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Spectral properties of close-packed monolayers consisting of metal nanospheres

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Abstract

We propose a method for the calculation of transmission and reflection spectra of close-packed monolayers formed from metal nanoparticles. The model takes into account the correlation effects and electrodynamic coupling in close-packed monolayers treated in the framework of multiple scattering of waves theory as well as the size dependence of the metal nanoparticle optical functions.

The transmission and reflection spectra for monolayers consisting of Ag nanospheres are calculated for various particle concentrations and sizes. The matrix influence on the spectral position of surface plasmon resonances for nanoparticle monolayers is considered. The concentration red shift of the plasmon attenuation resonances is shown and the reasons for its appearance are discussed.

1. Introduction

At the present time it is well known that planar structures of monodisperse metal nanoparticles with a high surface concentration are perspective materials for linear and nonlinear optics, laser physics, optoelectronics etc. In recent years there has been considerable advances in technology of the fabrication of such metal–dielectric nanomaterials with controlled sizes and packing factor values [1] and their unique electrical properties are actively being studied. The optical characteristics of such objects are investigated to a considerably lesser extent, both experimentally and theoretically. At the same time such research is certainly essential for the creation of metal–dielectric nanostructures with desirable and controllable selective absorbance, reflection and transmission.

The considerable distinctions between the optical properties of metal nanostructures and bulk materials are connected to the appearance of surface modes (plasmon resonances) on metal nanoparticles and the size dependence of their optical constants [2]. In the case of close-packed nanoparticle arrays these effects are of a collective nature. It was experimentally established that the collective interactions transform a structure of plasmon resonances and

have an influence on their spectral position [3–7]. This paper is dedicated to the theoretical investigation of the effect of a metal nanoparticles concentration on random monolayer spectral transmission and reflection within the plasmon resonance area.

For this purpose we have developed a theoretical scheme of collective electrodynamic processes into close-packed metal nanoparticles monolayers, based on the quasicrystalline approximation (QCA) [8–11] of the theory of multiple scattering of waves (TMSW). The size dependence of the metal nanosphere dielectric function has been described using a model of the limitation of the electron mean free path (LEMFP) [12].

2. Calculation method

A close-packed metal nanoparticles monolayer is a kind of composite material. Usually, spectral characteristics of composite materials are calculated using the effective dielectric constant (or permittivity) ε_{eff} that is involved by one of the models of effective media. Of these the best known are the Maxwell–Garnett theory (MGT) that results in the following relation:

$$\frac{\varepsilon_{\text{eff}} - \varepsilon_0}{\varepsilon_{\text{eff}} + 2\varepsilon_0} = f \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0}$$

or the Bruggeman approximation (BA)

$$0 = f \frac{\varepsilon - \varepsilon_{\text{eff}}}{\varepsilon + 2\varepsilon_{\text{eff}}} + (1 - f) \frac{\varepsilon_0 - \varepsilon_{\text{eff}}}{\varepsilon_0 + 2\varepsilon_{\text{eff}}}.$$

Here f represents the volume fill fraction of the inclusion particles and ε and ε_0 are dielectric constants of particles and a surrounding media, respectively.

However, the MGT is not intended for compounds with a significant inclusion concentration and the BA does not describe plasmon attenuation resonances of metal nanoparticles [7]. That is why one has to use more exact theoretical treatment of close-packed nanoparticle arrays in their plasmon resonance spectral ranges. At the present time the most effective means to realise this is the employment of approaches based on the TMSW.

The TMWS supposes that the resulting field in any point of space (both inside and outside of a disperse medium) is to be a sum of various multiple scattered waves taking into account their phase relations. In addition, each particle is not affected by an incident field \mathbf{E}_0 , but it is subjected to an effective field obtained as a composition of all the waves that are multiple scattered to the particle area of disposition. Consideration of phase correlations of multiple scattered waves, also called correlation effects, is especially important for space-ordered disperse systems, among which are the close-packed particle arrays characterized by short-range space ordering.

