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Surface Plasmon Resonance Dependence on Size in Metallic Nano-Spheres

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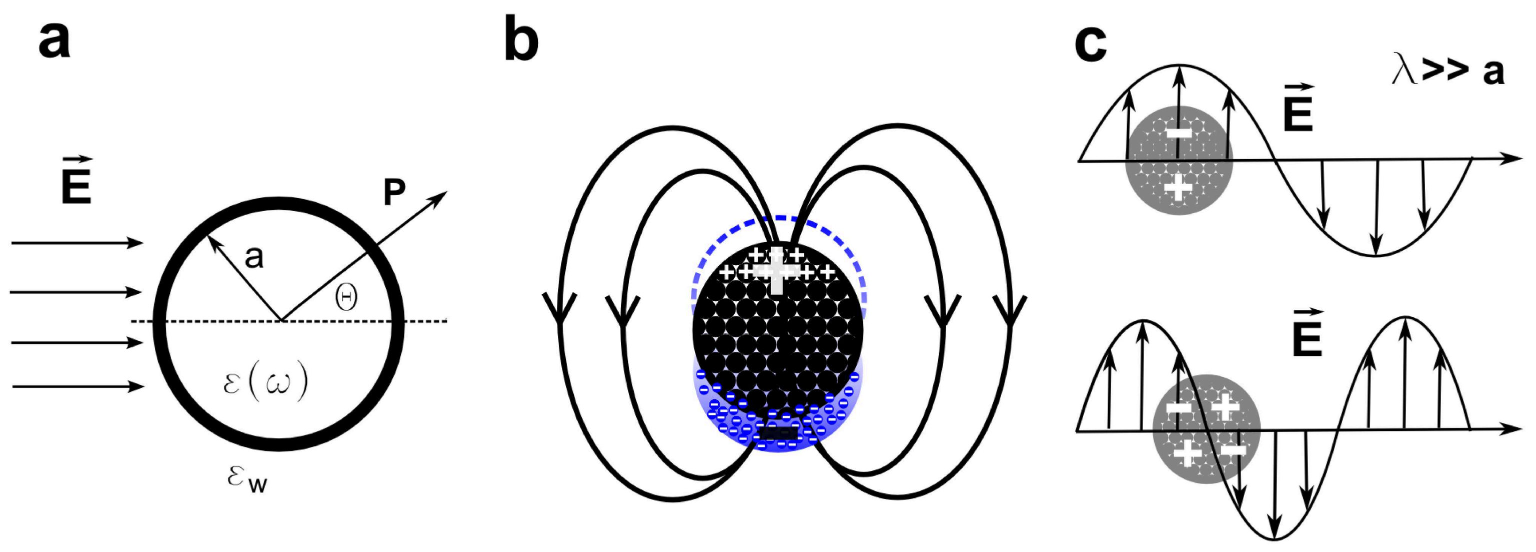
Surface plasmon resonance in metallic nanoparticles is highly and shape dependent, which enables varius applications in photovoltaics, photonics, sensing and even medicine. Particularly we observe redshift in plasmon resonance with increasing nanoparticle size. We investigate nanoparticle size influence on plasmon resonance within theoretical and numerical approach and compare results with experimental data.

Problem definition and assumptions

a. metallic nanoparticle with radius a located in dielectric media and in presence of dynamic electromagnetic field

b. Random phase approximation - jellium model - uniform positive ions field with free electron gas, electron oscillations induce electromagnetic field outside particle

c. In case of radius << incident wavelength only dipole type excitation occurs



Mathematical description:

electron density oscillations: two types of excitations

$$\frac{\partial^2\delta\rho_1(\mathbf{r},t)}{\partial t^2}=\frac{2}{3}\frac{\epsilon_F}{m}\nabla^2\delta\rho_1(\mathbf{r},t)-\omega_p^2\delta\rho_1(\mathbf{r},t)$$ → bulk plasmons

