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*WINTER COLLEGE ON OPTICS ON OPTICS AND PHOTONICS IN NANOSCIENCE AND NANOTECHNOLOGY*

**( 7 - 18 February 2005)**

# *"Fabrication and Properties of Metal Nanoparticles"-II*

**presented by:**

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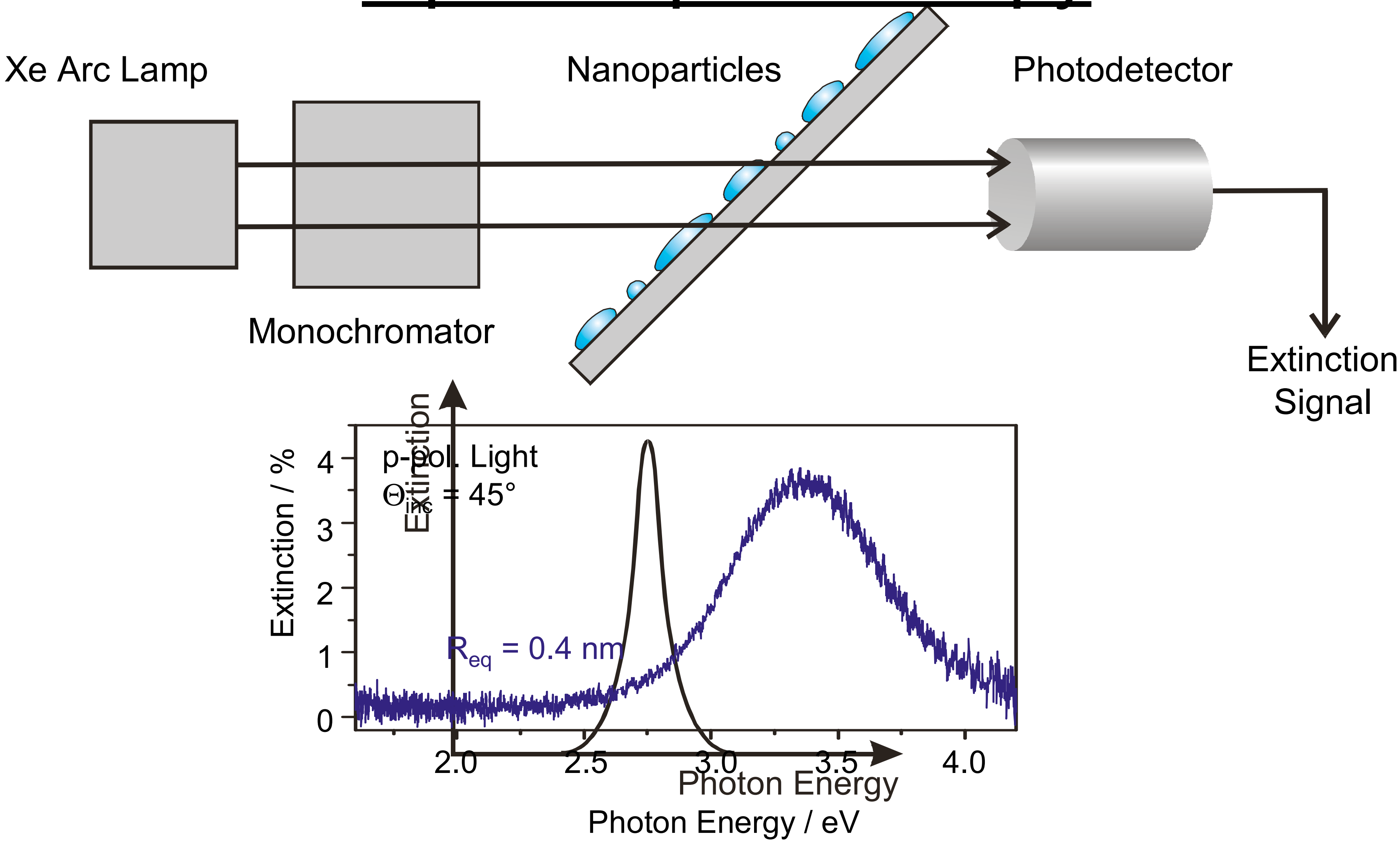
**Fachbereich Physik**
**Germany**

# Methods for observing and analyzing cluster and thin film growth

- Optical spectroscopy
- Atomic probe microscopy
- Electron microscopy
- Inelastic scattering of impinging atoms
- Reflection high energy electron diffraction (RHEED)
- . . .

# Optical spectroscopy

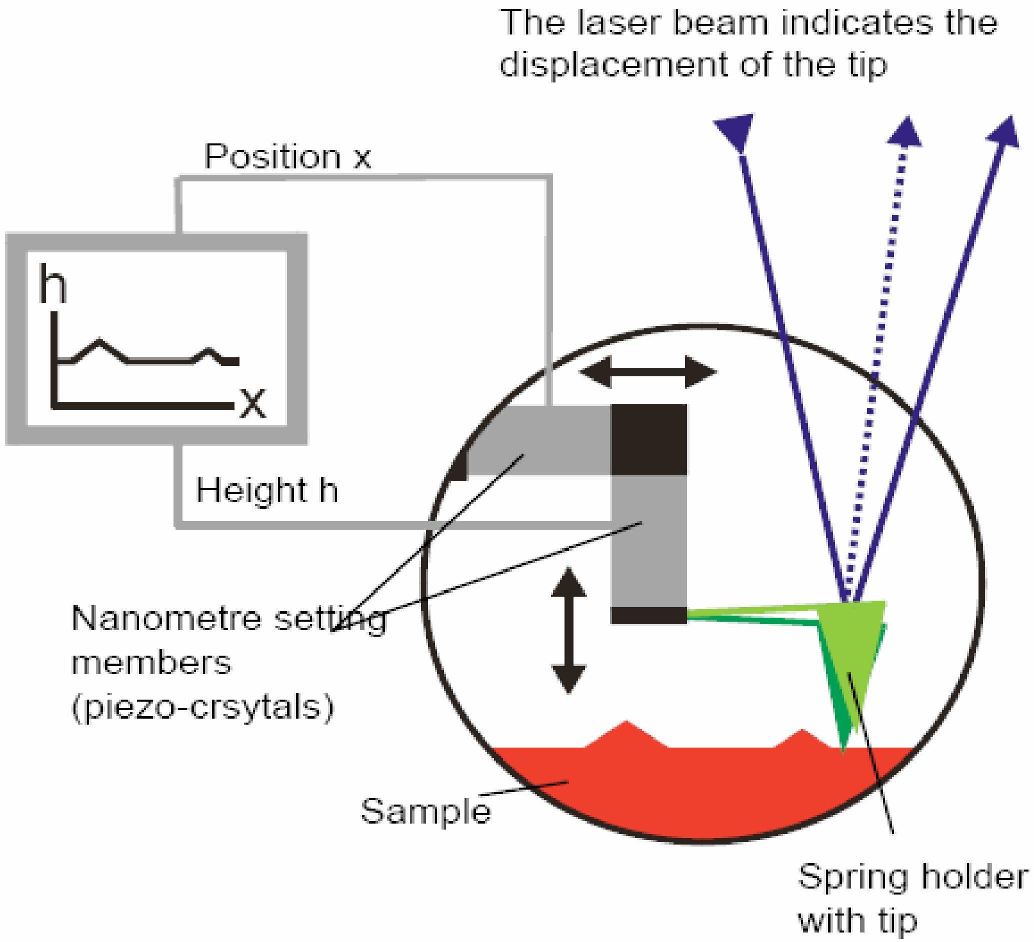


# Atomic force microscope

1) An atomically fine tip scans the surface of the sample.

2) A laser beam measures how far the tip is displaced by contact with the sample:

- Regulation of the tip holder (height h) for constant displacement
- The tip follows the contour profile

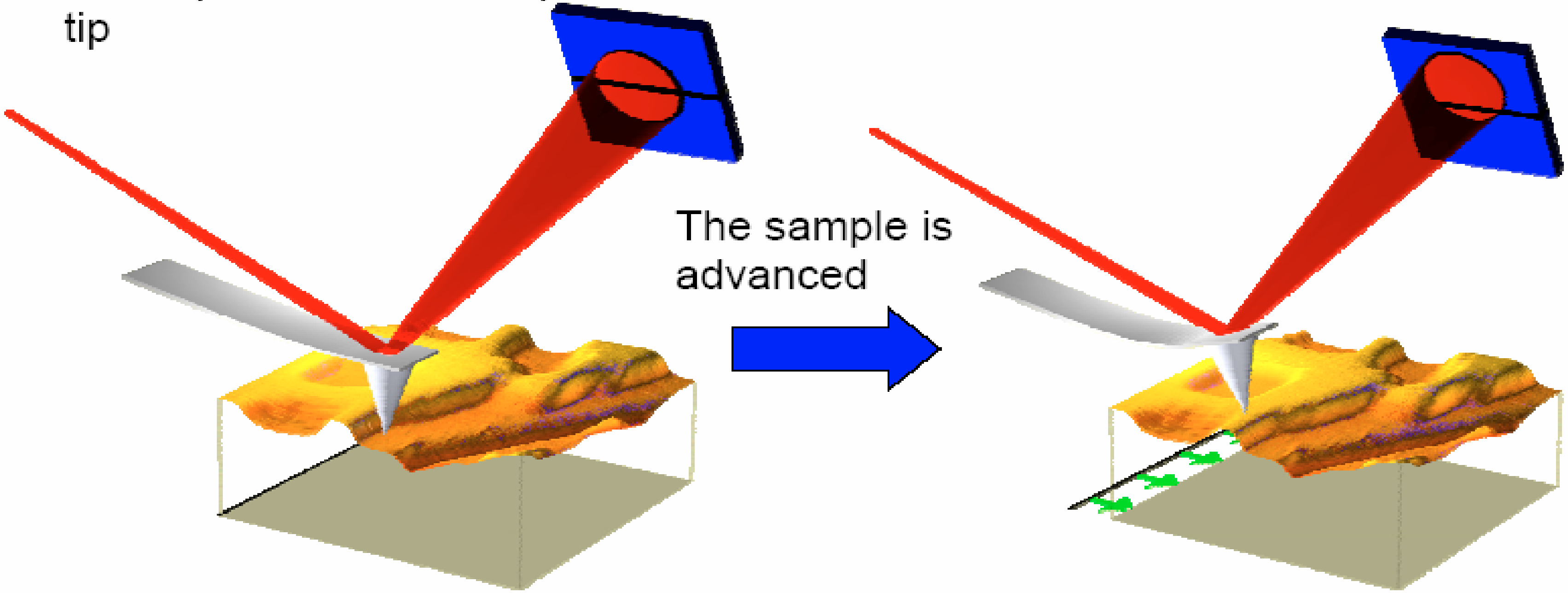



http://www.nanotruck.de/praesentationen/

# AFM in action

Laser beam for determining the displacement of the probe tip

The laser beam is deflected




Starting position of the cantilever

The surface roughness of the sample displaces the cantilever

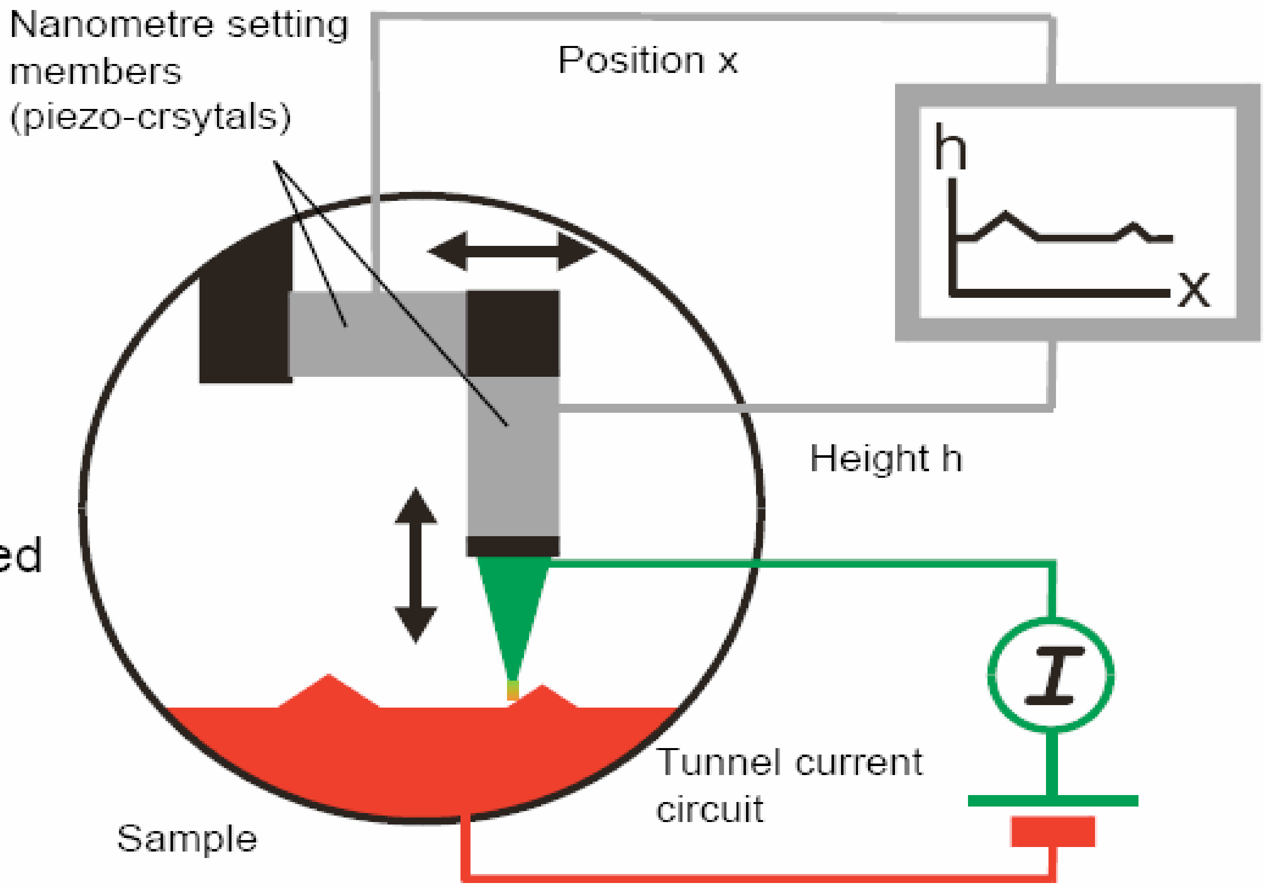
http://www.nanotruck.de/praesentationen/

# Scanning tunnelling microscopy

1) An atomically fine tip scans the surface of the sample.

