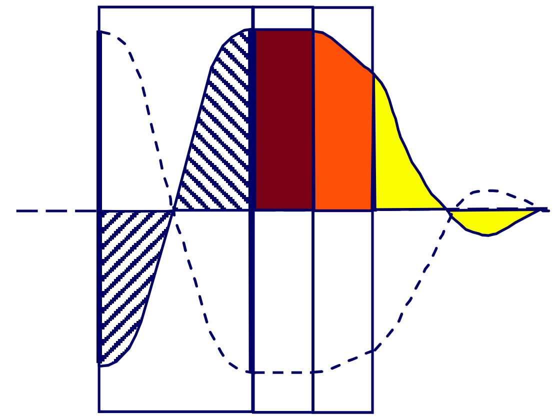


Finite viscoelastic film

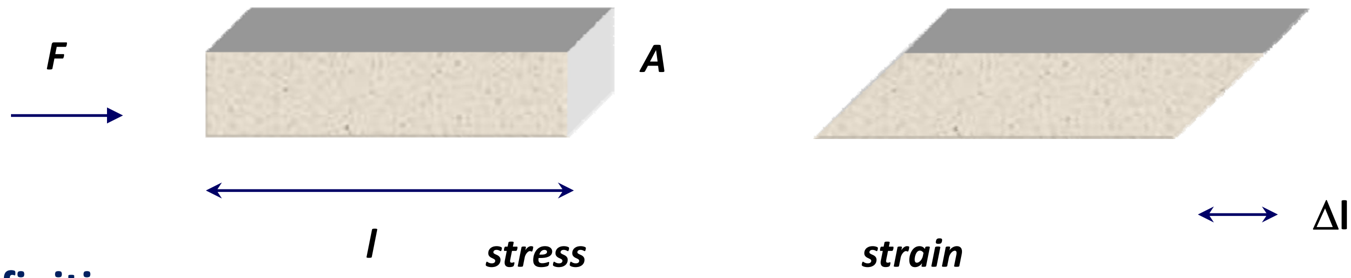


Composite resonator:

ideal mass layer
+ finite viscoelastic layer
+ semi-infinite liquid



Shear modulus

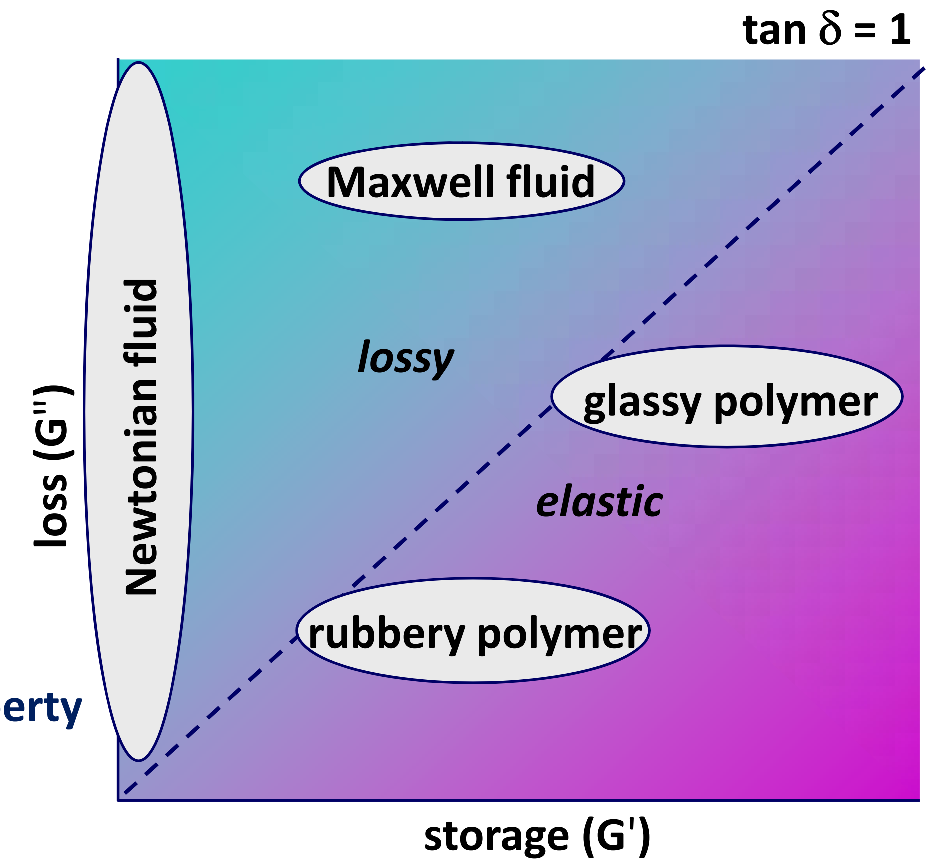


- **Definition**
  - ratio of shear stress to strain
  - "stiffness"
  - **G** = G' + jG"
- **Storage modulus (G')**
  - energy stored/recovered
- **Loss modulus (G")**
  - energy dissipated
- **Phase shift – a sample property**

$$\varphi = \gamma h_f = \omega h_f \sqrt{\rho_f}\sqrt{\frac{1+G'/|G|}{2|G|}}$$

- **Acoustic decay length – a material property**

$$\delta = 1/\gamma = \frac{1}{\omega\sqrt{\rho_f}}\sqrt{\frac{2|G|}{1-G'/|G|}}$$

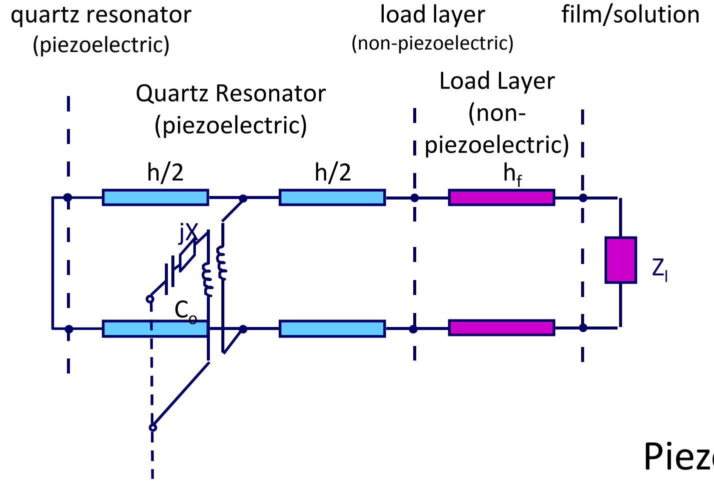


Objectives

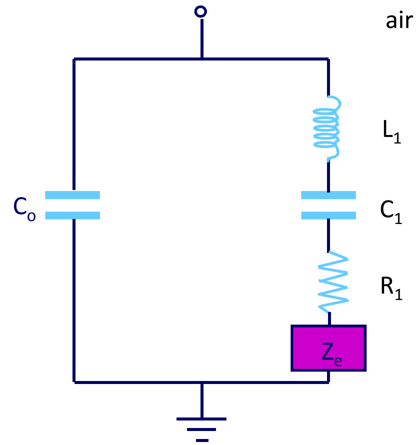
- **In situ application**
  - description of fluid damping
  - mass (population) changes of "rigid" films
- **Viscoelastic effects**
  - crystal admittance (full frequency response)
  - diagnose "rigid" *vs* viscoelastic films
  - recognition of film resonance ($\phi = \pi/2$)
- **Viscoelastic film characterisation**
  - simple model for Z_s & $Z_e = f(\mathbf{G}, h_f, \rho_f)$
  - extracting film parameters ("uniqueness of fit")
- **Models for practically useful structures**

Equivalent circuits

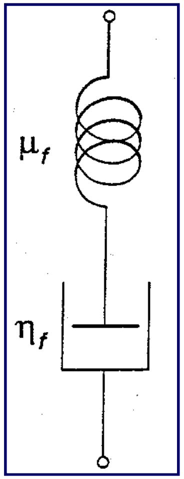
Transmission line model



Lumped element model



Maxwell model



Piezoelectric

ELECTRICAL

MECHANICAL

coupling

Voltage → charge motion (Z_e = V/I)

Stress → particle motion (Z_s = T/v)

Capacitance (C) → Mechanical elasticity of the system

Inductance (L) → Inertial mass changes

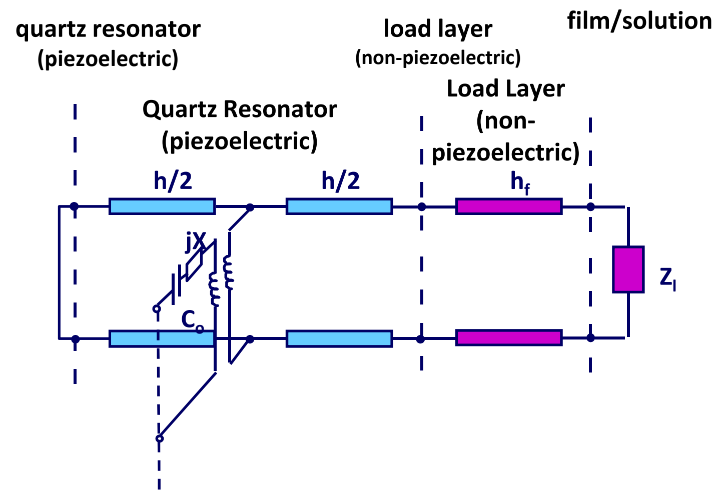
Resistance (R) → Energy dissipation (viscosity;friction)

Electrical and surface mechanical impedance

❑ Transmission line model

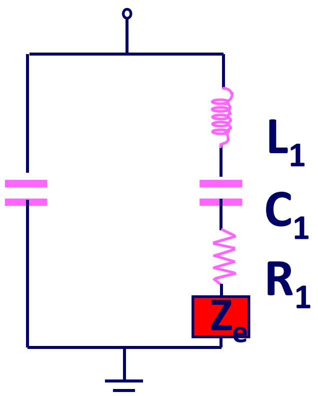
$$Z_m^1 = \frac{\varphi_q (Z_s/Z_q)}{4K^2\omega C_0}\left[1 - \frac{j(Z_s/Z_q)}{2\tan(\varphi_q/2)}\right]$$

Transmission line model



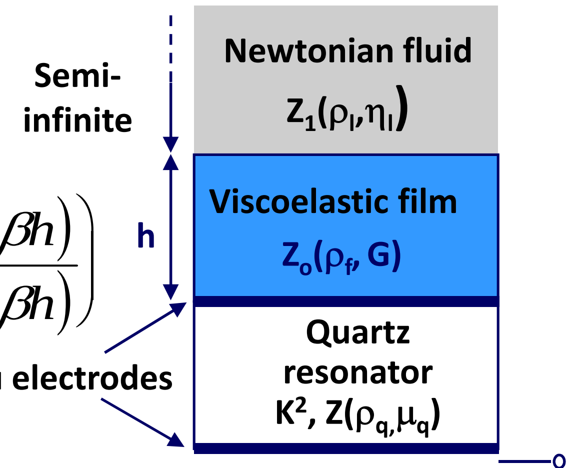
❑ Lumped element model

$$Z_m^1 \approx \frac{N\pi}{4K^2\omega C_0}\left(\frac{Z_S}{Z_q}\right)$$



❑ Surface mechanical impedance

$$Z_s = Z_0\left(\frac{Z_1 + Z_0\tanh(\beta h)}{Z_0 + Z_1\tanh(\beta h)}\right)$$



Acoustically thick film in fluid

- **General expression for Z_s**

$$Z_s = Z_0\left(\frac{Z_1 + Z_0\tanh(\beta h)}{Z_0 + Z_1\tanh(\beta h)}\right)$$

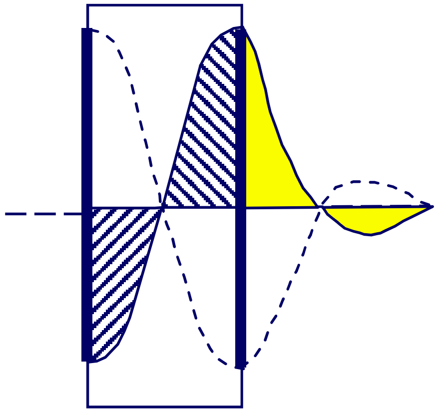
film $\quad Z_0 = (\rho_f G)^{1/2}$

liquid $\quad Z_1 = (\omega\rho\eta/2)^{1/2}(1+j)$

$$\beta = j\omega(\rho_f/G)^{1/2}$$

- **Let film thickness, h → ∞**

$$h > \delta = \frac{1}{\omega}\sqrt{\frac{2G}{\rho_f}} \qquad Z_s \approx Z_0 = (\rho_f G)^{1/2}$$



