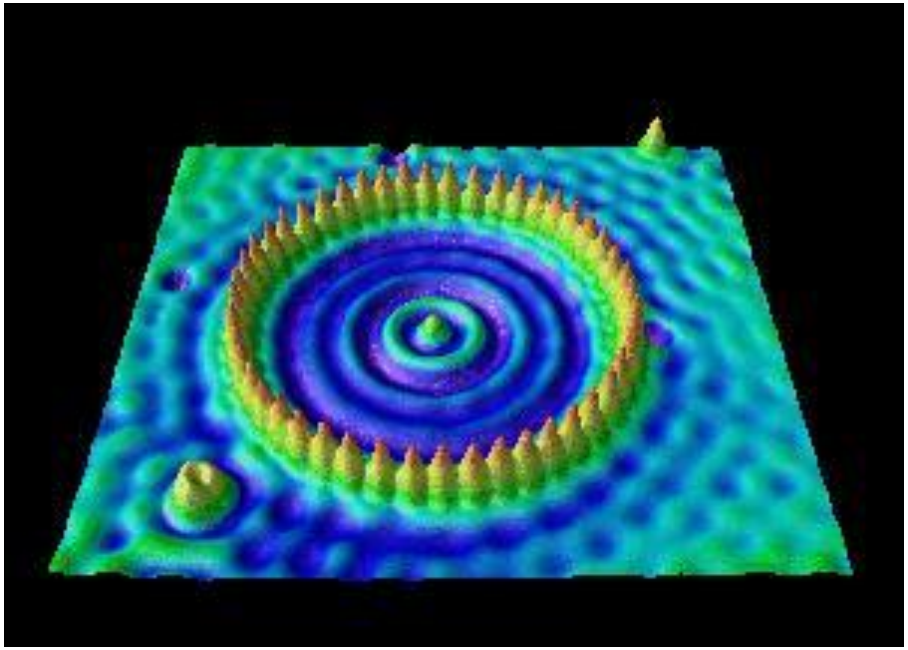
SCANNING TUNNELING MICROSCOPY



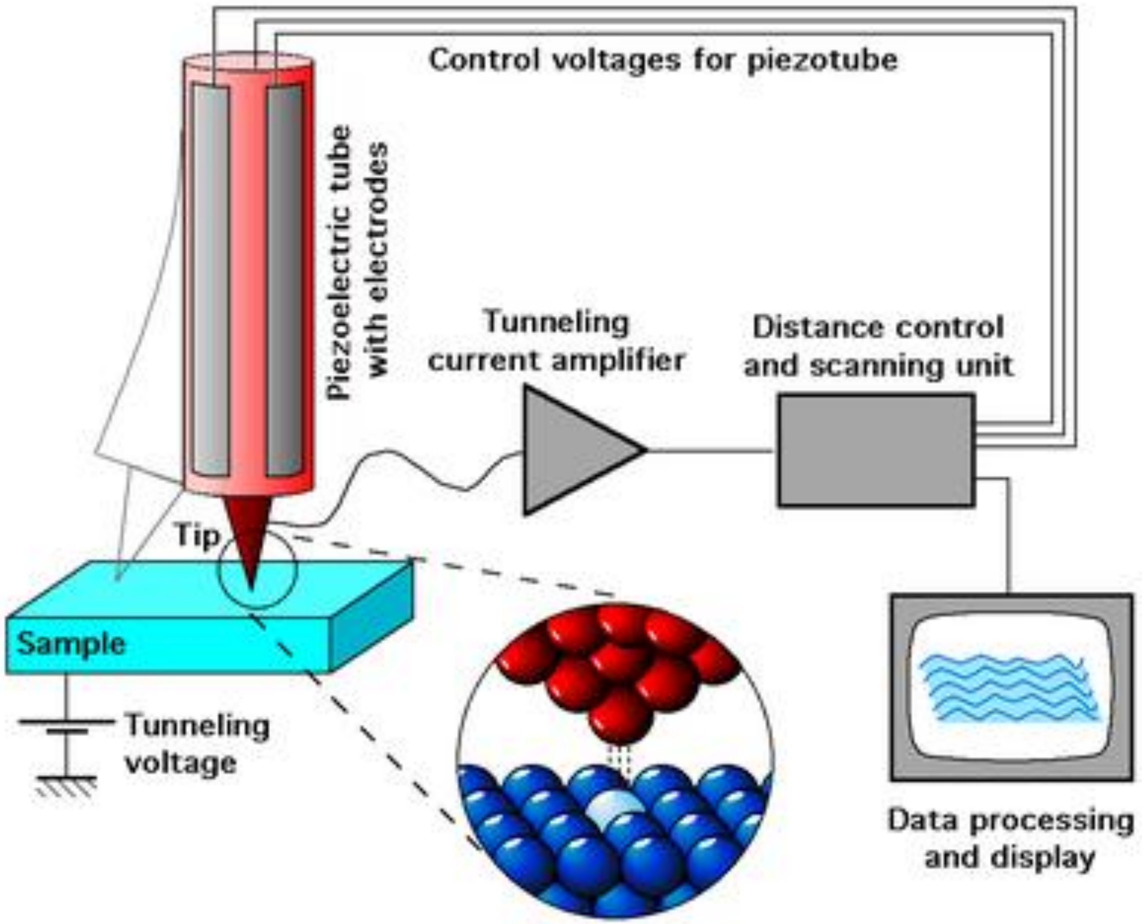
http://www.almaden.ibm.com/vis/stm/gallery.html

Scanning Tunneling Microscopy, *Jingpeng Wang, University of Guelp, GWC, CHEM 7513, (2006)*

STM - INTRODUCTION

- Tunnel effect
- Atomic resolution, better than the best EM
- Non-destructive measurements
- Tunneling current gives atomic information about the surface
- Scanning Probe Microscopes (SPM): designed based on the scanning technology of STM

SCANNING TUNNELING MICROSCOPY



http://www.iap.tuwien.ac.at/www/surface/STM_Gallery/index.htmlx

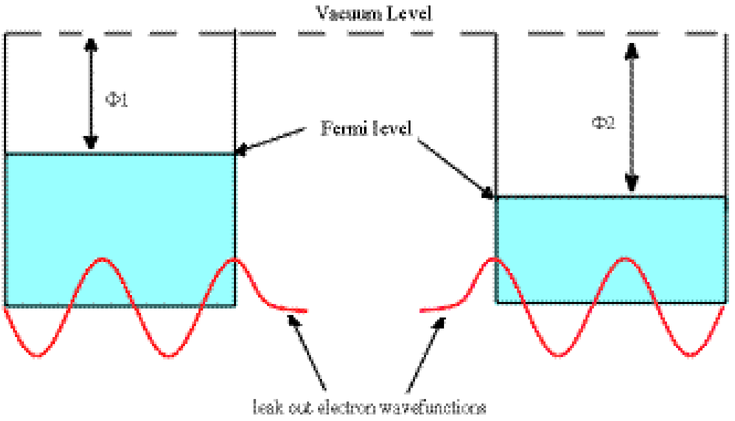
THEORY AND PRINCIPLES

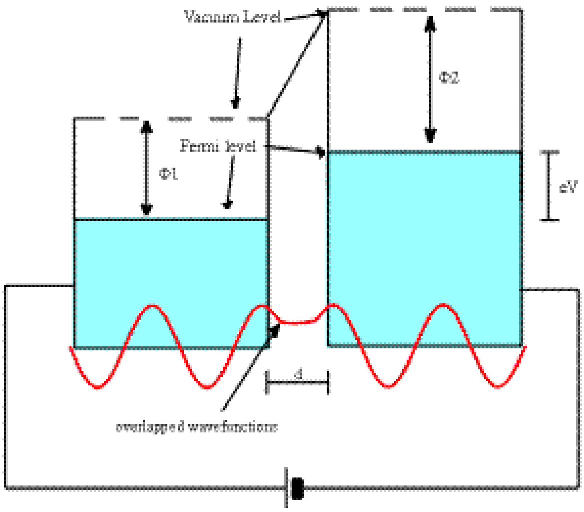
- In classical physics electron flows are not possible without a direct connection by a wire between two surfaces.
- On an atomic scale a quantum mechanical particle behaves in its wave function
- There is a finite probability that an electron will “jump” from one surface to the other of lower potential

http://www.chembio.uoguelph.ca/educmat/chm729/STMpage/stmdet.htm

THEORY AND PRINCIPLES

- If these leak-out waves overlap and a small bias voltage is applied between the tip and the sample, a tunneling current flows.
- The magnitude of this tunneling current does not give the nuclear position directly, but is directly proportional to the electron density of the sample at a point.

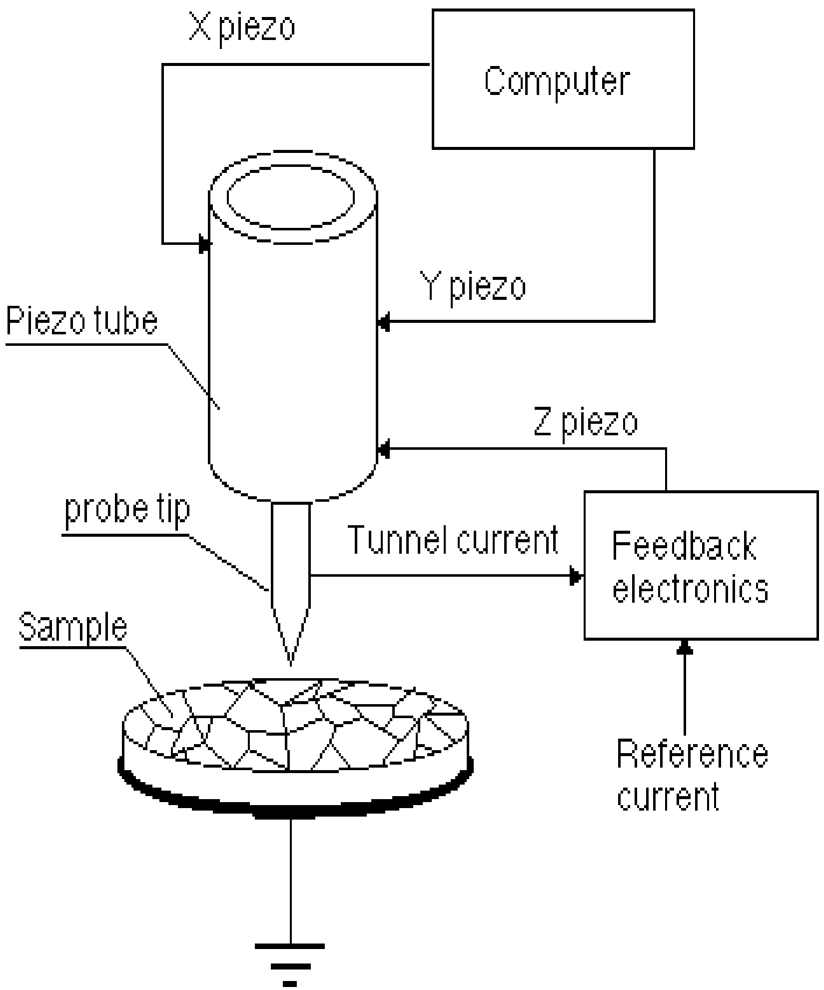




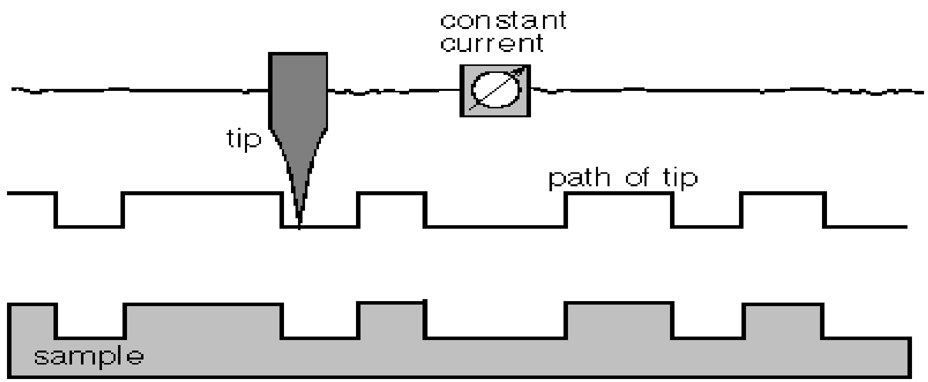
http://www.chembio.uoguelph.ca/educmat/chm729/STMpage/stmdet.htm

EXPERIMENTAL SETUP

- the *sample*
- a sharp *tip* on a piezo-electric crystal tube
- a mechanism to control the location of the tip in the x-y plane parallel to the sample surface
- a *feedback* loop to control the height of the tip above the sample (the z-axis)



EXPERIMENTAL SETUP



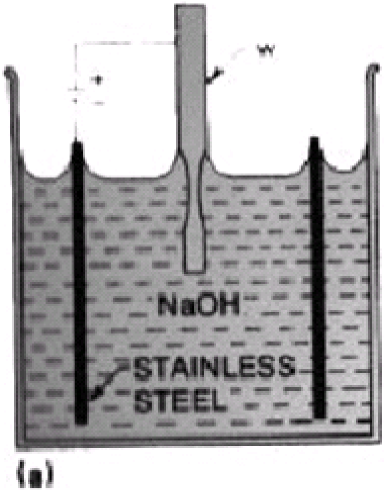
- Raster the tip across the surface, and using the current as a feedback signal.
- The tip-surface separation is controlled to be constant by keeping the tunneling current at a constant value.
- The voltage necessary to keep the tip at a constant separation is used to produce a computer image of the surface.

