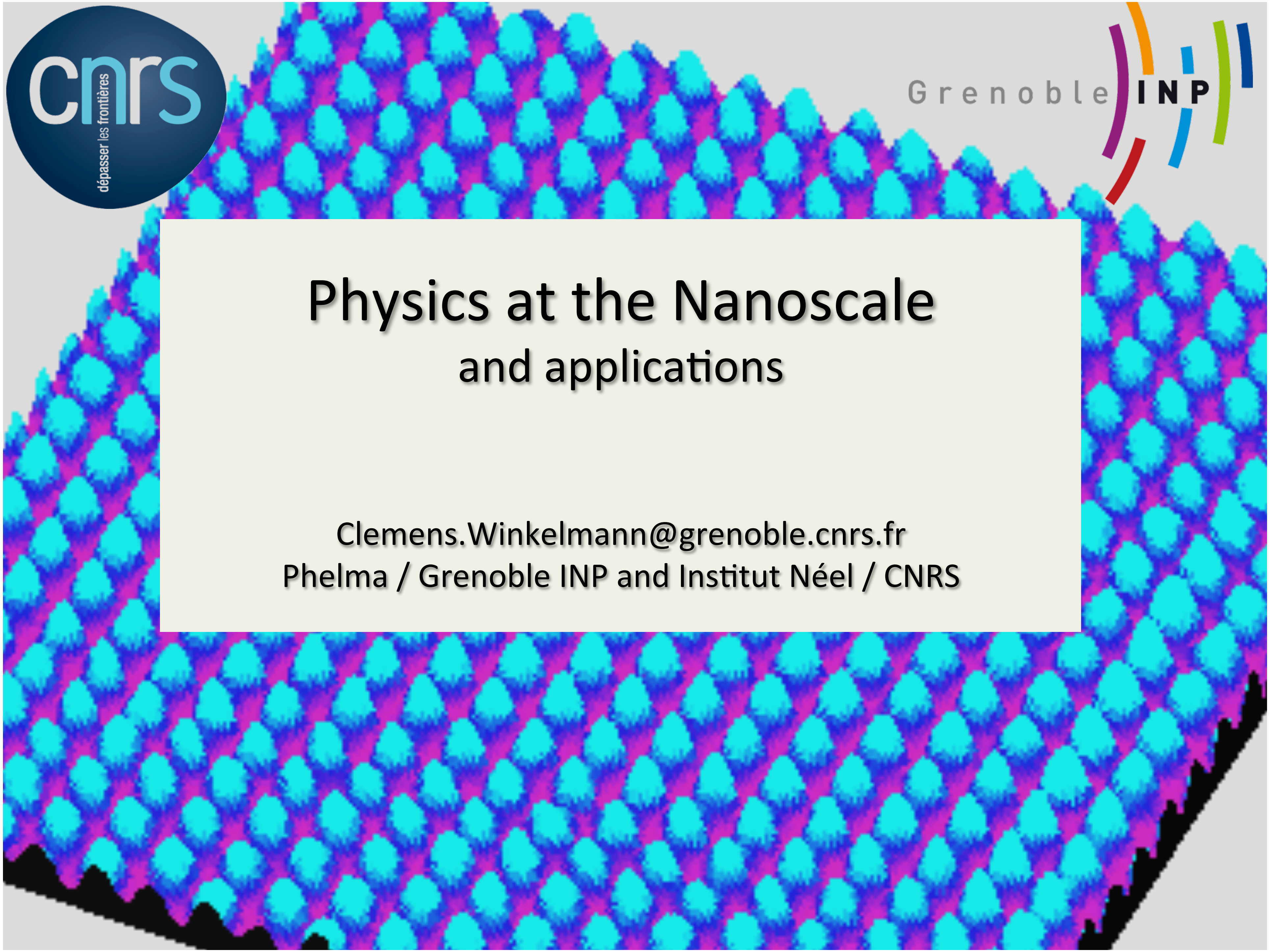


Physics at the Nanoscale
and applications

Clemens.Winkelmann@grenoble.cnrs.fr
Phelma / Grenoble INP and Institut Néel / CNRS

Physics at the Nanoscale

I Basics of quantum mechanics
II Statistical Physics
III Forces at the nanoscale and applications to AFM
IV Electron tunneling and applications
V Quantum electronic transport

Forces at the nanoscale

1/ Introduction.

2/ Capacitive forces.

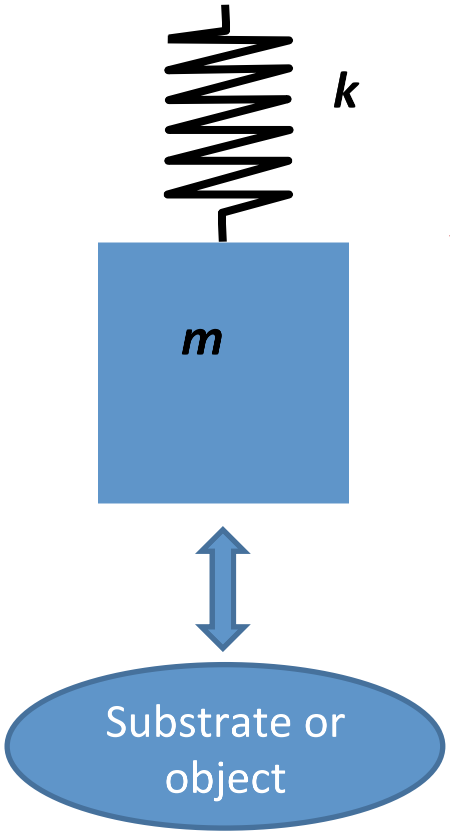
3/ van der Waals forces.

4/ Casimir Force.

5/ Application to Scanning Probe Microscopy.

Thanks to Thierry Ouisse for providing his lecture on the subject

General equation of a first-order mechanical system



2[nd] Newton's law: $$\mathbf{F} = m\gamma$$

$$m\ddot{z} = -kz - \beta\dot{z} + F_{exc} + F_{\text{int}}$$

spring force ($-kz$)

damping ($-\beta\dot{z}$)

forced excitation (F_{exc})

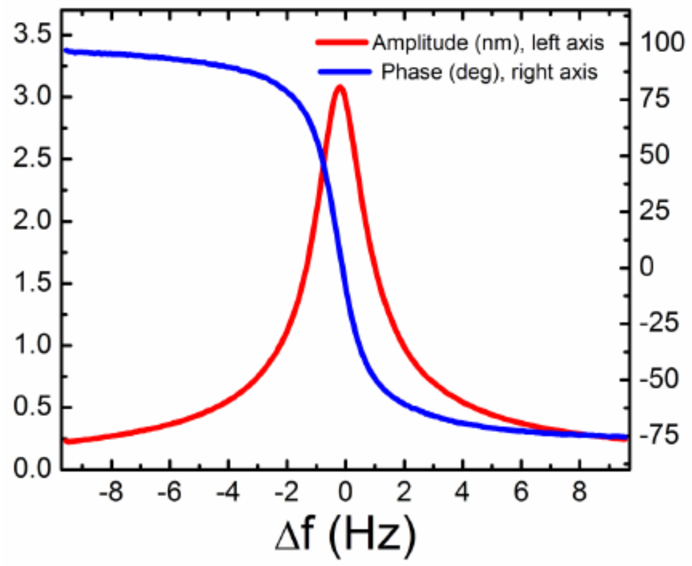
interaction with something else (F_{int})

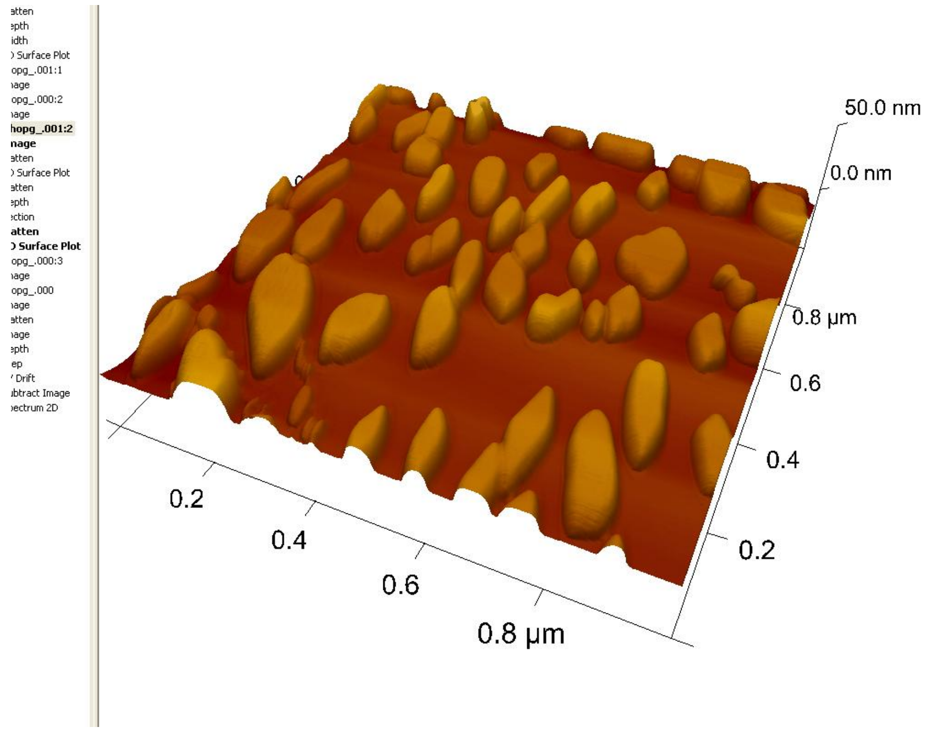
If interaction is small:

$$F_{\text{int}} = F\big|_{z=z_0} + (z - z_0)\frac{\partial F}{\partial z}\bigg|_{z=z_0} = F_0 + z\nabla F$$

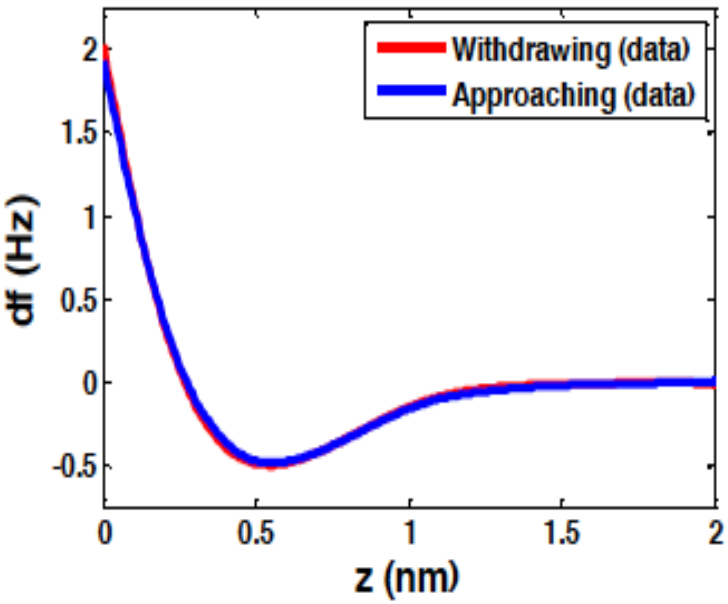
$$\ddot{z} + \frac{k - \nabla F}{m} z + \frac{\omega_0}{Q}\dot{z} = (F_{exc} + F_0)/m$$

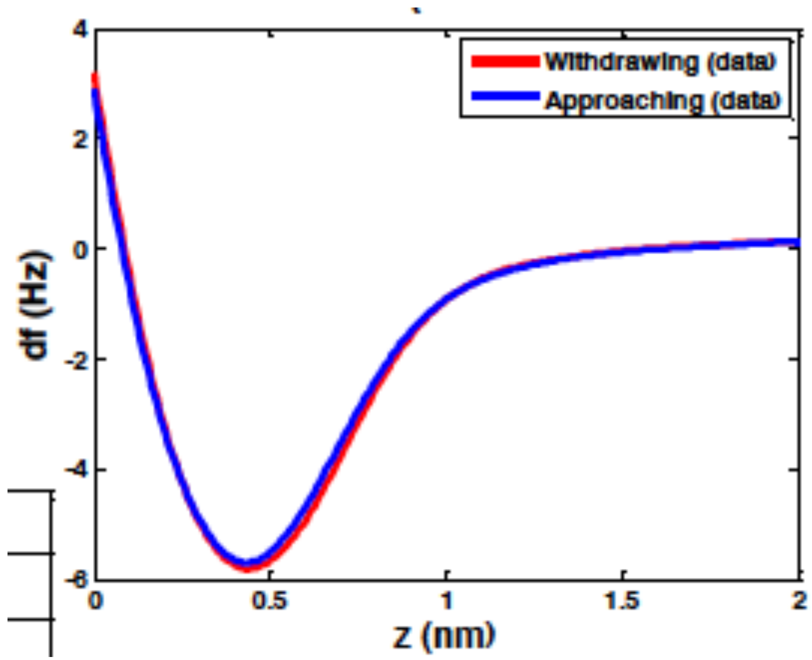
The only noticeable modification imposed by a small interaction is a variation of the spring constant equal to the gradient of the force.





$$\Delta f = f - f_0 = \frac{f_0}{2k}\left(\frac{\partial^2 U_{ts}}{\partial z^2}\right)$$

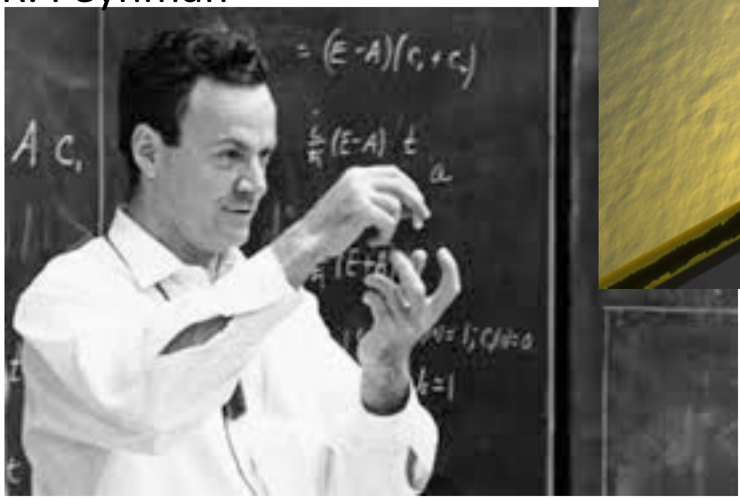


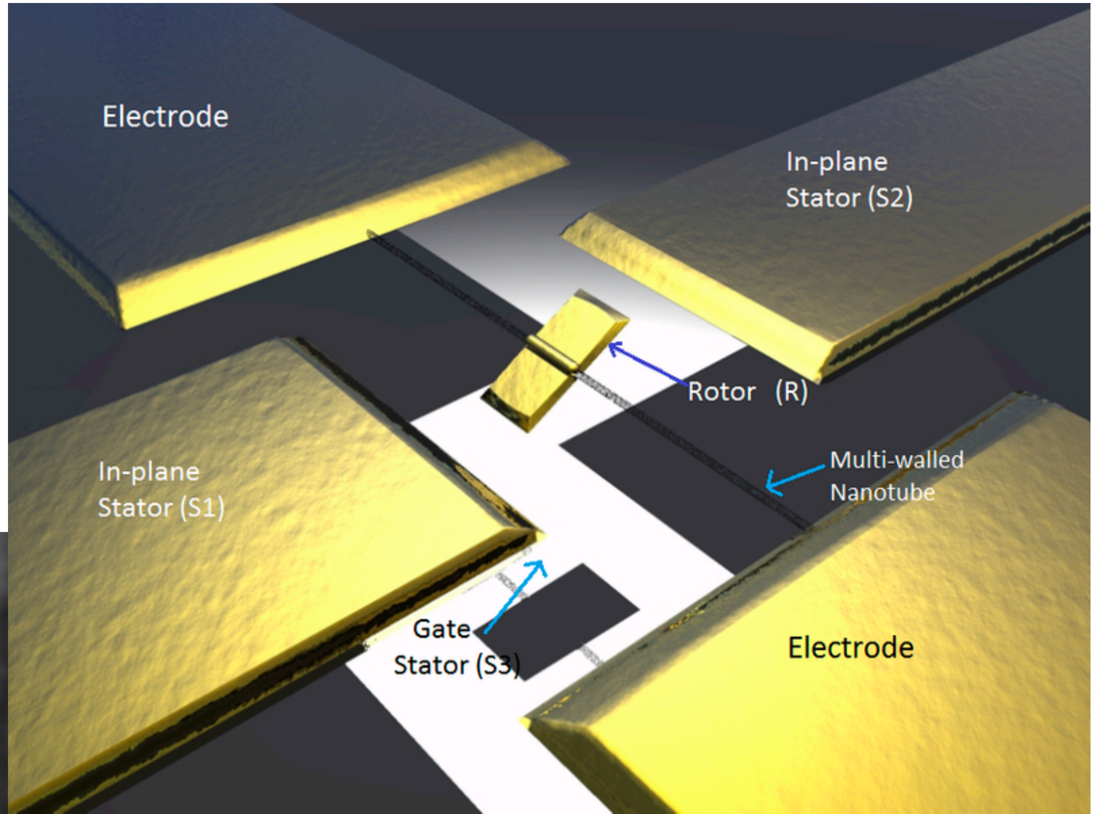


1.1 Introduction : Why study forces at the nanoscale ?

Nano-electromechanical systems (NEMS):
- **Size from 1 to 100 nm**
- **applications in sensors and actuators.**

