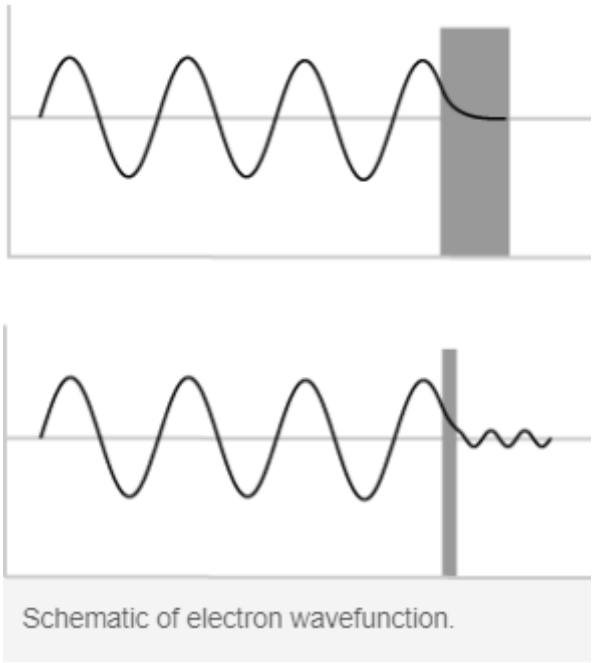
2. Nanomaterial Characterisation

F3370

Probe Force Measurement

Tunneling

- In the microworld, particles may pass through the energy barrier under certain conditions - tunnelling may occur
- This is due to their wave-particle nature

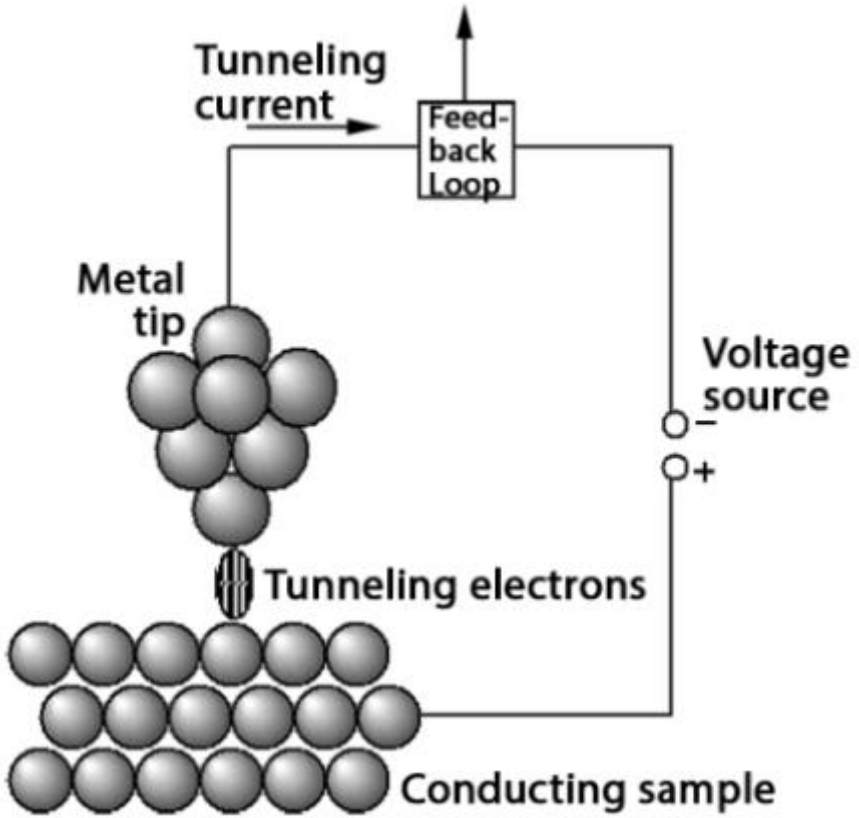


Schematic of electron wavefunction.

https://www.nanoscience.com/techniques/scanning-tunneling-microscopy/

Scanning Tunneling Microscopy (STM)