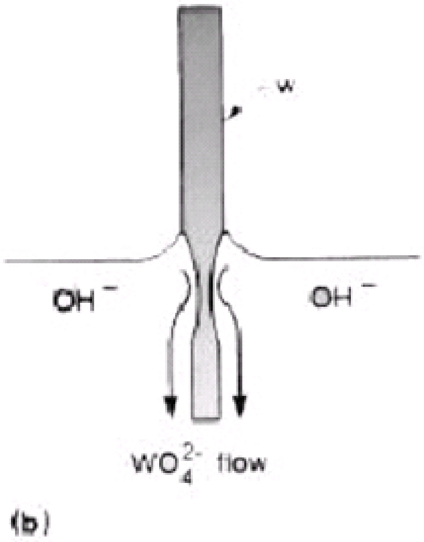
What does piezo-electric mean?

- In 1880 Pierre Curie: by applying a pressure to certain crystals induce a potential across the crystal.
- The STM reverses this process. Thus, by applying a voltage across a piezoelectric crystal, it will elongate or compress.
- A typical piezoelectric material used in an STM is Lead Zirconium Titanate.

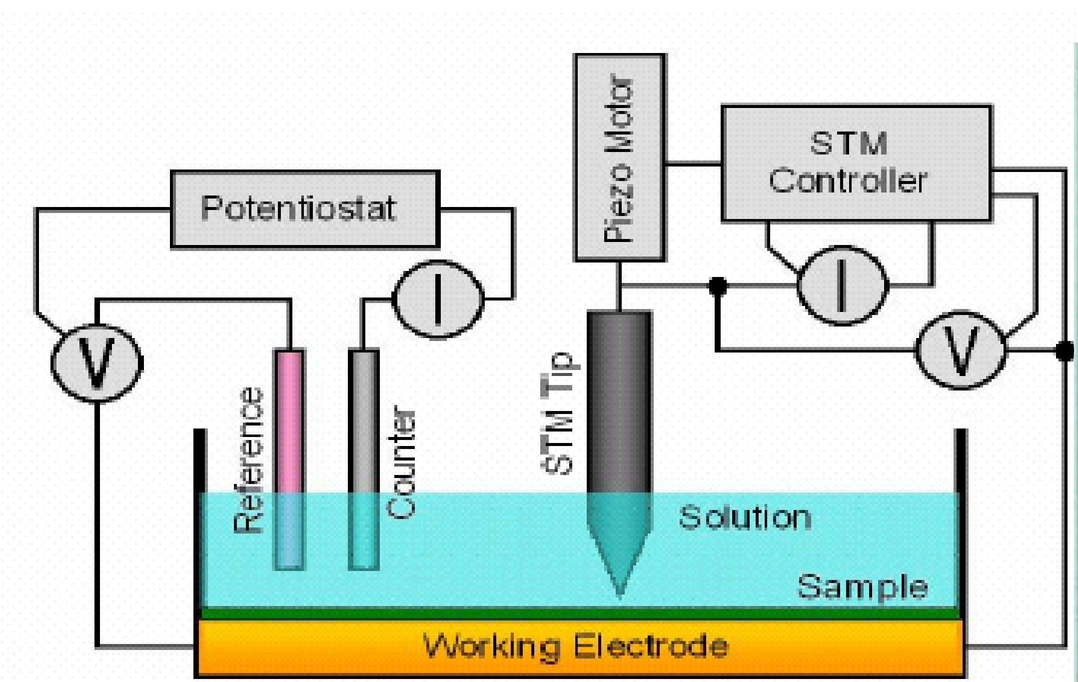
Experimental details: Tips preparation

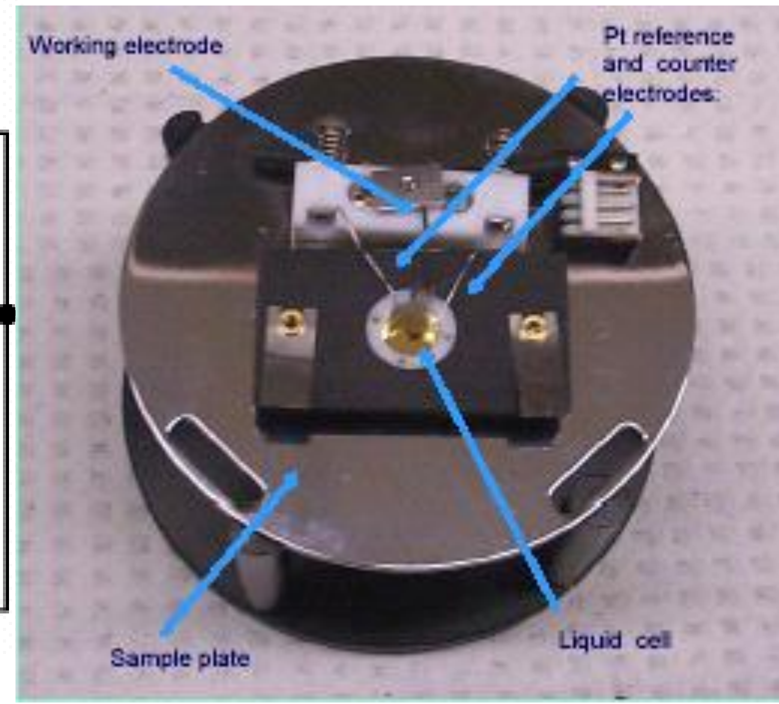
- STM tip - sharp needle and terminates in a single atom
  - Pure metals (W, Au) - Alloys (Pt-Rh, Pt-Ir)
  - Chemically modified conductor (W/S, Pt-Rh/S, W/C…)
- Preparation of tips: cut by a wire cutter and used as is cut followed by electrochemical etching





APPLICATIONS: Electrochemical STM



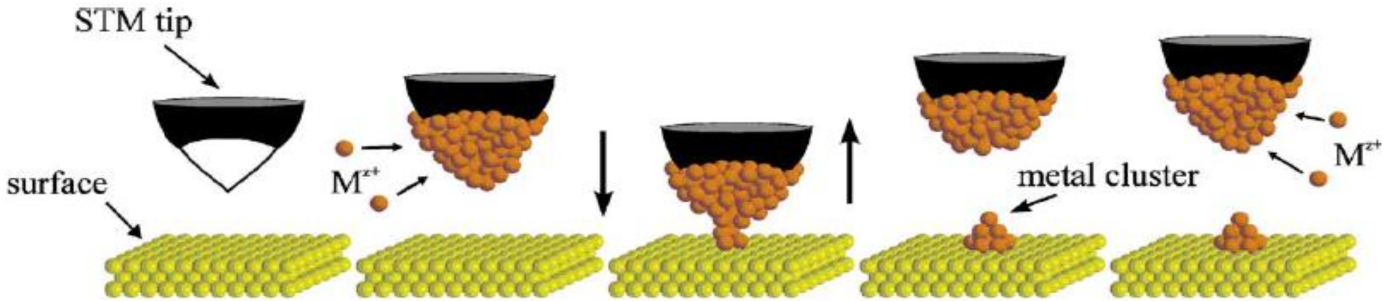


APPLICATIONS: Electrochemical STM

- Three-electrode system+ STM: the STM tip may also become working electrode as well as a tunneling tip.
- faradic currents several orders of magnitude larger than the tunneling current
- STM tip: a tool for manipulating individual atoms or molecules on substrate surface
- Tip crash method: (surface damaged) use the tip to create surface defects

APPLICATIONS: Electrochemical STM

- Electrochemistry can be used to manipulate the adsorbates



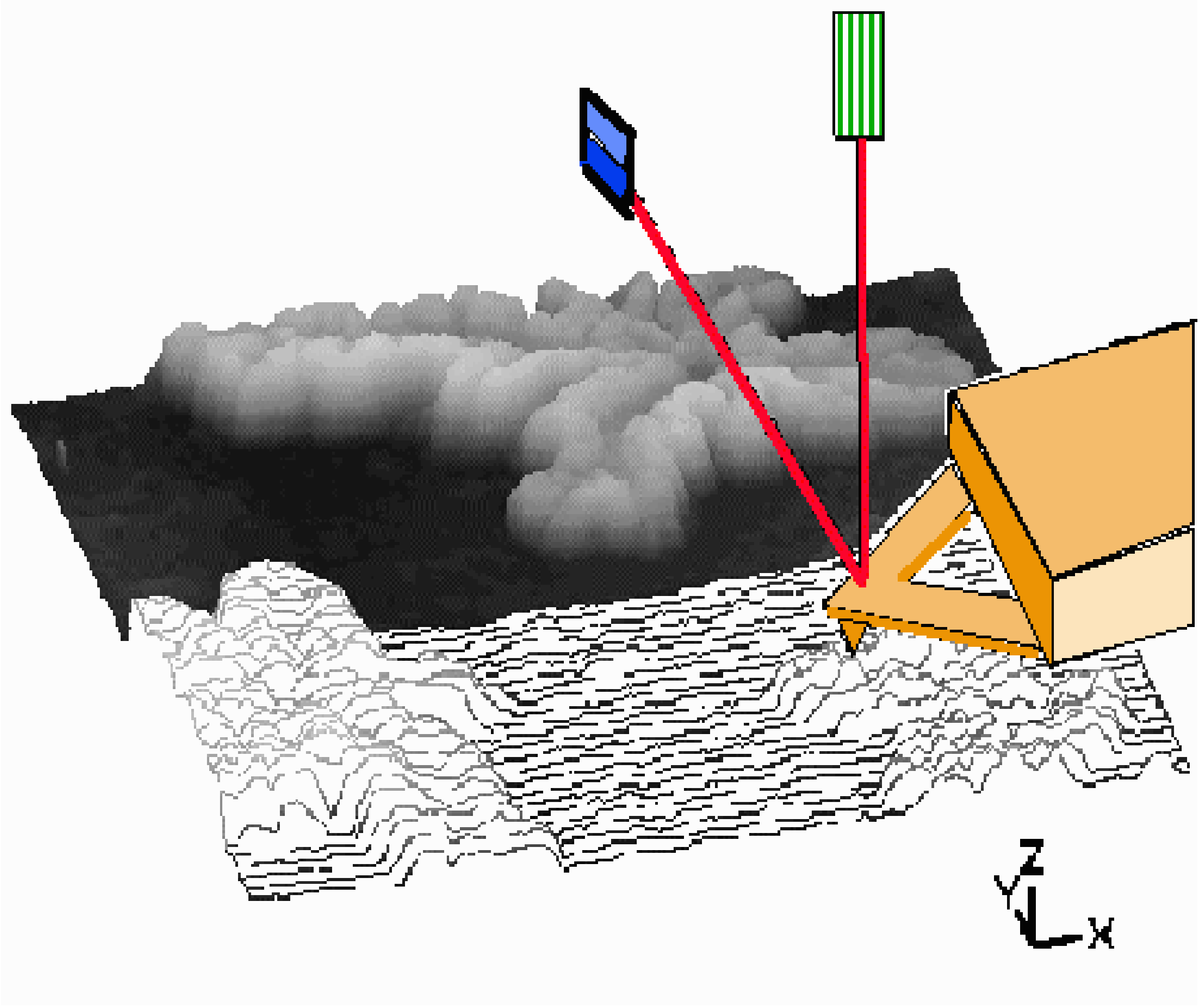
STM

STM is one the most powerful imaging tools with an unprecedented precision.

Disadvantage of STM:

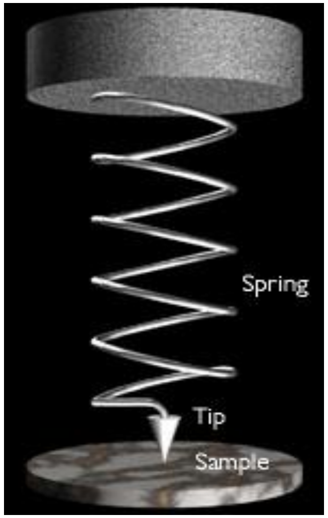
1. Vibrations from fans, pumps, machinery, building movements …
2. Ultra high vacuum
3. Do not work with nonconductive materials, such as glass, rock, etc.
4. Spatial resolution of STM is very good, but temporal resolution (around seconds) – no appropriate for fast kinetics of electrochemical process.