R. Feynman

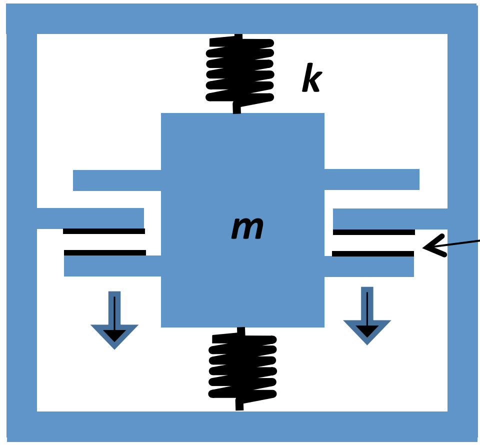




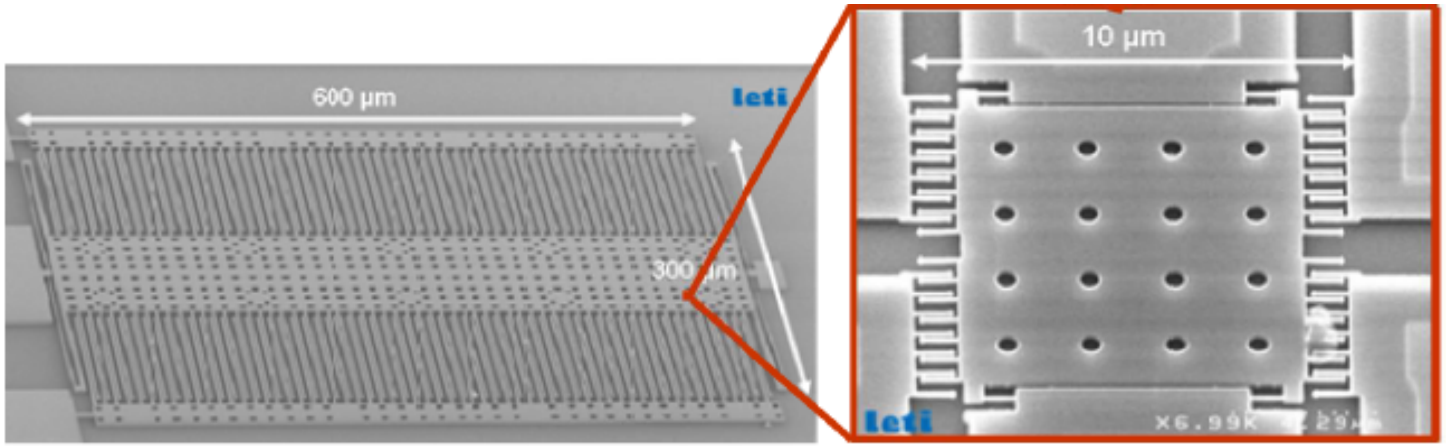
Carbon nanotube motor (A. Zettl, 2003)

Accelerometry

Applications : airbag (but no real need for miniaturisation), Ipod, videogames, mini-drones, etc.



$$I(t) = \frac{dQ}{dt} = \frac{\partial C}{\partial t} V$$

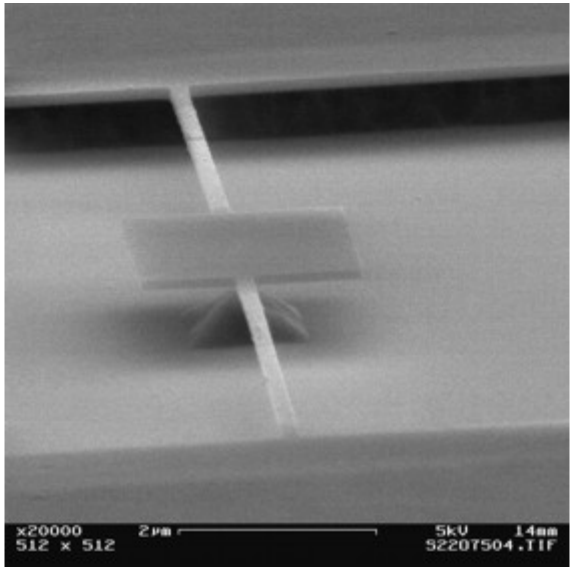


Micro-accelerometer

Nano-accelerometer

SEM images of micro and nano-systems fabricated at LETI-CEA (Grenoble)

Measuring small weight changes



Munich University

The smaller the resonator,
- the lower the power consumption and dissipation.
- the higher the operating frequency.

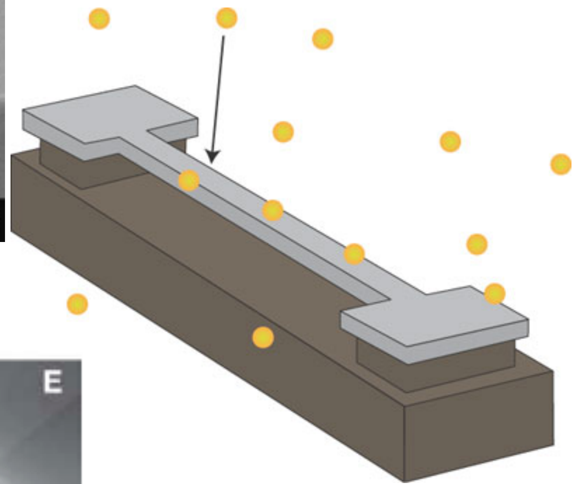
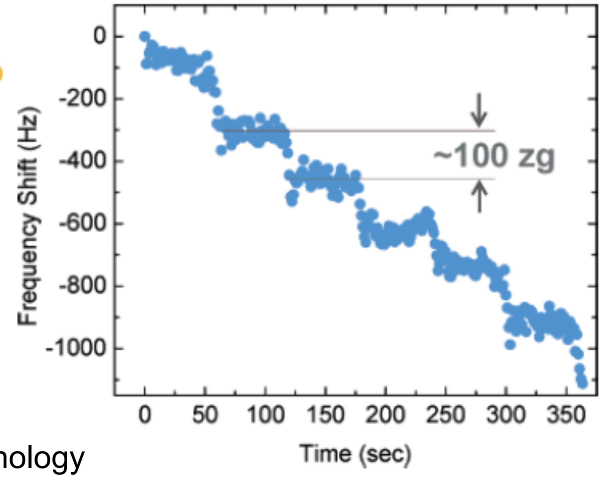
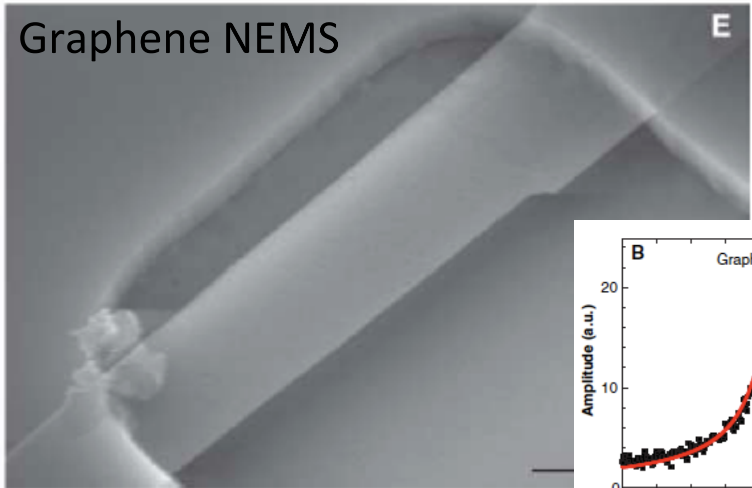
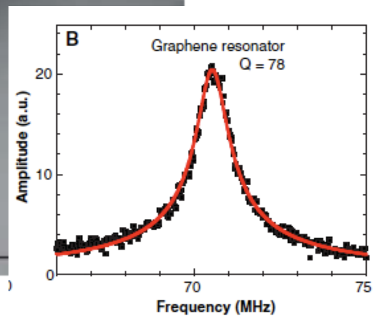


Image credit: Nature nanotechnology

Roukes group, Nanoletters 2006



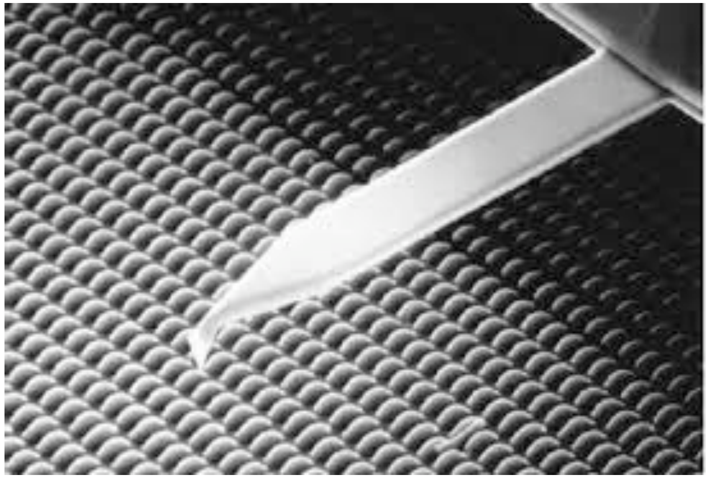




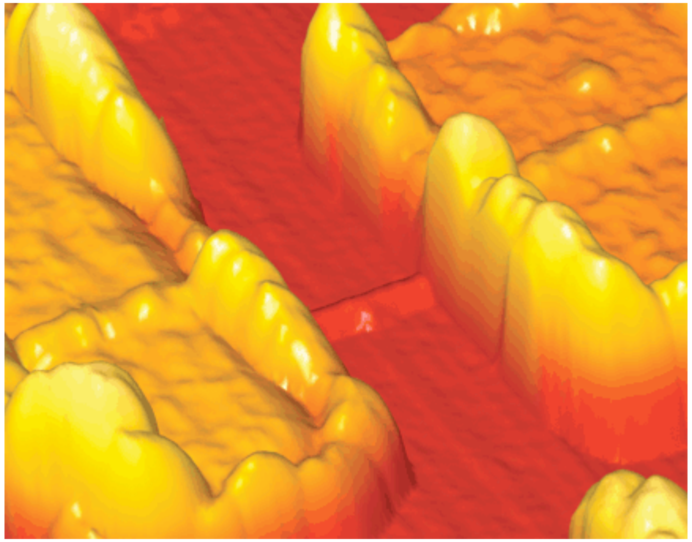
Bunch et al., Science 2007

Applications in chemical & biological detection

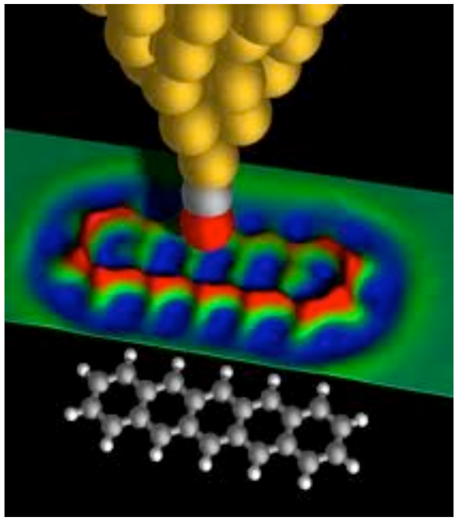
Atomic force microscopy

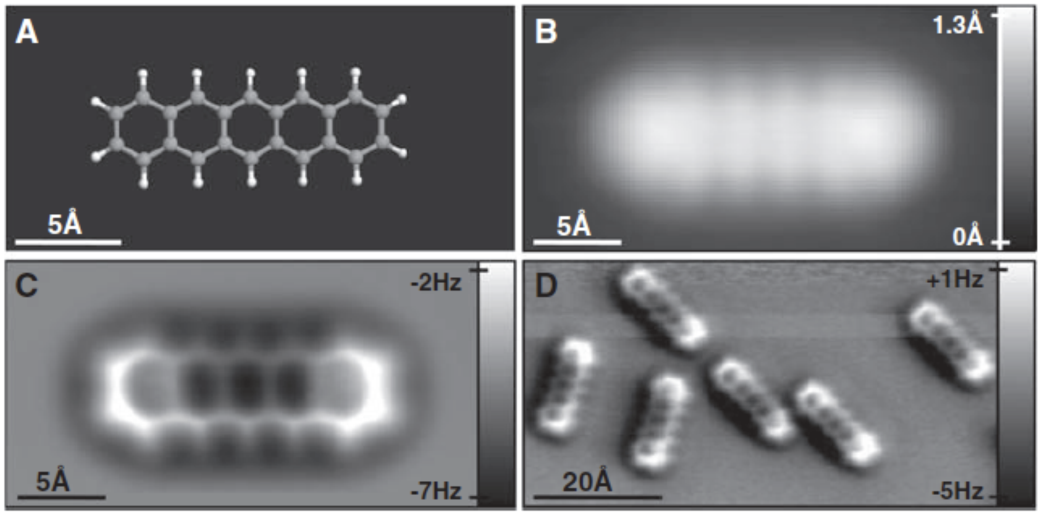


nc-AFM image of a carbon nanotube junction
Institut Néel



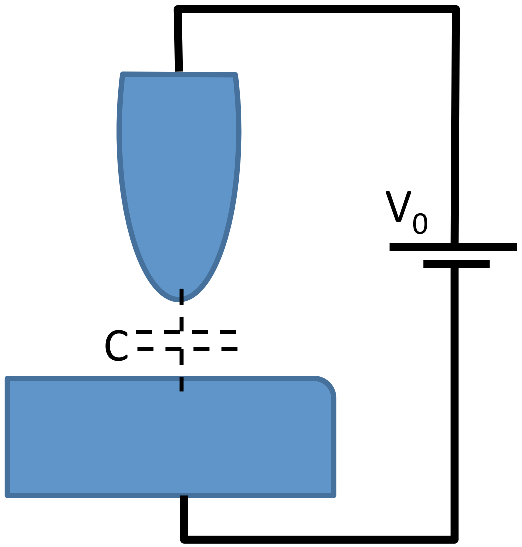
nc-AFM on pentacene
IBM Zürich





1.2 Capacitive forces

Capacitive forces often prevail when objects are conducting, but this depends on the applied voltage and surface areas.



