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An improved CVM entropy functional for binary fcc alloys

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ABSTRACT

We explore the possibility of modifying the multiplicity of the basic clusters in the entropy functional used in the cluster variation method so that the truncation errors arising due to finite size of the basic clusters may be corrected. The numerical values of the multiplicity of the basic clusters are found by requiring the modified CVM entropy functional in the tetrahedron–octahedron approximation for the face-centered cubic structure to yield the nearly exact critical temperatures for ordering and phase separating systems. This modification correctly reproduces the triple point in a prototypical fcc ordering system, using the same first neighbor pair interaction energy parameter for all the ordered ($L1_0$ and $L1_2$) and disordered (A1) phases, without increasing the computational burden and thereby making a long standing problem tractable. The modification also improves the agreement between the values of thermodynamic quantities (for ordered and disordered phases at arbitrary temperatures and compositions) obtained from CVM and Monte Carlo simulations.

1. Introduction

Computational Thermodynamics (CT) provides an integrated framework for representing thermodynamic properties, phase equilibria and phase diagrams of alloy systems. The advantage of such an approach is the capability to predict those features of phase equilibria which cannot be easily measured as well as to predict them for complex multicomponent systems using properties of lower order sub-systems. CT is most often based on the CALPHAD method [1]. Another approach for CT is cluster expansion–cluster variation method (CE–CVM) [2,3], which offers a theoretically sound alternative by providing an explicit description of Gibbs energy in terms of short-range order (sro) and long-range order (lro) parameters. However the latter is computationally more complex and time consuming in comparison with the former. Further, the accuracy of CE–CVM is limited by the size of the basic cluster(s) chosen in a particular approximation of the method. The present contribution develops and demonstrates a procedure for improving the accuracy of the CE–CVM for fcc systems, without increasing the computational burden.

We shall consider here phase diagrams and thermodynamic calculations only for first neighbor pair interactions, since theoretical or reliable Monte–Carlo simulation results which are required for comparison are available only for this case. Various approximations of CVM [2] are known to provide different levels of accuracy in the results. Sanchez et al. [4] and Finel and Ducastelle [5] have used the tetrahedron–octahedron (TO) approximation of CVM for the calculation of a phase diagram exhibiting order–disorder transformation in fcc alloys. One of the important achievements of these CVM calculations is in correctly locating the triple point at a finite temperature. Simulations by Lebowitz et al. [6] and Diep et al. [7] have confirmed the triple point at $RT/C_1 \approx 1.0$, where C_1 is the cluster expansion coefficient (CEC) corresponding to the first neighbor pair interactions. These studies were further refined by Kämmerer et al. [8]. The critical temperatures obtained by using the TO approximation of CVM and the best known values are given in Table 2.

It may be observed that, in general, critical temperatures obtained by using the TO approximation of CVM are overestimated in comparison with the best known results. This overestimation is as high as 20% in the case of triple point temperature. This necessitates a need to improve the CVM-TO entropy functional so as to improve its accuracy without increasing the computational effort. There have been some earlier efforts to improve the accuracy of CVM calculations. With particular reference to the fcc structure, a hybrid approach of MC simulations and CVM has been applied to ordering [9] and phase separating systems [10]. Ferreira et al. [11] have suggested a new functional for the entropy in the hybrid MC-CVM method. All these approaches are based on compute intensive MC simulations, which are impractical for multicomponent alloys. A slightly different approach has been taken by Oates et al. [12] in a modified version of CVM designated cluster site approximation (CSA). They have considered the tetrahedron approximation of CSA and treated the coefficient of the term corresponding to the basic cluster in the entropy functional as an

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adjustable system dependent parameter in addition to the cluster expansion coefficients (CEC), all of which would be determined by simultaneous optimization of experimental data.

The source of inaccuracy in the CVM entropy functional, particularly near phase transitions, can be attributed to the truncation of entropy functional corresponding to a basic cluster of finite size [13]. In the present communication, we propose a method of modifying the entropy functional for the TO approximation of CVM for binary fcc solutions. We shall then validate the new method by comparing it with MC simulation which is known to yield more accurate results.

2. Modification of CVM entropy functional

The configurational Gibbs energy of the fcc phase is expressed as

$$G = H - TS \tag{1}$$

where H and S respectively denote the configurational enthalpy and entropy. Configurational enthalpy may be expanded as [14]

$$H = \sum_i C_i m_i u_i \tag{2}$$

Here C_i, m_i and u_i respectively represent cluster expansion coefficient (CEC), multiplicity and correlation function of the ith cluster. We note that the enthalpy expression is exact since there is no truncation of the cluster expansion for the enthalpy and the infinite series terminates in practical situations as the CECs vanish for sufficiently large clusters.

