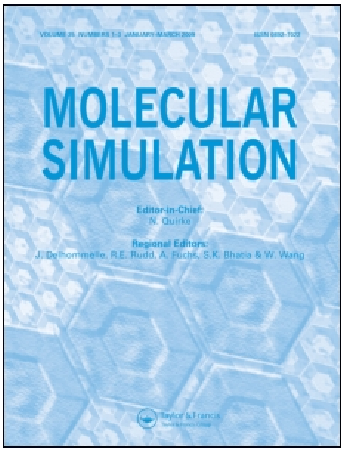

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Simulation of Ideal Crystal Superheating and Decay

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Molecular dynamics (MD) method is used to investigate time features of the transition of a superheated ideal crystal into liquid. Different levels of statistical description of the process are used. An approach to the calculation of the lifetime of a metastable crystal is developed. The homogeneous nucleation rate dependence on temperature is calculated. The decay under conditions of the constant rate heating is simulated as well. The limits of predictability of the MD method arising from chaotic properties of many-particle systems are shown for the problem concerned.

Keywords: Metastable states; Homogeneous nucleation; Molecular dynamics; Chaotic properties; Predictability

INTRODUCTION

Phase transitions are an important part of physics and chemistry for both fundamental science and applications. To obtain the information on their microscopic mechanisms on the level of individual particles one should solve complicated N-body problems. The only way to treat these problems is to use methods of molecular simulation [1].

The observation of solid and liquid phases was indicated just after the very beginning of the "simulation era" in Monte Carlo (MC) [2] and molecular dynamics (MD) [3] study of the hard-sphere model. The essential progress has been made in the understanding of melting transition since that time (e.g. see Refs. [4–14]).

The equilibrium melting temperature T_m is determined from the condition that the Gibbs free energies of solid and liquid phases are equal under the same pressure. It means that the solid–liquid interface exists in the equilibrium. MC was used to determine T_m for Lennard-Jones [4] and soft-sphere [5] potentials. Modern MD calculations [10] based on the direct observation of the solid–liquid coexistence give T_m values in a good agreement with experiment. The results of Ref. [14] show that MC and MD methods can give very precise data on the global phase diagram (i.e fluid–solid as well as vapour–liquid equilibrium).

It is known that first order phase transitions allow the formation of metastable states. The solid–liquid transition leads to supercooled liquid and superheated solid. Starting from the pioneering works [15,16] the supercooled liquid is much better explored via MD than the superheated solid since there are much more experimental findings on supercooled liquids, connected with physics of glasses and crystallization than experiments where superheated solid could be obtained.

In [6] MD was used to find the limit of stability of the superheated ideal Lennard-Jones crystal. The limit spinodal temperature T_s was determined by the condition that elastic constants vanish at T_s [17]. The lattice stability criteria formulated by Born were generalized for non-zero pressures and it was shown that elastic instabilities play the fundamental role in triggering unstable structural responses of homogeneous crystals [9]. The correspondence of Born and Lindemann criteria for melting was shown in Ref. [11].

Usually it is not possible to reach the temperature T_s experimentally. Defects act as the sites of the liquid nucleation. In Ref. [7] MD was used to simulate melting at a grain boundary. It was shown that the boundary is stable for $T < T_m$ and melts for $T > T_m$. The velocity of the melting front for metals at the moderate superheating was found to be $\sim 100\,\mathrm{m/s}$. In Ref. [8] MD results pointed out that the nucleation barrier is lower in the region of a dislocation than in the defect-free bulk.

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The role of defect-induced melting may be much lower under conditions of the ultrafast energy contribution. This is the case for the nanosecond metal wire explosions. The amount of energy up to several sublimation energies is put into the metal in 10–20 ns. There are indirect signs that the strongly superheated solid metal may be one of the transient states in such experiments [18,19]. The exact knowledge of thermophysical properties of metal in the process of wire explosion are important for the large-scale magnetohydrodynamic simulations of this phenomena which nowadays are not in a full agreement with the experimental data [20]. The preliminary estimates [21] show that one could improve the results by taking into account superheated solid states.

Another manifestation of transient solid superheating was observed in the Al crystals under tension at shock-wave loading [22]. Superheating can be interpreted as overstretching as well. This phenomenon is also discussed with respect to shock wave destruction of solid plates and crack formation.

In the second section, we discuss general features of metastable states description, the representation of solid-to-liquid transition in the phase space, the homogeneous nucleation, the model of nucleation as a random process and the features of the MD model. The third section is devoted to the calculation of lifetimes and the homogeneous nucleation rate. The crystal decay under constant rate heating is treated in the fourth section. The fifth section is connected with the influence of chaotic properties of many-particle systems on MD results. We summarize the results in the sixth section.

STATISTICAL DESCRIPTION OF A SUPERHEATED SOLID

Macroscopic Picture

Metastable states correspond to the local minima of a thermodynamic potential. Therefore, such states are stable with respect to small thermal perturbations. Instability takes place for a relatively large perturbation that leads to the formation of the viable nucleus of the competitor phase. Metastable system is in quasi-equilibrium. It holds that:

$$\{t_i = l/\nu_i\} \ll t^* < \bar{\tau}, \qquad (1)$$

where l is a linear size of the system, ν_i is a rate of the i-th parameter's relaxation, t_i is a characteristic relaxation time, t^* is a time of the (computer) experiment, $\bar{\tau}$ is an average time period before the first critical nucleus appears [23].

