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Effective cluster interactions from cluster-variation formalism. II

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Using the recently developed direct-configurational-averaging method, we have considered the expansion of formation energies of the random and ordered states in terms of effective cluster interactions (ECI's) for two model tight-binding binary-alloy systems. In particular, we have examined the rates of convergence of such expansions in two different averaging schemes. In the canonical scheme the ECI's depend on the concentration (c) of the alloy explicitly, while for grand-canonical averaging they do not. For a model system in which the ordering energies are highly asymmetric about $c=0.5$, we find that an expansion in canonical ECI's gives slightly better convergence. However, for the other system considered, both averaging schemes lead to similarly convergent expansions due to the symmetry of the system about $c=0.5$. We have also verified numerically formal relations between the ECI's in the two averaging schemes. Such relations provide a useful convergence criterion of expansions in terms of ECT's.

I. INTRODUCTION

In order to study the phase formation and stability of substitutionally disordered solid solutions, it is necessary to have reliable expressions for the configurational energy and entropy. These expressions are usually obtained within the context of an "Ising-like" system of atoms on a fixed lattice, and are most naturally formulated in terms of effective pair and multisite interactions. In conjunction with the cluster-variation method (CVM),[1–3] Monte Carlo techniques,[4–6] and other methods, these effective cluster interactions (ECI's) have been used to examine structural phase diagrams,[7–23] short- and long-range order,[16,24,25] and other thermodynamic properties of alloy systems. Thus, a detailed study of the ECI's is an essential step towards a more complete understanding of these alloy properties. In the first part of this paper[26] (hereafter called paper I), a formal derivation is given for expanding any function of configuration, $f(\sigma)$, in terms of an orthonormal set of "cluster functions." In particular, the internal energy is expanded in terms of ECI's. Two proposals for averaging over configurations are presented and it is shown that, not only the coefficients in the expansion (the ECI's), but also the basis functions are different in the two distinct schemes. In the first, the so-called grand-canonical (GC) scheme, the basis functions are defined to be orthonormal with respect to an average over all possible configurations of the system. This leads to GC-ECI's which are independent of the concentration (c) of the system, effectively averaging out any concentration and configuration dependence. The expectation value of the energy is written as

$$\langle E \rangle = V_0 + \sum_{\alpha} V_\alpha \xi_\alpha , \tag{1}$$

where V_α are the GC-ECI's for a given cluster α, and ξ_α are the correlation functions, given by the ensemble average

$$\xi_\alpha = \langle \sigma_{\mathbf{p}} \sigma_{\mathbf{p}'} \cdots \sigma_{\mathbf{p}''} \rangle , \tag{2}$$

where the σ's are the "spin" variables of the system, $\sigma_{\mathbf{p}} = +1\ (-1)$ designating an A (B) atom at site $\mathbf{p}$. The GC-ECI's are given by

$$V_\alpha = \rho_\alpha \sum_{\sigma_{\mathbf{p}}, \sigma_{\mathbf{p}'}, \ldots, \sigma_{\mathbf{p}''} = -1}^{+1} \sigma_{\mathbf{p}} \sigma_{\mathbf{p}'} \cdots \sigma_{\mathbf{p}''} \rho_{N-\alpha} \sum_{\{\sigma\}}{}' E(\sigma) , \tag{3}$$

where the primed sum represents the sum over all configurations, holding sites $\mathbf{p}, \mathbf{p}', \ldots, \mathbf{p}''$ fixed. The factors ρ_α and $\rho_{N-\alpha}$, are normalization factors, which, for the grand-canonical case, are simply $1/2^{n_\alpha}$ and $1/2^{N-n_\alpha}$, respectively, where n_α is the number of sites in the cluster α. A familiar example of Eq. (3) would be the effective pair interaction between sites $\mathbf{p}$ and $\mathbf{p}'$:

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

where E_{AA} is the total energy of the system with an A-A pair at sites $\mathbf{p}$ and $\mathbf{p}'$ and all other sites are averaged over all possible configurations. Similar definitions apply for E_{BB}, E_{AB}, and E_{BA}.

In the canonical (C) scheme, the expansion is expressed in terms of functions which are orthonormal with respect to a sum over all configurations which are consistent with a given concentration. Thus, the configuration dependence of these C-ECI's is again averaged out, but the concentration dependence is not, since the operation which actually defines the expansion is different at each concentration. The canonical expression for the internal energy is then

$$\langle E\rangle=\hat{V}_0(c)+\sum_{\alpha}\hat{V}_\alpha(c)\delta\hat{\xi}_\alpha\ , \tag{5}$$

where $\delta\hat{\xi}_\alpha$ are cumulants defined by

$$\begin{aligned}&\delta\hat{\xi}_\alpha=\langle(\sigma_{\mathrm{p}}-\bar{\sigma})(\sigma_{\mathrm{p}'}-\bar{\sigma})\cdots(\sigma_{\mathrm{p}''}-\bar{\sigma})\rangle\ ,\\&\bar{\sigma}=\langle\sigma_i\rangle=\xi_1=2c-1\ ,\end{aligned} \tag{6}$$

and $\hat{V}_\alpha$ are the C-ECI's given by an expression similar to the GC-ECI's where the primed summation over configurations is now restricted to those consistent with a given concentration of the system, with the appropriate normalization factor.

Successful phenomenological approaches for computing the ECI's have been used in the past.[27] More recently, several methods have been proposed for *ab initio* computations of ECI's.[28–37] Each of these techniques involves the determination of electronic structure as well as averaging over some set of configurations. It is precisely this averaging which is one of the most distinct aspects of the various methods. For a system of N lattice sites, the number of configurations in the GC scheme is 2^N, thus, calculating a sum over configurations exactly becomes rapidly intractable, even for relatively small N. Hence, one of the most widely used approximations to this sum involves setting up an average medium of A and B atoms. Thus, in this coherent-potential approximation[38] (CPA), rather than summing over all possible values of some observable, the average value of the observable is approximated by the value of the quantity evaluated in the average medium. The CPA has many merits, most notably that it restores periodicity to the lattice, thus facilitating the most sophisticated band-structure techniques.

By using this CPA medium to approximate the sum over configurations, one can calculate the appropriate quantities to obtain the ECI's. There are, in fact, several methods based on this idea, most notably the generalized perturbation method[28–31] (GPM) and the embedded cluster method[32,33] (ECM). In the GPM, the ECI are obtained by considering any given configuration of the system as a finite perturbation of the CPA medium. The ECM treats the ECI by embedding the cluster in the CPA medium, including all of the possible scatterings off the cluster. The equivalence of the ECM and GPM has been established previously,[39] and, in fact, the ECM gives the exact summation of the partially renormalized GPM to all orders. Also, it is noteworthy that ECI's from either the GPM or ECM are calculated in the canonical scheme simply by changing the average concentration of the reference medium.

