

MATHEMATICAL FORMULATION OF A KINETIC VERSION OF STEFAN PROBLEM FOR HETEROGENEOUS MELTING/CRYSTALLIZATION OF METALS

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Summary. Were analyzed possibilities of thermodynamic, kinetic and molecular dynamics approaches to the investigation of the kinetic properties moving interfaces in metals with different crystallographic lattices: Al, Cu (fcc) and Fe (bcc) in a wide range of solid phase overheating and overcooling of liquid - $(0.4 \div 0.6)T_m < T_{se} \leq 1.2 T_m$. On the basis of extensive molecular dynamics simulation, the values of the kinetic velocity $v(T_{se})$ for all metals in the specified range were determined. By approximating the results were built analytical expressions of velocity $v(T_{se})$ for all metals in the whole temperature range under consideration. Obtained analytical expressions for the velocity $v(T_{se})$ were used for the formulation of a kinetic version of Stefan problem in which eliminated the main contradiction of the classical Stefan problem associated with the use of equality of equilibrium melting temperature T_m to interface temperature T_{se} .

1 INTRODUCTION

The widespread use in the past two decades of an ultrashort pulse (picosecond and femtosecond) laser action on a variety of materials to generate nanoparticles and nanostructures [1,2], the creation of metamaterials [3], by ablation in gases and liquids [4,5] cause increased interest in the rapid phase transitions of the 1st kind. Analysis of the processes caused by pulsed laser action leads to the consideration of a number of important problems of the fundamental plan, which at high heating rates are attributed features of homogeneous and heterogeneous melting/solidification mechanisms and evaporation and the associated limit overheating and overcooling of material. Understanding the melting/solidification processes is also of great interest for applied problems of photonics [6], micromachining [7], the creation of new materials [8, 9], optimization of superfast modes of laser micromachining of materials [10], and others. In spite of the fact that the processes of melting/crystallization were studied over one hundred years, beginning with the famous Stephen's formulation [11] theme is still widely studied and keenly debated [12] – [14].

Melting of the solid and liquid solidification are a widespread phenomena in nature. There are two mechanisms of melting/crystallization of metals: heterogeneous (or it is also called surface or front) and homogenous (volumetric). In the first case, in the framework of classical thermodynamics [15], the melting of solids and liquid solidification relate to the phase transformation of the first kind flowing at a certain (equilibrium) temperature T_m , which

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corresponds to the equality of the Gibbs free energy of the solid and liquid states. Heterogeneous mechanisms for melting/crystallization corresponds to the motion of a continuous medium with a strong discontinuity surface, which abruptly changed thermophysical and optical characteristics: internal energy ε (enthalpy H), the coefficients of thermal conductivity λ and heat capacity C_p , density ρ , pressure p . Homogeneous melting mechanism is characterized by the birth of a new phase (liquid) in a volume of overheated crystal, and in this paper will not be considered.

A theoretical analysis of the dynamics of phase transitions of the first kind leads to different variants of the Stefan problem [16, 17], under which in mathematical physics implies a wide class of problems with moving boundaries, is described by equations of parabolic or elliptic type. The simplest approach to the mathematical formulation of the heterogeneous processes of melting/solidification was realized in the XIX century by Stephen [11] and others [18]. The classic version of the Stefan problem, includes a quasi-linear equation of heat conduction in the area with beforehand unknown moving boundary $\Gamma_{sl}(t)$ that separates the solid s and liquid l phases. Heterogeneous phase transition is described as the boundary conditions at the interface $\Gamma_{sl}(t)$

$$x = \Gamma_{sl}(t): \quad \lambda_s(T) \frac{\partial T_s}{\partial x} - \lambda_l(T) \frac{\partial T_l}{\partial x} = \rho_s L_m v_{sl} \quad (1)$$

$$T_{sl} = T_s = T_l = T_m, \quad (2)$$

Equation (1) is a differential Stefan condition, having a simple physical meaning: the speed of the phase boundary v_{sl} is determined by the difference between the heat flows with absorption or emission of on this boundary volumetric heat of phase transition L_m . The equality temperature (2) $T_s = T_l$ at the interface to the equilibrium melting point T_m is phenomenological equation of state, which determines the equilibrium ratio (or quasi-equilibrium) between the thermodynamic parameters of the system.

As is known, the lack of phase equilibrium is a necessary condition for the occurrence of a phase transition. However, in the classic version of Stefan problem nonequilibrium phase transformation is clearly not used (2). This approach and its various modifications are widely used to describe the phase transitions and are, of course, a certain area of applicability, but the issue of its boundaries for a number of practically important cases remain open.

The driving force of phase transitions of the first kind is the difference of Gibbs free energy ΔG at the interface between the two phases. One can show that at a constant pressure at the interface ΔG is linearly proportional to the overheating/undercooling ΔT

$$\Delta G = -S \cdot \Delta T = \frac{L \Delta T}{T_{eq}} \quad \text{where } \Delta T = T_{sl} - T_m$$

The appearance of condition $\Delta G \neq 0$ leads to that the processes at the interface solid-liquid $\Gamma_{sl}(t)$ can flow in conditions of significant violation of local thermodynamic equilibrium, characteristic for intensive external influence. In addition to the thermodynamic nonequilibrium interface of phase transitions of the first kind includes kinetic nonequilibrium associated with molecular-kinetic processes at the interface. In the case of melting-crystallization kinetic nonequilibrium characterized by motion speed of phase interface surface v_{sl} , depending on the deviation of the phase transition temperature T_{sl} from the

equilibrium temperature T_m , i.e. the magnitude of overheating/undercooling. A significant deviation from the equilibrium temperature makes inappropriate use of the phenomenological condition (2) of constancy of temperature at the interface $T_{sl}=T_m$ used in the classic version of the Stefan problem.

The aim of this work is a detailed study of the kinetic properties of interfaces of heterogeneous melting/crystallization of metals in a wide temperature range of solid overheating and undercooling liquid with follow-up using of the results for mathematical formulation of a kinetic version of Stefan problem.

