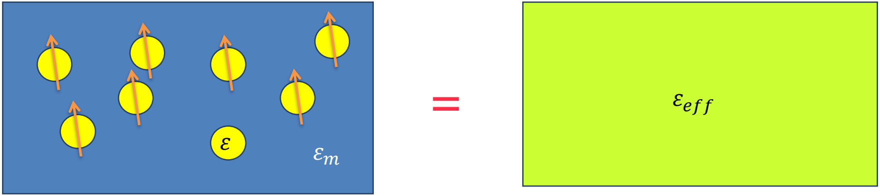
3. Interacting NPs

3.1 Effective Medium Approximation (EMA)

EMA



1. Maxwell-Garnett [1]: exact dipolar interaction

$$\frac{\varepsilon_{eff}-\varepsilon_m}{\varepsilon_{eff}+2\varepsilon_m} = f\,\frac{\varepsilon-\varepsilon_m}{\varepsilon+2\varepsilon_m}$$

f = filling fraction

$$f \equiv \rho\, V = \frac{N}{V_{tot}} V = \rho \frac{4\pi}{3} R^3 \in [0,1]$$

2. Bruggemann [2]: high f

$$f\,\frac{\varepsilon-\varepsilon_{eff}}{\varepsilon+2\varepsilon_{eff}} + (1-f)\,\frac{\varepsilon_m-\varepsilon_{eff}}{\varepsilon_m+2\varepsilon_{eff}} = 0$$

$$\gamma = \frac{4\pi}{\lambda_0} k_{eff}$$

$$\tilde{n}_{eff} = n_{eff} + i\,k_{eff}$$

$$\varepsilon_{eff} = \tilde{n}_{eff}{}^2$$

[1] J.C. Maxwell-Garnett, Phil. Trans. Roy. Soc. A 203 (1904) 385
[2] D.A.G. Bruggemann, Ann. Physik 5 (1935) 636

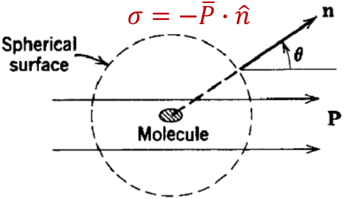
Maxwell-Garnett (EMA)

1. Simple case $\varepsilon_m = 1$

$$\bar{p}_{loc} = \varepsilon_0 \alpha \bar{E}_{loc}$$

$$\bar{P} = \rho \bar{p}_{loc} = \rho \varepsilon_0 \alpha \bar{E}_{loc}$$

$\sigma = -\bar{P} \cdot \hat{n}$



$$\bar{E}_{loc} = \bar{E}_0 + \bar{E}_p = \bar{E}_0 + \frac{\bar{P}}{3\varepsilon_0}$$

$$E_P = \frac{1}{4\pi\varepsilon_0} \iint_S \frac{-(-P\cos\theta)\cos\theta}{r^2} dS = \frac{P}{3\varepsilon_0}$$

$$\bar{P}\left(1 - \frac{\rho\alpha}{3}\right) = \rho\varepsilon_0\alpha\bar{E}_0 \quad \Rightarrow \quad \bar{P} = \frac{3\rho\varepsilon_0\alpha}{(3-\rho\alpha)}\bar{E}_0$$

$$\bar{P} = \varepsilon_0 \chi \bar{E}_0 = \varepsilon_0 (\varepsilon_{eff} - 1)\bar{E}_0 \quad \Rightarrow \quad (\varepsilon_{eff} - 1)\varepsilon_0 \bar{E}_0 = \frac{3\rho\varepsilon_0\alpha}{(3-\rho\alpha)}\bar{E}_0$$

$$\alpha = \frac{3(\varepsilon_{eff} - 1)}{\rho(\varepsilon_{eff} + 2)}$$

Maxwell-Garnett (EMA)

$$\alpha = \frac{3\left(\varepsilon_{eff} - 1\right)}{\rho\left(\varepsilon_{eff} + 2\right)}$$

$$f \equiv \rho V = \rho \frac{4\pi}{3} R^3 \in [0,1]$$

$$\alpha = 3V \frac{(\varepsilon - 1)}{(\varepsilon + 2)} \Rightarrow 3V \frac{(\varepsilon - 1)}{(\varepsilon + 2)} = \frac{3\left(\varepsilon_{eff} - 1\right)}{\rho\left(\varepsilon_{eff} + 2\right)}$$

$$\frac{\left(\varepsilon_{eff} - 1\right)}{\left(\varepsilon_{eff} + 2\right)} = \rho V \frac{(\varepsilon - 1)}{(\varepsilon + 2)} = f \frac{(\varepsilon - 1)}{(\varepsilon + 2)}$$

$$\frac{\left(\varepsilon_{eff} - 1\right)}{\left(\varepsilon_{eff} + 2\right)} = f \frac{(\varepsilon - 1)}{(\varepsilon + 2)}$$

