MATERIALS PHYSICS AND MECHANICS RESEARCH ARTICLE

Submitted: November 6, 2024 **Revised: December 10, 2024** **Accepted: February 24, 2025**

Influence of free surface on melting and crystallization in nickel and copper: molecular dynamics simulation

G.M. Poletaev [1], Y.V. Bebikhov [2], A.S. Semenov [2], R.Y. Rakitin [3], D.V. Novoselova [4]

[1] Polzunov Altai State Technical University, Barnaul, Russia

[2] Polytechnic Institute of North-Eastern Federal University, Mirny, Russia

[3] Altai State University, Barnaul, Russia

[4] Kuzbass Institute of the Federal Penitentiary Service of Russia, Novokuznetsk, Russia

✉ gmpoletaev@mail.ru

ABSTRACT

The influence of free surface on melting and crystallization processes in nickel and copper was studied using molecular dynamics simulation. It was shown that crystallographic orientation of the surface and, accordingly, the energy of atoms on the surface affect the melting onset temperature of the simulated metal cell. The melting onset temperatures from the surface are arranged in the following order of increase for the considered orientations: (110), (112), (100), (111). When studying the formation of crystalline nuclei during gradual cooling from the molten state, it was found that most of the nuclei are formed near the surface. The orientation of the crystal structure in the nuclei near the surface in most cases was such that the crystalline plane (111) was formed on the surface, which is the most energetically favorable.

KEYWORDS

molecular dynamics • melting • crystallization • surface

Citation: Poletaev GM, Bebikhov YV, Semenov AS, Rakitin RY, Novoselova DV. Influence of free surface on melting and crystallization in nickel and copper: molecular dynamics simulation. *Materials Physics and Mechanics*. 2025;53(1): 48–56.

http://dx.doi.org/10.18149/MPM.5312025_4

Introduction

The unique properties of metallic nanomaterials are largely due to the high volume fraction of surfaces and interfaces in them. One of these properties, important from the point of view of the operation and manufacturing technology of nanomaterials, is the dependence of the melting point on their effective size: grain size, film thickness, nanoparticle diameter. The so-called "size-dependent melting point depression phenomenon" has been most thoroughly studied for metallic nanoparticles. It is currently known that the melting point of round nanoparticles is inversely proportional to their diameter, which has been demonstrated both experimentally [1–5] and using molecular dynamics simulation [6–10], and also explained in theoretical works, in particular [11–16].

As for materials with a nanocrystalline structure, it was shown in [17–22] using molecular dynamics simulation that melting in them is not a homogeneous process; it usually begins from free surfaces and grain boundaries. A decrease in the average grain size in the aforementioned studies (in the range of sizes of about several nanometers) led to a decrease in the melting temperature of nanocrystalline Ag [18,19] and Al [20,21]. In [10,23], we also observed a decrease in the melting temperature for Ni nanoparticles

Publisher: Peter the Great St. Petersburg Polytechnic University

with a nanocrystalline structure compared to single-crystal particles. The crystallographic parameters of the surface and interfaces should obviously affect the temperature at which melting begins to initiate on them; however, this issue remains open at present. It can be assumed that this is affected by the energy of defect formation or, more precisely, the difference in the potential energy of atoms in the material from the energy in an ideal crystal, since it is precisely by this value that one should expect a decrease in the heat of fusion, which, in turn, is proportional to the melting temperature. The most effective method for studying this issue at present is computer simulation, namely the molecular dynamics method.

This work is devoted to the study of the influence of the crystallographic orientation of the free surface on the melting onset temperature of the modeled metal using the molecular dynamics method. Nickel and copper are considered as metals, which, on the one hand, have a wide practical application, and, on the other hand, the various properties of which are well reproduced in molecular dynamics models. In addition, this work studies the influence of the free surface on the crystallization process during gradual cooling from the molten state. In [10,24], when studying the crystallization of nickel and copper nanoparticles, we noted that the surface affects the probability of formation of crystalline nuclei: crystalline nuclei more often appeared near the surface, and as the temperature decreased in [10], an increase in the probability of formation of nuclei near the surface was noted. Obviously, in this case, there is an effect of two competing factors. On the one hand, atoms near the surface are more mobile than in the volume, and structural rearrangements, including the formation of crystalline nuclei, occur comparatively faster. However, on the other hand, the atoms on the surface are in shallower potential wells, and they are less stable and leave these wells more easily due to thermal vibrations, which, on the contrary, reduces the probability of forming a stable crystalline nucleus. We previously observed the effect of the surface on the formation of crystalline nuclei in [10,24] using the example of round metal nanoparticles. In this work, in addition to melting, we focused on studying the influence of a flat surface on the crystallization process in nickel and copper.

