

# ATOMISTIC MODELING OF THE DYNAMICS OF THE SOLID/LIQUID INTERFACE OF SI MELTING AND CRYSTALLIZATION TAKING INTO ACCOUNT DEEPLY SUPERHEATED/SUPERCOOLED STATES

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**Summary.** The velocity of the solid/liquid interface (SLI)  $v_{sl}$  plays an important role in the processes of crystallization and melting. It is one of the fundamental concepts of materials science. Based on the analysis of kinetic models of melting/crystallization with diffusion and collisional-thermal constraints, a modification of the transition state theory is performed. Using two interaction potentials (KIHS and SW), molecular dynamics modeling of Si melting/crystallization under deep overheating/undercooling was performed. From comparing the simulation results with the data of the modified kinetic model, we constructed the response function of interface  $v_{sl}$  in the region of the maximum allowable values of superheating/undercooling of Si. The temperature dependence of the velocity of the solid/liquid interface  $v_{sl}$  is diffusion-limited and is described by the same equation in the entire temperature range.

## 1 INTRODUCTION

Melting of solid body and liquid solidification are among the widely used and actively studied [1] phenomena. Two mechanisms of melting/crystallization of solids/liquids are known: heterogeneous (surface or frontal) and homogeneous (volume). In the first case, in the framework of classical thermodynamics [2], melting of solids and solidification of liquids belong to the first-order phase transformations that occur at a certain (equilibrium) temperature  $T_m$ , which corresponds to the equality of the Gibbs free energies of the solid and liquid states. The phenomena of heterogeneous melting and solidification are always non-uniform. They correspond to the motion of a continuous medium with a strong discontinuity surface, on which the mechanical, thermodynamic, thermophysical, and optical characteristics of a substance abruptly change.

The velocity  $v_{sl}(\Delta T) = v_{sl}(T_{sl})$  of the solid/liquid interface (SLI) is the function of the deviation  $\Delta T = T_{sl} - T_m$  from the equilibrium melting temperature  $T_m$  and is called the response function of the interface to overheating or undercooling, respectively, of the solid/liquid phase. The interface velocity  $v_{sl}(T_{sl})$  is a fundamental quantity that describes crystallization and melting processes and plays a fundamental role in materials science [3-5].

A significant part of the dynamics of melting and crystal growth from the melt is determined by the heat transfer from the moving interface. However, there are limiting circumstances in which the growth rate is regulated not only by the macroscopic heat flux. One of such circumstances is the emergence of fast phase transitions of the first kind, which

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are typical to the action of concentrated energy fluxes on materials. These processes have their own specifics [6]. Fast phase transitions are accompanied by the appearance of metastable, strongly superheated/undercooled states. Reaching the maximum permissible values of overheating/undercooling [7,8] leads to a number of interface instabilities.

Initially, experimental and theoretical studies were carried out more intensively in the field of crystallization/solidification of melts [9–11]. Along with the fundamental aspects [12], this is due to a large number of technological applications related to the production of metal glasses [13, 14] amorphous semiconductors [15], nanomaterials [16], etc.

However, the widespread use in the last two decades of ultrashort pulsed (pico- and femtosecond) laser irradiation on various materials causes increased interest in fast first-order phase transitions. An analysis of the processes caused by pulsed laser irradiation leads to the consideration of a number of important fundamental problems, which, at high heating rates, include the features of homogeneous and heterogeneous melting/solidification and evaporation mechanisms and the associated extreme overheating and supercooling of matter. An understanding of the melting/solidification processes is also of great interest for the applied problems of photonics [17], ultrafast laser microprocessing of materials [18, 19], generation of nanoparticles and nanostructures [20,21], etc.

Homogeneous melting/crystallization mechanisms are characterized by the nucleation of a new phase (liquid/crystal) in a certain volume of respectively superheated crystal and undercooled melt and will not be considered in this paper.

In the theoretical studies of the mobility of the solid/liquid interface and the kinetics of crystal and melt growth associated with it, kinetic models [10, 22–24] and atomistic modeling [25–28] are widely used. In most works, the studies of the temperature dependence of the stationary velocity  $v_{st}(T_{st})$ , as before, are carried out mainly in the temperature range of crystallization. Nevertheless, none of the models discussed describes the solidification process in the entire range of undercooling: from the minimum near the melting point  $T_m$  to the maximum in the region of amorphization (glass transition). In addition, the important question remains open about the possibility of using the analyzed kinetic models to determine the temperature dependence of the solid/liquid interface velocity for the melting process in the entire overheating region: from the minimum near the melting point  $T_m$  to the maximum in the spinodal region.

