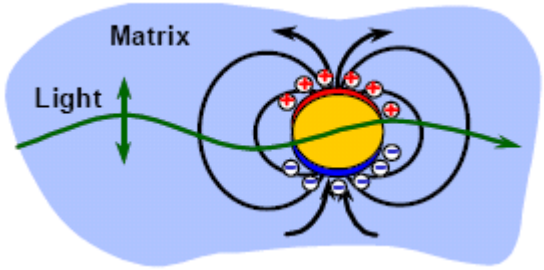
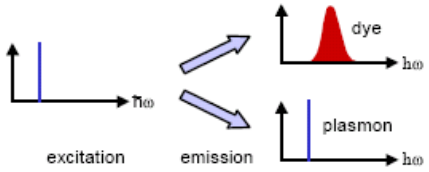
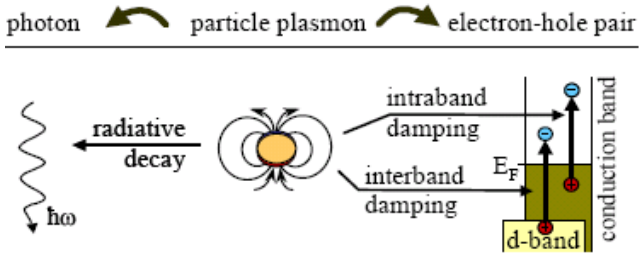
Localized surface plasmons (Particle plasmons)

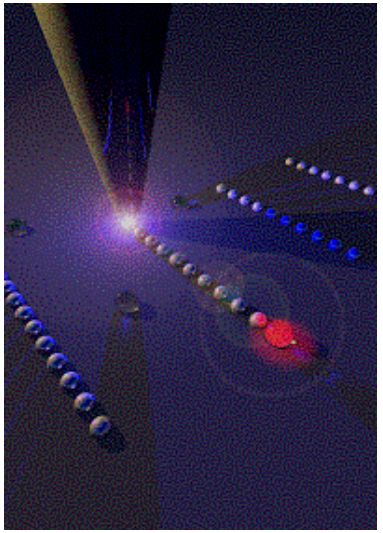
("Plasmons in metal nanostructures", Dissertation, University of Munich by Carsten Sonnichsen, 2001)

Lycurgus cup, 4th century
(now at the British Museum, London).
The colors originates from metal nanoparticles embedded in the glass. At places, where light is transmitted through the glass it appears red, at places where light is scattered near the surface, the scattered light appears greenish.

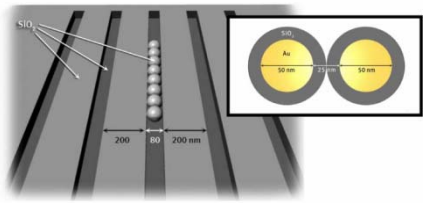








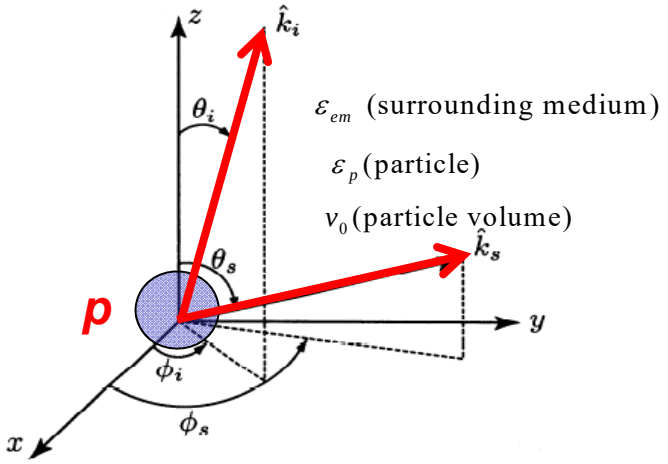
Focusing and guidance of light at nanometer length scales



Quasi-static approximation — Rayleigh scattering by a small particle

("*Scattering of Electromagnetic Waves: Theories and Applications*", Leung Tsang, Jin Au Kong, Kung-Hau Ding, 2000 John Wiley & Sons, Inc.

This approach effectively means that a region in space is investigated which is *much smaller than the wavelength of light*, so the *electromagnetic phase is constant* throughout the region of interest.
For small metal particles with diameters below 40 nm, this proves to be a reasonable simplification.



