# Electromechanical Coupling on the Nanoscale: Bonds, Cells, and Molecules

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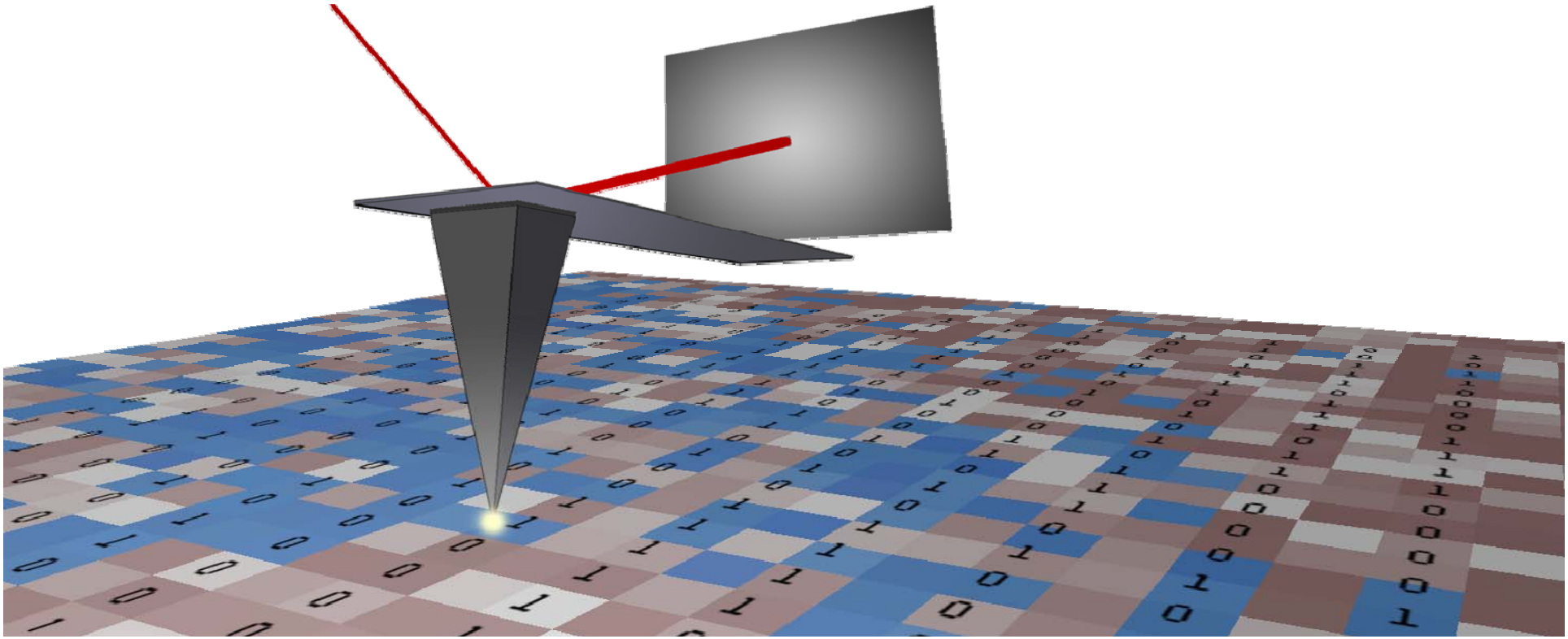
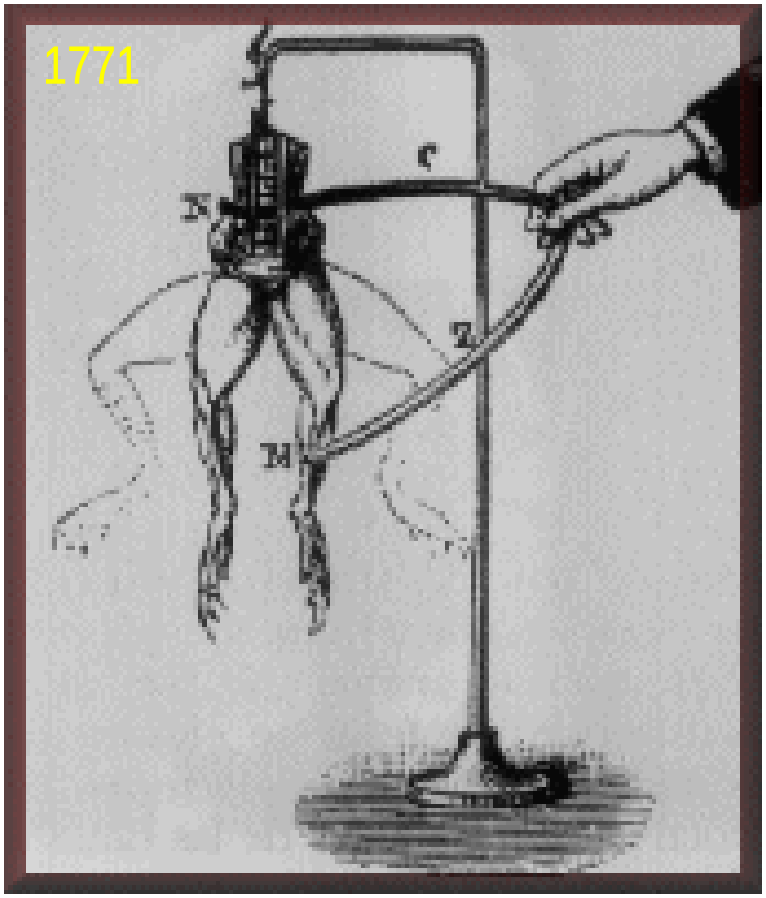
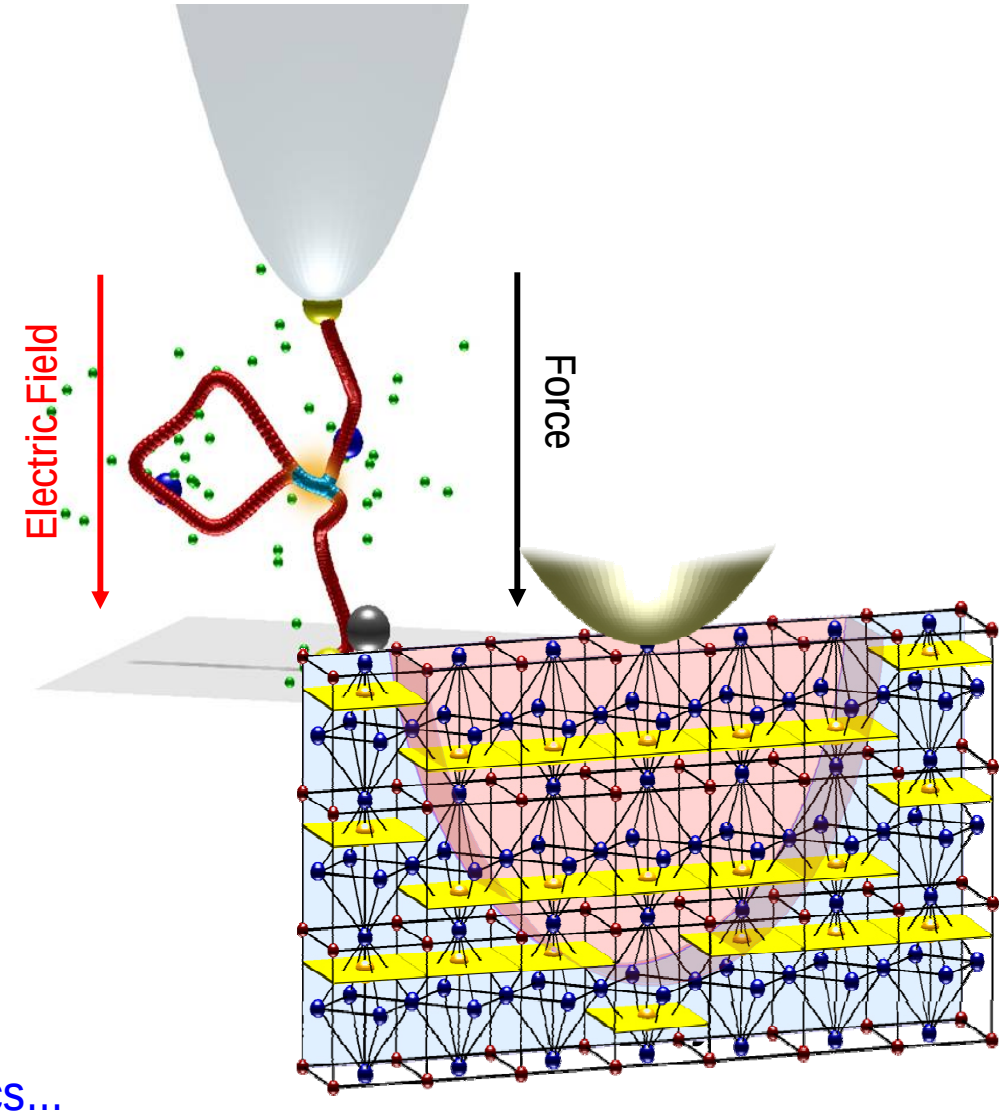


# Electromechanics and the Origins of Physics




18th Century

In the beginning, there was electromechanics…




And now is the time to revisit it

# Electromechanics on the Nanoscale

The fact that "small is different" is well established for a wide variety of phenomena including electrical, optical, magnetic and mechanical properties of materials. Untapped but potentially very important area of nanoscience involves the interplay of electricity and mechanics at the nanoscale.

## Rationale:

- How important are electromechanical phenomena on the nanoscale?

## Fundamental science:

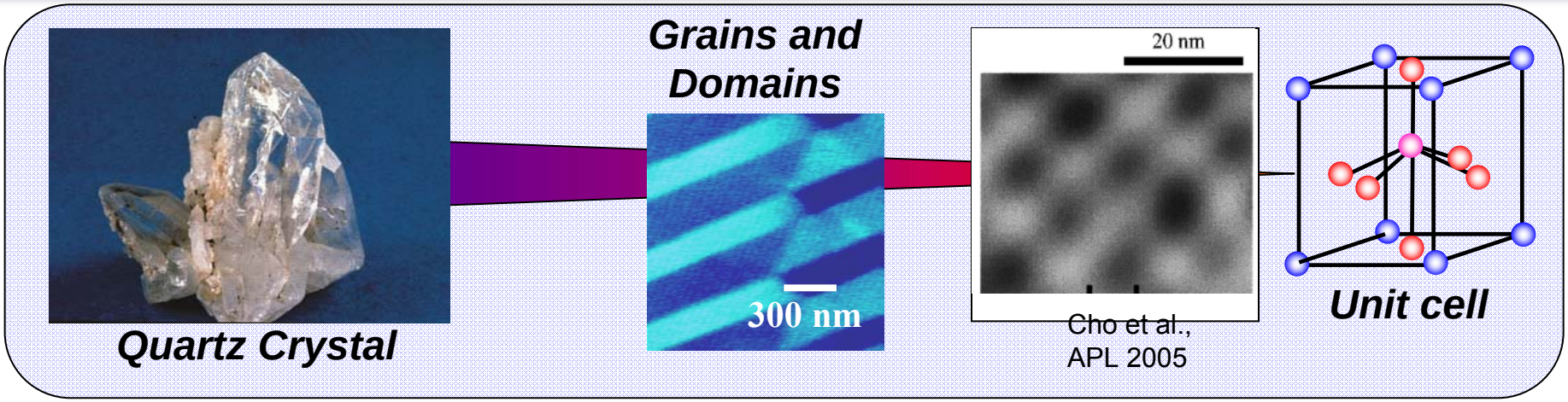
- Are there new behaviors in low dimensional systems?
- Is electromechanics expected to tell us something new about standard systems?

## Applications:

- Can we manipulate and control electromechanical energy conversion on the nanoscale?
- What do we need to do to harness it to real world applications?

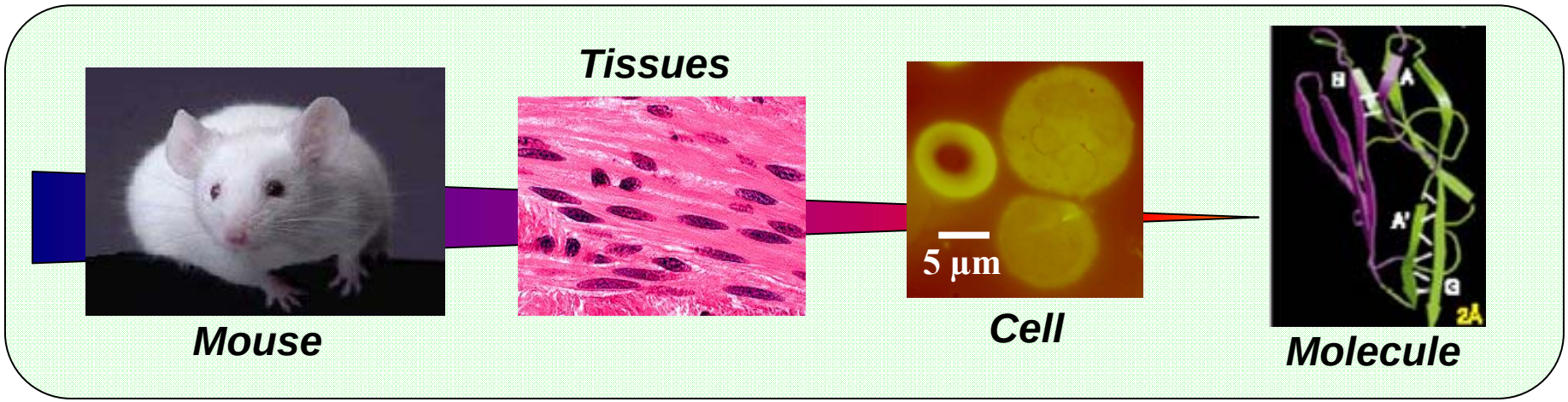
This Workshop: Electromechanical imaging, spectroscopy, and manipulation

# Electromechanics: The Next Frontier



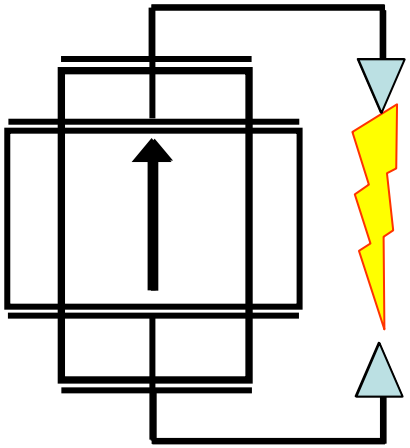

1 m | 0.1 m | 10 mm | 1 mm | 0.1 mm | 10 µm | 1 µm | 0.1 µm | 10 nm | 1 nm | 1 Å

**We need to understand structure and electromechanical behavior on the micron, nanometer, and ultimately molecular levels!**



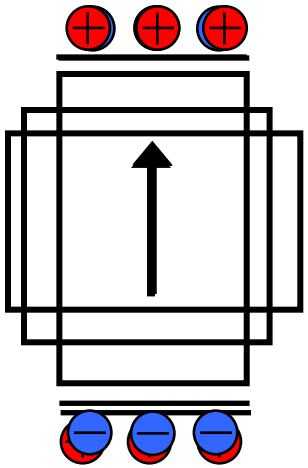
# Electromechanical Coupling

*Direct piezoelectric effect*



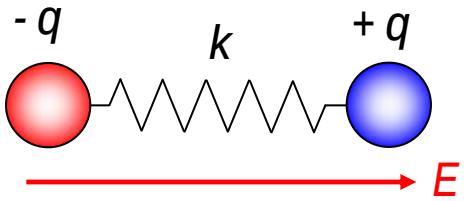
Charge = Force • $d_{33}$

*Inverse piezoelectric effect*



Strain = Bias • $d_{33}$

In crystals, $d_{33}$ ranges from ~2 pm/V (quartz) to ~500 pm/V (PZT)




External electric field

External force

Electrostatic force: $F_{el} = 2qE$

Change in bond geometry:

$$dl = (F + F_{el})/k = F/k + 2qE/k$$

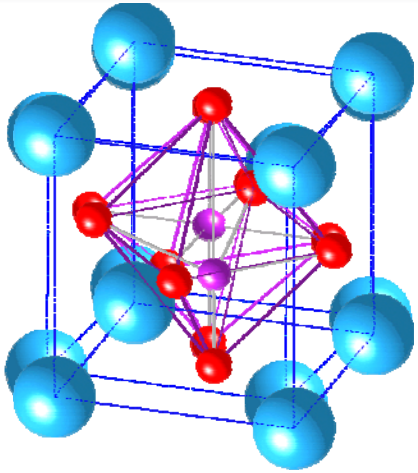
- Electromechanical coupling is ubiquitous in systems with polar bonds, if not forbidden by symmetry
- Surfaces, interfaces, and low dimensional systems with broken symmetry will have unusual forms of electromechanical coupling

Estimate for single chemical bond:

$$\left.\begin{array}{l} l = 1A \\ q = 0.3e \\ k = 100\,N/m \end{array}\right\} \Rightarrow \boxed{\begin{array}{l} d = 9.6\ pm/V \\ \text{or} \\ d = 9.6\,C/N \end{array}}$$

# Ferroelectrics: Structure and Applications

Phase transition is accompanied by symmetry change (elongation of the unit cell) and formation of electric dipole. Electric and mechanical phenomena are coupled.

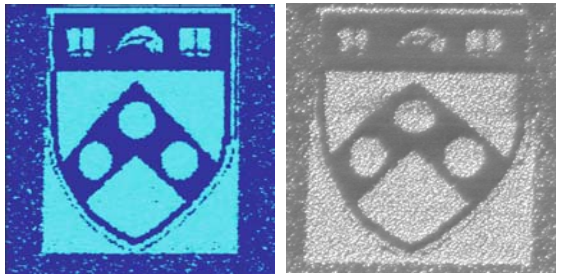


## Surface and Interface Charge

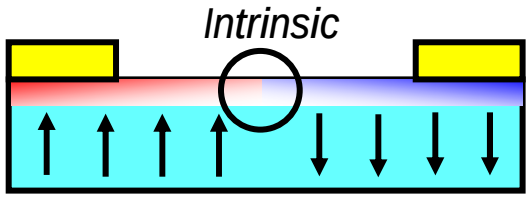
Polarization discontinuities: Charge $\sigma_{pol} = P \cdot n$

For $BaTiO_3$, $P$ = 0.26 C/m$^2$ (0.26 e-/unit cell) Sufficient to strongly affect the chemistry of ferroelectric surface or induce metal insulator transition in heterostructure.

