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

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Outline

Electrical Scanning Probe Microscopies

- Current Sensing - Atomic Force Microscopy (CS-AFM)
- Electrostatic Force Microscopy (EFM)
- Scanning Dielectric Microscopy (SDM)
- Scanning ElectroChemical Microscopy (ECM)
- Scanning Ion Conductance Microscopy (SICM)

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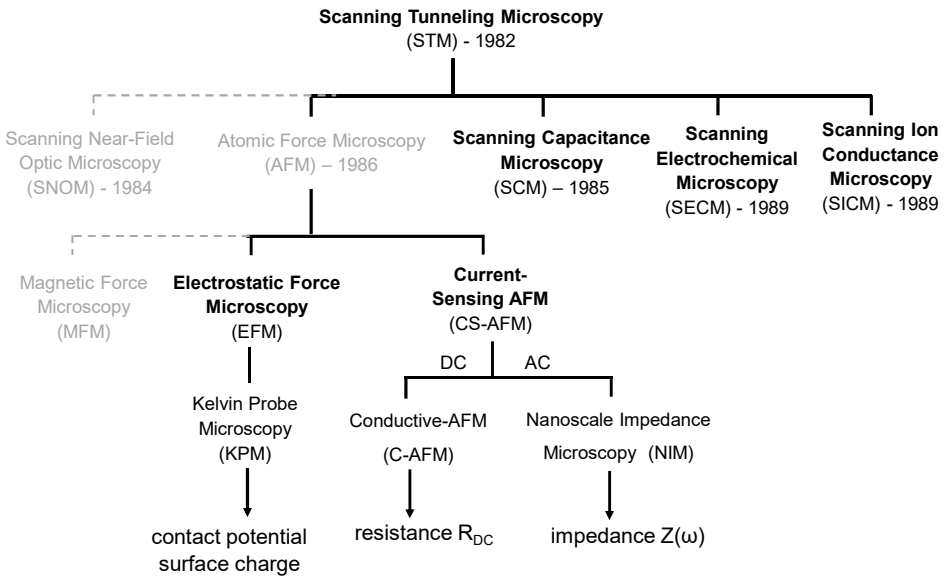
Electrical Scanning Probe Microscopies



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Question

How can we probe electrical properties on the nanoscale

1) **with no convolution with topography ?**
   beyond STM limitations

1) **on insulating samples ?**
   dielectrics and biological materials

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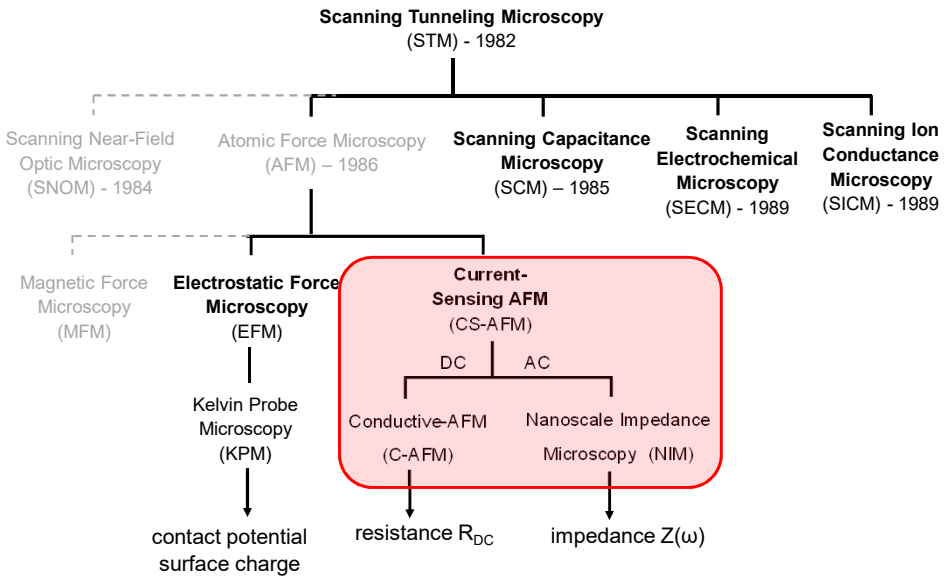
Electrical Scanning Probe Microscopies



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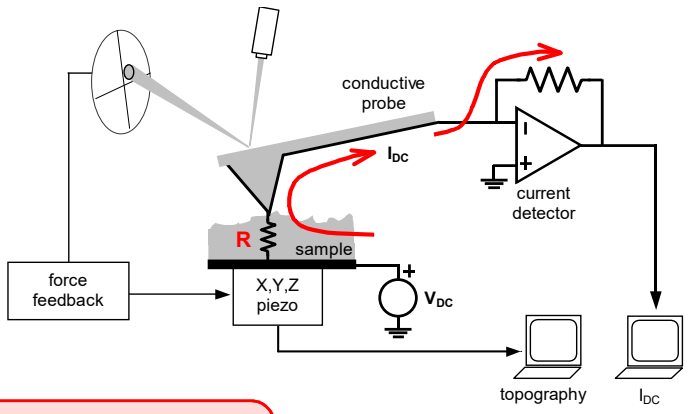
Current-Sensing AFM

A **DC voltage bias** is applied between a conductive tip and the sample on a conductive substrate. The current flowing through the tip is measured by a current detector, while the tip is maintained **in <u>contact</u> under force feedback control**.



<u>Advantage compared to STM</u>
topographic and electrical information are independent!

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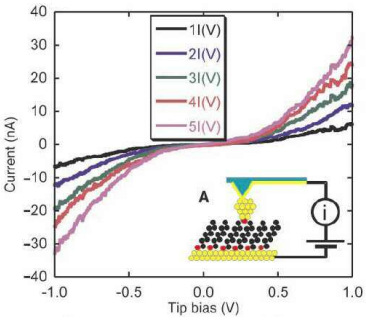
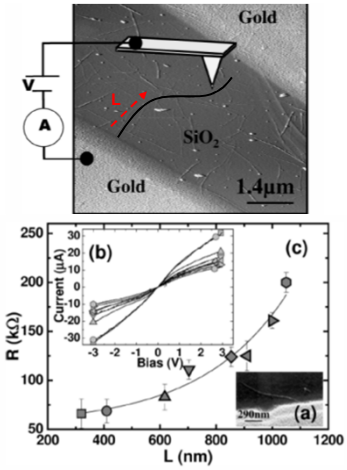
Probing single-molecule conductivity

Assisted by force feedback control (contact), the electrical conductivity of single molecules is probed at a given X,Y,Z position under minimum mechanical stress.



Current-to-voltage I(V) curves on octanethiols

Cui *et al. Science* 2001



SWNT resistance vs length (L)

DePablo *et al. PRL* 2002

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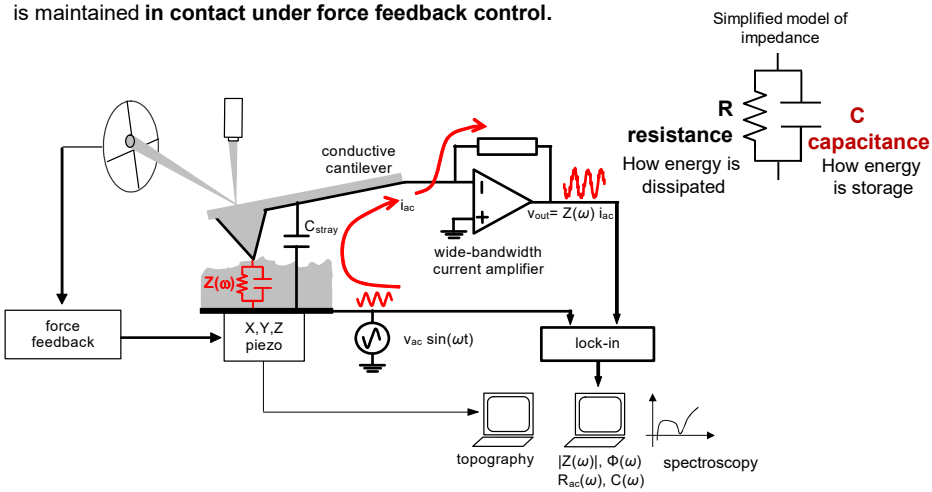
Scanning Impedance Microscopy