The incident wave to the direction of $\boldsymbol{k_i}$ is

$$\overline{E}_i = \left(\hat{a}_i E_{ai} + \hat{b}_i E_{bi}\right) e^{i\overline{k}_i \cdot \overline{r}} \qquad \hat{a}_i \text{ and } \hat{b}_i \text{ perpendicular to } \hat{k}_i$$

The far field radiated by a dipole $\boldsymbol{p}$ in the direction $\boldsymbol{k_s}$ is

$$\overline{E}_s = -\frac{k^2 e^{ikr}}{4\pi\epsilon r}\hat{k}_s \times (\hat{k}_s \times \overline{p})$$

The polarization per unit volume inside the particle is

$$\overline{P} = \varepsilon_0 \chi \overline{E} \;\; \& \;\; \varepsilon = \varepsilon_0(1+\chi) \;\rightarrow\; \overline{P} = \left(\varepsilon - \varepsilon_0\right)\overline{E}$$

$$\overline{P}_{\text{int}} = \overline{P}_{particle} - \overline{P}_{em} = (\varepsilon_p - \varepsilon_0)\overline{E}_{\text{int}} - (\varepsilon_{em} - \varepsilon_0)\overline{E}_{\text{int}} = (\varepsilon_p - \varepsilon_{em})\overline{E}_{\text{int}}$$

The dipole moment of the particle is $\overline{p} = v_o \overline{P}_{int}$ where v_0 is the volume of the particle.

$$\overline{E}_s = -\frac{k^2 e^{ikr}}{4\pi\epsilon r}(\epsilon_p - \epsilon)\, v_o\, \hat{k}_s \times \left(\hat{k}_s \times \overline{E}_{int}\right) = \frac{k^2 e^{ikr}}{4\pi\epsilon r}(\epsilon_p - \epsilon)\, v_o \left[\hat{a}_s(\hat{a}_s \cdot \overline{E}_{int}) + \hat{b}_s(\hat{b}_s \cdot \overline{E}_{int})\right] \longrightarrow \overline{E}_s = \hat{e}_s f(\hat{k}_s, \hat{k}_i) E_o \frac{e^{ikr}}{r}$$

For a sphere of radius a << λ, $\overline{E}_{int} = \dfrac{3\epsilon}{\epsilon_p + 2\epsilon}\overline{E}_i$

The power scattered is $\dfrac{P_s}{|\overline{S}_i|} = \int d\Omega_s |f(\hat{k}_s, \hat{k}_i)|^2 = \sigma_s$: scattering cross section, where $\overline{S}_i = \frac{1}{2}\text{Re}\left(\overline{E}_i \times \overline{H}_i^*\right)$

From Ohm's law, the power absorbed is $P_a = \dfrac{1}{2}\omega \int_V d\overline{r}\; \epsilon_p''(\overline{r})\left|\overline{E}_{int}(\overline{r})\right|^2 = \dfrac{1}{2}\omega\epsilon_p'' v_o \left|\overline{E}_{int}\right|^2$

Remember!!

Clausius-Mossotti Relation

Polarization of a solid

- Susceptibility: ----------→

$$\chi = \frac{P}{\varepsilon_0 E} = \frac{\sum_j N_j \alpha_j}{1 - \frac{1}{3}\sum_j N_j \alpha_j} \qquad \text{I}$$

- Limit of low atomic concentration:
  ….or weak polarizability:
  pretty good for gasses and glasses

$$\chi \approx \sum_j N_j \alpha_j \qquad \text{II}$$

Clausius-Mossotti

- By definition: $\varepsilon = 1 + \chi$
- Rearranging I gives

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{1}{3\varepsilon_0}\sum_j N_j \alpha_j \qquad \text{III}$$

- Conclusion: Dielectric properties of solids related to atomic polarizability
- This is very general!!

➔ *The Polarizability of a solid with volume V given by the Clausius-Mossotti relation is*

$$\alpha_{solid} = V\left(\sum_j N_j \alpha_j\right) = V\left[3\varepsilon_0\left(\frac{\varepsilon_r - \varepsilon_r^{embed}}{\varepsilon_r + 2\varepsilon_r^{embed}}\right)\right] = V\left[3\left(\frac{\varepsilon - \varepsilon^{embed}}{\varepsilon + 2\varepsilon^{embed}}\right)\right]$$

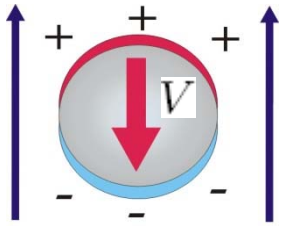
$$= \left(4\pi a^3\right)\left(\frac{\varepsilon - \varepsilon^{embed}}{\varepsilon + 2\varepsilon^{embed}}\right) \quad \textit{if the medium is a sphere with radius } a.$$

Rayleigh Theory for metal = dipole surface-plasmon resonance of a metal nanoparticle

("Plasmons in metal nanostructures", Dissertation, University of Munich by Carsten Sonnichsen, 2001)

$$\alpha_{solid} = \left(4\pi a^3\right)\left(\frac{\varepsilon_p - \varepsilon_{em}}{\varepsilon_p + 2\varepsilon_{em}}\right) \quad \textit{if the medium is a sphere with radius } a.$$

$$\vec{p} = \alpha\varepsilon_0\vec{E}_0 = \left(4\pi a^3 \frac{\varepsilon_p - \varepsilon_{em}}{\varepsilon_p + 2\varepsilon_{em}}\right)\varepsilon_0\vec{E}_0$$



