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Effective cluster interactions from cluster-variation formalism. I

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States of (partial) order in binary-alloy systems are described by means of expansions in a complete set of orthogonal cluster functions. The expectation value of the energy of such systems can then be expressed as a bilinear form in multisite correlation variables and effective cluster interactions (ECI's), as originally proposed by Sanchez, Ducastelle, and Gratias [Physica A **128**, 334 (1984)]. It is shown that ECI's are defined as interchange energies averaged over all atomic configurations with a fixed concentration or over all configurations and concentrations, depending on the orthogonal expansion considered. The former averaging process leads to concentration-dependent ECI's, the latter to concentration-independent ECI's. From their formal definitions, certain relations will be shown to hold between the interactions derived in the two averaging schemes in the thermodynamic limit. In particular, an interesting convergence criterion is established for the concentration-dependent ECI's.

I. INTRODUCTION

To understand the physical properties of an alloy system, a knowledge of the equilibrium phases and their limits with respect to experimentally controlled parameters, such as pressure, temperature (T), volume, concentration (c), etc., is essential. In particular, very accurate knowledge of the c-T phase diagram is crucial for technological applications. Therefore, much effort, both theoretical and experimental, has been devoted to the understanding of phase stability in alloy systems.

For an ideal crystalline binary alloy, one of the two types of atoms (denoted symbolically as A and B) occupies each site on a lattice. A given arrangement of these atoms specifies a configuration which may exhibit varying degrees of long-range or short-range order. The atomic configuration of a macroscopic system at equilibrium can be predicted given the knowledge of the free energy. Therefore, a theoretical study of phase stability in a binary alloy consists of trying to accurately describe the configurational dependence of the energy and the entropy.

For a lattice with N sites, 2^N possible configurations exist which make a straightforward calculation of the partition function intractable for macroscopic systems. For this reason, theoretical efforts in this field have made use of appropriate statistical models in which a finite set of effective cluster interactions (ECI's) are used to parametrize the energetics of the system. In general, the model Hamiltonian takes the form

$$H=\sum_{\alpha}\sum_{\mathbf{p}} V_\alpha(\mathbf{p})\Phi_\alpha(\mathbf{p}) \; , \tag{1}$$

where the sums are over sets of clusters α located at sites $\mathbf{p}$ in the lattice. The set of $\{V_\alpha(\mathbf{p})\}$ are the effective cluster interactions and the $\{\Phi_\alpha(\mathbf{p})\}$ are termed cluster functions. Equation (1) is a generalization of an Ising Hamiltonian for which the $\Phi_\alpha(\mathbf{p})$ are products of spin variables. In a first-principles study, one is left with the task of calculating the set of ECI's and solving the statistical mechanics of the model.

In Ref. 1, Sanchez, Ducastelle, and Gratias formulate a mathematical framework by which the different terms in Eq. (1) can be uniquely defined. In particular, these authors show that, in the space of the 2^N possible atomic configurations, a complete orthonormal basis set of cluster functions can be constructed. Therefore, any function of the atomic configuration can be expanded in the form of Eq. (1), and the $V_\alpha(\mathbf{p})$ are defined as generalized Fourier coefficients which are constant over the entire concentration range in the alloy. The formal definition of the ECI's is also discussed by Gonis *et al.* in Sec. V of Ref. 2 where these parameters are shown to depend explicitly on the composition of the alloy. In order to study how the ECI's, as formulated in Refs. 1 and 2, are related, we will extend the formalism of Sanchez, Ducastelle, and Gratias by constructing a complete orthonormal basis set of functions in the space consisting of all configurations with a fixed concentration, as originally proposed in Ref. 3, on a lattice in which the number of sites, N, becomes infinite.

As will be discussed in detail below, the ECI's are uniquely defined as interchange energies averaged over a certain set of atomic configurations. These ECI's are concentration dependent if only configurations with a fixed value of c are averaged over and are independent of c if all concentrations are traced over as well. Thermal effects such as phonons and increased scattering of the electrons will cause the energy of a given configuration, and hence the ECI's, to be temperature dependent. In practice, however, ECI's are usually calculated only at $T=0$.

In this paper, we will show that relations between concentration-dependent and concentration-independent ECI's can be obtained from the formal definitions of these parameters. That such relations exist is not surprising since the latter ECI's are obtained by averaging over the $N!/N_A!N_B!$ configurations [where $N_B=N(1-c)$ and $N_A=Nc$ are the number of B and A atoms, respectively] with fixed concentration c which are a subset of the 2^N configurations traced over for the former ECI's (note that $\sum N!/N_A!N_B!=2^N$). From these formal relations, an interesting convergence criterion for the concentration-dependent ECI's will be established which we will test numerically using the direct configurational averaging (DCA) method[4] in the companion paper (hereafter referred to as paper II, which follows).