1. Ferroelectric lithography
2. Ferroelectric gate transistor
3. Non-volatile ferroelectric memories



*Accumulation* *Inversion*




S.V. Kalinin, D.A. Bonnell *et al*, Adv. Mat. 16, 795 (2004), featured in Science 304, 415 (2004).
C.H. Ahn, K.M. Rabe, and J.-M. Triscone, Science 303, 488 (2004)

## Strong Electromechanical Coupling

1. Piezoelectricity/electrostriction:
   - transducers, actuators, MEMS

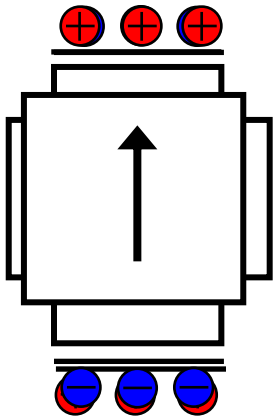
Piezoelectricity is tensorial:

$$x_j = d_{ij} E_i$$

Non-zero elements are determined by symmetry

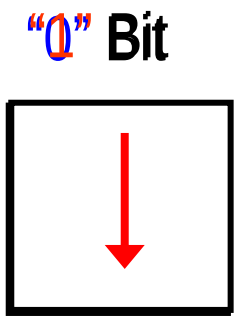
Tetragonal material (4mm):

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



## Switchable Polarization/Narrow Domain Wall

2. Ferroelectric memories (FeRAM)
   - non-volatile memory devices (Semiconductor Roadmap)
3. Ferroelectric Storage
   - Seagate, Samsung, etc…




How can we study piezo- and ferroelectrics on the nanoscale?

# Ferroelectrics: Structure and Applications

Does the nanometer scale brings new aspects to ferroelectric behavior?

Conventional description: ferroelectric size effects and dead layers

Depolarizing fields:

-instability of the polar phase

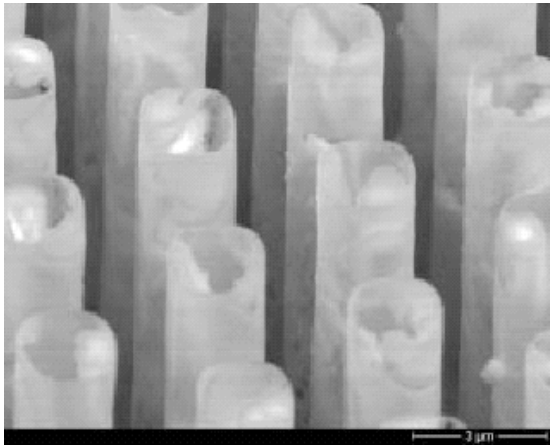
Surface effects:

- domain pinning

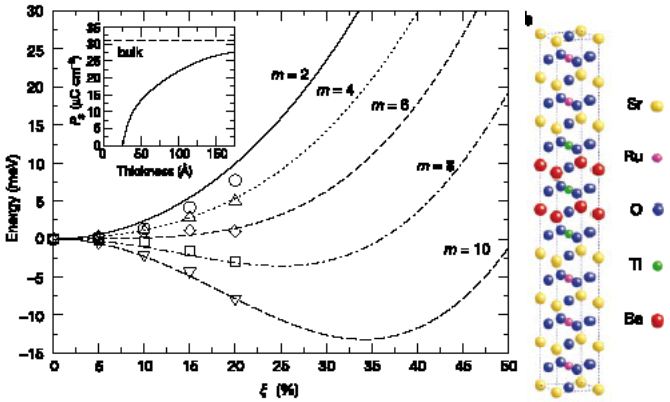
Domain structure:

- polydomain is not energetically favorable for particles <10 nm

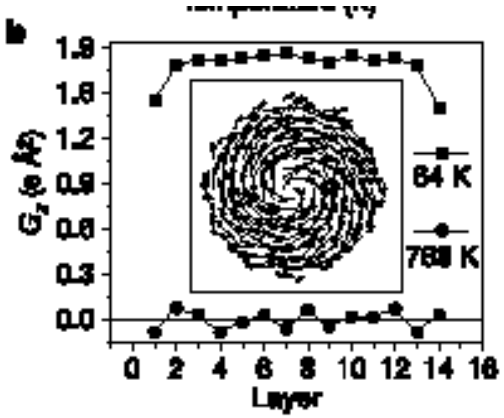
M. Dawber, K.M. Rabe, and J.F. Scott, Rev. Mod. Phys. 2005



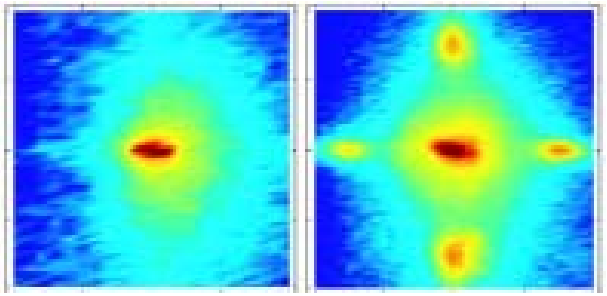
PZT nanotubes (M. Alexe, MPI, Halle)




J. Junquera, P. Ghosez, *Nature* 422, 506 (2003)

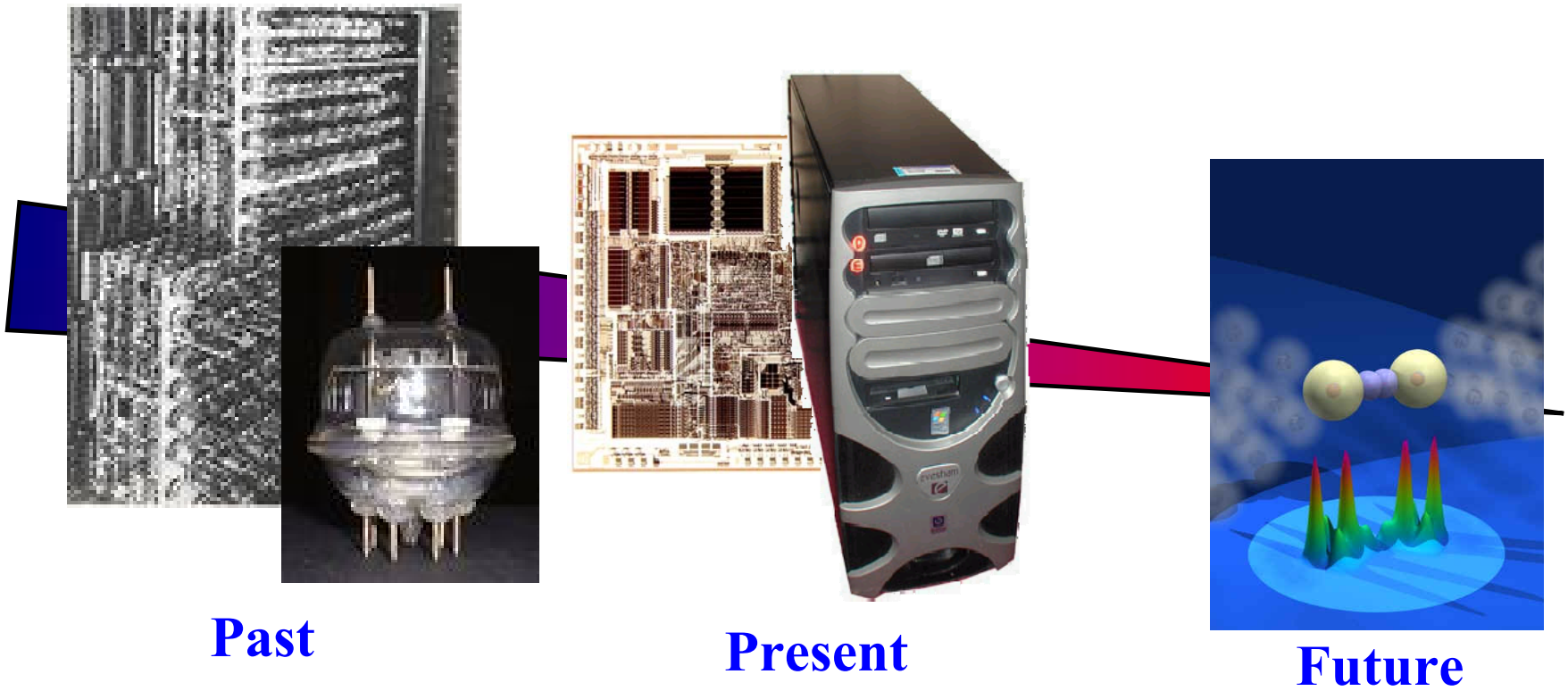



I. Naumov et al, Nature 432, 737 (2004)

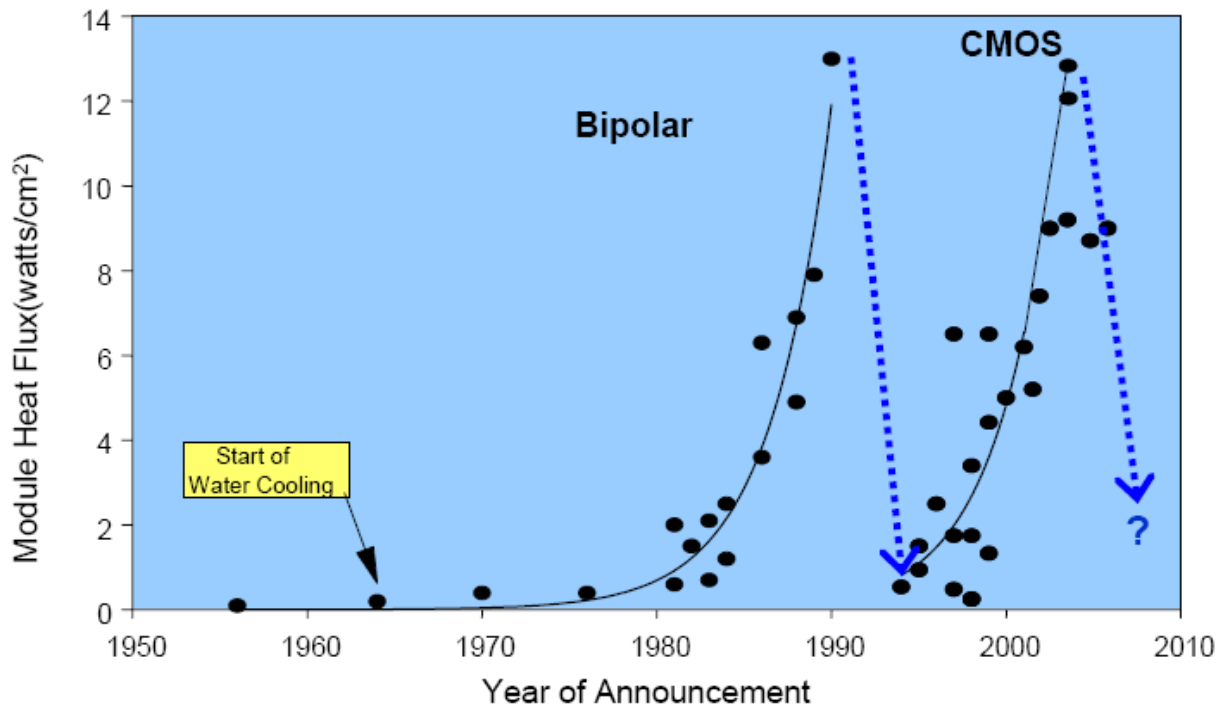


D.D. Fong et al, Science 304, 1650 (2004).

# Ferroelectrics in Information Technologies



# Ferroelectrics in Information Technologies




Switch parameters:

- Barrier height, $E_a$
- Particle mass, $m$

Determine

- Switching speed
- Stability
- Energy dissipation

International Technology Roadmap for Semiconductors

Energy → Computational state variables other than electronic charge

Noise → Non-equilibrium systems

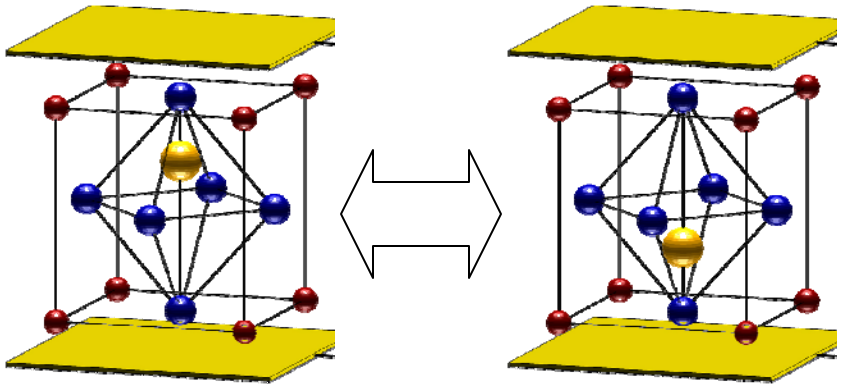
Interconnection → Novel energy transfer mechanisms

Heat → Nanoscale thermal management

Manufacturing cost → Directed self assembly

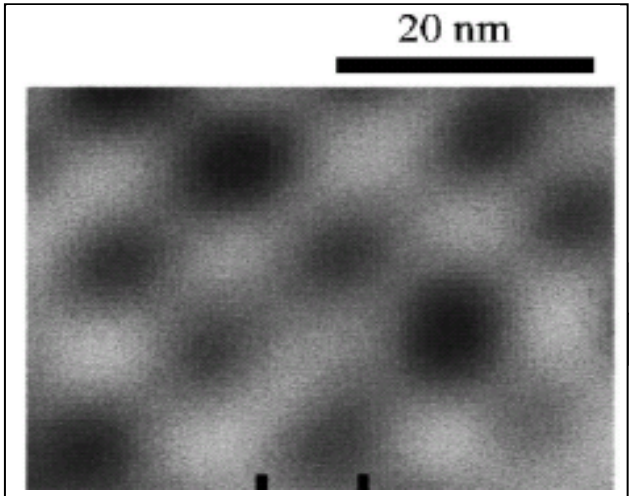
ITRS and NTI

# Ferroelectric Materials on the Nanoscale

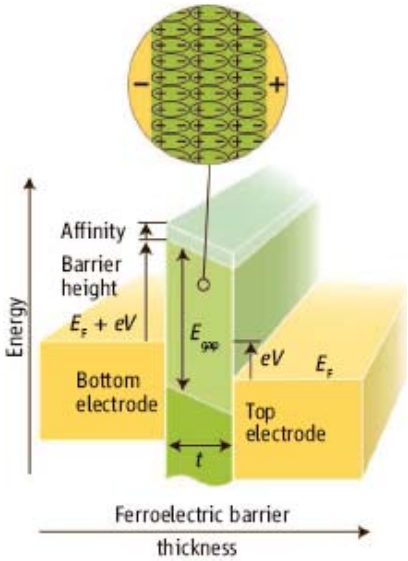


Perfect materials for information storage:

1. Non-volatile ferroelectric memories
   Fujitsy, Ramtron, TI
2. Data storage
   Samsung, Seagate, Intel
3. Resistive memories



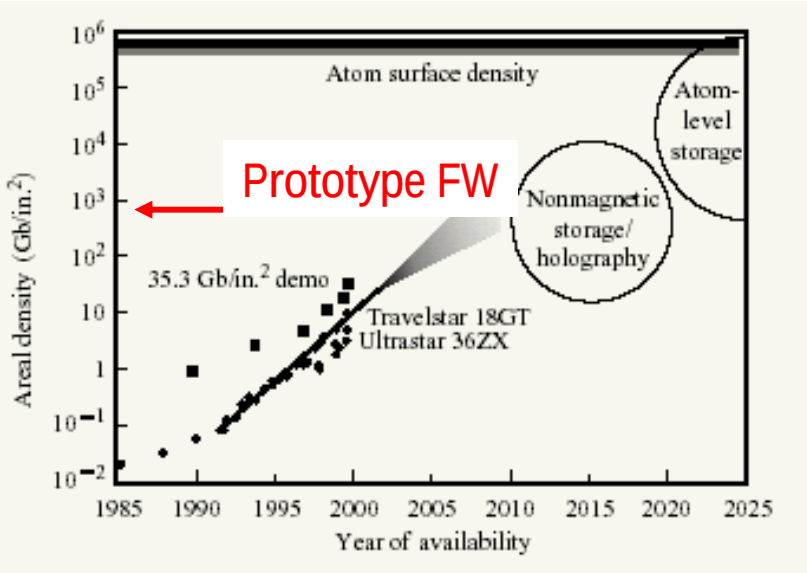

Cho et al., APL 2005

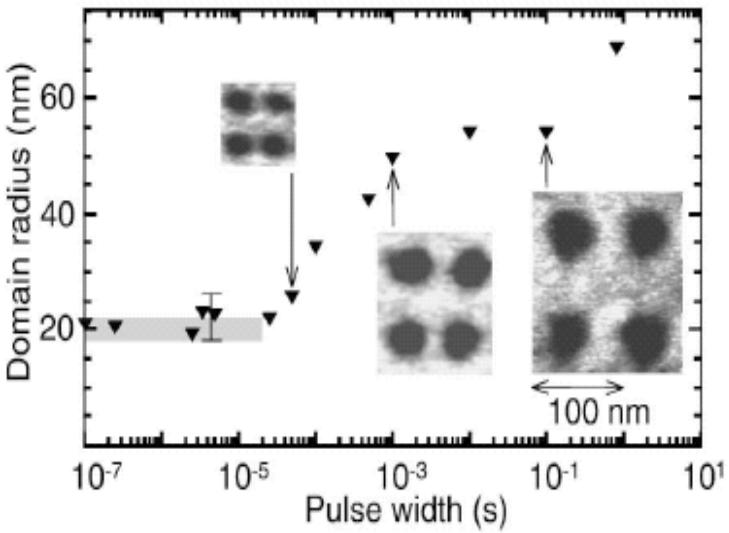



Kohlstedt and Tsymbal

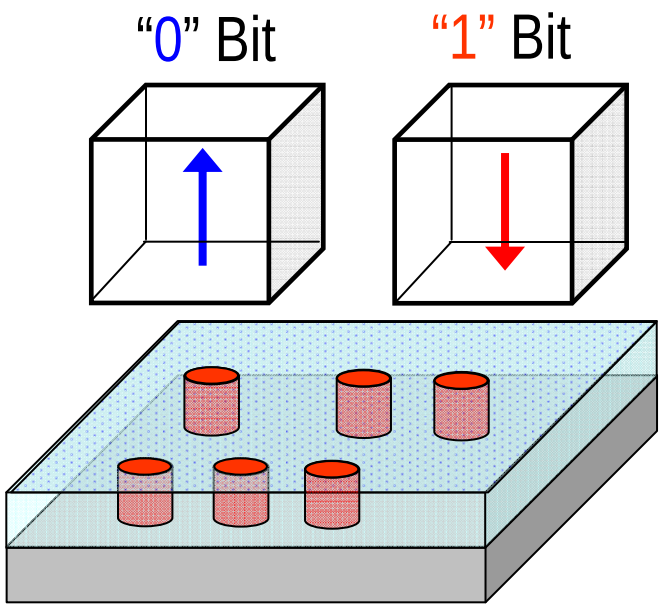
High speed: 50 ns vs 1μs – 1ms for Flash and EEPROM)
Low power: 1 pJ compared to 10 pJ-200 nJ for Flash and EEPROM
Endurance: $10^{12}$ cycles compared to $10^{6}$ for EEPROM
Scalable: 20 nm not a limit

