# Dipolar approximation (R << λ)



$$
\begin{cases}
\bar{E}_{in}(t) = \dfrac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m}\bar{E}_0 = f_e \bar{E}_0 e^{-i\omega t} \\
\bar{E}_{out}(t) = \bar{E}_0 e^{-i\omega t} + \dfrac{1}{4\pi\varepsilon_0\varepsilon_m}\dfrac{3\hat{r}(\bar{p}\cdot\hat{r}) - \bar{p}}{r^3} \\
\bar{p}(t) \equiv 4\pi R^3 \dfrac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}\varepsilon_0\varepsilon_m \bar{E}_0 e^{-i\omega t}
\end{cases}
$$

Quasi-static

# Dipolar approximation (R << λ)

## Near-field properties

$$\bar{p} = \epsilon_o \epsilon_m \alpha \bar{E}$$

$$\alpha = 4\pi R^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}$$

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 \in \mathbb{C}$$
$$\varepsilon_m \in \mathbb{R}$$

$$\bar{E}_{in} = \bar{E}_t = \frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m} \bar{E}_i = f_E \bar{E}_i$$

**Local field enhancement**

$$EF_{SERS} \propto |f_E|^4$$

$$\varepsilon_1(\omega_{SPR}) + 2\varepsilon_m = 0$$

**L-SPR resonance conditions (VIS)**

$$\varepsilon_1(\omega_P) = 0$$

**Bulk or Volume plasmons conditions (UV)**

$$\omega_P \equiv \sqrt{\frac{n\, e^2}{\varepsilon_0\, m}}$$

# Dipolar approximation (R << λ)



## Near-field properties

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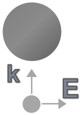
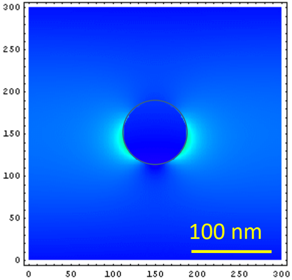
$$\bar{E}_{in} = \bar{E}_t = \frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m}\bar{E}_i = f_E \bar{E}_i$$

