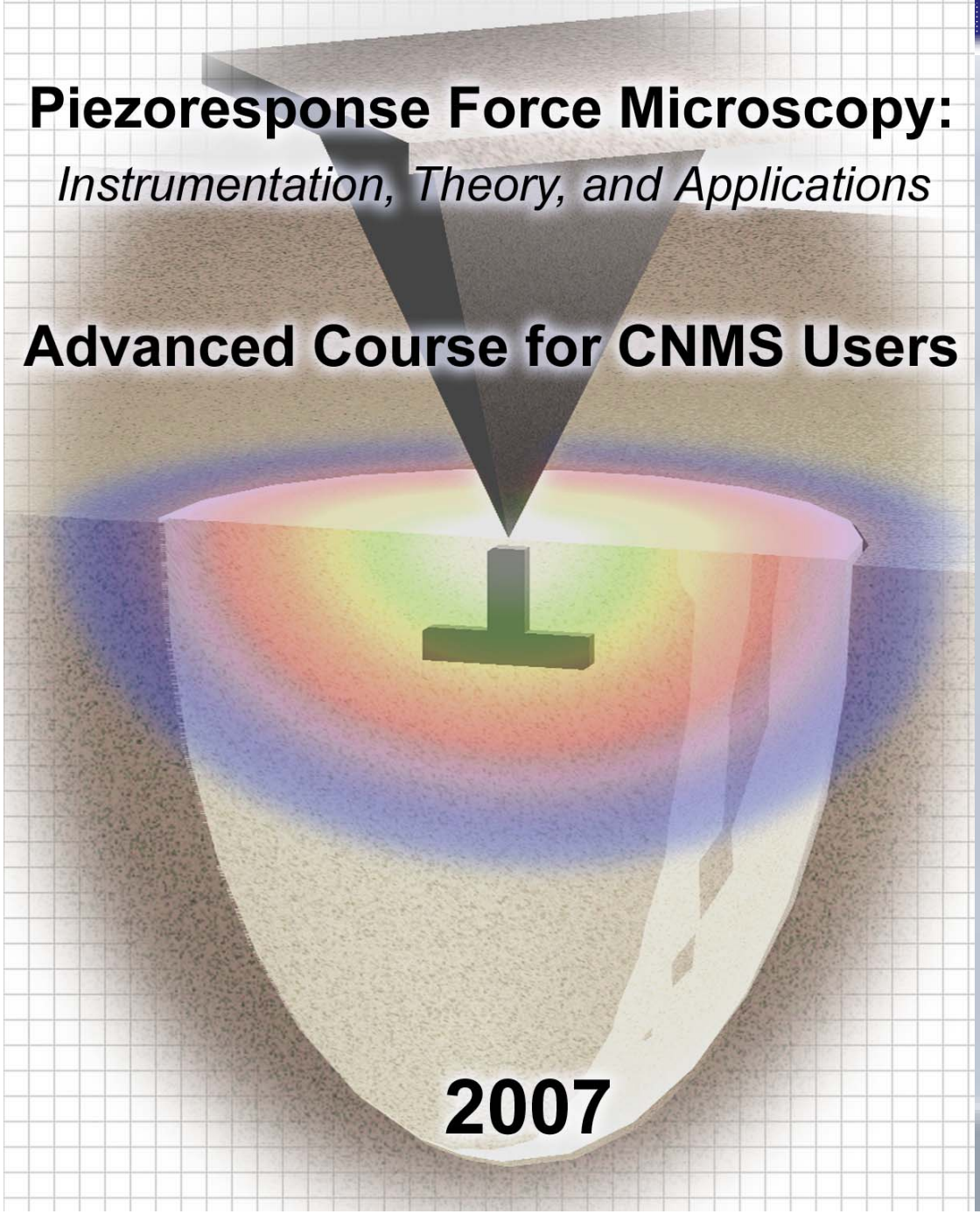
Piezoresponse Force Microscopy:

Instrumentation, Theory, and Applications

Advanced Course for CNMS Users



2007

Organizers:

Sergei V. Kalinin (ORNL)
Arthur Baddorf (ORNL)

Invited lecturers:

Alexei Gruverman (U. Nebraska-Lincoln)
Marty Gregg (U. Belfast)
Andrew M. Rappe (U. Pennsylvania)
S. Ducharme (U. Nebraska-Lincoln)
Stephen Jesse (ORNL)
E. Ward Plummer (U. Tenn./ORNL)

Experimental Labs:

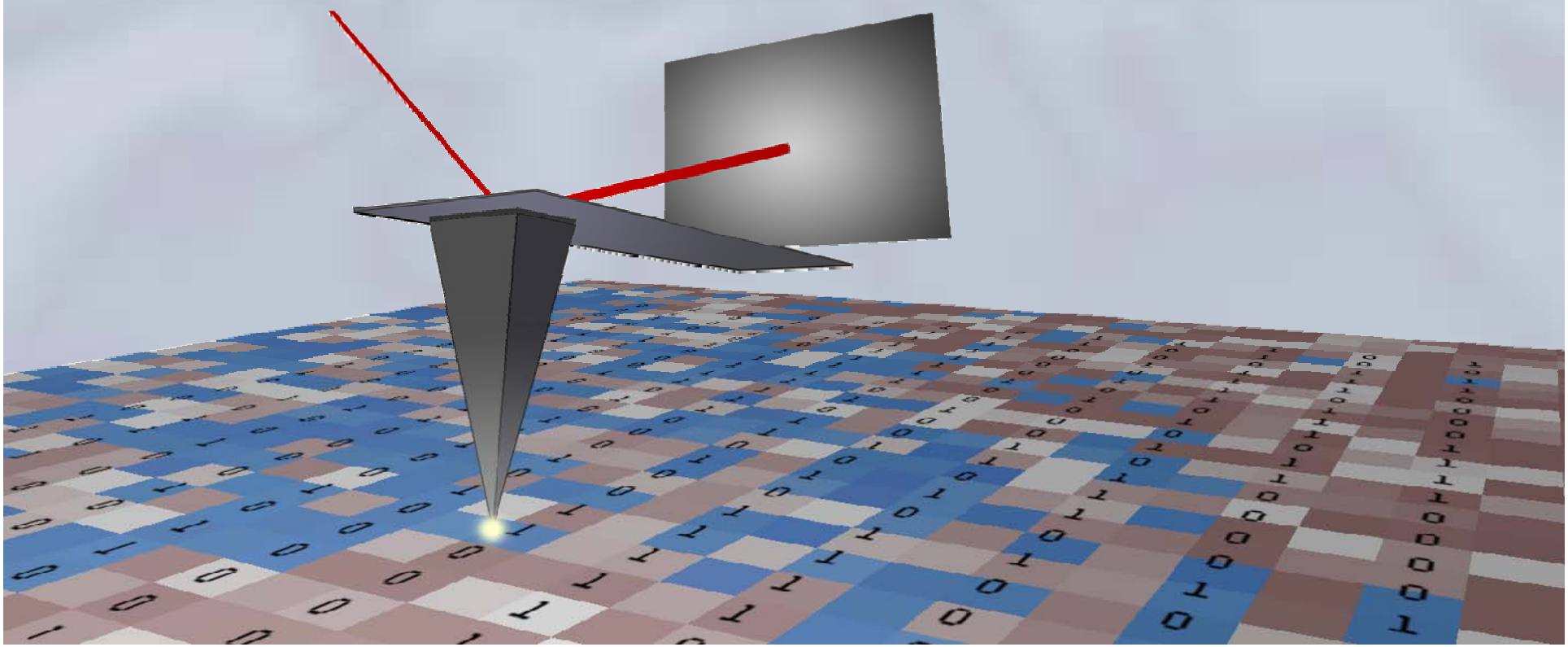
Katya Seal (ORNL)
Stephen Jesse (ORNL)
Keith Jones (Asylum Research)
B. Pittinger (Veeco)

Financial Support

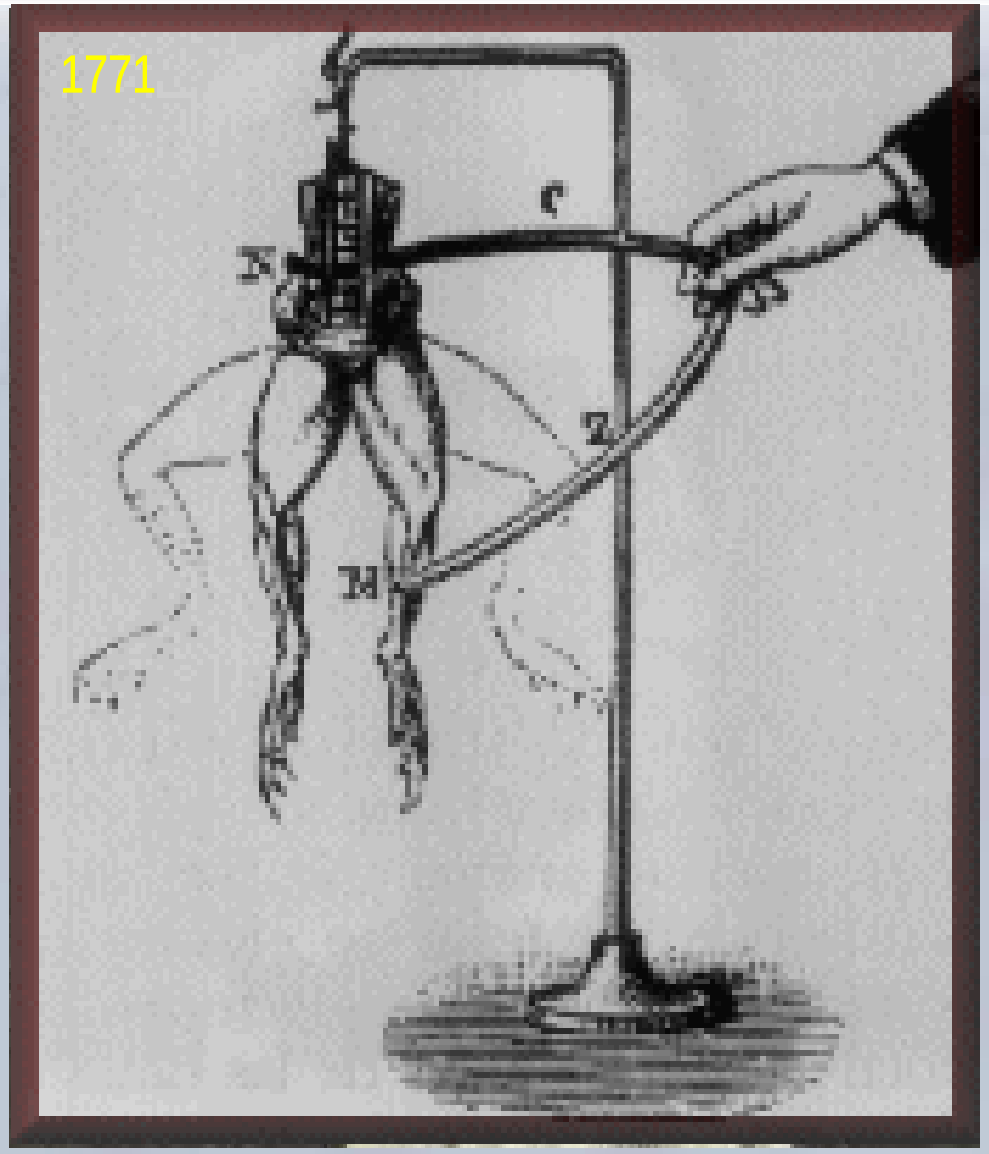
CNMS
Asylum Research

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

Sergei V. Kalinin
The Center for Nanophase Materials Sciences and Material Sciences and Technology Division,
Oak Ridge National Laboratory