# High Density Ferroelectric Data Storage



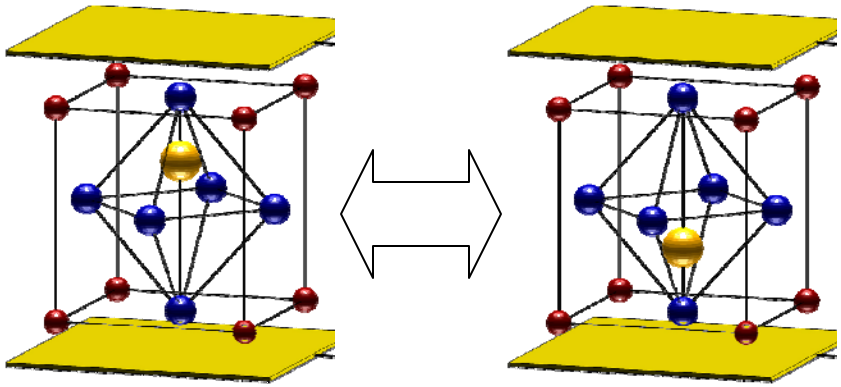

T. Tybell et al, PRL 89, 097601 (2002)




*Domain size control in PFM*

- Ferroelectric recording demonstrates ~40 nm bit size, corresponding to 400 Gbit/inch$^2$ density
- PFM provides a readout with ~3 nm resolution

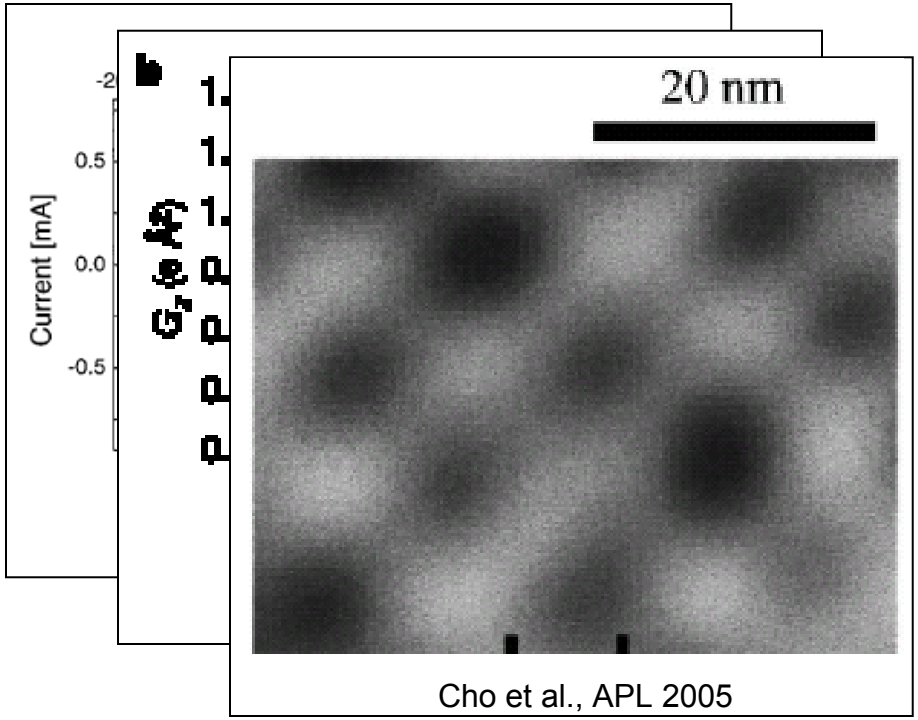
# Ferroelectric Materials on the Nanoscale



- Ferroelectricity in confined geometries
  - Stability of polar phase
  - Novel polarization ordering
  - Wall-lattice interactions
- Polarization Dynamics
  - Atomistic mechanisms for switching
  - Nucleation and growth times
- Ferroelectric surfaces and interfaces
  - Symmetry breaking
  - Surface chemistry
- Multiferroic materials
  - Complex order parameters

Perfect materials for information storage:

1. Non-volatile ferroelectric memories
   Fujitsy, Ramtron, TI
2. Data storage
   Samsung, Seagate, Intel
3. Resistive memories




Cho et al., APL 2005

*What are switching mechanisms in real materials?*

# Landauer Paradox

JOURNAL OF APPLIED PHYSICS VOLUME 28, NUMBER 2 FEBRUARY, 1957

The results of this treatment combined with previous estimates of a domain wall energy of 7 ergs/cm$^2$ lead to a variation of nucleus energy with domain size which would permit only implausibly large domains to expand in the presence of a typical coercive field.

- Landauer paradox
  - In 1957, Landauer analyzed ferroelectric switching in uniform fields and have shown that nuclei size and activation energies are extremely large (Landauer paradox)
  - Switching controlled by defects: typical behavior for 1$^{st}$ order phase transitions
  - Spatial and energy distribution is an integral part of theory (Kolmogorov-Avrami-Ishibashi)

*What are the nucleation centers?*

# Ferroelectric Nanodevices

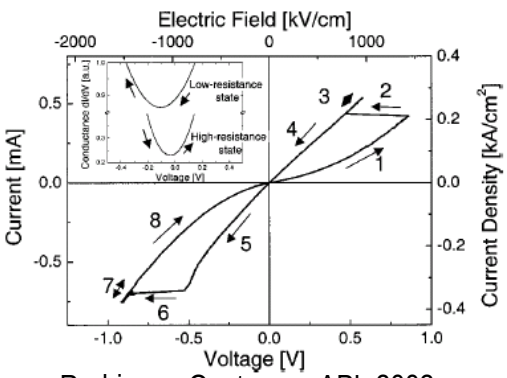
## Classical applications:

- Switchable polarization - nonvolatile FeRAM
- High dielectric constant - varistors, DRAM
- Piezoelectricity - transducers, actuators, MEMS
- Electro-optical activity - filters, switches
- Pyroelectricity - IR sensors

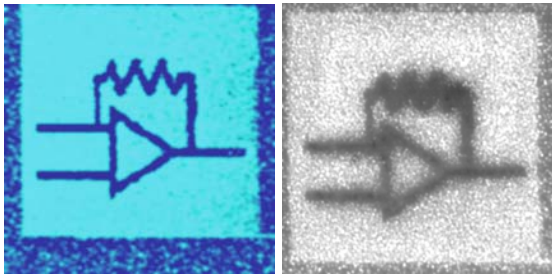
Fatigue – limited number of switching cycles
Imprint - writing failure
Retention loss - read-out failure
Ageing - degradation with time
Spatial variability - random bit failure

## Novel applications:

- Heterostructures: FeFET, tunneling junctions
- Ultra-high density data storage
- Ferroelectric lithography

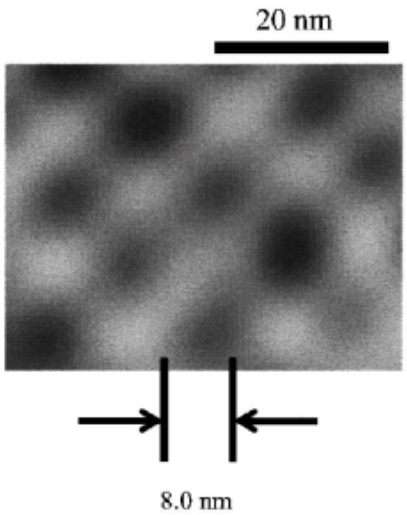



Rodriguez-Contreras, APL 2003



PFM Image Metal Deposition

Kalinin and Bonnell, Adv. Mat 2004

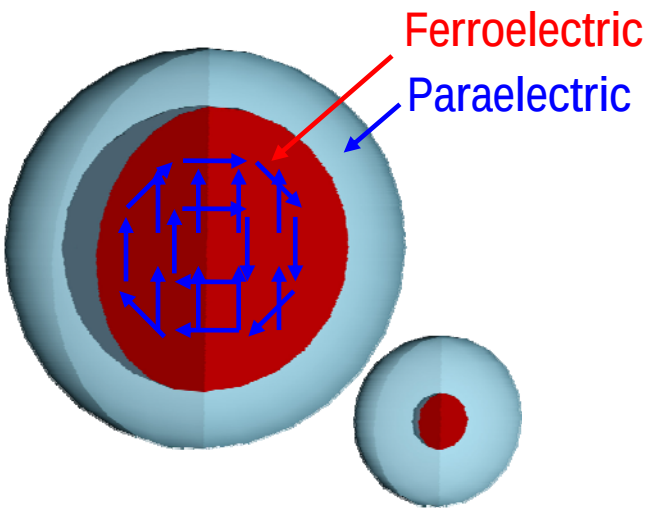



Cho et al., APL 2005

Probing the local properties of ferroelectrics on the nanoscale is the key to both device characterization and understanding of fundamental polarization controlled physical phenomena

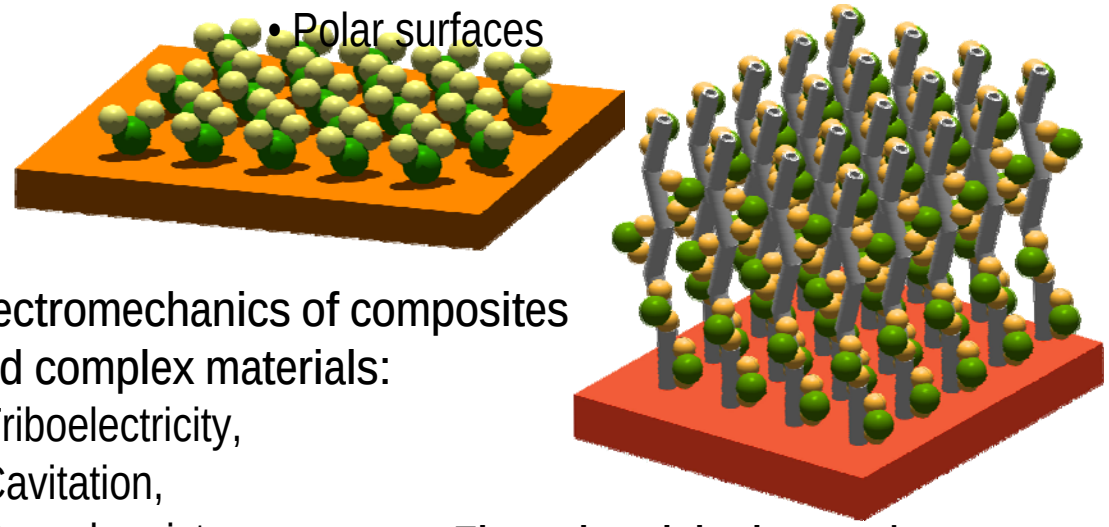
# Electromechanics on the Nanoscale

Classically, surface and dimensionality effects are considered as purely detrimental to ferro- and piezoelectricity.




Surface piezoelectricity:

- Ordered dipolar water layers
- Polar surfaces

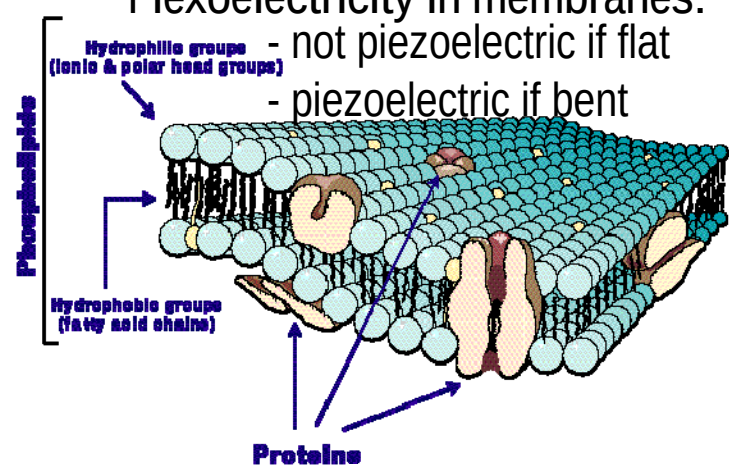


Electromechanics of composites and complex materials:

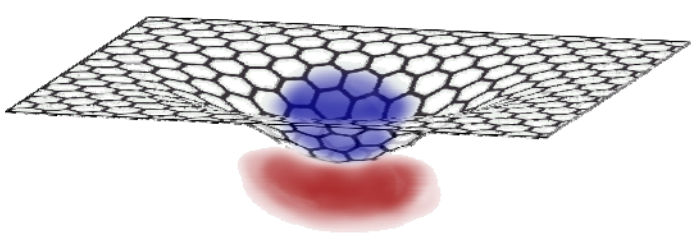
- Triboelectricity,
- Cavitation,
- Sonochemistry
- Sonoluminescence

Flexoelectricity in membranes:

- not piezoelectric if flat
- piezoelectric if bent

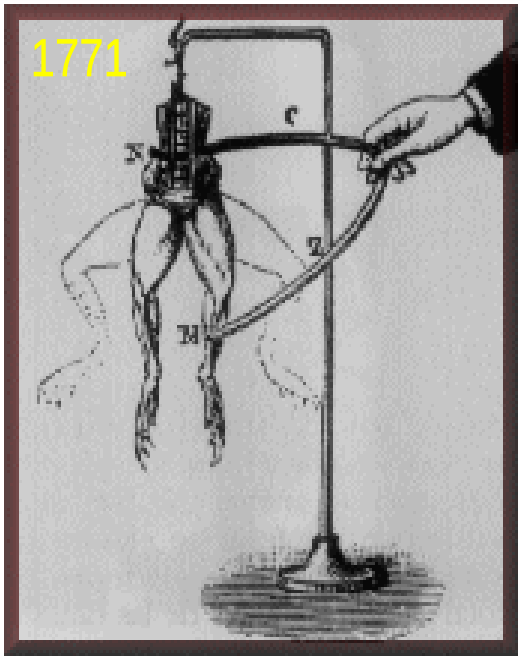



Flexoelectricity also exists in quantum systems:



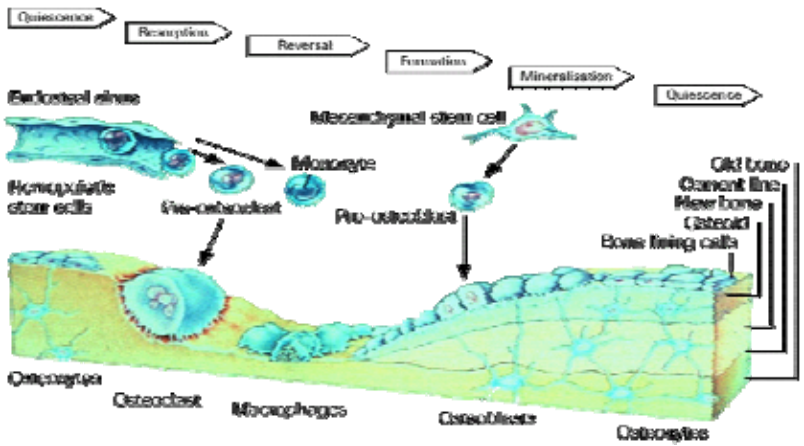
Nanoscale enables new forms of electromechanical coupling forbidden in the bulk

# Electromechanics in Biological Systems




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.

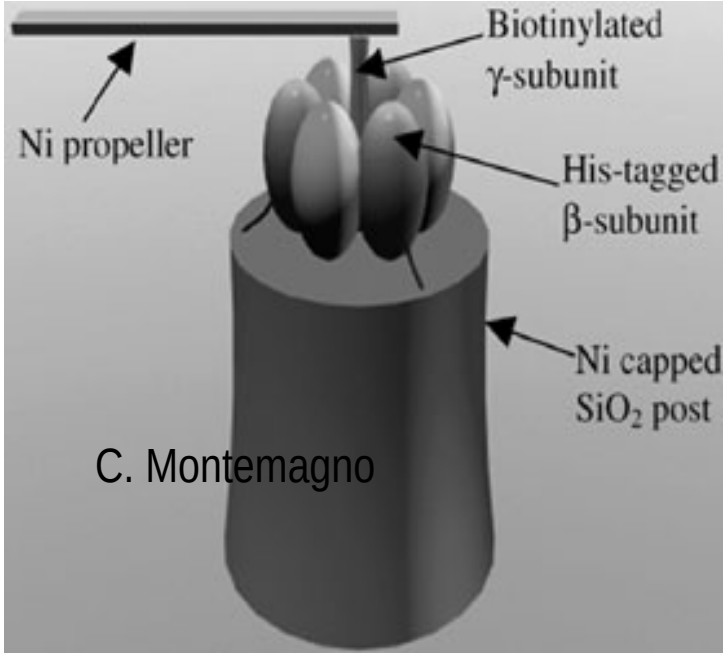


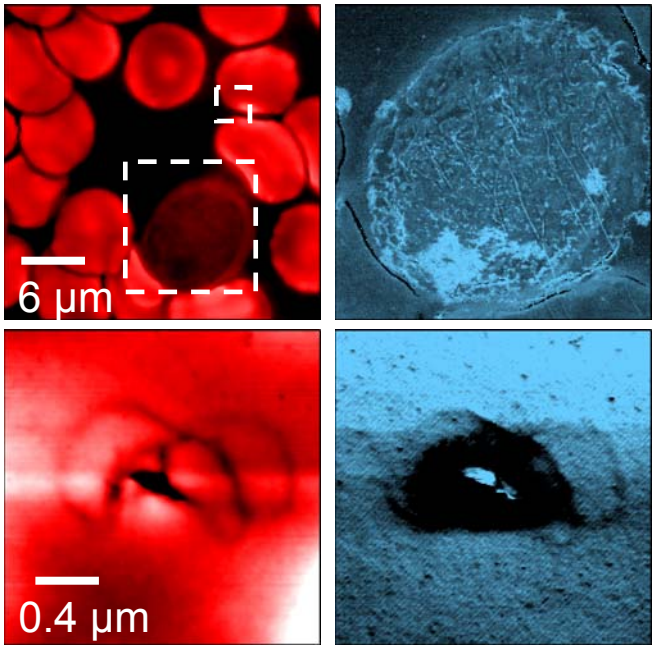

Bones remodel to respond to external stimuli (Wolff law)

- 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?

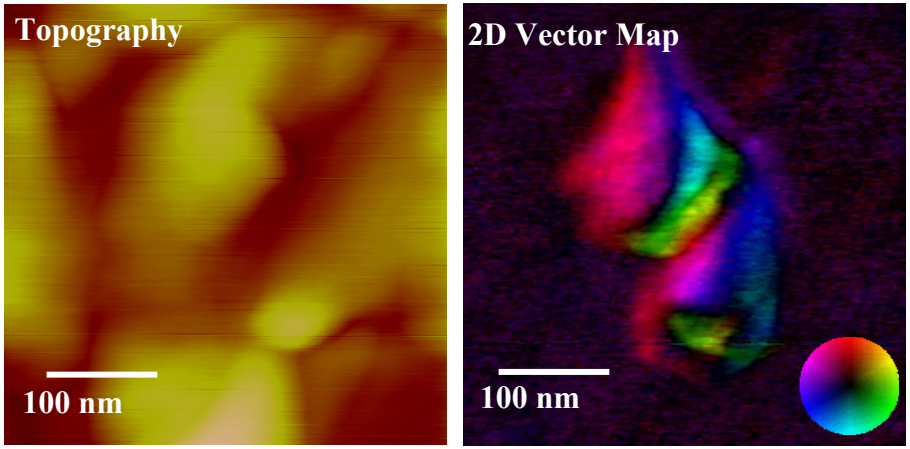
These are biological questions. However, they cannot be answered until physics of these phenomena can be studied!

