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# Formation of structure in Au, Cu and Ni nanoclusters: MD simulations

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**Abstract.** The molecular dynamics method with the modified tight-binding (TB-SMA) potential has been used to study structure formation in gold nanoparticles 1.6–5.0 nm in diameter. The formation of the internal structure of gold nanoclusters is studied in terms of canonical ensembles. The stability boundaries of various crystalline isomers are analyzed. The obtained dependences are compared with the corresponding data obtained for copper and nickel nanoparticles. The structure formation during solidification is found to be characterized by a clear effect of the particle size on the stability of a crystalline modification.

## 1. Introduction

The last two decades were marked by heightened interest of researchers in the development and study of different nanostructures. Nanostructures are of practical and scientific significance from the viewpoint of understanding fundamental electrical, magnetic, optical, catalytic, thermal, and mechanical properties of nanoscale materials, as well as from the viewpoint of fabrication of new technical devices on their basis. It is already clear that the quantum-mechanical effects implemented in nanostructures, such as the conductance quantization, band gap renormalization, Coulomb blockade, and others, can significantly improve functional characteristics of different electronic devices.

The determination of physical and chemical properties of individual elements of nanomaterials, i.e., nanoclusters, is of particular interest due to the possibility of studying the transition from free atoms and molecules to bulk condensed systems. Clusters, being the main unit of such evolution, are unique objects of study and can give a clue to understand the nature of different processes, including nucleation, dissolution, catalysis, adsorption, phase transitions, and others.

Furthermore, already in the early 1990s, the first experiments were performed on the development of electronic elements consisting of metal units of in fact nanometer size. Further experiments showed that the circuitry of such electronics can be developed based on metal nanoclusters exhibiting quantum conductance properties at room temperatures.

Thus, the main objective of this work is to study the possible effect of electronic and structural features on stability of free small gold, nickel and copper clusters, since clusters of exactly these metals are currently efficiently synthesized by different physicochemical methods. In this study, particular attention was paid to the internal nanoparticle structure stability, since a change in the atomic configuration of the cluster can have an effect on many other properties, in particular on its electronic structure. It is well known that clusters with different sizes and internal structures have different distances between energy levels, which cannot but attract interest from the technical point of view.



## 2. The computer model

In solid state physics, instead of expensive experiments, a model replacing a real object can be studied using modern computers. To date, many methods have been developed for simulating the nanocluster behavior, first of all, the molecular dynamics (MD) method. The MD method is based on the calculation of classical (Newtonian) trajectories of object motion in the phase space of coordinates and momenta of its atoms. In the simplest version of this method, classical trajectories of atomic motion in the force field of the empirical atom–atom potential, i.e., a detailed microscopic pattern of the internal thermal mobility is simulated in nanosecond time intervals.

MD simulation of nanostructures is completely based on a detailed description of particles composing them. In MD, the classical viewpoint is most often used, according to which atoms or molecules are represented as point masses interacting via forces depending on the distance between these objects. In the numerical analysis, such forces are calculated using different interatomic interaction potentials, and the confidence level of the results obtained is directly dictated by the used potential choice. Therefore, after analyzing different representations of the potential energy, metallic nanoclusters were simulated using well established tight-binding (TB-SMA) potentials [1] with fixed cutoff radius corresponding to the fifth coordination shell inclusive.

These potentials based on the approximation of the second moments of the tight-binding Hamiltonian were developed by Cleri and Rosato [1]. The modified tight-binding method proposed by them was successfully used in a number of cluster studies. The method is based on the fact that a large group of properties of transition metals can be fully defined using the density of states of outer  $d$ -electrons. The second moment of the density of state is  $\mu_2$ ; it was experimentally found that the cohesion energy of metals is proportional to the width of the density of states, which, in the approximation of the second moments, is simply  $\sqrt{\mu_2}$ .

