Melting and crystallization hysteresis in gold and nickel nanoclusters was simulated using molecular dynamics and the tight-binding potential. It has been found that at the structural level the hysteresis in question corresponds to a smooth crossover from the liquid state to the crystalline one. The crossover in question is much more smooth for Au nanoparticles. In particular, the coordination polyhedra distributions for Au nanoparticles have revealed not only basic fcc structure but also local hcp, ic (icosahedral) and pdp (a sort of decahedral) structures in a vicinity of the melting and crystallization temperatures.

1 INTRODUCTION

According to direct experiments [1, 2], our former molecular dynamics (MD) experiments [3–7] and MD results obtained by other authors [8, 9], nanoobjects, including Lennard-Jones particles and metal nanoclusters, are characterized by the hysteresis of melting and crystallization. The essence of this phenomenon is that the melting temperature $T_m$ is higher than the crystallization temperature $T_c$ and, according to the cited works, the temperature difference $\Delta T = T_m - T_c$, which may be interpreted as a quantitative measure of the hysteresis in question, can reach 400 K. MD results [10] for Ni nanoclusters predicted even a larger value $\Delta T \approx 1000$ K, which is at least twice as large as our results [3] and results obtained in [8].

In [11] we proposed and justified a hypothesis that large $\Delta T$ values should be explained primarily by non-equilibrium conditions of melting and crystallization of nanoparticles, i.e., by high heating and cooling rates. In particular, the computer experiments cited above were performed at rates of the temperature variation $\dot{T}$ of order of $1TK/s$. So high values of $\dot{T}$ were considered as appropriate for quasiequilibrium conditions of heating and cooling. In reality such conditions are far from equilibrium, although the possibility of crystallization of metal nanoclusters at such high cooling rates is in agreement with direct experiments on bulk phases of pure single-component metals: it is very difficult to transfer them into the amorphous state; i.e., they crystallize even at cooling rates above $10^{10}$ K/s [12].

At the same time, according to the experimental and theoretical results [13] for bulk phases, high rates of the temperature variation cannot be the only physical reason for the hysteresis of melting and crystallization. Indeed, according to [14], for bulk phases of chemically pure and homogeneous substances, the kinetic temperature curve, i.e., the dependence of the temperature $T$ on the time $t$, demonstrates the supercooling of the melt
below the equilibrium melting and crystallization temperature $T_m^{(\infty)}$. The curve in question is similar to the van der Waals loop on the volume dependence of the pressure. It is also well known that noticeable supercooling is typical for bulk low-melting-point metals. In particular, supercooling for liquid mercury can reach 21 K [15]. In [15] it was also mentioned that the overheating of a solid metal is the necessary condition of its melting, although the overheating under usual conditions (about 1 K) is not detected experimentally. Thus, the hysteresis of melting and crystallization seems to be characteristic for bulk metal phases as well, although large $\Delta T$ values as for metal nanoparticles are not observed. The aim of this work is to elucidate physical reasons for the hysteresis of melting and crystallization of nanoparticles.

2 DETAILS OF MD EXPERIMENTS

We have used our computer program, based on Verlet’s velocities algorithm [16]. The program has the modular structure and allows to use different pair and many-body potentials of the intermolecular (interatomic) interaction. When simulating metal nanoparticles, we use the tight-binding potential [17]. In this paper MD results are presented for nanoparticles of two fcc metals: Au and Ni. An initially spherical, to a lesser or greater extent, configuration is cut from the corresponding bulk metal fcc crystal. After placing it in the center of the simulation cell and relaxing at a selected low temperature, the nanocluster is uniformly heated and cooled, i.e. subjected to a predetermined number of the melting and crystallization cycles that allows to find the temperatures and heats of these processes averaged over all the cycles. Following our works [3–7] and works of other authors [8, 9], we determine the melting and crystallization temperatures from the jumps on the temperature dependences of the potential term in the specific (per atom) internal energy of the nanocluster $u$ (see Fig. 1).

