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 originate 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


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 $k_i$ is

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

The far field radiated by a dipole $p$ in the direction $k_s$ is

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

The polarization per unit volume inside the particle is

$$\overline{P} = \epsilon_0 \chi \overline{E} \quad \& \quad \epsilon = \epsilon_0 (1 + \chi) \rightarrow \overline{P} = (\epsilon - \epsilon_0) \overline{E}$$

$$\overline{P}_{\text{int}} = \overline{P}_{\text{particle}} - \overline{P}_{\text{em}} = (\epsilon_p - \epsilon_0) \overline{E}_{\text{int}} - (\epsilon_{em} - \epsilon_0) \overline{E}_{\text{int}} = (\epsilon_p - \epsilon_{em}) \overline{E}_{\text{int}}$$

The dipole moment of the particle is \( \overline{p} = \nu_0 \overline{P}_{\text{int}} \) where \( \nu_0 \) is the volume of the particle.

$$\overline{E}_a = -\frac{k^2 e^{ikr}}{4\pi\epsilon r} (\epsilon_p - \epsilon) \nu_0 \hat{k}_a \times (\hat{k}_s \times \overline{E}_{\text{int}}) = \frac{k^2 e^{ikr}}{4\pi\epsilon r} (\epsilon_p - \epsilon) \nu_0 \left[\hat{a}_s (\hat{a}_s \cdot \overline{E}_{\text{int}}) + \hat{b}_s (\hat{b}_s \cdot \overline{E}_{\text{int}})\right] \rightarrow \overline{E}_s = \epsilon_0 f(\hat{k}_s, \hat{k}_i) E_0 \frac{e^{ikr}}{r}$$

For a sphere of radius \( a << \lambda \), \( \overline{E}_{\text{int}} = \frac{3\epsilon}{\epsilon_p + 2\epsilon} \overline{E}_i \)

The power scattered is \( \frac{P_s}{|\overline{S}_i|} = \int d\Omega_s |f(\hat{k}_s, \hat{k}_i)|^2 = \sigma_s \) : 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 \( P_a = \frac{1}{2} \omega \int_V d\tilde{r} \epsilon_p' \left| E_{\text{int}}(\tilde{r})\right|^2 = \frac{1}{2} \omega \epsilon_p' \nu_0 |\overline{E}_{\text{int}}|^2 \)
The Polarizability of a solid with volume \( V \) given by the Clausius-Mossotti relation is

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

\[
= \left( 4\pi a^3 \right) \left( \frac{\varepsilon - \varepsilon^{\text{embed}}}{\varepsilon + 2\varepsilon^{\text{embed}}} \right) \text{ if the medium is a sphere with radius } a.
\]
Rayleigh Theory for metal = dipole surface-plasmon resonance of a metal nanoparticle

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

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

The polarizability $\alpha$ of the metal sphere is

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

$\varepsilon$ (surrounding medium, $\varepsilon_m$)

$\varepsilon_p$ (particle, $\varepsilon$)

The scattering and absorption cross-section are then

$$\sigma_s = C_{\text{scat}} = \frac{k^4}{6\pi} \left|\alpha/\varepsilon_0\right|^2 = \frac{k^4}{6\pi} \left(3V\right)^2 \frac{\left(\varepsilon_r' - 1\right)^2 + \varepsilon_r''^2}{\left(2 + \varepsilon_r'\right)^2 + \varepsilon_r''^2} = \frac{8\pi}{3} \left|\alpha_0\right|^2 = \frac{8\pi}{3} k^4 a^6 \left|\varepsilon_p - \varepsilon\right|^2$$

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

$$\sigma_t = \sigma_a + \sigma_s$$

Scattering and absorption exhibit the plasmon resonance where,

$$\varepsilon_r' = -2 \rightarrow \Re\left[\varepsilon_p(\omega)\right] + 2\varepsilon_{em} = 0$$

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) spheroid \((a > b = c)\),  
b) oblate (pancake-shaped) spheroid \((a = b > c)\)

The polarizability \(\alpha_i\) of such a spheroidal particle along the axis \(i\) is given by

\[
\alpha_i = \frac{V\varepsilon_0}{L_i} \left( \frac{1}{L_i} - 1 \right) + \varepsilon_r
\]

\(L_i\): 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

\[
L_a = \frac{1 - \varepsilon^2}{\varepsilon^2} \left( -1 + \frac{1}{2\varepsilon} \ln \frac{1 + \varepsilon}{1 - \varepsilon} \right), \quad \varepsilon^2 = 1 - \frac{b^2}{a^2}
\]

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:

\[ Q_{\text{scat}}^{(n)} = \frac{2}{x^2} (2n+1) (|a_n|^2 + |b_n|^2) \quad \text{with} \quad x = k r = \hbar \omega r N_{\text{medium}} / (\hbar c), \]

\[ Q_{\text{ext}}^{(n)} = \frac{2}{x^2} (2n+1) \text{Re}(a_n + b_n) \]

