

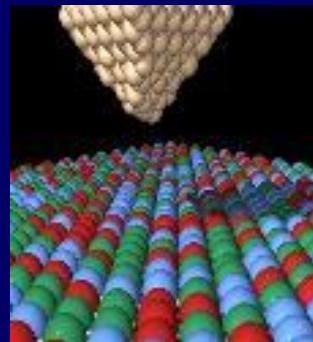
Dynamic Atomic Force Microscopy: Basic Concepts

Rubén Pérez

Nanomechanics & SPM Theory Group

Departamento de Física Teórica de la Materia Condensada

<http://www.uam.es/spmth>



Curso “Introducción a la Nanotecnología”

Máster en física de la materia condensada y nanotecnología

References

- R. García and R. Pérez, Surf. Sci. Rep. 47, 197 (2002)
F.J. Giessibl, Rev. Mod. Phys. 75, 949 (2003)
W. Hofer, A.S. Foster & A. Shluger , Rev. Mod. Phys. 75, 1287 (2003)

- C. J. Chen. “Introduction to Scanning Tunneling Microscopy”. 2nd Edition. (Oxford University Press, Oxford, 2008).
- S. Morita, R. Wiesendanger, E. Meyer (Eds). “Noncontact Atomic Force Microscopy”. (Springer, Berlin, 2002).
- S. Morita, F.J. Giessibl R. Wiesendanger (Eds). “Noncontact Atomic Force Microscopy”. Vol. 2 (Springer, Berlin, 2009).

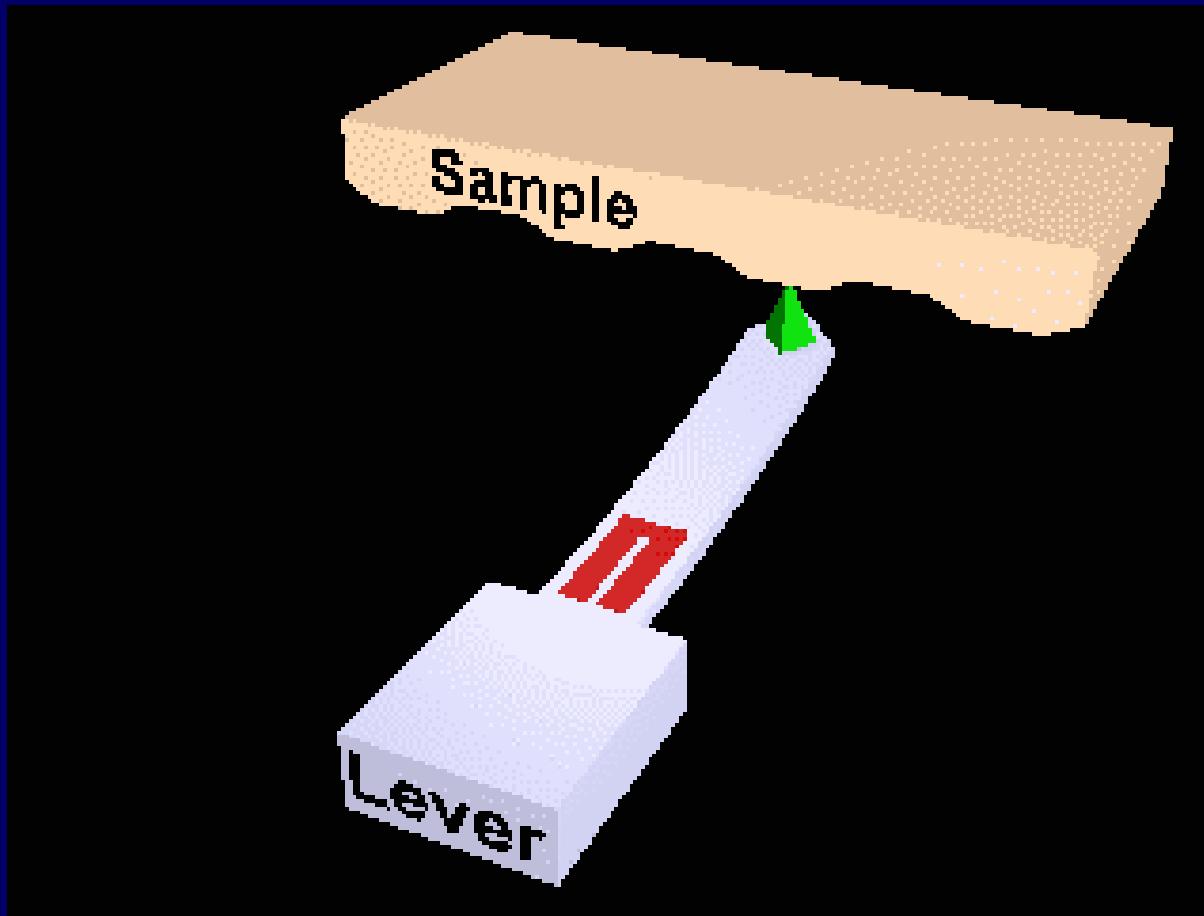
Outline

- Static vs Dynamic AFM: AM-AFM & FM-AFM.
- Amplitude Modulation AFM
- Frequency Modulation AFM

Static vs Dynamic AFM: Amplitude Modulation (AM) & Frequency Modulation (FM).

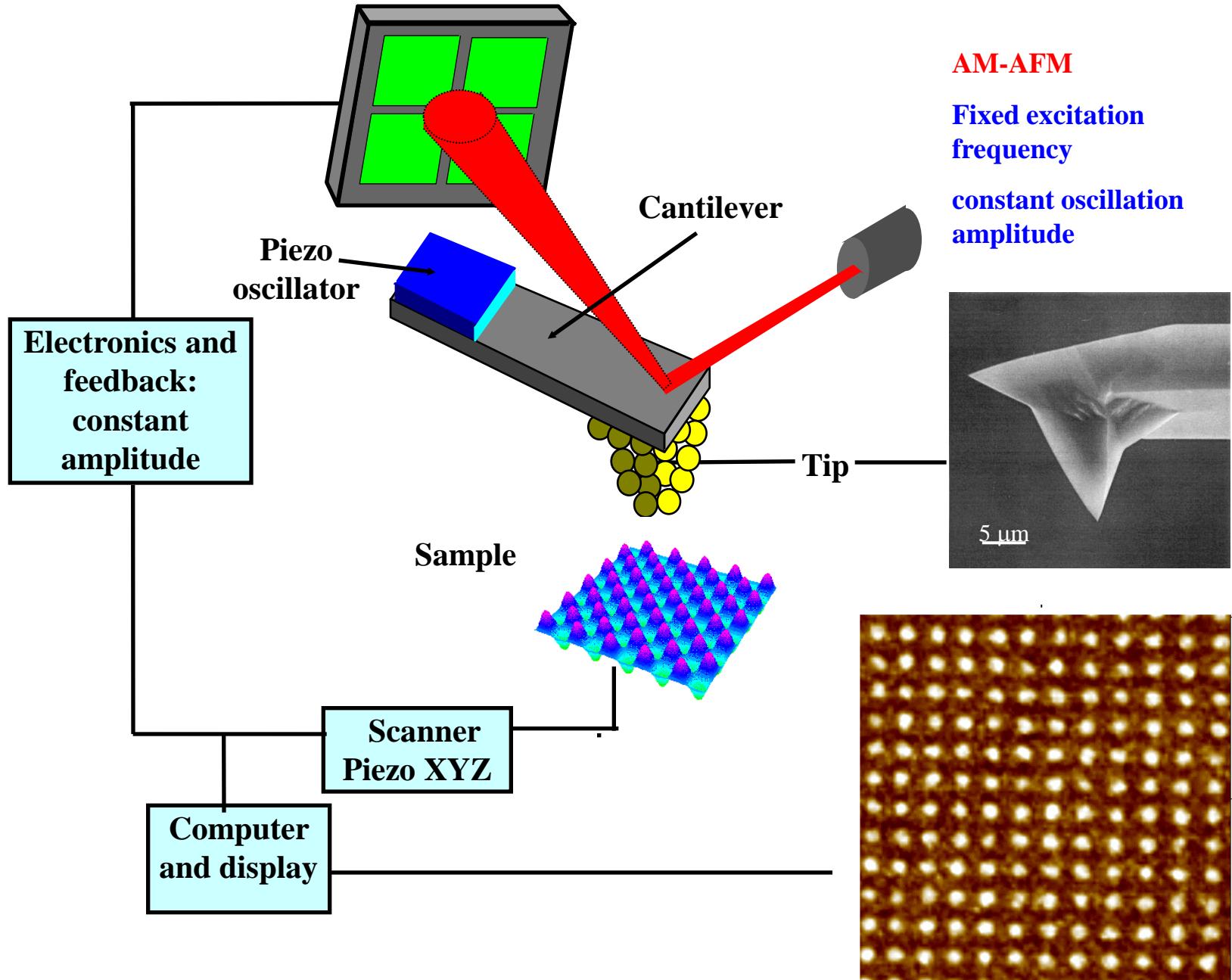
ATOMIC FORCE MICROSCOPY (AFM)

G. Binnig, C. Gerber & C. Quate, PRL 56 (1986) 930



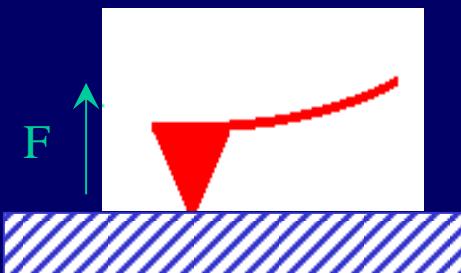
2nd most cited PRL: +5000 citations !!!

http://monet.physik.unibas.ch/famars/afm_prin.htm

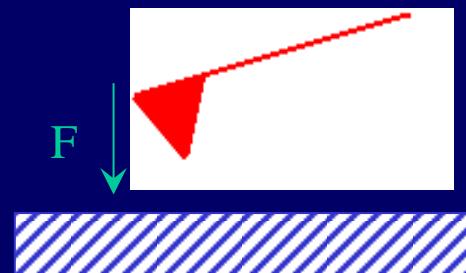


Limitations of static AFM

Contact



Non-contact



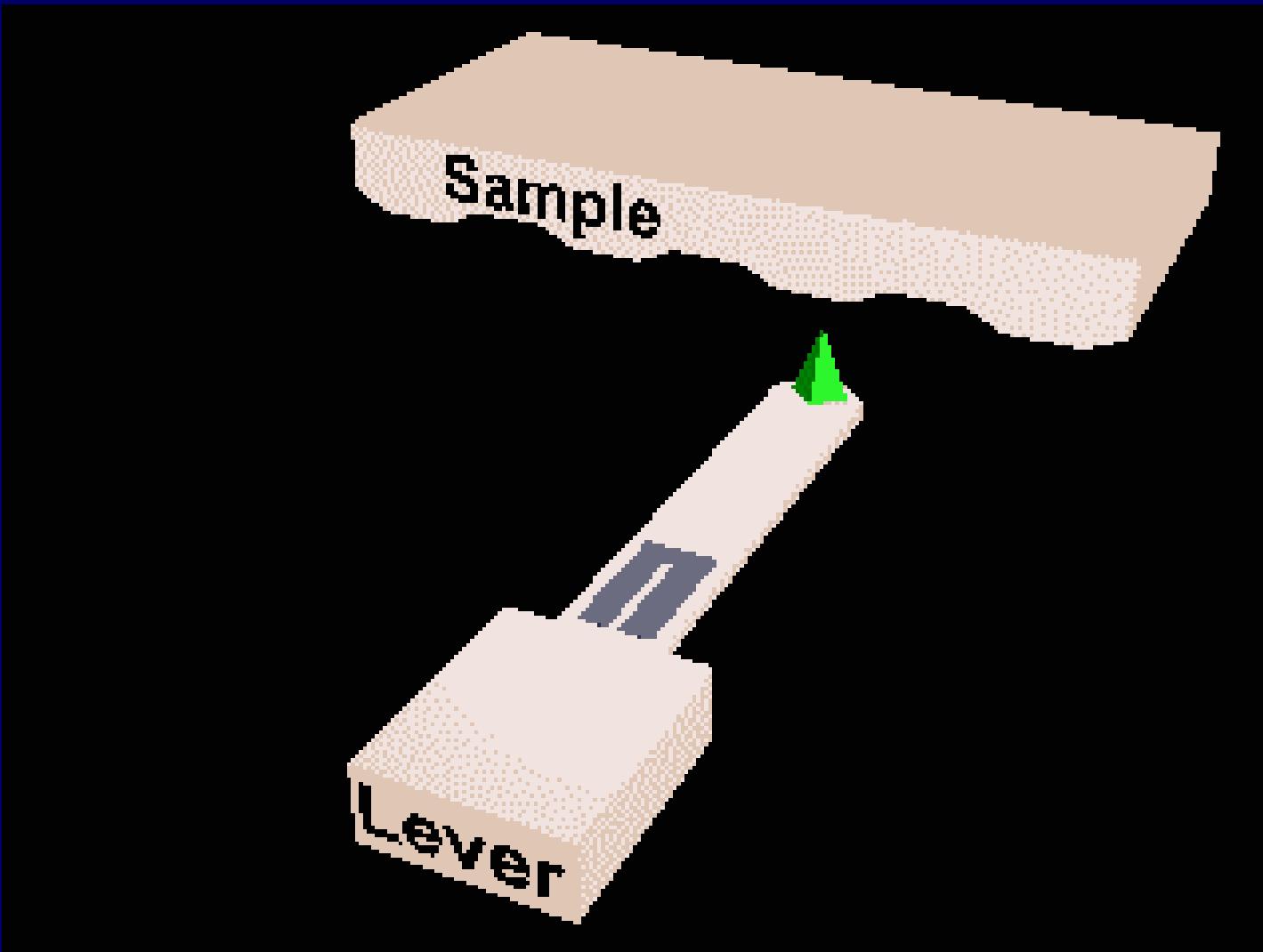
- Deformation, Friction
- No point defects observed

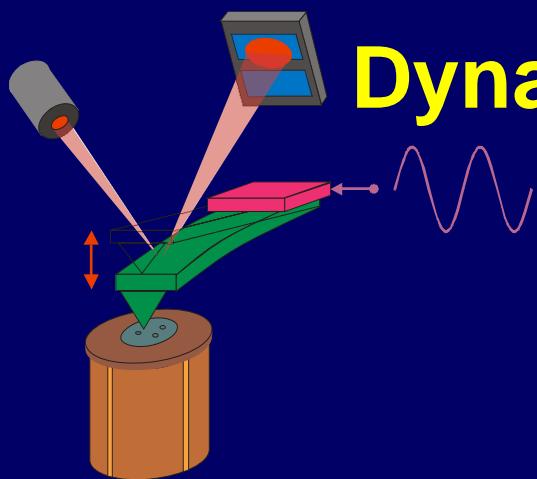
Atomic Resolution?

- Detection of small forces: soft cantilevers.
- “Jump to contact” : stiff cantilevers

AFM: G. Binnig, C. Gerber & C. Quate, PRL 56 (1986) 930

Dynamic AFM

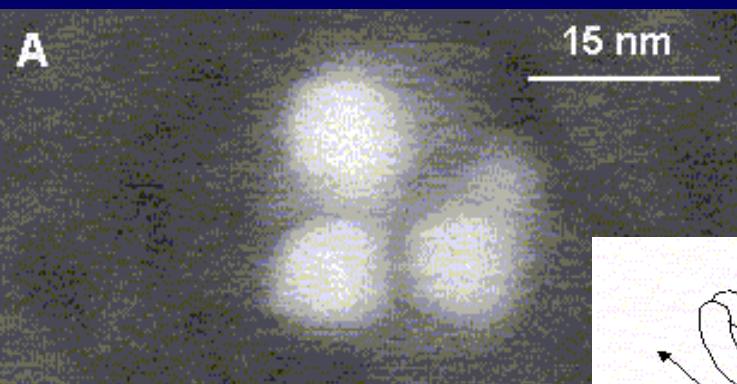




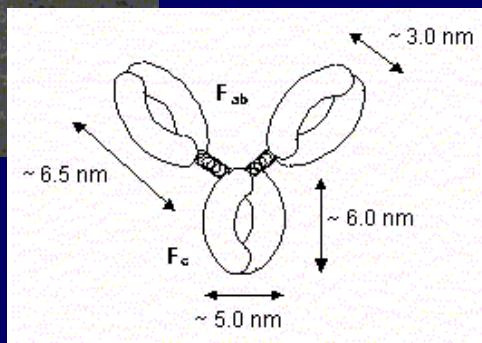
Dynamic AFM: Our Goal

Why changes observed in the dynamic properties of a vibrating cantilever with a tip that interacts with a surface make possible to:

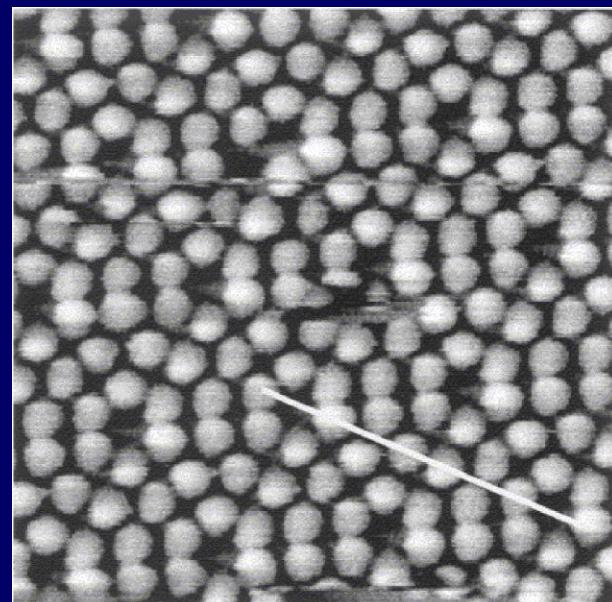
A



AM-dAFM

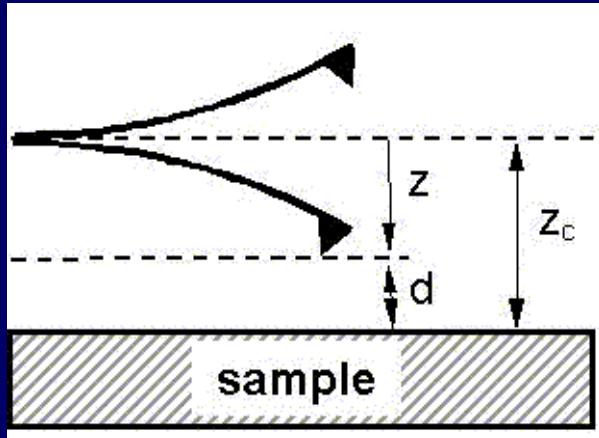


- Obtain **molecular resolution** images of biological samples in **ambient conditions**.