# Bioelectromotors and BioPiezoelectricity




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




Piezoelectric proteins in human dentin

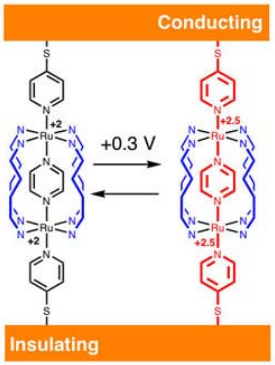
Electromechanical coupling in biomolecular systems and biologically-inspired motors

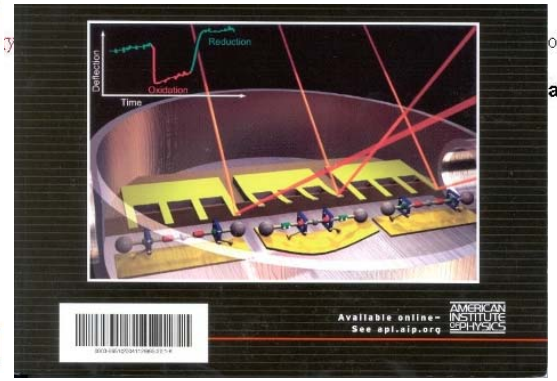
# Electromechanics on Molecular Level

REVIEW ARTICLE

## Making molecular machines work

In this review we chart recent advances in what is at once an old and very new field of endeavour — the achievement of control of motion at the molecular level including solid-state and surface-mounted rotors, and its natural progression to the development of synthetic molecular machines. Besides a discussion of design principles used to control linear and rotary motion in such molecular systems, this review will address the advances towards the construction of synthetic machines that can perform useful functions. Approaches taken by several research groups to construct wholly synthetic molecular machines and devices are compared. This will be illustrated with molecular rotors, elevators, valves, transporters, muscles and other motor functions used to develop smart materials. The demonstration of molecular machinery is highlighted through recent examples of systems capable of effecting macroscopic movement through concerted molecular motion. Several approaches to illustrate how molecular motor systems have been used to accomplish work are discussed. We will conclude with prospects for future developments in this exciting field of nanotechnology.

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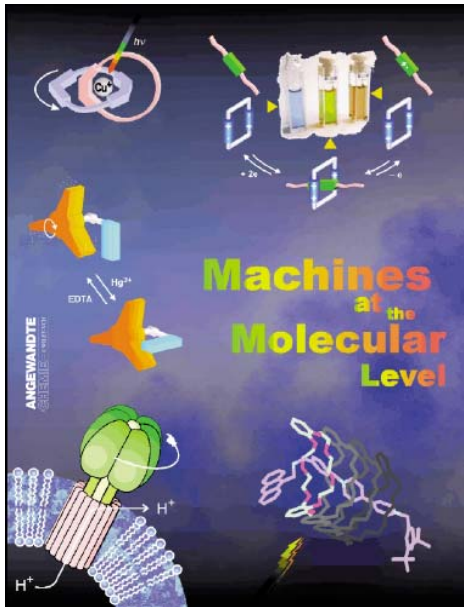
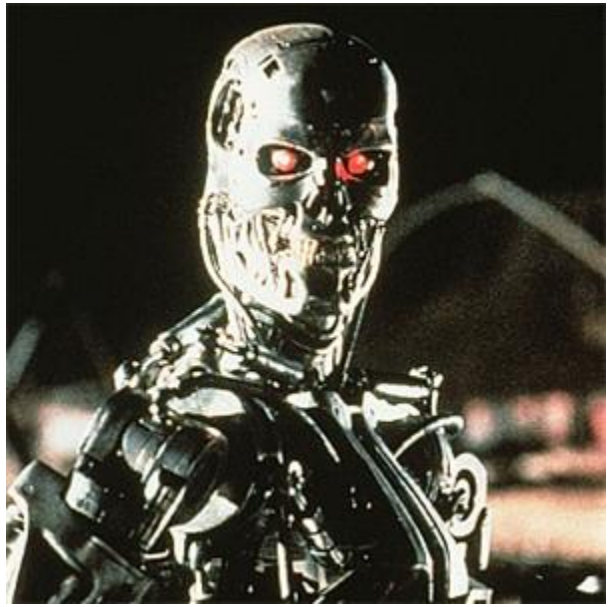
Direct electrical-mechanical conversion on molecular level

- Molecular MEMS and NEMS: fast, no reagents
- Energy harvesting
- Fundamental science

# Emerging Applications of Electromechanics



www.msnbc.msn.com/id/11858650/

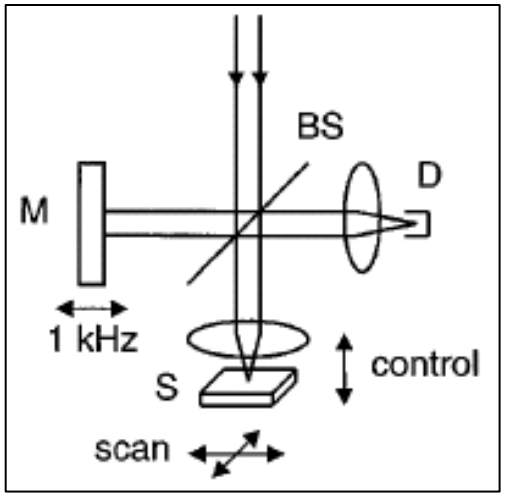


Direct electrical-mechanical conversion on molecular level

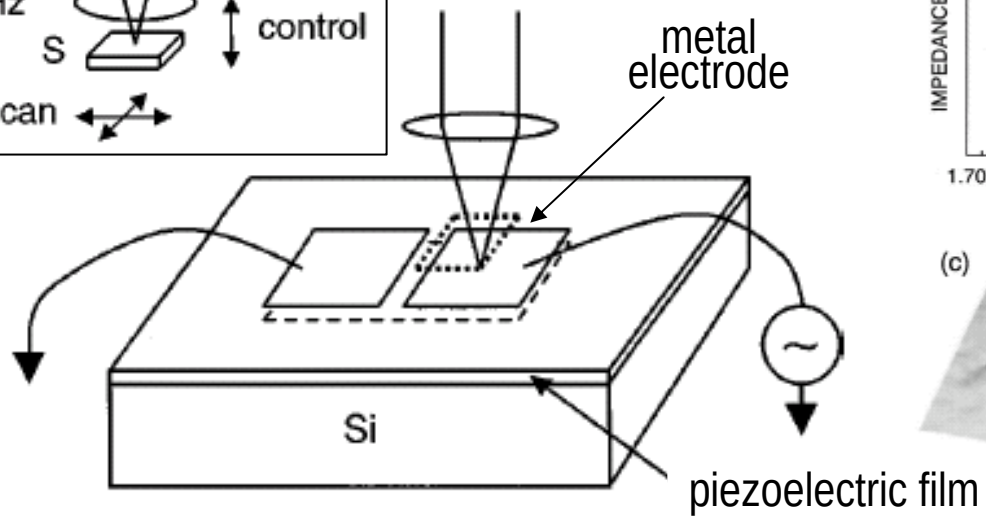
- Molecular MEMS and NEMS: fast, no reagents
- Energy harvesting
- Fundamental science

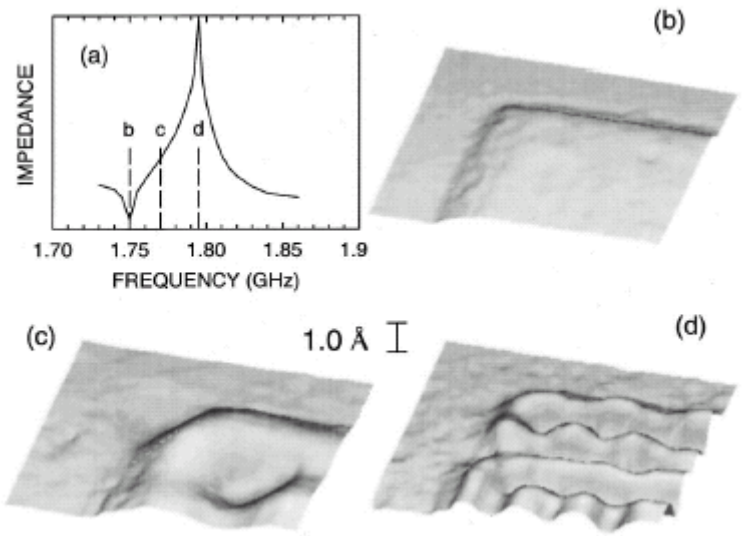
# Laser Interferometry for Ferroelectric Characterization

Michelson interferometer




- Vertical resolution – 0.003 Å
- Lateral resolution - 0.6 μm
- Frequency range <6 GHz



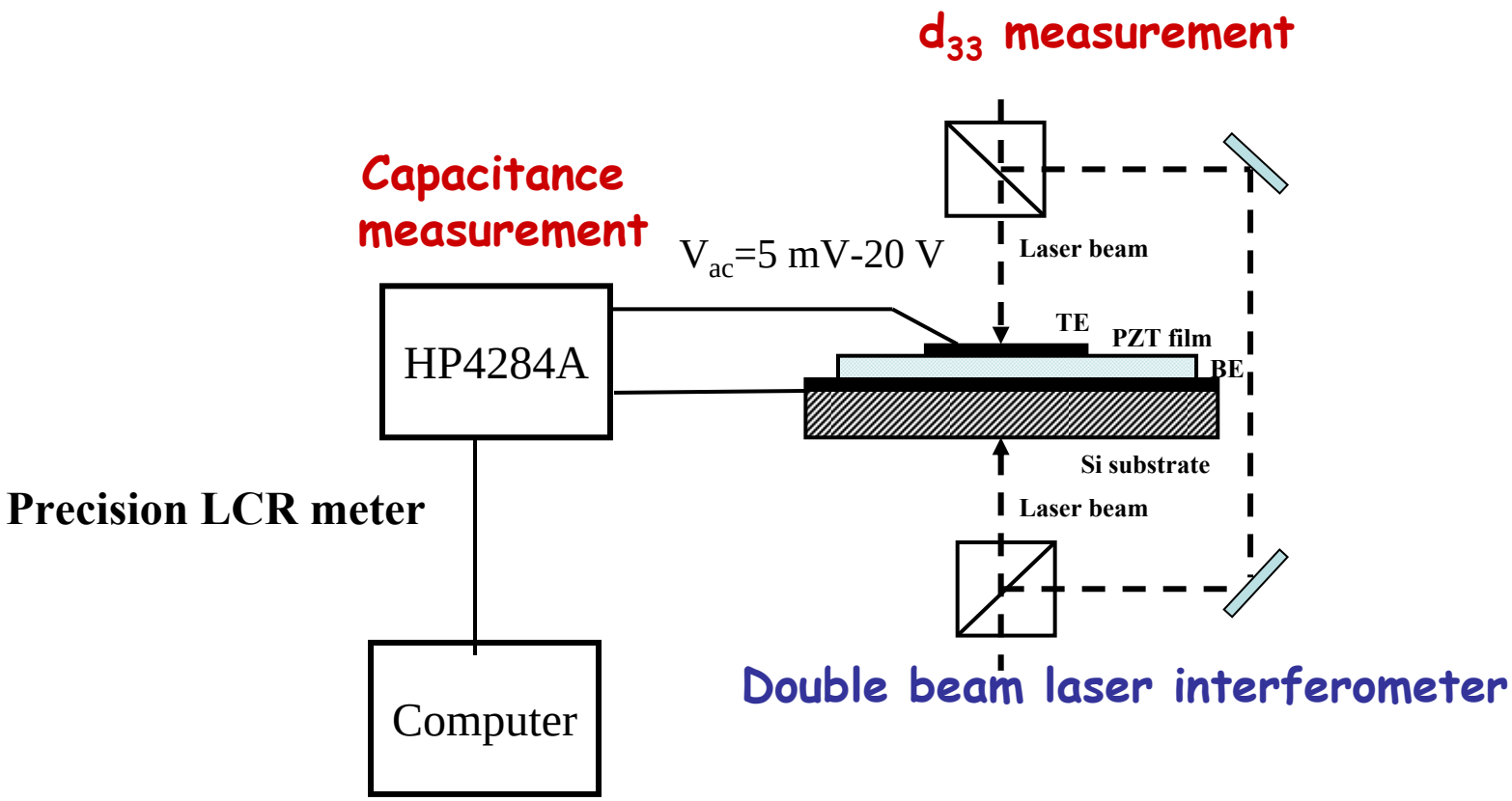




Graebner et al. Appl. Phys. Lett. 78 (2001)



