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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"-III

presented by:

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Ultra-Fast Electron Dynamics in Metal Nanoparticles: Principles and Application

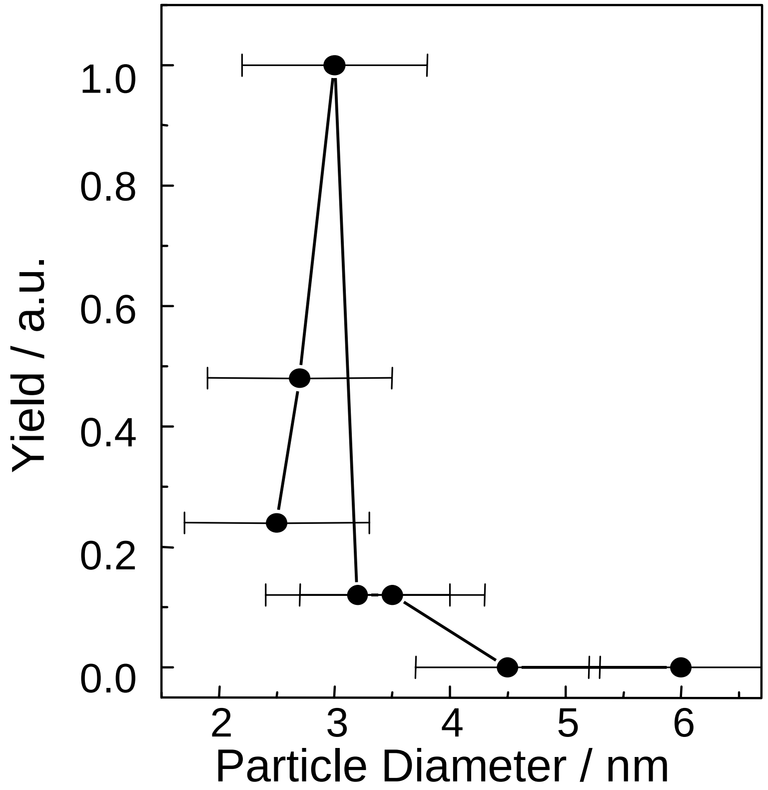
Properties of nanoparticles

How do the physical properties change as a function of particle size and shape?

For example investigation of:

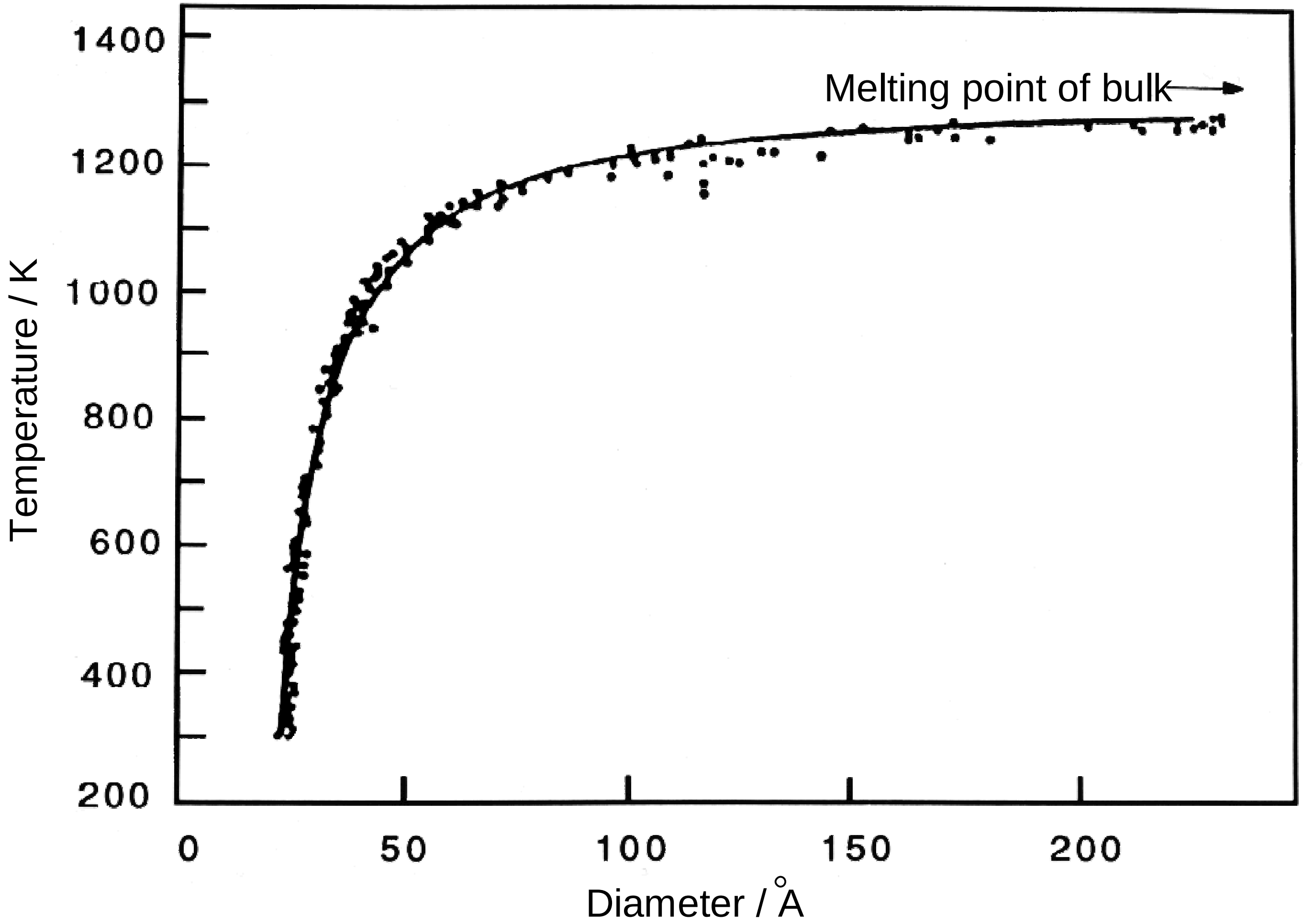
- chemical reactivity
- melting point
- optical spectra

Catalytic oxidation of CO by Au nanoparticles on TiO_2



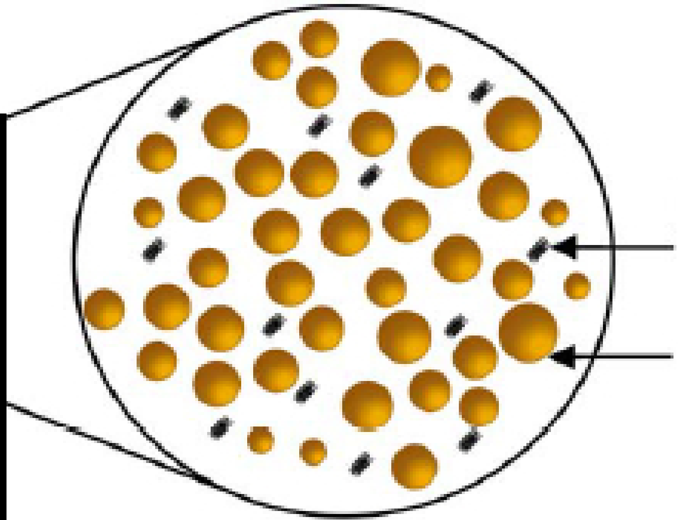
M. Haruta et al., Catal. Lett. **44**, 83 (1997)
D.W. Goodman et al., Science **281**, 1647 (1998)

Melting point of gold nanoparticles



Ph. Buffat, J.-P. Borel, Phys. Rev. A **13**, 2287 (1976)

Window from the Altenberger dome



The Lycurgus Cup

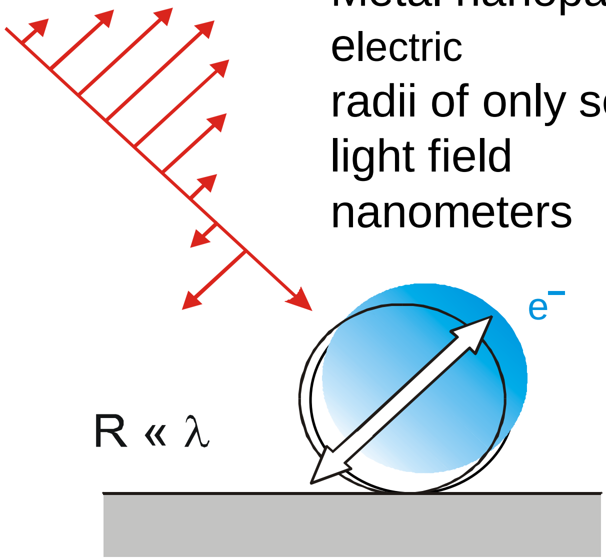
The Lycurgus Cup
(4th century AD)

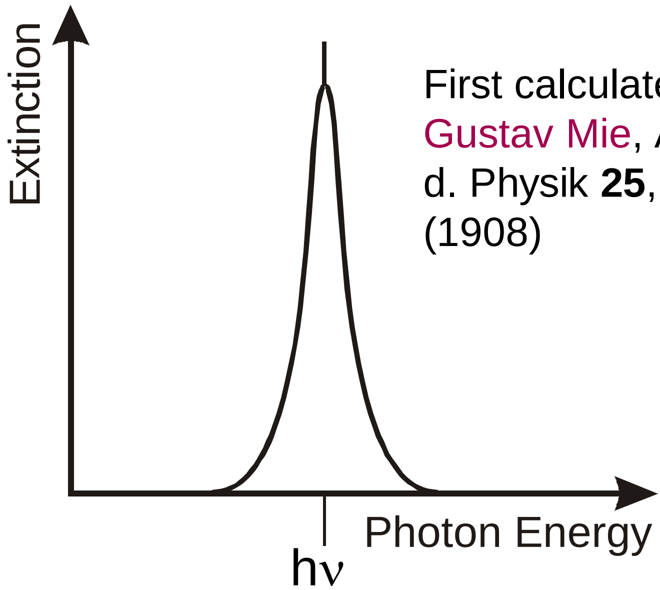
The British Museum, London

Gold Nanoparticles

The surface plasmon polariton

Metal nanoparticles with
electric
radii of only several
light field
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:

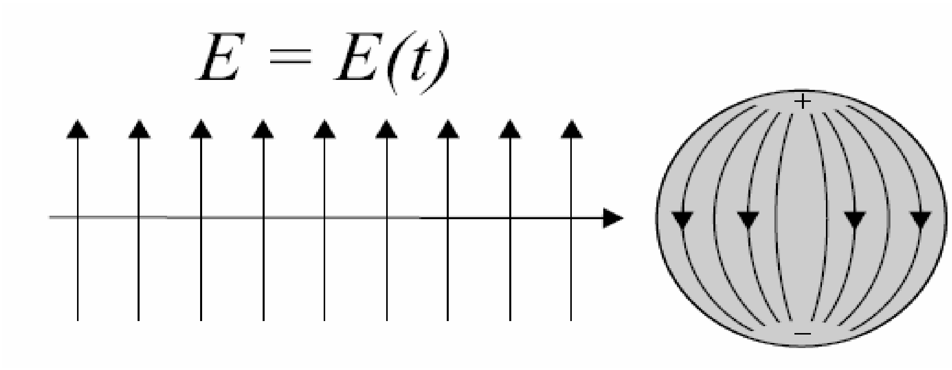
- material
- dielectric surrounding
- dimensions of the particles

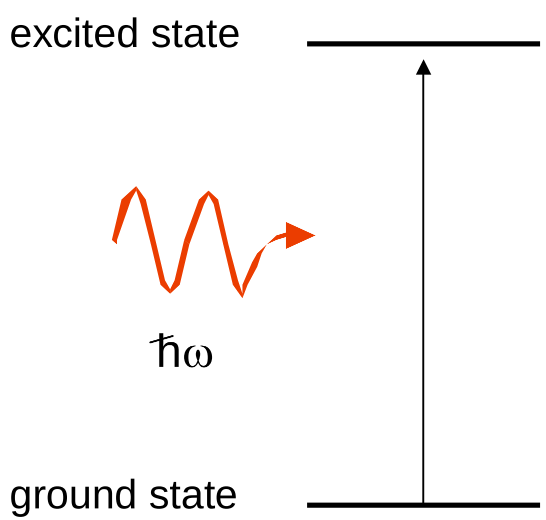
Excitation of the surface-plasmon-polariton

Surface-plasmon-polariton

collective oscillation of the electrons

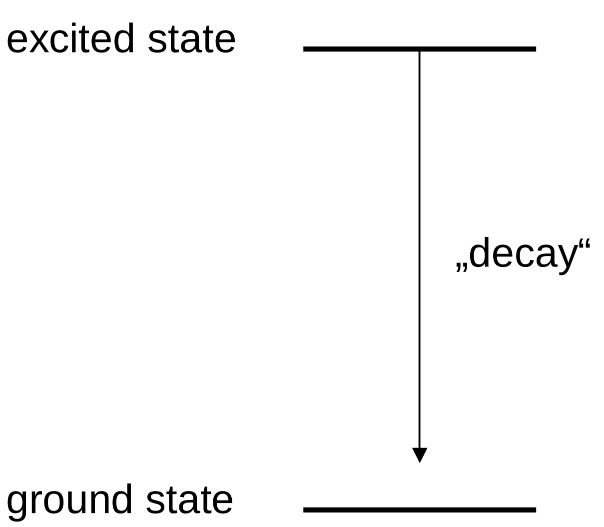
quasi-particle / electronic transition





The two-level-system

Two-level system



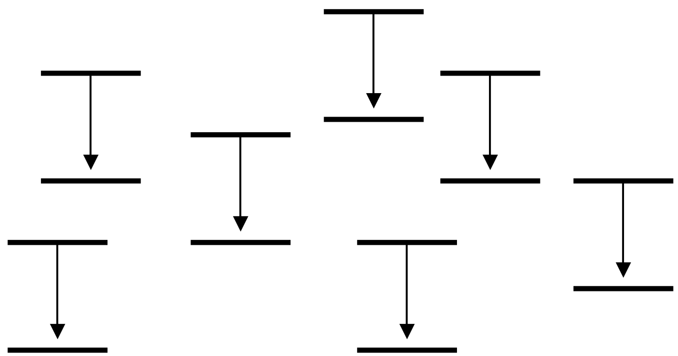
- Transition to the ground state has a natural linewidth Γ_{hom}
- Excited state has a life time τ

