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Random binary alloy. I. Formulation of the method of the distribution function

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We present a model of a binary alloy in which the pair interaction potentials (both nearest and next-nearest neighbor) are assumed to be randomly distributed over the lattice bonds. In this paper we derive the statistical mechanics of the alloy using the method of the distribution function. Substantial modification of the method is required to account for the nature of alloy ordering, which necessitates the introduction of sublattices of the basic lattice, and to accommodate the inclusion of second-neighbor interactions. We derive the thermodynamic potential for the alloy and show that it has the required stationarity properties.

I. INTRODUCTION

Studies of ordering in alloys have been carried out using many different techniques since the earliest theoretical discussion of the phenomenon by Bragg and Williams.[1] Describing a binary alloy using a lattice model, which is equivalent to an Ising model for an antiferromagnet, they applied a mean-field approximation to derive the behavior of the system. Subsequent work by Bethe[2] and Peierls,[3] Cowley,[4] and Clapp and Moss[5] included considerations of short-range order in such alloys. In all of these studies the model for the alloy was essentially the same and, in particular, the interaction potentials between atoms on neighboring sites were assumed to be constant over the entire lattice. The effect of any irregularities in the lattice was ignored. We attempt to include such features by allowing the interaction potentials between atoms to vary from site to site over the lattice. Also there have recently been developments in the preparation and study of metallic glasses which are formed by rapid cooling from a melt.[6] There is evidence[7] that some metallic glasses[8] possess a degree of chemical ordering. The model we present in this paper for an alloy with quenched randomness could describe such metallic glasses, provided the time scale for the ordering process (i.e., the interchange of atoms of different species) is shorter than the time scale for quenching the system.

We introduce a model which describes a randomly distorted, loose-packed structure. We maintain a lattice, but the distance, and therefore interaction, between atoms varies randomly. We describe the variation of the pairwise interatomic potentials (both nearest- and next-nearest-neighbor) using random probability distributions. In this paper we derive the thermodynamic potential of a random binary alloy (RBA) on a body-centered-cubic (bcc) or simple cubic (sc) lattice. Our model is closely related to the spin-glass model of Sherrington and Kirkpatrick[9] (SK) and the disordered lattice gas described by Inawashiro, Frankel, and Thompson[10] (IFT). However, our model is characterized by the presence in the Hamiltonian of random potentials (or random fields in magnetic terms). These random potentials are generated by the random pair interactions and hence the two terms in the Hamiltonian (see Sec. II) must always occur together. Since the work of Imry and Ma,[11] random-field problems in magnetic systems have been studied extensively.[12,13] Our model is therefore of interest as we are modeling systems (the metallic glasses) in which the effects of random interactions and random potentials may be observable at the same time. In magnetic systems, however, random-field problems can occur in systems without random interactions and, perhaps more importantly, random interactions do not necessarily imply the presence of random external fields.[9,14–18]

There are two main techniques used for deriving the statistical mechanics of random systems. The first, developed by Edwards and Anderson[14] in their original discussions of spin glasses, is the "n-replica" method. This approach was also used, within the framework of the mean-field approximation[19] (MFA), by SK to derive the order parameters and thermodynamic functions for the spin-glass phase. The second technique, the method of the distribution function, was initiated independently by Marshall[20] and Matsubara[21] and was used by IFT, also within the MFA, to study the disordered lattice gas. In this work we use the latter technique and follow closely the development of the method given by IFT.

The SK solution has been shown[22–24] to be incorrect at low temperatures (where it predicts negative entropy). In addition, Parisi[23] and Sompolinsky[24] have shown independently that the single Edwards and Anderson (EA) order parameter $\langle\langle s\rangle_T\rangle_R$ (where $\langle\ \rangle_T$ is a thermodynamic average and $\langle\ \rangle_R$ is an average over the randomness in the system), which is also used by SK, is insufficient to describe ordering in the spin-glass phase. A recent review by Young[25] describes the current theory of spin glasses and, in particular, discusses the nature of the order parameters required to describe the spin-glass phase. However, in this paper we only consider the simple one-parameter description of glasslike phases. The main interest in this work lies in determining whether there are any significant differences between the random order-disorder system and random magnetic systems.

In extending the method of the distribution function to study alloys, we encounter two problems. Firstly, the nature of alloy ordering requires the introduction of sublattices to describe the ordered state. For both the bcc and sc lattices a two-sublattice structure is considered here for simplicity. Of course, more complicated ordered structures other than those we have considered do exist, but they require the subdivision of the lattice into more sublattices. The second difficulty arises from the simultaneous treatment of both nearest- and next-nearest-neighbor interactions. The inclusion of both nearest- and next-nearest-neighbor interactions does however seem natural in view of the fact that to derive detailed numerical results[26] we need to work within the MFA.

