Evaluation of metastable region boundaries for liquid and solid states in MD simulations

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Abstract. An automatic method based on MD simulations was developed for detecting and tracing the boundaries of metastable states of superheated crystal and supercooled liquid. The main criterion of the detection of early nucleation of new phase is the self-diffusion coefficient temperature dependence. The scanning for nucleation events is performed at continuous temperature change. The set of independent nucleation events at a given pressure allows evaluation of temperature dependence of specific nucleation frequency. The collection of a large number of these calculations allows accurate approximation of pressure and temperature dependence of the specific nucleation frequency in both directions between phases. This dependence allows estimating the behavior of the free energy in the region between superheating and supercooling curves. In addition, dependence of nucleation frequency on pressure and temperature provides an opportunity to integrate the probability of nucleation under dynamic loading and subsequent release and thus to determine the likelihood of the crystallization and melting. The technique was applied to tin. MD simulation was carried out with the help of the EAM interatomic potential, well reproducing the properties of BCC phase.

1. Introduction

The macroscopic crystalline solids usually melt heterogeneously on the irregularities of crystal structure such as defects, grain boundaries and open surfaces. As the heterogeneous processes usually start without energy barriers, initiation of the melting process occurs in the phase equilibrium vicinity, and as a rule, even at temperatures below the melting point. After that a liquid phase appears at the irregularities and gradually penetrates into the bulk. But homogeneous phase transition occurs not just at the moment of crossing the line of the phase equilibrium. The transition of a superheated solid to the liquid phase starts from the rearrangement of destabilized atoms into disordered clusters. This process is a fluctuation in its nature and involves overcoming a barrier in free energy, which is determined by the work of formation of a critical-sized nucleus. The nucleation time of a new phase is strongly dependent on the difference of Gibbs thermodynamic energies in the solid and in the melted states at given pressure and temperature. At slow change of the thermodynamic parameters of the macroscopic sample the heterogeneous initiation of the phase transition process dominates over the homogeneous one. At high heating rates, on the contrary, the bulk homogeneous nucleation process plays a major role.
Analytical estimation of the nucleation time was made in [1] as part of the classical nucleation theory. But this estimation includes too many empirical values and needs verification and calibration of the nucleation frequency dependence on temperature. To obtain the information on microscopic mechanisms of the nucleation on the level of individual atoms one should solve complicated N-body problems [2]. So, the main objective of this work is to develop the automatic method of searching for the nucleation by scanning the isobars in the MD simulations.

2. Method

Here, we carried out molecular dynamics simulations of tin with the EAM potential [3]. Periodic boundary conditions were used. Simulations were started with atoms occupying ideal crystalline lattice positions in the BCC lattice and random velocities from a Maxwell distribution. Pressure was controlled using the Cell Dynamics method based on Parrinello-Rahman barostat [4]. Temperature of the system was changed by Berendsen thermostat [5]. As a result we scanned isobars with continuous temperature change at a constant rate.

New phase nucleation events obey Poisson distribution law. Correct modeling of the nucleation process requires a source of randomness. Uncertainty about arithmetic operations in the parallel code execution is such a source of randomness. The numerical experiments have shown that in the systems that are close to the nucleation state the dynamic chaos arises very quickly and within a few thousand MD steps the trajectories may be considered as independent. The figure 1 shows linear system size depending on MD step number for a series of calculations started from the same microscopic initial state.

![Figure 1](image1.png)

**Figure 1.** Linear system size along X direction depending on MD step number for a series of calculations started from the same microscopic state.

![Figure 2](image2.png)

**Figure 2.** The dependence of self-diffusion coefficient on MD steps at the preparing stage of the calculation. Light curve shows approximation of the self-diffusion coefficient for the crystal structure at the given pressure and temperature.

The most reliable and sensitive method for determining the nucleation of the new phase embryo is the evaluation of self-diffusion coefficient. For crystal phase it is more than two orders of magnitude lower than for liquid phase so that the nucleation of a new phase leads to a drastic change in the coefficient of self-diffusion. Initially, the isobars were scanned to roughly estimate the transition temperatures. Thereafter the isobars were scanned at low rate temperature changes both in the melting and crystallization area to prepare starting states for the nucleation searching. The preparing stages are shown in figure 2. As a result one has “State #1” for melting search and “State #2” for freezing search. These states of the system are the overheated crystal and the overcooled liquid, but temperature is still quite close to equilibrium transition temperature, so that the probability of nucleation is negligible. Heating from the state #1 and cooling from the state #2 were done at low temperature change rate of
about 0.1 K/ps, so that about a million of MD steps would proceed prior to the transition to a new phase. During this time, due to growth of the dynamic chaos the system completely forgot the microscopic state it had at the beginning of temperature change.