ε (surrounding medium, ε_m)

ε_p(particle, ε)

The polarizability *α of the metal sphere is*

$$\alpha = \left(3V\varepsilon_0\right)\left(\frac{\varepsilon_r - 1}{\varepsilon_r + 2}\right), \text{ where } \varepsilon_r = \varepsilon_r^{'} + i\varepsilon_r^{"} = \varepsilon_p / \varepsilon_{em}$$

The scattering and absorption cross-section are then

$$\sigma_s = C_{\text{sca}} = \frac{k^4}{6\pi}|(\alpha/\varepsilon_0)|^2 = \frac{k^4}{6\pi}(3V)^2\frac{(\varepsilon_r' - 1)^2 + \varepsilon_r''^2}{(2+\varepsilon_r')^2 + \varepsilon_r''^2} = \frac{8\pi}{3}|f_o|^2 = \frac{8\pi}{3}k^4a^6\left|\frac{\epsilon_p - \epsilon}{\epsilon_p + 2\epsilon}\right|^2$$

$$\sigma_a = C_{\text{abs}} = k\Im(\alpha/\varepsilon_0) = k3V\frac{3\,\varepsilon_r''}{(2+\varepsilon_r')^2 + \varepsilon_r''^2} = k\frac{\epsilon_p''}{\epsilon}\frac{4\pi a^3}{3}\left|\frac{3\epsilon}{\epsilon_p + 2\epsilon}\right|^2$$

Homework!

$$\boxed{\sigma_t = \sigma_a + \sigma_s}$$

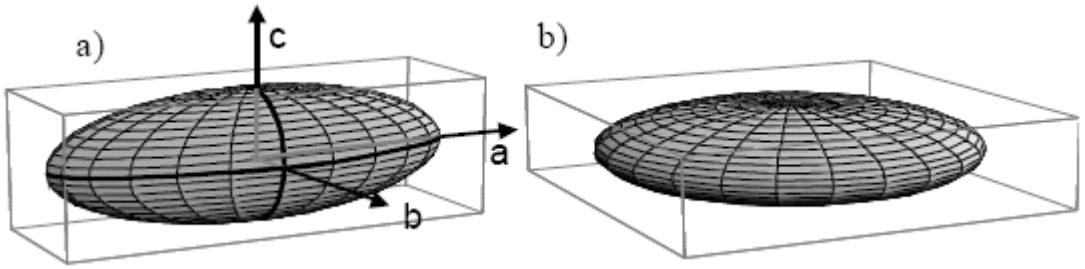
"Frohlich condition"

Scattering and absorption exhibit the plasmon resonance where, $\varepsilon_r' = -2 \rightarrow \text{Re}\left[\varepsilon_p(\omega)\right] + 2\varepsilon_{em} = 0$

For free particles in vacuum, resonance energies of 3.48 eV for silver (near UV) and 2.6 eV for gold (blue) are calculated.

When embedded in polarizable media, the resonance shifts towards lower energies (the red side of the visible spectrum).

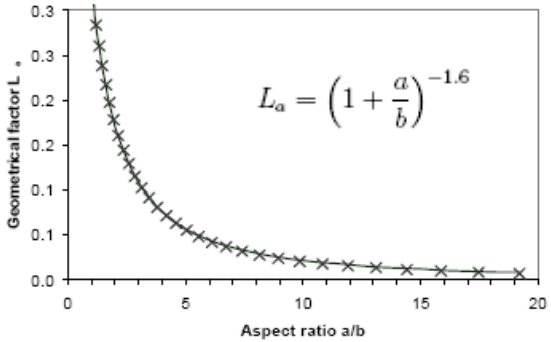
Rayleigh Theory : Scattering by elliptical particles



a) prolate (cigar-shaped) sheroid (*a* > *b* = *c)*, b) oblate (pancake-shaped) sheroid (*a* = *b* > *c)*

The polarizability α_i *of such a spheroidal particle along the axis i is given by*

$$\alpha_i = \frac{V\varepsilon_0}{L_i}\frac{1-\varepsilon_r}{(1/L_i - 1)+\varepsilon_r}$$



L_i: a geometrical factor related to the shape of the particle.

$L_a + L_b + L_c = 1$ holds

$L_i = \frac{1}{3}$ for spheres

$$L_a = \frac{1-e^2}{e^2}\left(-1+\frac{1}{2e}\ln\frac{1+e}{1-e}\right), \qquad e^2 = 1-\frac{b^2}{a^2}$$

for a prolate particles

Beyond the quasi-static approximation : Mie scattering Theory

For particles of larger diameter (> 100 nm in visible), the phase of the driving field significantly changes over the particle volume.
Mie theory ➔ valid for larger particles than wavelength, from smaller particles than the mean free-path of its oscillating electrons.
➔ Mie calculations for particle shapes other than spheres are not readily performed.