- **Surface mechanical impedance components**

$$\mathrm{Re}(Z_s) = \sqrt{\frac{\rho_f}{2}}\sqrt{|G| + G'} \qquad \mathrm{Im}(Z_s) = \sqrt{\frac{\rho_f}{2}}\sqrt{|G| - G'}$$

Acoustically thinner film in a fluid

- **Express in terms of film & fluid parameters**

$$Z_S = \left(\frac{\omega\rho\eta}{2}\right)^{1/2}(1+j) + j\omega h\rho_f + \frac{\omega^2\rho\eta h}{G} - j(\omega\rho\eta)\left(\frac{\omega\rho\eta}{2}\right)^{1/2}(1+j)\left(\frac{\omega h}{G}\right)^2 + \frac{\omega^2 h^2\rho_f}{G}\left(\frac{\omega\rho\eta}{2}\right)^{1/2}(1+j)$$

fluid — Kanazawa

film — Sauerbrey

film/fluid interaction terms

- **Express in terms of acoustic phase shift**

$$\phi = \omega h\sqrt{\frac{\rho_f}{G}}$$

$$Z_s = j\omega h\rho_f + \frac{\omega^2\rho\eta h}{G} + \left(\frac{\omega\rho\eta}{2}\right)^{1/2}(1+j)\left[1+\varphi^2\left(1-j\left(\frac{\omega\rho\eta}{\rho_f G}\right)\right)\right]$$

The fitting problem

❑ Theory

- use film parameters to calculate acoustic (electrical) impedance
  - $[h_f, \rho_f, G', G''] \rightarrow Z_S(\omega) = \mathrm{Re}(Z_S) + j\,\mathrm{Im}(Z_S)$
  - 4 input parameters $\rightarrow$ 2 output parameters...... ***no problem***

❑ Experimental application

- wish to use acoustic (electrical) impedance to calculate film parameters
  - $Z_S(\omega) = \mathrm{Re}(Z_S) + j\,\mathrm{Im}(Z_S) \rightarrow [h_f, \rho_f, G', G'']$
  - 2 input parameters $\rightarrow$ 4 output parameters ……***underdetermined***

❑ Previous (gravimetric) approaches

- restrict attention to acoustically thin films ($R_2 = 0$; $\varphi = 0$)

  $[\Delta f, Q] \rightarrow [h_f, \rho_f]$ …… ***no viscoelastic insight***
- acoustically thick films
  - assume $\rho_f = \rho_S$, ρ_P or 1
  - assume $G' \ll G''$ or value for loss tangent (G'/G'')
  - separately estimate h_f ……***assumptions to reduce to 2 parameter problem***
  - use higher harmonics ….. ***may assume information sought***

Strategy

First attempt

- 4 parameter fit, with “soft” constraints on 2 parameters
  - film density: $\rho_S \leq \rho_f \leq \rho_P$ or $\rho_S \geq \rho_f \geq \rho_P$
  - film thickness: $h_f \geq h_f^0$ — h_f^0 defined by Q and ρ_P
  - fit impedance response: $Z_S(\omega) \rightarrow [G', G'']$

……….…***imperfect***

New approach

- split into two separate 2-parameter problems, each fully determined

  acoustically thin film: $[\Delta f, \text{“X”}] \rightarrow [h_f, \rho_f]$

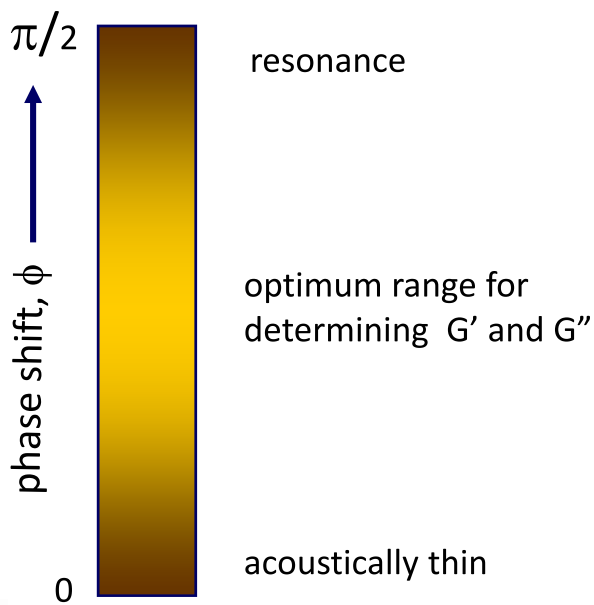
  - assume film homogeneity: $h_f \ \alpha$ “X”; ρ_f = constant
  - acoustically thick film: $Z_S(\omega) \rightarrow [G', G'']$

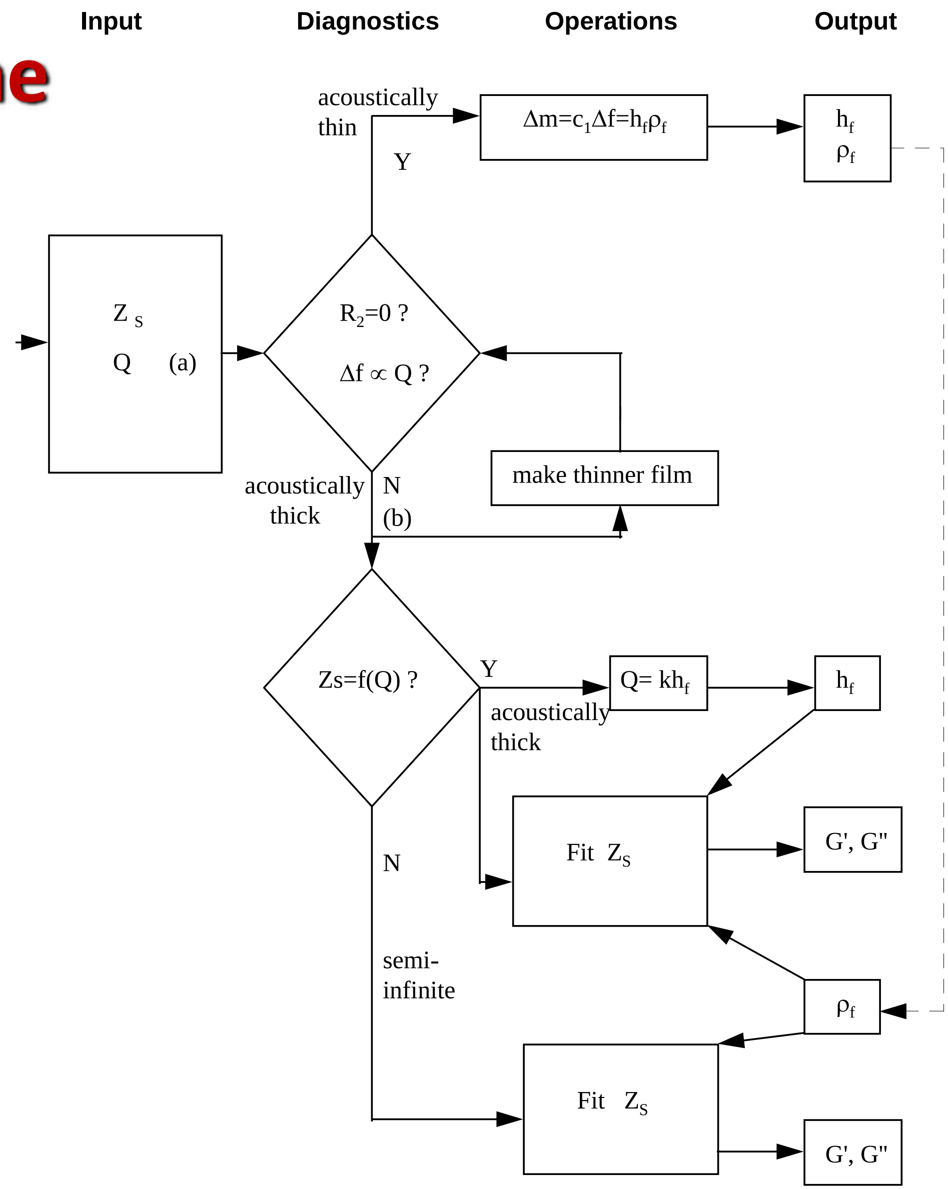
……….. ***unique fit***

[“X” = any measure of coverage, e.g. electrochemical charge Q]

“Unique fit” routine

Film characterized by four parameters: h_f, ρ_f, G', G''





See: Jackson: Anal. Chem., 73 (2001), 540.

2.1 Materials

		Phenomena								
Material class	Examples ⇓	Adsorption /desorption*	UPD	Bulk deposition /dissolution	Molecular recognition	Complexation	Ion exchange**	Wetting / solvation	Viscoelasticity	Stress / mechanical motion
	Presenter*** ⇒	RH	RH	HP	HP	RH	HP	RH	RH	RH?
Halides	Cl^-, Br^-, I^- (SCN^-, CN^-)	✓								
Thiols (SAMs)	$C_nH_{2n+1}SH$, ϕSH	✓			✓	✓		✓		
Organics	Calixarenes, DNA, antibodies	✓			✓	✓				
Dendrimers		✓			✓	✓				
Supramolecular systems				✓						
LbL films	?	✓								
Biological cells				✓	✓				✓	
Nanostructured films	PS/Pt			✓				✓		
Metals	Ag, Au, Cu, Pb, Sb ...		✓	✓				✓		✓
Metal (hydr)oxides	WO_3, IrO_2, $Ni(OH)_2$			✓			✓	✓		✓
Inorganic salts	Prussian Blue & analogues			✓			✓			
Semiconductors	CdSe, CdTe, ...??		✓	✓						✓
Insulating polymers	PPO & derivatives			✓						
Redox polymers	PVF, Os(PVP)			✓		✓	✓	✓	✓	✓
Conducting polymers	PPy, PAni, PT, PCz, PAz, PEDOT & derivatives			✓		✓	✓	✓	✓	✓

* Multiple examples illustrate monolayer vs multilayer films
** Use multiple examples to illustrate kinetics vs thermodynamics, anion vs. cation, special case of proton
*** Colour code indicates suggested presenter: HP or RH

University of Leicester

UPMC PARIS UNIVERSITAS

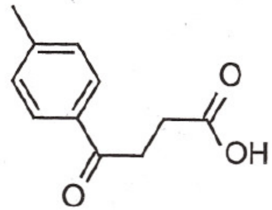
Adsorption …

… and related phenomena

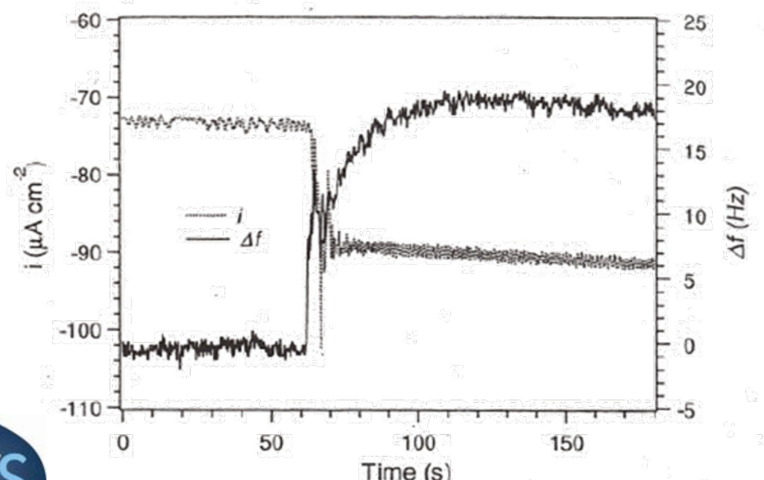
CNRS

Molecular adsorption

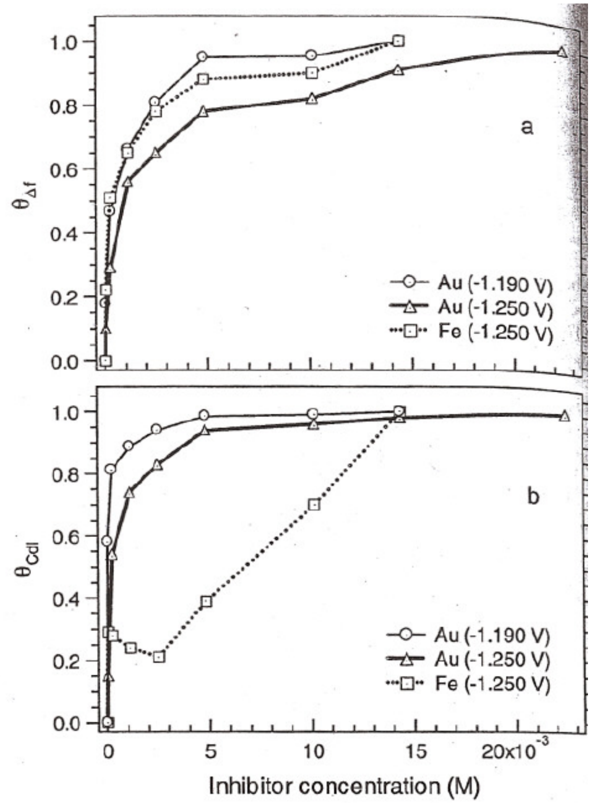
- Sophisticated EQCM / RDE
  - controlled mass transport
  - Au & Fe surfaces
  - adsorption of ω-benzoyl alkanoic acid
    - family of corrosion inhibitors



