MSE 160 – Ceramic synthesis

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MSE 160 class page: bowmanlab.eng.uci.edu/class

Final presentations

From syllabus:

Presentation Team:

You are to work in groups of two or three with another student in your lab period.

2

Lecture outline

Outline

- Ceramic characterization
  - Dynamic light scattering (DLS)
  - Scanning electron microscopy (SEM)

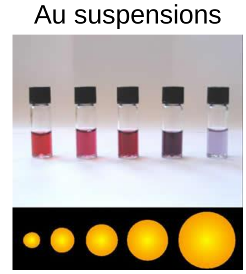
3

Colloidal methods

Wet chemistry processes where different ions are mixed to form insoluble precipitates

Used to produce **metals, metal oxides, organics, and pharmaceuticals**.

Au suspensions



Basic principles of colloidal preparation were known since antiquity. E.g. gold colloids used for high quality red and purple stained glass from medieval times to date. However, proper scientific investigations of colloidal preparation methods started only in 1857 when Faraday has published results of his experiments with gold.

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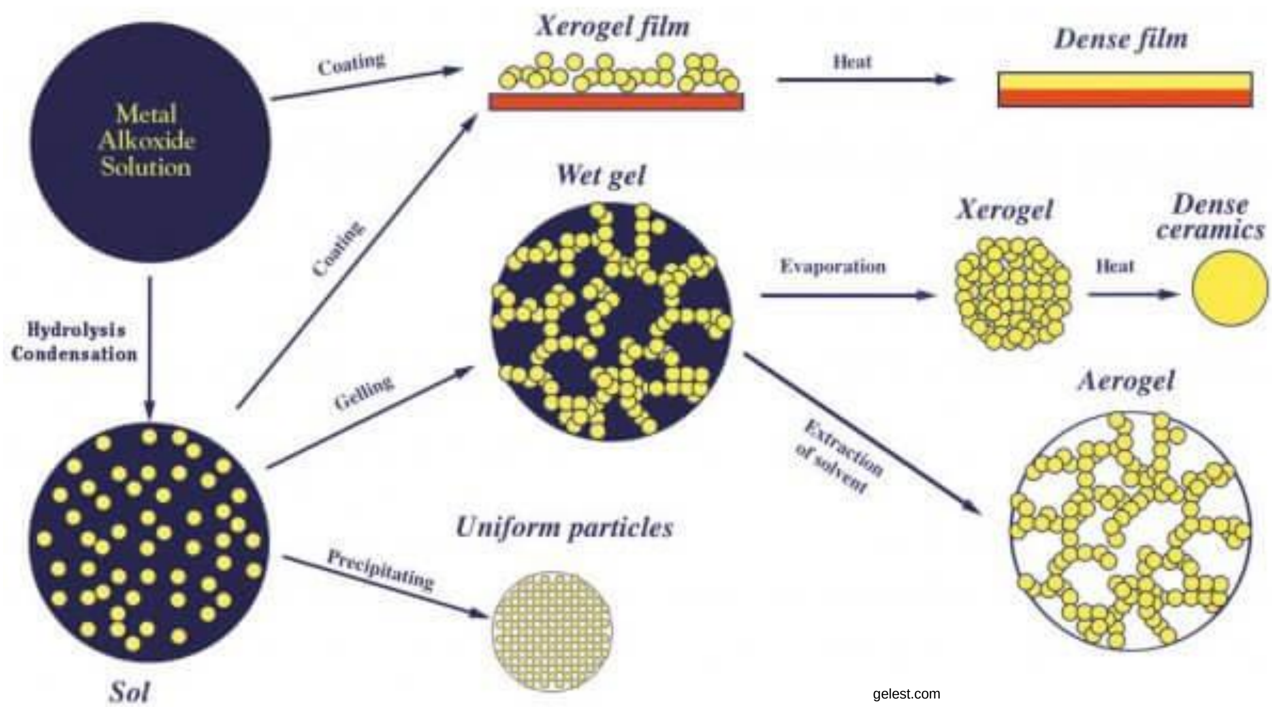

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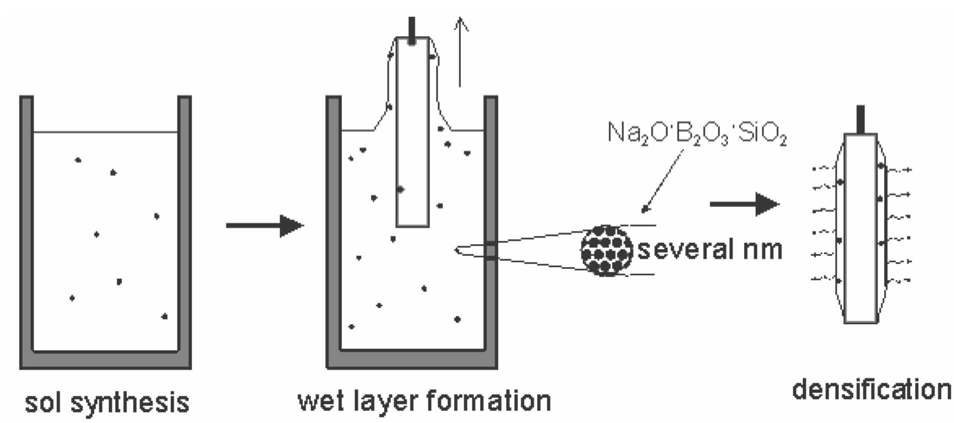
Common application - fabrication of coatings and films



Dip coating process
Substrate is immersed in a sol and withdrawn with well-defined speed under controlled temperature and atmospheric conditions. The sol forms a film with thickness mainly defined by the withdrawal speed, the solid content and the viscosity of the liquid. Gelation (densification) of the layer occurs by solvent evaporation, and finally annealing (heating) yields the oxide coating.

6

Dynamic light scattering (DLS)

Brownian motion

Correlation

Analyzing the correlation function

DLS is also called “photon correlation spectroscopy”

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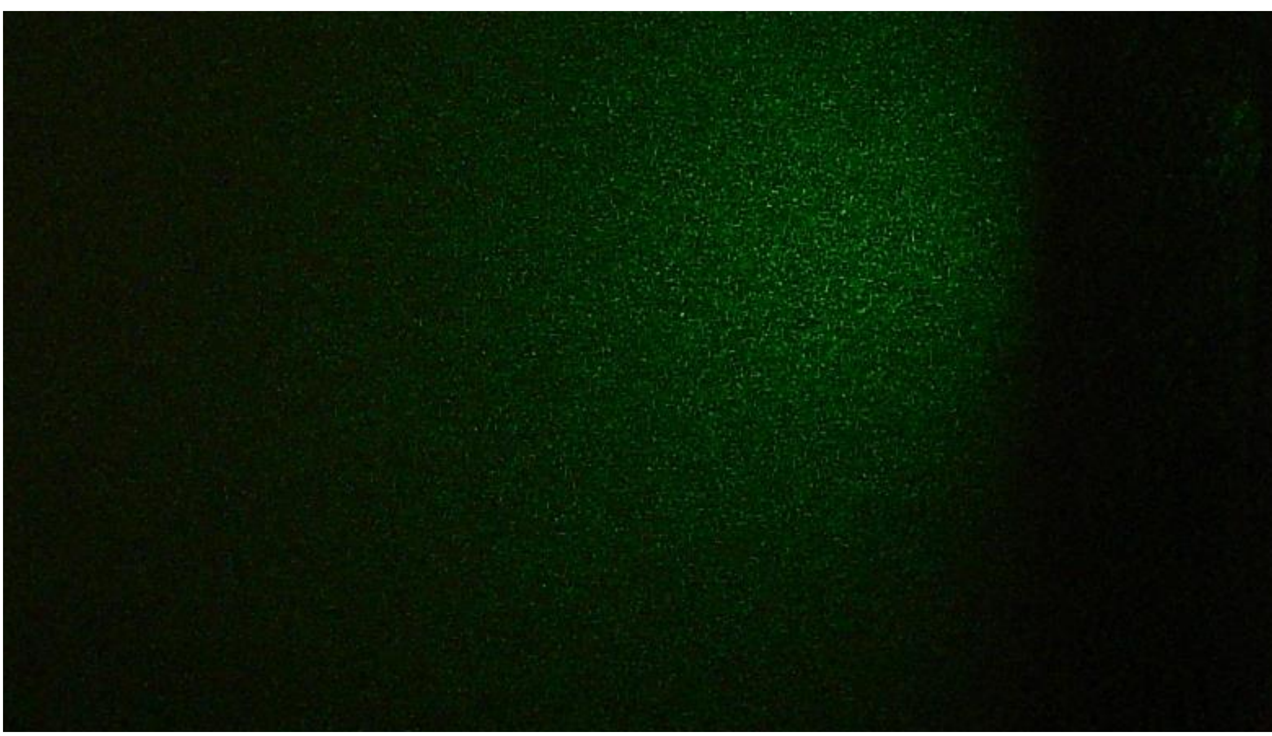

8

Applications of DLS

Determine the size distribution of particles in solution 1 nm – μms

Examples:

Engineering pigments in paint, dyes, inks
Drug delivery
Emulsions, colloidal systems
Etc.

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Dynamic Light Scattering and Brownian Motion

- Non-invasive technique for measuring the size of particles and molecules in suspension
- Brownian motion is the **random** movement of particles due to the bombardment by the solvent molecules that surround them

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Dynamic Light Scattering and Brownian Motion

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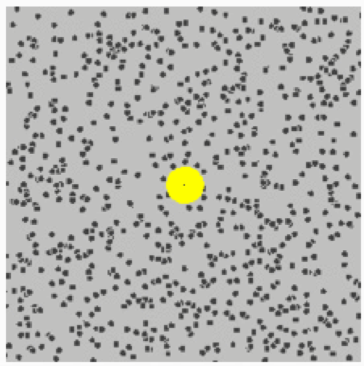

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Dynamic Light Scattering and Brownian Motion

- Non-invasive technique for measuring the size of particles and molecules in suspension
- Brownian motion is the **random** movement of particles due to the bombardment by the solvent molecules that surround them
- DLS measures the speed of particles undergoing Brownian motion
  - *Small particles diffuse rapidly*
  - *Large particles diffuse slowly*

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Brownian Motion

- Velocity of the Brownian motion is defined by the translational diffusion coefficient (D)
- The translational diffusion coefficient can be converted into a particle size using the **Stokes-Einstein** equation

$$d_H = \frac{kT}{3\pi\eta D}$$

d_H = hydrodynamic diameter
k = Boltzmann's constant
T = absolute temperature
η = viscosity
D = diffusion coefficient

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- Definition of Hydrodynamic Diameter (D_H):

The diameter of a hard sphere that diffuses at the same speed as the particle or molecule being measured

- Dependent on
  - Ionic strength
  - Surface structure
  - Shape

*Can correct for shape via rotational diffusion coefficient.

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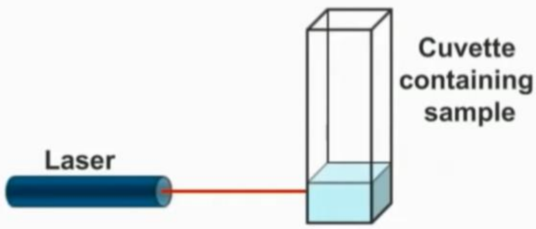
DLS Instrument Components



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DLS Instrument Components

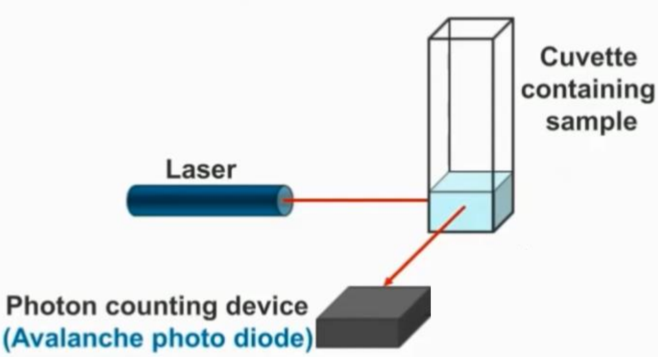

Photo diode has single-photon sensitivity

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DLS Instrument Components

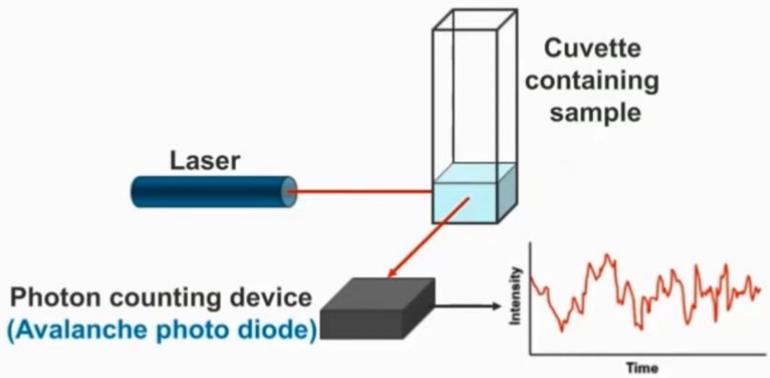

Photo diode has single-photon sensitivity with time resolution of nanoseconds

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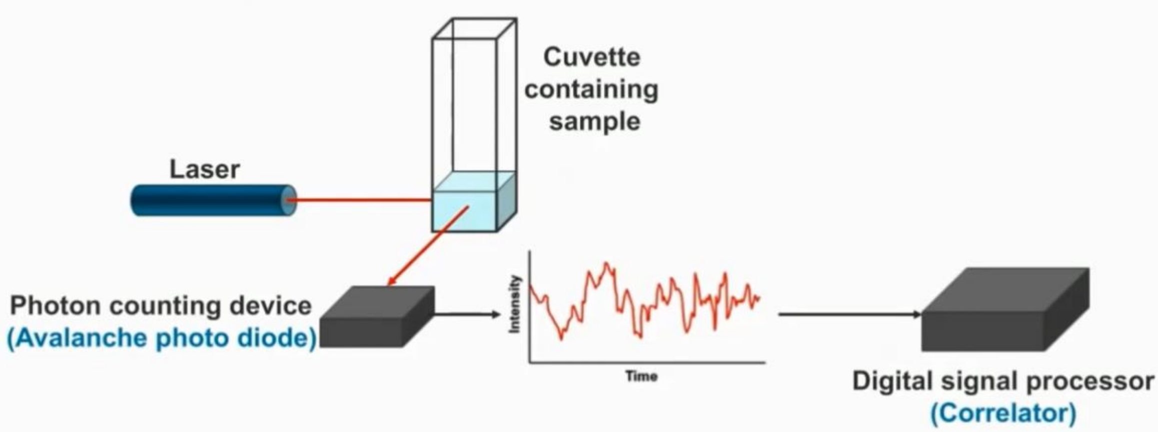
DLS Instrument Components



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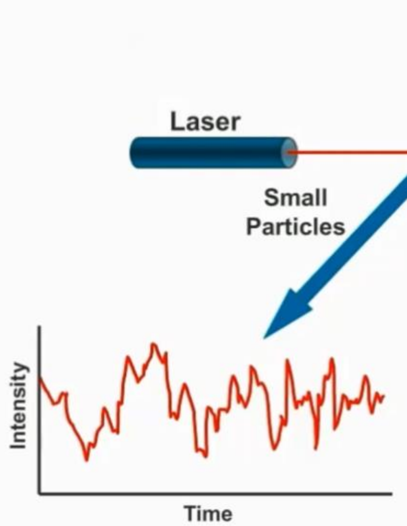
Fluctuation rate of intensity depends on particle size via velocity



