Scanning Probe Microscopy I

Scanning probe microscopy (SPM)

Operational principle:

1. Scan probe across surface
2. Collect data points
3. Plot data points as array to produce image

Resolution comes from:

- Good control of lateral (x-y) position
- Generation of local probe-sample interactions (small probe)
- Measurement of local probe-sample interactions
  * van der Waals forces (scanning FORCE microscopy)
  * tunneling current (scanning TUNNELING microscopy)
  * magnetic interactions (MAGNETIC force microscopy)

Contrast (z position) comes from changes in probe–surface interactions.

Quantitative data comes from statistical analyses of multiple images/spectra.

REVIEW ARTICLE:
"The Art of SPM: Scanning Probe Microscopy in Materials Science"
Joachim Loos, *Advanced Materials* (2005) **17**, 1821–1833.

Overview
STM
Characteristic interaction
Analyzing height data
Examples
Imaging molecules
Imaging bands
Imaging growth
Electrical properties
AFM
Characteristic interactions
Analyzing height data
Examples
Imaging protein conformation
Imaging processes
Force curves
Imaging adhesion
Comparisons
Probe issues
Substrate issues
Lab demo: MFM

Scanning tunneling microscopy (STM)

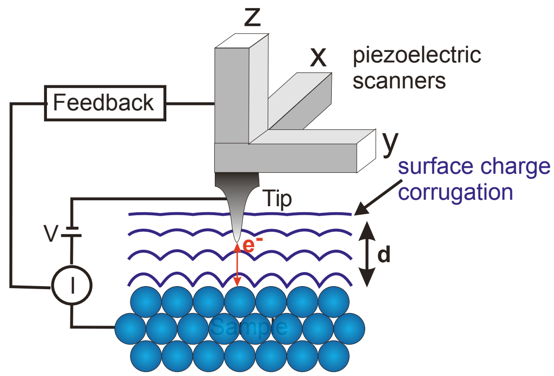
Use scanning tunnelling microscopy (STM) to investigate surface topology.

- Voltage bias between tip and sample causes electrons to jump the gap.

  $I_{tunnel} \propto exp(-d)$

- Feedback loop adjusts tip height to maintain constant tunnelling current while scanning.

  Tip movements mimic surface topography.

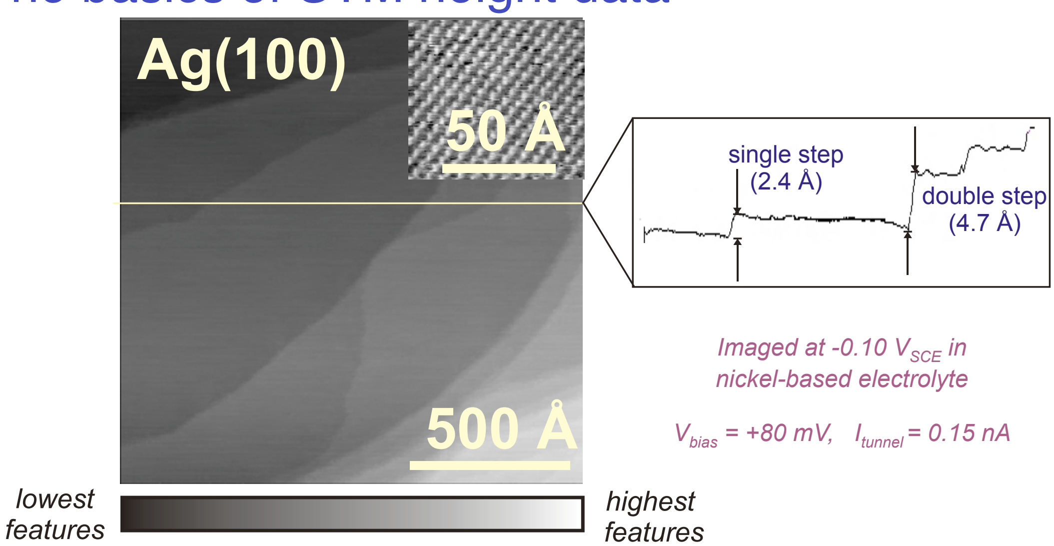


(after Boland group at www.unc.edu)

Exploit quantum mechanical effects to image small surface variations.

Tip-sample spacings ~ 0.5-1.0 nm

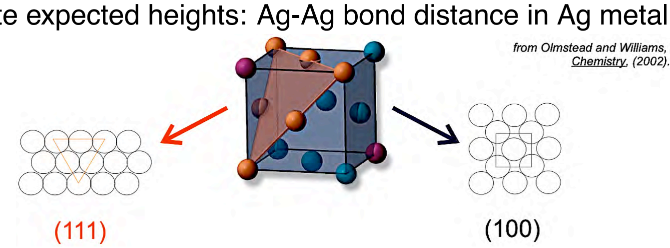
The basics of STM height data



Imaged at -0.10 V_{SCE} in nickel-based electrolyte

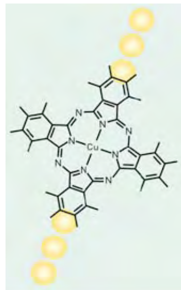
V_{bias} = +80 mV, I_{tunnel} = 0.15 nA

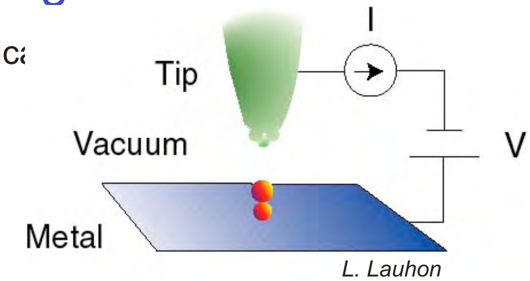
Calculate expected heights: Ag-Ag bond distance in Ag metal is 1.75 Å

