NACK NETWORK

Building College-University
Partnerships for Nanotechnology
Workforce Development

Advanced Scanning Probe Microscopy I

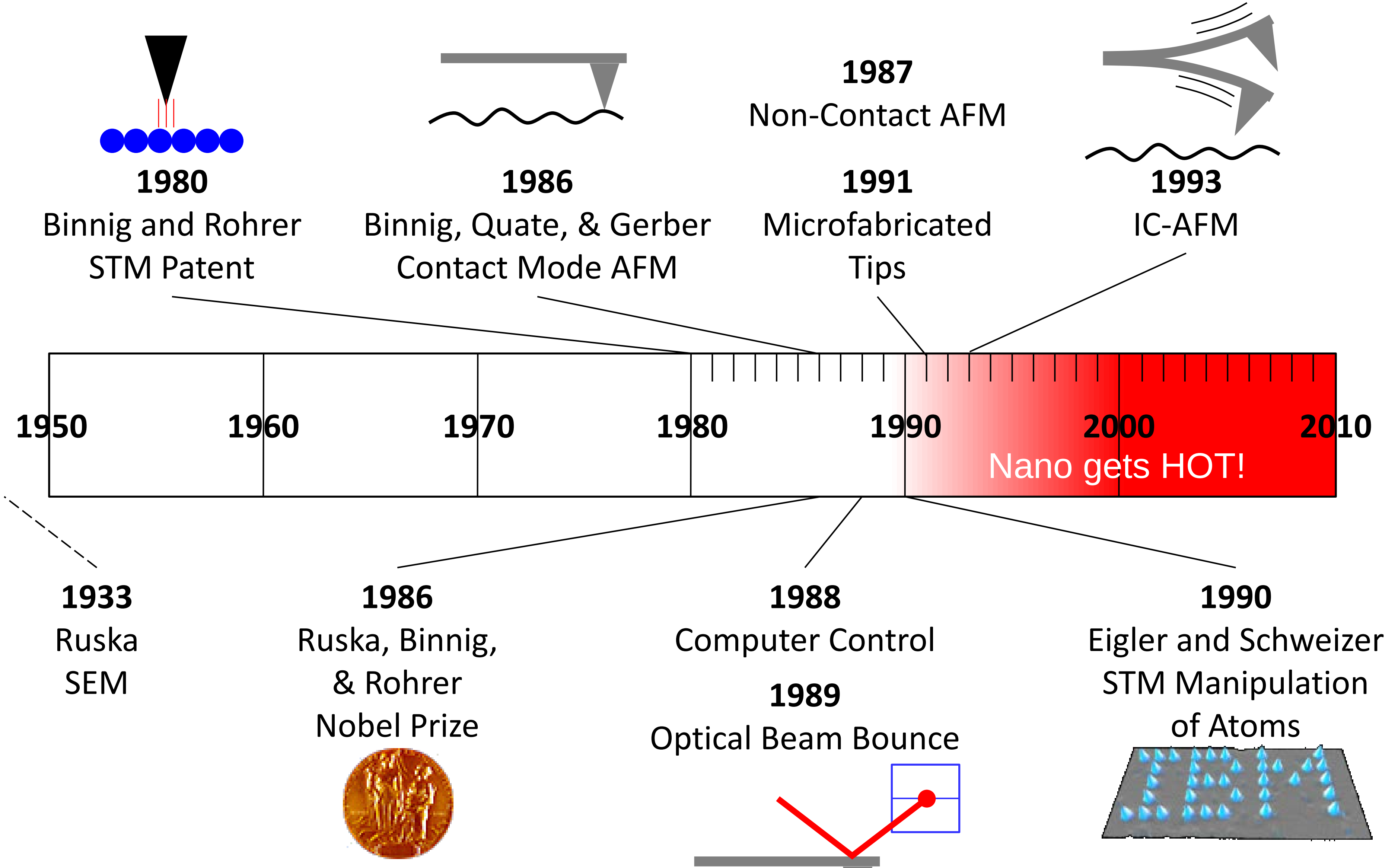
Outline

- Overview of Scanning Probe Techniques
- Scanning Tunneling Microscopy
- Atomic Force Microscopy
  - Hardware and Components
  - Tip/Sample Interactions
  - Common Modes of Operation
  - Pitfalls and Image Artifacts
- Example of Instrument Operation

Characterization on the Nanoscale

- Using nanoscale materials and understanding them are two different things.
- Modern tools help us to manipulate and characterize materials at the nanoscale.
- Two notable innovations:
  - FESEM: Field Emission Scanning Electron Microscopy
    - “seeing” at the nanoscale
  - SPM: Scanning Probe Microscopy (e.g., AFM)
    - “feeling” at the nanoscale

Timeline of Nanocharacterization



1980
Binnig and Rohrer
STM Patent

1986
Binnig, Quate, & Gerber
Contact Mode AFM

1987
Non-Contact AFM

1991
Microfabricated
Tips

1993
IC-AFM

1933
Ruska
SEM

1986
Ruska, Binnig,
& Rohrer
Nobel Prize

1988
Computer Control

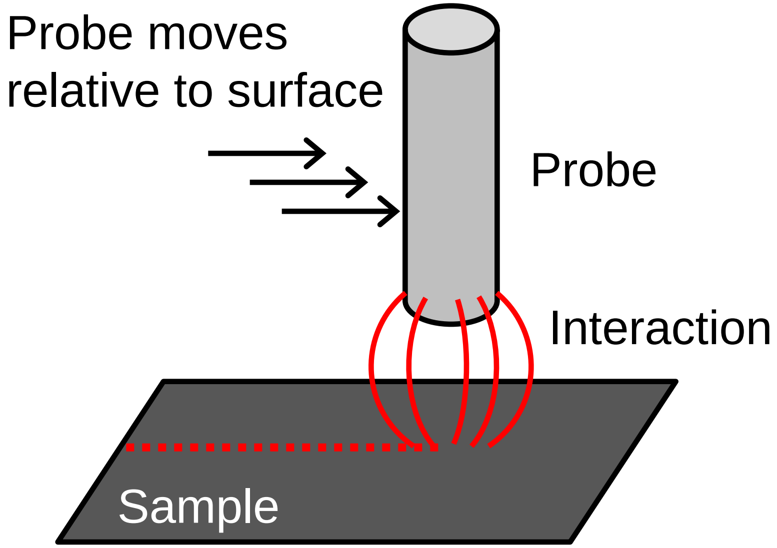
1989
Optical Beam Bounce

1990
Eigler and Schweizer
STM Manipulation
of Atoms

Eng. & Sci. 2005, 1-2, 16

A Sample of SPM Techniques

- Scanning Tunneling Microscopy (STM)
- Atomic Force Microscopy (AFM)
- Dynamic Force Microscopy (DFM)
- Scanning Near-Field Optical Microscopy (SNOM)



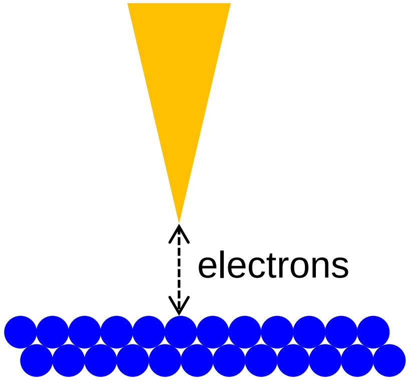
Selected Possible Interactions

Current Flow
Capacitance
Attractive and Repulsive Forces
Magnetic Forces
Absorption or Emission of Light
Flow of Heat

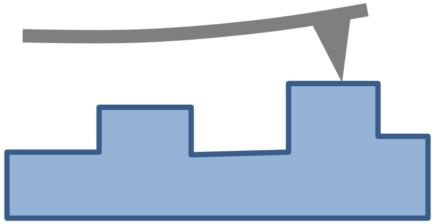
A Sample of SPM Techniques

For Example:

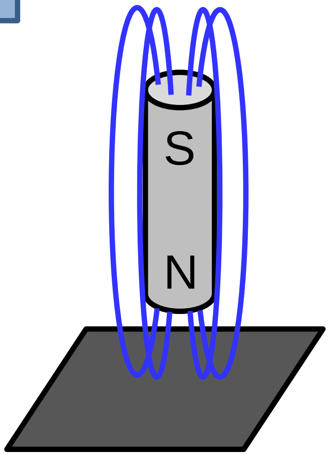
STM = electrical measurements



AFM = mechanical measurements



MFM = magnetic measurements



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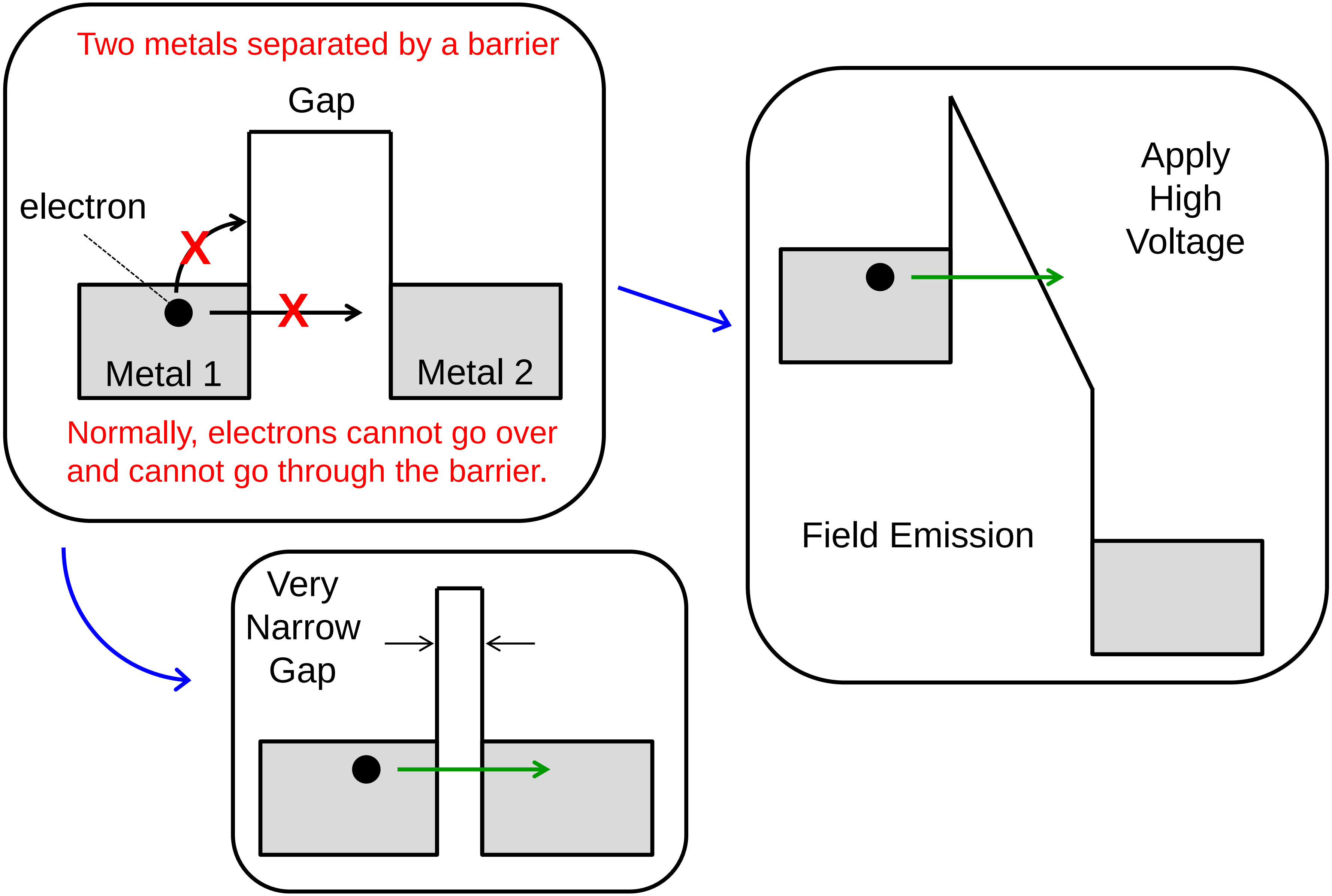
Scanning Tunneling Microscopy

- Utilizes a conducting tip, usually tungsten or gold, sharpened to the point of a single atom (ideally).
- A bias voltage is applied between the tip and the sample and the two are brought into close proximity (less than 10 Å).
- At this distance the electrons can quantum mechanically tunnel through the gap between tip and sample.

Scanning Tunneling Microscopy



Two metals separated by a barrier

Gap

electron

X

X

Metal 1

Metal 2

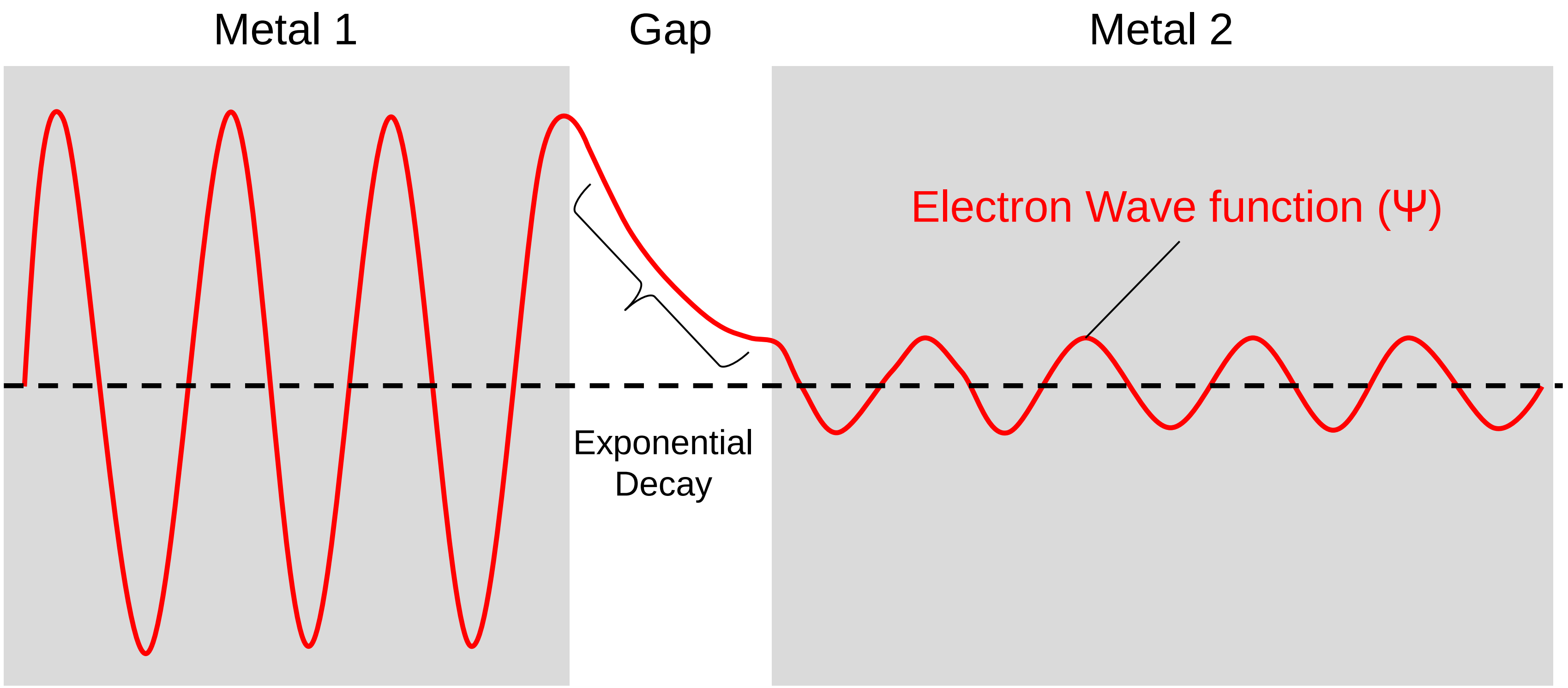
Normally, electrons cannot go over and cannot go through the barrier.