If Eq. (1) is valid then the thermodynamic properties (e.g. $P(V,T)$-dependence) can be quasi-statically continued from a stable to a metastable region in a unique way [23]. The inequality (1) means the large difference in times of relaxation without (t_i) and with ($\bar{\tau}$) breaking of homogeneity. The inequality (1) could be applied to the independent elements of volume ΔV. The smaller ΔV is the better Eq. (1) holds: t_i decreases as $(\Delta V)^{1/3}$ and $\bar{\tau}$ increases as $(\Delta V)^{-1}$. Therefore, a metastable state is in the local equilibrium if Eq. (1) is valid. Hence the thermodynamic description of a superheated solid is possible. However, one needs more information about a metastable system (the knowledge of $\bar{\tau}$) than about a stable one.

Microscopic Picture

Let us consider a system of N particles arranged in the f.c.c. crystal structure defined by vectors $\vec{R}_i = k\vec{e}_1 + l\vec{e}_2 + m\vec{e}_3$, where $(\vec{e}_i\vec{e}_j) = a^2\delta_{ij}$ and $k + l + m = 2i$, $i = 1, \ldots, N$. The system is considered to be in equilibrium at temperature T and volume V ($V = N/n$, where $n = 4/a^3$ is the corresponding number density). We assume that the system is in the periodic boundary conditions (PBC) in each dimension.

Let ρ denote the probability density in the phase space that corresponds to the NVT ensemble. The average value of some quantity $A(\Gamma)$ is defined by: $\langle A\rangle \equiv \int A(\Gamma)\rho(\Gamma)\mathrm{d}\Gamma$, where $\Gamma = (\vec{r}_1, \ldots, \vec{r}_N, \vec{v}_1, \ldots, \vec{v}_N)$ is the phase point, $\vec{r}_i$ and $\vec{v}_i$ are the coordinate and velocity of the i-th particle. $\langle A\rangle$ is a function of N, V and T.

For the classical f.c.c. crystal in equilibrium at the temperature T the following expressions are valid:

$$\int \rho\,\mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{r}_N = \exp\left(-\frac{1}{kT}\sum_{i=1}^{N}\frac{m\vec{v}_i^2}{2}\right), \qquad (2)$$

$$\langle \vec{r}_i - \vec{R}_i\rangle = 0, \quad \frac{\langle(\vec{r}_i - \vec{R}_i)^2\rangle}{\sqrt{2}a} = \delta_L, \qquad (3)$$

where δ_L depends on temperature T. The expression (2) stands for the fact that the velocity distribution is Maxwellian while the expression (3) tells that particles fluctuate near their ideal lattice sites. The raise of temperature leads to larger fluctuations and to the decay of the lattice.[†]

The introduced probability density $\rho = \rho(N, V, T)$ does not vary in time for stable states $T < T_\mathrm{m}$. For $T > T_\mathrm{m}$ the crystal is superheated and metastable: the density ρ is constant only for time intervals $t < \bar{\tau}$ (see Eq. (1)) until Eqs. (2) and (3) are valid.

The evolution of $\rho = \rho(t)$ can be expressed as the motion of individual phase points $\Gamma = \Gamma(t)$,

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[†] We use the term "decay" but not "melting" in order to emphasize the difference between the equilibrium melting at $T = T_\mathrm{m}$ (phase coexistence) and the spontaneous liquid nucleation inside the superheated solid at $T > T_\mathrm{m}$.

$\Gamma(0) = \Gamma_0$. The phase space of the N-body system considered can be subdivided into two regions, Δ_{crystal} and Δ_{liquid}. The former corresponds to the crystal structure, the latter to the liquid. One can determine the lifetime of the metastable crystal structure τ as:

$$\tau : \begin{cases} \Gamma(t) \in \Delta_{\text{crystal}}, & 0 < t < \tau \\ \Gamma(t) \in \Delta_{\text{liquid}}, & \tau + \Delta\tau < t \end{cases} \tag{4}$$

where τ is the moment when the decay starts and $\Delta\tau$ is a certain time of the transition from a metastable to an equilibrium state. The particular value of lifetime depends on the initial configuration: $\tau = \tau(\Gamma_0)$. The average lifetime of the metastable structure at temperature T is:

$$\bar{\tau} \equiv \langle\tau\rangle = \int \tau(\Gamma)\,\rho(\Gamma)\,\mathrm{d}\Gamma \tag{5}$$

Homogeneous Nucleation Rate

The solid-to-liquid transition in the bulk of an ideal metastable crystal can be described as the homogeneous nucleation, i.e. the spontaneous (fluctuational) formation of a liquid nuclei and their growth. This process is characterized by the nucleation rate J that is an average number of critical nuclei appeared in the unit volume in the unit of time. The temperature dependence the homogeneous nucleation rate is usually written as

$$J(T) = J_0 \exp\left(-\frac{W(T)}{T}\right), \tag{6}$$

where $W(T)$ is the activation energy of the process, i.e. the work for the critical nucleus formation. The standard approach gives [23]:

$$W(T) \propto \frac{T_m^2}{(T - T_\mathrm{m})^2}. \tag{7}$$

If the system considered in the previous section is not very large or small in comparison with the size of the critical nucleus one may assume that the transition from crystal into liquid goes by the fluctuational formation and subsequent growth of one liquid nucleus. This assumption finds its approval in the simulation results.

If this is the case, the nucleation rate is expressed as[‡]

$$J = 1/(\bar{\tau}V). \tag{8}$$

Unlike average lifetime $\bar{\tau}$ the homogeneous nucleation rate does not depend on the volume of the system. For the given number density n it depends only on temperature: $J = J(T; n)$.

