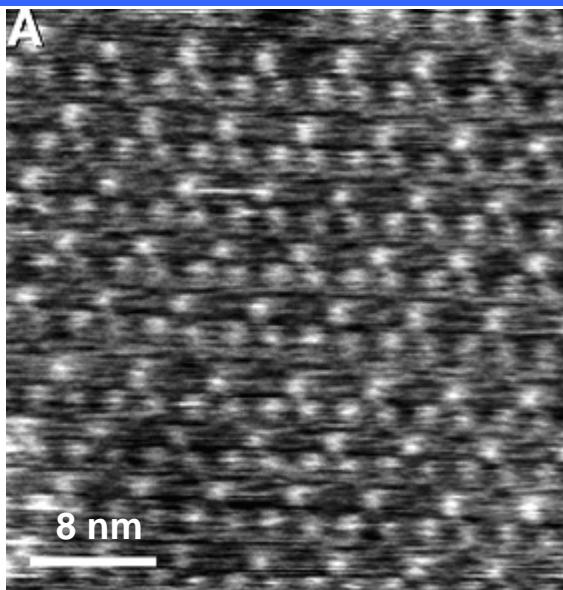


Frontiers of SPM, 5 Oct. 2006

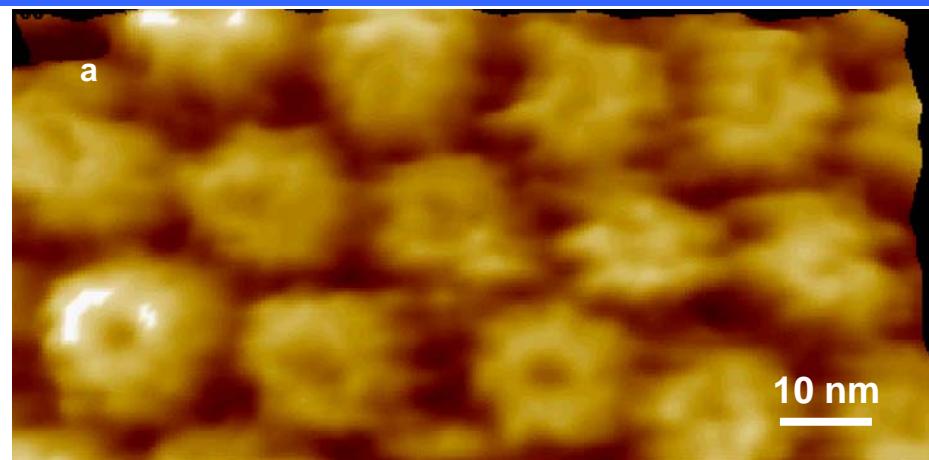
# The nanomechanics of Compositional Mapping by Amplitude Modulation AFM

## Outline

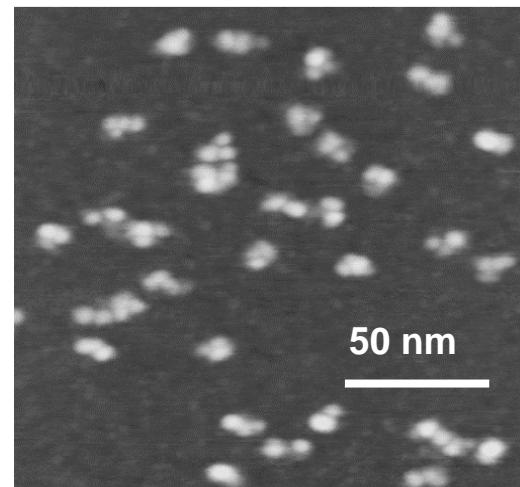
- i). Forces and molecular resolution
- ii). The physics of phase Imaging:  
elastic vs. Inelastic processes
- iii). Identification of energy dissipation  
Quantitative information
- iv). Enhancing Force Sensitivity: Beyond  
1st mode Imaging
- v). Summary



PM in liquid, D.J. Muller et al.  
Biophys. J. 77, 1150 (1999)



GroEL in liquid, T. Ando et al. PNAS 98, 12468 (2001)



IgG, SanPaulo, Garcia, Biophys.  
J. 78, 1599 (2000)

## Forces and Resolution in AM-AFM (biomolecules)

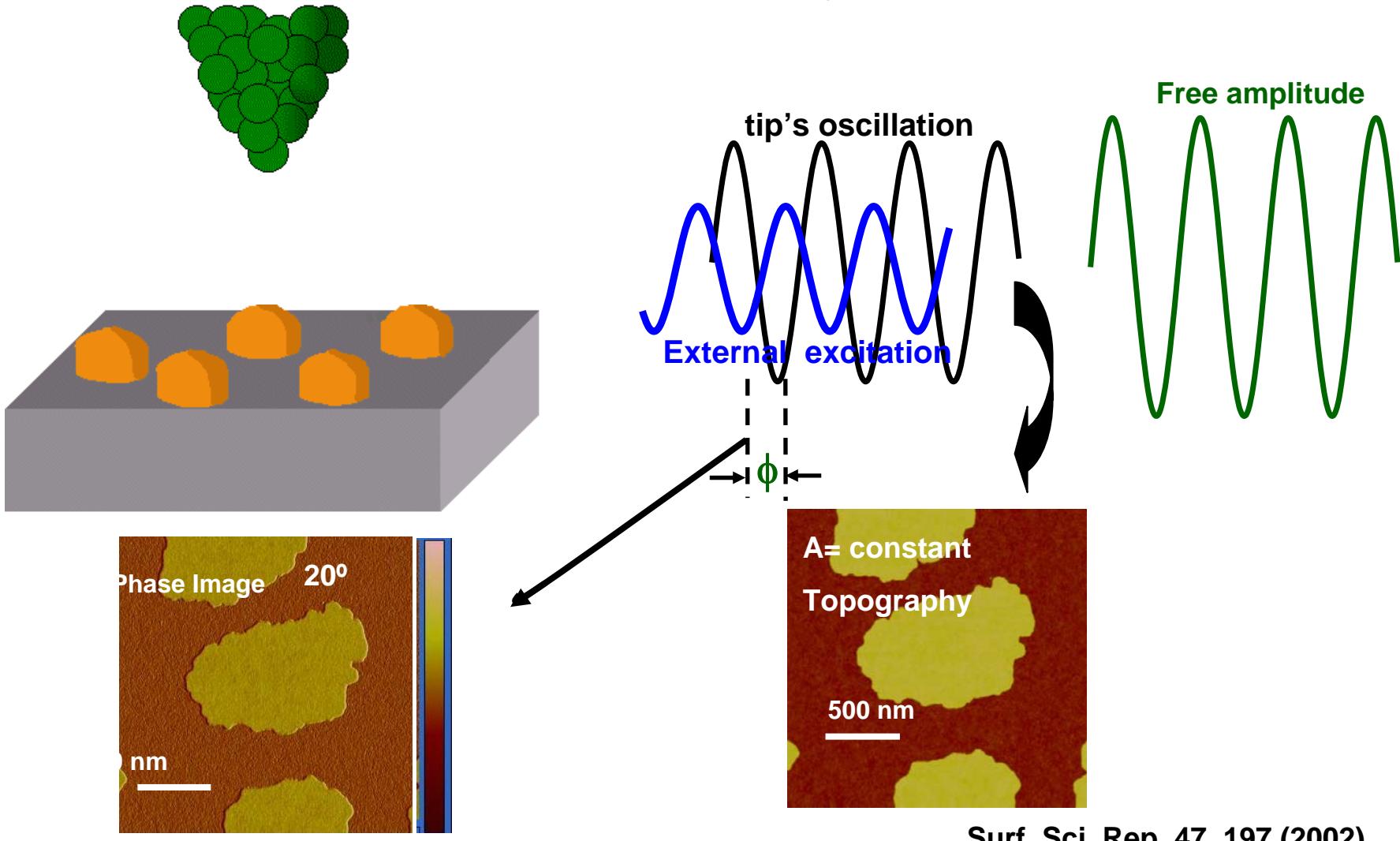
verified values

Medium	Force (pN)	Force sensitivity	Resolution* (nm)
Air IgG	300	0.1	3
Liquid 1 PM crystal	100	0.05	1.1
Liquid 2 GroEL patches	No available	No available	2

## Some forces in molecular biology

Process	Force (pN)	length scale
DNA entropic elasticity	0.01-10	0.8 L
DNA intrinsic elasticity	10-70	0.8-1 L
Protein unfolding	15-50	3-5 nm

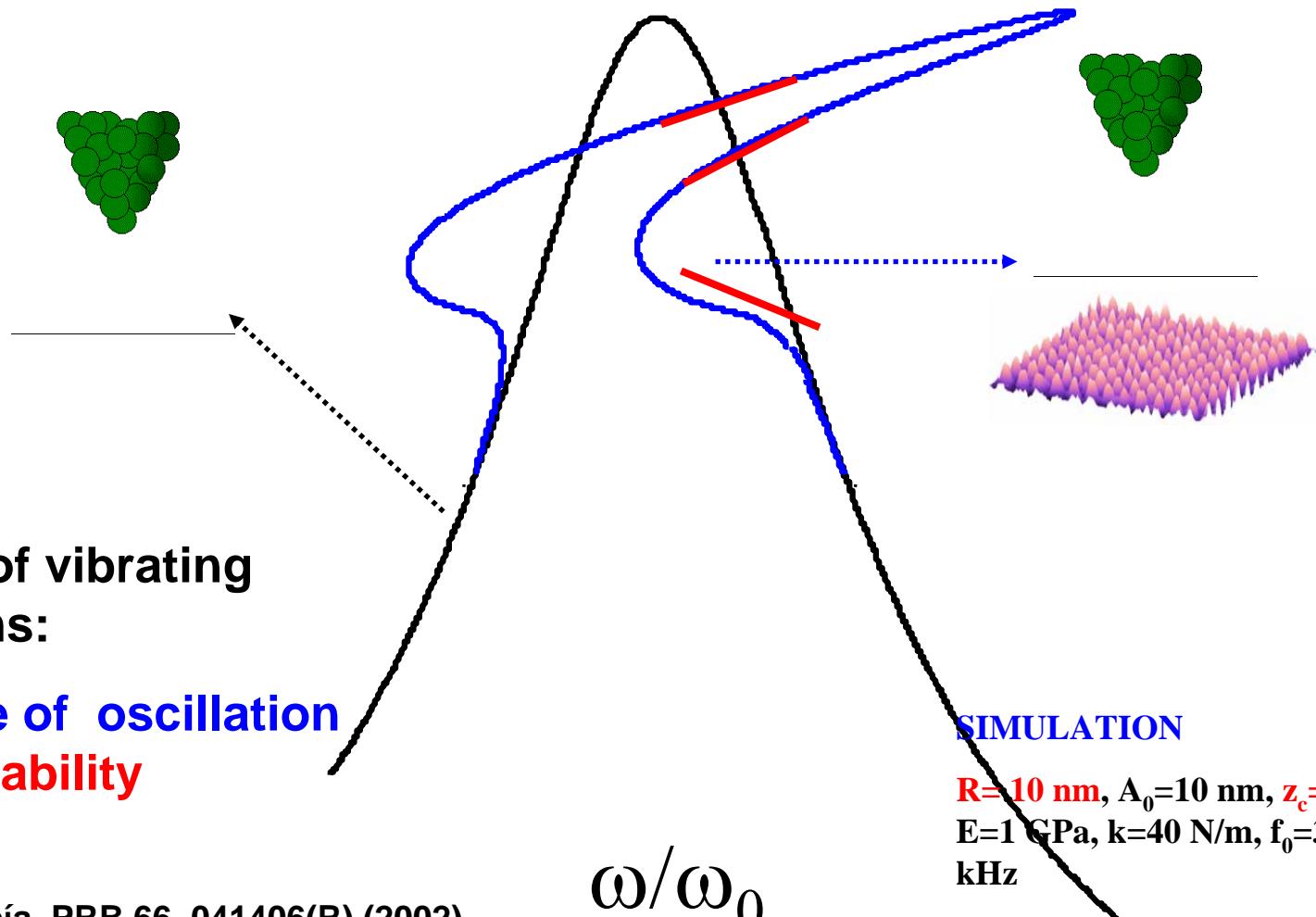
## Amplitude modulation AFM (AM-AFM) amplitude, phase-shift and resonance frequency