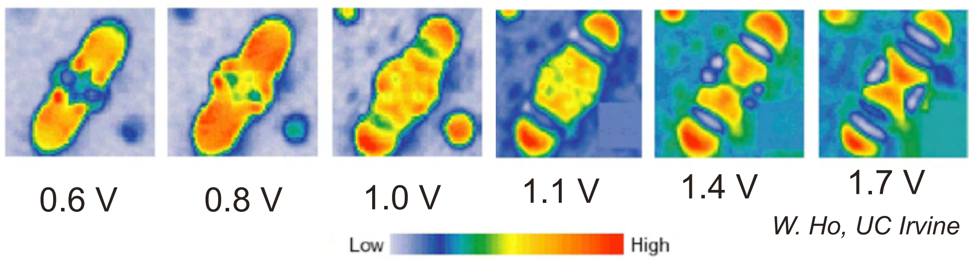


STM example 1: imaging molecular orbitals

Current from quantum mechanica



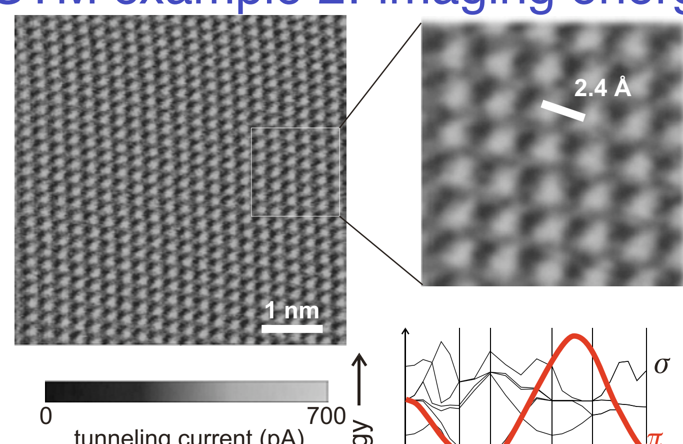


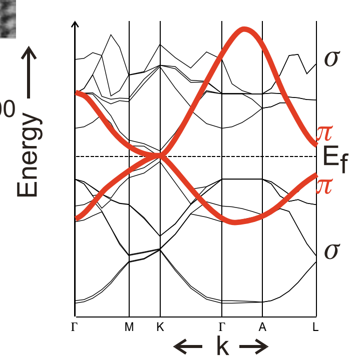


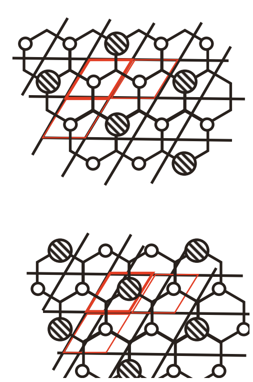
Change bias voltage (tip-sample) to view different molecular orbitals.

Requirements: low temperatures, low pressures, low density of molecules adsorbed to surface

STM example 2: imaging energy bands





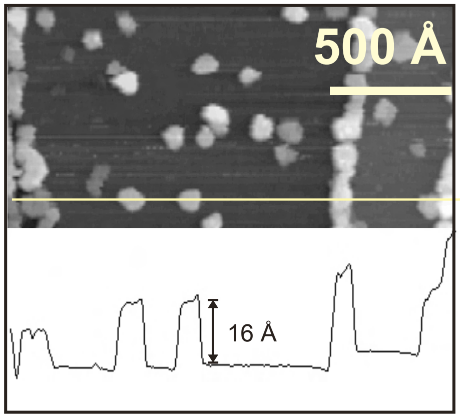


Graphite has C-C bond distance of 1.42 Å; bright spots observed at $\sqrt{3}(1.42)$ Å.

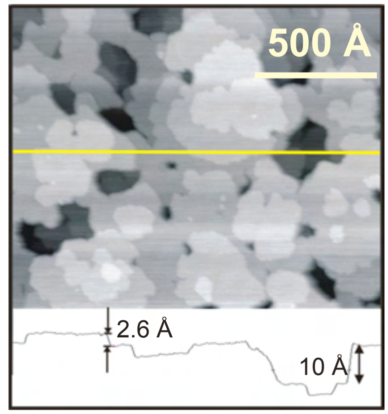
$$I_{tunnel} \propto V_{tunnel} \cdot \exp(const \cdot \sqrt{\Phi_{tunnel}} \cdot d)$$

STM example 3: imaging processes

nickel electrodeposition on Ag(111)



30 s deposition at -0.89 V_{SCE}



120 s deposition at -1.00 V_{SCE}

- Longer deposition times yield flat-topped, multi-layer islands that coalesce.
- Deep holes remain after islands merge.
- Flat-topped features consistent with proposed nucleation and growth model.

Morin et al. Phys. Rev. Lett. (1999) ***83****, 5066.*

Ni-Ni bond distance = 1.62 Å. Why might the measured distances be different?