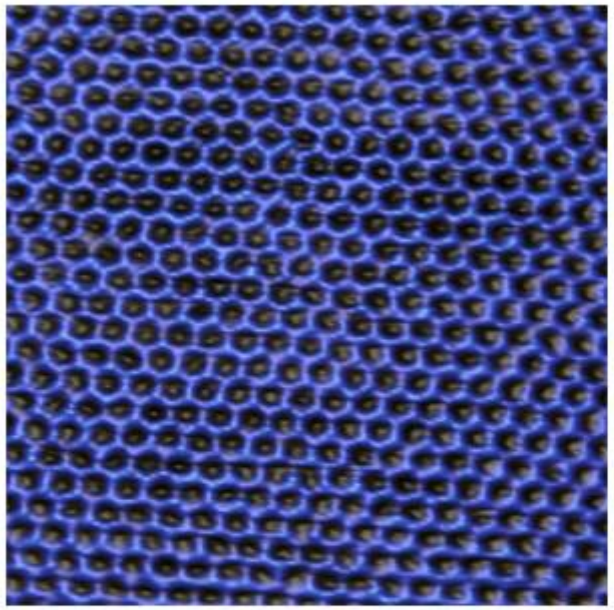
- The barrier is the vacuum between the conductive sample and the very sharp conductive tip
- Their distance must be very small - units of nm
- The sample is on a piezoelectrically actuated stage and is scanned under the tip



https://www.nanoscience.com/techniques/scanning-tunneling-microscopy/

STM Modes

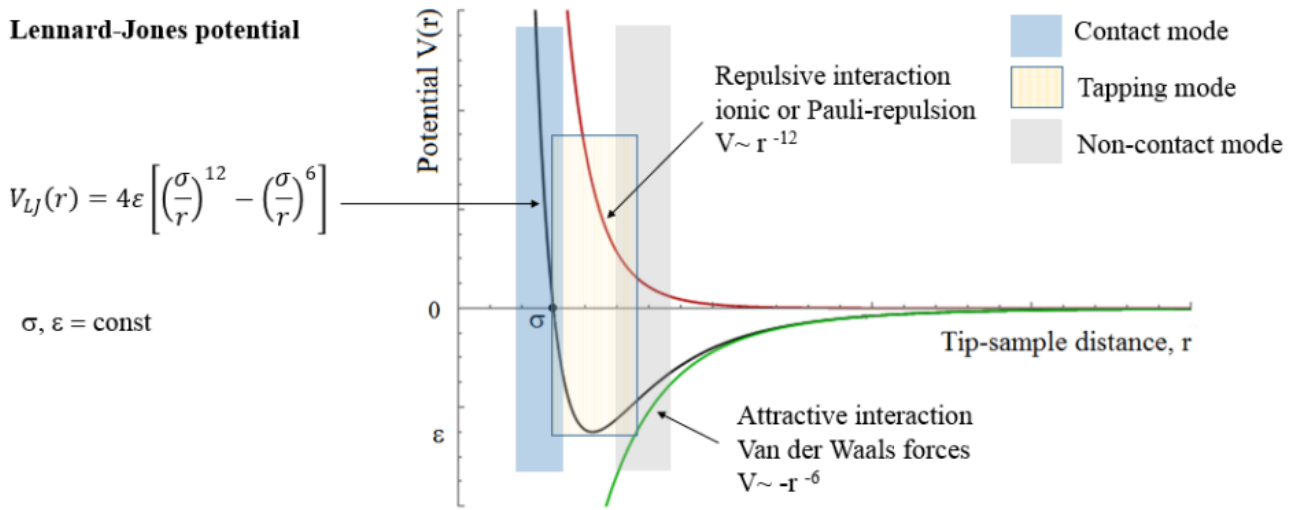
- Constant current mode
  - The tunneling current is measured - when it increases/decreases, the tip is raised/lowered by the feedback loop.
  - We obtain a 3D topography of the sample with a lateral resolution of 0.1 nm and a height resolution of 0.01 nm.
- Constant height mode
  - For very smooth samples. The tip height is stable and from the changes in tunneling current at the tip position and voltage we can determine the density of electron states, defects, molecular orbitals on the sample surface, etc.



