Techniques of Surface Physic

---STM and AFM(SPM)
• **Surface** is the boundary between identifiable phases of matter: solid/air, liquid/solid, solid/solid, and so on. In our course, we mainly focus on air/solid, and solid/solid interfaces.
Nanomaterials : Surface Domination

Nanomaterial surface physic is the study of physical phenomena (physical changes) that occur at the interface. Including surface states, surface diffusion, surface diffusion, surface reconstruction, surface phonons and plasmons, epitaxy and surface enhanced Raman scattering, the emission and tunneling of electrons, spintronics, and the self-assembly of nanostructures on surface.
The role of surface is more important as the size of object gets small.

\[
D \text{ (dispersion)} = \frac{\text{Number of surface atoms}}{\text{Total number of atoms}}
\]

Surface Chemistry and Catalysis
G. A. Somorjai (1994)
Visible by eyes

Optical microscope

SEM and TEM

SPM
Scanning Tunneling Microscopy

- tunneling phenomena:
Quantum Tunneling

Classical Picture

- electron
- electric field

In classical physics, the electron is repelled by an electric field as long as the energy of the electron is below the energy level of the field.
The phenomenon in tunneling in quantum mechanics describes an electron's penetration of an energy barrier, even though the electron's energy is below the height of the barrier. The tunneling situation can be seen as the following:

The probability that an electron penetrates the energy barrier is determined by the solutions to Schrödinger's wave equation in the three regions with the applicable boundary conditions.
Gerd Binnig
(born 20 July 1947) German physicist

Heinrich Rohrer
(born June 6, 1933) Swiss physicist

They shared half of the 1986 Nobel Prize in Physics with for the design of the scanning tunneling microscope (STM) (the other half of the Prize was awarded to Ernst Ruska).
• STM
The principle of STM

http://www.youtube.com/watch?v=47UgMpXFVj4
http://www.youtube.com/watch?NR=1&v=IR9-O_uwomc&feature=endscreen
The structure of STM
The manipulation of STM
Constant current image (topography) of an antiferromagnetic atomic layer iron on W(001) with defects and adatoms.
sharp tip

Constant Height Mode

sample surface
The Application of STM

- 1. Atomic Microscope
High performance STM image showing atomic resolution on Si(111) 7nm x 7nm

cobalt sulfide "nanoflower" structure synthesized on a Au(111) surface 9nm x 9nm
• 2. Manipulation of single atoms and single molecules
Desorption: Similar to vertical manipulation, but desorption of individual adsorbates directly into the surrounding gas phase.

Lateral manipulation: The transfer of atoms/molecules along the surface employing for example attractive/repulsive forces between the tip and the adsorbate.

Vertical manipulation: The reversible transfer of atoms/molecules between the surface and the STM tip employing additionally electronic/vibrational excitation of the adsorbate by inelastic tunneling.
positioned 48 iron atoms into a circular ring in order to "corral" some surface state electrons and force them into "quantum" states of the circular structure.

Example 1: Individual Cu atoms on Cu(111).
Size: 25 x 8 nm².
3. Single-molecule chemical reactions

**Synthesis:** Selective bond formation between two molecular units employing lateral manipulation followed by electronic/vibrational excitation.

**Dissociation:** Selective bond breaking within a molecule by means of inelastic tunneling processes.

**Change of Conformation**
Schematic illustration of the proposed mechanism of bond formation in the Au-PTCDA switch: In the nonbonded state, the atom and the molecule are both negatively charged and stabilized by the repulsive electrostatic interaction (a). By tunneling out of the occupied molecular resonance, the PTCDA is temporarily neutralized, and the electrostatic repulsion is weakened (b). This enables the Au atom to move towards the molecule and form the bond, ending up in the bonded state of the complex, which is only singly negatively charged.
4. Construct of molecular level electronics device

The terbium atom (red) is sandwiched between two organic molecules (grey and blue) to form a single-molecule magnet.
The advantages and disadvantages of STM

- **Advantages:**

  STMs are helpful because they can give researchers a three dimensional profile of a surface, which allows researchers to examine a multitude of characteristics, including roughness, surface defects and determining things about the molecules such as size and conformation.

  Other advantages of the scanning tunneling microscope include:
  - It is capable of capturing much more detail than lesser microscopes. This helps researchers better understand the subject of their research on a molecular level.
  - STMs are also versatile. They can be used in ultra high vacuum, air, water and other liquids and gasses.
  - They will operate in temperatures as low as zero Kelvin up to a few hundred degrees Celsius.
• **Disadvantages:**

The three major downsides to using STMs are:

• STMs can be difficult to use effectively. There is a very specific technique that requires a lot of skill and precision.

