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Self-Organized Aggregation of Small Metal Particles Controlled by an External Light Field

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Using simplest two- and three-particle models, it is shown that there exists a possibility of controlled aggregation of silver nanoparticles in an external light field. The aggregation occurs as a result of the dipole–dipole interaction of particles, whose energy has a minimum at a certain particle configuration and at corresponding frequency and polarization of the field.

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At present, it becomes more and more obvious that, in the coming few decades, one of the basic avenues of fundamental and applied research will be connected with the development of methods for creating nanosized systems and with the study of the properties and various applications of subminiature devices on their basis. In connection with this, great interest has been expressed by researchers in self-organization phenomena under the joint action of strong and weak intermolecular interactions, which depend on the structure of particular molecules and on the surrounding medium [1, 2]. The strategy based on self-organization is natural for organic chemistry and is the main for wildlife. For this reason, the use of physical actions and, in particular, of laser radiation for controlling the self-organization of nano-objects into clusters whose properties can be specified in the course of the construction of such nano-objects appears to be promising. Under the action of laser radiation, atoms, molecules, and other microparticles become polarized. On the one hand, this polarization, interacting with the laser radiation, gives rise to the so-called radiation forces, which make it possible to control the motion of particles and form structures whose size is of the order of the radiation wavelength [3–5]. On the other hand, if the interparticle distance is considerably smaller than the wavelength, the laser-induced polarization of particles also leads to interparticle interactions, which can be interpreted as the near-field effect [6]. This makes it possible to form structures whose size is considerably smaller than the wavelength of the polarizing laser radiation.

Most studies devoted to interparticle interactions deal with atoms whose transition frequency is close to the resonance with the laser radiation frequency [7–9]. In this case, attention is mainly focused on questions related to changing the frequency of the atomic transition [7] and on the formation of chemical bonds between atoms interacting in the field of optical radiation [6, 8, 9]. This study considers the possibility of formation of nanostructures with a given topology from metal nanoparticles in the course of their self-organization caused by electrodynamic interactions in an external field of quasi-resonance laser radiation.

An important distinctive feature of most absorption spectra of small metal particles is an intense band in the UV or visible spectral range, which is not observed in the spectra of macro samples. This band is caused by the surface plasmon resonance, which arises because the electric field of an incident electromagnetic wave displaces conduction electrons of a small particle with respect to its positively charged ion core. This polarizes the particle and, since the particle size is comparable with the electron free path, gives rise to electron density oscillations. These oscillations are collective in character, so that the motion of the electrons proves to be phase-correlated [10, 11].

In studies of hydrosols containing fractal aggregates of silver nanoparticles, a photochromic effect was revealed: laser pulses irradiating aggregates "burned" a narrow dip in their absorption spectrum near the laser radiation wavelength [11, 12]. In this case, the absorption spectrum with the dip had the same linear polarization as that of the laser pulses. The phenomenon revealed found a completely clear explanation in terms of the theory of the optical properties of fractal clusters, which takes into account the fractal geometry of these aggregates and the electrodynamic interactions between their particles [11–15]. It was shown in these studies that, as a result of electrodynamic interactions of particles, their absorption spectrum changes, and,

depending on the interparticle distance and polarization of the radiation, the band of the plasmon resonance is shifted by a value that is comparable with the frequency of the resonance. In addition, the estimations showed that, at moderate field amplitudes and near resonance frequencies, the energy of electrodynamic interaction between particles, leading to either their attraction or repulsion, can be comparable with the energy of the van der Waals interaction of particles, as well as with the energy of their thermal motion. This makes it possible to state that the possibility exists to control the aggregation of particles with the help of the parameters of an external (laser) field (its polarization and frequency). This study demonstrates the possibility of forming nanostructures of a given geometric shape from metal nanoparticles in an external field of laser radiation. Using the dipole approximation for the electrodynamic interaction, a simple variant of formation of a structure from a minimal number of particles (two or three) is considered.

BASIC RELATIONS

If particles are located close to each other, the oscillating dipole moments induced on them (in the dipole approximation of the electrodynamic interaction) begin to significantly affect each other, and the energy of the dipole (in the general case, multipole) interaction becomes comparable with the energy of interaction with the field of an individual particle (see, e.g., [11–15]).