Description of the model

To describe interatomic interactions in nickel in the molecular dynamics model, the EAM potential from [25] was used, and in copper – from [26]. These manybody EAM potentials were obtained based on comparison with experimental data and *ab initio* calculations for various properties of the metals under consideration. They reproduce well a wide range of their mechanical and structural-energetic properties [25–29], and have proven themselves well in various molecular dynamics studies, including the processes of melting, crystallization and self-diffusion in the melt [10,23,24,27,30].

The study was carried out using the software package for molecular dynamics calculations MDR [31]. The computational cells had the shape of a parallelepiped with the dimensions of approximately 28.2 × 11.3 × 18.3 nm^3 for nickel and 29.1 × 11.7 × 19.1 nm^3 for copper and contained about 380,000 atoms (Fig. 1). The boundary conditions along one axis were free (a free surface was modeled – the right and left edges of the computational cell in Fig. 1), and there were periodic conditions along the other two axes.

Four crystallographic surface orientations were considered: (100), (110), (111), and (112). Apart from the surface, the simulated fcc crystals of nickel and copper did not contain any defects. The NPT canonical ensemble in combination with the Nosé-Hoover thermostat was used in the model [30,32]. The time integration step in the molecular dynamics method was equal to 2 fs.

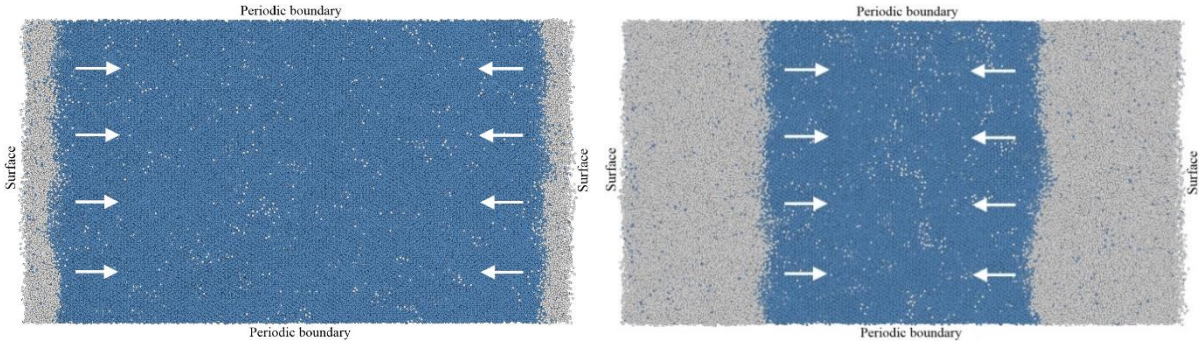


Fig. 1. Melting of the nickel computational cell from the (110) surface: (a) temperature 1770 K, time 30 ps; (b) temperature 1770 K, time 170 ps. Blue atoms represent the FCC crystal, while gray atoms represent the amorphous phase

