Limiting case of size and quantum-size effects in gold granules

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Abstract. The article is described the optical properties of nanostructures containing spherical gold nanoparticles with different radius. There is a deduction of the dielectric permittivity model describing absorption optical spectra of composites containing gold films of various sphere diameter. Conclusions following Mie theory of absorption of sphere of various diameter and dielectric permittivity are discussed. The applicability condition for different models was related to the particle radius. The boundary diameter for different dielectric permittivity model of the gold nanoparticles had been calculate and experimentally exam.

Introduction
The Mie theory [1] is based on the solution of Maxwell equations describing the fields when a plane monochromatic wave affects a spherical surface, while the physical properties of the latter should differ significantly from those of the environment. The physical meaning of this difference lies in dielectric permittivity [2], which is directly related to the extinction coefficient [3], a parameter measured in experiments.

\[ A = A_{abs} + A_{sc} = q\sigma_{ext} = q(\sigma_{abs} + \sigma_{sc}) \]  

where \( A_{abs} \) – absorption coefficient
\( A_{sc} \) – scattering coefficient
\( q \) – particle filling factor, specific volume occupied by particles
\( \sigma_{ext} \) – the effective cross section of one particle extinction
\( \sigma_{abs} \) – effective cross section of one particle absorption
\( \sigma_{sc} \) – effective cross section of one particle scattering

When the particle size is much smaller than the irradiation wavelength (\( a \ll \lambda \)), the formulas for the effective cross section of absorption and scattering look as follows [4]:

\[ \sigma_{abs} = 4\pi \frac{\omega}{c} n_0 a^3 Im \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} \]  

\[ \sigma_{sc} = \frac{8\pi}{3} c n_0 a^3 \varepsilon_0^2 \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0}^2 \]

where \( \omega \) – the frequency of the electromagnetic radiation incident on the particle
\( c \) – speed of light
\( n_0 \) – refractive index of the medium adjacent to the particle
\( a \) – particle size
\( \varepsilon \) – permittivity of the particle
\( \varepsilon_0 \) – permittivity of the medium adjacent to the particle

It is evident that, effective extinction cross section essentially depends on the permittivity model of the scattering and absorbing particles. So, a question arises of the limits of applicability of a particular model that describes the permittivity of absorbing or scattering particles. Thus, for a continuous metal film, the Drude theory [5] is applicable, which describes the reflection spectra well. This theory [5] gives the following expression for the permittivity:

\[ \varepsilon = 1 - \frac{\omega_p^2}{\omega^2 + i\nu\omega} \]  

where \( \omega_p = \sqrt{\frac{4\pi n_0 e^2}{m}} \) is the free electrons oscillation plasma frequency

This formula is based on the assumption that permittivity only relies on the free electron gas plasma in the metal rather than size effects. One of the first attempts to record size effects was made by Maxwell Garnet [6], who suggested that
individual metal spherical granules isolated from each other are distinguishable dipoles located on a non-absorbing dielectric substrate with permittivity \( \varepsilon_0 \). In this case [7], the effective permittivity of the colloid \( \varepsilon_{ef} \) is described by the equation:

\[
\varepsilon = (n - ik)^2 = 1 + \frac{3q n_m^2 - 1}{n_m^2 + 2} \tag{5}
\]

\( n \) and \( k \) – effective optical constants of the colloid
\( n_m \) – is the complex refractive index of the granule substance (assumed to be the same as that of bulk metal)

However, to derive the formula (5), the Lorentz-Lorenz equation [8] was used, which gives an unsatisfactory result in the case of a two-dimensional colloid of a granular film. On the other hand, the effective value of the complex dielectric constant of the film depends on the concentration of granules [9], which contradicts the equation (5).

Attempting to remove the contradictions Hampe [10] experimented on deposition of fine gold particles on fused quartz substrates. By annealing the prepared samples, making spectrophotometric measurements, and taking electron- microscopic photographs, Hampe showed that, despite the fact that the factor of filling the colloid with metal does not change during annealing, the absorption maximum increased and sharpened with increasing gold particle size, and its position in the spectrum changed. Thus, the Maxwell-Garnet theory showed a discrepancy with the experiment, since according to equation (5) the position of the absorption band maximum is determined only by the value of the filling factor \( q \). To solve the problem that arose, Hampe suggested that the appearance of an anomalous absorption band is associated with oscillations of free electrons inside the granules. However, Hampe did not take into account the dipole-dipole interaction between the granules. All of the above ideas were combined in the Hampe-Shklyarevskii theory [11], in which the values of the real and imaginary parts of the effective permittivity of a granular film were found in the following formula:

\[
\varepsilon_1 = n^2 - k^2 = \varepsilon_m q + (1 - q) \varepsilon_0 + \frac{q \omega_o^2 (\omega^2 - \omega_o^2)}{(\omega^2 - \omega_o^2)^2 + \gamma^2 \omega_o^2} \tag{6}
\]

\[
\varepsilon_2 = 2nk = \frac{q \omega_o^2 \gamma^2}{(\omega^2 - \omega_o^2)^2 + \gamma^2 \omega_o^2} \tag{7}
\]