If only  $dd\sigma$ -,  $dd\pi$ -, and  $dd\delta$ - orbitals are taken into consideration, then, according to this model, the band energy of atom  $i$  can be written as

$$E_B^i = - \left( \sum_j \xi_{\alpha\beta}^2 e^{-2q_{\alpha\beta}(r_{ij}/r_0^{\alpha\beta} - 1)} \right)^{1/2}. \quad (1)$$

It depends only on the distance between atoms  $i$  and  $j$ , i.e.,  $r_{ij}$ , and is formally the same as the embedding function in the embedded atom method. Furthermore, the model includes a term accounting for the repulsive interaction in the form of the sum of Born–Meyer ion pair potentials,

$$E_R^i = \sum_j A_{\alpha\beta} e^{-p_{\alpha\beta}(r_{ij}/r_0^{\alpha\beta} - 1)}, \quad (2)$$

where  $\alpha$  and  $\beta$  are different types of atoms. Thus, the total energy of the system is written as

$$E_c = \sum_i (E_R^i + E_B^i). \quad (3)$$

The quantities  $\xi_{\alpha\beta}$ ,  $p_{\alpha\beta}$ ,  $A_{\alpha\beta}$ ,  $q_{\alpha\beta}$ ,  $r_0^{\alpha\beta}$  and the potential cutoff radius  $r_c$  define the parameters of system elements. The values of  $\xi_{\alpha\beta}$ ,  $p_{\alpha\beta}$ ,  $A_{\alpha\beta}$ , and  $q_{\alpha\beta}$ , are determined by fitting the cohesion energy, lattice parameter, bulk modulus  $B$ , and elastic constants  $C_{44}$  and  $C'$  to experimental values. Despite the simple functional form, the tight-binding model quite adequately describes elastic properties, defect characteristics, and melting for a wide range of fcc and hcp metals. In our opinion, it is one of the most appropriate schemes for numerical analysis of small metal particles consisting of a few hundred atoms.

Clusters were simulated within the canonical ensemble using a Nose thermostat [2]. In this case, the number of particles  $N$ , volume  $V$ , and temperature  $T$  remain unchanged (NVT ensemble), and the total momentum  $p$  of the system is zero. The temperature during simulation was determined from the average kinetic energy of atoms, which was calculated based on the velocity Verlet algorithm [2] with time step  $h = 1$  fs. The simulation was performed with the MDNTP program developed by Dr. Ralf Meyer (Universität Duisburg, Germany).

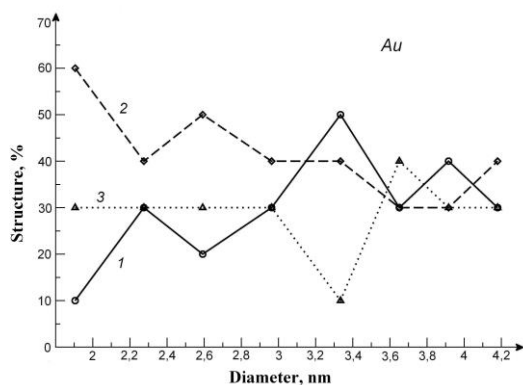
### 3. Results and discussion

To find the specific features of structure formation, we studied the role of the gold nanoparticle size on the isomer formation. A cluster structure was formed by melting of metallic nanoparticles of a certain size followed by their cooling into a crystalline phase. At the first stage, we used the Nose thermostat to perform a steplike change in the temperature: when simulating cooling, we decreased the temperature by 50 K and held clusters at every fixed temperature for 0.5 ns. To remove the side effects related to thermal noise, we held clusters in the solidification range at a fixed temperature for 2 ns but the temperature step was decreased to 5 and even 1 K, which corresponded to a total cooling time of 5–10 ns. The final temperature was taken to be 300 K, since most nanodevices should operate under these temperature conditions in practice.

When performing simulation, we found that all basic possible crystalline modifications (fcc, hcp, Ih, Dh) formed during such steplike cooling of nanoclusters from the liquid phase, and they began to

form once the solidification point was passed. It is interesting to study the dependence of the fraction of a certain structure on the cluster size, and particular emphasis was placed on the possibility of formation of pentagonal, namely, icosahedral and decahedral, structures.

To process the results of computer simulation, we applied not only visual inspection using graphics editors and radial distribution functions but also statistical analysis of the internal structures of gold clusters. When performing experiments with clusters of each size, we can draw a conclusion regarding the formation of various crystalline modifications at a finite temperature. The percentages of the structures forming during the solidification of Au nanoparticles of various sizes are shown in Fig. 1. The percentage probability of the appearance of a certain structure means that M clusters have this structure among the ensemble of N clusters of the same size.



