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Accurate Method to Calculate Liquid and Solid Free Energies for Embedded Atom Potentials

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Abstract

Using a perturbation theory with a hard-sphere reference system we have directly calculated free energies of fluid and solid phases of aluminum with an embedded atom model potential. Unlike other approaches such as thermodynamic integration, we do not require *any* simulations. Moreover, the free energies of the two different phases are calculated in a single approach, unlike approximations like the quasi-harmonic solid approach. The calculated free energies are with an average relative error 0.55% of the simulation values and the resulting melting temperature is within 5% of the simulation value.

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Using a perturbation theory with a hard-sphere reference system we have directly calculated free energies of fluid and solid phases of aluminum with an embedded atom model potential. Unlike other approaches such as thermodynamic integration, we do not require *any* simulations. Moreover, the free energies of the two different phases are calculated in a single approach, unlike approximations like the quasi-harmonic solid approach. The calculated free energies are with an average relative error 0.55% of the simulation values and the resulting melting temperature is within 5% of the simulation value.

Calculations of the melting line of materials are of fundamental interest, representing a fundamental understanding of the equilibrium properties of both the solid and liquid phases, and the competition between them. Traditionally, the liquid free energy is calculated from perturbation theory or variational theory with an appropriate reference system. The crystalline free energy may be calculated with quasiharmonic approximation.[1–4] For the free energy calculation of solids, the quasiharmonic approximation provides an accurate description when the temperature is far from the melting temperature; its accuracy becomes less reliable as the system gets close to the coexistence. For both the liquid and solid phases, thermodynamic integration has been used in combination with simulations, to perturb from a known system at some temperature, and then integrate the change in free energy needed to change to the system (and temperature) of interest.[5,6] Typically, a harmonic solid is used as a reference system for thermodynamic integration approaches for crystals, while an ideal gas is used as a reference for the liquid phase. As an alternative to calculating free energies, melting temperatures may be found directly from simulations.[7,8]

An alternative method to the quasiharmonic approximation is perturbation theory,[9,10] which has been successfully applied to simple model systems. In this Brief Report we will show that the perturbation theory with a hard sphere reference system yields free energies of liquid and solid free energies with an average relative error of 0.55% of the simulation values using an embedded atom model (EAM) potential of aluminum. The resulting melting temperature is within 5% of the simulation result.

The perturbation theory of liquid and solid is well known in chemical physics, and its applications to the coexistence of molecular model systems is well documented.[10,11] The most successful approach is the theory of Weeks, Chandler, and Anderson (WCA),[12] and its various extensions.[9–11] The original WCA theory divides the pair potential into a reference potential and a perturbation potential at the minimum of the potential well, since that is where the force ''felt'' by the particles tends to be zero. This division scheme is accurate in most fluid situations, and indeed it predicts accurate thermo-

dynamic properties of fluids for most densities. However, near the melting line, it gives a reference potential that is too stiff and that often requires an unrealistically large hardsphere diameter as a reference system, and thus leads to large errors in thermodynamic quantities. Kang and co-workers introduced an alternative division scheme to overcome this difficulty, and the modification gave very accurate results by comparison with simulations.[10,13] We will use this extended theory for the calculation of free energies of liquid and solid aluminum.

EAM potentials have been shown to be a useful potential for the study of melting processes of many metals and alloys.[5,14–16] These potentials are superior to pair potentials, at least for the aluminum used in our paper, by having a density-dependent term which includes many-body interactions. For aluminum extensive and accurate molecular simulations of the EAM potential have been published, and show that the potential can describe many properties of aluminum.[5,6] We will use the Mei-Davenport EAM potential for the calculation of free energies of liquid and solid aluminum, since its accurate simulation results are known.

