Recent Advances in PFM: Biological Imaging Polymers, and Imaging in Liquid Environmnet

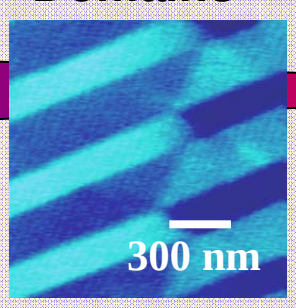
Sergei V. Kalinin

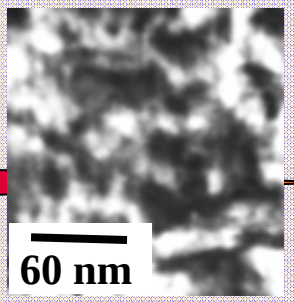
Material Sciences and Technology Division and The Center for Nanophase Materials Sciences,
Oak Ridge National Laboratory

Electromechanics: The Next Frontier

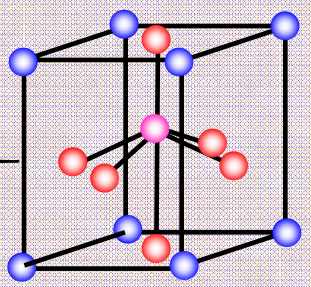
Quartz Crystal

Grains and Domains





Phase separation



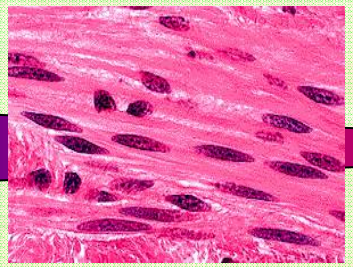
Unit cell

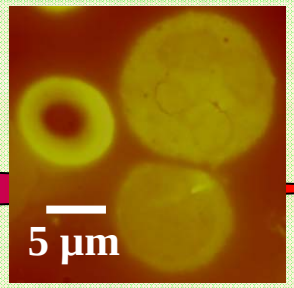
1 m | 0.1 m | 10 mm | 1 mm | 0.1 mm | 10 µm | 1 µm | 0.1 µm | 10 nm | 1 nm | 1 Å

We need Scanning Probe Microscopy to image elastic, electromechanical and electrical behavior !

Mouse

Tissues

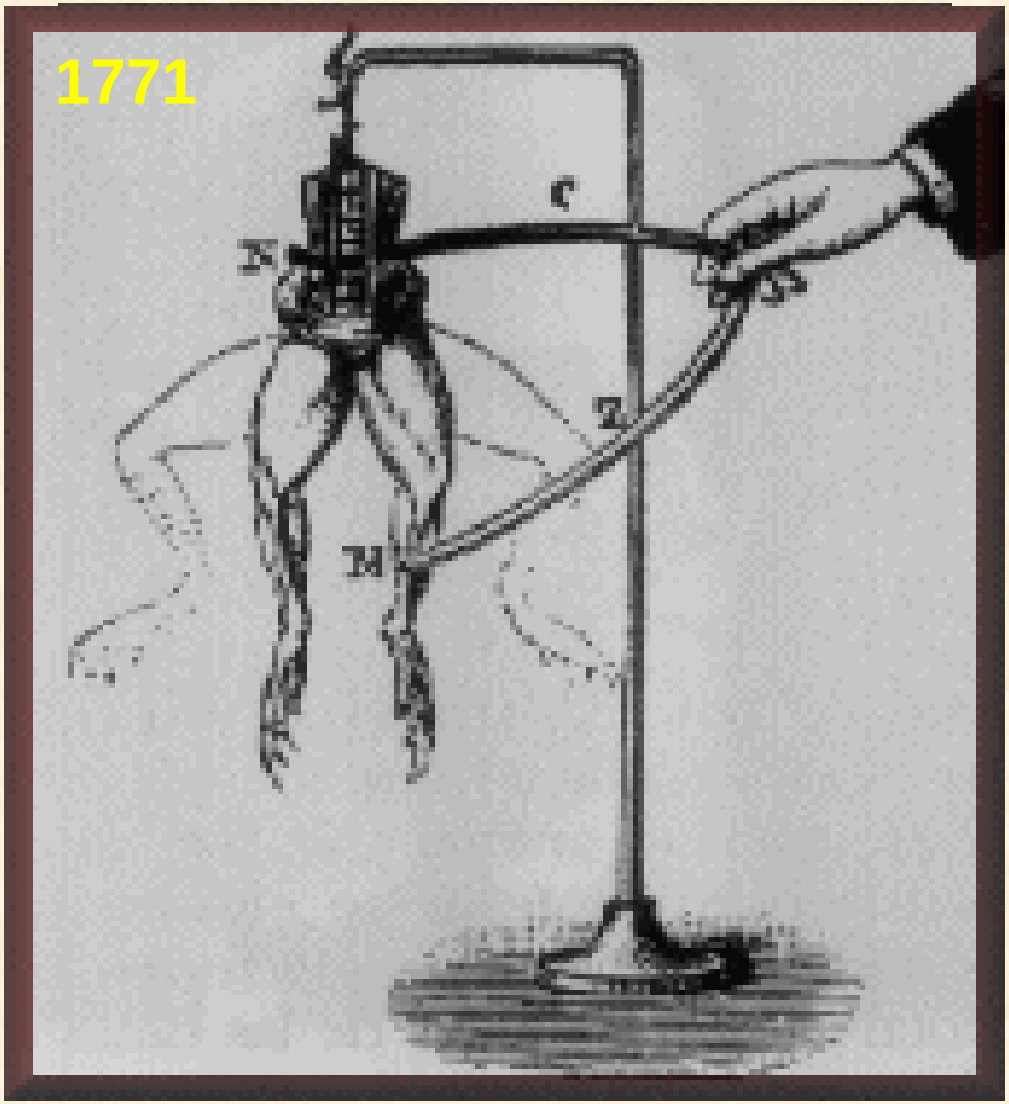




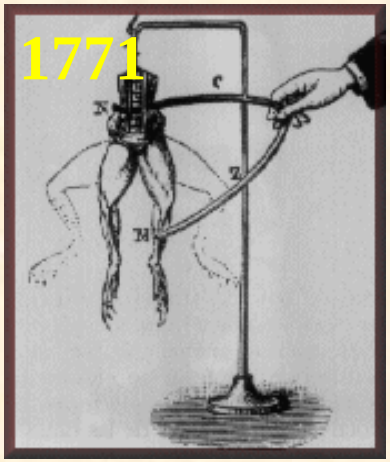
Cell

Molecule

Electromechanics and the Origins of Physics



Electromechanical Phenomena in Biosystems



1771: Galvani – discovery of electricity
1942: Wul - Ferroelectricity in $BaTiO_3$
1957: Fukada – piezoelectricity in bones
1996: Gruverman - Piezoresponse Force Microscopy

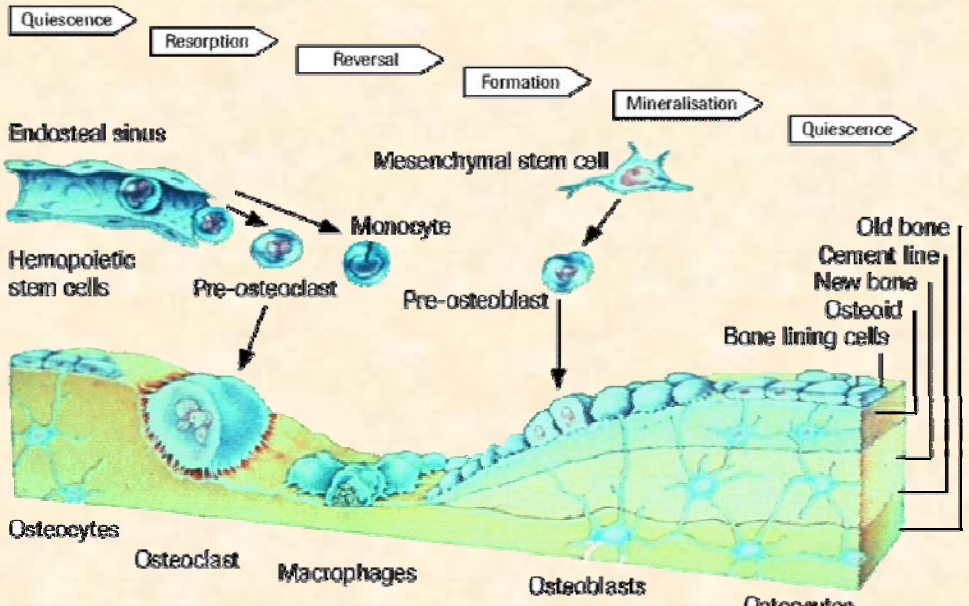
Since 1955, it was shown that many biomaterials, including collagen and cellulose, are piezoelectric. This piezoelectric activity was postulated to be directly related to biochemical functionality.

Bones remodel to respond to external stimuli (Wolff law):

Bones: d_{24} = 2-10 pC/N (similar to quartz)
As we know, bones regenerate

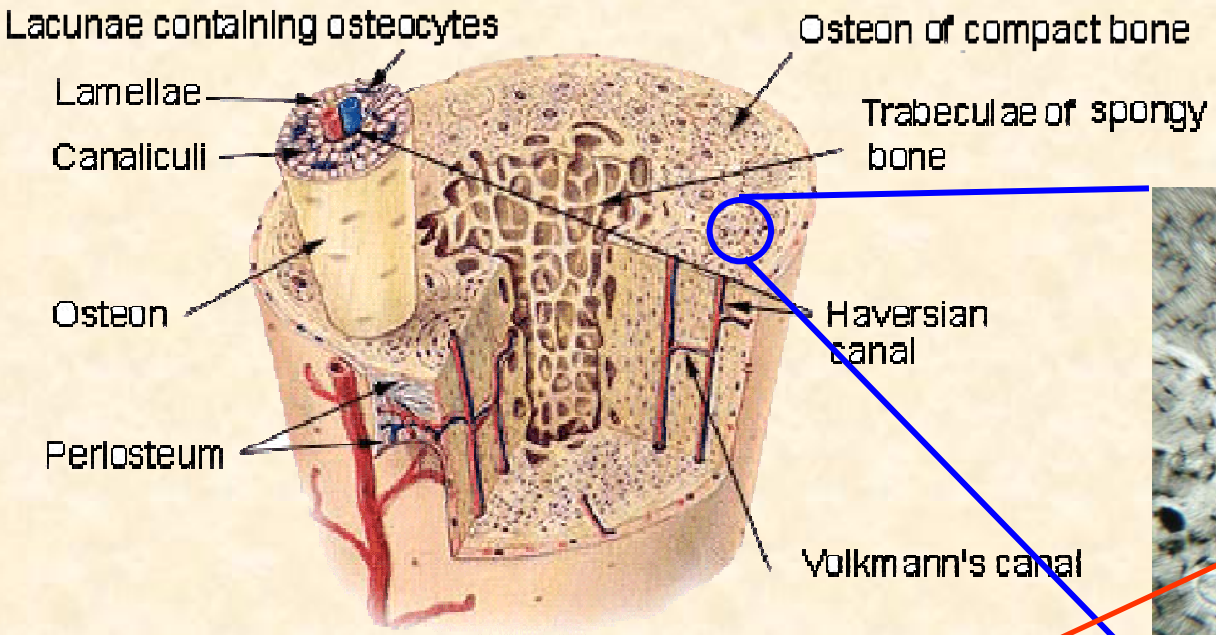
Teeth: d_{24} = 0.2 pC/N
And teeth don't…

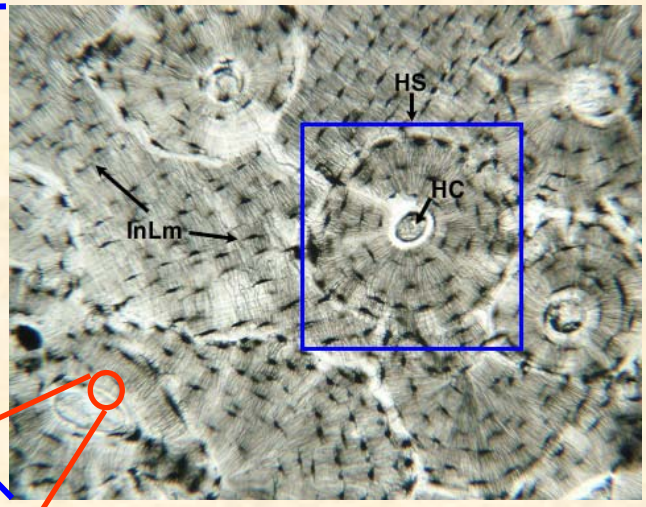
A number of approaches for bone treatments (osteoporosis, fracture) were suggested using periodic fields



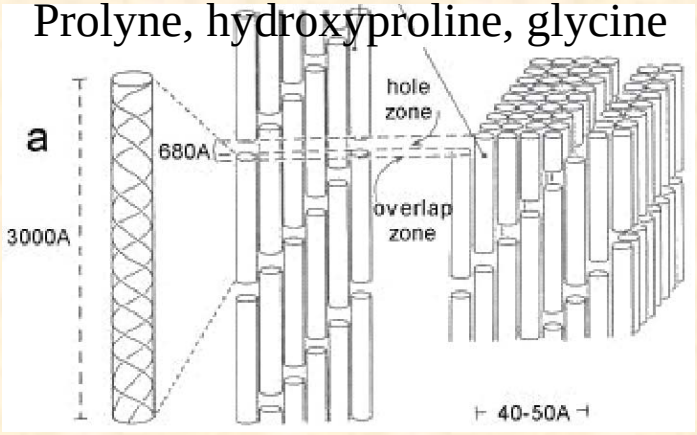
Piezoelectricity and Extinction of Dinosaurs

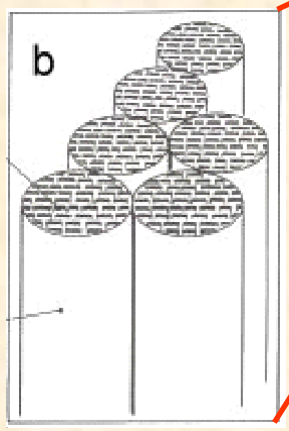
Piezoelectricity of Bones





Piezoelectric collagen: triple helix
Prolyne, hydroxyproline, glycine

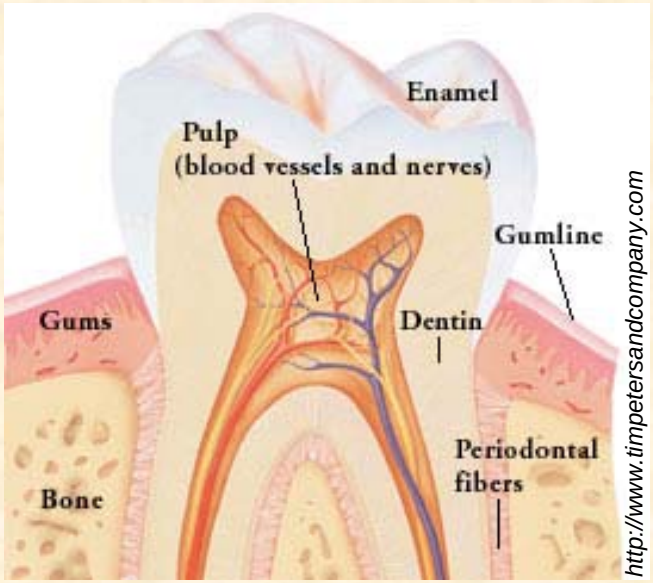




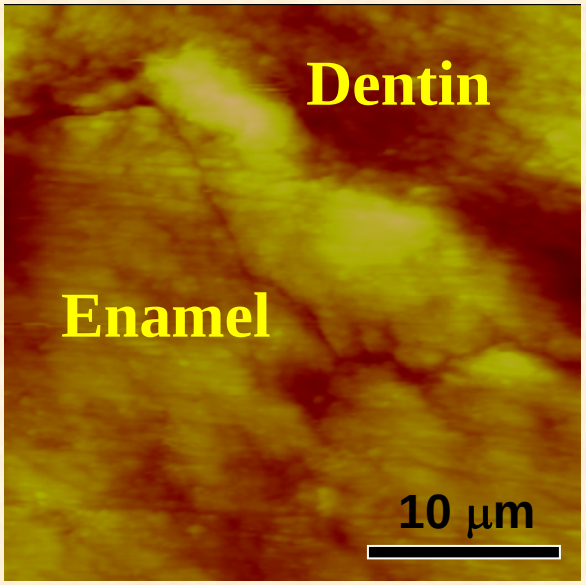
Bones are non-uniform:
Macroscopic piezoelectric measurements are not reproducible

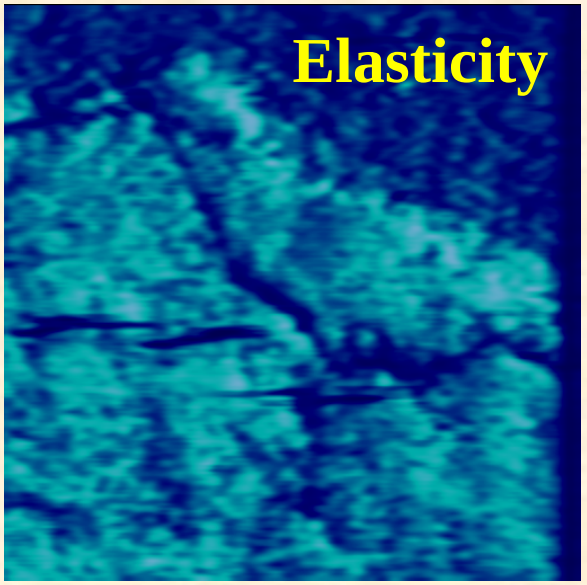
On sub-micron level:
20-30 nanometer apatite lamellae
~15 nanometer collagen fibrils
The detailed structure is virtually unknown…

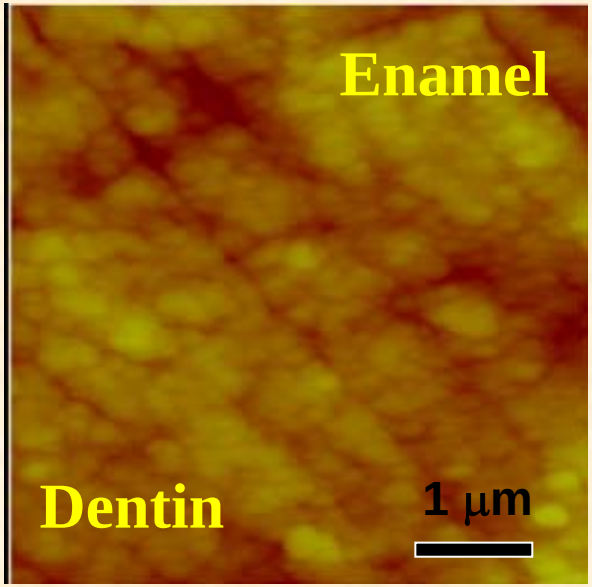
Dentin-Enamel-Junction as a Sample Model

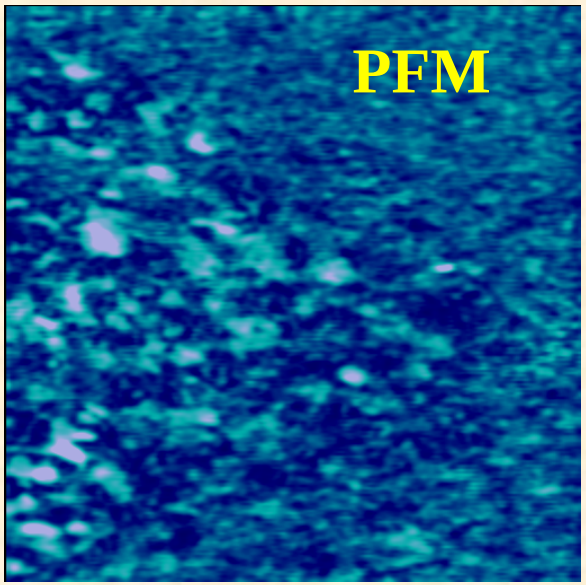


http://www.timpetersandcompany.com









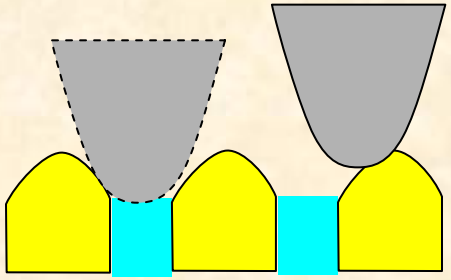
Clear contrast for both modes

What about higher resolution scans?

Sample courtesy of V. Grichko

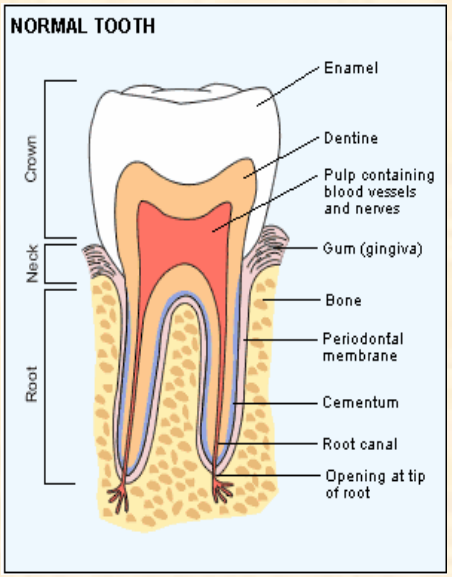
Nanoelectromechanics of Human Tooth - I

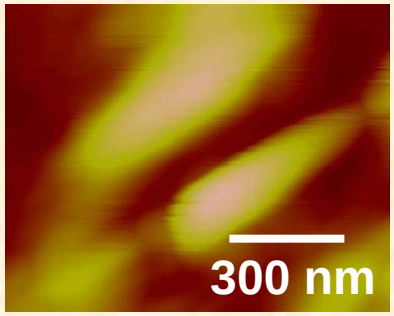
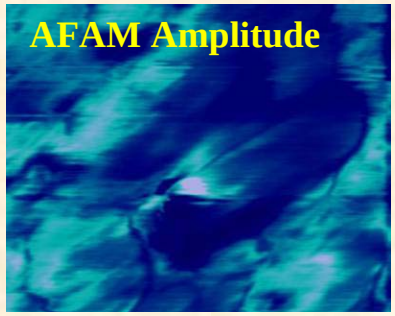
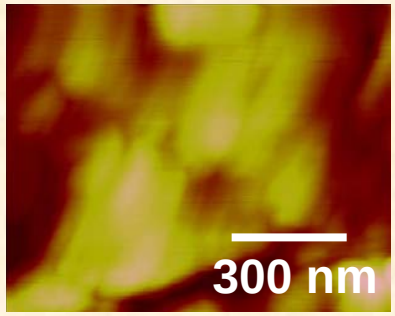
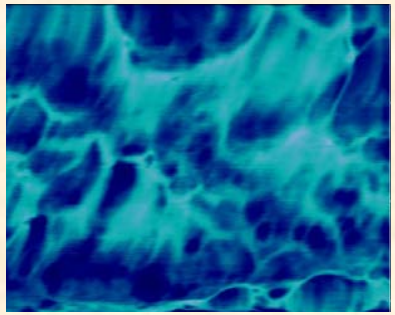
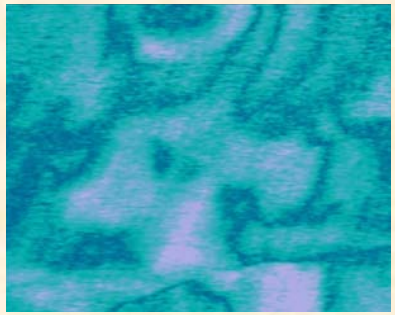
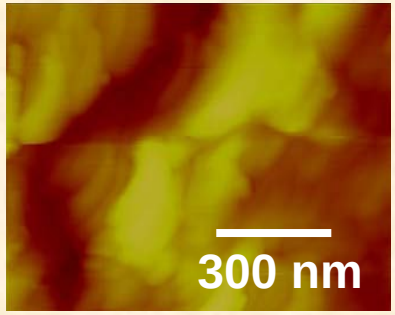
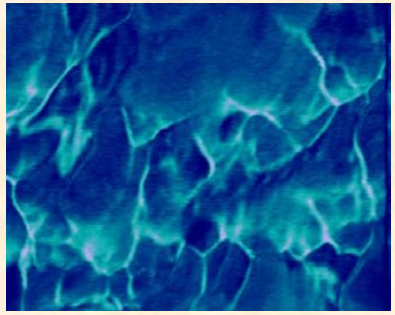
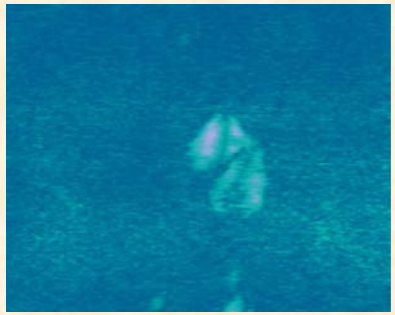
Dentine and enamel are based on hydroxyapatite, but have different mechanical properties as they differ by the content of organic fibers.



