

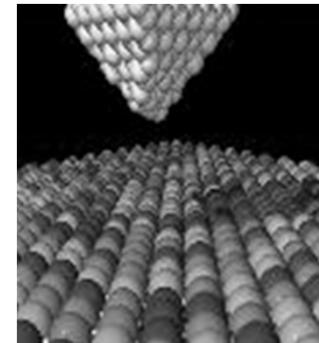
# **Dynamic Atomic Force Microscopy: Basic Concepts**

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<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).

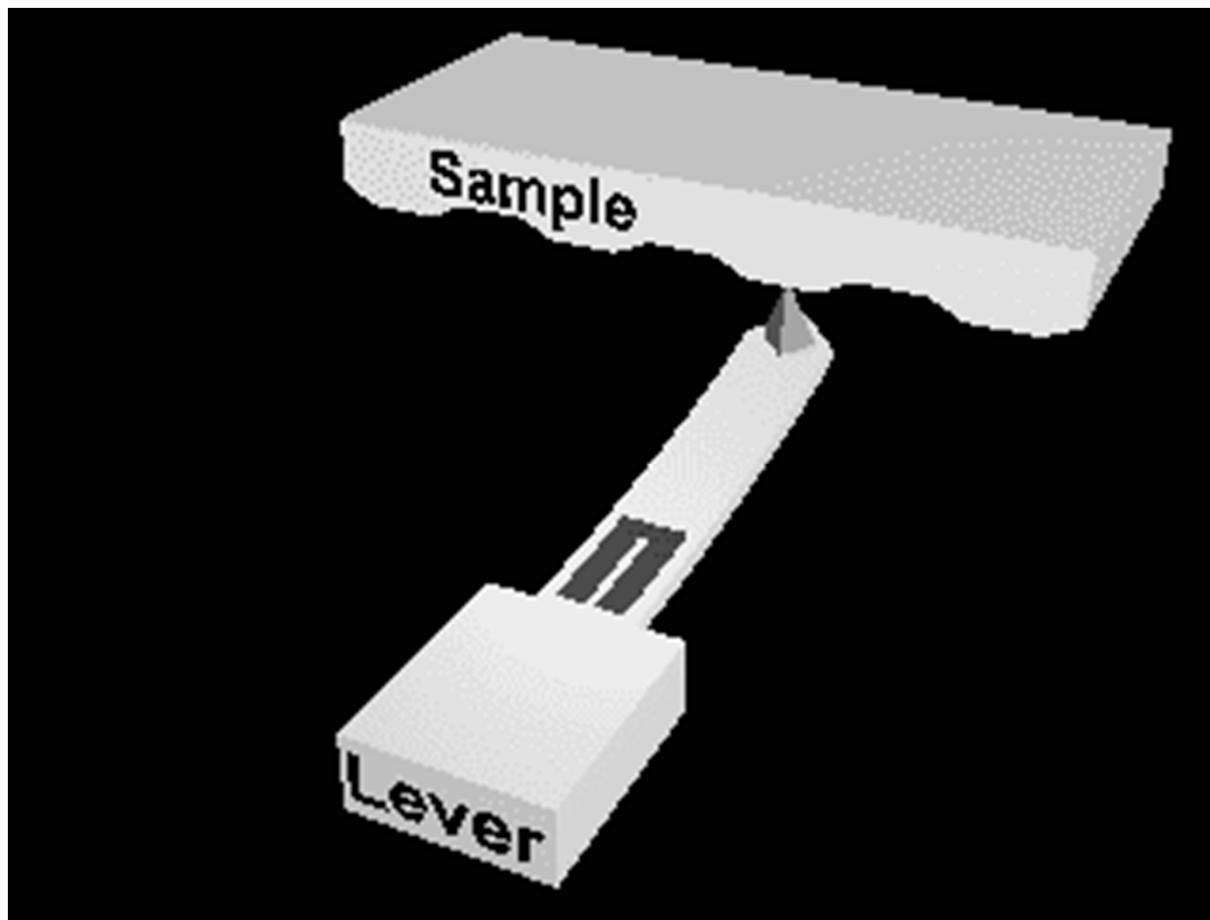
# **Outline**

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

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

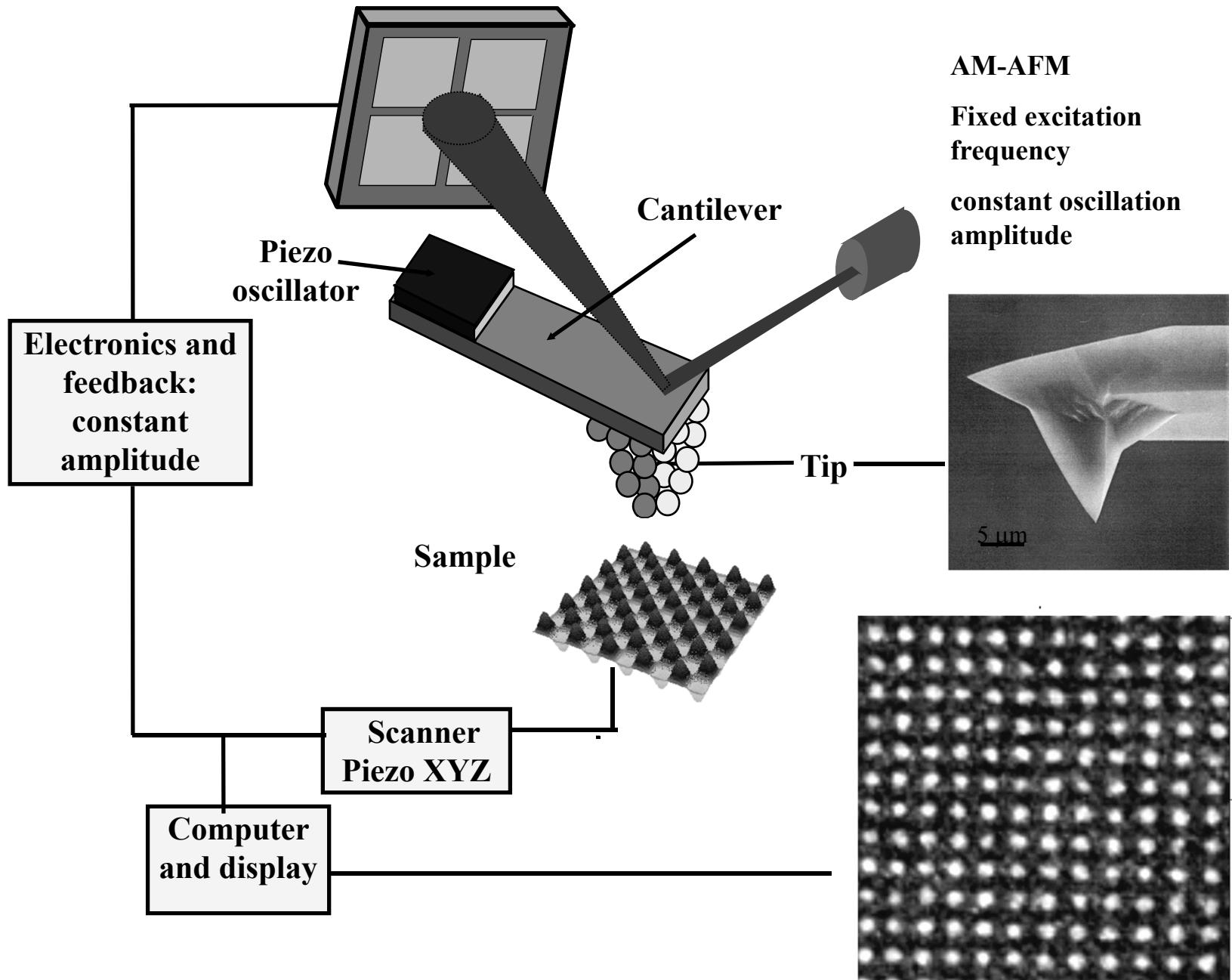
# ATOMIC FORCE MICROSCOPY (AFM)

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

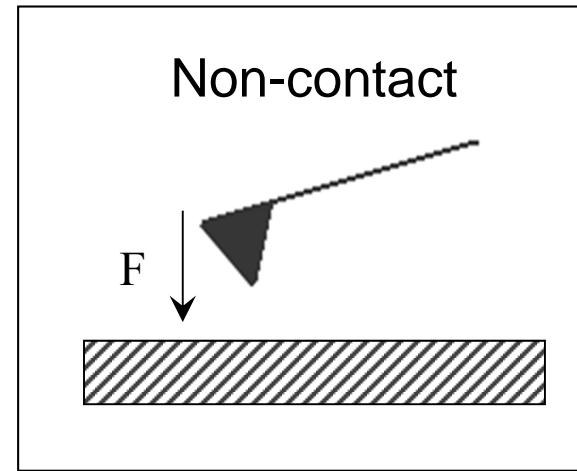
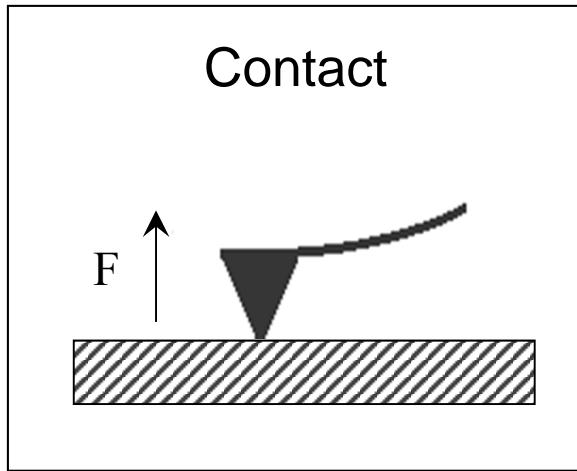


2nd most cited PRL: +5000 citations !!!

[http://monet.physik.unibas.ch/famars/afm\\_prin.htm](http://monet.physik.unibas.ch/famars/afm_prin.htm)



# Limitations of static AFM



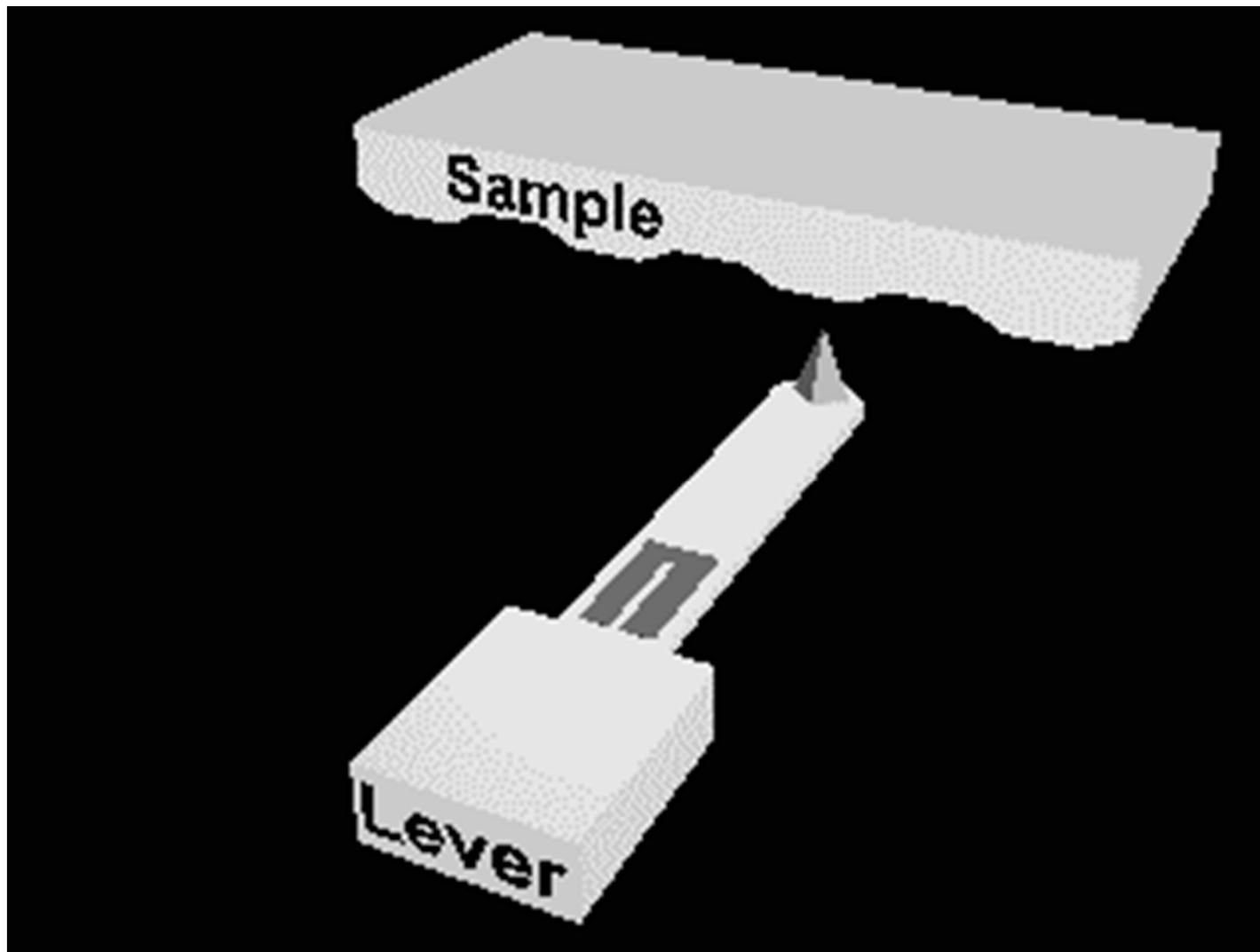
- Deformation, Friction
- No point defects observed

Atomic Resolution?

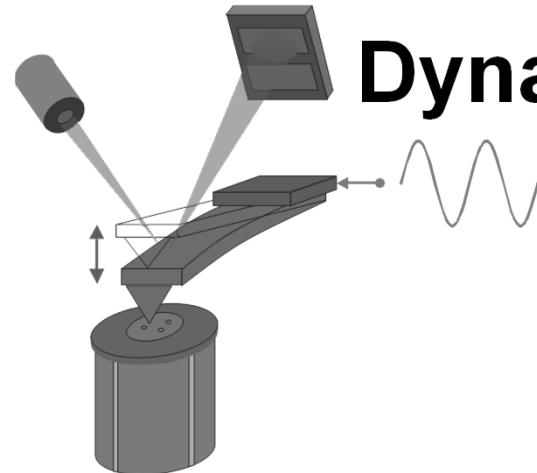
- Detection of small forces: soft cantilevers.
- “Jump to contact” : stiff cantilevers

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

# Dynamic AFM

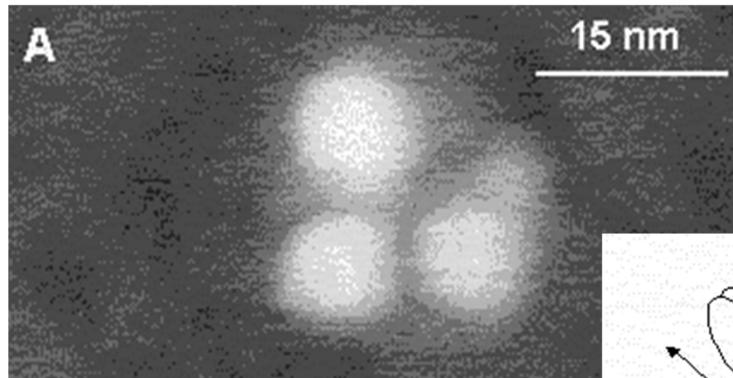


[http://monet.physik.unibas.ch/famars/afm\\_prin.htm](http://monet.physik.unibas.ch/famars/afm_prin.htm)

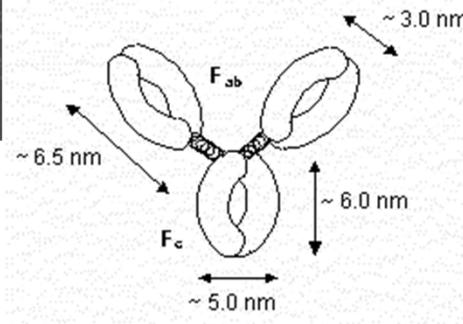


# Dynamic AFM: Our Goal

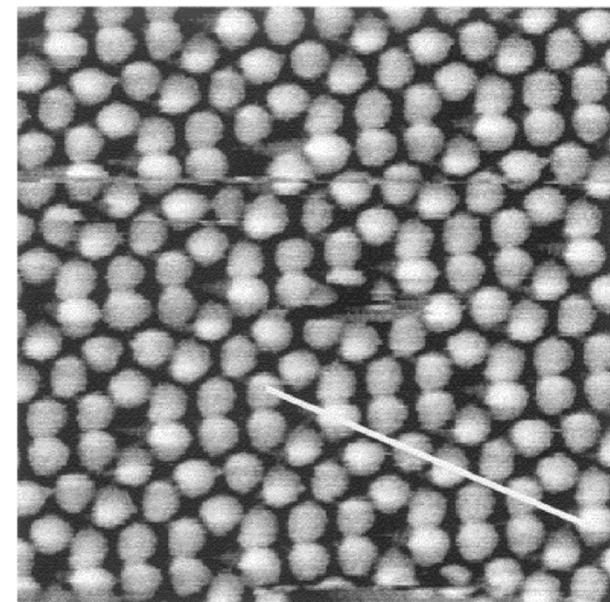
Why changes observed in the dynamic properties of a vibrating cantilever with a tip that interacts with a surface make possible to:



AM-dAFM



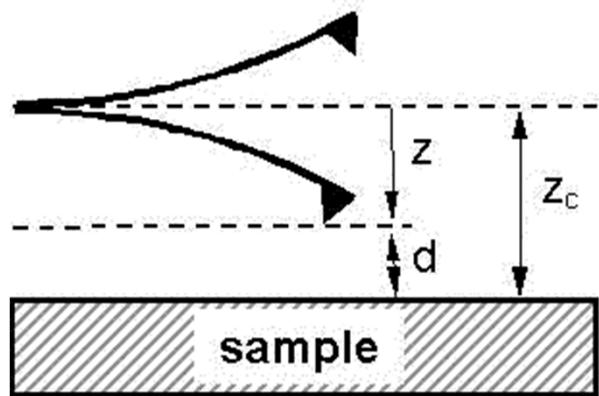
- Obtain molecular resolution images of biological samples in ambient conditions.



- Resolve atomic-scale defects in UHV.