$\Rightarrow$ Both are connected by the uncertainty relation:

$$\Gamma_{\text{hom}} = \frac{\hbar}{\tau}$$

Ensemble of two-level-systems

Ensemble of two-level-systems
or a set of oscillators



- Longitudinal relaxation time T_1:

  Relaxation of the stored energy

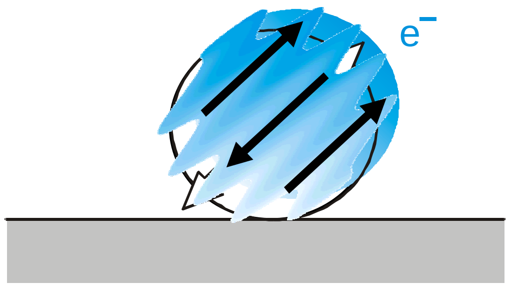
- Transversal relaxation time T_2:

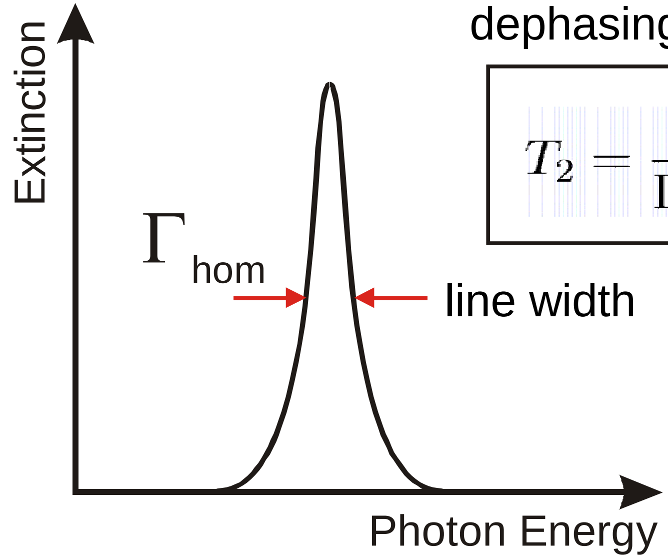
  Loss of phase coherence between the single osciallators

The decay of the surface plasmon polariton

Collective oscillation of conduction electrons

"dephasing"





dephasing time

$$T_2 = \frac{2\hbar}{\Gamma_{hom}}$$

Definition of the dephasing time

- time, in which the collective oscillation of the electrons gets out of phase

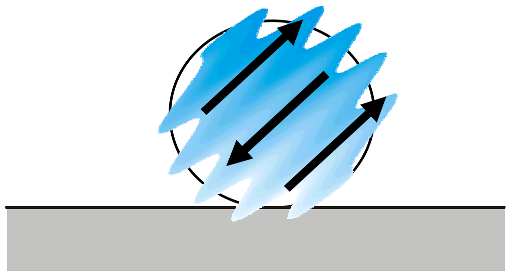
Measurement of T_2

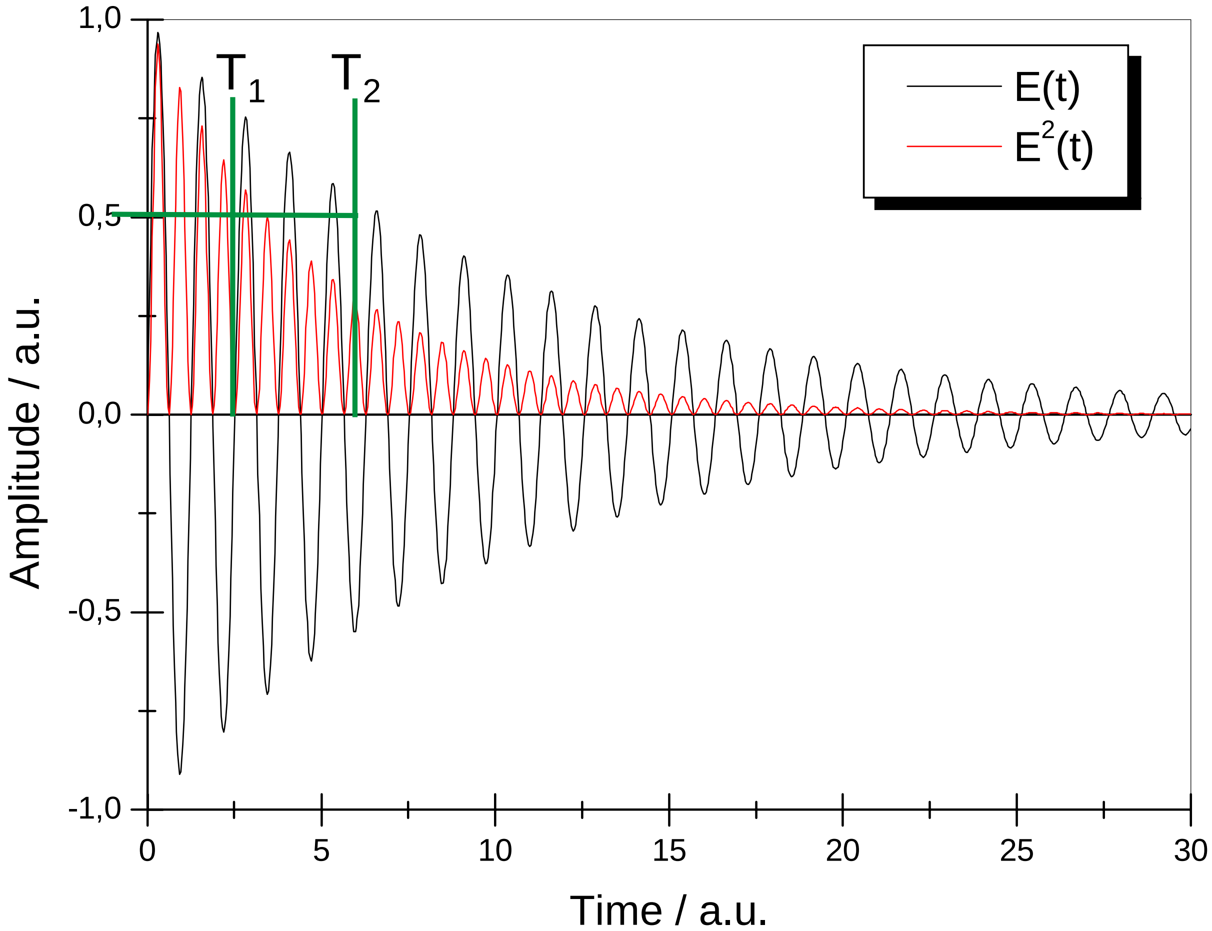
- clarify the role of different damping mechanisms
- optimize applications which are based on field enhancement

$f \sim T_2$

Definition of dephasing time

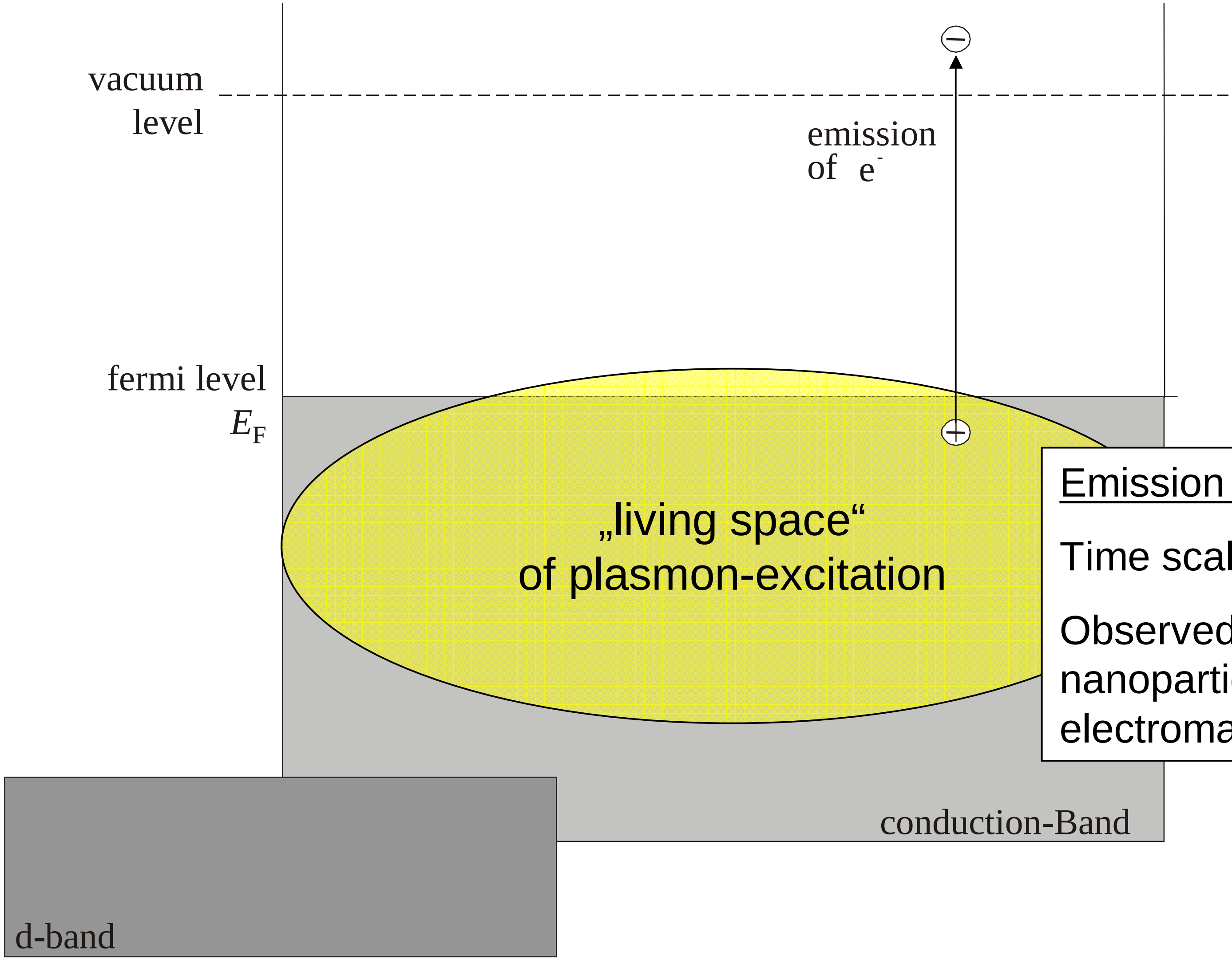
“dephasing“ of the collective oscillation





T_1 is connected with T_2: $T_2 = 2T_1 \Rightarrow$ $T_2 = \frac{2\hbar}{\Gamma_{\mathrm{hom}}}$

