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Adaptation of the Monte-Carlo method for modeling layer-by-layer growth of clusters and nanoalloys

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Abstract. In this paper, we study the layer-by-layer growth process of a bimetallic nanoparticle Au-Ag having face-centered cubic and decahedron structure. The Monte Carlo method was chosen to implement this problem combined with an approach from molecular dynamics. The Monte Carlo method allows solving of problems with periodic boundary conditions. Computer implementations of the method have been developed in two different software products Metropolis (Tver State University) and Tsuyoyama (Institute of Information and Communication Technologies). Interaction between atoms is calculated using multi-body tight-binding model. It is established that the order of addition of atoms (simultaneous or layered) affects the chemical ordering in the studied gold-silver equiatomic nanoalloys. In addition, the difference between the values of specific energy corresponding to Metropolis and Tsuyoyama software becomes quite small, supporting the inference that the numerical procedure for the layer-by-layer growth is adequate.

Keywords: computer simulation, Monte-Carlo method, molecular dynamics method, layer-by-layer growth, nanoalloy

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Адаптация метода Монте-Карло для моделирования послойного роста кластеров и наносплавов

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Аннотация. В данной работе исследуется процесс послойного роста биметаллической наночастицы Au-Ag, имеющей гранецентрированную кубическую и декаэдрическую

структуру. Для решения этой задачи был выбран метод Монте-Карло в сочетании с методом молекулярной динамики. Метод Монте-Карло позволяет решать задачи с периодическими краевыми условиями. Реализация метода производилась в двух разных программных продуктах Metropolis (Тверской государственный университет) и Tsuyoyama (Институт информационных и коммуникационных технологий). Взаимодействие между атомами описывается с использованием многочастичного потенциала сильной связи. Установлено, что порядок присоединения атомов (одновременный или послойный) влияет на химическую упорядоченность в исследованных эквиатомных наносплавах золото-серебро. Кроме того, разница между значениями удельной энергии, соответствующей использованию программ Metropolis и Tsuyoyama, становится достаточно малой, что подтверждает вывод об адекватности численной процедуры послойного роста.

Ключевые слова: компьютерное моделирование, метод Монте-Карло, метод молекулярной динамики, послойный рост, наносплав

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Introduction

To date, researchers around the world actively use the molecular dynamics method as a tool for conducting atomistic modeling of nanosystems. While the Monte Carlo method [1] is rarely used by researchers to study the properties of mono- and bimetallic nanosystems [2–4]. Most theoretical studies of the properties of metal clusters use the procedure of simple cutting of particles from a bulk crystal structure. Thus, in [5], we presented a method for obtaining a stable structure of one-dimensional bimetallic nanoobjects. The approach is based on applying the Metropolis algorithm [6] to a periodic lattice of nodes in combination with subsequent relaxation according to the molecular dynamics method. Here, the interaction between atoms is described in terms of the tight binding potential [7]. The main advantage of the many-body interaction potential, as compared to the simple pair potential, consists in its better reproduction of some of the main features of metallic systems.

The stochastic Monte Carlo method [8] is used to study model systems up to a million atoms in size at relatively high cooling rates [9, 10]. In particular, Monte Carlo simulation was performed in [11, 12] to study ordering in bimetallic nanoalloys of a wide range of sizes in combination with semiempirical potentials. Since the successful application of simulated annealing is critically dependent on proper temperature control, one of its most important parameters is the initial temperature, which must be sufficiently high to allow the system to explore different global configurations without hitting a local minimum too early. However, a lower initial temperature allows a solution to be obtained with fewer iterations of the Metropolis algorithm.

The problem of layer-by-layer growth of crystals was previously addressed by researchers. For example, in [13], a metric model of layer-by-layer self-similar crystal growth is studied for solving practical problems of single and mass crystallization. The problem of modeling layer-by-layer growth at the nanolevel has a number of fundamental features associated with both size effects and manifestations of symmetry types that are not typical for bulk crystals [14]. Au-Ag nanoparticles [15] are promising cocatalysts for photocatalytic hydrogen reduction. However, the effect of chemical ordering on the electronic properties of nanoparticles is not well

understood other than in terms of quantum effects due to small sizes. Thus, in [16], the structural properties of 147-atomic cuboctahedral Au-Ag clusters are studied, using empirical potentials in combination with the 'atomic-swap basin-hopping' metaheuristic optimization method and comparing with the minima obtained by the density functional theory. Calculations show that Au atoms predominantly occupy near- surface positions in bimetallic structures, which leads to the formation of a pseudo-onion structure for compositions enriched in Ag.

