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Physical and Chemical Analyses of Materials

Scanning probe microscopy: Basics

Introduction

⇨ Among the numerous scanning probe microscopy technics, we will focus on Scanning Tunnelling Microscopy STM and Atomic Force Microscopy AFM.

⇨ STM relates indirectly to electron microscopy and is based on the tunnelling effect of the electrons of a studied material.

↳ STM does not use an external electron beam as it is the case for TEM and SEM, but the intrinsic electrons from the sample to take its picture.

↳ The surface of the material is studied by the displacement of a stylus equipped with a sharp probe while recording a tunnelling current.

↳ The studied material must be indeed conductive.

↳ STM provides a structural and an electronic analysis of a material.

⇨ AFM is a derivative of STM. The two technics share the same key components.

↳ AFM is based on the measurement of the attractive or repulsive forces that the stylus undergoes along the scanned surface.

↳ AFM does not require any conductivity from the studied material.

↳ AFM provides some topographical information on a material surface. Moreover, AFM is used to measure some local forces at the material surface.

⇨ In contrast with STM for which the probe follows the surface profile, AFM can adopt several scanning modes:

↳ contact, resonating, tapping, pulsed, friction…

⇨ Compared to SEM and TEM, there is no beam-matter interaction that can modified the studied sample.

↳ STM and AFM can also provide chemical information about the studied surface. These information are different from those given by SEM and TEM.

⇨ The domain of study of STM and AFM is the following:

1 m	10^{-1} m	10^{-2} m	10^{-3} m	10^{-4} m	10^{-5} m	10^{-6} m	10^{-7} m	10^{-8} m	10^{-9} m	10^{-10} m
									scanning probe microscopy	

STM

Introduction

⇨ At the end of the 20's, the tunnelling effect of the electrons across a potential barrier was foreseen.

⇨ STM was developed in 1981 by Gerd Binnig and Heinrich Rohrer from IBM Zurich who received the Nobel prize of Physics in 1986.

⇨ The principle of STM lies on the tunnelling effect of electrons in metals and semiconductors.

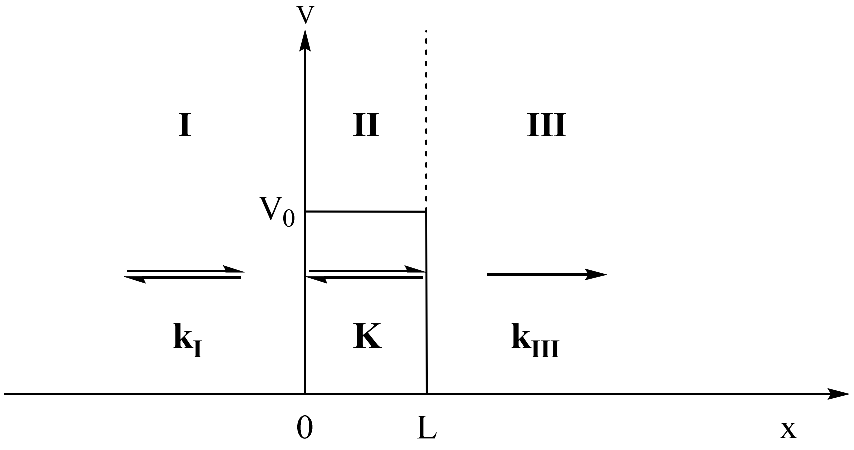
⇨ A Scanning Tunnelling Microscope from Directindustry.

⇨ The microscope is installed on a table uncoupled from the floor to prevent from any vibrations.

Principle

⇨ The principle is based on quantum mechanics and on the tunnelling effect of electrons in metals and semiconductors.

⇨ From a quantum mechanics point of view, most of the features of the tunnelling effect can be described by a simple symmetrical barrier of potential representing the energy that the electrons must overcome to "leave" the metal or semiconductor:



- Domain I: metal or semiconductor
- Domain II: potential barrier
- Domain III: vacuum
- Conservation of the energy **E**
- Conservation of the magnitude of the wave vector: $\mathbf{k_I = k_{III} = K}$