Damping mechanisms of the SPP

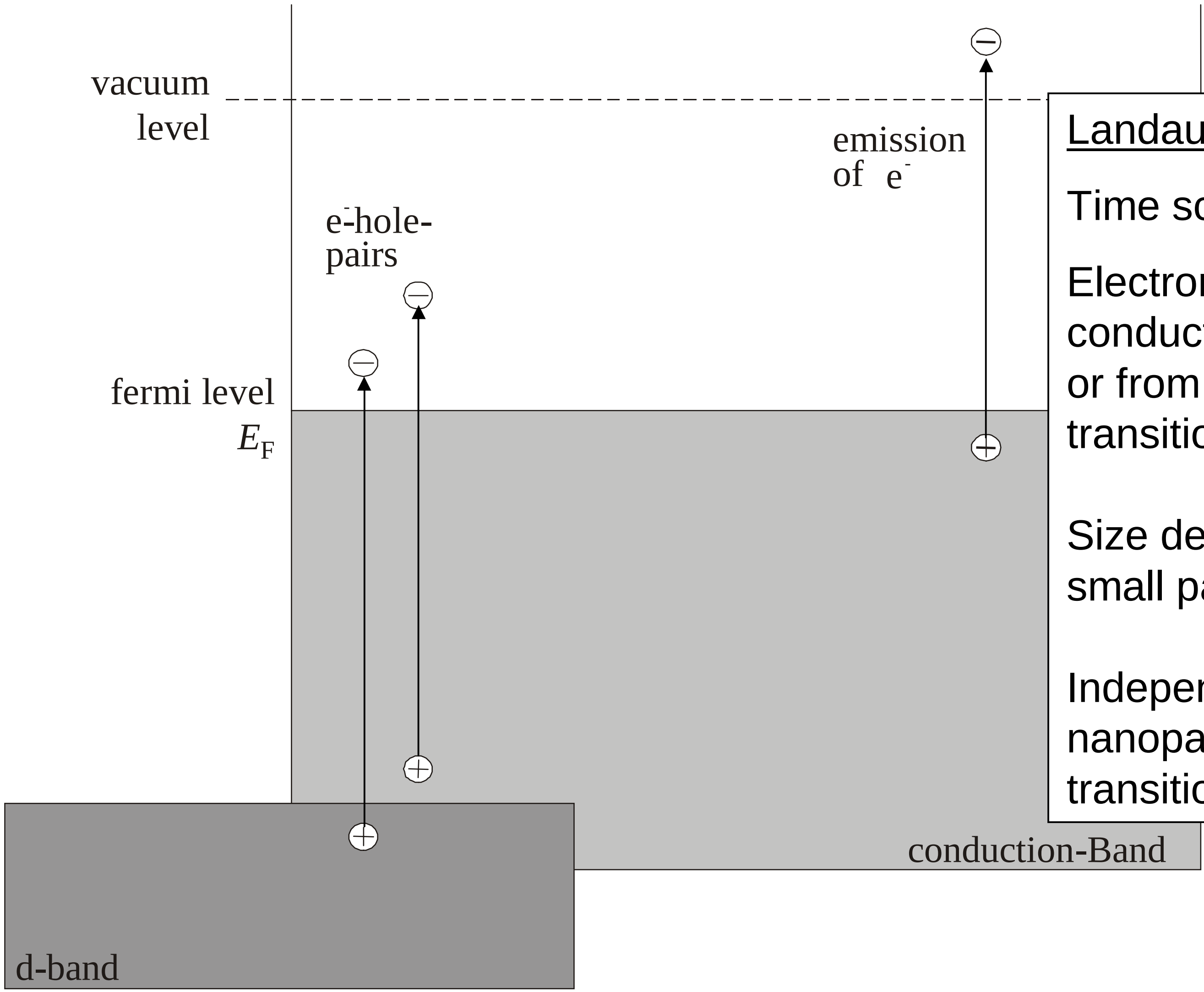


Emission of electrons:

Time scale 4 fs

Observed only for small nanoparticles and very high electromagnetic fields

Damping mechanisms of the SPP



Landau-Damping:

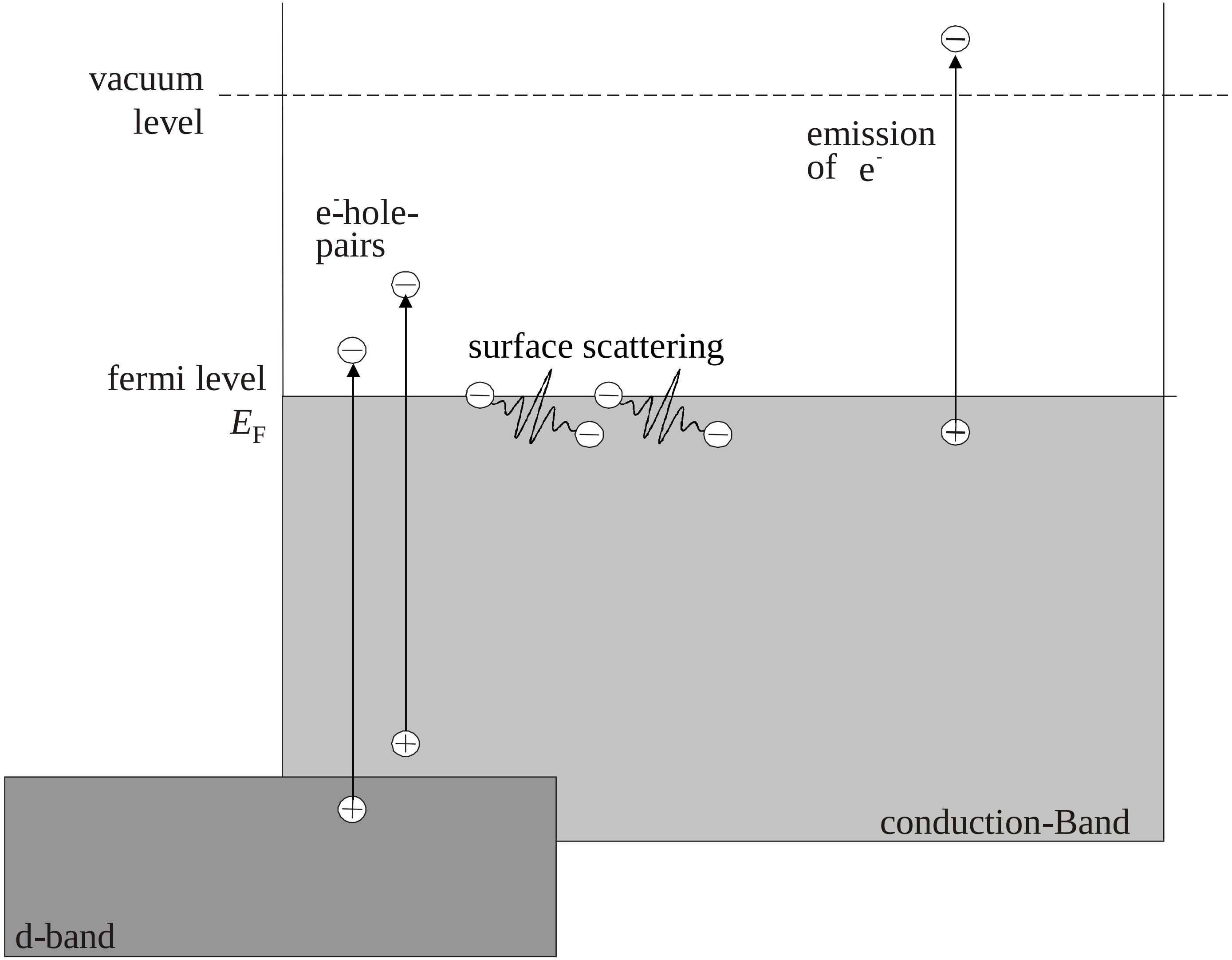
Time scale 6 - 20 fs

Electron-hole-pairs, within the conduction band (intraband transition) or from the d-band (interband transition).

Size dependent for small particles: $$\frac{1}{T_{2,\,\mathrm{Landau}}(R)} = \frac{A_{\mathrm{Landau}}}{R}$$

Independent of size for larger nanoparticles, where the band transitions are dominating.

Damping mechanisms of the SPP



Damping mechanisms of the SPP

Surface scattering:

Time scale 4 - 12 fs

Scattering of electrons at the particle surface. $1/T_2 \sim R^2 / R^3$

Depends on the velocity and free length of path of the electrons at the Fermi-level:

$$\frac{1}{T_{2,\,\mathrm{Surf}}(R)} = \frac{v_\mathrm{F}}{2}\left(\frac{1}{l_\infty} + \frac{\alpha_\mathrm{Surf}}{R}\right) = \frac{1}{T_{2,\,\mathrm{Drude}}^{\infty}} + \frac{A_\mathrm{Surf}}{R}$$

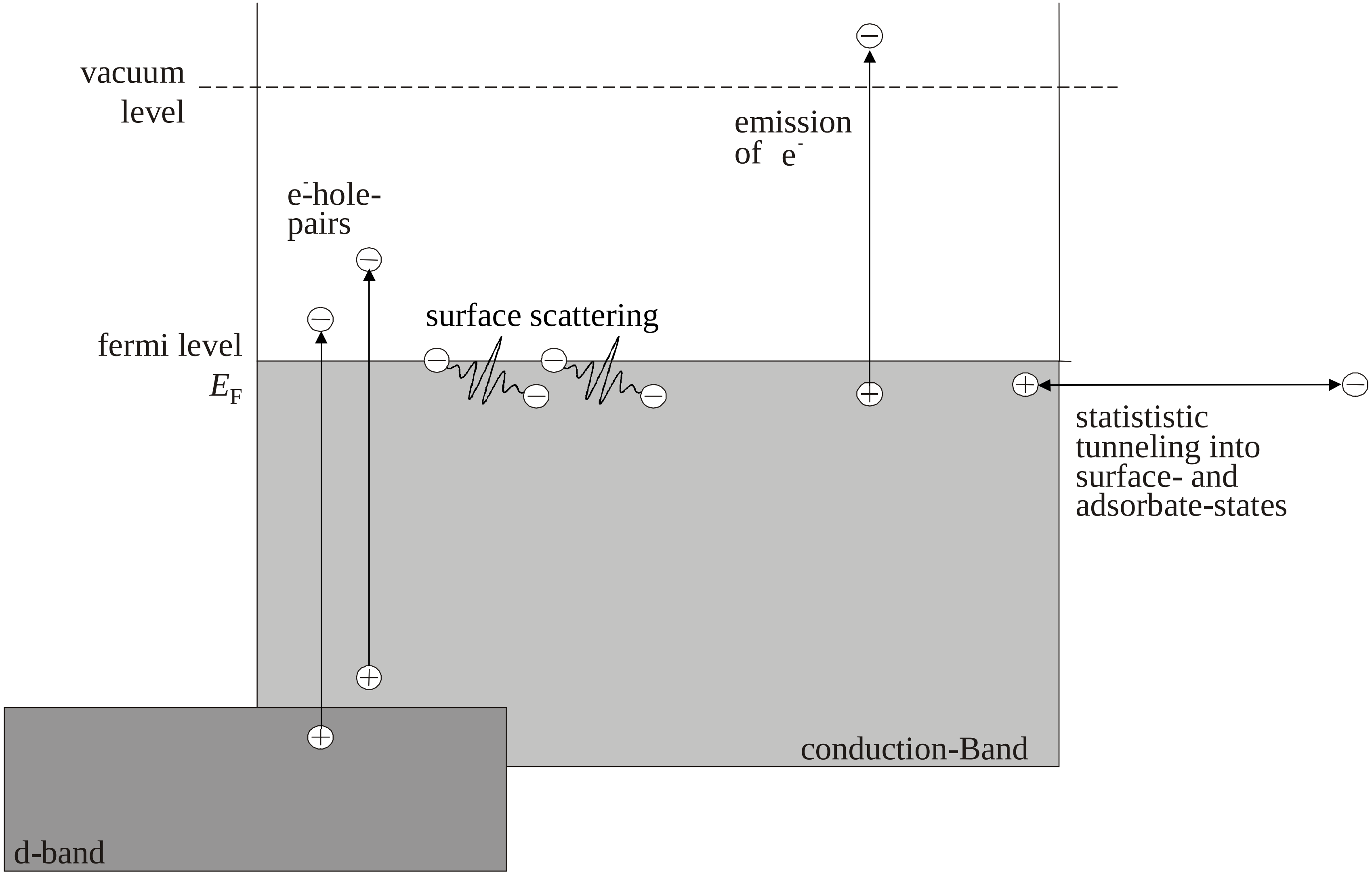
With α_{surf}=1 one obtains for gold:

$$A_\mathrm{Surf} = 0{,}7\,\frac{\mathrm{nm}}{\mathrm{fs}}$$

Result from quantum mechanics calculation for gold [Persson93]:

$$A_\mathrm{Surf}^\mathrm{Persson} \approx 0{,}2\,\frac{\mathrm{nm}}{\mathrm{fs}}$$

Damping mechanisms of the SPP



Damping mechanisms of the SPP

Chemical interface damping:

Time scale 3,5 - 5 fs

Interaction of the plasmon with the surrounding medium

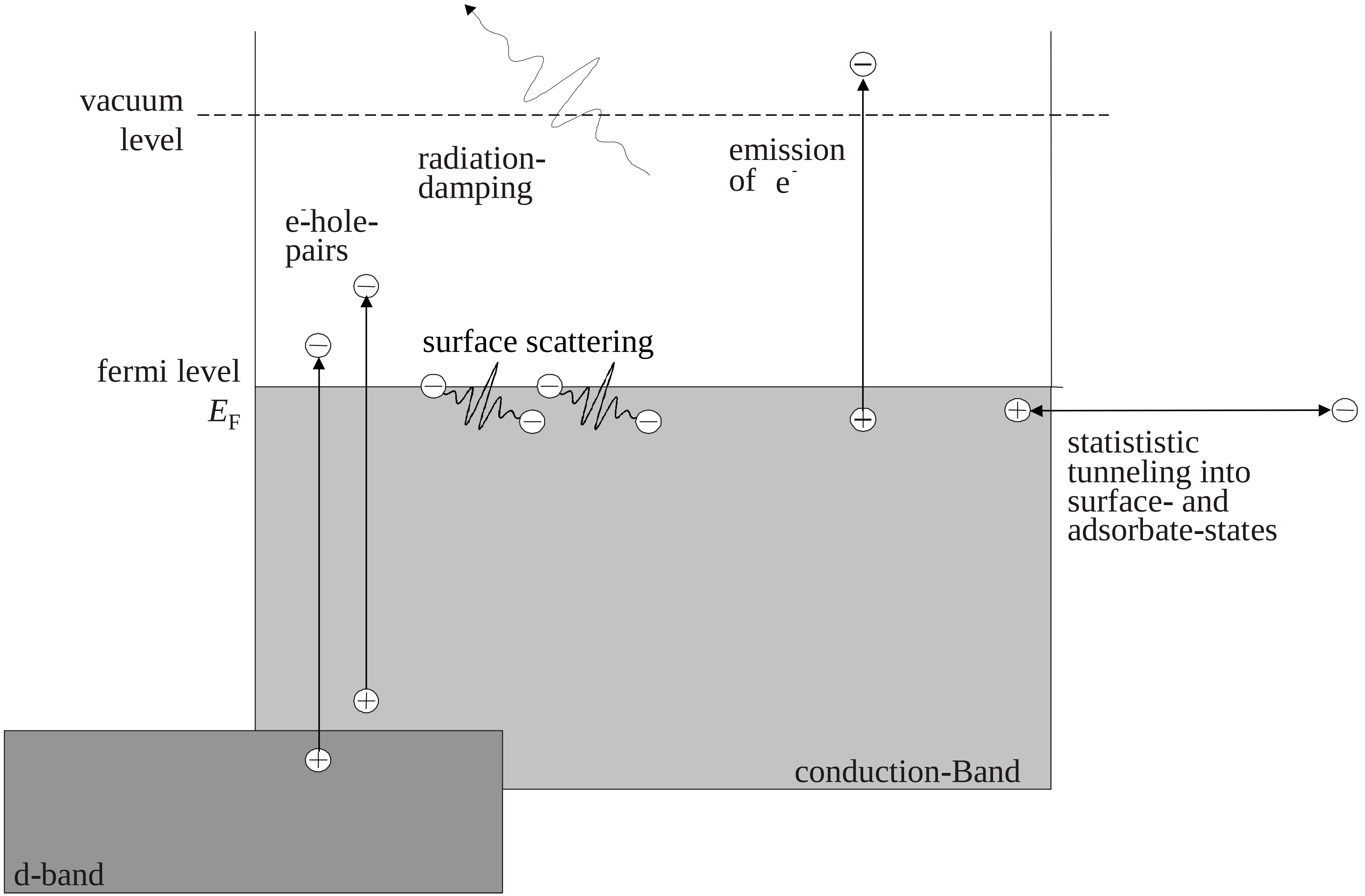
Static transfer of electrons in adsorbates changes density of states near fermi-level