- Resolve **atomic-scale** defects in **UHV**.
FM-dAFM

Dynamic description



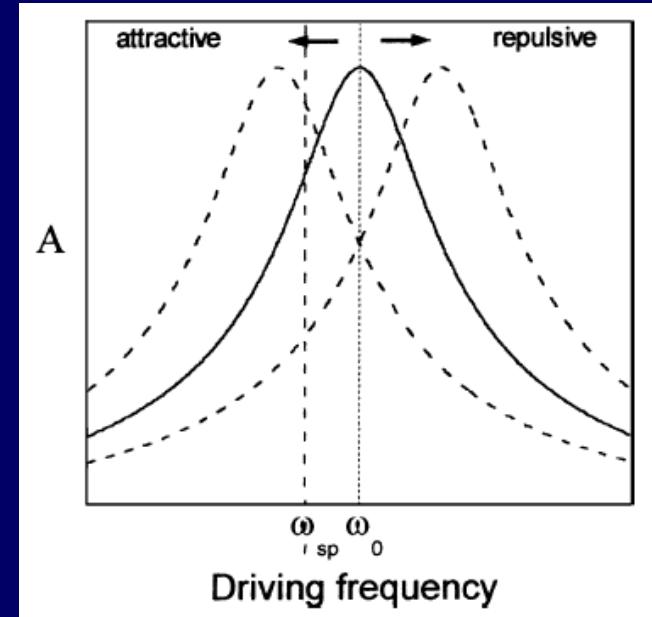
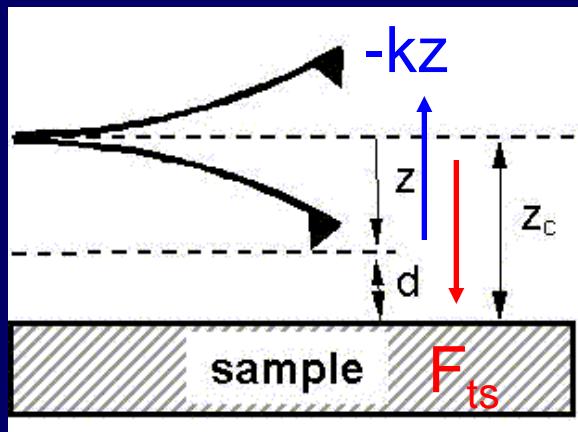
Cantilever-tip ensemble as a point mass spring described by a non-linear 2nd order differential equation

$$\ddot{z}(t) + \frac{\omega_0}{Q} \dot{z}(t) + \omega_0^2 z(t) - \frac{\omega_0^2}{k} F_{ts}[z_c + z(t)] = \omega_0^2 A_{\text{exc}}(t)$$

Amplitude
Resonance Frequency
Phase shift

} link the **dynamics** of a
vibrating tip to the **tip-surface**
 F_{ts} **interaction.**

Why do A and Δf ($\Delta\omega$) depend on F_{ts} ? (simple quasi-harmonic argument)



For small amplitudes and large distances

$$\omega = \sqrt{\frac{k + k_{ts}}{m}} \quad k_{ts} = -\frac{dF_{ts}}{dz} [z = z_c] \quad \Rightarrow \quad \frac{\Delta\omega}{\omega_0} = \frac{k_{ts}}{2k} \quad k \gg k_{ts}$$

New $\omega \Rightarrow$ new resonance curve \Rightarrow New amplitude for given ω_{exc}

BUT: Large amplitudes \Rightarrow Force gradient varies considerably during oscillation \Rightarrow Non-linear features in the dynamics

Two major modes: AM-AFM and FM-AFM

Amplitude Modulation AFM

- Excitation with constant amplitude A_{exc} and frequency ω_{exc} close or at its FREE resonance frequency ω_0 .
- Oscillation amplitude A as feedback for topography.
- Phase shift ϕ between excitation and oscillation: compositional contrast.
- Air and liquid environments.

Frequency Modulation AFM

- Constant oscillation amplitude at the current resonance frequency (depends on F_{ts}).
- Frequency shift Δf as feedback for topography.
- Excitation amplitude A_{exc} provides atomic-scale information on dissipation.
- UHV (now also liquids !)

Y. Martin et al, JAP 61, 4723 (1987)
Q. Zhong et al, SS 290, L688 (1993)

T.R. Albrecht et al, JAP 69, 668 (1987)
F.J. Giessibl, Science 267, 68 (1995)

Amplitude Modulation (AM) AFM

Outline: AM-AFM (or Tapping mode AFM)

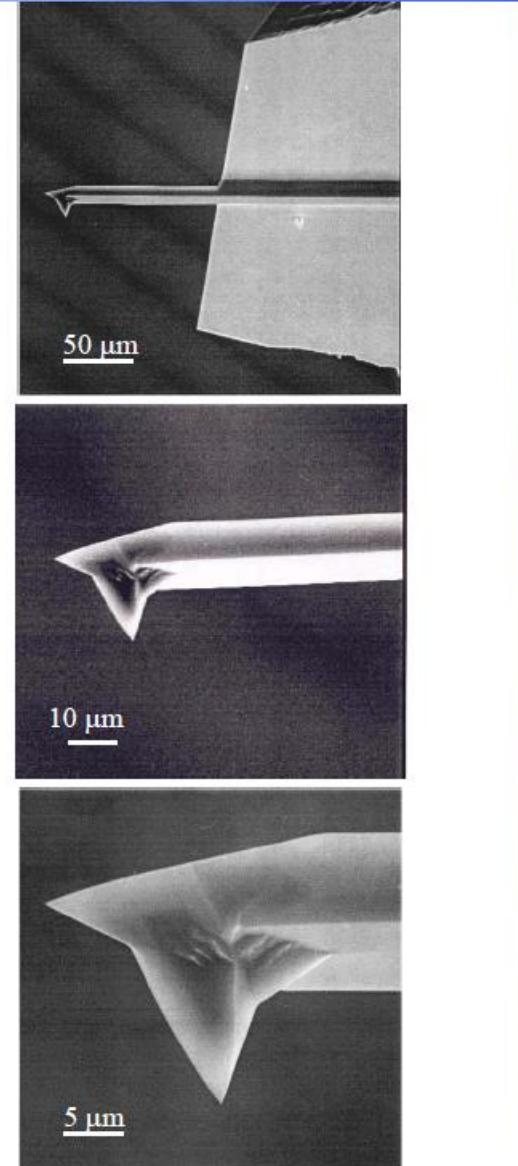
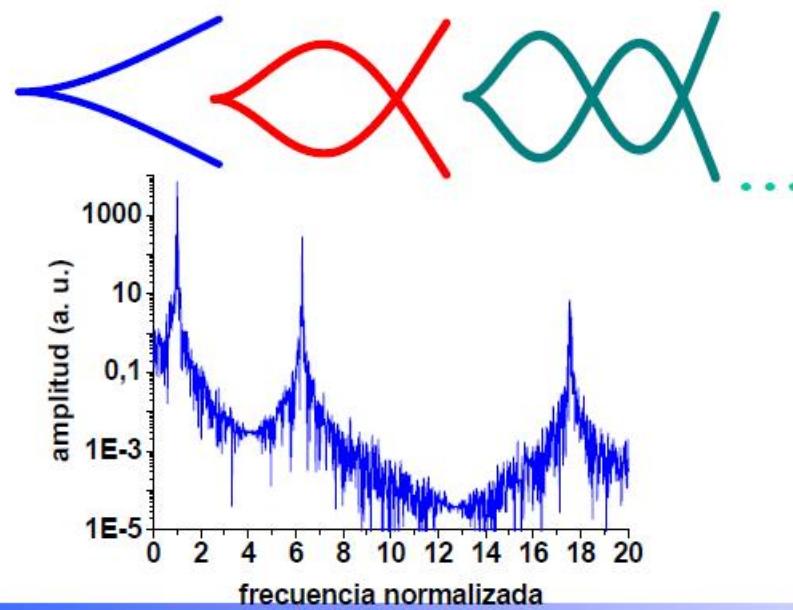
- Operation Parameters.
- Non-linear dynamics: Existence of two oscillation states (L & H): implications for imaging.
- Understanding amplitude reduction.
- Imaging materials properties: phase shifts and dissipation.
- Summary: things to remember...

Microcantilevers

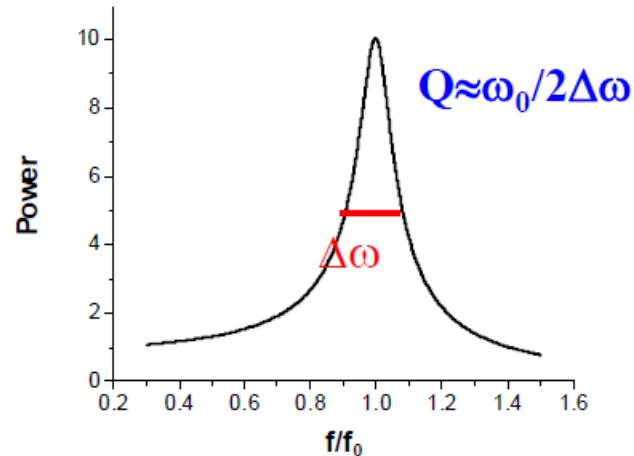
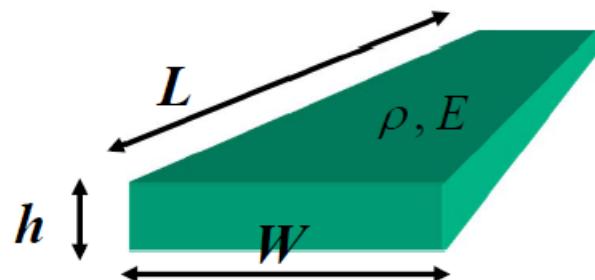
Mechanical device to detect and amplify tip-surface interactions,
Si or Si_3N_4

The dynamic response of the μ cantilever is characterized by three quantities: force constant k_n , resonant frequency f_n and quality factor Q_n

There are several resonances (eigenmodes) in a cantilever



Microcantilevers



$$f_n = \frac{1}{2\pi} \sqrt{\frac{k_n}{m_n}} = \frac{C_n^2}{2\pi} \frac{h}{L^2} \sqrt{\frac{E}{\rho}}$$

$$k = \frac{3EI}{L^3} = \frac{EWh^3}{4L^3}$$

Resonance frequency	Force constant	Q-factor
10^4 - 4×10^5 Hz	0.01-50 N/m	$1-10^5$

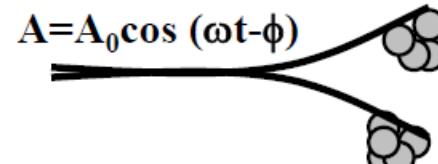
Forces: Equation of motion

Contact AFM



$$F_{ts} = -kz$$

dynamic AFM (amplitude modulation)

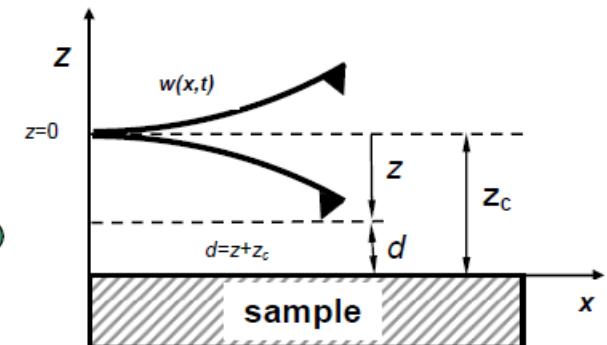


Point-mass model of the microcantilever

Respuesta elástica

$$m \frac{d^2 z}{dt^2} = -kz - \frac{m \omega_0}{Q} \frac{dz}{dt} + F_{ts} + F_0 \cos \omega t$$

Amortiguamiento del medio



Interacciones

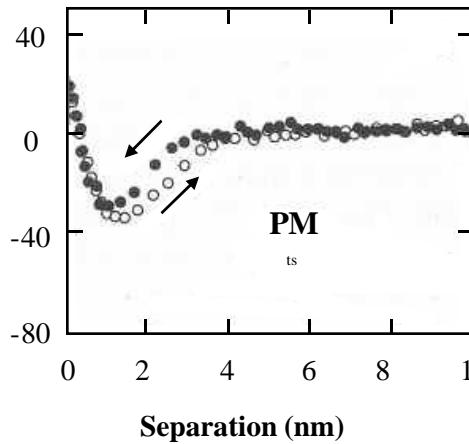
Fuerza externa

Forces in AFM

Restoring force cantilever

$$F_c = -kz$$

Force (nN)



Excitation force
 $F_0 \cos \omega t$

Hidrodynamic forces

$$F_h = \frac{m \omega_0}{Q} \frac{dz}{dt}$$

Short range repulsive forces (DMT)

$$F_{DMT} = E^* \sqrt{R} \delta^{3/2}$$

van der Waals forces

$$F_{vdw} = \frac{HR}{6d^2}$$

Capillary forces

$$F_a = 4\pi\gamma R$$

Adhesion forces

Forced damped harmonic oscillator

$$m\ddot{z}(t) + \frac{mQ}{\omega_0} \dot{z}(t) + kz(t) = kA_{exc} \cos(\omega_{exc} t)$$

$$\omega_0 = \sqrt{\frac{k}{m}}$$

$Q \equiv$ Quality factor (cantilever damping)

$$\gamma = \frac{\omega_0}{2Q}$$

$$z(t) = C \exp(-\gamma t) \cos(\omega_\gamma t + \delta) +$$

← (transient)

$$+ \frac{\omega_0^2 A_{exc}}{\sqrt{(\omega_0^2 - \omega_{exc}^2)^2 + (\omega_0 \omega_{exc}/Q)^2}} \cos(\omega_{exc} t - \phi)$$

$$\omega_0 = \omega_{exc} \Rightarrow A = Q A_{exc} \text{ (resonance)}$$

$$\tan \phi = \frac{\omega_0 \omega_{exc} / Q}{\omega_0^2 - \omega_{exc}^2}$$

BUT F_{ts} is nonlinear
 \Rightarrow anharmonic effects

Resonance Curves

Free oscillating tip (10 nm)



Interacting tip (10 nm size)



$$\omega/\omega_0$$

Mechanics of vibrating
nanosystems:

Coexistence of oscillation
states: Bi-stability

AS Paulo, R García, PRB 66, 041406(R) (2002)

SIMULATION

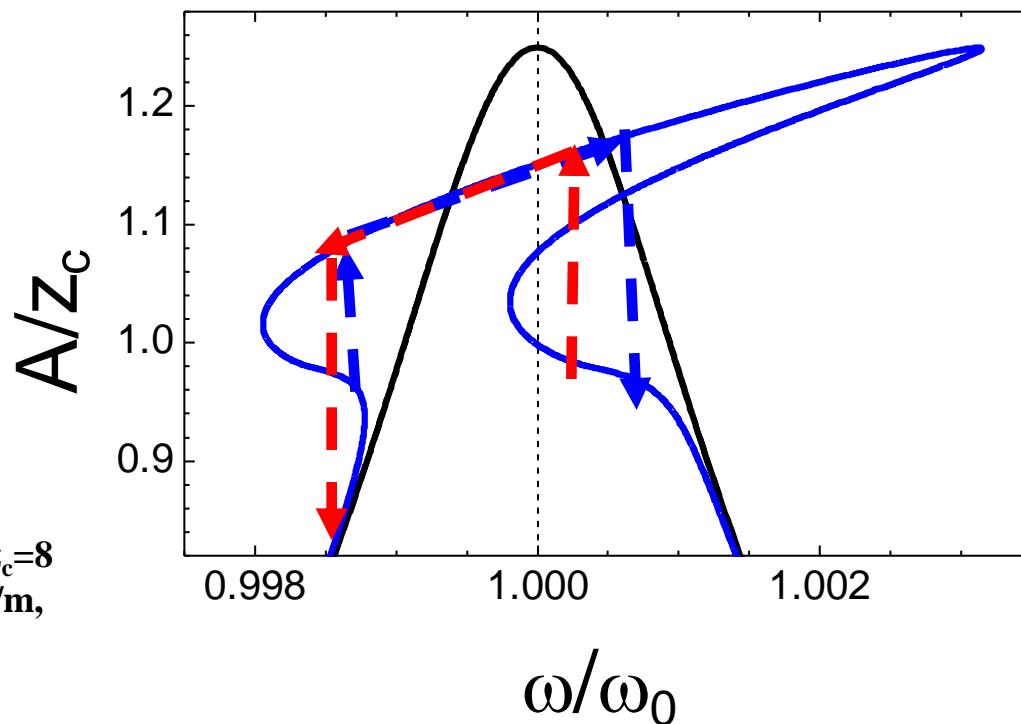
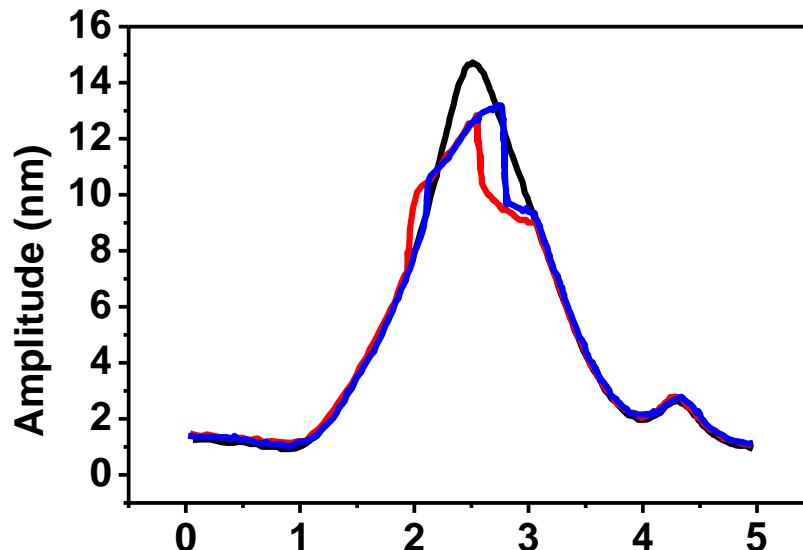
$R=10 \text{ nm}$, $A_0=10 \text{ nm}$, $z_c=8 \text{ nm}$,
 $E=1 \text{ GPa}$, $k=40 \text{ N/m}$, $f_0=325$
kHz

EXPERIMENT

Silicon, $A_0=15$ nm, $A=13$ nm, $f_0=295.64$ kHz

Low to high

high to low

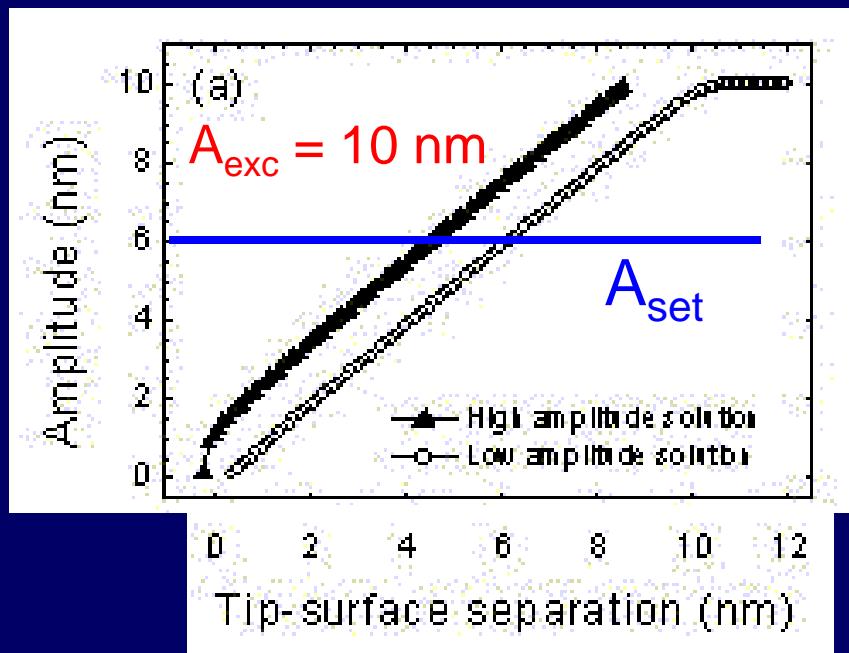


SIMULATION

$R=10$ nm, $A_0=10$ nm, $z_c=8$ nm, $E=1$ GPa, $k=40$ N/m, $f_0=325$ kHz

AM-AFM: Two stable oscillation states

$$z_{H(L)}(t) = z_c + A_{H(L)} \cos(\omega_{exc} t - \phi_{H(L)})$$



(two steady state solutions)

H: high amplitude state

L: low amplitude state

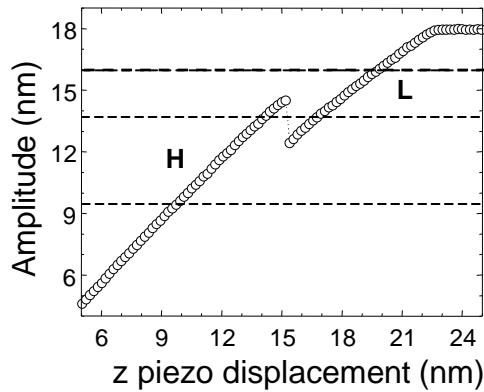
Amplitude curves: $A_{H(L)}$ vs z_c

- Collection of L and H solutions gives rise to L and H branches.
- $A_{H(L)}$ decreases linearly with z_c for both branches.
- Ambiguity in the operation: both branches can match the set amplitude A_{set} .

