# Atomic and molecular interactions.

# Scanning probe microscopy.

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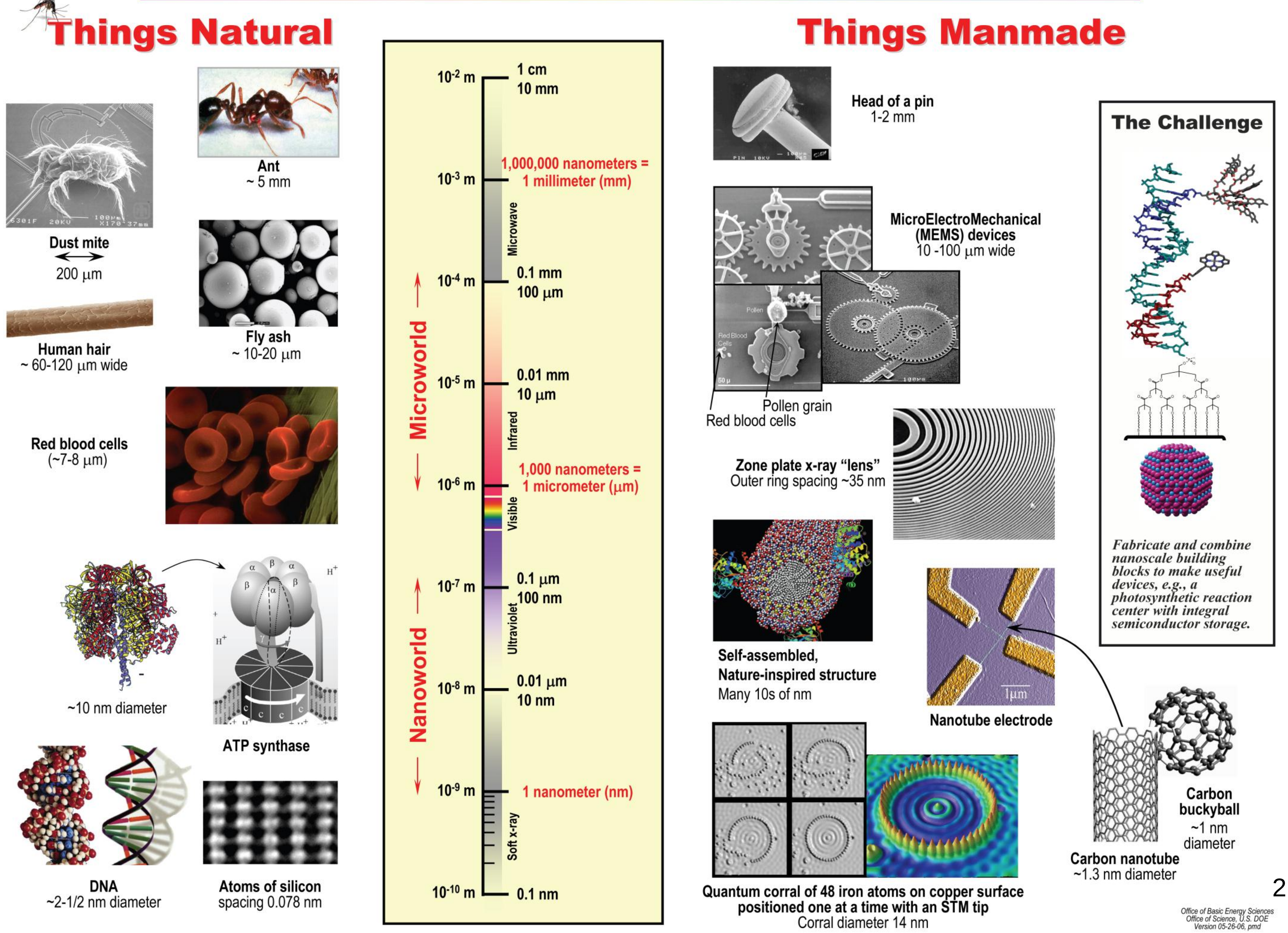
# The Scale of Things – Nanometers and More



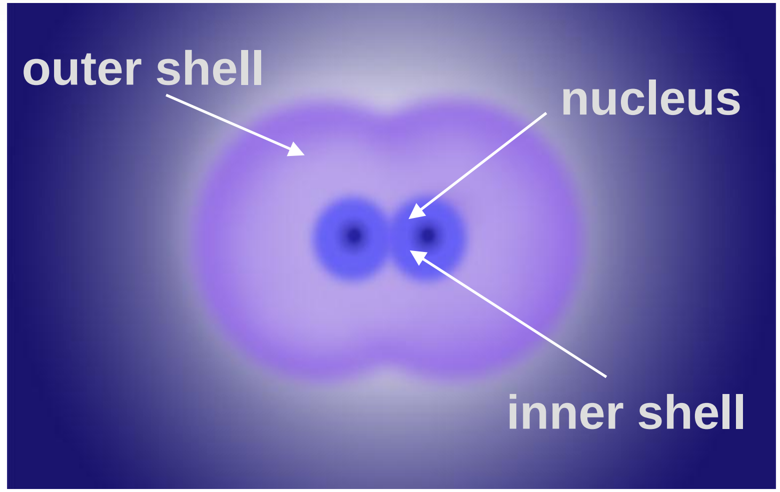
# Atomic interactions

**<u>short range</u>**

**interaction:**

**repulsion between nuclei**

(electron cloud overlap)

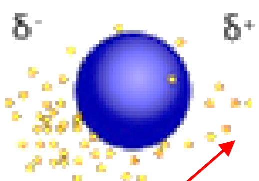


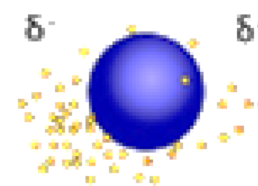

**<u>long range</u>**

**interaction:**

**coulombic attraction**

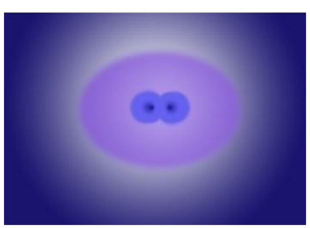
$$E_C = \frac{1}{4\pi\varepsilon_0}\cdot\frac{Q_A Q_B}{r}$$



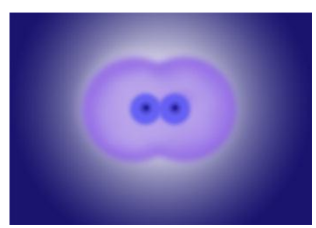

**repulsion**

**(inner shells and nuclei)**



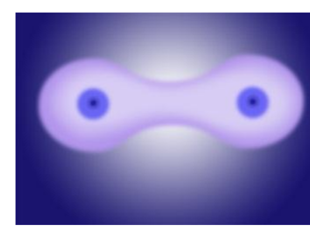
**equilibrium**

**attraction = repulsion**

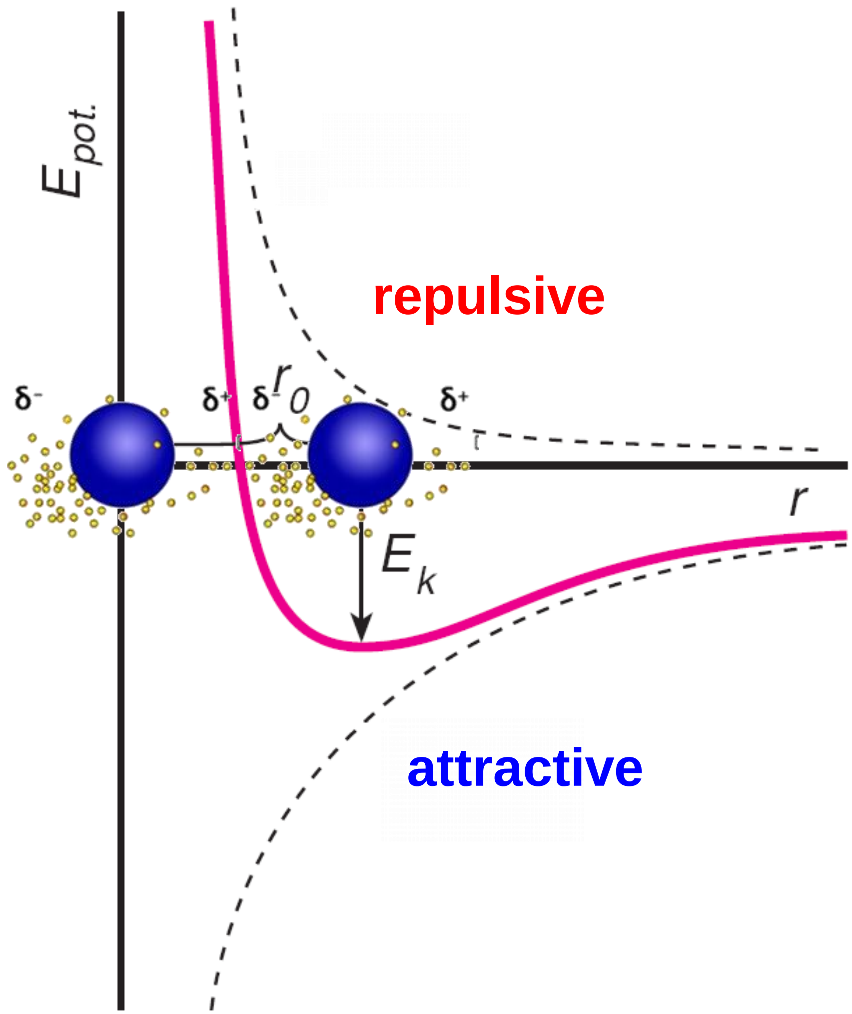


**attraction**

**(outer shells)**



# Atomic interactions




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

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

**A, B: interaction-specific constants**

**(atom-dependent)**

**n (attraction) < m (repulsion)**

**$r_0$: binding distance**

**$E_k$: binding energy**

# Primary bonds

**2-6 eV/bond**

~100 kJ/mol

| intramolecular | | intermolecular |
|---|---|---|
| strong | ⟷ | weak |
| primary | | secondary |

