hence $v_{01}(r)$, is unknown. We have found, in fact, that agreement with the experimental phonon spectrum of copper is improved if the parameter γ in Eq. (37) is increased from 8.43 to 13.4. This corresponds to increasing the magnitude of dv_{01}/dr and has the effect of deepening the first minimum in $v_{eff}(r)$ in Fig. 3. It also moves the calculated binding energy closer to the experimental value and moves the fcc curve in Fig. 8 downward with respect to the hcp curve, although not significantly in either case.

We finally point out that the separation of overlap energy from the band-structure energy here is really an artifact of the overlapping atomic d states. In the general theory given in Paper II, the d states are arbitrary as long as they are orthogonal to the core states. The need to calculate $v_{01}(r)$ could be eliminated by artifically constructing nonoverlapping d states. This is an attractive idea, but it does introduce a whole new series of problems related to the construction of such states. It remains to be seen whether or not such an approach can lead to simplified pseudopotential calculations of the total energy for d-band metals.

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Many-Site Interactions and Correlations in Disordered Binary Alloys

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An approximate method for obtaining the pair and higher-order correlation functions specifying the site-occupancy correlations in disordered substitutional binary alloys of arbitrary composition is described. The method is easily generalized from the usual pairwise interaction model to alloys with multi-site interactions. The value of $1/z$, where z is the number of sites interacting with a given site, is used as a parameter of smallness to obtain a set of quasilinear equations which may be solved numerically for the correlation functions. The long range of the interatomic interactions found in many alloys would make $1/z$ seem a good expansion parameter. The validity of the solution is discussed. We use the method in a numerical analysis to investigate the effect of three-site interactions in a disordered face-centered-cubic binary alloy with a nearest-neighbor pair interaction and a "nearest-neighbor-triangle" triplet interaction. A simple analytic solution for a corresponding idealized mean-field situation is also carried out. An enlightening result is that the mean-field solution and the more realistic computer solution have similar general features. We also compare our solution with others for a choice of parameters in which comparison is possible.

I. INTRODUCTION

The equilibrium arrangement of the atoms in a substitutional binary alloy at a given temperature depends on the part of the Hamiltonian which changes when the atoms of the alloy are rearranged on the crystal lattice, which in this paper is taken to be rigid. The most commonly used model

Hamiltonian is the pairwise one:

$$H(\{\sigma\}) = \tfrac{1}{4}\sum_{ij} V_{ij}\sigma_i\sigma_j \,, \tag{1}$$

where σ_i is an occupation operator which specifies the occupancy of site i:

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

The respective mole fractions of A and B atoms in the alloy are m_A and m_B so that $m_A + m_B = 1$. The pairwise interaction is given by

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

in which, for example, V_{ij}^{AB} is the energy of interaction between an A atom at site i and B atom at site j. See Ref. 1 for a more detailed discussion of the formulation of the pairwise model.

There are, however, contributions to H which are almost certainly present in binary alloys and which cannot be described in terms of the pairwise model. For example, the displacement of atoms from the average lattice sites which is due to the size discrepancy of the two kinds of atoms (size effect) makes the *interatomic* vector connecting two atoms different from the corresponding *intersite* vector by a difference vector which depends on the environment of the sites in question. Consequently, one expects that the mutual potential energy of the two sites depends not only on their occupancy, but also on that of neighboring sites. This is a multi-site effect. It has been shown (see, for example, pp. 50–55 of Ref. 2) that to second order in perturbation theory the effect of the conduction electrons may be represented by a contribution to the pair interaction V_{ij}. Higher orders in perturbation theory contribute to higher-order (three-site, four-site, $\cdots$) interactions. A third example is an alloy in which the component atoms have a tendency to form covalently bonded molecules; these covalent forces are often many body in character. See Clapp[3] for a review of the validity of the central-pairwise-interaction model of an alloy. For simplicity, our attention is confined to disordered binary alloys with Hamiltonian

$$H(\{\sigma\}) = \tfrac{1}{4}\sum_{ij} V_{ij}\sigma_i\sigma_j + \tfrac{1}{6}\sum_{ijk} W_{ijk}\sigma_i\sigma_j\sigma_k \,. \tag{3}$$

The interaction energies may depend on temperature and composition, but not configuration. The extension to interactions of higher order than the third is straightforward but tedious.

A useful formal restriction on many-site interactions is that an interaction is zero if two or more of its subscripts coincide. It is easily shown that, for example, the effect of W_{ijj} can be lumped with V_{ij} and a configuration-independent term, so that W_{ijj} might as well be zero. This often simplifies calculations considerably. We tacitly assume this property of the interactions in the remainder of this paper. Interactions also have permutational and translational symmetry [see properties (ii) and (iii) below].

If one investigates an alloy by an experimental technique which yields information about the atoms on a microscopic scale (such as x-ray, neutron, or electron diffraction), then the relevant parameters with which to characterize the equilibrium configuration of the alloy are the correlation functions. A correlation function is an ensemble average of products of the occupation operators in (2). Notice that $\langle\sigma_i\rangle = 0$ for all i because the composition is $m_A : m_B$. See Ref. 4 for the connection between correlation functions (defined slightly differently in this reference) and experimentally measured x-ray or neutron scattering intensities.

The correlation functions have some important formal properties.

(i) Whenever two or more sites in a correlation function coincide, it may be expressed in terms of lower-order correlations. These expressions are called "reduction relations" and are obtained by application of the identity

$$\sigma_i^n = A_n + B_n\sigma_i \,, \tag{4a}$$

where

$$A_n = 2^n[m_A m_B^n + (-1)^n m_A^n m_B] \,, \tag{4b}$$

$$B_n = 2^{n-1}[m_B^n - (-m_A)^n] \,. \tag{4c}$$

(ii) Correlation functions are invariant under permutation of site indices, e.g., $\langle\sigma_i\sigma_j\sigma_k\rangle = \langle\sigma_i\sigma_k\sigma_j\rangle = \cdots$.

(iii) Correlation functions are invariant under translation by a lattice vector, and one site index may always be chosen as the origin, e.g., $\langle\sigma_i\sigma_j\sigma_k\rangle = \langle\sigma_{i+n}\sigma_{j+n}\sigma_{k+n}\rangle = \langle\sigma_0\sigma_{j-i}\sigma_{k-i}\rangle$.

(iv) When the following replacements are made, $m_A \to m_B$, $V_{0i} \to V_{0i}$, $W_{0ij} \to -W_{0ij}$, then correlations among an even number of sites are invariant, and correlations among an odd number of sites change sign but have the same magnitude, i.e., $\langle\sigma_0\sigma_i\rangle \to \langle\sigma_0\sigma_i\rangle$, $\langle\sigma_0\sigma_j\sigma_i\rangle \to -\langle\sigma_0\sigma_i\sigma_j\rangle$, $\cdots$. This is easily shown by realizing that the replacement $m_A \to m_B$ is equivalent to interchanging the signs in (2). To reobtain the same physical alloy, this sign change must be accompanied by one in W_{ijk}, but not V_{ij} [see Eq. (3)]. Since the physical Hamiltonian is unchanged, we must have exactly the same arrangement of atoms, but each σ is changed in sign so the result follows. In the special case $m_A = m_B$ and $W_{ijk} = 0$, this shows that all odd-order correlations vanish, a result first shown by Clapp.[5]

So far most studies of short-range order in disordered binary alloys have concentrated on the theoretical[1,6–8] and experimental[9] determination of pair correlation functions. However, the work of Cowley[4] and Cowley and Murray[10] as well as the field-ion-microscopy experiments of Gold and Machlin[11] seem to indicate that it is possible to experimentally detect the effects of higher-order correlations. For this reason it appears that the inclusion of higher-order correlations into the description of an alloy should be investigated. We shall use only pair, triplet, and quadruplet correlations, because the inclusion of higher-order correlations is a straightforward extension.