The spherical symmetry suggests the use of a multipole extension of the fields, here numbered by *n*.
The Rayleigh-type plasmon resonance, discussed in the previous sections, corresponds to the dipole mode *n = 1.*

In the Mie theory, the scattering and extinction efficiencies are calculated by:

"Frohlich condition"

$$\rightarrow \mathrm{Re}\left[\varepsilon_p(\omega)\right] = -\varepsilon_{embedded}\left[\frac{n+1}{n}\right]$$

$$Q_{\mathrm{sca}}^{(n)} = \frac{2}{x^2}(2n+1)(|a_n|^2 + |b_n|^2) \qquad \text{with } x = k\,r = \hbar\omega\, r\, N_{\mathrm{medium}}/(\hbar c),$$

$$Q_{\mathrm{ext}}^{(n)} = \frac{2}{x^2}(2n+1)\mathrm{Re}(a_n + b_n)$$

k: wave vector, r: particle radius, N: refractive index,

and a_n, b_n the Mie coefficients, which are calculated by:

$$a_n = \frac{m\psi_n(m\,x)\psi_n'(x) - \psi_n(x)\psi_n'(m\,x)}{m\psi_n(m\,x)\xi_n'(x) - \xi_n(x)\psi_n'(m\,x)}$$

$$b_n = \frac{\psi_n(m\,x)\psi_n'(x) - m\psi_n(x)\psi_n'(m\,x)}{\psi_n(m\,x)\xi_n'(x) - m\xi_n(x)\psi_n'(m\,x)}$$

with $m = \sqrt{\varepsilon_r} = N_{\mathrm{particle}}/N_{\mathrm{medium}}$

the Riccati-Bessel functions ψ_n and ξ_n

For the first (n=1) TM mode of Mie's formulation is

$$\alpha_{\mathrm{Mie}} = \frac{1 - (1/10)(\varepsilon+\varepsilon_m)x^2 + O(x^4)}{\left(\frac{1}{3} + \frac{\varepsilon_m}{\varepsilon-\varepsilon_m}\right) - \frac{1}{30}(\varepsilon+10\varepsilon_m)x^2 - i\frac{4\pi^2\varepsilon_m^{3/2}}{3}\frac{V}{\lambda_0^3} + O(x^4)}V$$

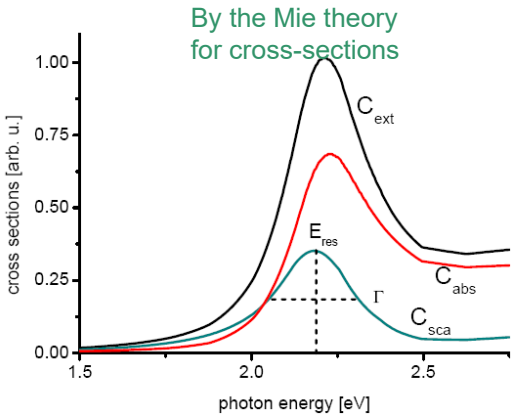
$x(=\pi a_{\mathrm{sphere}}/\lambda_0)$

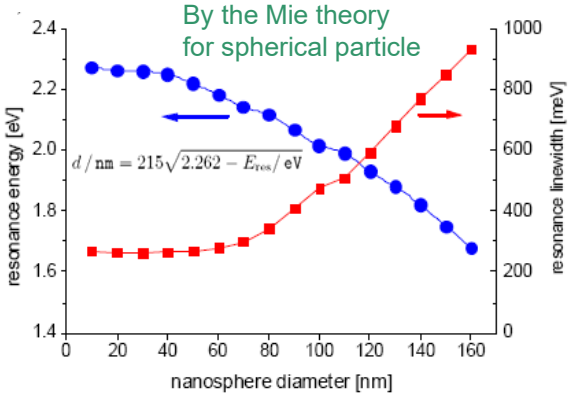
("Plasmons in metal nanostructures", Dissertation, University of Munich by Carsten Sonnichsen, 2001)

