Soft nanofluidics

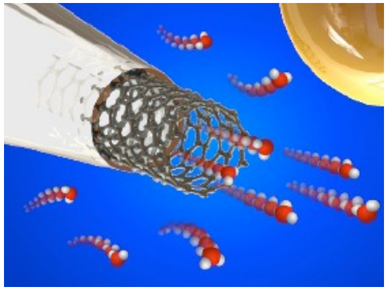
Anne-Laure Biance

Sub-nanometric transport in water

Anomalous behaviors reported :

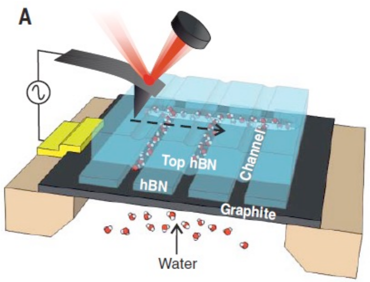
- in confined systems **(<1nm)**
- in the vicinity of van der Waals materials (graphene, hBN)

Friction



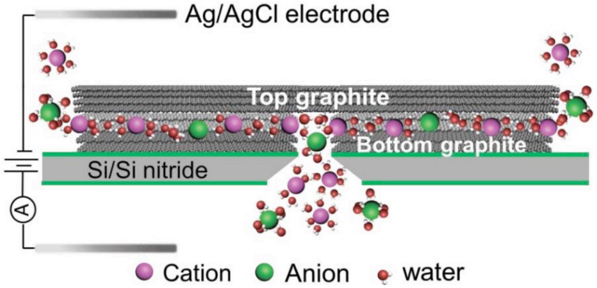
Secchi et al. 2016

Electric permittivity



Fumagalli et al. 2018

Ionic transport



Esfandiar et al. 2017

Effect of the confinement and/or of the material?

Motivations

Limitations of model experimental systems

-Not versatile (one size, one material)

-Difficult to build from a technological point of view

-Far from real systems for applications

→ Soft Matter!

Soft films as nanofluidic channels

Benjamin Franklin's experiment (1774)

Clapham pond before a drop of oil is added

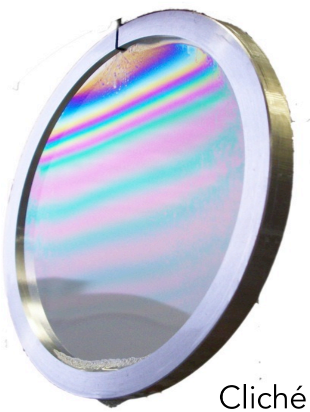
Clapham pond after a drop of oil (with contaminants) is added

https://edu.rsc.org/download?ac=11854

Liquid film of molecular thickness!

Soft films as nanofluidic channels

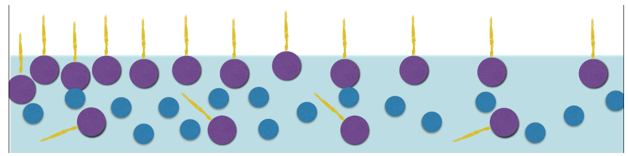
Soap films



Cliché P. Petit

Thickness: 5-100 nm

Complex boundary conditions, deformability



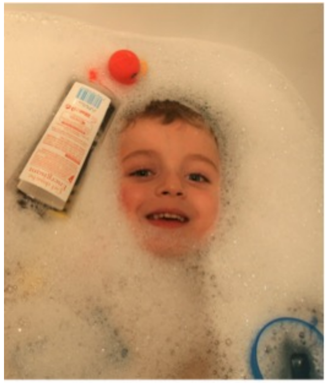
O. Bonhomme

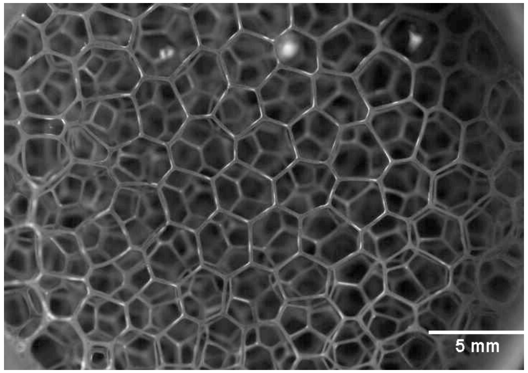
Condensed films

Thickness: 0.2-3 nm

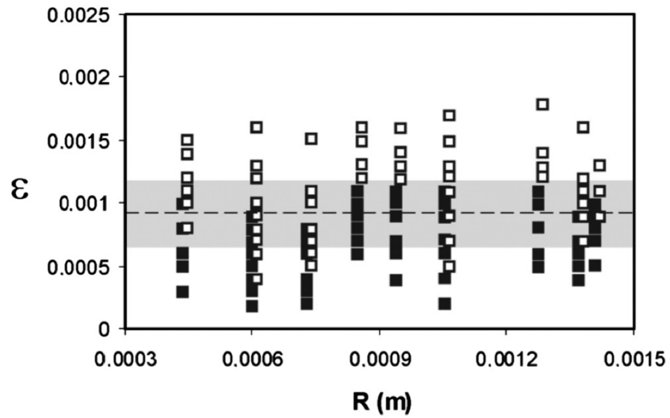
Ultimate confinement

Soap films: motivations



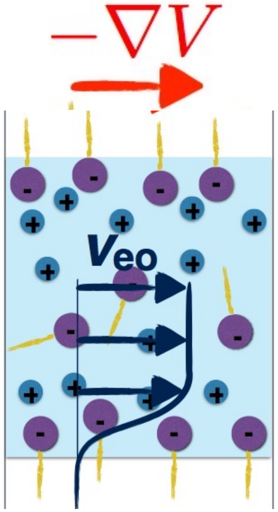


Stable: wet foams



Unstable: dry foams

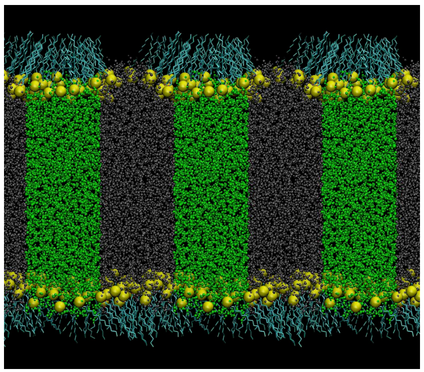
Biance, Delbos, Pitois, PRL 2011

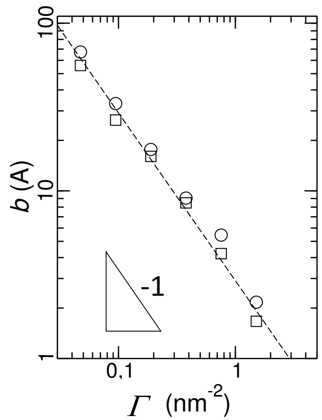


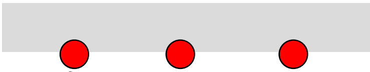
Electroosmosis!

Complex boundary condition

- **Slippage** depends on surfactant concentration (MD simulations)







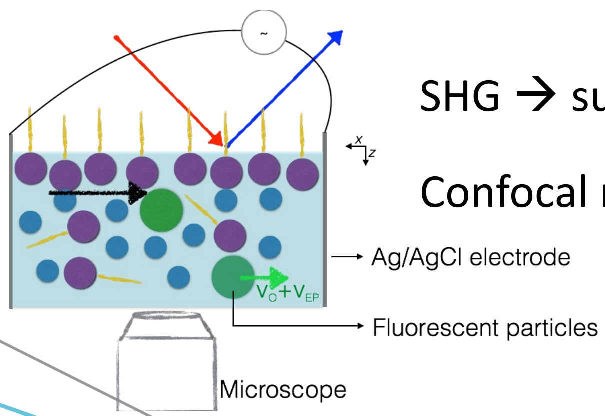
$$\lambda = 3\pi\eta a\Gamma$$

Friction on half-sphere

$$b = \frac{1}{3\pi\Gamma a}$$

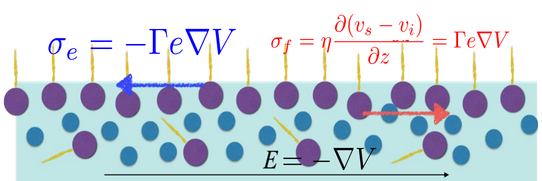
Joly, Detcheverry, Biance, PRL 2014

- Surfactant **distribution** at interface



SHG → surfactant distribution

Confocal microscopy → electroosmosis



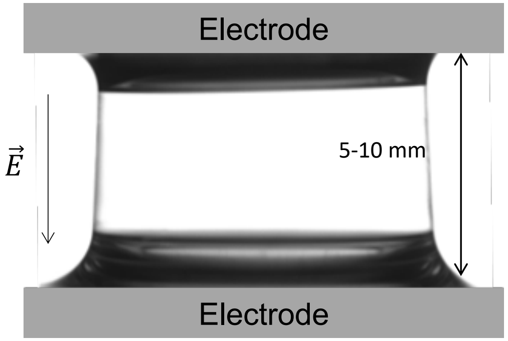
No Marangoni stress,
no net force on the surfactants