Nucleation as a Random Process

Nucleation of a new phase in the homogeneous system can be considered as a random process [23]. The probability of the formation of the critical liquid nucleus in the small time interval $(t,\ t + \delta t)$ can be written as $\lambda\delta t$. Then the probability of the absence of nucleation events is $1 - \lambda\delta t$. Let P_0 denote the probability that there is no critical nuclei in the system considered up to the moment $t + \delta t$. Then: $P_0(t + \delta t) = (1 - \lambda\delta t)P_0(t)$. In the limit $\delta t \to 0$: $\mathrm{d}P_0/\mathrm{d}t = -\lambda P_0(t)$.

Under stationary conditions $\lambda(t) = \text{const}$. The condition $P_0(0) = 1$ gives

$$P_0(t) = \exp(-\lambda t), \tag{9}$$

where λ^{-1} is the average time of the nucleus formation, i.e. $\lambda = \bar{\tau}^{-1} = JV$.

Under non-isothermal conditions λ depends on the temperature T (as J) and therefore on time t. In this case:

$$P_0(t) = \exp\left(-\int_0^t \lambda(t)\,\mathrm{d}t\right). \tag{10}$$

The probability density of the first critical nucleus formation is

$$\omega_1(t) = \frac{\mathrm{d}(1 - P_0(t))}{\mathrm{d}t} = \lambda(t)\exp\left(-\int_0^t \lambda(t)\mathrm{d}t\right). \tag{11}$$

If the heating rate is constant ($\dot{T} \equiv \mathrm{d}T/\mathrm{d}t = \text{const}$) the previous equation can be rewritten as:

$$\omega_1(T) = \frac{J(T)V}{\dot{T}} \exp\left(-\frac{V}{\dot{T}}\int_{T_0}^{T} J(T)\mathrm{d}T\right). \tag{12}$$

Molecular Dynamics Model

The MD simulation consists of the numerical integration of the classical equations of motion for the N-body system. The interaction forces are usually determined by the potential function $U = U(\vec{r}_1, \ldots, \vec{r}_N)$.

$$m_i \frac{\mathrm{d}\vec{v}_i(t)}{\mathrm{d}t} = -\frac{\partial U}{\partial \vec{r}_i}, \quad \frac{\mathrm{d}\vec{r}_i(t)}{\mathrm{d}t} = \vec{v}_i, \quad \Gamma(0) = \Gamma_0 \tag{13}$$

It is a Cauchy problem for $3N$ ordinary differential equations. For most dynamical systems the general fact of the theory is valid that the Cauchy problem has the unique solution $\Gamma(t)$ for the given initial conditions Γ_0. MD gives the approximation $\tilde{\Gamma}(t)$, $t = k\Delta t$, where Δt is the integration time step. The tilde denotes a quantity calculated via MD.

To simulate ideal crystal without open surface the 3D PBCs are applied. The soft sphere pair potential

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[‡] This expression was used in experimental investigations (e.g. see Refs. [23,24]) and MD calculations [13] of homogeneous nucleation rate).

is chosen: $U = \sum_{i<j} \epsilon(\sigma/|\vec{r}_i - \vec{r}_j|^{12})$. The potential cut-off radius is 1.6σ. The reduced units are used: ϵ for energy and temperature, σ for length, $(m\sigma^2/\epsilon)^{1/2}$ for time. All the data presented correspond to the number density $n\sigma^3 = 1$. The integration time step Δt is chosen to be 0.005 units of time. The wide range of system sizes is explored: from $N = 108$ up to 32000.

LIFETIME OF A SUPERHEATED CRYSTAL AT CONSTANT TEMPERATURE

In MD simulation of equilibrium thermodynamic properties, one can make the averaging over the calculated phase trajectory based on the expression

$$\langle A\rangle = \lim_{t\to\infty} \frac{1}{t}\int_0^t A(\Gamma(t))\mathrm{d}t. \qquad (14)$$

It means that ensemble averages are estimated by time averages [1]. The expression (14) is not useful to calculate non-equilibrium time-dependent properties. In this work we are concerned about the calculation of the lifetime of the metastable superheated crystal. To do this we sample the probability density ρ according to the following procedure:

1. The ideal lattice of N particles is generated for the fixed lattice constant a. Particle velocities are distributed randomly. The system is equilibrated. The resulting equilibrium state Γ_{00} corresponds to some temperature $T < T_{\mathrm{m}}$, where T_{m} is the equilibrium melting temperature for the given a.
2. A required degree of superheating $\Delta T \equiv T - T_{\mathrm{m}}$ is reached by the coupling of the system with the imaginary thermostat (e.g. the velocity rescaling method [25]). To prevent a spontaneous decay before the temperature T is reached, we use the artificial spherical restrictions on particle motion. Each lattice site $\vec{R}_i$ is surrounded by the imaginary spherical surface. The radius of these spheres is equal to one half of the nearest neighbour distance ($a/\sqrt{2}$ for the f.c.c. lattice). During thermal motion particles are reflected from such surfaces. The configuration obtained at this step is Γ_0^{r} (the index r means "restriction").
3. Starting with the configuration Γ_0^{r} MD trajectory $\tilde{\Gamma}^{\mathrm{r}}(t)$ is calculated. The *NVT* MD is used. The described restrictions on particle motion are applied. M independent phase points are selected on this trajectory: $\Gamma_j^{\mathrm{r}} = \tilde{\Gamma}^{\mathrm{r}}(k_j\Delta t),\ j = 1,\ldots,M$. We assume that the probability density

$$\tilde{\rho}(\Gamma) = \frac{1}{M}\sum_{j=1}^{M} \delta\Big(\Gamma - \Gamma_j^{\mathrm{r}}\Big), \qquad (15)$$

approximates $\rho(\Gamma)$ (δ is the delta-function). Apparently, the approximation becomes better as M increases.

