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Homogeneous and heterogeneous mechanisms of superheated solid melting and decay

Vladimir Stegailov

Institute for High Energy Density, Associated Institute of High Temperatures of RAS, Izhorskaya st. 13/19, 125412 Moscow, Russia

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Abstract

The kinetics of homogeneous nucleation in superheated solid and heterogeneous melting from the open crystal surface are investigated via molecular-dynamics method. The system under consideration is superheated copper in the EAM potential model. The temperature dependence of the lifetime of superheated crystal and the rate of homogeneous nucleation are calculated according to the previously developed approach. The temperature dependence of the melting front propagation velocity is calculated as well. The results on the homogeneous nucleation rate are compared with the theoretical estimates based on the classical nucleation theory.

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Keywords: Superheated solid; Homogeneous nucleation; Melting front velocity; Molecular dynamics

1. Introduction

First order phase transitions allow the formation of metastable states. The description of these states should combine the thermodynamical parameters (temperature, pressure, density, heat capacity, etc.) and the time-related kinetic parameters that determine the rate of phase transformation. Superheated solid is an actual object for developing computational approaches to the investigation of metastable states.

Usually superheated solid melts on heterogeneities of crystal structure such as open surfaces, grain boundaries and defects. If heterogeneous melting is suppressed (e.g., in the bulk of defect-free crystals) the homogeneous nucleation of melt becomes the mechanism the superheated solid decay. While heterogeneous processes usually start without energy barriers (that is the main limitation for superheating in experiments), initiation of homogeneous nucleation requires relatively high degrees of superheating. It can be achieved during rapid intensive heating when solid becomes essentially superheated before heterogeneous melting can develop. Experimental data on solid superheating were obtained in shock-wave experiments (e.g., [1,2]) and under fast laser heating (e.g., [3]).

In this work we apply molecular-dynamics (MD) method to investigate the kinetics of the homoge-

E-mail address: stegailov@ihed.ras.ru (V. Stegailov).

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neous nucleation in superheated solid as well as heterogeneous melting from the open crystal surface. We present the results for superheated f.c.c. copper in the EAM model according to the potential proposed by Mishin and coauthors [4]. We use the previously developed approach [5,6] to calculate the temperature dependence of the lifetime of superheated crystal and the rate of homogeneous nucleation. The velocity of melting front propagation is calculated by the technique that was used in the work of Nguen and coauthors for aluminum [7]. A comparison with theoretical estimates based on the classical nucleation theory (CNT) [8] is made.

2. Homogeneous nucleation of melt in the superheated lattice

MD simulations are performed for the f.c.c. crystal of $N = 6912$ particles in the 3D periodic boundary conditions (PBC). Classical equations of motion are integrated according to the velocity Verlet scheme.

The ensemble of M ideal crystal configurations are generated with different initial distributions of velocities ($M \sim 40$ are used). Then each of configurations is equilibrated at the given temperature using Nosé–Hoover thermostat scheme. During equilibration restrictions on the particle motion are applied in order to prevent uncontrolled formation of lattice defects. Restrictions imply that each particle can not leave the corresponding Wigner–Zeitz cell and reflects from its walls during vibrations. As a result we have an NVT ensemble of M independent configurations. From each of the configurations the MD trajectory is calculated in the NVE ensemble (with the time step $\Delta t = 8.1155$ fs). The calculation stops after the phase transition has happened.

The typical trajectory is illustrated on Fig. 1. Rapid increase of pressure (and decrease of temperature, not shown) corresponds to the transition to the liquid phase. Analysis a large number of configurations shows that this transition goes via formation of a localized nucleus of melt and its growth. The homogeneous nucleation is a result of spontaneous fluctuational ap-