A second averaging technique is to obtain the interactions from Eq. (1) itself:[35,40] Assuming that the sum in Eq. (1) converges (as will be shown below), it is permissible to truncate at some point. (The point of truncation has, of course, been the subject of some controversy.) Thus, calculating the total energies of n ordered structures, s, one can write n equations of the form

$$E^s=V_0+\sum_{\alpha\le\alpha_{\max}}V_\alpha\xi^s_\alpha\ . \tag{7}$$

Because the correlation functions of the ordered structures are obtained simply (practically by inspection), these equations each have m unknowns, where m is the number of interactions kept after truncation. Thus, provided $n\ge m$, the system may be inverted to obtain the interactions. Initially, it was proposed to use the method with $n=m$, however, recently, several schemes have been used successfully with $n>m$.[19,40] The question of which interactions and which ordered structures to use is of paramount importance, and hence, has been discussed extensively elsewhere.[19,40] Thus, the averaging over configurations is not explicitly performed, but rather is inherent in the formalism.

In direct configurational averaging[36,37] (DCA), it has been shown that it is possible to approximate the sum over configurations by restricting the sum to a small number of randomly chosen configurations. Since the ECI'S involve energies and differences of energies (all integrated quantities), the convergence with configurations is much faster than that of the density of states. The averaging philosophy of this approach, in contrast to the CPA, is that at least part of the sum over configurations is taken explicitly, however, this requires a nonperiodic structure, and hence a real-space method for diagonalizing the Hamiltonian. Also, the similarities between interactions calculated with DCA and those of the GPM and ECM have been established.[41] Interactions in the DCA may be calculated in either the grand-canonical or canonical averaging schemes by an appropriate restriction (or lack of it) on the sum over configurations, and therefore the DCA lends itself to a comparison of the two averaging schemes.

II. DIRECT CONFIGURATIONAL AVERAGING (DCA)

The DCA method is discussed in detail by Dreyssé *et al.*,[36] however, for completeness, we present the essential points here. The system is described by a tight-binding Hamiltonian

$$\begin{aligned}H=&\sum_{\mathrm{p},\lambda}|\mathrm{p},\lambda\rangle\varepsilon^{\lambda}_{\mathrm{p}}\langle\mathrm{p},\lambda|\\&+\sum_{\substack{\mathrm{p}',\mathrm{p}'',\mu,\nu\\(\mathrm{p}'\neq\mathrm{p}'')}}|\mathrm{p}',\mu\rangle\beta^{\mu\nu}_{\mathrm{p}'\mathrm{p}''}\langle\mathrm{p}'',\nu|\ ,\end{aligned} \tag{8}$$

where the Latin indices designate the lattice sites and the Greek indices label the orbitals. The ε's are the on-site energies and the β's are the hopping integrals. In this paper, we choose to restrict the Hamlitonian to d orbitals only. (Note that this is done merely to expedite the computational process, as the Hamiltonians for full *spd* system are readily calculated either semiempirically[42] or using a first-principles approach.[43,44]) Thus, one might expect that this Hamiltonian would reasonably represent a transition-metal alloy, since it is well known that the primary resonances in transition-metal systems occur in the *d* band. The hopping integrals are given their canonical (*not* related to the canonical averaging scheme) values of

$$(dd\sigma)=-0.6251\ \text{eV}\ ;$$
$$(dd\pi)=\frac{+|(dd\sigma)|}{2}\ , \tag{9}$$
$$(dd\delta)=0\ ,$$

leading to a *d*-band width of 5 eV, which is reasonable for a transition metal.

Determination of the on-site energies requires some care. Clearly, since it is only *differences* in energies which interest us, it is only the quantity $\delta=\varepsilon_B-\varepsilon_A$ that is relevant. As has been shown previously,[45] simply fixing δ arbitrarily is dangerous, as it can lead to significant charge transfers (up to ~ 0.5 electrons) between the *A* and *B* atoms. This is serious for a number of reasons: This charge transfer is *not* constant as a function of concentration, and because the concentration dependence (or lack of it) of various quantities is the primary focus of this paper, this sort of effect must not be overlooked. Also, the differences in energies needed to obtain the ECI's [as in Eq. (4)] are, in fact, differences in *total energies* of the system. However, in the DCA and CPA-based methods, usually only the band energy contribution is taken into account. In the absence of charge transfer, it has been shown[46] that the other contributions to the total energy tend to cancel. This cancellation presumably does not occur in systems with significant charge transfers. For these reasons, the value of δ is chosen so as to be consistent with local neutrality. Again, this approximation is certainly consistent with transition-metal alloys, where charge transfers are known to be negligible.

Next, the Hamiltonian for a given configuration is tridiagonalized using the recursion method.[47] Because this is a real-space method, the recursion cluster may have any configuration, i.e., the configuration need not be constrained by any symmetries. Given this transformed Hamiltonian, the Green's-function matrix element $G_{00}=\langle 0|G|0\rangle$ is obtained as a continued fraction, where G is given by

$$G(z)=(z-H)^{-1} \tag{10}$$

and $|0\rangle$ is the starting vector of the recursion. Thus, the local density of states (DOS) on atom 0 is obtained from

$$n_{00}=\frac{-1}{\pi}\text{Im}\,\text{Tr}G_{00}\ . \tag{11}$$

Of course, the recursion must be stopped at some stage, thus, a terminator must be applied to the Green's-function continued fraction. This terminator has been the topic of much research.[48] It has been shown[37] that the ECI are relatively insensitive the choice of the terminator (for transition-metal alloys), thus we use a simple quadratic one. Also, in this paper we use ten exact levels of recursion, which corresponds to a system of 3140 atoms.

Integrating the local DOS to the Fermi energy gives the band-structure term of the cohesive energy on a given atom in any configuration. Calculating the ECI's involves the differences in energies, e.g., the GC effective pair interaction (EPI), as in Eq. (4). However, computing each of the terms in Eq. (4) separately and then taking differences is difficult due to a large subtractive cancellations. The formalism of "orbital peeling"[49,50] may be applied to the problem of computing the ECI's. Using this method, one may obtain the differences in Eq. (4) directly, and thus bypass the numerical instabilities caused by simple subtractions. In Ref. 36, Dreyssé *et al.* show that, because of symmetries in the definition of the pair interactions, it is only necessary to "peel" on one of the atoms in the pair. It is important to note that this symmetry extends to triplets and higher-order ECI's, i.e., one only need "peel" a single atom in calculating *any* ECI.