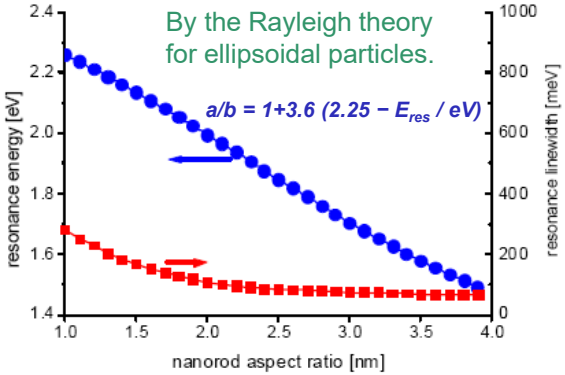
```
(* Needs : definition  of the (real) refractive  index of the medium Nmed and
         the (complex) refractive  index of the particle  material  Nparticle [w]
   Provides : Mie coefficients  a, b and
           scattering , extinction  and absorbtion  efficiencies  Qsca , Qext , Qabs
   Uses : Light  frequency  w (in eV)
          Particle  radius  r (in nm)
          Multipole  order  n
 *)
j[n_, x_] := (Sqrt[Pi / (2 x)]) BesselJ[n + 1/2, x]  (*  spherical  Bessel  function *)
y[n_, x_] := (Sqrt[Pi / (2 x)]) BesselY[n + 1/2, x]  (*  spherical  Bessel  function *)
h1[n_, x_] := j[n, x] + i y[n, x]    (*  spherical  Hankel  function  of first  kind *)
h2[n_, x_] := j[n, x] - i y[n, x]    (*  spherical  Hankel  function  of second  kind *)
psi[n_, x_] := x j[n, x]                          (*  Riccarti -Bessel -Funktion *)
xi[n_, x_] := x h1[n, x]                          (*  Riccarti -Bessel -Funktion *)
psidev[n_, x_] := Derivative[0, 1][psi][n, x]
xidev[n_, x_] := Derivative[0, 1][xi][n, x]
a[n_, x_, m_] := (m psi[n, m x] psidev[n, x] - psi[n, x] psidev[n, m x])
                 (m psi[n, m x]  xidev[n, x] -  xi[n, x] psidev[n, m x])
b[n_, x_, m_] := ( psi[n, m x] psidev[n, x] - m psi[n, x] psidev[n, m x])
                 ( psi[n, m x]  xidev[n, x] - m  xi[n, x] psidev[n, m x])
X[w_, r_] := w r Nmed / 197  (* w in eV, r in nm*)
M[w_] := Nparticle[w] / Nmed
Qsca[n_, w_, r_] := 2 / X[w, r]^2 (2 n + 1) (Abs[a[n, X[w, r], M[w]]]^2 + Abs[b[n, X[w, r], M[w]]]^2)
Qext[n_, w_, r_] := 2 / X[w, r]^2 (2 n + 1) Re[a[n, X[w, r], M[w]] + b[n, X[w, r], M[w]]]
Qabs[n_, w_, r_] := Qext[n, w, r] - Qsca[n, w, r]
```

MATHEMATICA™ script to calculate Mie coefficients

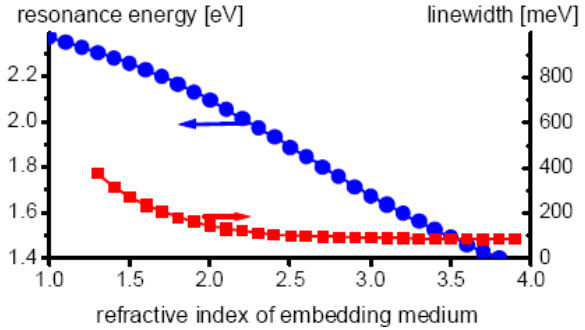
For a 60 nm gold nanosphere embedded in a medium with refractive index *n = 1.5.*
(use of bulk dielectric functions (e.g. Johnson and Christy, 1972))



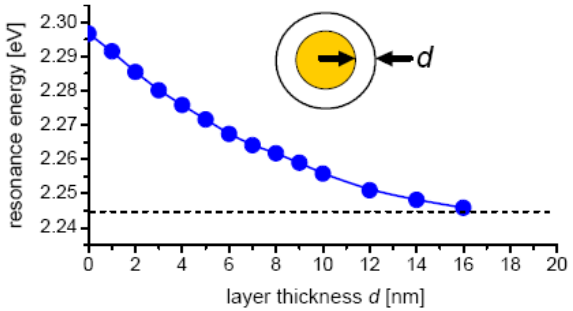




The red-shift observed for increasing size is partly due to increased damping and to retardation effects.
The broadening of the resonance is due to increasing radiation damping for larger nanospheres.



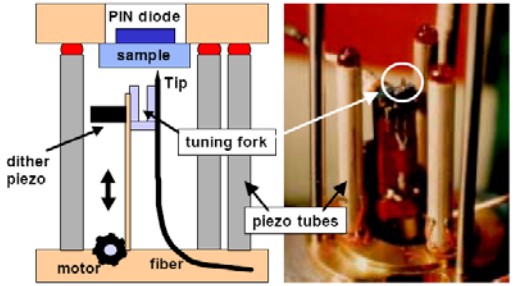
Influence of the refractive index of the embedding medium on the resonance position and linewidth of the particle plasmon resonance of a 20 nm gold nanosphere. Calculated using the Mie theory.



