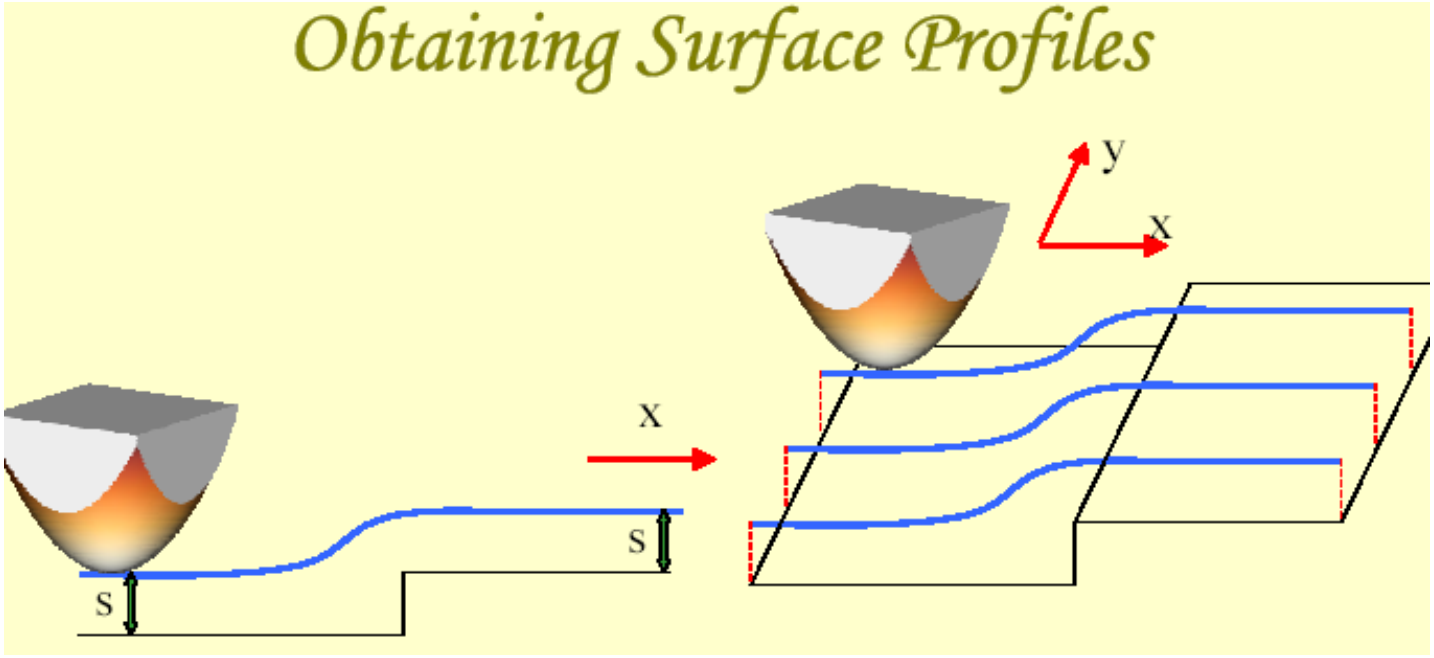
Lecture 4 Scanning Probe Microscopy (SPM)

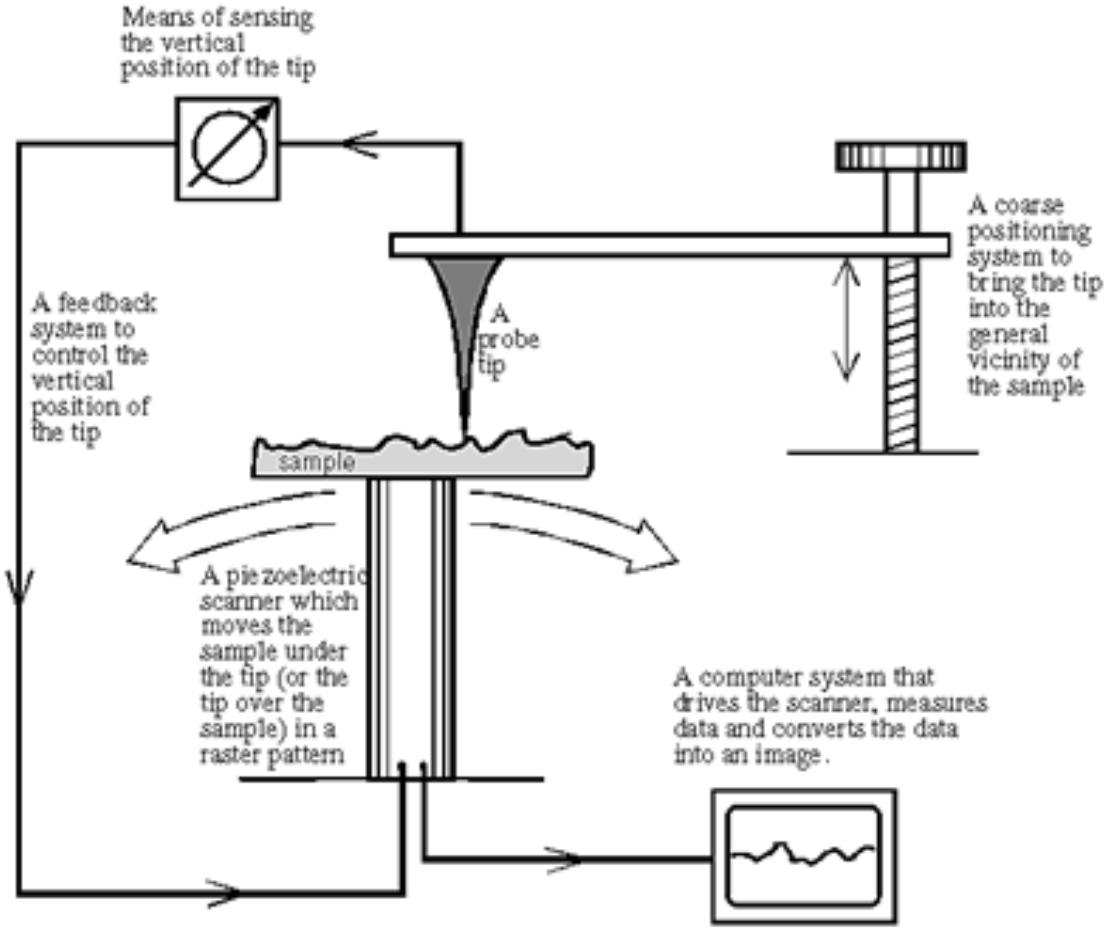
- General components of SPM;
- Tip --- the probe;
- Cantilever --- the indicator of the tip;
- Tip-sample interaction --- the feedback system;
- Scanner --- piezoelectric movement at x,y,z;
- Measurement artifacts: vibration must be isolated.

Generation of SPM image

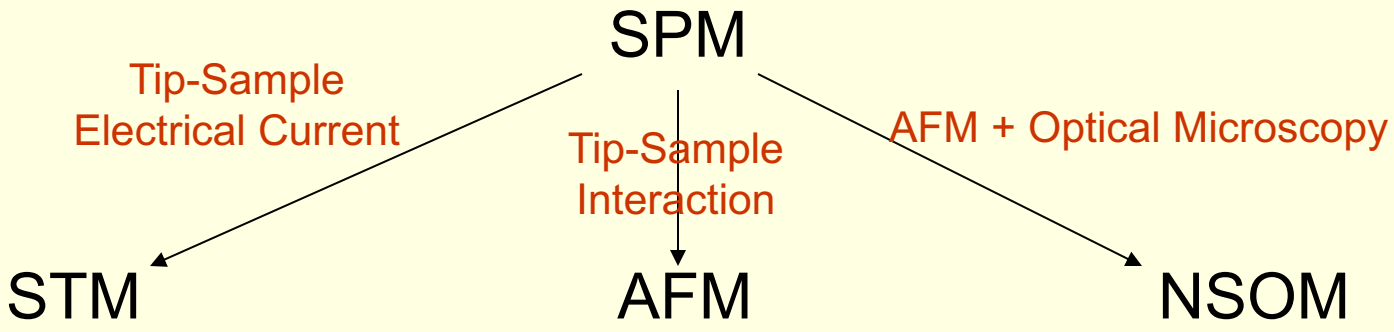
X-Y raster scanning;
Z-modulation (height) by feedback system.



Basic components of SPM: tip, cantilever, sensor for tip positioning, scanner, feedback loop (electronic control)



SPM Family



Extremely high Resolution at UHV.

Mechanic Force:

