PHYSICAL REVIEW B VOLUME 24, NUMBER 4 15 AUGUST 1981

Self-consistent theory for random alloys with short-range order

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(Received 17 November 1980)

In a previous paper, an analytic self-consistent cluster theory for random alloys was described; the only restriction on this theory was that the site-occupation random variables be independent (i.e., no short-range order). In this paper, we demonstrate that short-range order can be naturally included in this framework, thus providing a completely general theory for calculating the properties of random alloys. Using the augmented-space approach, we show that a short-range-order calculation requires little more than performing an independent-variables computation.

I. INTRODUCTION

Methods for calculating the properties of disordered solids have been investigated for many years.[1] The coherent potential approximation (CPA) of Soven[2] and Taylor[3] is recognized as the best single-site, self-consistent approximation for "diagonally disordered" Hamiltonians, and considerable effort has been directed toward eliminating the restrictions imposed by the CPA.[4–12] Mills and Ratanavararaksa,[13] still working with a diagonally disordered Hamiltonian, extended the CPA by including cluster scattering in an analytic self-consistent form. Soon thereafter, Kaplan *et al.*[14] (hereafter referred to as I) developed a generalization of the work of Mills and Ratanavararaksa which is applicable to general Hamiltonians (i.e., off-diagonal and environmental disorder). This theory is based on the augmented-space formalism[15,16] (ASF), and the only restriction is that the random variables describing the disordered system be independent. The purpose of the present paper is to show that short-range order (i.e., dependent random variables) can be naturally and simply included in this theory, thus completing the development of a general method for determining the properties of random alloys.

The approach used in this paper is based upon some basic theorems in measure theory; these theorems establish a relationship between the dependent random variables which describe the short-range order and the more tractable independent variables treated in I. As a consequence, computing the average Green's function for short-range order requires little more than performing an independent-variables calculation. This relationship and the averaging formalism are described in Sec. II with the detailed mathematical justification included in Appendix A. The approximations and their consequences are discussed in Sec. III. In Sec. IV model calculations for the electronic properties of a Markov chain are presented. While the formal presentation and model calculations are for electronic properties, the theory is applicable to any elementary excitations (phonons, magnons, excitons, etc.) Concluding remarks are presented in Sec. V.

II. FORMALISM

The theory presented in this paper is based on a relationship between the short-range-order problem and the independent-variables calculation (the problem solved in I). In this section we describe this relationship and then use the augmented-space formalism to solve for the configurationally averaged Green's function.

A. Mathematical introduction

The random alloy is constructed by occupying the lattice sites with atoms of type A or B. (We confine our discussion to binary alloys inasmuch as the extension to multicomponent systems is straightforward.) A random variable s_j is defined as equal to s_A or s_B if there is an A or B atom at site j, respectively. The short-range order is completely specified by the joint probability distributions $P_k(s_{j_1}, s_{j_2}, s_{j_3}, \ldots, s_{j_k})$ which determine the probability of finding any (finite) k sites of the alloy in a particular configuration. The simplest case that represents a realistic disordered alloy is one in which the random variables are independent,

$$P_k(s_{j_1}, s_{j_2},\ldots, s_{j_k}) = P_k^I(s_{j_1}, s_{j_2},\ldots,s_{j_k}) = P_1(s_{j_1})P_1(s_{j_2}) \cdots P_1(s_{j_k}) \,, \quad (2.1)$$

where $P_1(s_j)$ is the probability of occupying site j. It is this distribution for which a complete self-consistent approximation[14] for the averaged Green's function has been developed. In this paper we treat the general form of P where the random variables are dependent.

The key result that will be used is that there exists a function $\Phi(\{s_j\})$ such that

$$P(\{s_j\})\prod_j ds_j = \Phi(\{s_j\})\prod_j P_1(s_j)ds_j \,, \quad (2.2)$$

here $P(\{s_j\})$ is the short-range-order probability for a particular configuration of the entire solid. The proof of Eq. (2.2) is given in Appendix A [more precisely, it is shown that measures of the form given by the right-hand side of Eq. (2.2) converge "weakly" to the left-hand side]. The beauty of Eq. (2.2) is that it allows one to calculate configurational averages for a system with short-range order in terms of averages which are computed with respect to independent random variables. The price that is paid is the introduction of the unknown function Φ, but as will be shown, this presents no great difficulty.

B. Averaged Green's function

We begin by briefly reviewing the basic mathematical framework used in I; we refer the reader to that paper and the references cited therein for a more detailed treatment. The problem considered in I was to calculate the averaged Green's function $\bar G$,

$$\bar G_{nm}(E) = \int\int \cdots \int G_{nm}(\{s_l\},E)\prod_l P_1(s_l)ds_l \,, \quad (2.3)$$

where $G_{nm}(\{s_l\},E)$ is the n,m matrix element of the Green's function for the configuration $\{s_l\}$ and the random variables are independent as is indicated by the special choice of joint probability distribution, [Eq. (2.1)]. The calculation of $\bar G$ is accomplished by constructing the augmented space, $\Omega = \Psi \otimes \Theta$; Ψ is the Hilbert space of the original disordered Hamiltonian H, and Θ is the "disorder space" which allows for all possible configurations of the solid. The basis vectors for Ψ are denoted by $|n\rangle$ and there exists a vector $|f\rangle$ in Θ which is called the "ground state." The augmented-space Hamiltonian operator $\hat H$ acts on $|n\rangle \otimes |f\rangle \equiv |nf\rangle$ such that

$$\bar G_{n,m}(E) = \langle nf\,|(E\hat I - \hat H)^{-1}|\,mf\rangle \,. \quad (2.4)$$

The procedure for calculating $\bar G$ using Eq. (2.4) is discussed at length in I and it is not necessary to discuss it here. What is necessary for the present discussion is that calculations in I are carried out in terms of an orthonormal basis for Θ consisting of the vectors $|f_\sigma\rangle$, where σ is any finite set of lattice sites (by convention, $f = f_\emptyset$ where $\emptyset$ is the null set). The definition of $|f_\sigma\rangle$ can be found in Ref. 16.