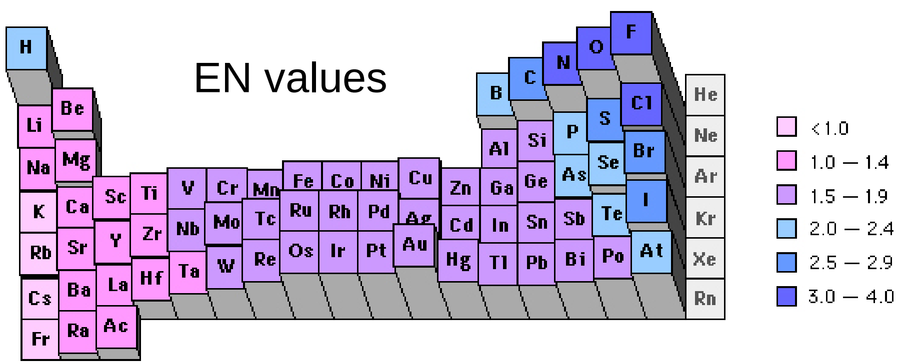
**0.01-0.1 eV/bond**

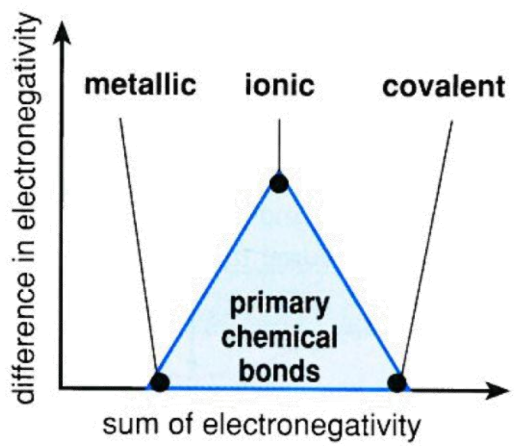
- **covalent:** common electron state around the participating nuclei
- **(metallic bond:** multi-atomic system**)**
- **electrostatic**
  - **ionic bond:** Coulomb-forces between ions
  - **dipole type charge distribution**

**type depends from electronegativity**

$$EN=(E_i+E_{ea})/2$$

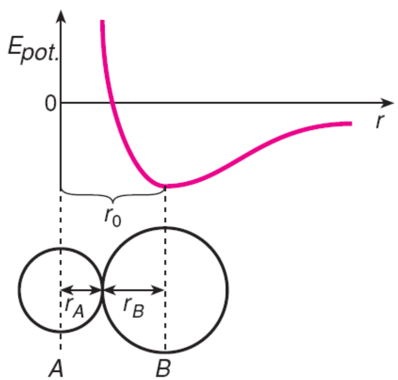
(Mulliken)



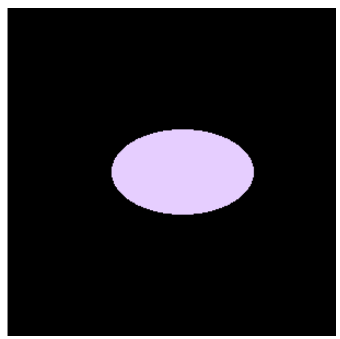



# Secondary bonds 1

- **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)**
  - **Van der Waals radius: $r_0=r_A+r_B$**

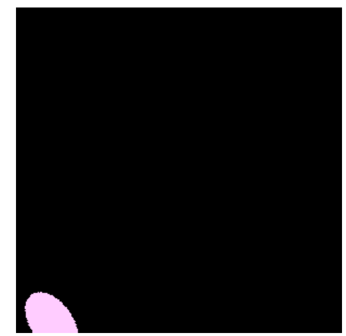



**fluctuation**



**ion-dipole**

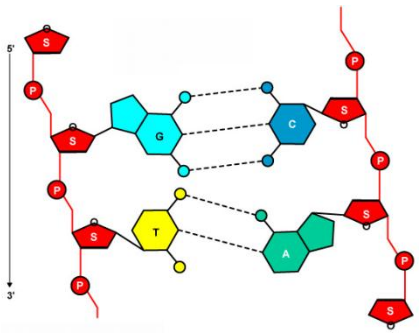
**induced dipole**



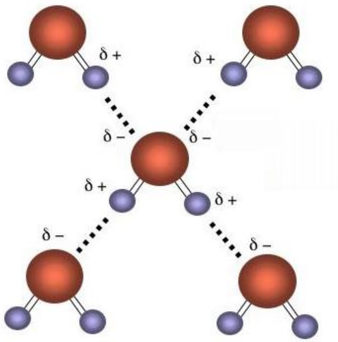
| **Interaction** | **Distance dependence of $E_{pot}$** | **Average binding energy (eV)** |
|---|---|---|
| Ion-dipole | $1/r^2$ | 0.1-0.2 |
| Dipole-dipole | $1/r^3$ | 0.02 |
| Dispersion | $1/r^6$ | 0.02 |
| Dipole-induced dipole | $1/r^6$ | 0.01 |

# Secondary bonds 2

- **H-bond**: the H-atom interbridges 2 other atoms (F, O, N) of high electronegativity
  - **r ~ 0.23-0.35 nm**
  - **E ~ 0.2 eV**

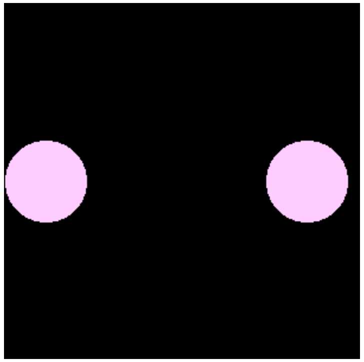


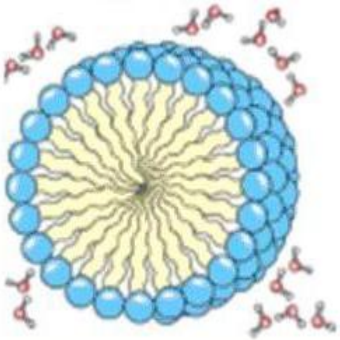
**DNA**



**water**

- **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)