2) A constant tunnel current flows between the tip and the sample:

- The distance from the surface (height) is regulated and kept constant
- The tip follows the contour profile

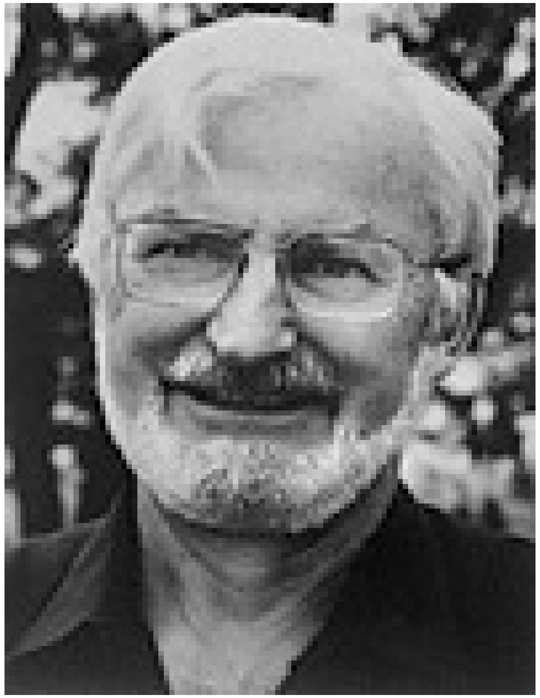



http://www.nanotruck.de/praesentationen/

# The Nobel Prize in Physics 1986


## Heinrich Rohrer

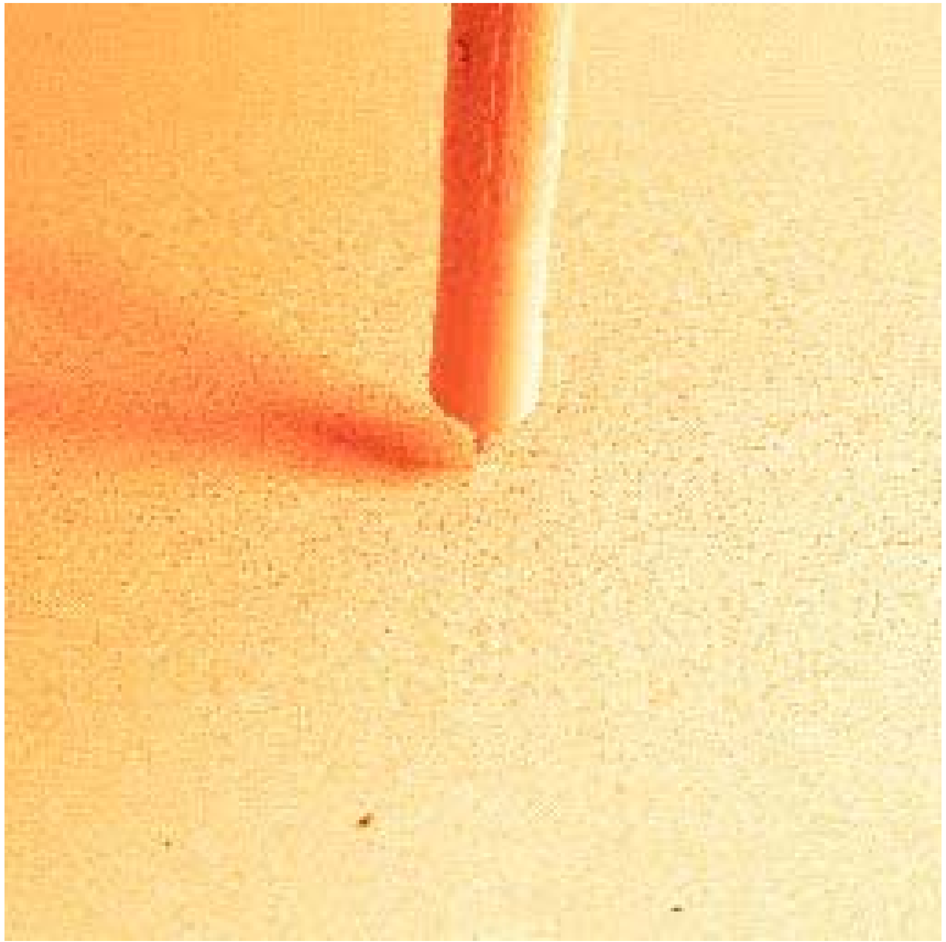
* 1933



### The New Nanometer World

„Miniaturization becomes a totally new game when we reach dimensions where physical laws and effects assume a different appearance, where size becomes comparable to characteristic length scales, where transport follows different laws, where surface and interface effects become dominant, and where concepts like dimensionality and symmetry are no longer readily useful or significant.“

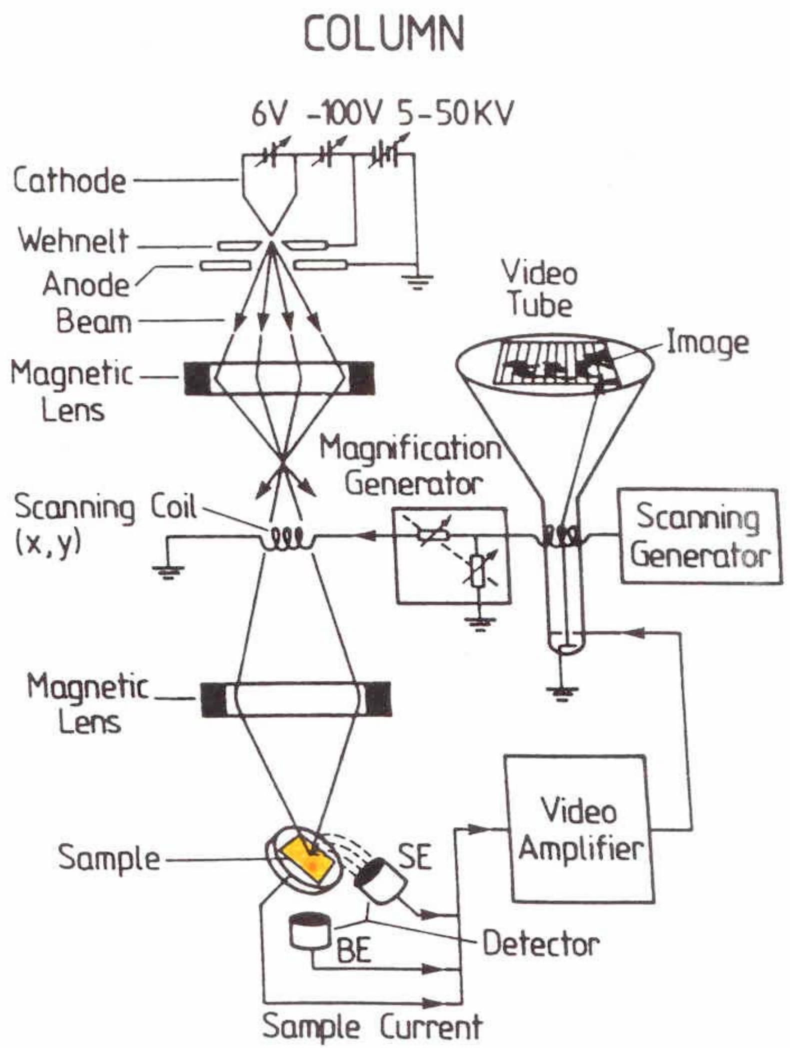
# STM in action



**SEM-movie during the STM measurement of a small Pb particle on Ru(001)**

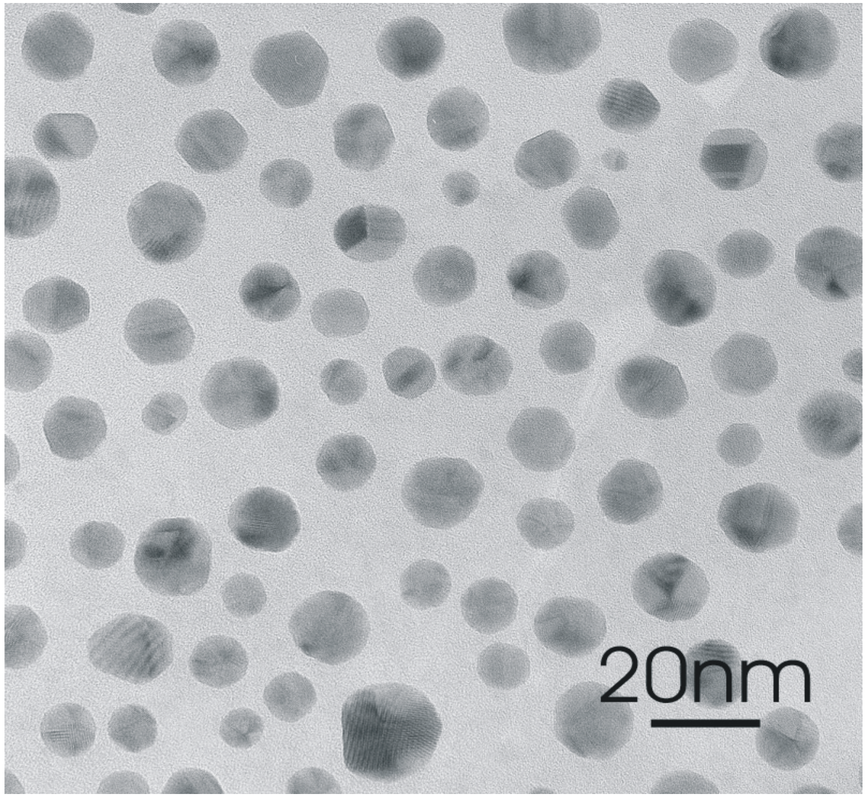
Emundts et al., Rev. Sci. Instrum. **72**, 3546 (2001).
http://www.fz-juelich.de/video/emundts/

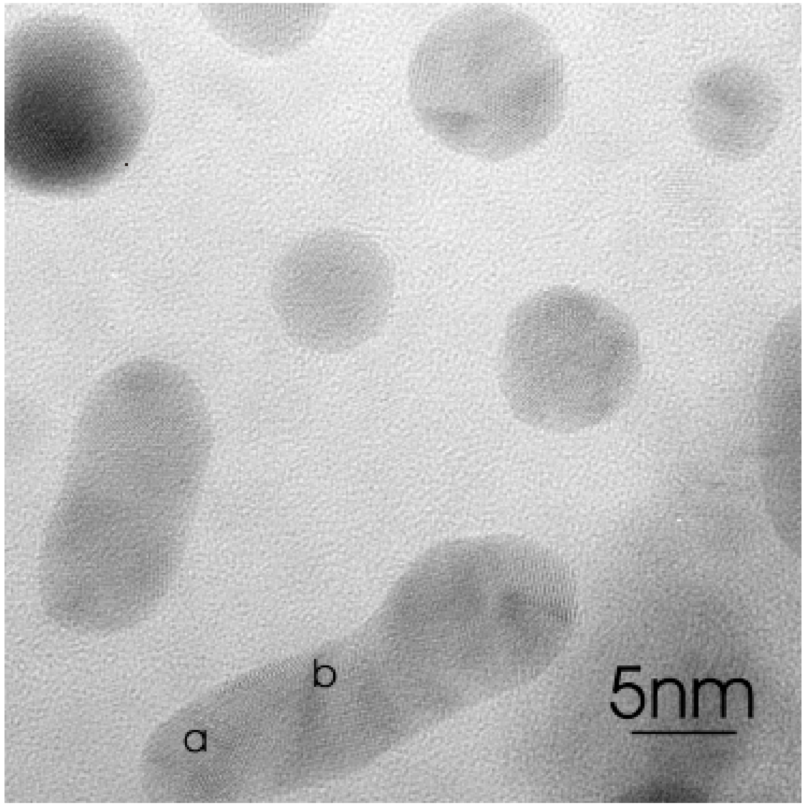
# Transmission electron microscopy and scanning electron microscopy