⇨ The wave functions and the Schrödinger equations for domains I, II and III are the followings:

$$\text{I:}\quad -\frac{\hbar^2}{2m_o}\frac{d^2\psi_I(x)}{dx^2} - E\psi_I(x) = 0 \;\Rightarrow\; \psi_I(x) = A_1e^{ikx} + B_1e^{-ikx}$$

$$\text{II:}\quad -\frac{\hbar^2}{2m_o}\frac{d^2\psi_{II}(x)}{dx^2} + (V_0 - E)\psi_{II}(x) = 0 \;\Rightarrow\; \psi_{II}(x) = A_2e^{Kx} + B_2e^{-Kx} \quad \text{if } E < V_0$$

$$\text{II:}\quad -\frac{\hbar^2}{2m_o}\frac{d^2\psi_{II}(x)}{dx^2} + (V_0 - E)\psi_{II}(x) = 0 \;\Rightarrow\; \psi_{II}(x) = A_2e^{iKx} + B_2e^{-iKx} \quad \text{if } E > V_0$$

$$\text{III:}\quad -\frac{\hbar^2}{2m_o}\frac{d^2\psi_{III}(x)}{dx^2} - E\psi_{III}(x) = 0 \;\Rightarrow\; \psi_{III}(x) = A_3e^{ikx} + B_3e^{-ikx} = A_3e^{ikx}$$

⇘ $k = (2m_oE/\hbar^2)^{1/2}$ and $K = (2m_oE/\hbar^2 - 2m_oV_0/\hbar^2)^{1/2}$

⇘ Tacking into account the continuity at each boundary, we can write:

$$\psi_I(0) = \psi_{II}(0), \psi_{II}(L) = \psi_{III}(L), \frac{d\psi_I(0)}{dx} = \frac{d\psi_{II}(0)}{dx}, \frac{d\psi_{II}(L)}{dx} = \frac{d\psi_{III}(L)}{dx}$$

- To describe the tunnelling effect, we must consider **E** < $\mathbf{V_0}$:

$$A_1 + B_1 = A_2 + B_2 \quad \text{and} \quad ik\left(A_1 - B_1\right) = K\left(A_2 - B_2\right)$$

$$A_2 e^{KL} + B_2 e^{-KL} = A_3 e^{ikL} \quad \text{and} \quad K\left(A_2 e^{KL} + B_2 e^{-KL}\right) = ikA_3 e^{ikL}$$

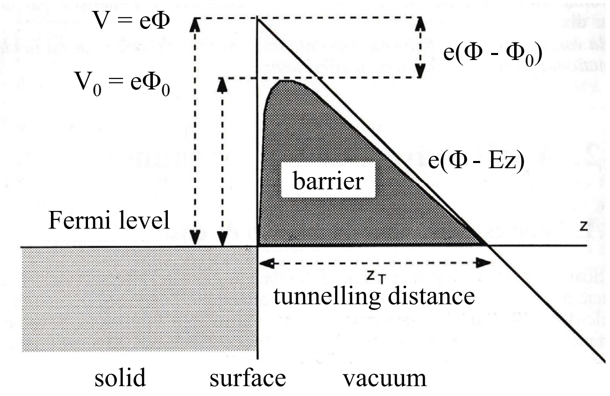
- Solving these equations leads to :

$$4ikKA_1 = \left[\left(K + ik\right)^2 e^{KL} - \left(K - ik\right)^2 e^{-KL}\right] A_3 e^{ikL}$$

- The transmission coefficient **T** and so the tunnelling effect probability is:

$$T = \left(\frac{A_3}{A_1}\right)^2 \approx \frac{16k^2K^2}{\left(k^2 + K^2\right)^2} e^{-2KL} \approx 16\left(\frac{E}{V_0}\right)\left(1 - \frac{E}{V_0}\right) e^{-2KL} \quad \text{for} \quad KL >> 1$$

⇨ Below is represented a real potential barrier at a metal / vacuum interface:



↳ **E** is the electric field ($V \cdot m^{-1}$)

↳ **z** is the distance from de surface (m)

↳ $\mathbf{\Phi_0}$ (V) is the extraction work of an electron from the material

↳ The tunnelling distance $\mathbf{z_T \approx \Phi_0 / E}$

Sample

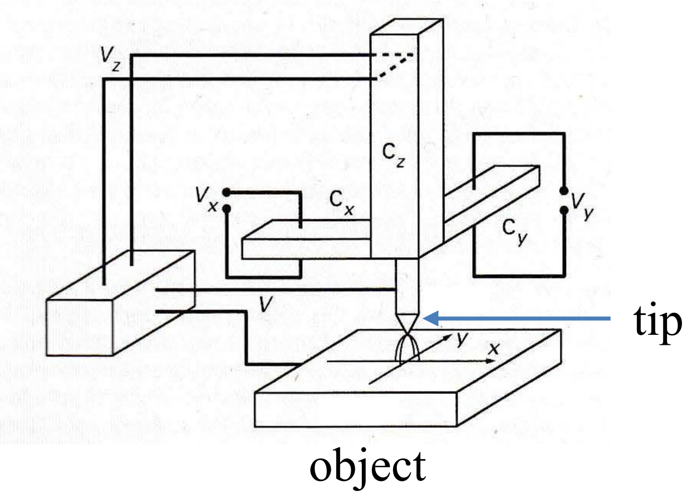
⇨ The sample must be a conductor or a semiconductor to generate a tunnelling current. Some conducting or semiconducting materials with a modified surface with organic molecules can also be studied by STM. The chemical nature the sample must allow analyses under vacuum if necessary.

