Thermodynamically Consistent Method for Calculation of Free Energy and Equilibrium Curves of First-Order Phase Transitions in Classical Molecular Dynamics

***A.V. Karavaev andV.V. Dremov**

Russian Federal Nuclear Centre – Zababakhin Institute of Technical Physics, Snezhinsk, Russia

State-of-the-art parallel computers allow performing MD simulations not only with substantial number of particles, but also using of complicated computationally intense many-body potentials of the interatomic interactions. One of the most important tasks for the computer-aided material science is accurate and extensive characterization of thermodynamic properties of the materials. An essential part of this characterization is the prediction of phase diagrams of the materials. Many-body model potentials of the interatomic interactions such as MEAM provide capabilities for accurate description of several phases. For a given functional form of model potentials the choice of their parameters requires a vast experimental and *ab-initio* calculation data including the data on the phase equilibrium. Thus, it is necessary to develop an accurate and universal method in the frames of classical molecular dynamics for calculations of thermodynamically consistent equilibrium curves of the first-order phase transitions between different phases of the material.

Key role in the description of the first-order phase transitions plays Helmholtz free energy, which unfortunately can not be measured directly in a simple numerical experiment. For calculation of free energies of various states of materials we use so called method of thermodynamic integration [1-3], which allows calculating 'absolute' values of free energy for various states of matter (different crystal structures, liquids) for given external parameter sets. Knowing the 'absolute' values of free energy (entropy, Gibbs thermodynamic potential) it is easy to retrieve dependence of these quantities along reversible iso-processes and calculate equilibrium phase transition temperatures. In the paper we present step-by-step method for calculation of equilibrium curves of the first-order phase transitions in the frames of classical MD by the example of Be with the MEAM potential [4] with the parameters [5]. We performed a number of numerical experiments to test accuracy and thermodynamic consistency of the method for many-body potentials.

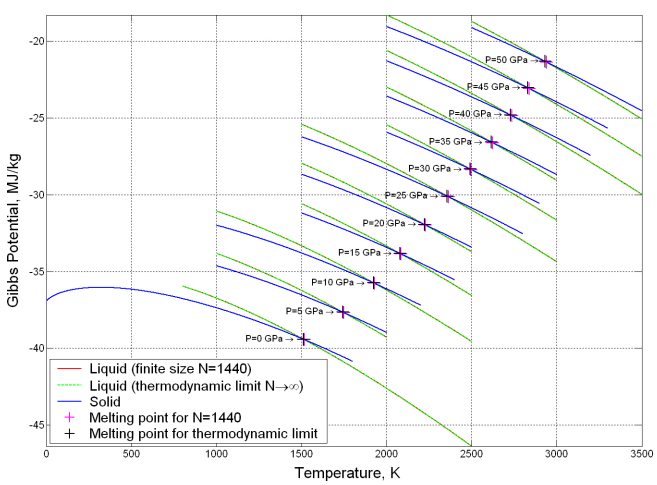

Figure 1. Specific thermodynamic Gibbs potential of HCP crystal and liquid phases of Be as a function of pressure and temperature.

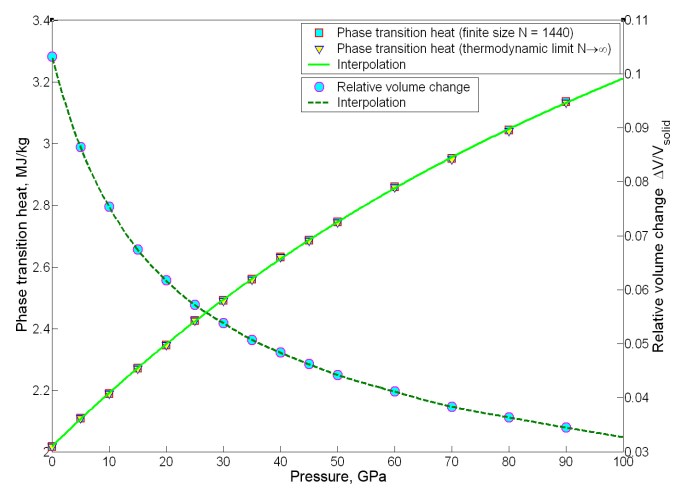

Figure 2. Specific heat of the first-order phase transition and relative volume change as functions of pressure.