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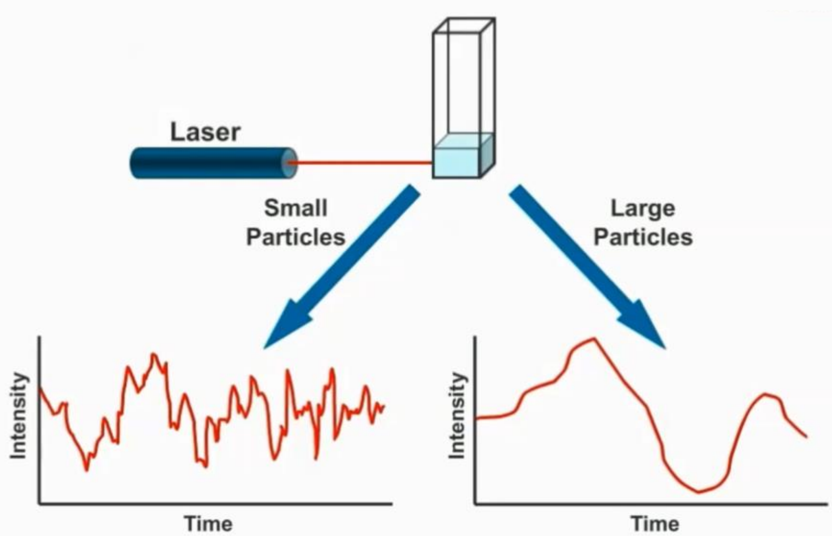
Fluctuation rate of intensity depends on particle size via velocity



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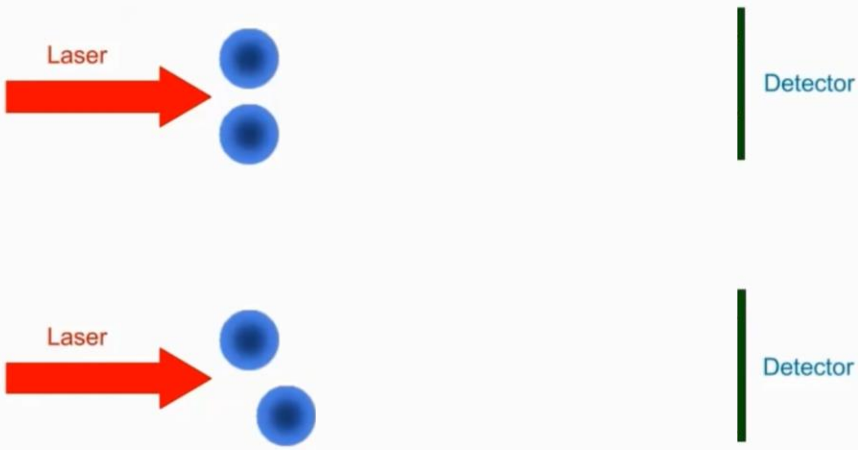
Constructive and Destructive Interference

Which scenario will produce destructive interference? Why?



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Constructive and Destructive Interference

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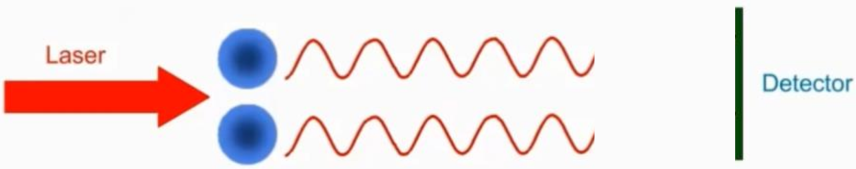
Constructive and Destructive Interference



*Photon scatter is isotropic

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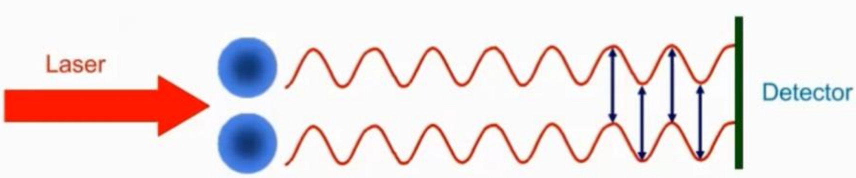
Constructive and Destructive Interference



Constructive Interference

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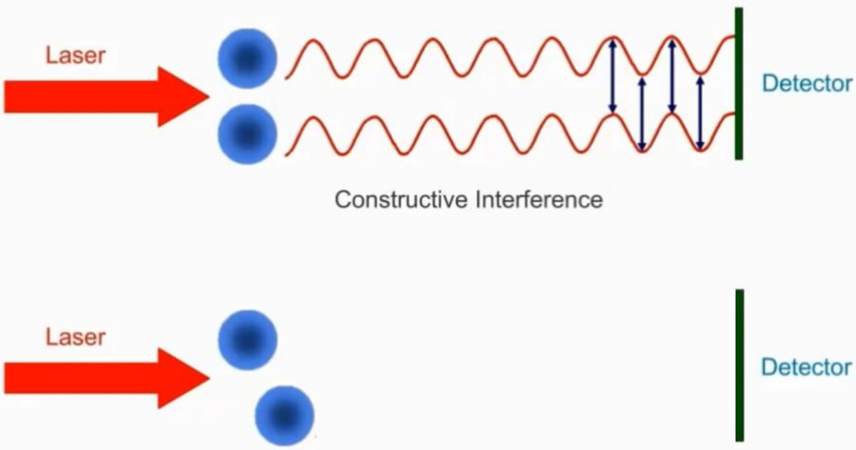
Constructive and Destructive Interference



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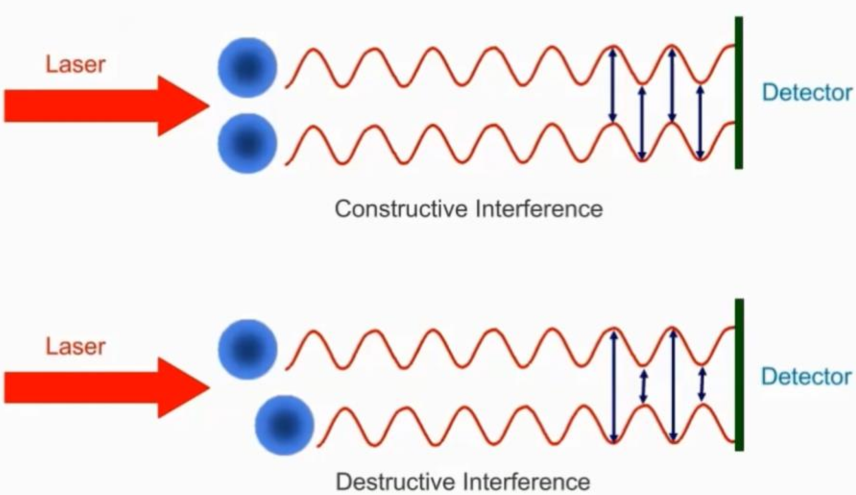
Constructive and Destructive Interference



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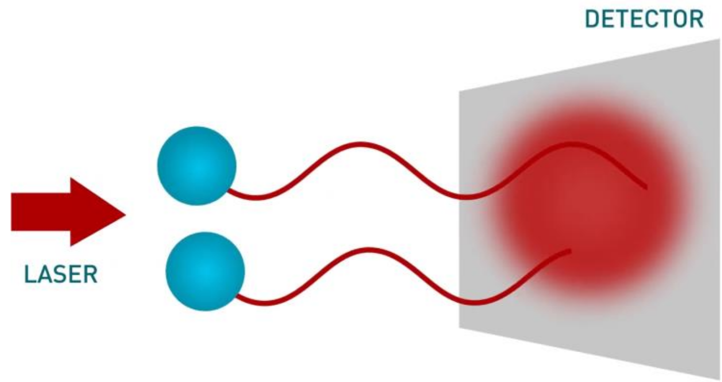
If particles are still, the intensity is fixed



27

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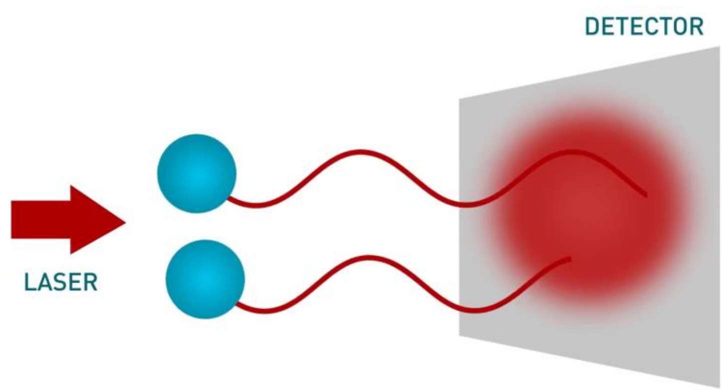

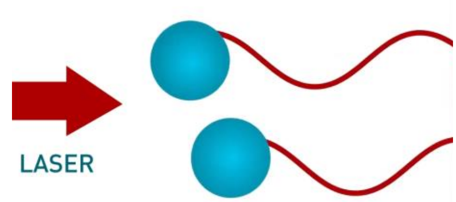

What happens to
signal in this case?

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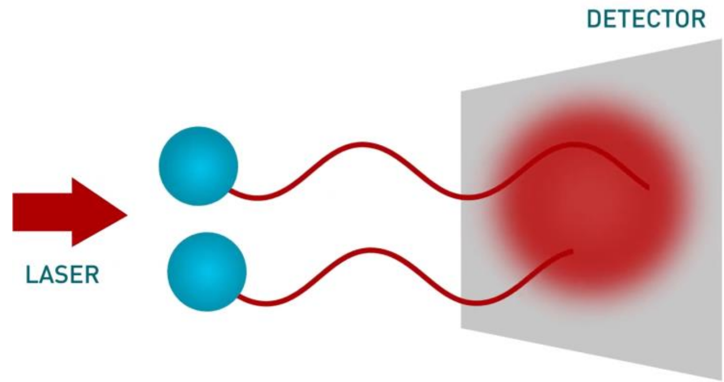
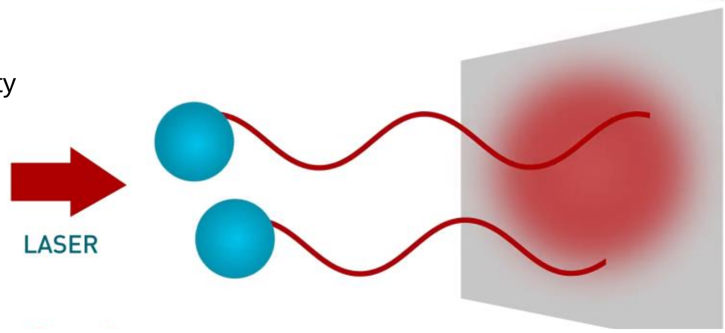
If particles are still, the intensity is fixed



In dispersion, particles move, and intensity fluctuates with time



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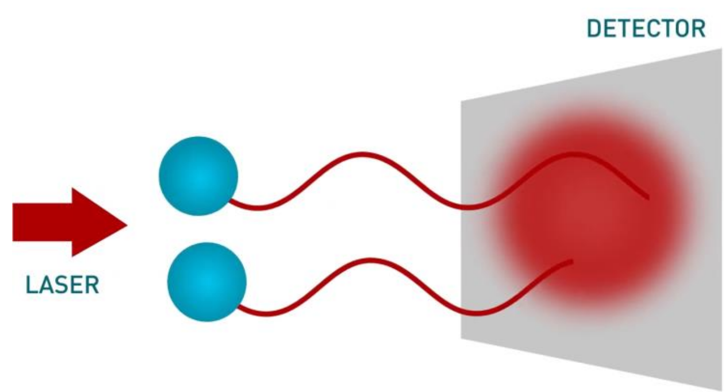
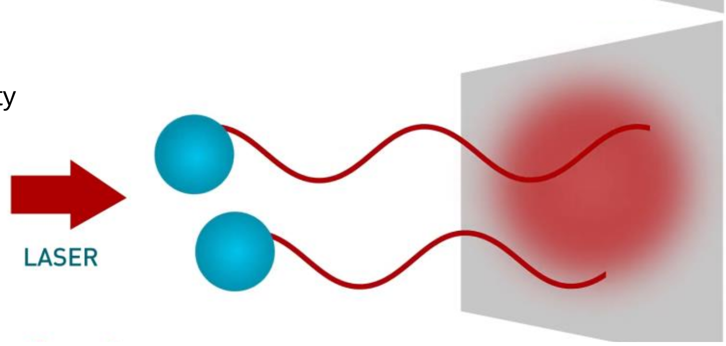


In dispersion, particles move, and intensity fluctuates with time

What is the qualitative relationship between particle size and intensity fluctuation rate?



Correlation in Dynamic Light Scattering

- Technique for extracting the time dependence of a signal in the presence of "noise"
- Time analysis carried out with a correlator
- Constructs the time autocorrelation function G(τ) of the scattered intensity according to

$$G(\tau) = \langle \frac{I(t_0) * I(t_0 + \tau)}{I(t_\infty)^2} \rangle$$

I = intensity
t = time
τ = delay time
t ∞ = seconds, practically

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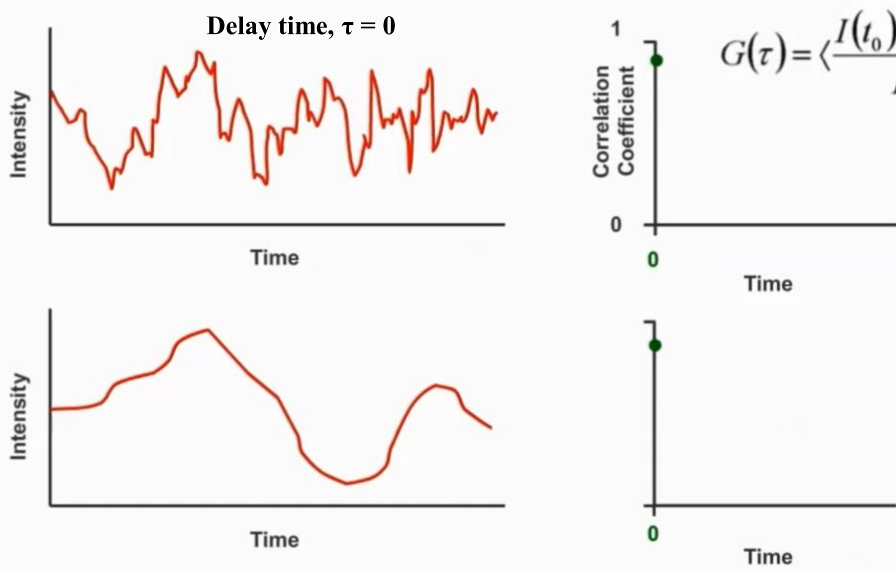
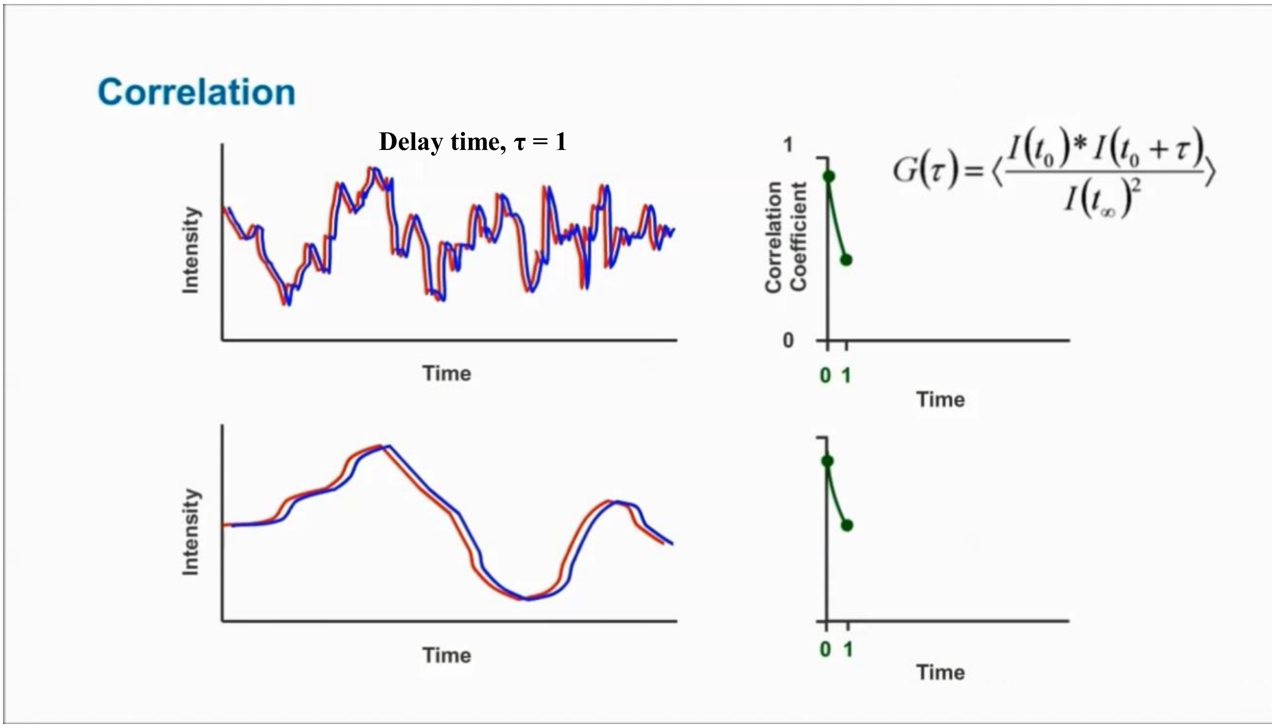
Correlation

