Dynamic Model of Melting – Investigation of Stability for Nanopyramid of Spherical Atoms

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Abstract : *A dynamical model of melting for simple metals is developed, constructed, and tested. Model is a trihedral pyramid of identical hard spheres, the base of which can be uniformly expanded in the horizontal plane. With the help of this mechanical model, the stability limit of nanoscale pyramidal clusters of elemental metals is investigated. Extrapolation of obtained results to the limit of infinite crystal should lead to the credible estimation of the relative thermal expansion of metallic crystals at which they start melting.*
Keywords - *dynamic modeling, hard sphere, melting, metal, nanopyramid*

I. INTRODUCTION

Since the atomic structure of a condensed substance determines its electronic structure, the step-wise changes in the atomic structure in result of melting are accompanied by radical changes in whole complex of physical-chemical properties. Studying the nature of condensed matter transformation during melting is not only of high academic interest – this problem is also important from the point of view of practical applications in metallurgy because many technological processes – industrial production of metals, welding, and soldering of metallic parts, etc. – are associated just with the melting process.

Why does the metal melt or what factors determine stability of its crystalline lattice? Obtaining answers to such questions remains to be one of most urgent problems of the solid state physics. From the thermodynamic point of view, melting refers to the first-order phase transformation. Historically, to explain this process various theories were proposed, which are based on the Debye–Einstein oscillating model for crystalline solids. Theories by Lindemann and Grüneisen are the most popular among them [1].

According to Lindemann, at melting temperature T_m the relative change in the dimensionless amplitude of atomic oscillations reaches a critical value x_m, at which the change in unit cell dimensional parameter r is so strong that the lattice loses stability – it melts. For elemental crystals, the melting temperature is related with these and some other characteristics of the cryatal: $kT_m \approx x_m^2 r^2 M (k\Theta)^2 / 9h^2$, where h is the Planck constant, k is the Boltzmann constant, M is the total mass of constituent atoms in the unit cell, and Θ is the Debye temperature. Hence, from the experimental melting temperatures one can estimate the critical value of the relative amplitude of atomic vibrations in crystals. It turns out [2] that for most of elemental crystals $x_m = 0.20 - 0.25$. The narrowness of this interval suggests that the melting of all the elemental substances is expected approximately at same relative expansion.

As for the Grüneisen approach to melting mechanism, when the crystal is expanded in volume from absolute zero of temperature by 6 – 8 %, atoms localization near the fixed lattice sites ceases to be stable and the substance melts: $3\alpha T_m \approx \mathrm{const} = 0.06 - 0.08$. Here α stands for the crystal coefficient of linear expansion averaged over the temperature interval from absolute zero to melting point. In the Debye–Grüneisen approximation, the crystal stability limit can be estimated [3] by quasi-thermodynamic relation between volumes V_0 and V_m of a solid sample, respectively, at absolute zero and melting point: $V_m / V_0 \approx 1.10$. Thus, the crystal cannot be too overheated: its resistance to melting is limited by expansion in volume by 6 – 10 %.

In present work, we briefly analyze different models of melting reported so far and propose a new prospective approach to the problem – dynamic modeling based on nanopyramidal cluster of the melting crystal.

II. GEOMETRIC APPROACH – HARD SPHERES MODEL

Melting is condensed substance transformation from one – crystalline – state to another – liquid – state. Therefore, its modeling primarily requires characterizing the geometry of condensed matter's atomic structure. When the gas of atoms is condensed, in the system there are formed interatomic bonds which, on the one hand, are strong enough to retain constant volume (at fixed temperature and pressure) and, on the other hand, weak

enough to be retained by atoms their individuality and then allow the unambiguous determination of the chemical composition. Acting together, these two factors shape the condensed matter as bound system of atoms, i.e., atomic structure. In view of this, here and below we use the term "atom" for all atom-like particles constituting crystals and liquids, which to greater or lesser extent differ in their effective parameters (radius, static charge, spin, etc.) from the isolated atoms of corresponding chemical elements.

Condensed matter of given chemical composition can exist only in two fundamentally different states: crystalline state with an ordered atomic structure and liquid state with a disordered structure. In both cases, for sites in atomic structure the parameter of key importance is the coordination number or the number of nearest neighboring sites. For most of substances, crystallinity makes it impossible the relative macroscopic displacements in the system without disruption its integrity. However, there are exceptions, for example, amorphous solids and liquid crystals. Consequently, in general the melting point of a substance is not equivalent to its fluidity limit point.

Since melting means condensed matter's transition from more ordered (or less randomized) state to more randomized (or less ordered) state, crystal and liquid, respectively, are low- and high-temperature phases of the substance and its melting is related to an increase in the entropy of the corresponding system of atoms.

In the ground state, each atom of the crystal performs zero-point vibrations near its equilibrium site in lattice. These oscillations are harmonic and, consequently, the average deviation of atoms from their equilibrium positions is zero. As for the standard atomic deviations, they certainly differ from zero, but almost always are less than the distances between nearest neighboring atoms. The only exception is helium, which crystallizes only under sufficiently high external pressure.

As the temperature rises, oscillations become anharmonic. This leads to displacements of atomic assemblies and, accordingly, to changes in the volume occupied by the crystal. More often, the thermal expansion takes a place. Rarely, the crystal thermal compressing occurs as well. As directions of atomic oscillations are random, local variations in interatomic distances are not homogeneous. Consequently, heating breaks ideality of the crystalline structure. But, up to a certain temperature, its topology as a whole and, in particular, coordination numbers of most of atomic sites remain unchanged. Emphasize that, mathematical sense of the term "topology" is related to the description of a system's structural property that changes only step-wise.

At melting temperature T_m the concentration of atomic sites with broken local crystalline topology reach such a critical value, which is sufficient for integration of local regions with broken topologies. Thus, melting process can be treated as transformation of an ordered crystalline topology into a randomized topology characteristic of liquids. As the relation between crystalline and liquid atomic geometries is determined by the physical nature of interatomic binding, it is advisable to consider here, at least briefly, geometric models of interatomic bonds of different types that occur in condensed matter. In doing so, we have to proceed from the fact that the atom is bounded system of heavy and, accordingly, practically fixed nucleus and cloud of significantly lighter electrons that move on closed orbits around nucleus forming electron-shells. Lower – core – shells are completely filled by electrons and, therefore, have spherical shapes. Only upper – valence – shells can be filled partially and then lead to aspheric distortions of the atom shape.

In atoms of inert elements, there are no valence shells. Therefore, in isolated state these atoms possess the ideal spherical shape, which practically does not change in their crystals with weak van der Waals polarization forces being responsible for binding. In all other types of crystals, binding is realized by valence electrons when atomic particles tend to states with filled valence shells, which are most stable energetically.

For metallic atoms, the valence shells are filled with electrons only slightly – less than in half. The tendency to filled shells leads to the moving of valence electrons into interatomic space, i.e. collectivization of valence electrons between atoms constituting crystal and, accordingly, to the growth in their coordination number. Metallic crystals can be imagined as systems of positive ions with filled shells and, therefore, of spherical shape, which "float" in negatively charged electronic "jellium".

