Thickness and viscosity of organic thin films probed by combined surface acoustic Love wave and surface plasmon resonance

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slides available at `http://jmfriedt.free.fr`

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Direct detection biosensor

Aim : detect DNA hybridation, antibody/antigen interaction without labeling (fluorescence, radiolabeling ...)

- *in-situ* measurement (not in dry state) : microfluidics ...
- time resolution $\simeq$1 s for kinetics measurements

$\Rightarrow$ detect mass bound to the surface : acoustic method (QCM, SAW)
$\Rightarrow$ detect optical index change (ellipsometry, SPR)
$\Rightarrow$ detect surface topography change due to adsorption (SPM)

- **Acoustic** methods beyond Sauerbrey : density, thickness, viscosity
- **Optical** methods : thickness, optical index
- **Scanning probe microscopies** : molecule conformation, density of molecules, thickness

Modelling is required for extracting quantitative information on the physical properties of the adsorbed layer

Various solvent concentrations

From QCM-D measurement we know that collagen and fibrinogen provide challenging properties :

- S-layer, IgG : behaves as a rigidly bound mass (Sauerbrey)
- collagen : displays a behaviour consistent with a predominantly viscous interaction
- fibrinogen : intermediate situation ...

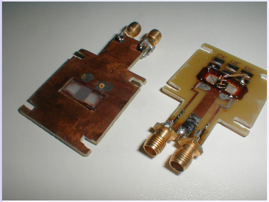
Analyte (bulk concentration, μg/ml)	$\Delta f_n/\sqrt{n}$ (Hz) QCM	$\Delta f_n/n$ (Hz) QCM	ΔD ($\times 10^{-6}$) QCM
S-layer	NO	45=900	3-5
CTAB	NO	8=160	0.2-0.5
collagen (30μg/ml)	1000	NO	100
collagen (300μg/ml)	1200	NO	>120
fibrinogen (46μg/ml)	110$\pm$5	55$\pm$5$\simeq$ 1110	4-10
fibrinogen (460μg/ml)	NO	100=1700	8-10

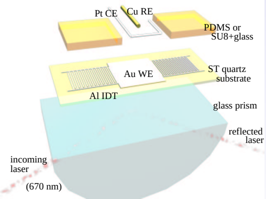
J.-M. Friedt *et al.*, J. Appl. Phys. **95** (4) 1677-1680 (2004)

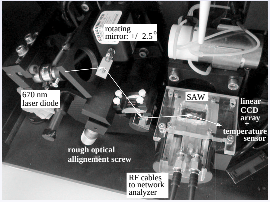
C. Zhou *et al.*, Langmuir **20** (14) 5870-5878 (2004)

SAW/SPR combination

- Objective : identify physical properties of protein films.
- Acoustic methods are sensitive to layer thickness, density and viscosity, but provide only insertion loss and phase variations.
- Combine with optical method : optical index and thickness.
- Assume that density and optical index vary linearly with solvent content ⇒ 3 unknowns and 3 measurements.

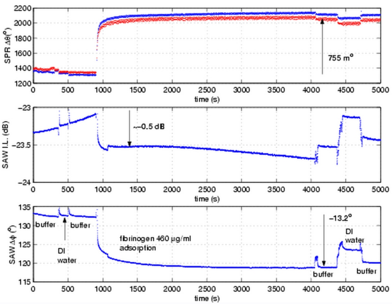


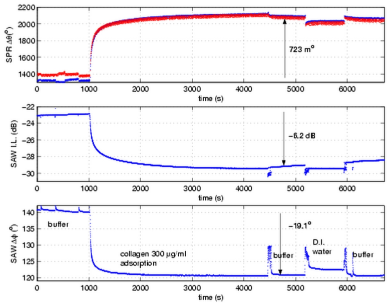




Data collected with combined SAW/SPR setup

- Globular protein (IgG, BSA, S-layer), fibrilar protein (collagen, fibrinogen) and polymers (pNIPAM) adsorption have been investigated.
- Globular proteins display a mostly rigid behaviour
- pNIPAM displays a behaviour dependent on temperature

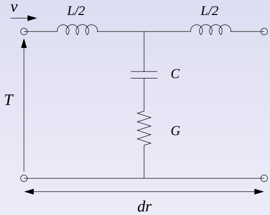




Data modelling approaches (acoustics)

Two complementary approches for modelling the acoustic data :