The theoretical problem with which we deal in this paper is the statistical mechanical evaluation of the various correlation functions, given the Hamiltonian (3). We are to evaluate the ensemble average of functions of configuration, $F(\{\sigma\})$. In the present application F is always a product of occupation operators. The ensemble average of F is defined as

$$\langle F\rangle = \sum_{\{\sigma\}} F(\{\sigma\})\rho(\{\sigma\}) \Big/ \sum_{\{\sigma\}}\rho(\{\sigma\}) \ . \tag{5}$$

The average is taken over a grand canonical ensemble in which we admit fluctuations in composition. This means that we can write ($N \equiv$ number of sites in the crystal)

$$\sum_{\{\sigma\}} = \sum_{\sigma_1=\pm}\ \sum_{\sigma_2=\pm} \cdots \sum_{\sigma_N=\pm} \ ,$$

where each summation over the two possible values of each occupation operator is done independently. The constraint on composition is obtained by determining the chemical potential λ in the grand canonical density operator

$$\rho(\{\sigma\}) = e^{-\beta H(\{\sigma\})+\lambda\Sigma_i\sigma_i} \tag{6}$$

by the condition $\langle\sigma_i\rangle = 0$. $\beta = 1/kT$, where k is the Boltzmann constant and T is the absolute temperature. An exact solution to the problem in hand would involve an evaluation of the sums in (5) in the thermodynamic limit ($N \to \infty$). This is a problem of the first magnitude even for a pairwise Hamiltonian since it is equivalent to the unsolved Ising theory of a three-dimensional ferromagnet in an external magnetic field.[12] Although there is no exact solution to the three-dimensional pairwise alloy, there are quite a number of approximate solutions,[1,6–8,13] the most important of which, from our point of view, are due to Clapp and Moss[1] and Tahir-Kheli.[8] All of these solutions have been for pairwise interactions and correlations, although Tahir-Kheli's method yields the high-temperature expansions of higher-order correlations as a by-product.[14] We show that Tahir-Kheli's work is quite easily extended to higher-order interactions. The work of Tahir-Kheli and the present paper are related. The essential difference is that in the former, β is used as a parameter of smallness, whereas in the latter $1/z$ is used. z is the number of sites interacting with a given site. This follows the spirit of Brout's work.[15,16] The characteristically long-range nature of the interactions in many alloys, principally due to the conduction-electron contribution to the configurational Hamiltonian[17–19] would make $1/z$ seem an excellent expansion parameter for alloys. The complication which arises in the case where an oscillatory interaction is present is discussed in Sec. IV.

II. SYSTEM OF EQUATIONS FOR THE CORRELATION FUNCTIONS

An infinite set of equations which may be solved for the correlation functions is obtained by what is, in essence, an expansion of (5) in powers of β, in which F is successively put equal to σ_o, $\sigma_o\sigma_i$, and so on. To facilitate this we first prove a theorem which is a simple generalization of that in the Appendix of Ref. 1.

We define the following average of $G(\{\sigma\})$:

$$\langle G\rangle_i \equiv \sum_{\sigma_i=\pm} G\rho \Big/ \sum_{\sigma_i=\pm}\rho \ .$$

The summation is only over the possible values of σ_i so that $\langle G\rangle_i$ depends on all σ's except σ_i. The theorem is that for two functions of configuration, $F(\{\sigma\})$ and $G(\{\sigma\})$,

$$\langle FG\rangle \equiv \langle F\langle G\rangle_i\rangle \ , \tag{7}$$

provided F does not have σ_i as one of its arguments. The proof is as follows: Using the definition (5) we have

$$\langle F\langle G\rangle_i\rangle \sum_{\{\sigma\}}\rho = \sum_{\{\sigma\}}{}' \sum_{\sigma_i=\pm} F\langle G\rangle_i\rho \ ,$$

where the prime indicates omission of the sum over σ_i, i.e.,

$$\sum_{\{\sigma\}} = \sum_{\{\sigma\}}{}' \sum_{\sigma_i=\pm} \ .$$

Since neither F nor $\langle G\rangle_i$ depend on σ_i, we may write the right-hand side as

$$\begin{aligned}\sum_{\{\sigma\}}{}' F\langle G\rangle_i \sum_{\sigma_i=\pm}\rho &= \sum_{\{\sigma\}}{}' F\Big(\sum_{\sigma_i=\pm} G\rho \Big/ \sum_{\sigma_i=\pm}\rho\Big)\sum_{\sigma_i=\pm}\rho \\ &= \sum_{\{\sigma\}}{}' F \sum_{\sigma_i=\pm} G\rho = \sum_{\{\sigma\}} FG\rho = \langle FG\rangle \sum_{\{\sigma\}}\rho \ .\end{aligned}$$

For our particular purpose we consider a special case of (7), namely $G = \sigma_o$ and $i = o$. First we need $\langle\sigma_o\rangle_o$. From the definition of $\langle G\rangle_i$ and (6) we have

$$\begin{aligned}\langle\sigma_o\rangle_o &= \sum_{\sigma_o=\pm}\sigma_o e^{-\beta H+\lambda\Sigma_i\sigma_i} \Big/ \sum_{\sigma_o=\pm} e^{-\beta H+\lambda\Sigma_i\sigma_i} \\ &= \sum_{\sigma_o=\pm}\sigma_o \exp\Big[-\tfrac{1}{2}\beta\Big(\sum_f V_{of}\sigma_f + \sum_{jk} W_{ojk}\sigma_j\sigma_k\Big)\sigma_o\end{aligned}$$

$$+\lambda\sigma_o]/\sum_{\sigma_o=\pm} e^{(\cdots)}$$

in which all parts not containing the operator σ_o have been cancelled from numerator and denominator. Evaluating the sums, one finds

$$\langle\sigma_o\rangle_o=\tanh(\beta E_o+\lambda)+(m_B-m_A)\ ,$$

where

$$E_o=-\tfrac{1}{2}\sum_f V_{of}\sigma_f-\tfrac{1}{2}\sum_{fg} W_{ofg}\sigma_f\sigma_g\ . \tag{8}$$

E_o is the effective field which an atom at a given site sees due to the configuration of the neighboring atoms. The special case of (7) is therefore written

$$\langle\sigma_o F\rangle=\langle[\tanh(\beta E_o+\lambda)+(m_B-m_A)]F\rangle\ , \tag{9}$$

where F does not depend on σ_o. This is an identity.

To find the required set of equations, (9) is expanded in powers of βE_o and F is set successively to 1, σ_i, $\sigma_i\sigma_j$, $\cdots$. Therefore, the set of equations is

$$\langle\sigma_o\rangle=\sum_{n=0}^{\infty} D_n\langle(\beta E_o)^n\rangle\ , \tag{10a}$$

$$\langle\sigma_o\sigma_i\rangle=\sum_{n=0}^{\infty} D_n\langle(\beta E_o)^n\sigma_i\rangle \qquad (i\neq o), \tag{10b}$$

$$\langle\sigma_o\sigma_i\sigma_j\rangle=\sum_{n=0}^{\infty} D_n\langle(\beta E_o)^n\sigma_i\sigma_j\rangle \quad (o\neq i\neq j\neq o), \tag{10c}$$

etc., in which

$$D_0=\tanh\lambda-(m_A-m_B)\ , \tag{11a}$$

$$D_1=\left.\frac{\partial\tanh(X+\lambda)}{\partial X}\right|_{X=0}=1-\tanh^2\lambda\ , \tag{11b}$$

$$D_2=\frac{1}{2}\left.\frac{\partial^2[\tanh(X+\lambda)]}{\partial X^2}\right|_{X=0}=\tanh^3\lambda-\tanh\lambda\ , \tag{11c}$$

$$D_3=\tfrac{1}{3}(-3\tanh^4\lambda+4\tanh^2\lambda-1)\ , \tag{11d}$$

etc. An infinite set of equations in terms of the correlation functions and the various interaction energies is obtained when (8) is substituted into (10) and the arbitrary subscripts on the left-hand sides of (10) are allowed to range over all permitted sites. The set of equations is linear in the correlation functions. The procedure is to find the solution for $\langle\sigma_o\rangle$, $\{\langle\sigma_o\sigma_i\rangle\}$, $\{\langle\sigma_o\sigma_i\sigma_j\rangle\}$, etc., as functions of the two parameters, $\tanh\lambda$ and β. For a given β, the solution which has the value of $\tanh\lambda$ such that $\langle\sigma_o\rangle=0$ is the required one.