This paper addresses these two problems and presents a formulation of the method of the distribution function which takes them both into account. In Sec. II we describe our model of the RBA and set up its Hamiltonian. We apply a pair approximation to this system in Sec. III. This requires the definition of several effective potentials at each lattice site, and in Sec. IV we introduce distribution functions for each effective potential. Here, we also derive integral equations which the distribution functions must satisfy. Section V contains a discussion of the thermodynamic potential for the RBA and we show that the integral equations for the distribution functions found in Sec. IV ensure the stationarity of the potential. Section VI contains a brief discussion of the results we have derived. In the following paper[26] we will present results of some detailed calculations on the RBA with specific forms chosen for the probability distributions of the pair interaction potentials and discuss the physical significance of our results.

II. THE MODEL AND HAMILTONIAN

Our model of the RBA is based on the lattice model of a binary alloy described by Huang[27] and Thompson.[28] We consider a regular bcc or sc lattice of N sites which is subdivided into two regular sublattices, denoted by λ and κ. Each sublattice contains $\frac{1}{2}N$ sites and they are arranged so that all sites in each sublattice have nearest neighbors only in the other sublattice. There are two species of atom, A and B, of concentrations n_A and n_B, respectively. At each lattice site there is an atom of type A or type B. We do not allow for the possibility of vacant lattice sites, consequently, we have the relation $n_A+n_B=1$. We assume throughout that $n_A \le n_B$. Operators t_i $(=0,1)$ are used to describe the occupation state of site i, where

$$t_i=\begin{cases} 1 \text{ if site } i \text{ is occupied by an } A \text{ atom },\\ 0 \text{ if site } i \text{ is occupied by a } B \text{ atom }. \end{cases} \tag{2.1}$$

The Hamiltonian for the RBA is given by

$$\begin{aligned} H=-\sum_{(ij)}\{&(W_{AA})_{ij}t_it_j+(W_{BB})_{ij}(1-t_i)(1-t_j)\\ &+(W_{AB})_{ij}[t_i(1-t_j)+(1-t_i)t_j]\}\\ &-\mu_A\sum_{i=1}^{N}t_i-\mu_B\sum_{i=1}^{N}(1-t_i)\ , \end{aligned} \tag{2.2}$$

where $(W_{XY})_{ij}$ represents the interaction potential between an X atom at site i and a Y atom at site j and μ_A and μ_B are the chemical potentials of species A and B, respectively. We assume that the interaction potentials $(W_{XY})_{ij}$ are randomly distributed with some specified probability distributions.

We simplify the Hamiltonian (2.2) by introducing two linear combinations of the interatomic potentials, $W_{ij}=(W_{AA})_{ij}+(W_{BB})_{ij}-2(W_{AB})_{ij}$ and $\mathcal{W}_{ij}=(W_{AB})_{ij}-(W_{BB})_{ij}$, and the chemical potential difference $\mu=\mu_A-\mu_B$. We now have

$$H=-\sum_{(ij)}W_{ij}t_it_j-\sum_{(ij)}\mathcal{W}_{ij}(t_i+t_j)-\mu\sum_{i=1}^{N}t_i\ , \tag{2.3}$$

which is the same as (2.2) to within an additive constant.

In this work it is necessary to distinguish interaction bonds between pairs of atoms on sites within the same sublattice (called here intrasublattice bonds) from interaction bonds between pairs of atoms on sites in different sublattices (called intersublattice bonds). We therefore introduce the following notation:

$$W_{ij}=\begin{cases} U_{ij} \text{ if sites } i \text{ and } j \text{ are in different}\\ \quad\text{sublattices (intersublattice)},\\ V_{ij} \text{ if sites } i \text{ and } j \text{ are in the same}\\ \quad\text{sublattice (intrasublattice)}, \end{cases} \tag{2.4}$$

$$\mathcal{W}_{ij}=\begin{cases} \mathcal{U}_{ij} \text{ for intersublattice bonds },\\ \mathcal{V}_{ij} \text{ for intrasublattice bonds }, \end{cases} \tag{2.5}$$

$$\begin{aligned} &\sum_{(ij)}{}' \text{ denotes a sum over pairs } (ij) \text{ with } i\\ &\qquad \text{and } j \text{ in different sublattices },\\ &\sum_{(ij)}{}'' \text{ denotes a sum over pairs } (ij) \text{ with } i\\ &\qquad \text{and } j \text{ in the same sublattice }, \end{aligned} \tag{2.6}$$

which enables us to write the Hamiltonian (2.3) as

$$\begin{aligned} H=&-\sum_{(ij)}{}'U_{ij}t_it_j-\sum_{(ij)}{}'\mathcal{U}_{ij}(t_i+t_j)-\sum_{(ij)}{}''V_{ij}t_it_j\\ &-\sum_{(ij)}{}''\mathcal{V}_{ij}(t_i+t_j)-\mu\sum_{i=1}^{N}t_i\ . \end{aligned} \tag{2.7}$$

We now consider the quantities U_{ij}, $\mathcal{U}_{ij}$, V_{ij}, and $\mathcal{V}_{ij}$ to be randomly distributed over the lattice bonds. Separate probability distributions are taken for the intrasublattice interactions (V and $\mathcal{V}$) and the intersublattice interactions (U and $\mathcal{U}$). We denote their respective joint probability distribution functions by $\mathcal{Q}(V,\mathcal{V})$ and $\mathcal{P}(U,\mathcal{U})$. We note that in general we would expect the interactions W_{AA}, W_{BB}, and W_{AB} to have the same type of distribution and these distributions would determine the probability distributions of U, $\mathcal{U}$, V, and $\mathcal{V}$.