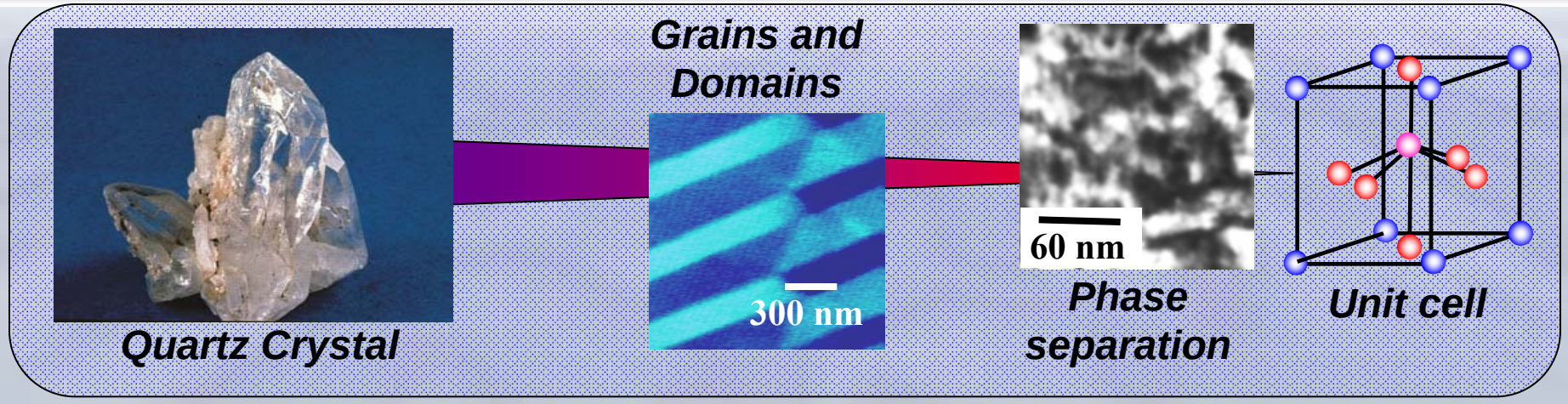


Electromechanics and the Origins of Physics



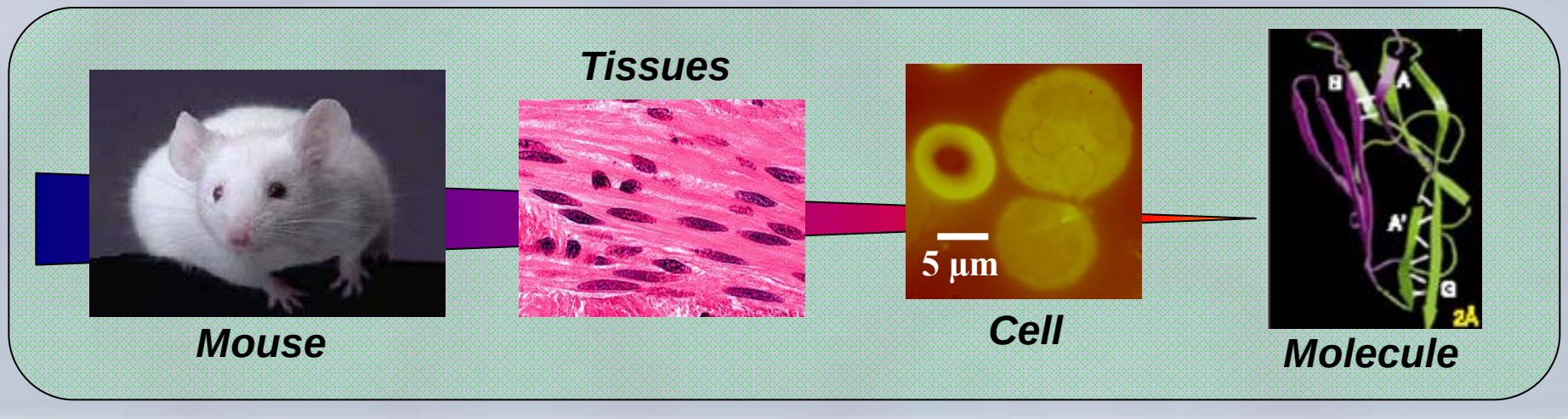
In the beginning, there was electromechanics…

Electromechanics: The Next Frontier



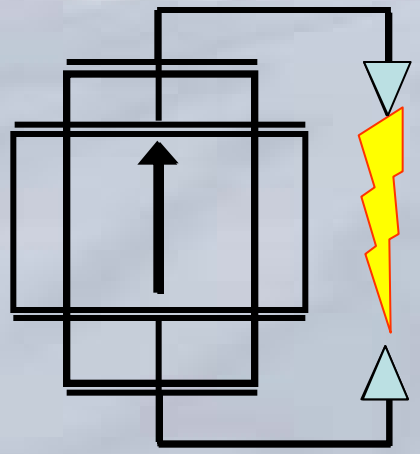
1 m | 0.1 m | 10 mm | 1 mm | 0.1 mm | 10 µm | 1 µm | 0.1 µm | 10 nm | 1 nm | 1 Å