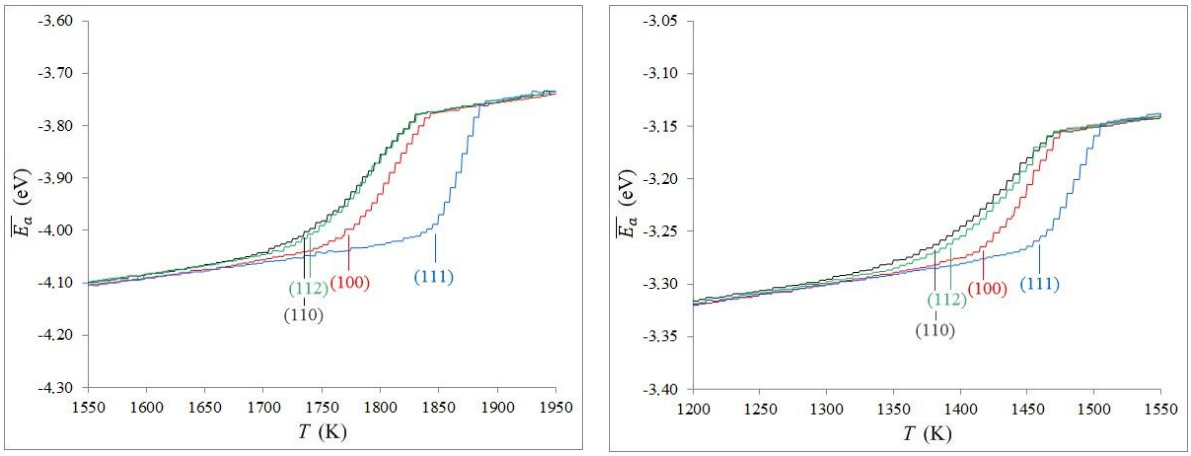
Figure 1 shows an example of the movement of the melting front from the (110) surface in nickel using a crystalline phase visualizer based on the CNA (Common Neighbor Analysis) method [33], which clearly illustrates that melting starts from the surface. For different surface orientations, the destruction of the crystal structure on the surface and the beginning of the melting front movement occurred at different temperature values. To determine the melting temperature of the computational cell, the gradual heating method was used with the plotting of the average potential energy of the atom as a function of temperature, which is often used in similar problems [6–10,23,24,34]. In this case, the rate of temperature change is usually set from 10^{11} to 10^{13} K/s. According to our previous works [10,23], the rate of 10^{12} K/s turned out to be optimal for our research. In the model, the temperature was increased linearly by a corresponding increase in the moduli of the atomic velocities after a certain time step (5 ps in this case).

Results and Discussion

With a gradual increase in the temperature of the computational cell, upon reaching a certain value, the crystalline structure on the surface was destroyed (Fig. 1). Then the crystal-liquid front moved from the surface to the center of the computational cell at a speed of about several tens of meters per second, which, however, depended on the temperature and increased with its increase [35,36]. The influence of the orientation of the crystal-liquid front in the crystal on its speed and dependence on temperature was considered in [37–41], where it was noted, in particular, that the highest speed of the front movement is observed at the orientation (100) compared to the orientations (110) and (111).

Figure 2 shows the dependences of the average potential energy of an atom on temperature for the computational cells of nickel and copper with gradual heating. With

increasing temperature, the average energy of an atom for the same phase increases almost linearly due to an increase in atomic oscillation and thermal expansion. A sharp increase in the average energy of an atom on the graphs corresponds to a phase transition, i.e. melting. In this case, melting of the computational cell did not occur instantly, as was already mentioned above – the front propagated from the surface to the center of the cell with a finite velocity. Therefore, we determined the melting temperature based on the moment of the phase transition onset, which, in turn, was determined by the intersection of the approximation lines before and after the onset of melting. The speed of the front increased with increasing temperature, due to which the slope of the part on the graphs corresponding to the movement of the melting front is steeper at a higher temperature. Having reached a liquid state in the entire computational cell, the average energy of an atom again grew linearly with increasing temperature.



(a) (b)