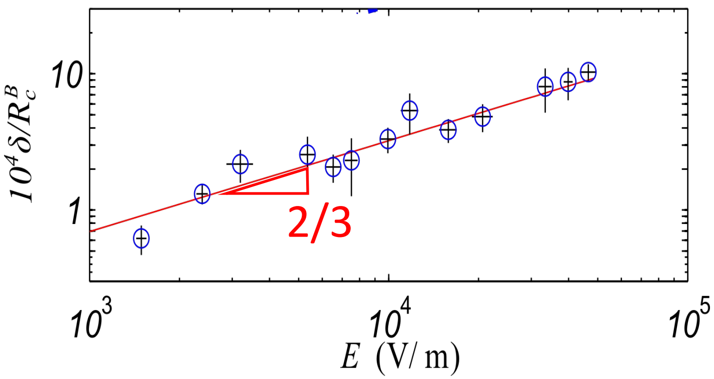
Similar to hydrophobic surfaces,
Huang et al., PRL 2007

Blanc, Bonhomme, Brevet, Benichou, Ybert, Biance, Soft Matter 2018

Soap films and foams

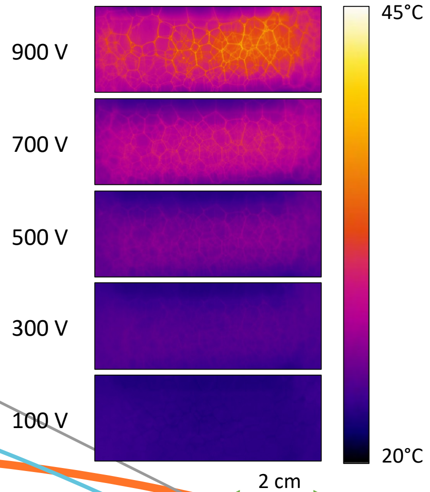
- **Deformable systems** – non-linearities

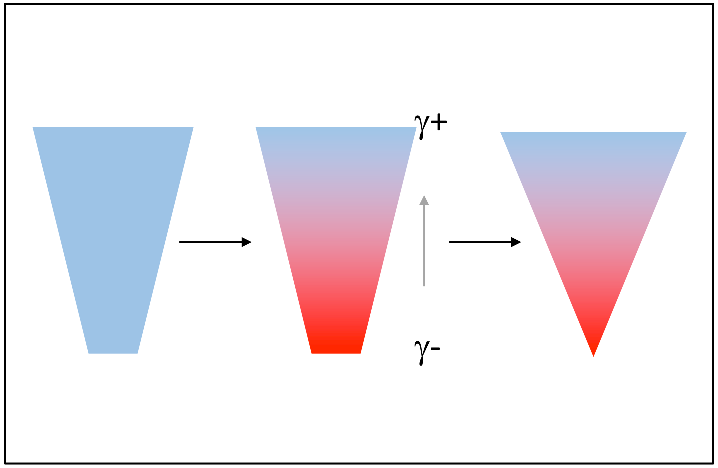




Bonhomme, Liot, Biance, Bocquet, PRL 2013

- Coupling with **thermal effects** (liquid foams)





Asymmetry + Joule effect

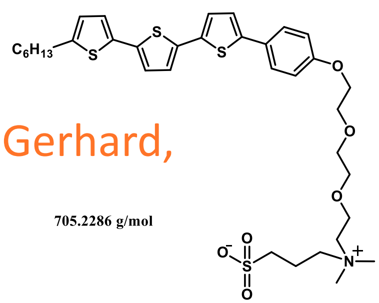
Enhanced electroosmosis (X100)

Bonhomme, Peng, Biance, PRX 2021

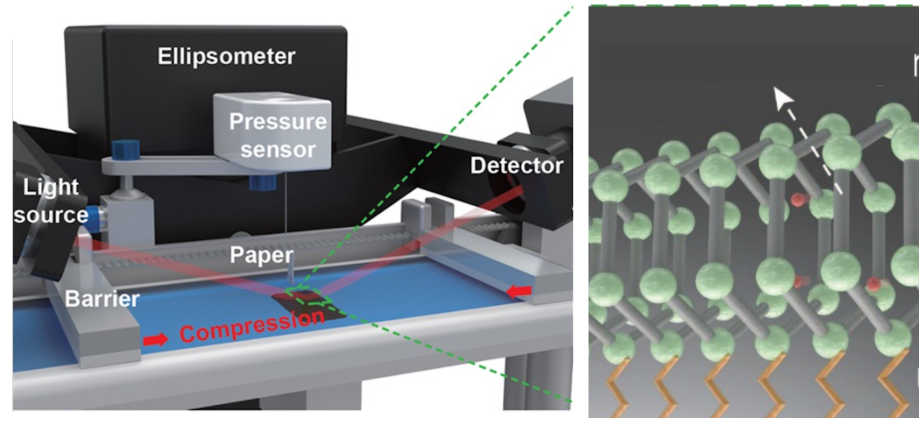
Coupling with electronic transport

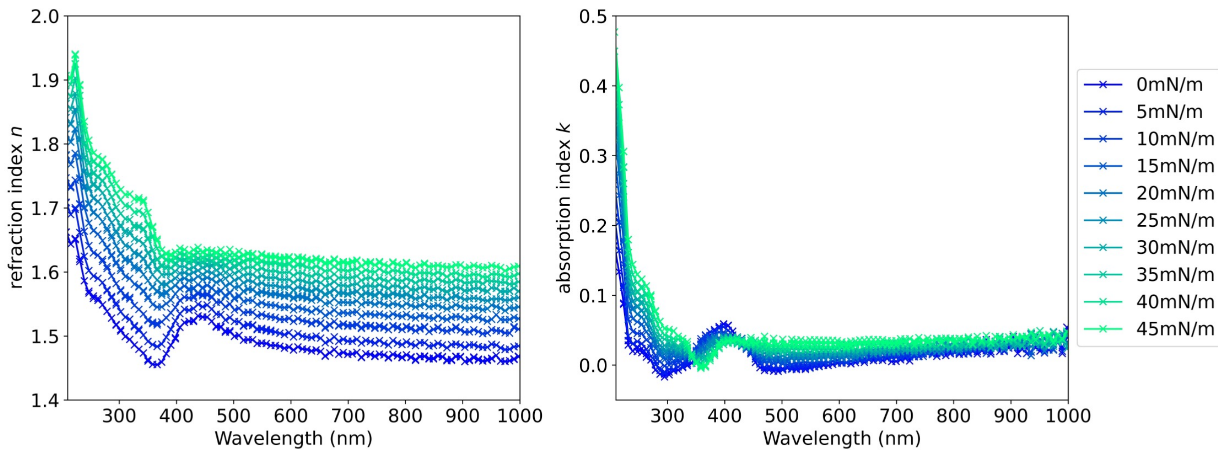
- **Electronic surfactants**

Isham Idriss,
Institut Charles Gerhard,
Montpellier



Spectrometric ellipsometry



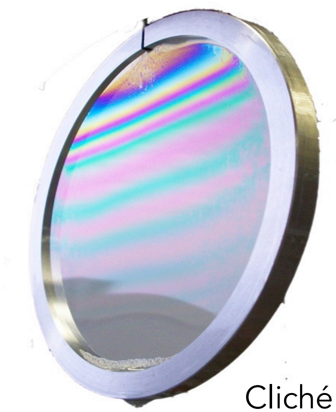


Blue shift,
π-π stacking,
electronic transport?