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



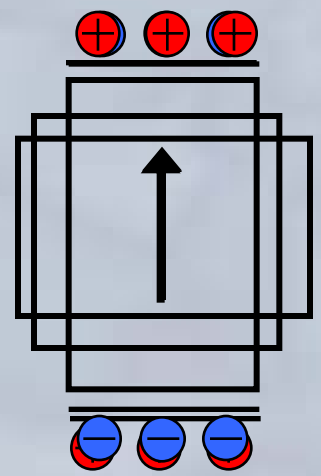
Electromechanical Coupling

Direct piezoelectric effect



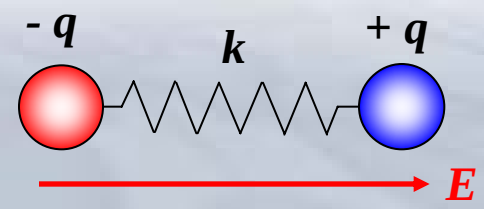
Charge = Force • d_{33}

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:

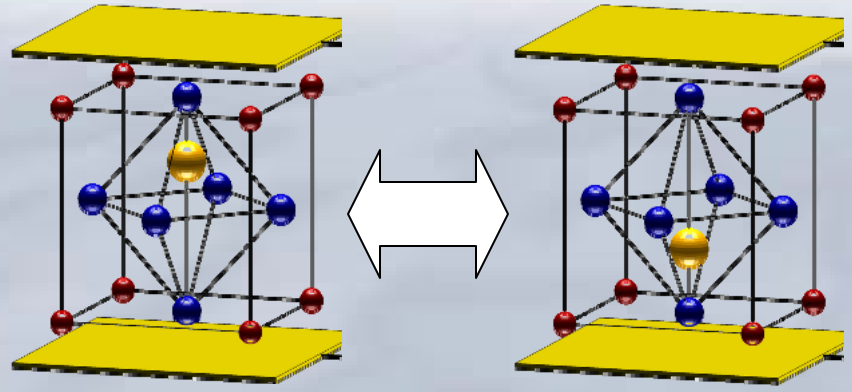
$$dl = (F + F_{el})/k = F/k + 2qE/k$$

- 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:

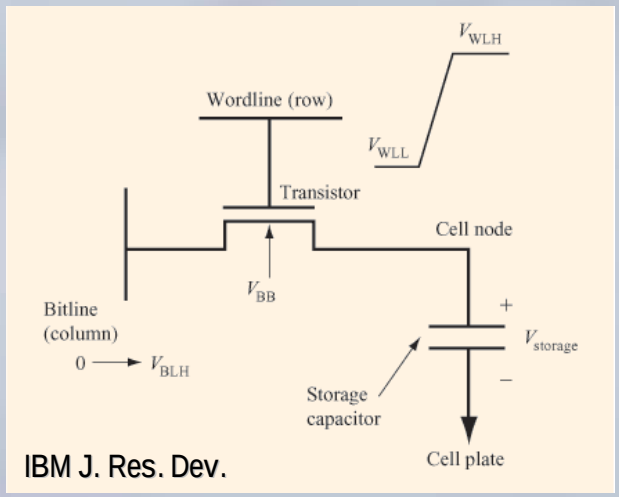
$$\left.\begin{array}{l} l = 1A \\ q = 0.3e \\ k = 100\,N/m \end{array}\right\} \Rightarrow \boxed{\begin{array}{l} d = 9.6\ pm/V \\ \text{or} \\ d = 9.6\,C/N \end{array}}$$

Ferroelectric Materials on the Nanoscale

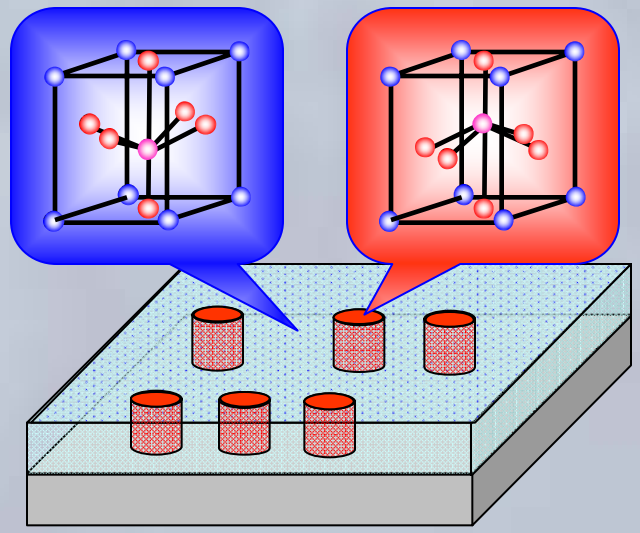


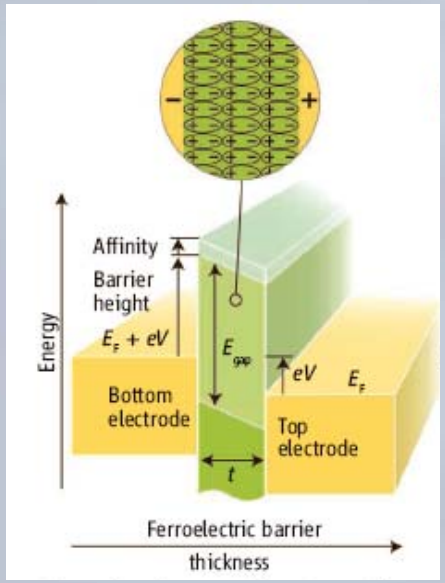
Perfect materials for information storage:

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



IBM J. Res. Dev.

