Atomic Force Microscopy :

A characterization and fabrication instrument at the Nanoscale

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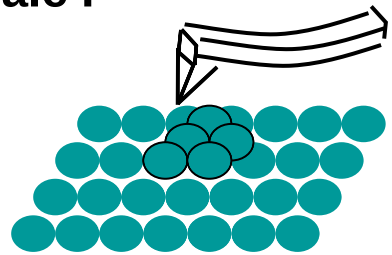
http://neel.cnrs.fr/

Forum MSL 2011

The Atomic Force Microscopy

Idea: To measure and use the nanoscopic and local tip-sample interactions to map the surface morphology and act at the nanoscale .



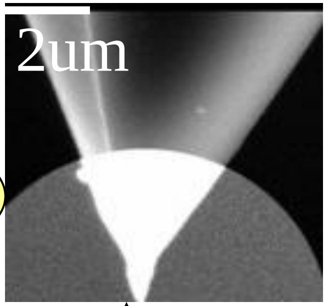
1. Review of the nanoscopic forces
2. The force detector: the AFM probe

   => link with G. Gillmann and A. Steinberger courses

3. Introduction to *three* main working modes:
   - Contact and friction mode
   - Dynamic mode : *intermittent mode* and non-contact mode (course of L. Nony)
   - Spectroscopy mode => course of Ph. Leclère
4. AFM probe used as a nanotool:
   - Nanolithography and nanofabrication:

   Local Nano-oxidation and Nanoxerography

Review of the main forces acting at the Nanoscale in air



$$\vec{F}_{t/s} = \vec{F}_{E/M} + \vec{F}_{cap} + \vec{F}_{VdW} + \vec{F}_{rép}$$

Tip-surface Gap (z)

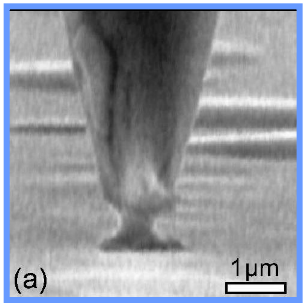
Electrostatic force ($1/z^n$; $1<n<2$) : Long range interaction => electric modes (course of B. Gautier)

$$F_{elect} = \frac{1}{2}\frac{\partial C}{\partial z}V^2 \prec \frac{1}{2}\frac{\varepsilon_0 \varepsilon_r S}{z^n}V^2$$

z > 20nm

Capillary Force

$$F_{cap} = f(\gamma, R, \theta_{p/eau}, \theta_{eau/surf}, z)$$



z> 5nm

Van der Waals Force

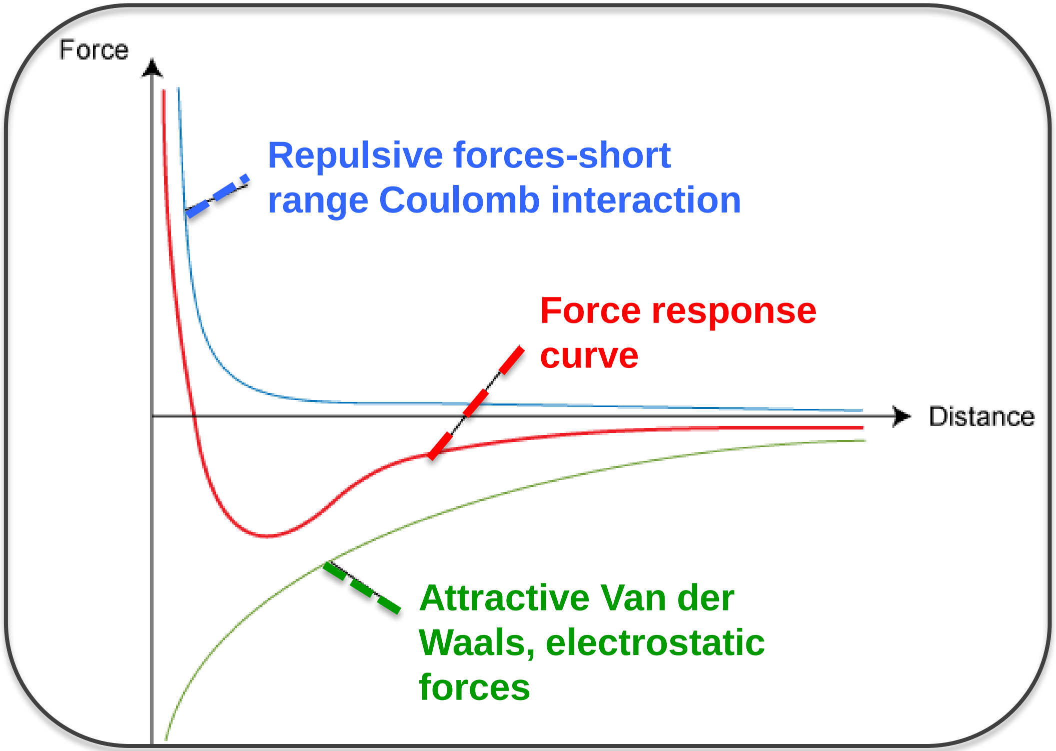
$$F_{VdW}(z) = \frac{HR}{6z^2}$$

z< 0.5nm

Repulsive Force (m>3)

$$F_{répulsion}(z) = \frac{A}{z^m}$$

Graphical representation of the tip-sample forces



Repulsive forces-short range Coulomb interaction

Force response curve

Attractive Van der Waals, electrostatic forces

$$F_{elect} = -\frac{1}{2}\frac{\partial C}{\partial z}V^2 \prec -\frac{1}{2}\frac{\varepsilon_0 \varepsilon_r S}{z^n}V^2$$

$$F_{VdW}(z) = -\frac{HR}{6z^2}$$

Sphere-surface geometry

$$F_{répulsion}(z) = \frac{A}{z^m}$$

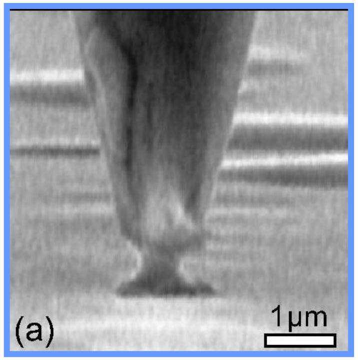
$$F_T = F_{rep}(z) + F_{VdW}(z) + F_{elect}(z) = \frac{A}{z^m} - \frac{HR}{6z^2} - \frac{1}{2}\frac{e_0 e S}{z^n}V^2$$

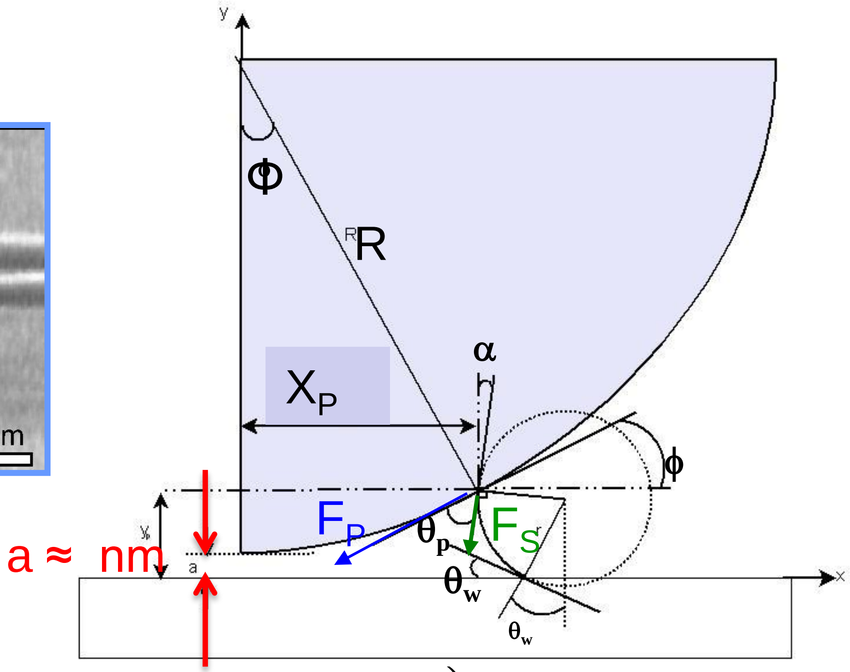
Value of n depends on the tip-surface geometry, cf B. Gauthier course, Publications of Th. Mélin of IEMN Lille, M. Ramonda and P. Girard University of Montpellier

Capillary force

M. Schenk et al, " Direct visualization of the dynamic behaviour of a water meniscus by scanning electron microscopy", J. Appl. Phys, 4880, (1998)

$$\vec{F}_{cap} = \vec{F}_p + \vec{F}_S$$





F_S is the surface tension force

F_P is the capillary pressure force

$$F_p = A_{xy}\Delta P = \pi \cdot x_p^2 \Delta P = \pi\gamma \cdot R\left(-\sin\phi + \frac{\cos(\theta_p + \phi) + \cos\theta_w}{a/R + 1 - \cos\phi} \times \sin^2\phi \right)$$

$$F_S = l\gamma\cos\alpha = 2\gamma\pi \times x_p \sin(\theta_p + \phi) = 2\pi\gamma \times R\sin\varphi\,\sin(\theta_p + \phi)$$

If $R >> a$ then ϕ very small

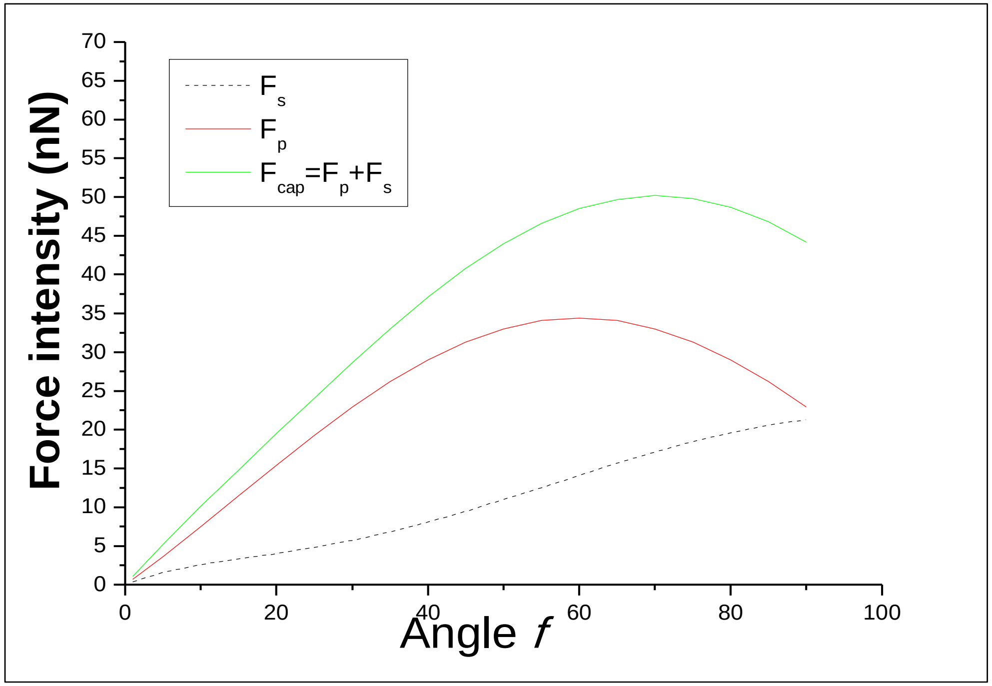
θ_p equal to θ_w

then

$$F_{cap} = F_P = 4\pi\gamma R\cos\theta$$

- 'Investigation of Humidity dependent capillary force', X. Xiao and L. Qian, Langmuir 16, 8153 (2000)
- 'Toward an accurate description of the capillary force in nanoparticle-surface interactions', O.H. Pakarinen and al, Modelling Simul. Mater. Sci. Eng. 13, 1175, (2005)

Graphical representation of capillary force and comparison with Van der Waals force



For small tip-surface distance, when RH <10%, Van der Waals interaction dominates