FM-dAFM

# Dynamic description



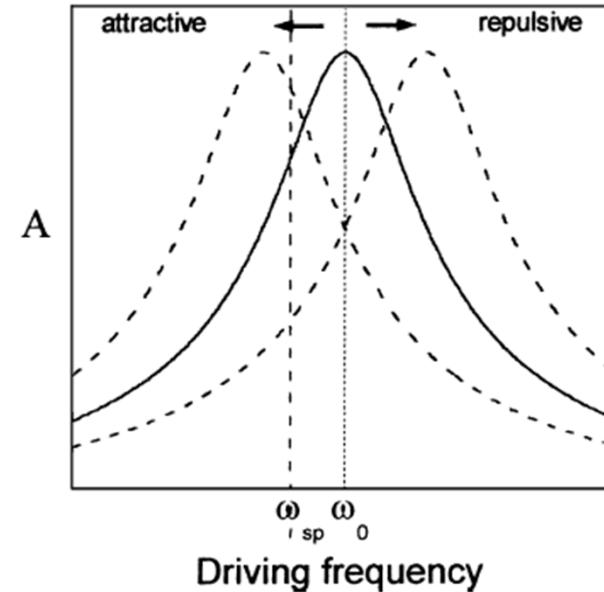
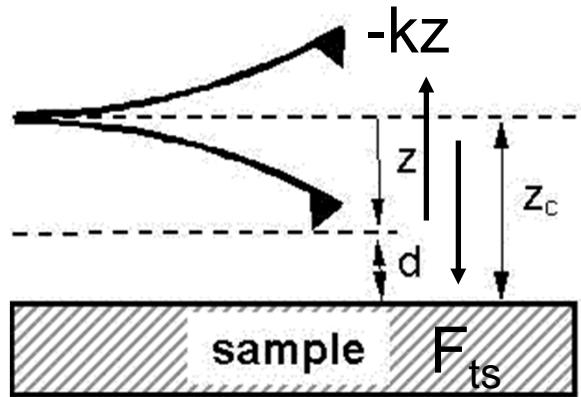
Cantilever-tip ensemble as a point mass spring described by a non-linear 2nd order differential equation

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

Amplitude  
Resonance Frequency  
Phase shift

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

# Why do A and $\Delta\omega$ ( $\Delta\omega$ ) 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  $\omega_{exc}$

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  $A_{\text{exc}}$  and frequency  $\omega_{\text{exc}}$  close or at its FREE resonance frequency  $\omega_0$ .
- Oscillation amplitude  $A$  as feedback for topography.
- Phase shift  $\phi$  between excitation and oscillation: compositional contrast.
- Air and liquid environments.

## Frequency Modulation AFM

- Constant oscillation amplitude at the current resonance frequency (depends on  $F_{\text{ts}}$ ).
- Frequency shift  $\Delta f$  as feedback for topography.
- Excitation amplitude  $A_{\text{exc}}$  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)**

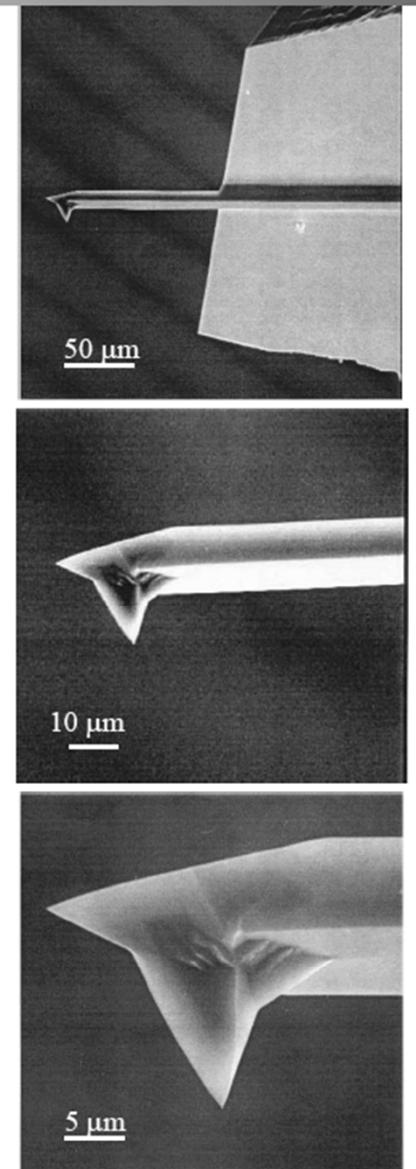
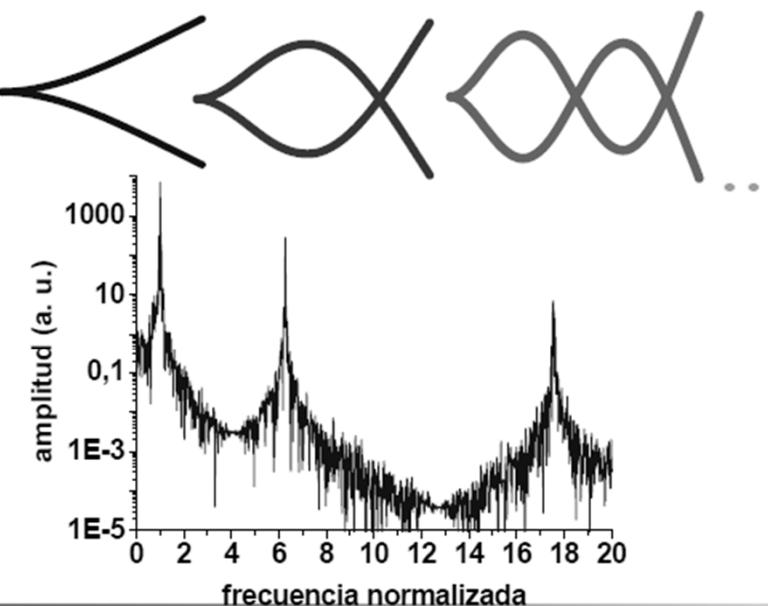
- Operation Parameters.
- Non-linear dynamics: Existence of two oscillation states (L & H): implications for imaging.
- Understanding amplitude reduction.
- Imaging materials properties: phase shifts and dissipation.
- Summary: things to remember...

## Microcantilevers

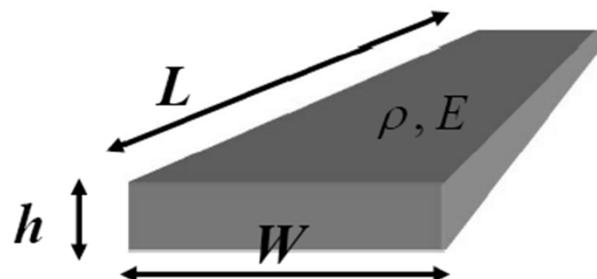
Mechanical device to detect and amplify tip-surface interactions, Si or  $\text{Si}_3\text{N}_4$

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

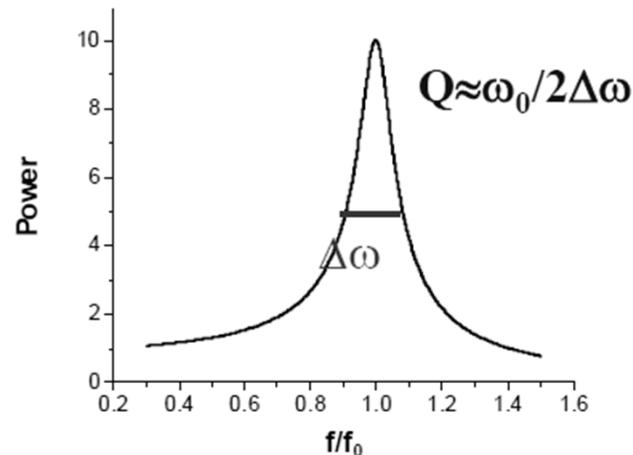
There are several resonances (eigenmodes) in a cantilever



## Microcantilevers



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

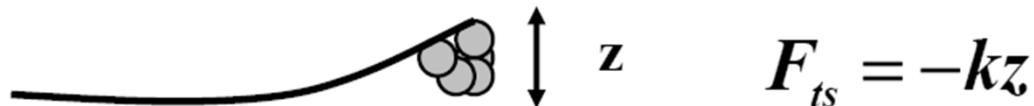


$$k = \frac{3EI}{L^3} = \frac{EWh^3}{4L^3}$$

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

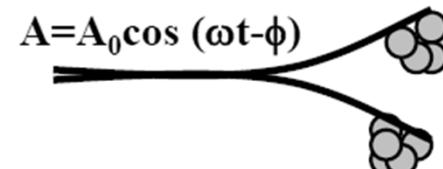
## Forces: Equation of motion

Contact AFM



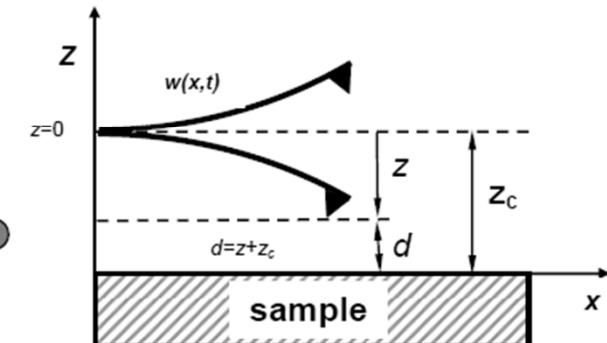
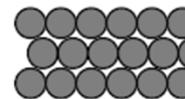
$$F_{ts} = -kz$$

dynamic AFM (amplitude modulation)



Point-mass model of the microcantilever

Respuesta elástica

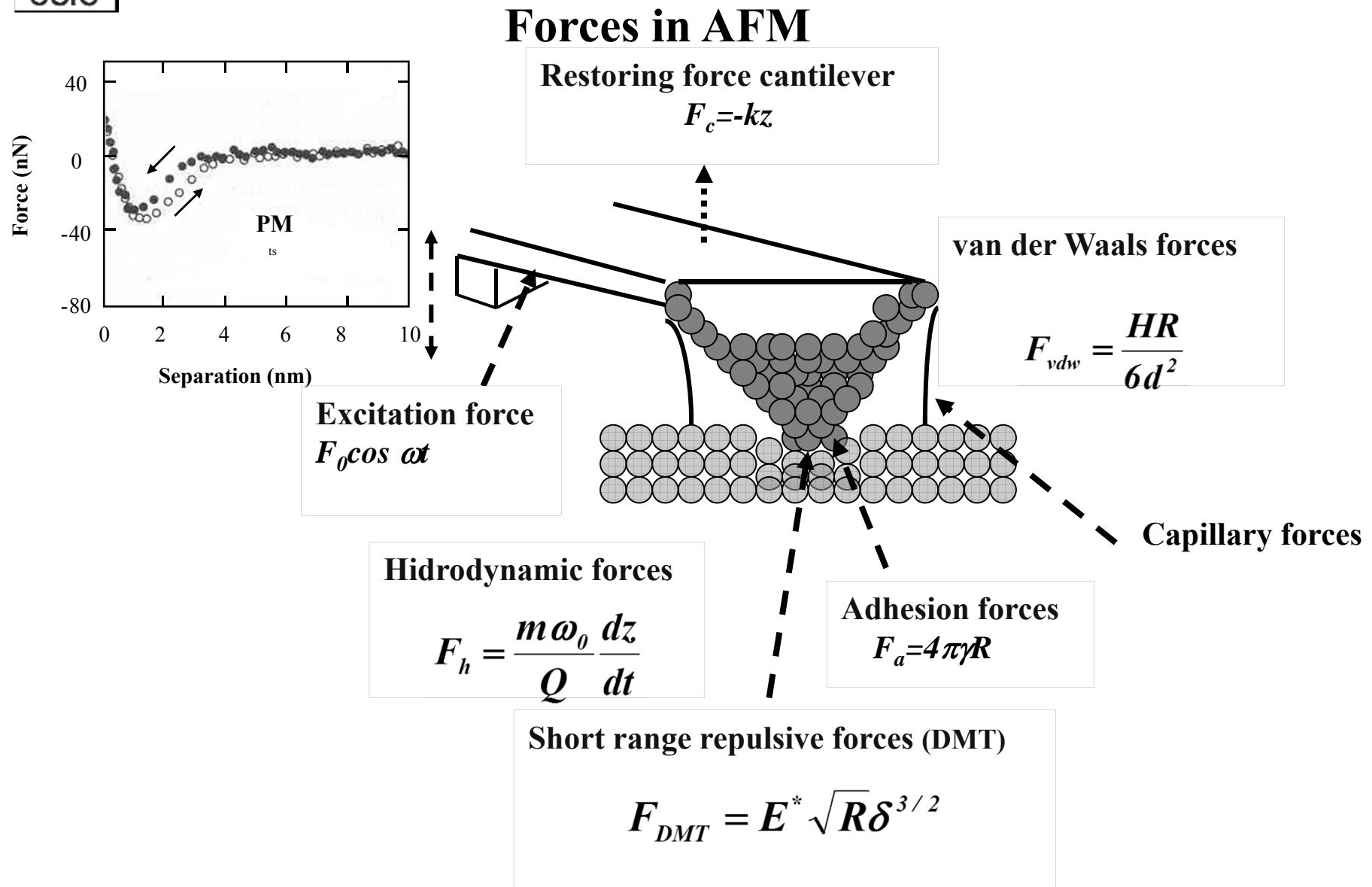


Interacciones

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

Amortiguamiento del medio

Fuerza externa



# Forced damped harmonic oscillator

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

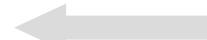
$$\omega_0 = \sqrt{\frac{k}{m}}$$

$Q \equiv$  Quality factor (cantilever damping)

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

(transient)

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



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

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

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

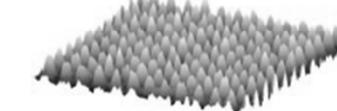
BUT  $F_{ts}$  is nonlinear  
 $\Rightarrow$  anharmonic effects

## Resonance Curves

Free oscillating tip (10 nm )



Interacting tip (10 nm size )



Mechanics of vibrating  
nanosystems:

Coexistence of oscillation  
states: Bi-stability

$\omega/\omega_0$

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

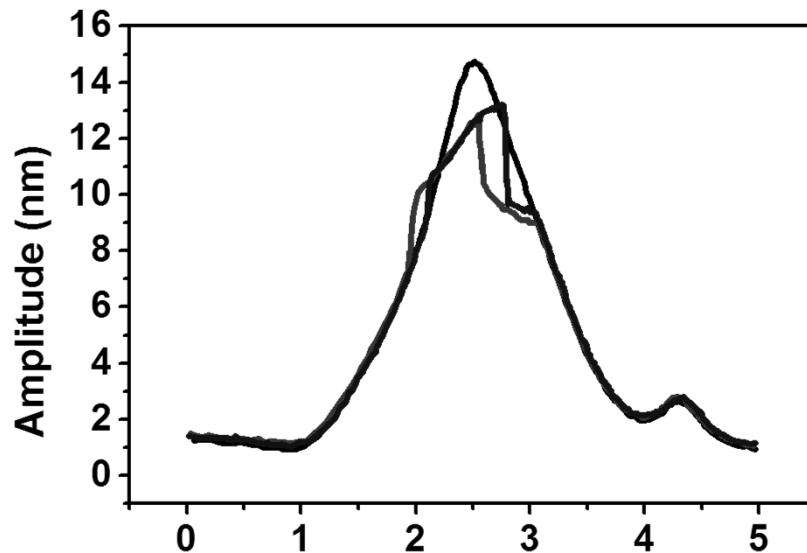
AS Paulo, R García, PRB 66, 041406(R) (2002)

## EXPERIMENT

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

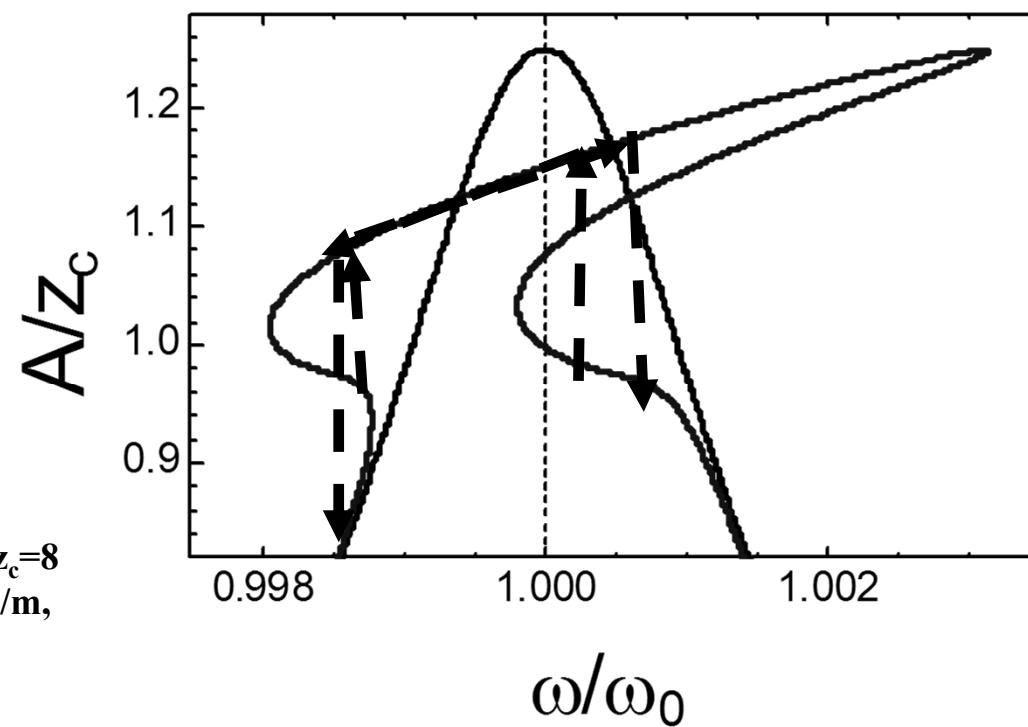
Low to high

high to low



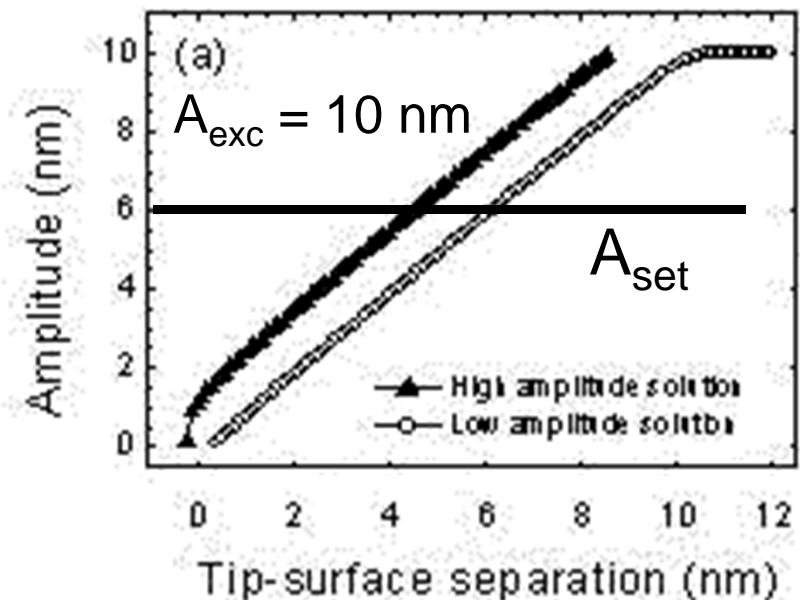
## SIMULATION

$R=10$  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

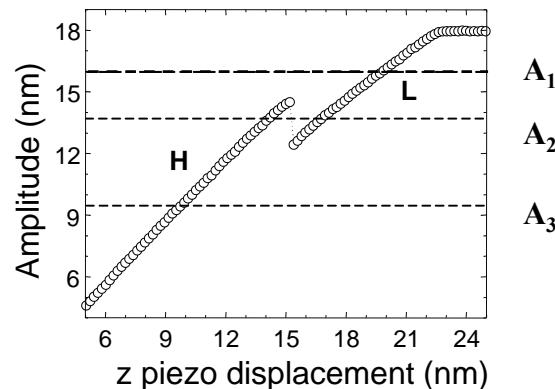
L: low amplitude state

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

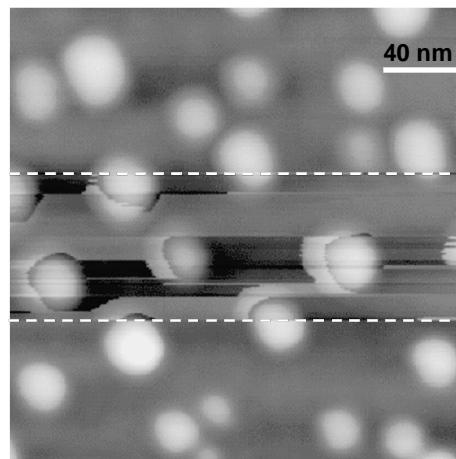
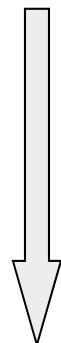
- Collection of L and H solutions gives rise to L and H branches.
- $A_{H(L)}$  decreases linearly with  $z_c$  for both branches.
- Ambiguity in the operation: both branches can match the set amplitude  $A_{set}$ .