We now consider the short-range-order problem of calculating the configurationally averaged Green's function,

$$[G_{n,m}]_{\rm av} = \int\int \cdots \int G_{n,m}(\{s_l\},E)P(\{s_l\})\prod_l ds_l \,. \quad (2.5)$$

($[G]_{\rm av}$ is used to distinguish averages over short-range order from the average over independent random variables $\bar G$.) Working directly with the augmented-space representation of the joint probability distribution P, as we did for independent random variables in I, is not possible, since the only formulation which is known for short-range order[17] is not translationally invariant. Translational invariance is essential in reducing the self-consistent equations in I to soluble form. There is the additional problem that for any physical system only a few of the joint probability distributions will be known. Therefore, one must approximate $[G]_{\rm av}$ in such a way that incorporates the known information and also "reasonably" approximates the unspecified distributions.

Appealing to Eq. (2.2), we have

$$[G]_{\rm av} = \int\int \cdots \int G(\{s_l\})P(\{s_l\})\prod_l ds_l = \int\int \cdots \int G(\{s_l\})\Phi(\{s_l\})\prod_l P_1(s_l)ds_l \,, \quad (2.6)$$

where $P_1(s_j = s_A) = c$ is the short-range-order concentration of A atoms. Using the standard techniques for independent random variables, we transform Eq. (2.6) to augmented space, with the result

$$[G_{n,m}(E)]_{\text{av}} = \langle nf \,|\, (E\hat{I} - \hat{H})^{-1}\hat{\Phi} \,|\, mf \rangle \ . \tag{2.7}$$

$\hat{G} = (E\hat{I} - \hat{H})^{-1}$ is the augmented-space Green's function constructed for independent random variables (with concentration c) and $\hat{\Phi} = I \otimes \tilde{\Phi}$, where $\tilde{\Phi}$ is the operator on Θ which corresponds to Φ and I is the identity on Ψ.

In order to use Eq. (2.7) we need to know $\tilde{\Phi}\,|f\rangle$. Using the basis $|f_\sigma\rangle$ for Θ we set

$$\tilde{\Phi}\,|f\rangle = \sum_\sigma a_\sigma |f_\sigma\rangle \ , \tag{2.8}$$

where the coefficients a_σ are to be determined. Substituting the expansion for $\tilde{\Phi}\,|f\rangle$ in Eq. (2.7) we have

$$[G_{n,m}(E)]_{\text{av}} = \sum_\sigma a_\sigma \langle nf \,|\, \hat{G}(E) \,|\, mf_\sigma \rangle = \sum_\sigma a_\sigma G'^{\sigma}_{n,m} \ . \tag{2.9}$$

The a_σ can be easily determined from the joint distribution functions. Since

$$\begin{aligned} 1 &= \int \cdots \int P(\{s_l\}) \prod_l ds_l \\ &= \int \cdots \int P^I(\{s_l\}) \Phi(\{s_l\}) \prod_l ds_l \ , \end{aligned} \tag{2.10a}$$

it follows that

$$\langle f \,|\, \tilde{\Phi} \,|\, f \rangle = 1 \ , \tag{2.10b}$$

and hence, $a_\varnothing = 1$. The first term in Eq. (2.9) is therefore the average Green's function $\bar{G}$ for independent variables. It is worth noting that the normalization of $[G]_{\text{av}}$ will always be correct since $\int_{-\infty}^{\infty} G'^{\sigma}_{00}(E)dE = 0$ except when $\sigma = \varnothing$. Therefore $\int_{-\infty}^{\infty} [G_{00}(E)]_{\text{av}} dE = \int_{-\infty}^{\infty} \bar{G}_{00}(E)dE$.

We evaluate the other coefficients by using $\tilde{\delta}(s_l = s_A)$, the projection operator on Θ which projects onto all configurations having an A atom at site l. (See Ref. 16 for a detailed definition of $\tilde{\delta}$.) To calculate a_l we use $\langle f \,|\, \tilde{\delta}(s_l = s_A)\tilde{\Phi} \,|\, f \rangle = P_1(s_l = s_A) = c$ to obtain

$$c = ca_\varnothing + [c(1-c)]^{1/2} a_l \ . \tag{2.11}$$

(a_l denotes a_σ where $\sigma = \{l\}$.) Thus, $a_\sigma = 0$ for all single-site subsets $\sigma = \{l\}$. This is not unexpected since a "single-site" calculation cannot use any information about correlations (which necessarily must involve two or more sites) and thus a "single-site short-range-order" calculation must reduce to an independent-variable approximation. We can systematically calculate the a_σ by using the relations

$$\begin{aligned} \langle f \,|\, \tilde{\delta}(s_l = s_A)\tilde{\delta}(s_{l'} = s_A)\tilde{\Phi} \,|\, f \rangle &= P_2(s_l = s_A, s_{l'} = s_A) \ , \\ \langle f \,|\, \tilde{\delta}(s_l = s_A)\tilde{\delta}(s_{l'} = s_A)\tilde{\delta}(s_{l''} = s_A)\tilde{\Phi} \,|\, f \rangle &= P_3(s_l = s_A, s_{l'} = s_A, s_{l''} = s_A) \ , \end{aligned} \tag{2.12}$$

etc. The details of these calculations are included in Appendix B; we list here a few of the results:

$$a_\varnothing = 1 \ , \tag{2.13a}$$

$$a_l = 0 \ , \tag{2.13b}$$

$$a_{ll'} = [P_{AA}(l,l') - c^2]/c(1-c) \ , \tag{2.13c}$$

$$a_{ll'l''} = \{P_{AAA}(l,l',l'') + 2c^3 - c[P_{AA}(l,l') + P_{AA}(l',l'') + P_{AA}(l,l'')]\}/[c(1-c)]^{3/2} \ , \tag{2.13d}$$

$$\begin{aligned} a_{l,l',l'',l'''} = \{ & P_{AAAA}(l,l',l'',l''') - 3c^4 + c^2[P_{AA}(l,l') + P_{AA}(l,l'') + P_{AA}(l,l''') + P_{AA}(l',l'') \\ & + P_{AA}(l',l''') + P_{AA}(l'',l''')] \\ & - c[P_{AAA}(l,l',l'') + P_{AAA}(l,l',l''') + P_{AAA}(l,l'',l''') + P_{AAA}(l',l'',l''')]\}/c^2(1-c)^2 \ . \end{aligned} \tag{2.13e}$$

In Eq. (2.13) we have used, for simplicity, $P_{AA}(l,l') = P_2(s_l = s_A, s_{l'} = s_A)$ and similar notation for the other distributions.