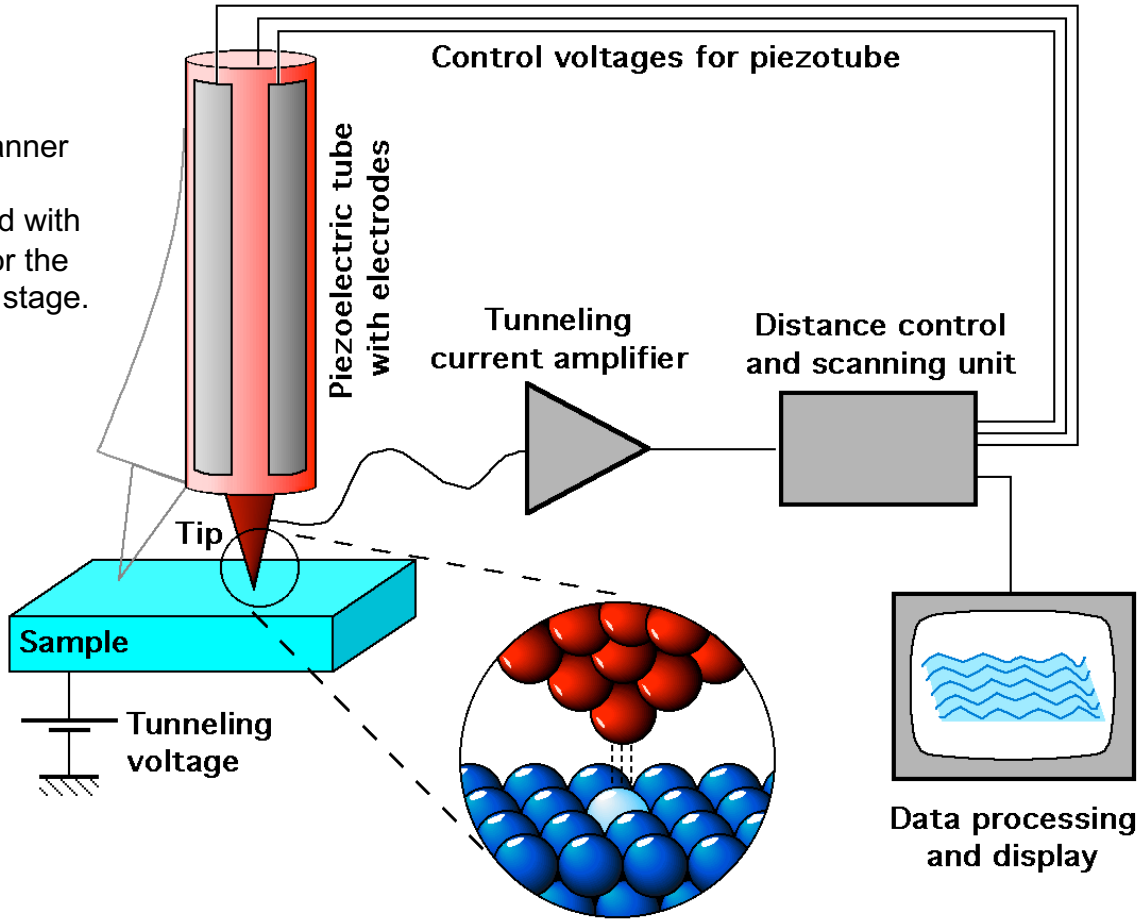
- **Contact mode**
- **Non-contact mode**
- **Tapping (intermittent) mode**

Other Interactions:

- **Electrostatic mode (scanning electrostatic potential microscope)**
- **Magnetic mode**
- **Chemical Force mode**

Basic components of STM:

The scanner can be mounted with the tip or the sample stage.

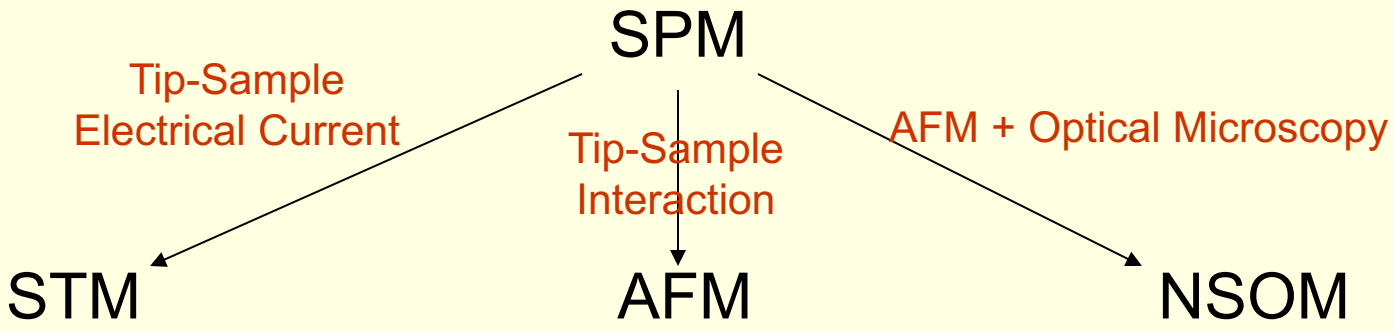


Five basic components:

1. Metal tip,
2. Piezoelectric scanner,
3. Current amplifier (nA),
4. Bipotentiostat (bias),
5. Feedback loop (current).

- Tunneling current from tip to sample or vice-versa depending on bias;
- Current is exponentially dependent on distance;
- Raster scanning gives 2D image;
- Feedback is normally based on constant current, thus measuring the height on surface.

SPM Family



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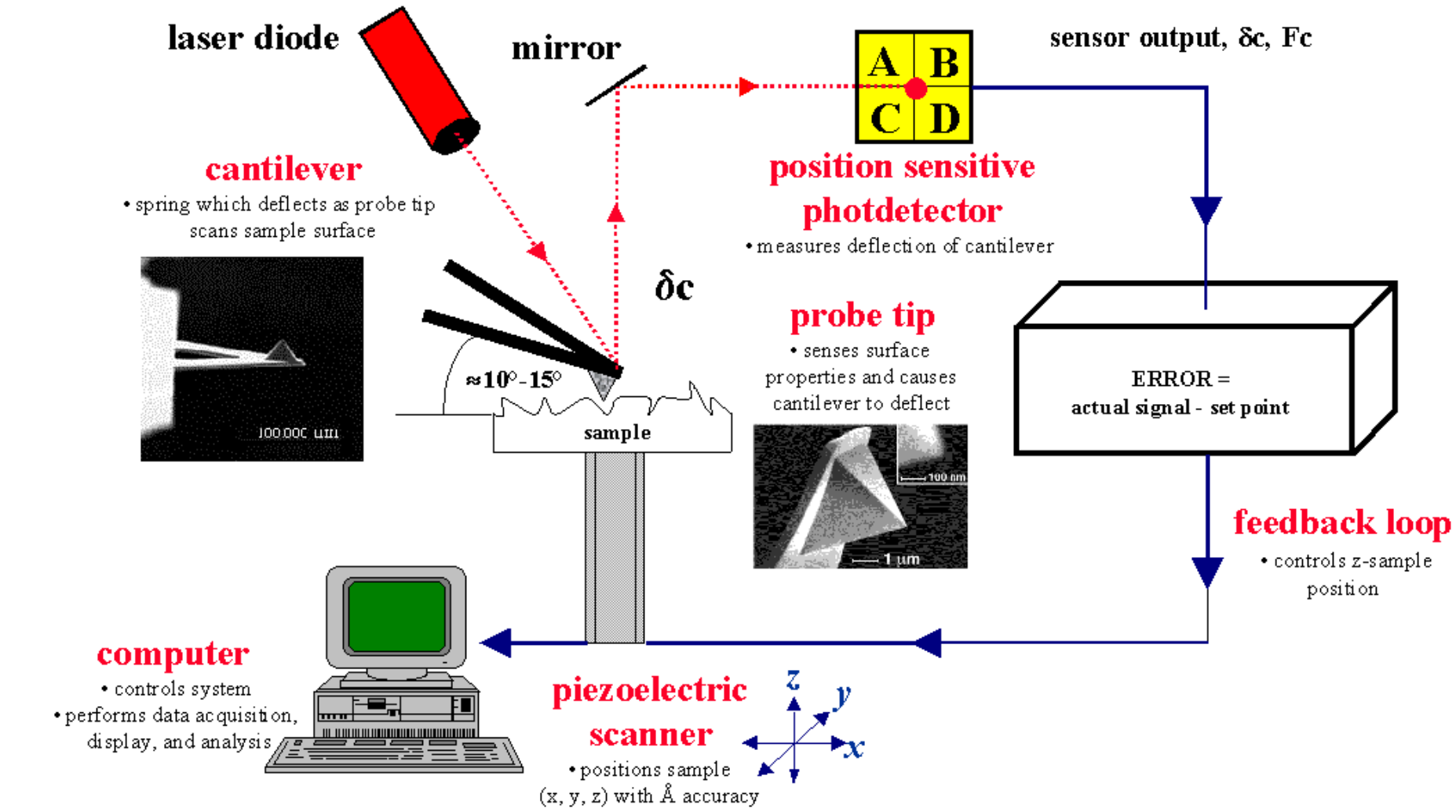
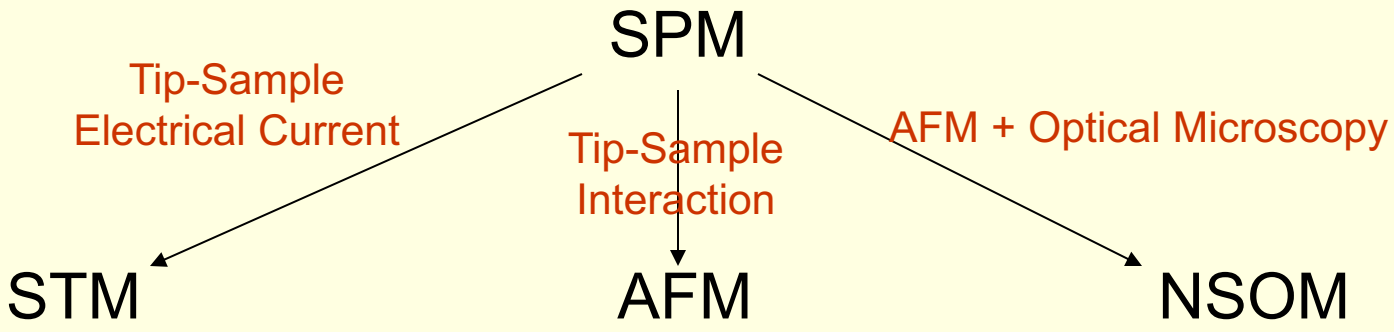
Atomic Force Microscopy (AFM) :