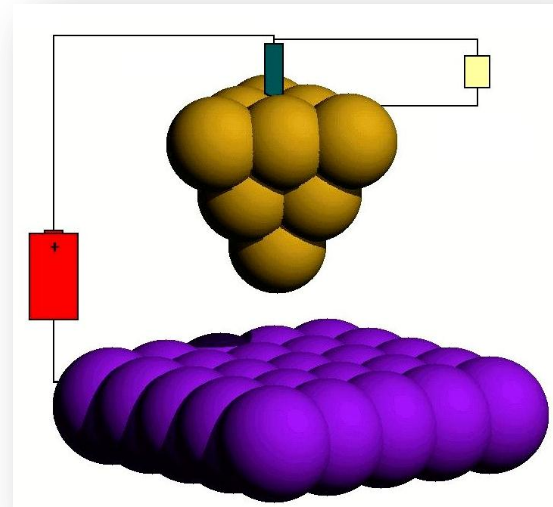




# Scanning Probe Microscopy- history

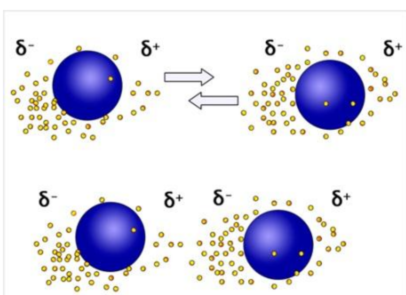
**1981: Binning, Rohrer – IBM**

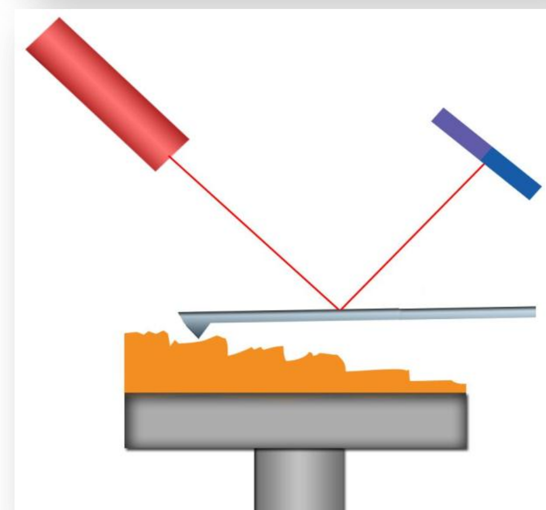
- scanning tunneling microscopy

**1986: Binning, Quate**

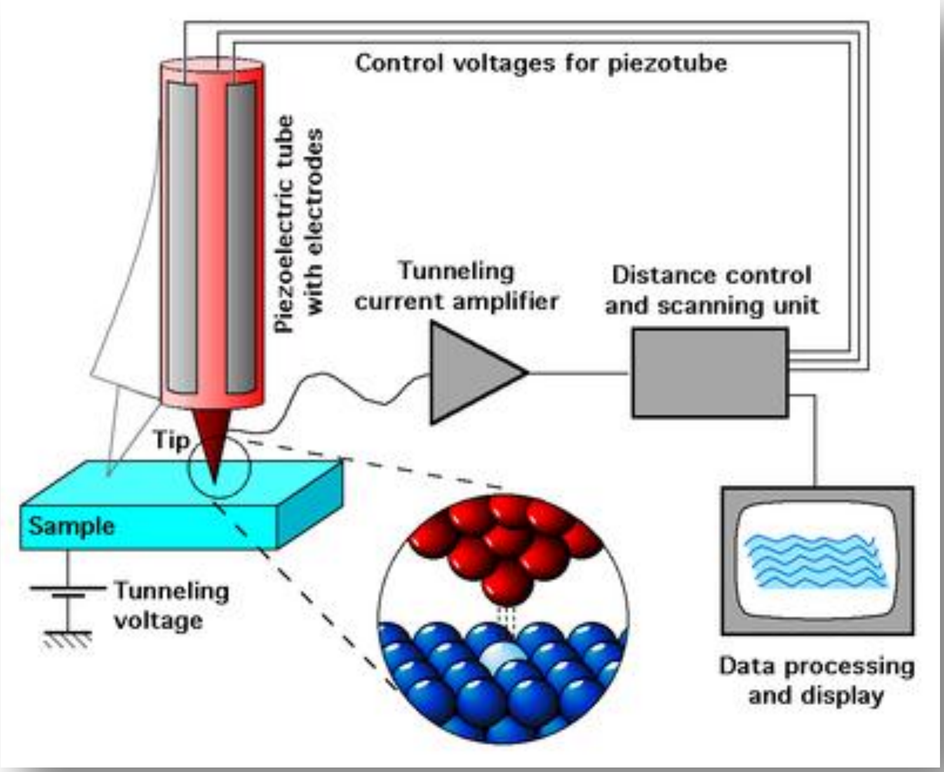
- atomic force microscopy



# Scanning Tunneling Microscopy

**<u>electron tunnelling:</u>** measurable electrical currents ($I$) between two conductors separated by a sufficiently thin uniform insulator




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

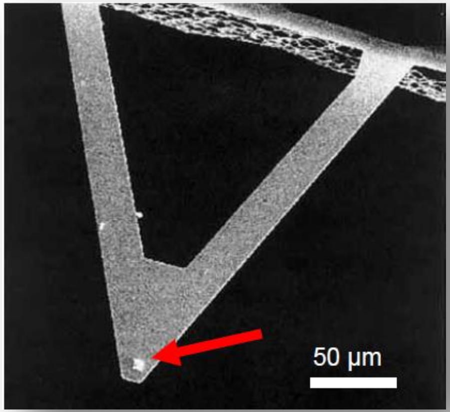
**z: distance (Z-axis)**

**κ: 2,2 $Å^{-1}$**

**I~ nA**

# Atomic Force Microscopy

**<u>aim:</u> to get rid of lens / optics: light is not favorable in direct imaging (Abbe's Principle limits the resolution)**




- **<u>„do it yourself”:</u>**
  - **thin, soft probe („point detector”)**

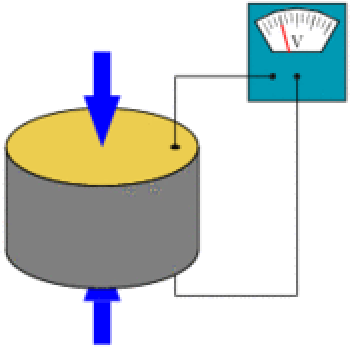
    to measure Van der Waals interactions between tip and surface

  - **smooth surface (mica)**

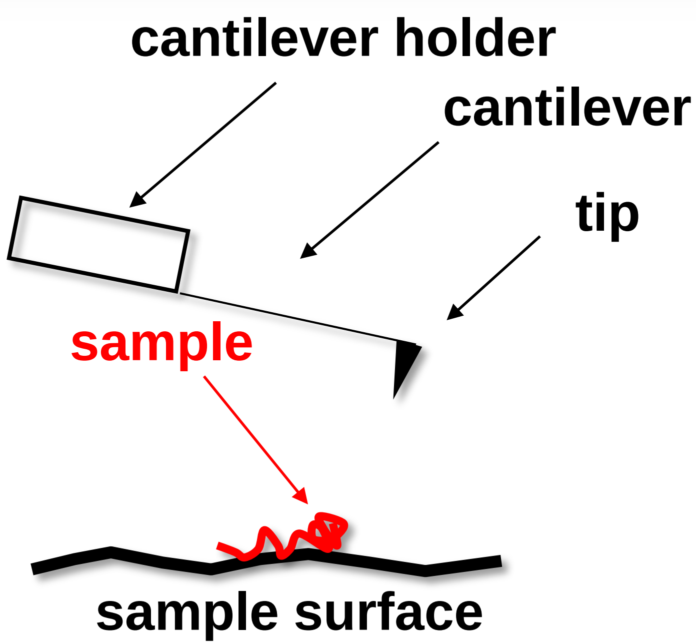
    clean, atomic layer

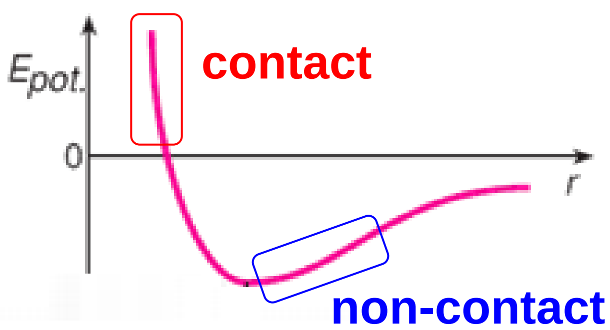
  - **stage: X/Y/Z piezoelectric actuators**

    translational motion in atomic steps: step size ~1Å (angstrom) = 0.1 nm



# Atomic force microscope (AFM)



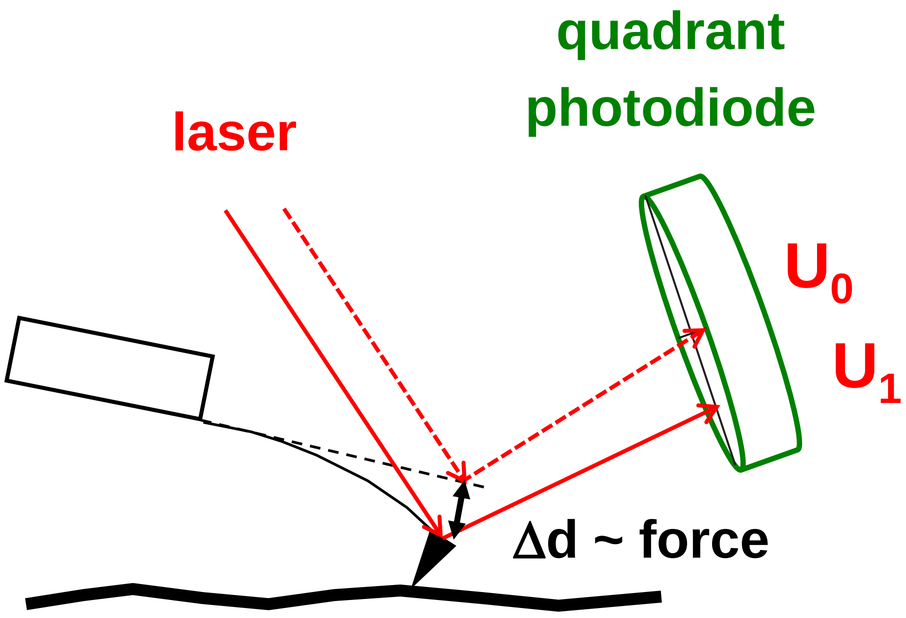

**operating modes:**

- **contact:** the tip touches the surface: cantilever deflection relates to the surface topography
- **non-contact:** the tip is being oscillated without contact with the surface: amplitude and resonant frequency changes
- **oscillating:** the cantilever is being oscillated near its resonant frequency

