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The spatial ordering effect on spectral properties of close-packed metallic nanoparticle monolayers

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Abstract

In the frame of the theory of multiple scattering of waves we have studied transmission spectra of monolayers of monodisperse spherical metallic nanoparticles surrounded by dielectric matrix at different nanoparticle arrangement types. The method being used takes into account collective effects of the coherent nature and electrodynamic coupling between particles.

The effect of the particle correlation degree on the surface plasmon absorption band has been investigated for random close-packed, polycrystalline quasiregular and chain-like planar particle arrays. We have established that the spatial ordering is mostly pronounced in transmission spectra of metal nanoparticle chain-like monolayers. Binary interactions in these structures cause the structure modification and the polarization dependence of the surface plasmon–polariton resonance. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Computer simulations; Light scattering; Silver

1. Introduction

At present a growing interest in optical properties of planar regular and partially ordered systems of metal nanoparticles embedded in matrix or deposited on substrates has been aroused [1–4]. Among them there are 2D fractal systems, close-packed island films as well colloidal nanostructures.

Regardless of packing type the metal–dielectric nanocomposite systems are characterized by resonance absorption caused by collective oscillations of conductive electrons at optical excitation of small metallic nanoparticles (so-called surface plasmon–polaritons (SPP)) [5]. Electrodynamic coupling in a spatially ordered nanoparticle ensemble gives rise to the influence of particle packing type on the spectral position and structure of resonance absorption bands. Theoretical investigation of disordering effects in a square lattice of metallic nanospheres (with the lattice constant being of the order of their size) has been presented in [2]. Both a red shift and narrowing of the dipole resonance band together with absorption increase in the high frequency region have been shown in this paper. Transformation of the SPP band with increasing the metal nanoparticles concentration into 2D random nanocomposites was studied by us [6] in the frame of the quasicrystalline approximation (QCA) of the theory of multiple scattering of waves (TMSW). A change from sparse to dense packing leads to appearance of the short order. The attendant intensification of metal nanoparticle

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electrodynamic coupling causes an amplification and a red shift of the SPP. This conclusion coincides with experimental data from [7].

In this paper we theoretically investigate the effect of collective interactions in plane spatially ordered systems of metallic nanoparticles on their transmission spectra. Triangular and square lattices as well as chain-like arrays are compared with macroscopically isotropic close-packed and sparse systems.

2. Calculation method

The TMSW is based on the assumption that the resulting field in any point of space is determined by a sum of various multiply scattered waves taking into account their phase relations. In addition, each particle is subjected to some effective field obtained as a composition of all waves multiply scattered to the particle's area of disposition. In the common case this effective field is not equal to the incident field E_0. Consideration of phase correlations of multiple scattered waves, also called correlation effects, is especially necessary for space-ordered disperse systems to regard the strong dependence of their optical properties on particle array morphology parameters [8,9].

In the QCA of the TMSW [10], after averaging on different configurations of a particle's 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:

$$\langle \mathbf{E}(\mathbf{r}) \rangle = \mathbf{E}_0(\mathbf{r}) + n_0 \int \mathrm{d}R \int \mathrm{d}\mathbf{r}' \overleftrightarrow{\Gamma}(\mathbf{r}, \mathbf{r}' + \mathbf{R}) \langle \mathbf{E}(\mathbf{r}' + \mathbf{R}) \rangle_{\mathbf{R}},$$

$$\begin{aligned} \langle \mathbf{E}(\mathbf{r} + \mathbf{R}) \rangle_{\mathbf{R}} = \mathbf{E}_0(\mathbf{r} + \mathbf{R}) \\ + \int \mathrm{d}\mathbf{r}' \overleftrightarrow{\Gamma}(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R}) \langle \mathbf{E}(\mathbf{r}' + \mathbf{R}) \rangle_{\mathbf{R}} \\ + n_0 \int \mathrm{d}\mathbf{R}' g(|\mathbf{R} - \mathbf{R}'|) \\ \times \int \mathrm{d}\mathbf{r}' \overleftrightarrow{\Gamma}(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R}') \langle \mathbf{E}(\mathbf{r}' + \mathbf{R}') \rangle_{\mathbf{R},\mathbf{R}'}. \end{aligned} \tag{1}$$

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

For a sparse medium the probability of a particle's location is constant for any $R \geqslant d$ (where d is the particle diameter), and correspondingly $g(R) = 1$. It means that the spatial arrangement of particles is disordered and their scattered wave phases are random. In contrast, crystals are characterized by long-distance topology ordering. Particles embedded at the specific sites in the crystal lattice are placed at well-defined distances from each other. For a perfect regular particle array the $g(|\mathbf{R} - \mathbf{R}'|)$ is a set of δ-functions, corresponding to the lattice sites $\mathbf{R}_i$.