In effect, Tahir-Kheli[8] has used the set of equations, with the E_o appropriate to pairwise interactions only, for generating high-temperature expansions for correlation functions. The extension of Tahir-Kheli's method to higher-order interactions is simply a matter of modifying E_o [see Eq. (4.6) in Ref. 8] appropriately and carrying the analysis through.[14] Although it is not central to the present paper, we have used Tahir-Kheli's method and present the results to $O(\beta^2)$:

$$\begin{aligned}\langle\sigma_o\sigma_i\rangle=&-8m_A^2m_B^2V_{oi}\beta+\Big[16m_A^3m_B^3\sum_f V_{of}V_{fi}+64m_A^3m_B^3(m_B-m_A)\sum_f(V_{of}+V_{if})W_{oif}+8m_A^2m_B^2(m_B-m_A)^2V_{oi}^2\\&+128m_A^4m_B^4\sum_{fg}W_{ofg}W_{ifg}+128m_A^3m_B^3(m_B-m_A)^2\sum_f W_{ofi}^2\Big]\beta^2+O(\beta^3)\qquad(i\neq o)\ ,\end{aligned} \tag{12}$$

$$\begin{aligned}\langle\sigma_o\sigma_i\sigma_j\rangle=&-64m_A^3m_B^3W_{oij}\beta+\Big[32m_A^3m_B^3(m_B-m_A)(V_{oi}V_{oj}+V_{oi}V_{ij}+V_{oj}V_{ij})+128m_A^3m_B^3(m_B-m_A)^2\\&\times(V_{ij}+V_{oi}+V_{oj})W_{oij}+128m_A^4m_B^4\sum_f(V_{of}W_{ijf}+V_{jf}W_{oif}+V_{if}W_{ojf})+256m_A^3m_B^3(m_B-m_A)^3W_{oij}^2\\&+512m_A^4m_B^4(m_B-m_A)\textstyle\sum_f(W_{oif}W_{ijf}+W_{ojf}W_{ijf}+W_{oif}W_{ojf})\Big]\beta^2+O(\beta)^3\qquad(o\neq i\neq j\neq o)\ ,\end{aligned} \tag{13}$$

$$\begin{aligned}\langle\sigma_o\sigma_i\sigma_j\sigma_k\rangle=&\Big[64m_A^4m_B^4(V_{oi}V_{jk}+V_{oj}V_{ik}+V_{ok}V_{ij})+256(m_B-m_A)m_A^4m_B^4(V_{oi}W_{ijk}+V_{oj}W_{ijk}+V_{ok}W_{ijk}\\&+V_{ik}W_{oij}+V_{jk}W_{oij}+V_{ij}W_{ojk}+V_{ik}W_{ojk}+V_{jk}W_{oik}+V_{ij}W_{oik}+V_{oi}W_{ojk}+V_{oj}W_{oik}+V_{ok}W_{oij})\\&+1024m_A^4m_B^4(m_B-m_A)^2(W_{oij}W_{ijk}+W_{oik}W_{ijk}+W_{ojk}W_{ijk}+W_{oij}W_{oik}+W_{oij}W_{ojk}+W_{ojk}W_{oik})\\&+1024m_A^5m_B^5\textstyle\sum_f(W_{oif}W_{jkf}+W_{ojf}W_{ikf}+W_{okf}W_{ijf})\Big]\beta^2+O(\beta^3)\qquad\text{(no coincidences)}\ .\end{aligned} \tag{14}$$

Our use of the set of equations differs from that of Tahir-Kheli in that we use several criteria [including the $O(1/z)$ criterion] to truncate the system of equations. This truncated set of equations is then solved self-consistently. This procedure has the advantage that, apart from the complications to be discussed in Sec. IV, it yields solutions good to a chosen order in $1/z$ for all $T\geq T_c$, where T_c is the characteristic disordering temperature. Apart from this, the $O(1/z)$ classification scheme seems a natural and potentially useful way to classify correlation functions in disordered alloys.

III. TRUNCATION OF THE SYSTEM OF EQUATIONS

Consider a clustering alloy (i.e., V_{ij}, $W_{ijk} < 0$ for $m_A < m_B$ and all noncoincident i, j, k) in which z sites interact with a given site through the energy term V_{ij}, and z' through W_{ijk}. When we remember the physical interpretation of (8), we see that the average configuration energy of a site is given by

$$-\langle \sigma_o E_o \rangle = \tfrac{1}{2} \textstyle\sum_f V_{of} \langle \sigma_o \sigma_f \rangle + \tfrac{1}{2} \textstyle\sum_{fg} W_{ofg} \langle \sigma_o \sigma_f \sigma_g \rangle .$$

For a clustering alloy, T_c occurs when the thermal energy per site is comparable with the minimum-possible configuration energy per site. Thus, we have

$$\begin{aligned} kT_c &\simeq \left| (-\langle \sigma_o E_o \rangle)_{\min} \right| \\ &= \tfrac{1}{2} \textstyle\sum_f |V_{of}| \langle \sigma_o^2 \rangle + \tfrac{1}{2} \textstyle\sum_{fg} |W_{ofg}| \langle \sigma_o^3 \rangle \\ &= 2 m_A m_B z \mathcal{V} + 4 m_A m_B (m_B - m_A) z'^2 \mathcal{W} , \qquad (15) \end{aligned}$$

where we have defined the average potentials by

$$\mathcal{V} = z^{-1} \textstyle\sum_f |V_{of}| \quad \text{and} \quad \mathcal{W} = (z')^{-2} \textstyle\sum_{fg} |W_{ofg}| .$$

This definition will also hold for potentials which may oscillate in sign. Physically, it seems unlikely that $\mathcal{W}$ will have much more than comparable strength with $\mathcal{V}$ (comparable when $z'^2 \mathcal{W} = z \mathcal{V}$). Given this, the upper and lower bounds on $\frac{1}{2} \beta \mathcal{V}$ for $0 < \mathcal{W} < \mathcal{V}/z$ are of the same order, and we may write conservatively,

$$\tfrac{1}{2} \beta \mathcal{V} \simeq \frac{\beta}{\beta_c} O\left(\frac{1}{4 m_A m_B z} \right) , \qquad (16a)$$

$$\tfrac{1}{2} \beta \mathcal{W} \lesssim \frac{\beta}{\beta_c} O\left(\frac{1}{4 m_A m_B z^2} \right) , \qquad (16b)$$

where we have replaced z and z' by the smaller of the two and relabeled it z. Notice that for very dilute alloys (16) will lead to failure of the scheme to be derived below, but this is not a severe restriction. With the understanding that we are not dealing with very dilute alloys we may leave out the composition-dependent parts of (16) when using them below.

The correlation functions may be classified according to powers of $1/z$. To see this, use (16) in (12) and note that each summation contributes a factor of z. We get, for $j \neq o$, but $|\vec{r}_{oj}|$ less than the interaction range:

$$\begin{aligned} \langle \sigma_o \sigma_j \rangle = 4 m_A m_B O(1/z) \Big(\beta/\beta_c + \{ O(1) + [8(m_B - m_A) + 8 m_A m_B + (m_B - m_A)^2 / 2 m_A m_B] O(1/z) \\ + 8 (m_B - m_A)^2 O(1/z^2) \} (\beta/\beta_c)^2 + \{ O(1) + \cdots \} (\beta/\beta_c)^3 + \cdots \Big) . \end{aligned}$$

The series in the large parenthesis is expected to have finite sum of order unity at $\beta \simeq \beta_c$ (cf. the exact curve labeled FS in Fig. 6). At $\beta = \beta_c$ we may therefore write $\langle \sigma_o \sigma_j \rangle = 4 m_A m_B O(1/z)$ for $j \neq o$ and $|\vec{r}_{oj}|$ within the interaction range. Naturally $\langle \sigma_o \sigma_j \rangle$ can be less than this depending on temperature and intersite separation, but the right-hand side is a conservative upper bound for $\langle \sigma_o \sigma_j \rangle$ in the ranges $\beta \lesssim \beta_c$ and $|\vec{r}_{oj}| < \infty$. Similarly, from Eqs. (13) and (14) we expect that at $\beta = \beta_c$, $\langle \sigma_o \sigma_i \sigma_j \rangle = O(1/z^2)$, and $\langle \sigma_o \sigma_i \sigma_j \sigma_k \rangle = O(1/z^2)$. Given these classifications and the fact that correlation functions decouple when groups of sites are moved to infinity, it is possible to find the classification of higher-order correlations. For example, $\langle \sigma\sigma\sigma\sigma\sigma\sigma \rangle - \langle \sigma\sigma \rangle \langle \sigma\sigma \rangle \langle \sigma\sigma \rangle = O(1/z^3)$. We always choose the decoupling which gives the lowest order in $1/z$. A likely classification scheme at $\beta = \beta_c$ can, therefore, be seen to be

$$\langle \sigma_i \cdots \sigma_{i+r} \rangle = O(z^{-v}) , \qquad (17)$$

where

$$v = \tfrac{1}{2} [r + 1 + \phi(r+1)]$$

and

$$\phi(x) = 1 \quad (x \text{ odd})$$
$$\quad\;\; = 0 \quad (x \text{ even}) .$$

The right-hand side of (17) may be interpreted as an upper bound on all possible $(r+1)$th-order correlation functions in the range $\beta \lesssim \beta_c$. In Appendix A we show the consistency of this scheme. It is probably also optimal. It should be noted that this classification depends on the property of the σ operators that $\langle \sigma \rangle = 0$.