A set of 2^N ECI's is defined by the formalism described above so that this approach to alloy phase stability studies becomes useful only if the model Hamiltonian (1) can be truncated to include a finite set of parameters. In paper II we will compare the convergence of the energy expansions in terms of the two types of ECI's for two model tight-binding binary alloy systems within the framework of the DCA method in order to study under which conditions a small set of either type of these interactions can be expected to describe the configurational dependence of the energy of a binary alloy system.

Several numerical techniques now exist for determining ECI's from first principles. In particular, the generalized perturbation method[5] (GPM), embedded cluster method[2] (ECM), and DCA method have been used to calculate the concentration-dependent ECI's which are discussed in Refs. 2 and 3. The Connolly-Williams method[6] and the DCA method can be implemented to calculate concentration-independent ECI's as defined in Ref. 1. These methods are all related in that they are used to determine ECI's which are defined within the context of the formalism discussed below. The $S^{(2)}(\mathbf{k})$ method[7] has also been used to derive parameters which describe ordering tendencies in binary alloys. The parameters in this method, however, are not completely equivalent to those defined below since they are derived within the context of linear response theory in the totally disordered alloy as characterized by the coherent-potential approximation.[8] The methods for calculating ECI's will be discussed in further detail in paper II.

In order to solve the statistical mechanics of Hamiltonians of the form (1), several techniques are available. Most notably, Monte Carlo (MC) simulation[9] and the cluster-variation method[10] (CVM) have been used in binary-alloy phase-stability studies. Detailed comparisons of MC simulations and CVM calculations on the fcc lattice[11] have established the accuracy of the latter method. As shown in Ref. 1, an expansion of the density matrix (which specifies the probability of observing a given atomic configuration) in terms of cluster functions provides a useful framework from which the CVM can be formulated.

The outline of this paper is as follows: after a general treatment of the formalism in the next section, the expansion of the internal energy will be discussed in detail in Sec. III. A comparison of the energy expansions will enable us to discuss how the ECI's are related in the two averaging schemes, as is shown in Sec. IV.

II. FORMALISM

Consider a binary-alloy system on a lattice with N sites. In order to specify the microscopic arrangement of atoms in this system, it is convenient to use spin variables $\sigma_{\mathbf{p}}$ which can take on values $+1$ or -1 depending on which type of atom occupies site $\mathbf{p}$. Any configuration on the lattice can be fully specified by the N-dimensional vector $\sigma=\{\sigma_{\mathbf{p}},\sigma_{\mathbf{p}'},\sigma_{\mathbf{p}''},\ldots\}$. We are interested in calculating functions on the configuration σ such as the energy $E(\sigma)$.

We begin by defining an inner product between two functions of configuration σ, $f(\sigma)$, and $g(\sigma)$, defined on the space of all configurations or in the subspace of configurations with a fixed concentration c:

$$\langle f(\sigma),g(\sigma)\rangle=\rho_0\sum_{\sigma}f(\sigma)g(\sigma)\ . \tag{2}$$

The sum in (2) is over all configurations in the space in question and ρ_0 is a normalization factor. Next, we use the Gram-Schmidt procedure to construct an orthonormal set of basis functions from the set

$$W(\sigma_{\mathbf{p}})=W_0=1$$

and (3)

$$W_1(\sigma_{\mathbf{p}})=\sigma_{\mathbf{p}}\ .$$

The result is

$$\theta_0=W_0=1$$

and (4)

$$\theta_1(\sigma_{\mathbf{p}})=\beta(\sigma_{\mathbf{p}}-\langle 1,\sigma_{\mathbf{p}}\rangle)\ ,$$

where β is defined by requiring $\langle\theta_1(\sigma_{\mathbf{p}}),\theta_1(\sigma_{\mathbf{p}})\rangle=1$. Provided the spins on different sites are independent, it follows that

$$\langle\theta_i(\sigma_{\mathbf{p}}),\theta_j(\sigma_{\mathbf{p}'})\rangle=\delta_{i,j}\delta_{\mathbf{p},\mathbf{p}'}\ , \tag{5}$$

where $\delta_{i,j}$ and $\delta_{\mathbf{p},\mathbf{p}'}$ are Kroenecker δ's. A completeness relationship can be shown to hold

$$\theta_0^2+\theta_1(\sigma_{\mathbf{p}})\theta_1(\sigma'_{\mathbf{p}})=\delta(\sigma_{\mathbf{p}},\sigma'_{\mathbf{p}})\ , \tag{6}$$

where $\langle f(\sigma_{\mathbf{p}}),\delta(\sigma_{\mathbf{p}},\sigma'_{\mathbf{p}})\rangle=f(\sigma'_{\mathbf{p}})$.

