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Bayesian statistical modeling of microcanonical melting times at the superheated regime

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ABSTRACT

Homogeneous melting of superheated crystals at constant energy is a dynamical process, believed to be triggered by the accumulation of thermal vacancies and their self-diffusion. From microcanonical simulations we know that if an ideal crystal is prepared at a given kinetic energy, it takes a random time t_w until the melting mechanism is actually triggered. In this work we have studied in detail the statistics of t_w for melting at different energies by performing a large number of Z-method simulations and applying state-of-the-art methods of Bayesian statistical inference. By focusing on a small system size and short-time tail of the distribution function, we show that t_w is actually gamma-distributed rather than exponential (as asserted in a previous work), with decreasing probability near $t_w \sim 0$. We also explicitly incorporate in our model the unavoidable truncation of the distribution function due to the limited total time span of a Z-method simulation. The probabilistic model presented in this work can provide some insight into the dynamical nature of the homogeneous melting process, as well as giving a well-defined practical procedure to incorporate melting times from simulation into the Z-method in order to correct the effect of short simulation times.

1. Introduction

It is well known that, under carefully controlled conditions, a solid can be heated above its melting temperature without triggering the melting process. This is known as superheating, and in it the solid enters a metastable state with interesting kinetic properties [1]. It is also possible to achieve such an homogeneous melting by ultrafast laser pulses [2]. As a complement to experiments, observation and characterization of this superheated state is especially clear in microcanonical simulations, particularly within the framework of the Z-method [3]. By using this methodology, it has been possible to establish the role of thermal vacancies [4,5] and their self-diffusion [6–8].

The Z-method, in fact, relies on the superheating metastable state to determine the melting temperature T_m. It establishes that in microcanonical simulations (i.e. with constant volume, constant internal energy, constant number of particles) there is a maximum energy E_{LS} (LS stands for Limit of Superheating), related to a temperature T_{LS}, that can be given to the crystal before it spontaneously melts. Beyond this point the solid unavoidably melts, showing a sudden, sharp drop in temperature, corresponding to the kinetic energy consumed as latent heat of melting. When a system melts at an energy $E_{LS} + \Delta E$ (with $\Delta E \to 0$), the final temperature T approaches T_m. Despite the current lack of a complete theory of first-order phase

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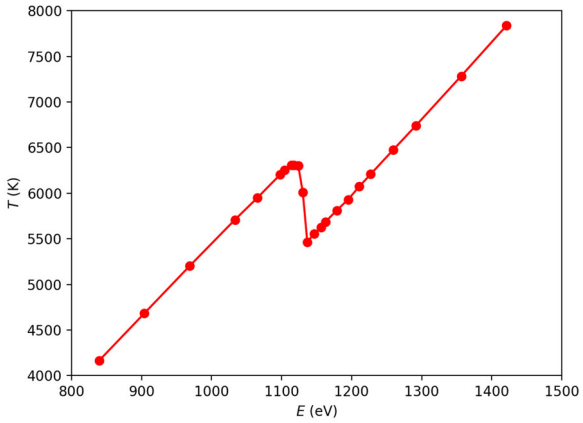

Fig. 1. Isochoric (Z) curve obtained from 23 different 50 ps simulations of high-density Ar, with initial temperatures T_0 ranging from 8000 to 17000 K. From this Z-curve we can determine $T_m \sim 5465$ K and $T_{LS} \sim 6307$ K. A clear drop of temperature is observed between $T_0 = 12500$ K and $T_0 = 12600$ K.

transitions and metastable states, there is plenty of accumulated evidence of the accuracy of the Z-method [9–11]. However, some issues remain concerning the uncertainties associated to T_m and T_{LS} due to the use of short simulation times. One important source of uncertainty is the random distribution of the elapsed time t_w from the beginning of the simulation until the melting process is triggered, even in a microcanonical setting. In previous work, Alfè et al. [12] reported statistics of t_w obtained from molecular dynamics (MD) simulations and postulated that t_w is exponentially distributed, and therefore the most probable value of t_w is close to zero for all temperatures.

In this work, we performed a large number of microcanonical simulations of a Lennard-Jones solid in order to generate statistically independent samples of t_w in a wide range of initial temperatures. We focused particularly in shorter times and a small system size and found that these "waiting times" are not exponentially distributed but gamma-distributed. Accordingly, we present a precise model that reproduces the gamma shape and scale parameters as functions of the initial temperature.

The rest of the paper is organized as follows. In Section 2 we give a detailed description of the simulations that were used to determine the melting temperature and the samples of waiting times (t_w). Section 3 describes the probability models proposed to represent the statistical distribution of t_w and assesses their likelihood given our simulated data. Next, Sections 4 and 5 present a concrete model for the distribution of t_w as a function of temperature fitted to our simulation data. Finally, Section 6 discusses the implications of our results for the process of melting in the superheating state for homogeneous solids.

2. Computational procedure

As a simple model of solid we considered the Lennard-Jones potential with $\epsilon/k_B = 119.8$ K and $\sigma = 3.41$ Å, as used in previous works on the Z-method [3,4]. A high-density, face-centered cubic (FCC) crystal, having 500 atoms and lattice constant $a = 4.2$ Å, was used as the starting point for all simulations. The use of such a high density (and therefore pressure) increases the superheating effect, revealing the melting process in a more salient way. All simulations were performed using the LPMD [13] molecular dynamics package. For every case we use a total simulation time $\tau_0 = 50$ ps and a timestep $\Delta t = 0.5$ fs with a Beeman integrator for Newton's equations of motion. Our aim is to completely characterize the statistical distribution of waiting times t_w for a small system size N and limited window of time, so that we can perform predictions for larger simulation times at the same N.

A set of 400 simulations with temperatures ranging from 50 K to 20000 K have been used to draw an isochoric $T(E)$ curve for this high-density argon model, in a standard application of the Z-method. We will refer to this $T(E)$ curve as the Z-curve, although the same name has been used in previous works to refer to the isochoric $T(P)$ curve. We prefer the use of the internal energy as the independent variable instead of the pressure is to be preferred because of the possibility of a non-monotonic trend of pressure and temperature, as observed for instance in the case of lithium [14]. In those cases where the melting curve has a region with negative $(\partial T/\partial P)_E$, the $T(P)$ isochore reverts direction while the $T(E)$ isochore is unaffected, as C_v is non-negative for solid and liquid equilibrium branches.

These results are shown in Fig. 1.

From the isochoric $T(E)$ curve, we have estimated the melting temperature T_m and the superheating limit T_{LS}. The sharp inflection at the higher temperature (6307 K) corresponds to T_{LS} and the lower inflection (5465 K) corresponds to T_m.

Once T_{LS} is estimated, and in order to collect statistically independent samples of waiting times, we performed a large number of classical MD runs for each of the 24 different initial temperatures T_0 in the interval from $T_0 = 12075$ K to $T_0 = 13300$ K. This was done as follows. For the temperatures between 12000 K and 12250 K, 10000 simulations per