## Experimental implications of the coexistence of states (I): Noise and stability

Sample: InAs quantum dots



A<sub>1</sub>  
A<sub>2</sub>  
A<sub>3</sub>



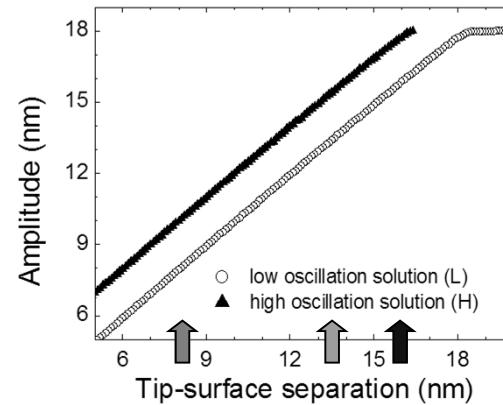
A<sub>1</sub> low amplitude branch

A<sub>2</sub>

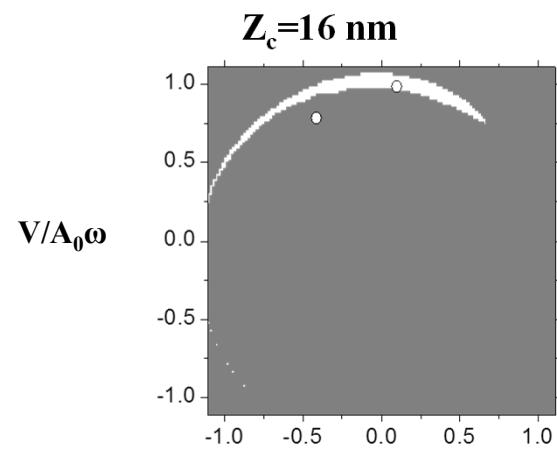
A<sub>3</sub> high amplitude branch

## Are both solutions equally accessible ?

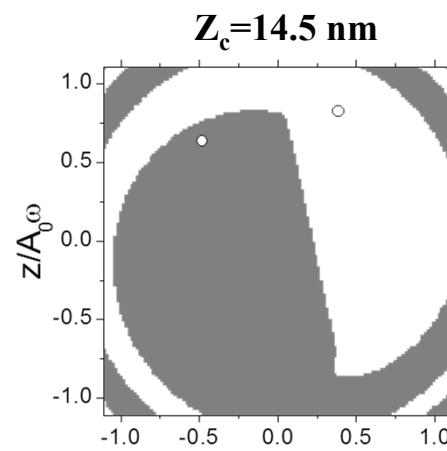
García and San Paulo, Phys. Rev. B  
61, R13381 (2000)



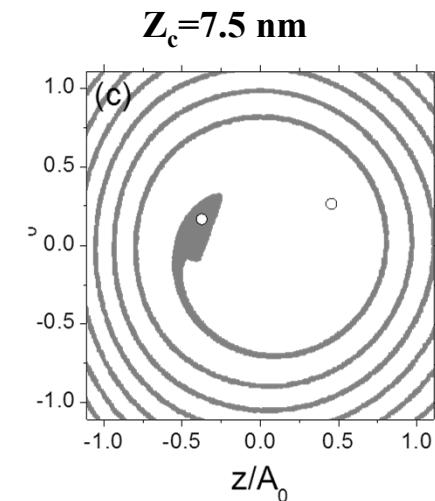
Phase space diagrams:  
Representation of the tip final state as a function of the initial velocity and positions



$Z_c=16 \text{ nm}$   
Phase space dominated by  
the L state=stable operation



$Z_c=14.5 \text{ nm}$   
Phase space diagram with  
significant H and L  
contributions=unstable  
operation

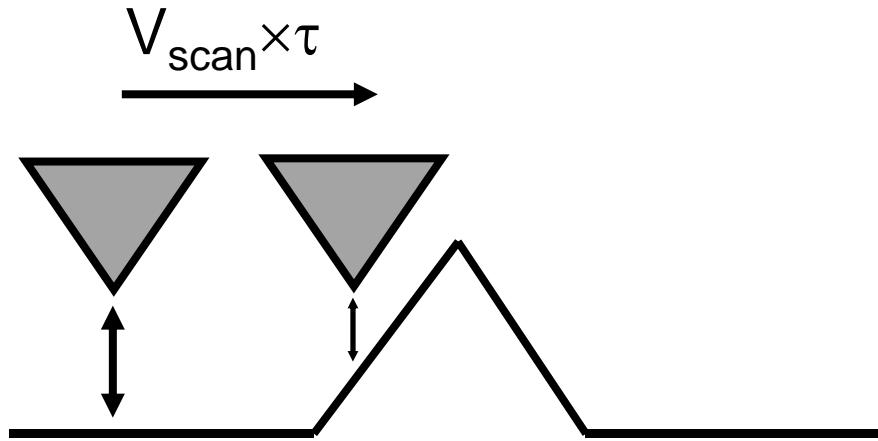


$Z_c=7.5 \text{ nm}$   
Phase space diagram  
dominated by the H  
state basin of  
attraction=stable  
operation

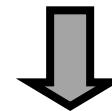
Tip should stay always on the same branch (deterministic) BUT...

# NOISE: Implications for scanning

Mechanical, electronical, thermal and feedback perturbations...



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



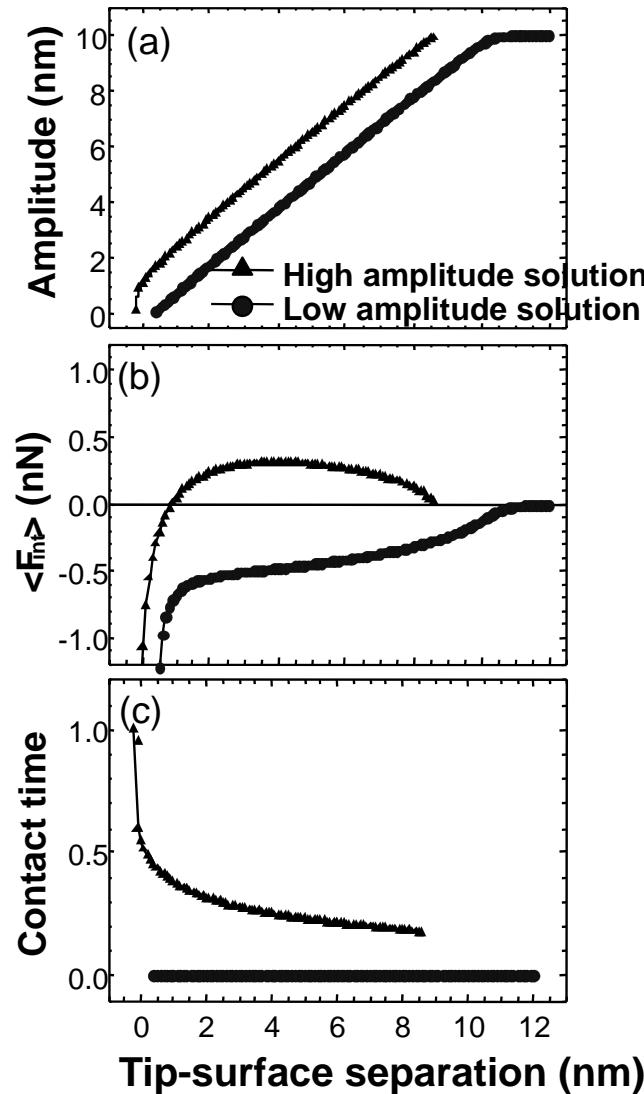
Change in separation can lead to transitions before the feedback takes over

- 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....

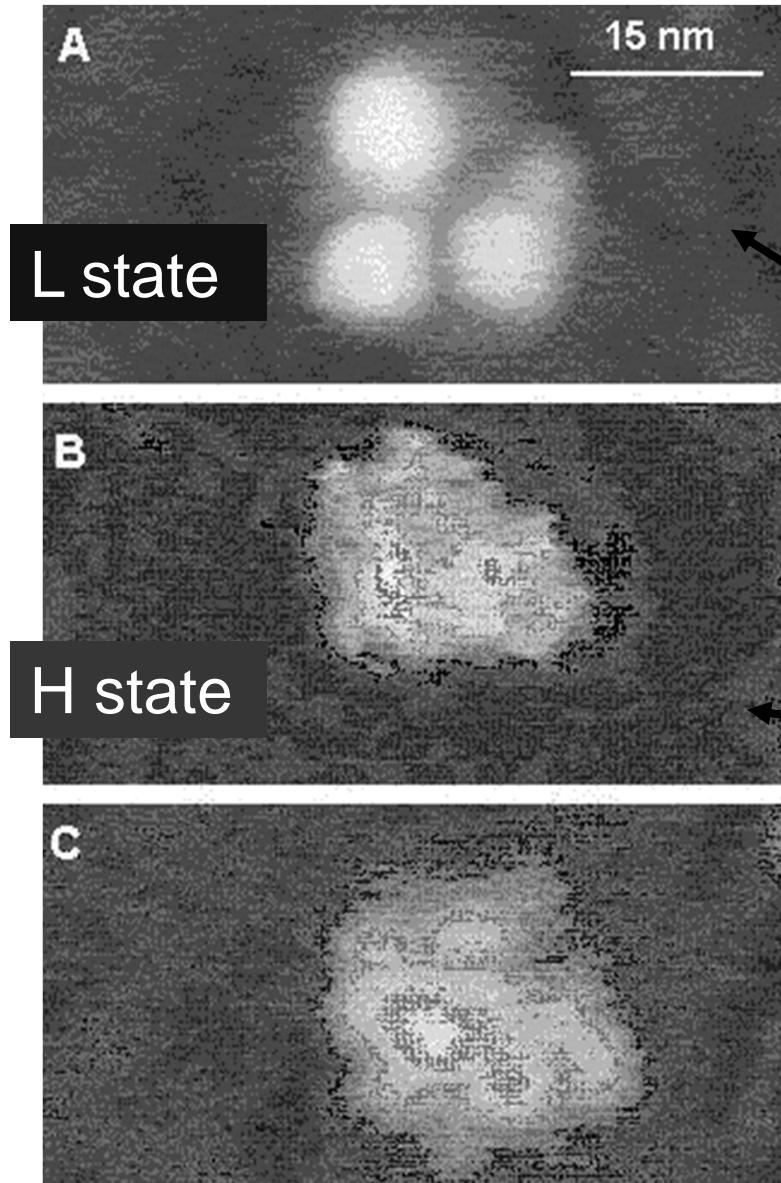
H and L states have different properties

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



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

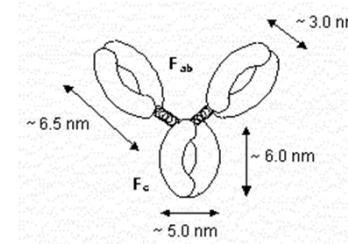
# Does resolution depend on the oscillation state chosen?



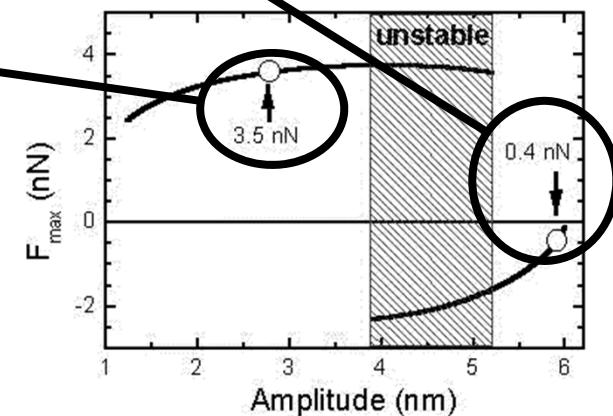
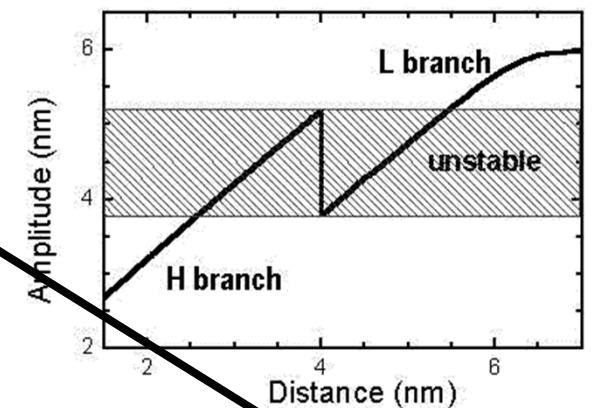
Morphology and dimensions of fragments clearly resolved

No domain structure

Irreversible deformation after imaging on H state



a-HSA antibody on mica



## Analytical Approximations

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

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

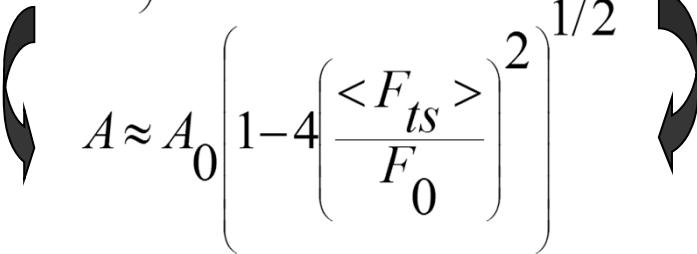
**The virial theorem and energy consideration allows  
to derive an analytical approximation**

$$\cos \phi = \frac{2Q}{k_c A A_0} \left[ \frac{\langle F_{ts} \rangle^2}{k_c} - \langle F_{ts} \cdot z \rangle + \frac{1}{2} k_c A^2 \left( 1 - \frac{\omega^2}{\omega_0^2} \right) \right] \quad \xrightarrow{\omega = \omega_0 \text{ and } A \gg z_0} \cos \phi \approx - \frac{2Q \langle F_{ts} \cdot z \rangle}{k_c A A_0}$$

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

**Negligible power dissipation**

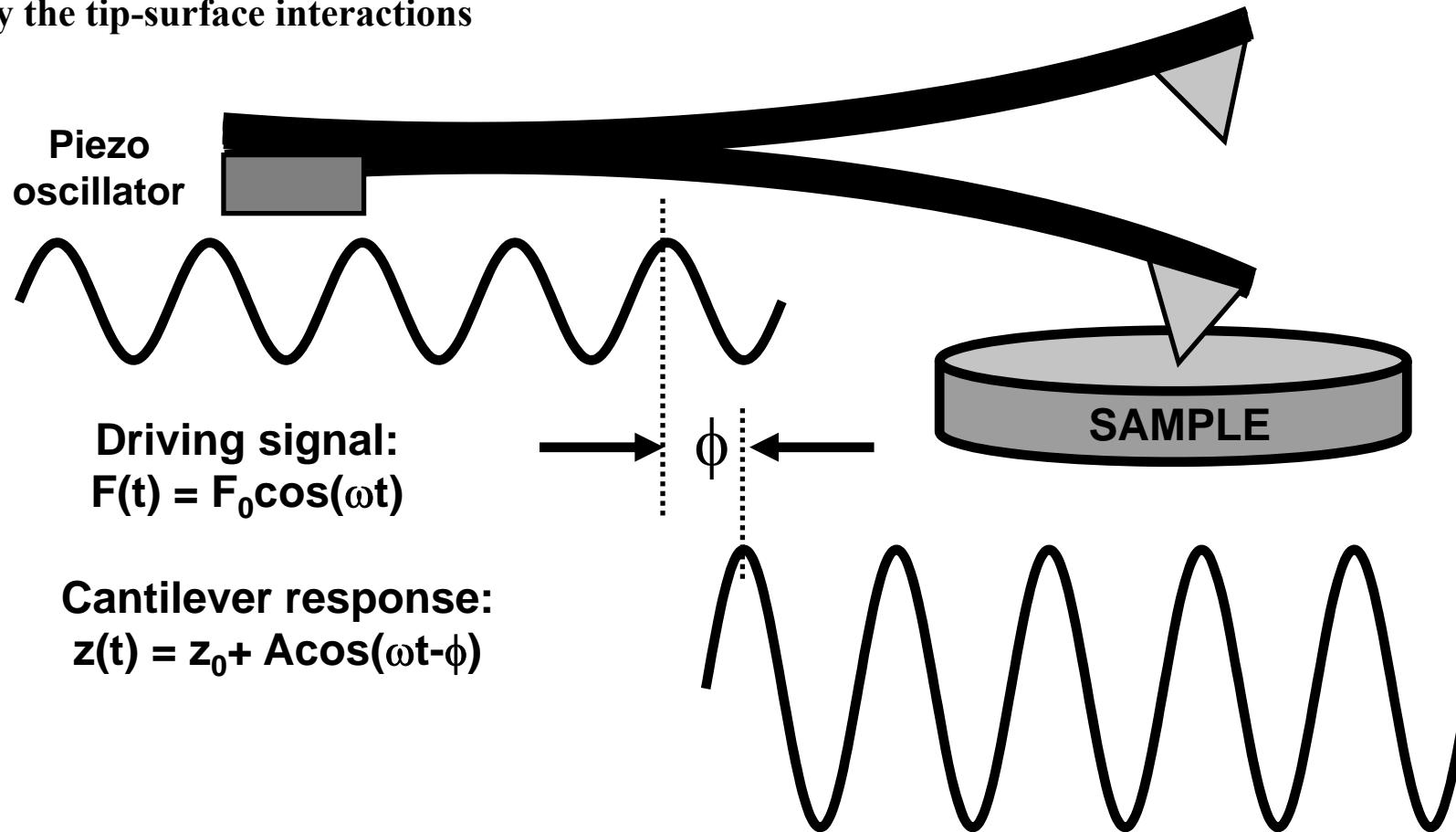
$$A \approx \frac{A_0}{\sqrt{2}} \left( 1 - \frac{2P_{ts}}{P_{med}} \pm \sqrt{1 - \frac{4P_{ts}}{P_{med}} - 16 \left( \frac{\langle F_{ts} \cdot z \rangle}{F_0 A_0} \right)^2} \right)^{1/2} \quad \xrightarrow{\quad} \quad A \approx \frac{A_0}{\sqrt{2}} \left( 1 \pm \sqrt{1 - 16 \left( \frac{\langle F_{ts}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