Changwoo Bae, Samuel Albert

Soft films as nanofluidic channels

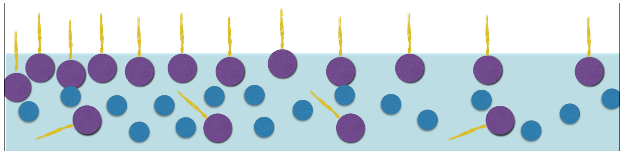
Soap films



Cliché P. Petit

Thickness: 5-100 nm

Complex boundary conditions, deformability

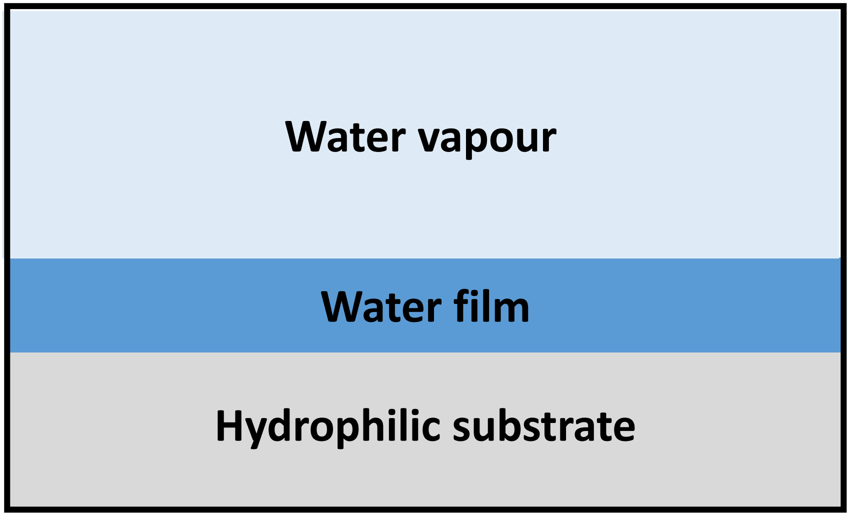


Condensed films

Thickness: 0.2-3 nm

Breakdown of continuous description:
Conductance measurements

Condensed film on a substrate

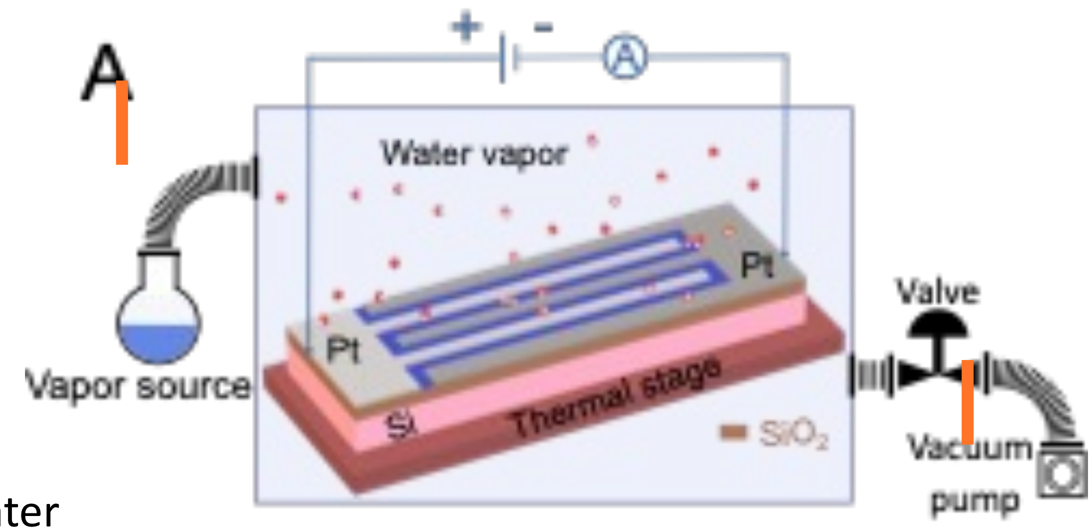


Spreading parameter

$$S = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV}) \geq 0$$

Humidity control

2: introduction of vapour at pressure $p_{vap}=p_{sat}(T_{source})$



1: vacuum

Thermostated water
T_{source}

3: variation of substrate temperature

$$RH[\%] = \frac{p_{vap}}{p_{sat}(T_{sub})} \times 100$$

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Condensed film experiments: set-up

Temperature controller

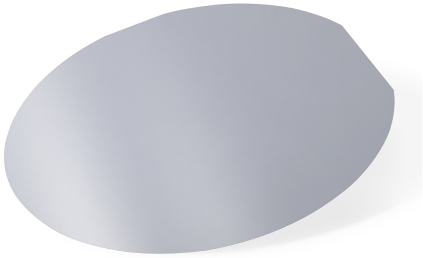
Thermostated bath

Vacuum pump

Condensed film thickness: ellipsometry

Material = Silica

- Silicon wafer with deposited layer of SiO_2



Cleaning

Substrate

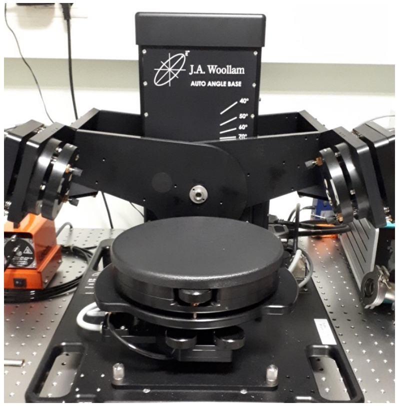
-Detergent + ultrasound

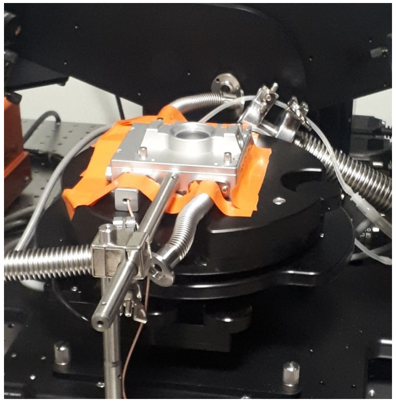
-3 min UV Ozone plasma

Cell and set-up

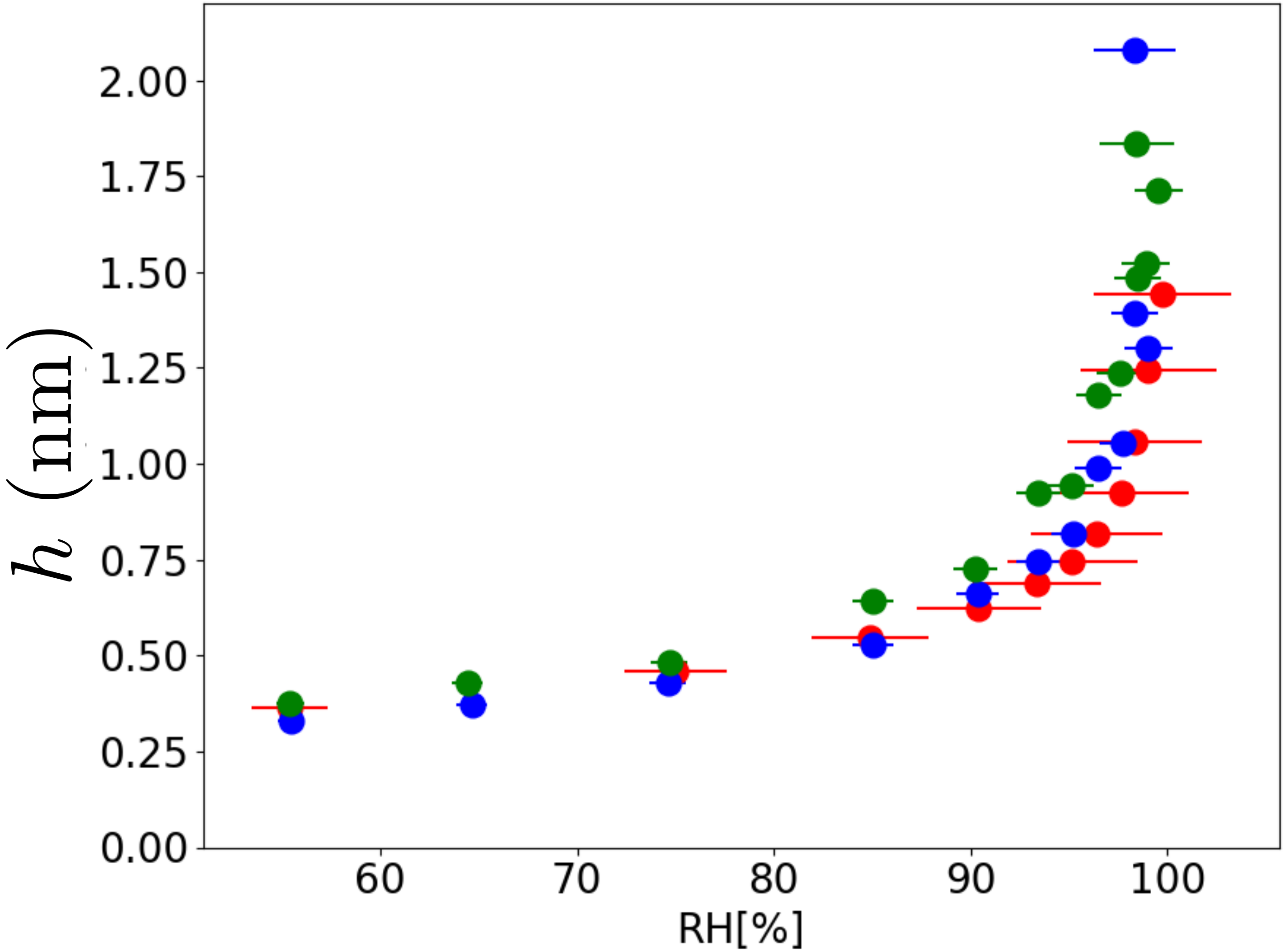
-Vacuum (10 Pa) during one week to remove dusts