To remove the capillary force, two solutions : to work in UHV, very dry environment (N_2) or in liquid

French ref :E. Charlaix Team – LPMCN

$$F_{VdW} = \frac{HR}{z^2}$$

Tip radius R : 50nm

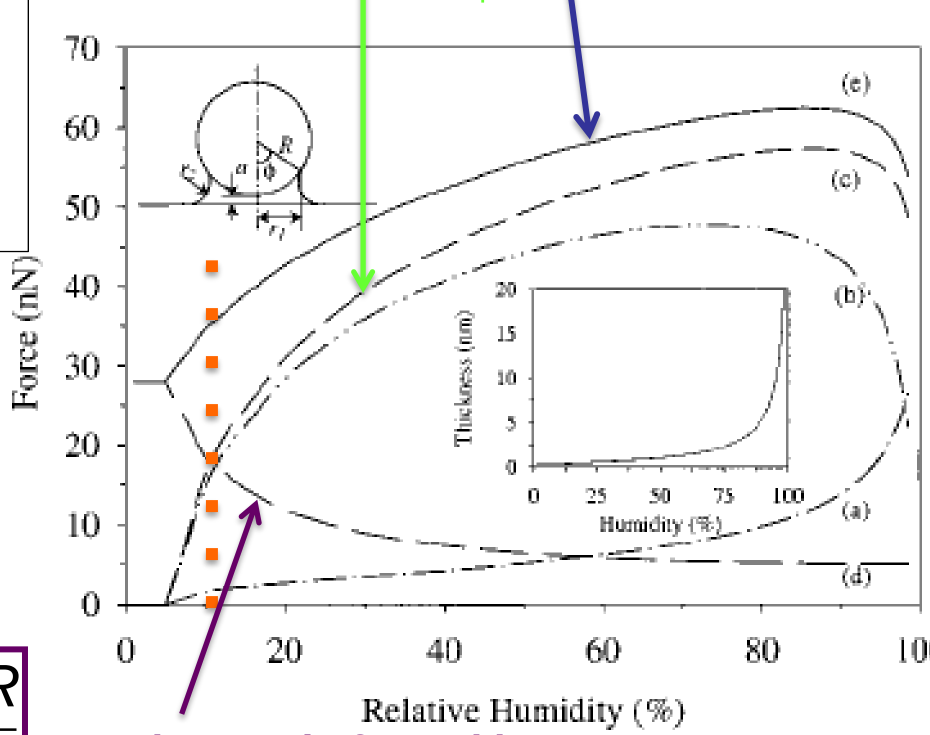
F_P: capillary pressure force

F_S : surface tension force

$F_{cap} = F_P + F_S$

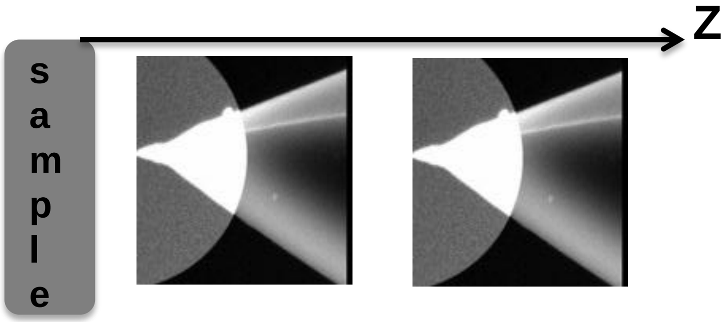
$F_T = F_{VdW} + F_{cap}$

Capillary force (F_{cap})



Van der Waals force (decrease because H varies with the media)

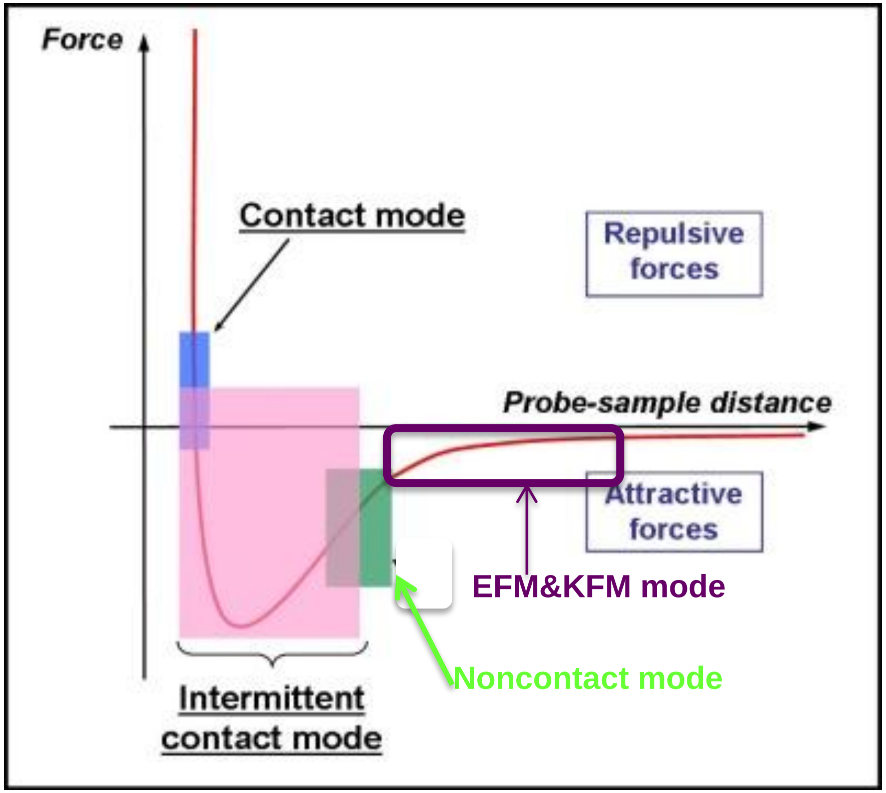
Working mode regions



Contact mode: the tip is in permanent and constant interaction with the sample in very closed to the sample : less than 1nm

Non-contact (nc) mode: the tip interacts with the sample only through long-range interactions

Electric modes based on nc mode: the tip interacts with the sample through attractive long range interactions
Tip-sample gap: several ten of nm

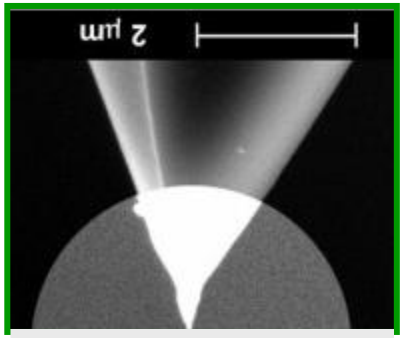


How to detect the force acting on the tip ?
➡ Need of a sensitive force sensor

AFM probe description : a clamp microlever + a fixed tip at the free end of the microlever

