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Disordered binary alloys. II. Decoupling schemes for many-site correlation functions

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General decoupling schemes for many-site site-occupation correlation functions in equilibrium-disordered substitutional binary alloys are presented and discussed. A justification for the decoupling schemes is given in terms of the order-in-$1/z$ criterion of accuracy developed previously, where z is the number of sites interacting with a given site. The present decoupling schemes apply directly to concentrated alloys with strongly clustering tendencies; they also apply to a lesser extent in other cases.

I. INTRODUCTION AND SUMMARY

Many-site site-occupation correlation functions are important parameters for obtaining a detailed understanding of many phenomena associated with binary alloys. For example, many-site correlation functions occur in: (i) theories of x-ray and neutron scattering from disordered alloys when the "size effect" is included,[1-3] (ii) expressions for the higher-order concentration derivatives of ensemble-averaged quantities,[4] (iii) the exact treatment of neutron scattering from disordered magnetic alloys [e.g., Eq. (40) in Ref. 4], (iv) treatments of the line shape in NMR[5] and the Mössbauer effect, and (v) the problem of differentiating between alternative possible structures when these have identical pair-correlation functions to all orders.[6] They are useful in helping to give simple pictures of the microstructure in disordered alloys[7,8] and may also be expected to be of value in theoretical calculations of the electronic structure of disordered alloys as these become more accurate.[9] Further, statistical-mechanical theories of ordering invariably involve some assumption as to the nature of these many-site correlation functions, and so improved theoretical methods for estimating them are useful in helping to improve the accuracy of equilibrium ordering theories—the goal to which the present series of papers is directed.

In a previous work[10] (hereafter cited as I), we laid a basis for the approximate statistical-mechanical calculation of pair- and many-site correlation functions using the order-in-$1/z$ criterion as a measure of accuracy, where z is the number of sites interacting with a given site. The purpose of the present work is to extend I by developing and justifying explicit (cf. Refs. 7 and 8) general decoupling schemes for many-site correlation functions. This is highly desirable because numerical evaluation of many-site correlations in the manner of I becomes intractable for large clusters and for widely dispersed sites in a cluster. Furthermore, explicit decoupling schemes are of particular value in the development of theories of disordered alloys because they can be used to help carry out simplifications of complicated algebraic expressions.

The emphasis of the present work is on developing approximate general methods which are suitable for a wide class of physically realistic Hamiltonians, rather than on obtaining highly accurate results for specific simplified cases (as might be derived for example by Monte Carlo or series-expansion methods). In this regard, the use of the order-in-$1/z$ criterion seems particularly appropriate because alloys are known to possess long-range interactions (see e.g., Ref. 11).

The outline of the present paper is as follows. In Sec. II, the fundamental equations are re-presented with new expressions for the coefficients and a brief resumé is given of the order-in-$1/z$ classification scheme. Section III contains the justification for the decoupling schemes[12] and describes several of their important properties. These results are intended to serve as a basis for the development of the improved ordering theories which are to be described in future papers.

II. HIERARCHY OF EQUATIONS FOR THE SITE-OCCUPATION CORRELATION FUNCTIONS

For the sake of simplicity, consideration in the present series of papers is henceforth restricted to the pair-wise configurational Hamiltonian

$$H = \frac{1}{4}\sum_{f,g} V_{fg}\sigma_f\sigma_g \qquad (2.1)$$

of an (A, B) binary alloy with mole fractions (m_A, m_B) and pair-interaction parameters V_{ij}. The site-occupation operators introduced in (2.1) are defined as

$$\sigma_i = \begin{cases} 2m_B & \text{for an } A \text{ atom at site } i \\ -2m_A & \text{for a } B \text{ atom at site } i\,, \end{cases} \tag{2.2a}$$

so that

$$\sigma_i^n = A_n + B_n \sigma_i\,, \tag{2.2b}$$

where the reduction coefficients in (2.2b) are found[10] to be

$$A_n = 2^n [m_A m_B^n + (-1)^n m_A^n m_B] \tag{2.2c}$$

and

$$B_n = 2^{n-1}[m_B^n - (-m_A)^n]\,. \tag{2.2d}$$

The pair-interaction parameter between sites i and j defined by lattice vectors $\vec{R}_i$ and $\vec{R}_j$ is

$$V_{ij} = \tfrac{1}{2}(V_{ij}^{AA} + V_{ij}^{BB} - 2V_{ij}^{AB})\,, \tag{2.3}$$

where V_{ij}^{AB}, etc. are assumed to be invariant to a translation by a lattice vector and also to be symmetrical with respect to inversion of sites i and j. A notational convention adopted throughout the present series of papers is that subscripts $i,j,k,\ldots$ relate to "fixed" or particular sites, whereas $f,g,h,\ldots$ relate to "floating" or summed over sites.