Energy of the capacitor:

$$W = \frac{1}{2} C V^2$$

Force exerted between the plates:

$$F_{el} = \frac{1}{2} \frac{\partial C}{\partial z} V^2$$

$$F_{\acute{e}l} = \frac{1}{2} \frac{\partial C}{\partial z} (V_0 + \Delta\varphi)^2$$

externally applied voltage

work function difference

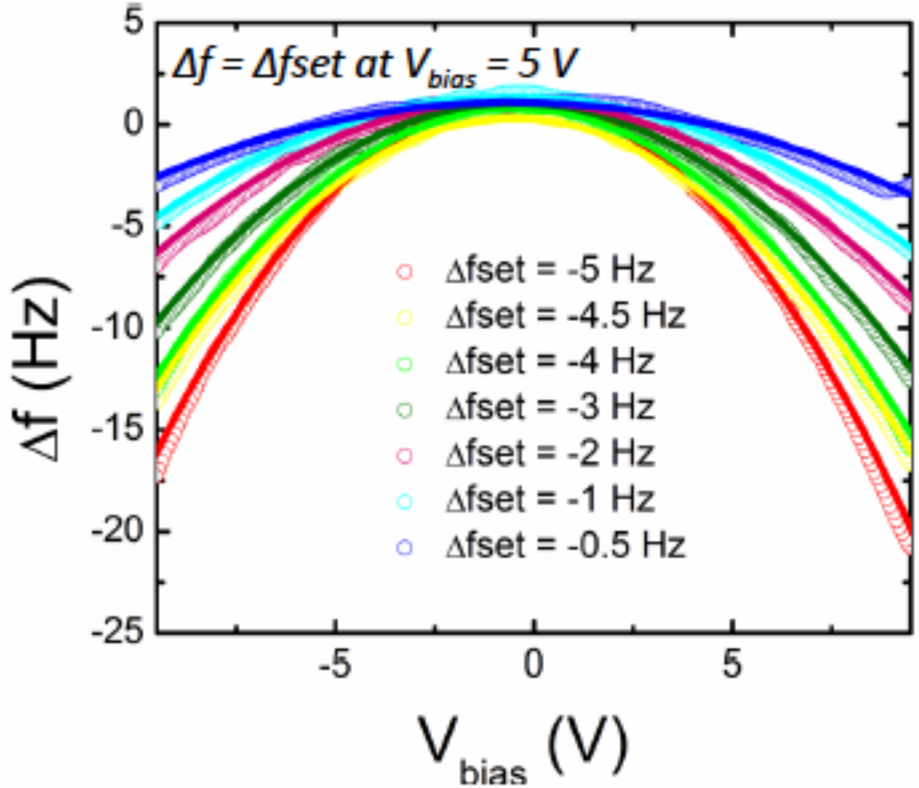
With an additional alternating voltage

$$V = \Delta\phi + V_P \cos(\omega t)$$

the force component at frequency ω is

$$F_{el}\ (at\ \omega) = \frac{\partial C}{\partial z} \Delta\phi \cdot V_P \cos(\omega t)$$

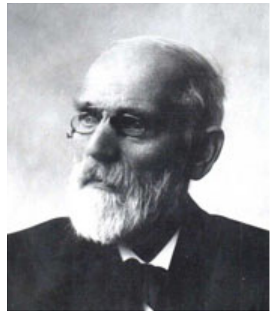
$$\Delta f = \frac{f_0}{4k}\frac{d^2C}{dz^2}(V - V_{CP})^2 + \frac{f_0}{2k}\frac{d^2U_{ts}}{dz^2}$$



(V_{CP})mean = (-0.51 ± 0.05) *volt*

Samaddar et al. (I. Néel)

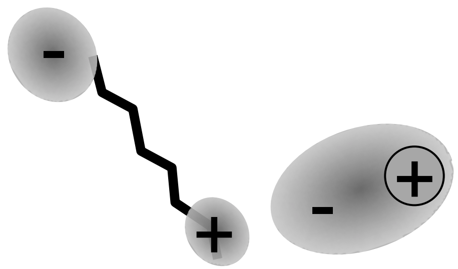
1.3 van der Waals forces



van der Waals forces : dipole or induced-dipole interactions

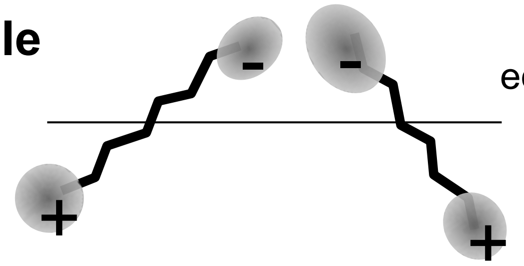
three possible contributions:

- Interaction between permanent and orientable dipoles (**Keesom interaction**).
- Interaction between polar and polarisable molecules (**Debye interaction**).
- Instantaneous dipolar interaction even between initially neutral atoms or molecules (**Dispersion** or **London forces**).

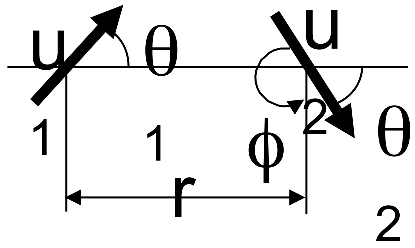


Keesom contribution :

Interaction between polar molecules with permanent and orientable dipoles.

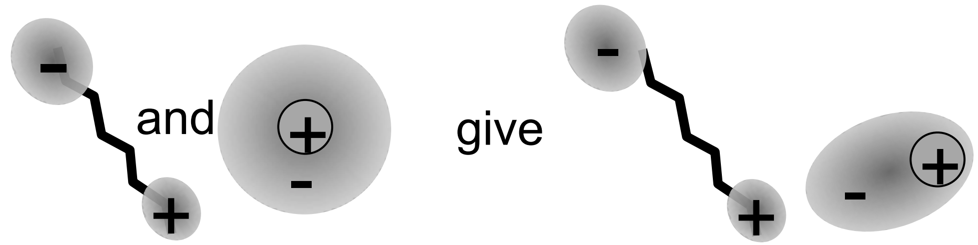


equivalent to



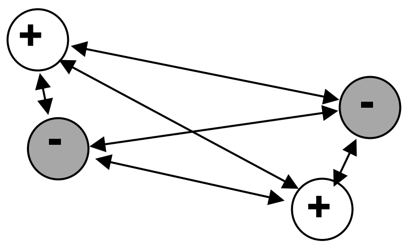
Debye contribution :

Interaction between a polar molecule and a neutral but polarisable atom

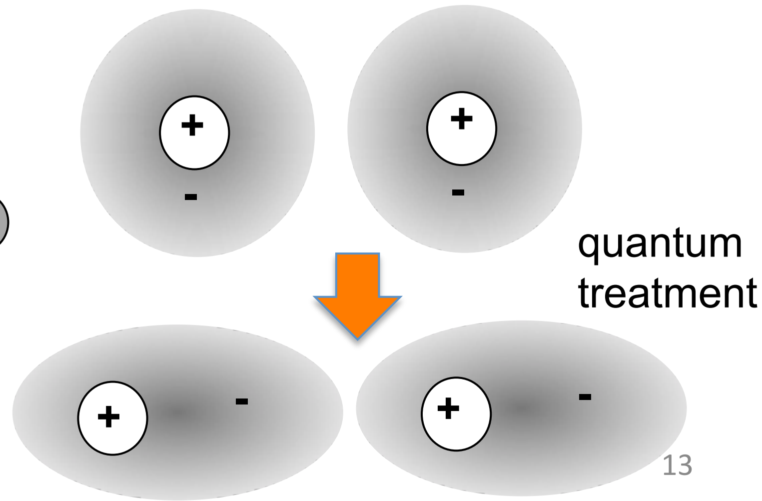


London (dispersion) forces :

Quantum term in systems with no associated dipolar momentum



« Instantaneous » interaction

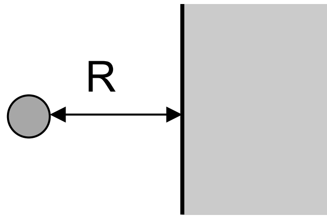


Extension of Van der Waals forces to 3D objects

Two atoms

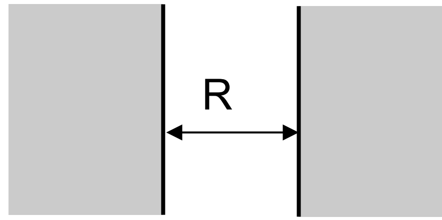
$$F = -\frac{C}{R^7}$$

atom-surface



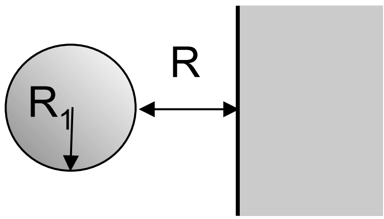
$$F = -\frac{\pi C \rho}{2R^4}$$

Two plane surfaces



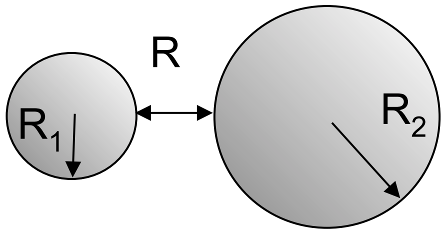
$$F = -\frac{H}{6\pi R^3}$$

Sphere-surface



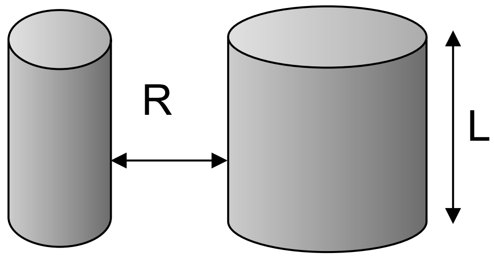
$$F = -\frac{HR_1}{6R^2}$$

Sphere-sphere



$$F = -\frac{R_1 R_2}{R_1 + R_2}\frac{H}{6R^2}$$

Parallel cylinders

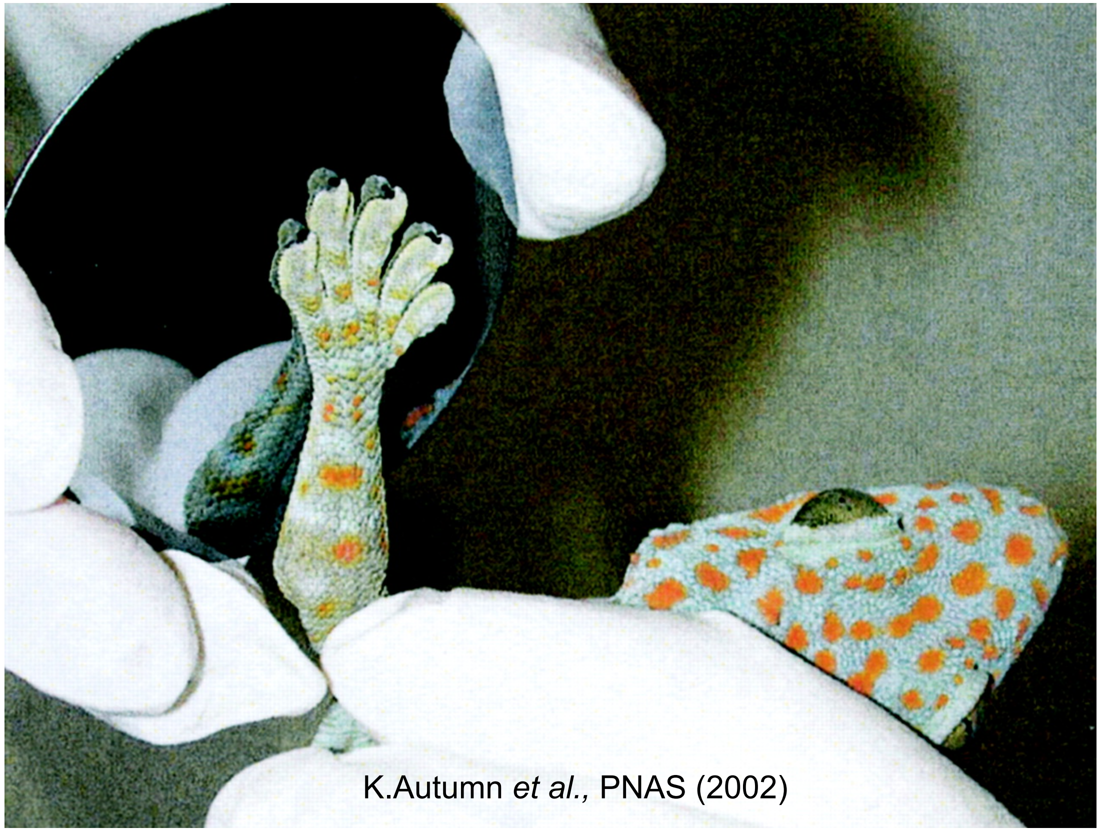


$$F = -\sqrt{\frac{R_1 R_2}{R_1 + R_2}}\frac{3HL}{24\sqrt{2}R^{5/2}}$$

Hamaker constant (material dependent)

$$H = \pi^2 C \rho_1 \rho_2 \approx 1eV$$

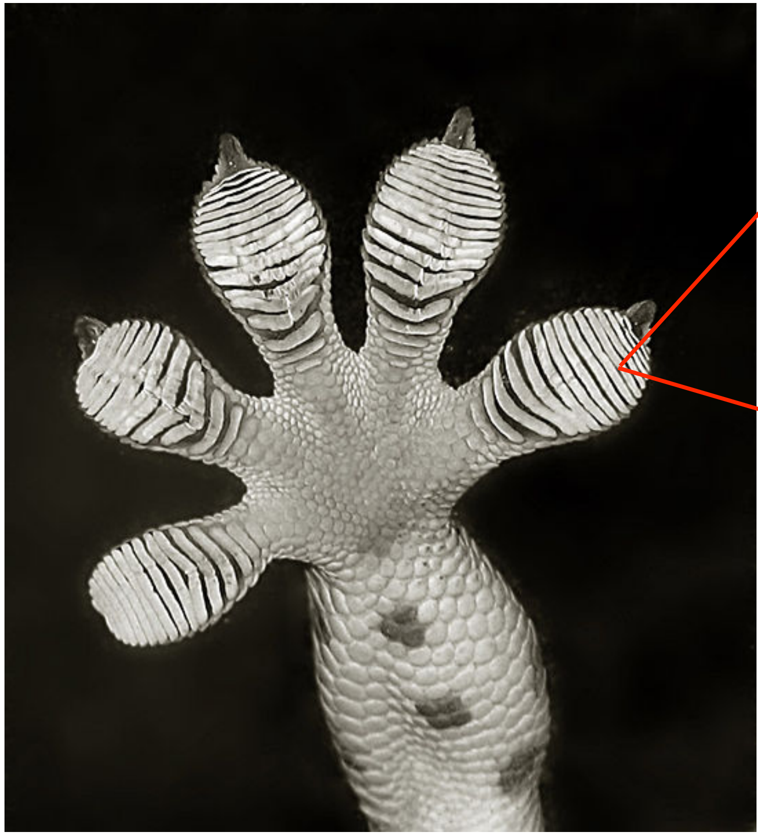
Van der Waals forces



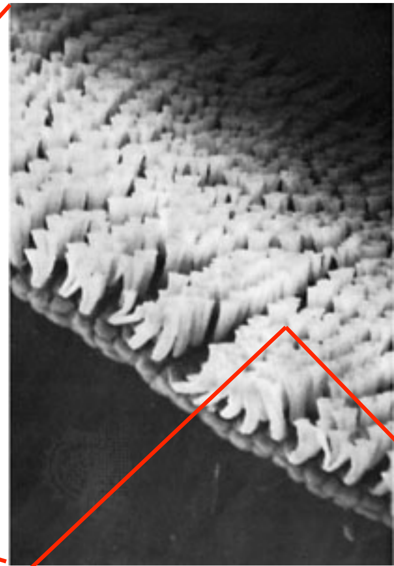
K.Autumn *et al.*, PNAS (2002)

A gecko sticking its legs onto a perfectly hydrophobic GaAs surface.

