Atomic and molecular interactions

As an example: atomic force microscopy

(Textbook chapters: I/1.1, I/1.2, I/1.3, I/1.4, I/2, X/2 Related practice: Resonance)

Tamás Bozó

Nanobiotechnology and Molecular Biophysics Workgroup

Department of Biophysics and Radiation Biology

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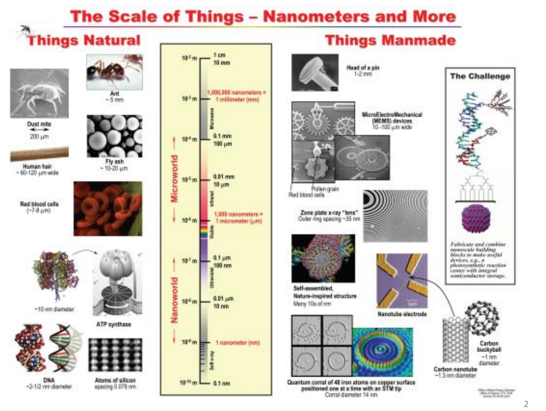

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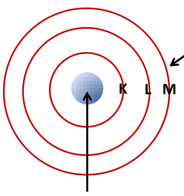
Atomic structure



energy levels (shells) with
K: max. 2 e^-
L: max. 8 e^-
M: max. 18 e^-

nucleus, including nucleons:
protons (p^+)
neutrons (n^0)

chemical properties!

Z: atomic number = number of protons (= number of electrons)
N: neutron number
A: mass number = Z+N
(Nuclear structure will be detailed in Lecture 11.)

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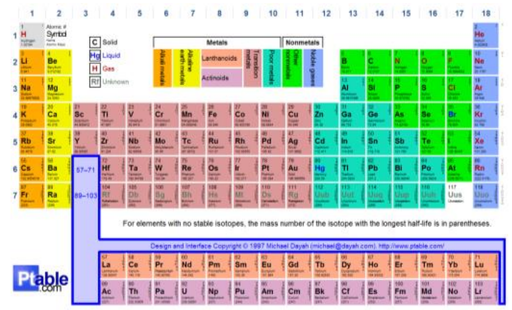
Atomic interactions

Noble gases: found in their atomic form in nature *(He, Ne, Ar, Kr, Xe, Rn)*

Other elements: form molecules held together by chemical bonds. *(e.g. H_2, HCl, H_2O, …)* Each atom has a (more or less) fixed position in the molecule.



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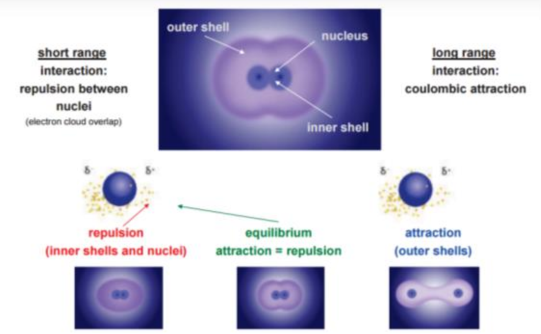
Atomic interactions



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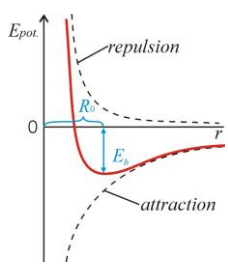
Atomic interactions

Bringing two atoms (ions/molecules/…) close to each other attractive and repulsive forces emerge between them resulting in a net potential energy function with an energy minimum at a certain distance:



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

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

E_{pot}: potential energy of the system
$E_{attraction}$: E contribution of attractive forces
$E_{repulsion}$: E contribution of repulsive forces
A and *B*: interaction-specific constants (atom dependent)
$n<m$
r: distance of atoms
E_b: bindig energy
R_0: binding distance

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Bond Types

Classification systems:

- Intra/intermolecular bonds
- According to the strength of bonds:
  - Strong/weak
  - Primary (covalent, metallic, ionic)
  - Secondary (dispersion, dipole-dipole, hydrogen)
- Other Bond types…

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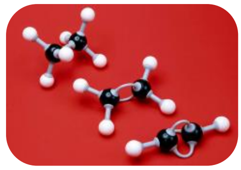
I. Covalent bond