2 KINETIC PROPERTIES OF INTERPHASE BOUNDARIES OF HETEROGENEOUS MELTING/CRYSTALLIZATION OF OF PURE METALS

Fast phase transformations of first kind including melting/solidification are characterized by the occurrence of metastable overheated/undercooled states. In recent years, in many theoretical and experimental studies special attention is paid to fundamental problems in which the solid can be overheated and the liquid can be undercooled.

The most important kinetic characteristic of heterogeneous phase transformations is the mobility of the interface defined by the speed $v_{sl} = v_{sl}(\Delta T) = v(T_{sl})$, depending on the magnitude of overheating/undercooling of the interface $\Delta T = T_{sl} - T_m$ [19]. To determine the temperature dependence $v_{sl}(\Delta T)$ there are several directions [20, 21], based on the thermodynamic, kinetic and molecular-dynamic approaches.

2.1 Thermodynamic approach

Thermodynamics is a macroscopic theory, in which from an energy point of view, we consider the properties of macroscopic bodies in a state of equilibrium. This allows conclusions of thermodynamics have a great communion. In equilibrium thermodynamics one way to describe the equilibrium processes is the theory of thermodynamic potentials. The method of the thermodynamic potentials is based on the possibility of introduction for equilibrium processes the functions of the state, total differentials of which describe the change of the state of a thermodynamic system. Basic equality of thermodynamics of equilibrium processes is usually presented in the form of

$$TdS = dU + p dV \quad \text{or} \quad dU = T dS = -p dV \quad (3)$$

Depending on the choice of two independent parameters, you can enter the thermodynamic potentials, the differentiation of which enables to determine the other unknown parameters of state. Generally, the thermodynamic potential can be a function of different parameters. In this record the internal energy is defined as a function of entropy and volume: $U=U(S,V)$. It is a function of the state and has a total differential with respect to its variables. By means of total differential dU you can determine the temperature T and the pressure p . However, the use as two independent variables entropy S and volume V is inconvenient in that it is very difficult to control it in the experiment. Therefore, usually as two independent variables selected pressure p and temperature T .

Sequentially converting the internal energy ε in the first in the enthalpy $H=H(S,p)$ and then in Gibbs energy $G=G(T,p)$

$$H = \varepsilon + pV , \quad (4)$$

$$G = H - TS = \varepsilon + pV - TS \quad (5)$$

The total differential of enthalpy considering the basic identity of thermodynamics (3) takes the form:

$$dH = d\varepsilon + pdV + Vdp = TdS + Vdp \quad (6)$$

Using (3) and (5) can obtain a total differential of the Gibbs energy,

$$dG = -SdT + Vdp \quad (7)$$

which is convenient because the independent variables T and p can be easily modified and controlled in the experiment.

After reaching the equilibrium state of the system Gibbs potential takes a minimum value and becomes constant: $dG=0$. It allows the use condition of the minimum of the Gibbs potential for describing equilibrium states in which $T=const$ and $p=const$.

The thermodynamic systems in equilibrium does not necessarily have to be a homogeneous medium. In equilibrium state can be system composed of several different phases with different physical and chemical properties, spatially separated by time invariant interfaces.

Most simply described multiphase thermodynamic systems, parts of which are in equilibrium states, and through the interphase boundaries is no matter, energy and momentum transport. In this case, such thermodynamic system is in equilibrium state and to describe it are applicable equilibrium thermodynamics methods.

Taking into account that during phase transformations each of the phases is a system with variable mass, in the thermodynamic description was introduced the concept of chemical potential $\eta(p,T)$, by which the system takes into account the exchange of not only energy, but also mass (particles). To define it, in the expression for thermodynamic Gibbs potential was introduced formally term, which takes into account the possibility of changing the number of particles in a homogeneous system (similarly we can proceed with other potentials):

$$dG = -SdT + Vdp + \eta dN , \quad (8)$$

where dN determines a number of system particles. If the thermodynamic potential is given as a function of temperature and pressure, the chemical potential value is expressed as:

$\eta = \left(\frac{\partial G}{\partial N} \right)_{p,T}$. The chemical potential can be expressed through other thermodynamic functions, but in this case it will be expressed through other state parameters:

$$\eta = \left(\frac{\partial G}{\partial N} \right)_{p,T} = \left(\frac{\partial U}{\partial N} \right)_{V,S} = \left(\frac{\partial H}{\partial N} \right)_{p,S} \quad (9)$$

If through the interphase boundaries is no macroscopic transfer, and the phases themselves are in a state of thermodynamic equilibrium, such a thermodynamic system, in spite of its heterogeneity, will be in a state of thermodynamic equilibrium. For the phase equilibrium in one-component two-phase system should be carried out at the same time conditions of the thermal and mechanical equilibrium $T_1=T_2=T_{eq}$, $p_1=p_2=p_{eq}$ as well as the condition of equality of the Gibbs energy, which consists in the requirement of absence of macroscopic

transport of molecules (atoms) of the substance from one phase to another: $\eta_1(p, T) = \eta_2(p, T)$. The equality $\eta_1(p, T) = \eta_2(p, T)$ can be solved with respect the variables T and p represent the curves and the equilibrium of two phases: in the form $T=T(p)$ or $p=p(T)$. In case of liquid-solid interface Γ_{sl} we will obtain equilibrium melting curve $T_m=T(p_{sl})$. For liquid-gas interface Γ_{lv} we will obtain curve of equilibrium evaporation – $p_{sat}=p(T_{lv})$.

It should be noted that as in the case of equilibrium of various phases and phase transformations the processes at the interface are statistical in nature. At the interface between a liquid and vapor occurs a constant process of moving molecules from liquid to vapor and back again. At equilibrium, these counter processes compensate each other, and at input and output of heat one of these processes (transfer of molecules from the water into vapor or vice versa) begins to dominate, and this leads to a change amount of the material in different states of aggregation.