# Resonance Curves

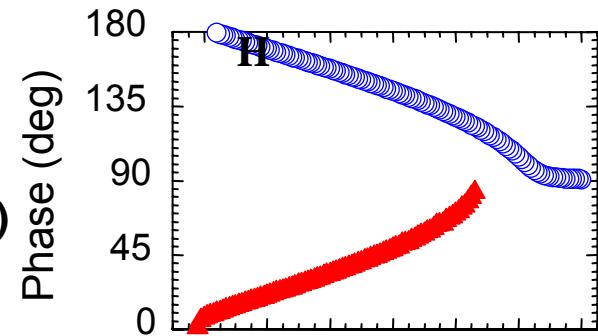
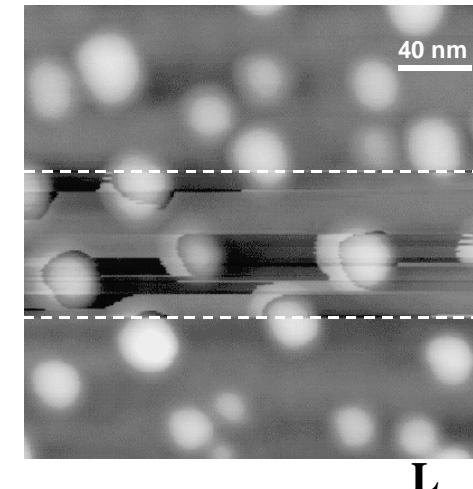
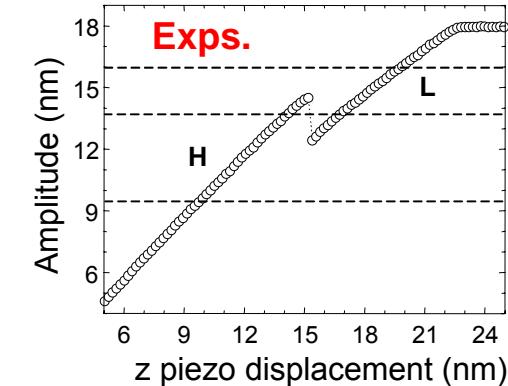
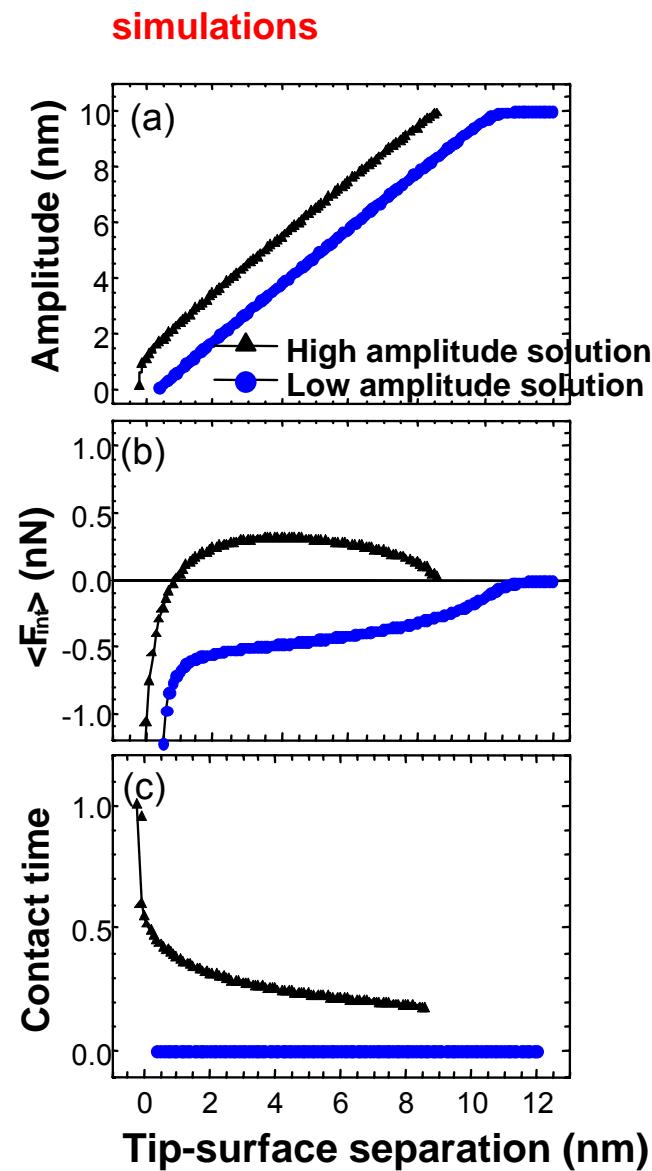
Free oscillating tip (10 nm )

Interacting tip (10 nm size )



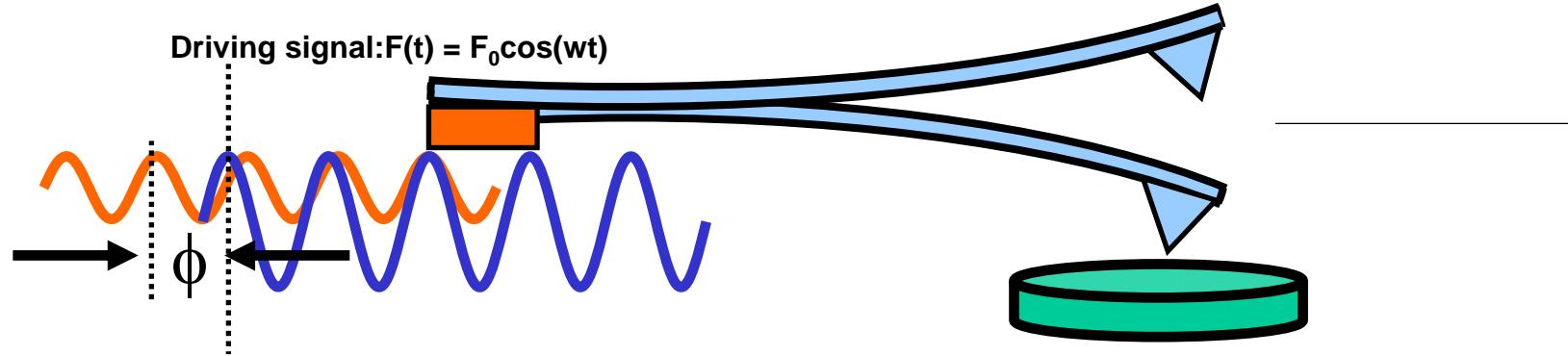
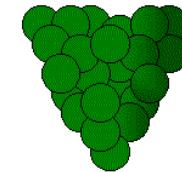
H and L states have different properties

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

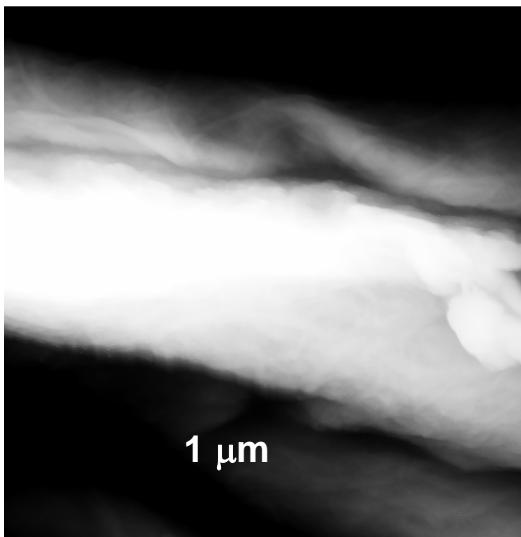


# Phase Imaging

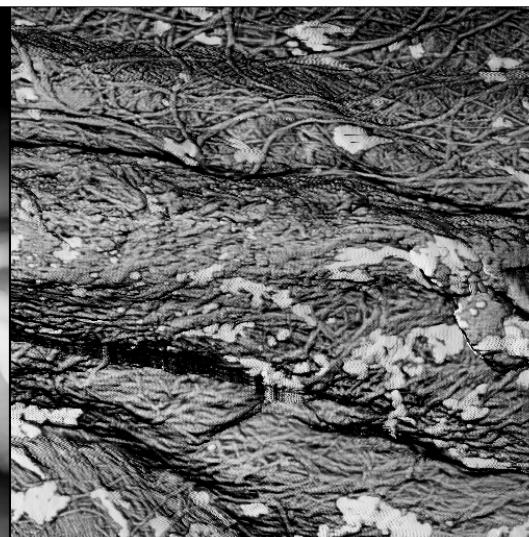
The dynamic response of the cantilever is modified by the tip-surface interactions