III. APPROXIMATIONS

In Sec. II, an exact expression [Eq. (2.9)] for the configurationally averaged Green's function was derived. To reduce the problem to a computationally tractable form, approximations are required; in this section, a method which meshes nicely with the theory of I is described.

The calculation of $[G]_{\text{av}}$ necessitates computing matrix elements of the (independent-variable) augmented-space Green's function $\hat{G}$. A self-consistent approximation for calculating the matrix elements $\langle nf \,|\, \hat{G} \,|\, mf \rangle$ (for any Hamiltonian) was described in I.[18] In I, the level of approximation is determined by the set T which consists of a finite number of classes of σ's (recall that σ denotes a finite subset of lattice sites; σ and σ' are in the same *class* if they are related by translational symmetry). For example, if $T = \{\sigma_1\}$, where σ_1 is the class of all single site σ, $\sigma_1 = \{\, \sigma = \{i\} \,\}$, we obtain the single-site approximation; if $T = \{\sigma_1, \sigma_2\}$, where $\sigma_2 = \{\, \sigma = \{i,j\},\ i,j \text{ nearest neighbors} \,\}$, we obtain the nearest-neighbor pair approximation.

Consider now $[G]_{\text{av}} = \sum a_\sigma G'^{\sigma}$, where the a_σ are determined by the joint probability distributions. The simplest (and we believe the most physical) approximation, is to restrict the summation to a finite number of classes of σ, i.e.,

$$[G]_{\text{av}} \sim \sum_{\sigma \in T} a_\sigma G'^{\sigma} . \tag{3.1}$$

The first term, $\sigma = \varnothing$, can be computed using the self-consistent approximation for the set T in I. Furthermore, once the self-consistent equations of I have been solved, it is a simple matter to compute the other needed matrix elements G'^{σ}, $\sigma \in T$. The details of this computation can be found in Appendix C. Thus the level of approximation to which the self-consistent theory is carried out is consistent with the choice of σ's included in the summation for $[G]_{\text{av}}$. Note that Eq. (3.1) is still an infinite sum, since there are an infinite number of σ's in each class, and $a_\sigma = a_{\sigma'}$ if σ and σ' are in the same class. However, the matrix elements $G'^{\sigma}_{n,m}$ die off as the sites denoted by σ get further away from n and m, and thus it is expected that only a finite number of terms need be calculated; we will illustrate this point in the next section.

In effect, we have set $a_\sigma = 0$ for $\sigma \notin T$; there are two consequences of this approximation. First, only a finite number of joint probability distributions can be included. This restriction is physically desirable since, for a real system, only a few distributions will be known. Indeed, the choice of T will generally be dictated by the known information. The second consequence of this approximation is that all distributions which are not specifically included are determined by the constraint $a_\sigma = 0$, $\sigma \notin T$. The effect of this constraint can best be demonstrated by example. Let us assume that the only known distribution other than $P_1(s_l = s_A) = c$ is for nearest-neighbor pairs l, l', i.e., $P_2(s_l = s_A,\ s_{l'} = s_A) = P_{AA}$ for $\{l, l'\} \in \sigma_2$. We thus have $a_\varnothing = 1$, $a_{\sigma_1} = 0$, $a_{\sigma_2} = (P_{AA} - c^2)/c(1-c)$ (σ_1 and σ_2 defined as above), and all other $a_\sigma = 0$. Let l, l', l'', l_1, and l_2 be such that of all possible pairs, only $\{l, l'\}$ and $\{l', l''\}$ are nearest neighbors. Using Eq. (2.13) and $a_\sigma = 0$ for $\sigma \notin T = \{\sigma_1, \sigma_2\}$, we find

$$P_{AA}(l, l_1) = c^2 , \tag{3.2a}$$

$$P_{AAA}(l, l_1, l_2) = c^3 , \tag{3.2b}$$

$$P_{AAA}(l, l', l_1) = c P_{AA} , \tag{3.2c}$$

$$P_{AAA}(l, l', l'') = 2c P_{AA} - c^3 . \tag{3.2d}$$

Equations (3.2a) and (3.2b) show that, in the approximation, non-nearest-neighbor sites are treated as independent, while Eq. (3.2c) shows that when a nearest-neighbor pair is taken together with a non-neighboring site, then the pair and the site are treated as independent. These are the results that would be anticipated from physical considerations. Equation (3.2d) points out the limitations of this approximation: When $P_{AA} < c^2/2$, the triplet probability is negative. If one considers Eq. (2.9) a perturbation series for $[G]_{\text{av}}$, with the independent variables $\bar{G}$ as the zeroth-order term, then it is reasonable to expect that the "stronger" the short-range order, the less reliable the truncated series (3.1). In this case the "strong" dependence of the random variables is indicated by $P_{AA} < c^2/2$. [Note that, for this example, P_{AAA} was studied; one must also check the other triplets (P_{ABA}, etc.) as well.] One consequence of allowing negative probabilities is that negative densities of states may occur (see Sec. IV).

