Scanned Probe Microscopy: measuring forces to map material properties

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MaNEP

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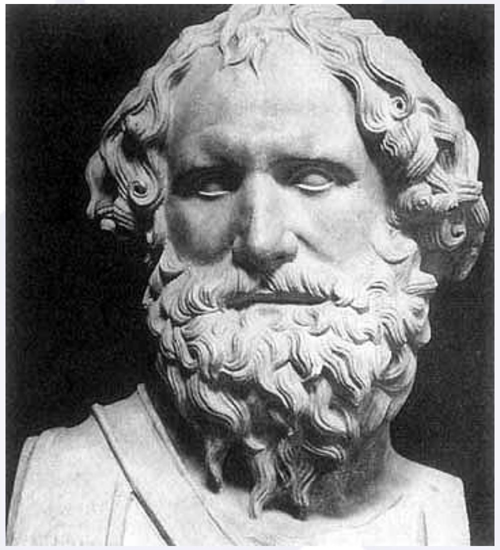
AFM - atomic force microscopy

Give me a lever long enough and a fulcrum on which to place it, and I shall move the world Archimedes



Give me a lever tiny enough and a functionalised probe tip, and I shall measure its interactions at the nanoscale

Goals of this lecture

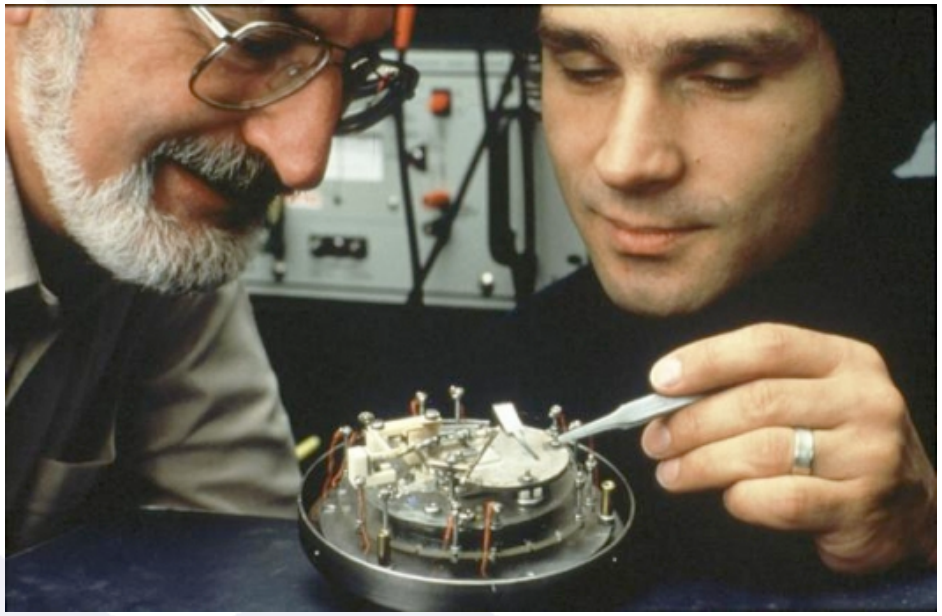
Review the basic principles of AFM

Present standard AFM modes beyond topographical imaging

Discuss AFM applications to nanopatterning

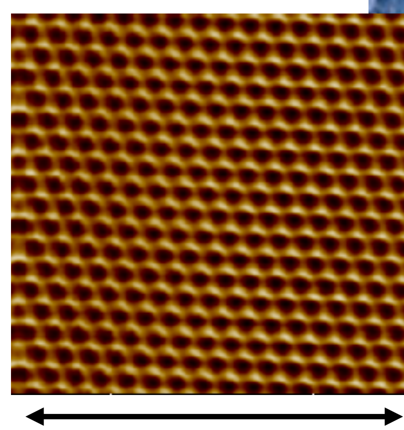
From STM to AFM

scanning tunneling microscopy



Rohrer and Binnig

UHV environment
metallic samples
(low temperatures)
(small scan range)

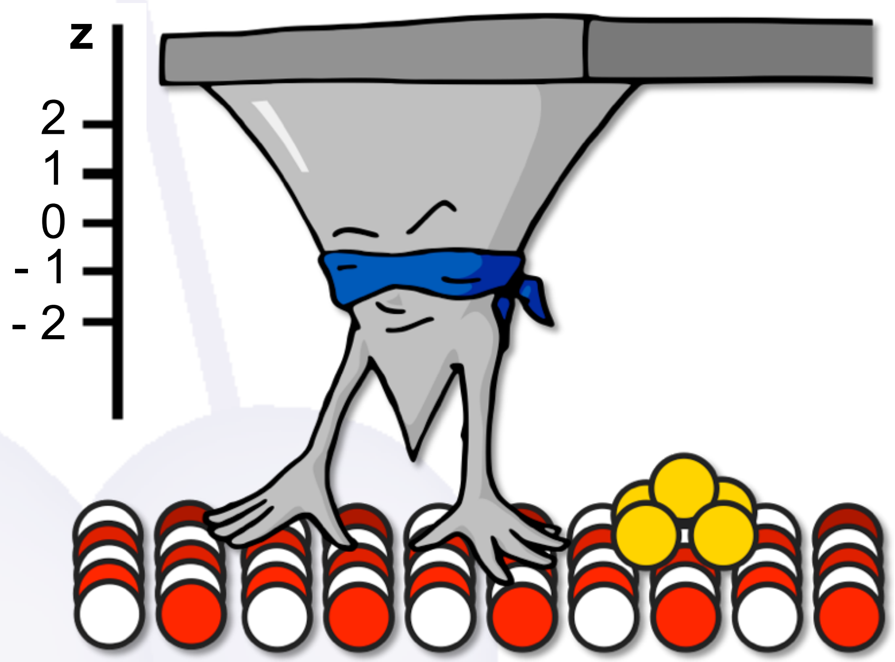


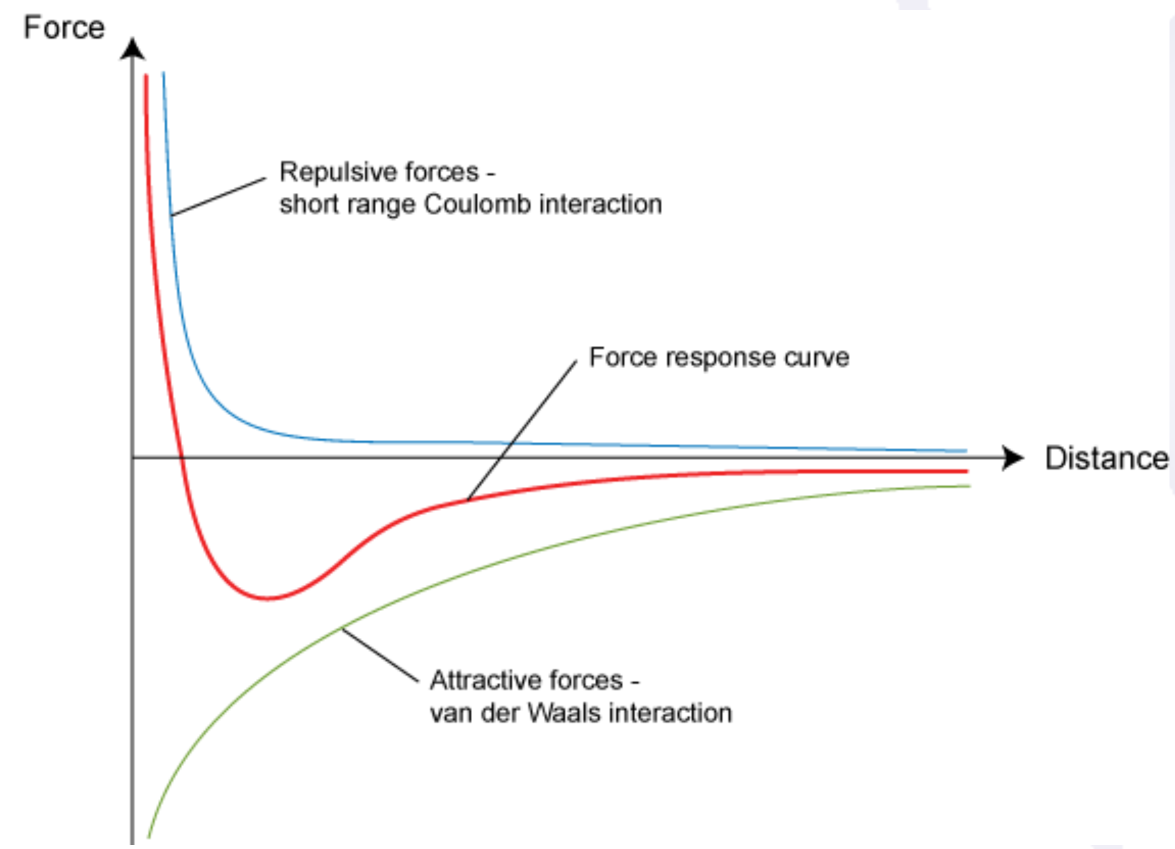
Want more general technique:
variable environment
all sample types
variable temperature
large scan range

Binnig, Quate and Gerber

How does AFM work?

$F = -kz$



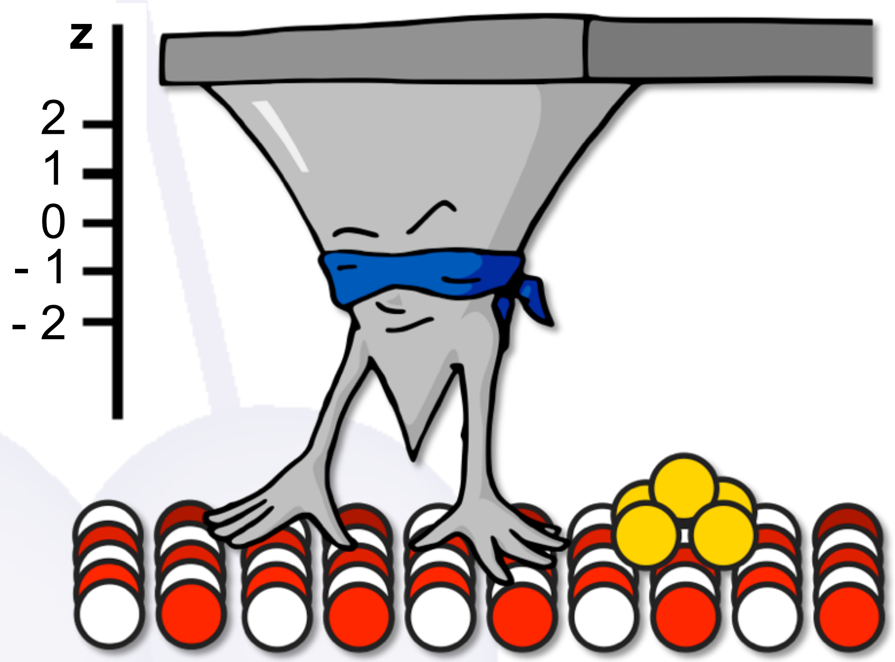


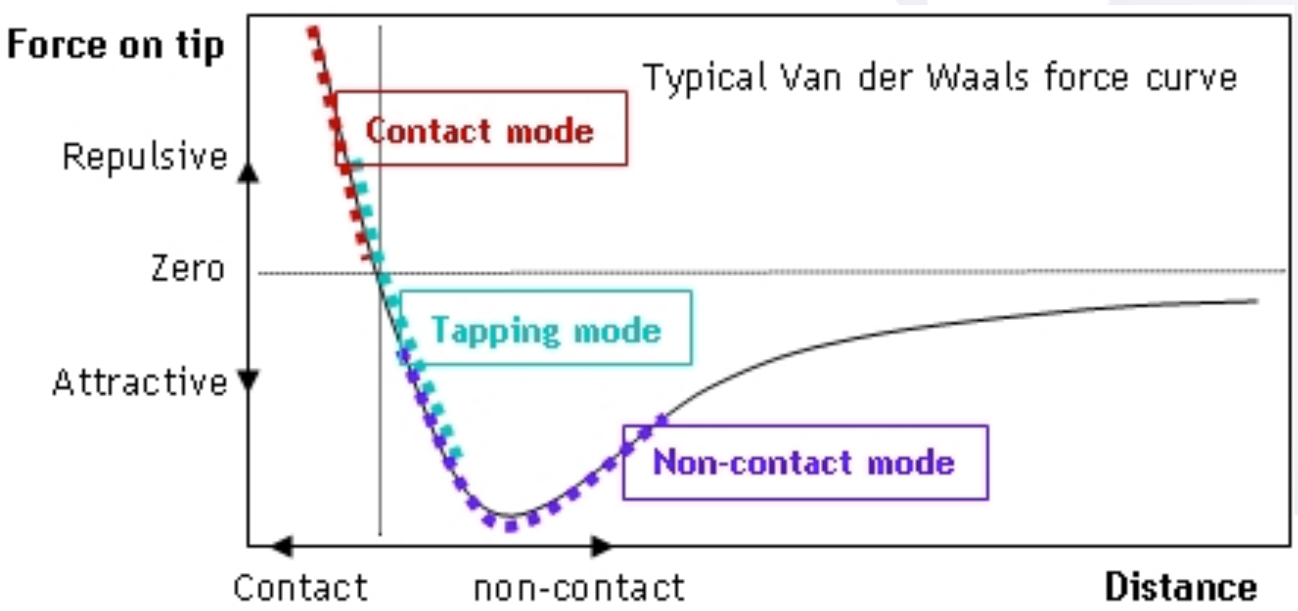
Interaction between a sharp probe tip and the sample → forces

Force can be measured via displacement of probe from its equilibrium position, need to calibrate spring constant k

How does AFM work?

$F = -kz$





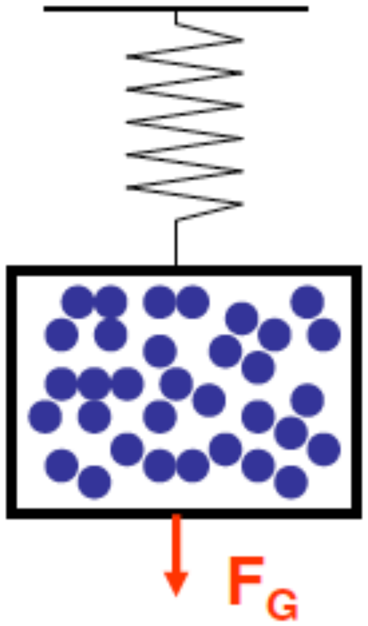
Interaction between a sharp probe tip and the sample → forces

Force can be measured via displacement of probe from its equilibrium position, need to calibrate spring constant k

How much force are we talking about here?

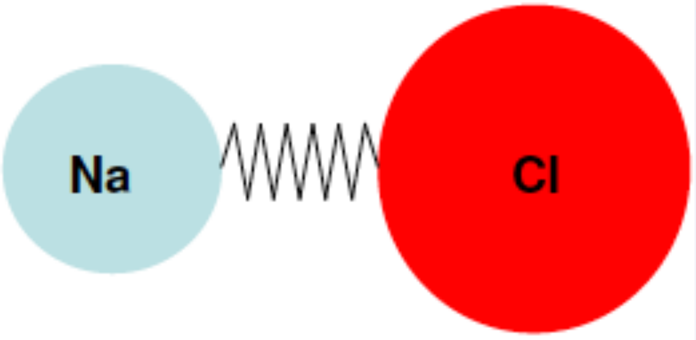
0.01 g

F= 0.1 mN = 10^5 nN



1 nm³ water (33 molecules)

$F_G = 10^{-23}$ N = 10^{-14} nN



Chemical bond

F_{chem} = 1eV/ 0.1 nm

1.6 nN

from E. Meyer

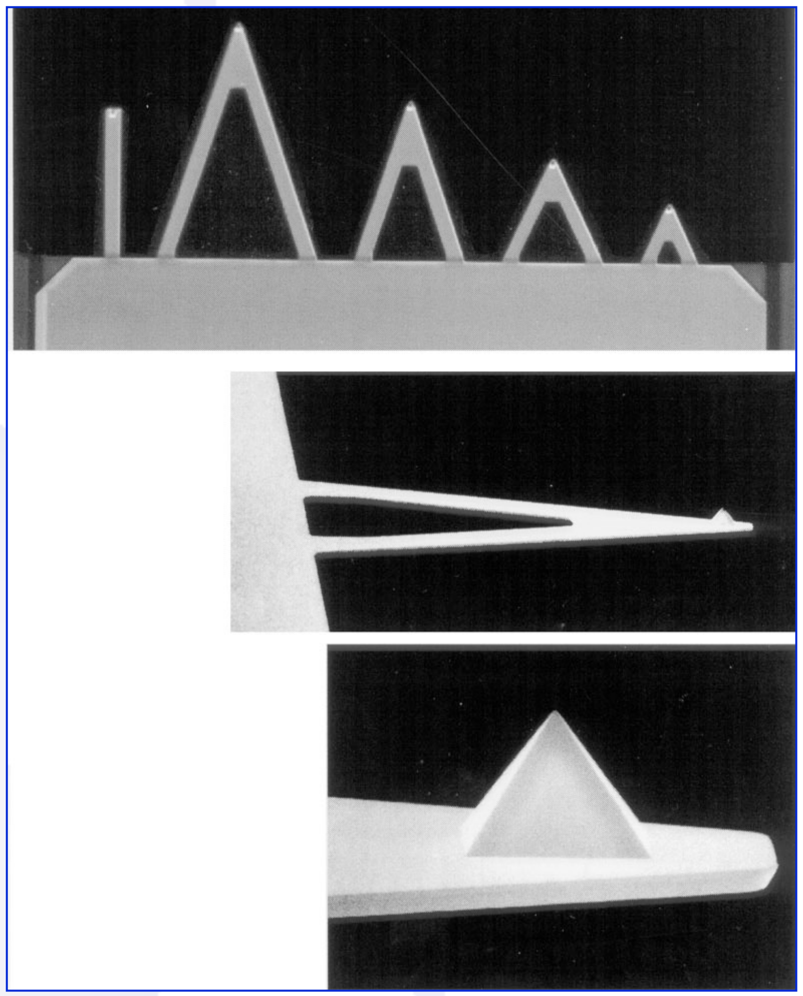
Want non-perturbative access to nanoscale interactions

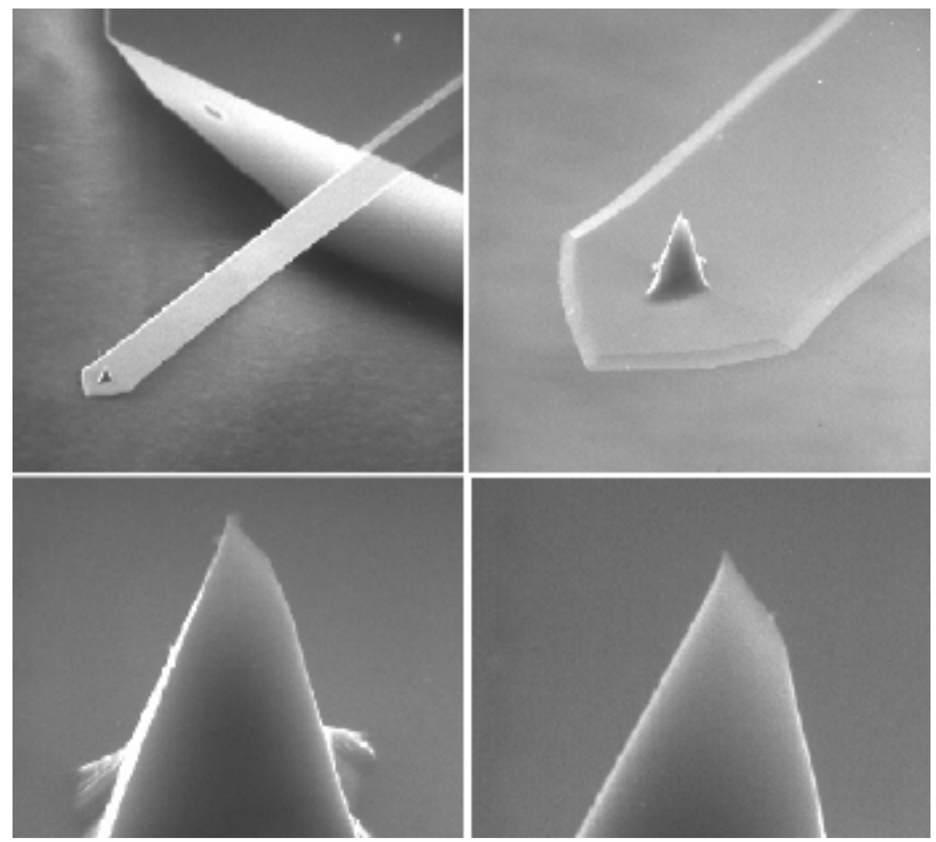
deflection: $z = 10^{-10}$m - 10^{-9} m

spring constant: k = 0.01- 10 N/m

forces: $z = 10^{-11}$N - 10^{-9} N

Tip-sample interaction gives rise to force on cantilever beam



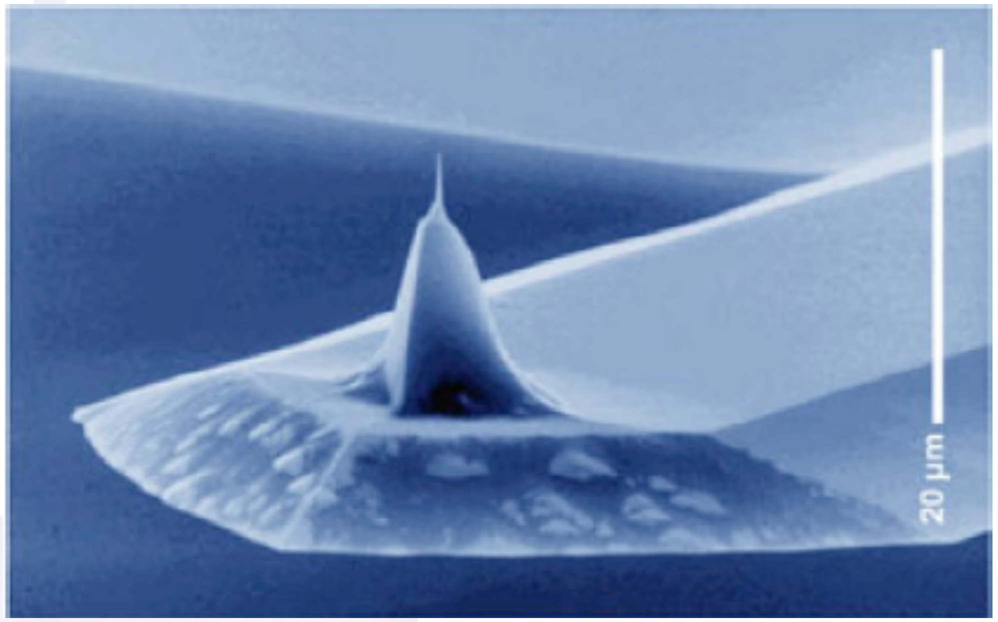


from E. Meyer

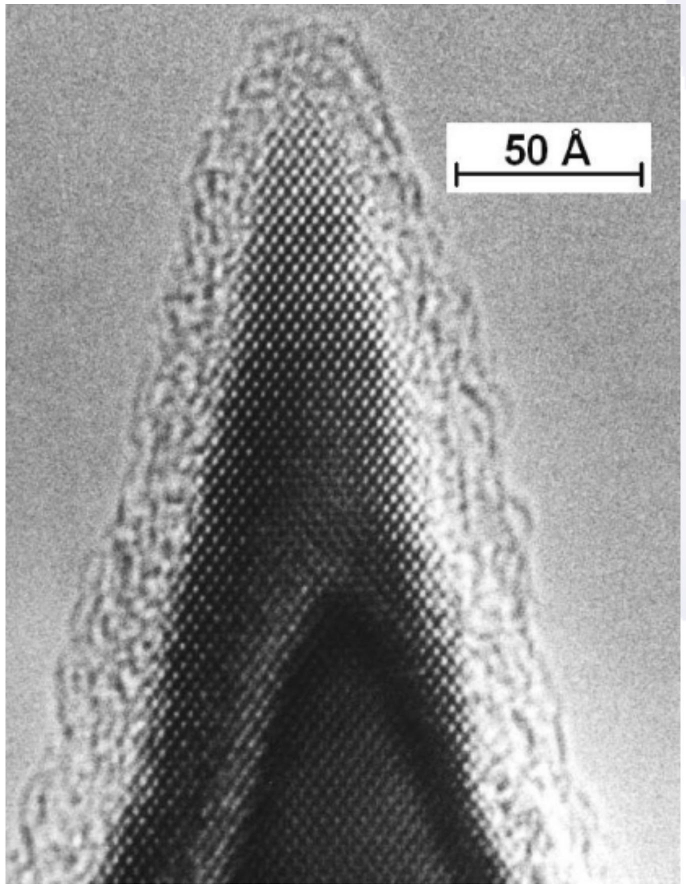
length : l = 450 μm
width : w = 45 μm
thickness: t = 1.5 μm

Tip height: 12 μm
Tip radius: 10 nm

Tip-sample interaction gives rise to force on cantilever beam



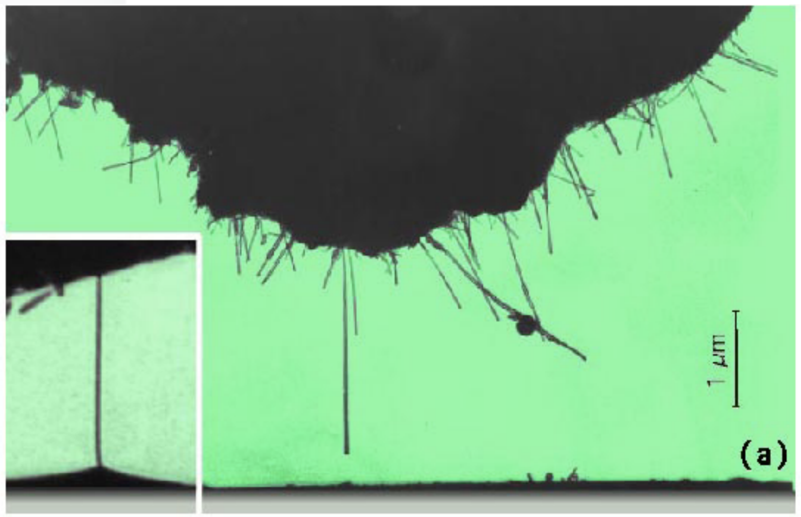
Pointprobe by Nanosensors GmbH



Marcus *et al*. APL **56,** 236 (1990)

Ultrasharp and/or functionalised tips can be engineered to probe specific interactions

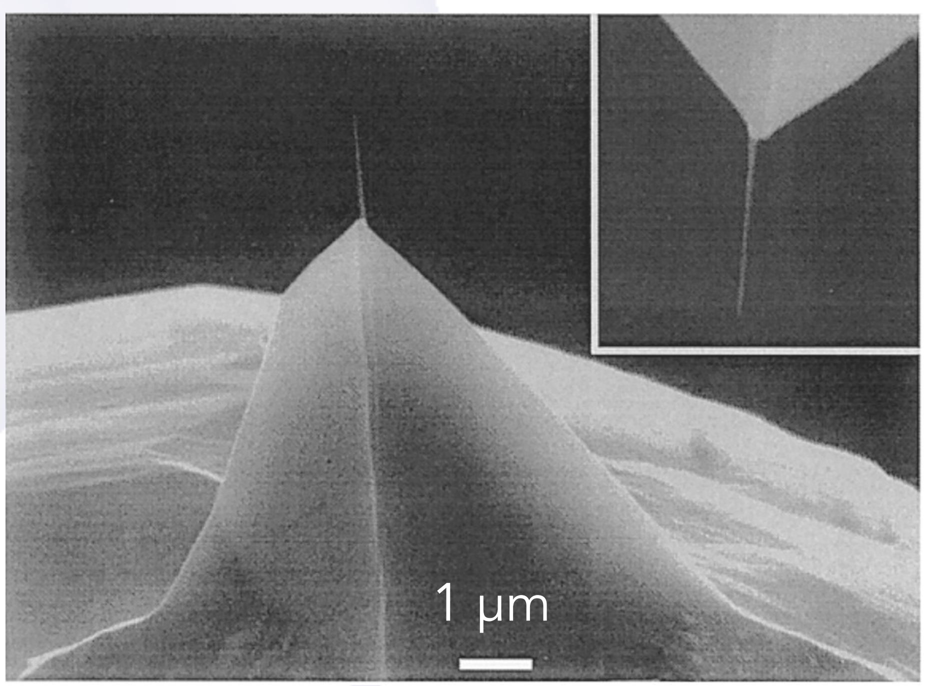
Improving tip performance using CNT



Poncharal, *et al.* JPCB **106**, 12104 (2002)

- Exceptional mechanical properties
- Ballistic conduction in metallic CNT
- Semiconducting CNT
  - quasi ideal 1D system
  - single molecule electronics

Dresselhaus, et al., **Carbon Nanotubes** Springer, Berlin (2001)



CNT AFM topography

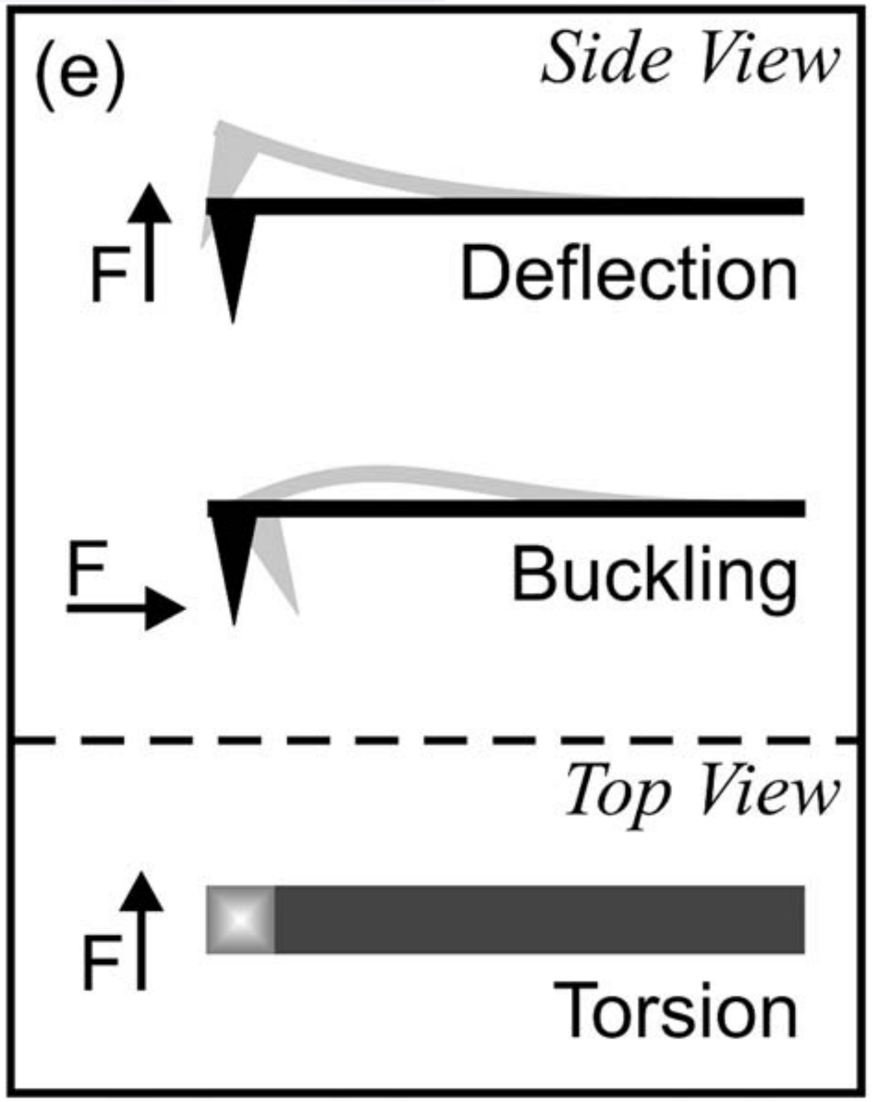
Hafner *et al.* Nat. **398**, 761 (1999)
Nishijima *et al*, APL **74**, 4061 (1999)