![Fig. 1. A melting-crystallization hysteresis loop for a Ni nanoparticle consisting of 500 atoms.](chart.png)
Fig. 2 shows the dependences $T_m(\dot{T})$ and $T_c(\dot{T})$ for nanoclusters of the metals indicated above. Despite a number of features inherent in nanoclusters of various metals, Fig. 2 demonstrates a general behavior: the melting temperature $T_m$ increases noticeably and the crystallization temperature $T_c$ decreases with an increase in the absolute value of the rate of temperature variation, the difference between $T_m$ and $T_c$ exceeds 100 K at heating and cooling rates of about 1 TK/s. However, as the heating and cooling rates decrease ($|\dot{T}| \to 0$), the melting and crystallization curves begin to approach each other, demonstrating that $\Delta T$ diminishes by an order of magnitude (down to 10 K) as compared to $\Delta T \sim 100$K, which was previously considered as typical of the hysteresis of melting and crystallization of nanoparticles.

Fig. 2. Melting temperature $T_m$ and crystallization temperature $T_c$ versus the heating and cooling rates, respectively, for nanoclusters consisting of (a) 500 Ni atoms and (b) 1000
Au atoms. The dashed line in panel (b) corresponds to the conditional equilibrium temperature between the crystal and liquid phases $T_0$, i.e., corresponds to the extrapolation of the $T_m(\dot{T})$ and $T_c(\dot{T})$ curves to the value $T_0$, corresponding to the equality $|dT/dt| = 0$.

3 CONCEPT OF A CONDITIONAL EQUILIBRIUM MELTING TEMPERATURE OF NANOCLUSTERS

The dependences $T_m(\dot{T})$ and $T_c(\dot{T})$ at low values of $\dot{T}$ were studied in more detail for Au nanoclusters. It was found that, as the heating and cooling rates were reduced to 0.35 BK/s, the difference between $T_m$ and $T_c$ decreased down to 10 K, and the extrapolation of melting and crystallization curves to the point $|\dot{T}| = 0$K/s gave $T_m = T_c = T_0 = 900\text{K}$. The characteristic temperature $T_0$ can obviously be interpreted as a conditional equilibrium melting temperature of nanoclusters. The new term is proposed because the term ‘equilibrium melting and crystallization phase transition temperature $T_m(\infty)$’, is applicable only to the infinite bulk phase. To clarify the physical meaning of the characteristic temperature $T_0$, we analyzed the behavior of the specific internal energy $u$ of Au nanoparticles consisting of $N = 1000$ atoms in a vicinity of the temperature $T_0 = 900\text{K}$. The results are shown in Fig. 3.

As is seen in Fig. 3b, fluctuations of the energy $u$ from the average value $\bar{u} = -3.48\text{eV/atom}$ toward higher and lower values are approximately equiprobable just at $T = T_0$. At the temperature $T = 875\text{K}$, which is lower than $T_0$ by only 25K (Fig. 3a), $\bar{u}$ decreases to $-3.50\text{eV/atom}$, which is characteristic of the solid phase, although some $u(t)$ values can exceed $u (T_0)$ with a noticeable probability. If the temperature of the nanocluster is $T = 925\text{K}$ (Fig. 3c), which is 25 K higher than the value $T_0 = 900\text{K}$, the region of fluctuations of the energy is shifted towards higher values ($-3.46 \geq u \geq -3.48\text{eV/atom}$), although some peaks correspond to its decrease down to $-3.52 \text{eV/atom}$, which is inherent in the crystal phase.

![Graph](image_url)
Fluctuations of the potential part of the internal energy $u$ at the annealing of the Au nanocluster containing $N = 1000$ atoms at (a) $T = 875$K, (b) $T = T_0 = 900$K, and (c) $T = 925$K. The reduced time $t^*$ is measured in numbers of simulation steps (one step corresponds to the time interval $\Delta t = 10^{-15}$s).