	R_0	E_b
$H_3C\text{-}CH_3$ ethane	154 pm	-331 KJ·mol^{-1}
$H_2C\text{=}CH_2$ ethylene	139,9 pm	-590 KJ·mol^{-1}
$HC\equiv CH$ acetylene	120,3 pm	-812 KJ·mol^{-1}

- Atoms are held together by electrons of common orbitals, called molecular orbitals.
- Valence electrons interact the most.
- Single, double or triple bond depending on the number of shared electrons.
- Some electrostatic component may be present (see later), but not predominant.
- Strong interaction: Eb>1 eV
- *(1 eV = 1.6*10^{-19}J = 96 kJ/mol ~ 100 kJ/mol)*

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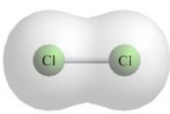
I. Covalent bond

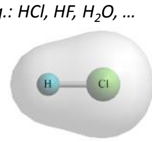
Apolar (nonpolar or homeopolar) bond

Center of (+) és (-) charges of the molecule coincides
Binding electron(s) shared equally
„purely covalent"
E.g. H_2, Cl_2, O_2, …



Polar (heteropolar) bond

Centers of (+) and (-) charges do not coincide
Electrostatic contribution appears
Electron cloud is polarized
Electric dipole is formed
E.g.: HCl, HF, H_2O, …



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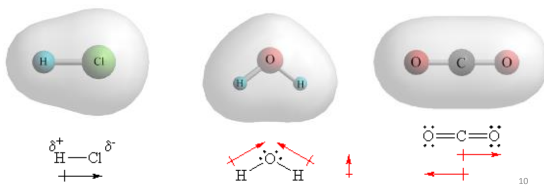
I. Covalent bond

Electric dipole moment: measure of the separation of positive and negative electric charges.

$$p = Q \cdot d$$

p: electric dipole moment
Q: charge (positive and negative)
d: distance of separation
[D, debye] *(1D = 3.34*10^{-30} Cm)*



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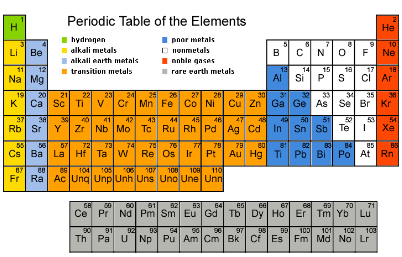
I./b Metallic bond

- Atoms are held together by common electrons (delocalized orbital)
- Valence electrons form continous electron band
- Strong interaction: E_b>1 eV
- Multi atomic systems



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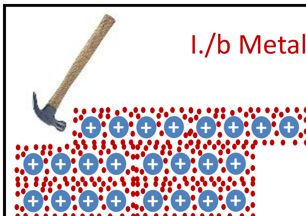
I./b Metallic bond



Metallic lattice: positively charged metal ions in a crystall lattice surrounded by a cloud of delocalized electrons.

Physical properties:
Metals are:

- Non transparent
- Ductile (shapeable)
- Good electric conductors
- etc.

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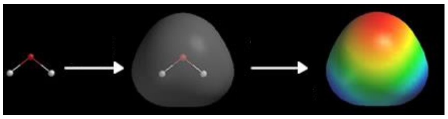
II. Bond types involving electrostatic interactions

Electronegativity

- is a chemical property that describes the tendency of an atom or a functional group to attract electrons towards itself.
- The higher the associated electronegativity number, the more an element or compound attracts electrons towards it.
- Approximately proportional to the sum of ionization energy and electon affinity.
- Calculated with different methods *(Pauling, Mulliken, Sanderson…)*



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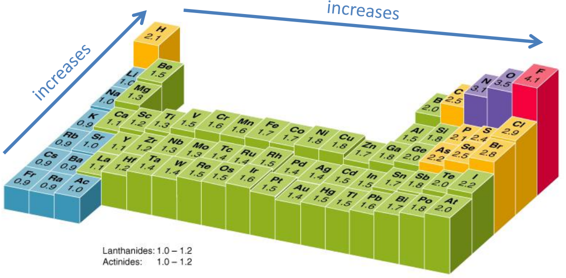
II. Bond types involving electrostatic interactions

Electronegativity according to L. **Pauling** (dimensionless units)



