Nanostructured Materials and Nanotechnology

2022-2023

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TÉCNICO LISBOA

Lab sessions:

- Synthesis

- Light scattering

- Electronic microscopy

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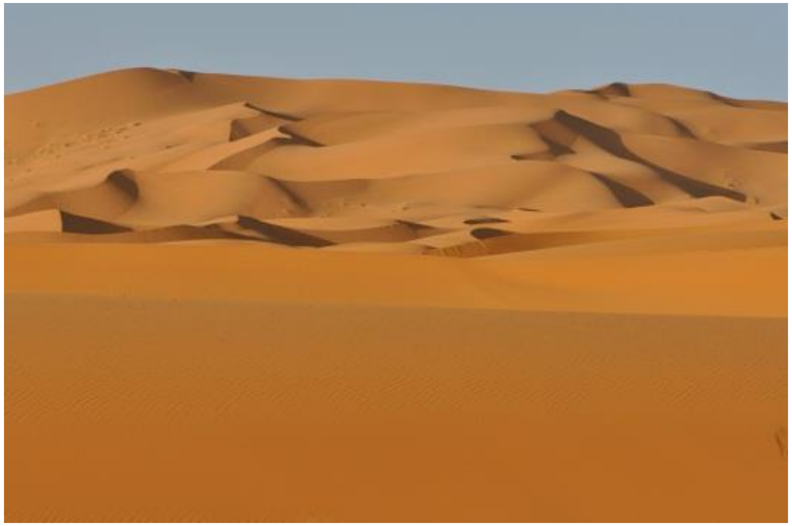
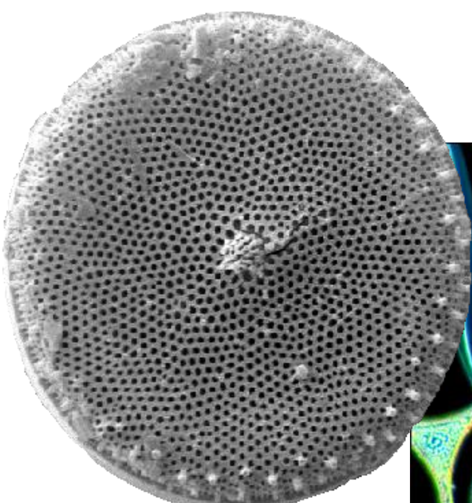
Silica