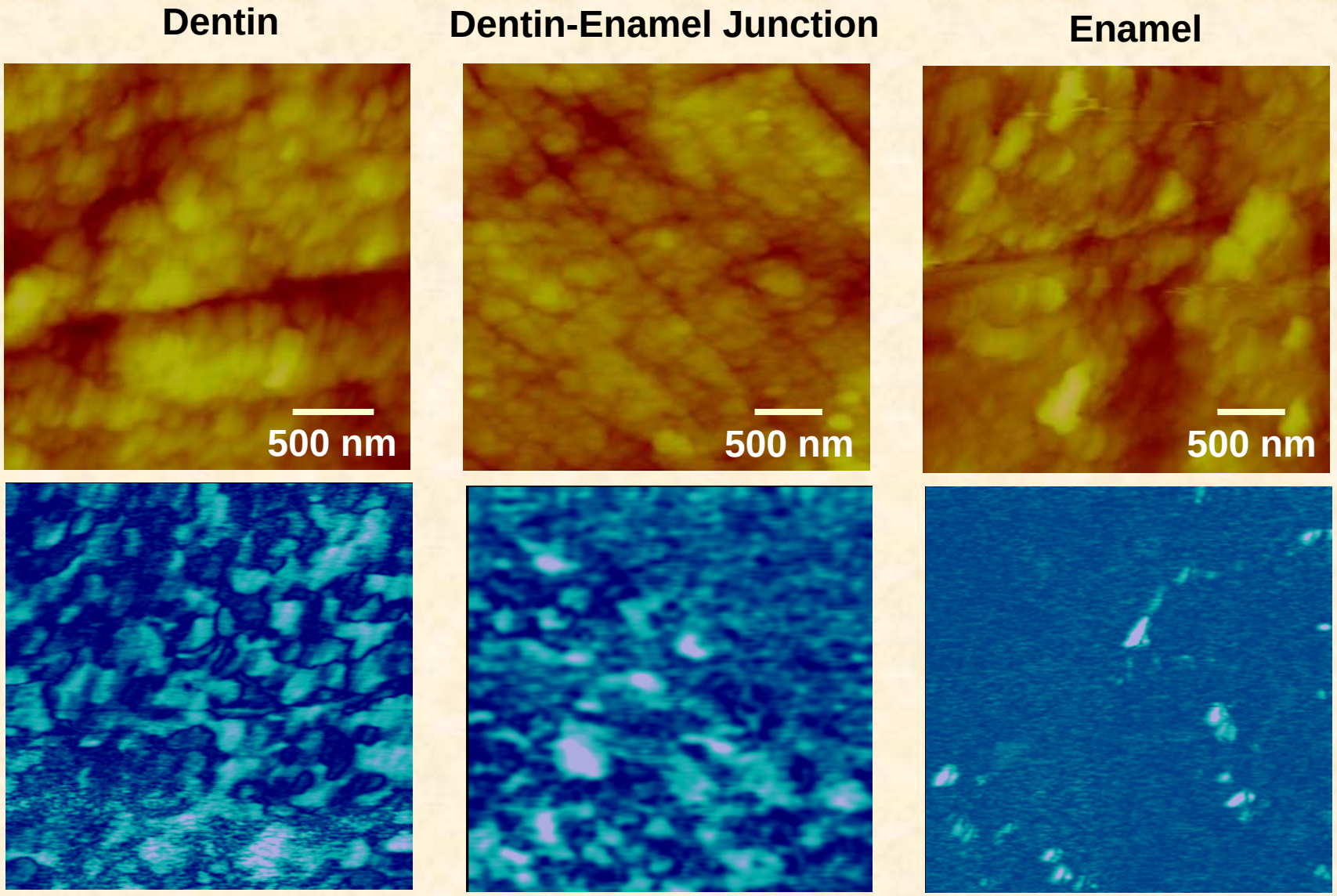
Soft
Piezoelectric

Hard
Non-piezoelectric

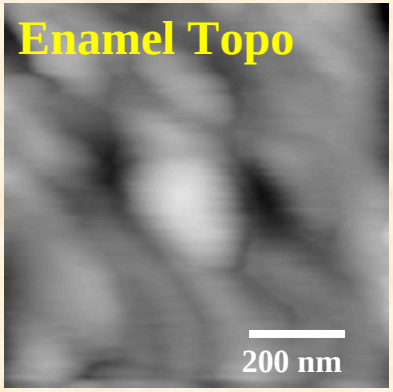


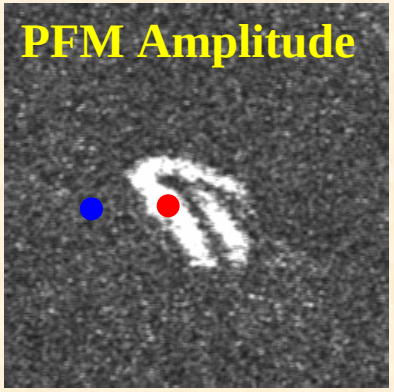
	Topography	Elasticity	Piezoelectricity
Pulp			
Dentine			
Enamel			

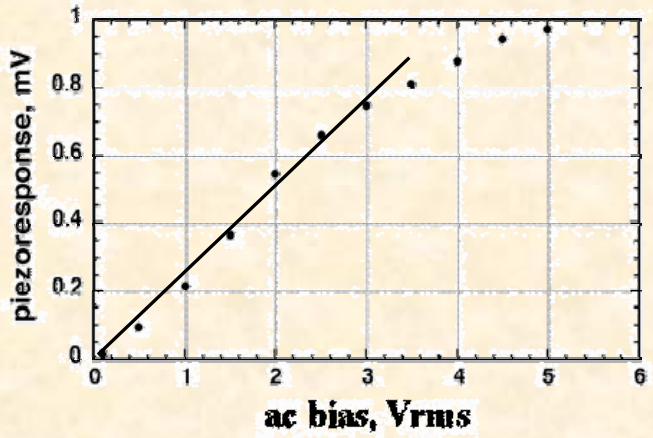
Nanoelectromechanics of Human Tooth - II



Piezoelectric Spectroscopy

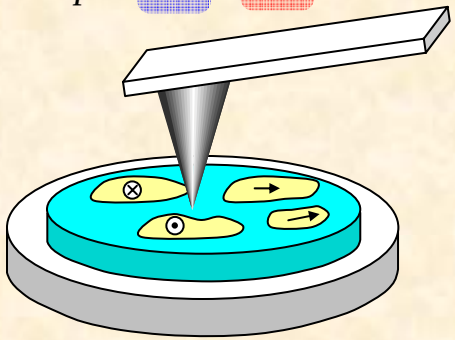


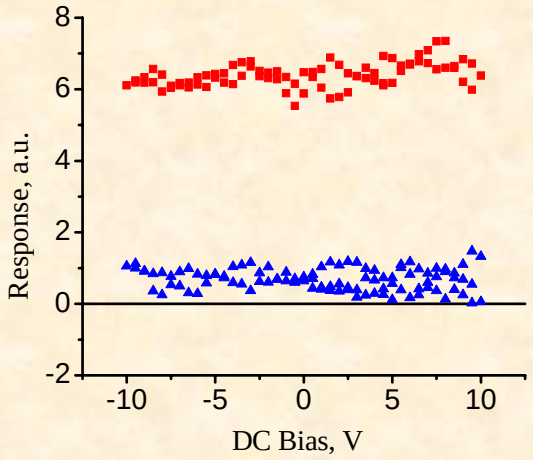


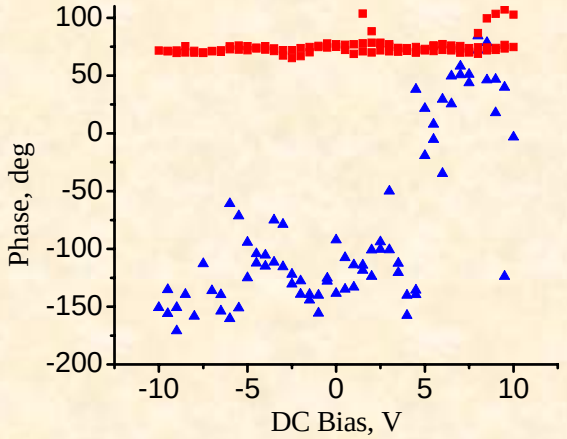


Hysteresis loops of a single protein fibril in tooth enamel

$$V_{tip} = V_{dc} + V_{ac} \sin \omega t$$



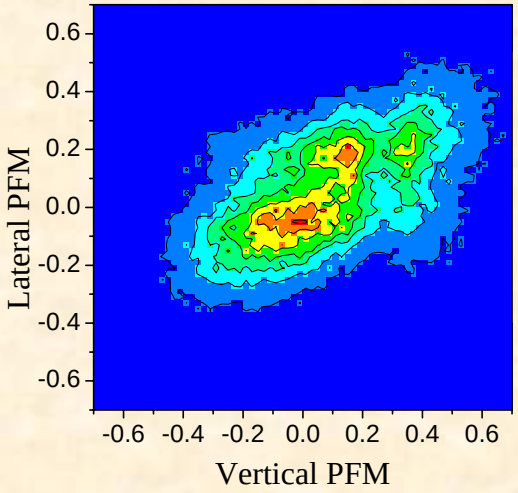


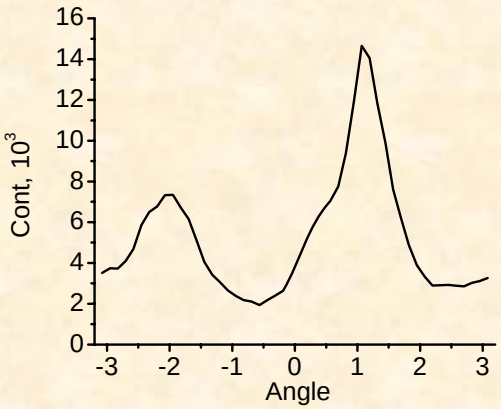


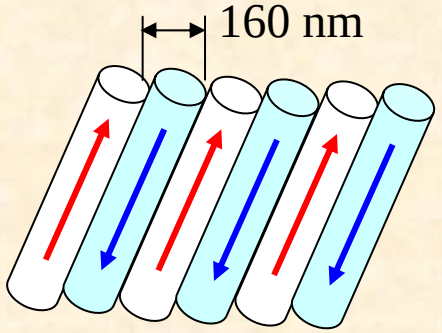
- Collagen is piezoelectric, but not ferroelectric.
- Response is almost linear in bias, d_{local} =0.5 - 2 pm/V

Microstructure of Dentin vs. Cartilage

Doubly histogram of vertical and lateral PFM shows that there are two dominant fiber orientations (significant disorder)

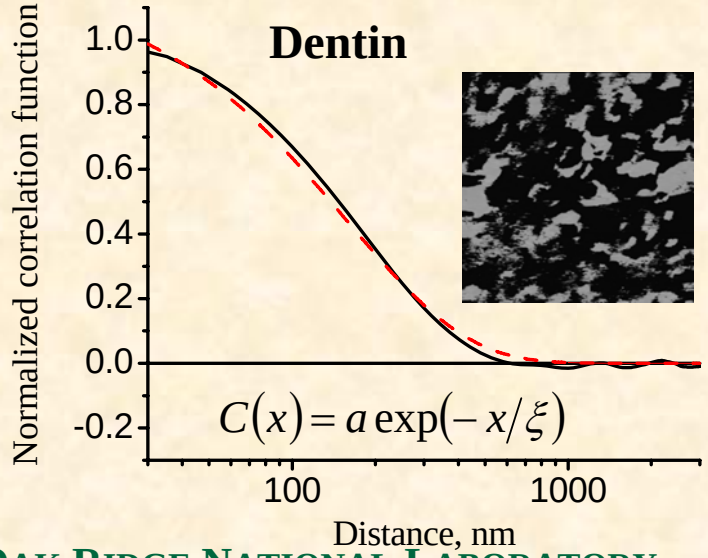


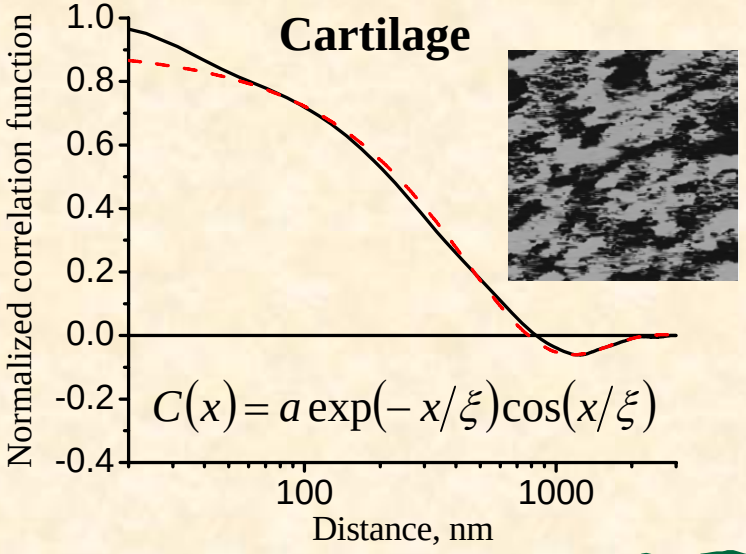




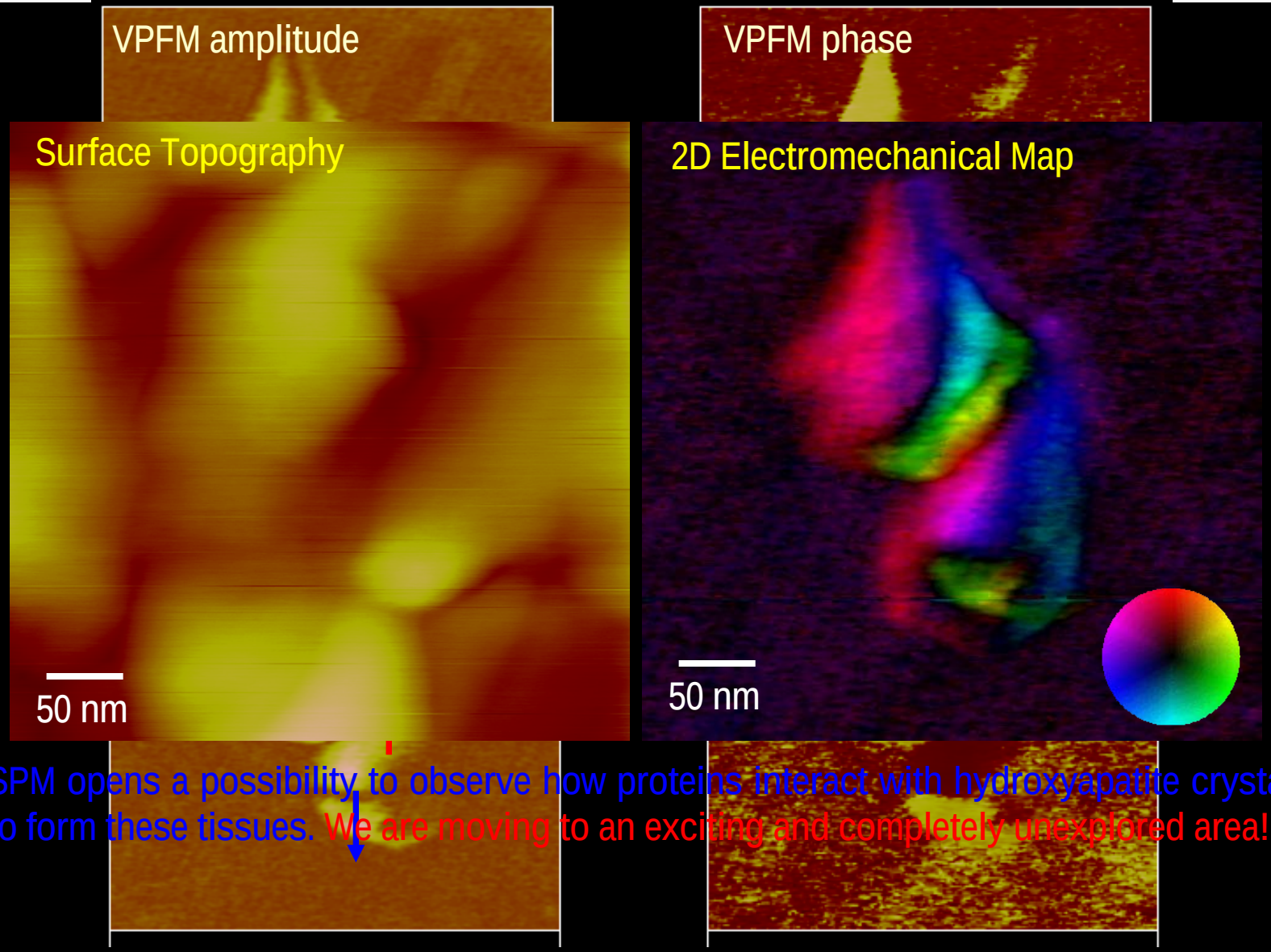
Microstructural model

Correlation function analysis





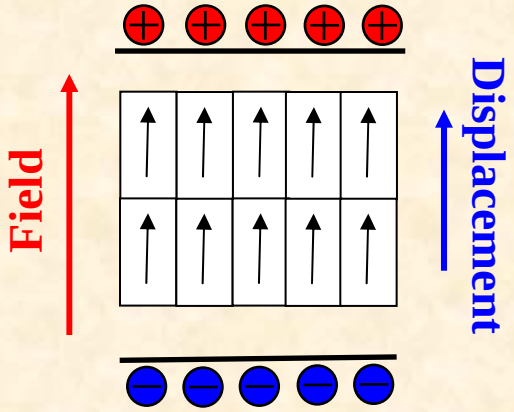
Toward Single Molecule Imaging



SPM opens a possibility to observe how proteins interact with hydroxyapatite crystals to form these tissues. We are moving to an exciting and completely unexplored area!

Principles of Orientation Imaging

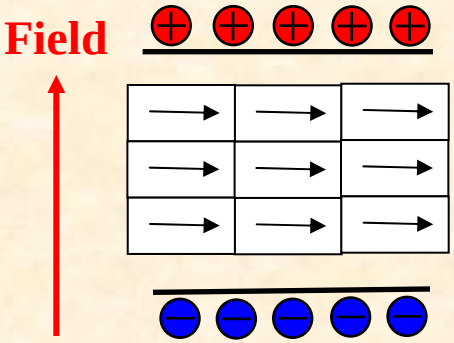
Experiment: measure the mechanical displacement in the applied electric field direction

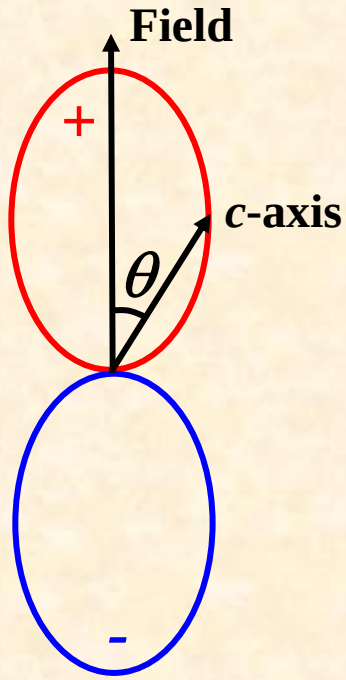


For tetragonal ferroelectric such as $BaTiO_3$, if the field is **parallel** to the c-axis, there is strong deformation of the crystal in the field direction

$$\delta z = d_{33} E_3 h \quad \text{or} \quad \delta z = 80V \text{ pm}$$

If the field is **perpendicular** to the c-axis, the deformation in the field direction is zero





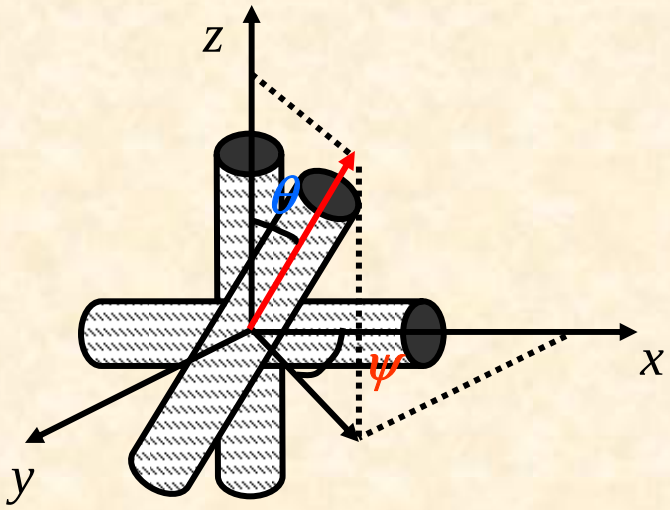
In the general case:

$$\delta z = (d_{15} + d_{31})\sin^2\theta\cos\theta + d_{33}\cos^3\theta$$

From known electromechanical response, we can determine crystal orientation!

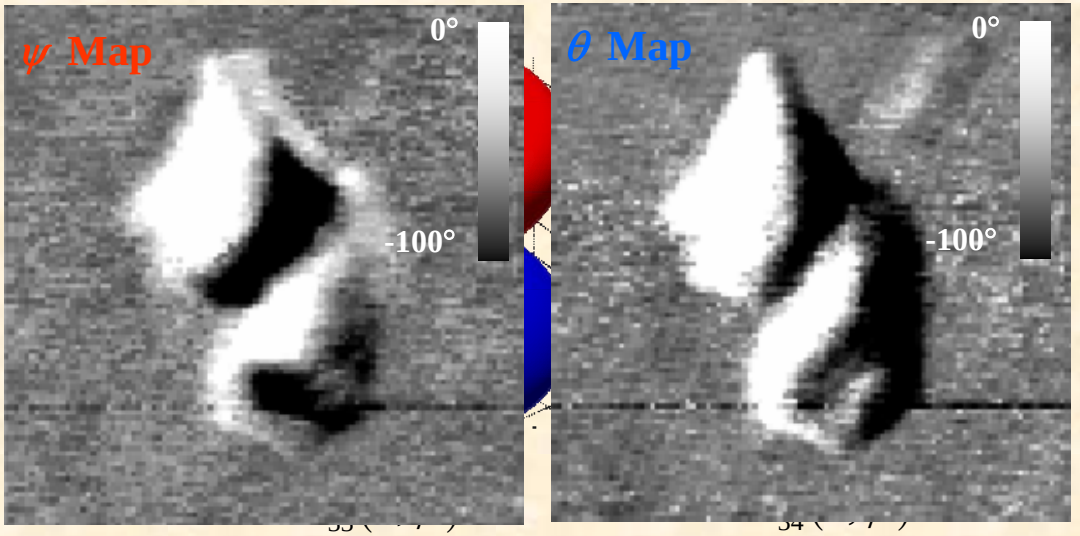
- small displacements (10-100 pm)
- spatially localized (< 1 μm)

Molecular Orientation from PFM Data



Semiquantitative Orientation Map for Collagen Fibril

Piezoresponse Surfaces for Collagen



Tetragonal material (4mm):

$$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & d_{15} \\ d_{31} & d_{33} & d_{31} & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & d_{15} & 0 & 0 \end{pmatrix}$$

Vertical PFM

Lateral PFM (*x*)

Lateral PFM (y)

$$d_{ij} = A_{ik}(\phi,\theta,\psi)\, d^{o}_{kl}\, N_{lj}(\phi,\theta,\psi)$$

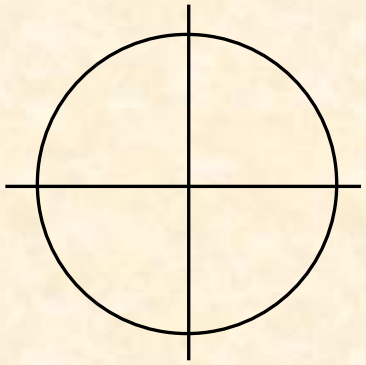
d_{ij} Piezotensor – lab coordinate system

d^{o}_{kl} Piezotensor – crystal coordinate system

$N_{ij}(\phi,\theta,\psi)$ $A_{ij}(\phi,\theta,\psi)$ Rotation matrices

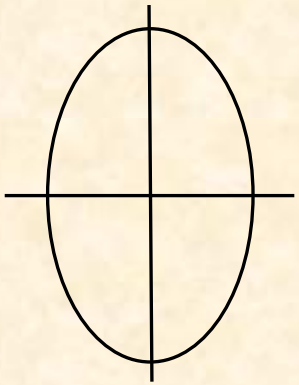
Can we do it any other way?

Scalar



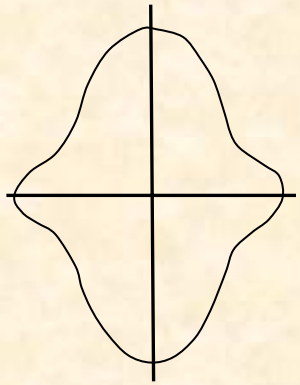
Temperature,
Potential, etc.

2nd order tensor



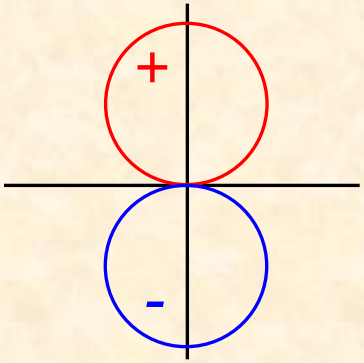
Dielectric constant
Thermal conductivity

4th order tensor



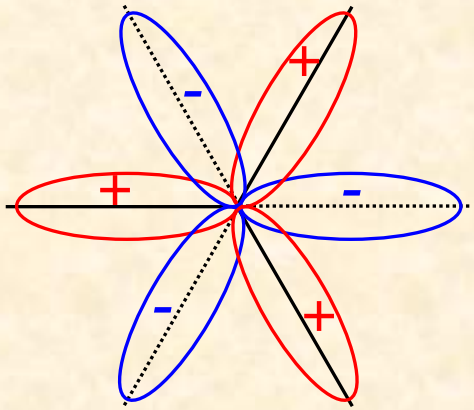
Elasticity, Kerr effect
Electrostriction

Vector



Polarization
Magnetization
Pyroelectricity

3d order tensor

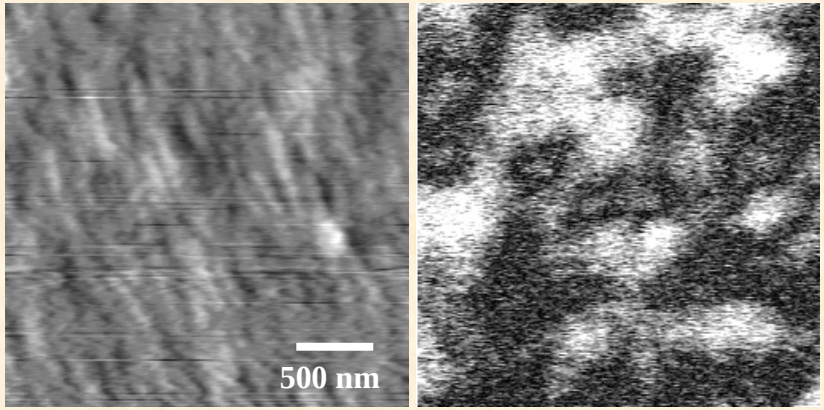


Piezoelectricity
Electrooptics, SHG

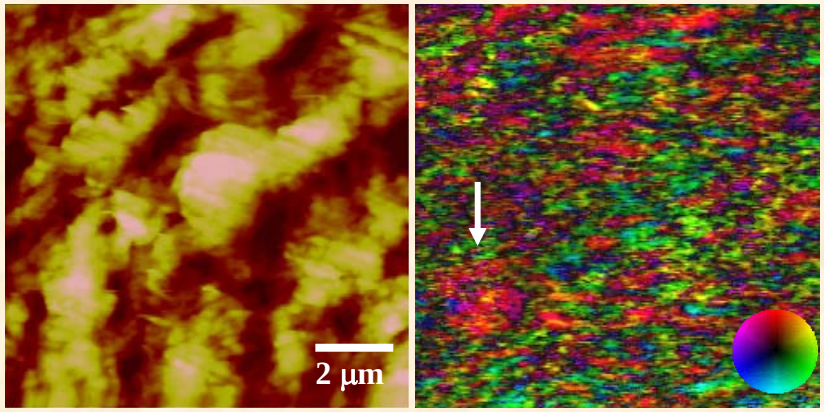
Electromechanical coupling coefficient can be measured by SPM with sub 10 nanometer resolution. Measurements are not sensitive to tip geometry, unlike elastic and dielectric measurements

Piezoelectricity in Biosystem

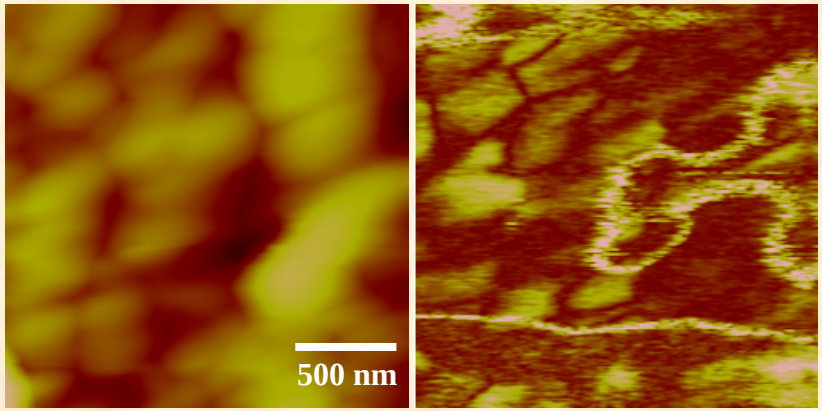
Artificial collagen film



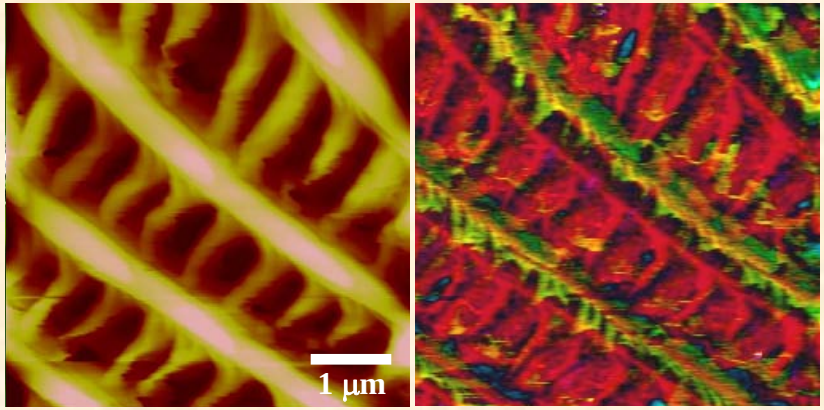
Cross-sectioned deer antler



Canine femur cartilage



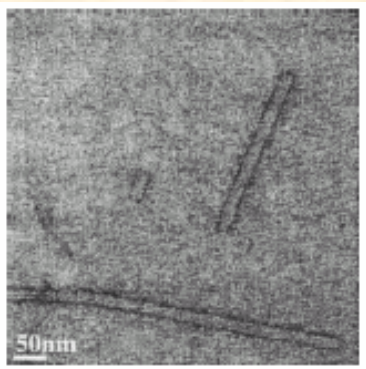
Vanessa Virginiensis wing

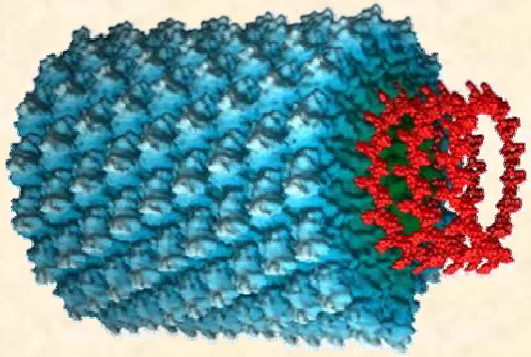


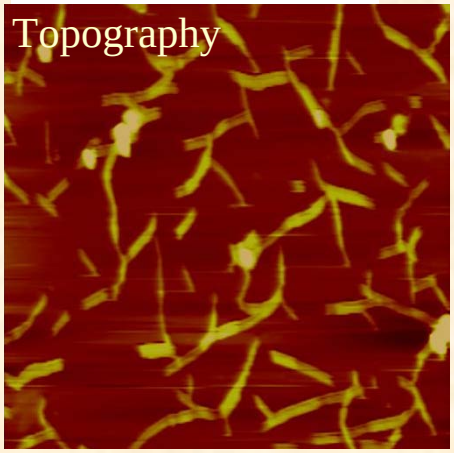
Nanoscale piezoelectricity is ubiquitous in biosystems, stemming from the combination of polar bonds and optical activity in biopolymers

