The nanoparticle shape's effect on the light scattering cross-section

D.V.Butenko, **P.M.Tomchuk**
Institute of Physics of NASU

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Introduction

Rayleigh's scattering: $d\Sigma \sim \omega^4 |\alpha(\omega)|^2,$

ω is the light frequency, and $\alpha(\omega)$ is the particle polarization.

Drude-Sommerfeld theory:

$$\epsilon(\omega) = 1 - \frac{\omega_{pl}^2}{\omega^2 + \nu^2} + i\frac{\nu}{\omega}\frac{\omega_{pl}^2}{\omega^2 + \nu^2},$$

ν is the collision frequency inside the particle bulk,
ω_{pl} is the frequency of plasma electron oscillations in the metal.

Size effect: $\nu \rightarrow \nu + A\frac{v_F}{R},$

v_F is the Fermi velocity, R refers to the particle radius,
A is an effective parameter.

Electric field

$$\epsilon''(\omega) = \frac{4\pi}{\omega}\sigma(\omega),$$

$\sigma(\omega)$ is the light-induced conductivity.

External field: $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 exp[i(\mathbf{kr} - \omega t)]$

$$\lambda_D \ll R \ll \lambda,$$

$$kR \ll 1,$$

λ_D is de Broglie wavelength.

$R = max(R_x, R_y, R_z).$

Internal field: $$E^j_{in} = \frac{E^j_0}{1 + L_j[\epsilon(\omega) - 1]},$$

L_j are depolarization factors in the jth direction.

Kinetic approach

$$f(\mathbf{r},\mathbf{v},t) = f_0(\varepsilon) + f_1(\mathbf{r},\mathbf{v})$$

$f_0(\varepsilon)$ is the Fermi distribution function.

Boltzmann equation:

$$(\nu - i\omega) f_1(\mathbf{r},\mathbf{v}) + \mathbf{v}\frac{\partial f_1(\mathbf{r},\mathbf{v})}{\partial \mathbf{r}} + e\mathbf{E}_{in}\mathbf{v}\frac{\partial f_0}{\partial \varepsilon} = 0.$$

Boundary conditions: $f_1(\mathbf{r},\mathbf{v})|_S = 0, \; v_n < 0,$

v_n is the velocity component normal to the particle surface.

$$f_1(\mathbf{r},\mathbf{v}) = -e\mathbf{E}_{in}\mathbf{v}\frac{\partial f_0}{\partial \varepsilon}\frac{1 - \exp[-(\nu - i\omega)t_0(\mathbf{r}',\mathbf{v}')]}{\nu - i\omega},$$

where the characteristic $t_0(\mathbf{r}',\mathbf{v}')$ is

$$t_0(\mathbf{r}',\mathbf{v}') = \frac{1}{v'^2}\left[\mathbf{r}'\mathbf{v}' + \sqrt{(\mathbf{R}^2 - \mathbf{r}'^2)\mathbf{v}'^2 + (\mathbf{r}'\mathbf{v}')^2}\right]$$

Tensor of complex conductivity

Electric current density:

$$\mathbf{j}(\mathbf{r},\omega) = 2e\left(\frac{m}{2\pi\hbar}\right)^3 \iiint \mathbf{v} f_1(\mathbf{r},\mathbf{v}) d^3v$$

Ohm law: $$j_\alpha(\mathbf{r},\omega) = \sum_{\beta=1}^{3} \sigma^c_{\alpha\beta}(\mathbf{r},\omega) E^\beta_{in}$$

$$k_B T/\varepsilon_F \ll 1 \quad \Rightarrow \quad \frac{\partial f_0}{\partial \varepsilon} \approx -\delta(\varepsilon - \varepsilon_F)$$

$$\sigma^c_{\alpha\beta}(\omega) = \left(\frac{m}{2\pi\hbar}\right)^3 \frac{2e^2}{\nu - i\omega} \int \frac{d^3r'}{V} \int d^3v \, v_\alpha \, v_\beta \delta(\varepsilon - \varepsilon_F) \left[1 - e^{-(\nu - i\omega)t_0(\mathbf{r}',\mathbf{v}')}\right]$$

