



Structure of matter, matter waves, atomic and molecular interactions

As an example: atomic force microscopy



Tamás Bozó
Nanobiotechnology and Molecular Biophysics Workgroup
Department of Biophysics and Radiation Biology

07 October 2015 1

Overview

Topics:

- atomic models
- atomic structure
- dual nature of electron
- propagation of free and bound electron
- quantum states
- atomic and molecular interactions
- atomic force microscopy

Related exam questions:

8. Proofs of particle-wave duality in case of electron. Matter waves in free and bound state.

9. General description of atomic and molecular interactions.

10. Principles of atomic force microscopy (AFM), working modes, applications.

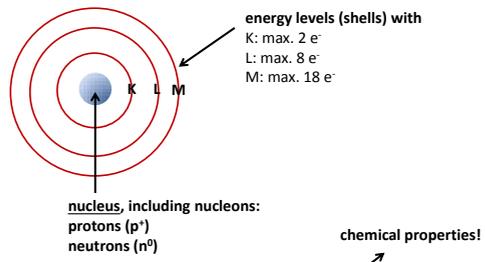
Textbook chapters: I/1.1, I/1.2, I/1.3, I/1.4, I/2, X/2

Related practices: Light emission, Light absorption, Resonance

History of the atom

<p>1803 </p> <p>1904 </p> <p>1911 </p> <p>1913 </p> <p>1926 </p>	<p>~ 400 B.C. Demokritos: atoms are miniscule quantities of matter.</p> <p>1803 J. Dalton: stoichiometric law, every elements consists of identical constituents, billiard ball model</p> <p>1900 M. Plack: Radiation law, quantum physics</p> <p>1904 J.J. Thomson: cathode ray: discovery of electron, mass of electron „plum pudding” model</p> <p>1910 R.A. Millikan: charge of electron</p> <p>1909-11 E. Rutherford: discovery of nucleus, planetary model</p> <p>1913 N. Bohr: discretet energy states, Bohr-model</p> <p>1914 J. Franck, G.L. Hertz: evidence of energy quanta</p> <p>1923 L.V. de Broglie: electron wave</p> <p>1926 E. Schrödinger: wave function, quantummechanical atomic model</p> <p>1927 W. Heisenberg: uncertainty relation</p> <p>1927-28 C.J. Davisson, L.H. Germer, G.P. Thomson: evidence of electron waves</p> <p>1932 J. Chadwick: discovery of neutron</p>
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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 (n⁰)

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.)

The wave nature of the electron

Wave-particle duality: Electron is at once a subatomic particle, with well defined mass and charge AND a wave. (See matter waves in Lecture 2.)

Wavelength of an electron (1923):



$$\lambda = \frac{h}{p}$$

h : Planck's constant
 p : momentum
 m_e : mass
 v : velocity

$$p = m_e \cdot v$$

Experimental proof of wave nature (1927-28):
Interference of electron beams on crystals and metal foils.
(J. Davisson, L.H. Germer and G.P. Thomson, see Lecture 2.)

5

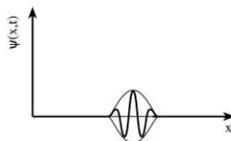
The wave nature of the electron



Propagation law of electron waves (1926):

A wave function(or state function) $\Psi(x,t)$ is used to describe the amplitude of the electron wave as a function of position (**x**) and time (**t**).
Electron is pictured as a continous charged cloud of finite size with a charge density proportional to Ψ^2 at any point in space.

visualization: wave package



location: where $\Psi(x,t) \neq 0$
momentum (p): given by the shape

6

Propagation law of free electrons (e.g. vacuum tube electron)

Since $\Psi(x,t) \neq 0$ holds for more than one point, the position cannot be determined with a simple numeric value. Momentum neither can be given by a single numeric value. The function is nonperiodic, thus it cannot be characterised by a single wavelength. Any λ between an approximate largest λ_1 and smallest λ_2 wavelength can characterize the wave package.