# Atomic force microscope (AFM)

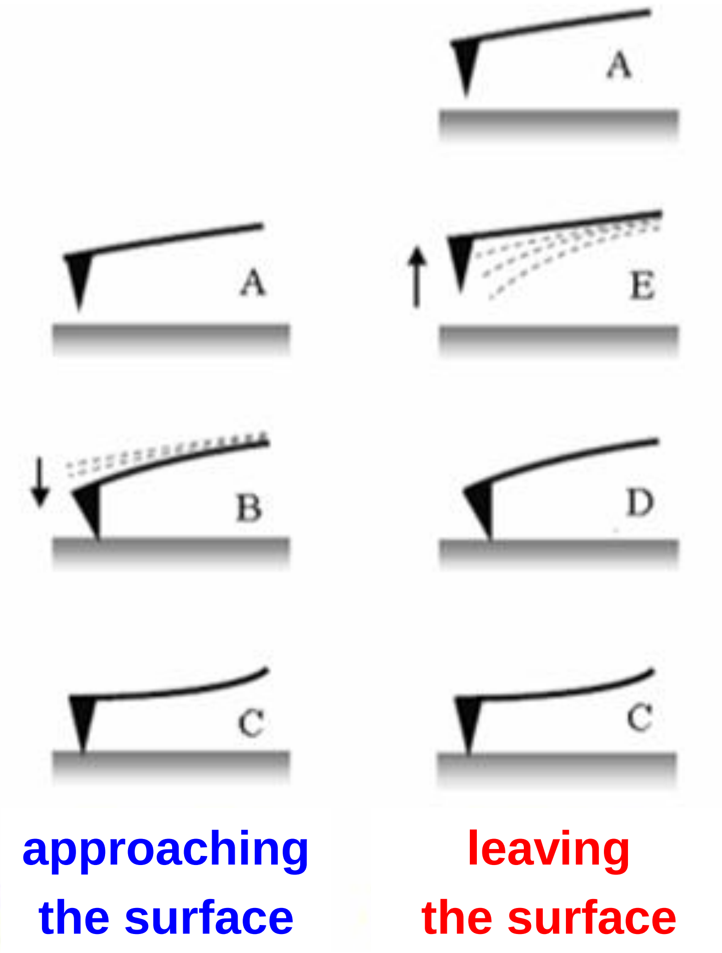
http://personal.ph.surrey.ac.uk/~phs1ad/MAT/MAT/Scanning%20Probe%20Micorscopies/Atomic%20Force%20Microscopy/modes%5B1%5D.swf

# Working principle of AFM 1
# contact mode




F = force = D Δd

Δd: deflection
D: spring constant

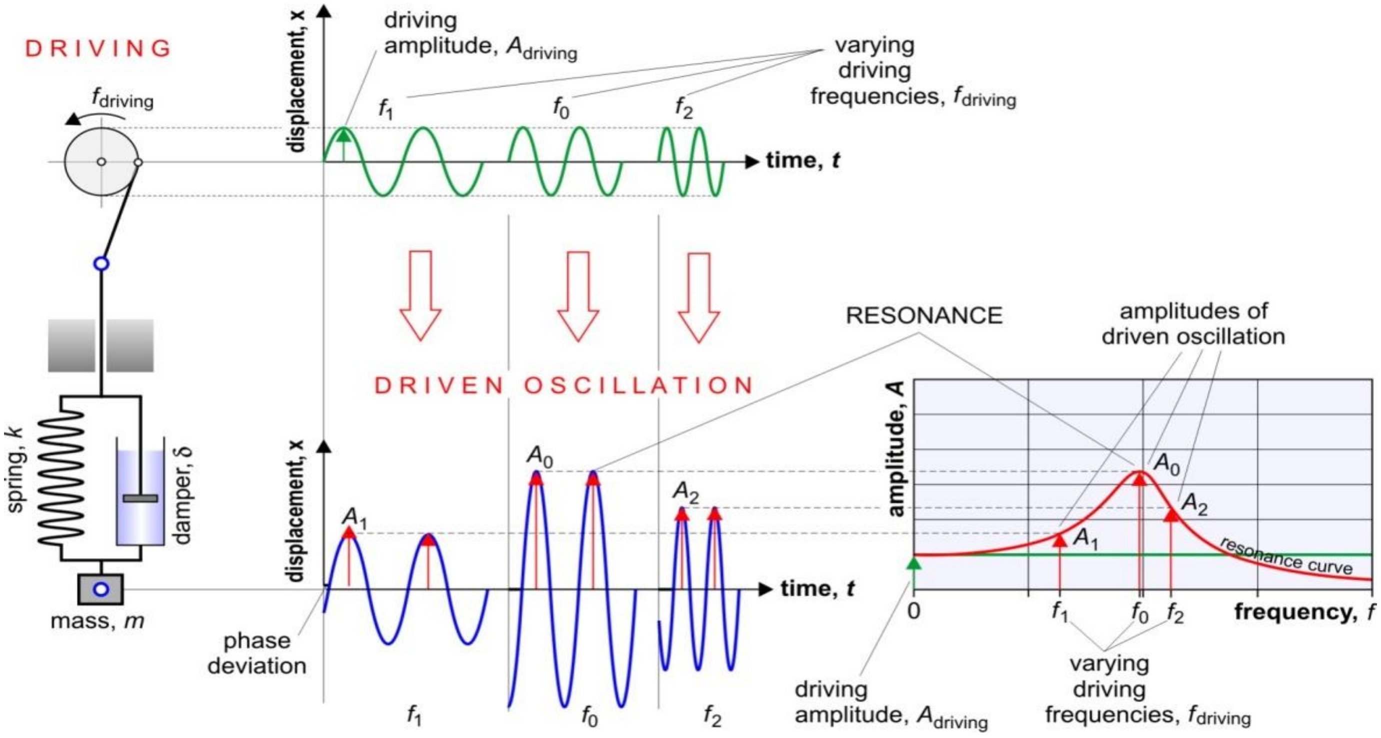


# Working principle of AFM 1 contact mode

http://personal.ph.surrey.ac.uk/~phs1ad/MAT/MAT/Scanning%20Probe%20Micorscopies/Atomic%20Force%20Microscopy/force-displacement%5B1%5D.swf

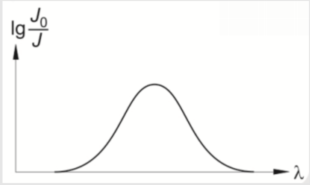
# Working principle of AFM 2 oscillating mode

**RESONANCE:** a driven oscillation occurring when the oscillatory system is exposed to a driving force with a frequency close to its eigenfrequency. Amplitudes may become extremely large.