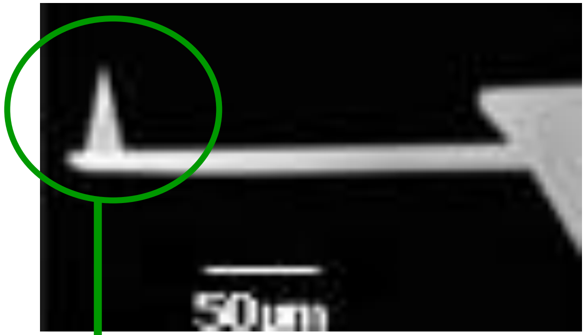
Rectangulaire chip,

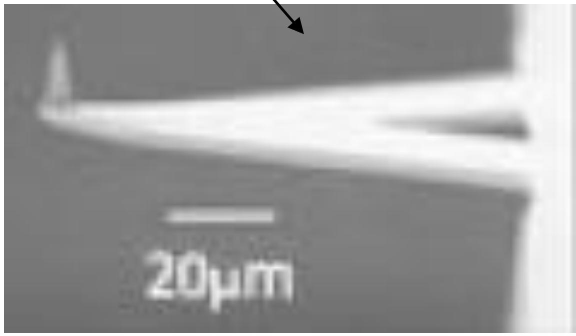
Chip size about few mm

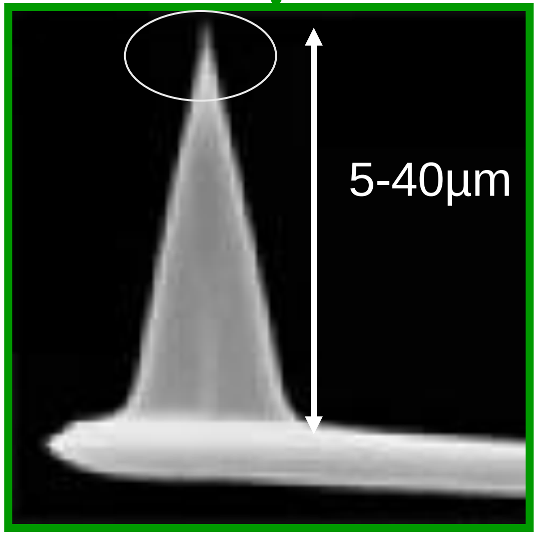


Radius of the tip apex : 1-50nm

2 standard shapes







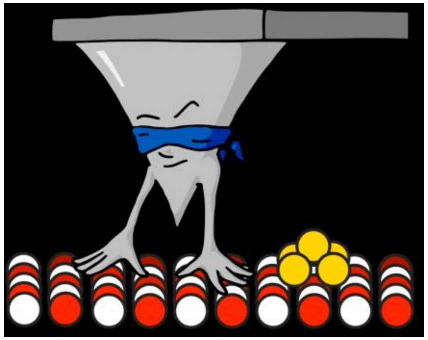
Mechanical Characteristics

$$K_Z = \frac{Ewe^3}{4l^3}$$

E : Young module of the lever material

e: thickness, *l*: length, *w*: width

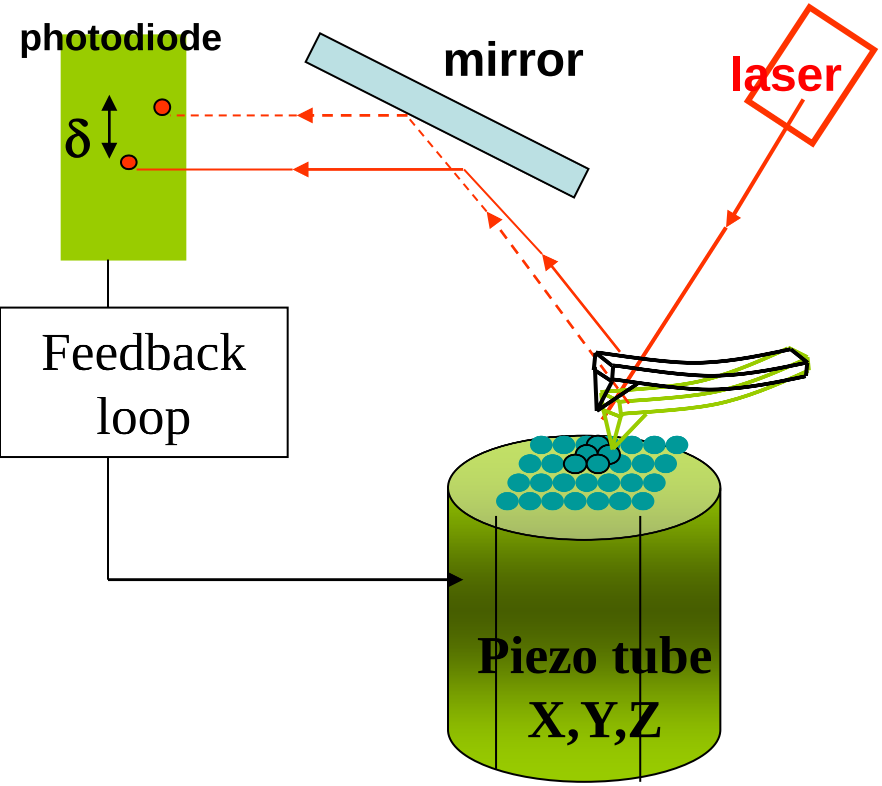
K_Z Є [0.001; 100] N/m

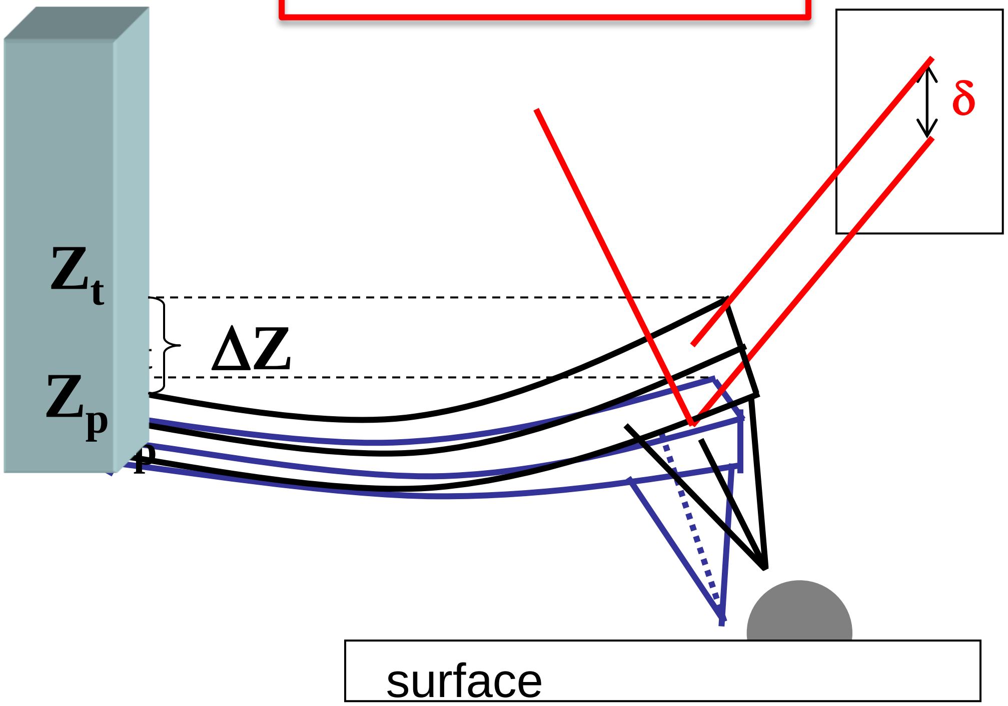


CONTACT Mode

On a homogeneous sample

$$\boxed{\vec{F}_{P/S}+\vec{F}_{P/L}=\vec{0}}$$





Measurement of δ ⇨adjustment of Z (tip-sample distance) to keep δ=0

⇨cantilever deflection constant,
⇨pressure force constant

$\delta \sim \Delta z$ and $F_i = K \bullet \Delta z = K (z_i - z_0)$

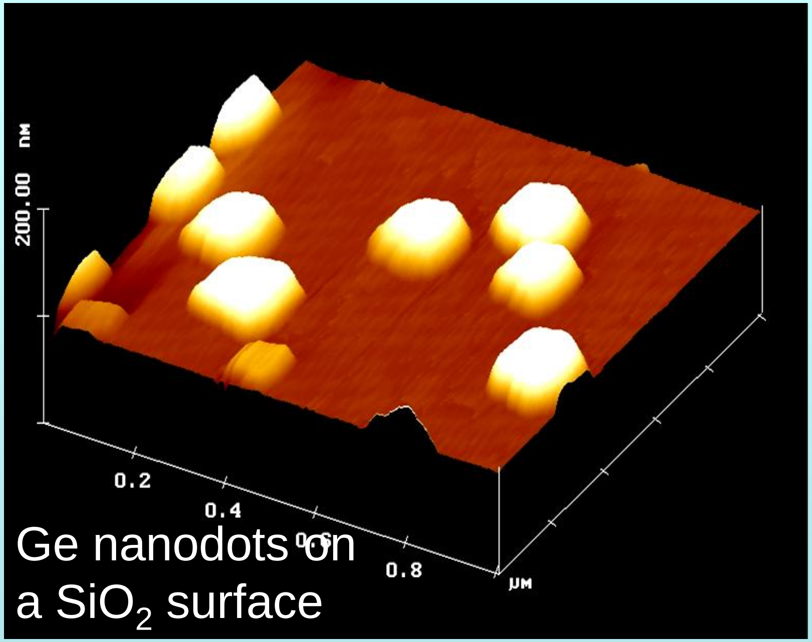
K Є [0.01; 1] N/m, soft lever

Δz Є [0.1-10^3]nm

⇨F_i Є [10^{-3}- 10^4]nN

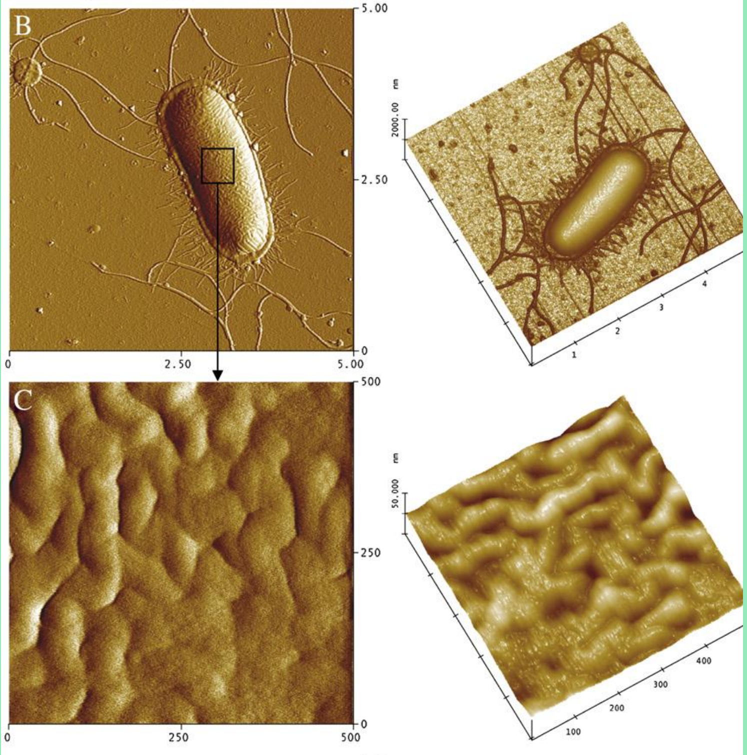
AFM Images in 3D obtained in contact mode in air

Material application



Ge nanodots on a SiO_2 surface

Biology application



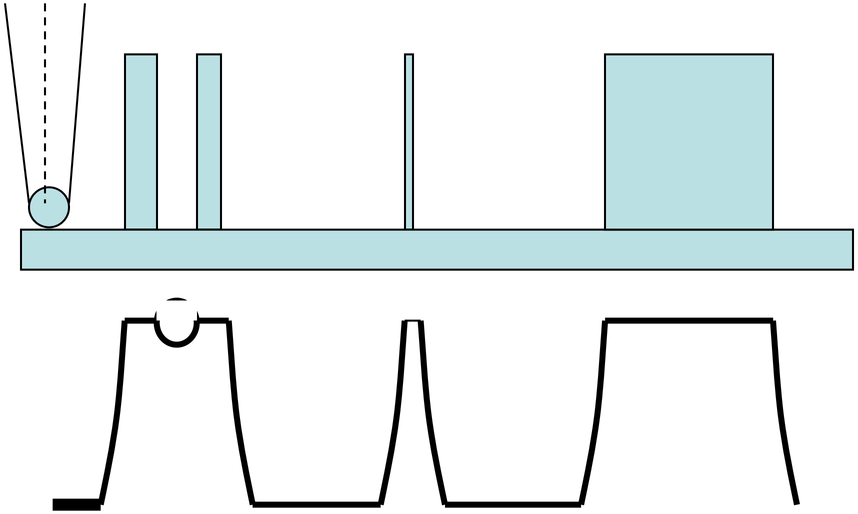
A. Li et al, Biochimica et Biophysica Acta 1768 (2007) 411–418

The contact mode is easy to use and it is well adapted for object in strong interaction with the substrate.

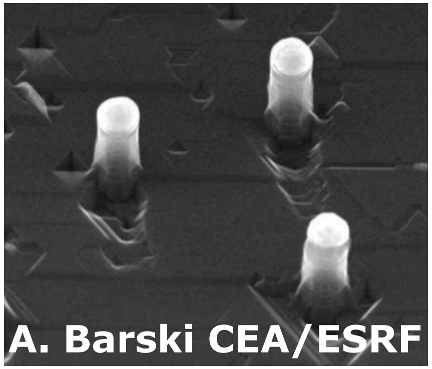
Can we trust the dimensions or shape of the scanned objects and structures from the SFM images ?