Thus, the fast alternation (“flicker”) of the structures corresponding to the solid and liquid states is characteristic of the nanoparticle near $T = T_0$: the probabilities of these phase states become identical at $T = T_0$. A fast change in the structure of nanoclusters at $T = T_0$ in a very short time interval (about 10 ps), as well as the probabilistic nature of such oscillations, is confirmed by the visual analysis of the corresponding configurations of Au nanoclusters two of which are shown in Fig. 4.
Fig. 4. Two configurations of the same Au nanocluster at $T = T_0 = 900$ K: (a) the crystal state, long-range translational order within the limits of the nanocluster corresponds to the distorted fcc structure, $u \approx -3.51$ eV/atom; (b) the liquid-like nanocluster (nanodroplet) without signatures of the long-range positional order, $u \approx -3.46$ eV/atom.

4 STRUCTURAL TRANSFORMATIONS IN THE COURSE OF MELTING AND CRYSTALLIZATION OF NANOPARTICLES

The hysteresis of melting and crystallization seems to be clearly manifested at the structural level at any, even minimum, heating and cooling rates. This assumption was confirmed by the study of the dynamics of change in the structure of nanoclusters consisting of 1000 and 2000 Au atoms in the process of their melting and crystallization, including premelting and post-crystallization phenomena (the last term was taken from [13]). We examined first of all the dynamics of change in the distributions of coordination polyhedrons (Voronoi polygons [18]) which characterize the local structure, i.e. the short-range order in the arrangement of atoms. Then, we analyzed groups of neighboring polyhedrons, interpreted as nuclei of a new phase, as well as the mesoscopic structure of crystalline nanoclusters. In this work, we report the results of analysis of the distribution of coordination polyhedrons for nanoclusters consisting of 2000 Au atoms. Nanoparticles with the perfect fcc structure at a quite low temperature $T = 400$ K were considered as the initial state (Fig. 5a). At the structural level the premelting corresponds to the transition of a small fraction (about 10%) of the local fcc structure into the hcp one (Fig. 5b). According to [19], since the surface tension of the liquid is smaller than the surface tension of the corresponding crystal, the melting of the particle should begin with its surface, whereas nuclei of the crystal phase can appear in any part of the droplet. Our results really demonstrate a smaller degree of ordering in the surface layer of the particle (see Fig. 3). At the same time, local hcp structures (anticuboctahedra) were also observed in the central part of the nanocluster near the melting temperature.
It is obvious that local hcp structures and other coordination polyhedrons characterize the local short-range order only and should not be treated as nuclei of the new phase. However, these polyhedrons can be considered as precursors of nuclei of the new phase as they are interpreted in Gibbs’ theory of homogeneous nucleation. At the melting temperature $T_m$, which is 1140 K for gold nanoclusters of this size, the fractions of fcc and hcp structures become close to each other. At the temperatures above $T_m$ by 10 K (Fig. 5c) the hcp structure becomes prevailing. At a higher temperature, icosahedral (ic) and decahedral (pdp) structures, which correspond to icosahedra and truncated decahedra (images of coordination polyhedrons can be found, e.g., in [18]), appear in addition to local fcc and hcp structures in the nanodroplet as well. At the same time, the fraction of atoms for which regular coordination polyhedrons cannot be constructed prevails at $T = 1600$ K (Fig. 5d). It is also worth noting that a pentagonal bipyramidal structure consisting of seven atoms, which was discussed in [20], is a component of both icosahedral and decahedral structures. It can be observed in nanoclusters both independently and in a group of coordination polyhedrons corresponding to icosahedral and decahedral structures, which are not considered in classical
crystallography. Local icosahedral and decahedral structures with the pentagonal symmetry are formed because they correspond to smaller values of the radius of the first coordination sphere and of the potential part of the internal energy.