We note that the Hamiltonian (2.7) can be rewritten yet again, introducing site-dependent potentials $\mathcal{U}_i$ and $\mathcal{V}_i$ which are sums over the appropriate neighbors of the site i of $\mathcal{U}_{ij}$ and $\mathcal{V}_{ij}$, respectively. In magnetic systems these would correspond to random applied magnetic fields. We prefer however to leave the Hamiltonian in the above form for the purpose of applying the pair approximation. Note that in a nonrandom alloy, the terms involving $\mathcal{U}_{ij}$

and $\mathscr{V}_{ij}$ would normally be absorbed into the chemical potential term in (2.7). Here, however, they must be retained in full. This makes the Hamiltonian (2.7) different from that of an antiferromagnet (AF) with random pairwise interactions, since for the AF the Hamiltonian does not contain a random applied field as a consequence of random pair interactions. We will discuss this further in the following paper.[26]

III. THE PAIR APPROXIMATION

We now derive the statistical mechanics of the RBA using the method of the distribution function. Following IFT (Ref. 10), we formulate the problem using the pair approximation. However, due to the sublattice structure inherent in lattice models of binary alloys, we must consider each type of site (λ sites and κ sites) separately, as well as consider three types of pairs of sites: $\lambda\kappa$ pairs, $\lambda\lambda'$ pairs, and $\kappa\kappa'$ pairs. Consequently, within the pair approximation for this model, we consider simultaneously two single-site Hamiltonians and three pair-site Hamiltonians and we require self-consistency between the pair-site density matrices and the single-site density matrices.

The two single-site Hamiltonians are given by

$$H_\lambda = -(\mu + l_\lambda^{(z)} + k_\lambda^{(z')})t_\lambda \, , \tag{3.1}$$

$$H_\kappa = -(\mu + l_\kappa^{(z)} + k_\kappa^{(z')})t_\kappa \, , \tag{3.2}$$

where $l_\sigma^{(z)}[k_\sigma^{(z')}]$ is the effective potential at a site in sublattice σ from the z $[z']$ nearest neighbors of the site in the other sublattice (in the same sublattice) (see Fig. 1). The effective potential $l_\sigma^{(z)}[k_\sigma^{(z')}]$ includes contributions from both the pair interaction term $U_{ij}t_it_j$ $[V_{ij}t_it_j]$ and the site-dependent potential term $\mathscr{U}_{ij}(t_i+t_j)$ $[\mathscr{V}_{ij}(t_i+t_j)]$ in (2.7). This must be taken into account when we consider the pair-site Hamiltonians. These are

$$H_{\lambda\kappa} = -Ut_\lambda t_\kappa - (\mu + l_\lambda^{(z-1)} + \mathscr{U} + k_\lambda^{(z')})t_\lambda - (\mu + l_\kappa^{(z-1)} + \mathscr{U} + k_\kappa^{(z')})t_\kappa \, , \tag{3.3}$$

$$H_{\lambda\lambda'} = -Vt_\lambda t_{\lambda'} - (\mu + l_\lambda^{(z)} + k_\lambda^{(z'-1)} + \mathscr{V})t_\lambda - (\mu + l_{\lambda'}^{(z)} + k_{\lambda'}^{(z'-1)} + \mathscr{V})t_{\lambda'} \, , \tag{3.4}$$

and

$$H_{\kappa\kappa'} = -Vt_\kappa t_{\kappa'} - (\mu + l_\kappa^{(z)} + k_\kappa^{(z'-1)} + \mathscr{V})t_\kappa - (\mu + l_{\kappa'}^{(z)} + k_{\kappa'}^{(z'-1)} + \mathscr{V})t_{\kappa'} \, , \tag{3.5}$$

where $l_\lambda^{(z-1)}(k_\lambda^{(z'-1)})$ represents an effective potential at the λ site of a $\lambda\kappa$ $[\lambda\lambda']$ pair which comes from its interaction with its $z-1[z'-1]$ nearest neighbors in the sublattice κ $[\lambda]$ outside the pair sites. The effective potentials $l_\kappa^{(z-1)}$ and $k_\kappa^{(z'-1)}$ have similar interpretations, while $l_\sigma^{(z)}$ and $k_\sigma^{(z')}$ are as defined for the single-site Hamiltonians. We will refer to the effective potentials $l_\sigma^{(m)}$ and $k_\sigma^{(m)}$ as m-bond potentials at σ, where it is understood that the former refers to intersublattice bonds and the latter to intrasublattice bonds (see Fig. 2). The single-site density matrices are given by

$$\hat{\rho}_\sigma = \exp(-\beta H_\sigma), \quad \sigma = \lambda, \kappa \tag{3.6}$$

and their traces are expressed as

$$\mathrm{Tr}\hat{\rho}_\sigma = Z_1(l_\sigma^{(z)} + k_\sigma^{(z')}) \, , \tag{3.7}$$

where

$$Z_1(x) = 1 + \exp[\beta(\mu + x)] \, . \tag{3.8}$$

There are three pair-site density matrices:

$$\hat{\rho}_{\sigma\sigma'} = \exp(-\beta H_{\sigma\sigma'}) \, , \tag{3.9}$$

where $\sigma\sigma' = \lambda\kappa$, $\lambda\lambda'$, or $\kappa\kappa'$ for the three types of pair sites we have to consider. Throughout this paper we will use σ and σ' to denote either λ or κ and $\sigma\sigma'$ to denote any of the (unordered) pairs $\lambda\kappa$, $\lambda\lambda'$, and $\kappa\kappa'$.