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

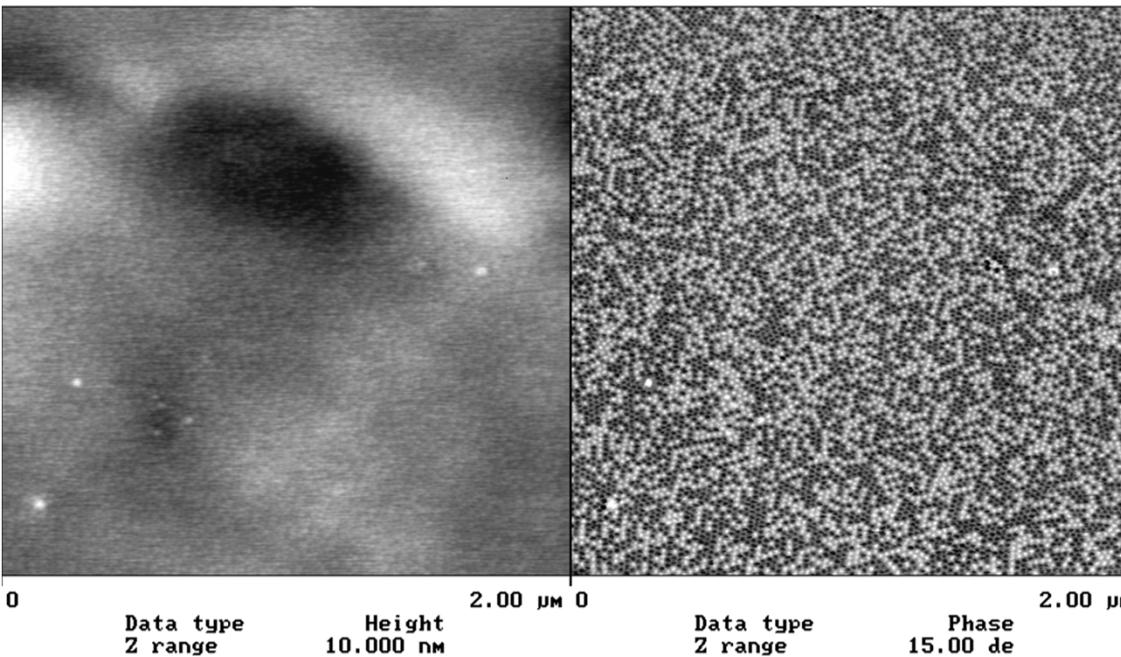
# Phase Imaging

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



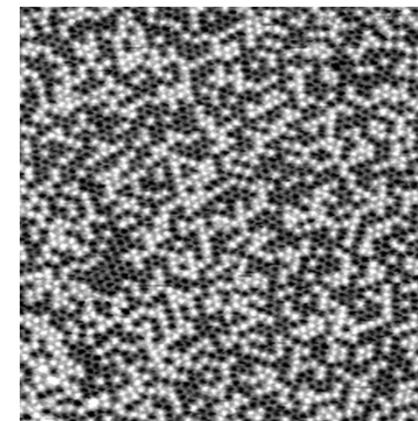
## Polymers: Morphology and Structure

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  
1 μm<sup>2</sup>

## 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)**

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

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

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

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

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

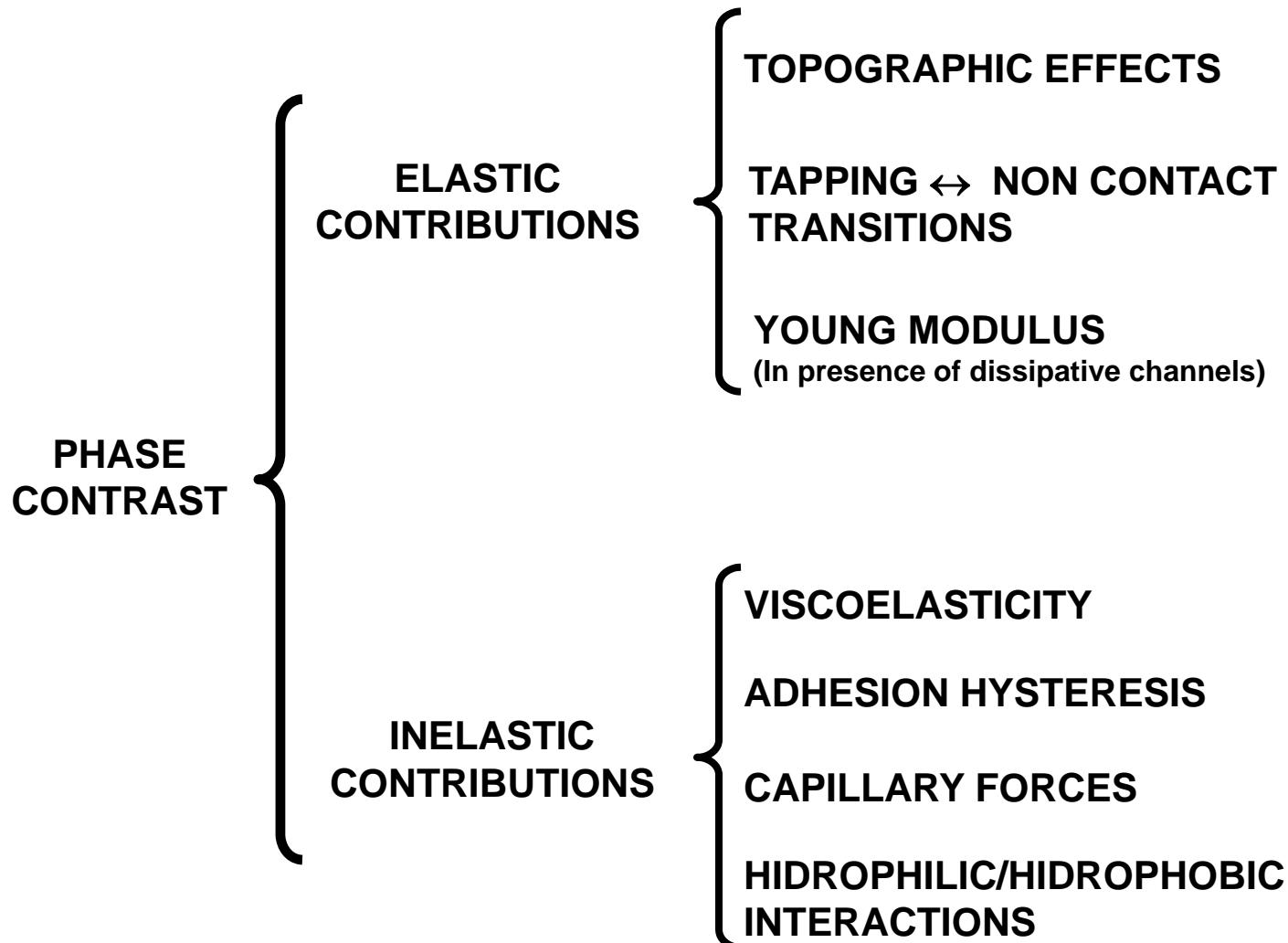
Cleveland et al. APL 72, 2613(1998)

Tamayo, García APL73, 2926 (1998)

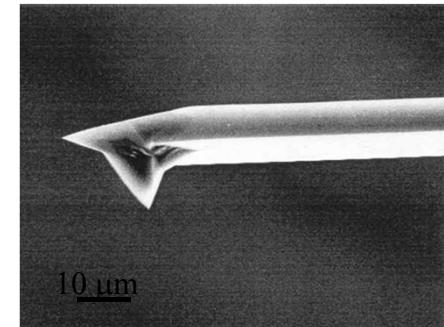
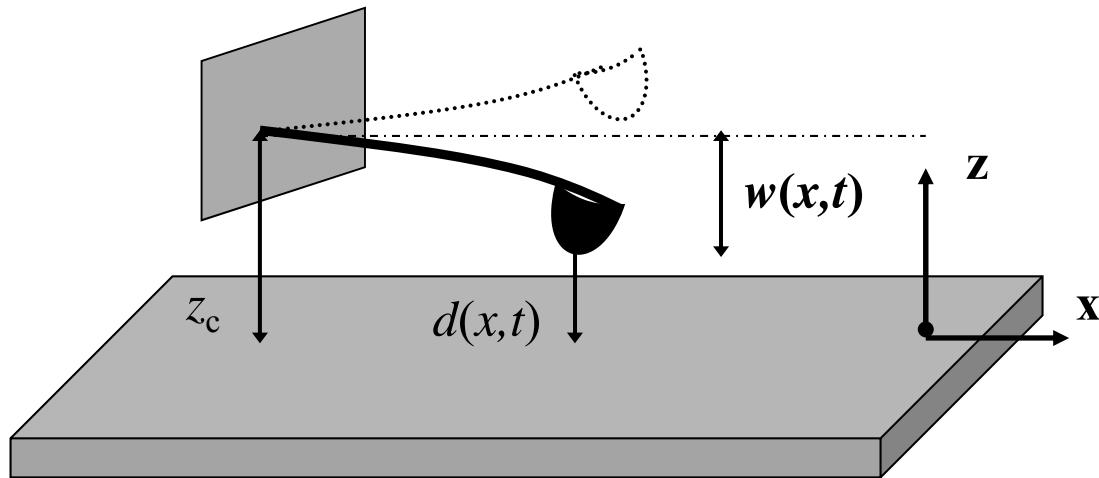
García et al. Surf. Int. Anal. 27, 1999)

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

# CONTRIBUTIONS TO CONTRAST IN PHASE IMAGES



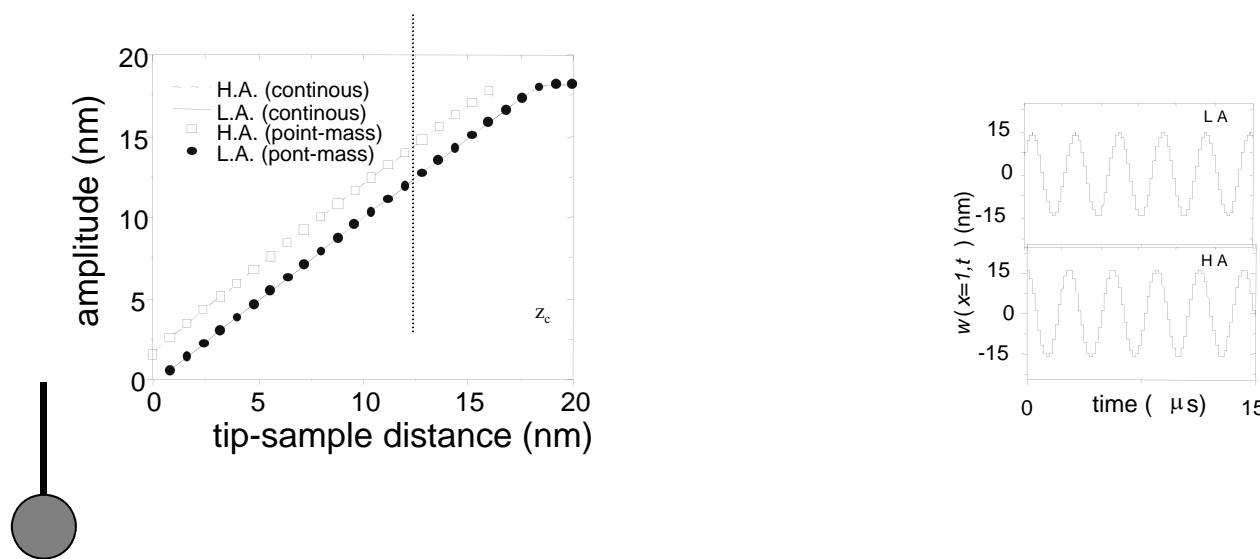
## Continuous Model for the Cantilever



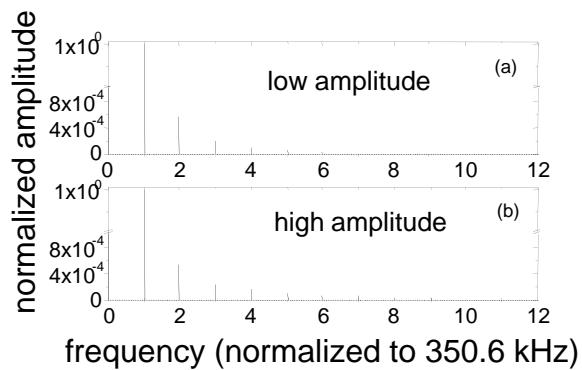
$$\frac{EI}{L^4} \frac{\partial^4}{\partial x^4} [w(x,t)] + bh\rho \frac{\partial^2 w(x,t)}{\partial t^2} = F_{ext} + F_{med} + F_{ts}$$

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

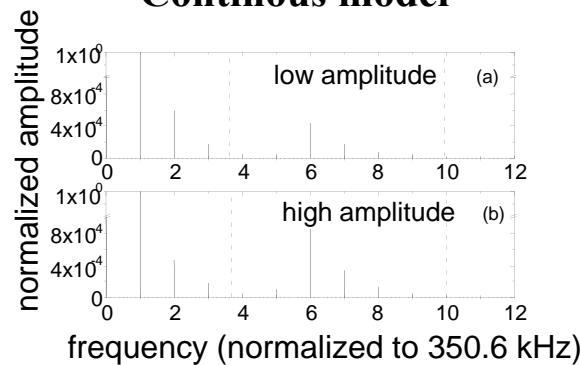
Rodríguez and García, Appl. Phys. Lett. 80, 1646 (2002)



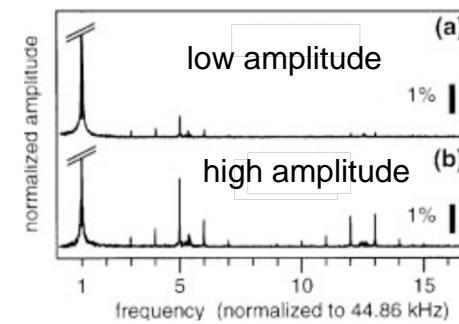
### Point -mass model



### Continous model



### Experimental results (Triangular cantilever)



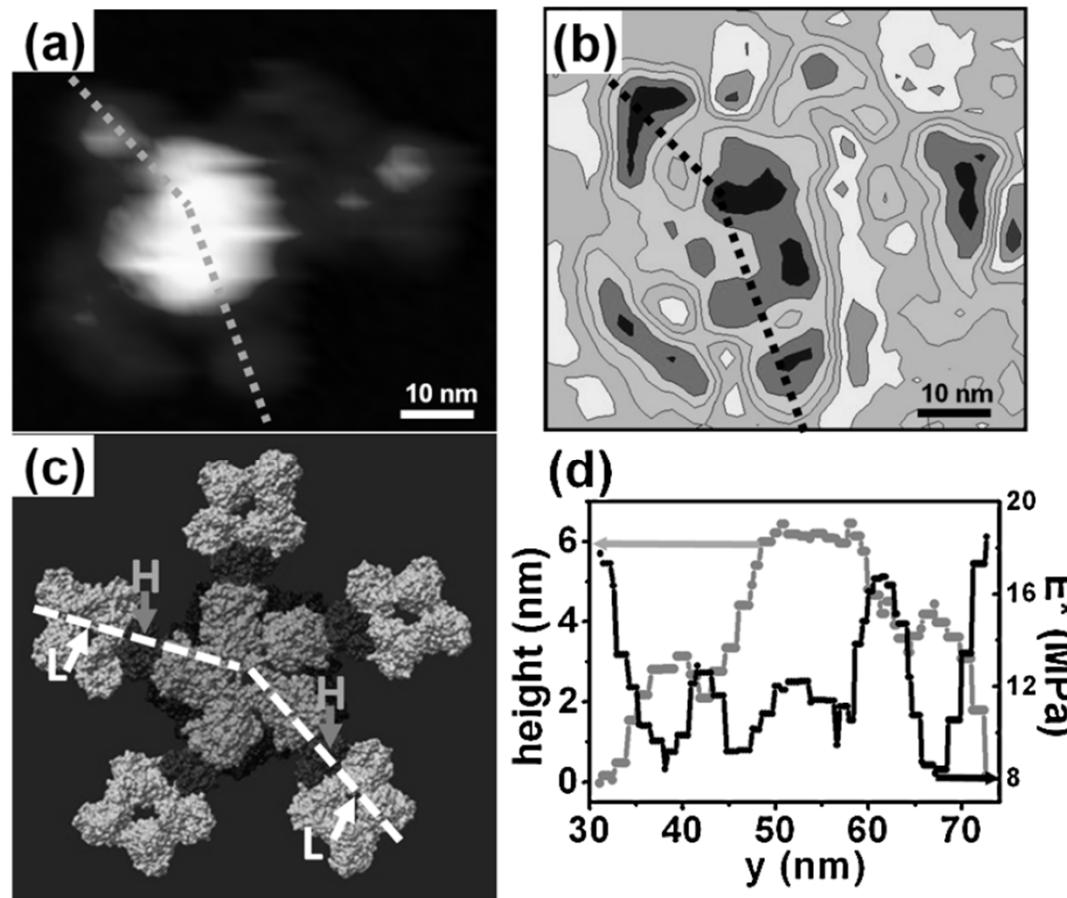
#### Parámetros de la simulación:

$f_p = 350.6 \text{ kHz}$ ,  $k = 40 \text{ N/m}$ ,  $A_0 = 18.22 \text{ nm}$ ,  $Q = 400$  (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):  $A_{\text{exc}}$ ,  $\omega_{\text{exc}}$ ,  $z_c$  &  $A_{\text{set}}$
- 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:  $\Delta f$  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  $A_{\text{exc}}$  and frequency  $\omega_{\text{exc}}$  close or at its FREE resonance frequency  $\omega_0$ .
- Oscillation amplitude  $A$  as feedback for topography.
- Phase shift  $\phi$  between excitation and oscillation: compositional contrast.
- Air and liquid environments.

