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Introduction into nanoplasmonics. Resonant absorption and scattering of light by metal nanoparticles

Nanoplasmonics. History

In the ancient and middle ages the metal micro and nanoparticles were used for colouring of the glass windows and ceramic pottery.

Lycurgus cup (Byzantine empire, 4th century A. D.): red colour in transmitted light and green colur in scattered light.

Stained glass windows (Gothic Cathedral in Chartres, France).

Nanoplasmonics. Today

What is it and why is it important!

Nanoplasmonics is an area of nanophotonics which deals with phenomena arising from the excitation of the surface coherent collective oscillations of free electrons (surface plasmons) on the metal nanostructure interfaces.

High relevance of the research in nanoplasmonics – high fundamental interest and great number of applications of the plasmonic nanostructures.

- Application as highly sensitive optical sensors.

- Plasmonic enhancement of the local EM-field near the surface of the metal nanostructure: surface enhanced spectroscopy (SERS, SEL, SEIRA, SHG, etc.).

- Considerably lower diffraction limit in metal plasmonic waveguides comparing to common dielectric ones. It allows to use the plasmonic waveguides for directional guiding and processing of light signals at the nanoscale level.

- High potential of plasmonic metal nanostructures in metamaterials fabrication.

1. The dielectric function of metals. Drude-Sommerfeld theory. Bulk plasmons

Equation of free electron (plasma) motion driven by force of external EM-wave $\mathbf{E}(t) = \mathbf{E}_0 \mathrm{e}^{-i\omega t}$

$$m\ddot{\mathbf{x}} + m\gamma\dot{\mathbf{x}} = -e\mathbf{E}$$

Induced electron oscillation:

$$\mathbf{x}(t) = \frac{e}{m(\omega^2 + i\gamma\omega)}\mathbf{E}(t).$$

Macroscopic polarization of medium:

$$\mathbf{P} = -\frac{ne^2}{m(\omega^2 + i\gamma\omega)}\mathbf{E}.$$

Dielectric function of free plasma:

$$\varepsilon_f(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}$$

$$\omega_p = \sqrt{\frac{4\pi ne^2}{m^*}}$$ - plasma frequency;

$\gamma = \gamma_{e-e} + \gamma_{e-ph} + \gamma_{e-d}$ - damping (scattering)rate

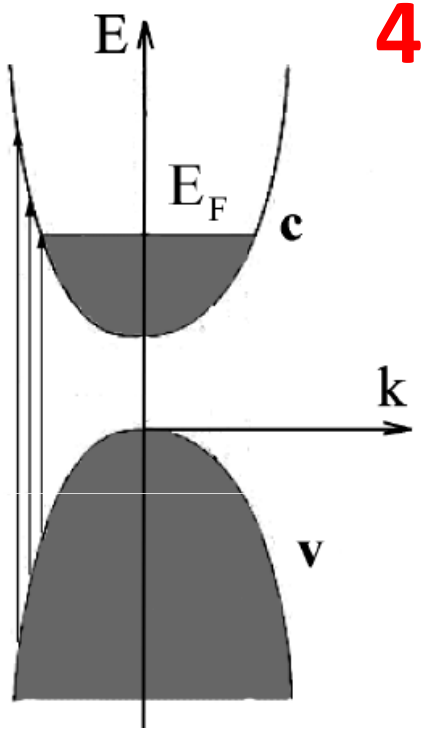
Dielectric function of metal with contribution of bound electrons (interband transitions)

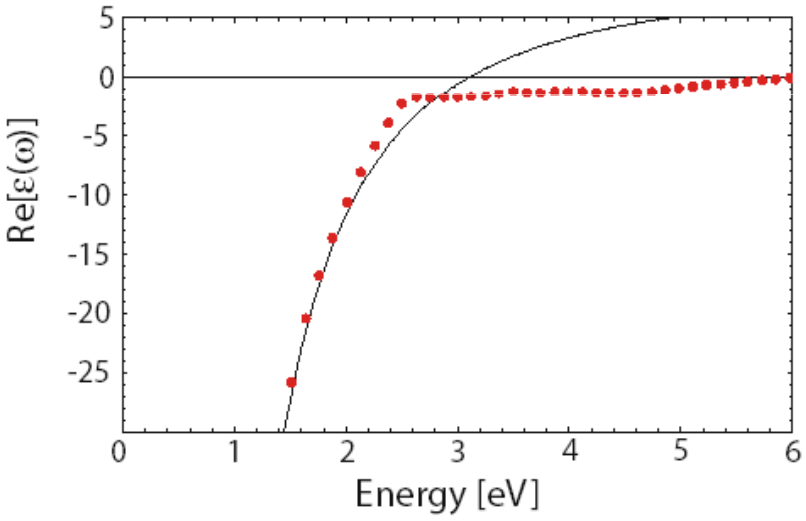
$$\varepsilon(\omega)=\varepsilon_b(\omega)+\varepsilon_f(\omega)=\varepsilon_b(\omega)+1-\frac{\omega_p^2}{\omega^2+i\gamma\omega}$$

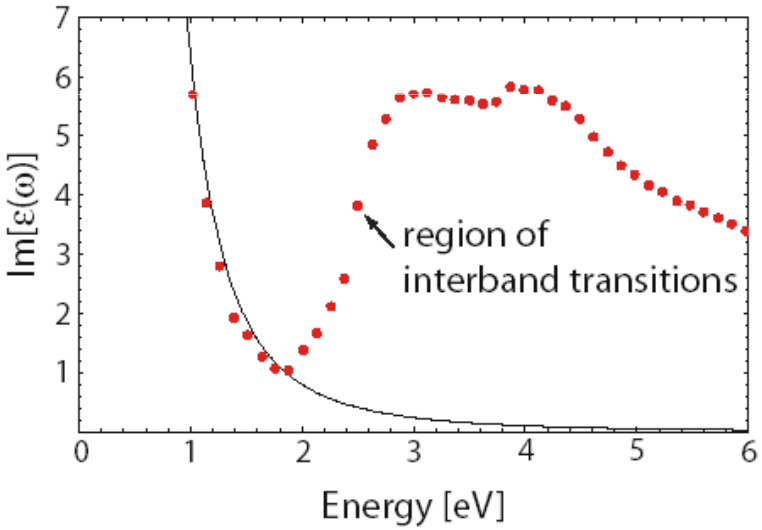
$$\Downarrow$$

$$\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)=$$

$$=\left[\varepsilon_b(\omega)+1-\frac{\omega_p^2}{\omega^2+\gamma^2}\right]+i\left[\frac{\omega_p^2\gamma}{\omega\left(\omega^2+\gamma^2\right)}\right]$$