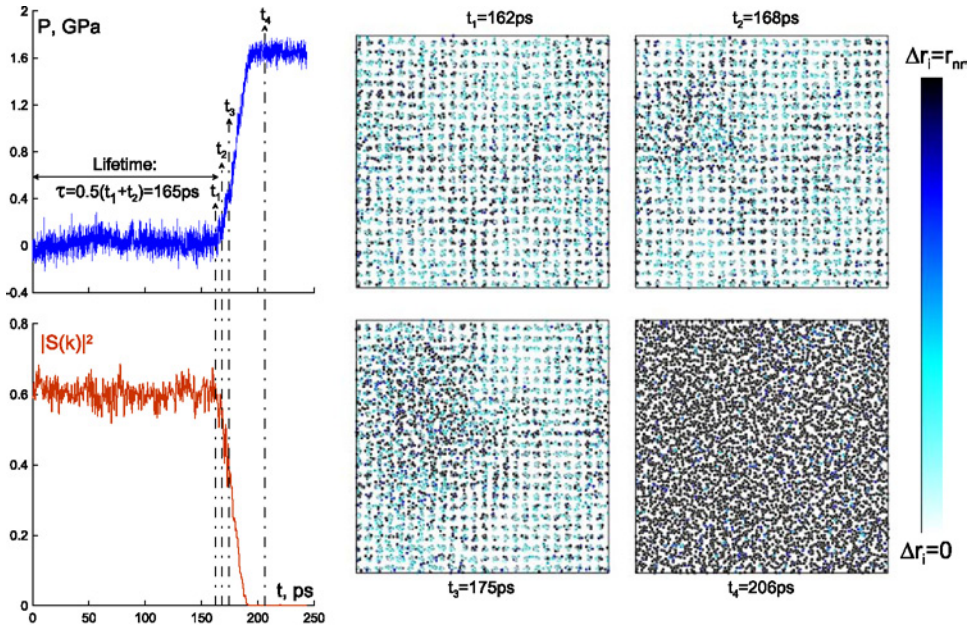

Fig. 1. Illustration of the spontaneous decay of superheated crystal. Initial temperature is $T = 1610$ K (superheating $\Delta T = 252$ K, 18.6%). Time dependencies of pressure P and static structure factor $|S(k)|^2$ are shown. The step corresponds to the birth and growth of the nucleus of melt that is illustrated by four orthogonal projections of the particle structure in the simulation box at subsequent time moments (color denotes the deviation from the ideal lattice sites Δr_i for each particle, r_{nn} is the nearest neighbor distance). The value of lifetime for the given MD simulation run are shown: $\tau = 165$ ps.

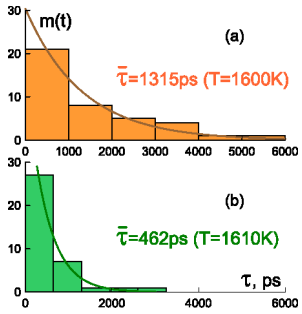

Fig. 2. Distributions of lifetime values $\{\tau_i\}$ $(i = 1, \ldots, M)$ for two temperatures T, solid lines correspond to the $m(t) = (M\delta\tau/\bar{\tau})\exp(-\tau/\bar{\tau})$, where $\delta\tau$ is the histogram bin size, $\bar{\tau} = \sum_{i=1}^{M} \tau_i$: (a) $T = 1600$ K ($\bar{\tau} = 1315$ ps, $M = 40$, $\delta\tau = 1000$ ps), (b) $T = 1610$ K ($\bar{\tau} = 462$ ps, $M = 37$, $\delta\tau = 650$ ps).

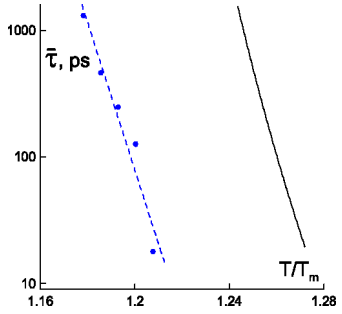

Fig. 3. Closed circles show the temperature dependence of the averaged lifetime $\bar{\tau}$ of the superheated crystal structure ($N = 6912$ particles in the 3D PBC) obtained from MD simulations. Dashed line is an exponential fit presented in order to guide the eye. Solid line is an estimate based on the work [8].

pearance of the critical (viable) nucleus and it can start at any point of the simulation box. For the considered system size PBCs do not influence on the formation of the critical nucleus, which consists of ∼100 particles according to the visual estimates. Although the stage of the nucleus growth depends, of course, on the size of the system.

The moment when a critical nucleus appears along the MD trajectory of the superheated crystal gives the lifetime of the superheated structure. As it was shown in the previous work [5,6] one can build a distribution of lifetime values for the ensemble of MD trajectories calculated from the ensemble of M initial configurations, examples are given on Fig. 2.