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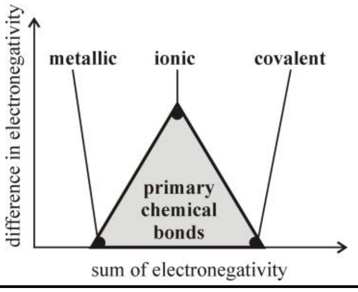
II. Bond types involving electrostatic interactions

Classic bonds classified according to electronegativity:

ΔEN : < 0.6 (apolar covalent) 0.6 – 2.1 (polar covalent) 2.1 < (ionic)



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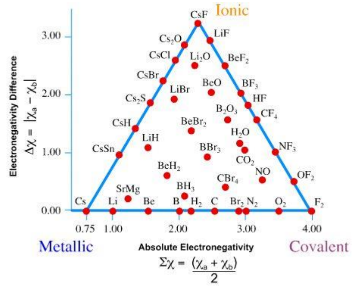
II. Bond types involving electrostatic interactions

Classic bonds classified according to electronegativity: an example



(This modell utilizes Norman (and not Pauling) EN values.)

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II./a Ionic bond

- Atoms are held together by Coulombic forces between (+) and (-) point charges
- „Limiting case of heteropolar bonds"
- Formed between atoms of significantly different electronegativity *(e.g.: NaCl, ΔEN = 3 – 0.9 = 2.1)*
- Can form between two atoms, but ions are usually multi-atom systems.
- Long range interaction - attraction is inversely proportional to the distance (decreases slowly with it).
- Electrostatic interction can be largely affected by other charged components *(eg. dissociation in water!)*
- Strong interaction (E_b > 1 eV)

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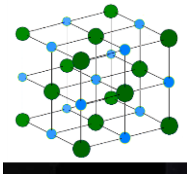
II./a Ionic bond



Ionic crystals: stochiometric ratio of positive and negative ions are structured into a periodic crystalline structure. *(e.g.:NaCl)*

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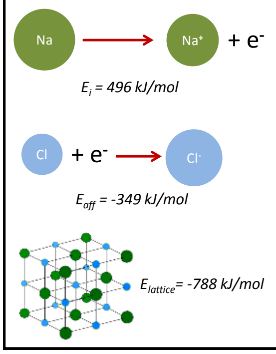
II./a Ionic bond



Ionization energy: is the energy *required* to remove electrons from gaseous atoms or ions.

Electron affinity: amount of energy *released* when an electron is added to a neutral atom or molecule to form a negative ion (measured in the gaseous state).

Lattice energy: measure of the strength of bonds in an ionic compound. Energy *required to* completely *separate* one mole of a solid ionic compound into gaseous ionic constituents.

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II./b Dipole-dipole interaction

- Constant charge distribution is present in a (given part of a) molecule
- Partially (+) and (-) segments are held together by electrostatic interactions (Coulombic forces)
- Intra/intermolekular interaction.
- Weak interaction (E_b = 0.003-0.02 eV)

- Energy of attracting interaction between dipoles:

$E_{attraction} = p\,E$

p: dipole momentum
E: electric field strength generated by the surrounding partners

($E_{repulsion}$: stems from the repulsion of the participant's electron cloud)

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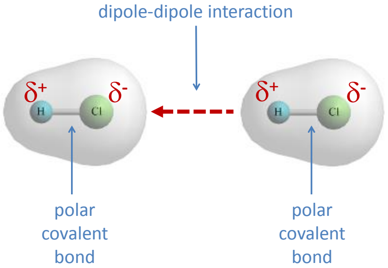
II./b Dipole-dipole interaction



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III. Van der Waals-interactions

- Sum of attractive and repulsive interactions between two apolar atoms, molecules or apolar molecular parts.
- The attractive contribution (also called *London*-, or *dispersion force*) is a result of temporarily created dipoles that can induce the polarization of other apolar molecule or molecular part.
- Intermolecular or intramolecular interaction.
- Important biological role: formation of organic structures.
- Week connection (E_b ~ 0.02 eV)

- *[according to other classifications Van der Waals interactions involve all types of weak electrostatic connections (permanent dipole-permanent dipole; permanent dipole-induced dipole, induced dipole-induced-dipole)]*