Slide courtesy of A. Kholkin, U. Aveiro

# Double Beam Interferometry and Capacitance Measurements



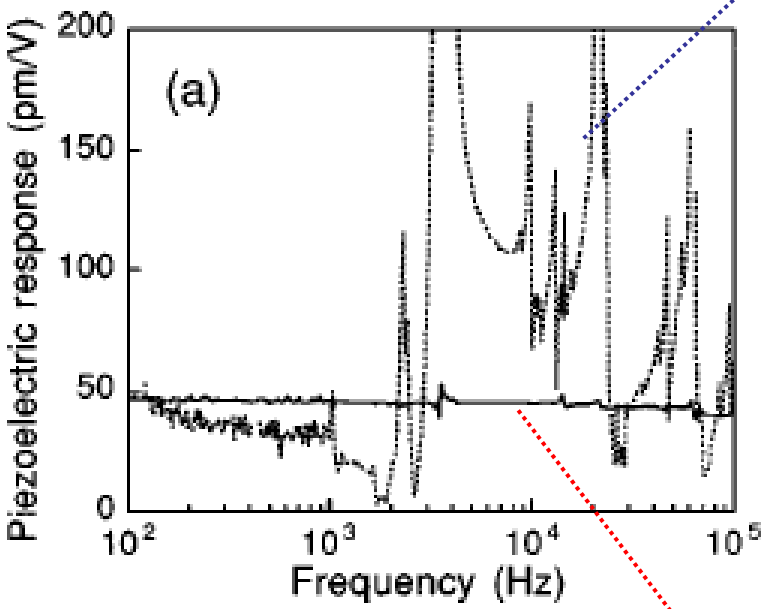

Kholkin et al., Rev. Sci. Instr. 1996

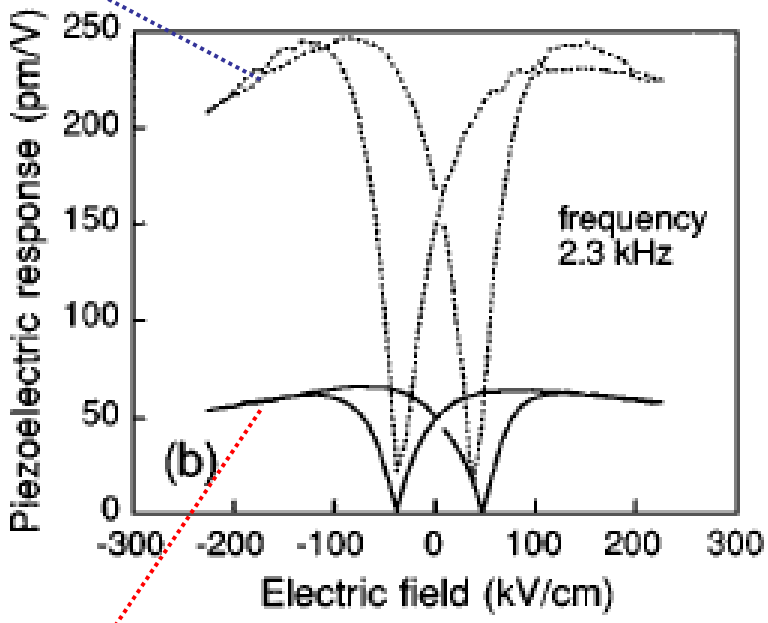


Slide courtesy of A. Kholkin, U. Aveiro

# Substrate Bending Elimination

single beam




double beam

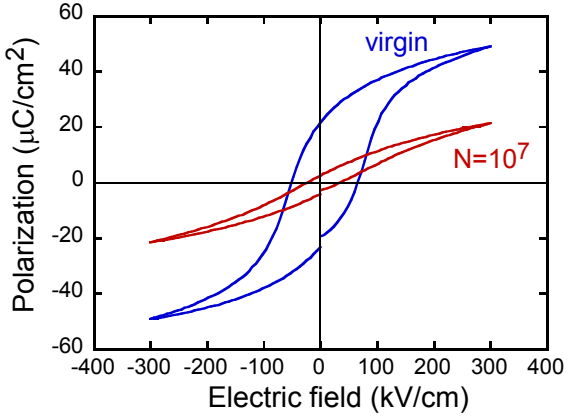
Kholkin et al., Rev. Sci. Instr. 1996



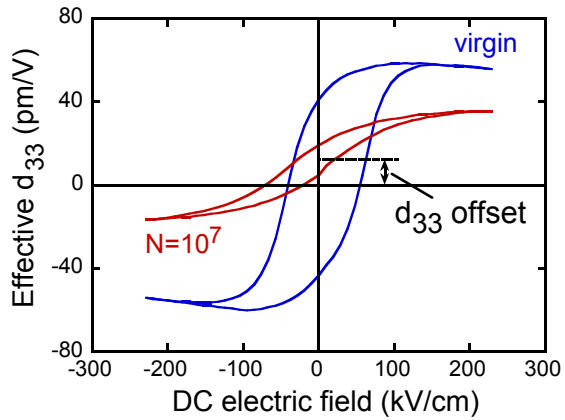
Slide courtesy of A. Kholkin, U. Aveiro

# Case Study: Ferroelectric Fatigue

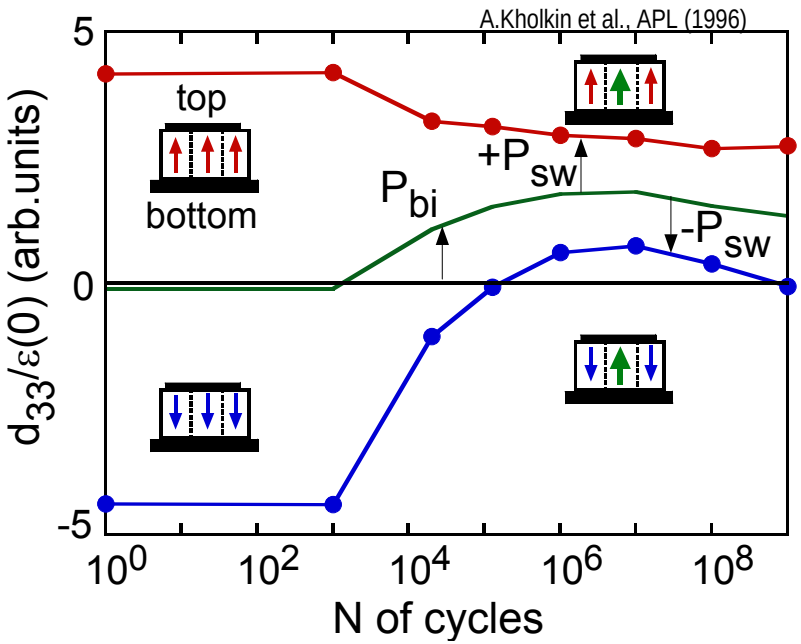
fatigue of polarization




fatigue of $d_{33}$




Polarization offset as a function of fatigue

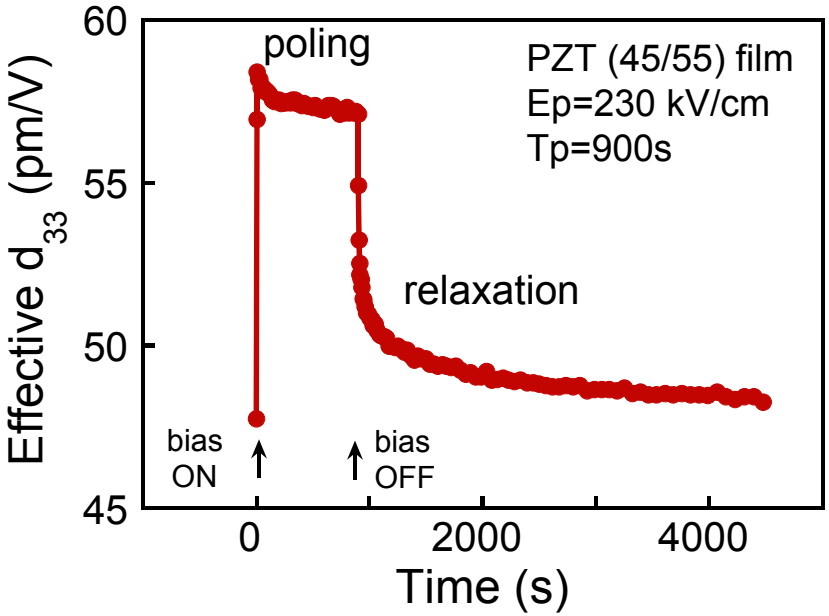


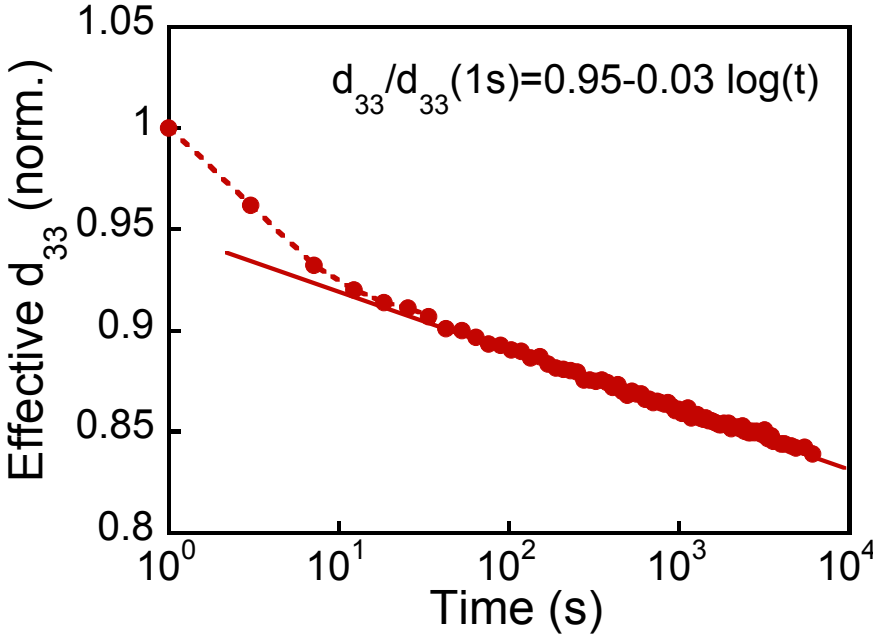

$$P_{bi}=d_{33}/(2Q_{eff}\varepsilon_0\,\varepsilon)$$

Slide courtesy of A. Kholkin, U. Aveiro

Kholkin et al Appl. Phys. Lett. (1996)

# Case Study II: Aging After Poling



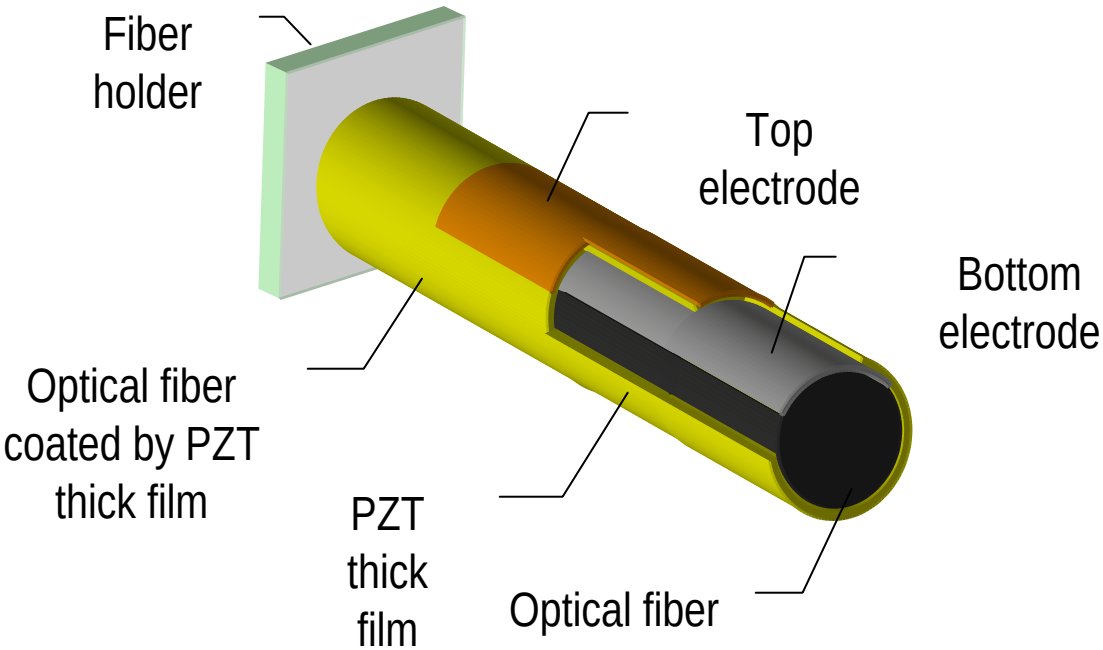




- two stages of $d_{33}$ relaxation: fast depoling and slow logarithmic decrease
- aging rates ≈ 2÷5 %/dec depending on poling time

A.Kholkin et al., Inegr. Ferroelectr. (1997)

Slide courtesy of A. Kholkin, U. Aveiro

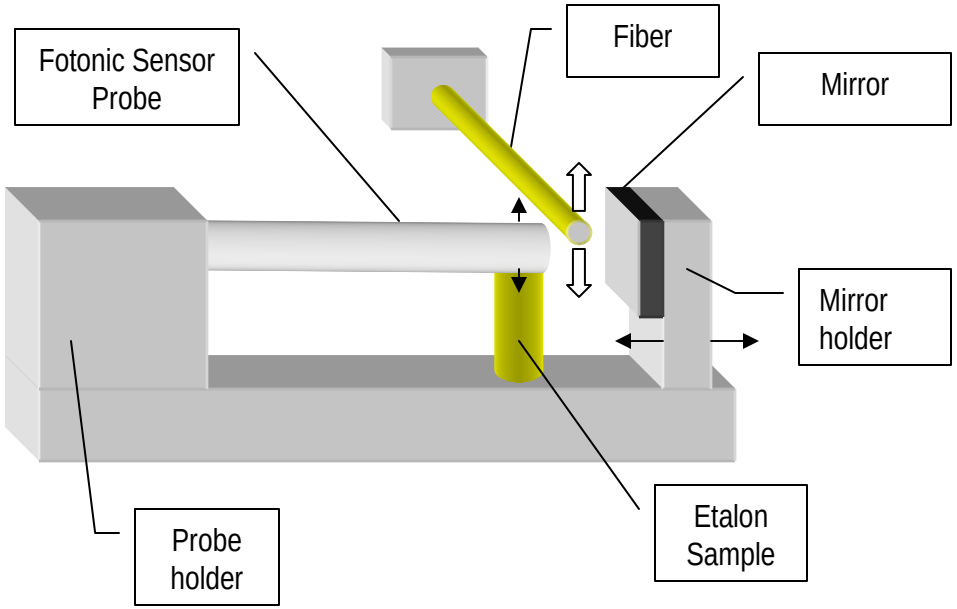
# Alternatives: Fiber Optic Cantilever Beam

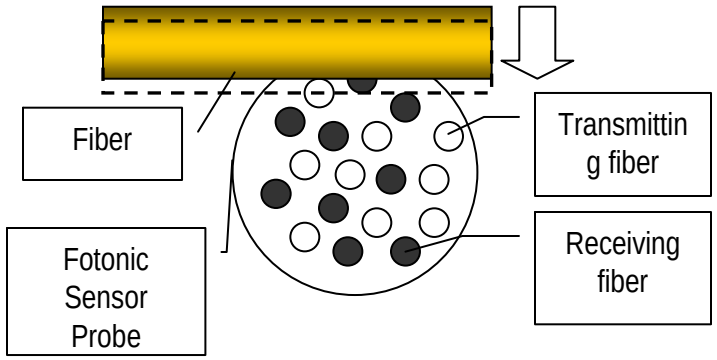



Slide courtesy of A. Kholkin, U. Aveiro

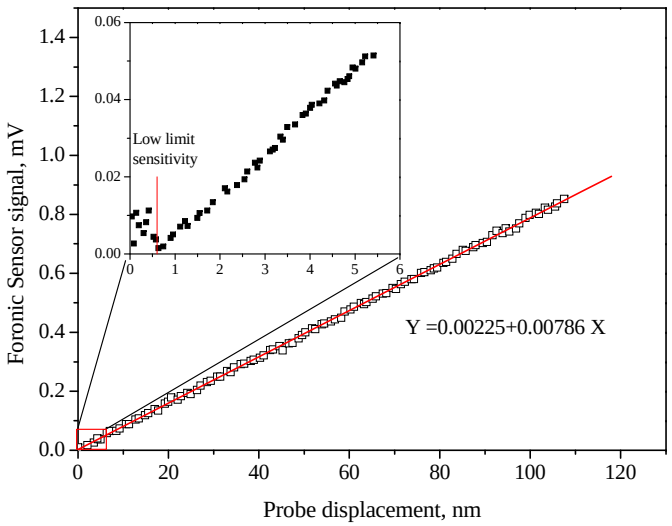
# Fiber Optic Cantilever Beam

The working configuration of Fotonic Sensor probe and studied fiber. Motion of the fiber down leads to shading of light transmitting and receiving fibers




Configuration of Fotonic Sensor probe, mirror and piezoelectric fiber sample for electromechanical measurement of fiber displacements.



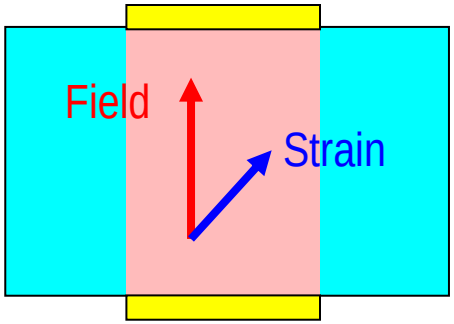

AC-field dependence of displacements

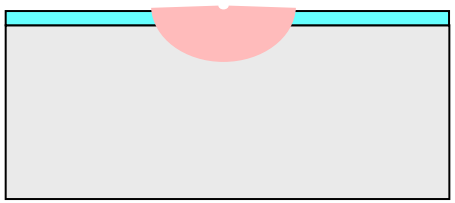
N. Vyshatko, P. Vilarinho, A. L. Kholkin, Rev. Sci. Instr. 78, 015107 (2008)

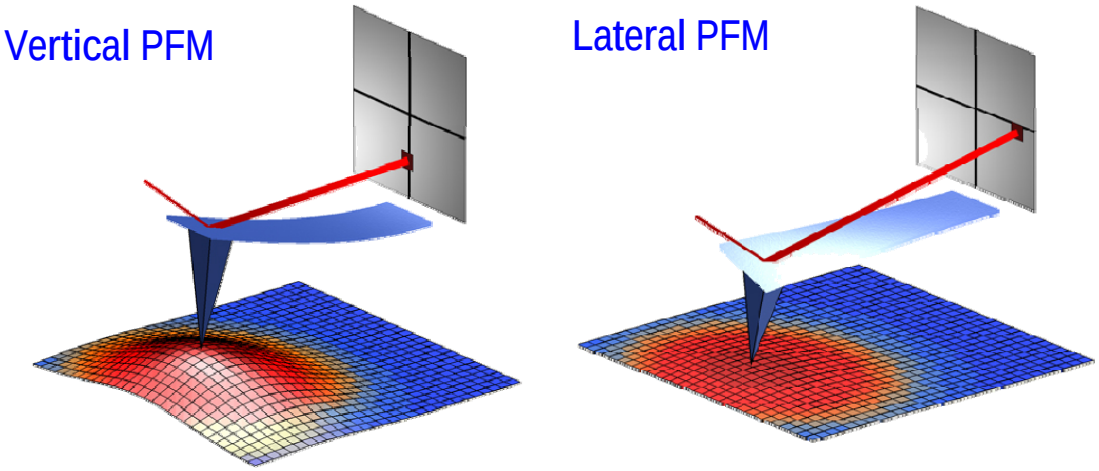
Slide courtesy of A. Kholkin, U. Aveiro

# Probing NanoElectromechanics

In macroscopic systems, we measure response to the uniform external field (interferometry, etc)






*Piezoresponse Force Microscopy*

Application of AC bias to the tip

$V_{tip} = V_{dc} + V_{ac}\cos(\omega t)$

results in cantilever deflection

$d = d_0 + A(\omega, V_{dc}) V_{ac} \cos(\omega t + \varphi)$

due to piezoelectric effect

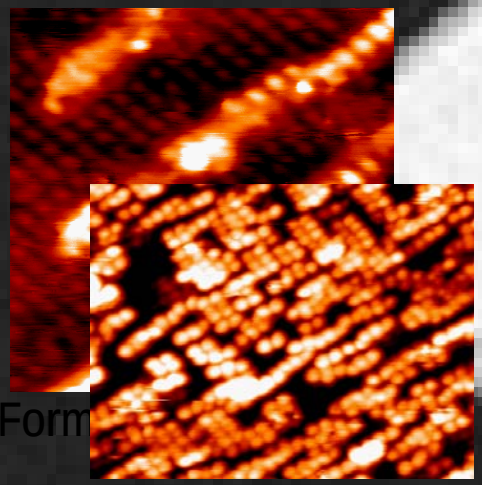
In nanoscale systems, we need

- Displacements of order of ~pm
- Currents of order of ~fA
- Length scales of ~1-10 nm

*PFM = Nanoelectromechanics*

# Philosophy of SPM

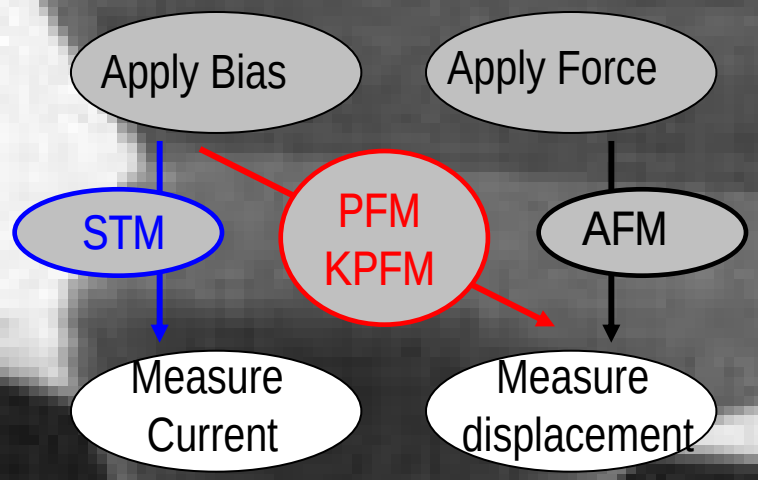
## Current techniques



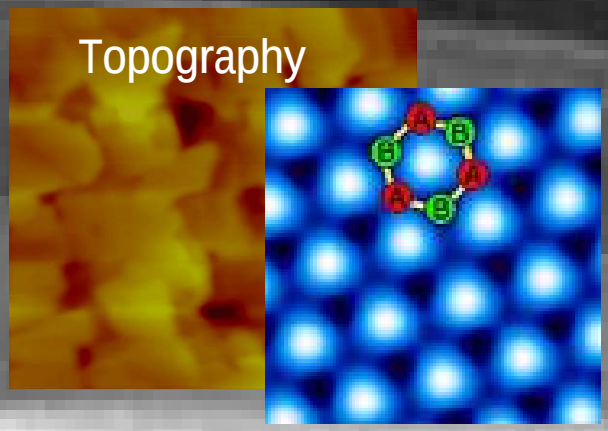
Form

$SrRuO_3$ (100)

- Atomic resolution imaging
- Spin-polarized imaging
- Vibrational spectroscopy



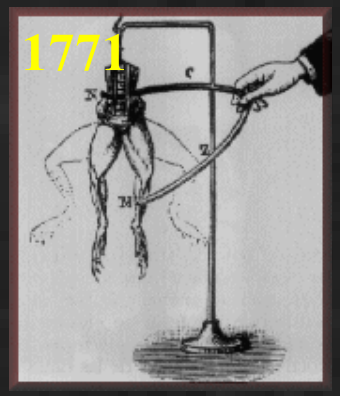

## Force techniques

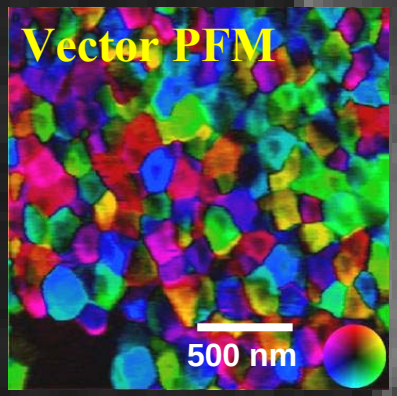


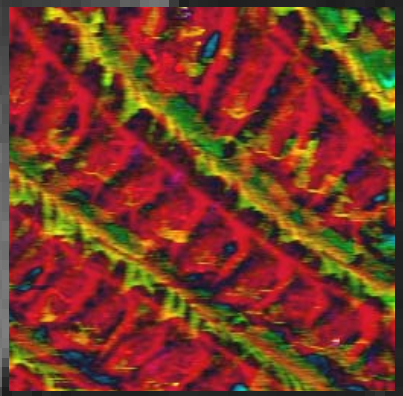

www.nanoscience.de

- Topography
- Adhesion
- Elasticity
- Magnetism

## Electromechanical techniques



- Imaging polar materials
- Local bias-induced transitions
- Biomaterials
- Spectroscopy