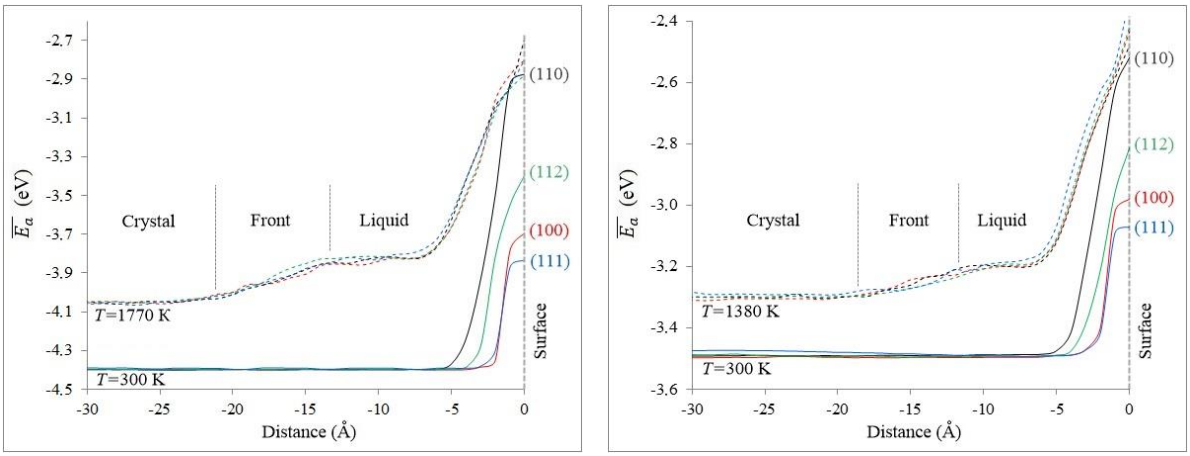
Fig. 2. Dependences of the average potential energy of an atom on temperature during heating for different surface orientations: (a) nickel; (b) copper

In Fig. 2, it is clearly seen that the orientation of the surface does influence the melting temperature of the computational cell. Moreover, this influence is quite strong in our case: the temperature at which melting began from the (111) surface was 6.5 % higher for nickel and 5.6 % higher for copper than the melting onset temperature from the (110) surface. It should be emphasized that the model is an idealized version, in which it is possible to single out one influencing factor and discard the others. The melting onset temperatures are arranged in the following order in ascending order: (110), (112), (100), (111). For nickel these are 1735, 1740, 1778, and 1847 K, respectively (Fig. 2(a)), for copper: 1381, 1393, 1417 and 1459 K (Fig. 2(b)).

Melting from the surface begins due to the comparatively easier destruction of the crystal structure on it, due to the fact that the atoms on the surface are in shallower potential wells compared to a pure crystal and it is easier for the atoms to leave them as a result of thermal vibrations. After the destruction of the structure on the surface, the formed front does not stand still (no static two-phase state was observed), it begins to move from the surface into the crystal volume. The atoms near the crystal-liquid front on the side of the crystal phase are also in comparatively shallower potential wells than in the crystal volume, due to the more disordered arrangement of the atoms on the side of

the melt. In addition, the melt has more intense self-diffusion and more free volume compared to the crystal, which is also the reason for the easier destruction of the crystal near the crystal-liquid front than inside the crystal volume, and the reason for the front movement.

To confirm all of the above, we constructed distributions of the average atomic energy depending on the distance from the surface for the crystalline state at a temperature of 300 K and at the moment of melting front movement (Fig. 3). In the second case, the crystalline structure was first destroyed from the surface and the front movement began, then the same temperature was set for all orientations (1770 K for nickel and 1380 K for copper) and the front movement was modeled to the same distance from the surface. This was done in order to then superimpose the energy distributions for different surface orientations under otherwise equal conditions. The distribution was constructed by calculating the average potential energy of an atom in layers 0.2 nm wide when moving with a step of 0.1 nm along the direction perpendicular to the surface.



(a) (b)

Fig. 3. Distributions of the average potential energy of an atom depending on the distance from the surface for the crystalline state at a temperature of 300 K and at the moment of movement of the melting front: (a) nickel; (b) copper

As can be seen, in the case of a crystalline state, the orientation of the surface significantly affects the average energy of an atom on the surface. Moreover, the average potential energy of an atom on the surface decreases in the same order among the considered orientations in which the melting onset temperature increases: (110), (112), (100), (111). The orientation of the surface affects the temperature at which the destruction of the crystalline structure begins, but further movement of the front, as was said above, depends on the temperature and the difference in energies in the crystalline and liquid phases. The front velocity, as noted in [37–41], depends on the orientation of the front relative to the crystal, but the distributions of the average atomic energy turned out to be identical for all considered orientations. In [41], it was suggested that the difference in the front velocity from the orientation in the crystal at the same temperature is due to different depths of the potential wells at the boundary of the forming crystal. Apparently, when calculating the average energy of all atoms in a layer (in our case the

layers were 0.2 nm thick), the orientation affects the range of values, but the average value itself is the same.