Thickness measurements: Ellispometry





Film thickness



Control of humidity → control of film thickness

Liquid-substrate interactions

- Film thickness set by the interaction energy (disjoining pressure)

$$\pi(h) = \rho_l kT \log(\mathrm{RH})$$

- Disjoining pressure origins

Wetting: statics and dynamics,
P. G. de Gennes, Rev. Mod. Phys. 57, 827, 1985

-Electrostatics (counter-ions only)

D. Andleman, Soft condensed matter physics in molecular and cell biology, 6, 2006

-Adsorption layer model

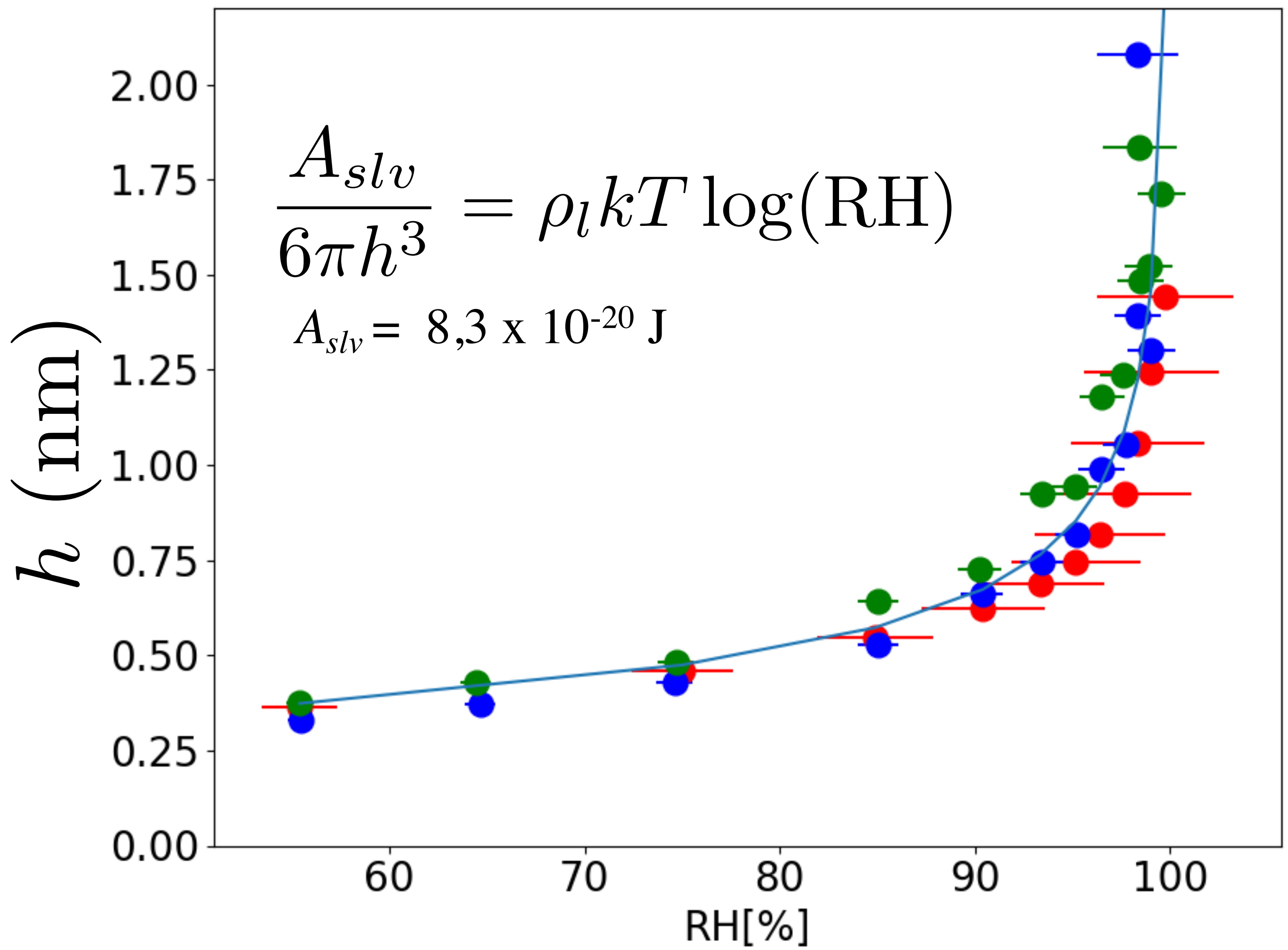
R. Pashley, Journal of colloids Int. Science, 78, 1980

$$\pi(h) \sim \frac{1}{h}$$

-Van der Waals

$$\pi(h) = \frac{A_{slv}}{6\pi h^3}$$

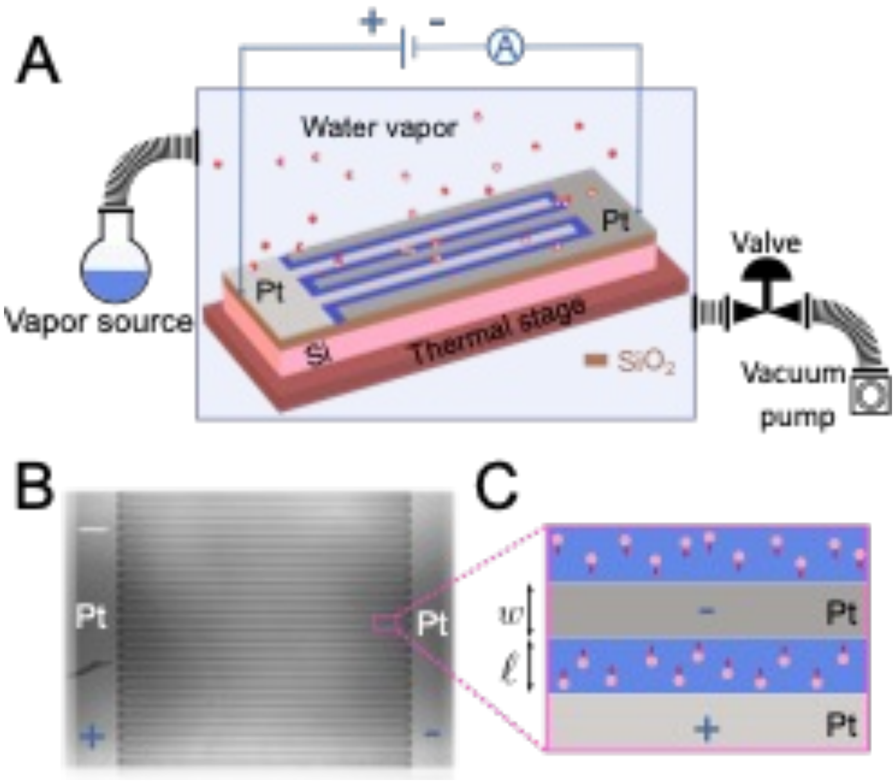
Film thickness: discussion



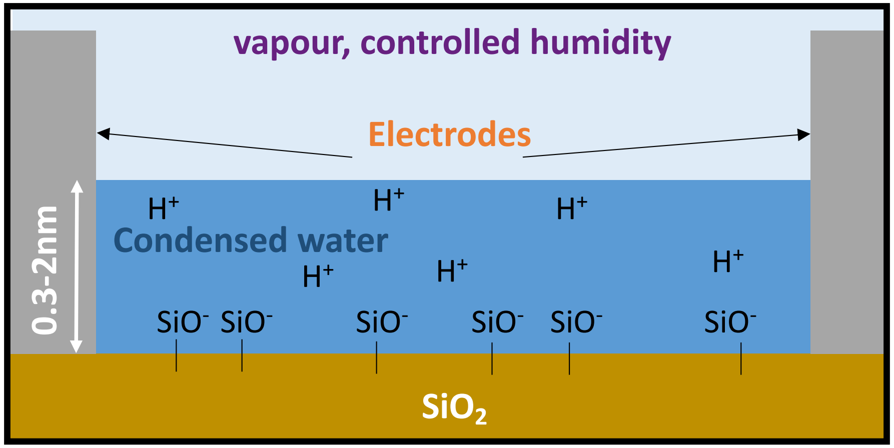
Calculated value of the silica/water/air Hamaker constant: 1-5 x 10^{-20} J

