# 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)*

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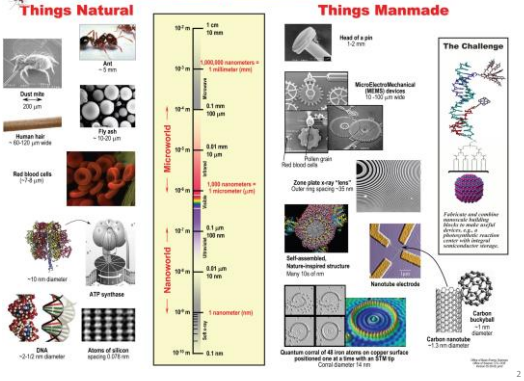
## The Scale of Things – Nanometers and More

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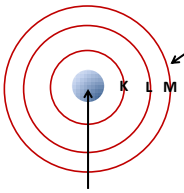
## Atomic structure




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

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

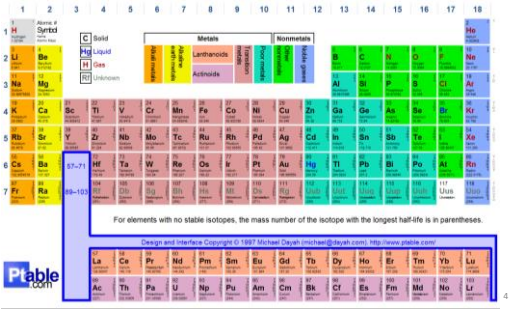
**chemical properties!**

***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.)*

## 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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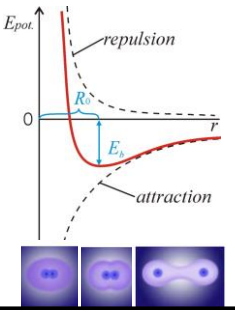
## Fundamental interactions in physics

| Interaction | acts on | effective range | relative strength |
|---|---|---|---|
| **Gravity** | any particle | infinite ( ~$1/r^2$) | $10^{-40}$ |
| **Electromagnetic** | charged particles | infinite (~$1/r^2$) | $10^{-2}$ |
| **Strong nuclear** | nucleons | $10^{-15}$ m | 1 |
| **Weak nuclear** | any particle | $10^{-18}$ m | $10^{-13}$ |

## 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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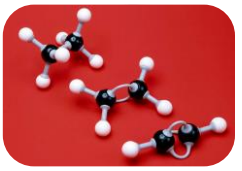
## Bond Types

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…



## I. Covalent bond



| | $r_0$ | $E_b$ |
|---|---|---|
| $H_3C$-$CH_3$ ethane | 154 pm | -331 KJ·mol$^{-1}$ |
| $H_2C$=$CH_2$ ethylene | 139,9 pm | -590 KJ·mol$^{-1}$ |
| HC≡CH acetylene | 120,3 pm | -812 KJ·mol$^{-1}$ |

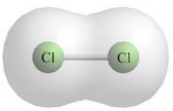
- Atoms are held together by electrons of common orbitals, called molecular orbitals.
- Valence electrons interact the most.
- Single, double or triple bond depending on the number of shared electrons.
- Some electrostatic component may be present (see later), but not predominant.
- Strong interaction: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



## I. Covalent bond

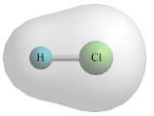
**Apolar (nonpolar or homeopolar) bond**

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, $H_2O$, …*



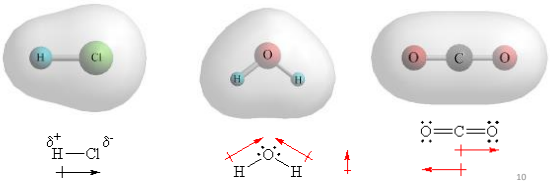



## I. Covalent bond

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

$$p = q \cdot d$$

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









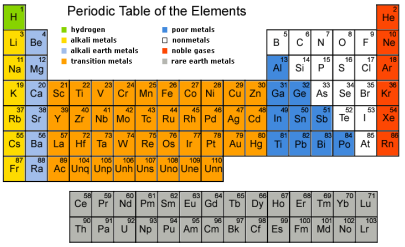






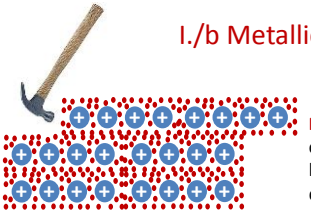
## I./b Metallic bond

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






## I./b Metallic bond



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

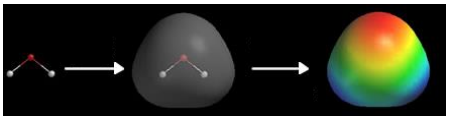

**Physical properties:**
Metals are:

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

## 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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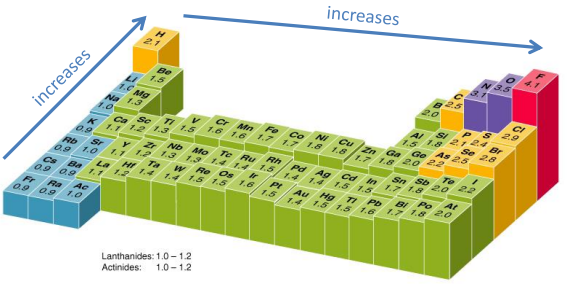
## II. Bond types involving electrostatic interactions