Thus, the averaging process of the DCA is to calculate the ECI with the medium surrounding the embedded cluster given as a random atomic configuration. This procedure is repeated for several configurations (in this paper, 20–50) and *then* averages are performed. The configurations generated are, of course, consistent with the averaging scheme used. For GC-ECI's, there is no constraint on the configuration. In other words, there are equal probabilities of any given lattice site in the medium being occupied by an *A* or a *B* atom. To compute C-ECI's, the configurations are constrained to a given concentration. Thus, the probability of each site in the medium being occupied by an *A* (*B*) atom is c_A ($c_B=1-c_A$).

III. MODEL SYSTEMS

We choose to look at *two* systems within the framework described. In the first system, there are 8 *d* electrons on an *A* atom and 3 *d* electrons on a *B* atom. We refer to this system as "8-3." The second system under investigation is the "9-4" system (where similar definitions apply). Physically, 8-3 might represent the Rh-Ti system, whereas 9-4 should describe Pd-V. Heuristically, one might expect that the 8-3 system will be strongly symmetric[51] about $c=0.5$. This is due to the fact that 8-3 is almost centered with respect to the *d* band. (This is, of course, assuming that the properties under consideration will be symmetric about the center of the *d* band.) This assumption is borne out by the shape of the nearest-neighbor pair interaction (NN EPI) as a function of band filling. A theorem based on the local moments of the density of states,[53,54] states that the NN EPI must have at lest two zeros as a function of band filling for the canonical *d* band Hamiltonian. Extensive work[55] in this area has also shown that, for this same Hamiltonian, the curve is indeed regular, has two zeros, and is sensibly symmetric about the center of the *d* band, although the degree of the asymmetry present can shift with concentration. Also, this research shows that more distant-neighbor pairs and higher clusters are not necessarily symmetric. However, since the NN EPI is expected to dominate all the other interactions, this heuristic prediction still has some merit. Based on the same sort of reasoning, one should expect that the 9-4 system will be strongly asymmetric about $c=0.5$. It is important to note that we have chosen two systems for study with the same $\Delta N = N_A - N_B$. Because ΔN is roughly proportional to δ, which is a direct measure of the diagonal disorder, the two systems should have approximately the same amount of this type of disorder. In this way, differences between the two averaging schemes that are influenced by the size of the diagonal disorder should be kept to a minimum. Thus, a comparison of grand-canonical and canonical averaging schemes for these two systems should provide an interesting test of the formalism.

The source of comparison between the averaging schemes cannot lie in the ECI's themselves, but rather in the energy expansions of Eqs. (1) and (5). Thus, it is necessary to choose a real, physical quantity associated with these expansions for the study. However, for computational reasons, it is difficult to calculate the empty cluster and point interactions with as much confidence as the pairs and higher order clusters. The choice of ordering energy bypasses these difficulties, as will be shown below. The ordering energy for a given structure s is defined to be the difference between the energy of that structure and the energy of the completely disordered state at the same concentration:

$$\Delta E^s_{\mathrm{ord}} = E^s - E_{\mathrm{rand}}(c_s) \ , \tag{12}$$

where c_s is the stoichiometric concentration of the structure s.

It is possible to compute the ordering energies by expanding both of the energies involved via the grand-canonical expansion of Eq. (1). The values of the correlation functions for both of these phases are easily obtained: For the *completely* disordered state, the correlation ξ_α, for a cluster α composed of n_α sites simply becomes $\xi_1^{n_\alpha}$, where ξ_1 is the point correlation given by $\xi_1 = 2c - 1$. Thus, combining Eqs. (1) and (12) gives

$$\Delta E^s_{\mathrm{ord}} = \sum_{n_\alpha\,(\neq 1)} V_\alpha(\xi^s_\alpha - \xi_1^{n_\alpha}) \ . \tag{13}$$

Note that the terms involving the empty cluster and point interactions cancel. (In the grand-canonical scheme, the empty cluster will vanish in any difference in energies, and the point interaction will vanish in differences in energies at the same concentration.) One can also write a similar formula for the case of canonical averaging. Again, the cumulants for the ordered phase are given by inspection, and for the completely disordered state, all of the cumulants vanish, leaving only $V_0(c)$. Thus, we have

$$\Delta E^s_{\mathrm{ord}} = \sum_{n_\alpha\,(\neq 1)} \hat{V}_\alpha \delta \hat{\xi}^s_\alpha \ . \tag{14}$$

Again, the only terms left in the sum are pairs and higher.

There are several reasons to look at the ordering energy: Since it involves the difference in energy between two structures at the *same* concentration, terms involving the empty cluster and point terms cancel in both averaging schemes. Also, the ordering energy is the *most critical* test of the formalism, because it is much smaller (typically ~ 0.1 eV or smaller) than other quantities relevant to alloying, such as the formation energy of the random state. The latter quantity can be five or more times larger than the ordering energy. Also, it is the ordering energy that is the relevant quantity when discussing order-disorder transitions and alloy phase stability.

IV. RESULTS

A. Convergence of the expansions

Because the two equations, (1) and (5), are in terms of a complete, orthonormal set of functions (the correlations and the cumulants, respectively), they are, in fact, *exact*, and the problem of computing the energy of any given configuration just becomes one of finding the correct coefficients in the sum (the ECI's). However, since the sums contain an infinite number of terms, this situation is certainly impractical. If the series were rapidly convergent, then perhaps it would be appropriate to truncate the sum at some suitably chosen cluster, throwing away the rest of the series as "negligible." For the series to have any chance at convergence, the following two conditions must hold: (1) cluster interactions must decay as any of the atoms in the cluster is "moved" away from the other atoms (an example of this is pair interactions decaying with distance between the pair), and (2) cluster interactions must decrease with the number of atoms in the cluster. In both cases the decay need not necessarily be monotonic, but it is vital that no "neglected" terms be of the same order of magnitude as the dominant terms which are kept in the sum.