Since $p = \frac{h}{\lambda}$, $v = \frac{p}{m_e}$ and $s = v \cdot t$

instead of having a well determined single value for momentum, velocity and displacement, they can be characterised by any value between p_1 and p_2 , v_1 and v_2 , s_1 and s_2 .

$\Psi(x,t)$ will disperse while propagating and new wave cycles appear on the graph.



Werner Karl Heisenberg
1901-1976

Heisenberg uncertainty relation (1927):

A wave function(or state function) $\Psi(x,t)$ is completely determined, although some pieces of the information it carries (e.g. position, momentum, velocity of the electron) are uncertain.

$\Delta x \cdot \Delta p \geq h$

Δx : uncertainty of position
 Δp : uncertainty of momentum
 h : Planck's constant

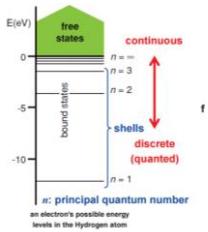
Conclusion: The more determined the position (x) of an electron, the less determined the momentum (p), and vice versa.

It can be extended to other pairs of physical properties (complementary variables) of a particle, eg. energy and time:

$\Delta E \cdot \Delta t \geq h$

What about electrons bound in an atom?

1. External force field is present due to the positively charged nucleus.
2. The field will move (distort) the state function of the electron to its own direction.
3. Electrons do not have enough energy to leave the proximity of the nucleus, they are in bound state.
4. Electrons disperse due to the uncertainty of their momentum.



As a result:
A dynamic equilibrium evolves between the attractive effect of nucleus and the dispersing nature of the state function. Constant, stationary, symmetric state functions emerge to form discrete, strictly differentiated, well defined atomic electron states.
 Δt uncertain, so E can be certain which leads to discrete energy levels.

Properties of quantized atomic electron states

Bound electrons – quantized energy levels. Their state of the electron can be described by **quantum numbers**:

quantum number	possible values	characterizes	describes
principal	$n=1,2,3...7$	electron shell	energy level
azimuthal	$l=0,1,2,...(n-1)$ or: s, p, d, f	subshell	magnitude of orbital angular momentum
magnetic	$m_l=-l,...,0,...,+l$	specific orbital within subshell	direction of orbital angular momentum
spin	$m_s=\pm 1/2$	intrinsic angular momentum (spin) of an electron	direction of the spin (magnitude is constant)

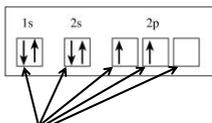
All the four quantum numbers are required to characterize a bound-state electron.

How will electrons occupy their quantum states?

Pauli exclusion principle: Within an atom there cannot be two electrons with all four quantum numbers being identical.

Principle of minimum energy: The total energy of the system should be minimized.

Hund principle: For a given electron configuration, the state with maximum total spin has the lowest energy.

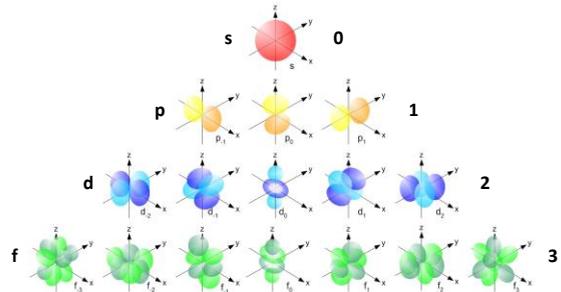


Carbon, Z=6

Electronic orbital: states characterized by n, l and m_l quantum numbers, which may be occupied by at most 2 electrons of opposite spins.

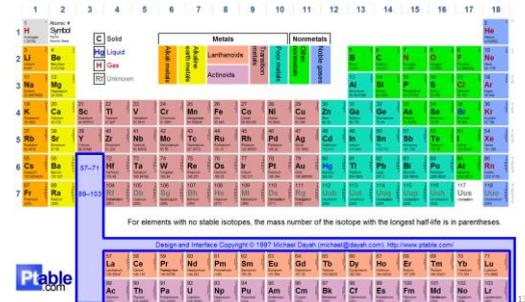
Configuration: Gives the (partially or fully) occupied subshells and the number of equivalent (same subshell) electrons.

