Electrical measurements
at the nanoscale
using Scanning Probe Microscopy
- Part 2 -

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Question

Can we probe the dielectric constant (electric permittivity) on the nanoscale?

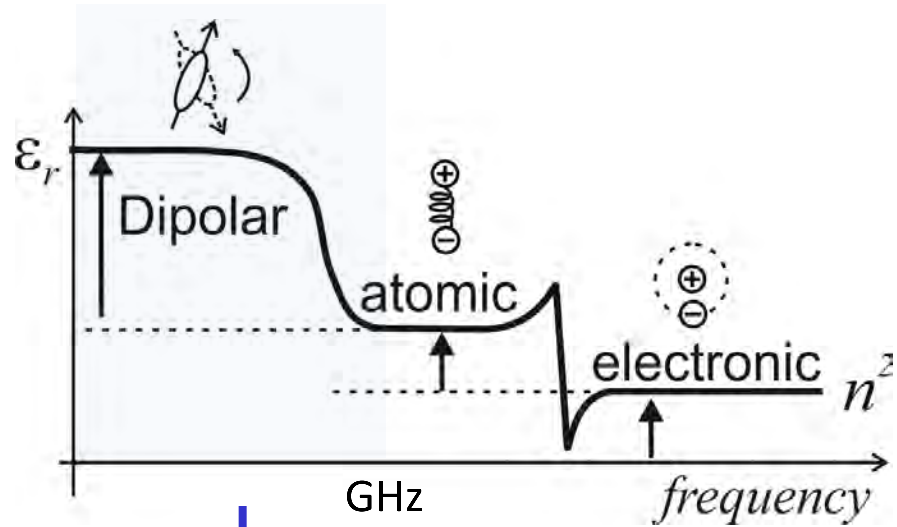
Basics of electric polarization

Macroscopic polarization

$$\vec{P}(\vec{r}) = \sum_i \vec{p_i} = \varepsilon_0(\varepsilon_r - 1)\vec{E}(\vec{r})$$

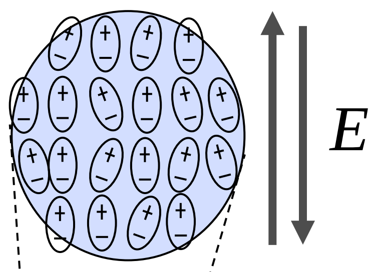
↓

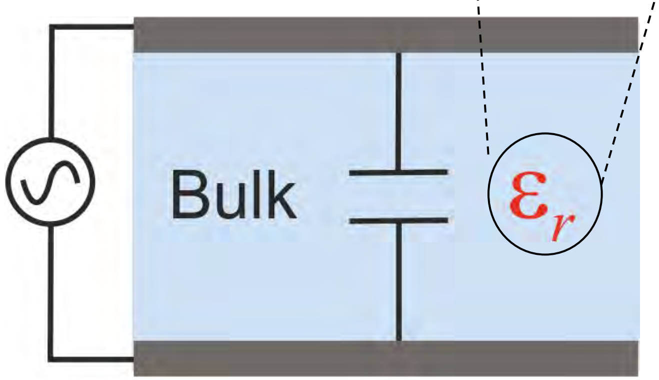
Dielectric constant
or permittivity



↓

Electric dipoles p_i
distribution, order,
rotational freedom





Capacitance measurement

$$C = \frac{\varepsilon_0 \varepsilon_r A}{h}$$

$A =$ area

$h =$ thickness

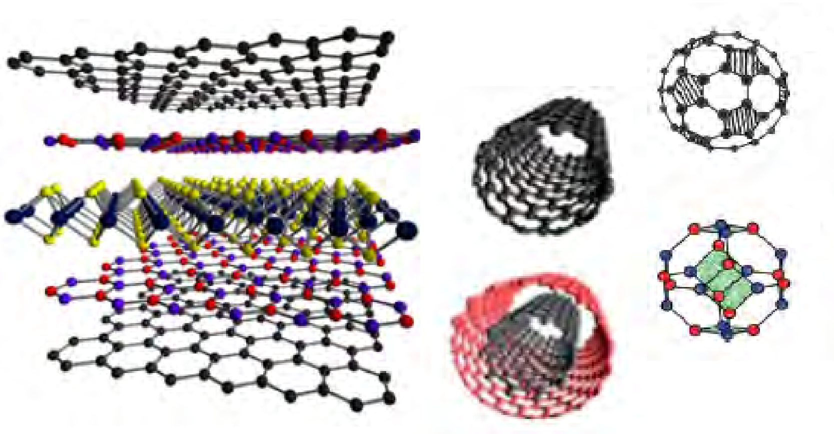
Unknown dielectric constants at the nanoscale

Lack of experimental tools with sufficient sensitivity

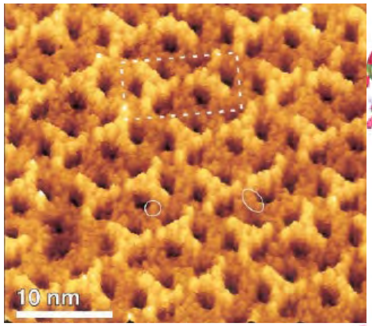
Theory to be established

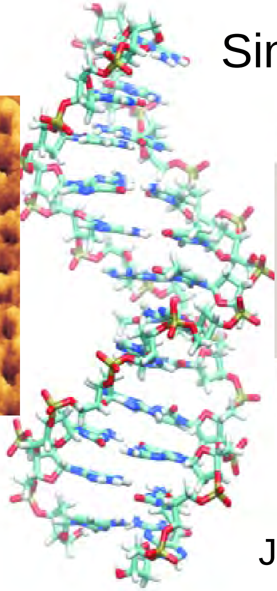
A multitude of systems still to explore

Low-dimensional systems

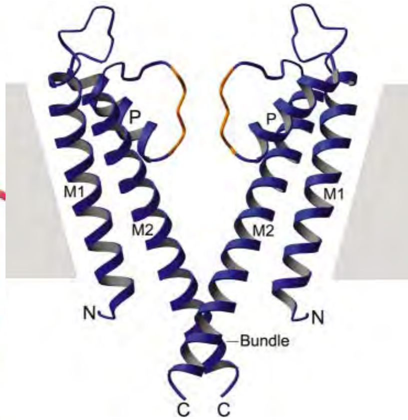


Biointerfaces





Single molecules



Bonaccorso *et al. ACS Nano* 2013

Goldberg *et al. ACS Nano* 2010

Jiang *et al. Nature* 2002

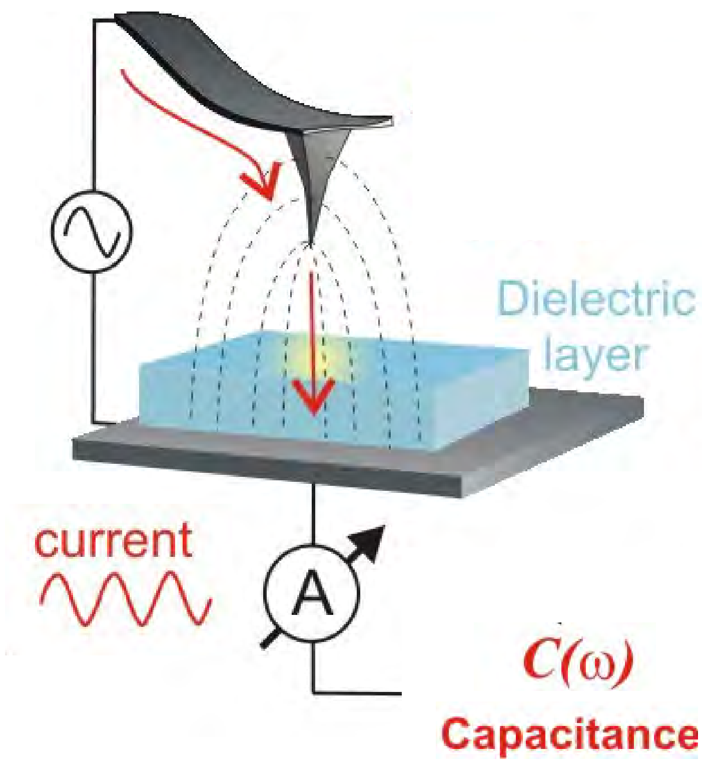
Engel *et al. Nat. Struct. Biol.* 2000

Physical Sciences

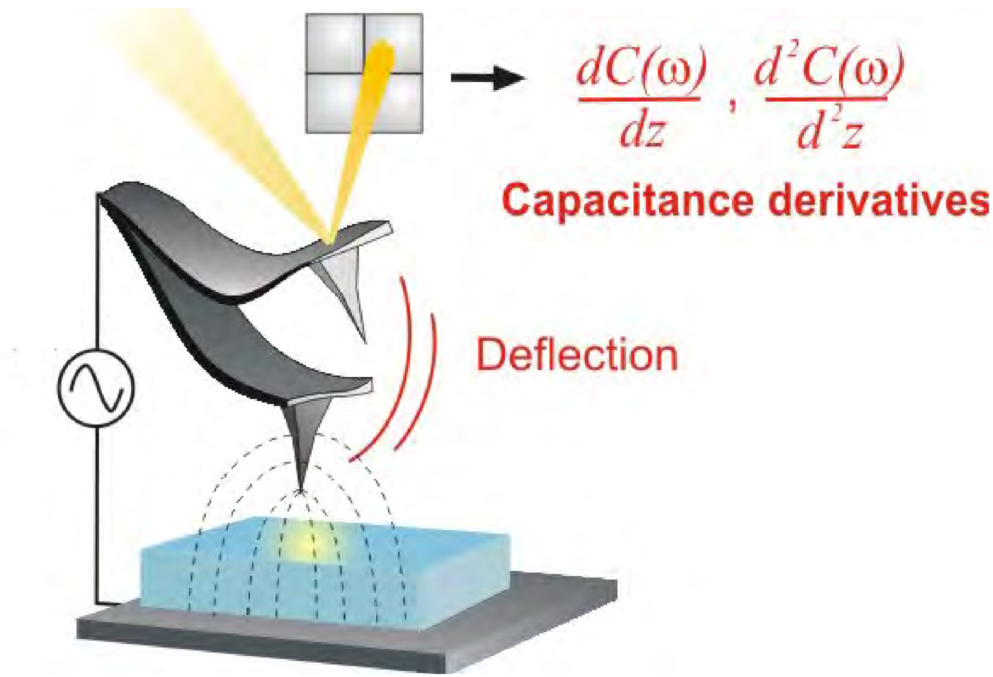
Chemistry and Biology

Scanning Dielectric Microscopy (SDM)

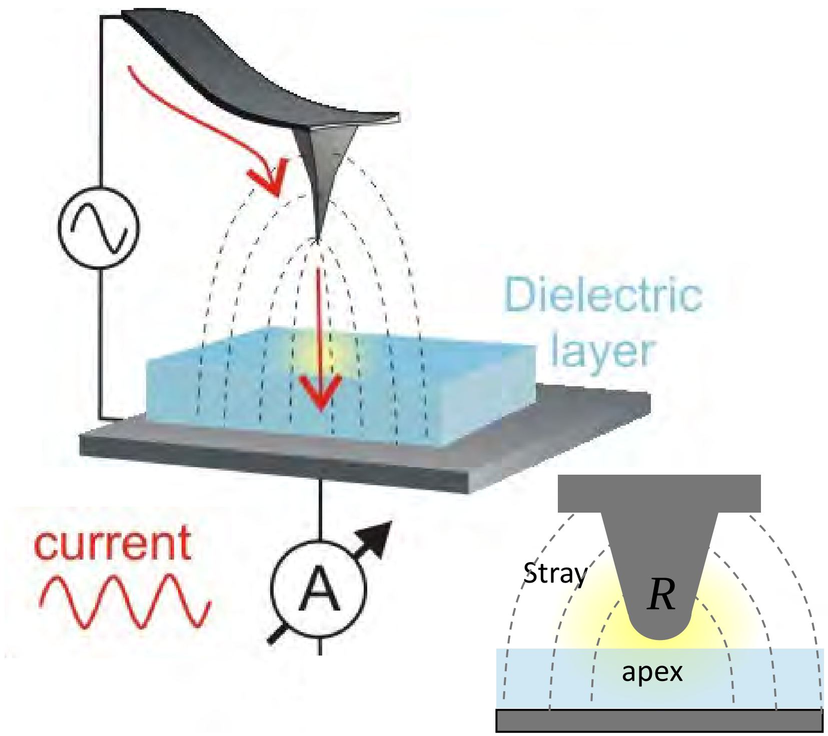
Current-sensing

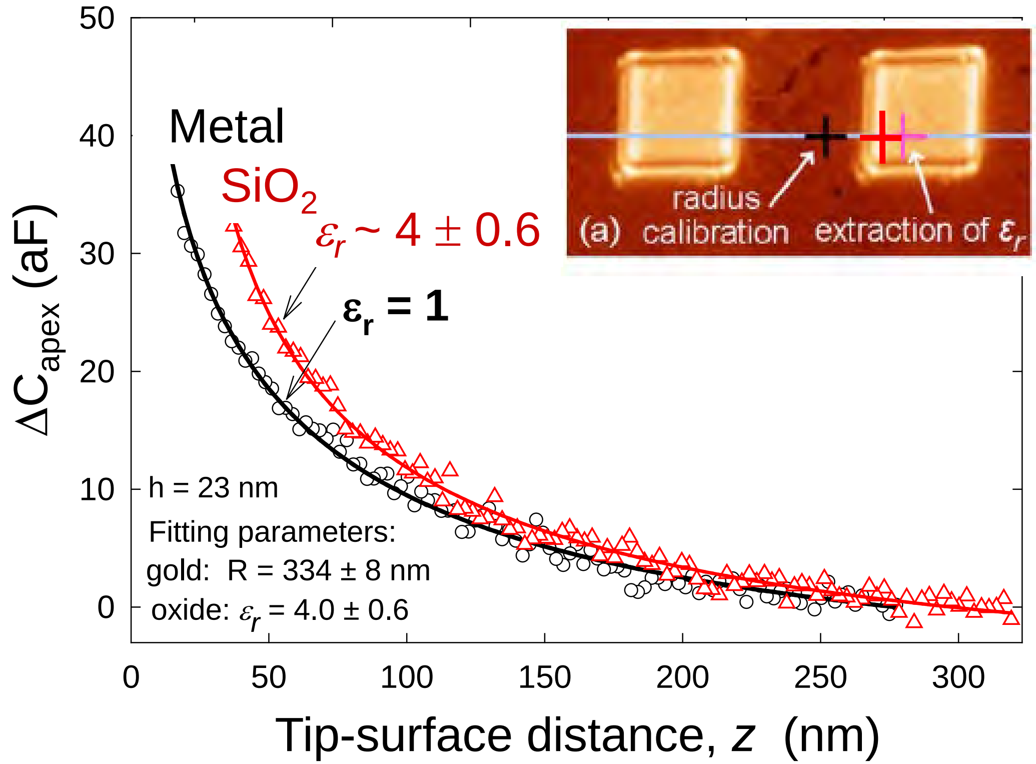


Electrostatic force-sensing



Dielectric constant measurement with CS-AFM





$$C_{total} = C_{apex} + C_{cone} + C_{cantilever} + C_{setup}$$

$$\Delta C_T \approx \Delta C_{apex} + k_{stray}(z_0 - z)$$

For thin dielectrics $h < 50$ nm

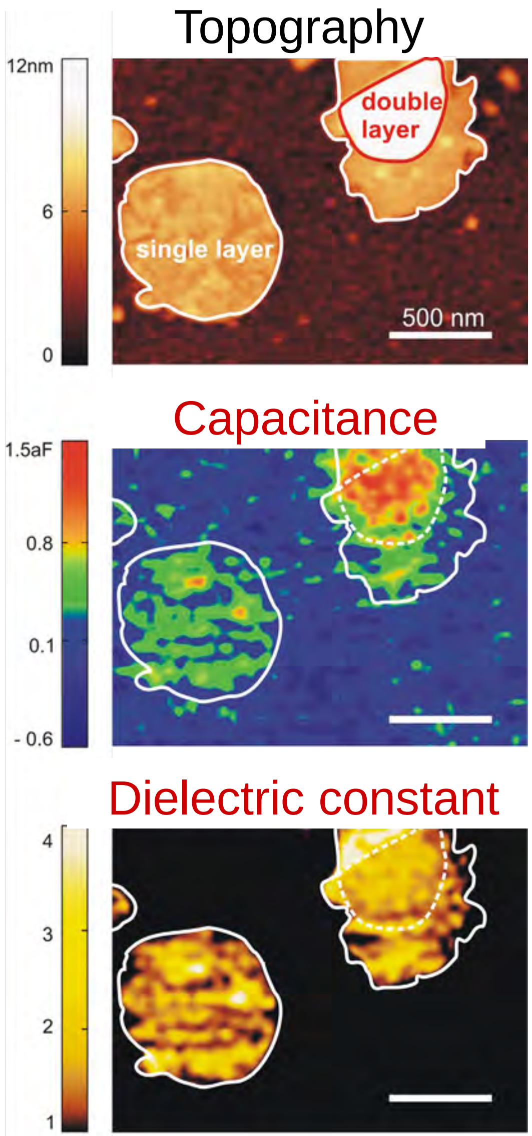
$$C_{apex}(z, h, R, \varepsilon_r) = 2\pi\varepsilon_0 R \cdot \ln\left(1 + \frac{R\cdot(1-\sin\theta)}{z + h/\varepsilon_r}\right) + c_0$$

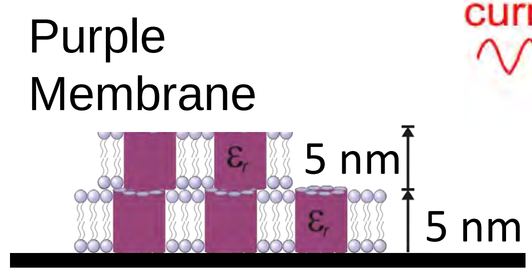
Logarithmically dependent on ε

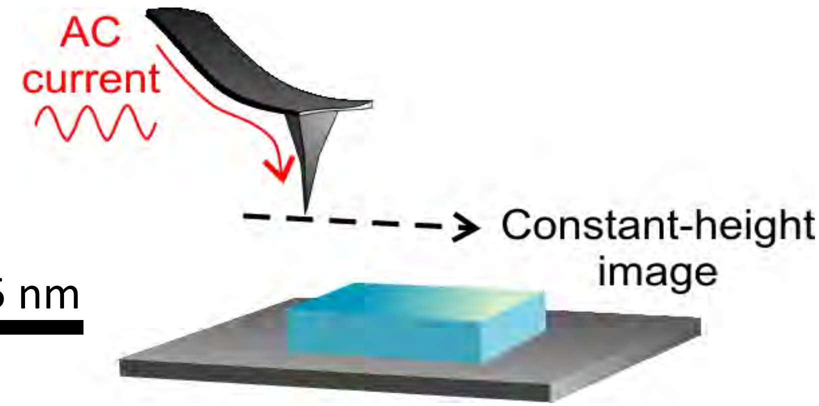
Proportional to the tip radius R

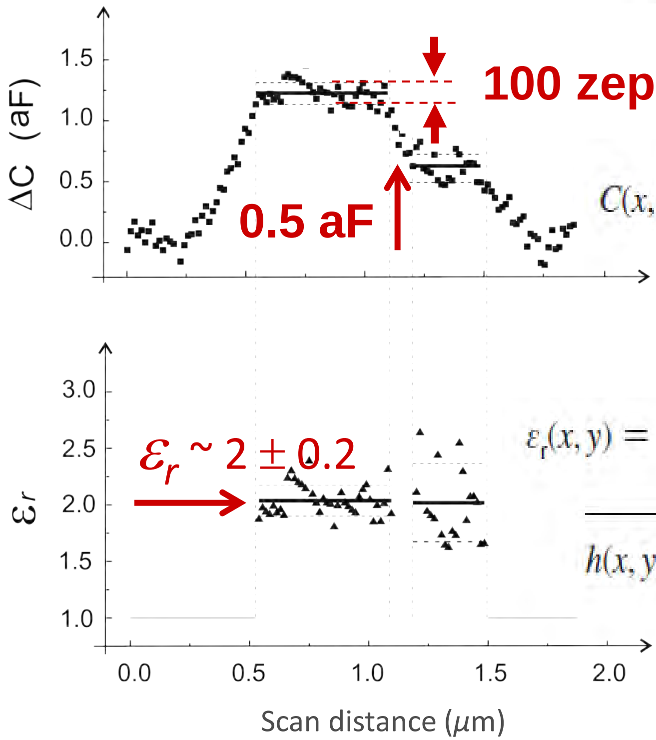
Fumagalli, Ferrari *et al. Appl. Phys. Lett.* 2007