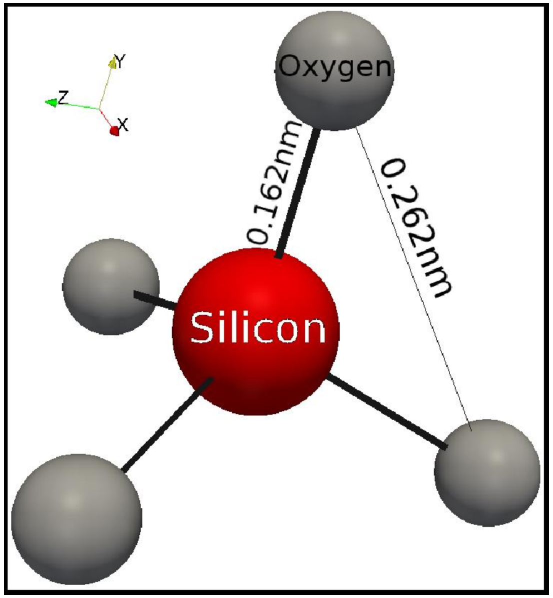


SiO_2

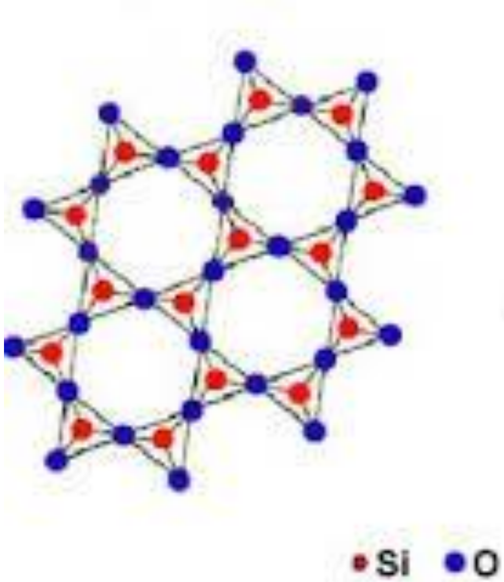
Density: 2 - 4.3 g/mL

Melting point: > 1600ºC

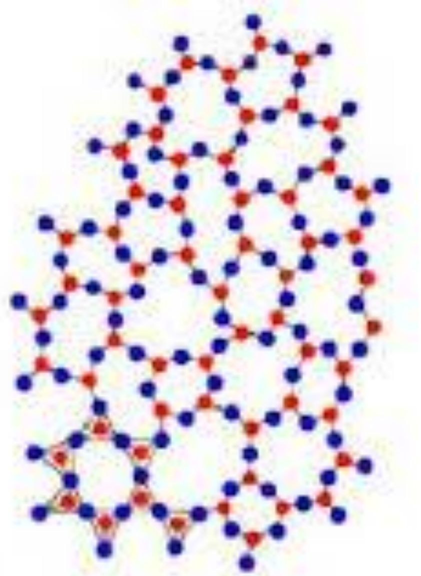
Boiling point: > 2200ºC



SiO_2 crystaline



SiO_2 amorphous



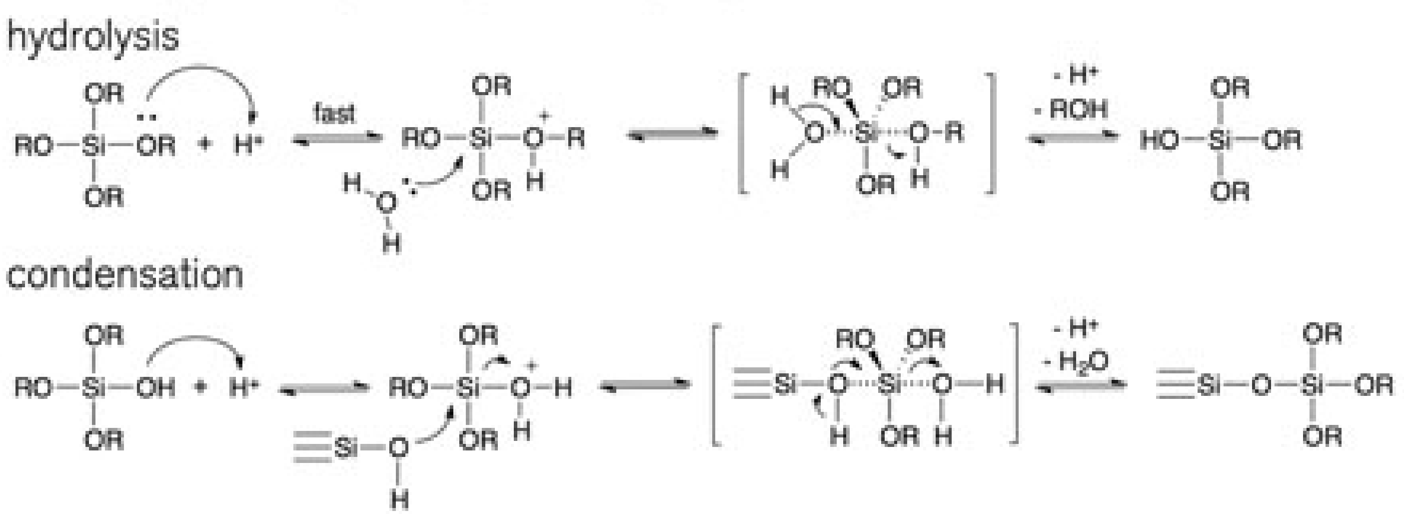
Sol-gel process

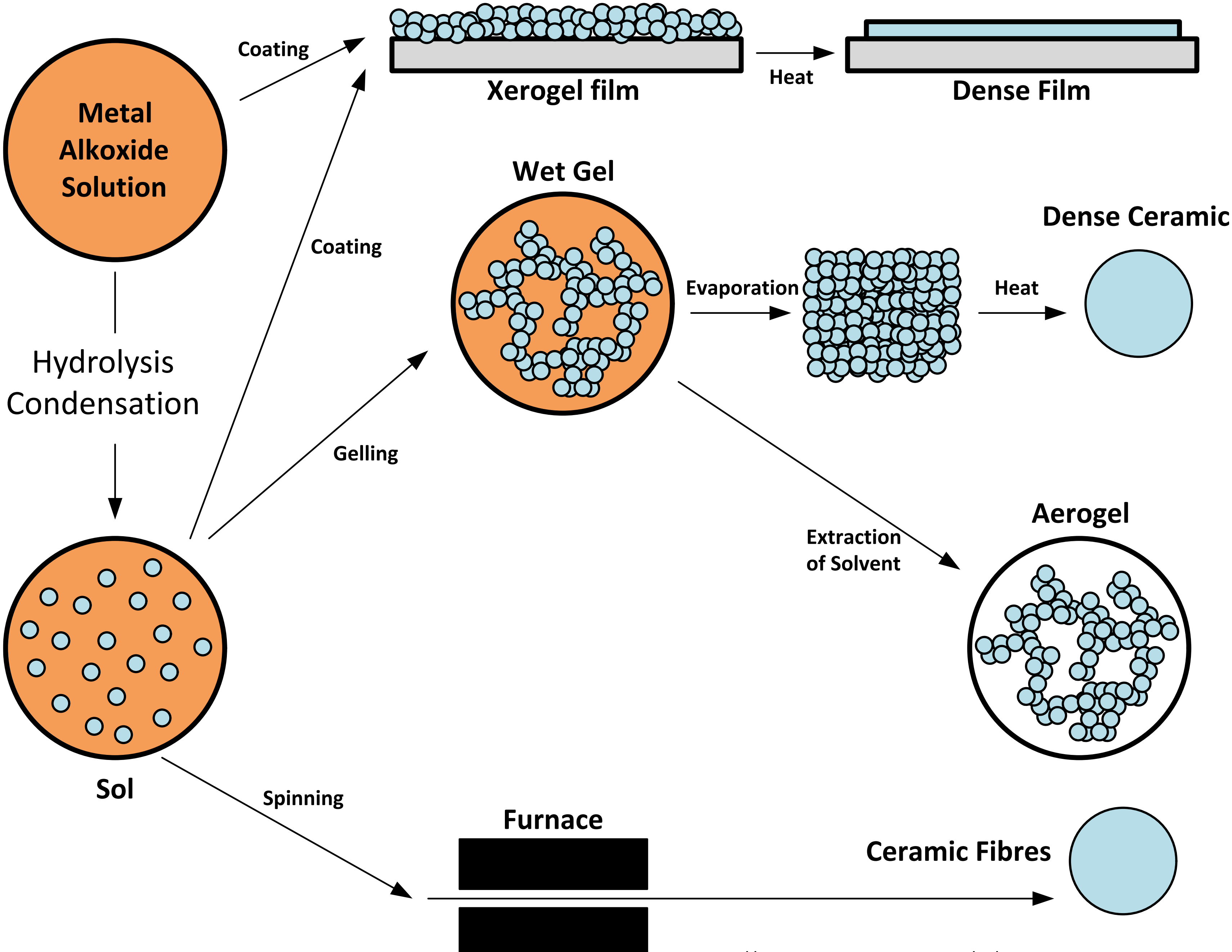
Sol = a stable suspension of colloidal solid particles or polymers in a liquid

Gel = porous, three-dimensional, continuous solid network surrounding a continuous liquid phase

Steps

- Hydrolysis
- Condensation
- Gelation
- Ageing
- Drying
- Densification





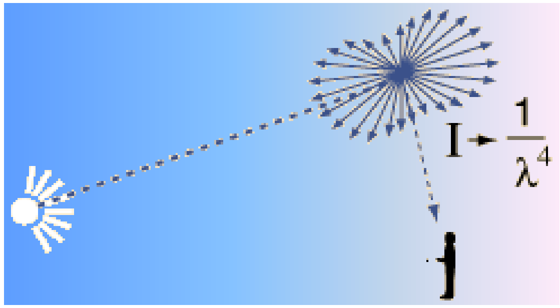
https://commons.wikimedia.org/w/index.php?curid=29869440

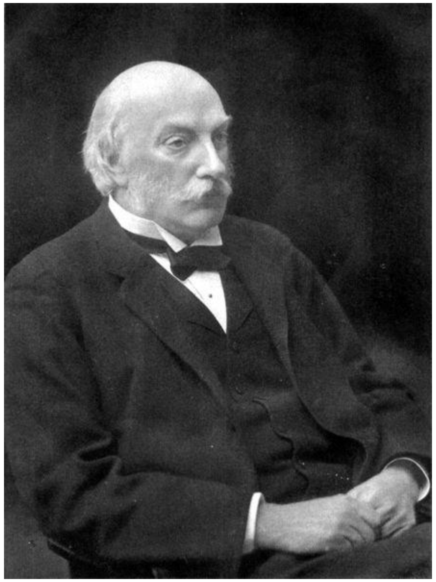
Light scattering

Radiation scattered without changing its wavelength

Rayleight scattering depends on the wavelength of the radiation and the polarizability of the scattering particles

The radiation electrical field induces an oscillating dipole on the scattering particles





John William Strutt, 3rd Baron Rayleigh (1842-1919) Nobel of Physics 1904

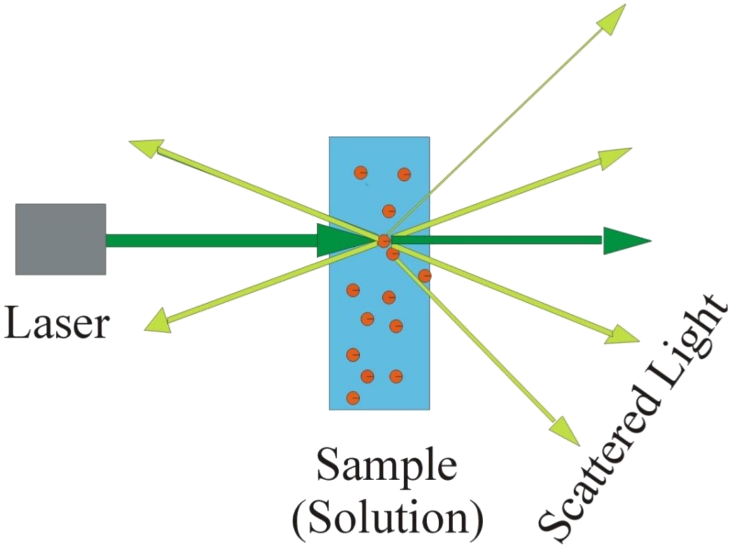
$$\vec{\mu} = \frac{\alpha}{4\pi\,\varepsilon_0}\,\vec{E}(0,t)$$