## Frequency Modulation AFM

- Constant oscillation amplitude at the current resonance frequency (depends on  $F_{\text{ts}}$ ).
- Frequency shift  $\Delta f$  as feedback for topography.
- Excitation amplitude  $A_{\text{exc}}$  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

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

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

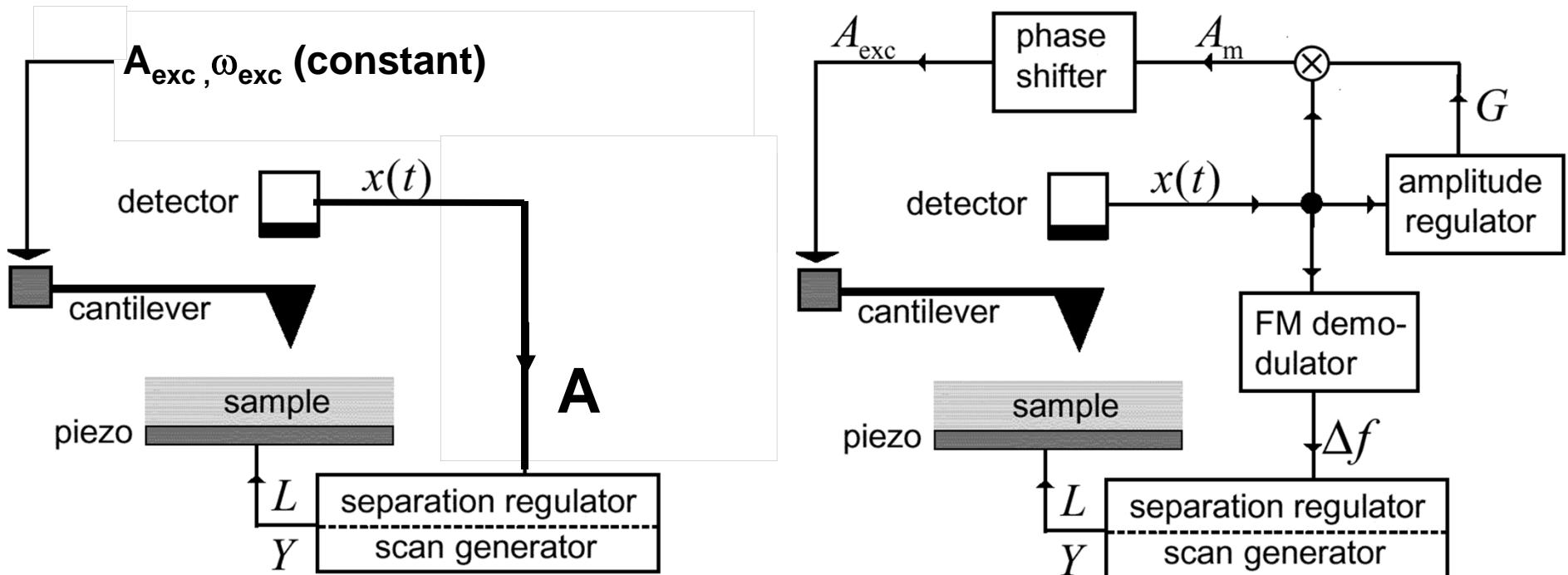
$$Q \text{ (air)} = 10^2 - 10^3 \Rightarrow \tau \text{ small}$$

$$\tau = \frac{1}{\gamma} = \frac{2Q}{\omega_0}$$
$$Q \text{ (UHV)} = 10^4 - 10^5 \Rightarrow \tau \text{ large}$$

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

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

# AM-AFM vs FM-AFM set-ups



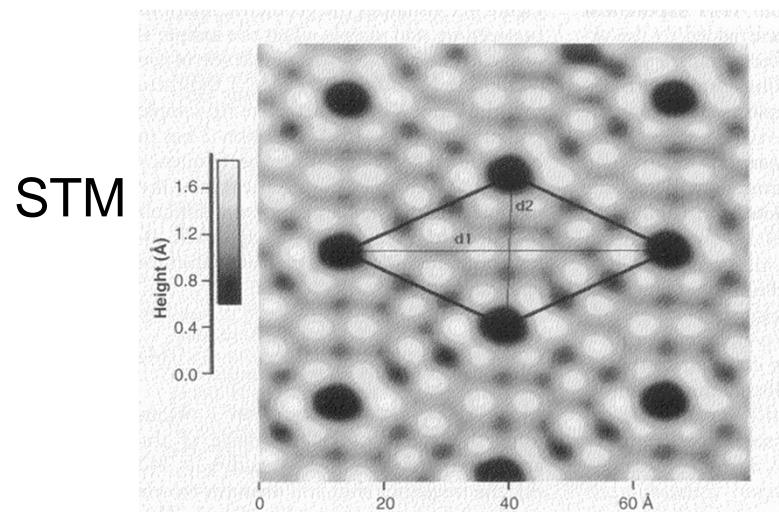
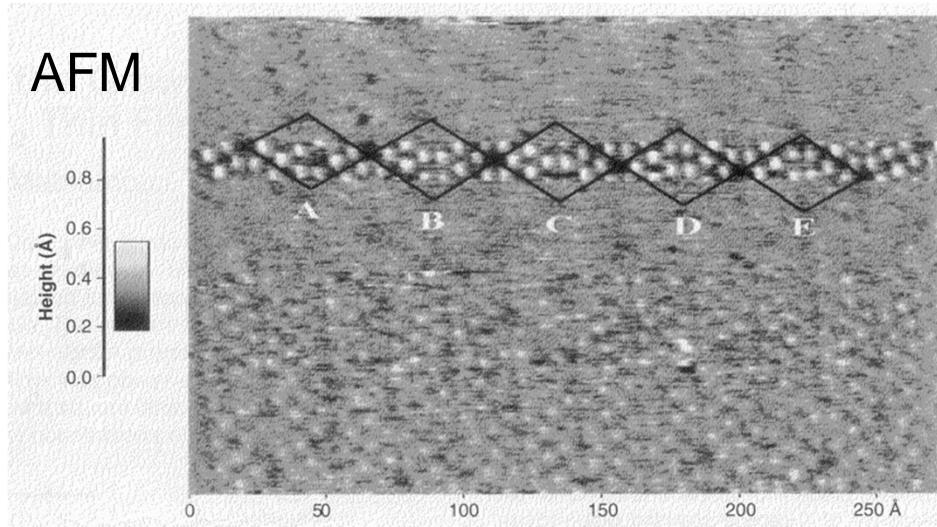
FM-AFM: cantilever regulated by electronics  $\Rightarrow$  stable and fast response.

Mechanical Stability Conditions

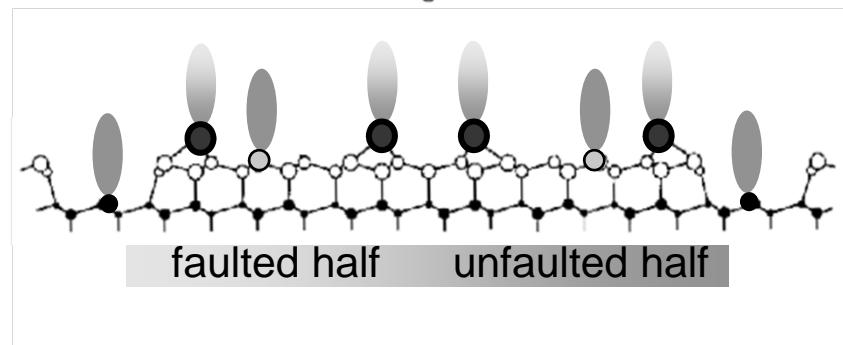
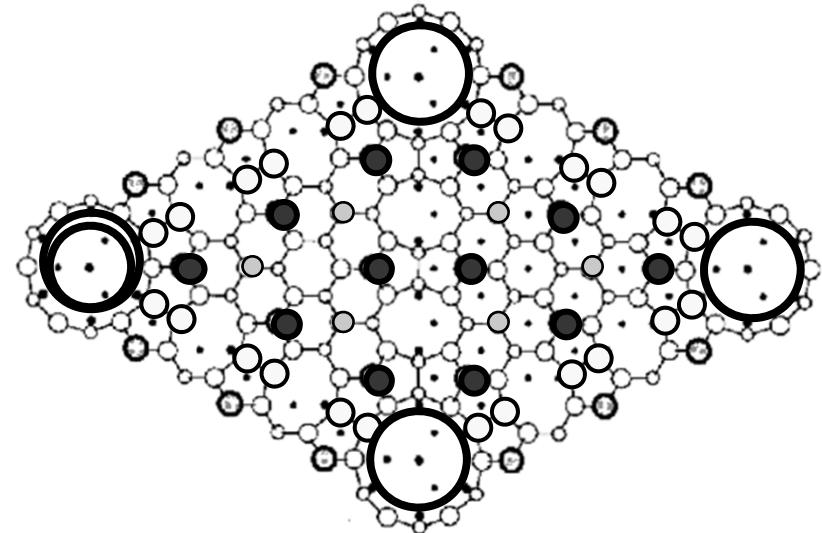
$$\tau_{\text{FM}} \approx \frac{1}{\omega_0}$$

$$\max \left| \frac{d^2 V_{\text{ts}}}{dz^2} \right| = k_{\text{ts}}^{\max} < k \quad \max \left| - \frac{dV_{\text{ts}}}{dz} \right| = |F_{\text{ts}}^{\max}| < kA_0$$

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



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



● 12 adatoms

○ 6 rest atoms

○ corner hole

○ dimers

# “Classical” FM-AFM operation conditions

## Stability Conditions

$$\max \left| \frac{d^2 V_{ts}}{dz^2} \right| = k_{ts}^{\max} < k \quad \max \left| -\frac{dV_{ts}}{dz} \right| = |F_{ts}^{\max}| < kA_0$$

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

$f_0 \sim 100 \text{ kHz}$

$Q \sim 30000$

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

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



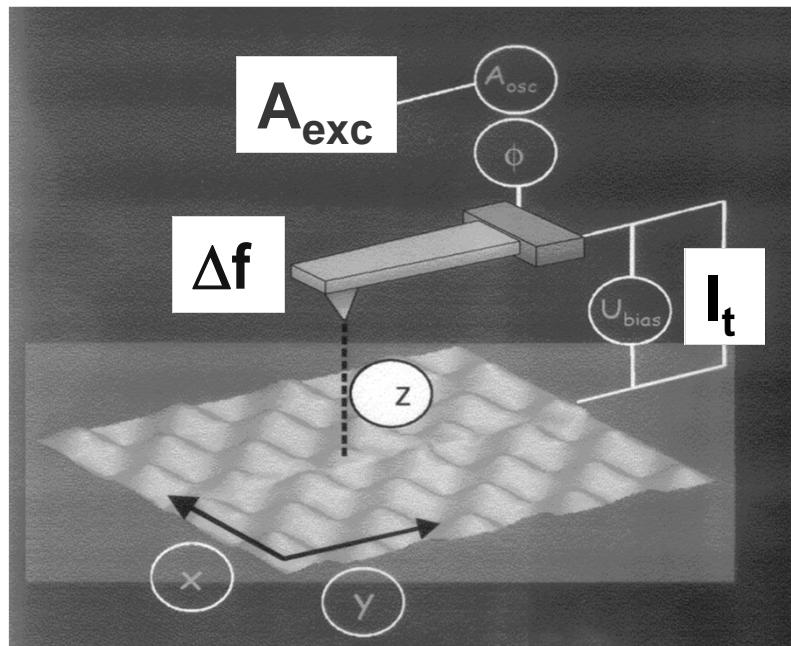
$$kA_0 \sim 600 \text{ nN} \gg F_{ts} \sim 1-10 \text{ nN}$$

(prevents cantilever instabilities)

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

(stable oscillation amplitudes)

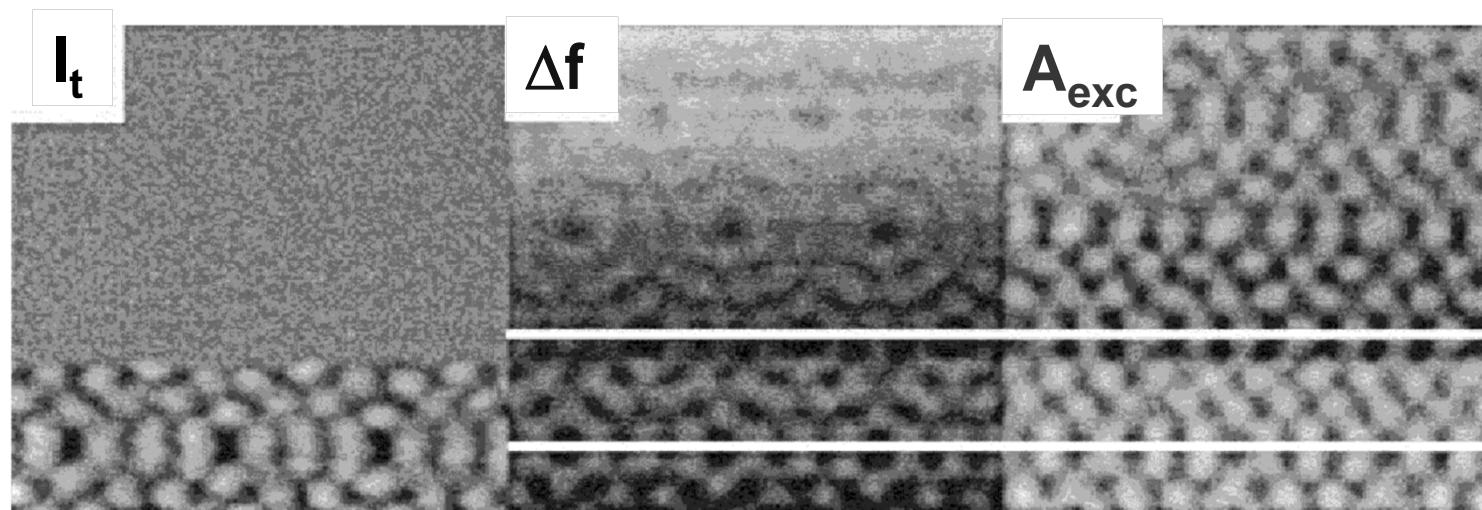
# FM-AFM: Contrast sources



$\Delta f$ : frequency shift

$A_{\text{exc}}$ : damping (excitation)

$I_t$ : mean tunneling current



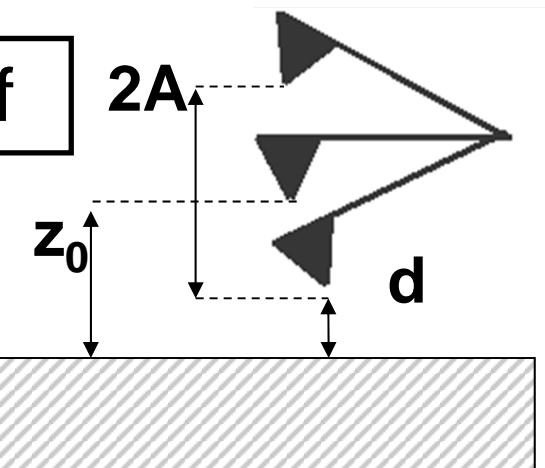
## **2. Cantilever dynamics : relation between the frequency shift and tip-sample interaction.**

# 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

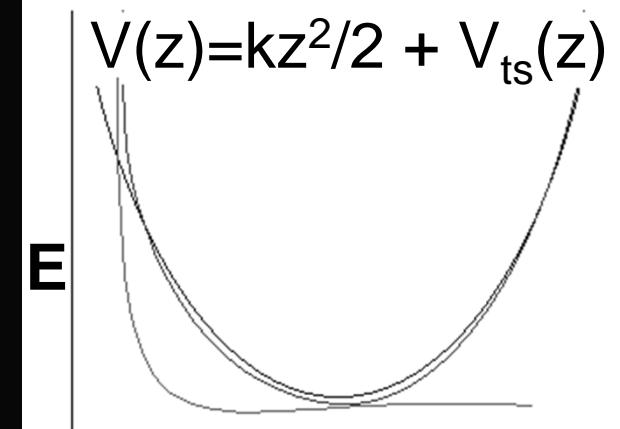
$$m\ddot{z}(t) + kz(t) - F_{ts}[z_o + z(t)] = 0$$



Perturbation theory

F.J. Giessibl, PRB 58, 10335 (1998)

$$\begin{aligned} \Delta f(d, k, A_0, f_0) &= -\frac{f_0}{kA_0^2} \langle F_{ts} z \rangle = \\ &= -\frac{1}{2\pi} \frac{f_0}{kA_0} \int_0^{2\pi} F_{ts}[d + A_0(1 + \cos\varphi)] \cos\varphi d\varphi \end{aligned}$$