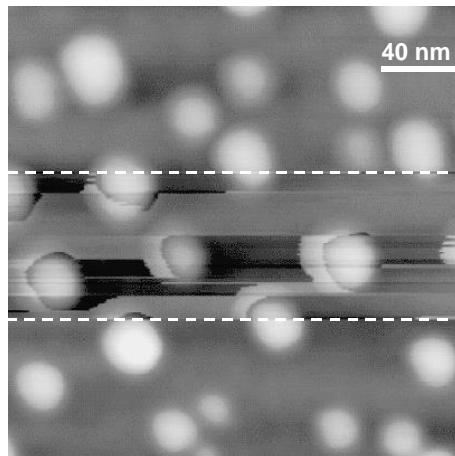
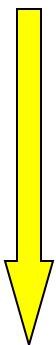
Experimental implications of the coexistence of states (I):

Noise and stability

Sample: InAs quantum dots



A₁
A₂
A₃



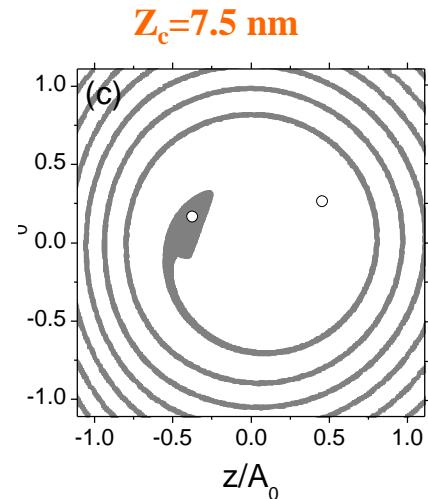
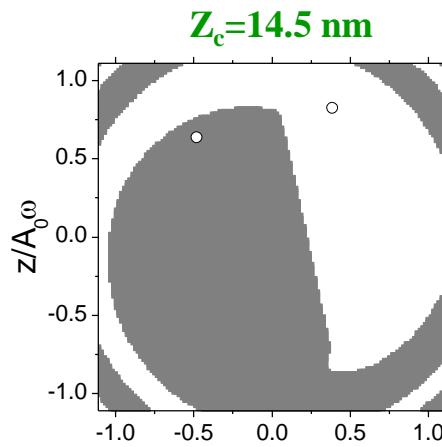
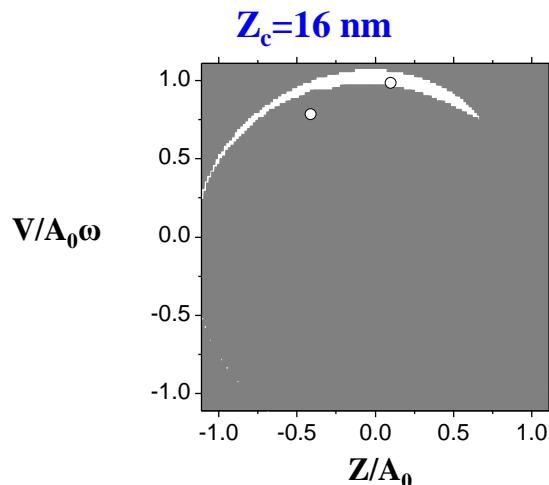
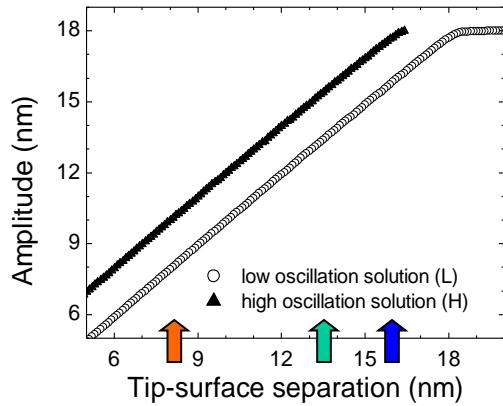
A₁ low amplitude branch

A₂

A₃ high amplitude branch

Are both solutions equally accessible ?

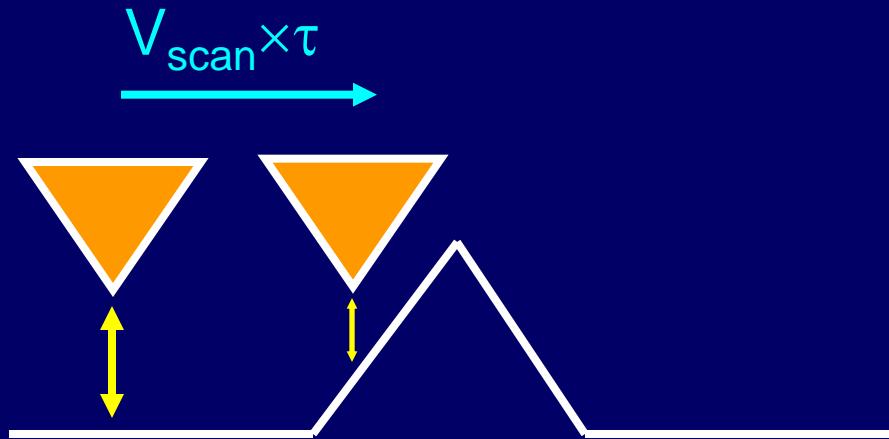
García and San Paulo, Phys. Rev. B
61, R13381 (2000)



Tip should stay always on the same branch (deterministic) BUT...

NOISE: Implications for scanning

Mechanical, electronical, thermal and **feedback** perturbations...



Finite time response of the feedback ($\tau \approx 10^{-4}$ s)

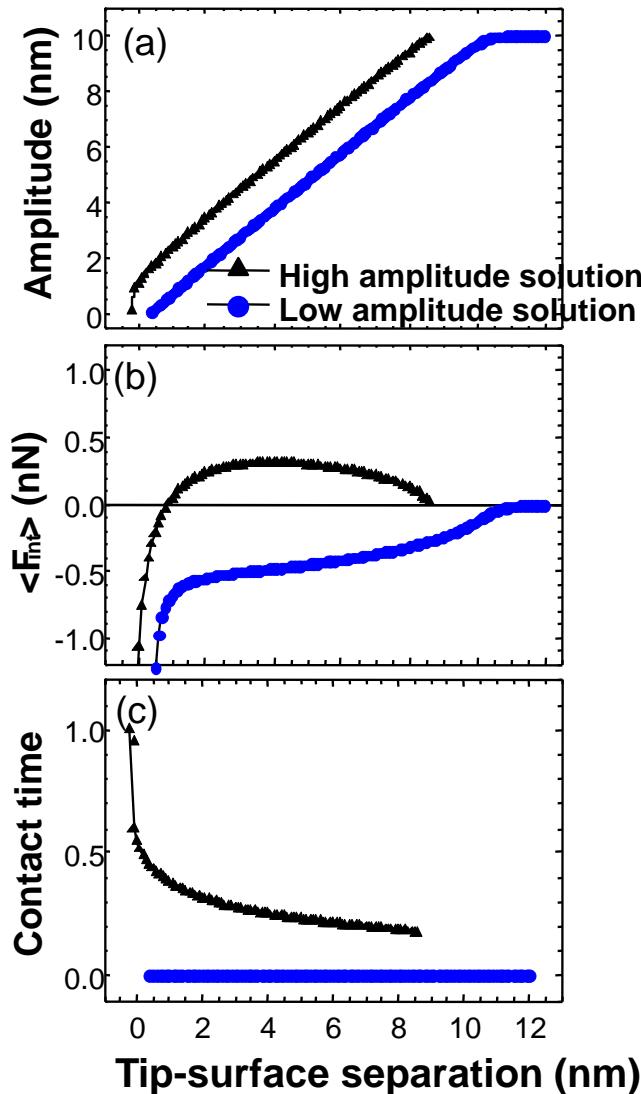


Change in separation can lead to transitions before the feedback takes over

- AM-AFM would operate properly if initial (unperturbed) and intermediate state belong to the same branch, otherwise instabilities and image artifacts will appear.
- Stable operation when one of the states dominates the phase space (tip oscillates in the state with the largest attraction basin).

Characterizing the physical properties of the two states....

H and L states have different properties

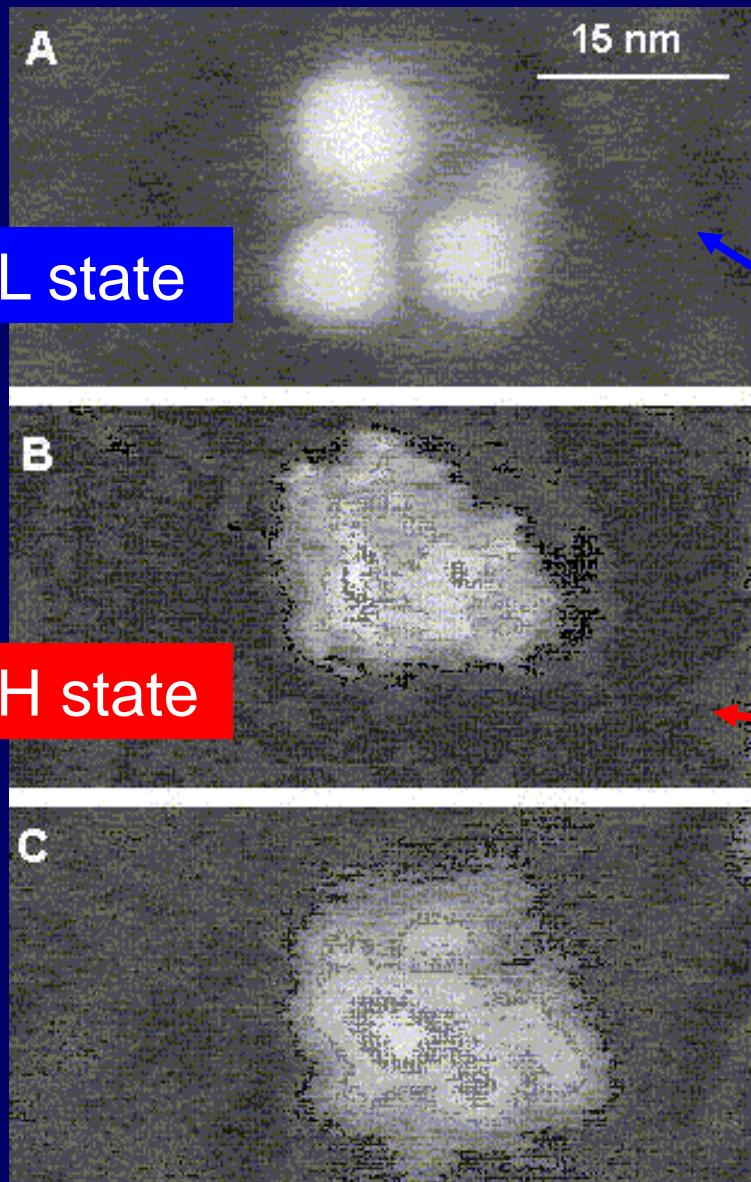


$$\langle F_{ts} \rangle = \frac{1}{T} \oint F_{ts}(t) dt$$

Simulation data: R=20 nm
 $f_0=350$ kHz, Q=400, H= 6.4×10^{-20} ,
 $E^*=1.52$ GPa

Does resolution depend on the oscillation state chosen?

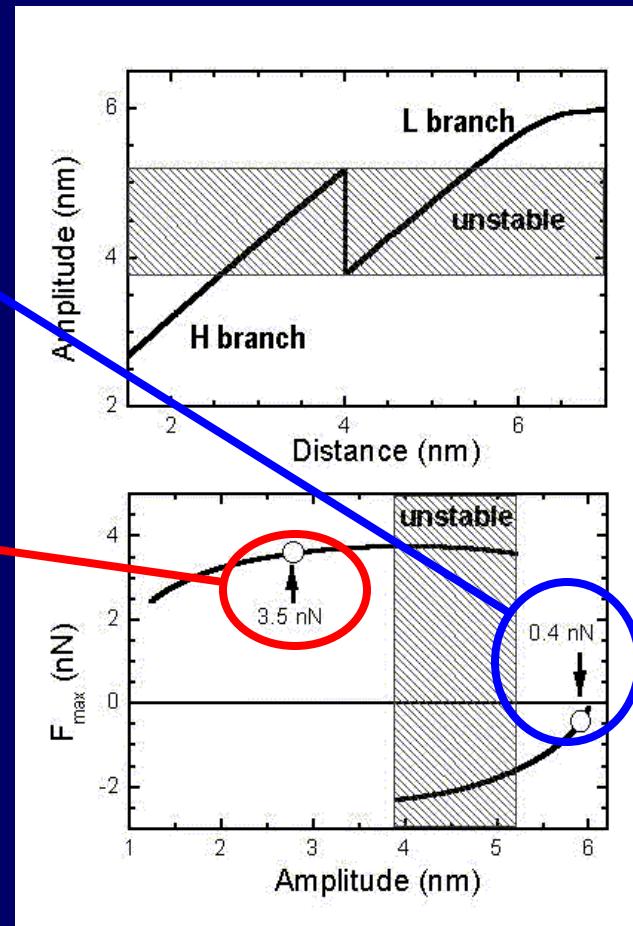
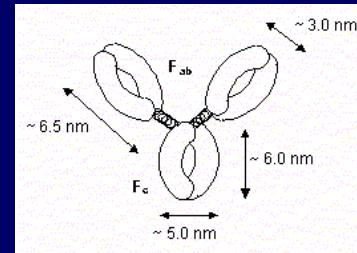
a-HSA antibody on mica



Morphology and dimensions of fragments clearly resolved

No domain structure

Irreversible deformation after imaging on H state



Analytical Approximations

(Understanding the amplitude reduction...: related to $\langle F_{ts} \rangle$??)

San Paulo and García,
PRB 64, 193411 (2001)

The virial theorem and energy consideration allows
to derive an analytical approximation

$$\cos\phi = \frac{2Q}{k_c A A_0} \left[\frac{\langle F_{ts} \rangle^2}{k_c} - \langle F_{ts} \cdot z \rangle + \frac{1}{2} k_c A^2 \left(1 - \frac{\omega^2}{\omega_0^2} \right) \right]$$

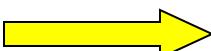
$$\omega = \omega_0 \text{ and } A \gg z_0$$

$$\longrightarrow \cos \phi \approx - \frac{2Q \langle F_{ts} \cdot z \rangle}{k_c A A_0}$$

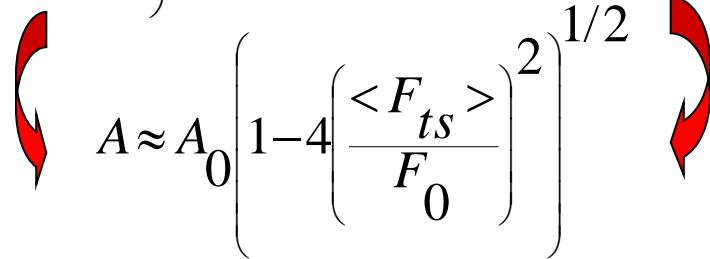
$$\sin \phi = \frac{A \omega}{A_0 \omega_0} + \frac{2Q P_{ts}}{k_c A A_0 \omega}$$

Negligible power dissipation

$$A \approx \frac{A_0}{\sqrt{2}} \left(1 - \frac{2P_{ts}}{P_{med}} \pm \sqrt{1 - \frac{4P_{ts}}{P_{med}} - 16 \left(\frac{\langle F_{ts} \cdot z \rangle}{F_0 A_0} \right)^2} \right)^{1/2}$$



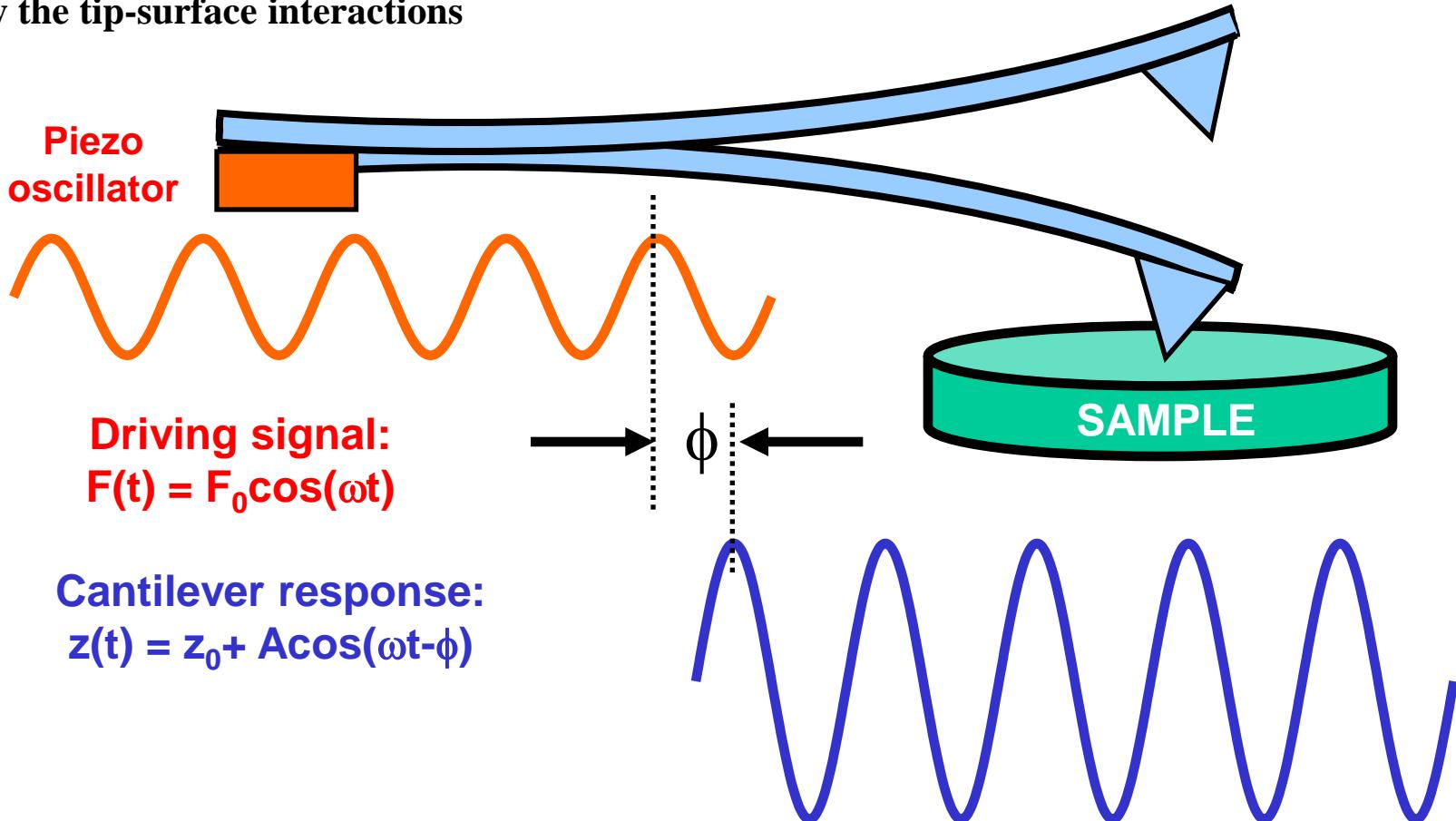
$$A \approx \frac{A_0}{\sqrt{2}} \left(1 \pm \sqrt{1 - 16 \left(\frac{\langle F_{ts} \cdot z \rangle}{F_0 A_0} \right)^2} \right)^{1/2}$$



$$A \approx A_0 \left(1 - 4 \left(\frac{\langle F_{ts} \rangle}{F_0} \right)^2 \right)^{1/2}$$