$$\frac{\partial^2\delta\rho_2(\mathbf{r},t)}{\partial t^2}=-\frac{2}{3m}\nabla\left\{\left[\frac{3}{5}\epsilon_F n_e+\epsilon_F\delta\rho_2(\mathbf{r},t)\right]\frac{\mathbf{r}}{r}\delta(a+\epsilon-r)\right\}$$
$$-\left[\frac{2}{3}\frac{\epsilon_F}{m}\frac{\mathbf{r}}{r}\nabla\delta\rho_2(\mathbf{r},t)+\frac{\omega_p^2}{4\pi}\frac{\mathbf{r}}{r}\nabla\int d^3r_1\frac{1}{|\mathbf{r}-\mathbf{r}_1|}(\delta\rho_1(\mathbf{r}_1,t)\Theta(a-r_1)\right.$$
$$\left.+\delta\rho_2(\mathbf{r}_1,t)\Theta(r_1-a))+\frac{en_e}{m}\frac{\mathbf{r}}{r}\cdot\mathbf{E}(t)\right]\delta(a+\epsilon-r)$$ → surface plasmons

for λ>> a - only dipole type surface plasmon occur

$$\delta\rho(r,t)=\begin{cases}0, r<a,\\ \sum_{m=-1}^{1}Q_{1m}(t)Y_{1m}(\Omega), r\geq a, r\to a+\end{cases}$$

corresponding dipole

$$\mathbf{D}(t)=e\int d^3r\mathbf{r}\delta\rho(\mathbf{r},t)=\frac{4\pi}{3}e\mathbf{q}(t)a^3$$

Surface plasmon oscillation equation

$$\left[\frac{\partial^2}{\partial t^2}+\frac{2}{\tau}\frac{\partial}{\partial t}+\omega_1^2\right]\mathbf{q}(\mathbf{t})=\frac{en_e}{m}\mathbf{E}(\mathbf{t})$$

$Y_{1m}(\Omega)$ spherical function

Q_{1m} dipole type function (l,m-angular momentum n.)

$$Q_{1,1}(t)=\sqrt{\frac{8\pi}{3}}q_x(t)$$
$$Q_{1,-1}(t)=\sqrt{\frac{8\pi}{3}}q_y(t)$$
$$Q_{1,0}(t)=\sqrt{\frac{4\pi}{3}}q_z(t)$$

ω_p bulk plasmon freq.

ω_1 Mie plasmon freq.

$$\omega_1=\omega_p/\sqrt{3}$$

Dissipation chanels

radiative losses - Lorentz Friction

$$\boldsymbol{E}_L=\frac{2}{3\varepsilon v^2}\frac{\partial^3\boldsymbol{D}(t)}{\partial t^3}=\frac{2e}{3\varepsilon v^2}\frac{4\pi}{3}a^3\frac{\partial^3\boldsymbol{q}(t)}{\partial t^3}\simeq\frac{\omega_1}{3}\left(\frac{\omega_1 a}{c}\right)^3$$

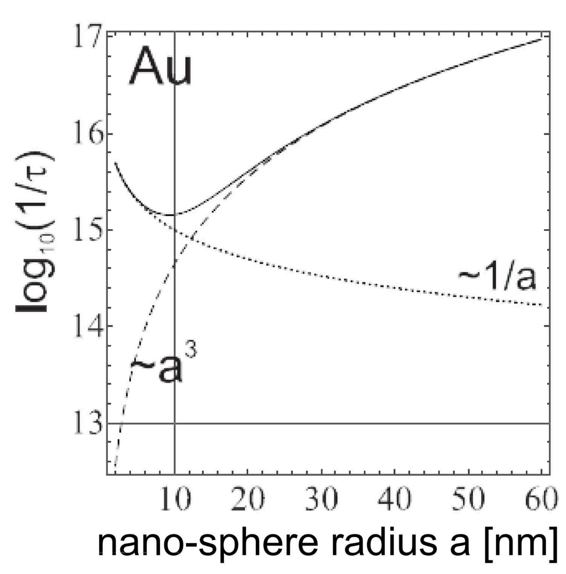
perturbative approximation

$$\frac{\partial^3\boldsymbol{q}(t)}{\partial t^3}\simeq-\omega_1^2\frac{\partial\boldsymbol{q}(t)}{\partial t}$$