The consistency relations which we require the density matrices to satisfy can be summarized as

$$\mathrm{Tr}_{\sigma'}\hat{\rho}_{\sigma\sigma'} \propto \hat{\rho}_\sigma \, , \tag{3.10}$$

where Tr_σ means partial trace with respect to the site σ. For the case $\sigma = \lambda, \sigma' = \kappa$, this condition gives us a relationship between the $(z-1)$-bond potential $l_\lambda^{(z-1)}$ and the z-bond potential $l_\lambda^{(z)}$ in terms of the $(z-1)$-bond and z'-bond potentials at the pair site $l_\kappa^{(z-1)}$ and $k_\kappa^{(z')}$, as we will now show.

Writing the pair-site density matrix $\hat{\rho}_{\lambda\kappa}$ in the form

$$\hat{\rho}_{\lambda\kappa} = \exp[\beta U t_\lambda t_\kappa + \beta(\mu + l_\lambda^{(z-1)} + \mathscr{U} + k_\lambda^{(z')})t_\lambda + \beta(\mu + l_\kappa^{(z-1)} + \mathscr{U} + k_\kappa^{(z')})t_\kappa] \, , \tag{3.11}$$

we evaluate the partial trace over the site κ to find

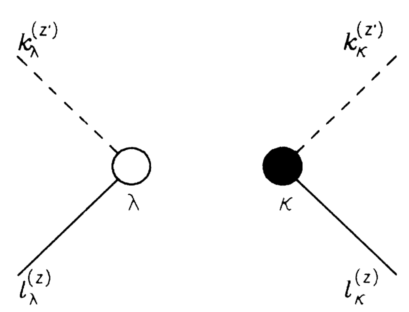

FIG. 1. z-bond and z'-bond effective potentials at each type of site. This diagram represents the single-site approximation.

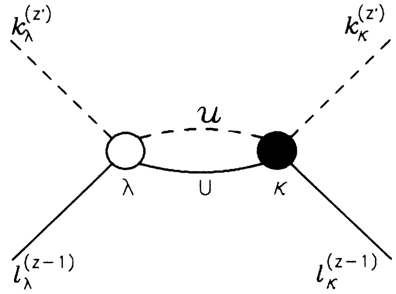

FIG. 2. $\lambda\kappa$ pair of sites and the effective potentials associated with each of them in the pair approximation. Similar diagrams can also be drawn for a pair of λ sites ($\lambda\lambda'$) or a pair of κ sites ($\kappa\kappa'$).

$$\mathrm{Tr}_\kappa\hat{\rho}_{\lambda\kappa}=\exp[\beta(\mu+l_\lambda^{(z-1)}+\mathscr{U}+k_\lambda^{(z')})t_\lambda]\\ \times\{1+\exp[\beta U t_\lambda+\beta(\mu+l_\kappa^{(z-1)}+\mathscr{U}+k_\kappa^{(z')})]\}\ . \tag{3.12}$$

This is simplified using the identity

$$e^{Xt}=1+t(e^{X}-1),\quad t=0,1 \tag{3.13}$$

to give

$$\mathrm{Tr}_\kappa\hat{\rho}_{\lambda\kappa}=Z_1(l_\kappa^{(z-1)}+\mathscr{U}+k_\kappa^{(z')})\exp[\beta(\mu+l_\lambda^{(z-1)}+\mathscr{U}+k_\lambda^{(z')})t_\lambda]\\ \times\left[1+t_\lambda\frac{(e^{\beta U}-1)\exp[\beta(\mu+l_\kappa^{(z-1)}+\mathscr{U}+k_\kappa^{(z')})]}{Z_1(l_\kappa^{(z-1)}+\mathscr{U}+k_\kappa^{(z')})}\right]\ . \tag{3.14}$$

Using (3.13) again on the term in large brackets, we find that

$$\mathrm{Tr}_\kappa\hat{\rho}_{\lambda\kappa}=Z_1(l_\kappa^{(z-1)}+\mathscr{U}+k_\kappa^{(z')})\exp[\beta(\mu+l_\lambda^{(z-1)}+\mathscr{U}\\ +L_\lambda+k_\lambda^{(z')})t_\lambda]\ , \tag{3.15}$$

where

$$e^{\beta L_\lambda}-1=\frac{(e^{\beta U}-1)\exp[\beta(\mu+l_\kappa^{(z-1)}+\mathscr{U}+k_\kappa^{(z')})]}{Z_1(l_\kappa^{(z-1)}+\mathscr{U}+k_\kappa^{(z')})}\ . \tag{3.16}$$