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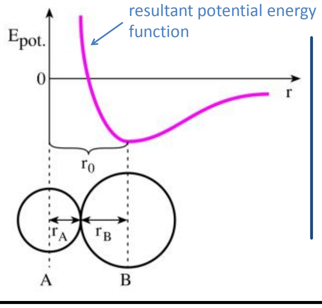
III. Van der Waals-interactions

Equilibrium distance of a Van der Waals interaction can be considered as one definition of atomic size.



r_0 : equilibrium (binding) distance

r_A and r_B : Van der Waals radii of atom A and B

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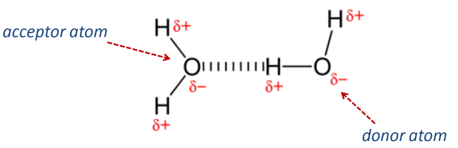
IV. Hydrogen bond

- Two atoms of high electronegativity are held together with a Hydrogen-bridge.
- Primarily between **F, N, O** atoms (pillar atoms).
- Intermolecular/intramolecular interaction
- Typical bond distance: 0.23 – 0.35 nm
- Well defined geometry.
- Important role in structural biology and biochemical reactions.
- Medium strong interaction (typical E_b = 0.2 eV)



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V. Hidrophobic interaction

- Appears in aqeous systems (like biological environments!)
- Apolar, hydrophobic molecules tend to aggregate (form bonds with each other) in aqeous environment in order to exclude the polar water molecules and minimize their surface area exposed to water.
- Intra/intermolecular interaction
- It has mostly entropic origin *(see later at Thermodynamics)* through reduction of highly structured water cage around the apolar surfaces. *(see Organisation of Water later)*
- Important role in structural biology and biochemical reactions.
- Weak interaction.

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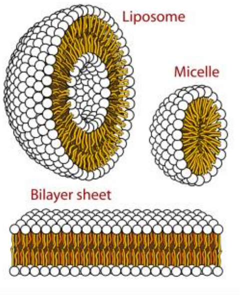
V. Hidrophobic interaction



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Scanning Probe Microscopy (SPM)

Family of instruments used for studying surface properties of various materials.

How do they work?

Etimology and function:

Microscopy: a method being able to form image of small objects.

How small? Size of resolvable objects spans from few pm-s to several μm-s.

They are not *„scope"*-s in the classic sense of the word: They do not *„see"* the object, they *„touch"* it.

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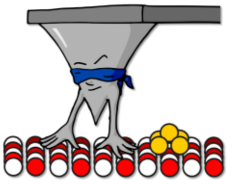
Scanning Probe Microscopy (SPM)

Probe:



- A tiny, specifically designed component particularly sensitive to *atomic interactions*.
- The probe is brought very closed to the sample surface.
- The sensed interactions can be correlated with the distance between the probe and the sample.
- Various interactions can be observed depending on the design of the probe.
- SPM methods are named after the type of atomic interaction sensed by a certain probe.

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Scanning Probe Microscopy (SPM)

Scanning:

- A scanner controls the precise *position* (X; Y) of the probe and its *distance* (Z) from the surface to be imaged.
- The probe can be moved with pm sensitivity in X; Y; Z directions.
- The surface of region of interest (ROI) is scanned point by point during a measurement.
- (The material that enables such precise positioning is *piezoelectric ceramic*. If voltage is applied on it, the ceramic changes its geometry. *See details in Ultrasound lecture, 2nd semester*)

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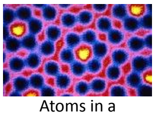
Scanning Tuneling Microscope (STM) 1981