*H. Lüth*
*Surface and Interfaces of Solids, 2nd Edition*
*Springer (1993)*

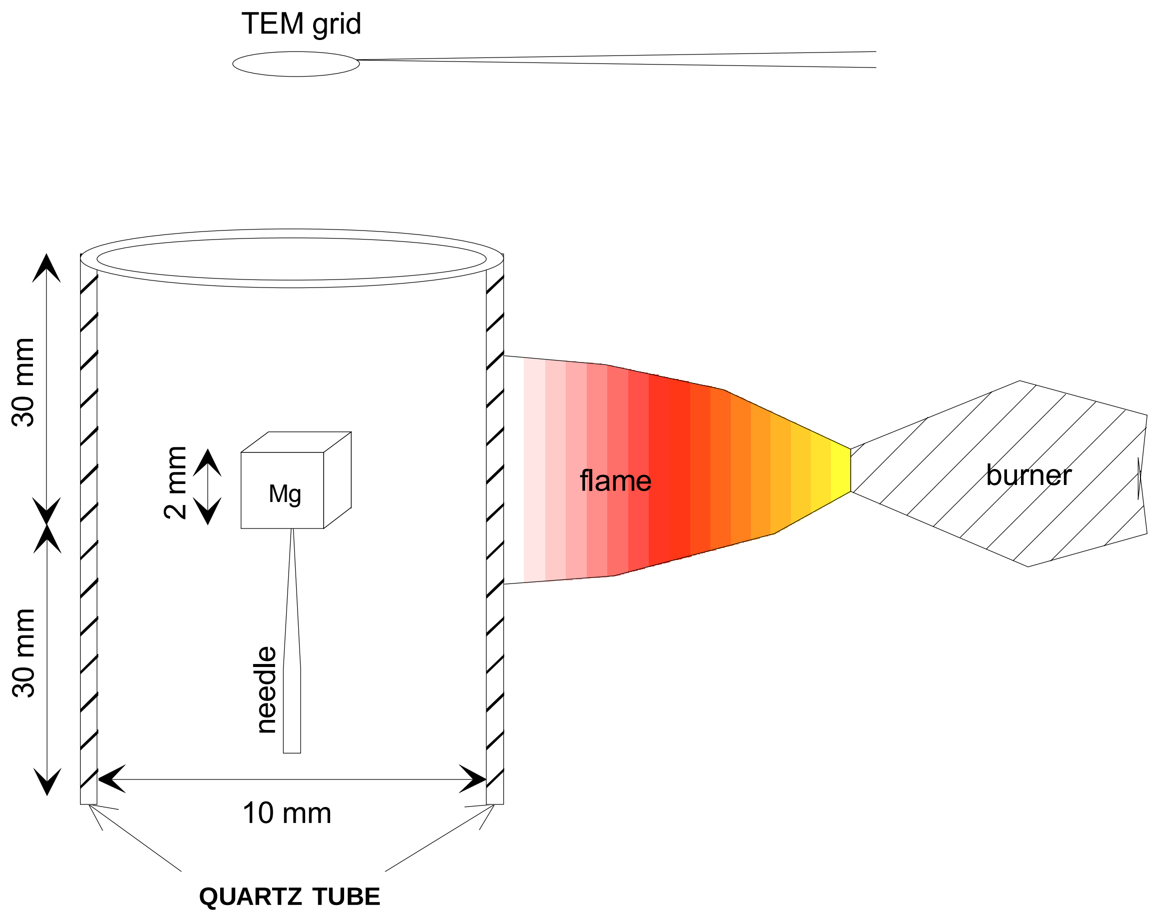
# High resolution TEM-images



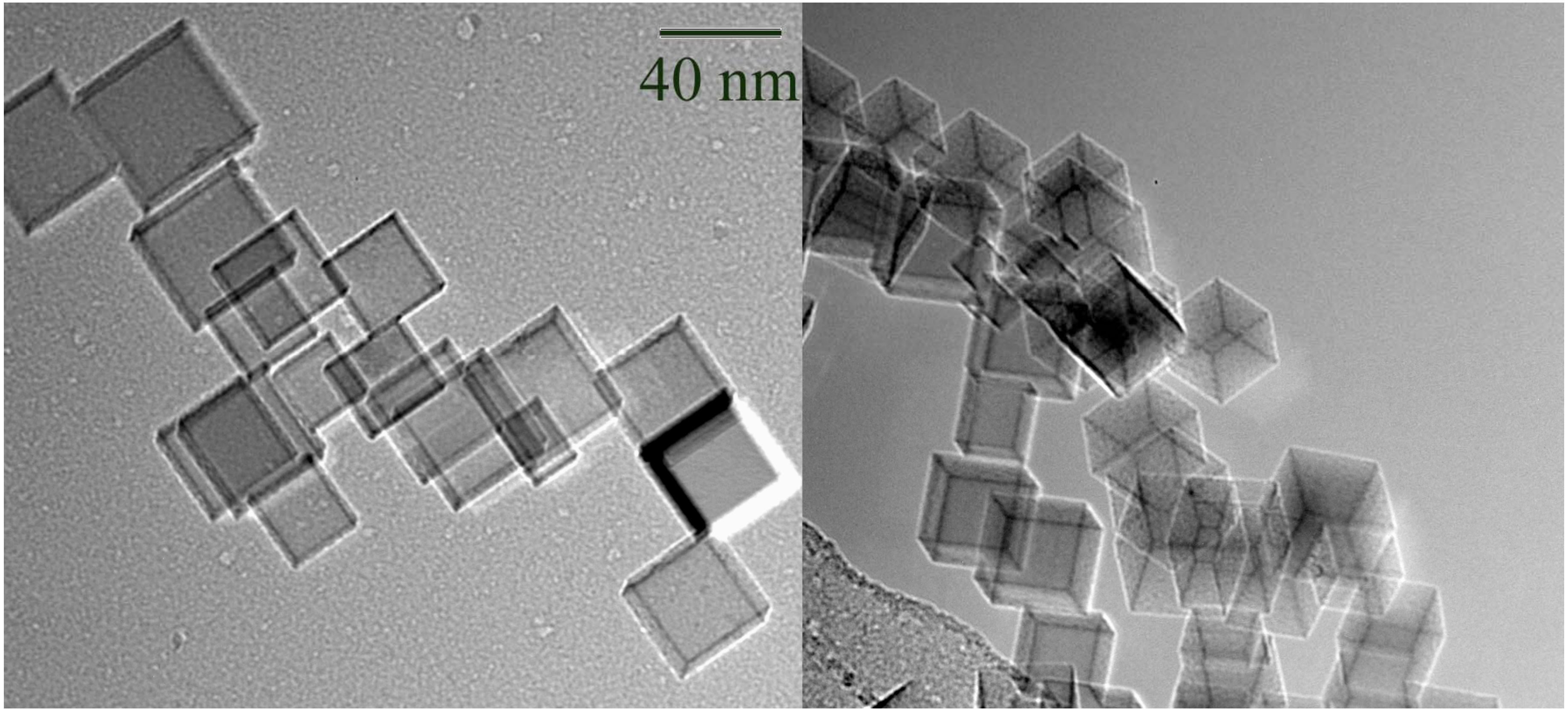




Gold nanoparticles on sapphire

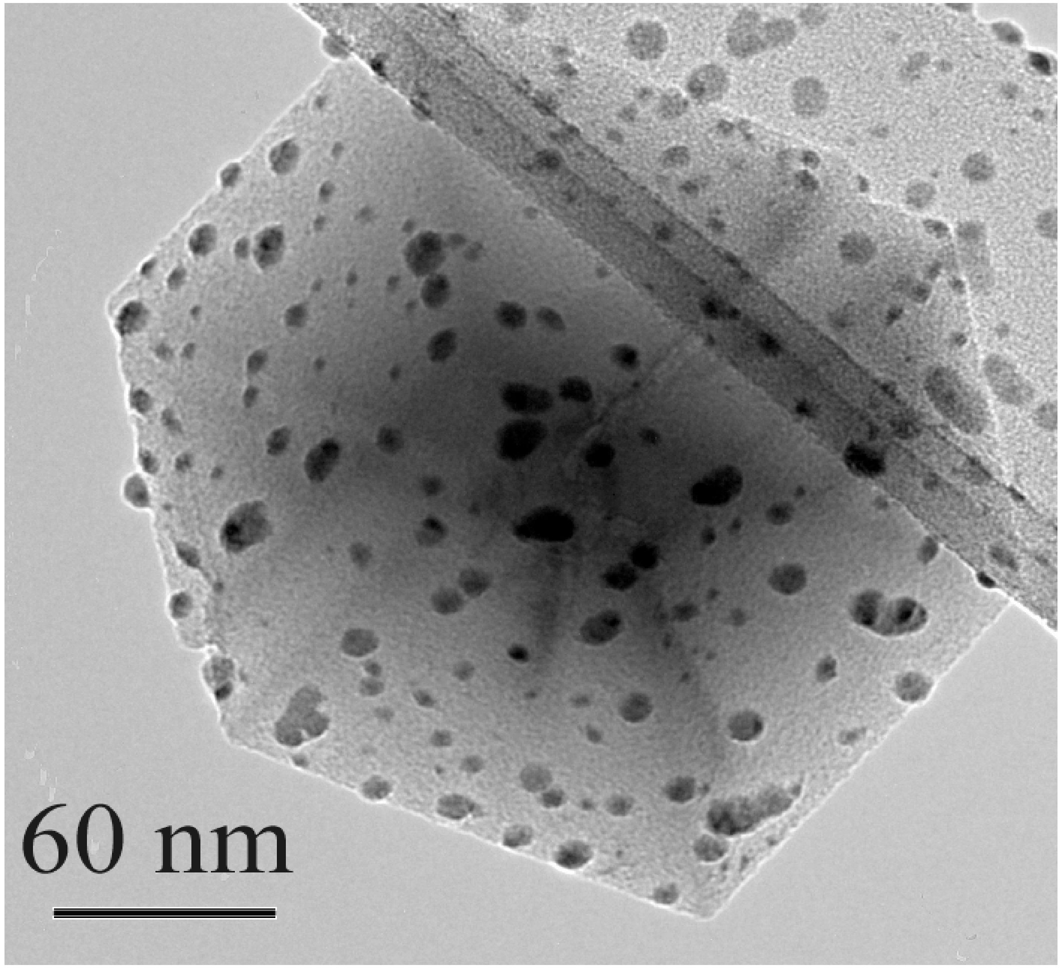
# Schematic presentation of MgO particle preparation and collection to TEM grid



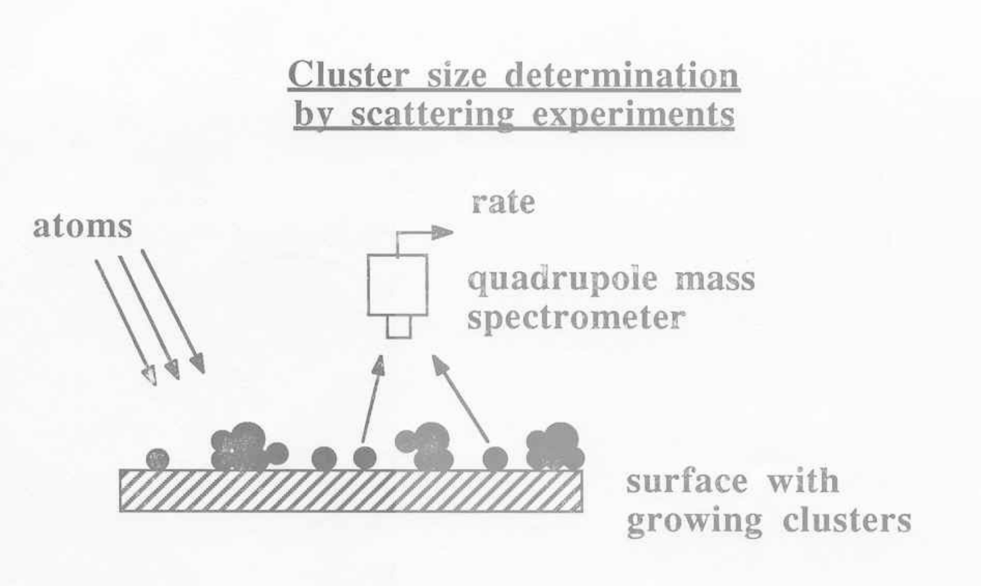
# TEM micrographs of MgO cubes



# Application: as substrates for TEM observations of polydispersed Ag nanoparticles



# Cluster size determination by scattering experiments

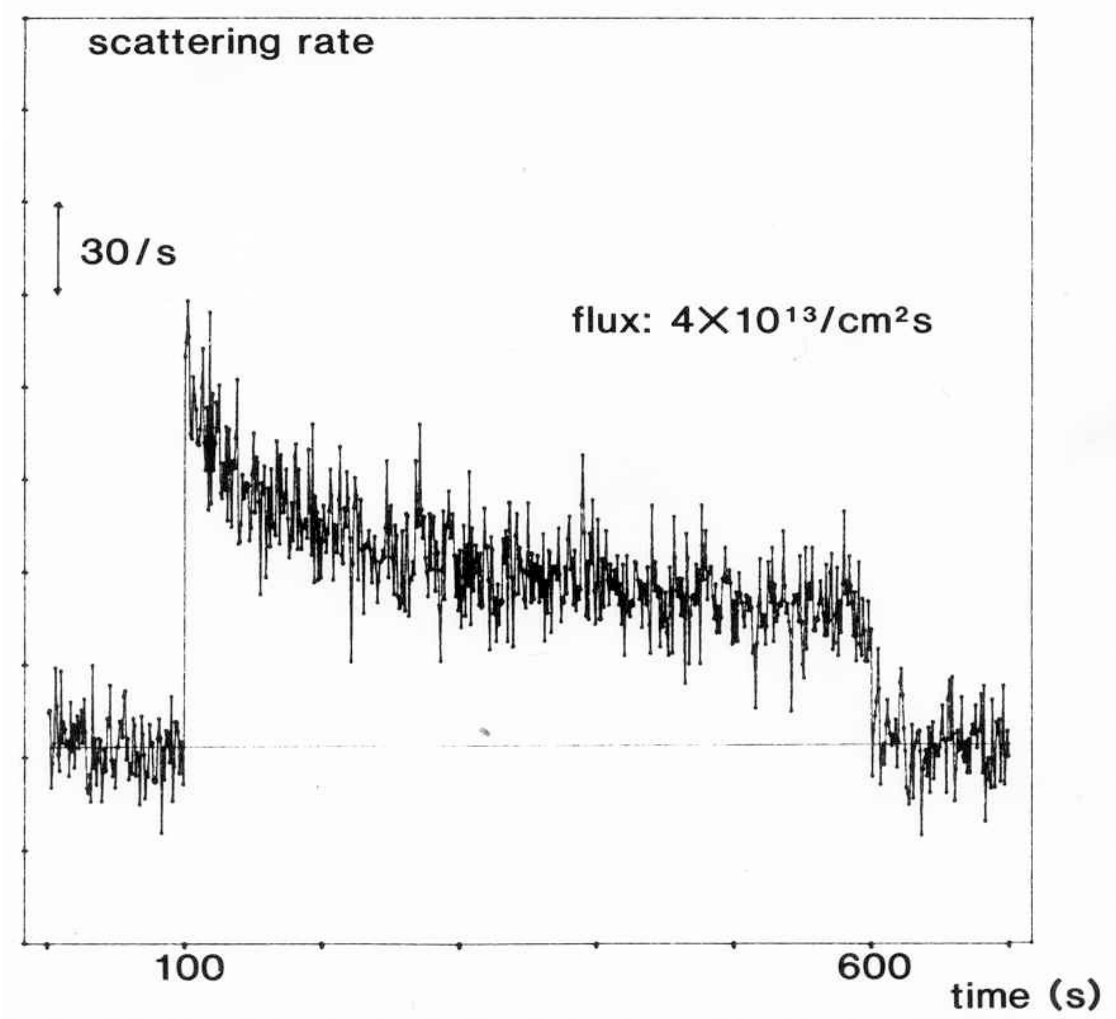



**idea:**

- direct a beam of metal atoms with constant flux on the surface
- detect the rate of inelastically scattered atoms as a function of time

The decrease of the scattering signal as a function of time reflects the growing fraction of the surface covered with clusters and therefore also the cluster size for each instant during the measurement.