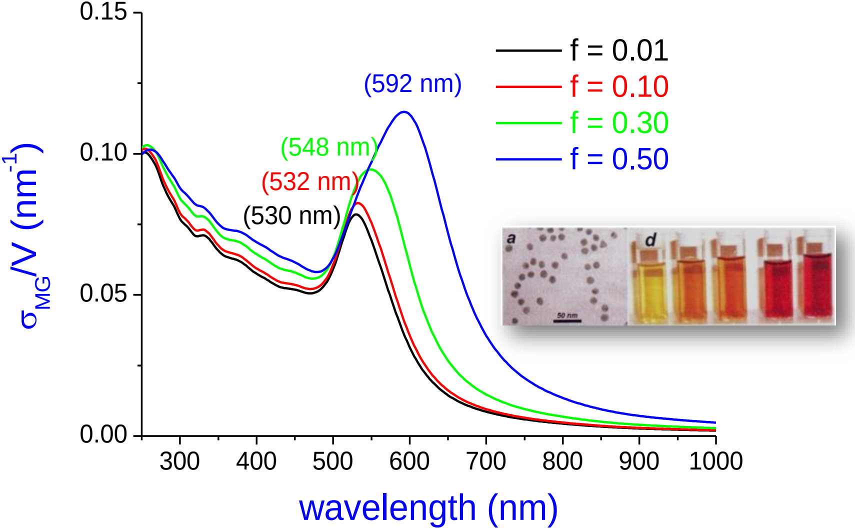
2. General case: $\varepsilon_m \neq 1$

$$\begin{cases} \varepsilon_{eff} \rightarrow \dfrac{\varepsilon_{eff}}{\varepsilon_m} \\ \varepsilon \rightarrow \dfrac{\varepsilon}{\varepsilon_m} \end{cases}$$

$$\frac{\left(\varepsilon_{eff} - \varepsilon_m\right)}{\left(\varepsilon_{eff} + 2\varepsilon_m\right)} = f \frac{(\varepsilon - \varepsilon_m)}{(\varepsilon + 2\varepsilon_m)}$$

Maxwell-Garnett

Red-shift vs. f



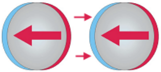
3. Interacting NPs

3.2 Multimers

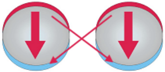
Interacting NPs

Polarization-dependent interaction

Isolated sphere is symmetric:
polarization effects are not relevant

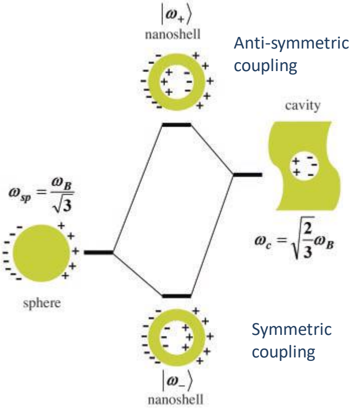


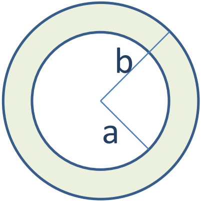
Longitudinal Polarization:
restoring force *reduced* by coupling to neighbour
→ Resonance shifts to lower energy



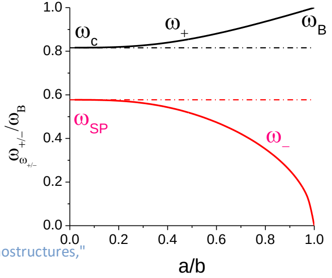
Transverse Polarization:
restoring force *increased* by coupling to neighbour
→ Resonance shifts to higher energy

L-SPR hybridization





$$\omega_{l\pm}^2 = \frac{\omega_B^2}{2}\left[1 \pm \frac{1}{2l+1}\sqrt{1+4l(l+1)\left(\frac{a}{b}\right)^{2l+1}}\right]$$