Dielectric constant imaging with CS-AFM







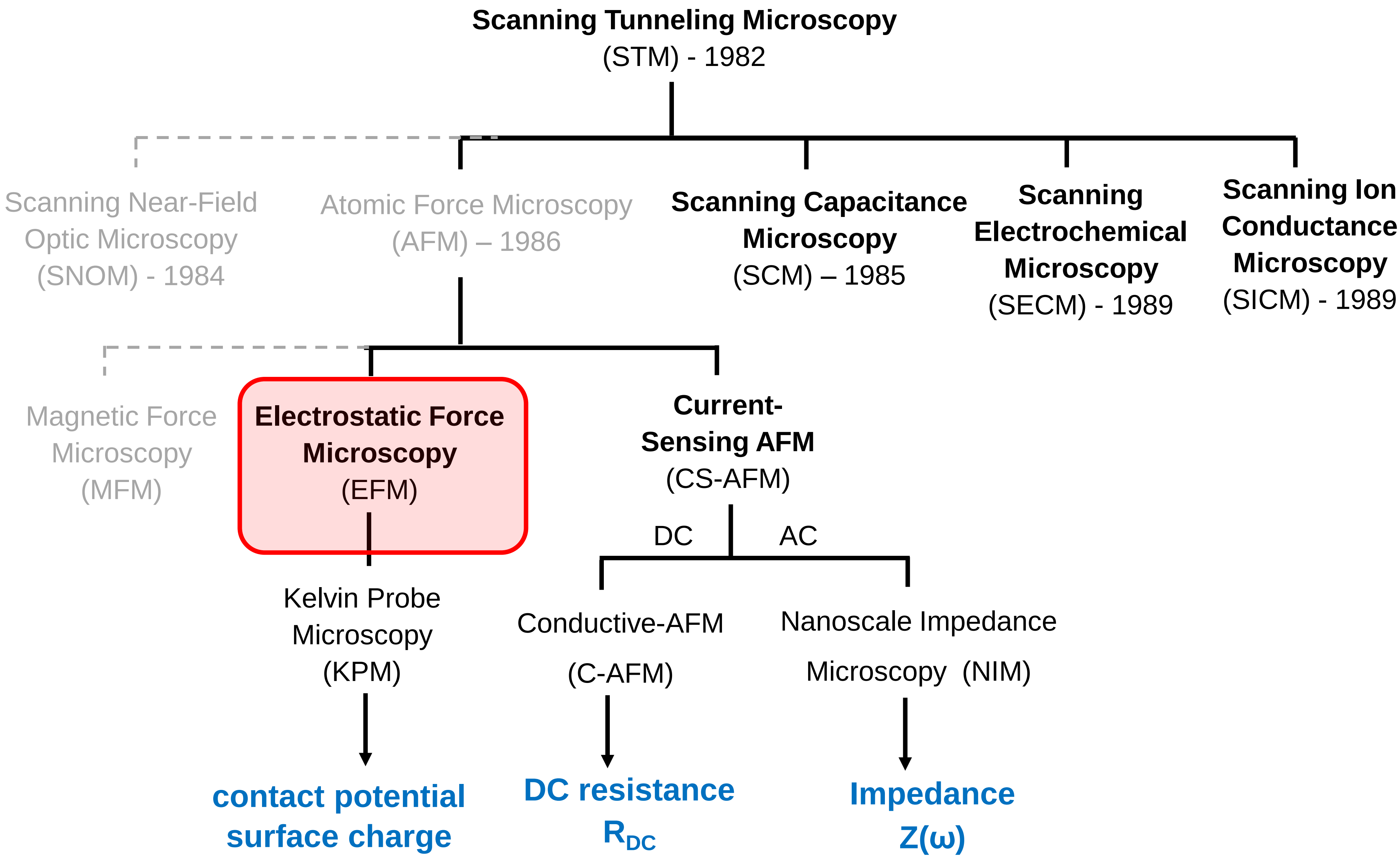


$$C(x,y,z_0) = 2\pi\varepsilon_0 R \ln\left[1 + \frac{R(1-\sin\vartheta)}{z_0 + \frac{h(x,y)(1-\varepsilon_r(x,y))}{\varepsilon_r(x,y)}}\right]$$

$$\varepsilon_r(x,y) = \frac{h(x,y)}{h(x,y) - z_0 + \frac{R(1-\sin\vartheta)}{\exp\left(\frac{\Delta C(x,y,z_0)}{2\pi\varepsilon_0 R}\right)\left(1 + \frac{R(1-\sin\vartheta)}{z_0}\right) - 1}}$$

Fumagalli, Ferrari, Sampietro *et al*. *Nano Lett.* 2009

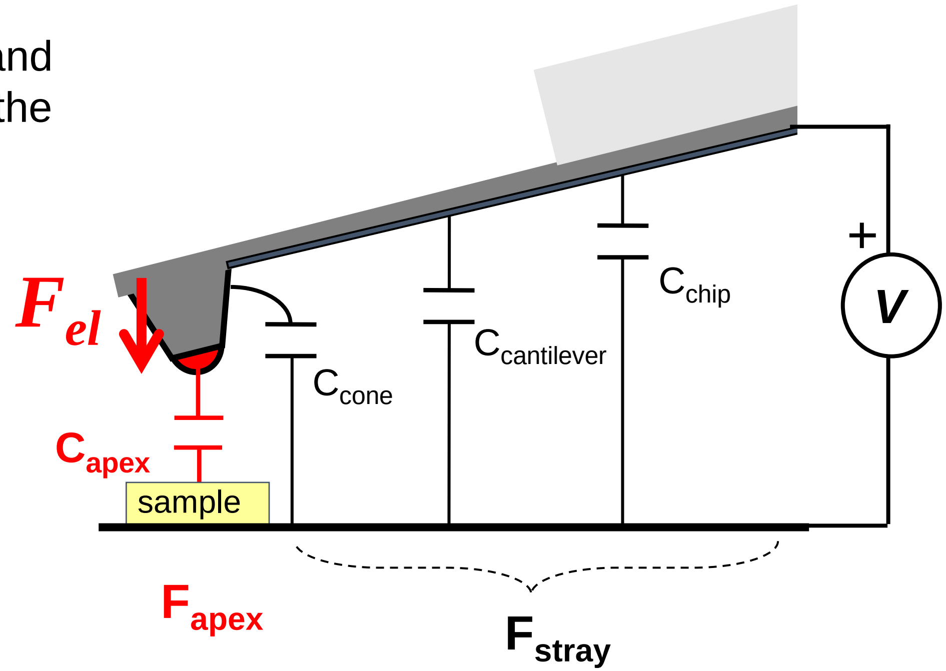
Electrical Scanning Probe Microscopies

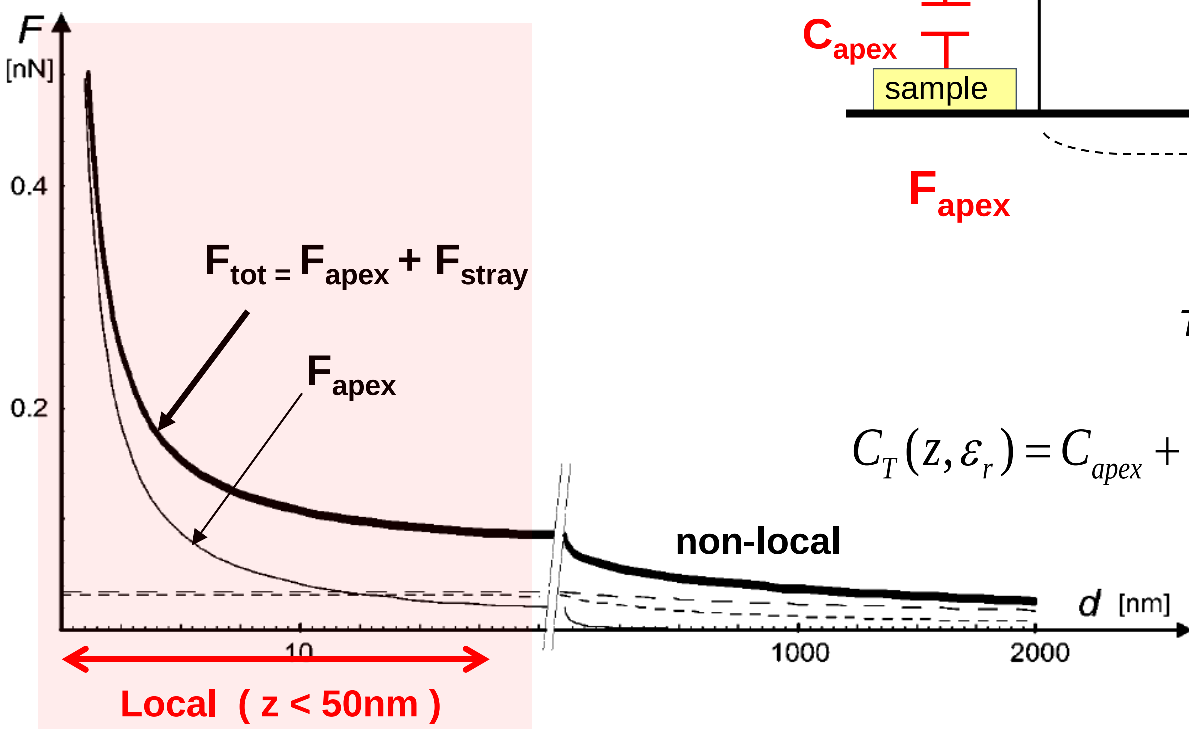


Electrostatic Force Microscopy (EFM)

When a voltage is applied between the tip and the cantilever kept **out of contact**, the cantilever detects an electrostatic force

$$F_{el}(z) = -\frac{1}{2}\frac{\partial C}{\partial z}V^2$$





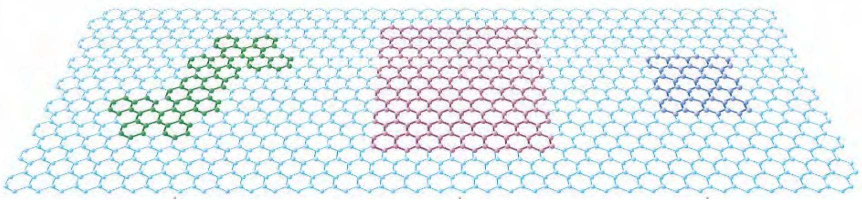
The cantilever is negligible

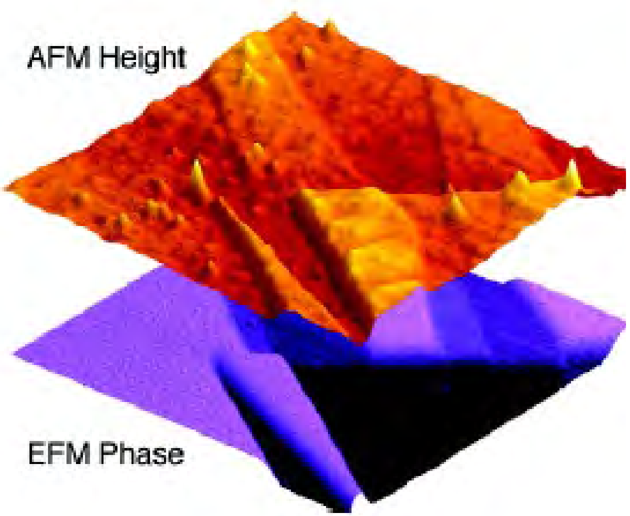
The chip not detected

$$C_T(z,\varepsilon_r) = C_{apex} + C_{cone} + C_{cantilever} + C_{chip}$$

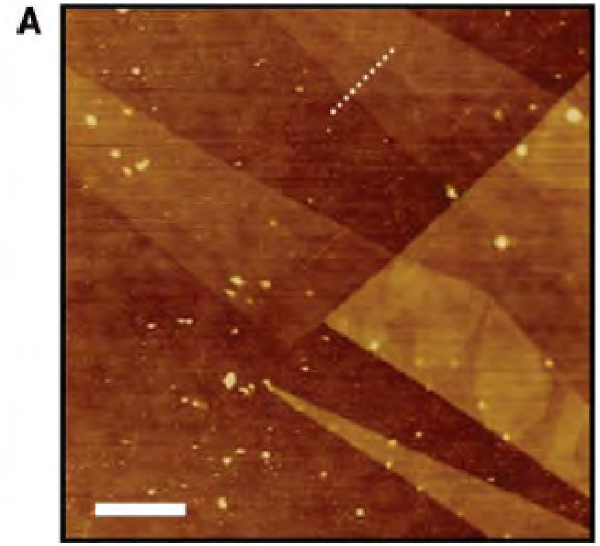
Electrostatic Force Microscopy (EFM)

Graphene
flat monolayer of carbon atoms
packed into a 2D sheet

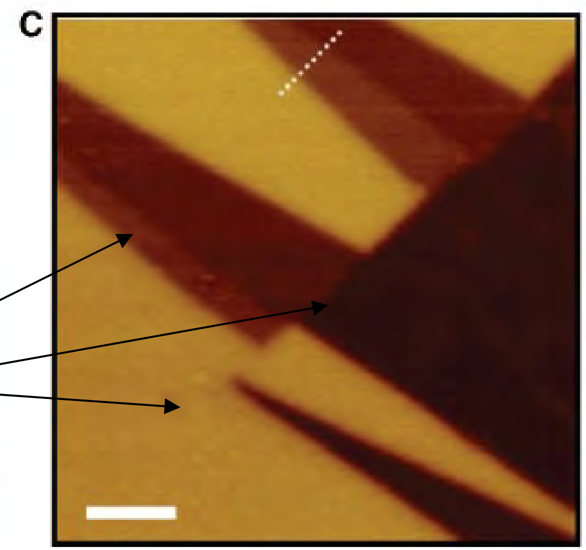




Topography



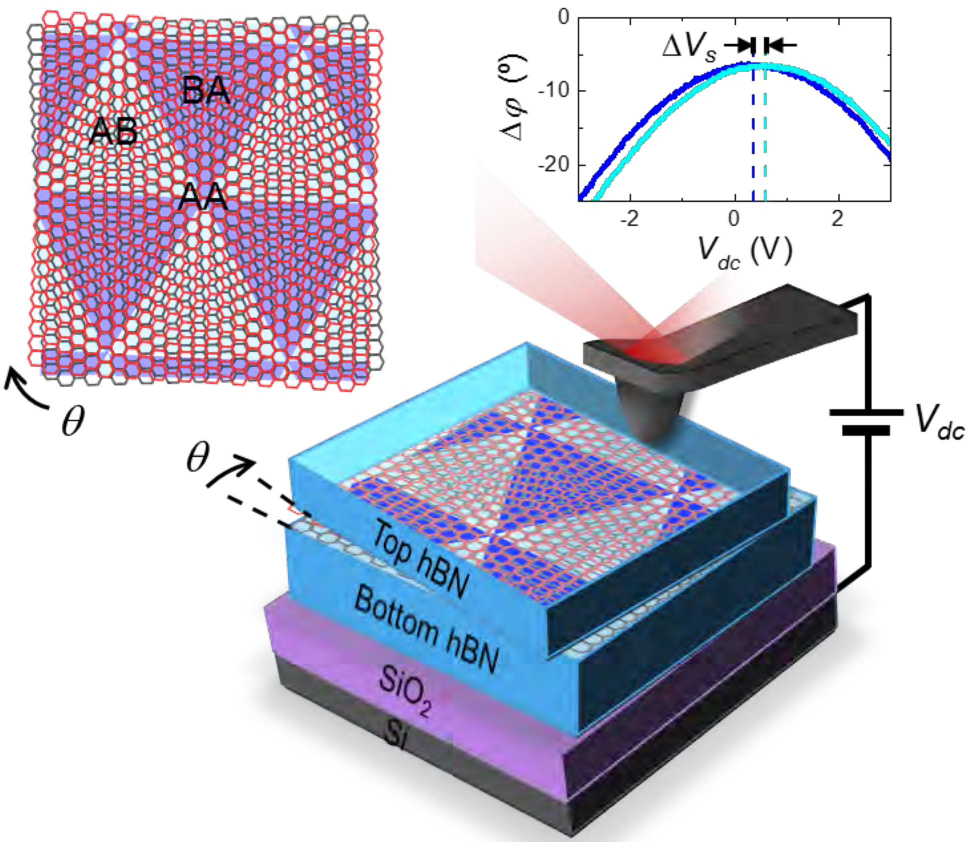
EFM



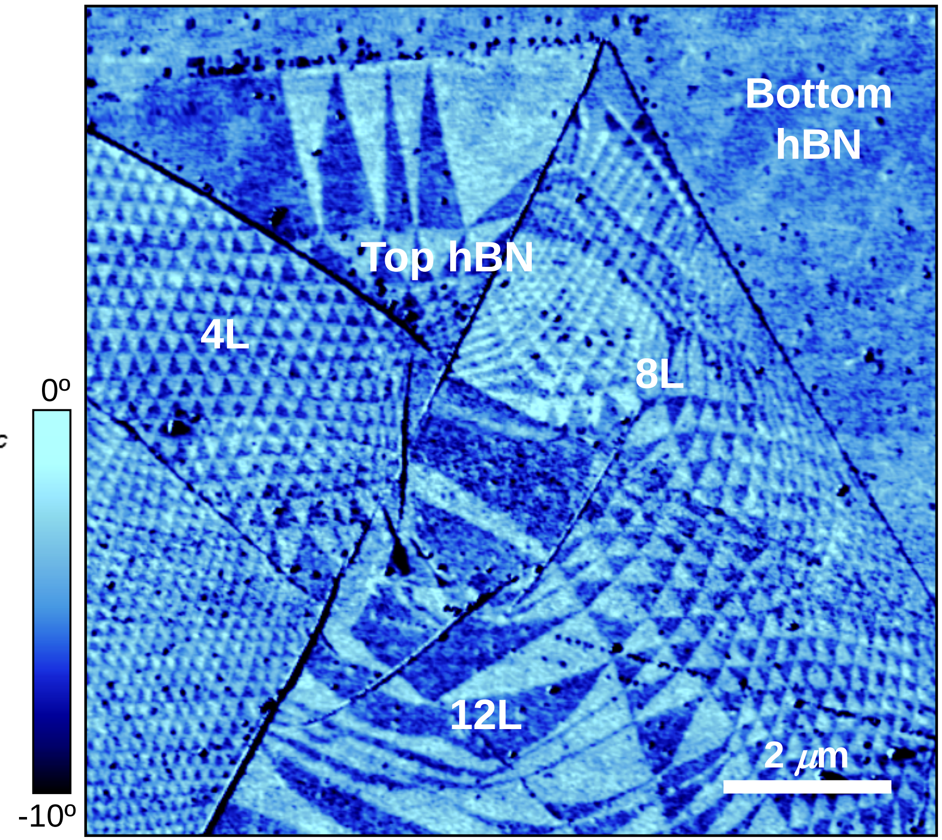
Sujit et al. NanoLetters 2008

Ferroelectric-like polarization in twisted hBN

Emergence of interfacial dipolar domains



EFM



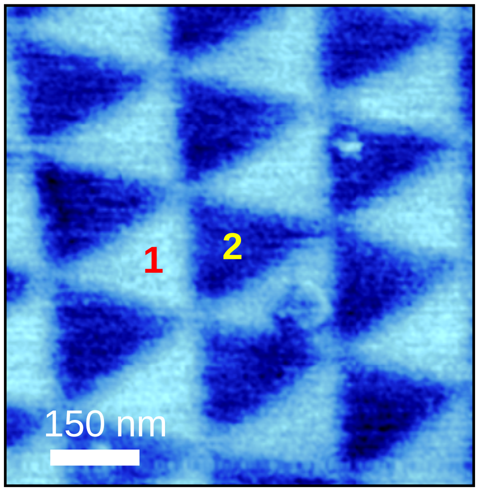
Oppositely charged domains
due to BN and NB interfacial dipoles
when twisting two insulating crystals

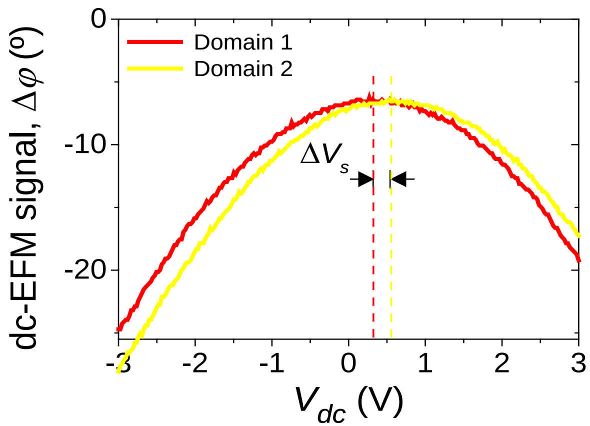
C. R. Woods *et al. Nature Comm. 2021*

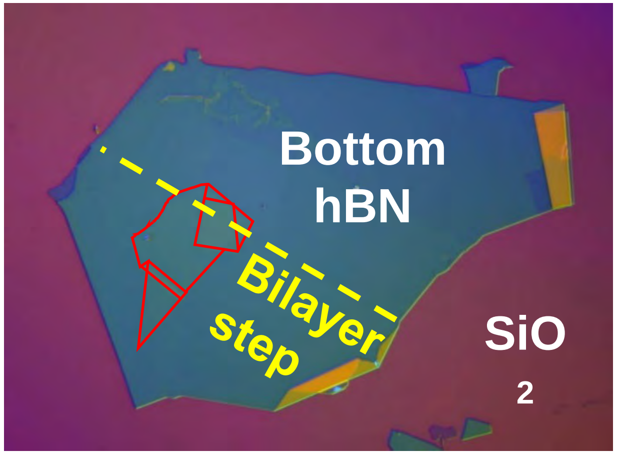
Ferroelectric-like polarization in twisted hBN

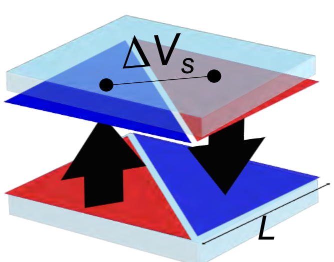
Emergence of interfacial dipolar domains