Very Narrow Gap

Apply High Voltage

Field Emission

Scanning Tunneling Microscopy

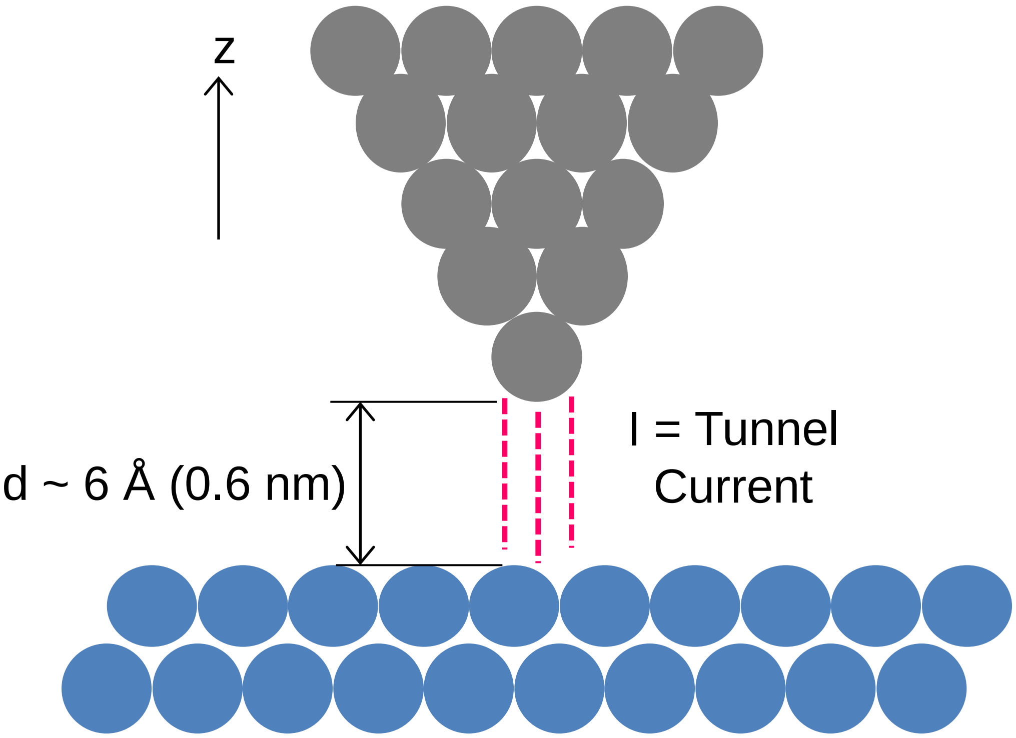


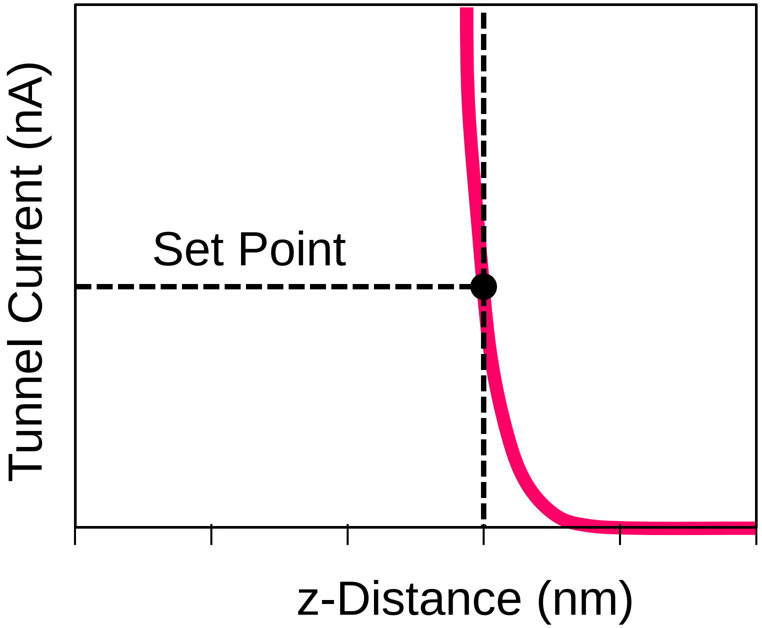
- The magnitude of Ψ is related to the probability of finding an electron in the material.
- If the gap is small enough, then the electron has some probability of crossing over from metal 1 to metal 2.
- In the absence of a high electric field, the gap must be less than a few nm to observe tunneling.

http://hyperphysics.phy-astr.gsu.edu

How Can Tunnel Current Be Used?

Tunnel current is very sensitive to the tip-sample separation distance.

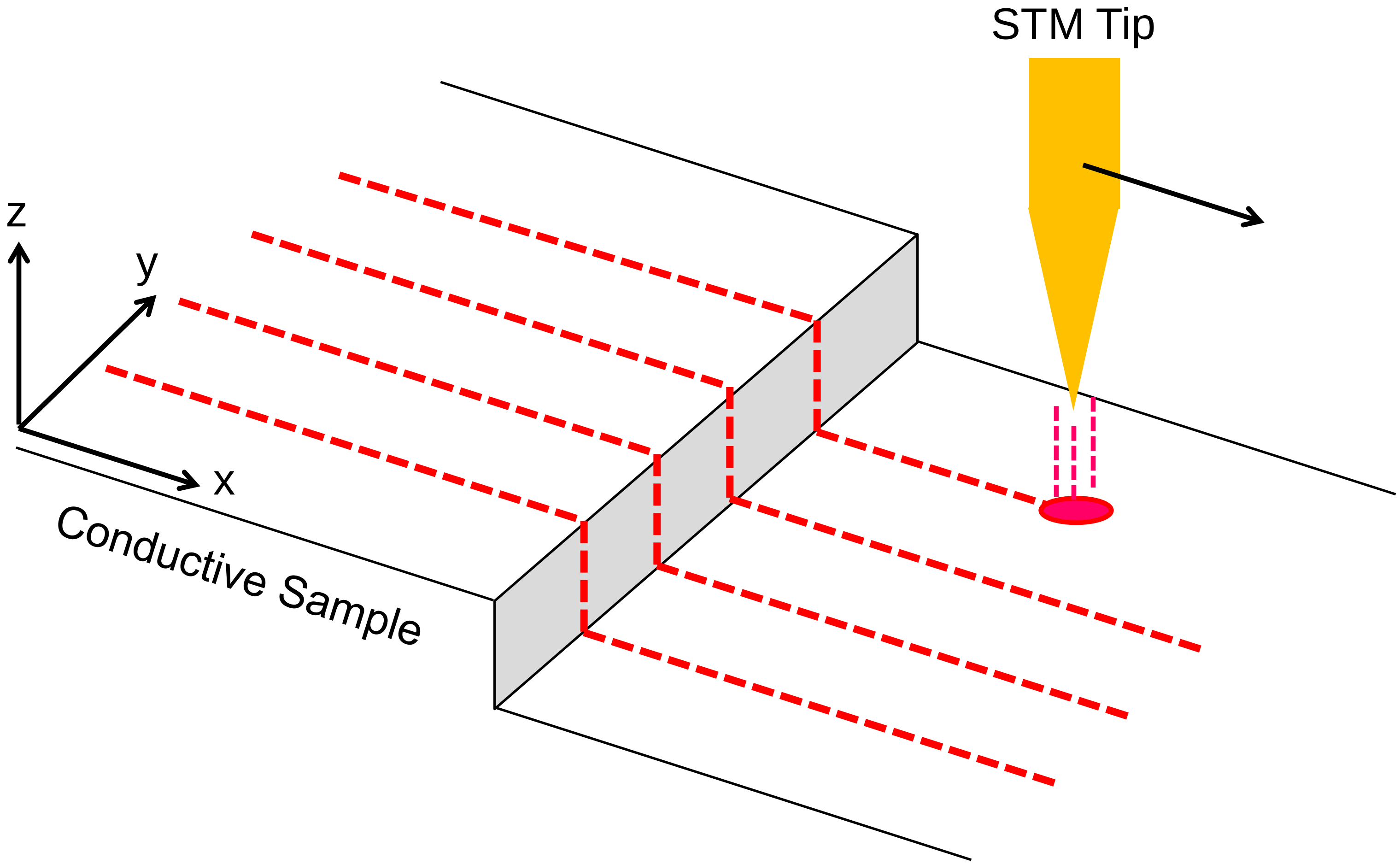




Under Ideal Circumstances

$I(z) \sim \exp[-2ad]$

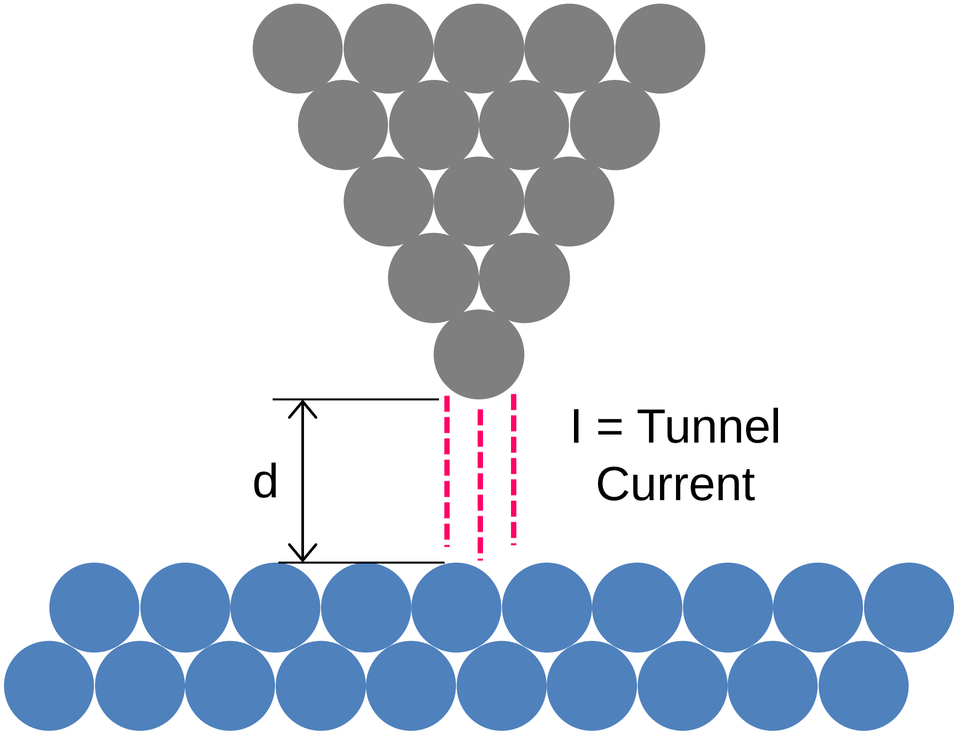
STM: Principle of Operation



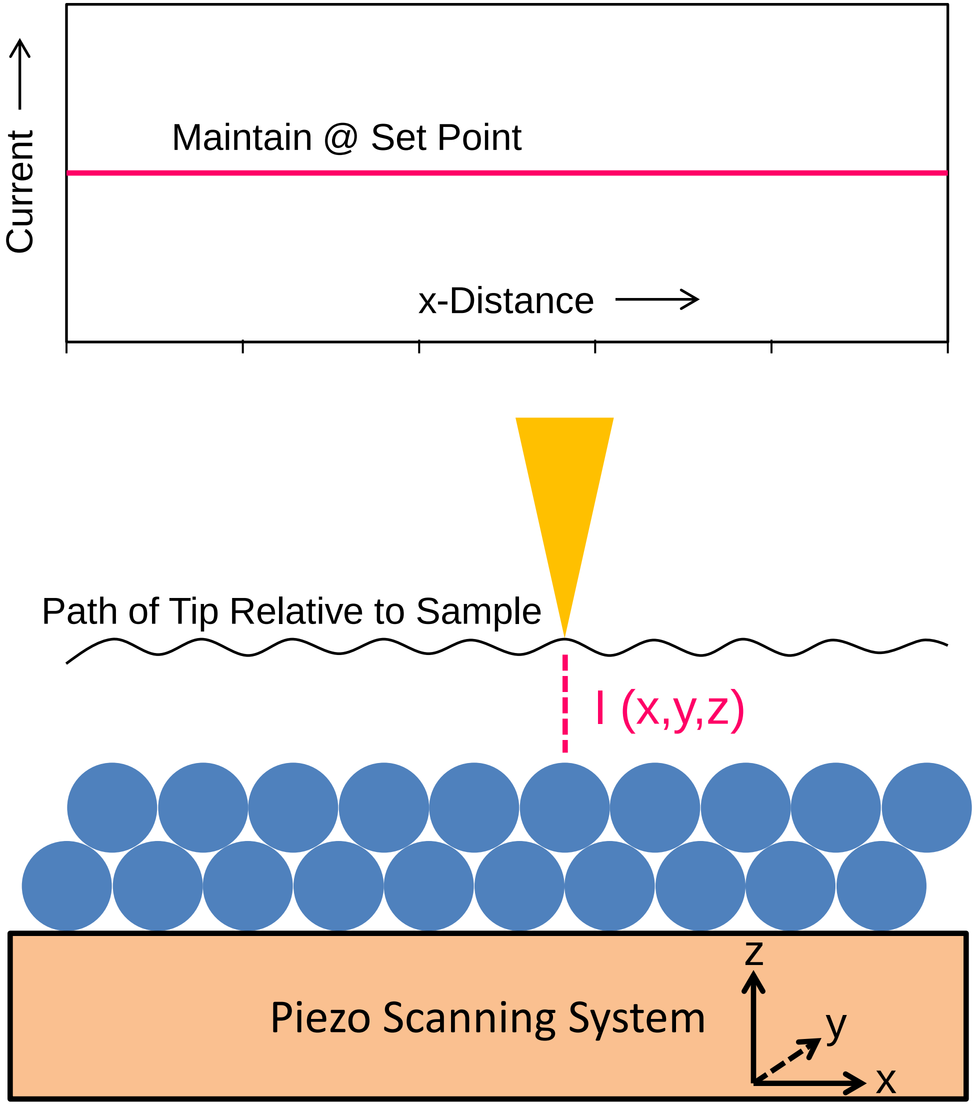
Gap is adjustable using piezoelectric material.
Tunnel current is maintained at set point by adjusting gap.
STM functions by scanning in a controlled manner while adjusting tip-sample distance.