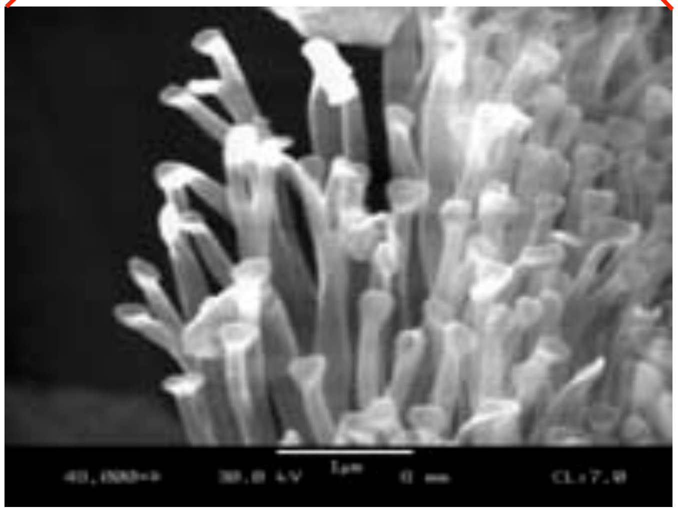
Van der Waals forces



Source: wikipedia



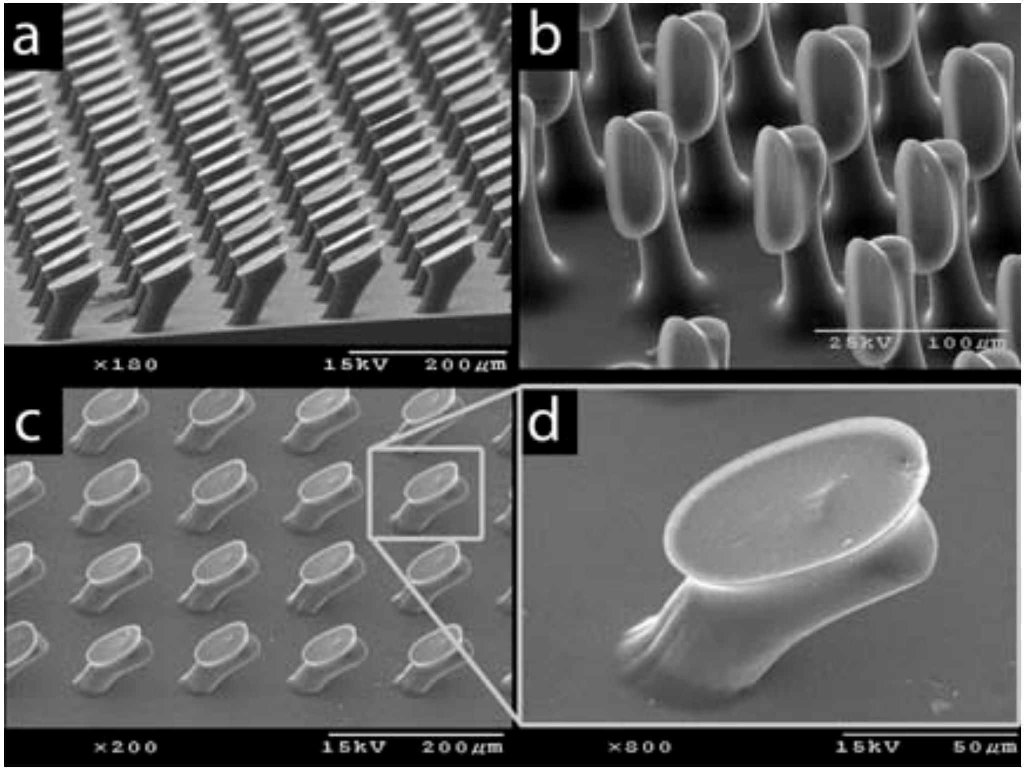
Source: S.F.Gennaro



Source: Nature publishing group

Details of a Gecko's leg, or how to get rid of surface roughness in order to walk on a ceiling.

Imitating the Gecko with nanostructures



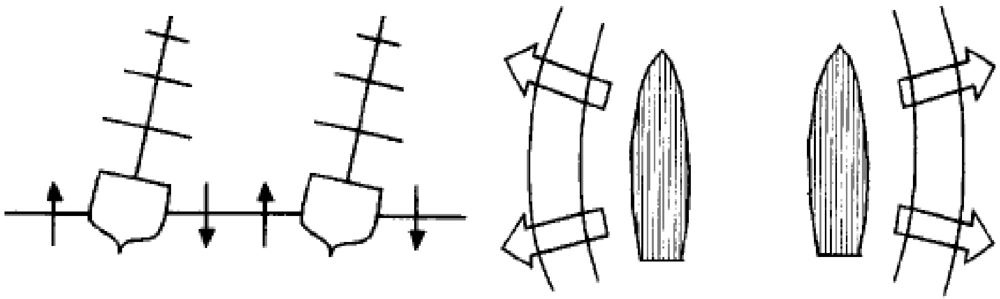
Murphy *et al* (Pittsburgh University 2009)

1.4 Casimir force: a classical analogy

Le Calme plat.

LORSQUE deux bâtiments sont en calme, ils tendent toujours à se rapprocher et finissent par s'aborder, étant attirés l'un vers l'autre par une certaine force attractive : dans ce cas, on se sert des canots pour s'éloigner, et on y parvient plus promptement en faisant remorquer l'un des bâtiments par les canots des deux. Les petits bâtiments ont de plus la ressource de leurs avirons de galère.

From J.C.Caussée, « l'album du Marin » (1836)



Casimir pressure between two plates

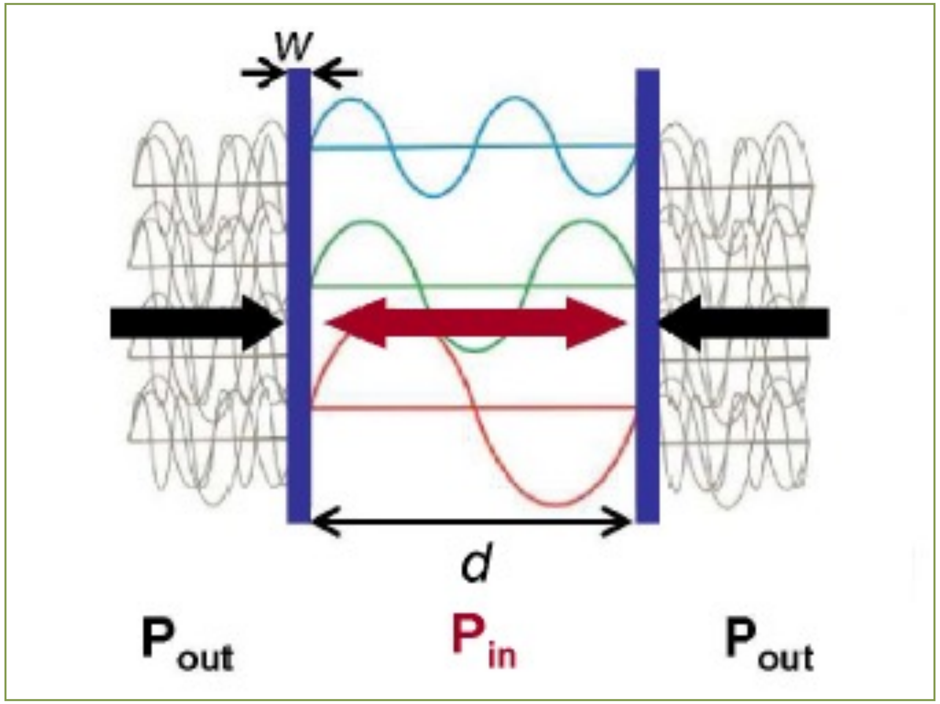
Interpretation :

• Quantum fluctuations create a radiation pressure.

• Two plates form an optical cavity:
The number of electromagnetic modes and the energy density are not the same as outside.

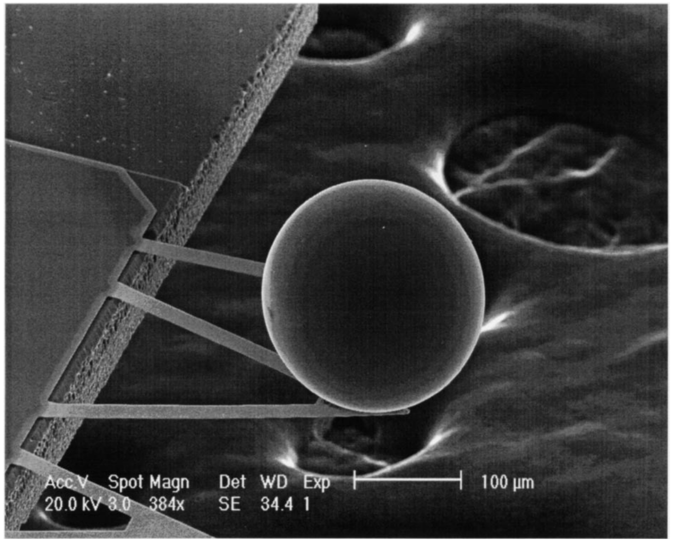
→ difference in the radiation pressure from quantum fluctuations inside and outside.

→ force which makes the plates get closer

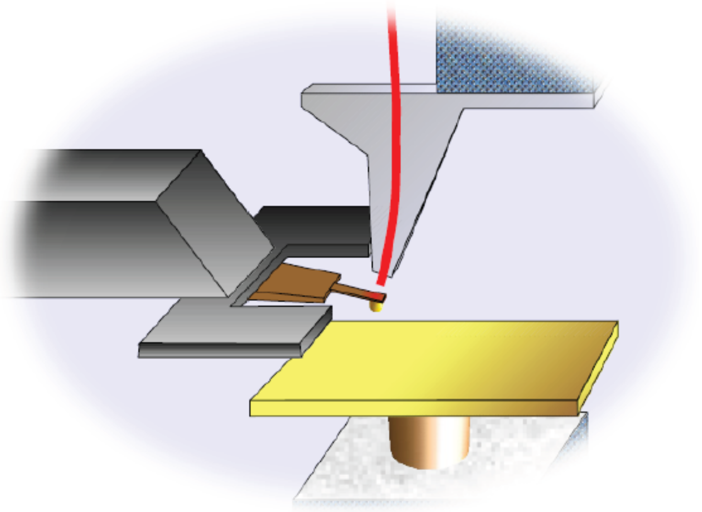


$$F_{Casimir} = \frac{\hbar c \pi^2}{240 d^4} A$$

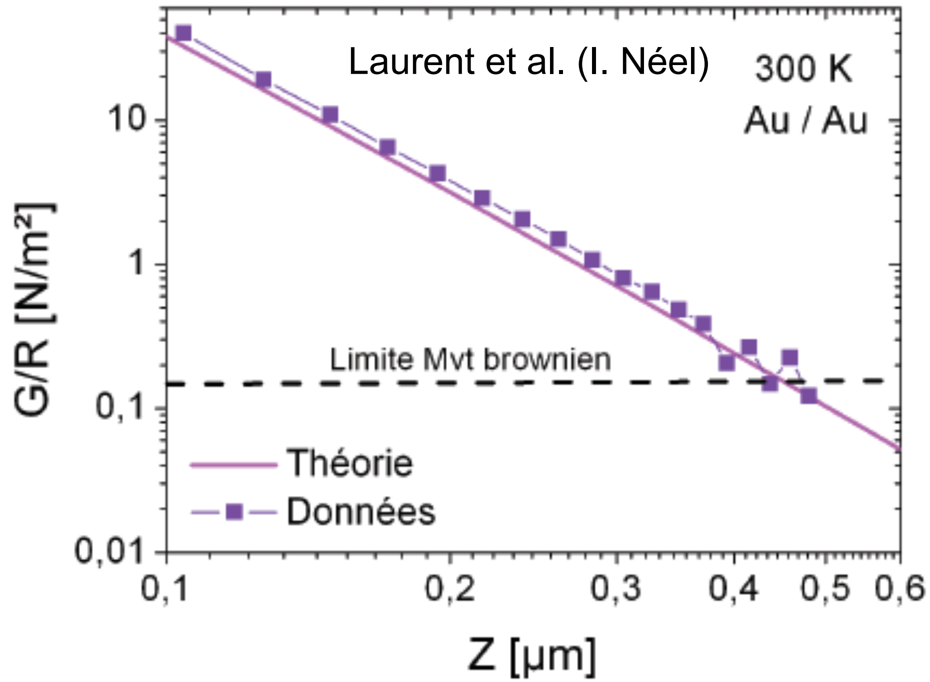
Casimir force between a sphere and a plane



Mohideen et al., Phys. Rev. Lett. 1999



Careful AFM measurements show the transition between the Van der Waals and Casimir regime.



Casimir : Relevance to NEMS

Casimir force can be rendered repulsive by changing the geometry or surface structure at the nanoscale

→ frictionless motion.

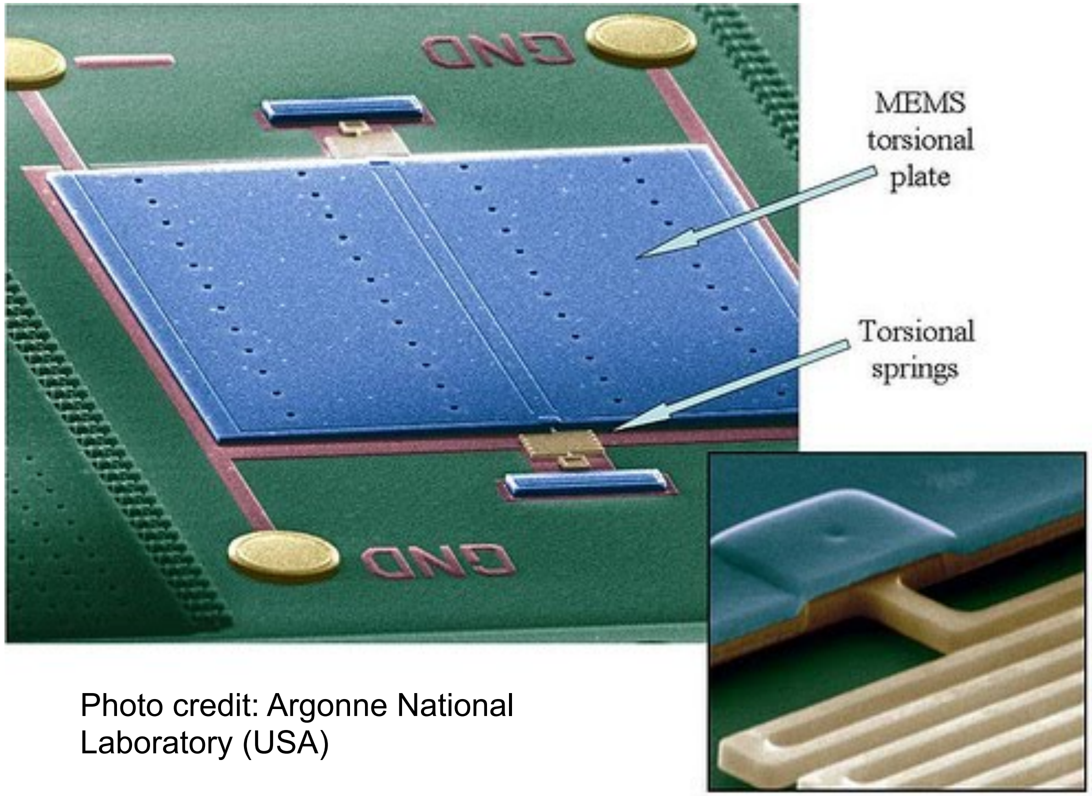
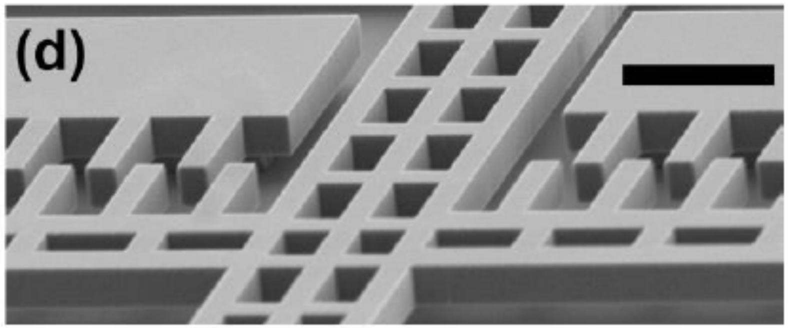


Photo credit: Argonne National Laboratory (USA)