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

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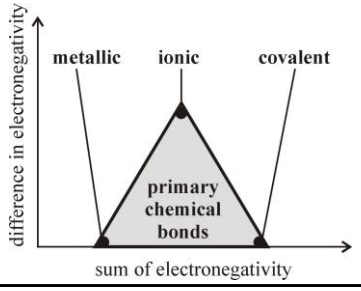
## II. Bond types involving electrostatic interactions

**Classic bonds classified according to electronegativity:**

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

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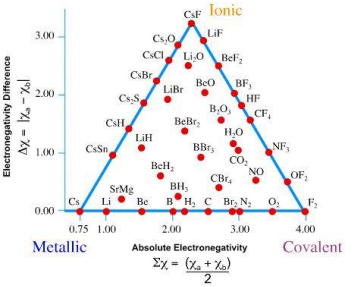
## II. Bond types involving electrostatic interactions

**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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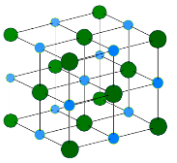
## II./a Ionic bond



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

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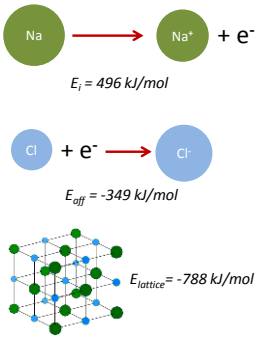
## II./a Ionic bond




**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:

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

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

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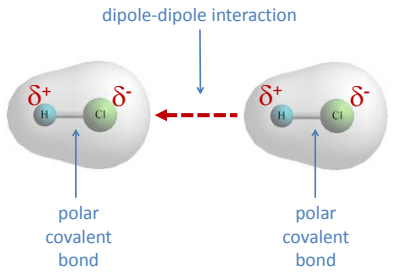
## II./b Dipole-dipole interaction

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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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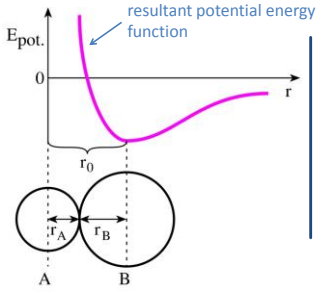
## III. Van der Waals-interactions

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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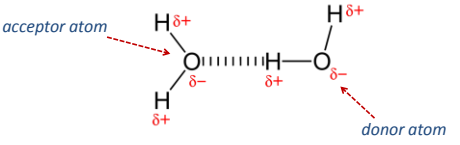
## IV. Hydrogen bond

- 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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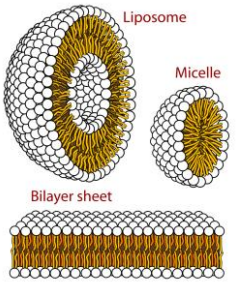
## V. Hidrophobic interaction

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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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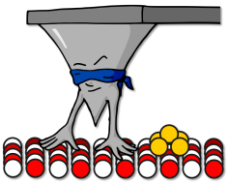
## Scanning Probe Microscopy (SPM)

**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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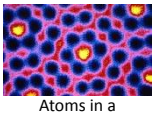
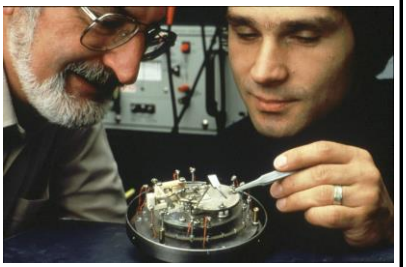
**Scanning Tuneling Microscope (STM) 1981**



Atoms in a silicon chip



Heinrich ROHRER and Gerd BINNING
Nobel prize: 1986

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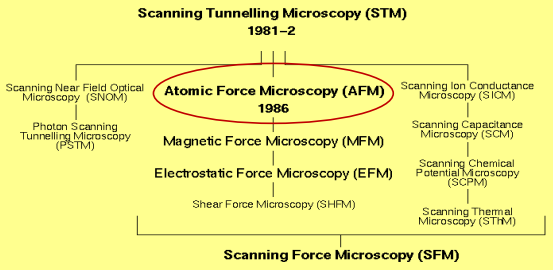
## Scanning Probe Microscopy "Family Tree" (SPM)

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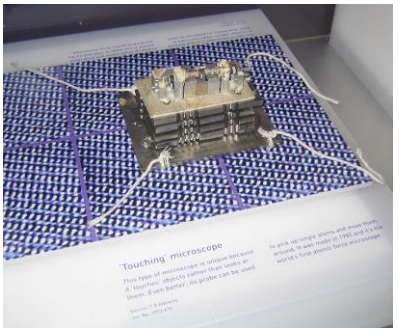
## Atomic Force Microscopy




The first one. 1986.

