

## Correlations and interactions in disordered binary alloys with atomic-radius disparity

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A theoretical method is developed for calculating the various correlations on which the diffracted intensity in an x-ray or elastic-thermal-neutron scattering experiment depends. The starting point is a Hamiltonian in which the atoms interact by pairwise "hard-core" potentials with different core radii. The hard-core condition, which should apply to transition and noble metals, simplifies the analysis by allowing the radius disparity to be used as a parameter of smallness for arbitrary composition. Classical statistical mechanics is used so that atomic-mass disparity has no effect on the correlations of interest. The Hamiltonian is analyzed in the quasiharmonic approximation, and some often-ignored terms are included because they may be important for short-wavelength fluctuations. Rigorous relations which express correlations involving atomic displacements and site occupancies in terms of correlations involving only site occupancies are derived, and they will hold even if diffusion is too slow for site-occupancy equilibrium to be established. These relations may be useful in the analysis of diffraction data. If the alloy can come to equilibrium with respect to site occupancy, then equilibrium statistical mechanics can predict the site-occupancy correlations, and an approximate mean-field theory is presented. The equations are not solved, but it is shown that in the disordered phase, away from the critical region, the site-occupancy correlations are those appropriate to a disordered binary alloy with no atomic-size disparity but with pair, triplet, and higher-order interactions. Expressions for the effective pair and triplet interactions are given.

### I. INTRODUCTION AND SUMMARY

A disordered substitutional binary alloy with atoms of different size may be visualized as a regular array of pairwise-interacting atoms which has become distorted because of differences in the three types of interatomic potential. If these differences are not great enough to disrupt the crystalline nature of the alloy, an "average lattice" with a one-to-one correspondence between atoms and lattice sites may be defined. In such an alloy the configuration may be specified by the average lattice structure and lattice parameter, by the set  $\{\vec{u}_i\}$  of displacements of atoms from average lattice sites, by the set  $\{\sigma_i\}$  of two-valued variables which specifies the site occupancies, and by the atomic momenta. These variables are defined in Sec. II, where a Hamiltonian which depends on them is derived in the quasiharmonic approximation. In the present work the lattice parameter is taken as constant at the empirical value for the entire ensemble used. Attention will be focused on the statistical mechanical evaluation of spatial correlations among the occupancy and displacement configuration variables, e.g.,  $\langle\sigma_0\sigma_i\rangle$ ,  $\langle\sigma_0\vec{u}_i\rangle$ , etc., where the angular brackets denote an ensemble average. This is because the orientation of the present work is toward the interpretation of x-ray or elastic-thermal-neutron scattering data. Relations between the intensity of kinematically scattered radiation and the spatial correlation functions are given in Appendix A.

In Sec. IV, a theorem derived in Sec. III is used to facilitate the derivation of relations which ex-

press displacement correlations (containing one or two atomic displacements) entirely in terms of concentration correlations (containing only site-occupancy variables). These relations are infinite series in ascending powers of "defect strength" and concentration. Physically, the defects are due to both force-constant and mass variations. Although the latter may be large, the present paper deals only with ensemble averages of momentum-independent quantities in the classical regime, so that mass variations have no effect. It will be shown that defect strength due to force-constant variation is "small" if the atoms are hard spheres (interacting by Born-Mayer repulsion) with small radius disparity. Consequently, it is possible to truncate the various series at a chosen order in defect strength for arbitrary composition. There is no restriction to dilute alloys or necessity to sum the concentration series as in the case of mass defects.<sup>1</sup> Aside from the necessary truncation, the relations derived in Sec. IV are exact within the harmonic approximation, and are valid even if the system is not in thermodynamic equilibrium with respect to the concentration variables  $\{\sigma_i\}$ . This may occur if diffusion rates are slow. It should be noted that if the series are truncated at the lowest order in defect strength and terms due to thermal vibration are dropped, then one recovers results derived by Krivoglaz<sup>2</sup> and by Cook and de Fontaine.<sup>3</sup>

A different application of theorem of Sec. III is made in Sec. V to obtain a set of linear equations in the various correlation functions. Displacement correlations may be eliminated in favor of concen-

tration correlations using the relations derived in Sec. IV, yielding a set of linear equations which in principle may be analyzed and solved in the disordered phase in the manner of Shirley and Wilkins.<sup>4</sup> In practice, however, this is too difficult, and a mean-field approximation following Clapp and Moss<sup>5</sup> is made. This approximation will be valid in the disordered phase away from the critical region. If the first two orders of defect strength are retained, one obtains a manageable set of equations which may be solved to obtain the pair, triplet, and quadruplet concentration correlations necessary to compute the scattered intensity correct to the first two orders in defect strength. The equations are not solved, but it is shown that in the disordered phase, away from the critical region, the concentration correlations are those appropriate to a conventional undistorted-lattice Ising-type model with long-range pair interactions. If the first three orders in defect strength are retained, then effective triplet interactions appear. The triplet interactions are one order higher in the defect strength than the pair interactions. Expressions for the effective pair and triplet interactions are given. The net effect of the analysis is to transform the distorted-lattice pairwise-interaction model into an undistorted-lattice multisite-interaction model.

## II. MODEL HAMILTONIAN

If the dependence of the electronic energy on the spatial configuration of the ion cores is taken into account to second order in perturbation theory,<sup>6</sup> the system Hamiltonian may be written

$$\begin{aligned}
 H' = & \sum_i (2m_i)^{-1} \vec{p}_i^2 + E(v) \\
 & + \frac{1}{2} \sum_{i \neq j} \{ V^{AA}(\vec{r}_{ij}) \sigma^A(\vec{r}_i) \sigma^A(\vec{r}_j) \\
 & + V^{BB}(\vec{r}_{ij}) \sigma^B(\vec{r}_i) \sigma^B(\vec{r}_j) + V^{AB}(\vec{r}_{ij}) \\
 & \times [\sigma^A(\vec{r}_i) \sigma^B(\vec{r}_j) + \sigma^A(\vec{r}_j) \sigma^B(\vec{r}_i)] \}, \quad (1)
 \end{aligned}$$

where  $\vec{r}_i$ ,  $\vec{p}_i$ , and  $m_i$  are the position, momentum, and mass of the  $i$ th nucleus, where  $\sigma^A(\vec{r}_i) = (1, 0)$  for an  $(A, B)$  atom at  $\vec{r}_i$  and  $\sigma^A(\vec{r}_i) + \sigma^B(\vec{r}_i) = 1$ , and where  $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$ . The structure-independent part of the electronic energy is contained in  $E$ , which depends only on the specific volume  $v$ . The interatomic potentials  $V^{AA}$ , etc., have a part which is induced by the electron-ion interactions as well as a Born-Mayer exchange-repulsion component that is particularly important in the noble and transition metals where the ion cores come into contact.<sup>7,8</sup> It is quite possible that anisotropies in the electronic structure will give rise to anisotropic pair potentials (noncentral forces) with the "orien-

tation" of the potentials defined by the average lattice. The theory developed below can accommodate this type of potential.

In the classical statistical mechanics of the Hamiltonian  $H'$ , the momenta are statistically independent of the other configuration variables. Consequently, the kinetic part of Eq. (1) may be ignored for the purpose of calculating ensemble averages of momentum-independent quantities, such as the correlation functions of interest in this paper. The Hamiltonian may be simplified further by assuming that each atom suffers only a small displacement from a site in the average lattice, and that there is a one-to-one correspondence between atoms and lattice sites. If the position of an atom is  $\vec{r}_i$  and its associated average lattice site is  $(\vec{r}_i)_{av}$ , then

$$\vec{r}_i = (\vec{r}_i)_{av} + \vec{u}_i, \quad (2)$$

where  $\vec{u}_i$  is a small displacement. In the present paper,  $\{(\vec{r}_i)_{av}\}$  defines a lattice of cubic symmetry. The one-to-one correspondence is written

$$\sigma^A(\vec{r}_i) = \sigma^A((\vec{r}_i)_{av}) \equiv \sigma_i^A, \quad (3)$$

and similarly for  $\sigma_i^B$ . Since  $\sigma_i^A + \sigma_i^B = 1$ , it is possible to express  $\sigma_i^A$  and  $\sigma_i^B$  in terms of a single variable  $\sigma_i$ . Thus,