**resonance in medical sciences:**

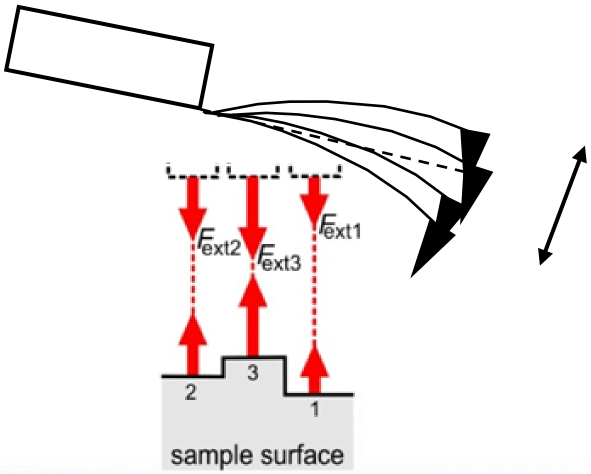
- light absorption

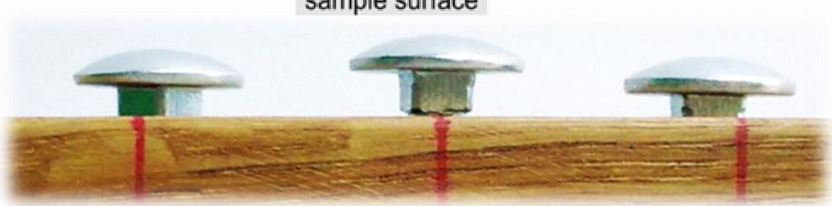


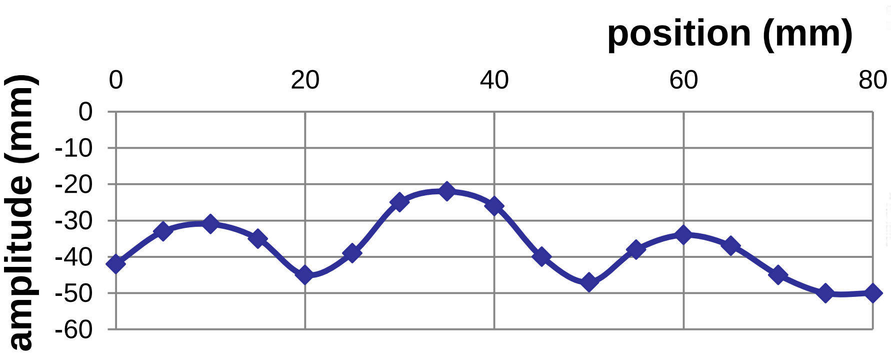

- MRI: magnetic resonance imaging
- FRET: fluorescence resonance energy transfer

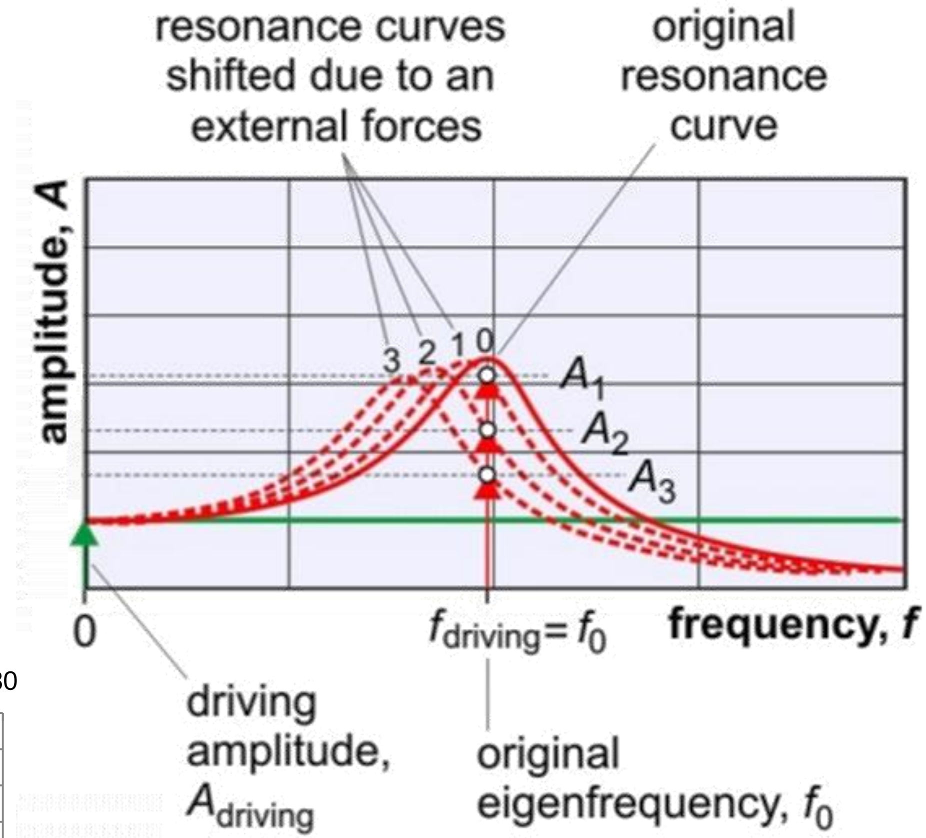
# Working principle of AFM 2

# oscillating mode



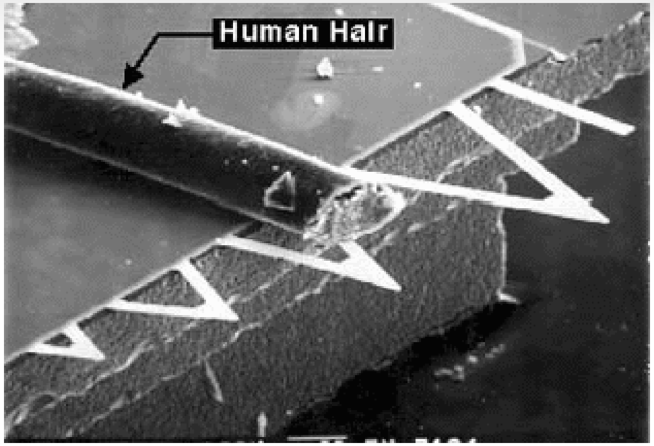


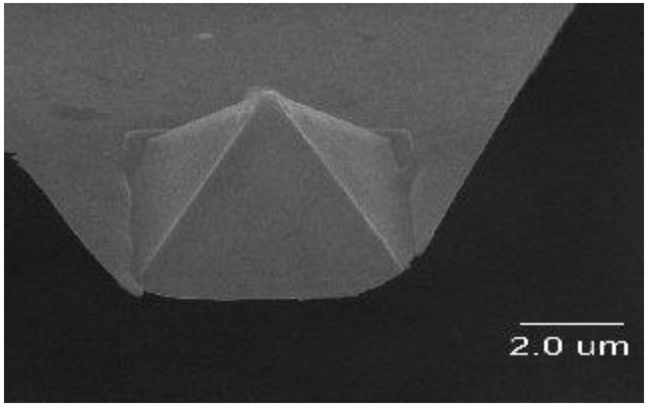



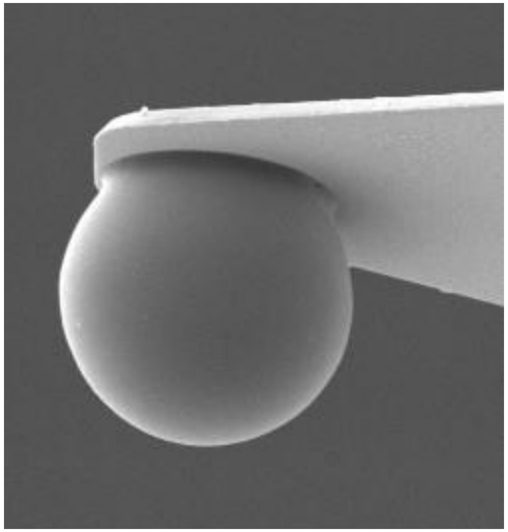

$$f_0 = \frac{1}{2\pi}\sqrt{\frac{D}{m}}$$

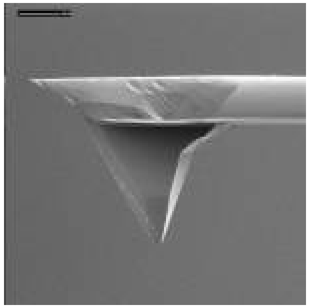
# Cantilevers

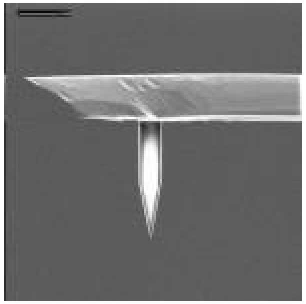
- material: silicon nitride (might be functionalized)
- tip radius: 0,1 nm- 100 µm
- spring constant ~ 0,1-10 N/m
- $f_o$ ~ 50-500 kHz



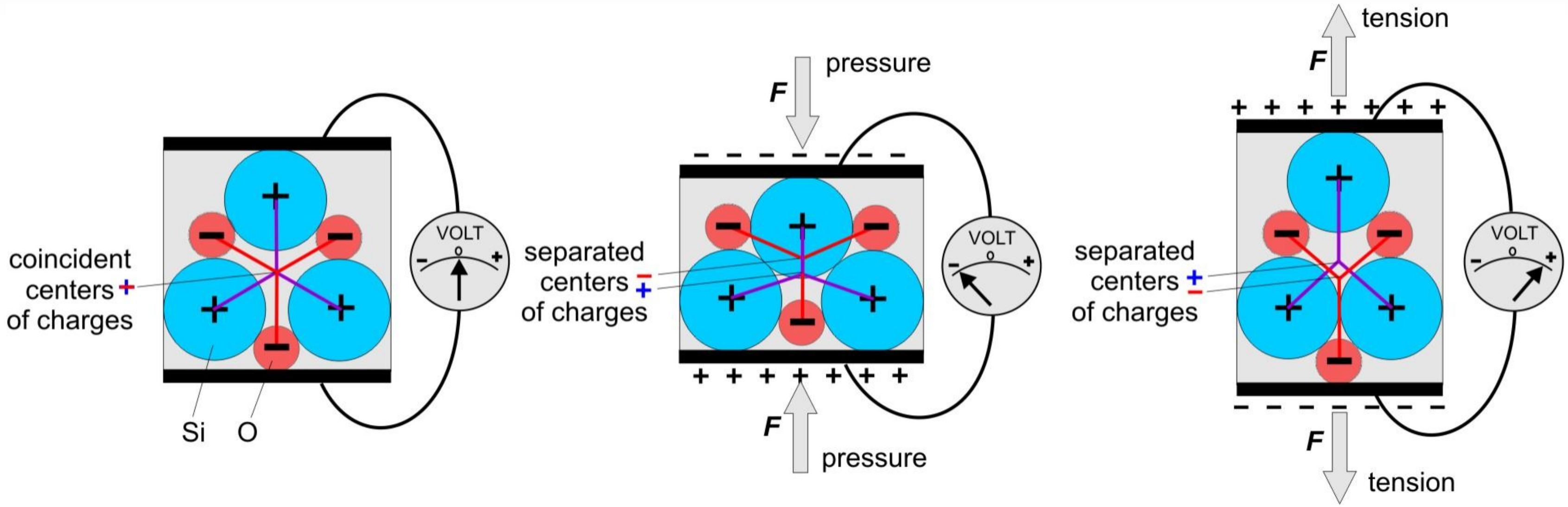





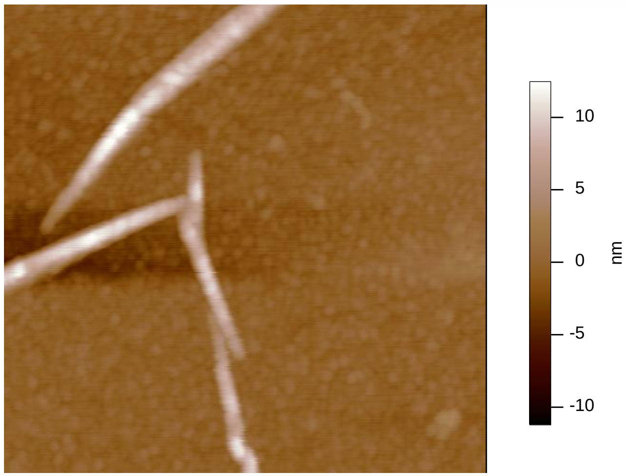


# Principle of scanning: piezoelectricity

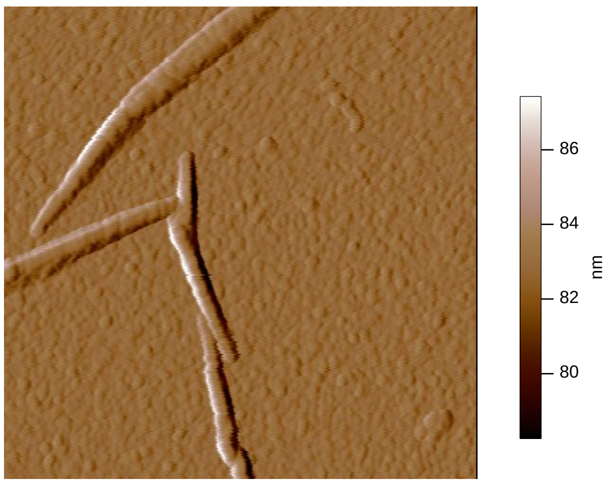



- **direct piezoelectric effect: deformation → voltage**
- **inverse piezoelectric effect: voltage → deformation**
- **X, Y, Z axes piezo: e.g. 150 V → 40 μm**

