Nano-Microscopy: Lecture 1

Scanning Tunneling and Atomic Force Microscopies Principles

Pavel Zinin
HIGP, University of Hawaii, Honolulu, USA

www.soest.hawaii.edu/~zinin
Axial and Lateral Resolutions of Optical Microscope

\[
\begin{align*}
 r_{\text{Airy}} &= \frac{0.61 \lambda}{\sin \alpha} = \frac{0.61 \lambda}{nNA} \\
 Z_{\text{axial}} &= \frac{\lambda}{n(1 - \cos \alpha)} \approx \frac{2 \lambda}{nNA^2}
\end{align*}
\]

How can we overcome these limits?

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Viruses</th>
<th>Red Blood Cells</th>
</tr>
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<tbody>
<tr>
<td>1 Å</td>
<td>1 nm</td>
<td>1 µm</td>
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<tr>
<th>Molecules</th>
<th>Computer Circuits</th>
<th>Hair</th>
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Diameter of one kopeika = 12.8 mm
Diameter of one cent = 1.8 mm
Generally nanotechnology deals with structures sized between 1 to 100 nanometer in at least one dimension, and involves developing materials or devices within that size.

\[
\frac{1\text{ meter}}{1\text{ nanometer}} = 10^9
\]
Carbon Nanoworld: Graphite, Fullerene, Nanotube, Graphene

Graphite

Fullerene

Graphene

Nanotube
Scanning tunneling microscopy (STM) is a powerful technique for viewing surfaces at the atomic level. Its development in 1981 earned its inventors, Gerd Binnig and Heinrich Rohrer (at IBM Zurich), the Nobel Prize in Physics in 1986. STM probes the density of states of a material using tunneling current. For STM, good resolution is considered to be 0.1 nm lateral resolution and 0.01 nm axial resolution.
Stylus Profiler (1929 – Schmalz)

The profiler, invented by Schmalz in 1929, utilized an optical lever arm to monitor the motion of a sharp probe mounted at the end of a cantilever. A magnified profile of the surface was generated by recording the motion of the stylus on photographic paper. This type of "microscope" generated profile "images" with a magnification of greater than 1000X.

- Generated profile images up to ~1000X magnification
- Problems with large features (bent probes)

http://www.pacifcnanotech.com/afm-history_single.html
In 1971 Russell Young demonstrated a non-contact type of stylus profiler. In his profiler, called the topographiner, Young used the fact that the electron field emission current between a sharp metal probe and a surface is very dependent on the probe sample distance for electrically conductive samples. In the topographiner, the probe was mounted directly on a piezoelectric ceramic used to move the probe in a vertical direction above the surface.

• The x and y piezo drivers scan the tip over and slightly above the specimen surface.
• The z piezo is controlled by a servo system to maintain a constant voltage, and hence a constant vertical separation between the tip and the surface.
• An electron multiplier detects the tiny fraction of the tunneling current which is scattered by the specimen surface.


FIRST SCANNING PROBE IMAGE.
Topographic map of a 180-line-per-mm diffraction-grating replica, obtained with the Topographiner, a non-contacting field-emission probe developed at NBS.

Scanning Tunneling Microscopy: Principle

The STM is based on the concept of *quantum tunnelling*. When a conducting tip is brought very near to the surface to be examined, a voltage difference applied between the tip and sample surface allows electrons to tunnel through the vacuum between them. The resulting tunneling current is a function of tip position, applied voltage, and the local density of states of the sample. Information is acquired by monitoring the current as the probe's position scans across the surface, and is usually displayed in image form.

Schematic view of an STM (From Wikipedia, 2009)
The Tunneling Phenomenon

The STM is an electron microscope that uses a single atom tip to attain atomic resolution.

- 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.

STM tips

Tips

- Cut platinum – iridium wires
- Tungsten wire electrochemically etched
- Tungsten sharpened with ion milling
- Best tips have a point a few hundred nm wide
Instrumental Design: Controlling the Tip

- Precise tip control is achieved with Piezoelectrics
- Displacement accurate to ± .05 Å

Raster scanning
The lateral resolution of STM can not be understood in terms of a Fraunhofer diffraction resolution. The corresponding wave length of the tunneling electron would be $> 10$ Å.