General Components and Their Functions



SPM Family



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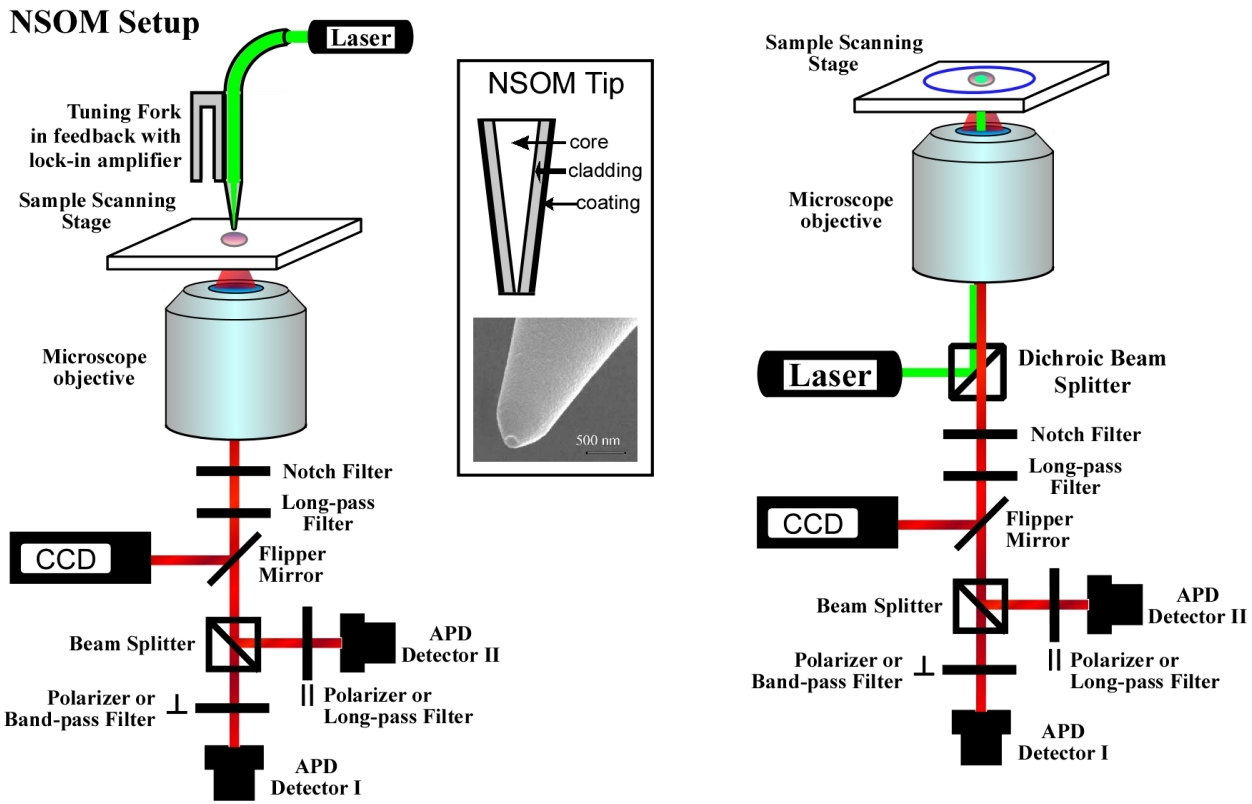
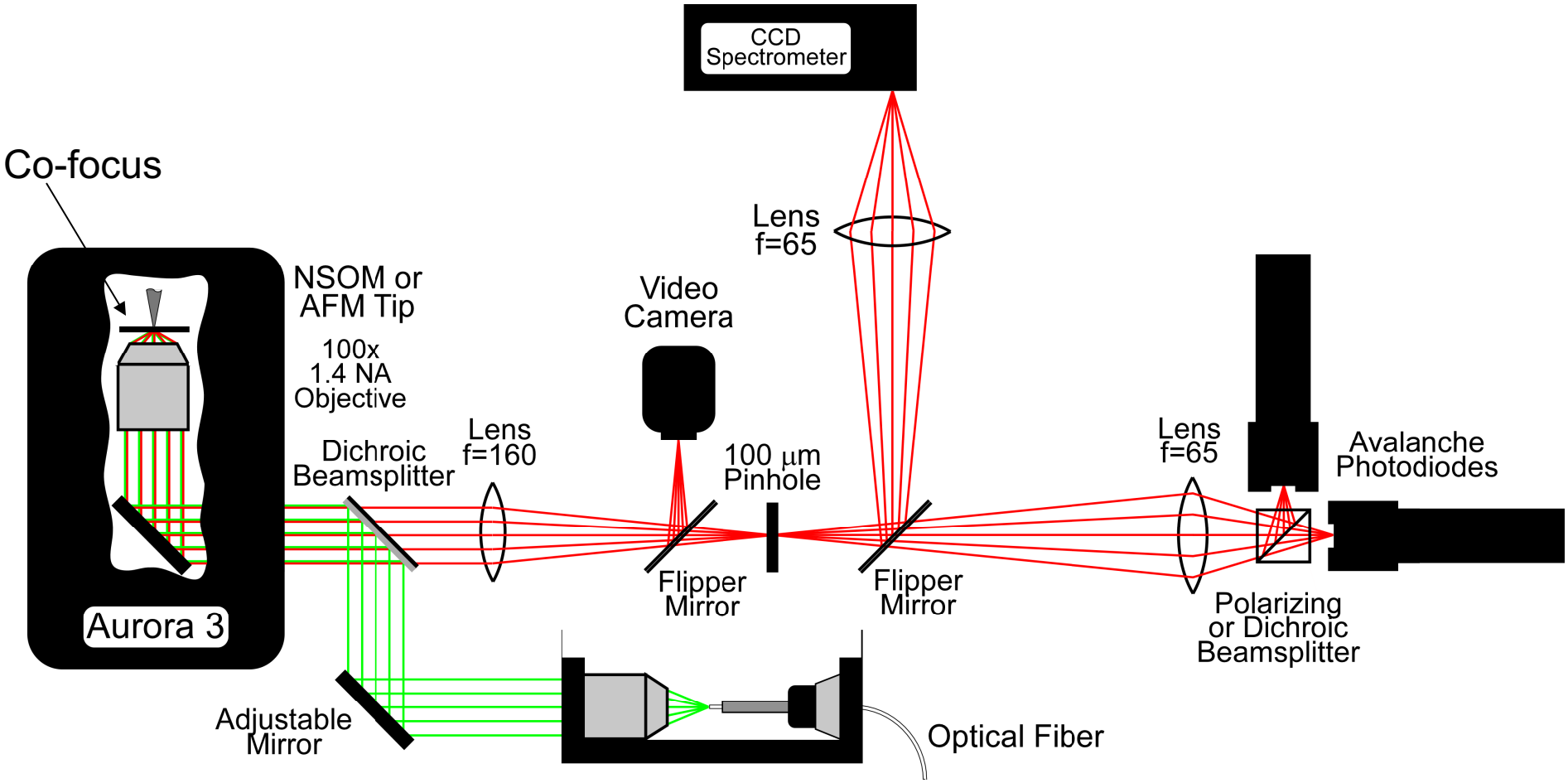
Scanning Confocal Microscopy from NSOM

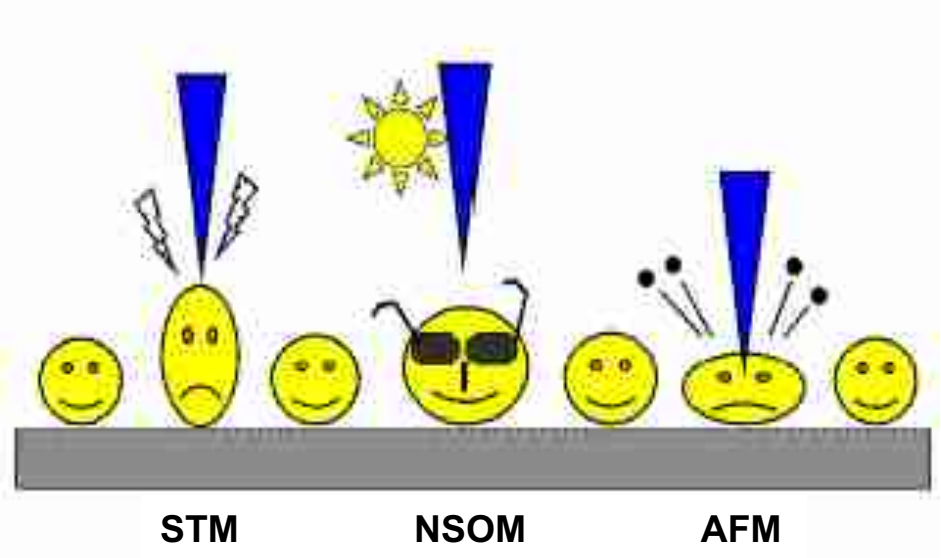


- NSOM can be modified to be a SCM simply by removing the tuning fork head, the tip.
- SCM uses the excitation beam through the same objective.
- Both the excitation and emission shares the same focus on the sample surface.
- Confocal requires high level alignment of optical accessories.

Principle of Scanning Confocal Microscope



Comparison of STM, AFM, NSOM



Comparison of Tips of STM, AFM, NSOM

- STM tip should be conducting, can be simply cut freshly by normal wire cutter.
- STM plays with the very top atom at the freshly cut tip, leading to atomic resolution.
- AFM tip should be sharp enough to get good resolution (fat-tip effect); recently atomically sharp tip obtained by binding a small molecule atop the tip.
- AFM tip should be stiff enough to sense the atomic interaction with sample surface (the distance).
- AFM tip is not necessary to be conducting.
- NSOM tip should be sharp enough to get good topography resolution.
- The aperture of NSOM tip should be small for better optical resolution.
- The outer surface of NSOM tip should be flat to avoid artificial effects from the scanning.

Brief History of Scanning Probe Microscopy (SPM): 1

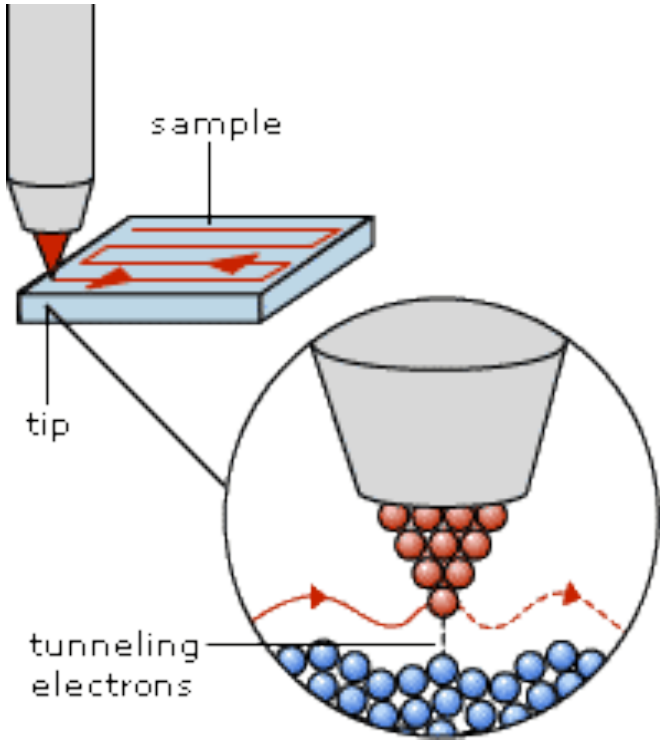
- The first member of SPM family, scanning tunneling microscopy (STM), was developed in 1980s.
- In 1982, Gerd Binnig and Heinrich Rohrer at IBM in Zurich created the ideas of STM (Phys. Rev. Lett., 1982, vol 49, p57). Both of the two people won 1986 Nobel prize in physics for their brilliant invention.