Ionic crystals are chemical compounds. In most stable species, total number of valence electrons in the unit cell is sufficient to completely fill valence shells of atoms of certain elements. Direction of valence electrons transfer is determined by the relative electronegativity of constituent elements. Therefore, ionic crystals are built of positive and negative ions with filled shells. It is clear that they are shaped as spheres of different radii.

Crystals with covalent bonds are constructed from atoms of a non-metallic element and the total number of valence electrons in their unit cells is sufficient to completely fill valence shells only of half of atoms. Such a situation in combination with the absence of pronounced transition direction for valence electrons leads to their exchange and formation of electron-density maxima in the middle of chemical bonds between neighboring atoms, as well as minimization of coordination numbers. It is experimentally proved that electron-density distribution in real covalent crystals with a good accuracy coincides with the simple superposition of averaged over time electron densities of isolated atoms, when they are fixed at corresponding sites of the

crystalline lattice. But, the time averages of electron density distributions of atoms are spherically symmetric. Thus, covalent crystals can be imaged as structures of partially overlapping identical spherical atoms.

Atoms of lightest element – hydrogen – have no filled shells: after removing its valence shell, hydrogen atom turns into a bare proton, radius of which should be neglected in comparison with that of ion of any other element with filled shell(s). Hydrogen-containing crystals are featured by so-called hydrogen-like bonds. In these crystals, hydrogen ions can be modeled as positively charged zero-radius spheres or material points serving for sources of Coulomb field.
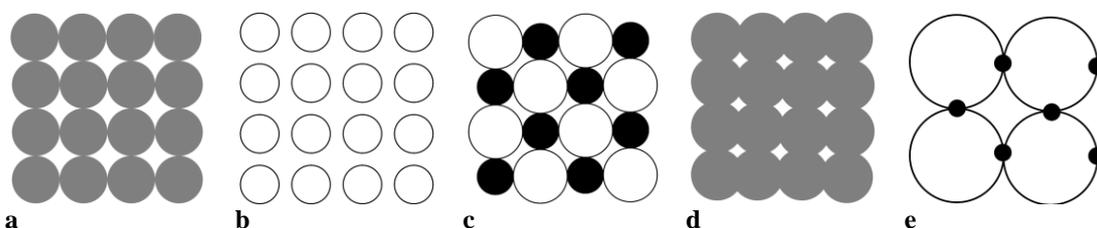

Figure 1. View of atomic geometries of crystals of (a) inert elements, (b) metals, (c) ionic compounds, (d) covalently bonded semiconductors, and (e) hydrogen-containing compounds with square lattice structure.

We come to the conclusion that any crystal can be represented as an ordered structure of spherical atomic particles. In **Figure 1**, such geometric models are presented for hypothetical quadratic crystalline lattice. Interaction between atoms of inert elements means the touching of atomic spheres, in metals – their approximation to certain distances, in ionic compounds – touching of atomic spheres of unlike ions with different radii, in covalent crystals – partial overlapping of atomic spheres, and crystals with hydrogen-like bonds – interactions with zero-radii atomic spheres, the central field sources. Of course, in real crystals one can face with combinations of different types of chemical bonding and then above geometric approach should be modified accordingly. For example, crystal with ionic–covalent bonding can be modeled by partially overlapping spheres of different radii.

With the increase in the crystal temperature and then its melting – transformation into liquid – the ordered crystalline atomic structure inherent to the ground state gradually randomizes, the average coordination number of constituent atoms increases, the number of directed bonds decreases as their directions become randomized as well. The joint action of all of these factors improves the applicability of the structural description based on substance geometric models with atoms in form of spherically symmetric objects. Thus, crystalline and liquid states both can be considered as systems of interacting spherical atomic particles. We believe that geometric approach based on well-known model of hard spheres characterizing crystalline and liquid structures (also morphology of powdered and porous materials) would be useful in solving the problem of melting as well.

Within the frames of hard spheres model, each atom constituting condensed matter is considered as an absolutely hard (rigid) sphere of fixed radius. Such "atoms" form bonds only in case of direct contact. The most important structural parameter of any of hard spheres structure is the packing ratio or relative part of the sample whole volume filled with spheres, i.e., "atoms". In particular, the model of close packed hard spheres satisfactorily describes the bulk and surface structures of most crystals of simple substances and a number of chemical compounds, as well as glasses and liquid metals. Foundations of corresponding geometric theory can be found, for example, in the book [4].

Mathematically strict upper limit of the packing ratio is: $\eta_{\mathrm{Limit}} = \sqrt{2}\,(3\arccos(1/3) - \pi) \approx 0.780$. It is clear that for periodic structures – crystals – packing ratio should be slightly smaller and when the crystalline structure of hard spheres changes, its value changes discretely. It was empirically established that in crystals the maximum possible density of $\eta_{\mathrm{Solid}} \approx 0.736$ is achieved in fcc (face-centered cubic) or hcp (hexagonally close-packed) structures. Because of the randomness of amorphous and liquid structures, the packing ratio of hard spheres varies continuously for them and its maximum value is lower than in crystals. For example, for a single-component liquid, i.e. randomly distributed hard spheres of same radii, it is obtained: $\eta_{\mathrm{Liquid}} \approx 0.637$.

Melting of the hard spheres "crystal" has to be accompanied by a change in the packing ratio and, consequently, the system volume. For structures with dense packing of spheres, an expansion is expected. Indeed, when melting most of real crystals extends. However, among crystals with low coordination numbers of atomic sites and, correspondingly, low packing ratio, there are ones (e.g. ice – crystal of water), for which melting is accompanied by the compression.

The volume effect of melting quantitatively is characterized by relative change in the condensed matter volume upon its transition from crystalline state into liquid one:

$$\frac{\Delta V}{V} = \frac{V_{\text{Liquid}} - V_{\text{Solid}}}{V_{\text{Solid}}} = \frac{V_{\text{Liquid}}}{V_{\text{Solid}}} - 1, \tag{1}$$

where V_{Solid} and V_{Liquid} are the volumes occupied by a substance sample, respectively, in solid and liquid states. In the model of solid spheres, we obtain:

$$\frac{\Delta V}{V} = \frac{\eta_{\text{Solid}} - \eta_{\text{Liquid}}}{\eta_{\text{Liquid}}} = \frac{\eta_{\text{Solid}}}{\eta_{\text{Liquid}}} - 1. \tag{2}$$

Apparently, model of hard spheres is best suited for crystals of inert elements. Let estimate the volumetric effect of melting for them. Using the values of close packing coefficients η_{Solid} and η_{Liquid}, respectively, in solid and liquid states theoretically – within the framework of hard spheres model – one obtains: $\Delta V / V \approx 15.5\,\%$. The experimental values [1] are: Ne (24.57) – 15.8, Ar (83.78) – 14.4, Kr (115.95) – 15.1, and Xe (161.36 K) – 15.1 %. Here melting temperatures are indicated in parentheses. We see that despite significant differences in melting temperatures, the volumetric melting effect in all crystals of inert elements is almost same. The average value of 15.1 % agrees rather well with the model result of 15.5 %.