By applying an **AC voltage signal** and measuring the AC current in a lock-in detection scheme, the **impedance** (resistance and capacitance) of the sample is measured, while the tip is maintained **in contact under force feedback control.**



Shao *et al. Appl.Phys.Lett.* 2003

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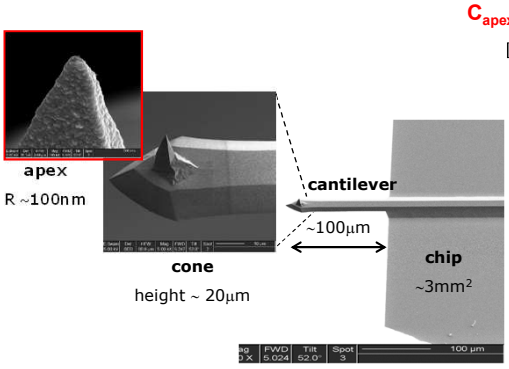
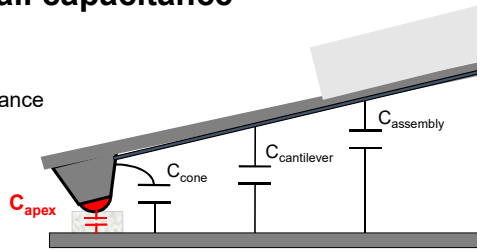
Extremely small capacitance

Tip apex capacitance is extremely small,
the dominant contribution due to stray capacitance





$$C_{meas} = C_{apex} + \underbrace{C_{cone} + C_{cantilever} + C_{chip}}$$

$C_{apex} \sim 1aF$ $\quad$ $C_{stray} \sim 0.1pF$

Only tip capacitance variation ΔC_{apex} can be quantified!

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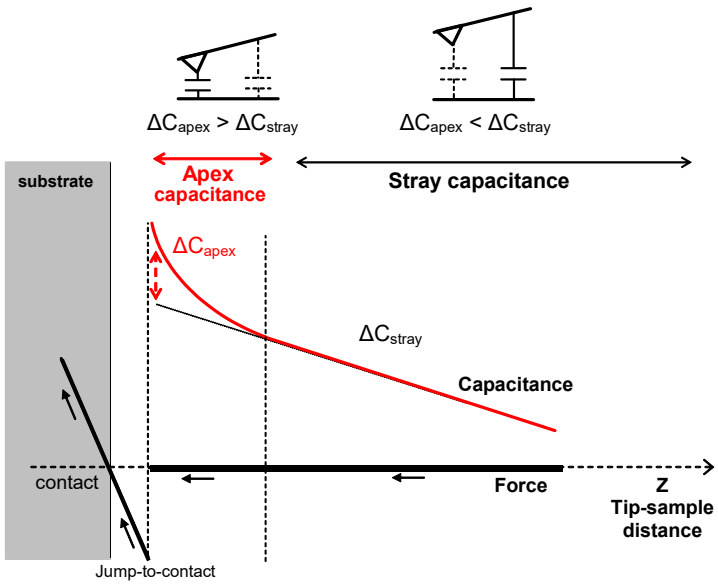
Capacitance-distance curves C(Z)



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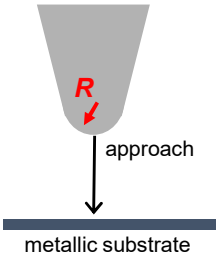
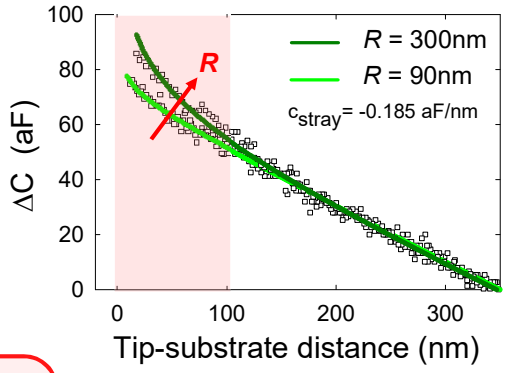
Measured capacitance-distance curves C(Z)

Needs low-noise preamplifiers, atto-zeptoFarad signals





By fitting the data with theoretical, the **apex radius R can be accurately measured (±1nm)**

Using the **tip - metal analytical model**
(Hudlet *et al. J.Appl. Phys.* 1998)

$$C_T(z) = C_{stray}(z) + C_{apex}(z)$$

$$C_{apex}(z) = 2\pi\varepsilon_0 R \cdot \ln\left(1 + \frac{R\cdot(1-\sin\theta_0)}{z}\right)$$

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

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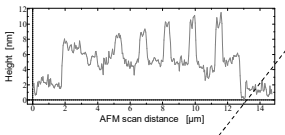
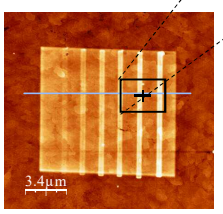
Local capacitance imaging

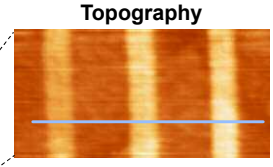
Needs low-noise preamplifiers, atto-zeptoFarad signals



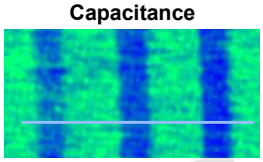


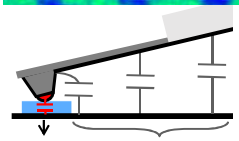
Nano-structured SiO_2 ultrathin film on gold (h_0 = 5nm thick)

Topography



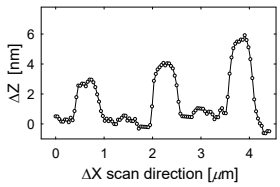
Capacitance

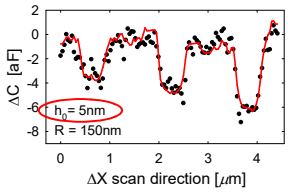




apex ~ 1 attoFarad

stray contribution ~ 1picoFarad





Fumagalli et al. *Nanotechnology* 2006

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Question

How can we probe electric polarization on the nanoscale ?

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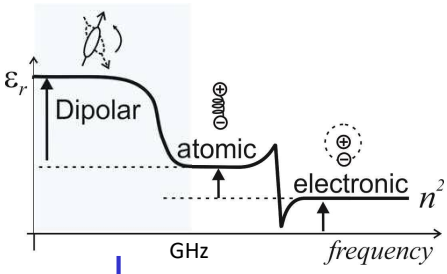
Basics of electric polarization

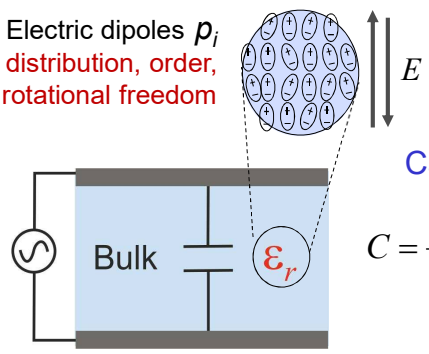
Macroscopic polarization

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

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

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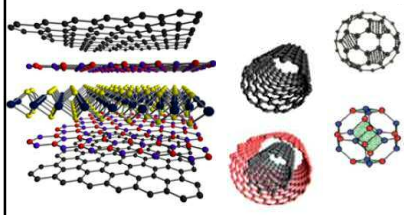
Unknown dielectric constants at the nanoscale