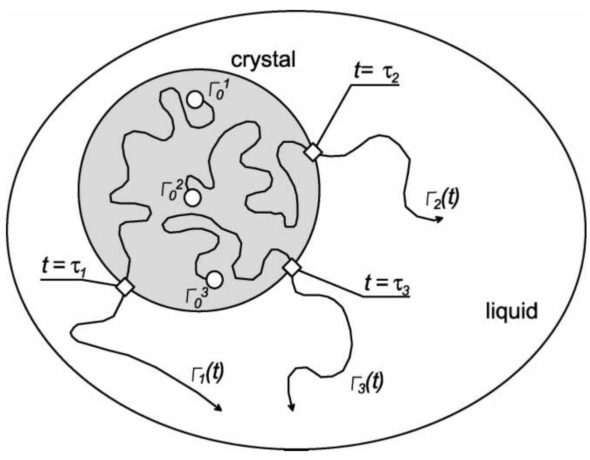

FIGURE 1 The scheme illustrates the motion of the many-particle system in the phase space. The grey area corresponds to the ordered configurations, which have the f.c.c. crystal structure. An ensemble of phase points Γ_0^k describes a metastable (superheated) crystal. Each of the outgoing phase trajectories $\Gamma_k(t)$ initially evolves in the domain of crystal but after some period τ_k undergoes the transition into the region of disordered (liquid) configurations.

4. For each of the selected phase points Γ_j^{r} the new trajectory is calculated. The conventional *NVE* MD is used *without* restrictions on particle motion. Each trajectory is calculated up to the complete disordering of the system, i.e. the transition from $\Delta_{\mathrm{crystal}}$ to Δ_{liquid}. The value of the lifetime τ_j of the metastable ordered crystal structure is obtained for each Γ_j^{r} (see Fig. 1).
5. The result of the described steps are a set of M lifetime values $\{\tau_j\}$. According to Eq. (5) and Eq. (15) one can express the ensemble average for the lifetime simply as an arithmetical average

$$\bar{\tau} \simeq (\tau_1 + \cdots + \tau_{\mathrm{m}})/M. \qquad (16)$$

The transition of the metastable crystal into liquid is shown on the pressure and temperature dependencies on time (Fig. 2). Such dependencies show that there is an initial period when the crystal "lives" in the superheated metastable state and then spontaneously melts. Lifetime values are different for the ensemble of initial configurations Γ_j^{r} corresponding to the same initial temperature.

The analysis of the structural transformation in the simulation cell shows that for $N < 2048$ the transition goes as simultaneous disordering of the crystal structure inside the cell. For $N \geq 2048$ it is possible to determine the nucleation process (Fig. 3). The birth of the nucleus corresponds to the moments τ_j.

One can consider these M lifetime values as a realization of the random process: the homogeneous nucleation in the superheated crystal. The probability (9) can be approximated as $P_0(t) \simeq \sum_j \theta(\tau_j - t)/M$, where θ is the Heviside function

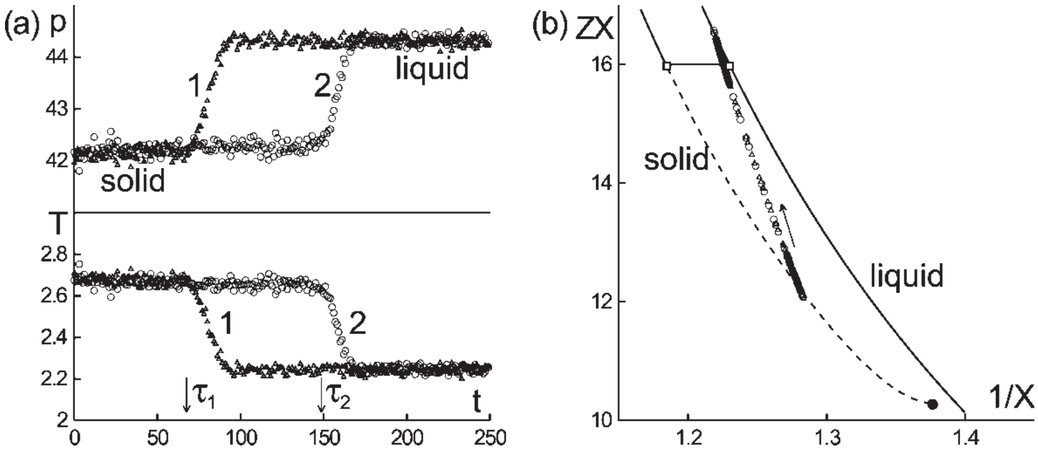

FIGURE 2 Synchronized pictures of the microscopic (a) and macroscopic (b) description of the spontaneous decay of superheated crystal: (a) The dependencies of the instantaneous pressure p and temperature T on time t for two MD trajectories (open circles and triangles, respectively). The initial conditions for these trajectories correspond to one ensemble of initial configurations with temperature $T = 2.66$. The distinctive step on the dependencies correspond to the transition from metastable crystal into liquid state. The lifetimes of the superheated crystal structure for these trajectories τ_1 and τ_2 are marked by arrows. $N = 6912$. (b) The transition is represented in the reduced thermodynamical variables $X = (n\sigma^3/\sqrt{2})(\epsilon/T)^{1/4}$ and $Z = p/(nT)$. The equation of state of the f.c.c. crystal and liquid (in variables $1/X$ and ZX) are shown as solid curves [5,12]; open squares indicate equilibrium Solid–liquid transition; metastable part of the solid branch are shown dashed; the fill circle is the spinodal point. Open circles and triangles correspond to the data on the subfigure (a).