# Philosophy of SPM

## Current techniques

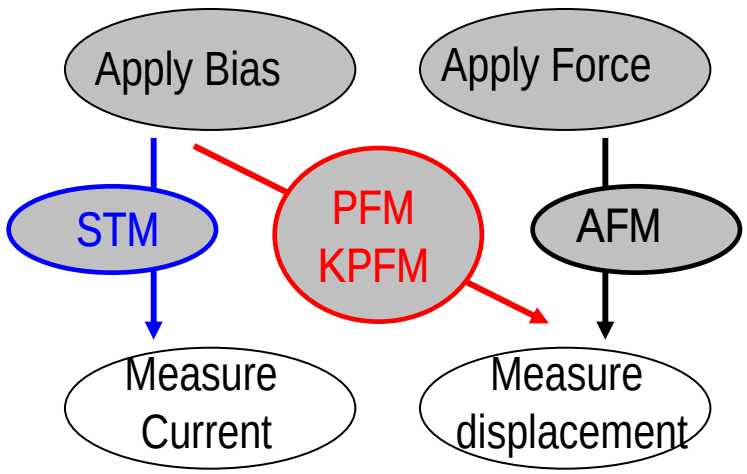
$$I = \Sigma V$$

Conductance scales as:

$\Sigma \sim a^1$ Classical

$\Sigma \sim a^2$ Sharvin

$\Sigma \sim a^0$ Tunneling




## Force techniques

Couples to vertical

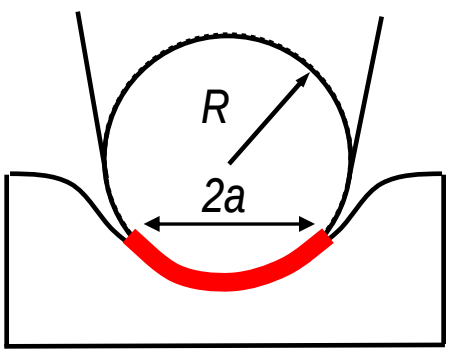
$$\begin{pmatrix} w_1 \\ w_2 \\ w_3 \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} F_1 \\ F_2 \\ F_3 \end{pmatrix}$$

Lateral AFM Vertical AFM

Contact stiffnesses scale as:

$a_{ij} \sim a^1$ Classical

$a_{ij} \sim a^0$ Single atom/molecule




## Electromechanical techniques

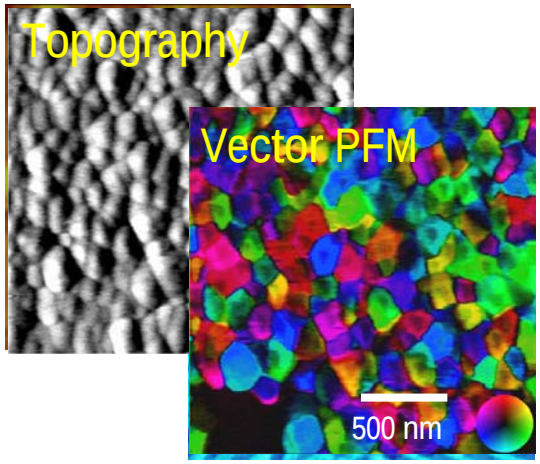
$$\begin{pmatrix} w_1 \\ w_2 \\ w_3 \end{pmatrix} = \begin{pmatrix} d_{34} \\ d_{35} \\ d_{33} \end{pmatrix} V$$

Responses scales as:

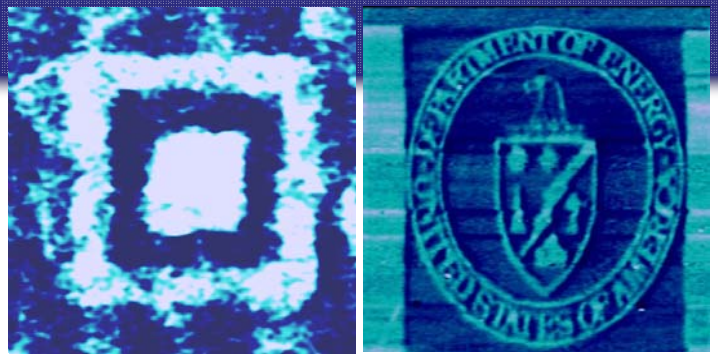
$d_{ij} \sim a^0$ Classical

$d_{ij} \sim ?$ Quantum limit

PFM is complementary to STM and AFM in terms of imaging mechanism!

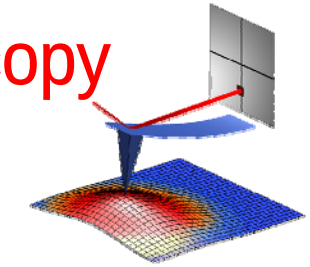


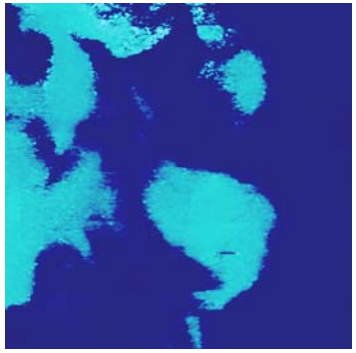

Domain imaging



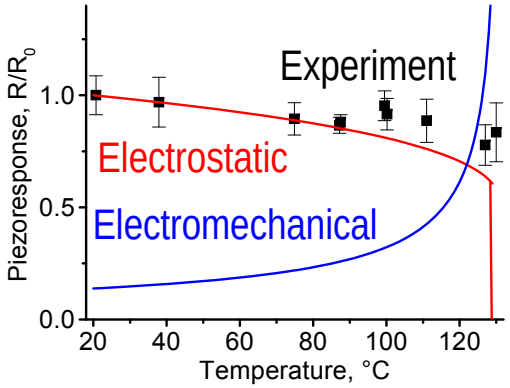
Domain writing

# Piezoresponse Force Microscopy

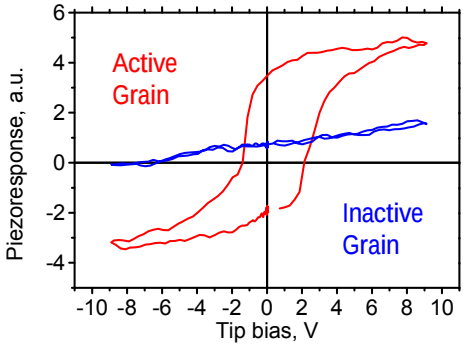




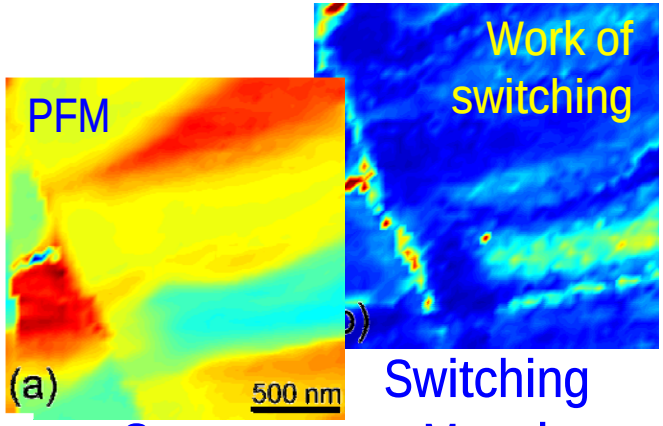
Domain dynamics and evolution




Temperature dynamics and phase transitions




PFM spectroscopy

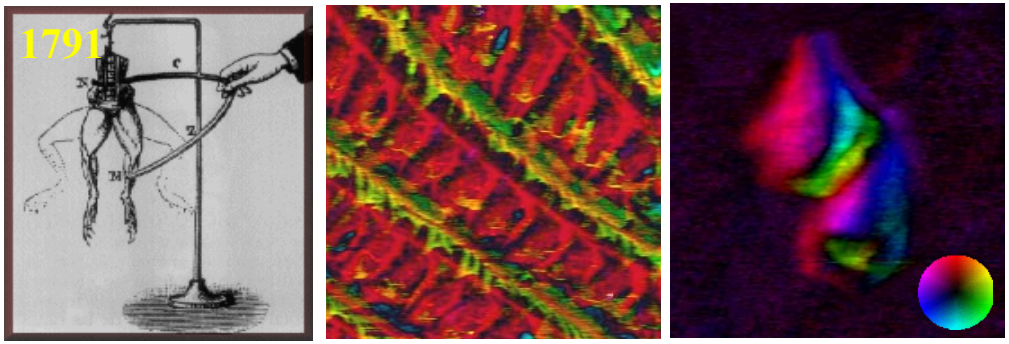



Switching Spectroscopy Mapping

# Electromechanical Coupling Beyond the Ferroelectrics

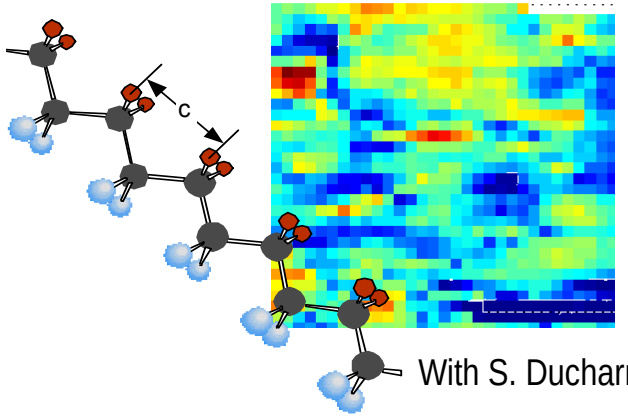
- In a decade, PFM has become the primary tool for characterization of ferroelectrics ($d_{eff}$ ~ 50-500 pm/V).
- Recently, PFM was extended to III-V semiconductors and and biopolymers ($d_{eff}$ ~ 1-10 pm/V).
- Sensitivity sufficient to probe single chemical bond!

*Imaging of calcified tissues*



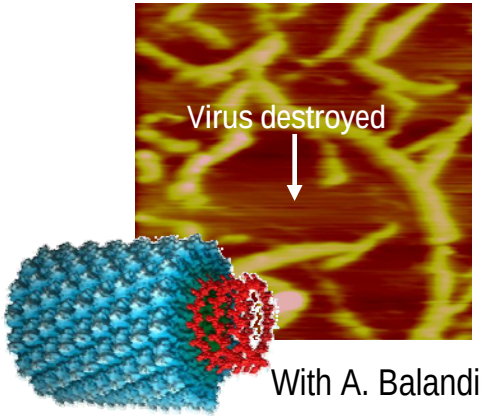

B.J. Rodriguez

*Ferroelectric polymers*



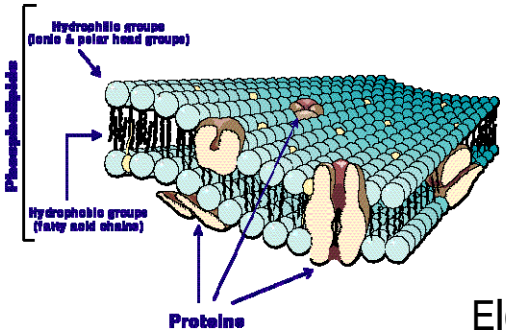

With S. Ducharme, UNL

*Electrical modification of TMV*

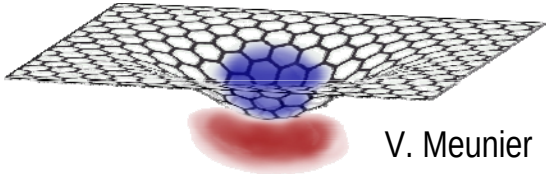



With A. Balandin, UCR

Membrane Flexoelectricity

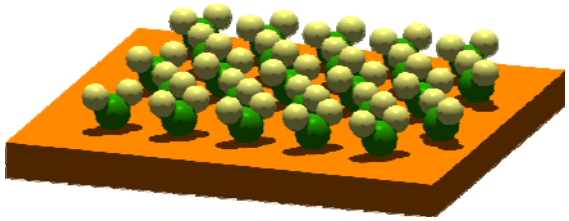



Quantum Flexoelectricity



V. Meunier
S.V. Kalinin

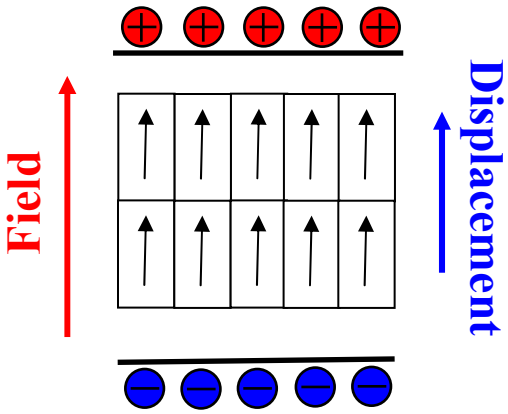
Surface piezoelectricity:
- Ordered dipolar water layers
- Polar surfaces



Electromechanics of complex materials:
- Triboelectricity,
- Cavitation,
- Sonochemistry
- Sonoluminescence

# Principles of Orientational Imaging

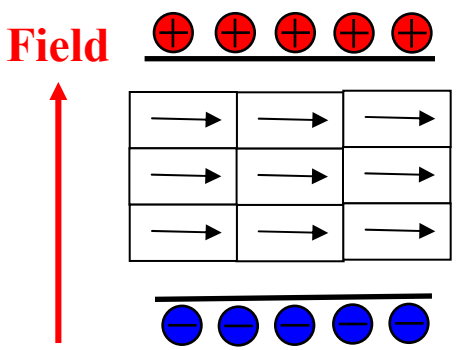
**Experiment:** measure the mechanical displacement in the applied electric field direction

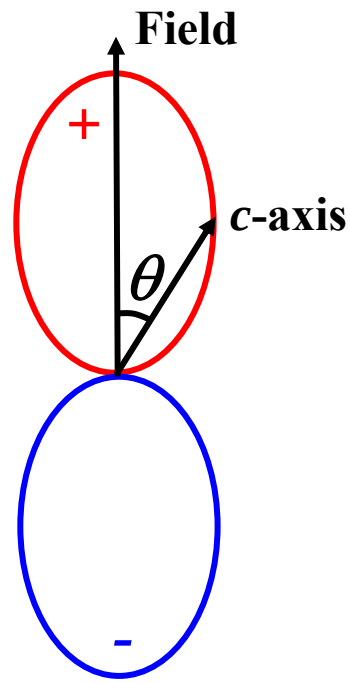



For tetragonal ferroelectric such as $BaTiO_3$, if the field is **parallel** to the c-axis, there is strong deformation of the crystal in the field direction

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

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



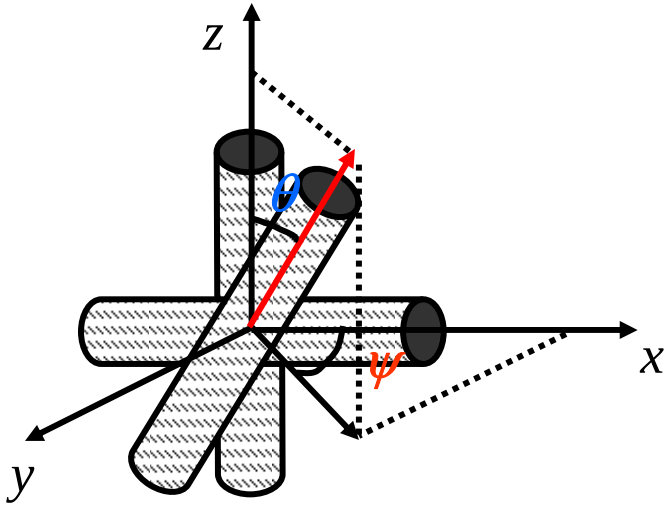

**In the general case:**

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

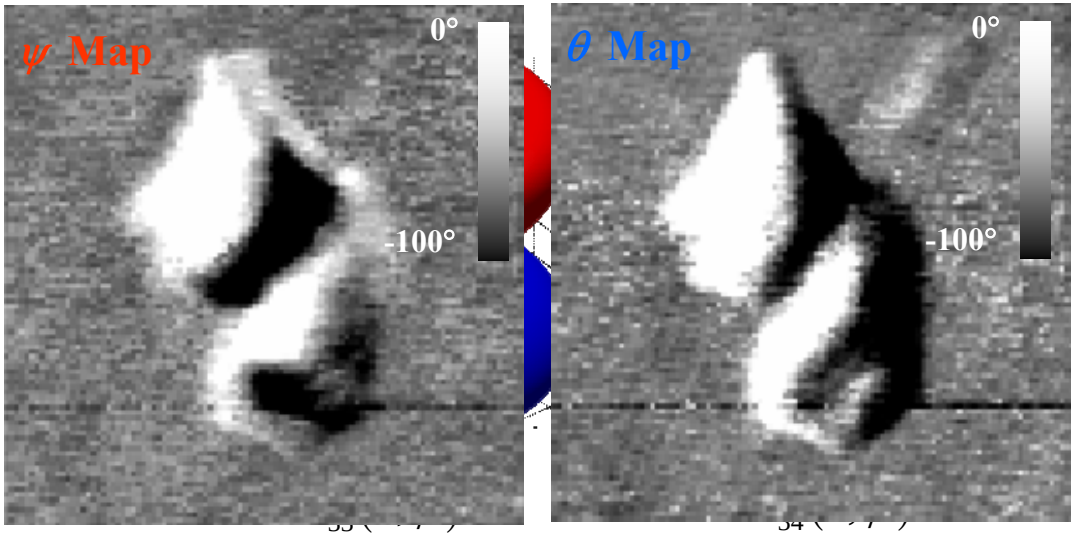
**From known electromechanical response, we can determine crystal orientation!**

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

# Molecular Orientation from PFM




**Semiquantitative Orientation Maps for Collagen Fibril Piezoresponse Surfaces for Collagen**




**Tetragonal material (4mm):**

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

**Vertical PFM**

**Lateral PFM (x)**

**Lateral PFM (y)**

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

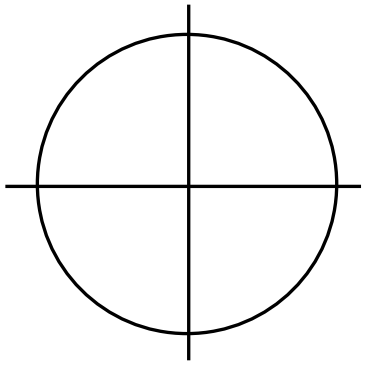
$d_{ij}$ Piezotensor – lab coordinate system

$d_{kl}^{o}$ Piezotensor – crystal coordinate system

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

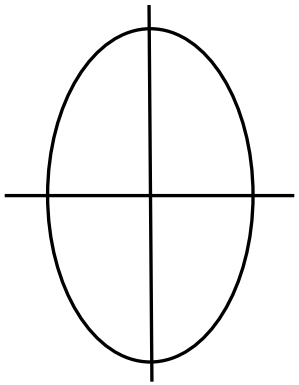
# Are there Alternatives?