According to [13], structural precrystallization effects in bulk phases should be much weaker than the premelting effects. However, according to our results, the precrystallization local structure of nanoclusters (Fig. 5e) is even more complex than the local structure corresponding to premelting (Fig. 5b): all above local structures are represented with comparable fractions in the distribution of coordination polyhedrons before the beginning of crystallization. The fcc structure corresponding to cuboctahedra again prevails after the end of crystallization (Fig. 5f). At the structural level, a nucleus of crystallization is formed as follows: a more or less regular coordination polyhedron (precursor) is supplemented by the same polyhedrons. However, an anticuboctahedron corresponding to the local hcp structure can sometimes be joined to a cuboctahedron corresponding to the local fcc structure. According to [20], the local bcc structure (coordination cube) plays a particular role as the precursor of the fcc crystal phase. However, we observed it only as a rare exception. Several nuclei of the fcc phase with different mutual orientations of the crystallographic axes are usually formed in the nanocluster. Then, growing nuclei adjoin each other. Various local structures can be treated at their junction. Thus, the crystallization of nanoclusters at the mesoscopic (intermediate in scale) structural level can be attributed to the formation of nanodislocations. So, for Au nanoparticles we observed no sharp structural changes at the temperatures $T_m$ and $T_c$. 
For Ni nanoparticles (Fig. 6) the crossover corresponding to the melting-crystallization hysteresis is less pronounced and less complicated. In particular, fractions of hcp and pdp in the coordination polyhedra are negligibly small, and local ic structures were not revealed at all. So, in general the melting and crystallization hysteresis in Ni nanoparticles reduces to the destroying (melting) and restoration (crystallization) of the fcc structure typical for bulk Ni. At the same time, about 25% of atoms in the final crystalline structure of Ni nanoparticles correspond to the not recognized local structure. This result means that after recrystallization Ni nanoparticles are far from ideal fcc structure corresponding to their initial configurations. Obviously, just less smooth crossover in comparison with Au nanoparticles results in a more regular (rhombic) shape of the melting-crystallization hysteresis loop for Ni nanoparticles (Fig 1).

5 CONCLUSION
Our MD results have shown that at the structural level melting and crystallization of metal nanoparticles correspond to a smooth enough crossover between crystalline and liquid states, and this crossover cannot be revealed by the usual method of the detection of phase transitions in nanoparticles used in computer simulation. This inherent crossover should obviously be considered as the main reason for the melting and crystallization hysteresis.

The value of $\Delta T = T_m - T_c$ depends not only on the rate of temperature variation but also on the particle size. Laboratory [1, 2] and computer [3–9] experiments indicate that the dependences $T_m(N)$ and $T_c(N)$ are complex enough. In particular, there is a tendency to the joining of melting and crystallization curves ($\Delta T \approx 0$K) at a certain small dimension of particles which corresponds to the characteristic number of atoms $N_{ch} = 300 - 500$ and the characteristic radius $R_{ch}$ about 1 nm. The authors of [19] predicted the coincidence of the $T_m(N)$ and $T_c(N)$ curves at $N < N_{ch}$. However, according to experimental data [1, 2] and our MD results, the detection of melting and crystallization phase transitions at $N < N_{ch}$ becomes hardly possible. With increasing the particle dimension, $\Delta T$ first increases and then somewhat decreases. However, even in laboratory experiments [1, 2], no tendency to the asymptotic joining of the $T_m(N)$ and $T_c(N)$ curves at $N \rightarrow \infty$ was observed. In particular, according to [2], for Pb nanoparticles, $R_{ch} \approx 2$ nm and the maximal $T$ value approximately equal to 150 K was observed at $R = 20$ nm, whereas $\Delta T$ decreased down to 130 K at $R = 40$ nm. A noticeable decrease in $\Delta T$ should be apparently observed at much larger dimensions inaccessible for computer simulation. At the same time, it remains unclear why a significant decrease in $\Delta T$ was not detected in laboratory experiments [1, 2, 19].

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