HKUST & MIT

1.6 Scanning Probe Microscopy

Diffraction limit to optical microscopy

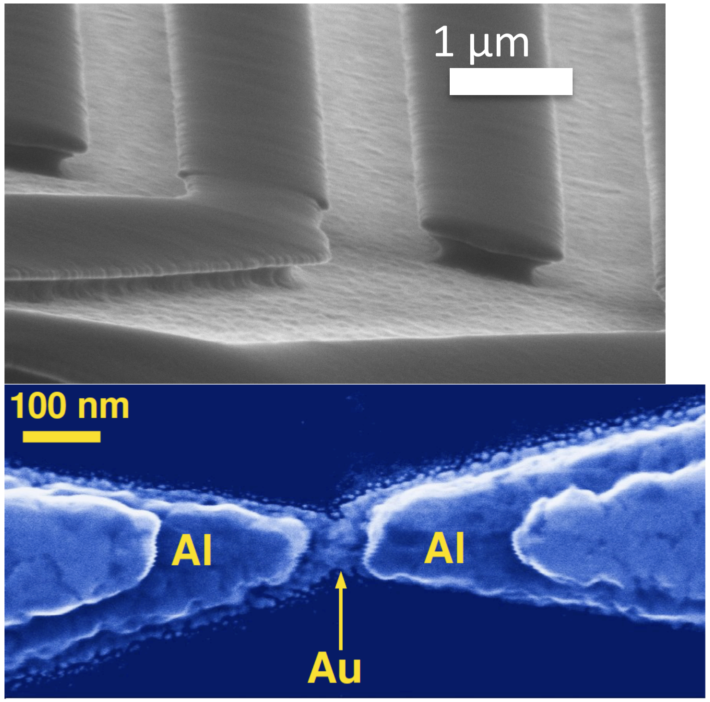
$$d = \frac{\lambda}{2n \sin \alpha}$$

Two strategies:

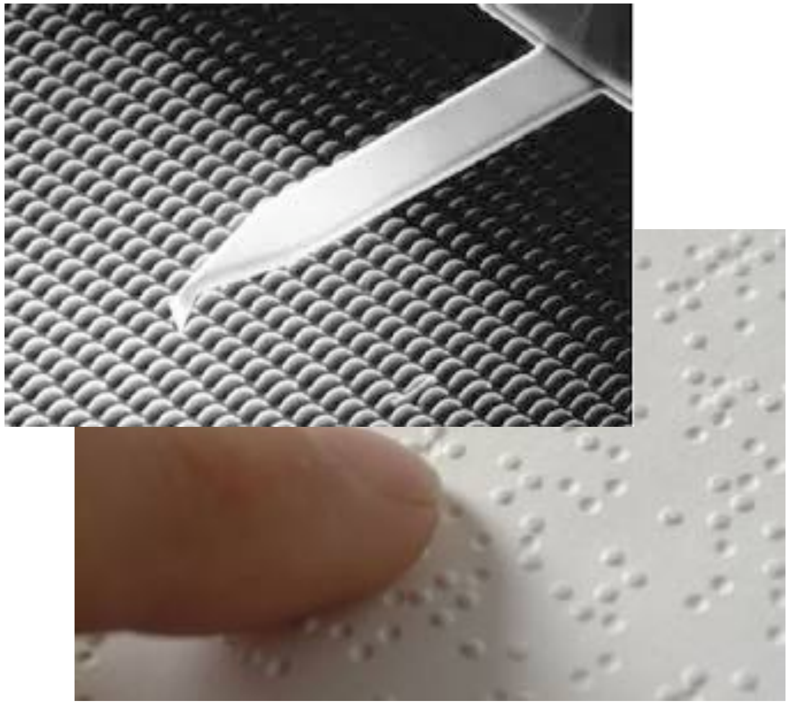
Smaller wavelength « bullets »

Avoid propagating information

Scanning electron microscopy



Scanning probe microscopy



Requirements

- **Sensing**

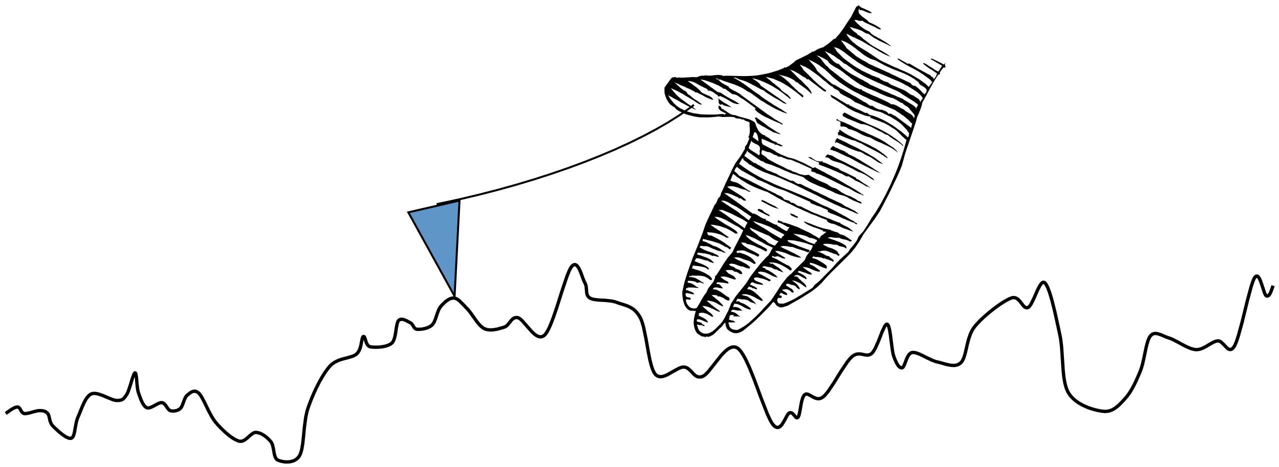
Evaluate the force between the tip and sample.
→ measure the deflection of the cantilever.

- **Actuating**

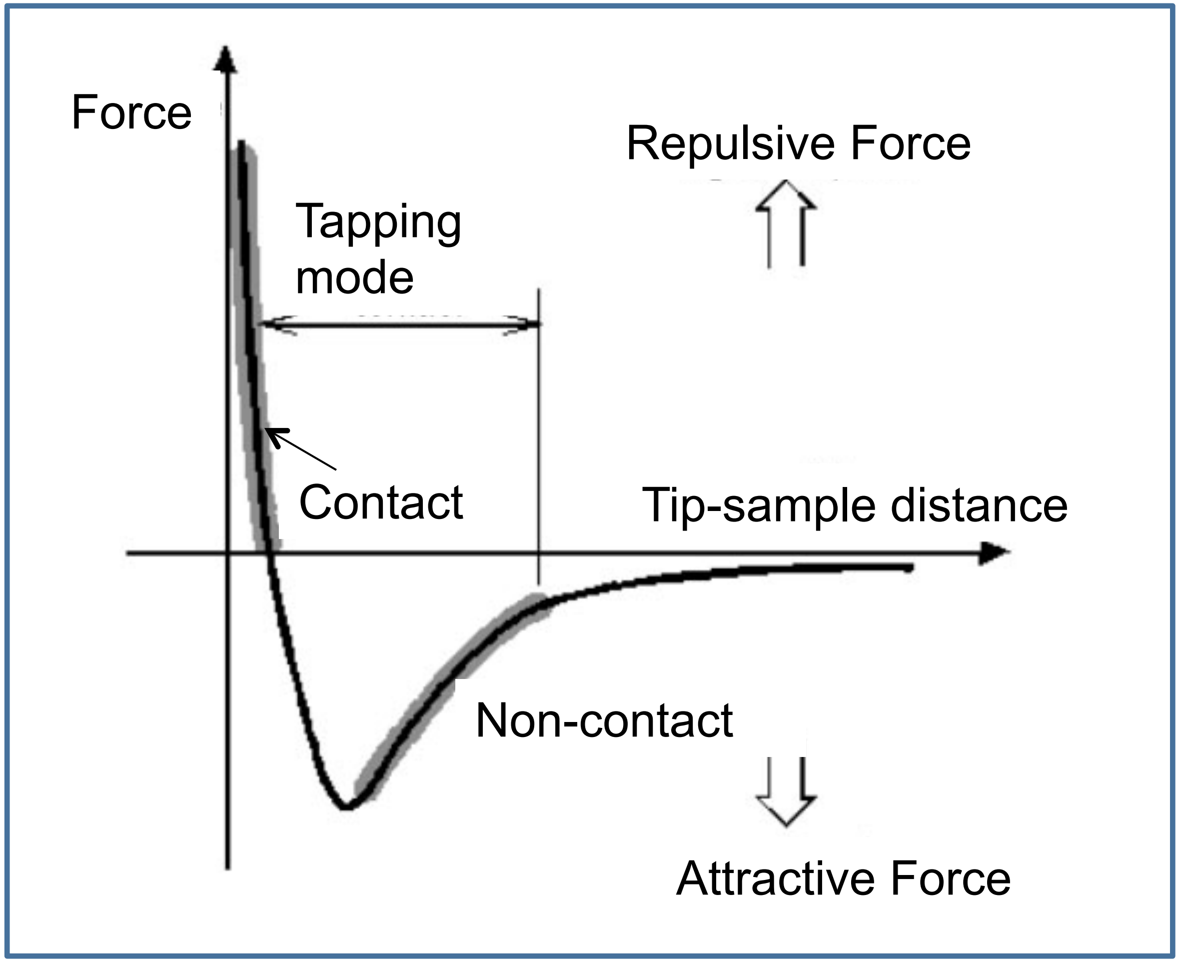
control the force between the tip and the sample

- **Feed-back loop**

Track the sample topography using a feed-back loop ensuring a constant deflection of the cantilever.



Contact forces



Just for 2 atoms:

Lennard-Jones potential

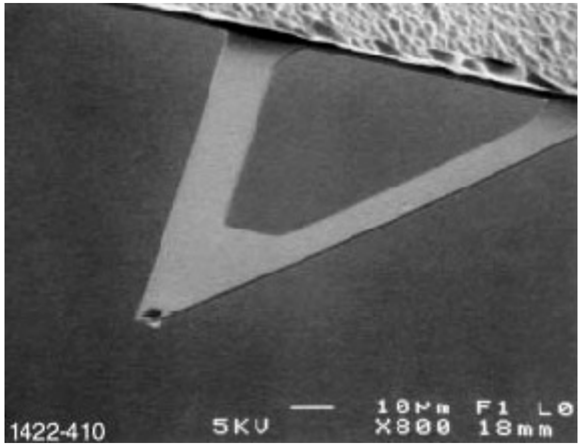
$$U(r) \propto \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}$$

Hard core repulsion
Electronic repulsion
and Pauli principle

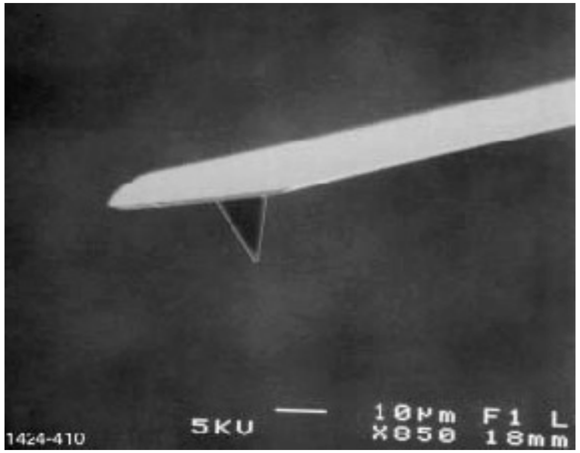
van der Waals term

$$F(r) = -\frac{\partial U}{\partial r}$$

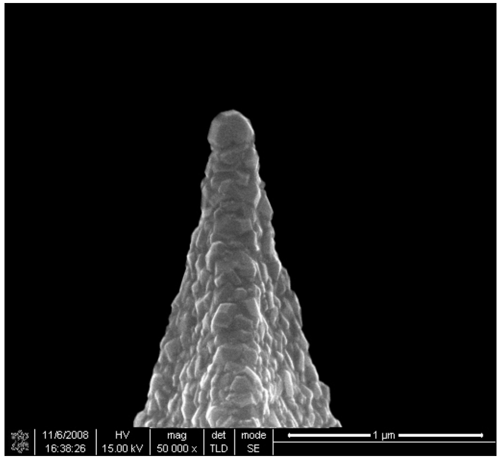
AFM cantilevers and tips



Silicon nitride (« harder »)

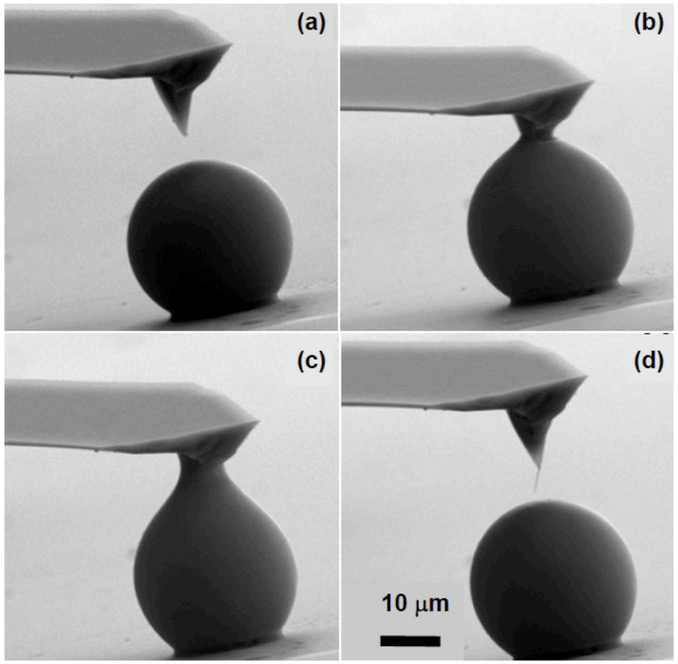


Silicon («more fragile »)

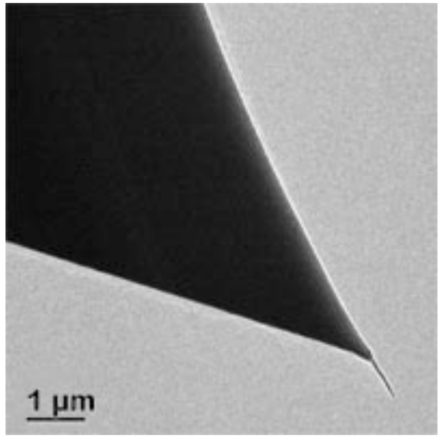


Diamond-coated tip (really hard)

- Probes can be metallized.
- Geometry designed for a given spring constant (= force), or a given resonant frequency.
- Tip geometry determined by the etching procedure and the material properties.