(Fig. 4(a)). These distributions are calculated for different values of superheating and are in a good agreement with Eq. (9) when λ is taken from Eq. (16).

Having carried out calculations of $\bar{\tau}$ for different temperatures and using Eqs. (6)–(8) one can estimate the temperature dependence of the homogeneous nucleation rate for the given number density (Fig. 4(b)). In spite of the fact that the mechanisms of the transformation for small systems and for large systems differ, the points on the $J - T$ plot fall on the same curve. Once obtained, $J(T)$ dependence can be extrapolated to the lower temperatures that are not reachable for the direct MD calculation because corresponding lifetimes increase exponentially fast and usually are beyond computational time limits.

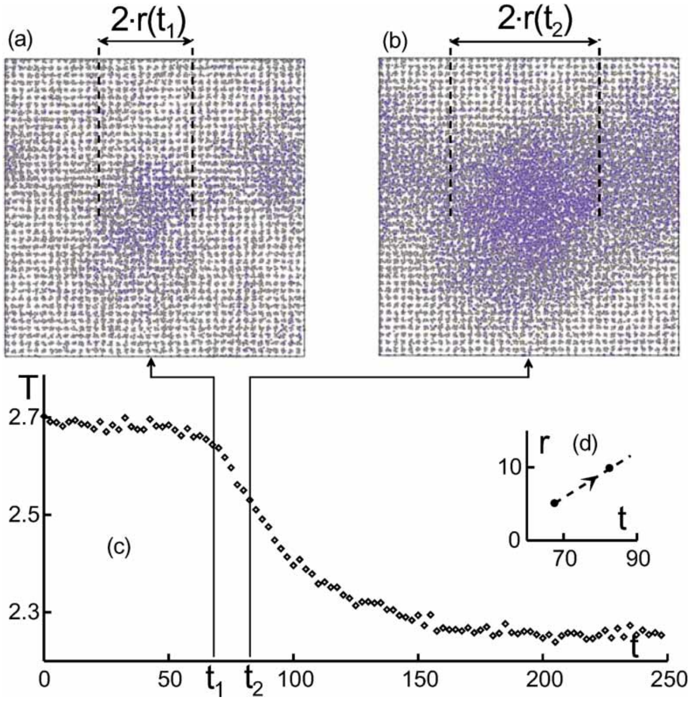

FIGURE 3 The synchronized illustration of the nucleation during the crystal-to-liquid transition in the MD cell. Subfigures (a) and (b) are the snap-shots of the particle structure in the simulation cell ($N = 32000$) for two moments of time t_1 and t_2 (the shift under PBC was made in order to move the nucleus in the center). Larger circles correspond to the particles, which displacements from the ideal lattice sites are greater than one half of the nearest-neighbor distance. Subfigure (c) displays the corresponding temperature dependence where the moments t_1 and t_2 are shown. The inset (d) gives the dependence of the radius of the liquid nucleus on time for this particular trajectory. (Colour version available online.)

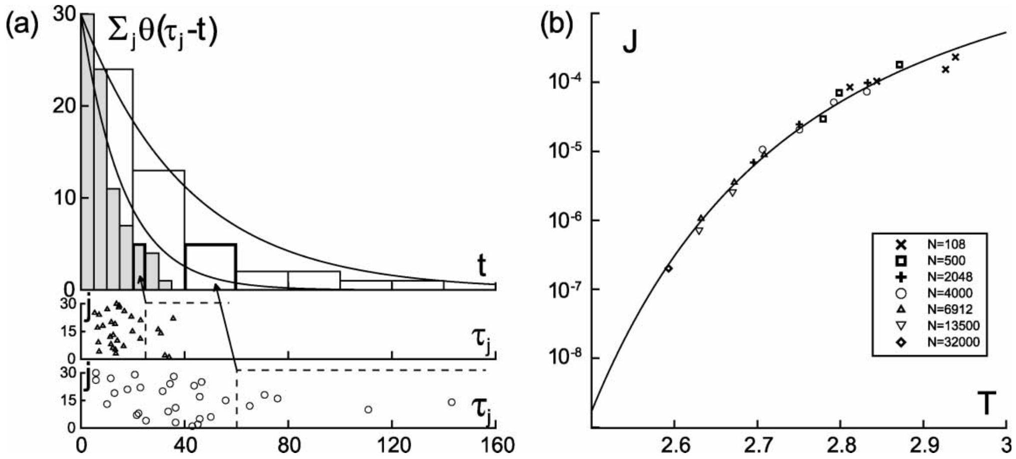

FIGURE 4 Direct (a) and processed (b) results of MD calculation of superheated crystal lifetimes for the ensemble of initial configurations: (a) Integral distributions of lifetimes of the superheated crystal: the number of trajectories, on which decay starts after moment t, i.e. $\sum_{j=1}^{M}\theta(\tau_j - t)$ (θ is the Heviside function). The method of distribution creation is illustrated by dashed lines and arrows. Data for two ensembles of trajectories with different values of temperature are shown ($M = 30$) : $T = 2.67$ (white), $T = 2.71$ (grey). $N = 6912$. Smooth solid lines are calculated as $M\exp(-t/(\sum_{j=1}^{M}\tau_j/M))$. (b) Symbols are the values of the homogeneous nucleation rate $J = (V\sum_{j=1}^{M}\tau_j/M)^{-1}$ calculated for different temperatures T and system sizes N (V is the volume of the simulation cell). Solid line is the best fit by Eqs. (6) and (7): $18.9\times10^{-3}\exp[-2.93T_m^2/(T(T-T_\mathrm{m})^2)]$, where $T_\mathrm{m} = 1.97$ [5].