scattering losses

$$\frac{1}{\tau_{sc}}=\frac{v_F}{2\lambda_B}+\frac{Cv_F}{2a}$$

↓ bulk scattering ↓ surface scattering



v_F Fermi velocity

C scatt. constant of unity order

λ_B mean free path

Effective attenuation rate as function of nano-sphere radius a. Two regimes: for small particles with a < 12 nm dominate scattering damping and effective attenuation rate scales as 1/a, for large particles a > 12 nm dominate radiative losses and effective attenuation rate scales as a^3.

Numerical calculation method

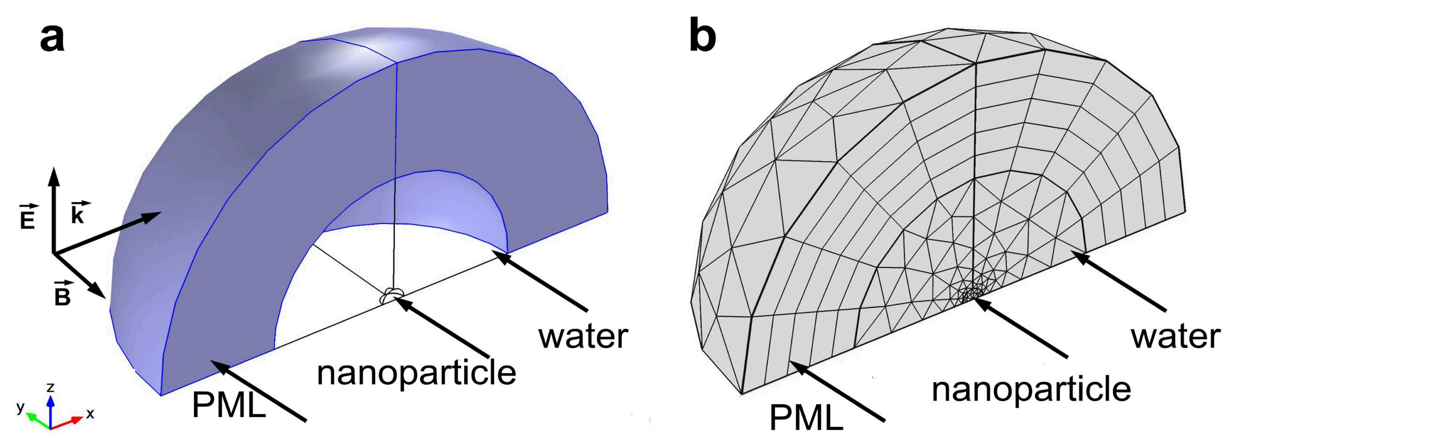
- Finite Element Method
- Software: COMSOL Multiphysics® 4.3 with RF Module
- Classical electrodynamics equations
- plasmon effects modeled via dielectric function of metal

Calculated parameters:

- extinction cross section $Q_{ecs}=Q_{scs}+Q_{abs}$

$$Q_{abs}=\frac{1}{\pi a^2}\frac{2}{\sqrt{\epsilon_0/\mu_0E_0^2}}\int U_{av}dV\qquad Q_{scat}=\frac{1}{\pi a^2E_0}\int|E_{far}|^2d\Omega$$

E_{far} is far field component of electromagnetic field (calculated on the boundary of PML and surrounding media), E_0 - incident electromagnetic field and U_{av} - resistive heat losses in nano-particle.