\( n \) and \( k \) – effective optical constants of the film.
\( \varepsilon_m \) – dielectric constant conditioned by interband transitions in a metal granule
\( \varepsilon_0 \) – dielectric constant of the medium surrounding the granules
\( \gamma \) – frequency relaxation of free electrons in a granule
\( \omega_o \) – frequency of the natural transition in the metal
\( \omega_o \) – plasma frequency of the i-transition

This approach confirmed the experiment [12], but did not provide explanations on the theoretical definition of the dielectric constant, which takes into account interband transitions. Thus, the idea of a hybrid or combined nature of plasma resonance arose. Thus we divided \( \varepsilon_1(\omega) \) [13] into two parts, one of which corresponds to free electrons, and the other is related to interband absorption. This work suggests that gold has zero values \( \varepsilon_1(\omega) \) when \( \omega \sim 3.2 \) eV. Thus, hybrid resonance can be associated with the collective nature of both d- and s-electrons behavior. The existence of such a resonance must depend, in particular, on the strength of the oscillator and on the frequencies of the transitions under consideration. Thus, in [14], we obtained permittivity formulas for a colloid containing small metal spheres, and analyzed the optical properties of a colloid containing small silver particles.

Based on the classical theory of dispersion, the complex dielectric constant can be as follows:

\[
\varepsilon^1(\omega) = 1 + \sum_{i=1}^{n} \frac{\omega_{pi}^2}{\omega_o^2 - \omega^2 + i\gamma_o^2} \tag{9}
\]

where \( \omega_{qi} \) – the natural frequencies of the i-transition,
\( \gamma_o \) – relaxation frequency
\( \omega_{pi} = \frac{4\pi n_i e^2}{m} \) – the plasma frequency of the i-transition in which \( n_i \) electrons participate (\( n_i = \)
where $f_i$ – the oscillator strength of the i-transition, $n$ – the total concentration of electrons).

The dielectric constant of the considered environment $\varepsilon$ can be found by summing the susceptibilities of the spheres and their environment using the ratio [14]:

$$\varepsilon(\omega) = \varepsilon_0 (1 - q) + q \frac{\sum (\omega_s^2 \epsilon_{ij} \omega_j)}{\prod \omega_i^2 + \sum \omega_s^2 \epsilon_{ij} \omega_j}$$

where $r_i = \frac{\omega_0^2 - \omega^2 + i \gamma_0 \omega}{\omega_i^2}$ is the denominator in the i-term in (9),

$$\omega_s^2 = \omega_p^2 (1 + 2 \varepsilon_0)^{-1},$$

and the products and the sum in (10) are taken according to the number of oscillators. Using this formula, one can calculate the optical properties of a colloid if the characteristics of individual oscillators $\omega_0i$, $\omega_p$, $\gamma_0i$, are known.

**Material and Methods**

The preparation of samples for further research was carried out according to the method described in detail in [15] with some improvements described below.

The Au film was deposited on a SiO$_2$ substrate in a $10^{-7}$ Torr vacuum, by means of thermal evaporation from a boat. The substrate was preliminarily cleaned in chromium peak and then processed by ion discharge in low vacuum (approximately $10^{-2}$ Torr). The initial film thickness had been 100 nm.

Then, for the first time, a specially developed modified laser implantation technology was used for thermal treatment of a gold film and partial implantation of gold nanoparticles into the near-surface layer of fused quartz in the most thermally active band.

The essence of the technology is that the gold film was exposed to thermal treatment using two lasers located on the same optical axis and heating the sample with the film from both sides. A 10 W Holmium doped yttrium aluminum lasers (Ho:YAG) laser with a wavelength of 2.1 μm operated on the side of the gold film. The opposite side of the substrate was heated by a 25 W CO$_2$ laser with a wavelength of 10.6 μm. The temperature gradient in SiO$_2$ was controlled by a *Fluke Ti400* thermal imager with a wavelength range of 8–15 μm. The Ho:YAG laser was taken due to the fact that the emissivity of gold at a wavelength of 2.1 μm is ~0.4 [16]. In other words, 40% of the laser radiation is absorbed by the gold film, and 60% is reflected. On the other hand, fused quartz has an absorption band at a wavelength of 10.2–10.6 μm, which leads to e-fold attenuation of the laser radiation at the depth of about 1–2 mm. Since the substrates used in the experiment are 5 mms thick, this leads to local heating by the CO$_2$ laser beam at half the depth of the substrate. Moreover, the coincidence of the optical axes of the lasers allows to locally heat the sample from both sides, which enables the creation of a local non-equilibrium condition, which is necessary for the structuring of the gold film.