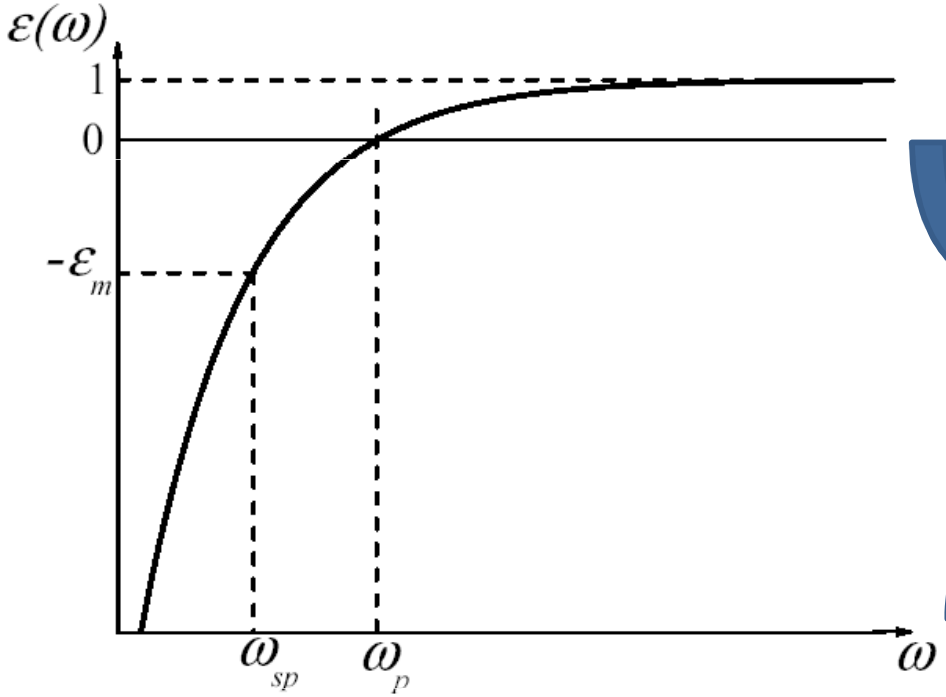




Dielectric function of gold: points – experiment), line – Drude-Sommerfeld theory

Noble metals (Ag, Au, Cu) – small damping and small bound electrons contribution. Dielectric function:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$$



$$\omega < \omega_p \;:\; \mathrm{Re}\,\varepsilon(\omega) < 0$$

- necessary condition for excitation of surface EM-waves (surface plasmons)

$$\omega > \omega_p \;:\; \mathrm{Re}\,\varepsilon(\omega) > 0$$

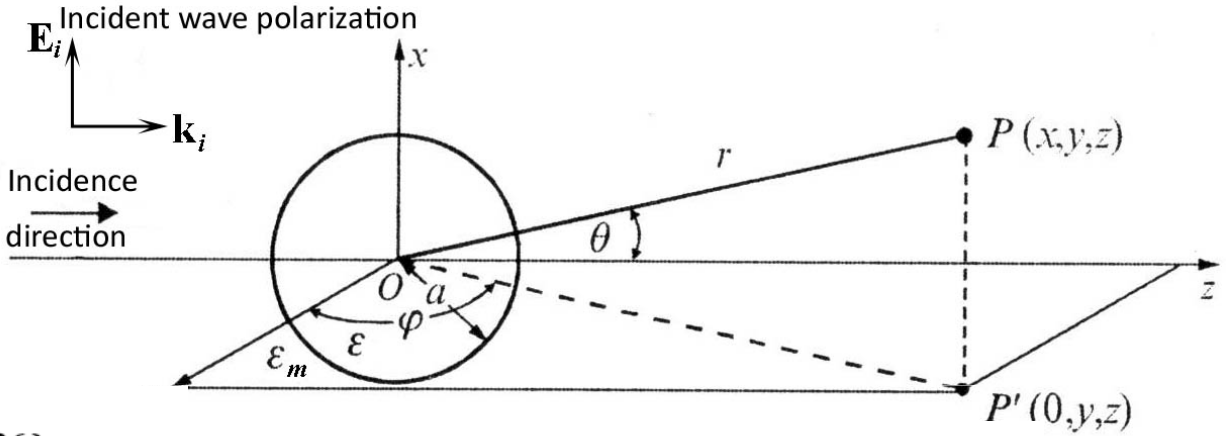
- metal is transparent for EM waves. The volume longitudinal EM waves are excited. The quanta – volume (bulk) plasmons. Due to longitudinal character, the volume plasmons do not interact with light. The dispersion relatio

$$\omega^2 = \omega_p^2 + \frac{6E_F K^2}{5m}.$$

2. Absorption and scattering of light by plasmonic nanocomposites

Unlike to bulk metals, the metal nanoparticles strongly absorb and scatter the light. The cause is excitation of local surface oscillation of free electrons – surface plasmons.

2.1. Mie theory for non-interacting spherical nanoparticles



$$rot\mathbf{H} = \frac{1}{c}\frac{\partial \mathbf{D}}{\partial t} = -i\frac{\varepsilon\omega}{c}\mathbf{E} \ ;$$

$$rot\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t} = i\frac{\varepsilon\omega}{c}\mathbf{H} \ ;$$

- Maxwell equations

$$div\mathbf{E} = 0 \ ;$$

$$div\mathbf{H} = 0 \ .$$

$$E_{i\theta} + E_{s\theta} = E_{l\theta} \ ,$$

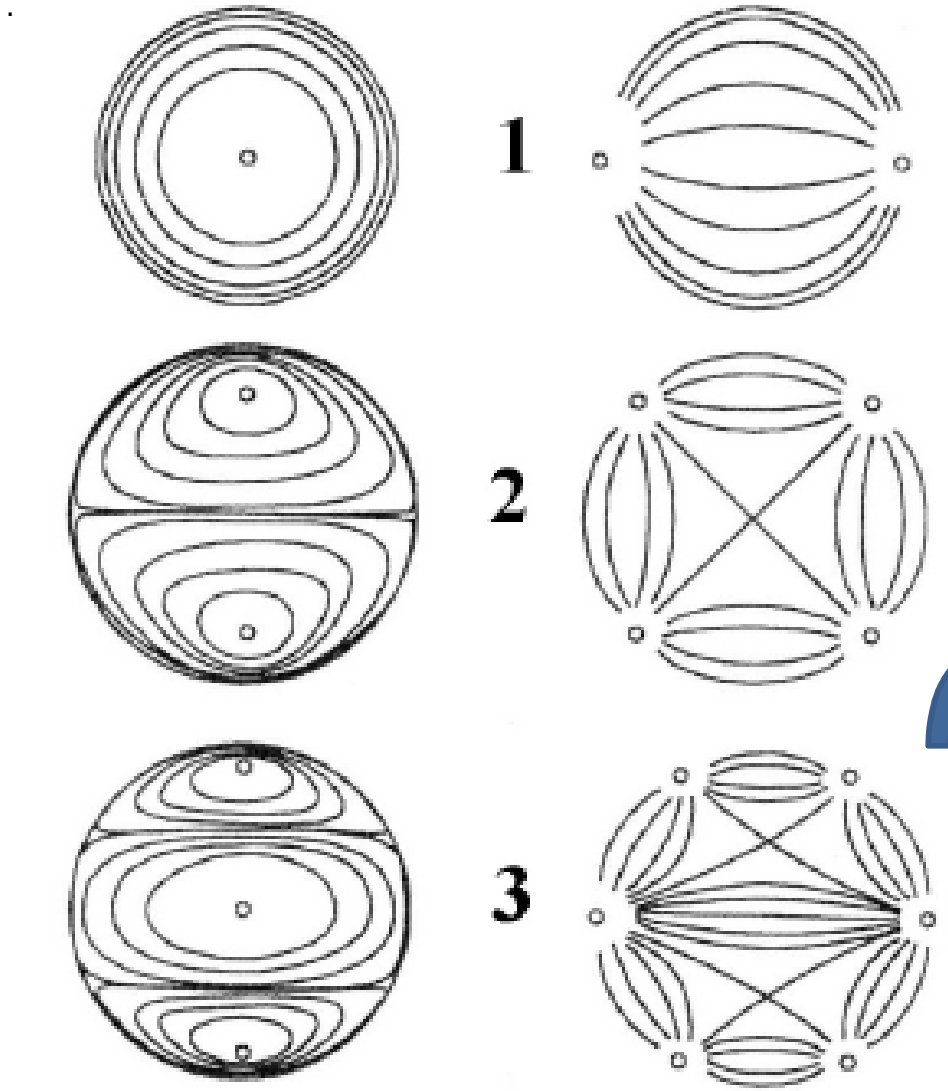
$$E_{i\phi} + E_{s\phi} = E_{l\phi} \ ,$$