The actual atomic resolution can only be understood in a quantum mechanical view.

- Maximum Lateral Resolution: 0.1 Å
- Maximum Axial Resolution: 0.01 Å
- Maximum Field of View: 100 μm

Over a typical atomic diameter of e.g. 0.3 nm, the tunneling current changes by a factor 1000!
First images were of the Si (111) reconstruction

The images vary depending on the electronic state of the material/tip.
The video shows a sequence of 155 individual scanning tunneling microscopy (STM) images total. Each image took about 30s for recording.

• “Topography” model good for large scale images, but not for the atomic level.

• Electron charge density model more accurate for atomic level images.

• Best model requires complex quantum mechanical considerations

Hence, the video covers a real time of about one and half an hour. You see three double layer high, parallel steps on a Cu(111) surface at 27°C. The displayed surface area is 24x24nm² and the surface height decreases from left to right. Due to atomic motion at the step edges, the steps do not remain straight and immobile, but undergo thermal fluctuations around their equilibrium position.

The movie shows a 200 x 200 nm² area of a Cu(111) surface at 36°C after deposition of several monolayers of copper. The deposited copper forms multi-layer high hexagonal islands. These islands are mobile due to atomic diffusion along the island edges and due to attachment/detachment of atoms.

Imaging of the graphite by STM

Overlay of structure shows only every other atom is imaged.

E. Stolyarova, et al., PNAS 2007
<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
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<tbody>
<tr>
<td>• No damage to the sample</td>
<td>• Samples limited to conductors and semiconductors</td>
</tr>
<tr>
<td>• Vertical resolution superior to SEM</td>
<td>• Limited Biological Applications: AFM</td>
</tr>
<tr>
<td>• Spectroscopy of individual atoms</td>
<td>• Generally a difficult technique to perform</td>
</tr>
<tr>
<td>• Maximum Lateral Resolution: 0.1 Å</td>
<td></td>
</tr>
<tr>
<td>• Maximum Axial Resolution: 0.01 Å</td>
<td></td>
</tr>
<tr>
<td>• Maximum Field of View: 100 μm</td>
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The Atomic Force Microscope was invented by Gerd Binning, Christoph Gerber, and Calvin F. Quate in the mid-eighties (Binning et al., *Phys. Rev. Letters* 1986), and is one of the scanning probe microscopes.
**Principle of operation:** An ultra-sharp tip on a spring cantilever is brought into contact with a surface and rastered across the sample. The change in forces – attractive and repulsive on the tip are measured as a function of tip position on the surface.

The position of the cantilever is measured by reflecting a laser off its backside and onto a 4 quadrant photodiode. Hence both up-down and sideways forces on the tip can be measured. Similarly to STM, the tip forces or tip height can be kept constant depending on the mode of operation.
One of the most important factors influencing the resolution which may be achieved with an AFM is the sharpness of the scanning tip. Best tips may have a radius of curvature of only around 5nm.

Another major application of AFM (besides imaging) is force spectroscopy, the measurement of force-distance curves. For this method, the AFM tip is extended towards and retracted from the surface as the static deflection of the cantilever is monitored as a function of piezoelectric displacement. These measurements have been used to measure nanoscale contacts, atomic bonding, Van der Waals forces, and Casimir forces, dissolution forces in liquids and single molecule stretching and rupture forces. Forces of the order of a few pico-Newton can now be routinely measured with a vertical distance resolution of better than 0.1 nanometer (Wikipedia, 2009).
Contact mode strong (repulsive) - constant force or constant distance. In contact mode, the tip is usually maintained at a constant force by moving the cantilever up and down as it scans.

• Non-contact mode weak (attractive). In non-contact mode or intermittent contact mode (tapping mode TM) the tip is driven up and down by an oscillator. Especially soft materials may be imaged by a magnetically-driven cantilever.