Since the Mei-Davenport EAM potential form is well documented in the literature,[5,6] we will not reproduce it here. As any theoretical calculations based on perturbation theory a pair potential is needed. Here we will use Foiles' method to extract a density-dependent effective pair potential of an EAM potential.[15] For an EAM potential the total energy of the system can be written as

$$E_{\text{tot}} = \sum_i U(\psi_i) + \frac{1}{2} \sum_{i,j} \phi_{ij}(r_{ij}), \qquad (1)$$

where ψ_i is the total electron density at atom i due to the rest of the atoms in the system. (We use ψ_i to indicate the electronic density at atom i, to avoid confusion with the atomic density ρ.) U_i is the embedding energy for placing an atom into that electron density, ϕ_{ij} is a short-range pair interaction representing the core-core repulsion, and r_{ij} is the distance between atoms i and j. To derive an effective pair potential we only need to define a two-body term from the embedding energy since the second term is already in pair form. Foiles'
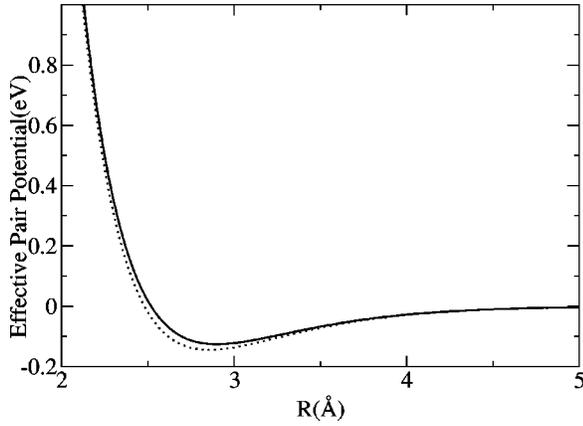
FIG. 1. The effective pair potential at two densities ($\rho = 0.055$ Å^{-3} with solid line and $\rho = 0.0519$ Å^{-3} with dotted line) from the Mei-Davenport EAM potential using Foiles' strategy. The so-obtained effective potential is density dependent.

strategy is to replace $U(\psi)$ with a Taylor expansion about an average electron density $\bar{\psi}$, hence, truncated to the second order yields an effective pair potential

$$V(r) = \phi(r) + 2U'(\bar{\psi})\psi(r) + U''(\bar{\psi})\psi^2(r), \qquad (2)$$

where $\bar{\psi}$ can be approximated by the average electron density for an fcc solid with a lattice constant such that the overall atomic density matches the liquid density. Foiles showed that radial distribution functions of liquid from the effective pair potential calculated from integral equations agree well the simulation ones with the full potential.[15] We also performed Monte Carlo simulations using the effective pair potential derived from the Mei-Davenport EAM potential using the above strategy (see Fig. 1). From these simulations, we obtained free energies of the liquid and solid from the effective pair potential that agree with the free energies from the full potential within 0.1%, which is well within the error of our perturbation theory calculations. Therefore, in this Brief Report, our perturbation theory calculations using the effective pair potential are directly compared with the simulation results using full potential.

We calculate the free energy by separating out a purely repulsive portion of the potential and approximating it by a hard-sphere system, then treating the remaining part of the potential $V_1(r)$ as a perturbation. The potential separation in the present perturbation theory can be written as

$$V(r) = V_0(r) + V_1(r), \qquad (3)$$

$$V_0(r) = \begin{cases} V(r) - F(r) & \text{if } r \leq \lambda \\ 0 & \text{if } r > \lambda, \end{cases} \qquad (4)$$

$$V_1(r) = \begin{cases} F(r) & \text{if } r \leq \lambda \\ V(r) & \text{if } r > \lambda. \end{cases} \qquad (5)$$

Here both λ and $F(r)$ are arbitrary, and the resulting thermodynamic properties depends on the choice of λ and $F(r)$ in the perturbation theory.

In the conventional WCA theory,[12] λ is chosen to be the intermolecular separation r^* at the minimum of the potential, and $F(r) = V(r^*)$. Such a separation is highly successful for fluid at normal densities.[11,12] At higher densities that occur near the freezing line, the WCA theory's hard-sphere diameter choice becomes so large that the resulting hard-sphere reference fluid lies in a metastable region and the application of WCA theory becomes difficult.[17] For the solid phase, the repulsive range λ is set to equal to the equilibrium lattice separation between particles, where the average repulsive and attractive forces of particles in the solid tend to be balanced out. Thus, a reasonable choice is $\lambda = a_c$, the nearest-neighbor distance of the crystal of interest (for example, $a_c = 2^{1/6}/\rho^{1/3}$ for fcc).

