The kinetics of homogeneous melting beyond the limit of superheating

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Molecular dynamics simulation is used to study the time-scales involved in the homogeneous melting of a superheated crystal. The interaction model used is an embedded-atom model for Fe developed in previous work, and the melting process is simulated in the microcanonical (N, V, E) ensemble. We study periodically repeated systems containing from 96 to 7776 atoms, and the initial system is always the perfect crystal without free surfaces or other defects. For each chosen total energy E and number of atoms N, we perform several hundred statistically independent simulations, with each simulation lasting for between 500 ps and 10 ns, in order to gather statistics for the waiting time τ_w before melting occurs. We find that the probability distribution of τ_w is roughly exponential, and that the mean value $\langle \tau_w \rangle$ depends strongly on the excess of the initial steady temperature of the crystal above the superheating limit identified by other researchers. The mean $\langle \tau_w \rangle$ also depends strongly on system size in a way that we have quantified. For very small systems of $\sim$100 atoms, we observe a persistent alternation between the solid and liquid states, and we explain why this happens. Our results allow us to draw conclusions about the reliability of the recently proposed Z method for determining the melting properties of simulated materials and to suggest ways of correcting for the errors of the method. © *2011 American Institute of Physics*. [doi:10.1063/1.3605601]

I. INTRODUCTION

The supercooling of liquids below their thermodynamic freezing point is familiar and easily observable, but the superheating of solids above their melting point is much more difficult to study. This is because melting is usually initiated at surfaces (grain boundaries and other defects may also initiate melting), so that superheating is generally possible only in solids that have no surfaces.[1] Melting from the defect-free superheated state, sometimes called "homogeneous melting," has been experimentally observed,[2–5] but there is still rather little detailed understanding of the kinetics of the process. Fortunately, computer simulation offers a rather straightforward way of studying superheated defect-free solids, and this has led to a recent resurgence of interest in the subject.[6] In addition to the purely scientific interest, it has recently been shown that the concept of the "superheating limit" leads naturally to a simulation technique known as the "Z method" that offers a new and potentially useful way of determining the melting properties of simulated materials.[7] In the present paper, we report new simulation results on the kinetics of homogeneous melting which shed light on the conditions needed for the Z method to yield reliable results.

The study of melting properties by computer simulation dates back over 50 years.[8] Two main approaches have become firmly established over that period. The first relies on the separate calculation of the free energies of the solid and liquid, and is based on the fact that the two phases coexist in thermal equilibrium when both the pressures and the chemical potentials in the solid and liquid are equal.[9–11] The second approach consists of the explicit simulation of coexisting solid and liquid in the same simulated system.[12] For any given interaction model, careful application of the two approaches to large enough systems should yield essentially identical results for the relation between melting temperature T_m and the pressure P on the melting curve, as well as other properties, including the heat and volume of fusion. The two approaches have been extensively used to determine the melting properties of a wide variety of systems interacting via classical potentials, including hard spheres,[8,13] inverse-power[14,15] and Lennard-Jones models,[16] as well as more complex models such as the Born-Mayer model of ionic liquids,[17] a variety of models for water,[18] and the embedded-atom model for metals.[19,20] In the past 15 years, there has been rapidly increasing interest in the determination of melting properties using *ab initio* molecular dynamics simulation (AIMD) based on density-functional theory (DFT). Initially, the free-energy route was used,[21–23] with thermodynamic integration employed to compute the difference of free energy between the *ab initio* system and an appropriately chosen reference system. The coexistence approach has also been extensively used, mainly with parameterised classical potentials tuned to data produced by DFT simulations on the solid and liquid. However, there have also been several studies in which direct *ab initio* simulations of coexisting solid and liquid have been performed on systems of several hundred atoms.[24–29]

The point of departure of the Z method[7] is an apparently simple question about the superheating of a solid. If a solid

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is allowed to evolve under the classical equations of motion at constant number of atoms N, volume V and internal energy E, what is the maximum energy E_{LS} it can have without eventually transforming completely into the liquid state? The proposed answer[7] is that it is the lowest energy on the given isochore within the field of thermodynamic stability of the liquid.[30] This energy E_{LS} corresponds to a temperature T_{LS} representing the limit of superheating, above which the solid, evolving at constant energy, will always melt. Since E_{LS} is the lowest energy of the liquid on the isochore, it should be the energy of the liquid in coexistence with the solid so that the energy E_{LS} of the liquid is associated with the melting temperature T_m:

$$E^{sol}(V, T_{LS}) = E^{liq}(V, T_m). \qquad (1)$$

The procedure for determing the point (T_m, P) on the melting curve belonging to a specified liquid-state V is then to perform a sequence of (N, V, E) MD simulations, monitoring T and P in each, the aim being to locate the threshold E_{LS} (equivalently, the threshold T_{LS}), above which the transition to the liquid always occurs, and below which it never occurs.[7]