The main tool for studying the kinetic rate of melting/crystallization in the region of the maximum allowable values of superheating/supercooling is atomistic modeling, the results of which are compared with the data of kinetic models. An acceptable match is achieved by introducing appropriate correction parameters in the model [25 - 30].

The main goal of the work is to construct a modified kinetic model with diffusion constraint that describes the mobility of the solid/liquid interface in a wide temperature range, including the region of maximum permissible values of superheat/supercooling. As the studied material, crystalline silicon (Si) was chosen, for which a series of MD calculations of the temperature dependence of the stationary melting/crystallization rate  $v_{st}(T_{st})$  were performed. MD results are compared with the data obtained from the modified kinetic model.

## **2 KINETICS THEORY OF THE SOLID/LIQUID INTERFACE**

Of the many solid/liquid interface kinetics theories that display various crystal growth mechanisms, two of the most commonly used and cited directions can be distinguished. The

first is described by original Wilson – Frenkel (WF) growth models [31, 32], in which the interface velocity is associated with the diffusion of atoms in the liquid phase. This theory is often called the transition state theory, since it assumes that melting or solidification occurs through some intermediate or transition state. In this theory, a diffusion limitation mechanism is used to control the speed of the crystallization-melting front. This mechanism is based on the assumption that atoms (molecules) must overcome the diffusion barrier upon transition from a liquid to a solid phase [31, 32]. The transition is accompanied by a significant restructuring of the interface. The rate of the crystallization process was assumed to be proportional to the diffusion coefficient, which is usually presented in the form of the Arrhenius equation

$$D = D_0 \exp\left(-\frac{Q}{k_B T_{sl}}\right) \quad (1)$$

where  $Q$  is the activation energy for the diffusive motion in liquid,  $k_B$  is the Boltzmann constant,  $k_B T$  is the average thermal energy of one atom,  $D_0$  is the prefactor, controlling the rate of the process.

In the final form, the velocity of the melting/crystallization front  $v_{sl}(\Delta T) = v_{sl}(T_{sl})$  with the diffusive limitation is formulated as [33]:

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

where  $C^{\text{WF}} = \frac{a^2}{\lambda^2} f$ ,  $a$  is the interatomic distance,  $\lambda$  is the mean free path of atoms for this process usually assumed being proportional to the lattice constant,  $a: \lambda < a$ ,  $f$  is the efficiency coefficient (a constant of the order of unity,  $f \leq 1$ ), characterizing the fraction of collisions of liquid atoms with the solid leading to crystallization. The values of  $\lambda$ ,  $f$ ,  $D_0$ ,  $Q$  do not have a strict definition and are difficult to measure. Moreover, they depend on the crystallographic orientation of the interface.

The second direction is based on the kinetic model originally proposed by Broughton, Gilmer and Jackson (BGJ) [34] as an improvement on the earlier model (WF). The BGJ model uses, as a limitation, the frequency of thermal collisions of atoms with an interphase boundary [35]. A modification of the transition state theory [31, 32] was motivated by the results of MD modeling with the Lenard – Jones interatomic potential [36], which showed that the growth of crystals of monatomic systems may not in all cases be limited by diffusion. In particular, far from the melting temperature in the region of very low temperatures, diffusion tends to zero, while, according to the simulation results, the SLI speed is still finite. On this basis, a conclusion was formulated on the unacceptability of the model with a diffusion restriction for crystallization in the entire temperature range.

The BGJ model [34] was based on the hypothesis formulated earlier that solidification of monatomic metals is limited only by the frequency of collisions of the melt atoms with the crystal surface [35]. Following this hypothesis, an assumption was made that the kinetic model with the collision-thermal restriction mechanism best fits the obtained simulation results. According to this limiting mechanism, the maximum crystallization rate is controlled by the average thermal velocity of the atoms in the melt. The result of such reasoning was the

replacement by the authors of the BGI model [34] of the diffusion term in (2) with the average thermal velocity of atoms  $v_T = \sqrt{3k_B T_{sl} / m}$ .

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

where  $C_{BGJ} = \frac{a}{\lambda} f_0$  is a dimensionless coefficient,  $m$  is the atomic mass.