The Nobel Prize in Physics 1986

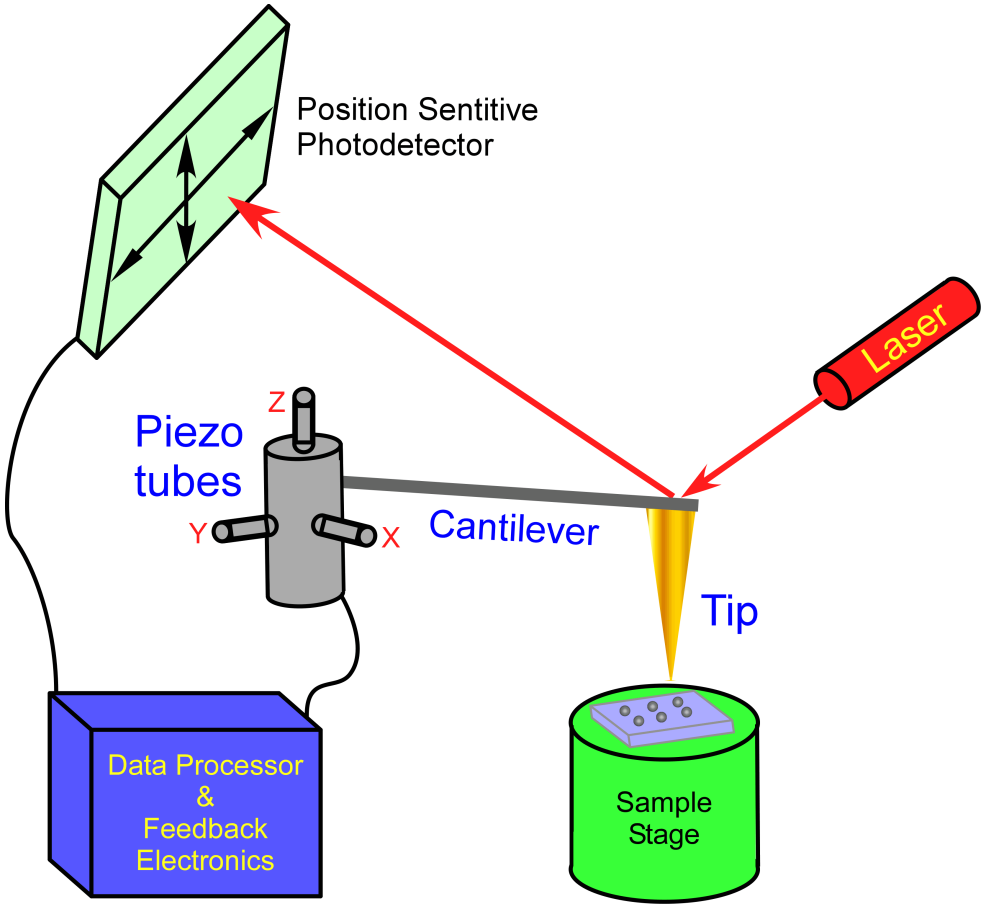
Shared with Ernst Ruska
(on electronic microscopy)

Heinrich Rohrer and Gerd Binnig

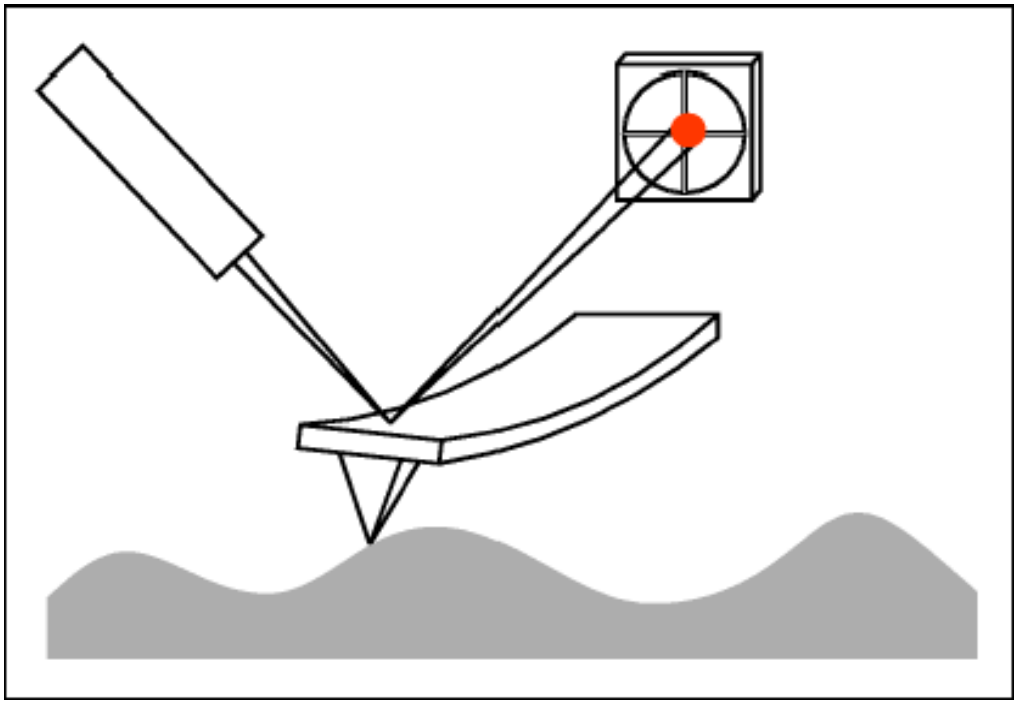
Brief History of Scanning Probe Microscopy (SPM): STM



Brief History of Scanning Probe Microscopy (SPM): AFM



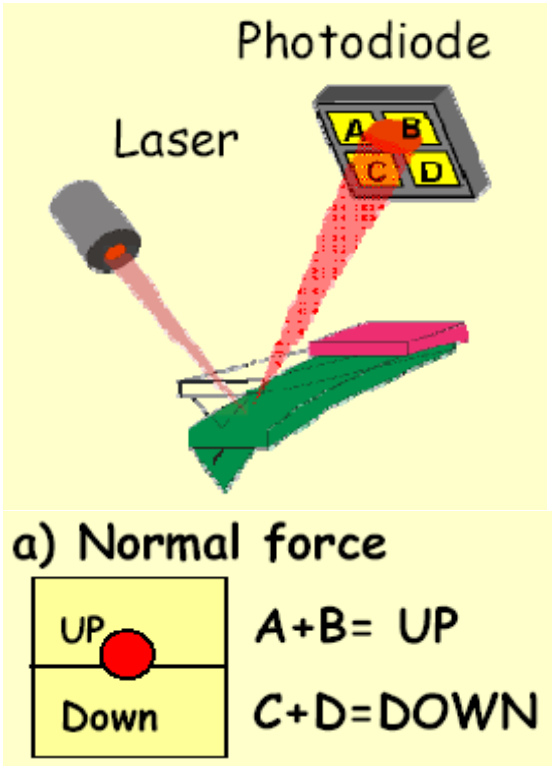
Cantilever: indicating the tip motion and rotation

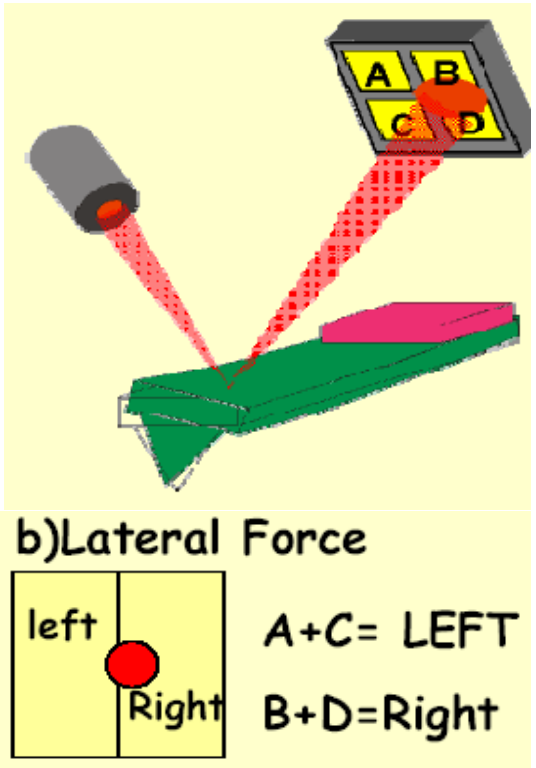


Laser sensing to monitor the position of cantilever:

1. Contact mode scanning: cantilever is usually not vibrating, but deflected due to friction or other forces. Such a deflection can be detected precisely by the sensitive photodiode.
2. Non-contact mode scanning: cantilever is in vibration with constant frequency (> 100 kHz). Such vibration can be monitored precisely by the laser sensing. To keep the resonance frequency (the constant height over the sample) during scanning, the Z-scanner has to adjust the height of the cantilever. Such adjustment can be recorded by the computer to create the scanning profile, the image.

Laser sensing both tilting and twisting of cantilever





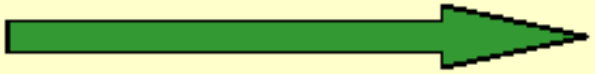
How to create vibration of cantilever?