J. Visser, Advances in Colloids and Interface Science, 1972, 331-363

Electrical measurements

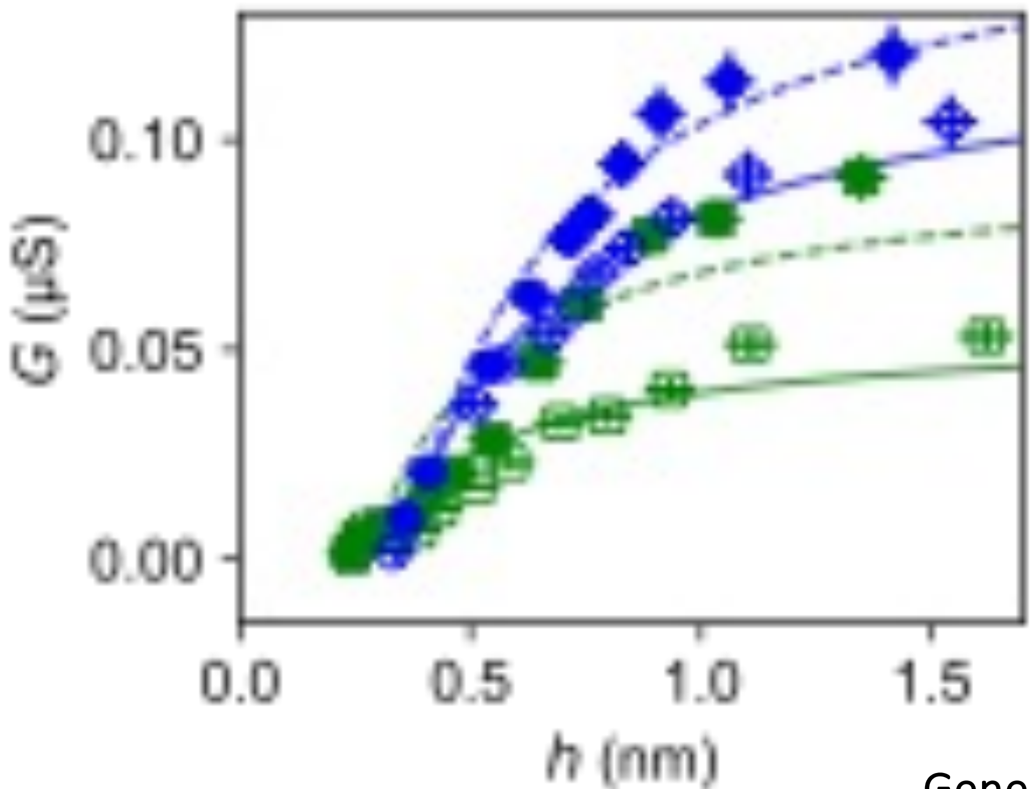


- L_{tot} = 78 cm
- Applied AC voltage, 10Hz, 1V



Side view

Conductance as a function of film thickness



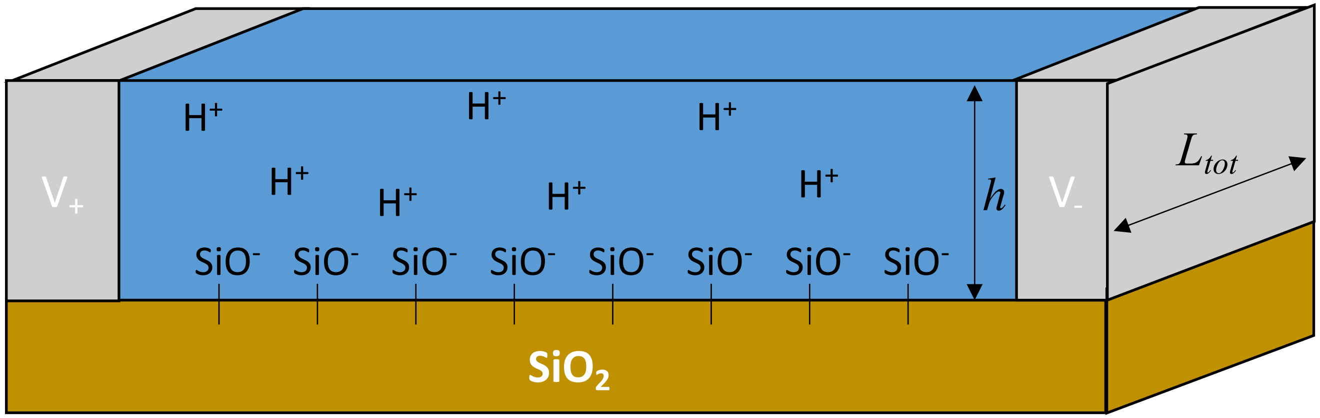
$T_{\mathrm{source}} = 6\,^{\circ}\mathrm{C}$

$T_{\mathrm{source}} = 16\,^{\circ}\mathrm{C}$

Generic Features:

- Non-linear Increase with h
- Conductance saturation

Conductance: continuous regime



Hypotheses:

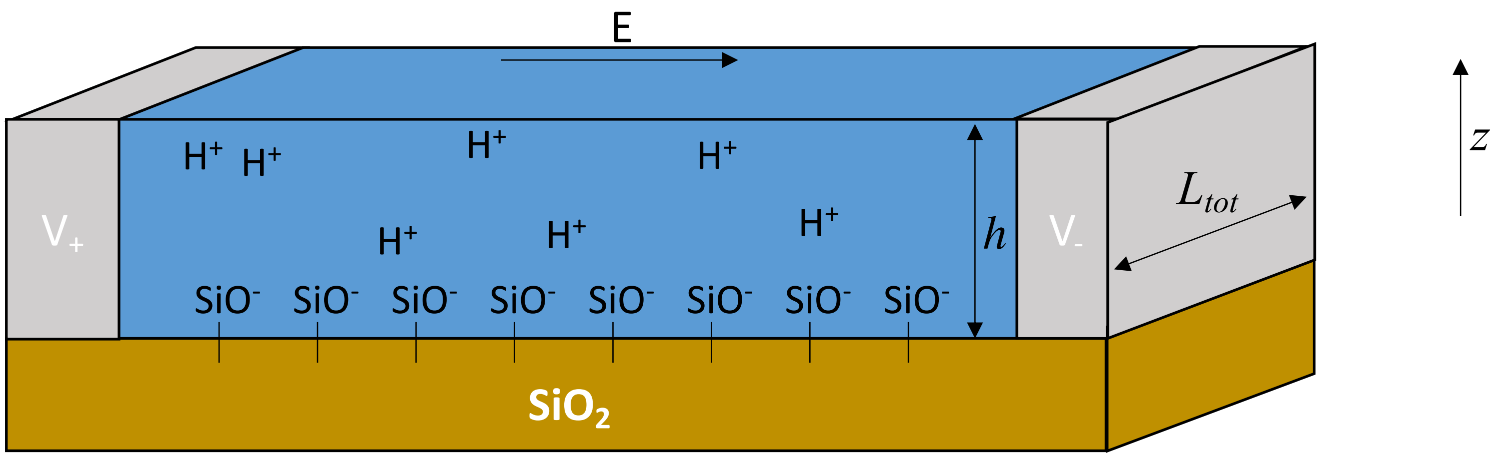
(i) Zero charge at the water/vapor interface
(ii) Ionic transport due to counter-ions (H^+)

$$I = e \times L_{tot} \int_0^h \rho_+(z) u_+(z) dz$$

$\rho_+(z)?$

$u_+(z)?$

Conductance: continuous regime



$$I = e \times L_{tot} \int_0^h \rho_+(z) u_+(z) dz$$

$$u_+(z) \simeq e\mu_+ E$$

+

Electroneutrality

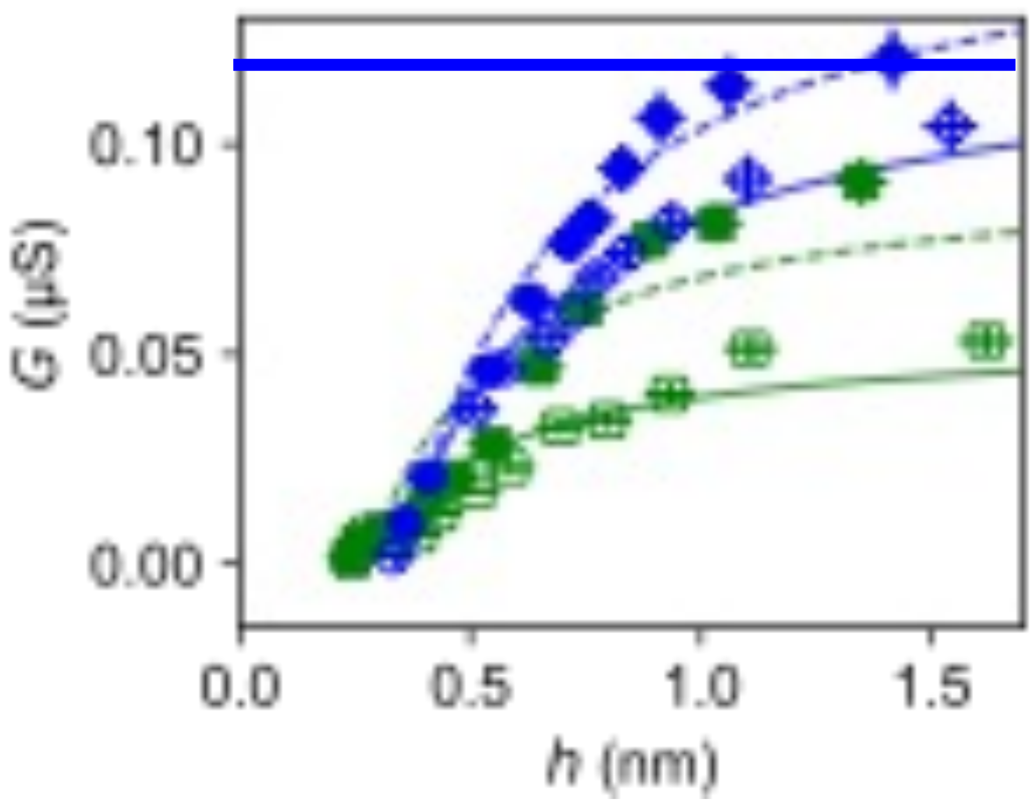
$$\int_0^h \rho(z) dz = [\mathrm{SiO}^-]_s$$