Scanning Tunneling Microscopy

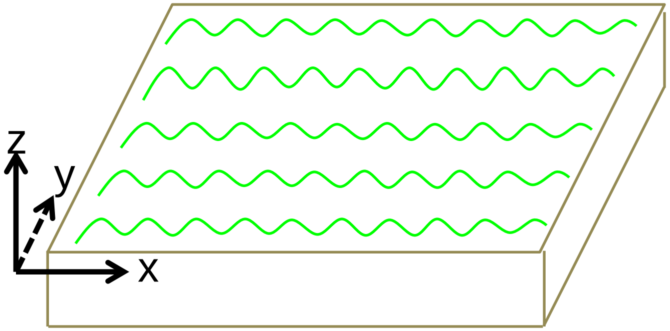
- The tunneling current changes exponentially with the distance between the tip and the sample.
- The changes are detected by a feedback loop which keeps the tunneling current constant by adjusting the tip-surface separation distance (d).
- The signal provides high resolution information about the surface topography and/or the electronic states of the surface.



STM: Principle of Operation



Data from many scans are compiled to form a 3-D representation of the surface.



STM: What can be measured?

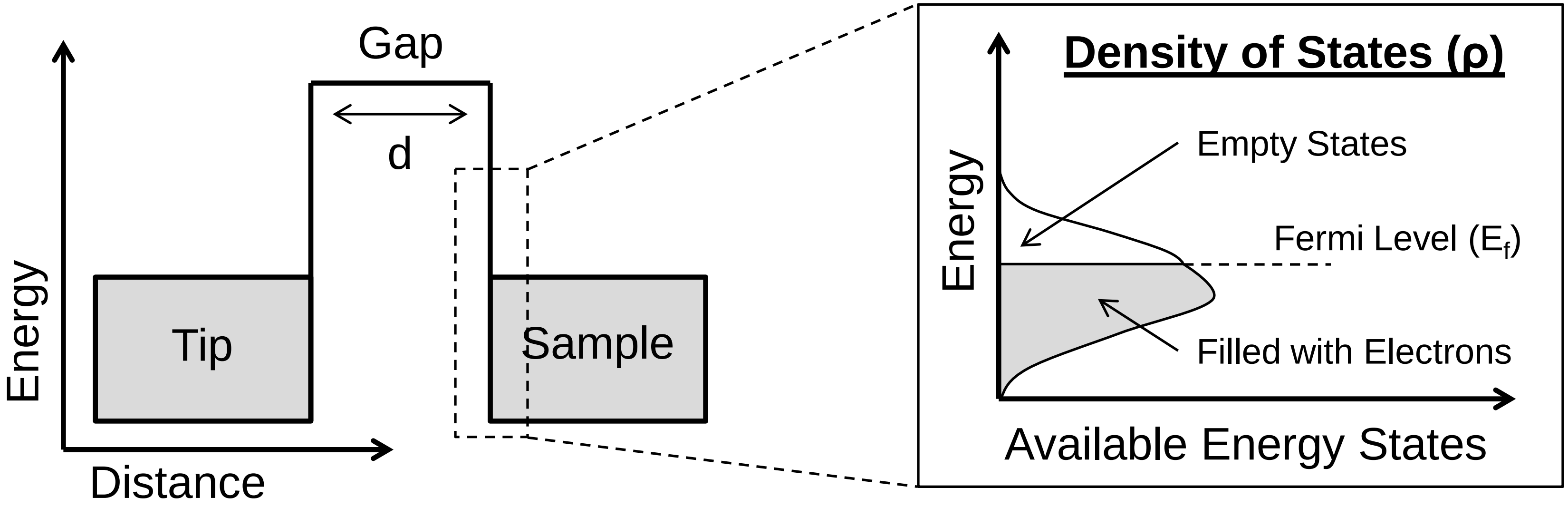
Bias Applied Between Tip and Sample

Tunnel Current

$$I = e\Delta V\rho$$

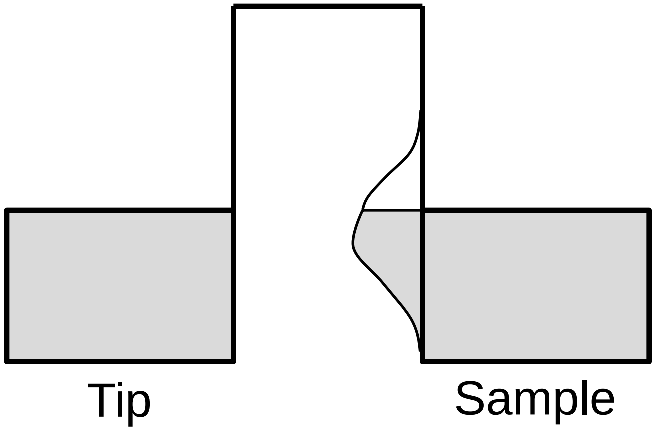
Charge on Electron

Complex Function That Describes the Electronic Structure of the Sample

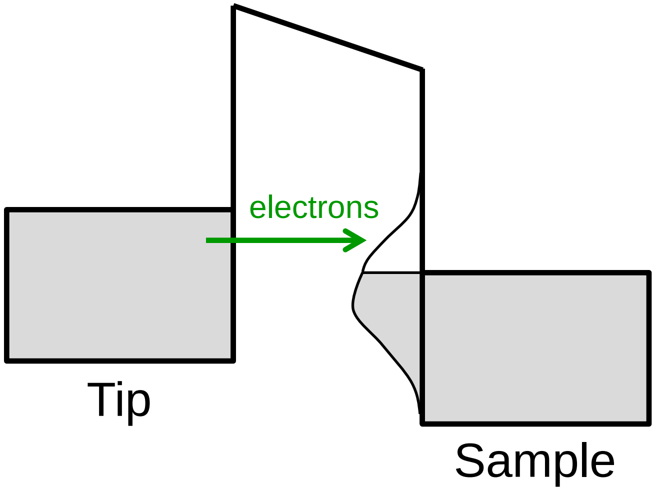


STM: What can be measured?

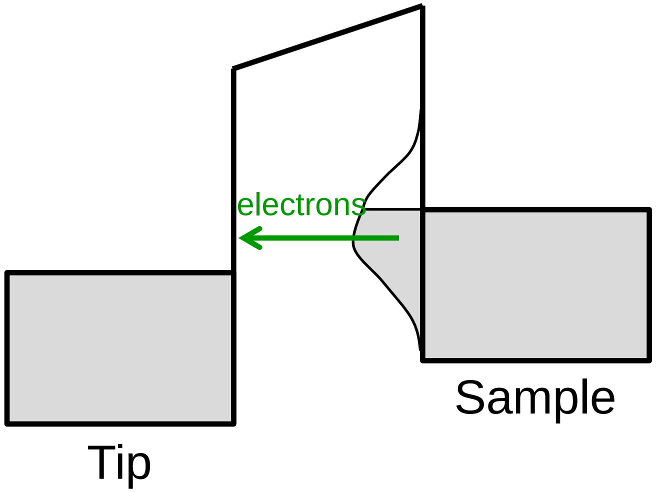
No Bias Voltage Applied



(-) Voltage on Tip



(+) Voltage on Tip



Current Imaging Tunneling Spectroscopy (CITS)

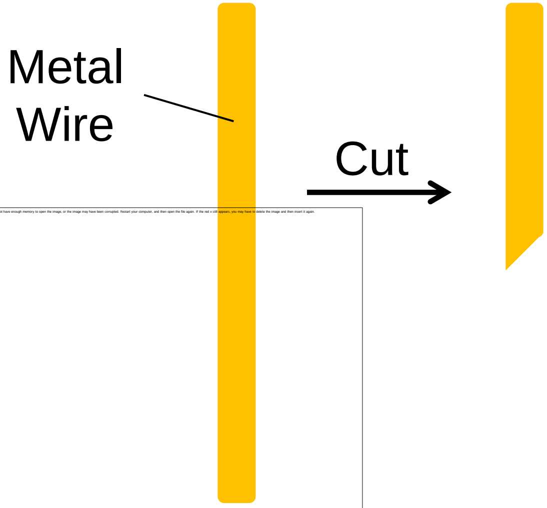
- Filled and unfilled electronic states can be examined by varying the tip-sample bias.
  - Negative bias on tip: electrons flow into unfilled states of the sample.
  - Positive bias on tip: electrons flow out of filled states of the sample.
- CITS = At each (x,y) point, acquire data at multiple (+) and (-) biases. This allows visualization of the local electronic structure of the sample.

STM: Requirements and Limitations

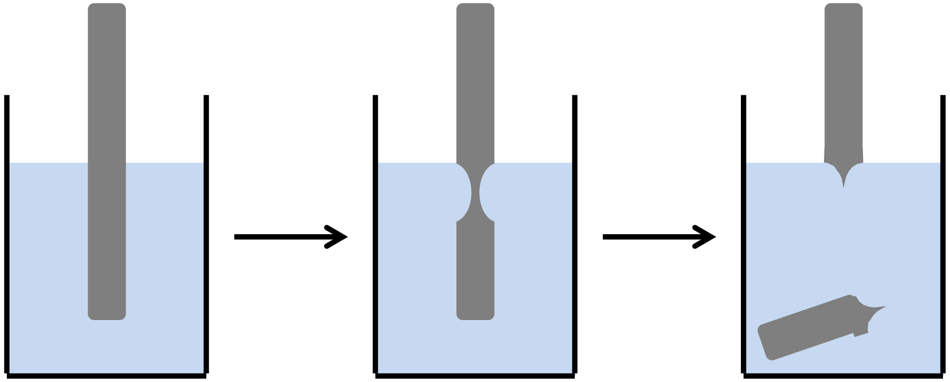
- Sample and tip must be conductive.
- Requires isolation from vibrations.
- Precise positioning mechanisms.
- Ability to measure very small currents.
- Samples must be flat on nm scale.
- Sample surfaces should be well-defined and stable over time.

STM: Requirements and Limitations

- “Good” tips are difficult to prepare.
- Only about 20% of tips produce meaningful results.
- Two ways to prepare tips:

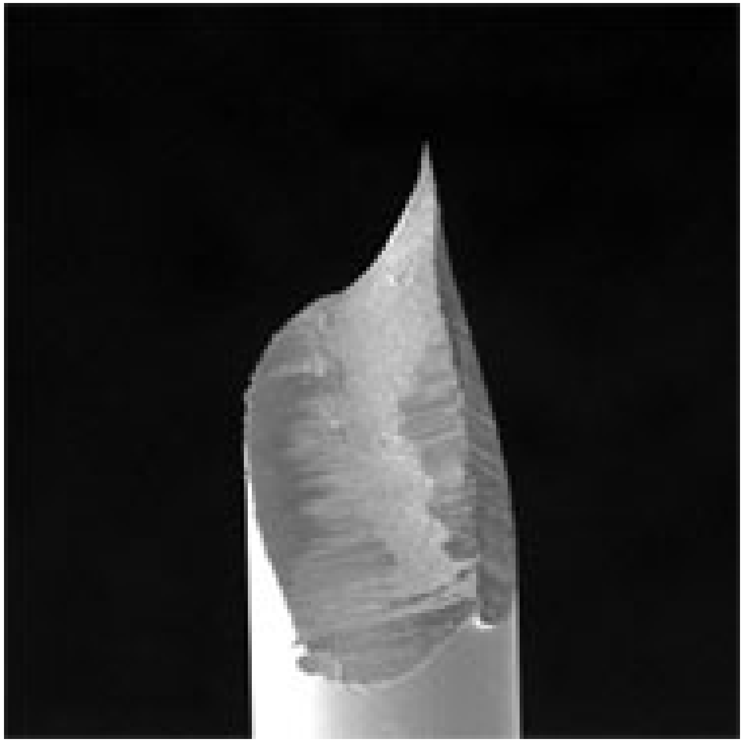


Electrochemical Etching



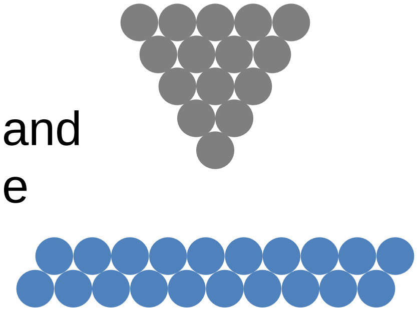
Scanning Tunneling Microscopy

- Sharpened, conducting tip with a bias voltage applied between the tip and the sample.
- Sample and tip must be conductors or semiconductors.
- How sharp is an actual tip?

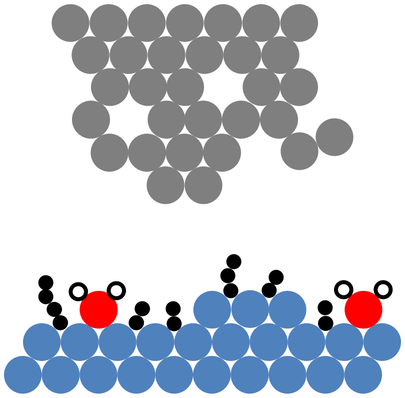


STM: Requirements and Limitations

- STM can be done in air, but best results are obtained in ultra high vacuum (UHV).
- Samples and tips must be stable:
  - Oxide layers do not form
  - UHV prevents adsorption of contaminates from ambient air



Ideal tip and sample



Real tip and contaminated surface

Interesting Surfaces for STM

- Surface reconstruction of Si(111) 7x7.
  - An early victory for STM.
  - STM images clearly showed the arrangement of atoms on the reconstructed surface for the first time.
  - Measurements done after annealing in UHV.
- HOPG (Highly-Oriented Pyrolytic Graphite)
  - STM images used to explain the packing of layers relative to each other.
  - How do the individual layers of graphene lay on top of each other? Do the atoms line up or not?

Phys. Rev. Lett. 1983, 50(2), 120.
Video of Si(111) Surface Reconstruction: http://www.vimeo.com/1086112

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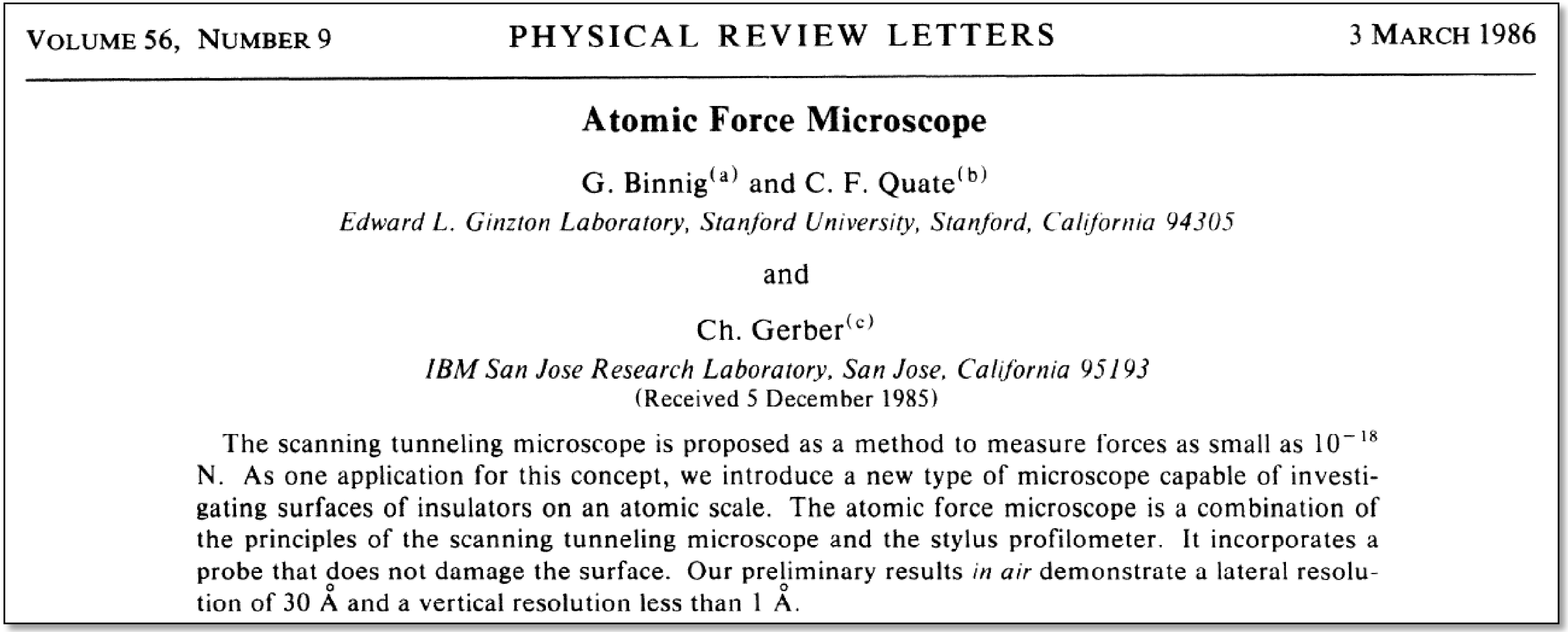
From STM to AFM

Many interesting surfaces and materials are not conductive. Can a technique similar to STM be used to characterize them? What other tip-sample interactions can be used and how can they be measured?