If components of the thermodynamic system are not in equilibrium with each other, then there are thermodynamic flows through their interfaces. At the same time will take place conversion process from one state to another, ie, the phase transformation. Assuming occurring in the system processes a quasi-static and flows – infinitely small, you can use the methods of equilibrium thermodynamics to describe a nonequilibrium system. In this case it is assumed infinitesimal difference in the thermodynamic parameters of the various parts of the system. Classic version of Stefan problem [11] is based on this assumption.

The driving force of phase transitions of the 1st kind is determined by the free energy difference between the two phases at the interface $\Gamma(t)$ (or overheating/undercooling value ΔT). Taking into account that in the process of phase transitions of the 1st kind at the interface number of variables undergo abrupt changes, in the thermodynamic equations the differential symbol would be replaced by difference between the corresponding value $dF \approx \Delta F$ at the equilibrium phase transition temperature T_{eq} and the excess Gibbs free energy for the two phases at the interface defined from (5) and (7) can be written in two ways:

$$\Delta G = (\varepsilon_1 - \varepsilon_2) + p_{eq}(V_1 - V_2) - T_{eq}(S_1 - S_2) = \Delta\varepsilon + p_{eq}\Delta V - T_{eq}\Delta S \quad (10)$$

$$\Delta G = V\Delta p - S\Delta T \quad (11)$$

where $\Delta p = p - p_{eq}$, $\Delta T = T - T_{eq}$, $\Delta\varepsilon = \varepsilon_1 - \varepsilon_2$, $\Delta V = V_1 - V_2$, $\Delta S = S_1 - S_2$, T_{eq} , p_{eq} – equilibrium temperature and pressure, respectively. In the case of melting, $T_{eq}=T_m$, $p_{eq}=p(T_m)$, in case of evaporation – $T_{eq}=T_b$, $p_{eq}=p_{sat}(T_b)$ where T_b - the equilibrium boiling temperature under normal conditions, p_{sat} - pressure of the saturated vapor.

Equilibrium. In equilibrium state $\Delta G=0$ equality (10) takes the form:

$$\Delta\varepsilon + p_{eq}\Delta V - T_{eq}\Delta S = \Delta H - T_{eq}\Delta S = 0$$

where the difference of enthalpy $\Delta H = \Delta\varepsilon + p_{eq}\Delta V$ is known as the equilibrium latent heat of transition

$$L_{eq} = \Delta H = T_{eq}\Delta S. \quad (12)$$

At constant pressure, $P=const$, from the equation (11) implies that the free energy difference is linearly proportional to undercooling (overheating):

$$\Delta G = -S \cdot \Delta T = \frac{L \Delta T}{T_{eq}} \quad (13)$$

In the future, identifying free-energy difference with the speed of phase transformation, we find that the rate of conversion in the thermodynamic approach, at constant pressure for small deviations from the equilibrium is linearly proportional to overheating (undercooling) ΔT

$$v \approx \mu \Delta T \quad (14)$$

where $\Delta T = T_{st} - T_m$, μ – the constant of proportionality between the normal speed of boundary and its undercooling. Equation (14) in appearance coincides with the well known relation for determining the linear crystal growth rate obtained on the basis of classical molecular-kinetic models, in which the proportionality constant μ is called the kinetic coefficient [22, 23]. The main use of the relation (14) and its different modifications [24, 25] has found in the description of processes of melting-solidification, where the coefficient μ is the main parameter characterizing mobility of the boundary crystal-melt. Disadvantages of this approach are that the constant, judging by its dimensions [$\text{cm s}^{-1} \text{ K}^{-1}$], has no clear physical meaning and is chosen experimentally for each material separately. Comparison with experiment shows that the equation (14) gives good agreement mainly at low degrees of undercooling [26, 27], ie in the vicinity of the temperature T_m . Despite the great importance of this feature, there are only a few successful experiments on measuring the kinetic coefficient in metals and alloys [28, 29]. The main difficulties of experimental determination related to the great complexity of the measurement of the melt undercooling at the solidification front.

Thus, the kinetic coefficient μ determined from the thermodynamic approximation, give a good description of the behavior of the front near the equilibrium melting point T_m , where the temperature dependence of the speed is mainly controlled by the difference in the free energies of the crystal and a liquid phase. However, the melting/solidification kinetics away from the equilibrium melting temperature differs greatly from the kinetics in the vicinity of T_m due to strong temperature dependence of the thermodynamic driving forces and atomic mobility.

Using an equilibrium theory of thermodynamic potentials to describe the phase transitions (non-equilibrium processes) allows to consider only a shallow entry into the metastable overheated/undercooled area and explore phase transformations near the equilibrium line. This identifies the main disadvantages of the thermodynamic approach. Since thermodynamics does not consider the internal structure of the bodies considered, that the number of its conclusions and the provisions are not sufficiently precise and physical clarity. Structural particles of matter are in constant motion are displayed in the main provisions of the molecular-kinetic theory, in which all processes are considered at the atomic or molecular level, and the particles have a Maxwellian velocity distribution.

2.2 Kinetic approach

Kinetic approach is based on the phenomenological theory of Wilson - Frenkel [30, 31] and some of its generalizations [26, 32, 33]. One of the directions based on the mechanism of diffusion limitations melting-solidification front speed using the assumption of the need to overcome by the atoms (molecules) diffusion barrier at the transition from liquid to solid

phase [30, 31]. The second one uses as limiting the frequency of thermal collisions of atoms with the interphase boundary [34, 35]. In the model of diffusion limiting the diffusion coefficient of the atoms in the liquid are usually in the form of the Arrhenius equation

$$D = D_0 \exp\left(-\frac{Q}{k_B T_{sl}}\right) \quad (15)$$

where Q - the activation energy for diffusion of motion in the fluid, k_B - Boltzmann constant, $k_B T$ - the average thermal energy for one atom, D_0 - pre-exponential factor (prefactor) on which the speed of the process depends.