**Local field enhancement**



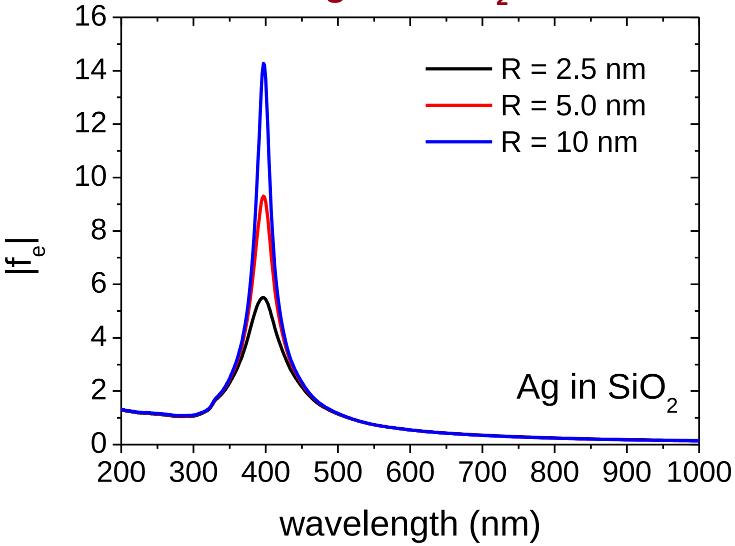




**Ag (R = 50 nm) in $SiO_2$**

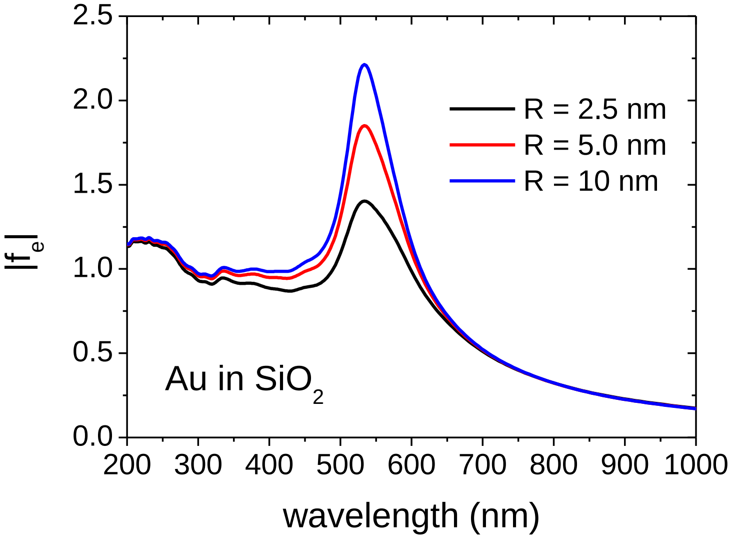
# Dipolar Local-Field



## Ag NP in $SiO_2$



## Au NP in $SiO_2$

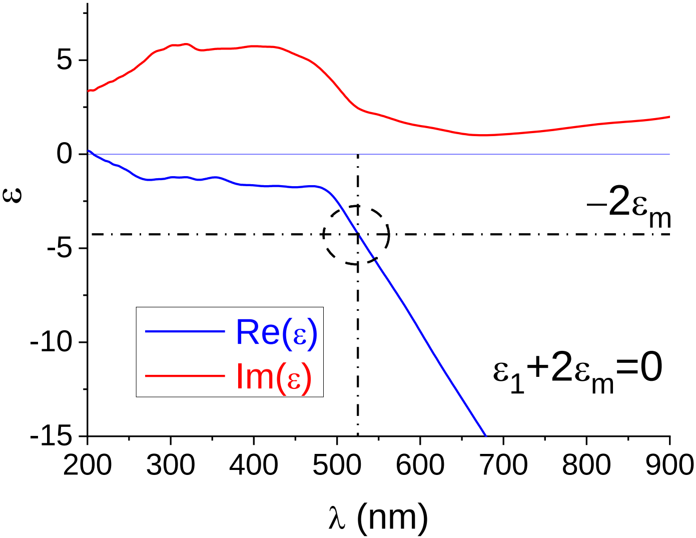

2.5
2.0
1.5
1.0
0.5
0.0
|f_e|
R = 2.5 nm
R = 5.0 nm
R = 10 nm
Au in SiO2
200
300
400
500
600
700
800
900
1000
wavelength (nm)

# Dielectric function Au



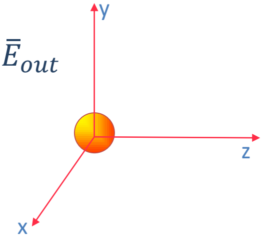
$\varepsilon_m(SiO_2) = 2.13$

Noble metals: Frölich condition in the visibile range



# Far-field properties






$$\begin{cases} \bar{S}' = \bar{E} \times \bar{H} \\ \dfrac{\partial u}{\partial t} + \bar{\nabla} \cdot \bar{S}' = -\bar{J}_f \cdot \bar{E} = 0 \\ u = \dfrac{1}{2}(\bar{E} \cdot \bar{D} + \bar{B} \cdot \bar{H}) \end{cases}$$

Poynting vector(W/m$^2$)

(no free charges)

E.M. Energy Density

$$I \equiv |\bar{S}'|$$

$$\bar{E} = \Re e(\bar{E}_c) = \Re e(\bar{E}_0 e^{-i\omega t})$$
$$\bar{H} = \Re e(\bar{H}_c) = \Re e(\bar{H}_0 e^{-i\omega t})$$

$$\bar{S} \equiv \langle \bar{S}' \rangle_t = \frac{1}{T}\int_0^T (\bar{E} \times \bar{H})\ dt = \frac{1}{2}\Re e\left(\bar{E}_c \times \bar{H}_c{}^*\right)$$

Time-averaged

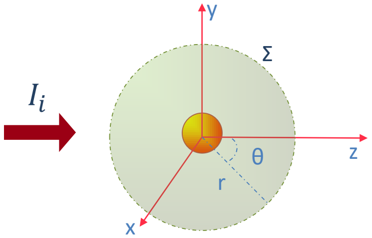
Poynting vector (time-averaged) outside the NP:

$$\bar{S}_{out} = \frac{1}{2}\Re e(\bar{E}_{out} \times \bar{H}^*_{out}) = \frac{1}{2}\Re e[(\bar{E}_i + \bar{E}_s) \times (\bar{H}^*_i + \bar{H}^*_s)] =$$
$$= \frac{1}{2}\Re e(\bar{E}_i \times \bar{H}^*_i) + \frac{1}{2}\Re e(\bar{E}_s \times \bar{H}^*_s) + \frac{1}{2}\Re e[(\bar{E}_i \times \bar{H}^*_s) + (\bar{E}_s \times \bar{H}^*_i)]$$
$$\equiv \bar{S}_i + \bar{S}_s + \bar{S}_{ext}$$