The aim of this work is to adapt the Monte Carlo method implemented in two different software products (Metropolis and Tsuyoyama) to simulate the layer-by-layer growth process using Au-Ag bimetallic nanoclusters with different structure (face-centered cubic – fcc and decahedron – dec).

Computer simulation results and discussion

The layer-by-layer growth scheme is implemented in the Metropolis software [1] as follows. At the first stage, the core energy of the nanoparticle in the initial configuration is minimized, after which the freezing process is initiated. At the second stage, the first layer is added and the process of minimizing its energy is commenced, followed by freezing of the first layer. This procedure is additionally repeated with subsequent layers.

The cyclical energy minimization procedure starting at 0 K takes place as follows. At the first step, a full cycle of Monte Carlo steps is processed, after which the energy value of the system is stored. At the second step, we again work out the entire cycle of Monte Carlo steps, after which the convergence condition is checked according to the equation

$$\left|E_{\min}(i) - E_{\min}(i-1)\right| < \varepsilon, \tag{1}$$

where $E_{\min}(i)$ is the energy at the current iteration, $E_{\min}(i-1)$ is the energy at the previous iteration, while the parameter ε is initially set manually. If it is necessary to minimize the energy at an arbitrary temperature, for example, at $T = 300$ K (this value was used in calculation), then the run_temperature(300) and config_minimize_energy(params) functions are used. Thus, before minimization (which is carried out at 0 K), the given configuration is maintained at $T = 300$ K, then the above-described algorithm is repeated when adding layers in a cycle.

The algorithm implemented in Tsuyoyama is described in [17]. For each layer, the growth atoms are first placed into random empty nodes, then a number of iterations are performed on the particle. At each iteration, one atom may jump into an empty node (both are chosen at random). If the jump would decrease the potential energy, it is performed unconditionally. Otherwise, it may or may not be performed, with the jump probability given as:

$$P = \exp(-\Delta E / kT), \tag{2}$$

where ΔE is the energy difference of the configurations and T is the current temperature of the system. The temperature, which is initially set at 2000 K, is then gradually decreased as the algorithm proceeds. We used a linear formula for the cooling, subtracting a small amount once every 10000 iterations. The algorithm ends after 500 million iterations, when the temperature reaches 100 K. After repeating each run of the algorithm 30 times, the two best results are chosen.

At the stage of approbation of the software product Metropolis [1], we simulated the layer-by-layer growth of a bimetallic nanoparticle having an initial size of 146 atoms (1.5 nm). Figures 1 and 2 show as example the sequence of growth of decahedral nanoparticles using alternative software products Metropolis [1] and Tsuyoyama [17]. As can be seen overall surface is

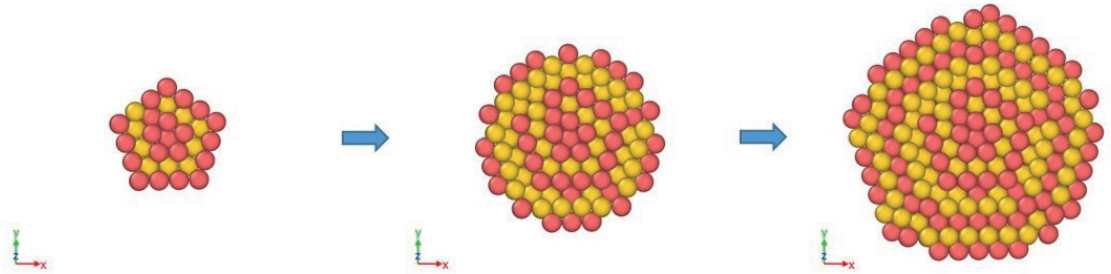

Fig. 1. Layer-by-layer growth of Au-Ag (dec) nanoparticles, in the (001) plane cross section. Metropolis software. Here and further, yellow atoms represent gold, while red atoms are silver

predominantly filled with Ag atoms (see Figure 1 and left picture in Figure 3), while the Au atoms present in sufficient quantity (see right picture in Figure 3) on the {111} faces of the resulting 3.5 nm nanoparticle. The "alternate" segregation of two metals on the near-surface layers of the nanoalloy was also revealed. Tables 1 and 2 present the calculations of specific energies per atom of Au-Ag nanoparticles, which were obtained by layer-by-layer growth procedure around the core. For the aforementioned software, two independent series of experiments are presented.