Implicit in these statements is an important question about timescales, i.e., about the kinetics of homogeneous melting. The original papers about the Z method[7] emphasise that in order to be reasonably certain whether the initial T is above or below T_{LS}, evolution must be allowed over a long enough time, which may be on the order of nanosecond, and the number of atoms N must also be large enough. (For simplicity, we assume here a single-component system of atoms.) This naturally raises a number of important questions, which we shall try to answer. First, since homogeneous melting in constant-(N, V, E) dynamics appears to be a rare-event process, we want to examine the probability distribution of waiting times τ_w before the transition occurs. This means repeating the simulation many times with the same (N, V, E) but with statistically independent initial conditions. Second, we want to study how the mean waiting time $\langle \tau_w \rangle$ depends on how far above T_{LS} the system is initiated. Third, we need to determine the dependence of $\langle \tau_w \rangle$ on the system size N. Naturally, the numerical answers to these questions will depend on the nature of the system and the number density $n = N/V$. Given the recent interest in using the Z method for the melting of metals,[31] particularly at high pressures,[32,33] we have decided to study the statistics of τ_w using an embedded atom model (EAM) for Fe, whose melting properties are already well known from previous work.[34] We will also present Z-method calculations on the melting of Fe using AIMD. We take a density corresponding to the megabar pressures typical of the Earth's core.

In Sec. II, we summarise the details of the interaction model and the simulation procedures. Our results on the statistical distribution of τ_w and the dependence of $\langle \tau_w \rangle$ on initial and final temperatures and system size from EAM and AIMD simulations are presented in Sec. III. In Sec. IV, we discuss the implications of our results for the understanding of homogeneous melting and for the reliability of the Z method, particularly in the context of *ab initio* simulations.

II. TECHNIQUES

The EAM for Fe used in our simulations is the one used as a reference system in our earlier work[34] on the *ab initio* melting curve of hcp Fe. Essentially the same EAM was also used in the very recent work of Belonoshko *et al.*,[33] in which they used the Z method to study the melting of Fe and an Fe/Si alloy. The model is actually a modification of a much earlier EAM developed originally by Belonoshko's group.[35] We recall that in an EAM scheme the total potential energy E_{tot} is expressed as a sum of atomic energies: $E_{tot} = \sum_i E_i$, with the sum running over the N atoms in the system. Each term is a sum of two parts: $E_i = E_i^{rep} + F(\rho_i)$. Here, E_i^{rep} consists of a sum of repulsive inverse-power pair potentials: $E_i^{rep} = \sum_j{}' \epsilon(a/r_{ij})^n$, where r_{ij} is the distance between atoms i and j, and the term $i = j$ is excluded. $F(\rho_i)$ is an "embedding function" which describes the metallic bonding. It has the form $F(\rho_i) = -\epsilon C \rho_i^{1/2}$, with $\rho_i = \sum_j{}' (a/r_{ij})^m$. The values of a and m are those in the original Belonoshko model,[35] while in Ref. 34 we showed how all the other parameters could be optimised by minimising the fluctuations of the difference between the EAM and *ab initio* energies in simulations of the liquid and the high-temperature solid. The numerical values of the parameters are $a = 3.4714$ Å, $m = 4.788$, $\epsilon = 0.1662$ eV, $n = 5.93$, $C = 16.55$. We apply the spatial cut-off $r_c = 5.5$ Å, so that terms in both E_i^{rep} and ρ_i for which $r_{ij} > r_c$ are set to zero, with the usual cutting and shifting used to ensure continuity.

Following previous work,[36–38] we focus here on the melting properties of Fe in the high-pressure region that is important for understanding the solid inner core and the liquid outer core of the Earth. Specifically, we confine ourselves to pressures $P \simeq 330$ GPa, which is the pressure at the boundary between the inner and outer core.[39] From extensive simulations with our EAM on large systems containing solid and liquid in stable coexistence,[34] we know that its melting temperature at $P = 323$ GPa is 6200 ± 100 K. We have recently refined these coexistence simulations so as to reduce the statistical errors, finding that a more accurate value of T_m at this pressure is 6215 ± 10 K.

All the simulations to be presented were performed at the same density corresponding to a volume per atom V/N $= 7.139$ Å^3, which gives pressures in the region of interest. In every simulation, we start from the perfect hcp crystal, with all atoms on their regular lattice sites, and we assign random velocities drawn from a Maxwellian distribution, the velocities then being shifted and scaled so that the total momentum is zero and the kinetic energy per atom K/N has a value corresponding exactly to a chosen initial temperature $T_i = 2K/3k_B N$. Verlet's algorithm[40] was used with a time-step of 1 fs, which ensures conservation of total energy with a drift of typically no more than ~10 K over times of several nanoseconds.

We shall present simulations on systems containing N $= 96, 150, 392, 972$, and 7776 atoms. For each N and for each initial temperature T_i, we have performed several hundred MD simulations of at least 500 ps (in some cases we have continued the simulations for over 10 ns), in order to gather statistical information about the melting process. For

the larger systems, the simulations were run on large parallel computers, with each individual simulation running on 24 cores, and with typically 350 such simulations running simultaneously. This mode of operation makes it possible, for example, to run an overall total of ~1 μs of MD on the 7776-atom system in only a few hours of wall-clock time. For the small systems, we ran the calculations on single processors using local facilities.