VOLUME 56, NUMBER 9 PHYSICAL REVIEW LETTERS 3 MARCH 1986

Atomic Force Microscope

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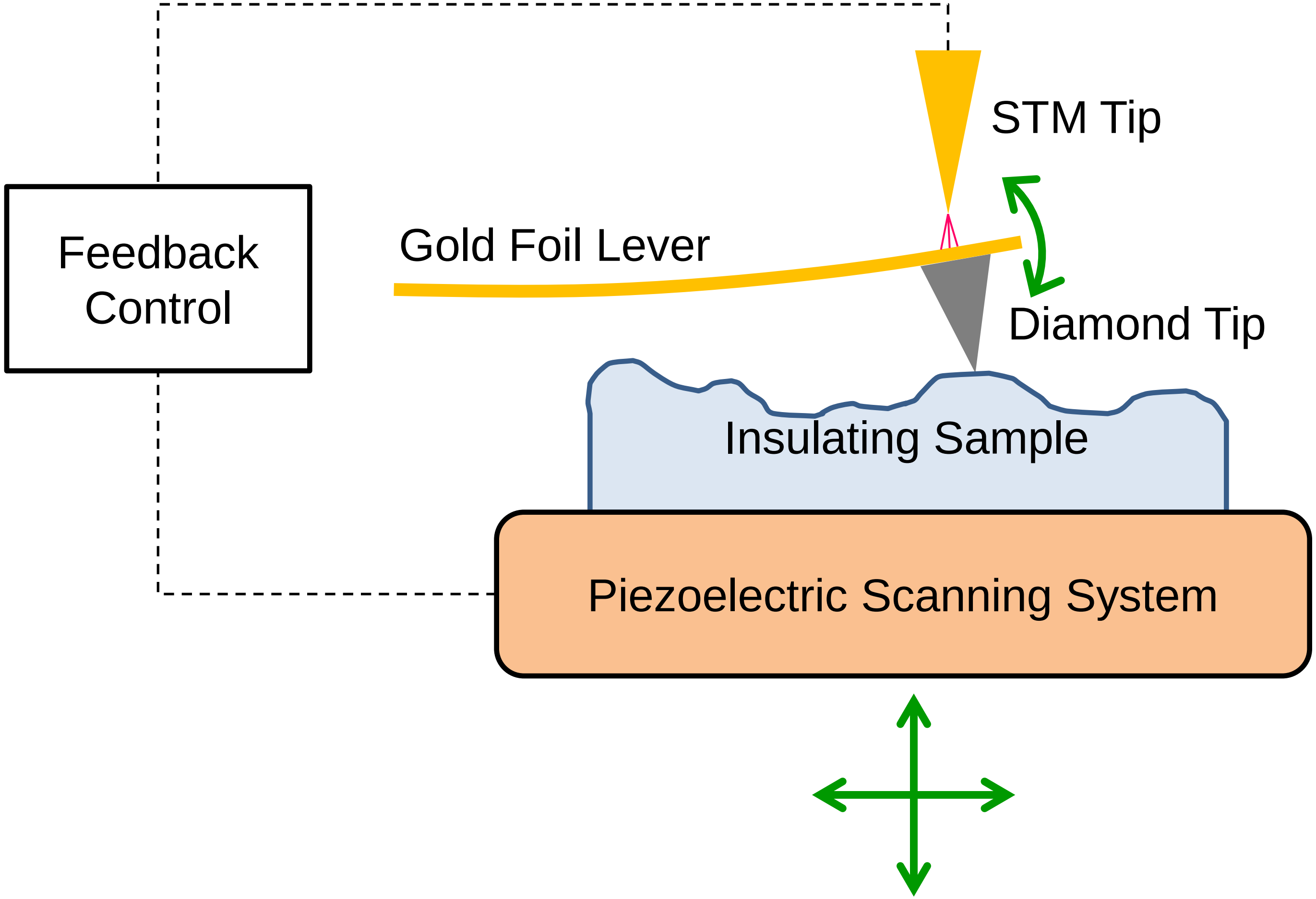
(Received 5 December 1985)

The scanning tunneling microscope is proposed as a method to measure forces as small as 10^{-18} N. As one application for this concept, we introduce a new type of microscope capable of investigating surfaces of insulators on an atomic scale. The atomic force microscope is a combination of the principles of the scanning tunneling microscope and the stylus profilometer. It incorporates a probe that does not damage the surface. Our preliminary results *in air* demonstrate a lateral resolution of 30 Å and a vertical resolution less than 1 Å.

Phys. Rev. Lett. 1986, 56(9), 930.

From STM to AFM



STM current is monitored and used to keep the diamond tip in contact with the sample surface.

Voltages are applied to the piezoelectric to move the sample relative to the tip.

Phys. Rev. Lett. 1986, 56(9), 930.

Atomic Force Microscopy (AFM)

- Traditional microscopes are limited by lens quality and diffraction loss.
- Scanning-probe instruments (like an AFM) do not use lenses to focus light.
- Instead, a small probe is rastered across the sample while a representative signal is monitored.
- Information gathered from the probe (e.g., height) can be reconstructed to form an “image” of the sample surface.

Atomic Force Microscopy

- The AFM is one of many scanning probe tools. All use a nanoscale probe to scan over a surface.
- An Atomic Force Microscope (AFM) is a tool for characterizing surfaces on a scale of about 0.1 nm to 100 microns.
- As the name implies, the instrument measures the forces acting between the tip and the sample.
- It also is commonly used as a type of microscope, due to its ability to gather high-resolution topographic information.
- The combination of force measurement and spatial resolution makes AFM a very versatile characterization technique.

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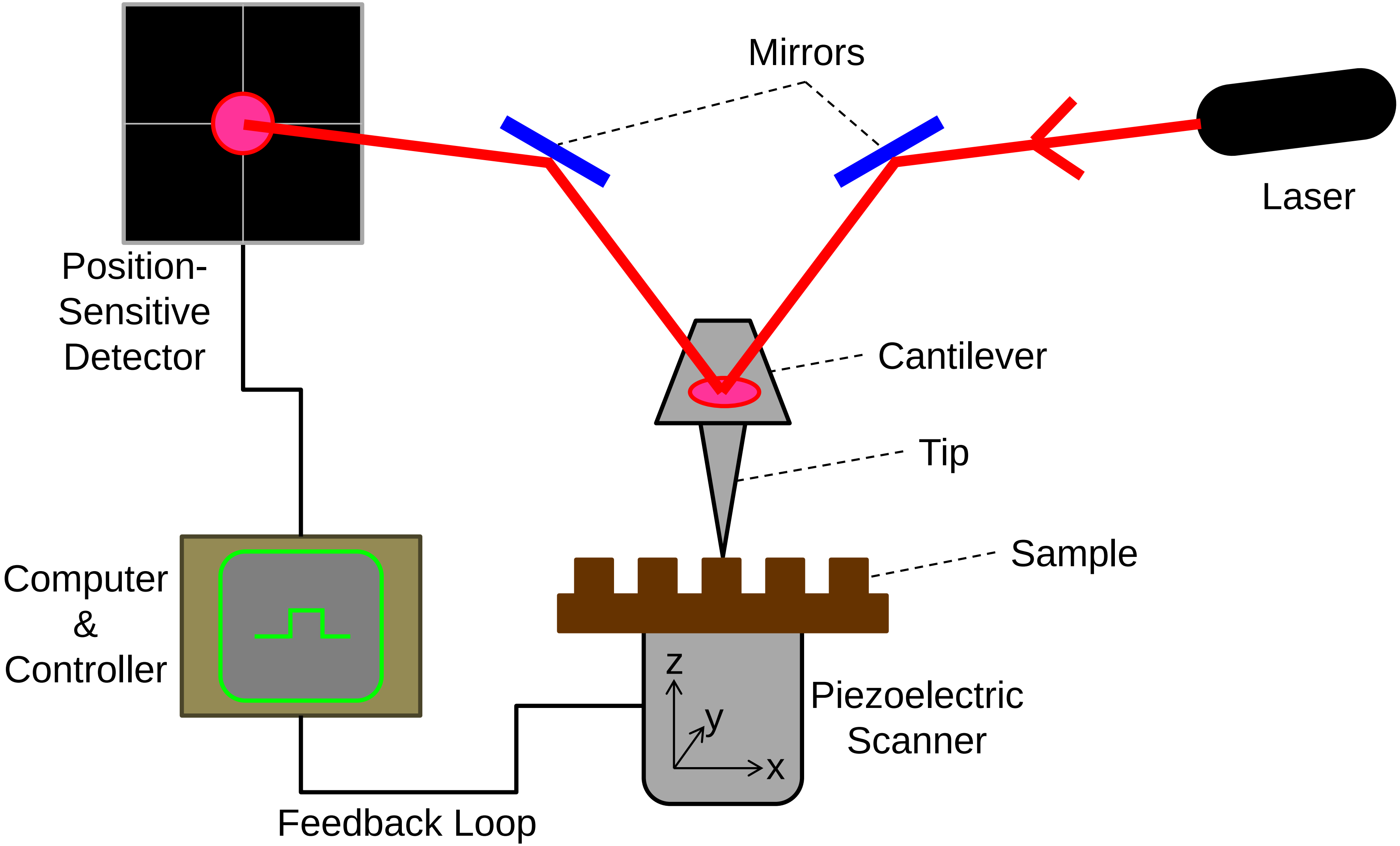
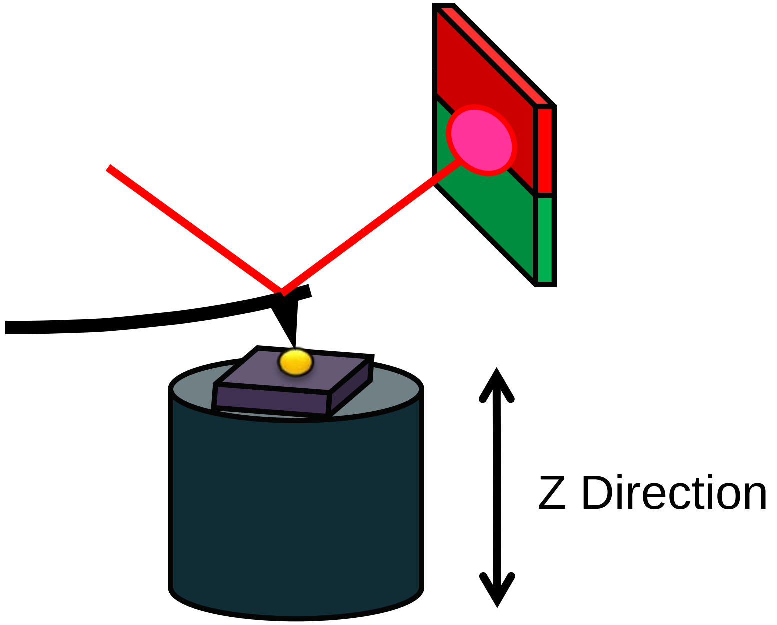
Principle of Operation



Principle of Operation

In its most basic mode of operation, AFM measures the surface by monitoring the deflection of the cantilever in the ***Z direction***. Detection is done by measuring the signal produced by a segmented photo-detector.

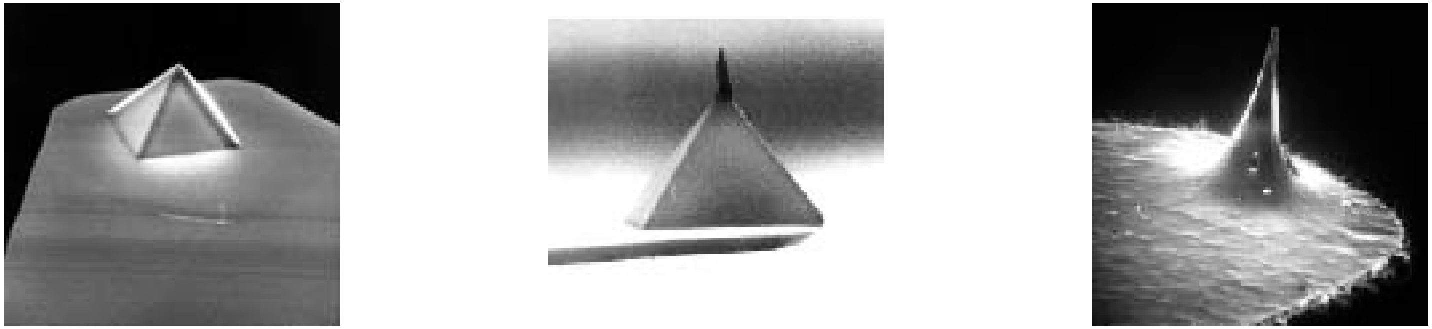


Hardware and Components

1. Sharpened tip on a cantilever.
2. A way of monitoring the deflection of the tip/cantilever (e.g., laser beam & detector).
3. Piezoelectric positioning and scanning system.
4. Computer-controlled feedback loop.

AFM Tip Technology

- Micro machining techniques can produce inexpensive, reasonably sharp tips.
- The photos below show three common tip configurations.
- All AFM tips have a finite radius. This “end radius” generally determines the resolution of the AFM.



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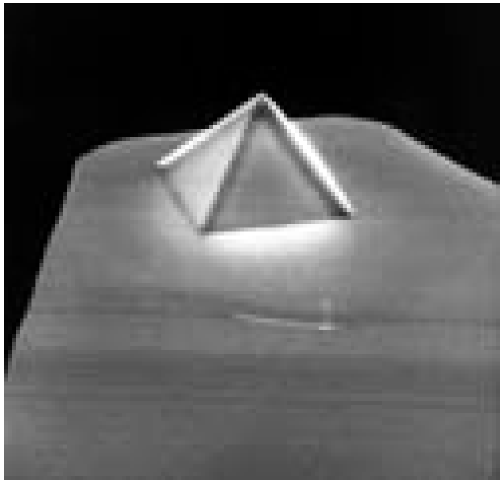
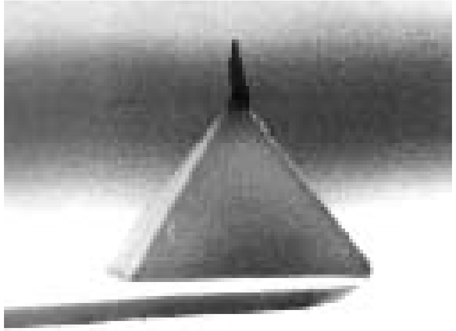
AFM Tip Technology

- The “standard” tip is about 3 um tall pyramid with a 30 nm end radius
- The electron-beam-deposited tip (EBD) is an improvement. An e-beam deposits carbonaceous material to effectively sharpen the radius.