STM example 4: electrical properties

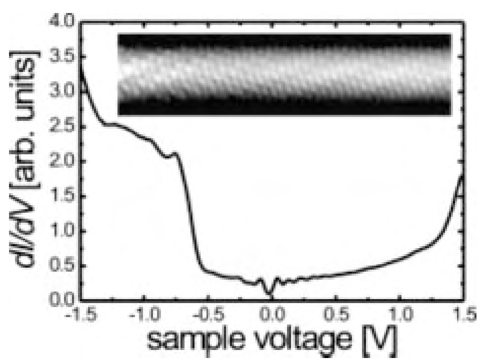


Figure 6. The differential current–voltage (dI/dV) spectrum of a metallic SWCNT. Subband features as well as oscillations near the Fermi energy are visible ($U = 1.5$ V, $I = 300$ pA). Inset: Atomically resolved STM image of a SWCNT ($I = 1$ nA, $U_{sample} = -50$ mV, 2.3 nm × 9 nm). Reprinted with permission from [73]. Copyright 2003 American Institute of Physics.

Local Density of States (LDOS) for a single-wall carbon nanotube

STM example 4: electrical properties

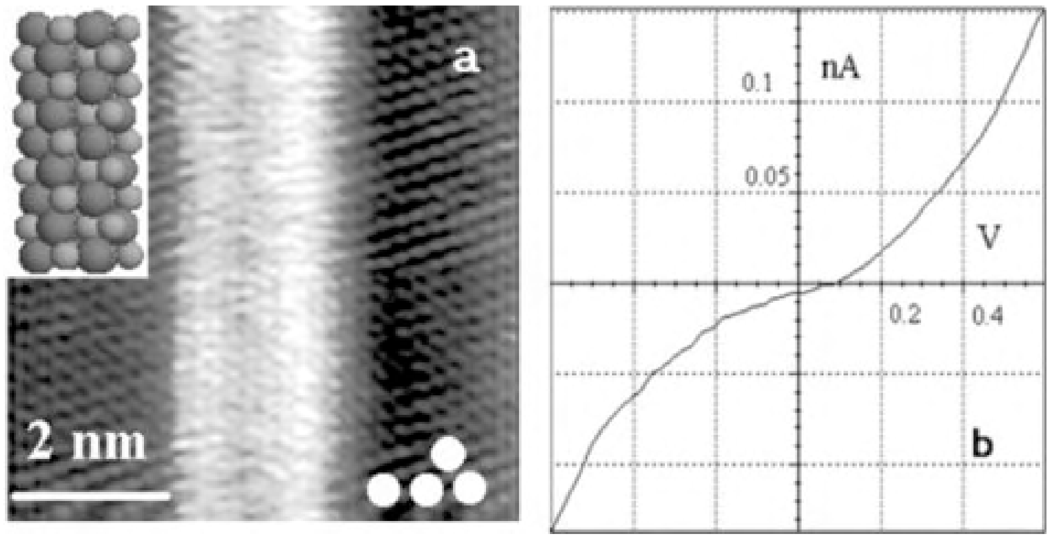


Figure 7. a) STM image of $MoS_{2-x}I_y$ nanotube bundle on a graphite substrate ($U = 1$ V, $I = 0.6$ nA). b) STS plot that reveals the metallic behavior of a single $MoS_{2-x}I_y$ nanotube. Reprinted from [75].

Scanning Tunneling Spectroscopy (STS) shows local current-voltage relations.

Atomic force microscopy (AFM)

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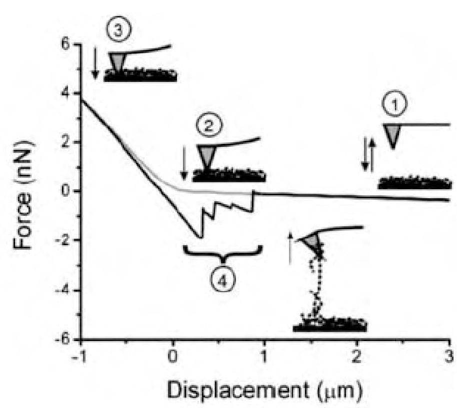
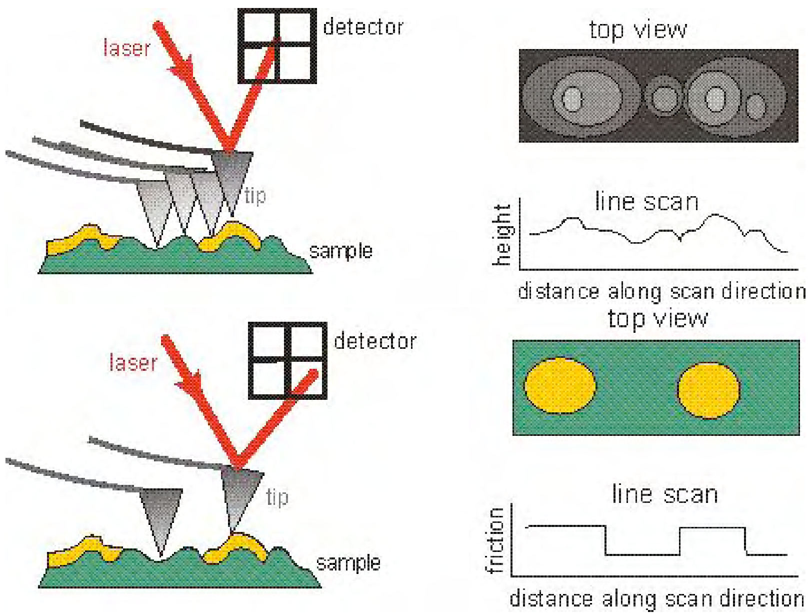
- van der Waals forces
- electrostatic (including capacitive forces
- capillary forces
- chemical forces (bonds)