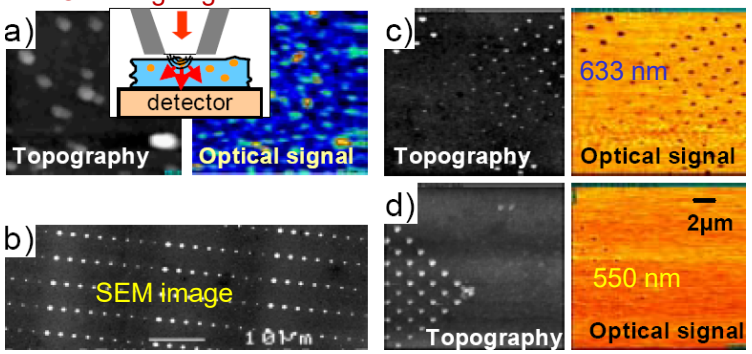
Resonance energy for a 40 nm gold nanosphere embedded in water (*n = 1.33) with increasing thickness d of a layer with refractive index n = 1.5.*

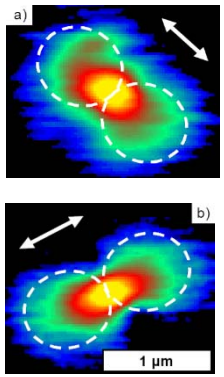
Experimental measurement of particle plasmons

Scanning near-field microscopy(SNOM)

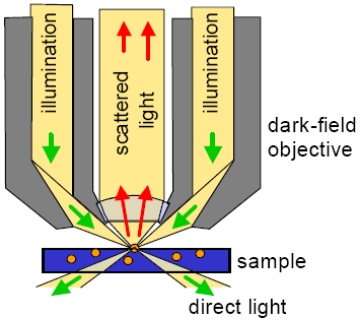


SNOM images gold nanodisks

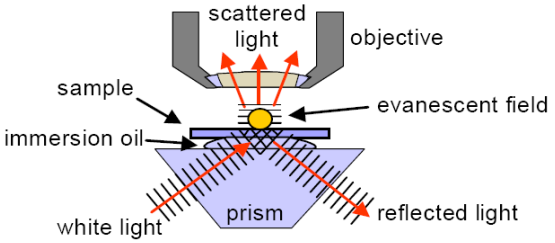




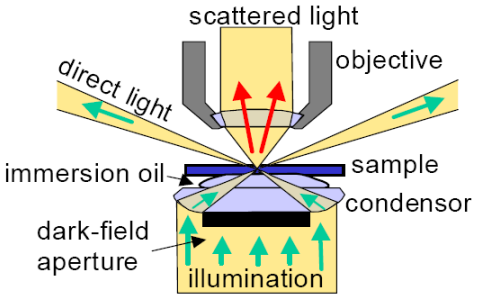
Dark-field microscopy in reflection

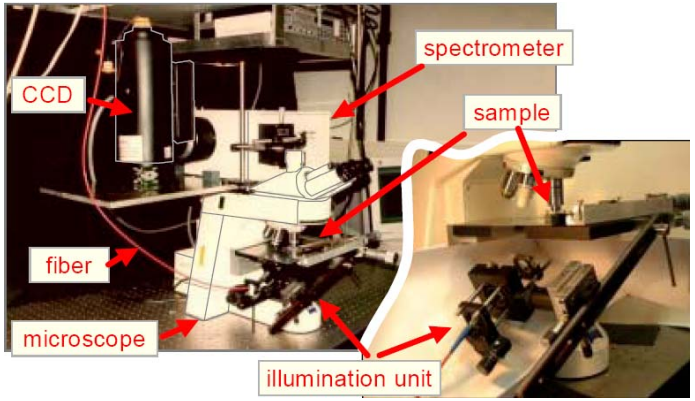


Total internal reflection microscopy(TIRM)



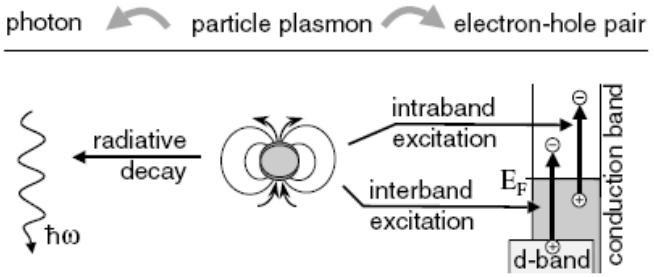
Dark-field microscopy in transmission





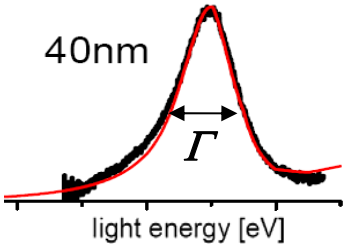
Plasmon Damping (Plasmon life time) in metal nanoparticles

C. Sönnichsen, et. al, “Drastic Reduction of Plasmon Damping in Gold Nanorods”, PRL, 88, 077402 (2002).



Radiative (left) and nonradiative (right) decay

The nonradiative decay occurs
via excitation of electron-hole pairs
either within the conduction band (intraband excitation)
or between the *d band and the conduction band* (interband excitation).