Determination of the cluster density and average cluster size.




$< R(t)> = 100$ Å - 1500 Å

$N = 5 * 10^8 /cm^2$

# Optical Properties of Metal Nanoparticles

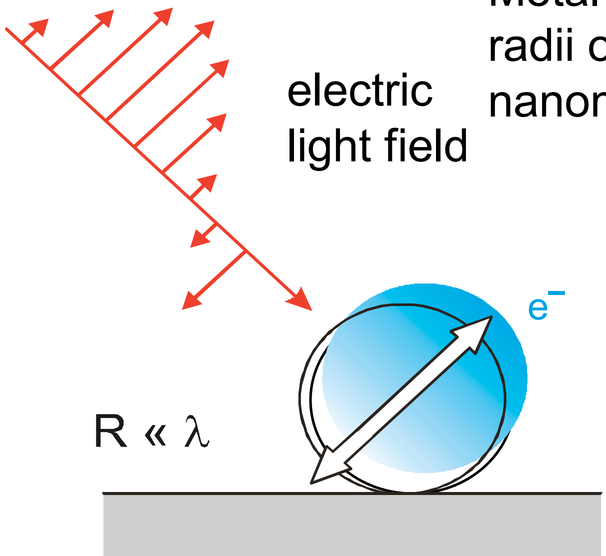
**Size range:**

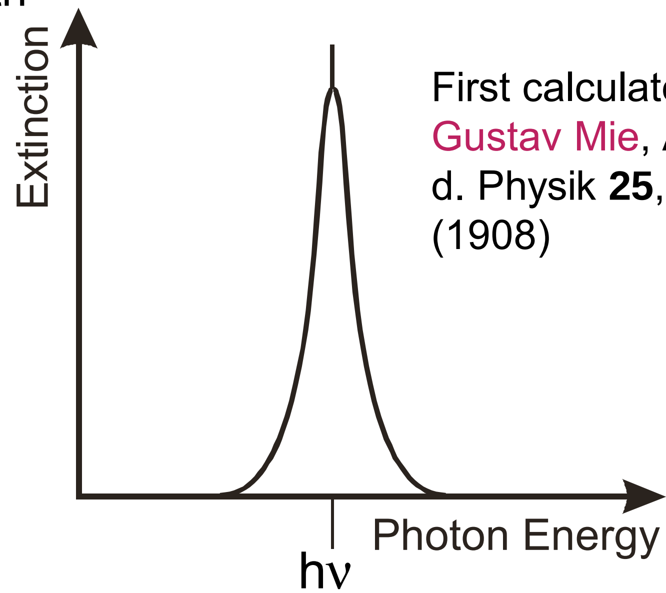
e.g.: Na

| | |
|---|---|
| 20 Atoms: | R = 0,55 nm |
| 500 Atoms: | R = 1,65 nm |
| $10^7$ Atoms: | R = 50,0 nm |

# The surface plasmon polariton

Metal nanoparticles with radii of only several nanometers




First calculated by Gustav Mie, Ann. d. Physik **25**, 377 (1908)

## Ideal case: spherical nanoparticles

**Interaction of small metal nanoparticles with light:**

- collective oscillations of the conduction electrons
- absorption of light at a specific wavelength

**Energetic position depends on:**

- material
- dielectric surrounding
- dimensions of the particles

# Of interest:

nanoparticles with R = 1 nm up to 10 nm

→ no quantuum size effects
→ no retardation effects
→ Position of the surface plasmon resonance independent of size
→ dipol approximation possible (calculations quasi static)

**Technical relevant:**
nanoparticles with pronounced resonances in the visible optical spectral range
→ e.g.: Ag, Au

# What is a plasmon ?

quant of a plasma oscillation

plasma oscillation = collective density oscillation of free electrons in the metal

a) volume-plasmon
collective oscillation of free electrons in the bulk material:
propagating three-dimensional wave

b) surface-plasmon
collective oscillation of free electrons in a thin film:
propagating two-dimensional wave

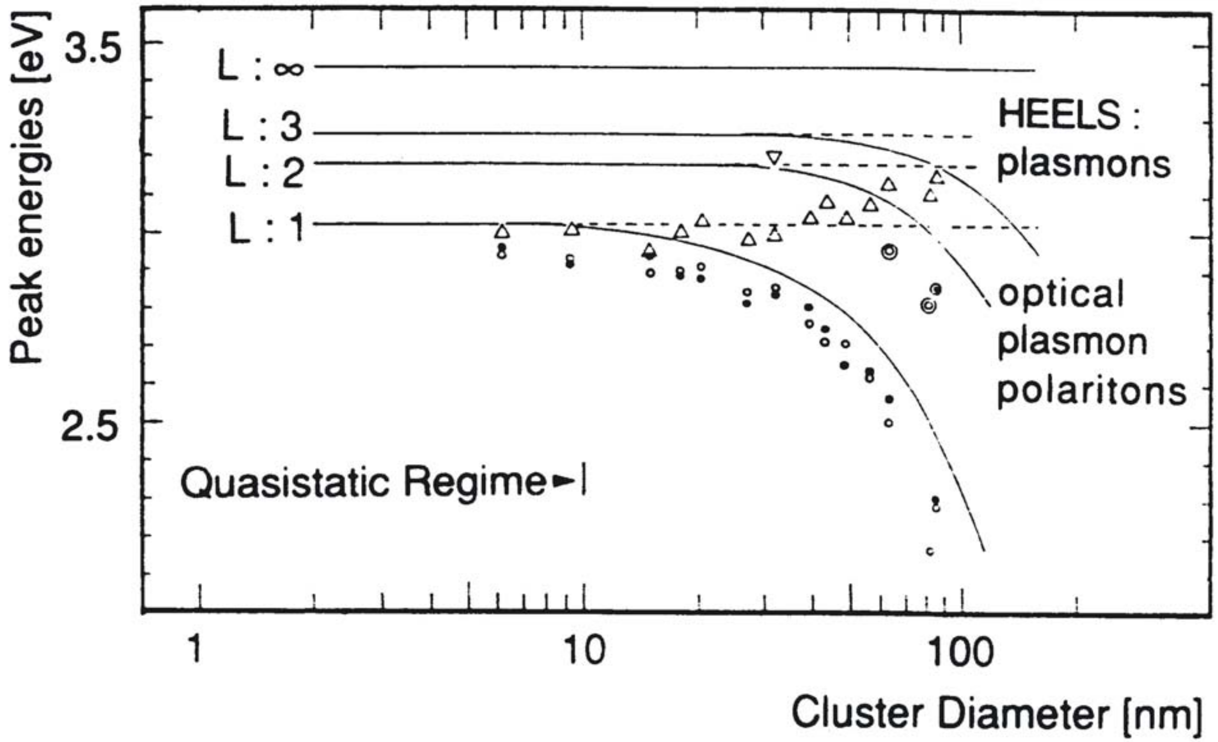
c) “free” surface-plasmon
collective oscillation of free electrons in nanoparticles
excited by e.g. fast electrons

d) surface-plasmon-polariton
collective oscillation of free electrons in nanoparticles
excited by electro-magnetic radiation, only

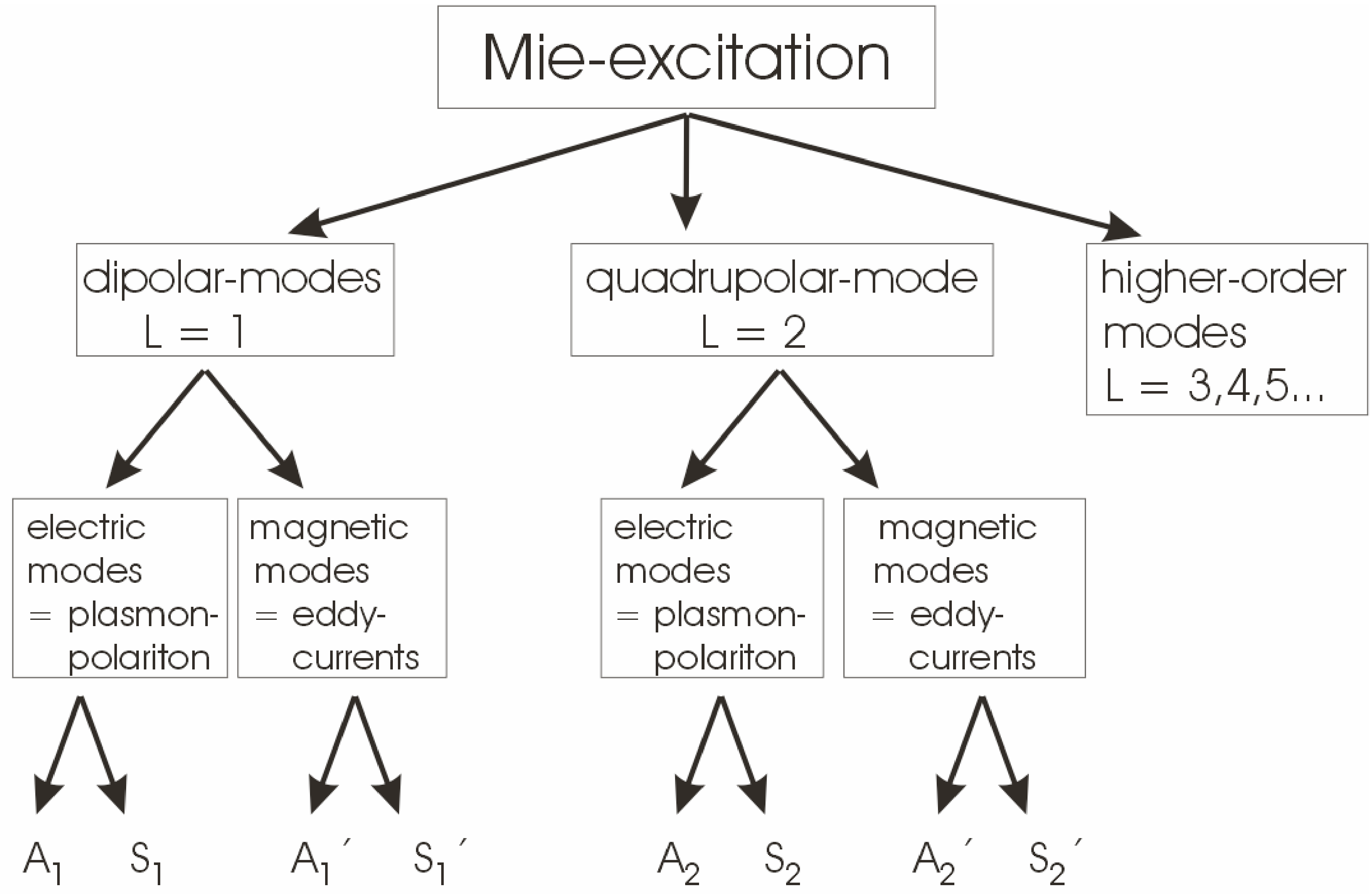
[e) Mie-plasmon]
Maxwell-equations applied to nanoparticles

# Differences between plasmon-polaritons and free plasmons

In nanoparticles with R > 10 nm, the position and the width of the resonance are different

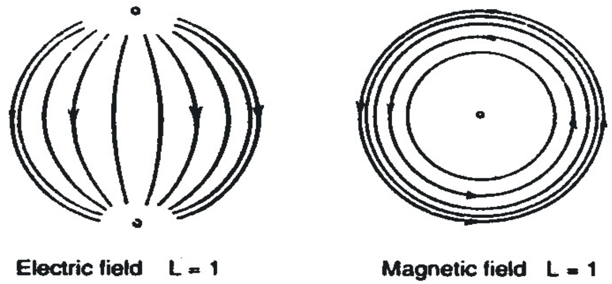



Reasons:
1) higher scattering (i.e. radiative damping) for plasmon-polaritons
2) at large λ, the electro-magnetic radiation suppress the excitation of multipoles