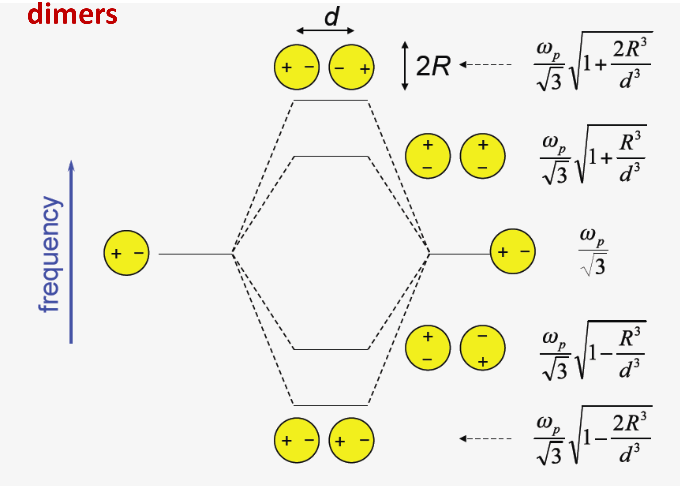


$$\omega_{1\pm} = \frac{\omega_B}{\sqrt{2}}\sqrt{1 \pm \frac{1}{3}\sqrt{1+8\left(\frac{a}{b}\right)^3}} \xrightarrow{a\to 0} \begin{cases} \omega_{1+} = \sqrt{\frac{2}{3}}\,\omega_B \\ \omega_{1-} = \sqrt{\frac{1}{3}}\,\omega_B \end{cases}$$

E. Prodan, et al., "A Hybridization Model for the Plasmon Response of Complex Nanostructures," Science **302**, 419–422 (2003).

L-SPR hybridization

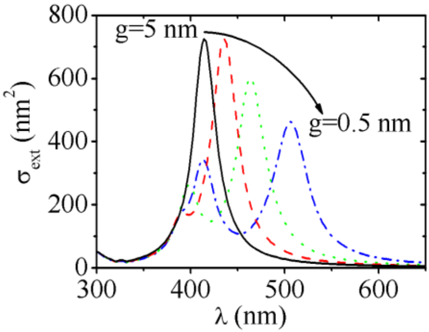
Bright and Dark Plasmon modes

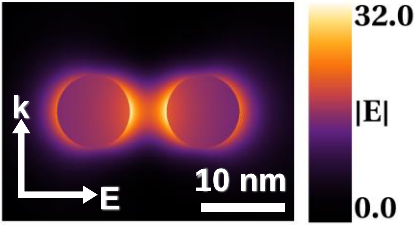


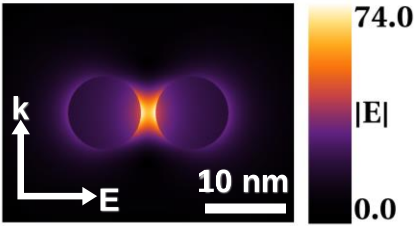
P. Nordlander, et al., "Plasmon Hybridization in Nanoparticle Dimers," Nano Lett. 4, 899–903 (2004).

Ag dimers

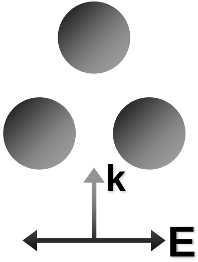
- Dimers Ag Local-Field
- Polarization ||
- D=10 nm
- g=5 nm, g=2 nm



