

Scanning Probe Microscopy

AFM, atomic force microscopy

Contact AFM

Non-contact AFM

Dynamic contact AFM

Tapping AFM

BEEM, ballistic electron emission microscopy

CFM, chemical force microscopy

C-AFM, conductive atomic force microscopy

ECSTM, electrochemical scanning tunneling mic.

EFM, electrostatic force microscopy

FMM, force modulation microscopy

KPFM, kelvin probe force microscopy

MFM, magnetic force microscopy

MRFM, magnetic resonance force microscopy

NSOM, near-field scanning optical microscopy

(or SNOM, scanning near-field optical mic.)

PFM, Piezoresponse Force Microscopy

PSTM, photon scanning tunneling mic

PTMS, photothermal
microspectroscopy/microscopy

SCM, scanning capacitance microscopy

SECM, scanning electrochemical microscopy

SGM, scanning gate microscopy

SHPM, scanning Hall probe microscopy

SICM, scanning ion-conductance mic.

SPSM, spin polarized scanning tunneling mic

SSM, scanning SQUID microscopy

SSRM, scanning spreading resistance mic.

SThM, scanning thermal microscopy

STM, scanning tunneling microscopy

STP, scanning tunneling potentiometry

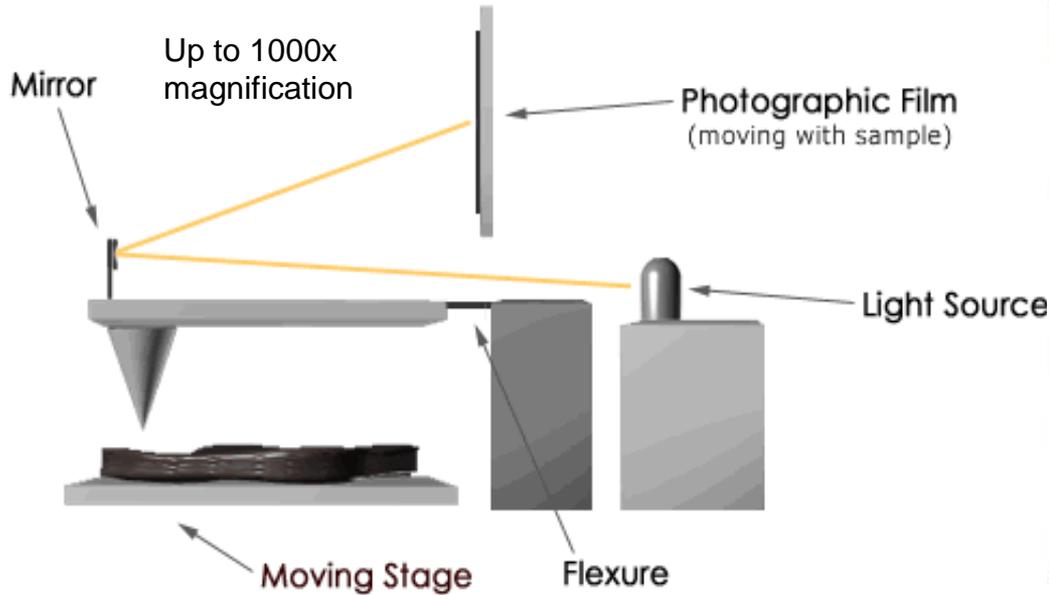
SVM, scanning voltage microscopy

SXSTM, synchrotron x-ray scanning tunneling
microscopy

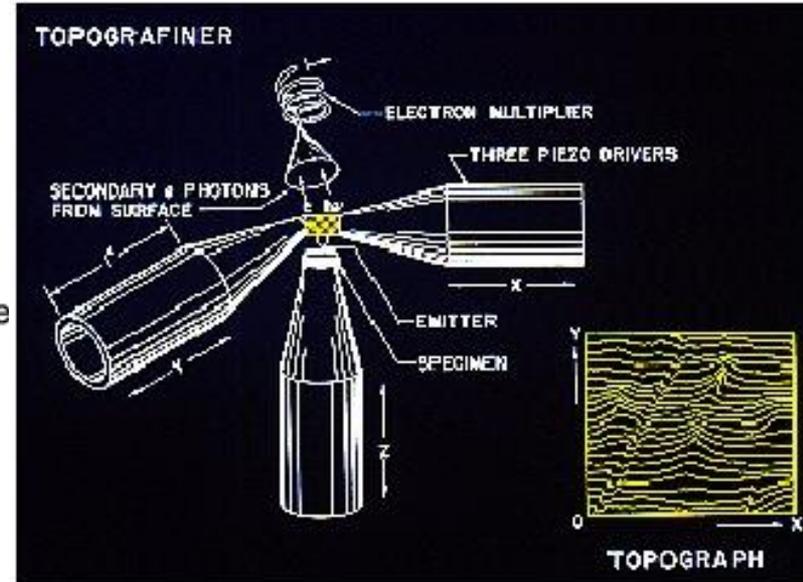
SSET, Scanning Single-Electron Transistor
Microscopy

Early SPMs

Stylus profiler (1929)



Topografiner (1971)



Field emission instead of tunneling current (STM) → lower resolution!

Scanning Tunneling Microscope (STM) 1981

Atomic Force Microscope (AFM) 1986

Surface topography imaged with topografiner
 180-line-per-mm diffraction grating replica
R. Young et al., Rev. Sci. Instrum. 43, 999 (1972)



The first AFM

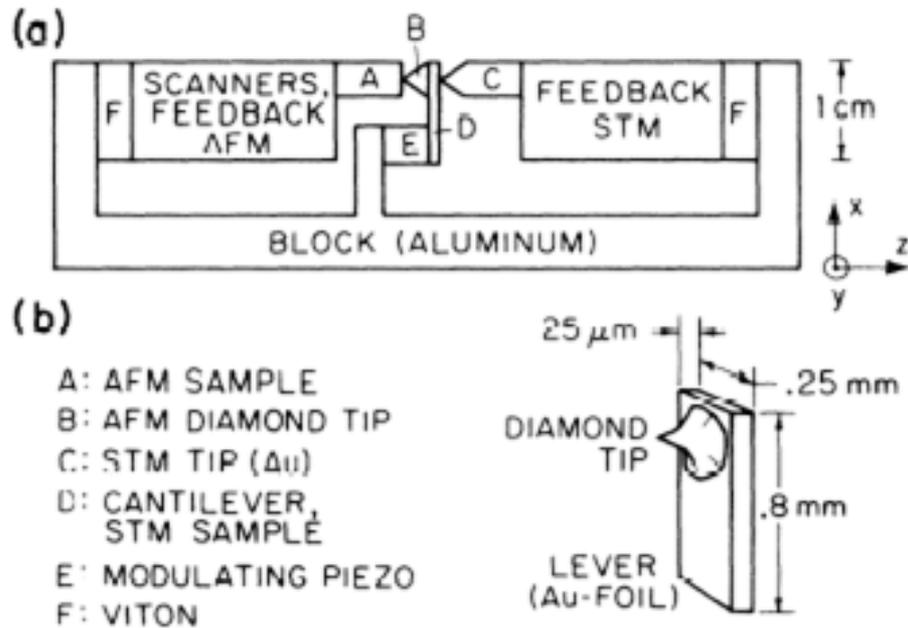
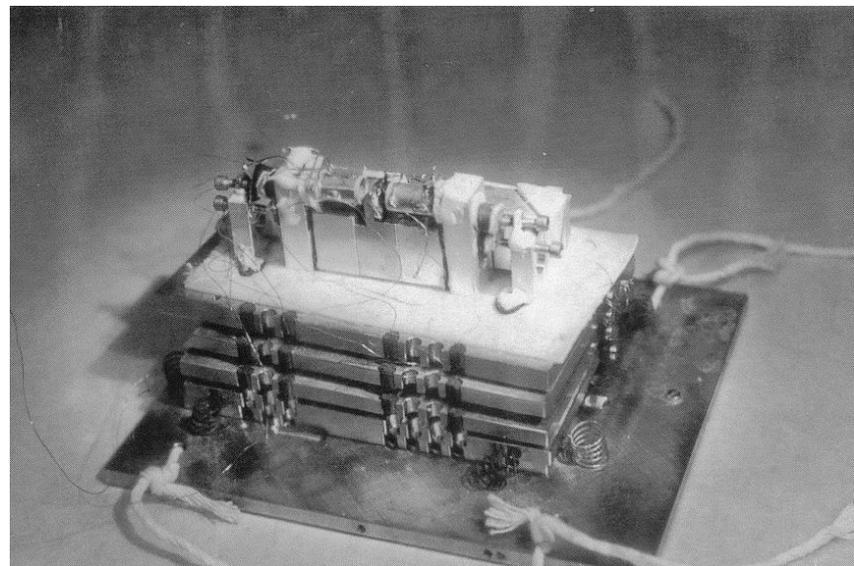
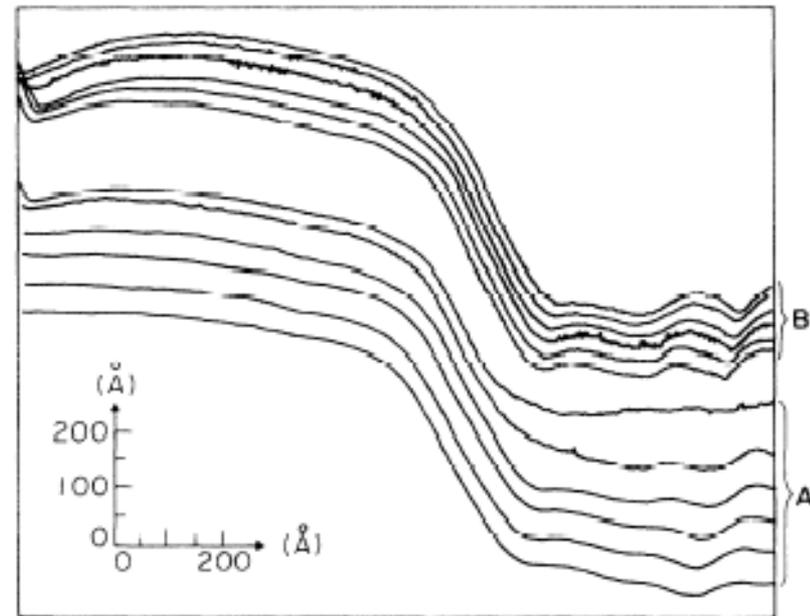


FIG. 2. Experimental setup. The lever is not to scale in (a). Its dimensions are given in (b). The STM and AFM piezoelectric drives are facing each other, sandwiching the diamond tip that is glued to the lever.

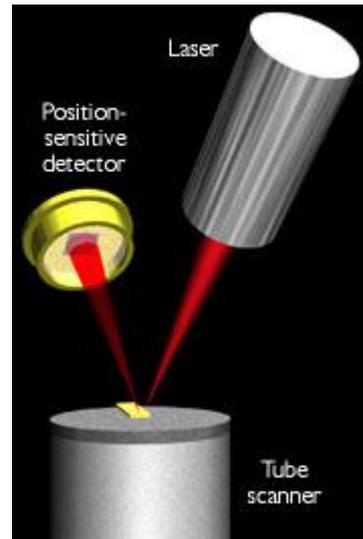
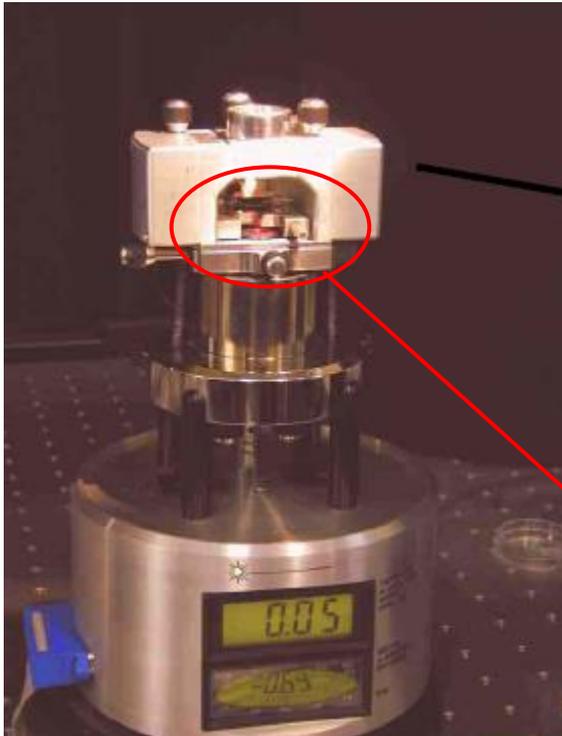
FIG. 4. The AFM traces for another area of the ceramic sample. The curves grouped under *A* were recorded with additional low-pass filtering. For this set the stabilizing force, f_0 , was reduced by thermal drifts as we moved from the lowest to the highest traces of set *A*. The force f_0 is near 10^{-8} N for the highest curve. We note that the structure vanishes on the traces when the sample-to-tip force is reduced below this level. The force f_0 was reset to a higher value near 5×10^{-8} N for the traces marked *B*.