Nanoscale electric field source

Dai *et al.* APL **73**, 1508 (1998)
Cooper *et al.*, APL **75**, 3566 (1999)

Further functionalisation possible

Cantilever response to applied forces

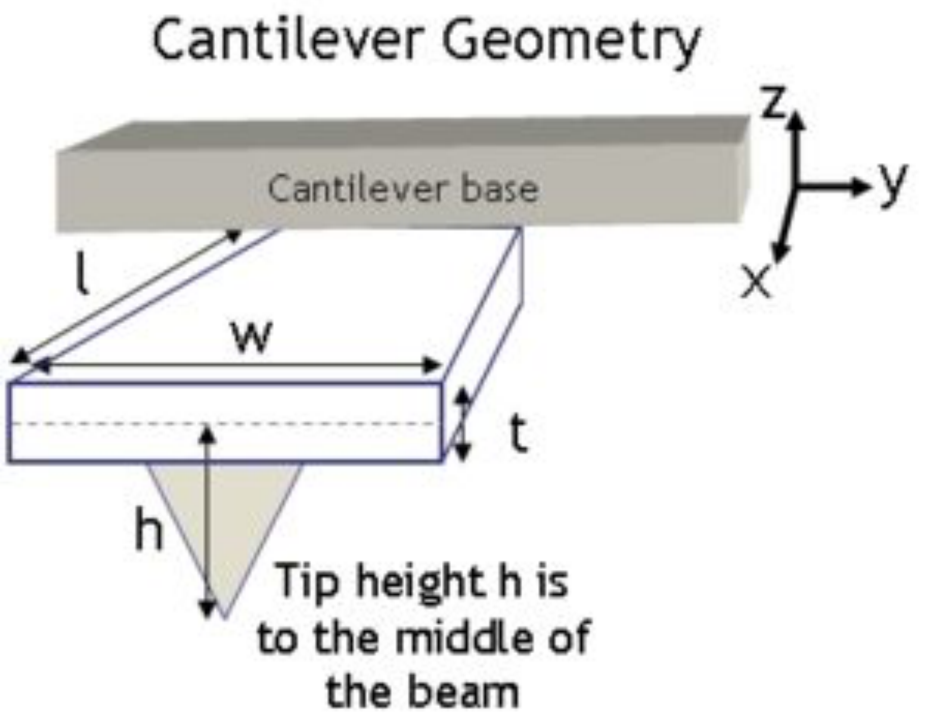


Jungk *et al.* APL **89,** 043901 (2006)

$$k_N = \frac{E \cdot w}{4}\left(\frac{t}{l}\right)^3$$

E : Young's modulus
w : cantilever width
l : cantilever length
t : cantilever thickness
G : shear modulus
h: probe height

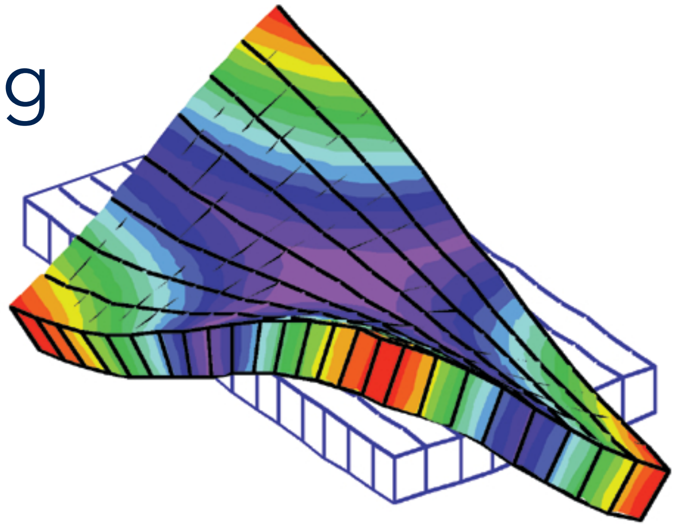
$$k_t = \frac{G \cdot w \cdot t^3}{3 \cdot l \cdot h}$$



Opensource Textbook of Nanoscience and Nanotechnology

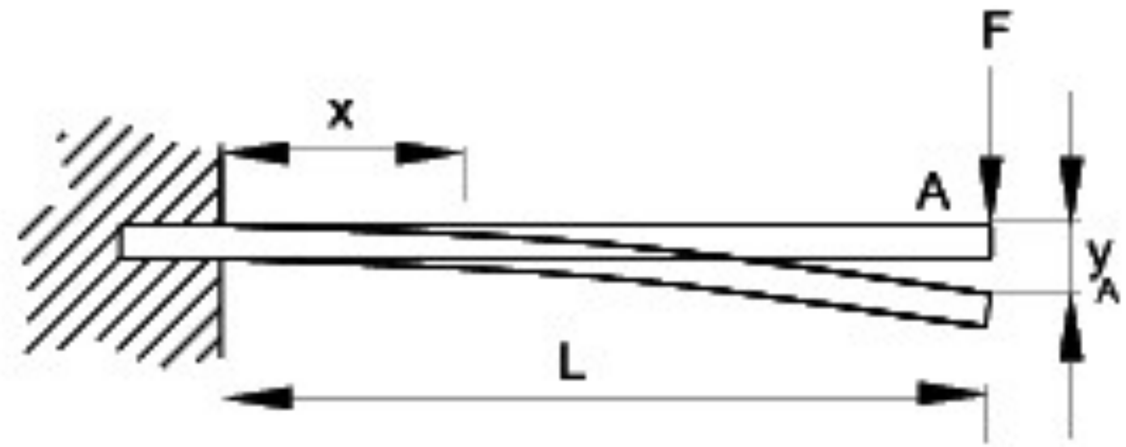
Cantilever responds with deflection, torsion, or buckling

… or some combination thereof



Contact mode: deflection of cantilever beam

beam bending:
one free end, one clamped end



E : Young's modulus
I : area moment of inertia

$$EI\frac{d^2y}{dx^2} = -F\,(L-x) \quad \text{Integrating}$$

$$EI\frac{dy}{dx} = -F\left(Lx - \frac{x^2}{2}\right) + C_1 \quad \text{.....}(C_1 = 0 \text{ because } dy/dx = 0 \text{ at } x = 0)$$

Integrating again

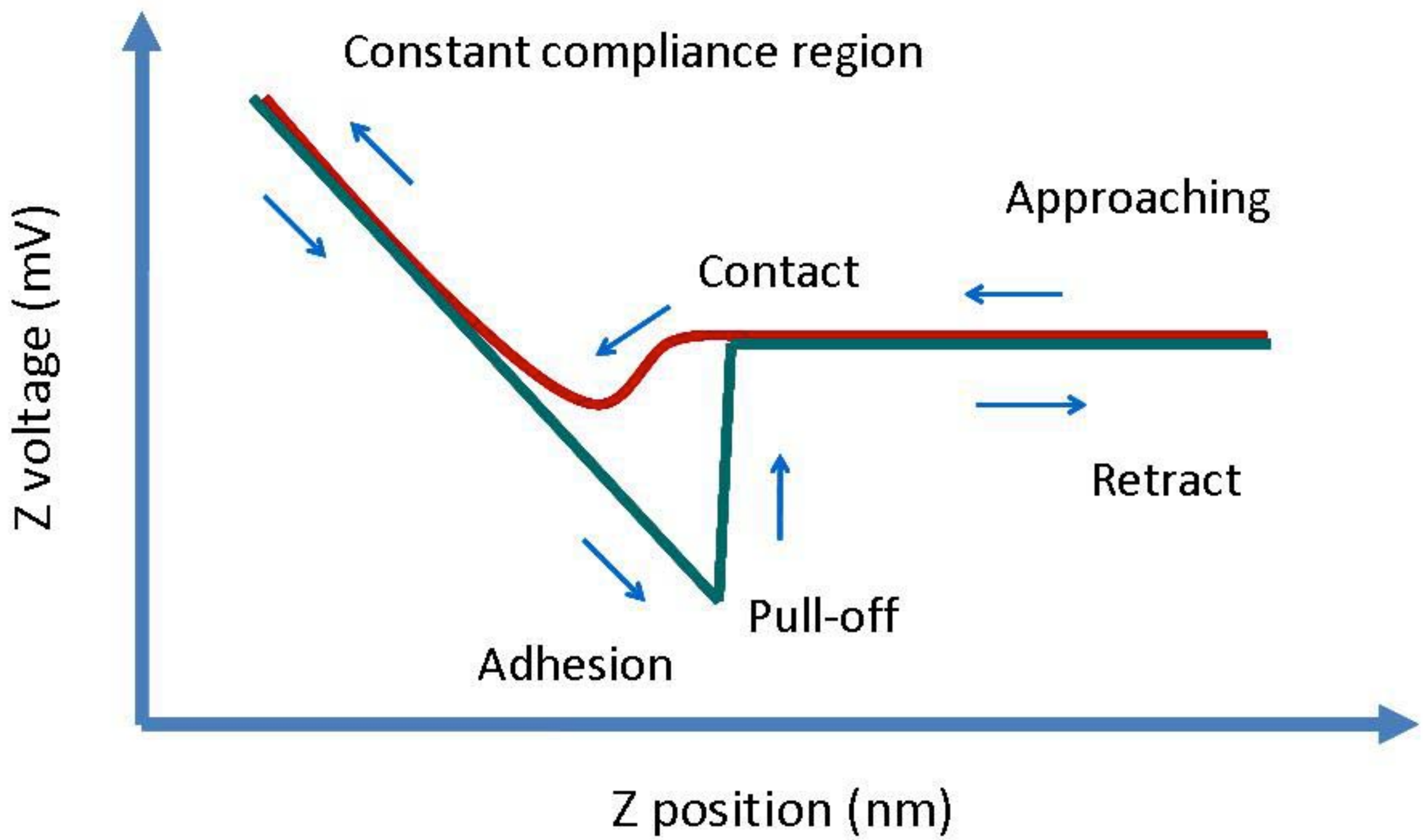
$$EI\,y = -F\left(\frac{Lx^2}{2} - \frac{x^3}{6}\right) + C_2 \quad \text{.....}(C = 0 \text{ because } y = 0 \text{ at } x = 0)$$

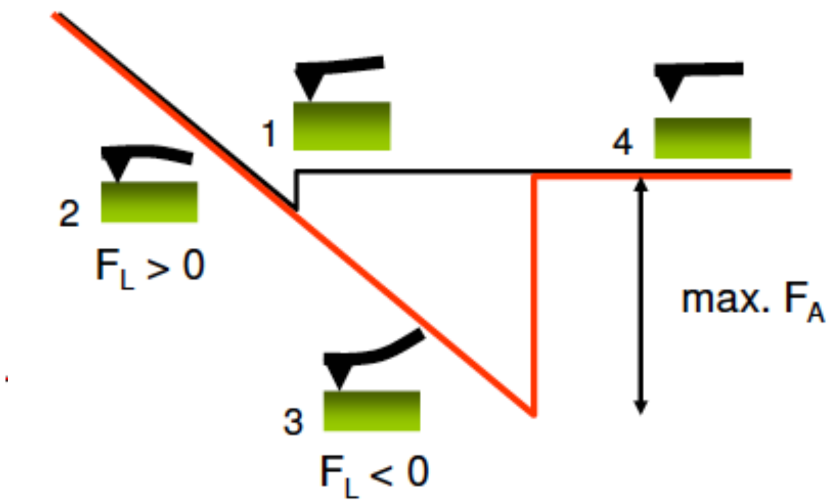
$$\text{At end A} \quad \left(\frac{dy}{dx}\right)_A = -\frac{F}{EI}\left(L^2 - \frac{L^2}{2}\right) = -\frac{FL^2}{2EI} \quad \text{and} \quad y_A = -\frac{F}{EI}\left(\frac{L^3}{2} - \frac{L^3}{6}\right) = -\frac{FL^3}{3EI}$$

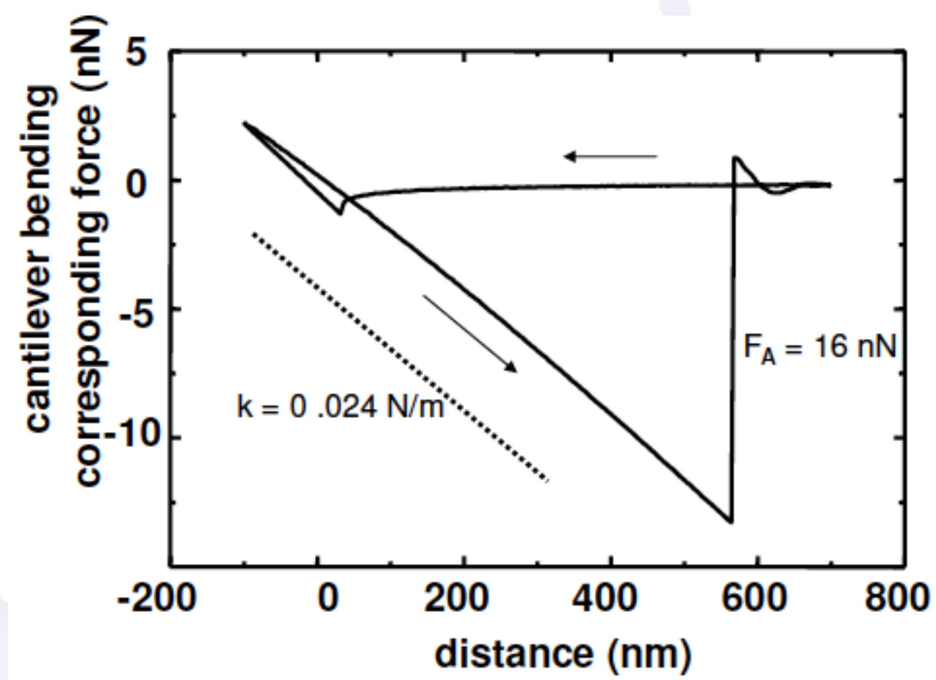
angle of deflection

elastic deflection

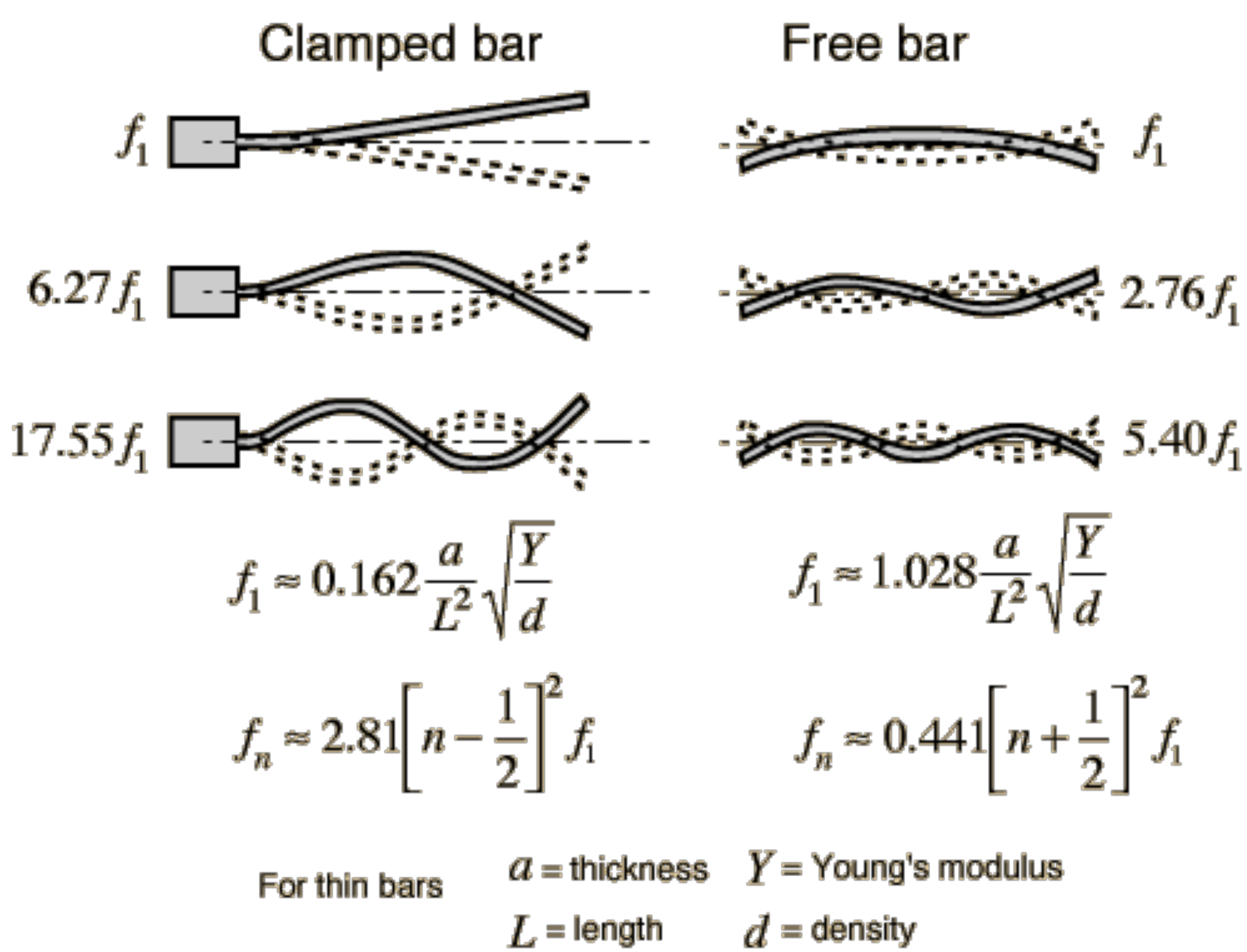
Force distance curve (approach/retract)

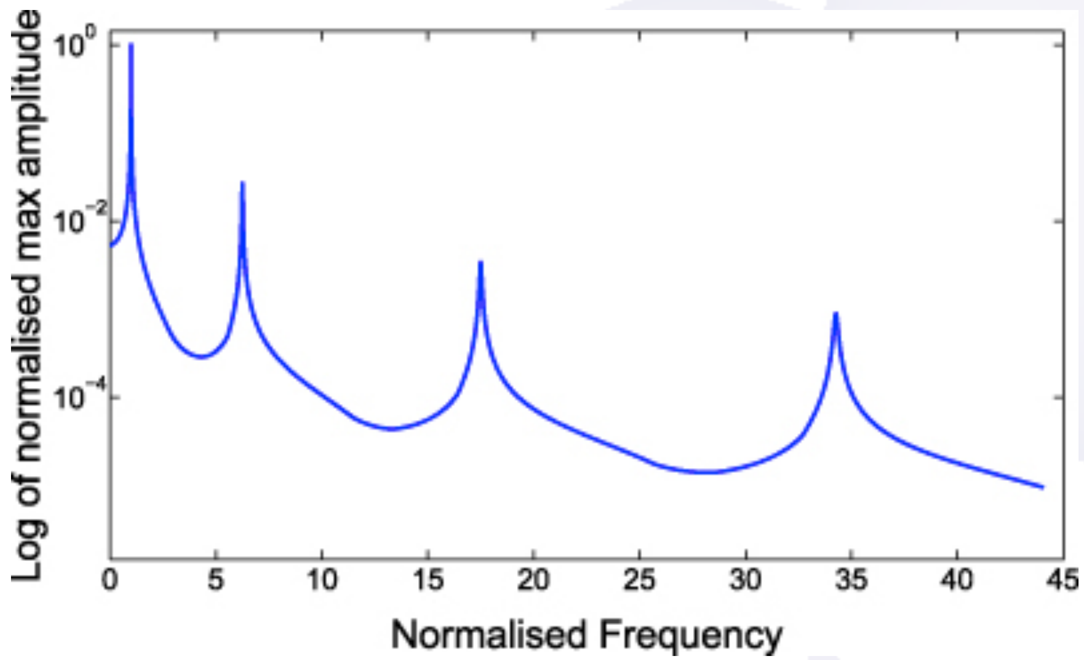






Resonant mode (tapping/non-contact) : oscillation of cantilever beam





Different modes of vibration of the cantilever, both vertical and torsional, are possible

Harmonic oscillator approximation

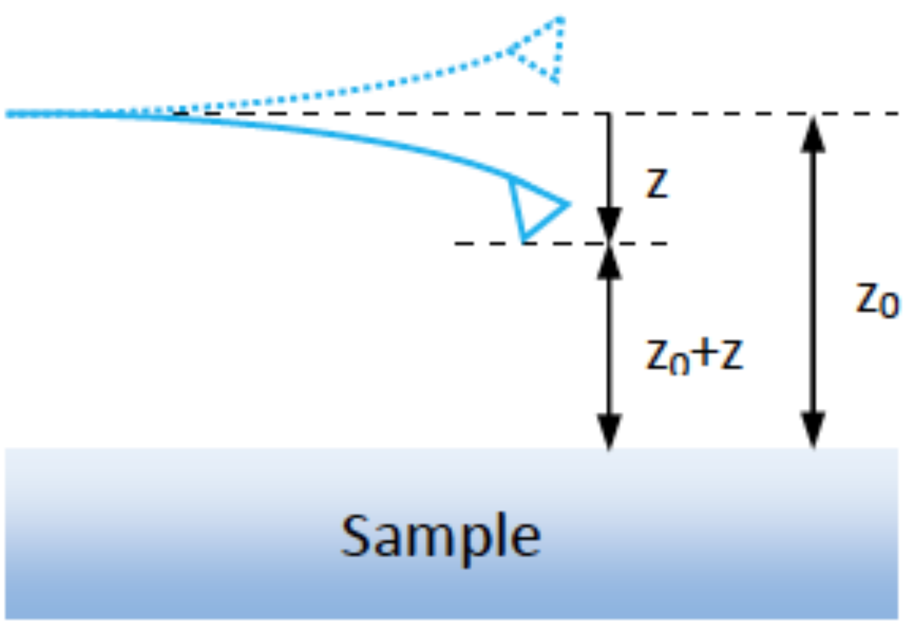
damping drive

$$m^*\ddot{z} + k_c z + \frac{m\omega_0}{Q_0}\dot{z} = F_{ts} + F_0\cos(\omega t)$$

with no interaction:

$$A(\omega) = \frac{F_0/m}{[(\omega_0^2-\omega^2)^2 + (\omega\omega_0/Q_0)^2]^{1/2}}$$

$$\tan\varphi = \frac{\omega\omega_0/Q_0}{\omega_0^2-\omega^2}$$



with interaction $F_{ts}(d = z+z_0)$:

$$F_{ts}(d) = F(z_0) - k_{ts}z$$

$$A(\omega) = \frac{F_0/m}{[(\omega_e^2-\omega^2)^2 + (\omega\omega_e/Q(z_0))^2]^{1/2}}$$

$$\omega_e = \sqrt{(k_c + k_{ts})/m^*} \qquad Q(z_0) = Q_0\frac{\omega_e}{\omega_0}$$

amplitude modulation

vs.

frequency modulation

Resonant mode: frequency modulation

Frequency modulation: $f_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m^*}}$ $\Delta f = -\frac{f_0}{2k}\frac{\partial F_{tot}}{\partial z}$

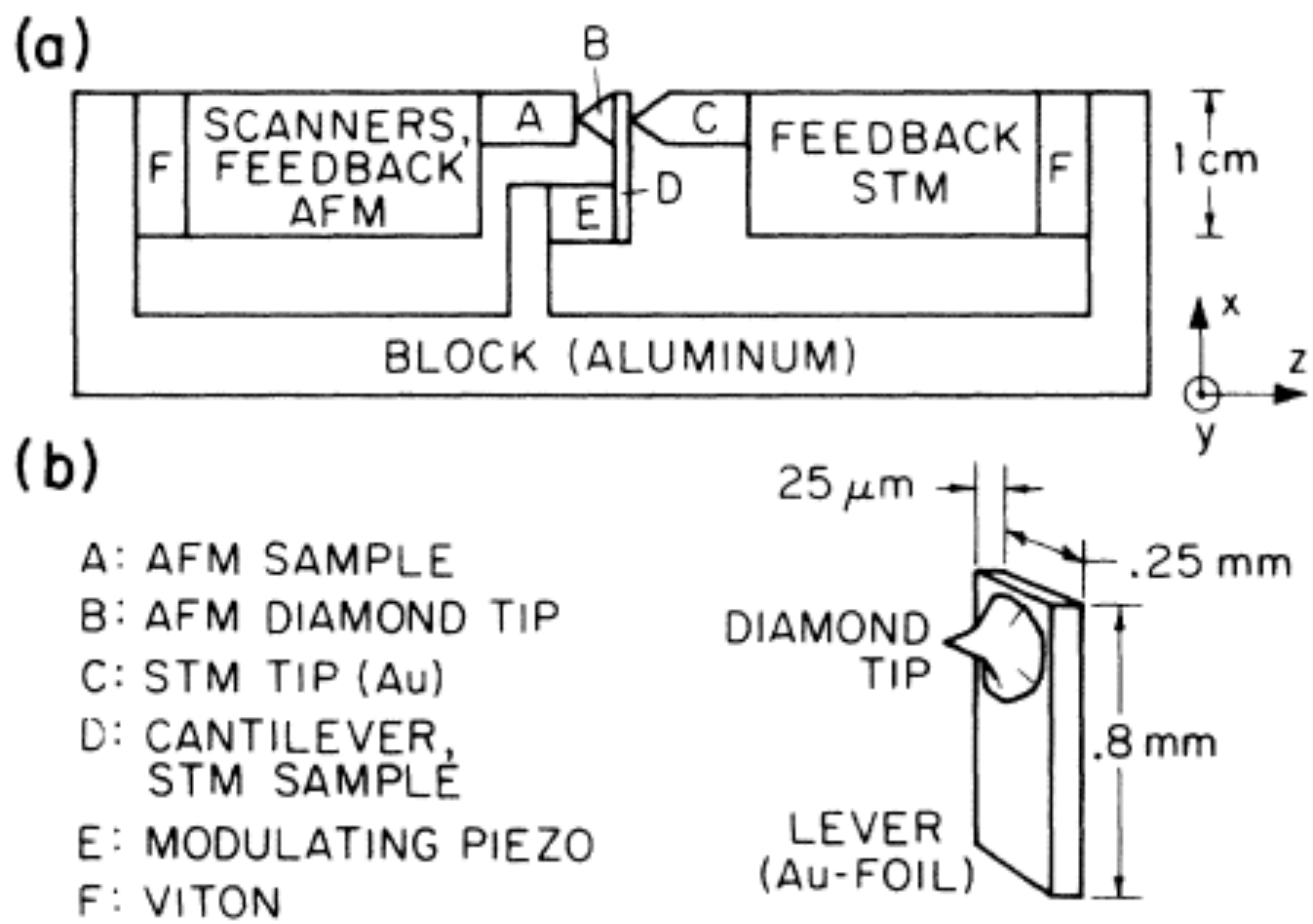
$\boxed{\Rightarrow \text{measured topography = surface of constant } \frac{\partial F}{\partial z}}$

from E. Meyer

Detecting the cantilever response

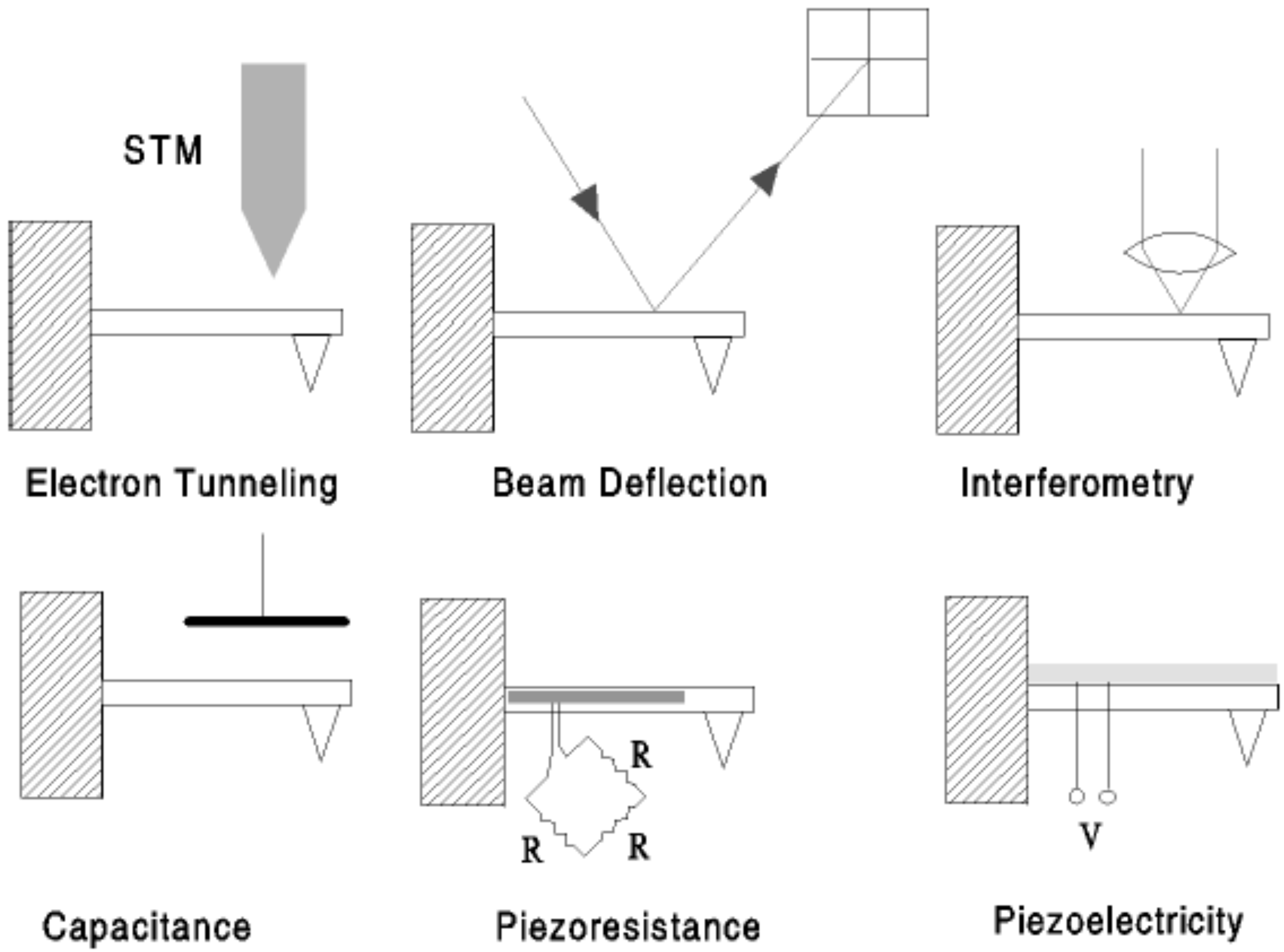
First approach: let's make things as complicated as possible….