We can now meaningfully truncate the infinite set of equations (10) and choose the correlation functions with which to characterize the alloy. The criteria are the following.

a. The order of the solution in $1/z$. In Appendix A it is shown that an upper bound to the leading order in $1/z$ of terms arising from Eqs. (10) when (8) is substituted is given, at β_c, by

$$\left| \left(-\frac{\beta_c}{2} \right)^{m+n} D_{m+n} \sum_{\{f,g,h\}} \prod_{p=1}^{n} V_{of(p)} \prod_{q=1}^{m} W_{og(q)h(q)} \left\langle \prod_{p=1}^{n} \sigma_{f(p)} \prod_{q=1}^{m} \sigma_{g(q)} \sigma_{h(q)} \prod_{s=1}^{r} \sigma_{i(s)} \right\rangle \right| \leqslant O(z^{-w}) , \qquad (18)$$

where each site index is summed over the whole lattice and where

$$w = \tfrac{1}{2}[r + n + 2m + \phi(r + n + 2m)] \ .$$

For $n + 2m \lesssim 2z$ the equality in (18) holds. The inequality (18) may be regarded as an upper bound in the range $\beta \lesssim \beta_c$ for terms arising from Eqs. (10). Notice from Eq. (10a) with $\langle\sigma\rangle = 0$ that $D_0 = O(1/z)$ so that the order in $1/z$ of the D_0 terms $(n + m = 0)$ is greater by one than given by (18) with $n + 2m = 0$. If we use (18) to write out Eqs. (10) with all terms which can be at most $O(1/z^3)$ in the range $\beta \lesssim \beta_c$ discarded, we obtain

$$\begin{aligned}\langle\sigma_o\rangle = D_0 &- \tfrac{1}{2}\beta D_1\Big(\sum_f V_{of}\langle\sigma_f\rangle + \sum_{fg} W_{ofg}\langle\sigma_f\sigma_g\rangle\Big) + \tfrac{1}{4}\beta^2 D_2\Big(\sum_{fg} V_{of}V_{og}\langle\sigma_f\sigma_g\rangle + 2\sum_{fgh} V_{of}W_{ogh}\langle\sigma_f\sigma_g\sigma_h\rangle \\ &+ \sum_{fghl} W_{ofg}W_{ohl}\langle\sigma_f\sigma_g\sigma_h\sigma_l\rangle\Big) - \tfrac{1}{8}\beta^3 D_3\Big(\sum_{fgh} V_{of}V_{og}V_{oh}\langle\sigma_f\sigma_g\sigma_h\rangle + 3\sum_{fghl} V_{of}V_{og}W_{ohl}\langle\sigma_f\sigma_g\sigma_h\sigma_l\rangle\Big) \\ &+ \tfrac{1}{16}\beta^4 D_4 \sum_{fghl} V_{of}V_{og}V_{oh}V_{ol}\langle\sigma_f\sigma_g\sigma_h\sigma_l\rangle \ , \qquad \text{(19a)}\end{aligned}$$

$$\begin{aligned}\langle\sigma_o\sigma_i\rangle = D_0\langle\sigma_i\rangle &- \tfrac{1}{2}\beta D_1\Big(\sum_f V_{of}\langle\sigma_f\sigma_i\rangle + \sum_{fg} W_{ofg}\langle\sigma_f\sigma_g\sigma_i\rangle\Big) + \tfrac{1}{4}\beta^2 D_2\Big(\sum_{fg} V_{of}V_{og}\langle\sigma_f\sigma_g\sigma_i\rangle + 2\sum_{fgh} V_{of}W_{ogh}\langle\sigma_f\sigma_g\sigma_h\sigma_i\rangle\Big) \\ &- \tfrac{1}{8}\beta^3 D_3 \sum_{fgh} V_{of}V_{og}V_{oh}\langle\sigma_f\sigma_g\sigma_h\sigma_i\rangle \ , \quad i \neq o \qquad \text{(19b)}\end{aligned}$$

$$\langle\sigma_o\sigma_i\sigma_j\rangle = D_0\langle\sigma_i\sigma_j\rangle - \tfrac{1}{2}\beta D_1\Big(\sum_f V_{of}\langle\sigma_f\sigma_i\sigma_j\rangle + \sum_{fg} W_{ofg}\langle\sigma_f\sigma_g\sigma_i\sigma_j\rangle\Big) + \tfrac{1}{4}\beta^2 D_2 \sum_{fg} V_{of}V_{og}\langle\sigma_f\sigma_g\sigma_i\sigma_j\rangle \ , \quad o \neq i \neq j \neq o \qquad \text{(19c)}$$

$$\langle\sigma_o\sigma_i\sigma_j\sigma_k\rangle = -\tfrac{1}{2}\beta D_1 \sum_f V_{of}\langle\sigma_f\sigma_i\sigma_j\sigma_k\rangle \ , \quad o,\ i,\ j,\ k \text{ noncoincident} \ . \qquad \text{(19d)}$$

When i, j, k are allowed to range over the entire lattice we see that we have an infinite dimensional set of linear equations to solve for the correlation functions of up to the fourth order. A very considerable simplification of this set of equations is obtained by use of the relation

$$\begin{aligned}\langle\sigma_o\sigma_i\sigma_j\sigma_k\rangle = \langle\sigma_o\sigma_i\rangle\langle\sigma_j\sigma_k\rangle &+ \langle\sigma_o\sigma_j\rangle\langle\sigma_i\sigma_k\rangle \\ &+ \langle\sigma_o\sigma_k\rangle\langle\sigma_i\sigma_j\rangle + O(1/z^3) \ , \qquad (20)\end{aligned}$$

which holds at β_c. This is proved in Appendix B. Thus, pair and triplet correlation functions completely characterize the system to $O(1/z^2)$ because we can substitute (20) for quadruplet correlation functions whenever they occur in (19). This makes the equations nonlinear, but convergence is rapid because $\langle\sigma\sigma\rangle$ is only needed to $O(1/z)$ in (20), but to $O(1/z)$ pair correlations do not depend on quadruplet correlations.

b. Spatial truncation. To make the set (19) finite, a spatial truncation is needed so that only a finite number of correlation functions of each order appears in the system of equations. For the $O(1/z^2)$ truncation the "boundary conditions" are simple because all pair and triplet correlation functions with one or more intersite vectors exceeding a certain length are assigned the value zero. For example, as site k moves away from sites i and j, $\langle\sigma_i\sigma_j\sigma_k\rangle \to \langle\sigma_i\sigma_j\rangle\langle\sigma_k\rangle = 0$. For higher-order truncations the boundary conditions are less simple because, for example, a possibility is that $\langle\sigma_i\sigma_j\sigma_k\sigma_l\rangle \to \langle\sigma_i\sigma_j\rangle\langle\sigma_k\sigma_l\rangle$ as sites k, l together move away from i, j. Spatial truncation effects are expected to be greatest near T_c, since the correlation range is longer there.

c. Symmetry. The number of order parameters which one needs can be considerably reduced by taking symmetries into account. For example, when the pair interaction between any two sites is the same, then we expect all pair correlation functions except the self-correlation $\langle\sigma_o^2\rangle$ to have the same value (mean-field case). When the pairwise interaction in a pairwise model is isotropic then each shell of sites has a distinct correlation function. In general correlation functions with "scaffoldings" of intersite vectors related by the point operations of the lattice are symmetrically equivalent. Correlation functions are also symmetric under permutation of site indices, which means that in the $(N-1)(N-2)$ equations (19c) each order parameter occurs on the left-hand side six times. The three distinct occurrences may be combined to give one permutationally symmetric equation for each correlation function:

$$\begin{aligned}\langle\sigma_o\sigma_i\sigma_j\rangle = \tfrac{1}{3}D_0(\langle\sigma_i\sigma_j\rangle + \langle\sigma_o\sigma_i\rangle + \langle\sigma_o\sigma_j\rangle) &- \tfrac{1}{6}\beta D_1\Big\{\textstyle\sum_f V_{of}\big[\langle\sigma_f\sigma_i\sigma_j\rangle + \langle\sigma_f\sigma_{-i}\sigma_{j-i}\rangle + \langle\sigma_f\sigma_{-j}\sigma_{i-j}\rangle\big] \\ &+ \textstyle\sum_{fg} W_{ofg}\big[\langle\sigma_f\sigma_g\sigma_i\sigma_j\rangle + \langle\sigma_f\sigma_g\sigma_{-i}\sigma_{j-i}\rangle + \langle\sigma_f\sigma_g\sigma_{-j}\sigma_{i-j}\rangle\big]\Big\}\end{aligned}$$

$$+\tfrac{1}{12}\beta^2 D_2 \textstyle\sum_{fg} V_{of}V_{og}\left[\langle\sigma_f\sigma_g\sigma_i\sigma_j\rangle+\langle\sigma_f\sigma_g\sigma_{-i}\sigma_{j-i}\rangle+\langle\sigma_f\sigma_g\sigma_{-j}\sigma_{i-j}\rangle\right], \quad o\neq i\neq j\neq o\ . \tag{19c$'$}$$

Note that Eqs. (19a), (19b), and (20) are already permutationally symmetric. Solution of permutationally symmetric equations will automatically yield solutions with the correct permutational symmetry.