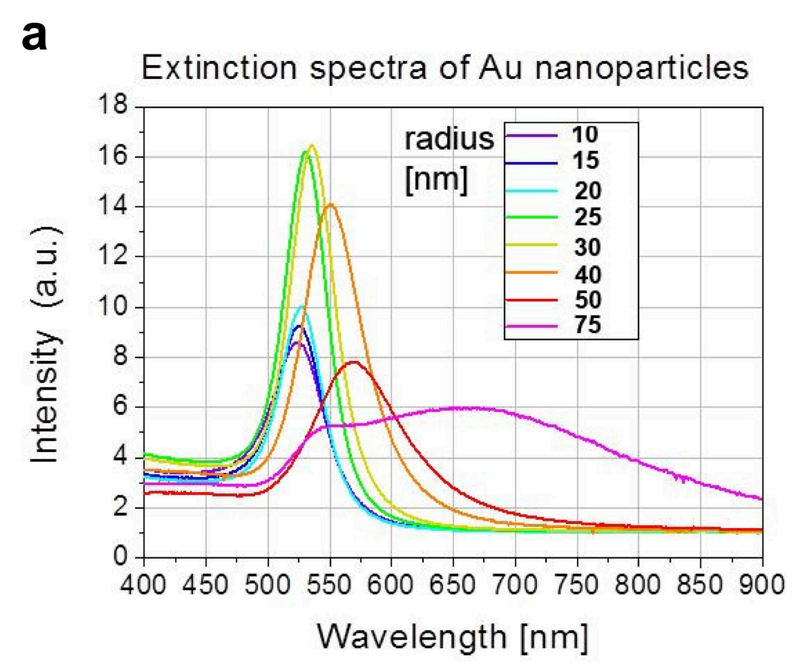


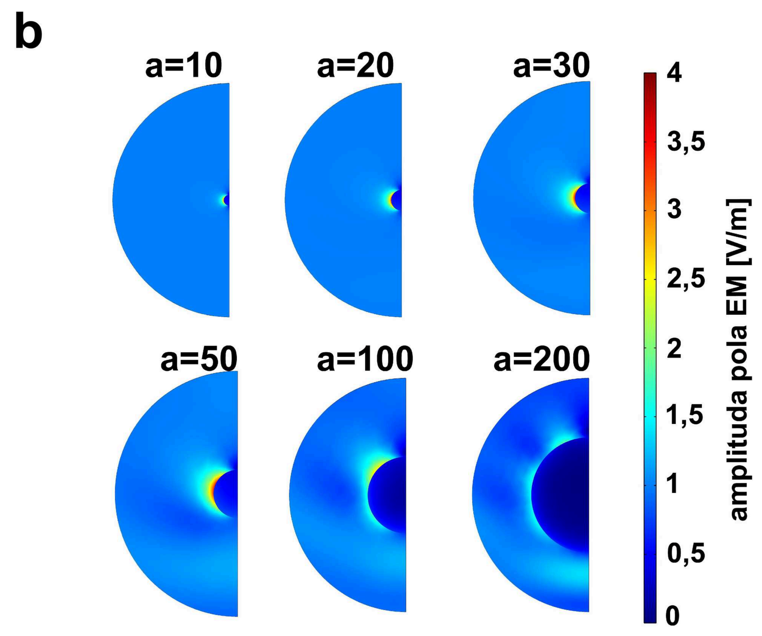
Schematic view on system geometry a and generated mesh b.

Experiment

- measurement of extinction spectra of colloidal solutions of Au nanoparticles in range 10-75 nm.

