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Vibrational spectrum and entropy in simulation of melting

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ABSTRACT

We present a detailed analysis of entropy reconstruction from a velocity autocorrelation function in molecular dynamics simulation for solid and liquid states. The reconstruction is based on the vibrational density of states (VDOS) and for the liquid phase is known as a two-phase thermodynamic (2PT) model. We show that adequate accuracy of VDOS is required for successful application of this technique in the solid phase. We study the convergence of VDOS and entropy on the number of particles, time step and simulation time using aluminum as an example. We also examine the influence of temperature upon VDOS. Our analysis demonstrates that systems containing less than 500 atoms of aluminum do not reproduce the phonon density of state (PhDOS) of the crystal. Nevertheless the error of entropy calculation decreases quickly with the increase of the number of particles in simulation. We note strong influence of high temperatures on VDOS and the difference between VDOS and PhDOS near melting. We show that a time step of 0.5 fs or less and trajectories of more than 10,000 time steps are required to obtain good accuracy of entropy in the solid phase. We use quantum molecular dynamics and the 2PT model with a memory function representation for the gas-like component to obtain a new point on the melting curve of aluminum at a pressure of 171 GPa, that agree well with previous experimental works and calculations.

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1. Introduction

Theoretical determination of solid–liquid phase boundaries is a long–standing problem in physics. A number of approaches exist in order to predict melting curves, however most of them require significant computational resources to achieve sufficient accuracy. Two groups of methods are usually considered. The first group studies conditions of stability of only one phase, while in the second liquid and solid phases are both taken into account. Vivid examples of the one-phase approach are direct molecular dynamics (MD) methods such as HUM (heat until it melts) [1], the Z-method [1–3] or the quasiharmonic approach based on the Lindemann criterion [4,5]. A direct simulation of two phases in coexistence [6–9] or a computation of the Gibbs potentials of both phases at the same pressure and temperature [10] are typical two-phase methods.

The shortcoming of the HUM approach is an overestimation of melting temperature. The Z method is more precise, however it is expensive computationally and requires various corrections [11,12]. The Lindemann criterion in the framework of the quasiharmonic approximation gives good results for metals [5] but not for compounds [13]. A simulation of two phases in equilibrium provides quite good results in comparison with experiment, but requires very long and accurate computations [7]. A recent statistical solid-liquid coexistence method seems to provide good accuracy with much lower computational cost, because the convergence of melting temperature is reached for simulations with only several hundreds atoms [14]. However the two-phase approach does not provide any information about entropies or free energies of the two phases.

Direct reconstruction of melting curves based on the equality of Gibbs energy for both phases sets a complicated task of entropy calculation, that remains the major impediment of this method. A rigorous technique of thermodynamic integration [15] is one of the best solutions to this problem however it is very challenging in realization, because it requires a considerable auxiliary architecture of tools, the choice of a good reference system for the problem at hand, and numerous integration points along the thermodynamic integration path. Another approach to compute liquid-state free energy is the Widom's particle insertion method, in which free energy is calculated through inserting a test particle

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into a liquid [16,17]. Recently this method has been applied to first-principle calculations [18,19]. Compared to the thermodynamic integration approach, the Widom's method holds a great advantage, since it does not require any reference system, but it is also computationally expensive.

A little more than ten years ago a promising approach to the direct calculation of entropy was suggested by Lin et al. [20]. This method uses a single simulation to compute entropy of a system through a decomposition of vibrational density of state (VDOS) or a vibrational spectrum (VS) into solid-like and gas-like subsystems, therefore it is called a two-phase thermodynamic (2PT) method. This method was developed and validated within the Lennard-Jones system, but in a short time it has been successfully applied to a wide variety of systems, including molecules [21] and mixtures [22]. On the one hand, the main advantage of the 2PT method is obviously its relative simplicity. On the other hand, this model is not rigorously substantiated and is sensitive to the choice of approximation for the gas-like component. It was shown that the hard sphere (HS) fluid approximation suggested by Lin et al. for the gas-like subsystem overestimates entropy for liquid metals [10,23]. A memory function (MF) representation for the gas-like component seems to solve this problem [10].

Thus the actively developing 2PT method has shown its availability for the entropy calculation of liquid. However, the entropy computation in the solid phase is not so easy as it may seem. Of course, the quasiharmonic approximation is a promising tool for this problem, because it allows to calculate the total free energy of a crystal, so it is possible to obtain all thermodynamic properties in a crystalline state. But in case of high temperatures close to melting the influence of anharmonic effects can be substantial, so additional methods and calculations may be necessary to determine the anharmonic contribution to free energy [24–26]. The use of a combination of quasiharmonic phonon calculations followed by the thermodynamic integration is another approach to the problem [10].