$$H_{i\theta} + H_{s\theta} = H_{l\theta} \ ,$$

$$H_{i\phi} + H_{s\phi} = H_{l\phi} \ .$$

- boundary conditions for interface particle-matrix

Maxwell equations with boundary conditions solution gives the expressions for extinction, scattering and absorption cross-sections:



$$\sigma_{ext} = \frac{2\pi}{k^2}\sum_{n=1}^{\infty}(2n+1)\,\mathrm{Re}\left(a_n + b_n\right),$$

$$\sigma_{sca} = \frac{2\pi}{k^2}\sum_{n=1}^{\infty}(2n+1)\left(\left|a_n\right|^2 + \left|b_n\right|^2\right),$$

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

presentation as a superposition of basic spherical EM-waves (spherical EM-modes).

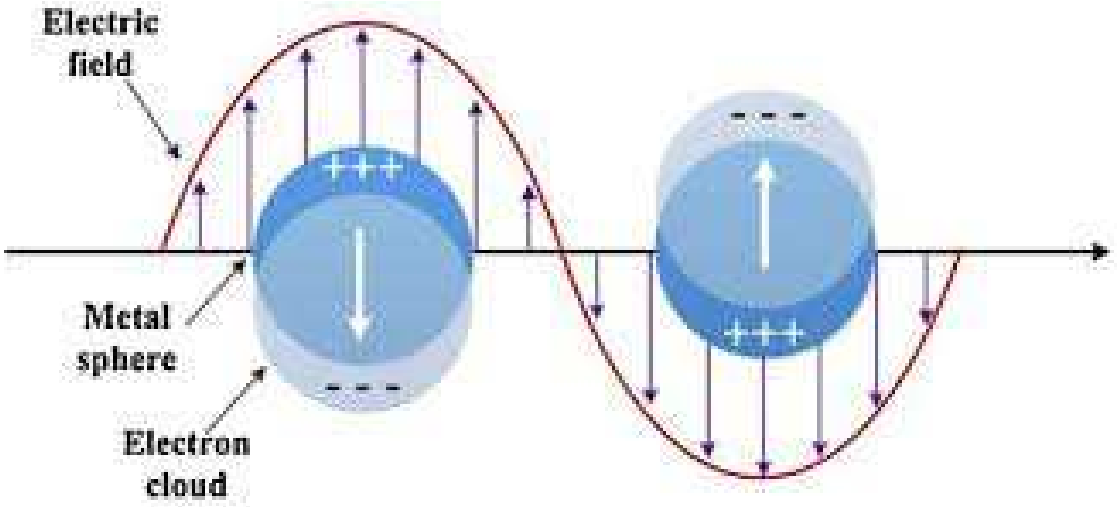
Distribution (force lines) of magnetic and electric fields near the surface of spherical particle:

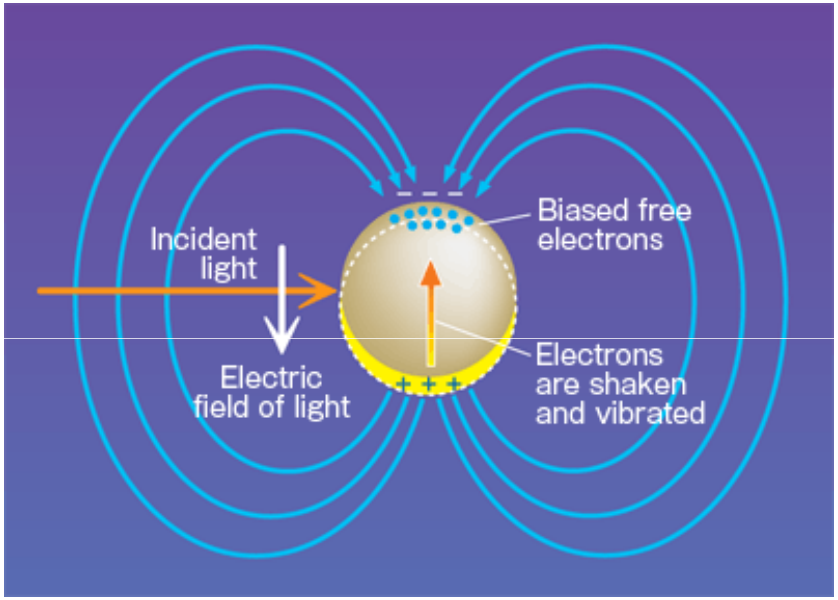
n=1 – dipole mode;

n = 2 – quadrupole mode;

n=3 – octupole mode.

For small nanoparticle much smaller than light wavelength $(a \ll \lambda)$ only dipole (n=1) surface plasmons are excited:





$$\mathbf{E_{in}} = \frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m}\mathbf{E}_0$$

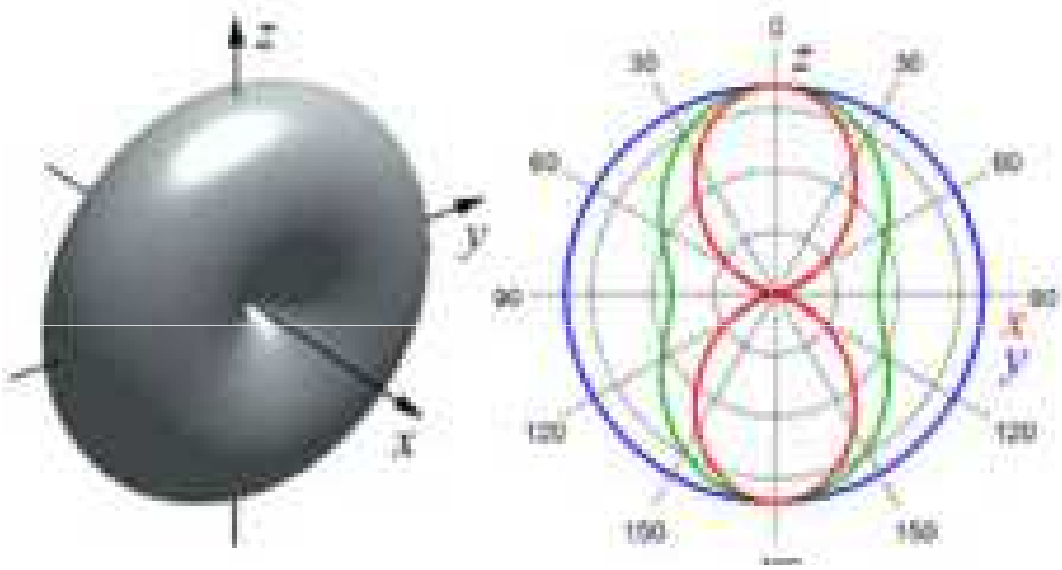
$$\mathbf{E_{out}} = \mathbf{E}_0 + \frac{3\mathbf{n}\,(\mathbf{n}\cdot\mathbf{p}) - \mathbf{p}}{4\pi\,\varepsilon_0\varepsilon_m}\frac{1}{r^3}.$$