The *ab initio* simulations were run with exactly the same technical details as described in Refs. 36–38, using the VASP code[41] with the projector augmented wave method[42,43] and an efficient extrapolation of the charge density.[44]

III. RESULTS

We start by showing some examples of homogeneous melting from our simulations on the system of 7776 atoms. Figure 1 displays the time-dependent temperature and pressure in four simulations that were all initiated from the perfect hcp crystal with exactly the same kinetic energy corresponding to the temperature $T_i = 15\,600$ K, but with statistically independent random velocities. As expected from equipartition, T drops rapidly to about half its initial value (this rapid drop is not shown in the figure), and it then fluctuates about a quasi-steady value $T_{sol} = 7590$ K for many picoseconds, before it drops again over a rather short period of ~8 ps, and then fluctuates again about a lower steady value $T_{liq} = 6315$ K. The second drop is due to melting, as we have verified by monitoring the self-diffusion of atoms via the time-dependent mean-square displacement $\langle \Delta r(t)^2 \rangle$. The appearance of atomic disorder throughout the system when the system melts is also easy to observe in movies prepared from the coordinate files. Melting is accompanied by an increase of P by ~10 GPa, which occurs over the same rather short interval as the drop in T. These effects are familiar from many previous reports on the Z method:[7,32,33] the drop in T is due to the latent heat of fusion, and the increase of P is associated with the volume increase that would occur on melting if the pressure were held

constant. We note that the waiting times τ_w that elapse before melting are different in the four examples shown. This is what we expect of a rare-event process and is consistent with the statements in earlier reports[7,32,33] that the time at which the melting transition occurs is not correlated with the details of the initial conditions. We find that the final mean temperature T_{liq} and pressure P_{liq} of the liquid are the same in all the examples. This is expected, because in every case the system settles into exactly the same thermodynamic state of the liquid. The temperature T_{liq} is somewhat above the melting temperature T_m at pressure P_{liq}, as expected because the system was initiated above the limit of superheating.

These observations naturally raise the question of the statistical distribution of waiting times τ_w. To investigate this, we have to repeat the simulations many times, starting always from the perfect lattice with exactly the same initial kinetic energy, but independent random velocities. To make the question well posed, we need a definition of τ_w. We note from Fig. 1 that the fluctuations of T about its mean value in the quasi-steady state of the solid before melting are much smaller than the drop of T during the melting process. We therefore define τ_w to be the elapsed time from the start of the simulation to the instant when T is mid-way between the mean quasi-steady temperature T_{sol} of the solid and the mean final temperature T_{liq} of the liquid.

For the 7776-atom system with $T_i \simeq 15\,800$ K, we repeated the simulations 350 times, with each run having a duration of 650 ps. We found that it melted in all cases, and we accumulated the histogram of τ_w shown in Fig. 2. We see that after a short incubation time of no more than ~20 ps, the probability distribution of τ_w decays in a quasi-exponential way. This is what we expect if melting is a random process having short memory time with a constant probability per unit time $1/\tau_0$ of occurring, given that it has not already occurred. In this case, the probability distribution of waiting times $p(\tau_w)$ would have the form $\tau_0^{-1} \exp(-\tau_w/\tau_0)$ and the mean waiting time would be $\langle \tau_w \rangle = \tau_0$. We show in Fig 2 a
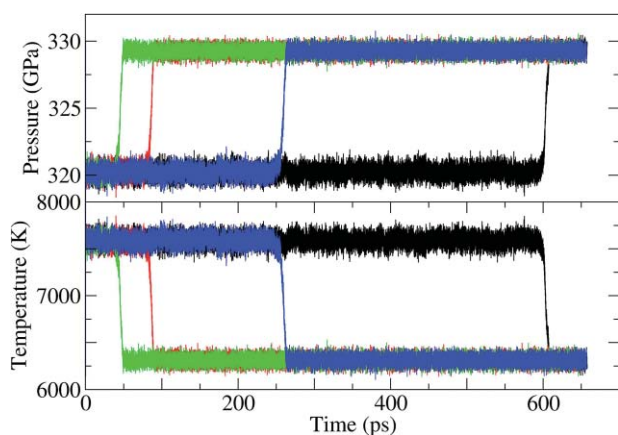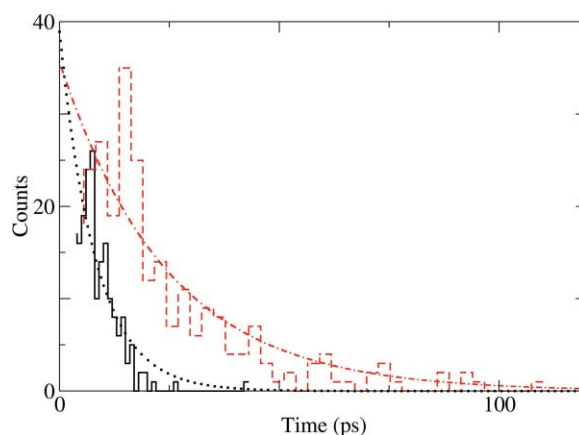

FIG. 1. Time-dependent temperature and pressure in four independent simulation runs, showing homogeneous melting from superheated hcp solid Fe in a system of 7776 atoms. All four simulations were initiated from perfect crystal positions, with initial random velocities corresponding to the same temperature $T_m = 15\,600$ K, the mean quasi-steady temperatures of the superheated solid and the final liquid being $T_{sol} = 7590$ K and $T_{liq} = 6315$ K.