Statistic tunneling into and out of adsorbate states

Depends on the surface of the particle, therefore a size dependence is expected

$$\frac{1}{T_{2,\mathrm{CD}}(R)} = \frac{A_{\mathrm{CD}}}{R}$$

Damping mechanisms of the SPP



Damping mechanisms of the SPP

Radiation damping:

Time scale 1 - 40 ps

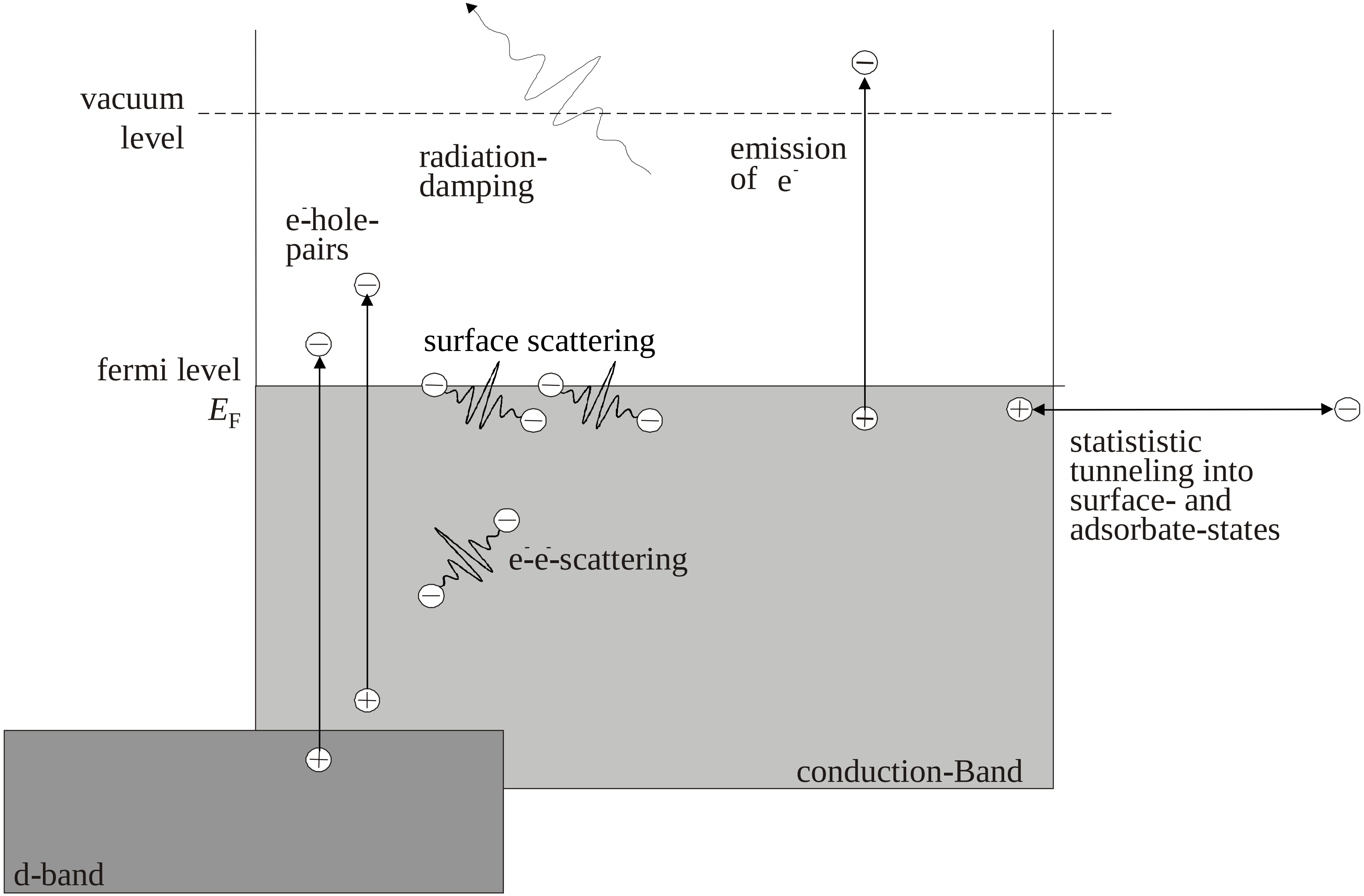
Emission of a photon destroys the plasmon completely

Calculations show that the inverse dephasing time is proportional to particle volume:

$$\frac{1}{T_{2,\mathrm{Rad}}(R)} = \frac{1}{3}\frac{\Omega^4 R^3}{c^3}$$

Radiation damping is directly connected to the scattering cross section by the Mie-theory.

Damping mechanisms of the SPP



Damping mechanisms of the SPP

Electron-Electron-Scattering:

Time scale 400 - 650 fs

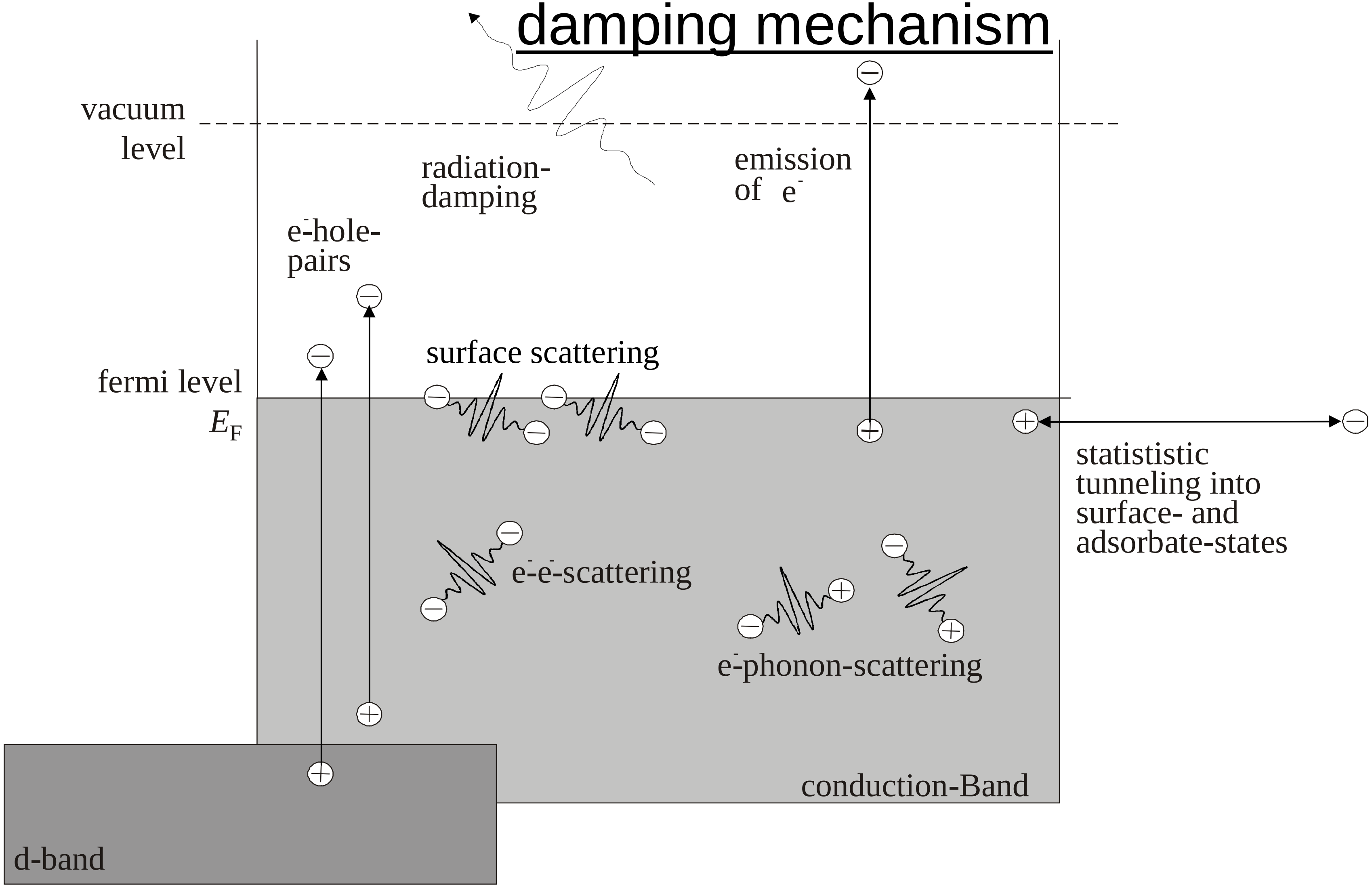
Interaction of electrons among each other.

Scattering probability depends strongly on electronic temperature.

At a temperature of 4000 K (excited by a fs-laser) the time scale of dephasing drops down to 10 fs.

Electron-Electron-interaction will increase for small nanoparticles, because the wavefunctions of the electrons can exceed the dimensions of the nanoparticles (so called „spill-out“).

Damping mechanisms of the SPOverview of the damping mechanism



Damping mechanisms of the SPOverview of the damping mechanism

Electron-Phonon-Scattering:

Time scale 1 ps

Follows all other damping mechanisms.

Scattering at the lattice of atoms, i.e. at phonons.

Energy-transfer to the lattice depends on electronic and lattice temperature.

Size dependence is caused by spillout of electronic wave functions (change in the screening of the ions).

Overview of the damping mechanism

	R = 3 nm	R = 10 nm	R = 30 nm
Emission of electrons[1]	4 fs		
From free electron gas (Drude)	29 fs	29 fs	29 fs
Landau damping[2,3]	6.1 fs	20.4 fs	61.2 fs
Surface scattering	4 fs	11.4 fs	24.6 fs
chemical interface damping[4]	3.5 fs	5 fs	
Electron-electron scattering[5]	400 fs	650 fs	
Radiation damping[2]	48 ps	1.3 ps	48 fs
Electron-phonon scattering[6]	1.2 ps		2.2 ps

[1]Calculation for small nanoparticles and high field power [Cal00, Ull98], [2]at a plasmon energy of 1.85 eV, [3]size dependent part, [4]experimental values for silver-nanoparticles/quartz [Bos02b], [5]silver-nanoparticles:sapphire [Voi00], [6]experimental values [Arb03]