Image Artefacts

- « Convolution » effect between the tip and the surface



SEM image of Si nanowires. Height: few µm, diameter 100nm



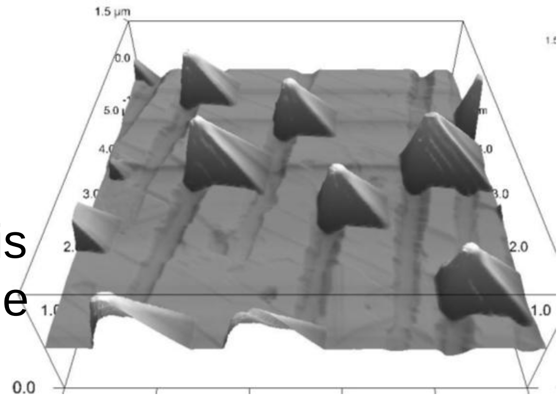
A. Barski CEA/ESRF

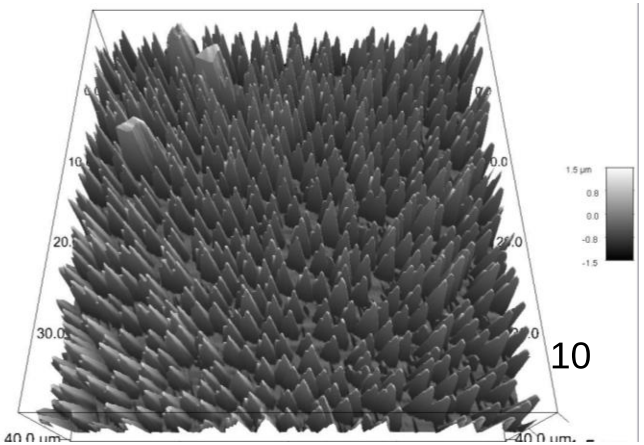
AFM Images of nanowires

Small area (5*5µm²)*1,5µm

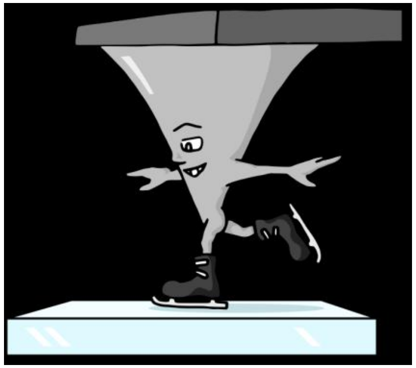
Large area (40*40µm²)*1,5µm

The Tip-sample convolution effect is visible on the image





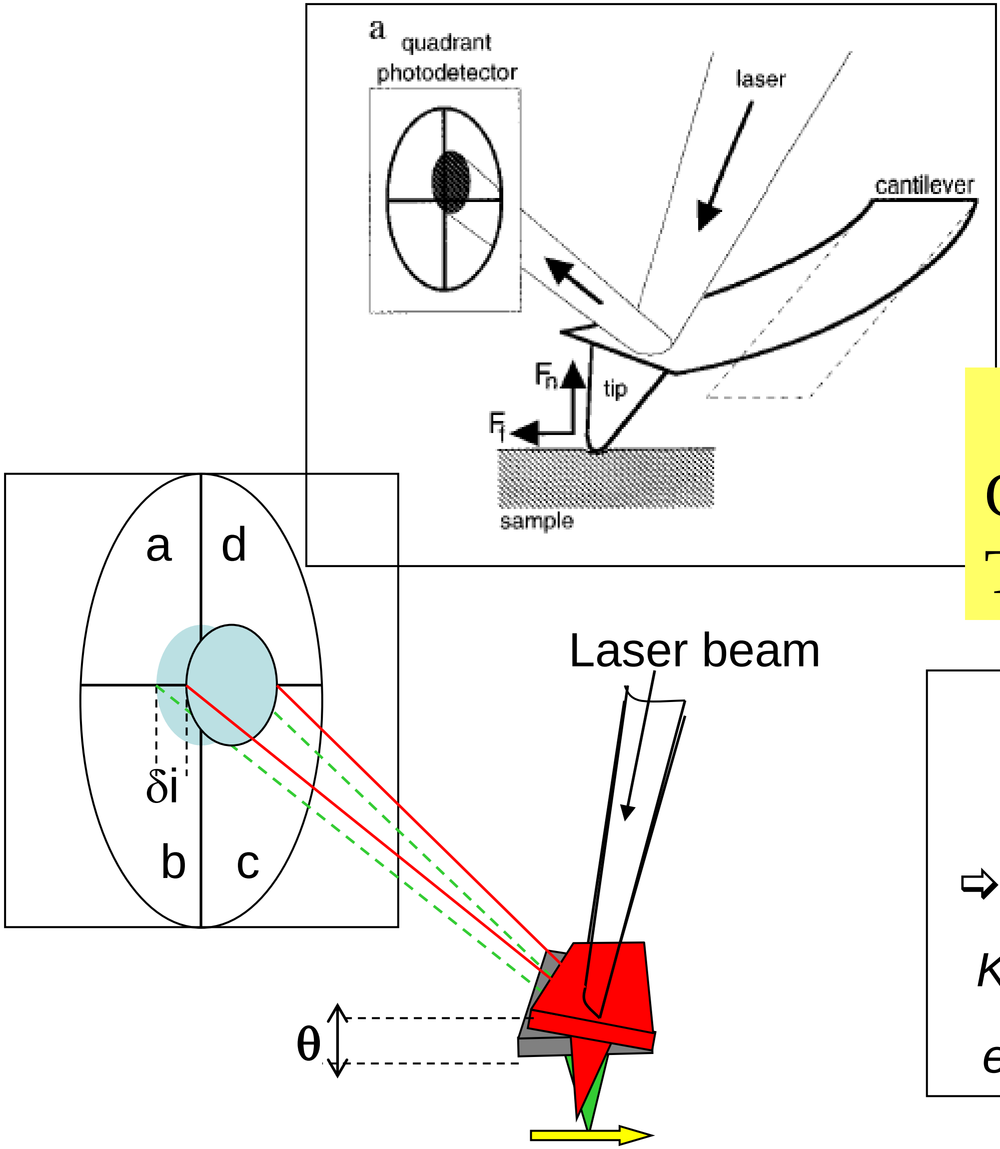
Friction mode



Friction ⇨ measurement of the tip torsion

Local measurement of friction:

contact AFM



Friction:

Constant tip velocity

Typical 10nm/sec-1micrometer/sec

$$\delta i \ \alpha \ \theta$$

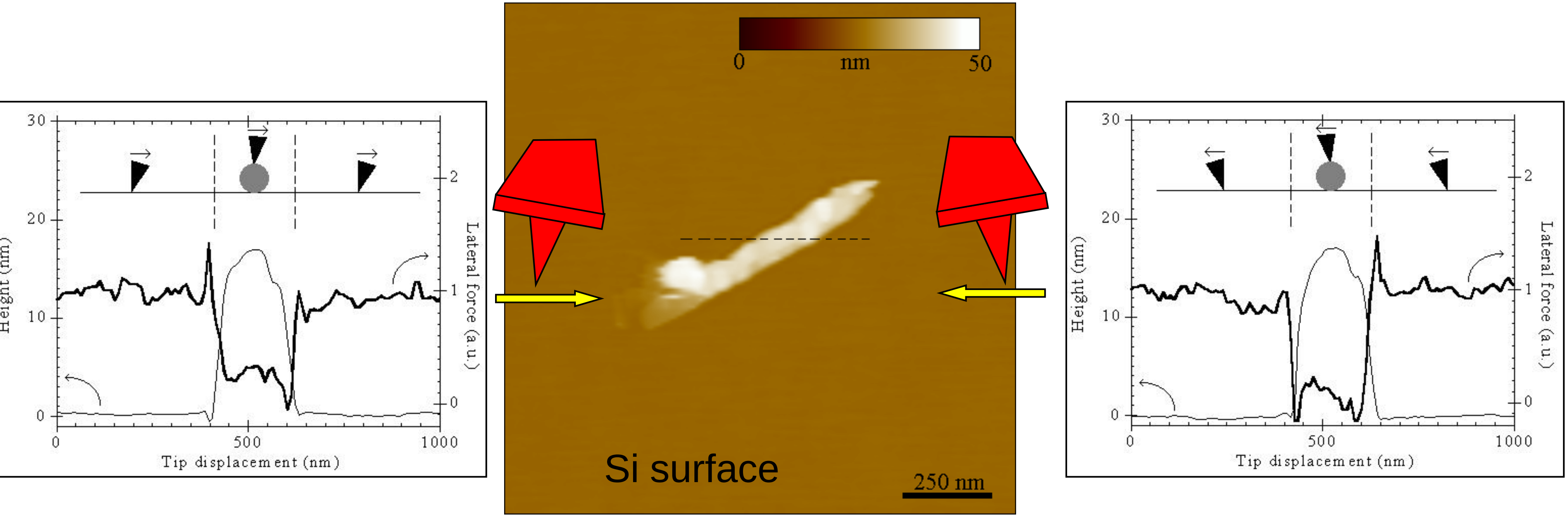
as $F_{friction} = K_{friction} \bullet \theta$

⇨δi *is a* *indirect* *measure of* $F_{friction}$

$K_{friction} = f\,(e, L, l, \text{Young module})$

e, L, l : geometry tip parameters

Friction measurement on isolated carbon nanotube



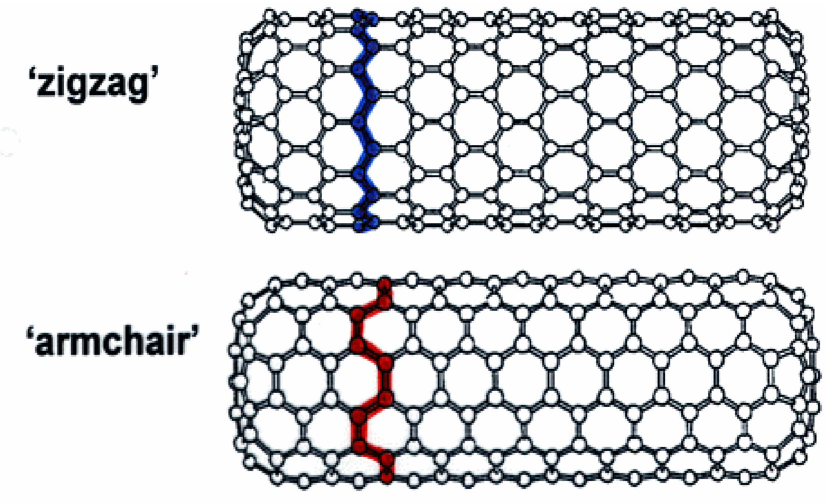
Whatever is the atmosphere (air or dry N_2):

$$\mathbf{Friction}_{\mathbf{Silicon}} \approx \mathbf{5} \times \mathbf{Friction}_{\mathbf{nanotube}}$$

Is this lower friction linked to individual properties of CNT or is it due to a geometry or shape effect ?

Individual properties of nanotubes

- Carbon nanotubes : *inorganic system*



- High dimension aspect ratio : L/d
- Hydrophobic
- Chemically inert
- Crystalline structure

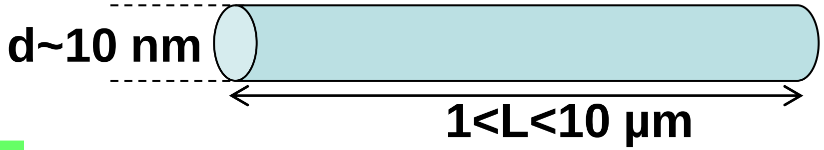
$$10 < \frac{\mathbf{L}}{\mathbf{d}} < 1000$$

- Tunicin whiskers : *a biologic nano-system*

Sea animal

Its external envelope contains cellulose filaments

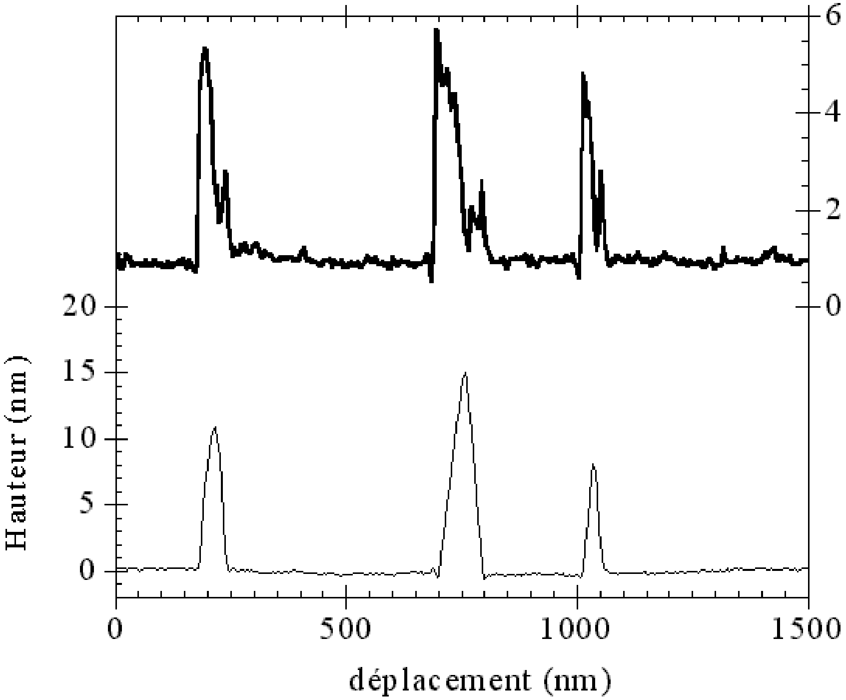
⇨ Rigidity

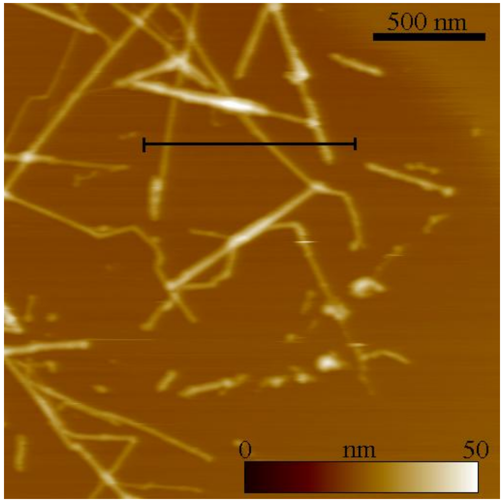


- Tunicin whisker is a full cellulose rod with a good crystalline structure
- Polarized molecules on surface whisker