As for other substances, at first glance model of hard spheres does not lead to the good agreement with experiments. For example, for metals with close packed crystal structures the experimental relative melting effect does not exceed ∼ 6 %. Main reason of the discrepancy undoubtedly is associated with difference in the crystal structure of real metals and close packed hard spheres. As it has been mentioned above, in real metals spherical ions do not touch each other, but always are separated (or glued) by layers of electron jellium of finite thickness. In details, structural models of metallic melts were analyzed by one of authors in the monograph [5].

Hard spheres model is the simplest one among possible geometric models of the condensed matter. Therefore, its success reveals applicability of the geometric approach to the problem of phase transformations, in general.

The characterization of low-temperature, i.e. almost perfect, crystalline structures does not make a problem. The problems are their description at high temperatures and during the melting process, as well as the structural characterization of the liquid state itself. Valuable information on the atomic structure evolution in condensed matter with temperature can be extracted from measurements of the system entropy. Based on the tabulated values of melting heat of elemental metals, we have calculated [6] their melting entropy and found out that, according to this parameter, metals are divided into two large groups with relatively low and relatively high average values, respectively, ∼ 1.7 and ∼ 2.3 cal/mol·K.

This result can be considered as one more argument of the geometric approach efficiency since such a division well coincides with the division according to their structures: the first group includes bcc (body centered cubic) structures (Li, Na, K, Rb, Cs, Tl, and Fe), while second – close packed fcc (Al, Co, Ni, Cu, Pd, Ag, Pt, and Au) and hcp (Mn, Zn, Cd, Ho, and Er) structures. Moreover, the division into these groups also coincides with average volume melting effects: ∼ 2.6 and ∼ 5.7 %, respectively [1].

Even the preliminary results [7, 8] of modeling by the system of hard spheres modified for binary metallic melts with different atomic volumes of components were found to be useful, for example, in calculating mixing volume and excess of thermodynamic functions of mixing.

Recently, we suggested [9] similar model for granular mixtures, which frequently serve for the starting reagents in the synthesis of a variety of special materials. As in the absence of heterogeneous inter-granular contacts chemical reactions are impossible, their number largely determines the successful development of such processes. It was used the simplest model of a granular medium, according to which the initial charge is considered as a statistical aggregate of spherical particles of two different diameters. An attempt was made to determine the optimum fractional ratio of diameters, which for given reagents mass composition ensures formation of the charge structure with maximum of heterogeneous contacts.

A generalization of such kind results by us has been formulated in form of a structural doctrine of hard spheres packing [5].

A simple model of the close packed structure of hard spheres interacting via long-range Newton-type attraction forces has been suggested in [10]. Based on DFT (density functional theory), the exact equation of state was obtained and the mutual transformations of crystal structures in such systems were explored.

III. PHYSICAL AND COMPUTER MODELING

As early as in the pioneering work on computer simulation of the condensed systems equation of state, some signs of a phase transition possible in the hard spheres system were discovered. According to [11], one of the main results reduces to the following: at melting point crystalline and liquid phases with relative densities, respectively, ∼ 0.736 and ∼ 0.667 are in equilibrium.

Computer experiments have established that thermal disorder even in the solid phase leads to the appearance of pentagonal faces. However, a comparison of the statistical distribution of polyhedra in types for

heated solid and liquid shows that the structural units with fifth-order symmetry in the "hot crystal" appear sporadically, whereas for a liquid they must be dominant [12].

Despite the fact that today a number of physical models of the liquid state of metals and alloys are suggested, among them there is no generally accepted one that would fully describe the nature of the liquid metal. Nevertheless, these models are to some extent useful for analyzing the melting process. In particular, several circumstances common to all liquid metals have been singled out by generalization of the experience accumulated by the modeling practice: (1) Near the metal melting point, the interatomic potential energy by order of magnitude exceeds the kinetic energy of thermal motion of atoms; (2) There is no long-range order in the arrangement of atoms; and (3) The system is fluid.

Conditionally, all the proposed models can be divided into two main groups. These are so-called quasi-gas and so-called quasi-crystalline models. The first list includes those models, in which the consideration is based on the motion of atoms. As for the second class of models, they take into account atomic interactions in local regions.

Sometimes, even hard spheres model becomes suitable for liquid metal. This is the most common model of quasi-gas type. In addition to diameter of spheres and packing ratio, its key characteristic is the pair interaction potential. Such modeling leads to the conclusion that for liquid metals the packing ratio should be in the range of 0.44 – 0.47. Further development of the model implies the introducing of rigid sticks to model the chemical bonds and hard disks to model the molten surface layer, as well as so-called elastic spheres and discs.

In further generalization of the geometric approach to melting process, alternatively to rigid sticks directional interatomic bonds can be taken into account by introducing anisotropy of the shape of atoms – replacing spheres with ellipsoids. This allows the manifestation of qualitatively new effects. For example, crystallization – freezing of the fluid, in the sense of inverse to melting process, can be considered in the 2D fluid model of hard circular or elliptical discs. It is known from computer simulations that 2D fluid of hard disc-like particles can freeze upon increasing density. According to the suggested freezing mechanism for such a system, the taking into account only three (out of six in total) alternating nearest neighbors of any particle is enough to describe both disordered and crystalline phases, as well as transition between them. The disordered phase becomes unstable when average center-to-center distance becomes shorter than two particles diameter. In [13], this mechanism was applied to understand freezing in case of elongated particles. There was found an intermediate range of particles anisotropy, when freezing is frustrated and monolayer proceeds continuously from a disordered phase to a crystalline one.

By operational definition, the glass transition is the point at which the viscosity of a structurally disordered liquid reaches its universal threshold value. But, when transition is a purely dynamic phenomenon ergodicity gets broken – the system becomes confined to some part of its phase space – and the thermodynamic properties of the liquid can remain unchanged across the transition. Such a phase transition would trigger the dynamic standstill and then be masked by it. In [14], the Monte Carlo simulations of a 2D system of polydisperse hard disks far within its glassy phase was performed and found no evidence for a thermodynamic phase transition up to very high densities: the glass remains indistinguishable from the liquid on purely thermodynamic grounds.

The model of free volume is based on the assumption that the structure of a metallic liquid is quasi-crystalline. Only repulsions between the neighboring atoms are taken into account regardless of motions of other atoms of the same "unit cell". Moreover, in this model the transfer of atoms between the "cells" is not allowed. The coefficient of the dynamic viscosity of a metallic liquid is expressed by the specific volume v as $c(v-b)$, where c and b are constants. In particular, parameter b is close to the sum of the intrinsic volumes of atoms. Consequently, the coefficient of viscosity is approximately proportional to the liquid metal free volume.

Frenkel's hole-model is based on the assumption that near the melting point liquid metal does not strongly differ from crystal by structural characteristics. As it is known, during melting metals expand by 3 – 10 %. This excess in fluid's volume is heterogeneously distributed – it consists of instantaneous and vanishing nano-voids or "holes" in different parts of the system. In order of magnitude, the radius of a nano-void is ~ 0.1 nm which is commensurable with the interatomic distances. According to the hole-model, the flow of a fluid consists in moving atoms from one position to another by overcoming energy barriers which average height approximately coincides with the molar heat of fusion.