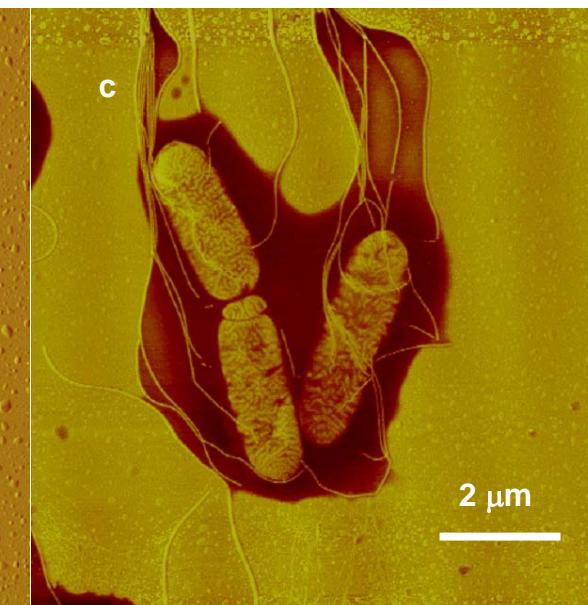
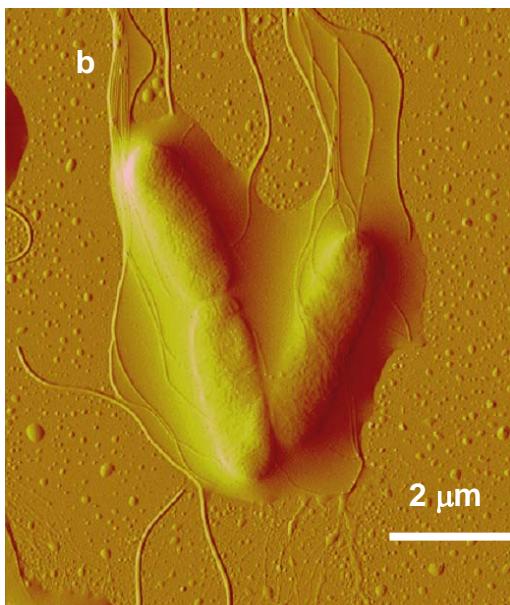
## Topography



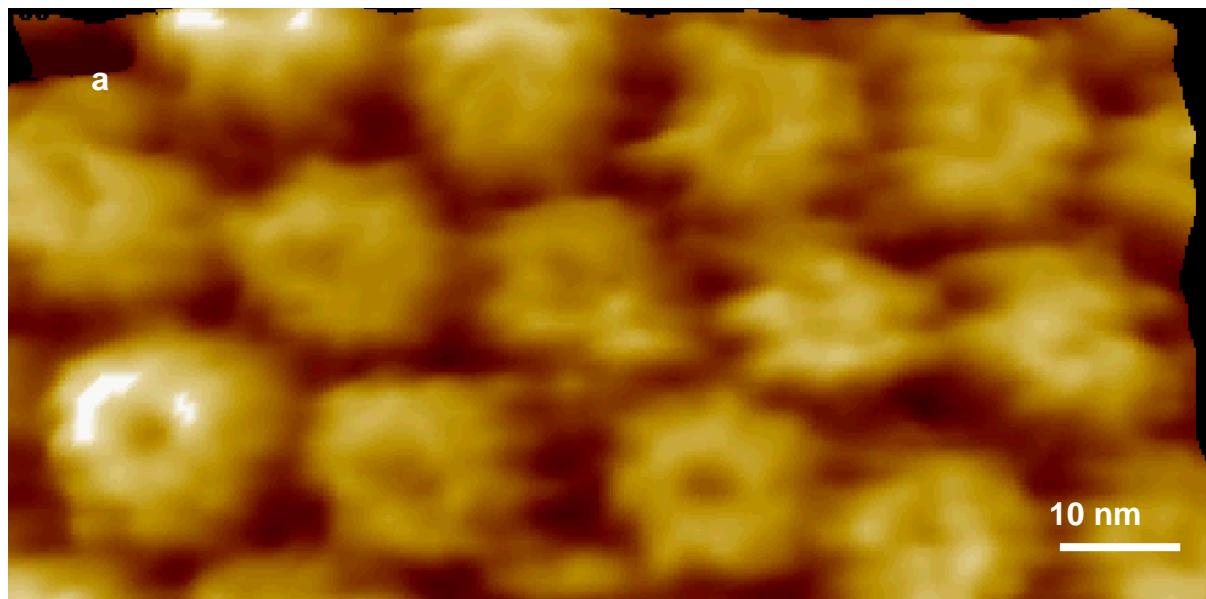
## Phase Image



Wood pulp fiber, D.A. Chernoff (1995)



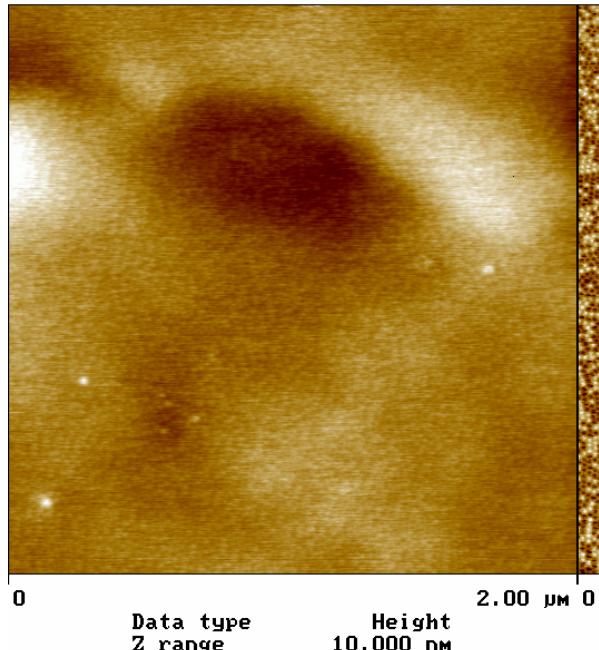
*S. Typhimurium* cells, R. Acvi, Biophys. J. (2006)



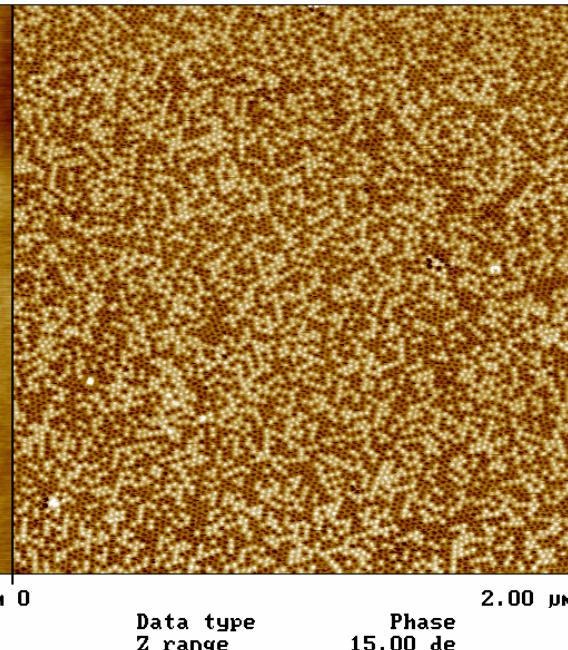
**GroEL in liquid, T. Ando et al. PNAS 98, 12468 (2001)**

# Polymers: Morphology and Structure

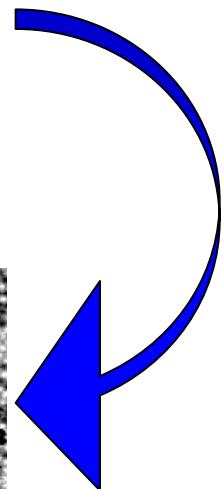
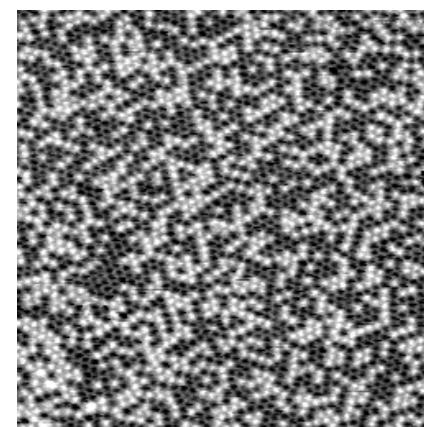
Topography



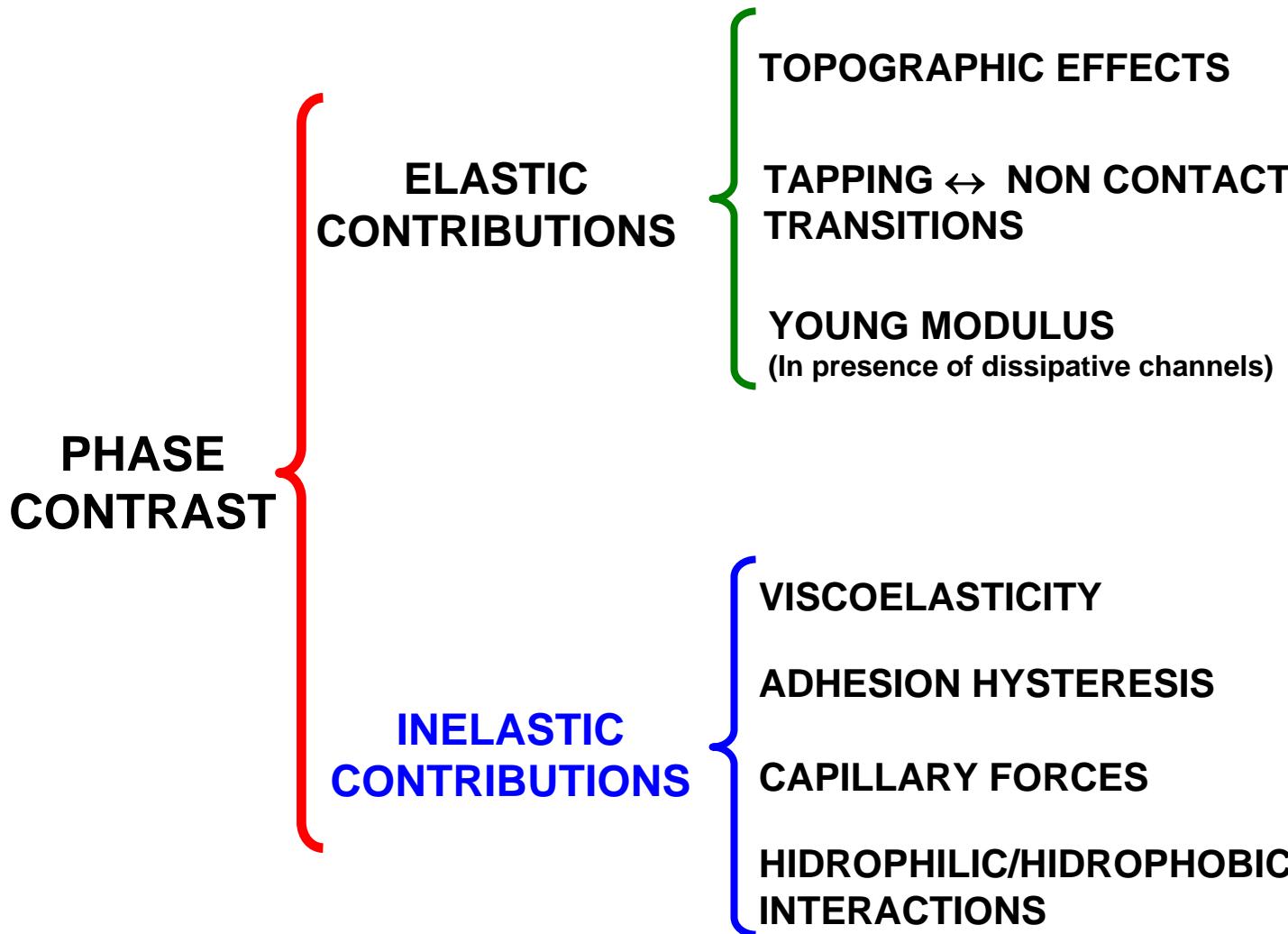
Phase Image



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)