- Inject inhibitor (1.1 ⇨ 2.5 mM)
  - monitor current & frequency
  - thin film, so gravimetric response



- Vary inhibitor concentration
  - determine isotherm
  - gravimetric & EIS routes



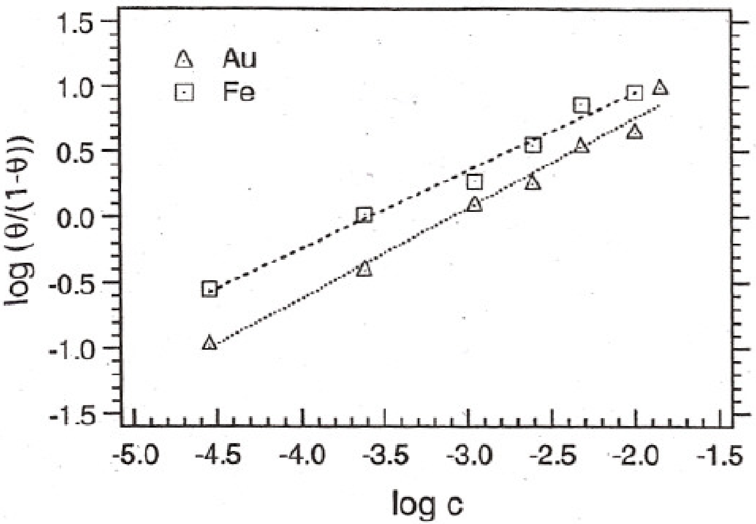
See: Landolt, *J. Electrochem. Soc.*, 148, 2001, B228.

Molecular adsorption

- Consider various models
  - Langmuir-Freundlich works best

$$\theta = \frac{(Kc)^h}{1 + (Kc)^h}$$

  - determine adsorption energetics

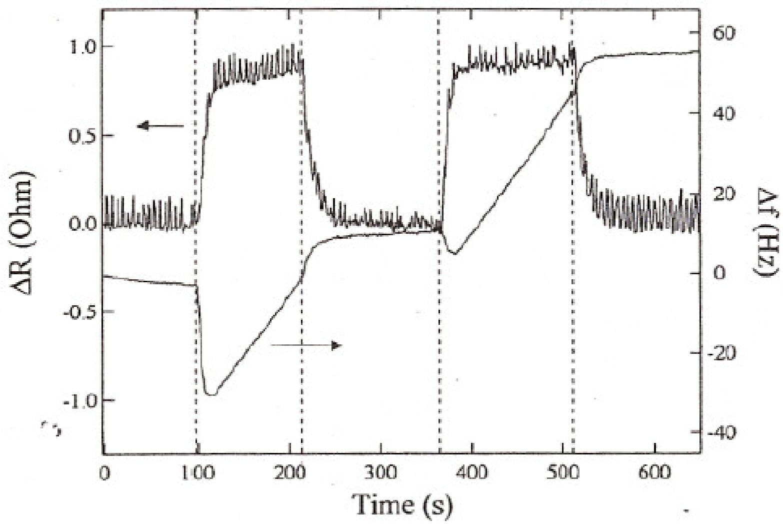


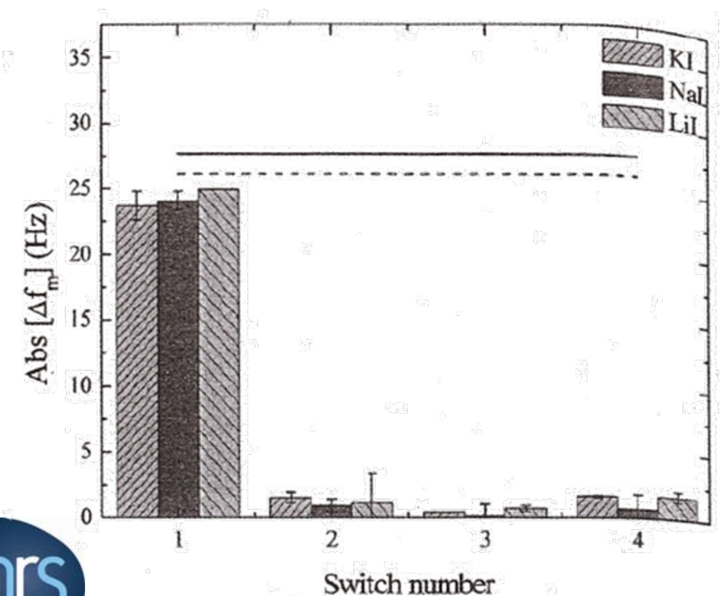
		Fe	Au
Langmuir-Freundlich	h	0.6	0.7
	K (L/mol)	3903	1250
	ΔG°_{ads} (kJ/mol)	−30.46	−27.63
	R^2	0.98	0.99
Multisite Langmuir	n	2.0	2.1
	L (L/mol)	8437	3157
	ΔG°_{ads} (kJ/mol)	−32.37	−29.93
	R^2	0.95	0.97
Flory-Huggins	x	2.0	2.1
	K (L/mol)	3216	1018
	ΔG°_{ads} (kJ/mol)	−29.98	−27.12
	R^2	0.95	0.97

See: Landolt, *J. Electrochem. Soc.*, 148, 2001, B228.

Adsorption & reaction

- EQCM / flow cell
  - controlled mass transport
  - Au surface exposed to I^-
- Changes at surface & in solution
  - solution viscosity alters ΔR
  - surface adsorption alters Δm
    - gravimetric interpretation





- Alternating solutions
  - 0.1 M $NaClO_4$ / 0.1 M $NaClO_4$ + 0.05 M LiI
  - E = 0.2 V (sufficient to dissolve "Au")
- Adsorption of iodide: $\Delta m \sim$ monolayer
- Oxidation of Au(0) to Au(I)
  - dissolution as $[AuI_2]^-$
  - at 0 V, no Au oxidation

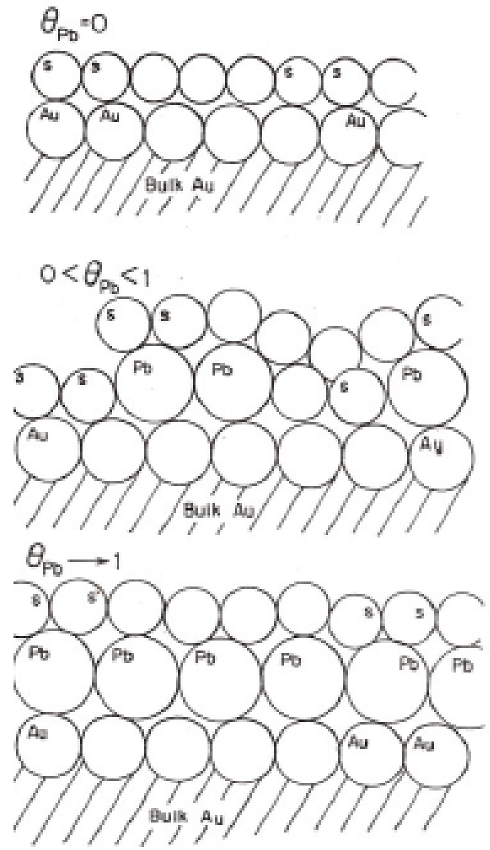
See: Landolt, *J. Electrochem. Soc.*, 150, 2003, B504.

Underpotential deposition (UPD)

UPD: the phenomenon

❑ Observation in electrodeposition of one metal another (“foreign”) metal surface

- some deposition occurs at a more positive potential than the reversible potential
- i.e. more readily than predicted by the Nernst equation
- many reported examples
  - Ag^{+}, Cu^{2+}, Hg^{2+}, Pb^{2+} on Pt
  - Cd^{2+}, *Tl^{+}*, Bi^{3+}, Zn^{2+} on Au
  - Pb^{2+}, Bi^{3+}, Sn^{3+}, Zn^{2+} on Ag



❑ Anodic potential shift

- related to difference in metal work functions
- usually: $\Delta E_p = \alpha\ \Delta\Phi$, where $\alpha = 0.5$ V eV^{-1}

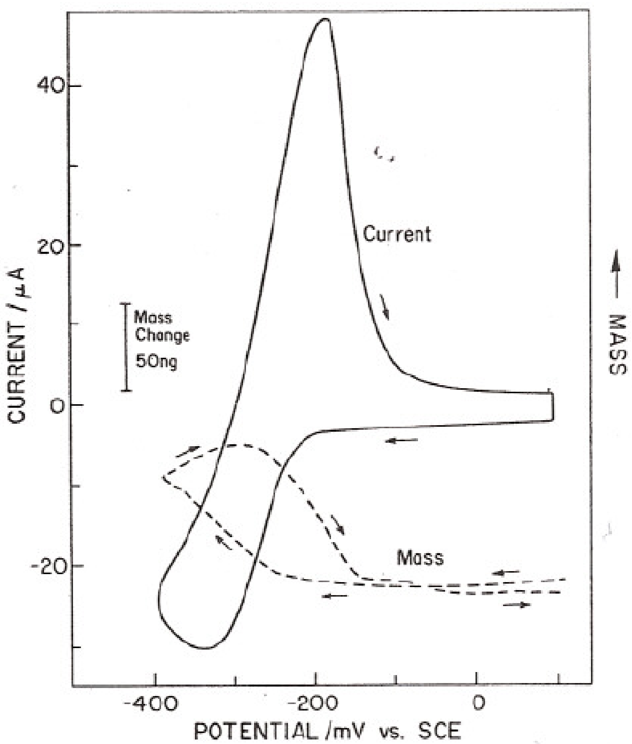
❑ Extent of UPD

- generally limited to monolayer

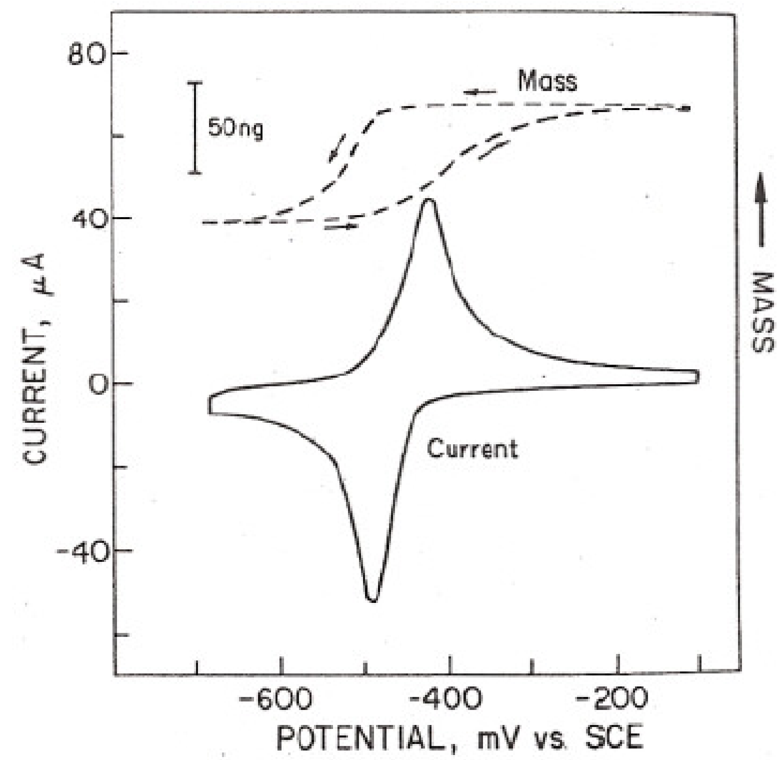
See: Kolb, *J. Electroanal. Chem.*, 54, 1974, 25; Swathirajan, *J.Electroanal. Chem.*, 28, 1983, 865; Hepel, *J. Electroanal. Chem.*, 266, 1989, 409; Conway, *J. Electroanal. Chem.*, 287, 1990, 13.