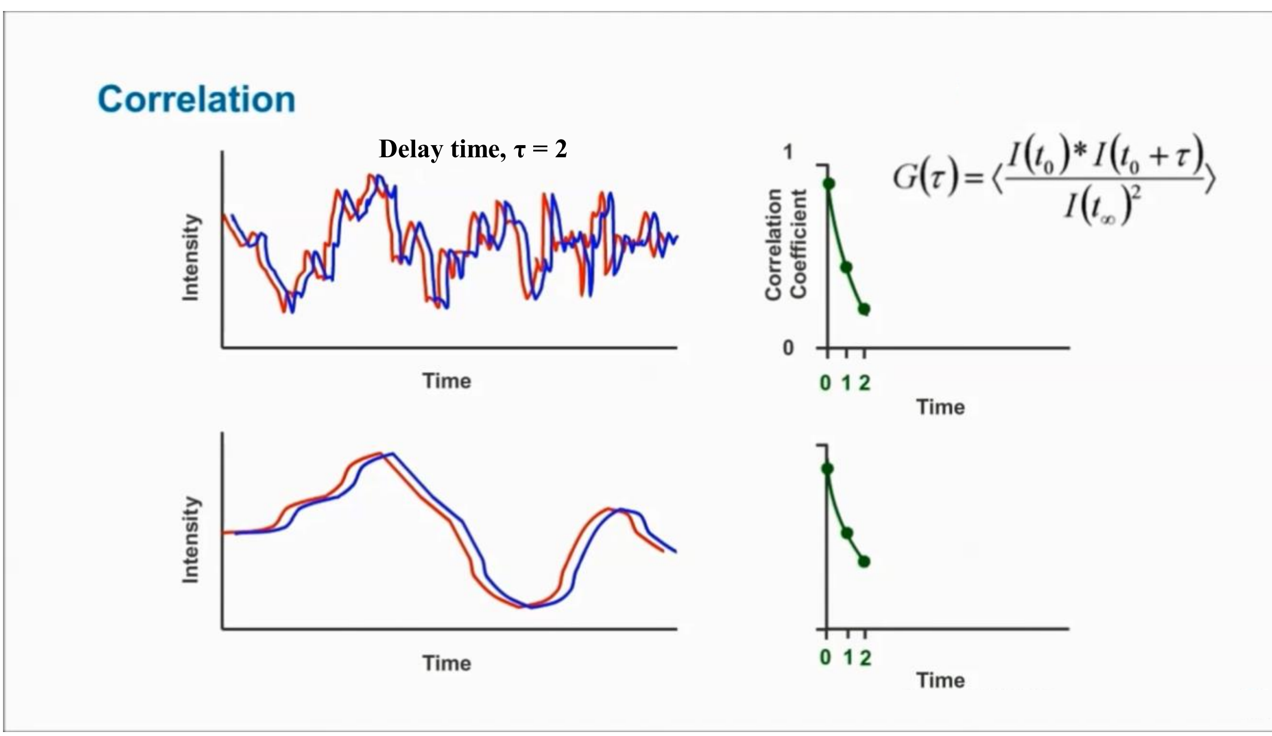


$$G(\tau) = \langle \frac{I(t_0) * I(t_0 + \tau)}{I(t_\infty)^2} \rangle$$

32


Correlation
Delay time, τ = 1
Intensity
Time
Intensity
Time
1
0
Correlation Coefficient
0 1
Time
0 1
Time
$G(\tau) = \langle \frac{I(t_0) * I(t_0 + \tau)}{I(t_\infty)^2} \rangle$

33


Correlation
Delay time, τ = 2
Intensity
Time
Intensity
Time
1
0
Correlation Coefficient
0 1 2
Time
0 1 2
Time
$G(\tau) = \langle \frac{I(t_0) * I(t_0 + \tau)}{I(t_\infty)^2} \rangle$

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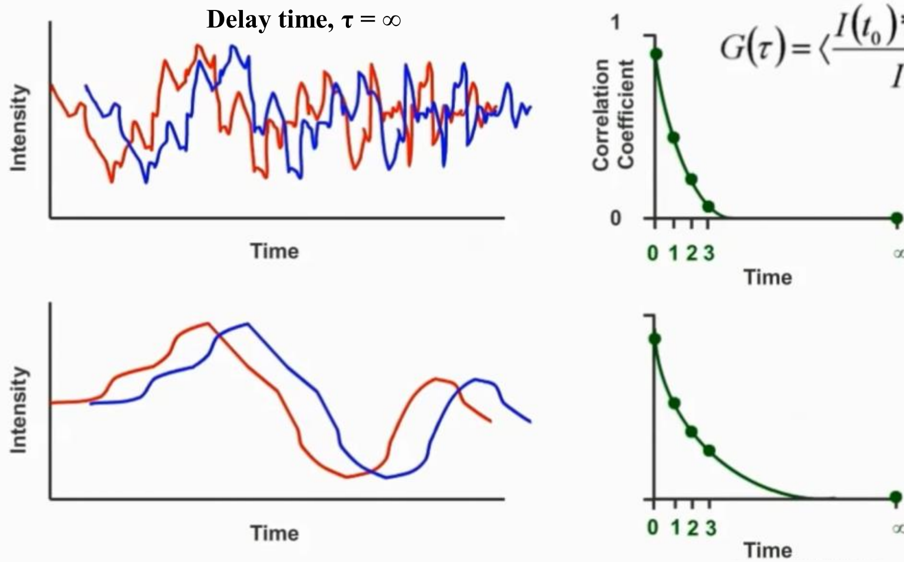
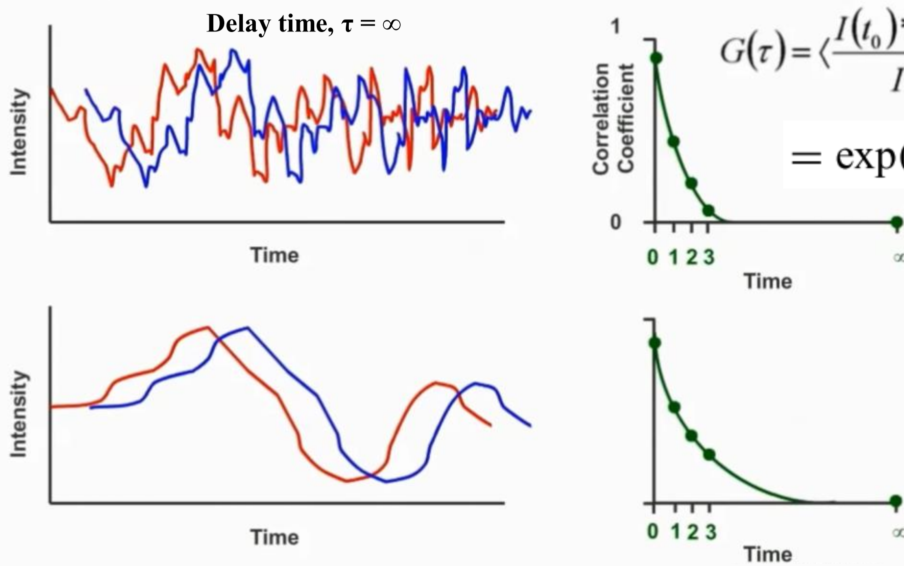
Correlation



$$G(\tau) = \langle \frac{I(t_0) * I(t_0 + \tau)}{I(t_\infty)^2} \rangle$$

35

Correlation



$$G(\tau) = \langle \frac{I(t_0) * I(t_0 + \tau)}{I(t_\infty)^2} \rangle$$

$$= \exp(-q^2 D t)$$

q = Scattering vector length

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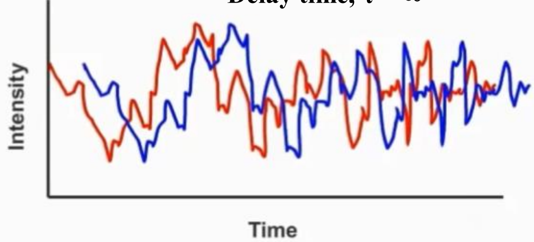
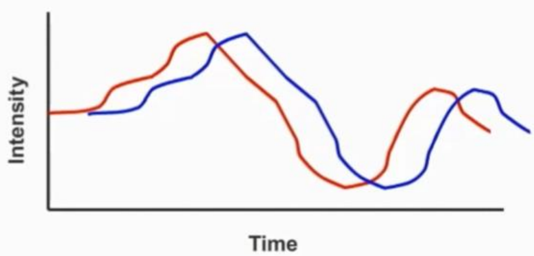
Correlation

Delay time, $\tau = \infty$

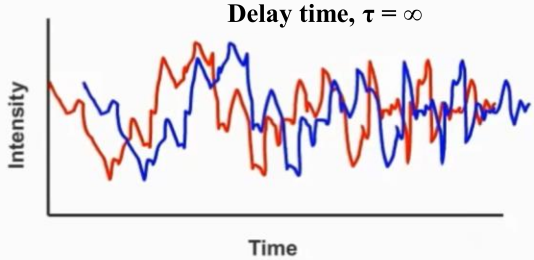


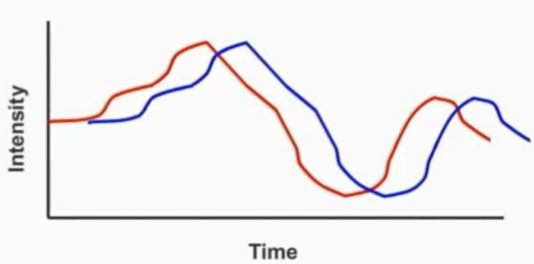


Re-plotted on semi-log scale on x-axis

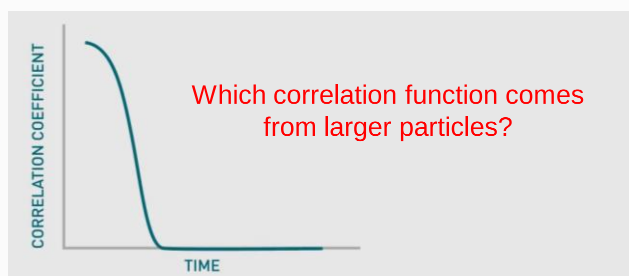
Correlation

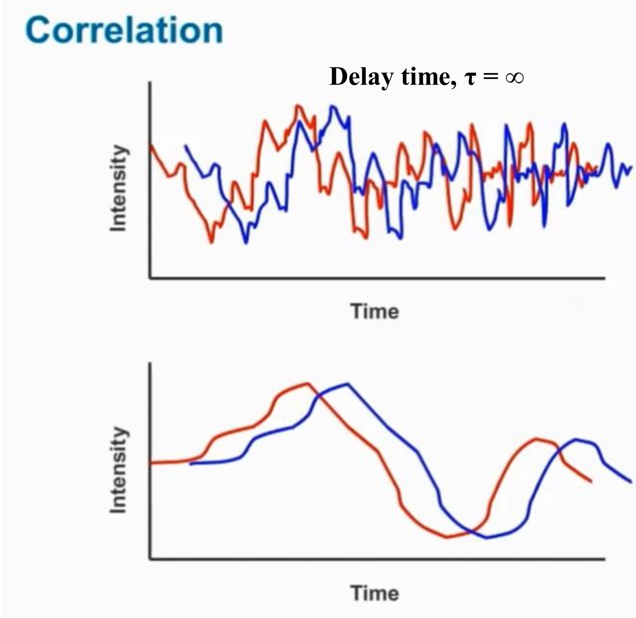
Delay time, $\tau = \infty$



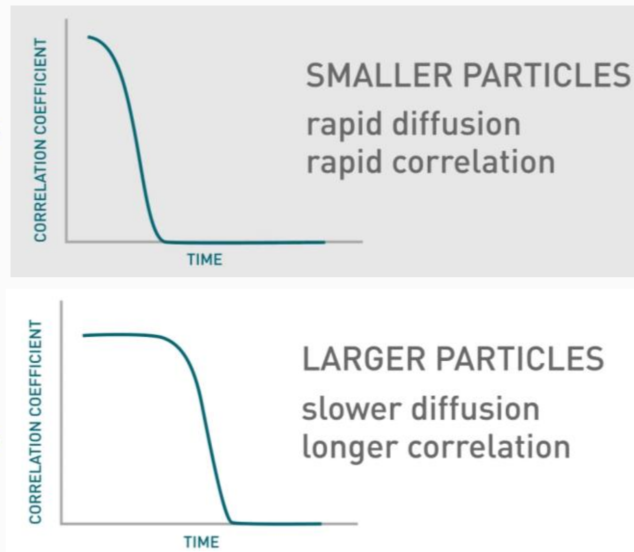


Re-plotted on semi-log scale on x axis





Re-plotted on semi-log scale on x axis



Lecture outline

- Ceramic characterization
  - Dynamic light scattering (DLS)
  - Scanning electron microscopy (SEM)

Why use electrons for microscopy?