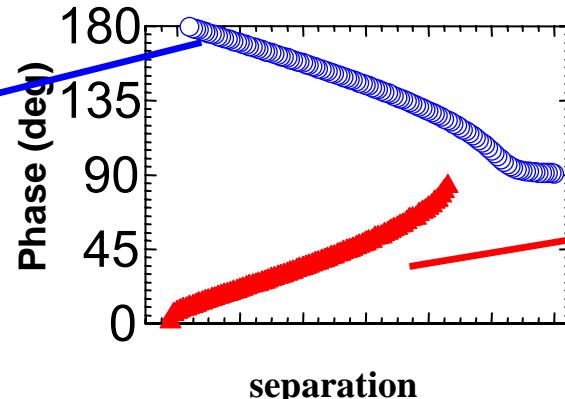


# Sources of Phase Imaging Contrast



# Phase shift and tip-surface interactions

Attractive regime (L branch)



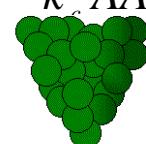
Repulsive regime (H branch)



The virial theorem applied to the tip allows to deduce

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

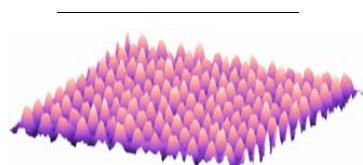
$$\cos \phi = \frac{2Q}{k_c A A_0} \left[ \frac{\langle F_{ts} \rangle^2}{k_c} - \langle F_{ts} \cdot z \rangle + \frac{1}{2} k_c A^2 \left( 1 - \frac{\omega^2}{\omega_0^2} \right) \right] \rightarrow \cos \phi \approx - \frac{2Q \langle F_{ts} \cdot z \rangle}{k_c A A_0}$$



Conservative interactions and small contact times

$$\cos \phi \approx 2 \frac{\langle F_{ts} \rangle}{\langle F_0 \rangle}$$

The phase shift depends on the sign of the interaction



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## **Phase shift and energy dissipation**

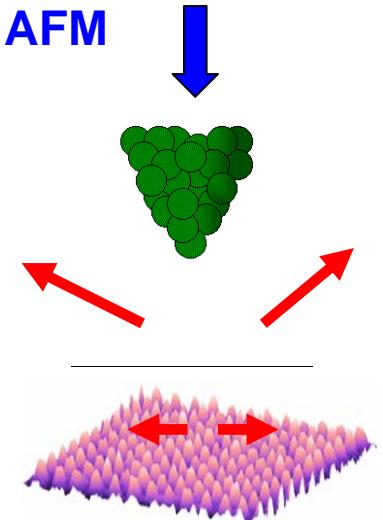
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## How to measure dissipation in amplitude modulation AFM steady state solution

$$Z = Z_0 + A \cos(\omega t - \phi)$$

Dynamic equilibrium in AM-AFM

$$\bar{E}_{ext} = \bar{E}_{med} + \bar{E}_{dis}$$



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

topography

composition

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

$$\sin \phi = \boxed{A_{sp}=cte} - + \frac{QE_{dis}}{\pi k A_0 A_{sp}}$$

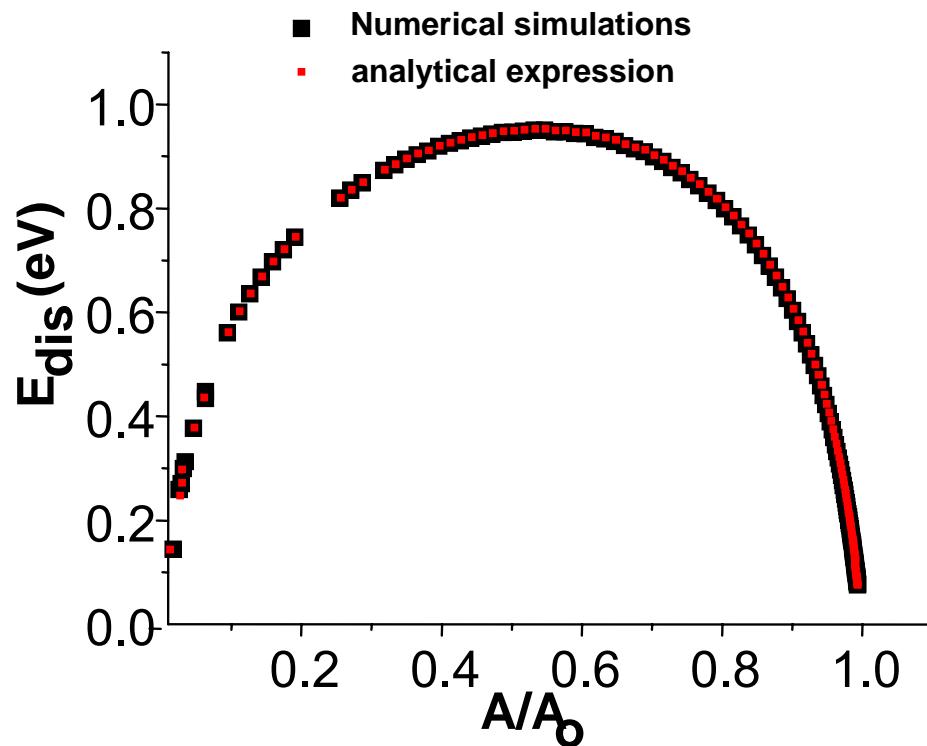
$$E_{dis} = \int (F_{ts}) \frac{dz}{dt} dt$$

**A<sub>sp</sub>=cte.; phase shifts are linked to tip-surface inelastic interactions**

Tamayo, García, APL 71, 2394 (1997)  
Tamayo, García APL73, 2926 (1998)

$$E_{dis} = (\sin\phi - \frac{A}{A_0}) \frac{A}{A_0} \frac{\pi k A_0^2}{Q}$$

$$E_{\text{dis}} = \left( \sin \varphi - \frac{A}{A_0} \right) \frac{A}{A_0} \frac{\pi k A_0^2}{Q}$$

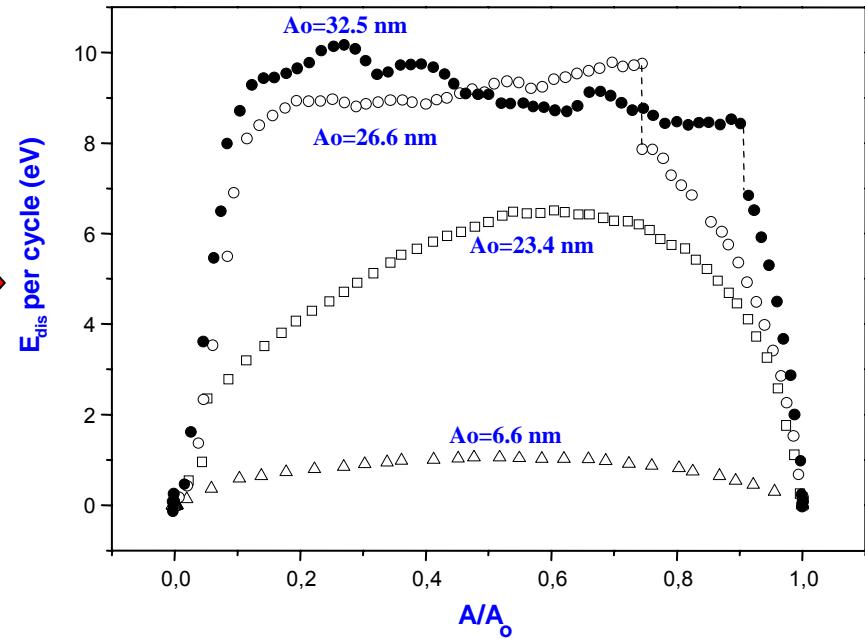
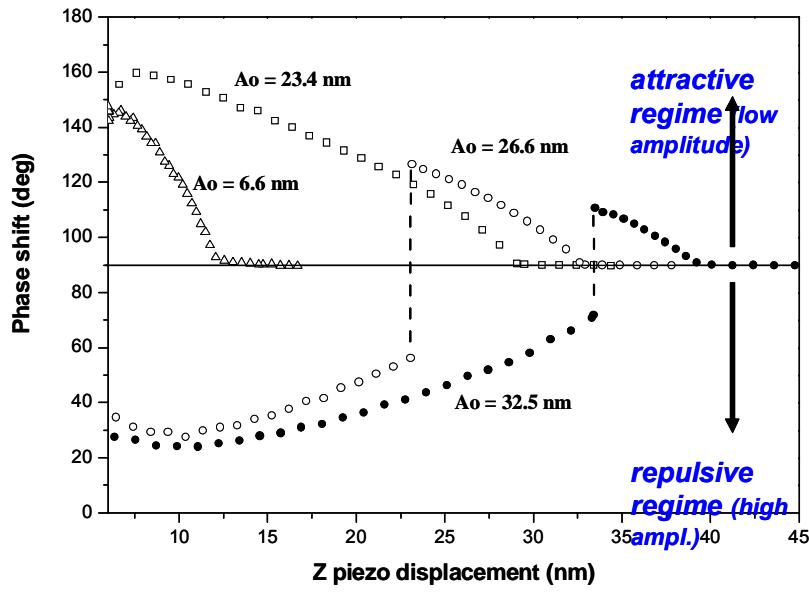


$$m \frac{d^2 z}{dt^2} = -k_z + \frac{m \omega_0}{Q} \frac{dz}{dt} + F_{ts} + F_0 \cos \omega t$$