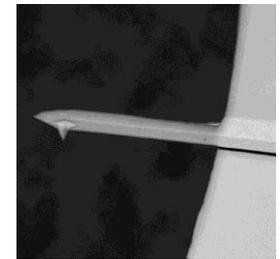
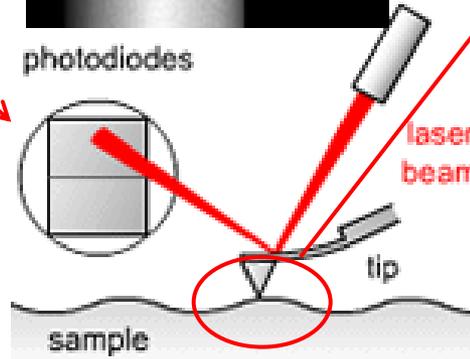
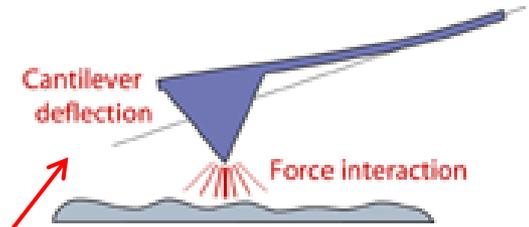
G. Binnig, Ch. Gerber and C.F. Quate, Phys. Rev. Lett. **56**, 930 (1986)



Atomic Force Microscope



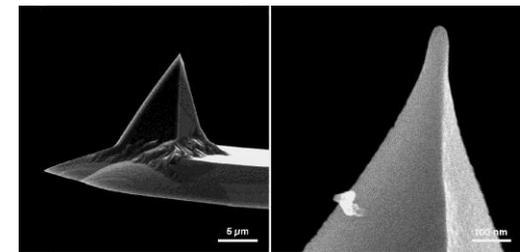
STM detection was cumbersome and soon cantilever motion was detected optically → similar to stylus profiler



Nanoscope III,
dI → Veeco → Bruker

4 main components:

- sensor (cantilever)
- scanner
- detector (photodiode)
- feedback



Commercially available tips

Cantilever fabrication

Microfabrication → silicon etching

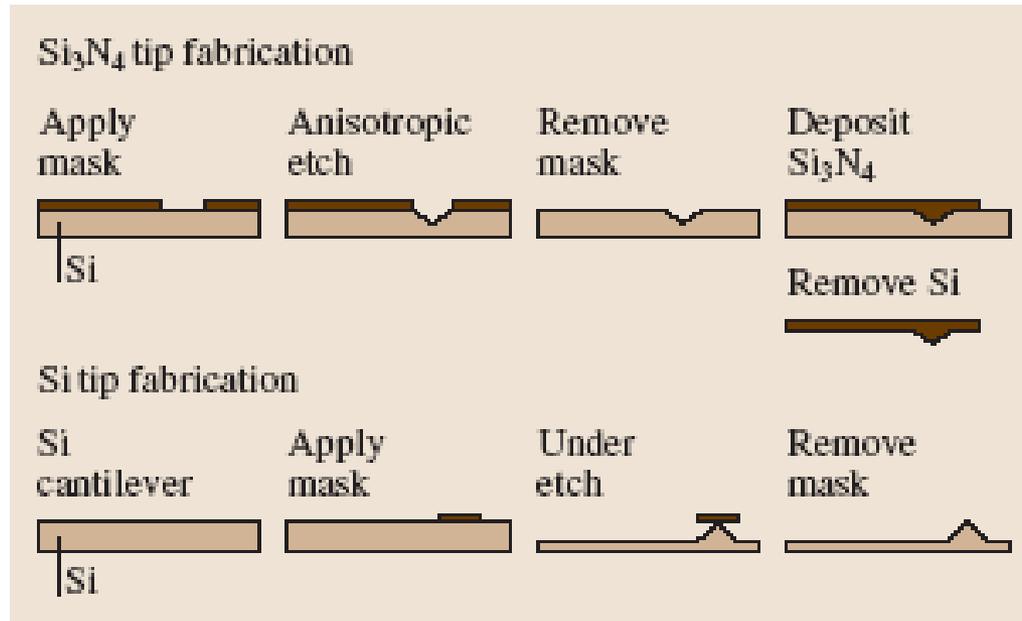


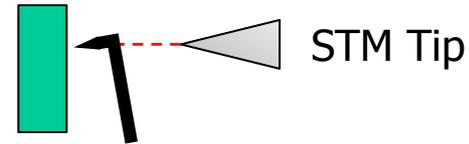
Fig. 12.3 A schematic overview of the fabrication of Si and Si₃N₄ tip fabrication as described in the text

Silicon tips are usually sharper than silicon nitride tips

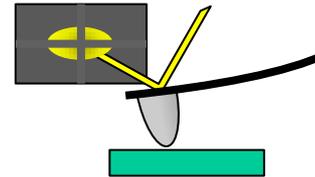
For contact mode imaging: usually silicon nitride
(thinner → lower normal k , but at the same time high lateral k)

Methods to detect cantilever deflection:

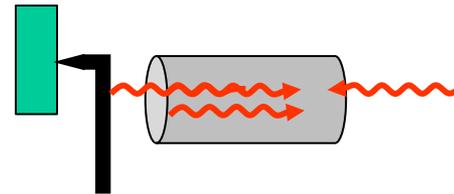
1. Tunneling (Binnig 1984)



2. Light beam reflection



3. Interferometry



4. Tuning forks: frequency shift

5. Piezo resistive cantilevers

6. Etc...

Instrumentation



Small sample AFM: sample moves, cantilever stationary;
(small sample means $\approx 10 \times 10 \text{ mm}^2$)

Large sample AFM: cantilever moves, fixed sample

Typ. scan sizes vary between 0.7 and $125 \mu\text{m}$ (depending on scanner!)

Piezo Tube Scanners

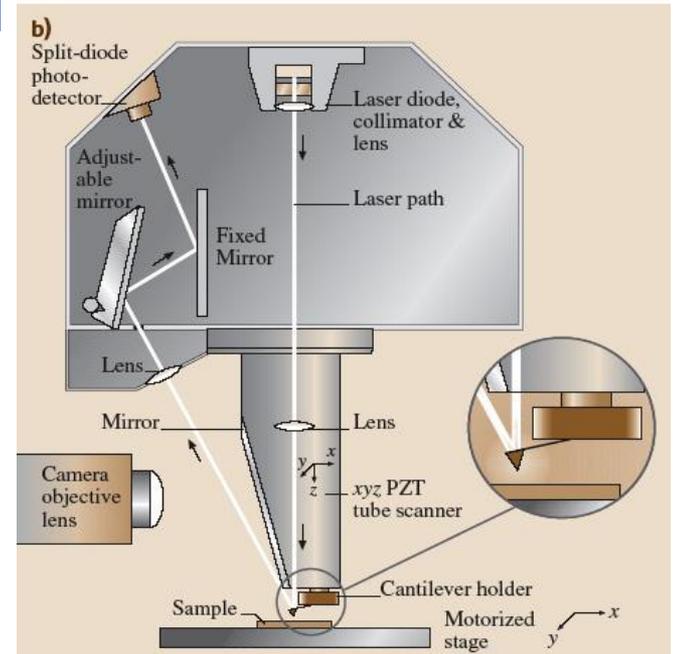
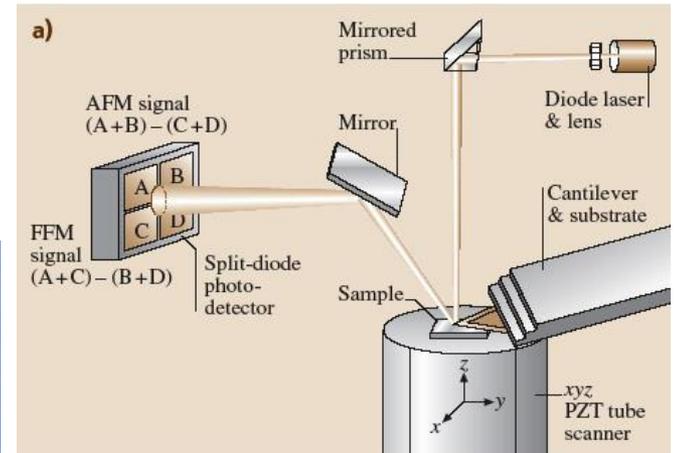
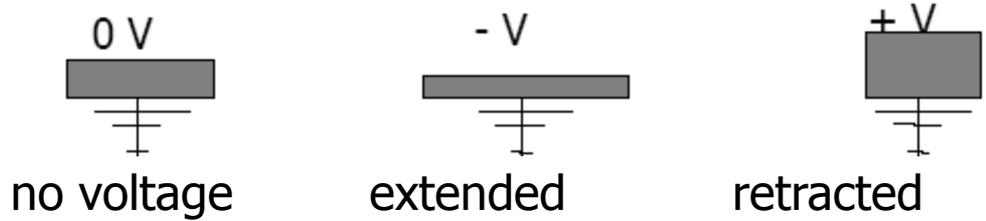


Fig. 11.9a,b Principles of operation of (a) a commercial small sample AFM/FFM, and (b) a large sample AFM/FFM

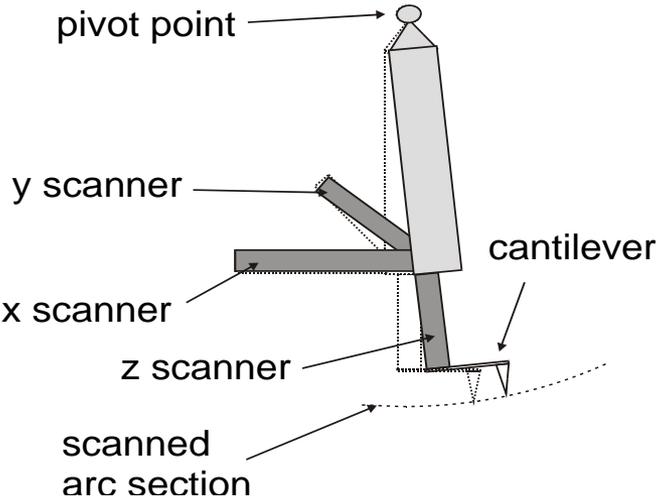
Scanner

Piezoelectric material → expansion / contraction due to applied voltage



1 V corresponds to ~1 nm

Tripod scanner



Tube scanner

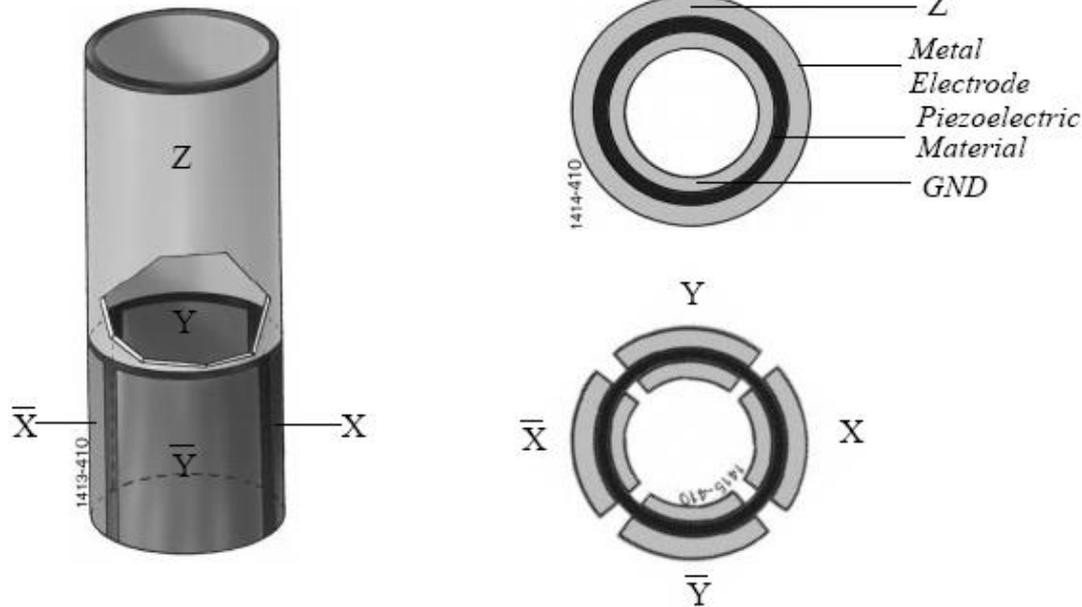
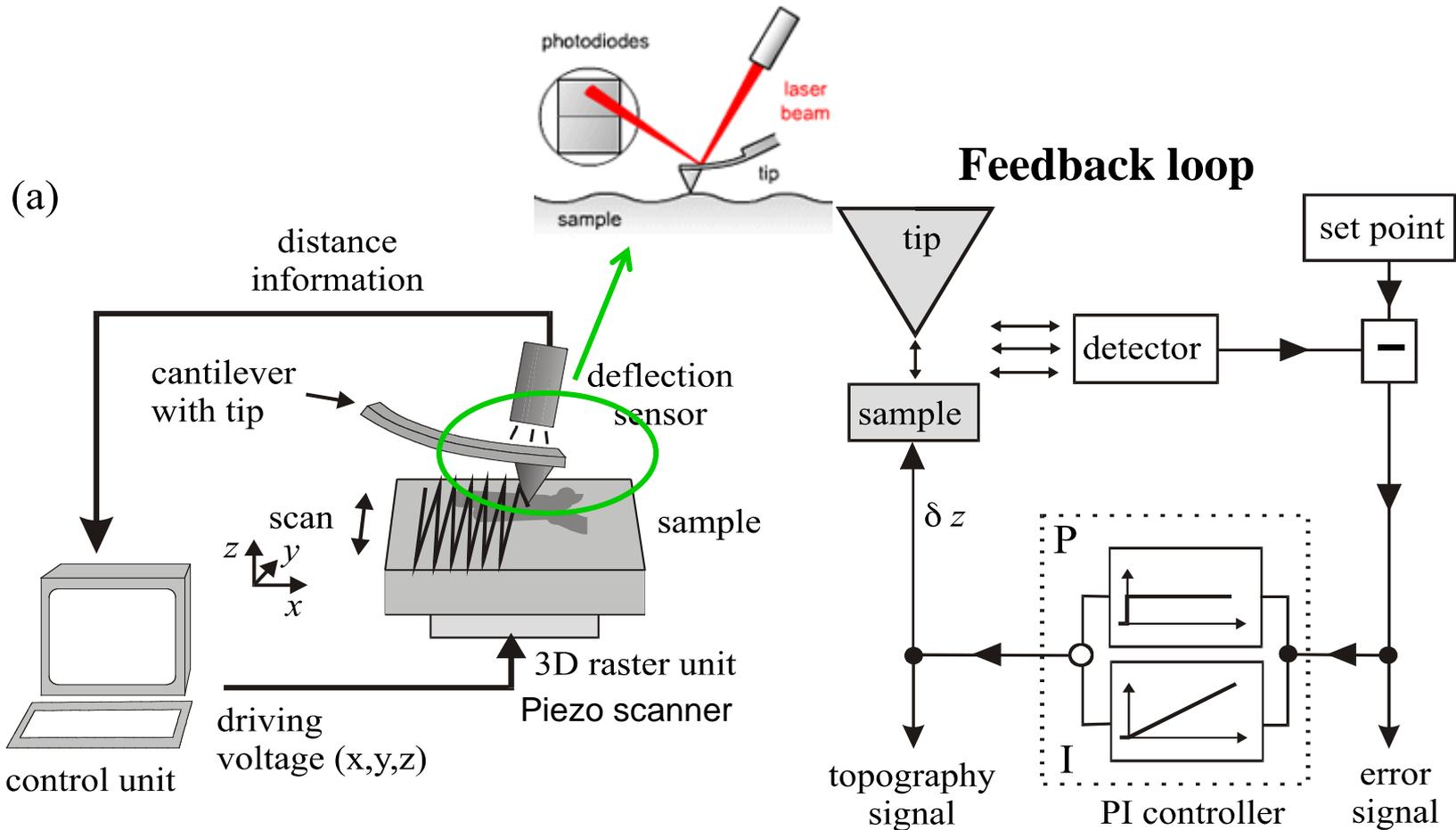


Figure 7.2 Typical scanner piezo tube and X-Y-Z configurations. AC Signals applied to conductive areas of the tube create piezo movement along the three major axes.

Feedback



Sample is scanned in raster pattern

Topography image formed by displaying z-motion of scanner (feedback) to maintain constant height or force

Mechanical Microscope

Cantilevers

Spring constant:

if $k=1 \text{ N/m} \rightarrow$ moves 1 nm per force of 1 nN

Manufacturer data:

Be careful with spring constant!

\rightarrow calibrate cantilever for force measurements (e.g. by thermal noise)!

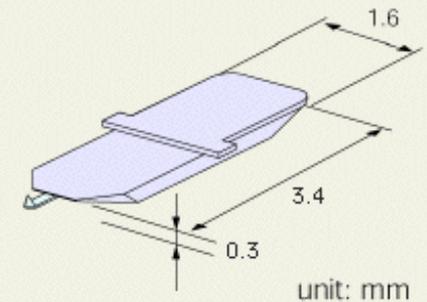
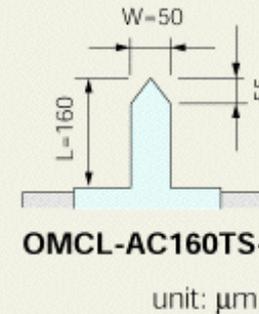
Why? \rightarrow thickness t of lever is hard to control during fabrication, but spring constant $\sim t^3$

$$k_{\min} : k_{\text{norm}} : k_{\max} = 0.3 : 1 : 2$$

OMCL-AC160BN series

Rectangular cantilevers with thin tetrahedral tips
Tip location: Just on end of cantilever

Chip size of silicon cantilever
One cantilever is extended from side edge of each chip



Technical Data	Nominal Value	Specified Range
Thickness / μm	7	6.0 - 8.0
Mean Width / μm	38	30 - 45
Length / μm	225	215 - 235
Force Constant /(N/m)	48	21 - 98
Resonance Frequency /kHz	190	146 - 236

Noise: The lever spring is excited thermally

From the equipartition theorem:

$$\frac{1}{2} k_B T = \frac{1}{2} k_L \cdot x^2$$

↓ ↓
Boltzmann Spring Cst.