First, the decay of the pair interactions with distance is checked. As the pairs are separated, heuristically, one would expect the pair energies to split into the constituent point energies [e.g., $E_{AB} \sim \frac{1}{2}(E_A + E_B)$ for large separations between A and B]. Thus, the expression for the pair interaction becomes

$$V_{\mathrm{pair}} = \tfrac{1}{4}(E_{AA} + E_{BB} - E_{AB} - E_{BA}) \Longrightarrow 0 \ . \tag{15}$$

(Note, in this section, these equations are valid for either averaging scheme, unless noted otherwise.) Figure 1 shows the logarithm of GC-EPI versus distance between the pairs for the 8-3 system. In this figure, we use an obvious extension of the notation of Table I: $V_{2,n}$ represents the nth-nearest-neighbor EPI. Clearly, the EPI do decay with distance, but even up to fourth nearest neighbor, the interactions could hardly be termed "negligible".

Also, as described above, cluster interactions must decrease as any of the atoms in the cluster become widely separated. As an example, consider the triplet interaction between sites $\mathbf{p}$, $\mathbf{p}'$, and $\mathbf{p}''$:

$$\begin{aligned} V_{\mathbf{pp}'\mathbf{p}''} = \tfrac{1}{8}(&E_{AAA} + E_{ABB} - E_{AAB} - E_{ABA} - E_{BAA} \\ &- E_{BBB} + E_{BBA} + E_{BAB}) \ . \end{aligned} \tag{16}$$

As $\mathbf{p}''$ becomes separated from $\mathbf{p}$ and $\mathbf{p}'$, the energies,

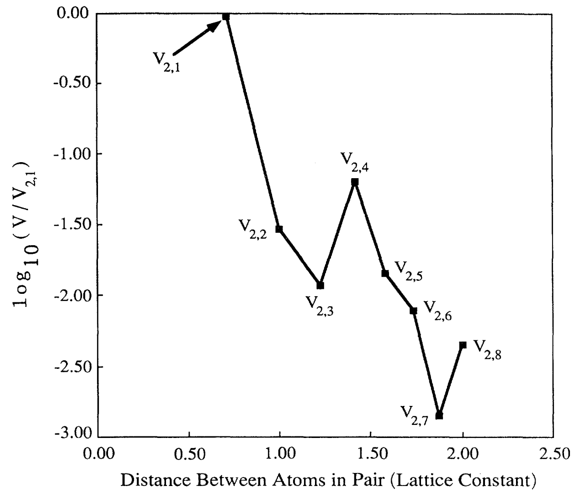


FIG. 1. Convergence of pair interactions with distance between pairs.

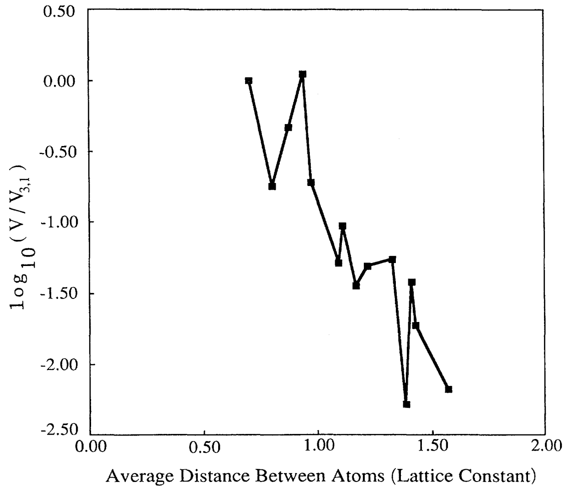
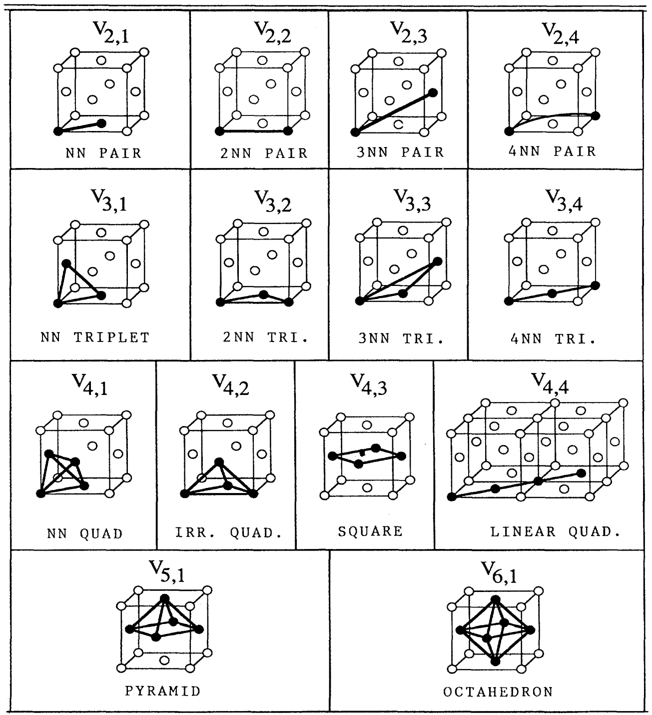


FIG. 2. Convergence of triplet interactions with average distance between atoms.

E_{AAB} separate into E_{AA} and E_B, and all of the other energies similarly decouple. Then, just as before, the expression for the triplet interaction, Eq. (16), tends toward zero. Figure 2 shows the convergence of triplet interactions made of a nearest-neighbor pair and a third atom for the system 8-3. Each point on the figure represents a different effective triplet interaction, and the horizontal scale is just the average of the three sides of the triplet, measured in lattice constants. As the distance between the third atom and the pair increases, the interactions decrease exponentially.

TABLE I. Effective cluster interactions for fcc lattice.



For convergence, the ECI must also decrease as the number of atoms in the cluster is increased. Consider the expression for the triplet interaction between sites **p**, **p**′, and **p**″ [Eq. (16)]. The first four terms are a pair interaction with the first atom held fixed as A. Also, the next four terms again are the pair interaction with the first atom being B. This motivates us to write the triplet interaction as a difference of pair interactions

$$V_{pp'p''}=\tfrac{1}{2}([V_{p'p''}]_{p=A}-[V_{p'p''}]_{p=B}) . \tag{17}$$

This formula is easily extended to any size cluster:

$$V_{pp'p''\cdots p'''}=\tfrac{1}{2}([V_{p'p''\cdots p'''}]_{p=A}-[V_{pp''\cdots p'''}]_{p=B}) . \tag{18}$$