From the $J(T)$ dependence one can estimate the kinetic limit of solid phase superheating [26,27]. It is also interesting to compare the homogeneous nucleation rate dependence on temperature obtained via the described approach with that calculated from phenomenological data (e.g. Ref. [26]) providing the realistic interatomic potential is used. This will be done in our future work.

CRYSTAL DECAY AT CONSTANT RATE HEATING

The slightly different scheme was used to simulate the decay under heating. The temperature of the crystal structure is increasing with a constant heating rate $\dot{T} \equiv \mathrm{d}T/\mathrm{d}t$ starting with the initial temperature $T \le T_\mathrm{m}$. We are interested in the value of the highest temperature T^h that can be reached until crystal begins to decay. Calculations are done according to the following steps:

1. The trajectory $\tilde{\Gamma}(t)$ was calculated from the equilibrium configuration Γ_{00} (see above). The *NVT* MD is used. M independent phase points are selected on this trajectory: $\Gamma_j = \tilde{\Gamma}(k_j\Delta t)$, $j = 1,\ldots,M$.
2. For each of the selected phase points the trajectories $\tilde{\Gamma}_j^\mathrm{h}(t)$ are calculated. Along each trajectory the temperature of the crystal is linearly

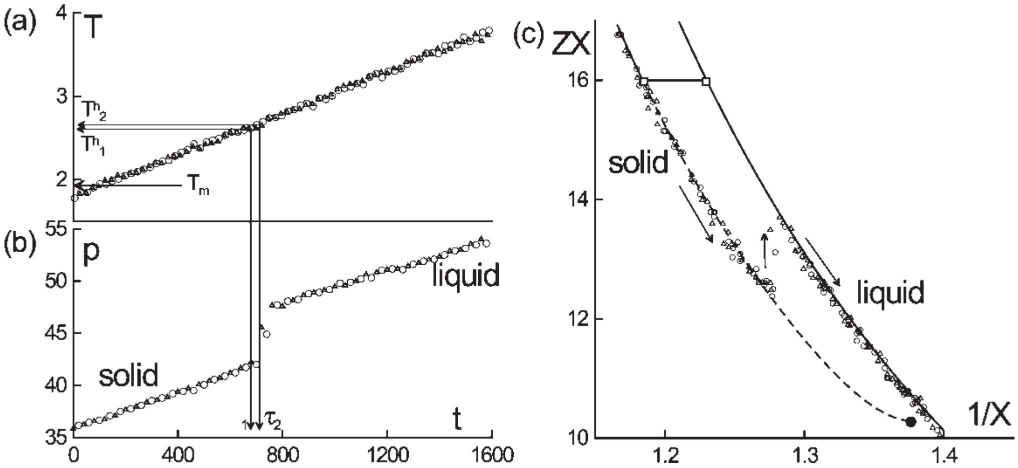

FIGURE 5 Synchronized pictures of the microscopic (a,b) and macroscopic (c) description of the crystal decay at the constant rate heating: (a) The dependence of the instantaneous temperature on time for two MD trajectories obtained with constant heating rate $\dot{T} = 1.25\times10^{-3}$ from different initial configurations (open circles and triangles). The equilibrium melting temperature $T_\mathrm{m} = 1.97$ is shown as well as the temperatures of the beginning of decay on each trajectory T_1^h and T_2^h. (b) The pressure-time dependence for these trajectories. The beginning of the decay is determined by the jump of pressure. The corresponding times τ_1 and τ_2 are marked by arrows. (c) The transition is represented in the reduced thermodynamical variables X and Z (see caption for Fig. 2(b).

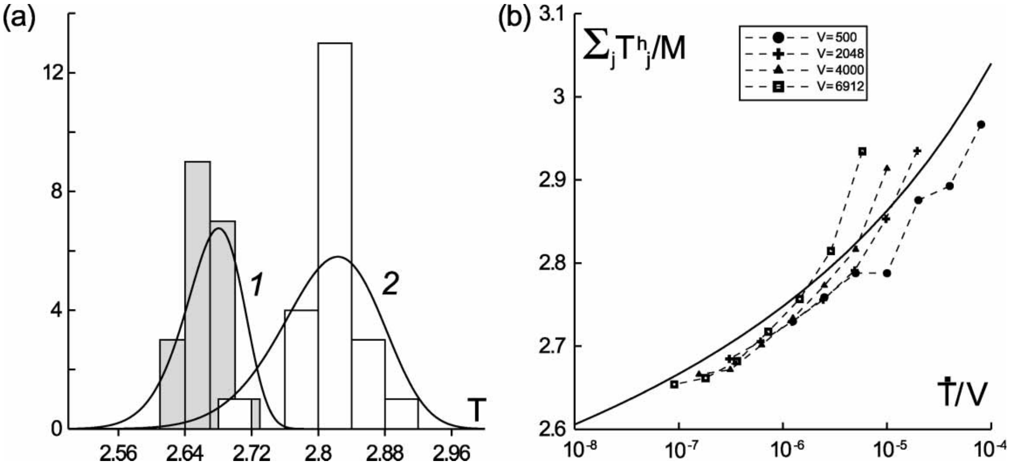

FIGURE 6 Direct (a) and processed (b) results of MD calculation of the crystal decay at the constant rate heating for the ensemble of initial configurations: (a) Hystograms give the number of trajectories from the ensemble of M trajectories on which decay starts in the temperature interval $(T, T + \Delta T)$, $\Delta T = 0.03$. $N = 4000$. Two distributions correspond to two different rates of heating: $\dot{T} = 2 \times 10^{-2}$ (white, $M = 22$), $\dot{T} = 6.25 \times 10^{-4}$ (grey, $M = 20$). Smooth solid lines are calculated as $M\Delta T\omega_1(T)$ (see Eq. (12)). (b) The average reachable temperature $\sum_{j=1}^{M} T_j^{\mathrm{h}}/M$ as a function of the ratio $\dot{T}/V$, where V is the volume of the simulation box. Symbols are data for different system sizes N; dashed lines connect the symbols in order to guide the eye. Solid line is obtained as the temperature of the maximum of $\omega_1(T)$ for different values of $\dot{T}/V$.