The pairwise form (2.1) for H should not be regarded as a necessary limitation of the present method, since the method may readily be extended to more complicated many-site-interaction Hamiltonians by using the order-in-$1/z$ classification scheme for irreducible many-site interactions introduced in I.

The basic starting point for the present treatment of the statistical mechanics of equilibrium-disordered binary alloys is the doubly-infinite hierarchy of equations for the pair- and many-site correlation functions given in Eqs. (10) of I. These equations are rewritten here in more compact form as follows:

$$\langle \sigma_1 \sigma_2 \sigma_3 \cdots \sigma_n \rangle \equiv \langle 123 \cdots n \rangle = D_0(t)\langle 23 \cdots n\rangle - \tfrac{1}{2}\beta D_1(t) \sum_f V_{1f} \langle f23\cdots n\rangle + \tfrac{1}{4}\beta^2 D_2(t) \sum_{f,g} V_{1f}V_{1g}\langle fg23\cdots n\rangle - \tfrac{1}{8}\beta^3 D_3(t) \sum_{f,g,h} V_{1f}V_{1g}V_{1h}\langle fgh23\cdots n\rangle + \cdots\,, \tag{2.4}$$

where n, the number of *distinct* sites in the cluster, successively takes the values $1, 2, 3, \ldots$. For the special case $n = 1$, the first term in the expansion (2.4) is simply $D_0(t)$. The expansion coefficients $D_m(t)$ are given by

$$D_0(t) \equiv t - (m_A - m_B) \quad \text{for } m = 0\,, \tag{2.5a}$$

and for $m \geq 1$,

$$D_m(t) \equiv \frac{1}{m!}\frac{d^m \tanh\lambda}{d\lambda^m} \equiv \frac{1}{m}(1-t^2)\frac{d}{dt}D_{m-1}(t) \equiv \frac{1}{m!}(1-t^2)\frac{d}{dt}(1-t^2)\cdots\frac{d}{dt}(1-t^2) \quad \left[\text{with } (m-1) \text{ factors } \frac{d}{dt}\right]. \tag{2.5b}$$

In these expressions, $t \equiv \tanh\lambda$, where λ is analogous to a chemical potential and as usual $\beta = 1/k_B T$, where k_B is Boltzmann's constant.

It should be noted that the development of these equations in I was carried out in a grand-canonical-like ensemble with the consequence that λ or equivalently t must be chosen for each β such that the solution to (2.4) satisfies the composition constraint $\langle \sigma_i \rangle = 0$ everywhere.

A. Order-in-$1/z$ classification scheme

The problem of finding a general solution to (2.4) is almost the same problem as trying to find a general solution to the many-neighbor Ising model in an applied field. In order to make the problem tractable, a method for selecting the dominant contributions in (2.4) was developed in I. This was based on the order-in-$1/z$ criterion of smallness. This classification scheme is most simply developed if only completely clustering (i.e., all $V_{ij} \leq 0$) alloys are considered initially; later extension of the classification scheme to alloys with arbitrary V_{ij} is possible, and was discussed in I.

The rules for classifying the order in $1/z$ of the general term with coefficient $D_m(t)$ in (2.4) are reproduced below for convenience: (a) Allow a factor of $z^{-(n-1)}$ for each n-site interaction in the general term. (b) Allow a factor of z for each summation over a floating (summed over) site in the general term. (c) Allow a factor of $z^{-\nu_n}$ for a correlation function with n sites (fixed plus floating), where ν_n is given by

$$\nu_n = \tfrac{1}{2}[n + \phi(n)] \quad \text{with } \phi(n) = (0, 1) \quad \text{for } n = (\text{even}, \text{odd})\,. \tag{2.6}$$

(d) Allow an additional factor of $1/z$ for any term which has coefficient D_0.

The special case (d) occurs because substitution of $\langle\sigma_i\rangle = 0$ into (2.4a) reveals that $D_0 = O(1/z)$, so that the order of a term containing D_0 is increased by one.

III. GENERAL DECOUPLING SCHEMES

The main results of the present work are the general decoupling schemes for the many-site correlation functions presented below and their justification in terms of the order in $1/z$ criterion.