Influence of the dimension on the dephasing time

- Drude theory: In the bulk material, electrons at the Fermi-level have a velocity v_F and have a mean free path of l_∞. The mean scattering rate is determined by:

$$\Gamma = \frac{v_F}{l_\infty}$$

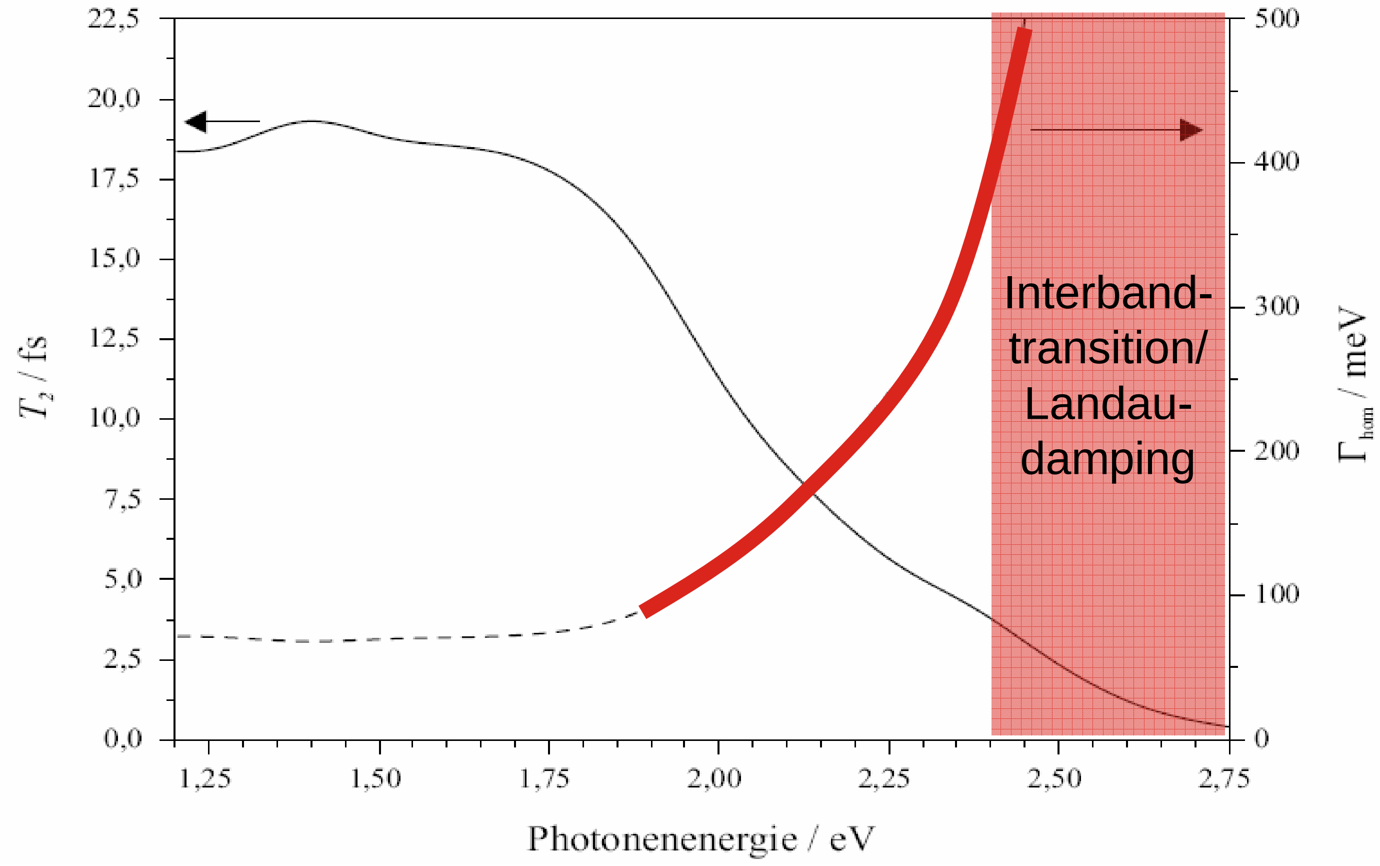
- For particles smaller than , the scattering rate is influenced by the nanoparticle surface and, thus the stray rate with the surface $\Delta\Gamma$ is proportional to the surface per electron:

$$\Delta\Gamma = \frac{A}{N} \propto \frac{4\pi R^2}{\frac{4}{3}\pi R^3} \propto \frac{\boldsymbol{A}}{R}$$

Dephasing times from electronic properties of the bulk

Calculation from the bulk dielectric function
(ε_1=real part, ε_2=imaginary part)

$$\Gamma(\Omega) = \frac{2\hbar\varepsilon_2(\Omega)}{\left|\frac{d\varepsilon_1(\omega)}{d\omega}\Big|_{\omega=\Omega}\right|}$$



Size dependent dielectric function

Assumption: Nanoparticle material can described as Drude-Metall

$$\varepsilon = \varepsilon_{\mathrm{frei}} + \varepsilon_{\mathrm{gebunden}}$$

The quasi-free electrons dominate the plasmon

$$\varepsilon_{\mathrm{frei}} = 1 - \frac{\omega_{\mathrm{p}}^2}{\omega(\omega + i/\tau)}$$

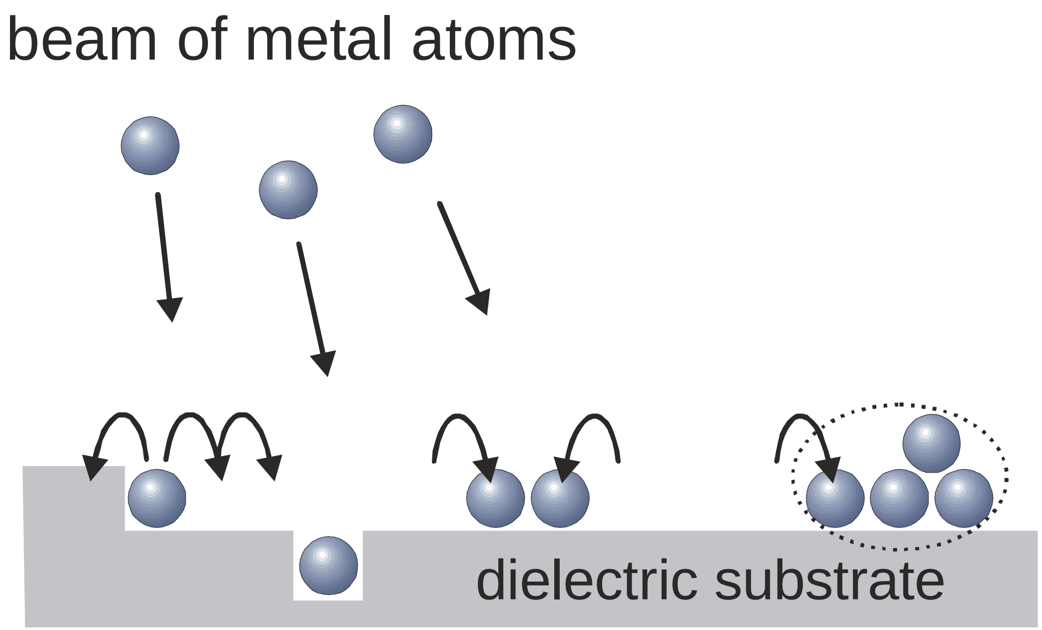
Size dependence can be introduced by 1/R-term

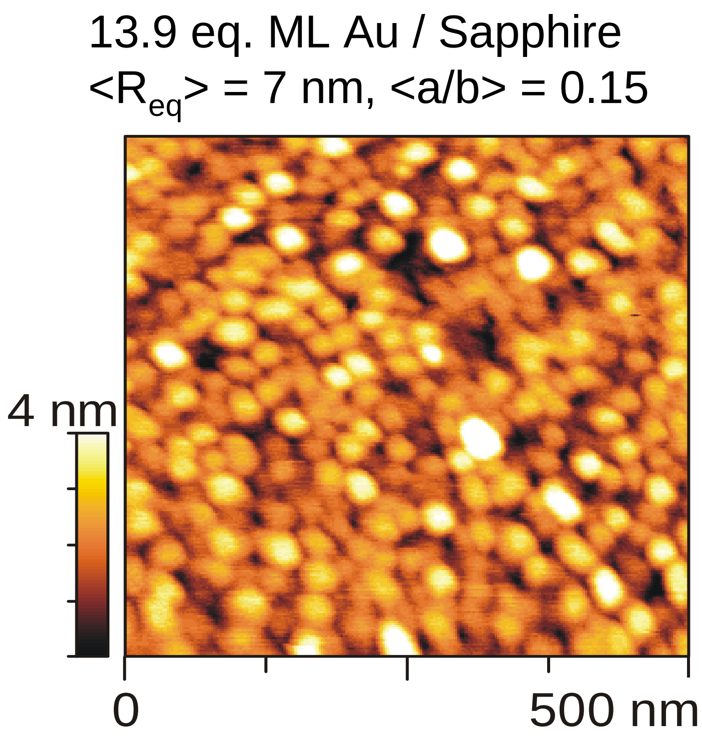
$$\frac{1}{\tau} = \frac{1}{\tau^{\infty}} + \frac{A}{R}$$

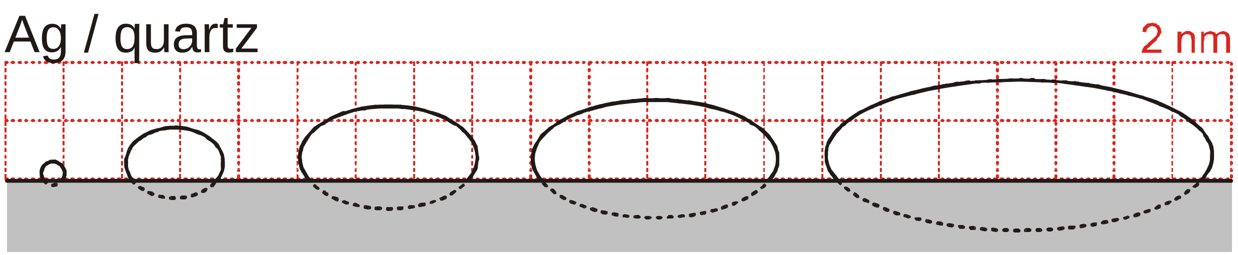
Final result: Size dependent dielectric function

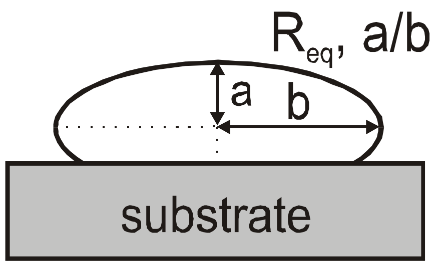
$$\varepsilon = \varepsilon_{\mathrm{gebunden}} + 1 - \frac{\omega_{\mathrm{p}}^2}{\omega\left[\omega + i\left(\frac{1}{\tau^{\infty}} + \frac{A}{R}\right)\right]}$$

Volmer-Weber-growth



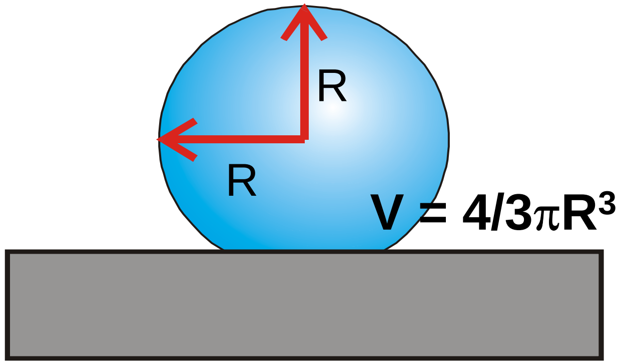




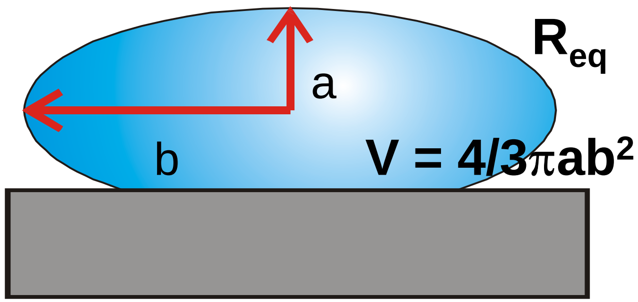


Mean radius of particles on surfaces

spherical particles

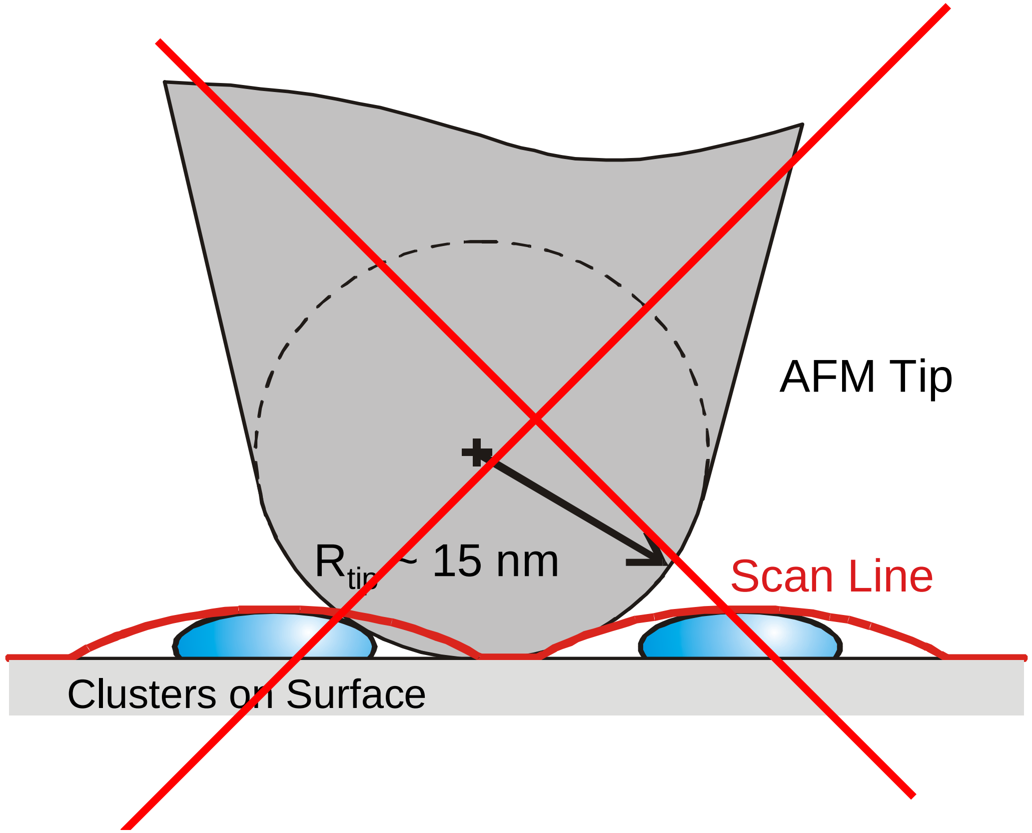


oblate particles
(rotational ellipsoids)