EFM

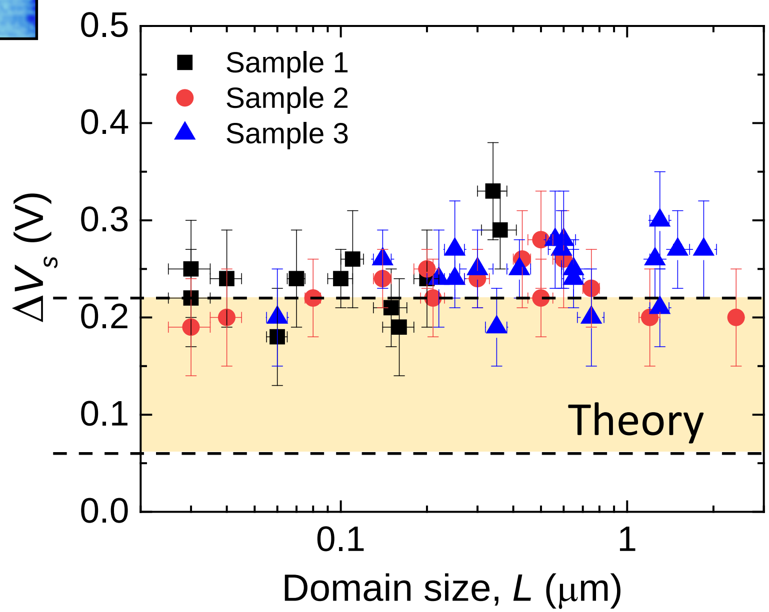


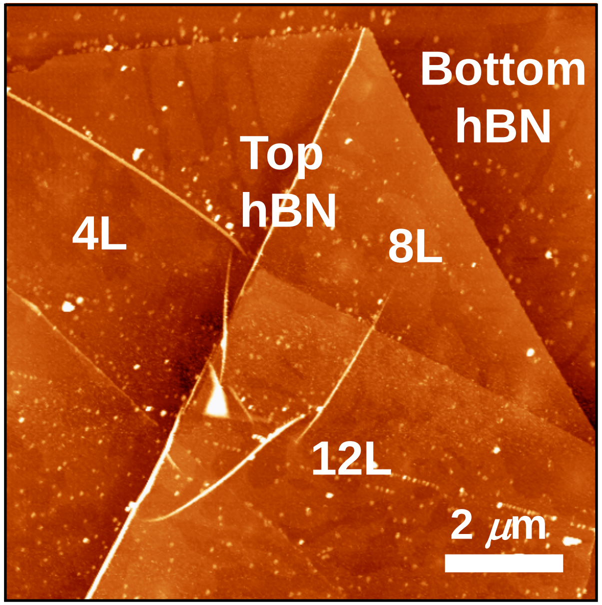




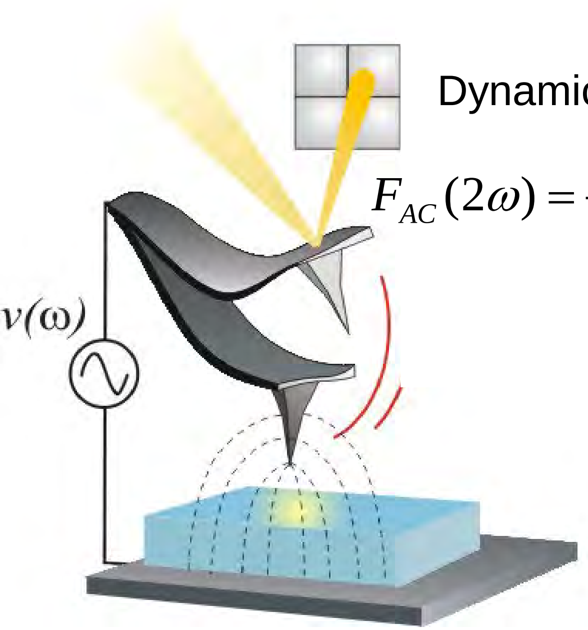


BN and NB interfacial dipoles



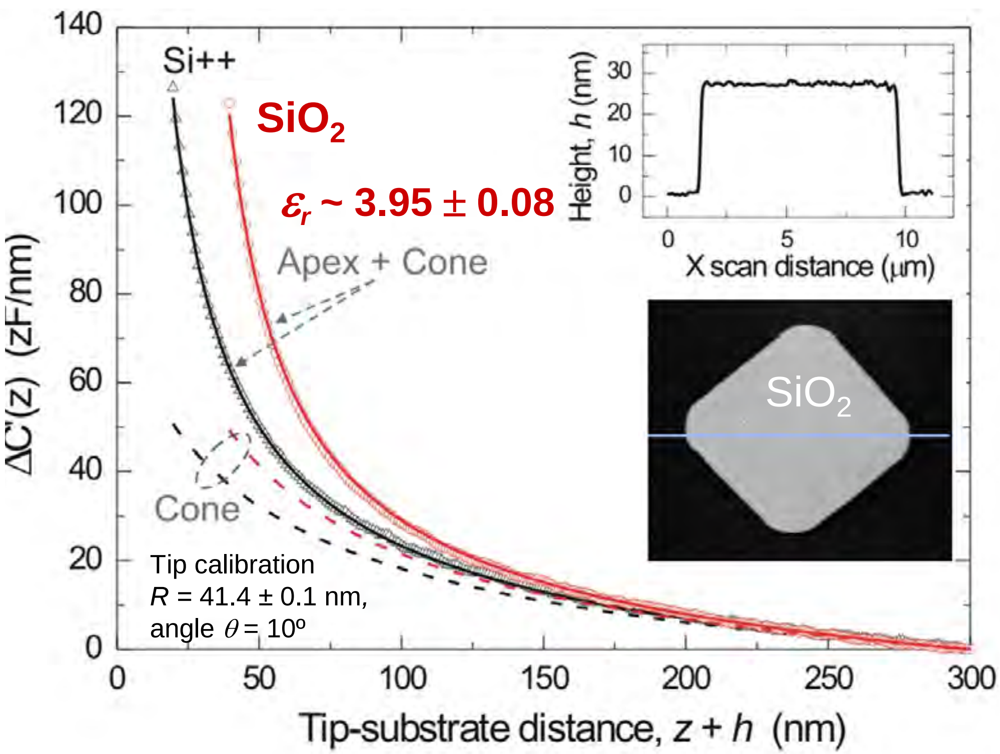


Dielectric constant measurement using EFM



Dynamic modes

$$F_{AC}(2\omega) = \frac{1}{4}\frac{dC}{dz}V_{AC}(\omega)^2$$



negligible

$$C_{total} = C_{apex} + C_{cone} + C_{cantilever} + C_{setup}$$

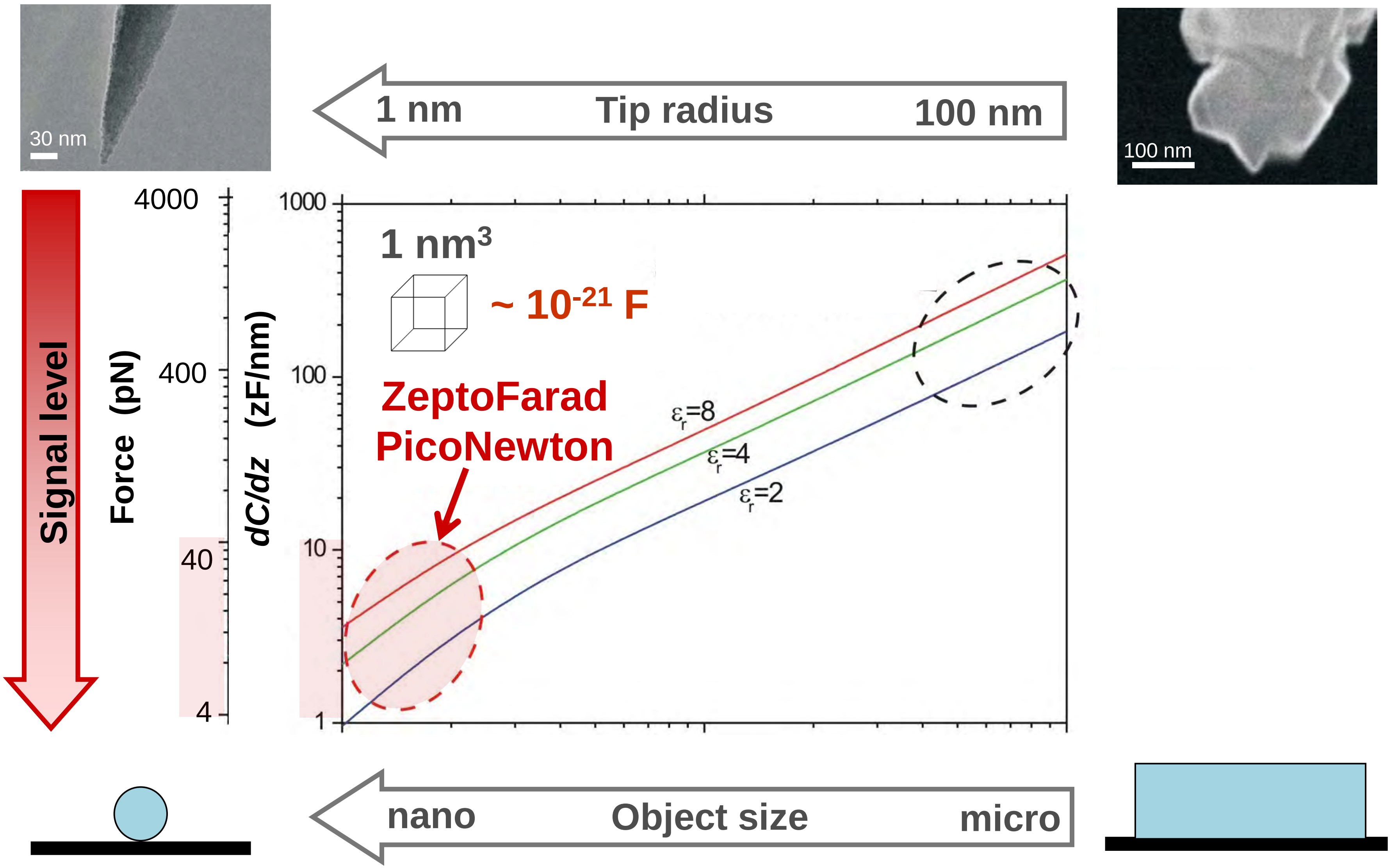
$$\frac{dC_{total}}{dz}(z, R, h, \varepsilon_r) \approx \frac{dC_{apex}}{dz} + \frac{dC_{cone}}{dz}$$

Advantages
Higher sensitivity, less parasitics

Disadvantages
Cantilever mechanical resonances, cantilever bandwidth

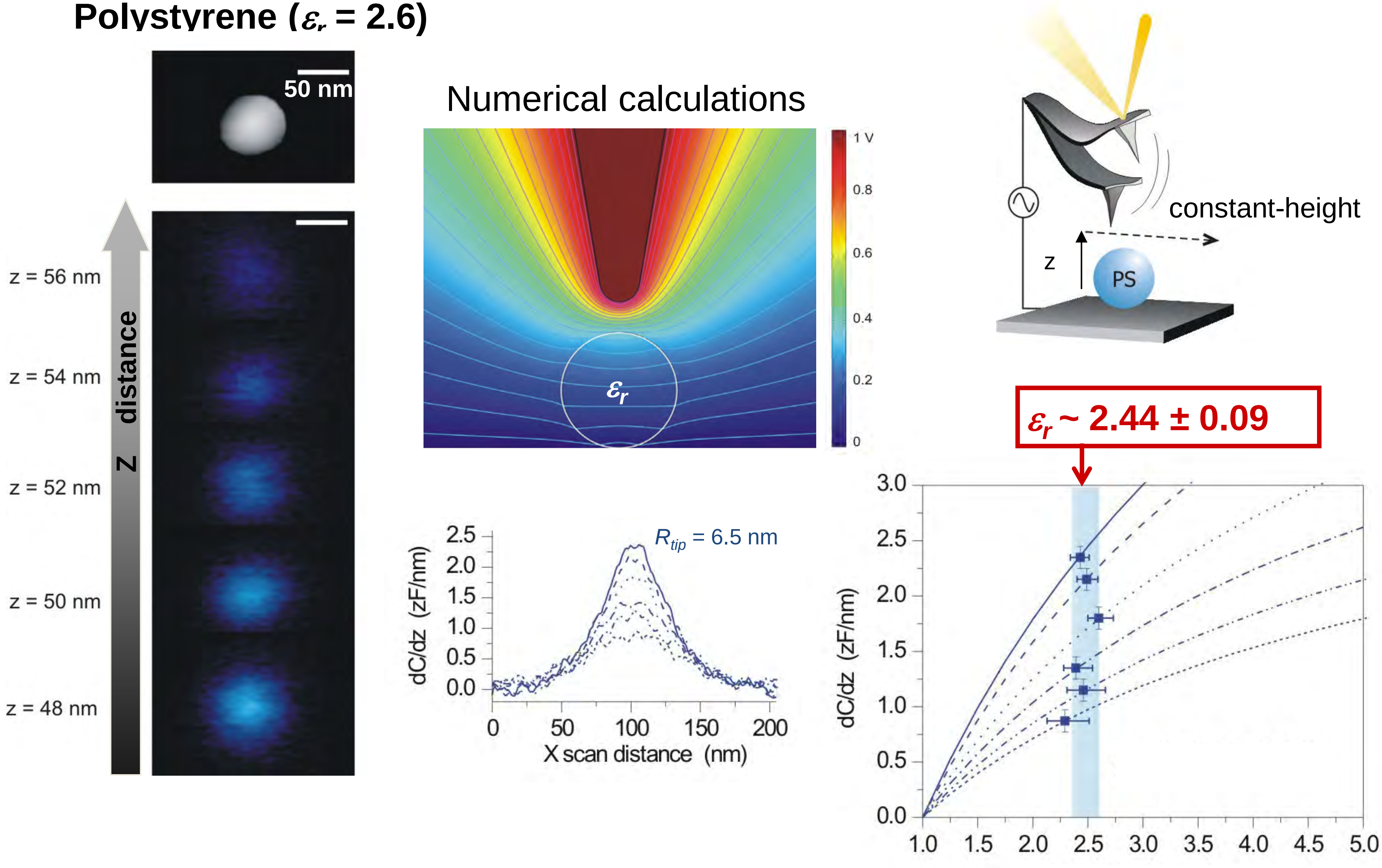
Fumagalli, Ferrari, Sampietro *et al. Appl. Phys. Lett. 2010*

Ultra-high sensitivity in capacitance is needed



Dielectric constant of a single nanoparticle

Polystyrene (ε_r = 2.6)



Fumagalli *et al.* *Nat. Mater.* 2012

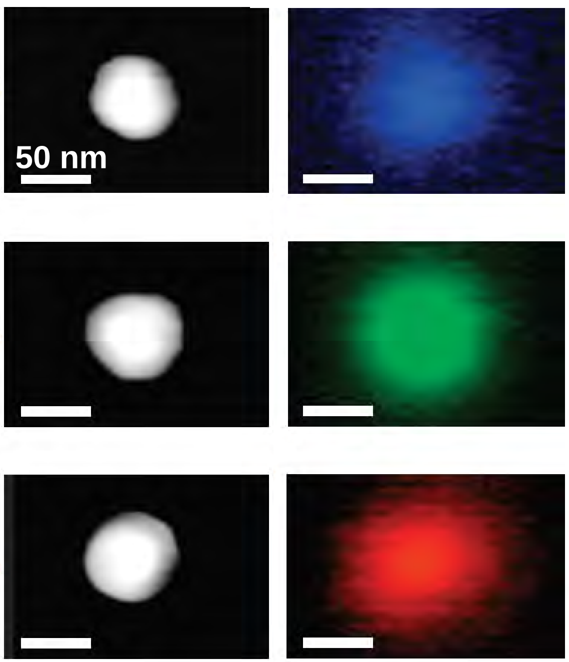
Dielectric constant of single nanoparticles

Topography **Dielectric image**

PS
ε_r **= 2.6**

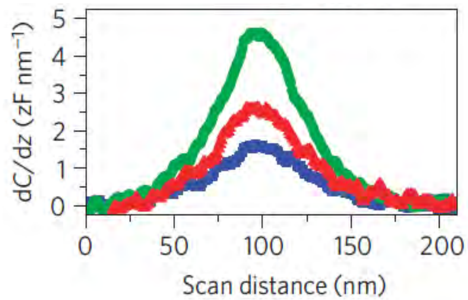
SiO$_2$
ε_r **= 3.9**

Al$_2$O$_3$
ε_r **= 9.4**

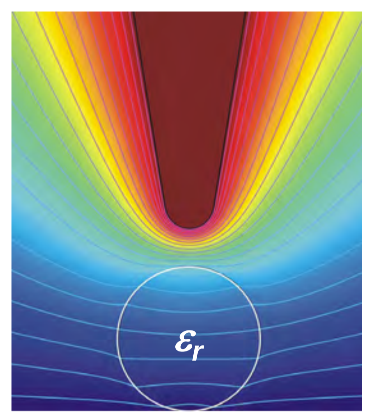


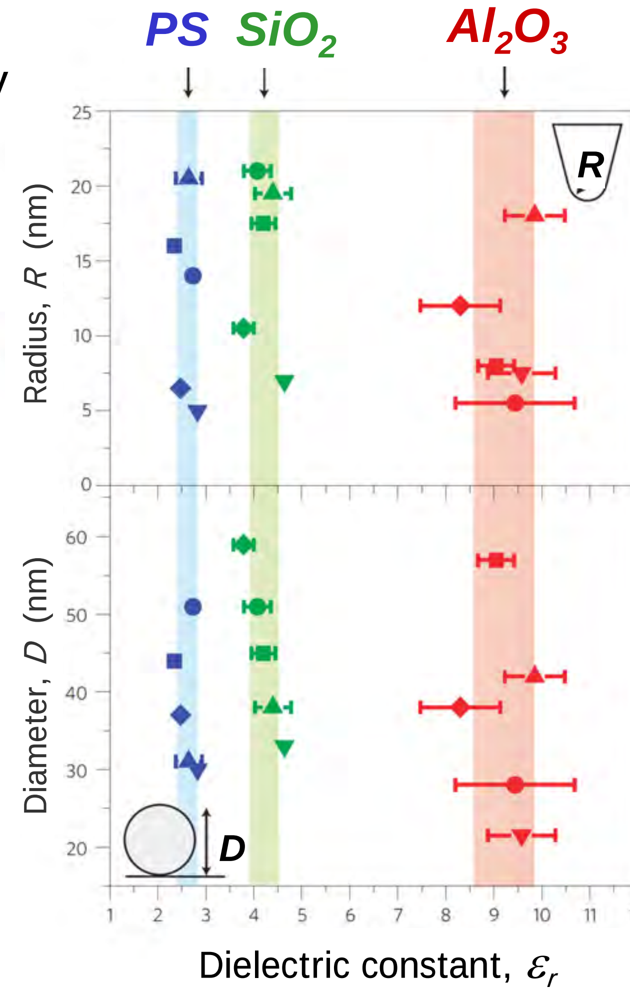
30 nm

Mixed
polarization + geometry



Numerical calculations





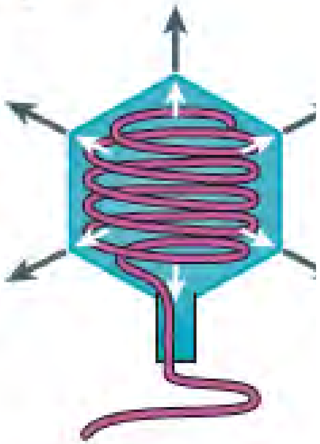
Independently from geometry

good precision $\delta\varepsilon$ < 7%

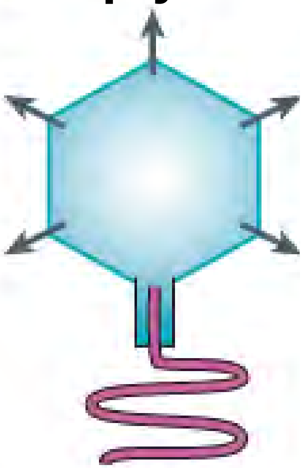
Fumagalli *et al.* *Nat. Mater.* 2012

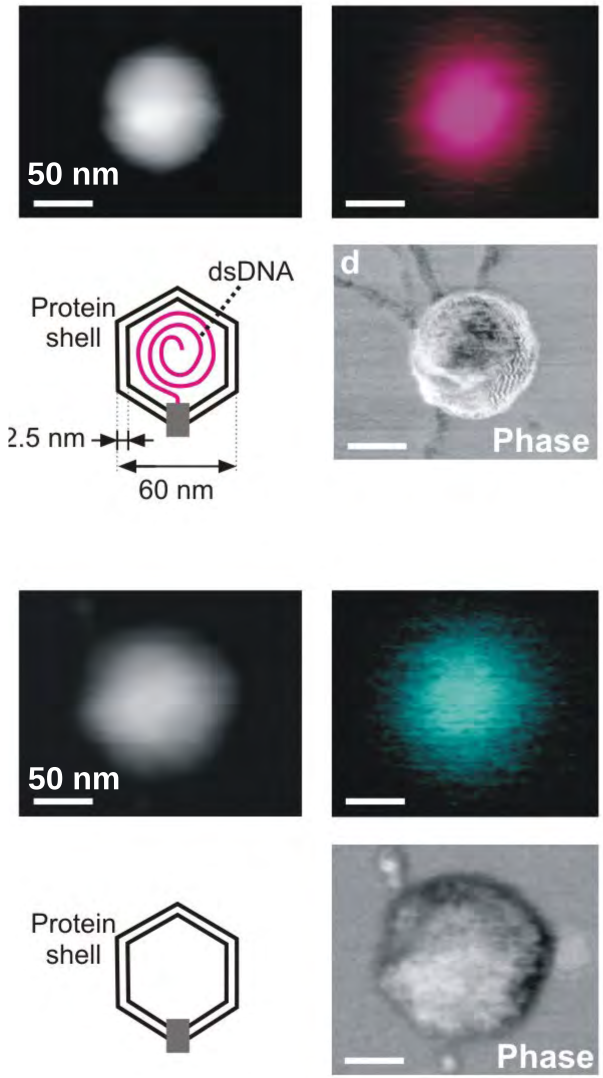
A nanoparticle of unknown properties

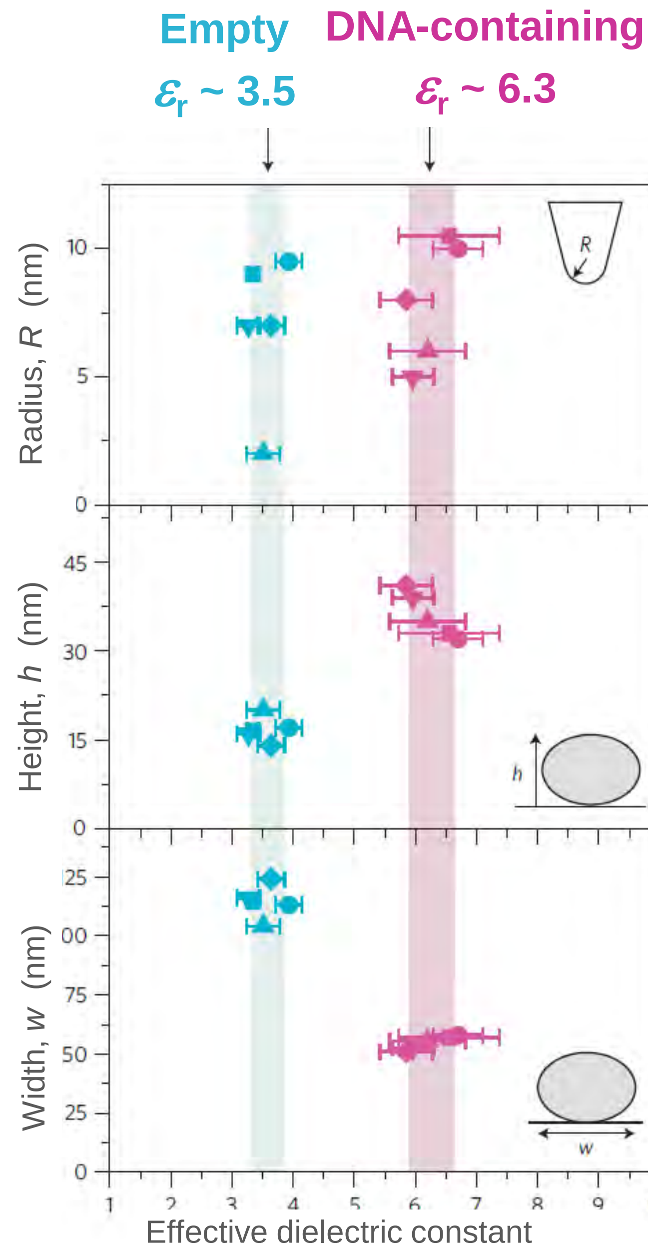
Full virus



Empty virus







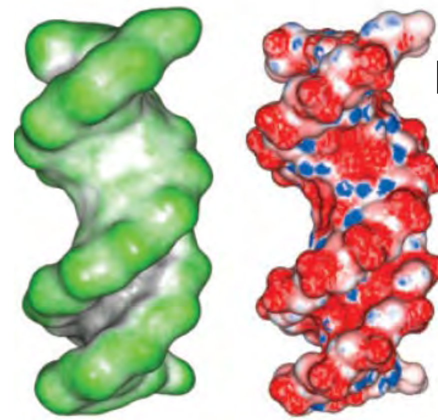
Dielectric polarization properties of DNA

$$\nabla \cdot \varepsilon(\vec{r})\nabla\phi(\vec{r}) = -[\rho_{\text{ions}}(\vec{r}) + \rho_{\text{perm}}(\vec{r})]$$

? Unknown

Complex structure
Interplay with solvent (water)

3D electrostatic potential maps depend on ε_{DNA} !