We now consider the set of configurations on the N lattice sites in the space in question. We assign point functions $\theta_0=1$ and $\theta_1(\sigma_{\mathbf{p}})$ to each point $\mathbf{p}$ and form the tensor product

$$\begin{bmatrix} 1 \\ \theta_1(\sigma_{\mathbf{p}_1}) \end{bmatrix} \times \begin{bmatrix} 1 \\ \theta_1(\sigma_{\mathbf{p}_2}) \end{bmatrix} \times \cdots \times \begin{bmatrix} 1 \\ \theta_1(\sigma_{\mathbf{p}_N}) \end{bmatrix} = \Phi_\alpha(\sigma) \ . \tag{7}$$

This equation defines 2^N cluster functions $\Phi_\alpha(\sigma)$ which have the form

$$\Phi_\alpha(\sigma) = \theta_1(\sigma_{\mathbf{p}})\theta_1(\sigma_{\mathbf{p}'}) \cdots \theta_1(\sigma_{\mathbf{p}''}) \ , \tag{8}$$

where the subscript α specifies the points in the cluster: $\alpha = (\mathbf{p}, \mathbf{p}', \ldots, \mathbf{p}'')$ [note that the $\mathbf{p}$ dependence of the cluster functions in (1) has been taken into the definition of α]. From Eqs. (5) and (6) it follows that the cluster functions are orthonormal,

$$\langle \Phi_\alpha(\sigma), \Phi_{\alpha'}(\sigma) \rangle = \delta_{\alpha,\alpha'} \ , \tag{9}$$

and complete

$$\sum_\alpha \Phi_\alpha(\sigma)\Phi_\alpha(\sigma') = \delta(\sigma, \sigma') \ . \tag{10}$$

Therefore,we can expand any function $f(\sigma)$ in the given configuration space as follows:

$$f(\sigma) = f_0 + \sum_\alpha f_\alpha \Phi_\alpha(\sigma) \ , \tag{11}$$

where

$$f_\alpha = \langle \Phi_\alpha(\sigma), f(\sigma) \rangle \tag{12}$$

is the generalized Fourier coefficient, and where we have extracted the configurationally invariant term $f_0 = \langle 1, f(\sigma) \rangle$ from the sum. In the approach of Sanchez, Ducastelle, and Gratias,[1] the entire configuration space consisting of the 2^N possible atomic arrangements is considered. Since the inner product in Eq. (2) is defined in terms of a sum over all configurations regardless of the concentration, we will refer to this approach as the grand-canonical scheme. Alternatively, we can limit the set of configurations to those with a given composition. In this second approach, which we will refer to as the canonical scheme, orthonormal cluster functions can only be defined in the limit of $N \to \infty$ since the spin variables become independent only in this thermodynamic limit.

In the grand-canonical scheme, it is easy to verify that

$$\theta_0 = 1$$

and

$$\theta_1(\sigma_{\mathbf{p}}) = \sigma_{\mathbf{p}} \tag{13}$$

since $\langle 1, \theta_1(\sigma) \rangle = 0$. Therefore, the cluster functions in this scheme are simply defined as products of the spins on a specified cluster:

$$\Phi_\alpha(\sigma) = \sigma_{\mathbf{p}}\sigma_{\mathbf{p}'} \cdots \sigma_{\mathbf{p}''} \ . \tag{14}$$

For an infinite system in the canonical scheme, it is seen that $\langle 1, \sigma_{\mathbf{p}} \rangle = \bar{\sigma}$, where $\bar{\sigma}$ is the average spin in the system and is related to the concentration by $\bar{\sigma} = 2c - 1$. Therefore, we have

$$\theta_0 = 1$$

and

$$\theta_1(\sigma_{\mathbf{p}}) = (\sigma_{\mathbf{p}} - \bar{\sigma})/(1 - \bar{\sigma}^2)^{1/2} \ , \tag{15}$$

where $(1 - \bar{\sigma}^2)^{1/2}$ is the reciprocal of β defined above. Aside from the normalization factor, we see that a canonical cluster function is given by the product of spin deviations away from the average spin $\bar{\sigma}$. It will be useful to consider unnormalized cluster functions in this scheme which are related to those defined in Eq. (7) by a factor of $1/(1 - \bar{\sigma}^2)^{n_\alpha/2}$, where n_α is the number of points in cluster α. The cluster functions used in this case are, therefore,

$$\hat{\Phi}_\alpha(\sigma) = \delta\sigma_{\mathbf{p}}\delta\sigma_{\mathbf{p}'} \cdots \delta\sigma_{\mathbf{p}''} \ , \tag{16}$$

where $\delta\sigma_{\mathbf{p}} = \sigma_{\mathbf{p}} - \bar{\sigma}$ and where the circumflex denotes canonical averaging. In Appendix A we show explicitly that these cluster functions are orthogonal.