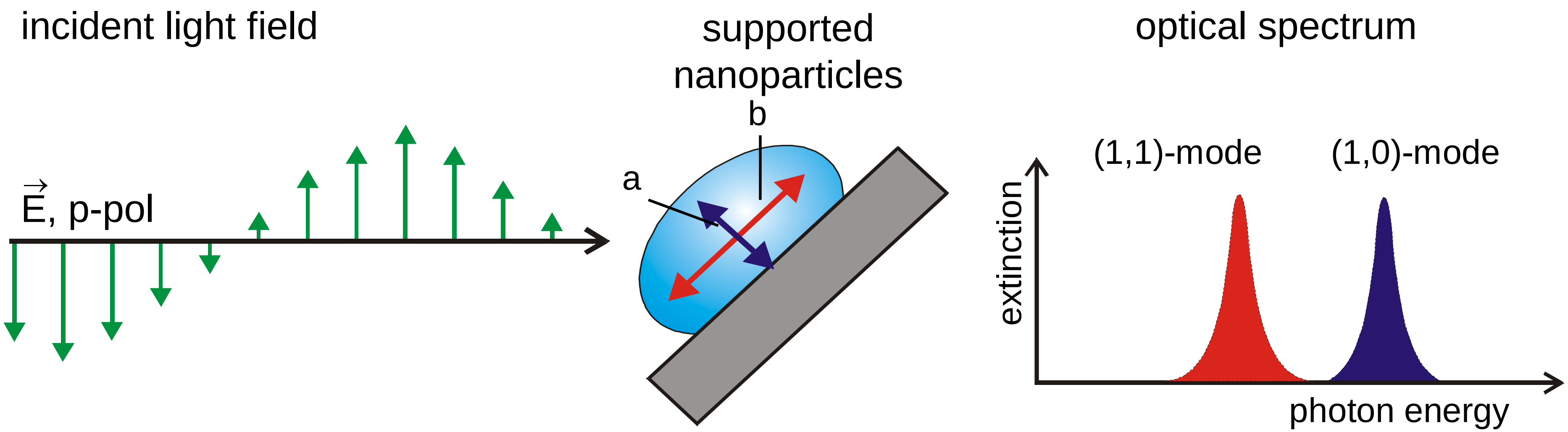


Particles are characterized by

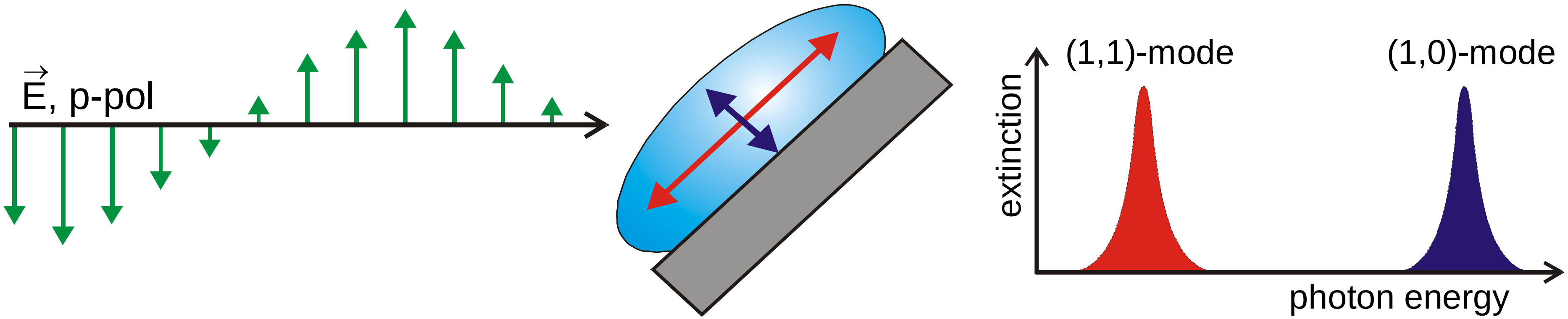
1. equivalent radius R_{eq}
2. axial ratio a/b



Surface plasmons of non-spherical particles

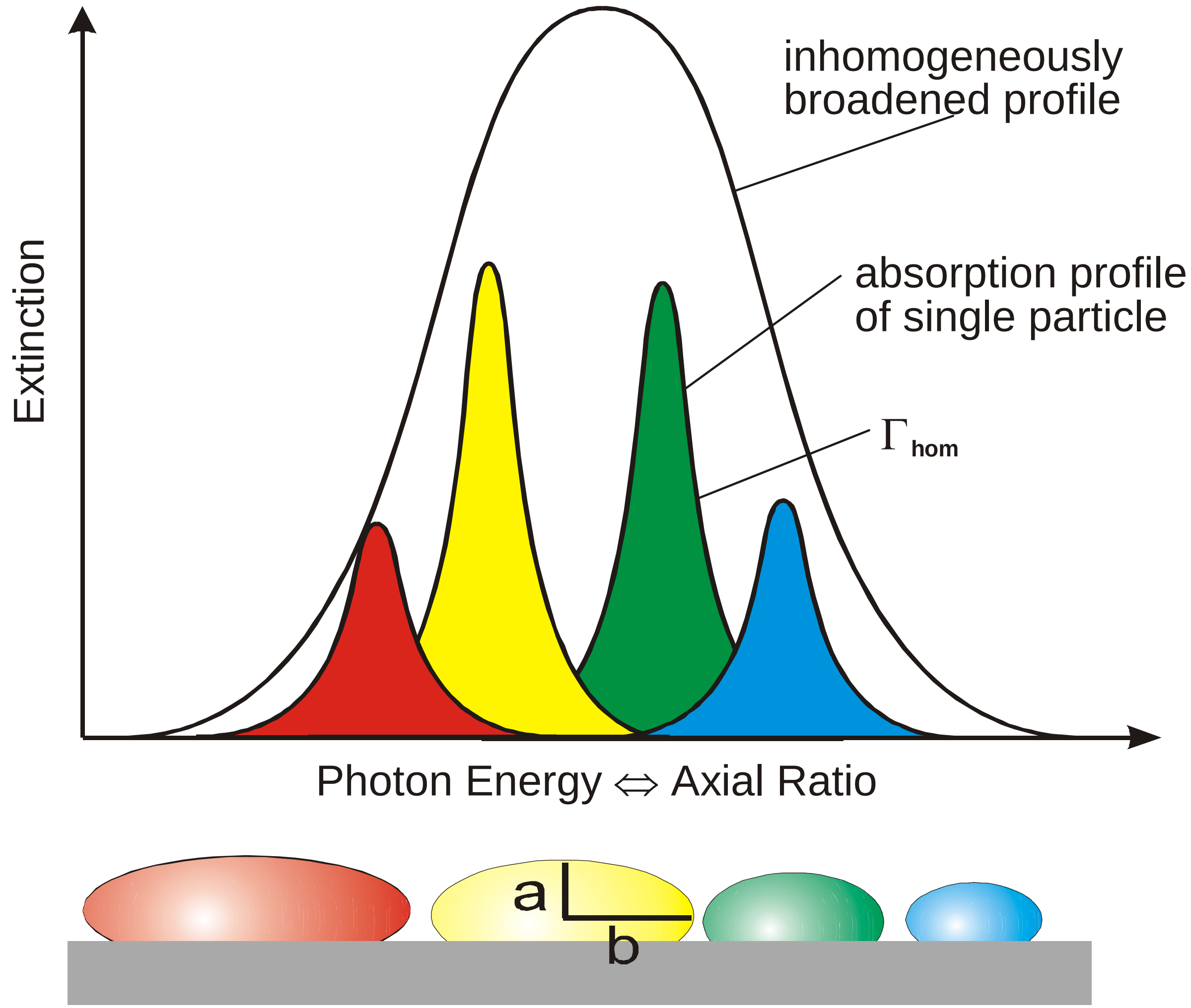


axial ratio: a_1/b_1



axial ratio: $a_2/b_2 < a_1/b_1$

Optical properties of a nanoparticle ensemble



Amount of inhomogeneous broadening is not known

⇒ Γ_{hom} and T_2 cannot be determined from the optical spectra

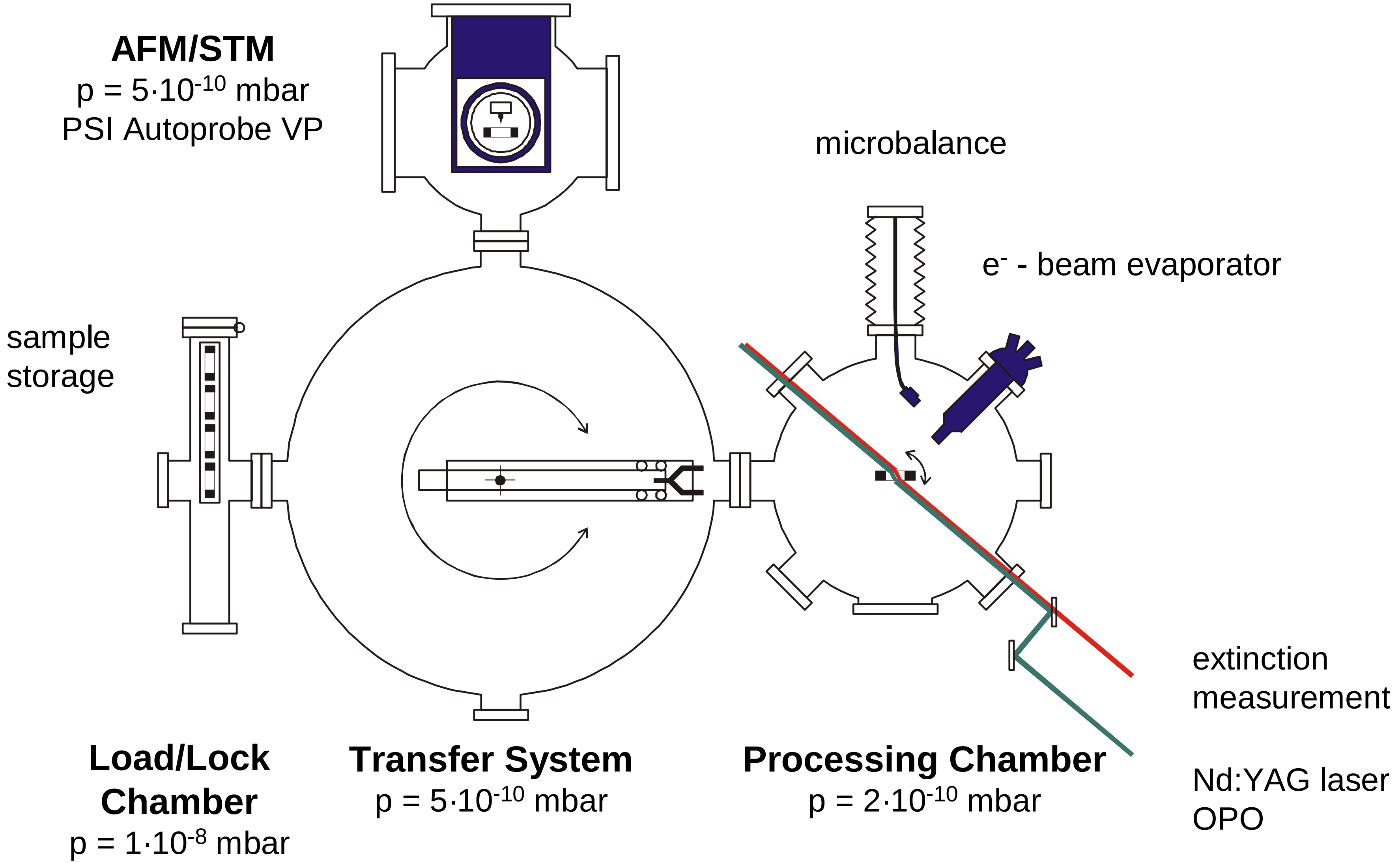
Inhomogeneous line broadening of the surface plasmon resonances of ensembles of nanoparticles can be exploited to

1. Measure the homogeneous linewidth and the dephasing time of surface plasmon excitation, i.e. examine the ultrafast electron dynamics in metal nanoparticles by persistent spectral holeburning