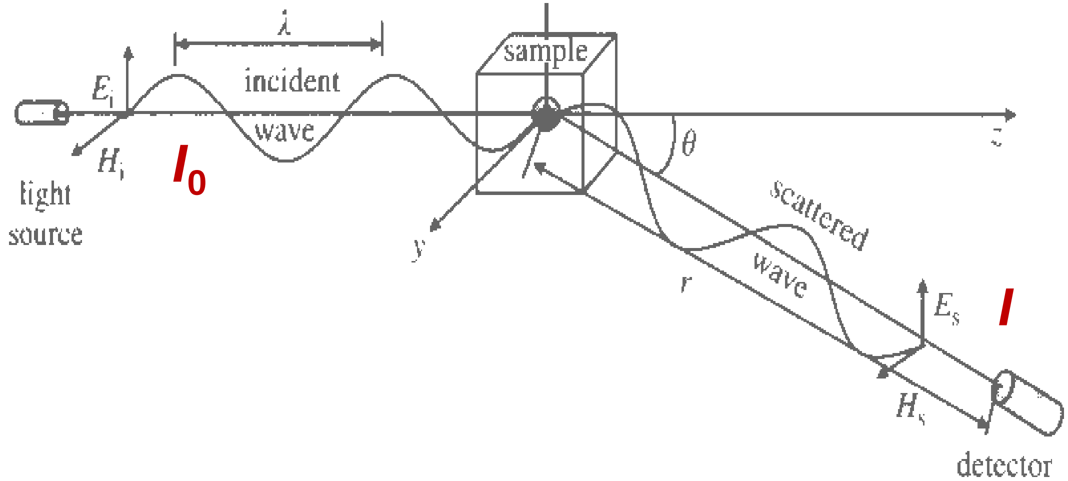
The induced dipole oscillates in resonance with the electrical field of the radiation, emitting with intensity proportional to the field and the ***polarizability*** α ***of the particle***

$$\frac{I}{I_0} = \frac{16\pi^4}{r^2\lambda_0^{\,4}} \times \left[\frac{\alpha}{4\pi\varepsilon_0}\right]^2$$

The polarizability of the scattering particles depends on their size

Light scattering





Intensity of scattered light by an isolated molecule smaller that λ / 20 (vertical polarized light)

$$\frac{I}{I_0} = \frac{16\pi^4}{r^2\lambda_0^4} \times \left[\frac{\alpha}{4\pi\varepsilon_0}\right]^2$$

Decreases with the squared distance to the detector

Increases with polarizability (intensity of scattered light changes with the square of the electromagnetic field)

Decreases sharply with the wavelength of the radiation

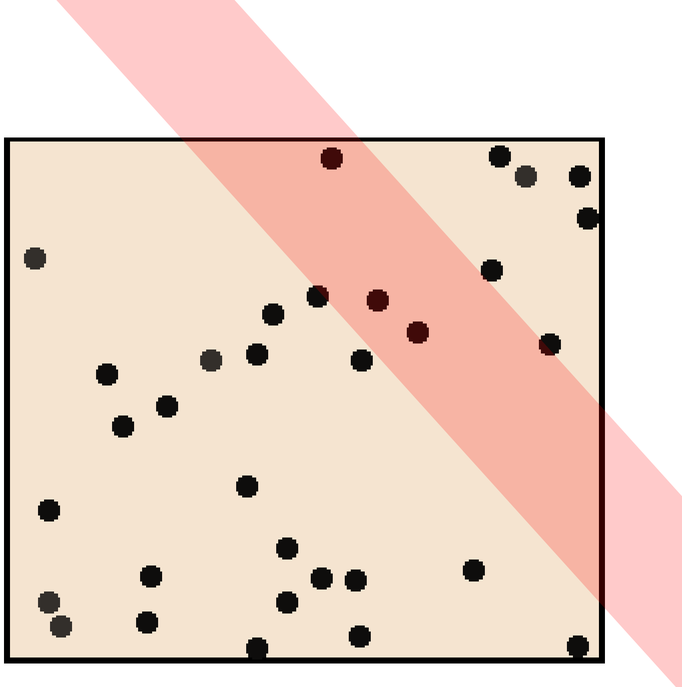
Rayleigh ratio

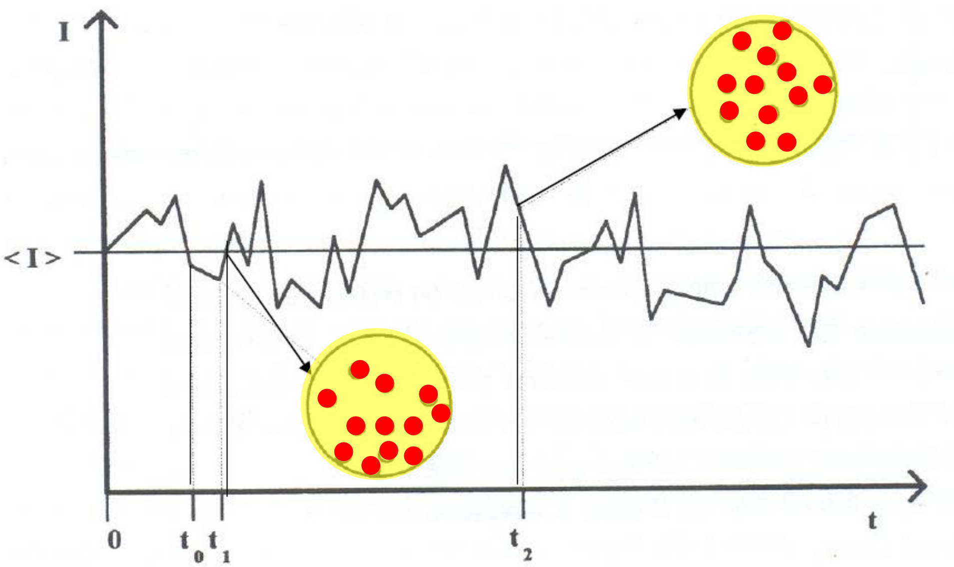
$$R_\theta = \frac{I \times r^2}{I_0}$$

$$R_\theta = \frac{16\pi^4}{\lambda_0^4} \times \left[\frac{\alpha}{4\pi\varepsilon_0}\right]^2$$

Dynamic light scattering (DLS)

Time-dependent interference of light dispersed from different molecules in the sample causes intensity fluctuations





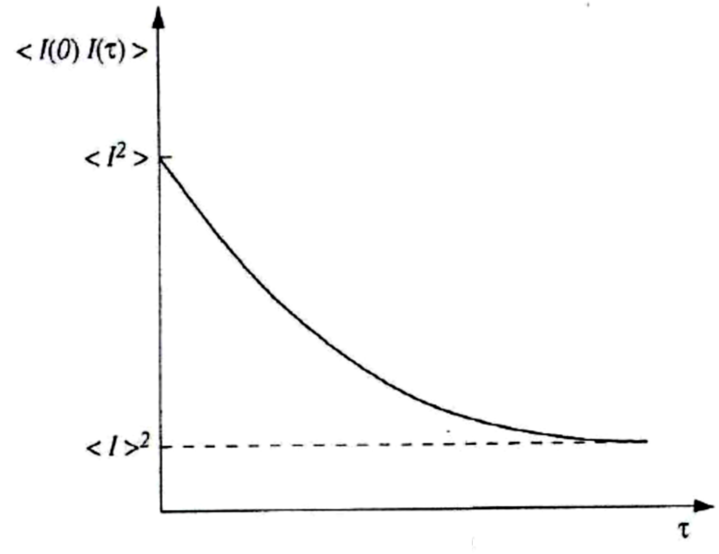
Intensity fluctuations depend on molecular motion, described by the diffusion coefficient

$$D = \frac{kT}{\zeta}$$

Einstein relation

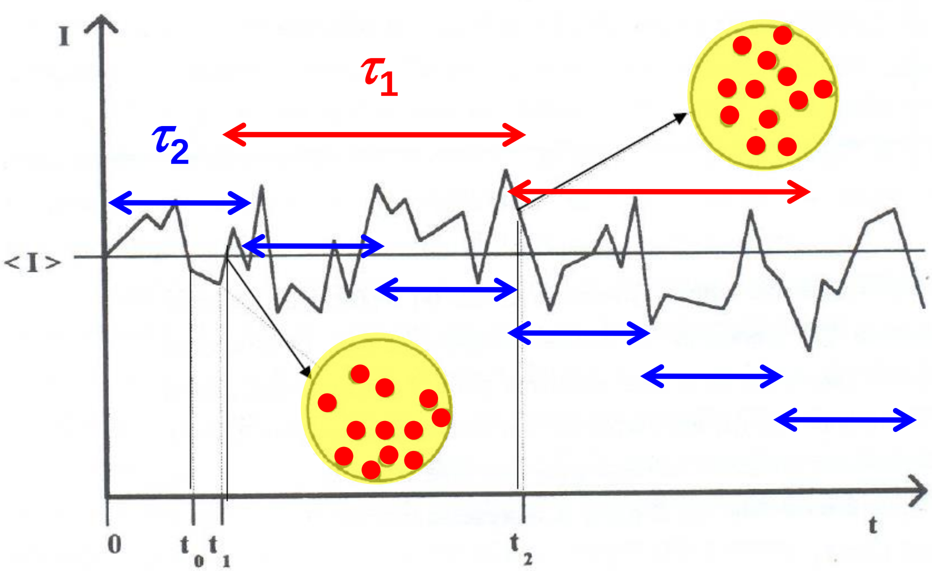
Friction coefficient ζ measures viscous dissipation opposing thermal motion