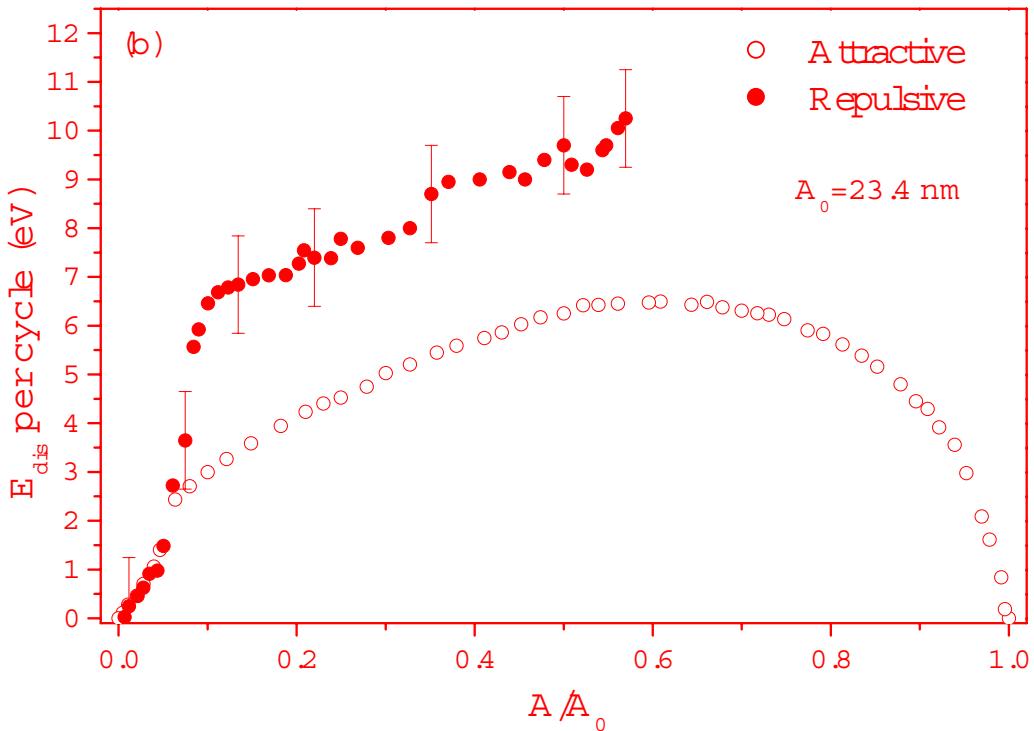
Fixed by the observer  $A_0, Q, k, \omega_0, \omega$

## From Phase shifts to energy dissipation

$$E_{\text{dis}} = \left( \sin\varphi - \frac{A}{A_0} \right) \frac{A}{A_0} \frac{\pi k A_0^2}{Q}$$



Martinez, Garcia, Nanotechnology 17, S167 (2006)



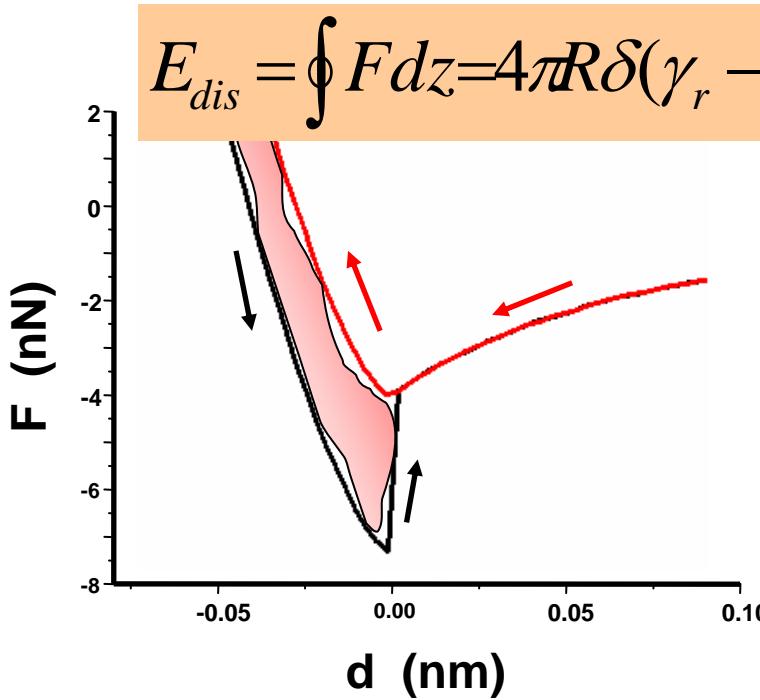
The dissipated energy is higher on the repulsive regime  
Dissipation avoids artefacts due to regime changes of contrast

## **Applications of Phase Imaging**

# **Identification of Nanoscale dissipation Processes**

# Dissipation at the Nanoscale: Surface Adhesion Hysteresis

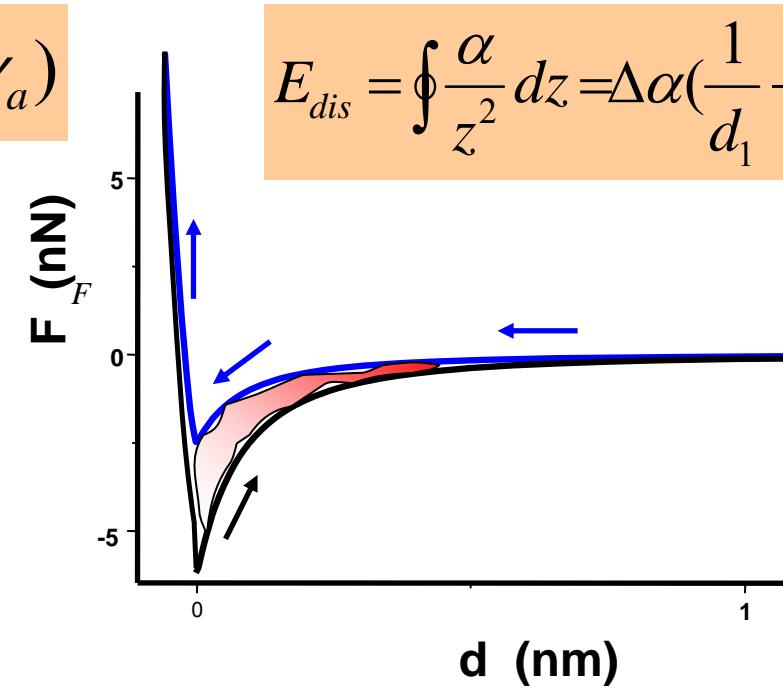
## Short range



$A_0 = 40$  nm,  $E = 150$  GPa,  $Z_c = 20$  nm;  $\Delta H = 1$   
 $E_i = 33$  mJ/m<sup>2</sup>;  $E_v = 66$  mJ/m<sup>2</sup>;  $k = 2$  N/m,  $Q = 150$

$$F_{DMT} = Y^* R^{1/2} \delta^{3/2} - 4\pi R \gamma$$

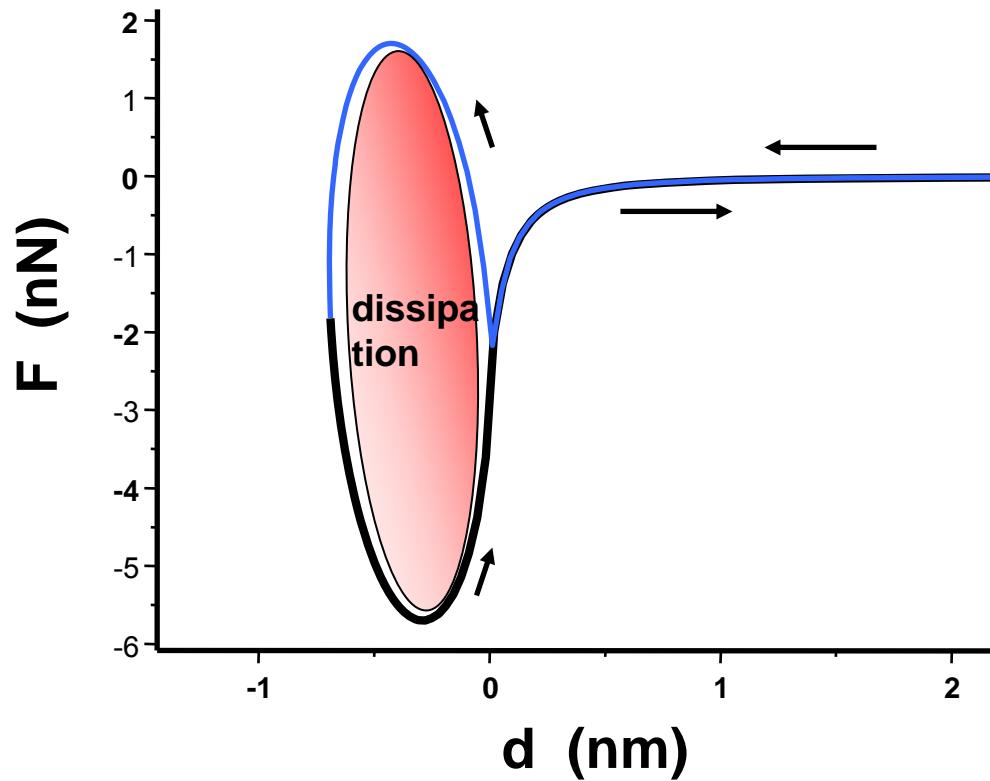
## Long range



$A_0 = 6.6$  nm,  $E = 150$  GPa,  $Z_c = 3$  nm.  $\Delta H = 2.5$   $E_i = 20$  mJ/m<sup>2</sup>.  $E_v = 40$  mJ/m<sup>2</sup>