- electric field of dipole surface plasmon inside and out the NPs

For small nanoparticles the scattering and absorption cross-sections:

$$\sigma_{sca}(\omega) = \frac{8\pi}{3}k_m^4 a^6 \left|\frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}\right|^2, \qquad \sigma_{abs}(\omega) = 4\pi k_m a^3\,\mathrm{Im}\left(\frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}\right)$$

Elastic (Rayleigh) scattering of light by small nanoparticle – dipole scattering:



$$I_{sca}(r,\theta) = I_i \frac{8\pi^4 n_m^4 a^6}{\lambda^4 r^2} \left| \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right|^2 (1+\cos\theta)$$

- for unpolarized light;

$$I_{sca}(r,\theta) = I_i \frac{8\pi^4 n_m^4 a^6}{\lambda^4 r^2} \left| \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right|^2 \cos\theta$$

- for light polarized parallel to incidence plane xz;

$$I_{sca}(r) = I_i \frac{8\pi^4 n_m^4 a^6}{\lambda^4 r^2} \left| \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right|^2$$

- for light polarized perpendicular to incidence plane xz;

Absorption of light by small nanoparticle – dipole absorption:

$$K = \sigma_{abs} n = \sigma_{abs} \frac{N}{V} = \sigma_{abs} \frac{V_0}{v_0} \frac{1}{V}, \qquad f = V_0 / V$$

Absorption coefficient for nanocomposite containing non-interacting spherical NPs

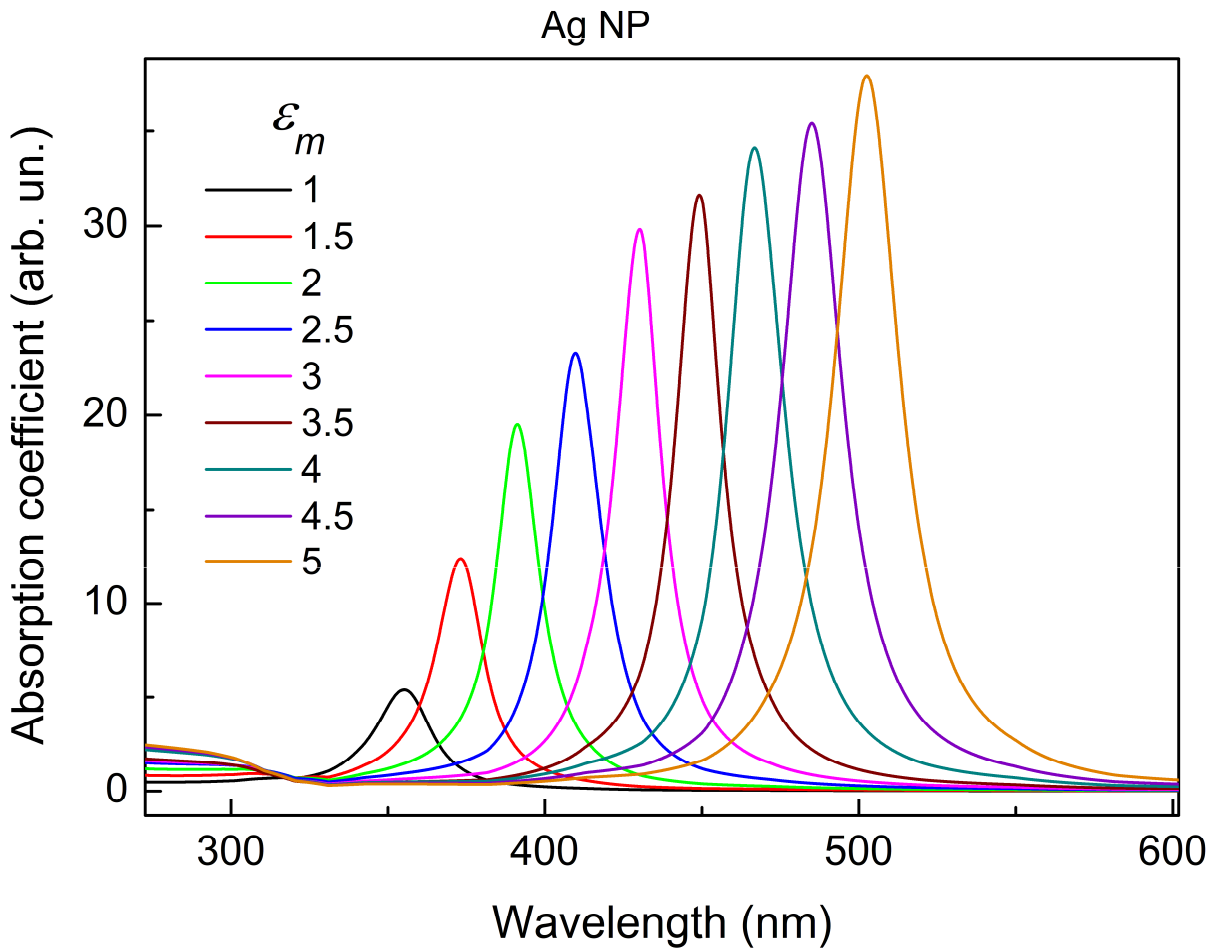
$$K = \frac{9 f \varepsilon_m^{3/2}}{c} \frac{\omega \varepsilon_2}{\left(\varepsilon_1 + 2\varepsilon_m\right)^2 + \varepsilon_2^2}$$

Strong resonant absorption at fulfillment of the condition of the excitation of dipole surface plasmon resonance (SPR)

$$\varepsilon_1 + 2\varepsilon_m = 0 \quad \Rightarrow \quad \varepsilon_1 = -2\varepsilon_m .$$

Dipole SPR excitation condition:

$$\varepsilon_1(\omega) = \varepsilon_b(\omega) + 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2} = -2\varepsilon_m \Rightarrow \omega_{sp} = \sqrt{\frac{\omega_p^2}{1 + 2\varepsilon_m + \varepsilon_{b1}} - \gamma^2}$$