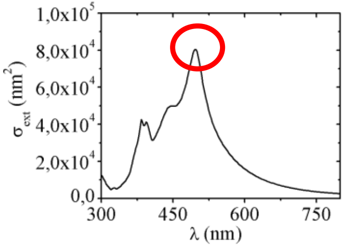


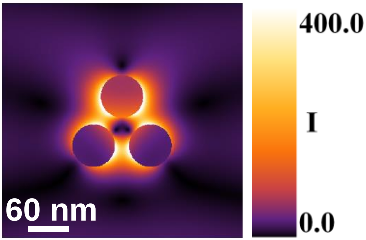


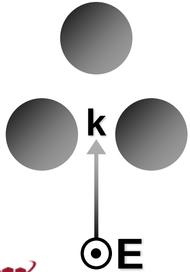
Ag trimers



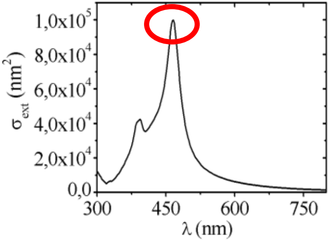
λ ~ 496 nm

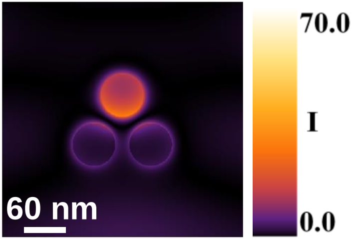






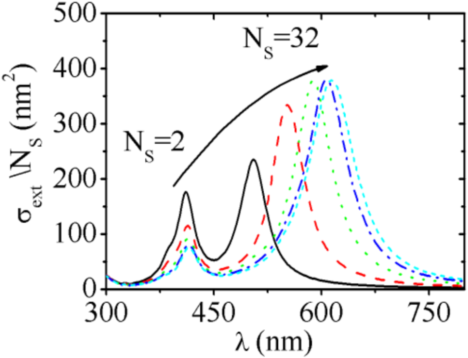
λ ~ 464 nm

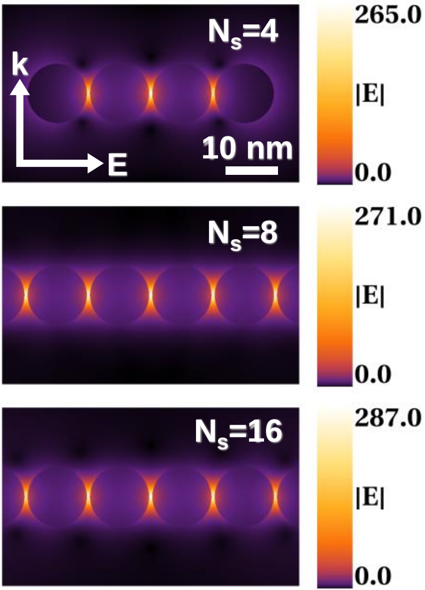




Ag linear chains

- Chains Ag Local-Field
- Polarization ||
- D=10 nm



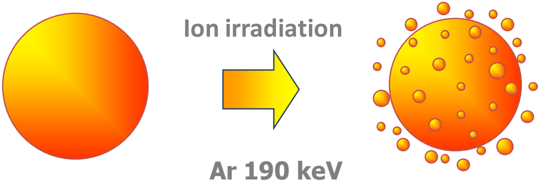


3. Interacting NPs

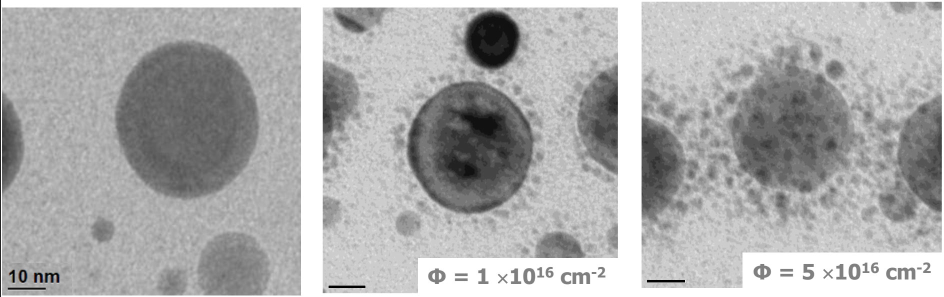
NanoPlanets

Plasmon tuning

Modification of the NCs electromagnetic environment



Core + Satellites
=
Nano-Planets

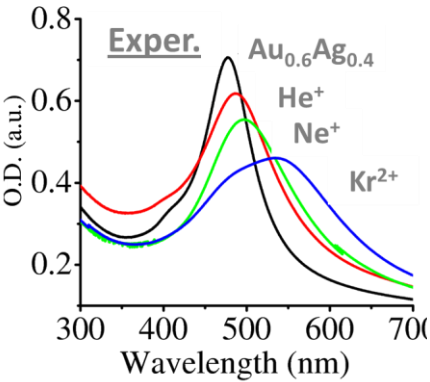


G. Mattei et al., "Chemical- or Radiation-Assisted Selective Dealloying in Bimetallic Nanoclusters," Phys. Rev. Lett. 90, 085502 (2003).