FIG. 2. Histograms of waiting times τ_w before the transition to liquid constructed from repeated simulations at two initial temperatures for the system of 7776 atoms. Histograms shown by dashed (red) and solid (black) lines result from initial temperatures of $T_i = 15\,800$ and 16 000 K, respectively, the quasi-steady solid and liquid temperatures in the two cases being $T_{sol} = 7640$ and 7740 K and $T_{liq} = 6410$ and 6505 K. Dashed and dotted curves show exponential functions fitted to histograms (see text).

fit of the exponential function to the histogram. The value of τ_0 given by this fit is $\tau_0 = 24.1$ ps, which agrees well with the value $\langle \tau_w \rangle = 24.7$ ps computed directly from the sample of 350 values of τ_w. We have checked that the final mean T_{liq} and P_{liq} of the liquid are the same in all cases, within statistical error, having the numerical values $T_{liq} = 6410 \pm 5$ K and $P_l = 330.4 \pm 0.3$ GPa.

For comparison, we show the results for $p(\tau_w)$ when we do exactly the same thing for the 7776-atom system, but now with a higher initial T_i of 16 000 K, the number of independent simulations in this case also being 350. As expected, melting occurs on average more rapidly with this T_i, the values of τ_0 from the exponential fit and from the directly computed $\langle \tau_w \rangle$ being 8.3 ps and 9.4 ps. The mean temperatures of the solid and the liquid in this case are are $T_{sol} = 7750$ K and $T_{liq} = 6510$ K, which, as expected, are higher than the values found with the lower T_i.

It is clear from these observations that the mean waiting time depends on the extent to which the temperature T_{sol} exceeds the limit of superheating T_{LS}. To study this further, we have repeated the simulations with T_i values of 16 000, 15 800, 15 600, 15 400, and 15 200 K. At the lowest of these T_i, melting was not seen in any of the simulations, even though we repeated them 350 times with statistically independent initial velocities, the duration of the simulation being 710 ps in every case. At $T_i = 15\,400$ K and $T_i = 15\,600$ K , melting was observed within 660 ps in only 14 and 283 out of 350 simulations, respectively. At all the other T_i values, melting occurred in all cases, and we were able to construct essentially complete histograms; the values of $\langle \tau_w \rangle$ and the value of τ_0 obtained by fitting $p(\tau_w) = \tau_0^{-1} \exp(-t/\tau_0)$ to the histogram agreed closely.

The final mean T_{liq} of the liquid is a monotonically increasing function of T_i, and it is convenient to examine the dependence of $\langle \tau_w \rangle$ on T_{liq}. We have found that it is helpful to plot the quantity $\langle \tau_w \rangle^{-1/2}$ against T_{liq}, as shown in Fig. 3. The points fall roughly on a straight line, and the indication is that $\langle \tau_w \rangle^{-1/2} \to 0$ (i.e., $\langle \tau_w \rangle \to \infty$) at a characteristic temperature. At the same time, P_{liq} also tends to a limiting value. We identify the characteristic temperature as the melting temperature T_m at the pressure P_{liq}, because T_m is the lowest possible final mean temperature of the liquid, namely the temperature found when $T_{sol} = T_{LS}$. The value of T_m obtained by this extrapolation is 6260 K, the extrapolated pressure being 328 GPa. These results agree very well with the value $T_m = 6215$ K from explicit coexistence simulations at the pressure $P = 323$ GPa (see Sec. II).

All the results presented so far are for the large system of 7776 atoms. We have performed simulations of essentially the same kind for systems of $N = 972, 392, 150,$ and 96 atoms, in each case initiating the simulations at sequence of initial temperatures T_i, repeating the simulations at each (N, T_i) a few hundred times, determining the liquid-state T_{liq} values for the cases where melting occurs, and extracting the $\langle \tau_w \rangle$ values. The plots of $\langle \tau_w \rangle^{-1/2}$ against T_{liq} for all the system sizes are displayed in Fig. 3. The results appear to be very coherent: for each N, the $\langle \tau_w \rangle^{-1/2}$ points fall reasonably well on a straight line, and the figure shows the linear least-square fits. These linear fits extrapolate to give T_m values that agree for the different system sizes to within ∼100 K, i.e., to within ∼2%. This agreement suggests that the Z method can be a robust way of obtaining T_m values close to the thermodynamic limit for systems that would be much too small for explicit coexistence simulations, provided very long simulations are performed and provided one extrapolates to the $\langle \tau_w \rangle \to \infty$ limit.

The plots of Fig. 3 show that for the given density n the mean waiting times $\langle \tau_w \rangle$ for different degrees of superheating and different system sizes can all be roughly represented by the formula $\langle \tau_w \rangle = A/(T_{liq} - T_m)^2$, where T_m is independent of T_{liq} and N but A depends on N. They also show that A increases with decreasing N. More extensive results would be needed to make precise statements about this N dependence, but we find that the inverse proportionality $A = B/N$ fits the results quite well. As evidence for this, we display a plot of $(N \langle \tau_w \rangle)^{-1/2}$ against T_{liq} in Fig. 4, showing that all our data are quite well reproduced by the formula