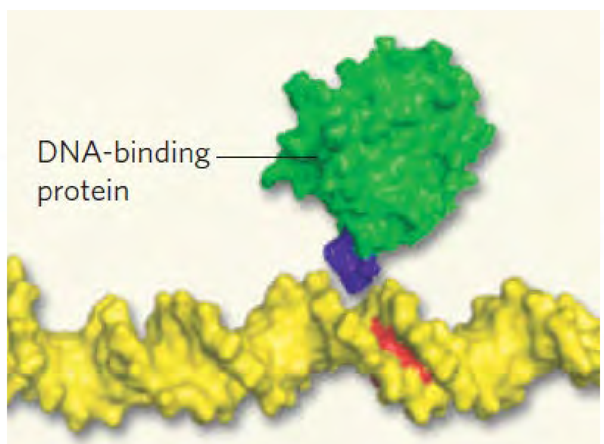
Electrostatic potential

Major therapeutic impact

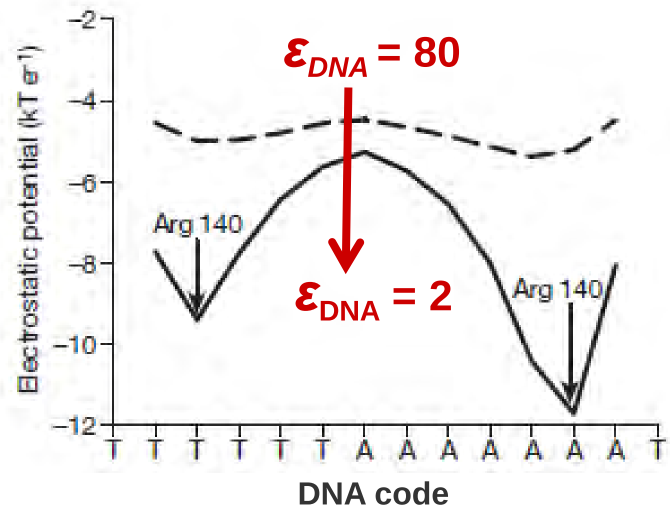
DNA structure

Molineux *et al. Nature Rev. 2013*

DNA-protein affinity



Rohs *et al. Nature* 2009

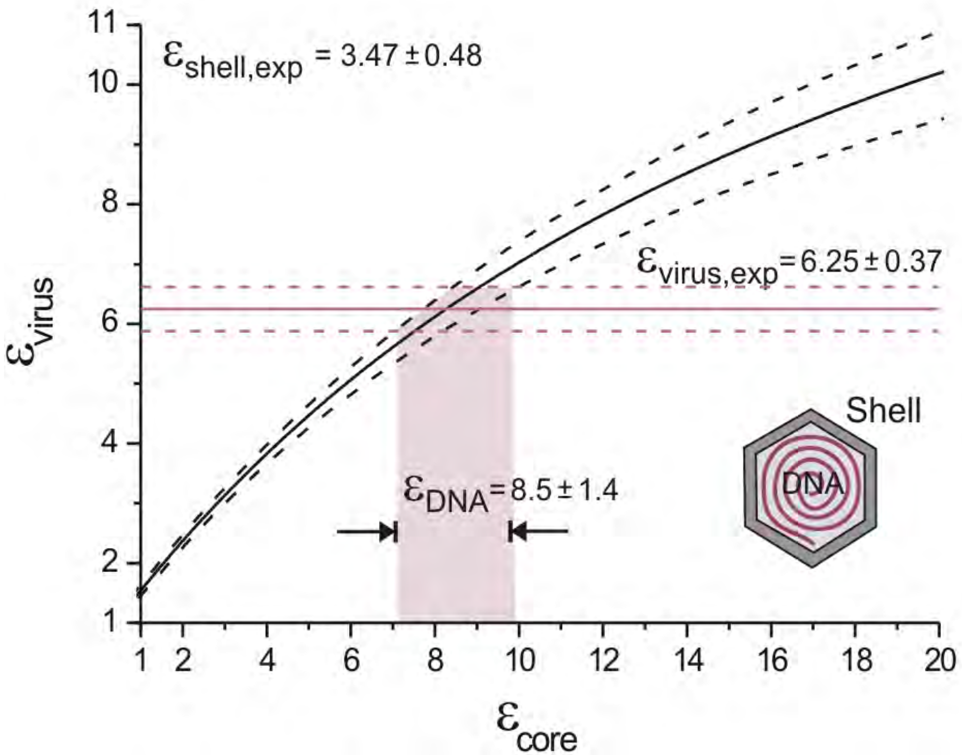


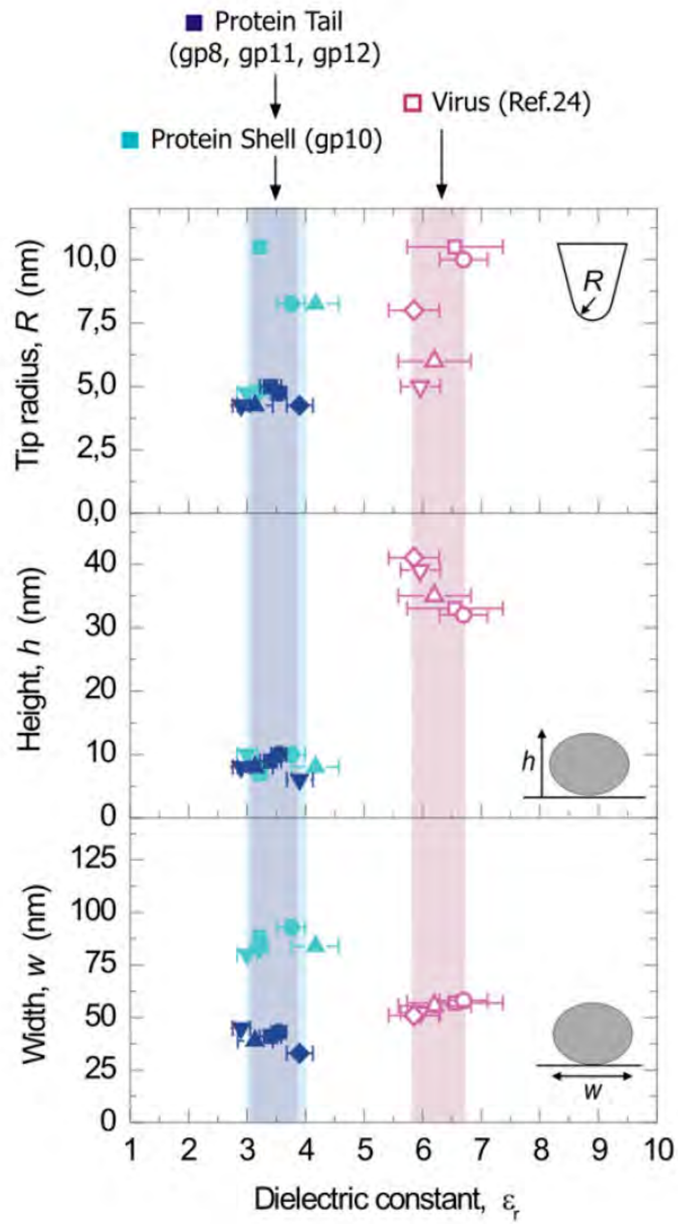
Dielectric polarization properties of DNA

Poisson-Boltzmann equation

$$\nabla \cdot \varepsilon(\vec{r}) \nabla \phi(\vec{r}) = -[\rho_{\text{ions}}(\vec{r}) + \rho_{\text{perm}}(\vec{r})]$$

ε_{DNA} = 8.5 ± 1.4 from our experiments
sensibly larger than normally assumed (2-4)





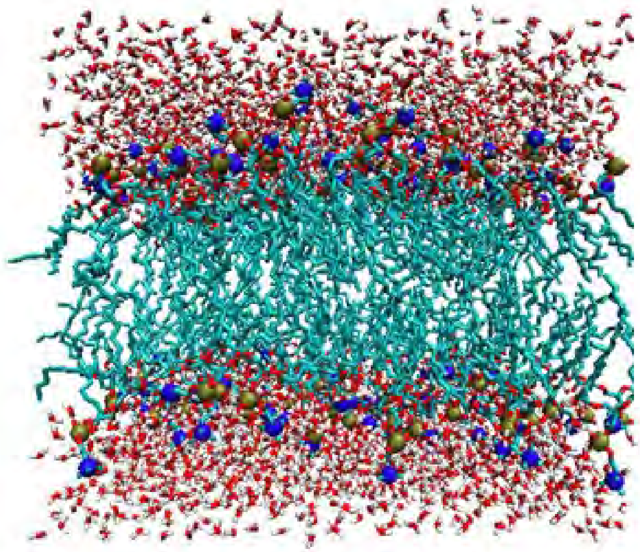
Cuervo *et al.* PNAS 2014

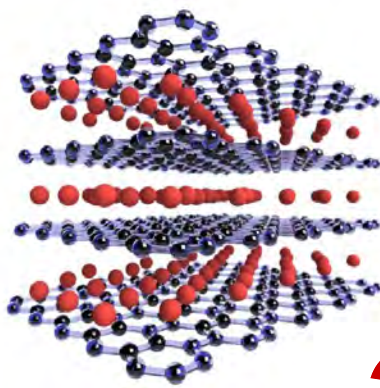
What is the dielectric constant of confined water?

Remained unknown

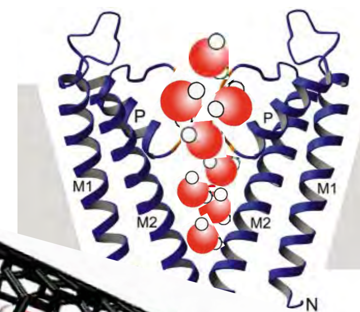
No experimental tools with enough sensitivity

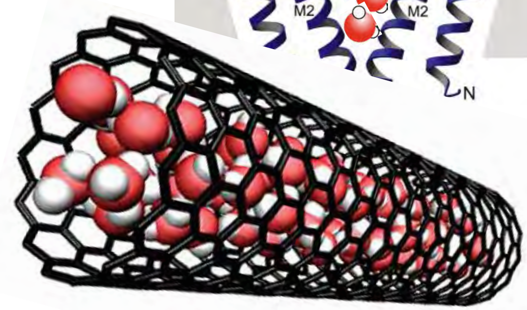
Interfaces

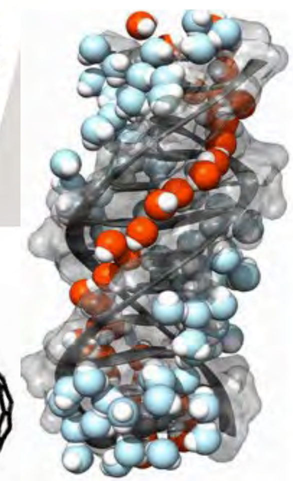




Nanocavities







?

ε_{water}

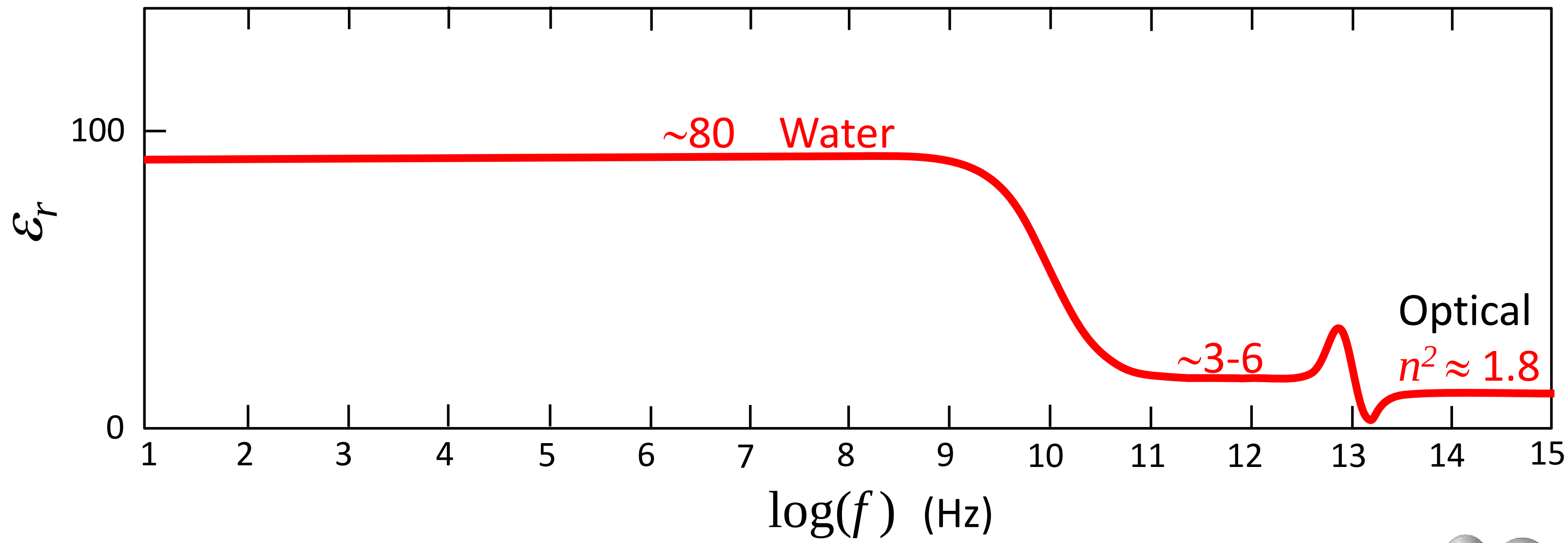
Ice-like hypothesis

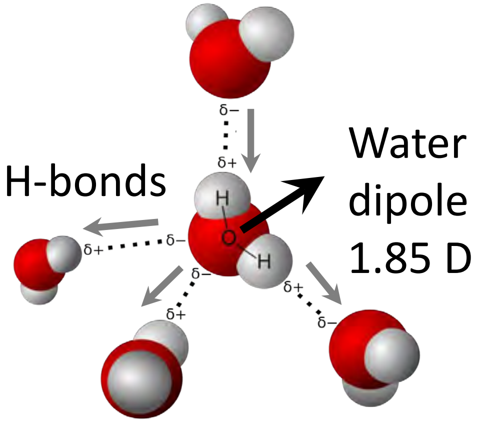
Dielectric constant expected to be different from bulk

Dielectric spectra of bulk water and ice

Large ε_r due to water dipole and H-bonds polarization

→ ability to dissolve substances - *"the solvent of Life"*





Dielectric spectra of bulk water and ice

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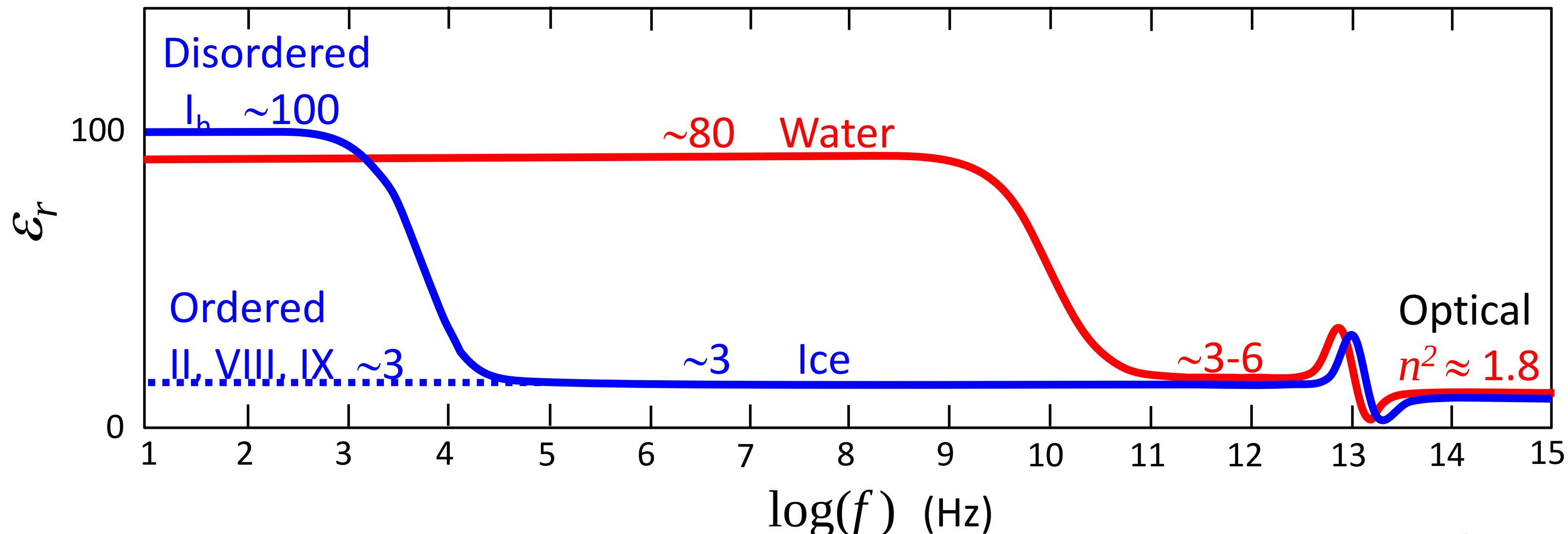
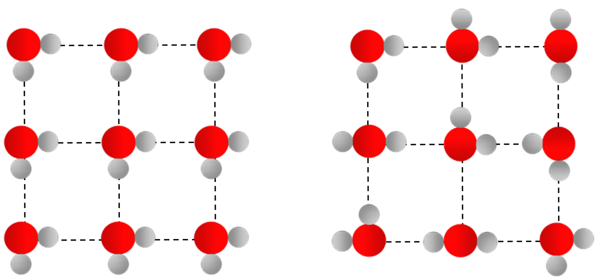


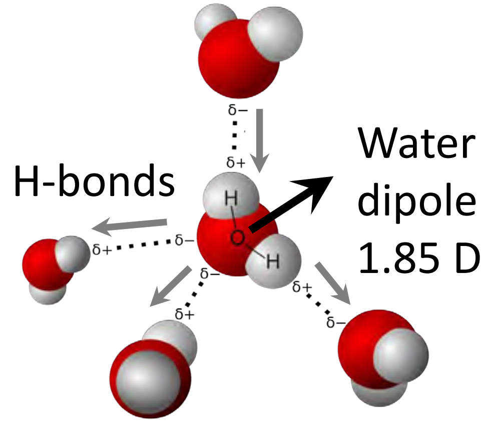
Many ice phases

H-ordered small ε_r

H-disordered large ε_r



Critical role played by hydrogen ordering

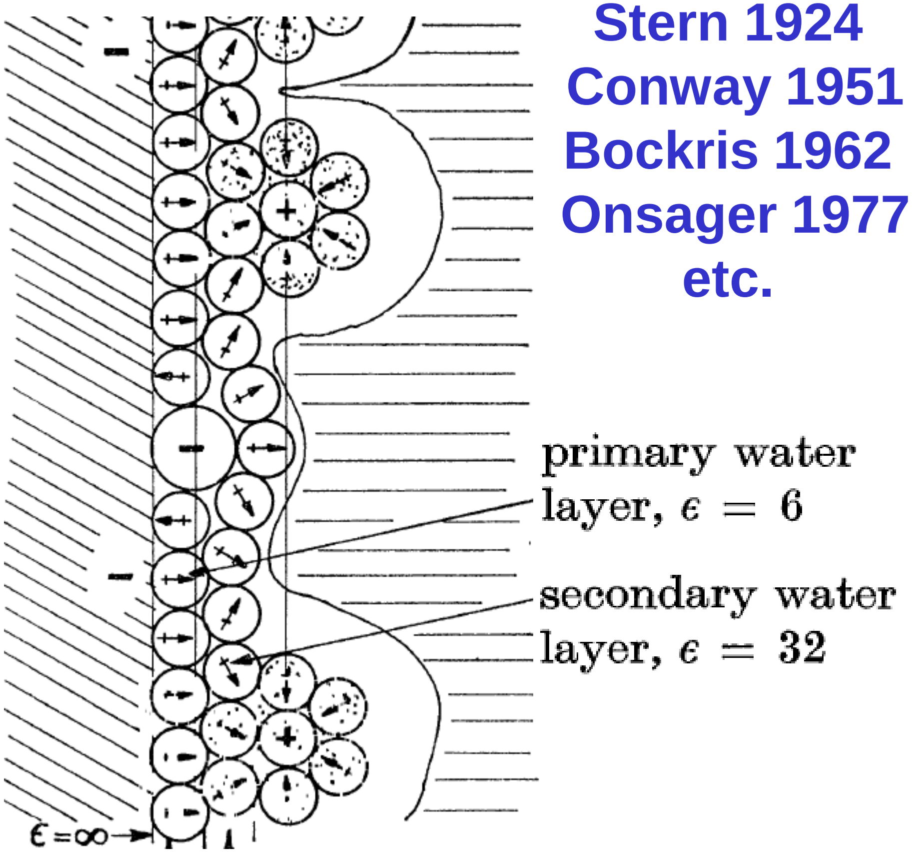


One-century long experimental challenge

Complex geometries, too many uncertainties at large scale

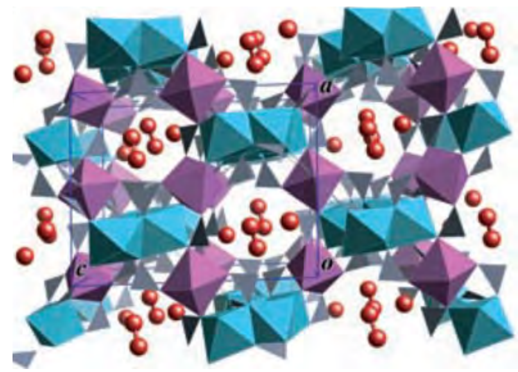
Interfacial layer thickness ?

Electric double layer



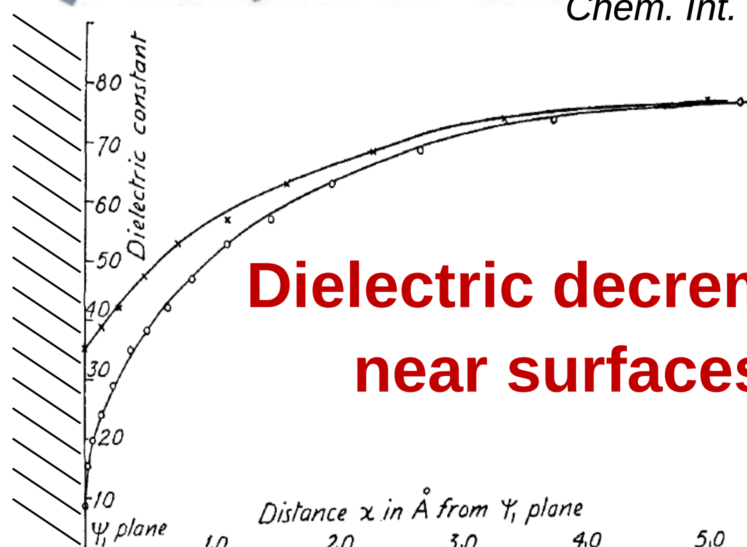
Stern 1924
Conway 1951
Bockris 1962
Onsager 1977
etc.