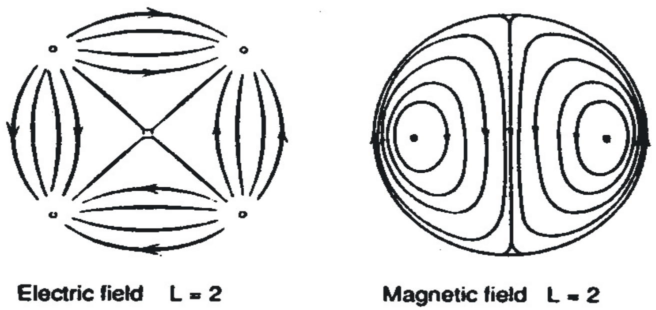



A = absorption, S = scattering

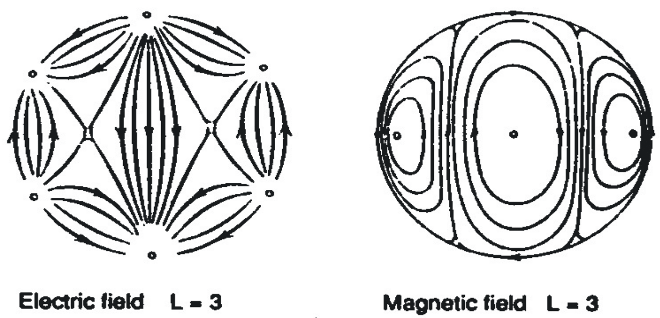
# Visualisation of the electric and magnetic fields




dipole

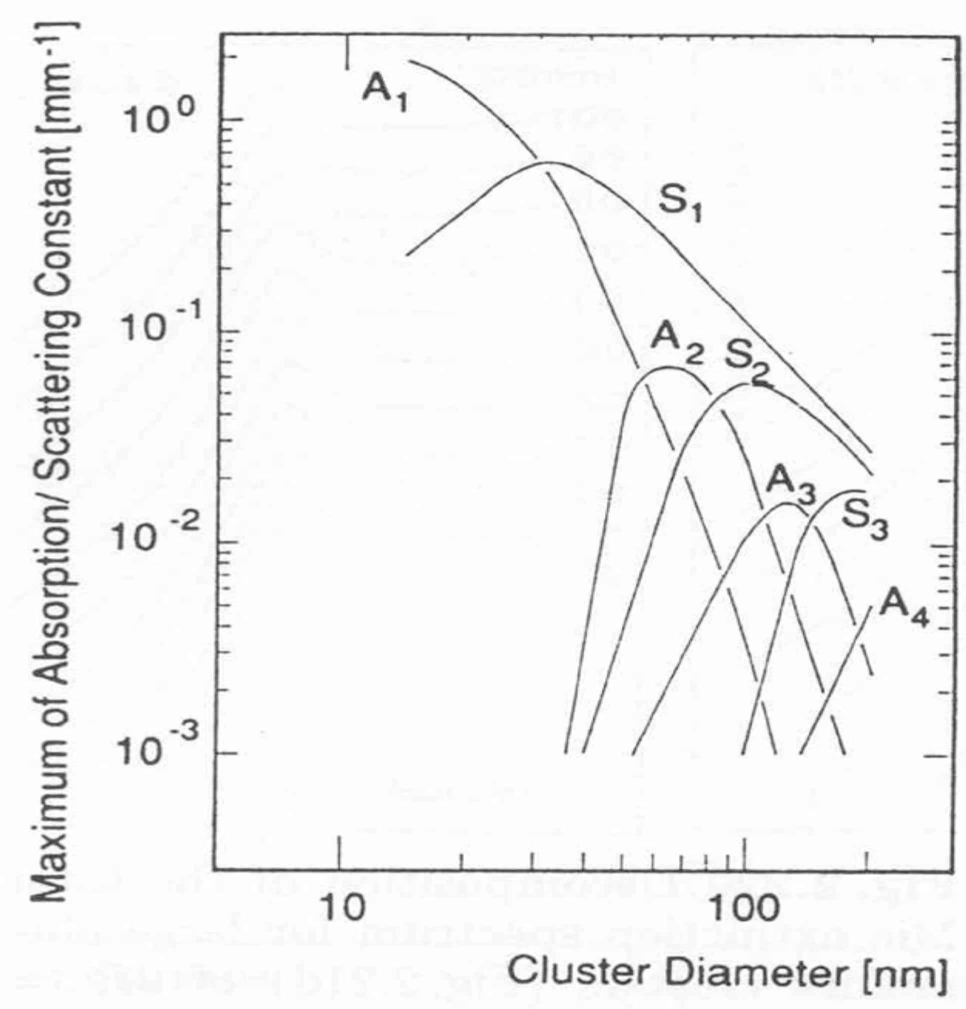



quadrupole




octupole

# Absorption and scattering contributions of the various multipolar plasmon modes for silver



# Linear optical properties of metallic nanoparticles / basics of linear spectroscopy

**Measurand**: extinction = absorption + scattering

For nanoparticles with R << λ yields:
absorption ~ $R^3$
scattering ~ $R^6$

→ if R < 10 nm, scattering is negligible

# Linear optical properties of metallic nanoparticles / basics of linear spectroscopy

**Results:**

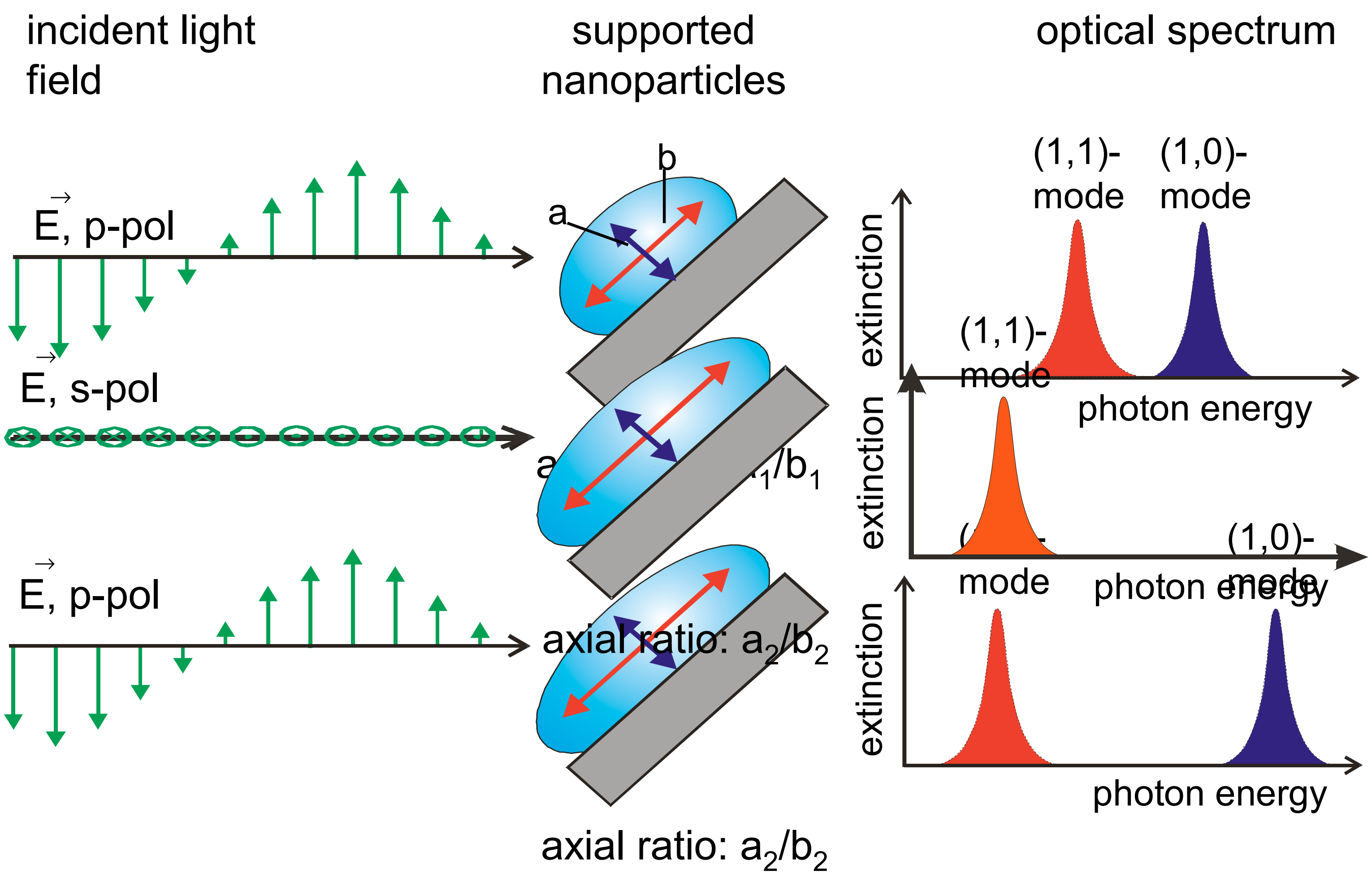
position of surface-plasmon resonance (SPR)
well known from Mie-Theory

width of SPR
inverse proportional to the dephasing time $T_2$
inverse proportional to the field enhancement
still open questions