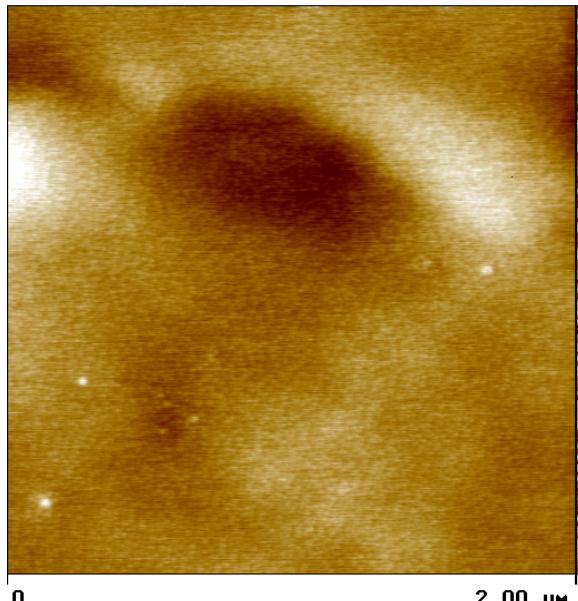
Phase Imaging

The dynamic response of the cantilever is modified by the tip-surface interactions

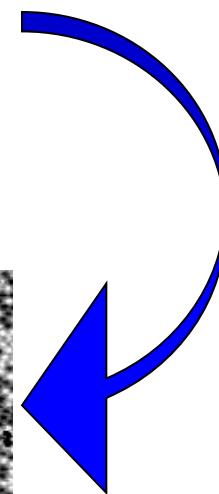
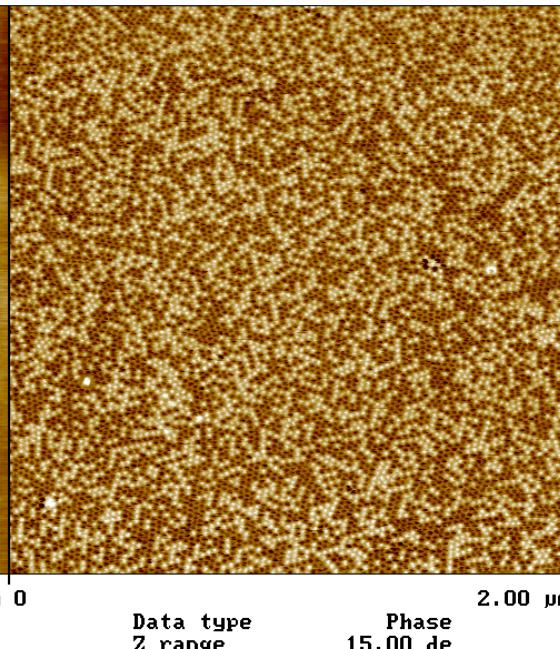


Polymers: Morphology and Structure

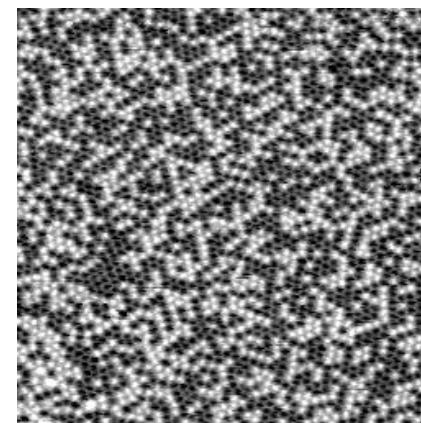
Amplitude image



Phase image



Polymer morphology and structure as a function of temperature. Hydrogenated diblock copolymer (PEO-PB). Crystallisation of PEO blocks occurs individually for each sphere (light are crystalline, dark amorphous). **Reiter et al., Phys. Rev. Lett.**
87, 2261 (2001)



Phase Image, size
1μm²

PHASE SHIFT AND ENERGY DISSIPATION IN AMPLITUDE MODULATIONAFM

Steady solution

$$z(t) = A(\omega) \cos(\omega t - \phi)$$

Dynamic equilibrium in AM -AFM (tapping mode)

$$E_{ext} = E_{med} + E_{dis} \quad \text{energy per period}$$

$$E_{ext} = \int F_0 \cos(\omega t) \frac{dz}{dt} dt = (1/Q)\pi k A_0 A(\omega) \cdot \sin\varphi$$

$$E_{med} = \int \left(\frac{m\omega_0}{Q} \frac{dz}{dt} \right) \frac{dz}{dt} dt = \frac{\pi k \omega A^2(\omega)}{Q \omega_0}$$

$$E_{dis} = \int (F_{ts}) \frac{dz}{dt} dt$$

$$\sin \phi = \frac{\omega}{\omega_0} \frac{A_{sp}}{A_0} + \frac{QE_{dis}}{\pi k A_0 A_{sp}}$$

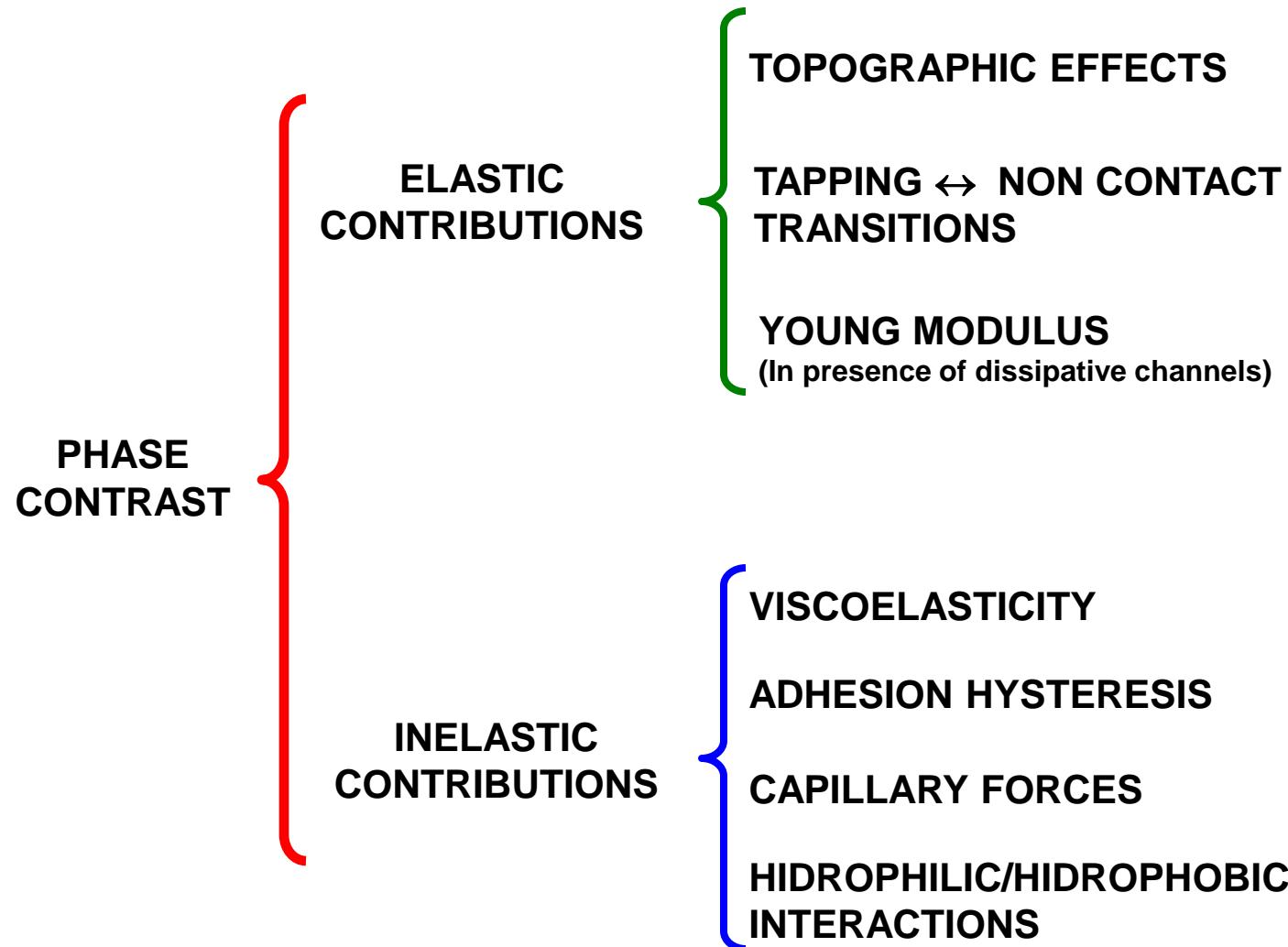
Cleveland et al. APL 72, 2613(1998)

Tamayo, García APL73, 2926 (1998)

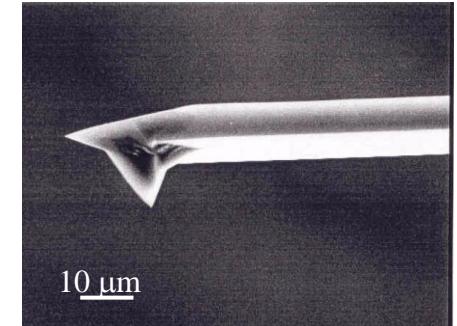
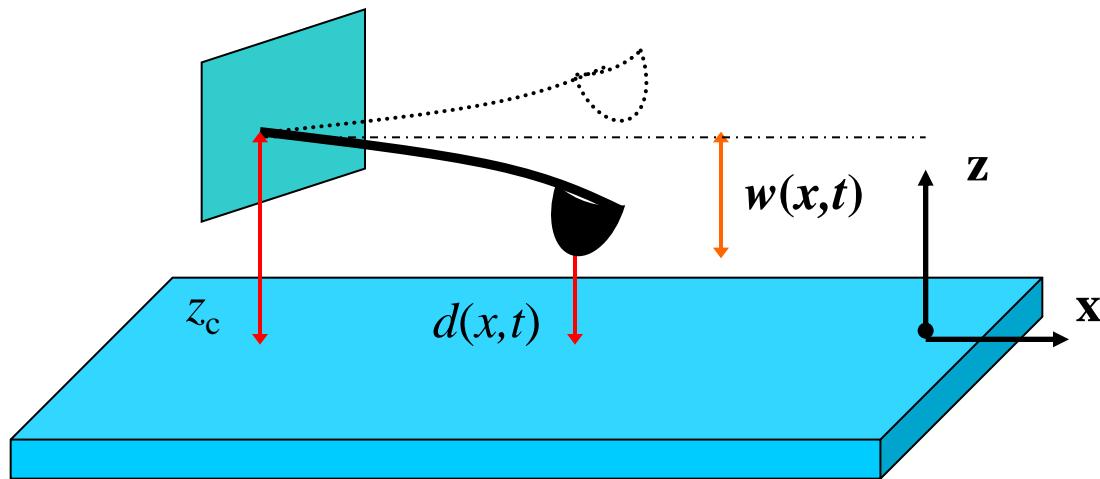
García et al. Surf. Int. Anal. 27, 1999)

At A_{sp} =constant phase shifts are linked to tip-surface inelastic interactions

CONTRIBUTIONS TO CONTRAST IN PHASE IMAGES



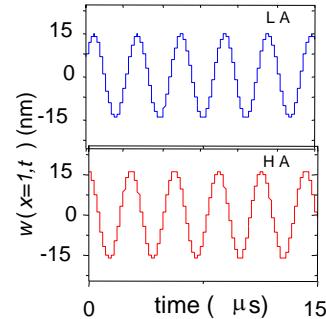
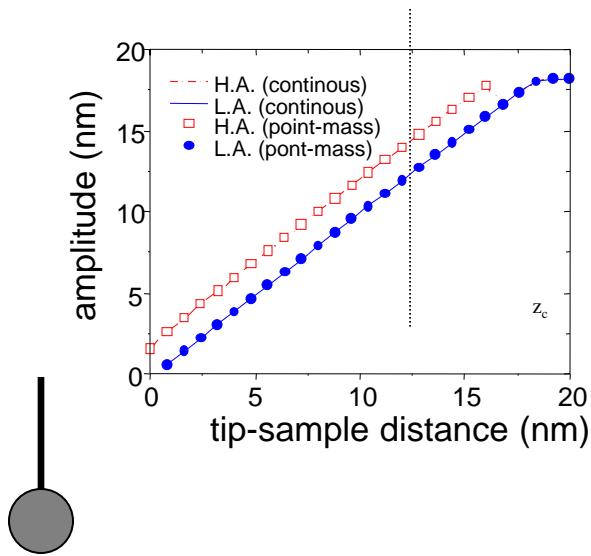
Continuous Model for the Cantilever



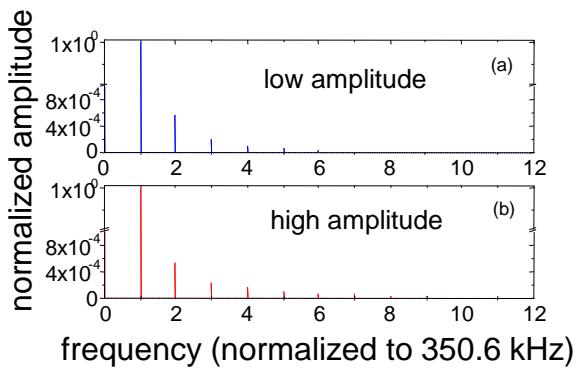
$$\frac{EI}{L^4} \frac{\partial^4}{\partial x^4} [w(x,t)] + bh\rho \frac{\partial^2 w(x,t)}{\partial t^2} = F_{ext} + F_{med} + F_{ts}$$

$$w(x,t) \Big|_{x=0} = \frac{\partial w(x,t)}{\partial x} \Big|_{x=0} = \frac{\partial^2 w(x,t)}{\partial x^2} \Big|_{x=1} = \frac{\partial^3 w(x,t)}{\partial x^3} \Big|_{x=1} = 0$$

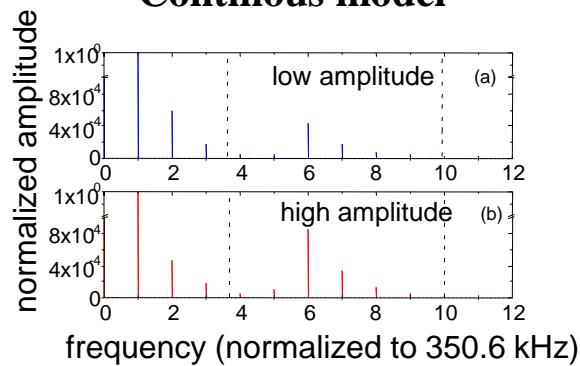
Rodríguez and García, Appl. Phys. Lett. 80, 1646 (2002)



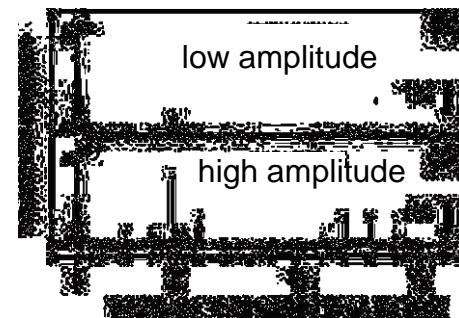
Point -mass model



Continous model



Experimental results (Triangular cantilever)



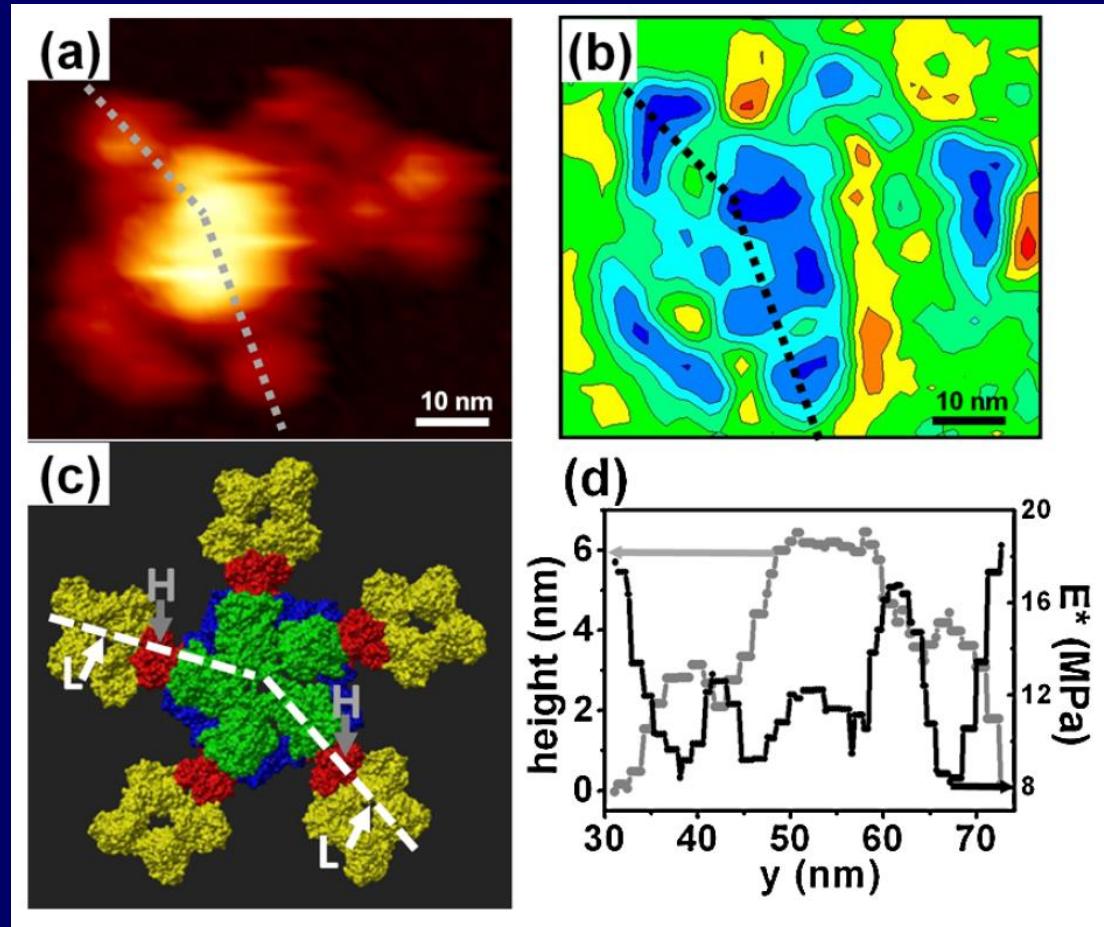
Parámetros de la simulación:

$f_0 = 350.6 \text{ kHz}$, $k = 40 \text{ N/m}$, $A_0 = 18.22 \text{ nm}$, $Q = 400$ (masa puntual, ajusta el primer modo libre).
 $l = 119 \mu\text{m}$, $h = 3.6 \mu\text{m}$, $b = 33 \mu\text{m}$, $E = 170 \text{ Gpa}$, $r_c = 2320 \text{ kg/m}^3$, $F = 1.85 \text{ nN}$, $a_0 = 1.28 \cdot 10^{-3} \text{ kg/m}\cdot\text{s}$,
 $a_1 = 0.2 \text{ ns}$, $a_2 = 10.037$ (modelo continuo que ajusta la curva A vs. f experimental libre)
 $R = 30 \text{ nm}$, $H = 6.4 \cdot 10^{-20} \text{ J}$, $E^* = 1.51 \text{ Gpa}$, $d_0 = 0.165 \text{ nm}$

Stark et al. APL 77, 3293 (2000)

Bimodal FM-AFM on Antibodies(IgM)

Noninvasive Protein Structural Flexibility Mapping



D. Martinez et al, PRL106, 198101(2011)

AM-AFM: Things to remember...

- Operation Parameters (OP): A_{exc} , ω_{exc} , Z_c . & A_{set}
- Two stable oscillation states: L (H) = low (large) amplitude.
- Choose OP to ensure that one state dominates phase space \Rightarrow stable imaging.
- Image soft materials with L state (avoid damage).
- Image stiff materials with H state (improved contrast).
- Amplitude reduction related to $\langle \mathbf{F}_{\text{ts}} \cdot \mathbf{z} \rangle$.
- Imaging material properties: Phase imaging.
- Phase shift related to $\langle P_{\text{ts}}^{\text{diss}} \rangle = \langle \mathbf{F}_{\text{ts}} \cdot d\mathbf{z}/dt \rangle$.
- Nanometric resolution (both amplitude and phase images).