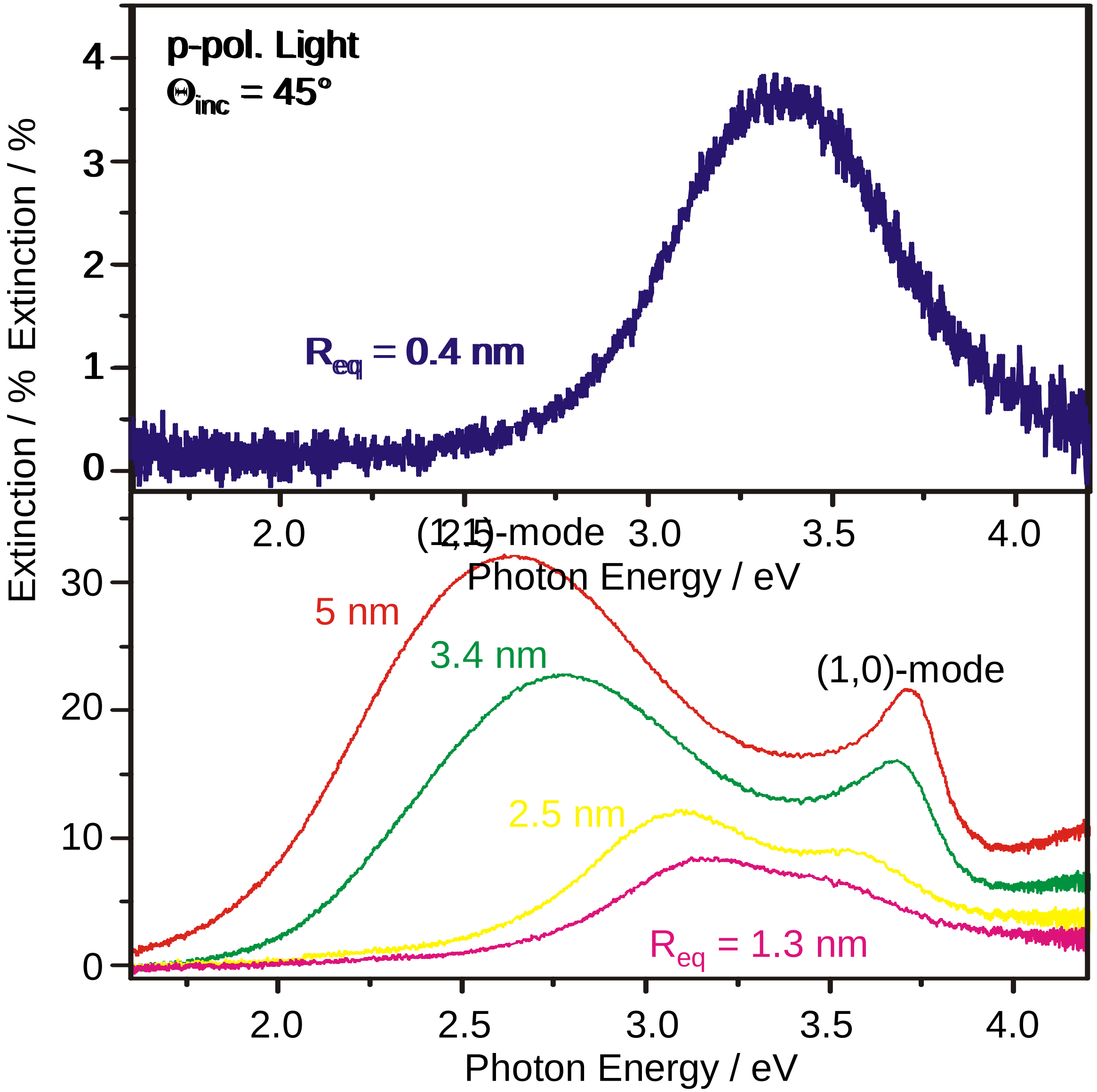
2. Tailormake nanoparticles with a predetermined size and a very narrow size distribution

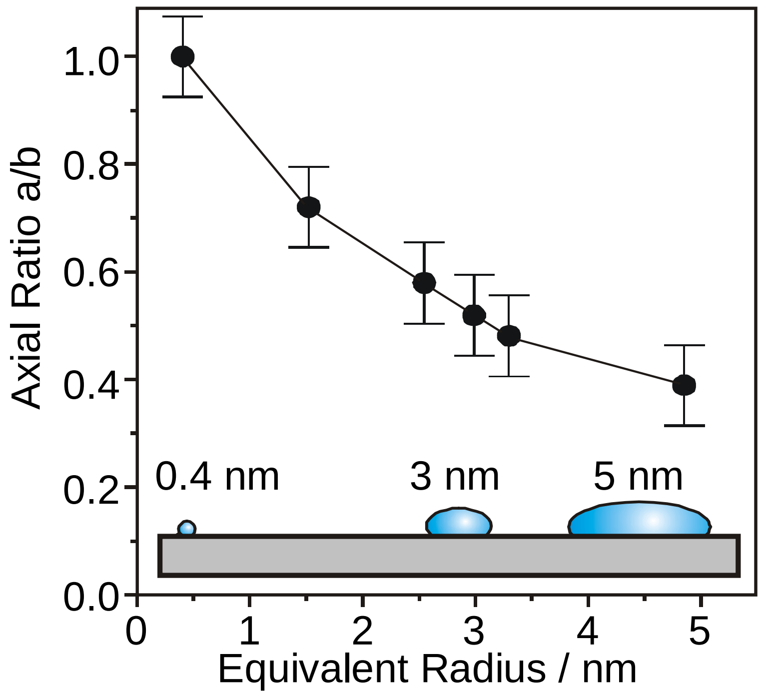
3. Measure the properties of metal nanoparticles, e.g. the chemical reactivity, as a function of size by spectral holeburning

Experimental setup



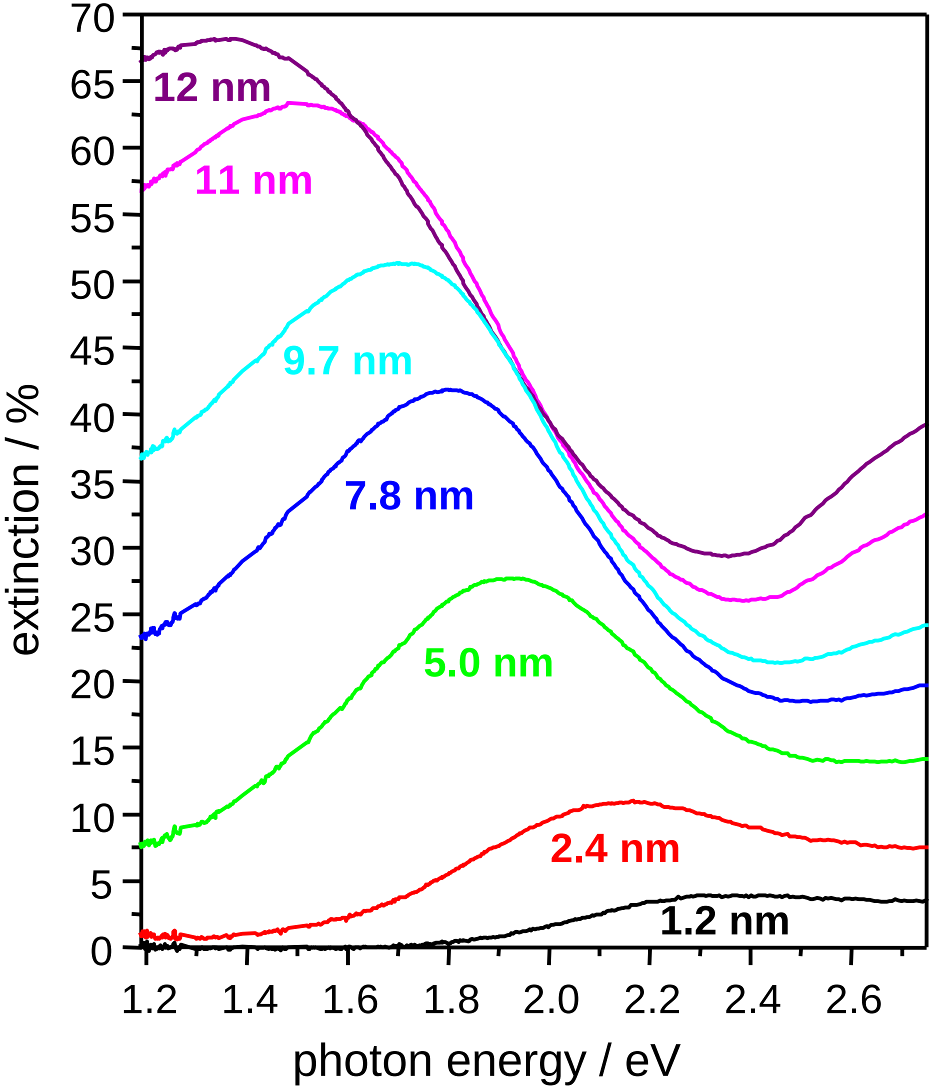
Ag nanoparticles on quartz

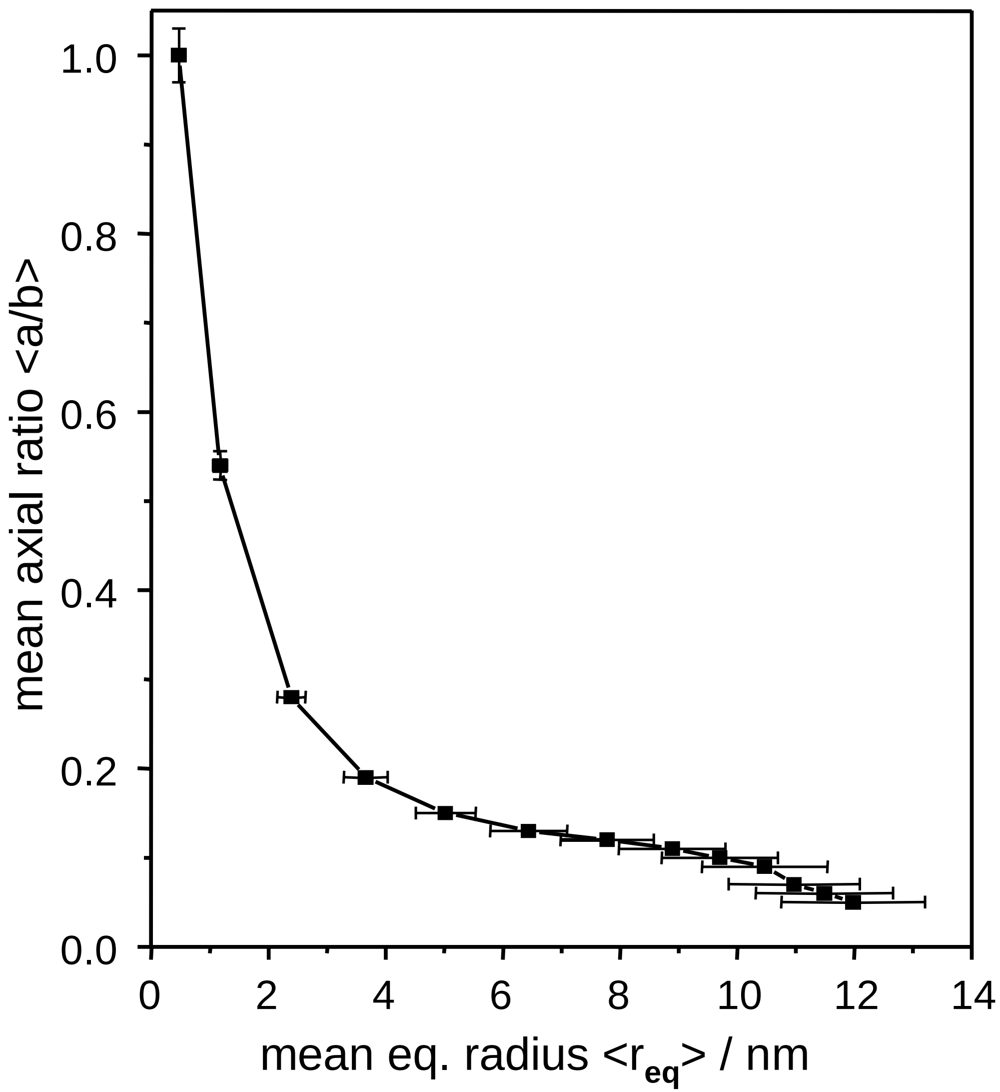




T. Wenzel, J. Bosbach, F. Stietz, F. Träger, Surf. Sci. **432**, 257 (1999)

Au/Sapphire: Natural particle growth





Methods to determine the homogeneous line width

a) Spectroscopy of single particles

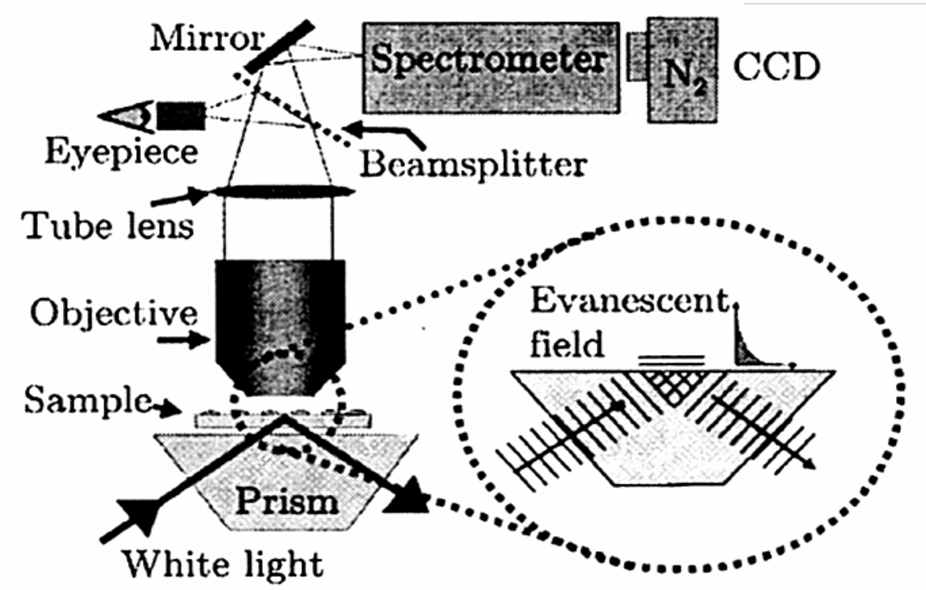
- no inhomogeneous broadening
- limited to particles with R_{eq} > 15 nm
- no defined chemical environment