In the QCA of TMWS [8], after averaging the different configurations of a particles ensemble, the mean field (also called the coherent field) $\langle \mathbf{E}(\mathbf{r}) \rangle$ at some point \mathbf{r} is determined by the following system of two equations:

$$\begin{aligned} \langle \mathbf{E}(\mathbf{r}) \rangle &= \mathbf{E}_0(\mathbf{r}) + n_0 \int d\mathbf{R} \int d\mathbf{r}' \vec{\vec{\Gamma}}(\mathbf{r}, \mathbf{r}' + \mathbf{R}) \langle \mathbf{E}(\mathbf{r}' + \mathbf{R}) \rangle_{\mathbf{R}} \\ \langle \mathbf{E}(\mathbf{r} + \mathbf{R}) \rangle_{\mathbf{R}} &= \mathbf{E}_0(\mathbf{r} + \mathbf{R}) + \int d\mathbf{r}' \vec{\vec{\Gamma}}(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R}) \langle \mathbf{E}(\mathbf{r}' + \mathbf{R}) \rangle_{\mathbf{R}} \\ &\quad + n_0 \int d\mathbf{R}' g(|\mathbf{R} - \mathbf{R}'|) \int d\mathbf{r}' \vec{\vec{\Gamma}}(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R}') \langle \mathbf{E}(\mathbf{r}' + \mathbf{R}') \rangle_{\mathbf{R}, \mathbf{R}'}. \end{aligned} \quad (1)$$

Here $\langle \mathbf{E}(\mathbf{r}) \rangle_{\mathbf{R}}$ is the averaged field with one fixed particle at the point \mathbf{R} ; $\langle \mathbf{E}(\mathbf{r}' + \mathbf{R}') \rangle_{\mathbf{R}, \mathbf{R}'}$ is the averaged field with two fixed particles at points \mathbf{R} and \mathbf{R}' , n_0 is the number of particles per unit area; $\vec{\vec{\Gamma}}(\mathbf{r}, \mathbf{r}')$ is the tensor Green function; $g(|\mathbf{R} - \mathbf{R}'|)$ is the radial distribution function

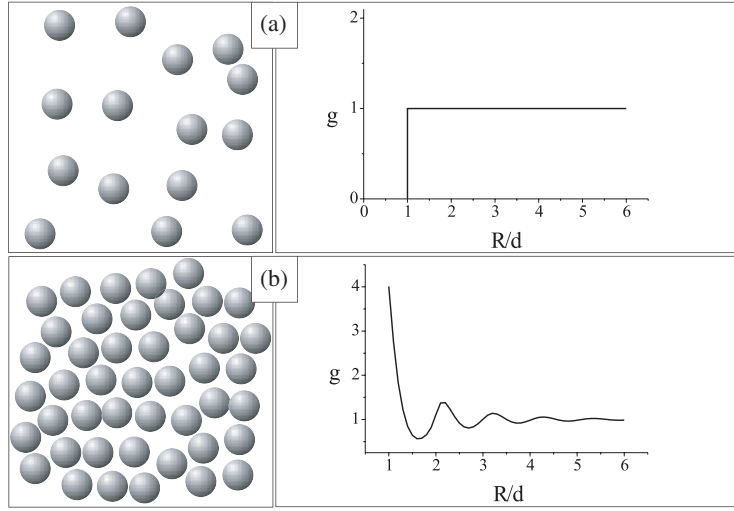


Figure 1. Schemes and radial functions of a sparse random (a) and a close-packed partially ordered (b) disperse layers.

characterizing the probability of the location of two particles at the points \mathbf{R} and \mathbf{R}' . For a statistically isotropic and uniform medium it depends only on the modulus $|\mathbf{R} - \mathbf{R}'|$.