There are two possible remedies for this situation. If the statistical information needed to evaluate more of the coefficients a_σ is available, one can enlarge the set T (thus doing a higher-order-cluster approximation for $\bar{G}$) and include more terms in the series (3.1). Alternatively, one can decide that $[G]_{\text{av}}$ and $\bar{G}$ are just too far apart for the "perturbation expansion" (3.1) to be useful, and that one must expand about a different "limit." Let G_p be the Green's function (assumed to be calculable) for this limit; for example, if the disorder is such that like atoms tend very strongly to group together, then G_p might be chosen as a linear combination of the A perfect-crystal and B perfect-crystal Green's functions. Using Eq. (2.9) we have

$$G_p = \sum_\sigma a^p_\sigma G'^{\sigma} , \tag{3.3}$$

and

$$\begin{aligned} [G]_{\text{av}} &= \sum_\sigma a_\sigma G'^{\sigma} - G_p + G_p \\ &= G_p + \sum_\sigma (a_\sigma - a^p_\sigma) G'^{\sigma} . \end{aligned} \tag{3.4}$$

The approximation would now insist that $a_\sigma - a_\sigma^p = 0$ for $\sigma \notin T$. Note that Eq. (2.13a) implies that $a_\varnothing = a_\varnothing^p = 1$, and thus the $\overline{G}$ term drops out of Eq. (3.4) as desired. It is possible that this approximation will also lead to negative probabilities, but it should give more reliable answers for the "strong" dependence limits. We will illustrate these ideas in the next section.

Finally, let us note that the self-consistent approximation of I produces Green's functions which are analytic and have the correct translational symmetry. Thus, this approximation for $[G]_{\text{av}}$ will also have these properties, as desired.[22]

IV. MARKOV CHAIN

The approximation described in Secs. II and III is quite general and can be applied to one-, two-, or three-dimensional alloys with any Hamiltonian and short-range order. In order to gain a better understanding of this approximation, we examine the simplest possible system for which the short-range order is easily defined and for which exact calculations are available for comparison, namely a Markov chain.[23] We calculate the electron density of states for an s-state tight-binding, binary A-B alloy with nearest-neighbor interactions,

$$\begin{gathered} H_{ij} = e(s_i)\delta_{ij} + W_{ij} , \\ e(s_i) = e_A \delta(s_i, s_A) + e_B \delta(s_i, s_B) , \\ W_{ij} = \begin{cases} W, & |i-j| = 1 \\ 0 & \text{otherwise} \end{cases} \end{gathered} \tag{4.1}$$

where $s_i = s_A$ or s_B with probabilities $c_A = c$ and $c_B = 1 - c$. For simplicity we have chosen to examine the case where only the diagonal element of the Hamiltonian is disordered.

In the case of a Markov chain,[23] all many-particle joint probability distributions can be written as an ordered product of pair distributions,

$$P_n(s_{l_1}, s_{l_2}, s_{l_3}, \ldots, s_{l_n}) = P_2(s_{l_1}, s_{l_2}) \frac{P_2(s_{l_2}, s_{l_3})}{P_1(s_{l_2})} \frac{P_2(s_{l_3}, s_{l_4})}{P_1(s_{l_3})} \cdots \frac{P_2(s_{l_{n-1}}, s_{l_n})}{P_1(s_{l_{n-1}})} , \tag{4.2}$$

where $l_1 < l_2 < l_3 < \cdots < l_n$. In fact all joint probability distributions are determined by the concentration c and the nearest-neighbor pair distribution $P_2(s_i = s_A, s_{i+1} = s_B) = P_{AB} = c - P_{AA}$, where $P_{AA} = P_2(s_i = s_A, s_{i+1} = s_A)$.

We approximate the averaged Green's function $[G]_{\text{av}}$ of the Markov chain by including the independent-variables-averaged Green's function $\overline{G}$, and the "first" correction, the nearest-neighbor pair terms. By symmetry all a_σ with $\sigma = \{i, i+1\}$ are equal and from Eq. (2.13c)

$$a_{i,i+1} = (P_{AA} - c^2)/c(1-c) . \tag{4.3}$$

All other a_σ are set equal to zero. Using (2.13) we find

$$P_{AA}(i,j) = c^2, \; j \neq i \pm 1 \tag{4.4a}$$

$$P_{AAA}(i, i+1, k) = cP_{AA}, \; k \neq i-1, i+2 \tag{4.4b}$$

$$P_{AAA}(i, i+1, i+2) = 2cP_{AA} - c^3 , \tag{4.4c}$$

$$P_{BBB}(i, i+1, i+2) = (1-c)(2P_{AA} + 1 - 2c - c^2) \tag{4.4d}$$

Using Eq. (3.1) and the nearest-neighbor (NN) pair approximation, the site-diagonal Green's function can be written as

$$[G_{00}(E)]_{\text{av}} = \overline{G}_{00}(E) + a_{01} \sum_{\substack{\sigma \\ \text{NN pairs}}} G_{00}^{\prime\sigma}(E) . \tag{4.5}$$

Note that the summation in Eq. (4.5) involves an infinite number of terms. Since $G_{00}^{\prime\sigma}$ drops off rapidly as $\sigma = \{i, i+1\}$ moves away from site 0, we anticipate that only a small number of terms is ever needed. This assumption proved true in all calculations for the Markov chain, where, as expected, the calculated Green's functions died off exponentially. Specifically only the first eight terms in Eq. (4.5) are needed to get three-significant-figure accuracy (the first 17 terms were actually calculated).

Equation (4.5), in conjunction with the self-consistent nearest-neighbor pair approximation described in I, was used to evaluate the density of states of the Markov chain. The details of evaluating $G_{00}^{\prime\sigma}$ are given in Appendix C. In Fig. 1, we compare the densities of states evaluated with the self-consistent pair approximation with essentially exact results obtained by node counting[24] for linear chains of 100 000 atoms with $e(A) = -e(B) = -2.5$, $W = 1.0$, $c = 0.5$, and $P_{AB} = 0.45 - 0.05$. $P_{AB} = 0.25$ corresponds to the independent-random-variables limit where the self-consistent approximation of I is applicable, $P_{AB} = 0.5$ corresponds to a perfect crystal of alternating A and B atoms, and $P_{AB}=0$ corresponds to a chain in which all the A atoms have segregated out from the B atoms producing two separate perfect chains. Only the positive energies are plotted since, for $c=0.5$ and the above choice of parameters, the density of states is symmetric about $E=0$. The small tails at the band edges are due to the small imaginary part which was added to E for computational purposes.