In general, a variational choice of λ, which is temperature and density dependent, will circumvent the above problem.[17] A simpler and more direct choice,

$$\lambda = r^* + S(\rho)(a_c - r^*),$$

$$F(r) = V(\lambda) - \left(\frac{dV(r)}{dr}\right)_{r=\lambda} (\lambda - r), \qquad (6)$$

turns out to give very accurate thermodynamic quantities for model systems.[13] Function $S(\rho)$ is defined as

$$s(\rho) = 0 \quad \text{if } \rho \leq \rho_1, \qquad (7)$$

$$= \frac{(\rho - \rho_1)^3 [6\rho^2 - 3(5\rho_2 - \rho_1)\rho + 10\rho_2^2 - 5\rho_1\rho_2 + \rho_1^2]}{(\rho_2 - \rho_1)^5}$$

$$\text{if } \rho_1 \leq \rho \leq \rho_2, \qquad (8)$$

$$= 1 \quad \text{if } \rho_2 \leq \rho \qquad (9)$$

which smoothly connects $\lambda = r^*$ at low ρ to $\lambda = a_c$ at high ρ. In this equation, $\rho_1 = 0.97\rho_c$, $\rho_2 = 1.01\rho_c$, and ρ_c is the density where $r^* = a_c$. For the fluid phase, this choice reduces to the WCA separation if $\rho \leq \rho_1$. At high densities near the freezing line an equilibrium nearest neighbor separation will lie closer to $r = a_c$ rather than $r = r^*$ due to the strong repulsion of other molecules. Such a choice makes the range of $V_0(r)$ [Eq. (3)] shrink with density; hence the corresponding hard-sphere diameter is also reduced, and the difficulty associated with the metastable hard-sphere fluid is avoided.

In the perturbation theory, the Helmholtz free energy A of the system can be expressed as the sum[11]

$$A = A_0 + A_1 + A_2 + \cdots, \qquad (10)$$

where A_0 is the free energy of the reference system specified by potential $V_0(r)$, and A_m contains all of the perturbation terms of order m with the inverse temperature as the expansion parameter.[11] In practical calculations the reference system is approximated by a hard-sphere system with an effective diameter $d(\rho, T)$ which is determined using various schemes.[11] Thus A_0 is approximated by a hard-sphere free energy. The first order free energy is calculated using the hard-sphere radial distribution function $g_{\mathrm{HS}}(r)$:

$$A_0 = A_{HS} + (\text{higher order terms}),$$

$$A_1 = \frac{1}{2}\rho \int d\mathbf{r} V_1(r) g_{HS}(r/d). \tag{11}$$

We define the hard-sphere cavity function, $y_{HS}(r/d)$, by

$$y_{HS}(r/d) = \exp[\beta V_{HS}(r)] g_{HS}(r/d), \quad \text{and} \quad \beta = 1/kT. \tag{12}$$

Thus an approximate pair correlation function for the reference system specified by $V_0(r)$ is given by

$$g_0(r) \approx \exp[-\beta V_0(r)] y_{HS}(r). \tag{13}$$

The key to the accurate determination of the free energy is the appropriate choice of the hard-sphere diameter d. Following the WCA approach, d is chosen so that the first order term in A_0 is zero:

$$\int d\mathbf{r} \{\exp[-\beta V_0(r)] - \exp[-\beta V_{HS}(r)]\} y_{HS}(r/d) = 0. \tag{14}$$

For the fluid phase, the Verlet-Weis $g_{HS}(r/d)^{18,19}$ of the hard-sphere fluid is used to solve the above equation to obtain the effective hard-sphere diameter. The hard-sphere free energy is given by the Carnahan-Starling equation.[11] Then the total free energy of the fluid phase is obtained from Eq. (11).

For the solid phase, Choi *et al.*'s parametrization $g_{HS}(r/d)$ based on Monte Carlo simulations of the fcc lattice[20] is used to solve Eq. (14) for the effective hard-sphere diameter. The fcc hard-sphere free energy of the solid phase is obtained from the Hall solid equation of state for hard spheres,[21] starting with the simulation free energy at packing fraction 0.545.[22] The free energy of the solid phase is obtained from Eq. (11).