For a lever of $k_L = 0.1 \text{ N/m}$

We get: $x^2 = \frac{0.025 \times 1.6 \times 10^{-19} \text{ N.m}}{0.1 \text{ N/m}} = 4 \times 10^{-21} \text{ m}^2$

$$\rightarrow x = 0.63 \text{ \AA}$$

How much force can we measure?

Cantilever stiffness and displacement sensitivity determine the magnitude of forces that can be measured.

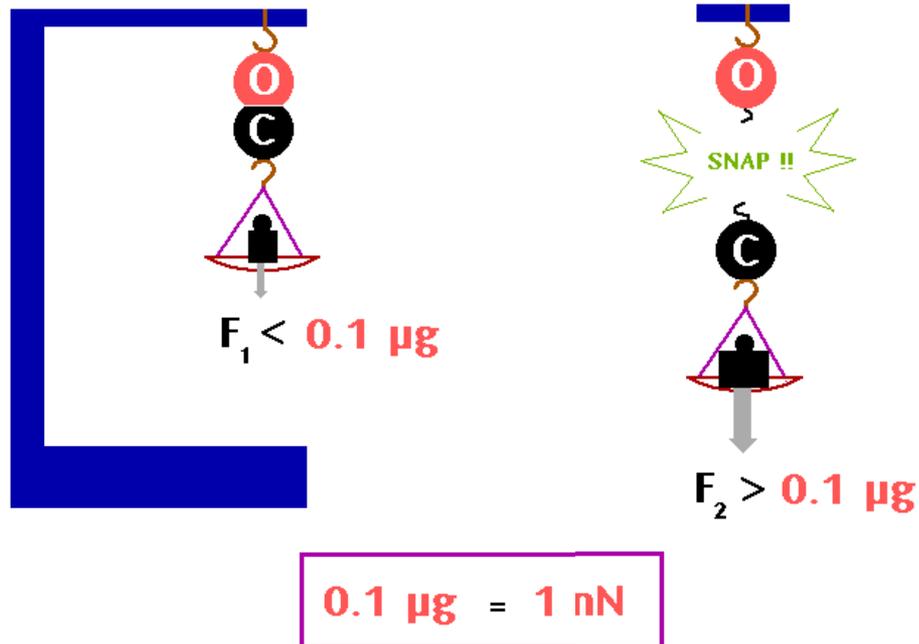
Measurable forces

resolution of contact mode AFM: 0.01 – 0.1 nm (vert), 0.2 nm (lat)
with 0.1 nm displacement sensitivity: forces down to 10 nN to 1 pN

Biological and chemical forces

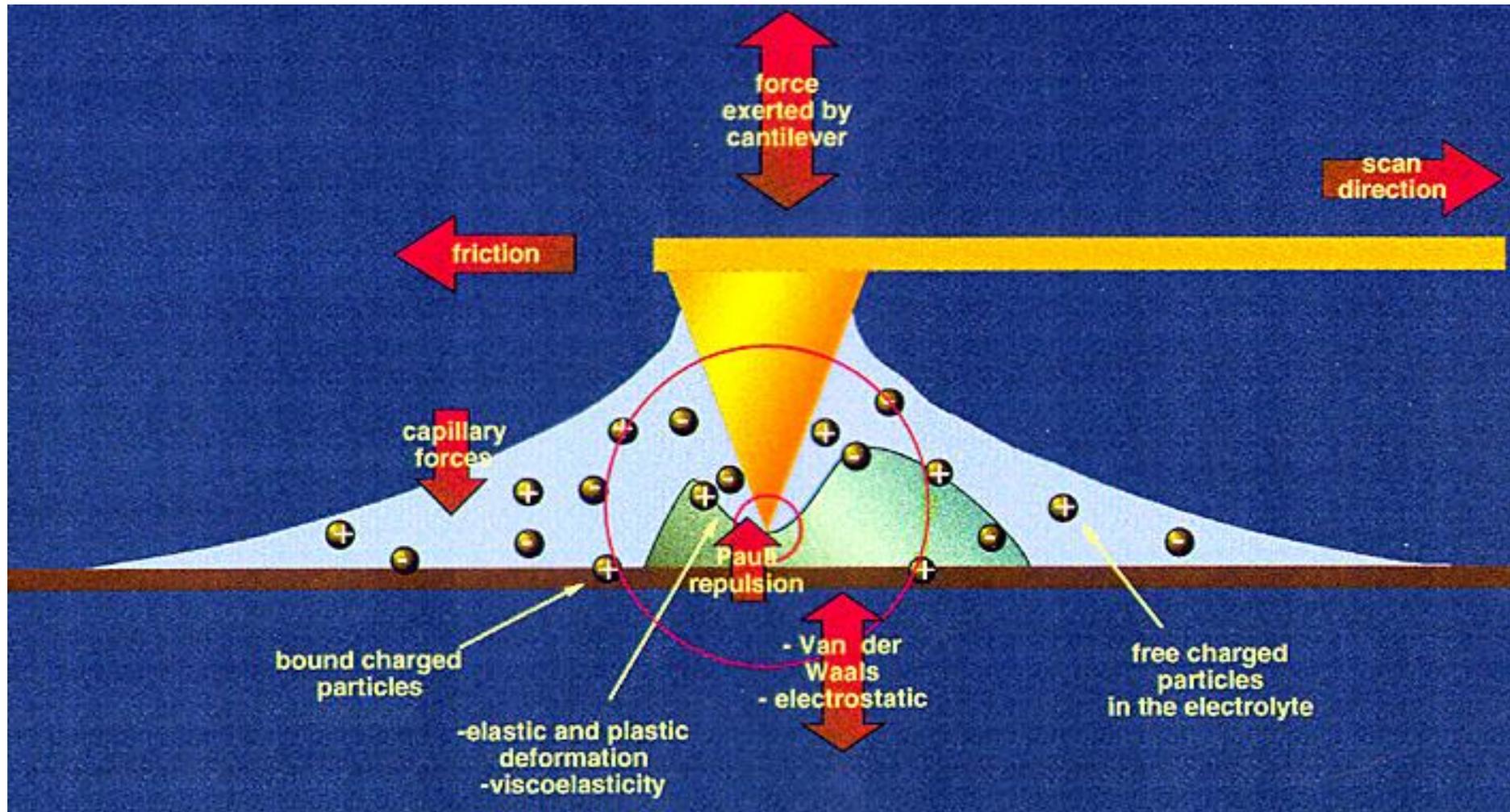
Chemical bonding:
0.1 μN (ionic bond),
10 pN (hydrogen bond)
Covalent bonds: 1 nN

Protein-protein: 10-50 pN
Biotin-avidin: 250 pN
DNA: 50 pN



Bond energy 1 to 10eV, separation between C and O (in CO) to break the bond $\sim 1\text{\AA}$

Types of forces relevant in AFM



- Attractive: van der Waals, electrostatic, magnetic, chemical bonding, capillary
- Repulsive: van der Waals in liquids of intermediate dielectric properties

Also magnetic forces if tip is coated with appropriate material.

AFM Approach curves (force-distance)

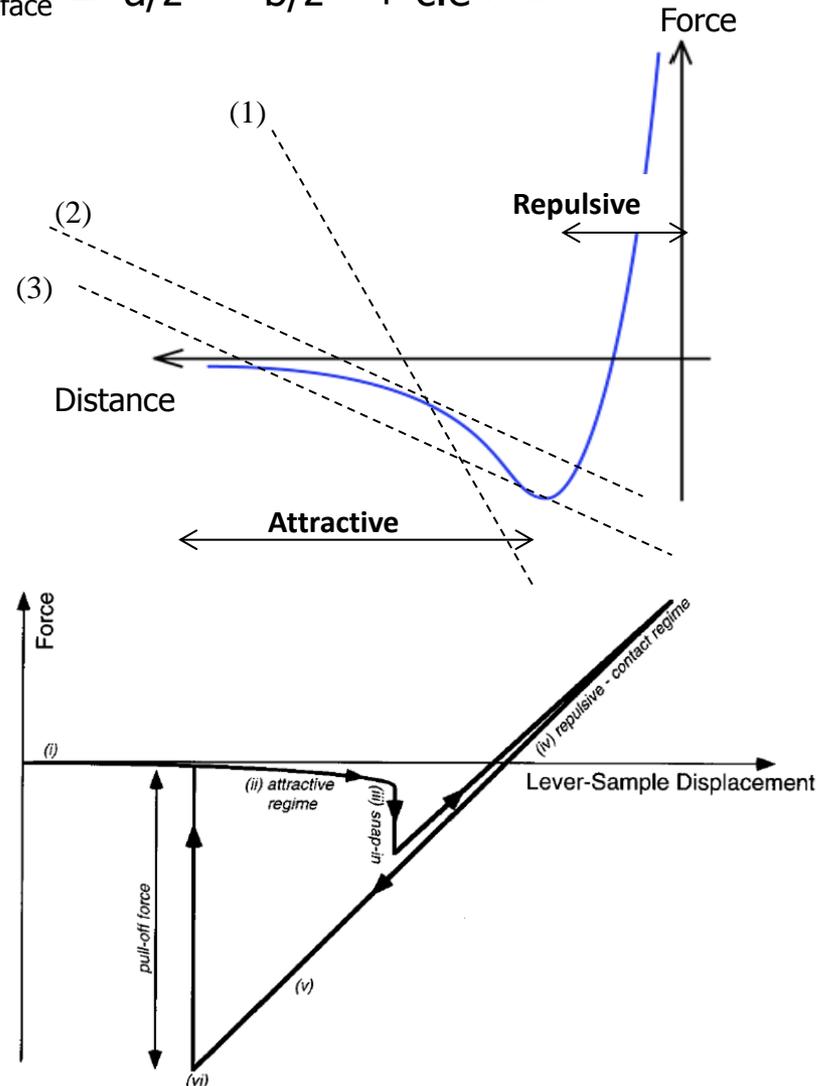
$$F_{\text{lever}} = -k.z$$

$$F_{\text{surface}} = a/z^{12} - b/z^n + c.e^{-(z-z_0)}$$

If the tip is mounted on a stiff cantilever (line (1)), it will move forward a bit and stop when the attraction and pulling forces are equal

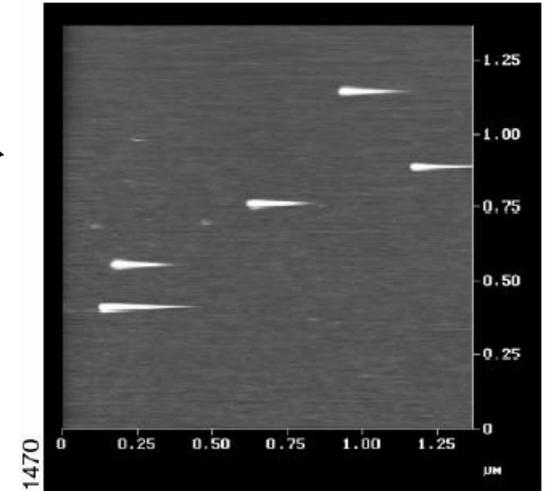
If the tip is mounted on a soft cantilever, the restoring force ($F = -kz$) could be smaller than the attraction force from the surface (line (2)). At the point where this happens the tip position is unstable and will jump to the surface.

Upon retraction, the soft lever will again experience an instability at a certain point and the tip will snap out of contact abruptly (curve (3)). Between the two unstable points the information about the force curve is lost.



Scanning artifacts

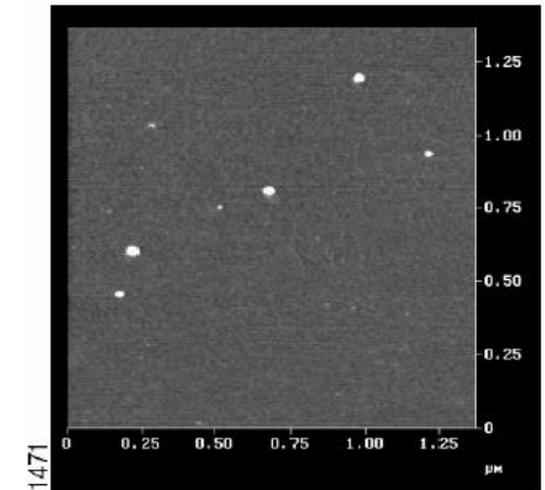
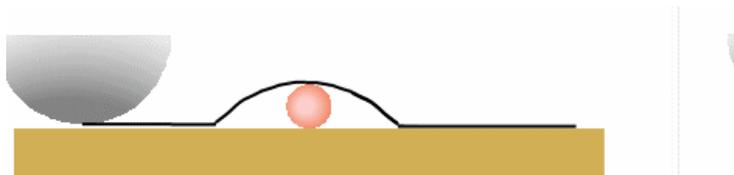
Scanning parameters
Feedback parameters
Scanner artifacts
Vibrations (mechanical, electrical)
Probe artifacts



No true 3 dimensional images
Image is convolution of tip and sample.