To calculate the radial-distribution function for the close-packed system of solid particles we used the following scheme. The $g(\mathbf{R}_1, \mathbf{R}_2)$ function may be expressed as $g(\mathbf{R}_1, \mathbf{R}_2) \equiv 1 + h(\mathbf{R}_1, \mathbf{R}_2)$, where $h(\mathbf{R}_1, \mathbf{R}_2)$ is the full correlation function satisfying the following self-consistent equation [13]:

$$h(\mathbf{R}_1, \mathbf{R}_2) = c(\mathbf{R}_1, \mathbf{R}_2) + n_0 \int c(\mathbf{R}_1, \mathbf{R}_3)h(\mathbf{R}_3, \mathbf{R}_2) d\mathbf{R}_3.$$

Here $c(\mathbf{R}_1, \mathbf{R}_2)$ is a part of the full correlation function $h(\mathbf{R}_1, \mathbf{R}_2)$ describing the direct correlation between two particles located at the points \mathbf{R}_1 and \mathbf{R}_2 . The most successful is the Percus–Yevick approximation for the direct correlation function

$$c(\mathbf{R}_1, \mathbf{R}_2) = [\exp(-\beta\phi(R_1, R_2)) - 1] \exp(\beta\phi(R_1, R_2)g(R_1, R_2))$$

where ϕ is the interparticle potential and β is the normalizing coefficient.

With the use of this approximation the integral equation for the full correlation function can be solved exactly when particles are solid spheres, i.e.

$$\phi(R_1, R_2) = \begin{cases} \infty & \text{for } |R_1 - R_2| < d \\ 0 & \text{for } |R_1 - R_2| > d. \end{cases}$$

The $g(R)$ function of a close-packed system is marked by pronounced maxima for R values corresponding to the most probable distances between the particles whereas for a sparse random disperse structure the particle space distribution is homogeneous and $g(R) = \text{const}$ (see figure 1). This behaviour of $g(R)$ reflects the appearance of the short-range ordering in the close-packed disperse system. The higher the particle packing density, the more extended the range of the particle ordering is. For particles located in this range the relations between phases of their scattered waves are not random. Scattered waves are partially coherent and their interference has to be taken into account as per (1).

When the particles are spheres it is convenient to solve (1) by an expansion of the electromagnetic fields and the tensor Green function on the vectorial spherical harmonics.

As a result we obtain the following relations for coherent transmission T_M and reflection R_M of a partially ordered monolayer of monodisperse particles [9, 10]:

$$T_M = \left| 1 - \frac{\pi}{k^2} n_0 \sum_l (2l+1)(b_{lM} + b_{lE}) \right|^2$$

$$R_M = \left| -\frac{\pi}{k^2} n_0 \sum_l (-1)^l (2l+1)(b_{lM} - b_{lE}) \right|^2$$

where k is the wavevector, the coefficients b_{lM} and b_{lE} are determined from the system of equations:

$$b_{lM} = b_l + n_0 b_l \sum_{l'} (P_{ll'} b_{l'M} + Q_{ll'} b_{l'E})$$

$$b_{lE} = a_l + n_0 a_l \sum_{l'} (P_{ll'} b_{l'E} + Q_{ll'} b_{l'M}).$$

Here a_l and b_l are the Mie coefficients, which define scattering and absorption properties of an individual particle with a diameter d and a complex permittivity ε [2]. The terms including the functions $P_{ll'}$, $Q_{ll'}$ appear as a consequence of a consideration of coherent particles irradiation. They depend on the radial-distribution function $g(R)$ in a complicated manner [9, 10]. When a single particles permittivity becomes size-dependent, one has to take this circumstance into account on the step of the Mie coefficient calculation.

We have considered size-effect modified permittivity ε in the framework of the classical electron mean free path model [14], which allows to obtain the size-dependent ε of metal spherical nanoparticles in the analytical form. Thus the LEMFP model argues that if the metal particle sizes are comparable with the mean free path of electrons in bulk material L_∞ the interaction of the conduction electrons with the particle surface becomes important as an additional collision process. This interaction results in the reduced effective mean free path L and, consequently, the increased damping constant γ_d . In accordance with [12] the appropriate size-dependent damping constant is defined as:

$$\gamma_d = \gamma_0 + \frac{v_F}{L} \quad (2)$$

where v_F is the Fermi velocity and γ_0 is the bulk damping constant. For diffuse electron scattering at the particle surface $L = \frac{1}{2}d$. Then, to obtain an appropriate size-dependent permittivity $\varepsilon(\omega, d)$, one can use the Drude–Lorentz–Sommerfeld model with the bulk damping constant γ_0 replaced by the size-dependent damping constant γ_d [2] as follows:

$$\varepsilon(\omega, d) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma_d \omega}. \quad (3)$$