STM detection
in first AFM



Binning *et al.* PRL **56,** 930 (1986)

Detecting the cantilever response



from E. Meyer

Piezoelectric detection using crystal tuning fork

Giessibl APL **73,** 3956 (1998)
Giessibl Rev. Mod. Phys. **75,** 949 (2003)

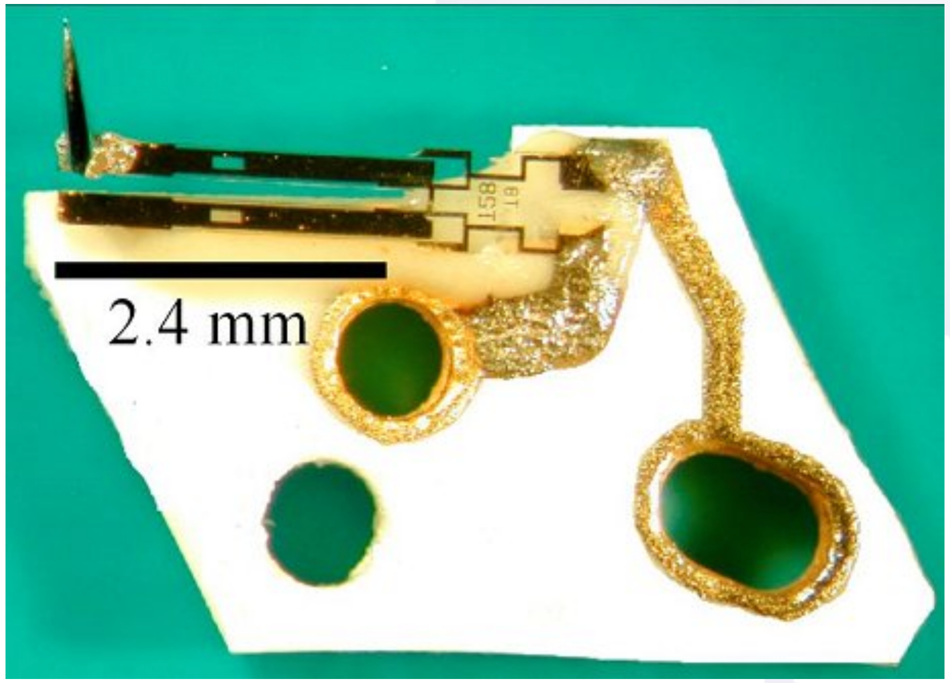
Minimising noise in resonant measurements

amplitude temperature

$$\delta z \propto \frac{\left(1+\sqrt{\frac{\pi}{2}}\left(\frac{A}{\lambda}\right)^{3/2}\right)}{A}\sqrt{TB}$$

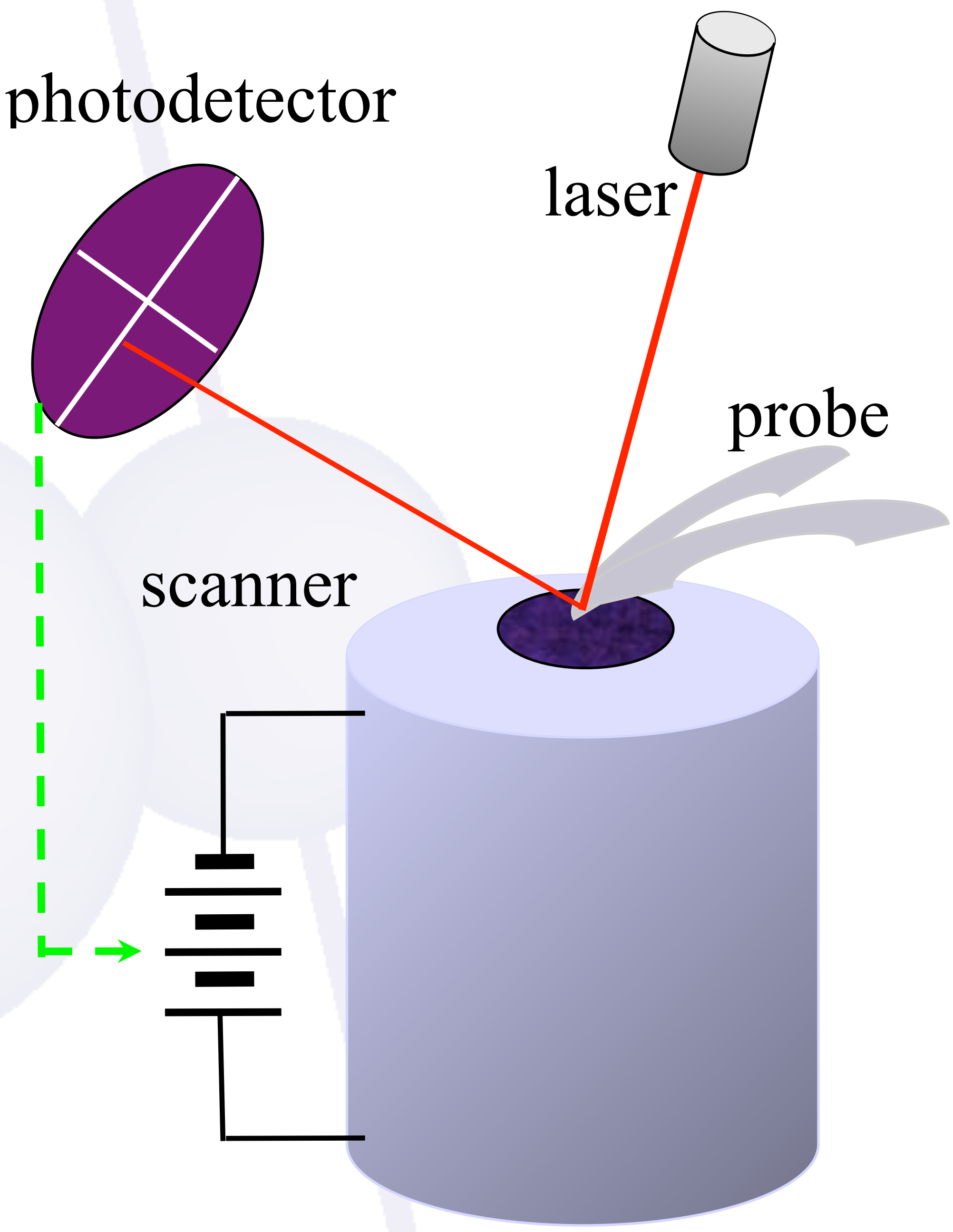
bandwidth

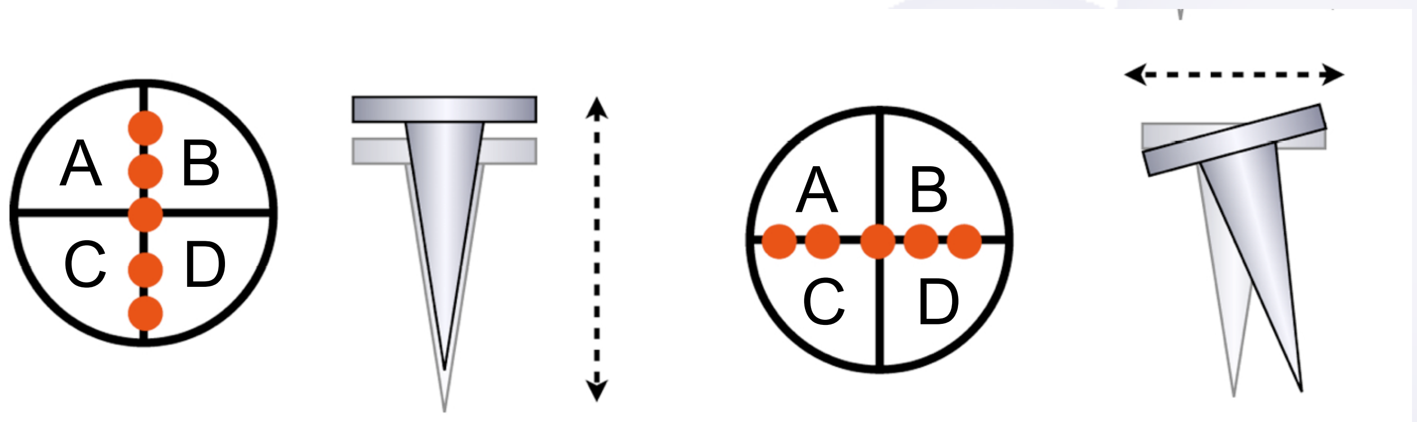
force interaction range



Best results for small amplitudes
Need extremely stiff cantilevers (k > 1000 N/m) → quartz

Beam deflection: laser reflection onto photodetector



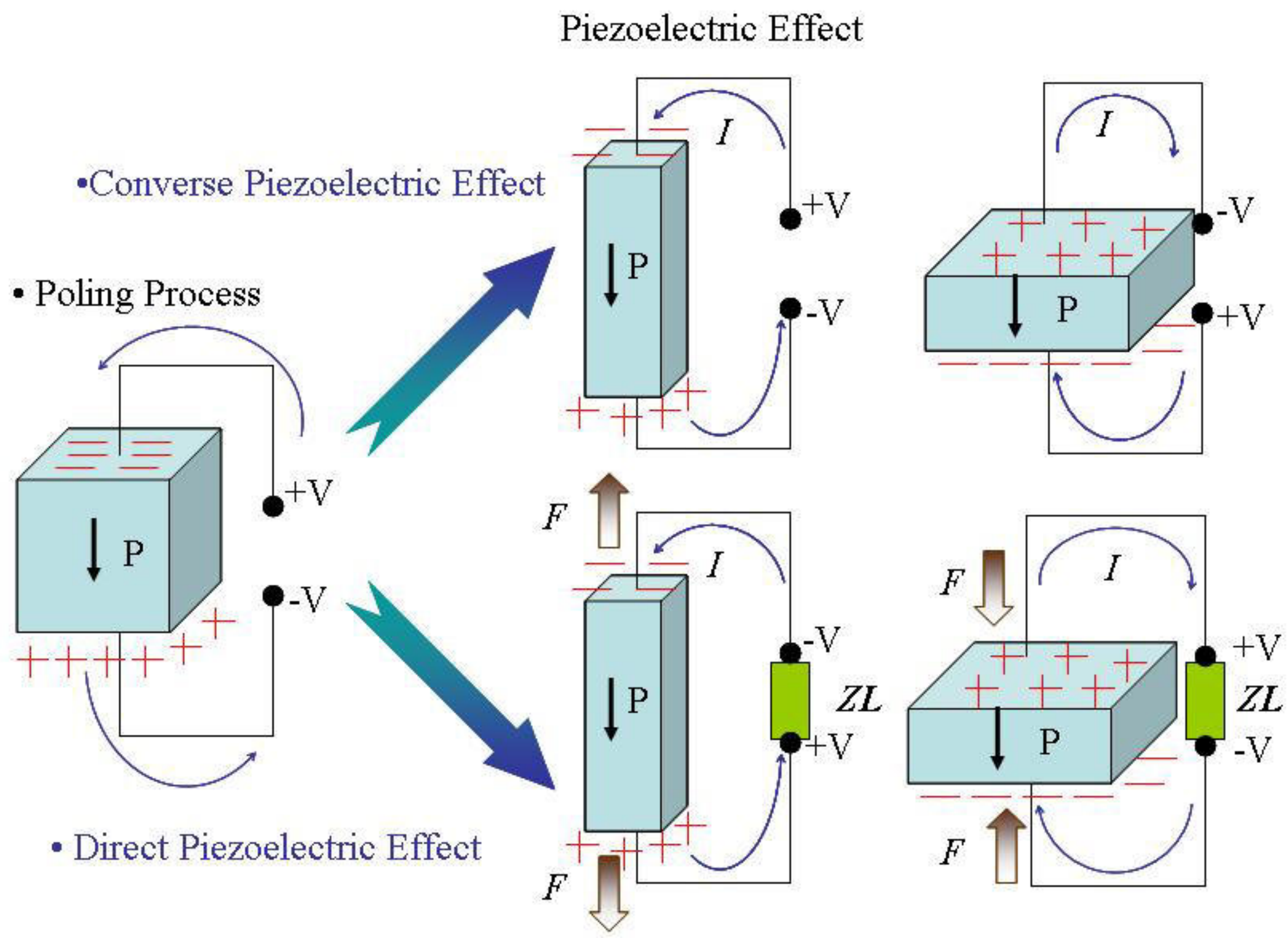


Vertical signal (deflection/buckling)
= (A+B) - (C+D)

Horizontal signal (torsion)
= (A+C) - (B+D)

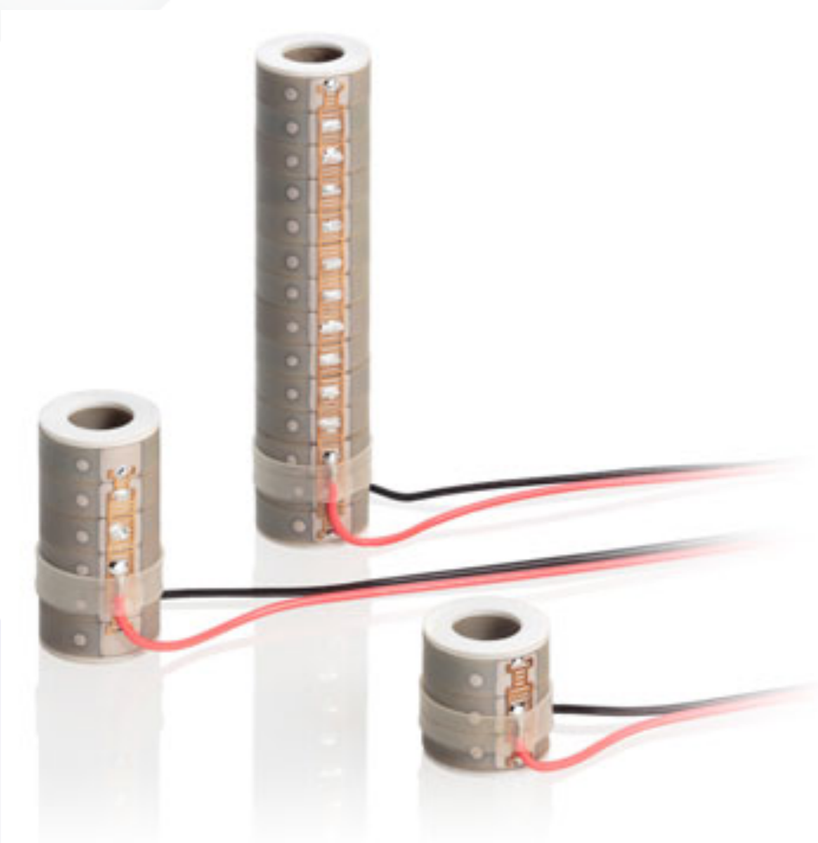
Feedback control of piezoelectric scanner displacement

Precise motion control by piezoelectric actuators

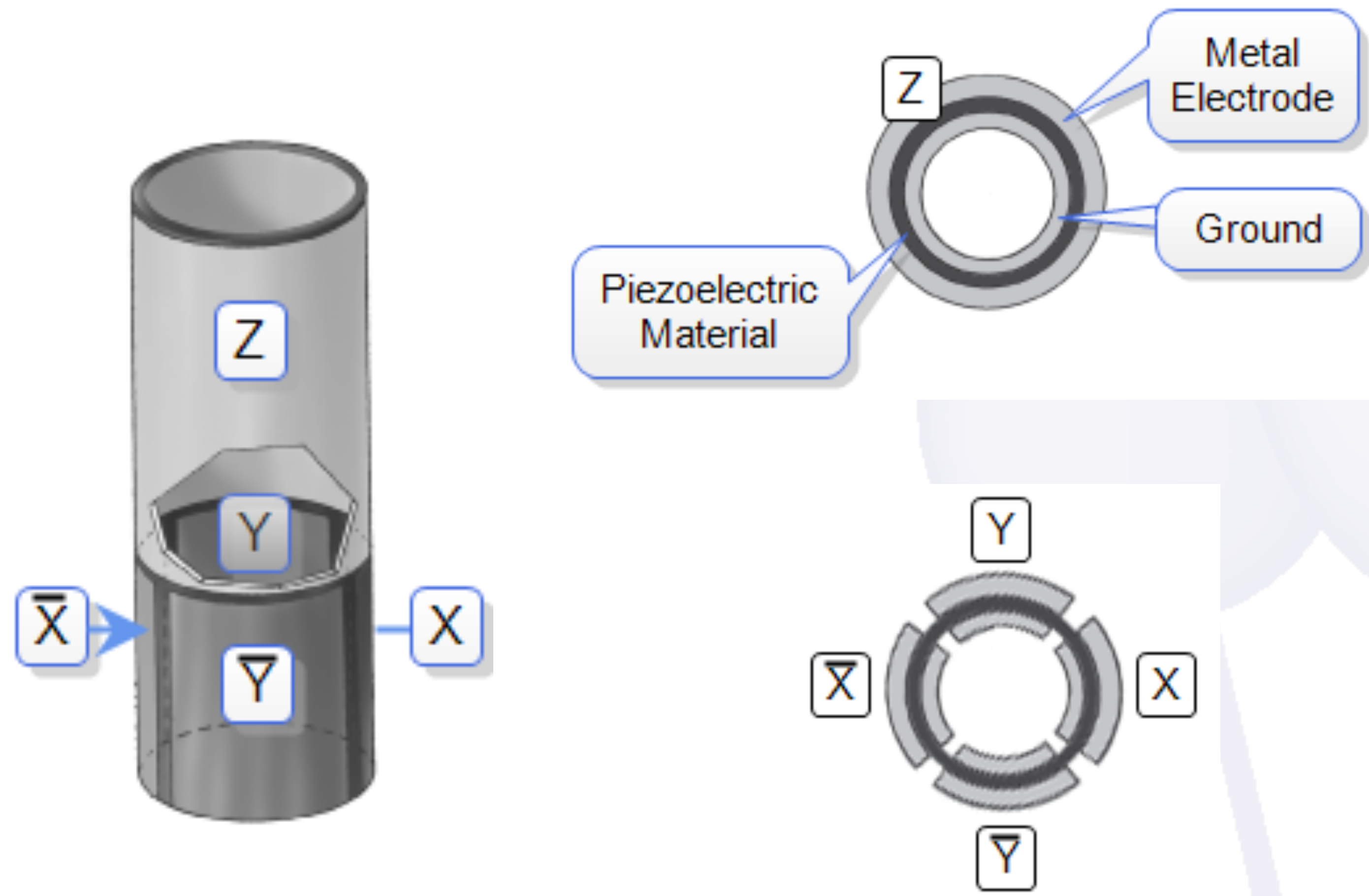


strain $X_j = d_{ij} E_i$ electric field

Precise motion control by piezoelectric actuators



Piezocolumns by Pi-USA



High voltage control of scanner displacement to adjust tip-sample distance following desired feedback (eg constant force, constant Δf)

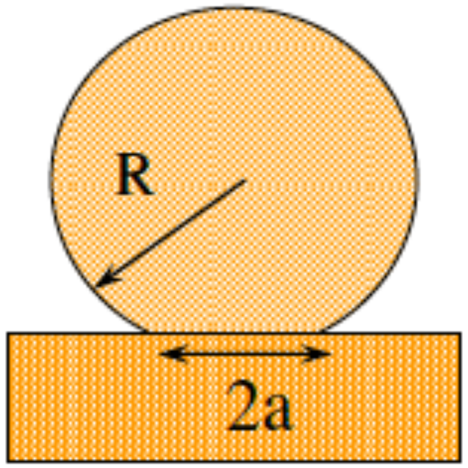
Need to consider scanner nonlinearities, thermal drift, and other sources of image distortion

Basic tip-sample interactions - uhv contact

The contact area is given by

$2a = 2\,E^*(F\,R)^{1/3}$ (Hertz theory)

- in air: 5-100nm
- in liqiuds: atomic resolution
  F. Ohnesorge and G. Binnig, Science 260, 1451 (1993)
- in ultra-high vacuum: 1-10 nm



from E. Meyer

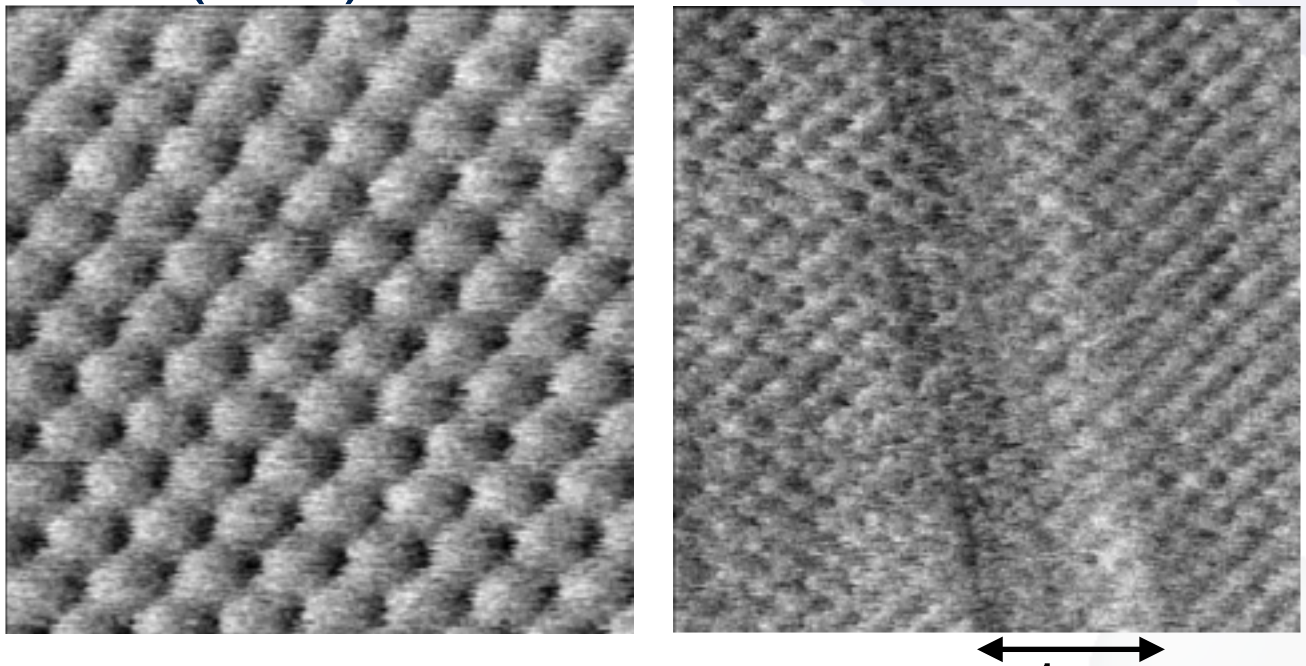
vertical deflection

C_{60} molecules
Lüthi *et al.* Z.f. Phys.B **95,** 1 (1994)

unit cell steps on NaCl
Howald *et al.* PRB **49,** 5651 (1995)

Si (111) 7x7 reconstruction
(chemically modified tip)
Howald *et al.* PRB **51,** 5484 (1995)

NaF (001)



from E. Meyer

can observe atomic periodicity but
distortion of step area of range of contact radius

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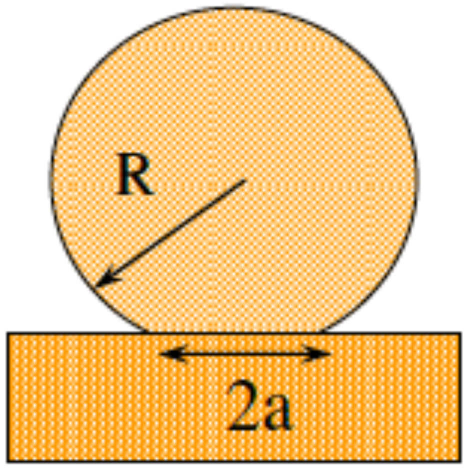
- in ultra-high vacuum: 1-10 nm

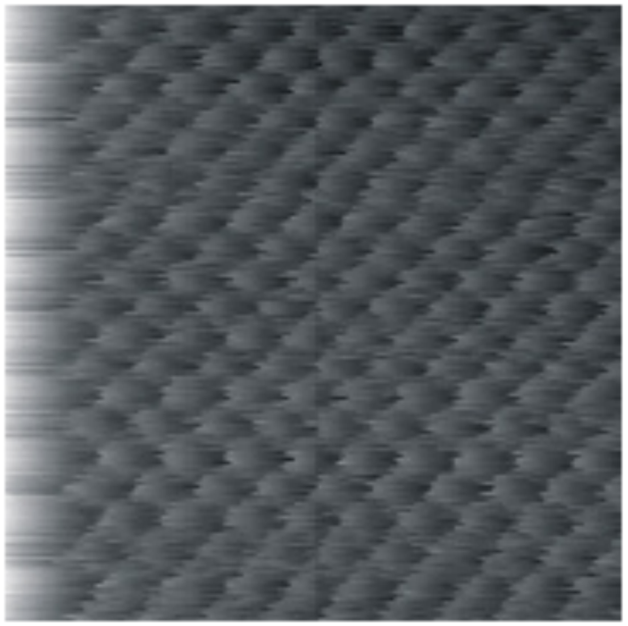
Best resolution in ultra-high vacuum:

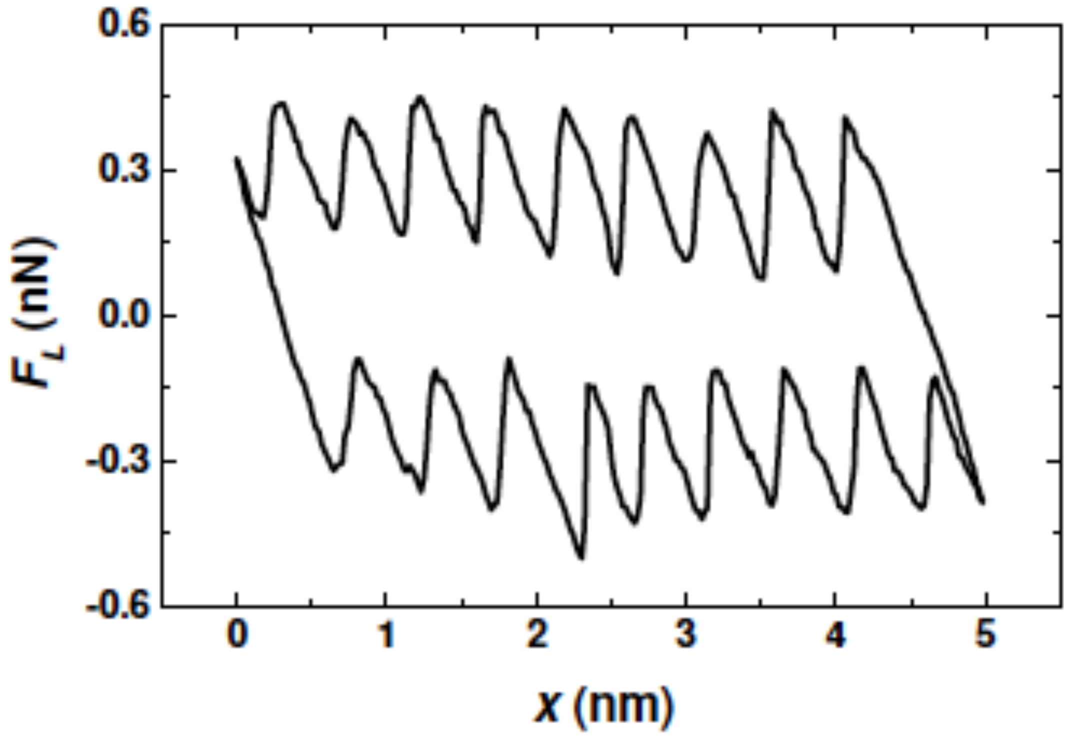


from E. Meyer

lateral torsion

NaCl (001)





from E. Meyer

atomic scale stick-slip motion

Basic tip-sample interactions - ambient

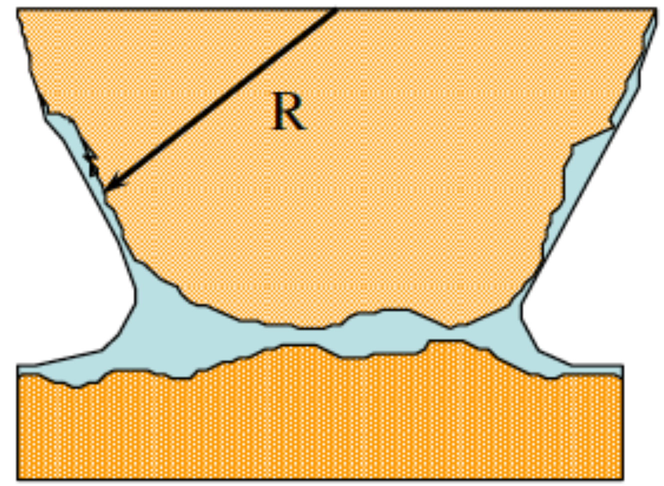
$F_{max} = 4\,\pi\, R\,\gamma \cos(\Theta)$