• STMs require very stable and clean surfaces, excellent vibration control and sharp tips. And STM only can be used to scan not easily oxidized good conductors samples.

• STMs use highly specialized equipment that is fragile and expensive.
Atomic Force Microscopy (AFM)

• 1986 --- Binnig, Quate and Gerber invented the first atomic force microscope
The principle of AFM

• When the tip is brought close to the sample, a number of forces may operate.

• Typically the forces contributing most to the movement of an AFM cantilever are the **coulombic** and **van der Waals** interactions.

**Coulombic Interaction**: This strong, short range repulsive force arises from electrostatic repulsion by the electron clouds of the tip and sample. This repulsion increases as the separation decreases.

**Van der Waals interactions**: These are longer range attractive forces, which may be felt at separations of up to 10 nm or more. They arise due to temporary fluctuating dipoles.

The combination of these interactions results in a force-distance curve similar to that below.
• As the tip is brought towards the sample, van der Waals forces cause attraction.
• As the tip gets closer to the sample this attraction increases.
• However at small separations the repulsive coulombic forces become dominant. The repulsive force causes the cantilever to bend as the tip is brought closer to the surface.
• There are other interactions besides coulombic and van der Waals forces which can have an effect.
The structure of AFM

Position Sensing Part

Force Sensing Part

Feedback System

Position Sensing photodetector
The manipulation of AFM

- Two scan modes:

  - Constant-height scan
  - Constant-force scan
The diagram illustrates force versus probe-sample separation in two modes: Contact Mode and Non-Contact Mode.

- **Contact Mode**: The probe is in direct contact with the sample, with forces acting to move it closer (attractive force) and away (repulsive force).
- **Non-Contact Mode**: The probe is not in direct contact with the sample, with forces acting to move it further away (repulsive force).

The diagram shows a curve representing the force as a function of the probe-sample separation, with different regions indicating the two modes.
Three primary imaging modes:

1. Contact AFM
   - < 0.5 nm probe-surface separation

2. Tapping mode AFM (Intermittent contact)
   - 0.5-2 nm probe-surface separation

3. Non-contact AFM
   - 0.1-10 nm probe-surface separation
1. Contact AFM

- In contact mode the tip contacts the surface through the adsorbed fluid layer on the sample surface.

- The detector monitors the changing cantilever deflection and the force is calculated using Hooke’s law:

\[ F = -kx \]  
\( F = \) force, \( k = \) spring constant, \( x = \) cantilever deflection

- The feedback circuit adjusts the probe height to try and maintain a constant force and deflection on the cantilever. This is known as the deflection setpoint.
2. Tapping mode AFM (Intermittent contact)

In tapping mode the cantilever oscillates at or slightly below its resonant frequency. The amplitude of oscillation typically ranges from 20 nm to 100 nm. The tip lightly “taps” on the sample surface during scanning, contacting the surface at the bottom of its swing.

Because the forces on the tip change as the tip-surface separation changes, the resonant frequency of the cantilever is dependent on this separation.

The oscillation is also damped when the tip is closer to the surface. Hence changes in the oscillation amplitude can be used to measure the distance between the tip and the surface. The feedback circuit adjusts the probe height to try and maintain a constant amplitude of oscillation i.e. the amplitude setpoint.
**Tapping mode in air:**
In this operating mode, a small piezoelectric crystal mounted in the multimode AFM tip holder makes the cantilever oscillate up and down at or slightly below its resonance frequency. The tip oscillates vertically, alternately contacts the surface and lifts off. The amplitude of this oscillation typically ranges from 20nm to 100nm. The oscillating tip lightly touches or ‘taps’ on the sample surface during scanning. When the tip comes close to the sample surface, forces like van der Waals force, dipole-dipole interactions, electrostatic forces, etc., act on the cantilever and lead to a decrease in the amplitude of oscillation. Thus, the image is obtained by imaging the force of the oscillating contacts of the cantilever tip with the sample surface.

**Tapping mode in fluids:**
Tapping mode operation in aqueous medium is a very useful tool for biologists because the samples are in a state that closely resembles the in vivo environment as compared to dehydrated samples.
3. Non-contact AFM

- In non-contact mode the cantilever oscillates near the surface of the sample, but does not contact it. The oscillation is at slightly above the resonant frequency. Van der Waals and other long-range forces decrease the resonant frequency just above the surface. This decrease in resonant frequency causes the amplitude of oscillation to decrease.

- In ambient conditions the adsorbed fluid layer is often significantly thicker than the region where van der Waals forces are significant. So the probe is either out of range of the van der Waals forces it attempts to measure, or becomes trapped in the fluid layer. Therefore non-contact mode AFM works best under ultra-high vacuum conditions.
The Properties of the different operation modes in AFM.