STM image of highly-oriented pyrolytic graphite (HOPG)
Acquired in air on an Asylum Research Cypher S scanning probe microscope, demonstrating the ability to resolve the atomic lattice structure. (5 nm scan size)

https://afm.oxinst.com/modes/scanning-tunneling-microscopy-stm

Atomic Force Microscopy (AFM)

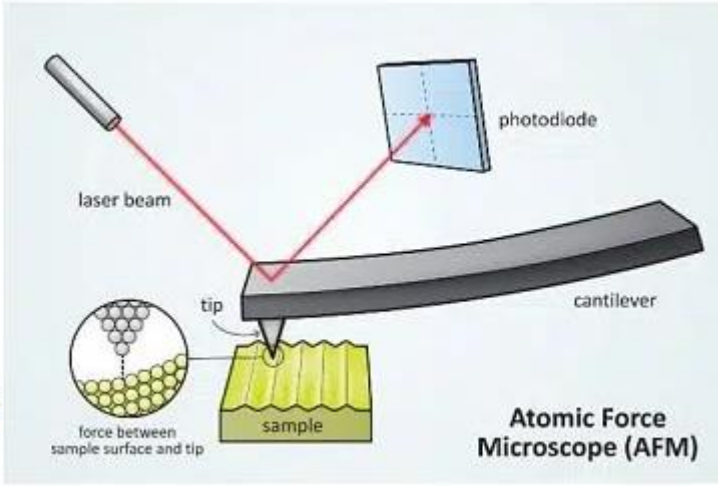


- Lennard-Jones potential - what forces are "felt" by two objects that we bring closer to each other - first they attract and then they start to strongly repel

J. Kámán, Investigationn of the Local ,Mechanical Properties with Atomic Force Microscopy Techniques, PhD Thesis, Budapest. 2020

AFM

- Measurement of small forces (on the order of nN) between the tip on the cantilever and the sample
- Very sharp tip with a radius of approx. 5 nm
- Also for non-conductive materials
- No vacuum required
- Lateral resolution 1-5 nm, vertical resolution 0.1 nm



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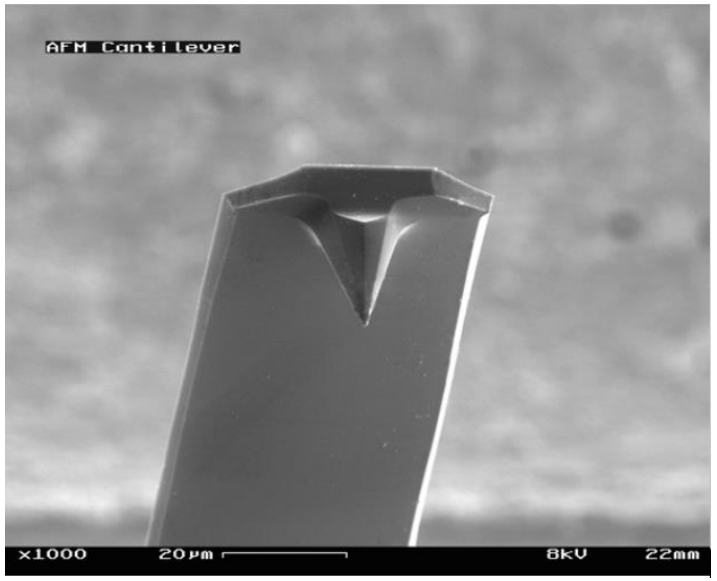

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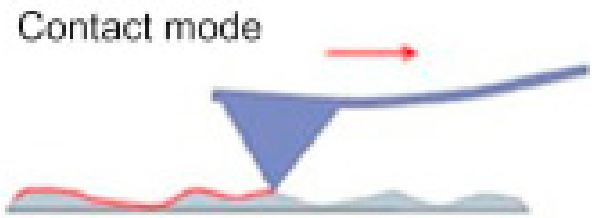
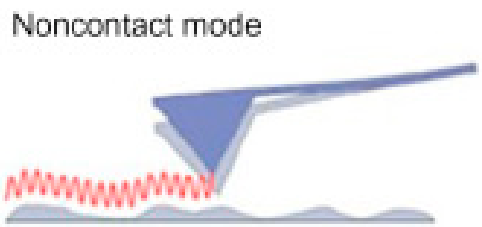
[1]https://www.atriainnovation.com/en/atomic-force-microscope-afm-the-key-tool-for-surface-analysis/
[2]https://nanohub.org/resources/25844/download/App_CantiL_PK14_PG.pdf