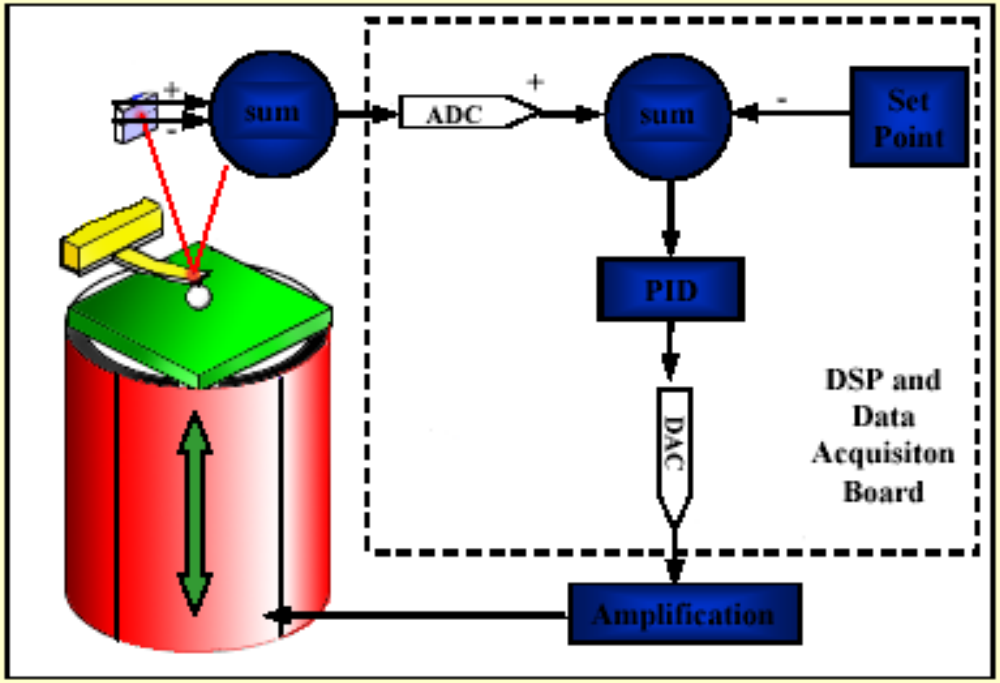
There are two ways to drive the cantilever into oscillation.

- One way is accomplished by indirect vibration, in which the cantilever is excited by high frequency **acoustic** vibration from a piezoelectric transducer attached to the cantilever holder. This is called the Acoustic AC mode (AAC).
- Another, more favored method that is much cleaner and gentler than Acoustic AC mode is a direct vibration method where the cantilever is excited directly without having to vibrate the cantilever housing or other parts. This is called Magnetic AC mode (MAC Mode™). To achieve MAC Mode imaging, a cantilever coated with a magnetic material is driven into oscillation by an **AC magnetic field** generated by a solenoid positioned close to the cantilever housing. The result of MAC Mode™ is a gentle, clean cantilever response that has no spurious background signals ("forest of peaks") like other AC modes can have. MAC Mode has even greater advantages when the cantilever is vibrated in liquid.

The Feedback in SPM with laser detection

Piezoelectric material: changes its shape when an electric potential is applied



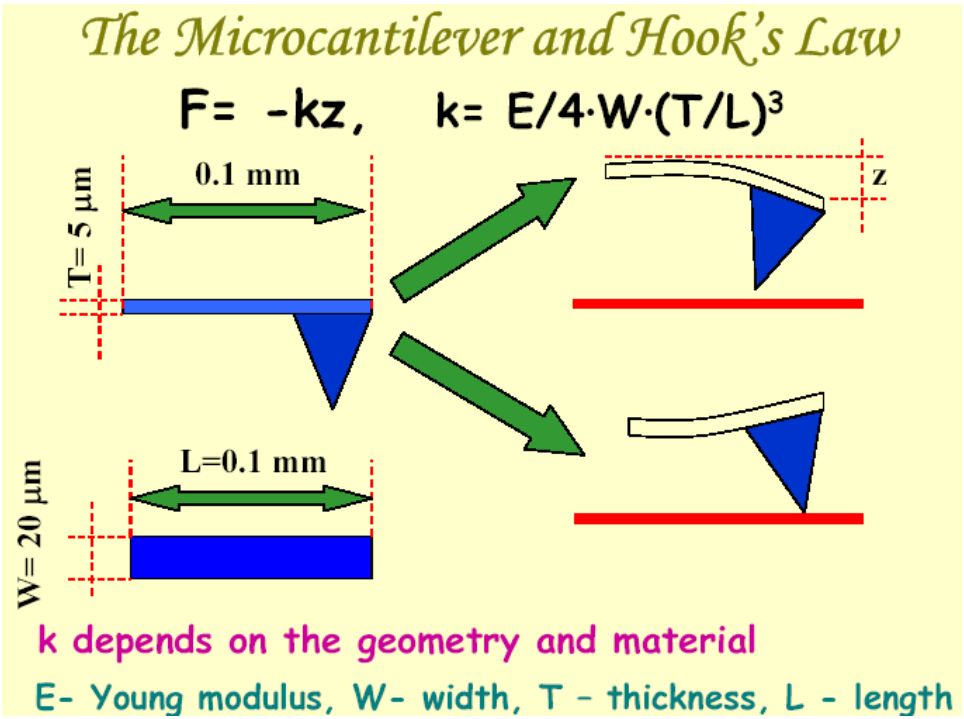


The normal force is kept constant using the feedback

Advantages:

- Negligible force on cantilever
- Not very sensitive to cantilever surface
- Disadvantage: Sample illumination

Resonance vibration of cantilever --- spring model



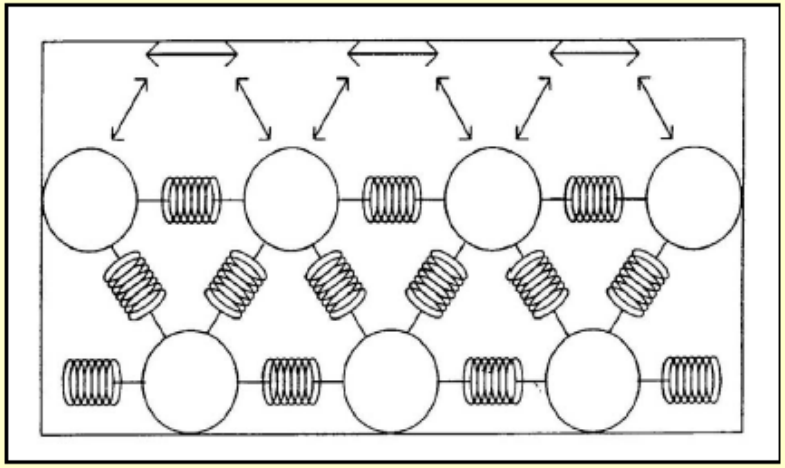
F: the force; k: the spring constant

Resonance frequency of the cantilever,

$$f_0 = \frac{1}{2\pi}\left(\frac{k}{m_0}\right)^{0.5} = \frac{1}{4\pi}\sqrt{\frac{EW}{m_0}}\left(\frac{T}{L}\right)^{1.5}$$

- k the spring constant, m_0 the effective mass of the lever.
- The softer the lever (smaller k), the more sensitive for detecting the deflection, but requires smaller mass to keep the high frequency. Why high f needed? (see next slide)

Atomic interaction (force)



$$f_0 = \frac{1}{2\pi}\left(\frac{k}{m_0}\right)^{0.5} = \frac{1}{4\pi}\sqrt{\frac{EW}{m_0}}\left(\frac{T}{L}\right)^{1.5}$$

- The vibration frequency of atoms, ω, at room temperature ~ 10^{13} Hz
- The mass, m, of an atom ~ 10^{-25} kg
- The effective spring constant, k, between atoms is:

$k = \omega^2 m \approx$ **10 N/m**

A distance of 0.1 nm (or 1 Å, typical chemical bond length) between tip and sample means a force of 10^{-9} Newton, which is enough for deflecting the cantilever (commercial cantilever has *k* between 10^{-2} N/m ≤ k_c ≤ 10^2 N/m).