The cluster-model is closely related to the hole-model. It also is based on the assumption of similarity between the structures of real metallic liquids and nanocrystalline solids. The model also assumes that in liquids, like crystals, the ordering is distributed to larger volumes with the difference that for a crystal such state is stable, while for liquid – changeable. The liquid at any time breaks up into large groups of atoms: clusters, within which atomic ordering is retained, and adjacent nano-volumes with disordered arrangements of atoms. The cluster fluid model is used to study properties of complex melts under the assumption that extensive properties of a real system are additively determined by corresponding properties of clusters.

Quasi-crystalline models can be considered as development of the cluster model. In such a model, the melt is a unity of two thermodynamically unstable structural components. These are: hard clusters with ordered arrangement of atoms and disordered zone that fills the regions between randomly oriented clusters. Because of energy fluctuations, these two components are continuously transformed into each other, but so that the lifetime of the cluster exceeds the period of atomic vibrations in the solid state.

The quasi-chemical model, being similar to cluster and quasi-crystalline models, assumes the structure of metallic liquid to be inhomogeneous. The application of the model is advisable for multicomponent melts, since in this model the differences in interaction energies of atoms of different chemical nature are taken into account. For this reason, at same temperature the coexistence of clusters with different composition and structure is permissible in the multi-component melt structure, and so is the stability.

Summarizing this variety of physical models of liquid metals, we can conclude that they differ in their assumptions about the spatial arrangement of atoms.

To develop a basis for physical model of metal melting in a geometric approach, we have analyzed the structures of those metal clusters that can exist in liquid state [15, 16].

Currently, it becomes possible to construct such mathematical models of liquid metal that allowed numerical simulation of their structures and properties at the atomic level. In particular, by computer simulation the motion of individual atoms are observed, as well as the time evolution of stability of a structure with short-range order changes with temperature, pressure, and other external parameters. Although, due to the computer memory limitations in a complex model it is not possible to study large (polyatomic) systems. For this reason, the objects of investigation often are so-called basic cells that cover a system of atoms of a certain (usually simple cubic) form. Since the structural characteristics depend on the atomic interactions, the main trend in modeling is to study the relation between system properties and pair potentials acting between its components.

An important special task of computer modeling of the metal melting is the compilation of an algorithm for generating the mostly dense disordered packing of hard spheres. Both theoretically and practically it is essential to establish the degree to which structures of densest unordered packing will be similar, when are constructed according to different algorithms. Anyway, the packing ratio will vary in a narrow range, 0.62 – 0.66, which lies well below the value of this characteristic for the ordered structure: 0.74.

The results of computer simulation of liquid metals confirm the existence of local spatial ordering. In this case, such a structure does not arise chaotically, but according to the effective interatomic potentials utilized in the model.

According to the review [17] of mathematical models of liquid metals, corresponding computer simulation methods, and obtained on their basis results, most part of suggested in the literature methods can be reduced to the widely known method of MD (molecular dynamics). The specificity of MD modeling for the melting process is related to the following two requirements: (1) The model should contain a sufficiently large number of atoms, since unlike the crystalline state, the use of periodic boundary conditions is unacceptable; and (2) The accuracy of the used interatomic potentials should be quite high, so that they simultaneously describe both the solid and liquid phases.

At present, the computer modeling results are available for many elementary metals, semimetals, and semiconductors, as well as a number of binary systems. However, the accuracy achieved in such modeling is not sufficient. Moreover, the analysis of MD simulation of amorphous metals carried out from the point of view of the theory of dynamical systems shows [18] that for such models structural instabilities are characteristic, because of which the specific structure of the amorphous metal a priori becomes unpredictable. We can state that the structure obtained by substance modeling in the melting process will not be single, but one from the set of possible structures.

A description of physical foundations of computer modeling of structure, atomic dynamics, and the properties of crystalline and amorphous metals and alloys, as well as melts, can be found, for example, in the book [19]. In particular, MD modeling of the thermal motion of atoms using the Lenard–Jones type interaction potential, which numerical values are established for a liquid, is presented in the melting process. Besides, based on quasi-crystalline approach and calculation of radial distribution functions of atoms in metallic melts, the computer simulation of liquid metals structure is conducted.

At first glance, newly captured [20] 4D atomic motion (3D movement of atoms at different times) contradicts older theories of how elements and alloys melt, crystallize, and evaporate. In particular, by electron microscope the iron–platinum alloy has been examined at ∼ 700 K. What was different was the nuclei created irregular shapes instead of almost round ones, which were the ones predicted as per previous long-standing theories. Another change was the fact that their borders became more jumbled, instead of sharp.

In [21], to exhaust the possibilities offered by the scaled particle theory of the hard spheres fluid, an approximate differential equation of state with the Helmholtz free energy and also the compressibility factor as unknown functions of the density was derived from the basic relations inclusive the thermodynamic condition.

IV. MECHANICAL MODELING

The possibility of effective mathematical modeling of the condensed matter, in particular, solid and liquid metals when they are considered as systems of hard spheres leads to the conclusion that valuable information on the nature of melting process can be obtained by its mechanical modeling as well.

Mechanical models can be static or dynamic. In this section, we first briefly describe available results on the static modeling of crystalline structures of and liquid substances. But, it is clear that such simulations could not be sufficient for the description of melting, the process of transition from a crystalline structure to a disordered structure characteristic of liquid state. To this end, we will introduce a dynamic model of melting.

What role does metals structure of play in the melting process? In general terms, the issue of the influence of space-structural characteristics on the stability of metals within the framework of static model of irregular structures was posed by us in [5, 16].

A number of mechanical models of molecular and crystalline structures are known. They, as a rule, serve for visual aids in the teaching stereochemistry. A good example of this kind is the model [22] constructed from spherical balls of different radii (atoms of different elements) connected by flexible cylinders (chemical bonds), which under external influences change their length and curvature and retain the acquired shape after removal of the effect.

Metallic nanoparticles frequently are modeled [23] in a pyramidal form (**Figure 2**).

Figure 2. Static model of gold nanopyramid.

For granular materials, it was demonstrated [24] experimentally that at their consecutive layer-by-layer packing monodispersed spherical granules form almost close packed structures.

As for simple liquid metals, Bernal constructed his well-known mechanical model in the form of identical balls connected by wires of different lengths [25]. This model demonstrated the fact that liquid has not only a single structure, but an infinite choice of mutually equivalent structures, and it constantly flows from one random structure to another. Bernal modeled mostly dense disordered structures of atoms using a vessel of irregular shape filled in with steel balls. From such a simple model it is possible to estimate the packing coefficient of disordered dense packing, and also to conclude that structural units with the fifth-order symmetry axis (frequently icosahedra) predominate. But, it is difficult to determine coordinates of centers of individual balls and then statistical characteristics of their spatial distribution.

In the mechanical model of fluid suggested in [26], atoms are modeled not by steel balls, but by soap bubbles. Soap bubbles are lighter than air and, therefore, it becomes possible to model entirely new effects, for example, the action of a force pushing out of the liquid. Many earlier experiments and simulations of packings of monodisperse hard spheres reported a dominance of the fcc structure in the limit case, even though it has no significant energetic or entropic gain over other close packed configurations. Combining simulations and experiments, there was demonstrated that a simple mechanical instability which occurs during the packing process may play an important role in selecting the fcc structure over other close packed alternatives. This argument is supported by detailed quantitative analyses of key configurations in packings of spheres and highlights importance of the packing dynamics. Proposed mechanism is elementary and should, therefore, play a role in wider range of systems of spheres.