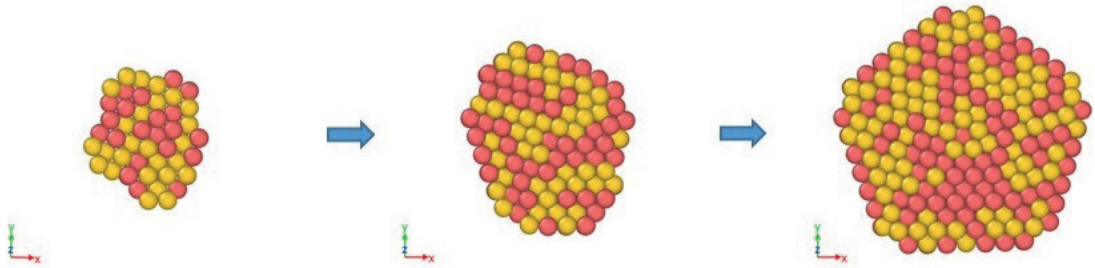

Fig. 2. Layer-by-layer growth of Au-Ag (dec) nanoparticles, in the (001) plane cross section. Tsuyoyama software

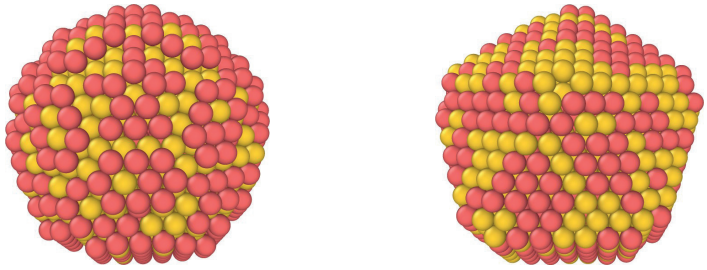

Fig. 3. Surface of the final grown decahedral Au-Ag nanoparticle: results of the Metropolis software on the left and Tsuyoyama software on the right, respectively

Table 1

Specific energy (eV/atom) of Au-Ag nanoparticles based on the FCC lattice

Layer number	Metropolis		Tsuyoyama		N, atoms	Total atoms
	Series 1	Series 2	Series 1	Series 2		
Core	–3.1141	–3.1144	–3.1512	–3.1531	146	146
+Layer 1	–3.2393	–3.2407	–3.2434	–3.2443	448	594
+Layer 2	–3.2825	–3.2829	–3.2820	–3.2831	906	1500

Table 2

Specific energy (eV/atom) of Au-Ag nanoparticles based on the dec lattice

Layer number	Metropolis		Tsuyoyama		N, atoms	Total atoms
	Series 1	Series 2	Series 1	Series 2		
Core	–3.1241	–3.1244	–3.1564	–3.1567	146	146
+Layer 1	–3.2375	–3.2410	–3.2395	–3.2417	448	594
+Layer 2	–3.2835	–3.2836	–3.2829	–3.2827	906	1500

Conclusion

An analysis of the data presented in Tables 1 and 2 suggests that both programs used predict a monotonic decrease of the specific energy of Au-Ag nanoparticles. In the size range under investigation, it is still impossible to unequivocally state which of the two structures (fcc or dec) will be more stable. With an increase in the number of atoms in Au-Ag nanoparticles, the difference between the values of specific energy corresponding to Metropolis [18] and Tsuyoyama software

becomes quite small, supporting the inference that the numerical procedure for the layer-by-layer growth is adequate. Thus, the study allows us to conclude that the order of atoms addition (simultaneous or layer-by-layer) affects the chemical ordering in equiatomic Au-Ag nanoalloys with a diameter of about 4 nm. Therefore, the growth parameters of bimetallic nanoalloys can affect their physical and chemical properties, as well as influencing the size effect [1].

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