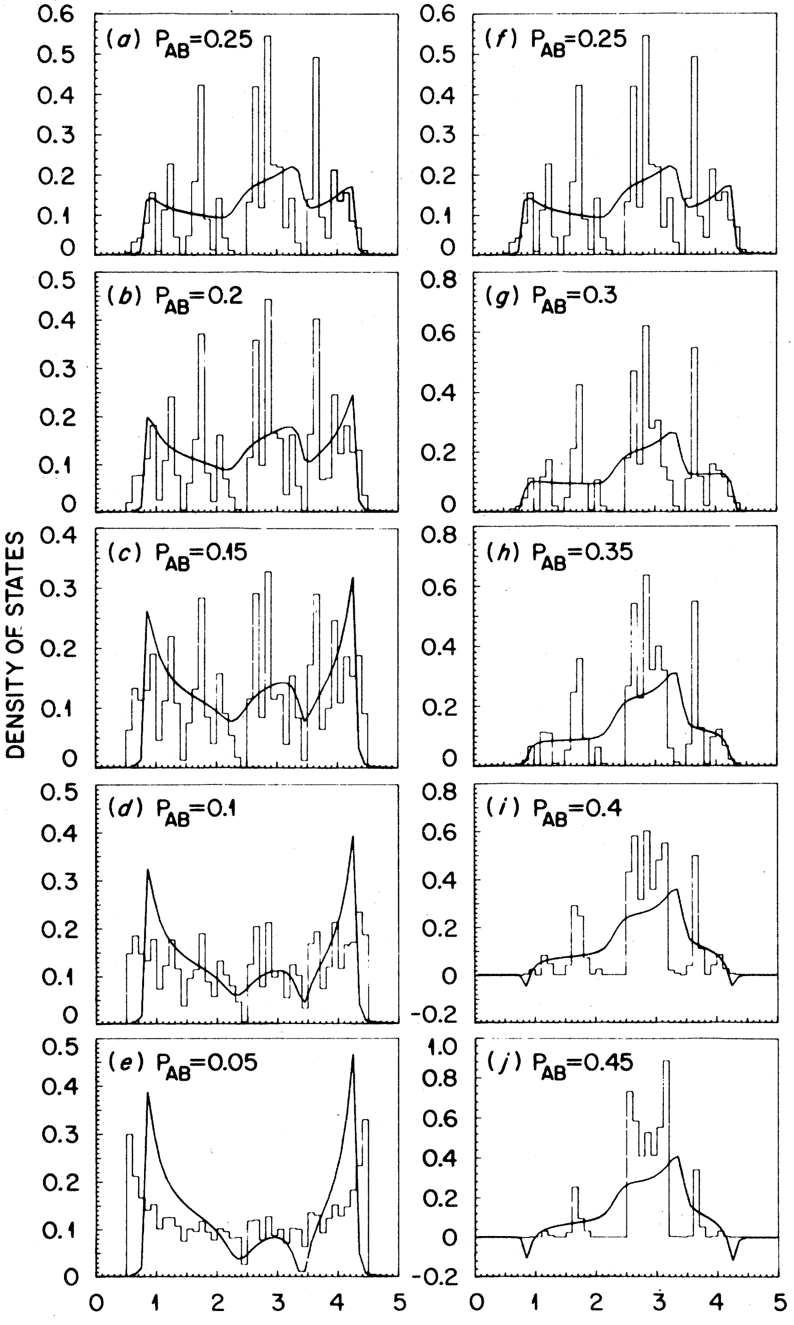

FIG. 1. Density of states for electrons in a Markov chain with $e(A)=-e(B)=-2.5$, $W=1.0$, $c=0.5$, and $P_{AB}=0.05-0.45$. Comparison of the exact results (histogram) with the nearest-neighbor-pair approximation expanded relative to the independent-random-variables average Green's function ($P_{AB}=0.25$).

In Figs. 1(a)—1(e), we have plotted the densities of states of the Markov chain as it changes from the independent case $P_{AB} = 0.25$ at the top, towards the almost segregated crystal $P_{AB} = 0.05$ at the bottom. In Figs. 1(f)—1(j), the changes from independent variables towards the almost perfect alternating crystal $P_{AB} = 0.45$ are plotted. The first column shows an increase near the band edges and a corresponding decrease at the center as P_{AB} decreases. The second column shows the opposite behavior for P_{AB} increasing. The approximation gives good agreement with the exact results in the range from $P_{AB} = 0.15-0.35$. The approximation does not pick up the extremely peaked behavior, but it does show good overall agreement with major structure in the density of states. Such agreement in one dimension indicates far superior results in three dimensions. A comparison of the one-[14] and three[13]-dimensional self-consistent results for diagonal disorder demonstrates this effect.

In the regime of stronger short-range order, where P_{AB} is very large or very small, the match with exact results is not as good. At $P_{AB} = 0.1$ and 0.05 the band edges show an excessively peaked structure which falls short of the band edge. The $P_{AB} = 0.4$ and 0.45 plots show regions of negative density just beyond the band edges. $P_{AB} = 0.1$ and 0.05 correspond to $P_{BBB} < 0$ [Eq. (4.4d)] and $P_{AB} = 0.4$ and 0.45 correspond to $P_{AAA} < 0$ [Eq. (4.4c)]. Solving Eqs. (4.4c) and (4.4d) for the transitions to negative distributions yields $P_{BBB} \leq 0$ for $P_{AB} \leq 0.125$ and $P_{AAA} \leq 0$ for $P_{AB} \geq 0.375$. As mentioned in Sec. III these negative distributions indicate where the pair approximation is less reliable.