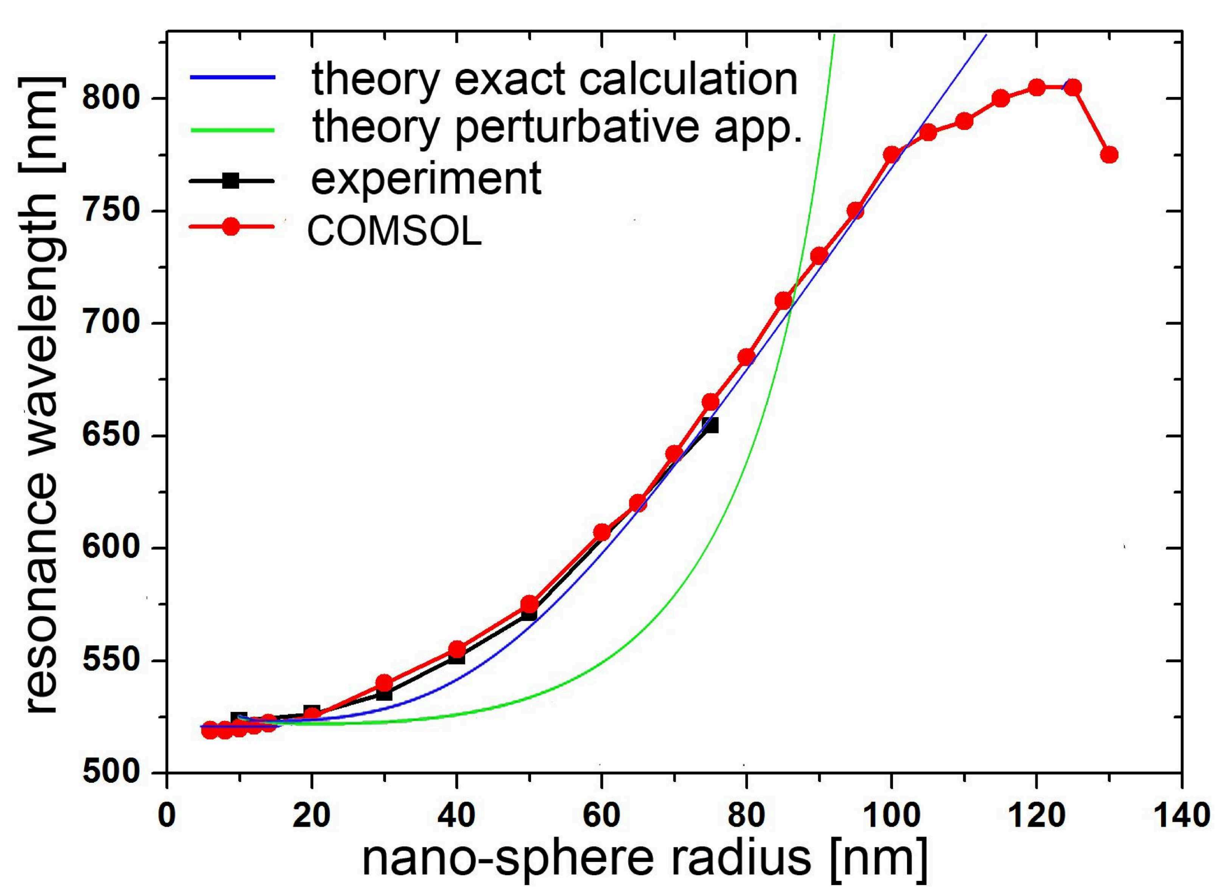
Results and discussion





a - Measured extinction spectra for gold nano-spheres. Visible redshift with increase of radius. In case of small (< 30 nm) and large (> 50 nm) particles we observe decrease in plasmon resonance intensity due to attenuation. Additionaly for radiuses larger then 50 nm we observe additional peak, which could be connected with bulk plasmon modes.

b - Electric field distribution around Au nano-spheres with different radii upon illumination with light of wavelength 400 nm. We observe dipole typeexcitations for small radii and higher modes for radii larger then 50 nm, whichshows that dipole approximation is not applicable.



Comparison of numerical and theoretical predictions to plasmon resonance redshift driven by nano-sphere radius for Au particles with experimental data. For small radii (10 - 20 nm) change resonance wavelength is relatively small, then we observe increase in redshift speed (20-60 nm) and stabilization (>60 nm).This behavior is strictly connected with effective attenuation rate of plasmon oscillations.

References:

1. W. Jacak et al., J. of App. Physics 107 p.124317 (2010)

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