$\gamma\,(H_2O) = 0.074$N/m R=100nm

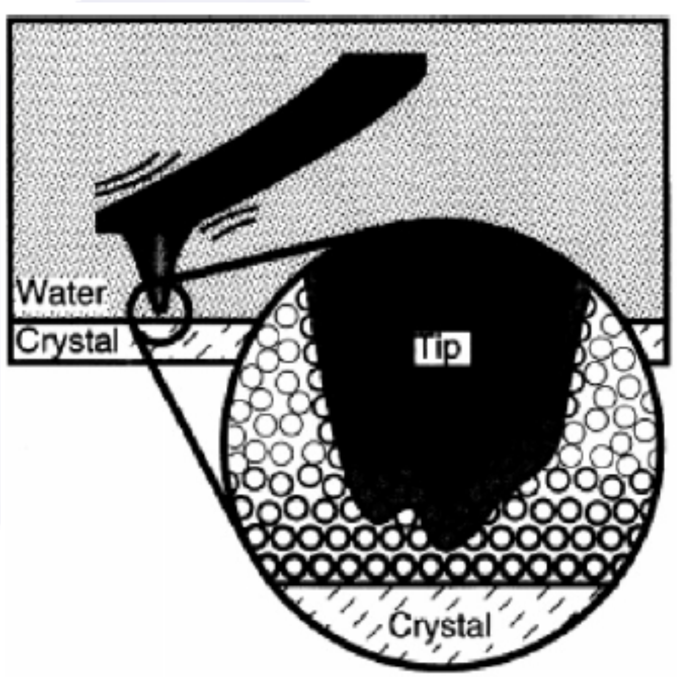
Contact angle foir hydrophilic surfaces $\Theta \approx 0°$

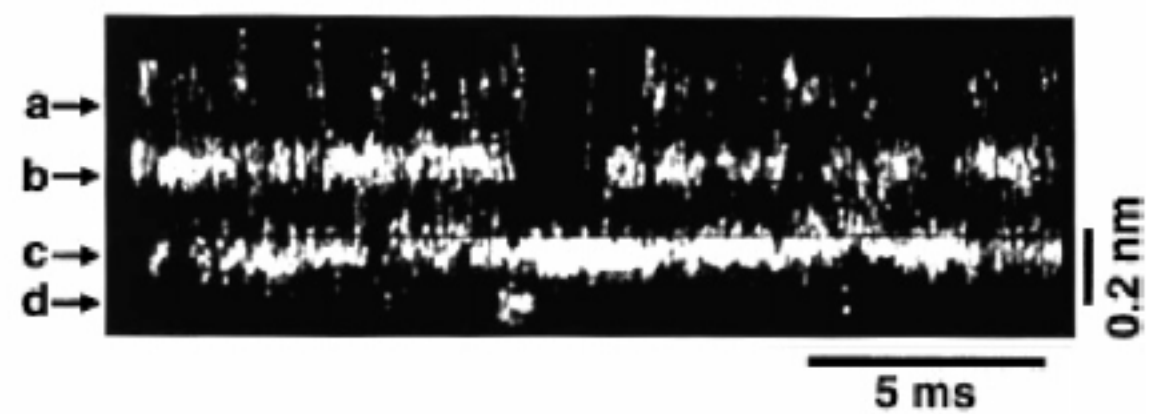
for

$\Rightarrow\ F_{max} = 90$nN



from E. Meyer





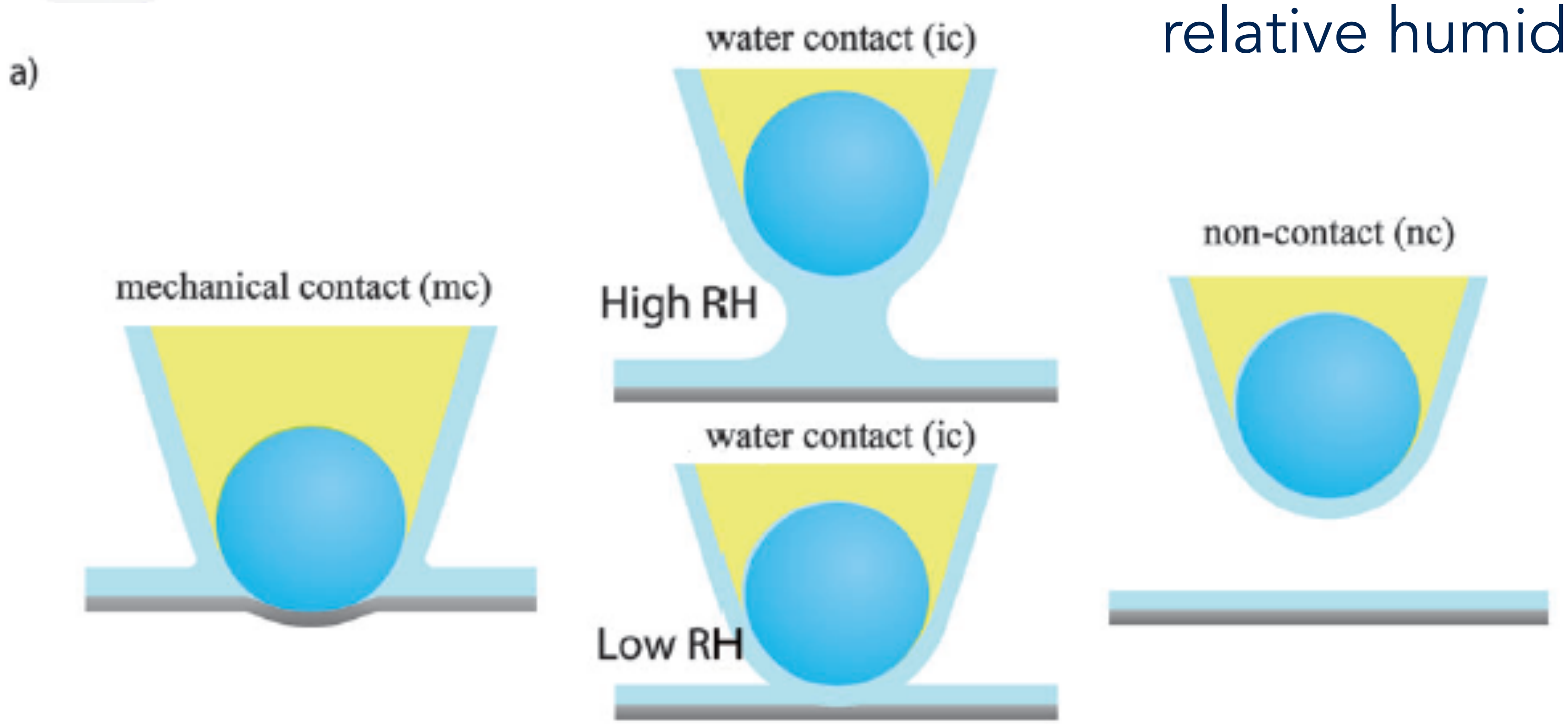
Cleveland *et al.* PRB **52,** R8692 (1995)

Tip hops between distinct states as it sequentially penetrates layers of water approaching the surface of the sample

Basic tip-sample interactions - ambient

Need to consider:

character of sample and tip
working distance
relative humidity



hydrophilic sample

Verdaguer *et al.* PCCP **14,** 16080 (2012)

Basic tip-sample interactions - vacuum

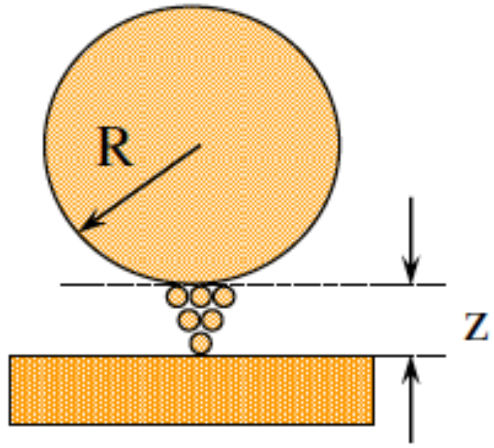
- No capillary forces (no water)
- Van der Waals and electrostatic forces dominate

$F_{vdW} = - B\ R/z^2 * 1/(1+z/2\ R)^2$

$B=3K/4\ (\varepsilon_s-1)(\ \varepsilon_t-1)/\ [(\varepsilon_t+1)(\ \varepsilon_t+2)]$
$K=1.41eV$

F.O. Goodman and N. Garcia,
Phys. Rev. B 43, 4728 (91)

$\Rightarrow$ R=100nm, z=1nm



graphite-graphite	8nN
diamond-diamond	17nN
metal-graphite	10nN
SiO_2-graphite	1.2nN

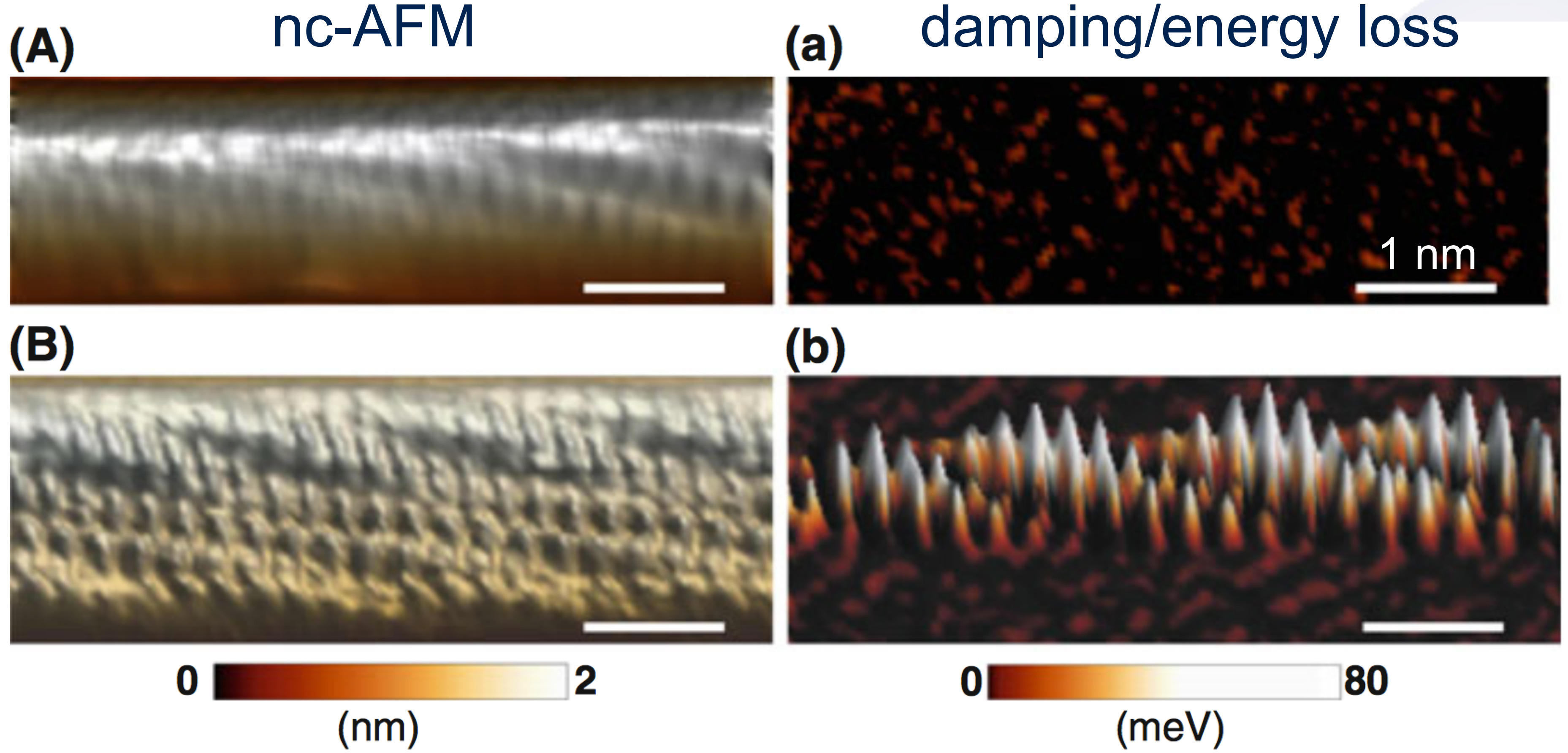
from E. Meyer

Atomic resolution in uhv nc-AFM

empty SWNT

nc-AFM

damping/energy loss



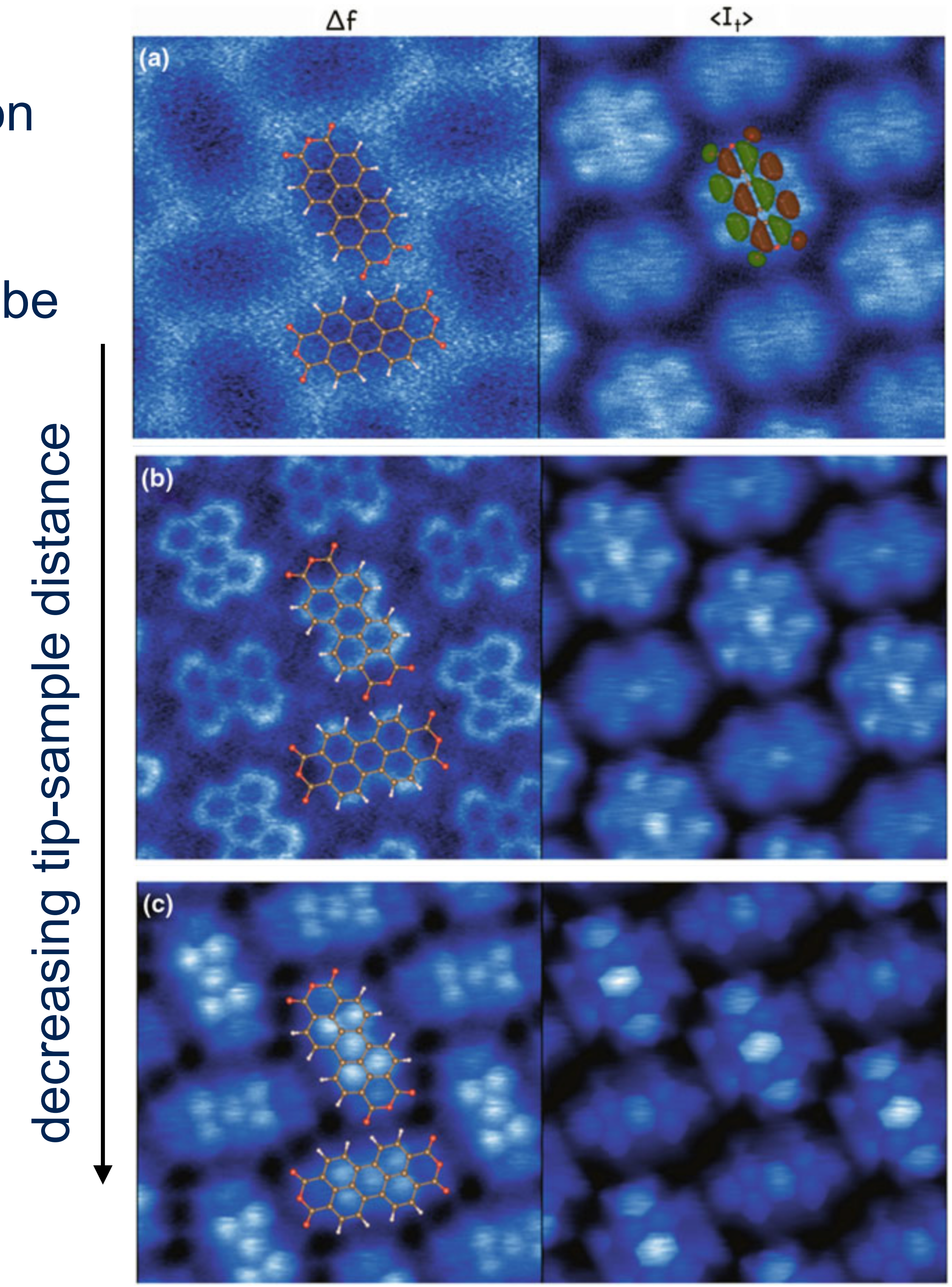
peapod w/ Dy@C_{82}

Ashino and Wiesendanger in Noncontact Atomic Force Microscopy, ed. Morita, Giessibl, Meyer, Wiesendanger

Submolecular resolution in uhv nc-AFM

PTCDA molecules on Ag (111)

Xe-functionalised probe



Hapala *et al.* in Noncontact Atomic Force Microscopy, ed. Morita, Giessibl, Meyer, Wiesendanger

Basic tip-sample interactions - liquids

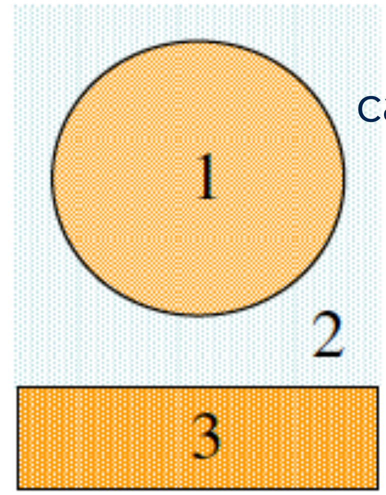
- capillary forces are eliminated
- Van der Waals can be repulsive:

  U » $(n_1^2 - n_3^2)(n_2^2 - n_3^2)$

  For $n_1 < n_2 < n_3$ result negative van der Waals forces.

  Mc Lachlan, *Proc. Roy. Soc.* A 271, 38 (1963)
- Observation of very weak forces (10pN) by Ohnesorge und Binnig. Atomic resolution of a calcite surface.

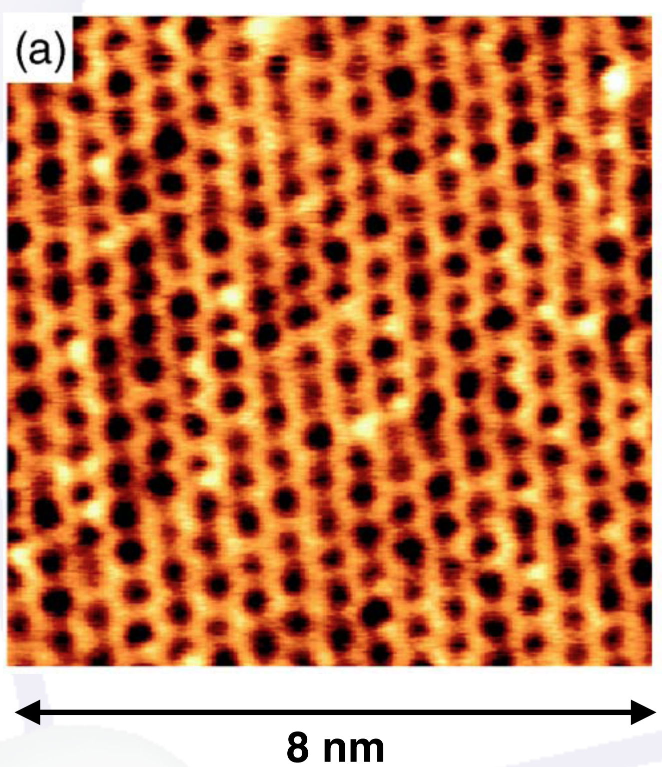
  F. Ohnesorge and G. Binnig, *Science* 260, 1451 (1993)
- For hydrophobic surfaces entrpoy effects can increase the net forces.

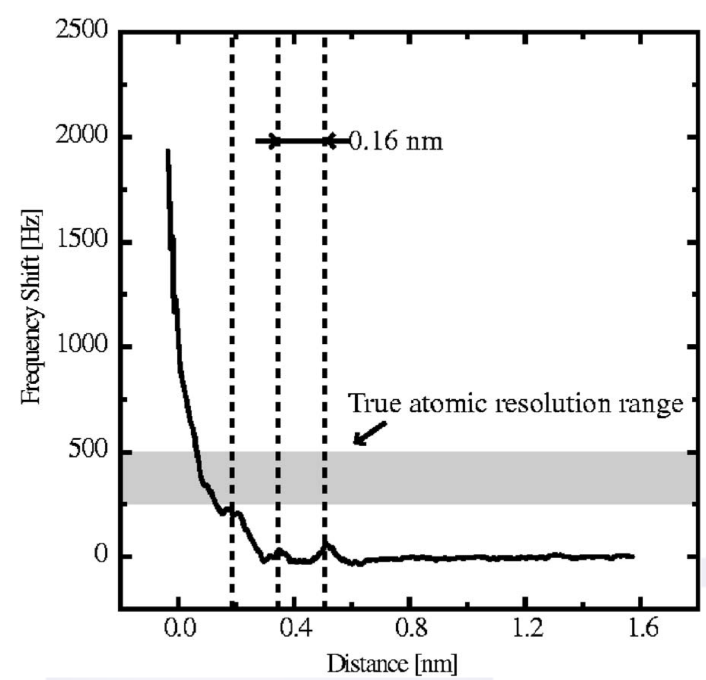


from E. Meyer

can manipulate Hamaker constant (1-3)
by the presence of a liquid (2)
depending on:
static dielectric constants (ε)
optical refraction indices (n)

cleaved (001)
muscovite mica





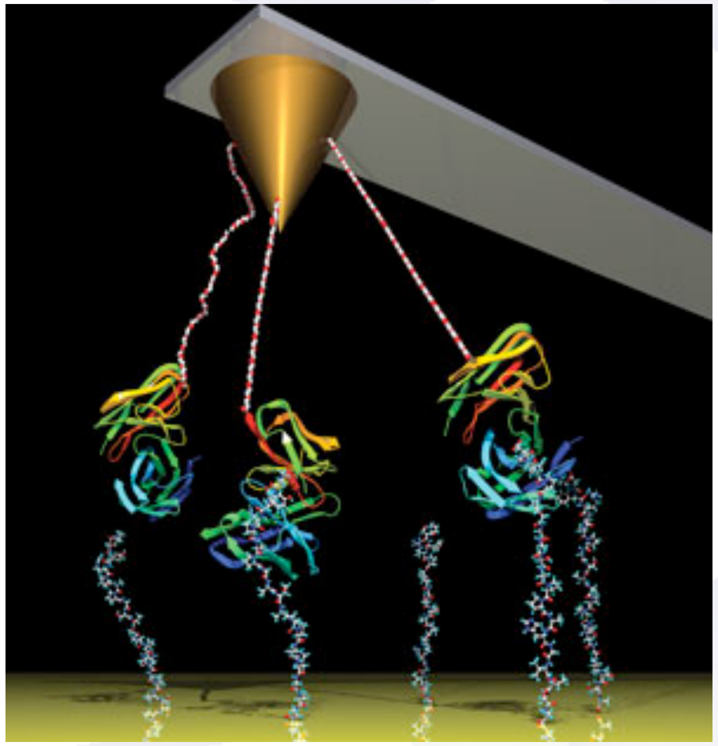
Fukuma *et al.* APL **87,** 034101 (2005)

Going beyond topographical imaging

Diverse forces between tip and sample

short-range repulsive forces (Pauli exclusion or ionic repulsion)
short-range chemical binding forces
van der Waals forces (always present, retarded beyond 100 nm)
long-ranged electrostatic forces
long-ranged magnetic forces

interactions in liquids:
hydrophobic / hydrophilic forces
steric forces
solvation forces



Noy Group
Lawrence Livermore Nat. Lab.

Sensitivity to interactions: double edged sword

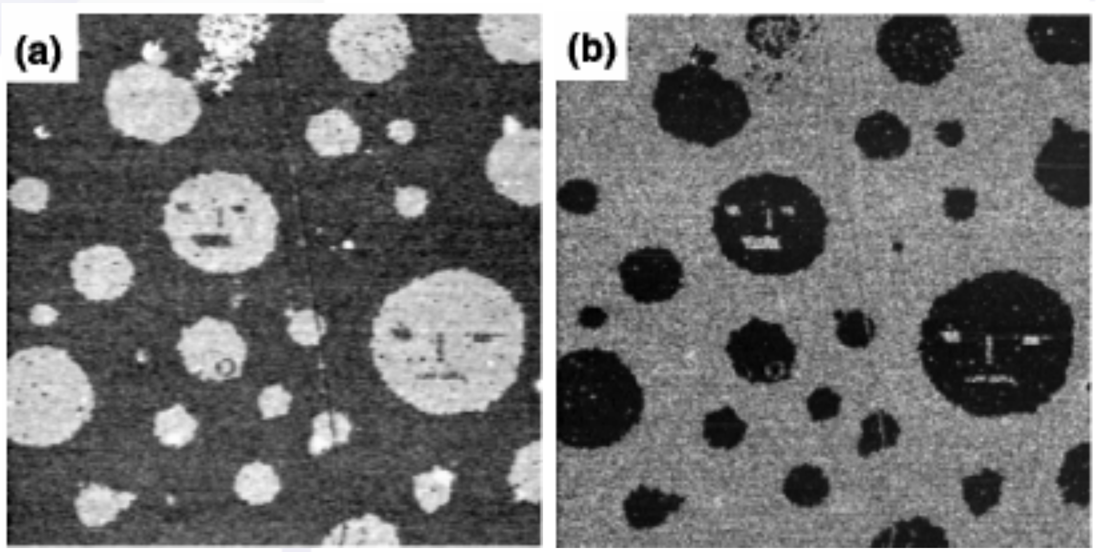
Different AFM modes to probe different interactions

Magnetic Force Microscopy MFM
Electric Force Microscopy EFM
Kelvin Probe Force Microscopy KPFM
Piezoresponse Force Microscopy PFM
Conductive Tip Microscopy CAFM
etc....

BUT parasitic interactions/artefacts can be a problem

Measuring friction contrast

Mixed Langmuir-Blodgett films

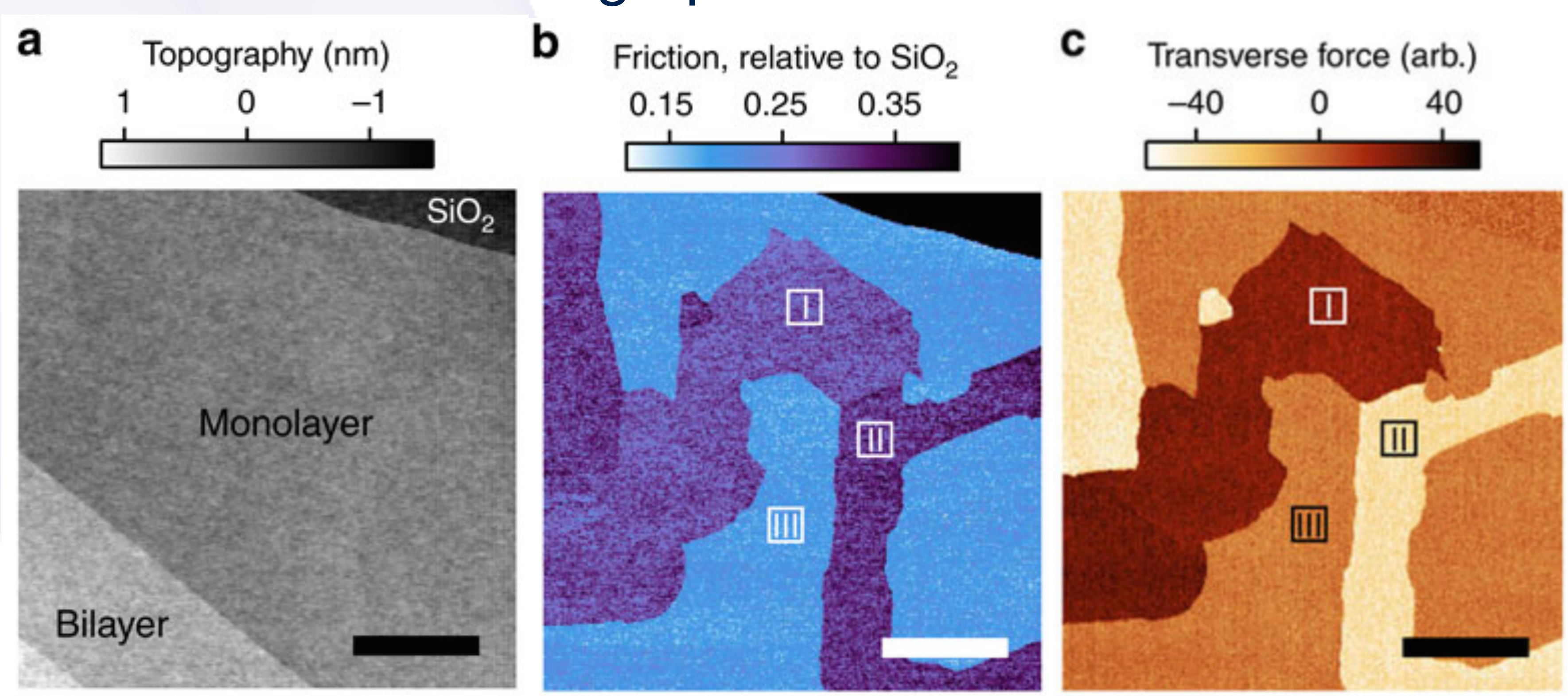


topography lateral force

Meyer *et al.* Thin Solid Films **220,** 132 (1992)

Friction measurements using either lateral force (torsion) or transverse force (buckling) access the adhesion between the tip and the sample