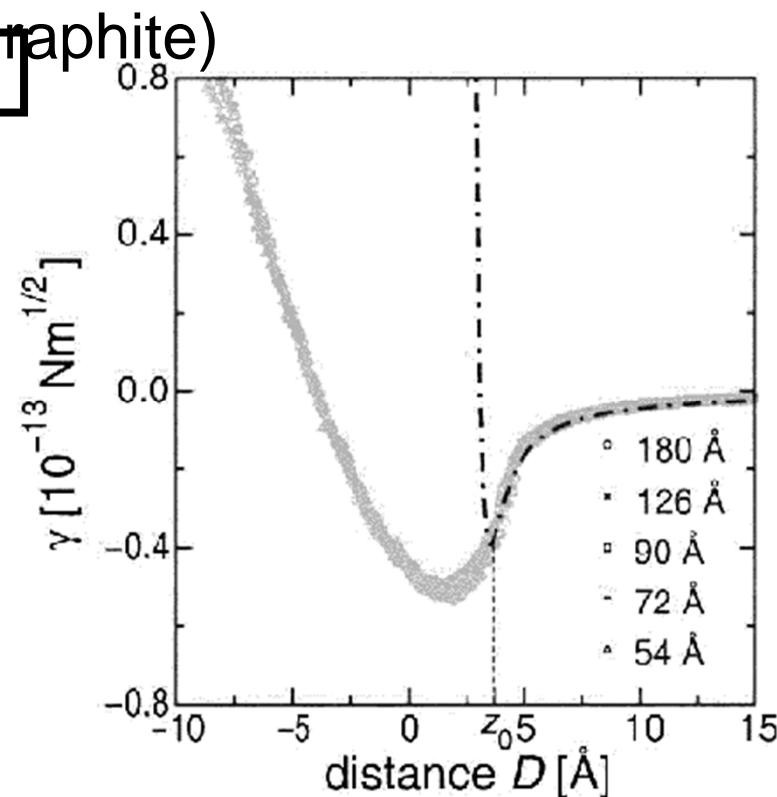
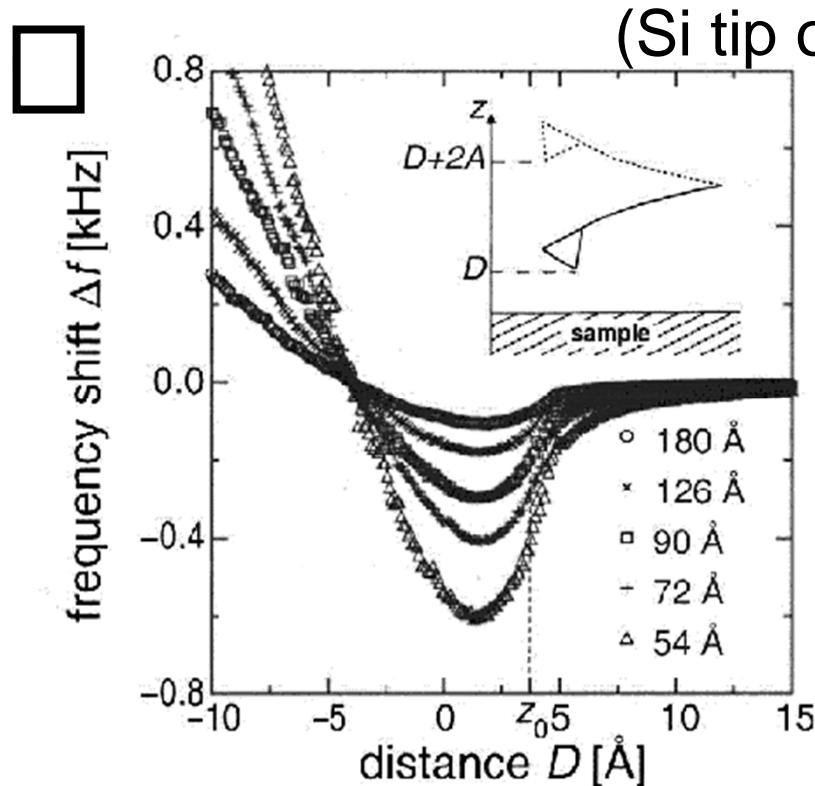
Confirmed by numerical simulations including the control electronics

M. Gauthier, R.P., T. Arai, M. Tomitori & M. Tsukada, PRL 87, 096801 (2001)

# Normalized frequency shift $\gamma$

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

$\gamma$  extracts the intrinsic contribution coming from  $F_{ts}$



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

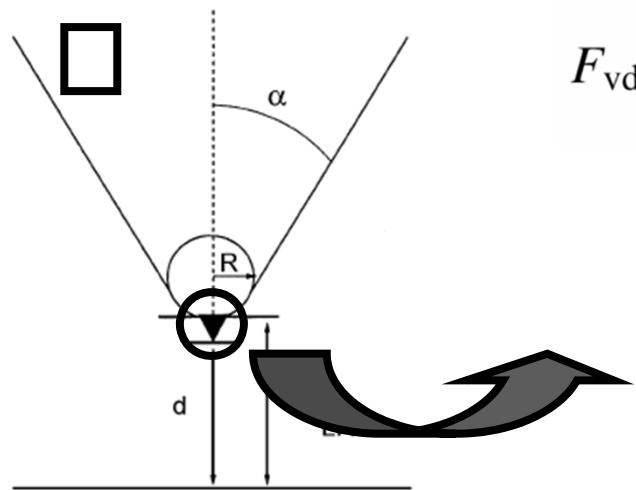
Not accurate for small tip-sample distances ( $2-3 \text{\AA}$ ) !!

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

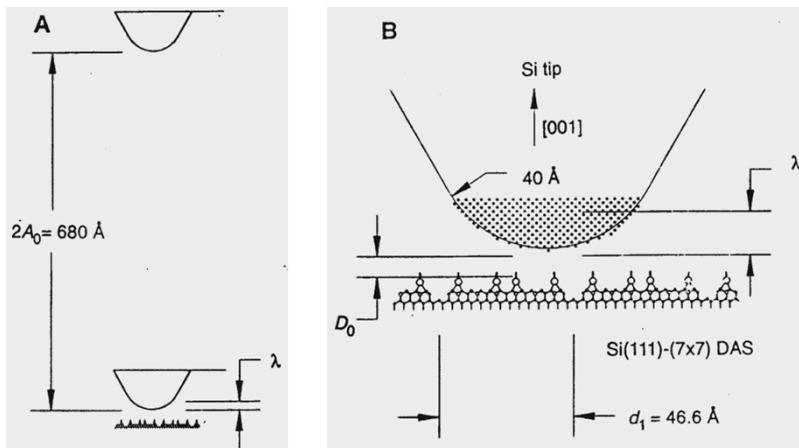
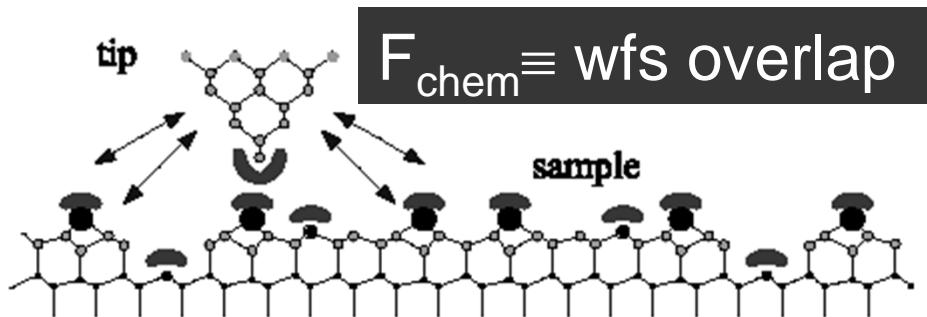
- Separation of LR and SR interactions
- Semiconductors
- Alkali halides & oxides
- Metals, weakly bonded systems & carbon-based materials (graphite, nanotubes, ...)

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

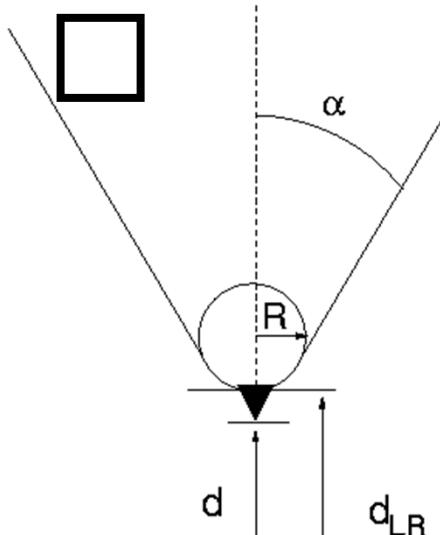
## Sensitivity to Short-Range Forces?

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

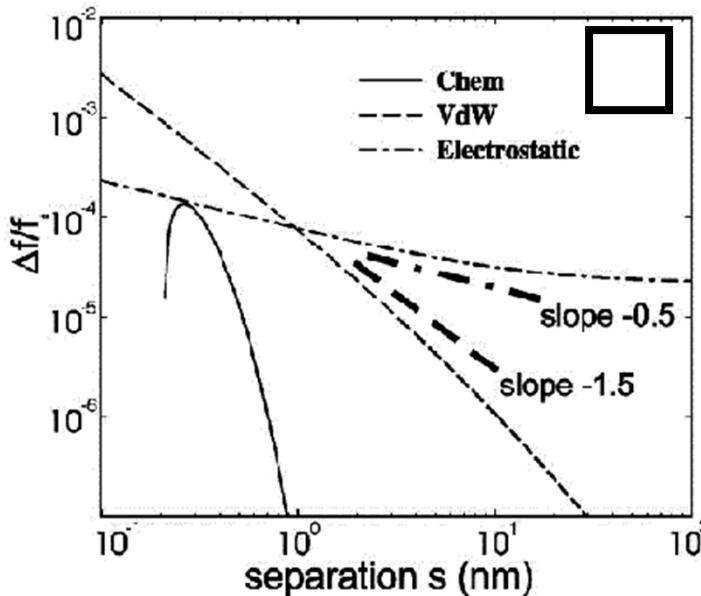
$$u = \cos(\omega t)$$

Weak singularity at  
turning points !!!

# Characterizing the “macroscopic” tip: Separation of interactions



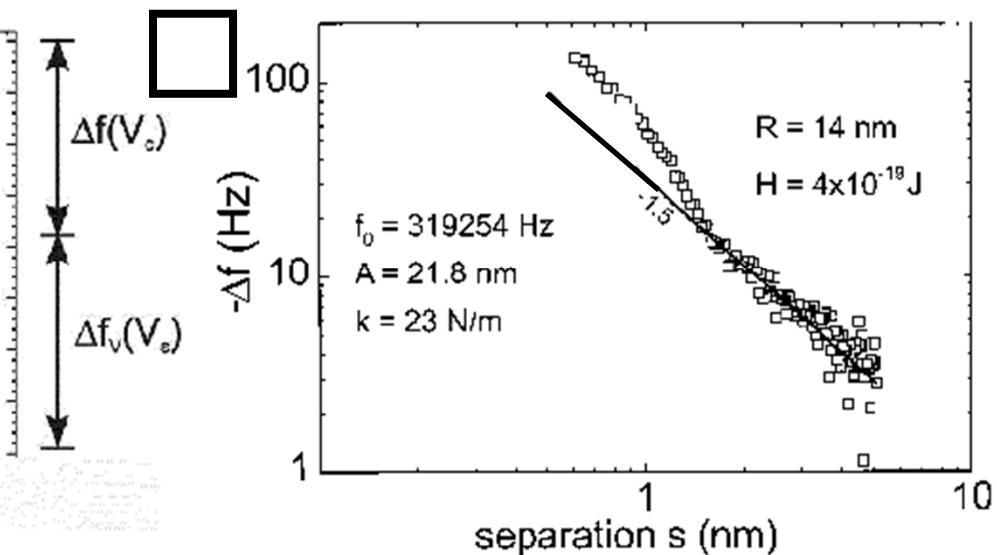
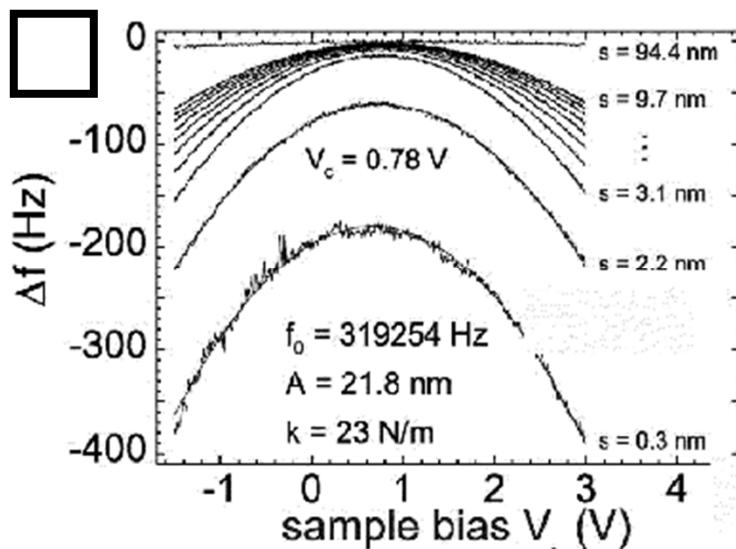
Electrostatic



Si tip on  
Cu(111)

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

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

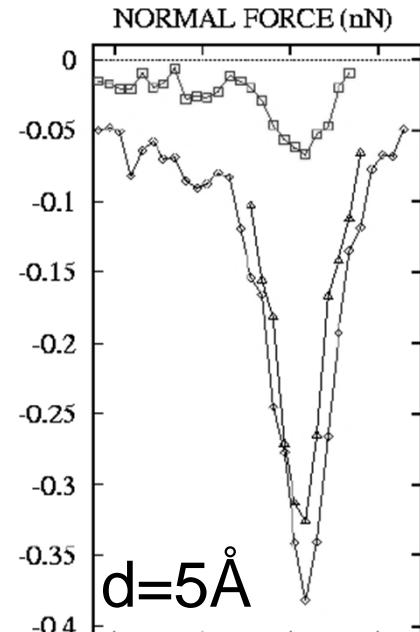
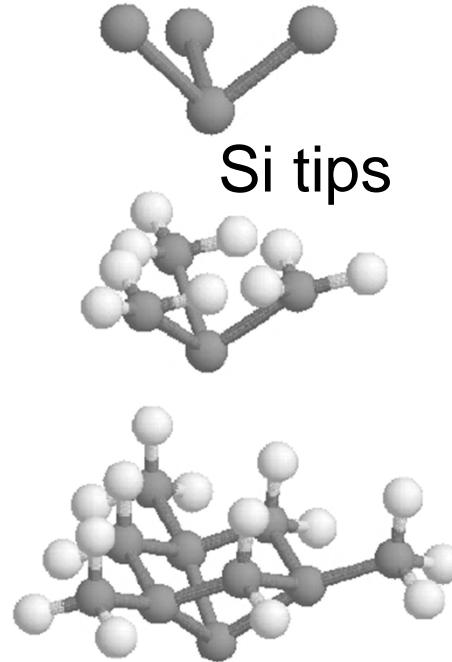
100 x

***Ab initio*  
quantum mechanics**

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

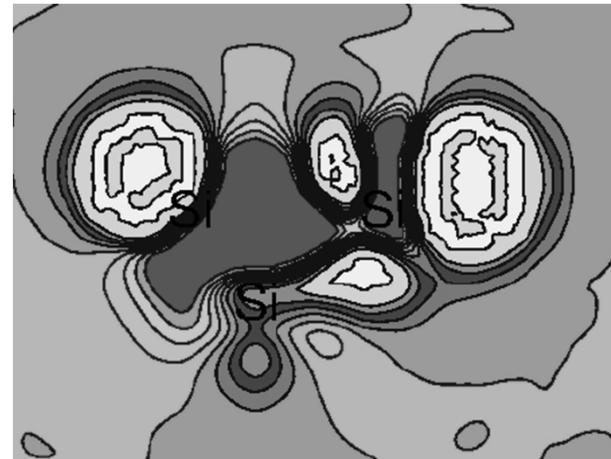
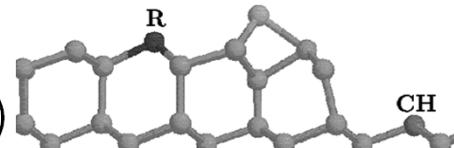
# Role of SR Covalent Bonding Interactions?

DFT-GGA plane wave pseudopotential calculations

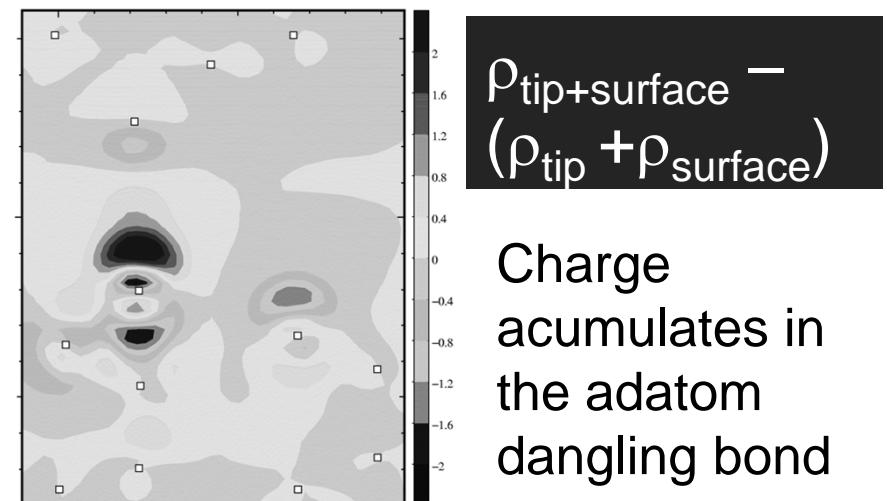


R. P. et al, PRL 78, 678 (1997)

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



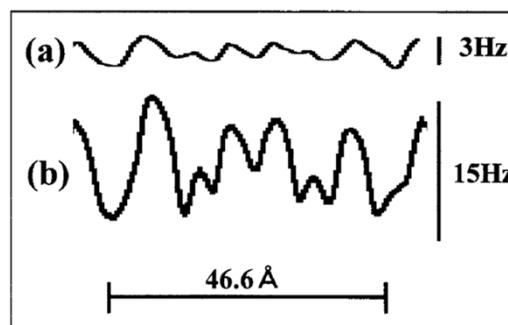
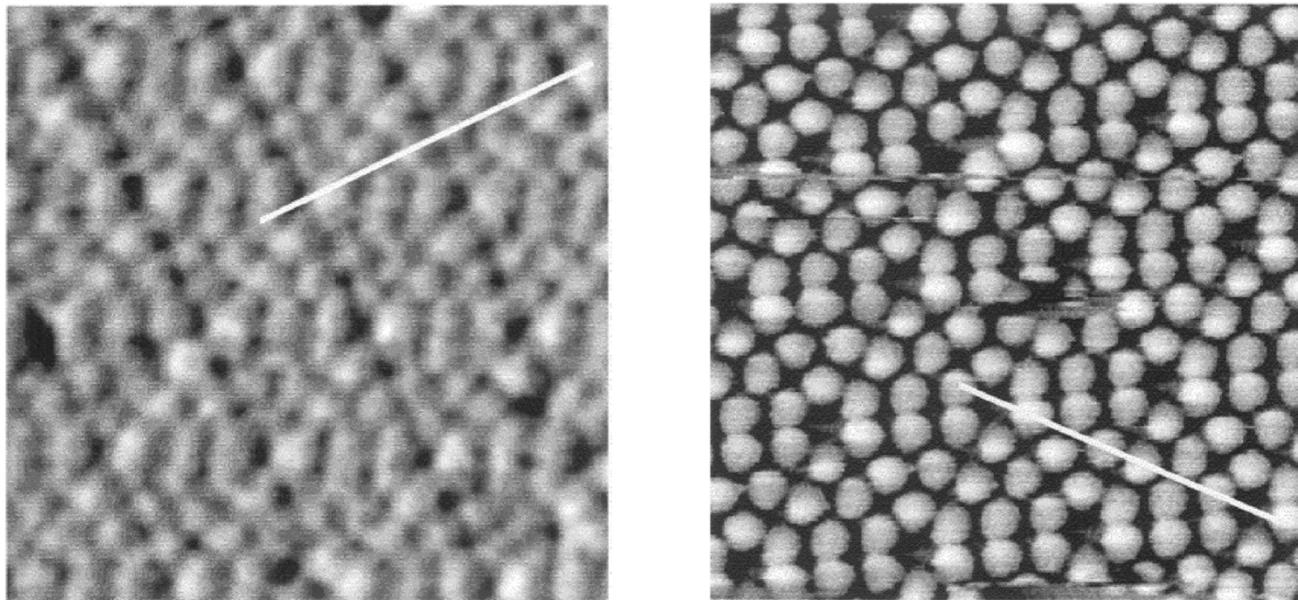
Charge density difference between tips