However, in later works [25, 29, 33], atomistic modeling showed that in the range of values close to the melting temperature, the crystallization process can be displayed with acceptable accuracy by the kinetic models with the diffusion (2) and collision-thermal constraints (3), as well as models of the density functional theory [24, 37].

A much smaller number of works is devoted to analysis of the possibility of using the analyzed kinetic models (2), (3) to determine the speed of movement of the solid/liquid interface  $v_{sl}(T_{sl})$  with acceptable agreement in the temperature region not only of crystallization, but also of melting with strong overheating of the solid phase.

In one of the first works [29], the results of molecular dynamics simulation were presented, in which the stationary rate of the silicon crystallization/melting interface was determined as a function of temperature in the conditions of strong undercooling/superheating. Particle interaction in the atomistic model was determined by the Stillinger – Weber potential [38]. The simulation results were compared with the data of the kinetic model with diffusion constraint (2). The model was adjusted to the simulation results by selecting the  $C^{WF}$  parameter. An analysis of the results showed that the transition state theory provides a reasonable qualitative description of heterogeneous crystallization and melting of silicon in the temperature range  $0.64 T_m \leq T_{sl} \leq 1.18 T_m$ . Close to the melting temperature, good agreement with experimental data was observed. In the region of deep undercooling, there was a strong discrepancy between the results of atomistic modeling and the crystallization rate data obtained from equation (2).

Similar studies using the kinetic model with the collision-thermal constraint mechanism (3) for metals were performed in [23, 26, 28, 30]. In an early work [30], the results of comparing the molecular dynamics simulation of crystallization and melting of sodium with the data of the kinetic model (3) in the temperature range  $0.2 T_m \leq T_{sl} \leq 1.26 T_m$  are presented. The comparison of the temperature dependence of the stationary velocity of motion solid/liquid interface  $v_{sl}(T_{sl})$  showed that the kinetic model data are in good agreement with the results of atomistic modeling in the entire crystallization region. However, an agreement was not obtained for the melting branch. A similar agreement was obtained with high accuracy for the model with a frequency-thermal limitation (3) in [23, 26, 28] for atomistic modeling with EAM potentials for aluminum (Al), copper (Cu), and iron (Fe) in the following temperature ranges:

$$\text{Al: } 0.3 \cdot T_m \leq T_{sl} \leq 1.26 \cdot T_m; \quad \text{Cu: } 0.61 \cdot T_m \leq T_{sl} \leq 1.2 \cdot T_m; \quad \text{Fe: } 0.6 \cdot T_m \leq T_{sl} \leq 1.15 \cdot T_m.$$

Nevertheless, the important question remains unanswered to date: which of the kinetic models and in which temperature range can be used to determine the stationary SLI motion velocity in the processes of metal melting/crystallization at high supercooling/overheating.

This problem is also crucial when using the continuum models describing the heterogeneous mechanisms of melting and crystallization.

### 3 MOLECULAR DYNAMICS STUDY

The molecular dynamics method was used to simulate the process of heterogeneous melting/crystallization of silicon under conditions when the melting/crystallization front propagates over the superheated/undercooled phase. Two series of numerical experiments were performed for two selected interaction potentials: KIHS [39] and Stillinger-Weber (SW) [38].

The calculated area of  $5.5 \times 5.5 \times 42.3$  nm in the form of a parallelepiped was filled with 64,000 particles interacting by means of the corresponding potential. In all three spatial directions, periodic boundary conditions are imposed on the boundaries of the computational domain. The particles form a layered structure containing two phases in contact: crystalline and liquid. The crystalline phase is formed by a diamond-like cubic lattice. The orientation of the lattice cells is such that the crystallographic direction [100] coincides with the large edge of the parallelepiped of the computational domain, and the melting/crystallization fronts propagate in this direction. At the initial stage, to study the melting process, the liquid phase occupies approximately 20% of the volume of the computational domain, and 80% in the study the crystallization process.

Using a thermostat in the entire calculation area, a fixed temperature value is set and maintained during the entire numerical experiment. At the same time, a constant value of external pressure is held by the barostat. The entire computational domain is divided into 30 layers of equal thickness along the long edge of the parallelepiped. Separately, in each layer, the thermostat controls the local temperature and keeps it equal to the target one. Thus, the inverse effect on the local temperature of the absorption/release of the latent heat of fusion  $L_m$  at the melting/crystallization fronts is leveled out.