Static modeling may not be sufficient even for choice of the equilibrium atomic structure of a condensed matter. One should expect more difficulties in modeling of processes like melting. Consequently, adequate mechanical model of melting necessarily must be dynamic.

Interesting dynamic model for not spherical but cubic particles was suggested in [27]. With its help the compaction dynamics of an ensemble of cubic particles submitted to a novel type of excitation has been experimentally analyzed. Instead of the standard tapping procedure used in granular materials the alternative twists to the cylindrical container was applied. Under this agitation, the development of shear forces among different layers of cubes leads to the particles alignment. As a result, the packing fraction grows monotonically with the number of twists. If the excitations intensity is sufficiently large, an ordered final state is reached where the volume fraction is the densest possible compatible with the boundary condition. This ordered final state resembles the tetratic or cubatic phases observed in colloids.

In the present paper, an attempt is made to find out how fcc lattices react to the expansion when and how the regular structure transforms into an irregular lattice and which geometric and topological factors determine the melting transition. In order to answer these questions, one must first of all investigate the mechanical stability of the structure itself as a 3D geometric object.
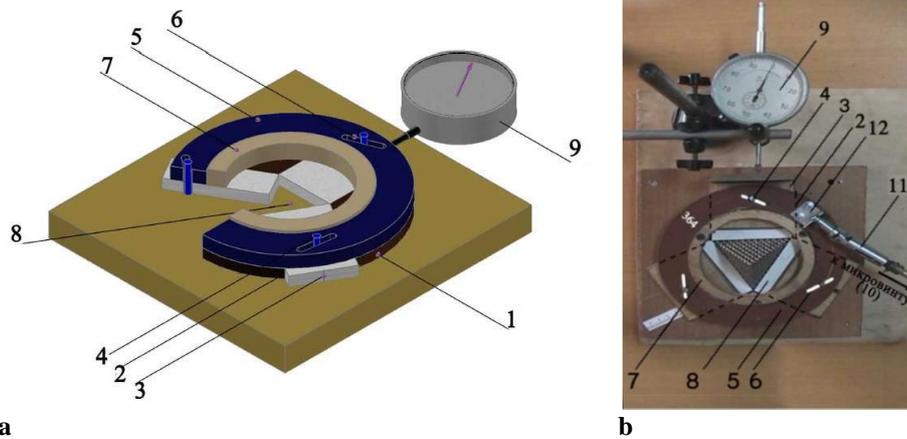

Figure 3. Device for determining of structure stability: (a) schematic drawing and (b) photo.

In order to determine the mechanical stability of fcc structures, we constructed special device – dynamic model (**Figure** 3), in which along the guide channels (2) oriented by angle of 120 ° relative to each other, rectangular plates (3) are at radial moving by rigid guides with pins (4). In the rotational ring (5), oblique cuts (6) are made for the pins (4). When the ring (5) rotates relative to the stationary centered ring (7), the oblique cuts (6) move plates (3) in radial directions. Consequently, it is possible to vary the size of barrier (8) in form of regular triangle shaped by plates (3) ends. The radial movement of plate (3) is measured by dial gauge (9) with accuracy of 0.01 mm. The smooth rotation of ring (5) and, consequently, radial movement of plates (3) are achieved by the micro-screw (10), which is connected to the rocker arm (12) by the gimbal joint (11).

With the help of this device, the stability limit of a trihedral pyramid constructed from identical steel (bearing) balls has been determined experimentally. At close packing of balls in such a structure, each ball comes into contact with six similar ones in the horizontal plane and three balls in each of two adjacent (upper and lower) layers. Thus, the fcc structure packed in the crystallographic plane (111) is obtained (**Figure 4a**). Similar colonies of balls – pyramidal clusters – contains N balls. Number of balls determined by so-called tetrahedral numbers of Pascal's triangle:

$$N = \frac{n(n+1)(n+2)}{6} = 1, 4, 10, 20, 35, 56, 84, \ldots, \qquad (3)$$

$$n = 1, 2, 3, 4, 5, 6, 7, \ldots, \qquad (4)$$

where n is the number of layers in the pyramid. The basal layer contains $n(n+1)/2$ balls. Stability of the pyramid in the gravity field is supported by the triangular barrier (8) formed by ends of plates (3).
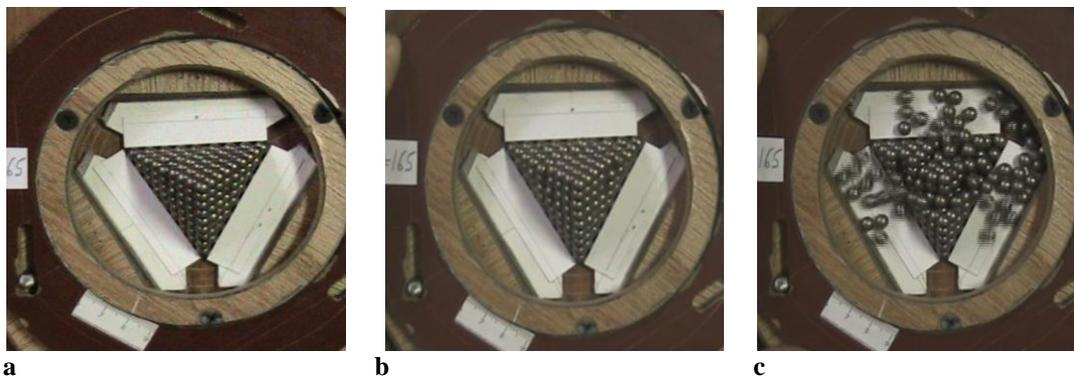

Figure 4. Pyramidal cluster of hard balls: (a) initial ordered state, (b) state of geometric disorder while preserving of initial topology, and (c) beginning of initial topology destruction.

When the ring (5) rotates (clockwise – in our case), the pyramid base dimensions increase, balls deviate from corresponding regular lattice sites stochastically, and the system of balls becomes geometrically

disordered. Although at the beginning it retains pyramidal shape, i.e., initial topology (**Figure 4b**). After increasing in size of the pyramid base side to a certain critical value, the structure loses its stability in the gravity field, collapses and goes into an unordered state, in other words, a topological transformation takes place in the system of balls (**Figure 4c**).

Obviously, stability limit of the structure for given N and identical processing (polishing) of ball surfaces, as well as device body, i.e., at fixed coefficients of friction should not depend on the balls diameter d.

At $N = 1$, the "pyramid" consists of a single ball.

The smallest pyramid with a structure is formed when $N = 4$. It is a tetrahedron formed by four balls, which "collapses" when three basal balls are displaced from each other at distances of $\sqrt{3}\,d$ allowing fourth to be placed in the created cavity. As a result, the 3D structure becomes the 2D one.

In contrast to these trivial cases, when $N > 4$ determining of the stability limit of a pyramidal structure is devoid of such clarity. However, this problem can be experimentally studied using the constructed device.

Our goal is to establish the stability of fcc structures in thermodynamic limit by extrapolating the stability limit of pyramidal colonies consisting of finite numbers of ball to the case of their infinite number in the pyramid: $N \to \infty$.