Frequency Modulation (FM) AFM

Outline: FM-AFM

- Dynamic AFM: AM-AFM vs FM-AFM.
- Cantilever dynamics: Δf vs F_{ts} .
 - Perturbation theory for the frequency shifts
 - Normalized frequency shift
- Atomic scale contrast and F_{ts} : tip as the key player.
 - Separation of long- and short-range interactions.
 - semiconductors, alkali halides, oxides, metals, nanotubes,...
- Recent developments.
 - Tuning forks: small amplitudes to enhance atomic contrast
 - Force spectroscopy: Chemical identification.
 - Single-atom manipulation, atomic-scale magnetic imaging
 - Operation in liquids
- Summary: things to remember...

1. Dynamic AFM: AM-AFM vs FM-AFM.

Two major modes: AM-AFM and FM-AFM

Amplitude Modulation AFM

- Excitation with constant amplitude A_{exc} and frequency ω_{exc} close or at its FREE resonance frequency ω_0 .
- Oscillation amplitude A as feedback for topography.
- Phase shift ϕ between excitation and oscillation: compositional contrast.
- Air and liquid environments.

Frequency Modulation AFM

- Constant oscillation amplitude at the current resonance frequency (depends on F_{ts}).
- Frequency shift Δf as feedback for topography.
- Excitation amplitude A_{exc} provides atomic-scale information on dissipation.
- UHV (now also liquids !)

Y. Martin et al, JAP 61, 4723 (1987)
Q. Zhong et al, SS 290, L688 (1993)

T.R. Albrecht et al, JAP 69, 668 (1987)
F.J. Giessibl, Science 267, 68 (1995)

Why not AM-AFM in UHV?: transient terms!!

$$\delta(\Delta f) = \delta(f - f_0) = \sqrt{\frac{f_0 k_B T B}{4\pi k Q \langle z_{\text{osc}}^2 \rangle}}$$

Increase Q to improve resolution
BUT... Q and B (bandwidth)
linked in AM-AFM

$$z(t) = C \exp(-\gamma t) \cos(\omega_\gamma t + \delta) + \xleftarrow{\text{(transient)}}$$

$$+ \frac{\omega_0^2 A_{\text{exc}}}{\sqrt{(\omega_0^2 - \omega_{\text{exc}}^2)^2 + (\omega_0 \omega_{\text{exc}} / Q)^2}} \cos(\omega_{\text{exc}} t - \phi)$$

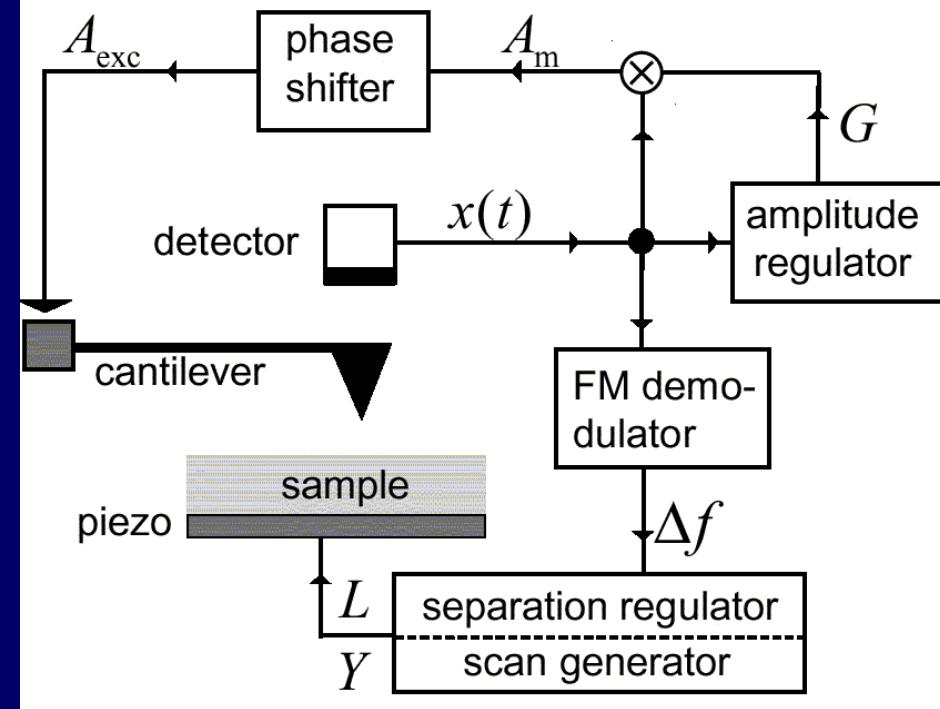
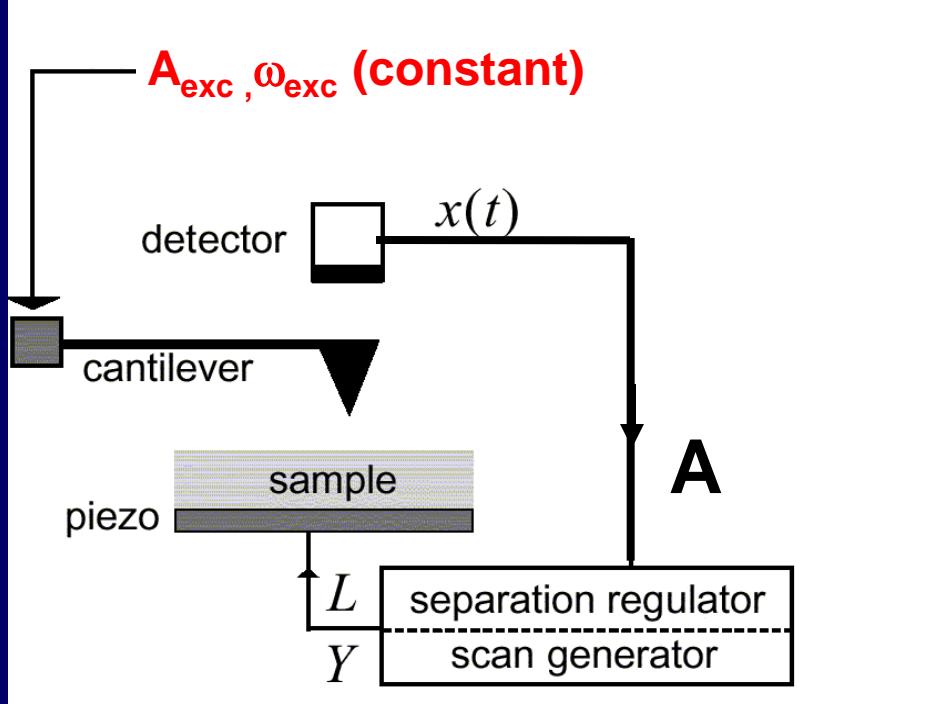
$$Q \text{ (air)} = 10^2 - 10^3 \Rightarrow \tau \text{ small}$$

$$Q \text{ (UHV)} = 10^4 - 10^5 \Rightarrow \tau \text{ large}$$

$$(Q=50000, \omega_0=50 \text{ kHz} \Rightarrow \tau = 2 \text{ s !!!})$$

We have to wait 2 s to record a single pixel... (small bandwidth)

AM-AFM vs FM-AFM set-ups



FM-AFM: cantilever regulated by electronics \Rightarrow stable and fast response.



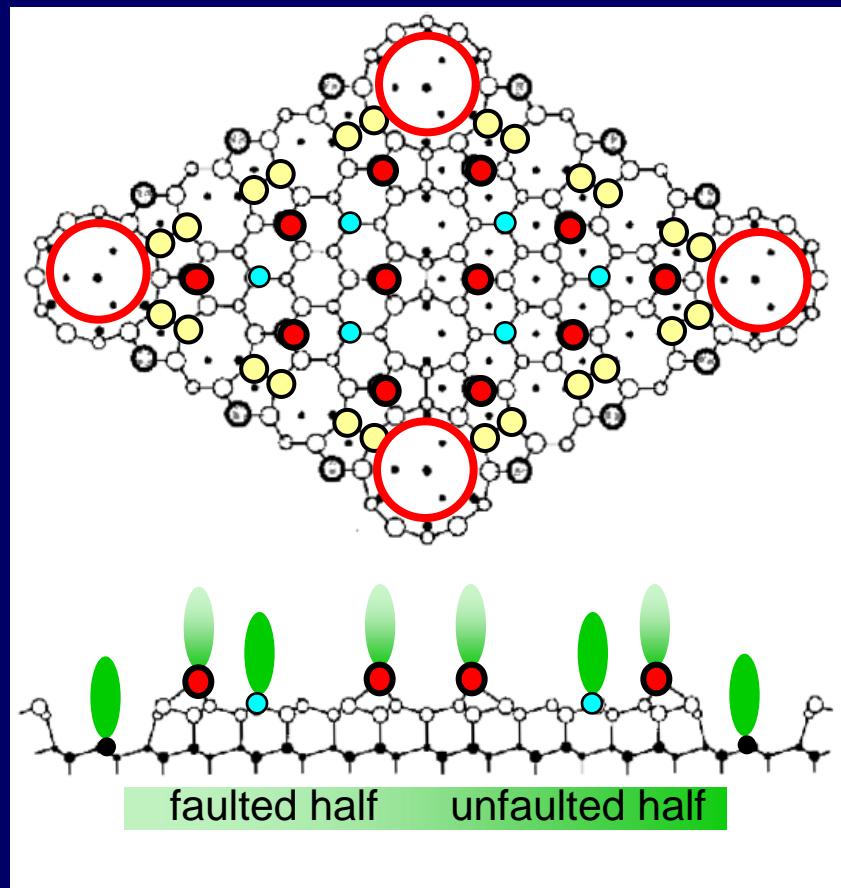
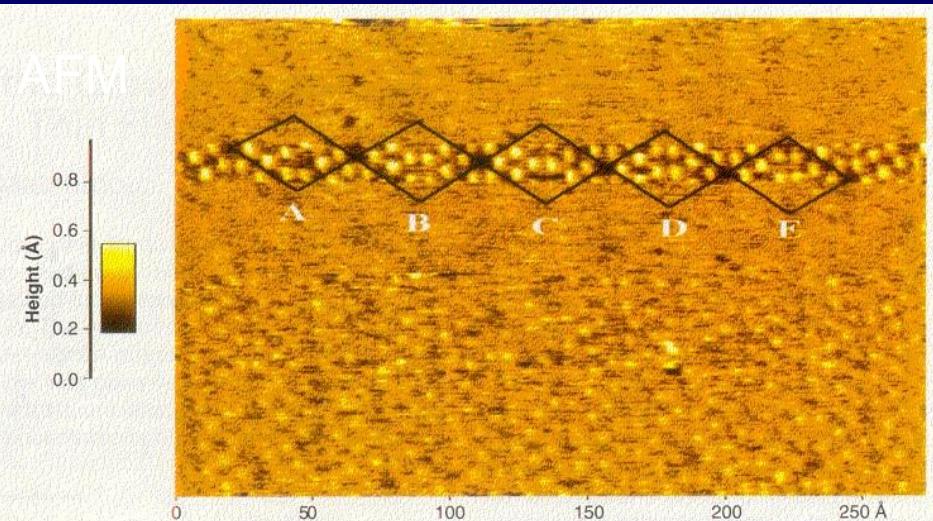
Mechanical Stability Conditions

$$\max \left| \frac{d^2 V_{\text{ts}}}{dz^2} \right| = k_{\text{ts}}^{\max} < k$$

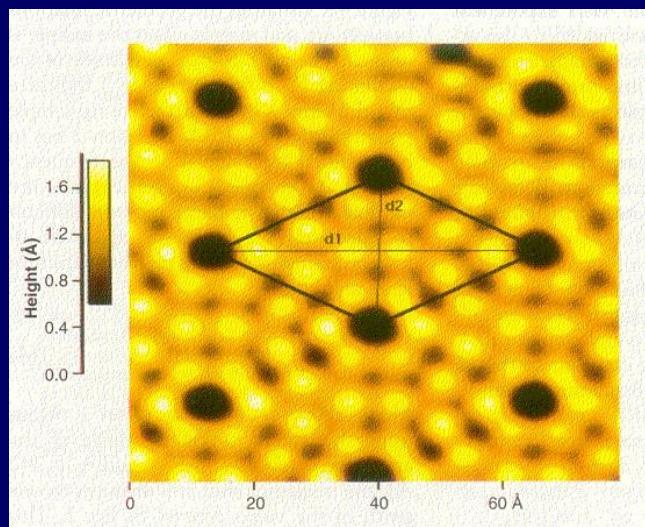
$$\max \left| -\frac{dV_{\text{ts}}}{dz} \right| = |F_{\text{ts}}^{\max}| < kA_0$$

$$\tau_{\text{FM}} \approx \frac{1}{\omega_0}$$

Atomic resolution in FM-AFM:Si(111)-7x7



STM



F.J. Giessibl, Science 267, 68 (1995)

“Classical” FM-AFM operation conditions

Stability Conditions

$$\max \left| \frac{d^2 V_{ts}}{dz^2} \right| = k_{ts}^{\max} < k$$

$$\max \left| -\frac{dV_{ts}}{dz} \right| = |F_{ts}^{\max}| < kA_0$$

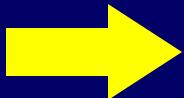
$k \sim 30 \text{ N/m}$

$f_0 \sim 100 \text{ kHz}$

$Q \sim 30000$

$A_0 \sim 200 \text{ \AA}$

$\Delta f \sim -(50-100) \text{ Hz}$



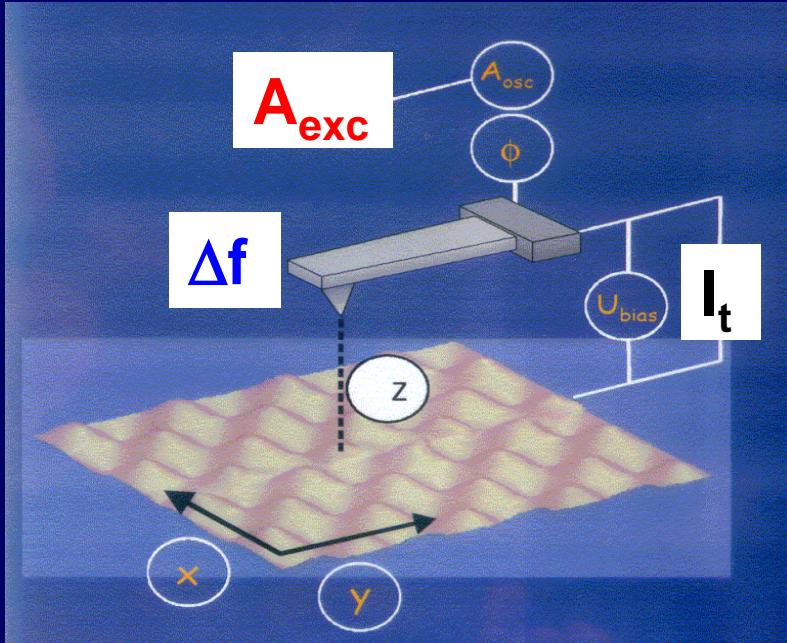
$$kA_0 \sim 600 \text{ nN} \gg F_{ts} \sim 1-10 \text{ nN}$$

(prevents cantilever instabilities)

$$1/2kA_0^2 \sim 3.75 \times 10^4 \text{ eV} \gg \Delta E_{ts}$$

(stable oscillation amplitudes)

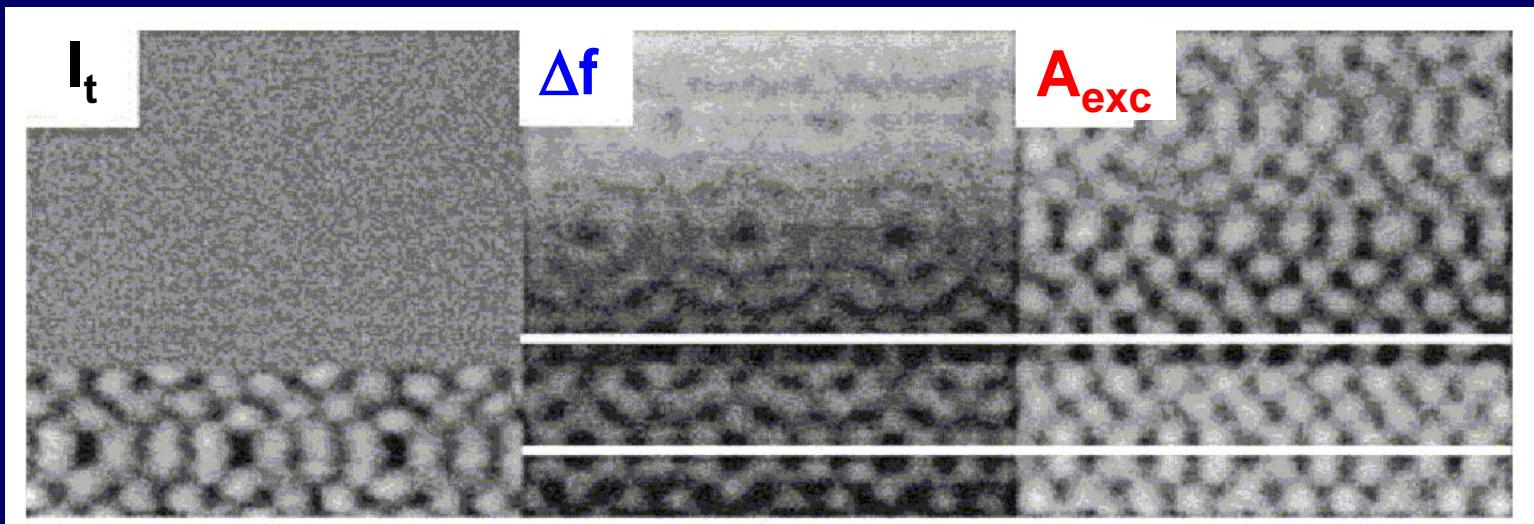
FM-AFM: Contrast sources



Δf : frequency shift

A_{exc} : damping (excitation)

I_t : mean tunneling current



2. Cantilever dynamics : relation between the frequency shift and tip-sample interaction.

Contrast source: frequency shift vs F_{ts}

$$m\ddot{z}(t) + \frac{m\omega_0}{Q} \dot{z}(t) + kz(t) - F_{ts}[z_o + z(t)] = kA_{exc}(t)$$

Electronics cancels damping exactly

$$m\ddot{z}(t) + kz(t) - F_{ts}[z_o + z(t)] = 0$$

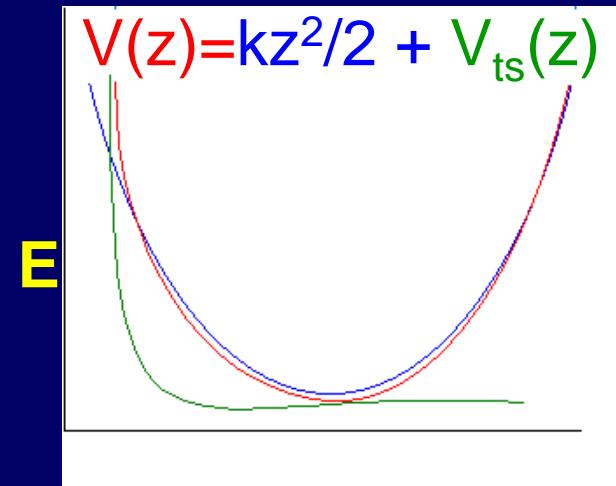
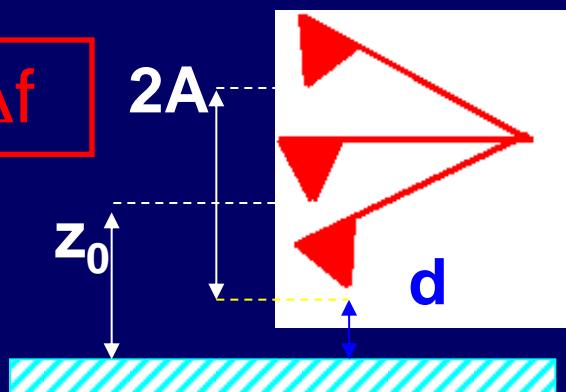
Perturbation theory