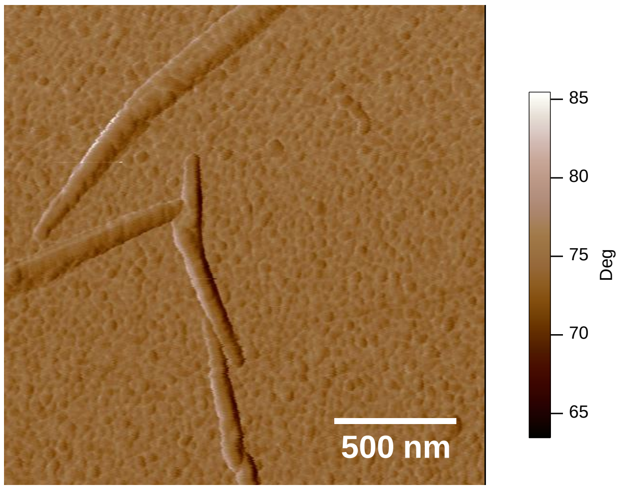
# Imaging, resolution



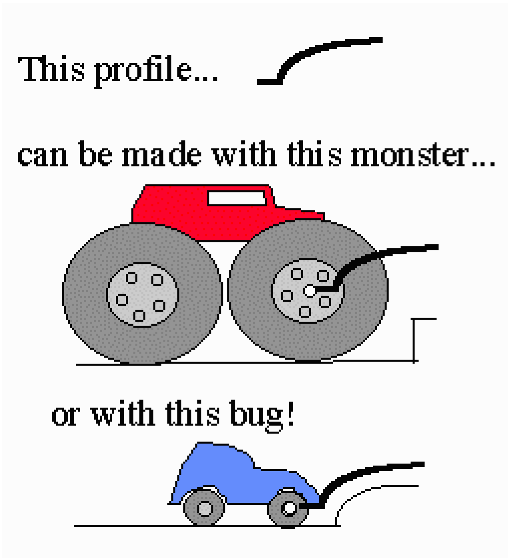

**height contrast**

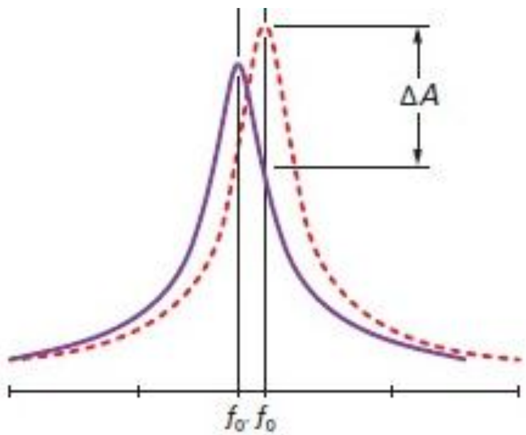


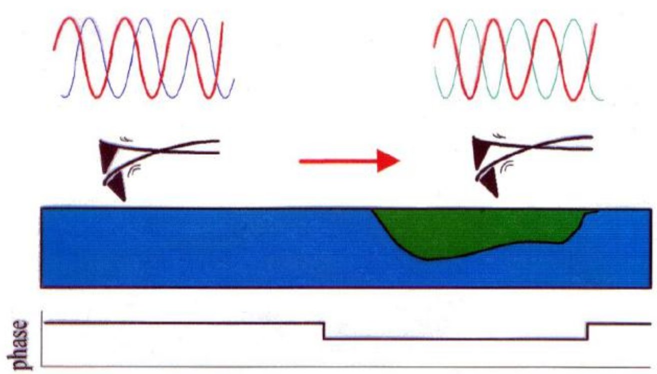

**amplitude contrast**




**phase contrast**



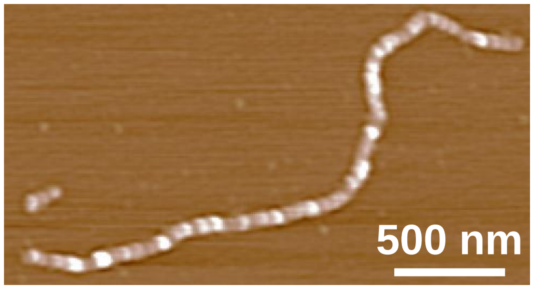



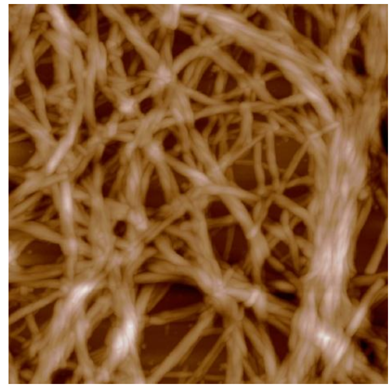

sensitive to viscoelasticity

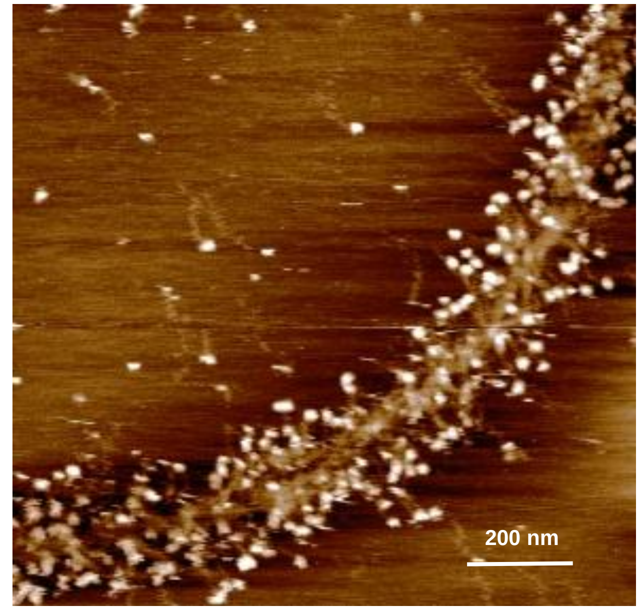
# Imaging artifacts

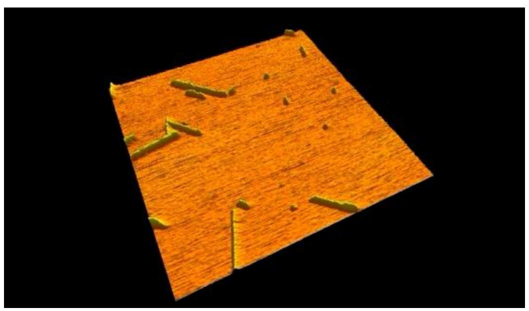
http://personal.ph.surrey.ac.uk/~phs1ad/MAT/MAT/Scanning%20Probe%20Micorscopies/Atomic%20Force%20Microscopy/sharp%2520v%2520blunt%2520tip%5B1%5D.swf