$$\sigma_i^A = m_A + \frac{1}{2} \sigma_i, \quad (4a)$$

$$\sigma_i^B = m_B - \frac{1}{2} \sigma_i, \quad (4b)$$

where  $\sigma_i = (2m_B - 2m_A)$  for an  $(A, B)$  atom on site  $i$ , and where  $(m_A, m_B)$  is the mole fraction of  $(A, B)$  atoms. Note that

$$\sum_i \sigma_i = 0. \quad (5)$$

Now if we use Eq. (3), substitute Eqs. (4) into Eq. (1), and ignore the kinetic term and the purely volume-dependent electronic term (since we shall be considering only isochoric changes at the empirical specific volume), we obtain the following effective Hamiltonian:

$$\begin{aligned}
 H'' = & \frac{1}{2} \sum_{i \neq j} [U(\vec{r}_{ij}) + V(\vec{r}_{ij})(\sigma_i + \sigma_j) \\
 & + W(\vec{r}_{ij}) \sigma_i \sigma_j], \quad (6)
 \end{aligned}$$

where

$$U(\vec{r}) = m_A^2 V^{AA}(\vec{r}) + m_B^2 V^{BB}(\vec{r}) + 2m_A m_B V^{AB}(\vec{r}), \quad (7a)$$

$$\begin{aligned}
 V(\vec{r}) = & \frac{1}{2} [m_A V^{AA}(\vec{r}) - m_B V^{BB}(\vec{r}) \\
 & + (m_B - m_A) V^{AB}(\vec{r})], \quad (7b)
 \end{aligned}$$

$$W(\vec{r}) = \frac{1}{4} [V^{AA}(\vec{r}) + V^{BB}(\vec{r}) - 2V^{AB}(\vec{r})]. \quad (7c)$$

When Eq. (6) is expanded to second order in the small displacements, it may be written (see Ref.

9 for details of the straightforward but tedious algebra)

$$H = \frac{1}{2} \sum_{i \neq j} W_{ij} \sigma_i \sigma_j + \sum_{ij} \vec{v}'_{ij} \sigma_i \vec{u}_j + \sum_{ij} \vec{w}'_{ij} \sigma_i \sigma_j \vec{u}_j + \frac{1}{2} \sum_{ij} \vec{u}'_i \vec{\Phi}_{ij} \vec{u}_j + \lambda \sum_i \sigma_i, \quad (8)$$

where<sup>10</sup>

$$\Phi_{ij} = \Phi_{ij}^U + \Phi_{ij}^V (\sigma_i + \sigma_j) + \Phi_{ij}^W \sigma_i \sigma_j - \delta_{ij} \sum_k (\Phi_{kj}^V \sigma_k + \Phi_{kj}^W \sigma_k \sigma_j), \quad (9)$$

and where the purely volume-dependent term

$$\frac{1}{2} \sum_{i \neq j} U_{ij}$$

has been ignored. The last term in Eq. (8) has been added because it will be convenient to satisfy the constraint of Eq. (5) in a grand canonical ensemble in which  $\lambda$  is determined by the condition

$$\langle \sigma_i \rangle = 0. \quad (10)$$

In Eqs. (8) and (9) the following abbreviation has been made ( $F$  is an arbitrary function):

$$F((\vec{r}_{ij})_{av}) \equiv F_{ij}.$$

In Eq. (8),  $\vec{v}'_{ij}$  is a column three vector with elements  $\partial V / \partial x | (\vec{r}_{ij})_{av}$ , etc., and  $\vec{v}'_{ij}$  is its transpose, where  $x$ ,  $y$ , and  $z$  are Cartesian coordinates referred to the three fourfold axes of the cubic lattice. A similar definition holds for  $\vec{w}'_{ij}$ , with  $W$  replacing  $V$ . For  $(\vec{r}_{ij})_{av} \neq 0$ ,  $\Phi_{ij}^U$  is a real-symmetric  $3 \times 3$  matrix with elements  $-\partial^2 U / \partial x^2 | (\vec{r}_{ij})_{av}$ ,  $-\partial^2 U / \partial x \partial y | (\vec{r}_{ij})_{av}$ , etc., and for  $(\vec{r}_{ij})_{av} = 0$  it is  $\bar{I} \sum_i \partial^2 U / \partial x^2 | (\vec{r}_{0i})_{av}$ , where  $\bar{I}$  is the unit matrix. It has the property

$$\sum_i \Phi_{0i}^U = 0.$$

The definitions of  $\Phi^V$  and  $\Phi^W$  have  $U$  replaced by  $V$  or  $W$  in the above. Note that  $\Phi$ , defined by Eq. (9), has the property

$$\sum_i \Phi_{0i} = 0$$

as it must.

The present analysis will be restricted to changes involving no homogeneous deformations of the crystal. This means that as well as requiring that there be no translation of the crystal as a whole, that is,

$$\sum_i \vec{u}_i = 0, \quad (11)$$

we also require that  $\langle \vec{u}_i \rangle$  be independent of  $i$ . Combined with Eq. (11), this implies that  $\langle \vec{u}_i \rangle = 0$ . This statistical equivalence of average lattice sites further implies that the correlation functions will

be invariant under translations by vectors of the average lattice, i. e.,  $\langle \sigma_i \vec{u}_j \rangle = \langle \sigma_{i+n} \vec{u}_{j+n} \rangle$ , etc., and that they will transform as basis functions of various representations of the point group of the average lattice. The system will be implicitly constrained to have no homogeneous deformation in the following analysis by assuming that  $\langle \vec{u}_i \rangle = 0$  and that the correlation functions have symmetries appropriate to the average lattice.

It is worth pointing out that some workers<sup>2,3</sup> have studied a Hamiltonian (or free-energy expansion) similar to Eq. (8) but with  $\vec{w} = 0$ ,  $\Phi^V = \Phi^W = 0$ , and with  $\{\sigma_i\}$  as continuous concentration variables. Such a Hamiltonian will adequately describe displacement waves with wavelengths considerably longer than the interatomic spacing (such as occur in spinodal decomposition) because little error will be introduced by replacing  $\sigma_i$  with the average composition of the region surrounding site  $i$  of linear dimension less than the wavelength [actually  $\sigma_i - 2(c_i - m_A)$ , where  $c_i$  is the concentration of  $A$  atoms]. The variables  $\{\sigma_i\}$  may then be thought of as continuous and small so that terms of third or higher order in *both* displacements and correlations may be dropped. However, for the interpretation of x-ray diffraction experiments which can resolve fluctuations with wavelengths comparable to interatomic spacings, it is necessary to study displacement waves with these wavelengths. Consequently, the two-valued nature of  $\sigma_i$  should not be ignored, and, because  $\sigma_i = O(1)$ , all the terms displayed in Eqs. (8) and (9) should be included.

### III. THEOREM

Let  $\sum_{c_i}$  denote summation (or integration) over the space of the configuration variable  $c_i$ , and define

$$\sum_{\{c\}} \equiv \sum_{c_1} \sum_{c_2} \dots \sum_{c_{4N}},$$

where there are  $4N$  configuration variables. There are  $N$  sites in the crystal. One may also define

$$\rho(\{c\}) = e^{-\beta H(\{c\})},$$

where  $\beta^{-1} = \kappa T$ . The absolute temperature is  $T$ , and  $\kappa$  is Boltzmann's constant. The ensemble average of a function  $P$  of configuration is therefore written

$$\langle P \rangle = \sum_{\{c\}} P(\{c\}) \rho(\{c\}) / \sum_{\{c\}} \rho(\{c\}). \quad (12)$$

We also define the following special average:

$$\langle P \rangle_{c_i} = \sum_{c_i} P \rho / \sum_{c_i} \rho. \quad (13)$$

The average is taken over  $c_i$ , so that  $\langle P \rangle_{c_i}$  is a function of possibly all the  $c$ 's except  $c_i$ . With

these definitions the following theorem may be proved.

*Theorem.* For two functions of configuration  $P(\{c\})$  and  $Q(\{c\})$ ,

$$\langle PQ \rangle = \langle \langle P \rangle_{c_i} Q \rangle,$$

provided  $Q$  does not have  $c_i$  as one of its arguments.