Note that, for $c = \frac{1}{2}$ ($\bar{\sigma} = 0$), the cluster functions become identical in the two schemes. As will be made more precise in Sec. IV, in the thermodynamic limit of $N \to \infty$, the two schemes become equivalent at $c = \frac{1}{2}$.

III. INTERNAL ENERGY

Consider now the internal energy which is defined as the ensemble average of the energy,

$$\langle E \rangle = \sum_\sigma \rho(\sigma) E(\sigma) \ , \tag{17}$$

where $\rho(\sigma)$ specifies the probability of observing the atomic configuration σ and where $E(\sigma)$ is the total energy of a given configuration, which we refer to as the configurational energy. We will be interested in the expansion of $E(\sigma)$.

In the grand-canonical scheme we have

$$E(\sigma) = V_0 + \sum_\alpha V_\alpha \Phi_\alpha(\sigma) \ , \tag{18}$$

where, using Eq. (12), we find, for the generalized Fourier coefficients,

$$V_\alpha = \langle \Phi_\alpha(\sigma), E(\sigma) \rangle \ . \tag{19}$$

These coefficients, which we will refer to as grand-canonical effective cluster interactions (GC-ECI's), are concentration independent since the inner product in (19) is defined in terms of a trace over *all* atomic configurations.

As an example of the GC-ECI's, consider the pair interaction: from Eq. (19), we have

$$V_{\mathbf{p},\mathbf{p}'} = \tfrac{1}{4}(E_{AA} + E_{BB} - E_{AB} - E_{BA}) \ , \tag{20}$$

where E_{AA} is defined as

$$E_{AA} = \frac{1}{2^{N-2}} \sum_\sigma{}' E(\sigma) \ , \tag{21}$$

with the prime indicating a restricted sum over configurations where sites $\mathbf{p}$ and $\mathbf{p}'$ are both occupied by A atoms. E_{BB}, E_{AB}, and E_{BA} are defined similarly with appropriate atoms occupying the two specified lattice sites. By definition, we see that the GC-ECI is an interchange energy averaged over all atomic configurations, regardless of the concentration. From Eq. (18) the internal energy can be written as

$$\langle E\rangle = V_0 + \sum_{\alpha} V_\alpha \xi_\alpha \ , \tag{22}$$

where $\xi_\alpha = \langle \Phi_\alpha(\sigma)\rangle$ are known as correlation functions.

In the canonical scheme, the expansion of the energy of a configuration with a specified concentration again has the form of Eq. (18):

$$E(\sigma) = \hat{V}_0 + \sum_{\alpha} \hat{V}_\alpha(c)\hat{\Phi}_\alpha(\sigma) \ , \tag{23}$$

where $\hat{V}_\alpha(c)$ is defined as

$$\hat{V}_\alpha(c) = (1-\bar{\sigma}^2)^{-n_\alpha}\langle E(\sigma), \hat{\Phi}_\alpha(\sigma)\rangle \ . \tag{24}$$

The factor $(1-\bar{\sigma}^2)^{-n_\alpha}$ in (24) comes from the normalization of the canonical cluster functions as specified in Eq. (A5) of the Appendix A. The coefficients in expansion (23) are now concentration dependent since the inner product in the definition (24) is defined in terms of the canonical trace defined earlier.

As an example of the $\hat{V}_\alpha(c)$, which we will refer to as canonical effective cluster interactions (C-ECI), consider the pair interaction (again in the thermodynamic limit). It is shown in Appendix B that this pair interaction has the form

$$\hat{V}_{\mathbf{p},\mathbf{p}'}(c) = \tfrac{1}{4}[\hat{E}_{AA}(c) + \hat{E}_{BB}(c) - \hat{E}_{AB}(c) - \hat{E}_{BA}(c)] \ , \tag{25}$$

where $\hat{E}_{AA}(c)$ is defined as

$$\hat{E}_{AA}(c) = \rho_{AA}(c)\sum_{\sigma}{}' E(\sigma) \ . \tag{26}$$

The restricted sum is over all configurations with a fixed concentration having A atoms at sites $\mathbf{p}$ and $\mathbf{p}'$, and ρ_{AA} is the inverse of the number of such configurations. The terms $\hat{E}_{BB}(c)$, $\hat{E}_{AB}(c)$, and $\hat{E}_{BA}(c)$ are again defined analogously. Therefore, the C-ECI's are now concentration dependent. As mentioned in the Introduction, the expansion (23) was formulated in Ref. 2 without the assumption of $N \to \infty$. For finite N, however, the cluster functions in the canonical scheme are no longer orthogonal and the coefficients in expansion (23) can no longer be interpreted as generalized Fourier coefficients.