⇨ The sample size is about 1 cm or less, big enough to be manipulated.

⇨ The sample images are grayscale and the colour is post-added to represent the recorded signal.

Instrument

⇨ The scheme below depicts the working principle of a STM:



⇨ The probe is a metallic tip made of tungsten or platinum on which a thin film of iridium is deposited. Sometimes pure iridium is also used.

↳ The choice of these metals are influenced by their ability to prevent for forming a oxidation layer that will hinder the tunnelling current.

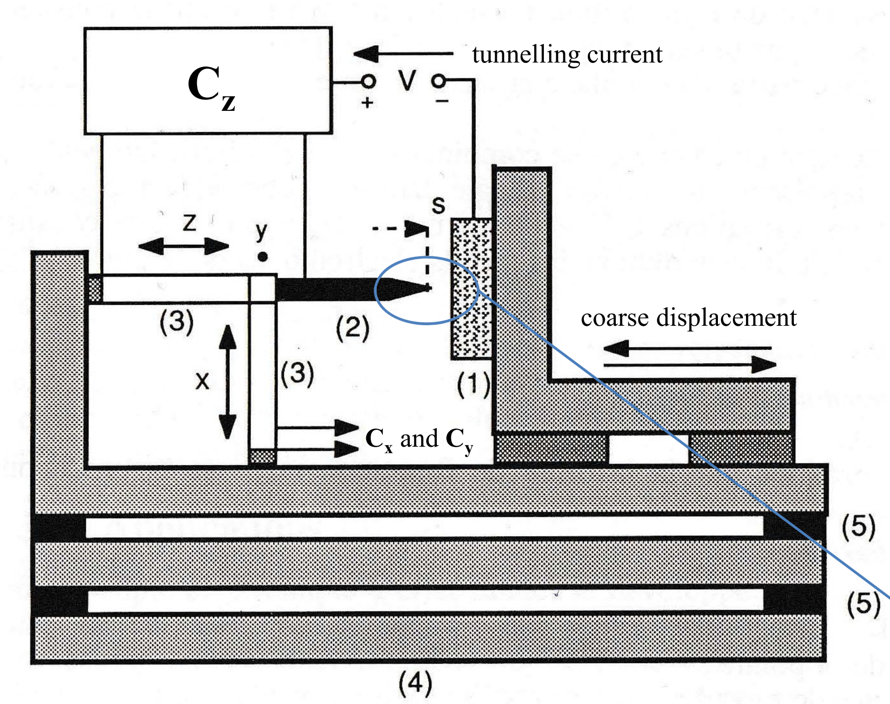
↳ The probe is prepared under inert conditions (N_2, He) or under vacuum.

↳ To get ride of such oxidation problems, STM is also performed under the same inert conditions or under vacuum.

↳ To get the atomic resolution, the tip must be terminated by a single atom. Several technics provide tips at the nanometric dimension.

⇨ The piezoelectric actuators **C_x**, **C_y** and **C_z** are activated by the tension **V_x**, **V_y** and **V_z**. They are moving the tip along the sample surface (stepper actuators from 0.05 - 5000 Å).

⇨ The following scheme represents the sample holder and the tip mechanics:

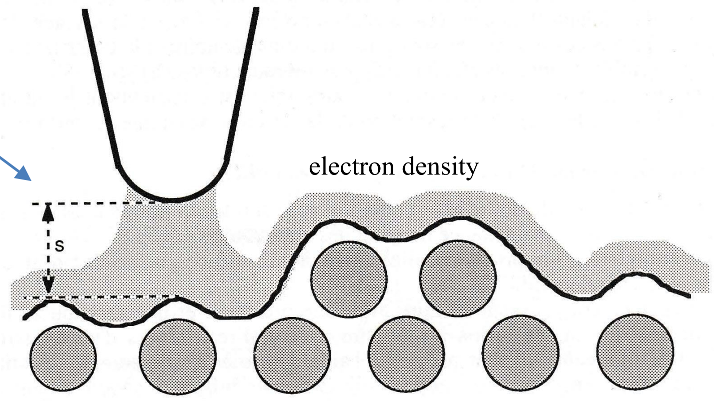


1: sample
2: tip situated at a distance **s** from the sample set at **V** > 0
3: piezoelectric actuators
4: anti-vibratory metallic pieces
5: vibration absorbers

↳ The tip moves in a volume of about a few mm^3.