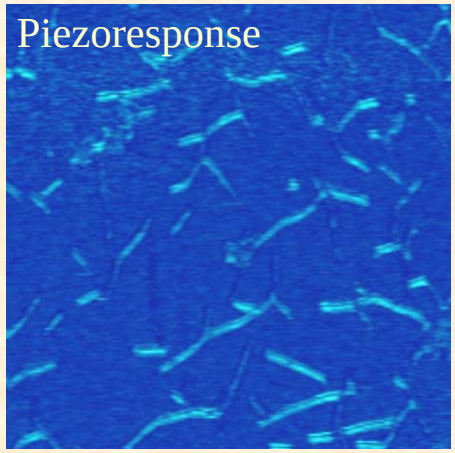
Flexoelectricity in Tobacco Mosaic Virus

More complex steps: tobacco mosaic virus and cells







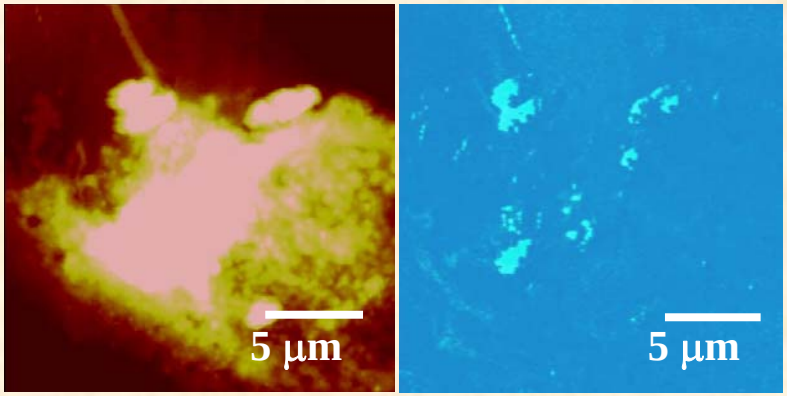


Collaboration with A. Balandin (UCR)

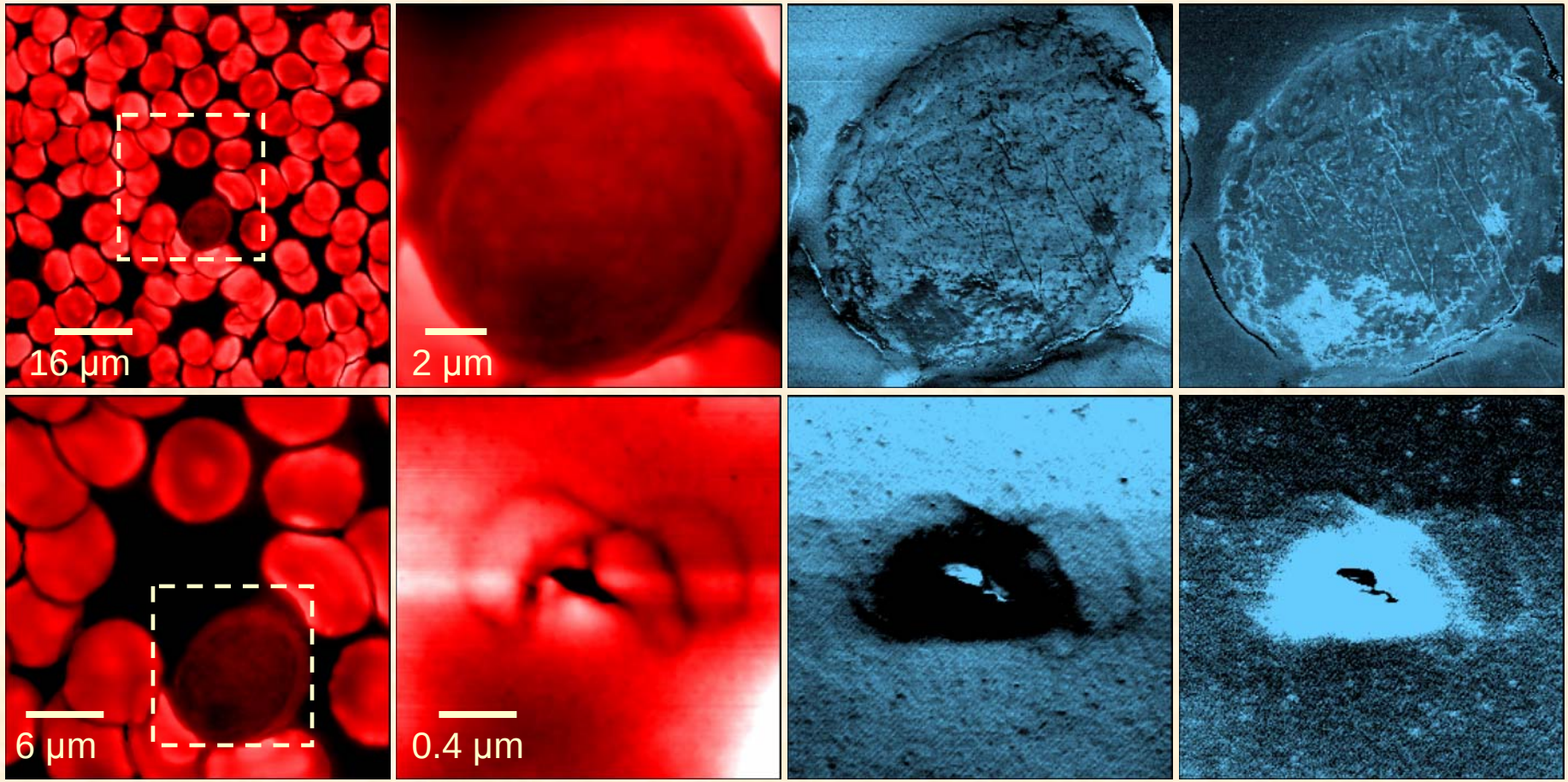
Electromechanical coupling in viruses is presumably flexoelectric due to symmetry limitations

Electrical modification of TMV

Cellular imaging (mouse lung cell):

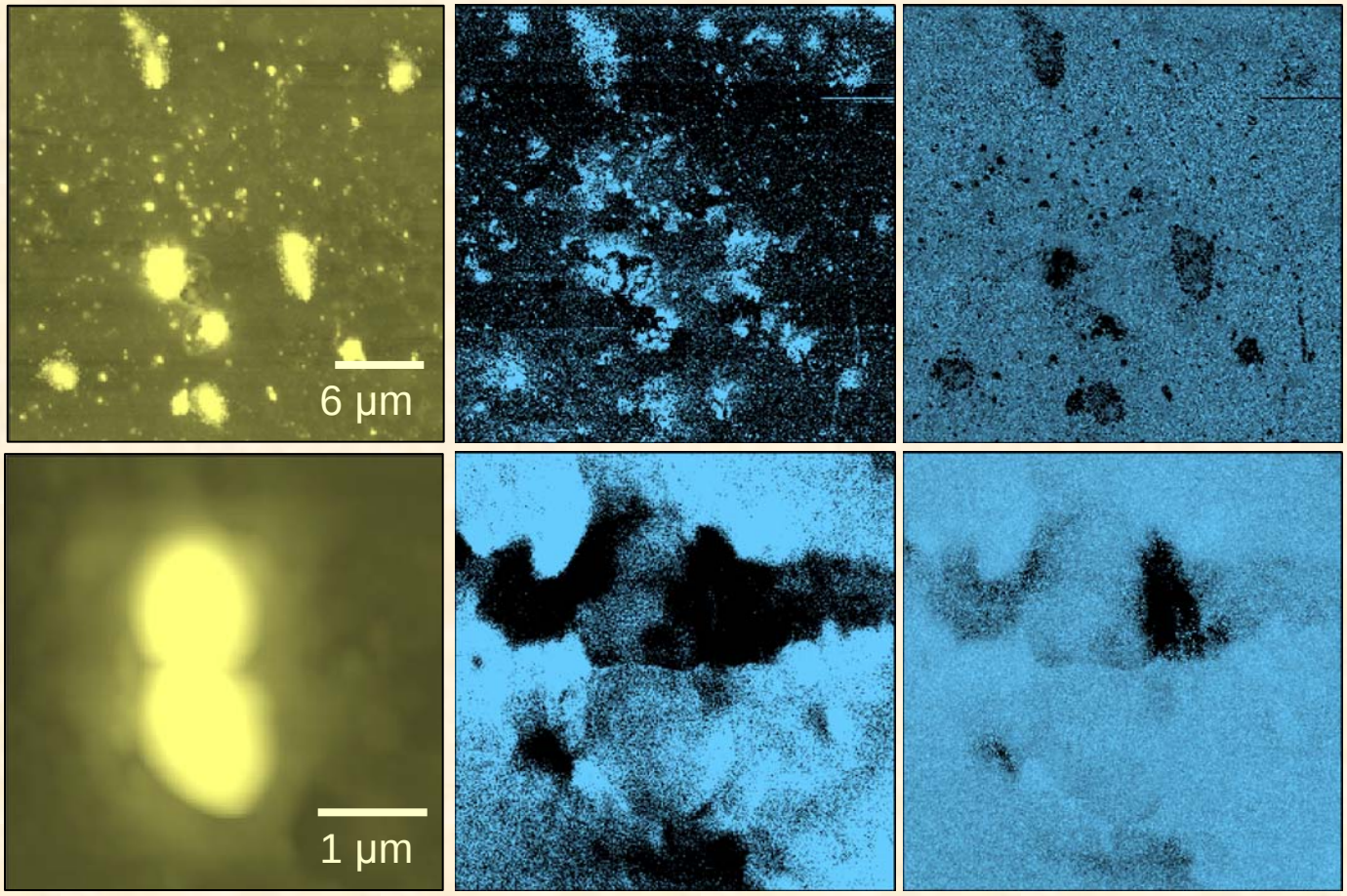


Towards Cell Imaging



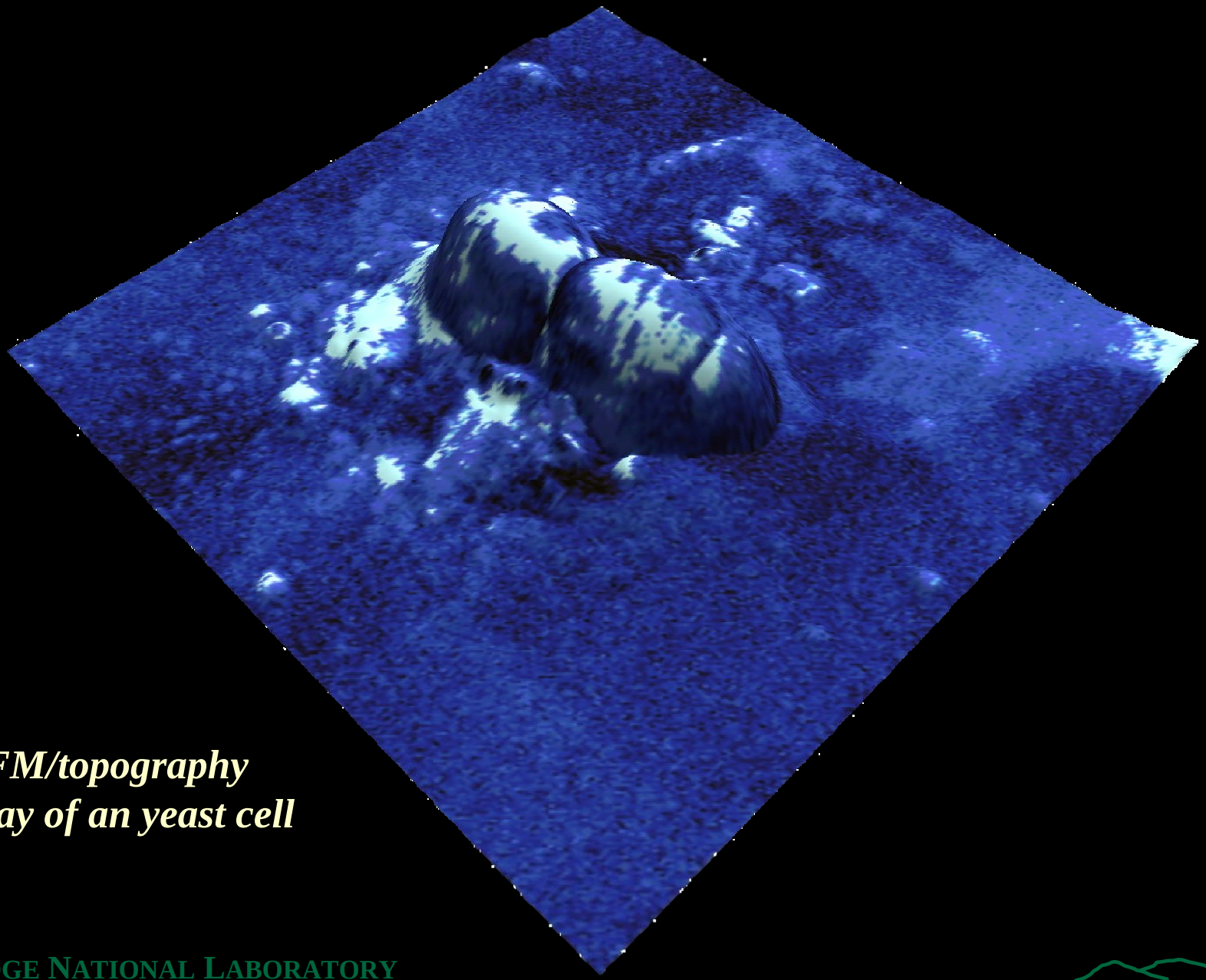
PFM of cells in ambient usually shows additional details of structure, beyond topographic contrast

Yeast in Action



PFM of cells in ambient usually shows additional details of structure, beyond topographic contrast

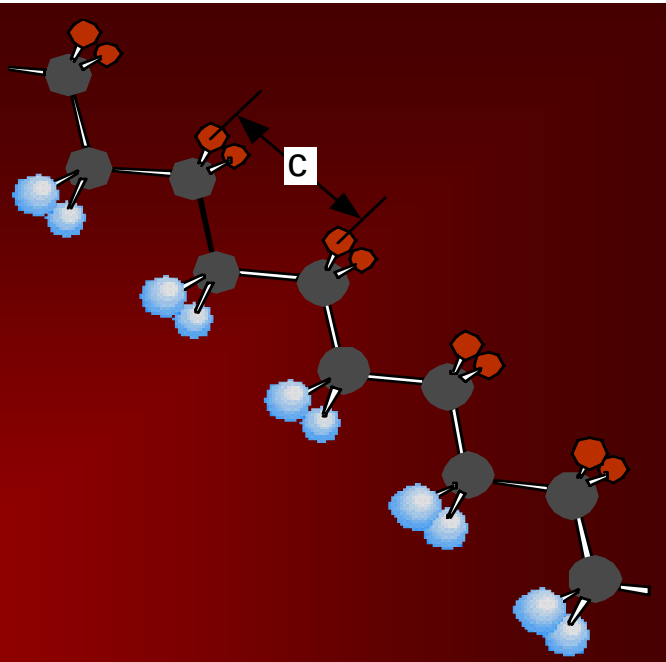
Fig. 7.



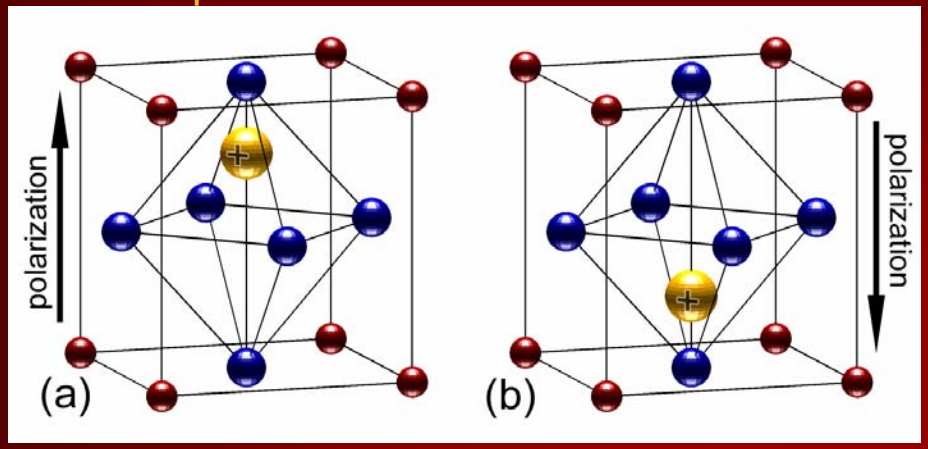
PFM/topography overlay of an yeast cell

OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

Motivation: Why PVDF?



Stable polarization states of traditional FE



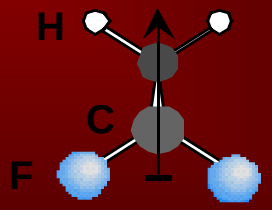
Inorganic FE: Subject to lattice phenomena

Which lead to imperfect behavior:

- interface phenomena
- chemical compatibility
- size effect

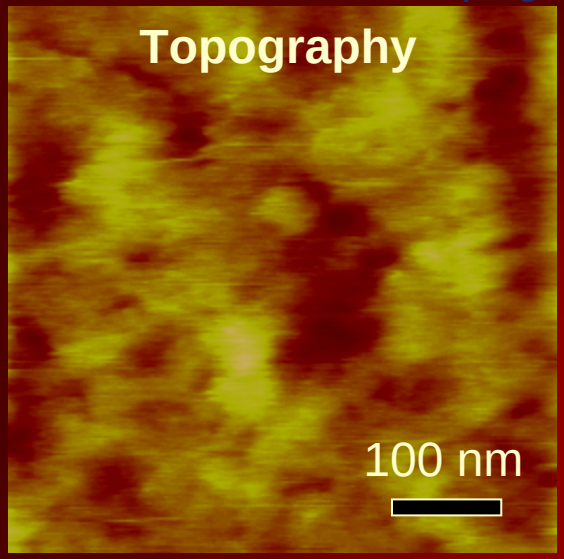
PVDF is a polymer that has polar bonds, is piezoelectric, pyroelectric and ferroelectric on the *molecular* scale

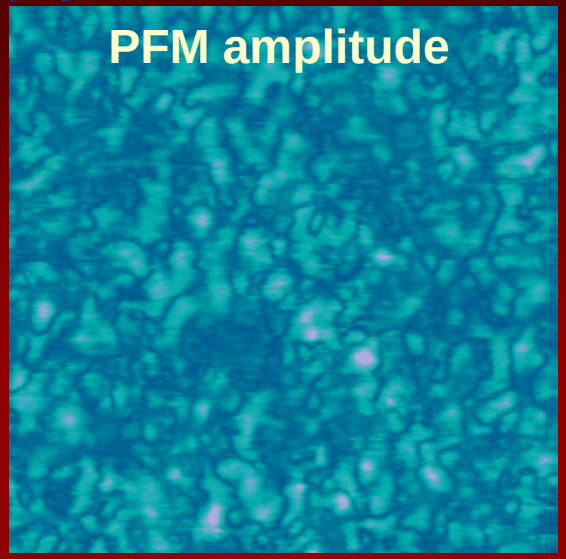
net dipole moment

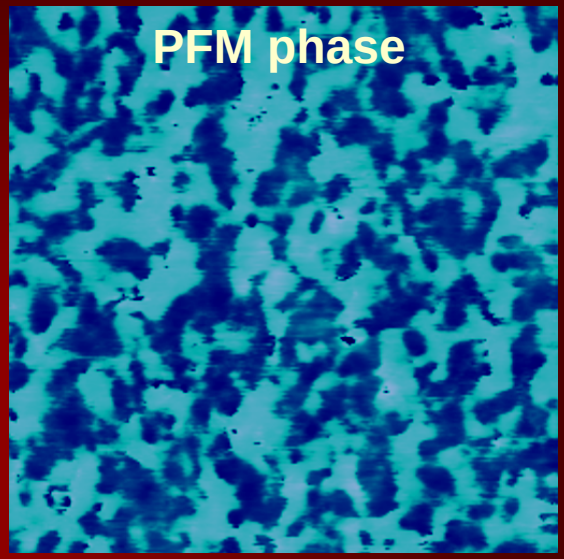


Imaging and Domain Structure

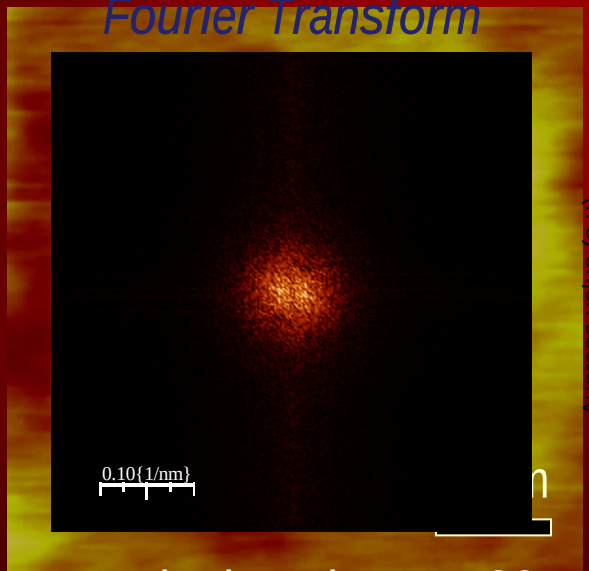
Topography *PFM Phase*



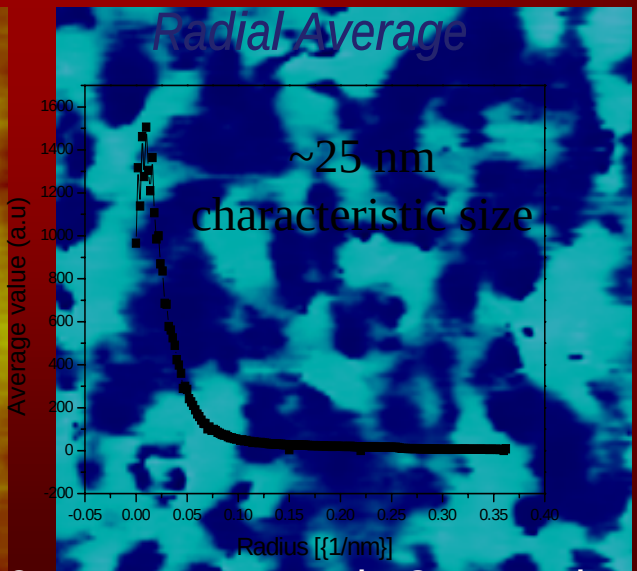




Fourier Transform



Radial Average

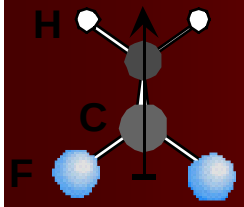


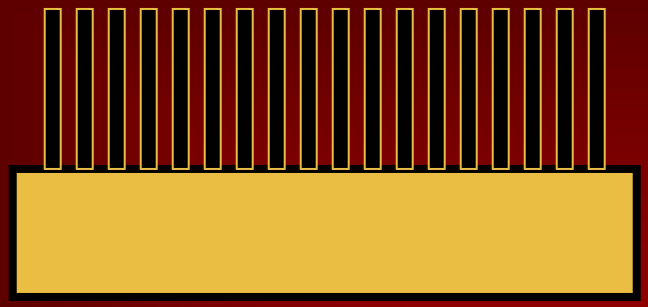
Annealed film reveal domain structure, random polarization, no topography

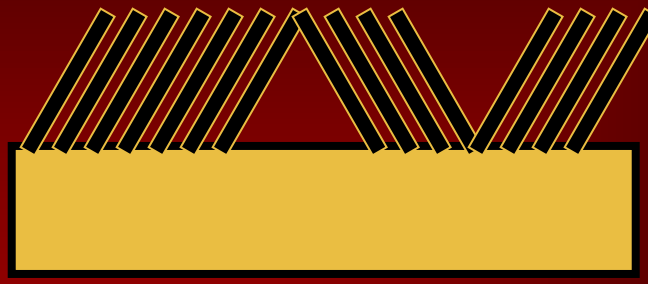
Image analysis reveals domains are 20-40 nm. FFT reveals 25 nm characteristic size

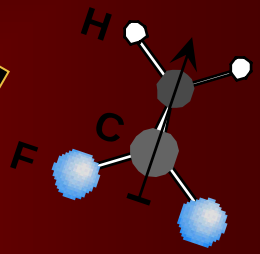
Domain Structure - Lateral PFM of PVDF

How are polymer chains aligned?