$$F_{LR} = -\frac{\alpha}{z^2}$$

# Dissipation at the Nanoscale: viscoelasticity



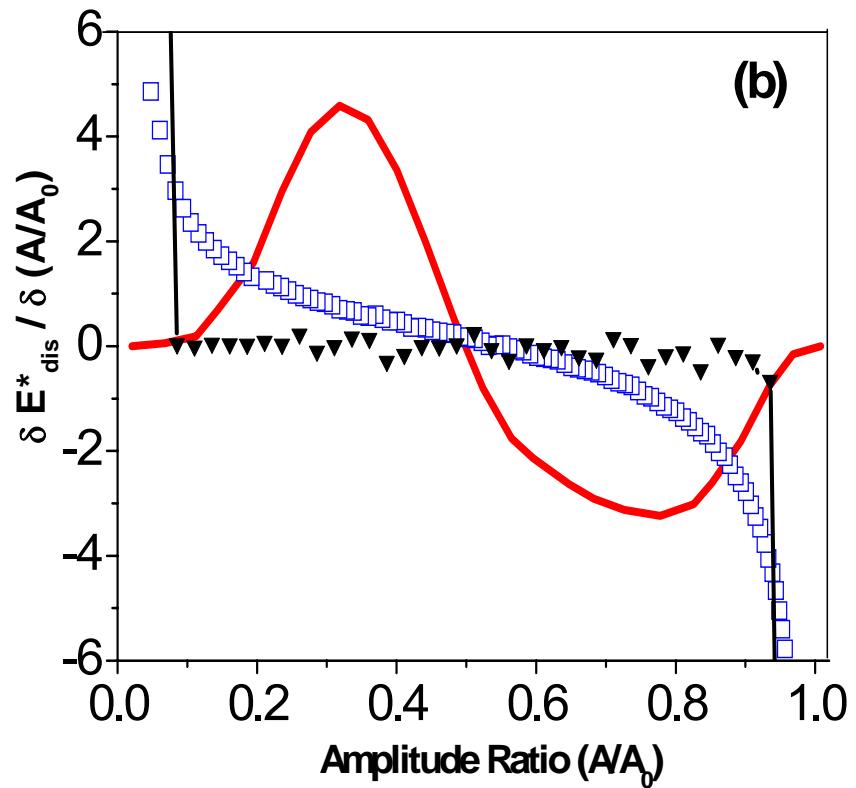
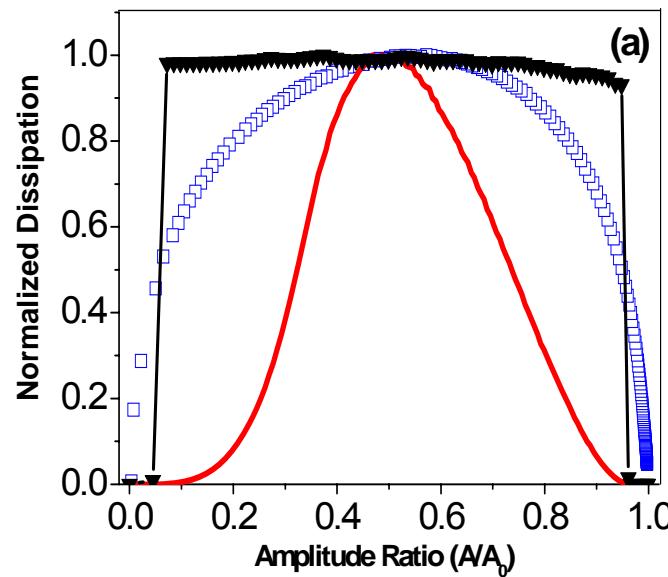
$A_0 = 15$  nm,  $\eta = 500$  Pa.s;  $E = 500$  MPa;  $Z_c = 6.5$  nm

$$F_v = \eta \sqrt{R \delta} \frac{d\delta}{dt}$$

Red: viscosity

Blue: long range adhesion hysteresis

Black: short range ad. hysteresis



The derivative of the dissipative energy singles out the dissipative process

Analogy: Tersoff-Hamann theory of STM

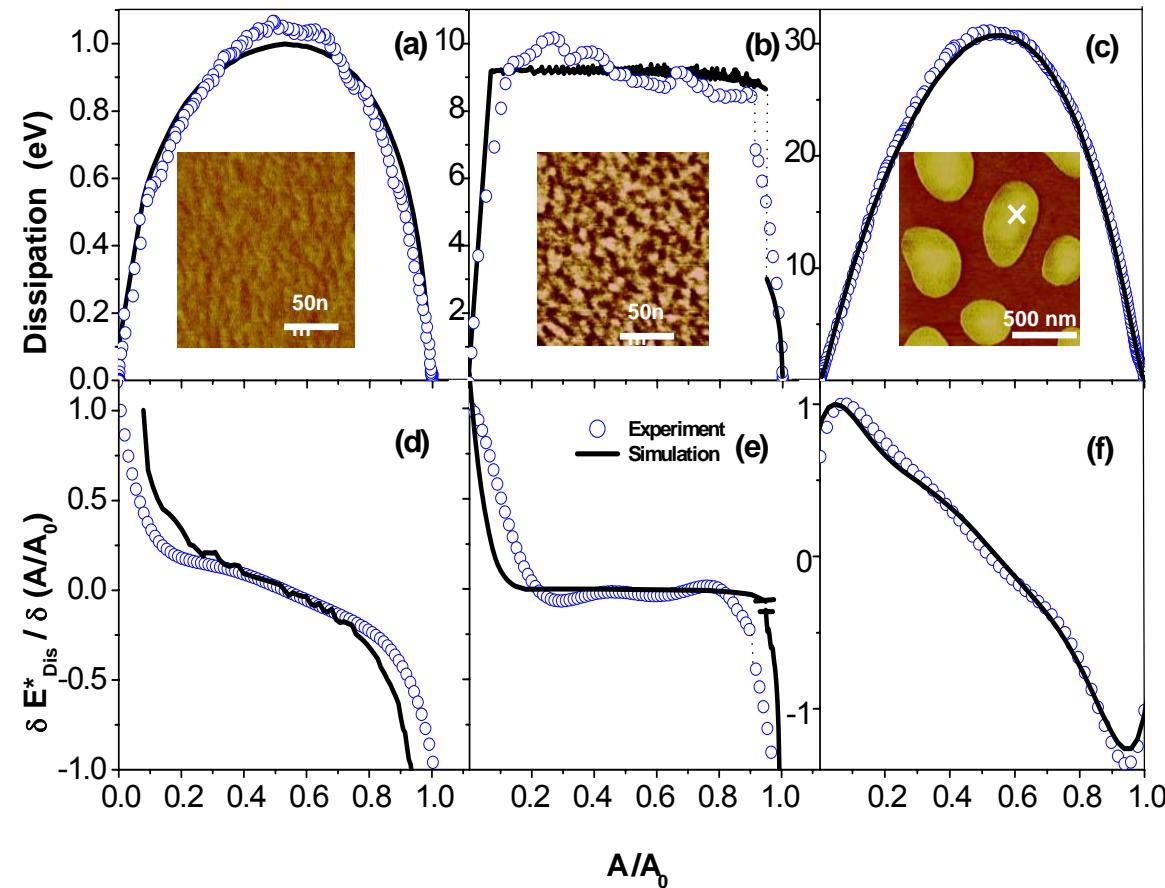
$$G \equiv \frac{dI}{dV} \propto \rho_{Sample}(E_F + eV) \times \rho_{Tip}(E_F) \times T(eV, z, \phi_p)$$

## Identification of dissipation mechanisms

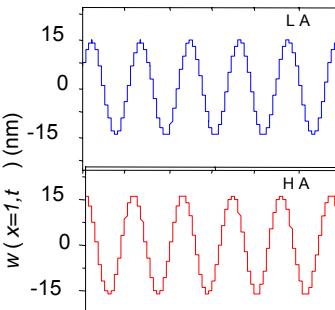
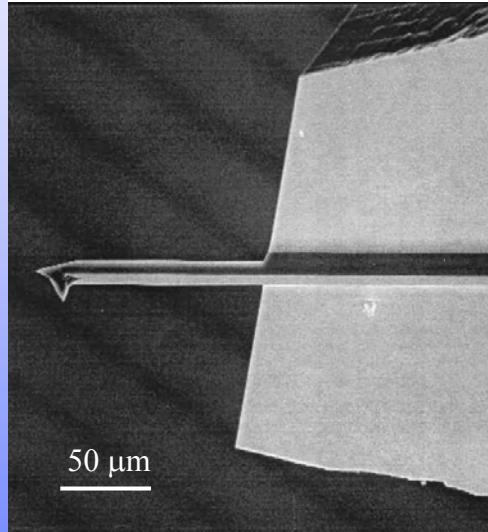
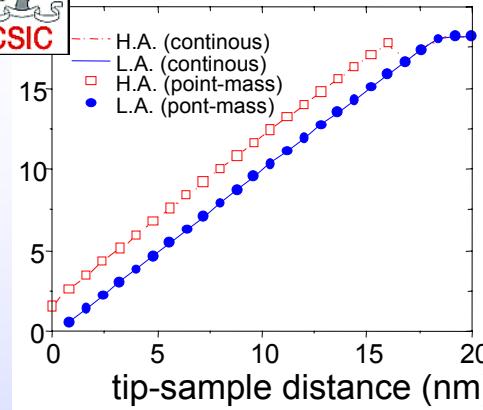
Long range dissipation      adhesion hysteresis      viscoelasticity

blue: exps.

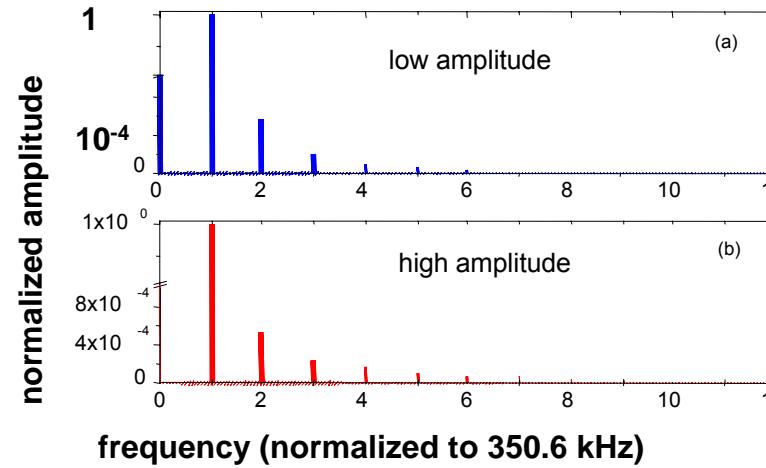
black: theory



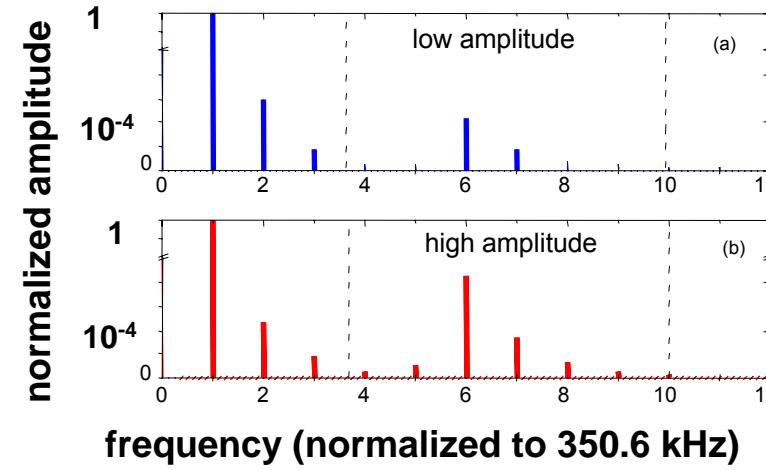
Garcia, Gomez, Martinez, Patil, Dietz, Magerle, Phys. Rev. Lett. 97, 016103 (2006).