This distributions correspond fairly well to the model of nucleation as the Poisson random process. The average value of lifetime $\bar{\tau}$ is a function of temperature T that is fixed for the ensemble of initial configurations. The homogeneous nucleation rate J (the average number of critical nuclei that appeared per unit time and unit volume) can be found as $J = (\bar{\tau}V)^{-1}$, where V is the volume of the simulation box. The rate of homogeneous nucleation is a kinetic parameter that characterize the rate of spontaneous phase transformation in the metastable state and does depend on the system size in contrast to $\bar{\tau}$. In [6] it was proved that the values of J calculated for different system sizes at different temperatures lies on one curve.[1] The described procedure of statistical averaging of lifetimes can be repeated for different temperatures that results in the temperature dependence of the lifetime (and the homogeneous nucleation rate). The results are shown on Fig. 3.

It is interesting to compare the predictions of the *macroscopic* theory of homogeneous nucleation (in the framework of the CNT) with the presented results of atomistic simulation. From the results of the work [8] one can obtain the temperature dependence of the homogeneous nucleation rate $J_{\mathrm{CNT}}(T)$ in superheated solid copper and to obtain lifetime values for the system size considered $\bar{\tau}_{\mathrm{CNT}}(T) = (V J_{\mathrm{CNT}}(T))^{-1}$ (solid line on Fig. 3). This variant of the macroscopic theory overestimates the values of superheating for a certain lifetime value. The discrepancy is about 7% in the presented range of lifetimes. However the estimate of the critical nucleus size agrees well with the result of MD simulation (approx. 100 particles). The deployed MD model of solid copper [4] proved to provide the good correspondence with experimental data (including the melting temperature—see below) and hence is expected to give adequate description of the strongly superheated solid as well. Therefore we can conclude that the discrepancy between the MD results and the macroscopic theory shows the insufficient accuracy of the latter in the region of strongly superheated solid.

[1] Although we should point out that in small systems ($N < 2 \times 10^3$) it is not possible to define nucleation process clearly due to the PBC influence—the phase transition goes as a collapse of the whole crystal structure in the simulation box. In large systems ($N > 30 \times 10^3$) it is possible to observe the independent birth of more than one nuclei.

3. Melting from the open surface

In order to simulate melting on the open crystal surface we use the simulation box elongated along the z direction ($10 \times 10 \times 50$ elementary f.c.c. unit cells, $N = 5000$). Crystal equilibration at the given temperature is performed in 3D PBC using Nosé–Hoover thermostat with restrictions on particle motion. Resulting configuration is used for simulation in 2D PBC (in x- and y-directions). Motion of the liquid–crystal phase boundary is analyzed via the calculation of the static structure factor $|S(k)|^2$ for the slabs, which subdivide the simulation box (the threshold value for phase separation is chosen $|S(k)|^2 = 0.3$). As illustrated on Fig. 4, for moderate superheating ($\lesssim$15%) melting front propagation goes at the constant rate. The temperature dependence of the melting front velocity is shown on Fig. 5. At higher degrees of superheating homogeneous nucleation in the bulk of the crystal prevents the reliable estimation of the melting front velocity.

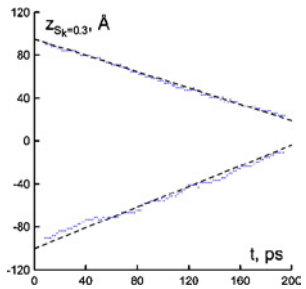

Fig. 4. Analysis of the melting front propagation from the open surfaces of the simulation box: propagation of the interphase boundary with time ($\Delta T = 63$ K, 5%). Dashed lines are linear fits of the data.

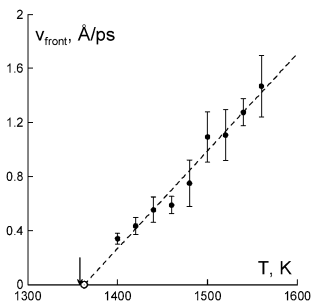

Fig. 5. Temperature dependence of the of the melting front velocity. Error bars shows the statistical scattering over 4 MD runs and 2 sides of the simulation box. The linear extrapolation gives the value of the equilibrium melting temperature (open circle) that is in a good agreement with experimental value (shown by arrow).

4. Conclusion

The temperature dependence of the homogeneous nucleation rate in superheated solid copper has been calculated. Results of atomistic simulation are found to be not in the agreement with the estimates based on the macroscopic nucleation theories. The temperature dependence of the melting front velocity has been obtained. The equilibrium melting temperature is found to agree well with the experimental value for copper.

Acknowledgements

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