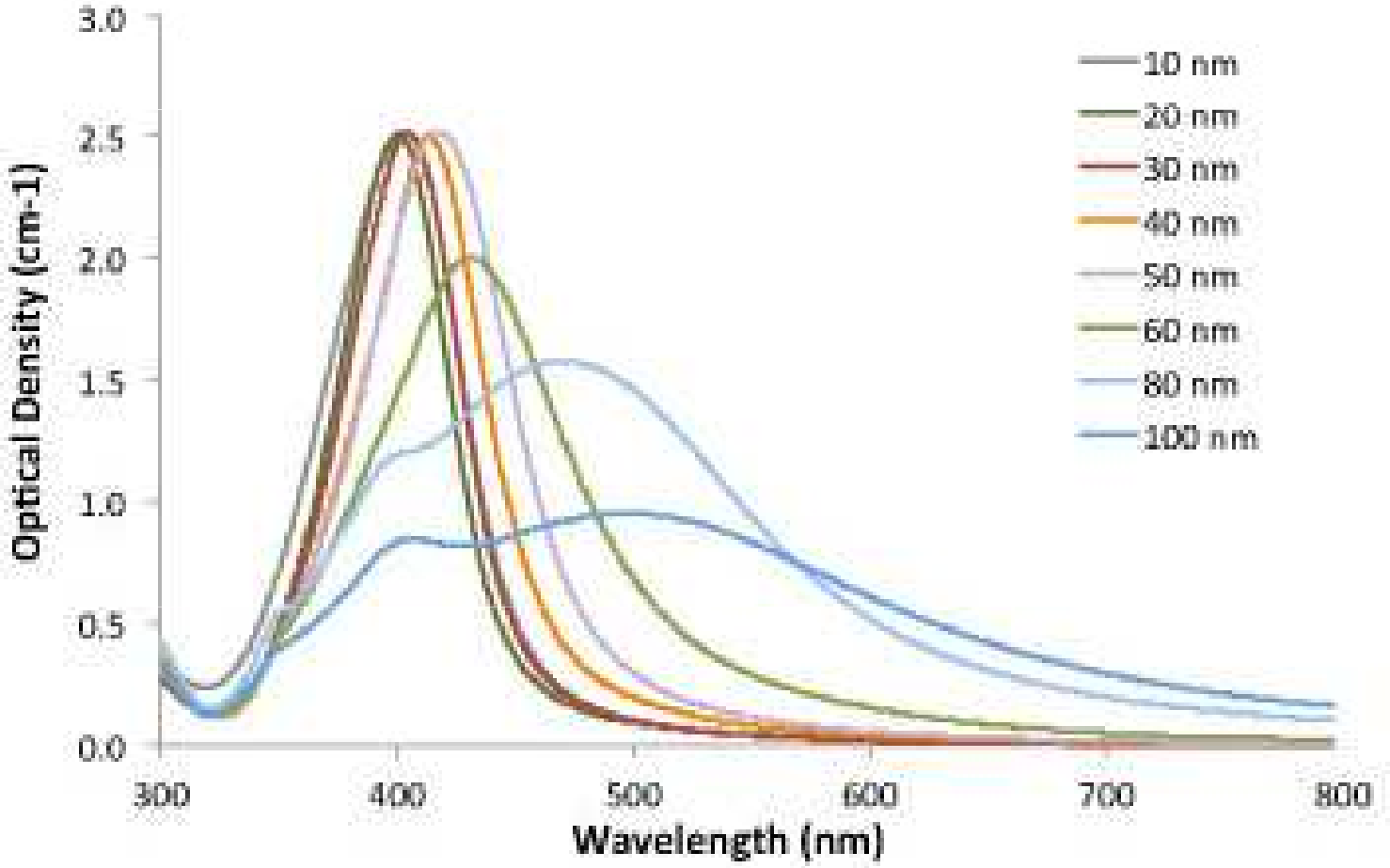
SPR peak wavelength depends on the dielectric permittivity of environment

High sensitive plasmonic optical sensors !

3. SPR modes: dependence on the particle size

$$\mathrm{Re}\,\varepsilon(\omega) = \varepsilon_1(\omega) = -\varepsilon_m \frac{n+1}{n}$$

- condition of the excitation of SPR mutipole modes of *n*-th order



1. Appearance of higher multipolar SPR modes.
2. Low-frequency (red) spectral shift and broadening of dipolar SPR absorption peak.

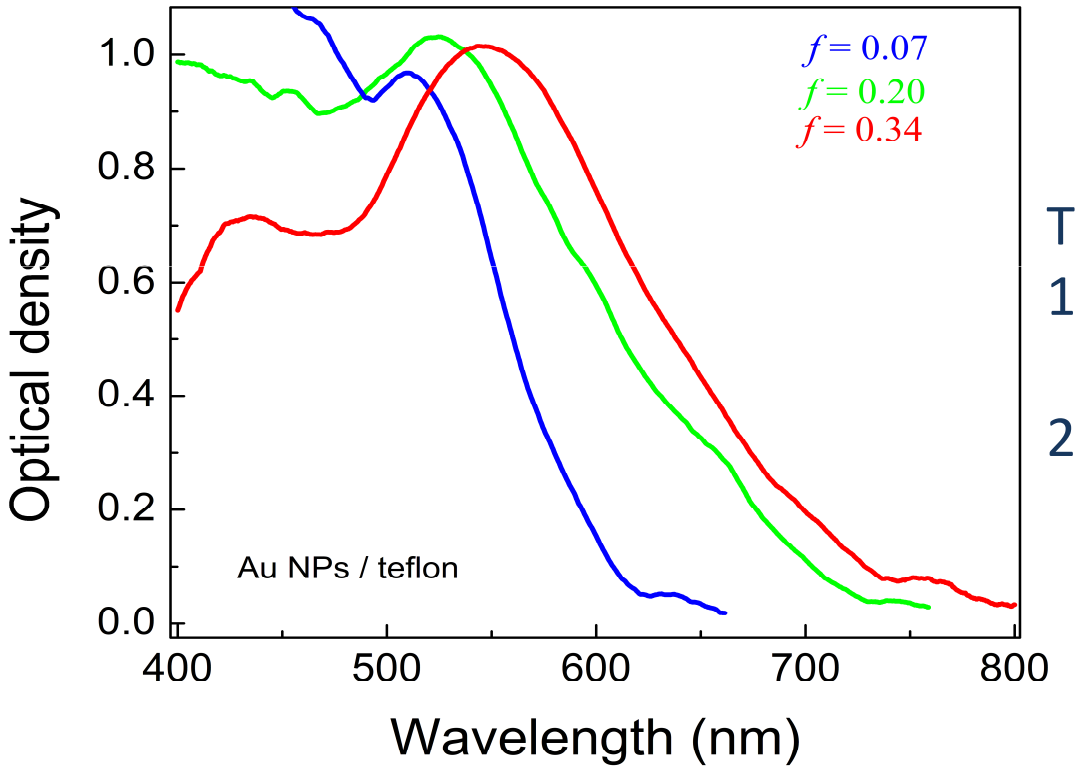
4. SPR modes: influence of the interparticle interaction

$$E(r) \sim \left(\frac{a}{r}\right)^{2n+1}$$

In dense nanocomposites the interparticle interaction can not be neglected.

The **models of effective medium** consider composite as isotropic homogenous medium with the effective dielectric function. In **Maxwell Garnett theory**, the dipole-dipole interparticle interaction is considered.