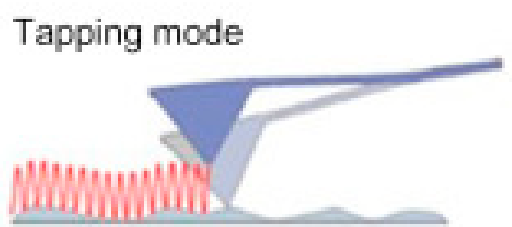
AFM Modes



- Contact mode
  - The tip is tenths of nm from the sample
  - The tip height is adjusted to keep the tip bend constant
  - Highest resolution
  - May damage the sample



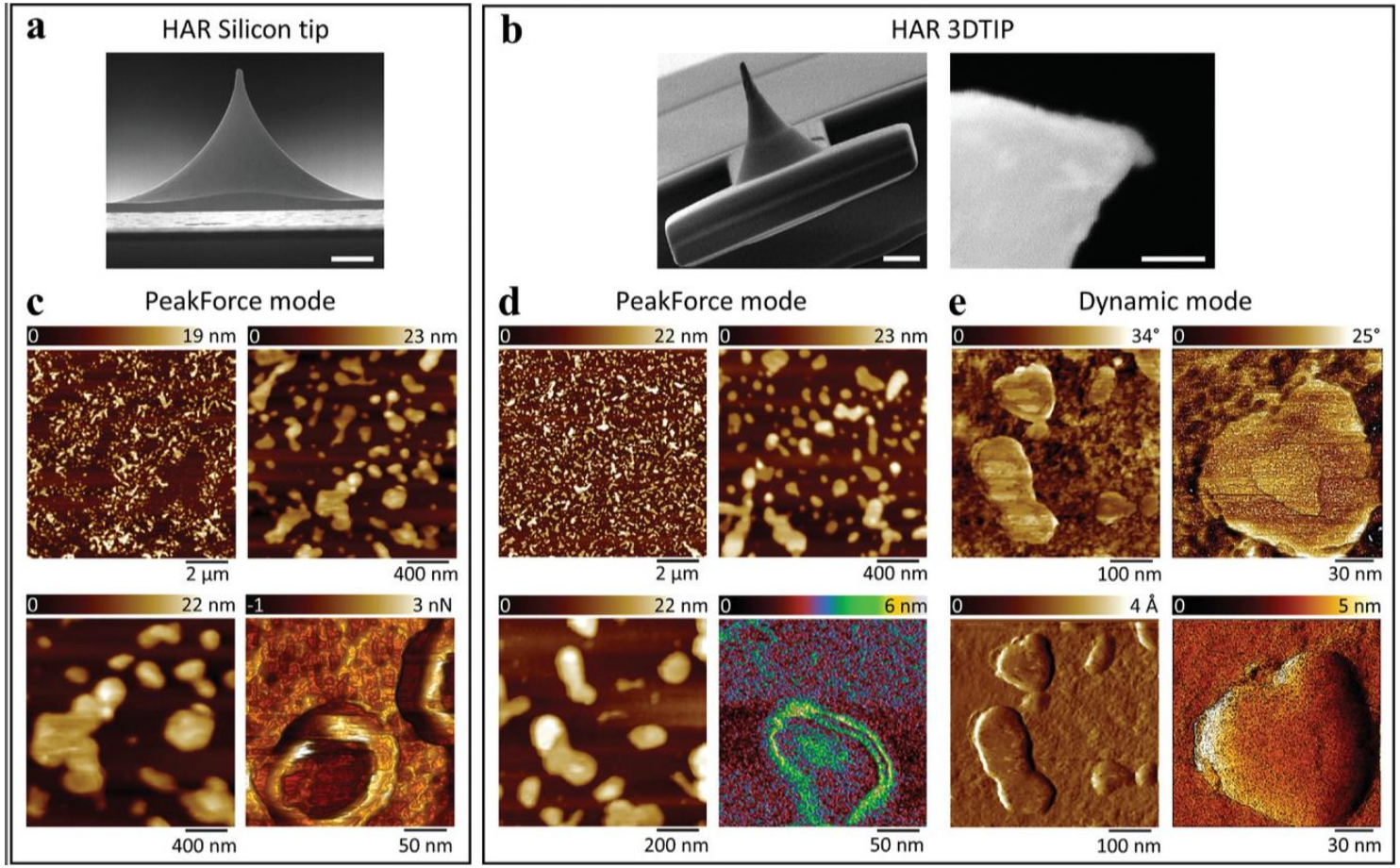
- Non-contact mode
  - Tip is tens of nm from the sample
  - The tip height is adjusted to keep the amplitude of its vibration constant
  - Lowest resolution
  - Non-destructive