Bockris *et al. Proc. R. Soc. Lond. A* 1963



Nanoporous crystals, powders, dispersions

Cui *et al. Angew. Chem. Int. Ed. 2005*



Dielectric decrement near surfaces

FIG. 3.—Dielectric constant against distance curves for the diffuse double layer for concentration = 0·01 g. ion/l.
× ψ = 0·1 V ⊙ ψ = 0·2 V

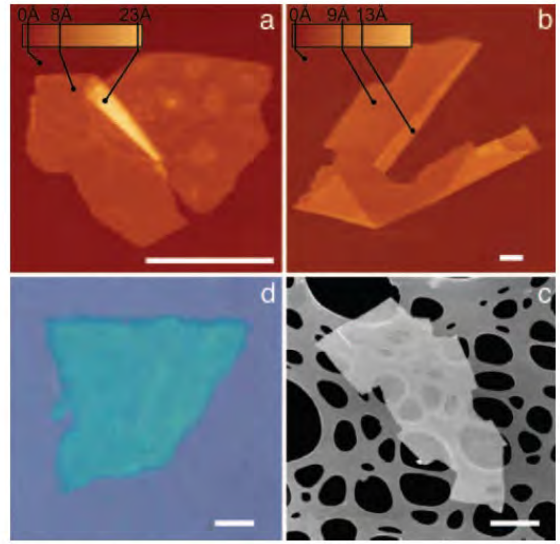
New approach: use of 2D atomically thin crystals

The University of Manchester

School of Physics & Astronomy

National Graphene Institute

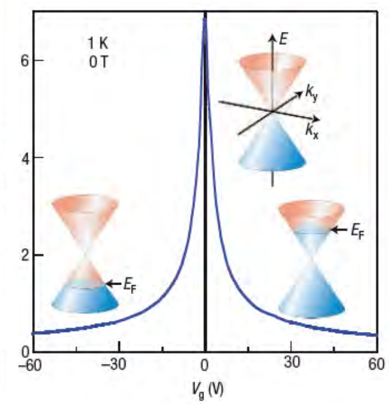
Graphene and other van der Waals crystals



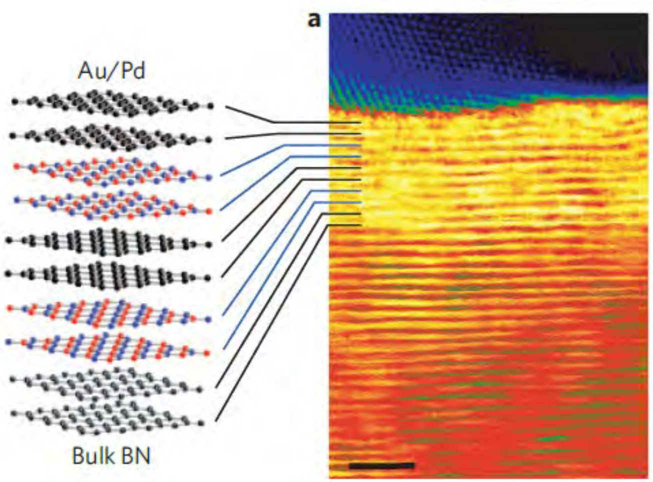
Novoselov & Geim

Science, *Nature* 2004

PNAS 2005



van der Waals heterostructures



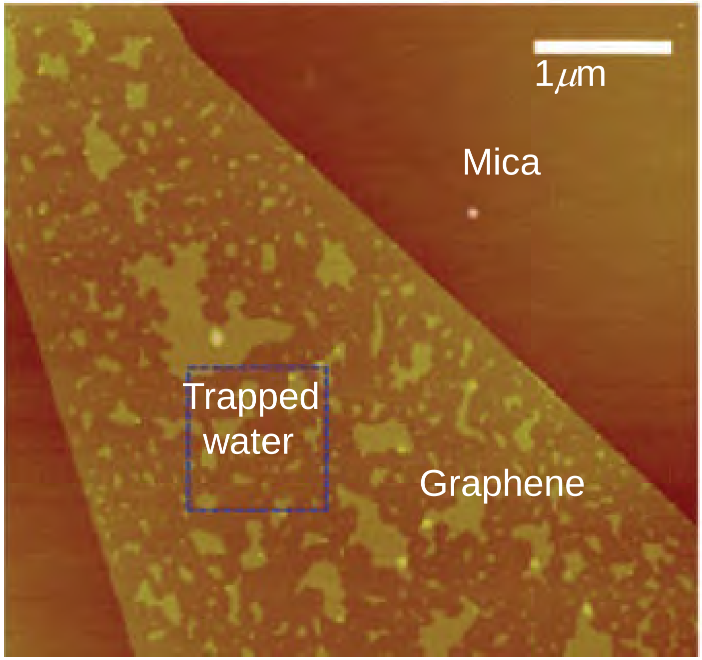
Geim and Novoselov,

Nobel Prize in Physics, 2010

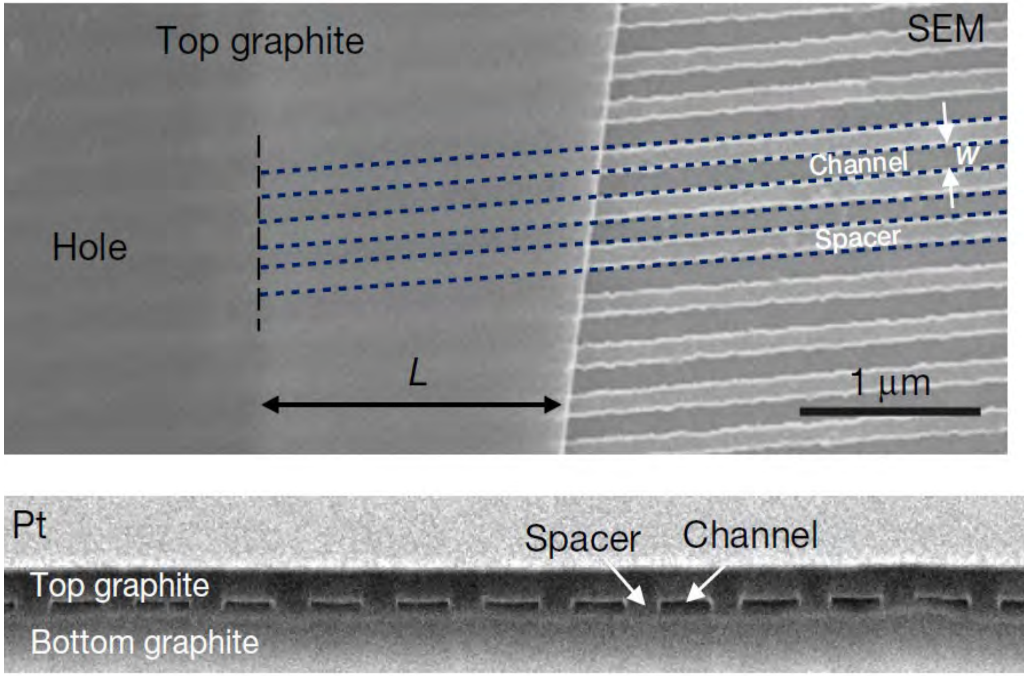
Water confined by van der Waals crystals

Ideal experimental platform

Atomically flat and smooth interface



Xu *et al. Science* 2010



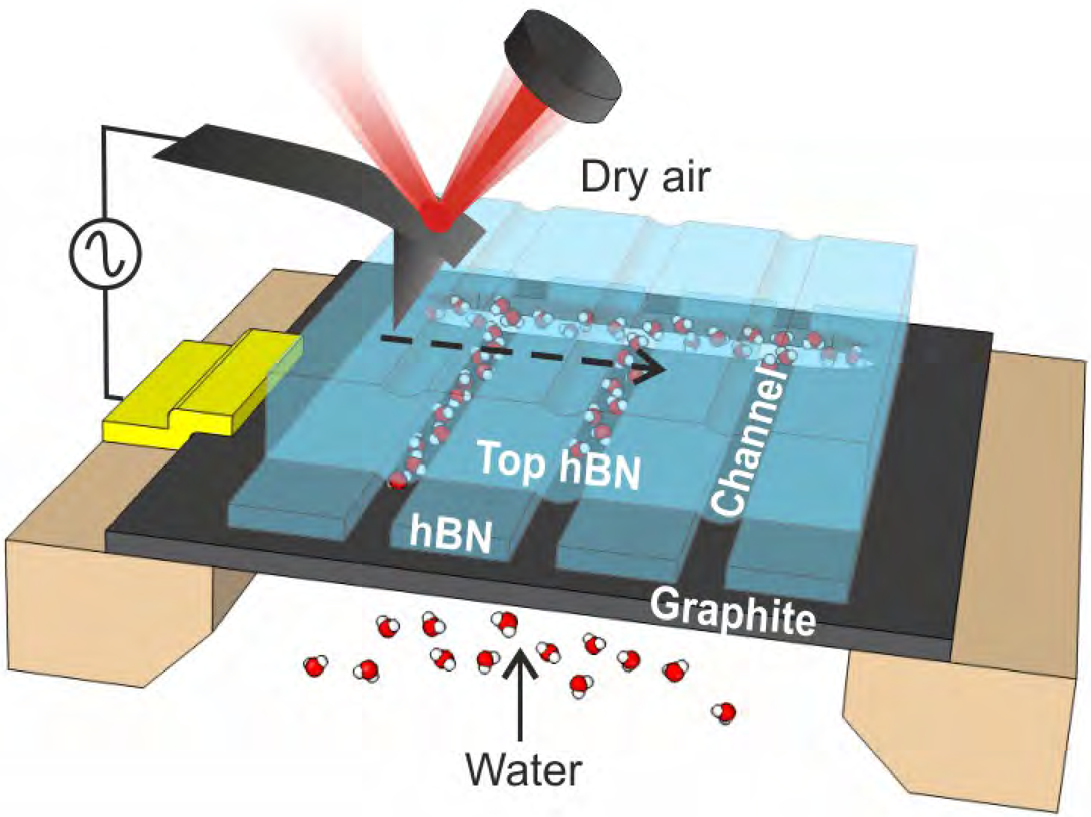
Radha *et al. Nature* 2016
Esfandiar *et al. Science* 2017

A. K. Geim's group (Manchester)

Dielectric imaging of single nanochannels

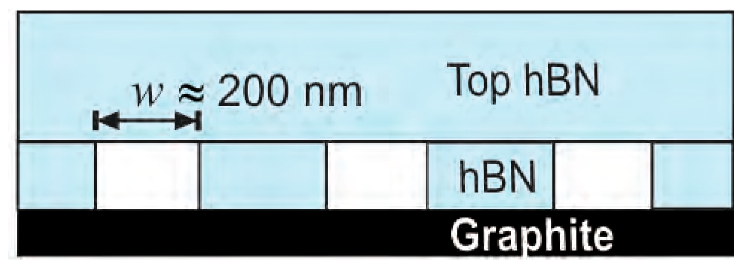
hBN/Graphite channels

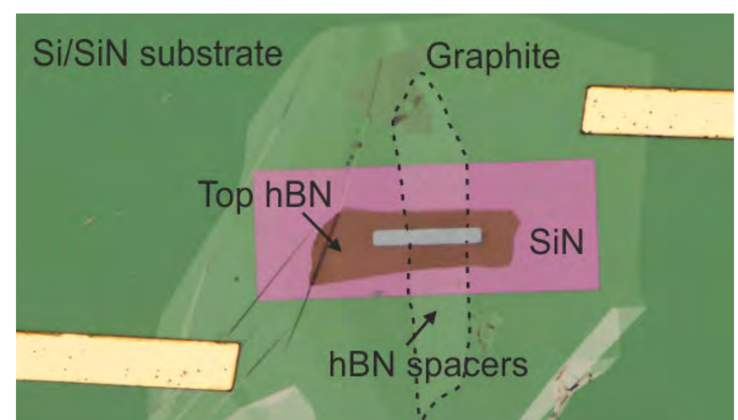
hBN as electrically transparent top layer



NB hBN spacers

Reference for ε_r ~ 3.5
(ordered ice)

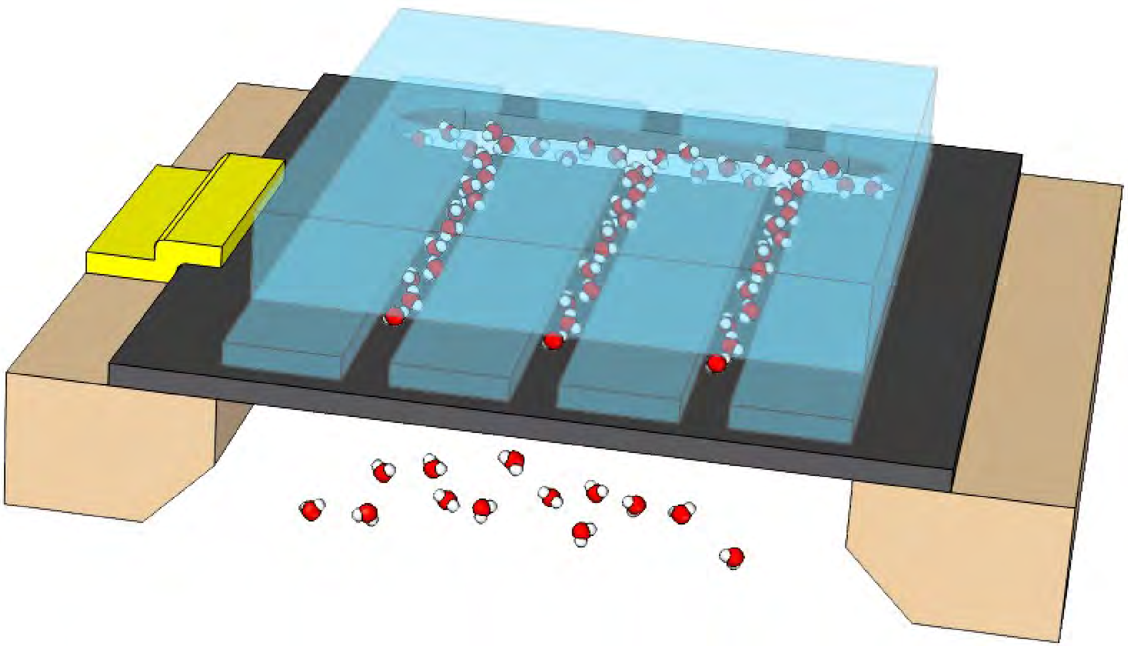


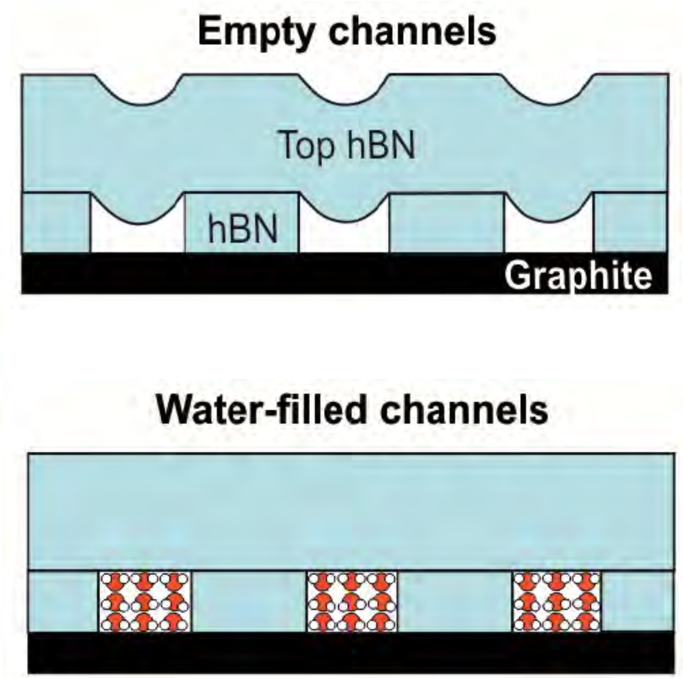


Fumagalli, Geim *et al.* *Science* 2018

Device built with sagged top layer

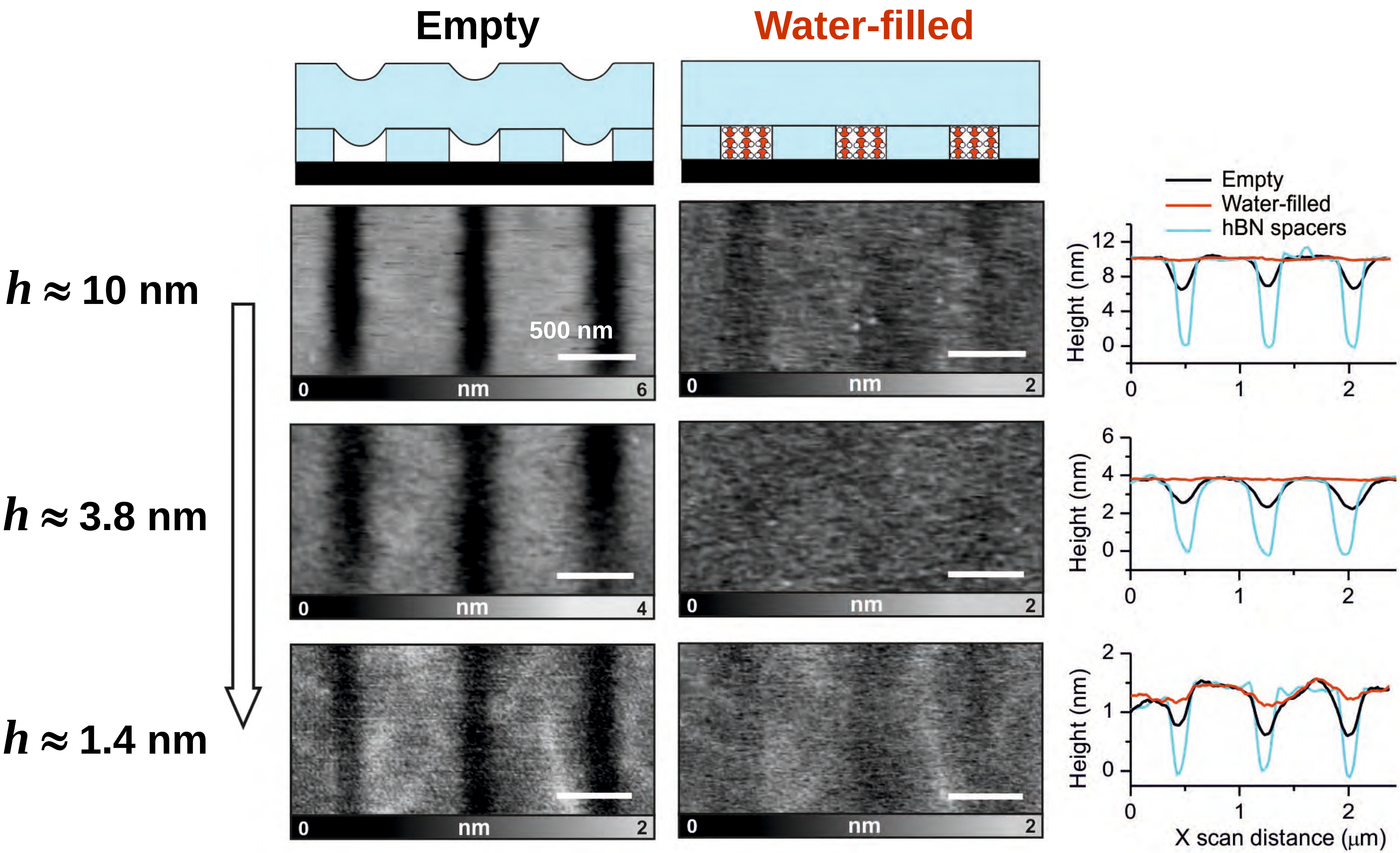
Fine-tuning of the top-layer thickness to avoid total collapse