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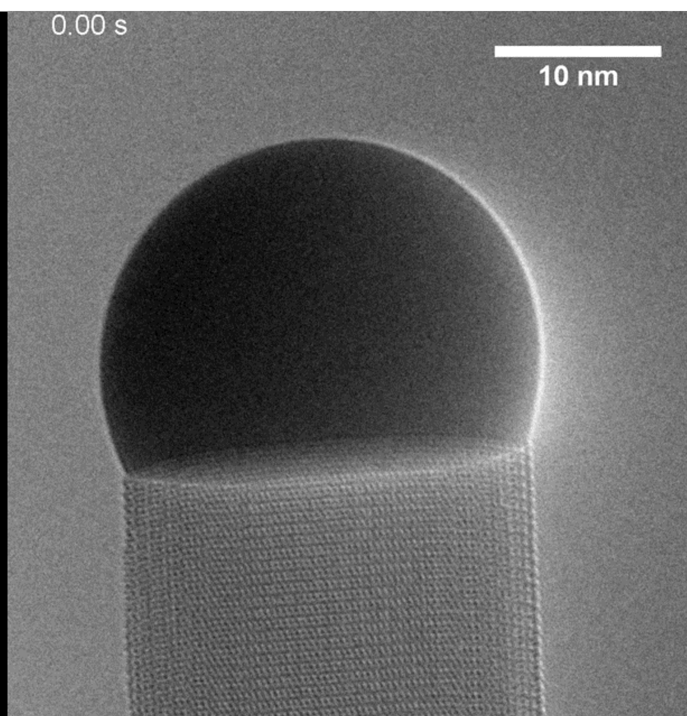

GaAs nanowire
CNRS France, *Phys. Rev. Lett.* (2019)

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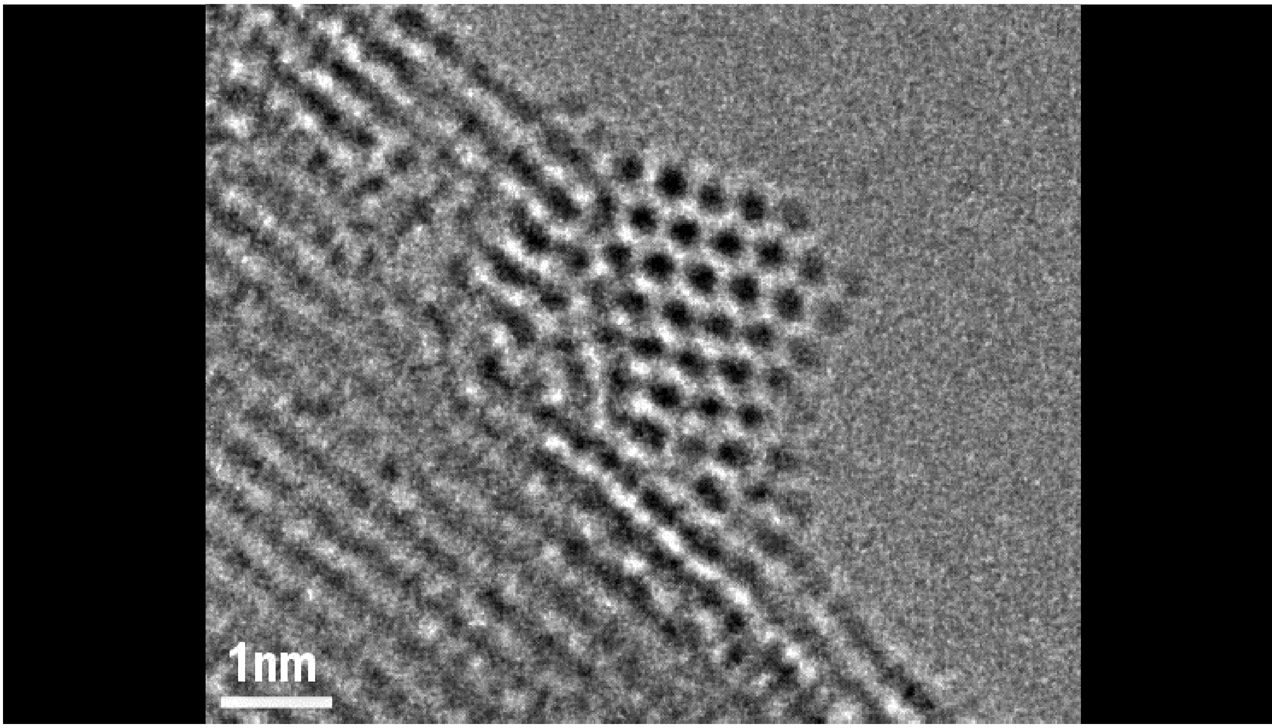
1nm

43


nature
ATOM-BY-ATOM ANALYSIS
Elements mapped by annular
dark-field electron microscopy
Krivanek *et al. Nature* (2010)

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Scanning electron microscopy

http://toutestquantique.fr/en/scanning-electron/

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Scanning electron microscopy

Similar to transmission electron microscopy (TEM)
Similar to scanning TEM (STEM)

http://toutestquantique.fr/en/scanning-electron/

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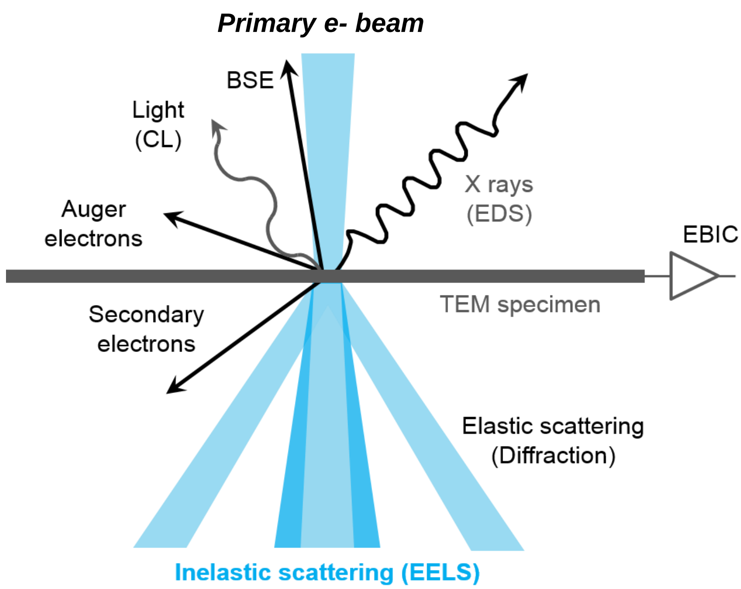
Many characteristic signals are generated during irradiation



Gatan.com

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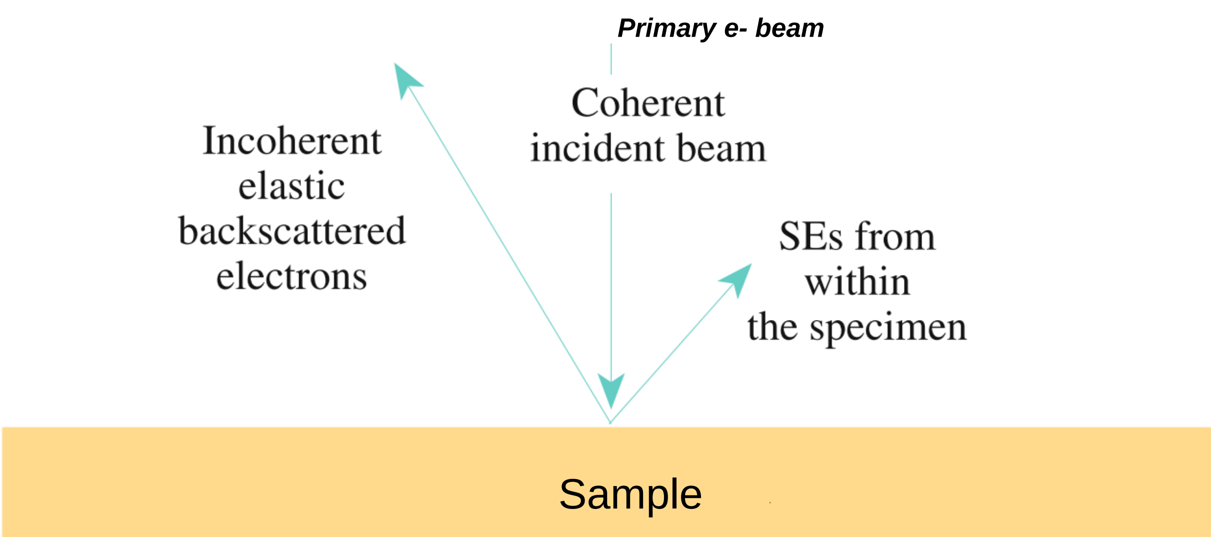
Many signals are generated during electron beam irradiation



D.B. Williams & C.B. Carter, *Springer* (2008)

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Scanning Electron Microscope

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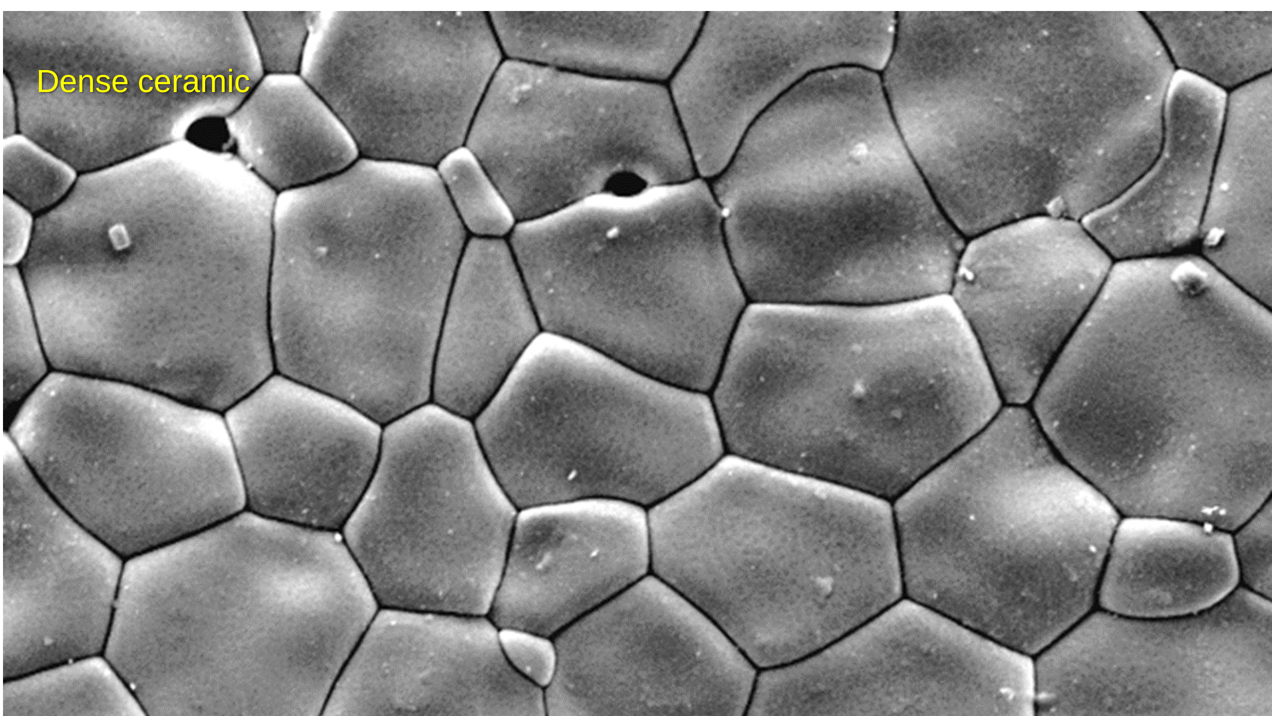

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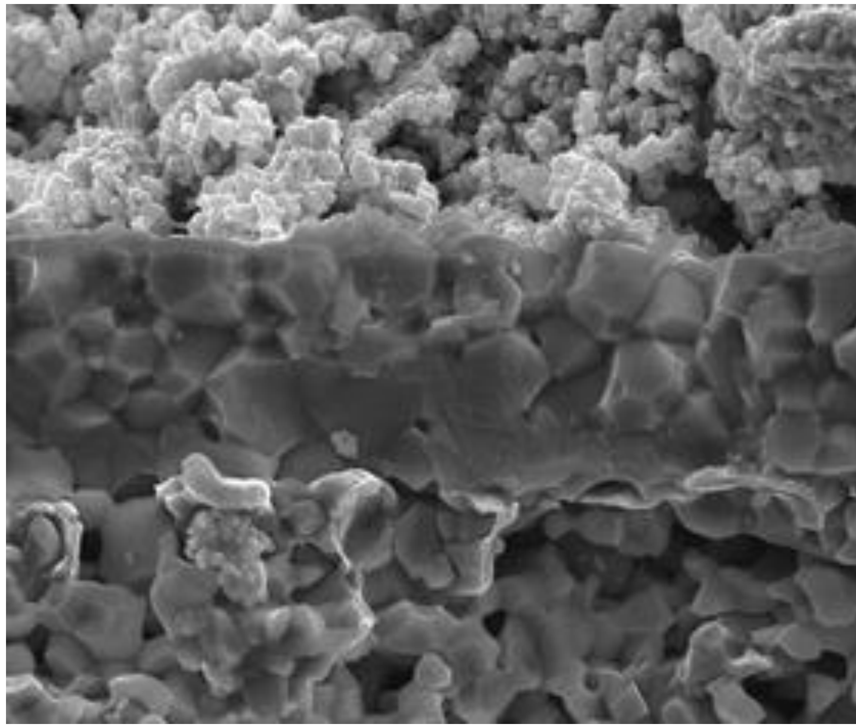
Cathode
Porous perovskite oxide

Electrolyte
Dense fluorite oxide

Anode
Porous ceramic-metal composite

C. Ding *et al.*,
Energy Environ. Sci., (2010)



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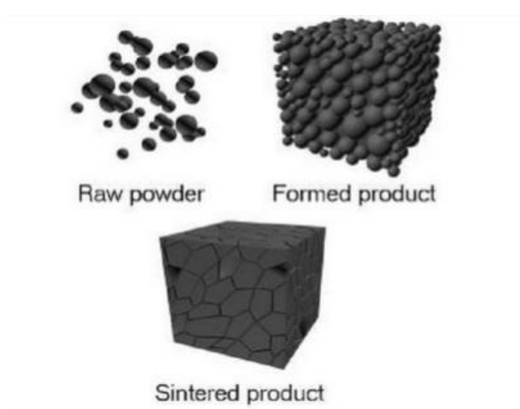
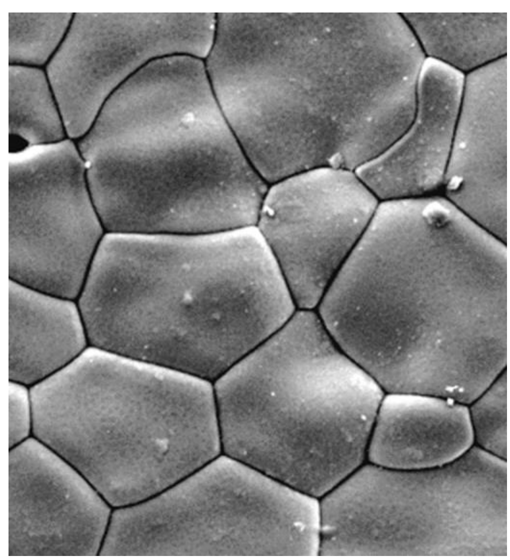
Powder processing – Sintering





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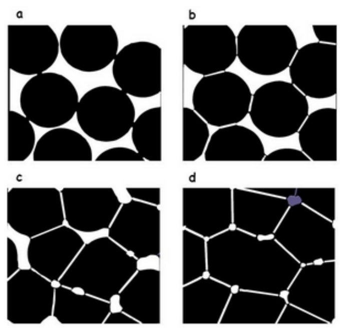
Sintering – Overview

Sintering is the process of transforming a powder into a solid body using heat.

The most important process in **making bulk dense and porous ceramics**, but also needed for **powder metallurgy**.



a) Green body, loose powder
b) Initial stage: increase of the interparticle contact area from 0 to 0.2 grain diameter, increase of the density from 60 to 65%
c) Intermediate stage: further increase of the contact area, stage characterized by continous pore channels along three grain edges, increase of the density from 65 to 90%.
d) Elimination of the pore channel along three grain edges, increase of the density to 95 - 99%

What are the features of the sintered microstructure?

