Invariance of truncated cluster expansions for first-principles alloy thermodynamics

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Cluster expansion methods for coupling electronic structure methods with statistical thermodynamics1–4 and for extensive ground-state predictions5–7 have become a widely used tool for understanding configurational aspects of crystalline solutions and alloys. In such cluster expansions (CEs) only clusters up to a certain size and range are included; excluded clusters are assumed to have a zero contribution to the property that is being cluster expanded. In this sense, practical CEs contain only rather compact clusters and are “truncated.” Recently, Zarkevich and Johnson presented an improved method for CEs of configurational properties of alloys.8 Although the “three rules ad vitam aut culpam” that define the method were argued via variational minimization (not presented), the rules were presented intuitively and on the basis of an improved agreement between theory and experiment for the properties of Ni3V. Thus, there is no consensus in the alloy theory community on the validity of these rules as demonstrated by the proliferation of methods.6,7,9 On the premise that a CE is defined by the clusters that it includes, and that once a set of clusters is selected for a cluster expansion it gives a specific value for the configurational energy of any particular structure, a proof for invariance of cluster expansions is presented. A cluster expansion is invariant under linear transformations of the site occupation variable when it includes all the subclusters of the included clusters. When the spin- or site-occupation variable is redefined, the consequence for an invariant cluster expansion is that the numerical values of the effective cluster interactions change, without there being any other changes. Therefore, the spin- or site-occupation variable can be defined at will, say, to optimize computational expediency.

\[ \langle \sigma_i \rangle = \left\langle \sigma_{i_1} \sigma_{i_2} \sigma_{i_3} \ldots \sigma_{i_n} \right\rangle, \]

where \( i_1, i_2, \ldots \) designate the sites in the cluster and \( n_a \) is the number of sites in cluster type \( \alpha \). It has been shown13 that all configurational properties of the alloy, including the configurational energy \( E \), can be written as a CE in terms of the ECIs \( E \) as

\[ E = \sum_{\alpha} J^{(\sigma)}(\langle \sigma_i \rangle), \]

where the cluster multiplicities have been absorbed in the ECI. It is understood that the CE includes the so-called empty cluster with zero sites that has a correlation function of unity. The superscript \( \sigma \) is attached to \( J \) because its numerical value depends on the definition of \( \sigma \). However, the assignment of values 1 and \(-1\) to \( \sigma \) is completely arbitrary. Thus, we impose that the CE gives the same results independent of the value assignment of \( \sigma \) by considering the linear transformation to the occupation variable \( s \) defined with \( \sigma_i = As_i + B \), where \( A, B \) are arbitrary but \( A \neq 0 \). Then it follows that:

\[ \langle \sigma_i \rangle = \sum_{\rho \subseteq \alpha} A^n \rho B^{n-a-n}(s_{\rho}), \]

where \( \beta \subseteq \alpha \) means that \( \beta \) is a subcluster of \( \alpha \), including the cluster \( \alpha \) itself and also including the empty cluster. The cluster expanded property \( E \) (e.g., energy) in Eq. (2) becomes

\[ E = \sum_{\alpha} J^{(\sigma)} \sum_{\rho \subseteq \alpha} A^n \rho B^{n-a-n}(s_{\rho}), \]

\[ = \sum_{\beta} \left[ \sum_{a \supseteq \beta} A^n \rho \sum_{\alpha \supseteq \beta} B^{n-a-n}(s_{\rho}) \right](s_{\rho}) = \sum_{\beta} J^{(\sigma)}(s_{\rho}), \]

where \( \alpha \supseteq \beta \) indicates clusters \( \alpha \) which have \( \beta \) as subcluster, inclusive. Hence, the new ECI are given as
\begin{equation}
J^{(s)}_{\beta} = A^{a_\beta} \sum_{\alpha \geq \beta} B^{a_\alpha - a_\beta} J^{(\sigma)}_{\alpha}.
\end{equation}

It is now important to point out that Eq. (5) introduces non-zero \( J^{(s)}_{\beta} \) for any subcluster of the original set of \( J^{(\sigma)}_{\alpha} \). Hence, if rule (2) is not satisfied, changing the definition of \( \sigma \) affects not just the values of \( J \) but also which terms are included and hence gives a different CE.\(^{14}\) Equation (5) shows that rule (2) must be satisfied for the CE to be independent of the representation of \( \sigma \).

An important consequence of Eq. (5) is that one is at liberty to choose the most convenient definition of \( s \). In Monte Carlo simulations, e.g., the definition of \( s = 0(1) \) for a site occupied by an \( A \) (\( B \)) species, can be very expedient when \( B \) is the minority species, because then \( \langle s_w \rangle \) corresponds to \( \alpha \) clusters consisting of pure \( B \). In other words, one could determine the many-body cluster correlation functions very quickly by considering the minority species \( B \) only. The exact transformation formulated in Eq. (5) guarantees that one obtains the same configurational energy as with the much more cumbersome definition \( \sigma = -1(1) \) for a site occupied by an \( A \) (\( B \)) species. In cluster variation method\(^{15,16}\) calculations with large maximal clusters,\(^{17}\) it is numerically advantageous to define the correlation functions such that they tend towards 0 because cluster probabilities are given as sums and differences of correlation functions. To evaluate accurately cluster probabilities, particularly for large clusters, it is advantageous to use two definitions for the site occupation: \( s = 0(1) \) for a site occupied by an \( A \) (\( B \)) species when \( B \) is the minority species, and \( s = 0(1) \) for a site occupied by a \( B \) (\( A \)) species when \( A \) is the minority species.

Based on the premise that a cluster expansion is defined by the clusters that it includes, and that once a set of clusters is selected for the cluster expansion it gives a specific value for the configurational energy of a structure, a proof was given for the so-called 2nd rule in Ref. 8 as a consequence of invariance under linear transformations of the site-occupation variable. A cluster expansion is invariant when it includes all the subclusters of the included clusters. Additionally, a conversion formula for the effective cluster interactions was derived that allows one to define the site occupation in such a manner that is computationally most efficient and accurate.

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\(^{9}\)A. van de Walle and G. Ceder, J. Phase Equilib. 23, 348 (2002).

\(^{10}\)This rule is mentioned also by van de Walle and Ceder (Ref. 9).

\(^{11}\)Actually for binary alloys only do the terms in a cluster expansion correspond to “clusters.” If there are three or more components, the “cluster expansion” is, in fact, over decorations of these clusters. Then, speaking of “figures” as in the terminology of Zunger (see Ref. 6) might be preferable.

\(^{12}\)This implies that the cross-validation score and least square fitting error are also independent of the definition of \( \sigma \).


\(^{14}\)Among other benefits of the 2nd rule are: (a) small clusters are favored over large clusters, in particular pairs over many-body clusters so that ground states stabilized by long-ranged interactions are described better; (b) CEs that more closely resemble those from analytic methods such as the generalized perturbation method; (c) CEs can be classified by its maximal clusters facilitating characterization and comparison.

\(^{15}\)R. Kikuchi, Phys. Rev. 81, 988 (1951).