In the 2PT method for a solid state the gas-like part is negligible. In this case a real VS is used for the calculation of entropy of the solid phase and effects of anharmonicity will be taken into account automatically. Therefore we can expect that the 2PT approach will be more proper at high temperatures than the quasiharmonic approximation which is based on the linear response theory.

An example of the entropy calculation of the solid phase through the VS was given by Lin et al. [20]. Using this technique possibility of calculation of melting curve was demonstrated recently by Robert et al. [27]. However the convergence of VDOS calculations in the crystalline state using MD modeling has not been properly investigated yet. In this work we study the problem of convergence of VDOS in the solid state on the number of particles, temperature and simulation time using classical MD calculations. We also show the applicability of the 2PT model in both solid and liquid states for simulation of melting of aluminum by quantum molecular dynamics (QMD).

2. Two-phase thermodynamic model, VDOS and entropy

The 2PT model is based upon the velocity autocorrelation function (VACF) and its frequency Fourier transform known as VDOS. Both values may be obtained from temporal trajectories of particles from MD simulations. In a crystalline state, however, there are alternative approaches to compute the VDOS as one should analyze only the vibrational movement of particles. A good approximation is to consider the harmonic vibrations; in this case only small displacements of particles from their equilibrium positions are taken into account. The shifts of the particles create small forces from which one can compute the dynamical matrix and the so-called phonon density of states (PhDOS) using the linear response theory. On the other hand, this approach may become ill-conditioned in case of bad accuracy of calculations [28]. In quantum computations this problem is avoided in the framework of the density functional perturbation theory (DFPT) which is widely applied for crystals with simple unit cells [29]. However, the computational cost of DFPT for large systems can be very high, so that QMD becomes more preferable. Moreover the VS reconstructed from the QMD VACF automatically includes anharmonic oscillations.

The VDOS function $F(\nu)$ can be obtained by the Fourier transform of the VACF $Z(t)$:

$$F(\nu) = \int_{-\infty}^{\infty} Z(t)\exp^{-i2\pi\nu t}\,dt, \tag{1}$$

with

$$Z(t) = \frac{\langle \boldsymbol{v}(t)\cdot\boldsymbol{v}(0)\rangle}{\langle \boldsymbol{v}(0)\cdot\boldsymbol{v}(0)\rangle}. \tag{2}$$

As can be seen from (2) the definition of $Z(t)$ contains a normalization factor such that $Z(0)\equiv 1$. The integration of the VDOS function over positive frequencies gives the total number of degrees of freedom of the system. Thus $F(\nu)$ as defined here has the following normalization

$$\int_0^{\infty} 12F(\nu)d\nu = 3. \tag{3}$$

Following Lin et al. the total spectrum is decomposed into the solid-like ($F_s(\nu)$) and gas-like ($F_g(\nu)$) components

$$F(\nu) = (1-f_g)F_s(\nu) + f_gF_g(\nu). \tag{4}$$

The total ionic entropy is decomposed into two terms as well

$$S_i = S_s + S_g \tag{5}$$

and S_s and S_g in turn can be written as integrals with appropriate weighting functions

$$S_s = Nk\int_0^{\infty} 12[F(\nu) - f_gF_g(\nu)]W_s(\nu)d\nu, \tag{6}$$

$$S_g = f_gNk\int_0^{\infty} 12F_g(\nu)W_gd\nu, \tag{7}$$

where the weighting function for the solid-like component is given by a quantum-corrected one-phase thermodynamic model

$$W_s(\upsilon) = \frac{h\upsilon/kT}{\exp(h\upsilon/kT)-1} - \ln[1-\exp(-h\upsilon/kT)]. \tag{8}$$

The gas-like component can be described as the HS system [20] or using the MF representation [10].

3. Simulation parameters

In this work classical MD simulation was performed by the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [30]. For metals, an embedded atom model (EAM) [31] is a good approximation that accounts for both a pair-wise interaction and a contribution of the electron charge density from nearest neighbors of an atom under consideration. We use an EAM potential of Zhakhovskii for aluminum [32]. This potential reproduces mechanical and thermodynamic parameters at normal conditions, gives a good agreement with the cold and Hugoniot curves, and describes well the phase diagram of aluminum [33]. The classical PhDOS is retrieved directly from MD simulation in the framework of the fluctuation-dissipation theory; the FixPhonon module of the LAMMPS code is used for this purpose [34].

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