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AFM Tip Technology

- The “ultralever” is manufactured using improved microlithography techniques. It offers high aspect ratio, and a nominal 10 nm end radius.

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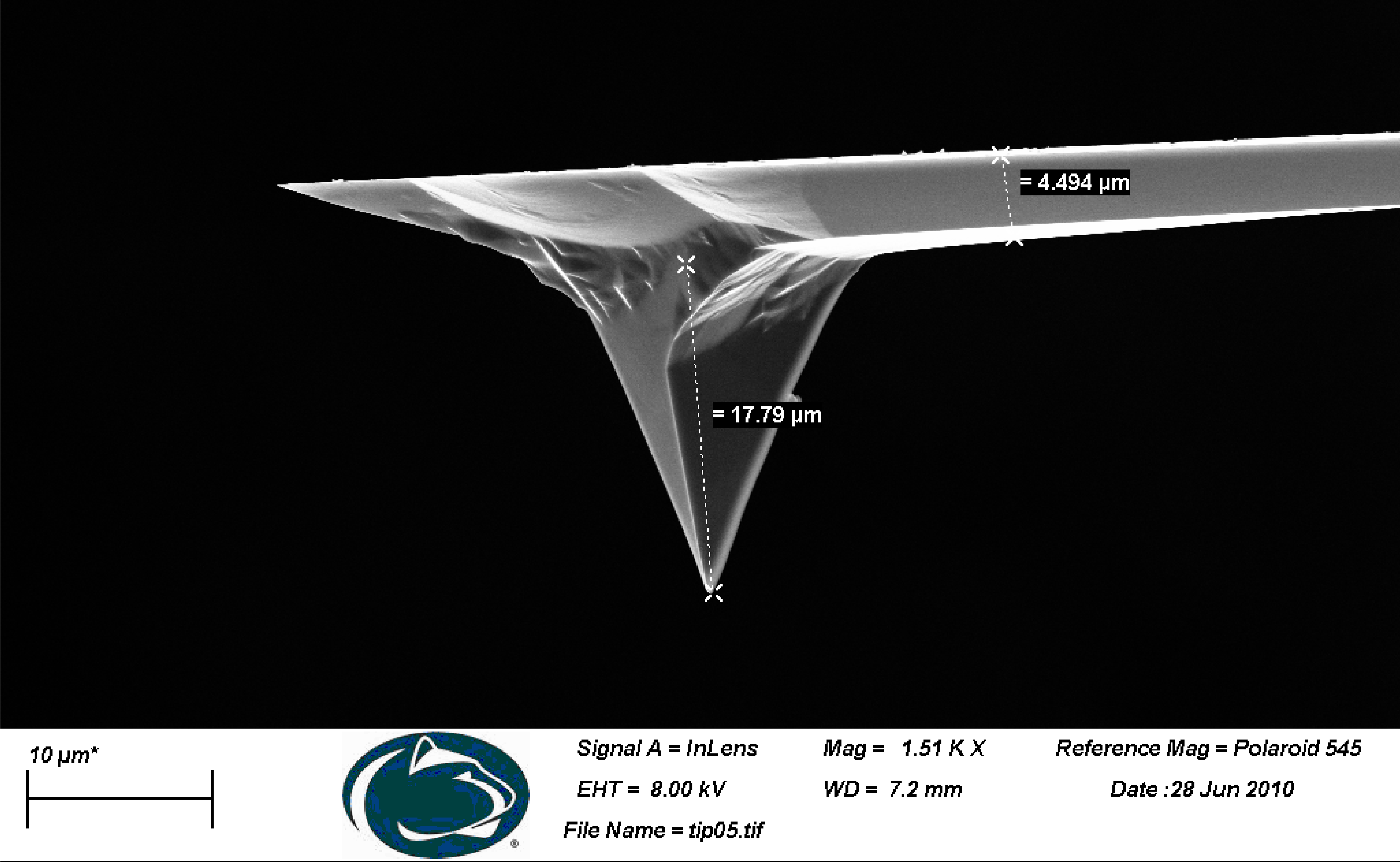
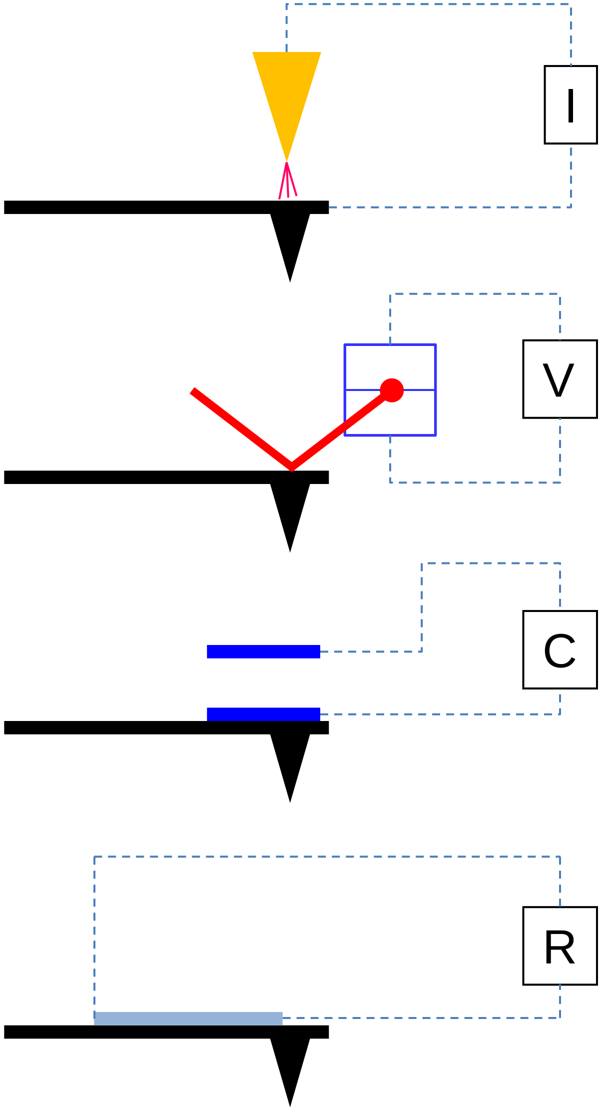
FESEM image of a typical tip/cantilever.



Signal A = InLens
EHT = 8.00 kV
File Name = tip05.tif
Mag = 1.51 K X
WD = 7.2 mm
Reference Mag = Polaroid 545
Date :28 Jun 2010

Detecting Cantilever Deflection



STM

Tunneling Current
Phys. Rev. Lett. 1986, 56(9), 930.

Optical Lever
(Beam Bounce)

Voltage from Photodiodes
Appl. Phys. Lett. 1988, 53(12), 1045.

Capacitance

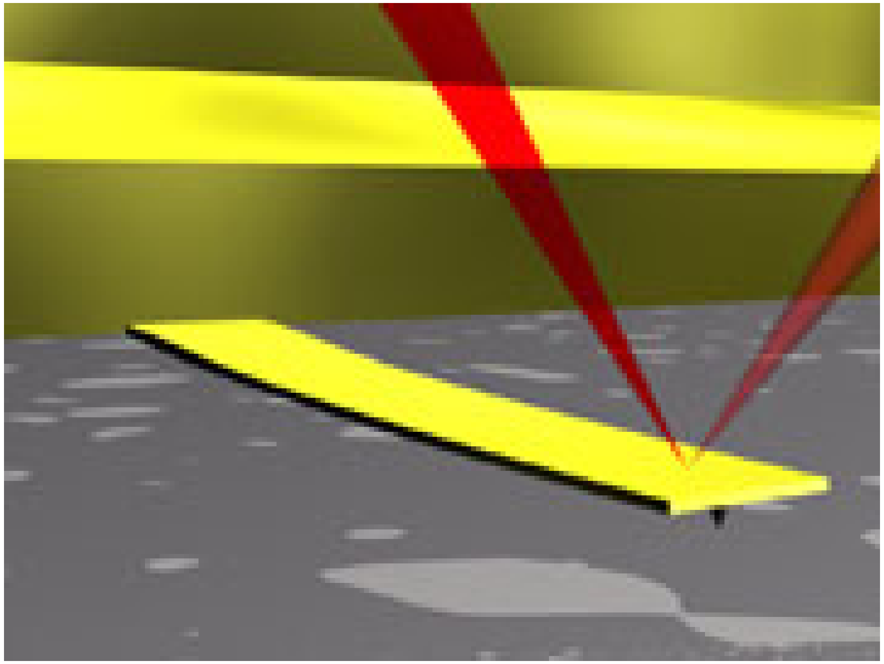
Change in Capacitance
J. Vac. Sci. Technol. A 1990, 8(1), 383.

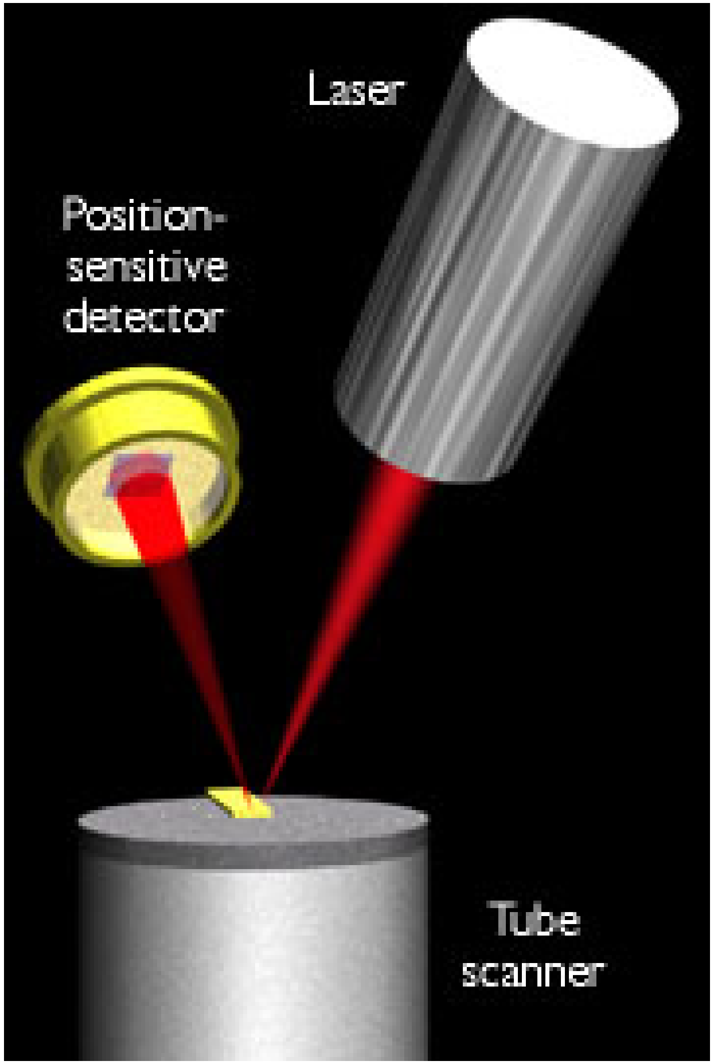
Piezoresistance

Change in Resistance
Appl. Phys. Lett. 1993, 62(8), 834.

AFM Optical Lever

Data from the detector is used to maintain or control tip-sample interactions.





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AFM Optical Lever

- The optical lever magnifies motions of the tip.
- The cantilever–detector distance is thousands of times the magnitude of the cantilever deflection.
- This magnification can approach 2000x, and the optical lever can theoretically obtain very low noise levels.
- This technique is inexpensive and accurate compared to other methods of measuring samples on the nanoscale.

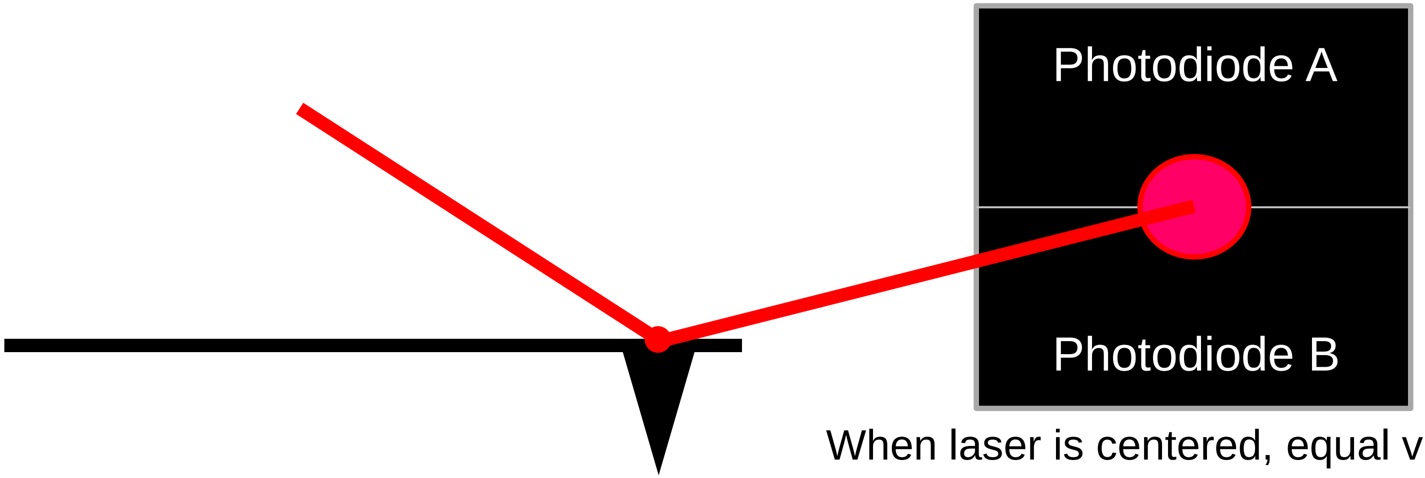
Photodiode Detector

Photodiode: A device that converts incident light into current or voltage.

The incident light comes from the laser beam reflecting off the cantilever.

The detector contains multiple (2 – 4) photodiodes.