One can improve the approximation by either including more distributions exactly or by using the expansion for the averaged Green's function which starts at a perfect-crystal limit of the short-range order. Since in the preceding model calculations we have experienced some difficulty near the perfect-crystal limits and since it is simplest to change the expansion, we have recalculated the examples in Figs. 1(c), 1(d), 1(i), and 1(j) using the latter of the two methods mentioned above. Using Eq. (3.4) and the nearest-neighbor-pair approximation, the site-diagonal averaged Green's function can be written as

$$[G_{00}(E)]_{\rm av} = G^{P}_{00}(E) + (a_{01} - a^{P}_{01}) \sum_{\substack{\sigma \\ \text{NN pairs}}} G'^{\sigma}_{00}(E) \; . \tag{4.6}$$

For $P_{AB} = 0$, where A and B atoms segregate into two separate chains we find, using Eq. (4.3),

$$G^{P}_{00}(E) = cG^{A}_{00}(E) + (1-c)G^{B}_{00}(E) \; , \tag{4.7a}$$

$$a^{P}_{01} = 1 \; , \tag{4.7b}$$

where $G^{A}_{00}(E)$ is the Green's function for a linear chain composed of only A atoms. For $P_{AB} = 0.5$, $G^{P}_{00}(E)$ is the Green's function for a perfect linear chain of alternating A and B atoms, and

$$a^{P}_{01} = -1 \; . \tag{4.8}$$

In Fig. 2, we have recalculated the densities of states for the model system of Fig. 1 with $P_{AB} = 0.05$ and 0.1 using the pair approximation expansion from the segregated crystal, $P_{AB} = 0$ [Eqs. (4.6) and (4.7)]. For $P_{AB} = 0.05$ [Fig. 2(b)], we notice a significant improvement over the expansion from independent random variables given in Fig. 1(e), particularly at the band edges. At $P_{AB} = 0.1$ the expansion with respect to $P_{AB} = 0$ is

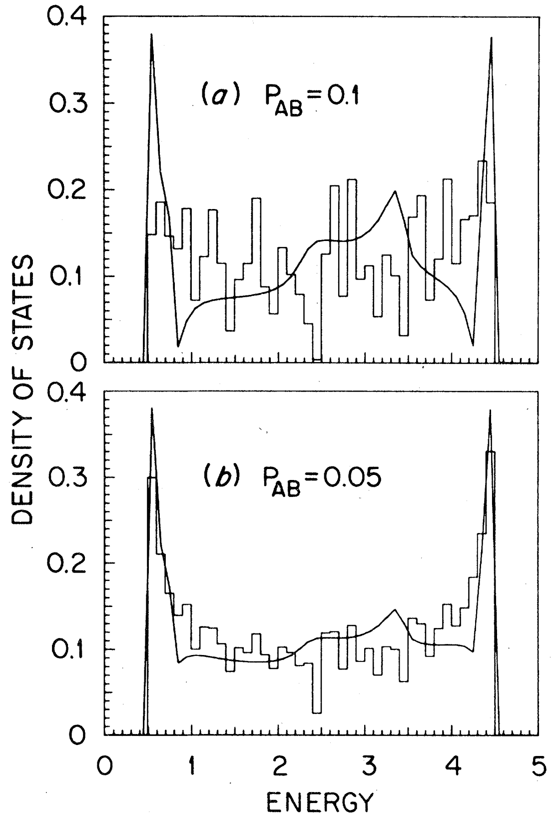

FIG. 2. Density of states for electrons in a Markov chain with $e(A) = -e(B) = -2.5$, $W = 1.0$, $c = 0.5$, and $P_{AB} = 0.05$, 0.1. Comparison of the exact results (histogram) with the nearest-neighbor-pair approximation expanded relative to the segregated perfect-crystal limit ($P_{AB} = 0$).

no longer good [Fig. 2(a)] and we would need to include more distributions exactly (i.e., use a high-order approximation) to improve the results.

In Fig. 3, we show examples of the pair-approximation expansion with respect to the perfect alternating crystal, $P_{AB} = 0.5$ [Eqs. (4.6) and (4.8)]. Again we have recalculated two of the cases treated in Fig. 1, $P_{AB} = 0.4$ and 0.45. For $P_{AB} = 0.45$ [Fig. 3(b)], we find the approximation picks up the sharp structure at the center of the band while only showing a general indication of the peripheral structure. Furthermore in the band gaps the density becomes slightly negative. The independent-random-variable approximation shown in Fig. 1(j) misses the sharpness of the central structure and shows a much smoother density which becomes negative at the band edges. In both cases the negative densities appear where the approximation is attempting to drive the density of states to zero. For $P_{AB} = 0.4$ [Fig. 3(a)], we again find that the approximation is no longer as good. Note that the expansion with respect to the independent-random-variables average has a significantly greater range of reliability than does either of the perfect-crystal expansions. This is to be expected since the expansions from the perfect-crystal limits are dominated by only one particular configuration of the alloy.

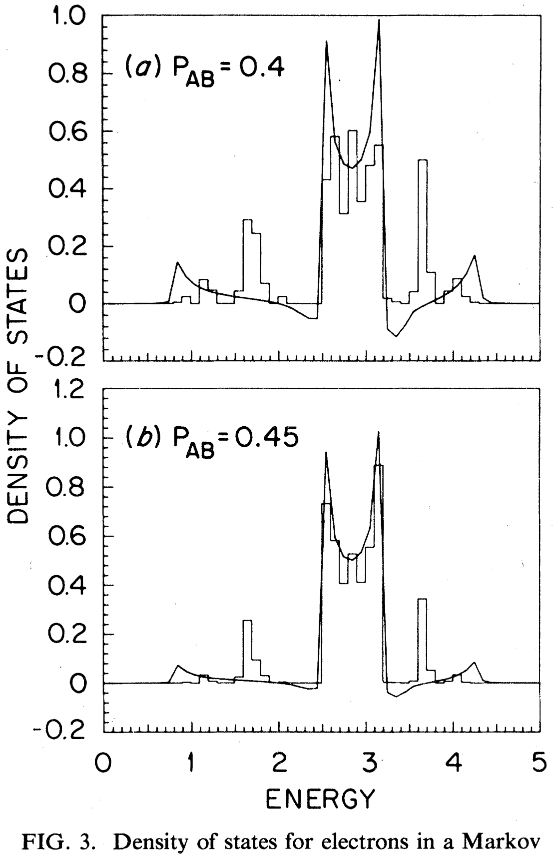

FIG. 3. Density of states for electrons in a Markov chain with $e(A) = -e(B) = -2.5$, $W = 1.0$, $c = 0.5$, and $P_{AB} = 0.4, 0.45$. Comparison of the exact results (histogram) with the nearest-neighbor pair approximation expanded relative to the alternating perfect-crystal limit ($P_{AB} = 0.5$).