Lack of experimental tools with sufficient sensitivity
Theory to be established

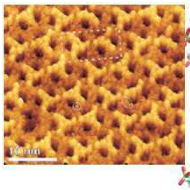
A multitude of systems still to explore

Low-dimensional systems

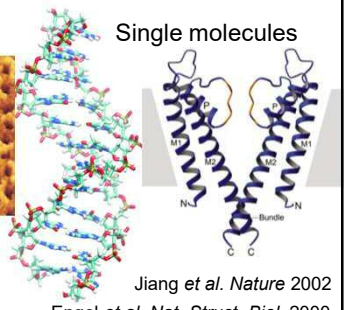


Bonaccorso *et al. ACS Nano* 2013
Goldberg *et al. ACS Nano* 2010

Biointerfaces



Single molecules



Jiang *et al. Nature* 2002
Engel *et al. Nat. Struct. Biol.* 2000

Physical Sciences

Chemistry and Biology

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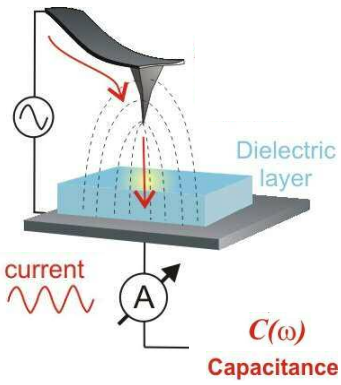
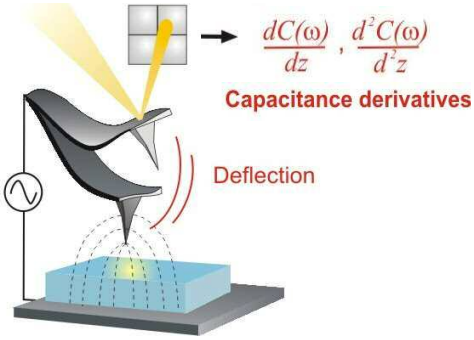
Scanning Dielectric Microscopy

Current-sensing



Electrostatic force-sensing



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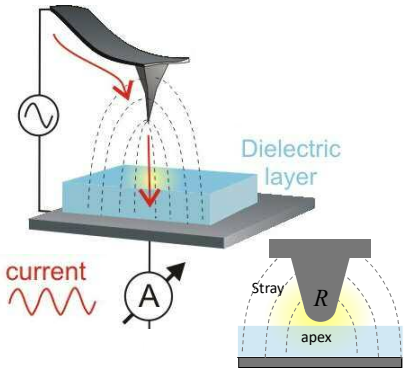
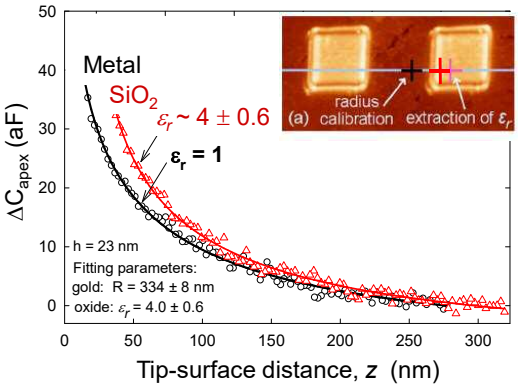
Dielectric constant measurement with CS-AFM





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

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

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 *et al. Appl. Phys. Lett.* 2007

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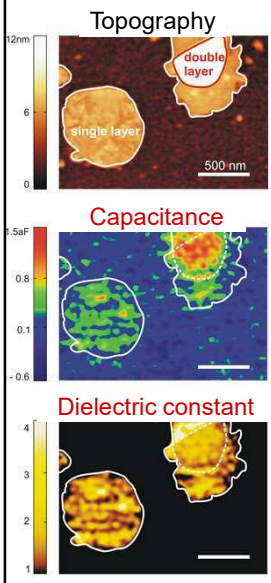
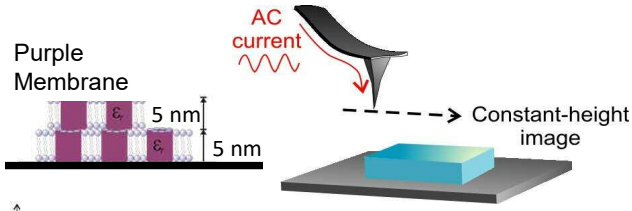
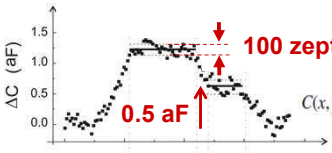
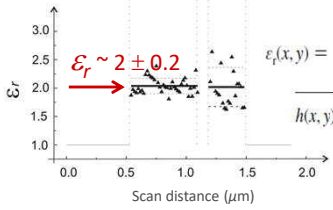
Dielectric constant <u>imaging</u> with CS-AFM







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



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

Fumagalli *et al. Nano Lett.* 2009

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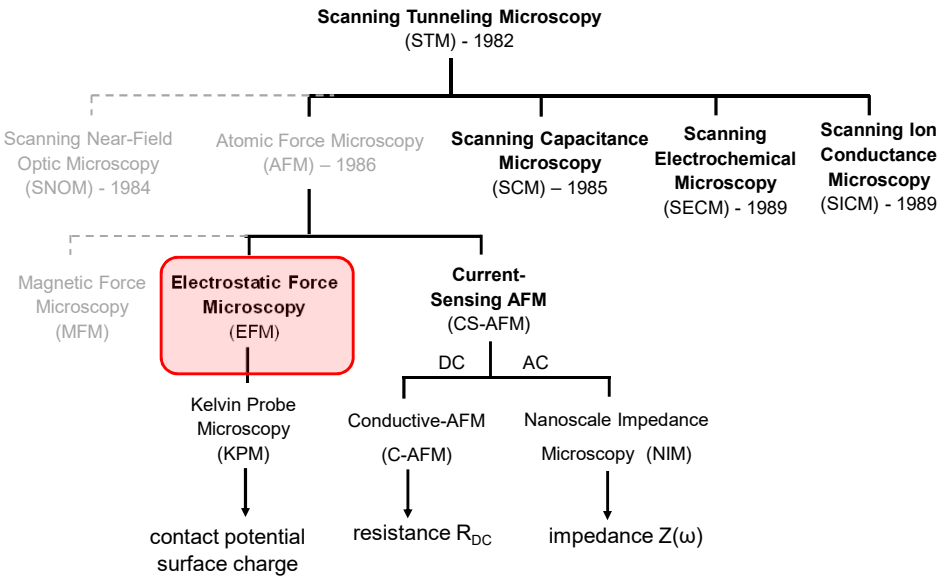
Electrical Scanning Probe Microscopies



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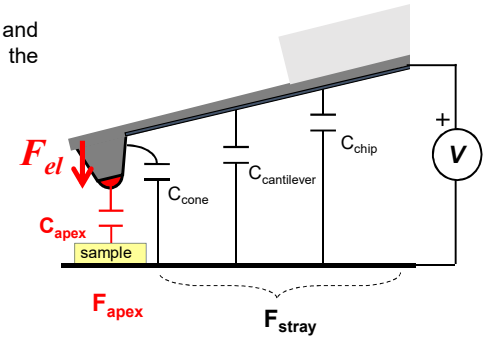
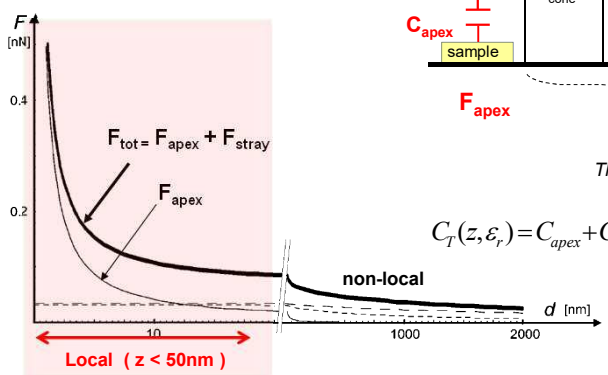
Electrostatic Force Microscopy (EFM)