# Changes of the surface plasmon excitation in supported metal nanoparticle arrays

# a) Splitting of the SPR in two modes

⇒ position of the modes depend on axial ration a/b



b) Shift of the SPR due to the higher refractive index

⇒ effective medium theory

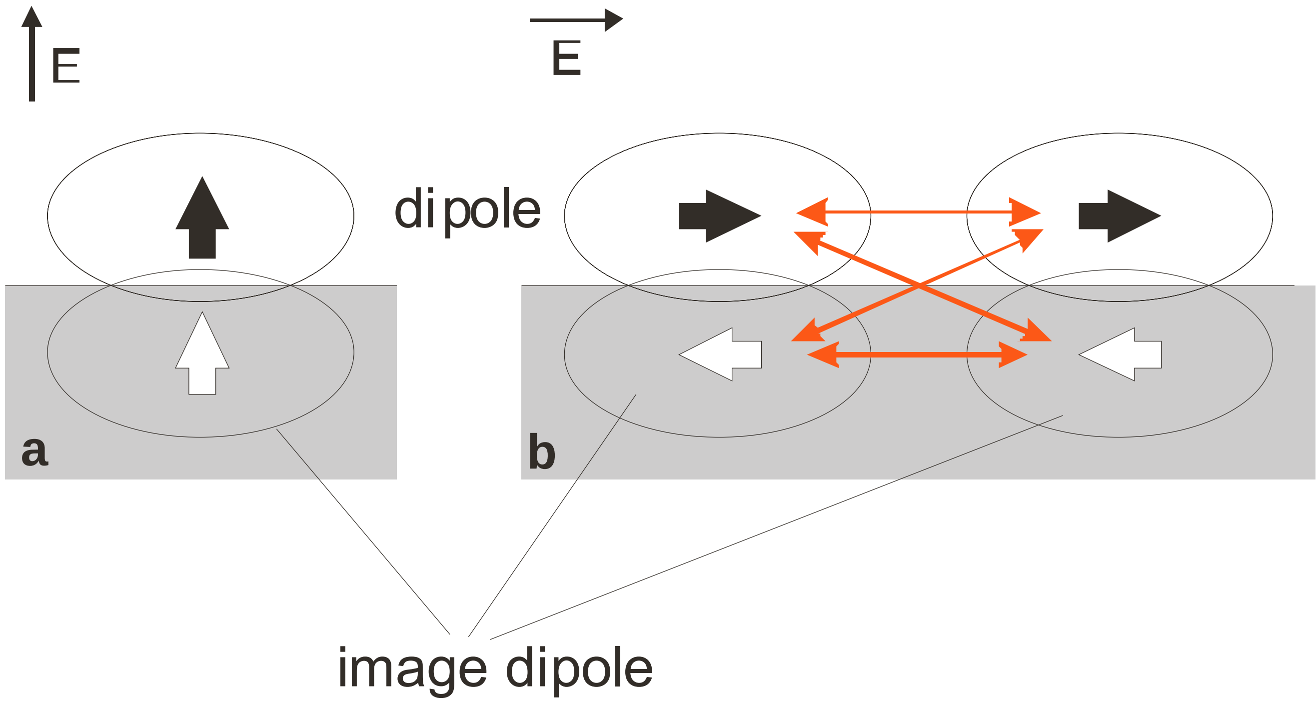
c) Chemical interface damping

⇒ electrons are able to tunnel in interface states

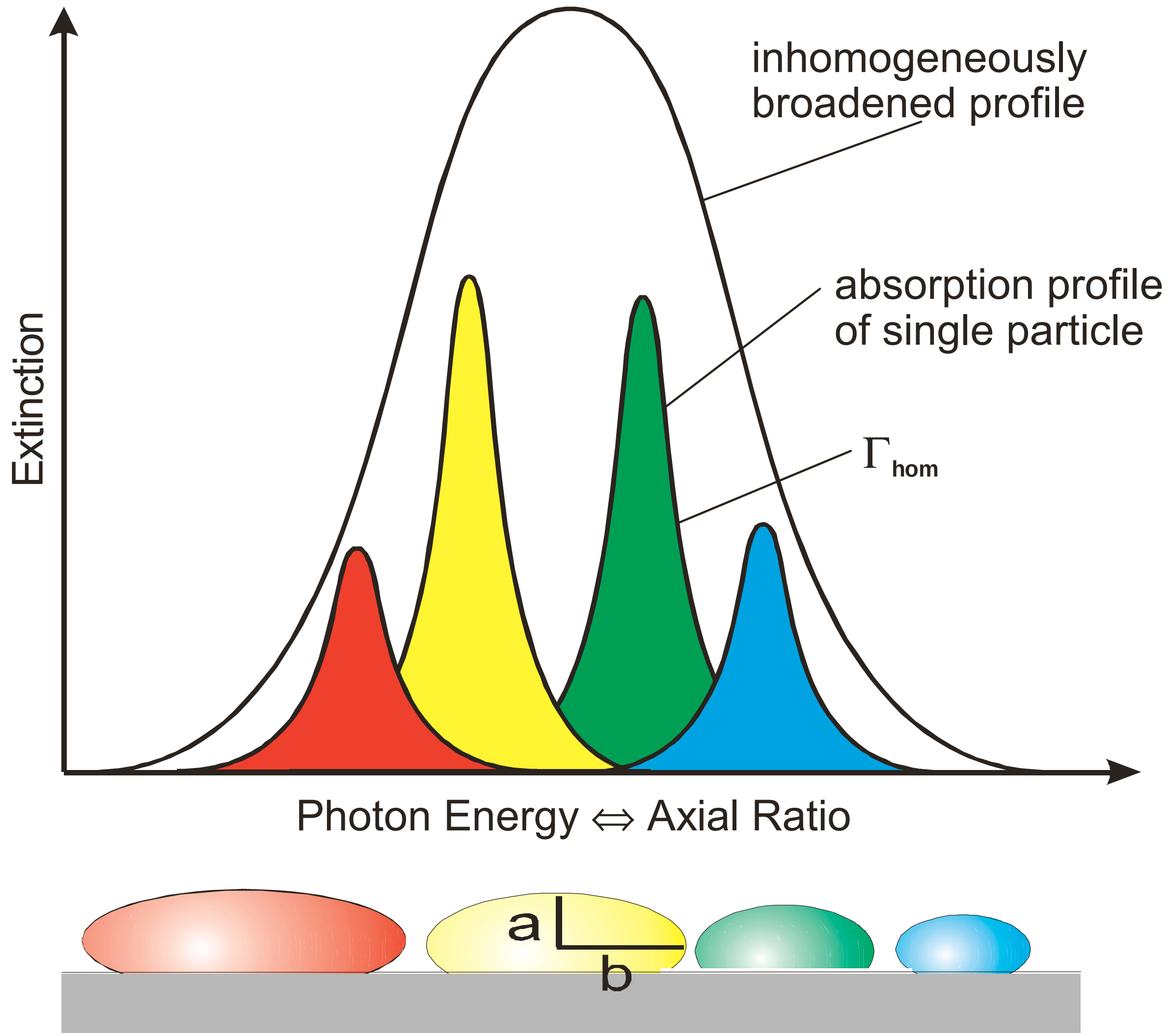
⇒ broadening of the SPR

d) The substrate influences the dipole oscillation due to image dipoles

$\Rightarrow$ Yamaguchi-theory



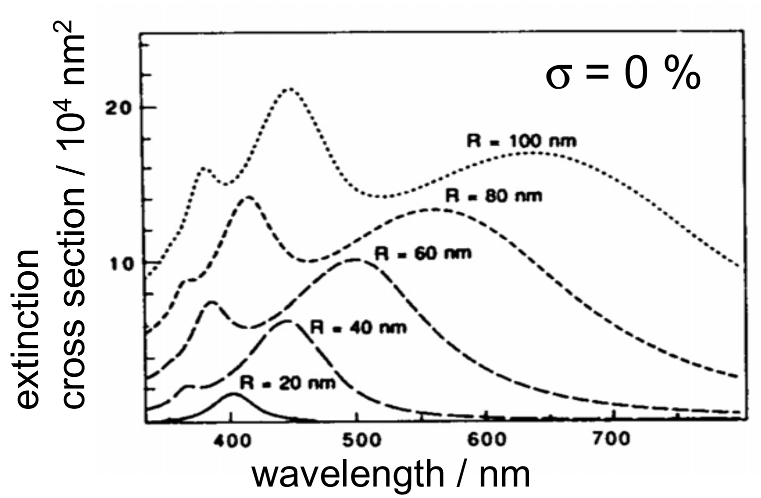
# e) Size and shape distribution $\Rightarrow$ broadening of the resonance

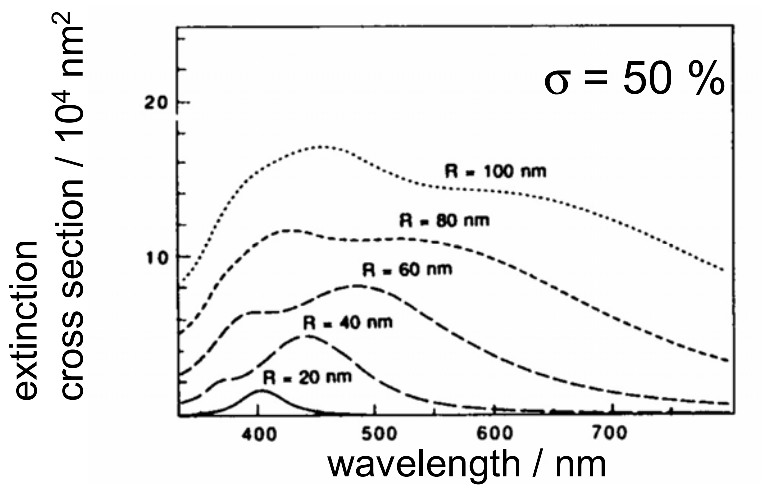


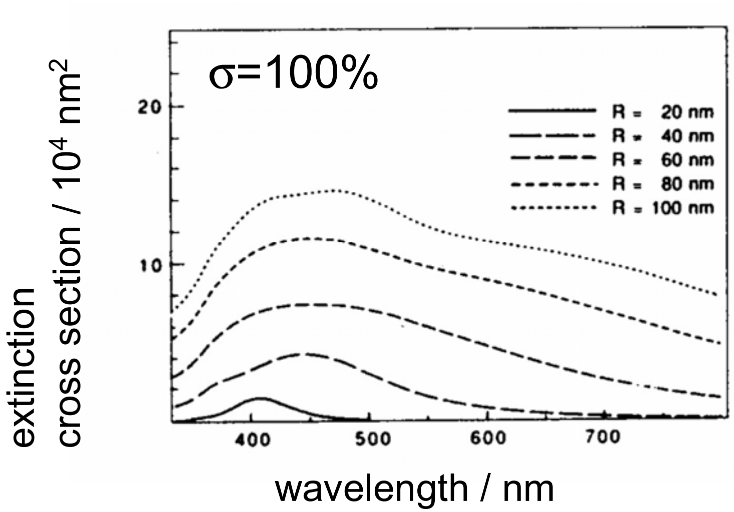

Amount of inhomgeneous broadening is not known

$\Rightarrow$ $\Gamma_{hom}$ and $T_2$ cannot be determined from the optical spectra

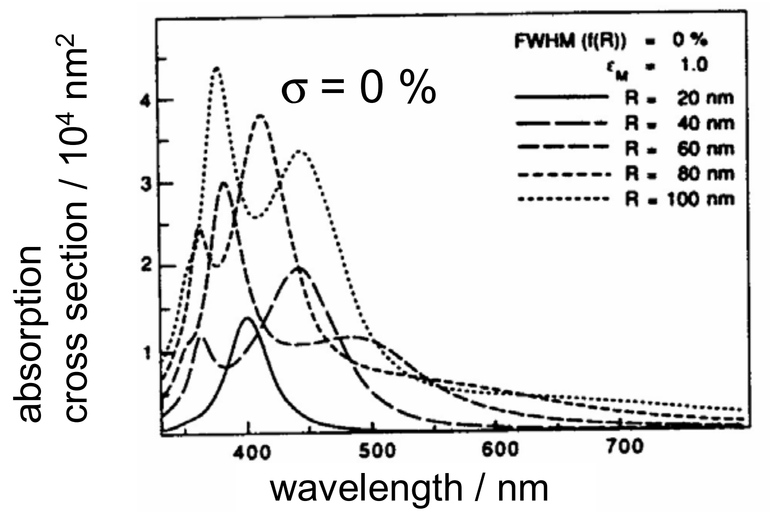
# Influence of the inhomogeneous size distribution to the extinction cross section