- Tapping mode
  - The tip touches the sample at the point of deepest deflection
  - The height of the tip is adjusted to keep the amplitude of its vibration constant
  - Better resolution
  - Non-destructive

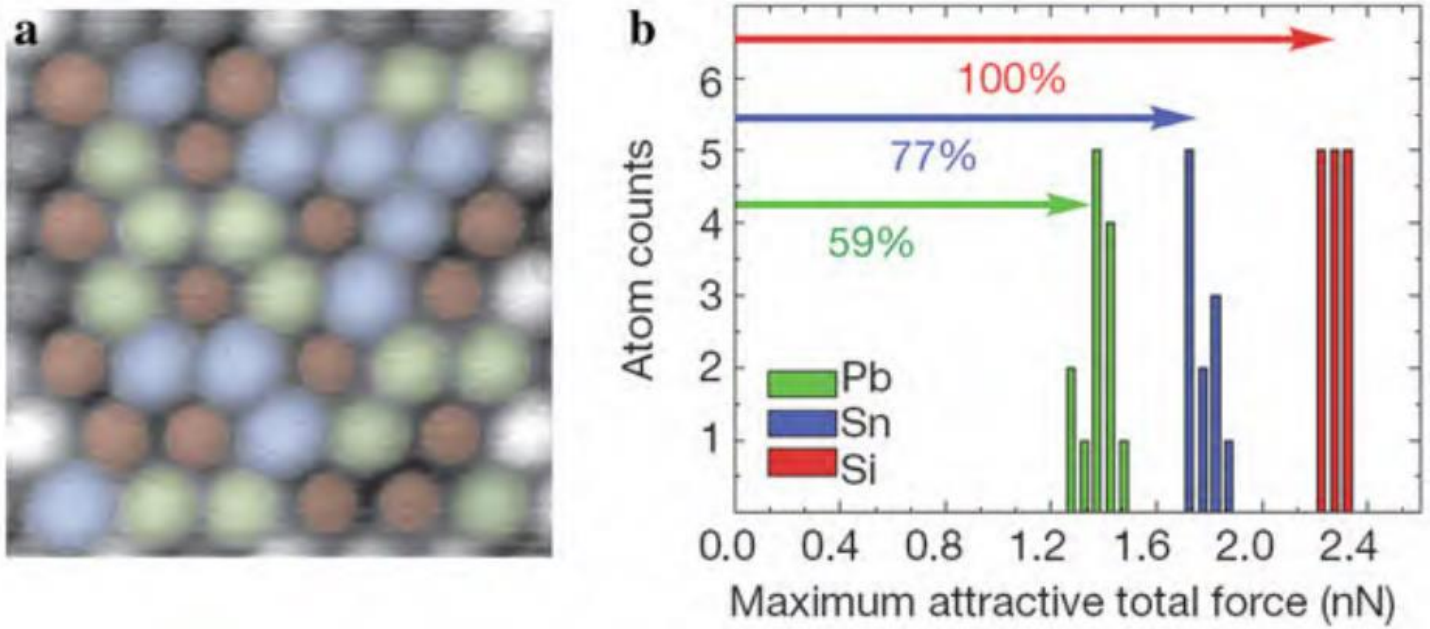
R. Asmatulu, W.S. Khan, Characterization of electrospun nanofibers, Synthesis and Applications of Electrospun Nanofibers, 2019

AFM Images



https://onlinelibrary.wiley.com/doi/full/10.1002/advs.202201489

AFM – Chemical Identification in Atomic-resolution



- Non-contact mode - forces from atoms of different elements acting on the tip are different - individual atoms of the alloy can be distinguished

H.E. Schaefer, Nanosciience: The Science of the Small in Physics, Engineering, Chemistry, Biology and Medicine, Springer, 2010