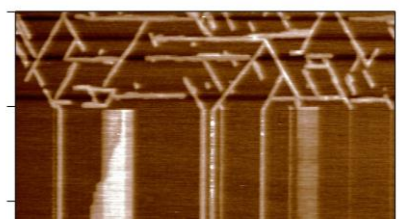
# Images were born in our lab…

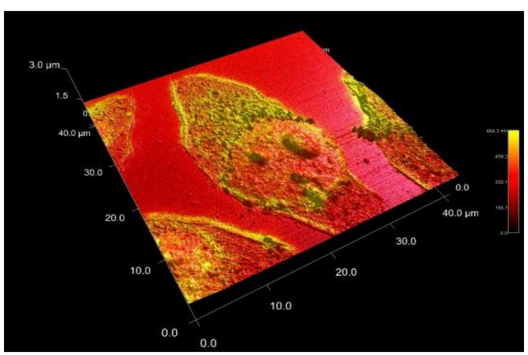


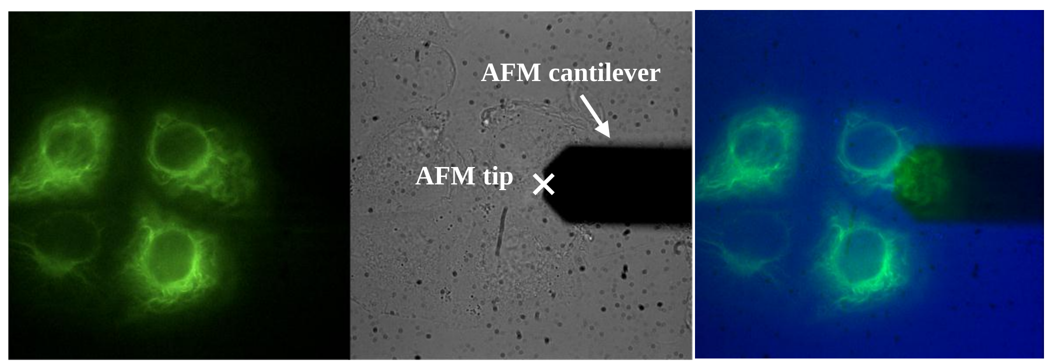





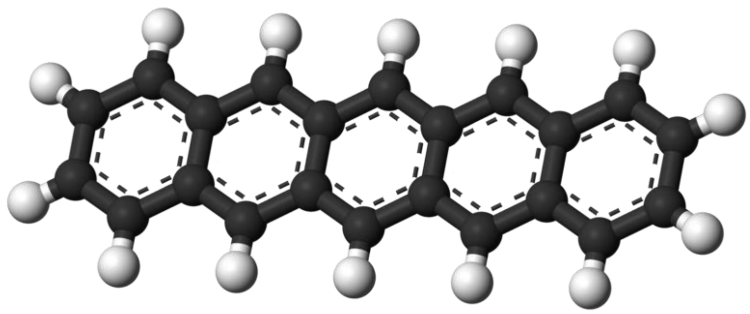





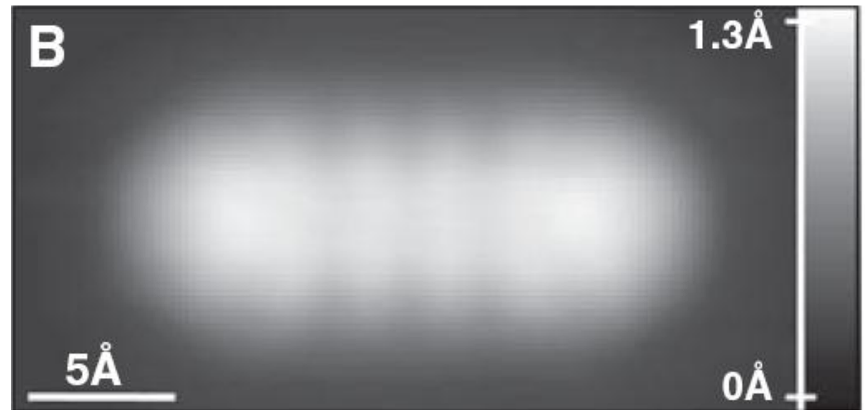


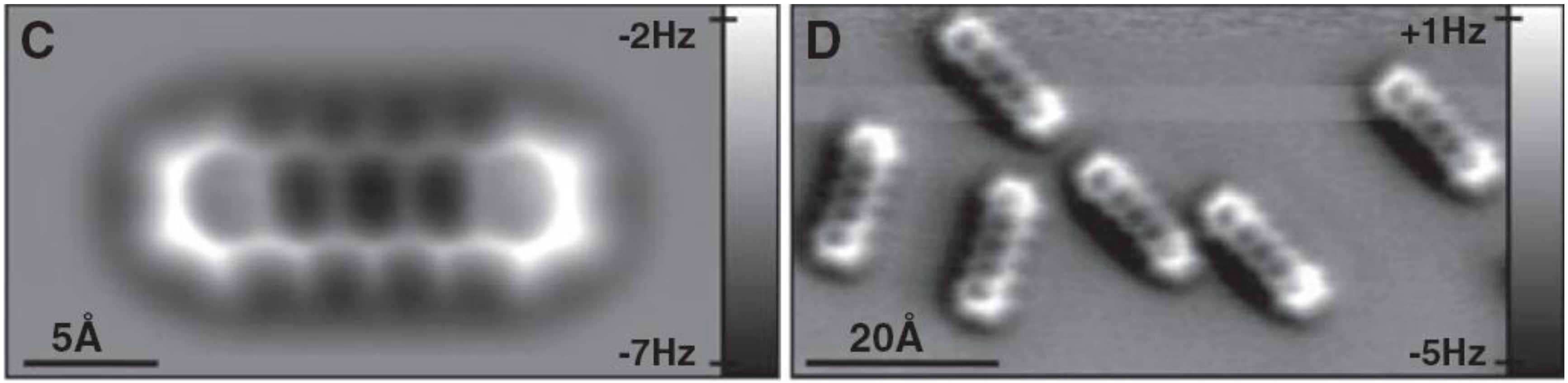
# Pentacene molecule



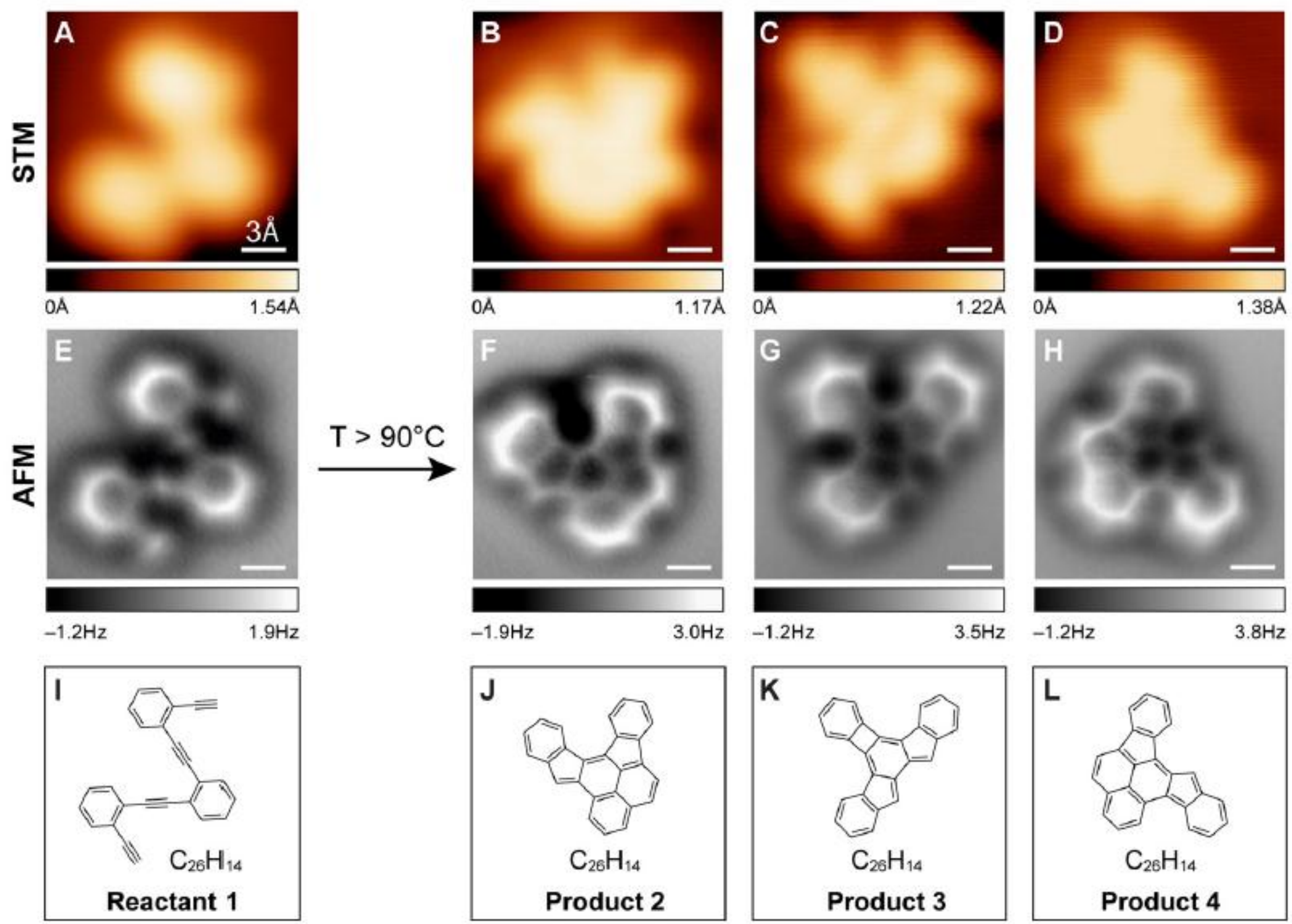
STM




AFM (tip covered with CO)



