Atomic and molecular interactions.

Scanning probe microscopy.

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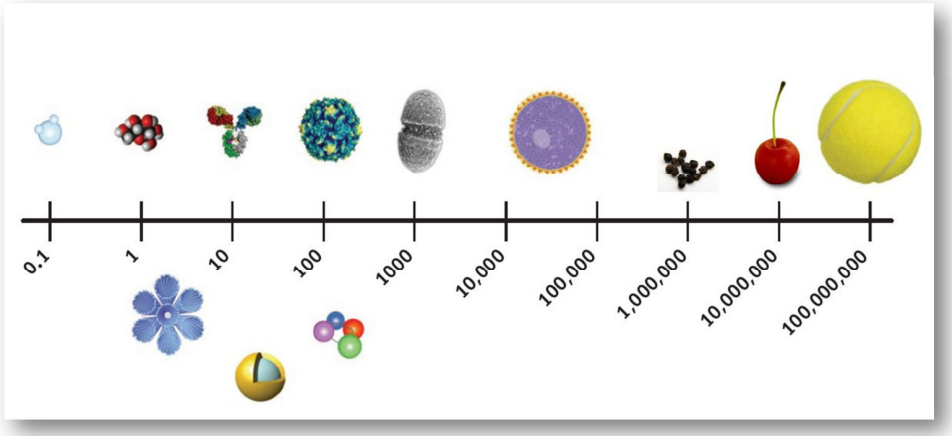
Nanoscale



Problem: Abbe's formula

$$\delta = 0{,}61\frac{\lambda}{n \sin \omega}$$

optical microscope

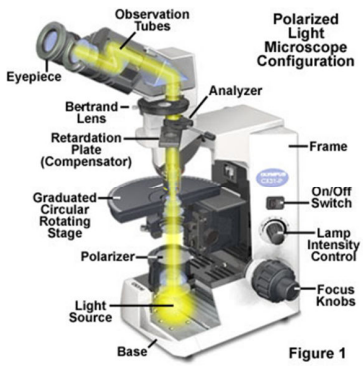
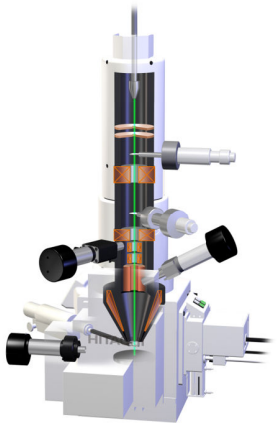


Figure 1

electron microscope



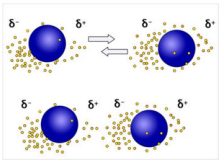
Probe microscopy- history

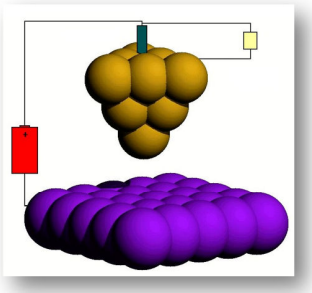
1981: Young, Binning, Rohrer – IBM

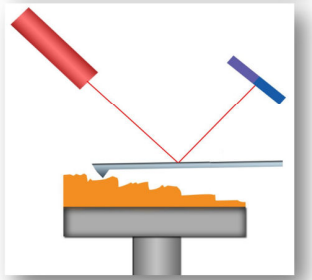
- **scanning tunneling microscopy**

1986: Binning, Quate

- **atomic force microscopy**

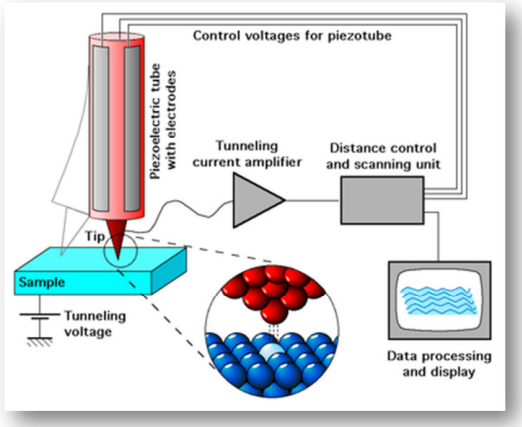






Scanning Tunneling Microscopy

electron tunnelling: measurable electrical currents between two conductors separated by a sufficiently thin uniform insulator