F.J. Giessibl, PRB 58, 10835 (1998)

$$\Delta f(d, k, A_0, f_0) = -\frac{f_0}{kA_0^2} \langle F_{ts} z \rangle =$$

$$= -\frac{1}{2\pi} \frac{f_0}{kA_0} \int_0^{2\pi} F_{ts}[d + A_0(1 + \cos\varphi)] \cos\varphi d\varphi$$

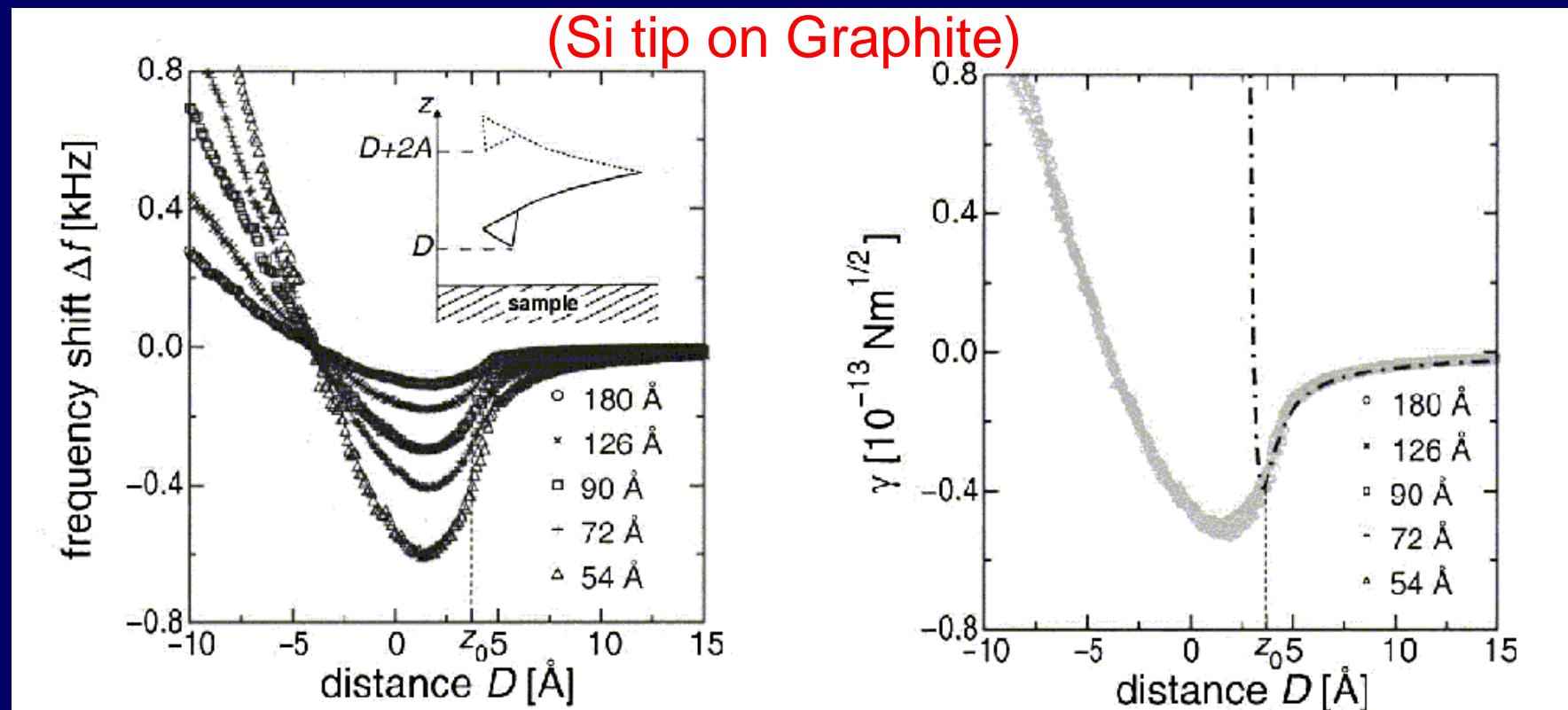
Confirmed by numerical simulations including the control electronics



Normalized frequency shift γ

$$\gamma(d) = \frac{kA_0^{3/2}}{f_0} \Delta f(d, k, A_0, f_0)$$

γ extracts the intrinsic contribution coming from F_{ts}



$$\gamma(d) \approx \frac{1}{\sqrt{2\pi}} F_{ts}(d) \sqrt{\frac{V_{ts}(d)}{F_{ts}(d)}}$$

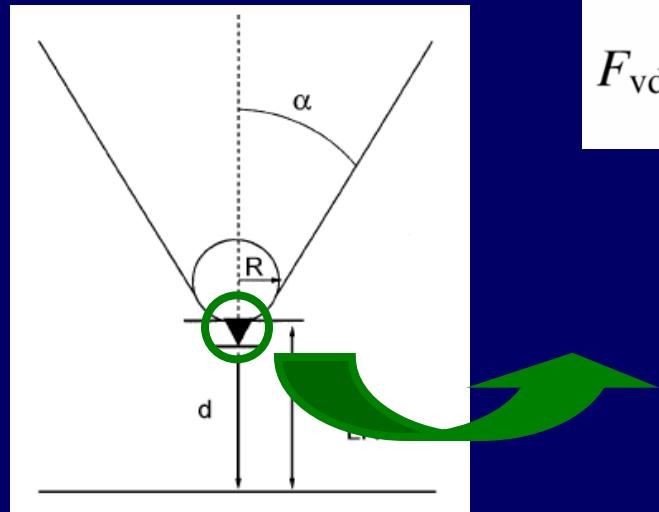
Not accurate for small tip-sample distances (2-3 Å) !!

3. Atomic-scale contrast and tip-sample interaction: tip as the key player

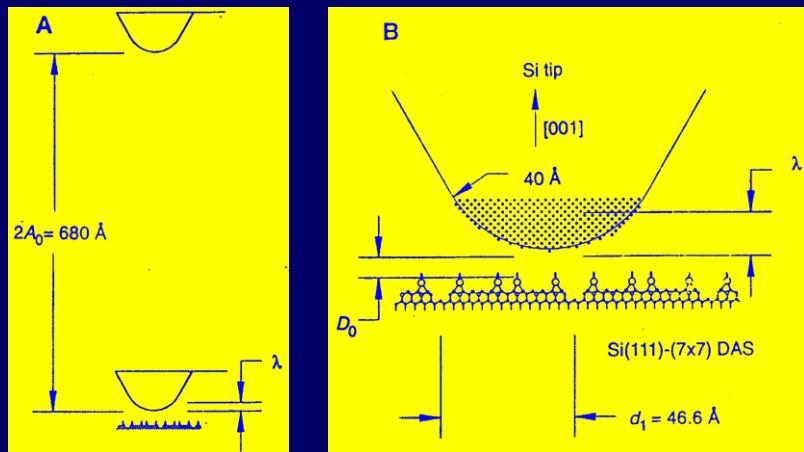
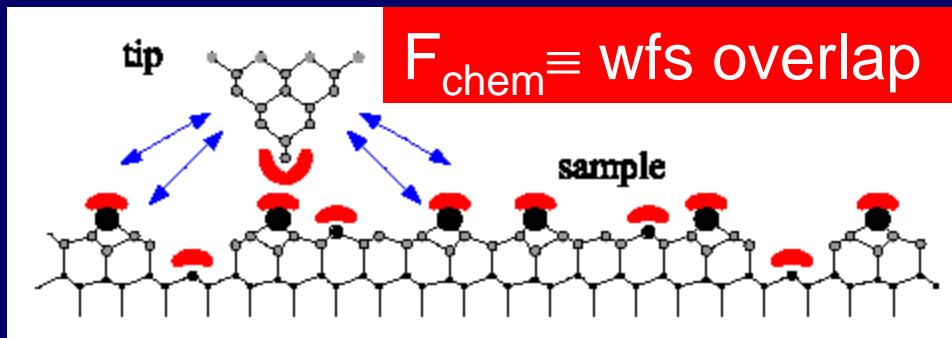
- Separation of LR and SR interactions
- Semiconductors
- Alkali halides & oxides
- Metals, weakly bonded systems & carbon-based materials (graphite, nanotubes, ...)

Tip-sample Interaction: $F_V + F_{vdW} + F_{chem}$

$$F_V = -\pi\epsilon_0(V_s - V_c)^2 \left\{ \frac{R}{d_{LR}} + s(\alpha) \left[\ln\left(\frac{L}{d_{LR} + R_\alpha}\right) - 1 \right] - \frac{R[1 - s(\alpha) \cos^2\alpha/\sin\alpha]}{d_{LR} + R_\alpha} \right\}$$



$$F_{vdW} = -\frac{H}{6} \left\{ \frac{R}{d_{LR}^2} + \frac{\tan^2\alpha}{d_{LR} + R_\alpha} - \frac{R_\alpha}{d_{LR}(d_{LR} + R_\alpha)} \right\}$$



Exp: $A = 340 \text{ \AA} !!!$, $R = 40 \text{ \AA}$

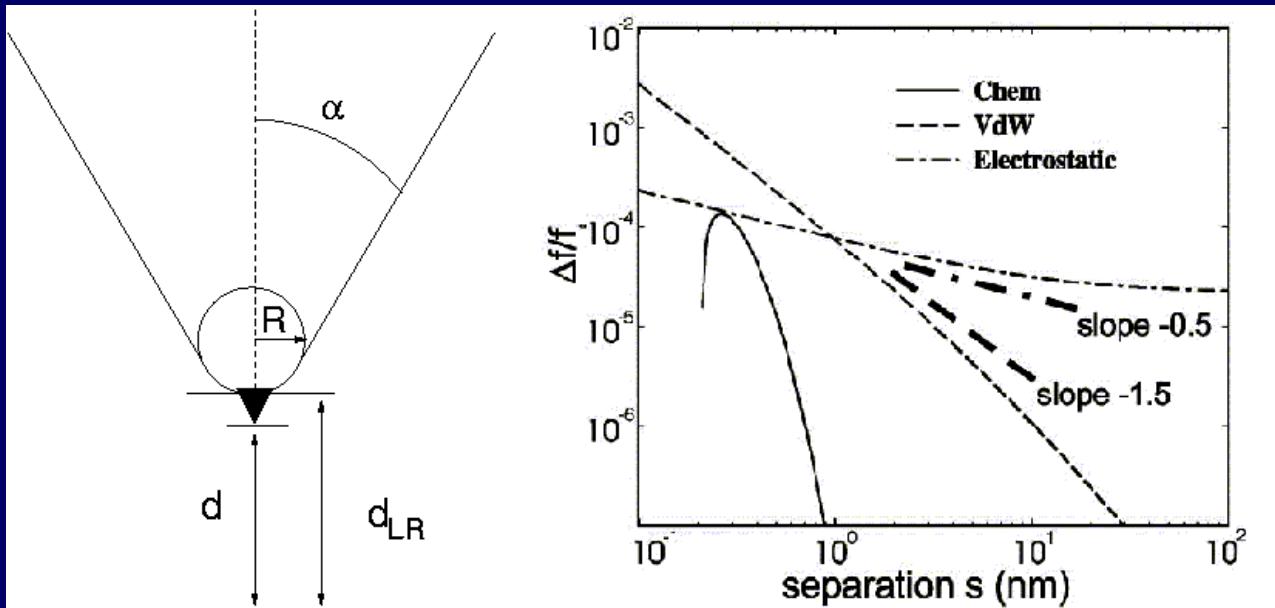
Sensitivity to Short-Range Forces?

$$\Delta f(d) = \frac{f_0}{\pi k a_1} \int_{-1}^1 F_{ts}[d + a_1(1 + u)] u \frac{du}{\sqrt{1 - u^2}}$$

$$u = \cos(\omega t)$$

Weak singularity at turning points !!!

Characterizing the “macroscopic” tip: Separation of interactions

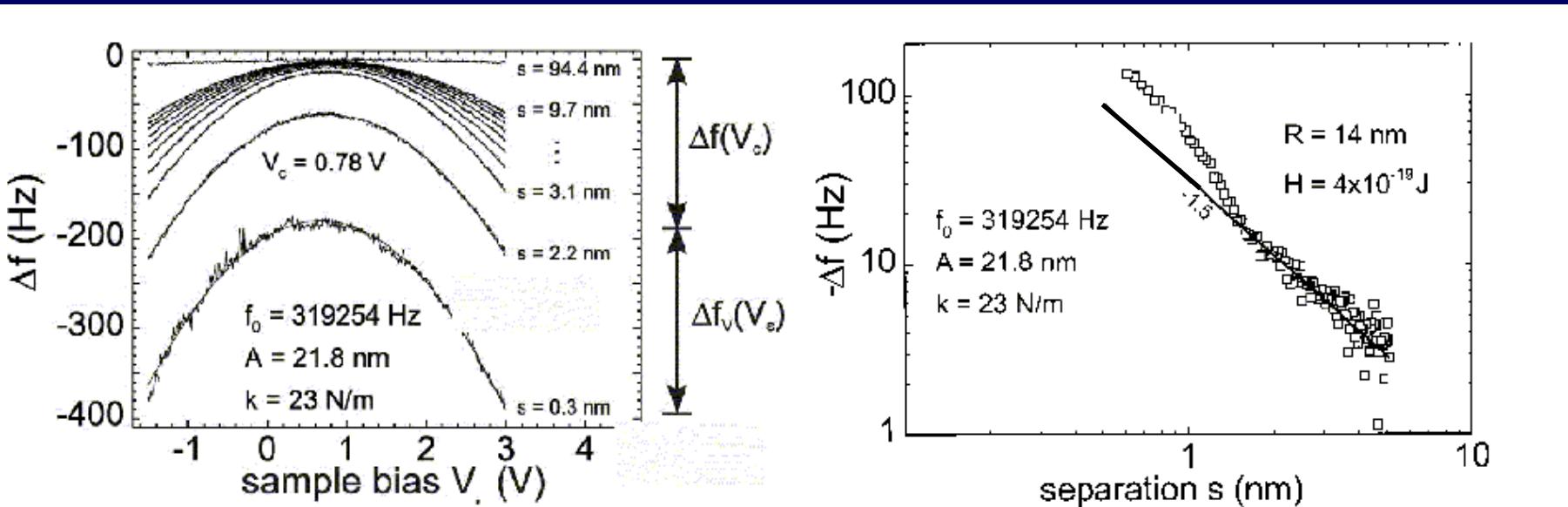


Si tip on
Cu(111)

M. Guggisberg et al,
PRB 61 (2000) 11151

Electrostatic

VdW



Computational approaches for SR F_{ts}

Empirical potentials

OK for ionic bonding

Weakly bonded systems??

Interatomic potentials +
some quantum mechanics

about 1,000 atoms

dynamics

reliable if carefully calibrated

10 x

Simplified and semi-empirical
quantum mechanics

about 1,000 atoms

simulated annealing, short dynamics

many features of first-principles, but faster

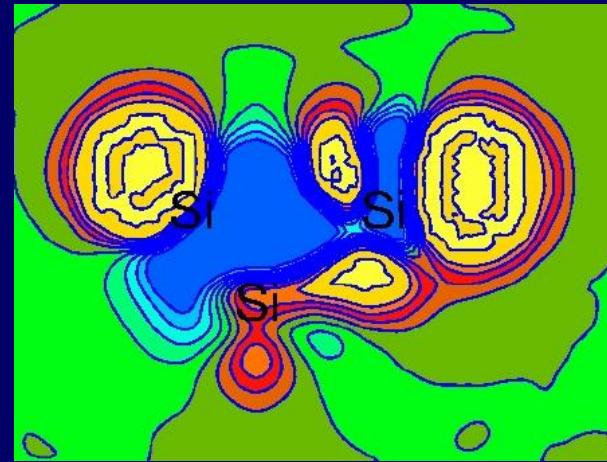
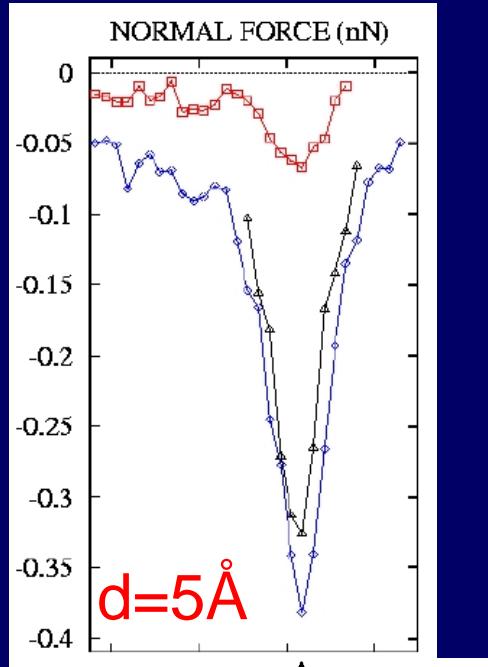
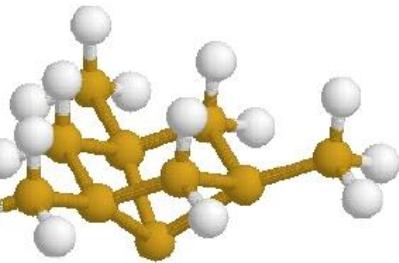
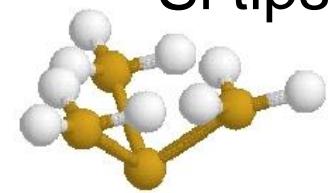
100 x

Ab initio
quantum mechanics

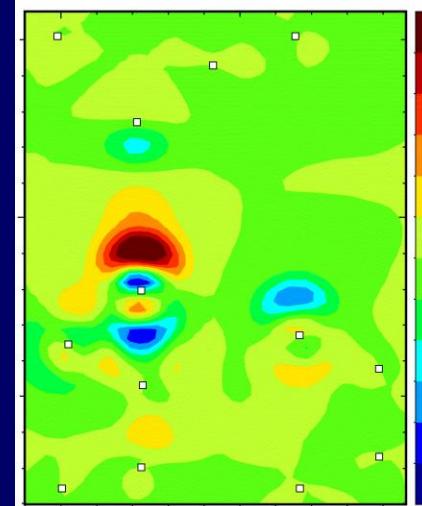
Necessary for covalent and
metallic bonding (semiconductors
and metals.)

Role of SR Covalent Bonding Interactions?