The speed of crystallization/melting front with diffusion restriction expressed by the equation of the type [26]

$$v(T_{sl}) = \frac{D_0 a}{\lambda^2} f_0 \exp\left(-\frac{Q}{k_B T_{sl}}\right) \left[1 - \exp\left(-\frac{L_m}{k_B T_m} \frac{\Delta T}{T_{sl}}\right)\right] = C^{WF} \frac{D}{a} \left[1 - \exp\left(-\frac{L_m}{k_B T_m} \frac{\Delta T}{T_{sl}}\right)\right] \quad (16)$$

where $C^{WF} = \frac{a^2}{\lambda^2} f_0$, a - interatomic distance, λ - the mean free path of the atoms in this process, it is assumed [36] that it is proportional to the lattice parameter, a : $\lambda < a$, f_0 - efficiency ratio (constant of order unity $f_0 < 1$), describing the part of collisions of atoms of the liquid with solid, leading to crystallization.

Equation (16) was used to study the kinetics of melting-crystallization of silicon in relatively small vicinity of the temperature T_m [37, 38]. The results were compared with the results of molecular-dynamic simulation with the Stillinger-Weber interaction potential [39] and the experimental data. The comparison showed an acceptable match. However, for pure metals, molecular dynamics simulation of crystallization kinetics [34] with the Lennard-Johnson potential [40] showed that at high degrees of undercooling, where the diffusion coefficient D is very small, growth rate of a new phase in one atomic metals was much higher than motion speed of interface determined from the equation (16).

This defect was eliminated by modification of Wilson-Frenkel theory [34] by means of introducing as a factor limiting the rate of solidification, the collision frequency of the atoms of the liquid phase with the planes of the crystal [35], instead of its diffusion. The result was a so-called BGJ (Broughton, Gilmer, Jackson) model, in which diffusion term (15) has been replaced by the average thermal velocity of the atoms $v_T = \sqrt{3k_B T_{sl}/m}$

$$v(T_{sl}) = \frac{a}{\lambda} f_0 v_T \left[1 - \exp\left(-\frac{L_m}{k_B T_m} \frac{\Delta T}{T_{sl}}\right)\right] = C^{BGJ} \sqrt{\frac{3k_B T_{sl}}{m}} \left[1 - \exp\left(-\frac{L_m}{k_B T_m} \frac{\Delta T}{T_{sl}}\right)\right] \quad (17)$$

where $C^{BGJ} = \frac{a}{\lambda} f_0$ - dimensionless coefficient, m - atomic mass.

The resulting relation (17) was used to study the kinetics of melting-crystallization of sodium [41, 42] in the vicinity of the temperature T_m . The results were compared with the results of molecular-dynamic simulation with Lennard-Johnson potential and experimental data. With an appropriate choice of fitting coefficients were obtained quite satisfactory agreement between the results.

Within the framework of the kinetic approach easy to formulate an analytical view of the kinetic coefficient μ . For temperatures in the vicinity of equilibrium melting temperature $T_s \approx T_m$ from equations (16) and (17) can obtain [25,27] coefficient μ in form:

$$\mu = C^{WF} \frac{D}{a} \frac{L_m}{k_B T_m^2} \Delta T \quad (18)$$

$$\mu = C^{BGJ} \sqrt{\frac{3k_B T_m}{m}} \frac{L_m}{k_B T_m^2} \Delta T \quad (19)$$

It is not difficult to notice that the equations (18) and (19) represent the first term in the decomposition of (16), (17) in the vicinity of T_m . Equations (18) and (19) have been widely used in studies mostly of solidification kinetics: dendritic solidification [43], solidification in area of glass-transition of metals [44] and silicon solidification [45].

The above approaches to the determination of melting and crystallization kinetics have two major drawbacks:

- a) all the equations (16) - (19) includes coefficients C^{WF} , C^{BGJ} containing quantities λ and f_0 for which there is no strict definition. Their presence is taken into account in the form fitting parameters, methods of selection of which are unknown at entering deep into the metastable region of overheated and undercooled states;
- b) a narrow temperature range (vicinity of the equilibrium temperature T_m) of overheated and undercooled states in which guarantee the adequacy of the results;

2.3 Molecular - dynamic approach

Currently, most of the information about the melting/crystallization kinetics obtained from the results of molecular dynamics simulation (MDM) [25-27, 34, 37,38, 41,42 - 52]. Statement of computational experiments (CE) is used to determine the basic equilibrium and nonequilibrium thermodynamic and kinetic properties of the interface solid - liquid. The simulation results contain information about excess free energy, kinetics of atom attaching to the interface (kinetic coefficient μ or kinetic speed $v(T_{sl})$) and other parameters that characterize the deviation from the chemical equilibrium at the interface between the solid-liquid interface.

Representation of physical processes on the atomistic level and then the MD simulation allows to looking newly at properties of interfaces crystal-melt relating to the melting and crystallization of strongly overheated/undercooled microstructures. The possibility of observing using MDM formation of metastable phases and the study of the kinetics of fast phase transitions represents new interesting possibilities, including in the field of mathematical description of the processes of heterogeneous melting/crystallization of in the continuum approximation [10, 21].

Statement of CE, atomistic model.

Determination of stationary temperature dependence of the melting/crystallization rate in the range of limit values of overheating/undercooling was carried out by means of computational experiment, consisting of a large series of calculations. In simulation have been involved atomistic simulation models for two types of metals: with the fcc lattice -

Aluminium (Al), copper (Cu) and with bcc lattice - iron (Fe). The basis of atomistic models is a model presentation of polyatomic molecular system in which all the atoms are represented as material points, the movement of which is described in the classical case by Newton's equations. Thus, there are N points particles, each of which

- has a mass, radius vector and velocity, respectively, $m_i, \vec{r}_i, \vec{v}_i$, where $i = 1 \dots N$;
- interacts with other by means of forces $\vec{F}_i = -\frac{\partial U(\vec{r}_1 \dots \vec{r}_N)}{\partial \vec{r}_i}$, where $U(\vec{r}_1 \dots \vec{r}_N)$ – the potential energy of interaction of the system of N particles;

- interacts with external fields by means of force \vec{F}_i^{ext} .