Fig.1 Experimental setup for the creation of nanoparticles cluster structure
a) neodymium-doped yttrium aluminum laser
b) sample with film (numbers indicate bands on the sample)
c) CO$_2$ laser
d) *Fluke Ti400* thermal imager
The temperature gradient was 384 °C per mm. The exposure time was 15 min. At the same time, pronounced color bands appeared on the surface of the sample:

1. the original film before irradiation had had a blue color

2. in the band, where the temperature during the first 15 minutes of laser irradiation had been 568 °C, (after 15 minutes of irradiation) the film acquired a greenish color in transmitted light

3. in the band, where the temperature during the first 15 minutes of laser irradiation had been 974 °C, (after 15 minutes of irradiation) the film acquired a pink color in transmitted light

4. in the band where the temperature during laser irradiation had been 1214 °C, after 15 minutes of irradiation, the color of the film could not be seen with the naked eye.

All four bands underwent spectrophotometric measurements with a Shimatzu UV2600 double-beam spectrophotometer. A clean quartz substrate from the same batch was used as reference samples, and the surface relief was measured with a 801NER Pro AFM microscope.

### Results

After the exposure of the sample to laser radiation, 4 pronounced bands with a typical color were obtained (Fig. 2). The optical and dimensional properties of the film in the bands are shown in Table 1. The spectra of all bands were photographed (Fig. 3) and the surface morphology of each band was studied with an AFM microscope (Fig. 4). The color of the bands depends on the filling factor $q$, on the size of the cluster structure, and on whether gold is implanted into the near-surface layer of fused quartz or not. In the central band of the sample, implantation of gold particles into the near-surface layer was observed. This fact was confirmed by the chemical and mechanical resistance of the central band of the laser beam impact and the stability of the optical characteristics after chemical or mechanical impact.

The initial thickness of the film was determined by the weight of the deposit and, according to calculations, was 100 nm, which corresponded to a continuous gold film. This fact is confirmed by photometric measurements: curve 1 in Fig. 2 is typical for a massive gold sample; the model for describing the dielectric constant of such a film is contained in the Drude theory.

| Bands             | Cluster size | Nanoparticle size | $\omega_s^{\text{exp}}$ | $\omega_s^{\text{theor}}$ |
|-------------------|--------------|-------------------|-------------------------|--------------------------|
| Blue              | Continuous film | 50 nm           | -                       |                          |
| Purple            | 500 nm       | 10-25 nm          | 3.316×10^{15} s^{-1}    | 3.25×10^{15} s^{-1}      |
|                   |              |                   | 568 nm                  | a~20 nm b~150 nm q=0.1   |
| Pink              | 300 nm       | 8-15 nm           | 3.443×10^{15} s^{-1}    | 3.4×10^{15} s^{-1}       |
|                   |              |                   | 547 nm                  | a~10 nm b~30 nm q=0.07   |
| Implantation band | -            | 2-6 nm            | 3.664×10^{15} s^{-1}    | 3.7×10^{15} s^{-1}       |
|                   |              |                   | 514 nm / 4.956×10^{15} s^{-1} | a~3 nm b~30 nm q=0.008   |
Further, exposed to laser beams, the films undergo morphological changes, leading to the appearance of plasma resonance bands (curves 2, 3, 4 in Fig. 3).

The AFM micrographs show the structural changes that the film undergoes in different thermodynamic bands. Plasma resonance bands and their positions indicate the appearance of a colloid on the substrate surface and partial evaporation of gold. It should be noted that structural changes in the film lead to a shift of the plasma resonance band to short wavelengths, which is well explained by the Hampe-Shklyarevskii theory. However, an additional absorption peak arises in the central impact band, which is not associated with plasma resonance. It must be associated with interband transitions in gold granules. In this case the Hampe-Shklyarevskii theory cannot be applied to describe the dielectric constant of metal granules. To describe this phenomenon a quantum mechanical approach is needed.

Discussion of the experiment results

The main goal of this work was to determine the applicability of the Hampe-Shklyarevskii theory to describe the dielectric constant of a granular colloid based on the size of the granules. The main assumption was the following: with particle approximately equal in size to wavelength, the Drude model is applicable; in case of an isotropic colloid, when \( b >> a \), the Maxwell-Garnett model is applicable; in case of clusters (b-a), the Hampe-Shklyarevskii model is applicable. However, the limits of applicability of the Hampe-Shklyarevskii theory depends on an increase in interband transitions.