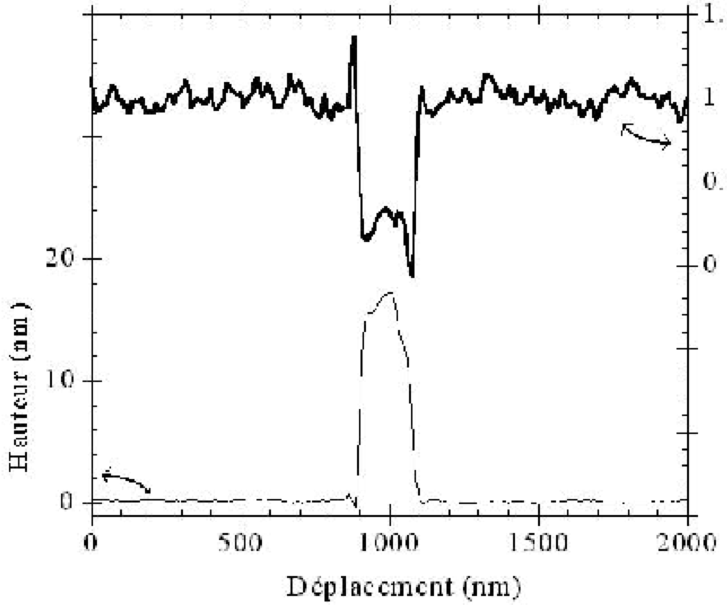
M. N. Angles and al, Macromolecules, 33, 8344, (2000)

Friction on tunicin whiskers deposited on silicon oxide surface





carbon nanotubes



- Lower friction force measured on CNT is NOT due to a geometry or shape effect

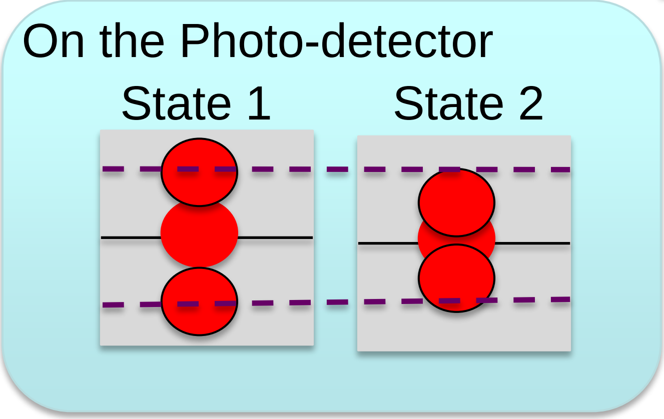
- AFM technique can give information on the friction property of an individual nano-object

Thesis of S. Decossas (2001)

Dynamic mode

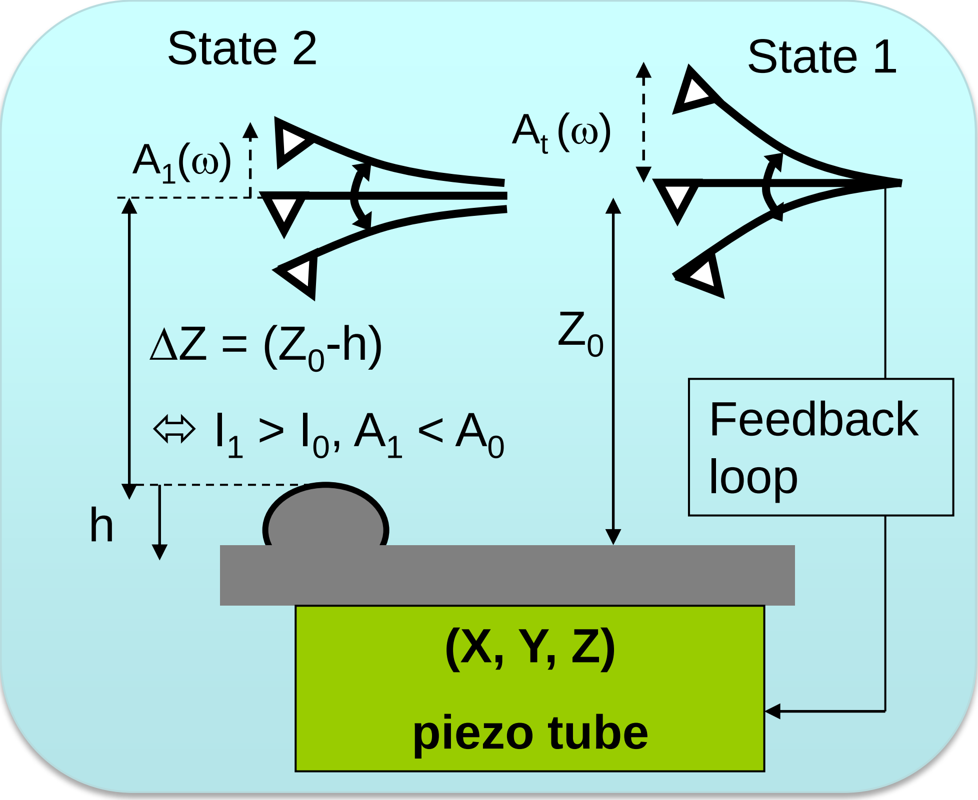
Key points:

- **When the probe is oscillating, the lever movement is sensitive to the tip-surface force gradient**
- **The tip apex is not in permanent mechanical contact with the sample: → reduction of the friction force**
  → well adapted for soft sample



- Cantilever stiffness k>10N/m to avoid jump to contact
- Measurement of δA ⇨ adjustment of $\Delta Z = Z_0$ by using the piezo tube

Record of ΔZ in each (X,Y) ⇨ 3D map

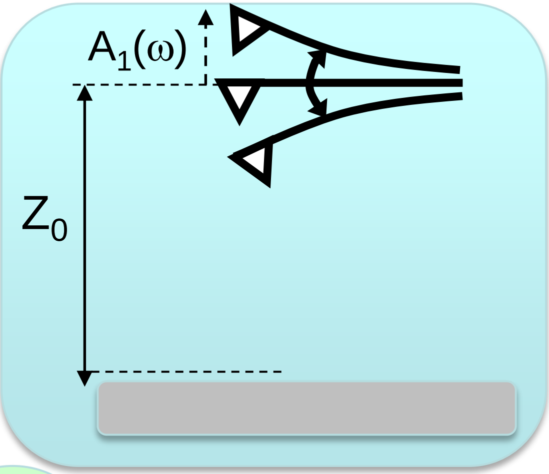


Small perturbation of the oscillator thanks to a light interaction

$$\ddot{Z}_T + \gamma\dot{Z}_T + \omega_0^2 Z_T = \frac{K_L Z_P}{m^*}\cos(\omega t) + \boxed{\frac{F(Z_{T/S})}{m^*}}$$

No direct solution because F($Z_{T/S}$) is not known

Hypothesis: small oscillations around Z_0



$$F(Z_{T/S}) \approx F(Z_0) + Z\frac{\partial F}{\partial Z}(Z_0)$$

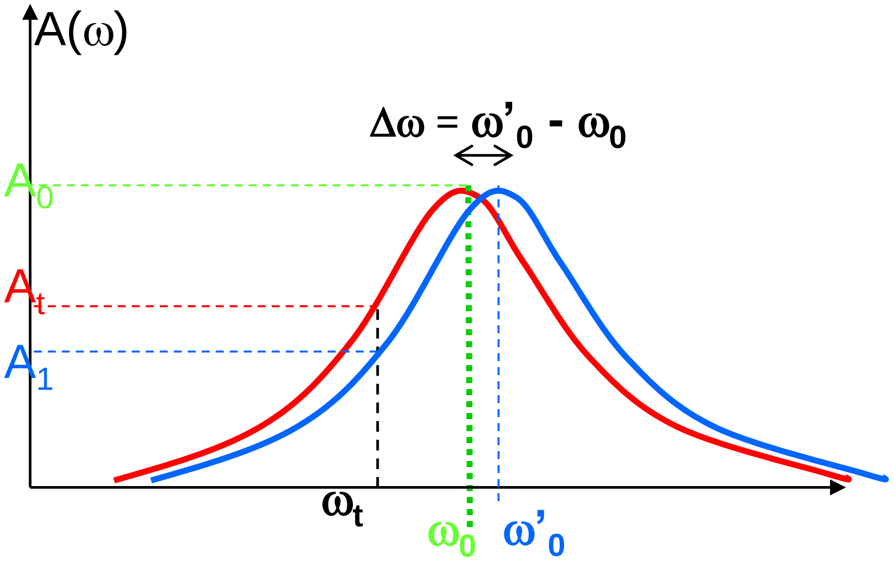
therefore:

$$\ddot{Z}_T + \gamma\dot{Z}_T + [\underbrace{\omega_0^2 - \frac{1}{m^*}\frac{\partial F}{\partial Z}(Z_0)}_{\omega_1^2}]Z_T = \frac{K_L Z_P}{m^*}\cos(\omega t) + \frac{F(Z_0)}{m^*}$$

Constant force :
Static deflection of the cantilever

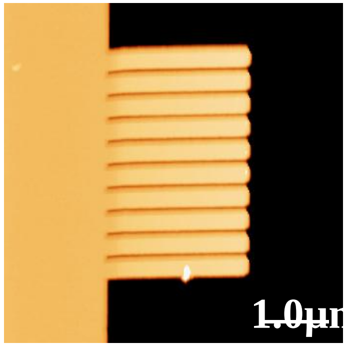
$$\boxed{\omega_1 \approx \omega_0\left(1 - \frac{1}{2K_L}\frac{\partial F}{\partial Z}(Z_0)\right)}$$

Effect of the Variation of Tip-surface interaction on the oscillator response : graphical representation



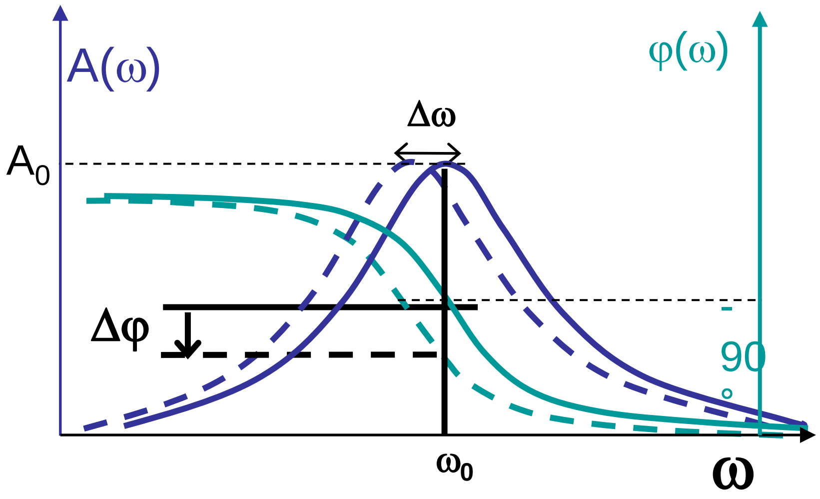
ω_0: AFM probe resonnance frequency

$$\omega_1 - \omega_0 = \Delta\omega = -\frac{\omega_0}{2K_L}\frac{\partial F}{\partial Z}(Z_0)$$



160 nm thickness,
100nm width

NEMS frabricated by LETI-CEA



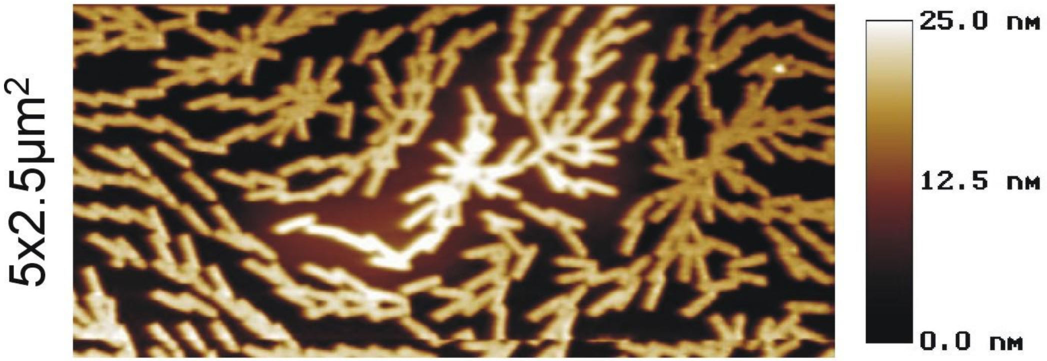
Attractive Force => Phase decrease: **$\Delta\varphi < 0$**