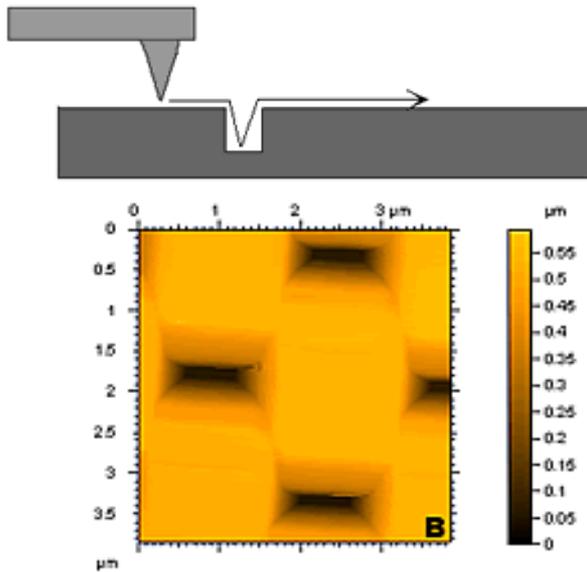
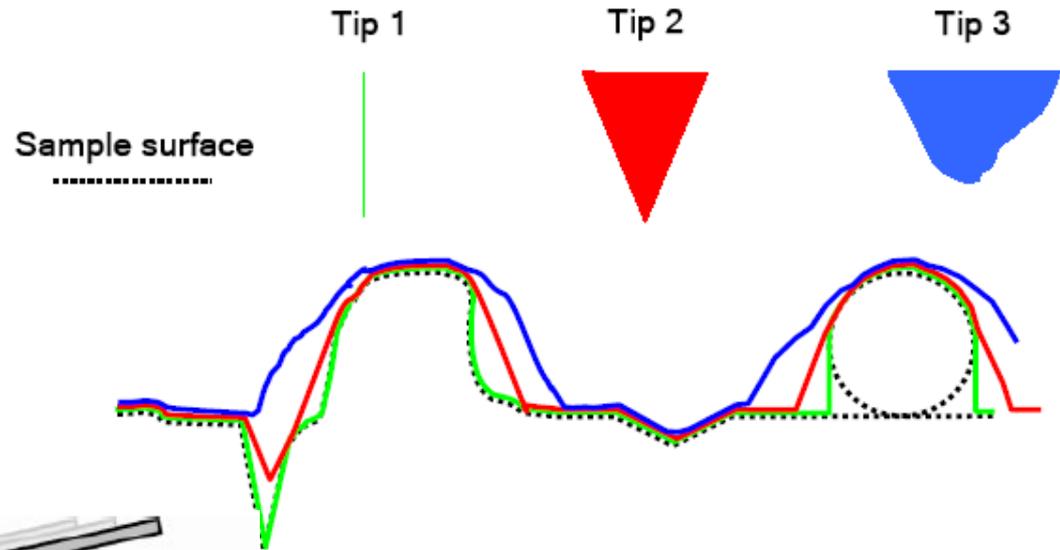
The signal is always a **convolution** of sample topography and tip topography

„The smaller thing images the bigger thing“

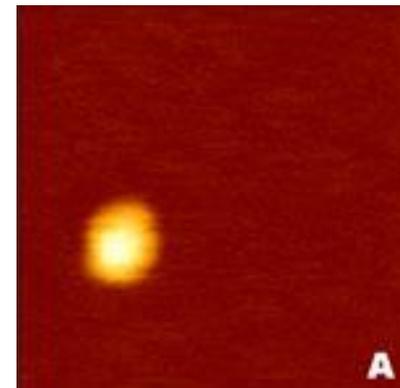
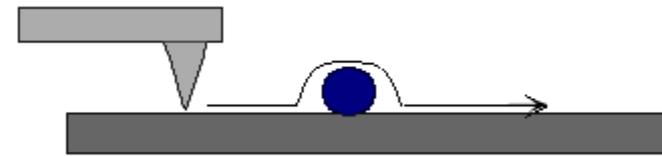
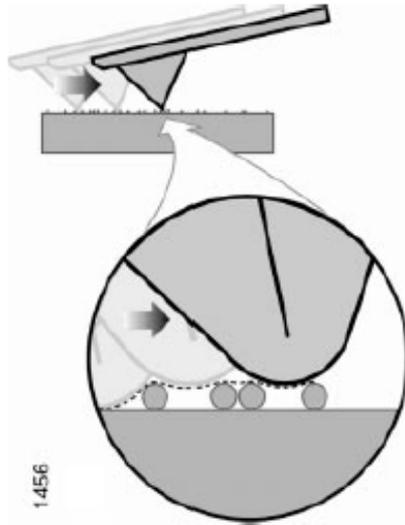


Probe artifacts – Tip convolution

- Features appear too large
- Strangely shaped objects
- Repeating strange patterns



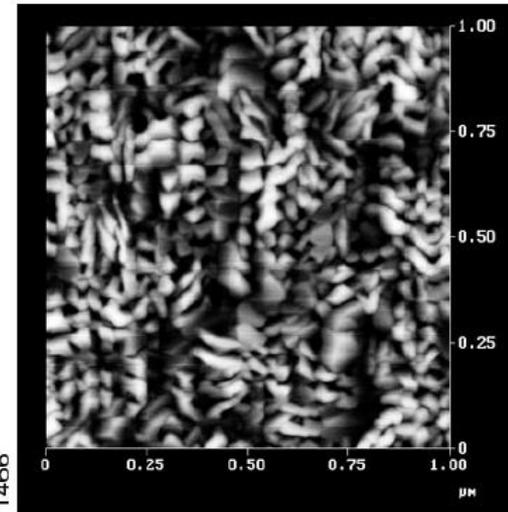
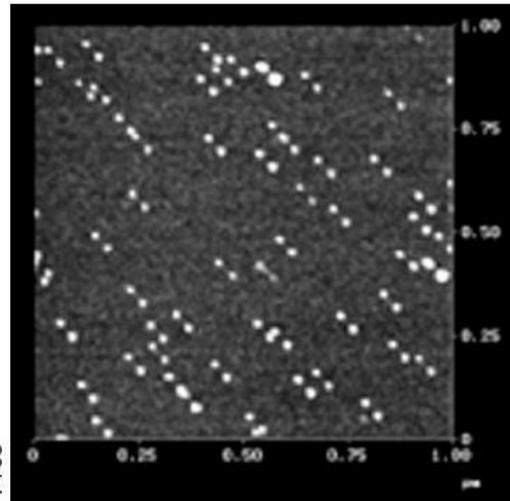
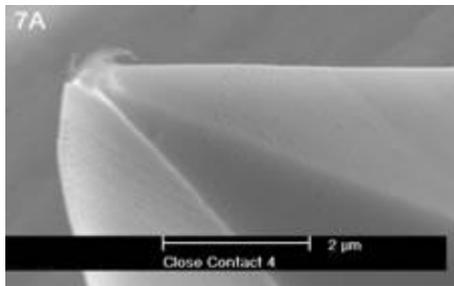
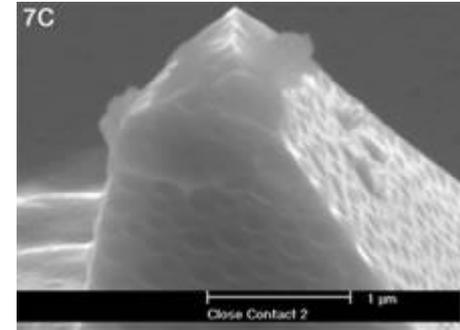
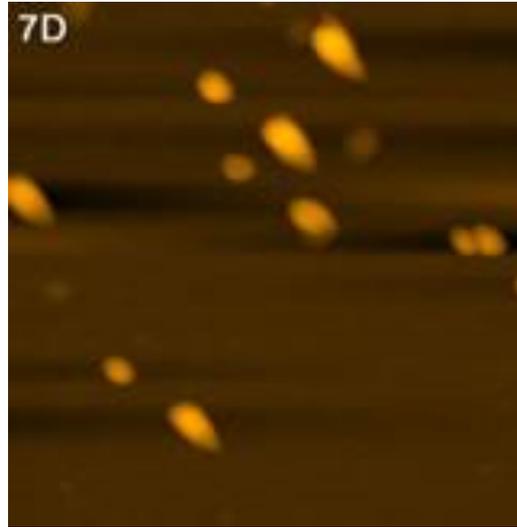
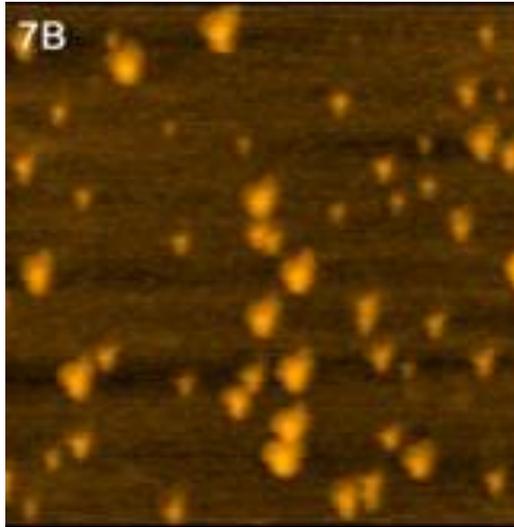
Should be squares...



Sidewalls of probe!
-> but height should be correct

Blunt tip effects

Tips may be blunt or have debris or dirt attached to it!



Double tip

„Strange“ shapes

Strange shapes? -> might be tip imaging!

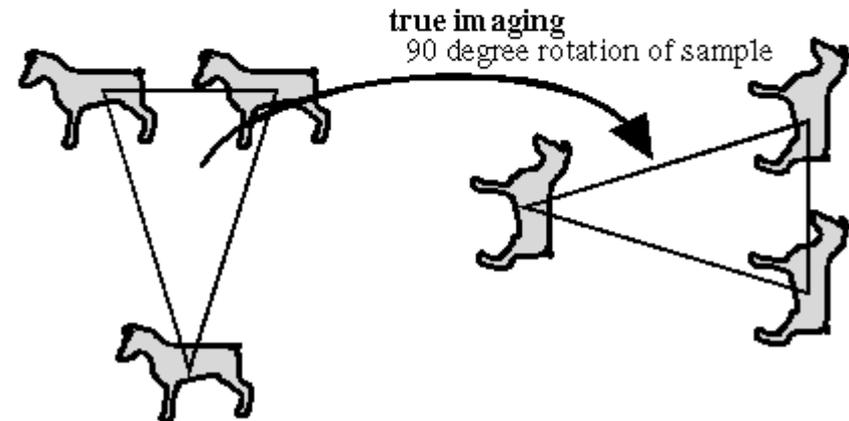
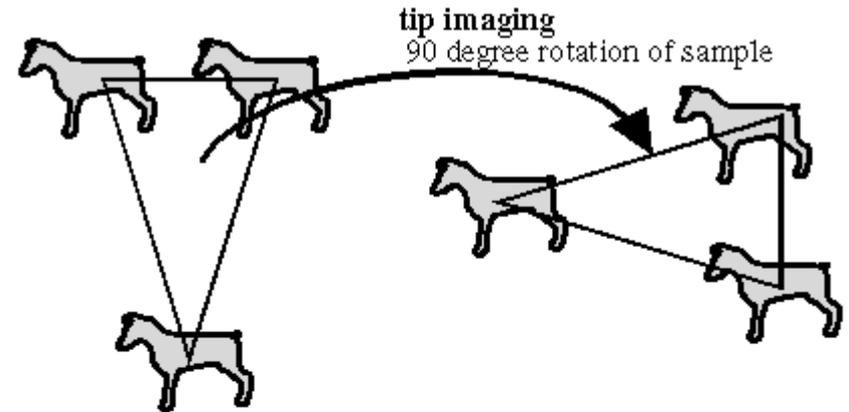
Shape can be different sizes, but maintains orientation!

Test:

Rotate sample by 90°

if orientation of shape stays
-> tip imaging / convolution
-> change tip!

if orientation changes
-> real image of the surface

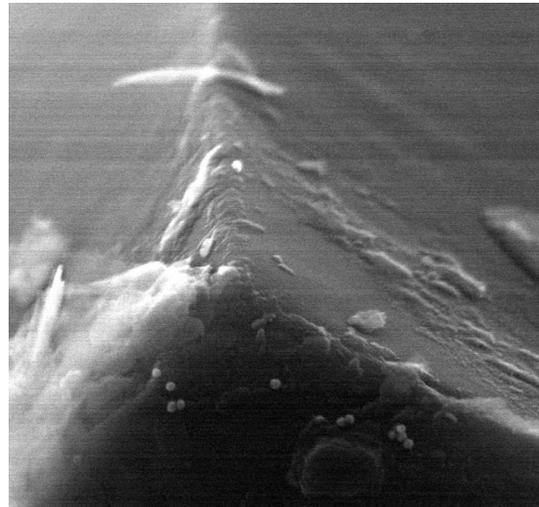
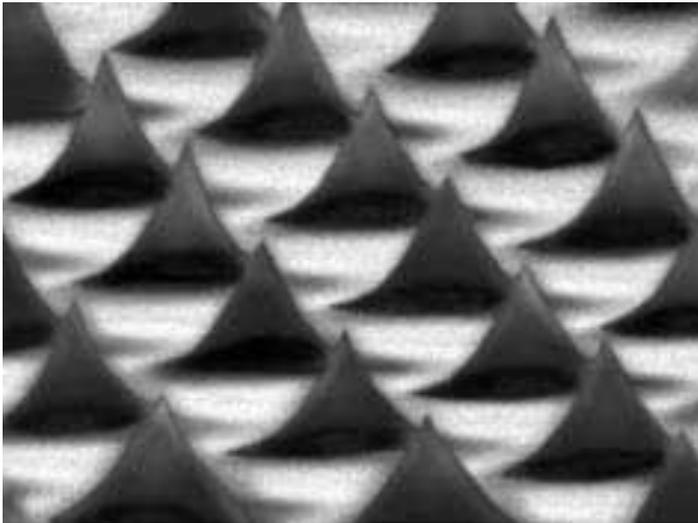
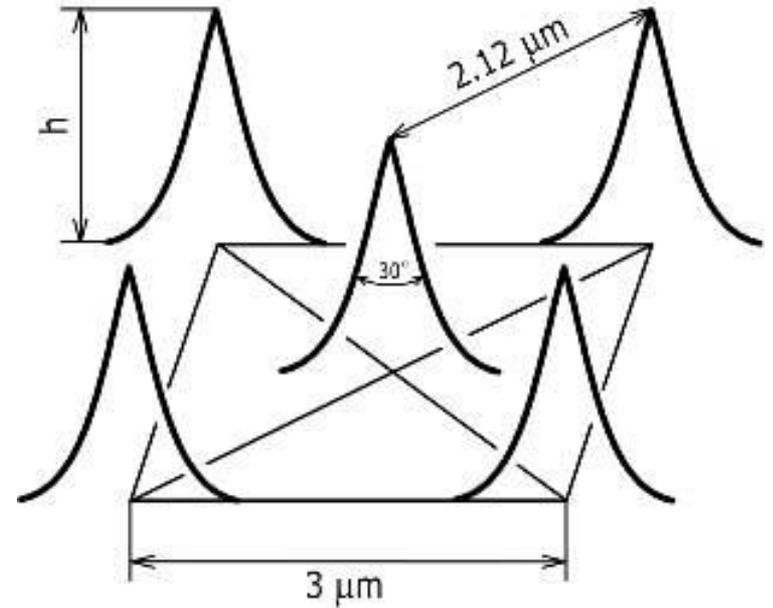


Tip visualization

Electron microscopy
(takes time...)

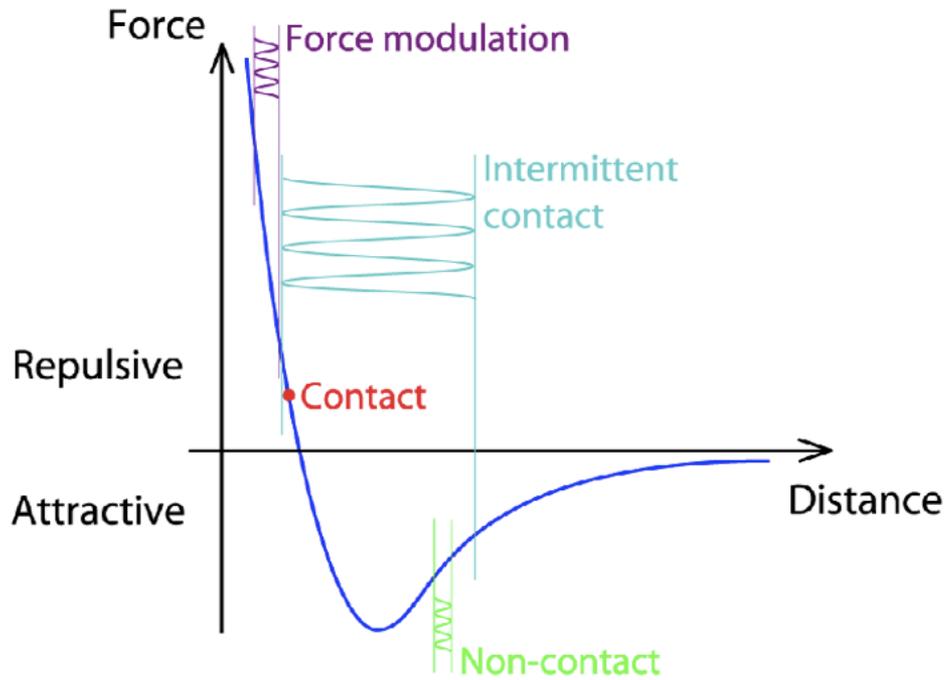
OR: Test gratings sharper than the tip!
(Reverse imaging)

Simply take a new tip.