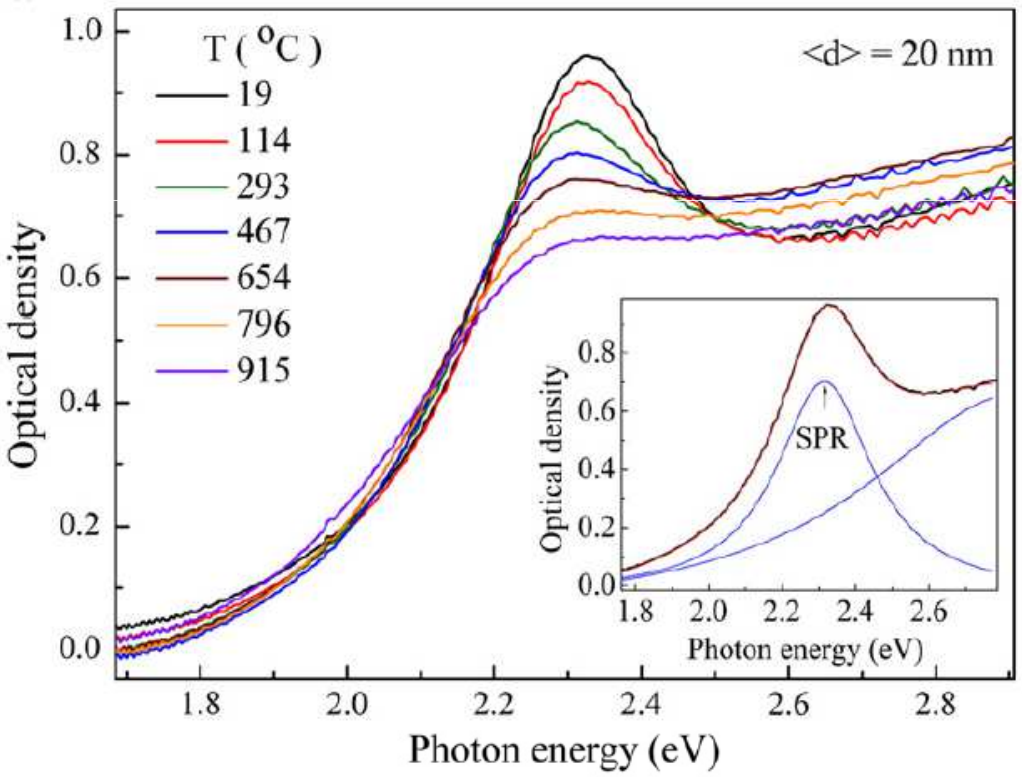
$$\tilde{\varepsilon} = \varepsilon_m \left[1 + 3f \frac{\varepsilon - \varepsilon_m}{\varepsilon(1-f) + \varepsilon_m(2+f)} \right] \quad \Rightarrow \quad K(\omega) = \frac{\omega}{c} \frac{\mathrm{Im}\,\tilde{\varepsilon}(\omega)}{\mathrm{Re}\,\overline{n}(\omega)}$$



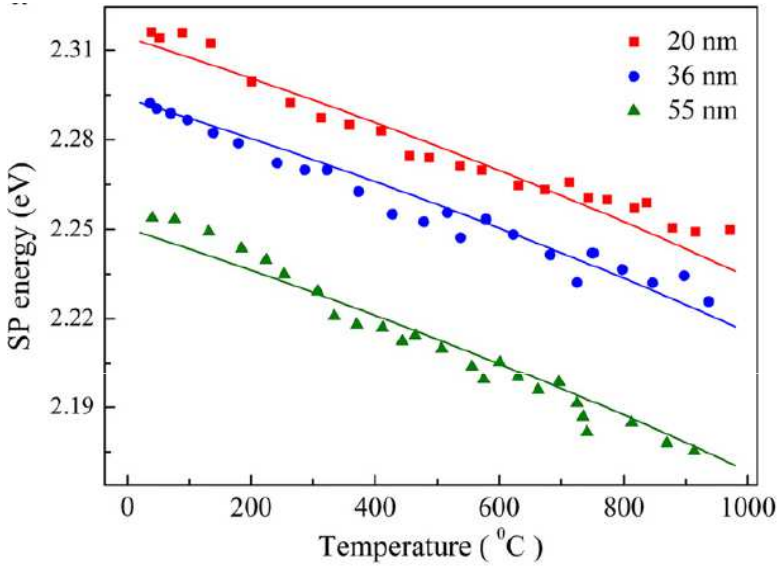
The increase of NP concentration leads to:

1. Red spectral shift of SPR absorption peak.
2. Its broadening.

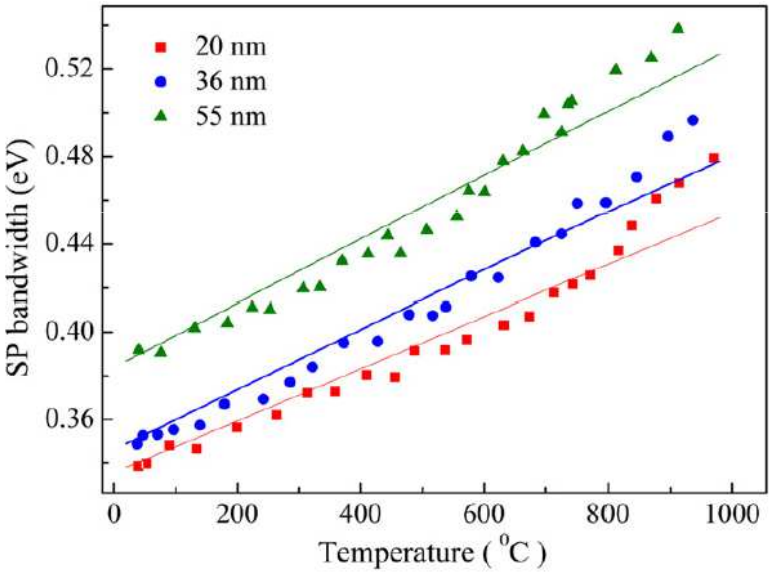
5. Temperature effects in plasmonic spectra of metal nanostructures



Temperature behaviour of absorption spectrum of 20 nm Au NPs in silica.



Temperature dependences of SPR energy for Au NPs of various size in silica (red shift).



Temperature dependences of SPR bandwidth for Au NPs of various size in silica (broadening).

Temperature influence on SPR frequency and bandwidth

SPR frequency temperature dependence

$$\omega_{sp}(T) = \sqrt{\frac{\omega_{p0}^2}{(1+2\varepsilon_m(T)+\varepsilon_{ib1})(1+\beta(T)\Delta T)} - \gamma^2(T)},$$