Evolution of this model described by the system of 2N ordinary differential equations of motion:

$$\begin{cases} m_i \frac{d\vec{v}_i}{dt} = \vec{F}_i + \vec{F}_i^{ext} \\ \frac{d\vec{r}_i}{dt} = \vec{v}_i \end{cases} \quad (20)$$

$i = 1 \dots N$

To integrate the system of equations (1) we need to know the coordinates and velocities $(\vec{r}_i, \vec{v}_i)|_{t=0}$ at the initial time $t=0$ of all the N particles. The computational domain was set as parallelepiped $5 \times 5 \times 4$ nm in size and filled with 57600 particles (Figure 1). Parallelepiped represented as a set of $100 \times 12 \times 12$ elementary cells of the lattice. In all three spatial directions on boundaries of computational domain were set periodic boundary conditions. MD calculations were carried out using various multiparticle EAM potentials: for aluminium [53], for copper [54, 55] and for iron [56] with the parametrization [57].

Thus, the mathematical model consists of a system of differential equations, their difference analogue (difference scheme), the interatomic interaction potential and specifically determined initial and boundary conditions.

Simulation.

For both types of metals temperature dependences of stationary kinetic melting/crystallization rate were determined in the crystallographic (100) plane in the range of limit values of overheating/undercooling. Initially, in computational domain the particles form a layered structure containing two phases in contact: crystal and liquid separated by a flat interface. Further interface speed was measured directly depending on its temperature. At the initial stage for investigation of the melting process, the liquid phase takes approximately 18% of computational domain; for investigation of the crystallization process $\sim 80\%$. Figure 1 shows the initial state of the computational domain for modeling heterogeneous metal melting process. The liquid layer in the middle part of the computational domain is highlighted with a dark color.

During the calculations by means of thermostat in the entire computational domain was established and maintained a fixed temperature during the whole numerical experiment. Simultaneously by barostat was maintained constant external pressure. It should be noted that was used thermostat which sought to keep the desired temperature at each point of the

computational domain, including the melting-crystallization fronts, not the average temperature in the entire volume. In [47] was called attention to the importance of such use of the thermostat. Thus, reverse effect on the local temperature of the process of emission/absorption of the latent heat of melting at the fronts was excluded. As a result, the process of heterogeneous melting/crystallization rapidly reaches a stationary state, and changing the amount of the new phase is almost linearly, Figure 2.

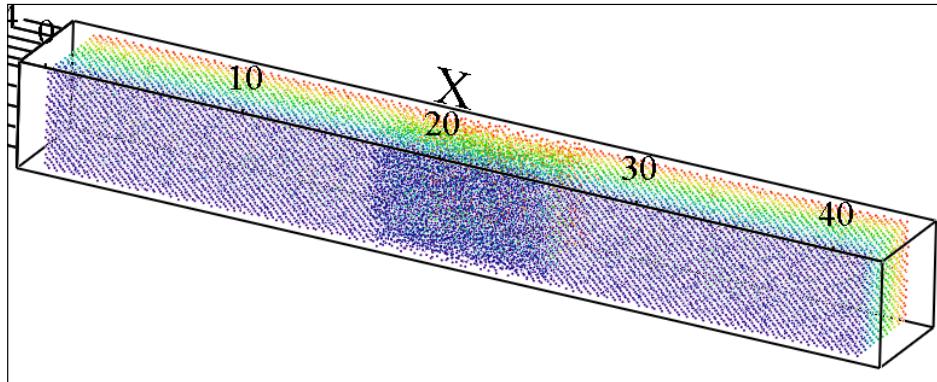


Figure 1. Computational domain of $5 \times 5 \times 41$ nm (57600 particles).

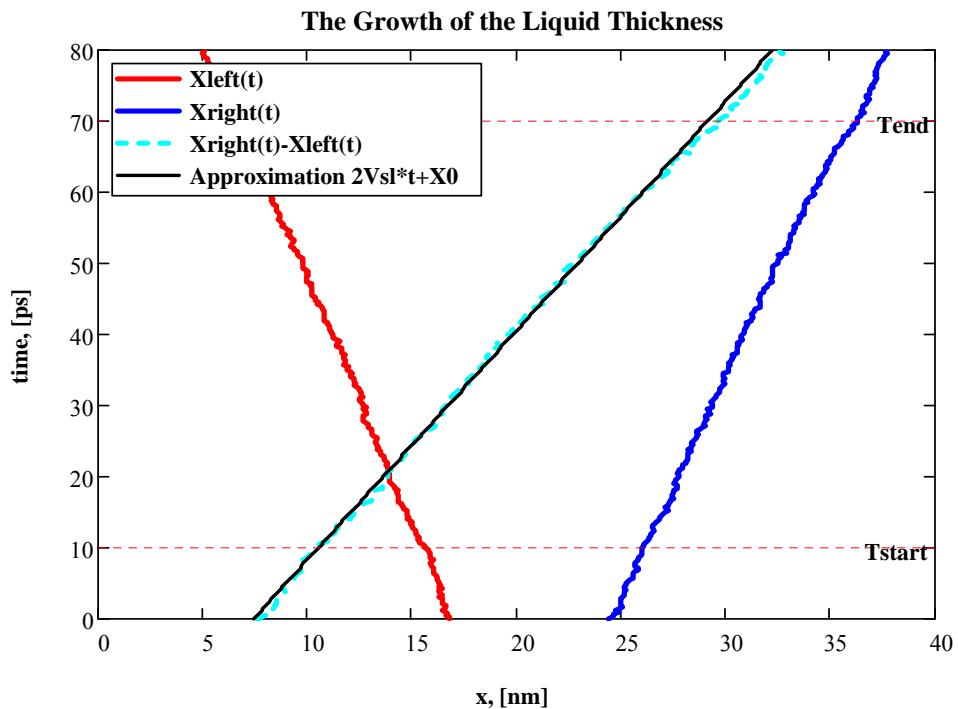


Figure 2. The positions of the melting front of Al and the thickness of the layer of the liquid phase via time in the numerical experiment with a temperature of 10^{25} K and zero pressure.