↳ The tip is set at a tension from 0 ± 5V against the sample.

↳ The **C_z** actuator position the tip at a few Å from the sample.

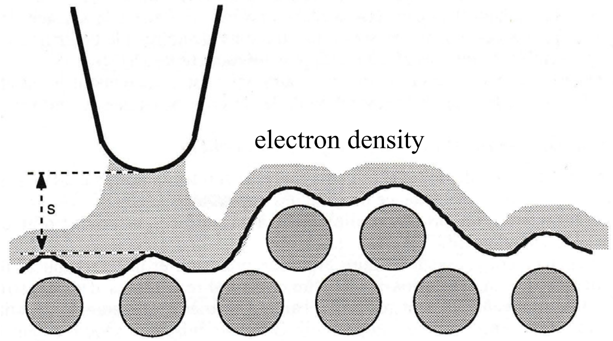


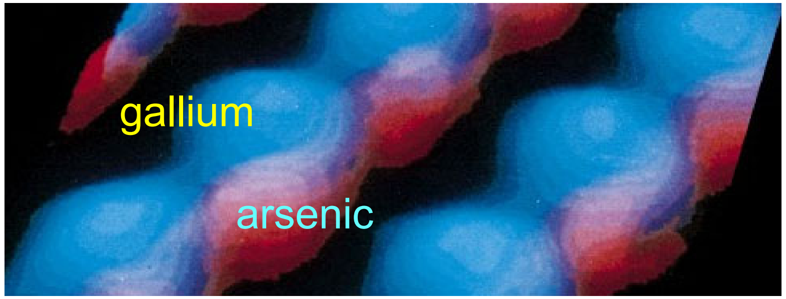
Imaging at a constant tunnelling current

Image formation

⇨ The tip is polarised at a voltage **V** from 0 to ±5 V.

⇨ The tip is positioned at the surface of the sample by the actuator $\mathbf{C_z}$ and is continuously moved along the **z** axis to provide a constant tunnelling current while scanning the surface.





↳ The distance between the tip and the surface ranges from 4 to 7 Å.

↳ The maximum measured depth is around 10 – 20 µm depending on the tip shape.

↳ The function $\mathbf{V_z = f\,(V_x, V_y)}$ corresponds to a 3-D map which represents the isocurrent of tunnelling leading to the surface topography of the sample.

⇨ The tunnelling current **I** is proportional to the applied potential **V**:

$$\mathbf{I} = \mathbf{aV}\exp\left(-\mathbf{s}\frac{4\pi\sqrt{2\mathbf{m}_0\mathbf{e}\Phi}}{\mathbf{h}}\right)$$

↳ In the current expression, **V** is the applied voltage at the tip (V), **a** is a constant, **s** (Å) is the distance between the tip and the surface, $\mathbf{m_0}$ (kg) is the electron rest masse, **e** is the elementary charge (1.60×10^{-19} C), **h** is the Planck constant (6.62×10^{-34} J·s) and **Φ** (V) is the average of the extraction work of an electron from the tip and the sample.

Image interpretation

⇨ A theoretical approach proposed by Tersoff and Hamann describes a situation of weak coupling between the electrons from the tip and the electrons from the scanned surface.

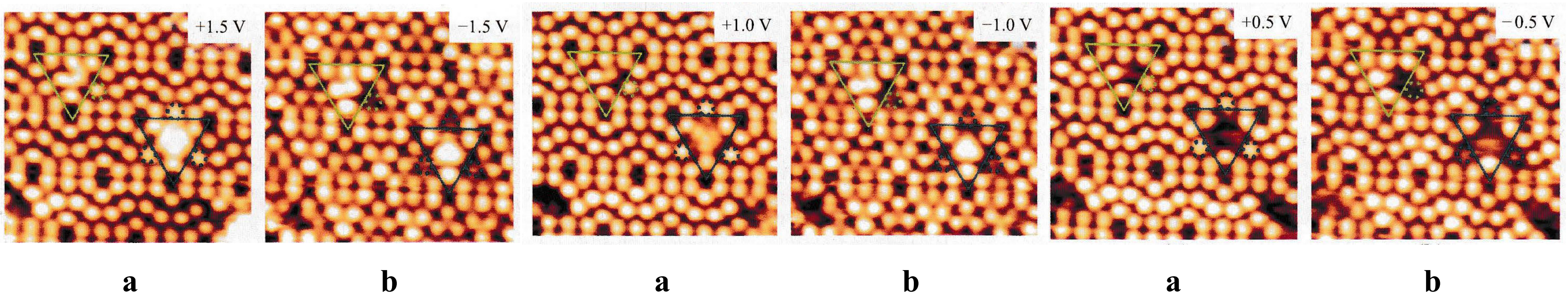
↳ The tip is represented by a spherical potential.