IV. VALIDITY OF THE SOLUTION

The derivation of Eqs. (19) assumed that all interactions favor clustering (i.e., V_{oi}, $W_{oij}\leq 0$ for all i, j and $m_A<m_B$). Since alloys do not in general satisfy this restriction, it is necessary to examine the domain of validity of Eqs. (19) for general interactions. We shall also consider the so-called "excluded-volume" effects which make our classification scheme fail near T_c.

To discuss general interactions, we introduce the notion of a conjugate alloy. The alloy conjugate to a given alloy has every pair interaction replaced by the negative of its absolute value (for all m_A), and every three-site interaction changed to the negative of its absolute value if $m_A<m_B$ or to the positive if $m_A>m_B$. The conjugate alloy has every interaction favoring clustering, so that it may be discussed in the manner of Sec. III. If the conjugate alloy has critical temperature T_c' then (16) gives $\frac{1}{2}\beta\mathcal{V}\simeq(\beta/\beta_c')O(1/z)$ and $\frac{1}{2}\beta\mathcal{W}\leq(\beta/\beta_c')O(1/z^2)$. If T_c is the critical temperature of the original alloy, then $T_c'\geq T_c$. This is easily shown for the $O(1/z)$ truncation (see below) in which $kT_c=2m_Am_B\times|V(\vec{k}_m)|$, where $V(\vec{k}_m)$ is the absolute minimum of the function

$$V(\vec{k})=\textstyle\sum_f V_{of}\,e^{2\pi i\vec{k}\cdot\vec{r}_{of}}\ .$$

Clearly

$$kT_c'=2m_Am_B\textstyle\sum_f|V_{of}| \quad\text{and}\quad |V(\vec{k}_m)|\leq\textstyle\sum_f|V_{of}|$$

so that the required inequality holds. For $\beta\leq\beta_c'$ terms of high order in $1/z$ cannot be greater in absolute magnitude than those of low order, but for $\beta_c'<\beta<\beta_c$ we have $\beta/\beta_c'>1$ so that the order of a term in β becomes of importance. Thus, in the range $\beta_c'<\beta<\beta_c$ the $1/z$ classification is no longer a criterion of smallness and we cannot gauge the validity of the solution.

In the region of T_c' terms of higher order in $1/z$ than have been explicitly displayed in Eqs. (19) begin to have appreciable effect. This corresponds to the excluded-volume effect discussed by Brout.[15] If we write down the $O(1/z)$ truncation of (19) we obtain the original Clapp-Moss[1] equation

$$\langle\sigma_o\sigma_i\rangle=-2m_Am_B\beta\textstyle\sum_f V_{of}\langle\sigma_f\sigma_i\rangle+C\delta_{oi} \tag{21}$$

to solve. The term $C\delta_{oi}$ removes the $i=o$ restriction. Solving by Fourier transformation we get

$$S(\vec{k})=C[1+2m_Am_B\beta V(\vec{k})]^{-1}\ , \tag{22}$$

where

$$C^{-1}=(4m_Am_B)^{-1}v_k^{-1}\int d^3\vec{k}\,[1+2m_Am_B\beta V(\vec{k})]^{-1}\ ,$$

in which the integration is over a Brillouin zone of volume v_k and where

$$S(\vec{k})=\textstyle\sum_f\langle\sigma_o\sigma_f\rangle\,e^{2\pi i\vec{k}\cdot\vec{r}_{of}}\ .$$

It would seem that this is the complete $O(1/z)$ solution but the cumulative effect of higher-order terms in (19b) makes a significant modification in the region of T_c'. Brout[15] shows that for the complete $O(1/z)$ solution (at least for $m_A=\frac{1}{2}$) (22) is modified to

$$S(\vec{k})=4m_Am_B[\chi+2m_Am_B\beta V(\vec{k})]^{-1}\ , \tag{23}$$

where χ is determined by

$$1=v_k^{-1}\int d^3\vec{k}\,[\chi+2m_Am_B\beta V(\vec{k})]^{-1}\ .$$

This is known as the spherical-model result.[20]

We have attempted to incorporate some of the excluded-volume effects by including terms which arise by the application of the reduction relations to higher-order terms in (19b). Of these higher-order terms we have taken all terms which are of $O(\beta^6)$ or less in the case $W=0$, so that a term like

$$\tfrac{1}{4}\beta^4 D_4\Big(4B_4V_{oi}^3\sum_{f\neq i}V_{of}\langle\sigma_i\sigma_f\rangle\Big)\ ,$$

which occurs in

$$\tfrac{1}{16}\beta^4 D_4\sum_{efgh}V_{oe}V_{of}V_{og}V_{oh}\langle\sigma_i\sigma_e\sigma_f\sigma_g\sigma_h\rangle$$

is classified $O(\beta^5)$ and is included in our solution. These extra terms begin to matter for $\beta\gtrsim\beta_c'$.

It seems that, apart from spatial truncation effects, our solution is good to the desired order in z^{-1} down to about β_c'. The failure of the $O(1/z)$ criterion for $\beta_c'<\beta<\beta_c$ and the excluded-volume effects are shortcomings of our approach which deserve closer study.[21] The former is especially so because many alloys seem to have long-range oscillating pair interactions.

V. SOLUTION OF THE SYSTEM OF EQUATIONS

To solve the set of equations (19a)–(19c) with the relation (20) and the extra terms mentioned in Sec. IV it is necessary to use symmetries to pick out distinct correlation functions, and to employ spatial truncation to make the set finite. We denote the mth-distinct nth-order correlation function by $\Gamma^n(m)$. It is also necessary to explicitly decompose correlation functions with coincident sites in the various summations by using the reduction relations.

In the computer program described below for a fcc binary alloy we used a spatial truncation in which pair and triplet correlation functions with one or more intersite vectors exceeding the tenth-neighbor distance were discarded. Thus, there were ten distinct pair correlations and 74 distinct triplet correlations included, so that an 85× 85 set of equations was solved. The $n=1$ correlation $\Gamma^1 = \langle\sigma_i\rangle$ was also included.

In the numerical solution of the truncated system of equations it is necessary to constrain Γ^1 to vanish. This is the composition constraint. At a given temperature one chooses a starting value for $\tanh\lambda$, obtained in general from two previous solutions at slightly higher temperatures. This defines all the D_n, so that Eqs. (19a)–(19c) may be solved by the standard technique, modified to account for the small amount of nonlinearity introduced by (20). This gives a value for Γ^1 which may be used in a *regula falsi* procedure to give a better estimate for $\tanh\lambda$. The new value of $\tanh\lambda$ is used in another solution of the set of equations, and the cycle is repeated until $\Gamma^1=0$ to within required limits. The values for the correlation functions corresponding to $\Gamma^1=0$ are the required solution at the given temperature. The procedure is carried out at successive closely spaced temperatures starting from $\beta=0$ (where $\tanh\lambda = m_A - m_B$), and continuing until the determinant of the 85×85 matrix (without the nonlinear part) vanishes or the solution becomes uninteresting.

The techniques of this paper are even more easily applied to the Ising ferromagnet problem than to the alloy problem because the magnetization (analogous to Γ^1) is determined by the applied magnetic field (related to λ) rather than *vice versa* as for an alloy.