Plasmon tuning

SPR Plasmon Tuning

Interaction between Au-Ag NPs (far-field properties)

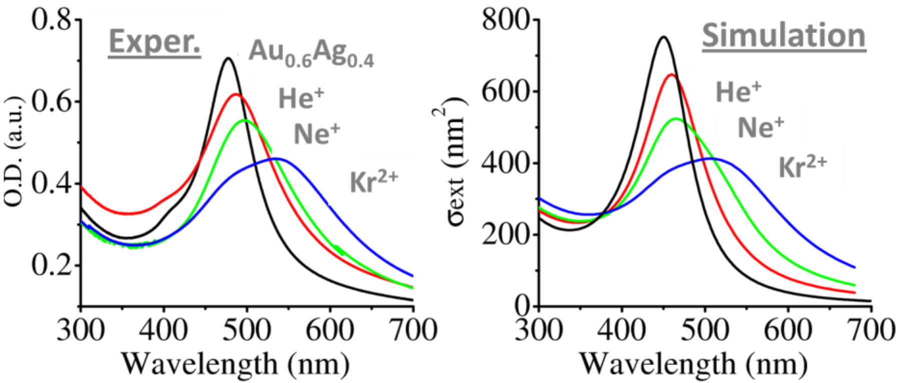


- SPR band red-shifts with increasing the irradiating ion mass

G. Pellegrini et al. "Local-field enhancement and plasmon tuning in bimetallic nanoplanets," Opt. Express **15**, 10097–10102 (2007).

Generalized Multiparticle Mie (GMM) Theory

Interaction between Au-Ag NPs (far-field properties)



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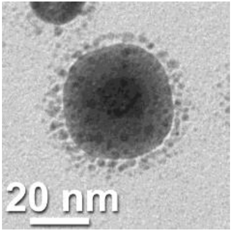
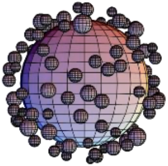
Plasmon tuning

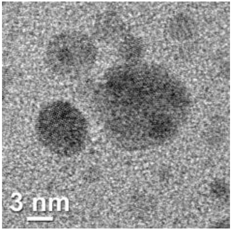
Generalized Multiparticle Mie (GMM) Theory

Interaction between Au-Ag NPs (<u>local-field properties</u>)

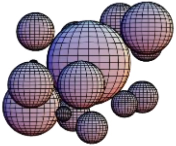


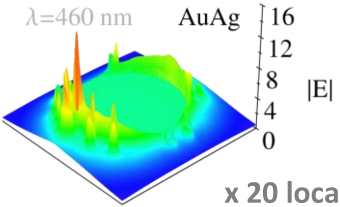
Ne^{+}

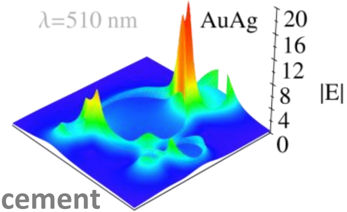




Kr^{2+}



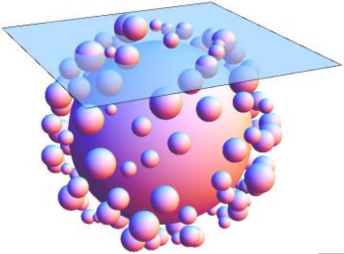


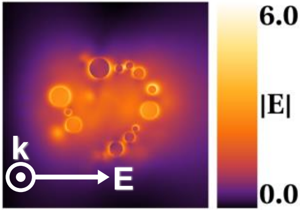


x 20 local field enhancement

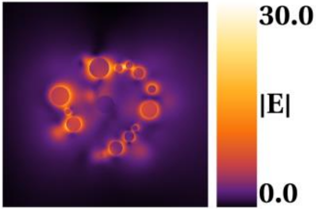
G. Pellegrini, et al. "Interacting metal nanoparticles: Optical properties from nanoparticle dimers to core-satellite systems," Materials Science and Engineering: C 27, 1347–1350 (2007).

NanoPlanets: AuAg vs. Ag





AuAg



Ag

G. Pellegrini et al. "Local-field enhancement and plasmon tuning in bimetallic nanoplanets," Opt. Express **15**, 10097–10102 (2007).