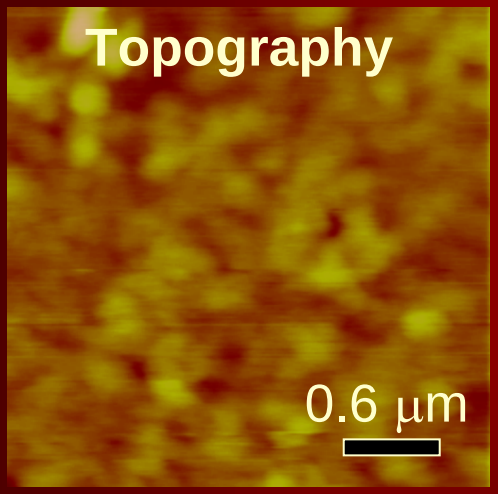


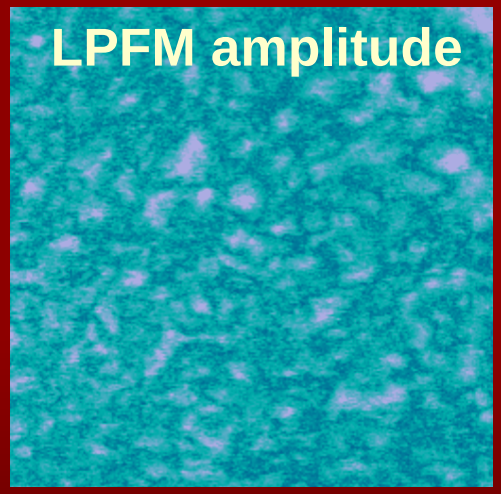


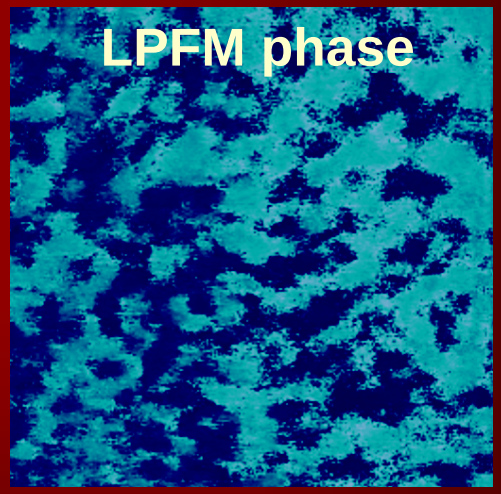


vertical alignment

lateral component





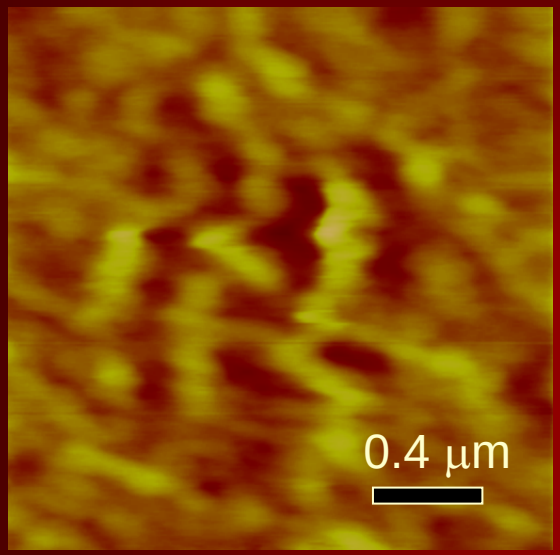


There is a lateral component to the PFM signal which implies that there is some angle between the polar axis of the polymer with respect to the substrate. The possible origins include:

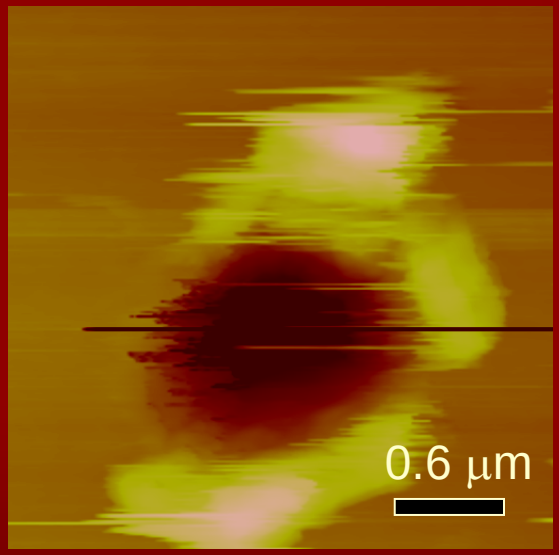
- tip-induced damage and subsequent molecular rotation
- intrinsic molecular orientation

Modification

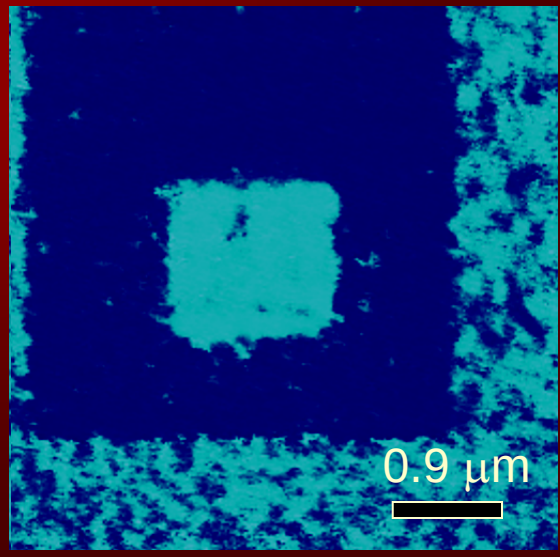
Alignment



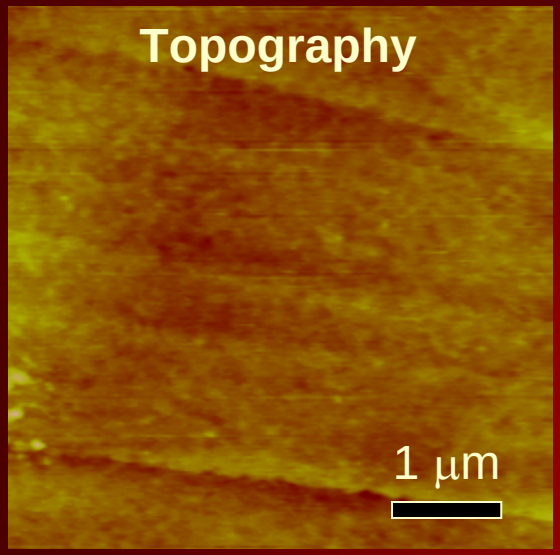
Breakdown

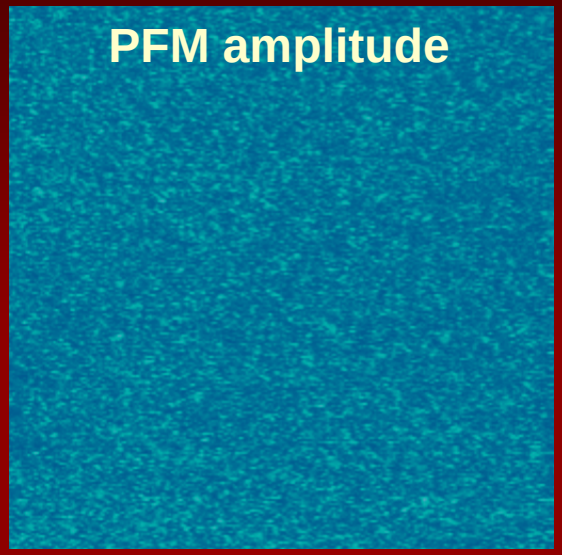


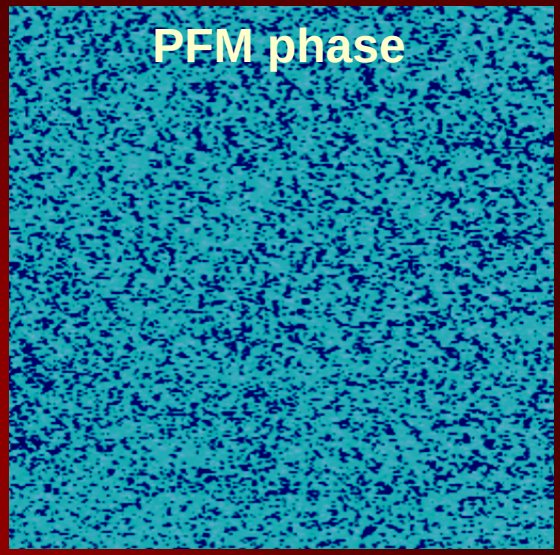
Patterning

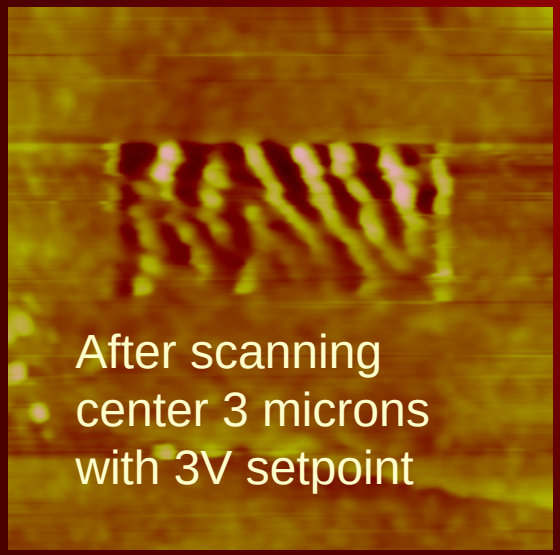


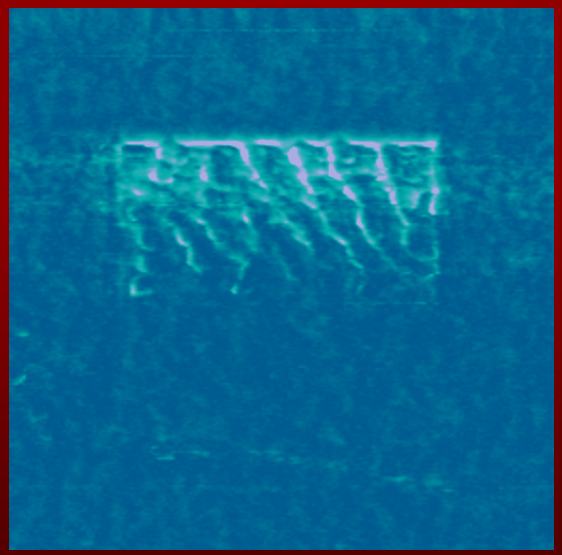
Effect of Mechanical Modification

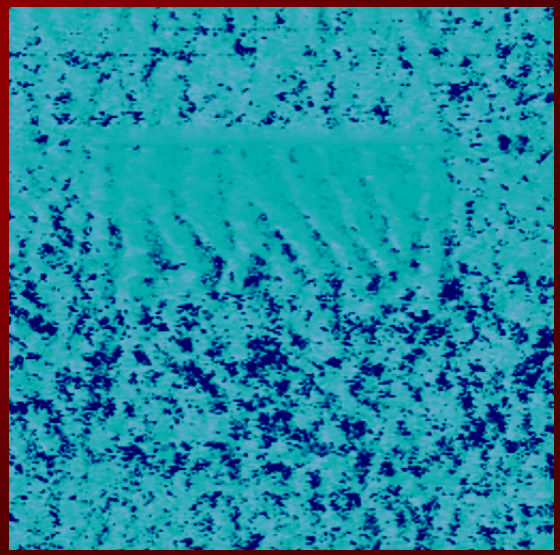






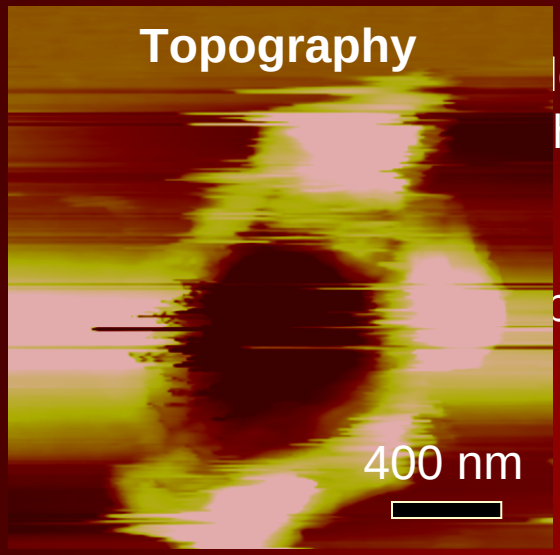


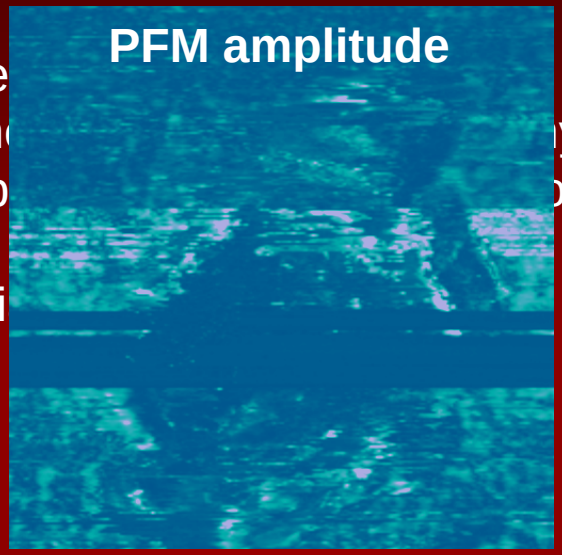


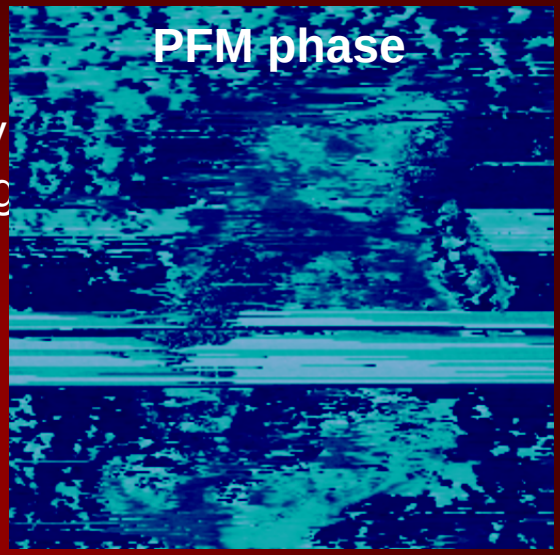


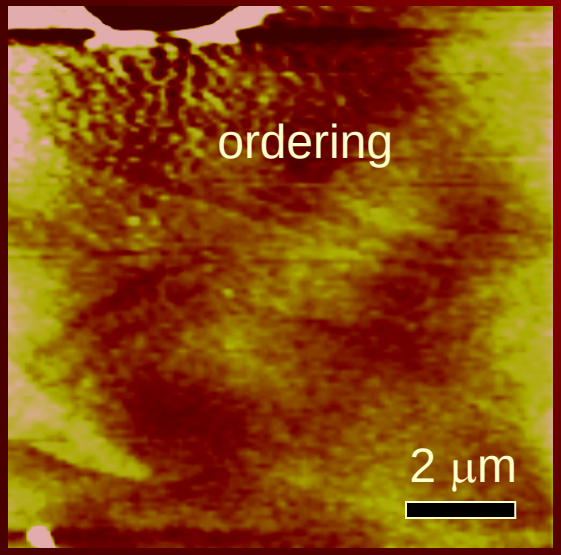
Continuous scanning with large indentation forces results in ordering of the film that can also be observed in PFM amplitude and phase images.

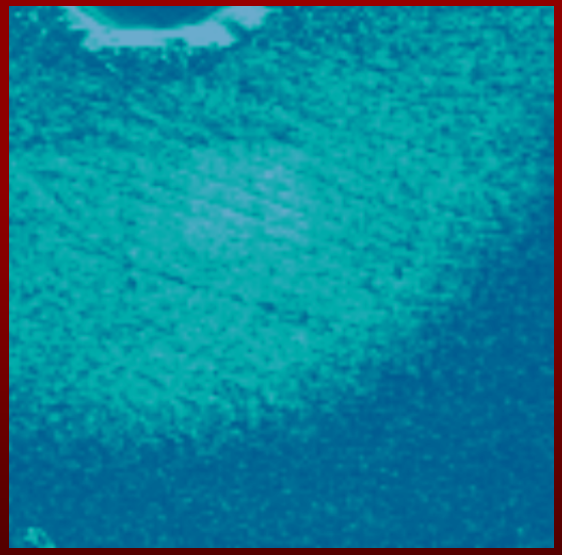
Modification – Breakdown

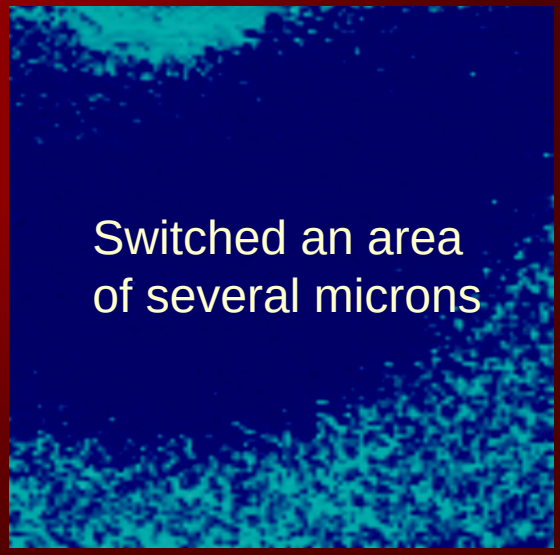






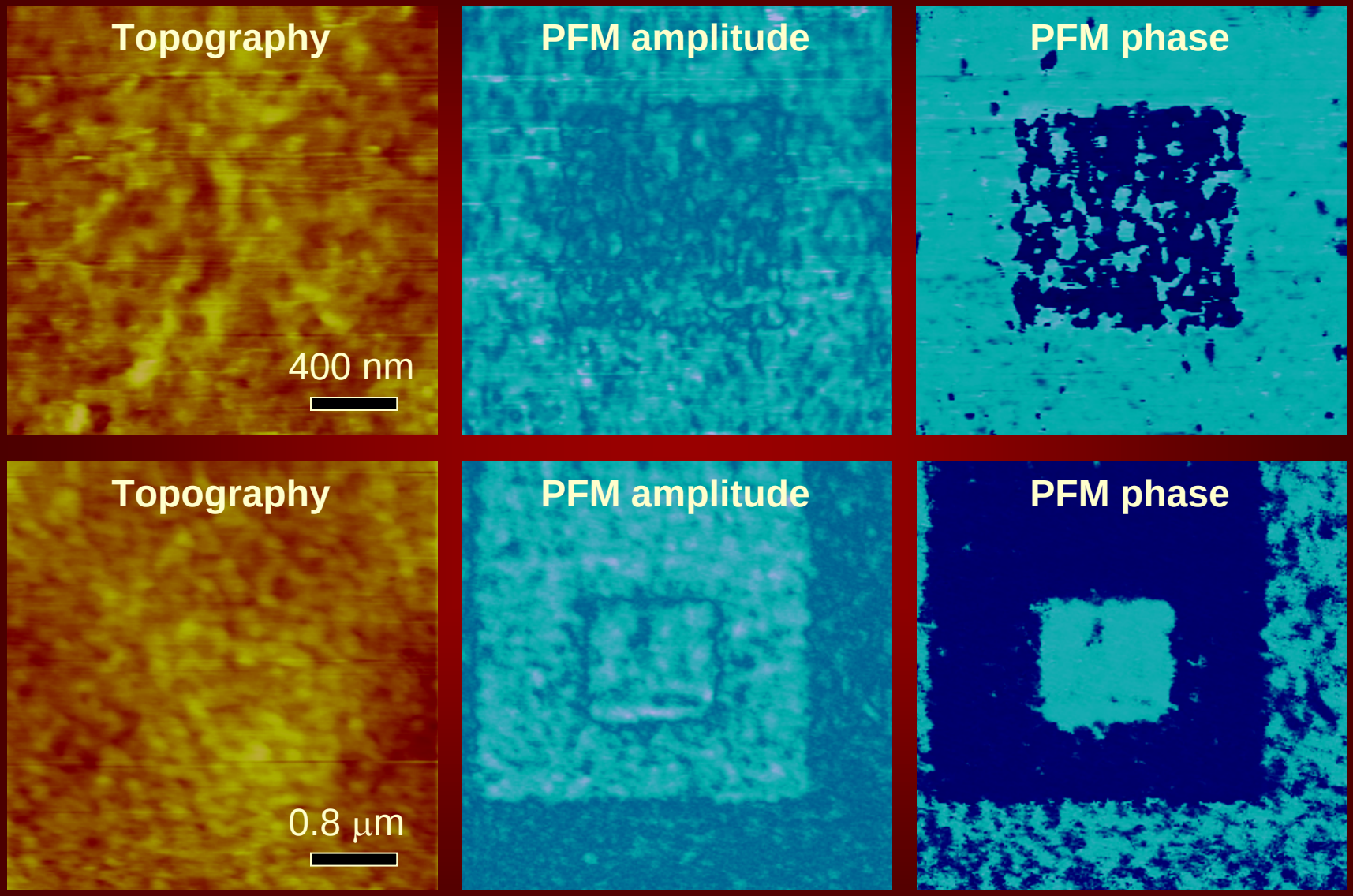






The PVDF film can be affected by dielectric breakdown, associated with partial poling of material over large length scales and local ordering. - Examples of what not to do!

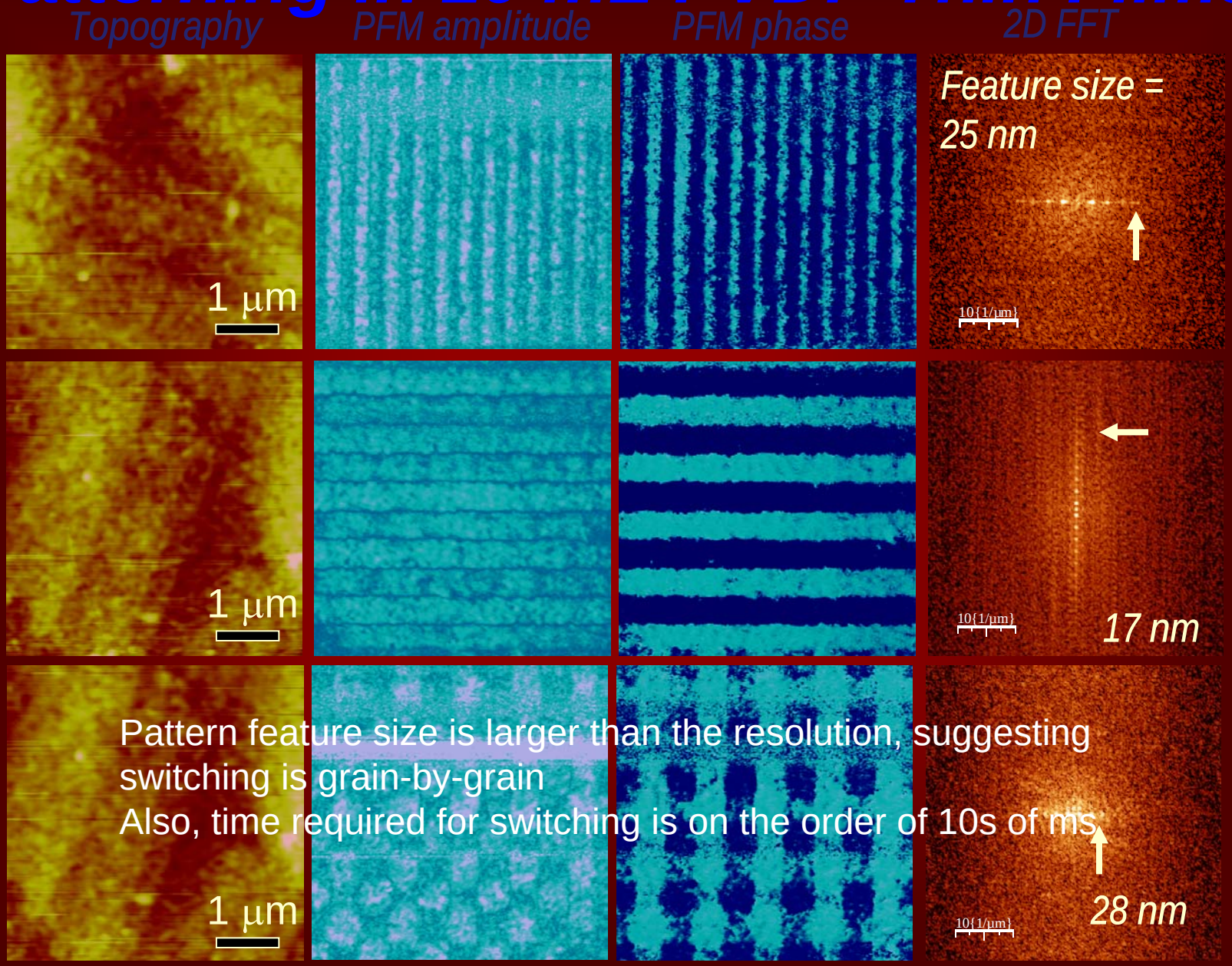
Modification – Switching



Inhomogeneous properties – some regions switch at low bias, others at high.
Also, note the roughness of the domain wall – it has an irregular shape

More complete switching at low bias

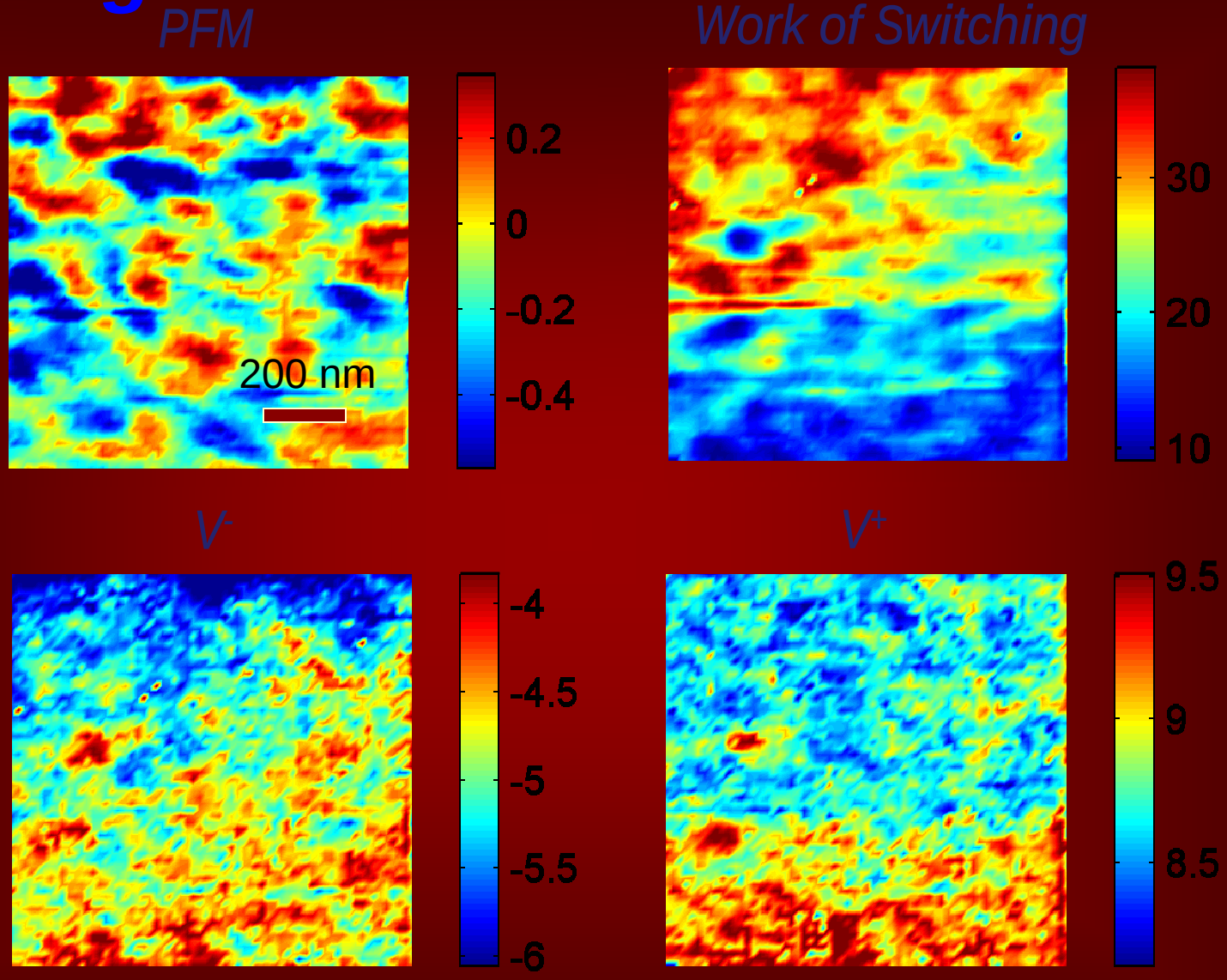
Patterning in 10 mL PVDF Thin Films



Pattern feature size is larger than the resolution, suggesting switching is grain-by-grain