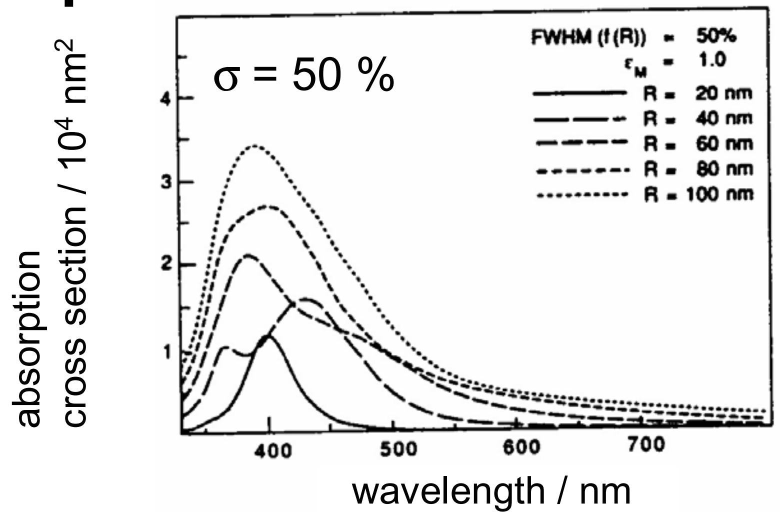


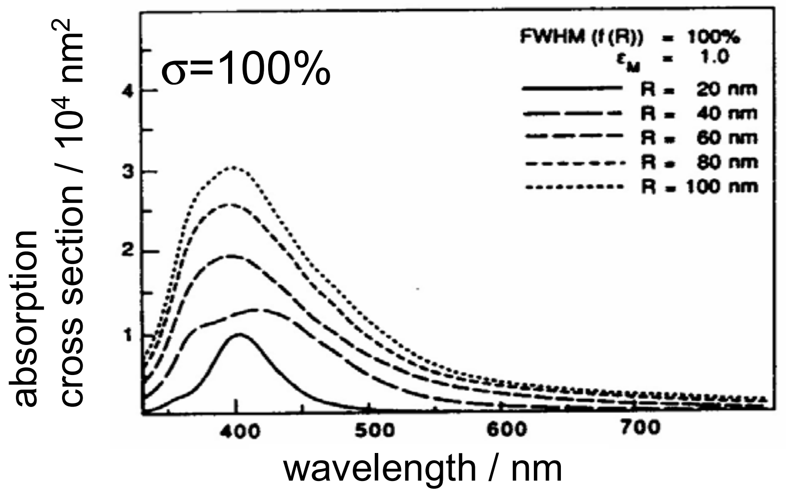



# Influence of the inhomogeneous size distribution to the adsorption cross section



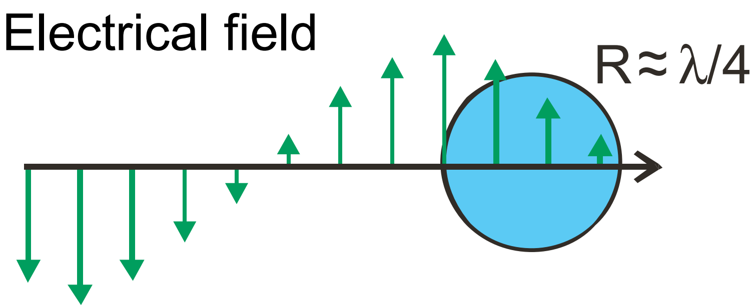



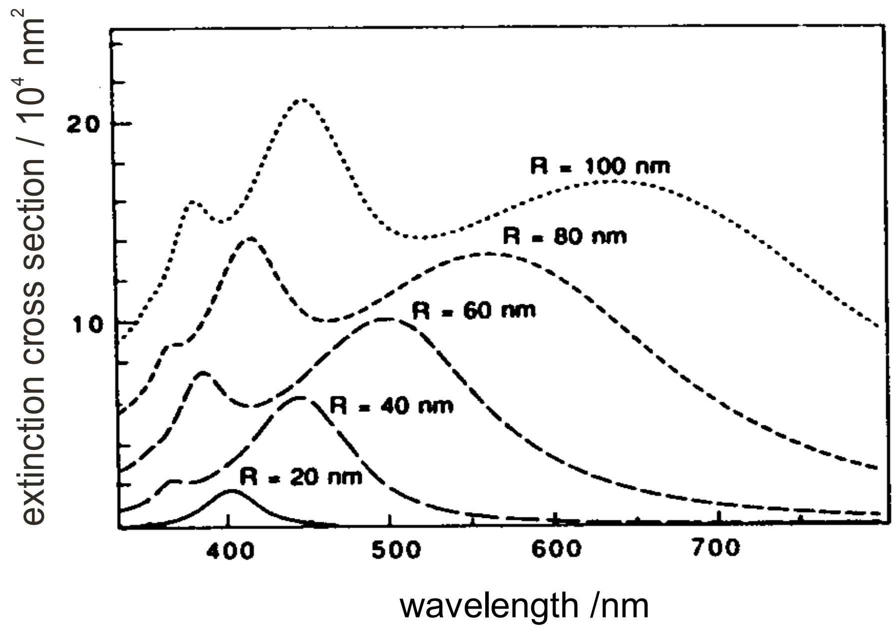



# Size effects

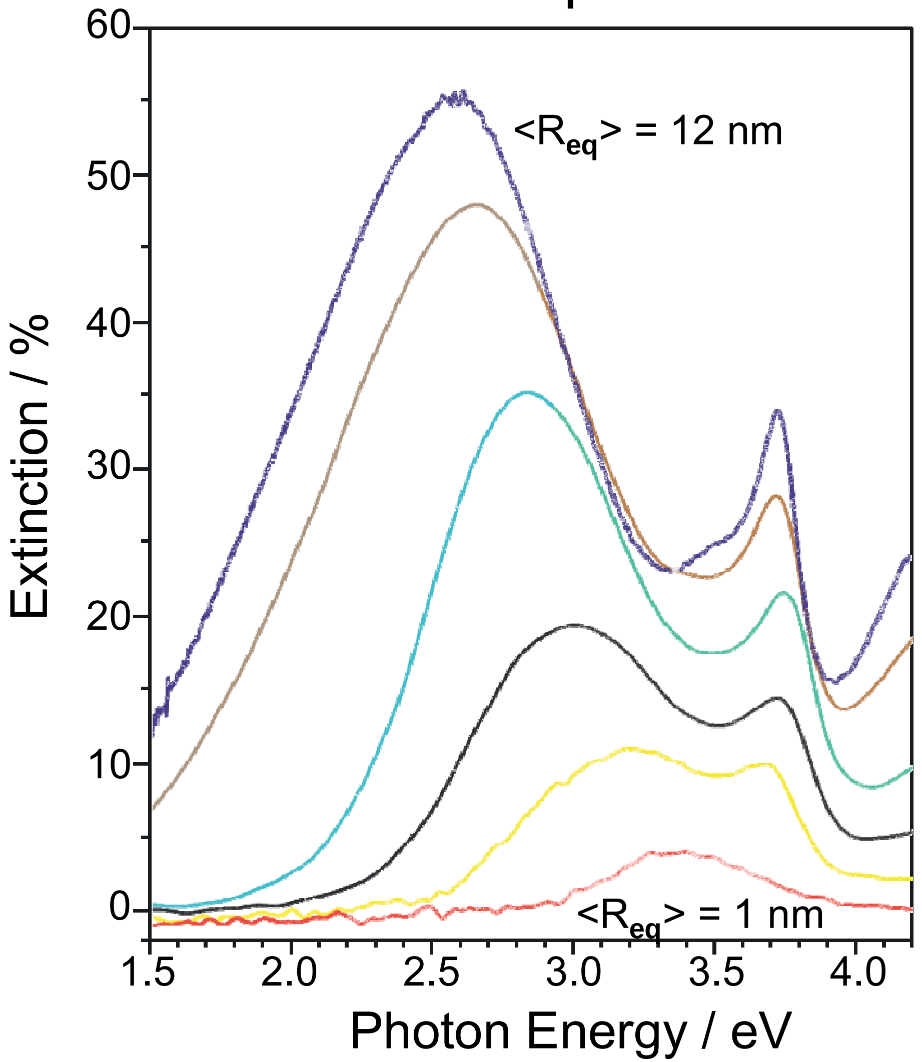
R>10 nm: retardation effects

- increased radiative damping
- SPR is red shifted
- quadrupole and higher-order resonances



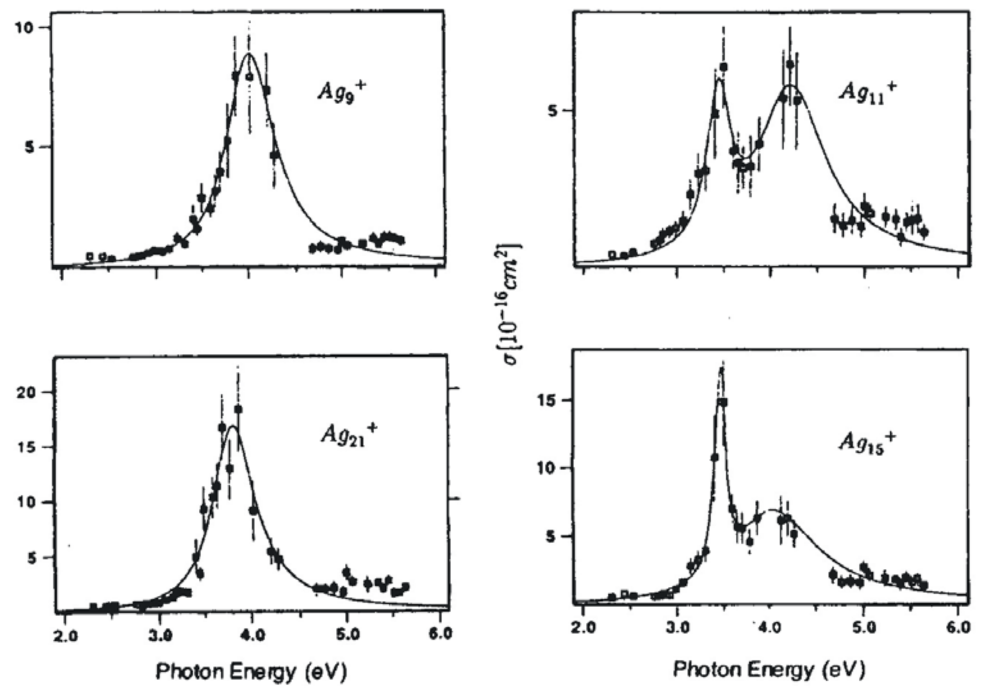



# ***Shape*** dependence of the absorption spectra of silver nanoparticles



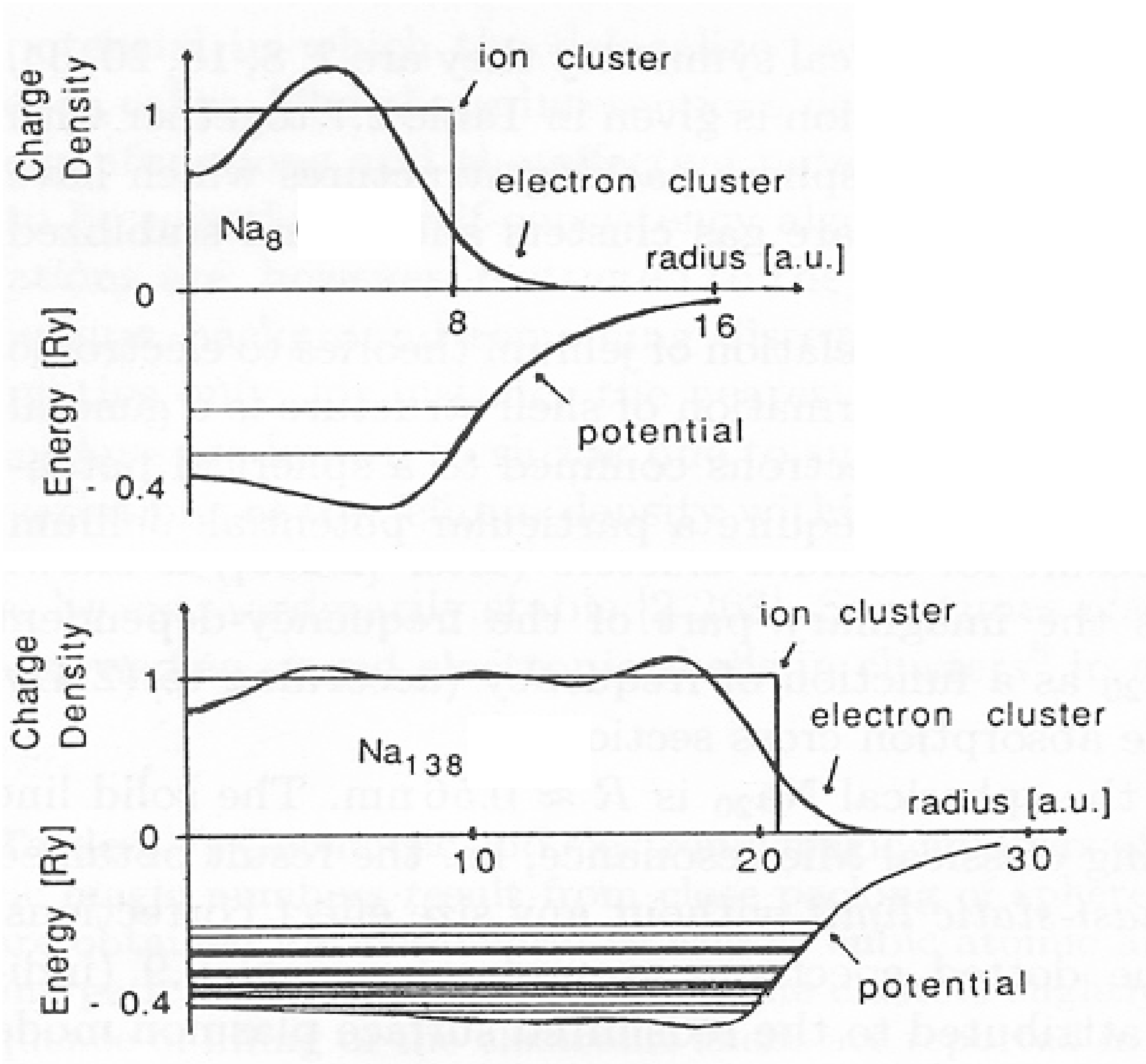
R < 1 nm (~ 200 atoms)

- quantuum size effects
- amount of surface atoms > than volume atoms
- spill-out is relevant.
- changes of
- bandstructure
- Fermi energy
- density of states
- and much more