*Proof.* From the definition [Eq. (12)] of an ensemble average,

$$\langle \langle P \rangle_{c_i} Q \rangle = \sum_{\{c\}} \rho = \sum_{\{c\}}' \sum_{c_i} \langle P \rangle_{c_i} Q \rho, \quad (14)$$

where

$$\sum_{\{c\}} = \sum_{\{c\}}' \sum_{c_i}.$$

Since neither  $\langle P \rangle_{c_i}$  nor  $Q$  depend on  $c_i$ , the right-hand side of Eq. (14) may be written

$$\begin{aligned} \langle \tilde{u}_0 \rangle_{\tilde{u}_0} = & \left( \int d^3 u_0 e^{-\beta H} \right)^{-1} \int d^3 u_0 \tilde{u}_0 e^{-\beta H} = \left( \int d^3 u_0 \exp \left\{ -\beta \left[ \left( \sum_i \tilde{v}'_{i0} \sigma_i + \sum_i \tilde{w}'_{i0} \sigma_i \sigma_0 \right. \right. \right. \right. \\ & \left. \left. \left. + \sum_i (1 - \delta_{i0}) \tilde{u}'_i \Phi_{i0} \tilde{u}_0 + \frac{1}{2} \tilde{u}'_0 \Phi_{00} \tilde{u}_0 \right] \right\} \right)^{-1} \int d^3 u_0 \tilde{u}_0 e^{(\dots)}, \end{aligned}$$

where Eq. (8) was substituted and parts not containing  $\tilde{u}_0$  have canceled from the exponentials. Both exponentials have the same argument.  $\delta_{i0}$  is the Krönecker  $\delta$ . Since  $\Phi_{ij}$ , and in particular  $\Phi_{00}$ , is real symmetric, the three-dimensional Gaussian integrals presented in Appendix B may be used, and one finds

$$\begin{aligned} \langle \tilde{u}_0 \rangle_{\tilde{u}_0} = & -\frac{1}{2} (\frac{1}{2} \beta \Phi_{00})^{-1} \beta \sum_i [ \tilde{v}_{i0} \sigma_i + \tilde{w}_{i0} \sigma_i \sigma_0 \\ & + (1 - \delta_{0i}) \Phi_{0i} \tilde{u}_i ] \end{aligned}$$

or

$$\begin{aligned} \Phi_{00} \langle \tilde{u}_0 \rangle_{\tilde{u}_0} + \sum_i (1 - \delta_{0i}) \Phi_{0i} \tilde{u}_i \\ = - \sum_i (\tilde{v}_{i0} \sigma_i + \tilde{w}_{i0} \sigma_i \sigma_0). \end{aligned} \quad (15)$$

When Eq. (15) is multiplied by a function  $J$  of  $\{\sigma\}$  only, an ensemble average is taken, and the theorem of Sec. III is applied, one obtains

$$\begin{aligned} \sum_i [ \Phi_{0i}^V \langle J \tilde{i} \rangle + \Phi_{0i}^W \langle \langle J 0 \tilde{i} \rangle \rangle + \langle J i \tilde{i} \rangle ] \\ + \Phi_{0i}^W \langle J 0 i \tilde{i} \rangle - \sum_k (\Phi_{k0}^V \langle J k \tilde{0} \rangle + \Phi_{k0}^W \langle J k 0 \tilde{0} \rangle) \\ = - \sum_i (\tilde{v}_{i0} \langle J i \rangle + \tilde{w}_{i0} \langle J i 0 \rangle). \end{aligned} \quad (16)$$

where Eq. (9) was used. The notation adopted in Eq. (16) is related to that used so far by the cor-

$$\begin{aligned} \sum_{\{c\}}' \langle P \rangle_{c_i} Q \sum_{c_i} \rho = \sum_{\{c\}}' \left( \sum_{c_i} P \rho / \sum_{c_i} \rho \right) Q \sum_{c_i} \rho \\ = \sum_{\{c\}}' \left( \sum_{c_i} P \rho \right) Q = \sum_{\{c\}} P Q \rho \\ = \langle P Q \rangle \sum_{\{c\}} \rho, \end{aligned}$$

thus proving the theorem.

#### IV. RELATIONS BETWEEN DISPLACEMENT CORRELATIONS AND CONCENTRATION CORRELATIONS

##### A. Displacement correlations with one displacement

First it will be convenient to calculate  $\langle \tilde{u}_0 \rangle_{\tilde{u}_0}$ , the average of  $\tilde{u}_0$  for fixed values of the other configuration variables. A special case of Eq. (13) is written

responses  $\tilde{u}_i \rightarrow \tilde{i}$ ,  $\tilde{u}'_i \rightarrow \tilde{i}'$ , and  $\sigma_i \rightarrow i$ .

The Green's function for the average lattice is defined by

$$\sum_i G_{0i} \Phi_{ii}^U = \bar{I} \delta_{0i}. \quad (17)$$

This Green's function is appropriate to a perfect crystal with interatomic potentials  $U(\tilde{r})$ , i. e., the average interatomic potential. It may be computed using, for example, the procedure of Flinn and Maradudin.<sup>11</sup> Replacing 0 by  $l$  in Eq. (16), multiplying by  $G_{0l}$ , and summing on  $l$ , one finds

$$\begin{aligned} \langle J \tilde{0} \rangle = & - \sum_{ii} [ G_{0i} \tilde{v}_{ii} \langle J i \rangle + G_{0i} \tilde{w}_{ii} \langle J i l \rangle \\ & + G_{0i} \Phi_{ii}^V (\langle J i \tilde{i} \rangle + \langle J l \tilde{i} \rangle - \langle J i \tilde{i} \rangle) \\ & + G_{0i} \Phi_{ii}^W (\langle J l i \tilde{i} \rangle - \langle J i l \tilde{i} \rangle) ]. \end{aligned} \quad (18)$$

This equation may be iterated to generate a series in ascending orders of the Green's function relating  $\langle J \tilde{0} \rangle$  to concentration correlations only. The criterion for truncating the series is considered in Sec. IV C.

##### B. Displacement correlations with two displacements

Using the Gaussian integrals of Appendix B, one may write<sup>12</sup>

$$\langle \tilde{u}_0 \tilde{u}_0 \rangle_{\tilde{u}_0} = \frac{1}{2} (\frac{1}{2} \beta \Phi_{00})^{-1} + \langle \tilde{u}_0 \rangle_{\tilde{u}_0} \langle \tilde{u}_0 \rangle_{\tilde{u}_0}.$$

Also, for  $l \neq 0$  one has

$$\langle \tilde{u}_i \tilde{u}_0 \rangle_{\tilde{u}_0} = \tilde{u}_i \langle \tilde{u}_0 \rangle_{\tilde{u}_0} = \langle \tilde{u}_i \rangle_{\tilde{u}_0} \langle \tilde{u}_0 \rangle_{\tilde{u}_0};$$

so, for arbitrary  $l$ ,

$$\langle \tilde{u}_i \tilde{u}_0 \rangle_{\tilde{u}_0} = \delta_{i0} \kappa T \Phi_{00}^{-1} + \langle \tilde{u}_0 \rangle_{\tilde{u}_0} \langle \tilde{u}_i \rangle_{\tilde{u}_0}$$

or

$$\Phi_{00} \langle \tilde{u}_i \tilde{u}_0 \rangle_{\tilde{u}_0} = \bar{I} \delta_{i0} \kappa T + \Phi_{00} \langle \tilde{u}_0 \rangle_{\tilde{u}_0} \langle \tilde{u}_i \rangle_{\tilde{u}_0}.$$

Using Eq. (15) this becomes

$$\begin{aligned} \Phi_{00} \langle \tilde{u}_i \tilde{u}_0 \rangle_{\tilde{u}_0} &= \bar{I} \delta_{i0} \kappa T \\ &- \sum_i [\tilde{v}_{i0} \sigma_i + \tilde{w}_{i0} \sigma_i \sigma_0 \\ &+ (1 - \delta_{i0}) \Phi_{0i} \tilde{u}_i] \langle \tilde{u}_i \rangle_{\tilde{u}_0}. \end{aligned}$$

If one multiplies this by  $J$ , an arbitrary function of  $\{\sigma\}$ , substitutes Eq. (9), applies the theorem of the previous section, and operates with the Green's function, one obtains

$$\begin{aligned} \langle J \bar{I} \bar{O} \rangle &= G_{0i} \langle J \rangle \kappa T - \sum_{ik} [G_{0k} \tilde{v}_{ik} \langle Ji \bar{I} \rangle \\ &+ G_{0k} \tilde{w}_{ik} \langle Jik \bar{I} \rangle + G_{0k} \Phi_{ik}^V (\langle Ji \bar{I} \bar{I} \rangle + \langle Jk \bar{I} \bar{I} \rangle \\ &- \langle Ji \bar{I} \bar{k} \rangle) + G_{0k} \Phi_{ik}^W (\langle Jik \bar{I} \bar{I} \rangle - \langle Jik \bar{I} \bar{k} \rangle)]. \end{aligned} \quad (19)$$

This equation may be iterated with Eq. (18) to give a series in ascending orders of the Green's function relating  $\langle J \bar{I} \bar{O} \rangle$  to concentration correlations only.