$$(N \langle \tau_w \rangle)^{-1/2} = C(T_{liq} - T_m), \qquad (2)$$

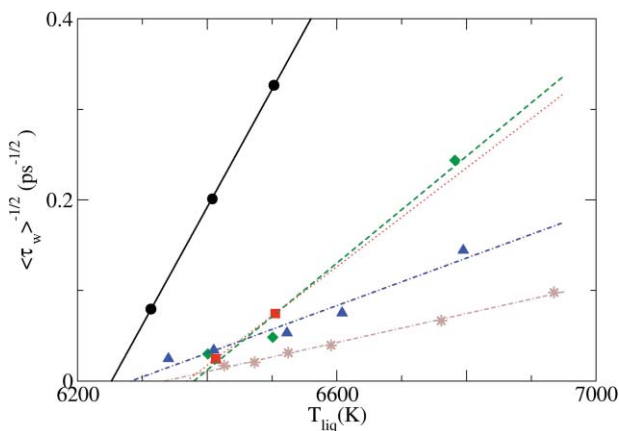where $T_m = 6315$ K and $C \equiv B^{-1/2}$ has the value 1.9×10^{-5} ps$^{-1/2}$ K^{-1}.

FIG. 3. Dependence of mean waiting time $\langle \tau_w \rangle$ on final liquid temperature T_{liq} for systems of $N = 7776$ (black circles), 976 (red squares), 392 (green diamonds), 150 (blue triangles) and 96 (brown stars) atoms. Quantity plotted is $\langle \tau_w \rangle^{-1/2}$ as function of T_{liq}. Straight lines are linear least-squares fits to the data for each N value.
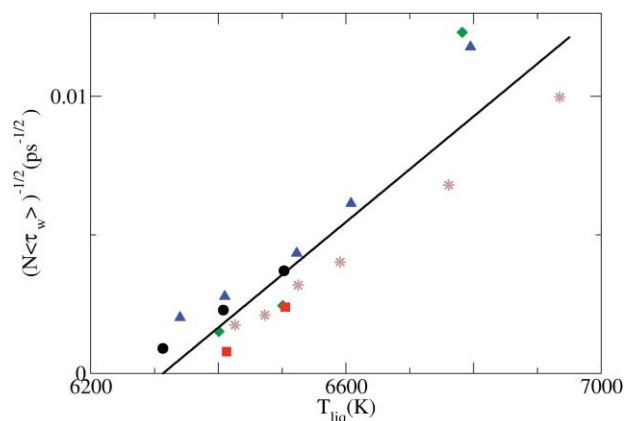

FIG. 4. Scaling of mean waiting times $\langle \tau_w \rangle$ with system size specified by number of atoms N. Quantity plotted is $(N \langle \tau_w \rangle)^{-1/2}$ as function of final liquid temperature T_{liq}.
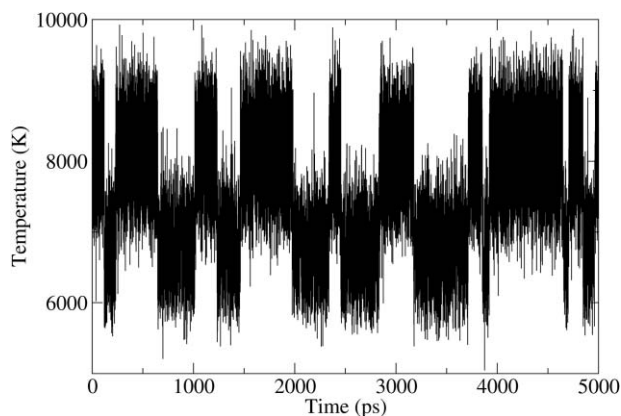
FIG. 5. Alternation between solid and liquid states: temperature as function of time in one of the constant-energy MD simulations on the system of 96 atoms, with total energy such that mean liquid-state temperature is $T_{liq} = 6760$ K, showing alternation between mean temperatures T_{sol} and T_{liq}.

FIG. 7. Fraction of time spent by the system in the liquid state for different liquid-state temperatures T_{liq} in simulations of 96-atom system.

For the system of 96 atoms, we observe a significant and interesting effect, which sheds further light on the kinetics of homogeneous melting. After the system has made the transition from superheated solid to liquid, it remains in the liquid state only for a finite time, before reverting back to the solid state. In fact, if the simulation is continued long enough, we observe a continual alternation between the solid and liquid states. An example of this behaviour is shown in Fig. 5, where we see that the temperature alternates between solid-like and liquid-like values T_{sol} and T_{liq}. This effect becomes very clear if we construct a histogram of temperature T obtained by sampling over the course of many simulations, all having exactly the same total energy E, and hence the same liquid temperature T_{liq}. The temperature histograms for the 96-atom system for different T_{liq} values are shown in Fig. 6. We see that in each case T has a bimodal distribution, being the superposition of the quasi-Gaussian distributions that would be found if the system were wholly in the solid state or wholly in the liquid state. In fact, we can fit the histograms
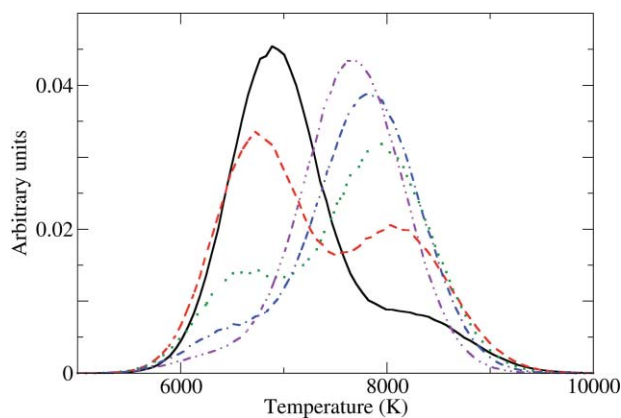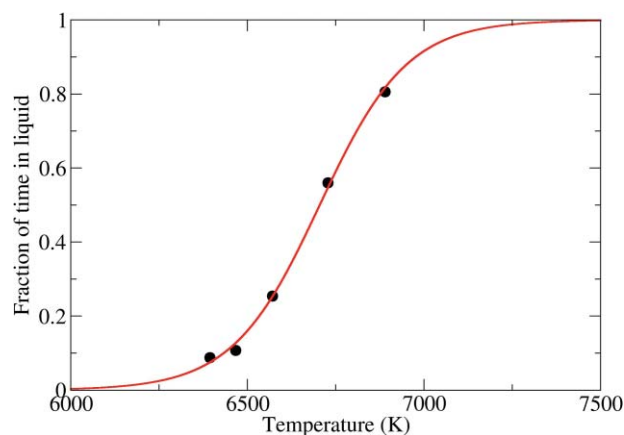