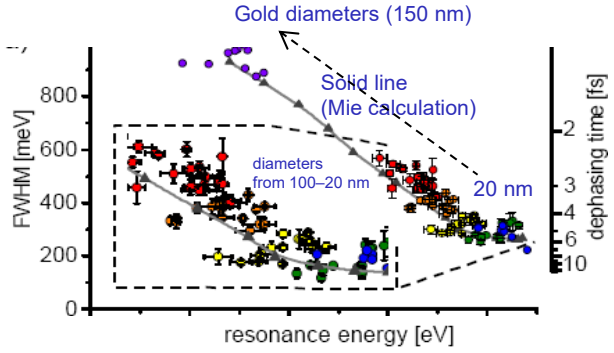


Dephasing times, directly relate to the plasmon lifetime, T_2 *can be deduced from the measured homogeneous* linewidths Γ

$$T_2 = \Gamma/2.$$

Quality factor of the resonance $Q = E_{res}/\Gamma$

Dephasing time decreases with increasing particle diameter, possibly due to increased radiation damping



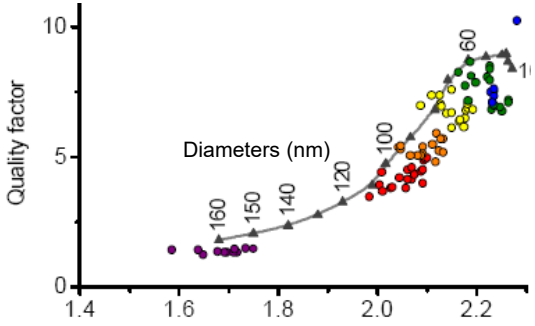


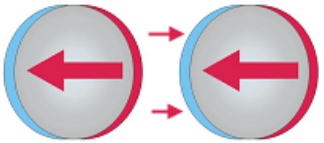
TABLE I. Summary of plasmon decay theories and parameters.

	Description	Expression	Half-width (cm^{-1})		Lifetime[a] (s)	Ref.
1	Total damping assuming homogeneous line shape	$\tau_T = 1/\pi c \Gamma_{obs}$	1500	(obs)	7.0×10^{-15}	16 This work
2	Width arising from conductivity expression for ϵ_2 for Ag spheres	$\Delta\lambda = \epsilon_0 + 2n_0^2 c/2\sigma$	1400 1157	(calc) (obs)	7.6×10^{-15}	16
3	Drude free electron gas–dc conductivity for bulk Au	$\tau_T \simeq 1/\epsilon_2(\omega_R)\omega_R$	1140		9.3×10^{-15}	15 22
4	Generalized free electron gas model for $\omega\rightarrow 0$	$\Delta\lambda = \epsilon_2(\omega_R)\left.\frac{\partial\epsilon_1}{\partial\omega}\right\|_{\omega=\omega_R}$	1407		7.5×10^{-15}	21–23, 25, 26
5	Quantum mechanical model for energy transfer to electrons	Results for $R = 50$ Å silver particles embedded in glass	750 1250	(calc) (obs)	1.4×10^{-14}	21 16
6	Radiation damping by photon emission	$\Delta\lambda = \frac{8\pi^3\epsilon_m\sqrt{\epsilon_m}}{2\epsilon_m+\epsilon_0}\left(\frac{R^3}{\lambda_R^2}\right)$	150 34	(Au) (Ag)	7.2×10^{-14} 3.1×10^{-13}	21
7	Radiation damping for metal spheres—Golden Rule approach	$\tau_R = \frac{3}{2}c^3/R^3\omega_R^4$	46 965	(Au) (Ag)	2.3×10^{-13} 1.1×10^{-14}	27
8	Radiative lifetime from absorption spectrum	$1/\tau_R \simeq 3\times10^{-9} n_0^2 \nu_R^3 \int\epsilon(d\ln\nu)$	13		8.0×10^{-13}	28 This work
9	Radiative quantum yield and photoacoustic study of Ag films	$\phi \simeq \tau_T/\tau_R \sim 0.2$	...		...	24 27

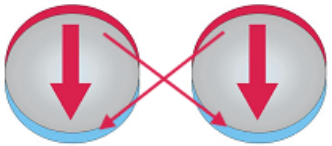
[a] Expression in 1 used to interconvert widths and lifetimes.