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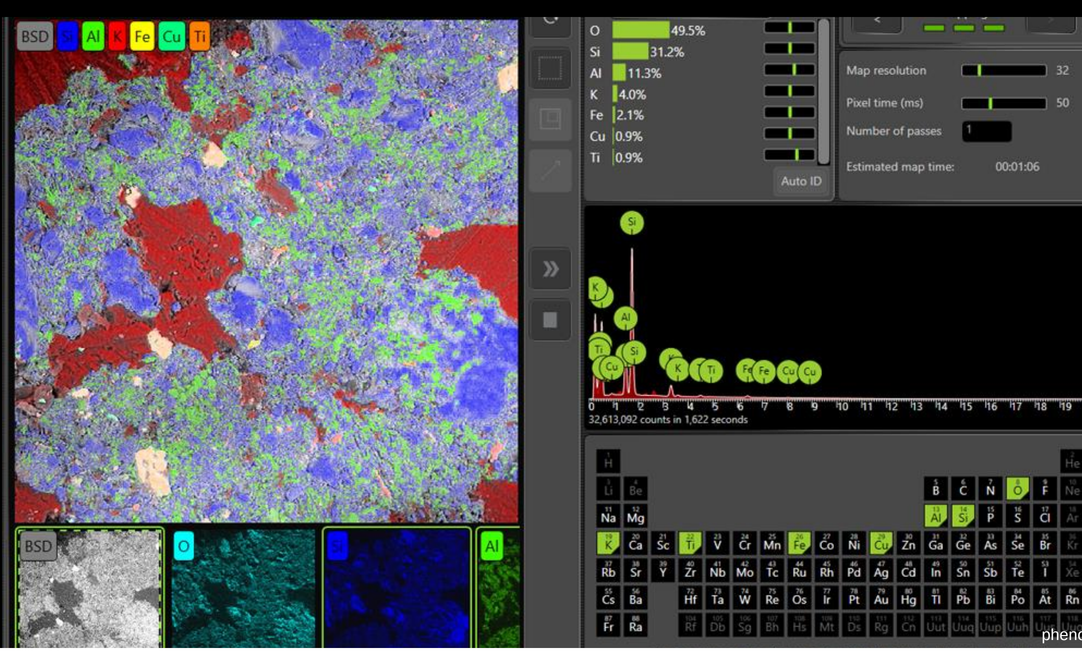
Imaging structure is useful, but ***spectroscopy*** tells us more…



phenom-world.com

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There are many microscopes at UCI

JEOL JEM-ARM300F Grand ARM

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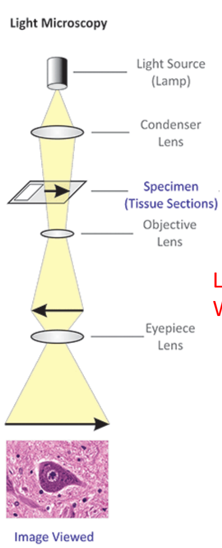
Visible light is the most common microscopy



Lenses (de)magnify beams.
What lenses did you bring to this lecture?

microbiologyinfo.com

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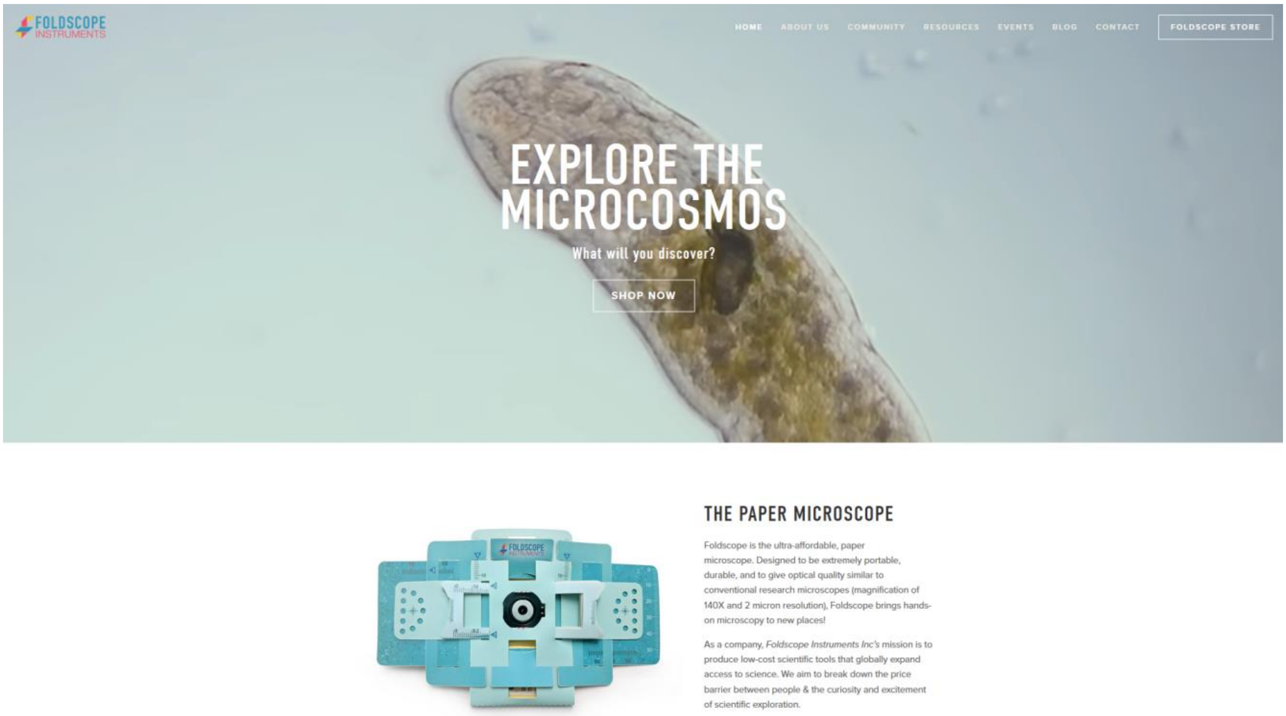

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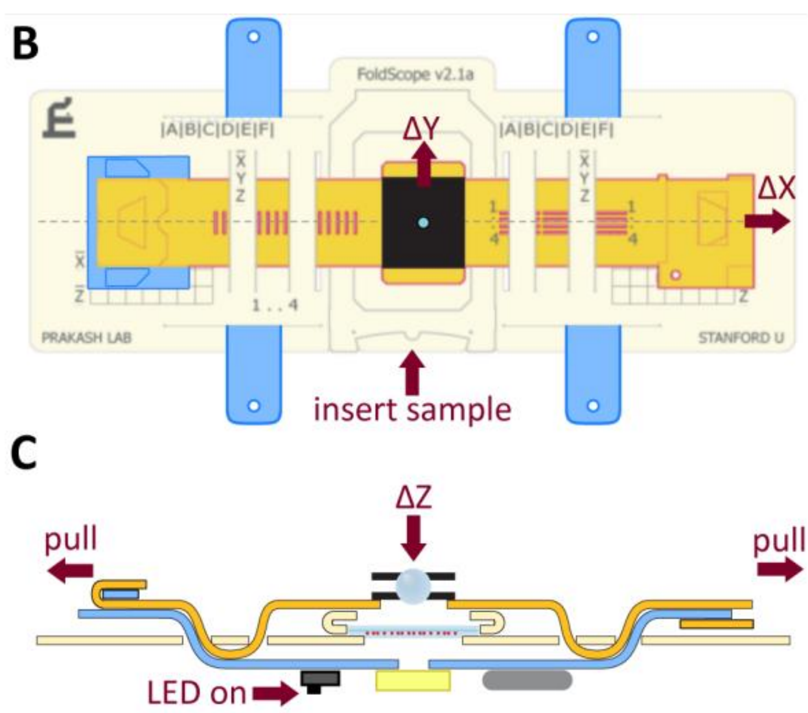

J.S. Cybulski … Manu Prakash, *PLOS One* (2014)

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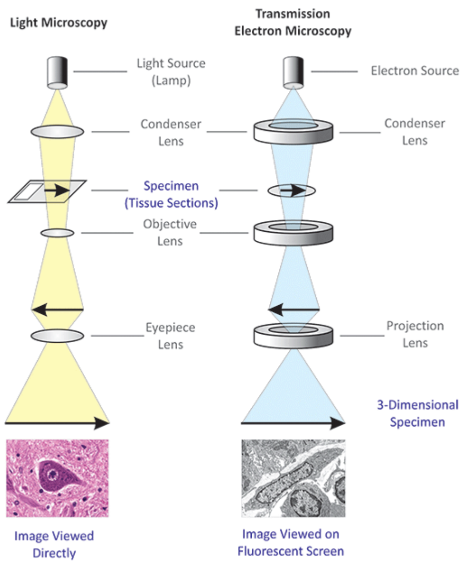
Electron microscopy is analogous to visible-light microscopy, but with higher ***resolution***



microbiologyinfo.com

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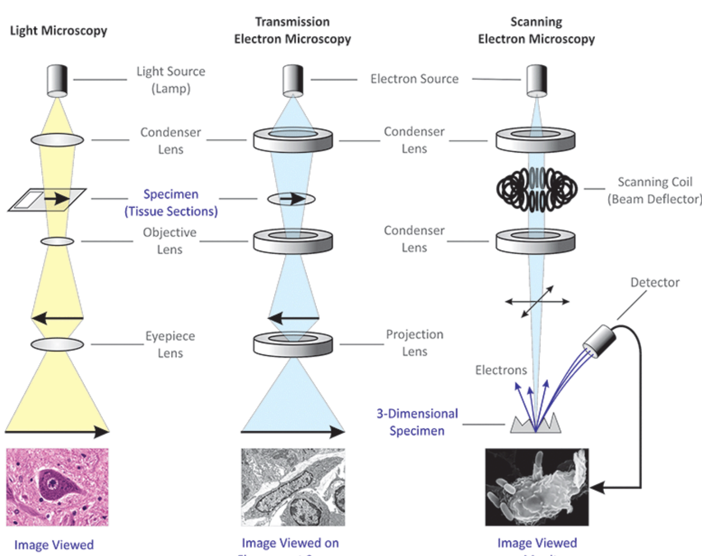
Electron microscopy is analogous to visible-light microscopy, but with higher ***resolution***



microbiologyinfo.com

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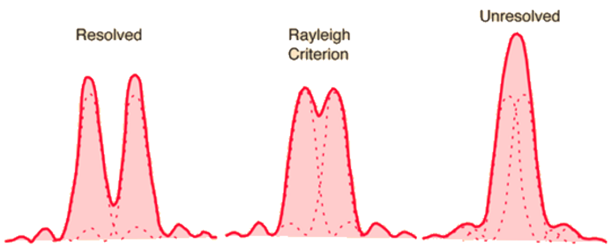
Resolution is the smallest distance that can be resolved



hyperphysics.com

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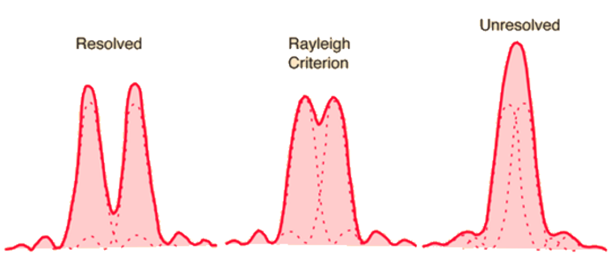

Resolution → δ; Wavelength → λ

$$\delta = \frac{0.61\,\lambda}{\mu\, sin\beta} \approx \frac{0.61\,\lambda}{1}$$

Refractive index of viewing medium → μ; Semi-angle of collection of magnifying lens → β

"Numerical aperture"

hyperphysics.com

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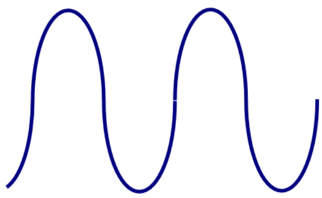
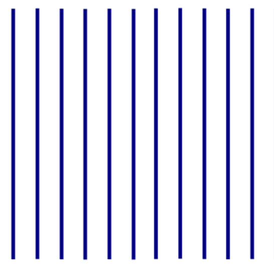
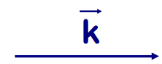
Wave number k is a vector that captures wave direction and wavelength



This is our plane wave …



Here we show it propagating, with the lines being the location of e.g. the peaks of the wave …



This is thus an equivalent representation of the wave …

Eric Stach "Elastic Scattering" *nanohub.org* (2008)

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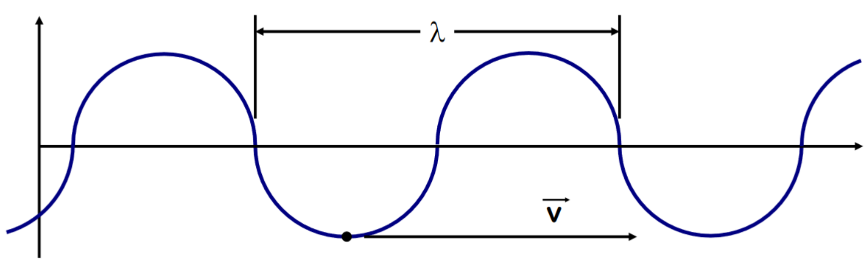
A wave is a periodic disturbance in both space and time



- **Wavelength (λ), velocity (v), frequency (ƒ):** $v = f\lambda$
- **Wave number (k):** $k = 1/\lambda$ *
- **Angular frequency (ω):** $\omega = f\,k$

* Sometimes written as: $k = 2\pi/\lambda$

Eric Stach "Elastic Scattering" *nanohub.org* (2008)

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Electron wavelength is inversely proportional to accelerating voltage

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

$$eV = \frac{m_0 v^2}{2}$$

$$p = m_0 v = (2 m_0 e V)^{1/2}$$

$$\lambda = \frac{h}{(2 m_0 e V)^{1/2}}$$

$$\lambda = \frac{h}{\left[2 m_0 e V\left(1 + \frac{eV}{2 m_0 c^2}\right)\right]^{1/2}}$$

TABLE 1.1 Fundamental Constants and Definitions

Charge (e)	(–) 1.602×10^{-19} C
1 eV	1.602×10^{-19} J
Rest mass (m_0)	9.109×10^{-31} kg
Rest energy (m_0c^2)	511 keV
Kinetic energy (charge × voltage)	1.602×10^{-19} N m (for 1 volt potential) = J
Planck's constant (h)	6.626×10^{-34} N m s
1 A	1 C/s
Speed of light in vacuum (c)	2.998×10^{8} m/s

TABLE 1.2 Electron Properties as a Function of Accelerating Voltage

Accelerating voltage (kV)	Non-relativistic wavelength (nm)	Relativistic wavelength (nm)	Mass (× m_0)	Velocity (× 10^8 m/s)
100	0.00386	0.00370	1.196	1.644
120	0.00352	0.00335	1.235	1.759
200	0.00273	0.00251	1.391	2.086
300	0.00223	0.00197	1.587	2.330
400	0.00193	0.00164	1.783	2.484
1000	0.00122	0.00087	2.957	2.823

D.B. Williams & C.B. Carter, *Springer* (2008)