$$I \sim e^{-\kappa z}$$

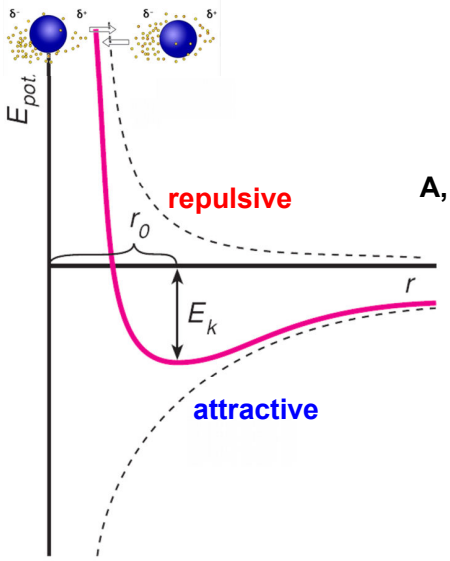
z: distance (Z-axis)

κ: 2,2 Å^{-1}

I~ nA

Atomic interactions

Lennard-Jones potential:



$$E_{pot} = E_{attraction} + E_{repulsion}$$

$$E_{pot} = -\frac{A}{r^n} + \frac{B}{r^m}$$

A, B: interaction-specific constants

n (attraction) < m (repulsion)

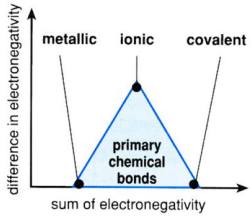
r_0: binding distance

E_k: binding energy

Bond types 1

intramolecular		intermolecular
strong	⟷	weak
primary		secondary

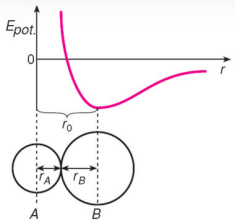
- **covalent: common electron state around the participating nuclei**
- **(metallic bond: multi-atomic system)**
- **electrostatic**
  - **ionic bond: Coulomb-forces between ions**
  - **dipole type charge distribution**

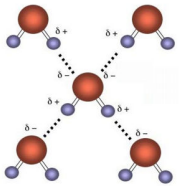


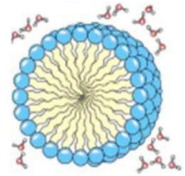
Interaction	Distance dependence of E_{pot}	Average binding energy (eV)
Ion-ion	1/r	2-3
Ion-dipole	$1/r^2$	0,1-0,2
Dipole-dipole	$1/r^3$	0,02
Dispersion	$1/r^6$	0,02

Bond types 2

- **Van der Waals: between atoms without permanent dipole moment (apolar)**
  - **temporarily created dipole interacts with an apolar molecule or atom thus converting it into a dipole (induced dipole)**
- **H-bond: the H-atom interbridges 2 other atoms (F, O, N) of high electronegativity**
  - **E ~ 0,2 eV**
- **hydrophobic interaction: weak Van der Waals interaction, but thermal motion (*kT*~0,025 eV) would disrupt the system**
  - **ordered water molecules exclude the apolar structures (minimized contact surface)**



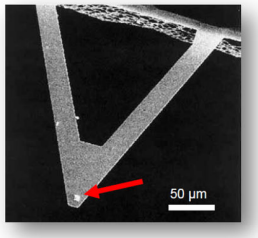




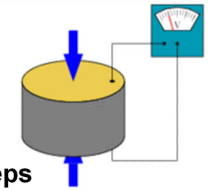
Atomic Force Microscopy

TB. page 579.