- transmission line model

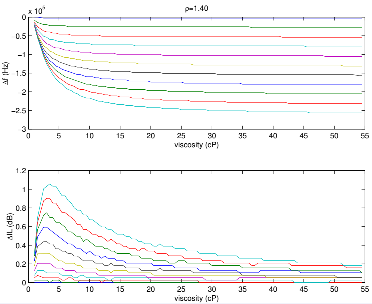


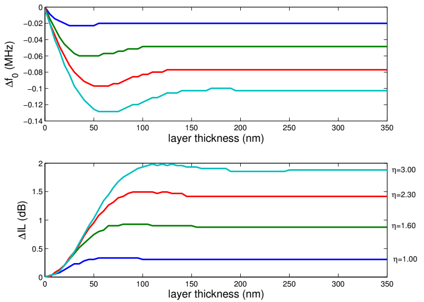
- harmonic admittance computation based on the Blötekjaër-model extended to include the viscous contribution of a newtonian fluid (linear response)

$$T_{ij} = -\left(P + j\omega\left(\frac{2}{3}\eta - \zeta\right)S_{kk}\right)\delta_{ij} + 2\omega\eta S_{ij}$$

Data modelling predictions (acoustics : Blötekjaër)

Parameters are : the layer thickness, its viscosity and density



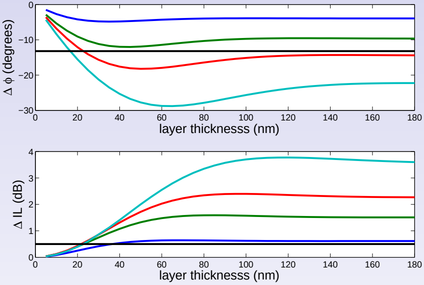


Varying the viscosity

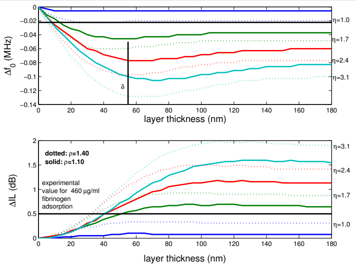
Varying the thickness

An insertion loss drop of **-6 dB cannot be modelled** by a newtonian fluid+rigid mass interactions.

Data modelling predictions (acoustics : TLM)



Transmission line model (η=[1, 1.5, 2, 3])



Blötekjaër

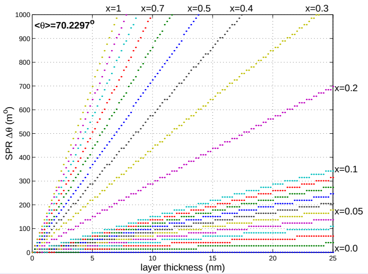
(harmonic admittance computation)

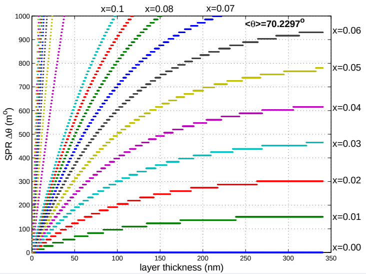
Here (left) we find a possible set of parameters for the fibrinogen data : **a viscosity around 2.6 cP and a thickness around 22.4 nm** assuming a density of 1.4.

Additional work requires sweeping the density parameter to extract water content.

Data modelling results (SPR)

2D model of reflected intensity of a laser by a stack of planar interfaces : requires optical index of all layers at a given wavelength+incident angle





Acoustic frequency shift+insertion loss and SPR angle shift
$\rightarrow$ density ρ, optical index n, viscosity and water content x **assuming**
$\rho = x \times \rho_{protein} + (1-x) \times \rho_{water}$ & $n = x \times n_{protein} + (1-x) \times n_{water}$
$\rightarrow$ with a thickness of 22.4 nm, SPR (755 m^o) tells us x$\simeq$0.25 *i.e.*
$\rho \simeq$1.10 **and iterate ...**

Conclusion and perspectives

- Experimental measurement of thin film adsorption by acoustic and optical means
- Simultaneously monitor using both techniques the *same* area in liquid with time resolution
- Implementation of models for the predictions of SPR angle shift and acoustic frequency shift and insertion loss as a function of adsorbed layer properties
- Models are incomplete : cannot justify large insertion loss decrease upon collagen adsorption
- Possible extension : add Maxwellian liquid behaviour (complex : non-linear, delayed effects, incompatible with transmission line model)