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*

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

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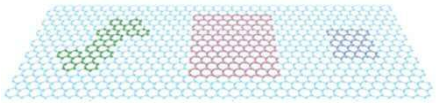
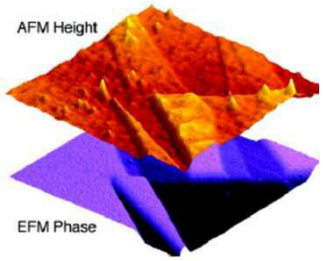
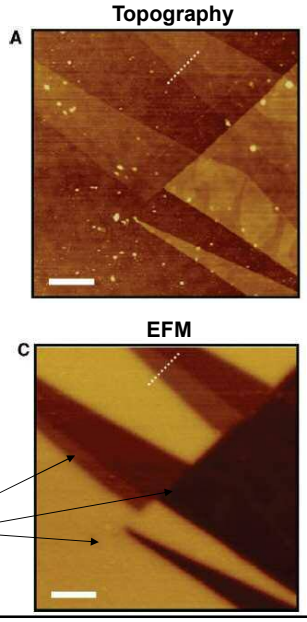
Electrostatic Force Microscopy (EFM)

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







Sujit et al. NanoLetters 2008

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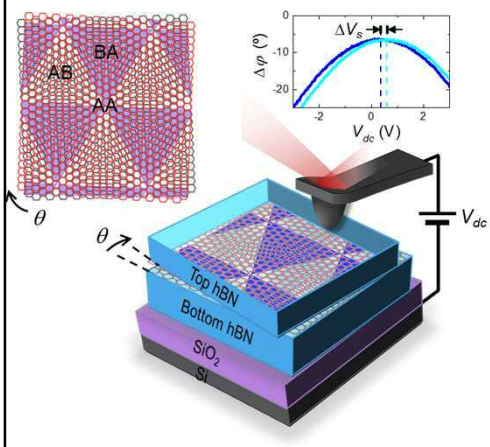
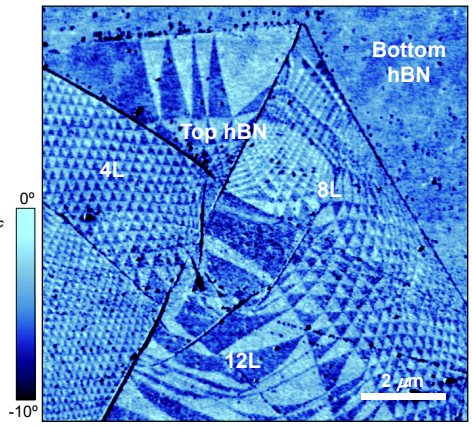
Ferroelectric-like polarization in twisted hBN

Emergence of interfacial dipolar domains



EFM



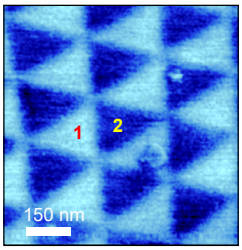
Oppositely charged domains
due to BN and NB interfacial dipoles
when twisting two insulating crystals

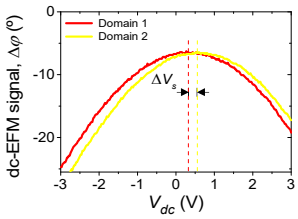
C. R. Woods *et al. Nature Comm. 2021*

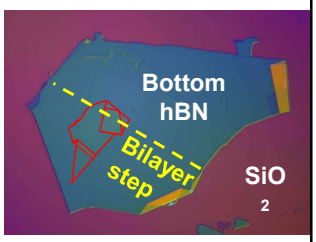
Ferroelectric-like polarization in twisted hBN

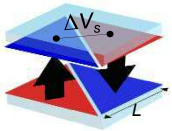
Emergence of interfacial dipolar domains

EFM

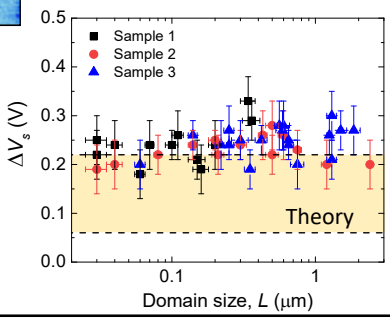


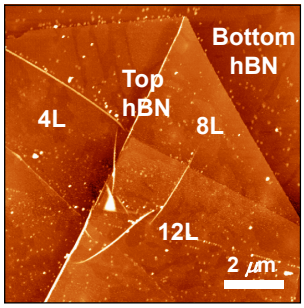




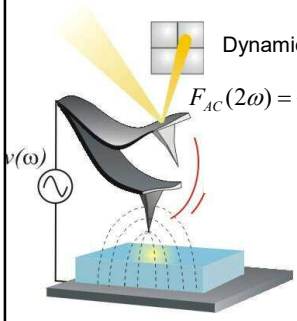


BN and NB interfacial dipoles





Dielectric constant measurement using EFM



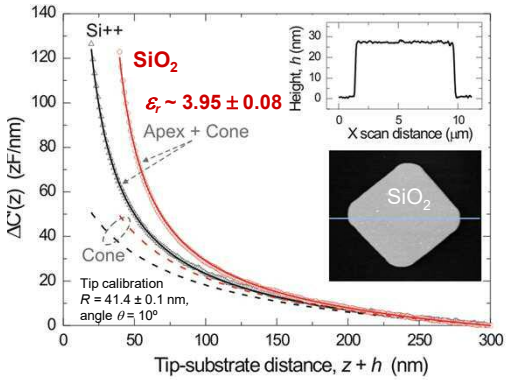
Dynamic modes

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

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 *et al. Appl. Phys. Lett. 2010*

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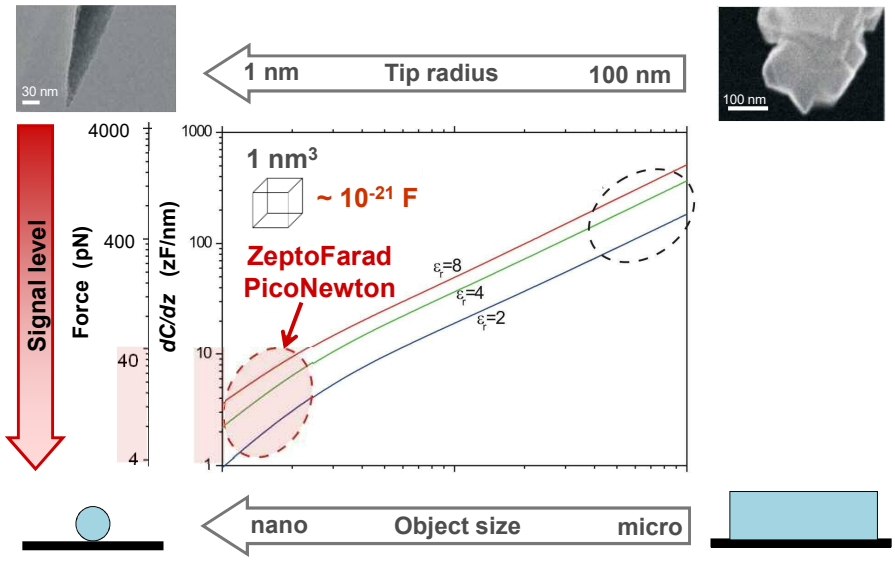
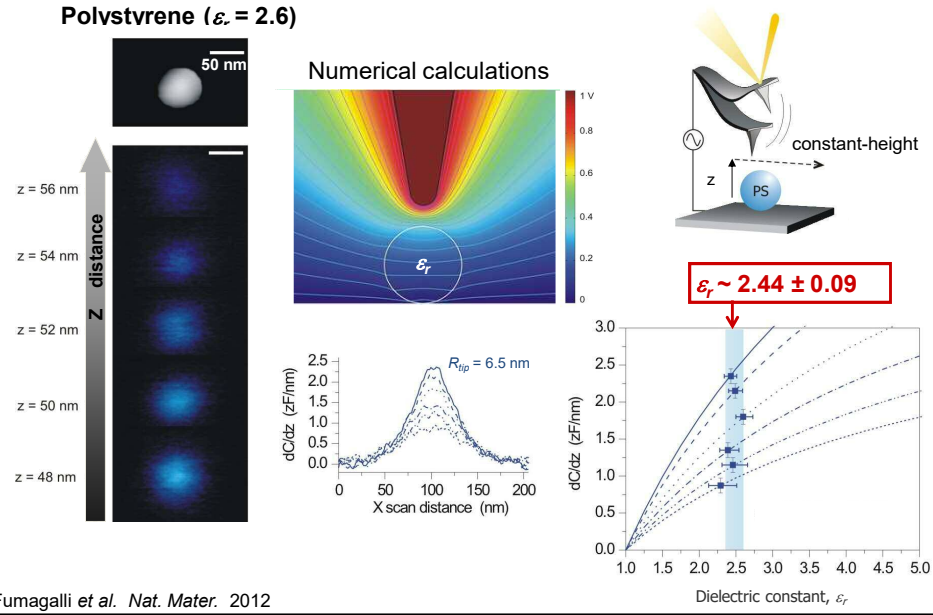
Ultra-high sensitivity in capacitance is needed

