The effect of shape and structure variation of metallic nanoparticles on localized plasmon resonances

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Surface plasmon resonances: from propagating to localized plasmons

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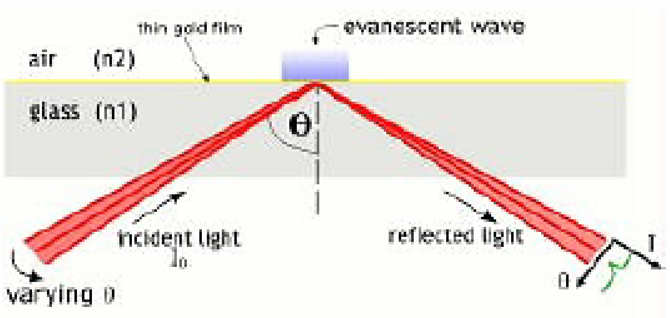
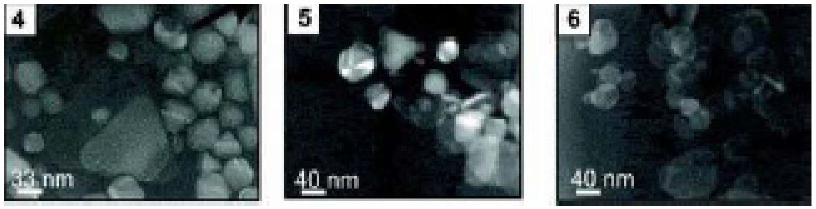
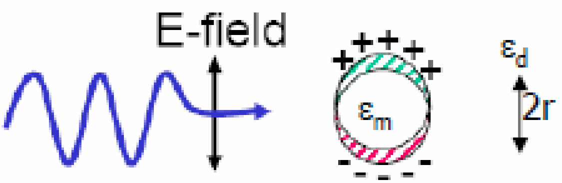
propagating



$$k_{sp} = k\left(\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}\right)^{1/2} = \frac{\omega}{c}\sqrt{\varepsilon_d}\sin\theta$$

localized





$$\omega_{res} = \frac{\omega_p}{\sqrt{3}}$$ Resonant frequency (geometry considerations)

Localized surface plasmon resonances (LSPRs)

In both cases resonance depends on dielectric permittivity

Calculation methods for LSPRs

1. discrete-dipole approximation (DDA).[1]
2. finite-difference time domain (FDTD).[2]
3. hybridization model (HB).[3]
4. operator method (quasistatic limit)[4] related to HB[5]

[1] B. T. Draine and P. J. Flatau, J. Opt. Soc. Am. A, **11** (1994) 1491.
[2] C. Oubre and P. Nordlander J. Phys. Chem. B **108** (2004) 17740.
[3] E. Prodan, *et al.* Science, **302** (2003) 419.
[4] D. R. Fredkin and I. D. Mayergoyz, Phys. Rev. Lett. **91** (2003) 253902.
[5] T. J. Davis *et al.* Nanoletters **10** 2618 (2010); T Sandu *et al.* Plasmonics (2011)

1 & 2 more complete but difficult to interpret.

3 & 4 provide direct physical interpretation.

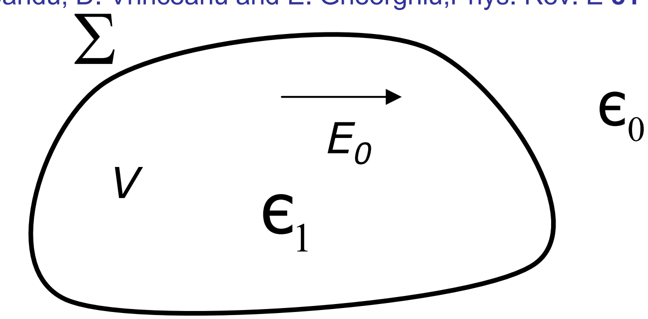
General Formalism quasistatic limit :

D. R. Fredkin and I. D. Mayergoyz, Phys. Rev. Lett. **91** (2003) 253902;
T. Sandu, D. Vrinceanu and E. Gheorghiu, Phys. Rev. E **81** (2010) 021913.