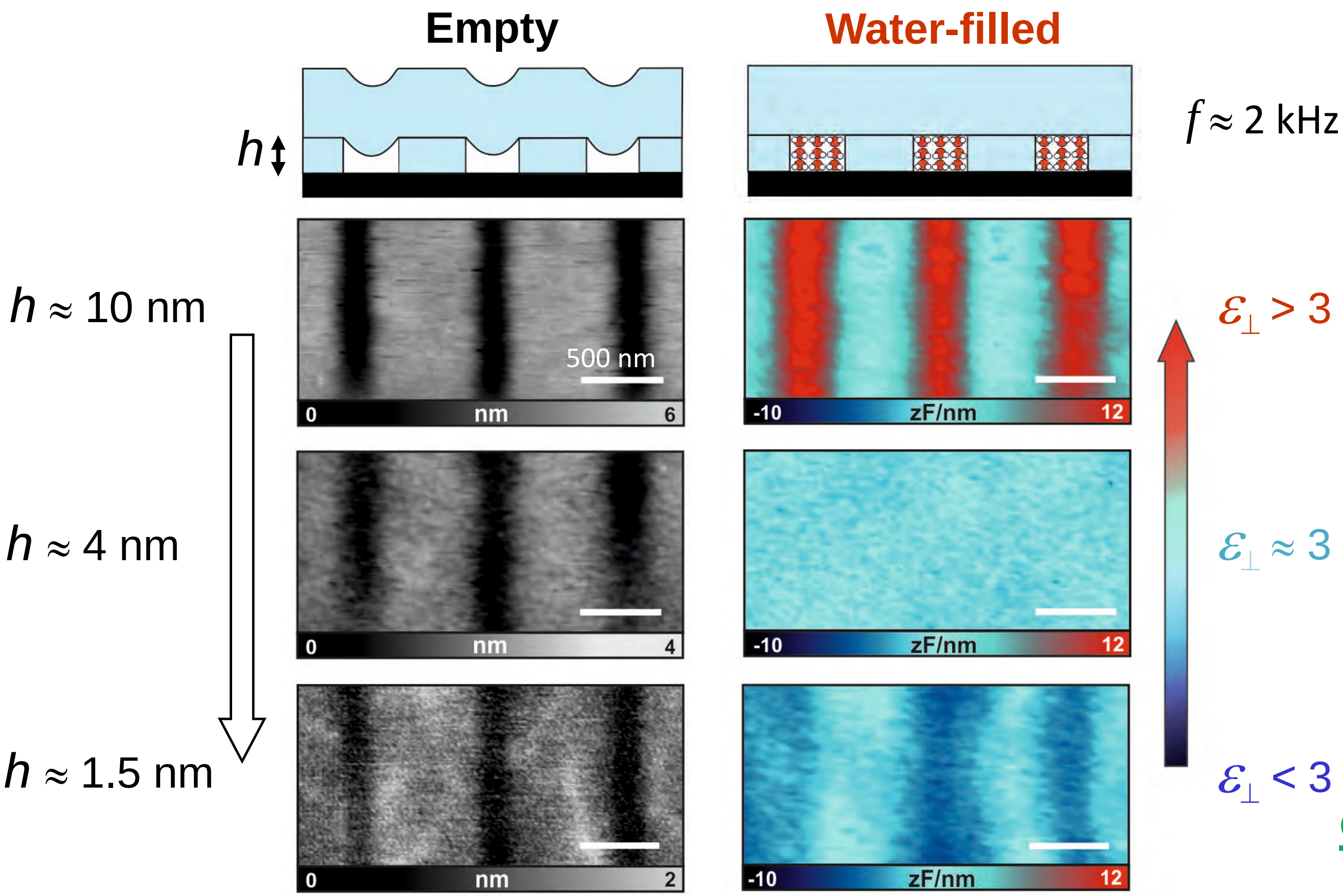


The top layer becomes straight when the channel is filled

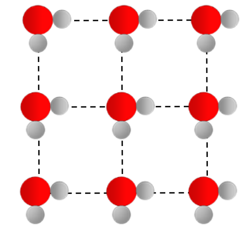
Nanochannels' thickness down to ~ 1 nm



Anomalously low out-of-plane ε_r of 2D water



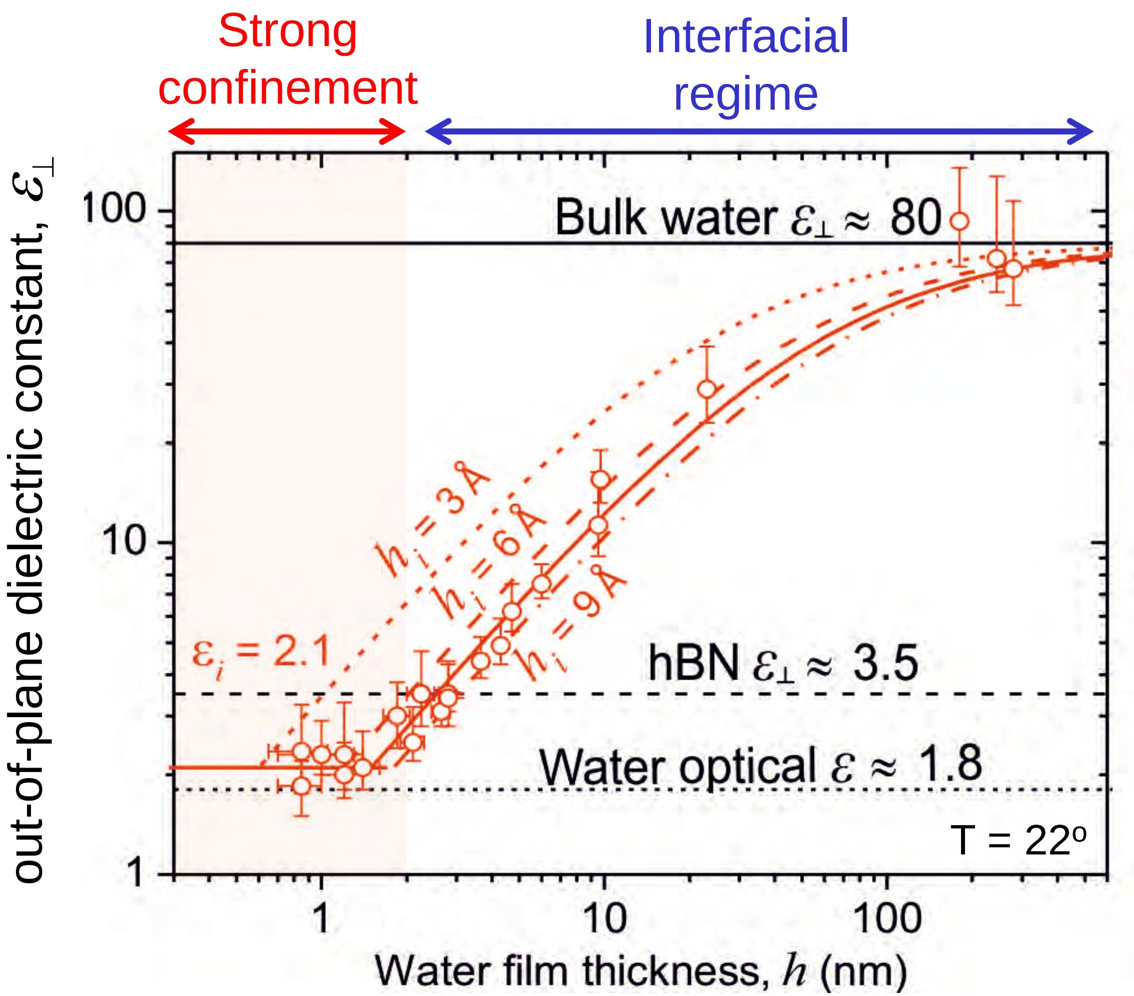
Smaller than in <u>ordered</u> ice!



Results independent of any data analysis or modelling

Out-of-plane ε_r of 2D confined water

Non-polarizable: dipolar and H-bond polarization are suppressed



TWO REGIMES

with same behavior

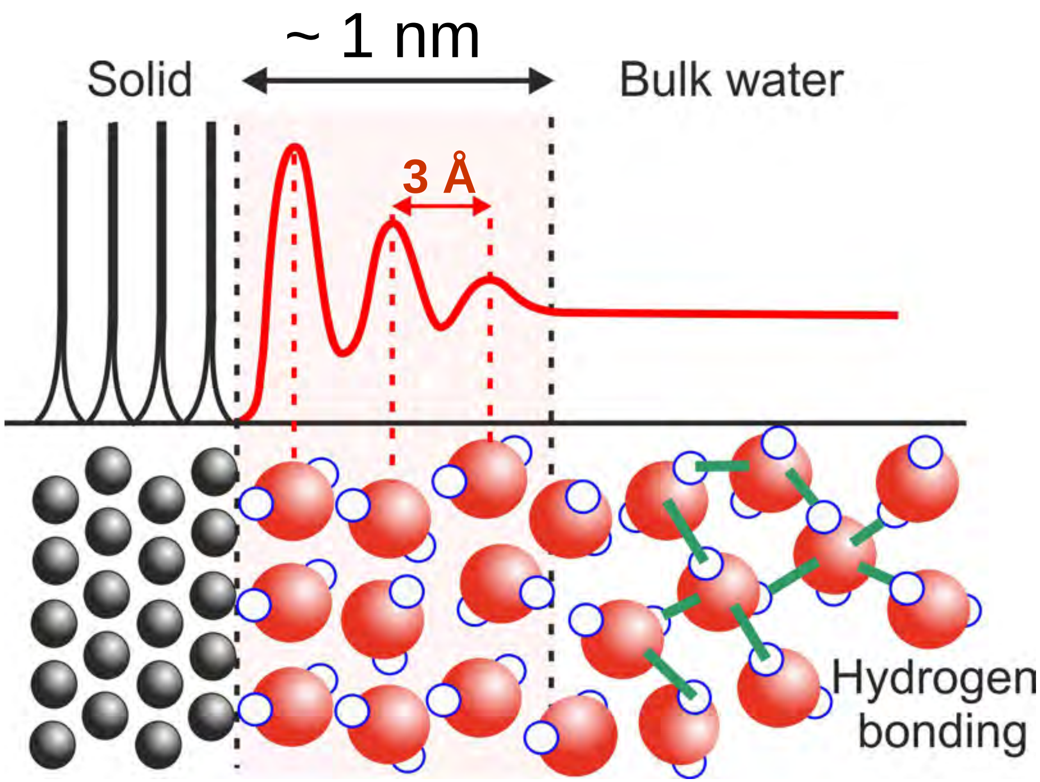
Residual electronic and atomic polarization

$\varepsilon_\perp \approx 2$

near the optical limit

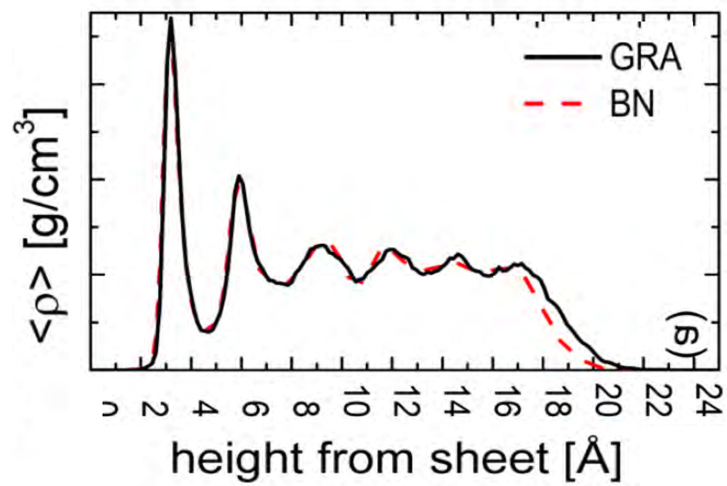
Layered structuring of water near surfaces

Molecular Dynamics density calculations



2-3 ordered layers are predicted

Tocci *et al. Nano Lett.* 2014

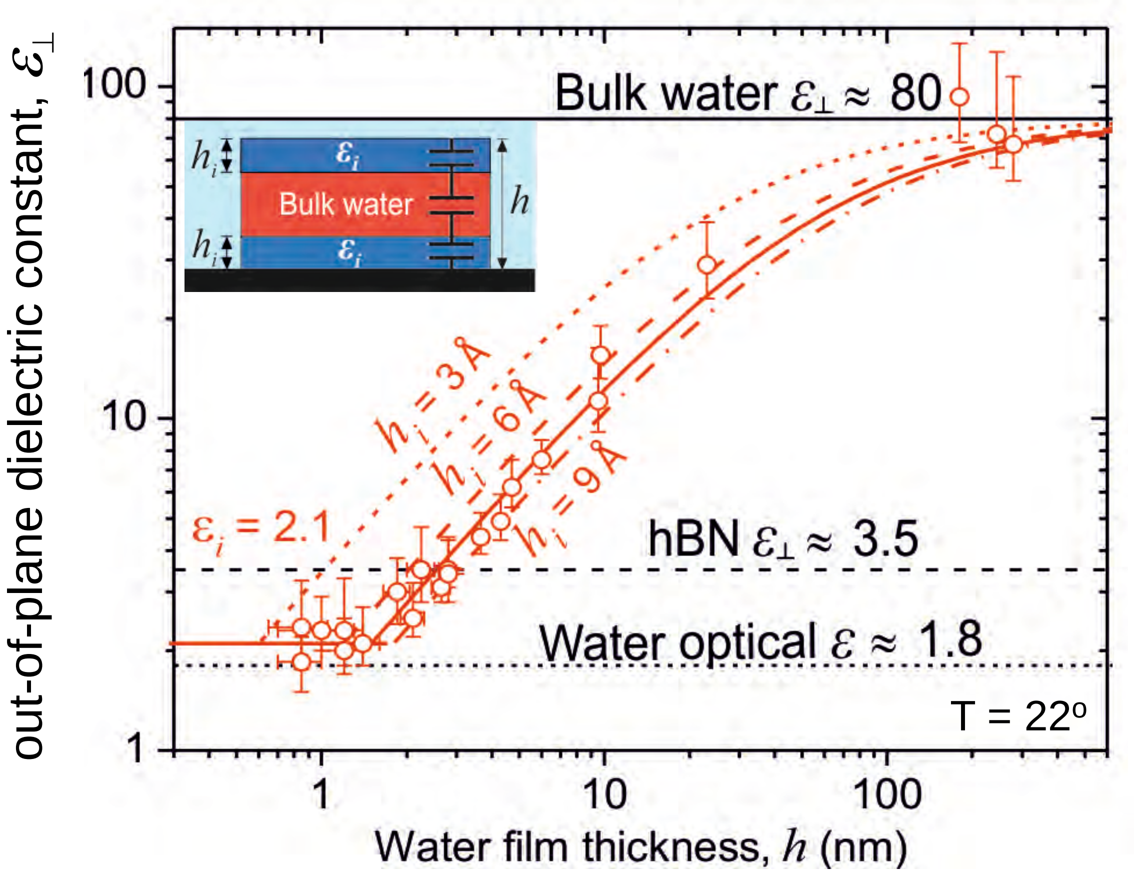


Same behaviour for hBN and graphite

Out-of-plane ε_r of 2D confined water

Electrically dead layer with $\varepsilon_\perp \approx 2$ extending ~2 water layers

Same behavior for interfacial and strongly confined water



Consistent with most MD predictions

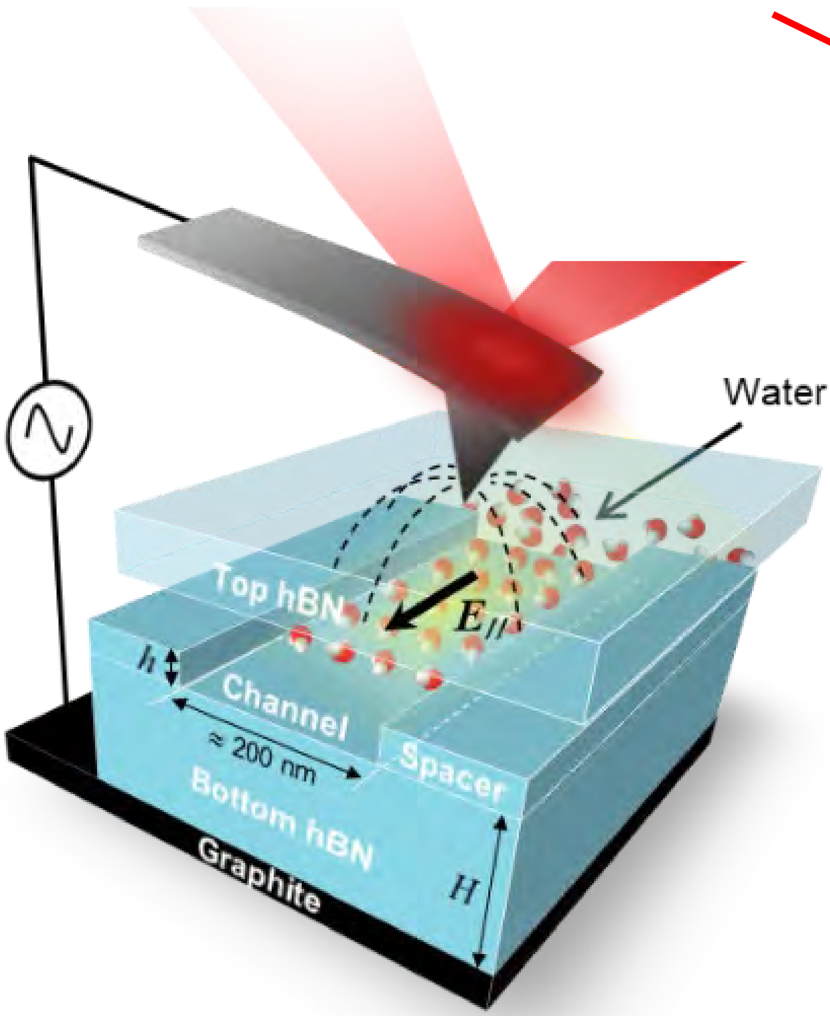
Netz 2011
Galli 2013
Aluru 2020
Marx 2020
Peeters 2021
Matyushov 2021
and many others

Question

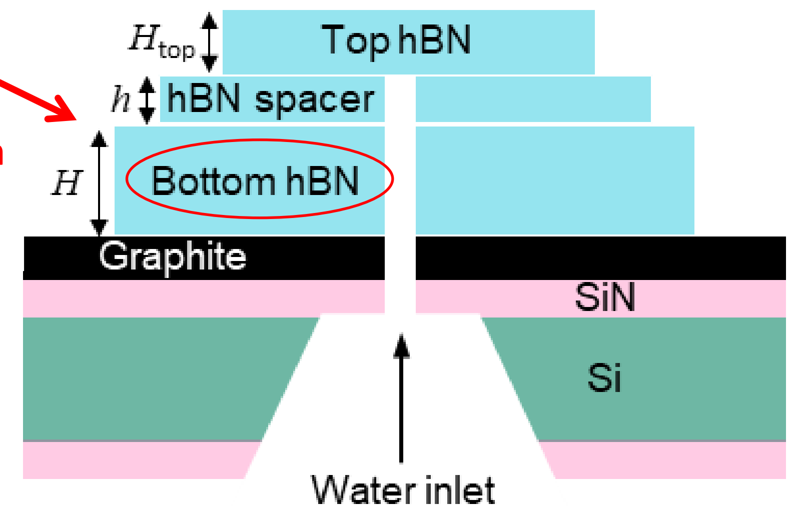
Can we probe the in-plane dielectric constant of 2D confined water?

In-plane dielectric imaging of 2D confined water

In-plane electric field inside the channel



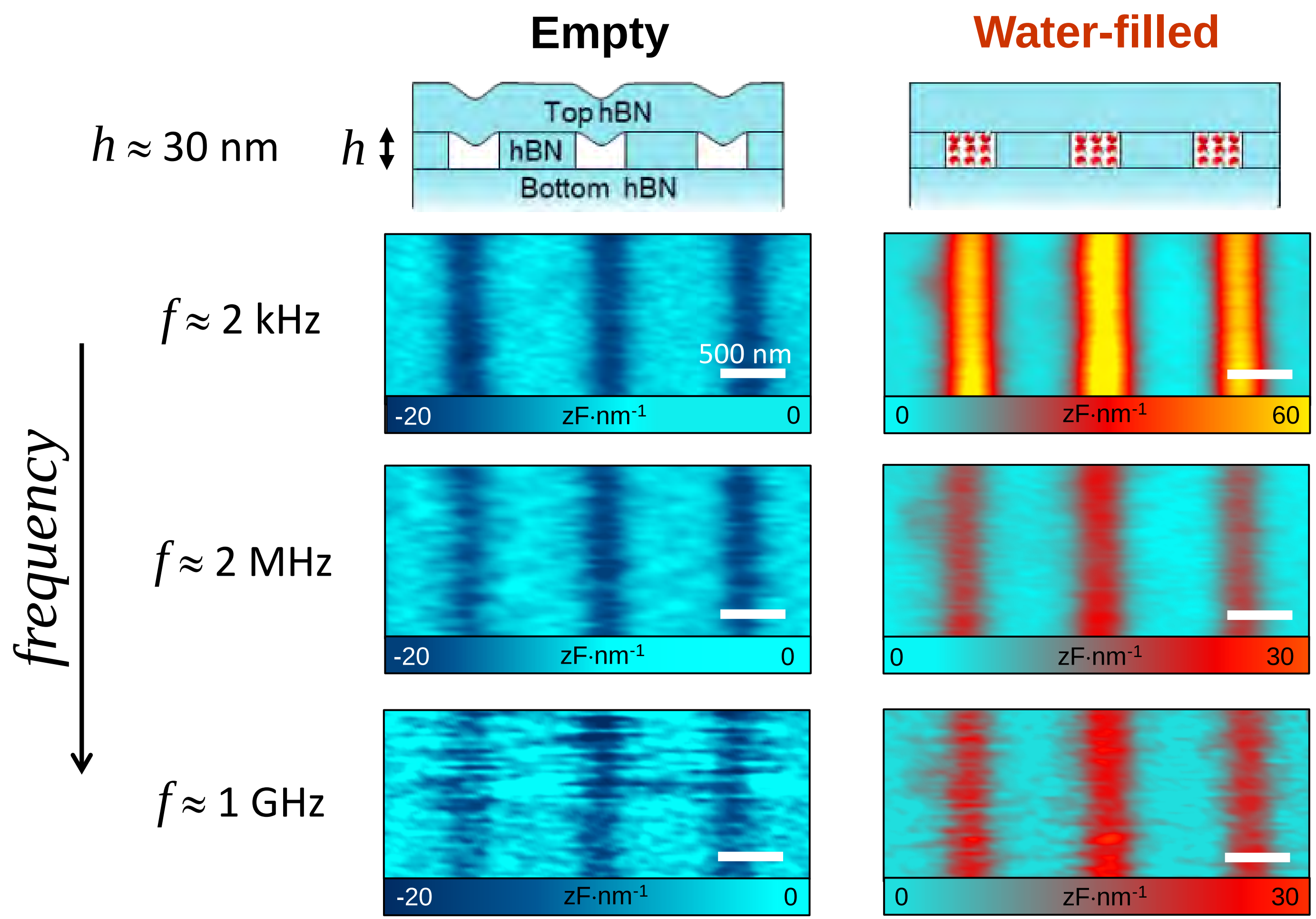
100-200 nm thick



M. Souilamas, R. Wang

R. Wang *et al.* Arxiv:2407.21538 (2024)

In-plane dielectric imaging of 2D confined water



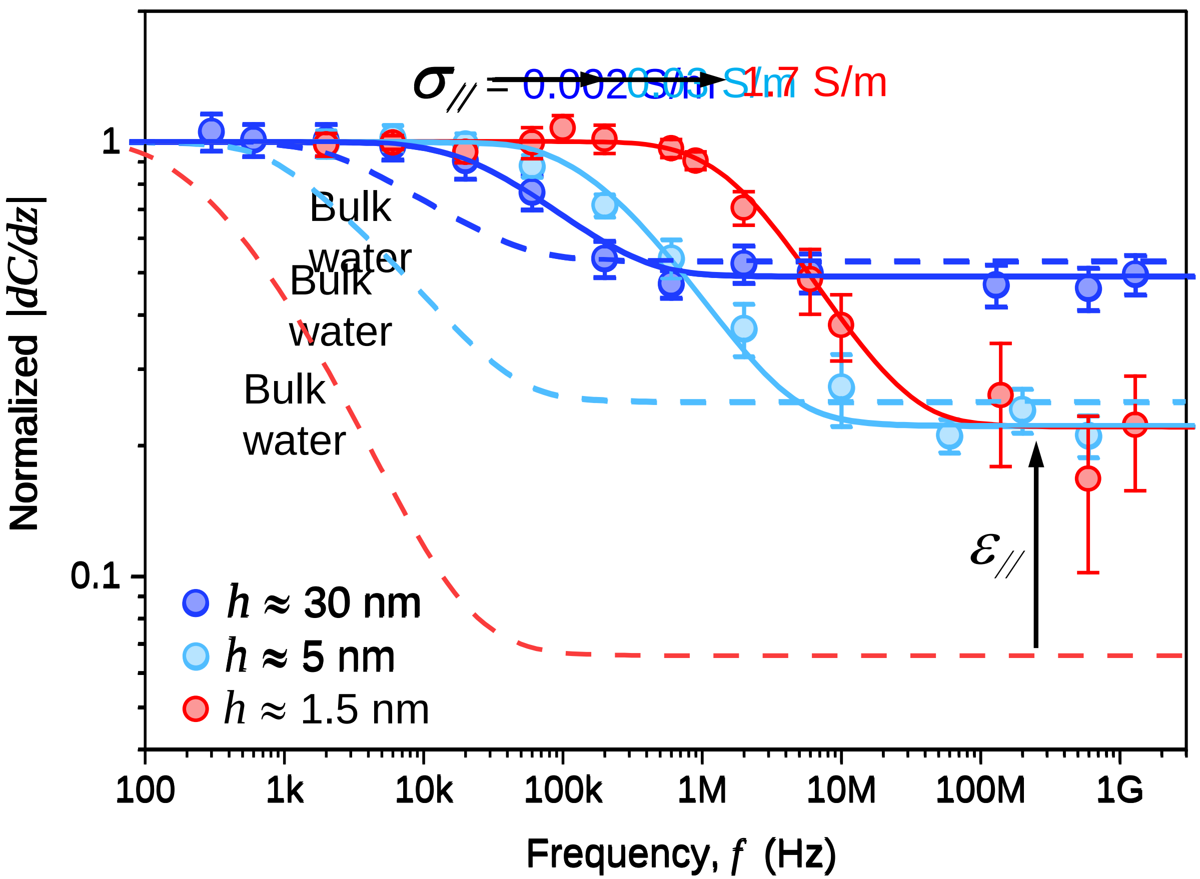
Large, positive response

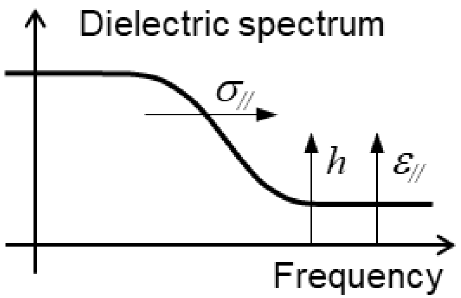
... still large at GHz frequencies!