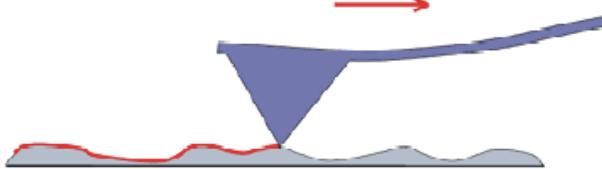


„Real“ tips

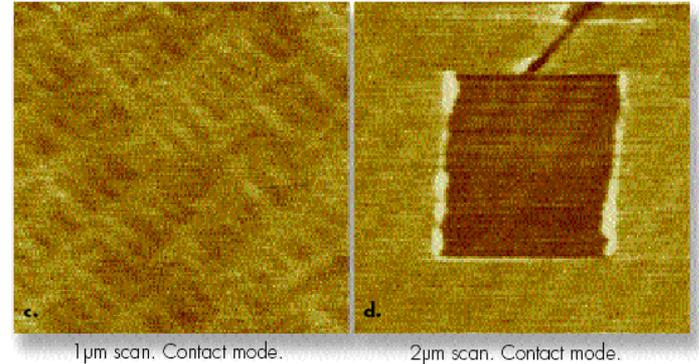
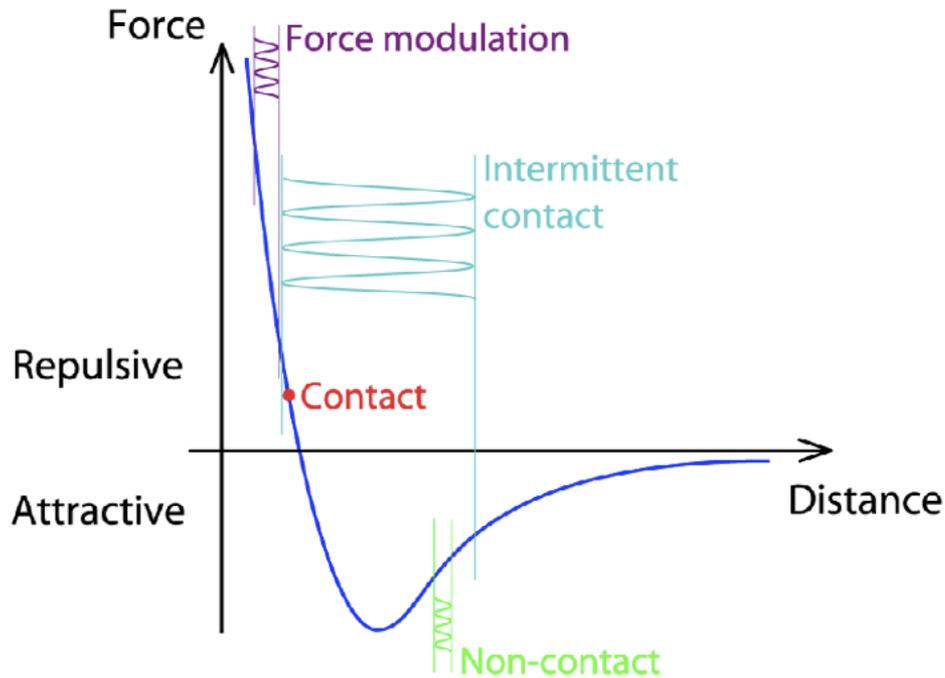
AFM Operation Modes



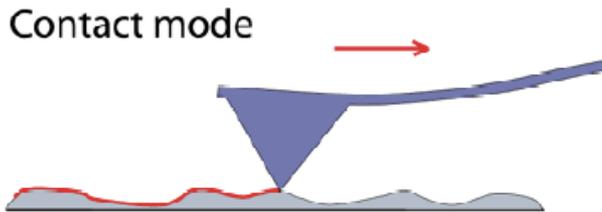
Contact mode



AFM Operation Modes

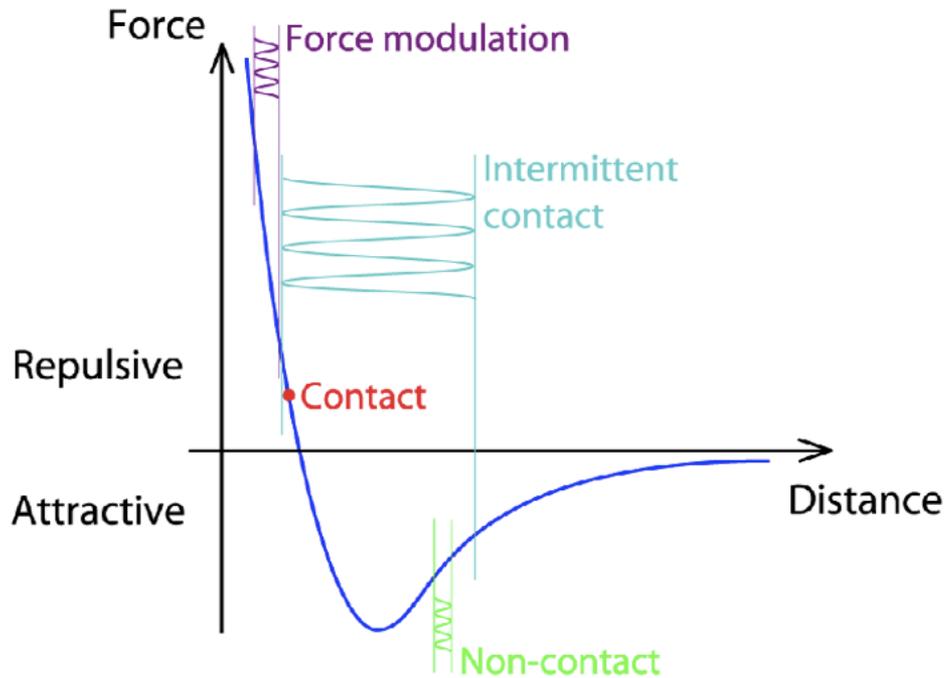


Long range attractive forces must be compensated through short range repulsive forces: risk of damage for delicate samples in contact mode!



Lateral Forces!

AFM Operation Modes



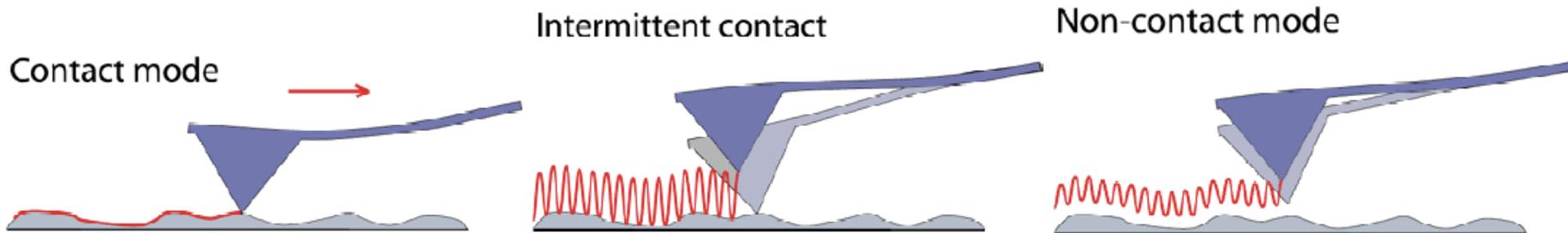
Advantage of dynamic AFM:

Less lateral forces

Possibility of obtaining more information about material properties

Higher lateral resolution achievable

Dynamic AFM



Dynamic AFM

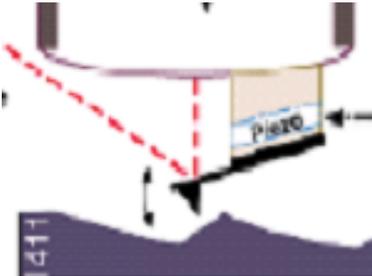
Vibrating Cantilever!

Excite cantilever at its eigenfrequency

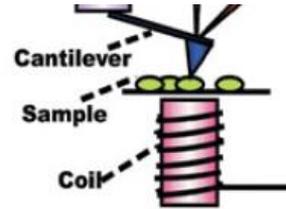
How to excite the cantilever?

-acoustic (piezoelectric actuator)

-magnetic (MAC mode)

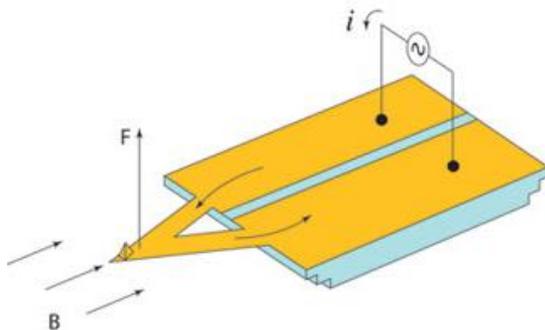


Piezo actuation
works for all cantilevers



Special Cantilevers
Good in liquids

-Lorentz Force (i-drive, Asylum Research)



Special cantilevers
Good in liquids

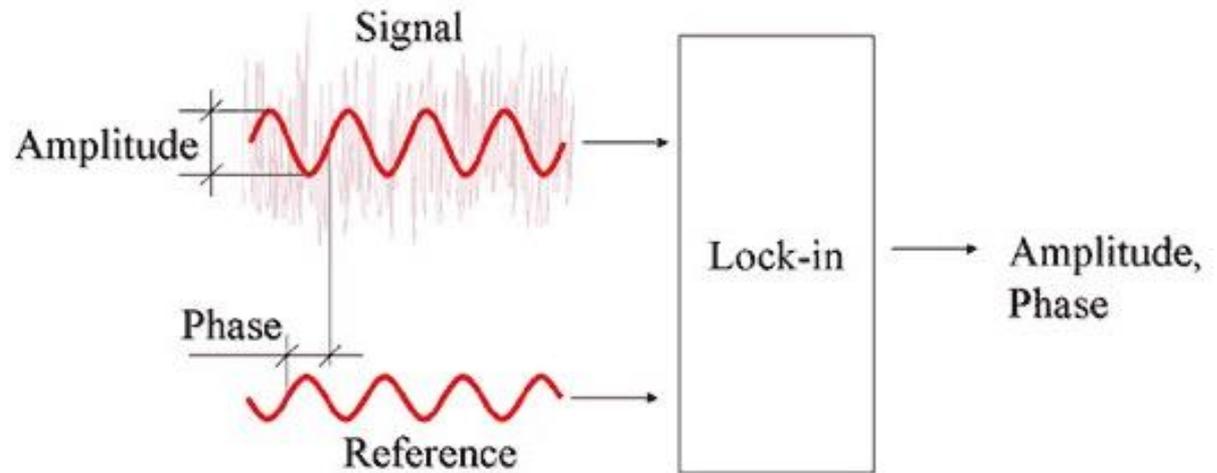
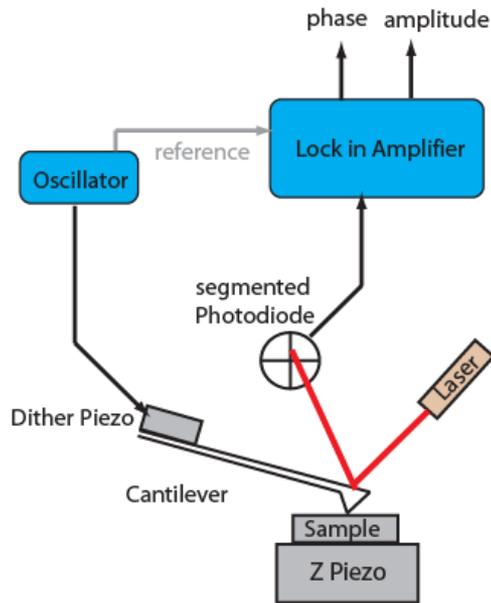
-Piezo electric cantilevers
-Tuning Forks (Quarz)

-**Photo Thermal Excitation**
use second laser at base of
cantilever (bimorph effect)

Dynamic AFM

Lock-in Amplifiers

compares cantilever deflection with reference signal (excitation)



Noise rejection, Filtering technique, Adjustable Bandwidth

The Cantilever Model

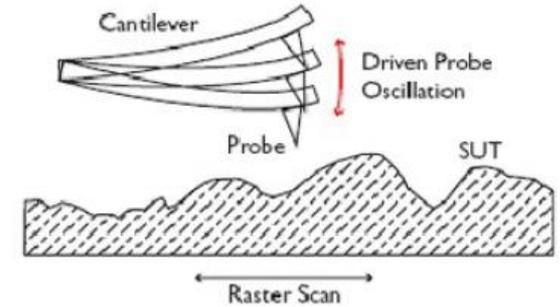
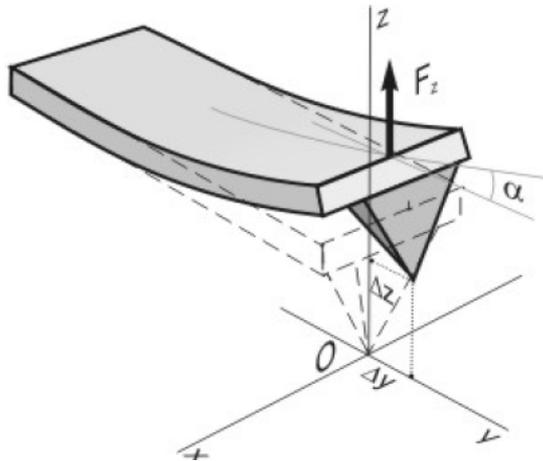
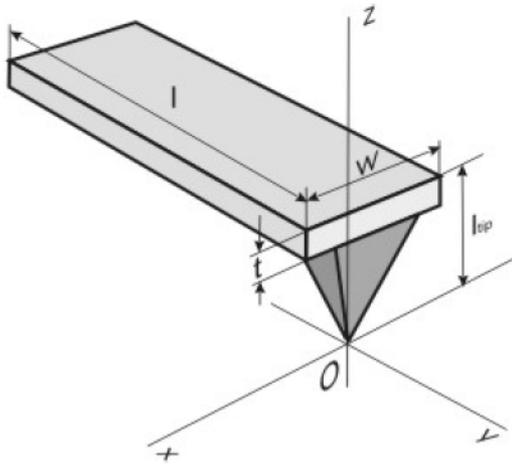


