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# A self-contained algorithm for determination of solid-liquid equilibria in an alloy system

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## ABSTRACT

We describe a self-contained procedure to evaluate the free energy of liquid and solid phases of an alloy system. The free energy of a single-element solid phase is calculated with thermodynamic integration using the Einstein crystal as the reference system. Then, free energy difference between the solid and liquid phases is calculated by Gibbs-Duhem integration. The central part of our method is the construction of a reversible alchemical path connecting a pure liquid and a liquid alloy to calculate the mixing enthalpy and entropy. We have applied the method to calculate the free energy of solid and liquid phases in the Al-Sm system. The driving force for fcc-Al nucleation in Al-Sm liquid and the melting curve for fcc-Al and Al<sub>3</sub>Sm are also calculated.

## 1. Introduction

Reliable free energy for both solid and liquid phases of an alloy is fundamental to achieving a microscopic understanding of freezing and melting phenomena, which remains a significant challenge in condensed matter physics and materials science [1]. The origin of the difficulty in free energy calculations is that free energy cannot be expressed as a simple average of a physical quantity over the phase space that can be conveniently evaluated in a single simulation with a standard sampling technique, such as Monte Carlo (MC) or Molecular Dynamics (MD) [2]. A variety of methods have been proposed for free energy calculations, emphasizing on computing the free energy *difference* between the target system and a reference system. These methods include multistage free energy perturbation [3], particle insertion/deletion [4–6], thermodynamic integration (TI) [7], Bennett analysis [8,9], weighted histogram [10], umbrella sampling [11], and adiabatic switching [12]. In addition to these equilibrium approaches, Jarzynski established a nonequilibrium equality to express the free energy difference in terms of the irreversible work along paths connecting the two systems. A path-sampling technique with the application of umbrella sampling has been formulated to improve the convergence of the original Jarzynski method [13], and has been applied on clusters [14], glasses [15] and crystalline alloys [16]. For binary fluids, alternatively, people have used relatively efficient methods such as energy partitioning method [17] and classical density-functional approach [18] to estimate the free energy.

When selecting a specific method, one strikes a balance between efficiency and accuracy according to the problem at hand. The main objective of the current paper is to develop a self-contained algorithm to *accurately* determine the free energy of both liquid and solid phases, in order to establish phase equilibria. The algorithm will be developed within the framework of TI, coupled with extensive GPU-accelerated MD simulations [19,20]. TI is based on the idea that derivatives of free energy are often well-defined ensemble averages that are measurable in a single MC or MD simulation. In this method, one evaluates the derivative of free energy along a reversible path connecting the reference system and a target realistic system. The integration of the derivative along this path gives the free energy difference between the two systems [2,7].

In principle, one can obtain the absolute free energy of solid and liquid phases by referencing to a harmonic crystal and the ideal gas, respectively, whose free energy can be analytically derived. However, it is generally not a good idea to treat the liquid and solid phases in separate frameworks when it is the free energy *difference* that controls phase stability [18]. Furthermore, many phenomena of interest such as crystal nucleation and growth occur when the liquid becomes supercooled, when it behaves so differently from the ideal gas that one needs to be very careful to obtain the required accuracy by using the ideal gas as the starting point. Here, we choose the harmonic crystal, such as the Einstein crystal [21,22] as a global initial reference system, since it can provide a reliable reference for pure solid phases in most cases. The general strategy is as follows: first, we calculate the absolute free energy

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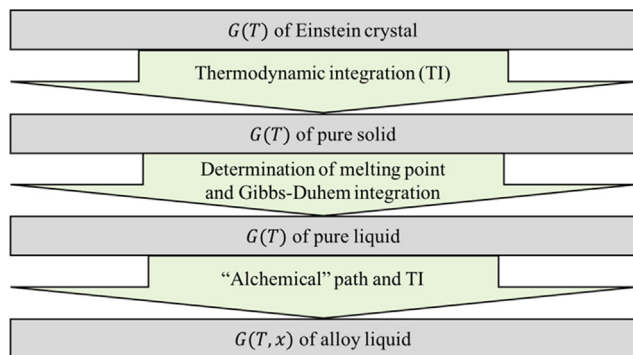


Fig. 1. Flowchart summarizing the algorithm for our free energy calculation.

of the solid phase directly using an Einstein-crystal reference; next, we determine the free energy difference between the solid and liquid phases at a specific state point; and finally, we use Gibbs-Duhem integration [23] to extend to other state points, such that all the free energy calculations are based on the same initial reference system. While the free energy difference at an arbitrary state point can be calculated by methods such as pseudosupercritical path integration [24,25], in this paper, we choose a special state point: the melting point, at which the free energy difference is zero. The accurate melting point is determined by monitoring the migration of a solid-liquid interface.

Next, we construct an “alchemical” path to transform a pure liquid to a liquid alloy, and apply TI to evaluate the mixing enthalpy and entropy during the process. Similar methods were frequently used previously to analyze affinity change upon substitution of certain atoms or functional groups in chemical or biochemical systems [26–28]. This strategy, together with a reliable method of determining solid/liquid free energy difference in single-element systems, forms a self-contained way of establishing phase equilibria in alloys. The algorithm is summarized in a flowchart shown in Fig. 1.