From the distributions shown in Fig. 3, one can estimate the width of the crystal-liquid front for the temperatures under consideration: approximately 0.8 nm for nickel at a temperature of 1770 K and 0.7 nm for copper at a temperature of 1380 K.

In addition to studying the influence of the surface on melting, this work also studied the influence of the surface on the process of initial formation of stable crystalline nuclei. As was already mentioned in the introduction, in this case there is an effect of two competing factors. On the one hand, self-diffusion on the surface and near it is higher than in the bulk of the material, i.e. all structural rearrangements near the surface should occur faster. However, on the other hand, the atoms on the surface are in shallower potential wells, due to which the position of such atoms is less stable than in the bulk, they more easily leave potential wells due to thermal vibrations, which, on the contrary, reduces the probability of formation of a stable crystalline nucleus.

In [10,24], when studying the crystallization of metal nanoparticles, we noted that crystallization most often begins from a free surface. In this paper, the formation of stable crystalline nuclei at the initial stage was studied using a rectangular computational cell with flat surfaces (Fig. 4). The computational cells for nickel and copper were the same as in the case of melting simulation, i.e., the boundary conditions along one axis were set as free, and along the other two, as periodic. First, the metal was melted by holding at a temperature above the melting point for a time sufficient to melt the entire volume of the computational cell. After this, gradual cooling was simulated. The forming crystalline nuclei were studied using a crystalline phase visualizer.

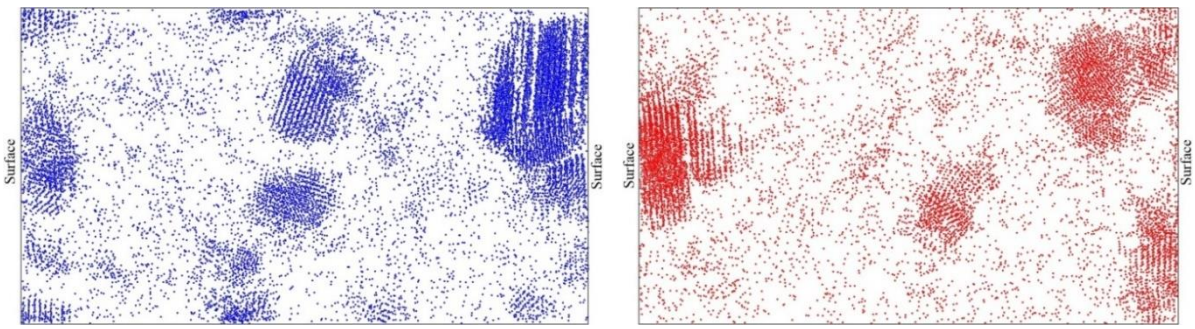


Fig. 4. Formation of crystalline nuclei during cooling of the melt at a rate of 10^{12} K/s: (a) nickel; (b) copper

Figure 4 shows examples of crystal nuclei formed during cooling of the melt in nickel (Fig. 4(a)) and copper (Fig. 4(b)). As can be seen, a significant portion of the nuclei are indeed formed near the surface, but no clear dominance of the surface factor was observed: nuclei also arose far from the surface. It should be noted that the orientation in the nuclei near the surface was, as a rule, such that a crystal plane (111) was formed on the surface, which, as shown above, is the most energetically favorable.

For a more detailed study, distributions of the fraction of the crystalline structure in the computational cell were constructed. For nickel and copper, four different experiments were carried out, and the resulting distributions were superimposed on each other (Fig. 5). The distributions were constructed by calculating the fraction of atoms

whose environment corresponded to the crystalline structure (mainly fcc, rarely hcp) in layers 0.2 nm wide when moving with a step of 0.1 nm along the direction perpendicular to the surface.