### C. Hard-core truncation criterion

The series generated by iterating Eqs. (18) and (19) must be truncated at a given order of some parameter of smallness, or they must be summed completely. In the present work the atomic-radius disparity is a natural parameter of smallness. The pair potentials in an alloy which is essentially hard core in nature with small atomic-radius disparity may be written:

$$V^{AA}(r) = D \exp[-r(b + \epsilon)^{-1}], \quad (20a)$$

$$V^{BB}(r) = D \exp[-r(b - \epsilon)^{-1}], \quad (20b)$$

$$V^{AB}(r) = D \exp(-rb^{-1}), \quad (20c)$$

where  $b$  is the nominal core radius and  $\epsilon/b$  is small. Small differences in  $D$  may be incorporated into  $\epsilon$ . Using Eqs. (7) to compute  $U$ ,  $V$ , and  $W$  to leading order in  $\epsilon/2b$ , one finds

$$U = D e^{-r/b},$$

$$V = D e^{-r/b} (r/b) (\epsilon/2b),$$

$$W = D e^{-r/b} (r^2 b^{-2} - 2r b^{-1}) (\epsilon/2b)^2.$$

For nearest-neighbor interactions, which are the most important in a hard-core alloy, it is apparent that  $V$  is smaller than  $U$  by a factor of  $\epsilon/2b$ , and that  $W$  is yet another factor of  $\epsilon/2b$  smaller.

This also holds for higher derivatives of  $U$ ,  $V$ , and  $W$ . The parameter of smallness we shall use to truncate the series obtained by iteration of Eqs. (18) and (19) is  $\epsilon/2b$ . It will be convenient to multiply  $V$  and its derivatives by a dimensionless parameter  $\gamma$  which will eventually be set to unity, and to multiply  $W$  and its derivatives by  $\gamma^2$ . In the equations below, the power of  $\gamma$  which multiplies a term is a label which indicates the order in  $\epsilon/2b$  of that term.

If the following replacements are made in Eq. (18):

$$G \rightarrow G, \quad \tilde{U} \rightarrow \gamma \tilde{U}, \quad \tilde{W} \rightarrow \gamma^2 \tilde{W}, \quad \Phi^V \rightarrow \gamma \Phi^V, \quad \Phi^W \rightarrow \gamma^2 \Phi^W,$$

and if Eq. (18) is iterated retaining terms only up to  $O(\gamma^2)$ , then one obtains

$$\langle J \bar{O} \rangle = -\gamma \sum_i \tilde{\xi}_{0i} \langle Ji \rangle - \gamma^2 \sum_{ij} \tilde{\xi}_{0ij} \langle Jij \rangle, \quad (21)$$

where

$$\tilde{\xi}_{0i} = \sum_k G_{0k} \tilde{v}_{ik}$$

and

$$\begin{aligned} \tilde{\xi}_{0ij} &= G_{0j} \tilde{w}_{ij} + \sum_k [G_{0k} \Phi_{ki}^V (\tilde{\xi}_{kj} - \tilde{\xi}_{ij}) \\ &- G_{0i} \Phi_{ki}^V \tilde{\xi}_{kj}]. \end{aligned} \quad (23)$$

Iteration of Eq. (19) retaining terms to  $O(\gamma^2)$  yields

$$\begin{aligned} \langle J \bar{I} \bar{O} \rangle &= \kappa T \left( G_{0i} \langle J \rangle + \gamma \sum_i \bar{P}_{0i} \langle Ji \rangle \right. \\ &\left. + \gamma^2 \sum_{ij} \bar{Q}_{0ij} \langle Jij \rangle \right) + \gamma^2 \sum_{ij} \tilde{\xi}_{0j} \tilde{\xi}_{ii} \langle Jij \rangle, \end{aligned} \quad (24)$$

where

$$\bar{P}_{0i} = \sum_k (G_{0k} \Phi_{ik}^V G_{ik} - G_{0k} \Phi_{ik}^V G_{ki} - G_{0i} \Phi_{ik}^V G_{ik}) \quad (25)$$

and

$$\begin{aligned} \bar{Q}_{0ij} &= G_{0j} \Phi_{ij}^W (G_{ij} - G_{ji}) + \sum_k (G_{0k} \Phi_{ik}^V \bar{P}_{kij} \\ &- G_{0k} \Phi_{ik}^V \bar{P}_{kij} - G_{0j} \Phi_{kj}^V \bar{P}_{kij}). \end{aligned} \quad (26)$$

The correlation functions appearing in the diffraction theory are [see Eqs. (A11)]  $\langle 0n \rangle$ ,  $\langle 0\bar{n} \rangle$ ,  $\langle 0n\bar{n} \rangle$ ,  $\langle \bar{0}\bar{n} \rangle$ ,  $\langle 0\bar{n}\bar{n} \rangle$ ,  $\langle 0\bar{0}\bar{n} \rangle$ ,  $\langle 0n\bar{n}\bar{n} \rangle$ , and  $\langle 0n\bar{0}\bar{n} \rangle$ . Consequently, only the special cases of Eqs. (21) and (24) given by  $J=1$ ,  $\sigma_0$ , or  $\sigma_0\sigma_n$ , and  $\bar{I} \rightarrow \bar{n}$  or  $\bar{0}$ , and  $\bar{O} \rightarrow \bar{n}$  are needed. Thus the diffracted intensity correct to  $O(\gamma^2)$  depends on pair, triplet, and quadruplet concentration correlations. Many of these correlations will have site coincidences. Such correlations may be expressed entirely in terms of lower-order correlations with no coincidences by the identity<sup>4</sup>

$$\sigma_i^n = A_n + B_n \sigma_i, \quad (27)$$

where

$$A_n = 2^n [m_A m_B^n + (-1)^n m_A^n m_B]$$

and

$$B_n = 2^{n-1} [m_B^n - (-m_A)^n].$$

It is not difficult to evaluate the above expressions for a particular model with the aid of a computer once the average-lattice Green's function  $G$  has been computed.<sup>9</sup> This is especially true if one considers special cases such as no short-range order, nearest-neighbor interactions, equiatomic composition, etc. A great simplification obtains if, as in Ref. 3,  $\Phi^V = \Phi^W = 0$ , for then Eqs. (18) and (19) do not need to be iterated. However, as indicated in Sec. II, there is no *a priori* justification for ignoring  $\Phi^V$  and  $\Phi^W$ . The main problem is in choosing an appropriate microscopic model.<sup>13</sup> There are no good theoretical estimates of  $V^{AA}$ ,  $V^{BB}$ , and  $V^{AB}$ , so one must choose reasonable phenomenological forms with a few parameters fitted to macroscopic data. A possible procedure is to use the elastic shear moduli  $C_{44}$  and  $C_{11} - C_{12}$ , measured at several compositions to determine the parameters in the interatomic potentials.<sup>9</sup> This is possible because the speed of the long-wavelength transverse waves in the alloy depends on the first and second derivatives of  $U(\vec{r})$ . Thus Born-Mayer potentials of the form of Eqs. (20) may be determined to within an additive constant. The additive constants have no effect on the theory presented except in a way to be shown in Sec. V.

The atomic displacements in alloys are often visualized as consisting of a rapidly time-varying component due to thermal agitation superimposed on a static distortion field. No such assumption has been made in the above analysis, but Eq. (21) and the explicitly temperature-independent part of Eq. (24) may be regarded as due to the static distortions, while the explicitly temperature-dependent part of Eq. (24) may be regarded as a thermal contribution.