In the canonical scheme for a lattice with an infinite number of sites, the internal energy takes the form

$$\langle E(c)\rangle = \hat{V}_0(c) - \sum_{\alpha} \hat{V}_\alpha(c)\widehat{\delta\xi}_\alpha \ , \tag{27}$$

where $\widehat{\delta\xi}_\alpha = \langle \delta\sigma_{\mathbf{p}}\delta\sigma_{\mathbf{p}'} \cdots \delta\sigma_{\mathbf{p}''}\rangle$ is the cumulant of the product of spins on a cluster α. Note that in the random alloy at concentration c we have $\widehat{\delta\xi}_\alpha = 0$ for all clusters α so that $\hat{V}_0(c)$ is the energy of this random alloy.

IV. RELATIONS BETWEEN GC-ECI AND C-ECI

In the previous section it was shown that the C-ECI's and GC-ECI's are both defined as interchange energies and differ only in the way they are averaged. In particular, the C-ECI's are obtained by averaging over a subset of the configurations used to obtain the GC-ECI's. Therefore, these two sets of ECI's are necessarily related. As we now show, the relations between these parameters can be used to establish a convergence criterion for the C-ECI's. Such a criterion is important since a common problem in this approach to alloy phase-stability studies is determining an appropriate level of truncation for expansions such as (22) and (27).

Consider the expansion for the internal energy in terms of C-ECI's given in Eq. (27). The cumulants can be expanded in terms of the correlation functions used in (22). In particular, for a disordered system in which all sites are equivalent by symmetry (i.e., $\langle\sigma_{\mathbf{p}}\rangle = \bar{\sigma}$ for all $\mathbf{p}$),

$$\delta\hat{\xi}_\alpha(\bar{\sigma}) = \xi_\alpha + \sum_{\gamma\subset\alpha} (-\bar{\sigma})^{n_\alpha - n_\gamma}\xi_\gamma \ , \tag{28}$$

where the sum is over all subclusters γ of cluster α. The expansion (27) can be rewritten using Eq. (28) as

$$\langle E(c)\rangle = \hat{V}'_0(c) + \sum_{\alpha} \hat{V}'_\alpha(c)\xi_\alpha \ , \tag{29}$$

where the primed ECI's are defined as

$$\hat{V}'_\alpha(c) = \left[\hat{V}_\alpha(c) + \sum_{\alpha\subset\gamma} (-\bar{\sigma})^{n_\beta - n_\alpha}\hat{V}_\beta(c)\right] \tag{30}$$

in which the sum is over all clusters β containing cluster α. By taking total derivatives of Eqs. (22) and (29) and equating the resulting expressions, it is found that the following relations exist between the GC-ECI's and the C-ECI's:

$$\begin{aligned} V_{\mathbf{p}} &= \hat{V}'_{\mathbf{p}} + \frac{\partial \hat{V}'_0(c)}{\partial\bar{\sigma}} + \sum_{\alpha} \frac{\partial \hat{V}'_\alpha(c)}{\partial\bar{\sigma}}\xi_\alpha \ , \\ V_\alpha &= \hat{V}'_\alpha(c) \ , \quad \alpha \neq 0,\mathbf{p} \ , \end{aligned} \tag{31}$$

where $\alpha = \mathbf{p}$ refers to the point cluster. In establishing these relations we have used the definition $\xi_{\mathbf{p}} = \bar{\sigma}$ and the fact that the correlation functions are independent variables. By equating the expansions (22) and (29) and using (31), the relation between the empty ECI's [defined as $\langle 1, E(\sigma)\rangle$] can also be obtained:

$$V_0 = \hat{V}'_0(c) - \left[\frac{\partial \hat{V}'_0(c)}{\partial\bar{\sigma}} + \sum_{\alpha} \frac{\partial \hat{V}'_\alpha(c)}{\partial\bar{\sigma}}\xi_\alpha\right]\bar{\sigma} \ . \tag{32}$$

The V_α are independent of concentration so that, from the second equality in (31), we know that the derivative of $\hat{V}'_\alpha(c)$ with respect to concentration is zero for all except the empty and point clusters. Relations (31) and (32) can therefore be simplified as

$$\begin{aligned} V_0 &= \hat{V}'_0(c) - \frac{\partial \hat{V}'_0(c)}{\partial\bar{\sigma}}\bar{\sigma} - \frac{\partial \hat{V}'_{\mathbf{p}}(c)}{\partial\bar{\sigma}}\bar{\sigma}^2 \ , \\ V_{\mathbf{p}} &= \hat{V}'_{\mathbf{p}}(c) + \frac{\partial \hat{V}'_0(c)}{\partial\bar{\sigma}} + \frac{\partial \hat{V}'_{\mathbf{p}}(c)}{\partial\bar{\sigma}}\bar{\sigma} \ , \\ V_\alpha &= \hat{V}'_\alpha(c) \ , \quad \alpha \neq 0,\mathbf{p} \ . \end{aligned} \tag{33}$$