Solving for L_λ gives

$$L_\lambda(U,\mathscr{U},l_\kappa^{(z-1)},k_\kappa^{(z')})\\ =\frac{1}{\beta}\ln\left[\frac{Z_1(l_\kappa^{(z-1)}+\mathscr{U}+U+k_\kappa^{(z')})}{Z_1(l_\kappa^{(z-1)}+\mathscr{U}+k_\kappa^{(z')})}\right]\ . \tag{3.17}$$

From the constraint placed on the pair-site density matrix by (3.10), we see that $\hat{\rho}_\lambda$ may be expressed as

$$\hat{\rho}_\lambda=\exp[\beta(\mu+l_\lambda^{(z-1)}+\mathscr{U}+L_\lambda+k_\lambda^{(z')})t_\lambda]\ . \tag{3.18}$$

This may be interpreted as saying that the z-bond potential $l_\lambda^{(z)}$ is the sum of a $(z-1)$-bond potential $l_\lambda^{(z-1)}$ and a single-bond potential $l_{\lambda 1}$, as illustrated in Fig. 3. Therefore, we can write

$$l_\lambda^{(z)}=l_\lambda^{(z-1)}+l_{\lambda 1}\ \text{with}\\ l_{\lambda 1}=L_\lambda(U,\mathscr{U},l_\kappa^{(z-1)},k_\kappa^{(z')})+\mathscr{U}\ , \tag{3.19}$$

where there are two distinct contributions to the single-bond potential $l_{\lambda 1}$: a contribution (L_λ) from the two-body interaction, and a contribution ($\mathscr{U}$) from the site-dependent potential term in (2.7). Finally, from (3.15) we see that the trace of $\hat{\rho}_{\lambda\kappa}$ can be expressed as a product of traces of single-site density matrices:

$$\mathrm{Tr}\hat{\rho}_{\lambda\kappa}=Z_1(l_\kappa^{(z-1)}+\mathscr{U}+k_\kappa^{(z')})\\ \times Z_1(l_\lambda^{(z-1)}+\mathscr{U}+L_\lambda+k_\lambda^{(z')})\ . \tag{3.20}$$

There are three other choices for σ and σ' in (3.10) which give different results, that is, establish relationships between $l_\kappa^{(z)}$ and $l_\kappa^{(z-1)}$ ($\sigma=\kappa,\sigma'=\lambda$), $k_\lambda^{(z')}$ and $k_\lambda^{(z'-1)}$ ($\sigma=\lambda,\sigma'=\lambda'$), and $k_\kappa^{(z')}$ and $k_\kappa^{(z'-1)}$ ($\sigma=\kappa$, $\sigma'=\kappa'$). The results which are used in this paper are summarized in Appendix A.

IV. DISTRIBUTION FUNCTIONS FOR THE EFFECTIVE POTENTIALS

In our model the single-bond potential at each site (l_λ and k_λ at each λ site and l_κ and k_κ at each κ site) vary from bond to bond. We introduce four single-bond distribution functions, denoted $g_\lambda(l_\lambda)$, $g_\kappa(l_\kappa)$, $f_\lambda(k_\lambda)$, and $f_\kappa(k_\kappa)$, which we assume describe the distribution of the four types of single bond over the entire lattice. Note that we consider separate distribution functions for each type of bond. We also introduce four multiple-bond distribution functions, which we denote by $g_\lambda^{(m)}(l_\lambda^{(m)})$, $g_\kappa^{(m)}(l_\kappa^{(m)})$, $f_\lambda^{(m)}(k_\lambda^{(m)})$, and $f_\kappa^{(m)}(k_\kappa^{(m)})$. We assume that these functions describe the distribution of the multiple-bond potentials at each site ($l_\lambda^{(z)},k_\kappa^{(z'-1)}$, etc.) over the entire lattice. The single-bond and multiple-bond distribution functions can be related to each other using the relationships given in Sec. III between the single-bond potentials at a site and the multiple-bond potentials at a neighboring site. For example, the single-bond potential at a κ site is related to the $(z-1)$-bond potential $l_\lambda^{(z-1)}$ and z'-bond potential $k_\lambda^{(z')}$ at a neighboring λ site through (3.19), and thus the single-bond distribution function $g_\kappa(l_\kappa)$ is related to the multiple-bond distribution functions $g_\lambda^{(z-1)}(l_\lambda^{(z-1)})$ and $f_\lambda^{(z')}(k_\lambda^{(z')})$ through

$$g_\kappa(l_\kappa)=\int\delta(l_\kappa-L_\kappa(U,\mathscr{U},l_\lambda^{(z-1)},k_\lambda^{(z')})-\mathscr{U})\\ \times\mathscr{P}(U,\mathscr{U})dU\,d\mathscr{U}\\ \times g_\lambda^{(z-1)}(l_\lambda^{(z-1)})dl_\lambda^{(z-1)}f_\lambda^{(z')}(k_\lambda^{(z')})dk_\lambda^{(z')}\ . \tag{4.1}$$