V. CONCLUSION

We have presented a self-consistent approximation for calculating the properties of disordered alloys with short-range order. The approximation is based on a relationship between the joint probability distributions for dependent and independent random variables. The approximation is constructed by coupling this relation with the operator methods of augmented space and the self-consistent theory for independent random variables.[14]

The use of the self-consistent theory guarantees that the averaged Green's function has the proper translational symmetry and is analytic. The theory also exhibits the proper behavior in the dilute, weak-scattering and strong-scattering limits. Furthermore, the major part of the computational effort which is involved in utilizing this approximation lies in solving the self-consistent equations of I. Once this solution is known it is relatively simple to calculate the Green's function for the short-range-order system.

The short-range order is included in the approximation in a physically realistic manner, i.e., only a finite number of the joint probability distributions for the alloy are needed to construct the approximation. For any real system only a few distributions will ever be known.

Example calculations for a Markov chain with nearest-neighbor-pair distributions show good overall agreement with exact results. In three dimensions we expect significantly better agreement since much of the structure in the exact density of states tends to disappear as each atom "sees" a more nearly average environment. A comparison of the results for the limiting case of diagonal disorder and independent random variables for one[14] and three[13] dimensions provides a clear demonstration of this point.

Although the theory and model calculations have been presented for a random alloy, formally this method is applicable to any disordered system with short-range order, such as amorphous solids. The continuous nature of the position random variables for an amorphous solid introduces significant computational difficulties in this theory. We hope to examine this problem in a future publication.

ACKNOWLEDGMENTS

The authors are grateful to R. L. Mills and P. L. Leath for helpful conversations. This research was sponsored by the Division of Materials Sciences, and the Applied Mathematical Sciences Research Program, Office of Energy Research, U. S. Department of Energy under Contract No. W-7405-eng-26 with Union Carbide Corporation.

APPENDIX A: MATHEMATICAL JUSTIFICATION OF EQ. (2.2)

As in Sec. II, we let s_j denote the site occupation random variable for site j; $s_j = s_A(s_B)$ if an A atom (B atom) is present at site j. The collection of variables $\{s_j\}_{j\in J} = S$, where J is the set of all sites, comprise a *strictly stationary stochastic process* ,[25] which means that all joint probability distributions $P_k(s_{j_1}, s_{j_2}, \dots, s_{j_k})$ are invariant under translation. These distributions characterize the process. A mathematically equivalent way of viewing stochastic processes is in terms of a measure[26] on the space of all possible realizations (configurations) of the process. The distributions P_k define a measure m_s on the space X of all functions f mapping J into the two-element set $\{s_A, s_B\}$; $X = \{ f \mid f: J \to \{s_A, s_B\} \}$. One can think of X as the space of all possible configurations of the solid, and the measure m_s indicates which configurations are "important" or highly probable.

There are two concepts concerning measures that will be used. If μ_1 and μ_2 are measures on the space Y, then μ_1 is said to be *absolutely continuous with respect to* μ_2, $\mu_1 < \mu_2$, if $A \subset Y$ and $\mu_2(A) = 0$ implies $\mu_1(A) = 0$. The measures μ_1 and μ_2 are called *singular,* $\mu_1 \perp \mu_2$, if there is a set B such that $\mu_1(B) = \mu_2(B^c) = 0$. Here B^c is the complement of B. Loosely speaking, absolute continuity and singularity are opposite extremes; the former says that μ_1 is "concentrated" on the same set (of configurations) as μ_2, while the latter condition requires that they be "concentrated" on disjoint sets.

A basic result about absolutely continuous measures goes under the name of the Radon-Nikodym theorem.[27]

Theorem. If $\mu_1 < \mu_2$, then there exists a function $\Phi(y): Y \to R$, where R is the real line, such that for any $A \subset Y$, $\mu_1(A) = \int_A \Phi(y) d\mu_2(y)$.

The function Φ is called the Radon-Nikodym derivative of μ_1 with respect to μ_2, and is denoted by $d\mu_1(y)/d\mu_2(y)$. This notation is often suggestive, in that correct results follow from formal manipulation. For example,[28]

$$\int_Y g(y) d\mu_1(y) = \int_Y g(y) \frac{d\mu_1(y)}{d\mu_2(y)} d\mu_2(y)$$

$$= \int_Y g(y) \Phi(y) d\mu_2(y) \, . \qquad \text{(A1)}$$

We may thus write

$$d\mu_1 = \Phi d\mu_2 \, , \qquad \text{(A2)}$$

which is precisely Eq. (2.2). In the situation of interest to us, μ_1 is the short-range-order measure m_S, and μ_2 is the measure generated by independent variables (with the same concentration of A atoms as m_S. Denote this measure by m_c.

Note that Eq. (A2) [or (2.2)] is valid under the assumption that $m_S < m_c$. However it follows from ergodicity[29] that $m_S \perp m_c$,[30] and therefore it might seem that the Radon-Nikodym theorem is of no use. Nevertheless, we are certainly free to *approximate* m_S by a measure m which does satisfy $m < m_c$ and apply Radon-Nikodym to m and m_c. The question then arises as to whether we can adequately approximate m_S by measures m which satisfy $m < m_c$ when in fact $m_S \perp m_c$. The following simple example is very instructive: let m_L be the uniform (Lebesgue) measure on the interval [-1,1], and m_D the Dirac-point measure at $x = 0$. Clearly, $m_L \perp m_D$. Now let m_ϵ be the measures corresponding to (truncated) Gaussian distributions with mean 0 and standard deviation ϵ. Note that $m_\epsilon < m_L$, and yet

$$\lim_{\epsilon \to 0} \int f(x) dm_\epsilon(x) = \int f(x) dm_D(x) \qquad \text{(A3)}$$

for any continuous $f(x)$. Thus m_ϵ converges "weakly" to m_D despite the fact that $m_\epsilon \perp m_D$ for all ϵ.