Analysis of fluctuating scattering intensity by an autocorrelation function



$$\langle I(0)\, I(\tau)\rangle = \lim_{T\to\infty} \frac{1}{T}\int_0^T I(t)\, I(t+\tau)\, dt$$

$$\langle I(0)\, I(\tau)\rangle = A + B\exp\left(-2 D q^2 \tau\right)$$



Stokes law: viscous dissipation of a sphere of radius R in a Newtonian fluid of viscosity η

$$\zeta = 6\pi\,\eta\, R$$

$$D = \frac{kT}{6\pi\,\eta\, R} \qquad D = \frac{kT}{\zeta}$$

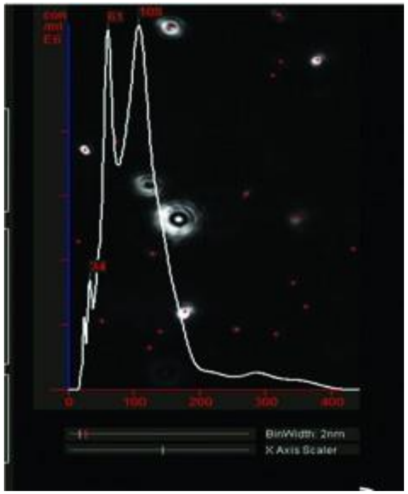
Stokes-Einstein relation

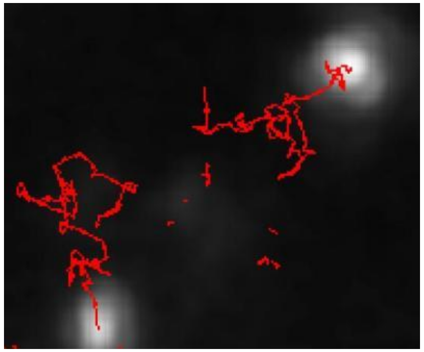
DLS used to obtain the hydrodynamic radius $\boldsymbol{R}_{\mathbf{h}}$

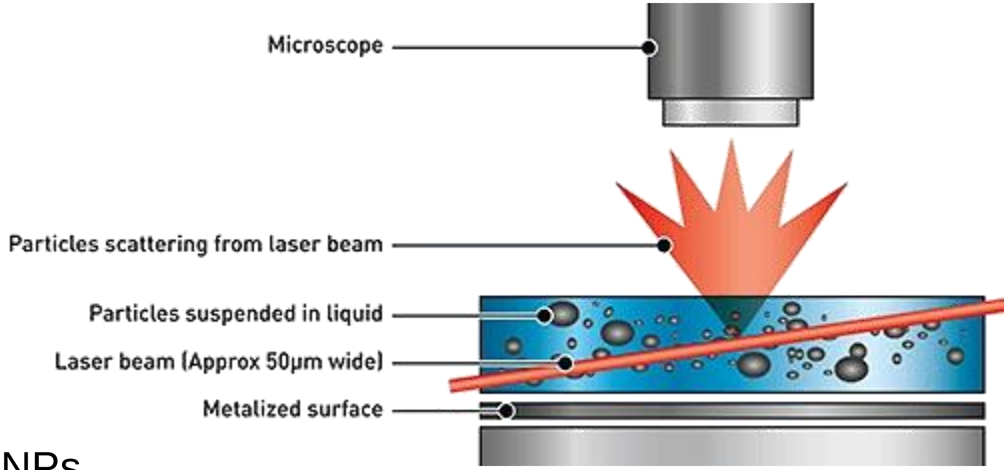
Nanoparticle tracking analysis (NTA)

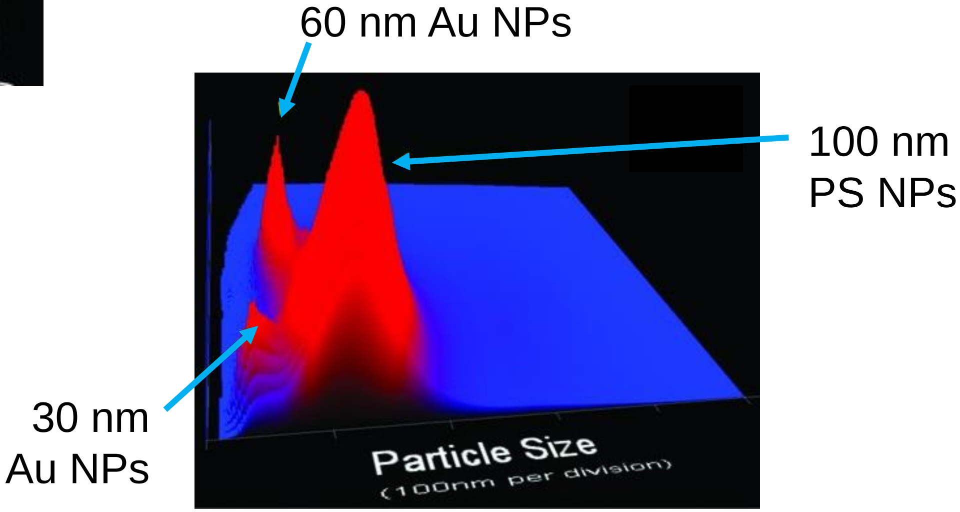
Distribution of R_h values, nanoparticle concentration

Detects light scattered from individual particles, measuring the *trajectory* of each particle to calculate the corresponding *diffusion coefficient*

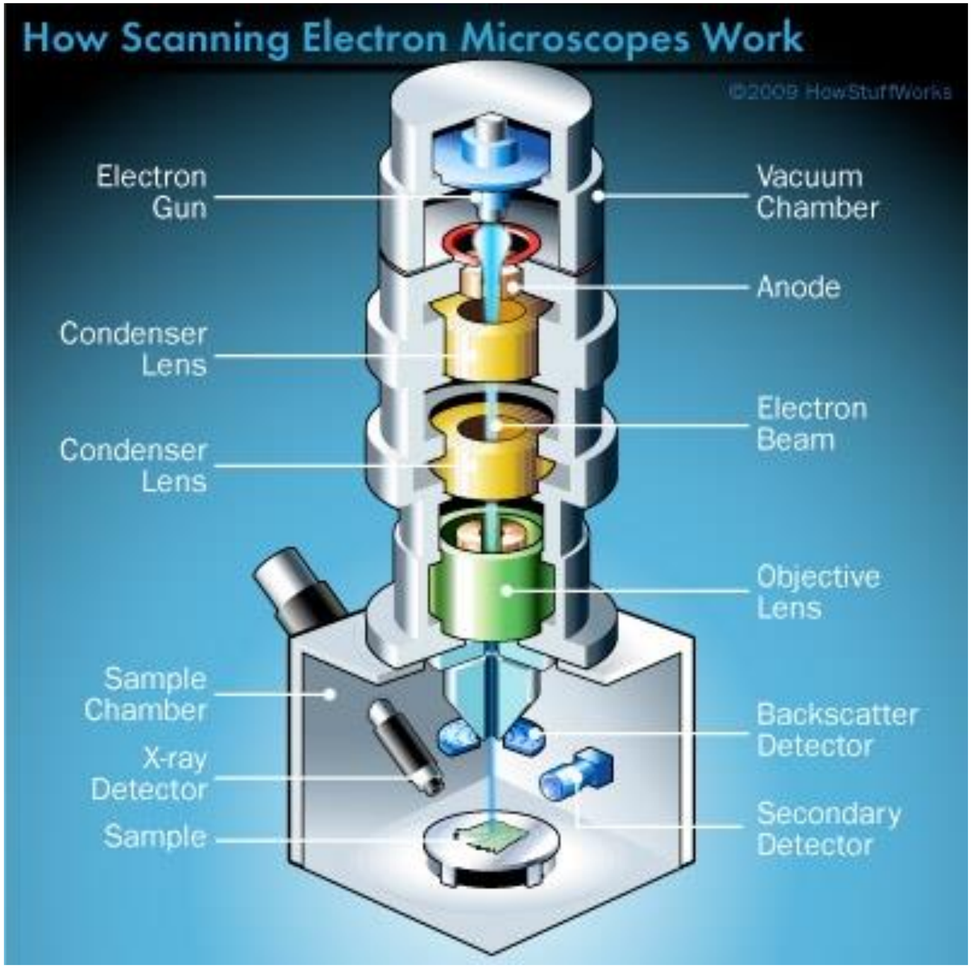








Scanning Electron Microscopy (SEM)



An electron gun generates electrons. A condenser focus the beam in the smallest point possible. Scanning coils deflect the beam and make it raster the sample surface.