Interaction between particles

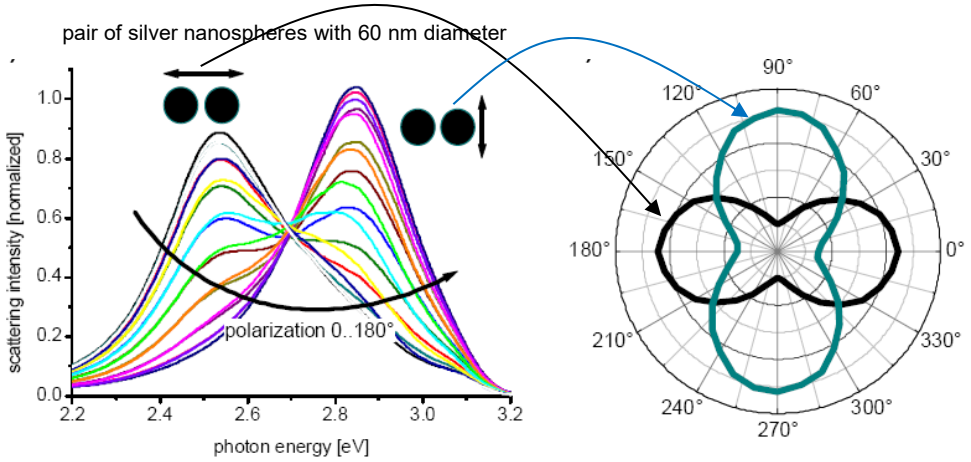
an isolated sphere is symmetric, so the polarization direction doesn't matter.



LONGITUDINAL:
restoring force *reduced* by coupling to neighbor
→ Resonance shifts to lower frequency

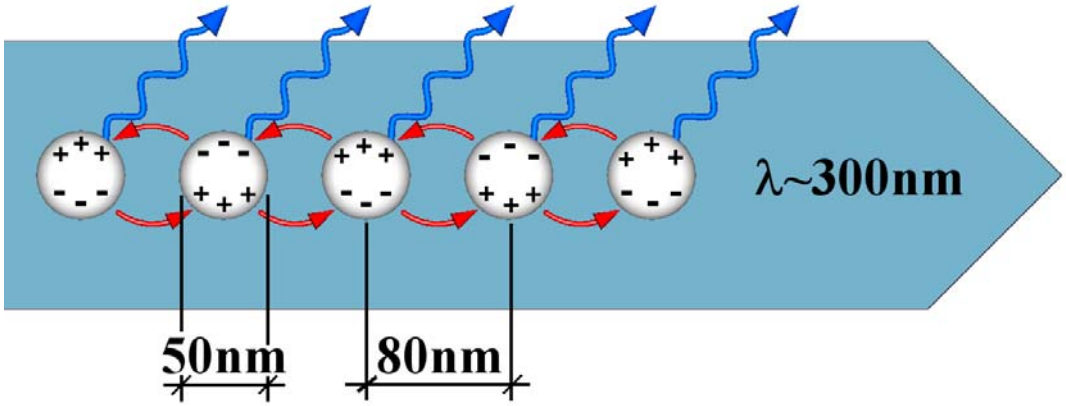


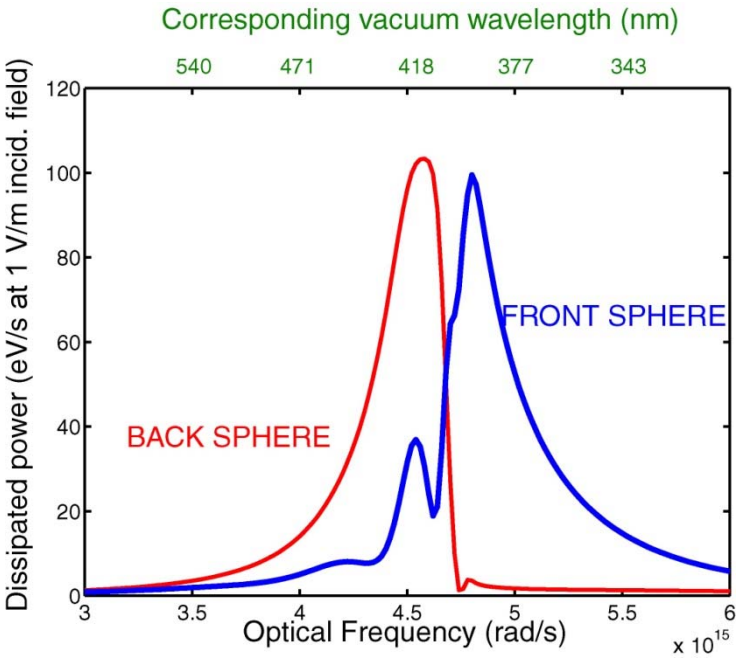
TRANSVERSE:
restoring force *increased* by coupling to neighbor
→ Resonance shifts to higher frequency



Plasmon Chains

- Spheres are resonant dipoles
- All dipoles are coupled
- Phase changes over the array
- Radiation & ohmic damping





For plane wave incidence:

- Strong fields localized on individual spheres
- Location of strongest field depends on λ

Nanolithography with a tunable mask !