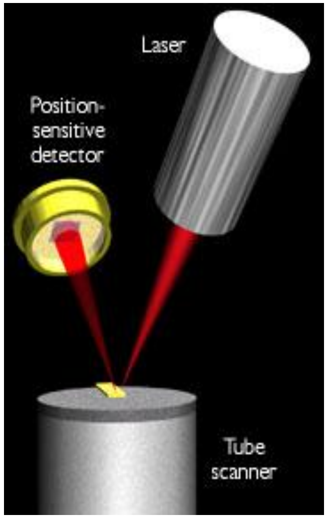
SPM -Principle



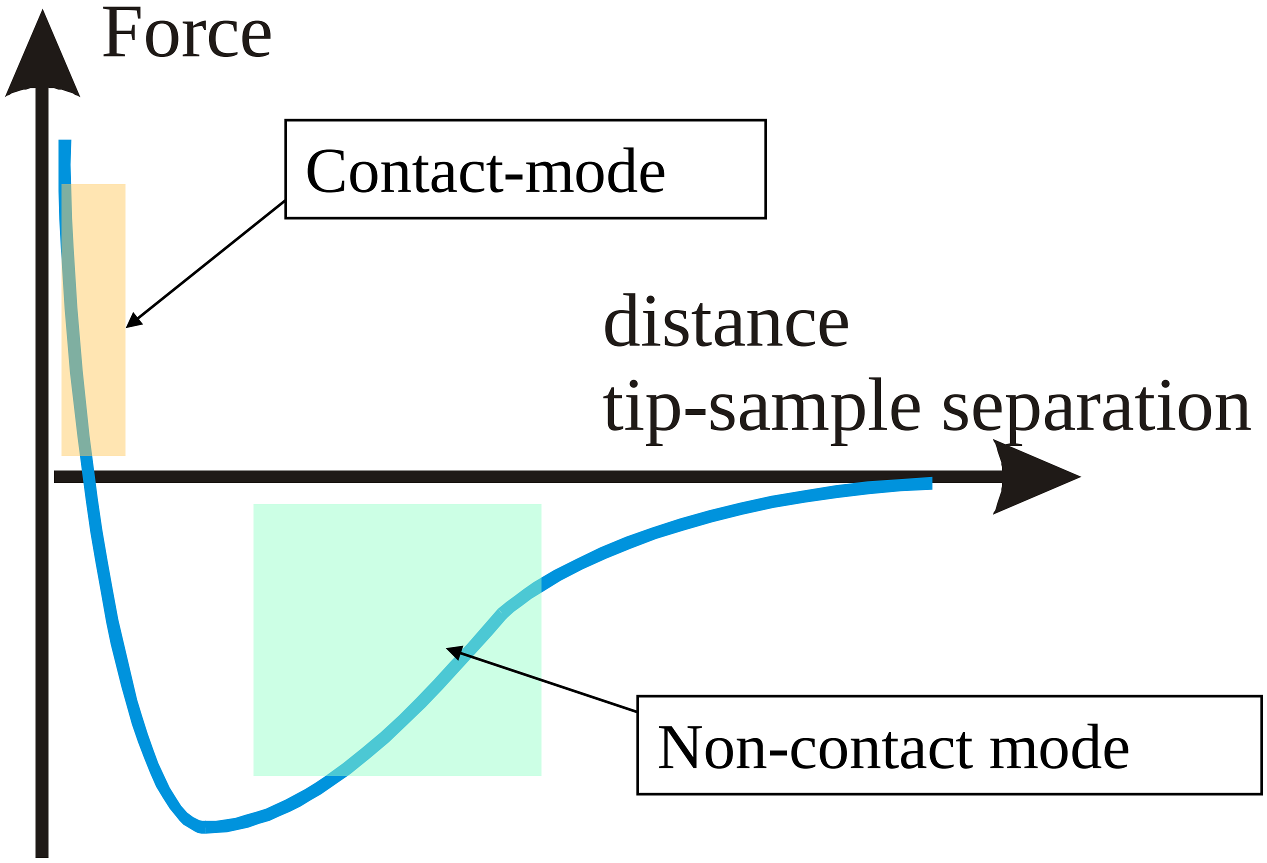
Scanning Probe Microscope

1. What does an AFM measure?
2. How does it work?
3. Tip and Cantilever
4. Laser Beam Deflection
5. Scanner and Feedback Control
6. Imaging Modes

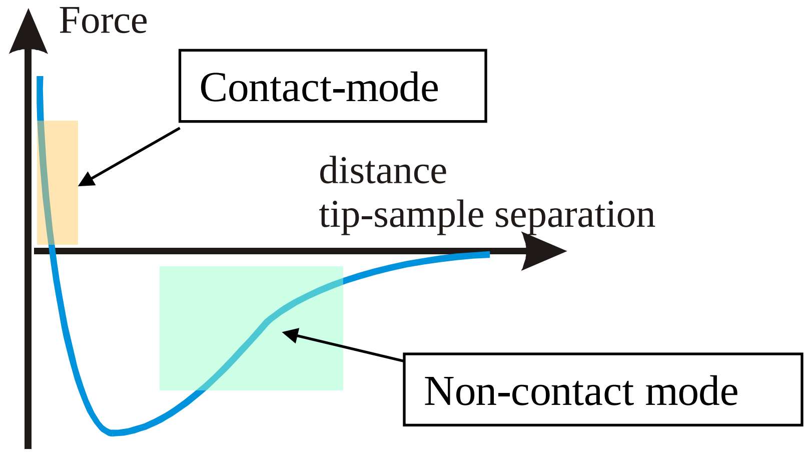




Forces in AFM measurements



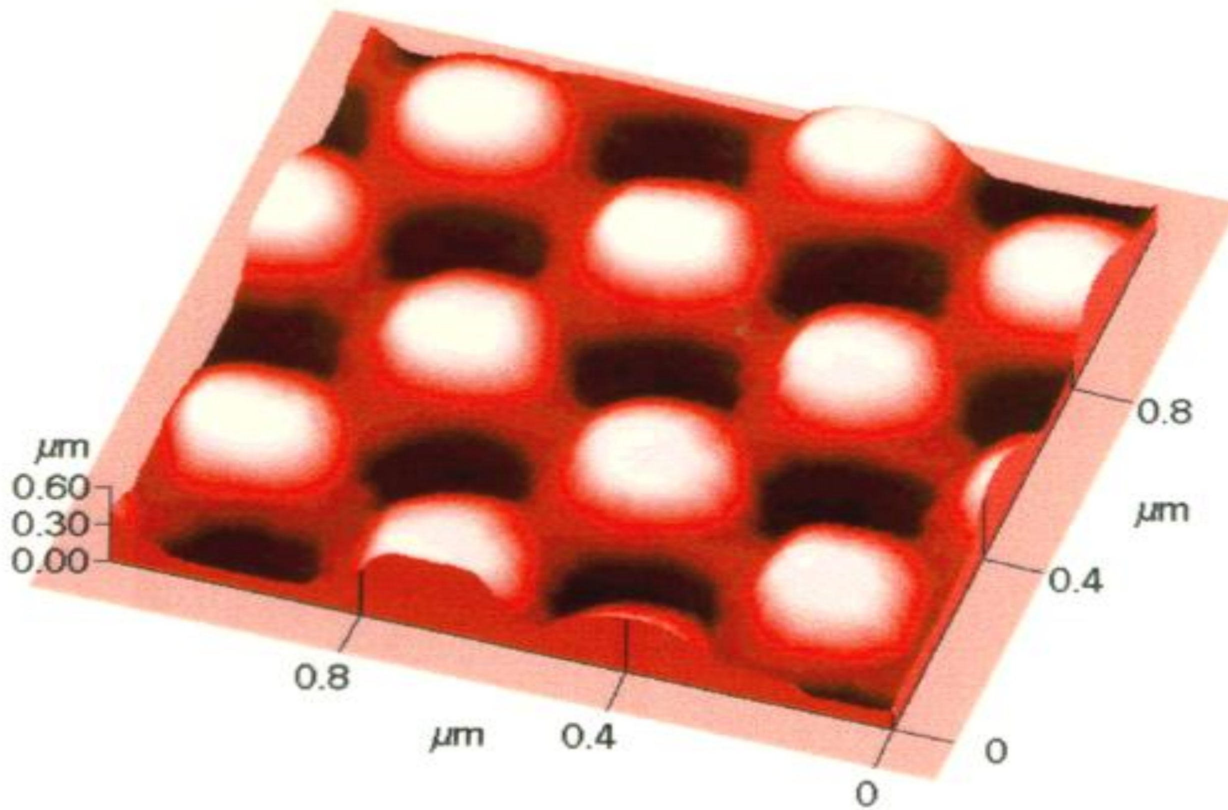
Forces in SPM measurements



Attractive forces between surface and tip:

- Electrostatic, magnetic forces (typical range 1000 nm) (surface dependent)
- Chemical bonding forces <1 nm (surface dependent)
- VdW forces < 5 nm (tip radius dependent)
- Capillary forces due to water film on surface (only in air)

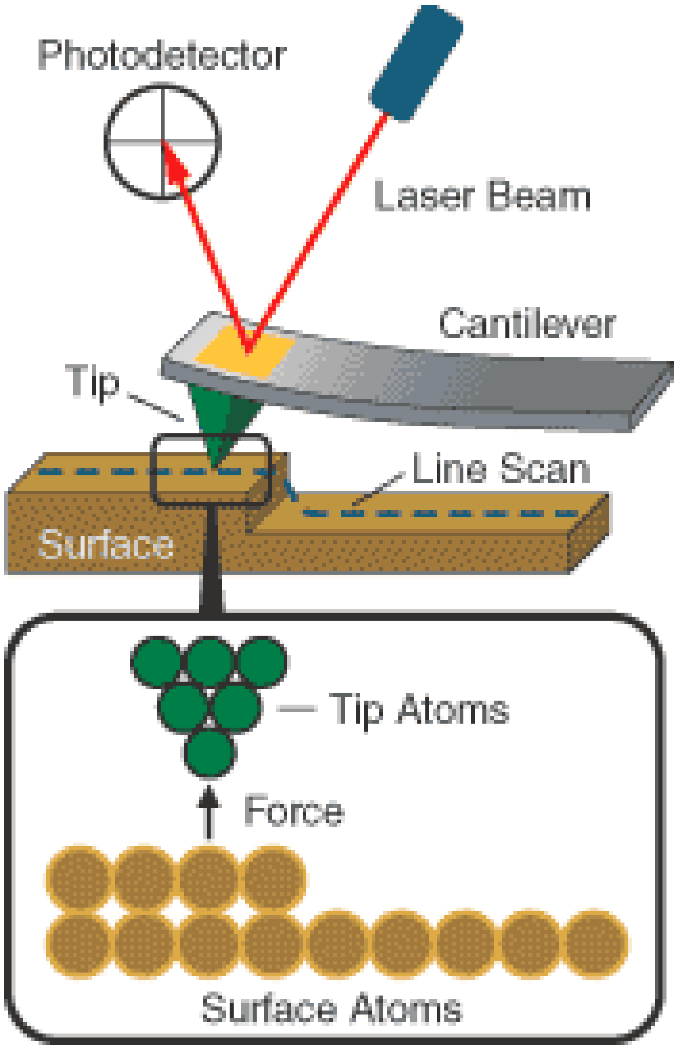
3D AFM image



Polymer pattern

Dr. Z. Barkai

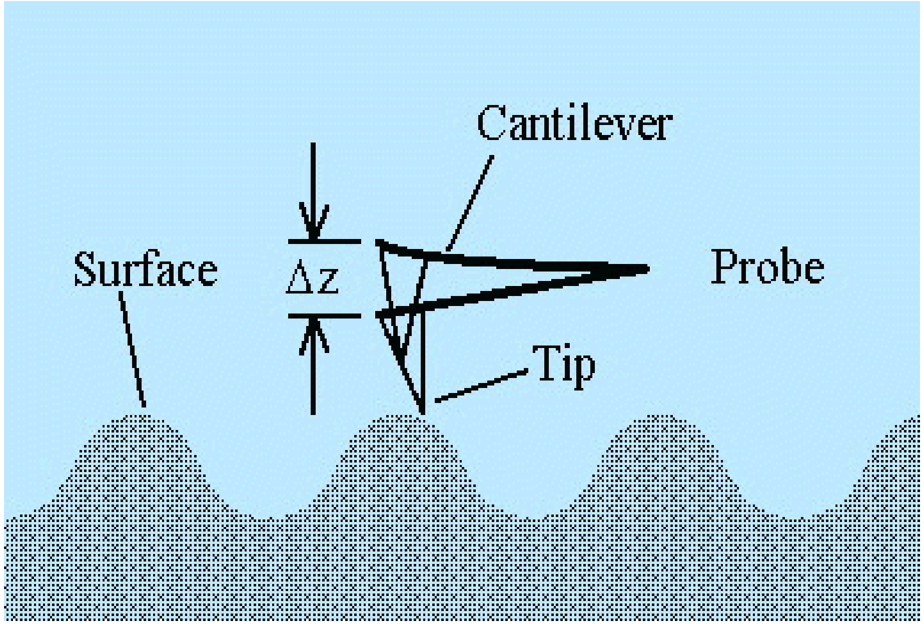
How It Works



http://www.molec.com/what_is_afm.html

- Cantilever
- Tip
- Surface
- Laser
- Multi-segment photodetector

Force Microscopy



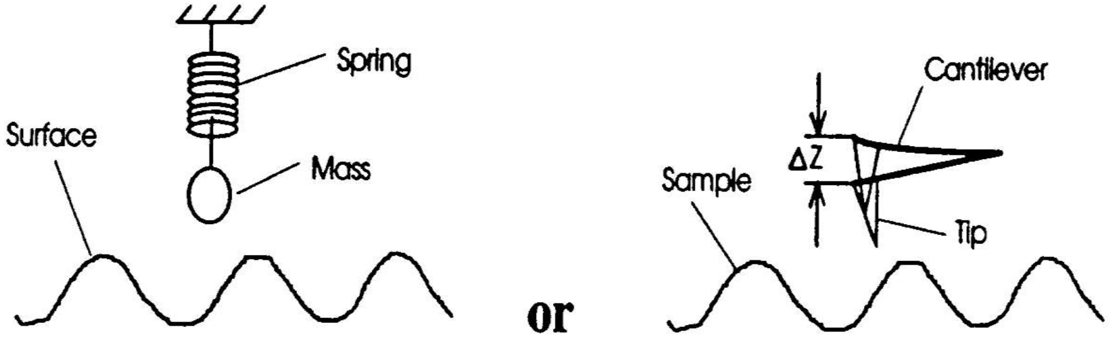
- 3-D Surface Topography
- Force: pico-Newton - nano-Newton range
- May be combined with other techniques

Force Microscopy

Basic Principle

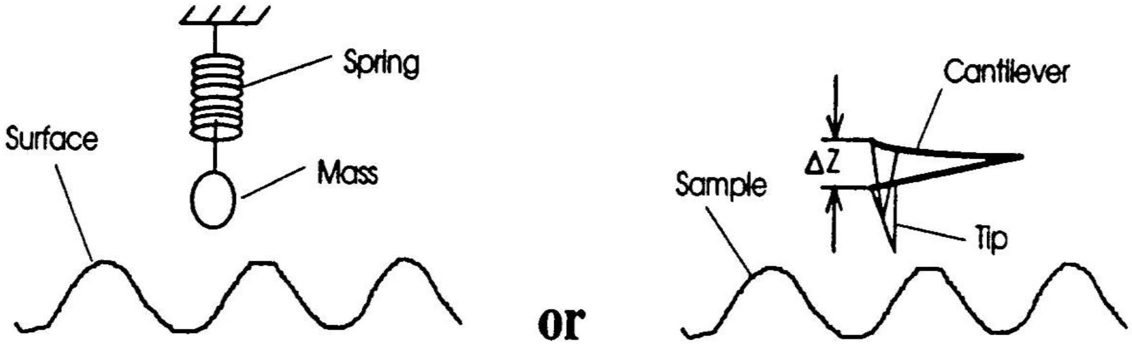
Detecting forces between a mass (tip) attached to a spring (cantilever)

Tip+cantilever feel some force when it is brought very close to the surface.