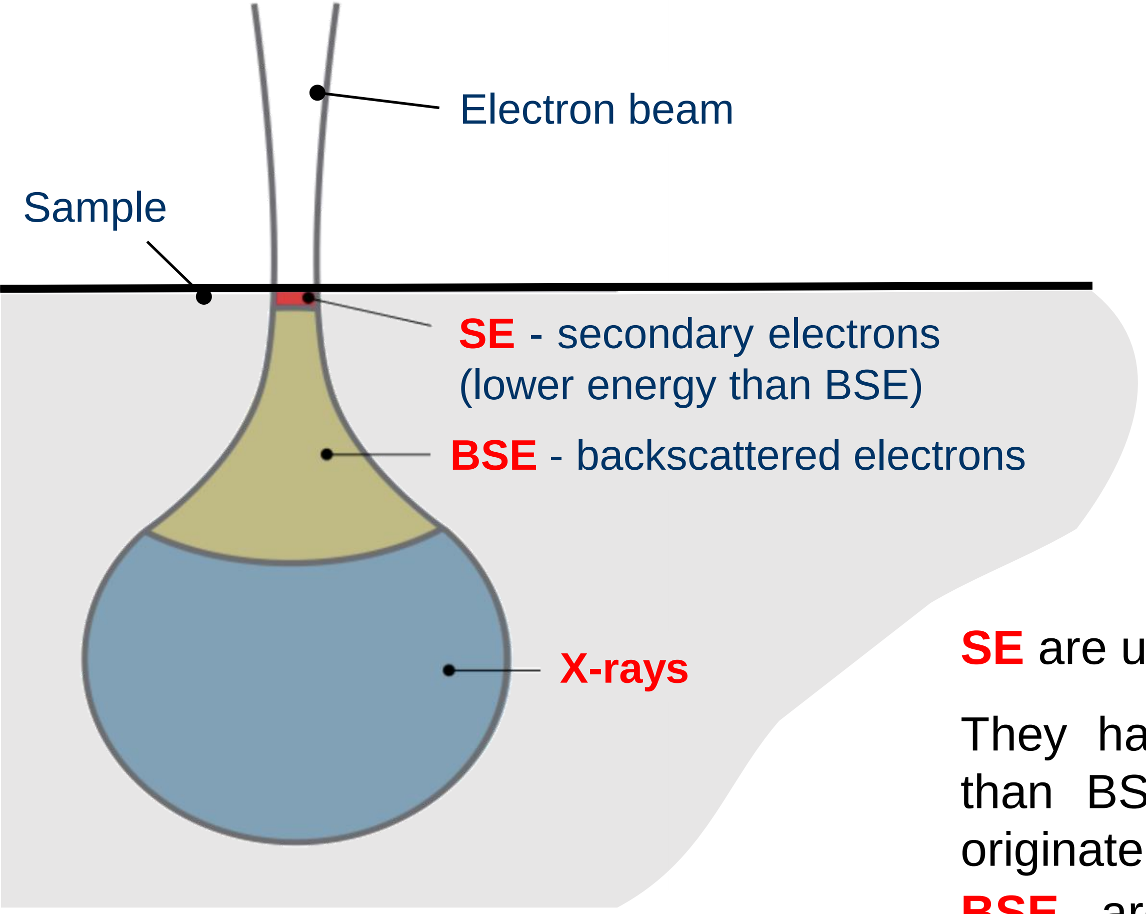
Magnifications from ca. 50x to over 100 000x

Local chemical information

JEOL 7100F FEG SEM - IST

Sample has to be made conductive

SEM beam/specimen interactions (signal types)

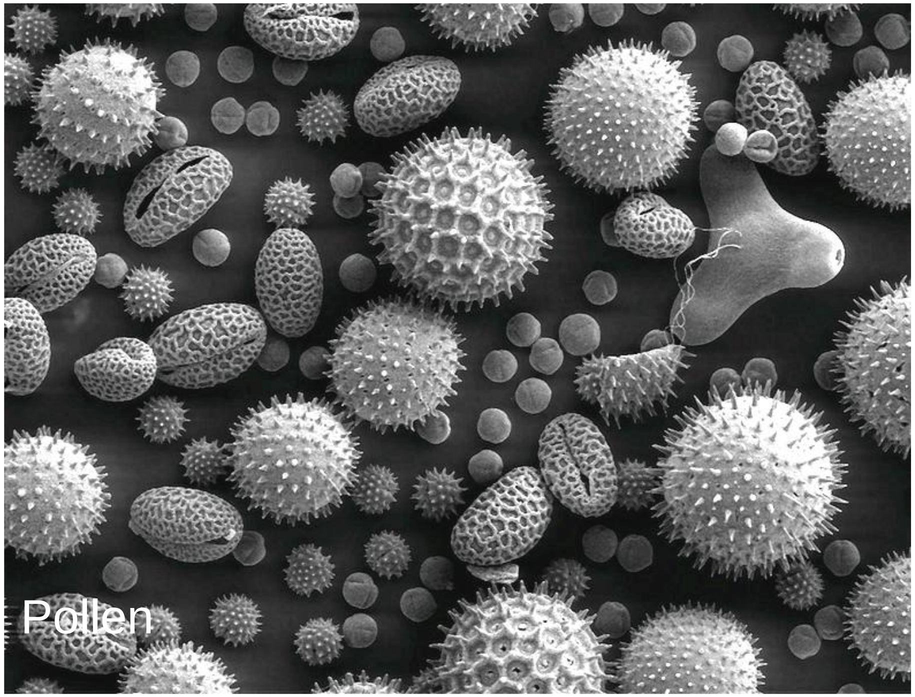


SE are used for *topographic contrast*.

They have higher spatial resolution than BSE because these electrons originate from a smaller volume

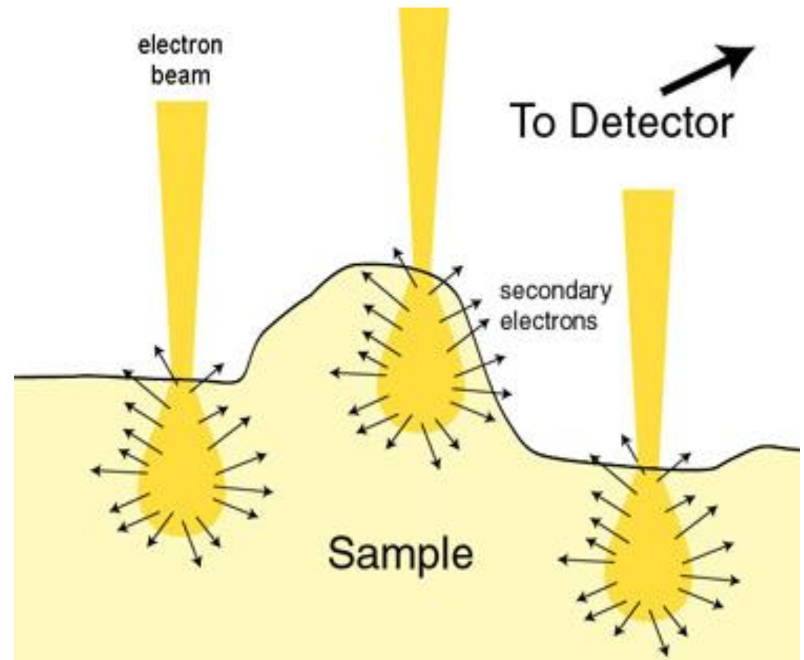
BSE are sensitive to the atomic number due to their high energy.