- aim: to get rid of lens / optics and light is not favourable in direct imaging
- „do it yourself”:
  - thin, soft probe („point detector”)

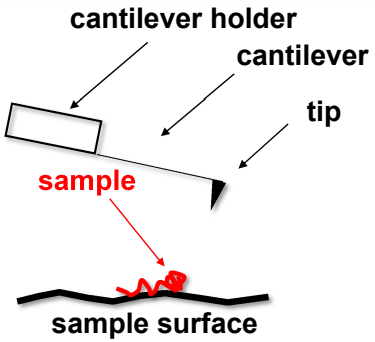


  - smooth surface (mica)



  - stage: X/Y/Z axis translational motion in atomic steps

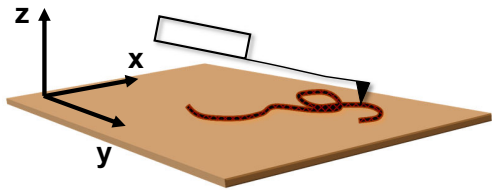
Atomic force microscope (AFM)

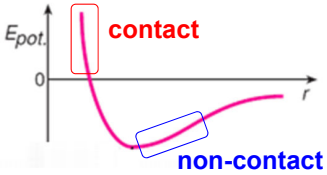


operating modes:

- contact: the tip touches the surface
- non-contact: the tip is away from the surface
- oscillating: the cantilever is being oscillated near its resonant frequency

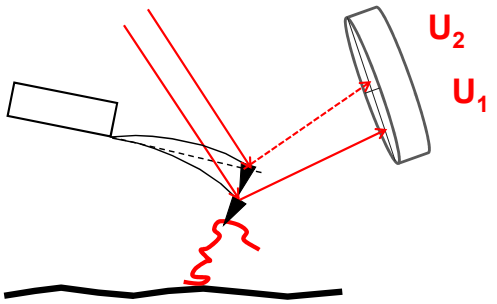
AFM

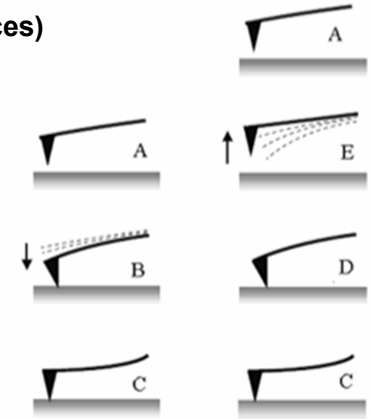




Working principle of AFM 1
contact and non-contact modes

quadrant (made of 4 pieces) photodiode



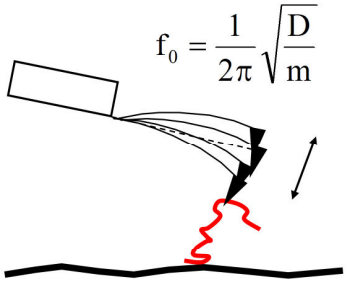


approaching the surface

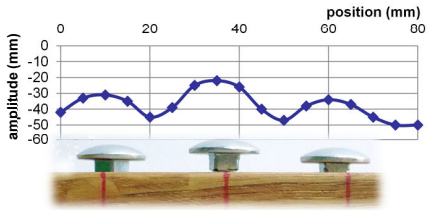
leaving the surface

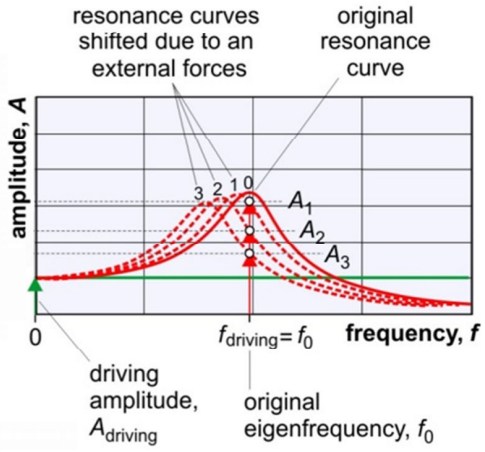
Resonance pract.