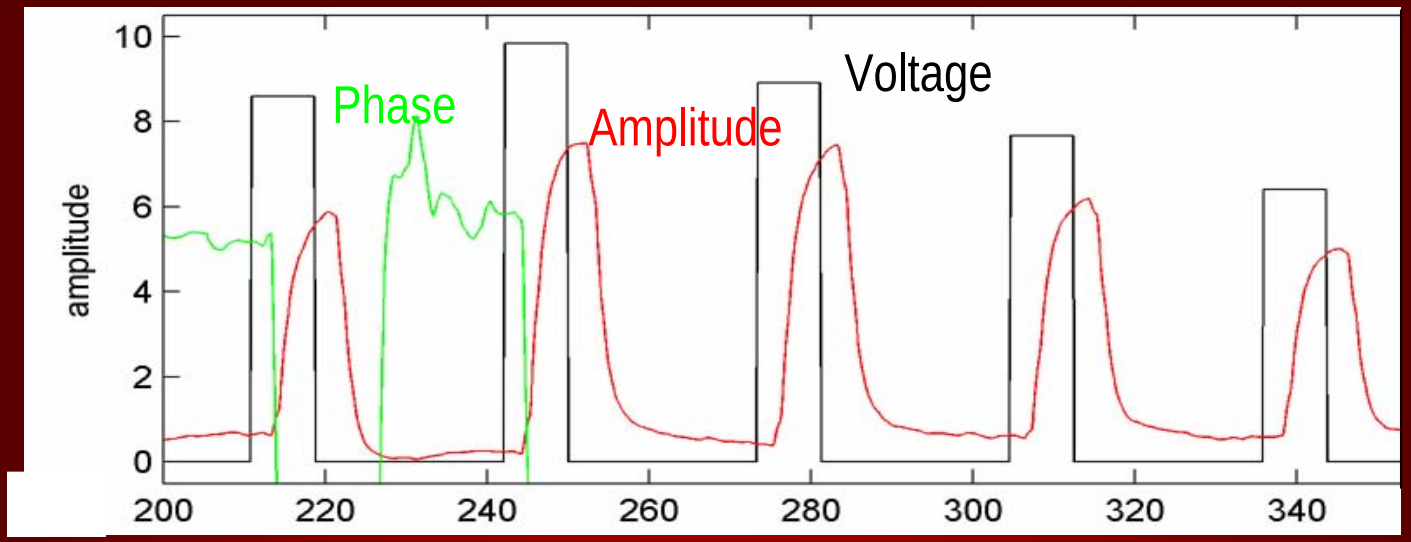
Also, time required for switching is on the order of 10s of ms

Ongoing: SS-PFM of PVDF Thin Films

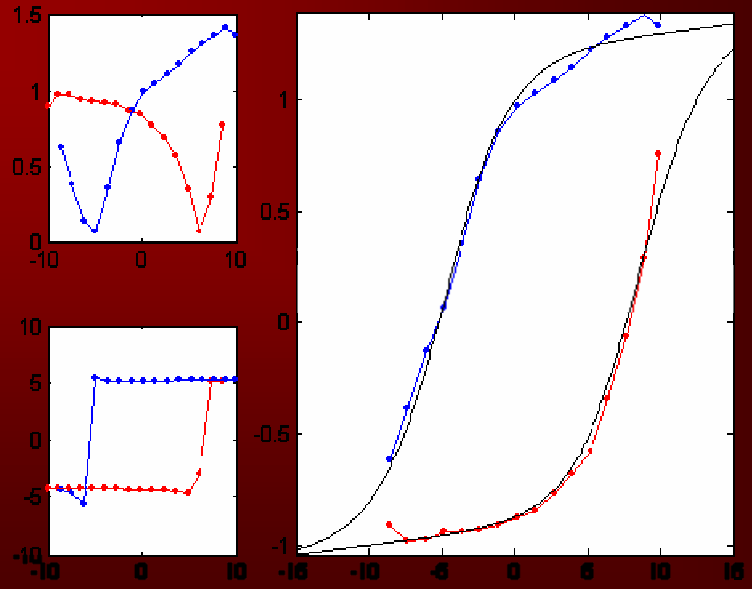


SS-PFM images of a 10 mL thick (18 nm) LB thin film of copolymer P(VDF-TrFE 70:30)
Variations of work of switching and imprint biases throughout the film are observed

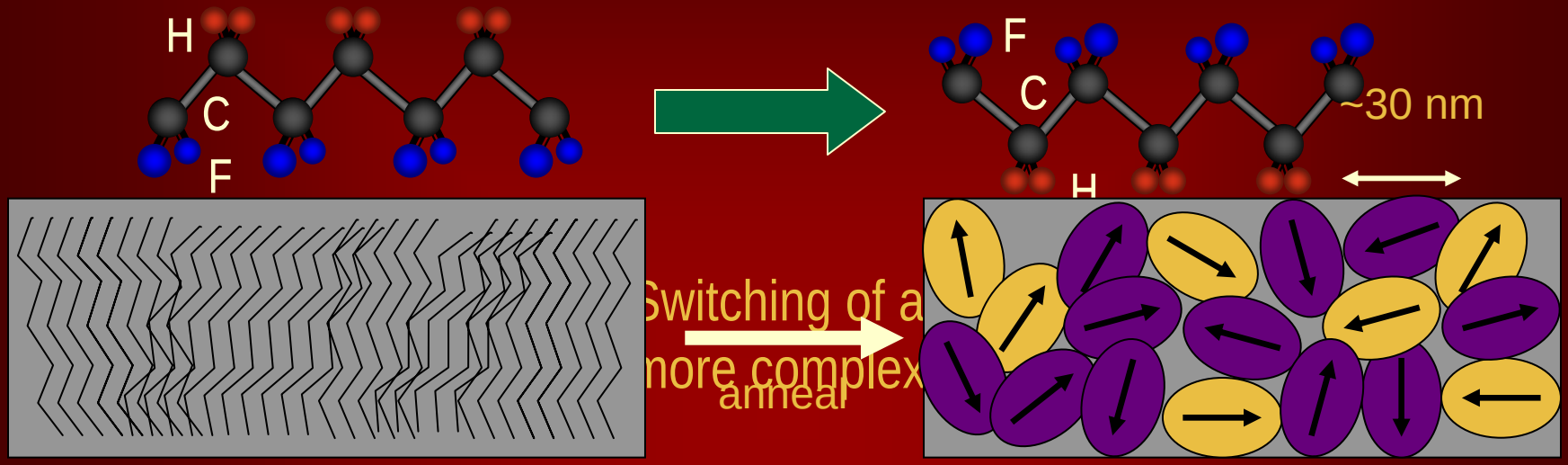
Ongoing Work - Relaxation Dynamics



The piezoresponse amplitude (red) to the applied bias is delayed. Additionally, once the bias is removed, the response appears to relax to a stable state. This behavior has not been observed on other ferroelectric ceramics, thin films, or nanoparticles.



Switching Dynamics



boundaries of switched areas are irregular and repeat the grain-pattern of the film

switching in the films occurs on a grain-by-grain basis

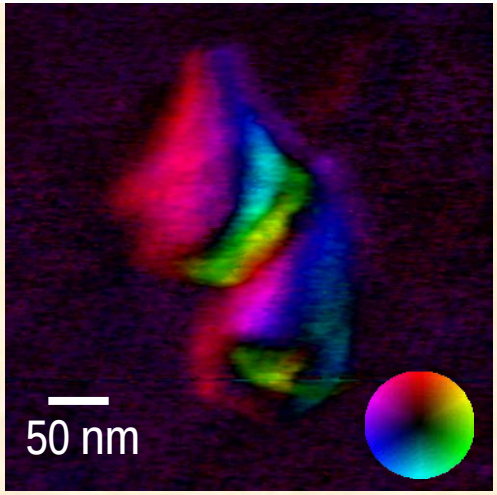
Interesting to see what happens when you try to switch a grain
Is there a difference between switching the center? The edge?
What is going on and can we see it?

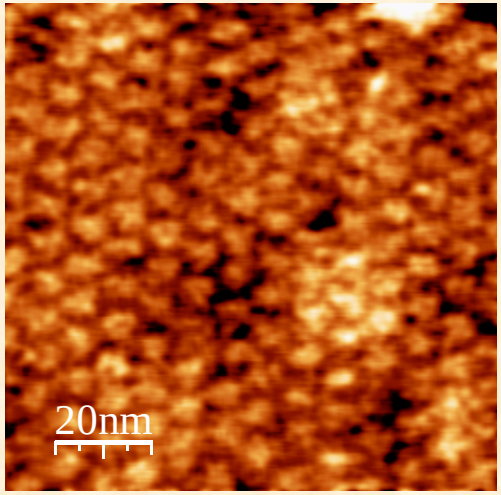
the switching was observed to be relatively slow and only prolonged applications of dc bias to the tip (> 1-100 ms) yield switched ferroelectric domains.

We attribute the observed behavior to the molecular nature of PVDF, in which a single dipole can not be rotated without changing the macromolecular conformation.

Motivation: from Ambient to Liquid

- Does the nanometer scale bring new aspects to ferroelectric behavior and can we see it?
- Can the electromechanical response of a single molecule be probed?
- Can electromechanical response of biosystems be imaged in a physiological environment?

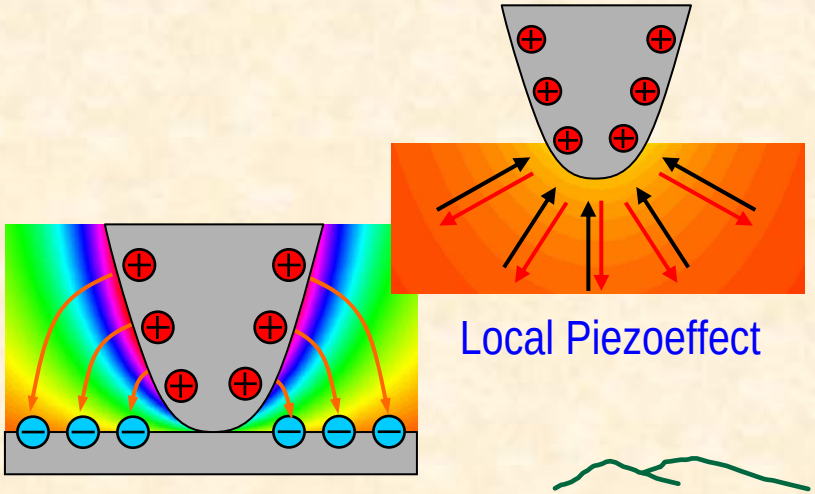




We need improved resolution and sensitivity for nanoferroelectrics, novel electromechanical phenomena, soft materials and biosystems

PFM Limitations: Contact Mode technique

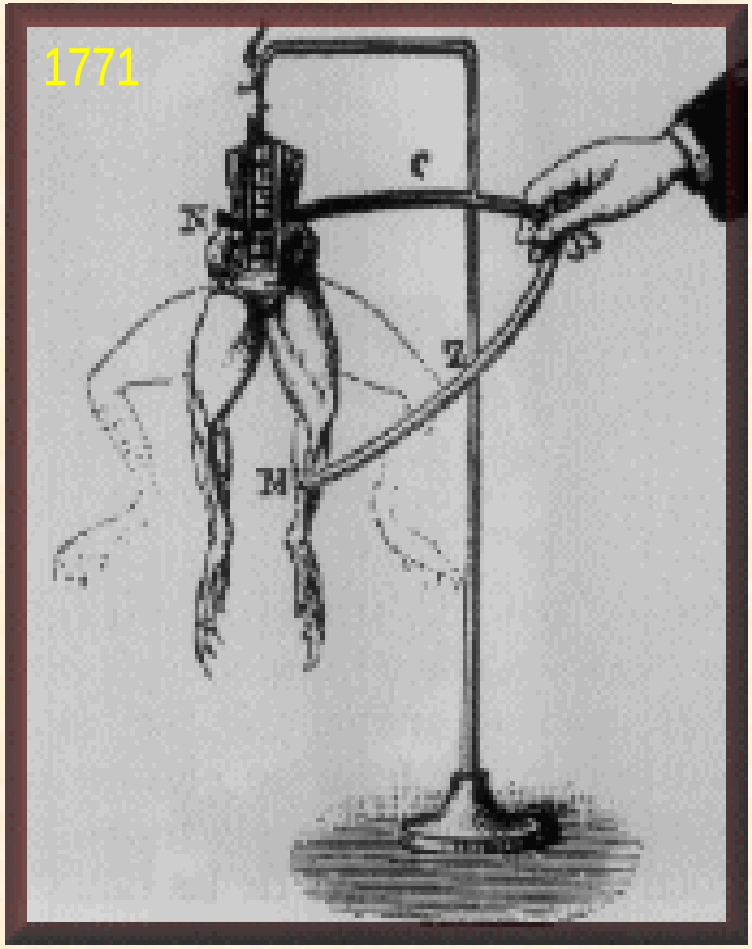
- Electrostatic tip-surface interactions
- Formation of liquid necks at the tip-surface junction
- Large contact force – large contact area



Local Piezoeffect

Local Electrostatic Force

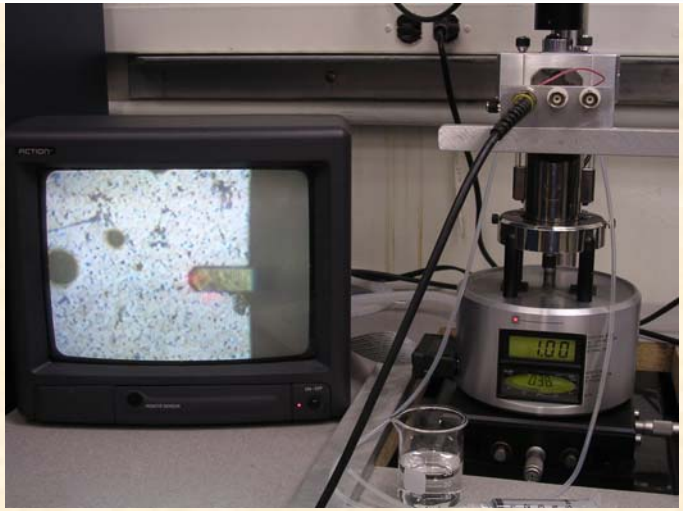
Electromechanics and the Origins of Physics



Electromechanics in biology: outer hair cell stereocilia, ion channels, electromotors, etc…

- Can we image electromechanics on a cellular level?
- Can we image activity in voltage-controlled ion channel?
- Can we image electromechanics on a single molecule level?

Experimental Setup for Liquid PFM



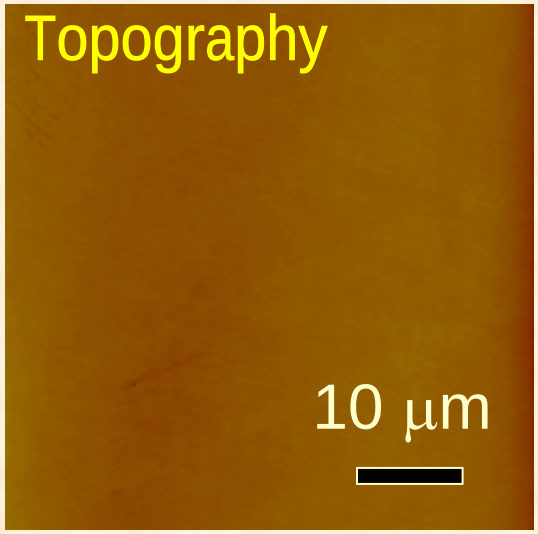
Advantages

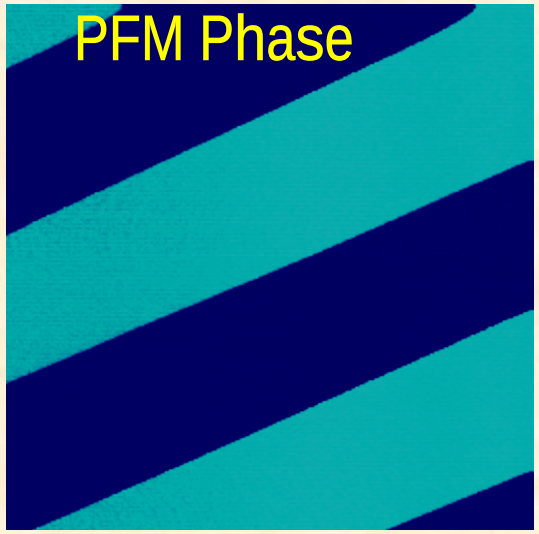
- Sign and magnitude of the Van der Waals interactions can be controlled
- Precise control of tip-surface interactions due to the lack of capillary forces
- Higher dielectric constant of liquid minimizes electrostatic contributions to the signal (force is reduced for $\kappa > 80$, force is repulsive for $\kappa < 80$)

Disadvantages

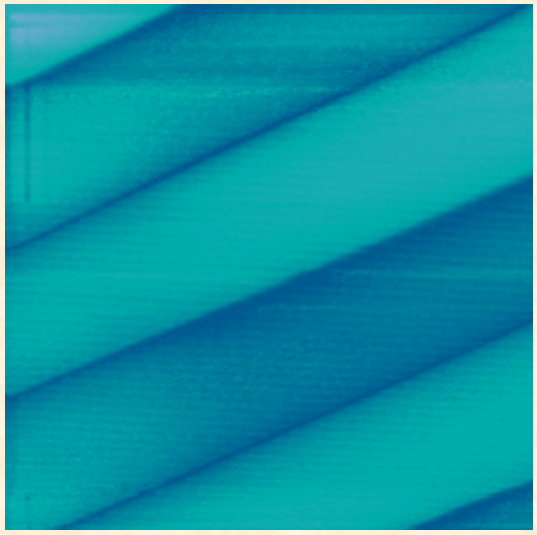
- Liquids are not a natural environment for ferroelectric materials
- Conductivity can result in stray currents and potential drops
- Viscous and added mass damping of the cantilever motion
- Formation of electric double layers and other surface effects such as hydrophobic interactions can complicate or preclude imaging

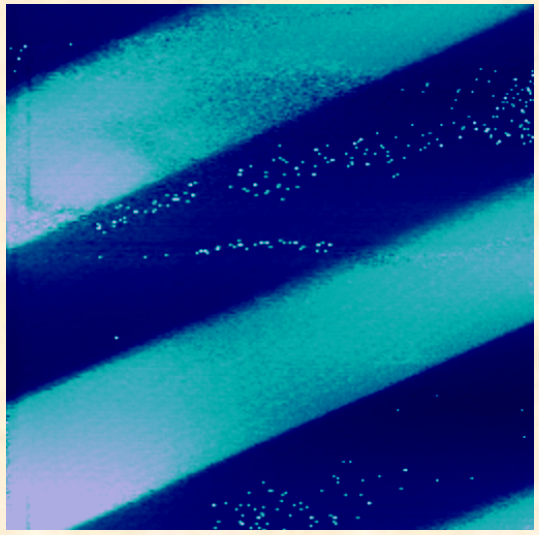
First Attempts - PPLN





5V 200kHz **ambient**

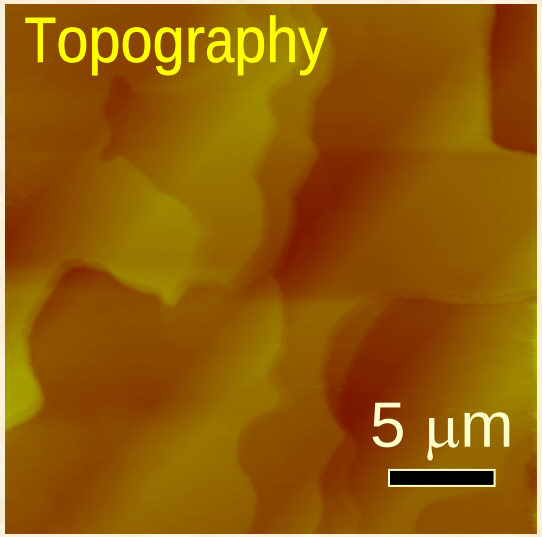


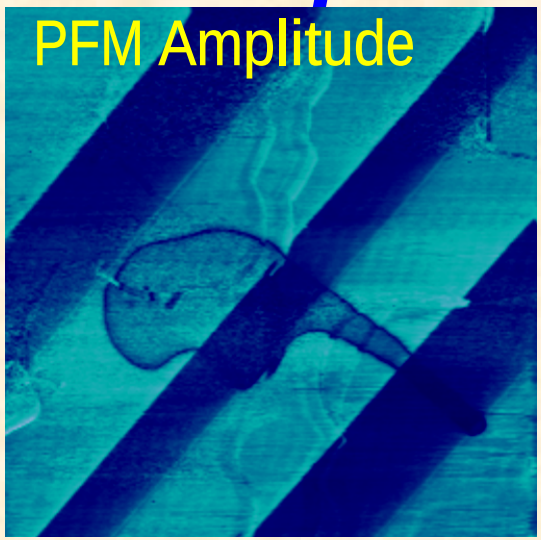


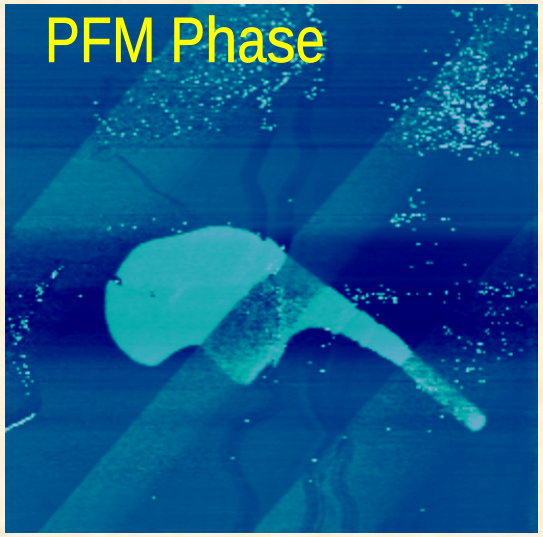
10V 790kHz **water**

Promising initial result:
Contrast associated with domains

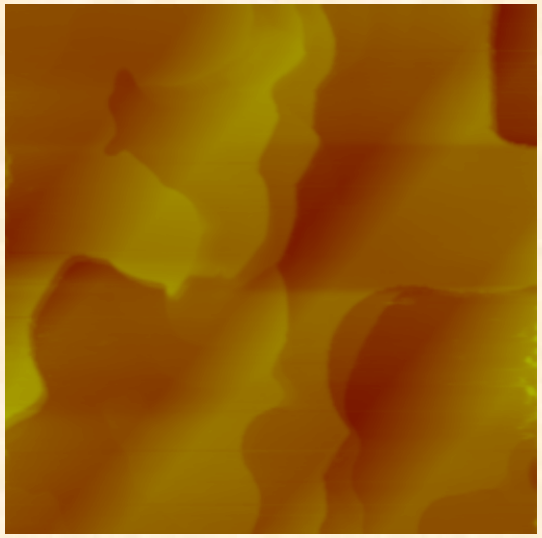
First Attempts - BTO

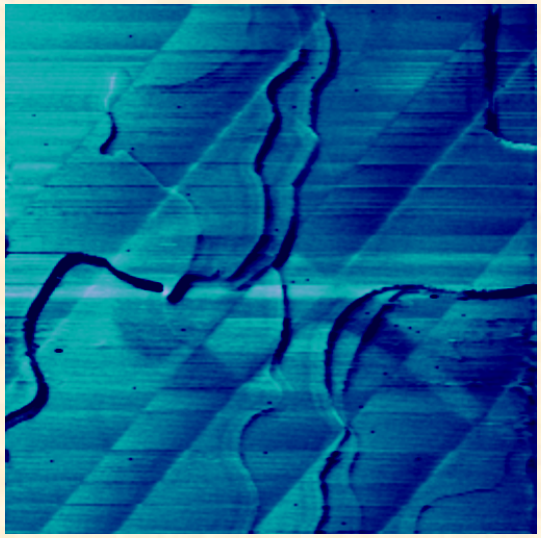


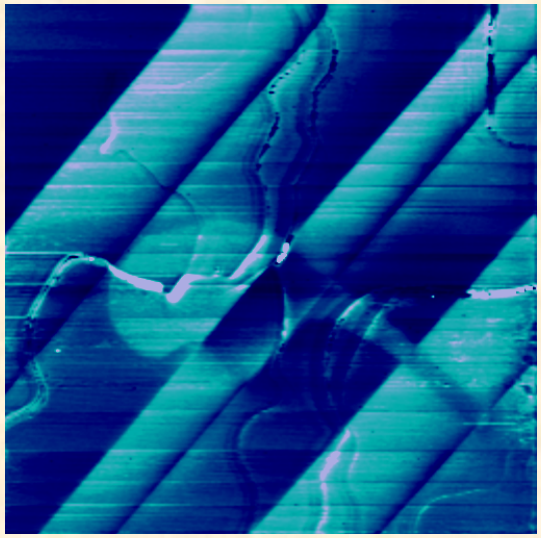




10V 630kHz **ambient**



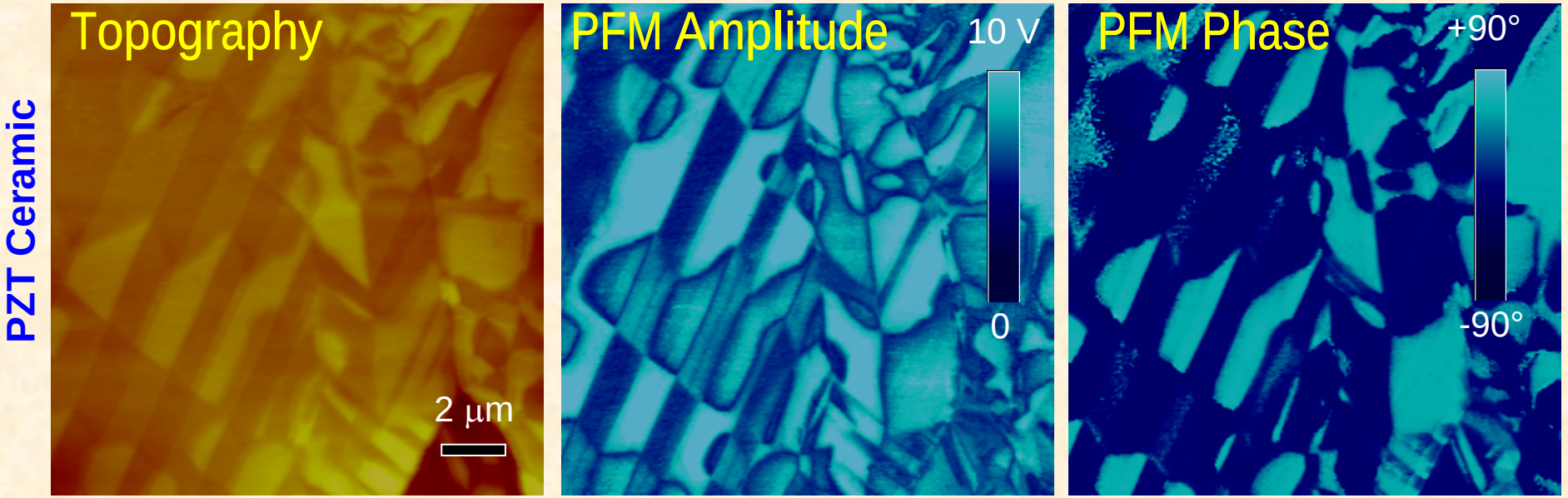




10V 1.8MHz **water**

Domain contrast and topo. cross-talk

PFM in Liquid - PZT



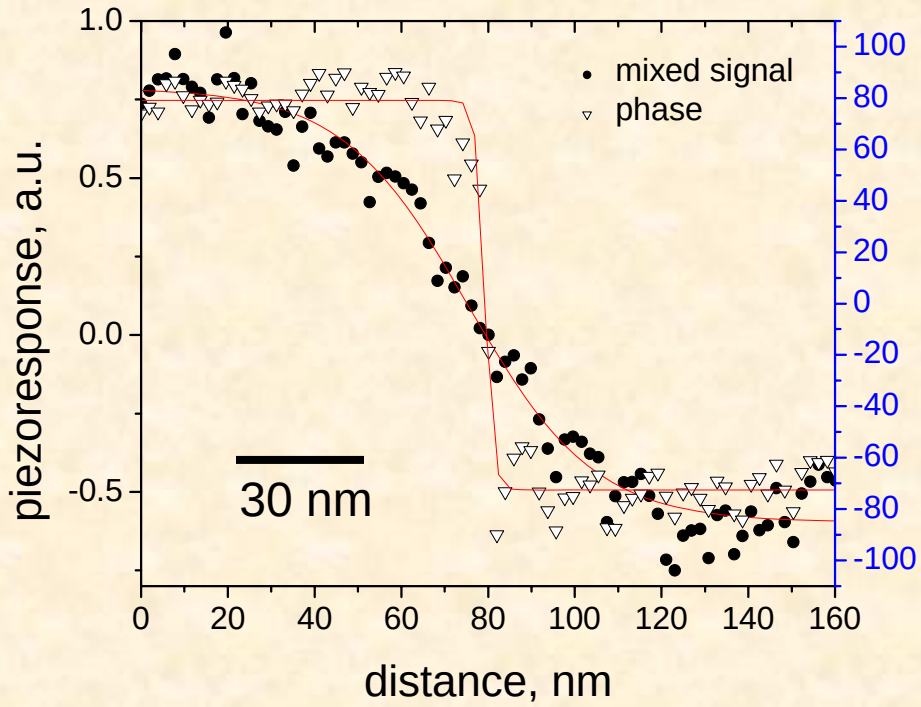
Liquid PFM imaging of PZT shows high-quality contrast.