Similar expressions may be found for the other single-

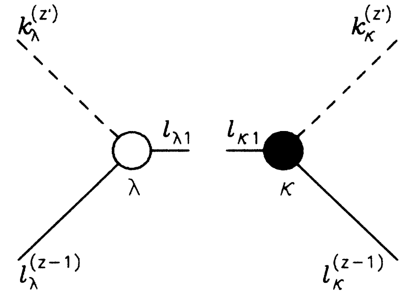

FIG. 3. $\lambda\kappa$ pair of sites showing the single-bond potentials $l_{\lambda 1}$ and $l_{\kappa 1}$. This diagram is equivalent to Fig. 1 with $l_\sigma^{(z)}=l_\sigma^{(z-1)}+l_{\sigma 1}$ ($\sigma=\lambda,\kappa$).

bond distribution functions using the results given in Appendix A:

$$g_\lambda(l_\lambda)=\int \delta(l_\lambda-L_\lambda(U,\mathcal{U},l_\kappa^{(z-1)},k_\kappa^{(z')})-\mathcal{U})\\ \times\mathcal{P}(U,\mathcal{U})dU\,d\mathcal{U}\\ \times g_\kappa^{(z-1)}(l_\kappa^{(z-1)})dl_\kappa^{(z-1)}f_\kappa^{(z')}(k_\kappa^{(z')})dk_\kappa^{(z')}\ , \tag{4.2}$$

$$f_\lambda(k_\lambda)=\int \delta(k_\lambda-K_\lambda(V,\mathcal{V},l_{\lambda'}^{(z)},k_{\lambda'}^{(z'-1)})-\mathcal{V})\\ \times\mathcal{Q}(V,\mathcal{V})dV\,d\mathcal{V}\\ \times g_\lambda^{(z)}(l_{\lambda'}^{(z)})dl_{\lambda'}^{(z)}f_\lambda^{(z'-1)}(k_{\lambda'}^{(z'-1)})dk_{\lambda'}^{(z'-1)}\ , \tag{4.3}$$

and

$$f_\kappa(k_\kappa)=\int \delta(k_\kappa-K_\kappa(V,\mathcal{V},l_{\kappa'}^{(z)},k_{\kappa'}^{(z'-1)})-\mathcal{V})\\ \times\mathcal{Q}(V,\mathcal{V})dV\,d\mathcal{V}\\ \times g_\kappa^{(z)}(l_{\kappa'}^{(z)})dl_{\kappa'}^{(z)}f_\kappa^{(z'-1)}(k_{\kappa'}^{(z'-1)})dk_{\kappa'}^{(z'-1)}\ . \tag{4.4}$$

In writing these relations we are ignoring any correlation between the multiple-bond distribution functions and the random distributions $\mathcal{P}$ and $\mathcal{Q}$ for U, $\mathcal{U}$, V, and $\mathcal{V}$.

We now assume that general m-bond distribution functions may be written in terms of single-bond distribution functions as

$$g_\sigma^{(m)}(l_\sigma^{(m)})=\int\delta\left[l_\sigma^{(m)}-\sum_{j=1}^{m}l_{\sigma j}\right]\prod_{j=1}^{m}g_\sigma(l_{\sigma j})dl_{\sigma j} \tag{4.5}$$

and

$$f_\sigma^{(m)}(k_\sigma^{(m)})=\int\delta\left[k_\sigma^{(m)}-\sum_{j=1}^{m}k_{\sigma j}\right]\prod_{j=1}^{m}f_\sigma(k_{\sigma j})dk_{\sigma j}\ . \tag{4.6}$$

With appropriate choices of σ and m [z or $z-1$ in (4.5) and z' or $z'-1$ in (4.6)], Eqs. (4.1)–(4.6) form a closed set of integral equations for the single-bond distribution functions of the effective potentials. We wish to find the $(z-1)$-bond and $(z'-1)$-bond distribution functions.[10] However, from the form of (4.1)–(4.4) it is clear that we will not find a closed set of equations for the $(z-1)$-bond and $(z'-1)$-bond distribution functions. Nevertheless, in the limit of infinite-range interactions $(z,z'\rightarrow\infty)$ we can solve the equations for the $(z-1)$-bond and $(z'-1)$-bond distribution functions. We will discuss this further in the following paper[26] and will now proceed to derive expressions for the $(z-1)$-bond [$(z'-1)$-bond] distribution functions in terms of other $(z-1)$-bond [$(z'-1)$-bond] distribution functions and z'-bond [z-bond] distribution functions.