The relations (33) lead us to conclude that the GC-ECI's are exactly equal to the C-ECI's at concentration $c=\frac{1}{2}$ ($\bar{\sigma}=0$) for all but the point cluster. Another way to establish this equality is to make use of the fact that the binomial distribution converges to a normal distribution which becomes peaked around $\bar{\sigma}=0$ for large N. In particular, consider the pair interaction in the two averaging schemes. As shown in Eq. (19), the grand-canonical interaction is defined as an interchange energy averaged over all atomic configurations on the lattice. Using the definitions of the terms in (20) and (25), it is possible to relate the pair interactions in the two averaging schemes. For example, the expression for E_{AA} can be rewritten in terms of that for $\hat{E}_{AA}(c)$ as

$$E_{AA}=\sum_{N_A=2}^{N}\rho_{AA}(N_A)\hat{E}_{AA}(N_A)\ , \tag{34}$$

where $\rho_{AA}(N_A)$ is the number of configurations with N_A the number of A atoms having an A atom at the specified sites normalized by the number of configurations having A atoms at these sites:

$$\rho_{AA}(N_A)=\frac{1}{2^{N-2}}\frac{(N-2)!}{(N_A-2)!(N-N_A)!}\ . \tag{35}$$

As shown in Appendix C, for large N we can use Stirling's approximation to show that, in the thermodynamic limit, $E_{AA}=\hat{E}_{AA}(\bar{\sigma}=0)$. Similar relations hold for the other terms in Eq. (20). Furthermore, the same considerations can be made for other clusters so that we again find that, for $N\rightarrow\infty$, the GC-ECI's are equivalent to the C-ECI's at concentration $\frac{1}{2}$. This argument applies even for the point cluster so that in order for the relation between V_{p} and $\hat{V}'_{\text{p}}(c)$ in (34) to be true, we must have

$$\left[\frac{\partial\hat{V}'_0(c)}{\partial\bar{\sigma}}\right]_{\bar{\sigma}=0}=0\ . \tag{36}$$

The relations (33) provide an interesting convergence criterion for the C-ECI's in the thermodynamic limit. Given a finite set of C-ECI's at different concentrations, the parameters can be renormalized according to Eq. (30). The set of C-ECI's at a given concentration is then increased until the relations (33) hold to within an acceptable error between this set and the set evaluated at $\bar{\sigma}=0$ which are equivalent to the GC-ECI's. Equivalently, the range of interactions can be increased until the C-ECI's become concentration independent. Clusters beyond this range will have little effect in renormalizing the already concentration-independent C-ECI's so that this condition for convergence will be satisfied. In paper II, a numerical study will be made to show that relations (33) are indeed valid.

V. CONCLUSIONS

The formal definitions of ECI's has been considered using the mathematical framework of expansions in complete sets of orthonormal basis functions. This framework has allowed us to establish that the difference between the two types of ECI's formulated in Refs. 1 and 2 is the set of atomic configurations over which they are averaged. In particular, by limiting the averaging to configurations with a fixed value of concentration, the ECI's defined in Ref. 2 are obtained while extending the averaging to all concentrations as well leads to the ECI's in Ref. 1.

The ECI's as defined in (19) and (24) can be interpreted as interchange energies of clusters embedded in an "average medium." It is commonly argued that this "medium" should reflect the dependence of the alloy properties on concentration so that the C-ECI's are a more valid choice of parameters to use in such studies. However, the complete set of GC-ECI's contain no less information than the set of C-ECI's at all concentrations since the "medium" for the former set of parameters contains all of the properties of the system at all concentrations. This is not to say, however, that an expansion of the energy in GC-ECI's will converge at a given concentration as rapidly as the similar expansion in C-ECI's. Indeed, for a system in which the physical properties are strongly dependent on concentration, fewer terms in expansion (27) might be expected to be needed to parametrize the energetics at a given concentration than for expansion (22). These considerations will be quantified in the numerical study of the second part of this paper.

For a system in which the number of atoms becomes infinite, we find that the C-ECI's and GC-ECI's are related as follows: By expanding the cumulants in the internal energy expression (27), it is found that the GC-ECI's are related to the set of C-ECI's at any concentration as given in (33). In particular, it is established that the GC-ECI's are actually equivalent to the C-ECI's at concentration $c=\frac{1}{2}$. This latter equivalence is true essentially because an exponentially greater number of configurations exist at $c=\frac{1}{2}$ than at any other concentration. These relations are derived using only the formal definitions of the ECI's and should therefore hold independently of the methods used to calculate them.