Let us consider an ensemble of N particles that are located at points r_i and interact with each other by means of dipoles induced by an external light field. We will assume that the size of the ensemble is much smaller than the wavelength of the incident radiation, which means that the external field E is considered to be uniform over the entire ensemble and the retardation effects are ignored. Then, the vector of the electric component of the field of the light wave can be represented in the form of a harmonic function that depends only on time, $\mathbf{E} = (1/2)\mathbf{E}_0\exp(i\omega t) + \text{c.c.}$ Near each particle, the contribution to the local field from all the remaining particles should be taken into account by summation of the fields of dipoles induced on all the particles. In this case, the vector of the dipole moment with the frequency ω induced on the ith particle has the form

$$\mathbf{d}_i = \chi_0\left(\mathbf{E} + \sum_{j\neq i}\mathbf{E}_j\right). \quad (1)$$

Here, χ_0 is the linear polarizability of the isolated particle and $\mathbf{E}_j$ is the field created by the jth particle of the ensemble at the point of location of the ith particle [11, 13, 15],

$$\mathbf{E}_j = \frac{3(\mathbf{d}_j\mathbf{r}_{ij})\mathbf{r}_{ij} - \mathbf{d}_j r_{ij}^2}{r_{ij}^5}, \quad (2)$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ is the distance between the ith and jth particles. The sum of the fields $\sum_{j\neq i}\mathbf{E}_j$ is the so-called self-consistent field, which is created by all the remaining particles of the aggregate at the point of location of the ith particle.

It is desired to solve the system of N equations with respect to the dipole moments of each particle, which are defined by expression (1). By this means, one can obtain the renormalized linear polarizability $\hat{\chi}_i$ of each particle, which, in the general case, is a tensor. The polarizability obtained relates the vector of the dipole moment induced on the ith particle to the electric field vector of the wave, $\mathbf{d}_i = \hat{\chi}_i\mathbf{E}$. The imaginary part of $\hat{\chi}_i$ determines the absorption of light by the ith particle.

The energy of interaction of the ith particle, whose dipole moment is $\mathbf{d}_i$, with the field $\mathbf{E}$ is given by

$$W_i = -\mathbf{d}_i\mathbf{E}. \quad (3)$$

If the polarizability $\hat{\chi}_i$ is complex, there exists a phase shift φ_d between $\mathbf{d}_i$ and $\mathbf{E}$, which is determined by the ratio of the real and imaginary parts of the polarizability. In this case, the dipole moment can be represented in the form $\mathbf{d}_i = (1/2)\mathbf{d}_{0i}\exp(i\varphi_d)\exp(i\omega t) + \text{c.c.}$ After transformations and averaging over time, we obtain

$$W_i = -\frac{1}{2}\mathbf{d}_{0i}\mathbf{E}_0\cos\varphi_d \sim |\mathbf{E}_0|^2. \quad (4)$$

Formula (4) makes it possible to calculate the force with which the field acts on a particle (the gradient force) in the case if the field of the wave is spatially nonuniform [3–5]. The energy of the interaction of the aggregate of N particles with the external field is equal to the sum of the energies of all the particles of the aggregate, $\sum_i W_i$.

Substituting expression (2) for the field created by the jth particle at the point of location of the ith particle into formula (4) for the energy, we obtain an expression for the energy of interaction between the ith and jth dipoles,

$$W_{ij}^{(d)} = \frac{1}{2}\frac{\mathbf{d}_{0i}\mathbf{d}_{0j}r_{ij}^2 - 3(\mathbf{d}_{0i}\mathbf{r}_{ij})(\mathbf{d}_{0j}\mathbf{r}_{ij})}{r_{ij}^5}\cos(\varphi_{di} - \varphi_{dj}). \quad (5)$$

The energy of the dipole–dipole interaction of the ith particle with all the remaining particles of the aggregate is equal to the sum $\sum_{i\neq j}W_{ij}^{(d)}$.