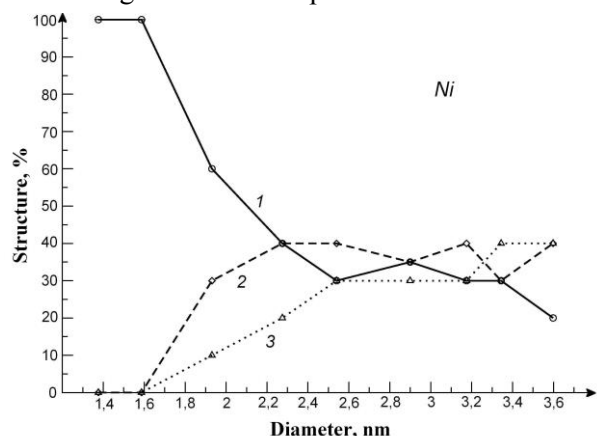
**Figure 1.** Structural configurations obtained for gold: (1) Ih, (2) Dh, and (3) fcc.

ance of a certain structure means that M clusters have this structure among the ensemble of N clusters of the same size.

It is clearly visible that the percentage of the appearance of icosahedra increases from 10 to 50% as the particle diameter increases from 1.6 to 3.33 nm. As the particle size increases further, the percentage passes through its maximum, and the probability of formation of gold clusters with this crystallographic type of structure decreases due to size effects. For example, this percentage fluctuates at a level of 30–40% for clusters 4.2 nm in diameter; at a cluster size of 5.0 nm, the percentage of appearance of the icosahedral modification is zero in all experiments. Since fivefold symmetry is prohibited for macrocrystals, the formation of large particles is inevitably related to the appearance of internal voids or elastic strains. The elastic strain energy, which is initially very low, increases in proportion to volume and exceeds the decrease in the surface energy for large icosahedral particles; as a result, this behavior destabilizes this crystallographic type.

The percentage of appearance of the decahedral phase, which can be actually called an intermediate phase between fcc and Ih, has a more complex character. The number of decahedra is 60% ( $D = 1.6$  nm) at the very beginning and then smoothly decreases to about 40% as the cluster size increases to  $D = 4.2$  nm. The number of decahedra then increases sharply because of the absence of the Ih modification. The percentage of appearance of an fcc (hcp) structure is almost independent of the cluster size in the range under study and is 30% on average, which points to the stability of formation of this structural modification in sufficiently small gold clusters. However, we should note an increase in this parameter to 40% in the largest clusters ( $D = 5.0$  nm). Thus, our experiments suggest that the process under study is characterized by a distinguishable effect of size N on the stability of a certain structural modification.

For comparison, we present the data of other authors regarding the determination of structures in gold nanoclusters in order to search for any common features. We can state that an amorphous state is most stable in clusters smaller than 1.5 nm at very low temperatures: this is supported by both an MD simulation and experimental data [3]. This conclusion is also true of clusters with a “magic” icosahedral size of 13 or 55 atoms. In the case of nickel and copper, an icosahedron is most stable at  $N = 13$  or 55 for any simulation, and the situation with gold is more complex. For example, at a cluster size  $N = 13$ , the authors of [4] found an amorphous structure using an ab initio method, and only some multi-particle potentials resulted in an icosahedral structure [4], which again points to the importance of choosing an interaction potential.

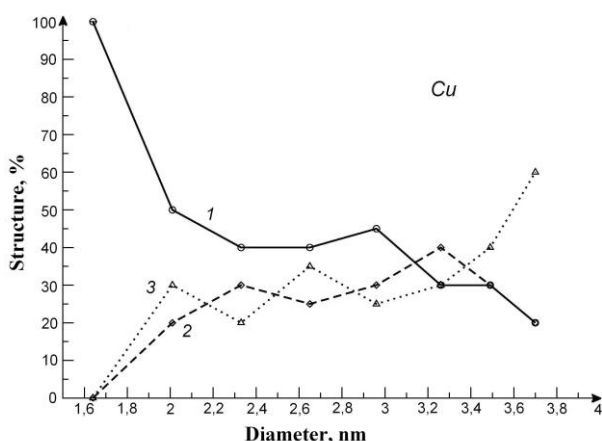


**Figure 2.** Structural configurations obtained for nickel: (1) Ih, (2) Dh, and (3) fcc.

ters, we performed an additional MD simulation of nickel and copper nanoclusters. In contrast to gold, the potential parameters in them demonstrated a high interaction; as a result, only ordered structures were found in the ground state. Other isomers were separated from them by a significant energy gap. The short-range interatomic interaction between surface atoms in gold clusters leads to uncoordinated

