Model of formation a metal nanoclusters under laser action in colloidal solution

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Abstract. The results of experimental studies of the production of metal nanoclusters in colloidal solutions are presented. Models based on the Smoluchowski equation for concentrations of nanoparticles of various sizes, as well as a model of cluster-cluster aggregation, are proposed, which can be useful in studying the processes of nanocluster formation in colloidal solutions.

1. Introduction
The synthesis of nanoclusters is of interest in the field of nanotechnology for producing materials with unique predetermined properties. The unique properties of such nanomaterials are mainly associated with size effects, when, upon reaching the nanoscale range, their properties begin to differ significantly from bulk samples [1]. Laser ablation of solids is one of the promising directions for obtaining nanoparticles with controlled properties. The action of laser radiation on targets in liquids makes it possible to form colloidal solutions containing nanoparticles.

2. Description of experimental studies on obtaining metal nanoclusters from colloidal solution
Initial colloidal systems containing metal nanoclusters (Ni, Cu, Ti) were obtained by laser irradiation of a solid target immersed in a liquid. The experimental setup and the method of obtaining such systems are described in detail in [2]. The sizes of the formed particles were determined using a particle size analyzer for dynamic light scattering - Horiba LB-550. For example, histograms of the particle size distribution for a copper target are shown in Fig. 1.

![Fig. 1. Distribution diagram of Cu particles: a) in glycerin; b) in ethanol.](image)

Particle shapes were examined using an atomic force microscope (AFM). For this, a drop of the solution was applied to a glass slide using a capillary with an inner diameter of 5 μm, after which the liquid was evaporated in a muffle furnace. The research results are shown in Fig. 2.
Fig. 2. AFM images of the region of laser deposition of copper particles: a) the structure of the deposited drop; b) approximation of precipitated particles.

From the data on the sizes of the synthesized particles, it can be concluded that the size of the synthesized particles is affected by both the intensity of the laser action, taking into account the pulse duration, and the properties of the liquid medium itself.

Moreover, the use of continuous laser radiation of moderate intensity makes it possible to obtain nanoparticles of the smallest size and seems to be the most promising for further use [3]. This may be due to the fact that, under the action of shorter laser pulses, clusters are initially formed in the jet of ablation products, which then only increase in size due to the attachment of smaller clusters and individual particles.

3. Nanocluster models

This behavior of the system during laser exposure can be described using the model of cluster-cluster aggregation for nanoclusters, as well as the Smoluchowski kinetic equation for their concentration.

The Smoluchowski equation is applicable to describe the dynamics of nanocluster concentration $n_k$:

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{p=1}^{k-1} K(k-p,p)n_{k-p}n_p - \sum_{p=1}^{k-1} K(k,p)n_kn_p,$$

where $K(k-p,p) = K(p,k-p)$ - a function that describes the probability of collision and adhesion of aggregates of $k$-p and $p$ particles, which is determined by the microphysics of motion and interaction of aggregates in the dispersion phase [4,5]. Fig. 3 shows histograms of distributions of aggregates - solutions of the Smoluchowski equation in MATLAB [6] at $K(k,p)=(k+p)(k^{2/3}+p^{2/3})$ [4].

Fig. 3. Histograms of the distribution of k-dimensional aggregates for $t = 0.1$ for the initial uniform distribution of concentrations (a) and normal (b).

The dynamics of the concentration of nanoclusters substantially depends on the initial distribution, when the maximum concentration is observed for nanoclusters with sizes from $[10; fifteen]$. Over time, localization of sizes occurs relative to the maxima, in addition, the number of one-measures begins to increase significantly, and k-dimensional aggregates larger than 15 disintegrate, and such a significant difference in histograms is not observed further. An important qualitative difference between Fig. 3a and 3b, suggests a significant effect of the rate and mode of heating the sample and the exposure time. It can be assumed that a decrease in the exposure time, which is directly related to the features of the formation of nanostructures in our experiments.
Modeling of the process of cluster formation was carried out within the framework of the cluster-cluster aggregation model on a two-dimensional computational domain. In the lower part of the computational domain, there was a target, from the surface of which model nanoparticles were separated due to the action of laser radiation. Their sizes $N$ were subdivided into 6 types - one-dimensional, two-dimensional, three-dimensional, four-dimensional, five-dimensional and multi-dimensional. The particles performed Brownian motion along the lattice sites, realized by the method of random walks. The method of random walks on the plane \[7\] is described through a random change in the coordinates $(x, y)$ of moving particles on the plane:

$$x_n = x_0 + \sum_{i=1}^{n} s t x_i, \quad y_n = y_0 + \sum_{i=1}^{n} s t y_i,$$

where $x_0, y_0$ are the coordinates of the start of the walk, $s t x, s t y$ are horizontal and vertical steps, respectively, $n$ is the number of steps.

When wandering particles hit the cells adjacent to the aggregates in accordance with the Moore neighborhood of the order of 1 \[8\] with a given probability $p$, they became elements of the aggregate or moved further. The speed of the $i$-th particle was inversely proportional to its size $v_i = v / N$, where $v$ is the maximum speed of a particle in the system. In addition, the particle velocity decreased with distance from the target. The effect of laser radiation on the system was also taken into account, when the probability of detachment of the monomer from the aggregate ($q$) was set in the region of its effect, and the value of $p$ became much less. In addition, the frequency of detachment of particles from the target was proportional to the radiation power.

Figure 4 shows the results of modeling the formation of clusters in the computational domain with a size of 100x100 rel. Units when the laser is acting on the target in while varying the time $t$ by $[500; 2500]$ rel. The maximum speed of motion $v$ was chosen equal to 10 relative units, the speed of detachment of particles from the target was 1 piece per unit time. The probability of particle attachment outside the laser impact zone was 80%, in the laser action zone (a square in the center of the computational domain with a side of 30 relative units) the probability of particle detachment from the cluster was 80%.

![Fig.4. Nanocluster aggregates at t = 500 (a), t = 1000 (b), t = 1500 (c) t = 2000 (d), t = 2500 (d).](image)

From Fig. 5, it is possible to estimate the effect of the maximum speed of movement $v$ on the nature of cluster aggregates 10 relative units (a), 20 relative units (b), 30 relative units (c). Figure 6 shows the results of modeling the formation of clusters when the probability of particle detachment from the cluster was 70% (a), 90% (b).

![Fig. 5. Nanocluster aggregates at t = 2000 for v = 10 relative units (a), v = 20 relative units (b), v = 30 relative units (c).](image)
4. Conclusion
Comparing the simulation results with the experimental ones, we can conclude that they are in agreement on a qualitative level. Thus, the proposed models can be useful in studying the formation of nanoclusters in colloidal solutions.

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