Here ω_p is the plasma frequency for the bulk metal where $\omega_p = N_0 e / m_e \varepsilon_0$ and N_0 is the free electron density, e and m_e are the electron charge and the effective mass, respectively.

3. Results and discussion

To study the role of the particle correlation effects in the plasma resonance absorption in the visible spectrum we have compared the spectral characteristics of metal nanoparticles monolayers with various particles' packing density and the corresponding sparse disperse layers. The monolayer overlap parameter $\eta = \frac{1}{4} n_0 \pi d^2$ was varied over the range 0.2–0.6 and for the each value of η the diameter of the particles was changed ($d = 2$ –10 nm). The corresponding sparse (or diluted) disperse layers are the structures consisting of particles with the same sizes and total numerical quantity as in the monolayer considered but with the volume

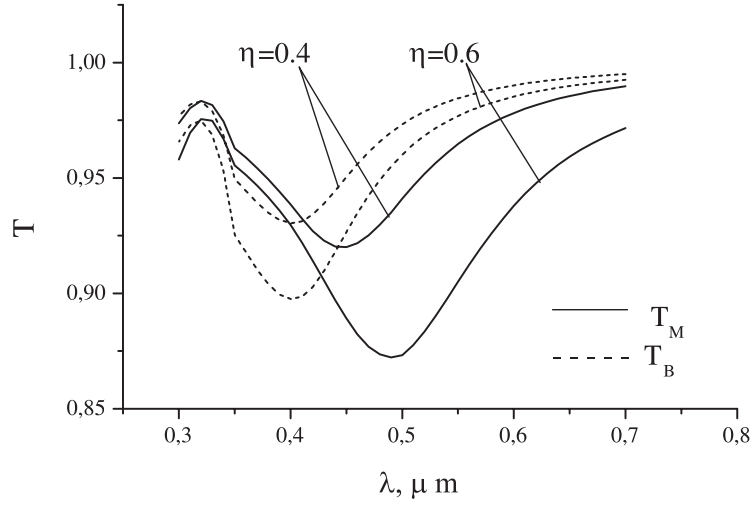


Figure 2. Coherent transmission of monolayers made of Ag nanospheres with the diameter $d = 2$ nm imbedded into a matrix with the refractive index $n_m = 1.4$.

fill fraction $f = 0.01$. With the overlap parameter values under consideration these sparse systems may be considered as optically thin disperse layers. In addition they are random and characterized by a homogeneous particle distribution. It means that the conditions of single independent scattering are fulfilled. This permits us to neglect the multiple scattered waves and to calculate the spectra of the sparse systems using the Bouguer law for the scattering media $T_B = \exp(-\eta Q_\lambda)$ [2]. Here Q_λ is the single particle extinction efficiency factor. For spherical particles the numerical values of Q_λ may be found using Mie theory [2].

The calculation of the coherent transmission and reflection spectra for Ag nanoparticle monolayers has been made with the help of the QCA-based algorithm stated in section 2. The special software for numerical simulations was developed earlier and is described in detail in [10, 15]. This scheme has been already successfully used for studying the optical properties of close-packed monolayers and stacks consisting of dielectric particles [10, 15], as well as bandgap formation in opal-based photonic crystals [16]. We now also introduce into this scheme the size-dependence of the metal nanoparticles permittivity.