Decreasing the thickness down to atomic scale

The dispersion clearly shifts → **Anomalously high $\sigma_{//}$ and $\varepsilon_{//}$**

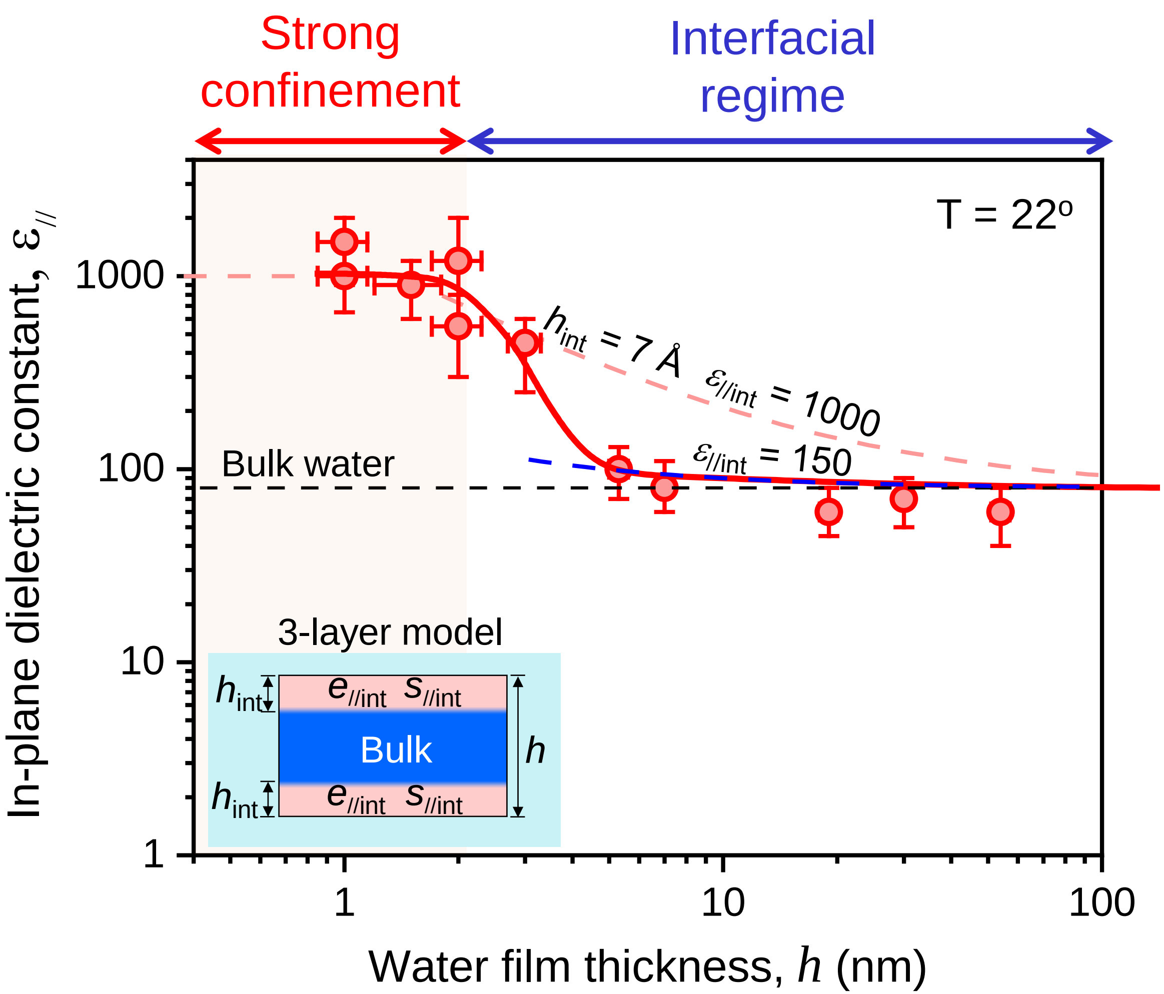
Results independent of any data analysis or modelling





In-plane ε_r of 2D confined water

Highly polarizable: values increase with confinement strength



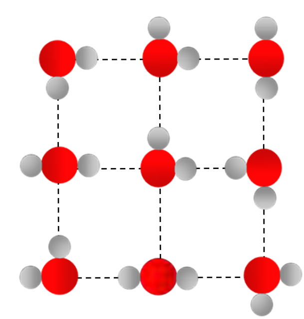
TWO REGIMES

with different behavior

Bulk-like or slightly higher in the interfacial regime

Ferroelectric-like values under strong confinement

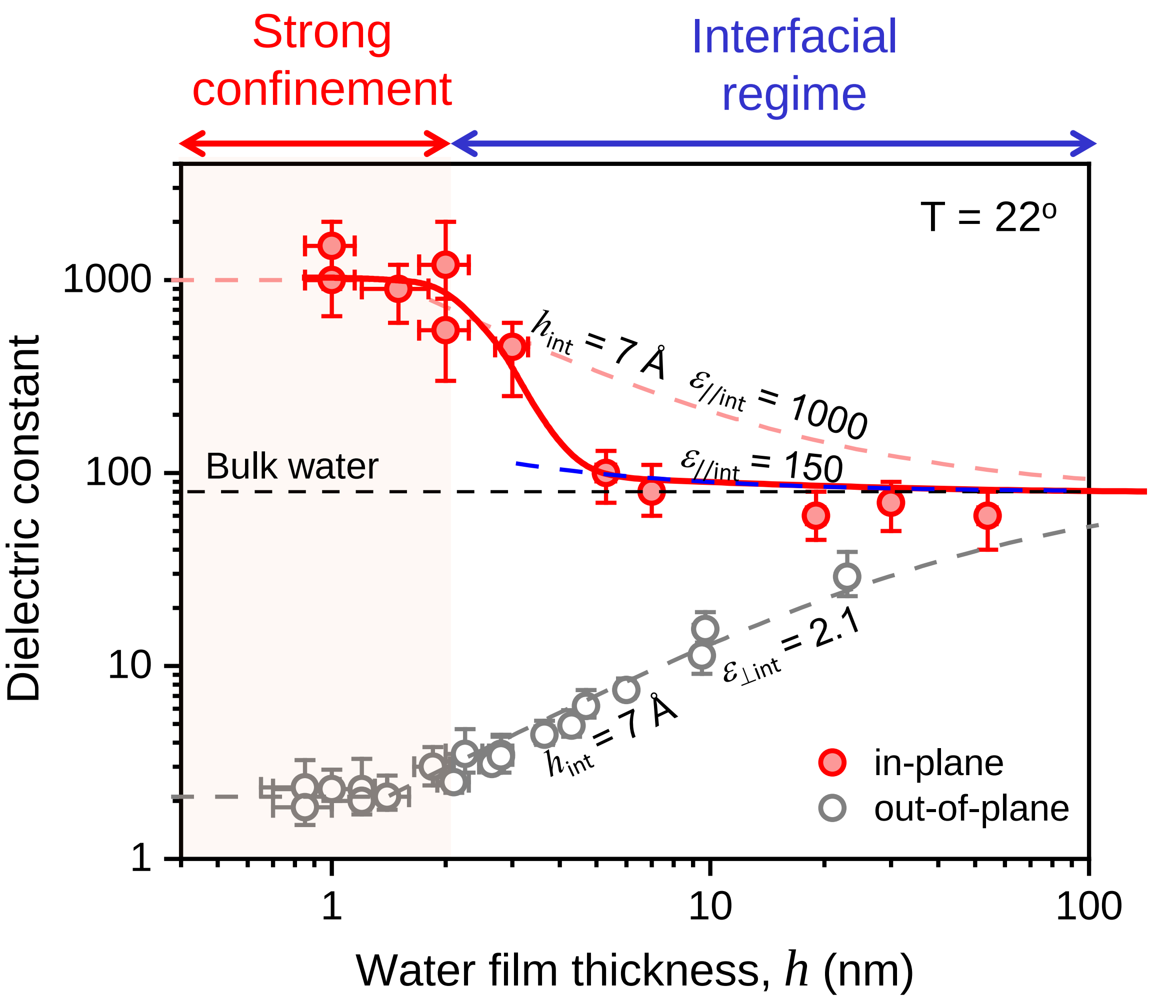
→ **Higher than in <u>disordered</u> ice**



R. Wang *et al.* Arxiv:2407.21538 (2024)

Dielectric constant of 2D confined water

Giant anisotropy in dielectric screening

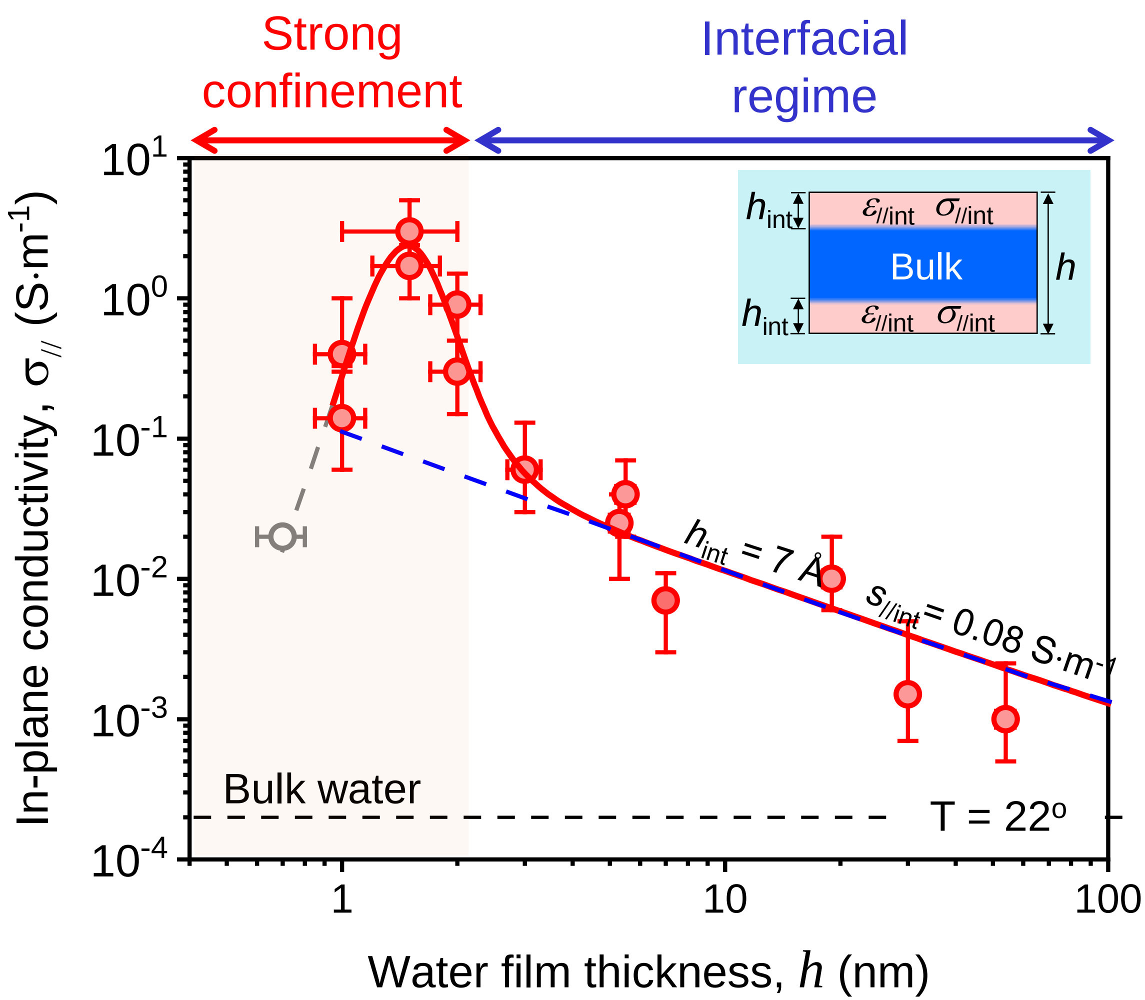


Consistent with most MD predictions (at least qualitatively)

Netz 2011
Galli 2013
Aluru 2020
Marx 2020
Peeters 2021
Matyushov 2021
and many others

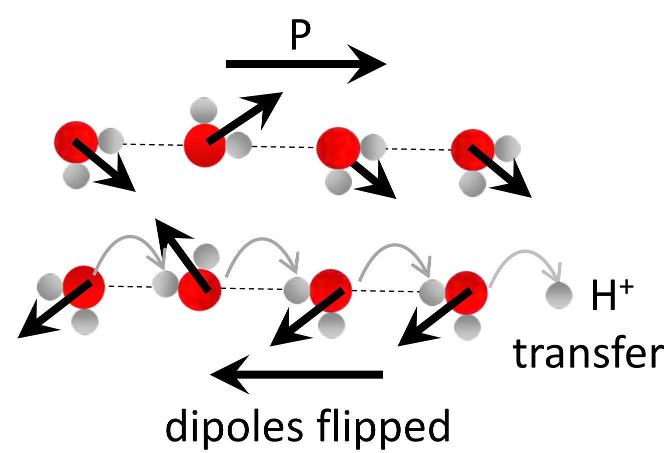
In-plane conductivity of 2D confined water

Increase up to superionic values under strong confinement



TWO REGIMES
with different behavior

Under strong confinement, similar to disordered ice:
H-disorder facilitates dipole-dipole correlation and Grotthuss-type fast proton transport



R. Wang *et al.* Arxiv:2407.21538 (2024)

Question

Can we probe local electric polarization in liquid environment?

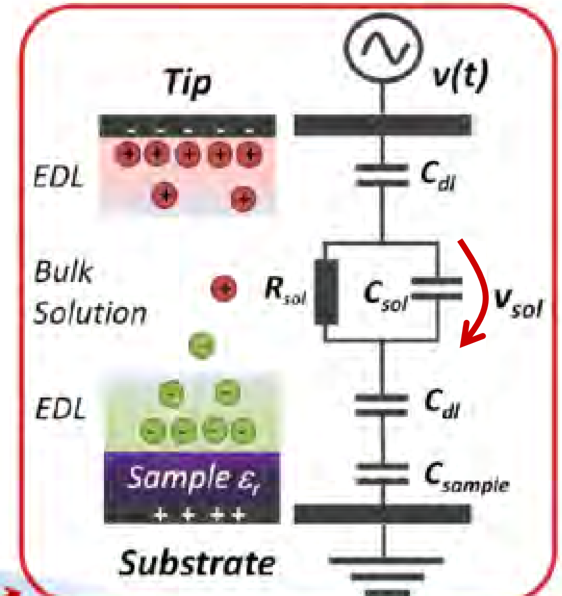
EFM in electrolyte solutions

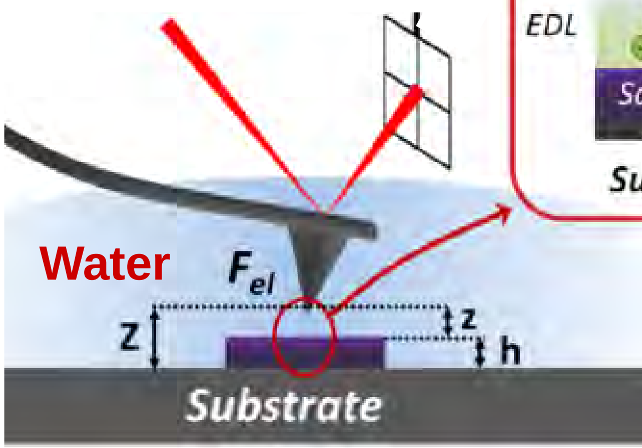
$$F_{elec}(z,t) = \frac{1}{2}\frac{\partial C_{sol}(z)}{\partial z} v_{sol}^2(z,t)$$

The voltage drop depends on frequency and ion concentration

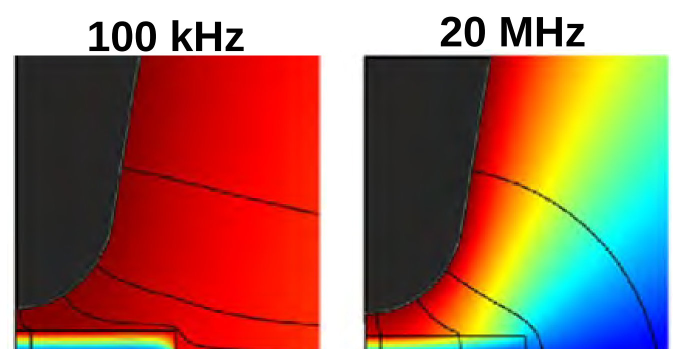
Advantage: higher dielectric environment $\varepsilon_r \sim 80$

Issues: ions conductivity and electric double layer



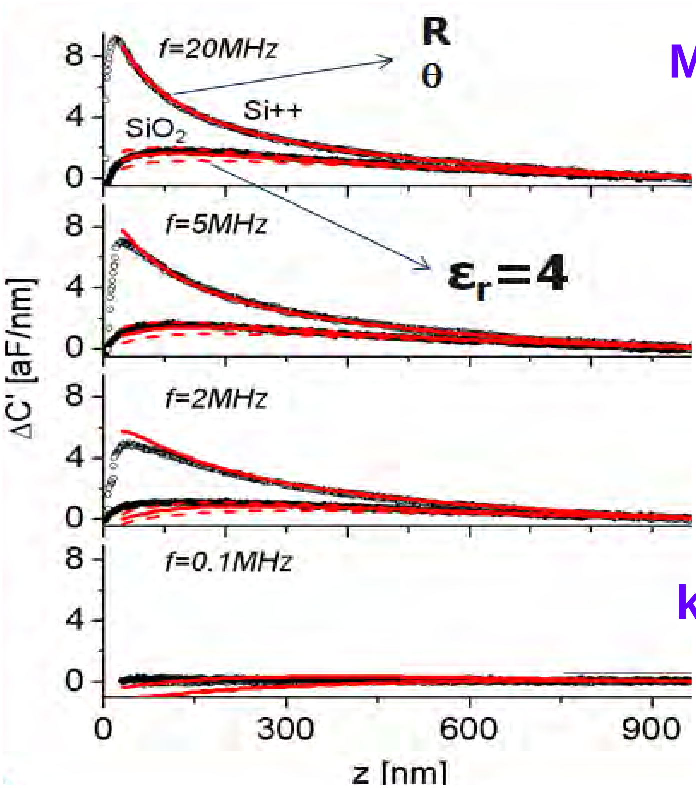


Tip apex interaction only at frequency > 1MHz

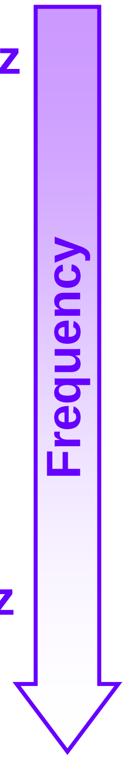


Gramse *et al. Appl. Phys. Lett.* 2012

EFM in electrolyte solutions at MHz frequencies

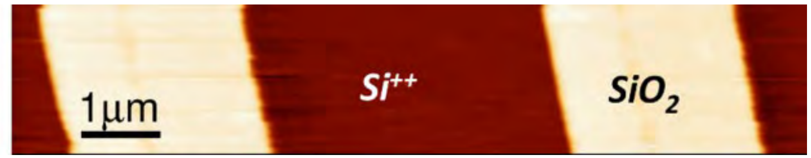


MHz

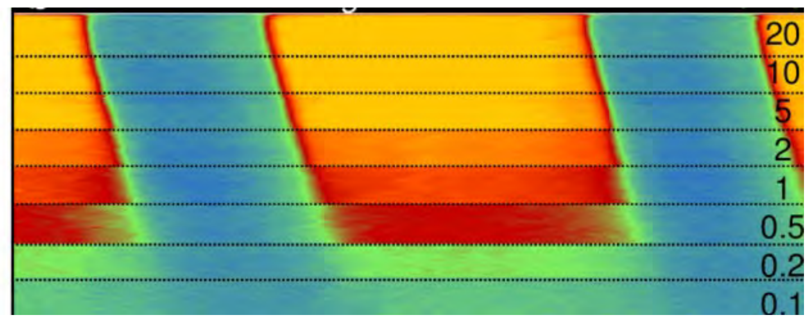


kHz

Topography



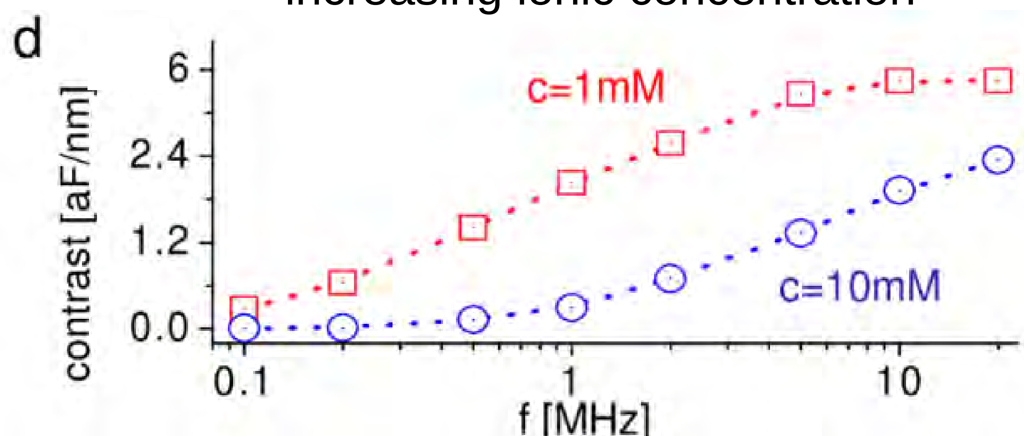
Dielectric image



MHz

kHz

Higher frequencies with increasing ionic concentration



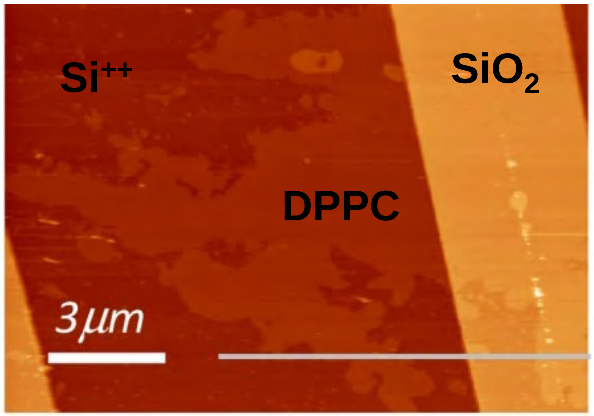
At high frequencies > MHz

it works as in air !