***Scalar***



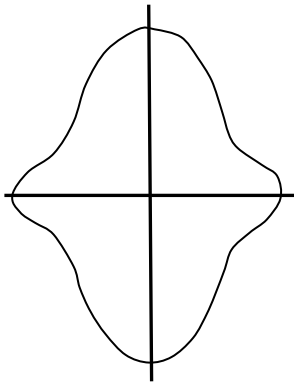
***Temperature, Potential, etc.***

***2nd order tensor***



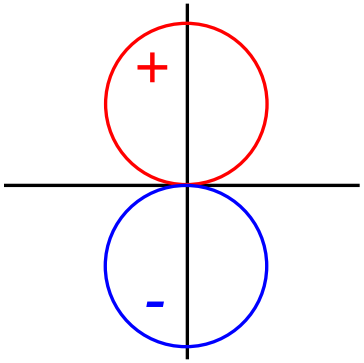
***Dielectric constant***
***Thermal conductivity***

***4th order tensor***



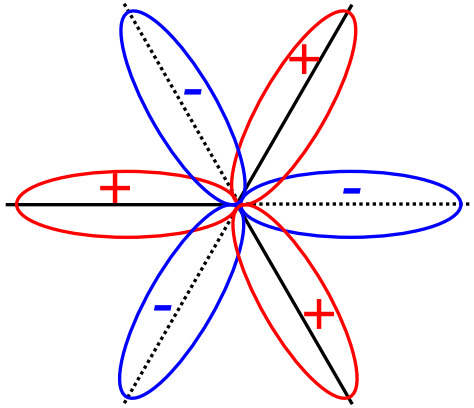
***Elasticity, Kerr effect***
***Electrostriction***

***Vector***




***Polarization***
***Magnetization***
***Pyroelectricity***

***3d order tensor***



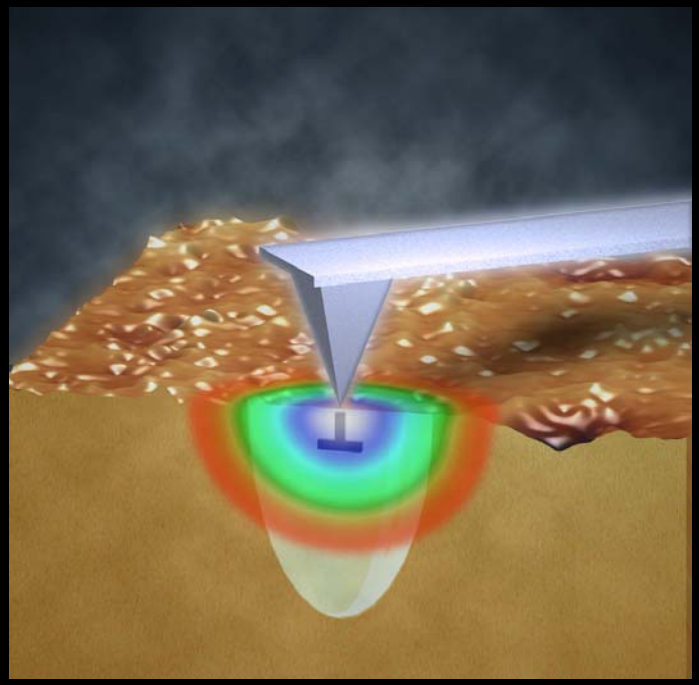

***Piezoelectricity***
***Electrooptics, SHG***

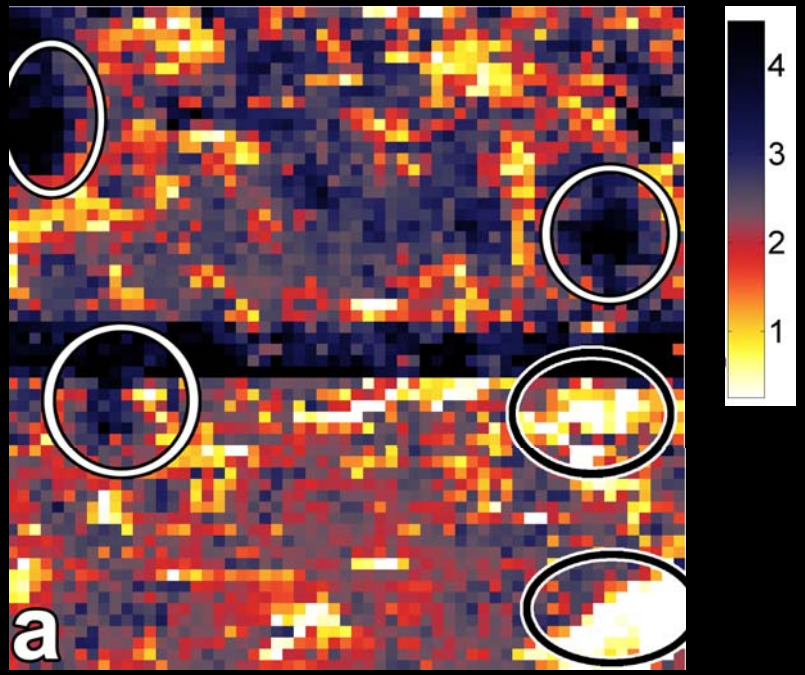
Electromechanical coupling coefficient can be measured by SPM with sub 10 nanometer resolution. Measurements are not sensitive to tip geometry, unlike elastic and dielectric measurements

# The hunt for the Snark: Imaging Nucleation Centers

- Macroscopic switching is determined by local switching centers (Landauer)
- From activation energies, centers should be well below 10 nm in size
- Centers will also affect local hysteresis loops and can be detected from local nucleation voltage

**Map of Nucleation Bias**



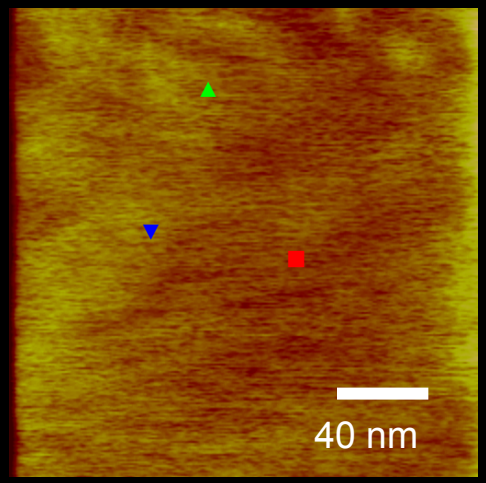



Nature Materials, March 2008

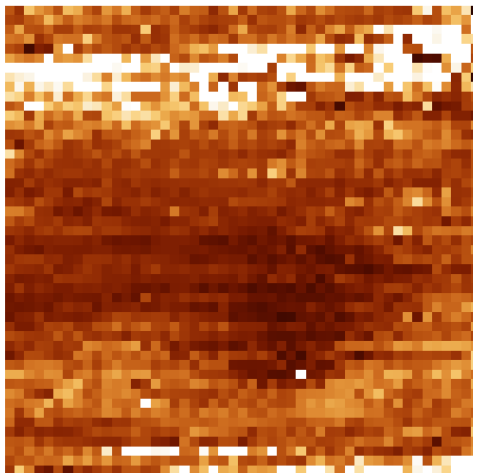
Nucleation bias maps yield information on spatial and energy distribution of switching centers and random bond / random field disorder potentials

# Hysteresis Loop Fine Structure: Imaging a Single Nucleation Center

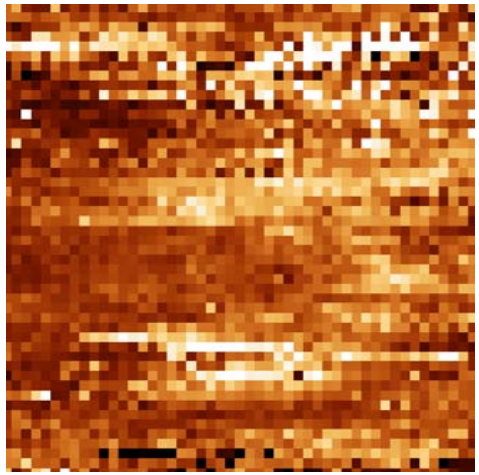
Topography

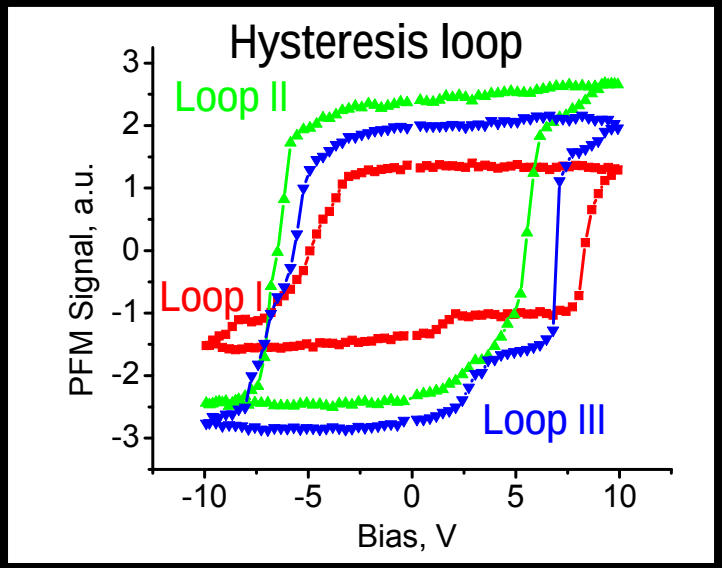


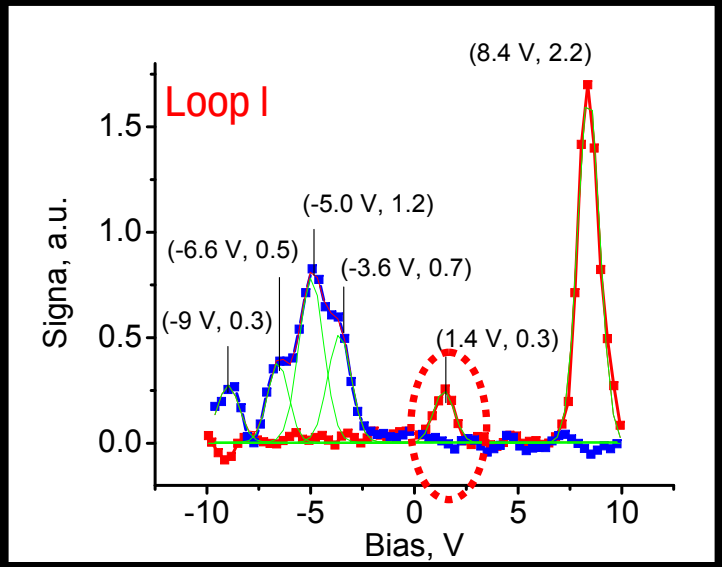

Nucleation bias map



Fine Structure Intensity Map





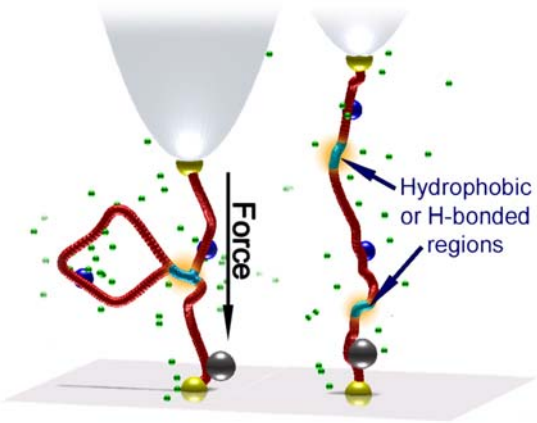

Thermodynamics and kinetics of phase transitions on a single defect level.

Phys. Rev. Lett. in print

# Future: Bias Induced Transformations

## Force-Induced Transitions

### Unfolding spectroscopy

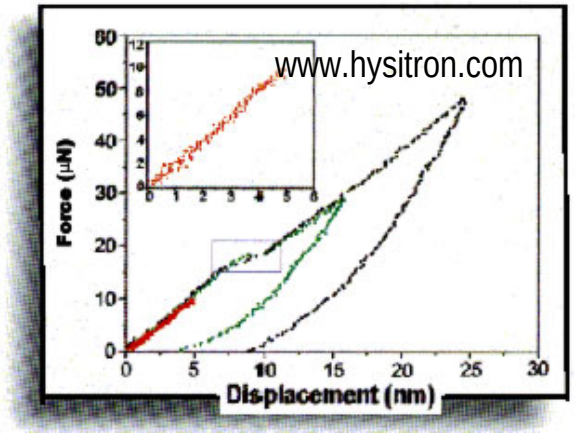



- Energies ~ kT: stochastic
- Reversible
- Only one parameter measured
- Need molecule hunting

**Single-molecule reactions**

- Thermodynamics
- Kinetics
- Statistical physics

### Nanoindentation

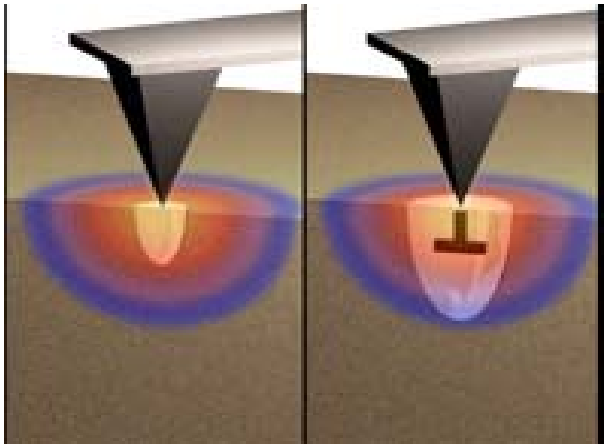



- Energies >> kT: deterministic
- (partially) Irreversible
- Only one parameter measured
- Strongly invasive

**Nanomechanics**

- Dislocation dynamics
- Pressure-induced transitions
- Cracking, etc

## Bias-induced transitions



- Energies either >> kT or ~kT
- Can be reversible
- Many parameters can be measured

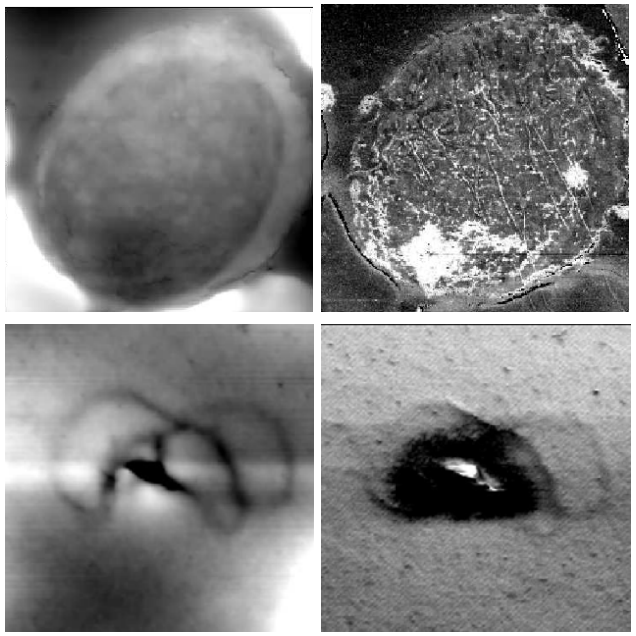
**Nanoelectromechanics**

- Polarization switching
- Electrochemical reactions
- Soft condensed matter
  - polyelectrolytes
  - biosystems
  - liquid crystals

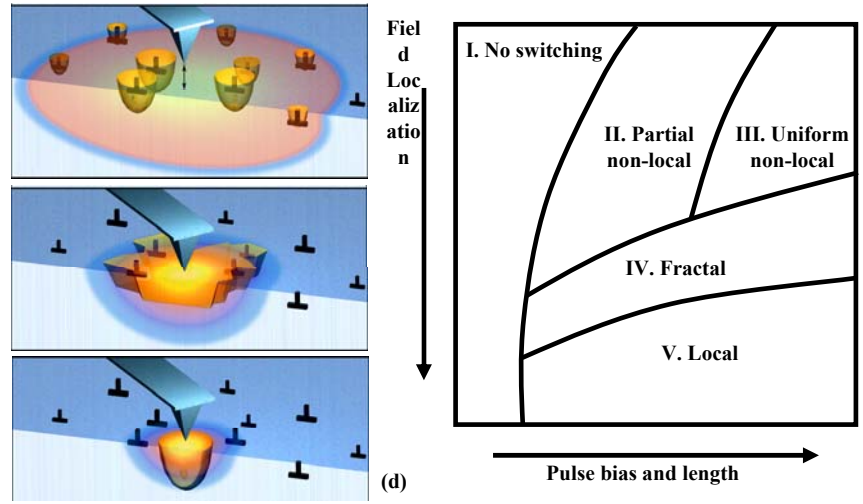
**Enabling tools in nanobiology and nanomechanics**

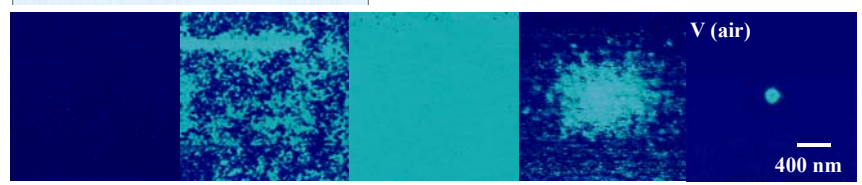
# Electromechanics in Biological Systems