↳ The chosen wave functions of the surface describe the movement of the electrons along the **x**, **y** and **z** axes.

⇨ At a constant tunnelling current, the tip follows a profile determined by an iso-density of electronic states.

Scanning probe microscopy: Basics

- When the tip is positively polarised, the image corresponds to the iso-density of the electronic states at the energy of the Fermi level $\mathbf{E_F}$ representing the filled surface states.
- Another possibility relies on polarising the tip negatively. The image will then correspond to the iso-density of the electronic states at an energy higher than the fermi level $(\mathbf{E_F + \varepsilon})$ representing the empty surface states. This mode is interesting for semiconductors.
- Below are represented the STM images of Si(111) surfaces, recorded at a constant current of 0.05 nA using a tungsten tip (Zhou et al., *Nano-Micro letters*, **2015**, *7*, 194-202):



empty **a** and filled **b** state STM images of Zn-induced nanocluster on an Si(111) surface. The bias voltages represent the polarisation of the sample.

Resolution

⇨ The lateral resolution **d** ranges from 2 – 6 Å, strongly depending on the tip preparation. The vertical resolution along the **z** axis is from 0.01 to 0.1 Å.

Imaging at a constant height

Image formation

⇨ The tip is polarised at potential **V** from 0 to ±5 V.

⇨ The tip is positioned at the surface of the sample by the actuator $\mathbf{C_z}$ and is kept at a constant distance from the scanned surface. The maximum measured depth is around 0.1 – 1 nm depending on the intensity of the tunnelling current.

⇨ This mode leads to an image made of current changes over the surface which can be related to surface charge densities. it provides a faster scan rate than the imaging at a constant current.

Image interpretation

⇨ The image interpretation is the same than for the imaging at a constant current, depending on the polarisation of the tip against the studied sample.

Spectroscopy by tunnelling effect

General features

⇨ The spectroscopic methods give some information on the distribution of the energy of the electronic states at a given surface location.

⇨ The nature of the atoms present at this surface location can be often identified.

⇨ These methods can be either run at a constant current or at a constant height.

Spectroscopy at a constant current

⇨ The goal is to study the dependency of the differential conductivity **dI/dV** of the sample as a function of the applied voltage **V** at the tip.

⇨ One obtains a differential conductivity spectrum which reproduces the spectrum of the density of states.

Spectroscopy at a constant height

⇨ For each probing point, one acquired a conventional image at a constant current for a voltage **V**. The position of the tip is then maintained, the voltage is changed and the variation of the current is recorded as a function of the applied voltage: **I = f(V)**.

⇨ The analysis of the **I / V** curve gives rise to the number of available electronic states for a given energy.

Emission of photons by tunnelling effect

⇨ When the energy of the electrons injected from the tip to the sample is higher than the energy of the Fermi level of the sample, the relaxation of these electrons gives rise to a local emission of photons.

⇨ The resulting image which depends on a local Fermi level energy can be used to probe the localisation of adsorbed chemical species on the sample surface.

⇨ Such a method is of interest in catalysis when the catalyst is a conducting or semiconducting material as it can ensure the localisation of catalytic sites, geometric surface modifications of the catalyst sites…

STM engraving

⇨ STM can provide the engraving of a surface at the nanometric scale.

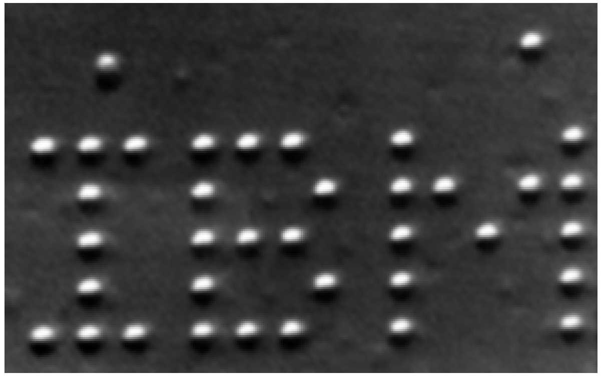
↳ STM allows the manipulation of atoms stuck at the STM tip.