NP volume thermal expansion (SPR red shift)

$$\gamma(T) = \gamma_\infty(T) + A\frac{v_F}{R(T)},$$

Damping constant temperature dependence

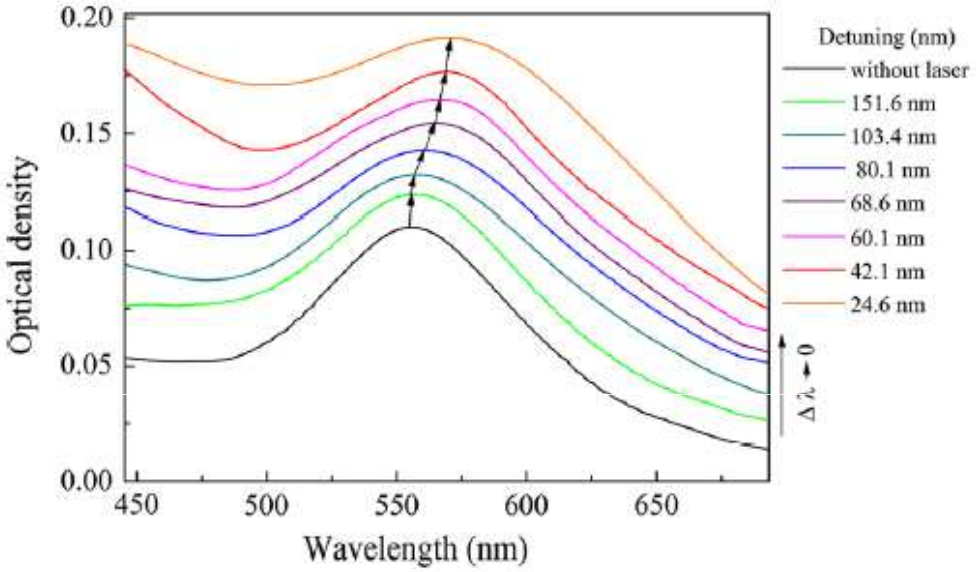
Surface scattering

$$\gamma_\infty(T) = K' T^5 \int_0^{\theta/T} \frac{z^4 dz}{e^z - 1}$$

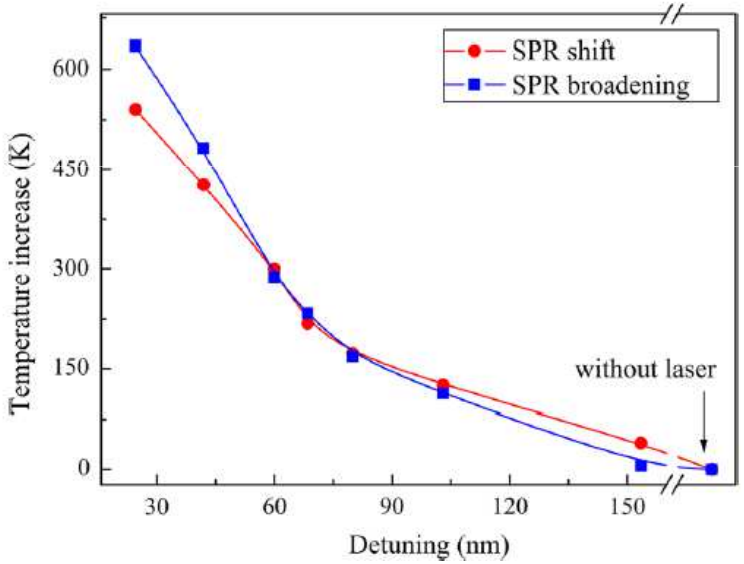
Electron-phonon scattering (SPR broadening)

Due to strong electron-phonon interaction, the excitation of surface plasmons in metal nanostructures by external light leads to high efficient transfer of the heat energy to surrounding environment – so called **"plasmon heating"**. Therefore, the metal nanostructures act as high efficient heaters at the nanoscale. This is used in such applications as thermo-magnetic recording of information, biology and medicine, catalysis, and fabrication of nanostructures and electronic chips.

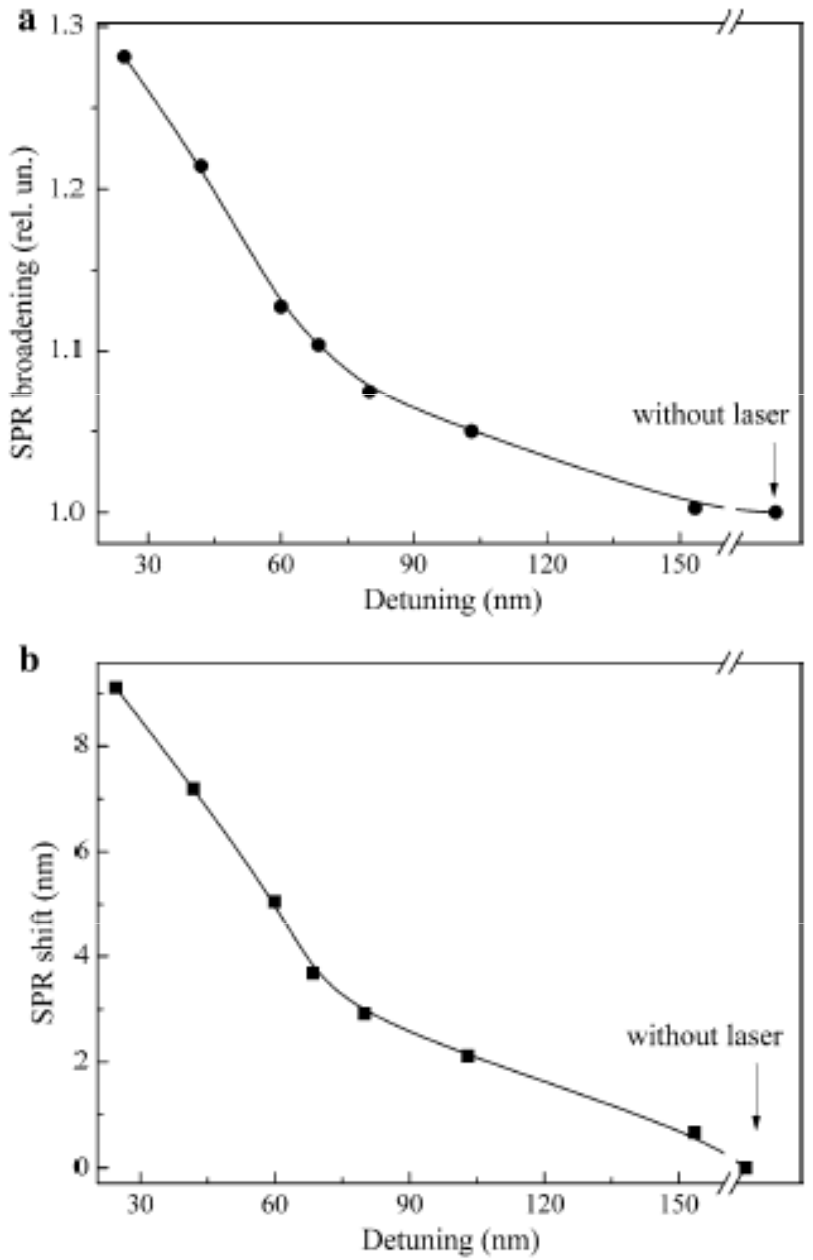
Plasmon induced laser heating of dense 2D Au nanoparticles array



Extinction spectra of 2D ensemble of Au NPs without and under simultaneous CW lasers excitation with various wavelengths.