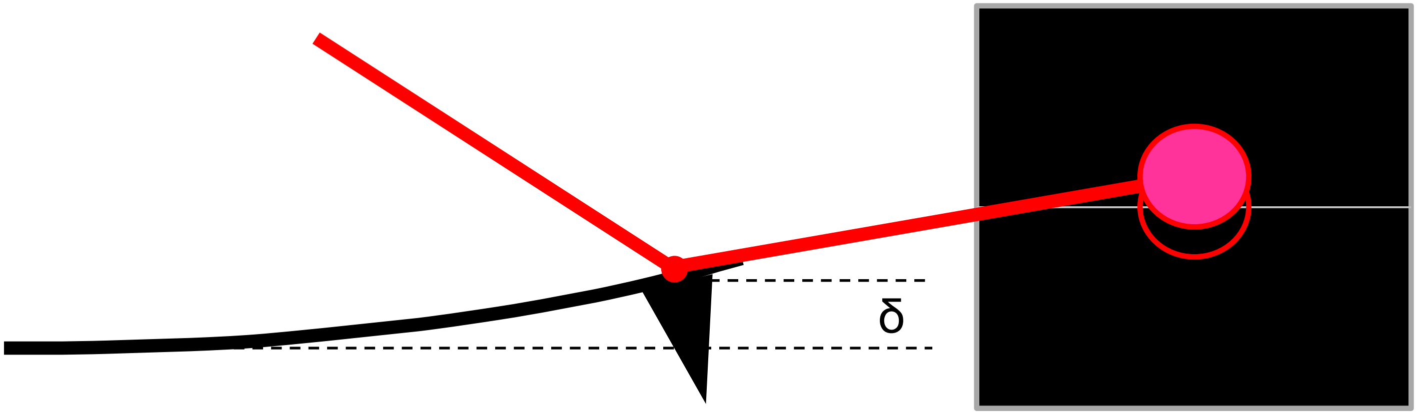
Comparison of the signals from the photodiodes creates a position-sensitive signal that measures the deflection (δ) of the cantilever.



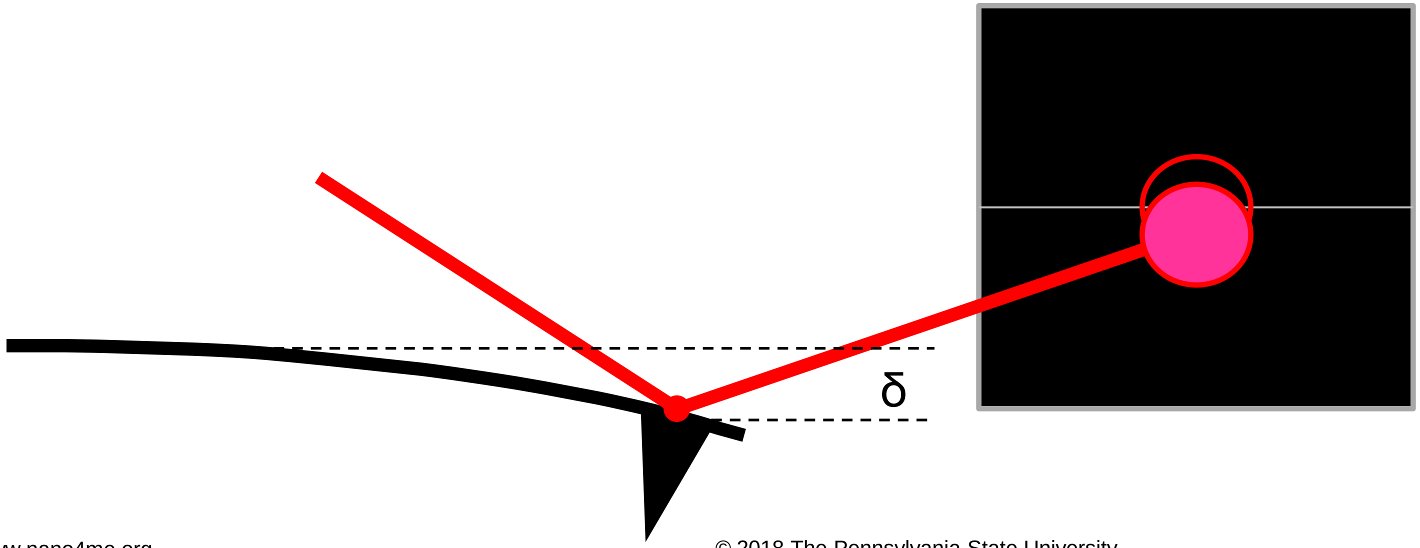
When laser is centered, equal voltages from top (A) and bottom (B) photodiodes.

A – B = 0

Photodiode Detector



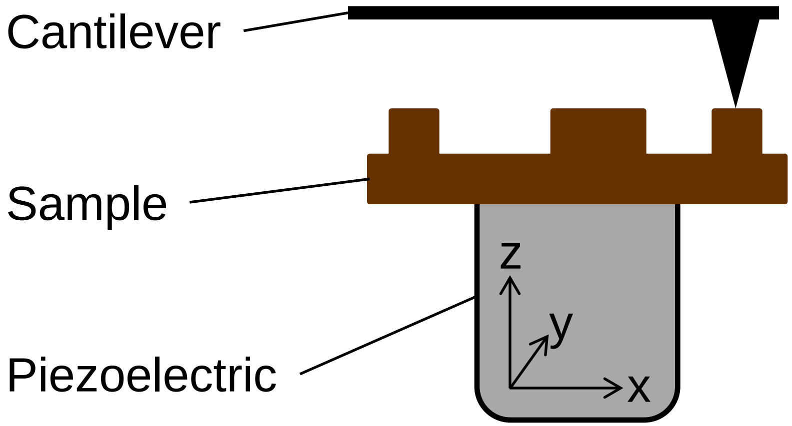
A – B = (+)



A – B = (-)

Piezoelectric Scanner

Piezoelectric Material: A material that changes shape in the presence of an electric field (Voltage).



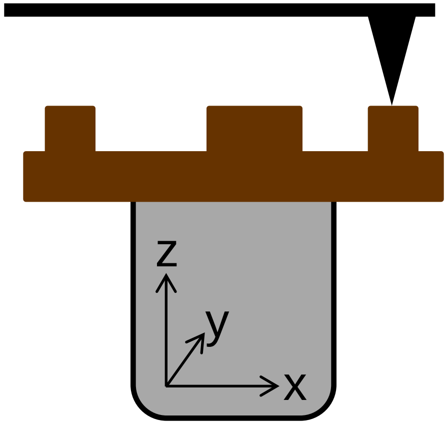
High electric fields produce only small changes in the size of the material (microns or less).

Since applied voltages can be controlled, this effect can be used to precisely position the sample.

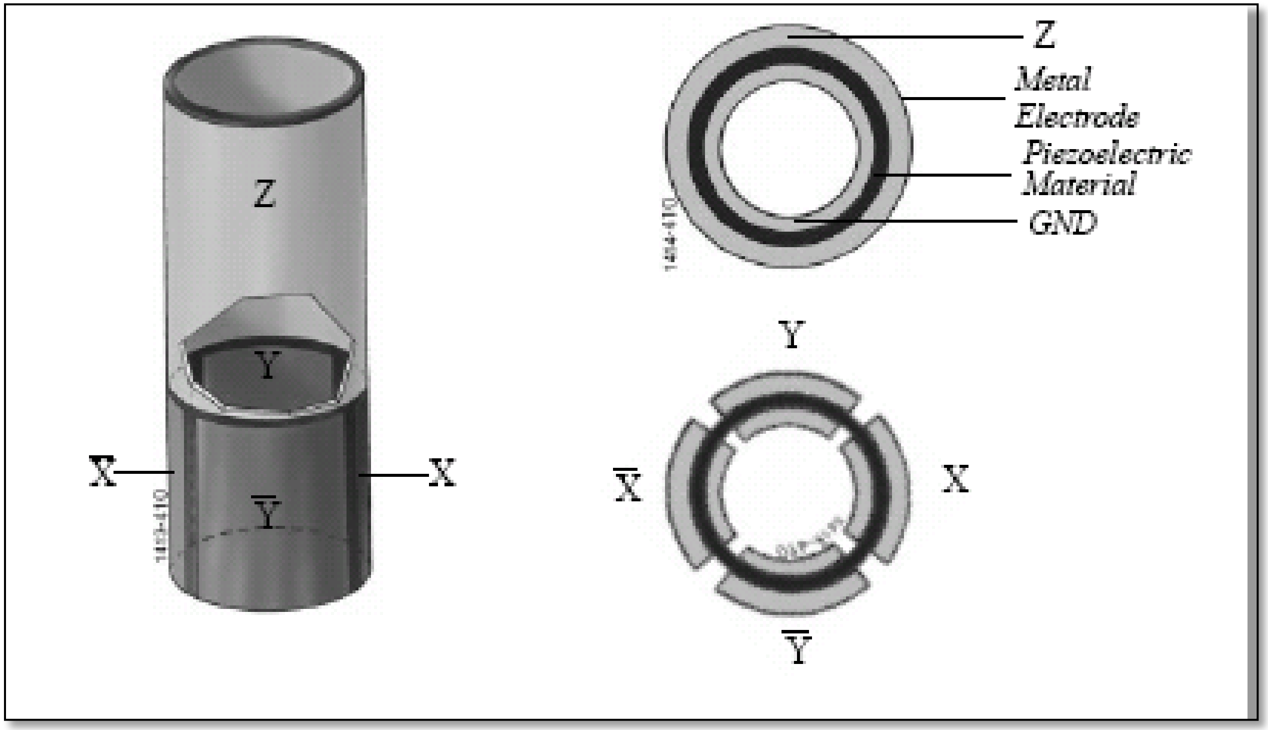
Piezoelectric Scanner

The tube-shaped scanner allows for movement in all three directions (x,y,z).

Metal electrodes on the tube of piezoelectric material allow for voltages to be applied.



Piezoelectric
Tube Scanner



Positioning the Sample

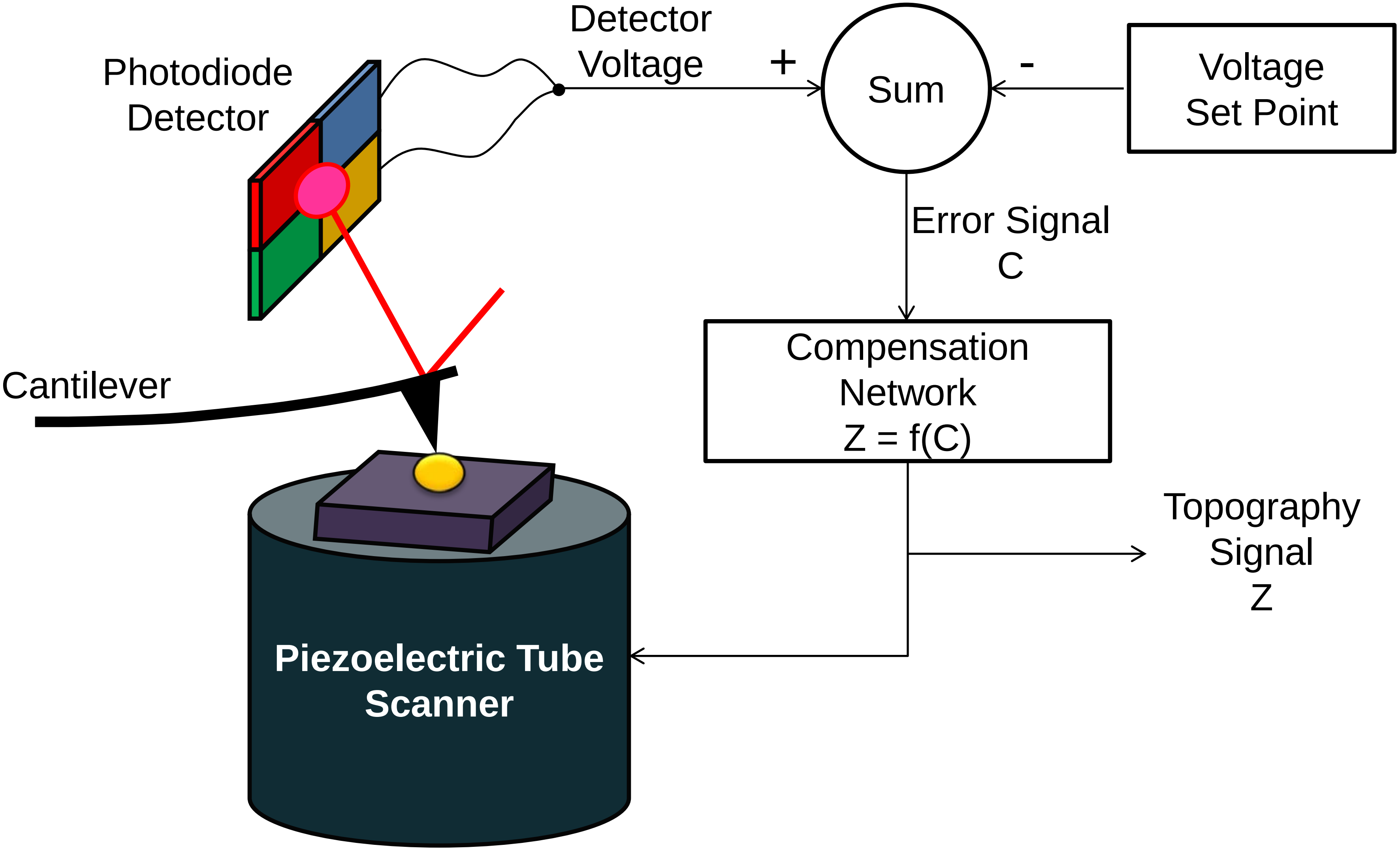
- An active platform is used to control the position of the sample, this is a distinct improvement compared to profilometers.
- The active platform is known as a tube scanner. It is made of a piezoelectric material that expands or contracts according to applied voltages.
- 4 outer electrodes control XY motion, while an inner electrode controls the height (Z).
- A compensation network (feedback loop) monitors the cantilever deflection and keeps it constant by adjusting the height of the sample or cantilever.

Positioning the Sample

This system can be analyzed in three areas.

1. Tube scanner controls the height of the sample.
2. The cantilever and optical lever measure the height of the sample.
3. A feedback loop keeps the cantilever deflection constant by adjusting the applied voltages to the scanner.

Feedback Loop



Photodiode Detector

Detector Voltage

+

Sum

-

Voltage Set Point

Error Signal C

Cantilever

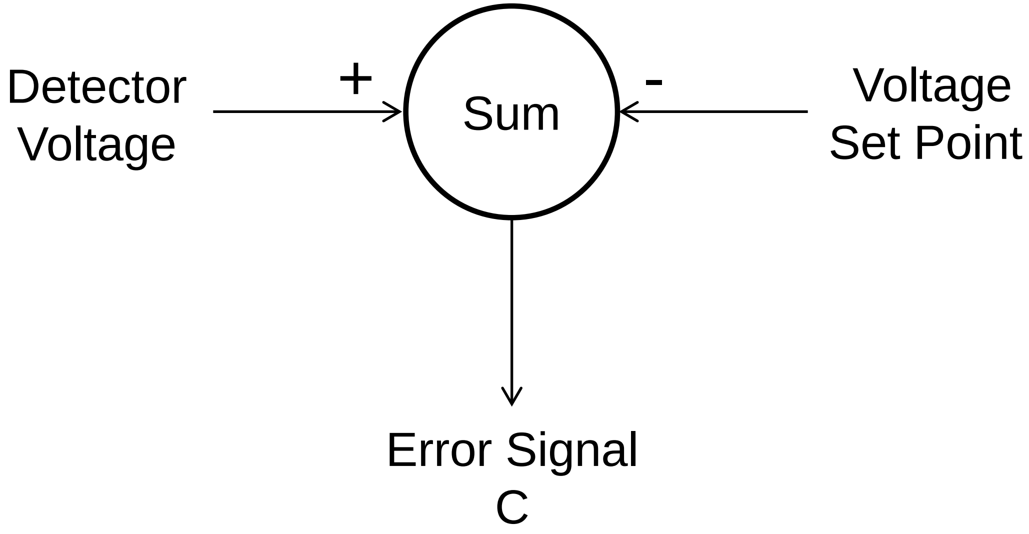
Compensation Network

Z = f(C)

Topography Signal Z

Piezoelectric Tube Scanner

Feedback Loop



Detector Voltage

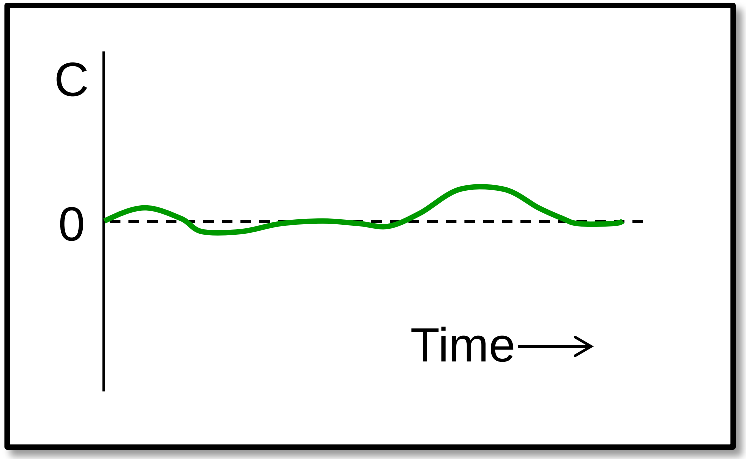
+

Sum

-

Voltage Set Point

Error Signal
C



If Detector Voltage = Voltage Set Point, then Error Signal is zero.
→ No action is required by the control system.