EQCM experiments for Pb UPD at Ag

0.2 mM Pb^{2+} / 10 mM acetate / pH 4.9
v = 50 mV s^{-1}



0.027 mM Pb^{2+} / 0.1 M boric acid / pH 9.1
v = 50 mV s^{-1}



- Pb^{2+} reduction:
  - electrode mass increases
  - Pb^0 deposited from solution …

    … from cationic species

- Pb^{2+} reduction:
  - electrode mass *decreases*
  - Pb^0 generated on surface …

    … from pre-adsorbed anionic species

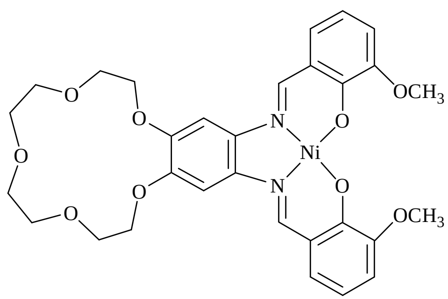
    observe *ejection of borate ligands*

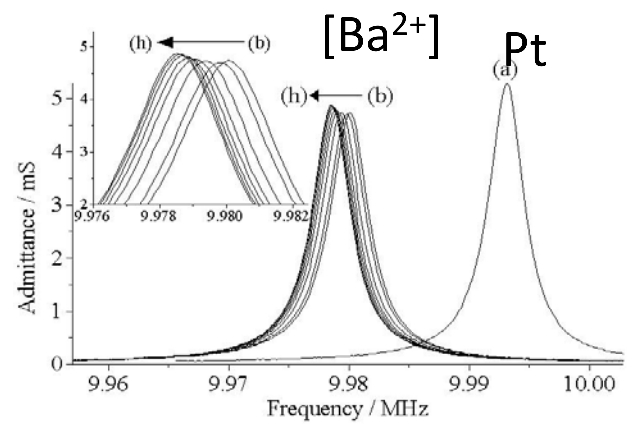
See: Hepel, *J. Electroanal. Chem.*, 266, 1989, 409.

Surface complexation chemistry

Metal ion complexation by surface-bound ligands

- [Ni(3-MeOsalophen-b-15-c-5)]
  - films electropolymerized on Pt
  - here, Γ = 77 nmol cm^{-2}
  - expose to Ba^{2+} (varying concentration)
  - voltammetry + admittance spectra



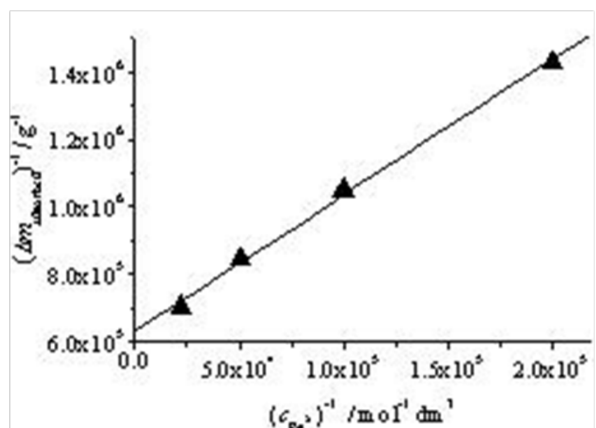


- Frequency decrease with [Ba^{2+}]
  - metal complexation by crown ether
- Admittance slightly decreased
  - small viscoelastic effect (ca. 3%)
  - interpret gravimetrically (Sauerbrey)

Langmuir isotherm

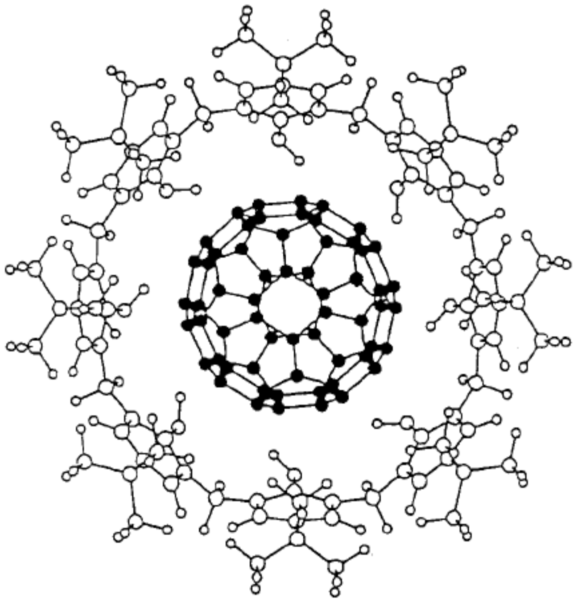
$$\frac{1}{\Delta m} = \frac{1}{\Delta m_{\infty}} + \frac{1}{\Delta m_{\infty} K c}$$

K = 1.56 x 10^5 mol^{-1} dm^3



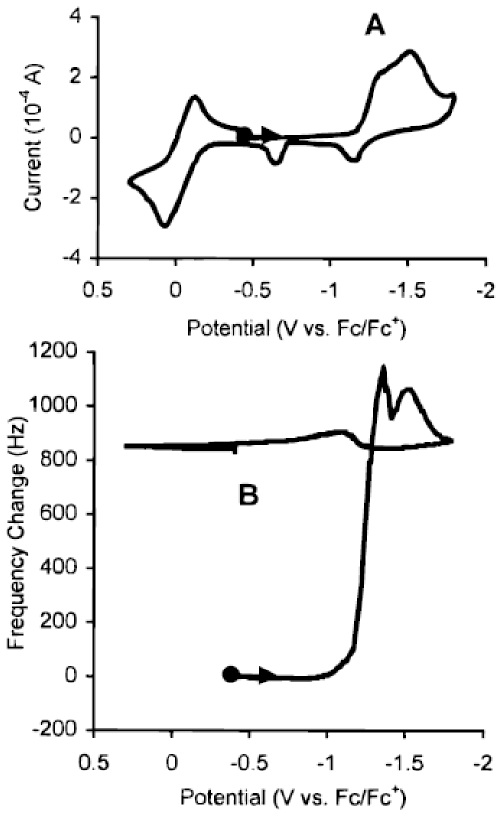
See: Martins, *Chem. Comm.*, 1998, 4146

Guest-host surface electrochemistry



- *p-tert*-butylcalix[8]arene-C_{60} complex
  - films cast on Au electrode
  - voltammetry + QCM + SECM
- C_{60} reduction results in complex decomposition
  - electrode mass decreases
    - ⇘ C_{60} lost to solution
  - electrode mass oscillations
    - ⇘ competing TBA^+ entry

- Au/calixarene-C_{60} film
  - 0.1 M $TBABF_4/CH_3CN$
  - v = 50 mV s^{-1}

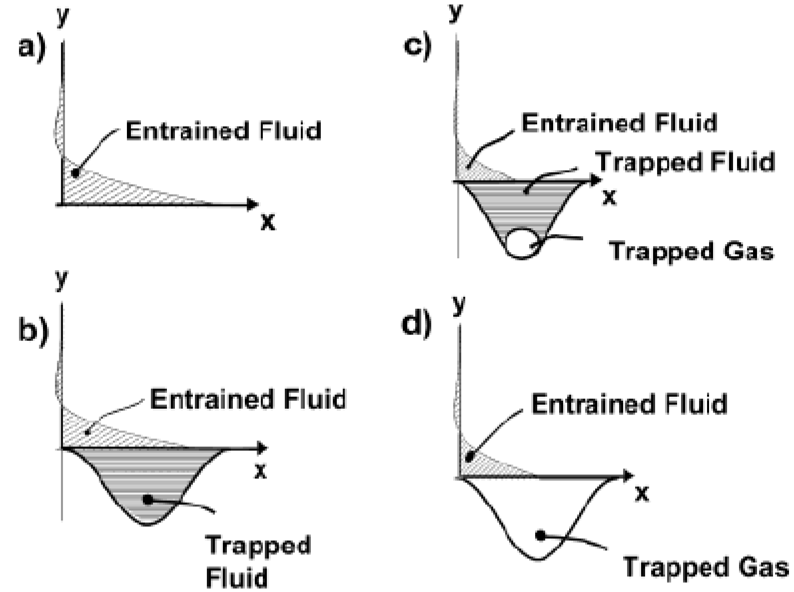


See: Bard, *Anal. Chem.*, 70, 1998, 4146

Interfacial wetting

Simple model

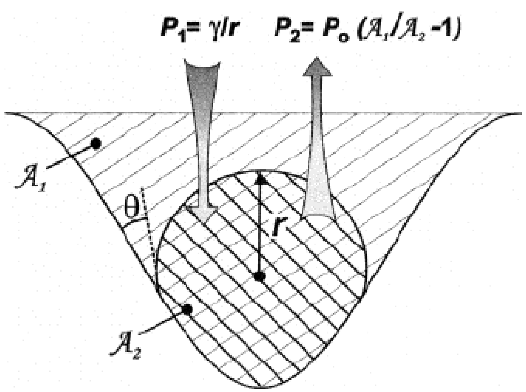
- Simplest case
  - surface (electrode) perfectly contacted by fluid
  - true for atomically smooth surface
    - not impossible, but practically rare



- Complete wetting:

$$-\frac{\Delta f}{\rho} = \frac{f_s^{3/2}}{N(\rho_q\mu_q\pi)^{1/2}}\left(\frac{\eta}{\rho}\right)^{1/2} + \frac{\pi f_s^{2} h}{N(\rho_q\mu_q)^{1/2}}$$

- Model surface
  - sinusoidal corrugations



- Real cases
  - gas / vapour trapped in surface features
    - extent dependent on surface
    - balance of interfacial forces

See: Theisen, *Anal. Chem.*, 76, 2004, 796.

Calculated meniscus ("bubble") profile

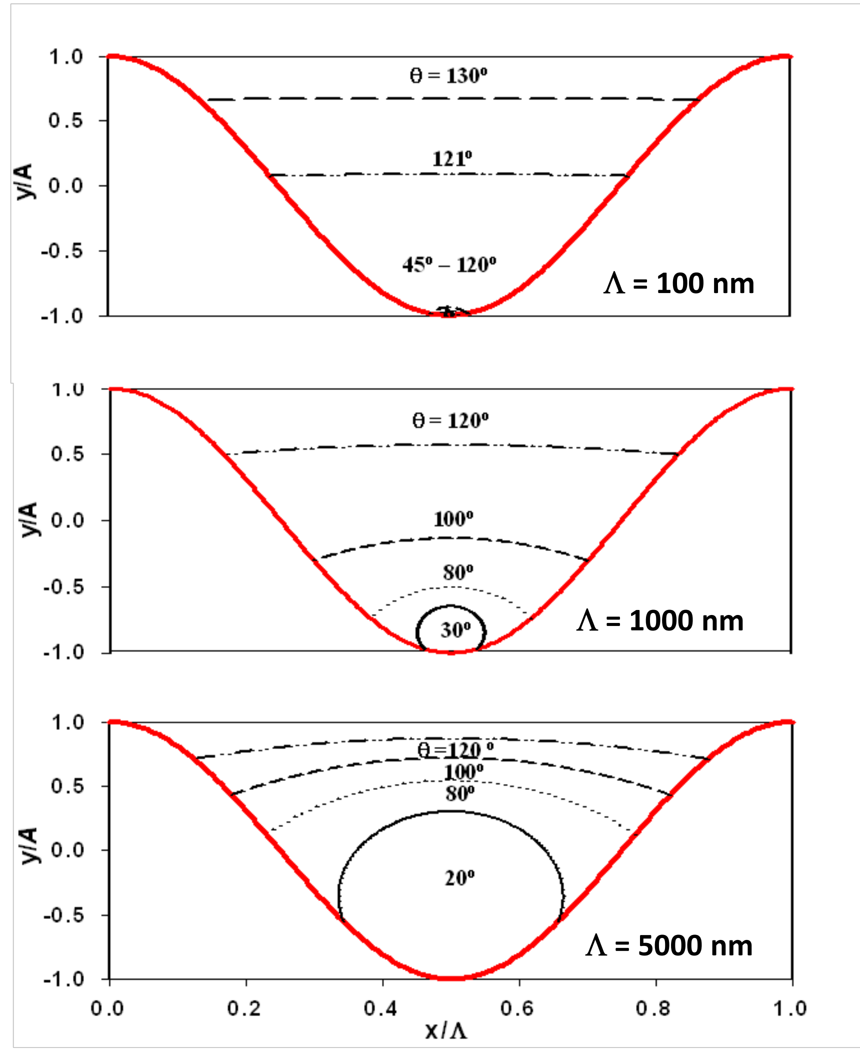
- At any fixed roughness (Λ)*:
  - increasing θ stabilises bubble
  - hydrophobicity drives de-wetting

- Wetting/de-wetting transition centred at $\theta \approx 100^{o}$ –120^{o}

- Decreasing feature size
  - shifts transition to higher θ
  - sharpens transition

  $\Delta\theta < 1^{o}$ for $\Lambda \leq 100$ nm

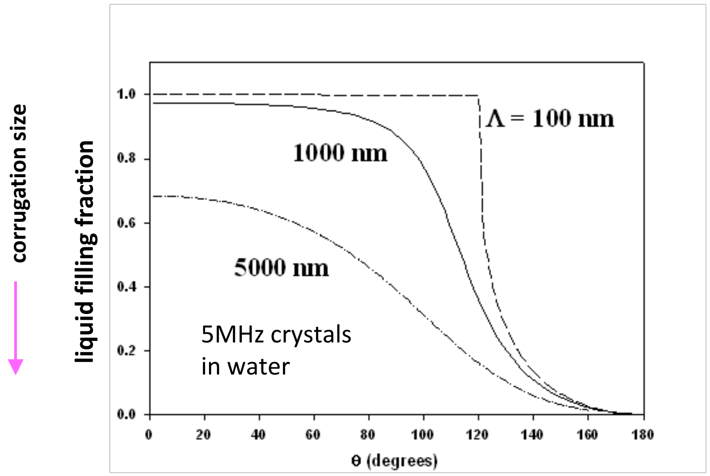
*Fixed "spherical abrasive" geometry: $h=\Lambda/2\pi$



See: Theisen, *Anal. Chem.*, 76, 2004, 796.