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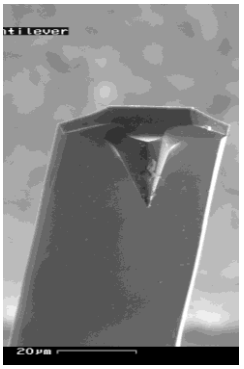
## Atomic Force Microscopy




- 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

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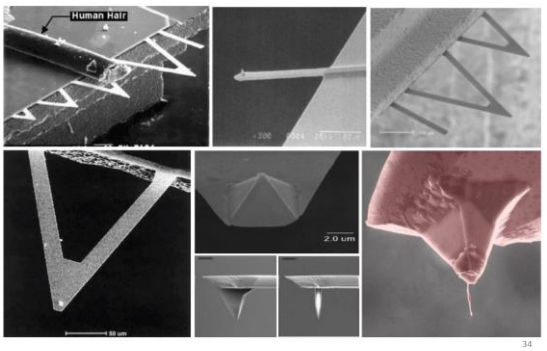
## Atomic Force Microscopy

Different types of AFM cantilevers.

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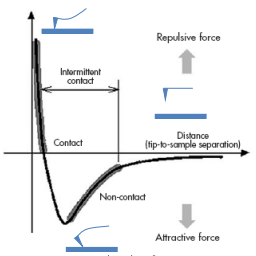
## Atomic Force Microscopy

- 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.

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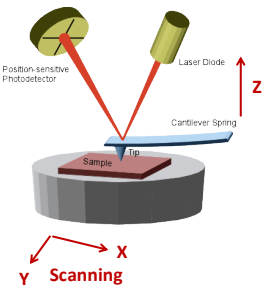
## Atomic Force Microscopy




- 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..

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## 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.

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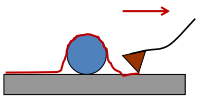
## Atomic Force Microscopy

**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.

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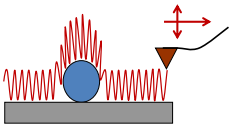
## Atomic Force Microscopy

**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.

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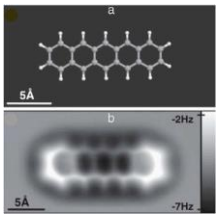
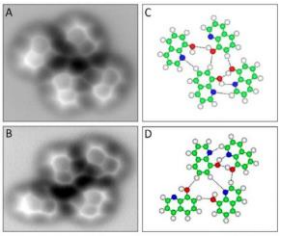
## Scanning Probe Microscopy (SPM)




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*

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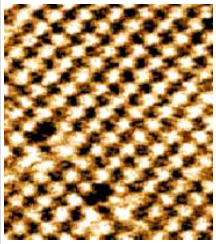
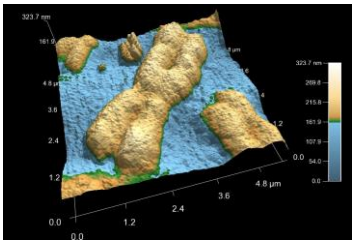
## Atomic Force Microscopy
Images



NaCl crystal surface



Human metaphase chromosomes

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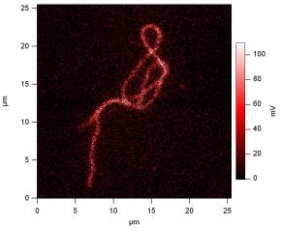
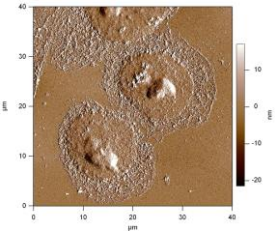
## Atomic Force Microscopy
Images



„The thinker"
a single actin polimer



HeLa cells on glass

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## Atomic Force Microscopy

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

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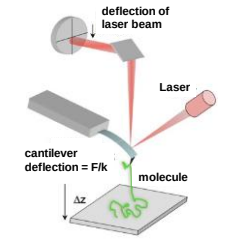
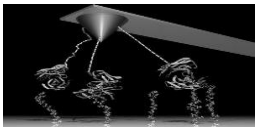
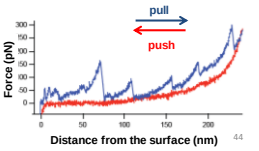
## Atomic Force Microscopy

**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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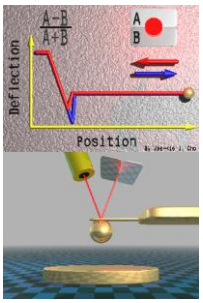
## Atomic Force Microscopy

**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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