DFT-GGA plane wave pseudopotential calculations



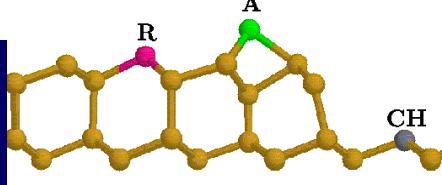
Charge density difference between tips



$$\rho_{\text{tip+surface}} - (\rho_{\text{tip}} + \rho_{\text{surface}})$$

Charge accumulates in the adatom dangling bond

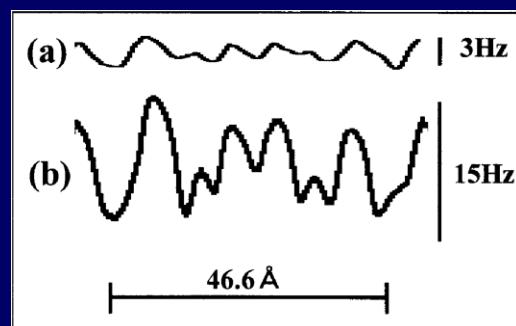
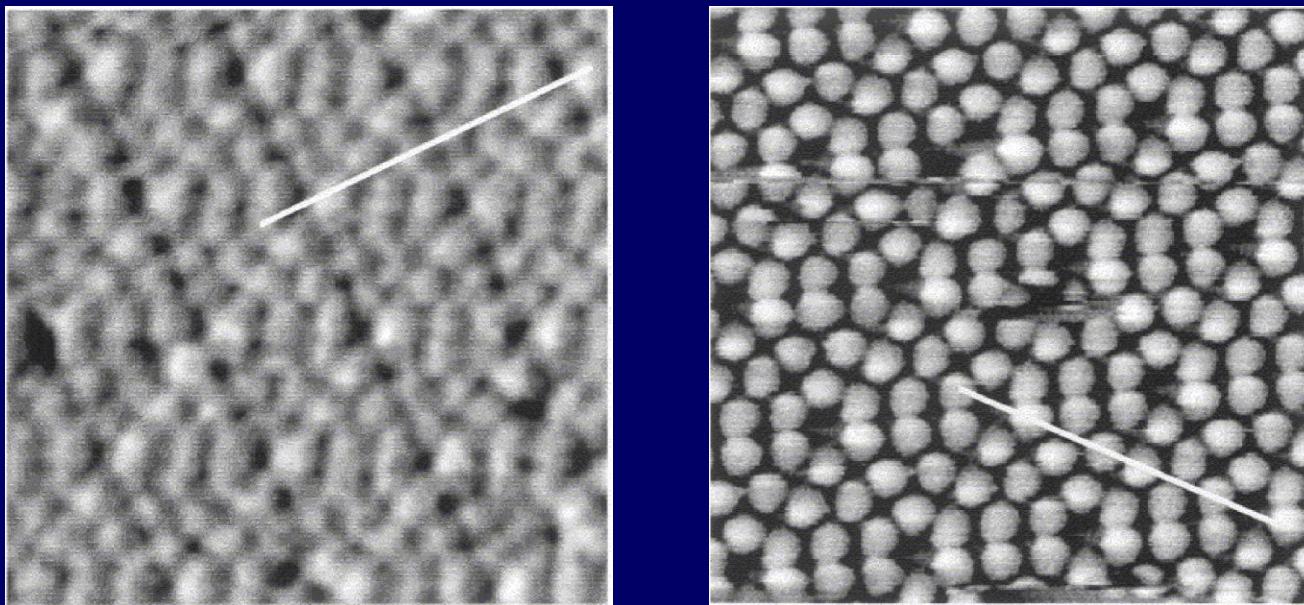
R. P. et al, PRL 78, 678 (1997)



R. P. et al, PRB 58, 10 835 (1998)

Atomic scale contrast in reactive semiconductor surfaces:
chemical tip-surface interaction (between dangling bonds)

Contrast dependence on tip preparation

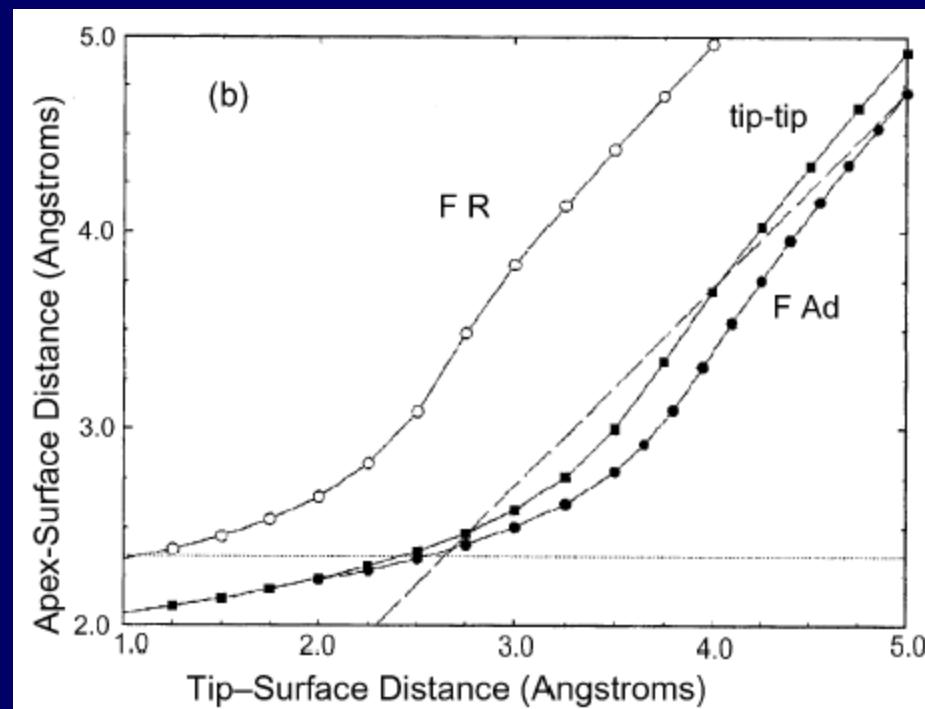
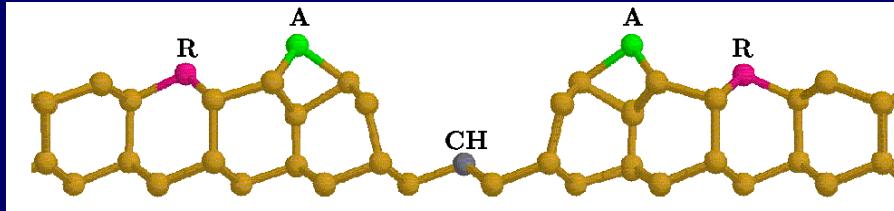
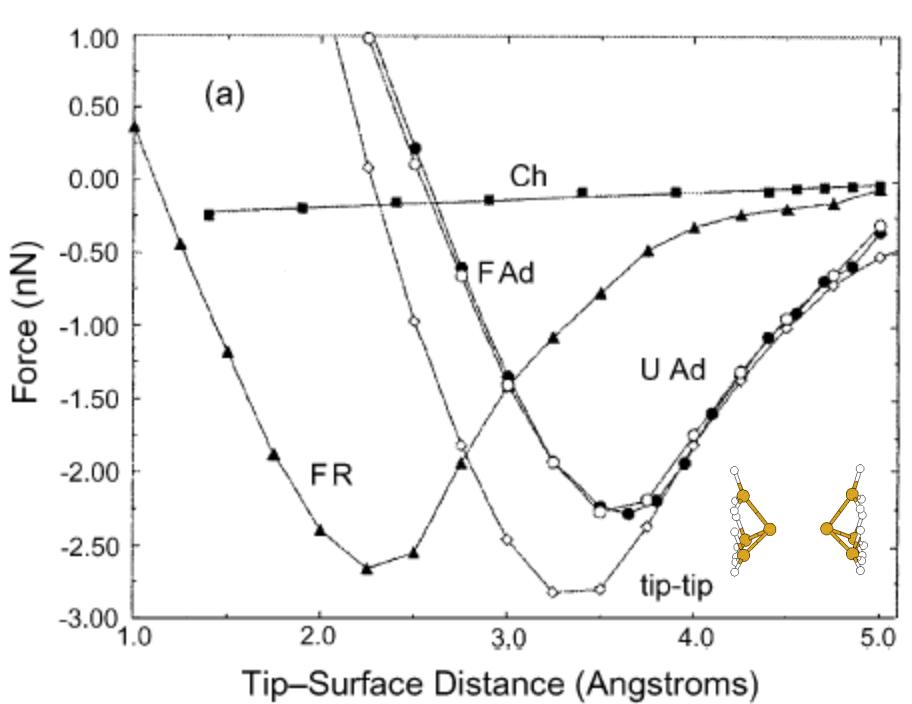


T. Uchihashi et al, PRB 56, 9834 (1997)

Force-distance curves & Atomic relaxations

R. P. et al, PRB 58, 10835 (1998)

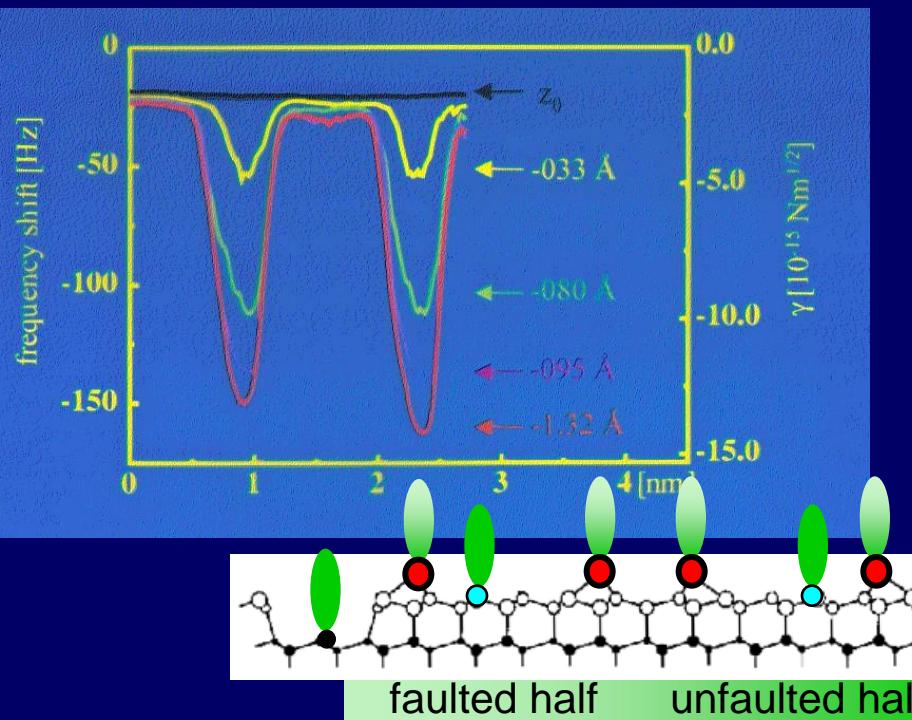
atomic relaxations due to
tip-surface interactions!!



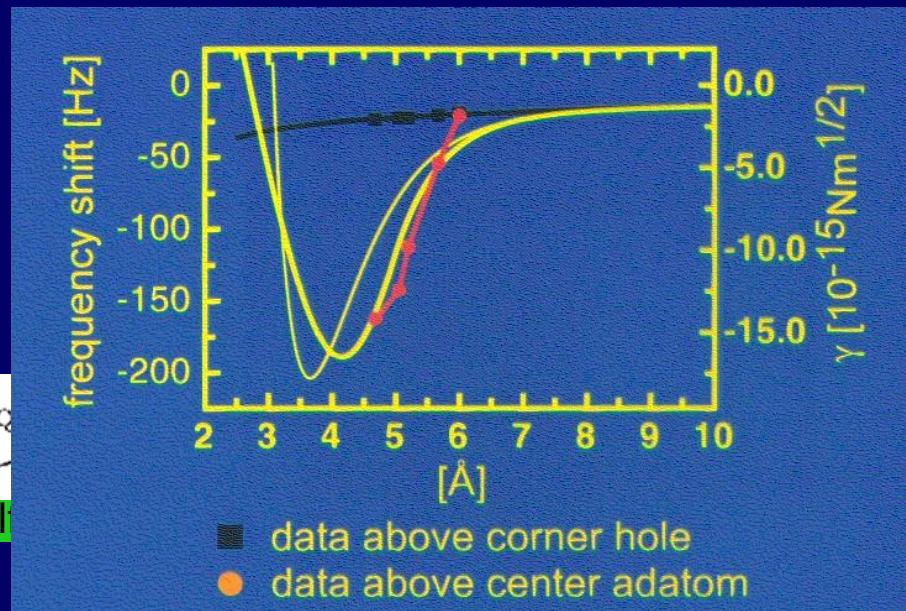
Force vs distance curves → prediction for Δf vs distance

$$\Delta f(d) = -\frac{1}{2\pi} \frac{f_0}{kA_0} \int_0^{2\pi} F_{ts} [d + A_o(1 + \cos\varphi)] \cos\varphi d\varphi$$

Comparison between theory and low-temperature FM-AFM experiments



M. Lantz et al, PRL 84, 2642 (2000)
M. Lantz et al, Science 291, 2580 (2001)



Separation of VdW and chemical interaction: subtracting the corner hole contribution.

Tip-surface interactions

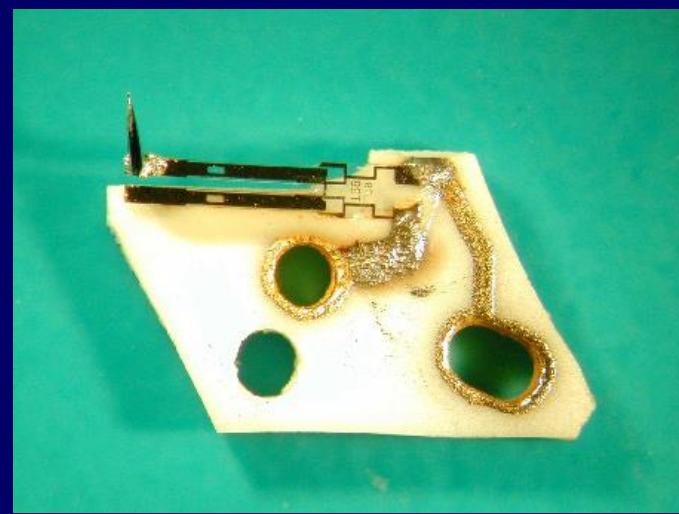
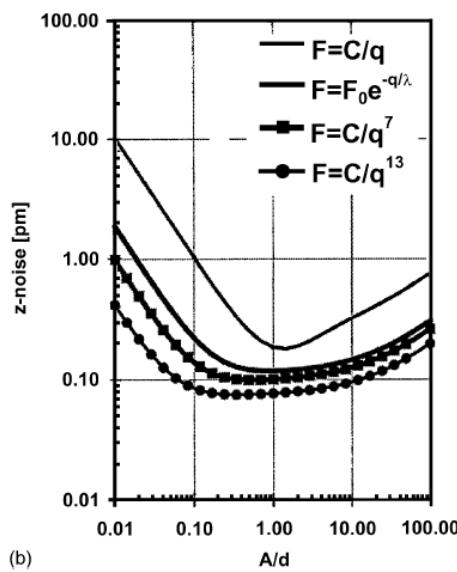
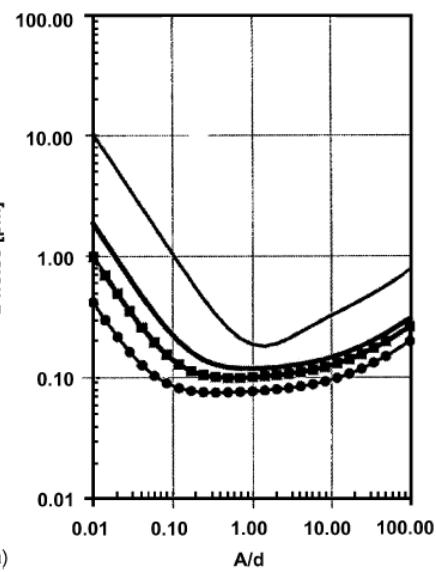
R. Pérez et al , PRL 78, 678 (1997)
R. Pérez et al , PRB 58, 10835 (1998)

4. Recent developments...

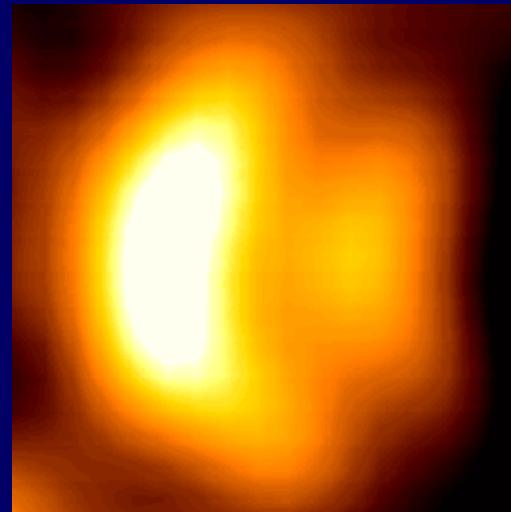
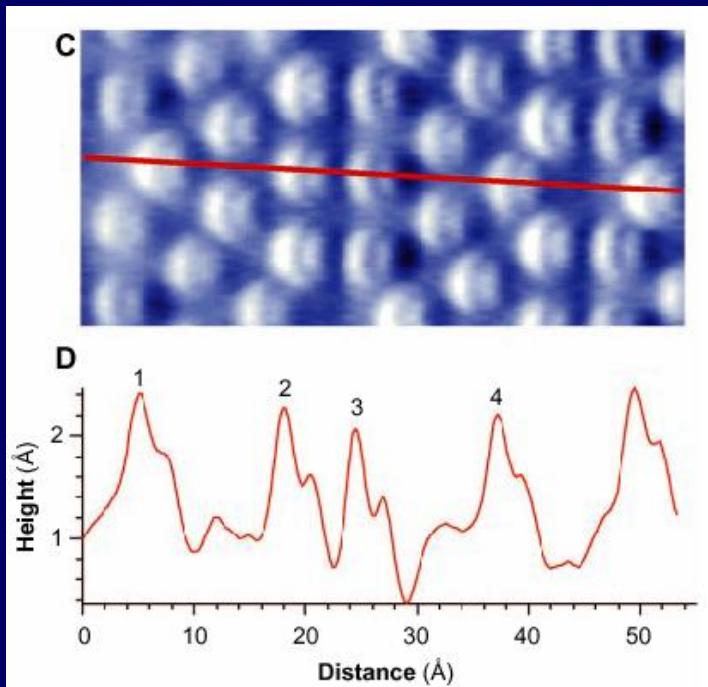
- Tuning forks: small amplitudes to enhance atomic contrast.
- Force spectroscopy: Chemical identification
- Single-atom manipulation at RT
- AFM detection of spin
- True atomic resolution in liquids

Other operating conditions: qPlus sensor

Smallest Noise for Å-size amplitudes!!!



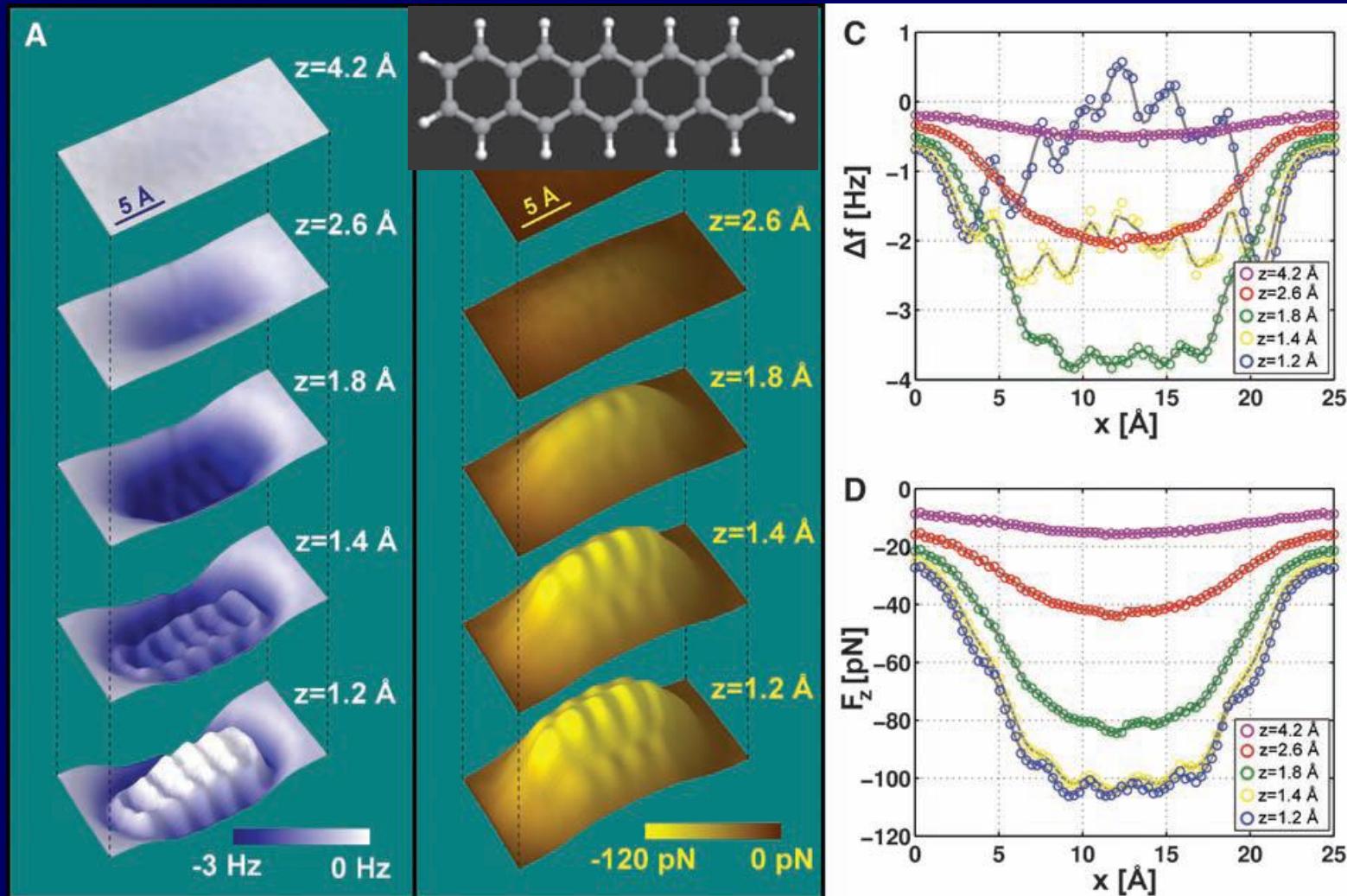
qPlus sensor made from a tuning fork ($k \sim 2000$ N/m)



Operating under repulsive SR forces (stabilize by LR electrostatics) !!!