The LEMFP method of calculation of the size-dependent ε has been applied to Ag nanospheres in the following manner. Metal permittivity was subdivided into two parts associated with the contributions of free and bound electrons, respectively. The part of permittivity defined by free electrons was considered to be size-dependent. Its values were calculated on the basis of (2) and (3) with the parameters: $\gamma_0 = 0.27 \times 10^{14} \text{ s}^{-1}$, $\omega_p = 1.38 \times 10^{16} \text{ s}^{-1}$, $v_F = 1.4 \times 10^6 \text{ m s}^{-1}$ [17].

In figure 2 one can see the spectra of coherent transmission in the visible spectrum for close-packed monolayers and corresponding sparse layers of 2 nm Ag particles in a gelatine matrix (refractive index $n_m = 1.4$) with different values of the particle-overlap parameter.

Recall that there are two possible ways of controlling the particle concentration of a disperse system. The first way is to regulate a system volume at the fixed number of particles (compare solid and dashed curves for $\eta = \text{const}$). The second way is to change the particle quantity at the same system volume (compare, for example, solid curves for different η values).

To analyse the concentration effects using the first method, when the number of particles remains constant, the spectra of monolayers (figure 2, solid curves) and corresponding sparse systems with the same η values (figure 2, dashed curves) were compared. As can be observed

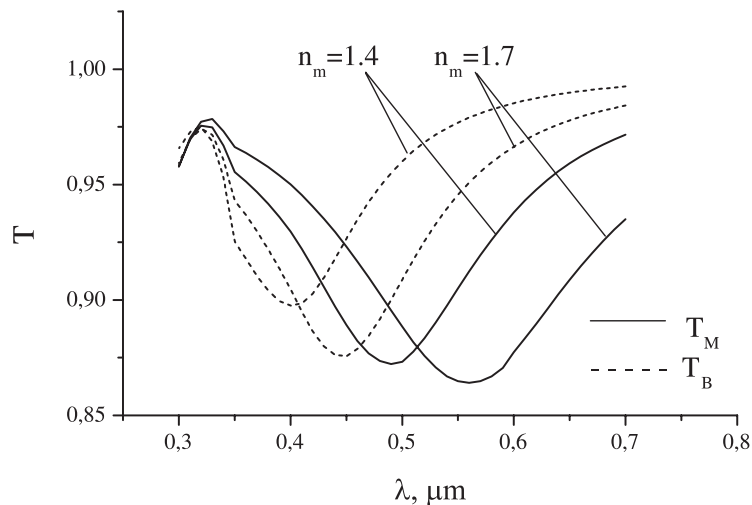


Figure 3. Coherent transmission of monolayers made of Ag spheres with $d = 2$ nm. The overlap parameter of monolayers is $\eta = 0.6$.

from figure 2, increasing the particles' packing density whilst keeping the size and quantity constant results in the red displacement of the plasmon resonance frequency. In addition, when the interparticle distances decrease, enhancing the electrodynamic coupling leads to strengthening of the plasmon resonance.

The second case, i.e. when the particle number is changed, has been realised experimentally for Ag nanospheres by Hovel *et al* [3]. Unfortunately, the absence of exact particle concentration values in that paper does not permit the detailed comparison of those experimental results with our theoretical data. But it does confirm the tendency to the red shift of plasmon resonances as the particle concentration in a monolayer increases (see figure 2). As it was noted in [3], the interference of waves scattered at close-packed nanoparticle aggregates acts, apparently, in the same manner as the growth of an isolated particle size. Aggregating particles is somewhat similar to enlarging them. At the QCA the appearance of close-packed nanoparticle aggregates is achieved by increasing short-range ordering. In particular it means that the radial-distribution-function values grow over the range of small interparticle distances.