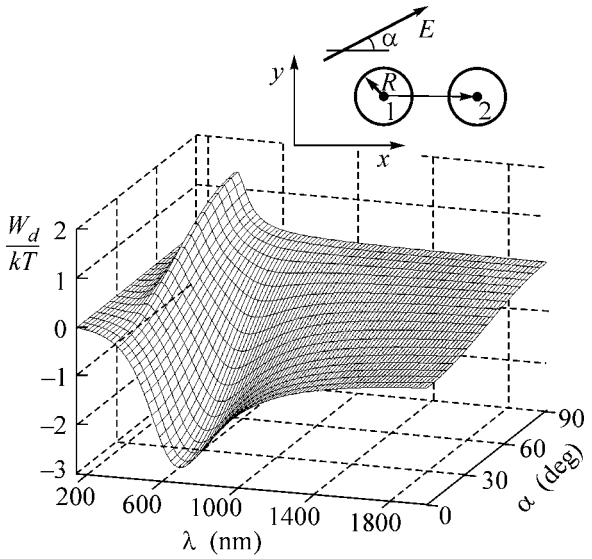

Fig. 1. Energy of the dipole–dipole interaction of two particles in an electromagnetic field in relation to the orientation angle of the field polarization and the wavelength.

In order to describe the dipole polarizability of particles, we will apply a two-level model characterized by a resonance at the frequency ω_0 and by the excitation relaxation rate (the homogeneous width) Γ. Then, the dipole polarizability of a particle in the vicinity of ω_0 can be represented as [11, 13, 15]

$$\chi_0 = R^3\omega_p/(\Omega + i\Gamma). \quad (6)$$

Here, ω_p is the characteristic excitation frequency, which is equal to the electron plasma frequency of the microsample (for silver, the wavelength corresponding to this frequency is $\lambda_p \approx 138$ nm [11]); R is the particle radius; and $\Omega = \omega_0 - \omega$ is the detuning from the resonance. In this study, we will consider nanoparticles of silver hydrosols, the initial absorption contour of which is that of the surface plasmon resonance (of the Lorentz type), which is characterized by the experimentally determined maximum at $\lambda_{pl} \approx 420$ nm and by the homogeneous width (at half maximum) $\Delta\lambda \approx 90$ nm, which corresponds to $\Gamma = 2\pi c\Delta\lambda/\lambda^2$.

CALCULATION OF THE ENERGY OF INTERACTION OF PARTICLES

Let us consider the simplest case of interaction between two identical spherical silver nanoparticles of a radius R and interparticle distance $r_{12} \equiv r$ (see Fig. 1). Let the polarization of an external light field be directed at an angle α to the straight line that connects the centers of the particles and is parallel to the x axis. According to (1), we obtain the following system of equations for determining the projections of the dipole moments of the particles onto the X and Y axes:

$$\begin{aligned} d_{1x} &= \chi_0(E\cos\alpha + 2d_{2x}/r^3), \\ d_{1y} &= \chi_0(E\sin\alpha - 2d_{2y}/r^3), \\ d_{2x} &= \chi_0(E\cos\alpha + 2d_{1x}/r^3), \\ d_{2y} &= \chi_0(E\sin\alpha - 2d_{1y}/r^3). \end{aligned} \quad (7)$$

Taking into account (6) and denoting the shift frequency as $\omega_s = \omega_m(R/r)^3$, we find that the solutions to this system are given by

$$\begin{aligned} d_{1x} = d_{2x} &= \frac{E\cos\alpha}{1/\chi_0 - 2/r^3} \\ &= \frac{r^3\omega_s E\cos\alpha}{\sqrt{(\Omega - 2\omega_s)^2 + \Gamma^2}}\exp\left(-i\arctan\frac{\Gamma}{\Omega - 2\omega_s}\right), \\ d_{1y} = d_{2y} &= \frac{E\sin\alpha}{1/\chi_0 + 1/r^3} \\ &= \frac{r^3\omega_s E\sin\alpha}{\sqrt{(\Omega + \omega_s)^2 + \Gamma^2}}\exp\left(-i\arctan\frac{\Gamma}{\Omega + \omega_s}\right). \end{aligned} \quad (8)$$

In view of (4), the energy of interaction of the dipoles of the two particles with the external field is expressed as

$$\begin{aligned} W &= -(\mathbf{d}_1 + \mathbf{d}_2)\mathbf{E} \\ &= -\frac{1}{2}r^3\omega_s|\mathbf{E}_0|^2\left(\frac{(\Omega + \omega_s)\sin^2\alpha}{(\Omega + \omega_s)^2 + \Gamma^2} + \frac{(\Omega - 2\omega_s)\cos^2\alpha}{(\Omega - 2\omega_s)^2 + \Gamma^2}\right). \end{aligned} \quad (9)$$