Visualization of subshell structure

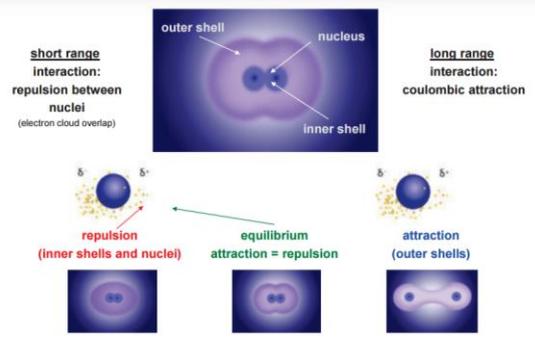


Atomic interactions

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.

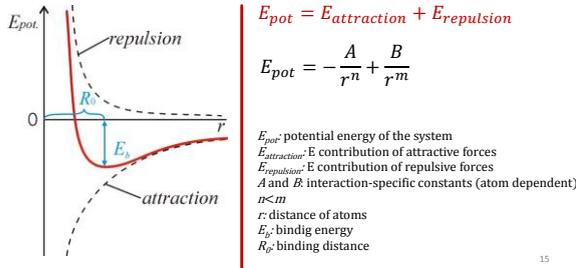


Atomic interactions



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:



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...



I. Covalent bond



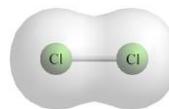
- Atoms are held together by electrons of common orbitals, called molecular orbitals.
- Valence electrons interact the most.
- Single, double or triple bond depending on the number of shared electrons.
- Some electrostatic component may be present (see later), but not predominant.
- Strong interaction: $E_b > 1 \text{ eV}$
 • ($1 \text{ eV} = 1,6 \cdot 10^{-19} \text{ J} = 96 \text{ kJ/mol} \sim 100 \text{ kJ/mol}$)

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

I. Covalent bond

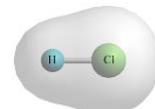
Apolar (nonpolar or homeopolar) bond

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 , ...

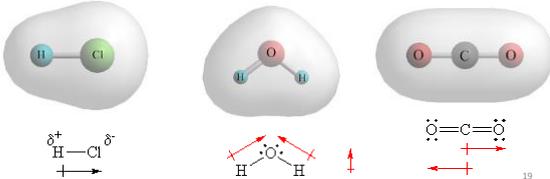


I. Covalent bond

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

$$p = Qd$$

p: electric dipole moment
Q: charge (positive and negative)
d: distance of separation
[D, debye] ($1D = 3,34 \times 10^{-30} \text{ Cm}$)

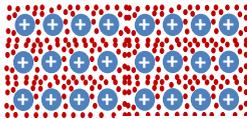


I./b Metallic bond

- Atoms are held together by common electrons (delocalized orbital)
- Valence electrons form continuous electron band
- Strong interaction: $E_p > 1 \text{ eV}$
- Multi atomic systems

Periodic Table of the Elements

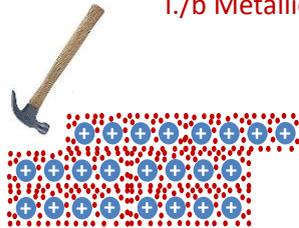
I./b Metallic bond



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



I./b Metallic bond



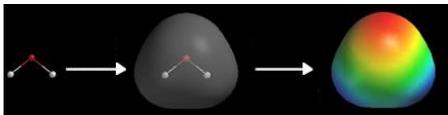
Physical properties:

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

II. Bond types involving electrostatic interactions

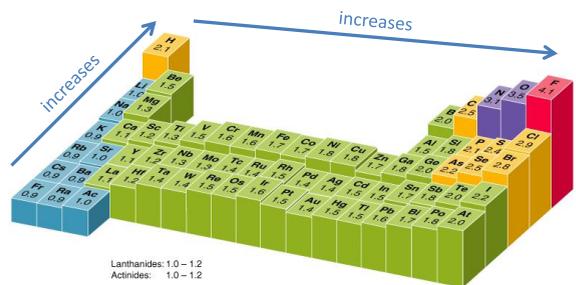
Electronegativity

- 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 electron affinity.
- Calculated with different methods (*Pauling, Mulliken, Sanderson...*)



II. Bond types involving electrostatic interactions

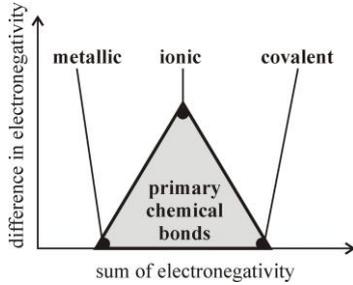
Electronegativity according to L. Pauling (dimensionless units)



II. Bond types involving electrostatic interactions

Classic bonds classified according to electronegativity:

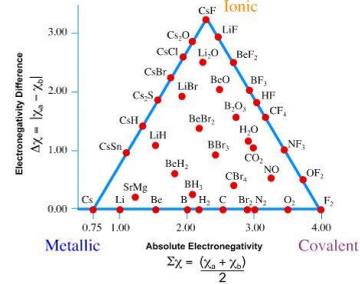
ΔEN : < 0,6 (apolar covalent) 0,6 – 2,1 (polar covalent) 2,1 < (ionic)



25

II. Bond types involving electrostatic interactions

Classic bonds classified according to electronegativity: an example



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

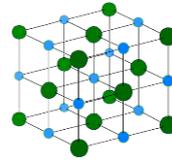
26

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, $\Delta EN = 3 - 0.9 = 2.1$)
- 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 interaction can be largely affected by other charged components (eg. dissociation in water!)
- Strong interaction ($E_b > 1$ eV)

27

II./a Ionic bond

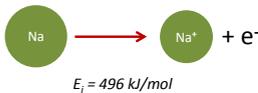


Ionic crystals: stoichiometric ratio of positive and negative ions are structured into a periodic crystalline structure. (e.g.: NaCl)

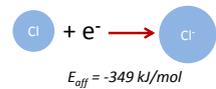


28

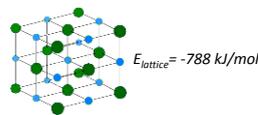
II./a Ionic bond



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.

29

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/intermolecular interaction.
- Weak interaction ($E_b = 0,003-0,02$ eV)

- Energy of attracting interaction between dipoles:

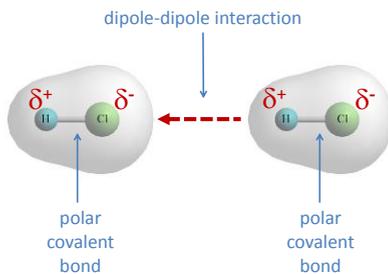
$$E_{\text{attraction}} = p E$$

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

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

30

II./b Dipole-dipole interaction



31

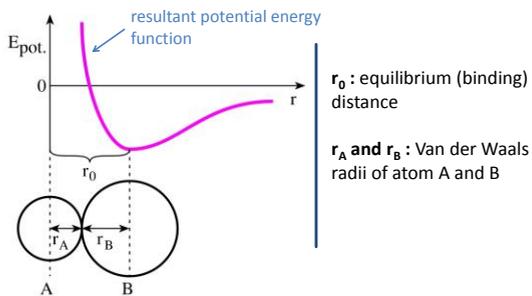
III. Van der Waals-interactions

- 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.
- Weak connection ($E_b \sim 0,02$ 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)]

32

III. Van der Waals-interactions

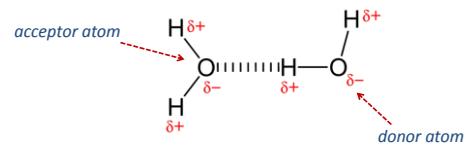
Equilibrium distance of a Van der Waals interaction can be considered as one definition of atomic size.