In Figs. 1–4 we have plotted the nearest-neighbor pair correlation $\Gamma^2(1)$ and the "equilateral-nearest-neighbor-triangle" triplet correlation $\Gamma^3(1)$ as a function of β for several choices of input parameters (V, W, m_A) in a fcc alloy with nearest-neighbor pair interactions of strength $V=\pm 1$ and equilateral-nearest-neighbor-triangle triplet interactions of strength W. When $W=0.1$, it has an effect comparable with that of V. On each of the graphs we indicate β_c' given by (15) with $W=0$. Nonvanishing W makes little difference to β_c' for the values of W considered. This value of β_c is also the value predicted by the Clapp-Moss equation (22) for a clustering alloy. The lower temperature limit for validity of our solution is about T_c'. On the graphs, a dot indicates termination of the solution due to a vanishing determinant, and an arrowhead indicates that the solution continues.

Some of the major features of the above solution may be interpreted in terms of a relatively simple analytical "mean-field" solution. The mean-field alloy has $V_{oi} \equiv \mathcal{V}$, $W_{oij} \equiv \mathcal{W}$ for all i, j except coincident sites.

The Hamiltonian is

$$H = \tfrac{1}{4}\mathcal{V}\sum_{ij}{}' \sigma_i\sigma_j + \tfrac{1}{6}\mathcal{W}\sum_{ijk}{}'\sigma_i\sigma_j\sigma_k ,$$

where the primes indicate omission of terms for which sites coincide. Let us define

$$w = N^2\mathcal{W} \text{ and } v = N\mathcal{V} .$$

By symmetry, the characteristic order parameters are

$$\langle\sigma_i\rangle \equiv \Gamma^1 \equiv \gamma^1 ,$$
$$\langle\sigma_o\sigma_i\rangle \equiv \Gamma^2 \equiv \gamma^2/N \text{ for } i \neq o ,$$
$$\langle\sigma_o\sigma_i\sigma_j\rangle \equiv \Gamma^3 \equiv \gamma^3/N^2 \text{ for } o \neq i \neq j \neq o,$$
$$\langle\sigma_o\sigma_i\sigma_j\sigma_k\rangle \equiv \Gamma^4 \equiv \gamma^4/N^2 \text{ no coincidences, etc.}$$

Thus, $\gamma^n = O(1)$ and all correlation functions of a given order are symmetrically equivalent. For an $O(1/N^2)$ truncation this symmetry reduces Eqs. (19) to 4×4 and obviates spatial truncation. It is easy, but messy, to write out Eqs. (19) for this mean-field case, but to simplify things we shall truncate each equation in (19) to *leading* order in $1/N$, rather than to $O(1/N^2)$. In Eq. (19a) we truncate to $O(1/N)$, not $O(1)$, because the condition $\gamma^1=0$ makes the $O(1)$ parts vanish.

The set of equations (19) may be written

$$\underline{G}\gamma = \delta ,$$

where the elements of the matrix $\underline{G}$ are

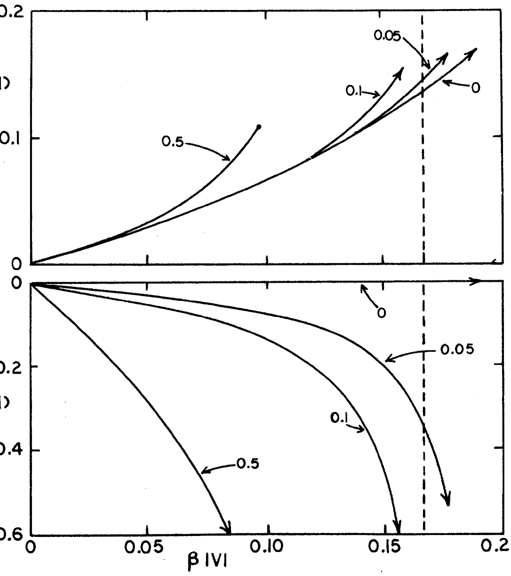

FIG. 1. Plots of $\Gamma^2(1)$ and $\Gamma^3(1)$ for $V=-1$, $m_A=\frac{1}{2}$, and various values of W. $\beta_c' = 0.167$ is marked.

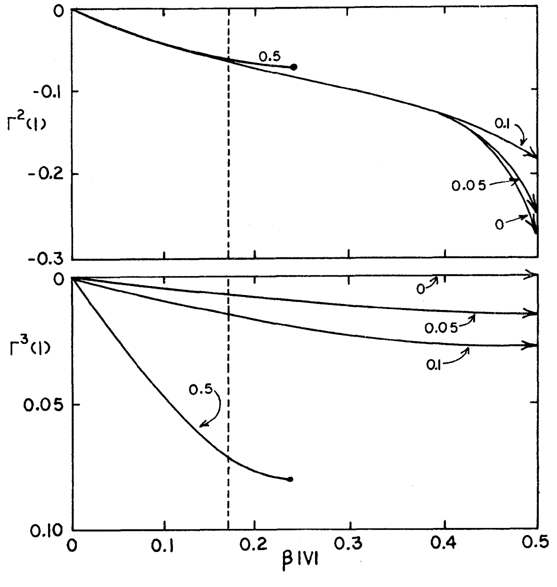

FIG. 2. Same as for Fig. 1, but with $V=1$.

$$G_{11}=N(1+\tfrac{1}{2}\beta D_1 v)\,,$$

$$G_{12}=\tfrac{1}{2}\beta D_1 w-\tfrac{1}{4}\beta^2 D_2 v^2\,,$$

$$G_{13}=G_{23}=G_{24}=G_{41}=G_{43}=G_{14}=0\,,$$

$$G_{21}=-ND_0+\tfrac{1}{2}\beta D_1(vB_2+2wA_2)-\tfrac{3}{4}\beta^2 D_2 A_2 v^2\,,$$

$$G_{22}=1+\tfrac{1}{2}\beta D_1 v=G_{33}=G_{44}\,,$$

$$G_{31}=\beta D_1 A_2 N v-\tfrac{1}{2}\beta^2 D_2 A_3 v^2\,,$$

$$G_{32}=-ND_0+\beta D_1(vB_2+2A_2 w)-\tfrac{5}{4}\beta^2 D_2 A_2 v^2\,,$$

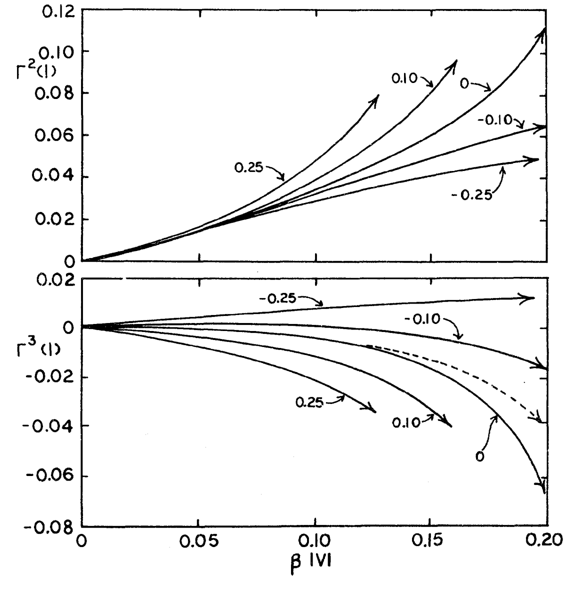

FIG. 3. Plots of $\Gamma^2(1)$ and $\Gamma^3(1)$ for $V=-1$, $m_A=\frac{3}{4}$, and various values of W. $\beta_c'=0.222$.

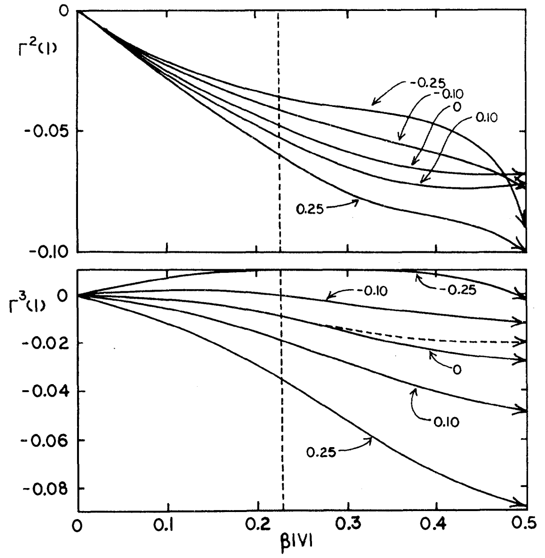

FIG. 4. Same as for Fig. 3, but with $V=1$.