As a result, the process of heterogeneous melting/crystallization quickly goes to the stationary mode, and the change in the amount of the new phase occurs almost linearly.

The integration of the equations of motion was carried out with a time step of 1 fs. Depending on the values of overheating/supercooling, from 400 thousand to 1 million steps were required to obtain each value of the melting/crystallization rate.

The values of the target temperature of the calculation region in each series were selected from the range of approximately  $-40\% \dots +30\%$  of the equilibrium melting temperature. An exit to the right outside the specified temperature range ended in failure, due to the beginning of the volume nucleation process, in which the solid / liquid interface became unstable. On the left outside this range, the crystallization process did not occur, the liquid “froze”, and an amorphous phase formed.

The control of the order parameter made it possible to automatically track the positions of the melting/crystallization fronts and to calculate the speed of their motion.

The discrete set of solid/liquid interface speed values thus obtained are presented in Table 1 and with markers on the curves in Figs. 1, 2. Subsequently, they were used to construct the analytical dependences  $v_{sl}(T_{sl})$  for each of the considered interaction potentials of model silicon.

| KIHS        |        |        |        |        |       |        |        |        |        |        |
|-------------|--------|--------|--------|--------|-------|--------|--------|--------|--------|--------|
| $T_{s\ell}$ | 1007.4 | 1175.4 | 1343.7 | 1428   | 1512  | 1595.8 | 1680   | 1844.9 | 2009.2 | 2171.9 |
| $v_{s\ell}$ | -0.04  | -0.41  | -8     | -13.7  | -14   | -10.03 | 0      | 30     | 81.75  | 160.22 |
| SW          |        |        |        |        |       |        |        |        |        |        |
| $T_{s\ell}$ | 839.5  | 1007.5 | 1175.6 | 1344.2 | 1512  | 1680   | 1845.2 | 2010   | 2174   | 2256   |
| $v_{s\ell}$ | -0.07  | -1.5   | -7.45  | -17.9  | -15.4 | 0      | 27.7   | 77.5   | 141.8  | 177    |

Table 1. The values of velocity  $v_{s\ell}(T_{s\ell})$ , obtained from MD calculations.

#### 4 MODIFIED KINETIC MODEL

In the theory of the transition state of Jackson and Chalmers [40], it is assumed that crystallization and melting proceed through an indefinite transition state, which is characterized by the presence of processes with two rates: one describes the melting rate  $R_{s \rightarrow \ell}$ , and another - solidification rate  $R_{\ell \rightarrow s}$ . The difference of these two gives the velocity of the solid/liquid interface:

$$v_{s\ell} = R_{s \rightarrow \ell} - R_{\ell \rightarrow s} \quad (4)$$

The intermediate state (intermediate phase) through which direct and reverse transitions take place has some Gibbs energy  $G^*$ . The driving force of these transitions is the difference between the Gibbs energy  $G^*$  and the one of the corresponding phase  $G_s, G_\ell$ , being in the Arrhenius exponent:

$$R_{s \rightarrow \ell} = \chi_s \exp[-(G^* - G_s)/kT] \quad (5)$$

$$R_{\ell \rightarrow s} = \chi_\ell \exp[-(G^* - G_\ell)/kT]$$

Here  $k$  is the Boltzmann constant,  $T$  is the temperature,  $\chi_s, \chi_\ell$  are the proportionality coefficients, which in classical theory are assumed to be equal to each other  $\chi_s = \chi_\ell = \chi$ .

Then the velocity is written as:

$$v_{s\ell} = \chi \exp\left[-\frac{(G^* - G_\ell)}{kT}\right] \left\{ \exp\left[\frac{(G_s - G_\ell)}{kT}\right] - 1 \right\} \quad (6)$$

The energy barrier in front of the curly bracket in the exponent can be interpreted as the activation energy of the process that limits the rate of melting/crystallization. In the Wilson-Frenkel phenomenological theory, this limiting process is associated with the diffusion of atoms in the liquid delivering the atoms to the crystallization front:

$$v_{s\ell} = \chi \exp\left[-\frac{Q}{kT}\right] \left\{ \exp\left[\frac{(G_s - G_\ell)}{kT}\right] - 1 \right\} \quad (7)$$