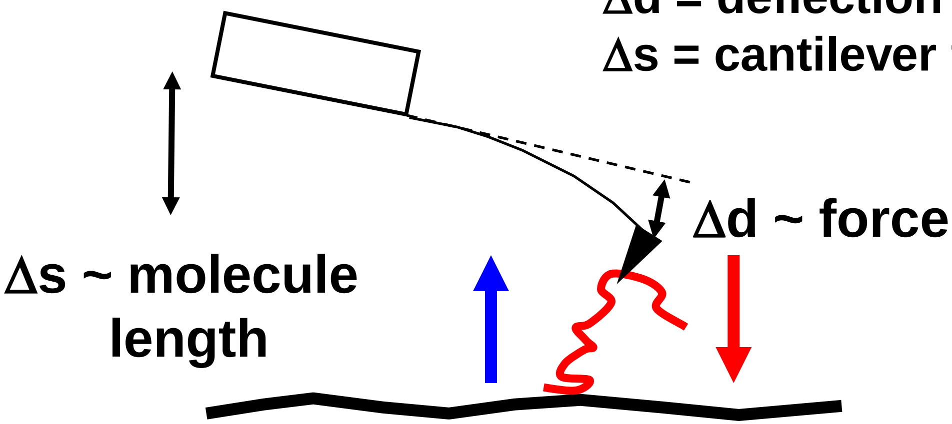
# Visualizing chemical reactions

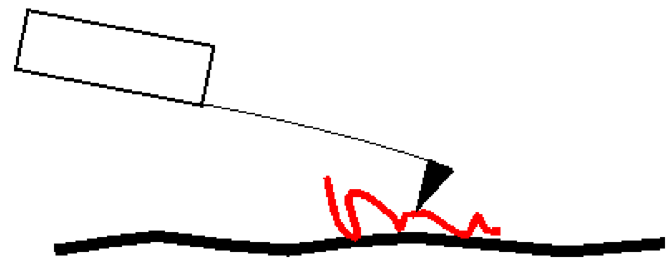


# Force measurement with AFM

**F = force = D Δd**

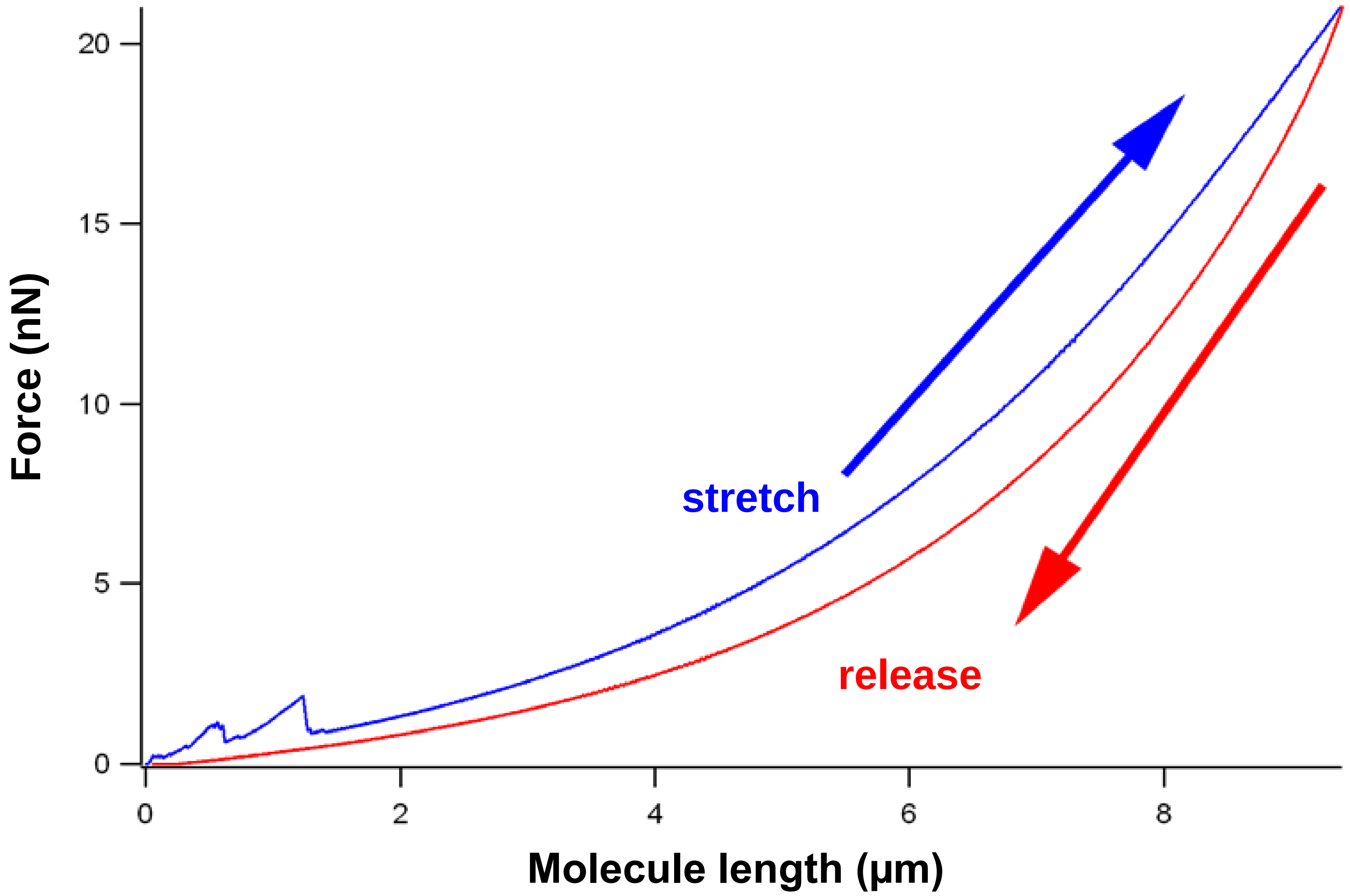
**Δd = deflection**
**Δs = cantilever travel**



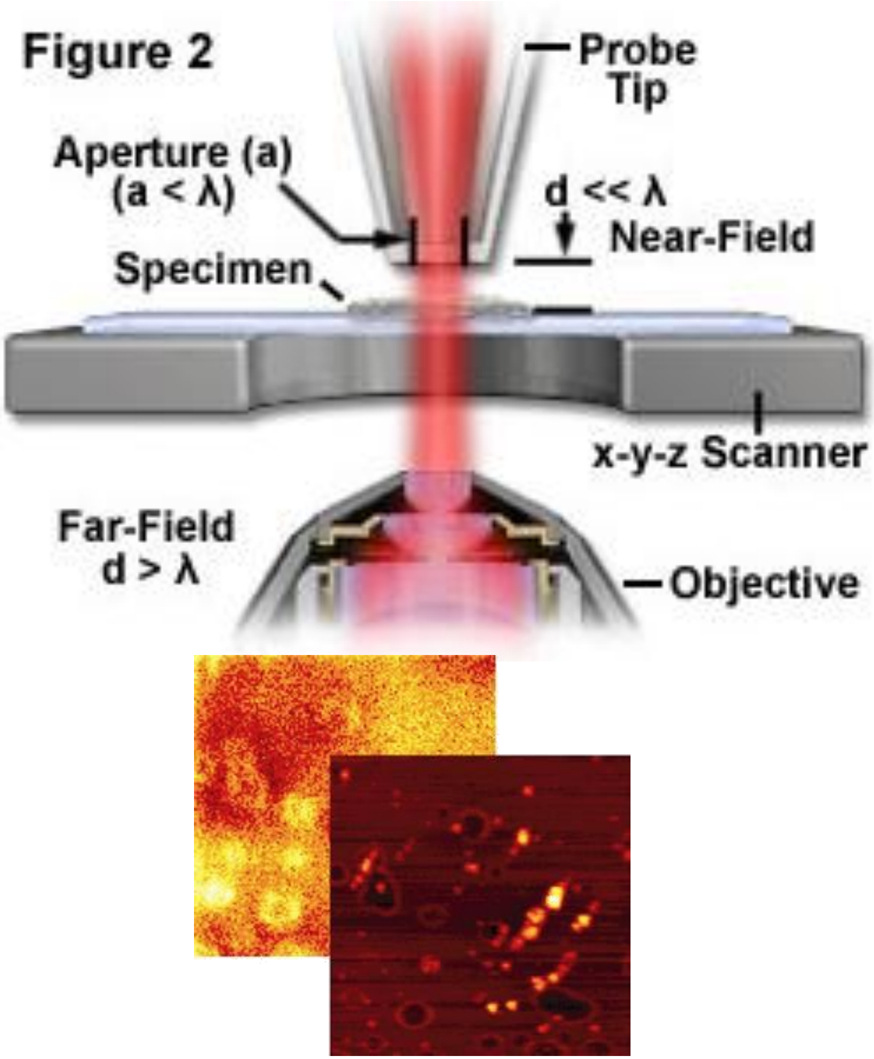



| Type of Force | Example | Rupture Force |
|---|---|---|
| Breaking of a covalent bond | C-C | ≡1600 pN |
| Breaking of a noncovalent bond | Biotin/streptavidin | ≡160 pN |
| Breaking of a weak bond | Hydrogen bond | ≡4 pN |
| Stretching dsDNA | to 50% relative extension | 0.1 pN |
| Developed by a molecular motor | Kinesin walking on microtubule | 5 pN (max) |

# 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)

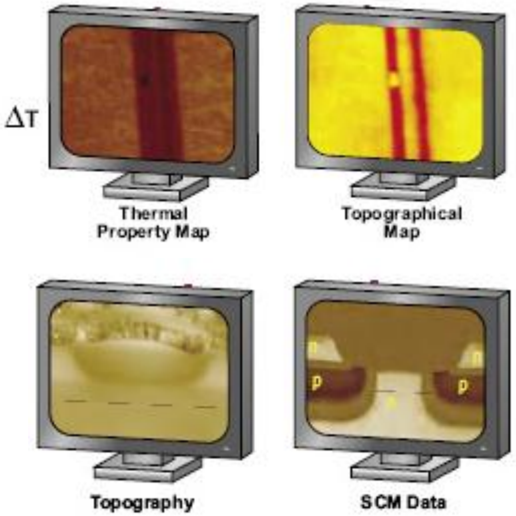
Lateral Force Microscopy (LFM)

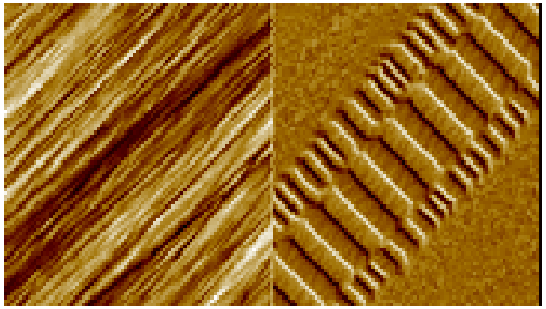
Electrical Force Microscopy (EFM)

Chemical Force Microscopy (CFM)

Magnetic Force Microscopy (MFM)

Scanning Tunneling Microscopy (STM)



**MFM: harddisk tracks**

# Thank YOU for your attention!