Interestingly, some of the domain walls in liquid demonstrate extremely small widths

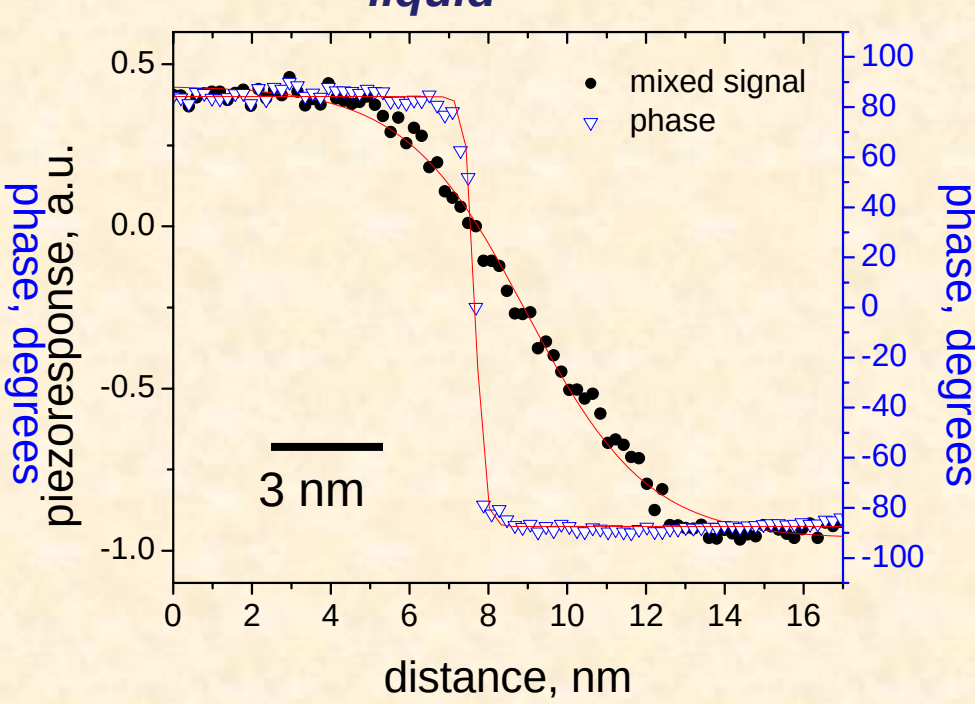
Sample from C. Watson, Sandia National Laboratory

Resolution: Ambient vs. Liquid

ambient



liquid



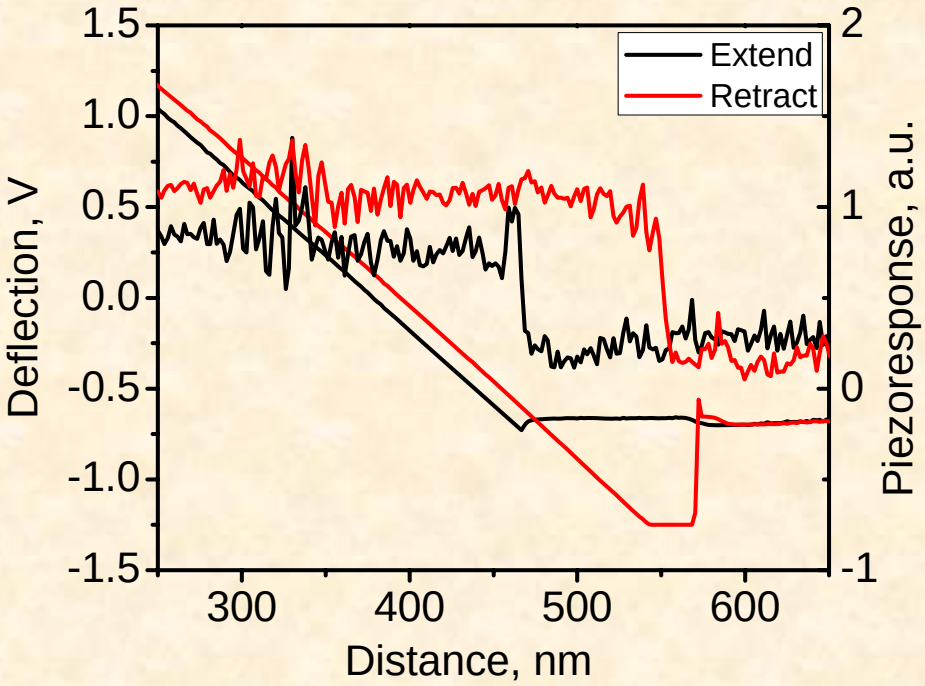
3 nm for the amplitude signal and 0.2 nm for phase, as compared to ~30 nm and 3 nm, respectively, typically observed in ambient!

Why does it work?

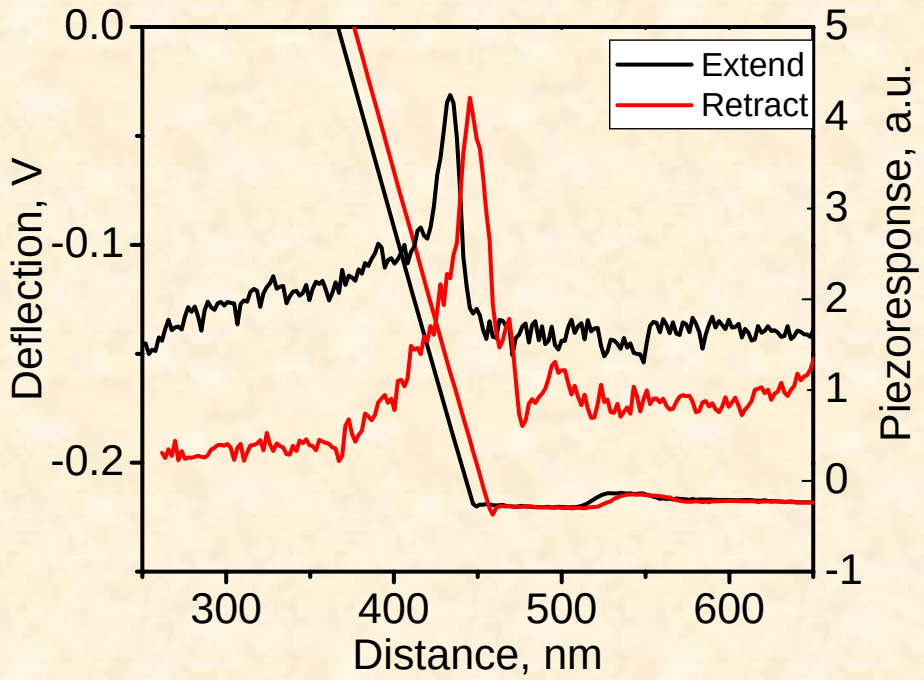
- The absence of long-range electrostatic forces due to screening by mobile ions in liquid
- The absence of capillary interactions.

Force-Distance Curves

Ambient



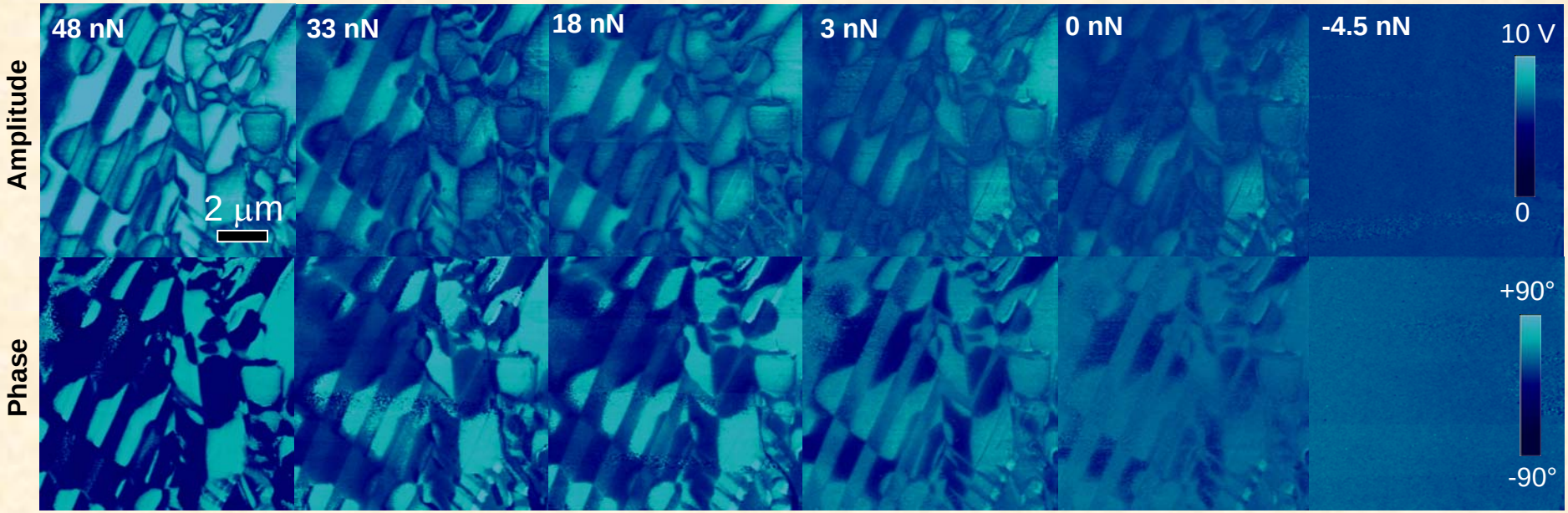
Liquid



There is no capillary hysteresis in liquid.

- In air, hysteresis of ~100 nm is observed, corresponding to 30 nN of capillary forces.
- This corresponds to ~3 nm contact area even under optimal conditions.
- The resolution is further reduced by liquid bridge formation.

Effect of Loading Force



A series of PFM amplitude (top) and phase (bottom) images obtained at different loading forces.

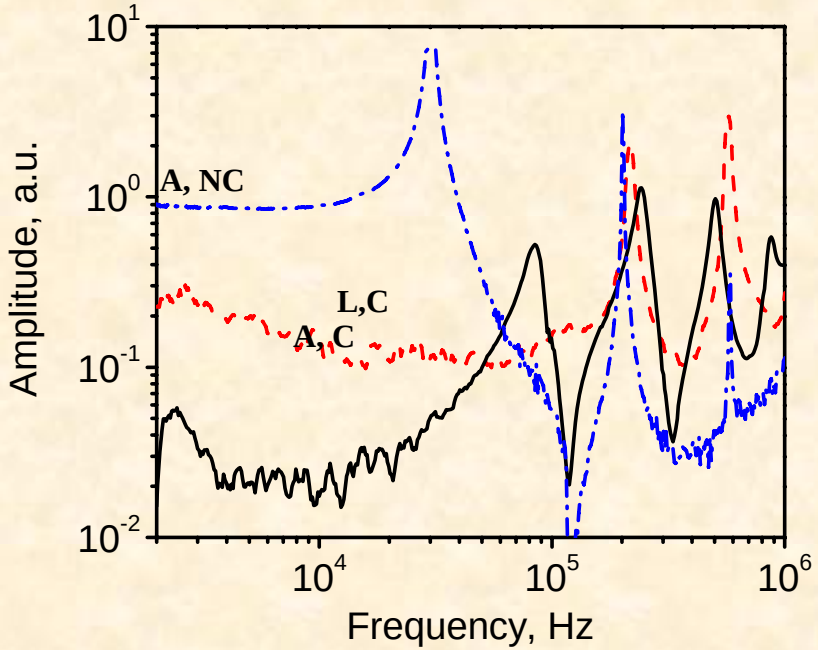
The contrast disappears above the surface

In ambient – contrast remains (EFM & SKPM)

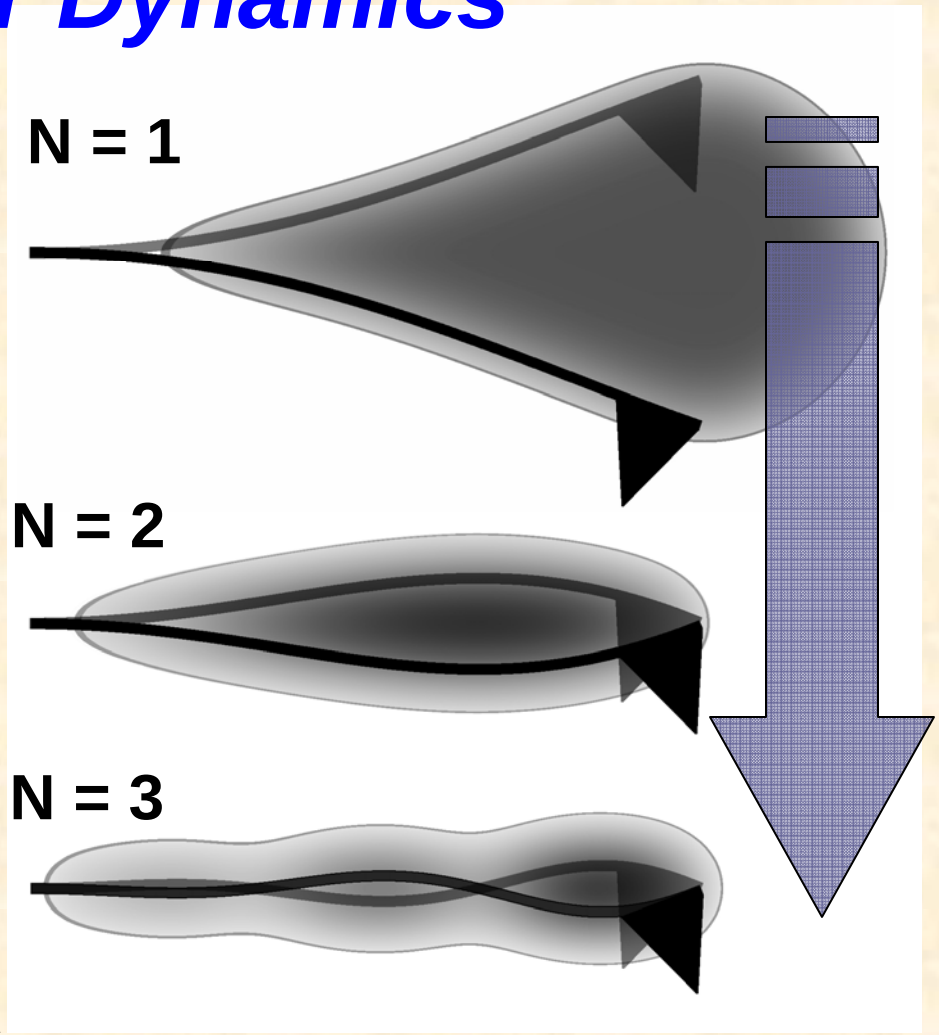
Cantilever Dynamics

PFM signal amplitude-frequency curves in ambient contact and non-contact regimes and in liquid.

Ambient vs. liquid



Note that response at resonances is comparable to ambient.



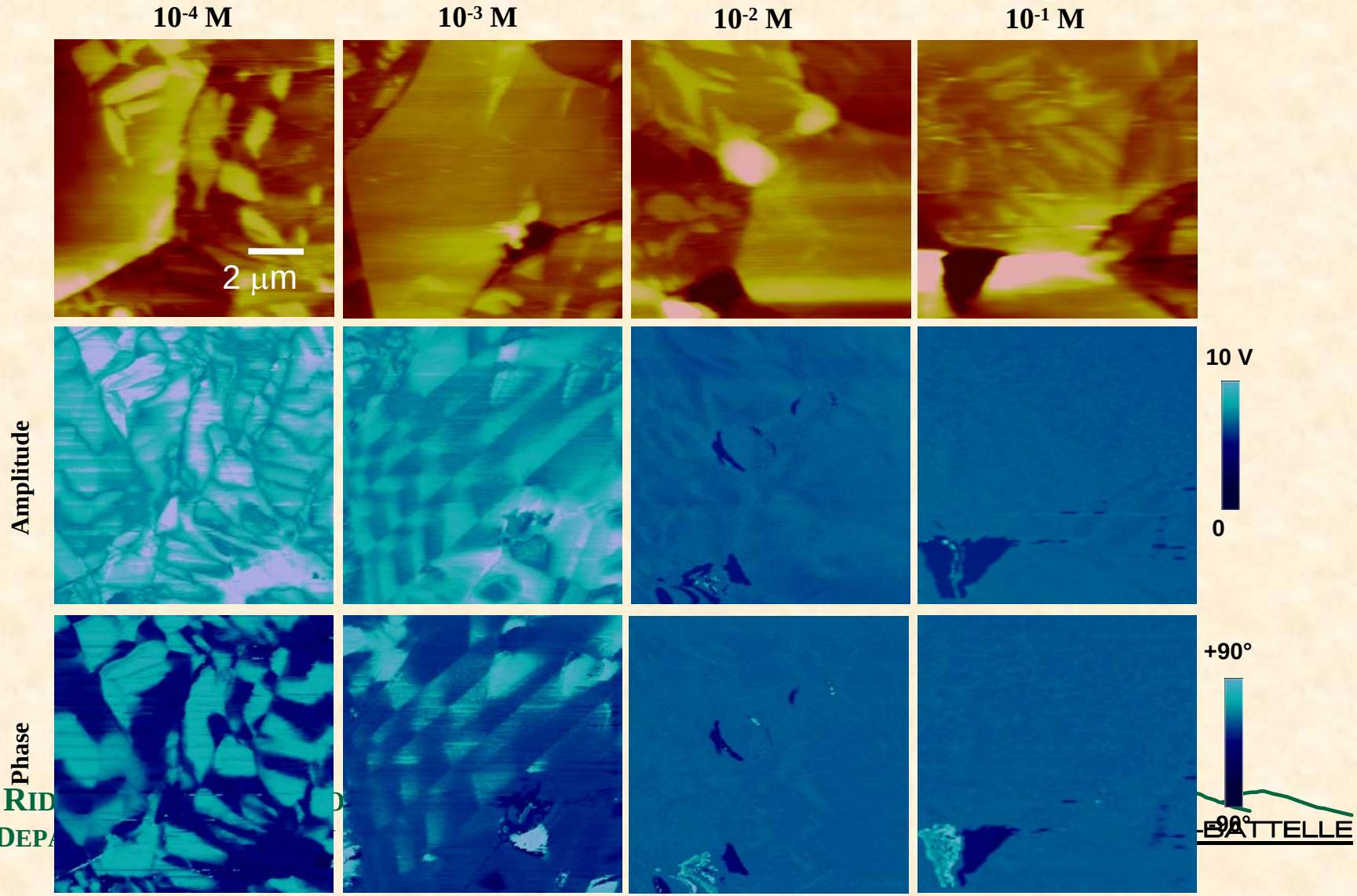
Excited volume is reduced at higher modes

Viscous damping and added mass effects on cantilever dynamics are reduced at high frequencies

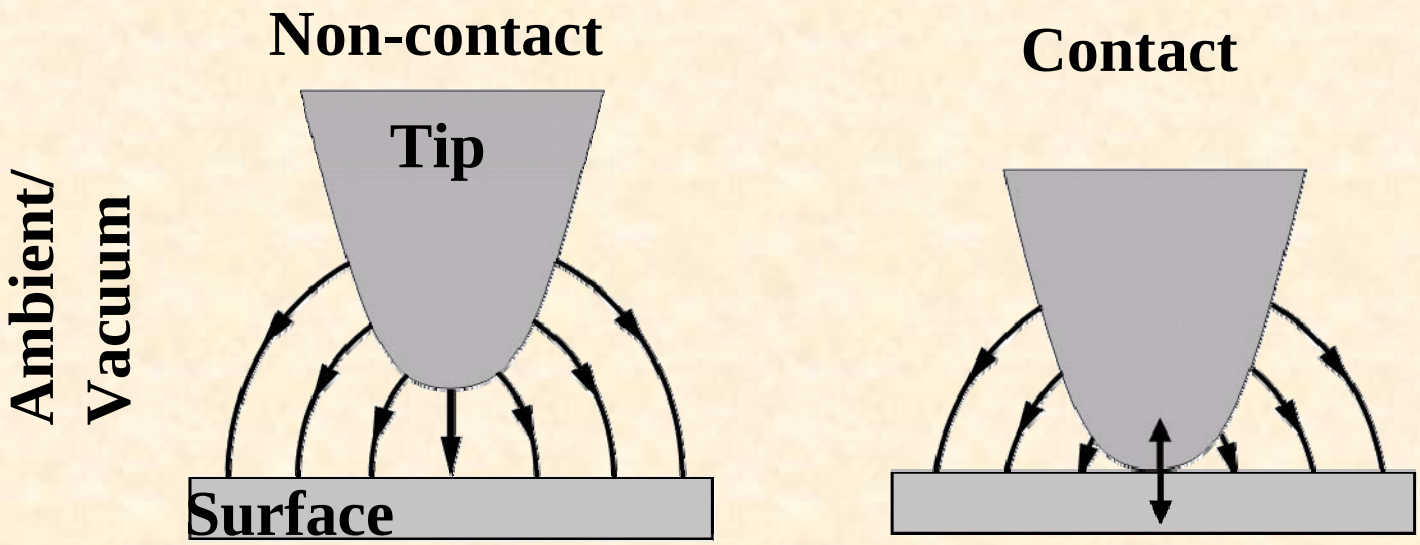
Effect of Salt Concentration

Concentration dependence of PFM images in NaCl solutions. The images were taken in different locations on the sample.

The signal disappears for high ionic strength of solution.



Theory: Ambient Model



long range electrostatic force

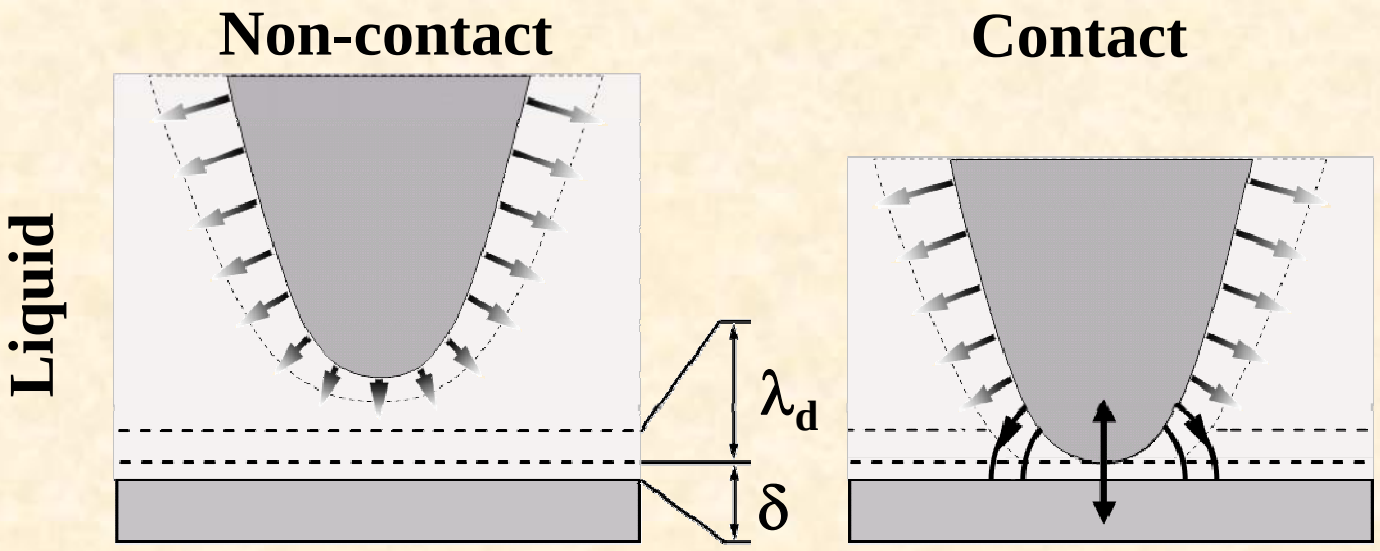
$$PR_{amb} = \alpha_a(h) d_{33} + F_{sphere}/k_1 + F_{cone}/k_1 + PR_{nl}$$

$\alpha_a(h)$ is the ratio of ac tip potential to the ac surface potential of the ferroelectric in ambient (i.e., the potential drop in the tip-surface gap)

k_1 is the spring constant of the tip-surface junction

Both electrostatic and electromechanical interactions are present in ambient

Theory: Liquid Model



short range electrostatic force

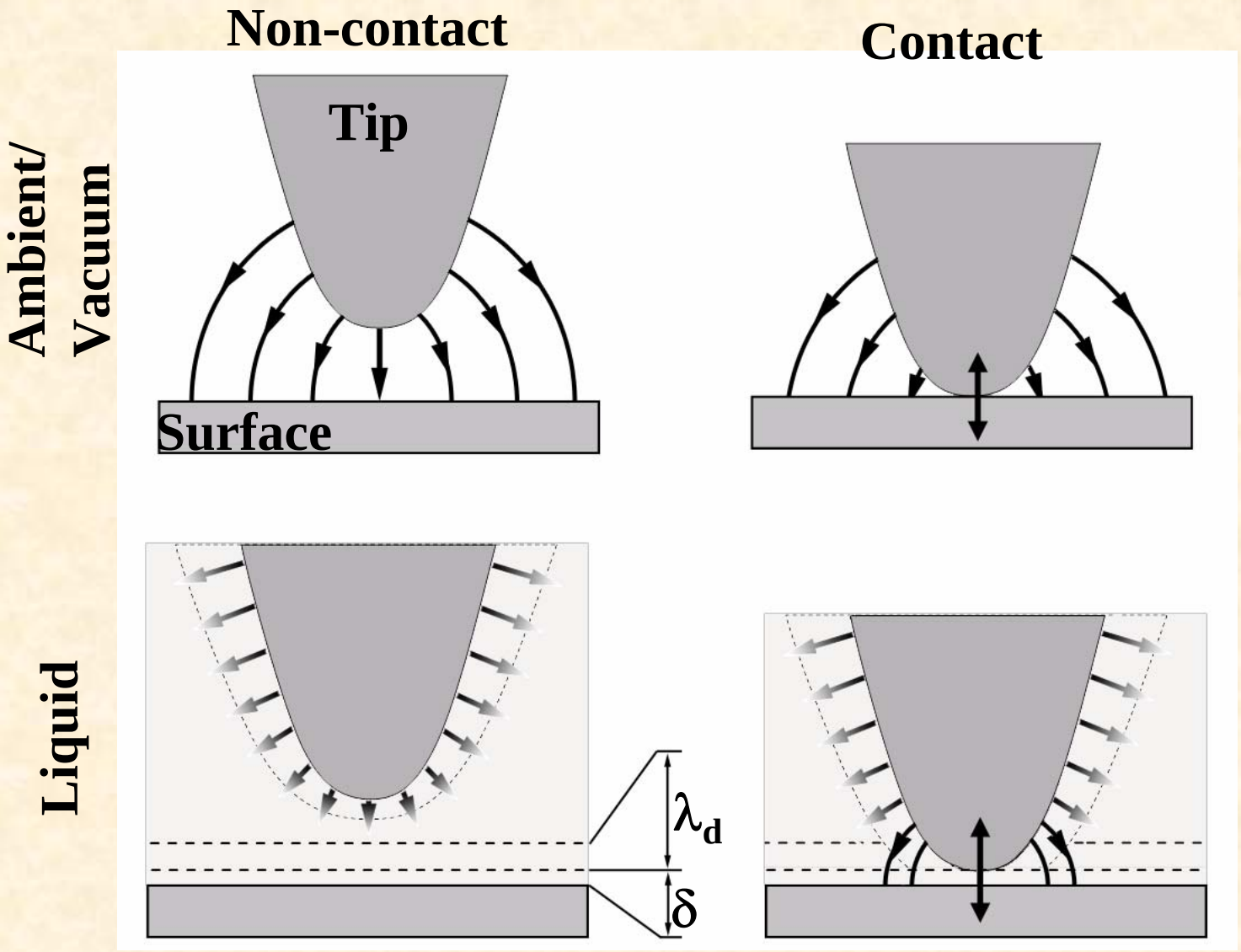
$$PR_l = \alpha(h)d_{33} + \frac{\varepsilon\varepsilon_0 R}{k_1\lambda_D}\frac{2V_s \exp(h/\lambda_D)}{\exp(2h/\lambda_D)-1}$$

electrostatic coupling in the double layer

contribution from the conical part of the tip and cantilever are absent
response decays on distances on the order of the Debye length of the solution, and the electrostatic contribution is significantly minimized compared to ambient or vacuum

electrostatic contributions are minimized in liquid

Theory: Electrostatics



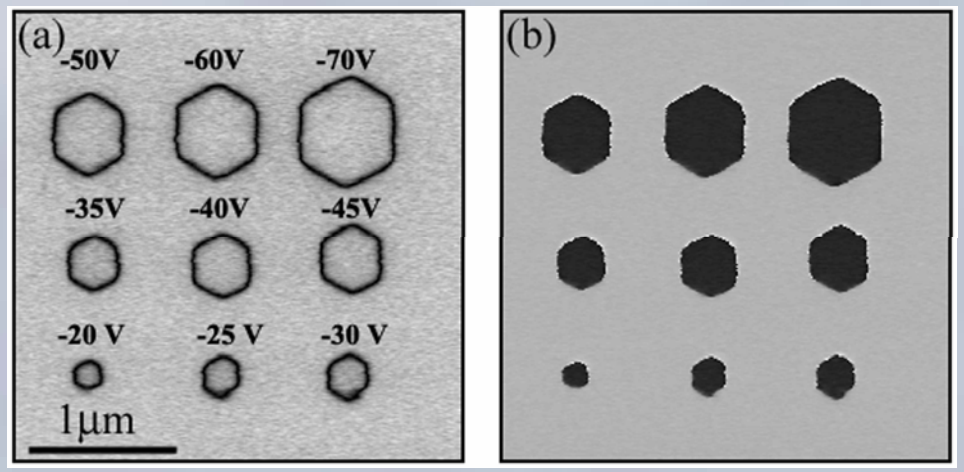
long range electrostatic force

short range electrostatic force

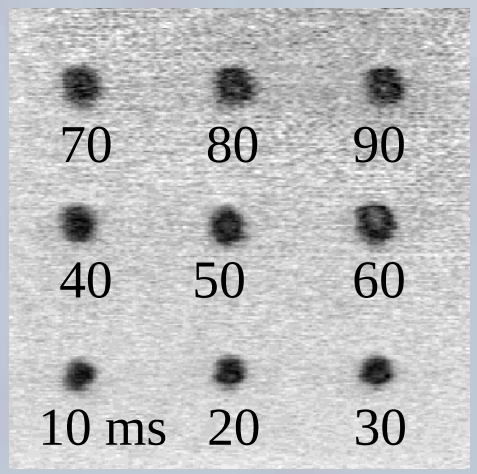
Schematic mechanism of electrostatic and electromechanical interactions in ambient and liquid environments and mechanism for PFM contrast enhancement.