Overview of Probe Force Measurements

Methods	Shortcut	Usage
Atomic force microscopy Lateral force microscopy Chemical force microscopy Magnetic force microscopy	AFM LFM CFM MFM	Topology and surface structure Surface energy Chemical analysis of the surface Magnetic properties
Scanning tunnelling microscopy Scanning tunnelling spectroscopy	STM STS	Topology and surface structure Electron density of states
Atomic probe microscopy Field ion microscopy Imaging atomic probe Atomic probe tomography	APM FIM IAP APT	3D imaging Chemical composition, atomic distances Surface imaging by emitted ions 3D position of atoms and their type

Spectroscopic (Photon) Methods

X-Ray Photoelectron Spectroscopy (XPS)

- X-ray photons hit the sample, knock out photoelectrons and we measure their energy

$$h\nu = \Phi + E_k$$

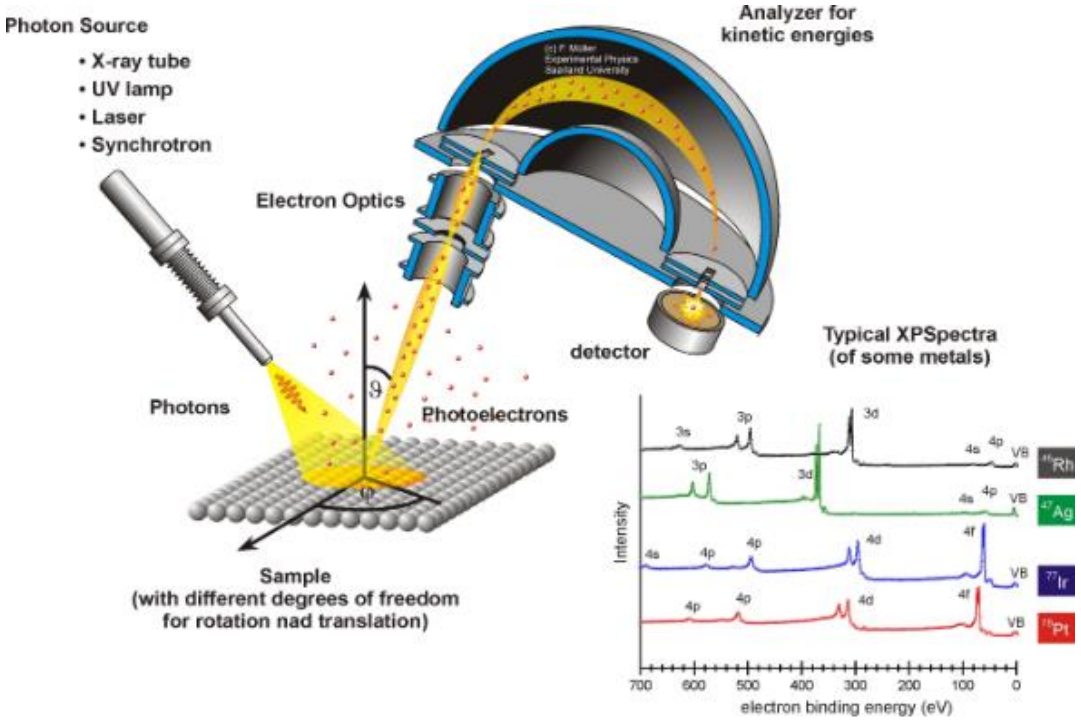
h – Planck constant

ν – frequency of the electromagnetic wave

Φ – work function

E_k – kinetic energy

- We get the chemical composition and information about the bonds of the atoms



http://www.rowbo.info/XPS.html

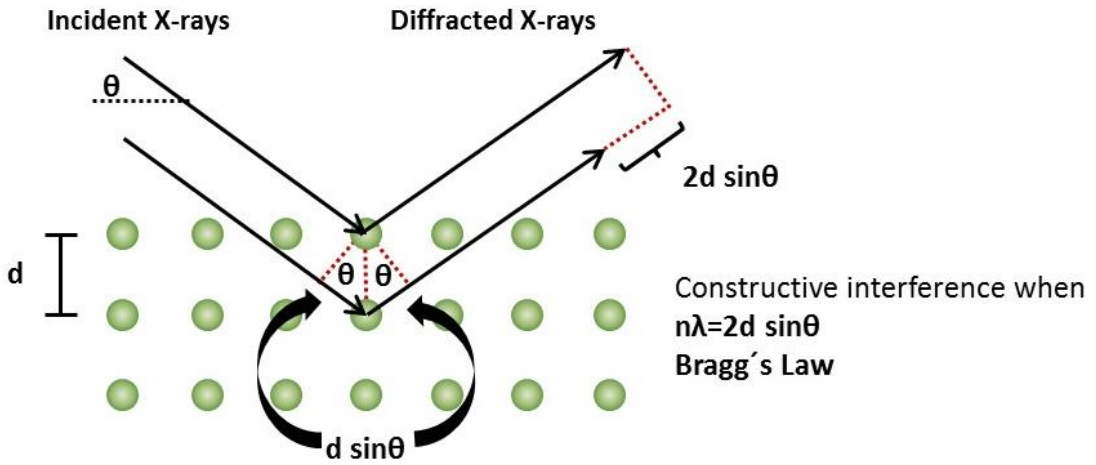
X-Ray Diffractometry (XRD)