33

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)



34

V. Hydrophobic interaction

- Appears in aqueous systems (like biological environments!)
- Apolar, hydrophobic molecules tend to aggregate (form bonds with each other) in aqueous 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.



35

V. Hydrophobic interaction



36

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.

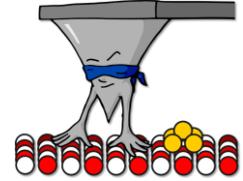
They are not „scope“-s in the classic sense of the word: They do not „see“ the object, they „touch“ it.

37

Scanning Probe Microscopy (SPM)

Probe:

- A tiny, specifically designed component particularly sensitive to *atomic interactions*.
- The probe is brought very close 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.



38

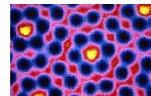
Scanning Probe Microscopy (SPM)

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)

39

Scanning Tuneling Microscope (STM) 1981



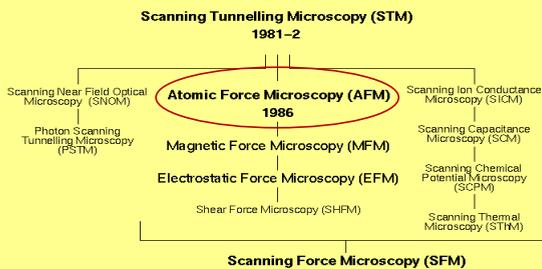
Atoms in a silicon chip



Heinrich ROHRER and Gerd BINNING
Nobel prize: 1986

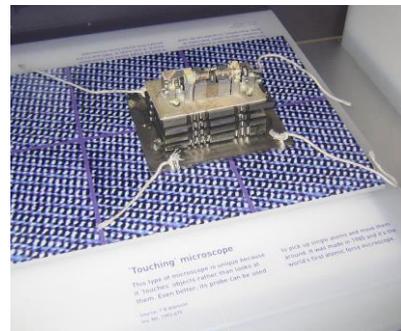
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Scanning Probe Microscopy "Family Tree" (SPM)



41

Atomic Force Microscopy



The first one. 1986.

42

Atomic Force Microscopy

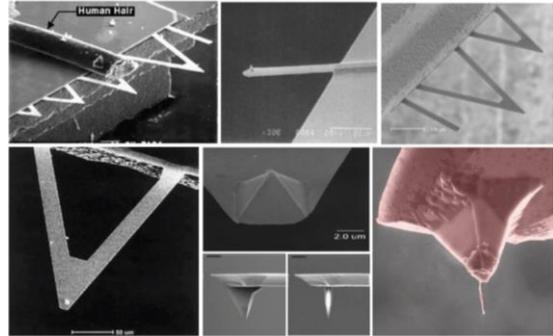


- The probe is a tiny, sharp tip, usually few μm -s tall, and only few nm-s in diameter at the apex.
- The tip is located at the free end of a cantilever that is usually 100-500 μm long.
- Material: usually silicon nitride
- May be coated with a thin metal layer.
- Radius: 0.1 nm – 100 μm
- spring constant: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

43

Atomic Force Microscopy

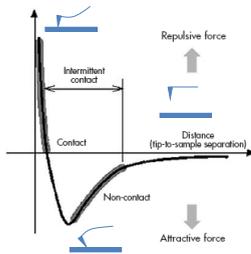
Different types of AFM cantilevers.



44

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.

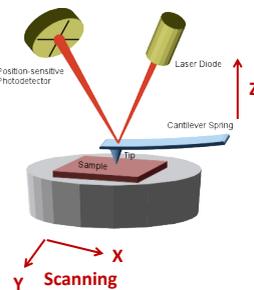


Depending on the tip-sample distance:

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

45

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- \AA sensitivity..