We choose the Al-Sm system for the current study, which is a typical member of Al-RE systems (RE: rare earth). At ~10 at% Sm, this system can form metallic glasses or nanocomposite materials with low-density-high-strength properties [29]. The evaluation of thermodynamic stability of relevant phases is necessary to understand the complicated phase selection of this system especially under supercooling, which is key to achieving the desired compositions and microstructures.

## 2. Computational details

All simulations are performed using the MD technique with a timestep of 2 fs, as implemented in LAMMPS GPU-accelerated package [19,20]. Systems are fully equilibrated in 500,000 timesteps in canonical ensemble ( $NVT$ ) or isothermal-isobaric ensemble ( $NPT$ ) with the Nose-Hoover thermostat [30,31]. The main purpose of performing MD simulations in this work is to calculate the ensemble average of certain quantities (details are shown below), which is equivalent to the temporal average under the ergodic hypothesis. The average is collected in another 500,000 timesteps after the equilibrium is reached. For efficient energy and force calculations, we use semi-empirical interatomic potential in the Finnis-Sinclair form [32], which was developed to reproduce pure Al properties, energetics of Al-Sm intermetallic alloys and Al-Sm liquid structures [33]. This potential was particularly designed to treat Al-rich alloys (at% Sm < ~10%).

## 3. Pure fcc-Al and Al liquid

We start with the calculation of free energy of the fcc-Al phase with TI, using the Einstein crystal as a reference system. The Helmholtz free energy of a classical Einstein crystal can be determined analytically as

$F_0 = 3Nk_B T \ln(h\nu/k_B T)$ , with  $N$  the number of atoms,  $h$  the Planck constant,  $\nu$  the vibrational frequency and  $k_B$  the Boltzmann constant. To implement TI, one generates intermediate systems with potentials  $U(\lambda) = (1-\lambda)U_E + \lambda U_{Al}$ , where  $U_E$  and  $U_{Al}$  stand for the potentials for the Einstein crystal and the real Al system, respectively. Then, the difference in Helmholtz free energy between the two systems can be expressed as

$$F_{Al,s} - F_0 = \int_0^1 \left\langle \frac{dU(\lambda)}{d\lambda} \right\rangle_{\lambda, NVT} d\lambda = \int_0^1 \langle U_{Al} - U_E \rangle_{\lambda, NVT} d\lambda. \quad (1)$$

In Eq. (1), the subscript  $s$  stands for solid, and  $\langle \dots \rangle_{\lambda, NVT}$  denotes the canonical ensemble ( $NVT$ ) average of fcc-Al with respect to the intermediate potential  $U(\lambda)$ . The volume is fixed at the equilibrium volume at ambient pressure, which is determined separately via MD simulation with the real FS potential for Al under  $NPT$  conditions. In this way, the Helmholtz free energy is equal to the Gibbs free energy at the same temperature.

As an example, we show in Fig. 1 the integrand of Eq. (1) for the implementation of TI at 800 K. The vibrational frequency  $\nu$  for the Einstein crystal is chosen to be 5 THz, which is close to the principal peak of Al phonon density of states [34]. The integration, performed based on cubic spline interpolation of discrete data points collected by separate MD runs (red open circles), gives the free energy difference between fcc-Al and Einstein crystal reference  $\Delta F = -3.872$  eV/atom (see Fig. 2).

To calculate the free energy of Al liquid, we first determine the melting point ( $T_m$ ) of fcc-Al under ambient pressure, at which the difference in Gibbs free energy between the solid and liquid phases  $\Delta G = 0$ . Following the method described in Ref. [35], we plot the solid-liquid interface (SLI) velocity, obtained from MD simulation for the [1 0 0] direction, as function of temperature (see Fig. 3). The melting temperature determined from these data is  $915.7 \pm 0.5$  K, which is slightly lower than the experimental value (933 K). The Gibbs free energy difference at other temperatures is readily available by integrating the Gibbs-Helmholtz equation

$$\left[ \frac{\partial(\Delta G/T)}{\partial T} \right]_P = -\frac{\Delta H}{T^2}, \quad (2)$$

where  $\Delta H$  is the enthalpy change in the liquid and solid phases, or, the latent heat. The absolute free energy for Al liquid can be obtained by combining the information on solid-liquid free energy difference and the absolute free energy for the solid fcc-Al calculated previously. The final results are shown in Fig. 4

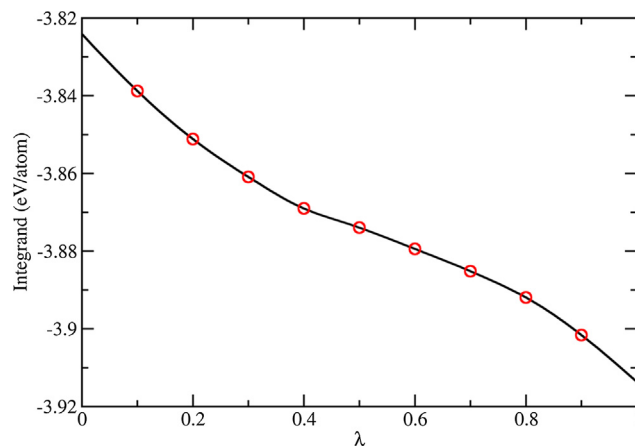


Fig. 2. The integrand of Eq. (1) for fcc Al at  $T = 800$  K. Open circles are data points collected in separated MD runs. The solid line is a cubic spline interpolation.

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