



Precise calculation of melting curves by molecular dynamics



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ARTICLE INFO

Article history:

Received 23 June 2016

Received in revised form 8 August 2016

Accepted 9 August 2016

Available online 22 August 2016

Keywords:

Liquid–solid coexistence

Phase transitions

Melting

Equilibrium melting curve

Molecular dynamics

ABSTRACT

The paper gives a brief review of methods to calculate melting curves by molecular dynamics and thoroughly investigates the so-called modified Z-method. The modified Z-method combines the ease of implementation inherent to the original Z-method with advantages the coexistence method offers, but, as it is shown, needs an improvement. In particular, the resulting liquid–solid states it gives are always not in hydrostatic equilibrium. To attain to hydrostatic equilibrium, it is necessary to equalize stress components in the calculation cell without changing its volume. In a series of simulations for aluminum, beryllium and iron we have demonstrated that the calculations by the modified Z-method with stress equalization are as accurate as those by the thermodynamic integration method but at much lower computational cost and do not depend on the system size. As a consequence calculated entropy changes across melting line allow us to evaluate solid–solid equilibrium lines between crystal phases involved. A system of $3 \times 3 \times 12$ fcc unit cells (432 atoms) was the smallest for which we were able to obtain reliable results. Such a small system size means that, in principle, the method could be used for the calculation of melting curves by the quantum molecular dynamics.

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1. Introduction

It is quite a challenge to quantitatively describe material melting within Classical Molecular Dynamics (CMD). The quantitative description/prediction of phase diagrams depends largely on the quality of interatomic potentials being used. However, the determination of equilibrium parameters for the first-order phase transitions proper to the model of interatomic interaction remains far from trivial because of a high hysteresis typical for the transitions, and the smaller the number of particles in the system, the higher the hysteresis. Accuracy, simplicity and reliability become the most important features of a method one uses to calculate melting curves by MD when melting temperature is a target parameter for a semiempirical interatomic potential parameters optimization procedure or in a modeling material melting from the first principles. There is a wide variety of methods used to calculate melting curves within MD. They are based on different theoretical background and estimate the melting temperature with different accuracy.

1. *The Heat Until it Melts (HUM) method* [1] is the easiest to implement and in some sense mimics real-life experiment on melting. Here the crystal which is modeled in periodic boundary

conditions in a fixed volume (or under a fixed pressure) is put in a thermostat whose temperature increases with time. In principle, this is the same as crystal heating in a fixed volume (or under a fixed pressure) in a real experiment except that the rate of heating is very high ($\sim 10^{11} - 10^{14}$ K/s) because of small time scales available for direct MD modeling. At some time the crystalline structure fails with a jump in pressure (volume). The temperature at which this happens is taken to be an estimate of the melting point, more exactly an upper estimate because the number of particles is small and the rate of heating is extremely high. The material gets highly superheated, and the degree of superheating depends on the size of the system and the rate of heating. But in general it is difficult to evaluate to what extent the system is superheated.

2. *The hysteresis method.* While the upper estimate T_m^+ of the melting temperature at a fixed pressure can be obtained with the HUM method, the temperature of ultimate liquid supercooling, T_m^- , at which crystallization starts can be obtained by cooling the liquid material at the same fixed pressure. T_m^+ and T_m^- are estimates for hysteresis bounds (that is why the method is referred to as the method of hysteresis [2]) and, respectively, the upper and lower bounds for the melting temperature. As stated in [2], the melting temperature T_m can be estimated as

$T_m = T_m^+ + T_m^- - \sqrt{T_m^+ T_m^-}$, but the formula lacks physical underpinning. Another shortcoming of the method is that the cooled

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liquid may crystallize into a solid phase which differs from the initial one and then, in general, the estimate T_m^- does not relate anyhow to the melting curve of the initial phase.

3. *The coexistence method.* Theoretically, if a material in a fixed volume is gradually heated, the isochore reaches the line of melting. After some time, nuclei of a liquid phase form in the material. As the temperature goes on increasing, they grow to a critical size and coalesce to produce a liquid phase which is in equilibrium with the crystal. The amount of the liquid phase increases under heating, but the system parameters (P, T) remain on the liquid-solid thermodynamic equilibrium line until the material completely melts. So, if we construct a system in such a way as to allow it stay partly in a solid phase and partly in a liquid phase for a rather long time, then the parameters of the system would lie on the line of liquid-solid thermodynamic equilibrium. The coexistence method, or the method of two phases [3–7], just constructs such systems and determines the parameters at which the liquid and solid phases coexist (stay in equilibrium) appreciably long. One of the ways to construct the system is as follows. One first defines a crystal under a pressure and a temperature slightly below the expected melting line. Then a half of atoms are “frozen” and a half are heated until the crystalline structure fails and then cooled to some temperature. After that the frozen atoms are released and the whole system is thermalized as NPT -ensemble. By varying P and T one can attain to stable states of equilibrium between liquid and solid on the melting curve.