The exact configurational entropy is given by the following infinite series.

$$S = \sum_{i=1}^{\infty} m_i g_i \tag{3}$$

Here g_i is a correction term, known as cumulant function, corresponding to the ith cluster. These are related to partial entropies S_i of the clusters. For the disordered fcc structure for which clusters and sites are shown in Fig. 1, the entropy expression becomes:

$$S = S_1 + m_2(S_2 - 2S_1) + m_3(S_3 - 2S_1) + m_4[S_4 - 3(S_2 - 2S_1) - 3S_1] + \cdots \tag{4}$$

where S_1, S_2, S_3, S_4... represent partial entropies of point (1), first neighbor pair (1,2), second neighbor pair (1,6), triangle (1,2,3) ... clusters respectively. The partial entropies in turn can be expressed in terms of the probability of occurrence of cluster configuration j on cluster type i, $\rho_{i,j}$ as follows:

$$-S_i/\mathrm{R} = \sum_j \rho_{i,j} \ln \rho_{i,j} \tag{5}$$

After simplifying Eq. (4) becomes,

$$S = -\mathrm{R}\sum_i \gamma_i m_i S_i \tag{6}$$

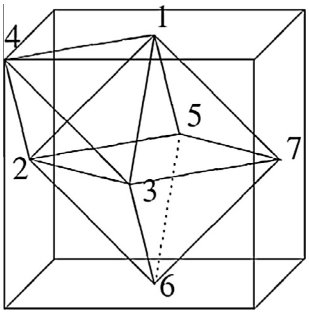

Fig. 1. Tetrahedron (1234) and octahedron (123567) clusters in an fcc unit cell [15].

where γ_i is Kikuchi–Barker overlap correction coefficient for the ith cluster.

In practice, configurational entropy is approximated by retaining a finite number of terms (up to cluster(s) of type K) of the infinite series expansion of the exact entropy in Eq. (3) and (4). The degree of approximation is determined by the number of terms retained in the entropy functional.

Limiting the basic cluster size thus leads to truncation error. The series given in Eq. (3) and (4) indicates that it is possible to modify the coefficient (that is the multiplicity) of the term corresponding to the basic cluster in a particular CVM approximation to account for the truncation error and reproduce the accurate value of some desirable feature such as the critical transformation temperature obtained either from MC simulation or from a higher order approximation of CVM. We shall apply this approach to fcc alloys to correct the CVM entropy functional for the TO approximation by using the best known results. We note that no modification of the multiplicity occurring in the expression for enthalpy is required since there is no truncation of that expression.

There are four invariant temperatures of interest in fcc phase separating and ordering systems, namely (i) consolute temperature for phase separation, (ii) critical temperature for A1 ↔ $L1_0$ ordering, (iii) critical temperature for A1 ↔ $L1_2$ ordering and (iv) triple point for A1, $L1_0$ and $L1_2$ equilibrium. There are two basic clusters in TO approximation of CVM for fcc, namely tetrahedron and octahedron. Multiplicities of these two basic clusters will be modified to best fit the 4 special temperatures in a least squares optimization. For this purpose, we define a merit function $\chi^2_{T_c}$ as

$$\chi^2_{T_c} = \sum_i \left(\frac{T^{M-CVM}_{c,i} - T^{exact}_{c,i}}{T^{exact}_{c,i}} \right)^2 \tag{7}$$

where the index i runs from 1 to 4 and corresponds to the four special temperatures mentioned above. In this, T_c^{M-CVM} represents the specific temperature of interest obtained by modifying the multiplicity of basic clusters in the CVM entropy functional whereas T_c^{exact} refers to its exact/best known value. Minimization of the merit function with respect to the multiplicities of the tetrahedron (m_T) and octahedron (m_O) clusters will provide optimum values of m_T and m_O. Since analytical derivatives of the merit function with respect to these multiplicities are not readily available, we shall use the conjugate gradient algorithm suggested by Powell [16] for the minimization, as it does not require derivatives. It may be noted that Kikuchi–Barker coefficients [3] of subclusters will also get modified owing to the variation of m_T and m_O as shown in Table 1. There are two ways in which multiplicities can be modified: (i) modifying multiplicities of the basic clusters only (henceforth referred to as M-CVM-1) and (ii) modifying multiplicities of the basic clusters along with those of clusters completely inside one of the two basic clusters (that is, non-overlapping clusters) with a similar factor so that their K–B coefficients remain zero (henceforth referred to as M-CVM-2). The number of independent variables is two in both the cases. It may be noticed that M-CVM-1 will be more computationally intensive than M-CVM-2 due to 5 additional partial entropy terms appearing in the entropy functional.

In order to compare the results of M-CVM calculations with exact (or more accurate) values, we have performed MC simulations and obtained values of enthalpies at various temperatures and compositions for both ordering and phase separating systems. All the simulations were performed on a 16^3 MC cell (having a total of 16,384 sites). In each case, the first 1000 MC steps per site (MCSS) were discarded. Averages were taken over the subsequent 4000 MCSS, each of which was separated by 2 MCSS to ensure uncorrelated equilibrium configurations.