Working principle of AFM 2
oscillating mode



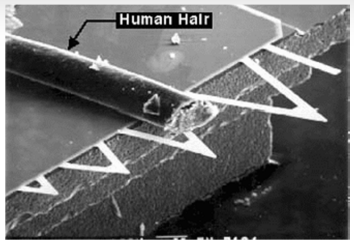
$$f_0 = \frac{1}{2\pi}\sqrt{\frac{D}{m}}$$

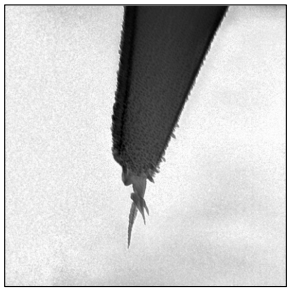


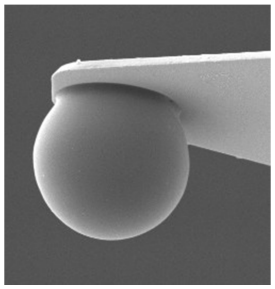


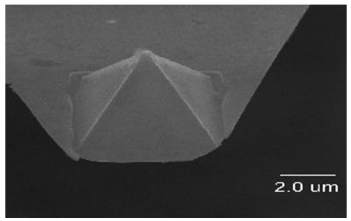
Cantilevers

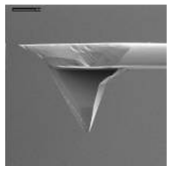
- material: silicon nitride (might be functionalized)
- tip radius: 0,1 nm- 100 µm
- spring constant ~ 0,1-10 N/m
- f_o ~ 50-500 kHz

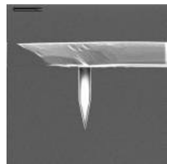




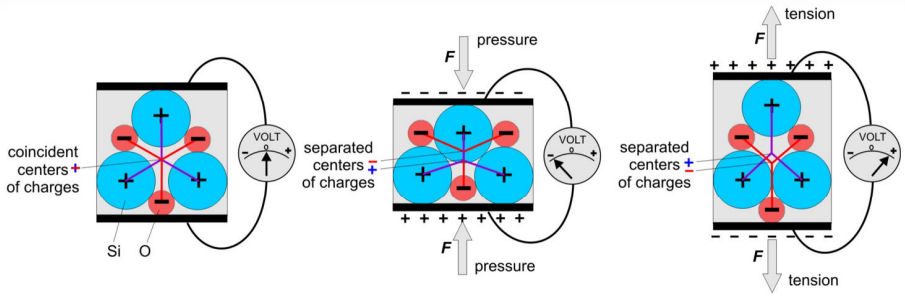






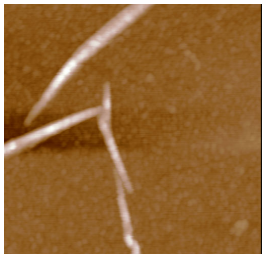


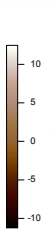
Principle of scanning: piezoelectricity

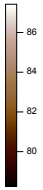


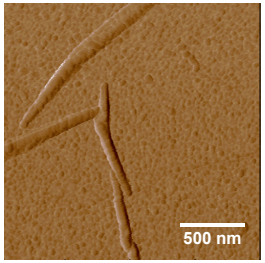
- direct piezoelectric effect: deformation → voltage
- inverse piezoelectric effect: voltage → deformation
- X, Y, Z axes piezo: e.g. 150 V → 40 µm