$$\Delta\Phi(\boldsymbol{x}) = 0; \quad \boldsymbol{x} \in \Re^3 \setminus \Sigma$$

$$\epsilon_0 \left.\frac{\partial\Phi}{\partial \boldsymbol{n}}\right|_{+} = \epsilon_1 \left.\frac{\partial\Phi}{\partial \boldsymbol{n}}\right|_{-}; \quad \boldsymbol{x} \in \Sigma$$

$$-\nabla\Phi(\boldsymbol{x}) \to \boldsymbol{E}_0, \quad |\boldsymbol{x}| \to \infty$$



Solution in terms of a single-layer potential: $\Phi(\boldsymbol{x}) = -\boldsymbol{x}\boldsymbol{E}_0 + \frac{1}{4\pi}\int_{y\in\Sigma} \frac{\mu_{E_0}(\boldsymbol{y})}{|\boldsymbol{x}-\boldsymbol{y}|} dS_y.$

$$\frac{1}{2\lambda}\mu_{E_0}(\boldsymbol{x}) - \hat{M}[\mu] = \boldsymbol{n}\boldsymbol{E}_0$$

$$\hat{M}[\mu] = \frac{1}{4\pi}\int_{y\in\Sigma} \frac{\mu(\boldsymbol{y})\,\mathrm{n}_x(\boldsymbol{x}-\boldsymbol{y})}{|\boldsymbol{x}-\boldsymbol{y}|^3} d\Sigma_y$$

$$\lambda = \frac{\epsilon_1 - \epsilon_0}{\epsilon_1 + \epsilon_0}$$

$$\hat{M}^{\dagger}[\mu] = \frac{1}{4\pi}\int_{y\in\Sigma} \frac{\mu(\boldsymbol{y})\,\mathrm{n}_y(\boldsymbol{x}-\boldsymbol{y})}{|\boldsymbol{x}-\boldsymbol{y}|^3} d\Sigma_y$$

$$\mu_{E_0} = \sum_k \frac{1}{\frac{1}{2\lambda} - \chi_k}\hat{P}_k[\boldsymbol{n}\boldsymbol{E}_0]$$

O. D. Kellogg, Foundations of Potential Theory, Springer, Berlin, 1929.
M. Putinar et al. Arch. Rational Mech. Appl. 185(10-), 143-184, (2007)

$\hat{P}_k = |v_k\rangle\langle u_k|$ (the projector as a function of eigenvectors of *M* and $M^{\dagger}$)

$$\alpha = \frac{1}{V}\sum_k \frac{1}{\frac{1}{2\lambda} - \chi_k}\left\langle \mathrm{r}\cdot \boldsymbol{N} \left| \hat{P}_k \right| \mathrm{n}\cdot \boldsymbol{N} \right\rangle = \sum_k \frac{p_k}{\frac{1}{2\lambda} - \chi_k}$$

Specific Particle polarizability

M and M^+ have the following properties :

- discrete and real spectrum that is bounded by the [-1/2, 1/2] interval.
- the number 1/2 is an eigenvalue irrespective of the particle shape.
- larger aspect ratios imply larger representative eigenvalues and tight junctions between particles imply additional eigenvalues close to 1/2.

Resolution of equations requires a complete basis of functions on the surface

$$\tilde{Y}_{lm}(\boldsymbol{x}) = \frac{1}{\sqrt{s(\boldsymbol{x})}} Y_{lm}(\theta(\boldsymbol{x}), \varphi(\boldsymbol{x})) \qquad dS = s(\boldsymbol{x})d\Omega_x$$

The surface is described either by a polar representation $r = r(\theta)$

or by the equation $\{x = g(z)\cos\varphi, y = g(z)\sin\varphi\}$

i.e mapping the surface onto unit sphere

Compact formula

Drude model for metals: $\epsilon = \varepsilon_m - \dfrac{\omega_p^2}{\omega(\omega + i\gamma)}$, Dielectrics: $\epsilon = \varepsilon_d$

Metal Nanoparticle polarization: eigenmode decomposition [T Sandu *et al.* Plasmonics (2011)].

$$\alpha_{plasmon}(\omega) = \sum_k \frac{p_k(\varepsilon_m - \varepsilon_{do})}{\varepsilon_{eff\_k}} - \frac{p_k}{1/2 - \chi_k} \frac{\varepsilon_{do}}{\varepsilon_{eff\_k}} \frac{\tilde{\omega}_{pk}^2}{\omega(\omega + i\gamma) - \tilde{\omega}_{pk}^2}$$

$$\tilde{\omega}_{pk}^2 = \frac{(1/2 - \chi_k)\omega_p^2}{\varepsilon_{eff\_k}} \qquad \varepsilon_{eff\_k} = (1/2 + \chi_k)\varepsilon_{do} + (1/2 - \chi_k)\varepsilon_m$$

$$\gamma \ll \omega_p \qquad \gamma = v_F\left(\frac{1}{l} + \frac{1}{L}\right)$$

ohmic damping

radiation damping: PRB **79**, 155423 (2009).