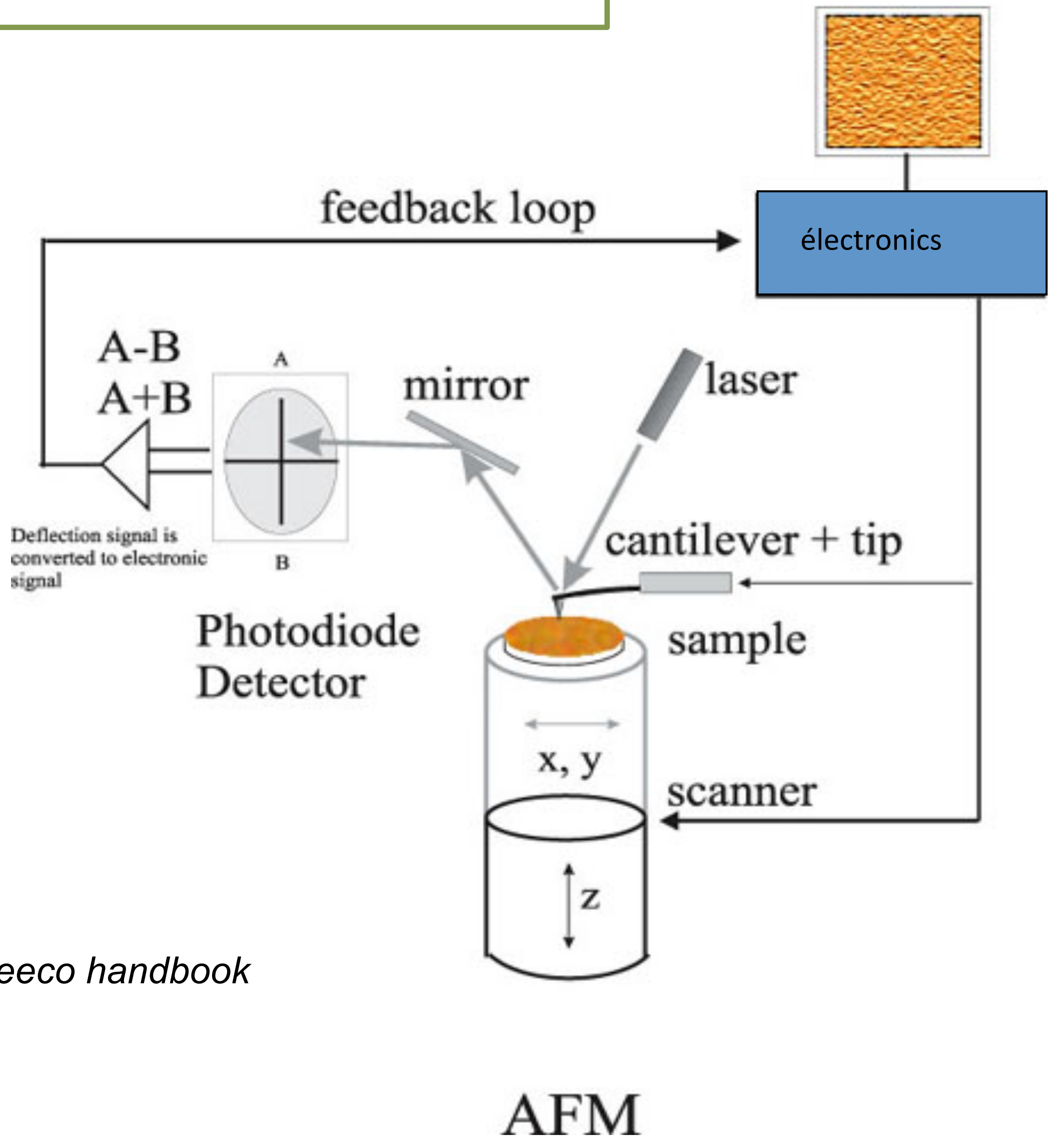


Nanowire tip (nauganeedles.com)



Carbon nanotube tip

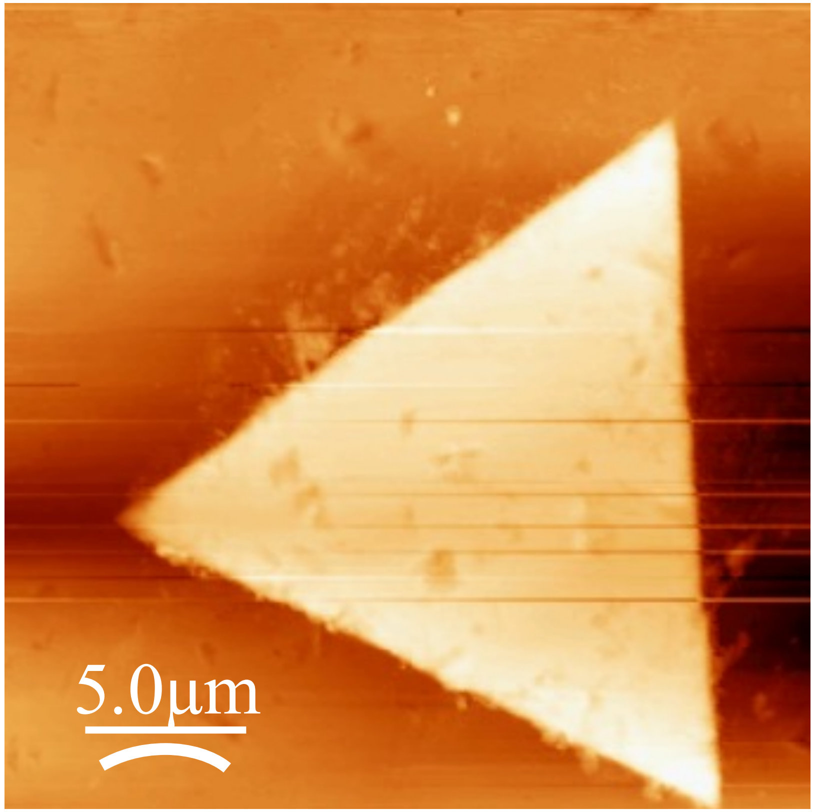
The AFM feed-back loop



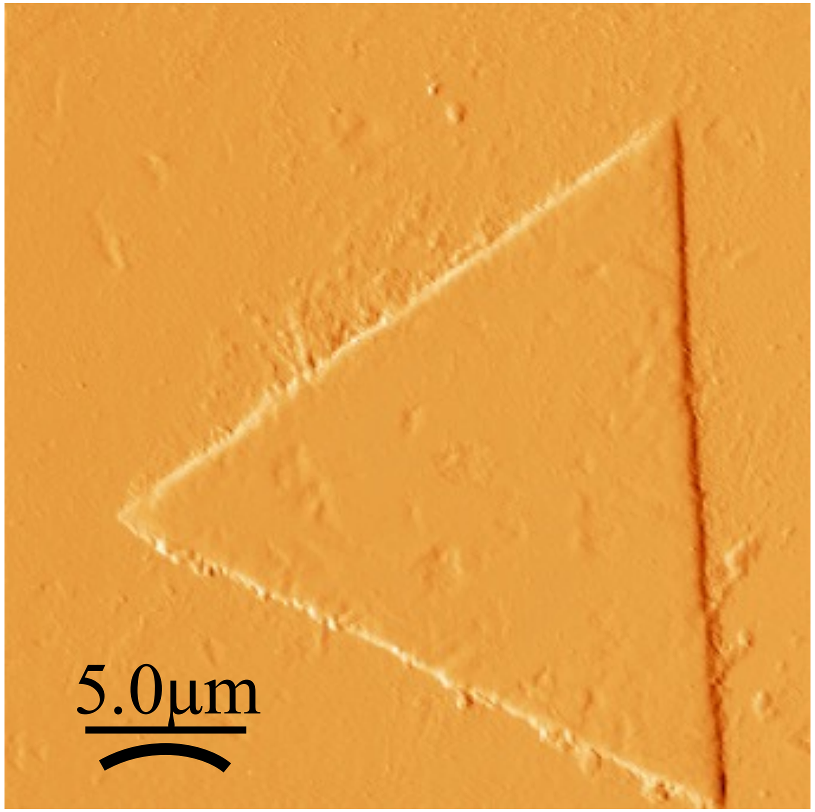
From Veeco handbook

What is a good image ?

Contact mode with deflection as the setpoint variable



Height

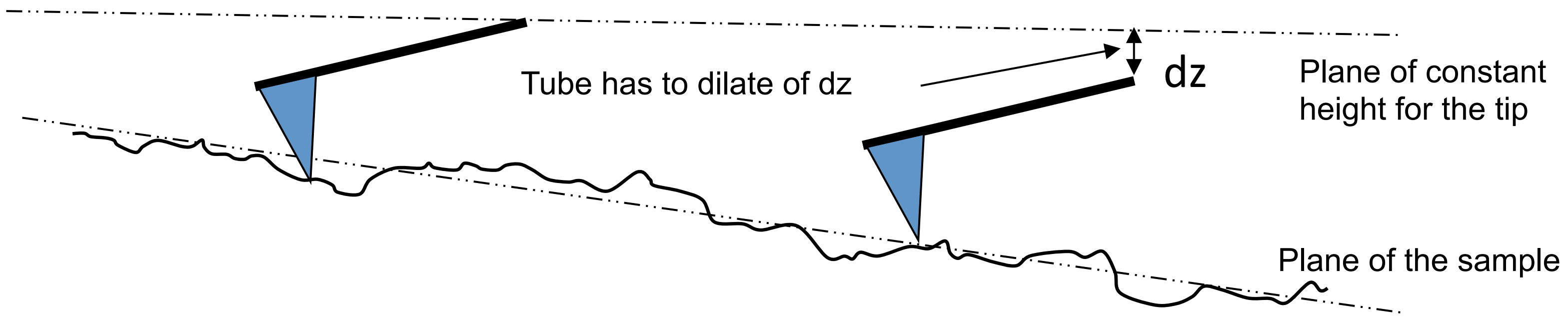


Deflection

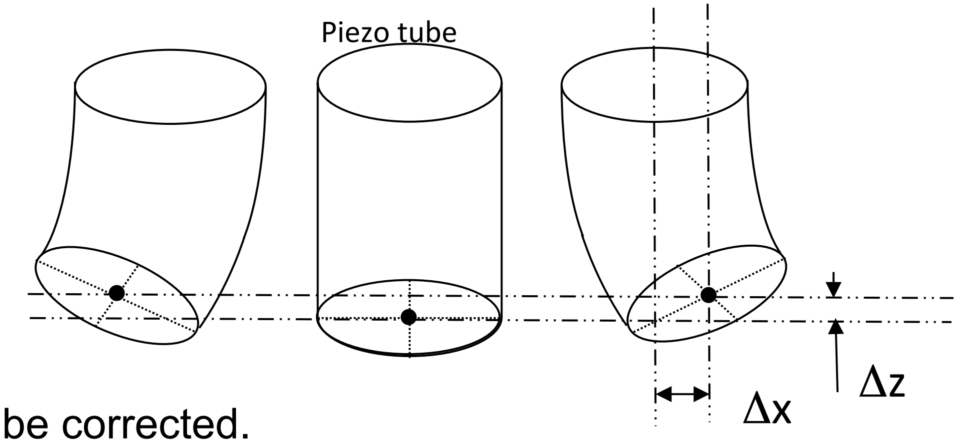
1/ Why do we obtain a contrast in the deflection image?
2/ How can we assess the image quality?

Correcting the raw data

- Imperfect parallelism between the sample and the scanning plane

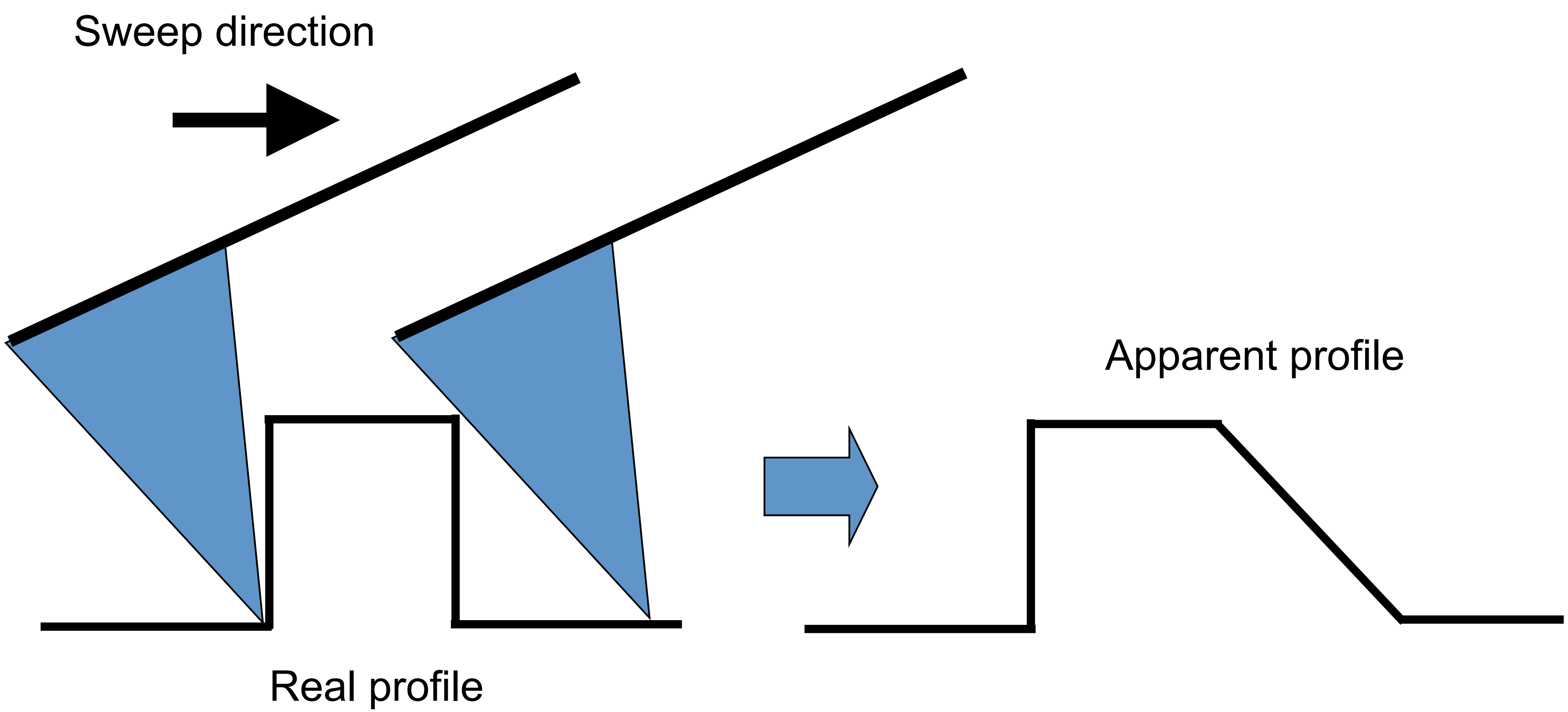


- For large x and y there is also a variation in z which has to be compensated by an additional dilatation of the piezotube.



Images have to be corrected.

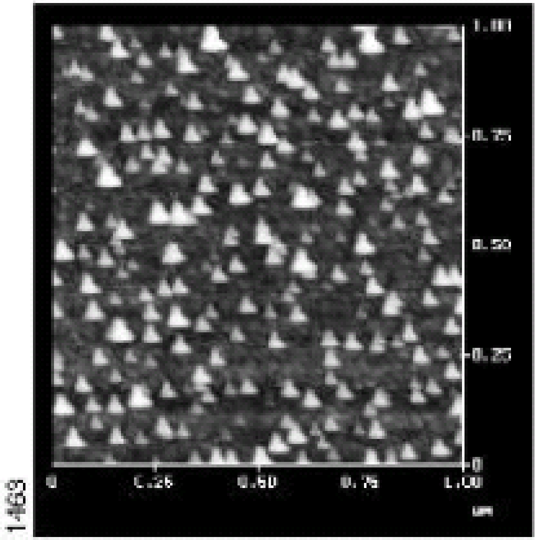
Artefacts related to the shape of the tip

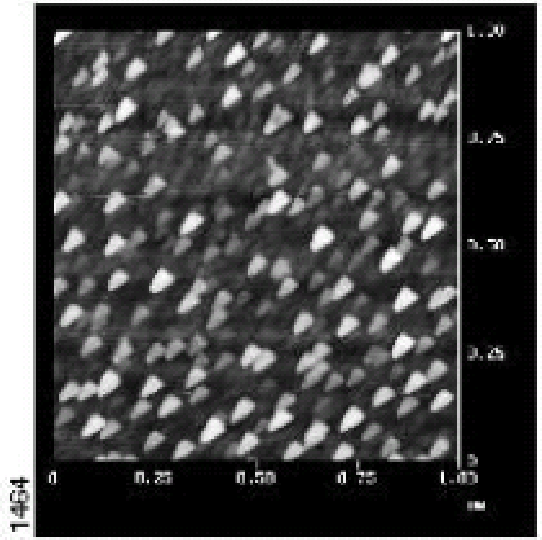


• The measured topography is a convolution of the real topography by the shape of the tip.

➡ To obtain good results the first condition is to use a sharp tip!