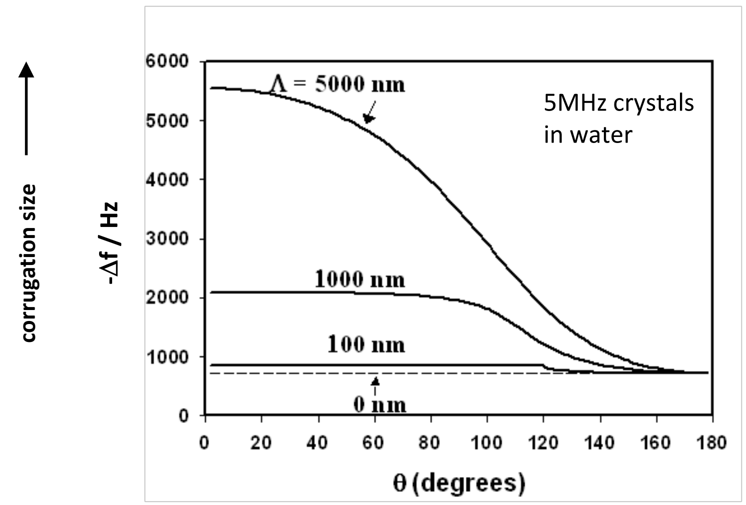
Partially de-wetted QCM response

- Integrate gas/fluid profiles to obtain fractional liquid filling of surface features



- Highlights sharpening of de-wetting transition of small surface features
- Responses are "normalised" with respect to feature size

- Input fluid density and assume synchronous motion
  - trapped fluid-derived Δf responses

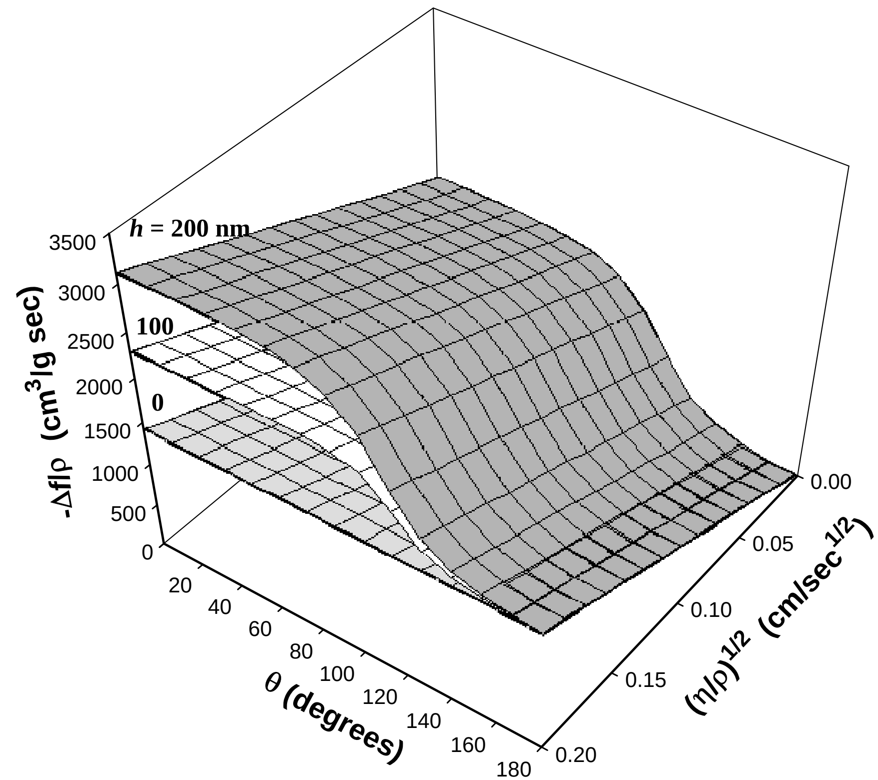


- Kanazawa result ("smooth" surface) provides baseline
- Responses not "normalised" with respect to feature size

See: Theisen, *Anal. Chem.*, 76, 2004, 796.

The complete picture

- QCM response depends on
  - surface topography (h)
  - fluid properties (η, ρ)
  - interfacial energetics (θ)
- For given topography (h) "master" surface of Δf/ρ



low θ → complete wetting → large variation with h

high θ → incomplete wetting → little variation with h

θ and $(\eta, \rho)^{1/2}$

- inter-related: mixed fluids
- separable: surfactants

See: Theisen, *Anal. Chem.*, 76, 2004, 796.

Full fluid mechanics approach

- QCM response on fluid & interface depends on characteristics sizes of:
  - vertical surface roughness (h ~ 10-100 nm)
  - lateral surface roughness (l ~ 10 nm – 1 μm)
  - fluid decay length (δ ~ 0.1-1 μm)
  - wavelength in quartz (λ ~ 1 mm)
- Generally:

  $h < \delta < \lambda$
- What about h & l?

- "Slight" roughness: h < l
  - vertical < lateral surface roughness
  - effect of roughness greatest for low fluid viscosity

- "Strong" roughness: h > l
  - vertical > lateral surface roughness
  - frequency shift independent of viscosity
  - frequency shift dependent on volume fraction & fluid density

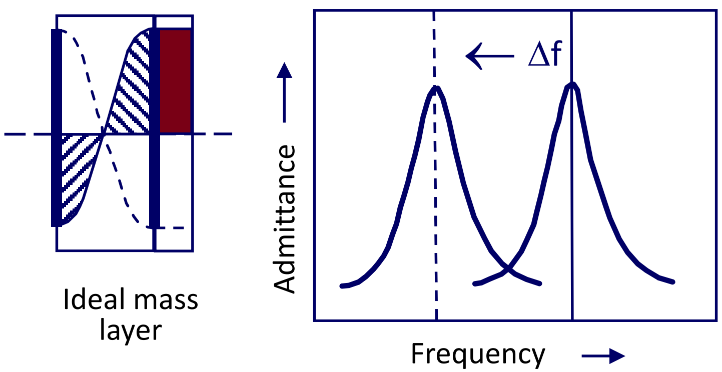
See: Urbakh, Langmuir, 10, 1994, 2386.

Viscoelasticity

Admittance spectra as a diagnostic tool

❑ Acoustically thin ("rigid") film

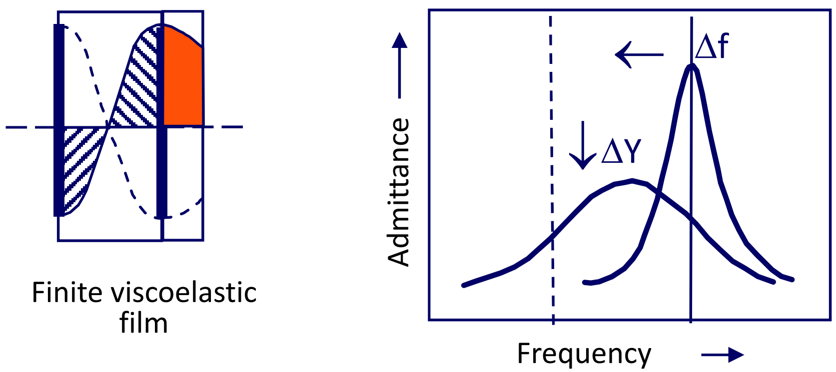
- no acoustic deformation



- energy storage, but no loss
- gravimetric probe of surface populations
  - film deposition
  - mobile species exchange
  - $\Delta f = -\left(\frac{2f_0^2}{\rho_q v_q}\right)\frac{\Delta m}{A}$ *gives* $\Delta\Gamma$

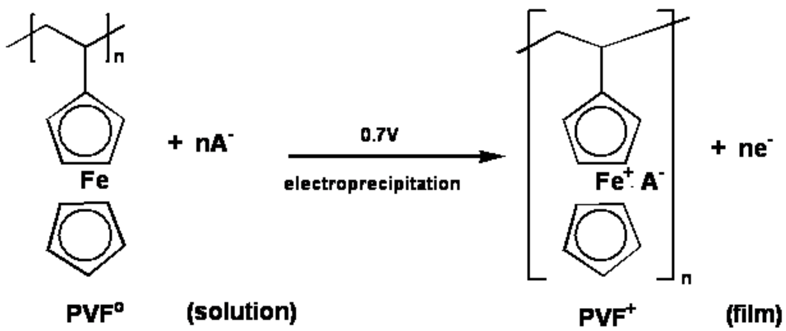
❑ Acoustically thick (viscoelastic) film

- acoustic deformation

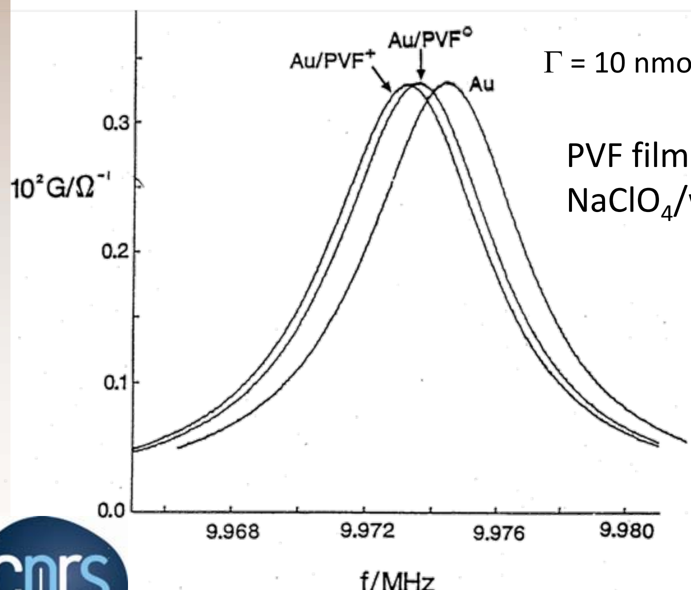


- energy storage and loss
- interfacial rheology probe
  - matrix dynamics
  - **Z** → **G** = G' + jG"

Polyvinylferrocene redox cycling



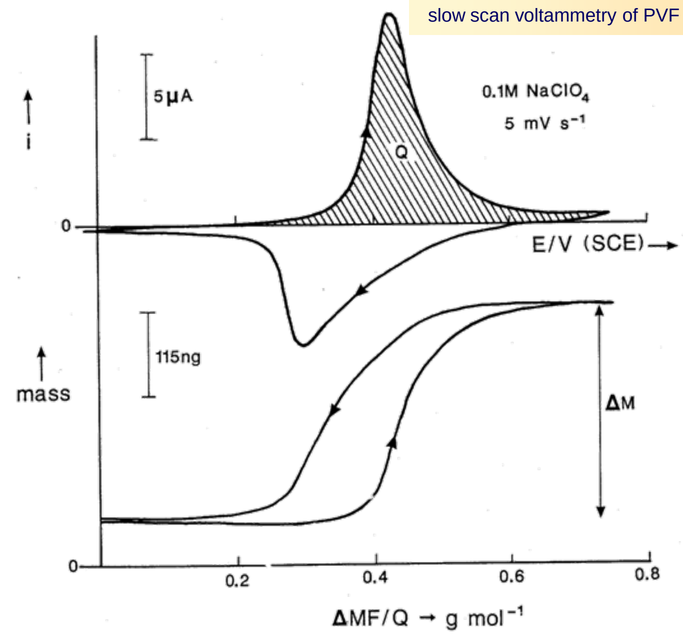
- **Typical EQCM experiment**
  - Low concentration:
    anion and solvent
    entry upon oxidation
  - High concentration:
    anion, solvent and salt
    entry upon oxidation