The contributions from each of these forces varies greatly with probe-sample separation distance, material properties and surface chemistries of probe/sample, relative humidity, *etc.*

The basics of AFM data

- Tiny probe
- Short-range interactions
- Detection and control of probe position



AFM example 1: protein conformation

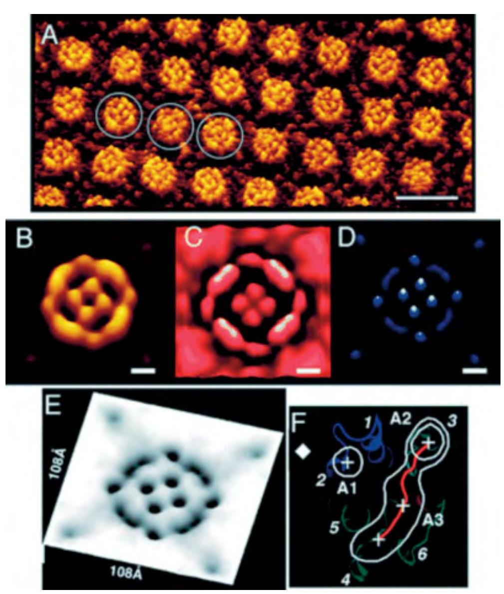
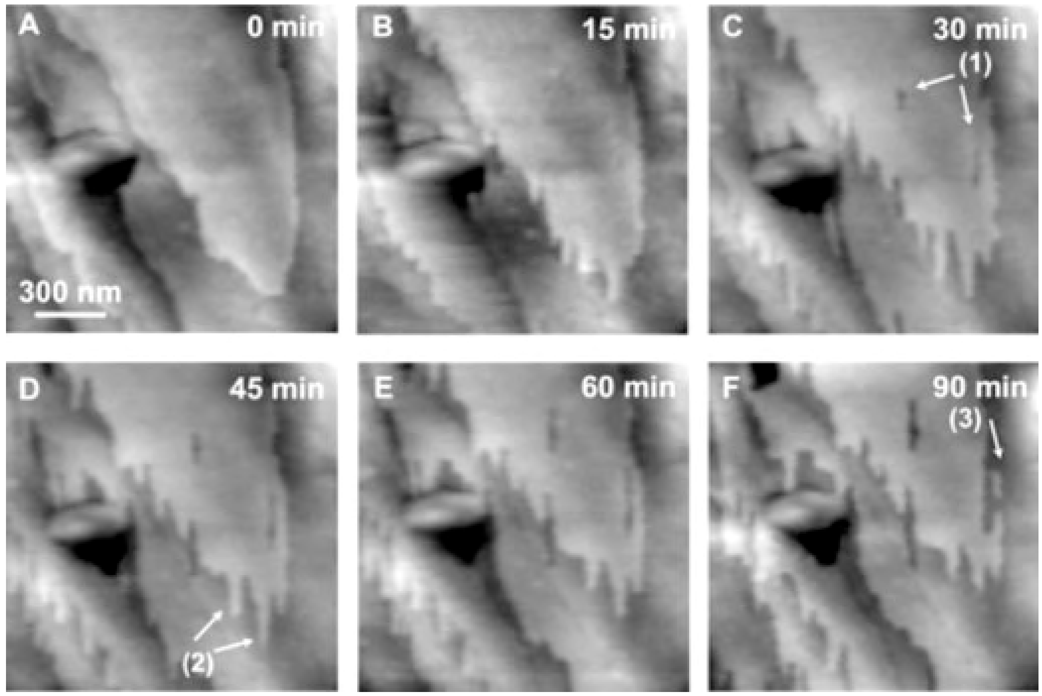


Figure 2. A) High-resolution raw data AFM image of an aquaporin-Z (AqpZ) 2D crystal. The circles indicate individual extracellular protein molecule surfaces. Scale bar, 10 nm; full gray scale, 1 nm. B) Topograph of a single protein from average of 1477 aligned trimers. Scale bar, 1 nm; gray scale range, 0.01–0.07 nm. C) Standard deviation map about the averaged structure in (B). D) Probability position map. Scale bar, 1 nm. E) Free-energy landscape calculated from (D). F) A monomer of the porin AqpZ atomic model with overlay of the full width at half maximum outline. Crosses indicate high-probability positions; the red line is the top probability tracing line of loop C. Transmembrane helices are numbered in italics. Helices 1 and 2 are connected by loop A1; helices 3 and 4 are connected by loop A3. Contour A2 corresponds to the protruding end of helix 3 out of the membrane surface. The colors of the helices indicate the pairing to form the loops. Reprinted with permission from [19]. Copyright 2003 AAAS.

Joachim Loos, *Advanced Materials* (2005) **17**, 1821–1833.

AFM is better for non-conducting (inhomogeneously conducting) samples.

AFM example 2: Imaging degradation



Joachim Loos, *Advanced Materials* (2005) **17**, 1821–1833.

Enzymatic degradation of poly[(R)-3-hydroxybutyric acid] in a phosphate buffer.