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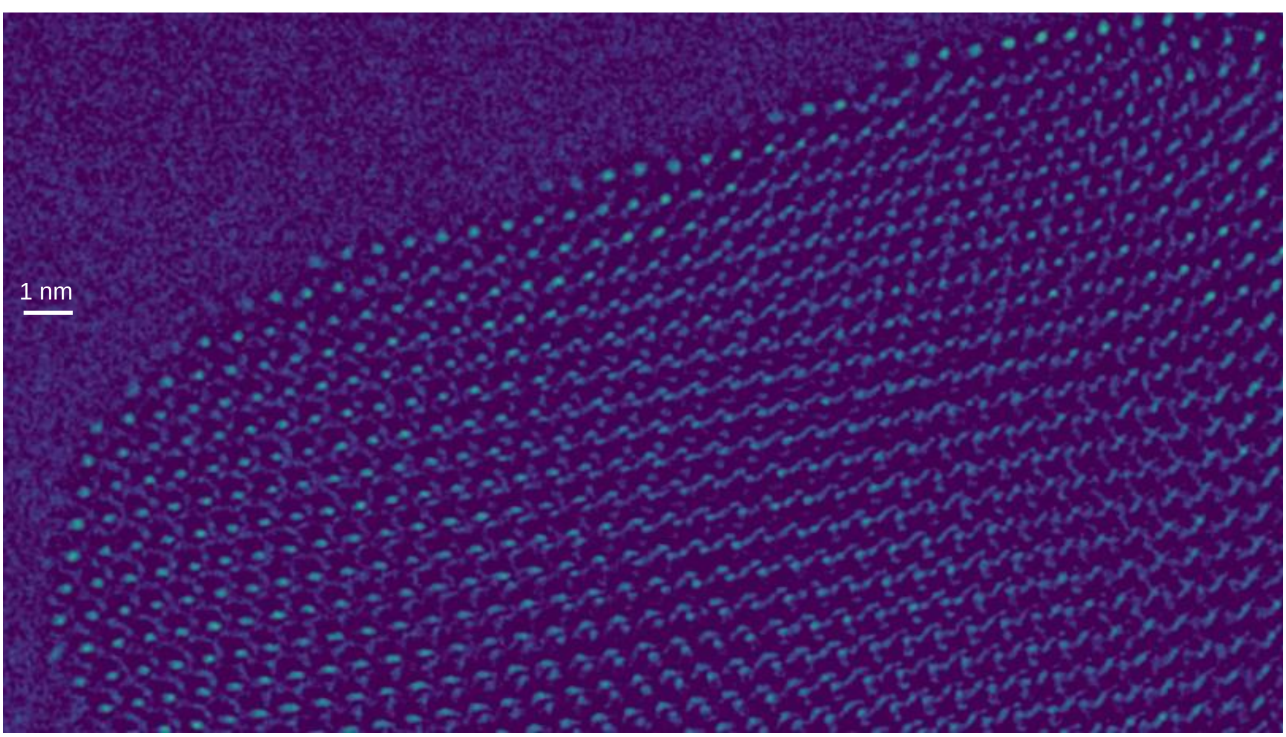

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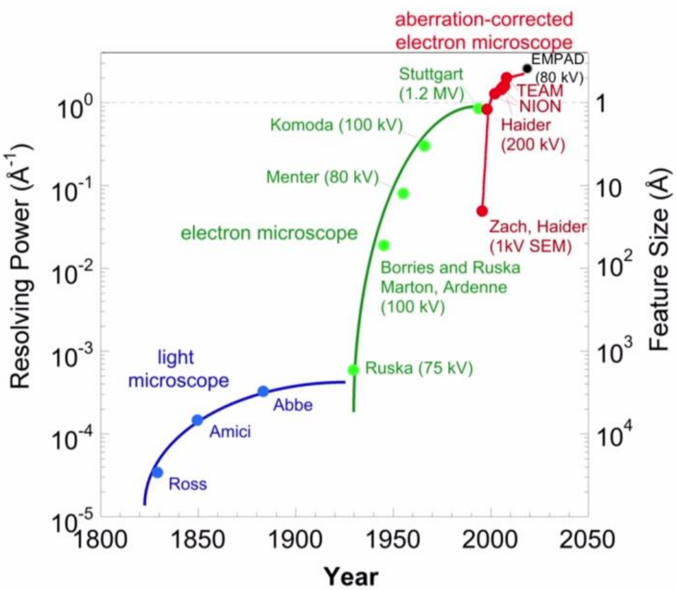
Resolution in Microscopes



Muller, DA et al. *Nature Materials*, **8**(2009)

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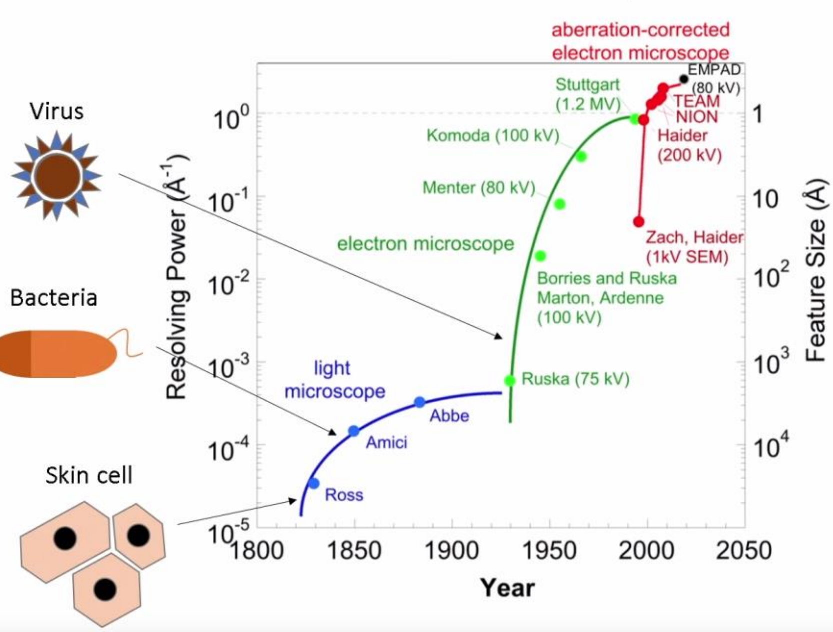
Resolution in Microscopes



Muller, DA et al. *Nature Materials*, **8**(2009)

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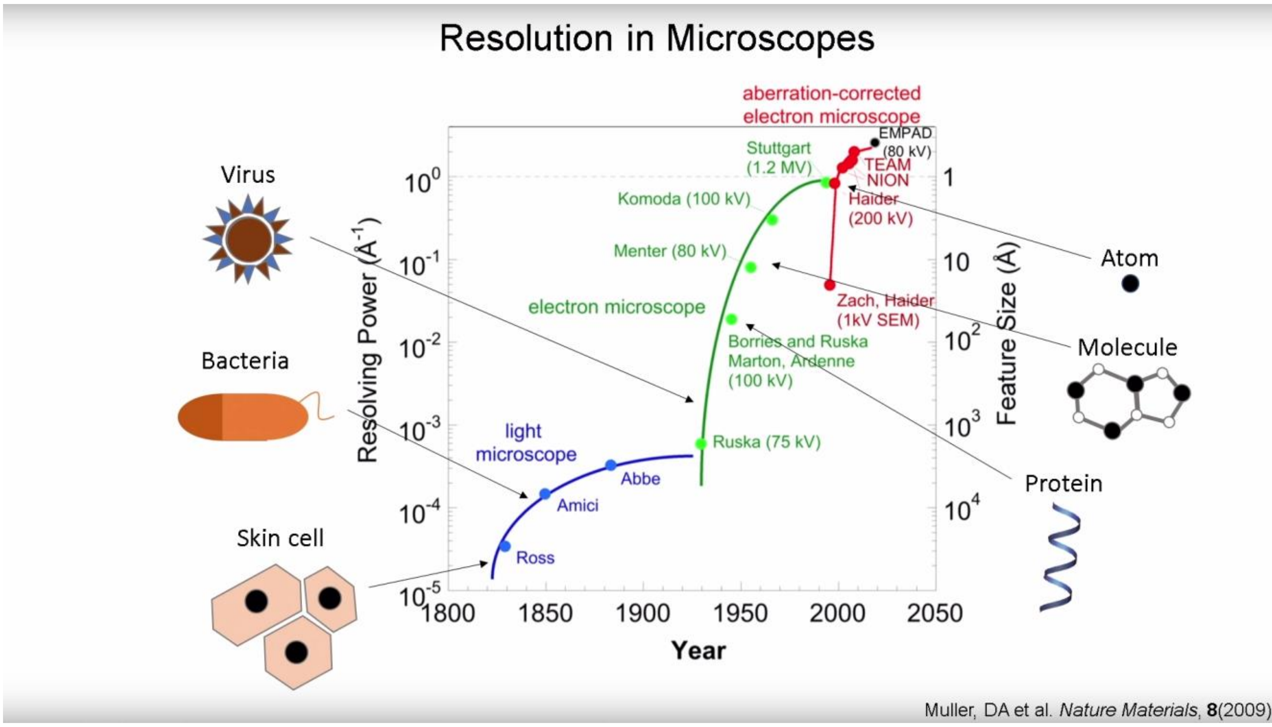
Resolution in Microscopes
aberration-corrected
electron microscope
EMPAD
(80 kV)
Stuttgart
(1.2 MV)
TEAM
NION
Haider
(200 kV)
Komoda (100 kV)
Menter (80 kV)
electron microscope
Zach, Haider
(1kV SEM)
Borries and Ruska
Marton, Ardenne
(100 kV)
Ruska (75 kV)
light
microscope
Abbe
Amici
Ross
Virus
Bacteria
Skin cell
Atom
Molecule
Protein
Resolving Power (Å-1)
Feature Size (Å)
Year
1800
1850
1900
1950
2000
2050
Muller, DA et al. Nature Materials, 8(2009)

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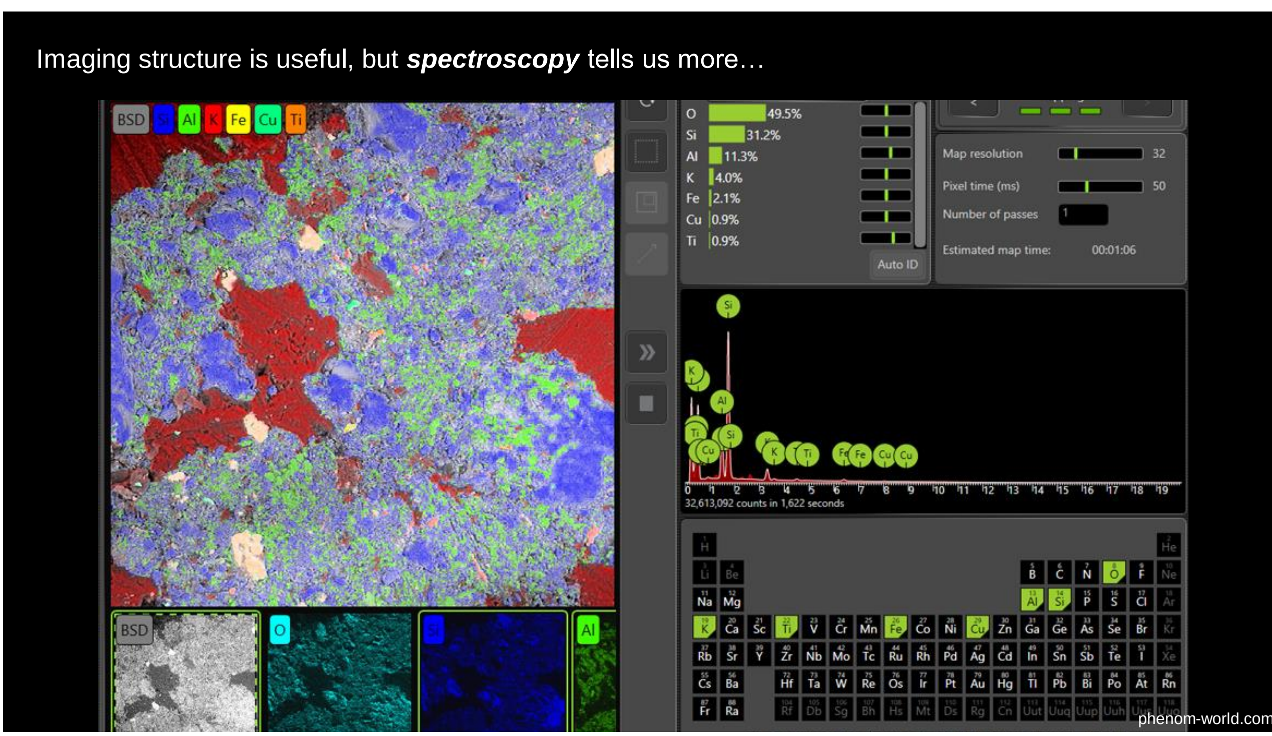
Imaging structure is useful, but ***spectroscopy*** tells us more…
BSD
Al
K
Fe
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Ti
O
Si
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49.5%
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Number of passes
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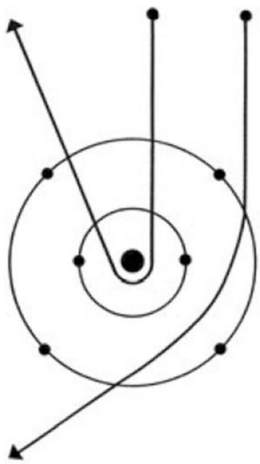
32,613,092 counts in 1,622 seconds
phenom-world.com

70

Beam-solid interactions produce characteristic chemical signals

Elastic scattering: ~0 energy trans
e.g. ‘backscattering’



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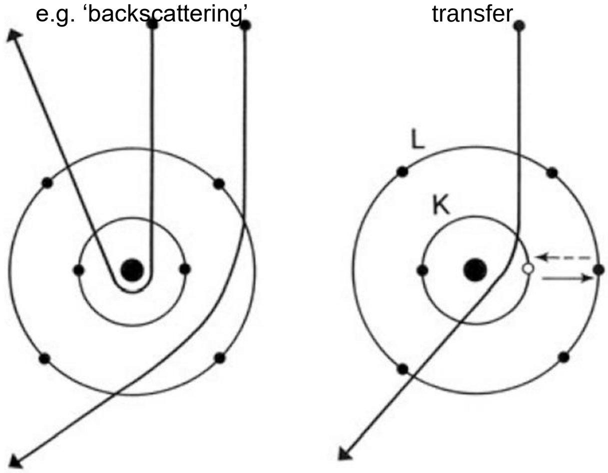
Beam-solid interactions produce characteristic chemical signals

Elastic scattering: ~0 energy transfer,
e.g. ‘backscattering’

inelastic scattering from core level: >0 energy transfer



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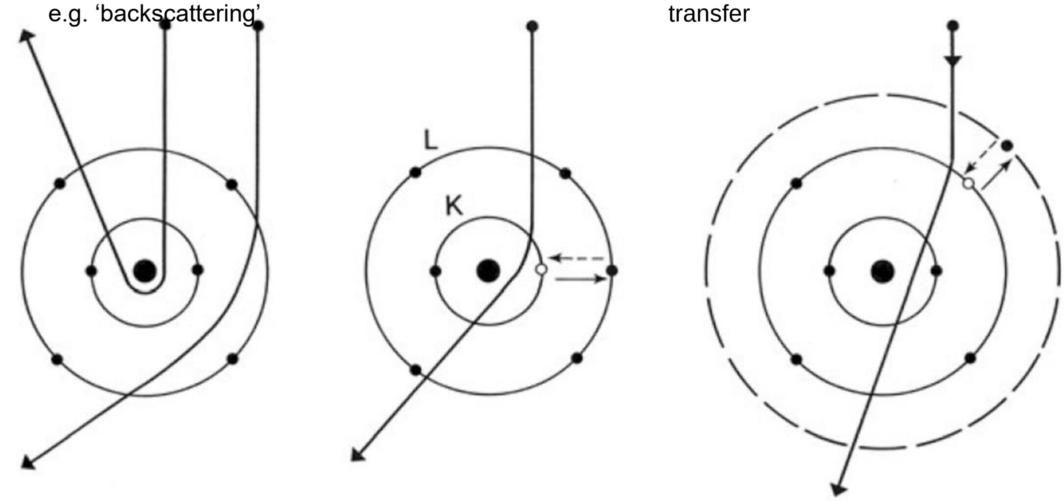
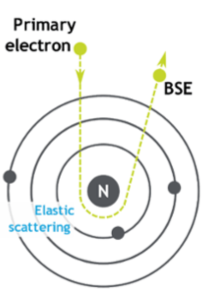
Beam-solid interactions produce characteristic chemical signals