$$\alpha_{plasmon} \sim p_k/(1/2 - \chi_k)$$

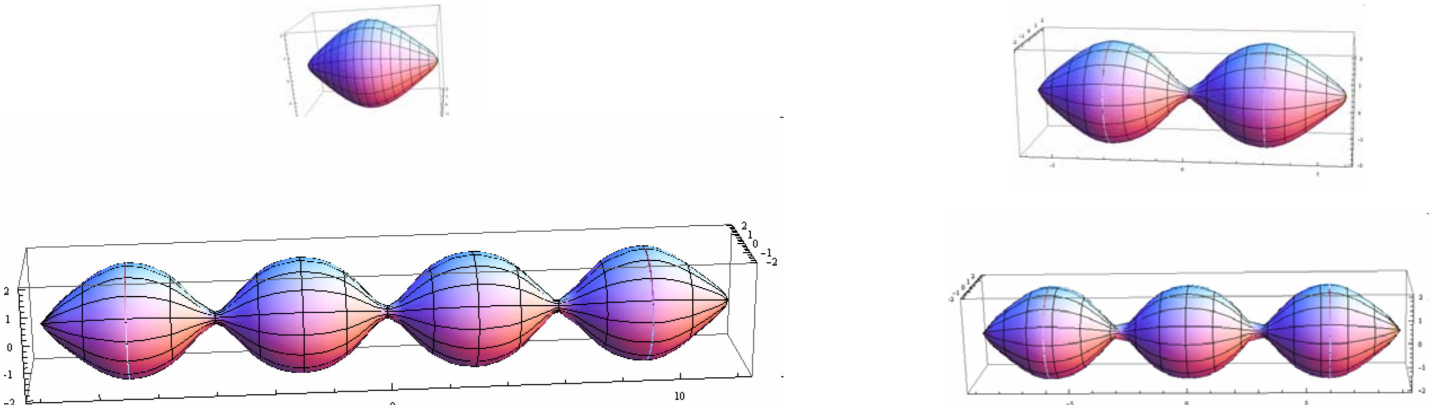
Oscillator strength boosted by a geometric factor (relevant for clusters)

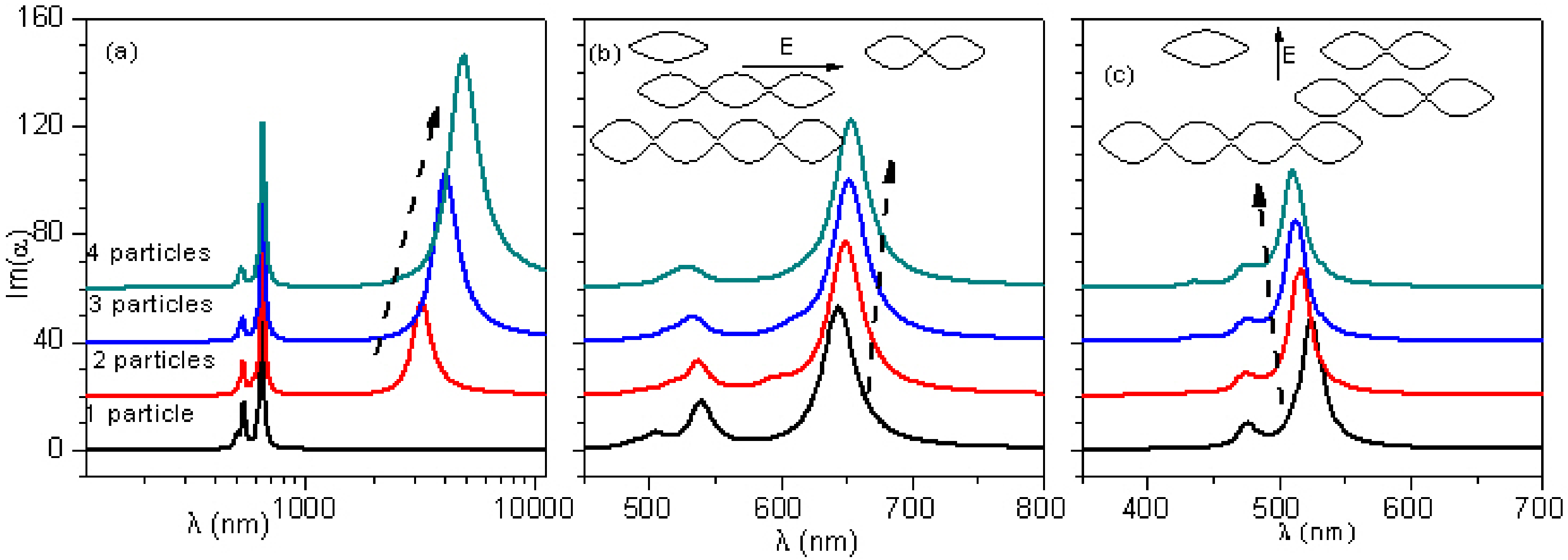
Direct calculation of refractive index sensitivity