SEM - Topographic contrast (SE)



Where do the shades come from?

SE are low energy electrons and can only escape the sample to reach the detector if emitted from an *interaction volume* near the surface.



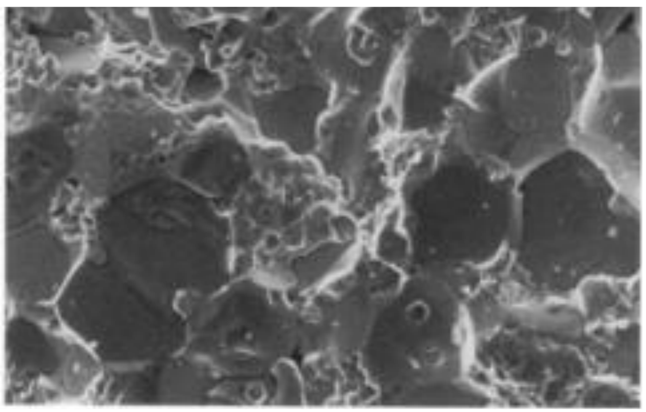
In ***hills*** there are more exposed surface, more SE escape and the signal is higher, originating ***brighter regions*** in the image.

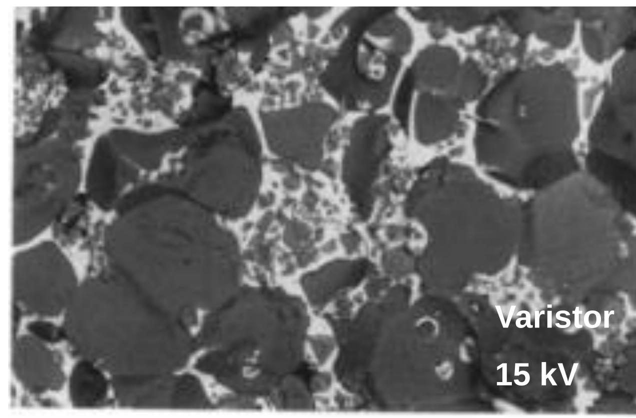
In ***valleys*** less *interaction volume* is exposed and less SE reach the detector, originating ***darker regions*** in the image.

SEM - Backscattered electron imaging

BSE are high energy electrons, sensitive to composition (atomic number).

BSE imaging is used in conjunction with SE (topological) imaging.



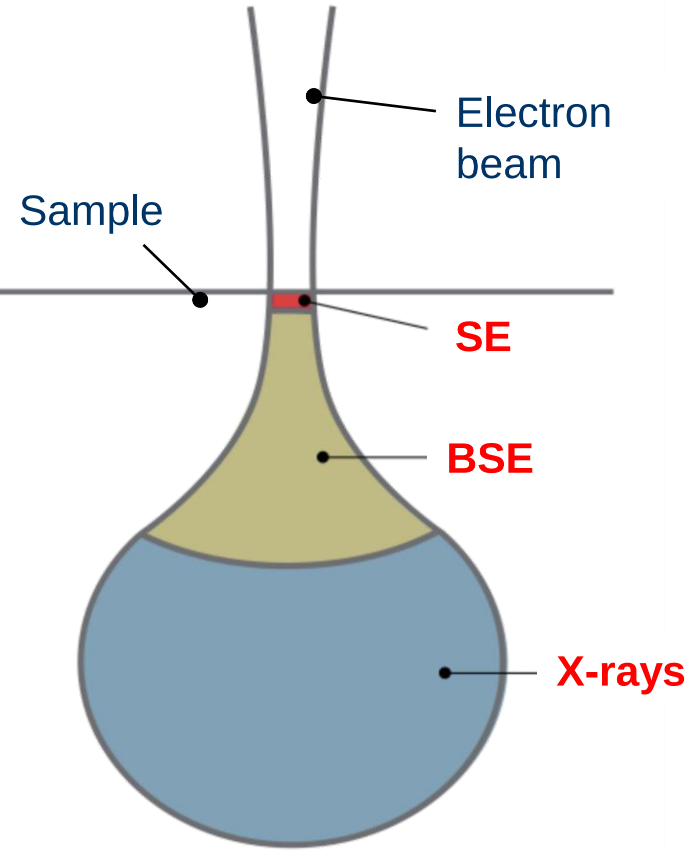


Topographic contrast (SE mode)

Atomic number contrast (BSE mode)

- Bright regions in ***SE*** images correspond to hills
- Bright regions in ***BSE*** images correspond to heavier elements

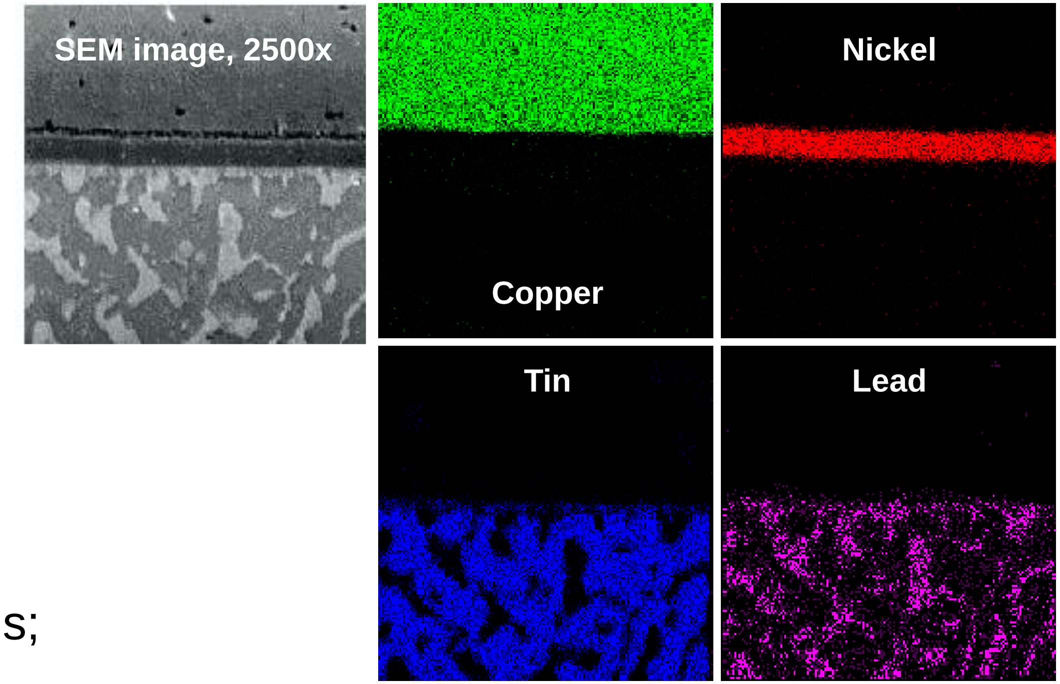
SEM - Energy dispersive X-ray spectroscopy (EDS)



X-rays are emitted from atoms when their electrons make transitions between inner atomic energy levels.

Each element has characteristic transition

In EDS, the SEM image is built from X-rays with specific energy, producing maps for each element



Analysis

- Qualitative: element identification;
- Semi-quantitative, without standards;
- Quantitative, with standards of similar composition.