Switching in solutions?

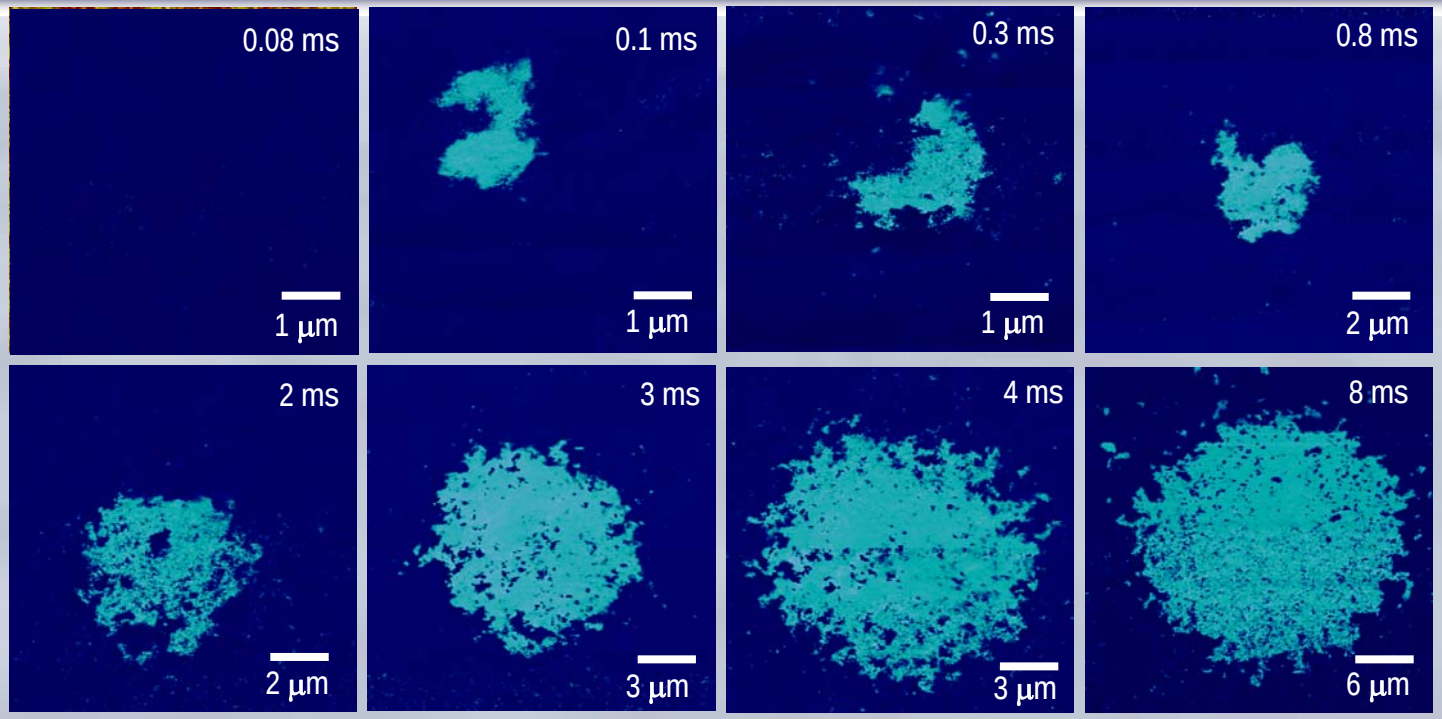
Bias dependence of domain size:



Time dependence of domain size

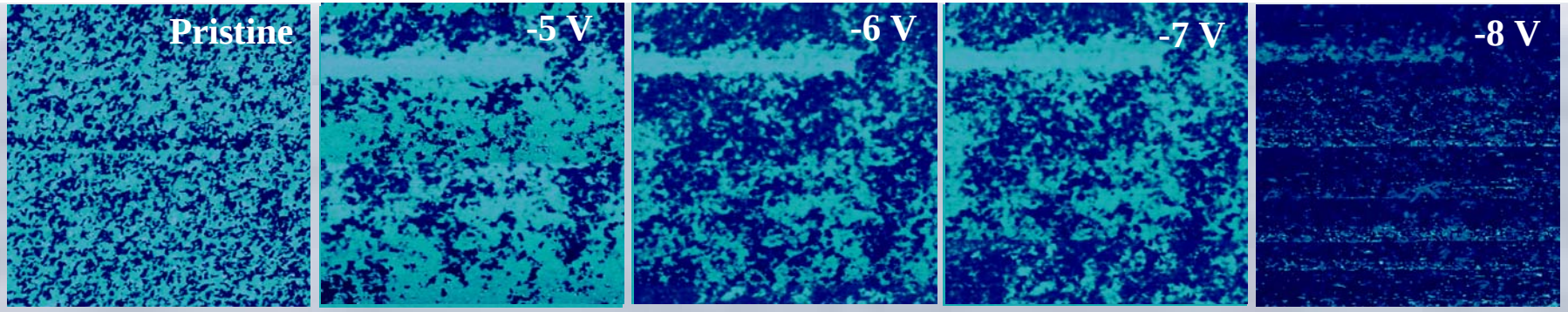


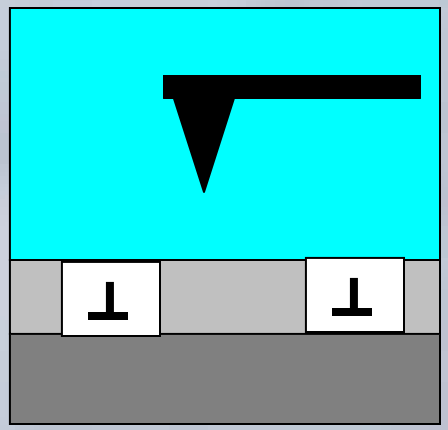
Localized Switching in Liquids

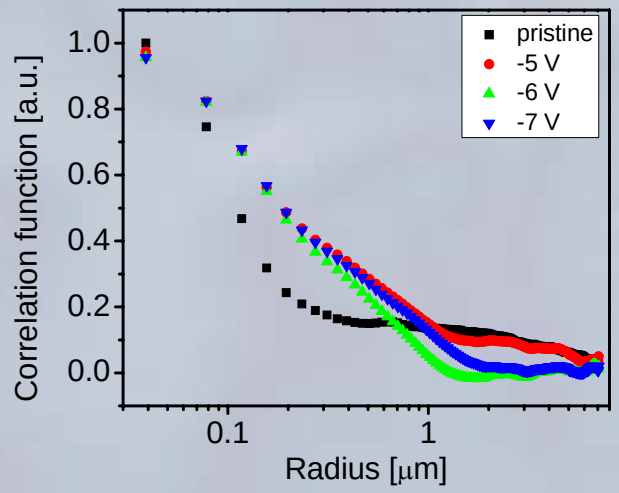


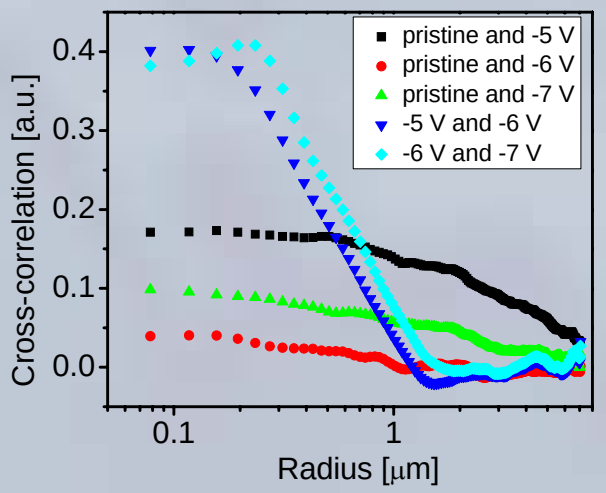
- Local switching is possible only in non-polar solvents.
- Imaging is possible even in polar solvents
- Localized switching (isopropanol) results in fractal clusters
- We cannot concentrate dc field!

Non-Local Switching in Liquids







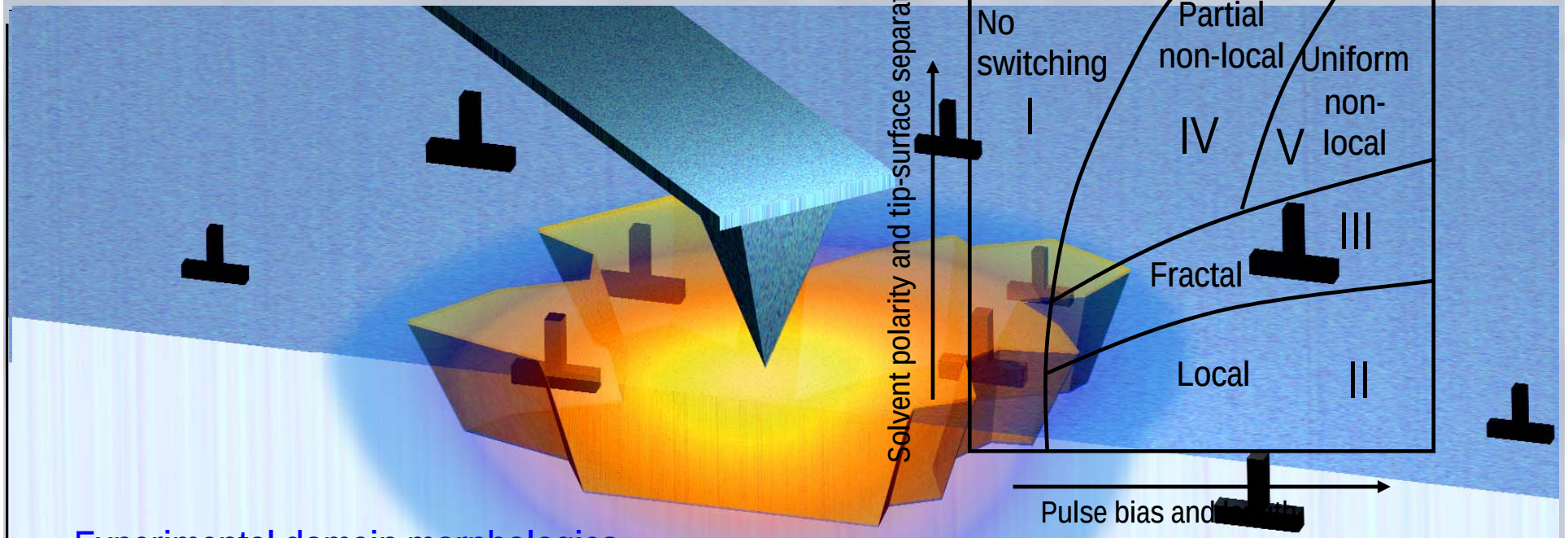


- Uniform switching in liquid allows mapping of switching centers
- Long range interactions are important
- Disorder is frozen

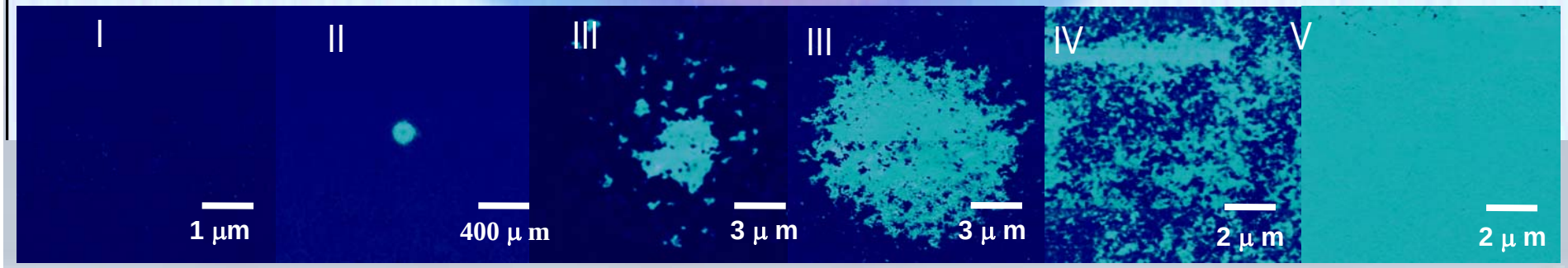
Solvent Polarity Control of Switching Mechanism

Switching mechanism

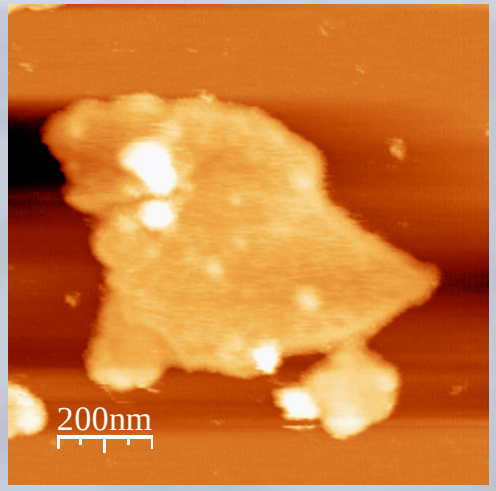
Switching map

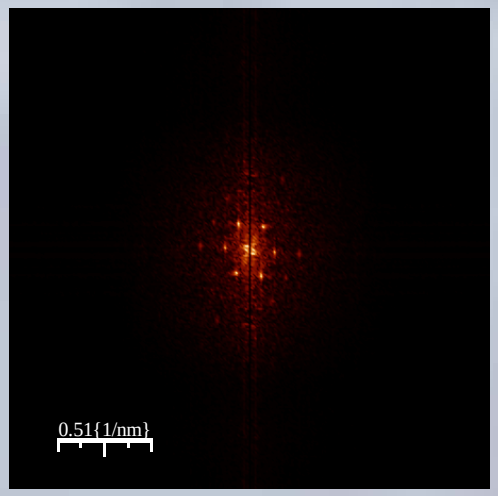


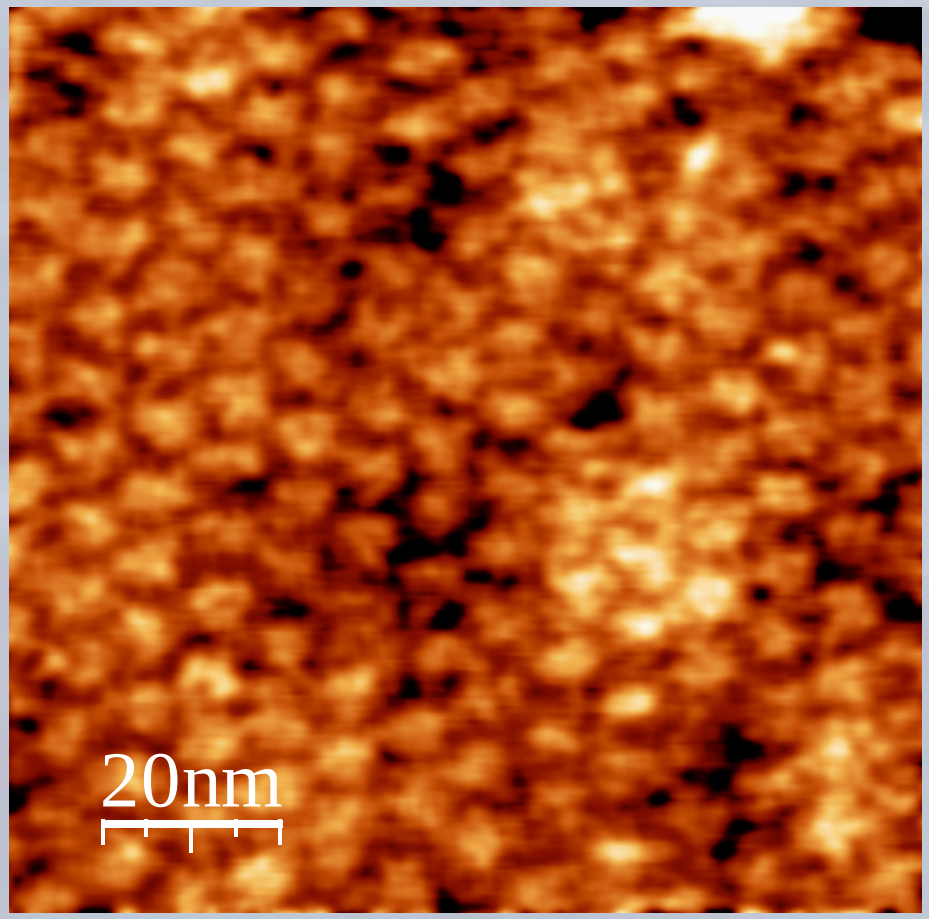
Experimental domain morphologies



Imaging Membranes with Metallized Tips

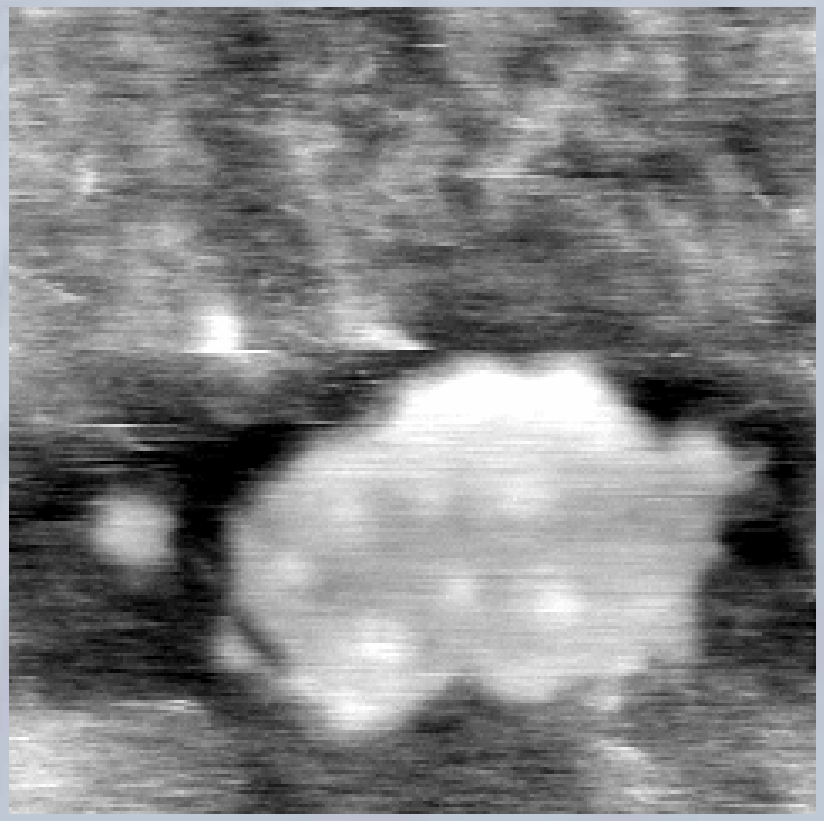


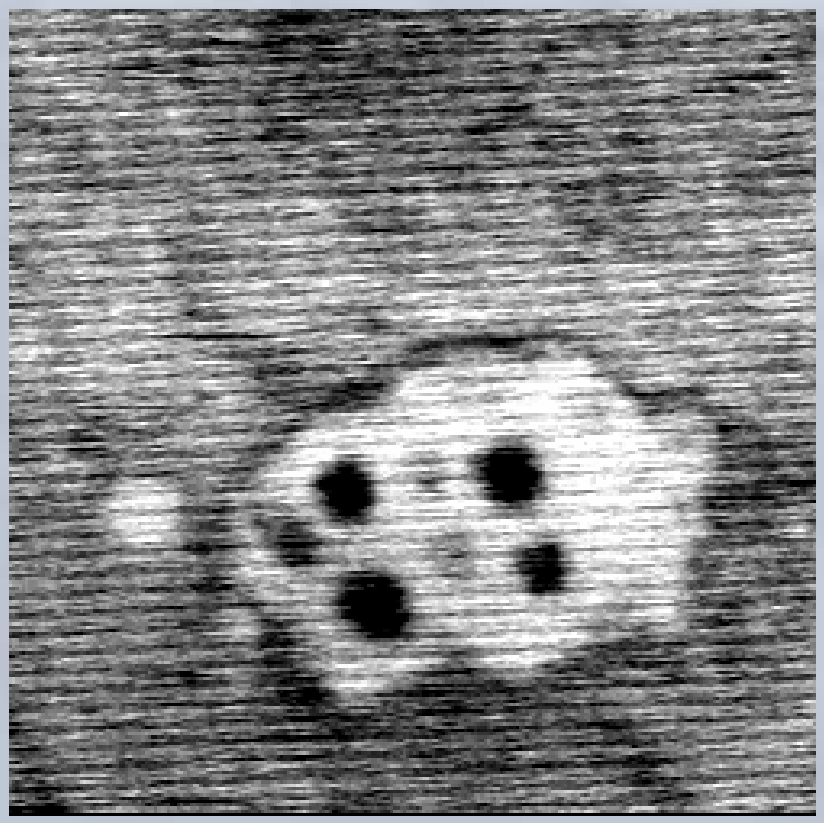




Tapping mode image

Liquid PFM of Protein Membrane



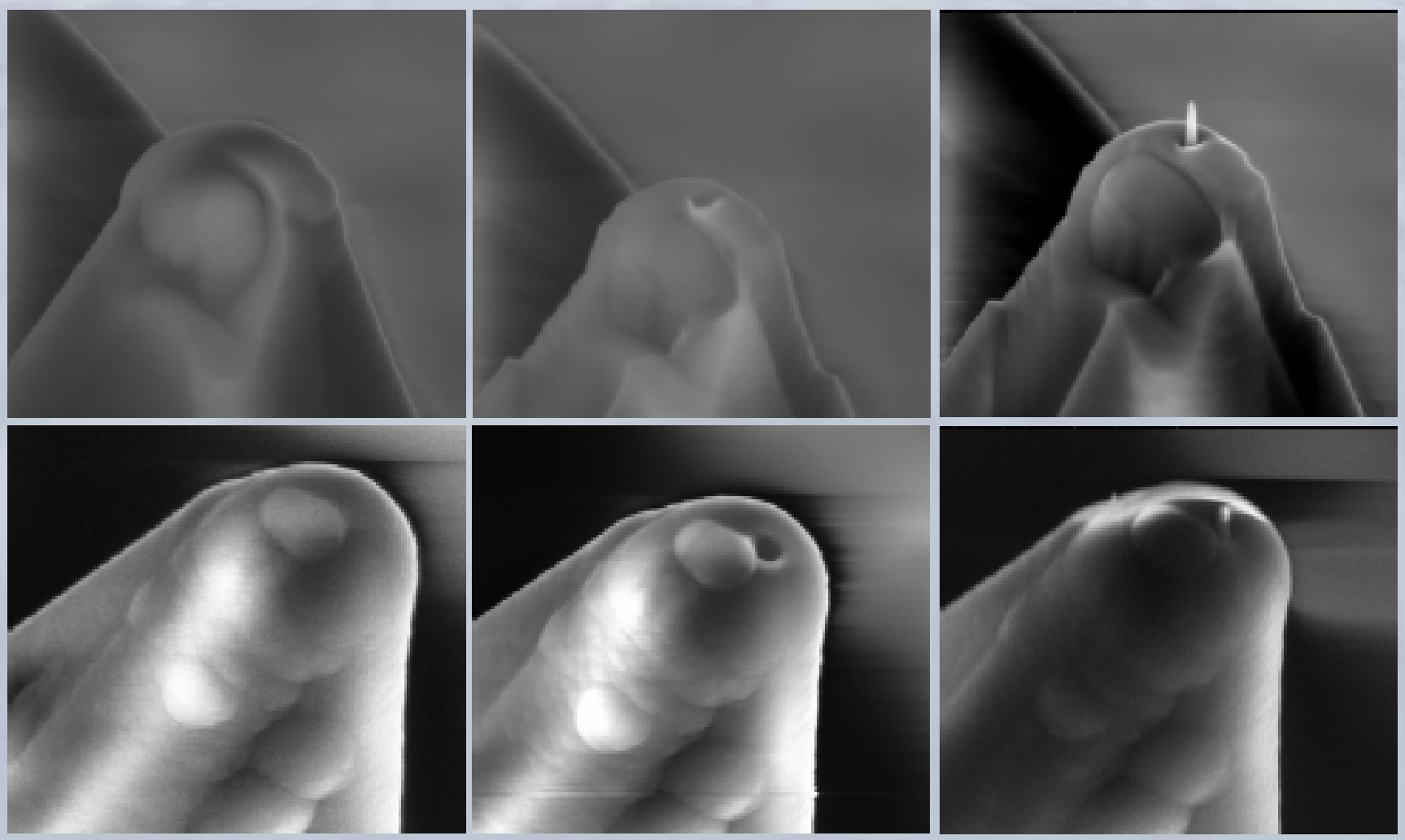


Imaging of the purple membrane, bacteriorhodopsin, with an ac-field in buffer solution reveals possible polarity induced contrast between extracellular and cytoplasmic regions.