In I, it was shown that *irreducible* (no sites coincident) four-site correlation functions could be decoupled correctly to lowest order in $1/z$ [i.e., to $O(1/z^2)$] into symmetrized products of pair correlation functions. More generally, it is possible to show that the following decoupling schemes for *irreducible* $2n$- and $(2n+1)$-site correlations apply to lowest order in $1/z$ [i.e., ν_n as given by (2.6)]:

$$\langle 123\cdots(2n-1)(2n)\rangle = \{\langle 12\rangle\langle 34\rangle\cdots\langle(2n-1)(2n)\rangle\} \quad [+O(1/z^{n+1})], \quad (3.1\text{a})$$

and

$$\langle 123\cdots(2n)(2n+1)\rangle = \{\langle 123\rangle\langle 45\rangle\cdots\langle(2n)(2n+1)\rangle\} \quad [+O(1/z^{n+2})], \quad (3.1\text{b})$$

respectively, where $\{\ \}$ denotes the sum over all *distinct* permutations of the sites. Permutations which differ only in the order of the sites inside an angle bracket or in the order of the correlation functions in a product are not distinct, so that, say, for distinct sites $1, 2, \ldots, 6$, the permutation terms $\langle 12\rangle\langle 34\rangle\langle 56\rangle$ and $\langle 43\rangle\langle 12\rangle\langle 65\rangle$ are *not* distinct. That is, all products of correlation functions which are formally identical, after algebraic manipulation if necessary, are counted only once. The decoupling schemes (3.1) are understood to be valid in the sense that for *fixed n* the error term becomes small as z becomes large.

The justification of (3.1a) follows in a similar manner to that used for four-site correlation functions in I, and so the details need not be given here. Suffice it to mention that the proof for the $2n$-site case proceeds by induction on $2n$ (see Ref. 13 for full details). By contrast, the justification of (3.1b) involves a more subtle argument, the details of which are given in the Appendix.

The decoupling schemes (3.1) have several important properties which are described below.

A. Properties of the decoupling schemes

(i) They are symmetrical with respect to site permutation—this is obvious from inspection of (3.1).

(ii) (3.1) is trivially *exact* for $m_A = \frac{1}{2}$ alloys since all irreducible odd-site correlation functions vanish, including $\langle 123\rangle$.

(iii) Validity of the decoupling schemes (3.1) under conditions of reducibility: Although the decoupling schemes (3.1) were only justified initially for irreducible site clusters, some very important and useful properties of (3.1) are the preservation of the validity of these schemes to residual lowest or leading order in $1/z$ when certain site coincidences are allowed to occur in the cluster (see also Ref. 13). These allowed classes of site coincidences are as follows: (a) For $2n$-site correlation functions, Eq. (3.1a) remains valid to leading order in $1/z$ if there are *at most* only pairwise coincidences between sites. To illustrate this result for a particular case, consider, say, (3.1a) for $n = 2$ with $\langle iijj\rangle$. Using the reduction relations (2.2b), we obtain for the left-hand side

$$\langle iijj\rangle = A_2^2 + B_2\langle ij\rangle = A_2^2 + O(1/z),$$

while the decoupled form on the right-hand side of (3.1a) gives

$$\langle iijj\rangle = \langle ii\rangle\langle jj\rangle + 2\langle ij\rangle\langle ij\rangle = A_2^2 + O(1/z),$$

and so the left- and right-hand sides of (3.1a) agree to leading order in $1/z$, i.e., to $O(1)$ in this case. (b) For $(2n+1)$-site correlation functions, Eq. (3.1b) also remains valid to leading order in $1/z$, if there are site coincidences such that there is at most one case of three coincident sites, and pairwise or no coincidences among the remaining sites.

(iv) Validity as sites in a cluster become more dispersed: The decoupling schemes (3.1) for irreducible many-site correlation functions are valid to *lowest* order in $1/z$, as given by (2.6). This shows that for given n the decoupling schemes (3.1) hold for the most strongly coupled n-site correlation functions. Physical intuition would suggest that the decoupling schemes should become more accurate as subclusters of sites "move" away from each other. In fact, we know that the decoupling scheme (3.1a), say, must become *exact* in the disordered alloy as pairs of sites move away from each other to infinity. This intuitive concept has been called "the principle of correlation weakening" by Bogolyubov[14] and provides a useful check on any results obtained for the decoupling of many-site correlations. It implies that the maximum attainable value of the n-site correlation functions must in fact become of higher order in $1/z$ than ν_n as the intersite separations become greater than the range of interaction. Therefore, it seems physically reasonable to conjecture that the decoupling schemes (3.1) hold to *leading* order in $1/z$, which may be greater than ν_n if the cluster is very dispersed. The assumption that (3.1) holds to *leading* order greatly increases the significance of the results obtained in, for example, I, because solutions for irreducible pair and triplet correlations then enable one to generate all the rest to *leading* order via (3.1).