• Lateral force mode frictional forces exert a torque on the scanning cantilever.

• Magnetic force the magnetic field of the surface is imaged.
Atomic Force Microscope (Nanoscope III)

- SPM tip
- tipholder
- sample
- piezo translator
- motor control

- photodiode
- laser beam
- mirror
- fluid cell
- fluid in
- fluid out
- O-ring
- x,y,z piezo translator
- sample

in air and in buffer solutions
Microcantiliver

Thermal tip

Diamond tip

PtIr/DLC coated tip for electricity meas.

Cantilever is mounted to a piece of silicon or glass

The tip (Si3N4, Si) has a diameter from 10 to 200 nm.
Crystal structure of graphite. The unit cell is shaded in green. (A) Top view on the surface layer. The hexagonal surface lattice is defined by two unit vectors, $u$ and $v$, in the $xy$ plane with a length of 246 pm and an angle of 120° forming a honeycomb web of hexagonal rings. The basis of the lattice consists of two carbon atoms $\alpha$ (white) and $\beta$ (red) with a distance of 142 pm. (B) Perspective view, showing the layered structure. The distance between layers is 2.36 times the next-neighbor distance of atoms within one layer, and the bond between layers is weak. The $\alpha$ atoms (white) are directly above an $\alpha$ atom in the layer directly underneath at a distance of 334.8 pm; the $\beta$ atoms (red) are over a hollow sites ($h$).

Hembacher S et al. PNAS 2003;100:12539-12542
One hexagonal surface unit cell with the two basis atoms \( \alpha \) (white) and \( \beta \) (red) is superimposed for clarity.

(A) Experimental image of graphite in constant-height dynamic STM mode. Only the \( \beta \) atoms appear in the image.

(B) Experimental image of graphite in constant-height dynamic AFM mode showing both \( \alpha \) and \( \beta \) atoms.

(C) The calculated charge density of graphite at the Fermi level. The maxima of Fermi level are at the \( \beta \) atom positions. The STM image reflects the charge density at the Fermi level.

(D) Calculated total charge density.
AFM images of areas on the surfaces of (a) turnip yellow mosaic virus crystals, and (b) brome grass mosaic virus (BMV) crystals. Scan areas are (a) 140 × 140 nm², (b) 275 × 275 nm². (from A. McPherson et al, Annu. Rev. Biophys. Biomol. Struct. 2000. 29:361-410.)
Single molecule (pentacene), one million times smaller than a grain of sand

The delicate inner structure of a pentacene molecule has been imaged with an atomic force microscope.

A computer-generated image of how we're used to seeing a molecule represented with balls and sticks.

A 3D view showing how a single carbon monoxide molecule was used to create the image using a 'tuning fork' effect (www.photonics.com, 2009: “Results by IBM scientists in Zurich”).
Oscillations of the Yeast cells by AFM

Typical deflection mode images of yeast cells are shown in (A and B). Yeast cells are about 5 µm in diameter and often have bud scars on the cell surface (arrow 1).

Mechanical trapping is used to study live cells in YPD medium at 30°C. In (B), a typical image of a living yeast cell (arrow 1) trapped in a 5-µm filter pore is shown [empty pores (arrow 2) are easily distinguishable from trapped cells in the image].

Forcedistance curves (C) can be obtained by monitoring the deflection of the cantilever as it is extended (up arrow) and retracted (down arrow) from the cell in order to measure the local cellular nanomechanical properties. The zero point on the displacement scale represents the point where the AFM tip first comes into contact with the cell. A force-distance curve on the cell body (black line, extension; and green line, retraction) and the bud scar (blue line, extension; and red line, retraction) are shown.

A schematic of the experimental setup (D) outlines the process of measuring the local nanomechanical motion of the cell wall. The AFM cantilever is positioned on top of a living cell, and the scan size is set to 0 nm. The deflection of the cantilever is measured with a photodiode (Pelling et al, Science, 2004).
Oscillations of the Yeast cells by AFM

Typical time traces of the motion of the cell wall of living yeast. The data in (A to G) are from one single cell and data in (H to J) are measurements on different individual cells on different days. In most experimental runs (70%), the amplitude of the motion was $\mu 3$ nm at 30°C (A to D) but is also consistent at other temperatures as well. Occasionally, amplitudes as large as 7 nm (F) and as small as 1 nm (G) were observed. Exposure of the cells to sodium azide for 1 hour (14) caused the motion to cease (H).

