Classical and quantum calculations of the temperature dependence of the free energy of argon

Wenwu Xu [a,b,c,*], Andrew P. Horsfield [d], David Wearing [d], Peter D. Lee [a,b]

[a] School of Materials, University of Manchester, Manchester M13 9PL, UK
[b] Research Complex at Harwell, Didcot OX11 0FA, UK
[c] Department of Mechanical Engineering, San Diego State University, San Diego 92182, USA
[d] Department of Materials, Imperial College London, London SW7 2AZ, UK

ABSTRACT

The free energy is central to statistical mechanics and thermodynamics, and its accurate calculation via. computational modelling is important for a large number of applications, especially when its experimental value is hard to obtain. Several established and general methods for calculating the Helmholtz free energy across different length scales, including continuum, atomistic and quantum mechanical, are compared and analyzed. A computational approach is then proposed to calculate the temperature dependences of internal energy and absolute Helmholtz free energy for solid and liquid phases with the coupling of thermodynamic integration (TI) and harmonic approximation calculations from both classical molecular dynamics (MD) and density functional theory (DFT). We use the Lennard-Jones system as an example (*i.e.* argon) for the demonstration of the approach. It is observed that the free energy transits smoothly from being describable by the harmonic approximation to including anharmonic effects at a transition temperature around $0.56 \, T_m$; below this temperature, the quantum behavior of atoms is important. At higher temperatures ($T > 0.56 \, T_m$), the TI and harmonic approximation results for the Helmholtz free energy functions become increasingly divergent with the increase of temperature. This work demonstrates that a multiscale approach employing TI, MD, and DFT can provide accurate calculations of the temperature dependence of absolute Helmholtz free energy for both solid and liquid phases.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The Helmholtz (volume constant) or Gibbs (pressure constant) free energy of a system is one of the most important thermodynamic quantities for condensed-phase systems [1]; it determines what the stable structures are, and the direction changes take. Bulk free energies can be derived from experiments, but interfacial free energies are much harder to obtain. While the calculation of bulk free energies and derivative thermodynamic quantities, and static energies for interfaces, are common and widespread applications of atomistic simulation techniques [2–4], the computation of solid-liquid interfacial free energies is still challenging.

Free energy functions can be used for studying important fundamental problems in materials sciences, such as phase and structural transitions [5,6], interfacial energies [7,8], or other critical phenomena [9–11]. There are several techniques available for calculating the absolute or relative free energy as a function of temperature of a system, an attractive option when experimental determination is difficult. In particular, we may obtain the crystal-melt (or solid-liquid) interfacial free energy as a function of temperature for systems in which the liquid and solid are formed from materials with different melting points based on the free energy functions of the solid and liquid phases. The interfacial energy would be the difference between the total free energy for a system with a solid-liquid interface, and the free energies of the bulk solid and liquid components [8]. In this case, the accurate computations of free energies for solid and liquid bulk phases become critical. Note that for the solid-liquid interface in a single material at its melting point, special methods are needed [12,13].

At a temperature sufficiently far below the melting point, one can compute absolute free energies quite accurately using the harmonic approximation (HA) [1]. To get free energies at higher temperatures, in particular when one of the materials is in the liquid state, one might perform thermodynamic integration (TI) from a lower temperature to a higher one. A problem with the usual TI approach is that one cannot integrate through the phase transition

to reach the liquid state, thereby obtaining an absolute free energy for the liquid. The difficulty is that at the melting temperature there is a discontinuity in the internal energy on going from the solid to the liquid states (the latent heat of melting) which makes it impossible to carry out a reversible calculation: there is a temperature that we must include at which the internal energy is not uniquely defined.

One way around this is to note that the free energies of the solid and liquid states are identical at the melting point. We can find the absolute free energy of the solid using available techniques to temperatures slightly above the melting point (superheated solid), and find the relative free energies of the liquid to just below the melting point (supercooled liquid). We can then match the free energies at the melting point. To do this we need techniques that allow us to compute the various contributions, all of which exist.

In this work, as a first step towards computing solid-liquid interfacial energies, we investigate some of these techniques of computing free energies of solid and/or liquid bulk phases and how these different methods can be combined. In particular we combine TI for classical molecular dynamics (MD) simulations with lattice dynamics calculations of the phonon spectrum. This allows us to compute the temperature dependence of the Helmholtz free energy of both the solid and liquid phases by using a Lennard-Jones system (argon) as an example. In Section 2 we introduce the method and modelling procedure which involves 3 aspects: (i) determination of the melting point; (ii) temperature dependence of the internal energy functions for both solid and liquid phases; (iii) a reference value of an absolute free energy at a specified temperature far below the melting point. In Section 3 we combine this information to produce the Helmholtz free energy as a function of temperature over a large temperature range, spanning both the solid and liquid states. We end with a summary of conclusions in Section 4.