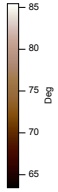
Imaging, resolution



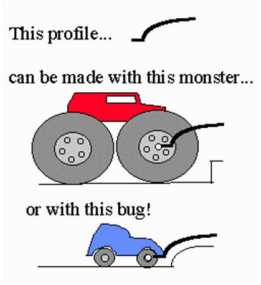


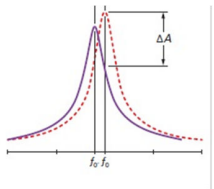


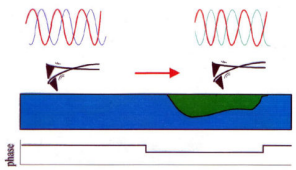




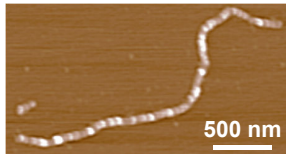
height contrast | **amplitude contrast** | **phase contrast**

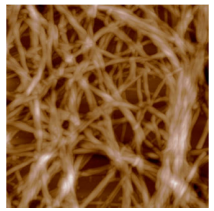


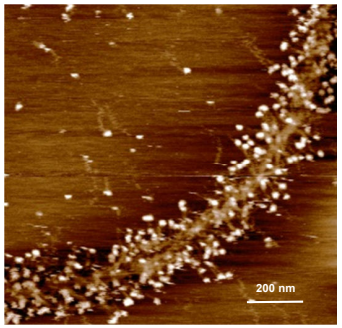


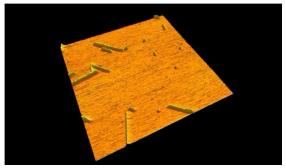


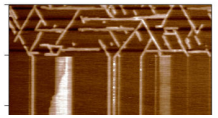
Images were born in our department…

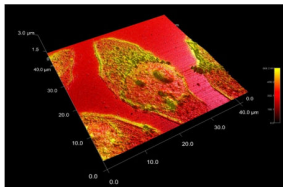


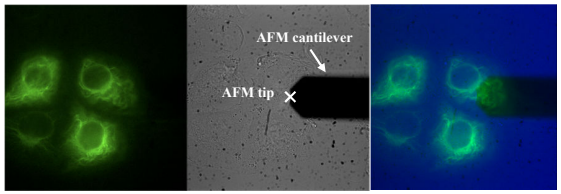




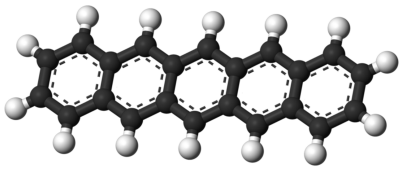






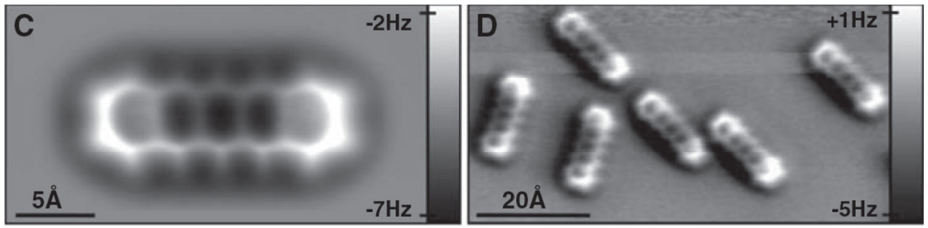


Pentacene molecule

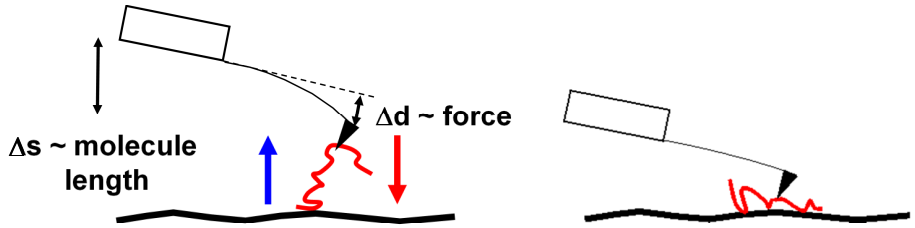


STM

AFM (tip covered with CO)