The experiment conducted with the help of this mechanical model consists in measuring the coefficient of linear expansion of sides of the built of balls pyramid base:

$$\alpha = \frac{l - l_0}{l_0}, \tag{5}$$

where l_0 is the initial length of these sides and l is their length at moment of losing the structural stability. However, the final interest is the relative coefficient of volumetric expansion

$$\beta = \frac{V - V_0}{V_0}. \tag{6}$$

Here V_0 is the initial volume of the pyramid, and V is its volume at the moment when it loses stability.

So, we need to establish the relation between coefficients α and β. Note that V_0 is calculated as the volume of a regular trihedral pyramid, i.e. tetrahedron:

$$V_0 = \frac{1}{3} S_0 H_0, \tag{7}$$

where

$$S_0 = \frac{\sqrt{3}}{4} l_0^2 \tag{8}$$

is the area of its base, and

$$H_0 = \sqrt{\frac{2}{3}} l_0 \tag{9}$$

is its height. Finally, we get:

$$V_0 = \frac{l_0^3}{6\sqrt{2}}. \tag{10}$$

Assuming that tetrahedron edges pass through the centers of edge balls, their length can determined by balls diameter and pyramid size, i.e., number n:

$$l_0 = (n - 1)\, d. \tag{11}$$

It leads to the pyramid initial volume in the following form:

$$V_0 = \frac{(n - 1)^3 d^3}{6\sqrt{2}}. \tag{12}$$

Up to its destruction, topology of the balls structure does not change – system retains the pyramidal shape. Therefore, we can assume that initial regular tetrahedron, when one of its faces (base of pyramid) is expanded, transforms into an equilateral pyramid. Its volume at the moment of destruction is calculated by the standard formula:

$$V = \frac{1}{3} SH, \tag{13}$$

where S is the area of pyramid base and H is its height. The area of the base is

$$S = \frac{\sqrt{3}}{4} l^2. \tag{14}$$

As for the height, when calculating it one has to note that up to destruction all the balls placed along lateral edges of the pyramid keep contacts with neighboring balls and, consequently, original length of these edges also remains the same: l_0. We have:

$$H = \sqrt{1 - \frac{l^2}{3l_0^2}}\, l_0 \cdot \tag{15}$$

In this way, we obtain:

$$V = V_0 \frac{l^2}{l_0^2} \sqrt{\frac{3}{2} - \frac{l^2}{2l_0^2}} \cdot \tag{16}$$

The ratio l/l_0 of base edge lengths after and before structure failure, introduced here, is determined experimentally – from the measured relative expansion coefficient of the model:

$$\frac{l}{l_0} = 1 + \alpha \cdot \tag{17}$$

It gives

$$V = V_0 (1+\alpha)^2 \sqrt{1 - \alpha - \frac{\alpha^2}{2}} \tag{18}$$

and

$$\beta = (1+\alpha)^2 \sqrt{1 - \alpha - \frac{\alpha^2}{2}} - 1 \cdot \tag{19}$$

Bearing in mind that up to the pyramid destruction the relative linear expansion of edges of its base remains small, $\alpha \ll 1$, we get

$$\beta \approx \frac{3\alpha}{2} \cdot \tag{20}$$

The obtained result significantly differs from the well-known relation, $\beta \approx 3\alpha$, which follows for a cube that is uniformly expanding in three directions. This is due to the fact that expansion of the horizontal base taking place in the gravity field is accompanied by pyramid compression in the vertical direction. The corresponding decrease in height is substantial and partially compensates the base area expanding effect. As result, coefficient of volumetric expansion reduces.

Physical justification of the suggested dynamic model is as follows.

Balls of all the overlying layers (by their weight) act on the balls of a given layer. In turn, the balls of a given layer by elastic forces of reaction act on balls of the upper neighboring layer. Hence, the magnitudes of forces of pair interaction between balls of adjacent layers depend on the height. They increase in the direction from the top of the pyramid to its base. Due to the finite size of layers – presence of boundaries, distribution of interaction forces in the horizontal directions are heterogeneous as well. This discrepancy between the model interactions and the real interatomic ones should not play an important role since the balls are almost rigid and inhomogeneous distribution of interaction forces does not affect their homogeneity by radii.

Modeled distribution of binding forces in some extent is similar to that in real close packed metallic structures. It was found [28] that hybrid bonds and exchange interaction can significantly affect the ratio c/a of crystal lattice periods a and c in hcp metals. Heterogeneity of the electron charge density distribution in such metals is indicated by smallness of structural factors experimentally measured at small scattering angles, as well as combination of major and minor components of the elasticity constant. As a result of this, during crystal compression along the c-axis, there is practically no mechanism for the transfer of stresses in directions lying in the basal plane, and vice versa.

The stability of the pyramid in the Earth gravity field is provided by the barrier in form of a regular triangle, which limits horizontal displacements of pyramid basal balls. Summarizing, we can say that atomic interactions are modeled by balls weight and reaction elastic forces of balls together with interaction of balls with triangular barrier and horizontal surface at pyramid basal plane.

Increase in the system temperature is modeled by the simultaneous action of two factors – uniform expansion of the pyramid base and friction between contacting balls (as well as balls of the pyramid base on the horizontal surface). Just friction leads to the randomization of distances between centers of balls.

The stability limit of such a structure for a given number of identical balls should not depend on balls diameter or average coefficient of friction between them.

V.   PRELIMINARY RESULTS OF DYNAMIC MODELING

Results of the preliminary experiments carried out with the help of our model are shown in **Table 1** and **Figure 5**. Here, the limit linear expansion coefficient is plotted along the ordinate axis.

It follows from **Figure 5** that the structure stability decreases monotonously with increasing in N. Obviously, this curve asymptotically tends to some non-zero limit, the exact estimate of which, if necessary, for a far extrapolation (by an infinite number of balls: $N \rightarrow \infty$) may be associated with ambiguous errors. The largest tested by us pyramid contained 364 balls, which corresponded to a stability limit of about 5.8 % or 8.7 % for volumetric expansion. In order of magnitude this value is quite reasonable. A more detailed quantitative comparison with data on the melting of metals requires pursuing of multiple measurements and statistical treatment of obtaned results.

Table 1. Limit coefficient of linear expansion of nanopyramid as function of number of hard balls in model.

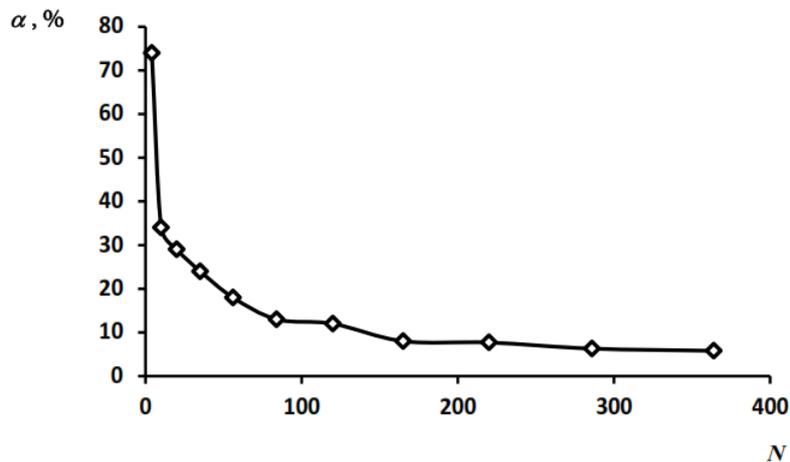| Number of hard balls in model pyramid N	Limit coefficient of linear expansion α, %
1	100
4	74
10	34
20	29
35	24
56	18
84	13
120	12
165	8.0
220	7.7
286	6.3
364	5.8

Figure 5. Dependence of limit coefficient of linear expansion of pyramidal structure on number of balls.