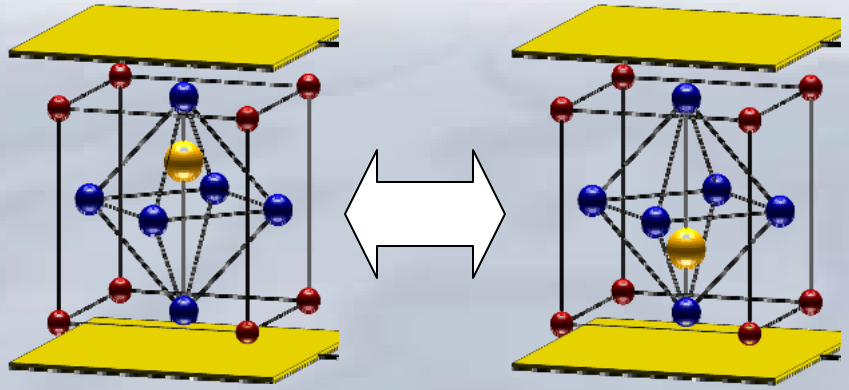




Kohlstedt and Tsymbal

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

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:

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   Fujitsy, Ramtron, TI
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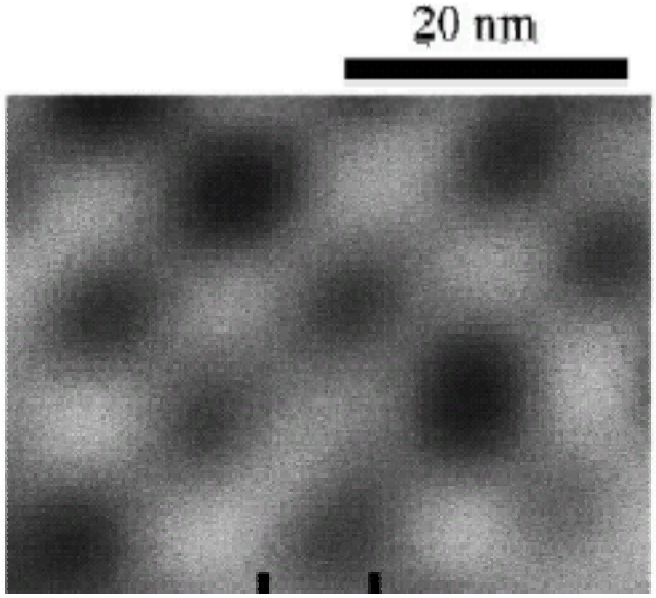
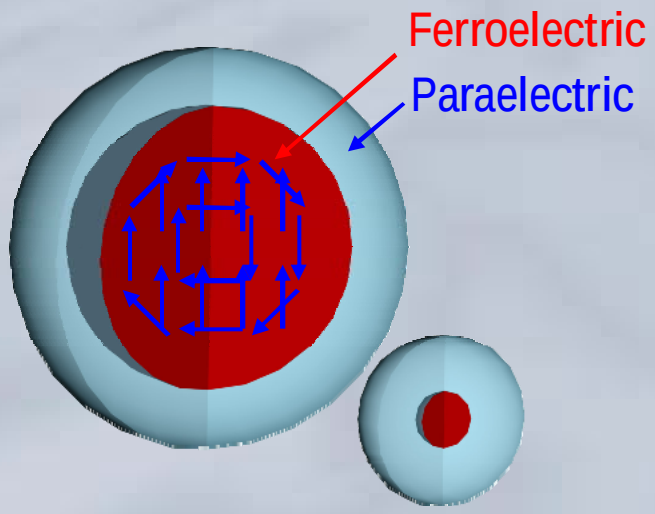


Cho et al., APL 2005

What are switching mechanisms in real materials?

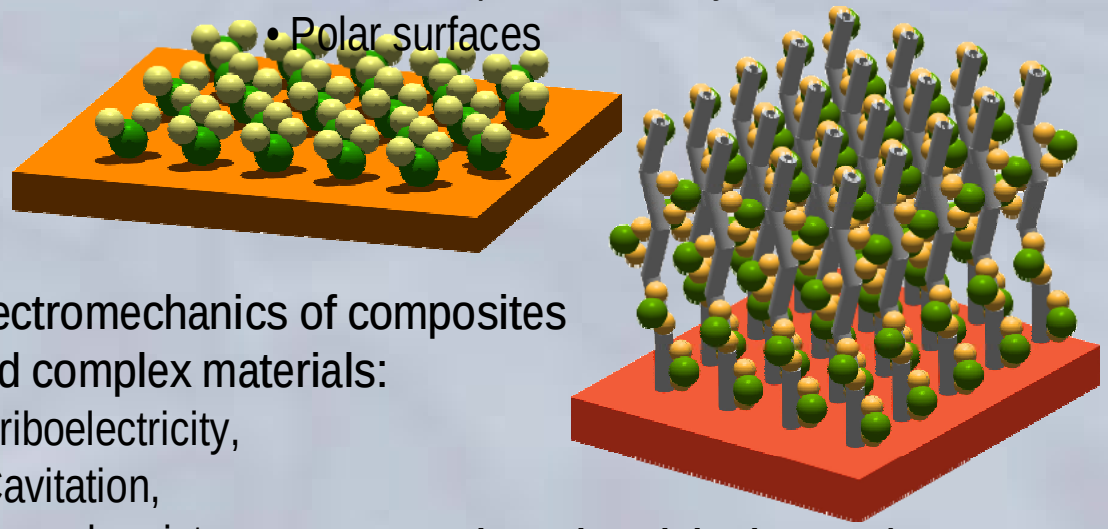
Electromechanics on the Nanoscale

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



Surface piezoelectricity:

- Ordered dipolar water layers
- Polar surfaces

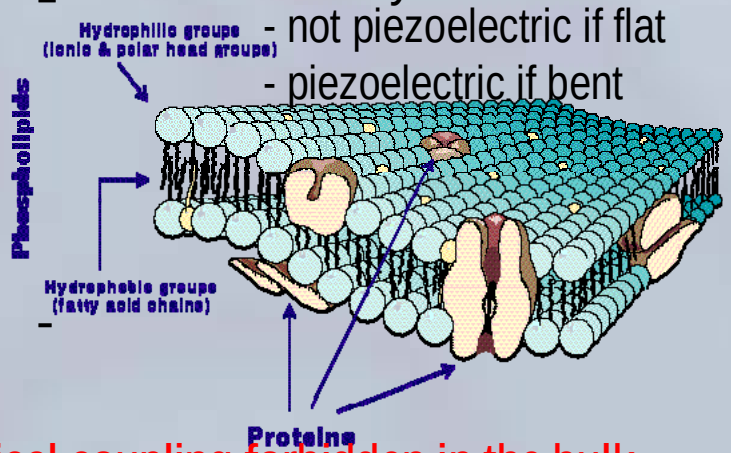


Electromechanics of composites and complex materials:

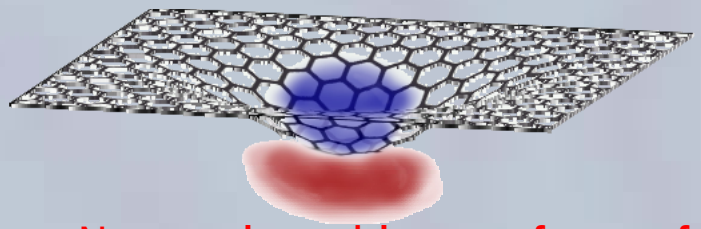
- Triboelectricity,
- Cavitation,
- Sonochemistry
- Sonoluminescence

Flexoelectricity in membranes:

- not piezoelectric if flat
- piezoelectric if bent

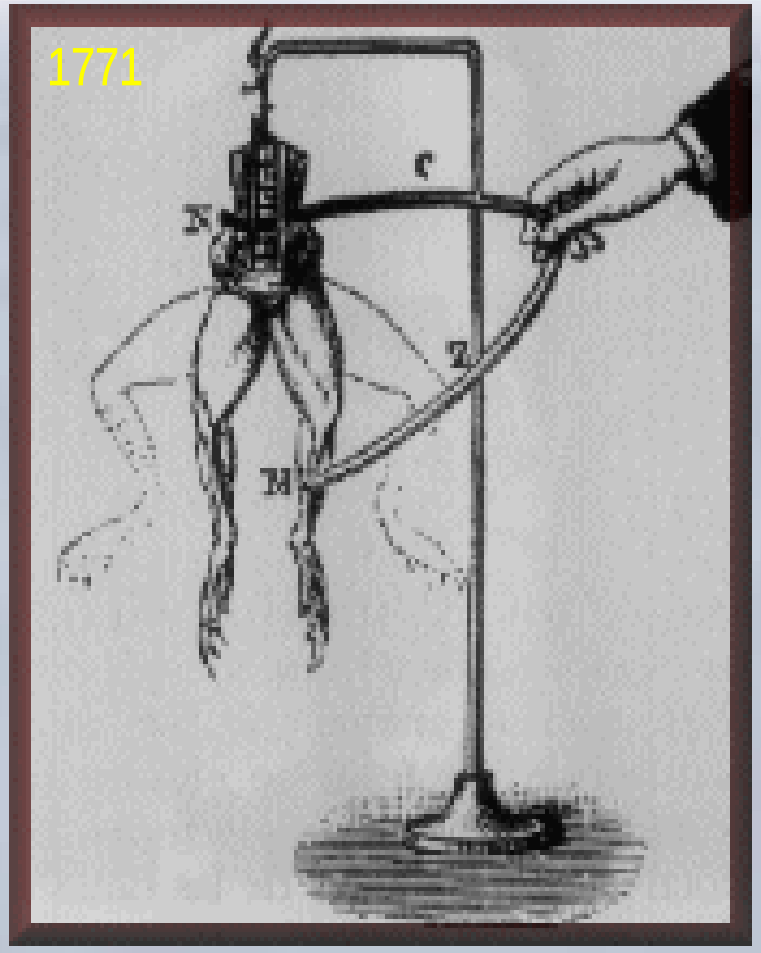


Flexoelectricity also exists in quantum systems:



Nanoscale enables new forms of electromechanical coupling forbidden in the bulk

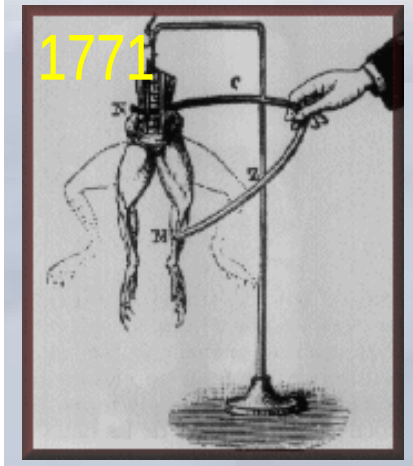
Electromechanics in Biological Systems



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?

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

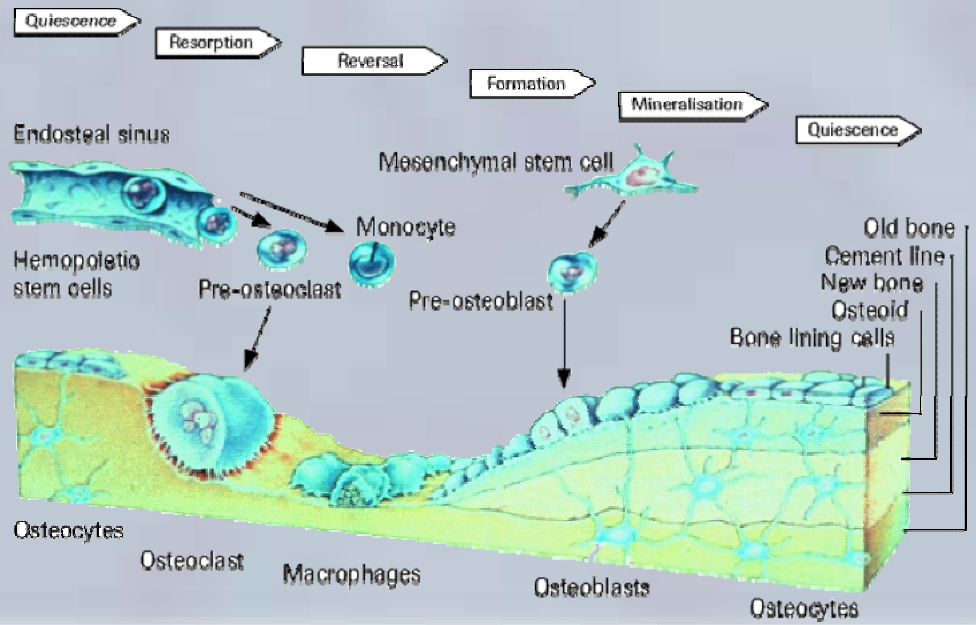
Since 1955, it was shown that many biomaterials, including collagen and cellulose, are piezoelectric. This piezoelectric activity was postulated to be directly related to biochemical functionality.