The cell wall of living *Saccharomyces cerevisiae* (baker’s yeast) exhibites local nanomechanical motion at characteristic frequencies. The periodic motions in the range of 0.8 to 1.6 kHz with amplitudes of 3 nm were measured using the cantilever of an atomic force microscope (AFM) (Pelling et al, *Science*, 2004).
AFM, SAM and FIB of defects in DLC coating

Left: Acoustical images taken in a Cr-DLC specimen at 1.0 GHz, in focus (a) and with a defocus of -4 µm (b). The field of view was 240×240 µm².

Right: AFM deflection mode contrast image of the Cr-DLC specimen (Field of view was 10 x 10 µm).

Sketch of the model of the subsurface defect in Cr-DLC film

SEM images of the defect BLD#C: (a) Defect C prior to sputtering, SEM image with 60° tilt; (b) Defect BLD#C after sputtering. The depth of the trench is approximately 1.9 µm. P1a denotes a distance between two crosses P1 and PR1.
Acoustic Atomic Force Microscope

Atomic Force Acoustic Microscopy is a new SPM measuring mode developed at the Fraunhofer Institute of Nondestructive Testing, Saarbruecken, Germany. This technique, licensed to NT-MDT, allows the measurement of qualitative and quantitative local elastic properties of different materials. The basic idea is to excite the cantilever of an atomic force microscope into flexural vibrations when the tip is in contact with the sample (Fig. 1). The frequency of the eigenmodes of the cantilever depends, amongst other parameters, on the stiffness of the tip-sample contact and on the contact radius, which in turn are both a function of the Young's modulus of the sample and the tip, the tip radius, the load exerted by the tip, and the geometry of the surface. Such a technique allows one to determine the Young's modulus from the contact stiffness with a resolution of a few tens of nanometers, mode sensitivity is about 5%.
Rhombic polyethylene crystal on mica substrate. Contact Mode Topography (left) and AFAM (right) images. Scan size: 7x7µm.
AFAM Applications

Stripes of low and high density polyethylene with different elasticity. Topography (1), AFAM amplitude (2), Force Modulation (3), and Phase (4) images and Young Modulus map (5). Scan size: 47x47µm.
In the Ultrasonic Force Microscope (UFM) four regions of fiber-matrix interface are easily distinguishable: 1. the SiC fibre; 2. the carbon layer; 3. the reaction region; 4. the mullite matrix.
Locally enhanced Raman spectroscopy with AFM

(Color online) (a) Schematic view of an apertureless near-field optical microscope. The right figure is the topographic image of silver nanoparticle immobilized tip obtained with the scanning electron microscope. (b) Topographic images of carbon onions. (Kodama, et al, *Appl.Phys. Lett.*, 27, 2006).
SERS spectra and the tip-SERS image of carbon onions

(a) The SERS spectra of carbon onions. Those were measured with the SNI tip. The solid, dotted, broken, and thin black spectra were measured at different positions of the sample surface with an input power of 25 µW (1.3×10⁴ W/cm²) and exposure time of 0.3 s.

(b) Tip-SERS image of carbon onions. The image resolution is 32×32. The image was measured by detecting the SERS signal at 1595 cm⁻¹ with an input power of 25 µW (1.3×10⁴ W/cm²) and exposure time of 0.3 s (Kodama, et al, Appl.Phys. Lett., 27, 2006)
Home Work

1. Describe the Principle of Scanning Tunneling Microscopy (Qihui).

2. Describe the Principle of Atomic Force Microscopy (Ben).

3. Describe locally enhanced Raman spectroscopy with AFM (Corey).


5. Lateral and axial resolutions of STM and AFM techniques (David).