FIG. 6. Histograms of temperature distribution at different constant total energies E in the system of 96 atoms. The histogram at each E was obtained by sampling over typically 128 simulations, each having a typical duration of 5 ns. Instead of giving E directly, we specify each histogram by the liquid-state temperature T_{liq}. Histograms shown by solid (black), dashed (red), dotted (green), chain (blue), and dotted-chain (black) lines are for $T_{liq} = 6935$, 6760, 6590, 6565, and 6473 K.

very well by a superposition of Gaussians, and the relative weights of the two Gaussians for a given T_{liq} tell us the relative amounts of time spent by the system in the solid and liquid states. We display the fraction of time α_{liq} spent in the liquid state as a function of T_{liq} in Fig. 7.

At first sight, the ceaseless alternation between solid and liquid might seem surprising, because it implies that homogeneous melting from the superheated solid is not the irreversible process that one might expect. However, in Sec. IV we will point out why this alternation is required by the principles of statistical mechanics, we give a simple formula that explains why α_{liq} depends on T_{liq} as shown in Fig. 7, and we discuss whether the alternation should also be seen in larger systems.

There has been considerable interest in using the Z-method with AIMD simulation (we refer to this as AIMD-Z) to obtain melting curves, particularly for metals.[32,33] To test the practical operation of AIMD-Z, we have performed our own calculations on the high-P melting of hcp Fe, on which there is already very extensive previous work based on both free-energy and explicit-coexistence methods, including a recent study of AIMD coexistence on systems of $N = 980$ atoms.[28] Before presenting our AIMD-Z results on this problem, it is useful to consider the errors that can be expected. Our AIMD-Z simulations were performed on systems of 150 atoms with duration of ~50 ps. Clearly, with a run of this duration, initiated above T_{LS}, we are unlikely to observe homogeneous melting unless $\langle \tau_w \rangle$ is ~50 ps or less. From the formula given in Eq. (2), we estimate that this will yield $T_{liq} - T_m \simeq 600$ K, and this is the error we may make if T_m is estimated as the lowest T_{liq} for which homogeneous melting is observed.

We present in Fig. 8 our AIMD-Z results for the melting of hcp Fe with $N = 150$ using 50-ps simulations. The figure also shows the melting curve obtained many years ago with exactly the same AIMD techniques but based on free-energy calculations,[37,38,44] as well as a point on the melting curve from AIMD coexistence using 980 atoms.[28] As expected, AIMD-Z overestimates T_m, and the amount of the overestimate $T_{liq} - T_m$ is similar to our prediction from Eq. (2).
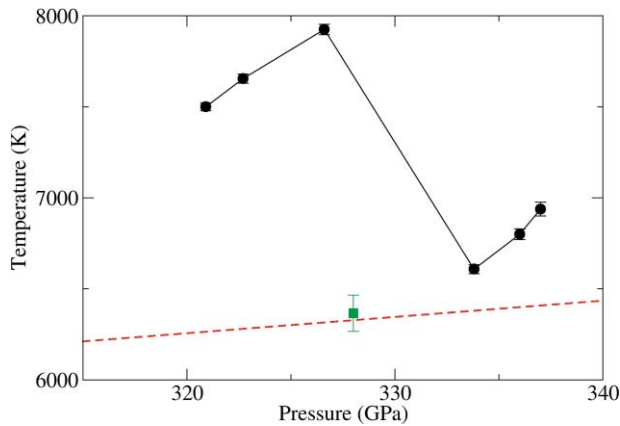
FIG. 8. Z plot from a sequence of constant-energy AIMD simulations on system of 150 atoms, duration of simulations being 50 ps. Black filled circles with error bars show final mean temperature and pressure, with upper-left branch corresponding to energies for which the system remains solid, and lower right branch to energies for which homogeneous melting occurs. Dashed (red) line shows the *ab initio* melting curve obtained in earlier work using the free energy technique, and green filled square with error bar shows point on *ab initio* melting curve obtained with *ab initio* MD simulations on a system of 980 atoms containing coexisting solid and liquid.