Repulsive force => shift of the amplitude curve *A=f(ω)* on the right (from red to blue)

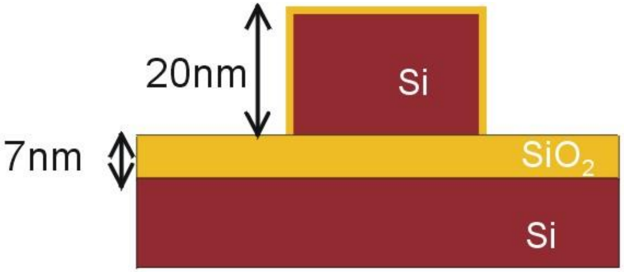
Attractive Force => opposite shift

Interpretation of dynamic mode image

Topography Image

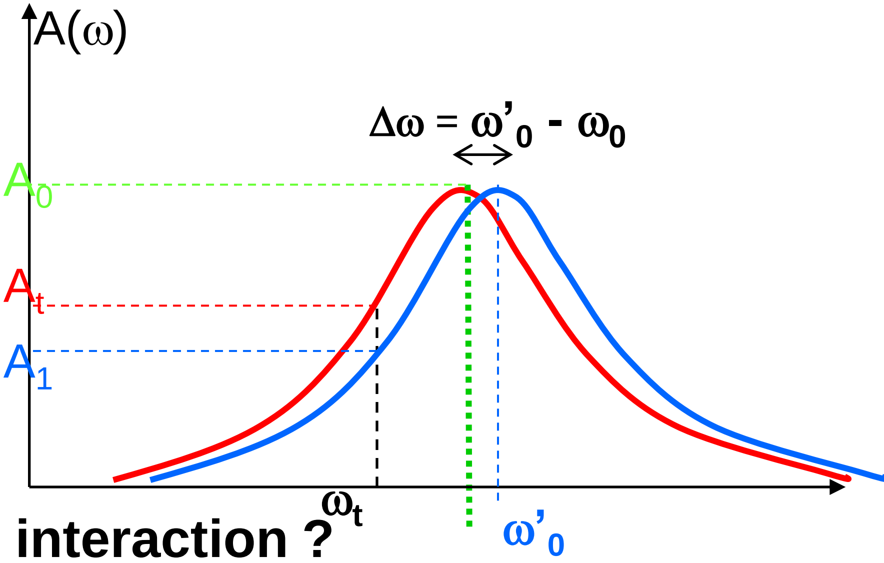


Sample description



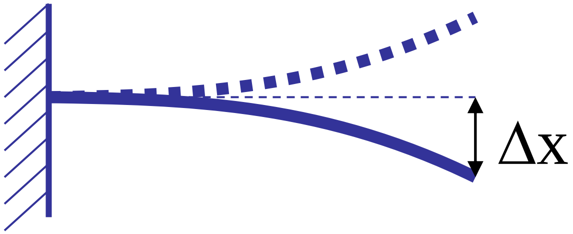
The highest feature on the image center : is it linked to a real morphology or a change of interaction ?

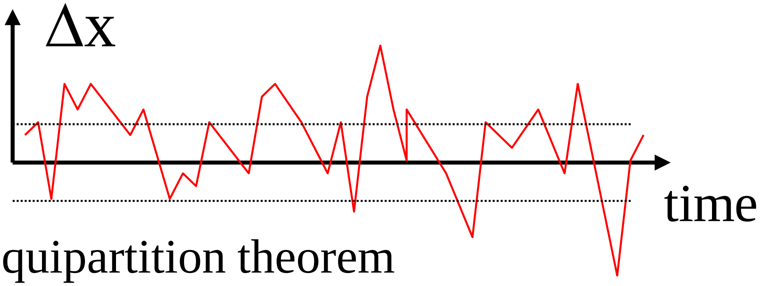
$$\omega_1 - \omega_0 = \Delta\omega = -\frac{\omega_0}{2K_L}\frac{\partial F}{\partial Z}(Z_0)$$



What is the minimum detectable interaction ?
What is it happening when A ≈ Z_0 ?

Thermodynamic Fundamental limits: Brownian motion





The Brownian motion of the lever is given by the equipartition theorem

$$\frac{1}{2}K\left\langle \Delta x^2 \right\rangle = \frac{1}{2}k_BT$$

$$\text{Average noise amplitude} = \sqrt{\left\langle \Delta x^2 \right\rangle} = \sqrt{\frac{k_BT}{K}} = \sqrt{\frac{1.38x10^{-23}x300}{0.02}} = \boxed{0.45\text{nm}}$$

$$\text{Average noise force} = K\sqrt{\left\langle \Delta x^2 \right\rangle} = \sqrt{K\,k_BT} = \boxed{9.1\text{ pN}}$$

Minimum detectable force gradient

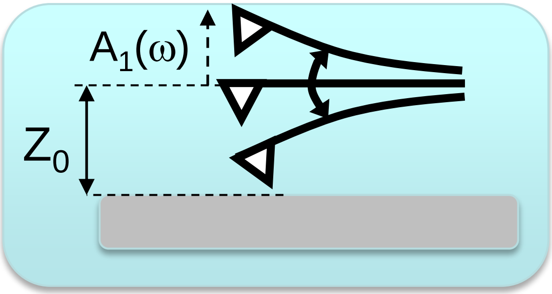
$$\left.\frac{\partial f}{\partial z}\right|_{min} = \frac{1}{A_m}\sqrt{\frac{27k_BTBk}{\omega_0 Q}}$$

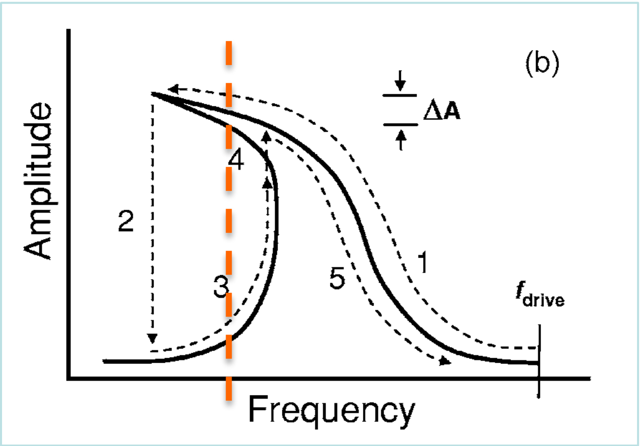
$$\left.\frac{\partial f}{\partial z}\right|_{min} \approx 10^{-5}\,N.m^{-1}$$

- A_m = 10-20 nm
- k_BT = 26 meV ambient temperature
- Q =100-300 ambient pressure
- k = 0.1-1 N/m
- ω_0 = 20 -100 kHz
- B = 500 Hz

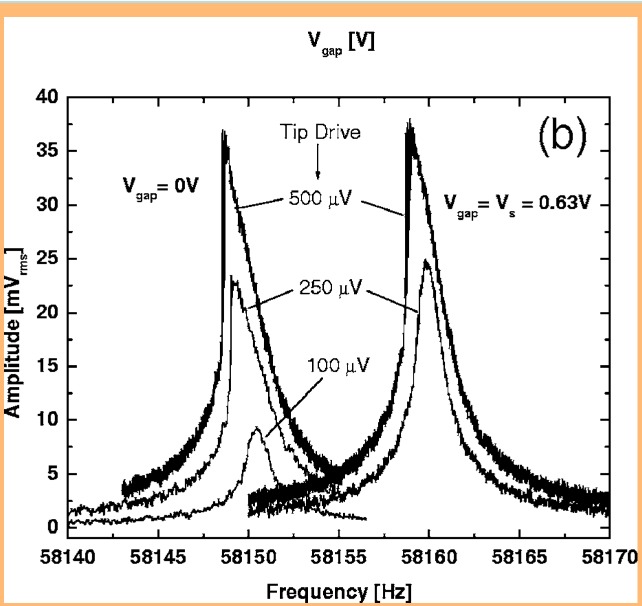
French ref : 3 rapports internes du LETI rédigés par F. Bertin et al et son manuscrit de HDR
Travaux de Ludovic Bellon – ENS Lyon

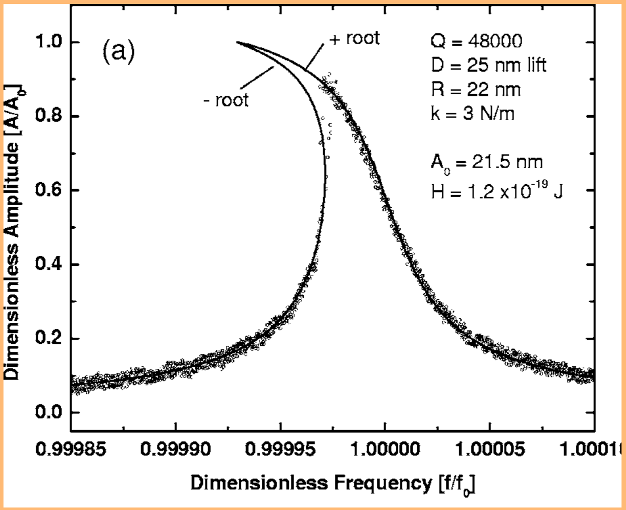
When the oscillation amplitude is about the same order of magnitude than the tip-surface distance…. Tapping mode





Presence of bi-stable positions for the cantilever: for a same f correspond two value of A



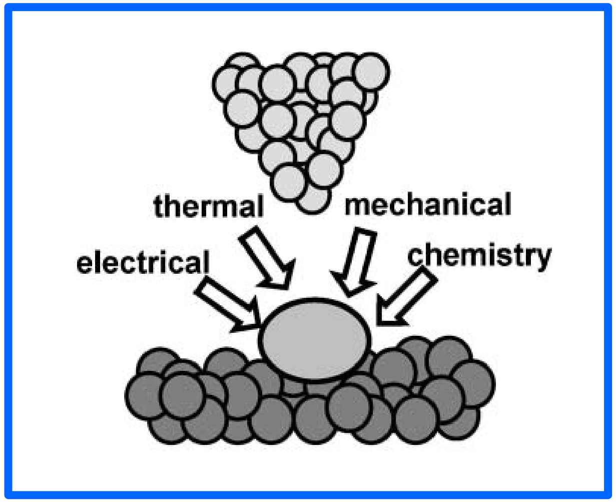


M. Gordon and T. Baron, Phy Rev B 72, 165420 (2005)

Travaux de J. P Aimé - Bordeaux

AFM tip : fabrication tool at the nanoscale Scanning Probe Lithography

Idea : To use the spatial confinement of a chemical, electrical, mechanical or thermal reaction, within a nanometer-size region define by the tip-sample gap.