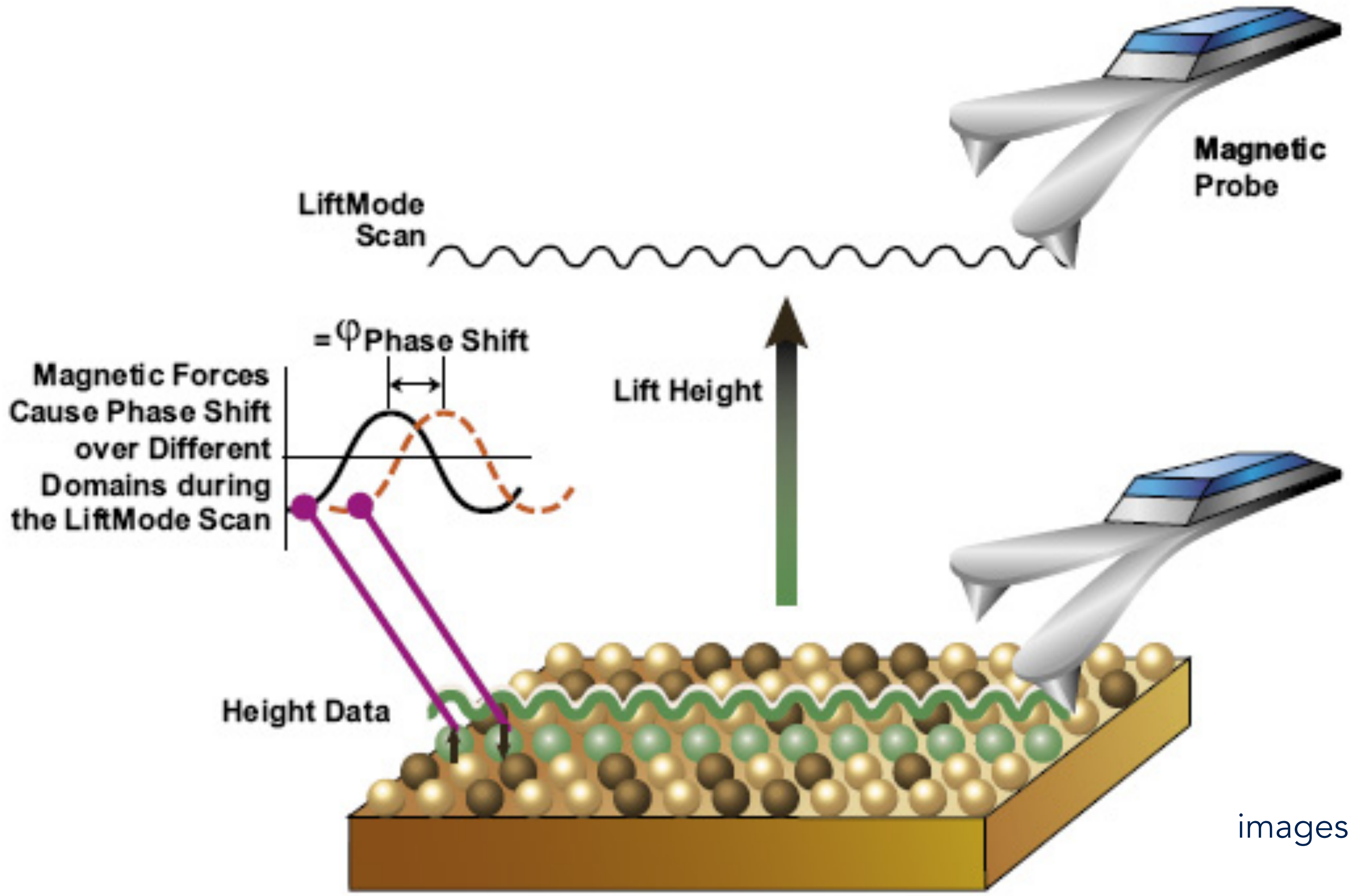
Adsorbates on graphene



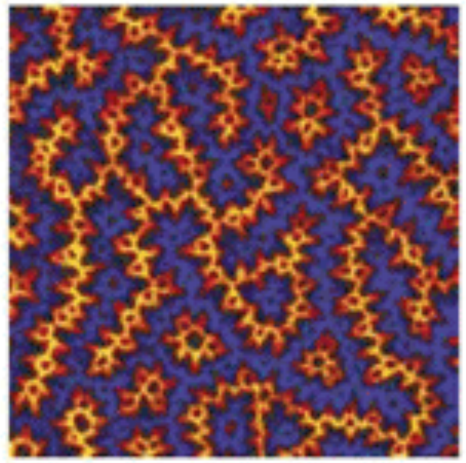
Gallagher *et al.* Nat. Comm. **7,** 10745 (2016)

Measuring magnetic interactions

Need functionalised (magnetically coated) tip



Magnetic domains in a steel sample



images from Bruker

2-pass technique, acquiring first topography, then MFM signal at a specific height above the sample to avoid topographical crosstalk

Magnetic force microscopy (MFM)

$$\Delta\varphi = -(Q/k)\cdot\partial F_z/\partial z,$$

$$F_z = \int_{\text{tip}} d^3r \int_{\text{sample}} d^3r' \, F_z^{ij}(\vec{r}-\vec{r}') m_i(\vec{r}) m'_j(\vec{r}'),$$

$$\hat{F}_z(\vec{r}-\vec{r}') \sim 1/|\vec{r}-\vec{r}'|^4$$

For high resolution, want sharp tips, which can be approximated as a point dipole

$$M = (1/6)\pi d_n^3 m_{\text{sat}}$$

$$\Delta\varphi_0(\vec{r}) = -(1/6)\pi d_n^3 m_{\text{sat}} \frac{Q}{k}\frac{\partial}{\partial z}\int_{\text{sample}} d^2r' \, F_z^i(\vec{r}-\vec{r}') m'_i(\vec{r}')\Big|_{z=d_n/2+d}$$

ideal measurement without noise

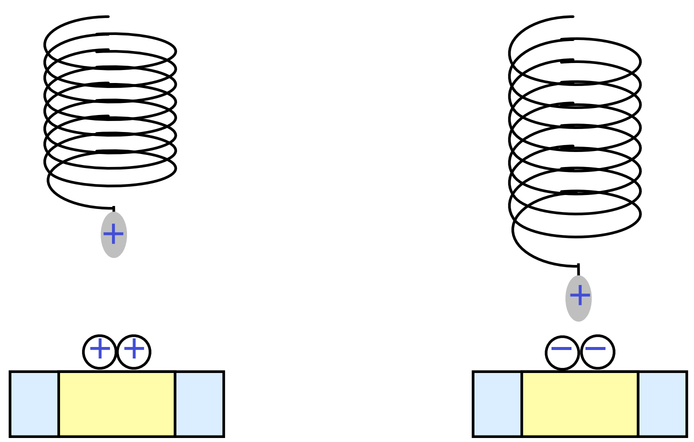
$$\sqrt{\langle\delta\varphi^2\rangle} = \sqrt{Qk_BT\Delta\nu/k\omega_0A^2},$$

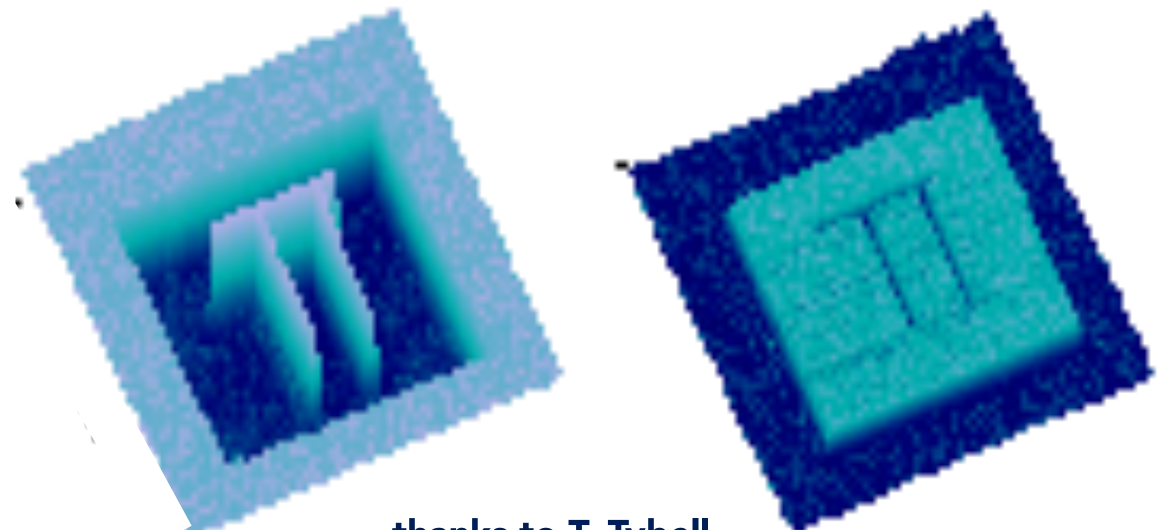
minimum detectable signal with thermal noise

Measuring electrostatic interactions

Need functionalised (metallic/charged) tip

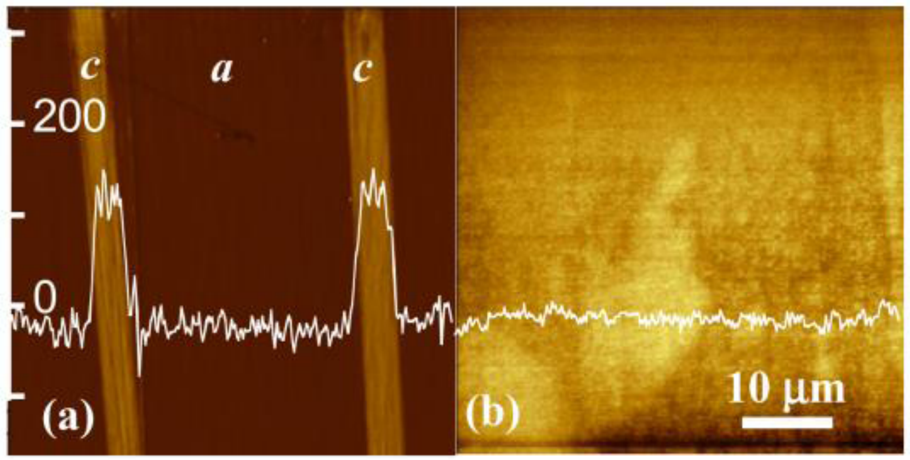
Screening charges on ferroelectric domains





2-pass technique, acquiring first topography, then EFM signal at a specific height above the sample to avoid topographical crosstalk

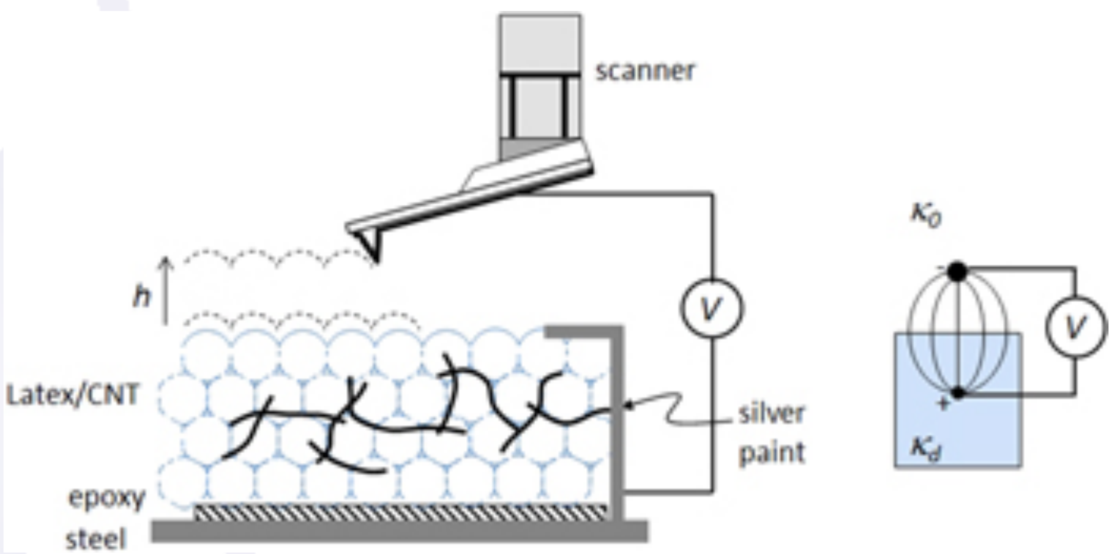
Very sensitive to relative humidity at ambient conditions

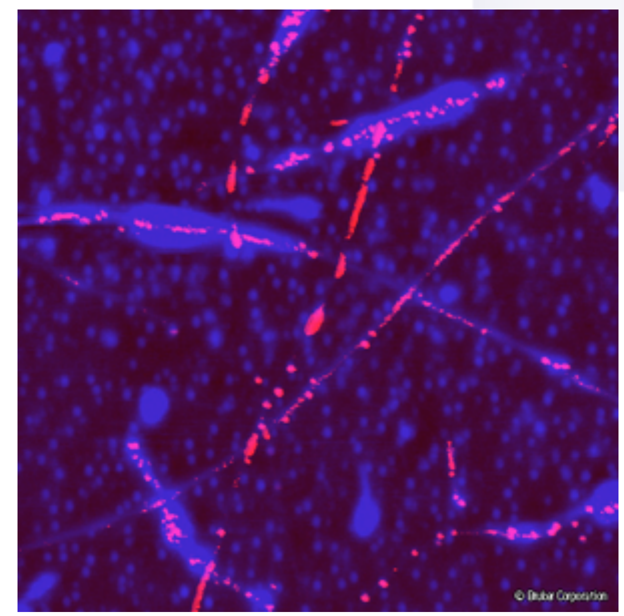


He *et al.* APL **98,** 062905 (2011)

Electric force microscopy (EFM)

Can image charge state of a sample surface OR look for metal/ insulator contrast using image charges

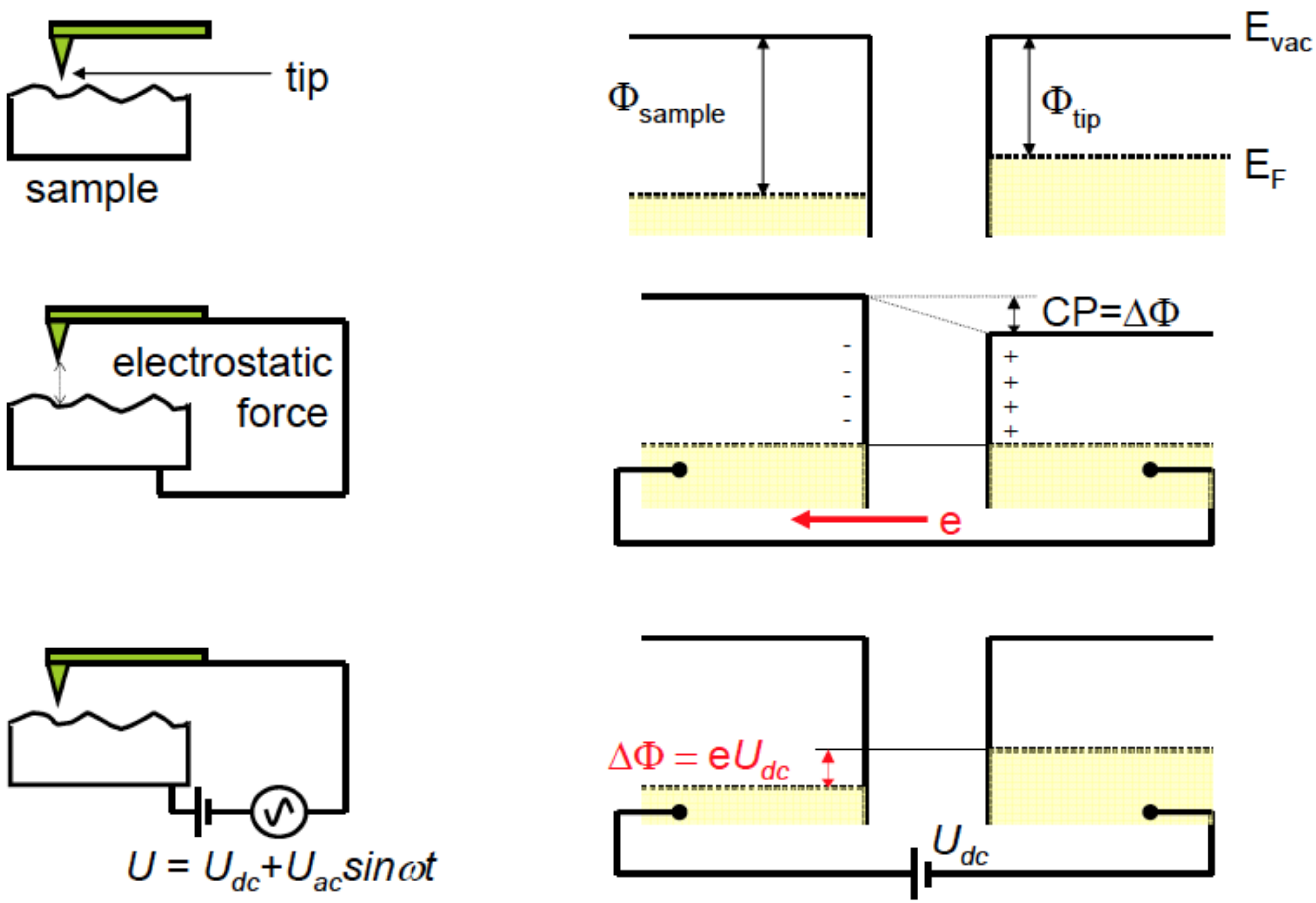




CNT (metallic) in latex (insulating)

Going further with a Kelvin probe approach

Kelvin Principle



Kelvin probe force microscopy (KPFM)

Principle of Kelvin Probe Force Microscopy

$$F_{el} = -\frac{1}{2}\frac{\partial C}{\partial z}V_{eff}^2 \quad \Rightarrow \quad F_{el} = -\frac{1}{2}\frac{\partial C}{\partial z}\left(V_{bias} - V_{CP}\right)^2$$

$$V_{CP} = 1/e \cdot \left(\Phi_{tip} - \Phi_{sample}\right)$$

contact potential

Φ - work function

apply bias: $$\boxed{V_{bias} = V_{dc} + V_{ac} \cdot \sin(\omega t)}$$

Kelvin probe force microscopy (KPFM)

$$F_{el} = -\frac{1}{2}\frac{\partial C}{\partial z}V_{eff}^2 = F_{dc} + F_{\omega} + F_{2\omega}$$

$$F_{dc} = -\frac{\partial C}{\partial z}\left[\frac{1}{2}\left(V_{dc} - V_{CP}\right)^2 + \frac{V_{ac}^2}{4}\right]$$

$$F_{\omega} = -\frac{\partial C}{\partial z}\left(V_{dc} - V_{CP}\right)V_{ac}\sin(\omega t)$$

$$F_{2\omega} = \frac{\partial C}{\partial z}\frac{V_{ac}^2}{4}\cos(2\omega t)$$

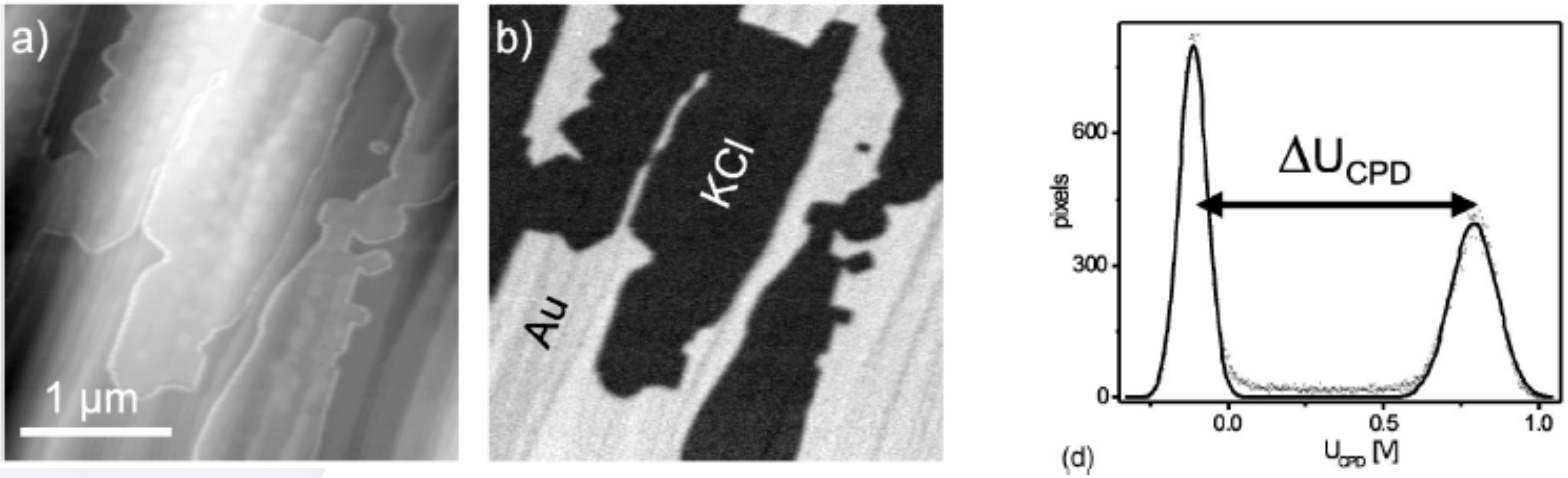
AM-KPFM
Amplitude Modulation

FM-KPFM
Frequency Modulation

Kelvin probe force microscopy (KPFM)

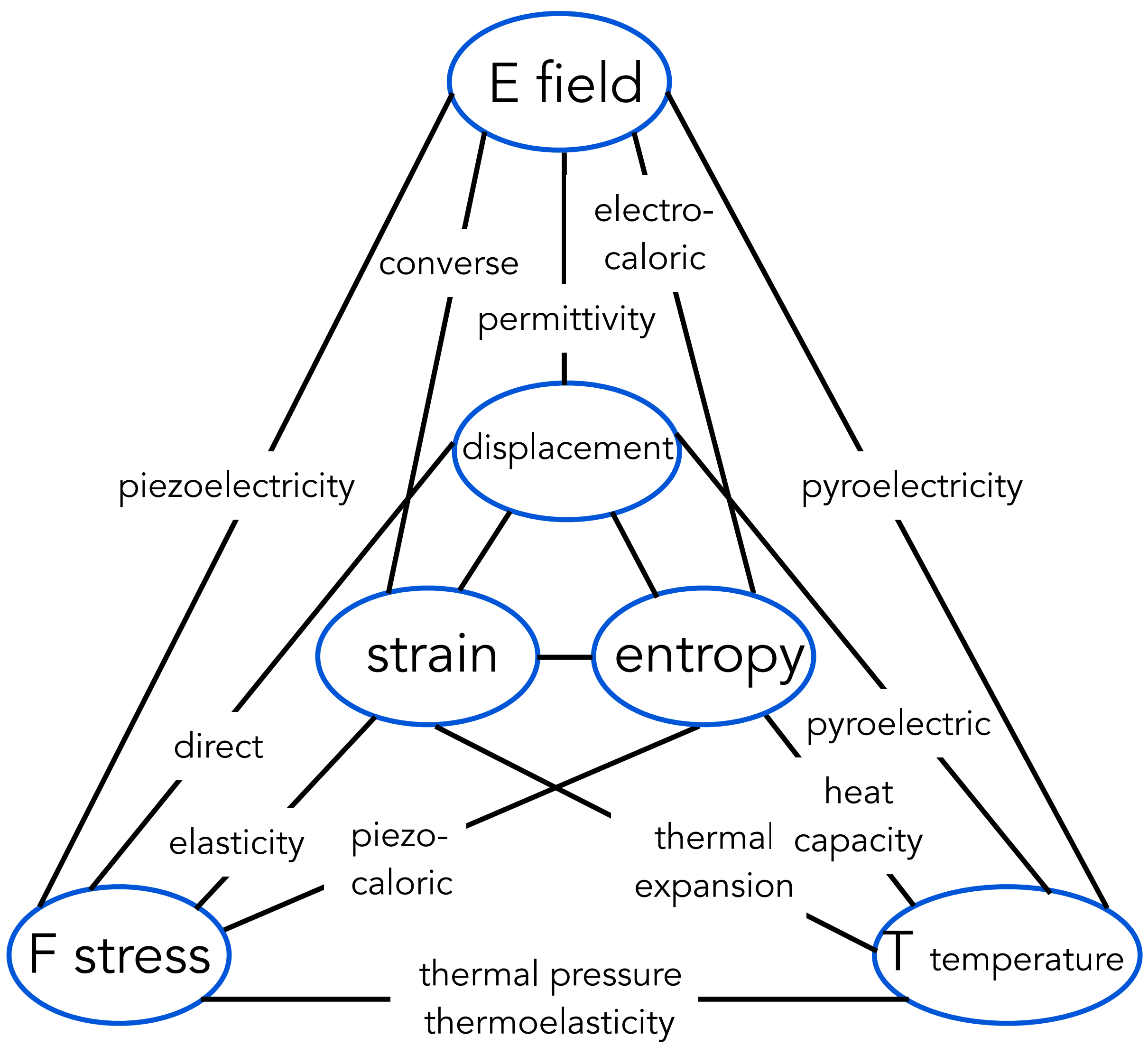
KCl on Au(111)

topography KPFM



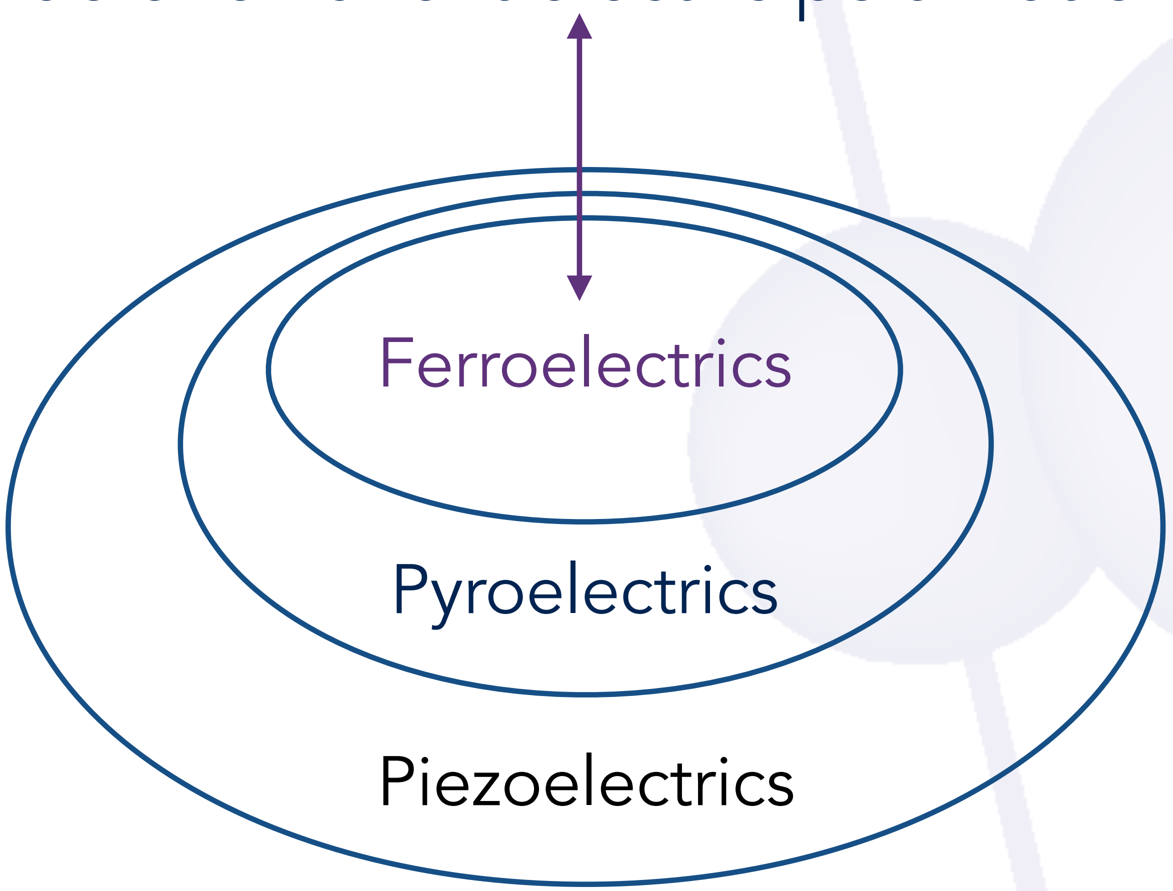
Zerweck *et al*. PRB **71,** 125424 (2005)

Measuring polar properties : ferroelectrics



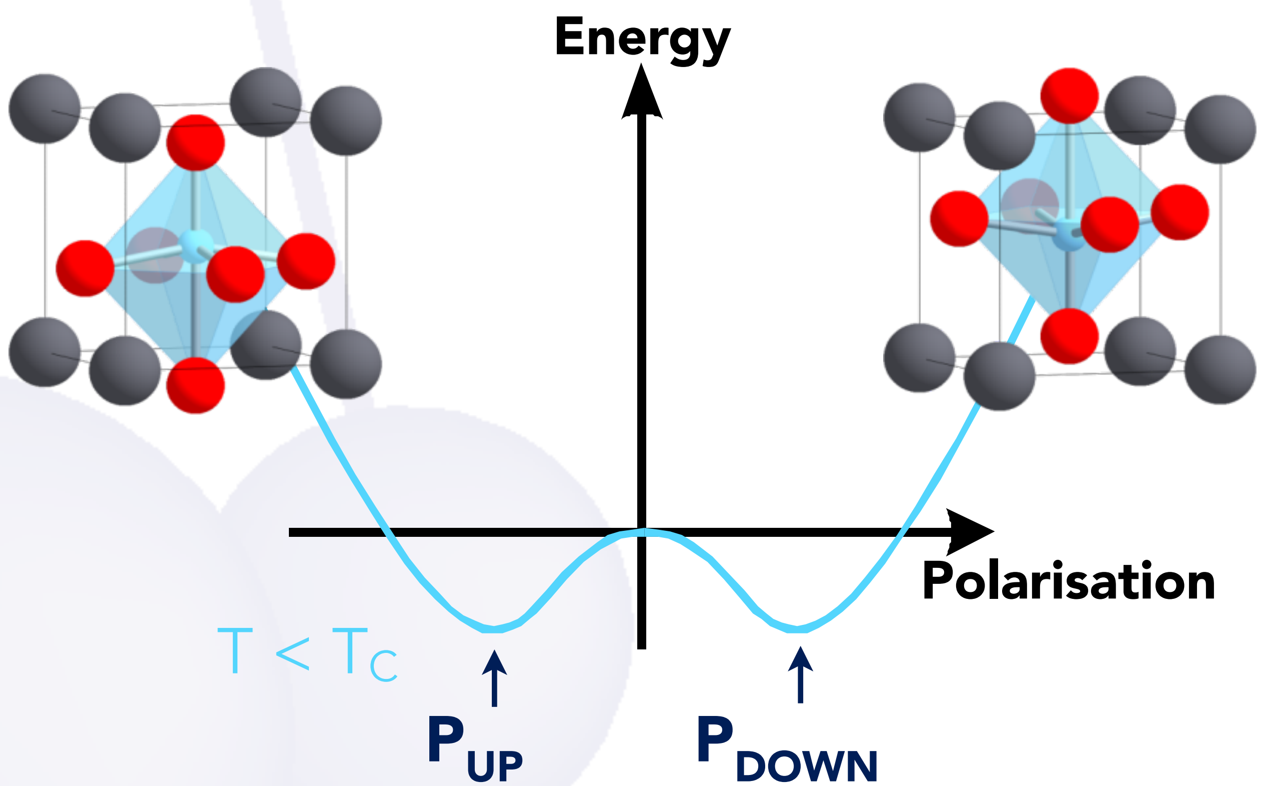
Behaviour of polar materials

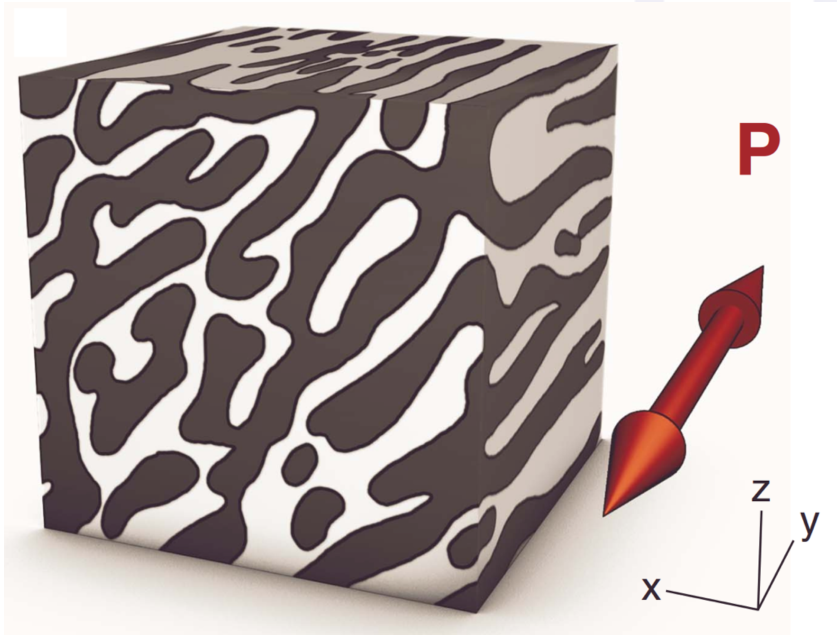
switchable remanent electric polarization



want to determine polarization

Domains and domain walls in ferroelectrics





thanks to D. Meier

Domain walls separate regions with different polarisation orientation

Piezoresponse force microscopy (PFM)