Table 1. Parameters of Equation 8

Parameter	Definition	Typical Values
m	Mass of tip	4 ng
k_c	spring constant of free cantilever	20 N/m
ω_0	Resonance frequency of free cantilever	272 KHz
Q	Quality factor of free cantilever	500
F_0	Drive amplitude	100 nm
ω	Drive frequency	271.90

$$f_0 = 0.162 \frac{t}{L^2} \sqrt{\frac{E_Y}{\rho}}$$

typically 20-500kHz

Harmonic
Oscillator

Harmonic oscillator - solution

$$\rightarrow \ddot{z}(t) + \frac{\omega_0}{Q} \cdot \dot{z}(t) + \omega_0^2 \cdot z(t) = A_d \cdot \omega_0^2 \cos(\omega t) \quad \text{Solution: } z(t) = z_1(t) + z_2(t)$$

Linear combination of 2 regimes:

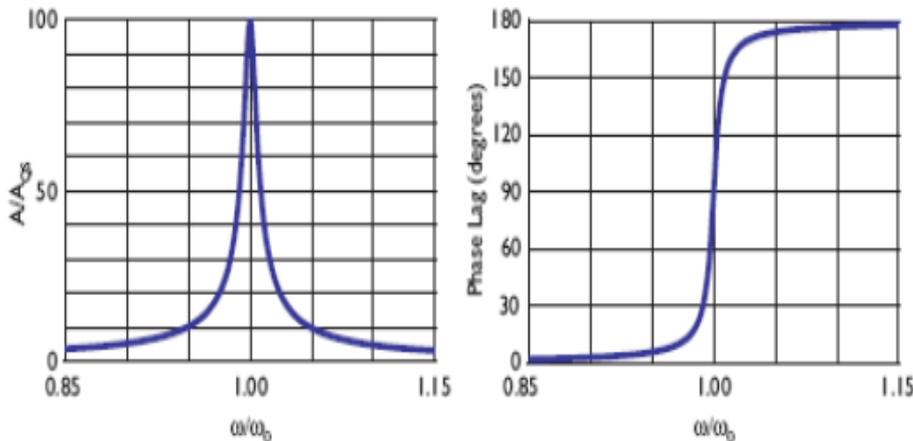
steady-state solution

$$z_1(t) = A_1 \cdot \cos(\omega t + \varphi)$$

transient regime

$$z_2(t) = A_t \cdot e^{-\frac{\omega_0 t}{2Q}} \cdot \sin(\omega_0 t + \varphi_t)$$

Amplitude and phase as function of ω :



$$A_0(\omega) = \frac{A_d \cdot Q \cdot \omega_0^2}{\left(\omega \cdot \omega_0^2 + Q \cdot (\omega_0^2 - \omega^2)\right)^{1/2}}$$

$$\varphi = \arctan\left(\frac{\omega \cdot \omega_0}{Q \cdot (\omega_0^2 - \omega^2)}\right)$$

Amplitude depends on:

- Cantilever properties (driving force)
- Medium (damping, Q)
- Operational parameters (ω/ω_0)

Response time

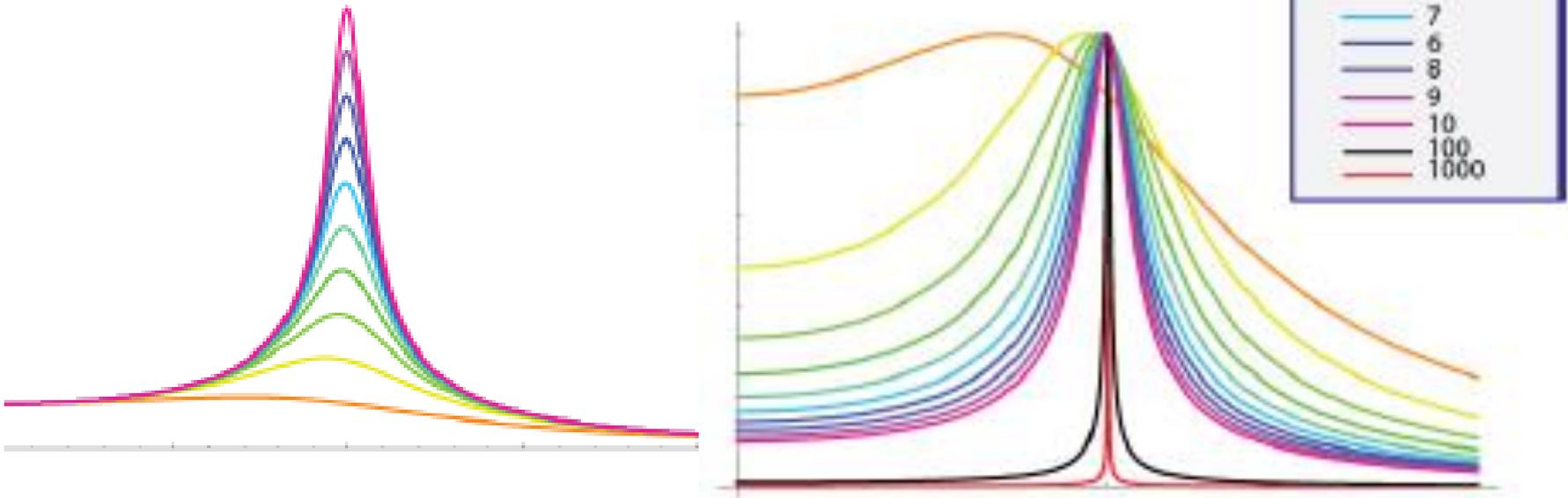
Damping! → Amax will be reached at $\omega \neq \omega_0$

→ shift in resonance frequency:
(negligible for $Q > 100$)

$$\omega_0^* = \omega_0 \cdot \left(1 - \frac{1}{2Q^2}\right)^{1/2}$$

Time constant:

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



Response time

Damping! → A_{max} will be reached at $\omega \neq \omega_0$

→ shift in resonance frequency:
(negligible for $Q > 100$)

$$\omega_0^* = \omega_0 \cdot \left(1 - \frac{1}{2Q^2}\right)^{1/2}$$

Time constant:

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

Vacuum: only internal dissipation $Q \geq 10,000$

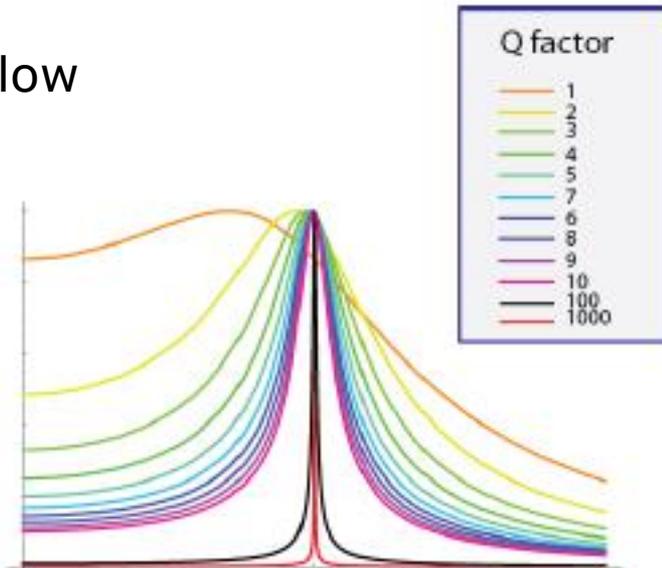
→ long transient regime (≈ 30 ms), too slow
Very high sensitivity

Air: viscous damping → $Q < 1000$

→ time constant < 1 ms,

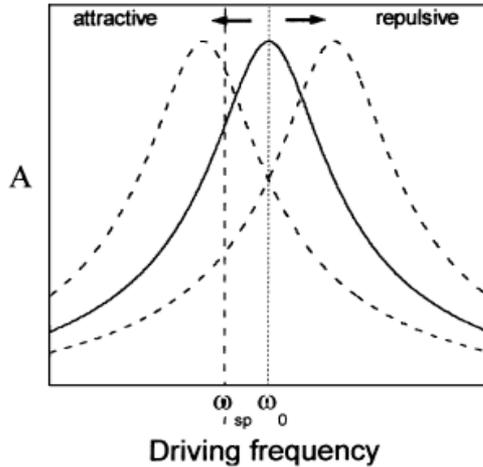
Liquids: $Q < 5$, nearly no mechanical gain

Viscous damping + added mass



Influence of tip-surface forces

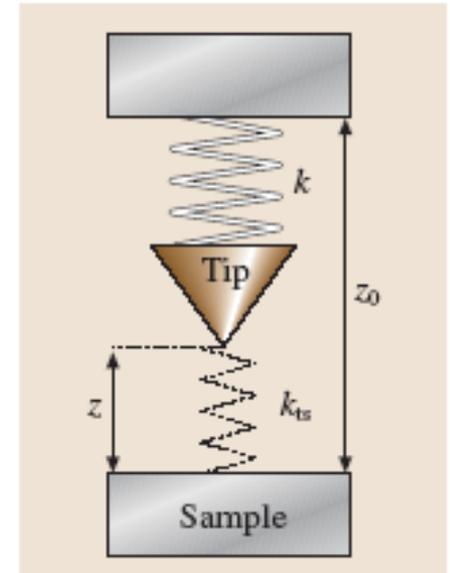
Approaching tip towards surface modifies resonance frequency, and, thus, also the vibration amplitude (attractive and repulsive forces)



$$\omega_e = \left(\frac{k - (dF_{ts}/dz)}{m} \right)^{1/2}$$

gradient of interaction

Model:
Point mass spring



$$m \cdot \ddot{z}(t) + c \cdot \dot{z}(t) + k \cdot z(t) = k \cdot A_d \cdot \cos(\omega t) + F_{ts}$$

The forces are non-linear in Tapping Mode, (no ideal harmonic oscillator)

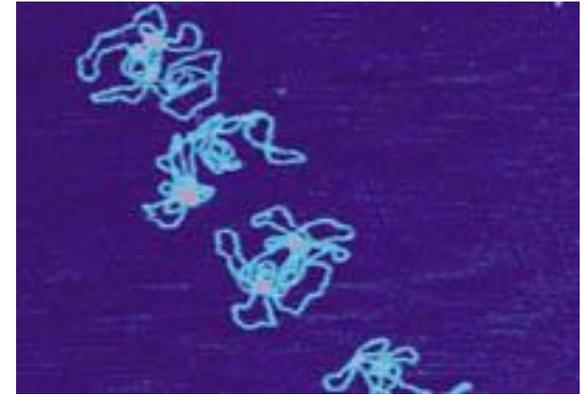
Dynamic AFM: Tip-surface interactions are measured by changes in oscillation behavior (Resonance frequency, amplitude, phase)

Z - Feedback in Dynamic AFM

2 major modes: Amplitude modulation (AM), Frequency modulation (FM)

AM excitation at or near resonance
parameters: amplitude and phase
amplitude as feedback
mostly performed in air or liquid

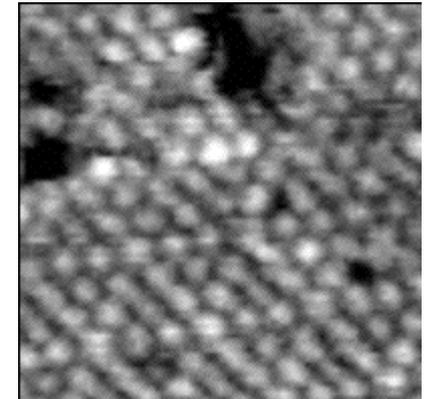
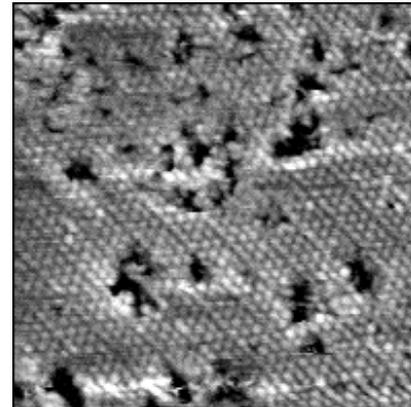
tapping mode, intermittent contact mode



DNA Molecules, 700nm scan

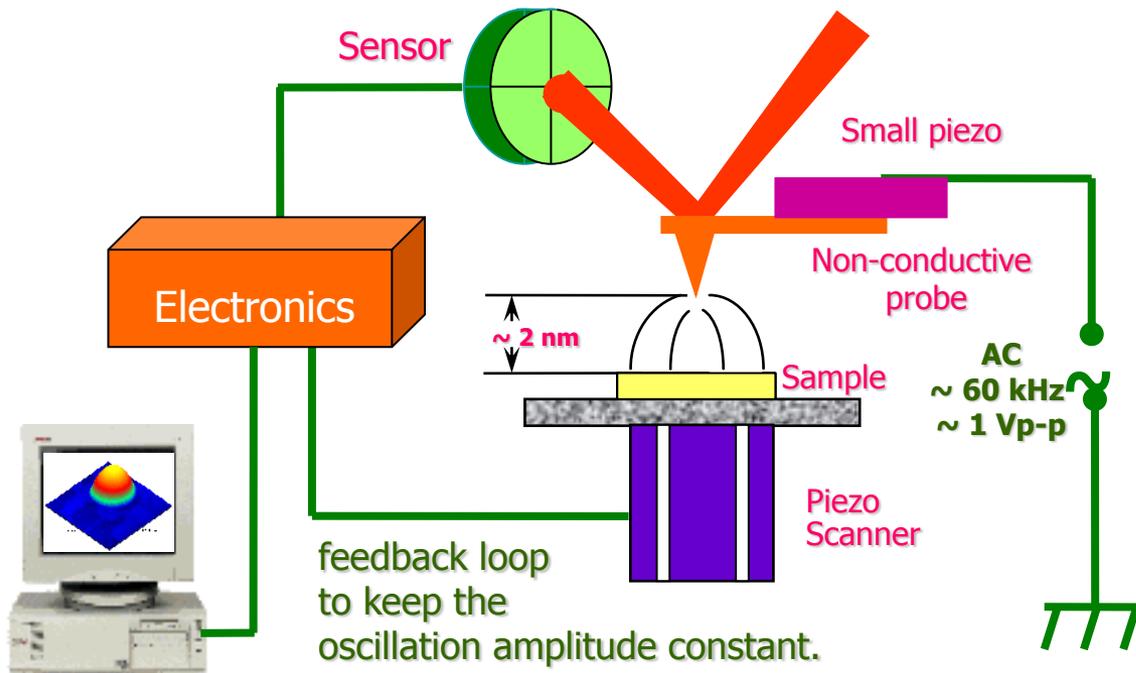
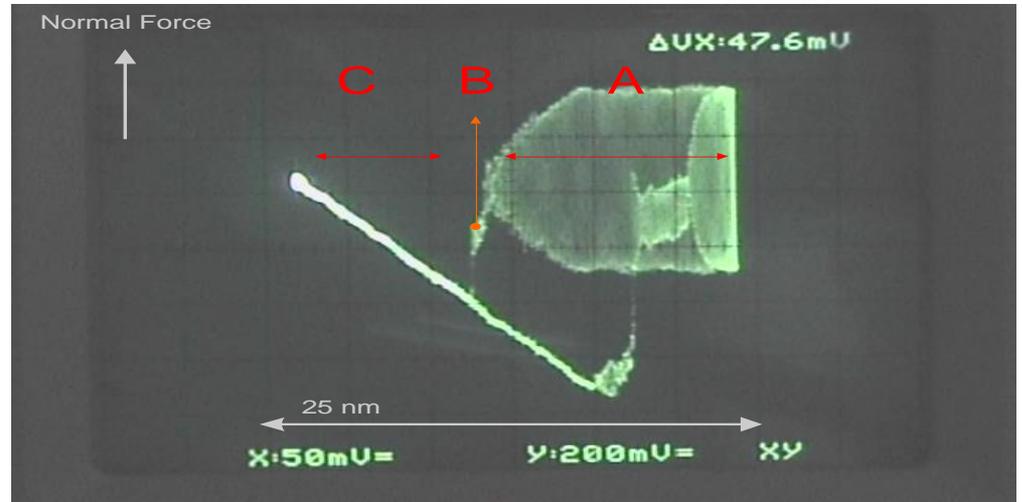
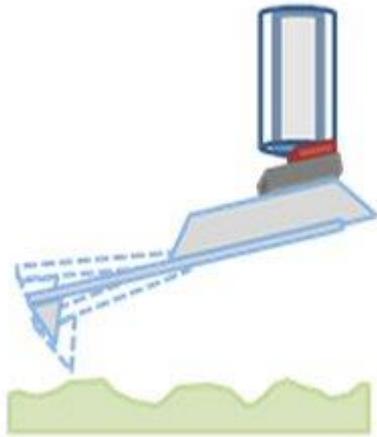
FM oscillation at resonance
frequency as feedback
no mechanical contact
dominant method in vacuum
Atomic Resolution

non-contact mode



Non contact UHV-AFM images, single crystal silicon, (111) plane
Scan area: 30nm x 30nm (Left), 9.8nm x 9.8nm (Right)
(Pictures : Prof.Morita, Hiroshima Univ. Japan (1995))