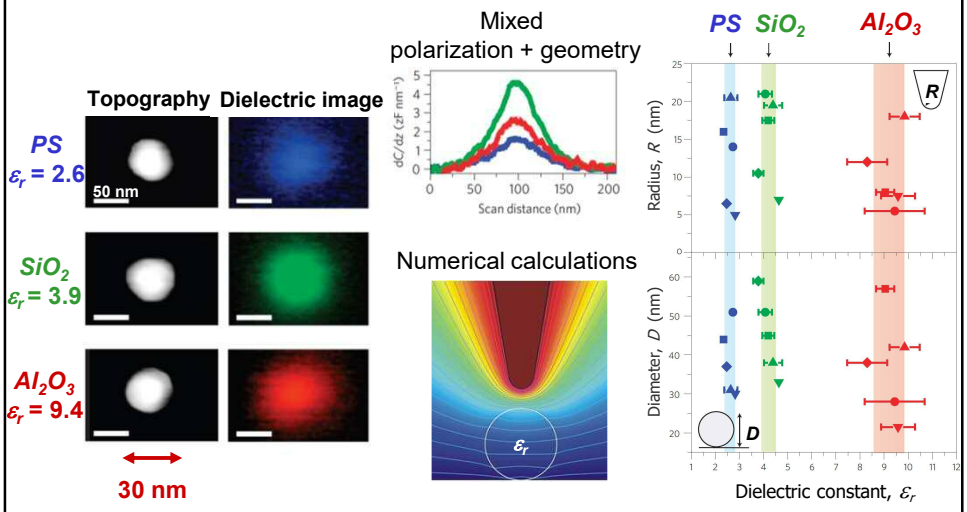


Dielectric constant of a single nanoparticle



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

Dielectric constant of single nanoparticles

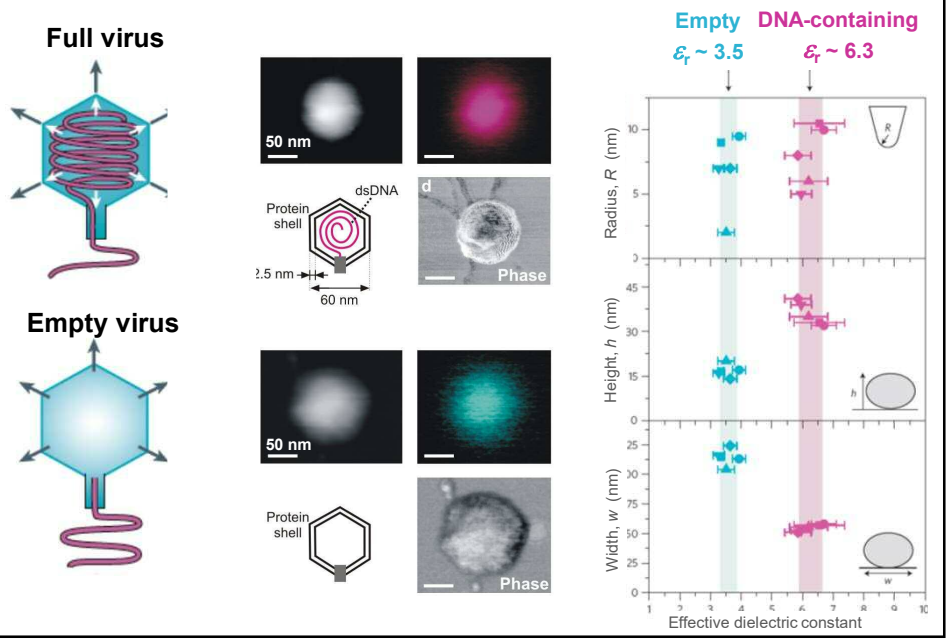


Independently from geometry good precision $\delta\varepsilon$ < 7%

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

27

A nanoparticle of unknown properties



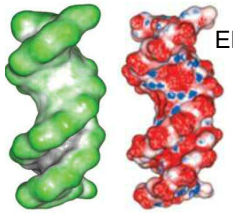
Polarization properties of DNA

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

? Unknown

Complex structure
Interplay with solvent (water)

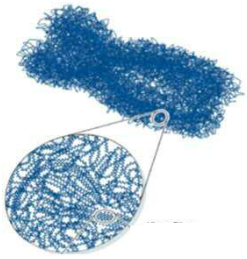
3D electrostatic potential maps depend on ε_{DNA} !



Electrostatic potential

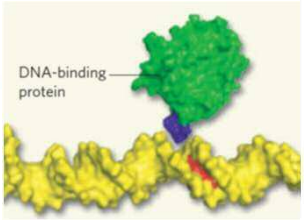
Major therapeutic impact

DNA structure

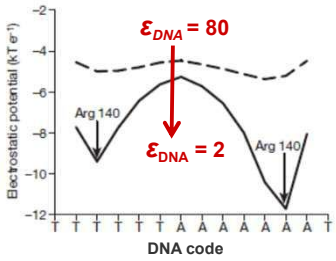


Molineux *et al. Nature Rev. 2013*

DNA-protein affinity



Rohs *et al. Nature* 2009



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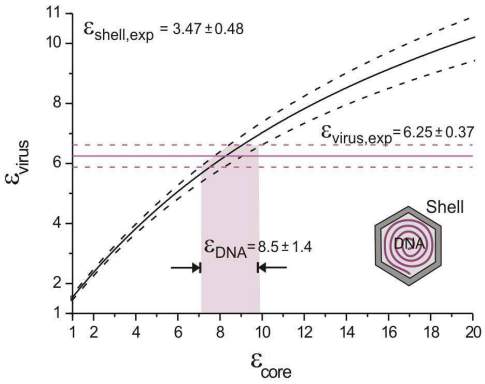
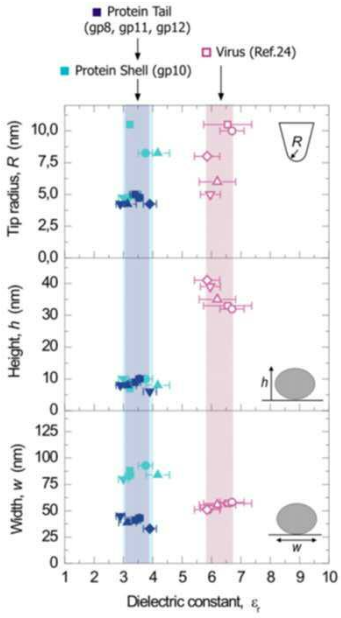
Polarization properties of DNA

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)





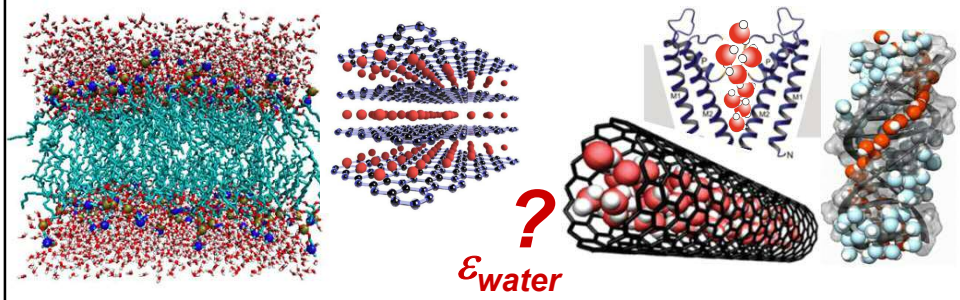
Cuervo *et al.* PNAS 2014

What is the dielectric constant of confined water?