Charge accumulates in the adatom dangling bond

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

# Contrast dependence on tip preparation

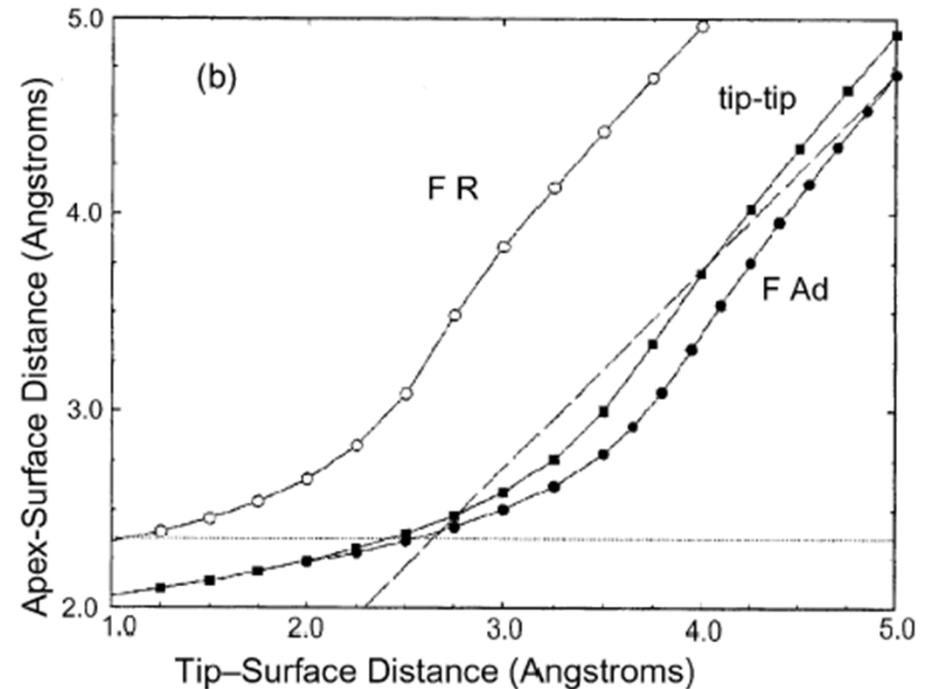
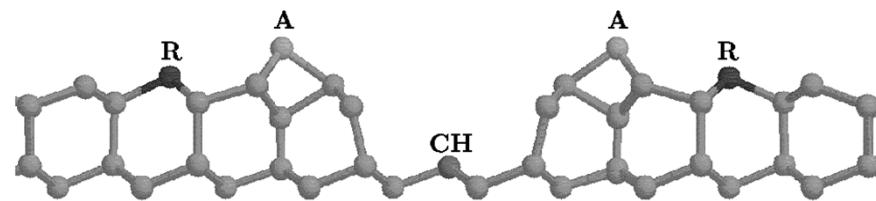
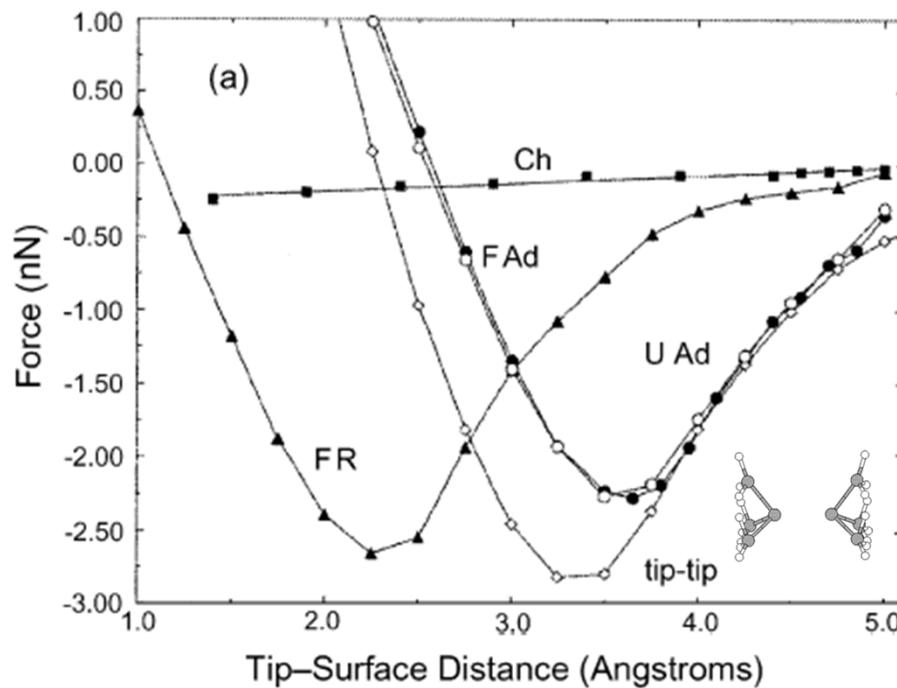


T. Uchihashi et al, PRB 56, 9834 (1997)

# Force-distance curves & Atomic relaxations

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

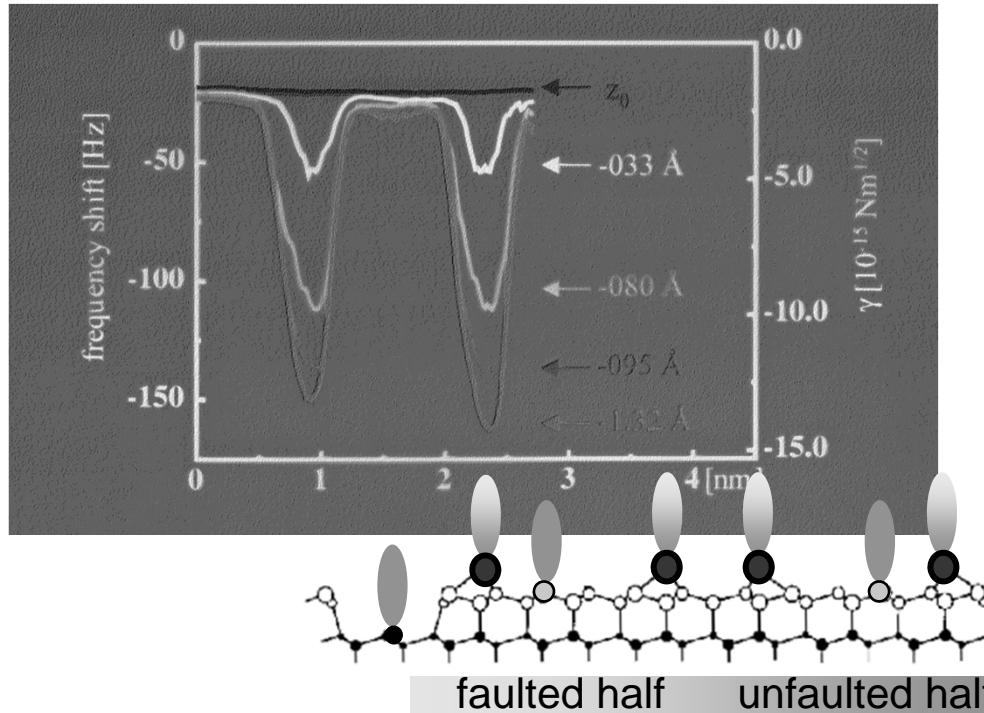
atomic relaxations due to  
tip-surface interactions!!



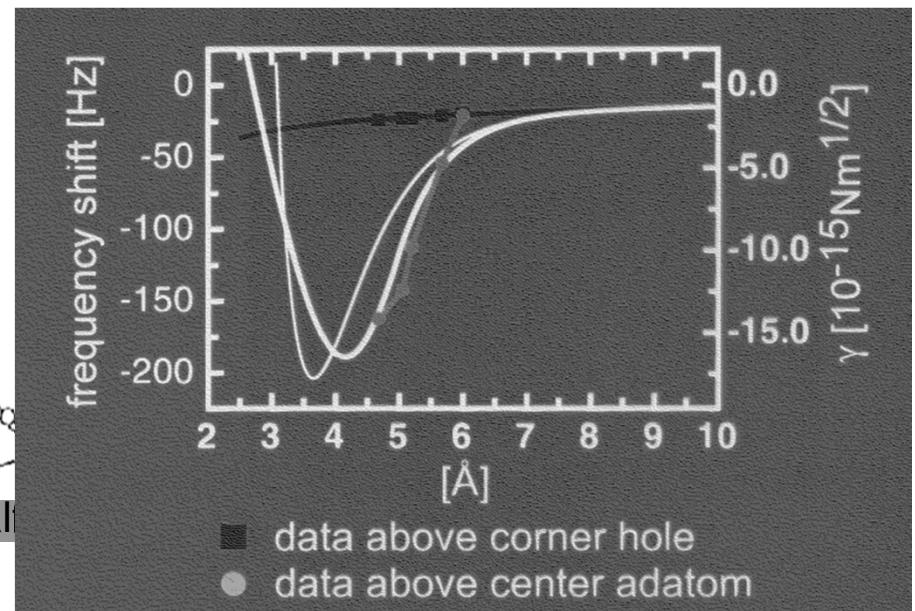
Force vs distance curves → prediction for  $\Delta f$  vs distance

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

# 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

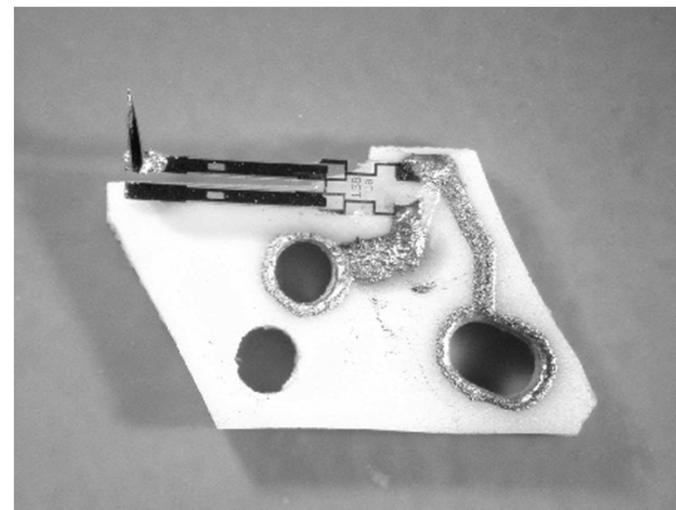
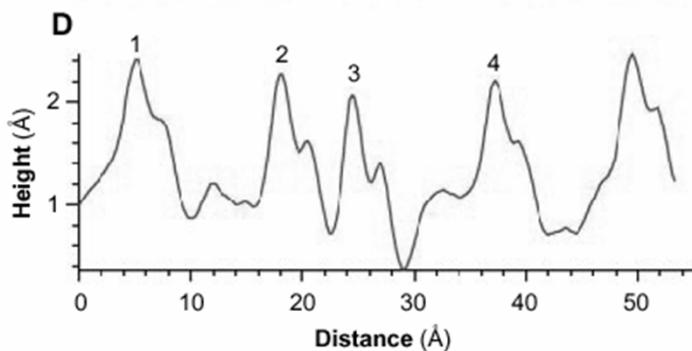
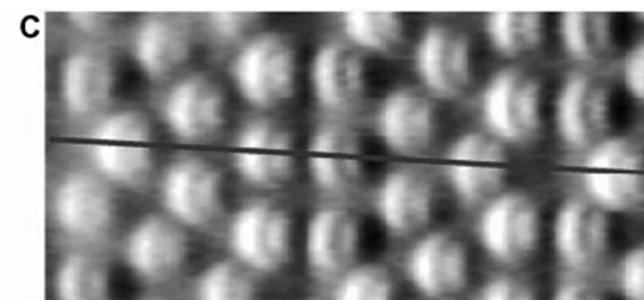
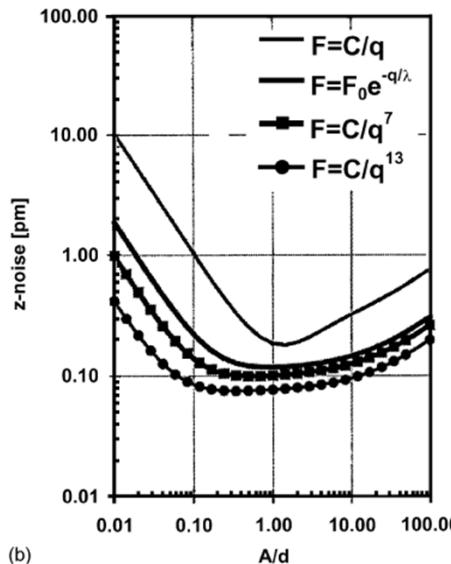
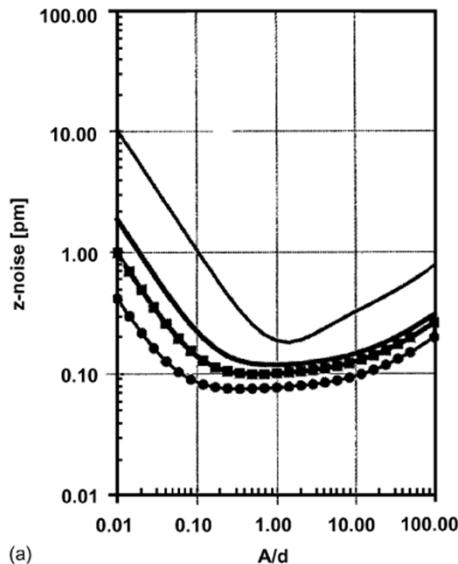
R. Pérez et al , PRL 78, 678 (1997)  
R. Pérez et al , PRB 58, 10835 (1998)

## **4. Recent developments...**

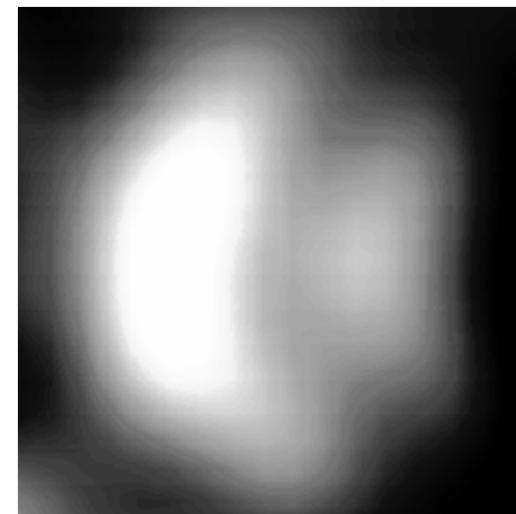
- Tuning forks: small amplitudes to enhance atomic contrast.
- Force spectroscopy: Chemical identification
- Single-atom manipulation at RT
- AFM detection of spin
- True atomic resolution in liquids

# Other operating conditions: qPlus sensor

Smallest Noise for Å-size amplitudes!!!