Transmission Electron Microscopy (TEM)

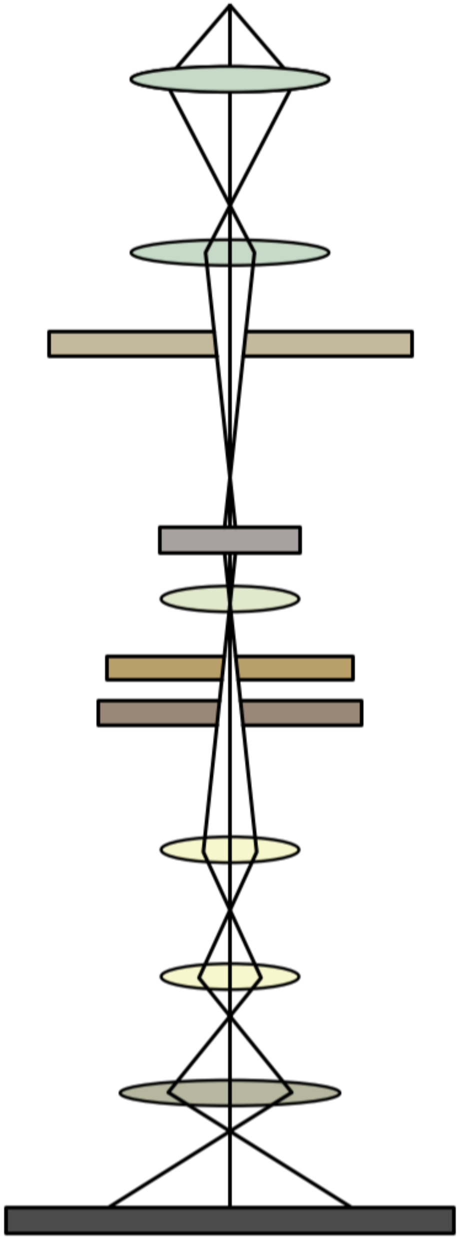
A TEM usually operates at 10^{-6} Torr in the column and 10^{-7} Torr in the electron gun chamber

Magnification up to 500 000x and resolution down to 0.2 nm (or better)

Hitachi 8100 - IST

Very thin sample

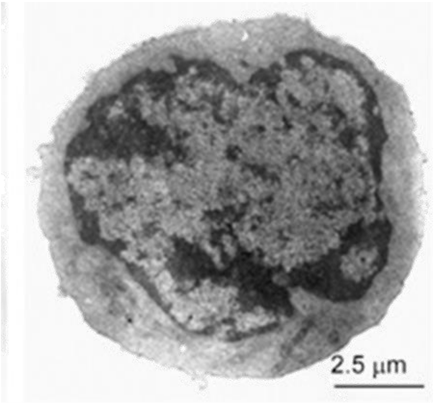
Conductive substrate



TEM contrast

The image contrast originates from:

- Diffraction: Crystalline materials
- Phase : High-resolution TEM (atomic resolution)
- Mass (amplitude) contrast: Polymers and biological materials



Sca-1^{+}lin^{-}CD45^{+} cell

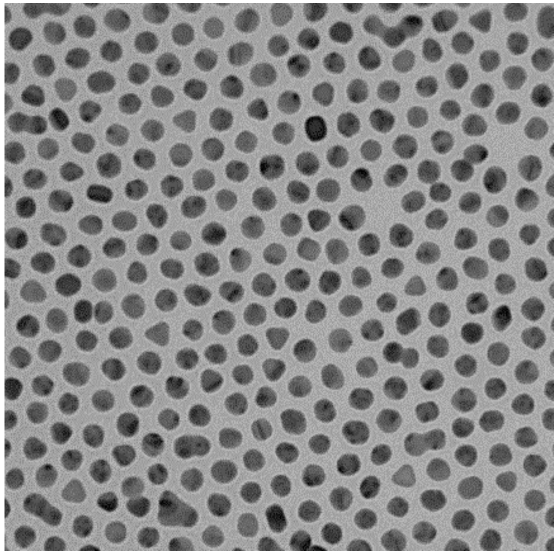
TEM mass contrast in soft matter

- Heavy atoms scatter more intensely (dark areas in the image).
- Fewer electrons are scattered at high electron accelerating voltages, since they have less time to interact with atomic nuclei in the specimen.

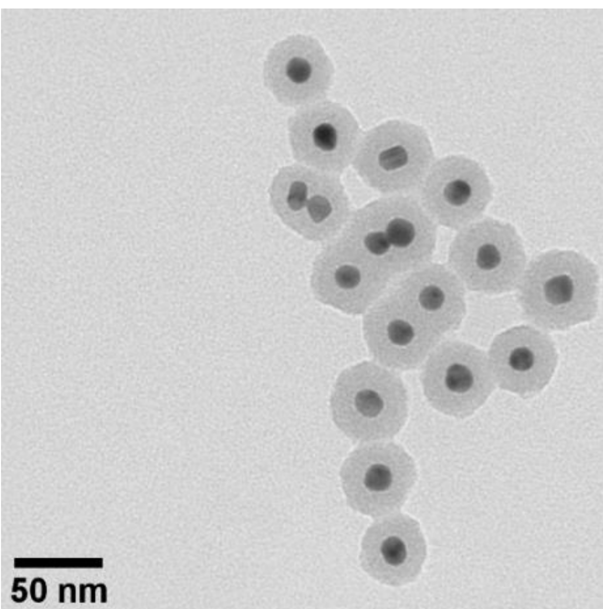
  However, high working voltages result in lower contrast and **damage polymeric and biological samples**

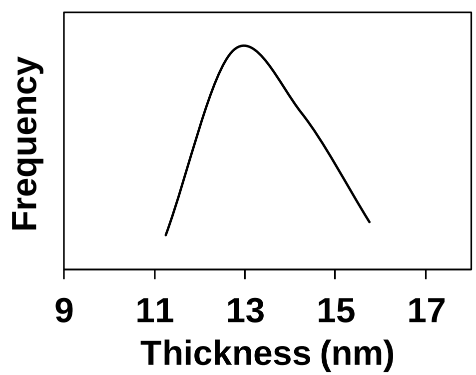
- Polymer and biological samples have low atomic number and similar electron densities. Staining increases the imaging contrast. Staining agents should be selectively absorbed in one of the phases (and appear dark in the image).

Example: Gold Nanoparticles



D = (15 ± 1) nm

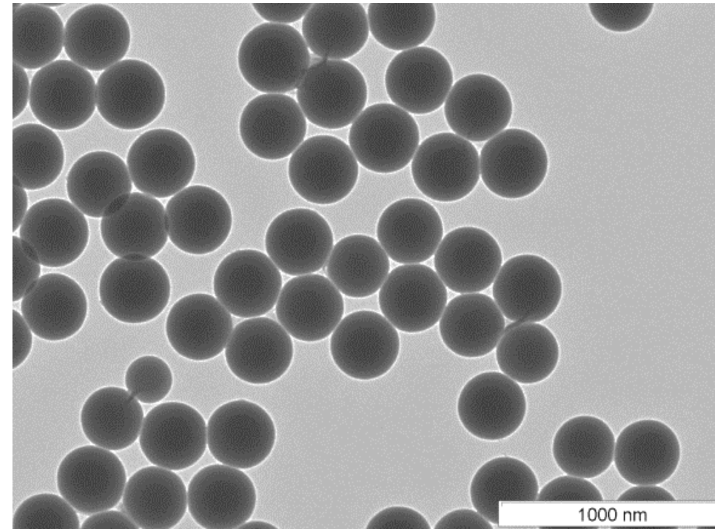




Silica shell: δ_{Si}= 13 nm

Scientific Reports 2017, *7*, 2440

Example: Silica Nanoparticles



Thursdays & Fridays

- **Week 1**: Introduction (Thursday)
- **Week 2**: Seminar coaching (ca. 1h, either Thursday or Friday)
- **Week 3**: Nanomaterials preparation (Complexo Interdisciplinar, ca. 1h, either Thursday or Friday)
- **Week 4**: Characterization (DLS, NTA at Complexo; SEM/TEM at Microlab, ca. 1h each, either Thursday or Friday)
- **Weeks 5 and 6**: Semionar presentation (both Thursday and Friday, ca. 3h/day)

Seminars

Seminar due dates

Topic for seminar and preliminary literature search: **September 27th** (week 2)

Submitted online

Seminar presentation: **October 12th** (week 4)

Submitted online

Topics for the seminars

Choose one of the areas:

1. Carbon nanomaterials
2. Metal nanoparticles
3. Semiconductor nanoparticles
4. Magnetic nanoparticles
5. Silica and metal oxide nanomaterials
6. Hybrid nanomaterials and nanocomposites

Specific application such as:

- Fabrication or characterization
- Energy applications
- Biomedical applications
- Catalysis, etc.