Position tracking of melting-crystallization fronts was carried out by means of the order parameter. Figure 2 shows the result of simulation of growth of thickness of Al liquid phase at a temperature of 1025K and zero pressure. Red and blue solid lines represent changes over

time of coordinate of left and right boundaries of the liquid phase, the blue dotted line - the thickness of the liquid phase, the solid black - approximation of a linear function. It is noted that only the middle section of the liquid thickness line was approximated because the initial and final sections contain errors associated with the process of establishing a stationarity of mode, as well as with surface effects, when the amount of the crystalline phase becomes too small.

The range of maximum permissible values of overheating/undercooling

The maximum permissible values of overheating/undercooling were determined relative to the equilibrium melting point T_m at zero pressure.

The maximum overheating of the solid phase in the calculation was fixed by loss of the mechanical stability of the crystal associated with the violation of the heterogeneity of the melting process. For stationary conditions of influence the value of the limit overheating at $T_{sl} \approx 1.2T_m$ which is in good agreement with the results of [58]. At unstationary influence the limit value of overheating reached value of $1.5T_m$ and more, that coincides with the estimates [59].

Limiting the deep entering to undercooling area is due to the formation of the intermediate (interstitial) phase for which the parameter of order is significantly greater than that of the liquid, but much smaller than the normal crystal. The appearance of the interstitial phase indicates the beginning of the glass transition process. The glass transition temperature of most metals is in the region $T_g \approx (0.3 \div 0.5)T_m$ [44]. Therefore, in the calculation the temperature of maximum undercooling of pure liquid was limited by temperature of beginning of liquid metal glass-transition and was assumed to be $T_{sl} \sim (0.4 \div 0.6)T_m$. At the same time crystallization front velocity slows down and is lower than in pure liquid crystallization. Thus, temperature range of maximum overheating/undercooling equal to $T_{sl} \approx (0.4 \div 1.2)T_m$.

Results

Investigation of the kinetics of melting - crystallization was carried out with statement of a series of computational experiments at undercooling of liquid phase and overheating of solid relatively to the equilibrium melting point T_m in the temperature range: $(0.4 \div 1.2)T_m$. For each of the selected metals was carried out two series of numerical experiments: for two external pressure values - 0 and 80 kbar.

The results of carried out molecular dynamics simulation was obtention a discrete ensemble of values of the phase front velocity $v(T_{sl})$ shown in Fig. 3,4,5 by markers, in a range maximum overheating and undercooling values for Al, Cu and Fe (in Fig. 3,4,5 circles and triangles).

3. CONSTRUCTION OF ANALYTICAL DEPENDENCIES $v(T_{sl})$

Obtained from molecular dynamics simulation discrete ensemble of values v_{sl} , as well as the shape of the temperature dependence of the kinetic velocity (BGJ model [34], equation (17)) was used to construct an analytical dependences $v(T_{sl})$ for all of metals under

consideration Al, Cu, Fe. For this purpose, using the expression (17) as an approximation function, a discrete ensemble $v(T_{sl})$ was approaching by the equation

$$v(T_{sl}) = \alpha \sqrt{\frac{3k_B}{m} T_{sl}} \left[\exp\left(\beta \frac{L_m}{k_B T_m} \cdot \frac{T_{sl} - T_m}{T_{sl}}\right) - 1 \right] \quad (21)$$

where α , β approximation parameters and $\alpha = C^{BGJ}$. Thus, not very precisely defined in BGJ model coefficients C^{BGJ} are found automatically from MD calculations. The introduction of additional parameters α before the whole expression and β into exponent achieved the required accuracy of the temperature dependence $v(T_{sl})$ over a wide temperature range.

Approximation of discrete ensemble was carried out taking into account the fact that in the equation (21) contains two thermophysical parameters - the value of the equilibrium melting point T_m and latent heat of melting L_m , which are due to the imperfection of used interaction potentials can in molecular dynamics calculations deviate slightly from reality. For the purity of the comparison of the two curves that approximated and calculated in equation (21) were used values T_m and L_m determined from the MDM. For their determination were used methodologies from [22-24]. MD calculations were performed with the same potentials [54-57]. The calculation results are shown in Table 1.

Metal	Pressure, [kbar]	T_m , [K]	L_m , [kJ/mole]
<i>Al</i>	0	949	8.90
	80	1332	11.30
<i>Cu</i>	0	1315	11.48
	80	1602	13.21
<i>Fe</i>	0	1775	15.57
	80	2062	17.14

Table 1. The calculation results.

The best agreement with the error not exceeding a few percent across the entire temperature range were achieved at values of approximating coefficients α and β presented in Table 2:

Pressure	<i>Al</i>		<i>Cu</i>		<i>Fe</i>	
	α	β	α	β	α	β
$P = 0$	0.344	5.01	0.416	5.74	0.365	6.34
$P = 80$ кбар	0.374	5.37	0.441	5.51	0.416	6.31

Table 2. Values of approximating coefficients α and β .

In the figures 3,4,5 solid red and blue dotted lines indicate simulation results of the approximation using the formula (21). The curves obtained for all metals have great generality. Melting branches with increasing overheating in area $T_m \leq T_{sl} \leq 1.2T_m$ are increasing in exponential, reaching the maximum values $v(T_{sl}) \sim 300 \div 350 \text{ m/s}$. The

crystallization process in the undercooling area $0.5T_m < T_{sl} \leq T_m$ occurs in more complicated manner. The velocity of crystallization $v(T_{sl})$ at all curves, Fig. 3-5, in the vicinity of $T_{sl} \sim 0.7T_m$ has an easy-to-see maximum, in which reaches a value $\sim 140\text{-}160$ m/s. It is noted the good coincidence of maximum crystallization rate for Fe with a similar data obtained in [44]. The appearance of a maximum in the crystallization rate is due to the beginning of the formation of interstitial (interstitium) phase, that slowing the velocity of the phase front. In this paper, we consider only crystallization processes in undercooled pure liquid. The process of glass-transition, flowing at undercooling $0 < T_{sl} \leq T_g$, excluded from consideration, since the complexity and importance of this process, in particular for the technological applications merit separate consideration.