# Far-Field



$I_i$




Net EM energy flux entering Σ

$$W_{in} = -\int_{\Sigma} \bar{S}_{out} \cdot \hat{u}_r \, d\Sigma = W_a$$

No energy production inside Σ (just absorption)

$$W_a > 0$$

$$W_a \equiv W_{abs} = W_i - W_s + W_{ext}$$

$$W_i \equiv -\int_{\Sigma} \bar{S}_i \cdot \hat{u}_r \, d\Sigma = 0$$

Non-absorbing medium

$$W_s \equiv W_{sca} \equiv \int_{\Sigma} \bar{S}_s \cdot \hat{u}_r \, d\Sigma$$

$$W_{ext} \equiv -\int_{\Sigma} \bar{S}_{ext} \cdot \hat{u}_r \, d\Sigma$$

$$W_{abs} = -W_{sca} + W_{ext}$$
$$W_{abs} + W_{sca} = W_{ext}$$

Normalize to incident intensity (W/m²)

$$I_i$$

$$\frac{W_{abs}}{I_i} + \frac{W_{sca}}{I_i} = \frac{W_{ext}}{I_i}$$

# Far-Field

Cross-sections ($m^2$)

$$\sigma_{abs} + \sigma_{sca} = \sigma_{ext}$$

$$\begin{cases} \sigma_{abs} \equiv \dfrac{W_{abs}}{I_i} \\ \sigma_{sca} \equiv \dfrac{W_{sca}}{I_i} \\ \sigma_{ext} \equiv \dfrac{W_{ext}}{I_i} \end{cases}$$

$$W_j = \int_{\Sigma} \bar{S}_j \cdot \hat{u}_r \, d\Sigma$$

Efficiencies (adimensional)

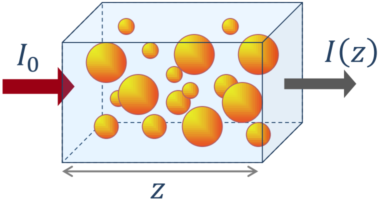
$$Q_{abs} + Q_{sca} = Q_{ext}$$

$$\begin{cases} Q_{abs} \equiv \dfrac{\sigma_{abs}}{A} \\ Q_{sca} \equiv \dfrac{\sigma_{sca}}{A} \\ Q_{ext} \equiv \dfrac{\sigma_{ext}}{A} \end{cases}$$

$$A \equiv \pi R^2$$

Spherical NP

# Far-Field




$$dI = -\rho\sigma_{ext} I \; dz = -\gamma I \; dz$$

$\varrho$ NP volumetric density

$\sigma_{ext}$ Extinction cross-section

$$\gamma = \varrho\sigma_{ext} = \varrho(\sigma_{sca} + \sigma_{abs})$$ Extinction coefficient

Neglecting multiple scattering $\gamma z \ll 1$

Lambert-Beer

$$I(z) = I_0 e^{-\gamma z}$$

Trasmittance

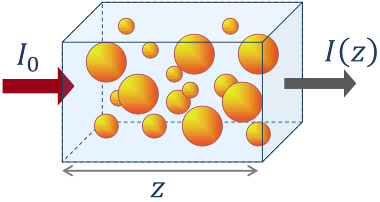
$$T \equiv \frac{I(z)}{I_0} = e^{-\gamma z}$$

Absorbance

$$A \equiv log_{10}\frac{1}{T} = \gamma \, z \, log_{10} e = log_{10}(e) \, z \, \varrho \, \sigma_{ext}$$

# Far-Field






$$I(z) = I_0 e^{-\gamma z}$$

$$\gamma = \varrho\sigma_{ext} = \varrho(\sigma_{sca} + \sigma_{abs})$$

$\varrho$ NP volumetric density

$$k = \frac{2\pi}{\lambda} = k_0 n$$

Dipolar Approx.

$$\sigma_{sca} = \frac{k^4}{6\pi}|\alpha|^2 \propto R^6$$ Scattering cross-section

$$\sigma_{abs} = k\,\mathrm{Im}(\alpha) \propto R^3$$ Absorption cross-section

$$\sigma_{ext} = \sigma_{sca} + \sigma_{abs}$$ Extinction cross-section

$$\sigma_{ext} = 9\frac{\omega}{c}\varepsilon_m{}^{3/2}\,\mathrm{V}\frac{\varepsilon_2}{(\varepsilon_1 + 2\varepsilon_m)^2 + (\varepsilon_2)^2}$$