Atoms in a silicon chip

Heinrich ROHRER and Gerd BINNING
Nobel prize: 1986

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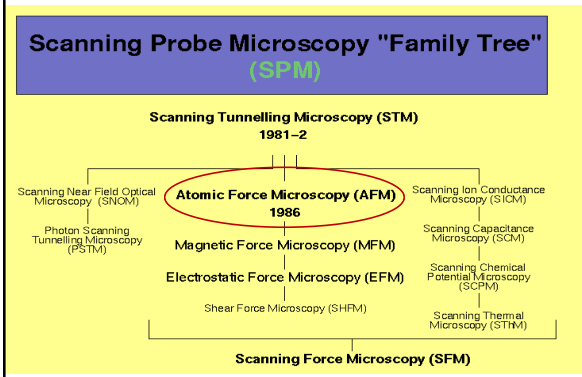
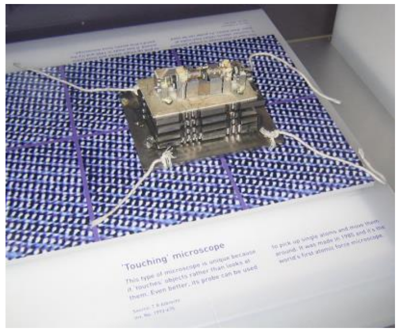
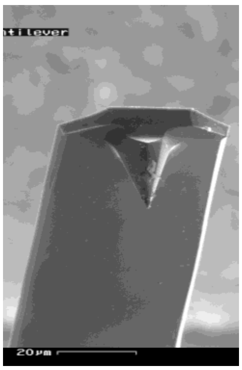


Atomic Force Microscopy



The first one. 1986.

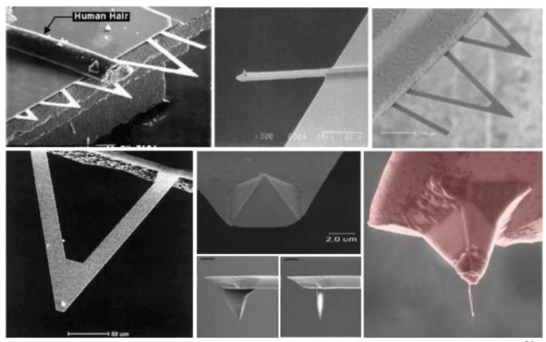
Atomic Force Microscopy



- The probe is a tiny, sharp tip, usually few µm-s tall, and only few nm-s in diameter at the apex.
- The tip is located at the free end of a cantilever that is usually 100-500 µm long.
- Material: usually silicon nitride
- May be coated with a thin metal layer.
- Radius: 0.1 nm – 100 µm
- spring constant: ~0.1-10 N/m
- f_0:~50-500 kHz

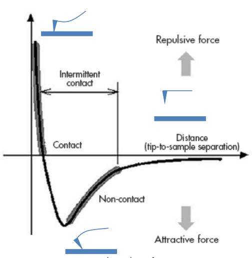
Atomic Force Microscopy

Different types of AFM cantilevers.



Atomic Force Microscopy

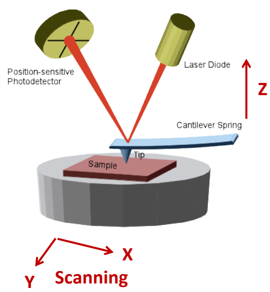
- Bringing the tip very close (few nm-s) to the sample atomic interactions arise between the very last atoms of it and the atoms of the sample.



Depending on the tip-sample distance:

- Net attraction or repulsion may occur.
- Attraction at „longer" distances.
- Repulsion at very short distances.

Atomic Force Microscopy



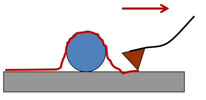
- Attractive and repulsive effects cause the cantilever to bend.
- Deflection of the cantilever is detected by an optical system.
- A laser beam is pointed at the very end of the cantilever, and reflected back to be sensed by a position-sensitive photodetector (PSD).
- Thus vertical deflection of the cantilever is amplified and can be detected with sub-Å sensitivity..

Atomic Force Microscopy (AFM)

- Topographic image is collected with ~10 pm vertical and somewhat worse horizontal resolution.
- Any surfaces (conductors, insulators and semiconductors) can be imaged.
- Works in air and in fluid environment as well.
- Usually does not require fixation or staining of the sample.
- Biological samples can be examined in their native state and physiological environment.

Atomic Force Microscopy

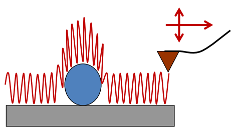
Contact mode:
- The tip is in perpetual contact with the sample surface.
- The deflection of the cantilever (i.e. the force exerted on the sample by the tip) is held constant.
- A Z feedback system is utilized to maintain the deflection at a constant value (setpoint) by lifting or lowering the cantilever.
- Topography data (i.e.: height) in each X;Y point is calculated from these Z movements



Disadvantage:
- Lateral forces exerted by the scanning tip may damage softer samples.