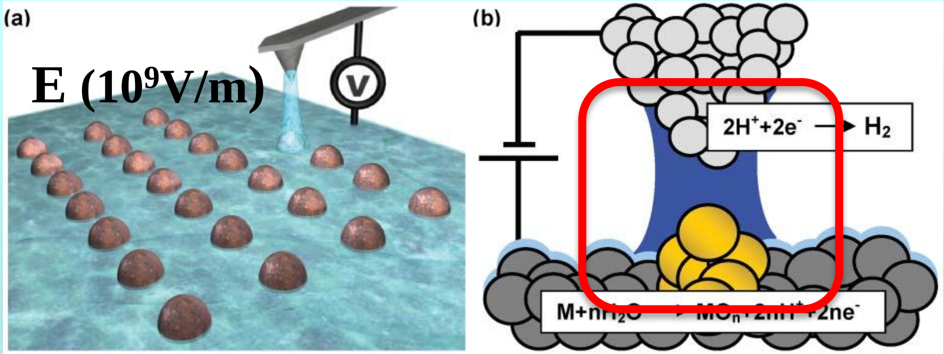
- **Dip pen nanolithography**
- **Nanoshaving, nanografting**
- **Local oxidation nanolithography**
- **Thermal nanolithography**

Aims: Design of smart and innovative nanoscale Devices for nano-electromechanic, nano-nose, optomechanics, nanoelectronics

Local oxidation nanolithography (LON) by AFM

Required conditions:

- **Ambient atmosphere**
- **Conductive Surface**
- **Conductive AFM tip**
- **Contact or dynamic mode**



Chemical Reactions in the nanocell:

Anodic reactions

$M + nH_2O \rightarrow MO_n + 2nH^+ + 2ne^-$ (a)

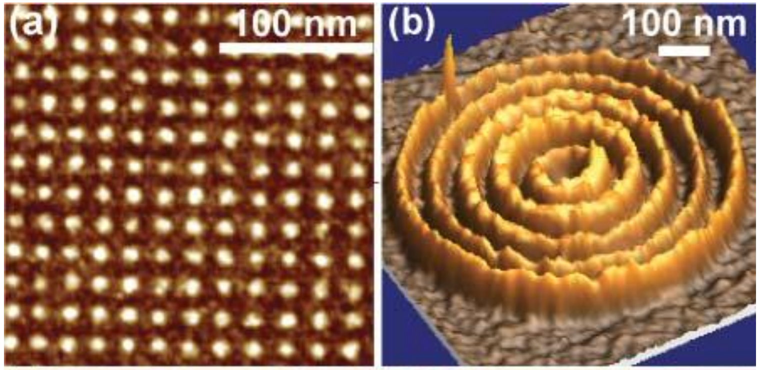
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ (b)

Cathodic reaction

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (c)

Nano-electrochemical cell:
Water: electrolyte
Tip : cathode
Lateral dimension : 20nm
5.10^4 molecules

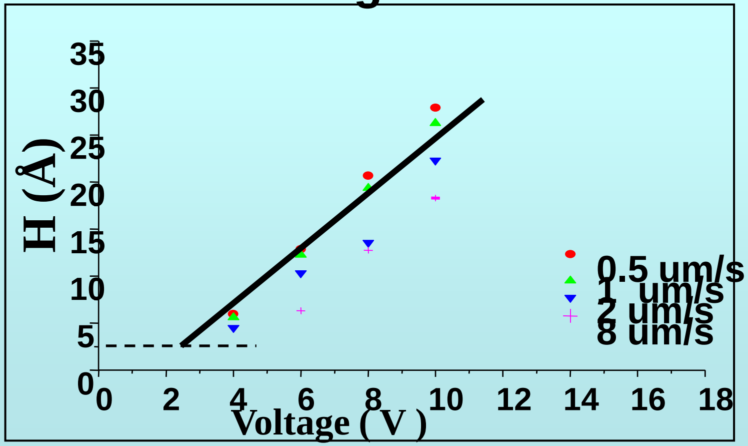
SiO_2 nanostructures



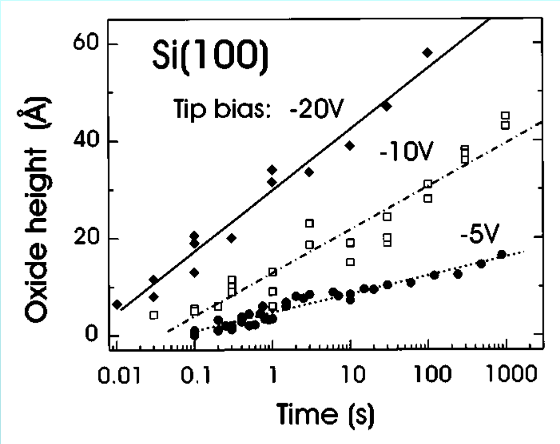
Ref : “Nano-chemistry and scanning probe nanolithographies”, R. Garcia and al, Chem. Soc. Rev, 35, 29-38 (2006)

Key parameters on the dimensions and chemical composition of the oxide nanopattern

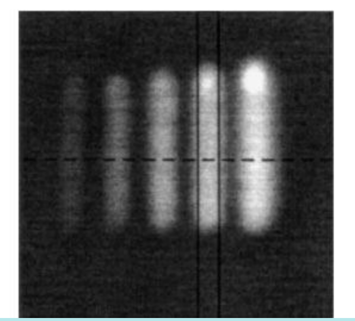
H versus Voltage : linear variation



H versus Speed : log variation



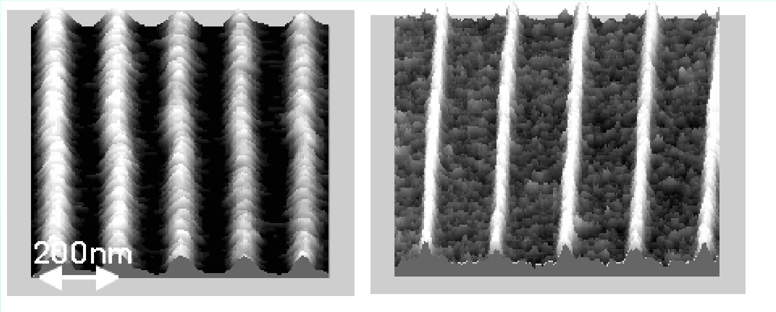
Working environment



NH_4 gaseous Si_3N_4 oxide pattern

J. L. Pyle, J. Vac. Sci. Technol. B 15, 38 (1997)

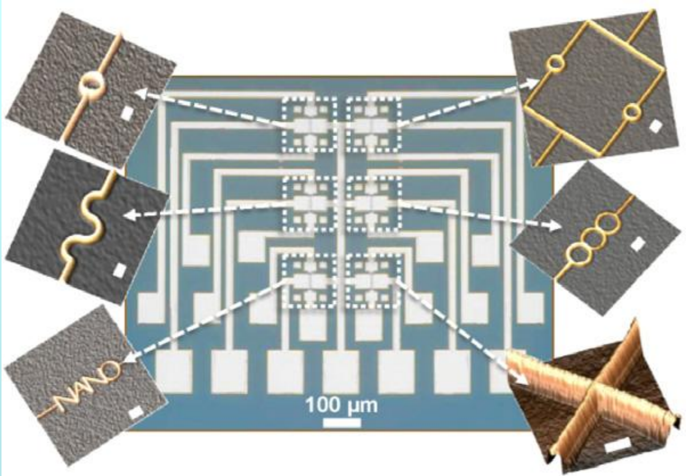
Humidity rate



Ph. Avouris Appl. Phys. Lett. **71**, 14 July 1997

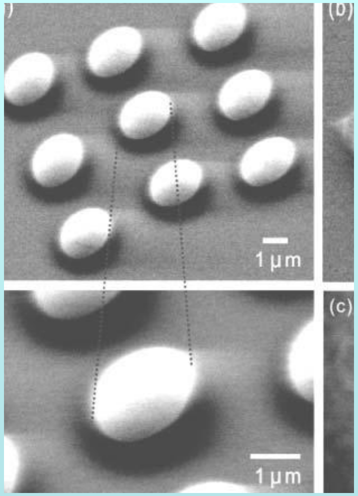
Examples of SC and metallic devices and micro-components fabricated by SPL

Silicon devices based on nanowires[1]

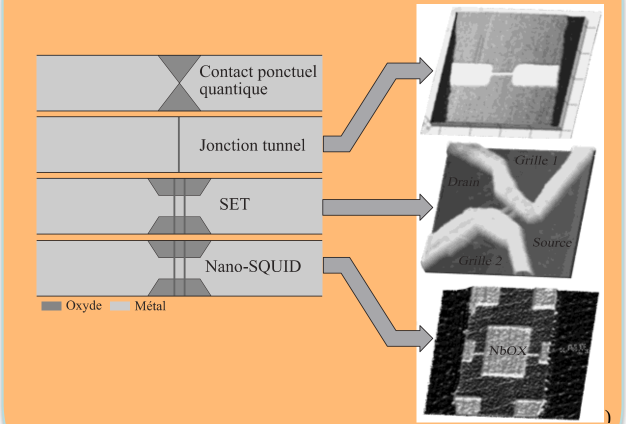


100nm

Si optics lenses[2]
MEOMS

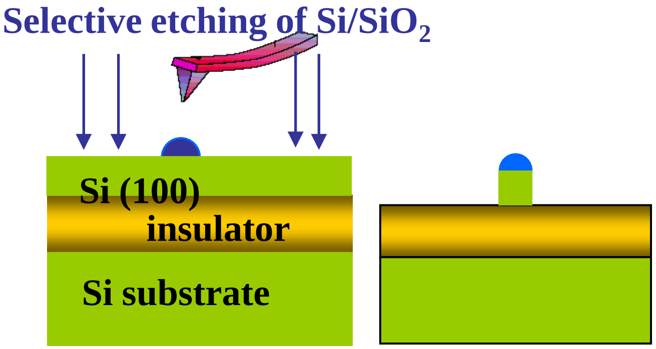


Metallic devices[3]



Nb, Ti

Oxide pattern as a mask on SOI substrate



[1] R V Martinez et al, Nanotechnology 21 (2010) 245301

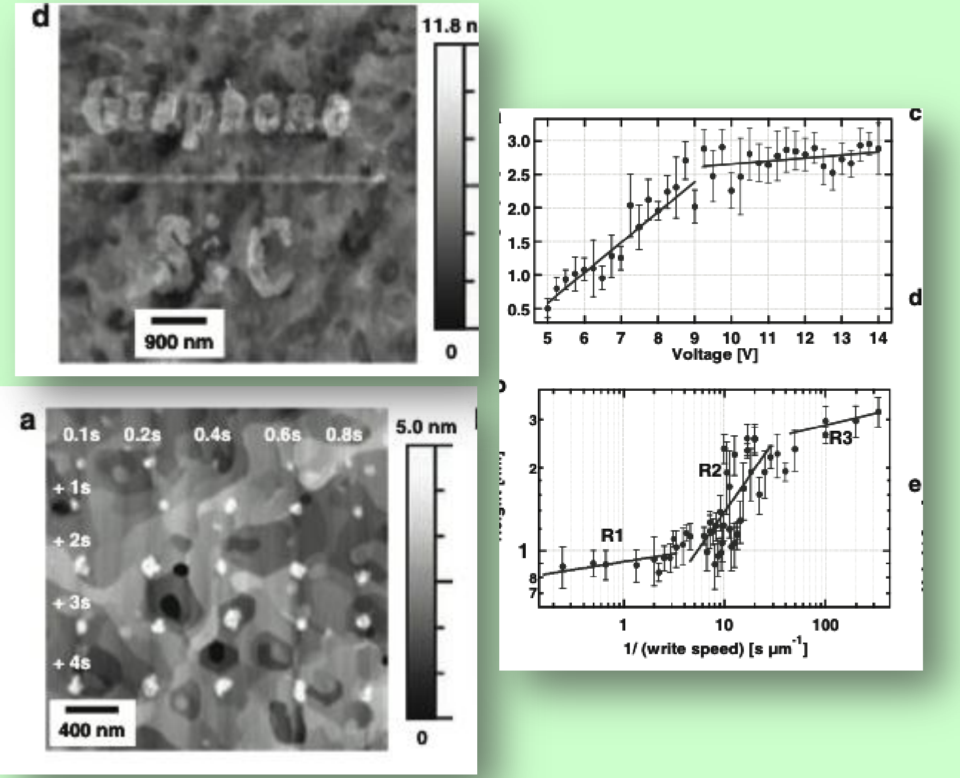
[2] C. F. Chen,et al, Opt. Lett., 2005, 30, 652.