In Figure 1 the calculated dependence of specific Gibbs potential on pressure and temperature for the pressure range $P = 0$ to $P = 50\,GPa$ are shown. Solid blue lines present the dependence $G(T)$ at various pressures P for the solid phase. Red solid lines are the dependence $G(T)$ for the liquid with the small number of particles $N = 1440$.

Green dashed lines show the dependence $G(T)$ for the liquid in the thermodynamic limit N ® ¥ . Note that green dashed lines lay slightly lower than red solid lines, since specific entropy of the liquid in the thermodynamic limit is higher than that of the finite size systems. This results in the melting points of the finite size system (magenta crosses in Fig. 1) laying slightly higher in temperature than those in the thermodynamic limit.

The most important criterion of the thermodynamic consistency of the calculated equilibrium curve of the melting is the satisfaction to the fundamental relation describing the first-order phase transition in the P - T plane, namely, Clapeyron-Clausius equation. Since we calculated the absolute values of entropy for the liquid and the crystal phases, we can easily calculate the values of entropy changes ΔS for the melting temperatures that were obtained by intersection of Gibbs potentials of the liquid and the crystal along isobars (See. Fig. 1). In Fig. 2 the calculated dependence of specific heat $T\Delta S$ and relative volume change $\Delta V / V_{solid}$ of the melting on pressure are presented. In Fig. 3 the calculated for Be with MEAM potential with the parameterization [5] melting line from HCP phase is shown. The squares and triangles in Fig. 2 represent calculated by the intersection of Gibbs potentials of the liquid and HCP crystal for the corresponding pressures for the finite size system and in the thermodynamic limit, respectively. Solid green curve is an interpolation of the points. By the inclined red and blue short lines near the each of the symbols the derivatives dT/dP of the melting line calculated using the data from Fig. 2 are shown. One can see that in all the range of pressure the slopes (that is the derivatives dT/dP) of the melting curve calculated using Clapeyron-Clausius equation and the slopes of the interpolation (green line), coincide with the high accuracy. Thus, the calculated first-order phase transition satisfies Clapeyron-Clausius equation, and is indeed thermodynamically consistent equilibrium curve of HCP crystal melting for the given form and the parameterization of the interatomic potential.

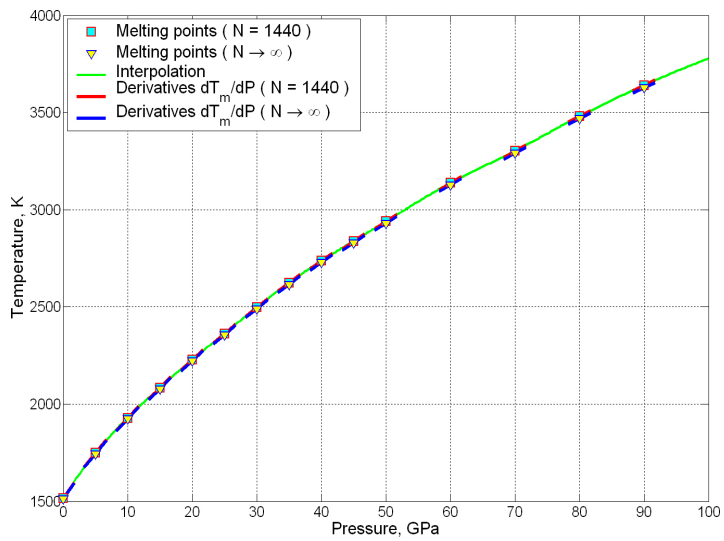

Figure 3. Equilibrium melting line of Be from HCP phase calculated for MEAM potential with the parameterization [5].

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