$$\frac{d\tilde{\lambda}_{pk}}{d\,n_o} = \frac{\tilde{\lambda}_{pk} n_o (1/2 + \chi_k)}{(1/2 + \chi_k)n_o^2 + (1/2 - \chi_k)\varepsilon_i}$$

High refractive index sensitivity is given by the red-shifted resonances that occur in elongated particles, as well as in clustered particles, and in nanoshells ([Nature Mat. **7**, 442 (2008); Chem Phys. Lett. **487**, 153 (2010)]

Applications: the effect of shape variations for clustered particles



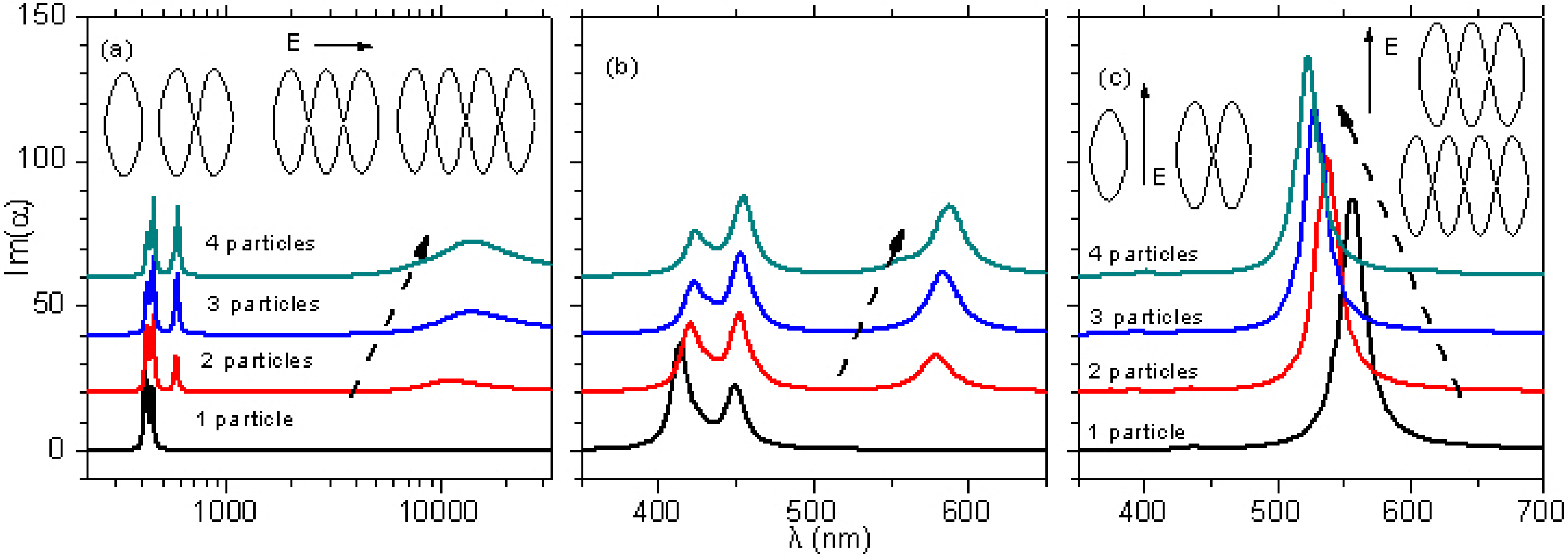


A new resonance in IR due to the junctions.