The growth of the refractive index for matrices containing Ag nanoparticles also gives rise to a red shift and to an intensification of the plasmon resonance (see figure 3). This effect is observed for various Ag particle sizes and concentrations. It is connected with changing the Frolich frequency ω_0 , that determines the spectral position of a plasmon resonance for a single dipole metal particle in a homogeneous nonabsorbing medium with the following conditions:

$$\begin{aligned} \operatorname{Re}[\varepsilon(\omega_0)] &= -2\operatorname{Re}[\varepsilon_m(\omega_0)] \\ \operatorname{Im}[\varepsilon(\omega_0)] &\approx 0. \end{aligned} \quad (4)$$

The influence of the particle size on the collective plasmon resonance characteristics is shown in figure 4. The growth of particle diameters over the range under consideration ($d < 10$ nm) is accompanied by the amplification and the narrowing of the plasmon attenuation peak, whereas the resonance spectral position for a system of such dipole particles is defined only by their concentration value. It should be emphasized, that allowing the optical constant size dependence leads to a broadening of the plasmon attenuation bands and decreasing its magnitude at all investigated values of d and η .

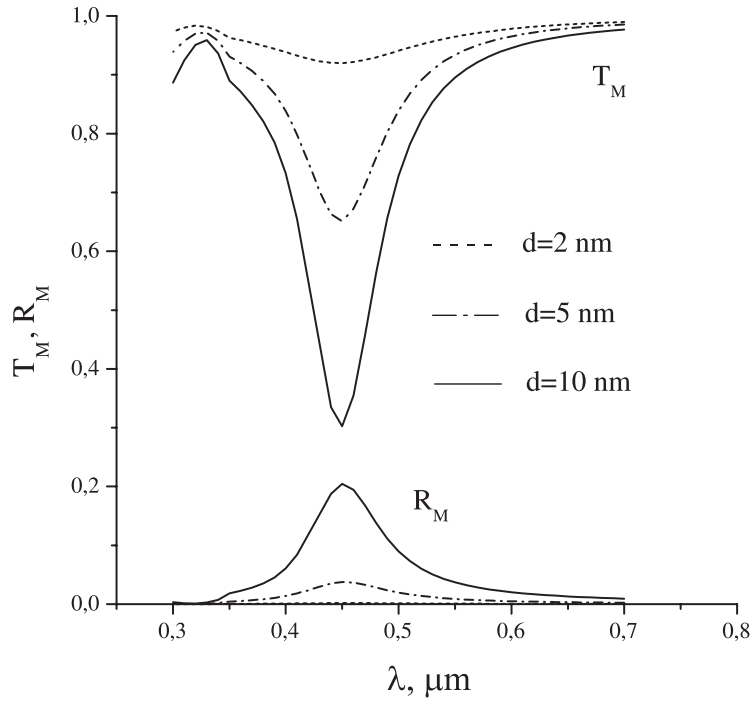


Figure 4. Coherent transmission and reflection of monolayers made of different-sized Ag spheres ($\eta = 0.4$, $n_m = 1.4$).

It is worthwhile noting, that selective reflectance within the plasmon resonance spectral region is significantly enhanced when the particle sizes increase. As depicted in figure 4, for Ag monolayers with $\eta = 0.4$ maximal reflectance increases from 5 to 20% when particle diameters change from 5 to 10 nm.

Analysis of the data in figures 2–4 allows us to propose that the concentration red-shift treatment is extended as opposed to the conclusions given in [3]. From our point of view this shift may be determined by two reasons. The first one, as already mentioned, consists of the appearance of the short-range order at a spatial particle arrangement accompanying the particle concentration increase. The closer the packing, the larger the correlation radius l_{cor} corresponding to the mean size of aggregates is. When l_{cor} is not infinitesimal compared with the incident light wavelength, the independence of the plasmon resonance spectral position on the aggregate size (that is characteristic for dipole scattering) is violated. This fact is exhibited by the red concentration shift of the collective plasmon resonance.

However, we suppose that there is one more possible explanation of the red concentration displacement. This shift may be defined not only by the short-range electrodynamic interactions, connected with particle aggregation and, consequently, with a change in the nearest surrounding particles. In addition, it may be caused by the effective-field modification as a whole when the particle concentration grows. Put more simply, the role of the effective field reduces to the assumption that a single inclusion is excited by a wave propagating in some effective medium associated with the average coherent field and characterized by the effective refractive index.