Alexei Gruverman


Sergei Kalinin


Stephen Jesse


Nina Balke


Lukas Eng


Roger Proksch


Elisabeth Soergel

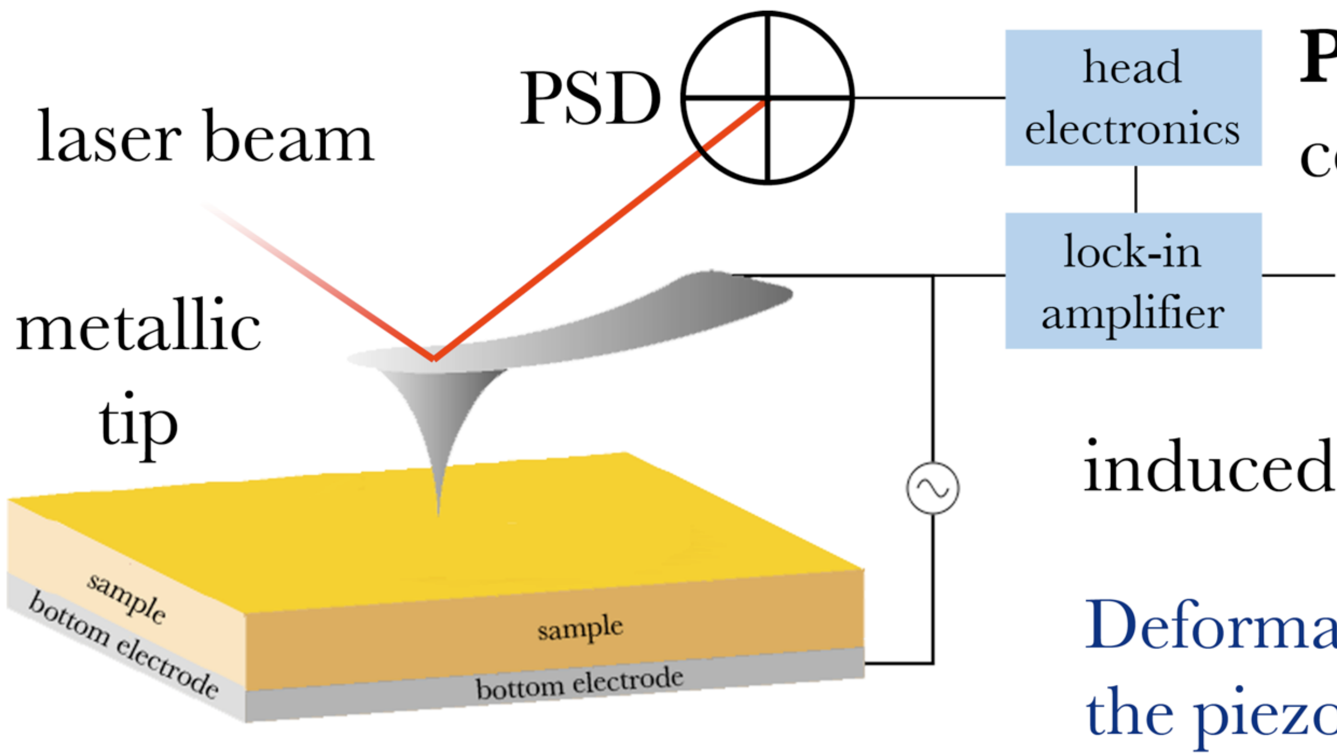

Catalin Harnagea


Seungbum Hong

Gruverman et al. APL 69, 3191 (1996)
Eng et al. APL 74, 233 (1999)
Tybell et al. APL 75, 856 (1999)
Eng et al. APL 74, 233 (1999)
Hong et al. JAP 89, 1377 (2001)
Kalinin et al. PRB 63, 125411 (2001)
Harnagea et al. APL 83, 338 (2003)
Jesse et al. RSI 77, 073702 (2006)
Jesse et al. Nanotech. 18, 435503 (2007)
Morozovska etal. PRB 80, 214110 (2009)
Johann et al. PRB 81, 094109 (2010)
Balke et al. ACS Nano 8, 10229 (2014)

21 years old this year:
can legally drink in the USA

Piezoresponse force microscopy (PFM)



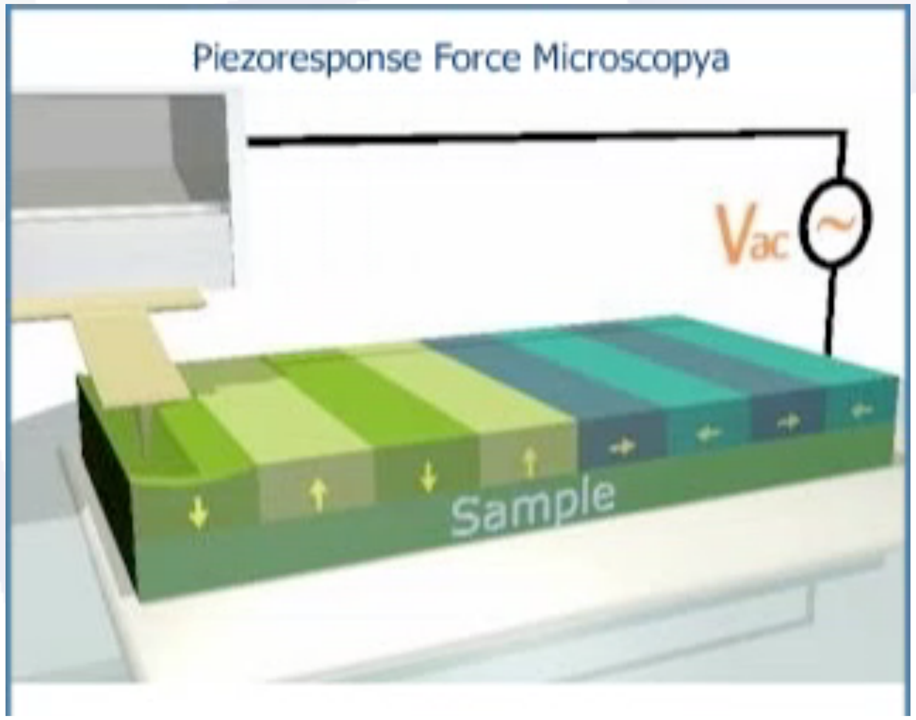
Piezoresponse : first harmonic component of tip deflection

$$A = A_0 + A_{1\omega} \cos(\omega t + \varphi)$$

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

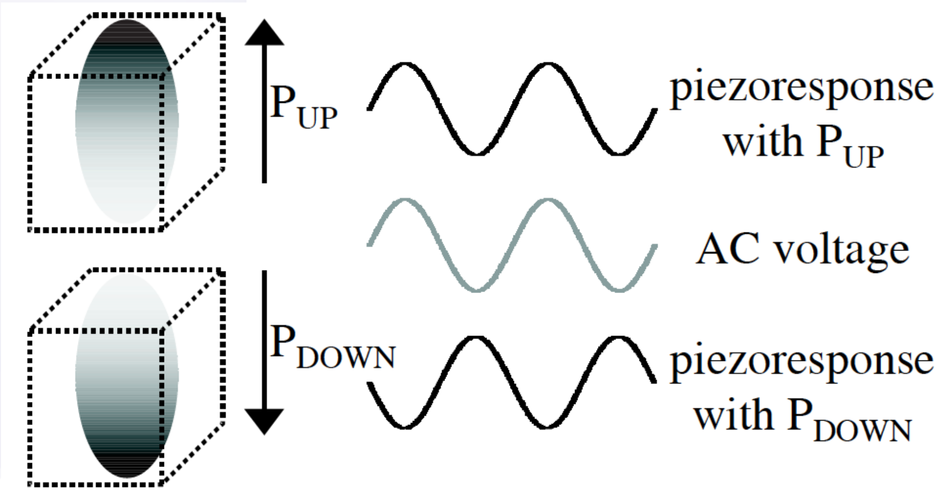
Deformation is given by the piezoelectric tensor : $X_j = d_{ij} E_i$

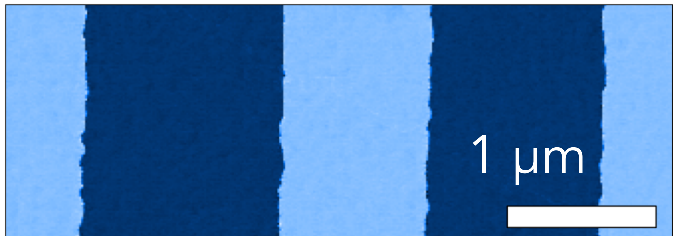
Imaging domains and domain walls



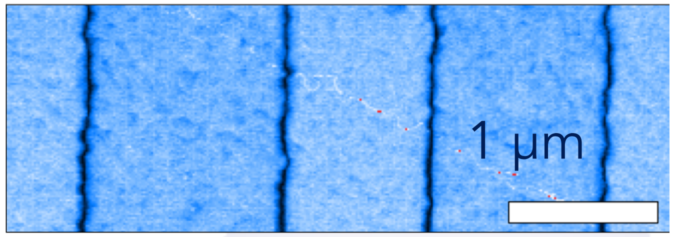
animation from NT-MDT

PFM is a key tool for nanoscale studies of ferroelectrics



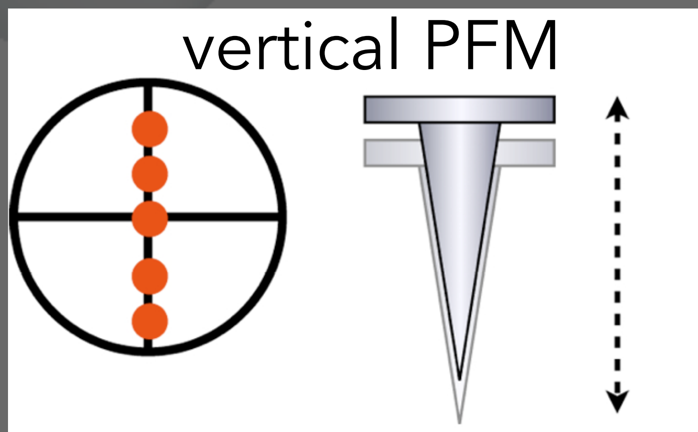


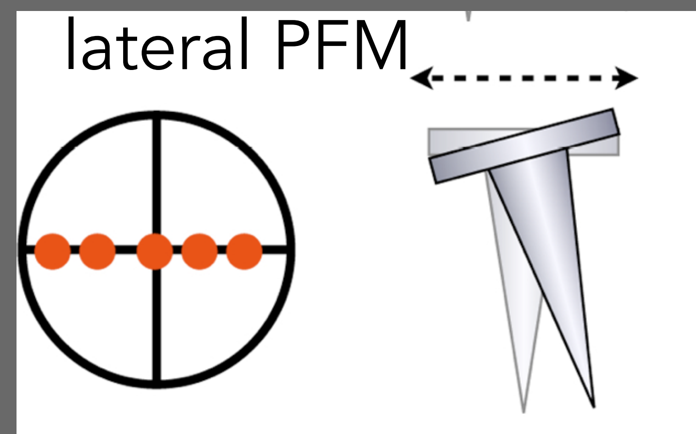
PFM - phase signal

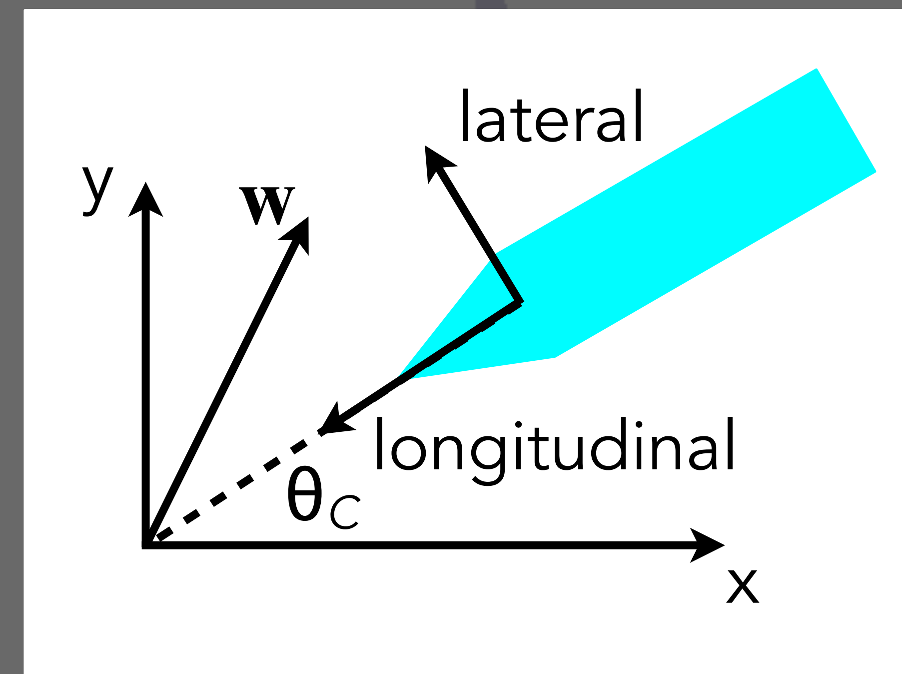


PFM - amplitude signal

Quantifying vertical and lateral PFM







surface displacement: $\mathbf{w} = (w_1, w_2, w_3)$

deflection   buckling

$$PR_v = aw_3 + c(w_1 \cos\theta_c + w_2 \sin\theta_c)$$

$$PR_l = b(-w_1 \sin\theta_c + w_2 \cos\theta_c)$$

torsion

choose θ_C = 0 for xPFM

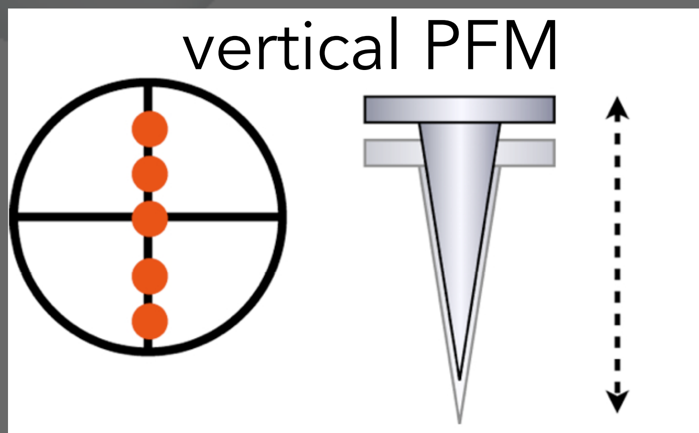
choose θ_C = π/2 for yPFM

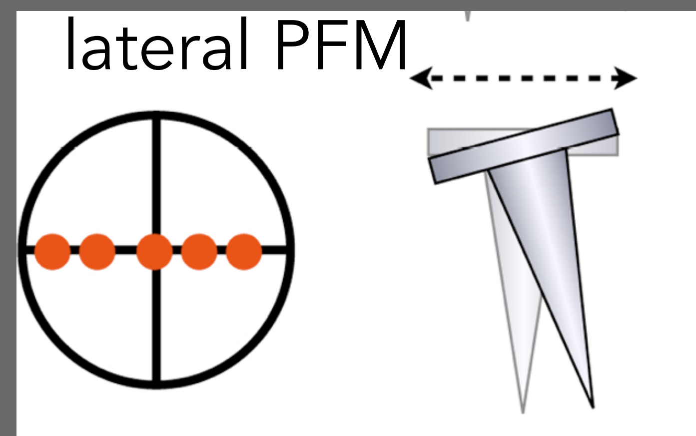
$$\begin{pmatrix} xPR_v \\ xPR_l \\ yPR_v \\ yPR_l \end{pmatrix} = \begin{pmatrix} c & 0 & a \\ 0 & b & 0 \\ 0 & c & a \\ b & 0 & 0 \end{pmatrix} \begin{pmatrix} w_1 \\ w_2 \\ w_3 \end{pmatrix}$$

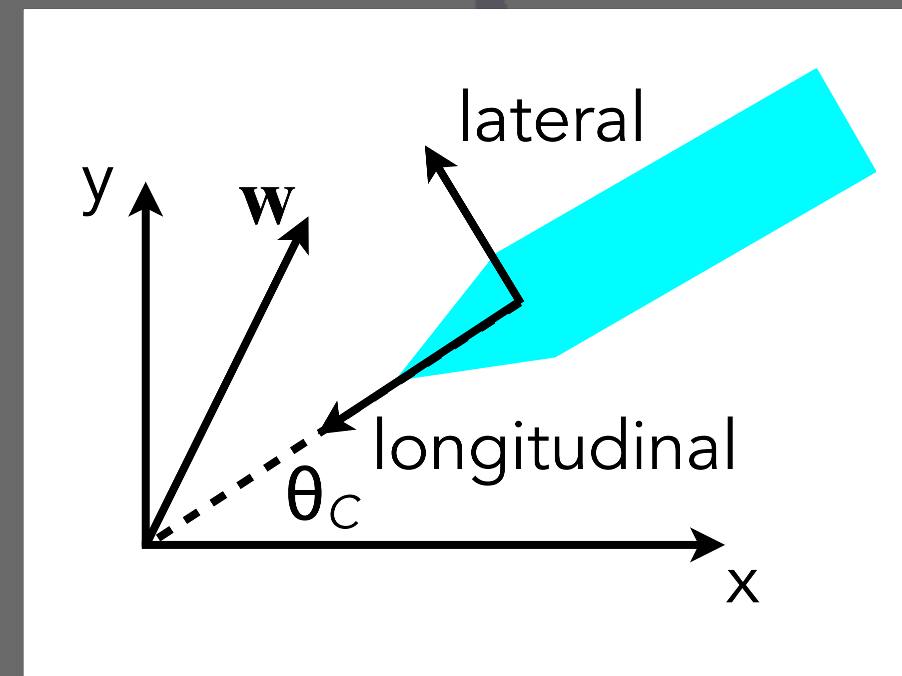
Jeon et al, Rev. Sci. Inst. **75**, 4841 (2004)

Kalinin et al, Microsc. Microanalysis **12**, 206 (2006)

Quantifying vertical and lateral PFM







surface displacement: $\mathbf{w} = (w_1, w_2, w_3)$

deflection buckling

$$PR_v = aw_3 + c(w_1 \cos\theta_c + w_2 \sin\theta_c)$$

$$PR_l = b(-w_1 \sin\theta_c + w_2 \cos\theta_c)$$

torsion

choose $\theta_C = 0$ for xPFM

choose $\theta_C = \pi/2$ for yPFM

eliminate buckling if possible :

$$\begin{pmatrix} xPR_l \\ yPR_l \\ vPR \end{pmatrix} = \begin{pmatrix} 0 & b & 0 \\ b & 0 & 0 \\ 0 & 0 & a \end{pmatrix} \begin{pmatrix} w_1 \\ w_2 \\ w_3 \end{pmatrix}$$

Jeon et al, Rev. Sci. Inst. **75**, 4841 (2004)

Kalinin et al, Microsc. Microanalysis **12**, 206 (2006)

Vector PFM - information in 3D (with care)

Eng et al, APL **74**, 233 (1999)
Eng et al, Adv. Sol. St. Phys. **41**, 287 (2001)
Harnagea et al, Integr. Ferro. **38**, 667 (2001)
Roelofs et al, APL **77**, 3444 (2002)
Rabe et al, J. Phys. D **35**, 2621 (2002)
Rodriguez et al, JAP **95**, 1958 (2004)

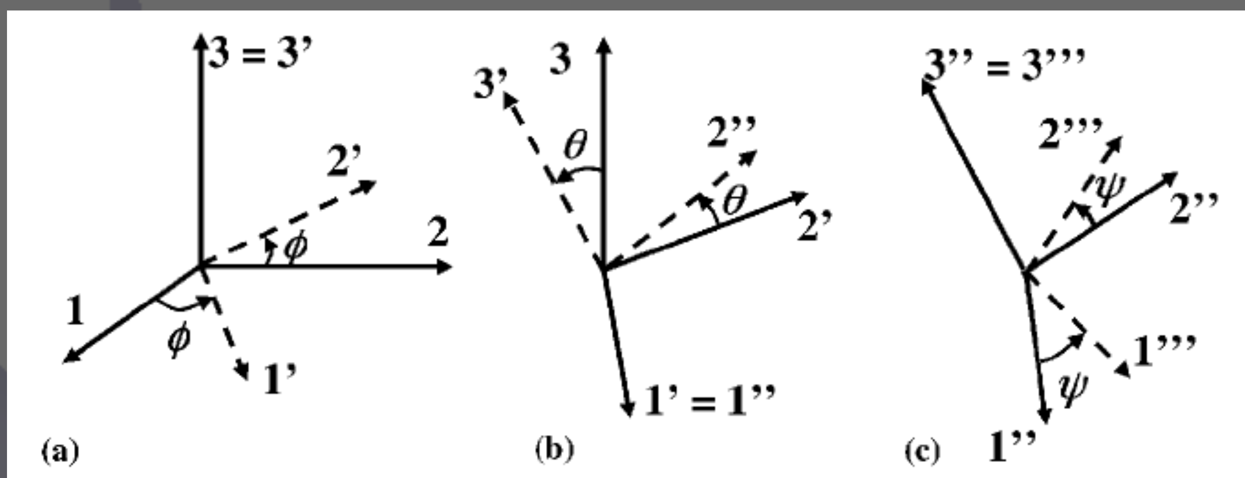
$$X_j = d_{ij} E_i$$

$$d_{ij} = A_{ik} d^0_{kl} N_{lj}$$

Useful rotation matrices

$$A_{ij} = \begin{pmatrix} (\cos\phi\cos\psi - \cos\theta\sin\phi\sin\psi) & (\cos\phi\sin\psi + \cos\theta\cos\phi\sin\psi) & \sin\theta\sin\psi \\ (-\cos\theta\cos\psi\sin\phi - \cos\phi\sin\psi) & (\cos\theta\cos\phi\cos\psi - \sin\phi\sin\psi) & \cos\theta\sin\psi \\ \sin\theta\sin\phi & -\cos\phi\sin\theta & \cos\theta \end{pmatrix}$$

Kalinin et al, Microsc. Microanalysis **12**, 206 (2006)



Transforming from crystal to laboratory coordinates

ϕ counterclockwise rotation around 3

θ counterclockwise rotation around 1′

ψ counterclockwise rotation around 3″

$$N_{ij} = \begin{pmatrix} a_{11}^2 & a_{21}^2 & a_{31}^2 & 2a_{21}a_{31} & 2a_{31}a_{11} & 2a_{11}a_{21} \\ a_{12}^2 & a_{22}^2 & a_{32}^2 & 2a_{22}a_{32} & 2a_{32}a_{12} & 2a_{12}a_{22} \\ a_{13}^2 & a_{23}^2 & a_{33}^2 & 2a_{23}a_{33} & 2a_{33}a_{13} & 2a_{13}a_{23} \\ a_{12}a_{13} & a_{22}a_{23} & a_{32}a_{33} & a_{22}a_{33} + a_{32}a_{23} & a_{12}a_{33} + a_{32}a_{13} & a_{22}a_{13} + a_{12}a_{23} \\ a_{13}a_{11} & a_{23}a_{21} & a_{33}a_{31} & a_{21}a_{33} + a_{31}a_{23} & a_{31}a_{13} + a_{11}a_{33} & a_{11}a_{23} + a_{21}a_{13} \\ a_{11}a_{12} & a_{21}a_{22} & a_{31}a_{32} & a_{21}a_{32} + a_{31}a_{22} & a_{31}a_{12} + a_{11}a_{32} & a_{11}a_{22} + a_{21}a_{12} \end{pmatrix}$$

Newnham, *Properties of Materials: Anisotropy, Symmetry, Structure* (2005)
Nye, *Physical Properties of Crystals* (1985)

Vector PFM - information in 3D (with care)

Eng et al, APL **74**, 233 (1999)
Eng et al, Adv. Sol. St. Phys. **41**, 287 (2001)
Harnagea et al, Integr. Ferro. **38**, 667 (2001)
Roelofs et al, APL **77**, 3444 (2002)
Rabe et al, J. Phys. D **35**, 2621 (2002)
Rodriguez et al, JAP **95**, 1958 (2004)

$$X_j = d_{ij} E_i$$

$$d_{ij} = A_{ik} d^0_{kl} N_{lj}$$

Need to know strain

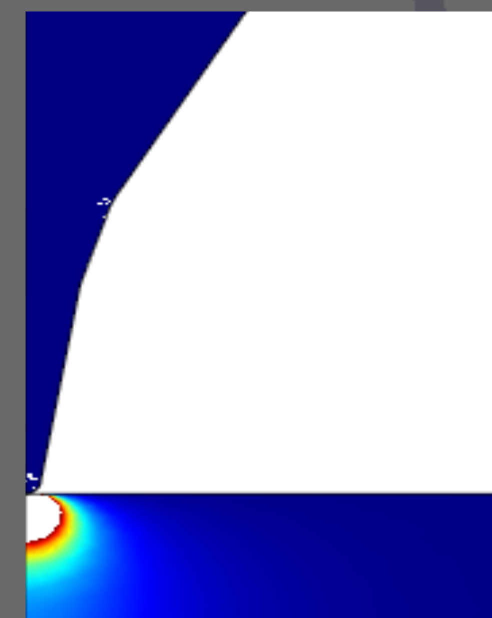
$$X_{ij} = \begin{pmatrix} \frac{\partial u_1}{\partial x_1} & \frac{1}{2}\left(\frac{\partial u_1}{\partial x_2} + \frac{\partial u_2}{\partial x_1}\right) & \frac{1}{2}\left(\frac{\partial u_1}{\partial x_3} + \frac{\partial u_3}{\partial x_1}\right) \\ \frac{1}{2}\left(\frac{\partial u_1}{\partial x_2} + \frac{\partial u_2}{\partial x_1}\right) & \frac{\partial u_2}{\partial x_2} & \frac{1}{2}\left(\frac{\partial u_2}{\partial x_3} + \frac{\partial u_3}{\partial x_2}\right) \\ \frac{1}{2}\left(\frac{\partial u_1}{\partial x_3} + \frac{\partial u_3}{\partial x_1}\right) & \frac{1}{2}\left(\frac{\partial u_2}{\partial x_3} + \frac{\partial u_3}{\partial x_2}\right) & \frac{\partial u_3}{\partial x_3} \end{pmatrix}$$

Kalinin et al, Microsc. Microanalysis **12**, 206 (2006)

Vector PFM - information in 3D (with care)

Eng et al, APL **74**, 233 (1999)
Eng et al, Adv. Sol. St. Phys. **41**, 287 (2001)
Harnagea et al, Integr. Ferro. **38**, 667 (2001)
Roelofs et al, APL **77**, 3444 (2002)
Rabe et al, J. Phys. D **35**, 2621 (2002)
Rodriguez et al, JAP **95**, 1958 (2004)

Highly inhomogeneous field of biased tip



Electric field E_z

$$X_j = d_{ij} E_i$$

$$d_{ij} = A_{ik} d^0_{kl} N_{lj}$$

Need to know strain
Need to know electric field

$$\mathbf{E} = \mathbf{z} E_3$$

$$X_j = d_{j3} E_s,\ j = 1, \ldots, 6$$

OR use macroscopic top electrode
$E = V/d$

ideal, uniform, freestanding piezoelectric capacitor

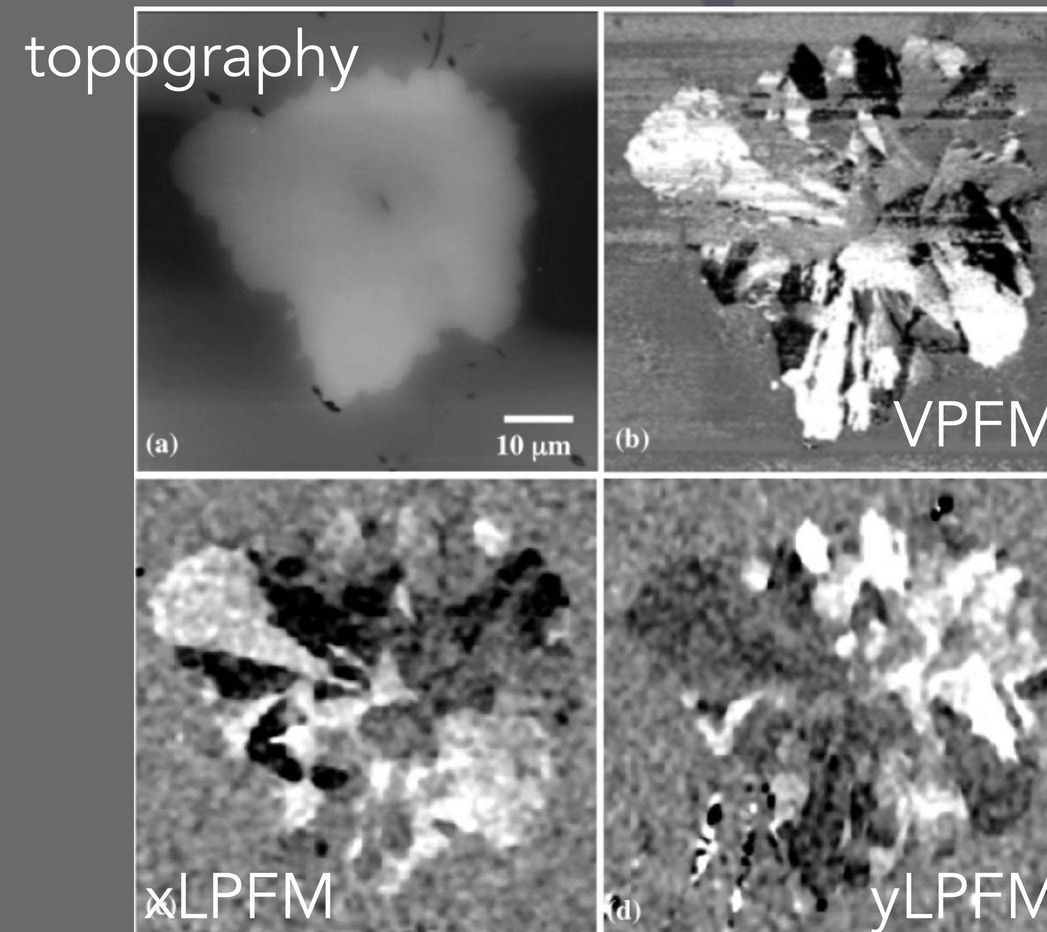
$$\mathbf{u} = (d_{35} V, d_{34} V, d_{33} V)$$