The experiment technique allowed to simulate the situation when massive islands with a diameter of about 150 nm exposed to \( \text{CO}_2 \) radiation transformed into clusters with islands with a 30 nm diameter and with distance between them equal to their diameter. Further irradiation led to the appearance of a colloid with a nanoparticle size of about 5 nm and a distance between nanoparticles of about
150 nm. Thus, it was possible to study absorption spectra and surface morphology on one sample, which led to controllability and repeatability in obtaining the given parameters, such as the filling factor, the size of nanoparticles, and the distance between them. Plasma resonance frequencies for various parameters of the colloid are given in Table 1. Theoretical calculations were based on formula 8, which allowed to calculate the Frohlich frequency taking into account the dipole-dipole interaction among the granules. The permittivity of quartz ε₀=2.15 [9] and the permittivity associated with interband transitions ε_m=2.13 were taken from work [9]. It should be noted that the position of the second maximum cannot be described by the Hampe-Shklyarevskii model, however, its estimation can be based on the energies of the levels in the metal granule described in the quantum theory of Sommerfeld [17].

We can be assume that, in the model of permittivity associated with interband transitions, the energy difference between the levels in a metal granule described in the Sommerfeld quantum theory [17] must be approximately equal to kinetic energy of an electron on the Fermi surface [18].

The eigenfrequencies of plasmons excited in small spheres can be determined with the help of the following vector equation [14]:

\[ \text{Re}\{\text{Det}|\mathbf{r}_i \delta_{ij} \mp \omega_{sji}^2|\} = 0 \] (11)

The availability of off-diagonal elements in (11) causes a difference between the eigenfrequencies of plasmons and \((\omega_{sji}^2 - \omega_{sji}^2)^{1/2}\), i.e., causes appearance of a hybrid resonance whose characteristics depend on the characteristics of all oscillators that determine the optical behavior of the environment. To understand this behavior, it is necessary to resort to the quantum-mechanical approach and consider the values of the electron energies in the metal. In this case, possible optical transitions on positive ions that form the core of a metal crystal are taken into account, that is, the ion component of the susceptibility \(\chi_{\text{ion}}\) is taken into account [19]. Thus, the contribution of ionic susceptibility to optical transitions in gold can be explained as follows. Au has the \(4f^{14}5d^{10}6s^1\) valence electron configuration [20]. When atoms condense into metal, electrons located in \(6s^1\) orbitals turn into free electrons. In crystals, the outer \(4f^{14}5d^{10}\) electrons form energy bands, and optical transitions from the \(5d\) band to the \(5s\) band partially filled with free electrons lead to an additional absorption band with a certain minimum threshold frequency \(\omega_b\) [21]. For gold, \(\omega_b\) lies in the visible area and, if \(\omega_b > \omega\), the ion susceptibility is a real value \((\chi_{\text{ion}}>0)\). So the eigenvalue of an electron in metal is determined by the expression [22]:

\[ E = \frac{2\pi^2 \hbar^2}{L^2 m} (l_1^2 + l_2^2 + l_3^2) \] (12)

where \(l_1, l_2, l_3\) – quantum numbers

\(m\) – electron mass

\(L\) – size of the side of a cube, and \(L\gg a\) – sides of an elementary cell in metal

The abovementioned mathematical assumption can be written as follows:

\[ \Delta E \sim m v_F^2 \] (13)

where \(v_F = 1.8 \times 10^8 \text{ cm/s}\) – the Fermi velocity (for gold [22])

Then substituting (12) into (13) and performing the corresponding calculations, we obtain

\[ L \sim \sqrt{\frac{\pi \hbar}{m v_F}} l \approx 5 \text{ nm} \] (14)

This estimation agrees with the values obtained with the AFM microscope, which showed that with size of about 5 nm, an increase in the absorption band associated with interband transitions is observed.

**Conclusion**

In this paper, the Limiting case of size and quantum-size effects in gold granules briefly study. Derivation of some permittivity model used when describing optical spectra of composites containing spherical gold
nanoparticles are presented. The experimental absorption investigation gives the ability to compare theoretical calculation of the maximum absorption band with experimental data. Conclusions are discussed following from the Mie theory dedication to the diffraction on sphere of various diameter and dielectric permittivity models. The applicability condition for different models was related to the particle radius. The boundary diameter for different dielectric permittivity model of the gold nanoparticles had been calculate and experimentally exam.

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