2. Method and simulations

Suppose we know the internal energy of a system U as a function of temperature T, and wish to compute the free energy F_2 at temperature T_2 given that we know the free energy F_1 at temperature T_1. The Gibbs-Helmholtz equation then gives

$$\frac{F_2}{T_2} - \frac{F_1}{T_1} = -\int_{T_1}^{T_2} \frac{U}{T^2} dT \qquad (1)$$

Thus, to calculate the absolute Helmholtz free energy as a function of temperature $F(T)$, we need to know its value at a reference temperature T_R, which we shall obtain using the result for a collection of quantum harmonic oscillators. Eq. (1) can now be written as

$$\frac{F(T)}{T} = \frac{F_R}{T_R} - \int_{T_R}^{T} \frac{U(T')}{T'^2} dT' \qquad (2)$$

As noted above, we emphasise that the temperature function of internal energy is not continuous across the solid/liquid transition (i.e. at the melting point, T_m), whereas $F(T)$ is continuous because the free energies of solid and liquid are equal at the melting temperature. The superscript prime symbol on temperature (T') corresponds to classical molecular dynamics simulations, and it is different from the temperature (T) in quantum calculations. This is because, at temperatures close to 0 K, there is a discrepancy between the temperatures used for classical molecular dynamics and for lattice dynamics (quantum) calculations, which originates from the quantum zero point energy [14]. This discrepancy, however, becomes small when the temperature of the crystal system exceeds ∼0.1T_m (T_m is the melting point) [14]. In summary, using Eq. (2), one can easily calculate the temperature dependence of the Helmholtz free energy of a system provided a value can be found for a reference temperature, and the internal energy as a function of temperature can be found for both the solid ($T_R < T \leq T_m$) and liquid ($T \geq T_m$) states.

There is one important technical point that we investigate here. At low temperatures, the atomic motion is quantum in nature, and thus we use a quantum mechanical expression suitable for harmonic motion. To extrapolate above low temperatures, we have to incorporate anharmonic terms, and the most straightforward way to do that is to perform TI with MD. However, for MD the atoms are treated as classical objects. Thus, to reach higher temperatures we simultaneously move from harmonic to anharmonic motion, and from a quantum to a classical description of the atoms. For this to work, the atoms need to be describable by classical mechanics before the harmonic approximation fails. Our calculations suggest the transition occurs smoothly.

A first step for this method is the accurate determination of the melting point. Here we obtain an accurate value of the melting point of argon by allowing the solid and liquid phases to reach equilibrium in a constant energy MD simulation [15]. Then, we compute the internal energies at a series of temperatures for both solid (10 K < $T \leq T_m$) and liquid ($T \geq T_m$) argon using constant volume and energy (NVE) MD simulations; constant temperature and pressure (NPT) MD simulations are used to establish a suitable volume. Lastly, the absolute value of the Helmholtz free energy at T_R = 10 K (the chosen reference temperature in the current work) is calculated using the standard expression that relates the free energy to the phonon frequency spectrum [16],

$$F(T) = E_{tot}(T) + k_B T \int^F (\omega) \ln \left[1 - \exp \left(-\frac{\hbar \omega}{k_B T} \right) \right] d\omega \qquad (3)$$

where the frequencies ω are computed from the dynamical matrix in quantum calculations. Here $E_{tot}(T)$ includes the contribution from zero-point energy. k_B and $\hbar$ are the Boltzmann and Planck constant, respectively. $F(\omega)$ is the phonon density of states. Based on the above calculations using Eqs. (1)–(3) one can compute the temperature dependence of the Helmholtz free energy for argon with the temperature ranging from the low reference temperature (e.g. T_R = 10 K) to temperatures well above the melting point ($T \geq T_m$).

2.1. MD simulations: melting point of argon

If not specified otherwise, our classical MD simulations are carried out by using an open-source code DL_POLY, which has been developed at Daresbury Laboratory by I.T. Todorov and W. Smith [17]. The Lennard-Jones 12-6 potential (with ε = 0.0104 eV and σ = 3.4 Å [18]) is employed to define the interactions between pairs of argon atoms. We determine the melting point of argon at atmospheric pressure (P = 1.0 atm.) by constructing a pressure versus temperature diagram from a series of solid/liquid co-existence simulations using the NVE (constant volume and energy) ensemble. These solid/liquid co-existence interface models equilibrate at a certain temperature and pressure, which is, by definition, the melting point at that pressure [15].

To perform one of these solid/liquid equilibrium simulations, we first create an initial configuration for the solid/liquid interface model that consists of about 50% solid by volume (42,592 atoms) with the rest being liquid (32,000 atoms): see below for a description of how the liquid is generated. These systems are pre-equilibrated at 10 K and 85 K (slightly higher than the experimental melting point of argon: 83.8 K [19]), respectively. Fig. 1(a) shows the front-view (projection of x-z plane) of a 3-D interface model, with the solid/liquid boundary indicated by a long-dashed line, perpendicular to the z-axis. This initial interface model is then relaxed and equilibrated at three different temperatures of 81 K, 83 K, and 85 K within the NVT (constant volume and temperature)