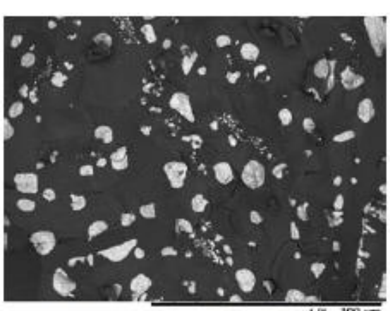
Elastic scattering: ~0 energy transfer, e.g. 'backscattering'

inelastic scattering from core level: >0 energy transfer



73





(a) Backscattered electron image

azom.com; hitachi-hightech.com

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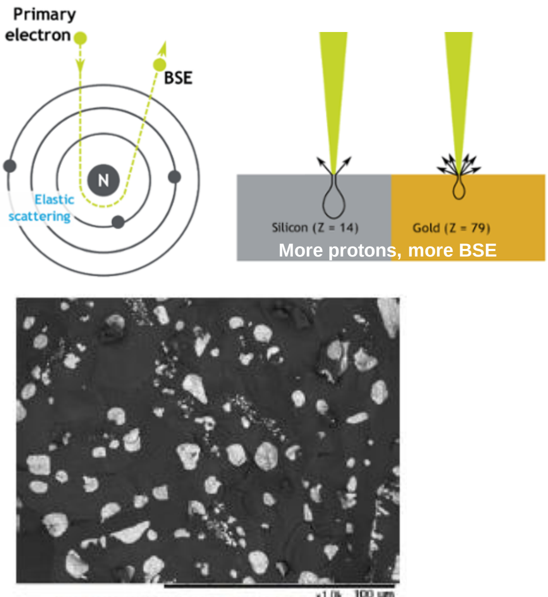
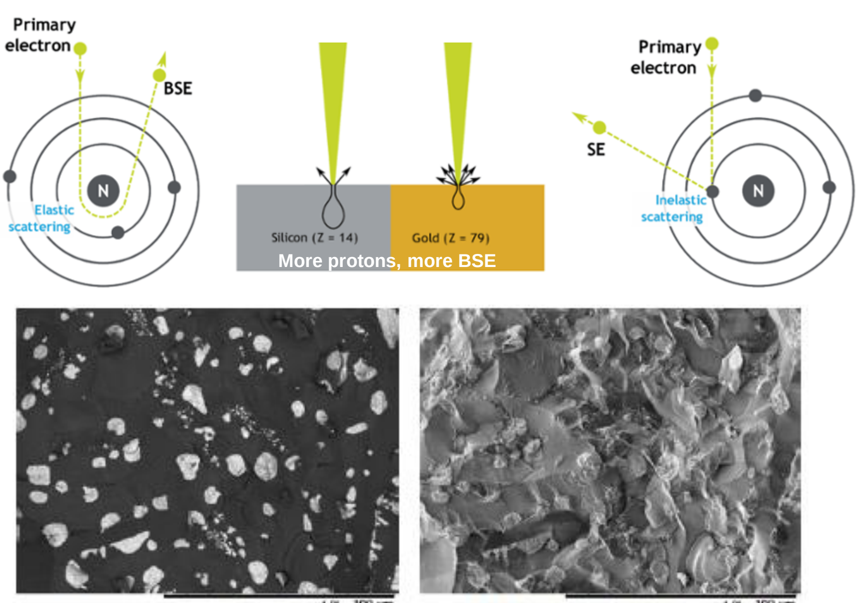


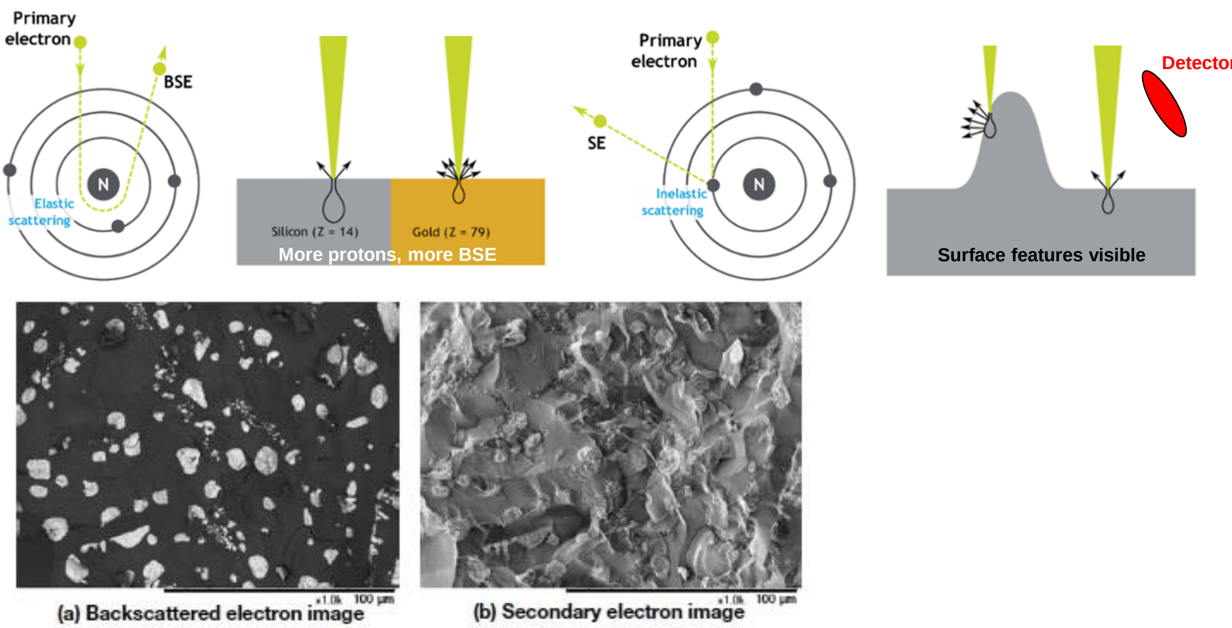
(a) Backscattered electron image

azom.com; hitachi-hightech.com

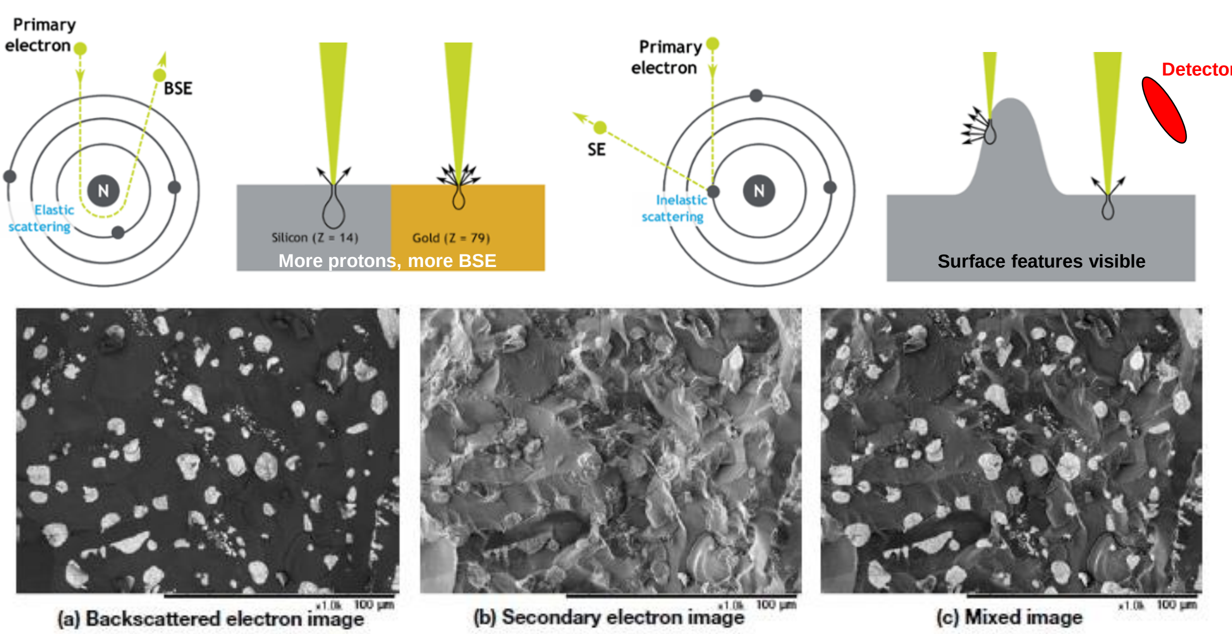


(a) Backscattered electron image (b) Secondary electron image

azom.com; hitachi-hightech.com

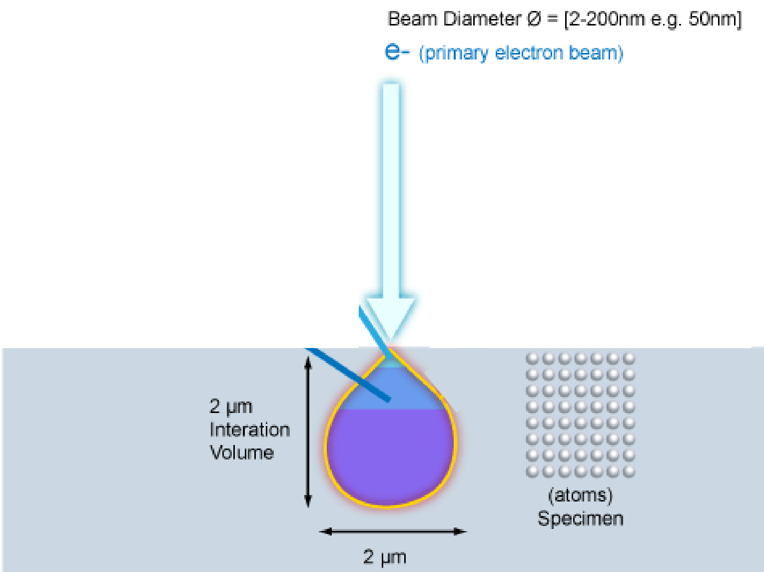


azom.com; hitachi-hightech.com



azom.com; hitachi-hightech.com

The spatial resolution is defined by the “interaction volume” between probe and specimen



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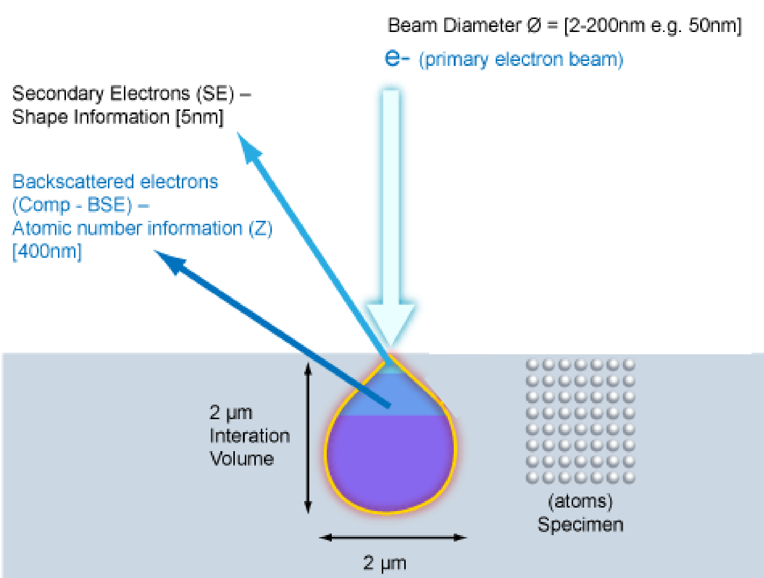
The spatial resolution is defined by the “interaction volume” between probe and specimen



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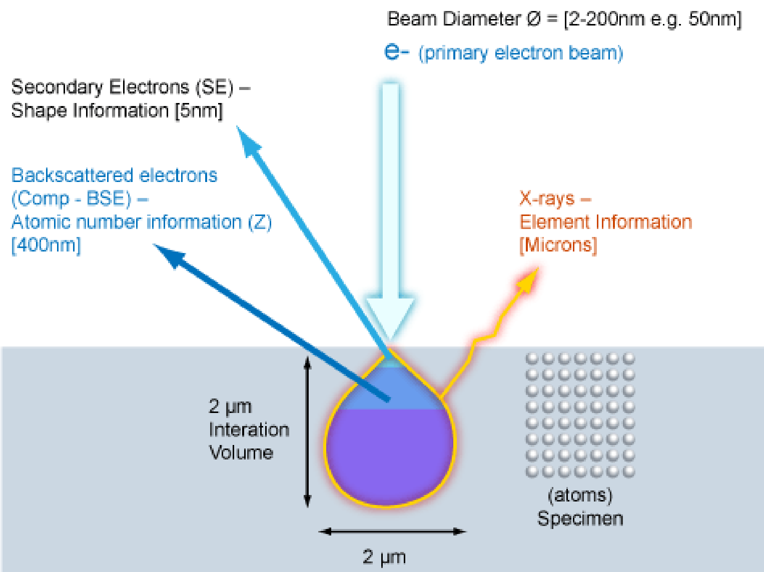
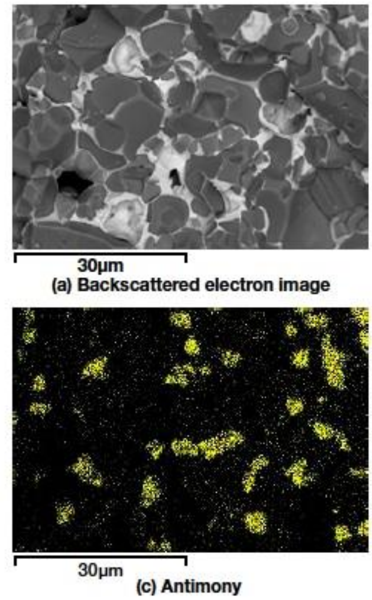
The spatial resolution is defined by the “interaction volume” between probe and specimen





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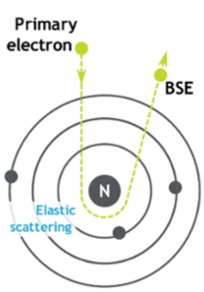
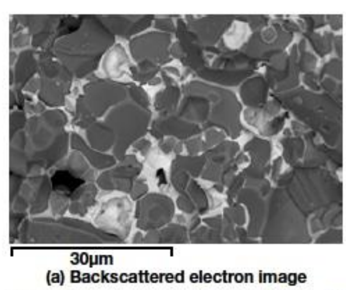
The primary beam undergoes elastic and inelastic scattering, the latter enables various ***spectroscopies***





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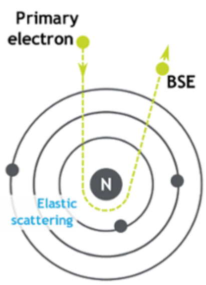
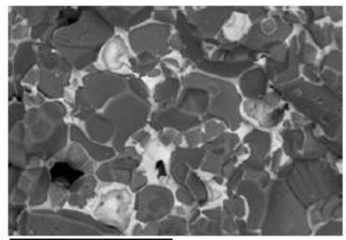
BowmanLab
UC IRVINE