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

\[ a_n = \frac{m \psi_n(m x) \psi'_n(m x) - \psi_n(x) \psi'_n(m x)}{m \psi_n(m x) \xi'_n(m x) - \xi_n(x) \psi'_n(m x)} \]

\[ b_n = \frac{\psi_n(m x) \psi'_n(m x) - m \psi_n(x) \psi'_n(m x)}{\psi_n(m x) \xi'_n(m x) - m \xi_n(x) \psi'_n(m x)} \]

with \(m = \sqrt{\varepsilon_r} = N_{\text{particle}} / N_{\text{medium}}\)

the Riccati-Bessel functions \(\psi_n\) and \(\xi_n\)

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

\[ \alpha_\text{mean} = \frac{1}{k} \left[ \frac{1}{3} \frac{e^{\varepsilon_m}}{e - e_m} - \frac{1}{30} \left( e + 10 e_m \right) x^2 - \frac{4 \pi^2 e_m^2}{3} \frac{V}{\lambda_0^2} + O(x^4) \right] \]

\[ x = \pi \sigma_{\text{sphere}} / \lambda_0 \]

("Frohlich condition")

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

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

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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))

By the Mie theory for cross-sections

By the Mie theory for spherical particle

By the Rayleigh theory for ellipsoidal particles.

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)**

**Dark-field microscopy in reflection**

**Total internal reflection microscopy (TIRM)**

**Dark-field microscopy in transmission**

SNOM images gold nanodisks

SEM image

633 nm

550 nm

measurement
The nonradiative decay occurs via excitation of electron-hole pairs either within the conduction band (intraband excitation) or between the \textit{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 $\Gamma$

$$T_2 = \frac{\Gamma}{2}.$$

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

Dephasing time decreases with increasing particle diameter, possibly due to increased radiation damping.
TABLE I. Summary of plasmon decay theories and parameters.

<table>
<thead>
<tr>
<th>Description</th>
<th>Expression</th>
<th>Half-width (cm(^{-1}))</th>
<th>Lifetime* (s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Total damping assuming homogenous line shape</td>
<td>(\tau_T = 1/\pi c \Gamma_{obs})</td>
<td>1500 (obs)</td>
<td>(7.0 \times 10^{-15})</td>
<td>16</td>
</tr>
<tr>
<td>2 Width arising from conductivity expression for (\varepsilon_2) for Ag spheres</td>
<td>(\Delta \lambda = \varepsilon_0 + 2n^2 c/2\sigma)</td>
<td>1400 (calc)</td>
<td>(7.6 \times 10^{-15})</td>
<td>16</td>
</tr>
<tr>
<td>3 Drude free electron gas–dc conductivity for bulk Au</td>
<td>(\tau_T \sim 1/\varepsilon_2 (\omega_R) \omega_R)</td>
<td>1140 (obs)</td>
<td>(9.3 \times 10^{-15})</td>
<td>15, 22</td>
</tr>
<tr>
<td>4 Generalized free electron gas model for (\omega \to 0)</td>
<td>(\Delta \lambda = \varepsilon_2 (\omega_R) \left</td>
<td>\frac{\partial \varepsilon_1}{\partial \omega} \right</td>
<td>_{\omega = \omega_R})</td>
<td>1407 (obs)</td>
</tr>
<tr>
<td>5 Quantum mechanical model for energy transfer to electrons</td>
<td>Results for (R = 50) Å</td>
<td>750 (calc)</td>
<td>(1.4 \times 10^{-14})</td>
<td>21, 16</td>
</tr>
<tr>
<td>6 Radiation damping by photon emission</td>
<td>(\Delta \lambda = \frac{8\pi^3 \varepsilon_m \sqrt{\varepsilon_m}}{2\varepsilon_m + \varepsilon_0} \left( \frac{R^3}{\lambda^2} \right))</td>
<td>150 (Au)</td>
<td>(7.2 \times 10^{-14})</td>
<td>21</td>
</tr>
<tr>
<td>7 Radiation damping for metal spheres—Golden Rule approach</td>
<td>(\tau_R = \frac{\sqrt{\varepsilon}}{2} R^3 \omega_R^2)</td>
<td>46 (Au)</td>
<td>(2.3 \times 10^{-13})</td>
<td>27</td>
</tr>
<tr>
<td>8 Radiative lifetime from absorption spectrum</td>
<td>(1/\tau_R \approx 3 \times 10^{-9} n_0^2 \nu_0^2 \epsilon(\nu))</td>
<td>965 (Ag)</td>
<td>(1.1 \times 10^{-14})</td>
<td>28</td>
</tr>
<tr>
<td>9 Radiative quantum yield and photoacoustic study of Ag films</td>
<td>(\phi \approx \tau_T/\tau_R \sim 0.2)</td>
<td></td>
<td>(8.0 \times 10^{-13})</td>
<td>24, 27</td>
</tr>
</tbody>
</table>

*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

pair of silver nanospheres with 60 nm diameter
For plane wave incidence:

- Strong fields localized on individual spheres
- Location of strongest field depends on $\lambda$

Nanolithography with a tunable mask!