After performing thermodynamic transformations of the Gibbs energy difference between the solid and liquid phases, the final expression is obtained. It is the main conclusion of the transition state theory as applied to melting/crystallization processes with diffusion constraint:

$$v_{s\ell}(T_{s\ell}) = \chi \exp\left[-\frac{Q}{kT_{s\ell}}\right] \left\{ \exp\left[\frac{L_m(T_{s\ell} - T_m)}{T_{s\ell}T_m}\right] - 1 \right\} \quad (8)$$

Here  $T_m$  is the equilibrium melting temperature,  $T_{s\ell}$  is the temperature of the melting front,  $L_m$  is the latent heat of melting at the melting temperature  $T_m$ .

The equation (8) showed an acceptable coincidence of the rate in the crystallization and melting region in a small vicinity of the equilibrium temperature  $T_m$  with the results of molecular dynamics modeling (MDM) and experimental data. However, in a wide temperature range in which the melting/crystallization processes can proceed with the maximum allowable values of superheating/undercooling, an acceptable agreement could not be obtained, since the kinetics of melting/crystallization far from the temperature  $T_m$  differs significantly from the kinetics in the vicinity of  $T_m$ .

To overcome this difficulty, it is necessary to modify the Wilson-Frenkel kinetic model with diffusion constraint (8). The proposed modification is based on the assumption that the processes of direct and reverse transitions (5) in the transition state are asymmetric. The simplest form of asymmetry can be represented as the absence of equality of proportionality coefficients  $\chi_s \neq \chi_\ell$ , and the relation  $\chi_s/\chi_\ell$  as a functional dependence on the temperature  $f(T_{s\ell})$ . Considering the relation  $\chi_s/\chi_\ell$ , the expression for the velocity (6) can be written as:

$$v_{s\ell} = \chi_\ell \exp\left[-\frac{(G^* - G_\ell)}{kT}\right] \left\{ \frac{\chi_s}{\chi_\ell} \exp\left[\frac{(G_s - G_\ell)}{kT}\right] - 1 \right\} \quad (9)$$

Or, repeating the above discussion,

$$v_{s\ell}(T_{s\ell}) = \chi_\ell \exp\left[-\frac{Q}{kT_{s\ell}}\right] \left\{ \frac{\chi_s}{\chi_\ell} \exp\left[\frac{L_m(T_{s\ell} - T_m)}{kT_{s\ell}T_m}\right] - 1 \right\} \quad (10)$$

To determine the functional dependence  $\chi_s/\chi_\ell = f(T_{s\ell})$  we use the following considerations. The relation  $\chi_s/\chi_\ell$  is generally different from unity. But in the state of equilibrium, when  $T_{s\ell} = T_m$  and  $G_s = G_\ell$ , the expression in the curly brackets in (9), (10) must be equal to zero. This means that functional dependence  $\chi_s/\chi_\ell = f(T_{s\ell})$  should in equilibrium take a value equal to unity.

As such a dependence satisfying the condition  $\chi_s/\chi_\ell = 1$ , one can use the ratio

$$\frac{\chi_s}{\chi_\ell} = \exp\left[\alpha \frac{T_{s\ell} - T_m}{T_m}\right], \quad (11)$$

where  $\alpha$  is a dimensionless coefficient.

In view of expression (11), the modified model with diffusion constraint takes the final form:

$$v_{s\ell}(T_{s\ell}) = D_0 \exp\left[-\frac{Q}{kT_{s\ell}}\right] \left\{ \exp\left[\left(\frac{L_m}{kT_{s\ell}} + \alpha\right) \frac{T_{s\ell} - T_m}{T_m}\right] - 1 \right\}, \quad (12)$$

where  $D_0 = \chi_\ell$  is a dimensional constant.

The modified equation (12) contains 3 constants  $D_0$ ,  $Q$ ,  $\alpha$ , the values of which were determined from a comparison with MD results. To do this, we used a procedure containing

the least squares criterion  $\sigma$  [41], which minimizes the deviation of the values of equation (12) with the selected parameters from the MD results. The values of the calculated parameters  $D_0$ ,  $Q$ ,  $\alpha$ , as well as the least squares criterion  $\sigma$  for each of the interaction potentials are shown in Table 2.

| Interaction potential | $D_0$ , [m/s] | $Q$ , [eV] | $\alpha$ | $\sigma$ , [m/s] |
|-----------------------|---------------|------------|----------|------------------|
| <i>KIHS</i>           | 83460.42      | 0.9241     | -1.1308  | 2.30             |
| <i>SW</i>             | 22816.30      | 0.7220     | -0.8994  | 1.76             |

Table 2. The values of the calculated parameters  $D_0$ ,  $Q$ ,  $\alpha$ , and the least squares criterion  $\sigma$  for each of the interaction potentials.