increasing. It is done by velocity rescaling [25]. The scaling is done at every time step by the constant determined as:

$$\chi = \left[1 + \frac{\Delta t}{t_{\mathrm{rel}}}\left(\frac{T_{\mathrm{ext}}}{\mathcal{T}} - 1\right)\right]^{1/2}, \qquad (17)$$

where $\mathcal{T}$ is the instantaneous temperature, T_{ext} is the thermostat temperature and t_{rel} is the time relaxation parameter. The thermostat temperature is incremented at every step: $T_{\mathrm{ext}}(k\Delta t) = T_{\mathrm{ext}}((k-1)\Delta t) + \dot{T}\Delta t$. The relaxation parameter is chosen so that $t_{\mathrm{rel}} \ll t_i$ (see Eq. (1)). Since the heating rates under consideration are relatively low ($\dot{T}\Delta t \ll T$) the system can be treated as equilibrium at every time step.

3. The ensemble of M trajectories $\{\tilde{\Gamma}_j^{\mathrm{h}}(t)\}$ is obtained at the given value of the heating rate $\dot{T}$. On the j-th trajectory the crystal structure decays at some particular temperature T_j^{h} (see Fig. 5).

These M values of temperature are realizations of the random process of nucleation under heating. The histogram of T_j^{h} values can be plotted (Fig. 6(a)). On the other hand the histogram can be checked according to Eq. (12) since the function $J(T)$ is known (see the previous section). The agreement between these two *independent* approaches is rather good, although distributions calculated directly via MD are somewhat higher and thinner than those obtained by the formula (12). The agreement is the evidence of the consistency of the results and their interpretation.

The highest average reachable temperature T^{h} can be estimated as $\sum_j T_j^{\mathrm{h}}/M$ (Fig. 6(b)). This value depends on the system size N (volume V) and on the heating rate $\dot{T}$. The same quantity can be estimated as the temperature of the maximum of $\omega_1(T)$ from Eq. (12). Figure 6(b) shows that the agreement of these approaches is generally good as well. It becomes worse for smaller system sizes and higher heating rates. However, it should be mentioned that the interpretation of the observed decay transition as nucleation is reasonable only for relatively large systems ($N \geq 2048$). High heating rates could lead to the artificial influence on the particle's dynamics that may be also the reason of the discrepancy of the results.

LYAPUNOV INSTABILITY AND CAUCHY PROBLEM IN MD

In this section, we would like to touch upon a question of the accuracy of MD calculations and some peculiarities connected with the simulation of the decay transition considered.

The set of equations (13) for MD systems is chaotic (exponentially unstable) [1,28–30]. The consequence is that two initially close phase trajectories diverge exponentially fast.

The measure of divergence at the moment t can be chosen as:

$$\langle \Delta r^2(t) \rangle \equiv \frac{1}{N}\sum_{i=1}^{N}(\vec{r}_i(t) - \vec{r}\,'_i(t))^2,$$

$$\langle \Delta v^2(t) \rangle \equiv \frac{1}{N}\sum_{i=1}^{N}(\vec{v}_i(t) - \vec{v}\,'_i(t))^2, \qquad (18)$$

where $\vec{r}_i$, $\vec{v}_i$ and $\vec{r}'_i$, $\vec{v}'_i$ are coordinate and velocity of the i-th particle on the 1st and the 2nd