According to (5), the expression for the energy of the dipole–dipole interaction between the two particles has the form

$$\begin{aligned} W_{dd} &= \frac{1}{2}r^3\omega_s^2|\mathbf{E}_0|^2 \\ &\times\left(\frac{\sin^2\alpha}{(\Omega + \omega_s)^2 + \Gamma^2} - \frac{2\cos^2\alpha}{(\Omega - 2\omega_s)^2 + \Gamma^2}\right). \end{aligned} \quad (10)$$

Consequently, as a result of the interaction of the two particles, their resonance frequency is shifted. If the field is directed along the straight line connecting the centers of the particles ($\alpha = 0$), the resonance frequency is determined by the condition $\Omega - 2\omega_s = 0$; i.e., it is shifted by $2\omega_s$ toward lower frequencies. If the field is orthogonal to this straight line, the resonance frequency is determined by the condition $\Omega + \omega_s = 0$; i.e., it is shifted by ω_s toward higher frequencies [13].

In accordance with formula (9), the energy of interaction of the two particles with the field depends on the angle α. If the field frequency is smaller than $\omega_0 - 2\omega_s$,

the energy of interaction of the pair of particles with the field will be negative, and, upon slow rotation of the plane of polarization, the straight line connecting the particle centers will follow this plane. This provides the possibility to transform the rotation of the plane of polarization of an electric field to the mechanical rotation of a nano-object.

Let us consider in more detail the expression describing the energy of interaction between particles. It is seen from (10) that the energy of the dipole–dipole interaction depends on such quantities as the laser radiation intensity, the detuning between the frequency of this radiation and the frequency of the plasmon transition, the angle between the polarization plane and the straight line connecting the particle centers, and the interparticle distance.

Figure 1 shows the ratio of the energy of the dipole–dipole interaction (10) to the energy of thermal motion calculated in relation to the frequency and the angle α. In the calculations, the quantities appearing in the equations were assumed to acquire the following values: the particle radius $R = 6$ nm, the interparticle distance $r = 15$ nm, the external field strength $E = 200$ esu (which corresponds to the highest field intensity of the order of 10^6 W/cm^2 at which silver particles still do not evaporate [11]), and the temperature $T = 300$ K. It is seen from the figure that the greatest depth of the potential well, about $-2.6\ kT$, is achieved at $\alpha = 0°$ and $\lambda \approx 680$ nm. Therefore, one can expect that, as a result of the thermal motion of particles, they fall into the potential well corresponding to their topological arrangement, where the energy of their interaction will be minimal. Hence, they will occupy the thermal equilibrium position in a self-organized fashion.

The numerical calculation confirms the qualitatively obvious conclusion that, as particles approach each other, the depth of the potential well increases even more at $\alpha = 0$, and the resonance frequency shifts toward the IR range. Thus, at $r = 12$ nm, the depth of the potential well increases approximately up to $-5.1\ kT$, and the resonance wavelength is shifted to $\lambda \approx 1750$ nm. If particles are spaced from each other by a distance greater than about 22 nm, the energy of the dipole–dipole interaction can be neglected in comparison with the energy of the thermal motion.

Of greatest interest is the possibility of formation of a potential well in which, by varying the radiation frequency and the angle α between the polarization plane of the radiation and the radius-vector r_{12} (see Fig. 2), it becomes possible to join a third particle at a given angle θ to a pair of particles. In this case, it is assumed that the pair of particles 1 and 2 acts as a single whole and that r_{12} can be oriented in space using auxiliary laser radiation in accordance with (9). It is difficult to obtain simple expressions of the type (8)–(10) for this situation; therefore, the problem was analyzed numerically using Eqs. (1)–(6). The distance between the particles of the pair was chosen to be $r_{12} = 2R = 12$ nm. In Fig. 2,