Select one specific topic to cover on your seminar

Literature review

1: Define a Topic

- Topic interesting to you
- Important aspect of the field
- Well-defined issue (otherwise there will be thousands of publications!)

2: Search and Re-search the Literature

- Keep track of the search items you use (and a list of the papers' pdf files)
- Look for research papers in the area, but also reviews and their references
- be thorough, use different keywords, look at who cited past relevant papers

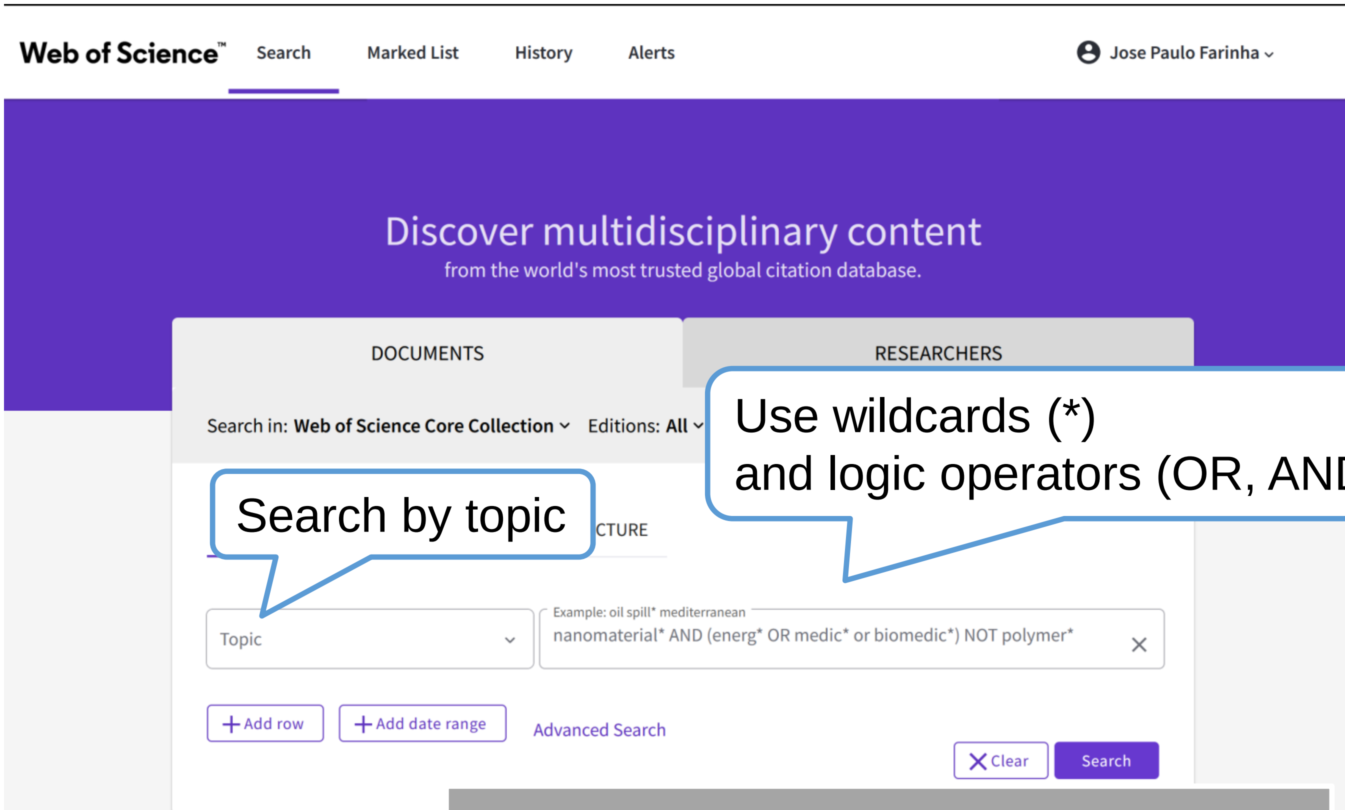
3: Be Critical and Consistent

- Not just summarize the work, but **discuss it critically**
- State major achievements, outstanding research questions…

4: Find a Logical Structure

- Draw a **conceptual scheme of the presentation** to define a logical order
- Give a introduction of the context and end with a take-home message
- Use a careful selection of figures

Literature Search *webofknowledge.com*



Search by topic

Use wildcards (*)
and logic operators (OR, AND, NOT)

Review papers for more general topics

Papers with more citations

More recent papers

Older papers cited by these

Newer papers that cite these

Literature Search – top journals in the field

- Nature Materials
- Nature Nanotechnology
- Matter
- ACS Nano
- Nano Letters
- Chemistry of Materials
- ACS Applied Materials and Interfaces (and family)
- Nanoscale
- Journal of Materials Chemistry (A/B/C)
- Materials Horizon
- Nanoscale Horizons
- Advanced Materials (and family)
- Advanced Functional Materials
- Small
- Particle and Particle System Characterization
- Nano Research

Seminar structure

- Introduction to the subject of your paper (use review papers)
- Critical discussion of the results of only 1 paper (preferably from one of the top journals) – one of the 3 papers you chose
- Includ goal of the work, novelty and expected impact
- *10 min presentation + questions*

To check

- *The font is readable (> 18pts)*
- *Information is clearly presented and organized*
- *Details are minimized so that main points stand out*
- *Do not read from slides*
- *Do not use more time than allocated for the talk*

Grading of Seminar Presentation

Components	Sophisticated A (18-20 points)	Competent B / C (14-17 points)	Not yet Competent D / R (10-13 points / fail)
Organization	Presentation is clear, logical, and very well organized.	Presentation is generally clear and well organized. A few minor points may be confusing.	Organization is haphazard; arguments are not clear.
Style	Presentation is a planned conversation, paced for audience understanding. Not reading. Speaker comfortable in front of the group and can be heard by all.	Level of presentation is generally appropriate. Pacing is sometimes too fast or too slow. Presenter seems slightly uncomfortable at times, and audience occasionally has trouble hearing him/her.	Aspects of presentation are too elementary or too sophisticated for audience. Presenter seems uncomfortable and can be heard only if listener is very attentive. Much of the information is read.

Grading of Seminar Presentation

Components	Sophisticated A (18-20 points)	Competent B / C (14-17 points)	Not yet Competent D / R (10-13 points / fail)
Responsiveness to Audience	Consistently clarifies, restates, and responds to questions. Summarizes when needed. Shows comfort interacting with audience	Generally responsive to audience questions. Shows some discomfort interacting with audience	Responds to questions inadequately. Shows reluctance to interact with audience

Grading of Seminar Presentation

Components	Sophisticated A (18-20 points)	Competent B / C (14-17 points)	Not yet Competent D / R (10-13 points / fail)
Communication Aids	Communication aids enhance the presentation. • The font is readable • Information is represented and organized to maximize audience comprehension • Details are minimized so that main points stand out	Communication aids contribute to the quality of the presentation. • Font size is mostly readable • Appropriate information is included • Some material is not supported by visual aids	Communication aids are poorly prepared or used inappropriately. • Font size is too small to read • Too much information • Details or unimportant information is highlighted, and may confuse the audience
Depth and accuracy of Content	Accurate and complete explanations of key concepts, theories and applications, drawing on relevant literature	For the most part, explanations are accurate and complete. No significant errors are made.	Explanations are inaccurate or incomplete. Enough errors to distract a knowledgeable listener. Listeners gain little from the presentation.