Thus, in the triplet case, if $(V_{p'p''})_{p=A\text{ or }B}$ is of the same order of magnitude as $V_{p'p''}$, then the triplet interaction is clearly smaller in magnitude than the pair. This sort of assumption is reasonable if one considers that GC-ECI's obey the following:

$$V_{p'p''}=\tfrac{1}{2}([V_{p'p''}]_{p=A}+[V_{p'p''}]_{p=B}) , \tag{19}$$

while

$$\hat{V}_{p'p''}=c_A[\hat{V}_{p'p''}]_{p=A}+c_B[\hat{V}_{p'p''}]_{p=B} \tag{20}$$

holds for C-ECI's. This same sort of argument would, in general, hold for all clusters. The decay of the cluster interactions in the 8-3 system can be evidenced in Fig. 3. Here, again, the logarithm of the interactions (normalized to the pair interaction) is plotted as a function of number of atoms in the cluster. Note that the convergence of the cluster interactions seems to be much more rapid than that of the pairs (over distance); however,

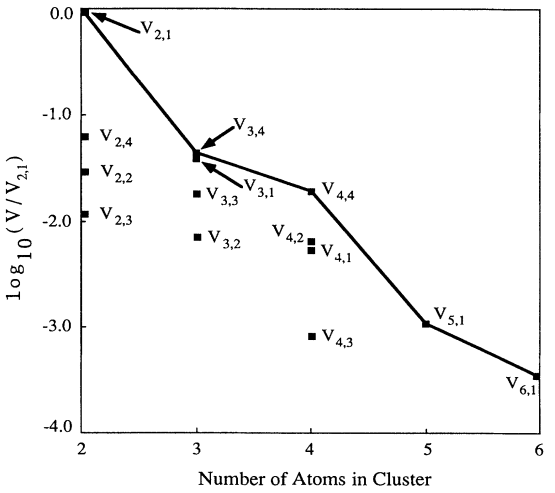


FIG. 3. Convergence of ECI's with number of atoms in the cluster.

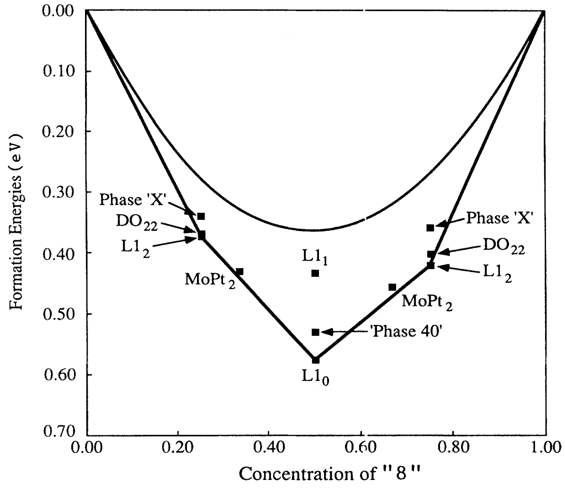


FIG. 4. Formation energies for system 8-3.

several of the triplets and quadruplets are as large as the second- and third-nearest-neighbor pair interactions, and thus, these interactions must not be considered negligible.

B. Comparison of grand canonical and canonical

For both the 8-3 and 9-4 systems, the interactions in Table I and the random formation energies were calculated as a function of concentration. Also, the formation energies of the following 11 ordered structures were calculated: $L1_0$, phase 40, $L1_1$, $L1_2$ (A_3B and AB_3), $D0_{22}$ (A_3B and AB_3), phase X (A_3B and AB_3), and MoPt_2 (A_2B and AB_2). All of these phases are superstructures of the fcc lattice and are defined in Ref. 56, except for phase X, which is defined in Ref. 40. The formation energy of a structure s is given by

$$\Delta E^s_{\mathrm{form}} = E^s - (c_A E^0_A + c_B E^0_B)\ , \qquad (21)$$

where the superscript 0 represents a pure element. The formation energies of the ordered phases were calculated by finding the cohesive energies of an A and a B atom in the structure (as described above), and then summing these energies weighted by the stoichiometry of the configuration. With the $D0_{22}$ and phase-X structures, there are three distinct types of atoms in the unit cell (as opposed to two types for all other phases). Thus, these systems were, in fact, treated as ternaries, with different on-site energies for each distinct atom, all generated by the condition of local neutrality. This sort of problem made the calculation of certain structures, namely, those with many distinct atoms in the unit cell, practically unfeasible. The formation energies of the random structures were found in much the same way, except that, of course, the cohesive energies of the A and B atoms were calculated in a random configuration, and these energies were averaged over many configurations, until there was a suitable convergence.

Figure 4 shows the formation energies for the 8-3 system. There is a correspondence between this system and an artificial one with only a single nearest-neighbor concentration-independent pair interaction. We will call this artificial alloy system a "perfectly symmetric" one since one of its characteristics would be the complete symmetry of ordered and random formation energies about $c=0.5$. Also, the ground states of the "perfectly symmetric" system[57] (including only the structures listed above) would be $L1_0$ (degenerate with phase 40) and $L1_2$ (degenerate with $D0_{22}$). The MoPt_2 structures would lie just above the tie line connecting $L1_0$ and $L1_2$. The same general properties are seen in the 8-3 system in Fig. 4. The random formation energy is nearly symmetric about $c=0.5$ and, although the exact degeneracies are, of course, broken, the other general features are kept as well: $L1_0$ is a ground state, as are both $L1_2$ phases. (The degeneracies with phase 40 and the $D0_{22}$ phases are lifted, but these phases are still very close in energy.) Also, both MoPt_2 phases still lie very close to the tie lines between $L1_0$ and $L1_2$. Figures 5–7 show the canonical

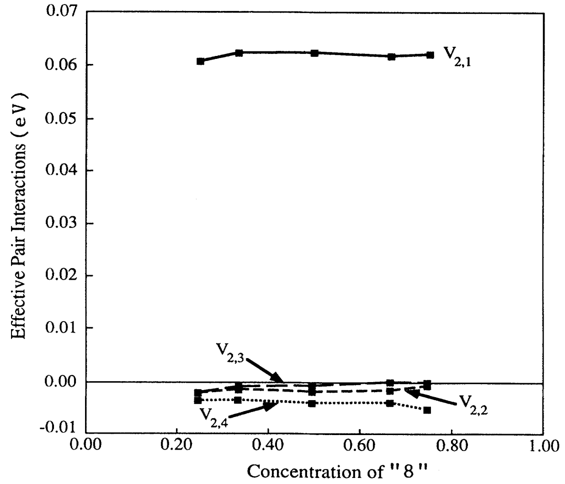


FIG. 5. Effective pair interactions vs concentration for system 8-3.