#### V. CALCULATION OF CONCENTRATION CORRELATIONS

Equations (21) and (24) will hold even if the system is not in equilibrium with respect to the  $\{\sigma\}$  configuration variables, as when the short-range order is quenched in. However, if the temperature is high enough, the system can equilibrate completely, and the concentration correlations can be calculated from equilibrium statistical mechanics. An approximate theory for computing the equilibrium-concentration correlations in the disordered phase away from the critical region is developed in the present section.

A special case of Eq. (13) is

$$\langle \sigma_0 \rangle_{\sigma_0} = \sum_{\sigma_0 = \pm} \sigma_0 e^{-\beta H} / \sum_{\sigma_0 = \pm} e^{-\beta H}. \quad (28)$$

When the Hamiltonian in the form of Eq. (6) is substituted (with the additional term involving the chemical potential added) and the sums are evaluated, one finds<sup>4</sup>

$$\langle \sigma_0 \rangle_{\sigma_0} = \tanh[\beta(E_0 + \lambda)] + (m_B - m_A), \quad (29)$$

where

$$E_0 = - \sum_{i \neq 0} [V(\vec{r}_{0i}) + W(\vec{r}_{0i}) \sigma_i]. \quad (30)$$

$E_0$  may be regarded as the field acting on site 0 due to the neighboring atoms. The next step is to expand  $E_0$  to quadratic terms in  $\{\tilde{u}\}$ :

$$\begin{aligned} E_0 = & - \sum_{i \neq 0} [V_{0i} + \vec{v}'_{0i}(\tilde{u}_i - \tilde{u}_0) - \frac{1}{2}(\tilde{u}'_i - \tilde{u}'_0) \\ & \times \Phi'_{0i}(\tilde{u}_i - \tilde{u}_0) + W_{0i} \sigma_i + \vec{w}'_{0i}(\tilde{u}_i - \tilde{u}_0) \sigma_i \\ & - \frac{1}{2}(\tilde{u}'_i - \tilde{u}'_0) \Phi''_{0i}(\tilde{u}_i - \tilde{u}_0) \sigma_i]. \end{aligned} \quad (31)$$

The restriction  $i \neq 0$  may be removed if  $V_{00} = 0$  and  $W_{00} = 0$ . In principle it may be possible to use Eqs. (29) and (31) as well as the relations derived in Sec. IV to derive and analyze an infinite linear set of equations in the concentration correlations in the manner of Shirley and Wilkins.<sup>4</sup> However, this would be very difficult, and it is simpler to employ a mean-field approximate theory. Such a theory is expected to be valid except in the critical region.

The derivation of the mean-field theory closely follows the derivation by Clapp and Moss<sup>5</sup> of Cowley's<sup>14</sup> theory for binary alloys with no size disparity. The mean-field approximation is conveniently expressed in terms of "subensemble" averages. The subensemble average of a function  $F$  is the average over configurations for which an  $A$  atom occupies site  $i$ , i. e.,

$$\begin{aligned} \langle F \rangle_{\sigma_i = +} & = \sum_{\{\sigma, \tilde{u}\}} \sigma_i^A F \rho / \sum_{\{\sigma, \tilde{u}\}} \sigma_i^A \rho \\ & = \frac{\langle \sigma_i^A F \rangle}{\langle \sigma_i^A \rangle} = m_A^{-1} (m_A \langle F \rangle + \frac{1}{2} \langle F \sigma_i \rangle), \end{aligned}$$

where Eq. (4a) was used. Thus

$$m_A \langle F \rangle_{\sigma_i = +} = m_A \langle F \rangle + \frac{1}{2} \langle F \sigma_i \rangle \quad (32a)$$

and

$$m_B \langle F \rangle_{\sigma_i = -} = m_B \langle F \rangle - \frac{1}{2} \langle F \sigma_i \rangle. \quad (32b)$$

These may be combined to give

$$\langle F \rangle = m_A \langle F \rangle_{\sigma_i = +} + m_B \langle F \rangle_{\sigma_i = -} \quad (33a)$$

and

$$\langle \sigma_i F \rangle = 2m_A m_B (\langle F \rangle_{\sigma_i = +} - \langle F \rangle_{\sigma_i = -}). \quad (33b)$$

We also have the identities

$$m_A - m_B = \langle \tanh[\beta(E_0 + \lambda)] \rangle \quad (34a)$$

and

$$\langle \sigma_0 \sigma_i \rangle = \langle \sigma_i \tanh[\beta(E_0 + \lambda)] \rangle \quad (i \neq 0), \quad (34b)$$

which were obtained via Eq. (29) and the theorem of Sec. III. Condition (10) was employed in Eqs. (34). Using Eqs. (33), Eqs. (34) may be written

$$m_A - m_B = m_A \langle \tanh[\beta(E_0 + \lambda)] \rangle_{\sigma_i=+} + m_B \langle \tanh[\beta(E_0 + \lambda)] \rangle_{\sigma_i=-}$$

and

$$\langle \sigma_0 \sigma_i \rangle = 2m_A m_B \{ \langle \tanh[\beta(E_0 + \lambda)] \rangle_{\sigma_i=+} - \langle \tanh[\beta(E_0 + \lambda)] \rangle_{\sigma_i=-} \} \quad (i \neq 0).$$

The mean-field approximation consists in replacing  $E_0$  by its average value in the appropriate sub-ensemble, i. e.,  $E_0 \rightarrow \langle E_0 \rangle_{\sigma_i=+}$  or  $\langle E_0 \rangle_{\sigma_i=-}$ . Therefore, one writes

$$m_A - m_B \simeq m_A \tanh[\beta(\langle E_0 \rangle_{\sigma_i=+} + \lambda)] + m_B \tanh[\beta(\langle E_0 \rangle_{\sigma_i=-} + \lambda)] \quad (35a)$$

and

$$\langle \sigma_0 \sigma_i \rangle \simeq 2m_A m_B \{ \tanh[\beta(\langle E_0 \rangle_{\sigma_i=+} + \lambda)] - \tanh[\beta(\langle E_0 \rangle_{\sigma_i=-} + \lambda)] \} \quad (i \neq 0). \quad (35b)$$

From Eq. (32a) we have

$$\langle E_0 \rangle_{\sigma_i=+} = \langle E_0 \rangle + (2m_A)^{-1} \langle E_0 \sigma_i \rangle,$$

and similarly for  $\langle E_0 \rangle_{\sigma_i=-}$ . When these expressions are substituted into Eqs. (35) and  $\langle E_0 \rangle + \lambda$  is eliminated between Eqs. (35), one obtains

$$(m_A + m_B \alpha_{0i})(m_B + m_A \alpha_{0i})(1 - \alpha_{0i})^{-2} = m_A m_B \exp[(m_A m_B)^{-1} \beta \langle E_0 \sigma_i \rangle] \quad (i \neq 0), \quad (36)$$

where  $\langle \sigma_0 \sigma_i \rangle = 4m_A m_B \alpha_{0i}$ . The term  $\alpha_{0i}$  is the Cowley-Warren short-range-order parameter.<sup>14</sup>

When the atoms are of identical size and thermal motion is ignored,  $\tilde{u}_i = 0$  for all  $i$ , and Eq. (31) reduces to  $E_0 = -\sum_j W_{0j} \sigma_j$ , where the irrelevant constant  $\sum_j V_{0j}$  has been dropped; and when

$$\langle E_0 \sigma_i \rangle = -\sum_j W_{0j} \langle \sigma_j \sigma_i \rangle = -4m_A m_B \sum_j W_{0j} \alpha_{ji} \quad (37)$$

is substituted into Eq. (36) and the index  $i$  is allowed to range over all sites except  $i=0$ , the set of nonlinear equations due to Cowley<sup>14</sup> results. In the disordered phase, further simplification is possible because<sup>4</sup>

$$\alpha_{0i} \lesssim O(1/z), \quad \beta \langle E_0 \sigma_i \rangle \lesssim O(1/z),$$

where  $z$  is the number of sites interacting with a given site ( $z=12$  in an fcc crystal with nearest-neighbor interactions). It is therefore not a bad approximation to replace Eq. (36) by its leading order expansion in  $1/z$ :

$$\langle \sigma_0 \sigma_i \rangle = 4m_A m_B \beta \langle E_0 \sigma_i \rangle \quad (i \neq 0). \quad (38)$$

If Eq. (37) is substituted into Eq. (38), the set of linear equations due to Clapp and Moss<sup>5</sup> results. Equation (38) may also be regarded as a high-temperature (small- $\beta$ ) approximation.