In addition to the above properties it is helpful here to note that many-site correlation functions must satisfy certain very general bounds[7,15] and sum rules.[4]

IV. APPENDIX

We wish to show that

$$\langle 12345\cdots(2n)(2n+1)\rangle=\{\langle 123\rangle\langle 45\rangle\cdots\langle(2n)(2n+1)\rangle\}\;[+O(1/z^{n+2})]\,. \tag{A1}$$

A. Proof

To leading order in $1/z$ (2.4) is

$$0=D_0(t)+\tfrac{1}{4}\beta^2D_2(t)\sum_{fg}V_{1f}V_{1g}\langle fg\rangle\quad\text{for } n=0\,, \tag{A2}$$

$$\langle 12\cdots(2n-1)(2n)\rangle=-\tfrac{1}{2}\beta D_1(t)\sum_{f}V_{1f}\langle f2\cdots(2n-1)(2n)\rangle\quad\text{for even-site clusters}\,, \tag{A3}$$

and

$$\langle 123\cdots(2n)(2n+1)\rangle=D_0(t)\langle 23\cdots(2n)(2n+1)\rangle-\tfrac{1}{2}\beta D_1(t)\sum_{f}V_{1f}\langle f23\cdots(2n)(2n+1)\rangle+\tfrac{1}{4}\beta^2D_2(t)\sum_{fg}V_{1f}V_{1g}\langle fg23\cdots(2n)(2n+1)\rangle\quad\text{for odd-site clusters}\,, \tag{A4}$$

where the sites $1,2,\ldots,(2n+1)$ are all distinct. Defining

$$G_{123\cdots(2n)(2n+1)}\equiv\langle 123\cdots(2n)(2n+1)\rangle-\{\langle 123\rangle\langle 45\rangle\cdots\langle(2n)(2n+1)\rangle\}\,, \tag{A5}$$

it may readily be shown by taking suitable combinations of (A2), (A3), and (A4) that, to $O(1/z^{n+1})$,

$$G_{123\cdots(2n)(2n+1)}=-\tfrac{1}{2}\beta D_1(t)\sum_{f}V_{1f}\langle f23\cdots(2n)(2n+1)\rangle+\tfrac{1}{4}\beta^2D_2(t)\sum_{fg}V_{1f}V_{1g}\times[\langle fg23\cdots(2n)(2n+1)\rangle-\langle fg\rangle\langle 23\cdots(2n)(2n+1)\rangle]-\{\langle 123\rangle\langle 45\rangle\cdots\langle(2n)(2n+1)\rangle\}\,. \tag{A6}$$

In order to continue the simplification of (A6), it is helpful to note the following two results:

$$\{\langle 123\rangle\langle 45\rangle\cdots\langle(2n)(2n+1)\rangle\}=\{\langle \underline{1}23\rangle\langle 45\rangle\cdots\langle(2n)(2n+1)\rangle\}+\{\langle 345\rangle\langle \underline{1}2\rangle\cdots\langle(2n)(2n+1)\rangle\}\,, \tag{A7}$$

and

$$\{\langle fg23\cdots(2n)(2n+1)\rangle\}=\{\langle \underline{fg}23\cdots(2n-2)(2n-1)\rangle\langle(2n)(2n+1)\rangle\}-n\{\langle \underline{fg}\rangle\langle 23\rangle\langle 45\rangle\cdots\langle(2n)(2n+1)\rangle\}\,, \tag{A8}$$

where a bar underneath a site label denotes a fixed (i.e., nonpermuted) site.

Substitution of (A7) into (A6), followed by the use of (A4) with $n=1$, leads to the equation

$$G_{123\cdots(2n)(2n+1)}=-\tfrac{1}{2}\beta D_1(t)\sum_{f}V_{1f}G_{f23\cdots(2n)(2n+1)}+\tfrac{1}{4}\beta^2D_2(t)\sum_{fg}V_{1f}V_{1g}[\langle fg23\cdots(2n)(2n+1)\rangle-\langle fg\rangle\langle 23\cdots(2n)(2n+1)\rangle-\{\langle \underline{fg}23\rangle\langle 45\rangle\cdots\langle(2n)(2n+1)\rangle-n\langle \underline{fg}\rangle\langle 23\rangle\langle 45\rangle\cdots\langle(2n)(2n+1)\rangle\}]\,, \tag{A9}$$