In numerical calculations one can represent the azimuthally averaged pair particle distribution function for quasiregular packing as a set of step-functions (Fig. 1). The step positions are determined by the lattice type and their half-width Δ is determined by a loose disturbance of the real particle systems and corresponds to a possible small deviation of the particle location from the lattice site:

$$g(R) = C \sum_{i=1}^{\infty} \frac{h_i}{2\pi \Delta R_i} \delta_{\Delta}(R - R_i);$$

$$\delta_{\Delta}(R - R_i) = \begin{cases} 0 & \text{for } R < R_i - \Delta/2, \\ 1 & \text{for } R_i - \Delta/2 \leqslant R \leqslant R_i + \Delta/2, \\ 0 & \text{for } R > R_i + \Delta/2. \end{cases}$$

Here h_i and R_i are the number of particles for the jth coordination sphere and its radius, respectively; C is the coefficient determined by the ordinary

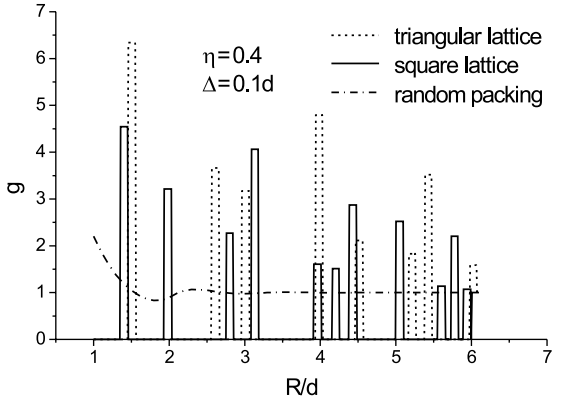

Fig. 1. Radial particle distribution function for different types of a plane structure.

normalization conditions for the pair particle distribution function [11].

Partially ordered structures occupy an intermediate place between sparse and regular systems. For example, they may be arrays of a polycrystalline structure. In this case the spatial scale of the ordering is limited by the domain boundaries and characterized by the correlation length L_c. At greater distances we can assume homogeneous distribution of particles. Thus, the pair particle distribution function of a polycrystalline sample is represented as

$$g'(R) = \begin{cases} g(R) & \text{for } r \leqslant L_c, \\ 1 & \text{for } r > L_c. \end{cases}$$

The second abundant type of partially ordered structures is the close-packed particle layer. The close-packed disperse media are characterized by short-range ordering. It means that space sites of neighboring particles become partially correlated due to their finite sizes and a high concentration. At this region the $g(R)$ function has sharply pronounced maxima for R corresponding to the most probable distances between particles. For particles located within this range the relations between phases of scattered waves are not random. Scattered waves are partially coherent and it is necessary to take into account their interference when the resulting field is determined. For a statistically isotropic and uniform close-packed system the $g(R)$ function depends only on the modulus $|\mathbf{R} - \mathbf{R}'|$ and can be calculated by the Percus–Yevick equation with the use of the solid spheres model [11] (see Fig. 1).

When the particles are spheres it is convenient to solve Eqs. (1) by an expansion of electromagnetic fields and the tensor Green function on the vectorial spherical harmonics. As a result for natural incident light we obtain the following relations for coherent transmission and reflection of a partially ordered monolayer of monodisperse spheres:

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

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

where the coefficients b_{lM} and b_{lE} are determined from the system of equations

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

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

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 relative refractive index $\tilde{n} = n_p + ik_p$ [5]. 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 [12,13]. When a single particle's permittivity becomes size-dependent, one has to take this circumstance into account in the step of the Mie coefficient calculation.