↳ STM allows also the generation of electrochemical reactions at a defined surface site. It can be either an electrooxydation or an electroreduction.

↳ Other electro-induced chemical reactions can be also envisaged.

↳ The Scanning ElectroChemical Microscope SECM is the evolution of STM dedicated to studies in aqueous or organic solutions.

↳ Below is the STM image resulting from the manipulation of 35 Xe individual atoms on a chilled crystal of Ni. From the IBM scientists in 1989:



AFM

Introduction

⇨ Atomic Force Microscopy was introduced by Gerd binnig, Calvin Quate and Christoph Gerber in 1986.

⇨ AFM was presented as an application of STM for insulating materials.

⇨ The principle of AFM lies on the measurement of the forces involved between a tip and the surface of the studied material.

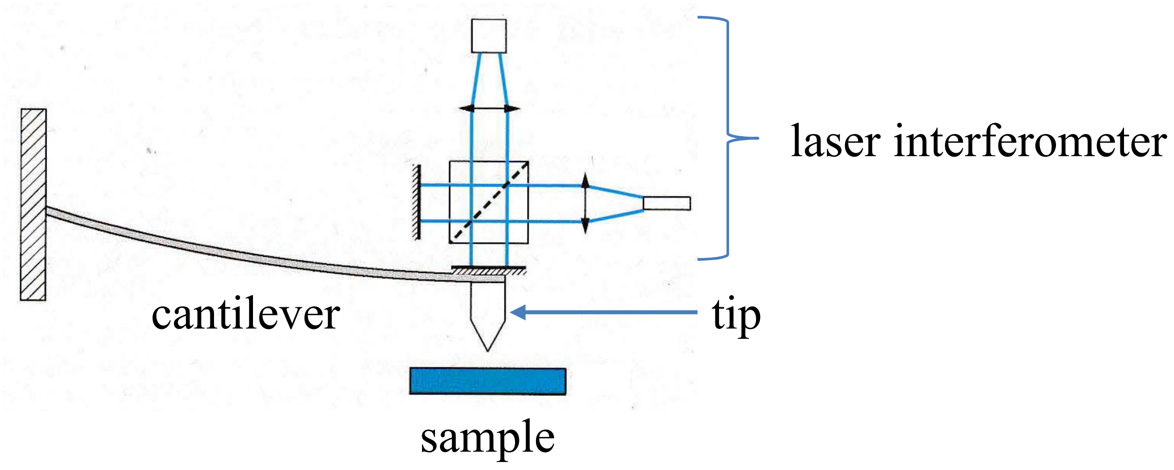
⇨ An Atomic Force Microscope from Park Systems.

⇨ The microscope is installed on a table uncoupled from the floor to prevent from any vibrations.

Principle

⇨ The principle is based on the monitoring of the deflection or the twisting of a cantilever ended by a tip when moving close to the studied surface.

⇨ The cantilever motion is measured with a laser interferometer.



⇨ The first cantilevers were made of a gold blade ended by a diamond tip.

⇨ The cantilevers can be made from an aluminium foil or etched tungsten wires.

⇨ Modern cantilevers are obtained from silicon micro-machining. The cantilevers, made of pur Si or Si_3N, integrate the tip.

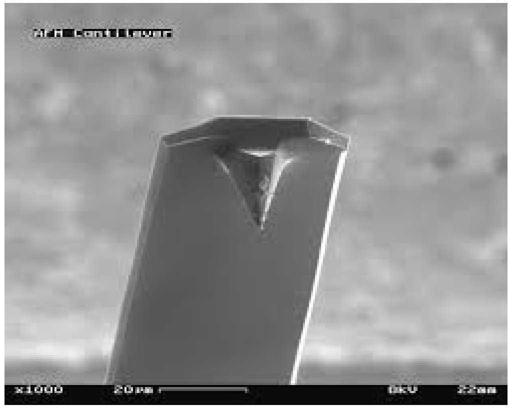
⇨ Cantilevers must meet several features:

↳ being terminated by a tiny tip to ensure a good lateral resolution

↳ having a resonating frequency of a few Hertz, greater than the acquisition frequencies

↳ exhibiting a particular rigidity: from 0.01 $N \cdot m^{-1}$ up to 100 $N \cdot m^{-1}$ for a good sensibility in force measurements