for G to $O(1/z^{n+1})$. Concentrating for the present on the term in square brackets in (A9), this part may be rewritten as

$$[\langle fg23\cdots(2n)(2n+1)\rangle+(n-1)\langle fg\rangle\{\langle 23\rangle\cdots\langle(2n)(2n+1)\rangle\}-\{\langle \underline{fg}23\rangle\langle 45\rangle\cdots\langle(2n)(2n+1)\rangle\}]=[\langle fg23\cdots(2n)(2n+1)\rangle-\{\langle fg\rangle\langle 23\rangle\cdots\langle(2n)(2n+1)\rangle\}]\,, \tag{A10}$$

where we have used (A8) and the decoupling scheme (3.1a), which may be shown independently to be correct to lowest order in $1/z$. The expression (A10) is of cumulant form, and from the property iii(a) of the decoupling scheme (3.1a) presented in Sec. III, it follows that this cumulant, and hence the second term in (A9), vanishes to lowest order in $1/z$ [i.e., $O(1/z^{n+1})$].

In order to complete the proof of (A1), we need only examine the first term in (A9), which involves G. For the case of two coincident sites, say "$1=2$," it is easily seen that

$$\begin{aligned} G_{1134\cdots(2n)(2n+1)} &= A_2\langle 34\cdots(2n)(2n+1)\rangle + B_2\langle 134\cdots(2n)(2n+1)\rangle - B_2\{\langle \underline{1}3\rangle\langle 45\rangle\cdots\langle(2n)(2n+1)\rangle\} \\ &\quad - A_2\{\langle 345\rangle\langle 67\rangle\cdots\langle(2n)(2n+1)\rangle\} \\ &\quad + \{\langle \underline{1}34\rangle\langle \underline{1}5\rangle\langle 67\rangle\cdots\langle(2n)(2n+1)\rangle\} + \{\langle 345\rangle\langle \underline{1}6\rangle\langle \underline{1}7\rangle\cdots\langle(2n)(2n+1)\rangle\} \\ &= O(1/z^{n+1}), \end{aligned} \tag{A11}$$

if it may be assumed that (3.1a) and (3.1b) are valid for "$n-1$." It is trivial to see that (3.1b) is valid for $n=1$, and hence, using the general argument of Appendix B in I applied to (A9), it follows by induction on n that

$$G_{123\cdots(2n)(2n+1)} = O(1/z^{n+2}) \tag{A12}$$

for each n, which is the desired result.

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[1] J. M. Cowley, Acta Crystallogr. A 24, 557 (1968).

[2] C. G. Shirley, Phys. Rev. B 10, 1149 (1974).

[3] N. H. March, S. W. Wilkins, and J. E. Tibballs, Cryst. Lattice Defects 6, 253 (1976).

[4] R. A. Medina and J. W. Garland, Phys. Rev. B 14, 5060 (1976).

[5] S. Nasu, H. Yasuaka, Y. Nakamura, and Y. Murakami, Acta Metall. 22, 1057 (1974).

[6] P. C. Clapp, in *Ordered Alloys: Structural Applications and Physical Metallurgy*, edited by B. H. Kear *et al.* (Claitor's, Baton Rouge, La., 1970), pp. 25–35.

[7] P. C. Clapp, J. Phys. Chem. Solids 30, 2589 (1969); Phys. Rev. B 4, 255 (1971).

[8] R. de Ridder, Physica (Utr.) 79A, 217 (1975).

[9] R. J. Elliott, J. A. Krumhansl, and P. L. Leath, Rev. Mod. Phys. 46, 465 (1974). See, in particular, p. 500.

[10] C. G. Shirley and S. W. Wilkins, Phys. Rev. B 6, 1252 (1972).

[11] S. W. Wilkins, Phys. Rev. B 2, 3935 (1970).

[12] Existence of this justification was briefly alluded to in S. W. Wilkins and C. G. Shirley, J. Appl. Crystallogr. 8, 107 (1975).

[13] S. W. Wilkins, Ph.D. thesis (University of Melbourne, 1972) (unpublished).

[14] N. N. Bogolyubov, in *Lectures on Quantum Statistical Mechanics* (Gordon and Breach, New York, 1970), Vol. 2.

[15] J. B. Cohen and J. Gragg, in *Critical Phenomena in Alloys, Magnets and Superconductors*, edited by R. E. Mills *et al.* (McGraw-Hill, New York, 1971).