It may be shown that for a close-packed system of particles under condition that one can neglect of the lateral electrodynamic coupling, formulae (2) transform into simple analytical expressions

$$T = 1 - \eta Q_S + \frac{4\pi\eta^2}{\rho^2} x_S(0) \Lambda_S Q_S,$$
$$R = \frac{4\pi\eta^2}{\rho^2} x_S(\pi) \Lambda_S Q_S. \tag{3}$$

Here Q_S is the single particle extinction efficiency factor, $x(\gamma)$ is the phase function, ΛQ is the scattering efficiency factor, $\rho = \pi d/\lambda$, $\eta = n_0 \pi d^2/4$ is the monolayer overlapping parameter. Note that these expressions were first obtained in the approximation of the coherent single scattering (CSSA), or the approximation of the amplitude-phase random screen, for large weakly refracting particles (see references in [9]).

In cases of more complete statistical anisotropic space ordering, for example, for chain-like particle arrays, expression (3) may be used to develop the simplified binary approximation (BA) for description of the lateral electrodynamic coupling. Taking into account binary interactions assumes that we use in (3) the values of effective single scattering indicatrix and extinction factors defined for a two-particle system with an interparticle distance l, that is determined by a particle concentration.

At this stage (for solving the two-body diffraction task) we used the volume integral equation formulation because it allows one to consider particles of an arbitrary shape, bisphere in particular.

3. Results and discussion

In Fig. 2 calculated spectra of coherent transmission of silver nanoparticle monolayers for the random close-packed system as well as for two types of a polycrystal plane array (square and triangular intradomain structure) are compared with that for the sparse medium of the same particles. The choice of silver as the metal under investigation was determined by the good appearance of Ag nanoparticle surface plasmon in vacuum in contrast to other noble metals, which have surface plasmons damped by electron relaxation effects and interband transitions near the plasmon frequency.

Size dependence of silver nanoparticle optical constants was studied using the model of the limitation of the electron mean free path [7]. The particle surface concentration is constant for all considered types of packing, $\eta = 0.6$.

It should be noted that calculated spectra of polycrystalline monolayers have been obtained for the step-like radial distribution function with the step half-width $\Delta = 0.1d$. The spatial scale of ordering (or the correlation length L_c) for the data of Fig. 2 was chosen equal to 5 lattice constants a.

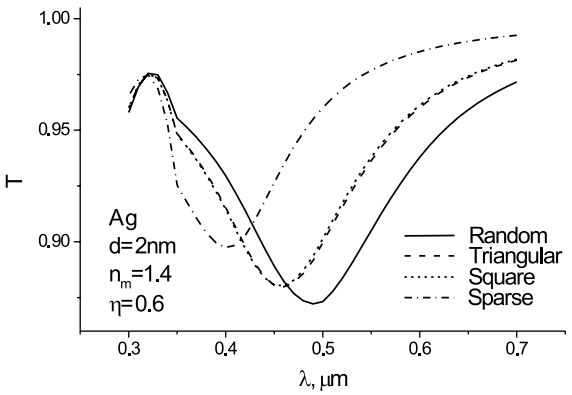

Fig. 2. Transmission spectral dependence calculated by the QCA for different packing types of a monolayer made of silver nanoparticles surrounded by gelatine ($n_m = 1.4$).

It is interesting that numerical results are hardly dependent on the correlation length at $L_c \geqslant 5a$. We are apt to believe that the reasons are the strong absorbance and the insignificant lateral scattering for given particle sizes near the SPP frequency, that limits the extension of a particle ensemble included into the essential lateral electrodynamic coupling.

The same circumstance together with the azimuth averaging of the monolayer coherent field results in hard pronounced spectral distinctions between triangular and square packing into domains at $a = \text{const}$.

When the particles are sparse arrayed the direct light attenuation is described by the Bouger law for scattering media $T = \exp(-\tau)$, where $\tau = Q_S\eta$ is the optical thickness of the scattering layer.

When the metal nanoparticle array is spatially ordered, electronic states are of a collective nature and plasmon resonance absorption bands become sensitive not only to particle sizes and shapes but also to particle space arrangement. The data for sparse and close-packed arrays shown in Fig. 2 confirm the tendency to concentration red shift of plasmon resonances. As it was noted in [7], interference of waves scattered at close-packed nanoparticle aggregates acts, apparently, in the same manner as the growth of an isolated particle size. The aggregation of particles is somewhat similar to their enlargement. At the QCA an appearance of close-packed nanoparticle aggregates is described by increasing the short-range ordering. Besides [14], this shift may be caused by the effective field modification as a whole when the particle concentration grows. 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, the concentration dependence of the effective Frolich frequency may be revealed as a red shift of collective plasmon frequency.