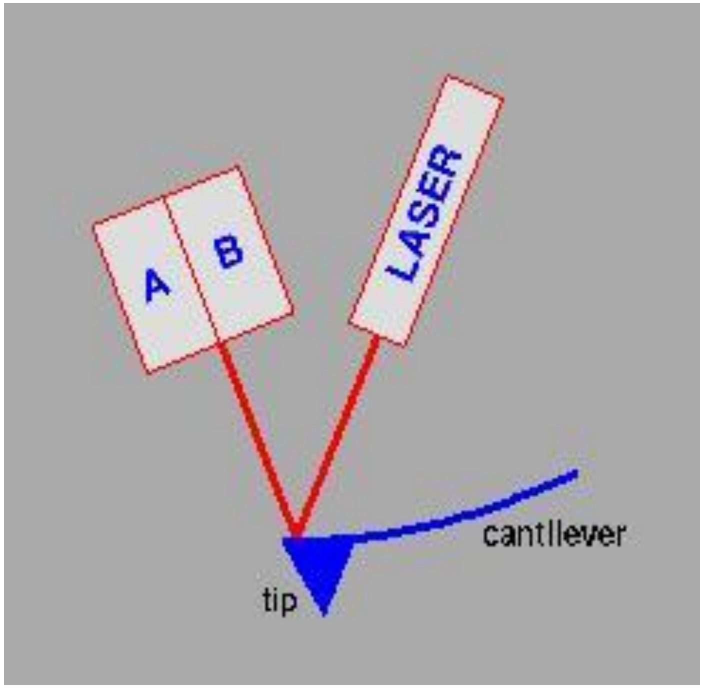


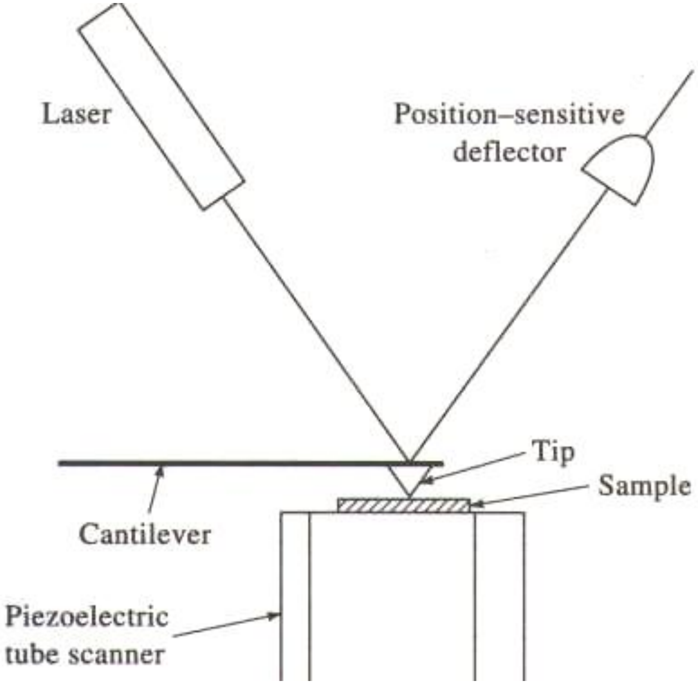
Force Microscopy

- Sensor: responds to a force
- The sensor: a cantilever beam with an effective spring constant k, moves in accordance with the forces acting on its tip
- Detector: measures the force by detecting the deflection in the cantilever



Force Microscopy

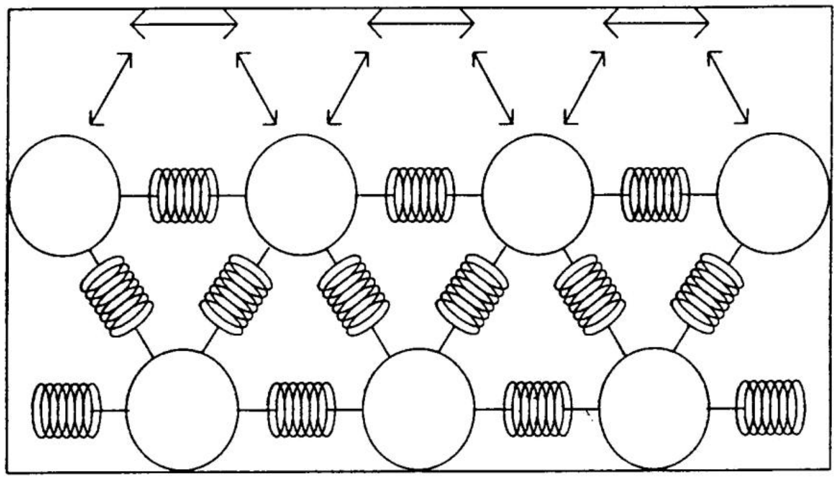




- Modern SPM use a split photo diode to detect the deflection
- System is sensitive to 0.01 mm as the tip scans the sample surface

http://spm.phy.bris.ac.uk/

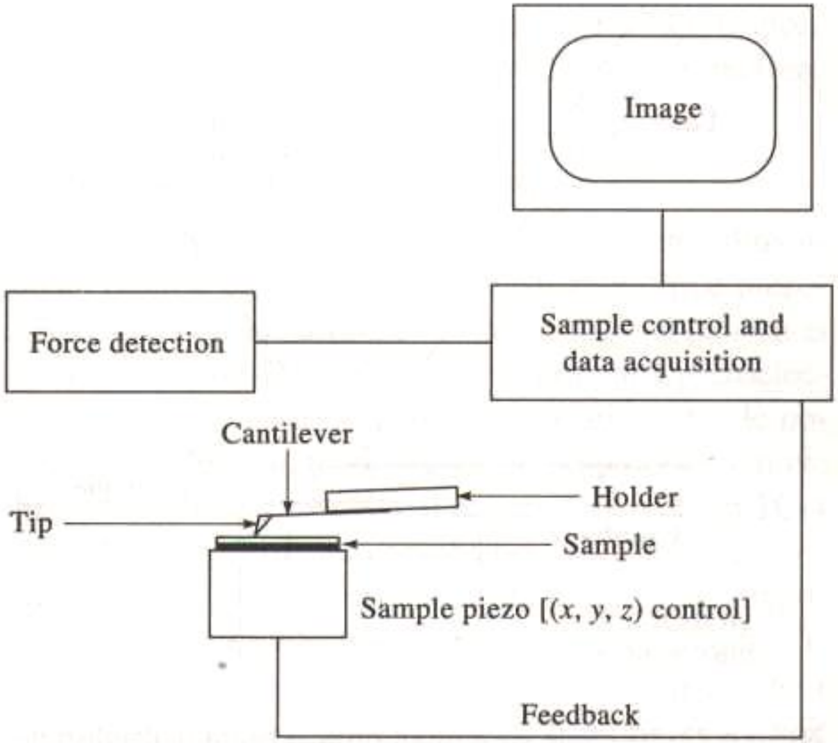
Force Microscopy



- Frequency of atoms vibration, f, at room temperature ~ 10^{14} Hz
- The mass, m, of an atom ~ 10^{-30} kg
- The effective spring constant, k, between atoms is

$$k=\omega^2 m \approx 1 N/m$$

Design of an atomic force microscope



AFM is performed by scanning a sharp tip on the end of a flexible cantilever across the sample while maintaining a small force.

Tip radii: 1nm to 10nm

http://www.nanoscience.com/education/AFM.html

Atomic Force Microscopy (AFM)

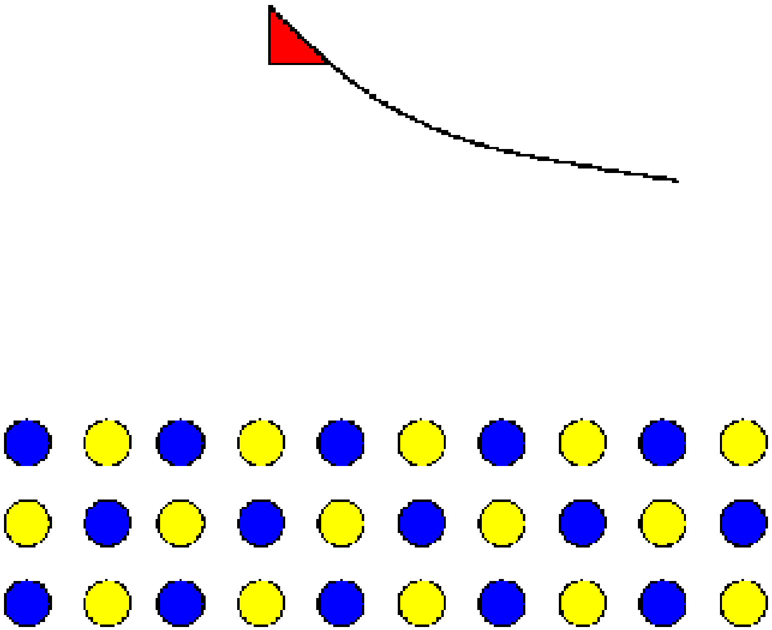
- AFM has two modes, tapping mode and contact mode.
- In contact mode, constant cantilever deflection is maintained.
- In tapping mode, the cantilever is oscillated at its resonance frequency

Contact Mode AFM

- A tip is scanned across the sample while a feedback loop maintains a **constant cantilever deflection (and force)**
- The tip contacts the surface through the adsorbed fluid layer.
- Forces range from **nano to micro N** in ambient conditions and even lower (0.1 nN or less) in liquids.

Non-contact mode AFM

(movie)



Tapping Mode AFM

- A cantilever and tip **oscillate at its resonant frequency** and scanned across the sample surface
- A **constant oscillation amplitude (constant tip-sample interaction)** are maintained during scanning. Typical amplitudes are 20-100nm
- Forces can be **200 pN or less**
- **The amplitude of the oscillations changes when the tip scans over bumps or depressions on a surface**

Non-contact Mode AFM

- The **cantilever oscillate** slightly above its resonant frequency
- Oscillation amplitude <10nm
- The tip does not touch the sample. Instead, t**ip oscillates above the adsorbed fluid layer**
- A **constant oscillation amplitude is maintained**.
- The resonant frequency of the cantilever is decreased by the **van der Waals forces** which extend from 1-10nm above the adsorbed fluid layer - **changing the amplitude of oscillation.**

Advantages and Disadvantages of contact mode

– Advantages:
  - High scan speeds
  - The only mode that can obtain “atomic resolution” images
  - Rough samples with extreme changes in topography can sometimes be scanned more easily

– Disadvantages:
  - Lateral (shear) forces can distort features in the image
  - The forces normal to the tip-sample interaction can be high in air due to **capillary forces** from the adsorbed fluid layer on the sample surface.
  - The combination of lateral forces and high normal forces can result in reduced spatial resolution and may damage soft samples (i.e. biological samples, polymers, silicon) due to scraping