Elasticity measurement performed with AFM

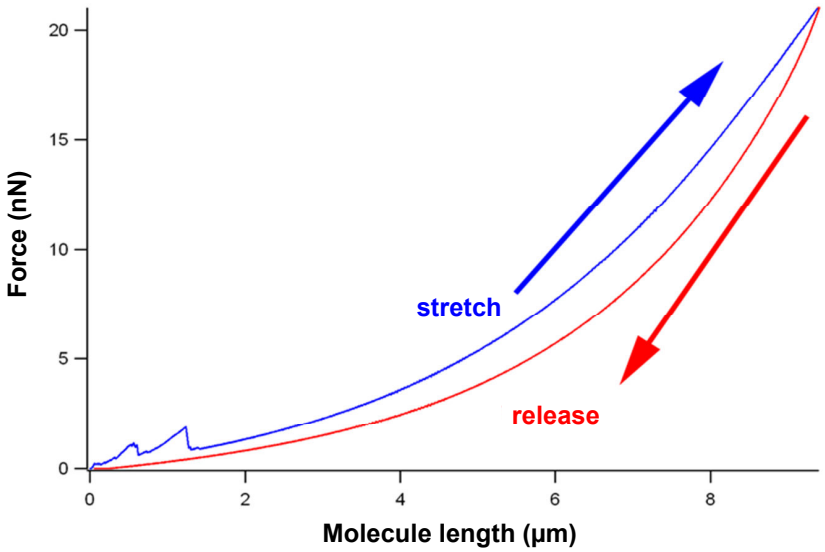


F = force = D Δd

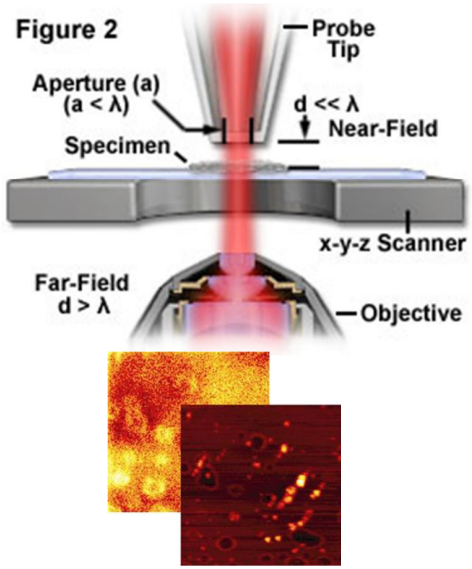
Δd = deflection

Δs = cantilever travel

Stretch-release curve measured with AFM



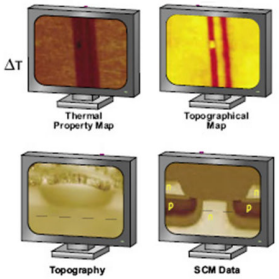
NSOM (Near Field Scanning Optical Microscopy)

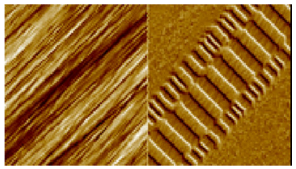


- optical fiber (probe)
- illumination by laser (excitation)
- beam diameter: a < λ
- close to the probe tip („near-field") no diffraction
- limit of resolution: 30-100 nm
- detector (commercial objective lens) in the „far-field"

Family tree of scanning probe microscopes

- Scanning Thermal Microscopy (SThM)
- Scanning Capacitance Microscopy (SCM)
- Near Field Scanning Optical Microscopy (NSOM)
- Scanning Force Microscopy (SFM)
  - Atomic Force Microscopy (AFM)
  - Lateral Force Microscopy (LFM)
  - Electrical Force Microscopy (EFM)
  - Chemical Force Microscopy (CFM)
  - Magnetic Force Microscopy (MFM)
- Scanning Tunneling Microscopy (STM)





MFM: harddisk tracks

Thank YOU for your attention!