On the contrary, when the spectra for close-packed and polycrystal arrays are compared, a blue shift of plasmon resonance is shown with particle ordering increase. We may suppose that it is a consequence of the absence of aggregation. Existence of a red shift versus a sparse particle

array may be connected with effective refractive index changing.

All previous investigations were carried out on the basis of the QCA only for unpolarized incident light. At the same time it was experimentally shown in [15] that transmission spectra of chain-like metal nanoparticle planar systems are sensitive to the polarization state of the incident light. In this paper the polarization effects are considered for planar silver nanosphere structures taking into account the binary interactions between two spheres in contact.

Comparison of transmission spectra calculated with the CSSA and with the BA for chain-like silver nanoparticle monolayers is made in Fig. 3. In the same figure one can see transmission spectra for a macroscopically isotropic random monolayer calculated considering only binary interactions in the QCA. It means a special choice of the radial distributional function as the homogeneous distribution for distances larger than the second coordination sphere radius R_2 with a single step located at the interparticle distance equal to the particle diameter.

Fig. 3 shows that polarization effects become very important for particle arrangements with marked directions and appear due to the binary interactions. In the case of parallel-oriented chain-like metal nanoparticle clusters, the binary coherent interactions lead to the dependence of the plasmon resonance frequency on the polarization state (see curves 1a, 1b). When the particle chains are formed, the absorption efficiency increases in the vicinity of the single particle plasmon frequency due to the binary interactions for the polarization state corresponding to the orientation of electrical vector along the particle chains (curve 1b).

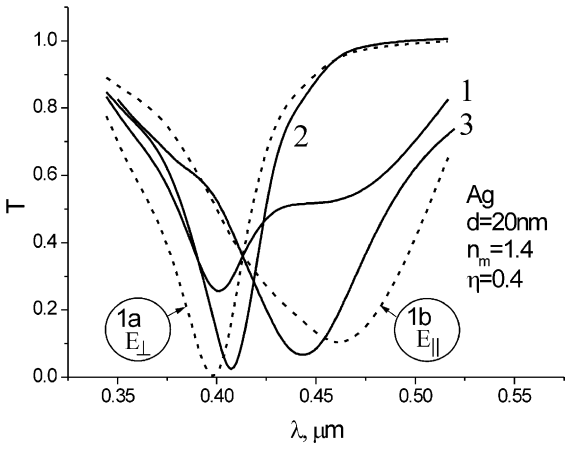

Fig. 3. Transmission spectra of natural incident light for a chain-like monolayer (curve 1) and a random monolayer with (curve 3) and without (curve 2) taking into account the binary interactions. Curves 1a and 1b corresponds with two polarizations of the incident light relative to chains.

It is worthwhile to note that the frequency separation between plasmon resonances for two orthogonal polarization states grows when interparticle distances decrease. For natural light the doublet structure of the SPP band is revealed (see curve 1). This effect was observed experimentally for granular chain-like indium films [15]. As one can see from curve 2, the doublet structure cannot be described without taking into account the lateral electrodynamic coupling between metal nanoparticles into a chain. Binary interactions averaged on the azimuth do not show the SPP doublet structure too (curve 3).

It is important that regarding the lateral interactions even in the simplest manner (taking into account only the binary interactions) leads to the red shift of the SPP for the random close-packed planar systems.

4. Conclusion

In summary, this paper has shown that numerical simulation with the help of the QCA of the TMSW is a good way to describe transmission and reflection spectra of partially correlated particle arrays of different space ordering. Almost disordered, close-packed and quasiregular structures may be regarded. For the first time polycrystalline monolayers with quasiregular packing of metal nanoparticles into domains were considered in this way. We have established the blue shift of SPP for polycrystalline monolayer relative to that for close-packed planar arrays at the same particle surface concentration.

We have also shown in the frame of the model of binary interactions that spatial ordering is most pronounced in spectra of metal nanoparticle chain monolayers and causes the broadening and

structure modification of a collective surface plasmon absorption band. Frequency dependence of plasmon resonance on polarization state and effect of packing density on the resonance spectral displacement have been established. The results of this simulation may be useful for the detection of nanoparticle chains' orientation in metallic planar nanostructures.

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