Artefacts related to the shape of the tip

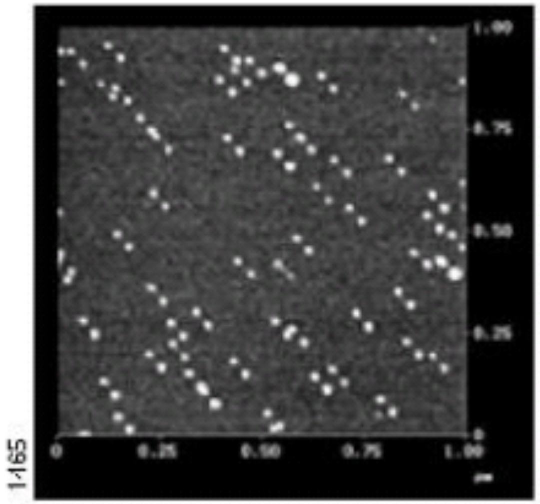


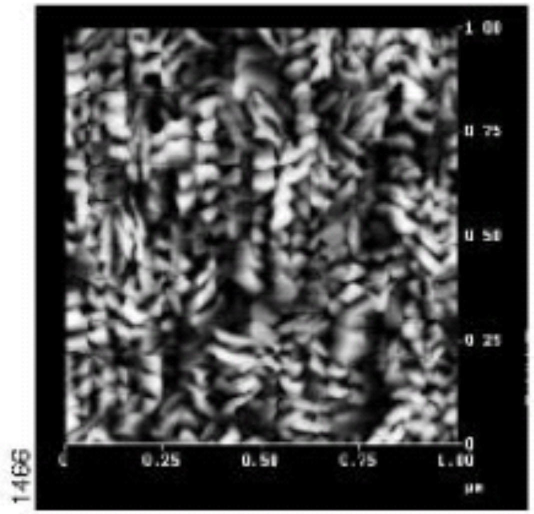


Dirty tip: all small patterns look similar.

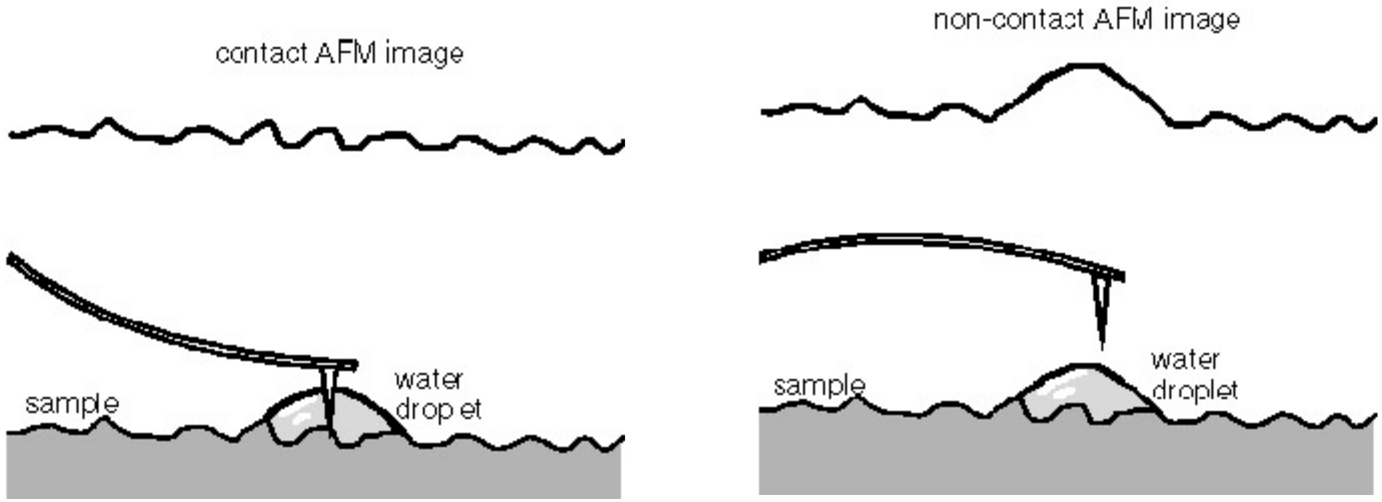
After Veeco handbook manual

Double-tip





Capillary forces



Atomic resolution requires ultra-high vacuum so as to get rid of the adsorbed water molecules.

Atomic scale imaging

Au(111) on a glass observed in contact mode AFM.

Requires ultra-high vacuum (UHV) conditions

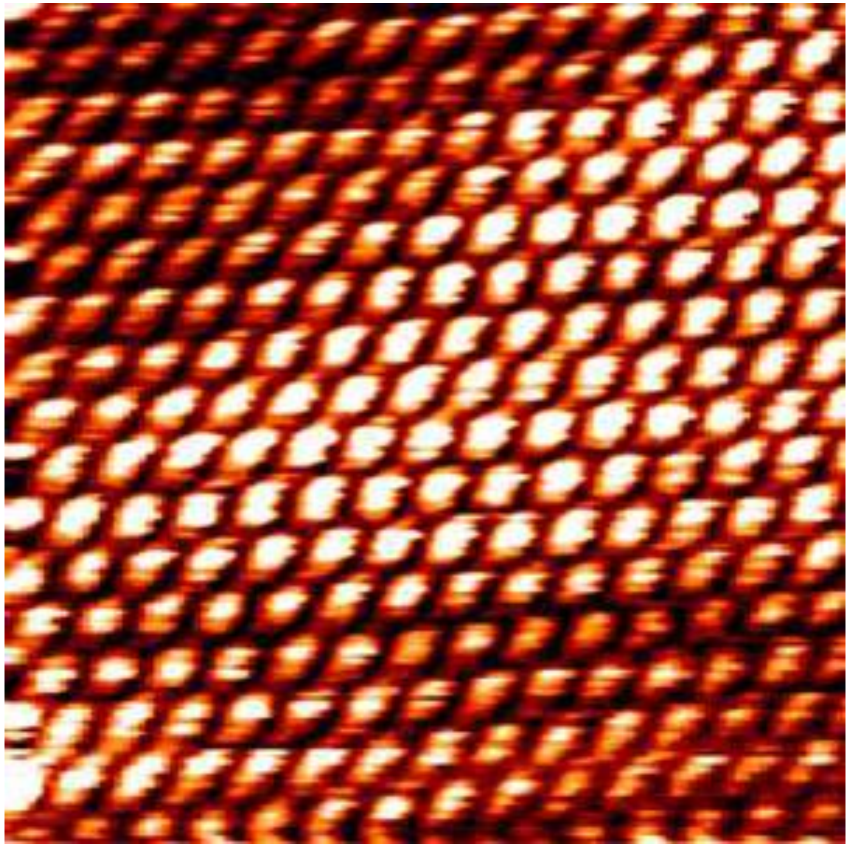
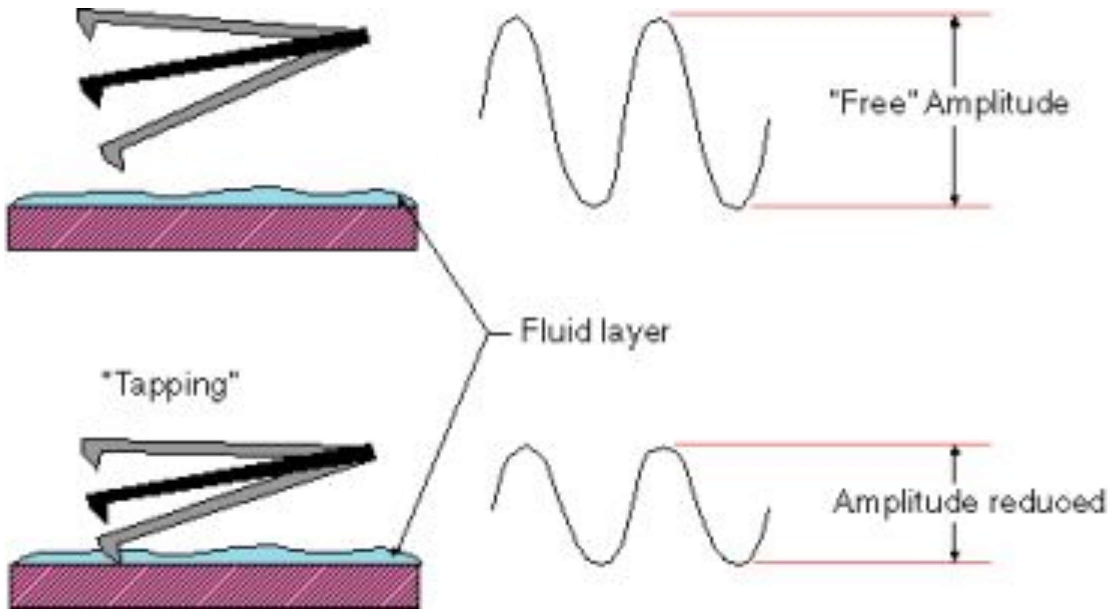


Image credit: Omicron

Tapping mode AFM

•The cantilever is excited by a piezo-electric actuator close to its mechanical resonance.

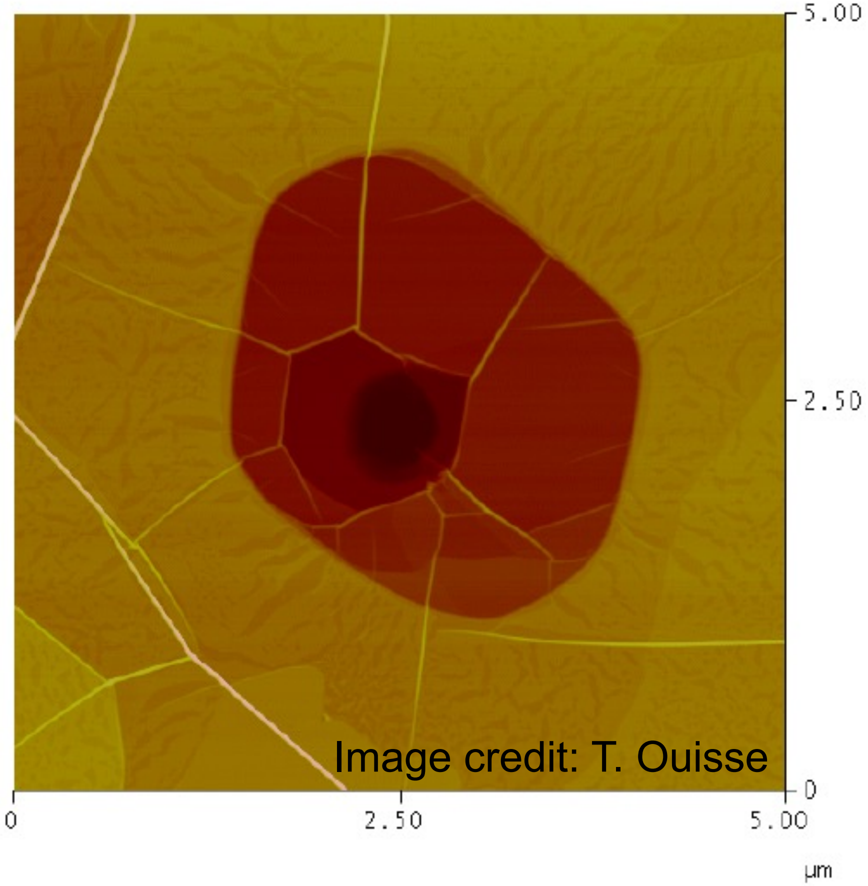
• Detect the modification of the forced oscillations by the small interaction between the tip and sample.



Feedback parameter: cantilever oscillation amplitude

Images in non contact mode

Graphene on a silicon carbide substrate



Feedback parameter: frequency shift

Si(111) 7x7

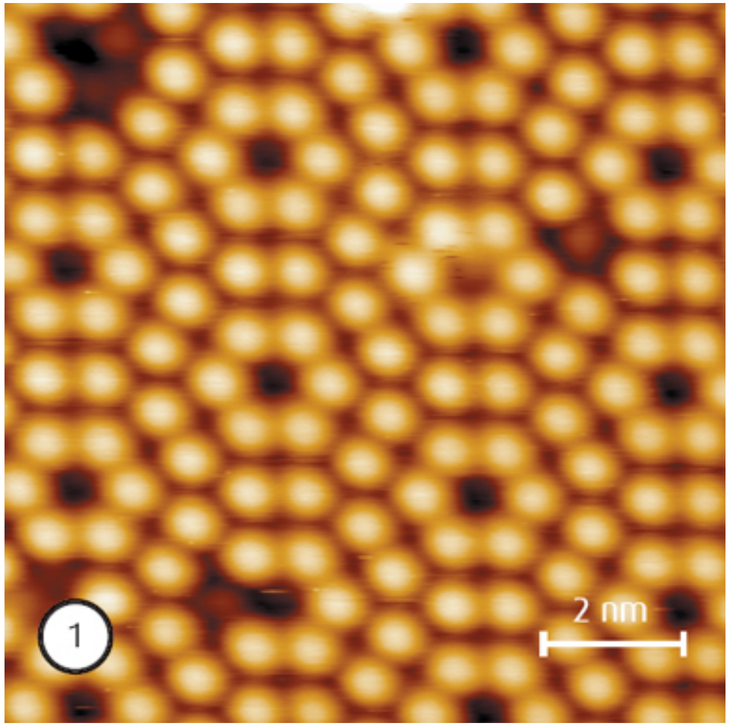
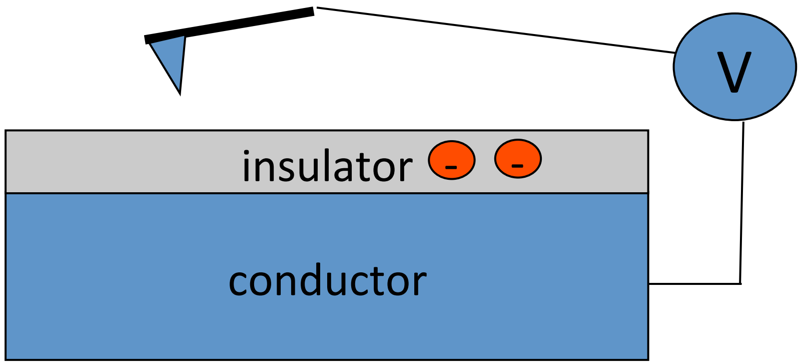


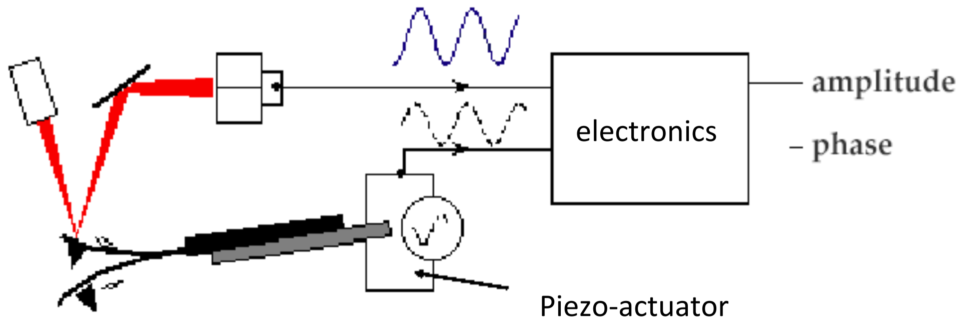
Image credit: Omicron

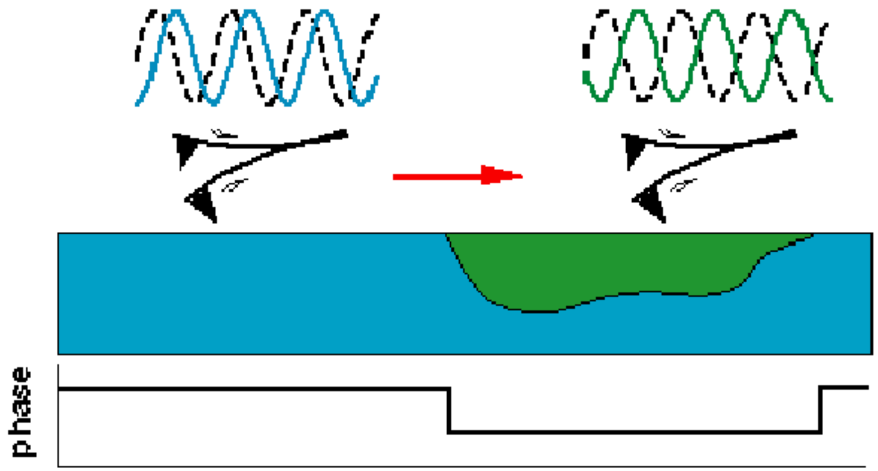
Electric Force Microscopy (EFM)