One thing can be said with certainty: if thousands of balls are contained, they will be sufficient to obtain reliable results. But for a real system, thousands of atoms correspond to the nanoscale substance. In this way, a nanopyramidal cluster can reflect bulk metal properties at melting point.

Thus, we believe that the limit of expansion of metals in solid phase and the limit of mechanical stability of model pyramid of balls with a similar structure should be comparable. Although reasons for their stability are of different physical natures: in first case the stability is due to atomic interactions, and in second case equilibrium of mechanical system of absolutely hard balls in homogeneous external (gravity) field under conditions of acting frictional forces between balls and fixed dimensions of the system in basal plane perpendicular to the field.

VI.   Discussion

In this section, we discuss the details of physical foundation of "mechanical" melting process considered as a transition in hard spheres system from ordered – close packed fcc – structure of to a disordered – close-packed one.

We have to start with description of fcc close packing. In this case, each ball is in contact with twelve identical balls. If center of an arbitrarily selected coordination sphere connect with centers of nearest spheres,

we obtain a figure with fourteen facets in the form of cube-octahedron having twelve vertices and twenty four edges (**Figure 6a**). As it is known, in an ideal lattice one always can choose unit cell with its full symmetry. Such a cell, for example, is the Wigner–Seitz cell. Obviously, for fcc structures the Wigner–Seitz cell has a form of rhombo-dodecahedron (**Figure 6b**).
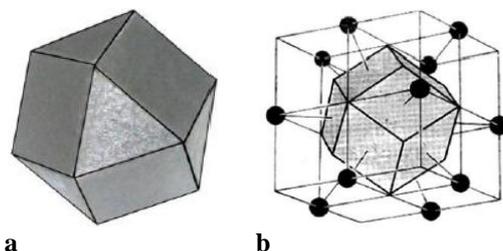

Figure 6. (a) Cube-octahedron – environment in fcc lattice and (b) rhomb-dodecahedron – Wigner–Seitz cell.

As for a random close packed system of balls, in which the lattice periodicity is completely broken and replaced by an irregular system of structure sites, above construction yields an ensemble of irregular Voronoi polyhedra. The study of polyhedra characteristic of monofractional irregular structures showed that the predominant part of their faces is represented by irregular pentagons. Of course, these polyhedra are not regular because in this case they cannot fill the space without overlaps. However, for small distortions and the presence of faces other than pentagons space is filled.

Thus, the disorder caused by the expansion has to lead to the appearance of pentagonal faces and destruction of the pyramid. However, reveling of fifth-order symmetry elements in this mechanical equivalent of the "hot crystal" will be episodic. In the irregular structure, the spatial distribution of particles is similar to the icosahedral configuration and characterized by the fifth order symmetry as well. Since icosahedron (**Figure 7a**) is conjugate to dodecahedron, it is obvious that for icosahedral structure Voronoi polyhedron will be dodecahedron (**Figure 7b**). Irregular packing cannot be described by lattice-type units, but can be considered as a set of well-defined cells – Voronoi polyhedra. They are irregular, not identical, and do not possess the lattice symmetry.
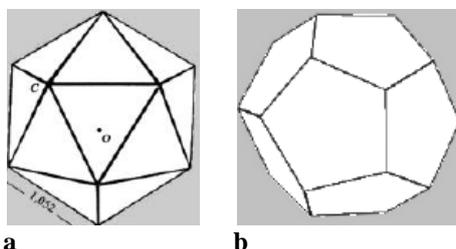

Figure 7. (a) Icosahedron and (b) its conjugate figure – dodecahedron.

Icosahedral clusters are expected in the amorphous state as well. By MD modeling, a mechanism of isothermal annealing has been established, in which formation of icosahedral structures occurs in nanoparticles of pure metals Al, Ni, and Cu [29].

According to the cluster-model of liquid, its structural units are crystal-like clusters that perform Brownian rotational motion and single atoms that fill the pores between them. On the basis of this theory, an expression for the material viscosity was proposed and metal clusters radii were estimated from corresponding expression and available experimental data: Cs – 5.18, K – 5.81, Li – 4.63, and Na – 5.18 Å [30]. Of course, these values are only indicative as correspond to different temperatures and pressures. Nevertheless, it is clear that these clusters contain tens of atoms, not more. Therefore, a model of thousands of atoms should be useful. On other hand, it is shown that a nanocrystalline phase may appear in melt near the melting curve, stability of which is provided by the nanoclusters rotation [31]. Upon cooling this phase can cause formation of an amorphous phase.

What does the phase transition mean from a geometric point of view? In the model under the consideration, melting is regarded as a jump-like change in topology. According to Bernal principle [25, 32], regular (crystalline) and irregular (random) packings are two alternative ways of filling the space with identical spherical particles. Topologies of an arrangement of balls in regular lattice and irregular structure are radically different. To emphasize importance of the topology, note that recently (in 2016) the Nobel Prize in Physics was awarded just for theoretical discovery of topological phases of matter and topological phase transitions [33].

At critical disturbance of the ordered structure, it loses stability and "melts". In terms of the model proposed, at this moment a topological jump takes place: the Wigner–Seitz cells are transformed into Voronoi polyhedra. "Geometric melting" occurs when topological characteristics of the structure change. In case of melting of fcc lattice of balls, the nearest environment of any ball in the form of cube-octahedron transforms into icosahedral configuration.

For our model, the volume of a cluster in form of a hard balls union, as well as other integral properties (such as the boundary area), play critical role. Analogous problems are too important for some other fields as well. In [34], there were proposed algorithms to compute volumes of unions of atoms (bounded by van der Waals forces) just from the Voronoi diagram of the system. These algorithms were implemented and thoroughly tested for big protein molecular structures.

Seemingly, the regular trihedral pyramid – tetrahedron is main structural motif not only of crystals, but also amorphous matter and liquids. It was demonstrated [35] the possibility of independent approaches to the construction of a dense quasicrystalline packing of regular tetrahedra in icosahedral symmetry. The resulting "icosahedral" quasicrystal has a packing density of 59.783 %. These geometrical considerations have experimental confirmations as well. The plasmonic single-crystalline seeds were used to track the growth of multiply twinned silver nanostructures [36]. They successively developed twin planes to form multiply twinned nanoparticles from seeds. Together these data demonstrated how a series of nanoparticles of different shapes and internal crystal structures are interrelated and developing from one another. Even growth starts from an almost spherical particle, it by obligatory takes intermediate form of tetrahedron and, finally, icosahedron. It was demonstrated [37] that by using the solution-phase method highly symmetric golden nanostars can be obtained from the icosahedral seed: the evenly distributed pyramidal arms are enclosed by the icosahedron facets.