Then, by analogy with the Frolich frequency ω_0 determining the particle plasmon spectral position in a homogeneous medium by the conditions (4), we introduce the effective Frolich

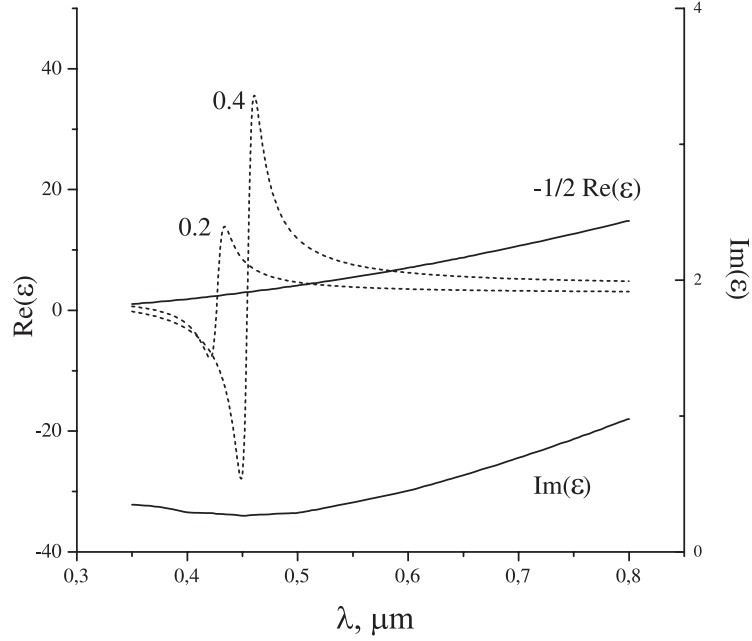


Figure 5. Spectral dependence of the bulk Ag permittivity (solid curves) and the real part of ϵ_{eff} (dashed curves) for a monolayer of Ag nanoparticles in the dielectric matrix ($n_m = 1.4$) calculated by the MGA at different overlap parameters η (see values next to the curves).

frequency ω'_0 , which determines the collective plasmon frequency as follows:

$$\text{Re}[\epsilon(\omega'_0)] = -2\text{Re}[\epsilon_{\text{eff}}(\omega'_0)] \quad (5)$$

$$\text{Im}[\epsilon(\omega'_0)] \approx 0 \quad \text{Im}[\epsilon_{\text{eff}}(\omega'_0)] \approx 0. \quad (6)$$

The concentration dependence of the effective Frolich frequency can be analysed, for example, by the application of the MGA for effective permittivity (see figure 5). As can be observed from figure 5, there are two roots of (5) for media with high particle concentrations and both of them are red displaced as the concentration is increased. Nevertheless, in figures 2–4 we find only a single red-shift collective plasmon resonance with the particle concentration growth. Apparently, the realization of a collective plasmon doublet structure is encumbered by breaking conditions (6) as a long-wave region is reached.

It is necessary to say that the second reason under consideration for the red concentration shift (associated with the concentration dependence of ϵ_{eff}) can also play a significant role if l_{cor} remains very small compared with a wavelength for small particle sizes. This conclusion is confirmed by a comparison of figures 2 and 4. Figure 4 demonstrates the size independence of a spectral position of the plasmon attenuation resonance at close-particle packing. However, if the spectral position of the plasmon attenuation resonance was determined by particle aggregation, we should see a red size shift for close-packed monolayers with $\eta = \text{const}$. This supposition is based on the fact that the dipole approximation is broken for aggregates consisted of Ag particles with diameters of 5–10 nm [14]. The absence of this size shift allows for the conclusion that in this case the main reason for a plasmon resonance concentration shift is the concentration change of the effective permittivity of the nanostructure.

4. Conclusions

In summary, this paper has shown that QCA-aided numerical simulation of the TMSW and LEMFP model is a good way of describing strong dependencies of spectral characteristics of close-packed metal nanoparticle monolayers on their sizes, concentrations and matrix refractive-index values. Such calculations may be useful for the preliminary estimation of microstructure parameters with desirable spectral characteristics for the creation of planar nanostructures with controllable selective absorbance, reflection and transmission properties.

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