Remained unknown

No experimental tools with enough sensitivity

Interfaces **Nanocavities**



Ice-like hypothesis

Dielectric constant expected to be different from bulk

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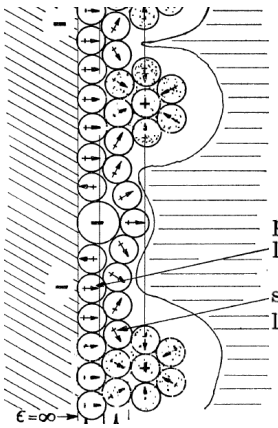
One-century long experimental challenge

Complex geometries, too many uncertainties at large scale

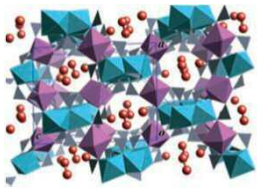
Interfacial layer thickness ?

Electric double layer



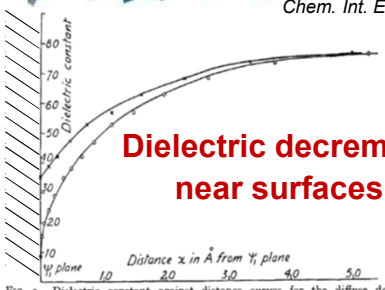
Bockris *et al. Proc. R. Soc. Lond. A* 1963

Stern 1924
Conway 1951
Bockris 1962
Onsager 1977
etc.



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.

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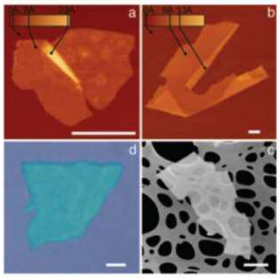
New approach: use of 2D atomically thin crystals

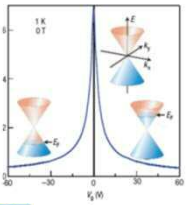
MANCHESTER 1824
The University of Manchester

School of Physics & Astronomy
National Graphene Institute

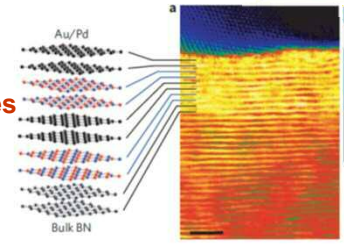
Graphene and other van der Waals crystals



Novoselov & Geim
Science, Nature 2004
PNAS 2005



van der Waals heterostructures



Geim and Novoselov,
Nobel Prize in Physics, 2010

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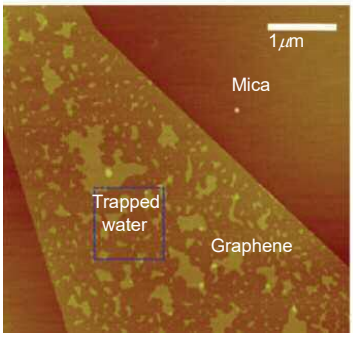
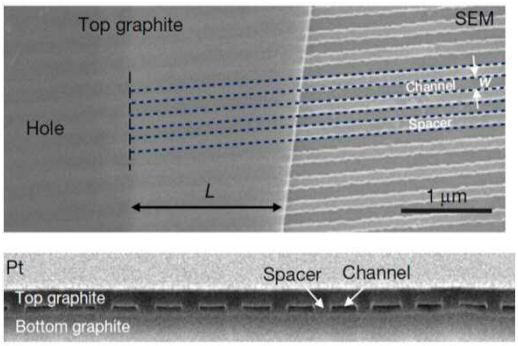
Water confined by van der Waals crystals

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)

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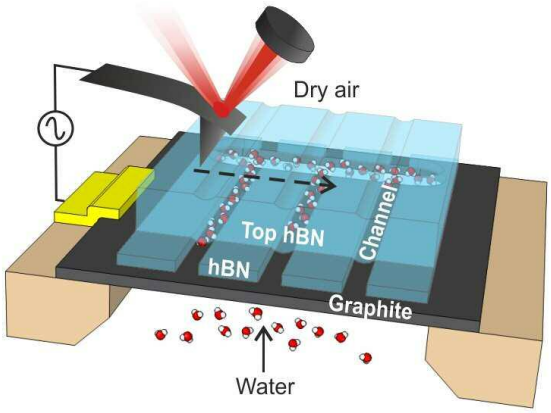
Dielectric imaging of single nanochannels

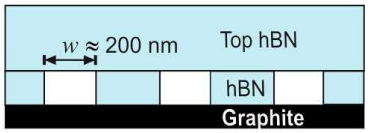
hBN/Graphite channels

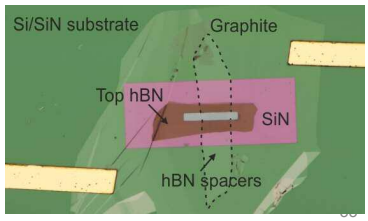
hBN as electrically transparent top layer



NB hBN spacers

Reference for ε_r ~ 3.5 (ordered ice)

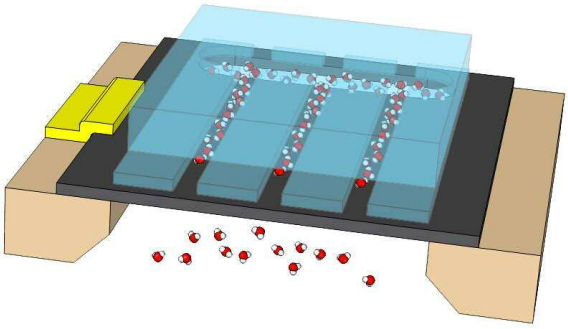




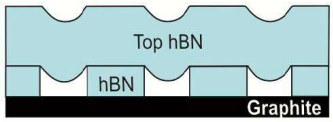
Fumagalli *et al.* *Science* 2018

Device built with sagged top layer

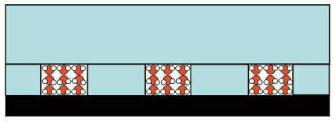
Fine-tuning of the top-layer thickness to avoid total collapse



Empty channels



Water-filled channels



The top layer becomes straight when the channel is filled

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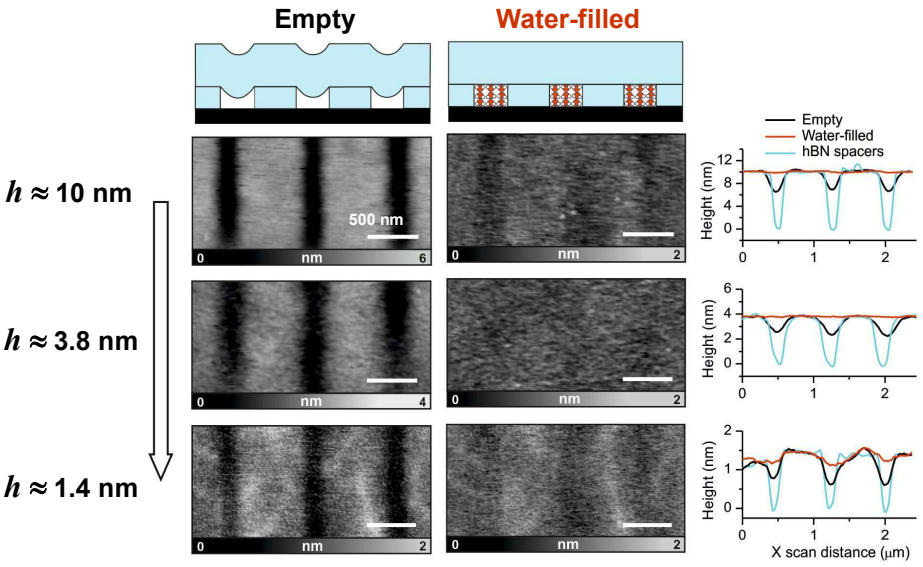
Nanochannels' thickness down to ~ 1 nm