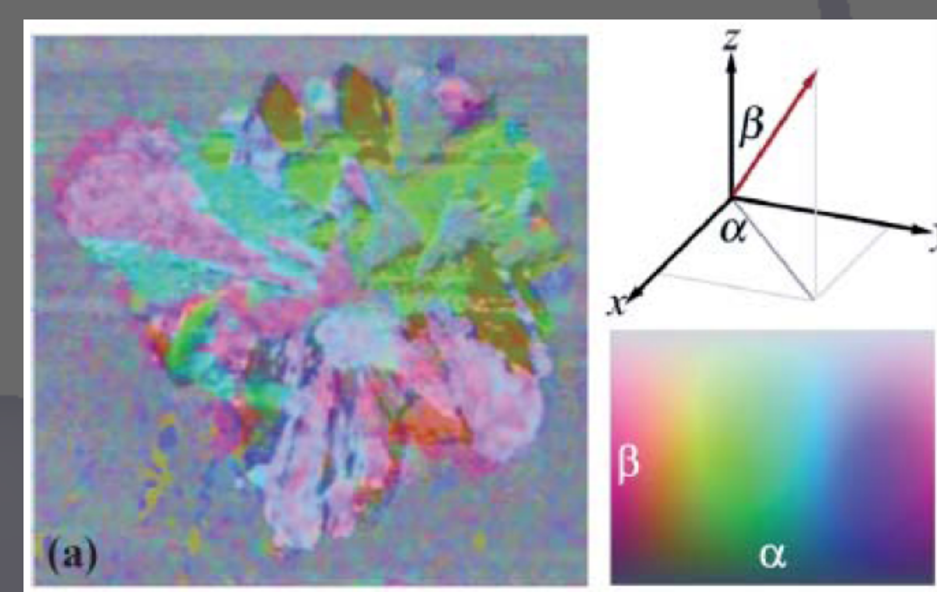
Quantitative information on d_{ij} in 2D or 3D

Option 1:
(work with materials with known symmetries)
full external calibration of tip displacement
homogeneous and well determined field

Option 2:
work with materials with known symmetries
self-calibration of tip displacement
(homogeneous) and well determined field

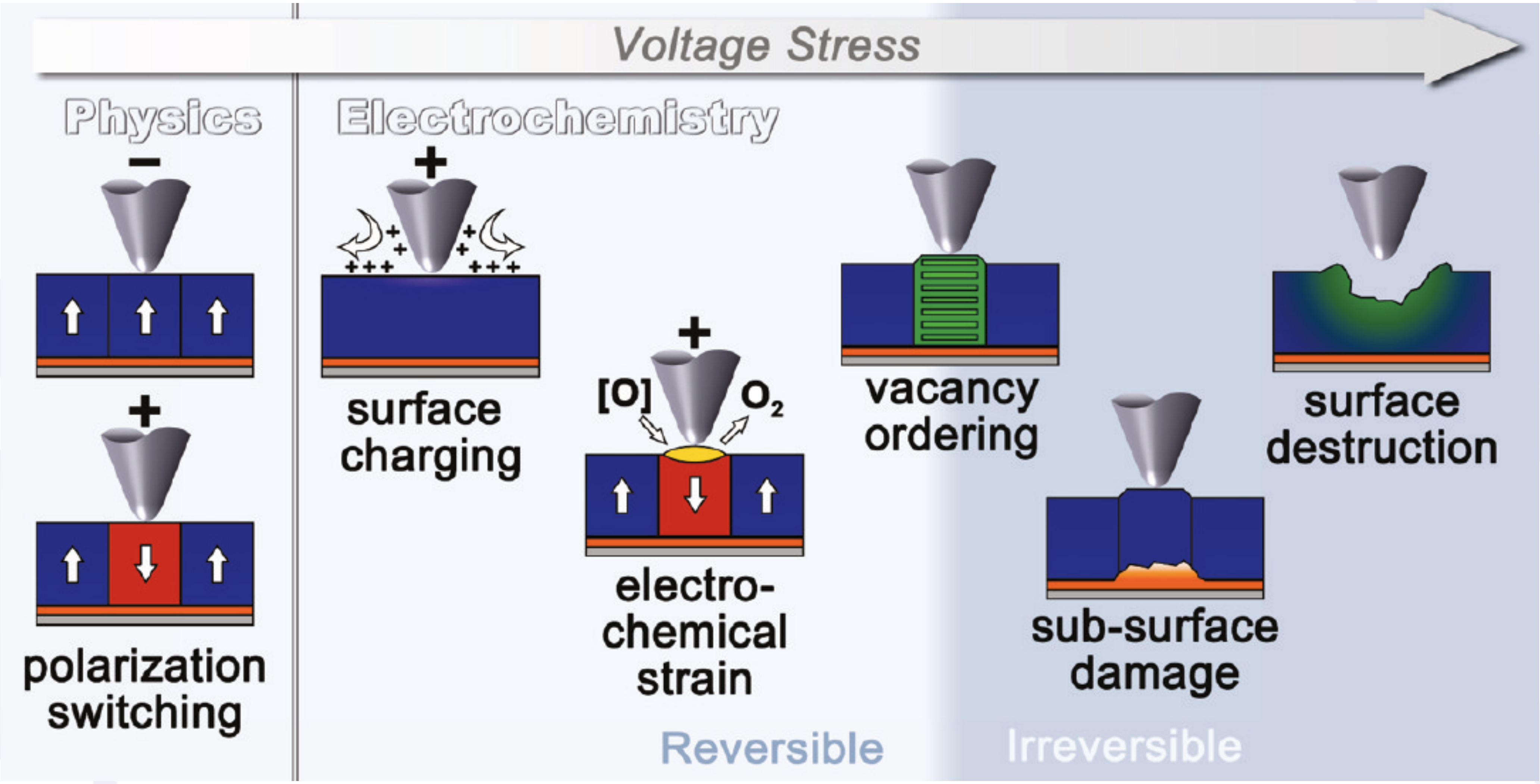
Consider external effects
eg. substrate clamping in thin films





Kalinin et al, Microsc. Microanalysis **12**, 206 (2006)

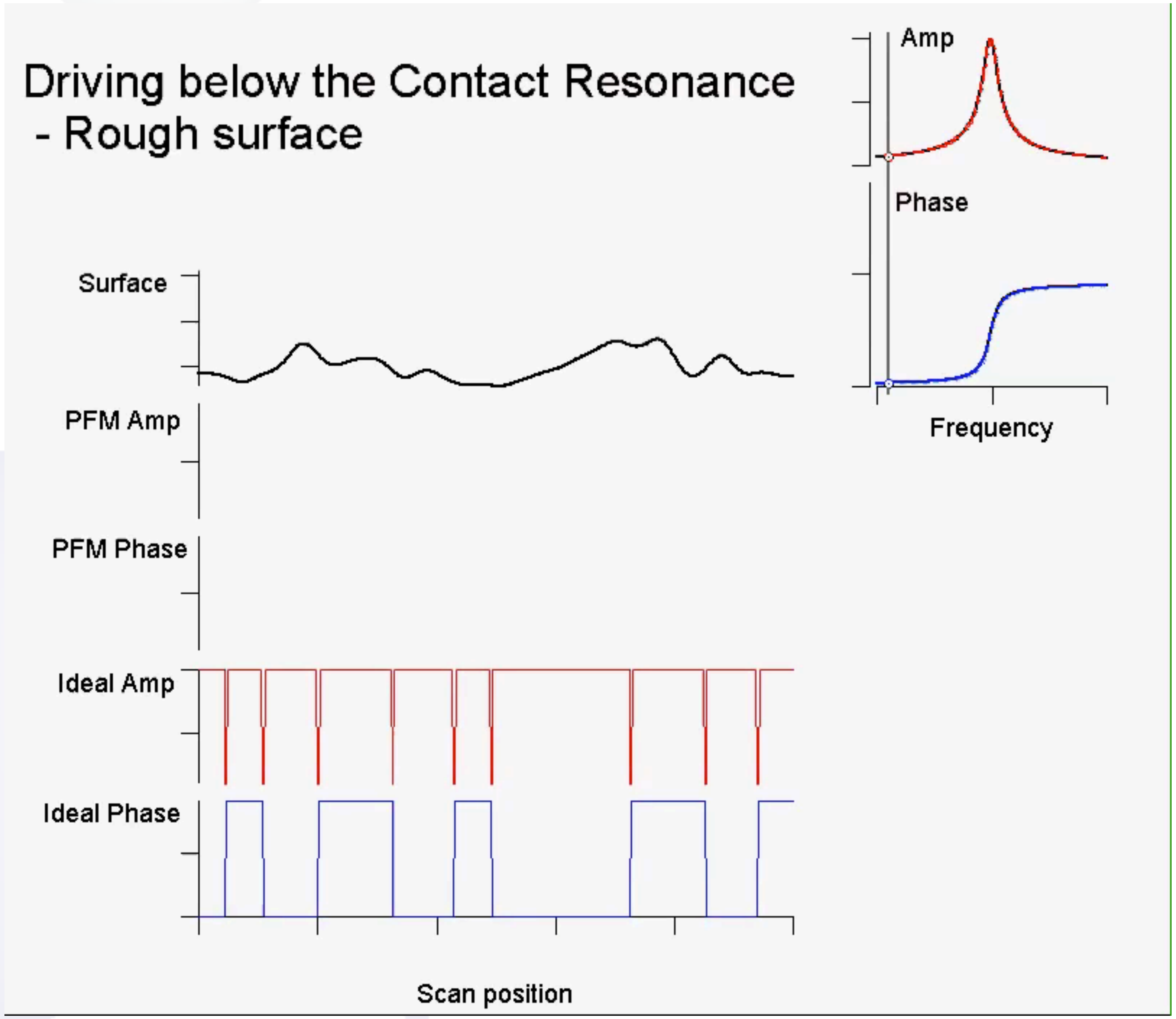
Significant role of electrochemical phenomena



Kalinin et al., ACS Nano **5**, 5683 (2011)

Artefacts - seeing is NOT believing

Nobody's perfect - including samples



animation from Asylum

Normal modes and "abnormal" signals

PFM at contact resonance

Dual frequency resonance tracking

Spectroscopy, Band Excitation etc

READ the literature, TALK to others, KNOW your system

Nano-transport: conductive tip AFM (CAFM)

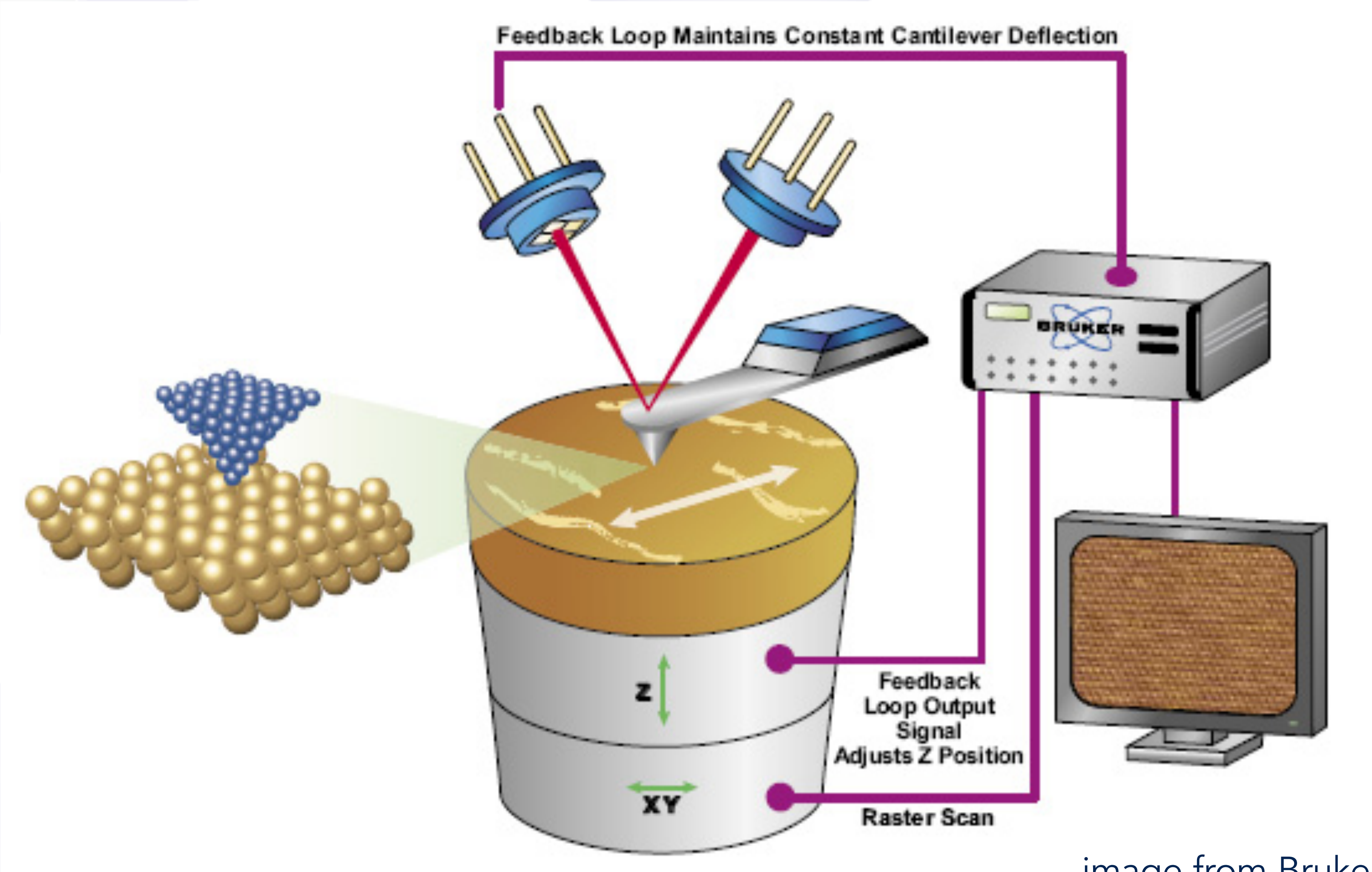
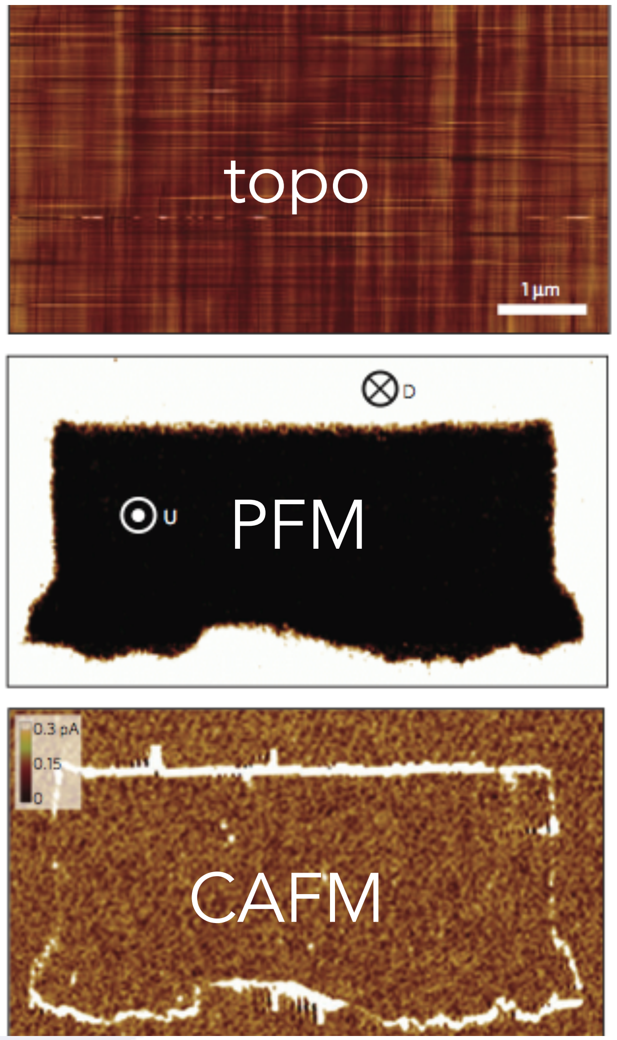


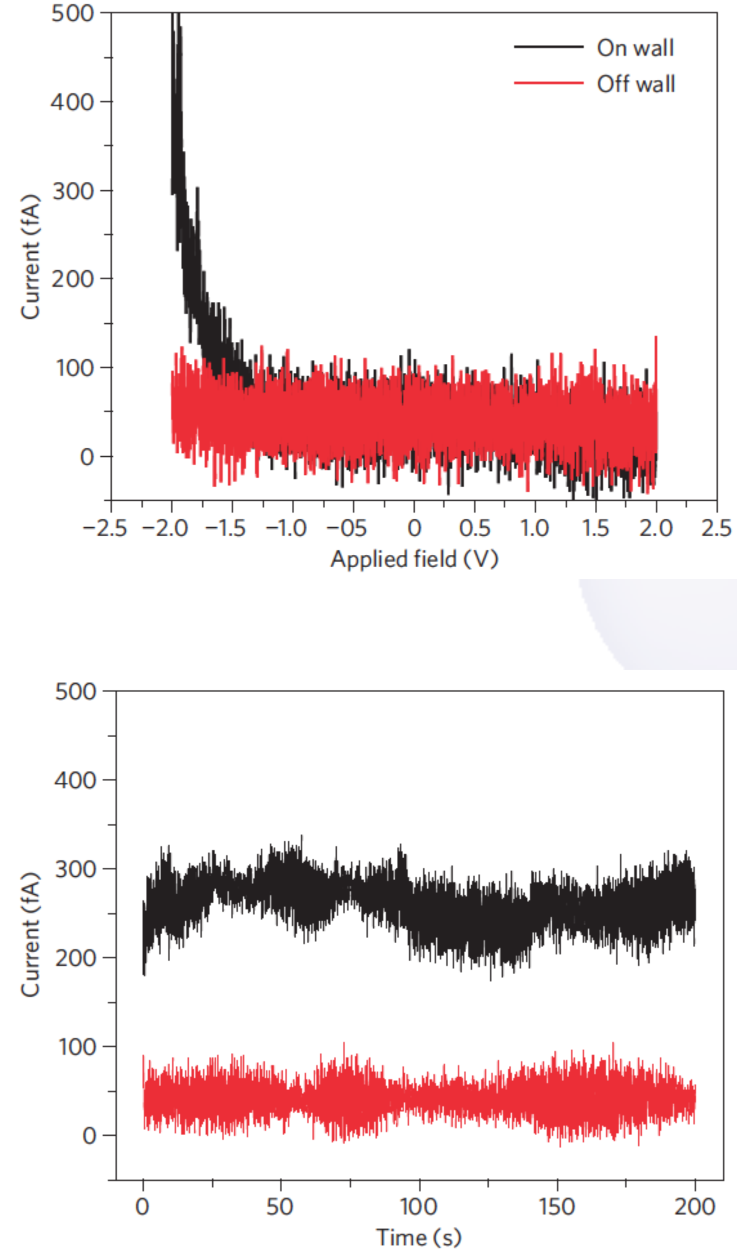
image from Bruker

local mapping of conductance
(currents down to 100 fA)
applicable to largely insulating samples

Nano-transport: conductive tip AFM (CAFM)

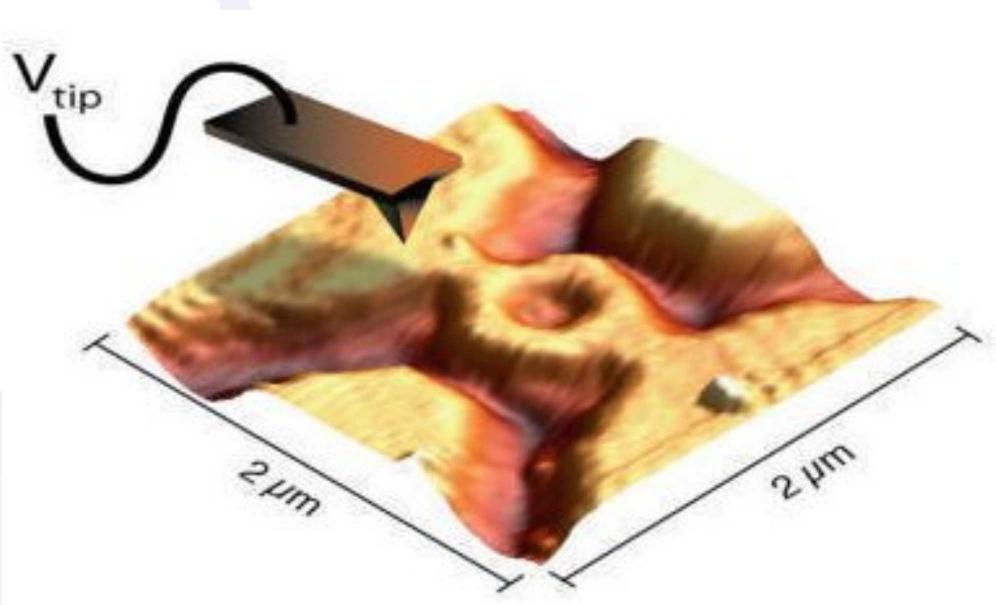


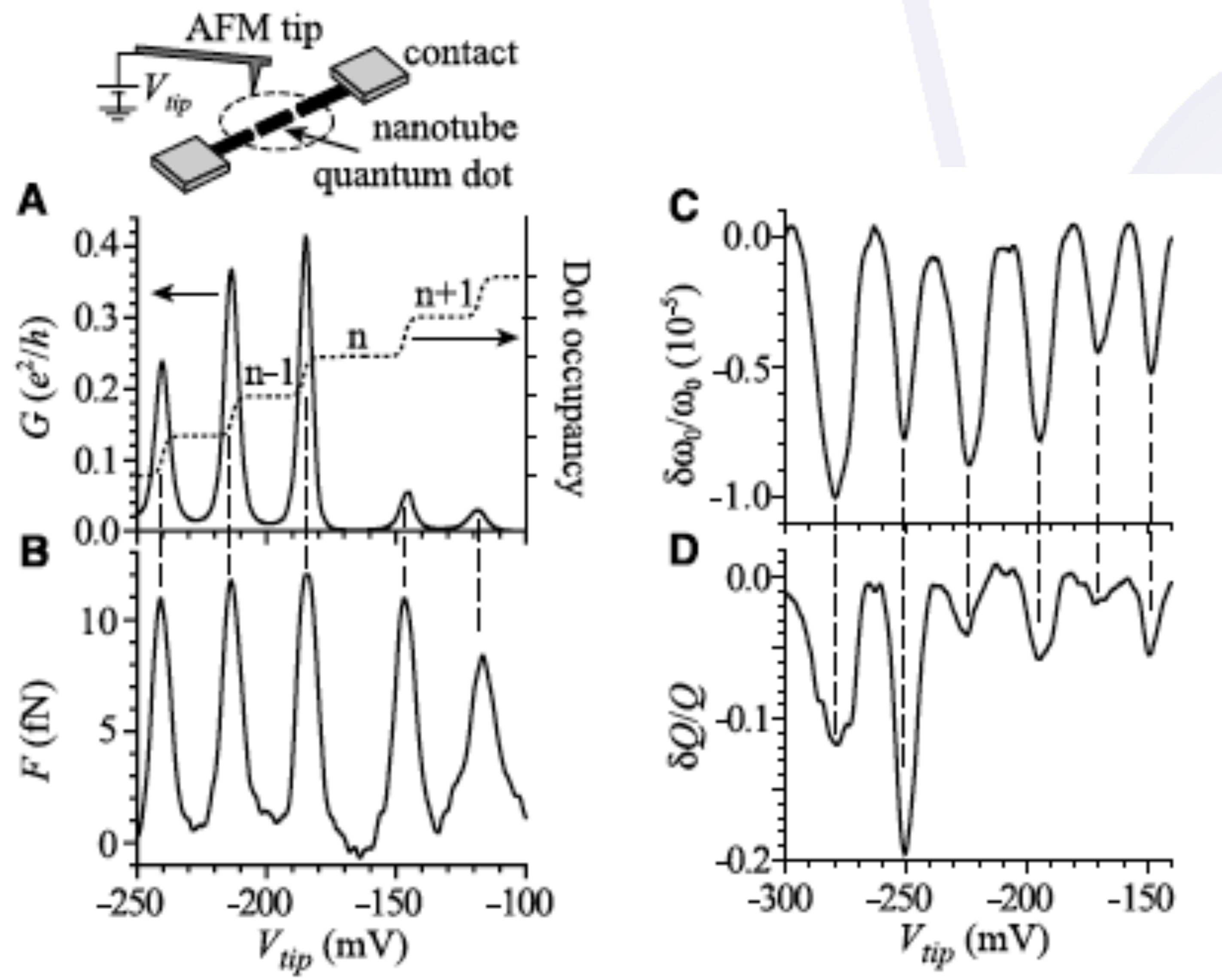
Seidel et al., Nat. Mat. **8**, 229 (2009)



Electrical conductance discovered at ferroelectric domain walls in otherwise insulating parent materials

Nano-transport: scanned gate microscopy

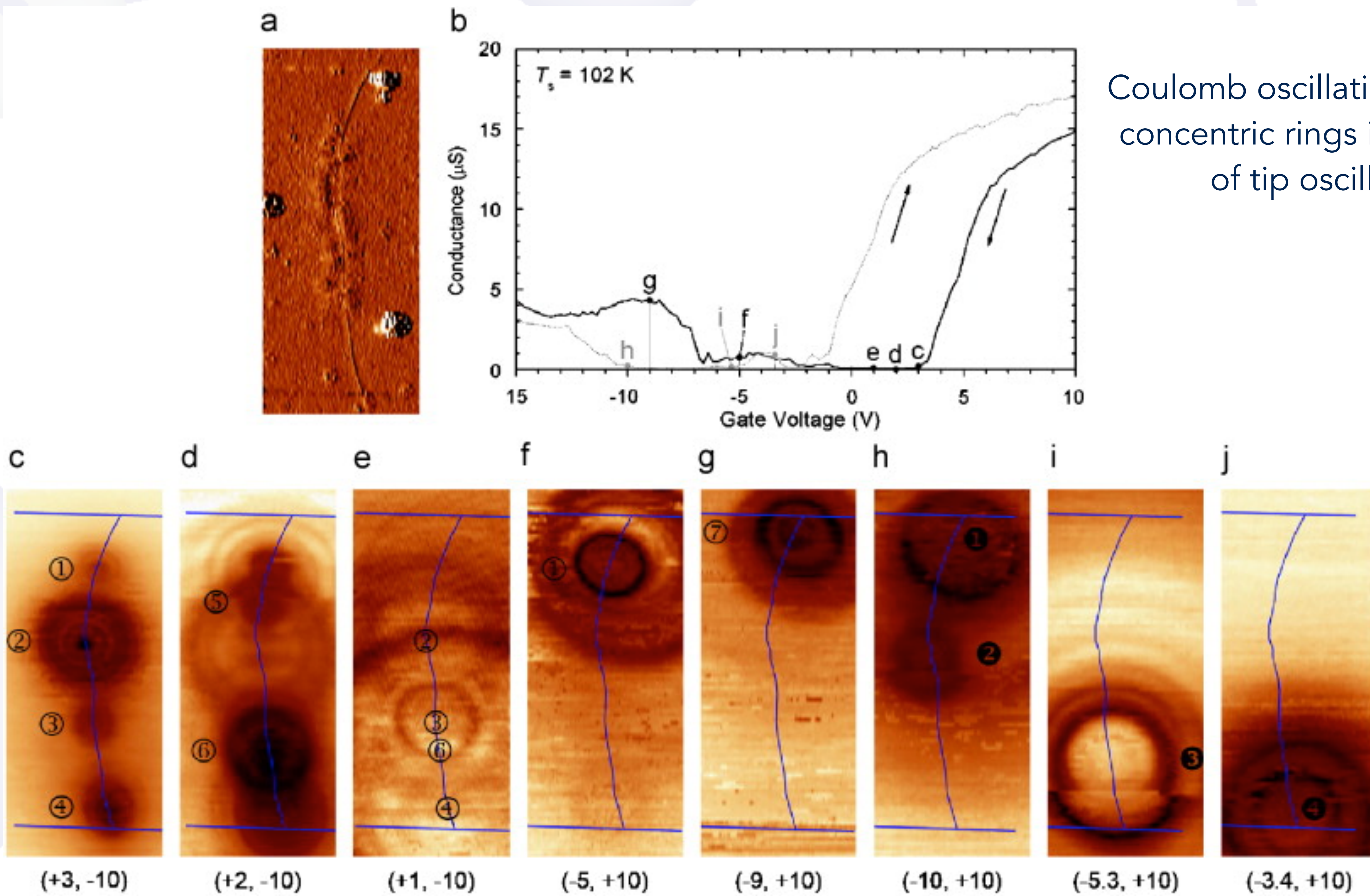




Woodside and McEuen, Sci. **296**, 1098 (2002)

Imaging transport through mesoscopic quantum devices as a function of tip voltage and position