If Detector Voltage ≠ Voltage Set Point, then Error Signal is not zero.
→ Control system must respond to bring the Error Signal back to zero.

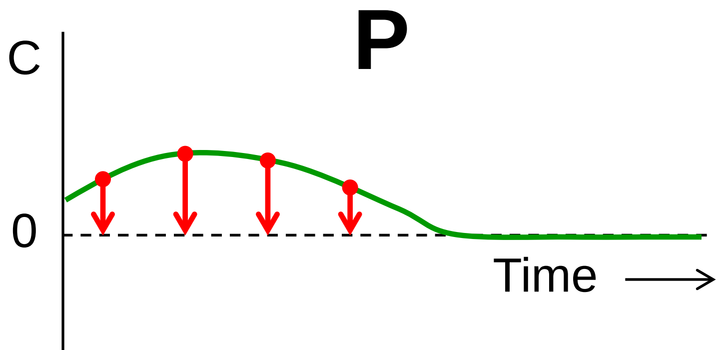
Feedback Loop: PID Control

Three components to control system:

- P - Proportional: Reacts to current value of error signal
- I - Integral: Reacts to sum of recent errors
- D - Derivative: Reacts to instantaneous rate of change of the error signal

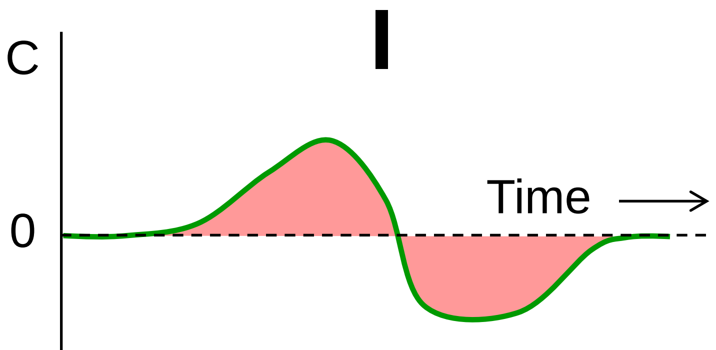
How would each of these components respond in real time?

Feedback Loop: PID Control



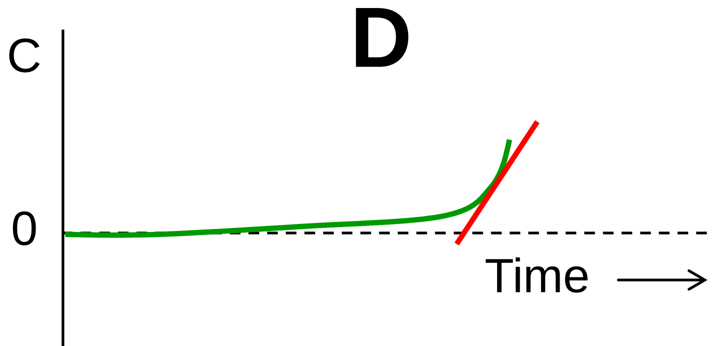
P

Depends on instantaneous value of error signal



I

Depends on history of error signal



D

Depends on rate of change of error signal

Each type of control addresses a unique aspect of the system response.

Tuning of the PID parameters is usually required to achieve robust control.

Tuning the Feedback Loop

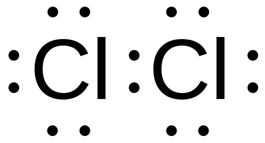
- Start with P = 1.00 and I = D = 0.00
- Increase P until <u>overshoot</u> begins to occur
- Then decrease P to just below maximum stable value (with no overshoot)
- Increase I and determine effect.
- Rule of Thumb: I = 0.3 x P
- D generally not needed. Keep D = 0.00

Outline

- Overview of Scanning Probe Techniques
- Scanning Tunneling Microscopy
- Atomic Force Microscopy
  - Hardware and Components
  - Tip/Sample Interactions
  - Common Modes of Operation
  - Pitfalls and Image Artifacts
- Example of Instrument Operation

Bonding and Forces Revisited

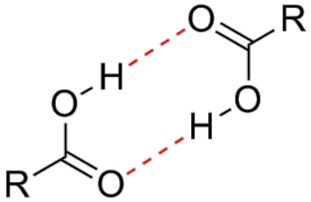
- Covalent Bonds



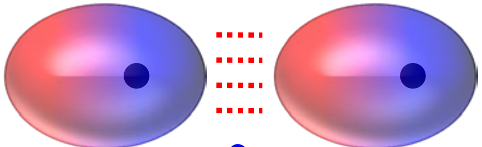
- Ionic (electrostatic)

$$F = \frac{Z_- Z_+ e^2}{r^2}$$

- Hydrogen Bonding

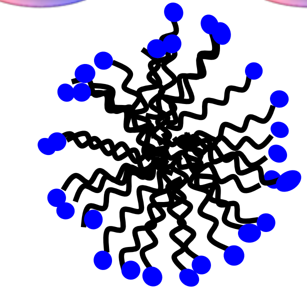


- van der Waals Forces



$$F \propto \frac{1}{r^6}$$

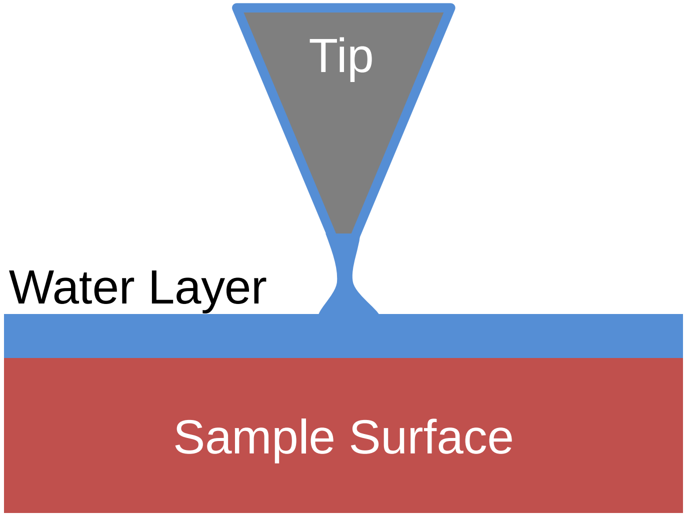
- Hydrophobic Interactions



Tip-Sample Interactions

Tip and sample may experience many possible forces and interactions. Each force acts over a characteristic length scale. Some are attractive, some are repulsive.

- Long-range electrostatic (up to 100 nm)
- Short range electrostatic
- Short-range polarization
- Dispersion forces (few nm)
- van der Waals forces
- Pauli repulsion (electrons)
- Capillary forces



Tip-Sample Interactions

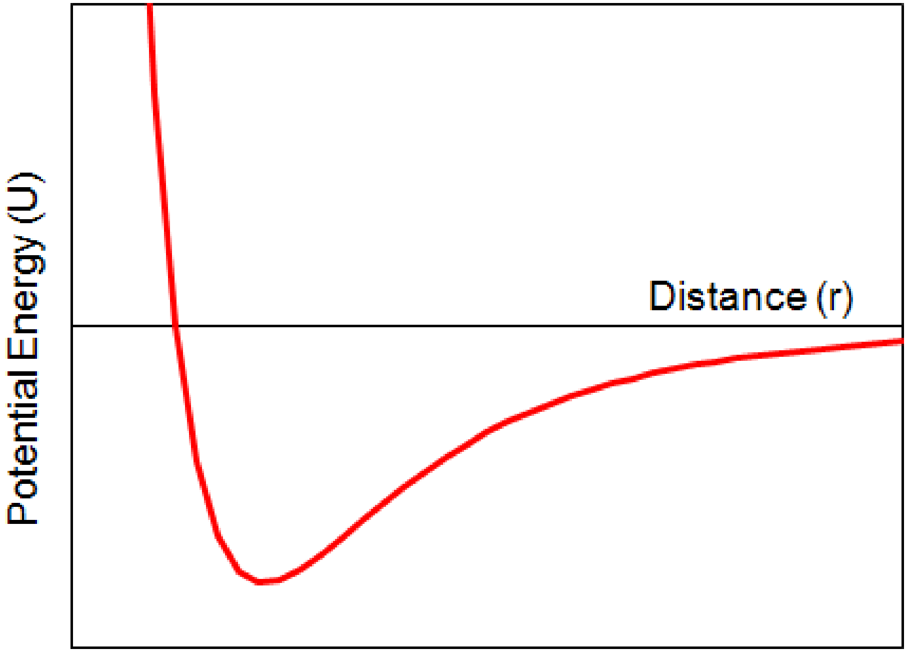
In addition to being a type of microscope, AFM can be used to measure the forces acting between the tip and the sample surface.

This data is useful because it can be related to surface energy of the sample.

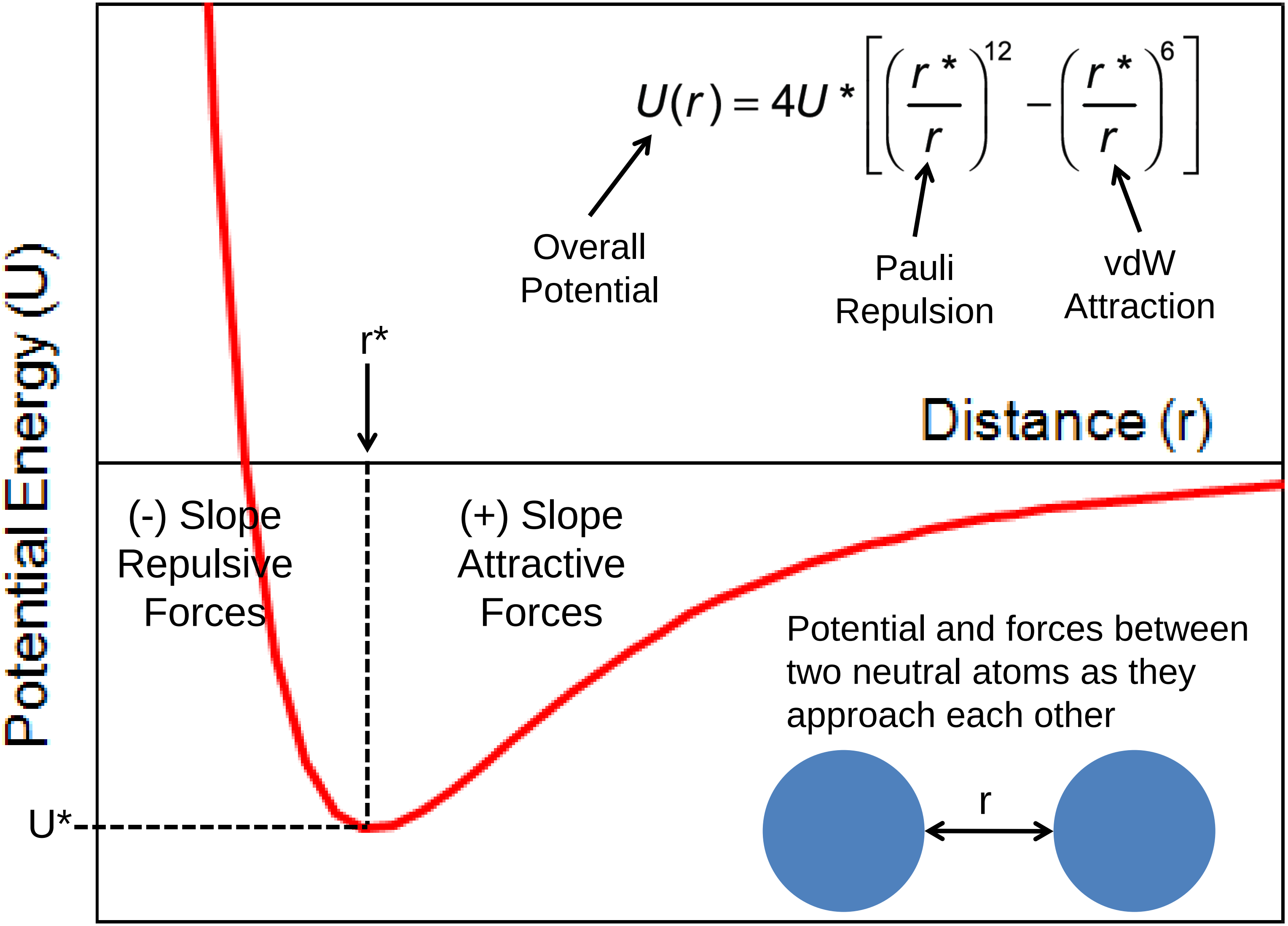
There are many theoretical approaches to modeling tip-sample interactions. Each model treats interactions in a slightly different way.

Results depend heavily on the geometry of the tip and the types of forces considered.

The Lennard-Jones potential is a simple model that combines dispersion (attractive vdW force) and Pauli repulsion (repulsion at very short distances due to overlapping electron clouds).



Lennard-Jones Potential



$$U(r) = 4U^* \left[\left(\frac{r^*}{r} \right)^{12} - \left(\frac{r^*}{r} \right)^{6} \right]$$

Potential and forces between two neutral atoms as they approach each other

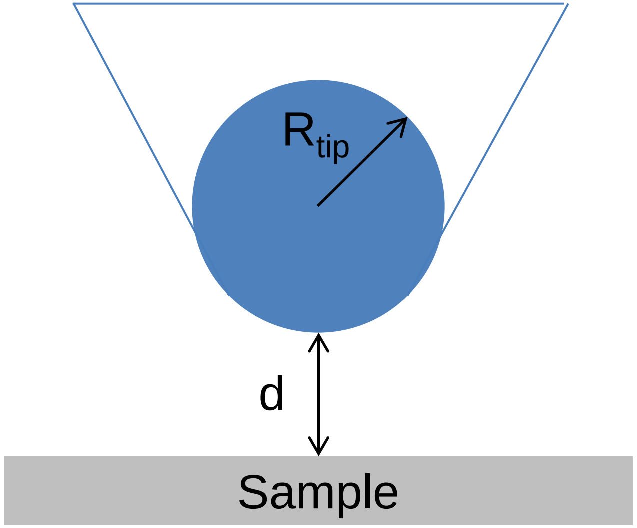
Tip-Sample Interactions

The simple Lennard-Jones potential on the previous slide considers what happens when two neutral atoms approach one another.