[3] M. Faucher et al, Physica C, 368, 211 (2002)

French groups : D. Tonneau-CINAM; D. Stievenard - IEMN Lille, V. Bouchiat –Insitut Néel Grenoble

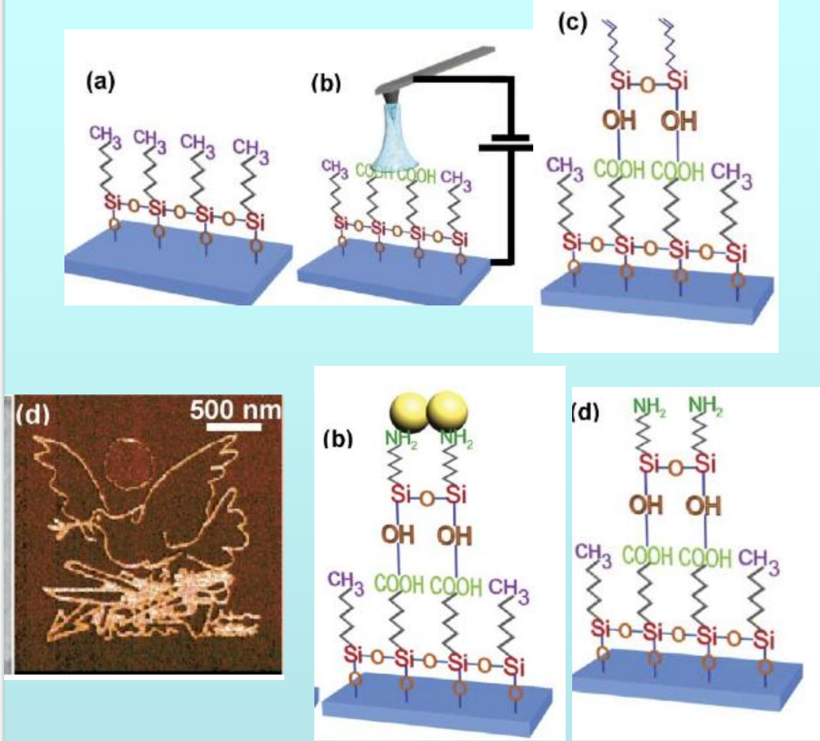
SPL on others materials : carbon like material and self-assembled monolayer

On Epitaxial Graphene on SiC (0001) in ambient conditions



Justice M. P. Alaboson et al, Adv. Mater., XX, 1–4 (2011)

Nanopatterming of self-assembled monolayer

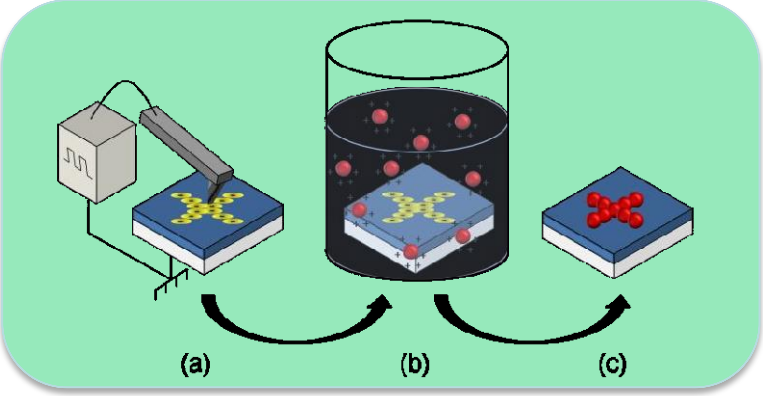


R. Maoz et al, Adv. Mater., 12, 725 (2000)
S. T. Liu et al, Nano Lett., 4, 845 (2004)

Nanoxerography

Nanoxerography

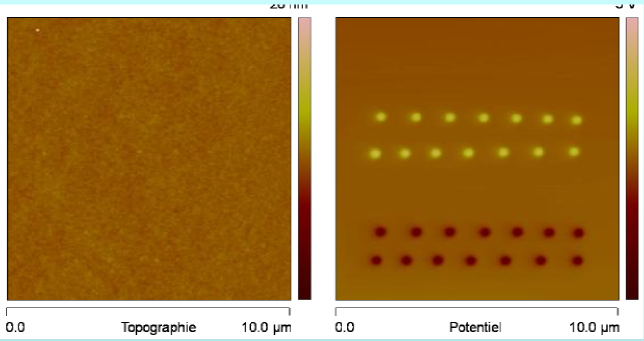
Principle: use the tip as a local electrode to inject electric charge in insulator film and use this local electric pattern to trap micro and nano-objects



- Gold particles 2-50nm
- 50-100 nm Polystyrene or silica spheres
- Biomolecules

S. Tzeng, et al, Template self-assembly of colloidal nanoparticules controleed by electrostatic nanopatterning on a $Si_3N_4/SiO_2/Si$ electret" , Adv. Mater., 18, 1147-1151 (2006).

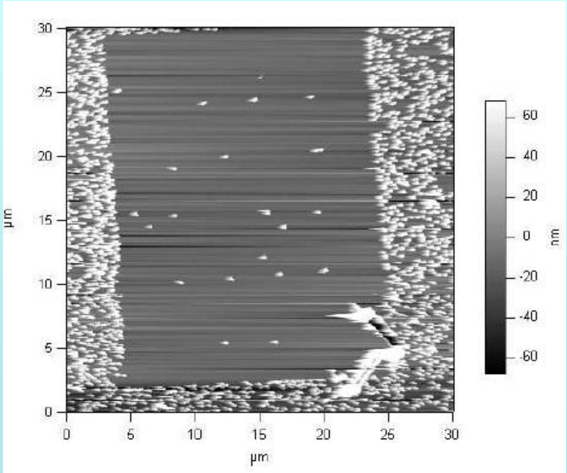
Local charged spots on PMMA layer on conductive substrate



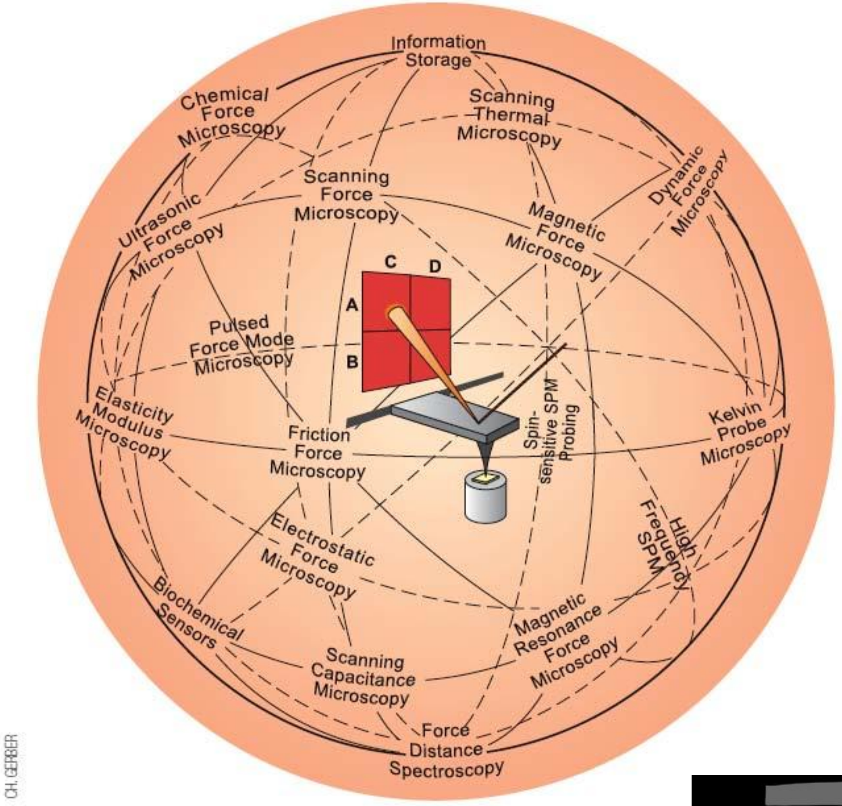
(a)

French ref : Laurence Ressier – LPCNO – Toulouse: HDR thesis

Individual Electric trap for 100nm latex nanoparticules

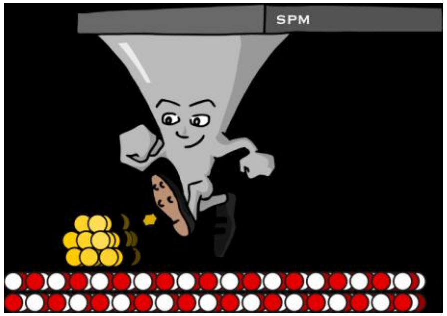


Conclusion…..



Gerber *et* Lang, 2006.

- **Two main AFM modes for imaging from micro to nanometer scale through wide range of forces.**
- **SPL : versatile, various and low cost technique for academic researcher to fabricate/imagine nano-structures**

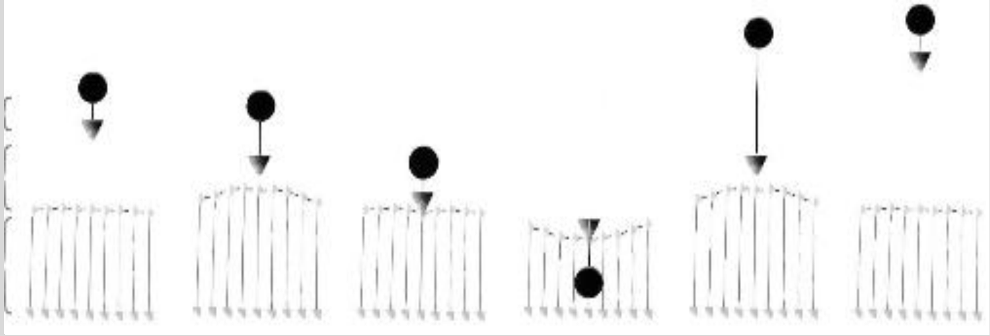


Nanomanipulation by AFM

Come to try the virtual force feedback nanomanipulateur !!!

● Nanomanipulateur virtuel: Scènes en 2D interactives et contrôlables via le système haptique

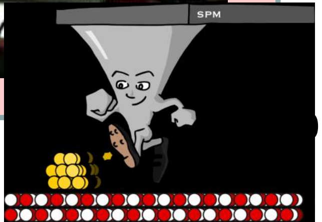
Scène multi-sensorielle en 1D : Spectroscopie de force

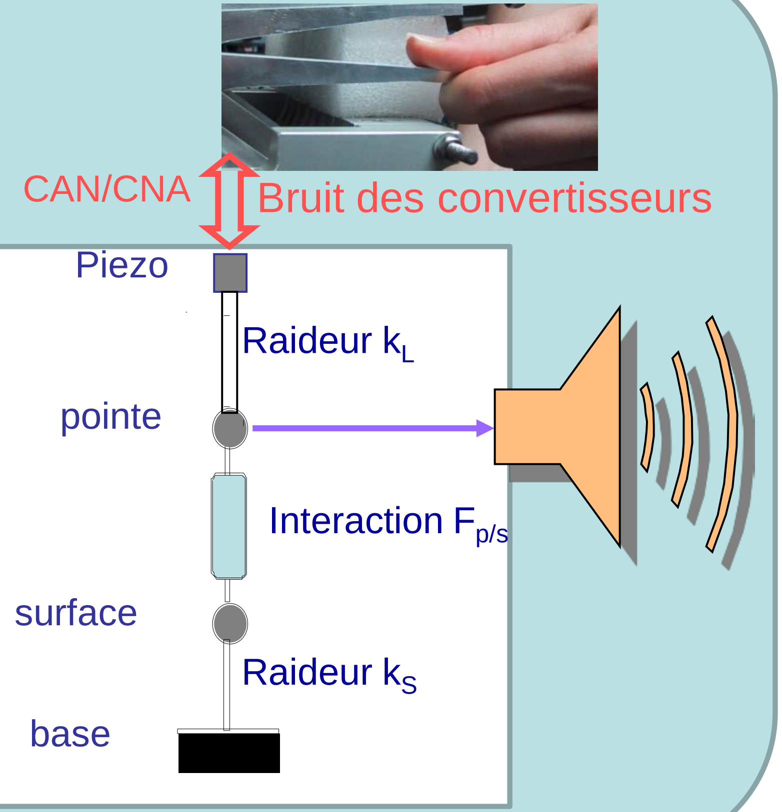


$F_l = -A/Z - B/Z^2 + C/Z^3$

Scènes virtuelles en 2D :

manipulation d'un nano-objet sur une surface





Atelier Nanomanipulateur à retour de force