AFM example 3: forces

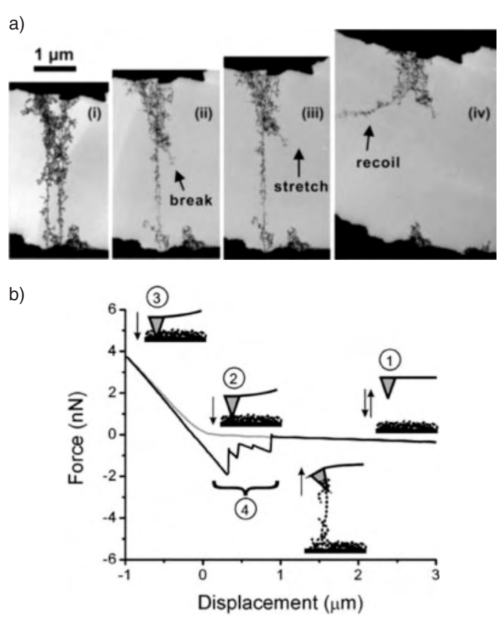
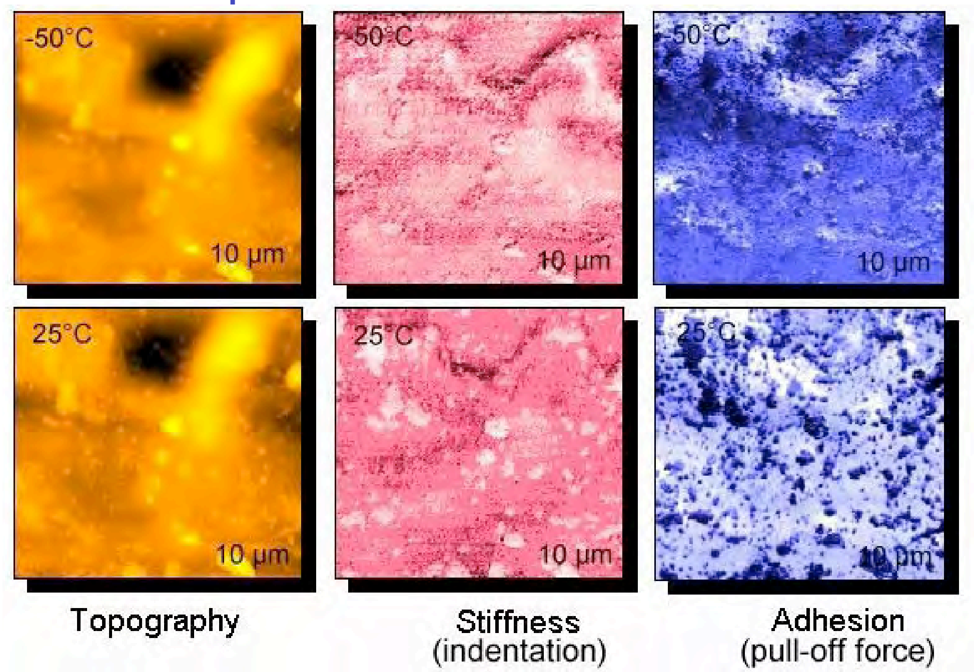


Figure 5. a) Transmission electron microscopy (TEM) photos showing the sequential stretching and breaking of single NCA chains. b) A typical force vs. displacement curve recorded as the AFM tip approaches (gray line) and retreats (black line) from an aggregate-coated silicon substrate. The light-gray curve represents the force acting on the tip as it moves toward the substrate surface (step 1), while at the contact point (step 2), and while it is indented into the sample (step 3). The black line is the force acting on the tip as it moves away from the surface (step 4). On aggregate-coated surfaces, multiple rupture events forming a sawtooth pattern were always observed during the retraction portion of the measurement. Reprinted with permission from [66]. Copyright 2004 American Chemical Society.

Joachim Loos, *Advanced Materials* (2005) **17**, 1821–1833.

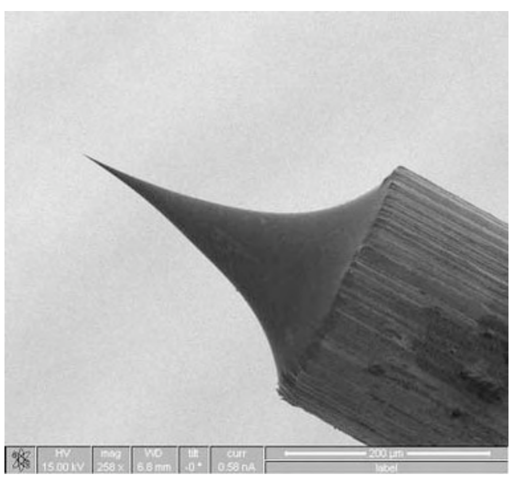
AFM example 4: adhesion effects



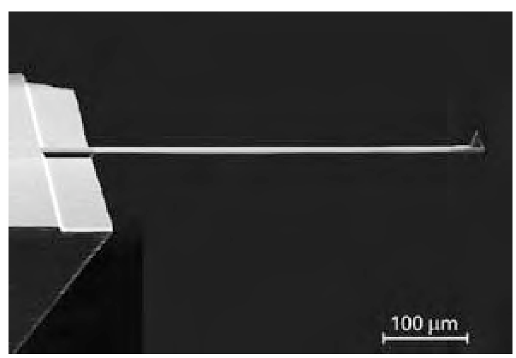
http://anasysinstruments.com/notes/afm6_1.jpg

Adhesion differences can be independent of stiffness or topography.