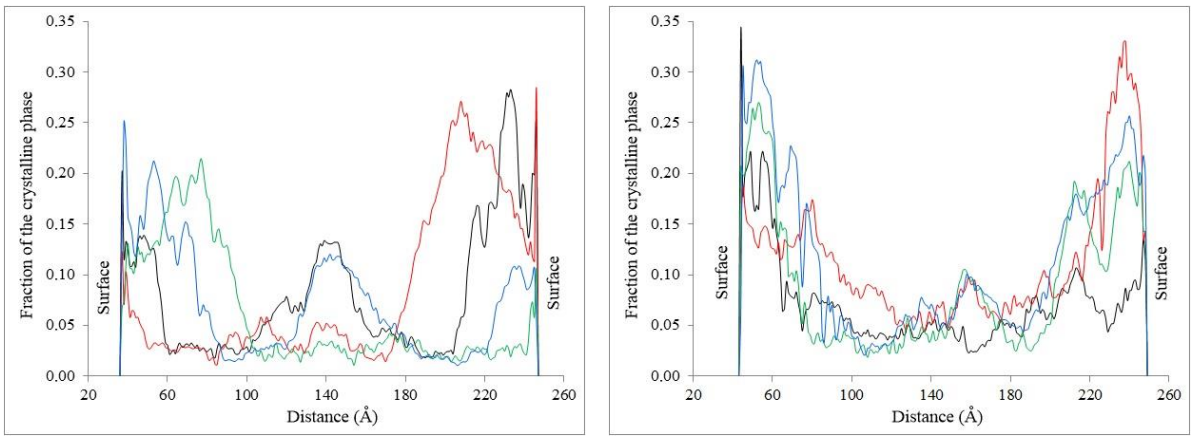


Fig. 5. Distribution of the fraction of the crystalline phase depending on the distance from the surface during the initial formation of stable crystalline nuclei: (a) nickel; (b) copper

As can be seen in Fig. 5, the fractions of the crystalline phase near the surface (on the left and right in the distributions) are indeed noticeably larger than in the volume of the computational cell. This was especially pronounced for copper (Fig. 5(b)). It can also be noted that the peaks of the distributions often do not coincide with the edge of the surface, but are located at some distance from it. This indicates that the centers of such nuclei are located at some distance from it, but, at the same time, their growth is due to the influence of the surface.

The two factors influencing the probability of crystalline nuclei formation and competing with each other, discussed above, more intense self-diffusion and relatively shallow potential wells, seem to make different contributions depending on the temperature. It can be assumed that at lower temperatures, for example, during the crystallization of metallic glasses, the so-called devitrification, an even more pronounced influence of the surface on the formation of the crystalline phase can be observed.

Conclusions

Using molecular dynamics simulation, the influence of the free surface on the processes of melting and crystallization in nickel and copper was studied. In the case of melting, the influence of the crystallographic orientation of the surface on the melting onset temperature of the simulated metal is considered. In the case of crystallization, the influence of the surface on the probability of the formation of stable crystalline nuclei during gradual cooling from the molten state was studied.

It is shown that with gradual heating, melting begins from the surface due to the comparatively easier destruction of the crystal structure on it, due to the fact that the atoms on the surface are in shallower potential wells compared to a pure crystal and it is easier for them to leave them as a result of thermal vibrations. In this case, the energy of surface atoms and the crystallographic orientation of the surface affect the melting onset

temperature: the lower the energy of surface atoms, the higher the melting onset temperature. For nickel and copper, the melting onset temperatures are arranged in the following order of increase for the orientations considered: (110), (112), (100), (111).

When studying the formation of crystalline nuclei during gradual cooling from the molten state, it was found that most of the nuclei were formed near the surface. The orientation in the nuclei near the surface was, as a rule, such that the crystalline plane (111) was formed on the surface, which is the most energetically favorable.

CRediT authorship contribution statement

Gennady M. Poletaev **:** conceptualization, writing – review & editing, writing – original draft; **Yuriy V. Bebikhov** **:** investigation, data curation; **Alexander S. Semenov** **:** investigation, data curation; **Roman Y. Rakitin** **:** investigation, data curation; **Darya V. Novoselova**: investigation, data curation.

Conflict of interest

The authors declare that they have no conflict of interest.