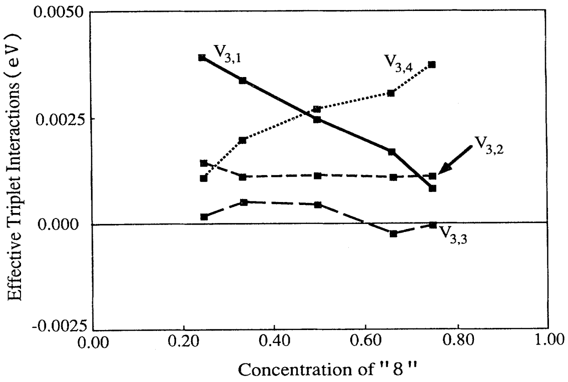


FIG. 6. Effective triplet interactions vs concentration for system 8-3.

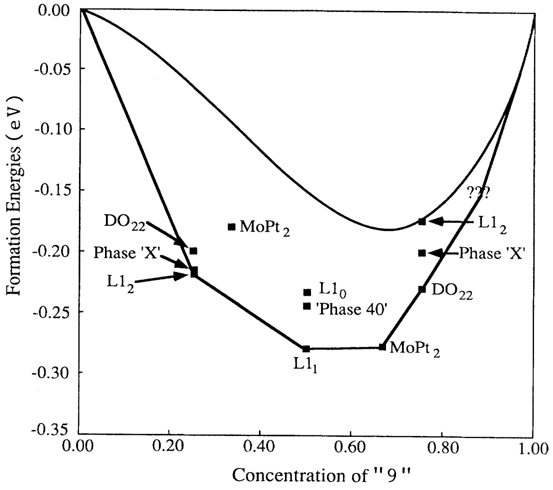


FIG. 8. Formation energies for system 9-4.

pair, triplet, and quadruplet interactions, respectively, versus concentration. As expected, the nearest-neighbor EPI dominates, and the higher-order interactions converge rapidly. Also, note that the concentration dependence of the pair interactions is extremely small. Thus, our qualitative predictions about the 8-3 system are verified.

The formation energies of the 9-4 system are shown in Fig. 8. In this system, the formation energies of the completely random states are not symmetric about $c=0.5$, but rather, the curve is asymmetric, with a minimum at $c \sim 0.7$. Also, note the strong asymmetry in the ordered formation energies: The $D0_{22}$ at 75% 9 is stable with respect to the $L1_2$, while at 25%, the situation is reversed. At 50%, the $L1_1$ is stable over $L1_0$ and phase 40. The two $MoPt_2$ structures also show the asymmetry. At $c=\frac{2}{3}$, $MoPt_2$ is stable with respect to decomposition into $L1_1$ and $D0_{22}$, while the $MoPt_2$ structure at $c=\frac{1}{3}$ is quite far from the tie line between $L1_1$ and $L1_2$. We have included the question marks at the 9-rich end of the concentration because of the possibility of the Pt_8V structure being stable in this system. Of course, this is also possible in the 8-3 system; however, it is much more likely in 9-4, since this system should represent the Pt-V system.

Due to all of the observations above, one would expect that the NN EPI in 9-4 should be strongly concentration dependent or perhaps the many-body interactions will be important (or both). In fact, both of these are found to be true. In Figs. 9–11, we show pairs, triplets, and quadruplets, respectively, for 9-4 system as functions of concentration. The NN EPI is a strong function of concentration, and the more distant pair interactions are larger with respect to the NN EPI in this system than in 8-3. Also, Fig. 10 illustrates that the triplet interactions are clearly relevant in 9-4. Note that the fourth NN triplet (which forms a straight line) is larger than all of the other triplets. The notion that ECI for clusters composed of self-retracing linear paths would be more important than those for compact clusters has been proposed before and studied with the tight-binding CPA-GPM.[58] Note also the large value of the linear quadruplet, even though it spatially extends to the ninth nearest neighbor.

In this paper, the main source of comparison between the canonical and grand-canonical ECI's is in how well they predict the ordering energies. The ordering energies for all 11 ordered structures are computed simply by taking the *ordered* (not ordering) energy of the structure, and then subtracting from that, the random energy at the

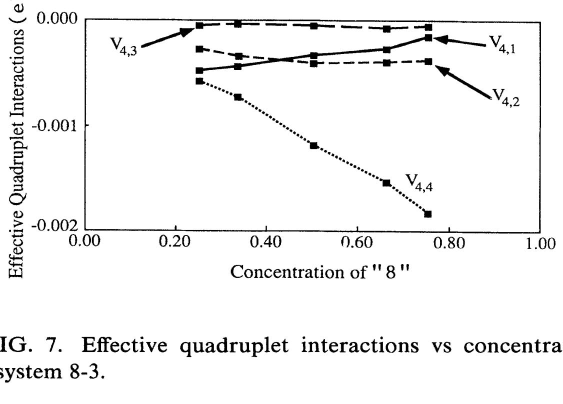


FIG. 7. Effective quadruplet interactions vs concentration for system 8-3.

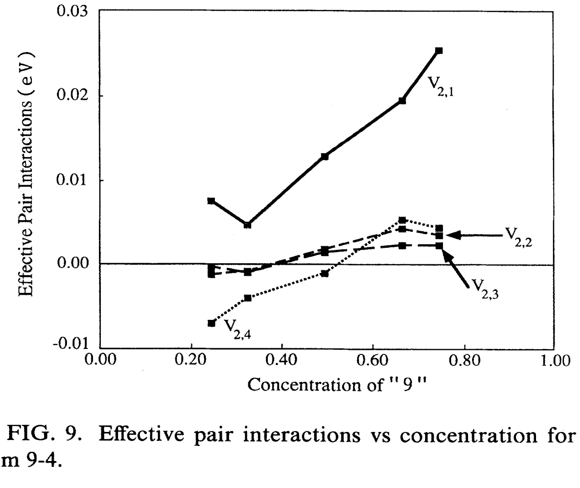


FIG. 9. Effective pair interactions vs concentration for system 9-4.