- X-rays are incident on the sample containing the crystallites and diffract

d – spacing between diffracting planes

λ – wavelength of the beam

ϑ – incident angle



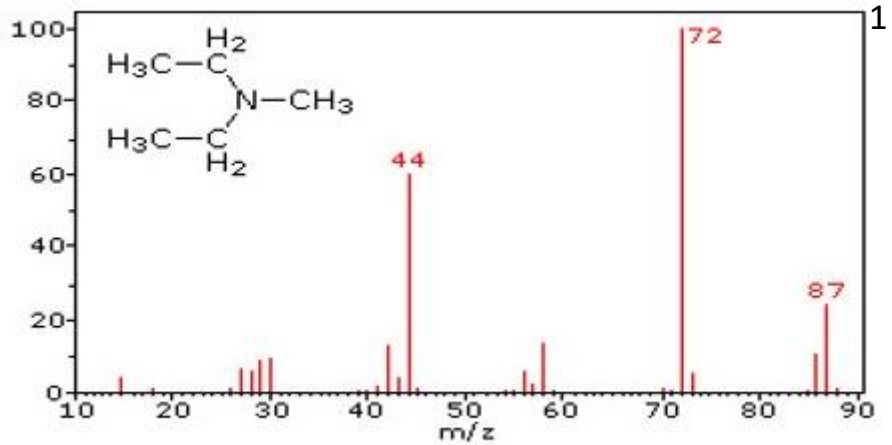
- We obtain information about the crystal structure (cell type, spacing between diffracting planes, lattice parameter, crystallite size, texture,...)

https://wiki.anton-paar.com/cz-cs/rentgenova-difrakce-xrd/

Particle Methods

Mass Spectrometry (MS)

- The sample to be studied is not in the form of a gas, we ionize it and use a magnetic field to separate the charged components based on its **m/q** ratio.



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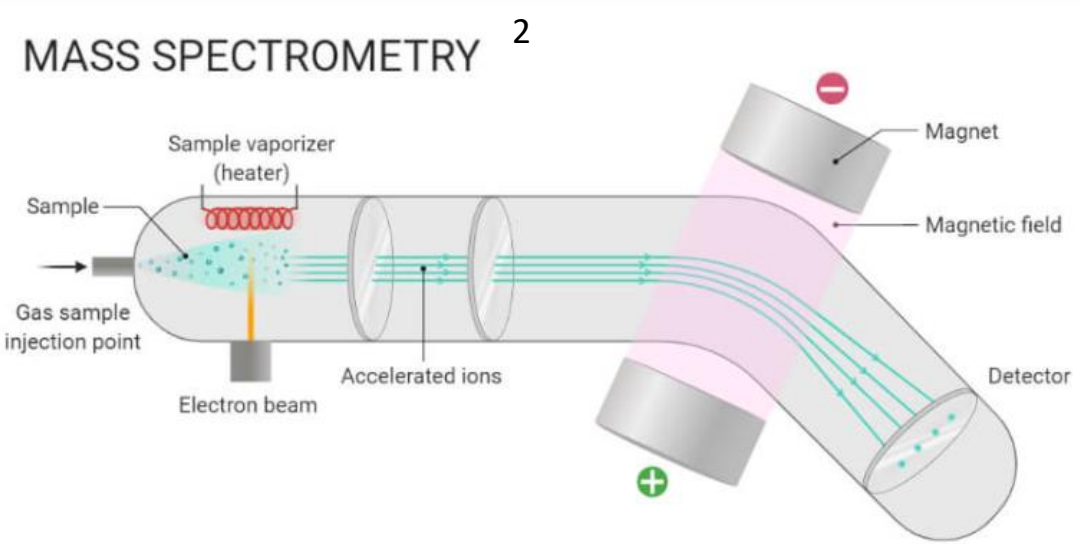