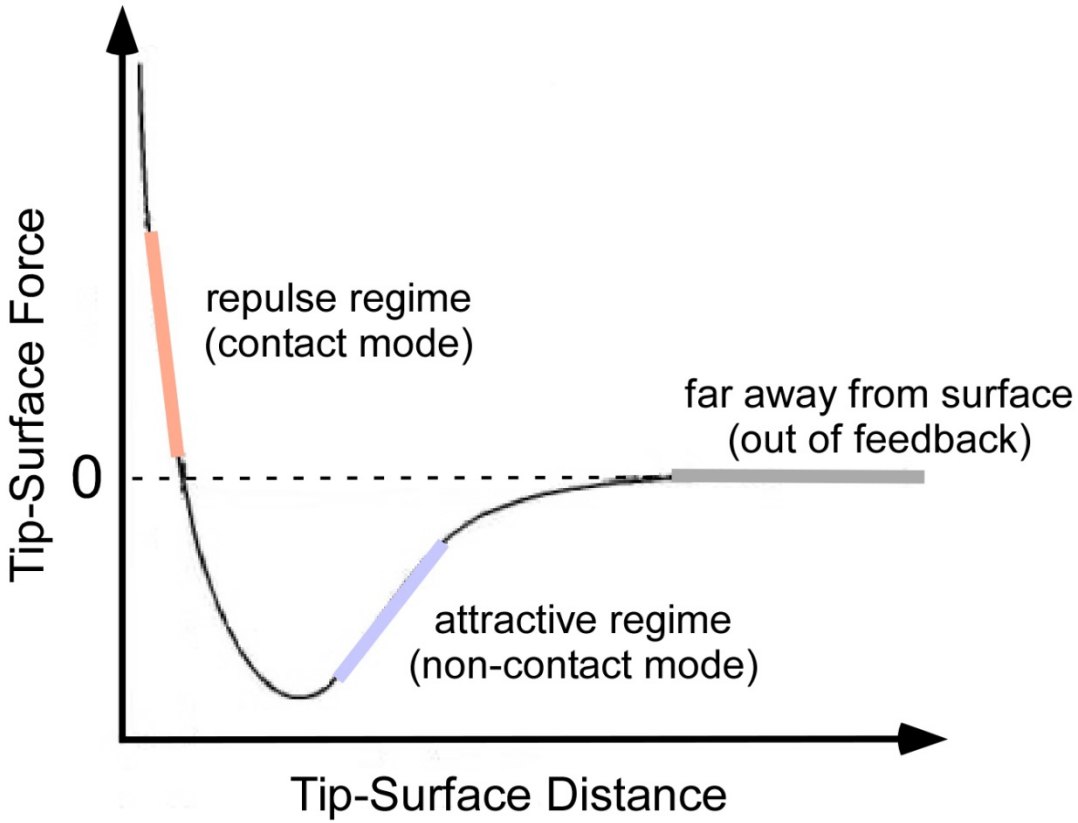
ω: the angular frequency, = $2\pi f_0$

Vibration between two atoms

- Taking m = 10^{-25} kg and $\omega_0 = 10^{13}$ Hz for atomic masses and vibrational frequencies, the spring constant of bi-atom vibration k_c = 10 N/m = 10 nN/nm. (proton mass = 1.672 621 71 × 10^{-27} kg, neutron mass = 1.674 927 29 × 10^{-27} kg, atoms mass ~ a few tens of protons or neutrons) (The **unified atomic mass unit** (**u**), or **dalton** (**Da**), is a small unit of mass used to express atomic and molecular masses. It is defined to be one twelfth of the mass of an unbound atom of ^{12}C at rest and in its ground state) (^{12}**C** is the most abundant of the two stable isotopes of the element carbon, accounting for 98.89% of carbon; it contains 6 protons, 6 neutrons and 6 electrons)

- Even smaller spring constants can be easily obtained by minimizing the cantilever´s mass. Commercial cantilevers have a typical spring constant in the range of 10^{-2} N/m ≤ k_c ≤ 10^2 N/m, typical resonant frequencies in the range of 1 kHz ≤ f_0 ≤ 500 kHz, a radius of curvature of the probing tip as small as 10 nm, and are usually fabricated of Si, SiO_2 or Si_3N_4.

Atomic interaction



Atomic interaction at different tip-sample distances

Repulsion:
At very small tip-sample distances (a few angstroms) a very strong repulsive force appears between the tip and sample atoms. Its origin is the so-called exchange interactions due to the overlap of the electronic orbitals at atomic distances. When this repulsive force is predominant, the tip and sample are considered to be in "**contact**".

Attraction (Van der Waals):
A polarization interaction between atoms: An instantaneous polarization of an atom induces a polarization in nearby atoms – and therefore an attractive interaction.

Environmental vibration should be isolated

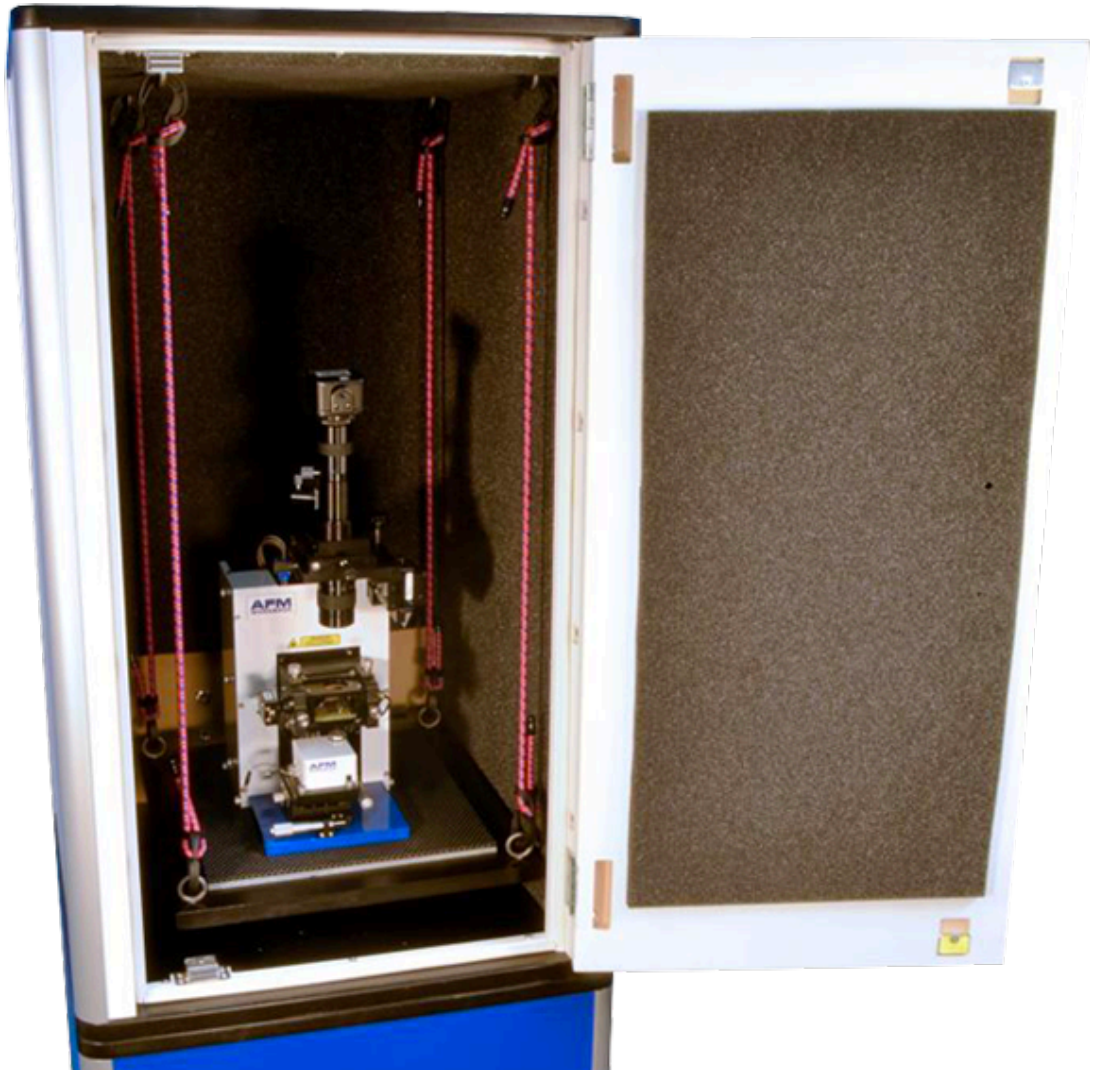
SPM is quite susceptible to external vibrations, which often cause fuzzy images. This is particularly true when measuring image down to scale of angstrom. To reduce external vibrations and obtain the highest-quality SPM images, environmental vibration should be isolated.

Methods of isolating vibration include: floating table or simply bungee option

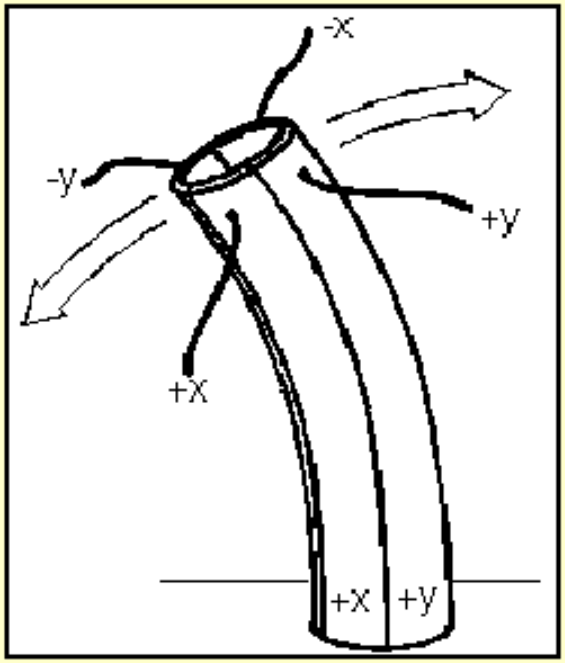
Environmental vibration should be isolated

Bungee option:

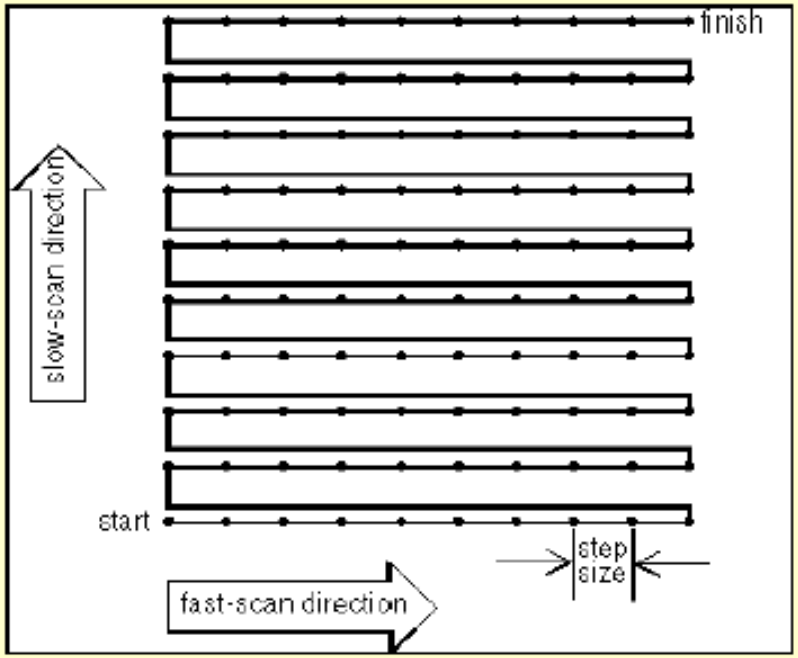
- Placing the SPM on a platform suspended by 4 bungee cords.
- Effective for vibration isolation.
- Relatively cost effective method