$$I \simeq e L_{tot} \times [\mathrm{SiO}^-]_s \times e\mu_+ E$$

(Independent of *h* if $[\mathrm{SiO}^-]_s$ is constant)

D. Stein et al., PRL 2004 among others

Conductance: continuous regime



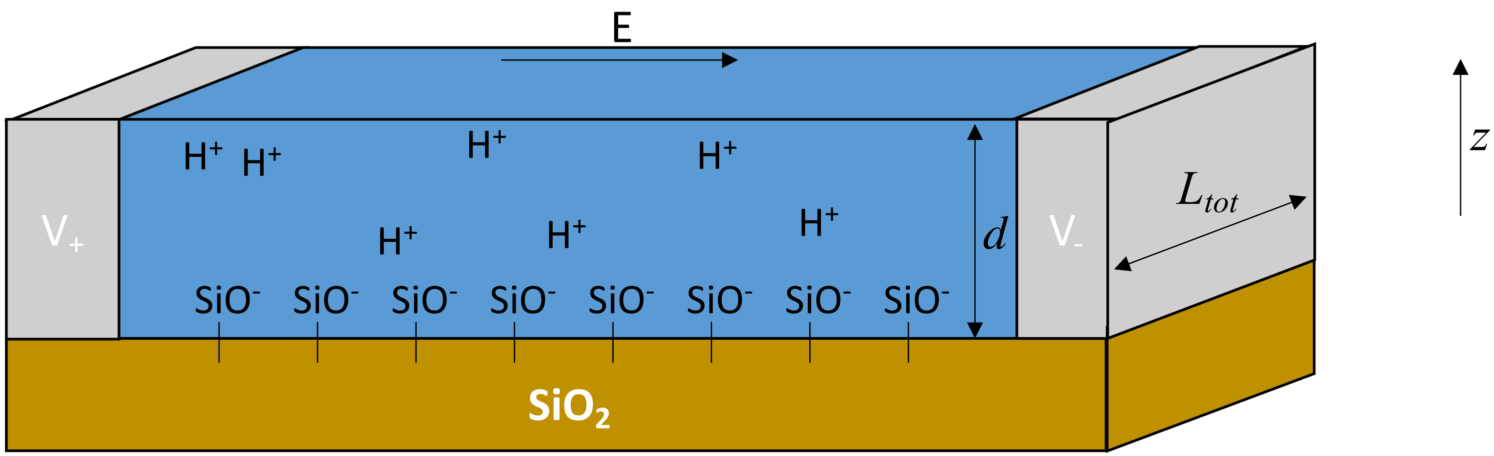
constant charge

- constant potential
- charge regulation

Not satisfying

Increase with *h* in the confined regime?

#Hypothesis: effect of surface friction



$$I = e \times L_{tot} \int_0^h \rho_+(z) u_+(z) dz$$

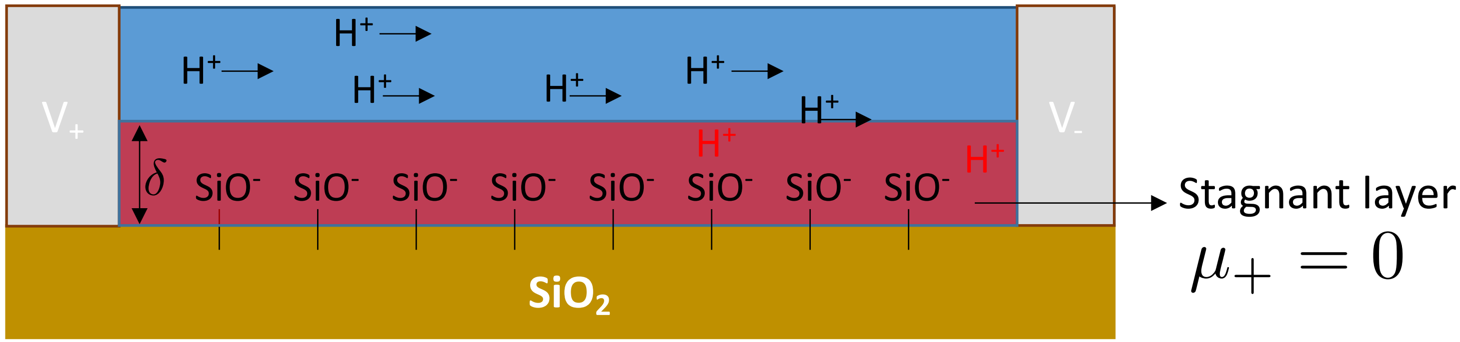
$$u_+(z) \simeq e\mu_+(z)E$$

Stagnant layer of ions?

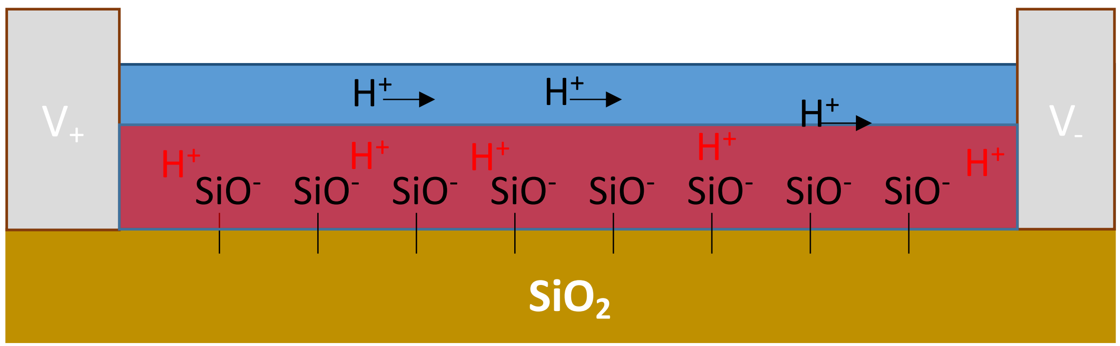
Measuring surface charge: Why experimental characterization and molecular modeling should be coupled?
Hartkamp, R., Biance, A. L., Fu, L., Dufrêche, J. F., Bonhomme, O., & Joly, L. (2018).
Current Opinion in Colloid & Interface Science, *37*, 101-114.

Naïve model: chemical layer with immobile ions

Larger h



Smaller h



Stagnant layer → conductance increases with h

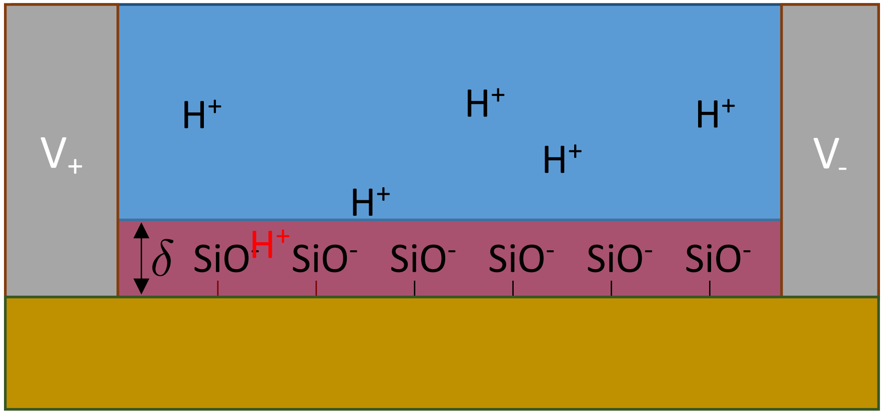
Detailed analysis: stagnant layers model

$$I \simeq E\ eL_{tot} \times [\mathrm{SiO}^-]_s \times \mu_+ \times \frac{h-\delta}{h}$$