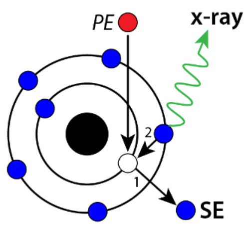
The primary beam undergoes elastic and inelastic scattering, the latter enables various ***spectroscopies***



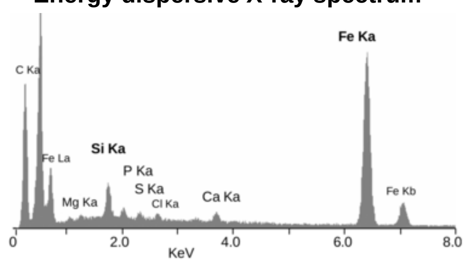


30µm
(a) Backscattered electron image

Inelastic scattering



Energy dispersive X-ray spectrum



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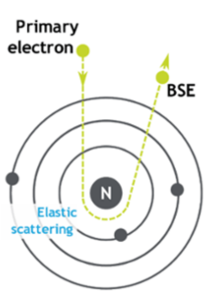
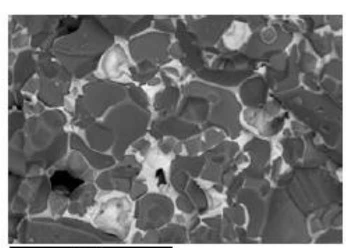
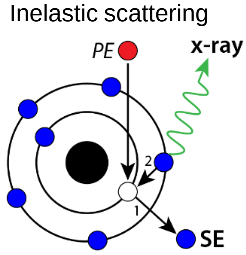
The primary beam undergoes elastic and inelastic scattering, the latter enables various ***spectroscopies***

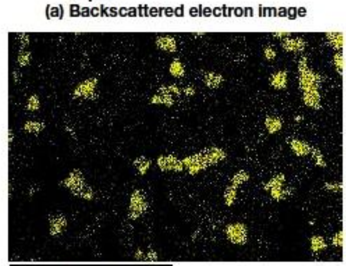




30µm
(a) Backscattered electron image

Inelastic scattering





30µm
(c) Antimony

energy dispersive x-ray spectroscopy (EDX)

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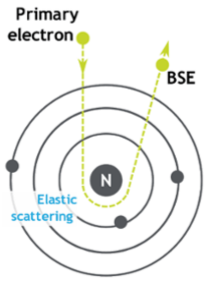
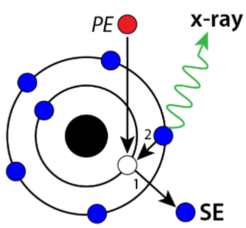
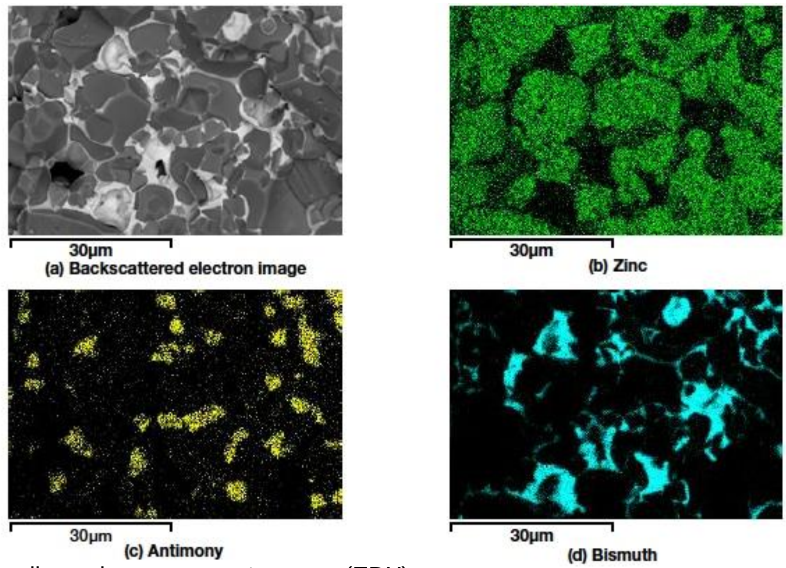
Energy dispersive x-ray spectroscopy is a common method for elemental mapping



Inelastic scattering





energy dispersive x-ray spectroscopy (EDX)

azom.com; hitachi-hightech.com

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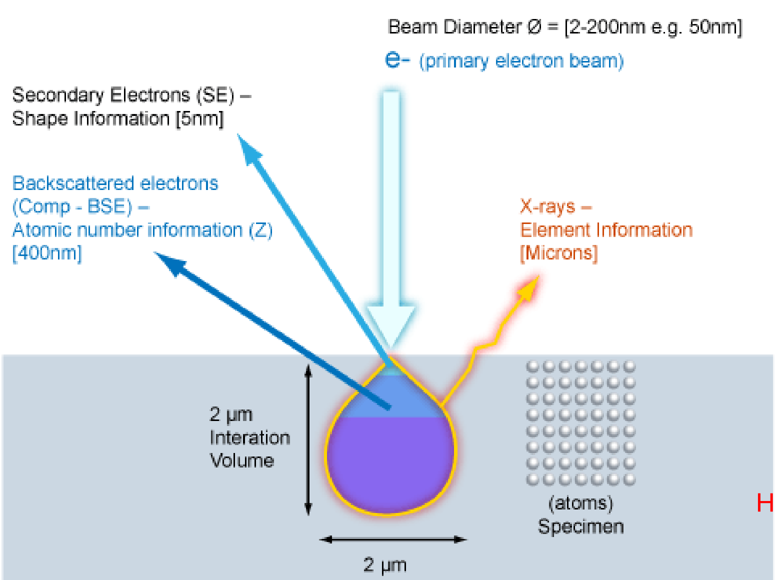
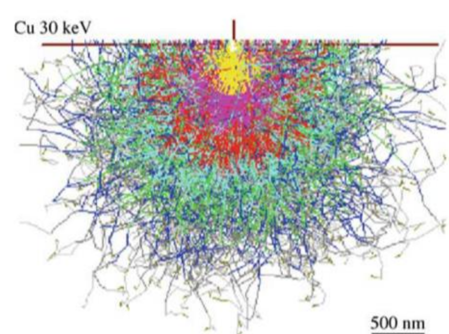
The spatial resolution is defined by the “interaction volume” between probe and specimen





How can the interaction volume be reduced to improve spatial resolution?

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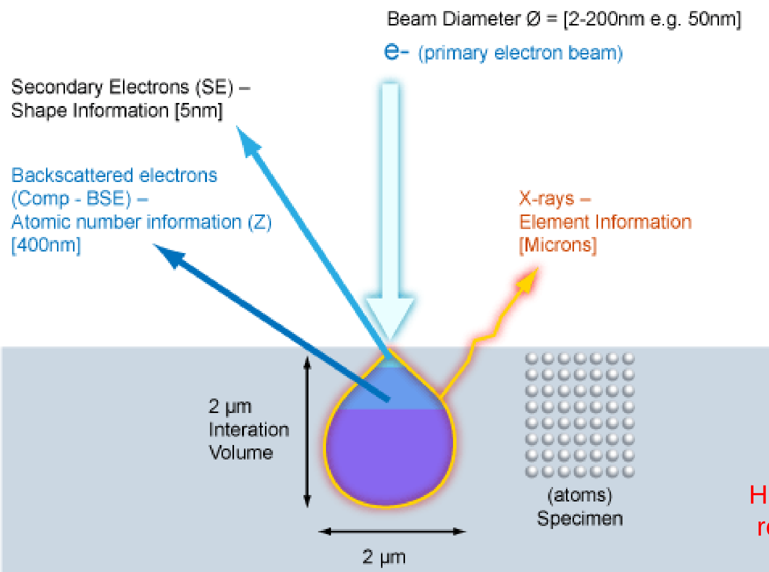
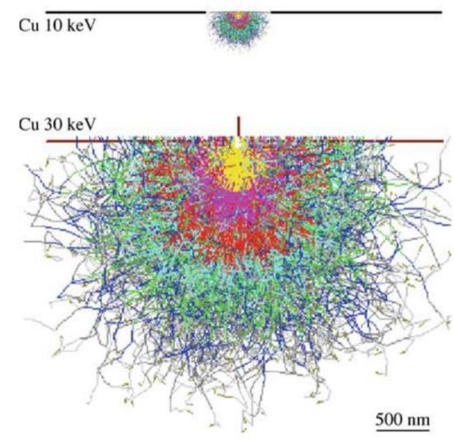
The spatial resolution is defined by the “interaction volume” between probe and specimen



Lower primary beam energy



How else can the interaction volume be reduced to improve spatial resolution?

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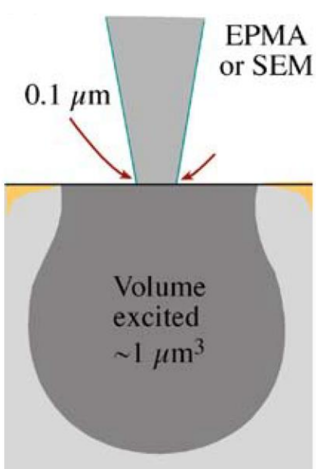
Electron microanalysis spatial resolution is better for ***thinner specimens***



Williams and Carter

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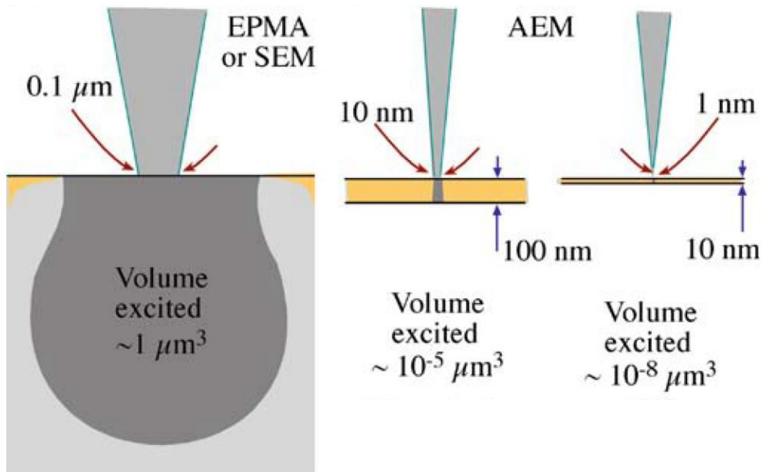
Electron microanalysis spatial resolution is better for thinner specimens



Williams and Carter

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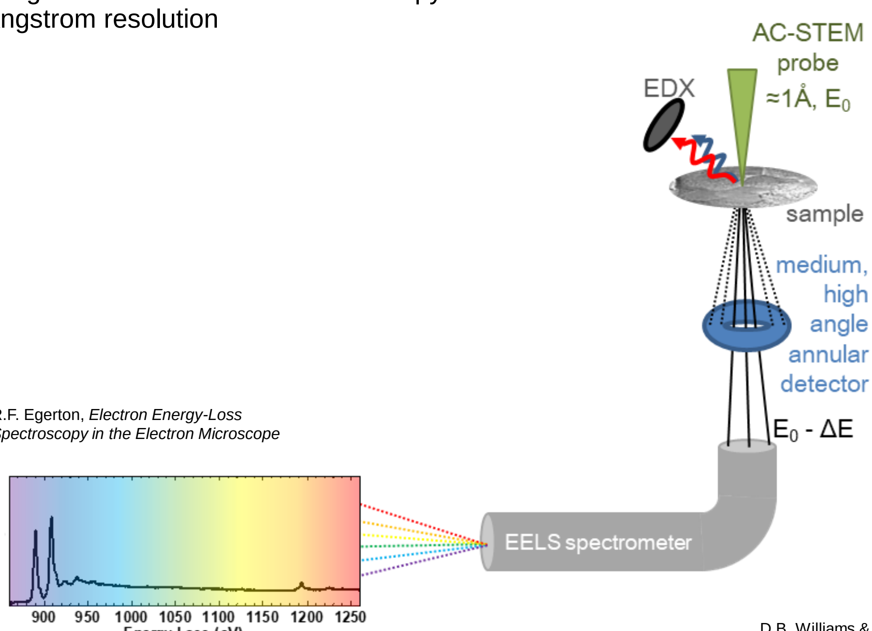
Modern scanning transmission electron microscopy obtains sub-Angstrom resolution



R.F. Egerton, *Electron Energy-Loss Spectroscopy in the Electron Microscope*

D.B. Williams & C.B. Carter, *Springer* (2008)
S.J. Pennycook & P.D. Nellist, *Springer* (2011)

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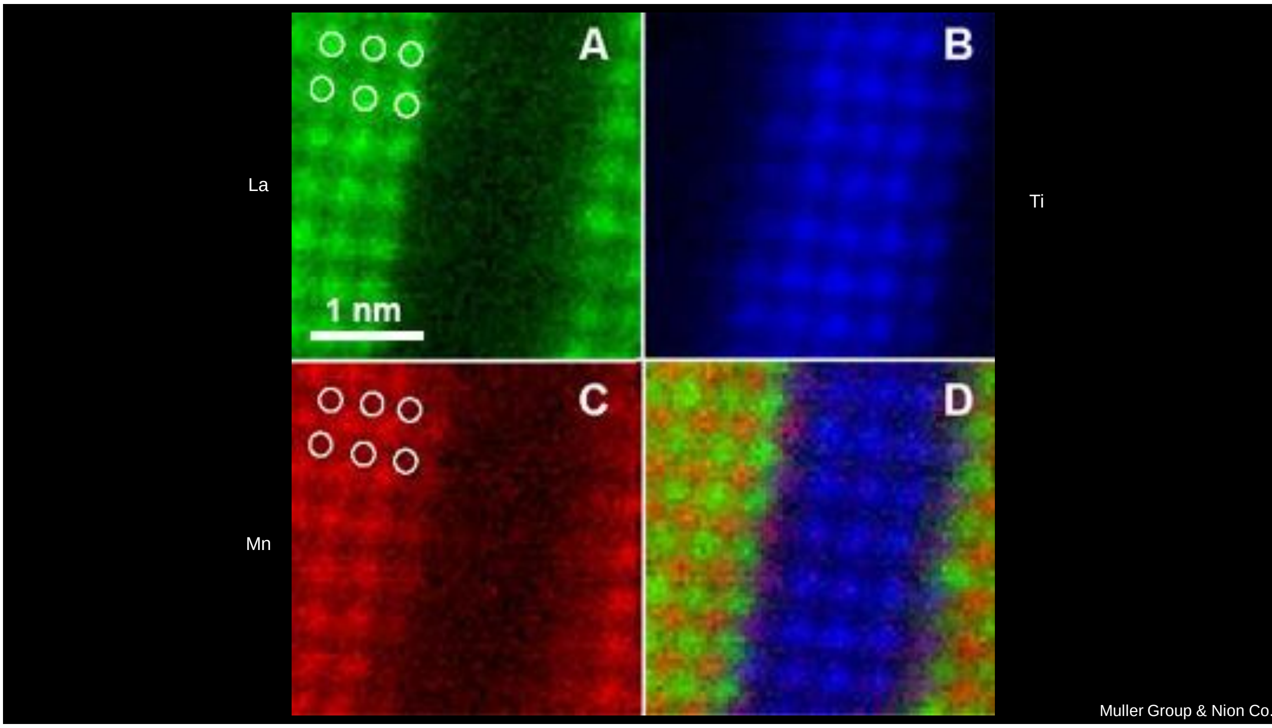

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References (see Class page)

DLS

R. Pecora (2000) Dynamic light scattering measurement of nanometer particles in liquids. *Journal of Nanoparticle Research*

Malvern Panalytical (2019) A basic introduction to Dynamic Light Scattering (DLS) for particle size analysis. www.youtube.com/watch?v=FaQM7C4oTz0

Electron microscopy

Throughout