



Approximate solutions to the cluster variation free energies by the variable basis cluster expansion



J.M. Sanchez ^{a,*}, T. Mohri ^b

^a Institute for Computational Engineering and Sciences and Texas Materials Institute, The University of Texas at Austin, Austin, TX 78712, USA

^b Institute for Materials Research, Tohoku University, Sendai, Japan

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ABSTRACT

In this paper we obtain approximate solutions to the Cluster Variation free energy by carrying out a cluster expansion of the probabilities appearing in the free energy functional in terms of concentration-dependent basis functions, and by truncating the expansion at different cluster levels prior to minimization. We show that a significant improvement over the Bragg–Williams approximation can be achieved by truncating the expansion of the cluster probabilities at relatively small clusters, thus dramatically reducing the number of equations that need to be solved in order to minimize the free energy. Furthermore, the free energy functional in the Cluster Variation Method offers a well-controlled case study to infer the effects of truncating the expansion of the energy of alloy formation in the commonly used Cluster Expansion method, versus the effects of truncating the expansion when using a concentration-dependent basis. Examples of the approach are given for simple Ising models for fcc- and bcc-based prototype alloy systems.

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1. Introduction

Since its inception by Kikuchi in 1951, the Cluster Variation Method (CVM) has been widely used to accurately account for the effect of short-range order in the free energy of binary and multicomponent alloys [1]. While the accuracy of the CVM generally increases with the size of the largest cluster included in the approximation, so does the computational effort involved in the minimization of the free energy functional. With increasing cluster sizes, the minimization needs to be carried out with respect to a relatively large number of configurational variables, a number that grows exponentially with cluster size. Within mean-field theories, at the other extreme of computational convenience is the commonly used Bragg–Williams approximation. While a significant body of research and applications have shown that the shortcomings of the Bragg–Williams approximation can be compensated with other terms in the configurational free energy, it is apparent that the use of increasingly accurate *ab initio* methods to calculate energies of formations calls for a similar increase in the accuracy of the configurational entropy.

A central task in the configurational theory of alloys is the description of functions of configurations in terms of a complete

set of configurational variables. A widely used approach to describe functions of configuration, formalized by Sanchez et al. [2], is the so-called Cluster Expansion (CE) method in which the functions are expanded in terms of pair and multisite correlation functions. These correlation functions form a complete and orthonormal basis in configurational space [2]. Subsequently, it was shown that the complete and orthonormal basis set introduced in Ref. [2], which will be referred here as the SDG basis, is a particular case of an infinite number of closely related complete and orthonormal basis sets in configurational space [3,4].

Presently, the CE in the SDG basis is the method of choice to obtain effective cluster interactions from the energies of a set of ordered compounds, which are typically calculated by means of some implementation of Kohn–Sham equations in Density Functional Theory. The approach is particularly appealing since, for the case of the energy of alloy formation, and after truncating the expansion at some maximum cluster size, the method casts the energy in the form of an Ising-like model with constant expansion coefficients. Such expansion coefficients are commonly referred to as Effective Cluster Interactions (ECIs). However, and despite the unquestionable success of the CE method in the SDG basis for the parametrization of the energy of alloy formation, the validity of truncating the expansion remains, at least at a fundamental level, an unresolved issue. In particular, if the energy has a non-linear dependence in the concentration of the alloy, like it is the

* Corresponding author.

E-mail address: jsanchez@austin.utexas.edu (J.M. Sanchez).

case for a regular solution model or for Fridel's square band model for transition metal alloys, it is straightforward to show that the CE in the SDG basis does not converge [4].

The existence of an infinite number of basis sets provides a straightforward path to address non-linear concentration dependences in the energy of the system [3,4]. The method consists in matching the basis sets to the overall concentration of the alloy under consideration, and is akin to doing the expansion in a canonical ensemble as first proposed by Asta et al. [5]. This particular implementation of the cluster expansion will be referred as the Variable Basis Cluster Expansion (VBCE) [4]. Unlike the expansion in the SDG basis, the ECIs in the VBCE are concentration dependent.

Although most current applications of the CE method are aimed at characterizing the energy of alloy formation, the method was initially motivated by the need to develop efficient algorithms to minimize the CVM free energy functional [7]. Such early studies were aimed at the calculation of prototype alloy phase diagrams based on Ising-like models for the description of the energy of formation, and on the CVM for the treatment of the configurational entropy [7–10]. The approach adopted in these early studies was to describe the probabilities appearing in the CVM configurational entropy in terms of a cluster expansion using the SDG basis functions, the expectation values of which are the so-called correlation functions. Since for a given cluster approximation the correlation functions form a complete and orthogonal basis set, they naturally constitute a full set of independent variables for the free energy minimization. In this paper we formulate the minimization of the CVM free energy in terms of a VBCE of the cluster probabilities, and show the effects of truncating the expansion at different cluster levels. In particular, the CVM free energy functional offers a well-controlled case study to investigate the truncation of the CE in the SDG basis versus the truncation of the CE in the Variable Basis. Our main result, to be presented in the following sections, is that truncating the CE of the probabilities in the SDG basis leads to large errors in the CVM free energy as we move away from the 50/50 concentration and, eventually, leads to negative values of the probability distributions. On the other hand, truncation of the CE in the Variable Basis gives a sequence of free energies that converge uniformly towards the full CVM free energy.