IV. DISCUSSION AND CONCLUSIONS

Our investigation has yielded several simple but important insights into the kinetics of homogeneous melting under (N, V, E) conditions. First, we have confirmed the existence of a "limit of superheating" T_{LS} proposed in previous work,[7] and we have shown that for a given "excess" quasi-steady temperature $T_{sol} - T_{LS}$ of the initial superheated solid, and for a given number of atoms N, there is a fairly well defined probability per unit time (reciprocal of mean waiting time $\langle \tau_w \rangle$) of making the melting transition. For given N, $\langle \tau_w \rangle$ appears to scale roughly as $A/(T_{liq} - T_m)^2$ with the excess of the final liquid temperature T_{liq} above the true thermodynamic melting temperature T_m associated with the specified liquid density. The coefficient A appears to be roughly proportional to $1/N$. These rather simple findings are clearly interesting, and it is natural to ask whether they will hold true for materials other than the particular transition metal studied here. At present, we have no way of answering this question and there is now a clear need to extend the investigation to materials of other kinds.

Another natural question concerns the relation between homogeneous melting and the kinds of metastable behaviour well known in, for example, supersaturated vapours or supercooled liquids. Of course, theories of such phenomena have an extremely long history, the point of reference often being called "classical nucleation theory" (CNT).[45] In CNT, the waiting time for the transition to the thermal equilibrium state (condensation, freezing, . . .) is governed by the time needed to form a "critical nucleus"; the associated free-energy barrier results from a competition between the lowering of bulk free energy resulting from the transition and the free energy increase due to the formation of interfaces (liquid-vapour, solid-liquid, . . .) during the transition. The metastable behaviour of a superheated solid that is only slightly beyond the thermal-equilibrium stability field of the solid should also be describ-

able by an appropriate CNT. However, it is possible that the formation of a critical nucleus described by such a CNT has little to do with the homogeneous melting observed in previous simulations[6] and in the ones presented here, for two reasons. First, CNT theories and other theories of nucleation would not predict a "superheating limit." Instead, they would predict a mean waiting time for nucleation that decreases continuously as we move further into the field of thermodynamic instability. Second, the transition associated with classical nucleation will generally lead to a final state in which both phases are present, rather than the single (liquid) phase seen in simulations of homogeneous melting.

The persistent alternation between solid and liquid states that we observe for the very small 96-atom system is relevant here.[46] To understand why this happens, and to know when we should expect to see it, we recall the ergodic principle, which is generally accepted to hold for condensed-matter systems. This states that the trajectory produced by (N, V, E) MD starting from any phase-space point (set of positions and momenta) having specified total energy E will, if continued long enough, pass arbitrarily close to an arbitrarily chosen phase-space point of the same E. The configurations we are concerned with here are either solid-like or liquid-like; in none of the simulations we have performed do we see solid and liquid simultaneously present, so that the configurations are either one or the other, except for the very small fraction of configurations that occur during the transitions from solid to liquid or vice versa. Now suppose that, starting from the superheated solid, the system has homogeneously melted and become liquid. Then the ergodic principle tells us that the given trajectory, if continued long enough, will eventually re-enter regions of solid-like configurations, so that it will re-freeze. Indeed, the trajectory will densely cover the entire constant-E manifold, and will spend well defined fractions α_{liq} and $\alpha_{sol} \equiv 1 - \alpha_{liq}$ in the liquid and solid states. This is exactly what we have seen, and Fig. 7 displays the value of α_{liq} as a function of T_{liq}.

It is straightforward to confirm that this explanation is correct. The fractions α_{liq} and α_{sol} are proportional to the numbers W_{liq} and W_{sol} of liquid-like and solid-like microstates on the given constant-E manifold. But these are related to the entropies S_{liq} and S_{sol} of the corresponding macrostates as follows: $S_{sol,liq} = k_B \ln W_{sol,liq}$. Hence, we have

$$\alpha_{liq}/\alpha_{sol} = \alpha_{liq}/(1 - \alpha_{liq}) = \exp((S_{liq} - S_{sol})/k_B). \quad (3)$$

This means that if we choose $E = E_0$ so that the system spends equal amounts of its time in solid and liquid states, then the entropies are equal. Let the temperatures in this situation be T_{sol}^0 and T_{liq}^0. If we go to a nearby energy $E = E_0 + \delta E$, then α_{liq} and α_{sol} change because

$$S_{liq} - S_{sol} = \left(\left(\frac{\partial S_{liq}}{\partial E} \right)_V - \left(\frac{\partial S_{sol}}{\partial E} \right)_V \right) \delta E. \quad (4)$$

But $(\partial S/\partial E)_V = 1/T$, and δE can be expressed as $\delta E \simeq C_{v,liq} \delta T_{liq}$, where $\delta T_{liq} = T_{liq} - T_{liq}^0$, and $C_{v,liq}$ is the isochoric specific heat of the liquid. From Eqs. (3) and (4), we then have

$$\alpha_{liq} = \frac{1}{1 + \exp(-\delta T_{liq}/T_{int})}, \quad (5)$$

where the temperature interval T_{int} over which the transition occurs is

$$\frac{1}{T_{int}} = (NC_{v,liq}/k_B)\left(\frac{1}{T_{liq}^0} - \frac{1}{T_{sol}^0}\right). \tag{6}$$

The Fermi function of Eq. (5) is the function we have used to fit our simulation results for α_{liq} as a function of T_{liq} (Fig. 7), and the parameters that emerge from this fit are $T_{liq}^0 = 6705$ K, $T_{int} = 124$ K. We can now check that this value of T_{int} obtained by empirical fitting is indeed consistent with the prediction of Eq. (6). From our EAM simulations of the liquid, we obtain the estimate $C_{v,liq}/k_B = 3.36$. Using the observed values of T_{sol}^0 and T_{liq}^0, we then obtain the prediction $T_{int} = 125$ K, which is very close (perhaps fortuitously close) to what we obtain from fitting.