$$G_{34}=\tfrac{1}{2}\beta D_1 w-\tfrac{1}{4}\beta^2 D_2 v^2\,,$$

$$G_{42}=\tfrac{3}{2}\beta D_1 A_2 v$$

and where the elements of the vector δ are

$$\delta^1=ND_0+\tfrac{1}{4}\beta^2 D_2 A_2 v^2,\qquad \delta^2=-\tfrac{1}{2}\beta D_1 A_2 v\,,$$

$$\delta^3=-\beta D_1 w A_2^2+\tfrac{1}{2}\beta^2 D_2 A_2^2 v^2\,,\quad \delta^4=0\,.$$

When eventually γ^1 is set to zero, the values of G_{21} and G_{31} become irrelevant, therefore we set them to zero. The equations are now quite easily solved. It is sufficient for the present order in $1/N$ to substitute $\tanh\lambda=m_A-m_B$ into (11) to determine the D_n. Also, one eliminates ND_0 from G_{32} by using the $\gamma^1=0$ condition in the equation involving δ^1. The solutions are

$$\gamma^2(4m_Am_B)^{-1}=(\beta/\beta_c)(1-\beta/\beta_c)^{-1}\,, \tag{24a}$$

$$\gamma^3(8m_Am_B)^{-1}=-[4m_Am_B|\beta/\beta_c|w'-3(m_B-m_A)(\beta/\beta_c)^2 +2(m_B-m_A)(\beta/\beta_c)^3](1-\beta/\beta_c)^{-3}\,, \tag{24b}$$

$$\gamma^4(48m_A^2m_B^2)^{-1}=(\beta/\beta_c)^2(1-\beta/\beta_c)^{-2}\,, \tag{24c}$$

where $\beta_c^{-1}=2m_Am_B|v|$, $w'=w/|v|$, and where $\beta>0$ corresponds to $v<0$ and $\beta<0$ to $v>0$. Notice that the relation (20) is verified for this case.

In Fig. 5 we have plotted γ^2 and γ^3 for $m_A=\frac{1}{2}$ and $m_A=\frac{3}{4}$ and several values of w'. When $|w'|=1$, then w has an effect comparable with that of v. The expressions for γ^2 and γ^3 are expected to typify correlation functions with all intersite vectors lying within the interaction range. Thus we can only compare γ^2 and γ^3 with $\Gamma^2(1)$ and $\Gamma^3(1)$ of the computer solution.

By comparing Figs. 1–4 with Fig. 5 one can see

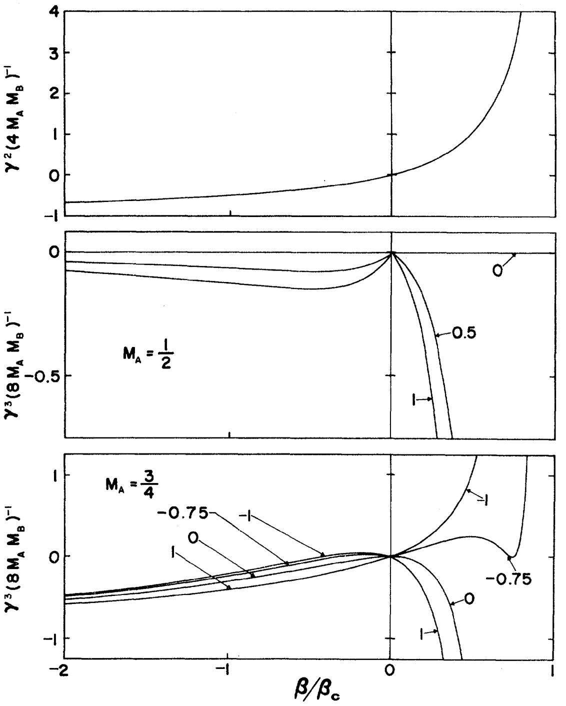

FIG. 5. Plots of γ^2 and γ^3 in the mean-field solution for $v=\pm 1$, $m_A=\frac{1}{2}$, $m_A=\frac{3}{4}$, and various values of w'. $\beta<0$ corresponds to $v=+1$ and $\beta>0$ corresponds to $v=-1$.

that for $|\beta| \lesssim \beta_c$ (or β_c' on Figs. 1–4) and even lower temperatures there is a very strong correspondence between the mean field curves and the corresponding computer solutions. This would indicate that certain aspects of the more realistic model's behavior may be interpreted in terms of the much simpler mean-field model.

VI. COMPARISON WITH OTHER SOLUTIONS

In Fig. 6 we compare the results of the above computation with other approximate solution methods by plotting $\Gamma^2(1)$ for a choice of input parameters for which a comparison is possible; that is, the equiatomic, nearest-neighbor, clustering, face-centered-cubic alloy with no three-site interactions. The spherical-model (SM) solution was obtained via (23). The prediction of Clapp and Moss[1] from Eq. (22) is labeled CM. For both of these curves the prescription of Lax[22] for the functions involved was used. The curve labeled FS was obtained by using Eq. (A5) of Ref. 23 which gives the internal energy of the fcc nearest-neighbor clustering alloy. The internal energy is proportional to $\Gamma^2(1)$. The FS curve closely approximates the exact result—to within 1 or 2% at the critical point and better elsewhere. The curve labeled TK is the prediction of Eqs. (5.4) and (6.1) of Ref. 8.

We have plotted $\Gamma^2(10)$ from our method in order to gauge the importance of spatial truncation effects. By comparing the analytical solution derived from (22) with the numerical solution of (21) done in the manner described in Sec. V (with the same spatial truncation) we found that when $\Gamma^2(10)$ was less than about 5% of $\Gamma^2(1)$, then the error in $\Gamma^2(1)$ was less than about 3%. Deviations of the curve labeled "present" in Fig. 6 can, therefore, not be attributed mainly to spatial truncation effects.

The present solution is certainly a considerable improvement over the CM solution and the SM solution in the range $0<\beta\lesssim\beta_c'$. In the range $\beta_c'\lesssim\beta$ the excluded volume corrections begin to matter and an improved treatment of these would probably yield better agreement with FS in this region. Although the TK curve gives agreement which is nearly as good as the present treatment, the derivation of Eqs. (5.4) and (6.1) of Ref. 8 was hard to justify and did not yield expressions for higher-order correlation functions, or indicate a way of deriving them in an orderly way.

A method for determining multi-site correlations based on an information-theory approach has recently been developed by Clapp[24,25] and used to calculate n-site probabilities for various alloys, with pair interactions only, from experimental or theoretical pair correlation functions. We have used the pair correlations generated by our program to calculate $\Gamma^3(m)$ by Clapp's method for a three-site cluster and compared them with $\Gamma^3(m)$ generated by our program. The dotted curves in Figs. 3 and 4 are Clapp's estimate of $\Gamma^3(1)$. In Figs. 1 and 2 Clapp's estimate is zero for all β by symmetry. In Fig. 4 the deviation of Clapp's estimate occurs outside the range of certain validity of our method, and so nothing can be concluded. However, in Fig. 3, at, e.g., $\beta=0.16$

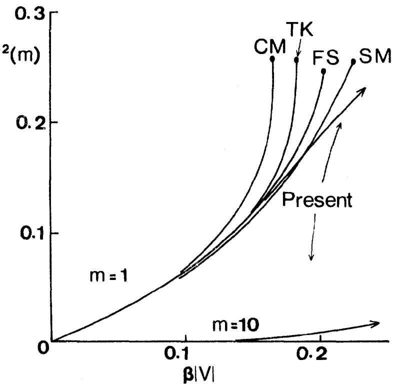

FIG. 6. Comparison of several solution methods in the $V=-1$, $m_A=\frac{1}{2}$, $W=0$ case with the exact (FS) result. The curves are the predictions of the Clapp-Moss approximation (CM), the spherical model (SM), and the approximation of Tahir-Kheli (TK), as well as $\Gamma^2(1)$ and $\Gamma^2(10)$ of the present approximation (Present).

the difference is 20% of our estimate of $\Gamma^3(1)$. This temperature is well above T_c' and $\Gamma^2(10)$ is small enough that spatial truncation effects can be ignored. The criteria of validity of our solution seem to be well satisfied so that Clapp's solution is probably in error. This suggests that the effect of varying the cluster size in Clapp's method for determining the higher-order correlation functions should be investigated.