Dielectric function: $$\epsilon_{\alpha\beta}(\omega) = \delta_{\alpha\beta} + i\frac{4\pi}{\omega}\sigma^c_{\alpha\beta}(\omega).$$

Spheroidal nanoparticle

$$R_x = R_y = R_\perp, R_z = R_\parallel$$

Polarization tensor of a spheroidal nanoparticle

$$\alpha_{\perp,\parallel}(\omega) = \frac{V}{4\pi}\frac{\epsilon_{\perp,\parallel}(\omega)-1}{1+L_{\perp,\parallel}[\epsilon_{\perp,\parallel}(\omega)-1]}$$

Nanoparticles are chaotically oriented in the ensemble of particles. After averaging over different orientations of nanoparticles, the light scattering cross-section is:

$$\langle\, d\Sigma\,\rangle = \frac{\omega^4}{15c^4}\left\{2\left|\alpha_\perp(\omega)-\alpha_\parallel(\omega)\right|^2 + \frac{1}{2}\left[3\left|2\alpha_\perp(\omega)+\alpha_\parallel(\omega)\right|^2 \right.\right.$$
$$\left.\left. +2\left|\alpha_\perp(\omega)\right|^2 + \left|\alpha_\parallel(\omega)\right|^2\right]\sin^2\psi\right\} d\Omega$$