When microscopic strains and thermal vibrations are present, one must evaluate  $\langle E_0 \sigma_i \rangle$  with  $E_0$  given by Eq. (31). Thus

$$\begin{aligned} \langle E_0 \sigma_i \rangle = & -\sum_n \{ \tilde{V}'_{0n} \langle i \tilde{n} \rangle - \frac{1}{2} \text{Tr}(\Phi_{0n}^V \langle i \tilde{n} \tilde{n} \rangle) \\ & + \text{Tr}(\Phi_{0n}^V \langle i \tilde{n} \tilde{0} \rangle) + W_{0n} \langle in \rangle + \tilde{W}'_{0n} (\langle in \tilde{n} \rangle - \langle in \tilde{0} \rangle) \\ & + \text{Tr}[\Phi_{0n}^W (\langle in \tilde{n} \tilde{0} \rangle - \frac{1}{2} \langle in \tilde{0} \tilde{0} \rangle - \frac{1}{2} \langle in \tilde{n} \tilde{n} \rangle)] \} \\ & (i \pm 0), \quad (39) \end{aligned}$$

where the following identity was used:

$$\tilde{u}' \bar{A} \tilde{v} = \text{Tr}[\bar{A} (\tilde{u} \tilde{v})],$$

where  $\bar{A}$  is real symmetric and the right-hand expression is the trace of the matrix product of  $\bar{A}$  and  $\tilde{u} \tilde{v}$ . If the x-ray scattering to  $O(\gamma^2)$  is required, it is only necessary to expand  $\langle E_0 \sigma_i \rangle$  to  $O(\gamma^2)$  in order to derive the set of equations which will yield concentration correlations which may be substituted into Eqs. (21) and (24). Here  $\langle E_0 \sigma_i \rangle$  is expanded to  $O(\gamma^3)$  because it is in this order that the triplet potentials appear, and these triplet potentials are of interest.<sup>4</sup> Substituting Eqs. (21) and (24) into Eq. (39) and retaining terms to  $O(\gamma^3)$ , one finds

$$\langle E_0 \sigma_i \rangle = -\sum_m \Gamma'_{0m} \langle mi \rangle - \frac{3}{2} \sum_{m,n} \Delta_{0mn} \langle mmi \rangle, \quad (40)$$

where  $\Gamma'_{0m}$  and  $\Delta_{0mn}$  will be defined below, and where the sums are unrestricted. To cast the theory into a familiar form it is necessary to restrict the sums. Consequently, we write

$$\begin{aligned} \langle E_0 \sigma_i \rangle = & -\sum_{m \neq 0} \Gamma_{0m} \langle mi \rangle - \frac{3}{2} \sum_{0 \neq m \neq n \neq 0} \Delta_{0mn} \langle mmi \rangle \\ & - \Gamma_{00} \langle 0i \rangle - 3 \sum_{m \neq 0} \Delta_{00m} \langle 0mi \rangle, \quad (41) \end{aligned}$$

where

$$\Gamma_{0m} = \Gamma'_{0m} + 3(m_B - m_A) \Delta_{0mm},$$

where Eq. (27) was used. Now because  $\langle 0i \rangle \lesssim O(1/z)$  and  $\langle 0mi \rangle \lesssim O(1/z^2)$  for  $0 \neq m \neq i \neq 0$  in the disordered phase (see Ref. 4) and because a summation contributes a factor of  $z$ , the last two terms in Eq. (41) are an order in  $1/z$  higher than the rest of the expression. The final term is always the smallest because it has the highest order in both  $1/z$  and  $\gamma$ , and we shall ignore it. The second-to-last term will be negligible if  $z \gg (\epsilon/2b)^{-1}$ . A good deal of manipulation yields the following expressions for  $\Gamma'_{0m}$ ,  $\Delta_{0mn}$ , and  $\Delta_{0mm}$ :

$$\Gamma'_{0m} = W_{0m} - \gamma^2 \left\{ \sum_k \bar{V}'_{0k} \bar{\xi}_{km} + \kappa T \text{Tr} \left[ \Phi_{0m}^W (G_{0m} - G_{00}) + \sum_{kl} (2\Phi_{0k}^V G_{0l} \Phi_{ml}^V G_{kl} - \Phi_{0k}^V G_{0l} \Phi_{ml}^V G_{km} - \Phi_{0k}^V G_{0m} \Phi_{lm}^V G_{kl} - \frac{1}{2} \Phi_{0k}^V G_{kl} \Phi_{ml}^V G_{kl}) \right] \right\}, \quad (42)$$

$$\Delta_{0mn} = \frac{1}{6} (\Delta'_{0mn} + \Delta'_{0nm} + \Delta'_{nm0} + \Delta'_{mno} + \Delta'_{n0m} + \Delta'_{m0n}), \quad (43a)$$

where

$$\Delta'_{0mn} = \gamma^3 \left\{ 2 \bar{\xi}'_{0n} \bar{W}_{mn} + 2 \sum_k \bar{\xi}'_{0m} \Phi_{0k}^V \bar{\xi}_{kn} + \sum_k \bar{\xi}'_{m k} \Phi_{0k}^V \bar{\xi}_{kn} + \kappa T \text{Tr} \left[ \sum_k \Phi_{0m}^W G_{0k} \Phi_{nk}^V (2G_{0n} - 2G_{mn} + G_{mk} - G_{0k}) + 2 \bar{A}_{0mn} \right] \right\}, \quad (43b)$$

where

$$\bar{A}_{0mn} = \sum_{jkl} \left( \frac{1}{3} \Phi_{0k}^V G_{kn} \Phi_{nj}^V G_{mj} \Phi_{ml}^V G_{0l} - \frac{1}{6} \Phi_{0k}^V G_{kl} \Phi_{ml}^V G_{lj} \Phi_{nj}^V G_{kj} - \Phi_{0k}^V G_{kn} \Phi_{nj}^V G_{jl} \Phi_{lm}^V G_{l0} + \Phi_{0k}^V G_{kj} \Phi_{jn}^V G_{mn} \Phi_{ml}^V G_{0l} + \Phi_{0k}^V G_{kj} \Phi_{nj}^V G_{jl} \Phi_{ml}^V G_{0l} - \frac{1}{2} \Phi_{0k}^V G_{kj} \Phi_{jn}^V G_{ln} \Phi_{ml}^V G_{l0} - \frac{1}{2} \Phi_{0k}^V G_{kj} \Phi_{jn}^V G_{jl} \Phi_{lm}^V G_{0m} \right), \quad (44)$$

and finally

$$\Delta_{0mm} = \frac{2}{3} \gamma^3 \left[ \bar{\xi}'_{0m} \bar{W}_{m0} + \sum_k (\bar{\xi}'_{0m} \Phi_{0k}^V \bar{\xi}_{km} + \bar{\xi}'_{0k} \Phi_{mk}^V \bar{\xi}_{km} + \frac{1}{2} \bar{\xi}'_{mk} \Phi_{0k}^V \bar{\xi}_{km}) + \kappa T \text{Tr} \left( \sum_k [\Phi_{0m}^W (G_{0k} - G_{mk}) \Phi_{mk}^V (G_{0m} - G_{00} + \frac{1}{2} G_{mk} - \frac{1}{2} G_{0k})] + \bar{A}_{0mm} + \bar{A}_{m0m} + \bar{A}_{mm0} \right) \right]. \quad (45)$$

Although these expressions are complicated, it is not difficult to evaluate them by computer once the Green's function is known.<sup>9</sup> As explained in Sec. IV, if the interatomic potentials are determined from elastic shear-modulus data, an arbitrary constant may be added to each of the interatomic potentials  $V^{AA}$ , etc. The only physically significant place in the theory where these constants show up is in the first term of Eq. (42). Therefore,  $W_{0m}$  is to be considered arbitrary, rather than  $O(\gamma^2)$ . In a nearest-neighbor-interaction model,  $W_{0m}$  can be determined from the critical-disordering temperature.