Nano-transport: scanned gate microscopy



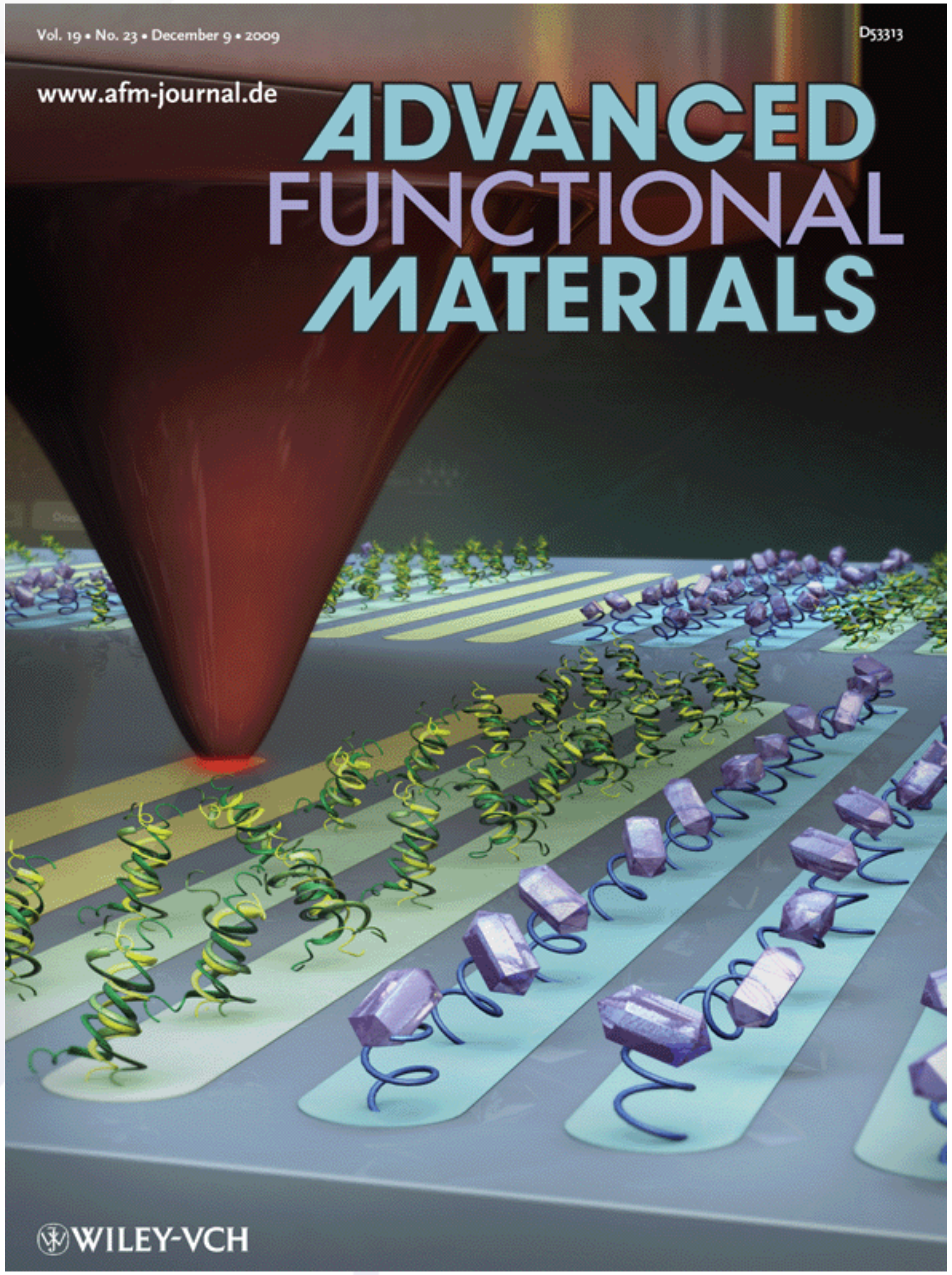
Coulomb oscillations visible as concentric rings in amplitude of tip oscillations

Zhu et al., Nano Lett. **8**, 2399 (2008)

imaging quantum dots in carbon nanotubes

AFM - applications to patterning

AFM Nanolithography



oxidation

charging

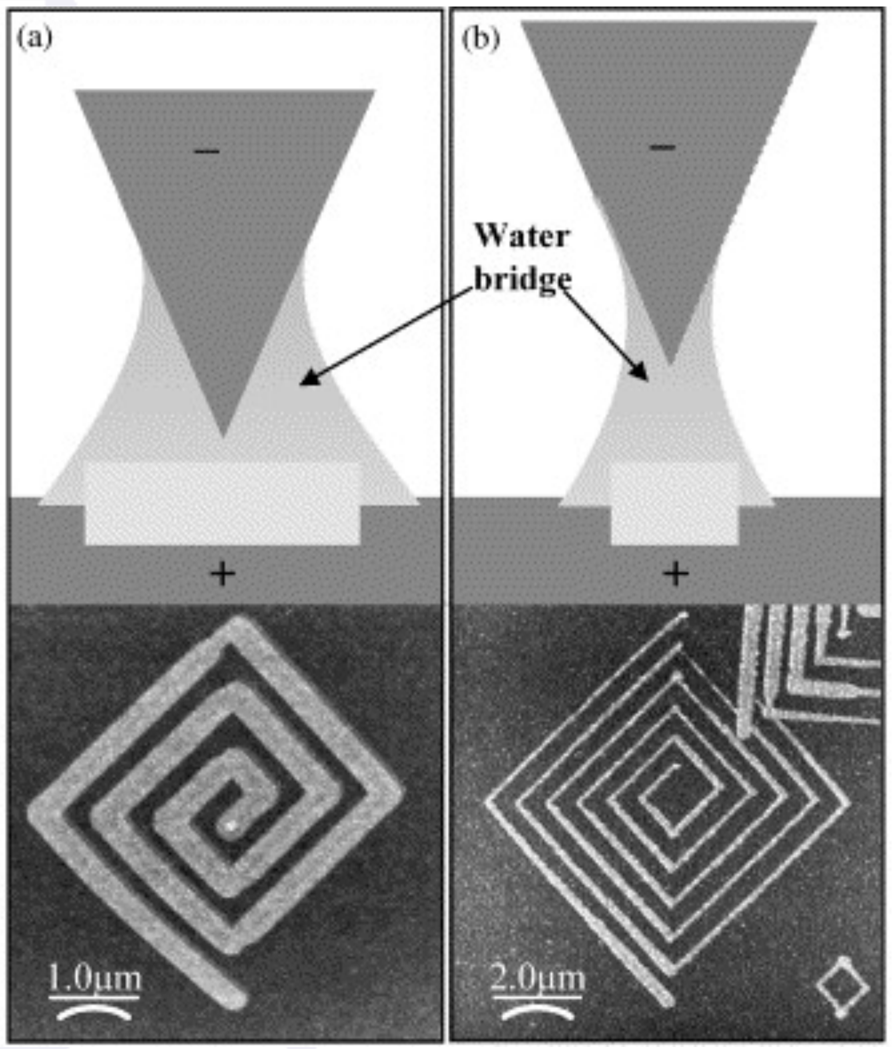
polarization switching

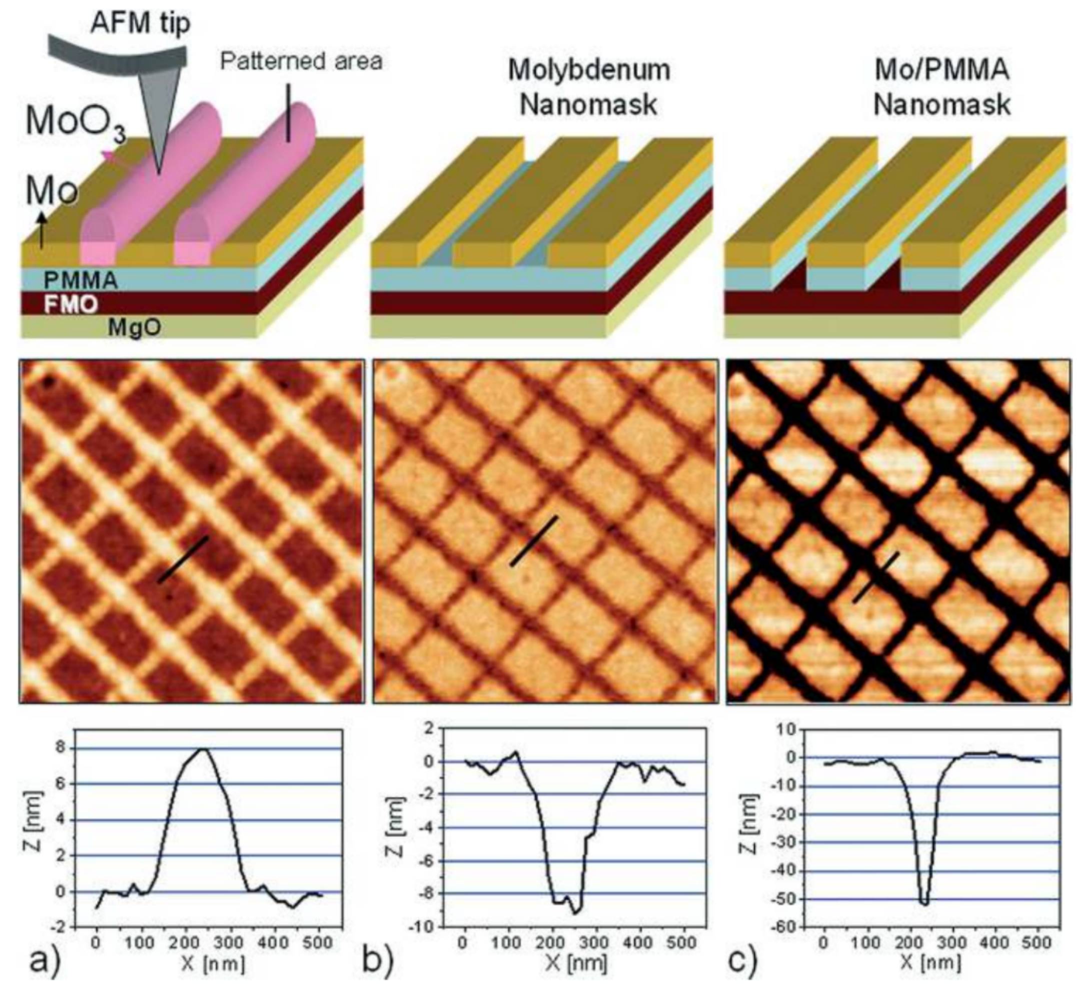
etching

....

AFM Nanolithography : using surface water

electrochemical reactions enhanced in the presence of surface water



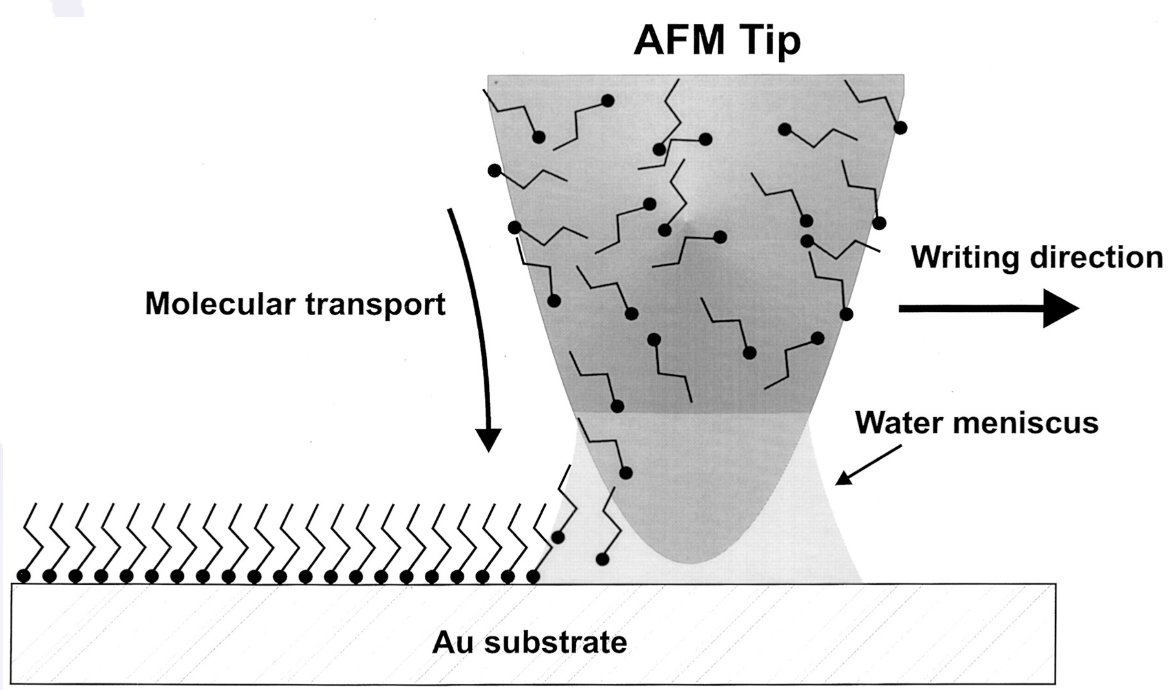


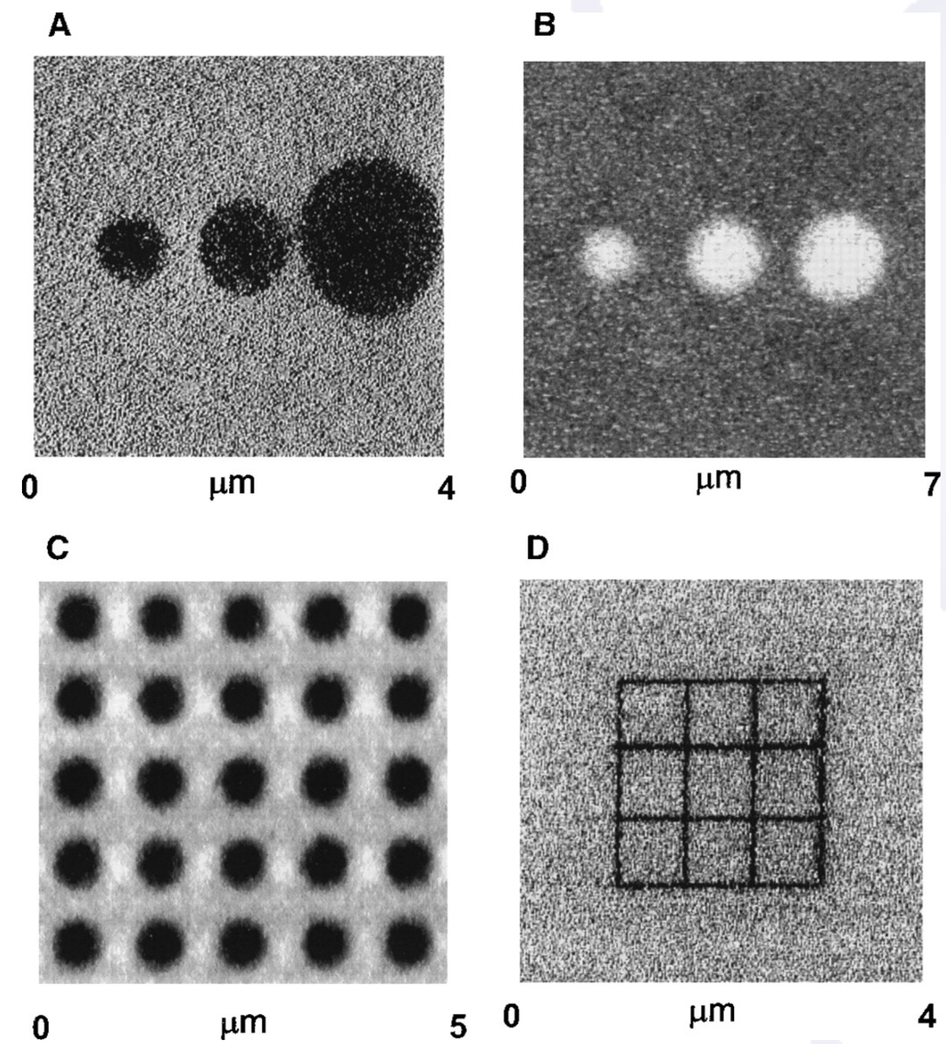
Pellegrino et al., Adv. Mat **18**, 3099 (2006)

feature sized controlled both by applied voltage AND by relative humidity

AFM Nanolithography : using surface water

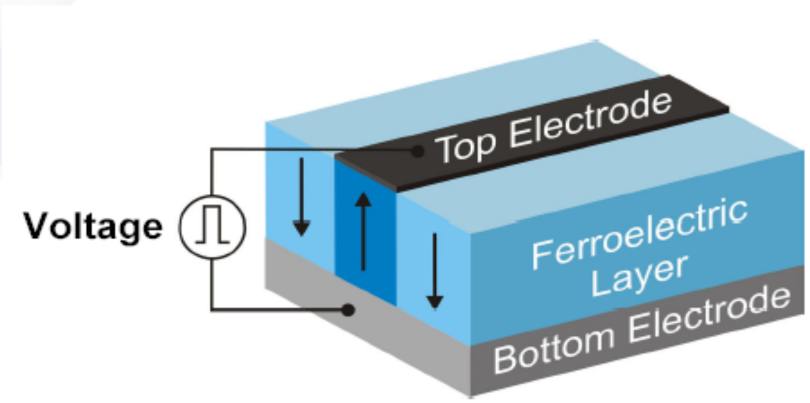
using AFM tip as a nanoscale "dip-pen"

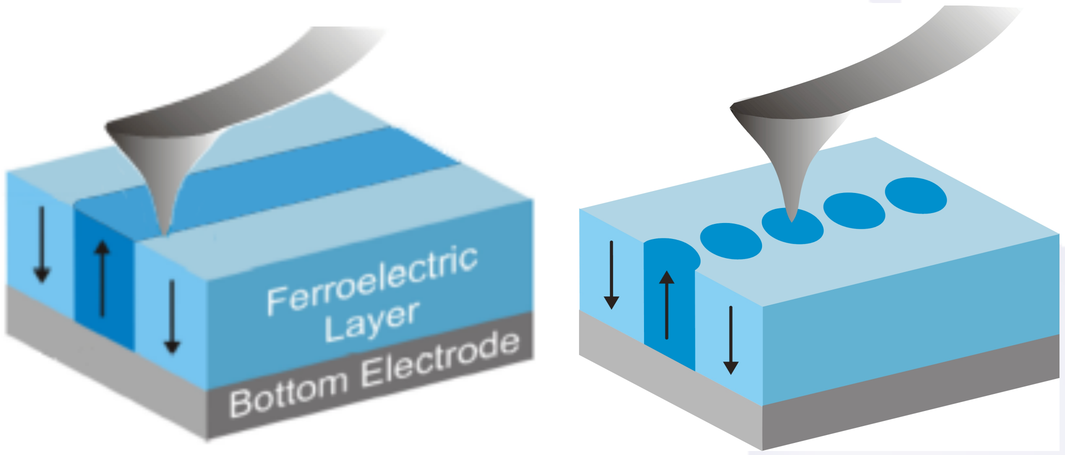


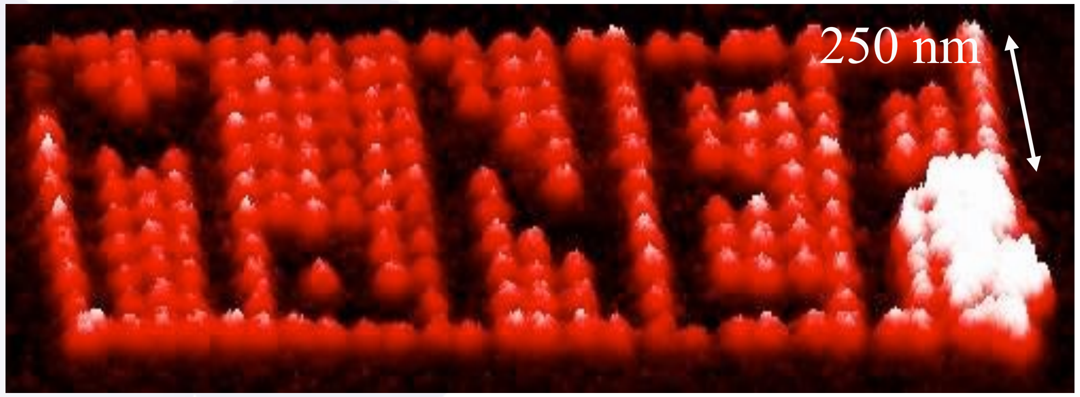


Piner et al., Sci. **283**, 661 (1999)

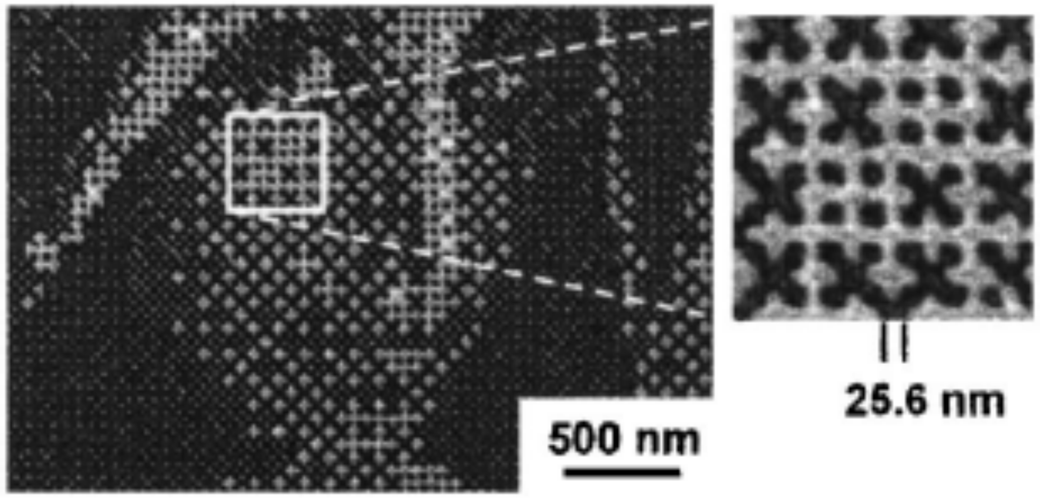
AFM Nanolithography: polarisation switching







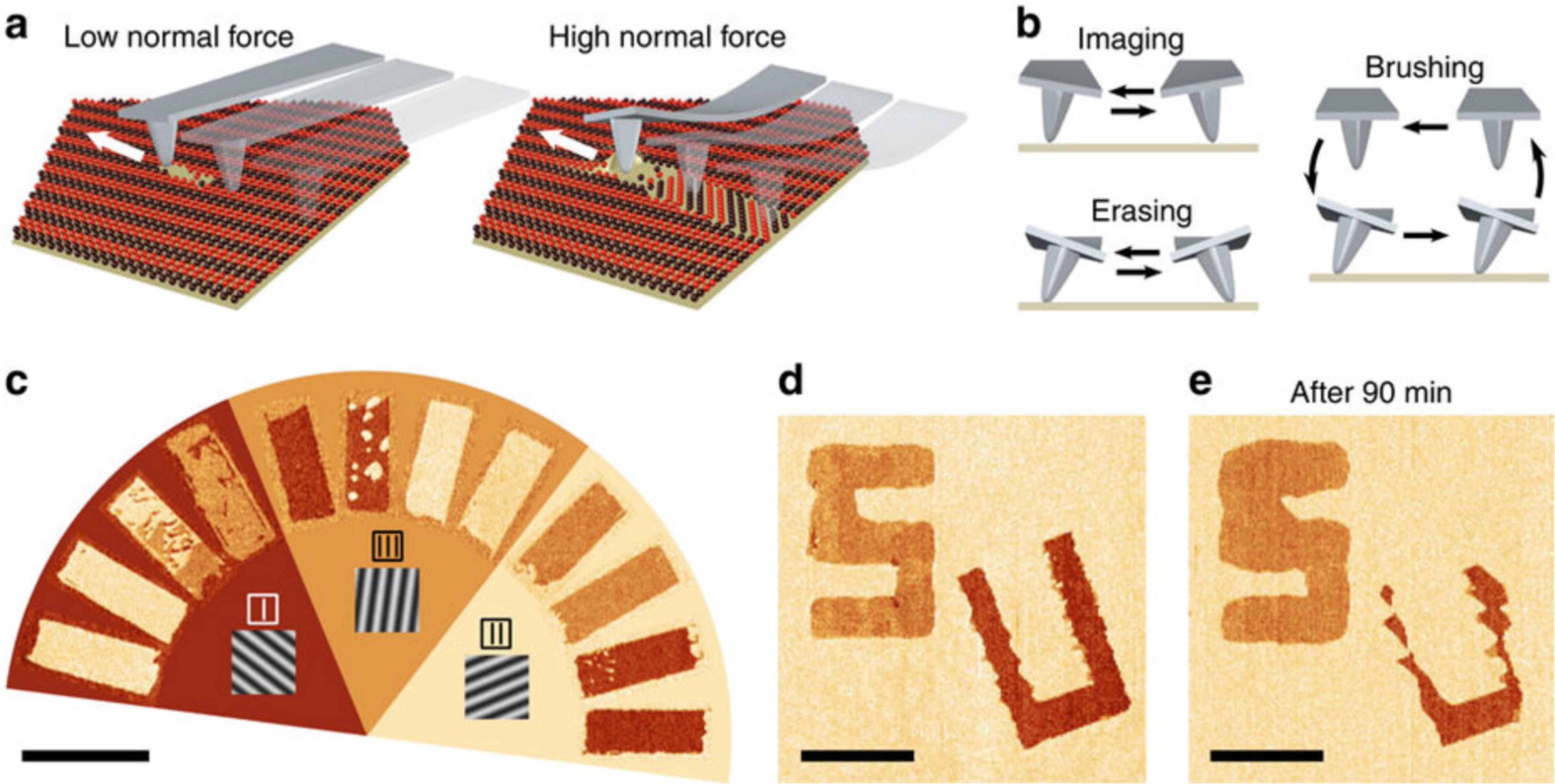
Paruch et al APL **79**, 530 (2001)



Cho et al APL **87**, 232907 (2005)

Local electric field application with a metallised probe tip allows the formation of very small domains

AFM Nanolithography: friction domains

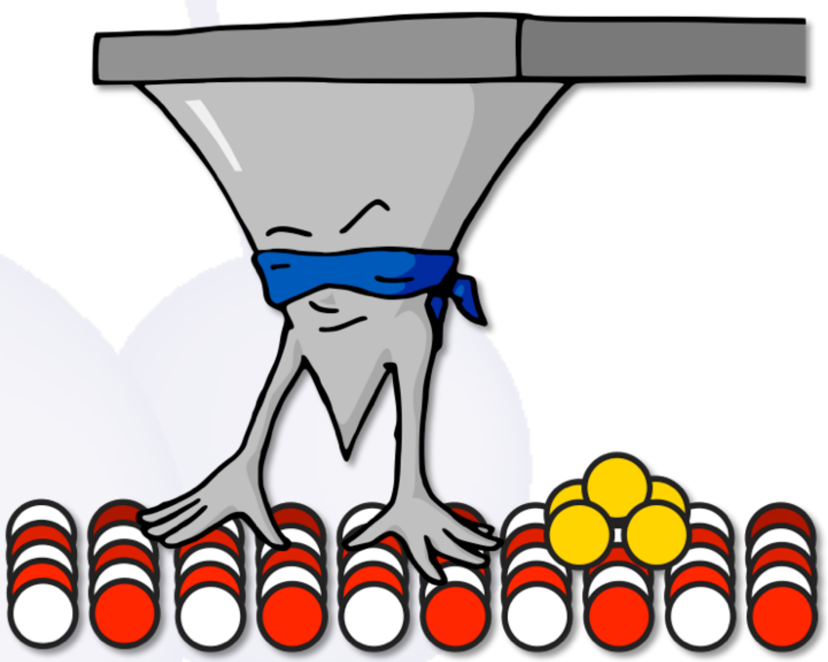


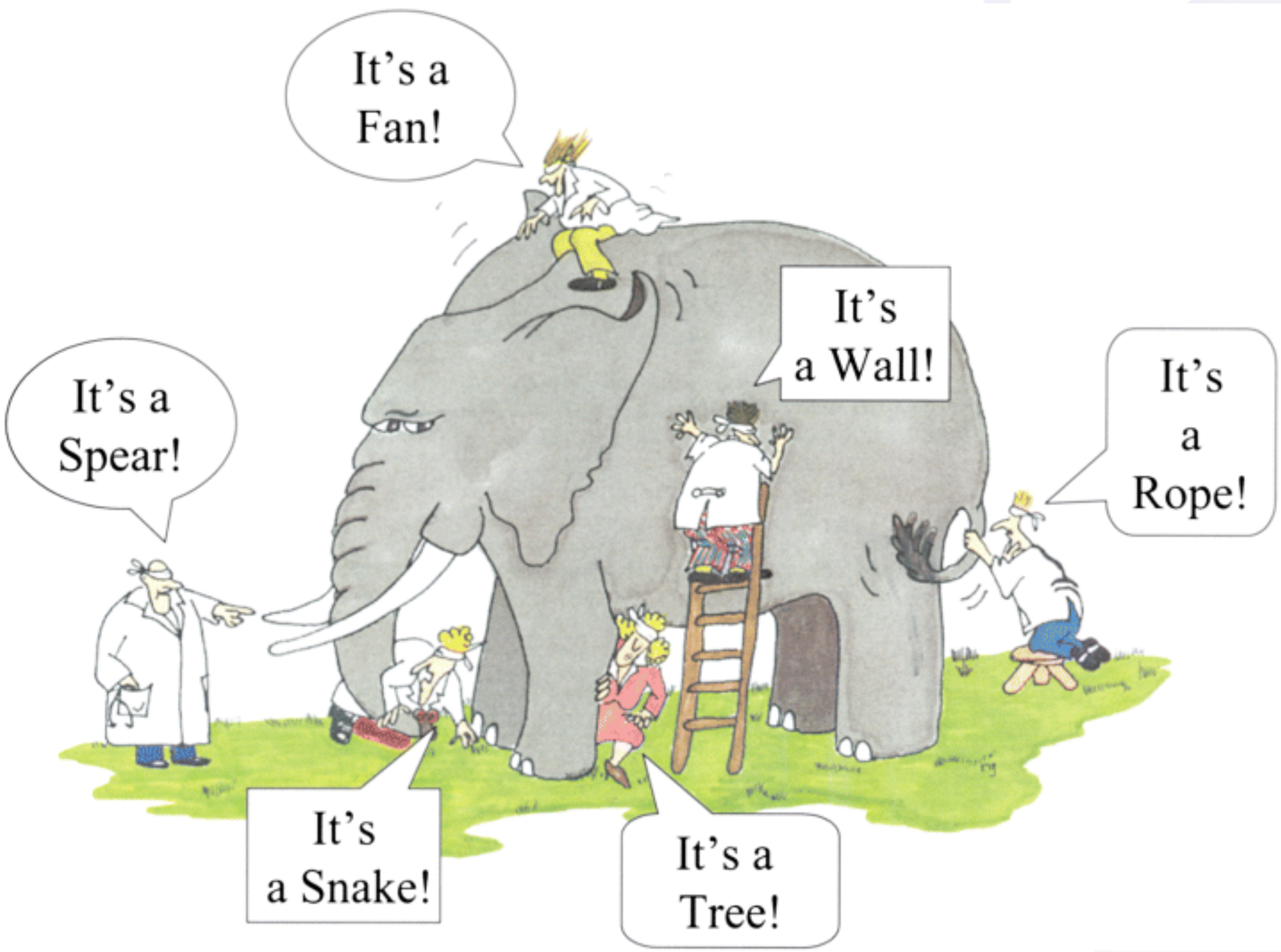
Gallagher *et al.* Nat. Comm. **7,** 10745 (2016)

Force applied to adsorbates on graphene surface reorients them, which gives a different torsion and buckling response

Conclusions

AFM allows an incredibly diversity of physical interactions to be locally probed with nanoscale resolution





YOU need to know what you are searching for AND expect many potential artefacts