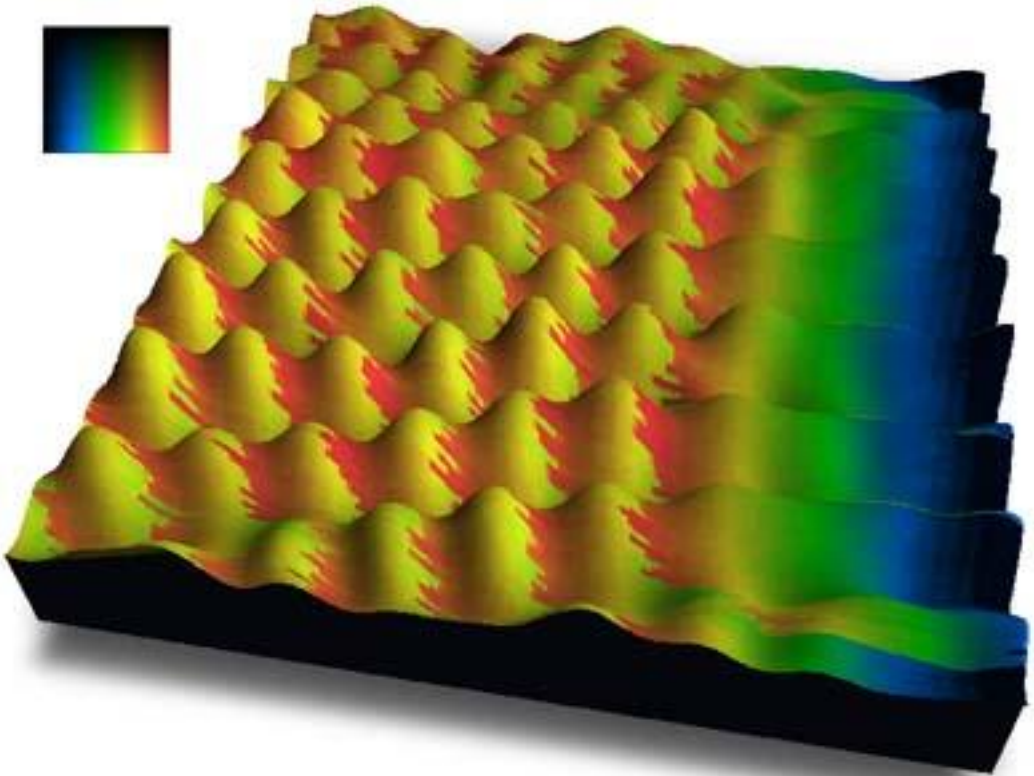
Advantages and Disadvantages of tapping mode

- Advantages:
  - Higher lateral resolution on most samples (1 to 5nm)
  - Lower forces and less damage to soft samples imaged in air
  - Lateral forces are virtually eliminated so there is no scraping
- Disadvantages:
  - Slightly lower scan speed than contact mode AFM

AFM Modes: comparison

- Contact Mode
  - High resolution
  - Damage to sample
  - Can measure frictional forces
- Non-Contact Mode
  - Lower resolution
  - No damage to sample
- Tapping Mode
  - Better resolution
  - Minimal damage to sample

Topography

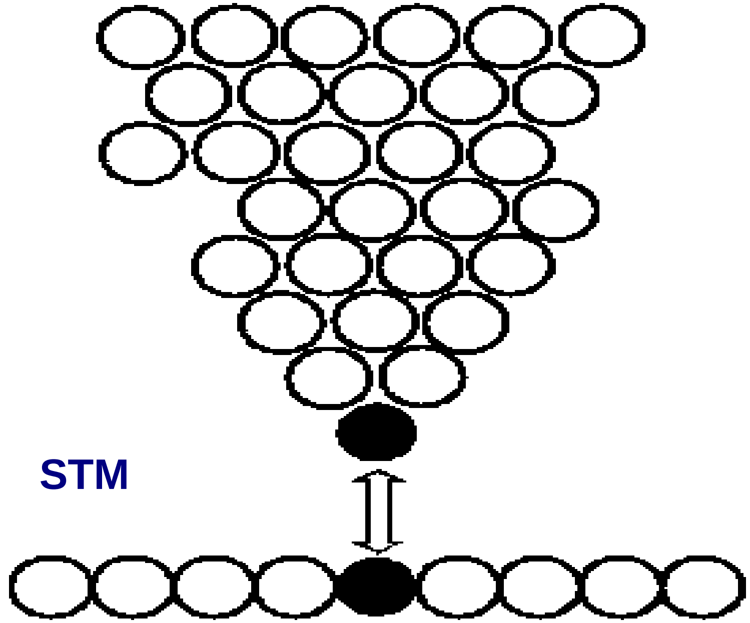


2.5 x 2.5 nm simultaneous topographic and friction image of highly oriented pyrolytic graphic (HOPG). Bumps represent topographic atomic corrugation, while coloring reflects the lateral forces on the tip.
Scan direction: right to left

http://stm2.nrl.navy.mil/how-afm/how-afm.html#imaging%20modes

AFM -Resolution

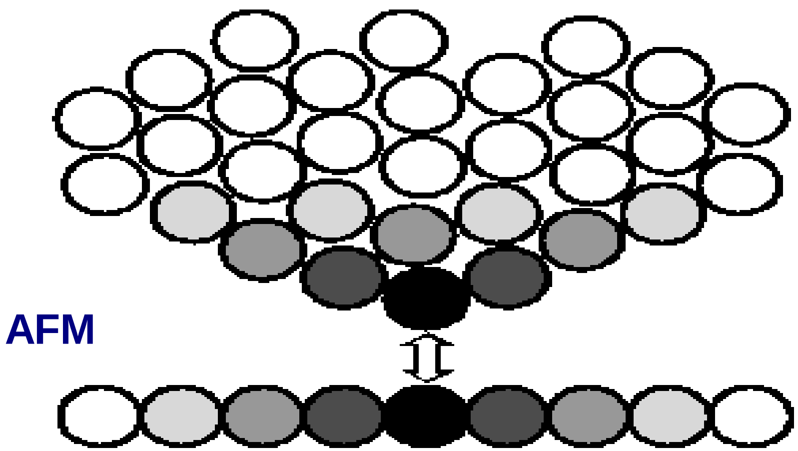
- **STM-single atom interaction**



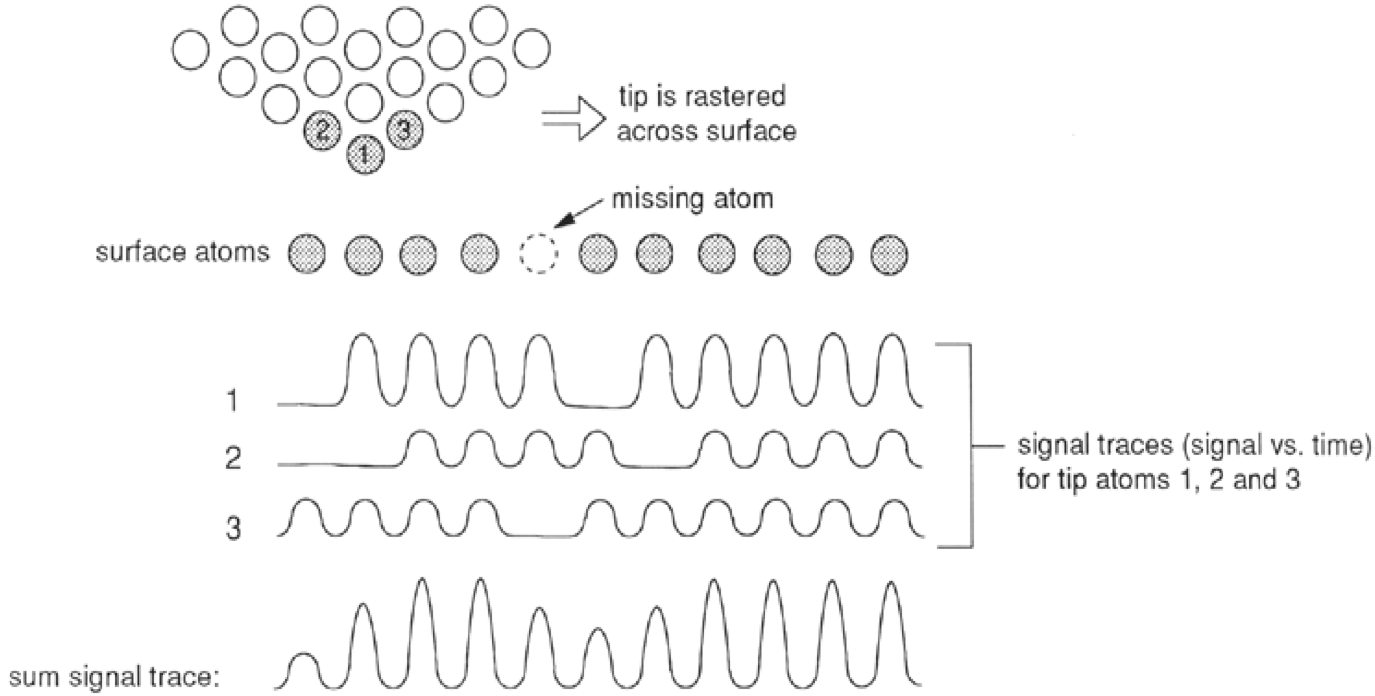
- **AFM-several atoms on tip interact with several atoms on surface**

- **In contact, not necessarily a single atom contact, radius of contact ~$(Rd)^{1/2}$**

(d-penetration depth, R-radius of tip)