Stagnant layer

$$\mu_+ = 0$$

$$v = 0$$



$$I = E\frac{4\epsilon K}{2\pi\ell_B\eta}\left(\frac{\ell_B}{3r_h}\tan(K\frac{h-\delta}{2}) + \tan(K\frac{h-\delta}{2}) - \frac{K\delta}{2}\right)$$

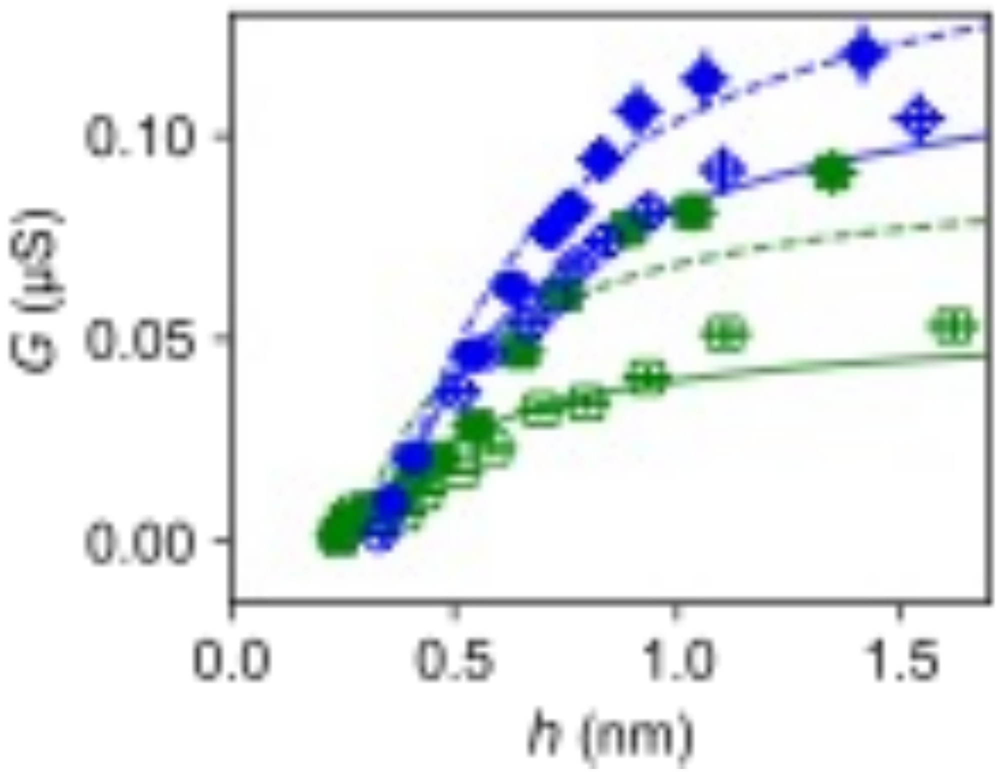
$$Kh \times \tan(Kh) = \frac{h}{\ell_{GC}}$$

electrophoretic contribution

electroosmosis contribution

Bocquet, Charlaix, Chemical Society Reviews, 2011

Back to experiments



Fitting parameters

$$\delta = 0.3\text{nm}$$

Surface charge $20\ \mu\text{C/m}^2$
→ OK with literature
(charge regulation)

Stagnant layer
→ In contrast with so-called Stern layer
→ In agreement with statics and hydrodynamics

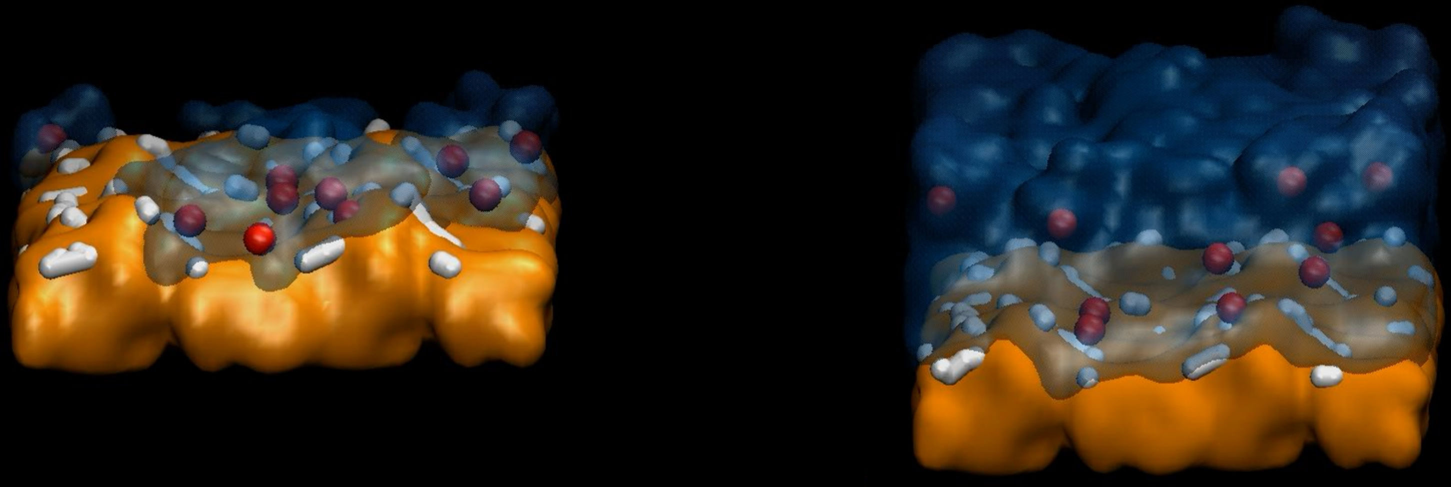
Georges, S Millot, J Loubet, A Tonck,1993.
M Cieplak, J Koplik, JR Banavar, Phys. Rev. Lett., 2001.

Allemand, Zhao, Vincent, Fulcrand, Joly, Ybert, Biance, PNAS (in press)

Origins of the stagnant(s) layer?

h=0.284 nm

h=1.73 nm



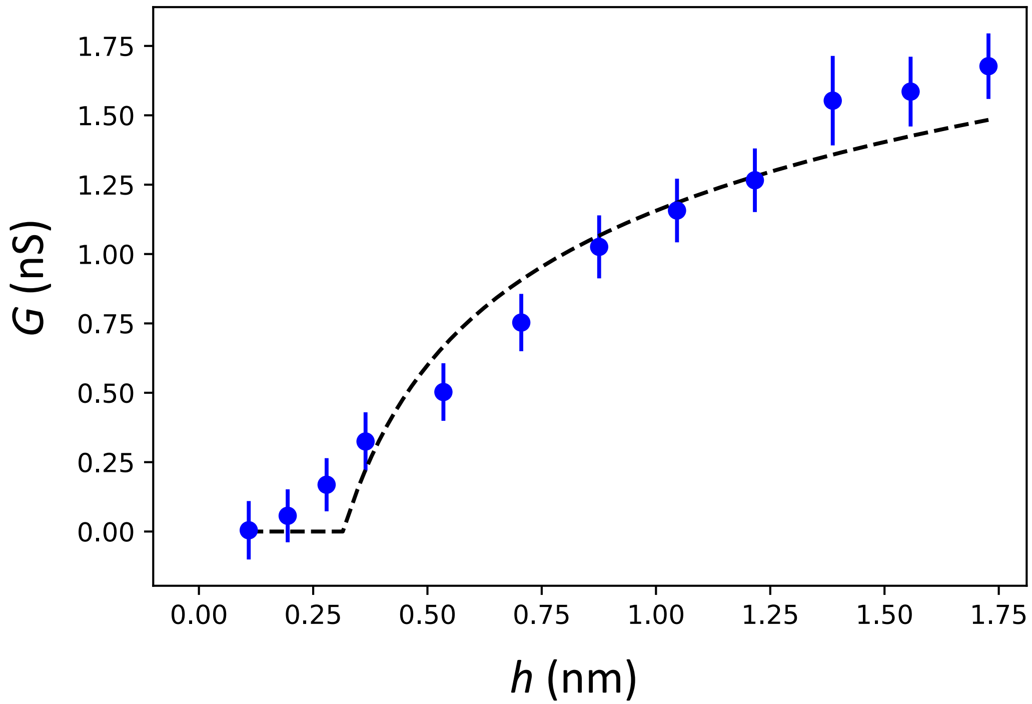
Fixed ionized groups
$[SiO^{-}]_{S}$=10

-Silanol -Silica
-Cation -Water

MD simulations
dt=50ps

Conductance measurements: MD

$$I \simeq E\, eL_{tot} \times [\mathrm{SiO}^-]_s \times \mu_+ \times \frac{h-\delta}{h}$$