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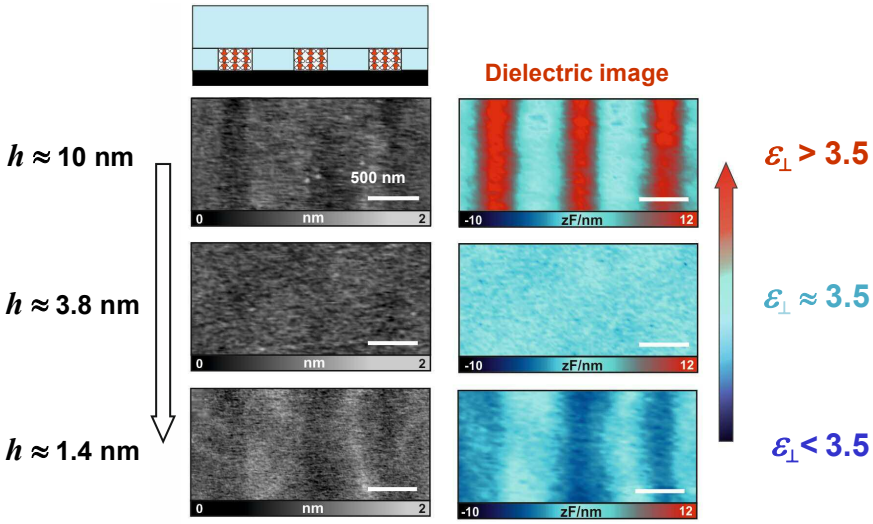
Anomalously low $\varepsilon_\perp$ of confined water

Smaller than in ordered ices, independently of the modelling



Fumagalli *et al.* *Science* 2018

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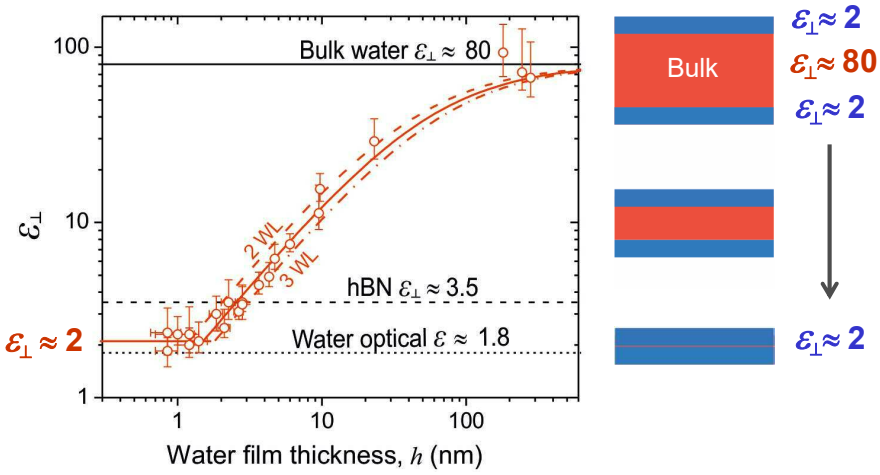
Confined and interfacial water

Dead layer of $\varepsilon_\perp \approx 2$ that extends 2-3 water layers



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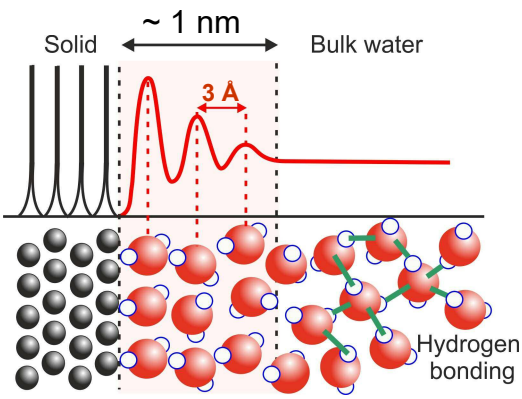
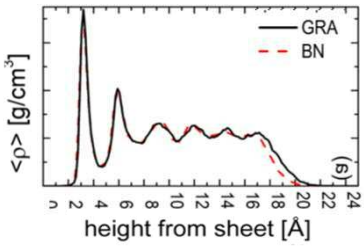
Layered structuring of water near surfaces

Molecular Dynamics density calculations



2-3 ordered layers are predicted

Tocci *et al. Nano Lett.* 2014



Same behaviour for hBN and graphite

40

Question

Can we probe electric polarization in liquid environment?

41

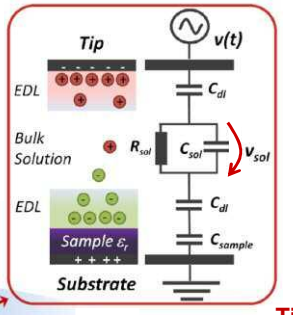
EFM in electrolyte solutions

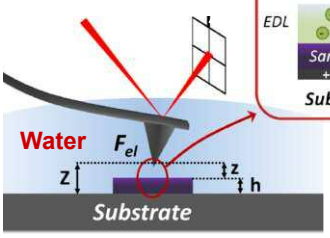
$$F_{elec}(z,t) = \frac{1}{2}\frac{\partial C_{sol}(z)}{\partial z} v_{sol}^2(z,t)$$

The voltage drop depends on frequency and ion concentration

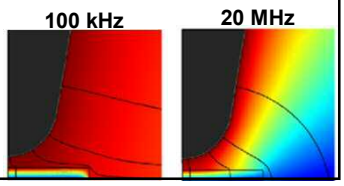
Advantage: higher dielectric environment $\varepsilon_r \sim 80$

Issues: ions conductivity and electric double layer



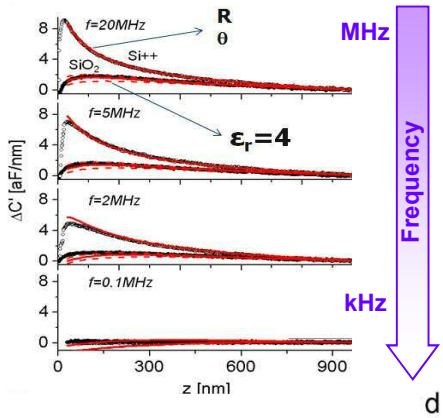


Tip apex interaction only at frequency > 1MHz



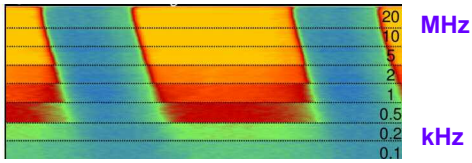
Gramse *et al. Appl. Phys. Lett.* 2012

EFM in electrolyte solutions at MHz frequencies

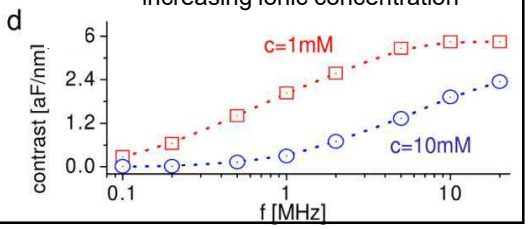


Topography

Dielectric image



Higher frequencies with increasing ionic concentration

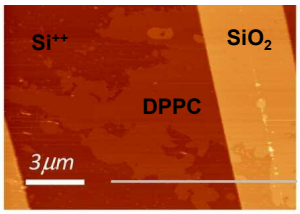


At high frequencies > MHz it works as in air !