where ψ is an incidence angle

Numerical calculations

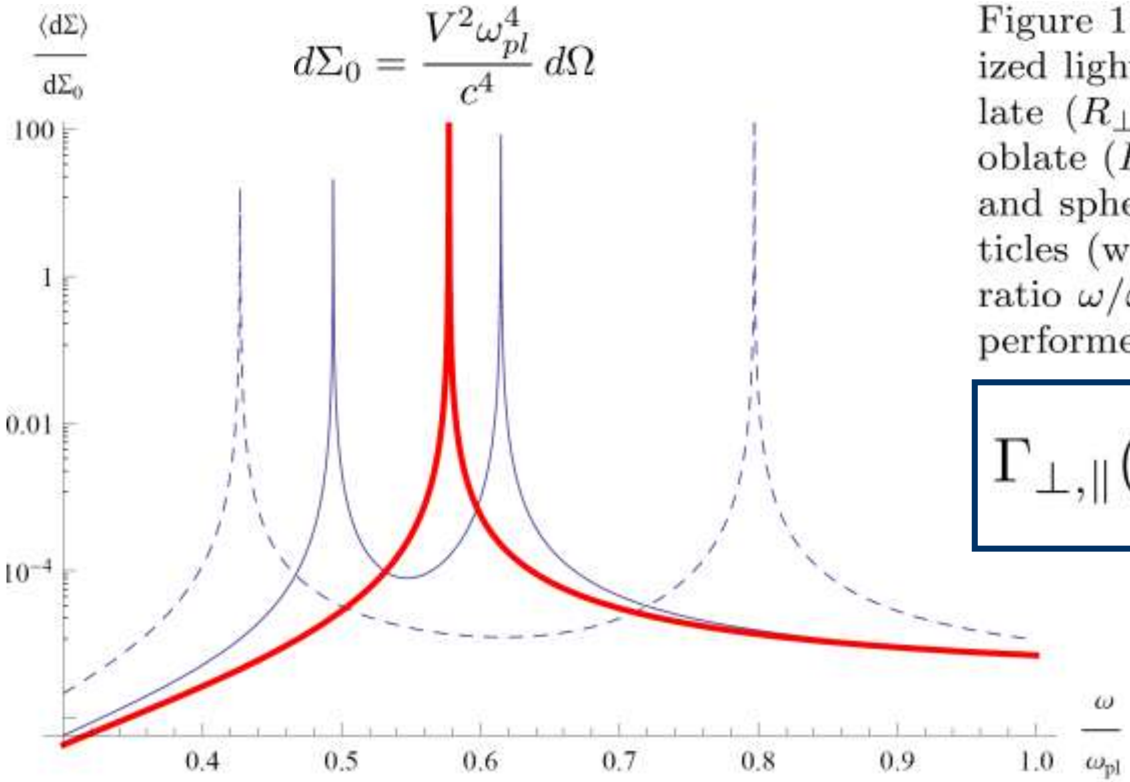

Figure 1: The dependence of the normalized light scattering cross-section for prolate ($R_\perp / R_\parallel = 0.7$, solid (blue) curve), oblate ($R_\perp / R_\parallel = 3$, dashed (blue) curve) and spherical (thick (red) curve) Au particles (with $R = 20nm$) vs the frequency ratio ω/ω_{pl}. The numerical evaluation is performed for the angle $\psi = \pi/4$.

$$\Gamma_{\perp,\parallel}(\omega) = 2\pi L_{\perp,\parallel}\sigma_{\perp,\parallel}(\omega)$$

$\nu = 3.39 \cdot 10^{13}$ at $0°C$, $n = 5.9 \cdot 10^{22} cm^{-3}$, $v_F = 1.39 \cdot 10^8 cm/s$.

Numerical calculations

$$|\alpha_\perp(\omega)|^2_{\omega=\omega_\perp} / |\alpha_\parallel(\omega)|^2_{\omega=\omega_\parallel} \approx \left[\frac{L_\parallel \sigma_\parallel(\omega_\parallel)\omega_\parallel}{L_\perp \sigma_\perp(\omega_\perp)\omega_\perp} \right]^2$$

for $R_\perp \gg R_\parallel$ $\quad |\alpha_\perp(\omega)|^2_{\omega=\omega_\perp} / |\alpha_\parallel(\omega)|^2_{\omega=\omega_\parallel} \approx 4.$