Prolate shape, aspect ratio >1

Applications: the effect of shape variations for clustered particles

Oblate shape, aspect ratio <1



- •A new resonance shows up beginning with 2 particle clusters for oblate shapes*.
- • Transverse LPSRs redshift and longitudinal LSPRs blueshift.
- •Clusters candidates for SEIRS-surface enhanced IR spectroscopy.

$$\alpha_{plasmon} \sim p_k/(1/2 - \chi_k)$$

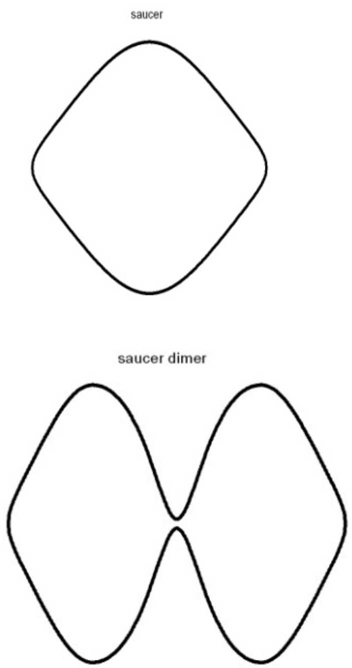
*M. Danckwerts, L. Novotny, Phys. Rev. Letters 98, 026104 (2007); I. Romero et al., Optics Express 14, 9988 (2006)

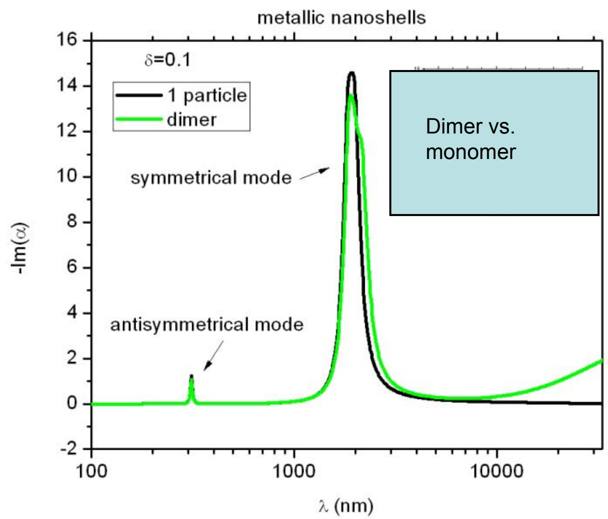
Structure variation: nanoshells

Metal Nanoshell polarization: eigenmode decomposition

$$\alpha_{shell}(\omega) \approx \sum_k \frac{p_k(\varepsilon_{di}-\varepsilon_{do})}{\varepsilon_{eff\_k}} - \frac{p_k}{1/2-\chi_k}\frac{\varepsilon_{do}}{\varepsilon_{eff\_k}}\left(\frac{\tilde{\omega}'^2_{pk}}{\omega(\omega+i\gamma)-\tilde{\omega}'^2_{pk}} + \frac{\tilde{\omega}''^2_{pk}}{\omega(\omega+i\gamma)-\tilde{\omega}''^2_{pk}-\omega_p^2/\varepsilon_m}\right)$$

$$\tilde{\omega}'^2_{pk} = \frac{\delta(1/2+\chi_k)(1/2-\chi_k)\omega_p^2}{\varepsilon_{eff\_k}} \qquad \tilde{\omega}''^2_{pk} = \frac{\delta(1/2-\chi_k)^2\omega_p^2}{\varepsilon_{eff\_k}}\frac{\varepsilon_{di}}{\varepsilon_m}$$





Dimer vs. monomer

Conclusions

- Operator method allows eigenmode decomposition of NP polarizability with compact formulae for NP and nanoshells.
- Oscillator strength $\sim p_k/(1/2-\chi_k)$
- Direct calculation of refractive index sensitivity.
- Due to the junctions, a new LSPR appears in IR for clustered particles.
- Also beginning with 2-particle clusters of oblate shapes there is an additional LSPR in visible.
- Transverse LPSRs blueshift and longitudinal LSPRs redshift.
- Clusters candidates for SEIRS-surface enhanced IR spectroscopy.
- Nanoshell LSPR is moved toward IR with respect to metal NP.

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