The classical coexistence method [3–7] aims to construct a system where liquid and solid phases stay in equilibrium for a long time at some values of internal energy E and volume V . This corresponds to a point (P_m, T_m) on the equilibrium melting curve. There is also a non-equilibrium approach [8,9] which does not seek for equilibrium, but models a small system being initially half solid and half liquid under constant pressure P and temperature T . Due to the barostat and thermostat the small system spontaneously overcomes the potential barrier and fully melts or crystallizes, and the probability to fully melt or crystallize is defined by the position of P and T relative to the equilibrium melting curve. For each pair of P and T , one can do a series of statistically independent calculations starting with the mixed state and determine the temperature of melting at a given pressure from the frequency of transitions into purely liquid or purely solid final states.

4. *Thermodynamic integration method (TIM).* Thermodynamics goes that the Helmholtz free energy, $F = E - TS$, of a system at fixed volume V , number of particles N , and temperature T which is in equilibrium is minimal. Similarly, the Gibbs thermodynamic potential, $G = F + PV$, is minimal for a system which is in thermodynamic equilibrium at constant pressure P , number of particles N , and temperature T . That is, in order to determine which of the phases α or β is thermodynamically stable at given T and V , one should compare appropriate free energies $F_\alpha(T, V)$ and $F_\beta(T, V)$ (or Gibbs thermodynamic potentials $G_\alpha(T, P)$ and $G_\beta(T, P)$ for fixed T and P). The melting curve is found as the intersection of surfaces $G(T, P)$ for the solid and liquid phases. Unfortunately, one cannot calculate free energy, entropy or Gibbs potential directly in a numerical experiment (as well as to measure them in real-life experiment) as some thermodynamic averages or functions of averages without model approximations. However, one can calculate the absolute values of thermodynamic potentials for the liquid and solid phases with the Thermodynamic Integration Method (TIM) [10–12]. The method gives the absolute values of free energy (entropy or Gibbs potential) for different metastable states by integrating the energy characteristics of the system along the reversible

quasi-equilibrium path from the state of interest to the state for which the free energy is known. This method of calculating the curves of equilibrium between different phases (including crystal modifications) is most difficult to implement algorithmically and computationally. But if everything is done accurately, the resulted phase equilibrium curve satisfies the basic equation for the equilibrium first-order phase transitions - the Clapeyron-Clausius equation.

Besides the equilibrium methods that calculate the absolute values of thermodynamic potentials through thermodynamic integration along the reversible thermodynamic path [10–12], there also exist the non-equilibrium methods [13], where the difference between the free energies of a reference state and the state of interest is calculated along a particular non-equilibrium transition rather than along a thermodynamically equilibrium one. The error from the difference between irreversible and equilibrium transitions is proposed to be removed by implementing the reverse non-equilibrium transition. So, according to [13], if a non-equilibrium transition proceeds rather slowly, it satisfies the linear response approximation. Then the integrals obtained for the direct and reverse transitions will identically differ from a true value calculated for the equilibrium process, and the slower the transition is, the smaller the difference. By doing integration in the direct and reverse non-equilibrium transitions one can find the average difference between the free energies of the state of interest and the reference state and avoid the systematic error.

We have to mention here other free energy methods as well. For example in [14] authors introduced an alternative approach to directly calculate free energies of fluid and solid phases that does not require performing any simulations of the transition from the state of interest to the reference state. Using the perturbation theory [15–17] with a hard sphere reference system authors directly calculate the free energies of liquid and solid phases in a single approach with an average relative error 0.55% of the values calculated with TIM.

5. *The Z-method* [18,19] implements modeling in the following way. A crystal of a fixed volume of interest is imparted a fixed thermal energy E (the kinetic energy of atoms) and then a micro-canonical (NVE) ensemble is modeled for a quite long time. In parallel, calculations for different values of E are started. This gives an isochore for volume V and different values of internal energy E , which in the (P, T) -plane looks like the letter Z, giving the name to the method. Since the Z-method is rather simple in realization and works for relatively small systems it is widely used to study melting of various materials using *ab initio* molecular dynamics [19–24]. The authors of the Z-method claim that if the time of calculation is rather long, the crystal with the highest superheating relative to the true melting curve must melt into a liquid state with parameters lying on the melting curve [18,19]. According to the developers of the Z-method [18] they demonstrate, by molecular dynamics simulations, that the total energy of a solid at T_{LS} (limit of superheating) is equal to the total energy of its liquid at T_m (melting temperature) at the same volume. However it is not true, and researchers (even the developers themselves [25]) later found numerous counterexamples. As for the prediction of the actual melting temperature, the Z-method is no better than HUM and only gives an upper estimate for the melting temperature as well.
6. *The modified Z-method* was proposed in [26]. The modification is as simple to implement as the Z-method and as accurate and physics-based as the coexistence method. So, the authors propose doing calculations by the Z-method with periodic cells which are elongated in one of the directions. The modification

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