formation of disordered regions, which form an amorphous structure. With a computer simulation, the authors of [3] studied a huge ensemble of various random atomic configurations in clusters ( $N = 55, 75$ ) at a temperature of  $10^{-9}$  K and found that amorphous structures had the maximum density of states. At  $N = 55$ , approximately 80% of the structures with the minimum energies corresponded to an amorphous state and only 20% corresponded to an icosahedral state. At  $N = 75$ , a decahedron was detected among the ground states and the majority of clusters had a disordered state. As the temperature increases to room temperature, crystalline modifications, such as fcc, Ih, and Dh, begin to appear at noticeable fractions.

To understand the cause of the intense appearance of amorphous structures in small gold clusters, we performed an additional MD simulation of nickel and copper nanoclusters. In contrast to gold, the potential parameters in them demonstrated a high interaction; as a result, only ordered structures were found in the ground state. Other isomers were separated from them by a significant energy gap. The short-range interatomic interaction between surface atoms in gold clusters leads to uncoordinated



**Figure 3.** Structural configurations obtained for copper: (1) Ih, (2) Dh, and (3) fcc.

Most initial particles had an Ih morphology, and some of the particles corresponded to a decahedral structure. An ensemble of gold particles of close sizes (3.5 nm in diameter) was experimentally formed in [5], and structural analysis performed there shows that an icosahedron is stable.

In addition, the authors of [7] supported the operation of the size effect during the formation of a fixed structure. They found that the number of fcc clusters in particles 3–6 nm in diameter remained

formation of disordered regions, which form an amorphous structure. When the cluster size increases to 2.0 nm, the decahedral modification becomes preferable, which follows from the results of our simulation and the data in [5]. The so-called equivalent theory of crystals developed in [6] demonstrates that a decahedron begins to appear in gold at zero temperature when a cluster has more than 150 atoms and that fcc clusters appear at  $N > 180$ , which agrees with our data even at  $T = 300$  K.

At a cluster diameter of 3.0–3.5 nm, an icosahedron is considered to be most stable among all possible structures, which was experimentally supported in [7, 8]. In [7], clusters were formed when gold was cooled to room temperature in helium vapors and then placed onto an amorphous carbon film.

almost the same. As the cluster size increased, the number of icosahedra decreased, which led to an increase in the number of decahedra [7]. We made a similar conclusion when simulating the structure formation in gold clusters of diameter  $D = 4\text{--}5$  nm. At sufficiently large sizes ( $D > 5\text{--}6$  nm), most researchers believe that an fcc structure is predominant [9].

It is interesting to compare our results with the data of a similar investigation of nickel and copper (Figs. 2, 3). The percentage of the icosahedral modification for small clusters of these metals is 100%. For the largest simulated cluster ( $N = 2243$ ), an icosahedral structure appeared in 20% of the experiments and 60% clusters had the fcc structure characteristic of bulk samples. As the nickel cluster size increased, the number of icosahedra also decreased with the corresponding increase in the fraction of the fcc phase. The fraction of decahedra was almost independent of the cluster size and fluctuated about a certain value specific for each metal.

Thus, our experiments suggest that the structure formation during solidification is obviously characterized by the effect of the cluster size on the stability of a certain structure. Nickel and copper clusters exhibit certain common features in the formation of structural properties of nanoparticles, and gold clusters demonstrate much more complex behavior.

#### 4. Conclusions

Using an MD simulation, we studied the formation of the internal structure in gold clusters up to 5 nm in size. To analyze the formation processes, we used the structureless clusters formed upon melting of primary fcc Au nanoparticles and cooled them to room temperature. To create fixed cluster structures during solidification, we used various techniques that can be applied in experiments. Various structural modifications were shown to form in cooling from a liquid phase, and some criteria of their stability were determined. In simulating, we revealed the role of the size factor and the heat removal rate in the structure formation in Au clusters. A comparative analysis of our results and the data on structure formation in nickel and copper clusters shows that they exhibit common features in the formation of structural properties, whereas gold clusters demonstrate much more complex behavior, which is often in conflict with the laws characteristic of nickel and copper particles of the same size. This discrepancy in the behavior is thought to be caused by the physicochemical nature of gold, which is a rather soft and ductile material; as a result, the formation of an ideal (from a crystallography standpoint) structure is hindered.

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