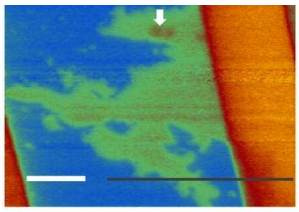
Gramse *et al. Appl. Phys. Lett.* 2012

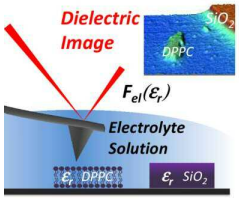
Dielectric constant of lipid bilayers in liquid

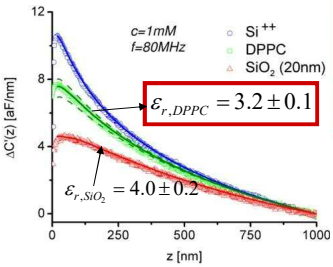
Topography

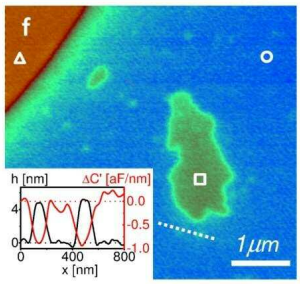


Dielectric image









→ $\varepsilon_r \sim 3$

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

Gramse *et al. Biophys. J.* 2013

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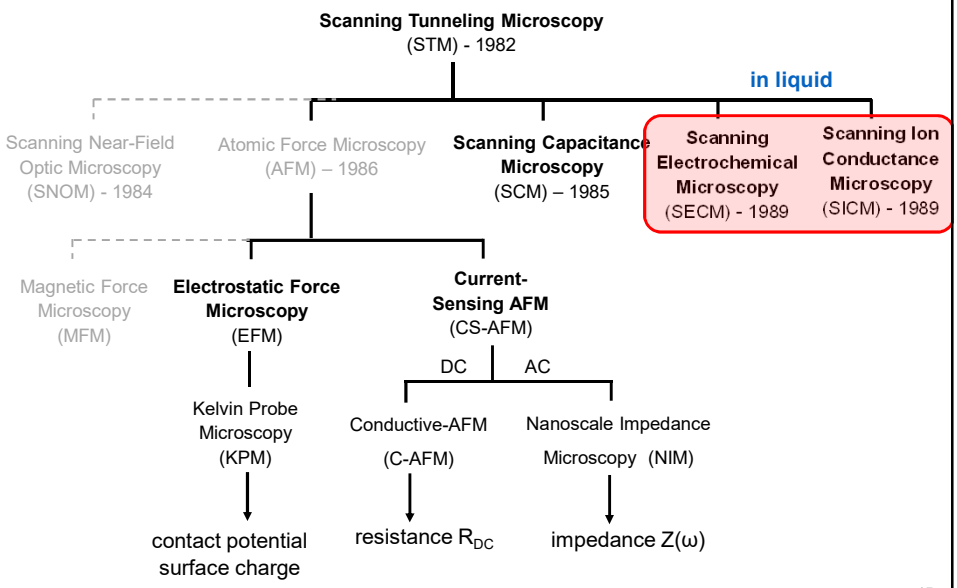
Electrical Scanning Probe Microscopies



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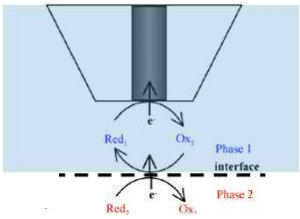
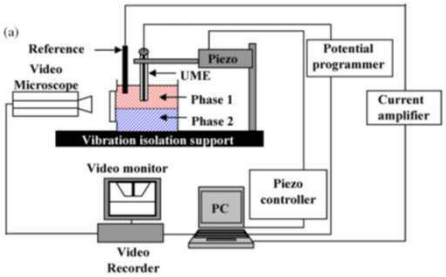
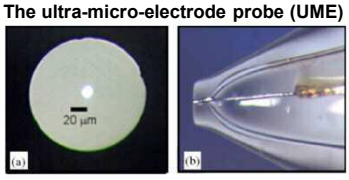
Scanning ElectroChemical Microscopy (SECM)

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 μm) 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

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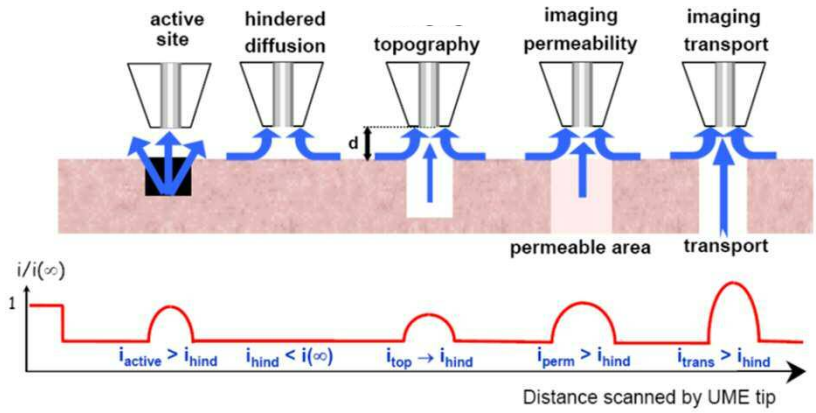
Scanning ElectroChemical Microscopy (SECM)

Major limitations compared with other SPM techniques

- **Convolution of topography and electrochemistry (like STM)**
- **spatial resolution limited to microscale**



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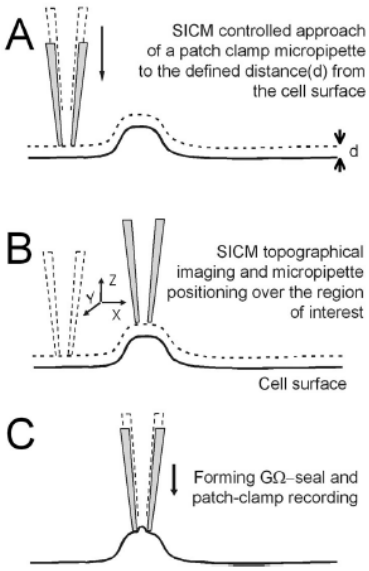
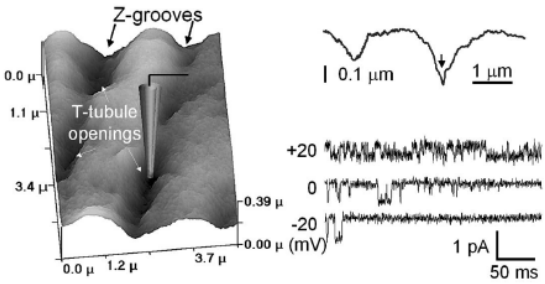
Scanning Ion Conductance Microscopy (SICM)



Patch-clamp with nanoscale positioning



Biophysical Journal 83(6) 3296–3303

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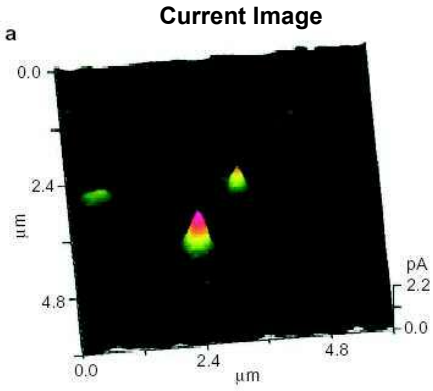
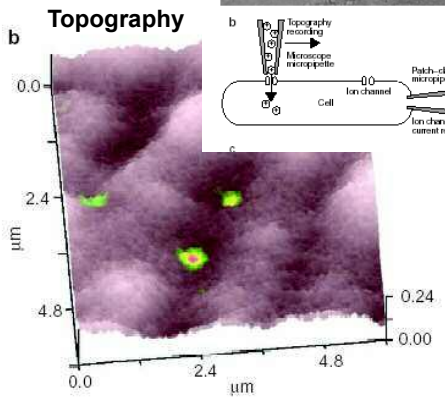
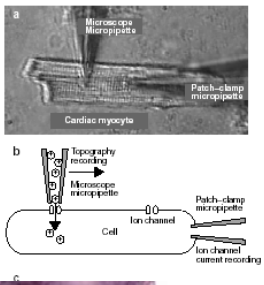
Scanning Ion Conductance Microscopy (SICM)

Detecting ion channels in living cells







Nature Cell Biology 2, 616 (2000)

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THANK YOU!

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Dept. of Physics & Astronomy
Condensed Matter Physics

PhD students and postdocs positions available
laura.fumagalli@manchester.ac.uk