⇨ Below is depicted a micro-machined tip ended cantilever in Si:



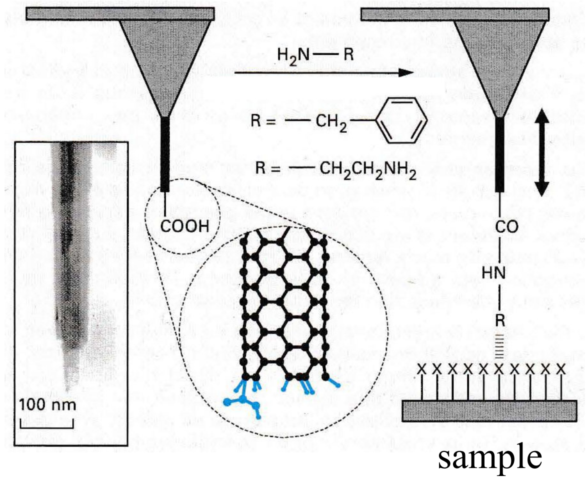
tip ended cantilever

⇨ The cantilevers are from 100 to 200 µm long and a fraction of micrometre thick.

⇨ The tip curvature ranges from 2 to 50 nm.

⇨ Some cantilevers ended with a diamond tip are still used for scratch tests and tests of resistance to contact.

- For specific applications, the tip can have specific properties like electrical, magnetic properties…



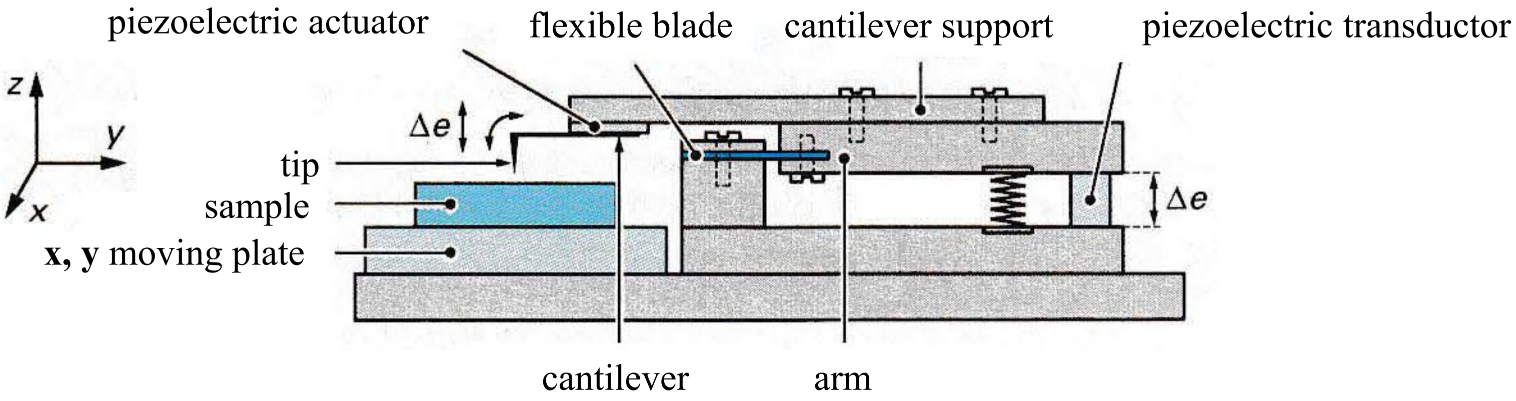
- Some tip can be ended by colloids, carbon nanotubes or specific molecules for biological purposes.
- The functionalised tips can be inert or chemically reactive.

Sample

- The sample can be a conductor, a semiconductor or an insulator.
- The AFM experiment can be run under vacuum, under controlled or natural atmosphere, in liquid medium…
- The sample size is about 1 cm or less, big enough to be manipulated.
- Compared to STM, AFM offers a higher hands on flexibility with a rather similar accuracy.

Instrument

⇨ The scheme below depicts the working principle of an AFM:



⇨ During an AFM experiment the cantilever can be static or animated by an oscillating movement induced by the piezoelectric actuator.

⇨ Due to its soft rigidity, the cantilever is sensitive to temperature gradients.

⇨ Therefore, AFM gives rise to three principal running modes: static, dynamic (oscillating) and thermic.

↳ These three different running modes provide different information on the studied sample.