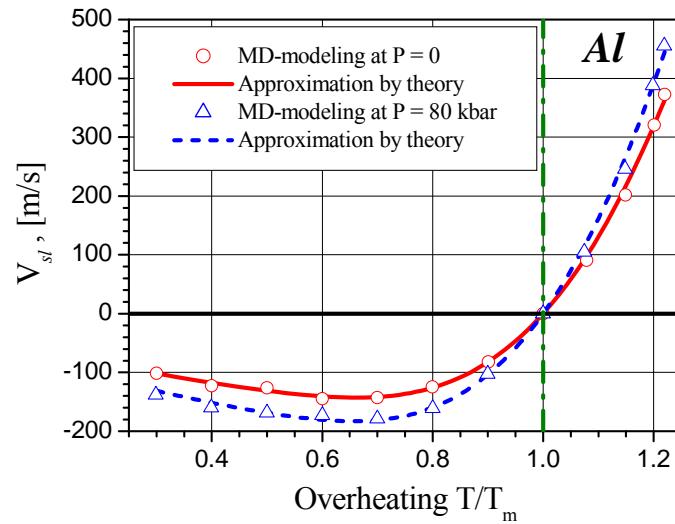


Figure 3. The dependence of the melting/crystallization front velocity via the magnitude of overheating/undercooling for aluminum.

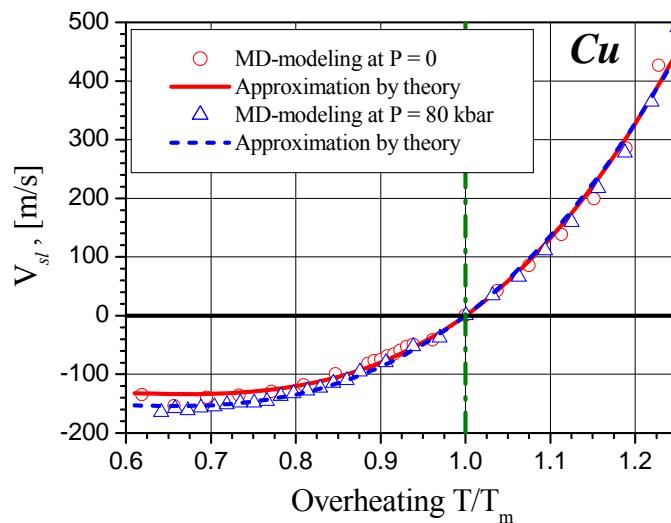


Figure 4. The dependence of the melting/crystallization front velocity via the magnitude of overheating/undercooling for copper.

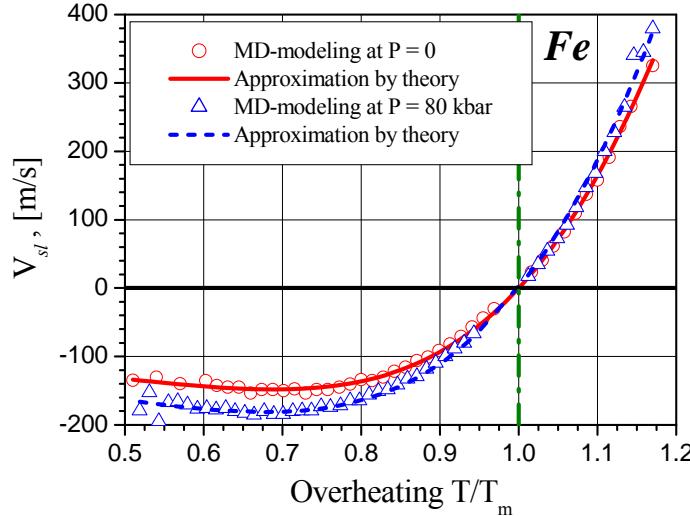


Figure 5. The dependence of the melting/crystallization front velocity via the magnitude of overheating/undercooling for iron

External pressure ($p = 80$ bar) has no significant influence with the behavior of kinetic velocity throughout overheating/undercooling range under the consideration - blue curves. But the maximum value of the melting and crystallization rate however increasing to 350-450 m/s and 160-180 m/s, respectively.

4 KINETIC VERSION OF STEFAN PROBLEM

In a rather general statement, but without taking into account hydrodynamic processes, Stefan problem can be reduced to a boundary value problem for a quasilinear parabolic equation with piecewise continuous coefficients having discontinuities of the first kind on a priori unknown moving surfaces. In the case of laser action on metals the processes of heterogeneous melting/crystallization, are usually considered together with the processes of the surface (heterogeneous) evaporation and volumetric or surface absorption of laser radiation. The mathematical description of these processes realized by a system of nonlinear equations of heat conduction and transfer of laser radiation with moving interphase boundaries $x = \Gamma_{s\ell}(t)$ and $x = \Gamma_{\ell\nu}(t)$ at which are formulated ratios describing the mechanisms of heterogeneous melting/crystallization and evaporation:

$$\left[\frac{\partial(\rho H)}{\partial t} = \frac{\partial}{\partial x} \lambda(T) \frac{\partial T}{\partial x} - \frac{\partial G}{\partial x} \right]_k, \quad H = C_p(T)T, \quad k = s, \ell, \quad (22)$$

$$\left[\frac{\partial G}{\partial x} + \kappa(\rho, T)G = 0 \right]_k, \quad G(t) = G_0 \exp\left(-\left(\frac{t}{\tau}\right)^2\right) \quad (23)$$

$$x_0 < x < \Gamma_{s\ell}(t) \cup \Gamma_{s\ell} < x < \Gamma_{\ell\nu}(t), \quad -\infty < t < \infty.$$