To find a linear set of equations in the concentration correlations, one substitutes Eq. (41), without the final term, into Eq. (38). This gives

$$\langle 0i \rangle = -4m_A m_B \beta (1 + 4m_A m_B \beta \Gamma_{00})^{-1} \times \left( \sum_m \Gamma_{0m} \langle mi \rangle + \frac{3}{2} \sum_{m,n} \Delta_{0mn} \langle mni \rangle \right) \quad (i \neq 0), \quad (46)$$

where it is understood that in the sums,  $\Gamma_{0m}$  and  $\Delta_{0mn}$  vanish if subscripts coincide. It is not possible to solve the set of Eqs. (46) as it stands because there are too many unknowns. However, if the term involving  $\Delta_{0mn}$ , which is an order in  $\gamma$  higher than the rest of the expression, is regarded as a perturbation, then Clapp's<sup>15</sup> relation between pair and triplet correlations may be used. This relation is based on the assumption that triplet or higher-order interaction potentials (i. e.,  $\Delta_{0mn}$ ) vanish. Thus triplet correlations obtained in this way will be correct to  $O(\gamma^2)$ , and they may be substituted properly into Eq. (46) to yield pair correlations correct to  $O(\gamma^3)$ . The short-range-order

component of the x-ray scattering may be computed to  $O(\gamma^3)$  using these pair correlations. To compute the other components to this order, it is necessary to take Eqs. (21) and (24) to another order in  $\gamma$ , and to determine fourth and higher-order concentration correlations, possibly by Clapp's procedure.<sup>15</sup> If we were to study the statistical mechanics of a disordered binary alloy with no atomic size disparity but with "effective" Hamiltonian

$$H = \frac{1}{2} \sum_{m,n} \Gamma_{mn} \sigma_m \sigma_n + \frac{1}{2} \sum_{lmn} \Delta_{lmn} \sigma_l \sigma_m \sigma_n,$$

where the last term is regarded as a perturbation and where  $\Gamma_{mn}$  and  $\Delta_{lmn}$  vanish for coincident subscripts, then we would obtain<sup>4</sup> exactly Eq. (46), except that  $\Gamma_{00} = 0$ . The equations could be solved in the same manner as above. Thus  $\Gamma_{mn}$  and  $\Delta_{lmn}$  may be regarded as effective pair and triplet interaction potentials.<sup>16</sup> There is also a rescaling of the temperature between the effective alloy and the "real" alloy given by

$$\beta_{\text{real}} = \beta_{\text{eff}} (1 - 4m_A m_B \beta_{\text{eff}} \Gamma_{00})^{-1}.$$

It is simpler if one needs the x-ray scattering correct to  $O(\gamma^2)$ , for then one needs to solve just

$$\langle 0i \rangle = -4m_A m_B \beta (1 + 4m_B m_A \beta \Gamma'_{00})^{-1}$$

$$\times \sum_m \Gamma'_{0m} \langle mi \rangle + C \delta_{0i},$$

where the last term removes the  $i \neq 0$  restriction. This has the Clapp-Moss form,<sup>5</sup> and their method may be used to solve for the pair correlations. The effective pair potential  $\Gamma'_{0m}$  given by Eq. (42)



has three parts. The term  $W_{0m}$  is present even without atomic size disparity. There is another temperature-independent term given by

$$\begin{aligned} \Gamma_{0m}'' &= -\sum_k \bar{v}'_{0k} \bar{\xi}_{km} = -\sum_{k,l} \bar{v}'_{0k} G_{kl} \bar{v}_{ml} \\ &= -\frac{1}{N} \sum_{\bar{q}} \bar{v}'(\bar{q}) [\Phi^U(\bar{q})]^{-1} \bar{v}(-\bar{q}) \cos(\bar{q} \cdot \bar{r}_{0m}), \end{aligned} \quad (47)$$

where

$$\bar{v}_{0k} = \frac{1}{N} \sum_{\bar{q}} \bar{v}(\bar{q}) \exp(-i\bar{q} \cdot \bar{r}_{0k}),$$

etc., and where Eq. (17), written as  $G(\bar{q}) = [\Phi^U(\bar{q})]^{-1}$ , was used. Equation (47) has exactly the same form as the interaction between point defects derived by Hardy and Bullough,<sup>17</sup> which makes the physical interpretation of this term clear. The third part of  $\Gamma_{0m}'$  is a temperature-dependent part which is probably less important than the other two for temperatures below the melting point, but it gives rise to the interesting result that the correlations become asymptotic to nonzero values as  $T \rightarrow \infty$ . To compute the x-ray scattering other than the short-range-order scattering, one needs to substitute the pair, triplet, and quadruplet concentration correlations into Eqs. (21) and (24). The triplets and quadruplets may be found by Clapp's relations,<sup>15</sup> or the quadruplets may be found by the following relation<sup>4</sup>:

$$\langle ijkl \rangle = \langle ij \rangle \langle kl \rangle + \langle ik \rangle \langle jl \rangle + \langle il \rangle \langle jk \rangle + O(1/z^3).$$

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#### APPENDIX A

An up-to-date account of the experimental analysis of small momentum-transfer kinematical-diffraction data and the associated diffraction theory has been given by Gragg and Cohen.<sup>18</sup> The results of this type of experiment may be compared quite directly with the predictions of the theory in this paper, and this appendix derives the relationship between the experimentally measured quantities and the various correlation functions.

The intensity distribution in reciprocal space of x rays or of elastic thermal neutrons scattered by a substitutional binary alloy is given in the kinematical approximation by

$$I(\bar{q}) = \left\langle \sum_{ij} f_i f_j \exp(i\bar{q} \cdot \bar{r}_{ij}) \right\rangle, \quad (A1)$$

where  $f_i$  is the atomic scattering factor (x rays) or the nuclear scattering length (neutrons) of the atom at site  $i$ . Ignoring possible isotopic variations in the case of neutrons, one may write

$$f_i = \sigma_i^A f_A + \sigma_i^B f_B = \bar{f} + \Delta f \sigma_i, \quad (A2)$$

where  $\bar{f} = m_A f_A + m_B f_B$  and  $\Delta f = \frac{1}{2}(f_A - f_B)$ , where Eqs. (4) were used, and where  $(f_A, f_B)$  is the atomic scattering factor of an atom of type (A, B). From Eq. (2) one obtains

$$\bar{r}_{ij} = (\bar{r}_{ij})_{av} + \bar{u}_j - \bar{u}_i. \quad (A3)$$

Substitution of Eqs. (A2) and (A3) into Eq. (A1) and expansion to second order in displacements yields

$$\begin{aligned} I(\bar{q}) &= \left\langle \sum_{ij} [\bar{f}^2 + \bar{f} \Delta f (\sigma_i + \sigma_j) + (\Delta f)^2 \sigma_i \sigma_j] \right. \\ &\quad \times \{ 1 + i\bar{q}'(\bar{u}_j - \bar{u}_i) - \frac{1}{2} [\bar{q}'(\bar{u}_j - \bar{u}_i)]^2 \} \\ &\quad \left. \times \exp[i\bar{q} \cdot (\bar{r}_{ij})_{av}] \right\rangle. \end{aligned} \quad (A4)$$