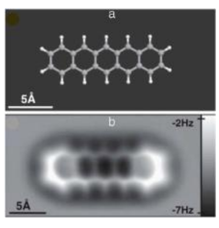
Atomic Force Microscopy

Oscillating mode: (Tapping mode, Non-contact mode)
- Cantilever is oscillated close to its resonant frequency.
- The tip taps the surface gently
- The amplitude of cantilever oscillation changes with surface topography.
- A Z feedback system is utilized to maintain the amplitude at a constant value (setpoint) by lifting or lowering the oscillating cantilever.
- Topography data (i.e.: height) in each X;Y point is calculated from these Z movements



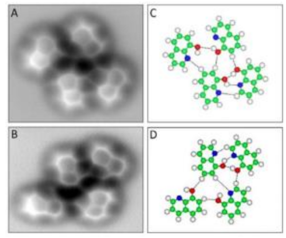
Advantage:
- Virtually eliminated lateral forces.
- Allows more gentle imaging.
- Applicable for soft samples.

Scanning Probe Microscopy (SPM)



Pentacene molecule imaged with AFM

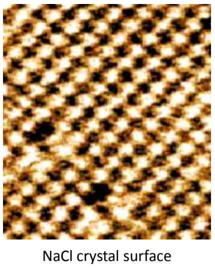
Nature Chemistry ***1****, 597 - 598 (2009)*



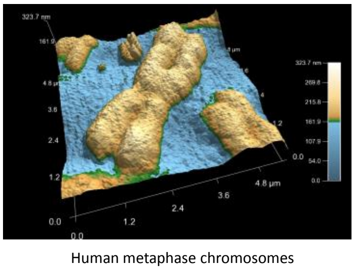
Hydrogen bonds between 8-hydroxiquinoline molecules scanned with AFM

Science, 2013: 342 (6158), 611-614

Atomic Force Microscopy
Images

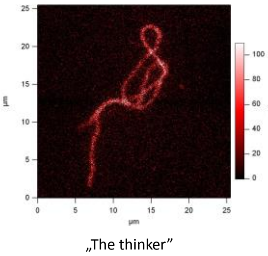


NaCl crystal surface

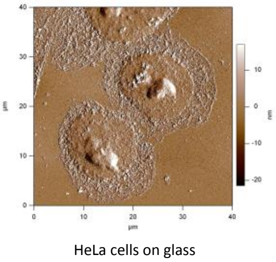


Human metaphase chromosomes

Atomic Force Microscopy
Images



„The thinker"
a single actin polimer



HeLa cells on glass

Atomic Force Microscopy

http://www.youtube.com/watch?v=BrsoS5e39H8

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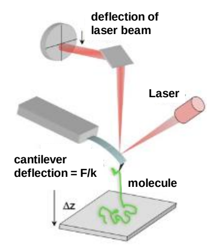
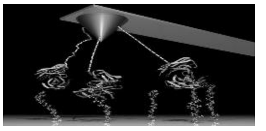
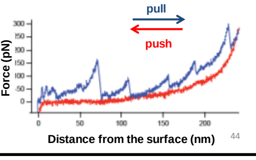
Atomic Force Microscopy

Force spectroscopy: Force-distance traces registered upon push-pull cycles of the AFM tip (movement only in Z direction)
~10 pN sensitivity







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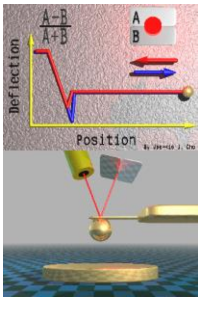
Atomic Force Microscopy

Force spectroscopy:



Deflection of the cantilever (Δx) is proportiaonal to the force (F) (Hooke's law):

$$F = k \cdot \Delta x$$

k : spring constant of the cantilever

Binding forces, viscous and elastic properties can be measured perturbing the sample with the tip and registering the force response.

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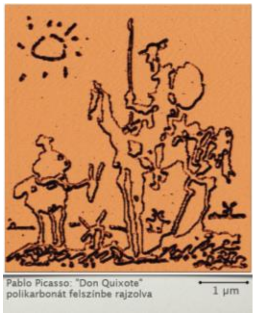
Thank you for your attention!



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