In light of the well-known historical discussion between Frenkel and Landau on the atomic mechanism of transition from long-range order to near-range one and based on modern experimental data on metallic materials nanostructuring by means of superplastic or intense megaplastic deformations, there was found one more argument for our model assumption that melting begins at the multiplication of defects in local areas of the structure. Namely, physical aspects of structural phase changes in nonequilibrium grain boundaries were described [38] and found out that it is possible to change periodically the grain boundaries state in Zn–Al and other metallic alloys from the equilibrium state with negligible density of lattice dislocations to the first limiting – nonequilibrium crystalline state with their extremely high density and energy close to the melting energy of the material, subsequently to the second limiting – liquid state and then return to the initial state. Such a model corresponds simultaneously to provisions of Landau's theory about impossibility of a continuous transition from the long-range to short-range order in the crystal, and the Frenkel's theory of crystal amorphization or melting at low temperature by introducing critical number of lattice defects. Thus, during and after plastic deformations amorphous and liquid phases can exist within micro- and nanoregions in metals.

At first glance, the modeling of a macroscopic sample by a nano-sized cluster can be considered as problematic if take into account that melting temperature depends on the particle size. Analysis based on the chemical bonds weakening mechanism of melting leads to the conclusion that melting temperature decreases with decreasing nanonoparticle in size [39]. The statistical theory of the nanocrystalline state also leads to the conclusion that as the crystal size decreases, the pressure of the phonon gas directed outward increases and properties of the crystal, including its melting point, change [40]. However, it must be kept in mind that these and other possible nanoscale effects influencing melting point of real samples completely absent in the model.

According to the localization criterion for the crystal–liquid phase transition suggested in [41], melting starts at temperature T when the ratio E_d / kT reaches the boundary value $E_d(S) / kT_m$, above which solid phase and below which liquid phase are located in the phase diagram. Here, E_d and $E_d(S)$ are energies of delocalization of an atom, respectively, at T and melting point T_m for solid phase. This localization criterion is applicable for both normally melting substances and substances melting with a decrease in the volume. Besides, it explains the inequality $T_c < T_m$, where T_c is the crystallization temperature. Greatest value of ratio T_c / T_m and small value of Grüneisen parameter are likely to be characteristic of bcc crystals. Later, it was demonstrated [42] that localization criterion for the crystal–liquid phase transition introduced for macrostructures is valid for nanocrystals as well. Investigation of variation of activation processes (formation of vacancies and self-diffusion) parameters with a decrease in the nanocrystal size shows that at low temperatures nanocrystalline lattices are more perfect than that of macrocrystals, while at high temperatures nanocrystals are activated by mobile vacancies to a greater extent.

Melting of crystalline surfaces needs a special consideration.

An equation for the surface energy σ as a function of sample size and shape was obtained [43] for nanocrystal in form of parallelepiped with square base with the ratio f between side and base edge lengths determining the system shape. The σ value decreases as the number N of atoms in the nanocrystal decreases,

and the larger is the difference between the shape parameter f and 1, the stronger is the $\sigma(N)$ dependence. At high temperatures, the surface Helmholtz energy decreased as the temperature increased, and the smaller is the size of the nanocrystal of given shape or the stronger is deviation of nanocrystal shape at given N from thermodynamically stablest cubic shape, the larger is the $-\partial\sigma/\partial T$ value. Nanocrystals were shown to melt, when their surface energy is decreased to a certain value independent of their size and shape. From the assumption that pressure exerted on nanocrystal surface under melting passes into the Laplace surface pressure, an expression for relative volume, within which the solid phase of the nanosystem remains stable at different pressures, can be derived [44]. Such a "surface" criterion of melting slightly depends on crystal size and external pressure, and is solely determined by interatomic potential parameters. Calculations for macrocrystals (with van der Waals bonding) demonstrate good agreement with experimental data for the relative crystal volume at melting point. By proposing a simple quasi-chemical approximation for the square lattice fluid model with blocked sites (obstacles) and attractive or repulsive nearest neighbor interactions, expressions for chemical potential, thermodynamic factor, and distribution functions were obtained [45]. Generalizing this method on lattice systems, in which order–disorder phase transitions can occur, and applying the Monte Carlo simulation it was shown that the critical temperature linearly increases with the concentration of blocked sites.

Some features of melting process are characteristic for nanocrystals.

An analysis of results of studying the size dependence of vacancy concentration in nanoparticles presented in [46] demonstrates that an increase in the vacancy concentration with decreasing nanoparticle size is the most argued conclusion with assumption for relationship between melting temperature, binding energy, and energy of vacancy formation. Expressions for the melting point, crystallization temperature, entropy change per atom, latent heat, and volume change for the solid–liquid phase transition were derived [47] from model of a nanocrystal in the form of parallelepiped with variable surface shape. These quantities were studied as functions of number of atoms N and nanoparticle shape. In particular, calculations carried out based on these relations show good agreement with the results of computational experiments for copper nanoparticles. It was shown that entropy change, latent heat, and volume change vanish in a certain range of cluster dimension N_0 and a hysteresis between melting point and crystallization temperature disappears: $T_c(N_0) = T_m(N_0)$. In such a cluster, the phases become physically identical. For nanocopper, this dimension falls into the range $N_0 = 49 - 309$ and grows when the shape of the nanoparticle deviates from the energetically most favorable one. Using dependences of melting and crystallization points on the number of atoms in a spherical silicon crystal calculated by MD method, it was estimated [48]: (1) Number of atoms at which the latent heat of the solid–liquid phase transition disappears, and (2) Temperature below which solidifying nanoclusters remain noncrystalline. These values were found to be $N_0 \approx 23$ and $T_0 \approx 400$ K, respectively. The N-dependences for silicon melting parameters, namely, jump of entropy of melting, latent melting heat, slope of the melting line, and jumps in surface energy and volume, were derived as well. Size dependence of the melting point of Si nanoparticles also was investigated [49] using MD and thermodynamic simulation based on the Thomson's formula. The atomistic modeling data obtained using the Stillinger–Weber potential agreeing well with reported results and thermodynamic-simulation data predict a decrease in the melting point with an increase in particles reciprocal radius $1/R$ according to linear law. The available experimental data predict lower T_m values, including the limiting value $T_m(\infty)$, which corresponds to the linear extrapolation of experimental points to the radius $R \to \infty$. The underestimation was $200 - 300$ K as compared with the reference melting point of silicon: 1688 K. It is concluded that the MD data on $T_m(1/R)$ dependence obtained using the Stillinger–Weber potential are more adequate than the available experimental data.

Above discussion on current analysis of the melting process physics argues applicability of our dynamical modeling with pyramidal nanoparticles of close packed elemental metals.

VII. Conclusion

In summary, we have argued, developed, and tested a novel dynamic model useful for studying phase transformations in condensed matter. For model serves a pyramid constructed from close packed identical hard balls with variable basal area. Preliminary modeling carried out by this device show that elemental metals have to melt at temperature when their volumetric expansion achieves $\sim 8.7\ \%$. This value well coincides with both experimental and theoretical ones reported previously.

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