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Comment on “Cluster expansion and the configurational theory of alloys”

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Comment on “Cluster expansion and the configurational theory of alloys”

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Abstract

Cluster expansions with concentration-independent interactions have been widely used to model the formation energies of alloys. In the paper “Cluster expansion and the configurational theory of alloys”, this practice is called into question based on the argument that a truncated cluster expansion with concentration-independent interactions cannot be used to represent the formation energy of a random alloy if the formation energy is a nonlinear function of concentration. To clarify the validity of using cluster expansions with concentration-independent interactions, I demonstrate that this argument is not necessarily correct.

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In the paper “Cluster expansion and the configurational theory of alloys” (reference [1]) the validity of using cluster expansions with concentration-independent interactions for modeling alloy formation energies is called into question. In this Comment I will demonstrate that the central claim that leads to this conclusion, that a truncated cluster expansion with concentration-independent interactions cannot be used to represent the formation energy of a random alloy if the energy is a nonlinear function of concentration, is not necessarily correct.

Cluster expansions are generalized Ising models [2, 3] that have been widely used to model alloys and other materials with substitutional disorder [4]. For simplicity and clarity, throughout

this Comment I will use the example of a binary A-B alloy, in which every site on a lattice can be occupied by either an A atom or a B atom, but it is straightforward to extend this analysis to the more general case.

In a cluster expansion the structure of an A-B alloy is mapped to a set of site variables, \mathbf{s} , where $s_i = +1$ if an “A” atoms occupies the i^{th} site and $s_i = -1$ if a “B” atoms occupies the i^{th} site. For an infinite lattice, a property of the material (per unit cell) can be expanded as a linear combination of functions of \mathbf{s} :

$$F(\mathbf{s}) = V_0 + \sum_{\alpha} V_{\alpha} m_{\alpha} \varphi_{\alpha}(\mathbf{s}) , \quad (1)$$

where $F(\mathbf{s})$ is the material property, α are sets (a.k.a orbits) of symmetrically equivalent clusters of sites, m_{α} is the number of clusters in set α per unit cell, and V_{α} are coefficients known as effective cluster interactions (ECIs). A “cluster of sites” can be any subset of sites in the material. The correlation function, $\varphi_{\alpha}(\mathbf{s})$, is defined as

$$\varphi_{\alpha}(\mathbf{s}) = \frac{\sum_{cluster \in \alpha} \left(\prod_{i \in cluster} s_i \right)}{N_{\alpha}} , \quad (2)$$

where the sum is over all clusters in α and N_{α} is the number of clusters in α . It is commonly assumed that the infinite sum in equation (1) can be truncated to a sum over a finite number of terms representing spatially compact clusters with little loss of accuracy. The remaining ECIs of the cluster expansion are typically fit to a set of training data (often generated using density functional theory [5, 6]), and the resulting expansion can be used to very rapidly predict the value of $F(\mathbf{s})$ for different arrangements of atoms on the lattice.

In reference [1], in explaining the value of using concentration-dependent ECIs in a cluster expansion, the author provides the example of a hypothetical Hamiltonian for a binary alloy in which the energy is the square of the “concentration” (x) of the material, i.e.

$$E(\mathbf{s}) = x^2. \quad (3)$$

Here “concentration” is defined as a function of the number of A atoms (N_A) and the number of B atoms (N_B) on the lattice:

$$x = \frac{N_A - N_B}{N_A + N_B}. \quad (4)$$

It is correctly demonstrated that the cluster expansion for the Hamiltonian in equation (3) is a sum over an infinite number of symmetrically distinct, equally-weighted pair interactions and thus cannot be truncated to a sum over a finite number of terms. From this result, the following conclusion is drawn:

“...therefore, functions that have a nonlinear dependence on $[x]$ cannot be described by a finite sum of Fourier transform or cluster coefficients. With regard to the energy of formation of binary alloys, such a nonlinear dependence in concentration is always present in the energy of the totally disordered or random configuration. Thus, an important and dominant component of the energy of formation, namely, the energy of the random alloy *cannot* be expressed in the form of an Ising-type model with concentration-independent interactions. This fact brings into question the validity of essentially all applications of the cluster expansion to date...”

This result is surprising and at apparent odds with the successful application of the cluster expansion with concentration-independent ECIs to a variety of problems in materials science (see refs [4, 7-29] for some examples). This conflict can be resolved by recognizing that there is a subtle but important flaw in the above argument. It is clearly demonstrated that the cluster

expansion fails to converge in a case where the energies of *every possible arrangement of atoms*, even well-ordered ones, are a simple nonlinear function of concentration. However this does not imply that localized cluster expansions fail to converge if the energy of a *random* alloy is a nonlinear function of concentration.