## Blood cells (with Asylum Research)

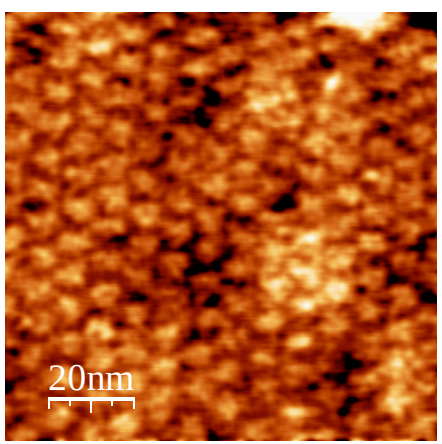


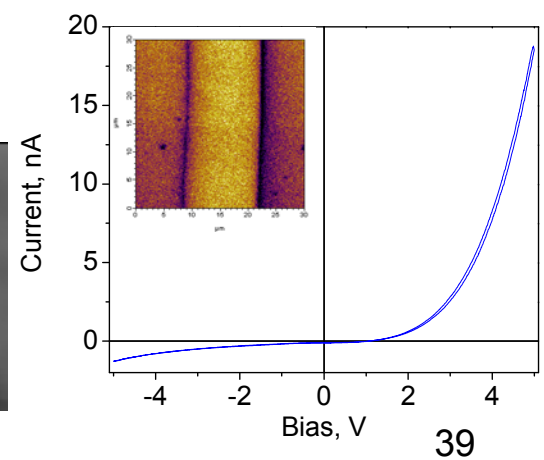
## Problems in liquid Imaging



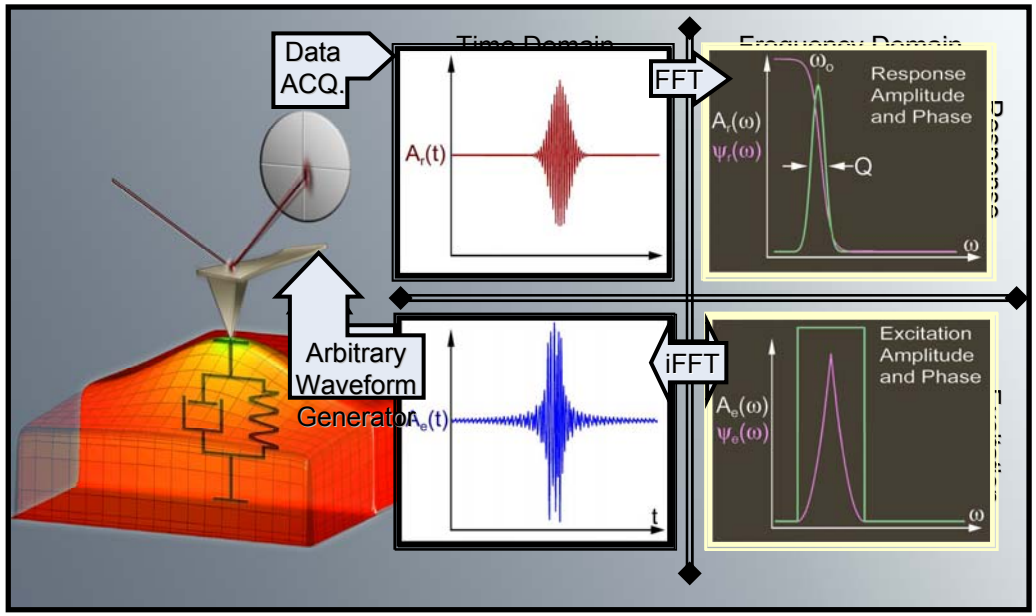

## Solution: Insulated Probes (P. Rack)



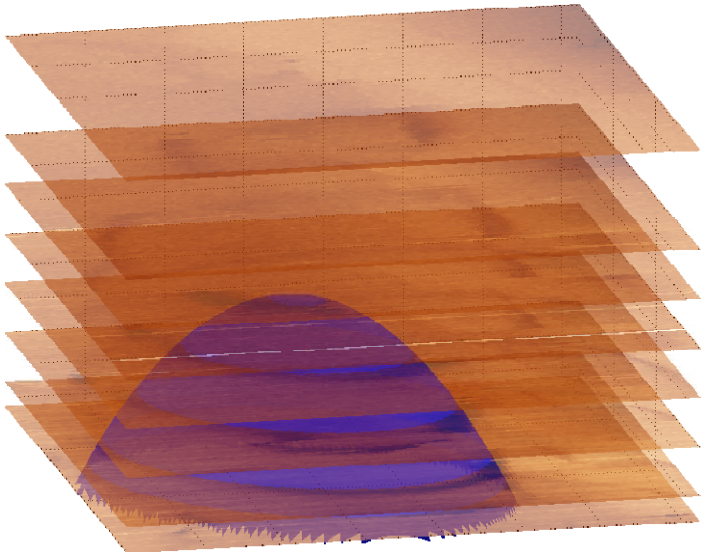


# Resonance Enhancement in PFM: Band-Excitation SPM

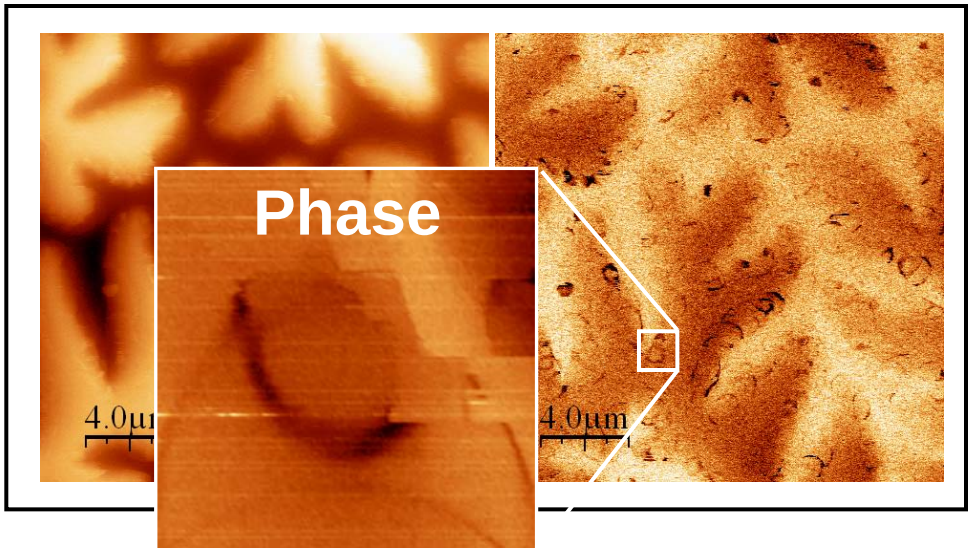
## Band Excitation Principle



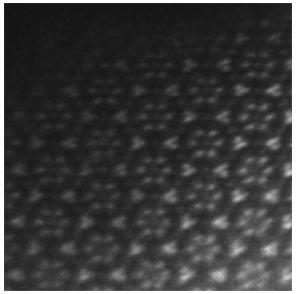

## Height Slices



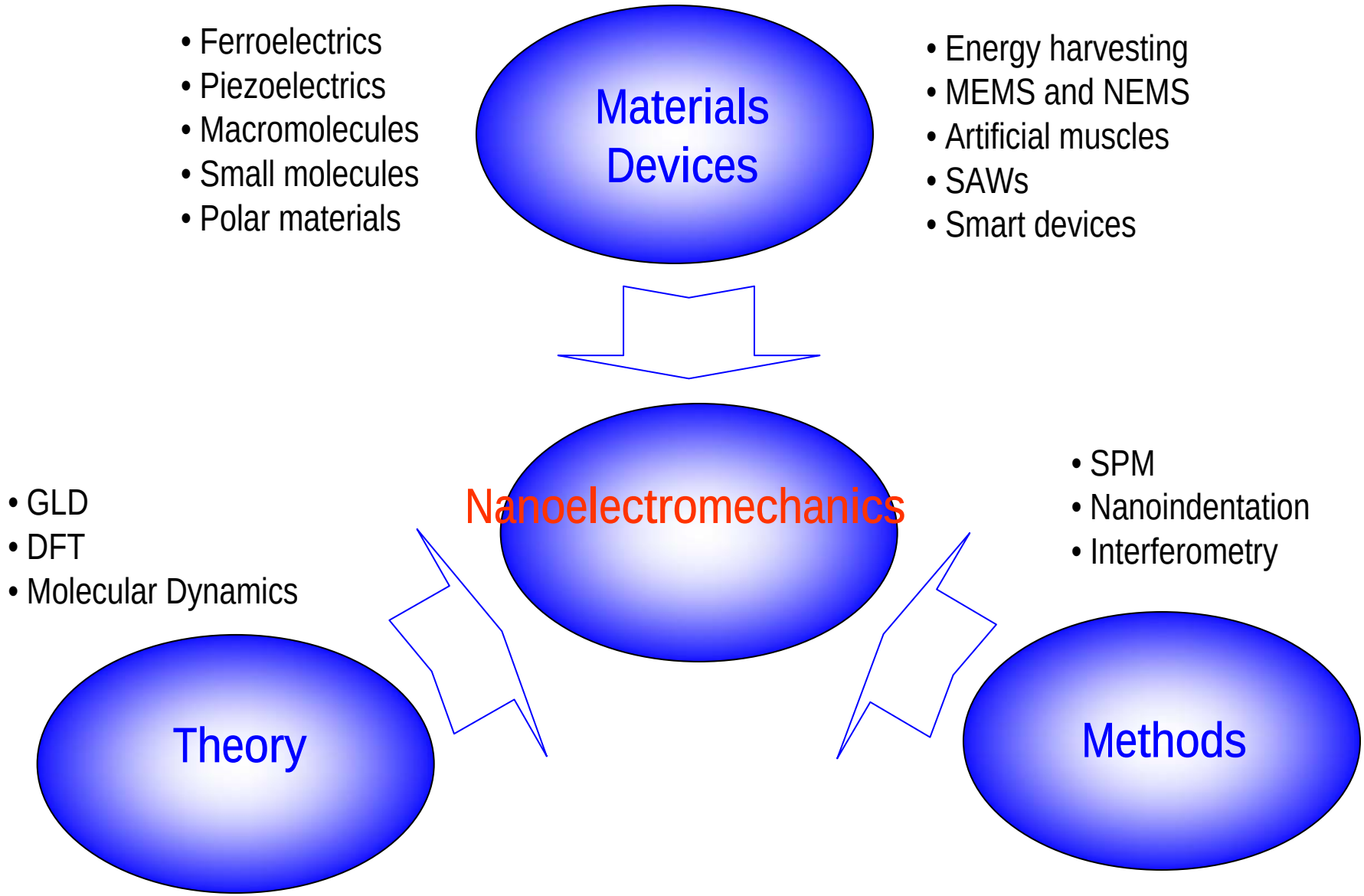
## Magnetic Dissipation in Garnet



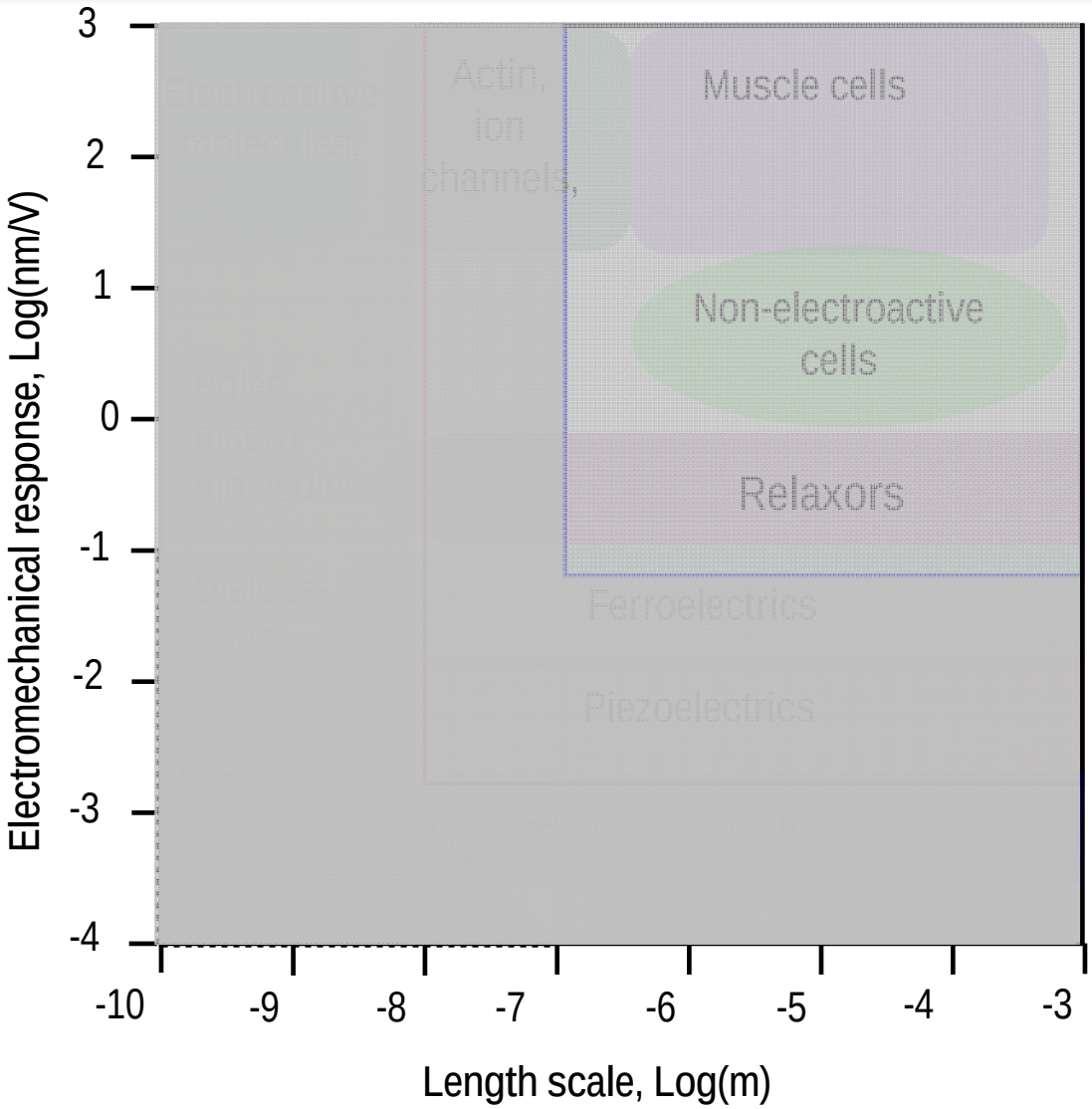

## Next step: what are the defects?



- STEM (Pennycook)
- Lorentz Microscopy (ANL)
- Modelling (Stocks)


• Ferroelectrics
• Piezoelectrics
• Macromolecules
• Small molecules
• Polar materials
Materials
Devices
• Energy harvesting
• MEMS and NEMS
• Artificial muscles
• SAWs
• Smart devices
Nanoelectromechanics
• GLD
• DFT
• Molecular Dynamics
Theory
• SPM
• Nanoindentation
• Interferometry
Methods

# Roadmap for Nanoelectromechanics




Sensitivity and resolution for nanoindentation

Sensitivity and resolution for Scanning Probe Microscopy

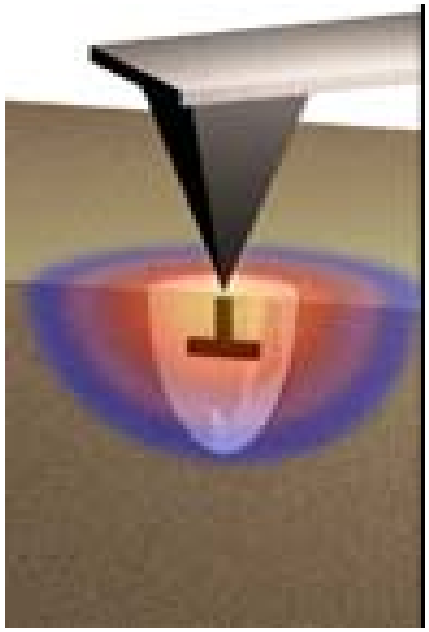
Theoretical limits are well below!

- Resonance enhancement
- UHV/Low T platforms
- Liquid environment
- Small levers
- Low-noise laser sources

Scientific need drives instrumentation development!

# Future PFM Development

In a decade, PFM has become the primary tool for characterization of ferroelectrics ($d_{eff}$ ~ 50-500 pm/V).
Recently, PFM was extended to III-V semiconductors and and biopolymers ($d_{eff}$ ~ 1-10 pm/V).
Sensitivity sufficient to probe single chemical bond!



## PFM Development vectors

Quantitativeness:

- development of probes with well controlled geometries
- understanding of probe dynamics

Resolution: pushing resolution to molecular and atomic scales

Bandwidth: dynamic processes

Sensitivity: weak coupling, or voltage dependent phenomena

Environments: operation in aqueous and liquid environments

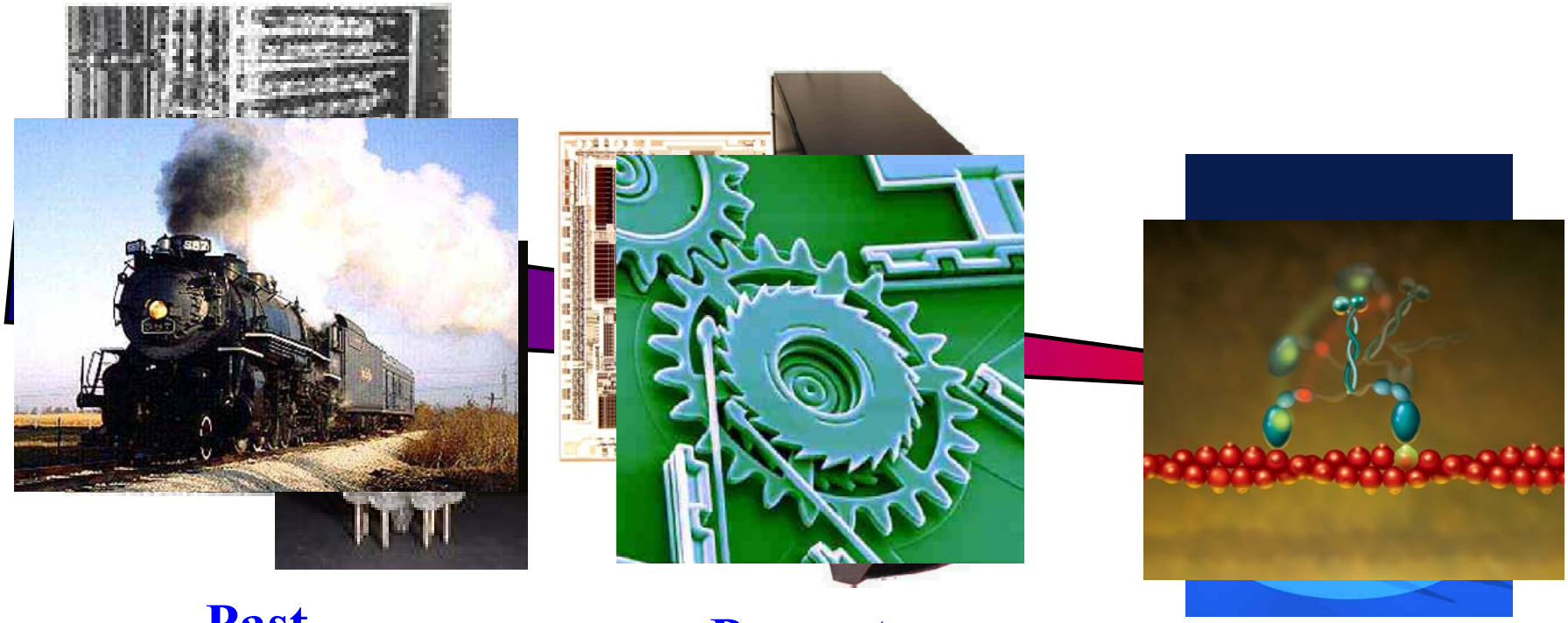
- control of chemical potentials
- local electrochemistry

Control: bias-induced phase transitions and electrochemical reactions

Theory: relate measured signal to local physics

- contact mechanics
- probe dynamics
- bias-induced dynamic phenomena

# Future: Molecular Electromechanical Machines



**Past** **Present** **Future**

To go beyond purely electronic functionality in nanodevices, we need efficient transduction between electricity and mechanical motion

- materials that can efficiently transform electrical energy to mechanical and vice versa
- experimental techniques capable of addressing electromechanical energy transformations on the submicron, nanometer, and molecular scale