Comparing STM and AFM: probes



www.mse.engin.umich.edu (Millunchick group)



mrsec.wisc.edu

STM tips are etched metal wire; AFM tips are fabricated on cantilevers.

STM typically has better lateral resolution due to smaller tips (greater curvature).

AFM is better for poorly conducting samples.

Typical STM tip problems

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Imaging processes
Force curves
Imaging adhesion
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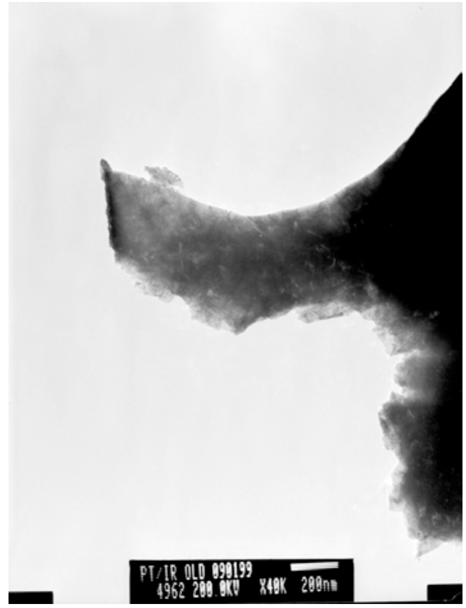

www.physics.purdue.edu/ nanophys/uhvstm/tip.html

Tips can have imperfections or can be damaged during use.

Artifacts: an example

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STM
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Characteristic interactions
Analyzing height data
Examples
Imaging protein conformation
Imaging processes
Force curves
Imaging adhesion
Comparisons
Probe issues
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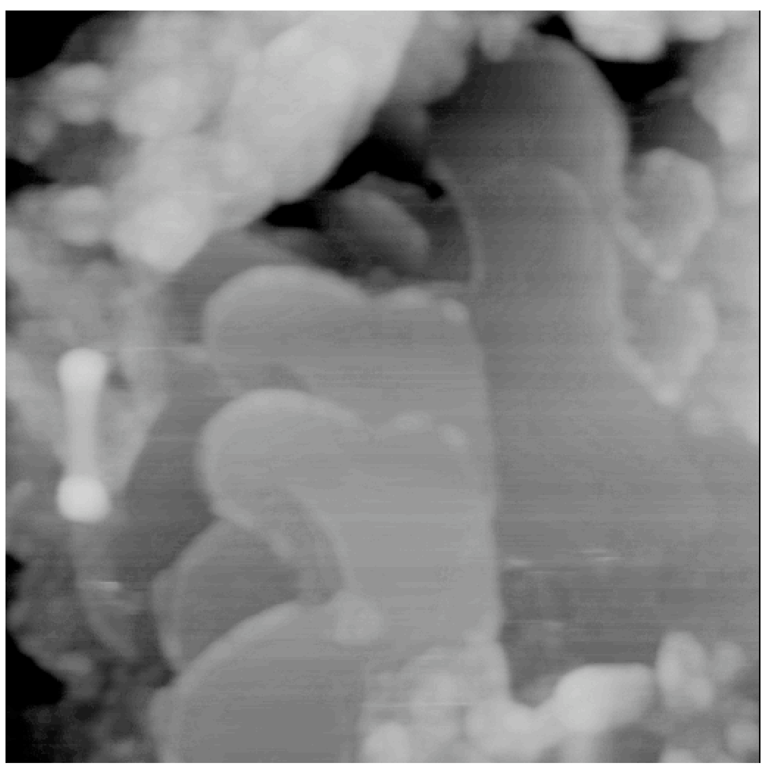
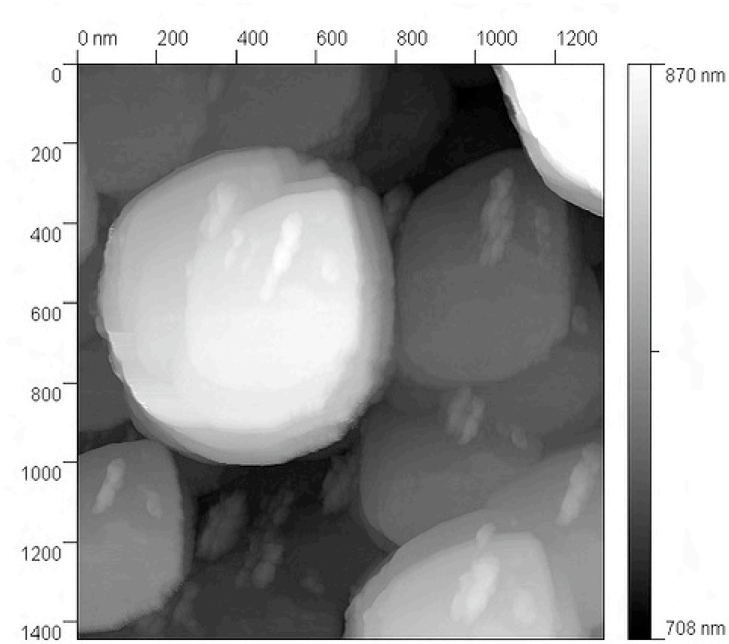


www.weizmann.ac.il (Peter Markiewicz)

Multiple tips or tip damage can yield artifacts (false effects) in images.