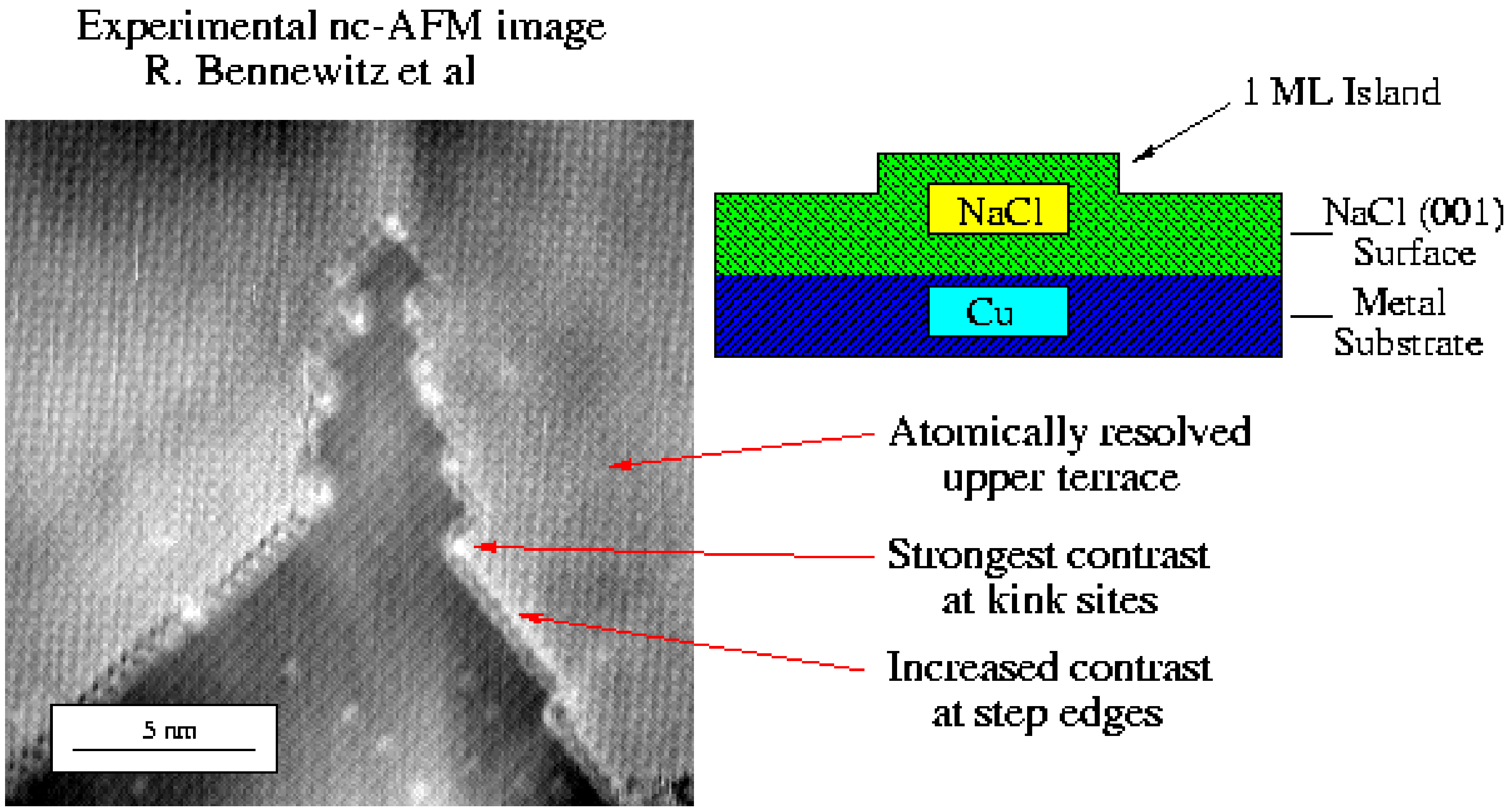


AFM -Resolution



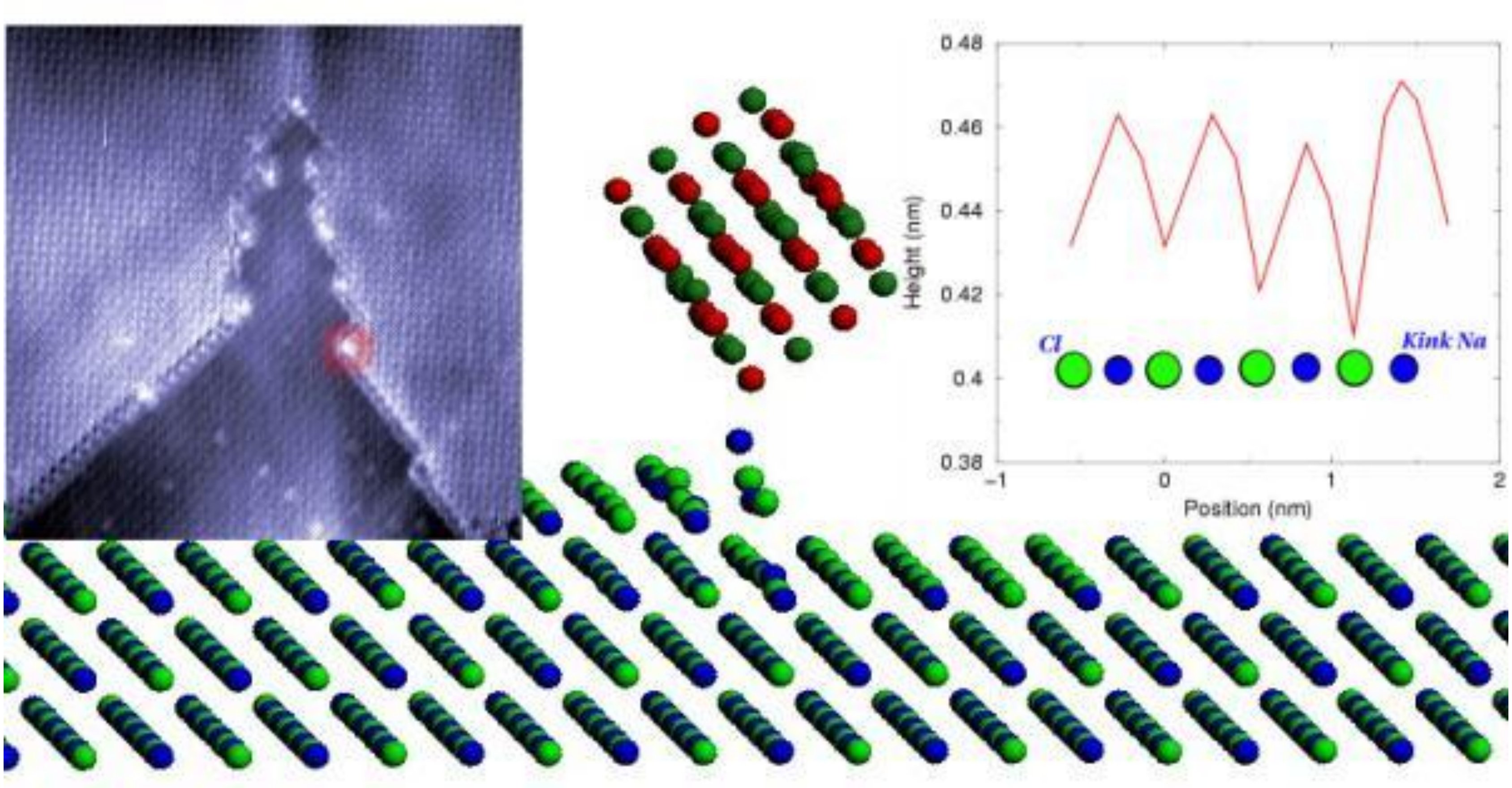
- **Interaction of atom 1 different from interaction of atom 3,2**
- **Each tip atom produces a signals with offset to each other**
- **Periodicity reproduced but no true atomic resolution**

AFM -Resolution



R. Bennewitz, University of Basel, Switzerland

Origin of increased contrast of step-edges and kinks: tip-sample interactions.

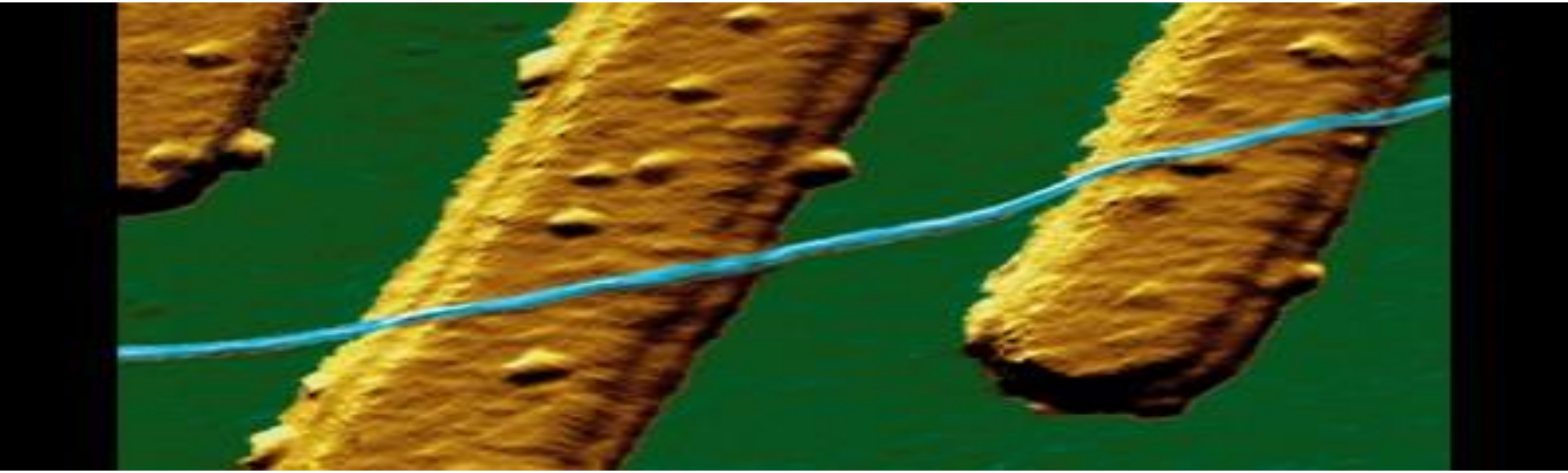


R. Bennewitz, University of Basel, Switzerland

AFM Images - Au (111)

High resolution scan of Au (111) surface, with reconstruction strips (inset) hexagonal atomic structure.
Scan size: 5nm; inset: 20 nm

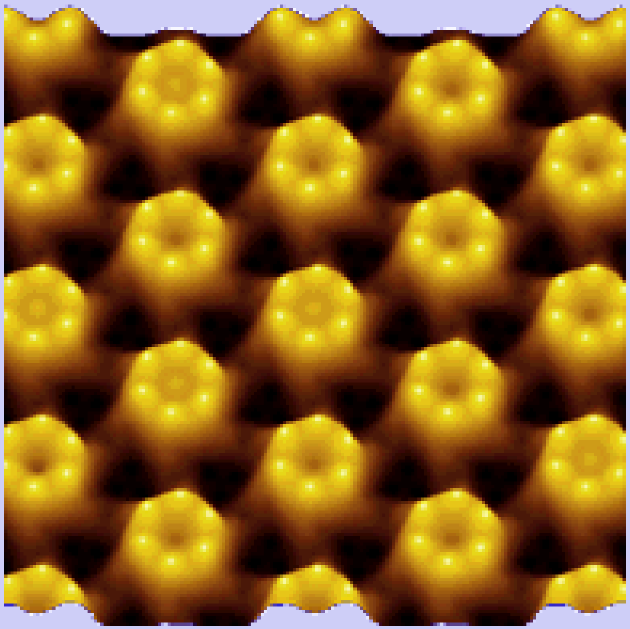
AFM Images



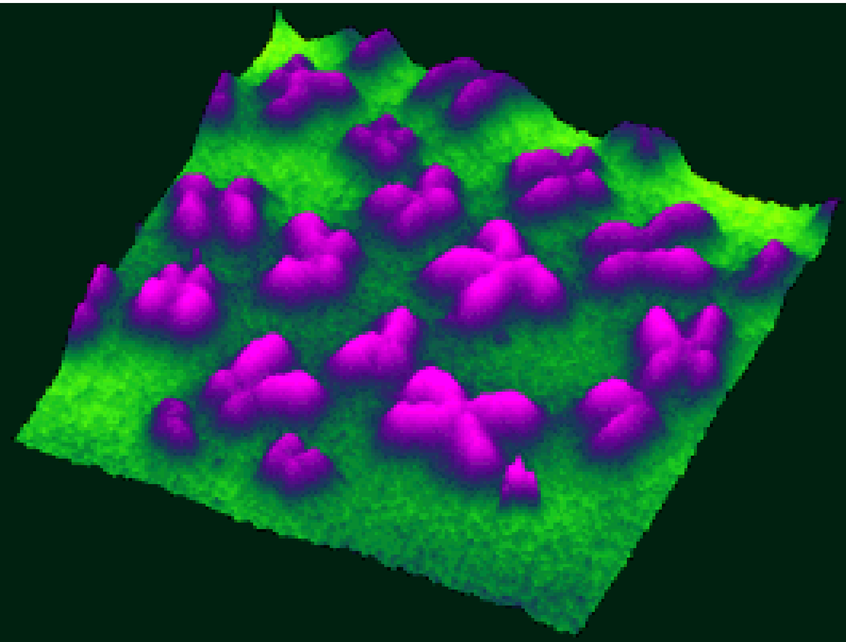
Tapping-Mode AFM image of a single carbon-nanotube molecule on electrodes. 530nm x 300nm scan

C. Dekker and Sander Tans, Delft University of Technology, Department of Applied Physics and DIMES, The Netherlands.

AFM Images: biological specimens



Protein surface layer of D. Radiodurans. Courtesy of Digital Instruments.

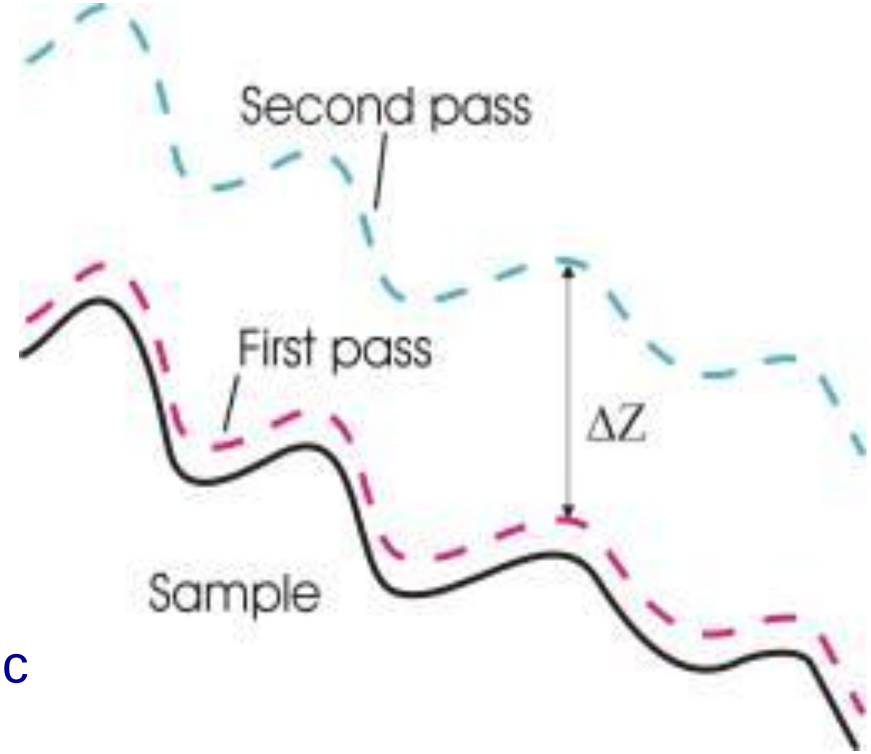


Human Chromosomes. Thanks to Digital Instruments for the picture.