Raster scanning of piezoelectric scanner



Piezo tube

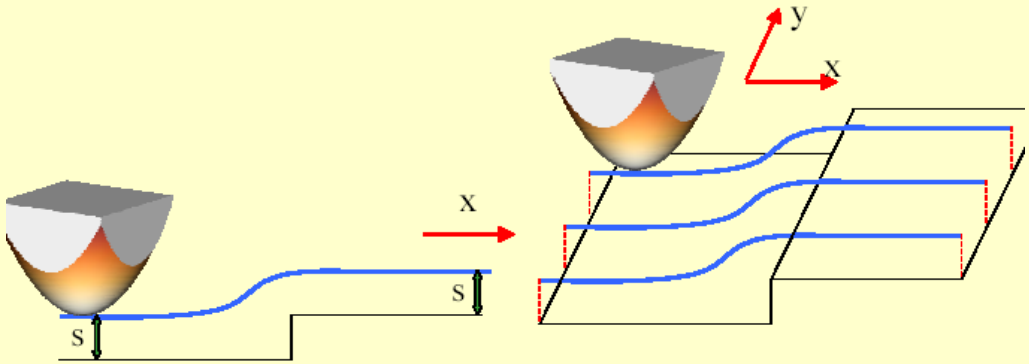


Raster scan

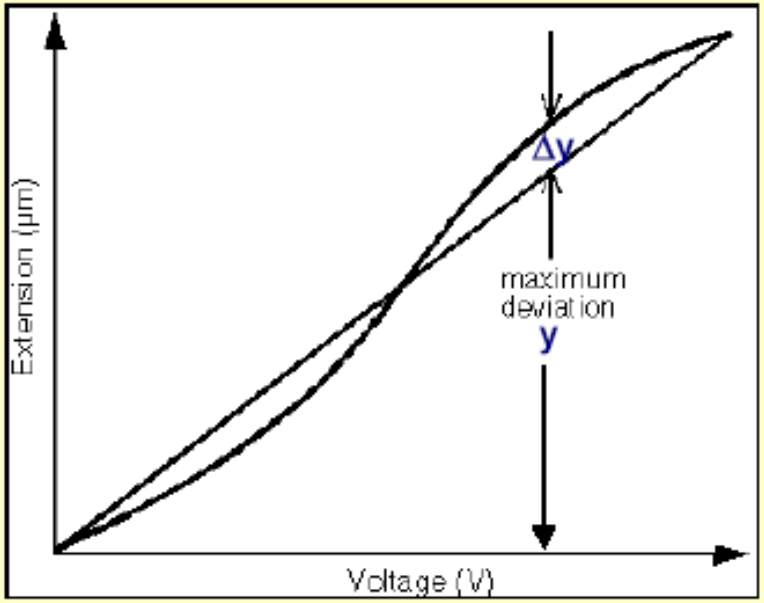
S – Strain [Å/m],
d – Strain coefficient [Å/V],
E – Electric field [V/m]

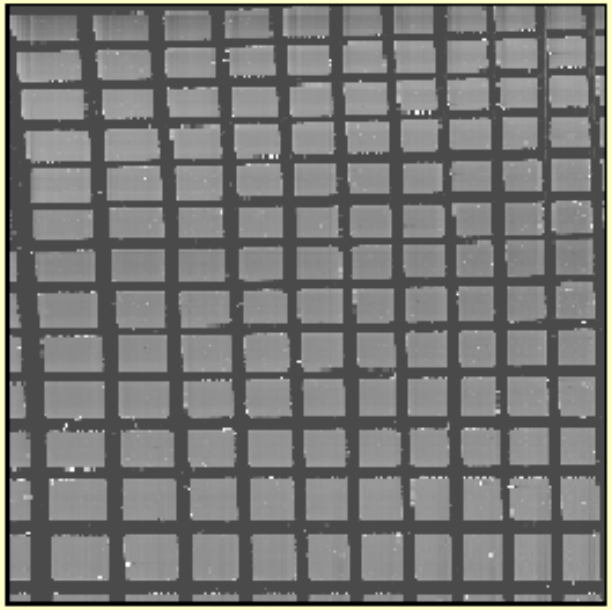
Ideally, a piezoelectric scanner varies linearly with applied voltage.
Scanning step (resolution): 0.1 nm

Obtaining Surface Profiles



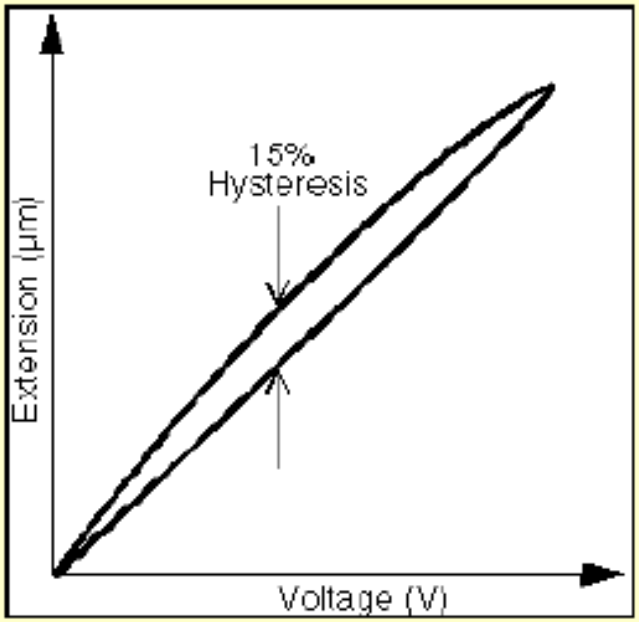
Scanner Intrinsic Nonlinearity

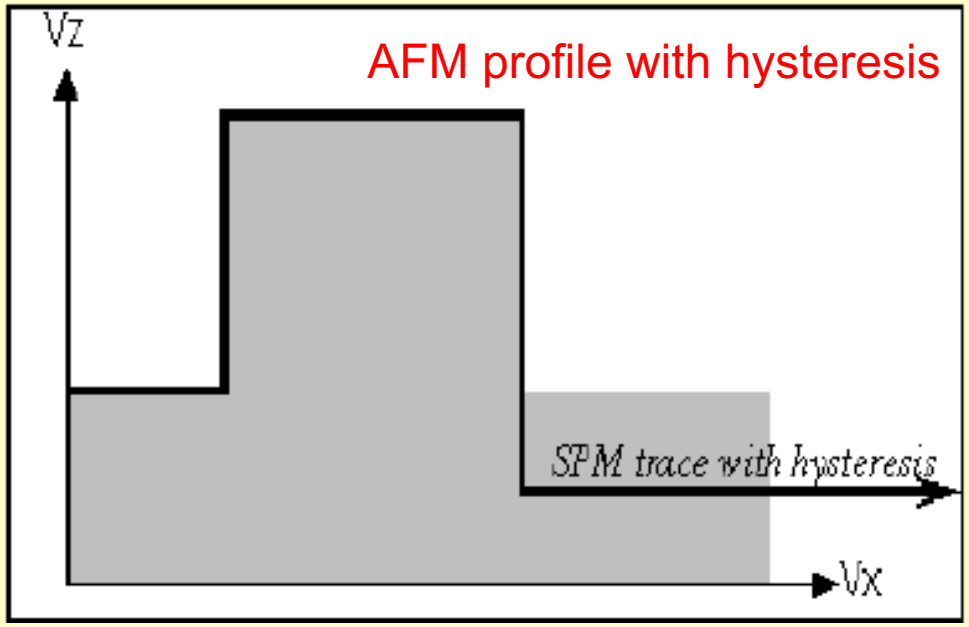




Ideally, the intrinsic nonlinearity is the ratio $\Delta y/y$ of the maximum deviation Δy from the linear behavior to the ideal linear extension y at that voltage. It is in the range 2-25%.

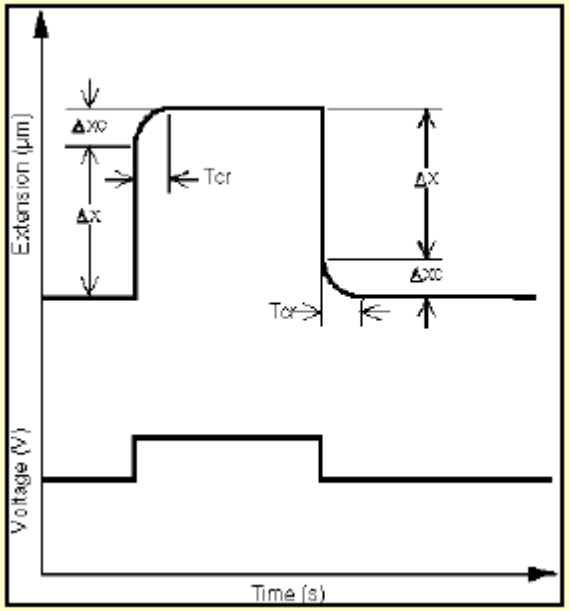
Scanner Hysteresis



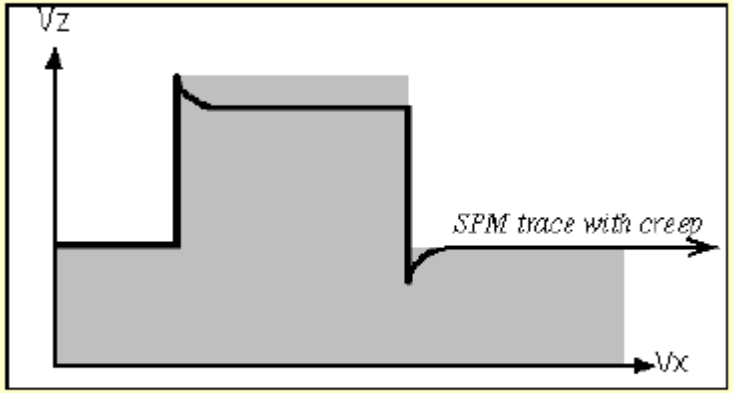


The hysteresis of a piezoelectric scanner is the ratio of the maximum divergence between the two curves to the maximum extension that a voltage can create in the scanner: $\Delta Y/Y_{max}$. Hysteresis can be as high as 20% in piezoelectric materials.