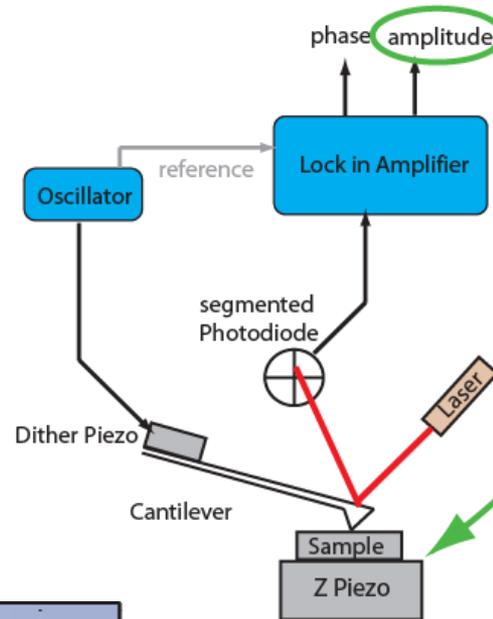
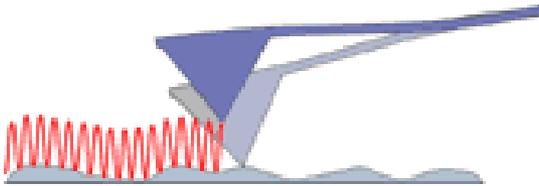
Amplitude Modulation Scanning Force Microscopy



Amplitude Modulation

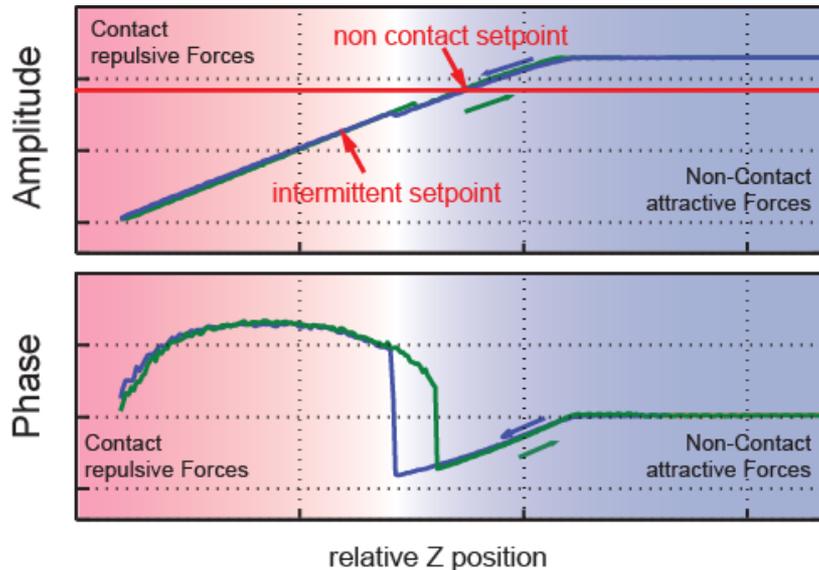
Tapping mode /
intermittent contact

Intermittent contact



In a tapping mode or amplitude modulation configuration the cantilever is excited near to its resonance. Amplitude and phase of the cantilever's oscillation are measured by a lock-in amplifier.

The topography is obtained by setting the Z-piezo controller to a constant amplitude.



-Typical amplitudes are 20-100 nm

-Amplitude Setpoint

-Phase Imaging

Tapping Mode Applications

- **Most commonly used** imaging mode (no or small problems with friction / adhesion like in CM, and less problems with electrostatics like in NC)

- Robust imaging technique
(Amplitude decreases monotonously)

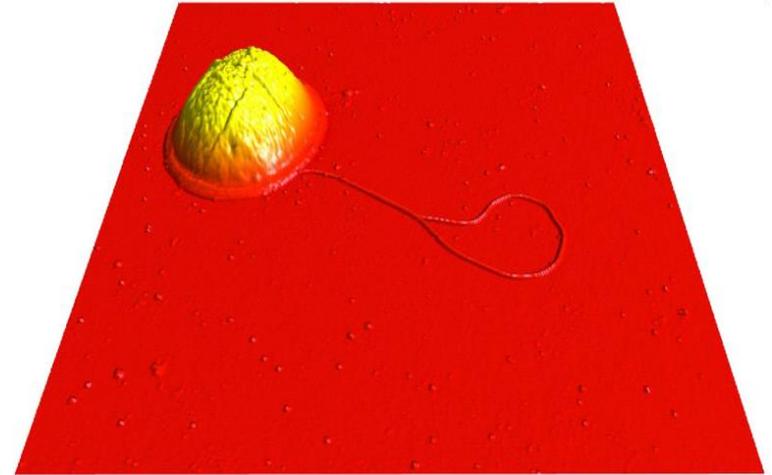
- No lateral forces!

- Phase information (material properties)

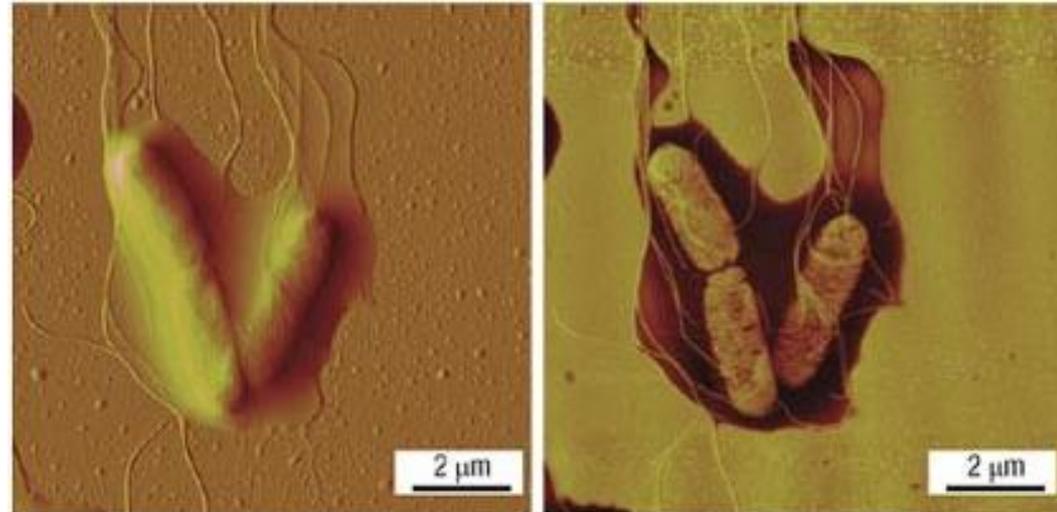
- In **ambient and liquid**

- TM particularly suited for:

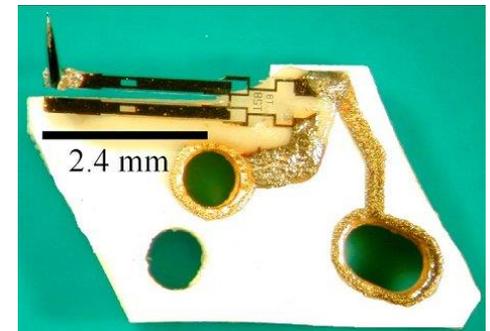
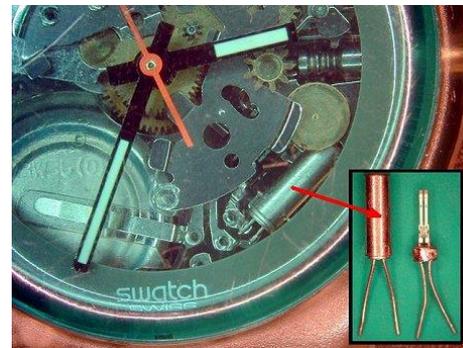
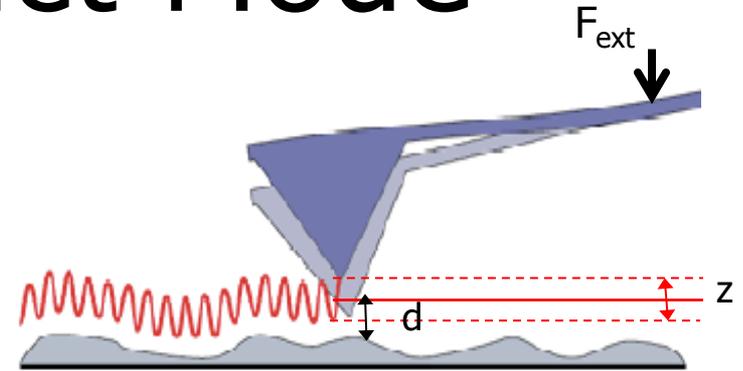
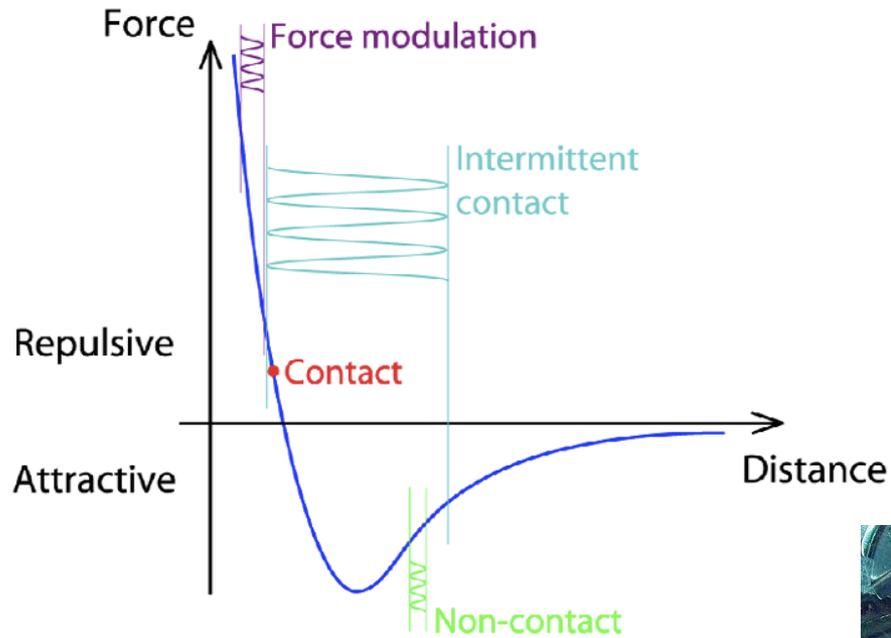
- Biomolecular imaging
- Polymers
- Life Science



Single E. coli bacterium on glass, 6 μ m scan.



Non-contact Mode



Quartz resonators: stiff, no snap-in, small amplitude

Vacuum: only internal dissipation $Q \geq 10,000$
→ long transient regime (≈ 30 ms), too slow for AM feedback

Non-contact Mode (Frequency Modulation)

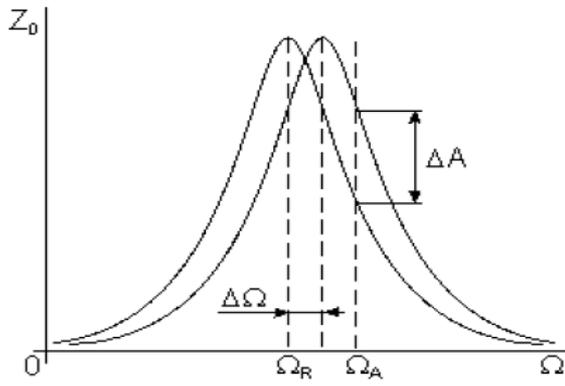


Fig. 4.3. Variation of the oscillations amplitude with resonant frequency.

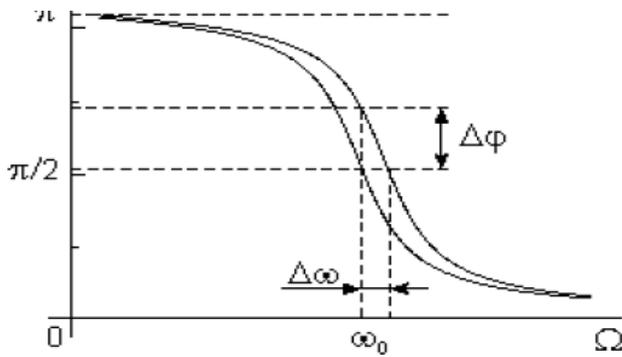
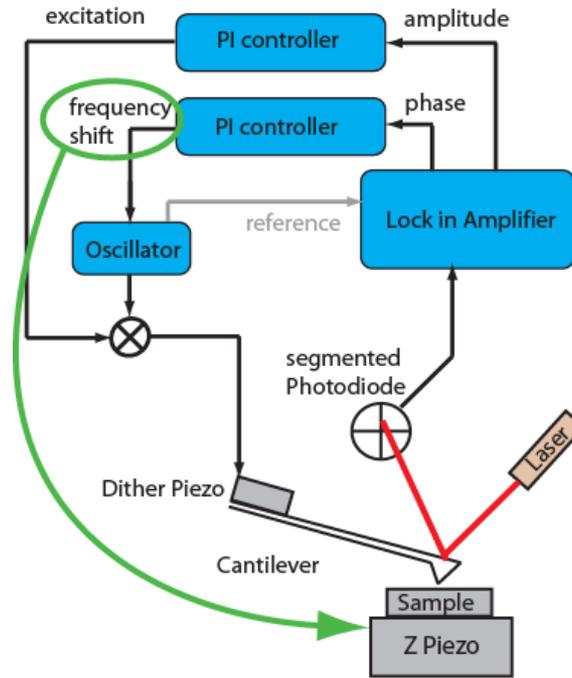


Fig. 4.2. Variation of the oscillations phase with resonant frequency.