Magnetic Force Microscopy (MFM)

- Coated with a magnetic covering
- Two modes of operation
  - Non-vibrating for larger magnetic fields
  - Vibrating for weaker fields that require a greater sensitivity

Magnetic Force Microscopy (MFM)

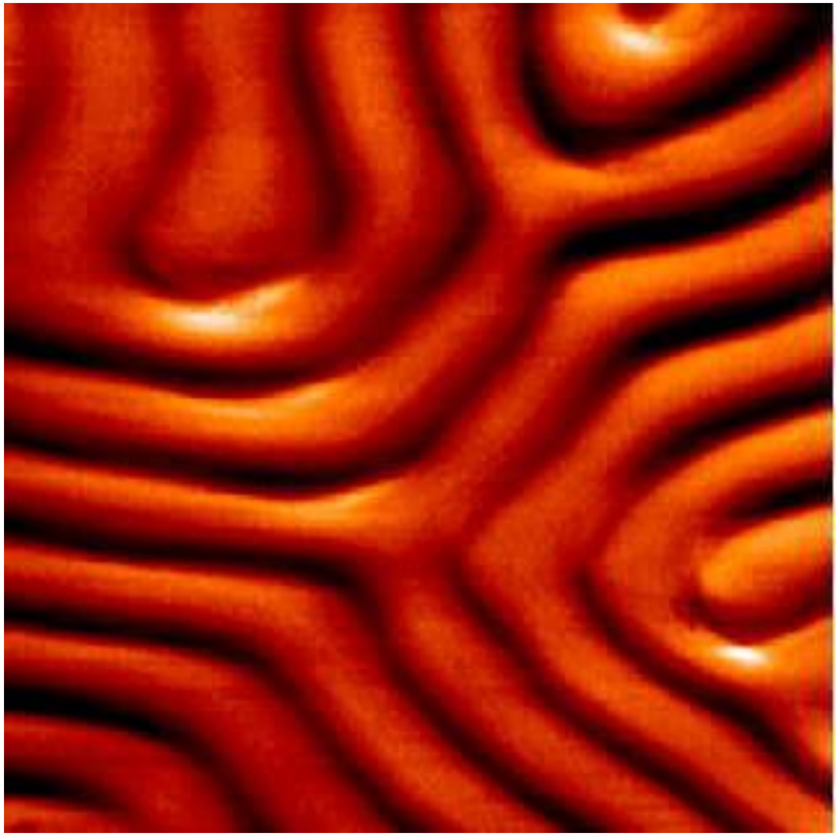


- Uses a two steps technique
  - First pass finds topography of sample
  - Second pass finds the magnetic field
- On the second pass tip is kept at a constant height

http://www.ntmdt.ru/SPM-Techniques/SPM-Methodology/Magnetic_Force_Microscopy_MFM/text45.html

Magnetic Force Microscopy (MFM)

Imaging of ferromagnetic surfaces

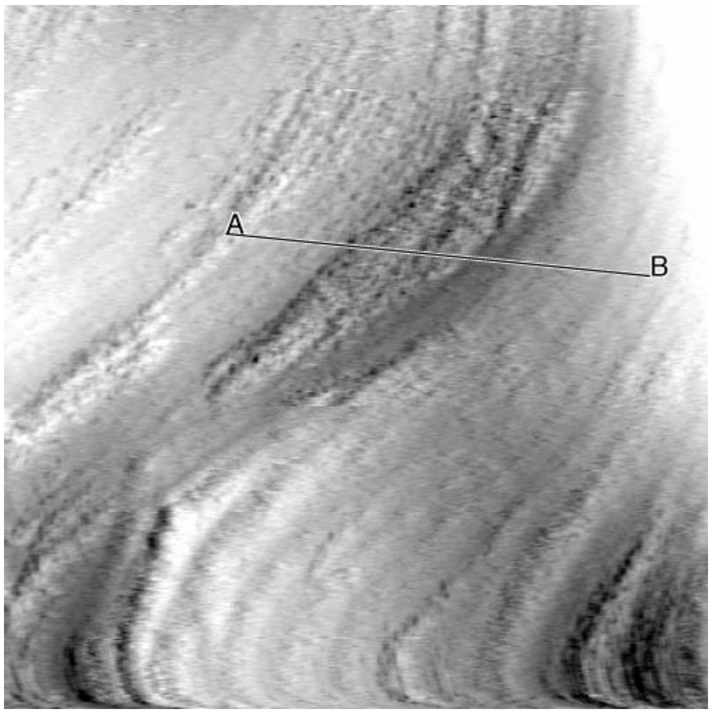


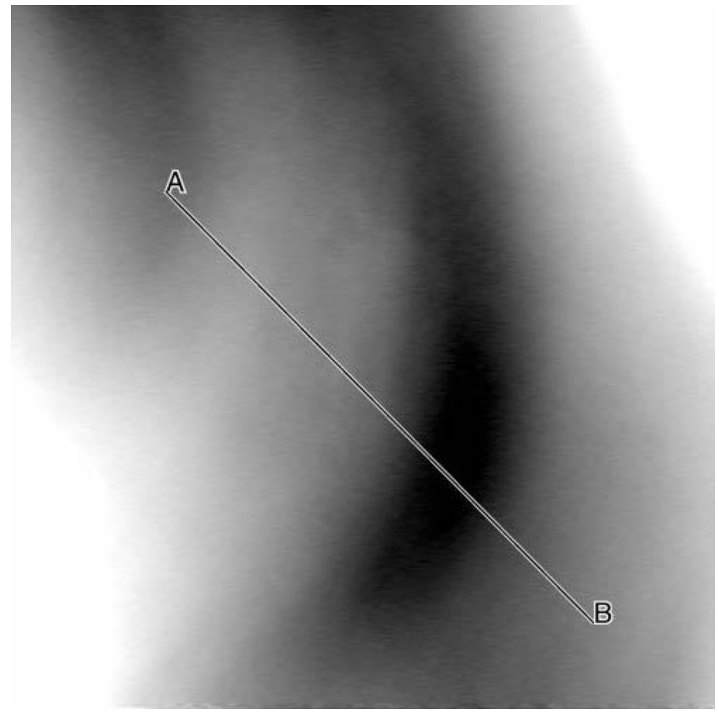
Magnetic domain walls on $BaFe_{12}O_{19}$, measured with iron coated AFM tip.

A. Wadas et al., University of Hamburg, Germany

Topographic and Magnetic Images

corrugation 4nm   Scan of 500 x 500 micrometer



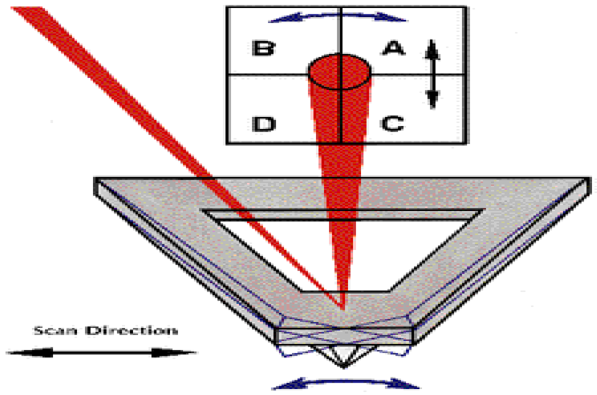


Comparison betweeen corrugation and magnetic structure information detected with an MFM cantilever, identical position

Electrostatic Force Microscopy (EFM)

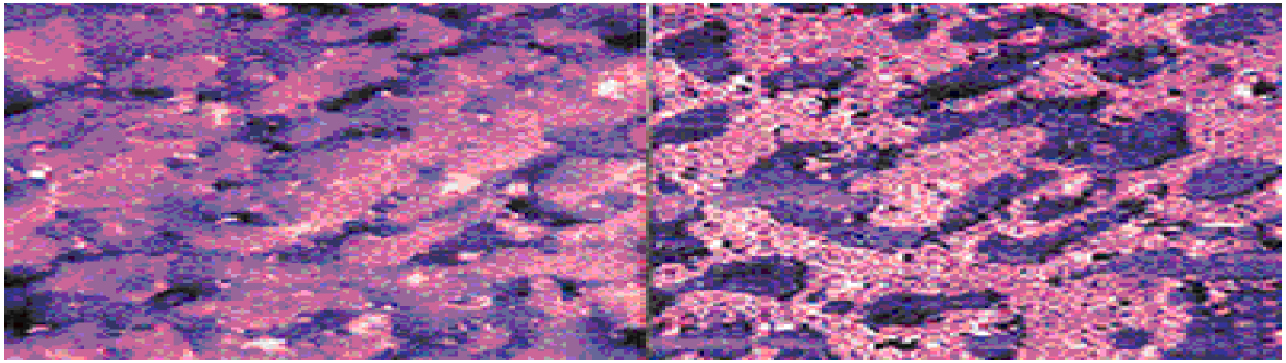
- A bias is used to create an electrostatic field between the tip of the probe and the sample
- Two uses
  - Determine which regions are conducting and which are insulating
  - Determine the electric potential at different points

Lateral Force Microscopy



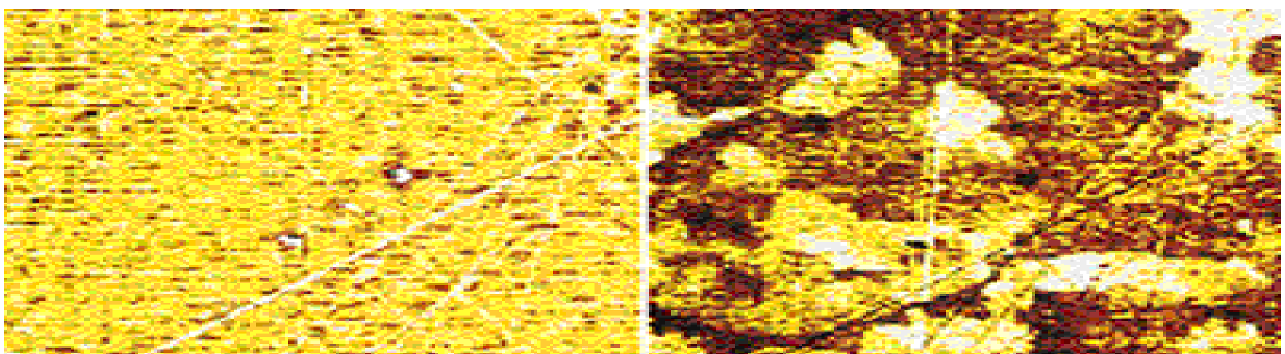
- Tip is scanned sideways. The degree of torsion of the cantilever is used as a **relative measure of surface friction** caused by the lateral force exerted on the tip.
- Identify **transitions between different components** in a polymer blend,in composites or other mixtures
- This mode can also be used to **reveal fine structural details** in the sample.

Lateral Force Microscopy



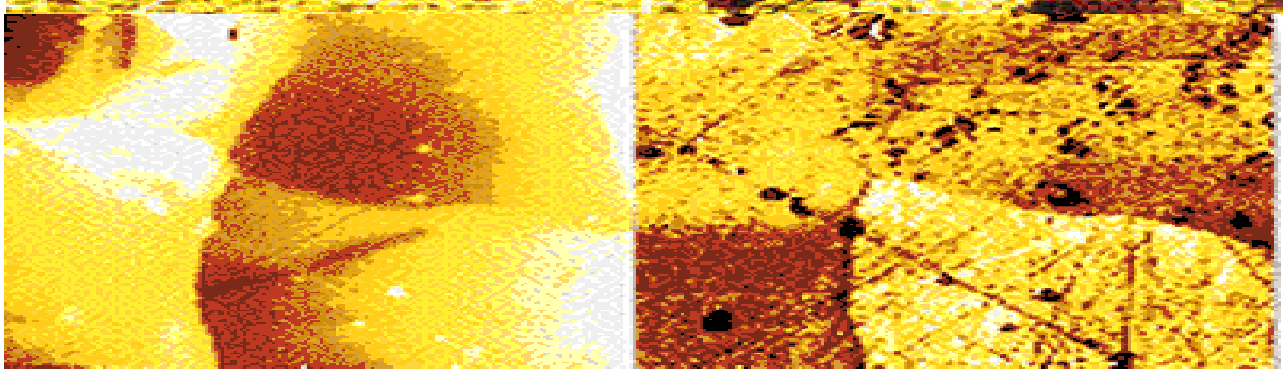
Natural rubber/
EDPM blend

20 micron scan



Polished polycrystalle
silicon carbide film.
Grain structures

30 micron scan



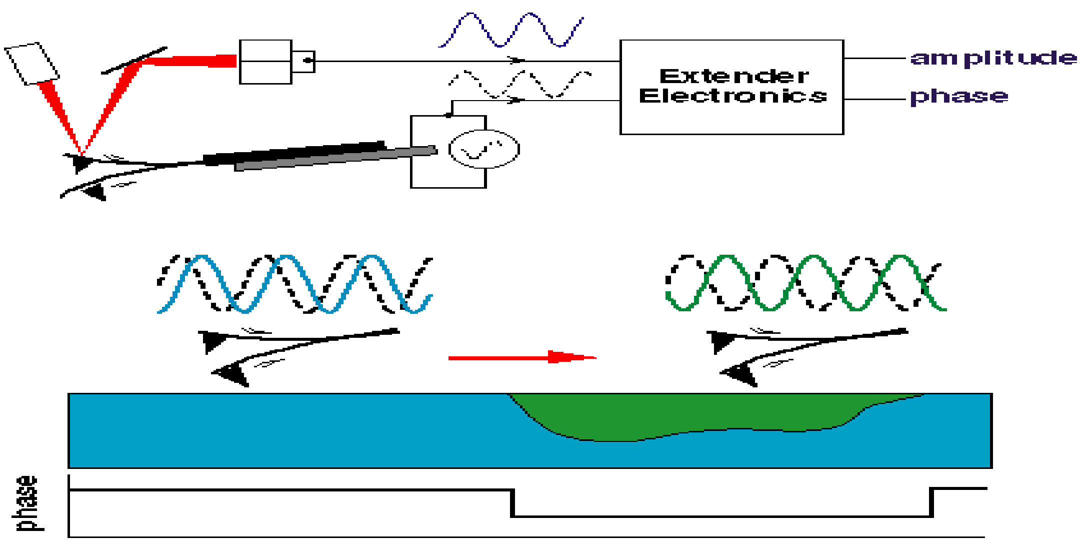
Magnetic recording
Head

Al oxide grains
and contamination
800nm scan

Images/photo taken with NanoScope® SPM, Digital Instruments

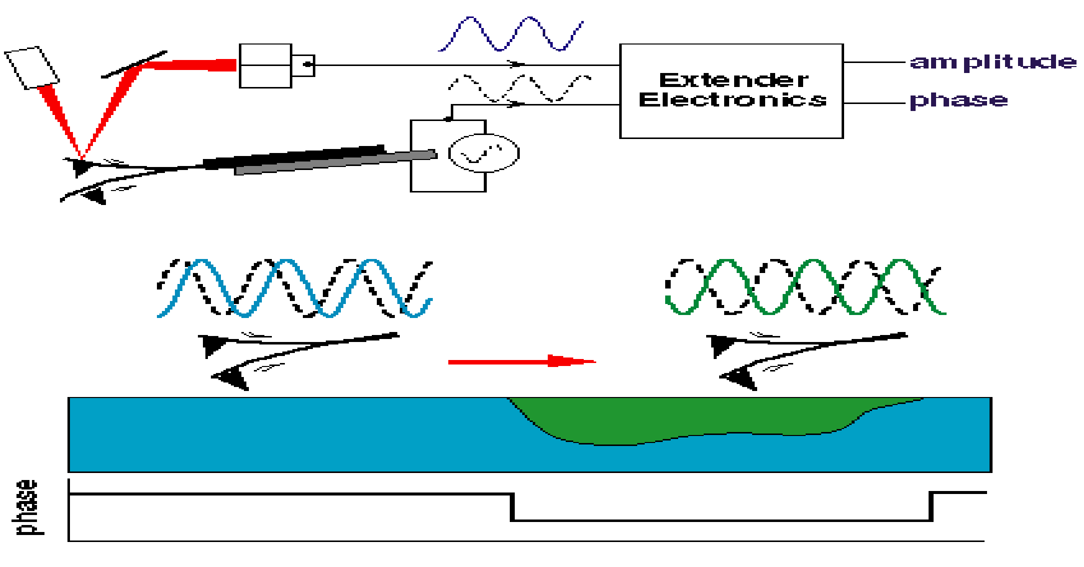
Phase Imaging

- Accessible via Tapping Mode
- Oscillate the cantilever at its resonant frequency. The amplitude is used as a feedback signal.
- The phase lag is dependent on several things, including composition, adhesion, friction and viscoelasticity properties.