ACKNOWLEDGMENTS

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APPENDIX A

Consider a general term on the right-hand side of Eqs. (10) at $\beta = \beta_c$:

$$(-\tfrac{1}{2}\beta_c)^{m+n} D_{m+n} \sum_{\{f,g,h\}} \prod_{p=1}^{n} V_{of(p)} \prod_{q=1}^{m} W_{og(q)h(q)} \times \left\langle \prod_{p=1}^{n} \sigma_{f(p)} \prod_{q=1}^{m} \sigma_{g(q)} \sigma_{h(q)} \prod_{s=1}^{r} \sigma_{i(s)} \right\rangle .$$

All the indices f, g, h are summed over (floating), but $i(1) \cdots i(r)$ are fixed and uncontracted. For Eq. (10a) $r=0$, for (10b) $r=1$, etc. No contractions can occur among indices on the same W [e.g., $o \neq g(s) \neq h(s) \neq o$]. Various special cases in the summations corresponding to different contractions of indices contribute to different orders in $1/z$, and we seek an upper bound on the leading-order contribution from the general term.

For our purposes it is sufficient to specify an over-all contraction arrangement by $\{S_t\}$, where S_t is the number of t-fold contractions. For a given $\{S_t\}$ the number of distinct sites in the lowest-order correlation function in the expression for the reduced (by contraction) $(r+n+2m)$th-order correlation function appearing in the general term is

$$u = r + n + 2m - \sum_{t \geq 2} t S_t . \tag{A1}$$

We have used Eqs. (4). Thus, assuming the scheme (17), the lowest-order correlation function arising from the contraction is $O(z^{-p})$, where

$$p = \tfrac{1}{2}[u + \phi(u)] . \tag{A2}$$

The number of summations in the general term will be reduced from $n+2m$ by contractions. A t-fold contraction among floating sites reduces the number of summations by $t-1$. A t-fold contraction can include one (but no more) fixed site, and when it does, $t-1$ summations are eliminated. If there are S_t t-fold contractions, among floating or fixed and floating sites, then $S_t(t-1)$ summations are eliminated. The total number of summations is therefore q where

$$q = n + 2m - \textstyle\sum_t S_t(t-1) . \tag{A3}$$

In these q summations coincidences must be avoided, for otherwise we would be considering a term arising from another contraction. If there are s fixed sites among the z sites within the interaction range then the q summations actually contribute a factor of $(z-s)(z-s-1)\cdots(z-s-q-1) < z^q$. We shall use the upper bound, z^q. Notice also that $q < z-s$, since for $q > z-s$ floating site coincidences are unavoidable.

With $\frac{1}{2}\beta_c \mathcal{V} = O(1/z)$ and $\frac{1}{2}\beta_c \mathcal{W} = O(1/z^2)$ an upper bound to the lowest-order contribution from the general term is $O(z^{-w})$, where

$$w = p - q + n + 2m = \tfrac{1}{2}[r + n + 2m + \textstyle\sum_t (t-2) S_t + \phi(u)] .$$

In this we need a lower bound for the value of $\sum_t (t-2)S_t$. Now $(t-2)S_t \geq 0$ so $[\sum_t (t-2)S_t]_{\text{lb}} = 0$. When this lower bound (lb) can actually occur, $\sum_t S_t t$ is even, so from (A1), $\phi(u) = \phi(r+n+2m)$. For $n+2m \gtrsim 2z$, the condition $q < z-s$ coupled with (A3) implies that this lower bound on $\sum_t (t-2)S_t$ will not actually be achieved, but in any case we may always write a lower bound on w as

$$w = \tfrac{1}{2}[r + n + 2m + \phi(r+n+2m)] , \tag{A4}$$

which is the desired result. The lower bound on w is attained for $n+2m \lesssim 2z$.

To show the consistency of the classification scheme (17) we compare the order in $1/z$ of the left- and right-hand sides of an arbitrary equation (arbitrary r) in the set of equations (10). The left-hand side is $O(z^{-v})$ where $v = \frac{1}{2}[r+1+\phi(r+1)]$ and a general term on the right-hand side is $O(z^{-w'})$, where $w' = \frac{1}{2}[r+n+2m+\phi(r+n+2m)] + \delta_{2m+n,0}$ provided that $n+2m \lesssim 2z$. The Kronecker δ is added to account for the fact that $D_0 = O(1/z)$. It is easy to show that

$$v - w' = \tfrac{1}{2}[(n+2m-1) + (-1)^{r+1}\phi(n+2m-1)] + \delta_{2m+n,0} . \tag{A5}$$

By inspection of (A5) with $r+1$ odd or even we see that (i) $v - w' \geq 0$, (ii) there exist values of $n+2m$ (0, 1 or 2) which are less than approximately $2z$ (24 for fcc) for which $v - w' = 0$. This means that for each equation (10), the leading order in $1/z$ of the right-hand side is the same as the left-hand side. Therefore, the scheme (17) is consistent.

APPENDIX B

We wish to show that when no sites coincide and $\beta=\beta_c$,

$$\langle\sigma_i\sigma_j\sigma_k\sigma_l\rangle=\langle\sigma_i\sigma_j\rangle\langle\sigma_k\sigma_l\rangle+\langle\sigma_i\sigma_k\rangle\langle\sigma_j\sigma_l\rangle+\langle\sigma_i\sigma_l\rangle\langle\sigma_j\sigma_k\rangle+O(1/z^3).$$

Proof. To $O(1/z^2)$ the function

$$G_{ijkl}=\langle\sigma_i\sigma_j\sigma_k\sigma_l\rangle-\langle\sigma_i\sigma_j\rangle\langle\sigma_k\sigma_l\rangle-\langle\sigma_i\sigma_k\rangle\langle\sigma_j\sigma_l\rangle-\langle\sigma_i\sigma_l\rangle\langle\sigma_j\sigma_k\rangle$$

satisfies

$$G_{oijk}=-\tfrac{1}{2}\beta D_1\textstyle\sum_f V_{of}G_{fijk}\qquad\text{(none of } o,i,j,k \text{ coincident)},$$

because to $O(1/z^2)$,

$$\langle\sigma_o\sigma_i\sigma_j\sigma_k\rangle=-\tfrac{1}{2}\beta D_1\textstyle\sum_f V_{of}\langle\sigma_f\sigma_i\sigma_j\sigma_k\rangle,$$

and

$$\langle\sigma_o\sigma_i\rangle\langle\sigma_j\sigma_k\rangle=-\tfrac{1}{2}\beta D_1\textstyle\sum_f V_{of}\langle\sigma_f\sigma_i\rangle\langle\sigma_j\sigma_k\rangle,\ \text{etc.}$$

Now, we have

$$\begin{aligned}G_{iikl}&=\langle\sigma_i^2\sigma_k\sigma_l\rangle-\langle\sigma_i^2\rangle\langle\sigma_k\sigma_l\rangle-2\langle\sigma_i\sigma_k\rangle\langle\sigma_i\sigma_l\rangle\\&=A_2\langle\sigma_k\sigma_l\rangle+B_2\langle\sigma_i\sigma_k\sigma_l\rangle-A_2\langle\sigma_k\sigma_l\rangle-2\langle\sigma_i\sigma_k\rangle\langle\sigma_i\sigma_l\rangle\\&=O(1/z^2)\quad\text{at }\beta=\beta_c,\end{aligned}$$

where we have used (4). Therefore, at $\beta=\beta_c$,

$$\begin{aligned}G_{oijk}&=-\tfrac{1}{2}\beta_c D_1(V_{oi}G_{iijk}+V_{oj}G_{jijk}+V_{ok}G_{kijk})-\tfrac{1}{2}\beta_c D_1\sum_{f\neq i,j,k}V_{of}G_{fijk}\\&=O(1/z^3)-O(G_{oijk}),\end{aligned}$$

so

$$G_{oijk}=O(1/z^3)\ \text{at}\ \beta=\beta_c,\ \text{Q.E.D.}$$

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[14] While this manuscript was in preparation the recent work of G. B. Taggart and R. A. Tahir-Khell, Progr. Theoret. Phys. (Kyoto) 46, 1960 (1971) came to our notice. They calculate the high-temperature expansions of the pair and triplet correlations in an alloy with pair and triplet interactions. The differences between their expressions for the correlations and ours [Eqs. (12) and (13)] may be traced to a different choice of occupation operator. Their choice is S_i^z, where $S_i^z=\frac{1}{2}(m_A-m_B+\sigma_i)$, in which σ_i is defined by (2). Consequently, their $I_2(ij)$ and $I_3(ijk)$ are not exactly comparable to our V_{ij} and W_{ijk}, and their expressions for the correlation functions are much more complicated than ours. Moreover, except for $m_A=\frac{1}{2}$, with this occupation operator their triplet (and all higher-order) correlations have an $O(1/z)$ leading term. It seems that a more computationally convenient and physically natural hierarchy of correlation functions is obtained through the use of occupation operators such that $\langle\sigma\rangle=0$ for *all* compositions.

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