Substituting (4.1) and (4.2) into (4.5), with $m=z-1$ and the appropriate choice for σ, and evaluating the integrals over $l_{\sigma j}$, we find that

$$g_\sigma^{(z-1)}(l_\sigma^{(z-1)})=\int\delta\left[l_\sigma^{(z-1)}-\sum_{j=1}^{z-1}[L_\sigma(U_j,\mathcal{U}_j,l_{\sigma' j}^{(z-1)},k_{\sigma' j}^{(z')})+\mathcal{U}_j]\right]\prod_{j=1}^{z-1}[\mathcal{P}(U_j,\mathcal{U}_j)dU_j d\mathcal{U}_j g_{\sigma'}^{(z-1)}(l_{\sigma' j}^{(z-1)})\\ \times dl_{\sigma' j}^{(z-1)}f_{\sigma'}^{(z')}(k_{\sigma' j}^{(z')})dk_{\sigma' j}^{(z')}]\ . \tag{4.7}$$

Here, U_j and $\mathcal{U}_j$ are the interaction potentials between the site σ and each of the $(z-1)$ neighboring sites (in the other sublattice) which are contributing to $l_\sigma^{(z-1)}$, while $l_{\sigma' j}^{(z-1)}$ and $k_{\sigma' j}^{(z')}$ are the effective potentials felt at each of these neighboring sites from all their neighbors excluding the site σ. We may rewrite (4.7) in a more convenient form using the relation

$$\delta(x-a)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-is(x-a)}ds\ , \tag{4.8}$$

which gives

$$g_\sigma^{(z-1)}(l_\sigma^{(z-1)})=\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(-isl_\sigma^{(z-1)})[G_\sigma(s)]^{z-1}ds\ , \tag{4.9}$$

where

$$G_\sigma(s)=\int\exp\{is[L_\sigma(U,\mathcal{U},l_{\sigma'}^{(z-1)},k_{\sigma'}^{(z')})+\mathcal{U}]\}\mathcal{P}(U,\mathcal{U})dU\,d\mathcal{U}\,g_{\sigma'}^{(z-1)}(l_{\sigma'}^{(z-1)})dl_{\sigma'}^{(z-1)}f_{\sigma'}^{(z')}(k_{\sigma'}^{(z')})dk_{\sigma'}^{(z')}\ , \tag{4.10}$$

which is the Fourier transform of the single-bond distribution function g_σ.

Turning our attention now to the distribution functions for intrasublattice bonds, we substitute (4.3) and (4.4) into (4.6), with $\sigma=\lambda, m=z'-1$ and $\sigma'=\lambda', m=z'-1$, respectively, and find

$$f_\sigma^{(z'-1)}(k_\sigma^{(z'-1)})=\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(-isk_\sigma^{(z'-1)})[F_\sigma(s)]^{z'-1}ds\ , \tag{4.11}$$

with

$$F_\sigma(s)=\int\exp\{is[K_\sigma(V,\mathcal{V},l_{\sigma'}^{(z)}k_{\sigma'}^{(z'-1)})+\mathcal{V}]\}\mathcal{Q}(V,\mathcal{V})dV\,d\mathcal{V}\,g_\sigma^{(z)}(l_{\sigma'}^{(z)})dl_{\sigma'}^{(z)}f_\sigma^{(z'-1)}(k_{\sigma'}^{(z'-1)})dk_{\sigma'}^{(z'-1)}\ , \tag{4.12}$$

which is the Fourier transform of the single-bond distribution function f_σ.

The z-bond distribution functions $g^{(z)}$ $[f^{(z')}]$ can be expressed in terms of $G[F]$ by replacing $z-1$ $[z'-1]$ by z $[z']$ in (4.9) [(4.11)]. Then (4.10) and (4.12) constitute a closed set of integral equations for the Fourier transforms of the single-bond distribution functions, G and F. These equations are useful for numerical calculation of the distribution functions in the case of a finite coordination number.

Equations (4.9)—(4.12) are in a convenient form for further calculations and we shall return to them in the following paper when we specify the probability distributions $\mathscr{P}(U,\mathscr{U})$ and $\mathscr{Q}(V,\mathscr{V})$ and derive detailed results for the order parameters of this system.

It is also possible to derive expressions for the single-bond distribution functions in terms of other single-bond distribution functions using (4.1)—(4.6). Substituting (4.5) and (4.6), with appropriate choices of σ and m, into (4.1), we find that

$$g_\sigma(l_\sigma)=\int\delta\left[l_\sigma-L_\sigma\left[U,\mathscr{U},\sum_{j=1}^{z-1}l_{\sigma'j},\sum_{i=1}^{z'}k_{\sigma'i}\right]-\mathscr{U}\right]P(U,\mathscr{U})dU\,d\mathscr{U}\prod_{j=1}^{z-1}g_{\sigma'}(l_{\sigma'j})dl_{\sigma'j}\prod_{i=1}^{z'}f_{\sigma'}(k_{\sigma'i})dk_{\sigma'i} \tag{4.13}$$

and

$$f_\sigma(k_\sigma)=\int\delta\left[k_\sigma-K_\sigma\left[V,\mathscr{V},\sum_{j=1}^{z}l_{\sigma'j},\sum_{i=1}^{z'-1}k_{\sigma'i}\right]-\mathscr{V}\right]\mathscr{Q}(V,\mathscr{V})dV\,d\mathscr{V}\prod_{j=1}^{z}g_{\sigma}(l_{\sigma'j})dl_{\sigma'j}\prod_{i=1}^{z'-1}f_{\sigma}(k_{\sigma'i})dk_{\sigma'i}\ , \tag{4.14}$$

with the general relations

$$l_\sigma^{(m)}=\sum_{j=1}^{m}l_{\sigma j},\quad k_\sigma^{(m)}=\sum_{j=1}^{m}k_{\sigma j}\ , \tag{4.15}$$

where, as usual, $\sigma=\lambda$ or κ. This means we can consider the m-bond potentials as sums of m single-bond potentials, as illustrated in Fig. 4.