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

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

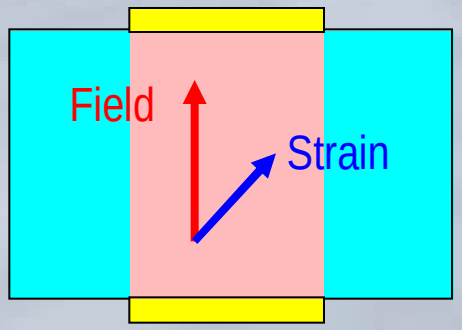
Teeth: d_{24} = 0.2 pC/N
And teeth don't…

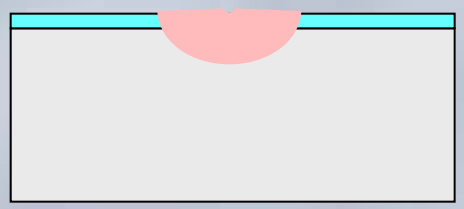
A number of approaches for bone treatments (osteoporosis, fracture) were suggested using periodic fields



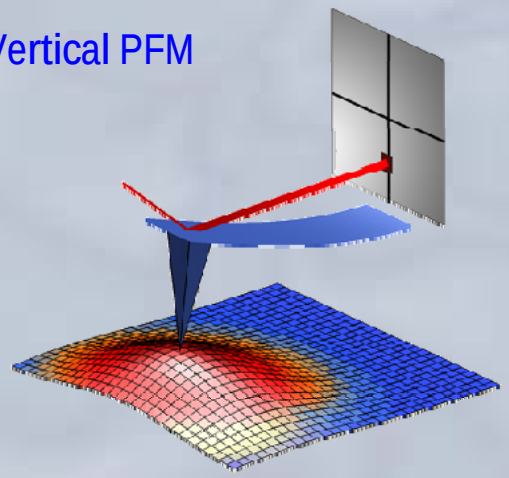
Probing NanoElectromechanics

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

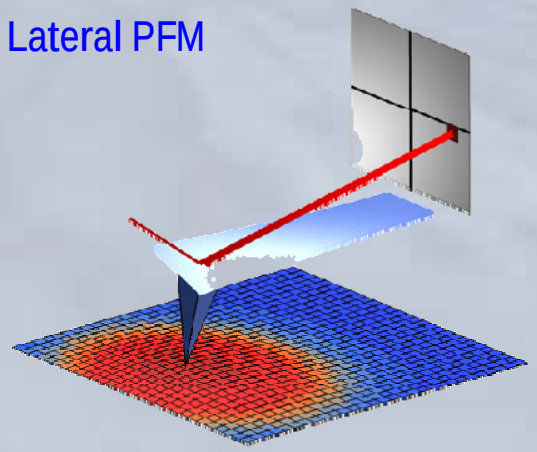




Vertical PFM



Lateral PFM



Piezoresponse Force Microscopy

Application of AC bias to the tip

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

results in cantilever deflection

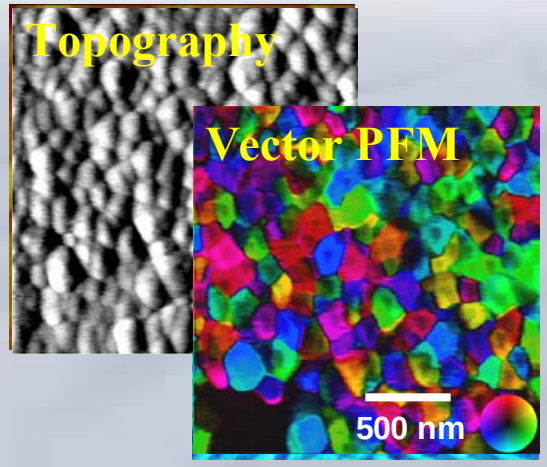
$d = d_0 + A(\omega, V_{dc}) V_{ac} \cos(\omega t + \varphi)$