The organization of the paper is as follows: we begin with a review of the CVM in Section 2 and place the emphasis on the expansion of the cluster probabilities in the different basis sets. An explicit example of how to connect the CE in the SDG basis with the expansion in the Variable Basis is presented in Section 3 for the tetrahedron approximation in the fcc lattice. We also present examples of approximate solutions to the standard Ising model for several CVM approximation in the fcc and bcc lattices. We conclude in Section 4 with a summary and observations on the proposed set of approximate solutions to the CVM free energy.

2. The cluster variation method

The CVM, based on the variational principle of classical statistical mechanics, provides approximations to the exact configurational free energy functional in terms of a cumulant expansion of cluster entropies [1,11–13]. The general form of the CVM free energy functional is:

$$F(\{X_\eta\}) = \langle E \rangle - k_B T \sum_\eta a_\eta \sum_{\vec{\sigma}_\eta} X_\eta(\vec{\sigma}_\eta) \log(X_\eta(\vec{\sigma}_\eta)) \quad (1)$$

where $\langle E \rangle$ is the expectation value of the configurational energy, $X_\eta(\vec{\sigma}_\eta)$ is the probability of observing a finite cluster of type η in the configuration $\vec{\sigma}_\eta$, and the a_η are geometric coefficients.

As mentioned in the Introduction, the energy of the alloy can always be expanded in any one of an infinite number of complete

and orthonormal basis sets. The basis functions in question are given by [3,4]:

$$\Phi_\alpha^x(\vec{\sigma}) = \prod_{p \in \alpha} \frac{(\sigma_p - x)}{\sqrt{1 - x^2}} \quad (2)$$

where $\alpha = \{\eta, p, v\}$ stands for a cluster of type η , with its center of mass located at point p in the lattice, and where v labels all distinct orientations of the cluster obtained by applying the symmetry operations of the point group of the lattice.

For a given value of x in Eq. (2), the scalar product of two functions of configuration is defined as:

$$\langle f, g \rangle_x = \sum_{\vec{\sigma}} \left(\frac{e^{\mu(\vec{\sigma})}}{2 \cosh(\mu)} \right)^N f(\vec{\sigma}) g(\vec{\sigma}). \quad (3)$$

with μ such that $\tanh(\mu) = x$ and with $\langle \sigma \rangle$ the point correlation given by:

$$\langle \sigma \rangle = \frac{1}{N} \sum_{p=1}^N \sigma_p \quad (4)$$

It follows from the completeness of the basis functions $\{\Phi_\alpha^x\}$, that the expectation value of the energy can be written as:

$$\langle E \rangle = \sum_\eta \omega_\eta J_\eta(x) z_\eta^x \quad (5)$$

where ω_η is the number of clusters of type η per lattice point, z_η^x is the expectation value of the basis function Φ_η^x , and $J_\eta(x)$ is the ECI for cluster η obtained by projecting the energy E onto the basis function Φ_η^x [3,4].

From Eqs. (2) and (3) we see that a choice of a fixed basis with a value of $x = 0$ corresponds to the commonly used SDG basis. On the other hand, in the VBCE, we use, for each configuration $\vec{\sigma}$, a basis such that $x = \langle \sigma \rangle$.

Several methods [1,11–13] have been developed to calculate the coefficients a_η , with the approach introduced by Barker [11] being perhaps the simplest. In Barker's approach, one starts by selecting a maximum cluster, or clusters, to be used in the approximation, say η_0 . The coefficient for the maximum cluster a_{η_0} equals the number of clusters of type η_0 per lattice point, i.e. $a_{\eta_0} = \omega_{\eta_0}$. The remaining coefficients for clusters $\eta \subset \eta_0$ are given by the following recursive formula:

$$a_\eta = \omega_\eta - \sum_{\eta' \supset \eta} M_\eta^{\eta'} a_{\eta'} \quad (6)$$

where $M_\eta^{\eta'}$ stands for the number of cluster of type η contained in a cluster of type η' .

The main computational task in implementations of the CVM is the minimization of the free energy functional, Eq. (1), with respect to the cluster probabilities $X_\eta(\vec{\sigma}_\eta)$. In order to facilitate the minimization step, it is convenient to introduce a set of independent variables to describe all the cluster probabilities involved in a given CVM approximation. Such full set of independent variables can be identified quite straightforwardly by cluster expanding the probability distributions $X_\eta(\vec{\sigma}_\eta)$. As mentioned in the Introduction, the CE method was initially developed to expand the cluster probabilities in terms of the expectation values of the correlation functions in the SDG basis [7]. In such a basis, the expansion is:

$$X_\eta(\vec{\sigma}_\eta) = \sum_{\alpha_{\eta'} \subseteq \alpha_\eta} \langle X_\eta, \phi_{\alpha_{\eta'}}^0 \rangle_0 \phi_{\alpha_{\eta'}}^0(\vec{\sigma}_{\eta'}) \quad (7)$$

with the coefficients $\langle X_\eta, \phi_{\alpha_{\eta'}}^0 \rangle_0$ taking a particularly simple form [7]:

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