Γ = 10 nmol cm^{-2}

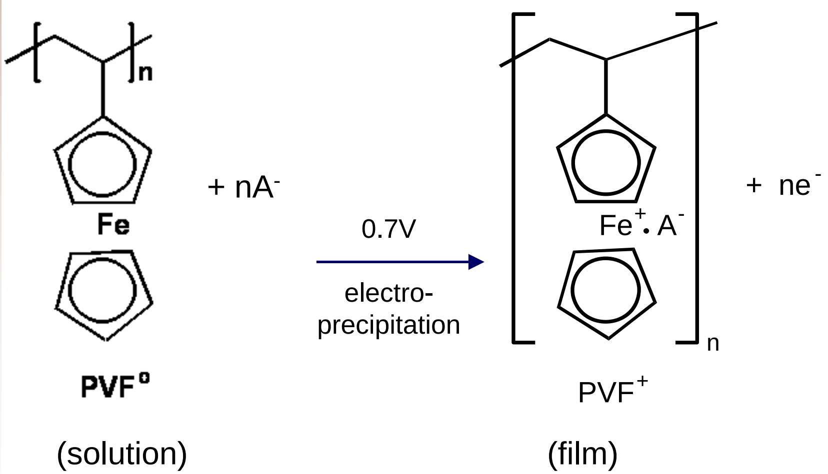
PVF films in 0.1M $NaClO_4$/water are rigid

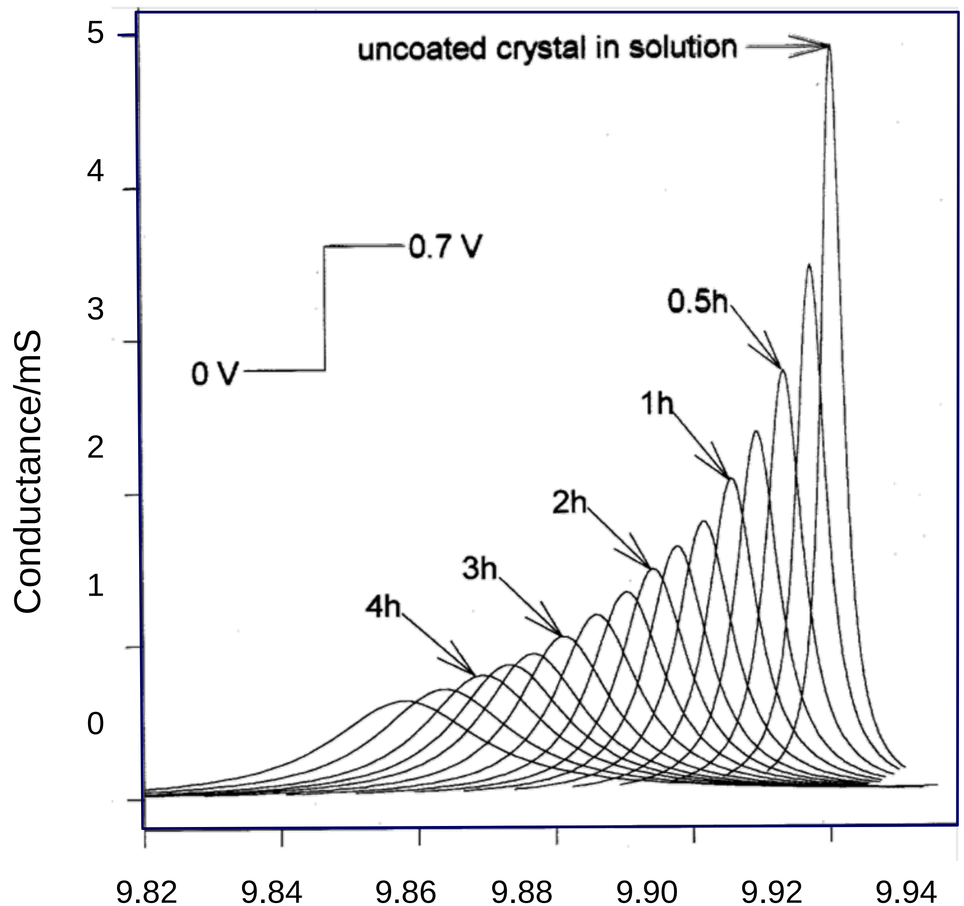
slow scan voltammetry of PVF



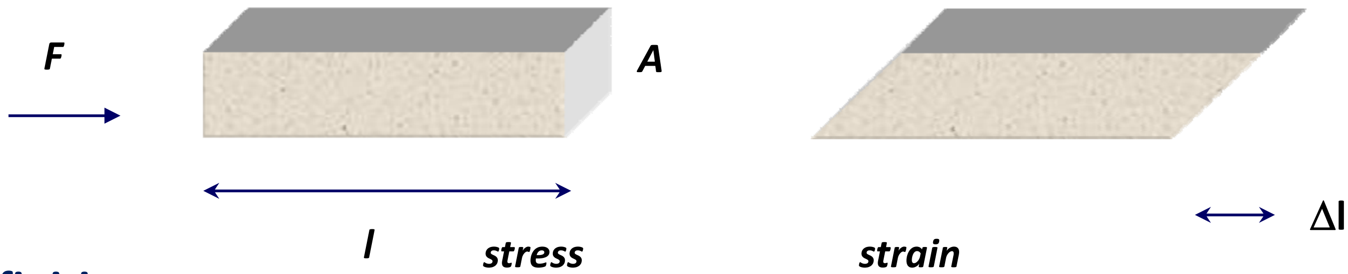
PVF Electroprecipitation

- **Principle**
  - PVF^0 is a soluble in CH_2Cl_2,
  - PVF^+A^- is not
- **Process**
  - electrochemically oxidize
  - $PVF^0 \rightarrow PVF^+$





Shear modulus

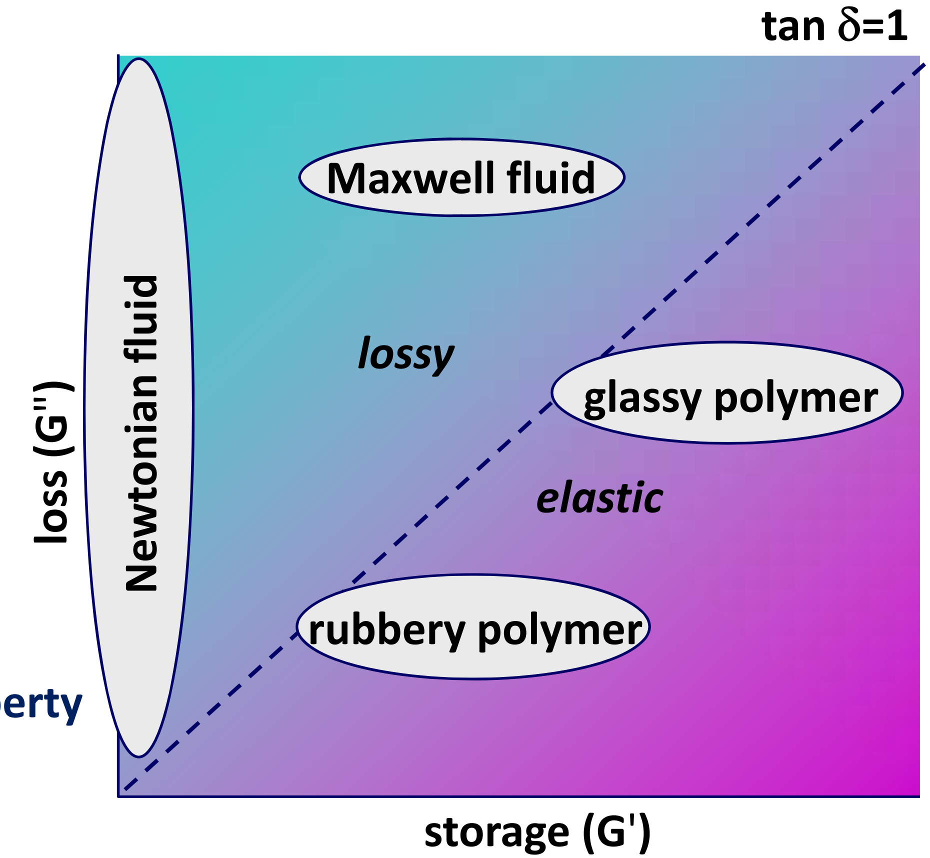


- **Definition**
  - ratio of shear stress to strain
  - "stiffness"
  - **G** = G' + jG"
- **Storage modulus (G')**
  - energy stored/recovered
- **Loss modulus (G")**
  - energy dissipated
- **Phase shift – a sample property**

$$\varphi = \gamma h_f = \omega h_f \sqrt{\rho_f} \sqrt{\frac{1 + G'/|G|}{2|G|}}$$

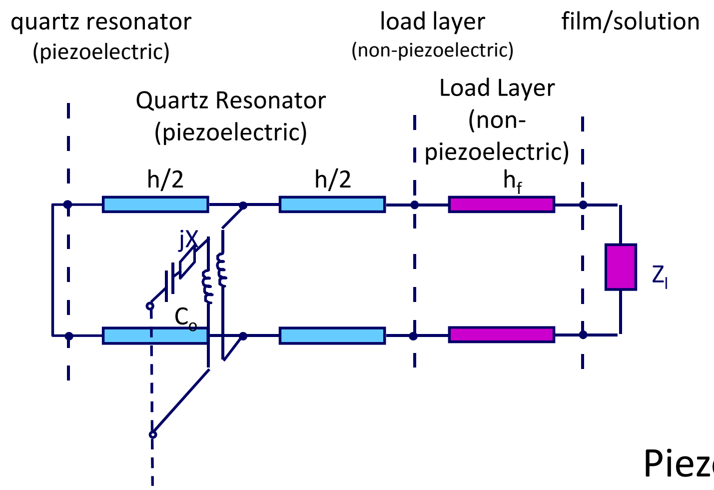
- **Acoustic decay length – a material property**

$$\delta = 1/\gamma = \frac{1}{\omega \sqrt{\rho_f}} \sqrt{\frac{2|G|}{1 - G'/|G|}}$$

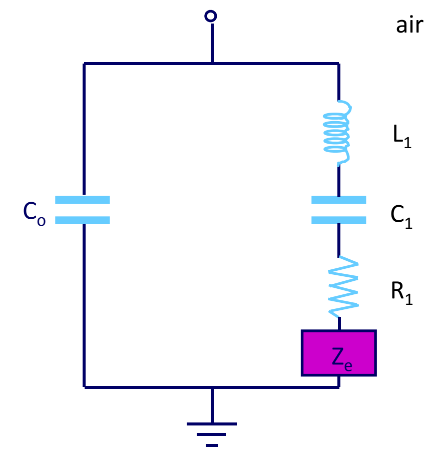


Equivalent circuits

Transmission line model



Lumped element model



Piezoelectric

ELECTRICAL

MECHANICAL

coupling

Voltage → charge motion (Z_e = V/I)

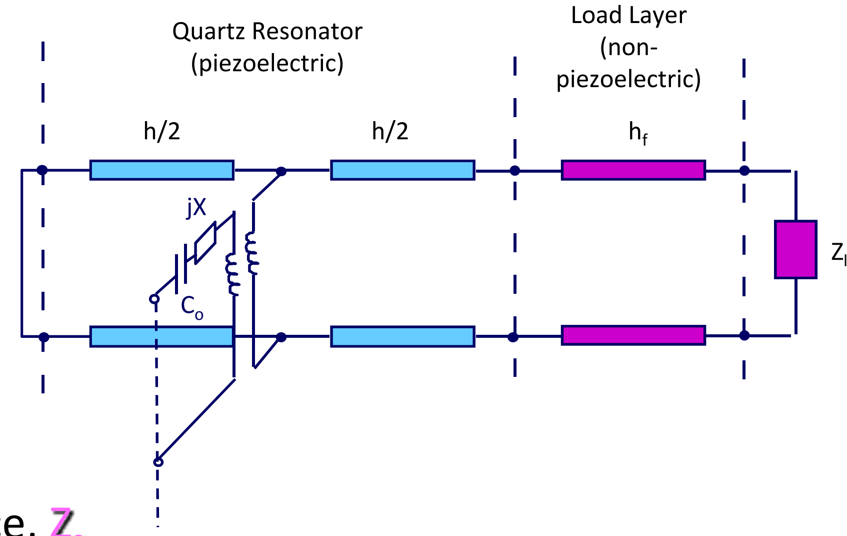
Stress → particle motion (Z_s = T/v)

Capacitance (C) → Mechanical elasticity of the system

Inductance (L) → Inertial mass changes

Resistance (R) → Energy dissipation (viscosity;friction)

Model



❑ Composite resonator

❑ Strategy

- reflectance, S
  - electrical impedance, Z_e
    - surface mechanical impedance, Z_s
      - shear modulus, G = G' + jG"

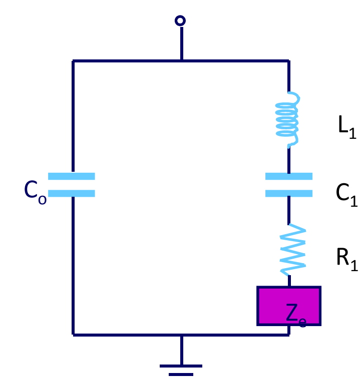
❑ Implementation

- transmission line model:

$$Z_e = \frac{N\pi}{4K^2\omega_s C_0}\left(\frac{Z_s}{Z_q}\right)\left(1 - \frac{j(Z_s/Z_q)}{2\tan(\omega\pi/2\omega_s)}\right)^{-1}$$