Actual tips and samples are comprised of many atoms arranged in a specific (unknown) geometry.

Often, the problem is simplified to a planar sample being approached by a spherical tip.

When the interactions between all atoms are considered, the potential varies as 1/d and the force varies with $1/d^2$.



$$U_{vdW} = \frac{-HR_{tip}}{6d}$$

Tip-Sample Interactions

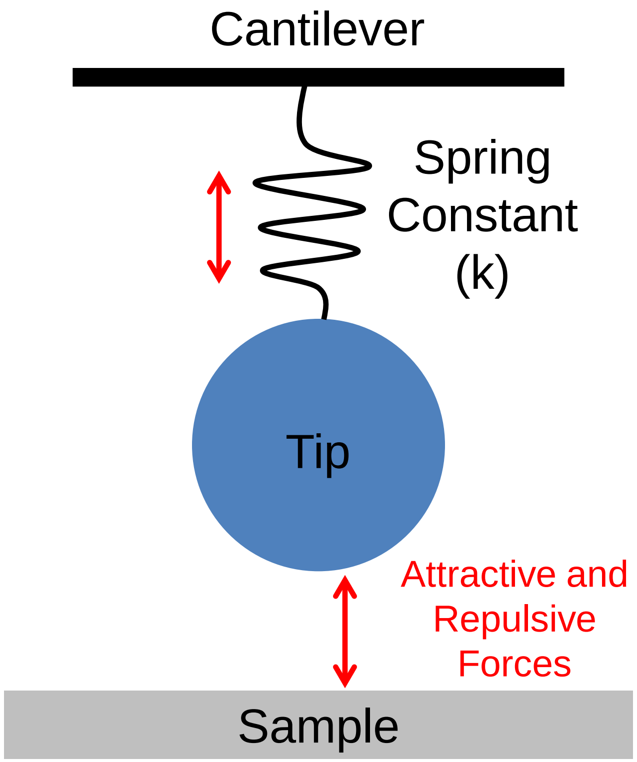
The tip is mounted at the end of a cantilever.

The cantilever is flexible and behaves like a spring.

As the tip approaches the surface, it will experience forces due to tip-sample interactions.

The spring-like action of the cantilever also acts on the tip.

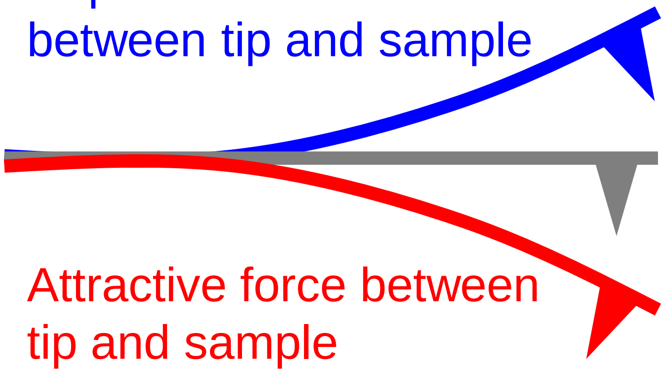
A force balance can be set up that models all forces acting on the tip as it approaches the sample.



Tip-Sample Interactions

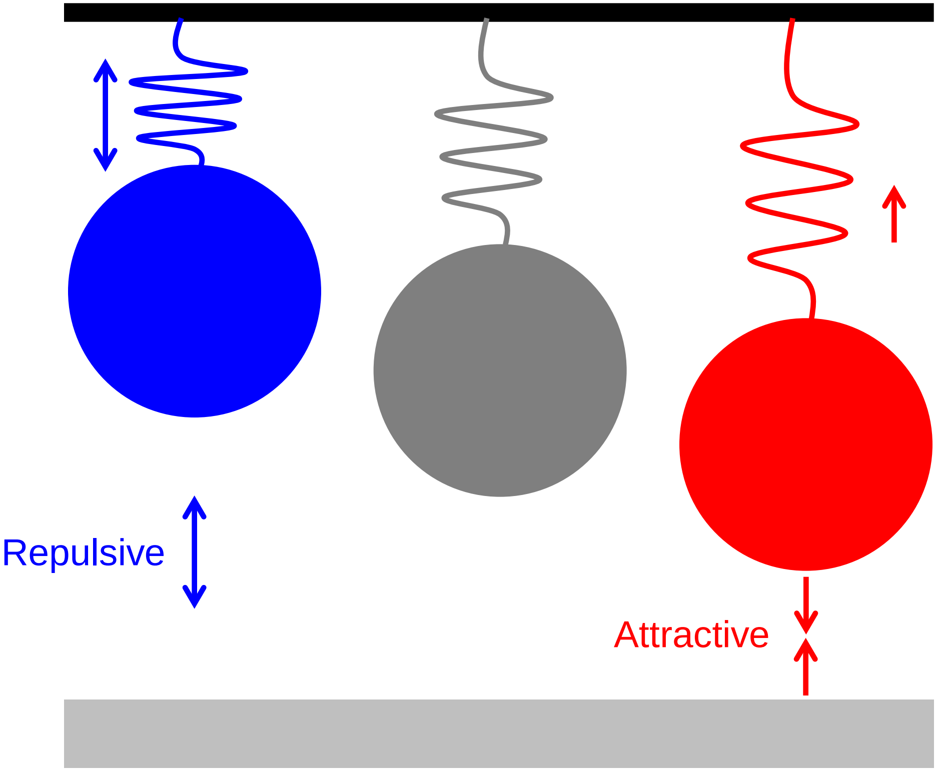
Examples of
Cantilever Deflection

<u>Note</u>: If the tip is not moving,
the forces must be balanced.



Repulsive force
between tip and sample

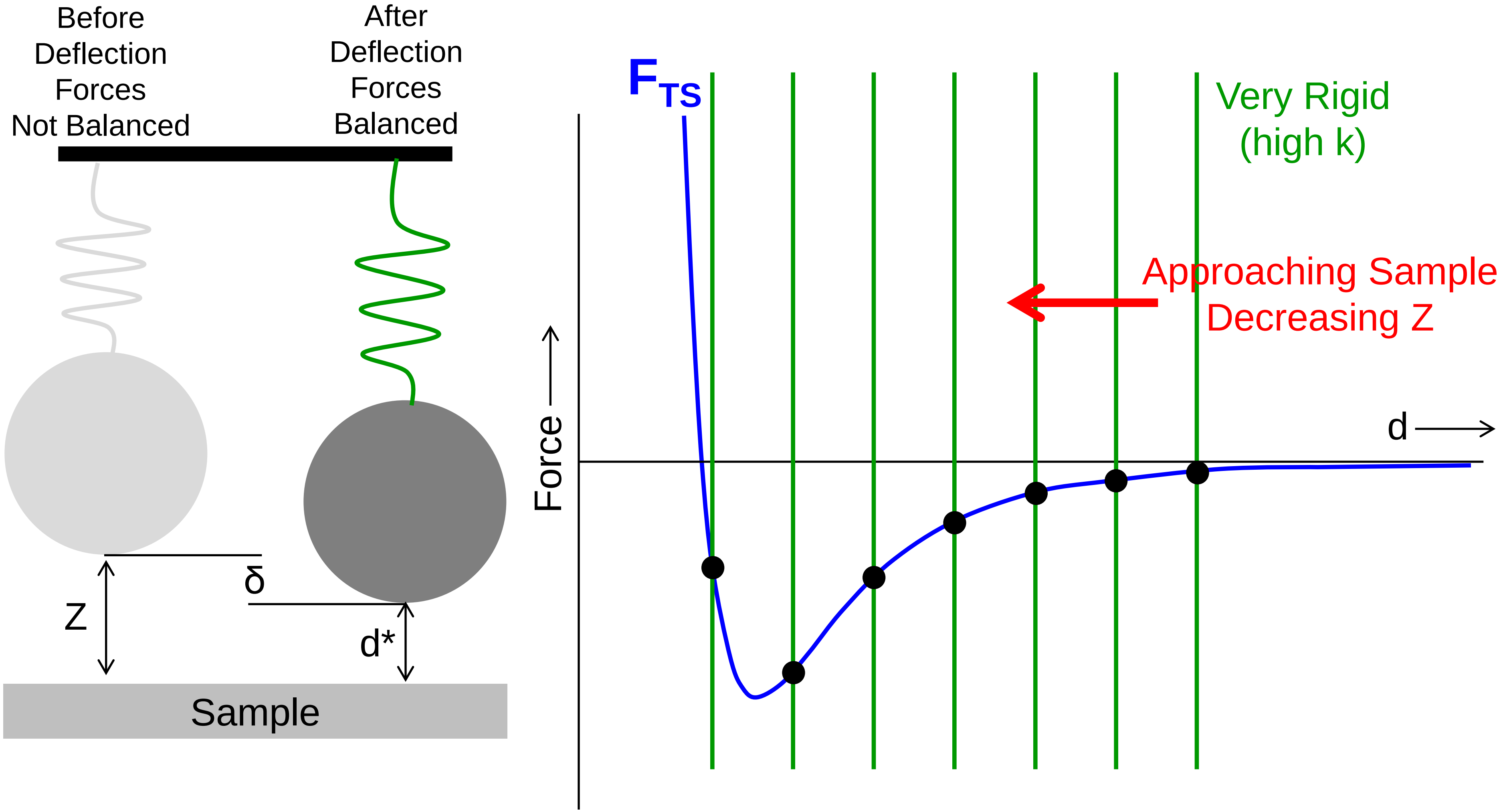
Attractive force between
tip and sample



Repulsive

Attractive

Cantilever Spring Constant

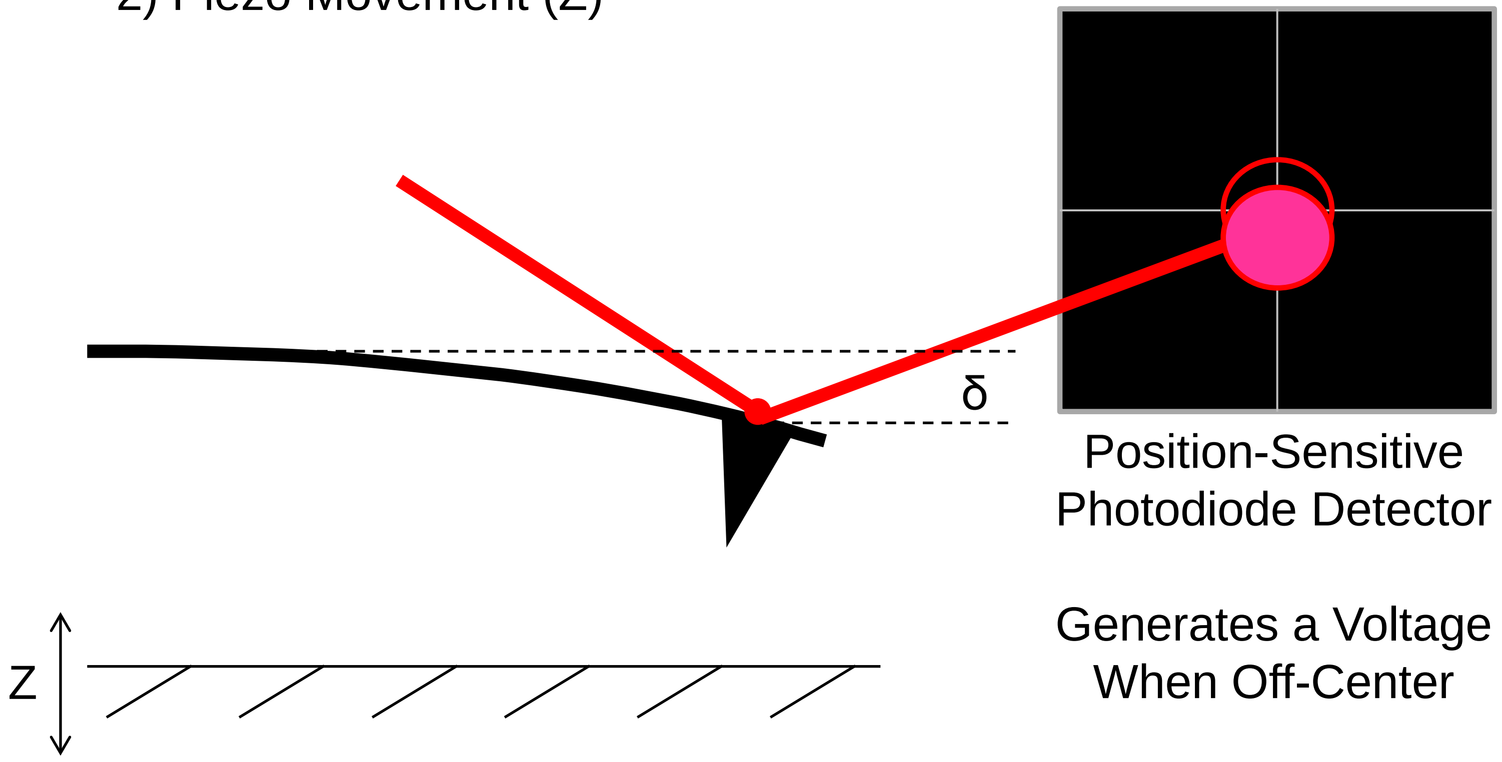


Cantilever is so rigid that the tip does not snap onto the surface. All d’s are accessible.

AFM Signals and Measurements

What signals or variables are measured by the AFM instrument?

1) Cantilever Deflection (δ)
2) Piezo Movement (Z)



Position-Sensitive Photodiode Detector

Generates a Voltage When Off-Center

What do these signals look like as the tip approaches the sample surface?

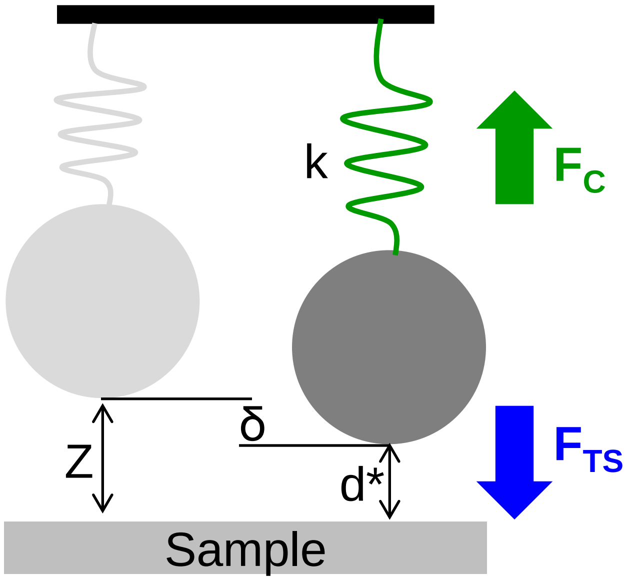
Force-Distance Curves

The data collected as the tip approaches, contacts, and retracts from the surface can be used to construct Force-Distance curves.

The collected data is a series of (Z, δ) data points.

These curves give information about the interaction forces between the tip and the surface.

The data points can be converted to (d, F_{TS}) data as follows:



At equilibrium

$$F_{TS} = F_C$$

$$F_{TS} = F_C = k\delta$$

$$d^* = d = \delta + Z$$

Plug each (Z, δ) into these equations to convert to (d, F_{TS}).

This generates a Force-Distance curve.

Principle of Operation