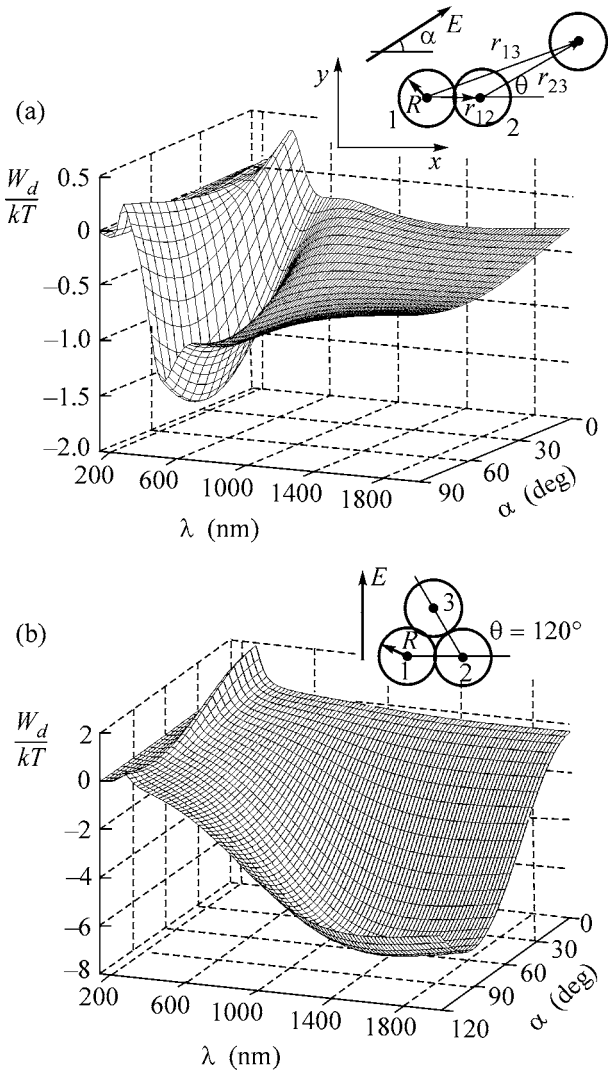

Fig. 2. Energy of interaction of a third particle with two others in an electromagnetic field in relation to the orientation angle of the field polarization and the wavelength; the angle θ = (a) 90° and (b) 120°.

r_{23} is the distance between the second and third particles, and θ is the angle between the straight lines r_{12} and r_{23}. The polarization of the external light field is directed at an angle α to the straight line that connects the centers of the first two particles and is parallel to the x axis.

Figure 2 presents the energy of the dipole–dipole interaction of the third particle with the two others in relation to the frequency and the angle α. The values of the particle radius, the external field strength, and the temperature were the same as in the above case with two interacting particles; the distance between the pair of aggregated particles and the third one was $r_{23} = 15$ nm, and the angle of arrangement of the third particle was equal to $\theta = 90°$. It is seen from Fig. 2a that the minimum of the dipole–dipole interaction energy,

approximately equal to –1.7 *kT*, is attained at the angle of orientation of the external field polarization $\alpha \approx 65°$ and at the radiation wavelength $\lambda \approx 500$ nm.

Similarly to the above case of two interacting particles, as the particles approach each other, the potential well becomes deeper, while the resonance frequency is shifted toward the IR range. For example, for the particle arrangement as in Fig. 2b, i.e., at $\theta = 120°$ and $r_{23} = 12$ nm, the minimum of the potential well at $\lambda \approx 1600$ nm amounts to –6.9 *kT*. The field in this case should be oriented at the angle $\alpha = 90°$, which is consistent with qualitative views.

In addition, the numerical calculation shows that a decrease in the angle θ also leads to a shift of the resonance frequency toward the IR range and to a small deepening of the potential well, as well as to its shift toward smaller angles α. Thus, at $r_{23} = 15$ nm and $\theta = 0°$, the calculated minimum, equal to –2.2 *kT*, is observed at $\lambda \approx 3500$ nm and $\alpha = 0°$.

Therefore, using simplest two- and three-particle models as an example, we showed that there exists a fundamental possibility of self-organized aggregation of metal nanoparticles in an external light field. The self-organization occurs due to the dipole–dipole interaction of particles, whose energy has a minimum at a certain configuration of particles and at a corresponding choice of the frequency and polarization of the field. The procedure described can be used for determining the values of the laser radiation frequency and the angle α upon successive assemblage of aggregates with a specified configuration for any number of particles.

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