It is clear from what we have said that solid-liquid alternation is only an important effect for small systems. The key feature that makes it easy to observe in our 96-atom system is that the temperature distributions of the solid and liquid states overlap significantly (Fig. 6). Since the rms temperature fluctuation of a single-phase system in the microcanonical ensemble is proportional to $1/\sqrt{N}$, the overlap becomes negligible for large systems. The same conclusion is clear from Eqs. (5) and (6), which show that temperature interval T_{int} goes as $1/N$. For a large system, once the quasi-steady temperature T_{sol} of the initial solid exceeds T_{LS}, the homogeneous melting transition is effectively irreversible.

Our results shed light on the Z method for the determination of melting properties. This method is simple to use, but our work shows that it generally gives only an upper bound to the melting temperature associated with a given liquid density, unless measures are taken to correct it. This is because melting may not be observed even when the quasi-steady temperature T_{sol} of the solid is above T_{LS}. Indeed, melting is very unlikely to be seen if $T_{sol} - T_{LS}$ is such that $\langle \tau_w \rangle$ is much longer than the duration of the simulation. This is a particular problem for AIMD, where we have shown for the case of hcp Fe that, even with 50 ps simulations on a system of 150 atoms, melting is unlikely to be seen until $T_{sol} - T_{LS} \simeq 300$ K, in which case the final liquid temperature will overestimate T_m by ~ 300 K. For the systems of less than 100 atoms and simulations of less than 10 ps used in some recent AIMD-Z work,[32,33] the overestimation is likely be much worse.

It is clearly desirable to have ways of correcting for the overestimate of T_m given by the Z method. Our work demonstrates that calculation of the mean waiting time $\langle \tau_w \rangle$ provides one way of doing this. For large enough $T_{sol} - T_{LS}$, melting will occur rapidly, and $\langle \tau_w \rangle$ can then be estimated by repeating the simulation many times so as to reduce the statistical errors on $\langle \tau_w \rangle$. If this is done at two or more values of $T_{sol} - T_{LS}$, we then have information about the dependence of $\langle \tau_w \rangle^{-1/2}$ on T_{liq}, from which the necessary correction can be made. This would be a somewhat expensive procedure for AIMD, but would have the great advantage of being simple and automatic, since many simulations could be run simultaneously on a large compute cluster. The relation with parallel replica methods[47] will be noted. As an alternative, it may well be possible to use Bayesian techniques to extract the informa-

tion needed for corrections from the sequences of simulations that are required in any case by the Z method. On a completely different line of thought, we remark that since homogeneous melting is a rare-event problem, it may be possible to exploit techniques used for other rare-event problems to accelerate melting in the Z method. Metadynamics[48] might be one such technique, since it would be easy to adopt "collective variables" that would discourage the system from remaining too long in the solid state.[49] We plan to investigate some of these possibilities in the future.

Before concluding our discussion of the Z method, we comment that further study of its theoretical basis is very much needed. It appears to have been assumed by its originators[7] that when homogeneous melting of the superheated solid occurs, the final state will always consist entirely of liquid, rather than of coexisting solid and liquid. This is indeed what we have observed in the present work (apart from the solid-liquid alternation for small systems). But the assumption cannot be true in general. For a large enough system initiated in the solid state, but superheated only slightly beyond the field of true thermodynamic stability of the solid, basic thermodynamics tells us that the final state must consist of coexisting solid and liquid, simply because at constant internal energy this state has a higher entropy than pure solid or pure liquid. In this sense, the whole concept of a "limit of superheating" is questionable. We conjecture that the reason why we do not observe final states of coexisting solid and liquid even for systems consisting of several thousand atoms is that the solid-liquid interface plays remains important enough to make coexisting states entropically unfavourable. This conjecture clearly needs investigation.

In conclusion, our MD simulations on the homogeneous melting of the transition metal Fe confirm the existence of a rather well defined limit of superheating, beyond which melting occurs on a typical time-scale of nanosecond or less. We have shown that the statistical distribution of waiting times τ_w before melting displays a typical "rare event" character, consistent with a probability per unit time for melting to occur. The mean waiting time $\langle \tau_w \rangle$ lengthens rapidly as the superheating limit is approached from above, being roughly proportional to the inverse square of the excess beyond the limit; it also lengthens as the system size (number of atoms N) decreases, being roughly proportional to $1/N$. This means that the Z method for calculating melting temperatures can be subject to large errors if it is applied to small systems over short times, though the method can work successfully under suitable conditions. We have noted that these conditions have not always been satisfied in earlier work.

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