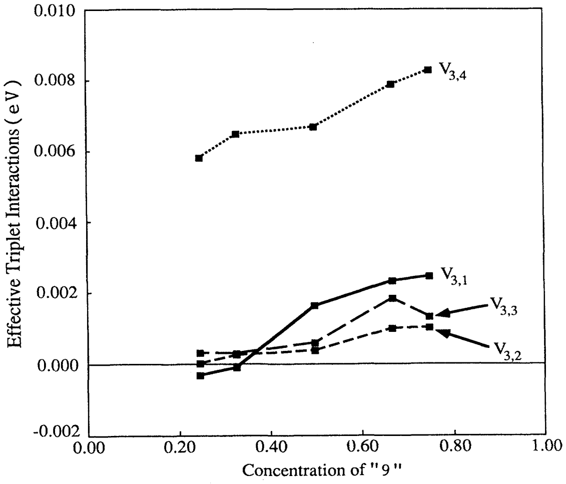


FIG. 10. Effective triplet interactions vs concentration for system 9-4.

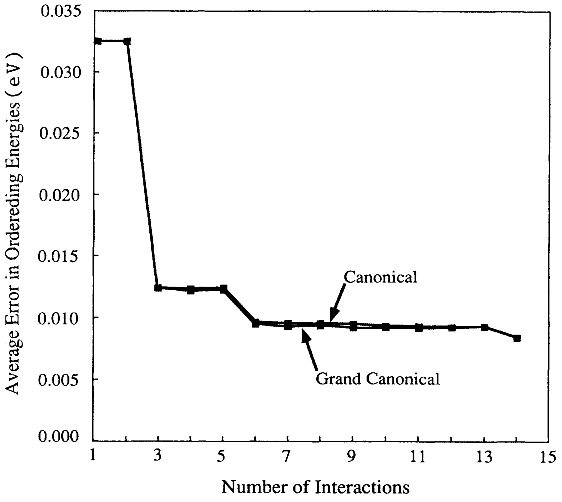


FIG. 12. Convergence of averaging schemes for system 8-3.

same concentration. The ordering energies determined in this way will be termed "exact". It is also possible to determine the ordering energies through either Eq. (13) or Eq. (14). Using the grand-canonical or canonical ECI's, the terms in the summations of Eqs. (13) and (14) are calculated. Then, these results are subtracted from the "exact" results, and a root mean square is formed. This quantity, for whichever set of interactions, is termed the error in ordering energy for that set. Thus, the convergence of the expansions should be seen if this error is plotted versus the number of terms kept in the sum. These results appear in Figs. 12 and 13 for the 8-3 and 9-4 systems, respectively. The interactions are added in the order of Table I, except for the pyramid and octahedron interactions, which are negligible for both systems. Thus, the first ECI to be used is the empty cluster. Since this interaction does not appear in Eqs. (13) and (14), the root-mean-square error of the ordering energies is simply the root mean square of the exact ordering energies themselves (for instance, 0.033 eV in the 8-3 case). Similarly, the error does not change with the point interaction, since this ECI also does not appear in the sums. It is not until the NN EPI is included that the error drops significantly. The leveling out of the curves with large number of interactions implies that the sum has mostly converged and additional interactions are not appreciably changing the average error in the ordering energies.

Figure 12 shows the convergence for the 8-3 case. For this case, both the grand-canonical and canonical interaction are able to describe the system relatively well. Both curves show a huge drop in error at the NN EPI interaction, and a smaller drop in error at the fourth NN EPI. Both curves level off at slightly less than 0.01 eV, and since the "exact" results for the random formation energies are only expected to be accurate on this sort of energy scale, we say that the system is described by both sets equally well. This is consistent with the fact that the NN EPI dominated this system, and was, for all intents and purposes, concentration independent. Thus, we expect

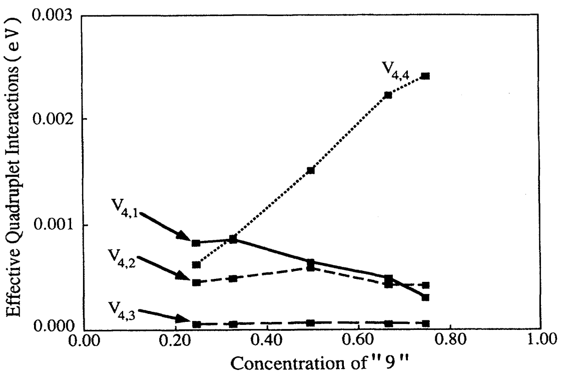


FIG. 11. Effective quadruplet interactions vs concentration for system 9-4.

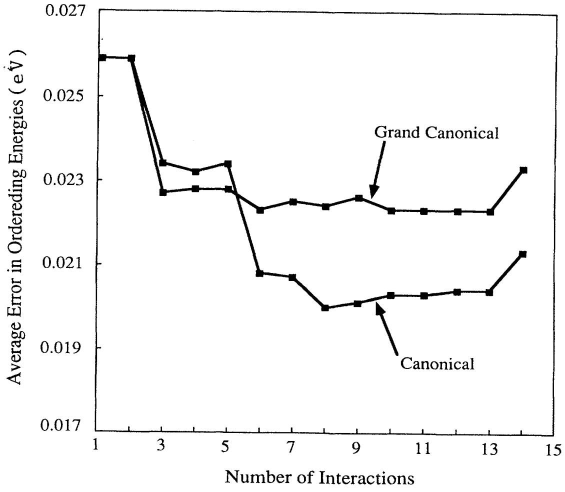


FIG. 13. Convergence of averaging schemes for system 9-4.

that there would be little or no difference between the two averaging schemes for this system.

Figure 13 gives the results for the 9-4 system. Again, there is a large drop in the error with the NN EPI. The grand-canonical interaction is actually slightly lower than the canonical interaction at this point. It is not until the fourth NN pair that the canonical interactions actually prove to more accurately describe this system than the grand-canonical interactions. However, it should be noted that *both* the grand-canonical and canonical interactions have quite a bit more difficulty in describing this asymmetric system than they did in the symmetric, 8-3 case. (Note the lower end of the energy scale on Fig. 13.) Also, both averaging schemes undergo a sharp rise in error with the linear quadruplet, indicating that neither set of interactions has completely converged at this point. Thus, a larger set of interactions is needed to adequately describe the 9-4 system.

C. Relations between GC-ECI's and C-ECI's

In paper I, the equivalence of the grand-canonical and canonical expansions was proved. In identifying the expansions terms for term, the following expression was derived relating the GC-ECI's and C-ECI's:

$$V_\alpha = \hat{V}_\alpha(c) + \sum_{\alpha\subset\beta} (-\sigma)^{n_\beta - n_\alpha} \hat{V}_\alpha(c) \ . \tag{22}$$

Thus, the concentration-independent GC-ECI's may be expressed as linear combinations of the concentration-dependent C-ECI's. If the canonical interactions are properly renormalized by the triplets and higher-order interactions, they will tend towards their grand-canonical counterparts or, in other words, will tend to lose their concentration dependence. Figure 14 shows the concentration dependence of the NN EPI for the 9-4 system. As state previously, the unrenormalized interaction is strongly concentration dependent. However, as expected from Eq. (22), the EPI becomes less concentration dependent when renormalized by the triplet interactions, and even less so when renormalized with triplets and quadruplets. This simple test provides an extremely strong verification of the formalism, and also gives valuable insight into the similarities between the two seemingly distinct averaging schemes.