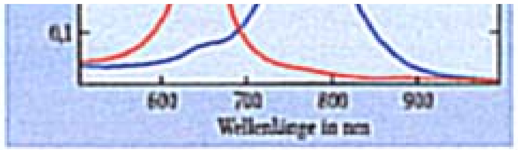
b) Spectroscopy with nanoparticle arrays with narrow size and shape distribution

- small inhomogeneous broadening
- dipole-dipole interaction controllable
- limited to particles with R_{eq} > 40 nm

c) Autocorrelation measurements

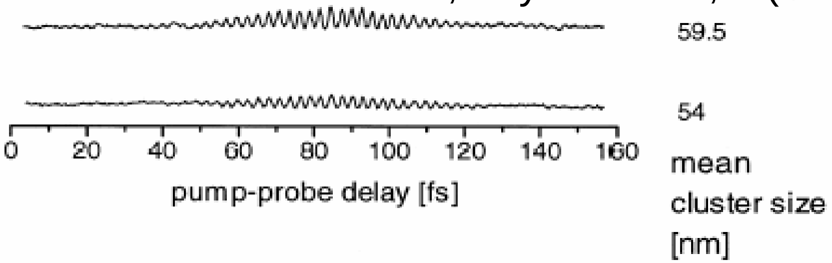
- inhomogeneous broadening causes a narrowing of the autocorrelation traces





C. Sönnichsen et al., Appl. Phys. Lett. **77**, 19 (2000)

J. R. Krenn et al., Phys. Jour. **1**, 3 (2002)



M. Simon, F. Träger, A. Assion, B. Lang, S. Voll, G. Gerber, Chem. Phys. Lett. **296**, 579 (1998)

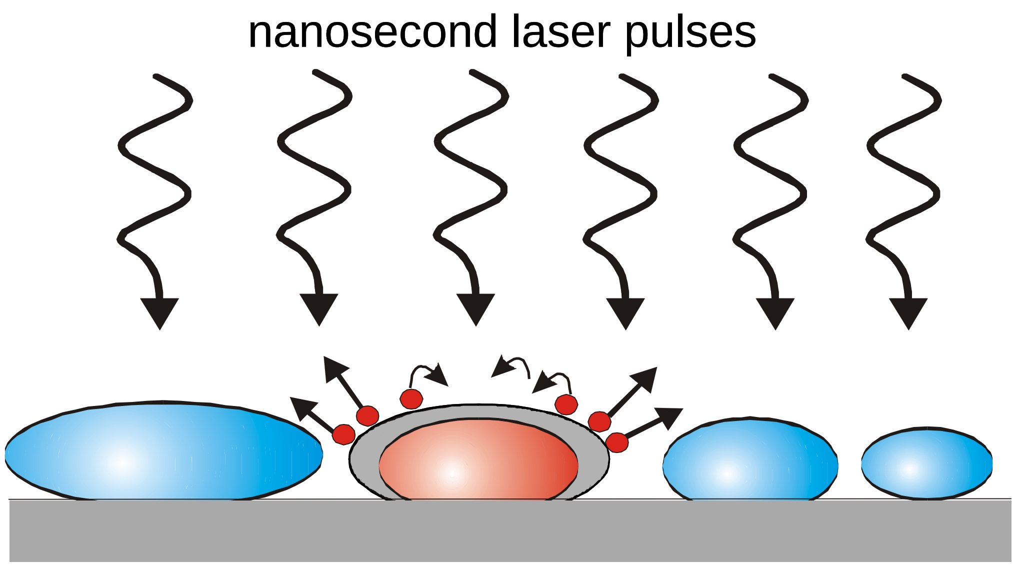
New method to determine the homogeneous line width/dephasing time is urgently needed.

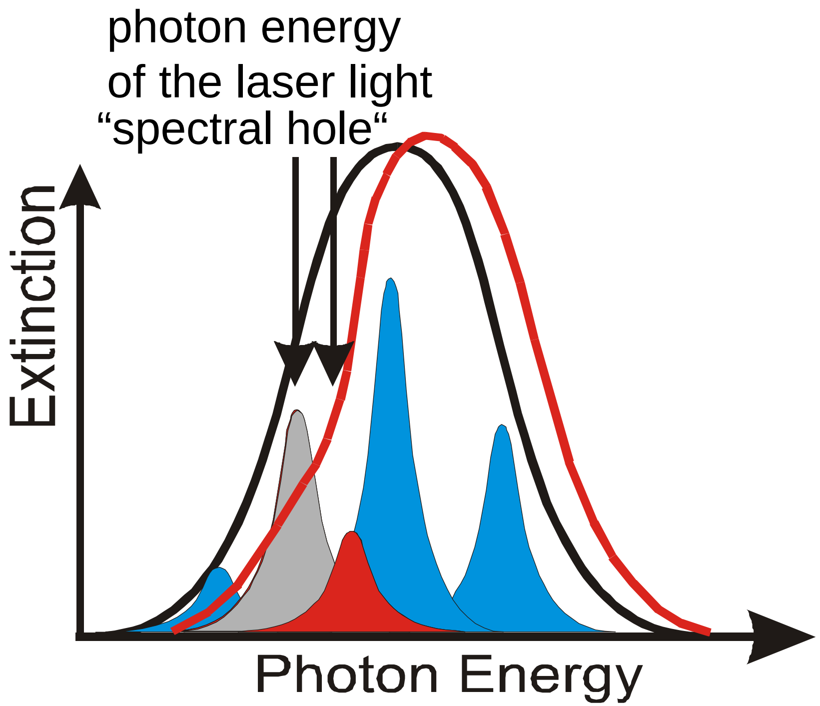
Should be applicable to

- many materials
- wide size range, especially below 10 nm
- different dielectric and chemical surroundings

$\Rightarrow$ Spectral hole burning in the optical spectra of metal nanoparticles

Method of spectral hole burning





only resonant particles
are selectively heated

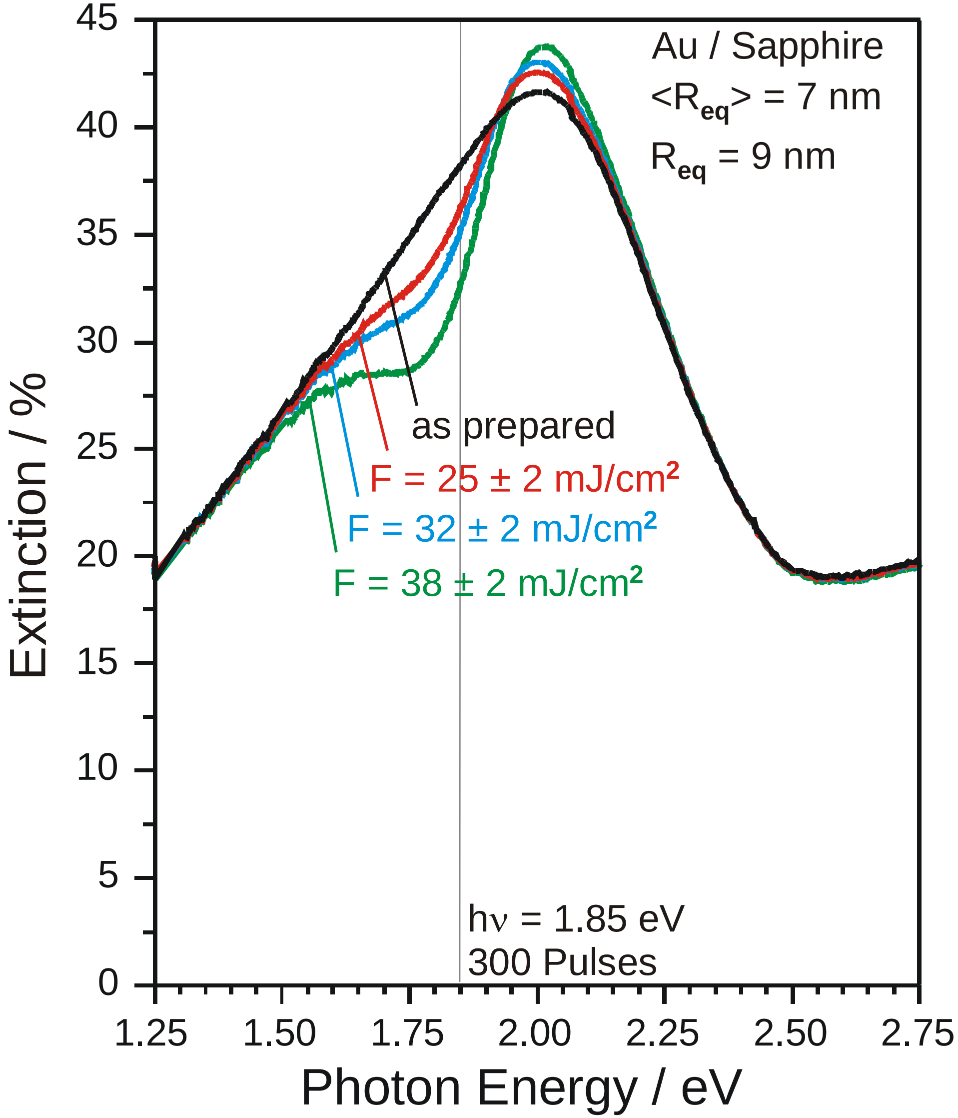
diffusion and
desorption of atoms

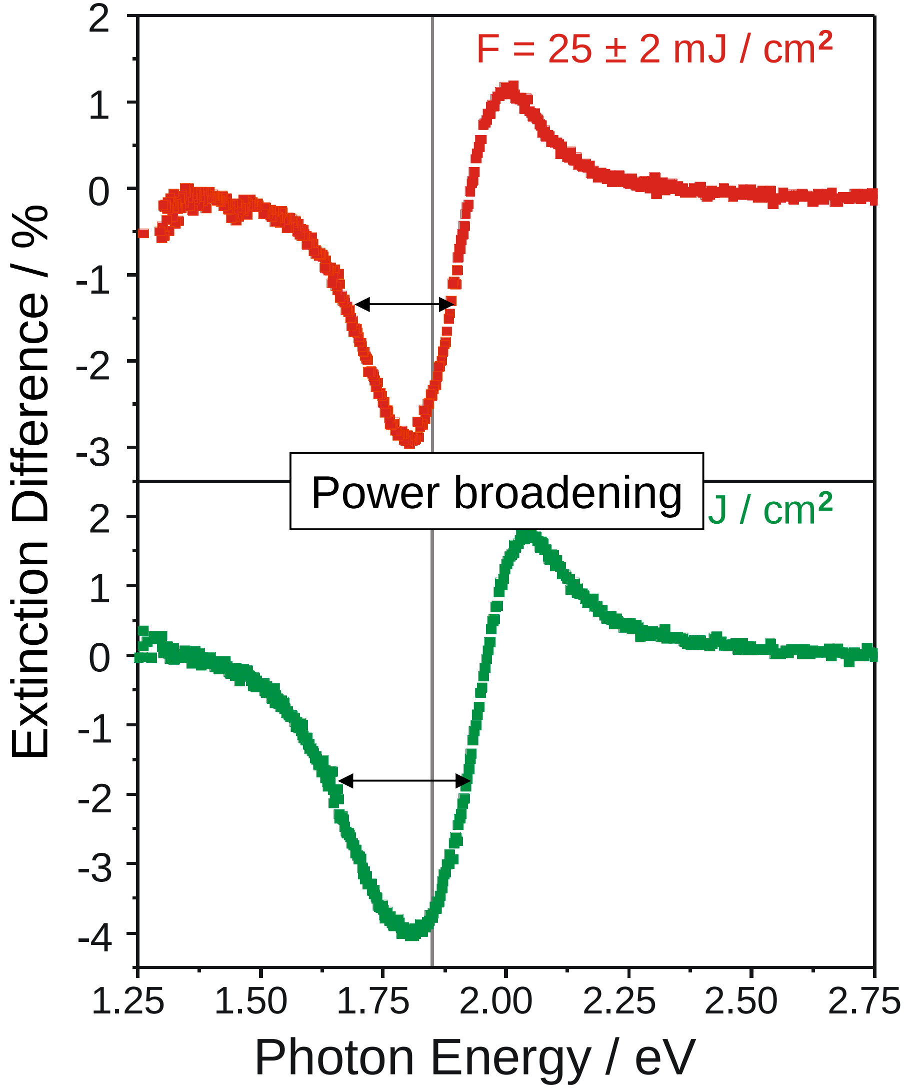
particles get smaller
and more spherical

blue shift and decrease
of plasmon resonance

F. Stietz, J. Bosbach, T.Wenzel, T. Vartanyan, A. Goldmann
and F. Träger, Phys. Rev. Lett. 84, 5644 (2000)

Spectral hole burning with gold nanoparticles





Exact but straightforward theoretical modelling is important to determine the homogeneous width precisely because

- Spectral holes are asymmetric since the population next to the hole is increased

  Usually the homogeneous width is described by a symmetric curve

  $\Rightarrow$ Lorentzian

- Width of the hole depends on laser fluence $\Rightarrow$ Gaussian profile

  Reason: Absorption of nanoparticles with neighboring size, i.e. similar axial ratio

Theoretical modelling: T. Vartanyan, J. Bosbach, F. Stietz, F. Träger,
Appl. Phys. B **73**, 391 (2001)