46

Atomic Force Microscopy (AFM)

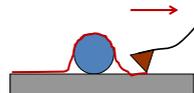
- Topographic image is collected with $\sim 10\text{ pm}$ vertical and somewhat worse horizontal resolution.
- Any surfaces (conductors, insulators and semiconductors) can be imaged.
- Works in air and in fluid environment as well.
- Usually does not require fixation or staining of the sample.
- Biological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

47

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:

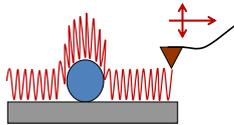
- Lateral forces exerted by the scanning tip may damage softer samples.

48

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

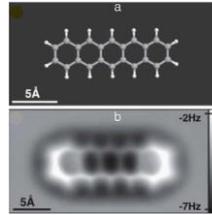


Advantage:

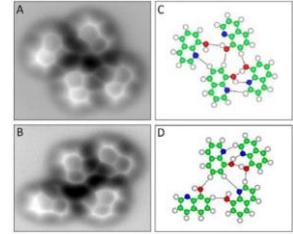
- Virtually eliminated lateral forces.
- Allows more gentle imaging.
- Applicable for soft samples.

49

Scanning Probe Microscopy (SPM)



Pentacene molecule imaged with AFM
Nature Chemistry 1, 597 - 598 (2009)

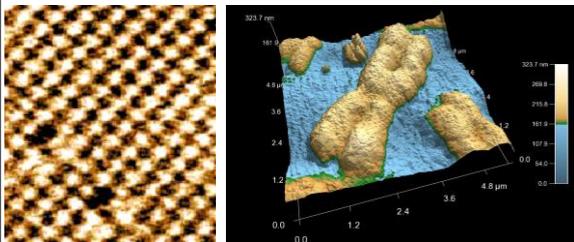


Hydrogen bonds between 8-hydroxyquinoline molecules scanned with AFM

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

50

Atomic Force Microscopy Images

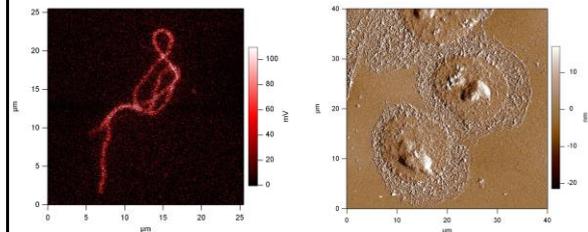


NaCl crystal surface

Human metaphase chromosomes

51

Atomic Force Microscopy Images



„The thinker“ a single actin polymer

HeLa cells on glass

52

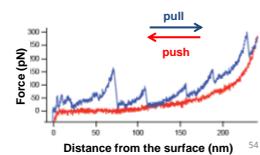
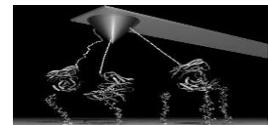
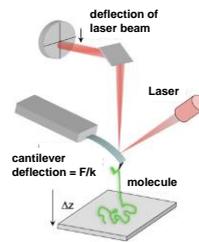
Atomic Force Microscopy

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

53

Atomic Force Microscopy

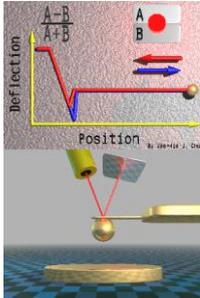
Force spectroscopy: Force-distance traces registered upon push-pull cycles of the AFM tip (movement only in Z direction)
~10 pN sensitivity



54

Atomic Force Microscopy

Force spectroscopy:



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

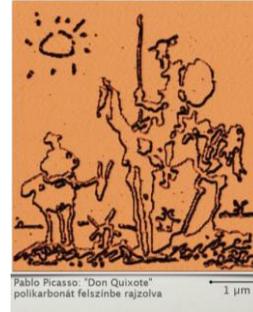
$$F = k \cdot \Delta x$$

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.

55

Thank you for your attention!



56