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APPENDIX A

In general, cluster functions constructed by forming a tensor product of point functions, as is done in Eq. (7), will be orthonormal provided these point functions are independent and orthonormal according to Eq. (5). In particular, consider the canonical cluster functions defined in Eq. (16). In order to show explicitly that the $\hat{\Phi}_\alpha(\sigma)$ are orthogonal, use will be made of the following equality:

$$\rho_0 \mathrm{Tr}[\sigma_{\mathrm{p}_1}\sigma_{\mathrm{p}_2}\cdots\sigma_{\mathrm{p}_n}=\bar{\sigma}^{\,n} , \tag{A1}$$

where the trace and normalization are those for canonical averaging. To prove the above equality, consider a lattice with N sites:

$$\begin{aligned}\rho_0 \mathrm{Tr}[\sigma_{\mathrm{p}_1}\sigma_{\mathrm{p}_2}\cdots\sigma_{\mathrm{p}_n}]&=\frac{N_A!N_B!}{N!}\sum_{i=1}^{n}\frac{n!}{(n-i)!i!}\frac{(N-n)!}{(N_B-i)!(N_A-n+i)!}(-1)^i\\&=\frac{1}{N^n}\sum_{i=1}^{n}\left[\frac{n!}{(n-i)!i!}(N_A)^{n-i}(-N_B)^i\right]+O(1/N)\\&=\left[\frac{N_A-N_B}{N}\right]^n+O(1/N)=\bar{\sigma}^{\,n}+O(1/N) ,\end{aligned} \tag{A2}$$

so that (A1) is true in the limit of $N\to\infty$.

Now, consider the inner product of two cluster functions written explicitly as

$$\langle\hat{\Phi}_\alpha(\sigma),\hat{\Phi}_{\alpha'}(\sigma)\rangle=\rho_0\mathrm{Tr}[(\sigma_{\mathrm{p}_1}-\bar{\sigma})^2\cdots(\sigma_{\mathrm{p}_i}-\bar{\sigma})^2(\sigma_{\mathrm{p}_{i+1}}-\bar{\sigma})\cdots(\sigma_{\mathrm{p}_j}-\bar{\sigma})] , \tag{A3}$$

where the points $[p_1,p_2,\ldots,p_i]$ are in both clusters (i being the number of such points) and where j is the number of *distinct* points in clusters α and α' (so that $n_\alpha+n_{\alpha'}-j=i$). Equation (A3) can be expanded as follows:

$$\begin{aligned}\langle\hat{\Phi}_\alpha(\sigma),\hat{\Phi}_{\alpha'}(\sigma)\rangle=\sum_{n_1=0}^{1}\sum_{n_2=0}^{1}\cdots\sum_{n_j=0}^{1}&[(1+\bar{\sigma}^{2})^{i-(n_1+n_2+\cdots+n_i)}(-\bar{\sigma})^{j-i-(n_{i+1}+n_{i+2}+\cdots+n_j)}\\&\times(-2\bar{\sigma})^{(n_1+n_2+\cdots+n_i)}\rho_0\mathrm{Tr}(\sigma_{\mathrm{p}_1}^{n_1}\sigma_{\mathrm{p}_2}^{n_2}\cdots\sigma_{\mathrm{p}_j}^{n_j})] ,\end{aligned} \tag{A4}$$

which can be rewritten using Eq. A1 as follows:

$$\langle\hat{\Phi}_\alpha(\sigma),\hat{\Phi}_{\alpha'}(\sigma)\rangle=[1-\bar{\sigma}^{2}]^i[\bar{\sigma}-\bar{\sigma}]^{j-i} . \tag{A5}$$

From Eq. (A5) it is seen that, if α and α' are identical clusters (so that $i=j=m/2=n_\alpha$), $\langle\hat{\Phi}_\alpha(\sigma),\hat{\Phi}_{\alpha'}(\sigma)\rangle=(1-\bar{\sigma}^{2})^{n_\alpha}$, while if any points in α are distinct from those in α', we have $\langle\hat{\Phi}_\alpha(\sigma),\hat{\Phi}_{\alpha'}(\sigma)\rangle=0$. That these cluster functions are not normalized follows from their definition in Eq. (16).

APPENDIX B

From Eq. (25), the canonical effective pair interaction is defined by

$$\hat{V}_{\mathrm{p,p'}}(c)=(1-\bar{\sigma}^{2})^{-2}\langle E(\sigma),\hat{\Phi}_\alpha(\sigma)\rangle , \tag{B1}$$

where the inner product is defined by Eq. (2) in terms of a trace over all configurations with a fixed concentration c. For a lattice with N sites, Eq. (B1) can be written explicitly as

$$\hat{V}_{\mathrm{p,p'}}(c)=(1-\bar{\sigma}^{2})^{-2}\frac{N_A!N_B!}{N!}\sum_{\sigma}[(\sigma_{\mathrm{p}}-\bar{\sigma})(\sigma_{\mathrm{p'}}-\bar{\sigma})]E(\sigma) . \tag{B2}$$