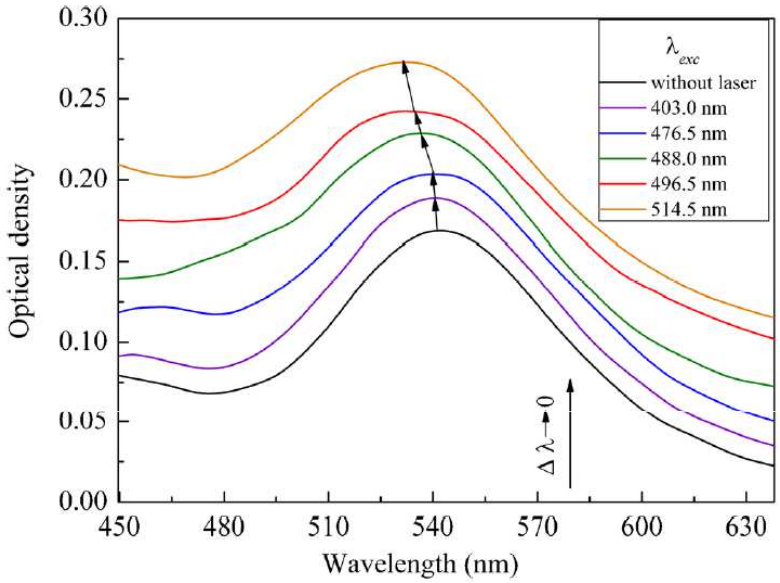


Increase of temperature of 2D Au NPs array laser wavelength at decrease of laser detuning from SPR.

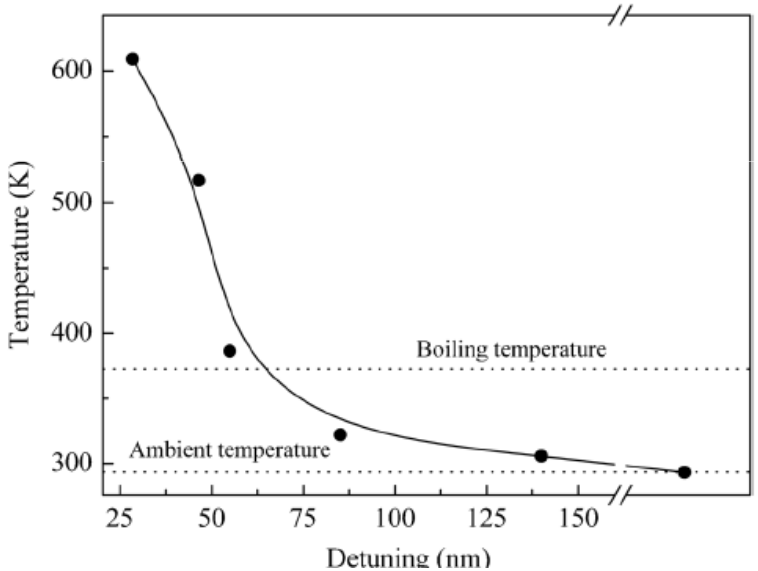


Dependence of SPR extinction band broadening (a) and shift (b) on detuning of the laser wavelength from SPR.

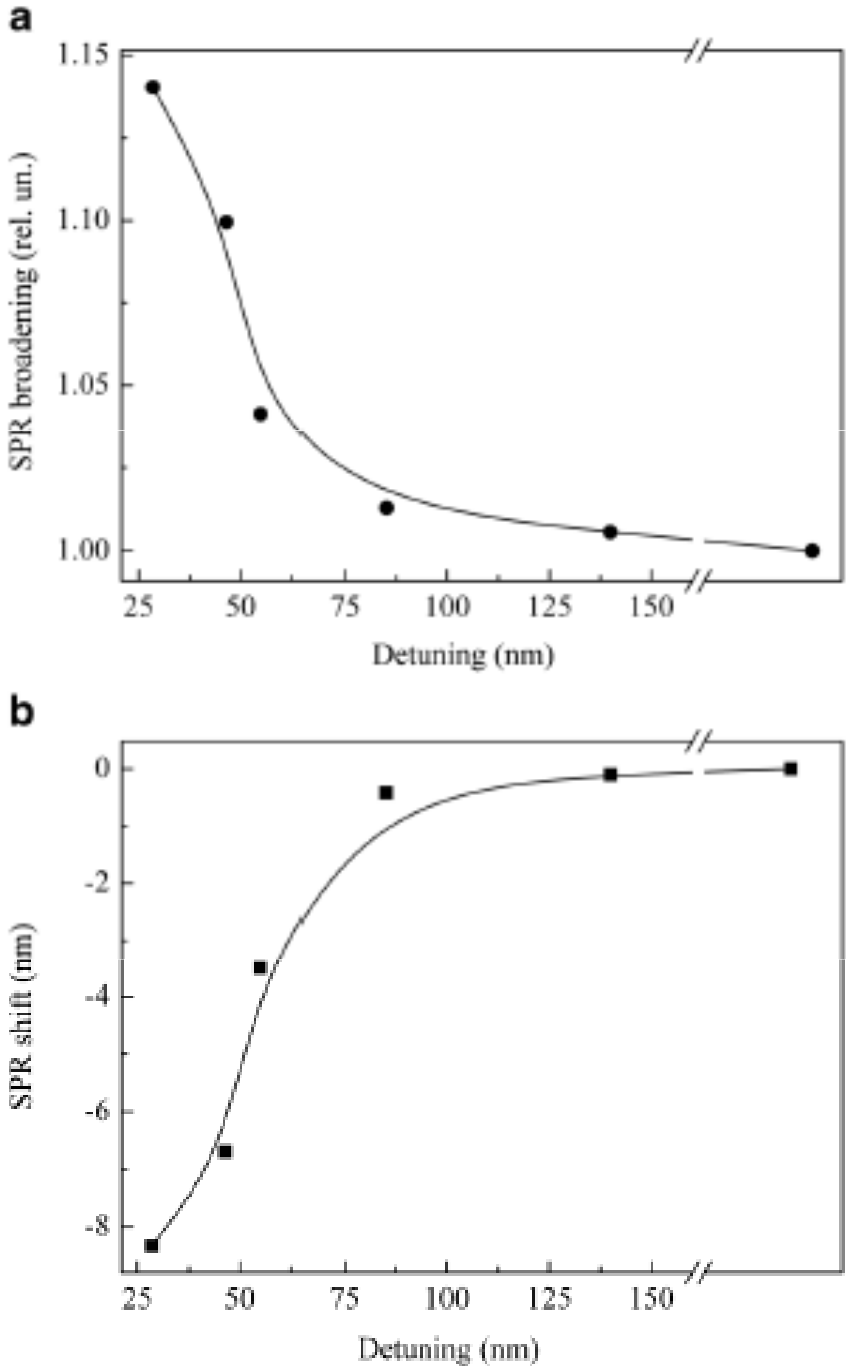
Plasmon induced laser heating of Au nanoparticles colloids



Absorption spectra of Au NPs in colloid without and under simultaneous CW laser excitation with various wavelengths.



Temperature of the Au NPs versus the laser wavelength detuning from SPR.



Dependence of SPR peak broadening (a) and shift (b) on detuning of the laser wavelength from SPR.

Conclusions

1. The excitation of surface plasmons in metal nanoparticles is an origin of strong light absorption and scattering.

2. The dependence of the frequency of SPR in metal nanoparticles on the dielectric permittivity of the surrounding environment is the physical basis of the using of the metal nanostructures as optical sensors.

3. The variation of the nanoparticle size and interparticle distance allows wide efficient tuning of the optical response of the nanoparticles.

4. Metal nanostructures act as high efficient heaters at the nanoscale. This is used in such applications as thermo-magnetic recording of information, biology and medicine, catalysis, and fabrication of nanostructures and electronic chips.

THANK YOU
FOR ATTENTION !