For a description of phase transitions melting - crystallization at the interface $x = \Gamma_{s\ell}(t)$ uses differential Stefan condition (1) and the expression for the kinetic velocity (21):

$$x = \Gamma_{s\ell}(t): \quad \lambda_s(T) \frac{\partial T_s}{\partial x} - \lambda_\ell(T) \frac{\partial T_\ell}{\partial x} = \rho_s L_m v_{s\ell} \quad (24)$$

$$v(T_{s\ell}) = \alpha \sqrt{\frac{3k_B}{m}} T_{s\ell} \left[\exp\left(\beta \frac{L_m}{k_B T_m} \cdot \frac{T_{s\ell} - T_m}{T_{s\ell}}\right) - 1 \right] \quad (25)$$

The system of equations (22) - (25) is an kinetic version of Stefan problem. The principal difference from the classic version is that the movement of the interface, whose velocity is determined from the expression (25), it is possible only if its overheating or undercooling, i.e. when $\Delta T = T_{s\ell} - T_m \neq 0$. The differential equation (24), in contrast to the classical version of Stefan problem is used to determine the temperature of the interface $T_{s\ell}$, which coincides with a temperature T_m only in case of phase equilibrium.

In the kinetic version are removed all the contradictions associated with the use of condition of temperature equality (2). At the same time numerical implementation of kinetic version of Stefan problem imposes strict limitations on the choice of the solution algorithm, consisting in the requirement of explicit separation of the phase boundary $x = \Gamma_{s\ell}(t)$, that making it impossible to use the enthalpy approach [60 - 62] widely used in the solution of the classical Stefan problem.

Heterogeneous evaporation of metals are usually described in the approximation of one-phase Stefan problem, supplemented by the ratios on nonequilibrium Knudsen layer [63 - 67]. For this purpose, on evaporating surface $x = \Gamma_{kv}(t)$ are written 3 conservation laws

$$x = \Gamma_{kv}(t),_{k=s,\ell}: \rho_k v_{kv} = \rho_v (v_{kv} - u), p_k + \rho_k v_{kv}^2 = \rho_v (v_{kv} - u)^2, \quad \lambda_k(T) \frac{\partial T_k}{\partial x} = \rho_k L_v v_{kv} \quad (26)$$

where ρ_k , p_k , T_k - density, pressure and temperature of condensed phase, v_{kv} - evaporation front velocity.

ρ_v , p_v , T_v , - are the vapor density, pressure and temperature, on the outer side of the Knudsen layer. Their values are determined from Krut model [63,67],

$$T_v = \alpha_T(M) T_k, \quad \rho_v = \alpha_\rho(M) \rho_{sat}, \quad P_v = \alpha_T(M) \alpha_\rho(M) P_{sat}(T_k), \quad (27)$$

where

$$M = \frac{u_v}{u_{sound}}, \quad u_{sound} = (\gamma R T)^{1/2}, \quad P_{sat}(T_k) = P_b \exp\left[\frac{L_v}{R_\mu} \left(\frac{1}{T_b} - \frac{1}{T_k}\right)\right], \quad \rho_{sat} = P_{sat}(T_k) * (R_\mu T_k)^{-1};$$

α_T , α_ρ are the Crout coefficients, ρ_{sat} , P_{sat} are the density and pressure of the saturated vapor, P_b , T_b , are the equilibrium boiling pressure and temperature, u , u_s - gasdynamic the vapor flow velocity and the speed of sound, M is the Mach number at the outer side of the Knudsen layer, which characterizes the degree of kinetic nonequilibrium of phase transition. The maximum nonequilibrium of evaporation process corresponds to the value $M = 1$: at which $T_v = 0.633 T_\ell$, $\rho_v = 0.328 \rho_{sat}$.

For the transport equation of the laser radiation on evaporating surface was written

condition

$$G_k = A(T_k)G(t), \quad (28)$$

where $A(T_k)$ - absorptivity of the surface.

The mathematical model (22) - (28) is a combined version of Stefan problem with two moving phase boundaries.

Due to strong nonlinearity these problems require a numerical solution, which can be carried out using a specially developed method of dynamic adaptation [68-70]. The method allows to perform the numerical solution of non-stationary boundary value problems of 1D [71] and 2D [72,73] with an arbitrary number of moving interfaces [74-77], discontinuous solutions such as shock waves contact boundaries [78-80].

In the case of fast phase transitions typical for pulse influence of concentrated flows of energy [17] the characteristic velocity of propagation of the phase fronts of which are in the range $(10 \div 10^3 \text{ m/s}) \leq v_{se} \leq u_{sound}$ for a correct description of phase transformations is necessary to use a complete set of continuum equations for mass, momentum and energy flow.

5 CONCLUSIONS

Was considered and analyzed the possibility of different approaches: thermodynamic, kinetic and molecular dynamics to investigation of kinetic properties of moving interfaces in metals with different crystallographic lattices: Al, Cu (fcc) and Fe (bcc) in a wide range of overheating/undercooling.

On the basis of extensive molecular dynamics simulations the values of the kinetic velocity $v(T_{se})$ of interfaces movement for all metals in the range of $(0.4 \div 0.6)T_m < T_{se} \leq 1.2 T_m$.

By approximating the simulation results by expression for the kinetic velocity near equilibrium were built analytical expressions for speed $v(T_{se})$, containing two approximating coefficients for all metals in whole considered range of overheating of solid phase and undercooling of the liquid. Approximation error does not exceed a few percent.

Obtained analytical expressions for the velocity $v(T_{se})$ were used for the formulation of a kinetic version of Stefan problemin which was eliminated the main contradiction of the classical Stefan problem associated with use of equality equilibrium melting temperature T_m to the interface temperature T_{se} .

Was formulated a mathematical model describing the dynamics of phase transitions (melting/crystallization, evaporation) in the case of laser action on metals.

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