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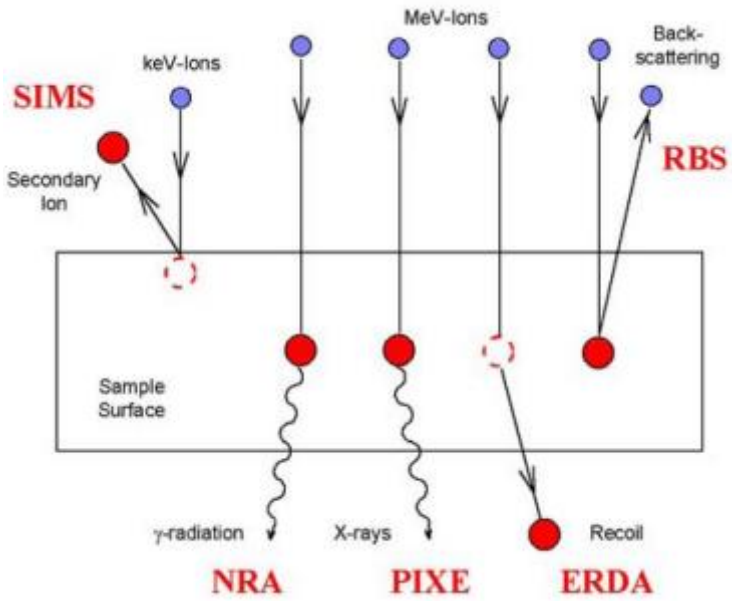
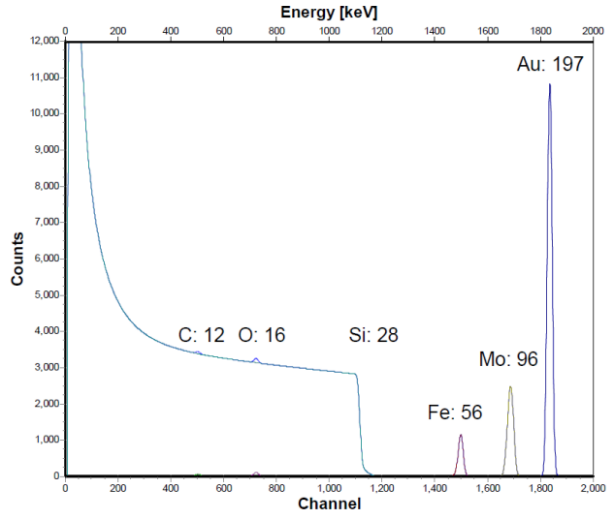
[1] https://assignmentpoint.com/mass-spectrometry/
[2] https://microbenotes.com/mass-spectrometry-ms-principle-working-instrumentation-steps-applications/

Rutherford Backscattering Spectrometry (RBS)

- Light energetic ions are incident on the measured sample and reflected from the sample nucleus. Their energy is studied.
- The chemical composition of the surface (~ hundreds of nm) layer of the sample is obtained. The measurement is very sensitive for heavy elements and less sensitive for light elements. The measurement is non-destructive.





https://physics.uwo.ca/~lgonchar/research/links/June3_2013/RBS_June3_2013_slides.pdf

Thermodynamic Methods

Thermodynamic Methods

- **TGA – thermogravimetric analysis**
  - Measurement of weight loss/gain as a function of temperature
- **DTA – differential thermal analysis**
  - Thermal differences between measured and reference sample
  - State changes, reaction heat, reaction kinetics
- **DSC – differential scanning calorimetry**
  - Comparison of heat flux changes per measured and reference sample
  - More modern version of DTA, extra heat

- Thermodynamics is based on the assumption of a large number of particles. This may not be fulfilled for nanostructures.

Conclusion

- We have introduced different types of methods used to investigate nanostructures
  - Optical
  - Electron imaging
  - Probe
  - Spectroscopic
  - Particle
  - Thermodynamic