Image by B. Rodriguez, I. Revenko, and S. Holbauch

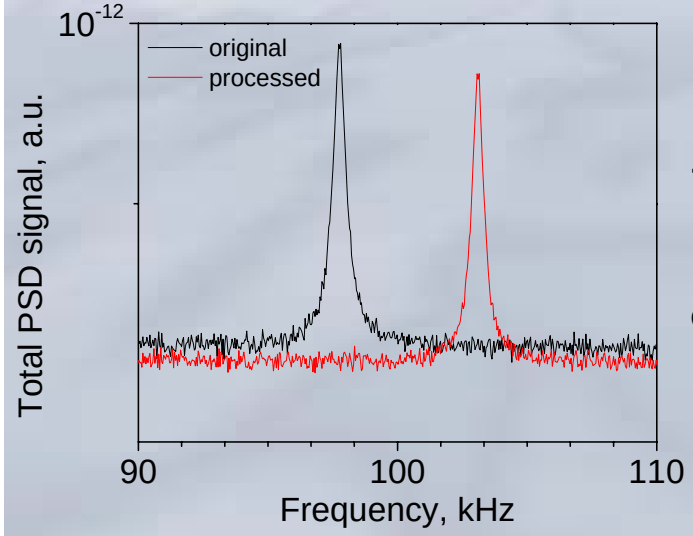
Development of Shielded Probes

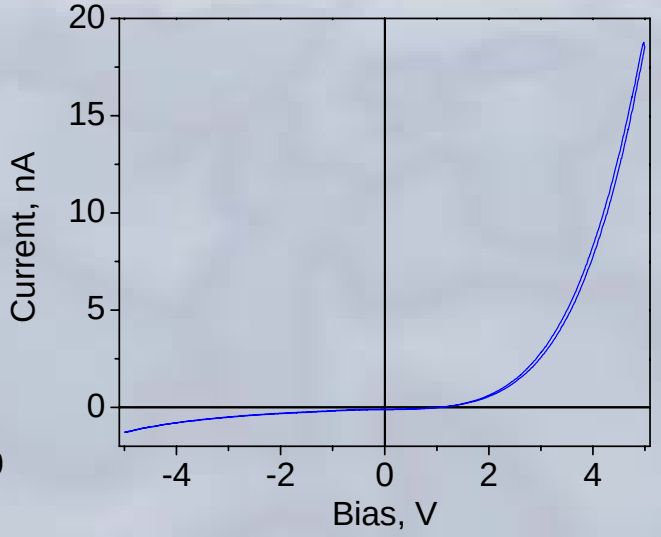
Electromechanical imaging in liquids requires insulated and shielded probes

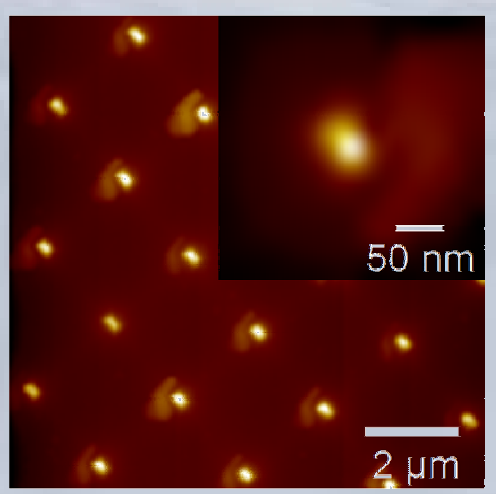


Development by P.D. Rack, ORNL/UT

Probe Characterization: Dynamics and Conductivity



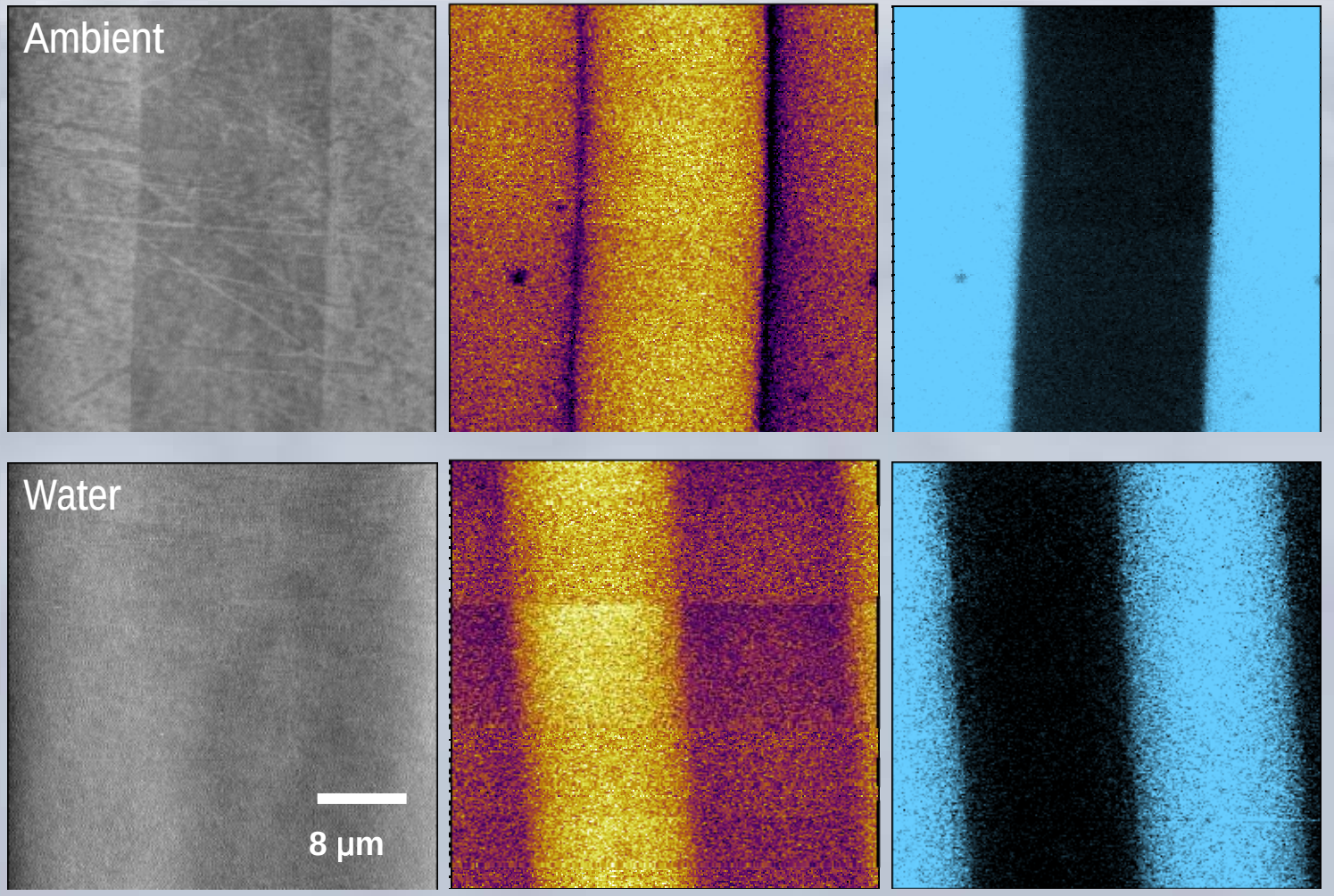




Tip	Sum (V)	Resonance (kHz)	Q	k (N/m)	InvOLS (nm/V)
Tip 1 before	4.14	97.76	288	9.82	95.43
Tip 1 after	4.25	103.10	335.6	13.42	87.78
Tip 2 before	5.61	66.74	156	1.78	75.75
Tip 2 after	5.49	76.14	244.2	3.59	79.72

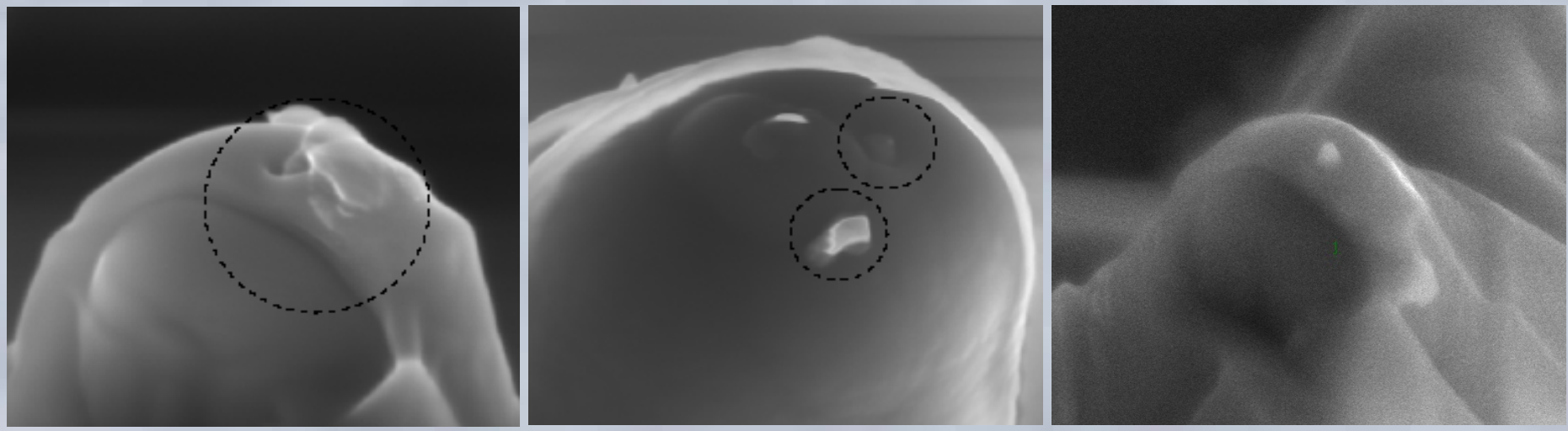
Stiffness increases. Conductance is non-ohmic.

Probe Characterization: Dynamics and Conductivity



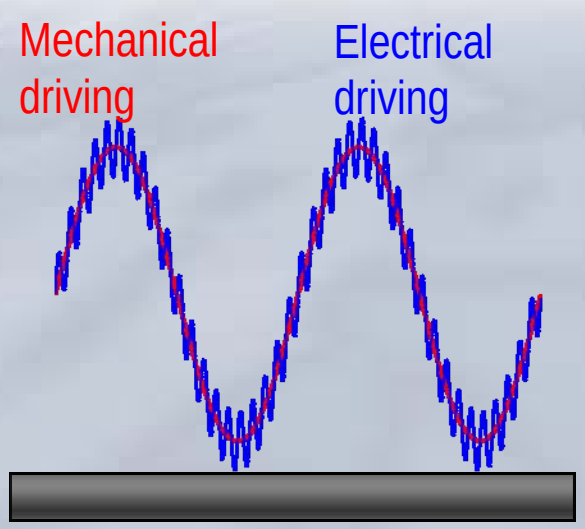
Tip allow PFM contrast both in ambient and in liquid environments.

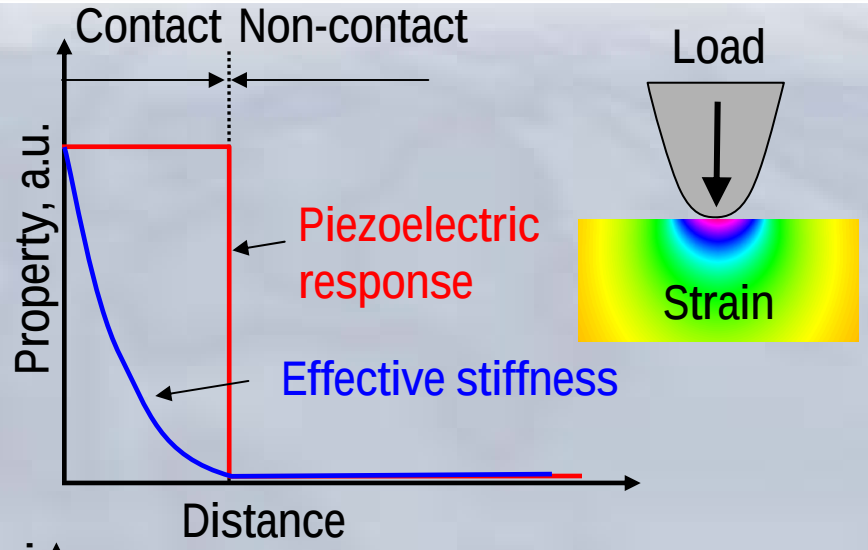
Probe Modification and Repair

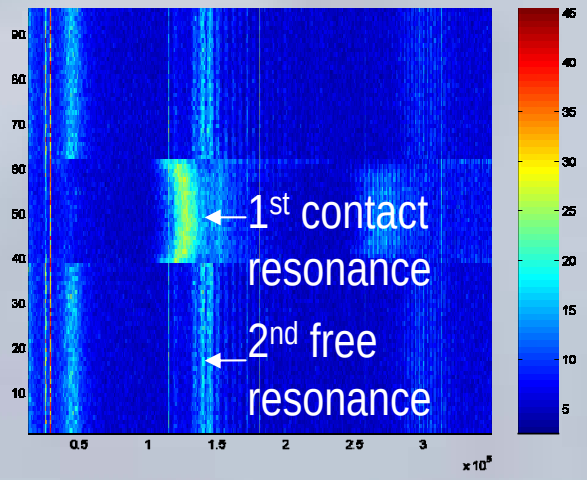


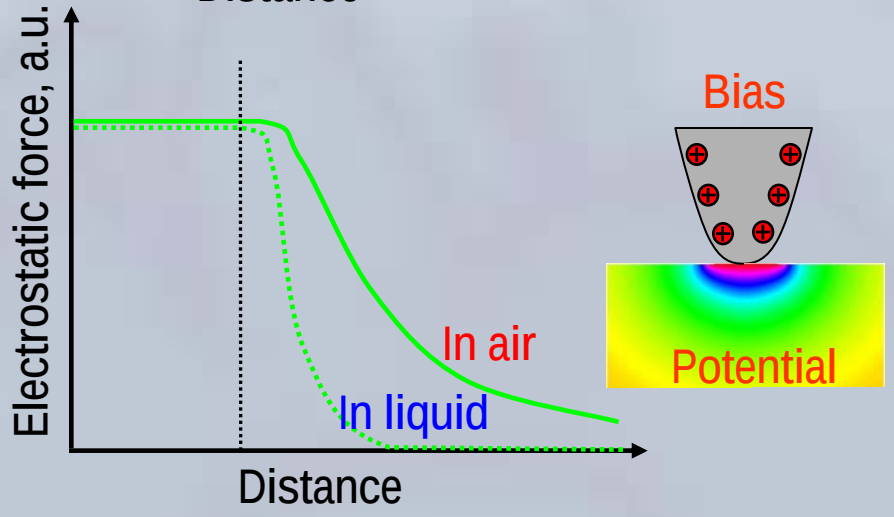
Tips can be repaired.

Intermittent Contact Mode PFM?



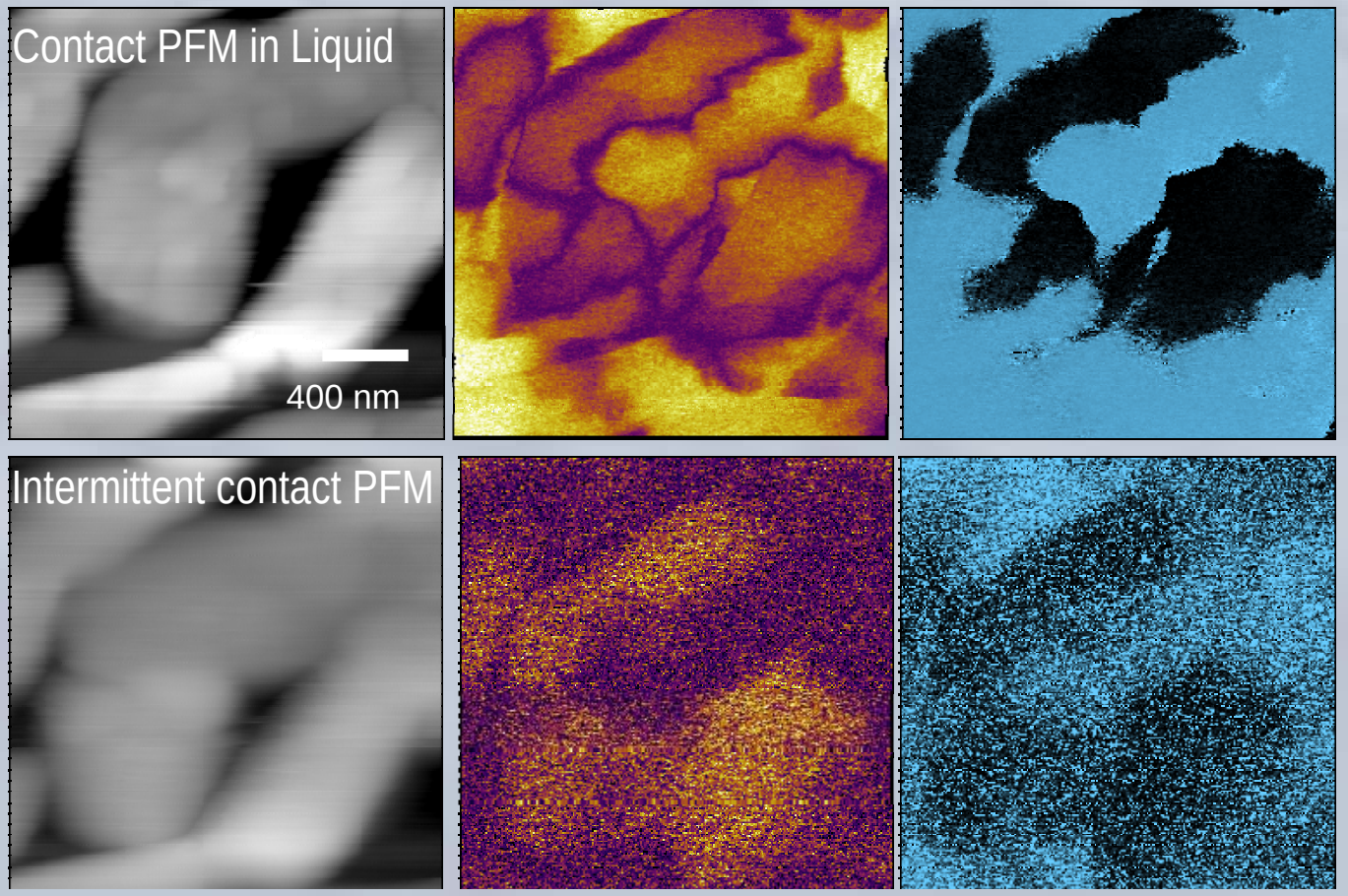




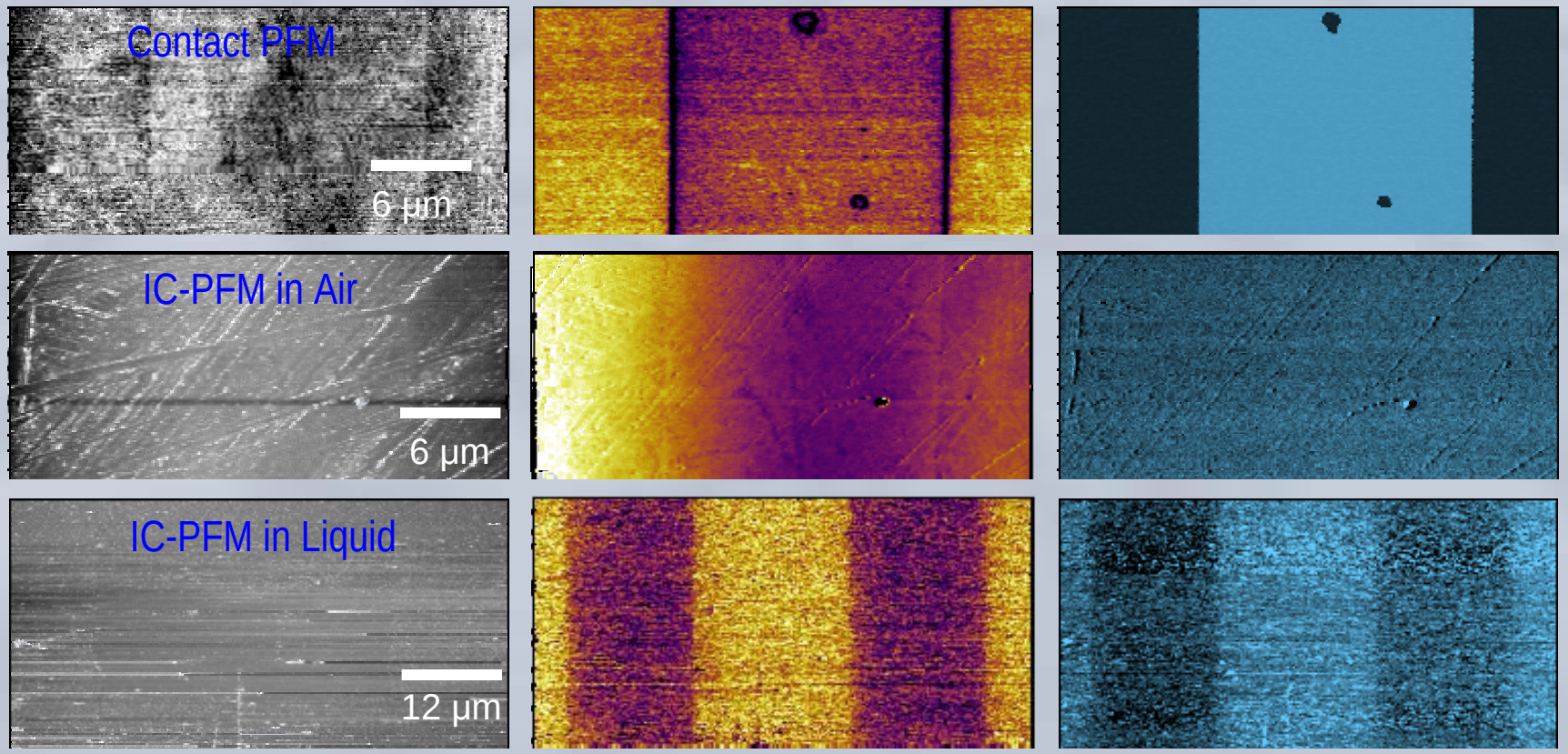


Intermittent contact PFM would be perfect for high resolution imaging. However, electrostatic forces are long range and are expected to dominate signal. ..

First Results: PZT



First Results: PPLN

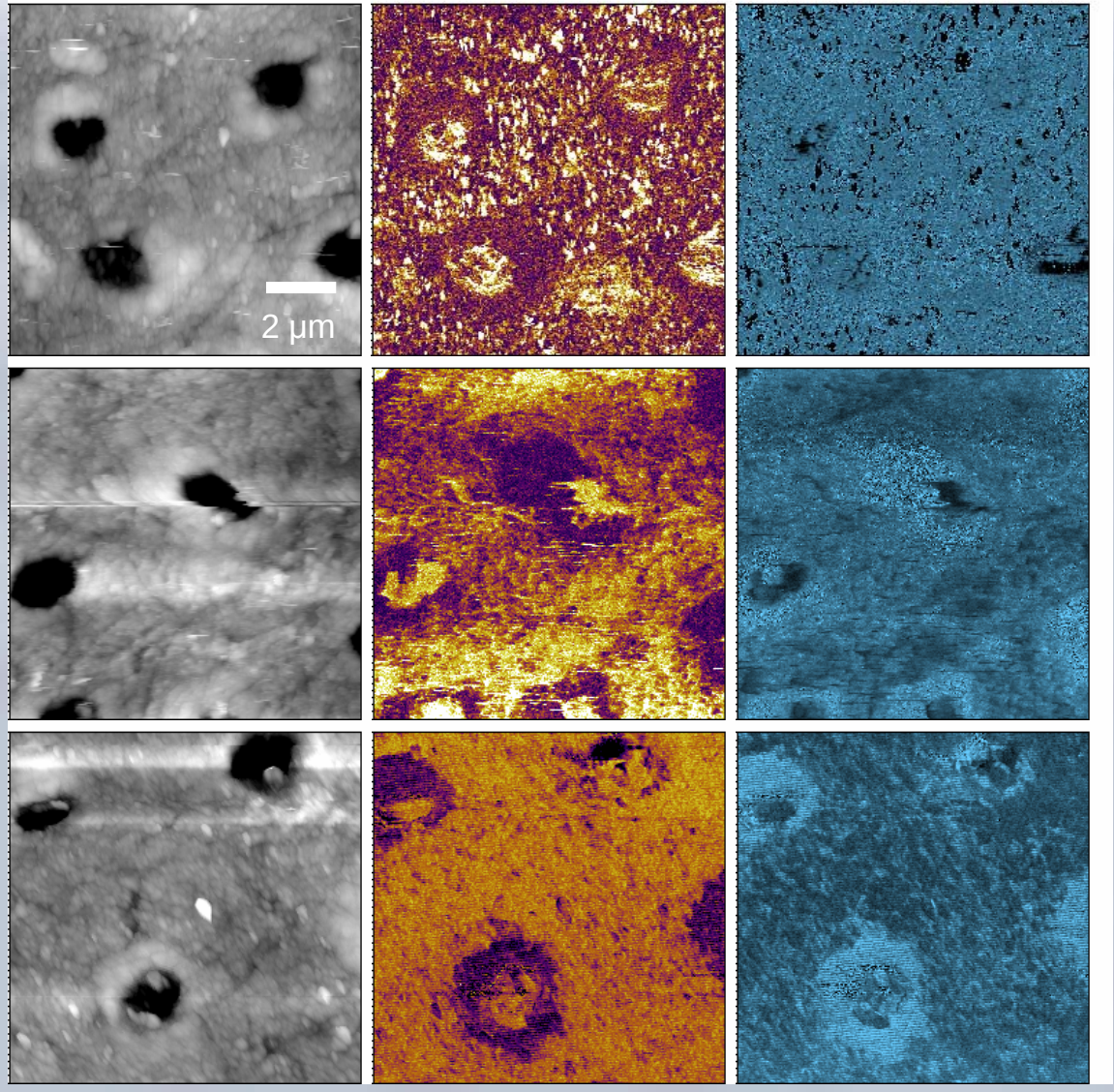


First Results: Dentin

Contact PFM

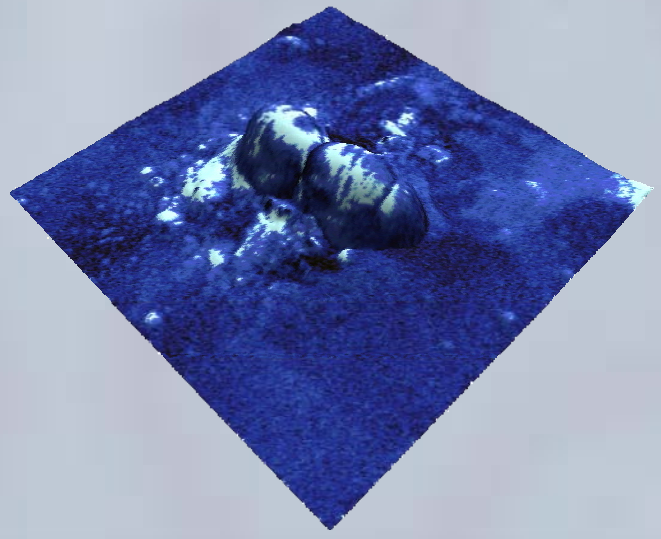
PFM in Liquid

IC-PFM in Liquid



Summary

- In the decade since invention, PFM has become a primary tool for imaging, spectroscopy, and modification of ferroelectric materials on the nanoscale.
- PFM is applicable for high resolution imaging of ultrastructure of connective and calcified tissues utilizing piezoelectricity of collagen and proteins
- PFM in liquids opens pathways to many interesting and unusual phenomena, including electromechanics of biological systems
- Kelvin Probe and Electrostatic Force Miscopies can be implemented in Liquid




MSTD


MSTD