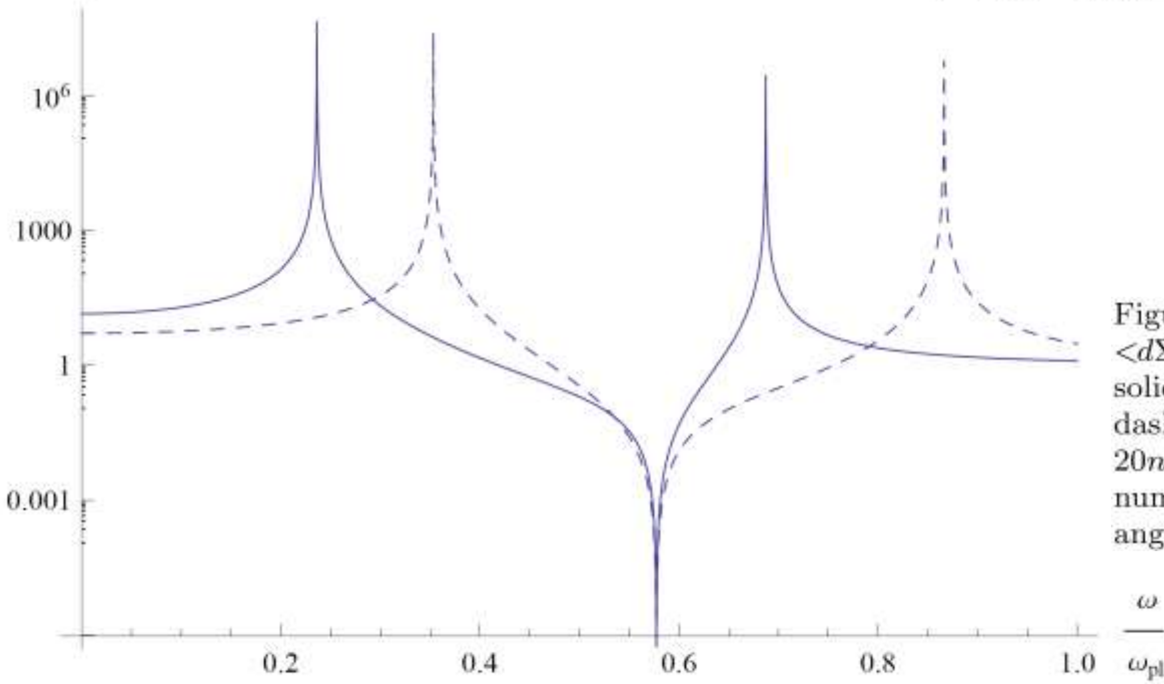

Figure 2: The dependence of the ratio <$d\Sigma$>$/d\Sigma_{sph}$ for prolate ($R_\perp/R_\parallel = 0.2$, solid curve) and oblate ($R_\perp/R_\parallel = 5$, dashed curve) Au particles (with $R = 20nm$) vs the frequency ratio ω/ω_{pl}. The numerical evaluation is performed for the angle $\psi = \pi/4$.

Numerical calculations

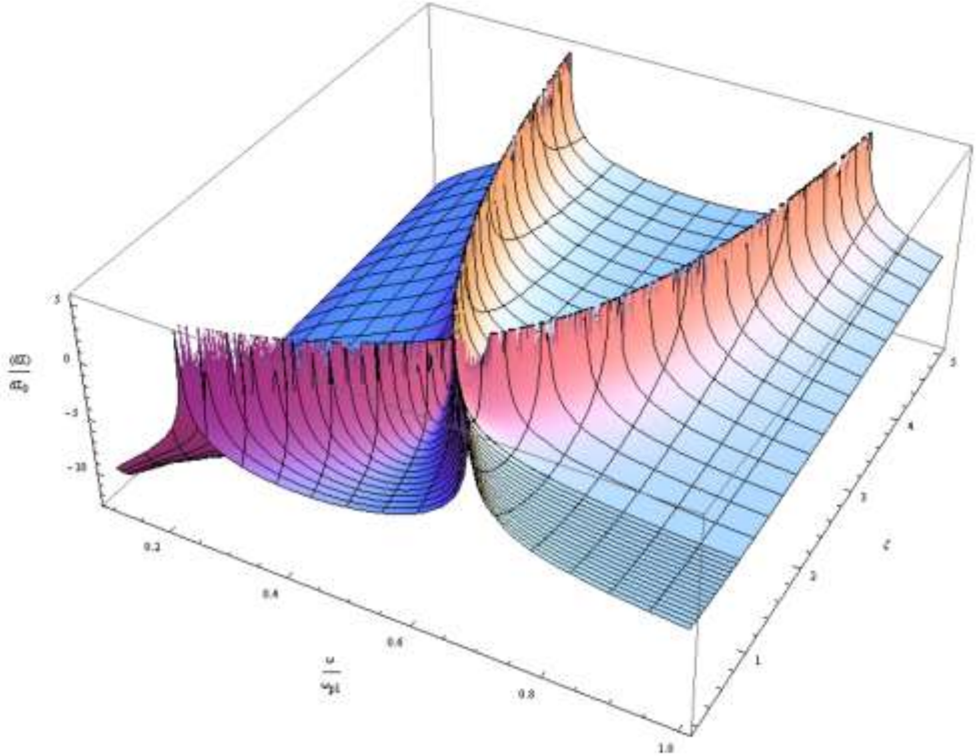

Figure 3: The dependence of the ratio $< d\Sigma > / d\Sigma_0$ for spheroidal Au particles (with $R = 5nm$) vs the frequency ratio ω/ω_{pl} and the semiaxes ratio $R_\perp / R_\parallel \equiv \zeta$. The numerical evaluation is performed for the angle $\psi = \pi/4$.

Conclusions

- When a size of the particle becomes less than a free electron path, the conductivity of an asymmetrical particle becomes a tensor quantity, and the diagonal elements of this tensor define the half-widths of plasmon resonances. The half-widths in turn define an intensity of light scattering in a region of frequencies close to resonances.
- It has been shown that in the collection of chaotically oriented identical asymmetrical particles averaging over different directions of particles does not change distinctive features of asymmetrical particles. A spectrum of light scattering has two peaks at the frequencies of plasmon resonances in contrast to a spectrum for spherical particles that has only one peak.
- Regarding to the effect of particle's shape on the plasma resonance half-widths, one may obtain results that can differ several times from the results obtained without regarding to this effect.

Thank You for Your Attention