due to piezoelectric effect

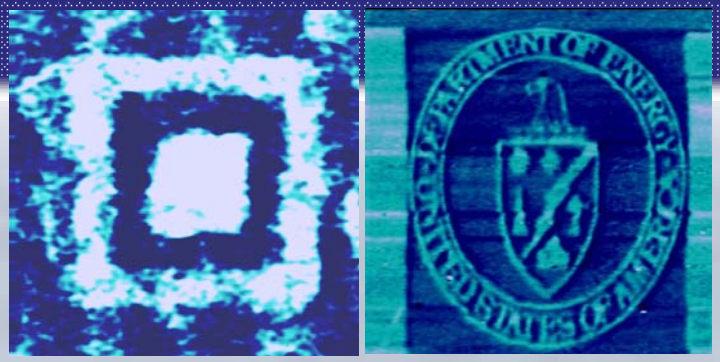
In nanoscale systems, we need

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

PFM = Nanoelectromechanics

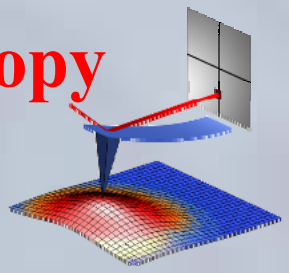


Domain imaging

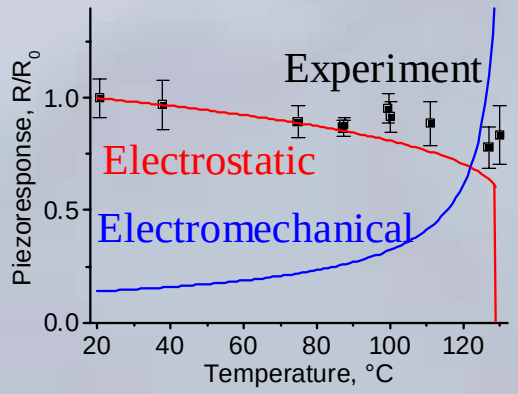


Domain writing

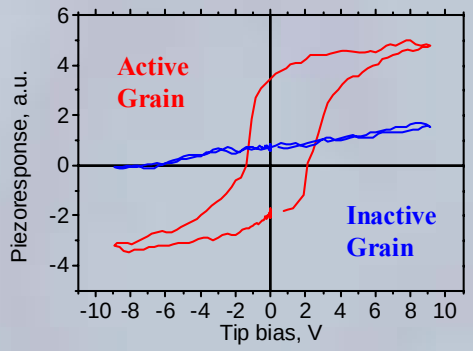
Piezoresponse Force Microscopy



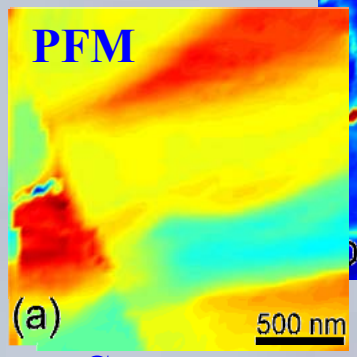
Domain dynamics and evolution

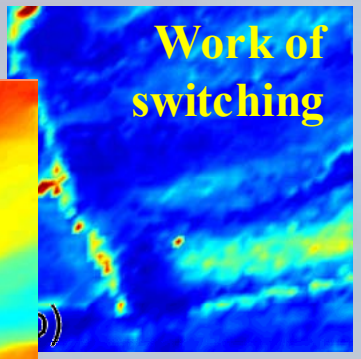


Temperature dynamics and phase transitions



PFM spectroscopy





Switching Spectroscopy Mapping

Monday, October 8

8.00 a.m – 8.20 a.m.	Introduction: Electromechanical Coupling on the Nanoscale: Bonds, Cells, and Molecules (S. Kalinin, ORNL)
8.20 a.m. – 10 a.m.	**Invited tutorial** "Nanoscale Ferroelectrics: Where Size Really Does Matter" (M. Gregg, U. Belfast)
10.00 a.m. – 10.30 a.m.	Coffee break
10.30 a.m. – 12.00 p.m.	Principles and Instrumental aspects of Piezoresponse Force Microscopy (A. Gruverman, UNL)
12.00 p.m – 1.00 p.m.	Lunch
1.00 p.m. – 2.30 p.m.	PFM of piezoelectric materials: contact mechanics, cantilever dynamics, and resolution theory (S.V. Kalinin, ORNL)
2.30 p.m. – 3.00 p.m.	Coffee break
3.00 p.m. – 4.30 p.m.	**Invited tutorial** "Phase transitions, domain structure & dynamics, and surface chemistry in ferroelectrics studied by x-rays" (S. Streiffer, Argonne National Lab.)
4.30 p.m. – 6.00 p.m.	PFM studies of polarization dynamics in ferroelectric films and capacitors (A. Gruverman, UNL)

Tuesday, October 9

8.30 a.m. – 10.30 a.m.	**Invited tutorial** "First-principles and multiscale modeling of ferroelectrics" (Andrew M. Rappe, University of Pennsylvania)
10.30 a.m. – 11.00 a.m.	Coffee break
11.00 a.m. – 12.30 p.m.	Local polarization switching and PFM spectroscopy (S. Kalinin, ORNL)
12.30 p.m – 1.30 p.m.	Lunch
1.30 p.m. – 3.00 p.m.	**Invited tutorial** "Structure and Properties of Ferroelectric Polymers at the Nanoscale" (Stephen Ducharme, UNL)
3.00 p.m. – 3.30 p.m.	Coffee break
3.30 p.m. – 5.00 p.m.	Advanced topics in PFM: Macromolecular and biological systems and imaging in liquids (S.V. Kalinin, ORNL)
5.00 p.m. – 5.45 p.m.	Advanced modes in PFM: Band Excitation Method and Energy Dissipation on the nanoscale (S. Jesse, ORNL)
5.45 p.m. – 6.30 p.m.	Polarization dynamics and atomic structure on *in-situ* grown ferroelectric films (A. Baddorf, ORNL)

Wednesday – Friday

Lab 1: Imaging (Veeco Nanoman V, lead by Katya Seal, ORNL, and Bede Pittinger, Veeco)

8.1.1. Basic experimental set-up for PFM

8.1.2. Imaging at high frequencies and topographic cross-talk

Lab 2: Imaging, Patterning, and Switching (Asylum MFP-3D, led by Keith Jones, Asylum Research)

2 machines

8.2.2. Switching Spectroscopy PFM

8.2.3. Polarization dynamics in capacitors

Lab 3: Polarization dynamics in films (Nanonis/MultiMode, led by Stephen Jesse, ORNL)

8.2.1. PFM spectroscopy

8.2.2. Switching Spectroscopy PFM

Questions:

Workshop logistics:	Art Baddorf
CNMS and user program:	Tony Haynes
Labs and such:	Sergei Kalinin