This is, in effect, what is done in Sec. III. The measure m_S is approximated by a measure m_T such that $m_T < m_c$ (and thus Radon-Nikodym can be used). The accuracy of the approximation is determined by the size of the set T, or equivalently, by how many joint probability distributions are used to define m_T (recall that m_T is defined by $a_\sigma = 0$ for $\sigma \notin T$ and a_σ for $\sigma \notin T$ as computed using the joint distributions). It follows directly from the definition of the integral that this sequence (more precisely, net) of approximating measures converges (as the set T becomes large) weakly to m_S,and thus in this limit, Eq. (2.9) is correct.

APPENDIX B: EVALUATION OF a_σ

In order to evaluate the a_σ's in Eq. (2.9) we need only the normalization condition Eq. (2.10), the expressing of the joint probability distributions in terms of augmented-space projection operators, Eq. (2.12), and the relation[16]

$$\widetilde{\delta}(s_l = s_A)\,|f\rangle = c\;|f\rangle + [c(1-c)]^{1/2}\,|f_l\rangle \;. \tag{B1}$$

Using the expansion for $\widetilde{\Phi}$ [Eq. (2.8)] and its normalization we have

$$\langle f\,|\,\widetilde{\Phi}\,|\,f\rangle = a_\emptyset = 1 \;. \tag{B2}$$

Next we use the single-particle distribution:

$$\begin{aligned} P_1(s_l = s_A) = c &= \langle f\,|\,\widetilde{\delta}(s_l = s_A)\widetilde{\Phi}\,|\,f\rangle \;,\\ &= c a_\emptyset + a_l[c(1-c)]^{1/2} \;. \end{aligned} \tag{B3}$$

Using (B2) we find $a_l = 0$. For the two-particle distribution we have

$$\begin{aligned} P_{AA}(l,l') &= \langle f\,|\,\widetilde{\delta}(s_l = s_A)\widetilde{\delta}(s_{l'} = s_A)\widetilde{\Phi}\,|\,f\rangle \;,\\ &= a_\emptyset c^2 + a_{ll'}c(1-c) \;. \end{aligned} \tag{B4}$$

solving for $a_{ll'}$ yields,

$$a_{ll'} = [P_{AA}(l,\,l') - c^2]/c(1-c) \;. \tag{B5}$$

Similarly for three-particle distribution we find

$$\begin{aligned} P_{AAA}(l,l',l'') &= \langle f\,|\,\widetilde{\delta}(s_l = s_A)\widetilde{\delta}(s_{l'} = s_A)\widetilde{\delta}(s_{l''} = s_A)\widetilde{\Phi}\,|\,f\rangle \\ &= c^3 + c^2(1-c)(a_{ll'} + a_{l'l''} + a_{ll''}) + [c(1-c)]^{3/2}a_{ll'l''} \;. \end{aligned} \tag{B6}$$

Substituting the expression for $a_{ll'}$ in (B5) gives

$$P_{AAA}(l,l',l'') = c^3 + c\,[P_{AA}(l,l') + P_{AA}(l',l'') + P_{AA}(l,l'') - 3c^2] + [c(1-c)]^{3/2}a_{ll'l''} \tag{B7}$$

and

$$a_{ll'l''} = \{P_{AAA}(l,l',l'') + 2c^3 - c\,[P_{AA}(l,l') + P_{AA}(l',l'') + P_{AA}(l,l'')]\}/[c(1-c)]^{3/2} \;.$$

All other a_σ can be determined in the same manner using higher-order distribution functions.

APPENDIX C: CALCULATION OF G'^{σ} USING THE SELF-CONSISTENT APPROXIMATION

In this appendix we describe how to compute the matrix elements $G'^{\sigma}_{m,n} = \langle mf\,|\,\hat{G}\,|\,nf_\sigma\rangle = \langle nf_\sigma\,|\,\hat{G}\,|\,mf\rangle$ which are needed to approximate $[G_{m,n}]_{\text{av}}$ in Eq. (2.9). The procedure is similar to that used in Appendix D in Paper I. We follow the notation used there. If $n = i + \alpha$ and $m = i + \beta$, then by translational invariance

$$\begin{aligned} G'^{\sigma_u(i)}_{m,n} &= \langle nf_{\sigma_u(i)}\,|\,\hat{G}\,|\,mf\rangle \\ &= \frac{1}{N}\sum_i \langle (i+\alpha)f_{\sigma_u(i)}\,|\,\hat{G}\,|\,(i+\beta)f\rangle \;. \end{aligned} \tag{C1}$$

Using rèlation (D5) of I, we have

$$G'^{\sigma_u(i)}_{m,n} = -\frac{1}{N}\sum_{ijr}\sum_{lu'} F^{\sigma_u(i)\sigma_{u'}(l)}_{i+\alpha,j}\, K'^{\dagger\sigma_{u'}(l)}_{j,r}\, \overline{G}_{r,i+\beta} \;. \tag{C2}$$

If we Fourier transform on the sites in the disorder space according to Eq. (3.8) of I we have

$$\begin{aligned} G'^{\sigma_u(i)}_{m,n} = -\frac{1}{N^2}\sum_{ijr}\sum_{u'l}\sum_{\vec{q}} F(\vec{q})^{\sigma_u,\sigma_{u'}}_{\alpha,j-l}\, e^{i\vec{q}\cdot\vec{R}_{il}} \\ \times K'^{\dagger\sigma_{u'}}_{j-l,n-l}\,\overline{G}_{n,i+\beta} \;. \end{aligned} \tag{C3}$$

If we now Fourier transform $\overline{G}$ on real site indices the equation can be reduced to the form

$$\begin{aligned} G'^{\sigma_u(i)}_{m,n} = -\frac{1}{N}\sum_{u'}\sum_{ss'}\sum_{\vec{q}} F(\vec{q})^{\sigma_u\sigma_u'}_{\alpha,s'} \\ \times K'^{\dagger\sigma_{u'}}_{s',s}\, e^{i\vec{q}\cdot\vec{R}_{s\beta}}\,\overline{G}(\vec{q}) \;. \end{aligned} \tag{C4}$$

Every term in (C4) is evaluated in the course of solving the self-consistent equations except those elements of F outside of the space projected by the P^σ (which are defined in I). However, by using the matrix $P^\sigma G^\sigma P^\sigma$ and Eqs. (3.16) and (3.17) of I, one can generate any matrix element of F.

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