The equilibrium temperatures  $T_m$  and latent heat of melting  $L_m$  corresponding to the potentials *KIHS* [39] and *SW* [38] are taken from [42, 43] and are shown in Table 3.

| Interaction potential | $T_m$ , [K] | $L_m$ , [kJ/mole] |
|-----------------------|-------------|-------------------|
| <i>KIHS</i> [42,43]   | 1680        | 35                |
| <i>SW</i> [42,43]     | 1680        | 32                |
| Reference data [44]   | 1688        | 45,3              |

Table 3. Equilibrium values of temperature  $T_m$  and latent heat  $L_m$ .

## 5 DISCUSSION OF THE RESULTS

Figs. 1a, b, present the results of the molecular dynamics simulation, in which the stationary rate of the Si crystallization/melting interface was determined as a function of temperature in the conditions of strong undercooling/superheating. The interaction of particles in the atomistic model was determined by the potentials of *SW* [38] and *KIHS* [39]. The simulation results were compared with the data of the modified kinetic model with diffusion constraint (12). The approximation of the model to the simulation results was carried out by selecting 3 parameters  $D_0$ ,  $Q$ ,  $\alpha$ . In the deep undercooling region, the modified kinetic model (12) showed that the data on crystallization rate obtained from the equation (12) is almost completely identical to the results of atomistic modeling for both potentials. Thus, the introduction into the theory of the transition state of a functional temperature dependence of direct and reverse transitions makes it possible to eliminate the main drawback of the Wilson-Frenkel model, which shows that in the region of very low temperatures, diffusion tends to zero faster than modeling data indicating that the velocity solid/liquid interface is still finite.

In particular, far from the melting temperature in the region of very low temperatures, diffusion tends to zero, while, according to the simulation data, the SLI speed is still finite.

An analysis of the results showed that the modified theory of the transition state gives a reasonable qualitative description of heterogeneous crystallization and melting of silicon in the temperature range  $0.596T_m \leq T_{sl} \leq 1.28T_m$  for the *KIHS* potential and  $0.49T_m \leq T_{sl} \leq 1.35T_m$  for the *SW* potential.