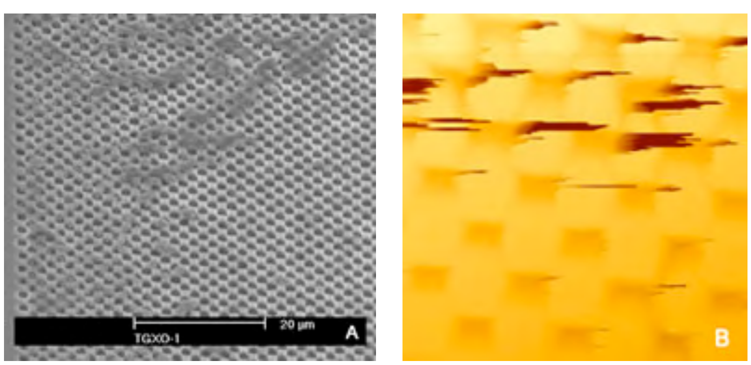
Artifacts: another example

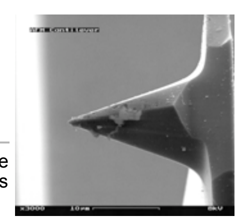


flickr.com

Multiple tips or tip damage can yield artifacts (false effects) in images.

Substrate issues



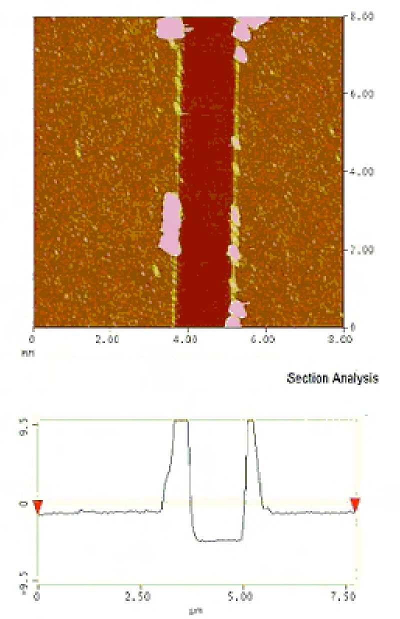


Figures 26A-B: (A) SEM image of a test pattern that is contaminated. (B) AFM image of the same test pattern that is covered with contamination. The contamination is identified by the streak marks at the top of the scan.

pacificnanotech.com en.wikipedia.org/wiki/Atomic force microscope

Poorly anchored materials can stick to SPM probes and cause streaking in images.

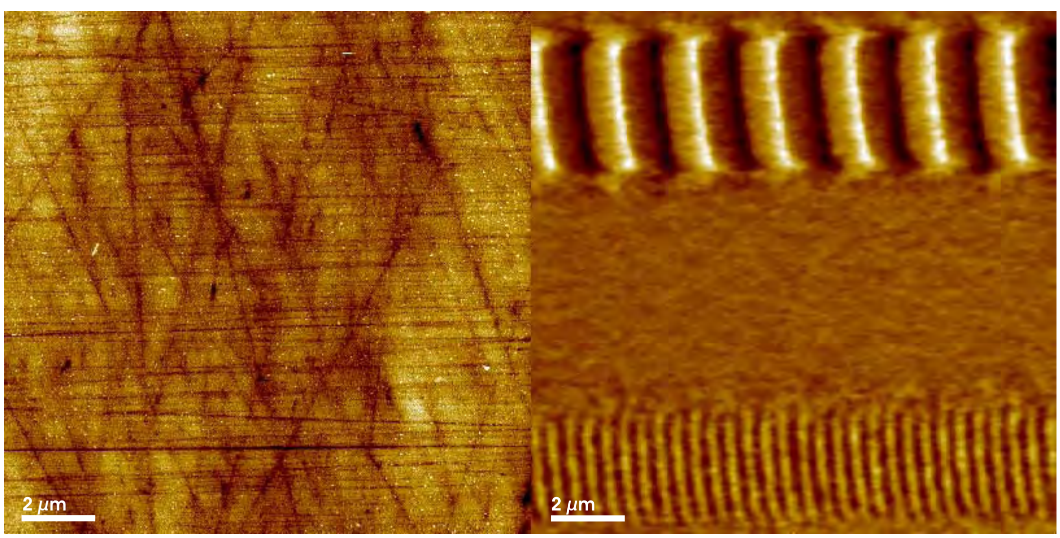
Substrate issues



www.macdiarmid.ac.nz

- AFM tips can scratch soft materials if the force between tip and sample is too great.
- If the sample is harder than the tip, the tip can break during imaging.
- Useful variations on these problems include lithography (intentional scratching) or indentation studies (assessing sample hardness).
- Imaging with the same tip used for lithography or indentation is convenient, but may not yield the best image quality.