To understand the difference between these two claims, it is useful to consider a cluster expansion of a random binary alloy on an infinite lattice. For a random binary alloy in the limit of infinite crystal size, the average value of s_i at each site is x . Because the occupancies of different sites are not correlated in a random material, the value of the correlation function for an orbit of clusters of n sites is [29, 30]

$$\varphi(\mathbf{s}) = x^n. \quad (5)$$

The value of the correlation function depends only on composition and is otherwise independent of \mathbf{s} , the vector of site variables. Thus, from equation (1), the cluster expansion of a property of a random binary alloy per unit cell is:

$$F(\mathbf{s}) = V_0 + \left(\sum_{\alpha \in \text{sites}} V_\alpha m_\alpha \right) x + \left(\sum_{\alpha \in \text{pairs}} V_\alpha m_\alpha \right) x^2 + \left(\sum_{\alpha \in \text{triples}} V_\alpha m_\alpha \right) x^3 + \dots \quad (6)$$

where “sites” is the set of all orbits of single-site clusters, “pairs” is the set of all orbits of 2-site clusters, “triples” is the set of all orbits of 3-site clusters, etc. Equation (6) can be used to express the formation energy of a random alloy in the form of an Ising-type model with concentration-independent interactions. Importantly, it demonstrates that this is possible even if the energy is a non-linear function of concentration, in contrast to the claim of reference [1]. If the energy of a random alloy is a linear function of concentration, then it can be expressed by a cluster expansion containing only single-site terms. If it is a quadratic function of concentration, then it can be expressed by a cluster expansion using up to 2-site terms. A cubic function can be

expressed using a cluster expansion containing up to 3-site terms, and so on. If the cluster expansion is truncated, then the sums in equation (6) only need to be evaluated over the clusters that are included in the expansion. For example, a simple cluster expansion that only includes single-site, nearest-neighbor 2-site, and nearest-neighbor 3-site interactions is capable of representing the formation energy of a random alloy as a third-order polynomial of the concentration.

A well-known example illustrating the validity of equation (6) is the regular solution model, which can be used to explain a variety of observations in real-world alloys [31]. In the regular solution model, enthalpy of formation for a random alloy is given by

$$H(\mathbf{s}) = \omega \frac{(1-x^2)}{4}, \quad (7)$$

where ω is a constant and x is as defined in equation (4). Consistent with equation (6), the regular solution model can be expressed as a cluster expansion containing only pair interactions [31]. The general cluster expansion approach can be thought of as an extension of the regular solution model by allowing for the inclusion of additional pair and higher-order interactions.

It is worth exploring why a truncated cluster expansion with concentration-independent ECIs can accurately reproduce the energy of a random alloy in the regular solution model (equation (7)), but not the Hamiltonian in equation (3). The difference is that the Hamiltonian in equation (3) assigns the same energy to every possible arrangement of atoms at a given composition, even well-ordered ones. This is a pathological example that is, for most systems, physically unrealistic. In most real-world alloys there exist well-ordered ground states with lower energy than a random structure, an observation that is well-described by truncated cluster expansions with concentration-independent ECIs. Because truncated cluster expansions typically capture the most significant contributions to the total energy, they are able to accurately represent the

energies of well-ordered ground states, completely random structures, and intermediate structures that are only partially disordered.

The analysis in this Comment does not necessarily contradict an important conclusion of reference [1], that the quality of a cluster expansion can be improved by using concentration-dependent ECIs. The truncation of a cluster expansion for a physically realistic Hamiltonian always introduces some non-zero error into the model. (Nature may be near-sighted, but there is no distance in the material at which it is completely blind.) In many cases, the most significant physical interactions are sufficiently localized to make this error acceptably small; this is why truncated cluster expansions with concentration-independent ECIs have been successfully used to model many systems. However in some situations there might be a relatively large non-local contribution to the property of interest, and in some such cases the use of concentration-dependent ECIs can significantly reduce the prediction error of a truncated cluster expansion [32]. Concentration-dependent ECIs may also be used to reduce the number of local clusters that must be included in a cluster expansion to reach a sufficient level of accuracy [33, 34]. On the other hand, the use of concentration-dependent ECIs cannot completely resolve the well-known inability of truncated cluster expansions to predict the energies of long-period coherent superlattices, due to the anisotropy of the elastic constants [35, 36].

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