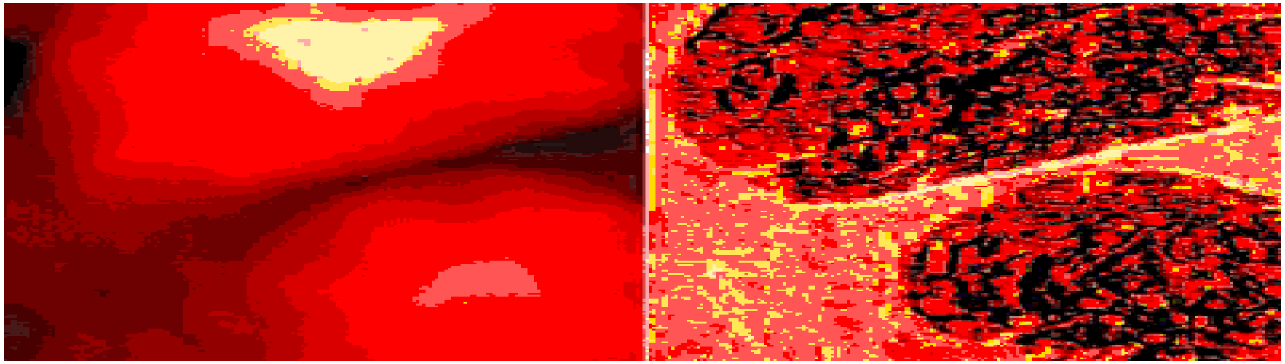


Phase Imaging

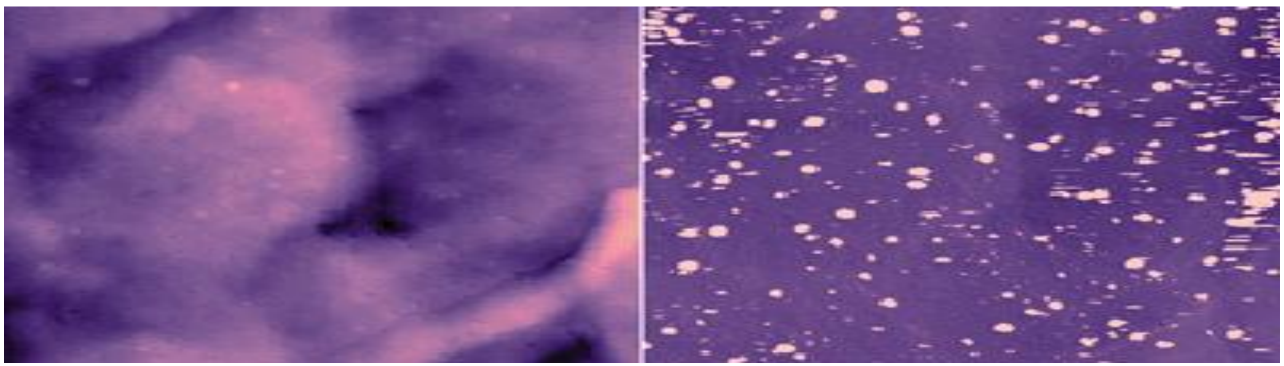
- Identify two-phase structure of polymer blends
- Identify surface contaminants that are not seen in height images
- Less damaging to soft samples than lateral force microscopy



Phase Imaging

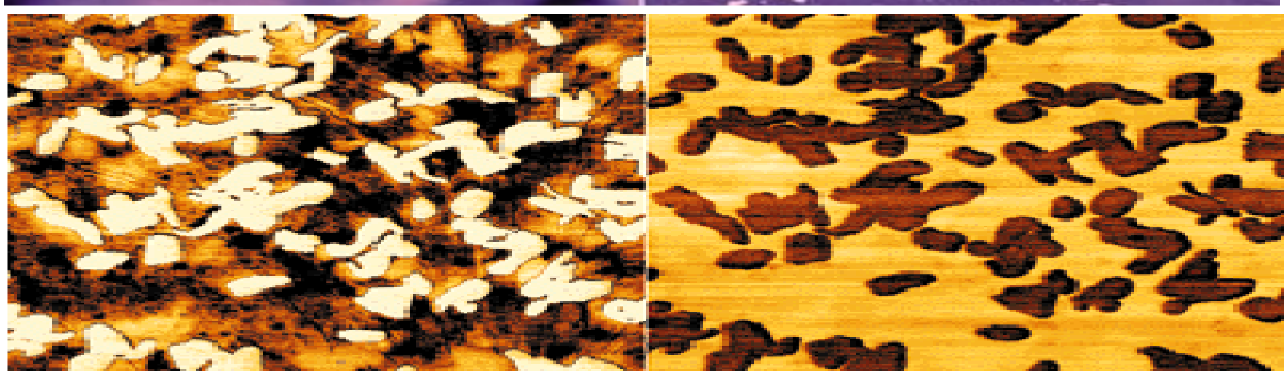


Composite polymer
imbedded in a matrix
1 micron scan



Bond pad on an
integrated circuit
Contamination

1.5 micron scan



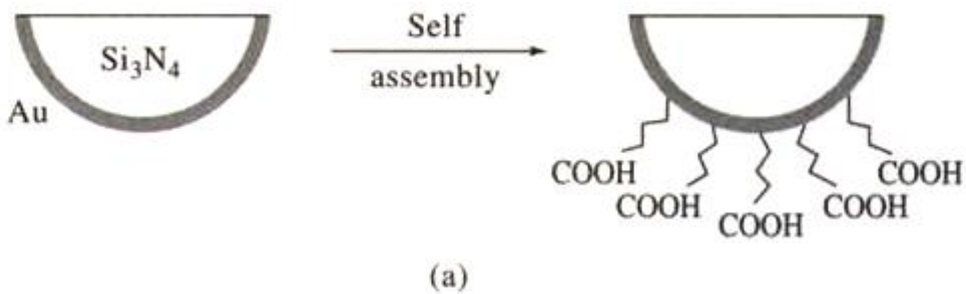
MoO_3 crystallites
on a MoS_2 substrate

6 micron scan

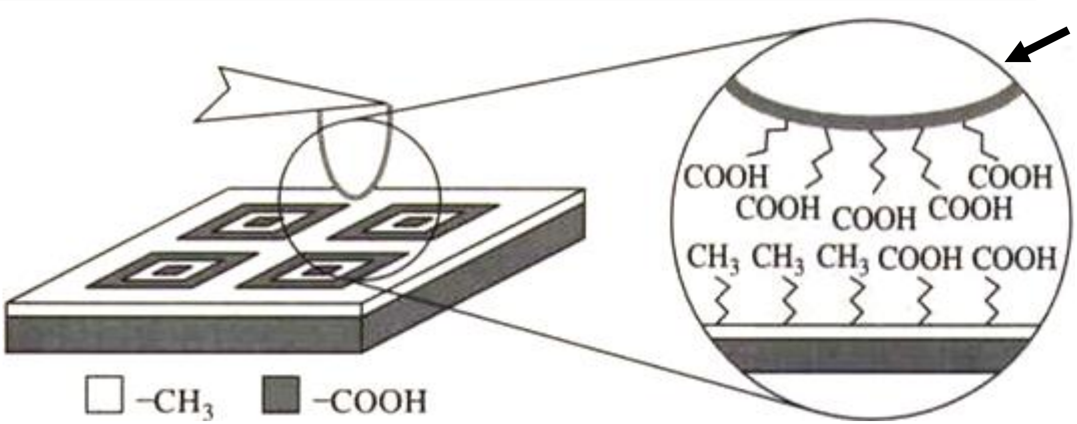
Image/photo taken with NanoScope® SPM, courtesy Digital Instruments

Chemical Force Microscopy

Detection of a functional group by atomic force microscopy



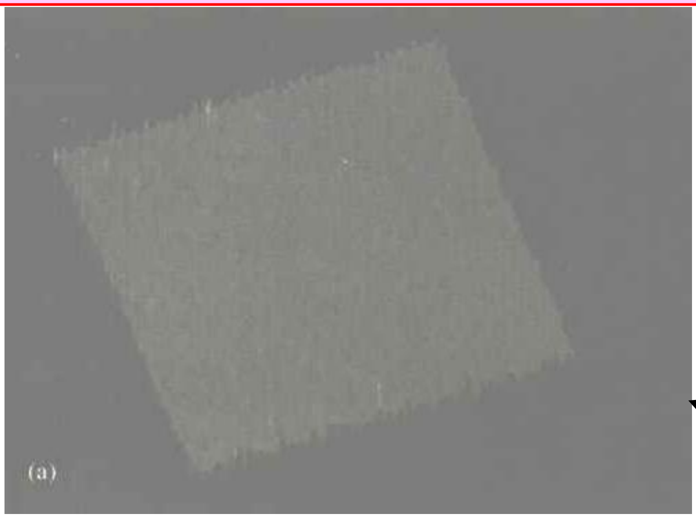
Carboxylic acid groups are chemically attached to a gold-coated AFM tip

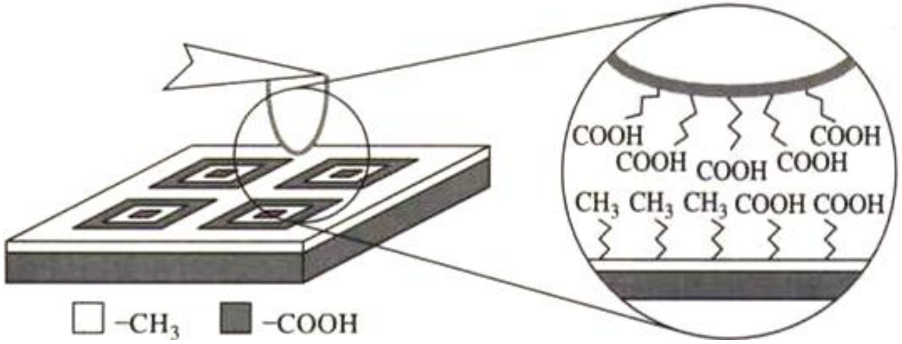


Showing interaction between the gold tip coated with –COOH groups and the sample coated with both –CH_3 and -COOH

Schematic views of the experiment

Chemical Force Microscopy

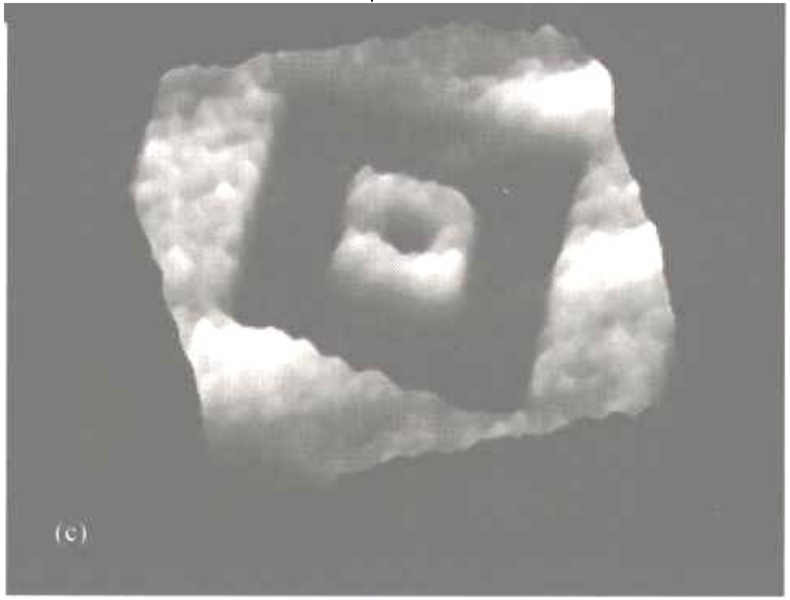




Ordinary AFM scan (without chemically modified tip)

When tip is coated with $-CH_3$ groups

When tip is coated with –COOH groups



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