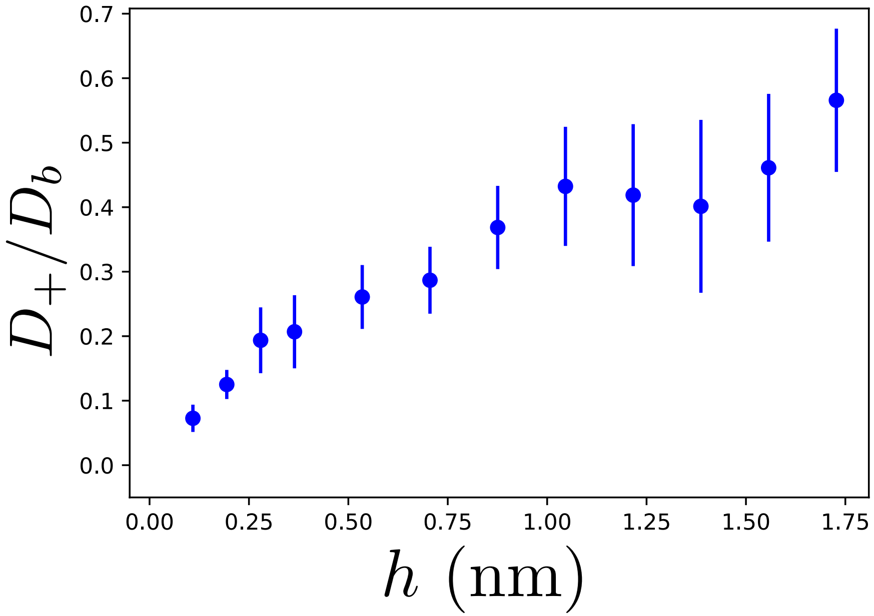
Fitting parameters

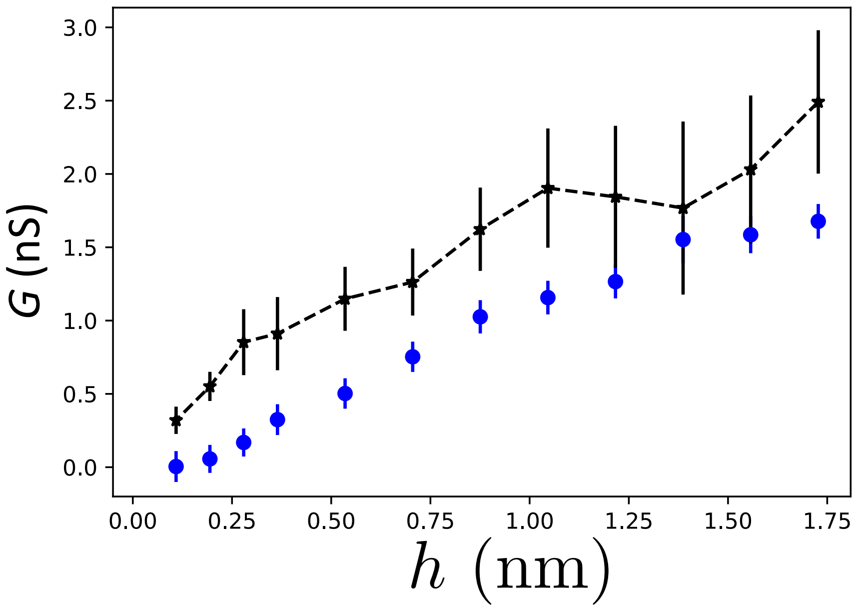
$$\delta = 0.3\mathrm{nm}$$

$[\mathrm{SiO}^-]_s = 3$ (instead of 10)

→ Mismatch

Diffusion coefficient of the ions: MD





$$D_+(z) = \mu_+(z)kT$$

$$u_+(z) = e\mu_+(z)E + u_{EO}$$

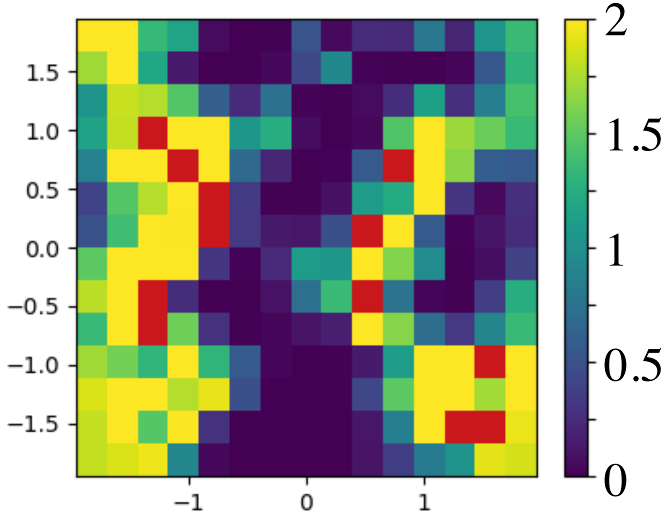
$$I = e \times L_{tot} \int_0^h \rho_+(z)u_+(z)dz$$

- Good agreement

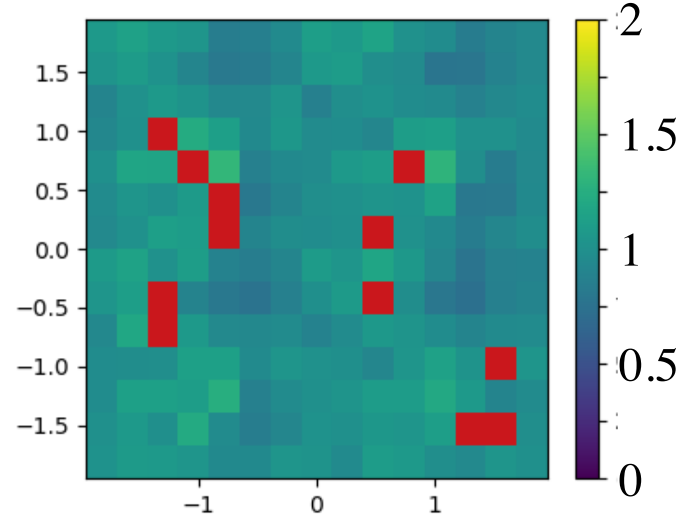
Origins of the hindered diffusion layer

Normalized local time averaged thickness maps
(top view on the film)

Thin film
h = 0.284 nm



Thick film
h =1.78 nm



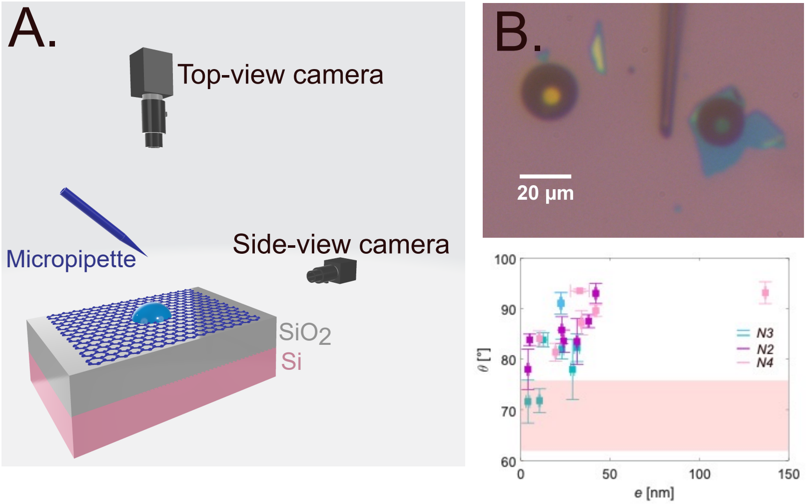
■ SiO^- group

Dry spots on neutral zones?

Take-home messages

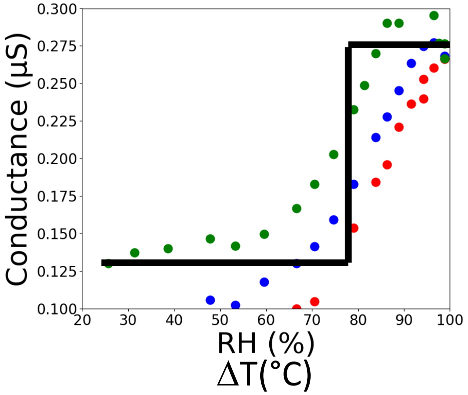
- **Experiments** to measure **transport in subnanometric** water films.

- Break-down of continuous description **< 0.3 nm**.
  → *Effect of the material?*
  (F. Vialla, M. Zhao)
  → *MD with reactive interface*



- Design of an **ionic gate**, activated by humidity or temperature.
  → *Optical activation?*

- Out-of-equilibrium response for humidity gradients?
  → *Macroscopic results*



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Christophe Ybert

Olivier Vincent

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ANR

SOFT NANOFLU

Team Liquid and Interfaces