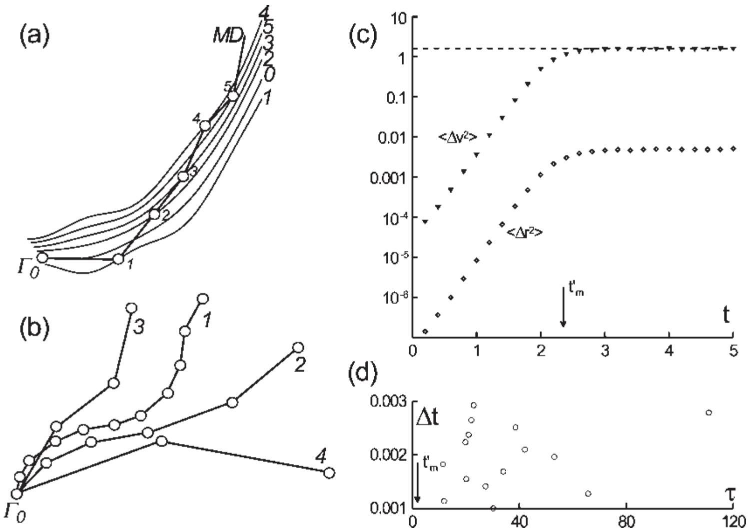

FIGURE 7 Schematic (a,b) and numerical (c,d) pictures, which illustrate the approximate character of the MD method: (a) MD trajectory (open circles) is the approximation of the hypothetical exact solutions of the Cauchy problem. Solid lines represent such solutions for each phase point on the MD trajectory. There are no two MD points that belong to the same exact solution of the Cauchy problem. (b) An illustration of the bundle of trajectories calculated from the same initial configuration with different integration time steps. Open circles are phase points on the MD trajectories taken every thousand (for example) of steps. (c) Divergencies of coordinates $\langle \Delta r^2 \rangle$ and velocities $\langle \Delta v^2 \rangle$ for two MD trajectories calculated from the same initial configuration with different time steps $\Delta t = 0.001$ and $\Delta t' = 0.0001$. The arrow marks the time t'_{m} when these two trajectories lost any correlation. The dotted horizontal line corresponds to the level of saturation of the velocity divergence at $2\langle v_T^2 \rangle = 6T$, where $T = 2.67$ is the temperature of the crystal. $N = 13500$. (d) The values of lifetime τ for trajectories calculated with different time step Δt from the one and the same initial configuration.

trajectory, respectively. If $\langle \Delta r^2(0) \rangle > 0$ and/or $\langle \Delta v^2(0) \rangle > 0$ then

$$\langle \Delta r^2(t) \rangle = A \exp(Kt), \quad \langle \Delta r^2(t) \rangle = B \exp(Kt), \qquad (19)$$

where A and B are constants depending on the magnitude of the initial perturbation ($\langle \Delta r^2(0) \rangle$ and $\langle \Delta v^2(0) \rangle$), K is the maximum averaged Lyapunov exponent.

The crucial consequence of such an instability is that MD trajectories calculated from the same initial configuration with different integration time steps Δt and $\Delta t'$ diverge exponentially fast as well. Let us assume that $\Delta t' = \Delta t/2$. The finite-difference character of integration scheme leads to the fact that the resulting trajectories do not coincide just after the first several time steps: $\langle \Delta r^2(\Delta t) \rangle \neq 0$. This is the priming perturbation leading to the subsequent exponential divergence (Fig. 7).

The divergence observed in simulation changes its exponential character after a certain period t'_{m}. At the moment t'_{m} divergence goes to the saturation. This moment separates two stages: when $0 \le t < t'_{\mathrm{m}}$ two trajectories partially retain initial correlation, after ($t > t'_{\mathrm{m}}$) they become completely uncorrelated and "forget" that the their initial configurations are the same. The maximum value $\langle \Delta v^2 \rangle_{\max} = 2\langle v^2 \rangle$, since $\langle \vec{v}(t)\vec{v}'(t) \rangle = 0$ for $t > t'_{\mathrm{m}}$. The divergence of coordinates $\langle \Delta r^2(t) \rangle$ switches to the diffusive regime (in liquids it is more likely a kind of random walk regime [31]). This behaviour can not be clearly distinguished on the presented plot (Fig. 7(c)) because it corresponds to the crystal state where the diffusion coefficient is extremely small.

The value of t'_{m} depends on the time steps Δt and $\Delta t'$. One can fix the time step Δt using for calculation of the 1st trajectory and choose $\Delta t' = \Delta t/2, \Delta t/4, \Delta t/8, \Delta t/16, \ldots$. Calculations showed that the dependence of t'_{m} on $\Delta t'$ is rather weak [32]. The limiting value $t_{\mathrm{m}} = \lim_{\Delta t' \to 0} t'_{\mathrm{m}}$ is called *dynamical memory time* [32]. This quantity gives the maximum time of correlation of the exact solution of Eq. (13) $\Gamma(t)$ and the numerical MD trajectory $\tilde{\Gamma}(t)$.

Therefore, MD simulation results in a bundle of diverging trajectories instead of a unique trajectory for the Cauchy problem.

A good illustrating example is the calculation of the lifetime. We choose a particular configuration corresponding to the superheated crystal and calculate trajectories with different time steps $\tilde{\Gamma}(t; \Delta t_k)$ for one and the same initial conditions. Then the set of lifetime values is obtained. The example is given on Fig. 7(d). We see that the scatter of the resulting values τ_k is very broad. There is no convergence in the limit $\Delta t \to 0$. Therefore, we cannot determine or even estimate the exact value of lifetime for the particular initial configuration if it is larger than the dynamical memory time.

However, we can determine a distribution of values $\{\tau_k\}$. Calculations show that such distribution does not depend on the values $\{\Delta t_k\}$. These distributions can be presented in the form similar to Fig. 4(a).

The usage of MD trajectories calculated with different timesteps for the same initial conditions gives an alternative method of obtaining distributions of lifetime. Computer simulations performed show that these distributions obtained are very close to those presented in Fig. 4(a).

CONCLUSION

The approach is developed to calculate the ensemble averages of time-dependent properties in non-equilibrium processes for the case of the superheated solid decay.

The wide range of system sizes is investigated. It is shown that decay goes via nucleation for relatively large systems. Disordering of the crystal structure goes simultaneously in the whole simulation cell for small systems.

The temperature dependence of the homogeneous nucleation rate is calculated. Its shape corresponds to that derived in the classical theory of nucleation. The calculated dependence along with the formulas of the theory of non-isothermal nucleation give a good description of the decay under constant heating.

The approach gives reasonable results both for distributions and for average values. The results of the simulations in the stationary case and in the case of constant heating are shown to be consistent.

It is shown that MD method allows one to calculate the exact dynamical trajectories only for times limited by the dynamical memory time. This time is much shorter than characteristic times of interest (lifetimes in our case). Therefore, only statistical description is possible on larger timescales. This fact is generally important for the simulation of time-dependent properties in non-equilibrium processes (e.g. conformations of biomolecules and folding [33]).

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