References

1. Castro T, Reifenberger R, Choi E, Andres RP. Size-dependent melting temperature of individual nanometer-sized metallic clusters. *Physical Review B.* 1990;42: 8548–8556.
2. Dick K, Dhanasekaran T, Zhang Z, Meisel D. Size-denpendent melting of silica-encapsulated gold nanoparticles. *Journal of the American Chemical Society.* 2002;124: 2312–2317.
3. Hirasawa M, Orii T, Seto T. Size-dependent crystallization of Si nanoparticles. *Applied Physics Letters.* 2006;88: 093119.
4. Tang S, Zhu S, Lu H, Meng X. Shape evolution and thermal stability of Ag nanoparticles on spherical SiO_2 substrates. *Journal of Solid State Chemistry.* 2008;181: 587–592.
5. Kim HK, Huh SH, Park JW, Jeong JW, Lee GH. The cluster size dependence of thermal stabilities of both molybdenum and tungsten nanoclusters. *Chemical Physics Letters.* 2002;354: 165–172.
6. Qi Y, Cagin T, Johnson WL, Goddard III WA. Melting and crystallization in Ni nanoclusters: the mesoscale regime. *The Journal of Chemical Physics.* 2001;115: 385–394.
7. Shim JH, Lee BJ, Cho YW. Thermal stability of unsupported gold nanoparticle: a molecular dynamics study. *Surface Science.* 2002;512: 262–268.
8. Li X. Modeling the size- and shape- dependent cohesive energy of nanomaterials and its applications in heterogeneous systems. *Nanotechnology.* 2014;25: 185702.
9. Chepkasov IV, Gafner YY, Vysotin MA, Redel LV. A study of melting of various types of Pt-Pd nanoparticles. *Physics of the Solid State.* 2017;59: 2076–2081.
10. Poletaev GM, Gafner YY, Gafner SL. Molecular dynamics study of melting, crystallization and devitrification of nickel nanoparticles. *Letters on Materials.* 2023;13(4): 298–303.
11. Nanda KK, Sahu SN, Behera SN. Liquid- drop model for the size- dependent melting of low-dimensional systems. *Physical Review A.* 2002;66: 013208.
12. Qi WH, Wang MP, Zhou M, Shen XQ, Zhang XF. Modeling cohesive energy and melting temperature of nanocrystals. *Journal of Physics and Chemistry of Solids.* 2006;67(4): 851–855.
13. Luo W, Hu W, Xiao S. Size effect on the thermodynamic properties of silver nanoparticles. *The Journal of Physical Chemistry C.* 2008;112: 2359–2369.
14. Luo W, Deng L, Su K, Li K, Liao G, Xiao S. Gibbs free energy approach to calculate the thermodynamic properties of copper nanocrystals. *Physica B.* 2011;406: 859–863.
15. Li H, Han PD, Zhang XB, Li M. Size-dependent melting point of nanoparticles based on bond number calculation. *Materials Chemistry and Physics.* 2013;137: 1007–1011.