In frequency modulation the excitation frequency is constantly adjusted to work at the resonance peak of the cantilever (phase=90°). Additionally the amplitude of oscillation is held constant by varying the excitation.

The topography is obtained by setting the Z-piezo controller to a constant frequency shift.

-Phase Locked Loop, (PLL)

-adjusts excitation frequency to keep phase at 90° (=tracking of eigenfrequency)

-Response time of PLL is independent of Q

Non-contact Mode (Frequency Modulation)

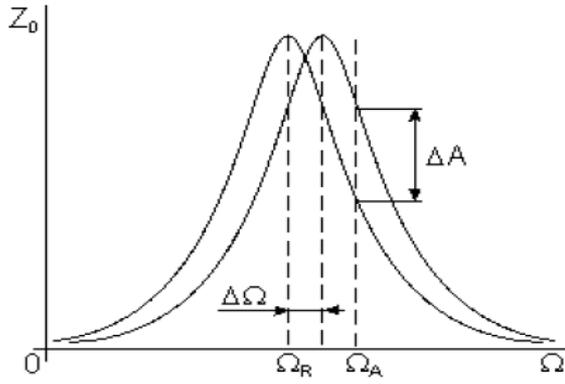


Fig. 4.3. Variation of the oscillations amplitude with resonant frequency.

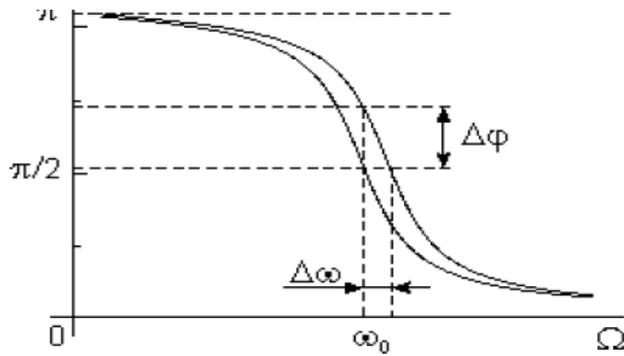
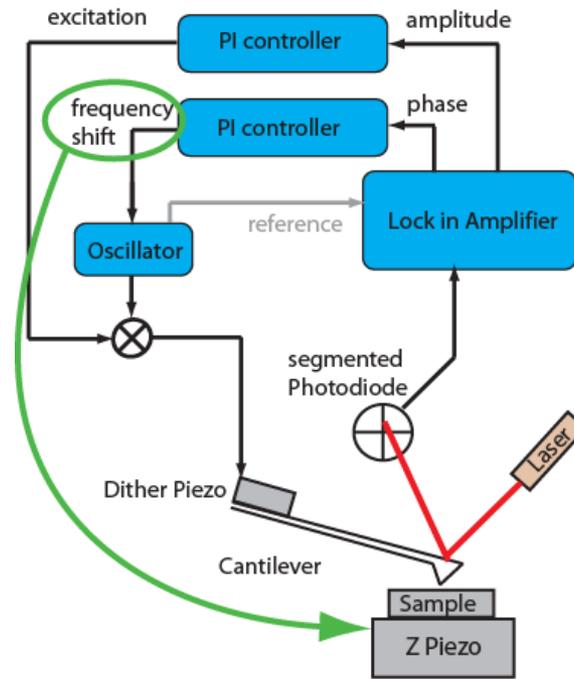
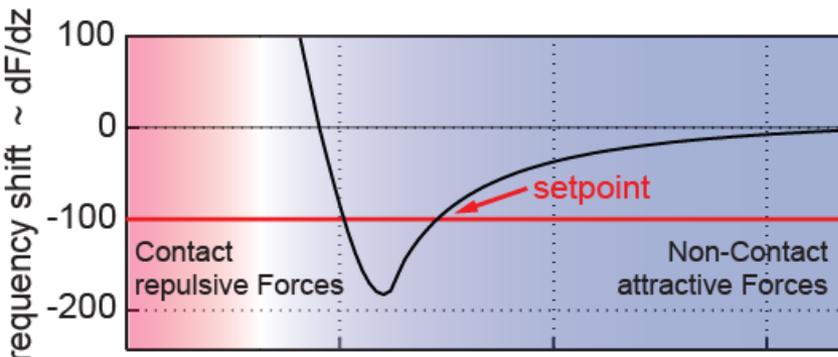


Fig. 4.2. Variation of the oscillations phase with resonant frequency.



In frequency modulation the excitation frequency is constantly adjusted to work at the resonance peak of the cantilever (phase=90°). Additionally the amplitude of oscillation is held constant by varying the excitation.

The topography is obtained by setting the Z-piezo controller to a constant frequency shift.

-typical frequency shift setpoint -10 to -200Hz

-frequency shift proportional to force gradient

-Z feedback on negative frequency shift attractive forces

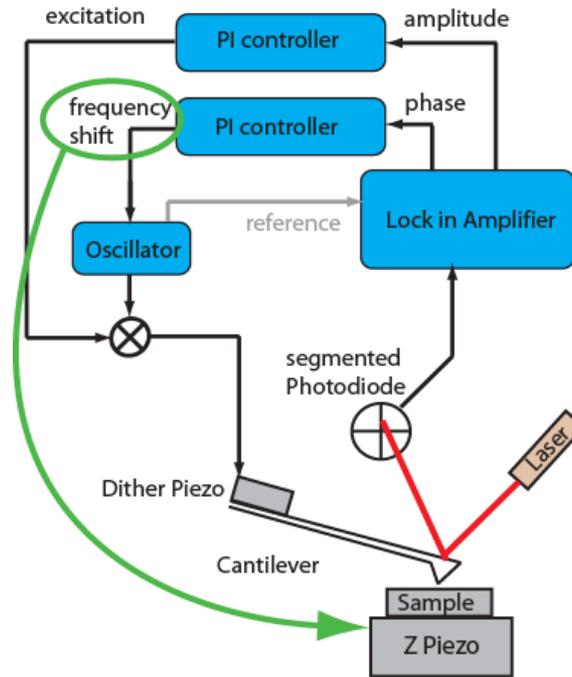
Non-contact Mode (Frequency Modulation)

Amplitude can be held constant by continuous adjustment of excitation amplitude. (AGC automatic gain control)

Risk of tip crash!

Usually smaller scan areas

Flat samples



In frequency modulation the excitation frequency is constantly adjusted to work at the resonance peak of the cantilever (phase=90°). Additionally the amplitude of oscillation is held constant by varying the excitation.

The topography is obtained by setting the Z-piezo controller to a constant frequency shift.

In vacuum increased sensitivity through higher Q!

attractive forces in the range of pN (10^{-12})

$$\frac{\delta f_0}{f_0} = \sqrt{\frac{2k_B T B}{\pi^3 k A^2 f_0 Q}}$$

Chemical identification of individual surface atoms by atomic force microscopy

Yoshiaki Sugimoto, Pablo Pou, Masayuki Abe¹, Pavel Jelinek, Ruben Perez, Seizo Morita¹ & Oscar Custance. **Nature** Vol 446, 64, 2007

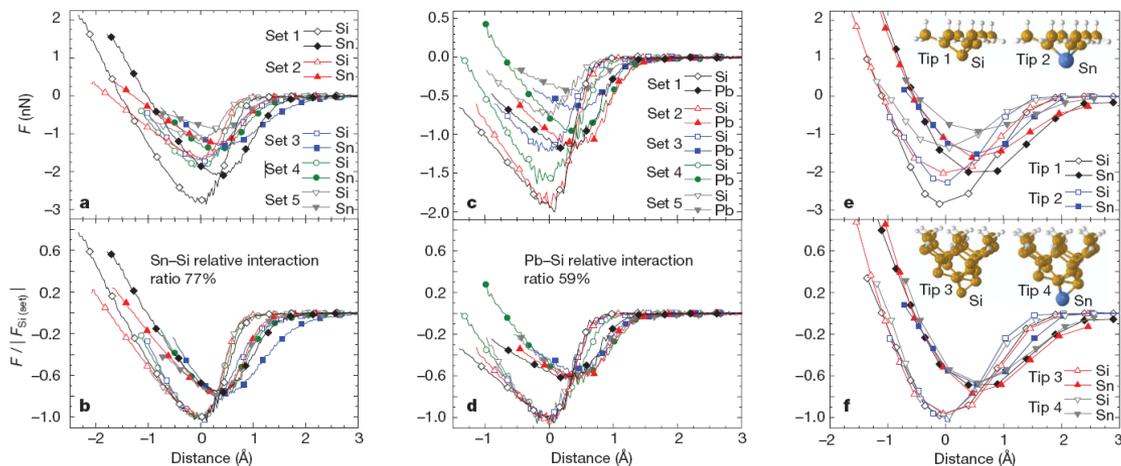
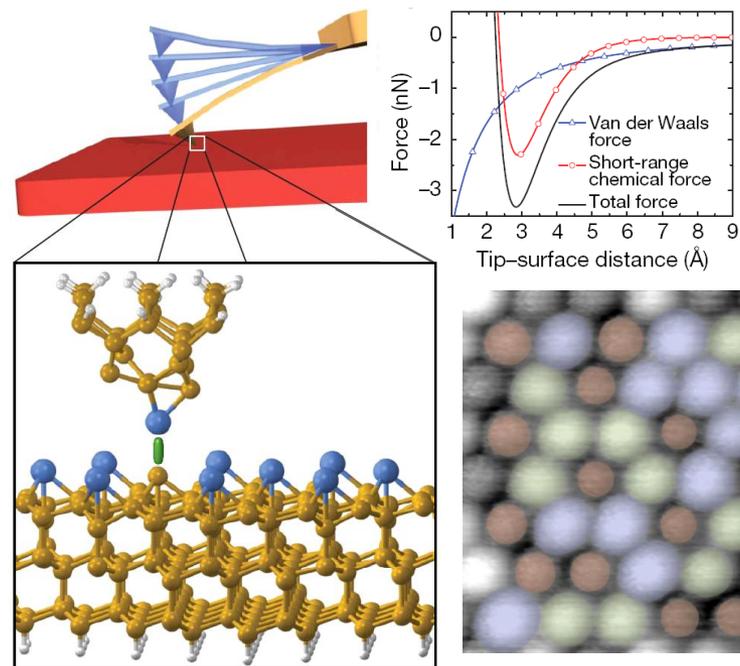


Figure 2 | Probing short-range chemical interaction forces. **a**, Sets of short-range force curves obtained over structurally equivalent Sn and Si atoms. All curves are obtained using identical acquisition and analysis protocols, but the tips differ from set to set. **b**, The same force curves as in **a**, but the curves in each set are now normalized to the absolute value of the minimum short-range force of the Si curve ($|F_{\text{Si}}^{\text{(set)}}|$). **c, d**, Sets of short-range force curves for Pb and Si, obtained in the same way as for Sn and Si, before (**c**) and after (**d**) normalization. The average relative interaction ratios calibrated against Si, or the maximum attractive short-range forces for Sn and Pb relative to those of Si (77% and 59%, respectively), provide an intrinsic signature for

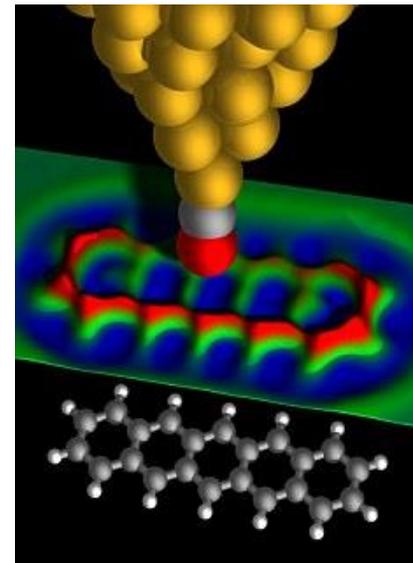
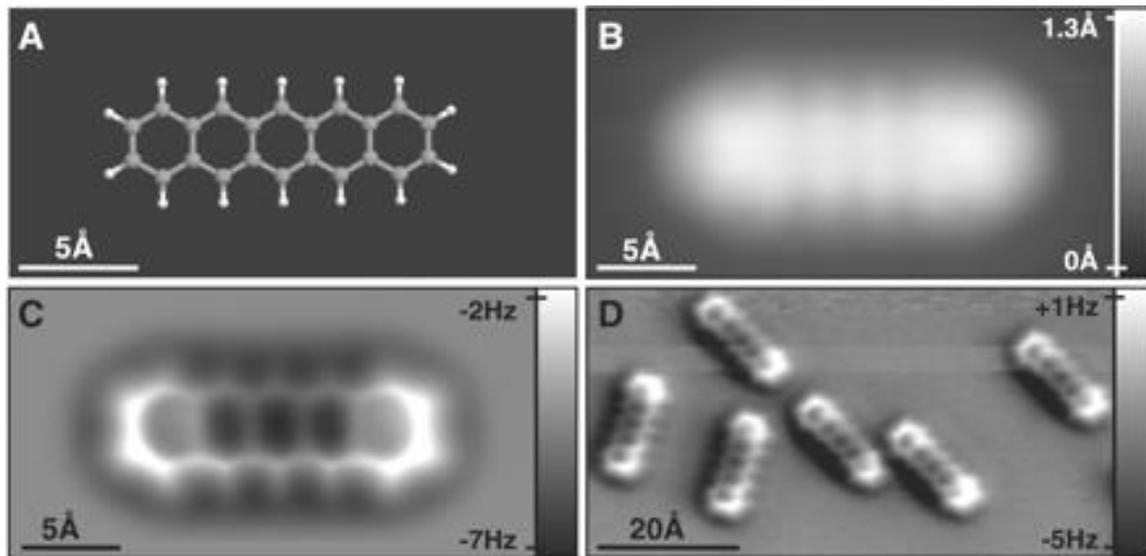
the chemical identification of individual atoms. Each experimental force characteristic shown here was obtained from the measurement of a hundred spectroscopic curves (see Methods for details). The acquisition parameters are available in the Supplementary Information. **e, f**, Chemical force curves calculated for different tip-apex models (see insets for structural and chemical characteristics) over the Sn and Si atoms of the $(\sqrt{3} \times \sqrt{3})$ R30° surface model shown in Fig. 1b. The curves are shown before (**e**) and after (**f**) normalization. In both the experimental and the calculated short-range force curves, the distance axes denote the tip-sample relative displacement (see Methods for details).

Non-contact image of pentacene

Science

Vol. 325 no. 5944 pp. 1110-1114
DOI: 10.1126/science.1176210

The Chemical Structure of a Molecule Resolved by Atomic Force Microscopy



STM and AFM imaging of pentacene on Cu(111). (A) Ball-and-stick model of the pentacene molecule. (B) Constant-current STM and (C and D) constant-height AFM images of pentacene acquired with a CO-modified tip. Imaging parameters are as follows: (B) set point $I = 110$ pA, $V = 170$ mV; (C) tip height $z = -0.1$ Å [with respect to the STM set point above Cu(111)], oscillation amplitude $A = 0.2$ Å; and (D) $z = 0.0$ Å, $A = 0.8$ Å. The asymmetry in the molecular imaging in (D) (showing a "shadow" only on the left side of the molecules) is probably caused by asymmetric adsorption geometry of the CO molecule at the tip apex.