- low loading near resonance:

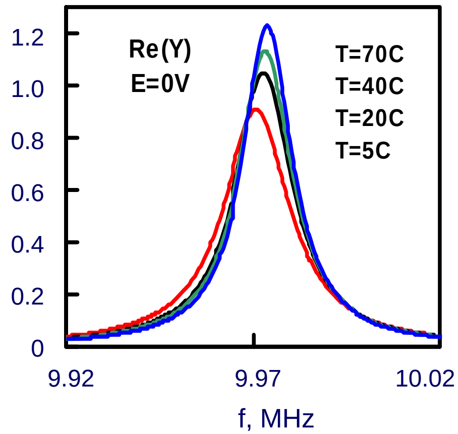
$$Z_e = \frac{N\pi}{4K^2\omega_s C_0}\left(\frac{Z_s}{Z_q}\right) = R_2 + j\omega L_2$$



lumped element model

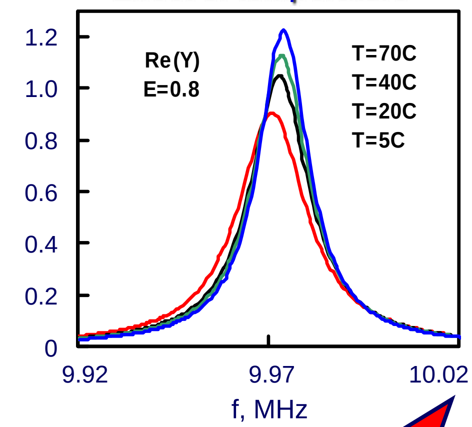
PEDOT p-doping and undoping

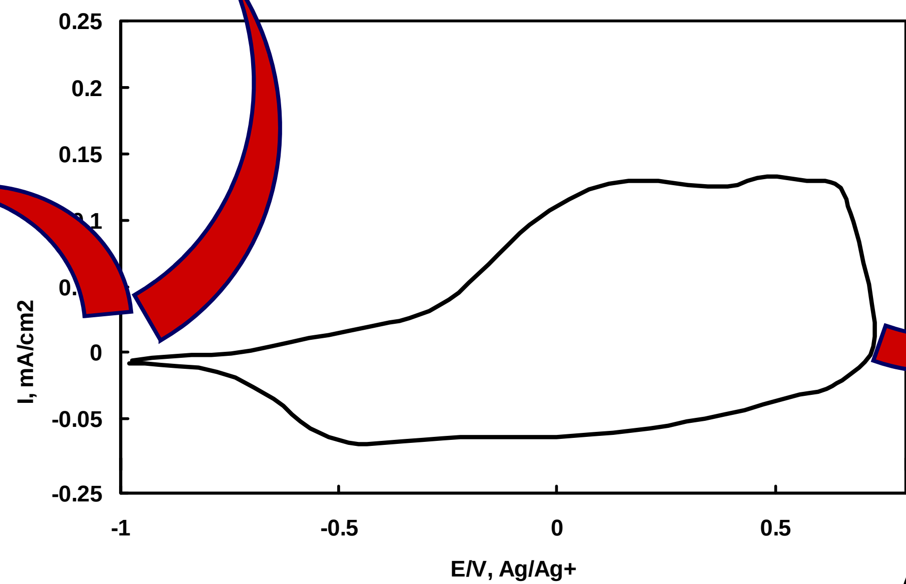
Effect of temperature



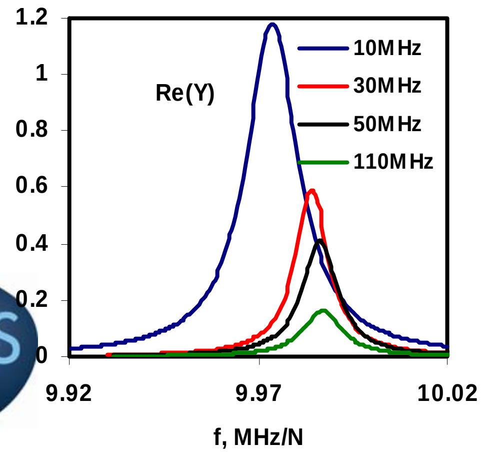
Fundamental (10 MHz)

Effect of temperature

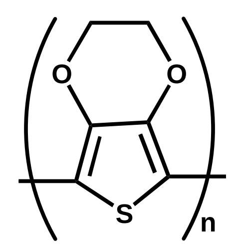




Effect of timescale



T = 20 °C



The problem

- Theory
  - use film parameters to calculate acoustic (electrical) impedance

    $[h_f, \rho_f, G', G''] \Rightarrow Z_S(\omega) = \mathrm{Re}(Z_S) + j\,\mathrm{Im}(Z_S)$

    4 input parameters ➡ 2 output parameters ***...... no problem***
- Experimental application
  - wish to use acoustic (electrical) impedance to calculate film parameters

    $Z_S(\omega) = \mathrm{Re}(Z_S) + j\,\mathrm{Im}(Z_S) \Rightarrow [h_f, \rho_f, G', G'']$

    2 input parameters ➡ 4 output parameters ***......underdetermined***
- Previous (gravimetric) approaches
  - restrict attention to acoustically thin films ($R_2 = 0$; $\phi = 0$)
  - $[\Delta f, Q] \Rightarrow [h_f, \rho_f]$ ***...... no viscoelastic insight***
  - acoustically thick films

    assume $\rho_f = \rho_S$, ρ_P or 1

    assume $G' \ll G''$ or value for loss tangent (G'/G'')

    separately estimate h_f

    ......assumptions to reduce to 2 parameter problem

    use higher harmonics ***..... may assume information sought***

Strategy

First method

- 4 parameter fit, with "soft" constraints on 2 parameters
  - film density: $\rho_S < \rho_f < \rho_P$ or $\rho_S > \rho_f > \rho_P$
  - film thickness: $h_f > h_f^0$ h_f^0 defined by Q and ρ_P
  - fit impedance response: $Z_S(\omega)$ ➡ [G′, G″]

...........imperfect

Better approach

- split into two separate 2-parameter problems, each fully determined

  acoustically thin film: [Δf, "X"] ➡ [h_f, ρ_f]
  - assume film homogeneity: h_f α "X"; ρ_f = constant
    - acoustically thick film: $Z_S(\omega)$ ➡ [G′, G″]

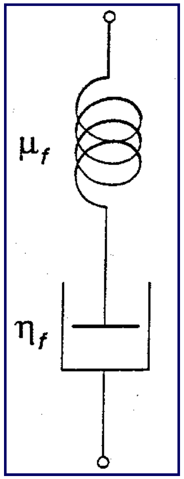
.... unique fit

["X" = any measure of coverage, e.g. electrochemical charge Q]

See: Jackson, Anal. Chem., 73, 2001, 540.

Mechanical models for viscoelasticity

Maxwell model



Stress (T) and strain (S): G = T/S

Elastic deformation of film: T = μS (*Hooke's Law)*

model: spring, stiffness m_f

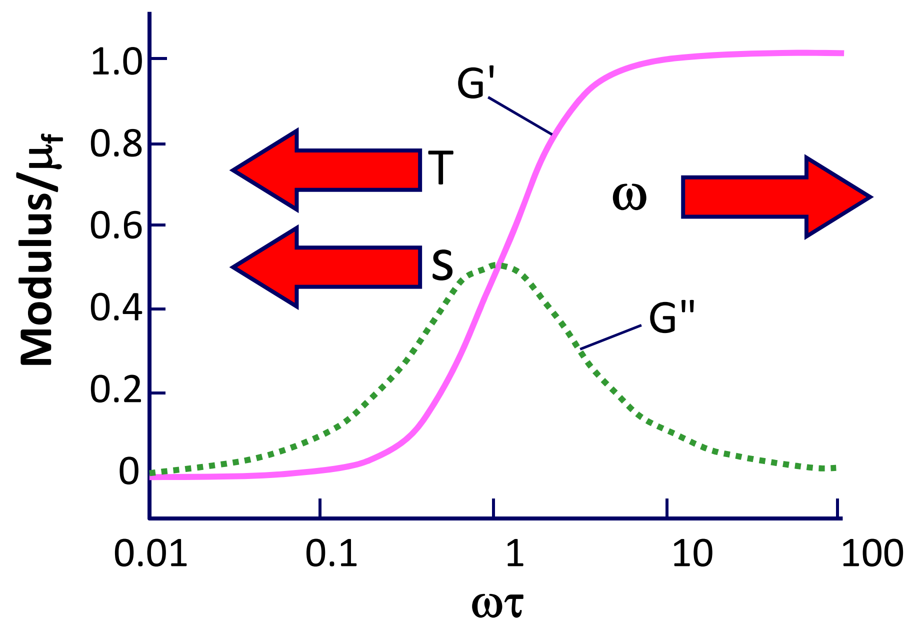
Viscous dissipation of energy: T = η(dS/dt) (Newtonian fluid)

model: dashpot, viscosity η_f

$$\tau = \frac{\eta_f}{\mu_f} = \tau_0 \exp[\Delta H_a / RT]$$

$$G' = \frac{G_0 + \omega^2\tau^2 G_\infty}{1+\omega^2\tau^2}$$

$$G'' = \omega\tau \frac{G_\infty - G_0}{1+\omega^2\tau^2}$$



τ = f(T) ... so G' & G" = f(T)

Mechanical properties: importance of timescale

Low temperature

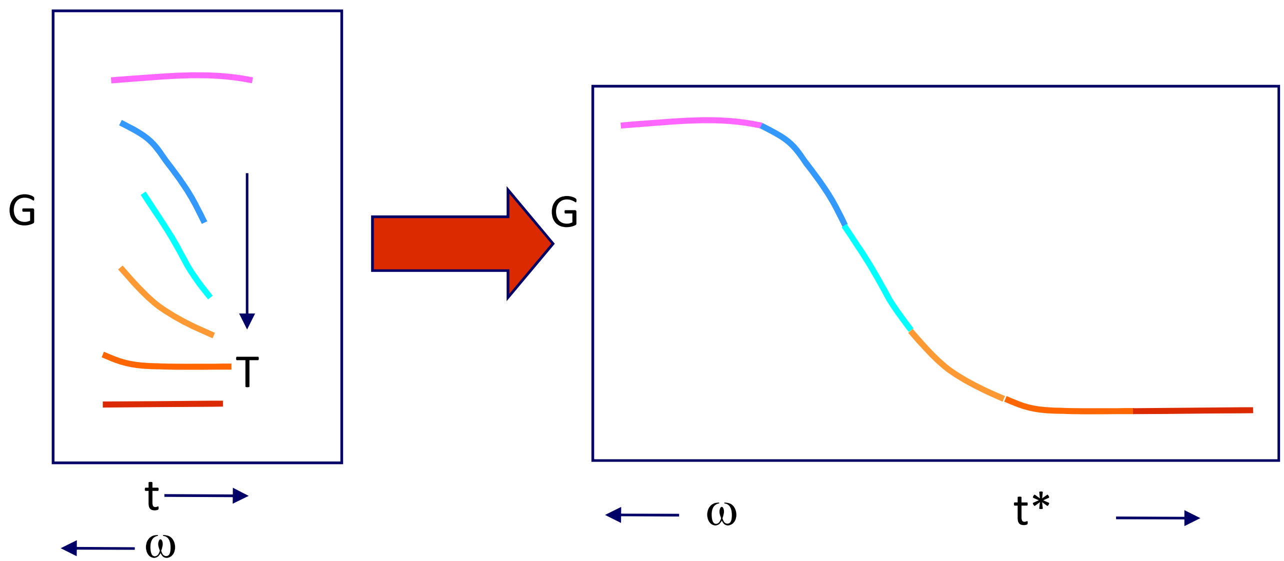
High temperature

Rigid solid

Fluid

Time-temperature equivalence concept

- **Explore effect of timescale on dynamics through G**
  - directly via frequency, ω (harmonics)
  - indirectly via temperature, T (relaxation time, τ)



time-temperature equivalence

$$G(T_1,t) = G(T_2,t/a_T)$$

Stress effects in electrodeposited films

Film mass, stress & adhesion

The QCM responds to mass and stress

$$\Delta f = -\left(\frac{\Delta m}{A}\right)\left[\frac{f_Q^2}{\rho_Q N_Q}\right] + K\Delta S\left[\frac{f_Q^2}{N_Q}\right]$$

Δf / s^{-1} = measured frequency change
Δm / g = change in mass
ΔS / N m^{-1} = change in stress