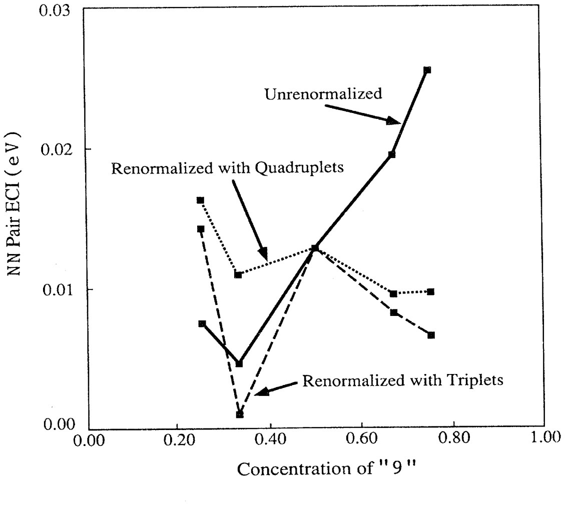


FIG. 14. Renormalized nearest-neighbor pair ECI for system 9-4.

V. DISCUSSION

The notion of expansion in orthonormal cluster functions was introduced by Sanchez, Ducastelle, and Gratias[34] (SDG) who showed that the cluster-variation method did not need to be considered as a *variational* method at all. In fact, cluster function expansions provide an unambiguous way of obtaining the optimal description of the state of order in a (partially) disordered system for a given cluster approximation. Additionally, such expansions also provide a rigorous formalism for determining effective cluster interactions which, in turn, determine the thermodynamics of the system. The original SDG formalism produced concentration-independent ECI's but we have now shown, in this paper and in I, that concentration-dependent ECI's could be defined within the same orthonormal expansion formalism: it was merely necessary to modify the method of summation which enters into the definition of the scalar product to the vector space.

It was then possible to prove that energy expansions based on concentration-independent and concentration-dependent interactions are strictly equivalent, and could be identified term for term. Thus, by Eq. (22), the renormalized effective interactions beyond the "point" ECI despite the manifest concentration dependence indicated in Eq. (22), turn out to be concentration independent. It follows that the expansion in concentration-dependent interactions proposed, for example, in Eq. (5.9) of Ref. 39, can, in fact, be written as an expansion in concentration-independent ECI's (beyond the point interaction) via this renormalization. The formal proof given in I is well substantiated here: in Fig. 14, the NN pair interaction for a highly "asymmetric" system becomes progressively less concentration dependent as the renormalization is extended to higher clusters (triplets, quadruplets).

From a practical standpoint, however, it may be preferable to approximate the energy of a system in terms of a small number of concentration-independent pair interactions. It will not do, of course, to expand the energy in concentration-independent pair interactions only. A phase diagram perfectly symmetric about the central concentration would result, which would be generally incorrect. Hence, with GC-ECI's, it is necessary to include cluster interactions beyond the pair. In some cases, this may be the best way to proceed computationally. Although the GC expansion may require a large set of interactions to accurately represent the energy, this set can be used throughout the entire range of concentrations of the system. Whereas, with the C expansion, it is perhaps permissible to use only a small number of pair interactions, these interactions must be calculated individually for each concentration. Thus, for phase-diagram calculation, the GC scheme might actually require fewer ECI calculations than the C scheme.

Calculated C and GC-ECI's will, of course, be numerically different. Their physical meaning will also differ. However, both sets of interactions may be interpreted physically as interchange energies averaged over a specified set of configurations. Thus, neither set may be said to be more or less physically meaningful than the other. In any case, what matters is that the actual energy expression be invariant to the choice of ECI definitions. In the GC expansion, the whole burden of the concentration dependence of the expectation value of the ordering energy is placed on the correlation functions, ξ, in the C expansion, the concentration dependence is shared by both the $\hat{V}_\alpha$ and the $\delta\hat{\xi}_\alpha$ parameters of Eq. (5).

What is not available at present is a universally valid criterion for series termination. On the basis of present considerations, we may state merely that multiplet interactions are contributing significantly to the ordering energy up to the point where the "renormalized" C-ECI's become practically concentration independent. Thus, although this criterion allows the declaration of convergence with some degree of confidence, it does not indicate *which interactions* are most relevant for a given system. At present, this choice is still somewhat arbitrary.

VI. CONCLUSIONS

In this paper, we have examined the formalism for defining a complete set of cluster functions which can be constructed so as to be orthonormal in *both* types of averaging schemes: An average over all configurations of the system (the GC scheme), or an average with the constraint that only configurations at a given concentration are to be included (canonical). The former leads to an energy expansion in which the ECI's are independent of the concentration of the system, whereas the latter gives concentration-dependent ECI's. We have also seen that the DCA is a practical, viable method for obtaining the ECI's in either averaging scheme. Both types of averaging schemes have been shown to be rapidly convergent. This was evidenced in part by the decay of cluster interactions (pair and triplets) as the distance between atoms was increased and also by the decay of interactions as more points were added to the cluster. With respect to the numerical comparisons made for a symmetric, or concentration-independent system, canonical and grand-canonical interactions seem to describe the system about equally as well. For a strongly asymmetric system, both of the methods have much more trouble giving correct values for random and ordered energies. In these systems, canonical interactions seem to do slightly better than grand canonical. Thus, generalizing from these two systems, we can say that DCA with either GC or C ECI's seems to be a reliable method for obtaining the correct trends in binary-alloy systems; however, quantitatively, the best choice, unfortunately, seems to be system dependent. We have also numerically studied relations between the interactions in the two averaging in schemes. These relationships establish links between the concentration-dependent and -independent interactions which prove the complete and formal equivalence of the two expansions. Thus, we have seen in I that two distinct averaging schemes are available and can be justified theoretically under the same general framework. The choice of which scheme to adopt for a given calculation is clearly dictated by the system under study as well as practical concerns, such as computer time or the constraints imposed by the numerical minimizations of the CVM free-energy functional.

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