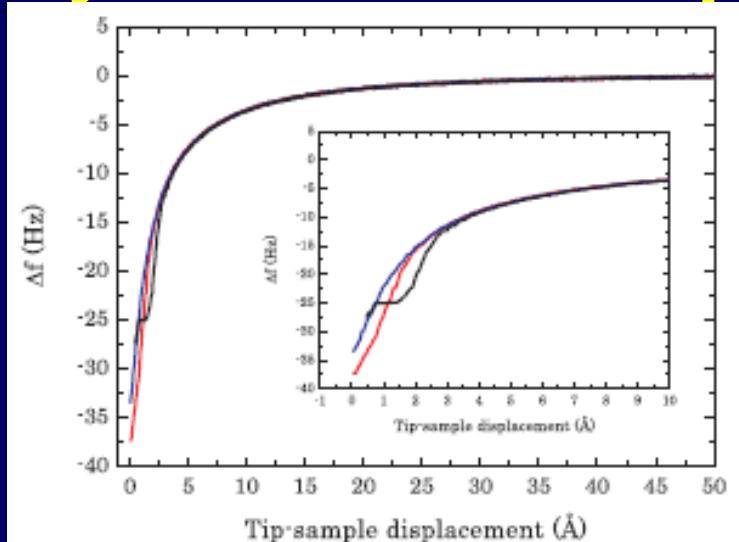
F.J. Giessibl et al,
Science 289 (2000) 422

The Chemical Structure of a Molecule Resolved by Atomic Force Microscopy

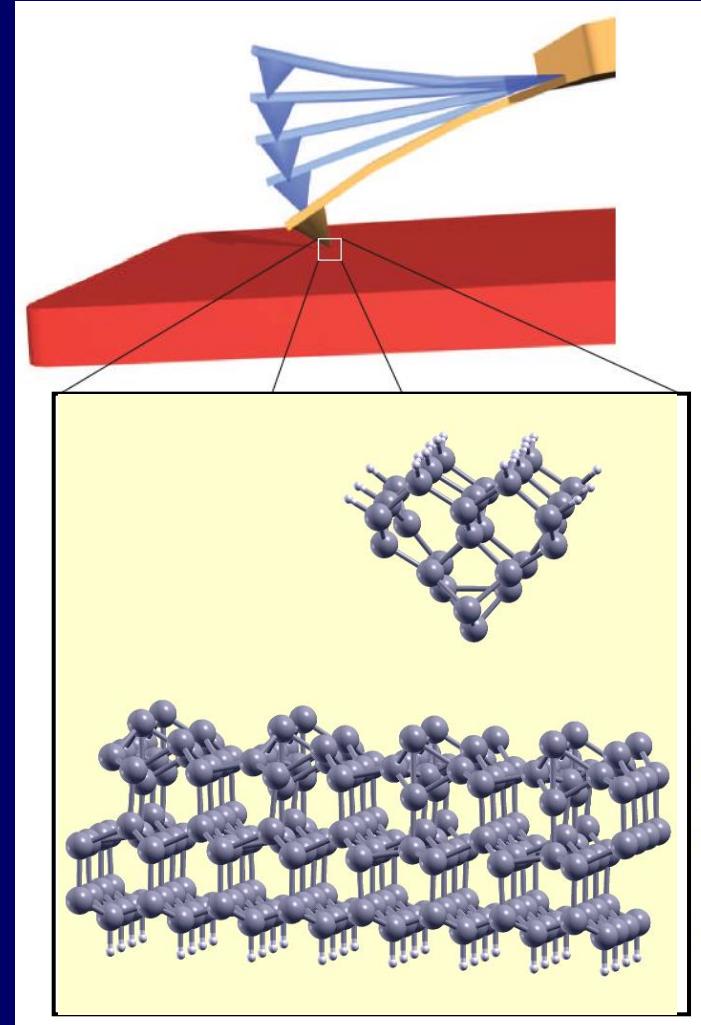
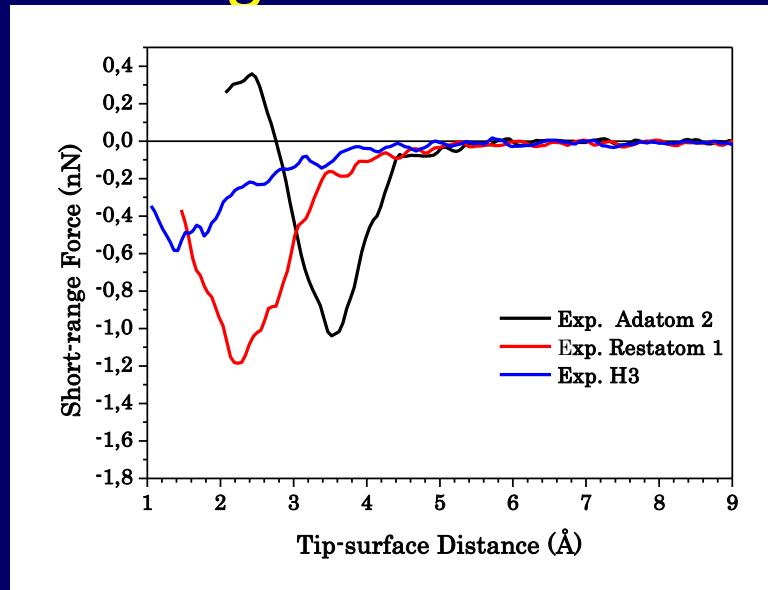


L. Gross et al, Science 325, 1110 (2009)

Dynamic Force Spectroscopy: Access to F_{ts}



↑ Inversion
algorithms ↓

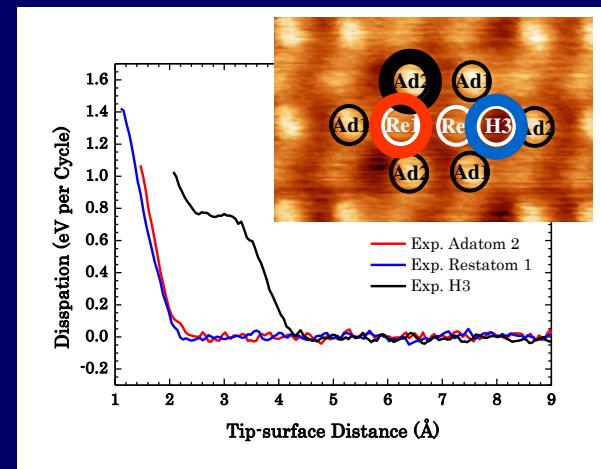


SR forces amenable to
ab initio calculations

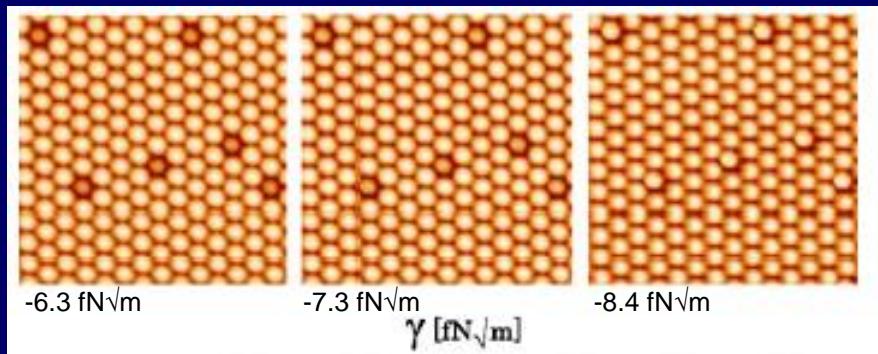
Developments based in Force Spectroscopy

1. DISSIPATION: Characterizing the tip structure and identifying a dissipation channel due to single atomic contact adhesion.

N. Oyabu et al. Phys. Rev. Lett. 96, 106101 (2006).



2. IMAGING: changes in topography: access to the real surface structure?

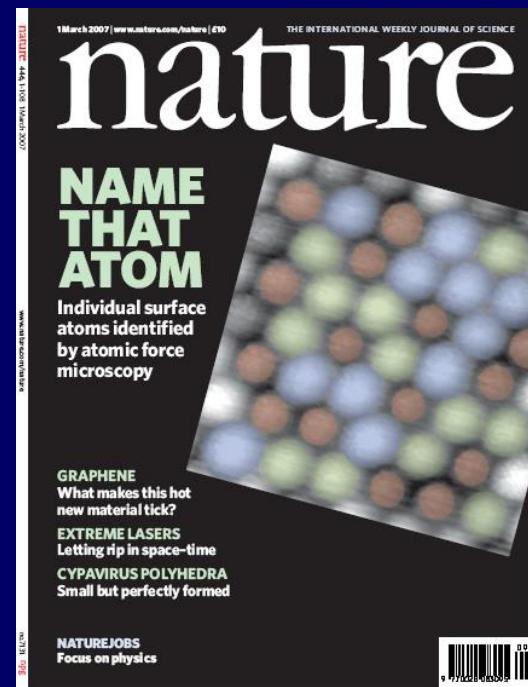


3. CHEMICAL IDENTIFICATION:

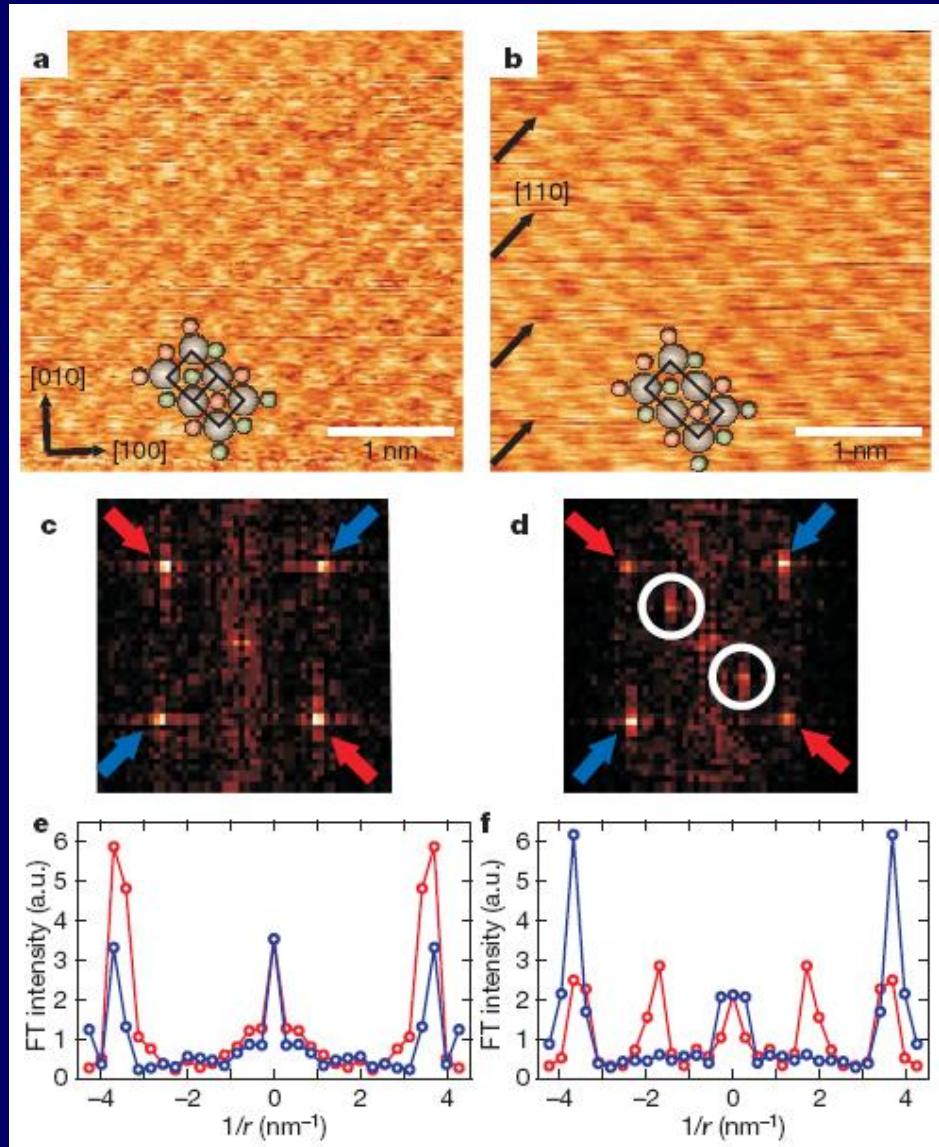
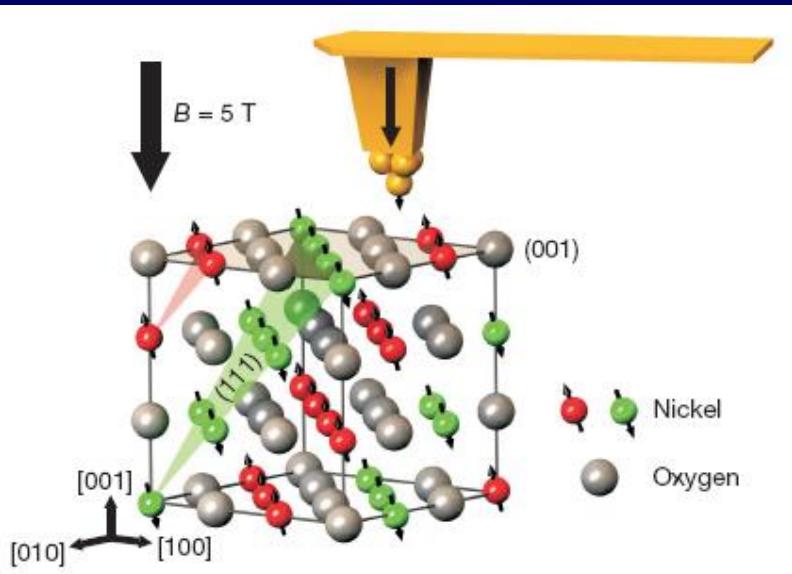
based on the relative interaction ratio of the maximum attractive force measured by dynamic force spectroscopy

Y. Sugimoto et al. Nature 446, 64 (2007).

Y. Sugimoto et al
Phys. Rev. B 73, 205329 (2006).



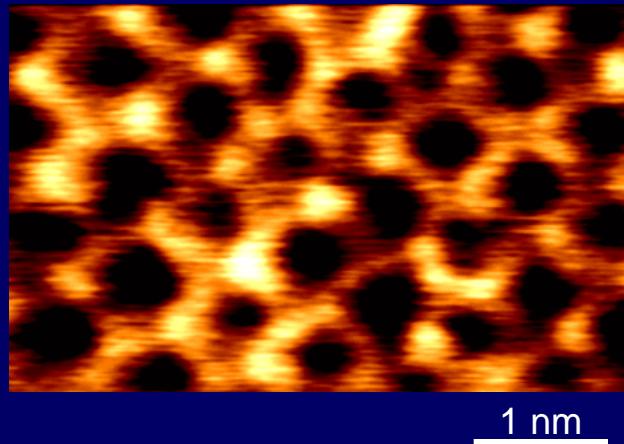
Magnetic exchange force microscopy with atomic resolution



High-Resolution FM-AFM Imaging in Liquid

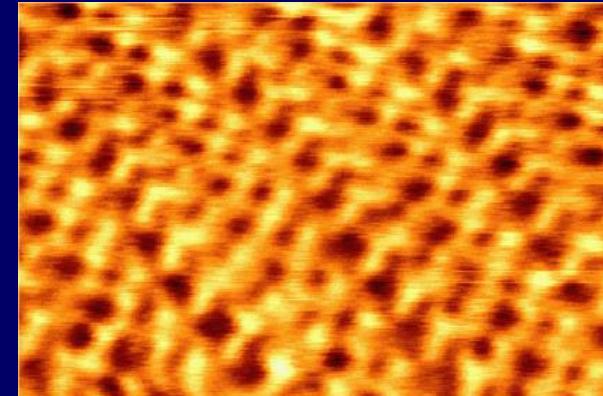
True Atomic Resolution (2005)

FM-AFM Image of Mica in Water

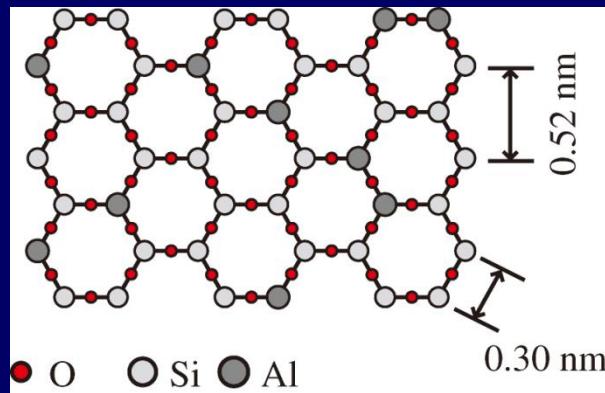


True Molecular Resolution (2005)

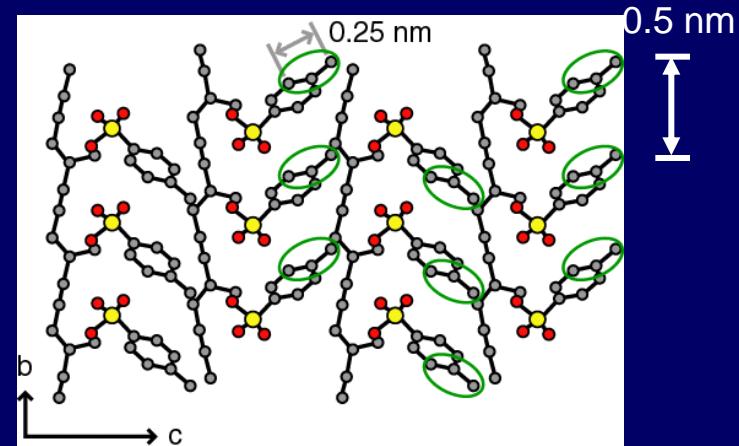
Polydiacetylene Single Crystal in Water



Cleaved Mica Surface



bc-plane of Polydiacetylene Crystal



Fukuma et al. APL 87 (2005) 034101

Fukuma et al. APL 86 (2005) 193108

FM-AFM: Things to remember...

- Frequency shift as the contrast source.
- True atomic resolution. (UHV & Liquids !!!)
- self-driven oscillator: More complicated operation and electronics, but simpler behaviour (amplitude feedback “linearizes” the behaviour).
- Short-range (chemical, electrostatic) interactions are responsible for the atomic resolution.
- Separation of interactions + inversion formulae \Rightarrow spectroscopic capabilities (in combination with theory).
- Different channels (frequency shift, tunneling currents, energy dissipation) recorded simultaneously