## Point-mass model



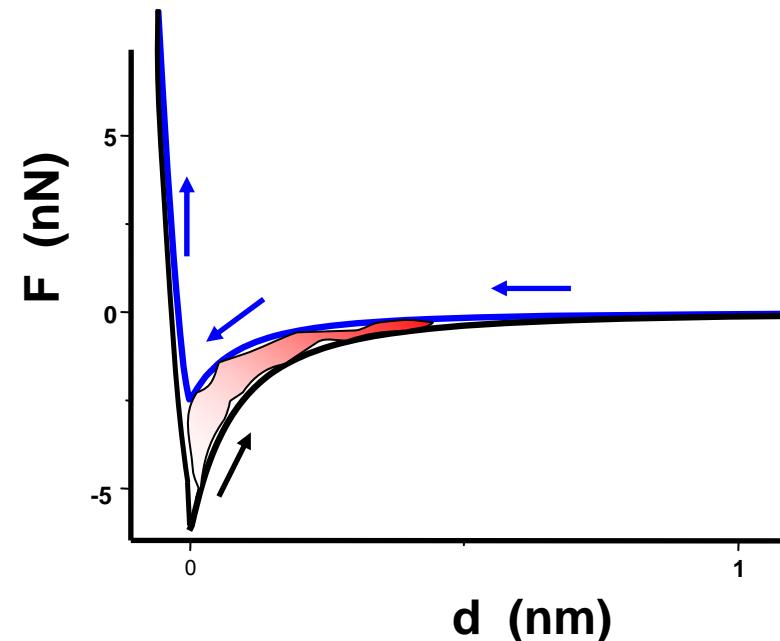
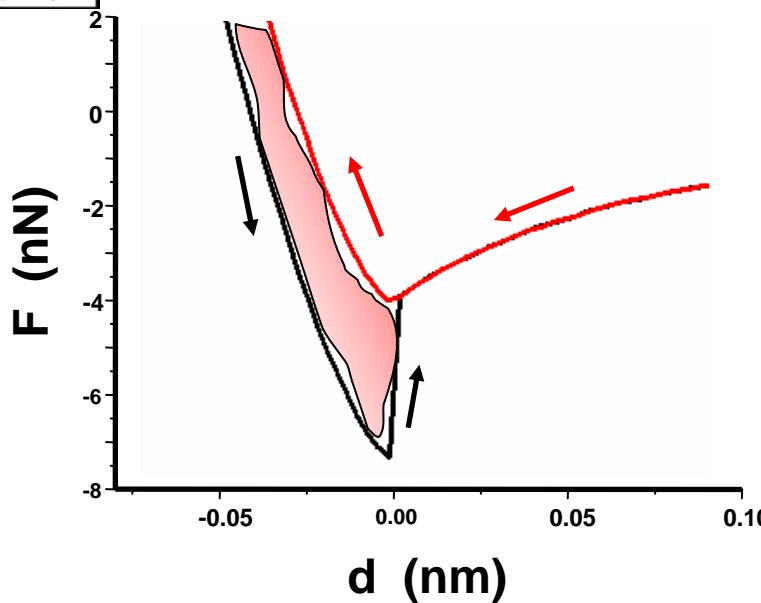
## Continuous model



The components of higher order modes and harmonics are several orders of magnitude smaller than the fundamental

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

# Forces and Molecular Resolution in AM-AFM



## Some forces in molecular biology

Process	Force (pN)	length scale
DNA entropic elasticity	0.01-10	0.8 L
DNA intrinsic elasticity	10-70	0.8-1 L
Protein unfolding	15-50	3-5 nm

## **Improving force sensitivity**

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## **Beyond 1st mode Imaging**

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ABSTRACT + LINKS

APPLIED PHYSICS LETTERS

VOLUME 84, NUMBER 3

19 JANUARY 2004

## Compositional mapping of surfaces in atomic force microscopy by excitation of the second normal mode of the microcantilever

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(Received 4 August 2003; accepted 20 November 2003)

We propose a method for mapping the composition of a surface by using an amplitude modulation atomic force microscope operated without tip-surface mechanical contact. The method consists in exciting the first two modes of the microcantilever. The nonlinear dynamics of the tip motion, the coupling of its first two modes, and the sensitivity of the second mode to long-range attractive forces allows us to use this mode to probe compositional changes while the signal from the first mode is used to image the sample surface. We demonstrate that the second mode has a sensitivity to surface force variations below  $10^{-11}$  N. © 2004 American Institute of Physics.

[DOI: 10.1063/1.1642273]

$$\frac{EI}{L^4} \frac{\partial^4}{\partial x^4} \left[ w(x,t) + a_1 \frac{\partial w^2(x,t)}{\partial t^2} \right] + \mu b h \frac{\partial w^2(x,t)}{\partial t^2} = \text{Forces}$$

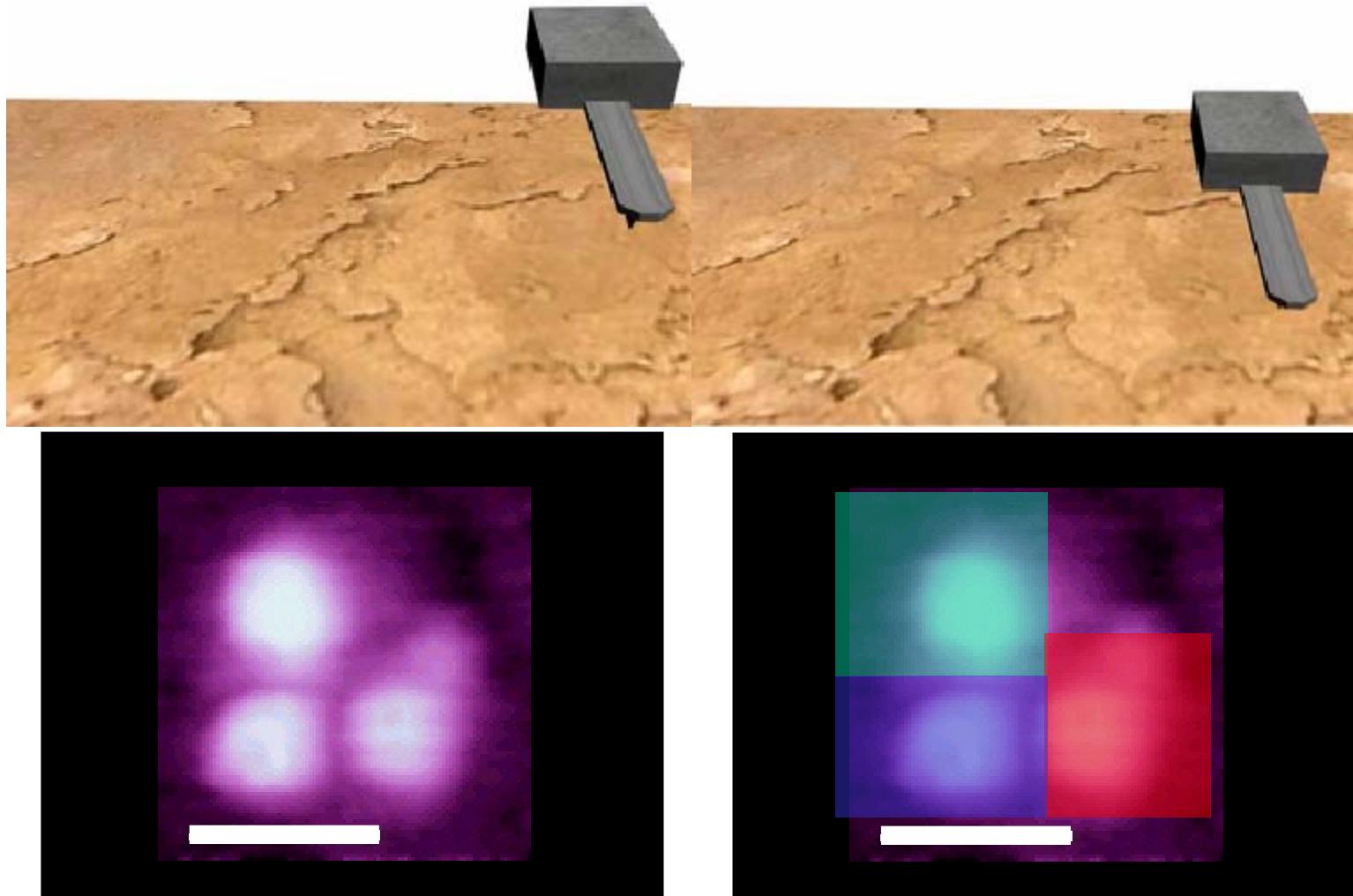


## Multipurpose Force Tool for Quantitative Nanoscale Analysis and Manipulation of Biomolecular, Polymeric and Heterogeneous Materials

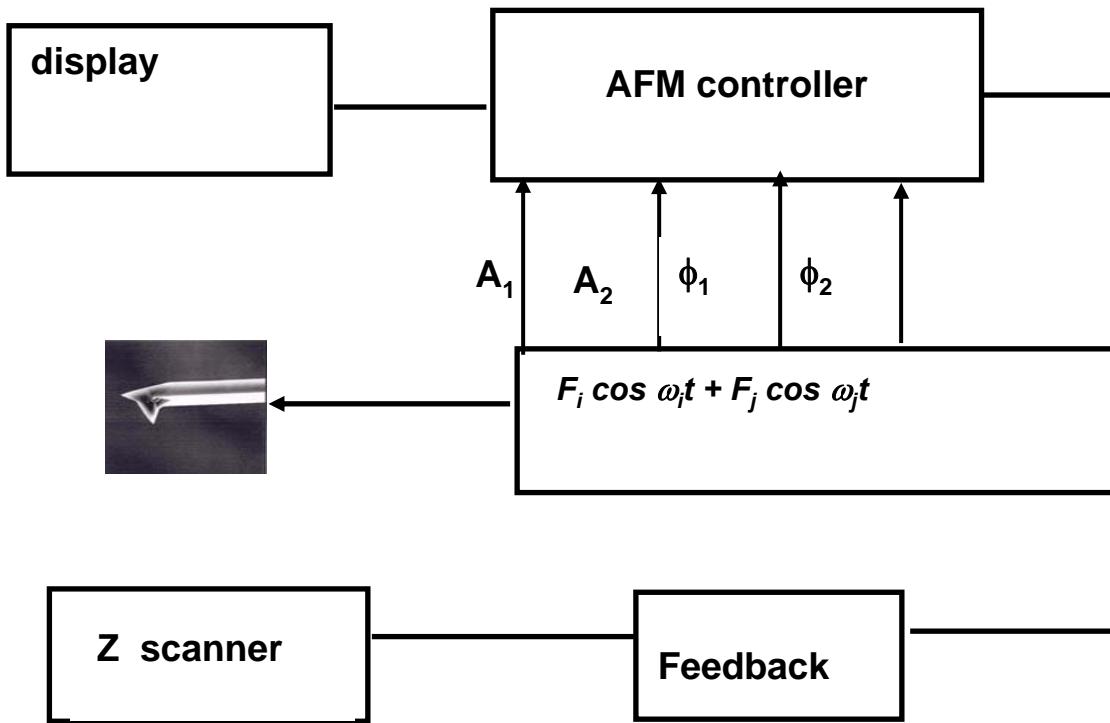


**CSIC, CNR (F. Biscarini) , Utwente (J. Vancso) , Ludwig-Maximilians-Universität (R. Stark), Chemnitz University of Technology (R. Magerle) , Universidad Autónoma de Madrid (R. Pérez), Nanoworld (C. Ritchter ) , Johannes-Kepler University (P. Hinterdorfer) , Electrónica y Diseño Aguado (I. Rodriguez)**