Once the total free energy as a function of density is obtained, the thermodynamic relation $P = -[\partial A/\partial(1/\rho)]_T = 0$ yields the free energy at zero pressure, as well as the corresponding density. These results can be directly compared with the simulation values from the same potential.[6] In Fig. 2, we compare the free energies. As shown in the figure, even such a simple perturbation calculation can produce very accurate free energies for both the fluid and solid phases. On the other hand, the melting point from perturbation calculations still has a relatively large error because of the sensitivity to the slope of the free energies. The average relative error in the free energies is 0.5%. The melting temperature from perturbation calculation is 863 K, 5% higher than the simulation value of 825 K. Nevertheless, our calculations show that perturbation theory with accurate radial distribution functions of hard-sphere solid can yield accurate thermodynamic quantities.

Furthermore, the perturbation theory also yields reasonable radial distribution function for the liquid. Figure 3 shows the comparison between results from computer simulations of the liquid at the melting temperature, and the reference $g_0(r)$ calculated using Eq. (13). Note that $g_0(r)$ is calculated only using $V_0(r)$, which is purely repulsive. Thus
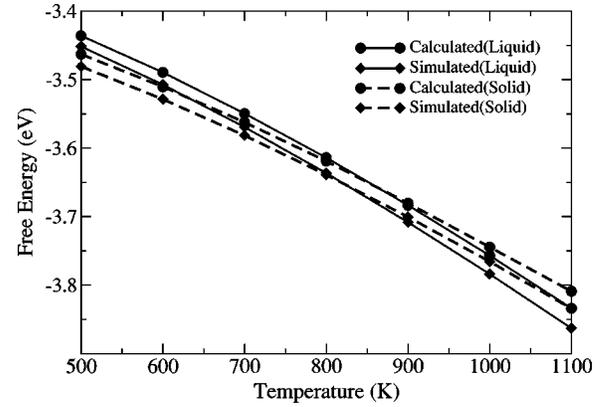

FIG. 2. The free energies at $P=0$ of aluminum fluid and solid phases from Mei-Davenport EAM potential using perturbation theory and computer simulations.

the strong agreement of the systems indicates that the liquid responds essentially like an effective hard-sphere system. The inset shows that the first peak position occurs at a slightly smaller distance for $g_0(r)$ than that of the simulations. In the figure, we also include $g(r)$ from simulations of the liquid calculated using the approximate pair potential $V(r)$, demonstrating that the pair correlations of the many-body potential and its approximate pair potential are extremely close. The difference is again largest at the first maximum, as can be seen in the inset of the figure.

This paper shows that accurate free energies of fluid and solid phases can be obtained from a single theoretical framework. Once an accurate radial distribution function of the reference system is known, perturbation theory gives very accurate thermodynamic quantities. An accurate radial distribution function of a hard sphere system in fluid phase is well
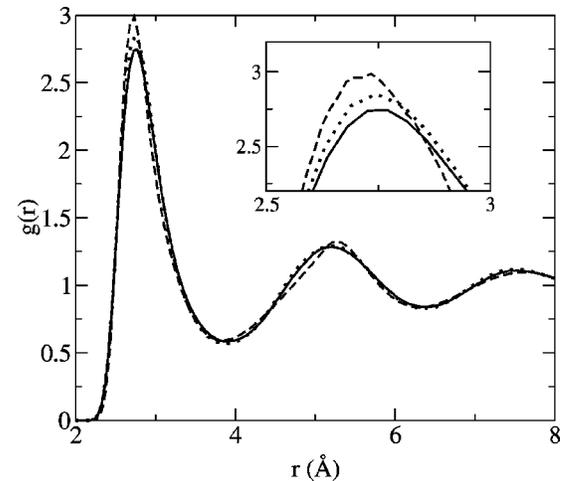

FIG. 3. The radial distribution function of aluminum fluid from Mei-Davenport EAM potential using perturbation theory and computer simulations. The solid line is from simulation with the full EAM potential and the dotted line is from simulation with the effective pair potential shown in Fig. 1. The dashed line is from perturbation calculation. The inset shows the region near the maximum of the first peak, where the discrepancies are largest.

established.[11,18] Using density functional theory, an accurate radial distribution function of a hard sphere system in solid phase can also be obtained,[23] and the strategy can be extended to mixtures. Thus, an extension of the current approach to alloy phase diagrams will be interesting.

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