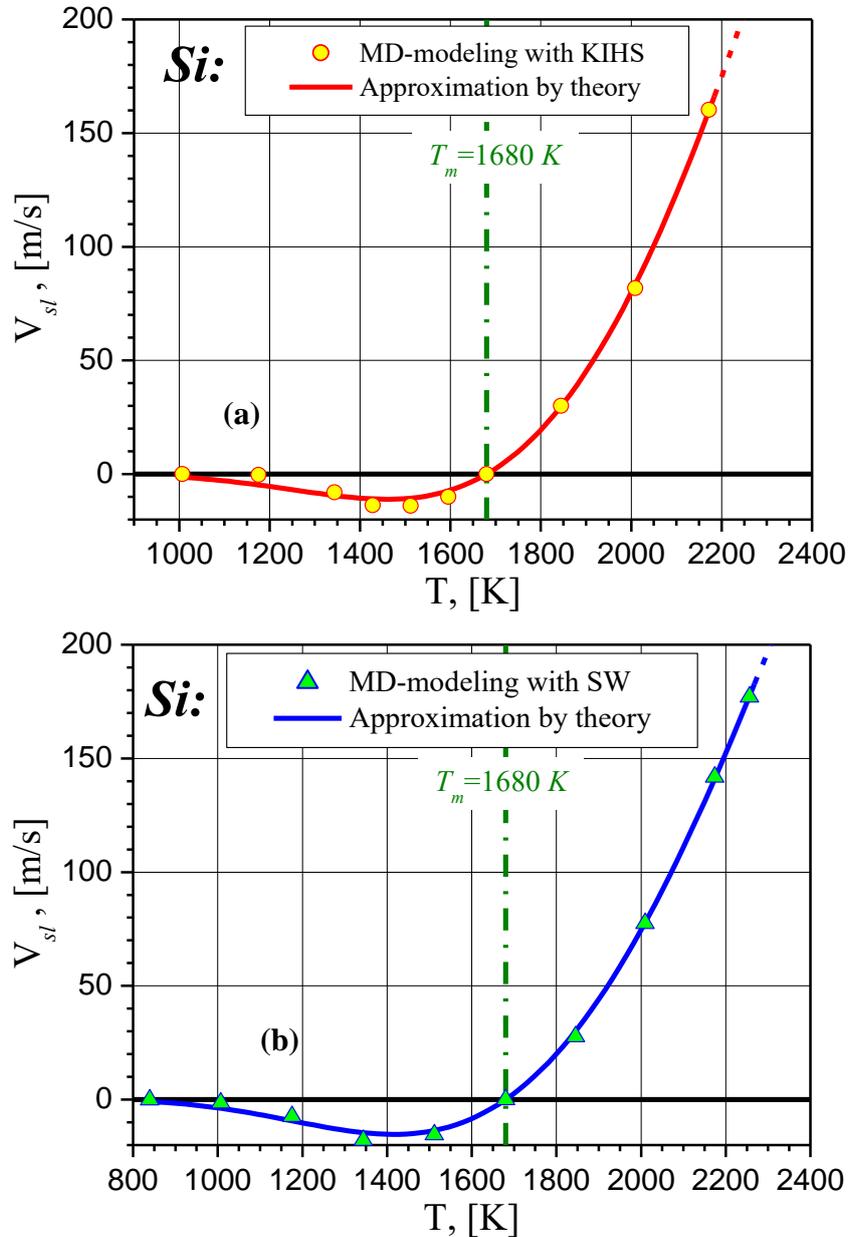


Fig.1. Temperature dependence of the melting/crystallization front for silicon: MD modeling and approximation. KIHS potential (a), SW potential (b).

In the vicinity of the melting temperature  $T_m$ , a smooth change in the temperature dependence of the velocity, determined from the simulation, is observed without breaking the slope when passing through the melting point for both potentials.

At the same time, the calculation results demonstrate a pronounced asymmetry of the curve  $v_{sl}(T_{sl})$  relative to the melting point  $T_m$ , i.e. between undercooling and overheating. The velocity profiles approach large undercooling and large superheating in different ways, since the solidification kinetics far from the melting temperature differs significantly from the melting kinetics in a very superheated state. The crystal growth rates in the melt are largely

determined by the structural order parameter, which measures the local degree of crystallinity. When crystals grow, each atom on the interface must go to a specific place in the lattice. As the melt grows, the crystal melts and turns into a liquid without any structural limitations for atoms passing from the interface to the melt. Thus, structurally, it is easier for a crystal to transform into a liquid than to melt into a crystal. These structural differences in the processes lead to the asymmetry observed in the crystal/melt growth rate. The structural factor also has a great influence on the velocity profiles when approaching severe overheating and undercooling. Near the limiting superheating, the metastability state reaches its maximum and upon further heating, the crystal becomes unstable due to homogeneous nucleation, which leads to the disappearance of the solid/liquid interface. With large undercoolings, the mobility of the melt decreases significantly, reducing the value of the interface velocity.

## 6 CONCLUSION

1. A modification of the transition state theory for melting/crystallization processes is proposed using the Wilson-Frenkel kinetic model as an example. The modification consists in replacing the constant coefficients in the rate of direct and reverse transitions with a functional dependence on the temperature of the solid/liquid interface  $T_{sl}$ .

2. Atomistic modeling of Si melting / crystallization processes under the conditions of deep overheating/undercooling was performed using two interaction potentials KIHS and SW.

3. From comparing the simulation results with the data of the modified kinetic model, the interface response function is constructed in the region of the maximum allowable values of superheating/undercooling in Si. The crystallization part of the interface response function, as well as the second part of the interface response function for melting, are diffusion-limited and are described by the same equation over the entire temperature range.

4. The temperature dependence of the speed of the solid/liquid interface determined from the simulation results using both interaction potentials shows a clear asymmetry with respect to the melting point  $T_m$ . This is explained by the strong difference between the solidification kinetics in a highly undercooled state and the melting kinetics in a very superheated state.

5 The change in the temperature dependence of the velocity  $v_{sl}(T_{sl})$  upon passing through the melting point  $T_m$  occurs smoothly without a kink of the slope.

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