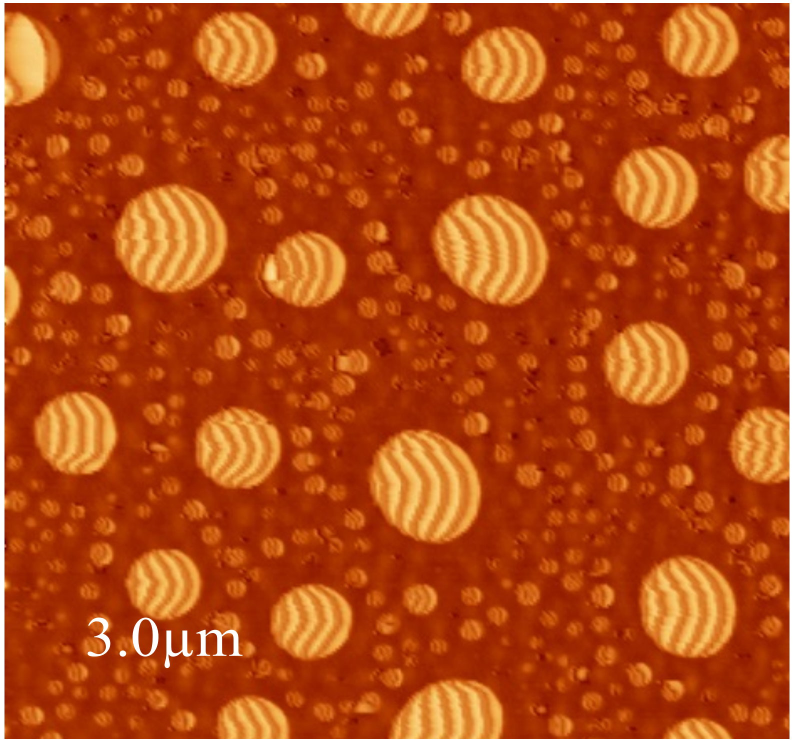
$$U = \frac{1}{2} C V^2 \quad \Rightarrow \quad F = \frac{1}{2} \frac{\partial C}{\partial z} V^2$$

Operates even in the absence of topographic variations

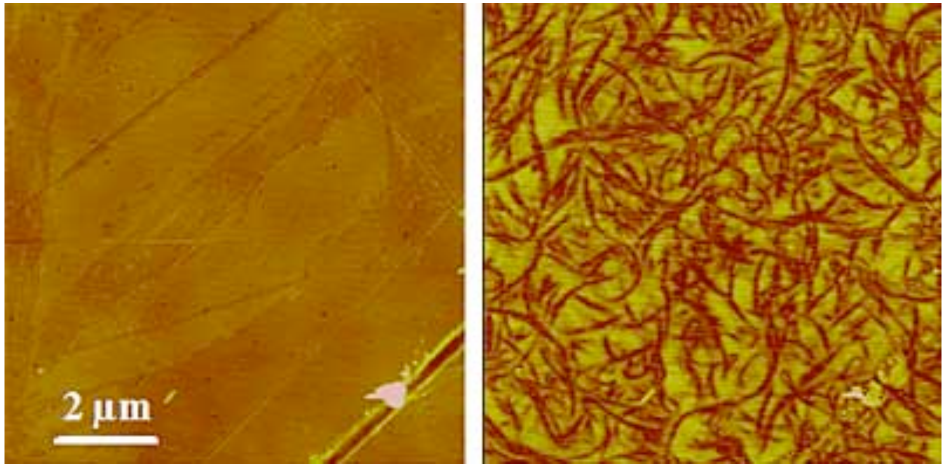




Electric Force Microscopy (EFM)

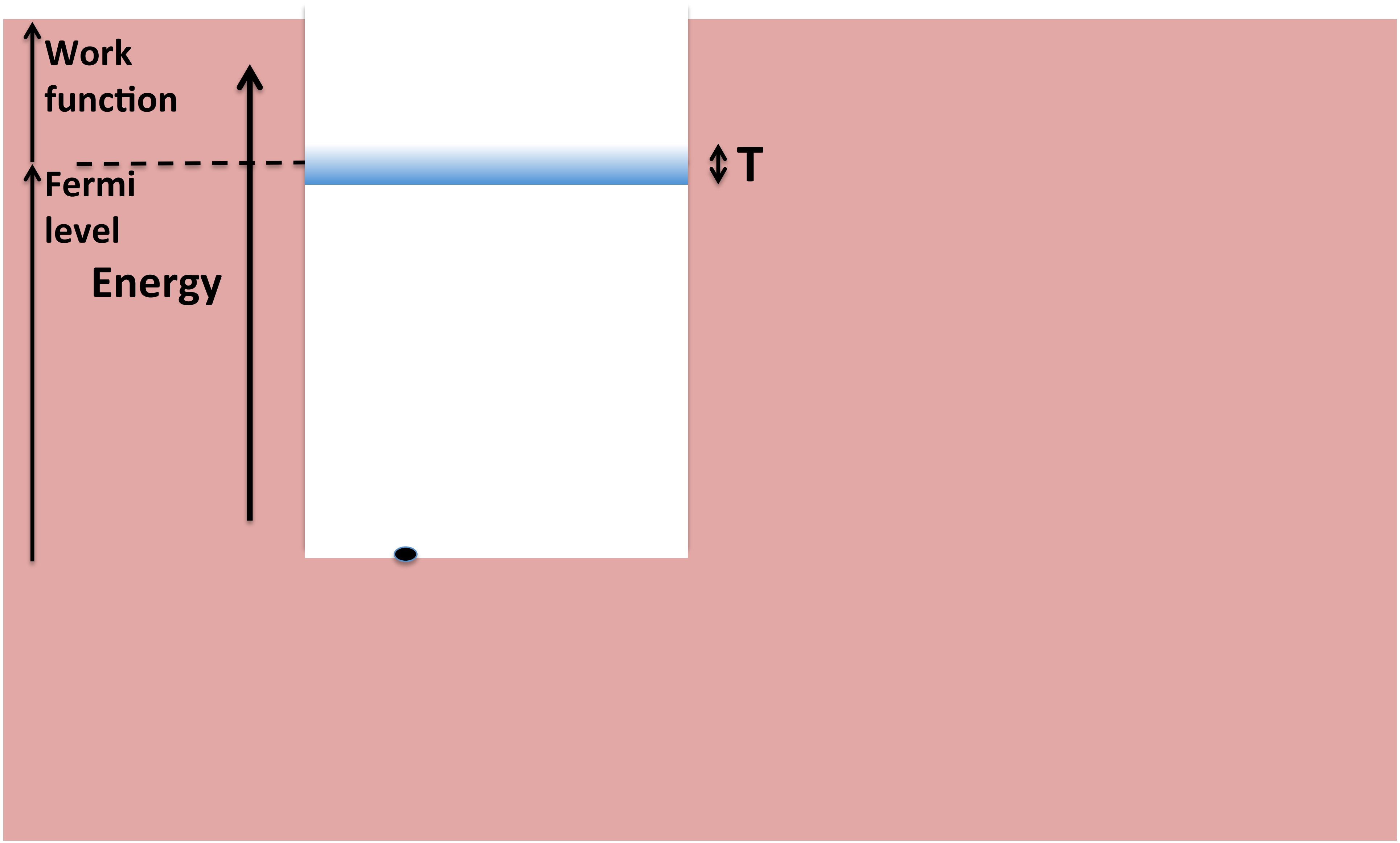


EFM phase imaging of a thin layer made from a blend of polyfluorene and molten salt. Sample topography is totally flat
(from T. Ouisse/ LMGP Grenoble)

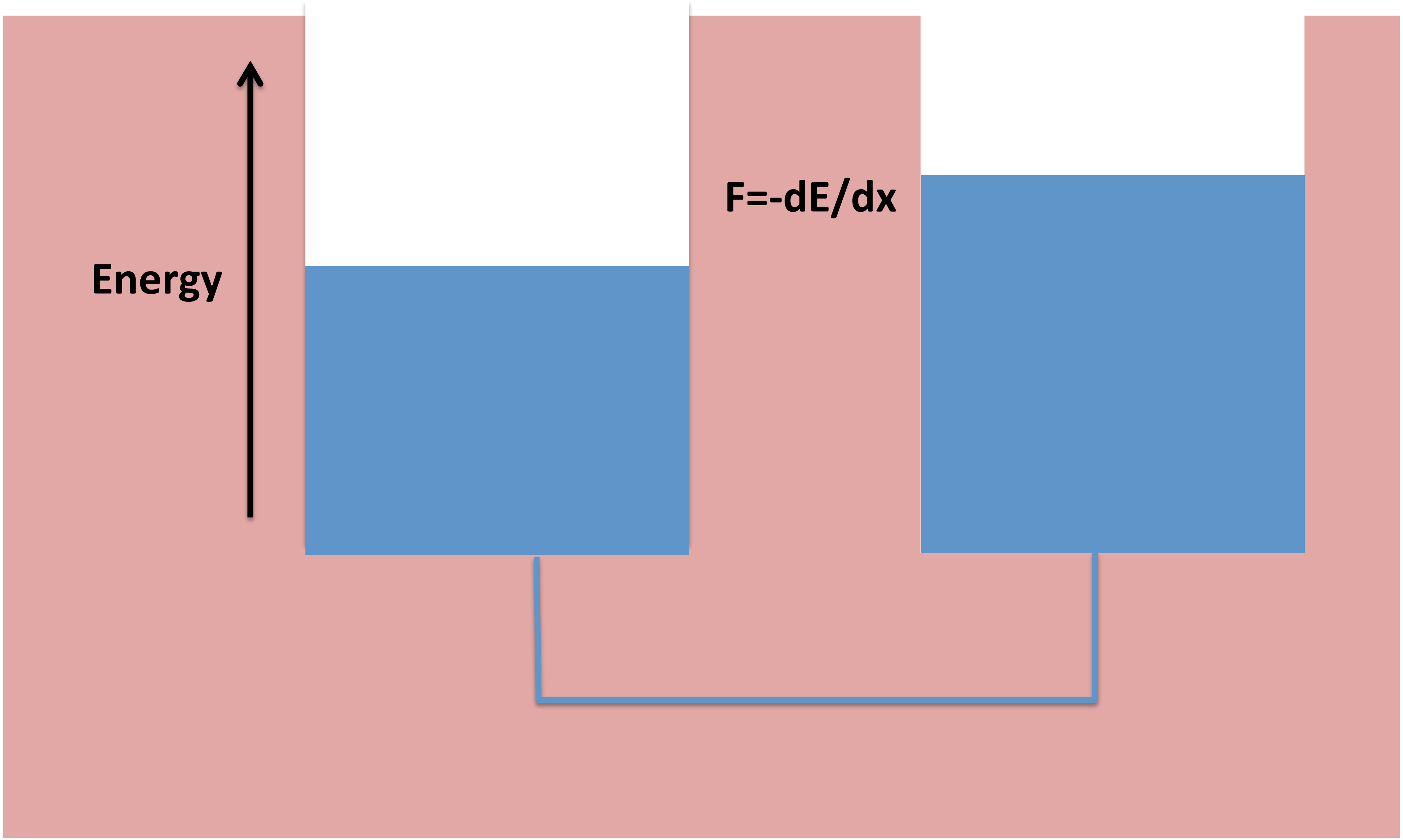


Subsurface imaging of carbon nanotubes in a polymer composite
(Zhao, Nanotechnology, 2010)

Fermi level and work function



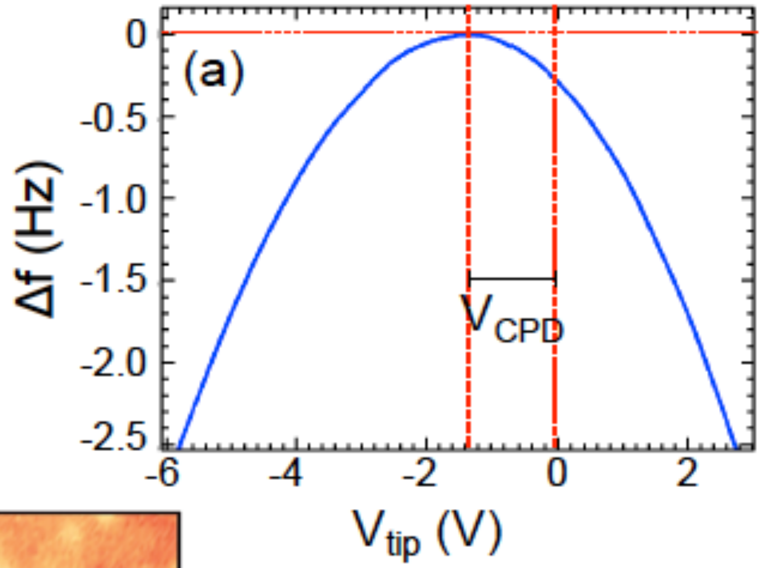
Kelvin probe force microscopy

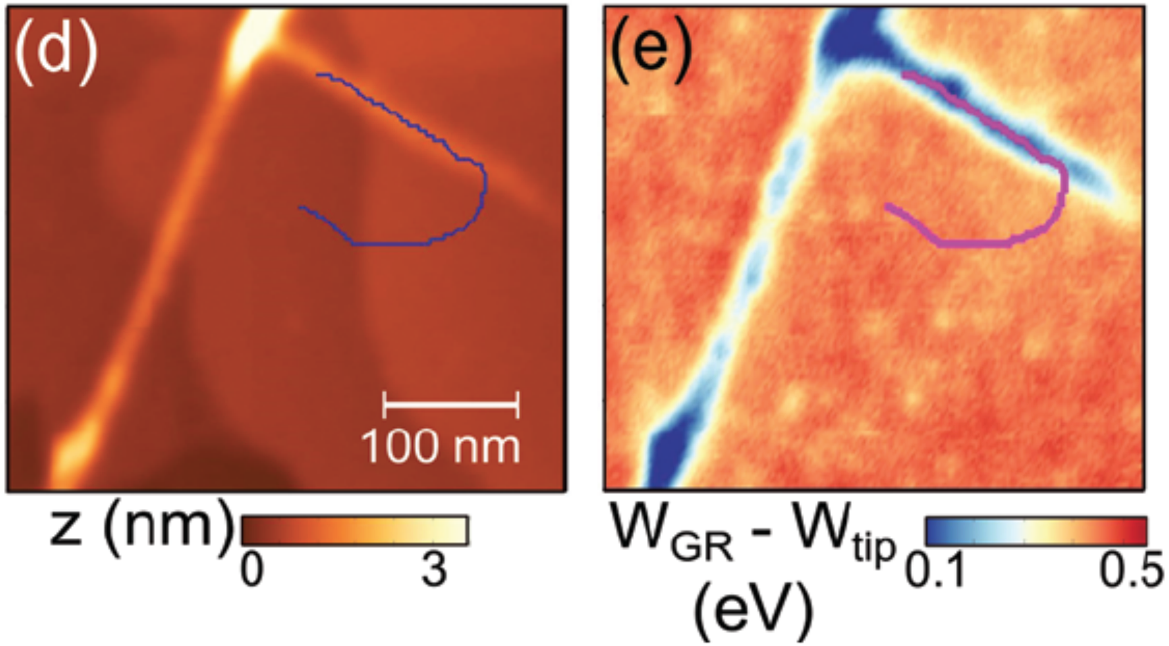


Kelvin probe force microscopy

Force vs. bias curve of W tip on graphene:
Contact potential difference

$$V_{\mathrm{CPD}} = W_{sample} - W_{tip}$$





topography

Local workfunction

Graphene delaminations from Iridium substrate
Samaddar *et al.,* Nanoscale 2016