16. Zhu J, Fu Q, Xue Y, Cui Z. Accurate thermodynamic relations of the melting temperature of nanocrystals with different shapes and pure theoretical calculation. *Materials Chemistry and Physics.* 2017;192: 22–28.
17. Phillpot SR, Lutsko JF, Wolf D, Yip S. Molecular-dynamics study of lattice-defect-nucleated melting in silicon. *Physical Review B.* 1989;40: 2831.
18. Xiao S, Hu W, Yang J. Melting behaviors of nanocrystalline Ag. *The Journal of Physical Chemistry B.* 2005;109(43): 20339–20342.
19. Xiao S, Hu W, Yang J. Melting temperature: from nanocrystalline to amorphous phase. *Journal of Chemical Physics.* 2006;125(18): 184504.
20. Wejrzanowski T, Lewandowska M, Sikorski K, Kurzydlowski KJ. Effect of grain size on the melting point of confined thin aluminum films. *Journal of Applied Physics.* 2014;116(16): 164302.
21. Noori Z, Panjepour M, Ahmadian M. Study of the effect of grain size on melting temperature of Al nanocrystals by molecular dynamics simulation. *Journal of Materials Research.* 2015;30: 1648–1660.
22. Poletaev GM, Sitnikov AA, Yakovlev VI, Filimonov VY, Novoselova DV. Study of the melting nanocrystalline aluminum by the molecular dynamics method. *Materials Physics and Mechanics.* 2024;52(2): 106–113.
23. Poletaev GM, Bebikhov YV, Semenov AS. Molecular dynamics study of the formation of the nanocrystalline structure in nickel nanoparticles during rapid cooling from the melt. *Materials Chemistry and Physics.* 2023;309: 128358.
24. Poletaev G, Gafner Y, Gafner S, Bebikhov Y, Semenov A. Molecular dynamics study of the devitrification of amorphous copper nanoparticles in vacuum and in a silver shell. *Metals.* 2023;13(10): 1664.
25. Purja Pun GP, Mishin Y. Development of an interatomic potential for the Ni-Al system. *Philosophical Magazine.* 2009;89: 3245–3267.
26. Williams PL, Mishin Y, Hamilton JC. An embedded-atom potential for the Cu-Ag system. *Modelling and Simulation in Materials Science and Engineering.* 2006;14: 817.
27. Levchenko EV, Ahmed T, Evteev AV. Composition dependence of diffusion and thermotransport in Ni-Al melts: a step towards molecular dynamics assisted databases. *Acta Materialia.* 2017;136: 74–89.
28. Muser MH, Sukhomlinov SV, Pastewka L. Interatomic potentials: achievements and challenges. *Advances in Physics: X.* 2023;8: 2093129.
29. Drewienkiewicz A, Zydek A, Trybula ME, Pstrus J. Atomic level insight into wetting and structure of Ag droplet on graphene coated copper substrate – molecular dynamics versus experiment. *Nanomaterials.* 2021;11: 1465.
30. Poletaev GM, Bebikhov YV, Semenov AS, Starostenkov MD. Self-diffusion in melts of Ni-Al and Ti-Al systems: molecular dynamics study. *Letters on Materials.* 2021;11(4): 438–441.
31. Poletaev GM. *Molecular dynamics research (MDR).* Certificate of state registration of a computer program No. 2015661912 dated 12 Nov 2015.
32. Poletaev GM, Starostenkov MD. Mutual diffusion at the interface in a two-dimensional Ni-Al system. *Technical Physics Letters.* 2003;29(6): 454–455.
33. Tsuzuki H, Branicio PS, Rino JP. Structural characterization of deformed crystals by analysis of common atomic neighborhood. *Computer Physics Communications.* 2007;177: 518–523.
34. Poletaev G., Rakitin R., Bebikhov Y., Semenov A. Molecular dynamics study of melting initiation at tilt grain boundaries depending on their misorientation angle in aluminum. *Physica Scripta.* 2025;100: 015988.
35. Chan W-L, Averback RS, Cahill DG, Ashkenazy Y. Solidification velocities in deeply undercooled silver. *Physical Review Letters.* 2009;102: 095701.
36. Zhang HY, Liu F, Yang Y, Sun DY. The molecular dynamics study of vacancy formation during solidification of pure metals. *Scientific Reports.* 2017;7: 10241.
37. Mendelev MI, Zhang F, Song H, Sun Y, Wang CZ, Ho KM. Molecular dynamics simulation of the solid-liquid interface migration in terbium. *The Journal of Chemical Physics.* 2018;148: 214705.
38. Zhang HY, Liu F, Yang Y, Sun DY. The molecular dynamics study of vacancy formation during solidification of pure metals. *Scientific Reports.* 2017;7: 10241.
39. Mendelev MI, Rahman MJ, Hoyt JJ, Asta M. Molecular-dynamics study of solid-liquid interface migration in fcc metals. *Modelling and Simulation in Materials Science and Engineering.* 2010;18: 074002.
40. Sun DY, Asta M, Hoyt JJ. Kinetic coefficient of Ni solid-liquid interfaces from molecular-dynamics simulations. *Physical Review B.* 2004;69: 024108.
41. Poletaev GM, Karakulova IV, Rakitin RY. Crystallization front motion velocity in nickel depending on orientation and supercooling temperature: molecular dynamics simulation. *Russian Physics Journal.* 2022;65(8): 1323–1327.