**ForceTool AFM**  
**Non-linear dynamics Nanomechanics, material design**



## ForceTool AFM

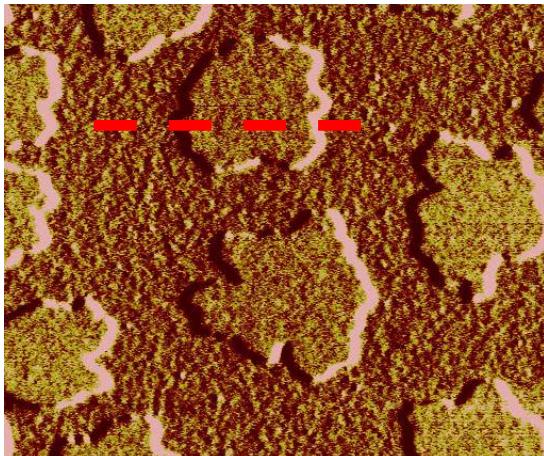


Patents: PCT/ES 2006/070016; PCT/ES 2006/070096

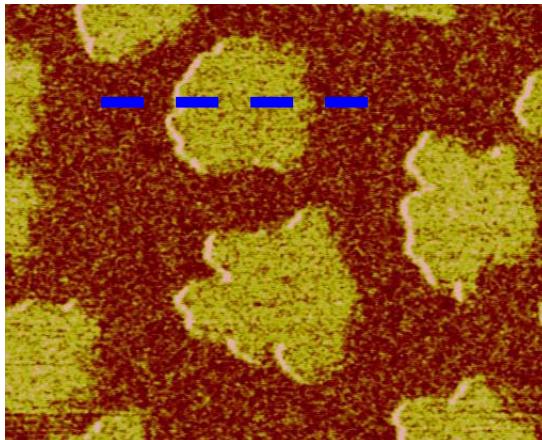
ForceTool: Proposal submitted: 12 May 2004; final: 28 October 2004;

Project started: 1 February 2005

## Tapping mode versus ForceTool phase shift

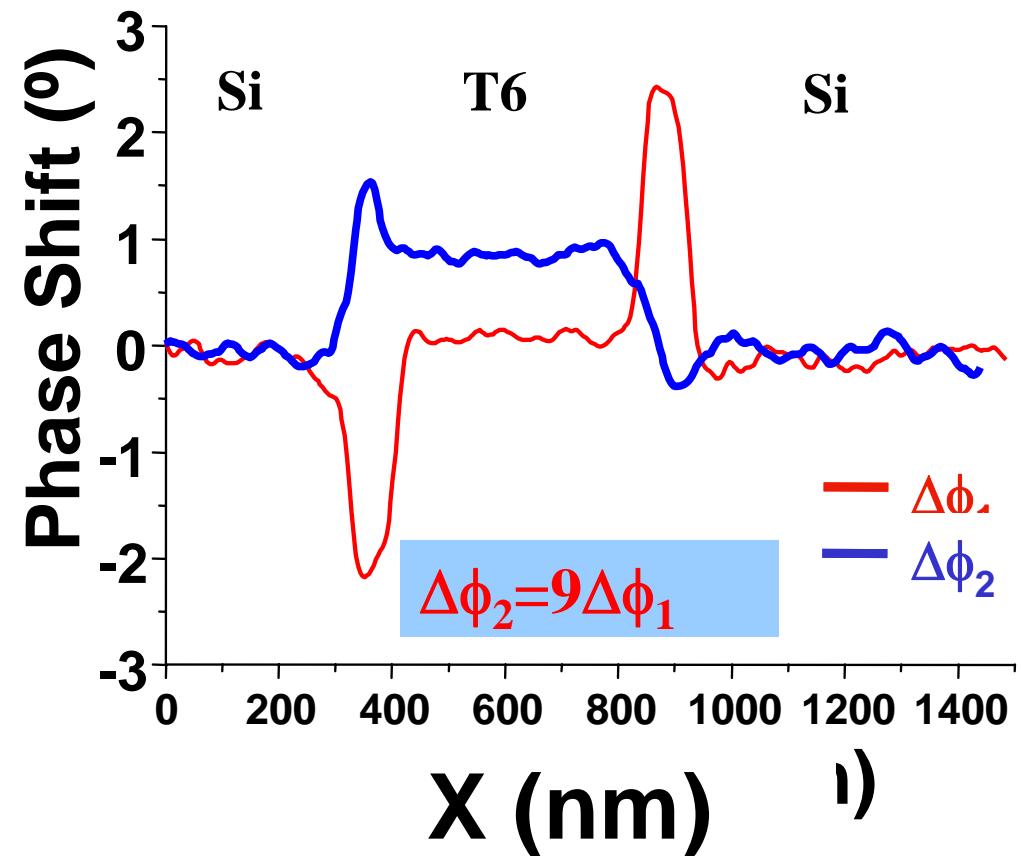


Tapping mode PHASE SHIFT

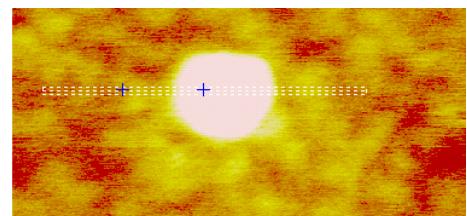


ForceTool Phase shift

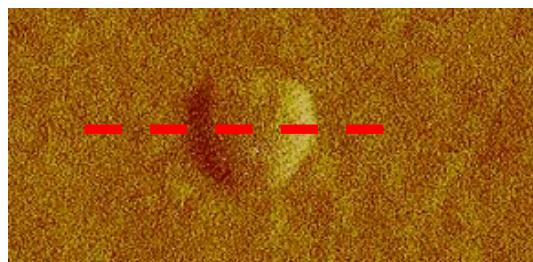
Sexithiophene on Si(100)



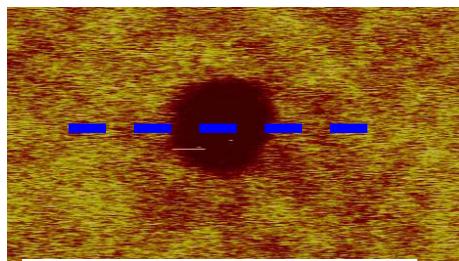
## Tapping mode vs. ForceTool mode



topography

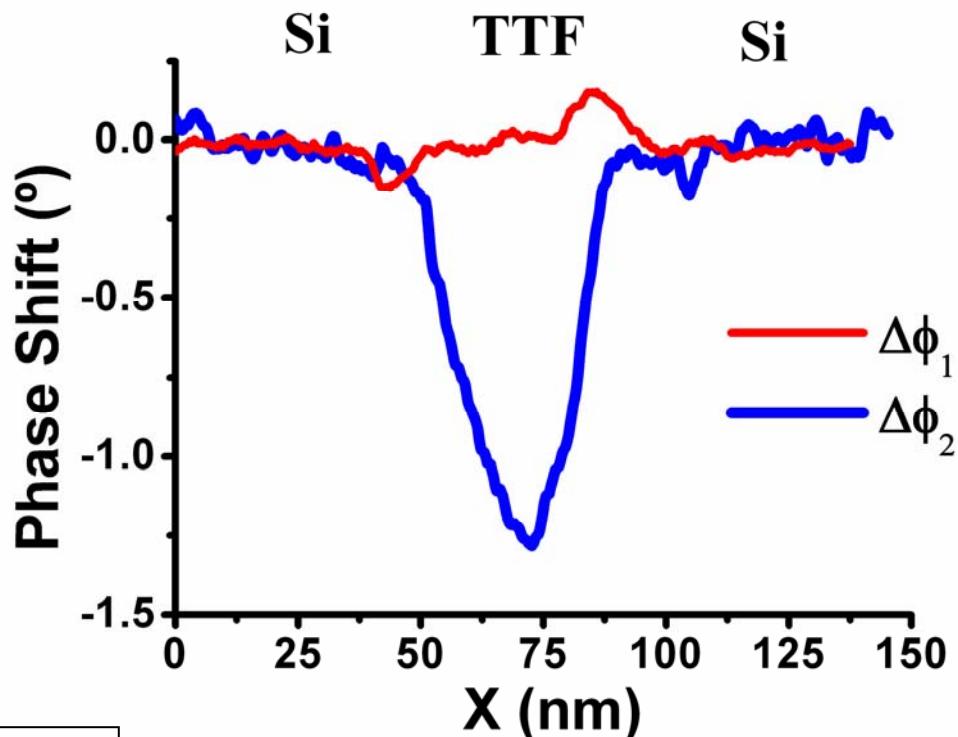
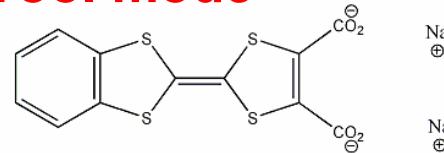


Tapping mode  
phase shift



ForceTool  
Phase shift

DB-TTF



$$\Delta\phi_1 = 0.1^\circ$$

$$\Delta\phi_2 = -1.3^\circ$$

$$\Delta\phi_2 = 13 \Delta\phi_1$$

**Two routes to compositional contrast: Conservative and non-conservative processes.**

---

### **Phase Imaging**

**Application 1: Identification of nanoscale energy dissipation processes**

**Application 2: Measurement of material properties**

---

**The 3D character of the microcantilever allows to develop methods based on elastic processes. ForceTool Sensitivy is 100 times higher than in AM-AFM.**

## Agradecimientos



Prof. Ricardo  
García



Dr. Shiva Patil



Nicolás F.  
Martínez



Carlos  
Gómez

# Thank you for your attention!

[+José L. Lozano](#)

[+Elena Tomás](#)

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Programa Nacional de Materiales, MEC; CAM

European Commission: **ForceTool**