<table>
<thead>
<tr>
<th>Operation mode</th>
<th>Contact mode</th>
<th>Non-contact mode</th>
<th>Tapping mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>tip loading force</td>
<td>low → high</td>
<td>low</td>
<td>low</td>
</tr>
<tr>
<td>contact with sample surface</td>
<td>yes</td>
<td>no</td>
<td>periodical</td>
</tr>
<tr>
<td>manipulation of sample</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>contamination of AFM tip</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
</tr>
</tbody>
</table>
### Advantages and Disadvantages of AFM Modes

<table>
<thead>
<tr>
<th>Mode</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
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</table>
| **Contact Mode**| - High scan speeds
- “Atomic resolution” is possible
- Easier scanning of rough samples with extreme changes in vertical topography. | • Lateral forces can distort the image
• Capillary forces from a fluid layer can cause large forces normal to the tipsample interaction
• Combination of these forces reduces spatial resolution and can cause damage to soft samples. |
| **Tapping Mode**| - Higher lateral resolution (1 nm to 5 nm).
- Lower forces and less damage to soft samples in air.
- Almost no lateral forces. | • Slower scan speed than in contact mode |
| **Non-contact Mode** | - Both normal and lateral forces are minimised, so good for measurement of very soft samples
- Can get atomic resolution in a UHV environment | • Slower scan speed than tapping and contact modes to avoid contacting the adsorbed fluid layer
• Lower lateral resolution, limited by tip-sample separation.
• Usually only applicable in extremely hydrophobic samples with a minimal fluid layer. |
The application of AFM

1. Imaging

AFM 3D image of a detail of the free surface of an artificial opal

The figure illustrates 800 nm wide and 10 nm high Pd/Fe/Pd thin film dots fabricated using electron lithography.
NCAFM image of the Ge/Si(105) surface, 4.2 nm x 4.2 nm

PMMA spheres scanning range 45x45 μm

AFM image of human plasma fibrinogen
2. Measuring forces (and mechanical properties) at the nanoscale

Illustration of an Atomic Force Microscope (AFM) tip measuring the force it takes to move a cobalt atom on a crystalline surface. The ability to measure the exact force it takes to move individual atoms is one of the keys to designing and constructing the small structures that will enable future nanotechnologies. (Credit: Image courtesy of IBM) [http://www.youtube.com/watch?v=BUq2bQkL1zo](http://www.youtube.com/watch?v=BUq2bQkL1zo)
Schematic of experiment to measure the force between particles in an electric field.

Force as a function of applied voltage

http://www.youtube.com/watch?v=MZb8C0f7Kdg
Single-molecule force microscopy uses a target molecule at the end of an AFM cantilever to probe surface molecules for those with a strong attractive or adhesive force. These force measurements can subsequently be mapped out as an image.
• 3. As a nanoscale tool

for bending, cutting and extracting soft materials (such as Polymers, DNA, and nanotubes), at the submicron scale under high-resolution image control

Manipulation of a nanotube on a silicon substrate. The AFM tip is used to create the Greek letter "theta" from a 2.5 micron long nanotube.
Schematic of the several applications of AFM in biomaterials. (a) high-resolution imaging of cortical bone and individual collagen fibril (inset); (b) measurement of viscoelastic and rate-dependent properties of individual living cells; (c) characterization of electro-mechanical coupling in individual collagen fibrils; (d) mapping the local strain field in situ tensile experiments; (e) penetration of living cell membrane by a nanoneedled-probe; and (f) nano-injection of living cells by local rupture of the cell membrane for drug delivery at the single-cell level.
A single nanotube (in red) originally on an insulating substrate (SiO₂, shown in green) is manipulated in a number of steps onto a tungsten film thin wire (in blue), and finally is stretched across an insulating tungsten oxide barrier (in yellow).
The advantage and disadvantage of AFM

**Advantages**:
1) it generates true, high-resolution 3-dimensional surface images;
2) it does not require special sample treatments that can result in the sample's destruction or alteration;
3) it does not require a vacuum environment in order to operate (it can operate in both air and liquid);
4) could used for organic materials

**Disadvantages**:
1) the image size that it provides is much smaller than what electron microscopes can create;
2) it is slow in scanning an image, unlike an electron microscope which does it in almost real-time.
3) tip convolution--not true sample topography, but the interaction of the probe with the sample surface
4) expensive tips
Tip convolution----Tip Related Artifacts

Protrusions appear wider, depressions narrower than they are in reality.

Variables that determine the resolution of the scan.