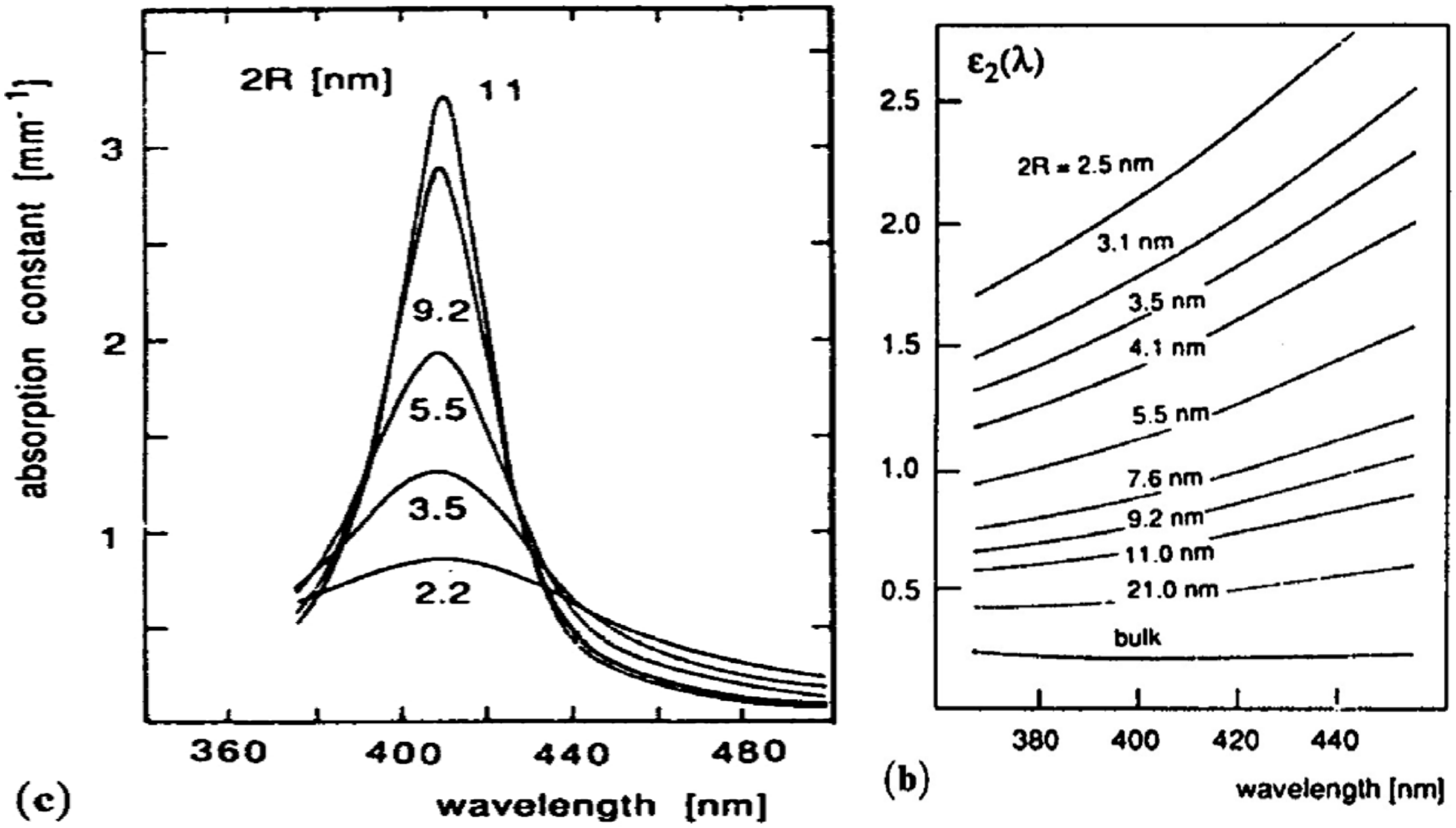



**optical properties of small unsupported nanoparticles**

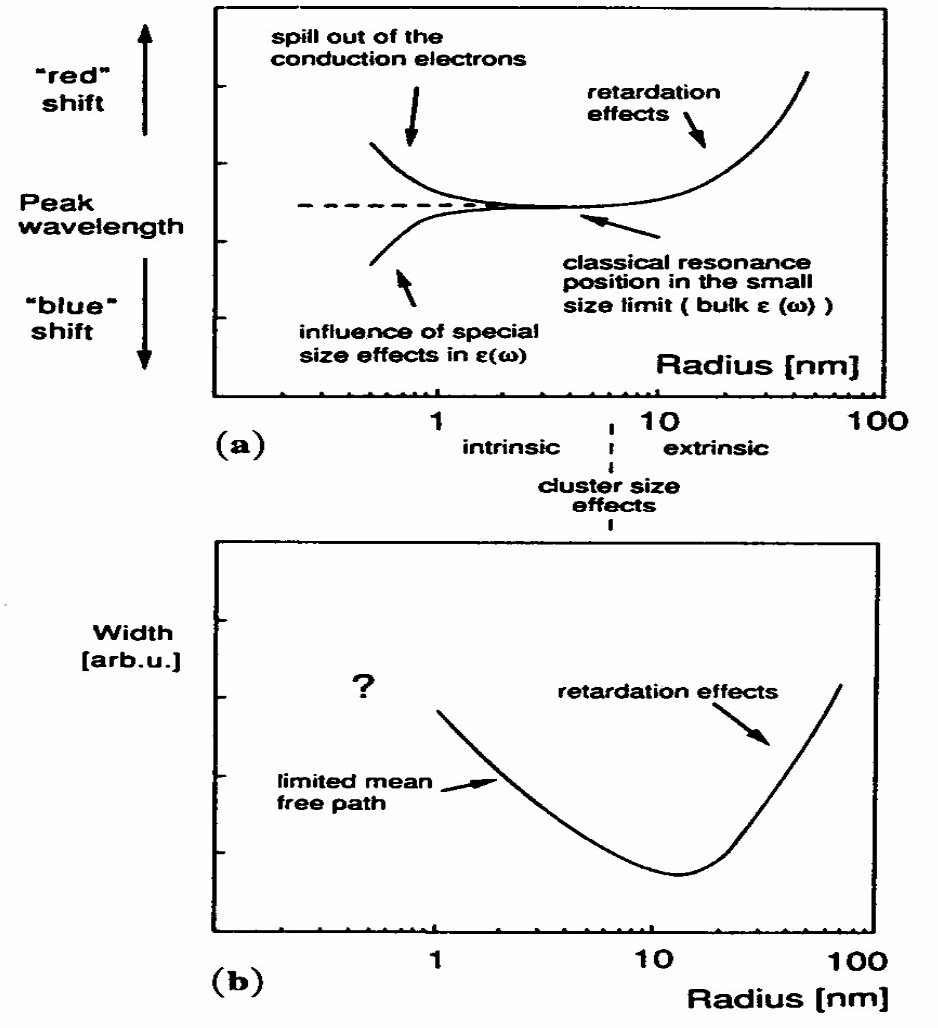
# Spill out


Charge Density
1
0
ion cluster
electron cluster
$Na_8$
radius [a.u.]
8
16
Energy [Ry]
- 0.4
potential
Charge Density
1
0
ion cluster
electron cluster
$Na_{138}$
radius [a.u.]
10
20
30
Energy [Ry]
- 0.4
potential

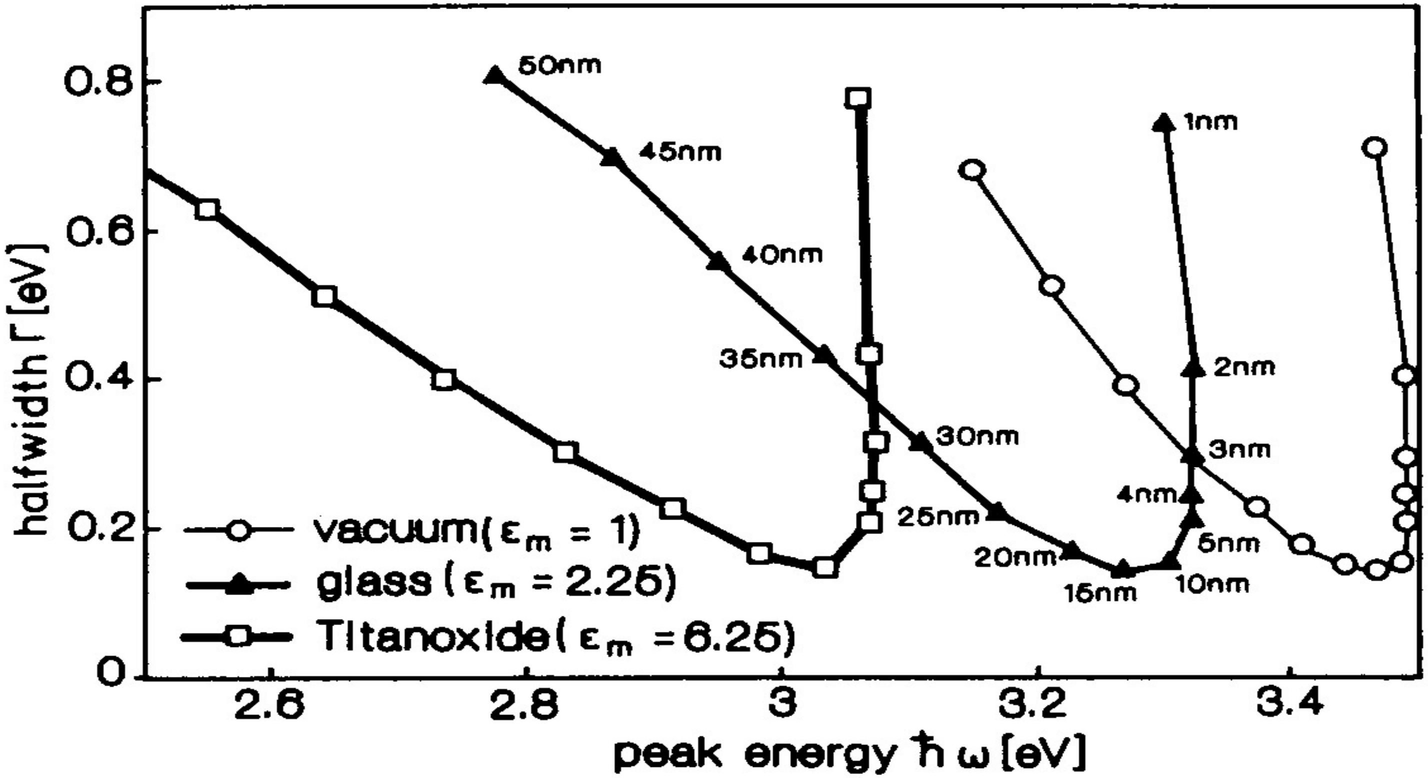
# Size dependence of dielectric function calculated by including the limited mean free path



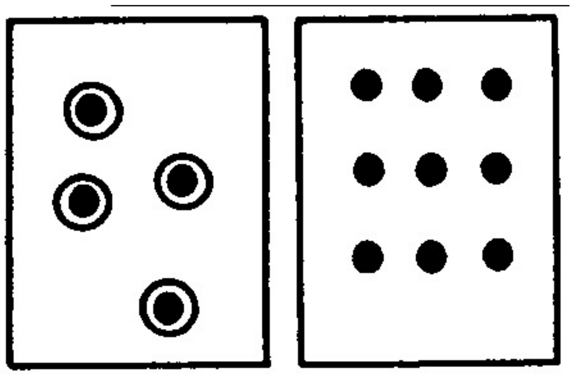
# Schematic dependence of the position and width of the dipolar SPR



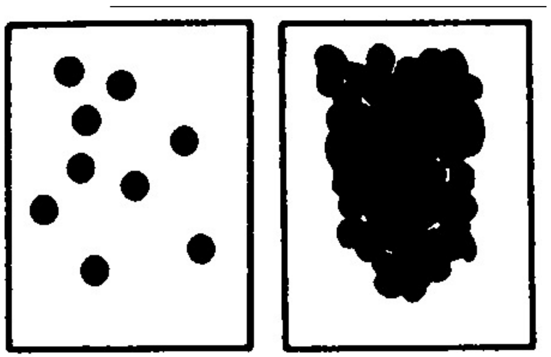
# Half width of the dipolar SPR of silver nanoparticles versus the respective peak energy for several embedding media



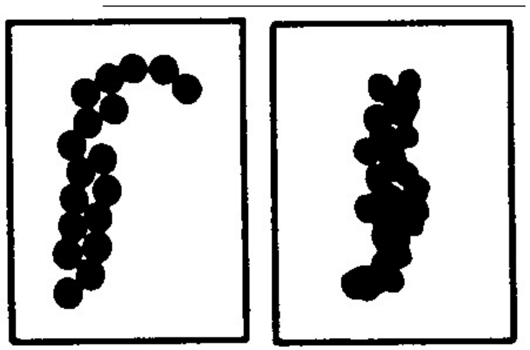
# Nanoparticle matter



core-shell regular topology

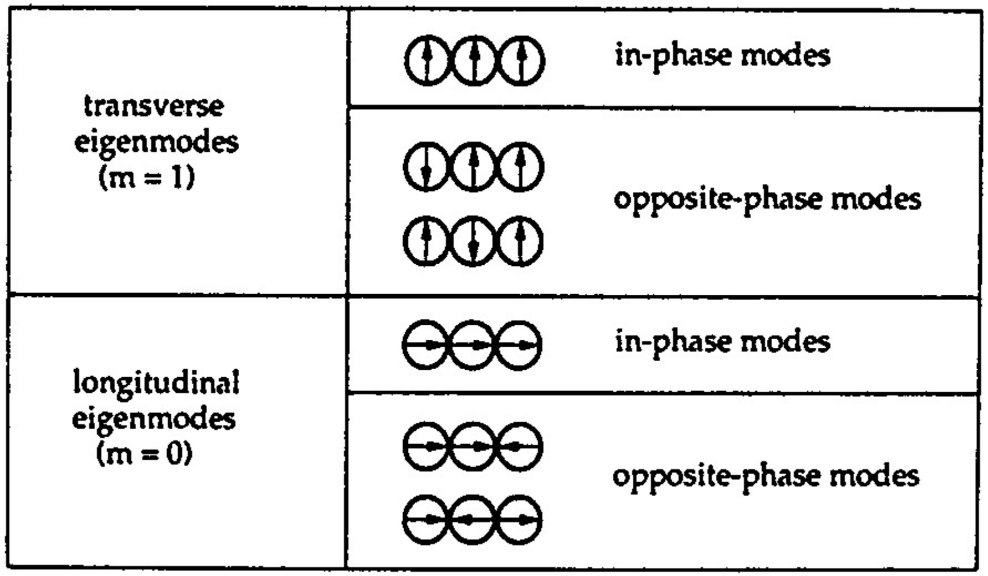


random topology „nugget“

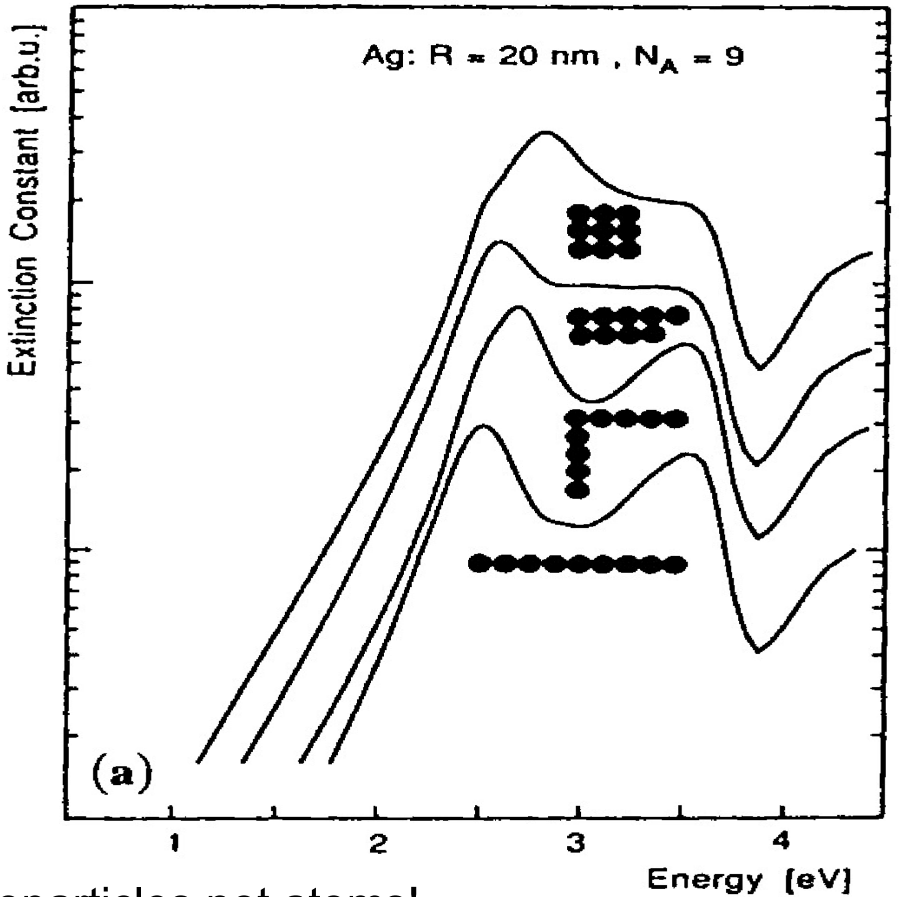


coagullation coalescence

## Eigenmodes of a linear 3-nanoparticle chain




## Extinction spectra for silver nanoparticles of different topologies




Note: depicted are nanoparticles not atoms!

# Absorption spectra and according dielectric functions for two different filling factors