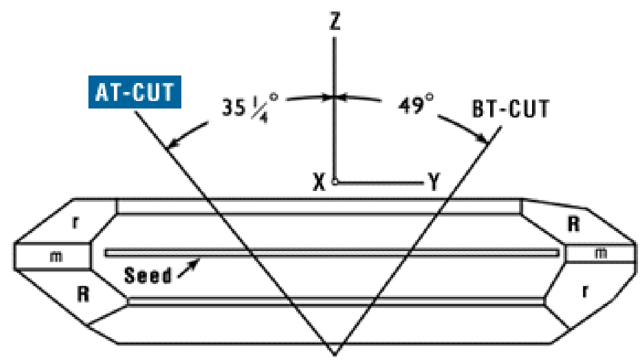
f_Q / s^{-1} = fundamental frequency
r_Q / g cm^{-3} = quartz crystal density
N_Q / m s^{-1} = crystal frequency constant
K = constant

Limiting case of zero stress

- ΔS = 0 ⇨ **Sauerbrey equation**

Double resonator technique

- Measure responses of two crystal cuts
  - ↳ distinctive (known) N_Q & K values
- AT- and BT-cut
  - ↳ similar mass responses
  - ↳ very different stress responses
- solve simultaneous equations for Δm & ΔS

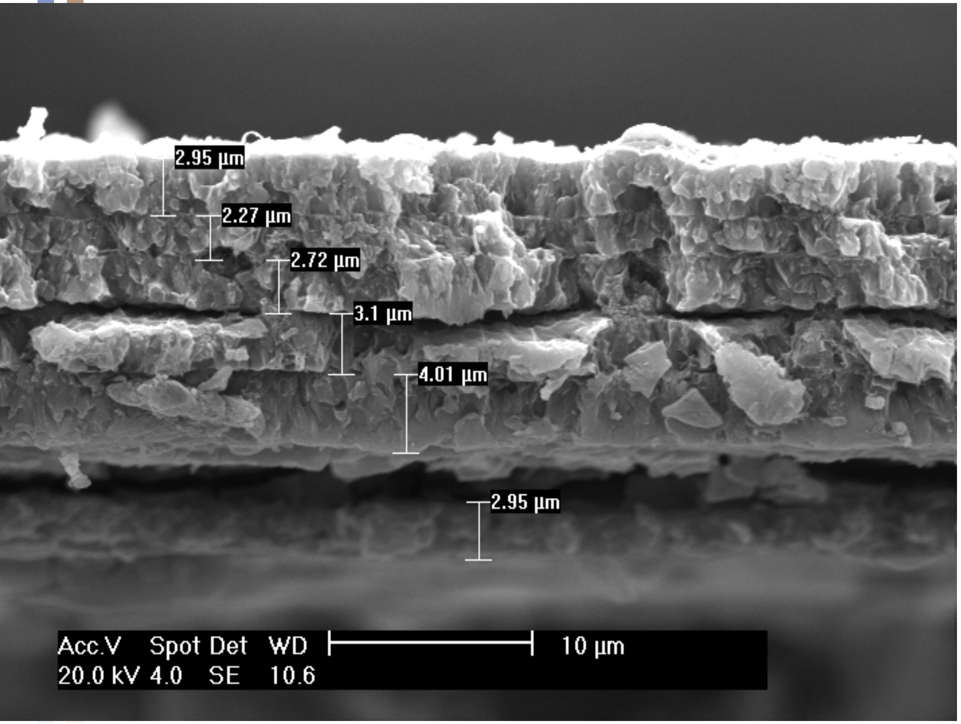


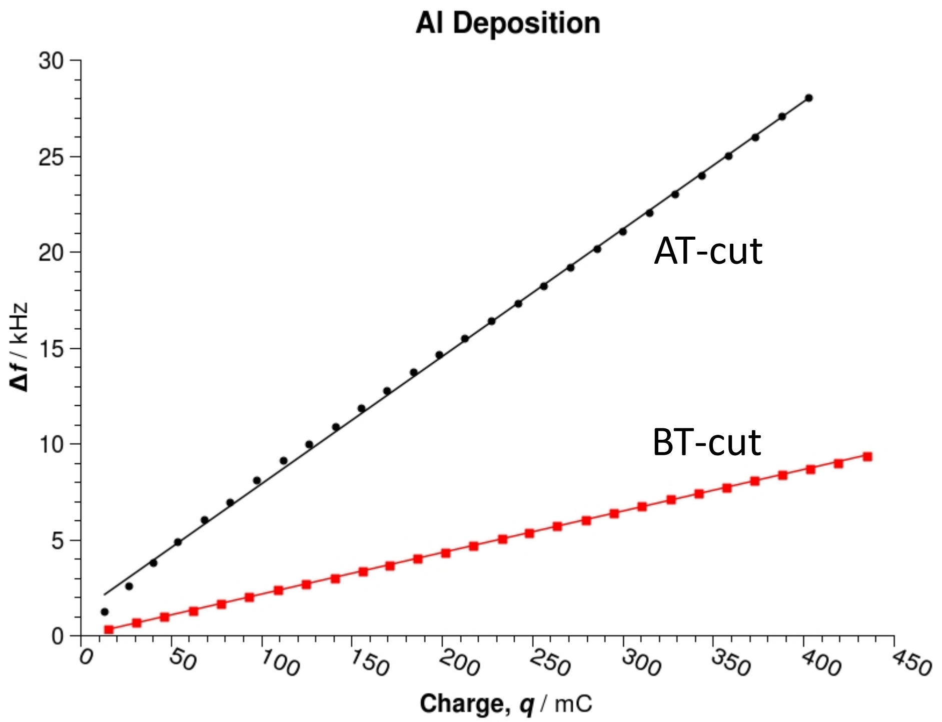
d = quartz resonator thickness

Al plating: stress & adhesion

❑ Stress during Al plating?

- Electroplating of multiple layers of Al on Au / quartz crystals (AT and BT cut)

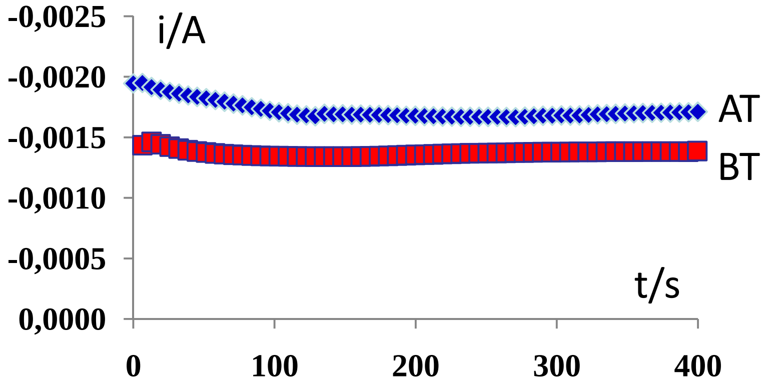




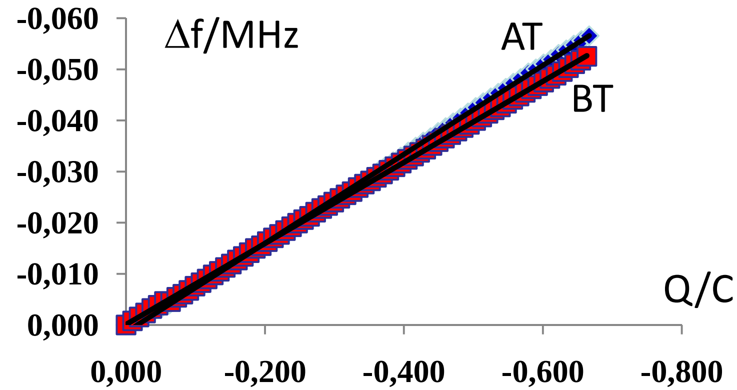
Stress can cause delamination and failure of complex thin film architectures

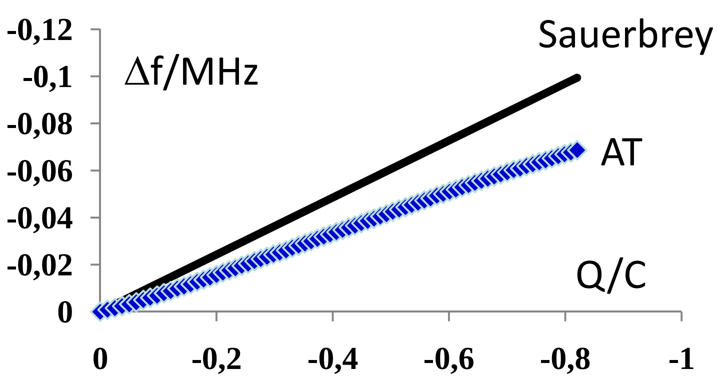
Low temperature deposition (T = 5°C)

Current



Frequency

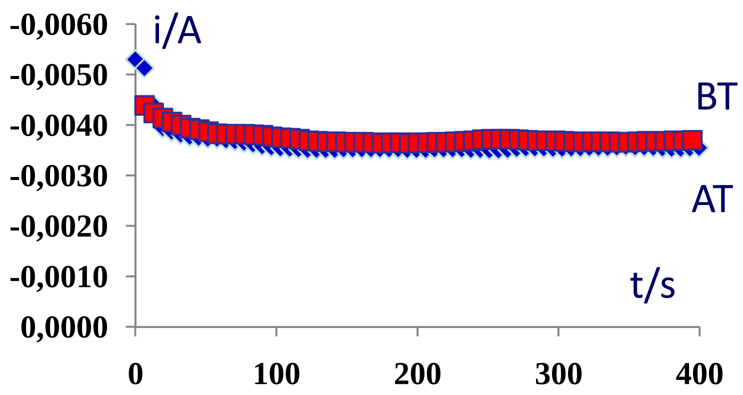




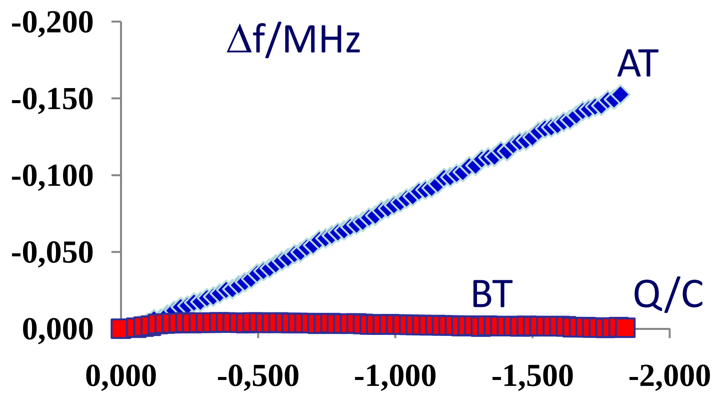
- Current response
  - independent of cut
    - ↳ minor area difference
- Frequency response
  - slightly dependent on cut
    - ↳ stress present
- Comparison with Sauerbrey
  - mass dominant

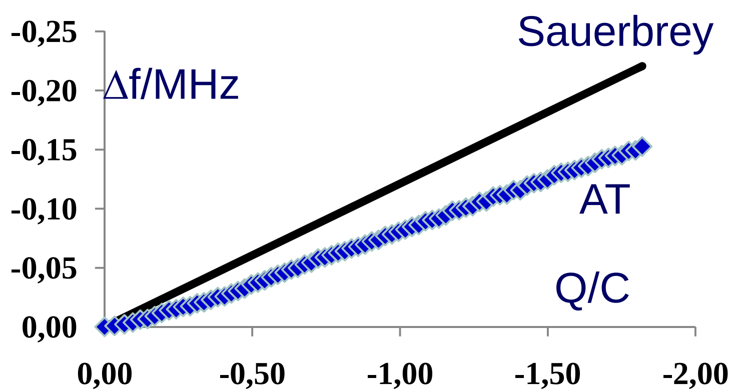
High temperature deposition (T = 55°C)

Current



Frequency





- Current response
  - independent of cut
    - minor area difference
- Frequency response
  - slightly dependent on cut
    - stress present
- Comparison with Sauerbrey
  - stress significant

Stress and mass effects

General case

$$\frac{\Delta f^{AT}}{\Delta f^{BT}} = \left(\frac{N_Q^{BT}}{N_Q^{AT}}\right) \frac{\left[\left(K^{AT} Af_Q \,\Delta S/\Delta m\right)-1\right]}{\left[\left(K^{BT} Af_Q \,\Delta S/\Delta m\right)-1\right]}$$

Stress dominant (ΔS >> Δm):

$$\frac{\Delta f^{AT}}{\Delta f^{BT}} \rightarrow \frac{N_Q^{BT}}{N_Q^{AT}} \cdot \frac{K_Q^{AT}}{K_Q^{BT}}$$

Mass dominant (ΔS << Δm):

$$\frac{\Delta f^{AT}}{\Delta f^{BT}} \rightarrow \frac{N_Q^{BT}}{N_Q^{AT}}$$