The expansion is valid for

$$|\bar{q}| \langle (u^2) \rangle^{1/2} \ll 1, \quad (A5)$$

or

$$4\pi(\sin\theta)\lambda^{-1} \langle (u^2) \rangle^{1/2} \ll 1. \quad (A6)$$

Equation (A5) gives meaning to the term "small-momentum transfers," and Eq. (A6) shows that this is equivalent to small scattering angles  $\theta$ , and/or small displacements compared to the wavelength of the radiation  $\lambda$ . Separating Eq. (A4) into the Bragg and diffuse components, one finds

$$N^{-1} I(\bar{q}) = I_{\text{Bragg}} + I_{\text{Diff}}, \quad (A7)$$

where

$$\begin{aligned} I_{\text{Bragg}} &= \bar{f}^2 \left( 1 - \frac{1}{3} q^2 \langle \bar{u}_0^2 \rangle - \frac{1}{3} \eta^{-1} q^2 \langle \sigma_0 \bar{u}_0^2 \rangle \right) \\ &\quad \times \sum_i \exp(i\bar{q} \cdot \bar{r}_{0i}) \end{aligned} \quad (A8)$$

and

$$\begin{aligned} I_{\text{Diff}} &= [4m_A m_B (\Delta f)^2] \\ &\quad \times [A(\bar{h}) + \bar{h}' \bar{B}(\bar{h}) + \bar{h}' \bar{C}(\bar{h}) \bar{h} + \bar{h}' \bar{D}(\bar{h}) \bar{h}], \end{aligned} \quad (A9)$$

where  $\bar{q} = 2\pi \bar{h} a^{-1}$  ( $a$  is the lattice parameter) and  $\eta = \bar{f}/\Delta f$ . The term in the first parentheses in Eq. (A8) is the Debye-Waller factor. In Eq. (A9) the diffuse scattering has been separated into components which Borie and Sparks<sup>19</sup> have shown can be isolated by processing the diffraction data in a way which exploits the different symmetry of each component. The component  $A(\bar{h})$  is known as the short-range-order scattering and is perfectly periodic in reciprocal space. The component

$\vec{h}'\vec{B}(\vec{h})$  is the size-effect scattering, and  $\vec{h}'[\vec{C}(\vec{h}) + \vec{D}(\vec{h})]\vec{h}$  contains both the thermal-diffuse scattering and the Huang scattering. The thermal-diffuse scattering and the Huang scattering have the same symmetry in reciprocal space, but in the classical harmonic theory the thermal-diffuse scattering is proportional to the absolute temperature whereas the Huang scattering is independent of temperature provided lattice-site occupancy is frozen. Thus thermal-diffuse scattering and Huang scattering may be separated by measurement of  $\vec{h}'[\vec{C}(\vec{h}) + \vec{D}(\vec{h})]\vec{h}$  at two temperatures and extrapolation to the absolute zero of temperature. Fourier coefficients for each component of the diffuse scattering are defined as follows (see Ref. 18):

$$A(\vec{h}) = \sum_{lmn} \alpha_{lmn} \cos(\pi h_x l) \cos(\pi h_y m) \cos(\pi h_z n), \quad (\text{A10a})$$

$$B_x(\vec{h}) = \sum_{lmn} \gamma_{lmn}^x \sin(\pi h_x l) \cos(\pi h_y m) \cos(\pi h_z n), \quad (\text{A10b})$$

$$C_{xx}(\vec{h}) = 0, \quad (\text{A10c})$$

$$C_{xy}(\vec{h}) = \frac{1}{2} \sum_{lmn} \epsilon_{lmn}^{xy} \sin(\pi h_x l) \sin(\pi h_y m) \cos(\pi h_z n), \quad (\text{A10d})$$

$$D_{xx}(\vec{h}) = \sum_{lmn} \delta_{lmn}^x \cos(\pi h_x l) \cos(\pi h_y m) \cos(\pi h_z n), \quad (\text{A10e})$$

$$D_{xy}(\vec{h}) = 0. \quad (\text{A10f})$$

The other elements of  $\vec{B}$ ,  $\vec{C}$ , and  $\vec{D}$  are found by permutation of  $x$ ,  $y$ , and  $z$ . The summations in Eqs. (A10) are over all triplets of integers  $(l, m, n)$  which obey one of the following conditions: (i) for an fcc crystal  $l + m + n$  is even, or (ii) for a bcc crystal  $l, m$ , and  $n$  are either all even or all odd. The precise nature of the symmetry of each of the components of the diffuse scattering is evident in Eqs. (A10). The sets of Fourier coefficients  $\{\alpha\}$ ,  $\{\gamma\}$ ,  $\{\epsilon\}$ , and  $\{\delta\}$  are the experimentally determined quantities in a diffraction study of an alloy.

It is clear from Eq. (A4) that each component of the diffuse scattering may be written explicitly in terms of the correlation functions (e. g.,  $\langle ij \rangle$ ,  $\langle i\bar{j} \rangle$ ,  $\langle \bar{i}\bar{j} \rangle$ , etc.), and when these expressions are compared with Eqs. (A10), relations between the ex-

perimentally determined Fourier coefficients and the correlation functions studied in this paper may be written down. These relations are the following:

$$\alpha_{lmn} = \langle \sigma_0 \sigma_{lmn} \rangle / 4m_A m_B, \quad (\text{A11a})$$

$$\gamma_{lmn}^x = -(\pi m_A m_B a) (\eta \langle \sigma_0 x_{lmn} \rangle + \langle \sigma_0 \sigma_{lmn} x_{lmn} \rangle), \quad (\text{A11b})$$

$$\begin{aligned} \epsilon_{lmn}^{xy} = & - [ 2\pi^2 / (m_A m_B a^2) ] (\eta^2 \langle x_0 y_{lmn} \rangle \\ & - \eta \langle \sigma_0 x_{lmn} y_{lmn} \rangle + 2\eta \langle \sigma_0 x_0 y_{lmn} \rangle \\ & - \langle \sigma_0 \sigma_{lmn} x_{lmn} y_{lmn} \rangle + \langle \sigma_0 \sigma_{lmn} x_0 y_{lmn} \rangle), \quad (\text{A11c}) \end{aligned}$$

$$\begin{aligned} \delta_{lmn}^x = & [ \pi^2 / (m_A m_B a^2) ] (\eta^2 \langle x_0 x_{lmn} \rangle - \eta \langle \sigma_0 x_{lmn}^2 \rangle \\ & + 2\eta \langle \sigma_0 x_0 x_{lmn} \rangle - \langle \sigma_0 \sigma_{lmn} x_{lmn}^2 \rangle \\ & + \langle \sigma_0 \sigma_{lmn} x_0 x_{lmn} \rangle), \quad (\text{A11d}) \end{aligned}$$

where  $x_{lmn}$  ( $y_{lmn}$ ) is the  $x$  ( $y$ ) component of  $\vec{u}$  at site  $(l, m, n)$ . These expressions show that the Cowley-Warren short-range-order parameters  $\{\alpha_{lmn}\}$  are the only true Fourier coefficients because  $\gamma$ ,  $\epsilon$ , and  $\delta$  all depend on position in reciprocal space through  $\eta$ . However,  $\eta$  is often quite slowly varying, and this dependence is weak. For neutrons,  $\eta$  is constant because the scattering lengths are constant and all of the Fourier coefficients are "true."

#### APPENDIX B

If  $\vec{B}$  is a real-symmetric matrix and  $\vec{A}$  is a vector, the three Gaussian integrals

$$\mathcal{I}_1 = \int \exp(-\vec{A}'\vec{x} - \vec{x}'\vec{B}\vec{x}) d^3\vec{x},$$

$$\mathcal{I}_2 = \int \vec{x} \exp(-\vec{A}'\vec{x} - \vec{x}'\vec{B}\vec{x}) d^3\vec{x},$$

$$\mathcal{I}_3 = \int \vec{x}\vec{x} \exp(-\vec{A}'\vec{x} - \vec{x}'\vec{B}\vec{x}) d^3\vec{x}$$

are given by

$$\begin{aligned} \mathcal{I}_1 = & \pi^{3/2} (\Lambda_{xx} \Lambda_{yy} \Lambda_{zz})^{-1/2} \exp(C_x^2 \Lambda_{xx}^{-1} \\ & + C_y^2 \Lambda_{yy}^{-1} + C_z^2 \Lambda_{zz}^{-1}), \end{aligned}$$

$$\mathcal{I}_2 = -\frac{1}{2} \vec{B}^{-1} \vec{A} \mathcal{I}_1,$$

$$\mathcal{I}_3 = \mathcal{I}_1 (\frac{1}{2} \vec{B}^{-1} + \vec{\mathcal{I}}_2 \vec{\mathcal{I}}_2^{-1} \mathcal{I}_1^{-2}),$$

where  $\vec{B}$  is diagonalized by an orthogonal matrix, so  $\vec{B} = \vec{S}' \vec{\Lambda} \vec{S}$ , where  $\vec{S}' \vec{S} = \vec{I}$  and  $\vec{\Lambda}$  is diagonal with elements  $\Lambda_{xx}$ , etc. The vector  $\vec{C}$  is given by  $\vec{C} = \frac{1}{2} \vec{S} \vec{A}$ .

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- See also Ref. 9.
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