Scanner Creep

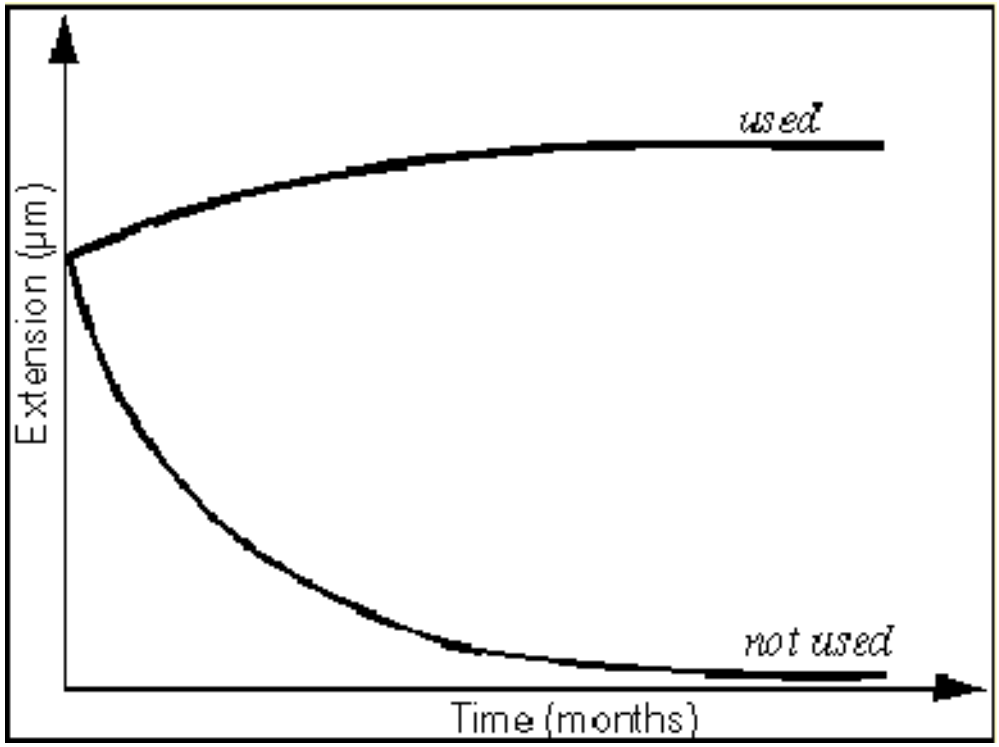


AFM profile with creep



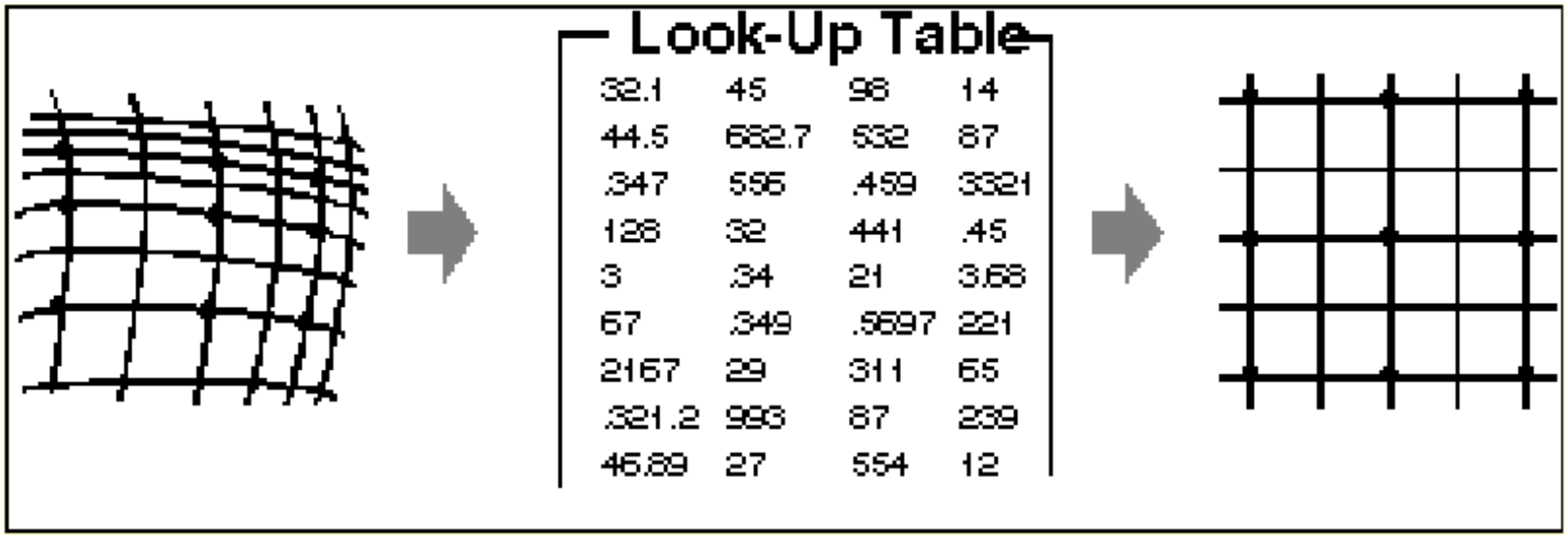
- When an abrupt change in voltage is applied, the piezoelectric reacts in two steps: the first step takes place in less than a millisecond, the second on a much longer time scale. The second step, Δxc, is known as creep.
- Creep is the ratio of the second dimensional change to the first: Δx c /Δx. It ranges from 1%to 20%, over times of 10 to 100 sec.

Scanner Aging

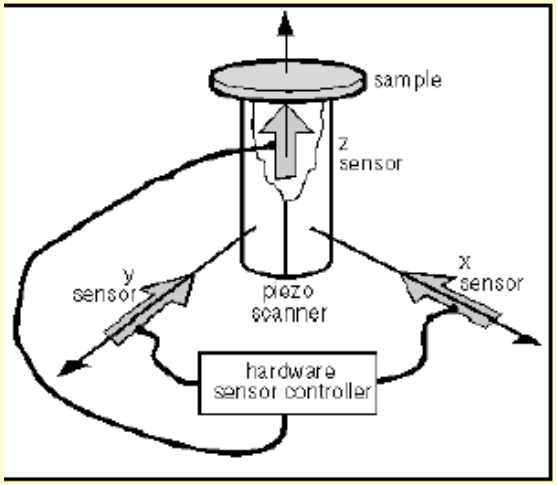


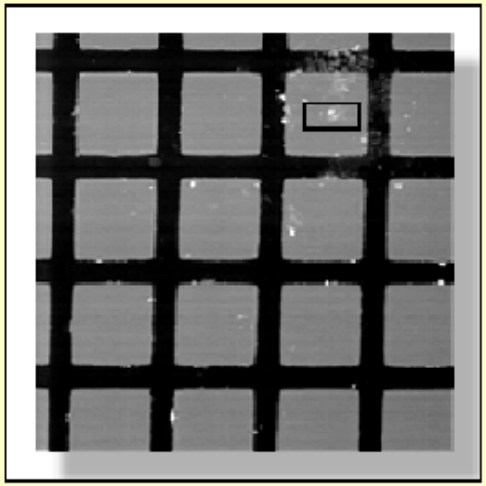
The aging rate is the change in strain coefficient (Å/V) per decade of time. The piezoelectric strain coefficient, changes exponentially with time: increases with regular use, decreases with no use.

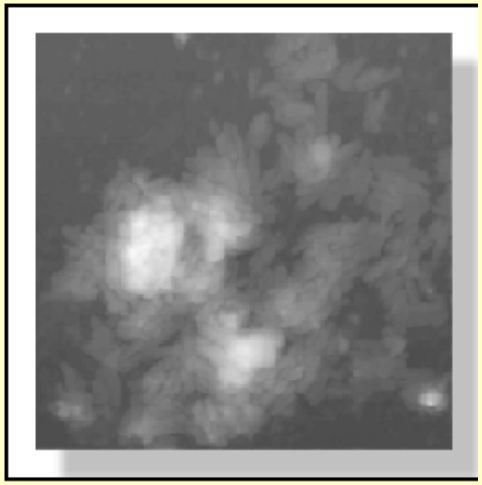
Software correction of scanner



Hardware correction of scanner







A sensor “reads” the scanner actual position, and a feedback system applies voltage to drive the scanner to the desired position, the total nonlinearity can be reduced to 1%.

Scanning artifacts

- Not-in good feedback (tip far from the sample surface).
- Electrical noise (particularly the periodical noise added to the internal signal).
- Environmental vibration (particular when the frequency is close to that of the tip oscillation).
- Fat-tip effect.
- Unknown tip-sample interaction (slowing down the scanning speed…).

Test of scanning artifacts

- Repeat the scan to ensure that it looks the same.
- Change the scan direction and take a new image.
- Change the scan area size and take an image to ensure that the features scale properly.
- Rotate the sample and take an image to identify tip imaging
- Change the scan speed and take another image (especially if you see suspicious periodic or quasiperiodic features).

Advantages of Scanning Probe Microscopy (SPM)

- Angstroms (atoms) to Nanometers (molecules);
- Digitalized and Computerized;
- Experimentally Versatile;
- Highly Tunable and Flexible to be Combined with Others;
- Wide Application in Surface and Nanotechnology.

Scanning Probe Microscopy (SPM)

Double functions: **scanning** and **probing**.

Scanning: piezo raster 2D (X-Y) scanning;

Probing: sharp tip mounted to a Z-scanner.

Comparison between traditional optical and electron microscopes and SPM

	probe	Mechanism	Sample	Resolution
Traditional optical / electronic microscope	Light/electron	Using properties of waves: diffraction, deflection, scattering	High vacuum chamber, Strict sample pre-treatment (e.g. conducting stain) required	Å – μm, good for X-Y lateral imaging
SPM	Tip	Using interaction between tip and sample: mechanic, electrostatic, magnetic.	Usually under ambient conditions, though high imaging resolution also requires high vacuum to keep clean surface, Highly flexible with other techniques	Å – nm, good for Z-height measurement, thus topography imaging

- SPM cannot replace electron microscopes, but complementary each other.
- SPM is not just superior in high resolution imaging, but more importantly it can target and manipulate just ONE atom or molecule.