The spin variables σ_{p} take on values $+1$ or -1 if site **p** is occupied by an A or B atom, respectively. Therefore, Eq. (B2) can be rewritten as

$$\begin{aligned}\hat{V}_{\mathrm{p,p'}}(c)=(1-\bar{\sigma}^{2})^{-2}\frac{N_A!N_B!}{N!}&\left[(1-\bar{\sigma})^2\frac{(N-2)!}{(N_A-2)!N_B!}\hat{E}_{AA}(c)+(1+\bar{\sigma})^2\frac{(N-2)!}{N_A!(N_B-2)!}\hat{E}_{BB}(c)\right.\\&\left.-(1-\bar{\sigma}^{2})\frac{(N-2)!}{(N_A-1)!(N_B-1)!}\hat{E}_{AB}(c)-(1-\bar{\sigma}^{2})\frac{(N-2)!}{(N_A-1)!(N_B-1)!}\hat{E}_{BA}(c)\right] ,\end{aligned} \tag{B3}$$

where the terms such as $\hat{E}_{AA}(c)$ are defined in Eq. (27) and where the explicit expressions for ρ_{AA}, ρ_{BB}, ρ_{AB}, and ρ_{BA} have been used. Equation (B3) can be further simplified to order $1/N$ using the relations $N_A=N(1+\bar{\sigma})/2$ and

$N_B=N(1-\bar\sigma)/2$ as follows:

$$\hat V_{\mathrm{p,p'}}(c)=(1-\bar\sigma^2)^{-2}\left[(1-\bar\sigma)^2\frac{(1+\bar\sigma)^2}{4}\hat E_{AA}(c)+(1+\bar\sigma)^2\frac{(1-\bar\sigma)^2}{4}\hat E_{BB}(c)\right.$$
$$\left.-(1-\bar\sigma^2)\frac{(1-\bar\sigma^2)}{4}\hat E_{AB}(c)-(1-\bar\sigma^2)\frac{(1-\bar\sigma^2)}{4}\hat E_{BA}(c)+O(1/N)\right], \tag{B4}$$

which becomes, in the thermodynamic limit of $N\rightarrow\infty$,

$$\hat V_{\mathrm{p,p'}}(c)=\tfrac{1}{4}[\hat E_{AA}(c)+\hat E_{BB}(c)-\hat E_{AB}(c)-\hat E_{BA}(c)] \tag{B5}$$

as in Eq. (26).

APPENDIX C

In order to show that $E_{AA}=\hat E_{AA}$ $(\bar\sigma=0)$ in the thermodynamic limit, it is necessary to show that, for large N, $\rho_{AA}(N_A)$ as defined in Eq. (35) converges to a normal distribution centered around $\bar\sigma=0$. From Stirling's approximation it can be shown that, for large N, the following relation holds:

$$\frac{1}{2^N}\frac{N!}{N_A!(N-N_A)!}\approx\frac{2}{\sqrt{2\pi}}\frac{1}{\sqrt{N}}\exp\left[\frac{-2(N_A-N/2)^2}{N}\right], \tag{C1}$$

so that Eq. (36) can be rewritten as

$$E_{AA}\approx\frac{8}{\sqrt{2\pi}}\frac{1}{\sqrt{N}}\frac{1}{N(N-1)}\times\sum_{N_A=2}^{N}N_A(N_A-1)\times\exp\left[\frac{-2(N_A-N/2)^2}{N}\right]\hat E_{AA}(N_A)\ . \tag{C2}$$

The sum in (C2) can be rewritten as an integral (using a Euler-MacLaurin series) which becomes, after changing variables from N_A to $\bar\sigma$,

$$E_{AA}\approx\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{N}}\frac{N^3}{N(N-1)}\times\int_{-1+2/N}^{1+2/N}(1+\bar\sigma)\left[1+\bar\sigma-\frac{2}{N}\right]\times\exp\left[\frac{-N\bar\sigma^2}{2}\right]\hat E_{AA}(\bar\sigma)\,d\bar\sigma\ . \tag{C3}$$

In the thermodynamic limit, (C3) can again be rewritten as

$$E_{AA}=\frac{1}{\sqrt{\pi}}\int_{-1}^{1}\sqrt{N/2}(1+\bar\sigma)^2\exp\left[\frac{-N\bar\sigma^2}{2}\right]\hat E_{AA}(\sigma)d\sigma$$
$$=\hat E_{AA}(\bar\sigma=0)\ , \tag{C4}$$

where, in the second equality, we have made use of the fact that

$$\sqrt{N/2}\exp[-N\bar\sigma^2/2]\rightarrow\sqrt{\pi}\delta(\bar\sigma) \tag{C5}$$

in the thermodynamic limit of $N\rightarrow\infty$, where $\delta(\bar\sigma)$ is the usual Dirac δ function.

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