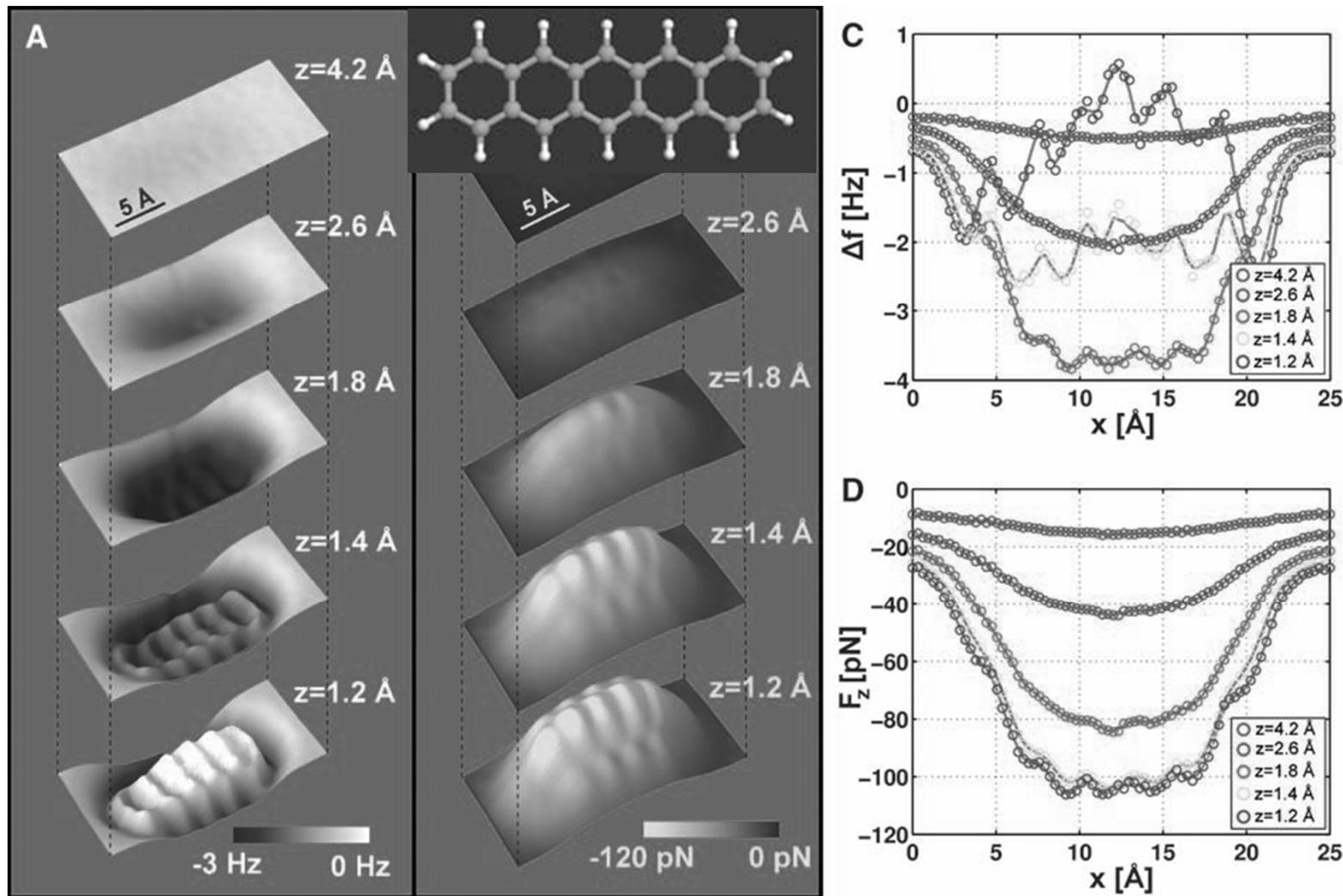
qPlus sensor made from a tuning fork ( $k \sim 2000$  N/m)



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

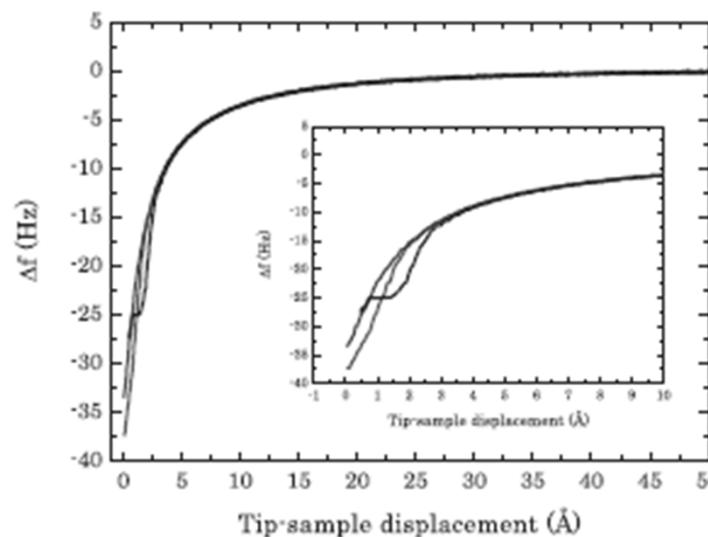
F.J. Giessibl et al,  
Science 289 (2000) 422

# The Chemical Structure of a Molecule Resolved by Atomic Force Microscopy

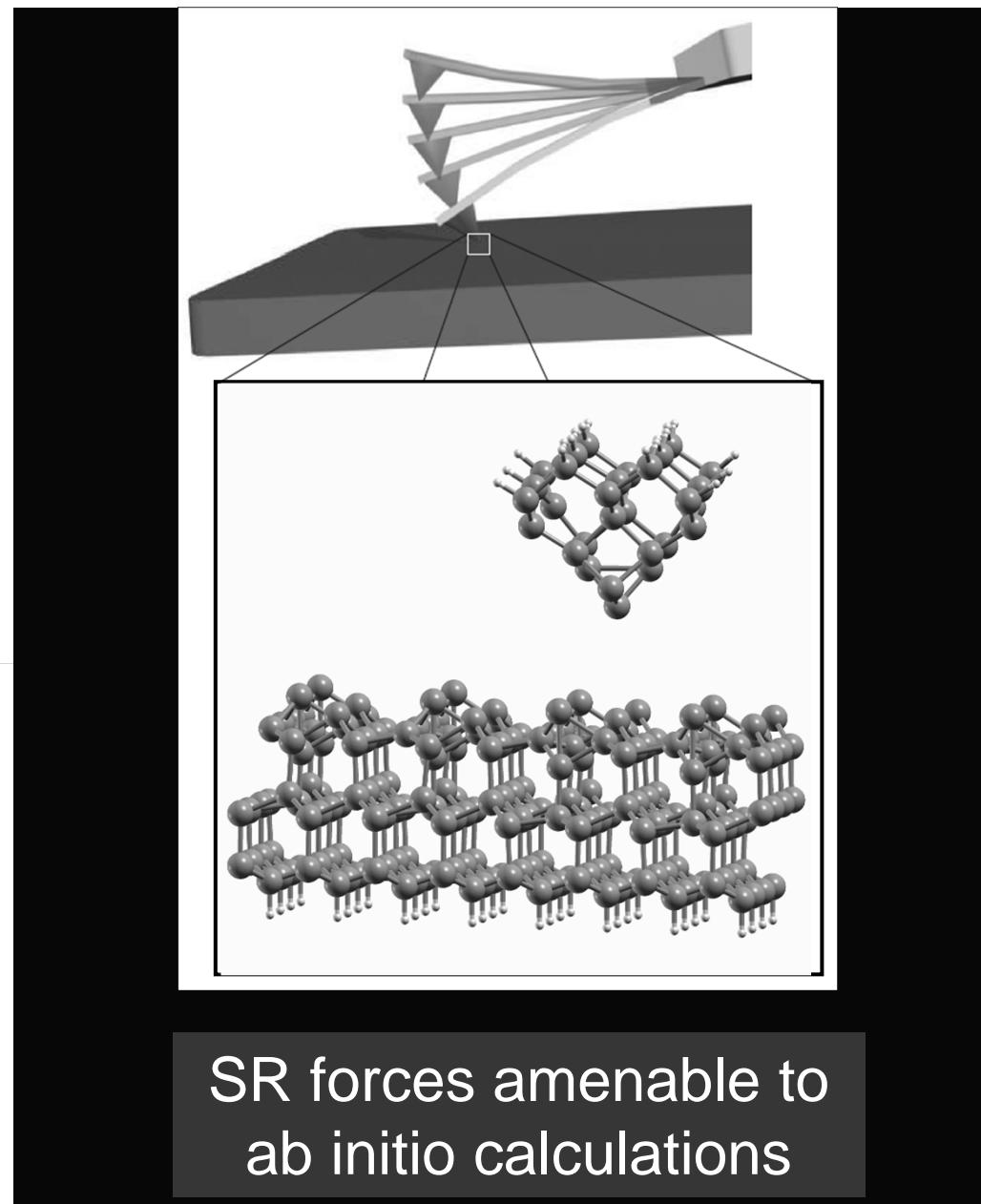
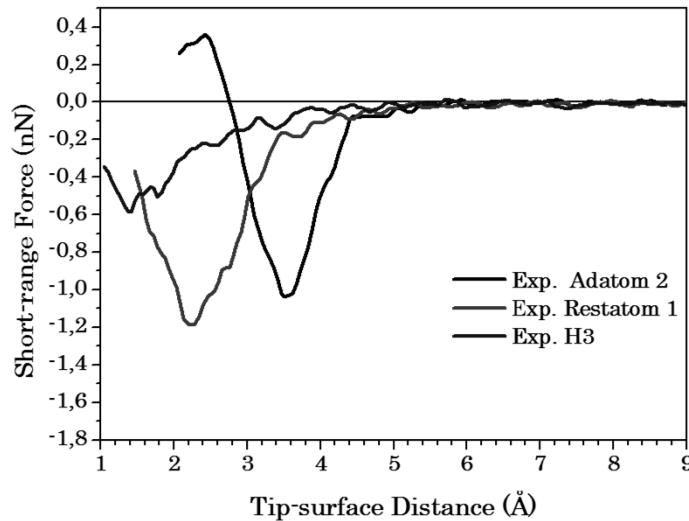


L. Gross et al, Science 325, 1110 (2009)

# Dynamic Force Spectroscopy: Access to $F_{ts}$



Inversion  
algorithms



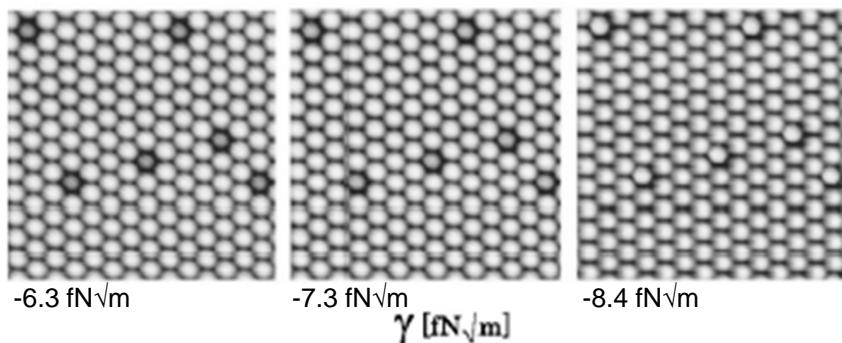
SR forces amenable to  
ab initio calculations

# 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).

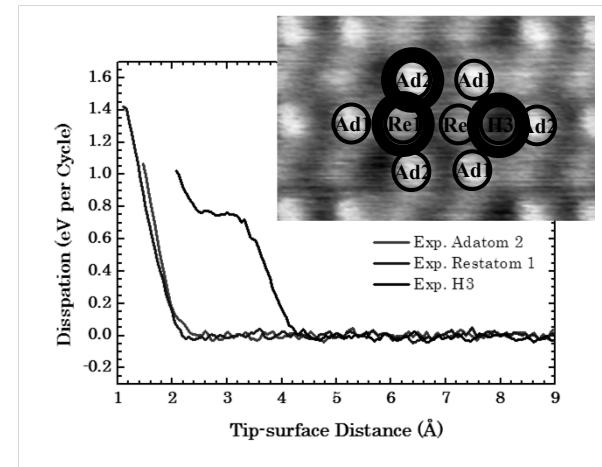
2. IMAGING: changes in topography: access to the real surface structure?



## 3. CHEMICAL IDENTIFICATION:

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

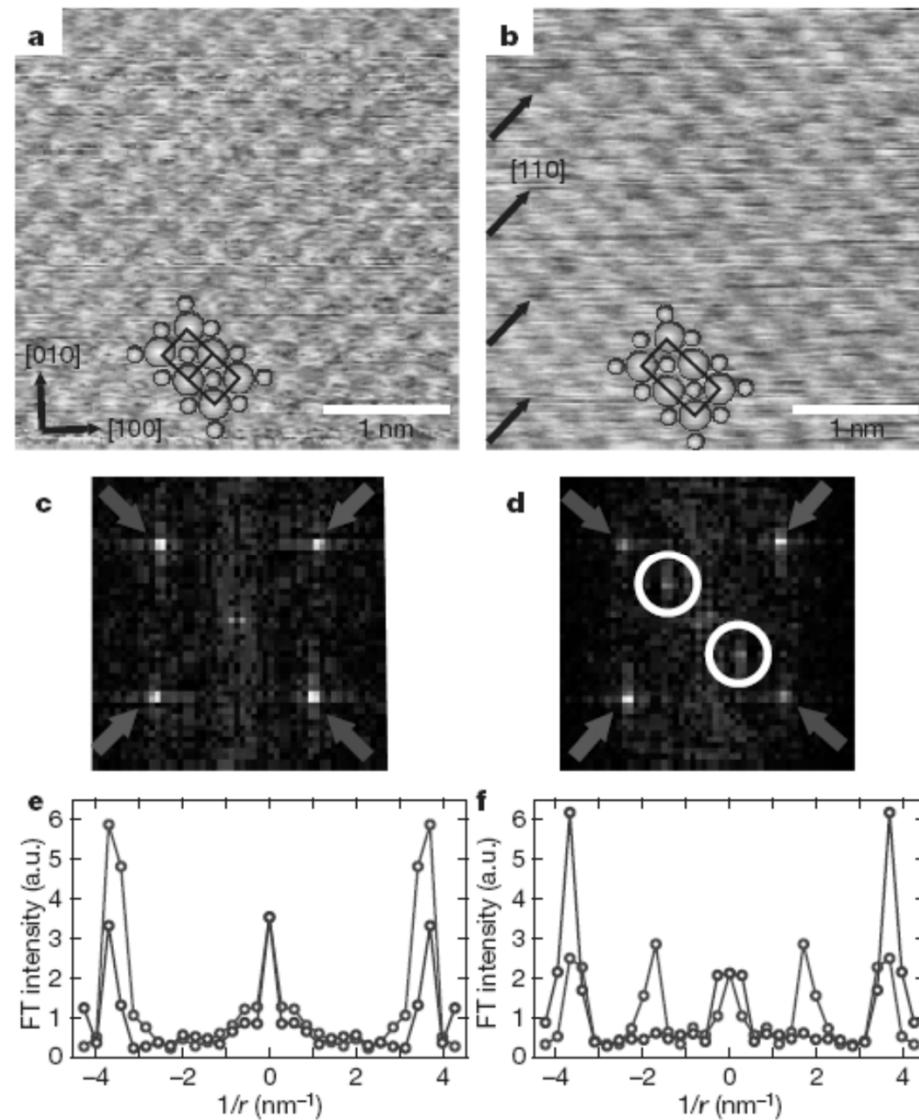
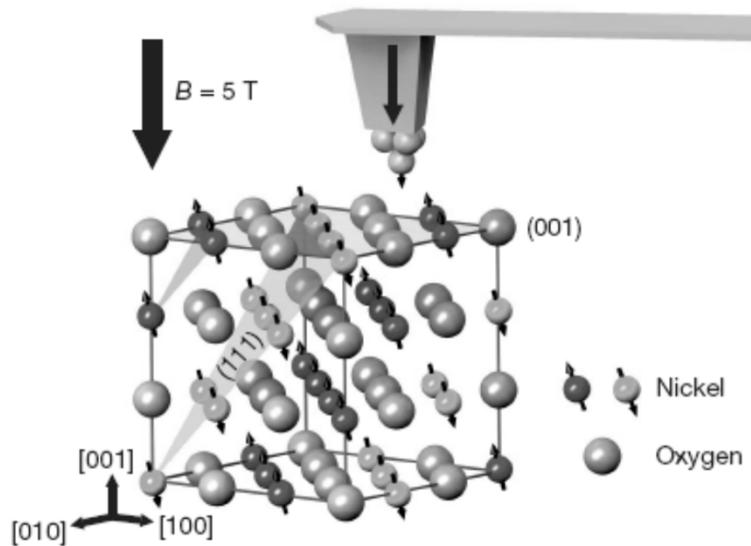
Y. Sugimoto et al Nature 446, 64 (2007).



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



# Magnetic exchange force microscopy with atomic resolution

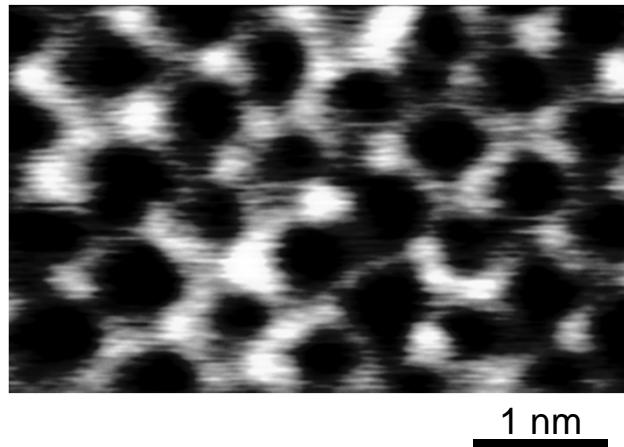


U. Kaiser, A. Schwarz & R. Wiesendanger, Nature 446, 522 (2007)

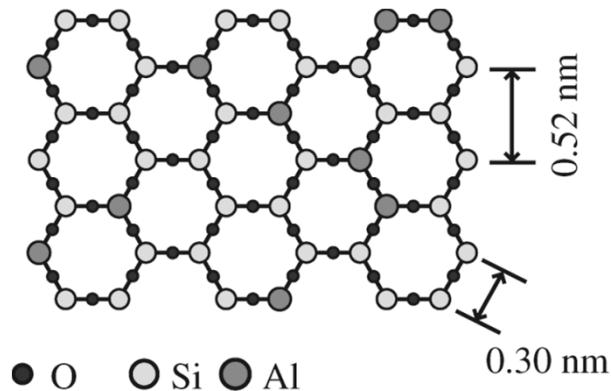
# High-Resolution FM-AFM Imaging in Liquid

True Atomic Resolution (2005)

FM-AFM Image of Mica in Water



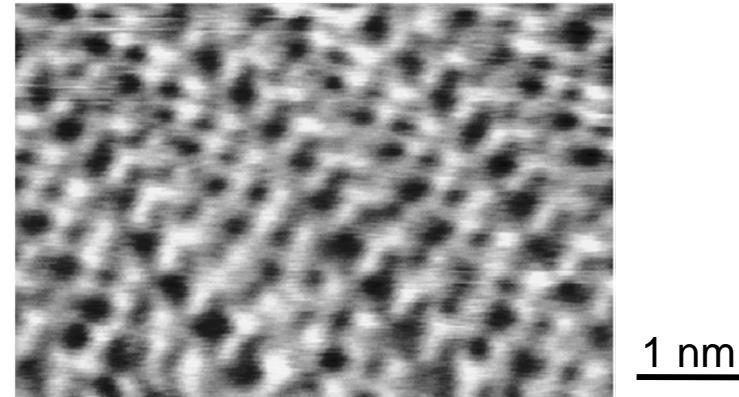
Cleaved Mica Surface



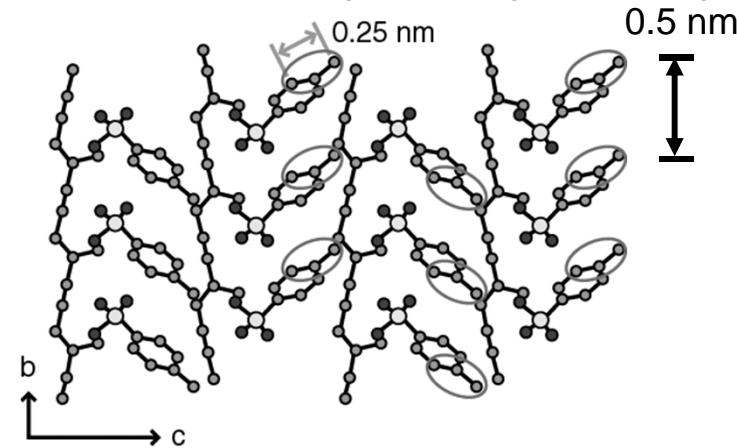
Fukuma et al. APL 87 (2005) 034101

True Molecular Resolution (2005)

Polydiacetylene Single Crystal in Water



bc-plane of Polydiacetylene Crystal



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