Magnetic Force Microscopy (MFM)

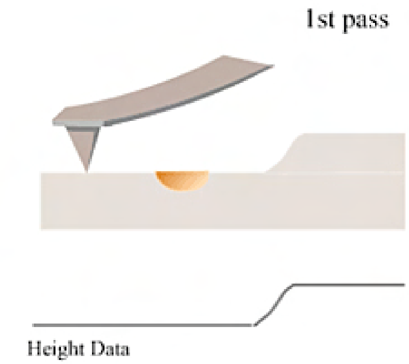


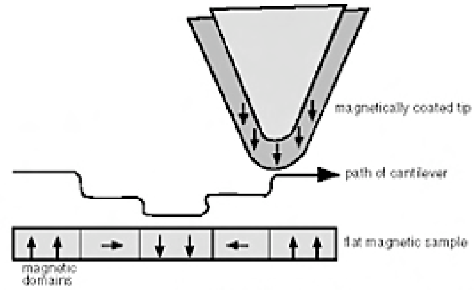
Topography (left) and magnetic frequency shift image (right) of an experimental hard disk (courtesy of IBM) measured with a PPP-MFMR probe (z-range topography: 72nm, magnetic image scale: 22.5Hz).

nanosensors.com

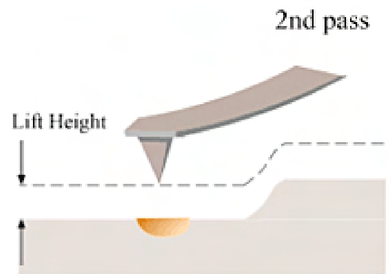
Magnetic tips can provide both topographic and magnetic information.

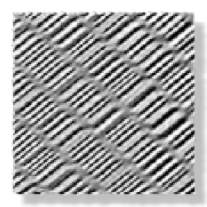
MFM measurement basics





MFM maps the magnetic domains of the sample surface.





MFM image showing the bits of a hard disk.
30μm. scan

veeco.com

Two passes are required to get topographic and magnetic information.

Relating MFM to sample magnetization

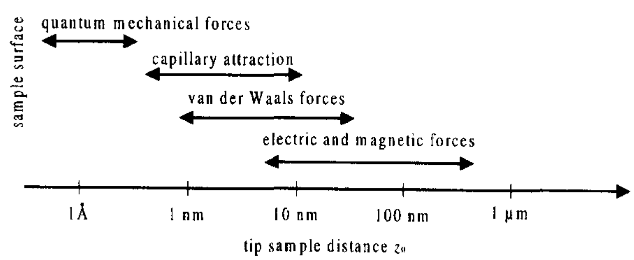


Fig. 3. Different forces acting on a magnetic tip and the distance region where they dominate the MFM signal.

- Cantilever movement depends on interactions between tip's magnetic moment and sample's magnetic field.

$$F = \mu_0 \int \nabla(M_{tip} \cdot H_{sample}) dV_{tip}$$

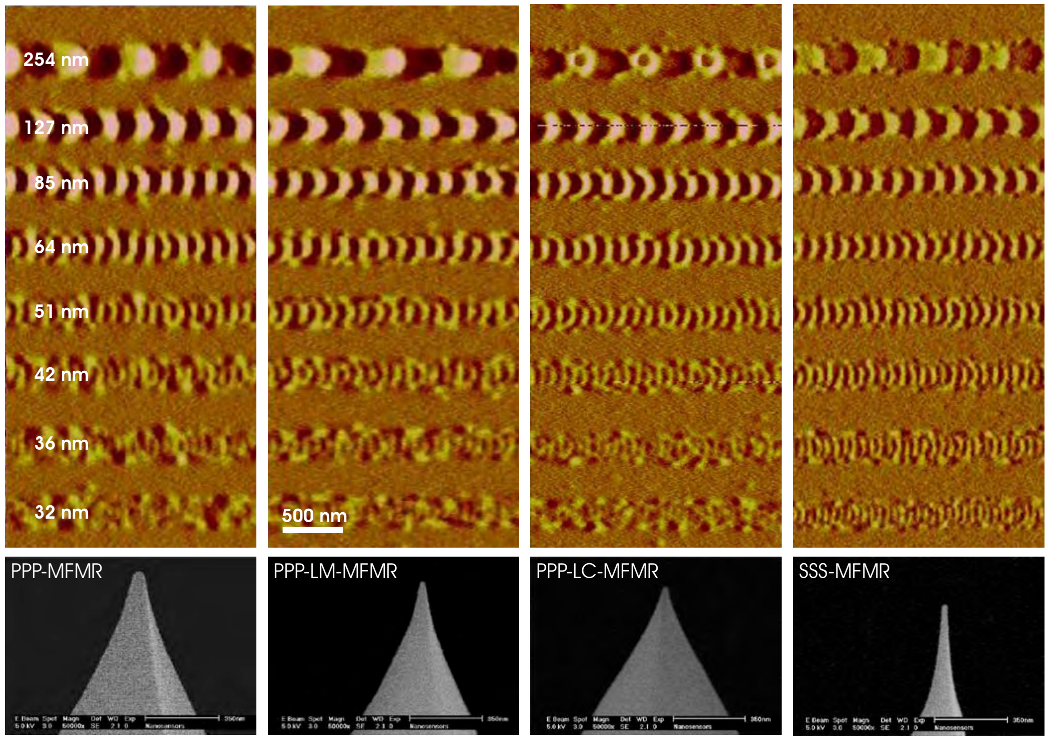
(integrate over tip volume, so approximations (dipole) simplify calculations)

- Sample magnetization cannot be determined uniquely from MFM field map. *Model sample magnetization, calculate MFM response, then compare.*

S. Porthun, L. Abelmann, C. Lodder *J. Magn. Magn. Mater.* **182** (1998) 238-273.
E.D. Dahlberg and J.-G. Zhu *Physics Today* (1995) 34-40.

MFM and probe effects

- Comparison of Lateral Resolution



Magnetic images (phase shift) of an experimental hard disk with varied bit length (courtesy of Maxtor).