Accumulating nucleation events are the initial data for the construction of a function of the nucleation frequency density depending on temperature. From the distribution of the nucleation events it is easy to find the frequency dependence on temperature. Indeed, let the density of nucleation frequency depending on temperature is $J(T)$, then the probability of nucleation is $J(T) dt\tau$, where $V$ is the volume of the system. Then the probability of the absence of the nucleation in the system since the beginning of the temperature change is

$$1 - F(T(t)) = \exp\left(-\int_{0}^{t} J(T(\tau)) V d\tau \right)$$  \hspace{1cm} (1)$$

from equation (1) one easily finds that

$$-\ln(1 - F(T(t))) = \int_{0}^{t} J(T(\tau)) V d\tau$$ \hspace{1cm} (2)$$

and time derivative of equation (2) is

$$J(T) = \frac{\dot{T}}{V} \frac{F'(T)}{1 - F(T)}$$ \hspace{1cm} (3)$$

We approximate the distribution function by the expression

$$F(T) = \frac{1}{2} \left(1 + \text{erf}\left(a + b(T - T_0) + c\left(T - T_0\right)^2 + d\left(T - T_0\right)^3\right)\right)$$ \hspace{1cm} (4)$$

then

$$F'(T) = \frac{b + 2c\left(T - T_0\right) + 3d\left(T - T_0\right)^2}{\sqrt{\pi}} \exp\left(-\left(a + b(T - T_0) + c\left(T - T_0\right)^2 + d\left(T - T_0\right)^3\right)^2\right)$$ \hspace{1cm} (5)$$

Now one can get the function $J(T)$ from the MD simulation series of nucleation in a continuous change of temperature at constant pressure. To do this, we approximate the normalized distribution function found in the MD simulation by equation (4), choosing the coefficients with the help of least squares method. Another approximation of $F$ used is

$$F(T) = \frac{1}{2} \left(1 + \text{erf}\left(k(T - T_0)\right)\right)$$ \hspace{1cm} (6)$$

Knowing the rate of temperature change $\dot{T}$ one can use equation (5) and get the density of nucleation frequency according to equation (3). The results of such calculation are shown in figure 3 for tin sample with the size 10x10x10 of the BCC unit cells in periodic boundary conditions under pressure 5 GPa. The MD distribution function is equal to the number of independent MD trajectories where the nucleation occurred before the achieving of given temperature. The error function in equation (6) poorly approximates the MD data on nucleation events. Function depending on the first three powers of temperature difference in the equation (4) approximates the MD distribution function much better.
The approximation of the distribution function allows us to obtain a smooth dependence of nucleation frequency on temperature with respect to its deviation from the exponential function which can be used in further research of nucleation mechanism.

![Graph of nucleation of liquid tin under 5 GPa](image)

**Figure 3.** Distribution functions and the density of nucleation frequency of liquid tin as dependent on temperature. Solid line – MD simulation events, dash line – approximation by equation (6), dot line – approximation by equation (4), dash-dot line is density of nucleation frequency according to equation (3). Approximations were made for normalized distribution functions.

The evaluation of the nucleation frequency function can be done for different pressures, as a result one obtains the surface $J(P, T)$. Knowing this function it is easy to find the probability of new phase nucleation along any path in the plane PT within time intervals from 0 to $t$

$$p = 1 - \exp \left( -V \int_0^t J(P(\tau), T(\tau)) d\tau \right)$$

(7)

We explored the function $J(P, T)$ for tin in pressure range 0-150 GPa both for melting and crystallization transitions. Since the nucleation process is random in its nature and may occur at various temperatures at given pressure, it is impossible to speak certain about critical temperature at which new phase nucleation occurs instantaneously. Phase transition of a sample might occur at different temperatures. The larger sample and longer waiting time provide for lower transition temperature. The PT diagram shows the curves of superheating and supercooling, which correspond to the frequency of nucleation $3 \cdot 10^{-8}$ ps$^{-1}$ Å$^{-3}$. At this frequency, the nucleation probability of transition of the studied samples in the MD simulation is about 0.5 at the given conditions. In contrast, the function $J(P, T)$ is invariant relative to the sample size and rate of temperature change. It determines the kinetics of the transition to a new phase at given pressure and temperature.
Also tin was studied by the method of thermodynamic integration. The method allows finding consistent values of the Gibbs thermodynamic potential for the solid and the liquid for any pressure and temperature and hence to determine equilibrium melting line.

Equilibrium melting curve and curves of superheating and supercooling (which correspond to the frequency of the nucleation $3 \times 10^8 \text{ps}^{-1} \text{Å}^{-3}$) are shown in figure 4. Melting points from the experimental measurements and from ab-initio calculations [6] are close to equilibrium melting curve obtained here.

![Figure 4](image)

**Figure 4.** The equilibrium melting curve for BCC-liquid transition in tin are shown with green (black line is B-spline approximation of raw data). Curves of nucleation frequency $3 \times 10^8 \text{ps}^{-1} \text{Å}^{-3}$ for superheated solid (orange curve) and supercooled liquid (blue curve) obtained in a series of MD calculations for tin BCC 12x12x12 sample at pressures of 0-150 GPa. For comparison, equilibrium melting data from [6] are shown.

3. **Conclusion**

The method for automatic determination of new phase nucleation rate was developed. The method is implemented in the code written in the CUDA language for GPU, allowing gathering a sufficient number of nucleation events in a reasonable timescale of several days. Together with the thermodynamic integration technique the method proved to be a useful tool for the investigation into the mechanisms of phase transitions. Tin was explored in pressure range 0-150 GPa and the curve of phase equilibrium as well as superheating and supercooling curves for given frequency of the nucleation were evaluated. We simulated samples with box sizes 10x10x10, 12x12x12 and 15x15x15, and for each size get the same nucleation frequency for given pressure and temperature.
References

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