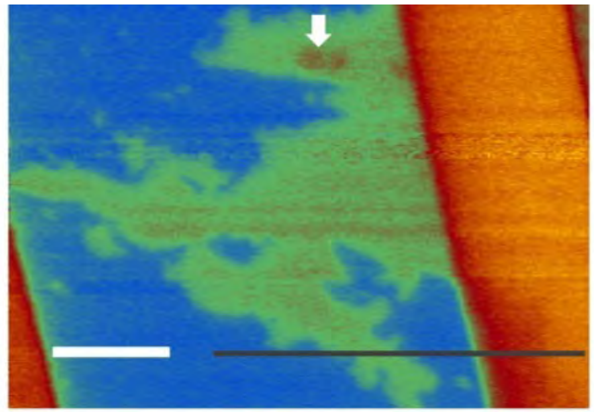
Gramse *et al. Appl. Phys. Lett.* 2012

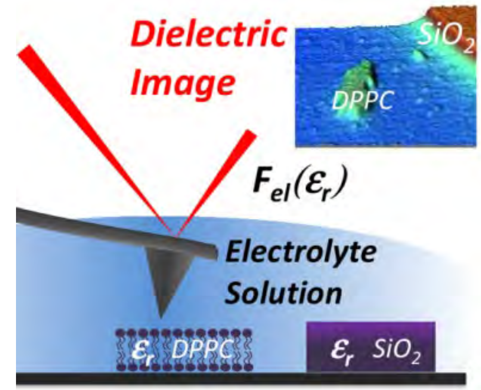
Dielectric constant of lipid bilayers in liquid

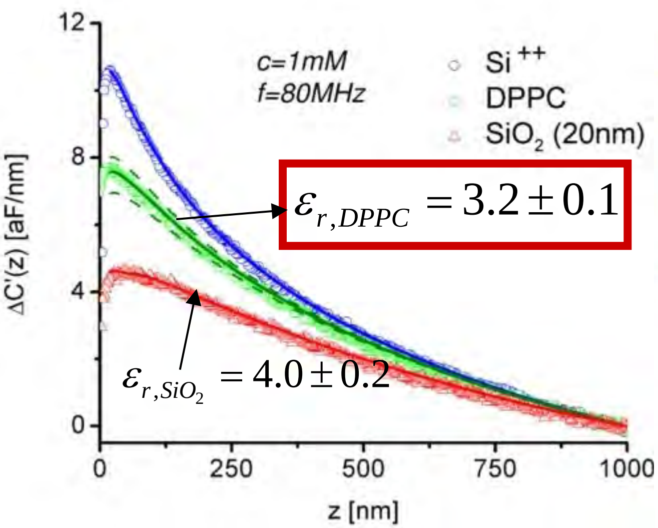
Topography

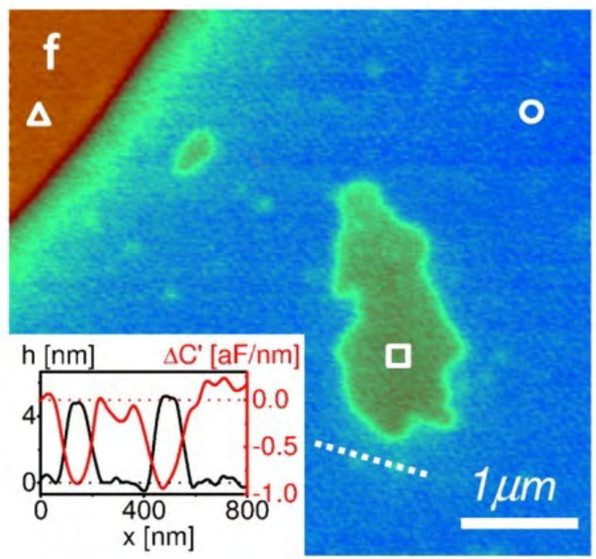


Dielectric image







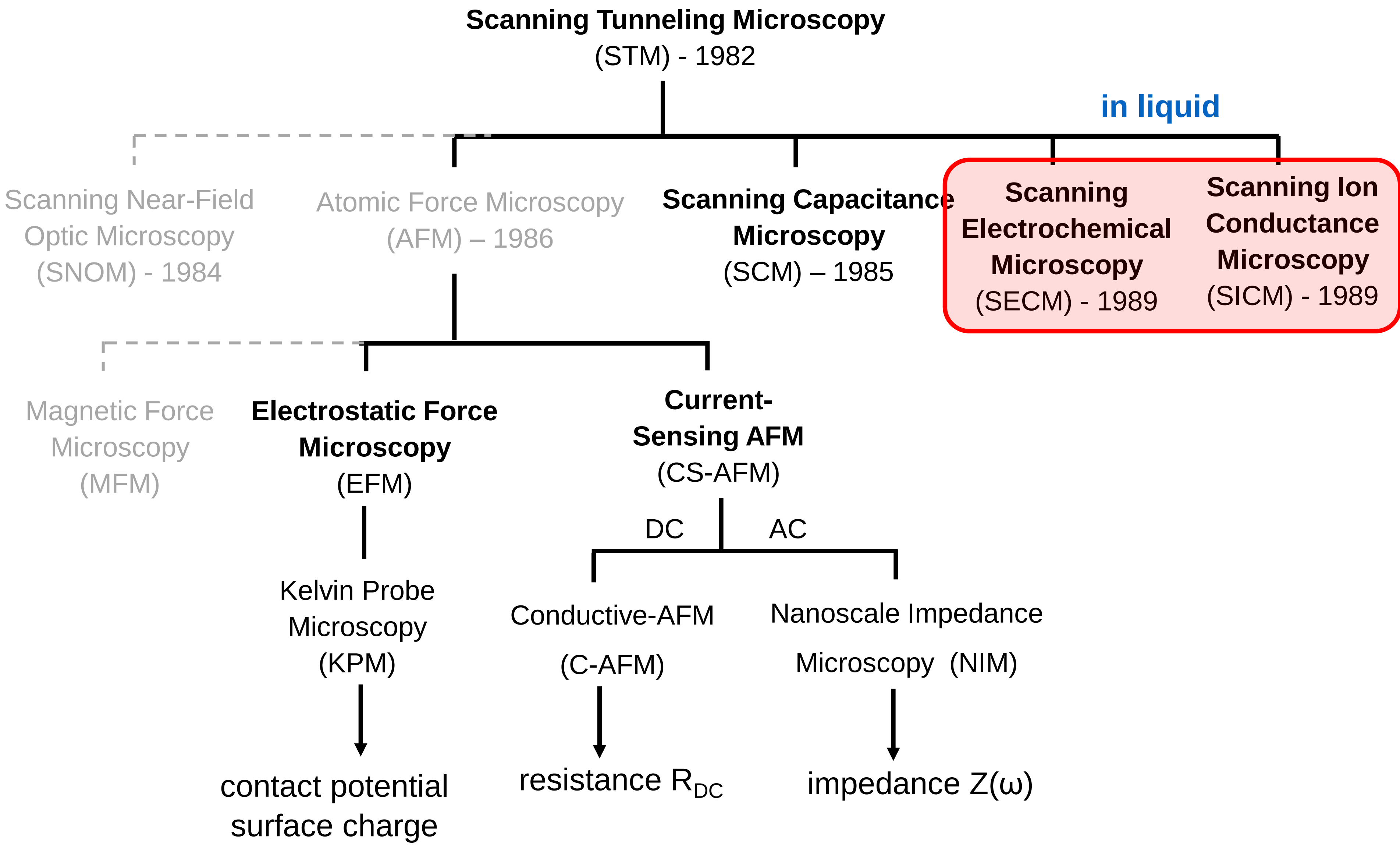


→ ε_r ~ 3

larger than in air (~ 2) due to the hydration of the polar head

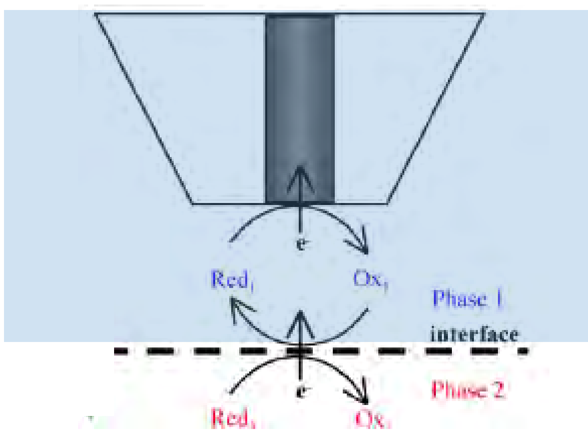
Gramse *et al. Biophys. J.* 2013

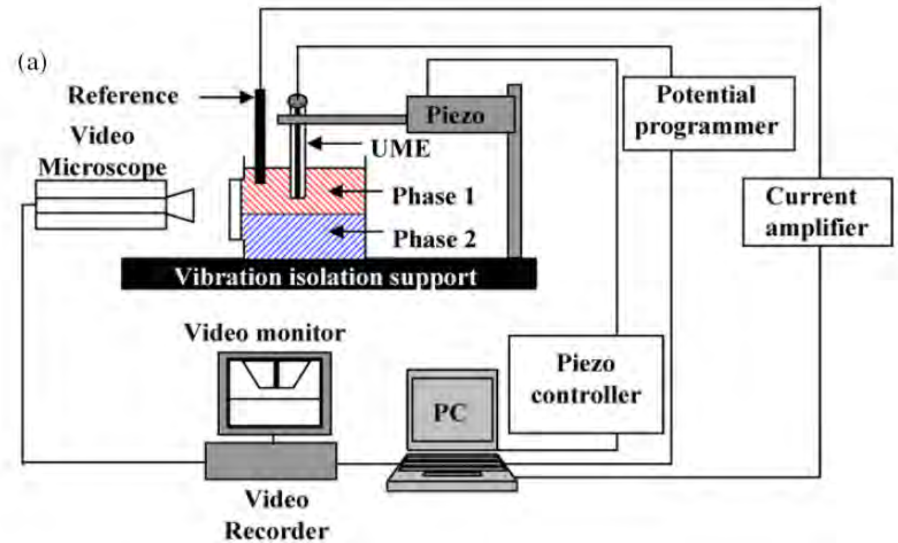
Electrical Scanning Probe Microscopies



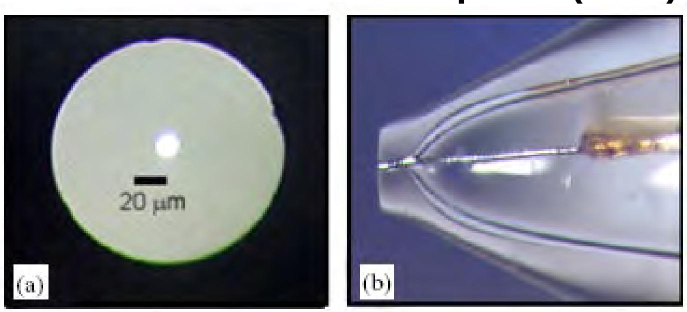
Scanning ElectroChemical Microscopy (SECM)

A scanning ultra-micro-electrode probe in solution, either amperometric or potentiometric, to investigate the **local eletrochemical activity** (oxidation-reduction) of an interface.





The ultra-micro-electrode probe (UME)

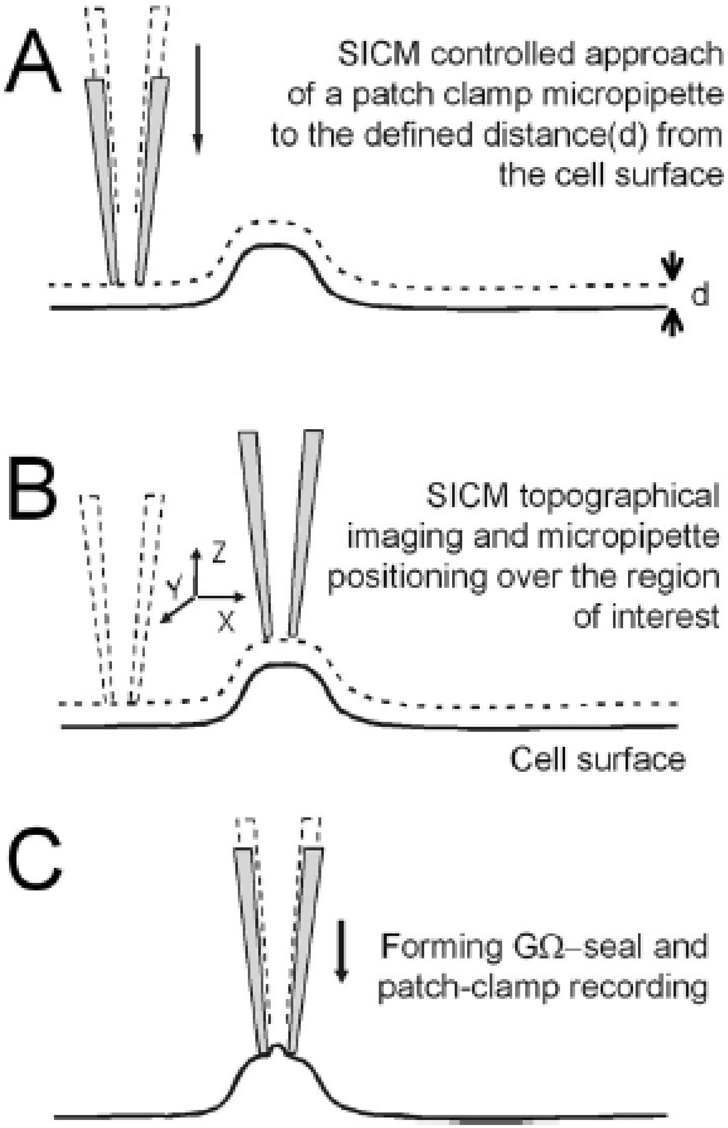


a disc-shaped electrode (a diameter of 0.6–25 *µ*m) with a sealed conductive wire in a glass capillary

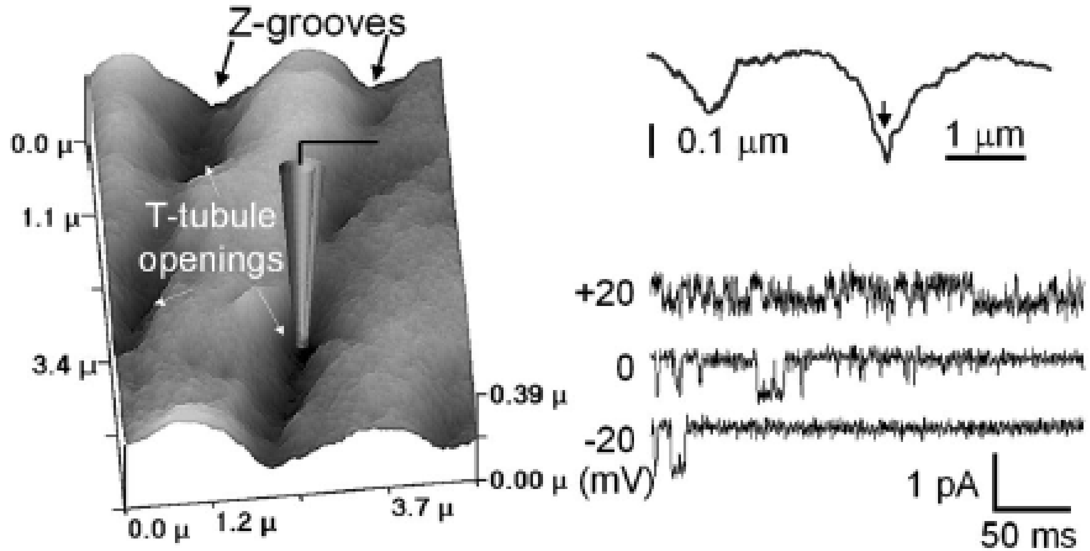
Kwak J and Bard A. J. *Anal. Chem.* 1989

Edwards M. A. *et al* Physiol. Meas. 2006

Scanning Ion Conductance Microscopy (SICM)



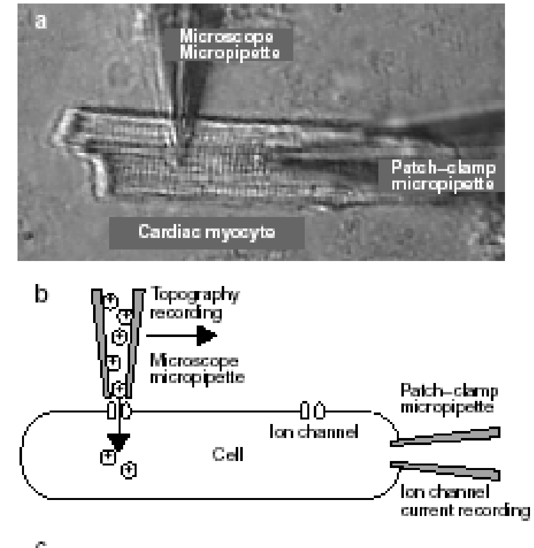
Patch-clamp with nanoscale positioning



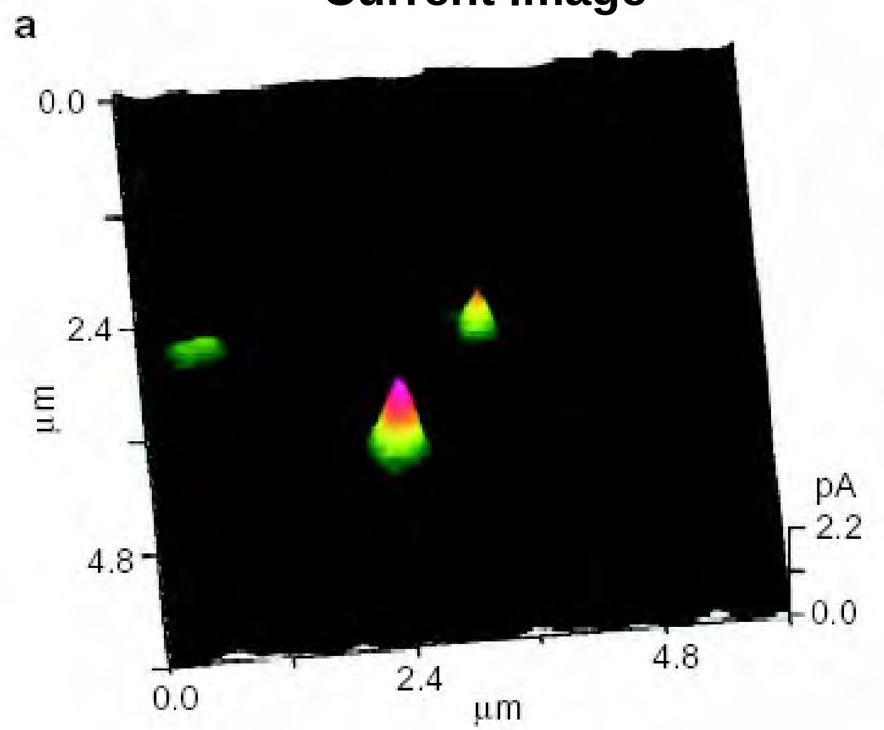
Biophysical Journal 83(6) 3296–3303

Scanning Ion Conductance Microscopy (SICM)

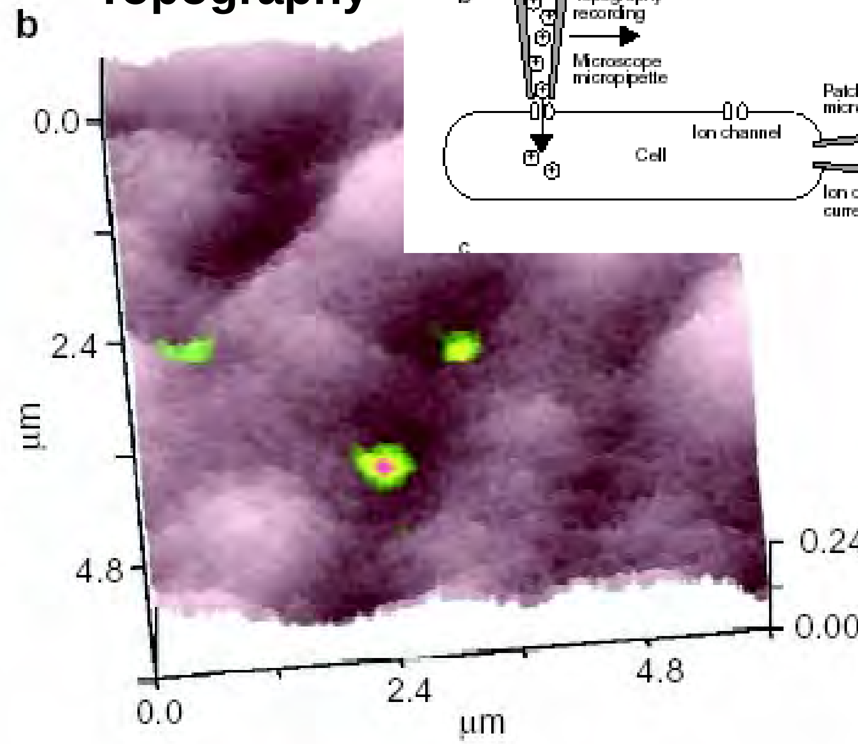
Detecting ion channels in living cells



Current Image



Topography



Nature Cell Biology 2, 616 (2000)

Questions?

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Dept. of Physics & Astronomy
Condensed Matter Physics

PhD students and Postdoctoral positions available

laura.fumagalli@manchester.ac.uk