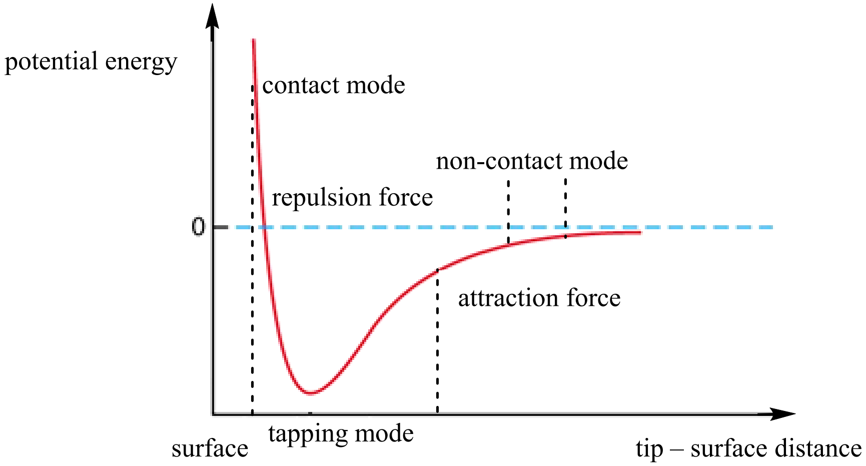
AFM imaging

General features

⇨ For imaging, only the static and the dynamic modes are of interest. The maximum measured depth is around 10 – 20 µm depending on the tip shape.

⇨ The thermic mode, which studies the deflection of the cantilever as a function of the temperature finds some applications in calorimetry like in the quantification of heat exchanges during a chemical reaction probed by the AFM tip.

⇨ When dealing with the static and the dynamic modes, the tip undergoes an attraction or a repulsion force from the sample surface described by a interactomic potential curve:



⇨ The static mode regroups the contact and the friction modes. Only the contact mode provides images, the friction mode is related to tribology.

⇨ The dynamic mode regroups the tapping and the non-contact modes which both provide images.

Contact mode

⇨ The contact mode operates in the neighbourhood of the repulsion wall of the interatomic potential curve.

⇨ The tip touches the surface and the measured deflection of the cantilever reproduces the topography of the scanned surface.

⇨ Another possibility relates to a constant height mode in which the cantilever is static.

⇨ The surface topography is obtained from the potential applied to the piezoelectric actuator to counteract the cantilever natural deflection along the scanned surface.

⇨ The contact mode requires a cantilever of soft rigidity: from 0.01 to 5 $N \cdot m^{-1}$.

⇨ The contact mode provides an easy and rapid surface mapping.

⇨ The lateral resolution **d** of this operating mode is about 0.5 nm.

⇨ The vertical resolution is determined by the vertical scanner and can be up to 1 Å.

Non-contact mode

⇨ The non-contact mode operates with the vibration of the cantilever either at its resonant frequency or just above it with a small amplitude *i.e.* from a few picometre to a few nanometre (< 10 nm).

⇨ The tip is far from the surface, the AFM tip and/or the sample do(es) not suffer from damages. This mode is indicated to image soft and fragile materials.

⇨ When set at its resonant frequency, one can observe a frequency modulation when scanning a material surface.

↳ In this mode, the changes in the oscillation frequency give some information about the tip – surface interactions.

⇨ When set above its resonant frequency, one can observe an amplitude modulation when scanning a material surface.

↳ In this mode, the changes in the oscillation frequency can distinguish different types of surface of the scanned material *i.e.* soft and hard domains.

⇨ The lateral resolution **d** of this operating mode is also about 0.5 nm. It also provides a vertical resolution at the atomic scale when operates in high vacuum conditions.

Tapping mode

⇨ The tapping mode operates with the vibration of the cantilever either at or near its resonant frequency with a bigger amplitude than in non-contact mode, *i.e.* from a few nanometre to 200 nm.

↳ The oscillations of the cantilever are maintained constant by the tuning of the height of the tip during the scan. The tuning of the height of the tip constitutes the recorded signal. The image relates to the forces involved between the tip with the studied surface during the intermittent contact.

⇨ The tapping mode is the most widely used mode (ambient atmosphere and in liquids). The lateral and vertical resolutions are similar to that of the other modes.

⇨ Due to its intermittent contact with the surface, it prevents from surface damaging and from any sticking at the surface when the tip approaches the attraction force domain of the surface as it is the case in the contact mode. At each oscillation cycle, the tip brush the repulsion wall of the surface.

⇨ The tapping mode is used to image soft adsorbed materials like lipid bilayers.

⇨ When recording the oscillation phase changes, one can obtain some information on the elasticity or the wettability of the studied surface for example.