The thermal and configurational average of a function of the operator t_σ can be written in terms of the density matrix at a site in sublattice σ $(\hat{\rho}_\sigma)$ and the distribution functions of the effective potentials by

$$\langle\langle A(t_\sigma)\rangle_\sigma\rangle_R=\int\left[\frac{\mathrm{Tr}[A(t_\sigma)\hat{\rho}_\sigma]}{\mathrm{Tr}\hat{\rho}_\sigma}\right]\prod_{i=1}^{z}\prod_{j=1}^{z'}g_\sigma(l_{\sigma i})dl_{\sigma i}f_\sigma(k_{\sigma j})dk_{\sigma j}\ , \tag{4.16}$$

and also using the pair density matrix $\hat{\rho}_{\sigma\sigma'}$ as

$$\langle\langle A(t_\sigma)\rangle_{\sigma\sigma'}\rangle_R=\int\left[\frac{\mathrm{Tr}[A(t_\sigma)\hat{\rho}_{\sigma\sigma'}]}{\mathrm{Tr}\hat{\rho}_{\sigma\sigma'}}\right]\mathscr{P}(U,\mathscr{U})dU\,d\mathscr{U}\,\mathscr{Q}(V,\mathscr{V})dV\,d\mathscr{V}\prod_{\tau=\sigma,\sigma'}\prod_{i=1}^{z}g_\tau(l_{\tau i})dl_{\tau i}\prod_{j=1}^{z'-1}f_\tau(k_{\tau j})dk_{\tau j}\ . \tag{4.17}$$

Clearly for our theory to be consistent, we must have that

$$\langle\langle A(t_\sigma)\rangle_\sigma\rangle_R=\langle\langle A(t_\sigma)\rangle_{\sigma\sigma'}\rangle_R$$

for all σ and σ'. We show in Appendix B that the relations we have derived among the distributions functions do ensure that the different ways of taking the average do give the same result.

V. THE THERMODYNAMIC POTENTIAL

We are now in a position to calculate the thermodynamic potential per bond of the binary alloy in the pair approximation. We begin by defining three pair potentials $\phi_{\lambda\kappa}$, $\phi_{\lambda\lambda'}$, and $\phi_{\kappa\kappa'}$ which are given by

$$\phi_{\lambda\kappa}=-k_BT\int\ln(\mathrm{Tr}\hat{\rho}_{\lambda\kappa})\mathscr{P}(U,\mathscr{U})dU\,d\mathscr{U}\times\prod_{\substack{i=1\\j=1}}^{z-1}g_\lambda(l_{\lambda i})dl_{\lambda i}g_\kappa(l_{\kappa j})dl_{\kappa j}\times\prod_{\substack{m=1\\n=1}}^{z'}f_\lambda(k_{\lambda m})dl_{\lambda m}f_\kappa(k_{\kappa n})dk_{\kappa n}\ , \tag{5.1}$$

$$\phi_{\sigma\sigma'}=-k_BT\int\ln(\mathrm{Tr}\hat{\rho}_{\sigma\sigma'})\mathscr{Q}(V,\mathscr{V})dV\,d\mathscr{V}\times\prod_{\substack{i=1\\j=1}}^{z}g_\sigma(l_{\sigma i})dl_{\sigma i}g_\sigma(l_{\sigma'j})dl_{\sigma'j}\times\prod_{\substack{m=1\\n=1}}^{z'-1}f_\sigma(k_{\sigma m})dk_{\sigma m}f_\sigma(k_{\sigma'n})dk_{\sigma'n}\ , \tag{5.2}$$

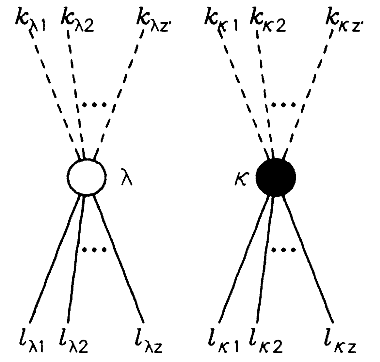

FIG. 4. Single-bond potentials $l_{\sigma j}$ and $k_{\sigma j}$. Figure 4 is equivalent to both Figs. 1 and 3 using Eq. (4.15).

where σ and σ' represent sites in the same sublattice and $\mathrm{Tr}\hat{\rho}_{\lambda\kappa}$ is given by (3.20) and (A4), $\mathrm{Tr}\hat{\rho}_{\lambda\lambda'}$ by (A8), and $\mathrm{Tr}\hat{\rho}_{\kappa\kappa'}$ by (A12). We also define two single-site potentials ϕ_λ and ϕ_κ by

$$\phi_\sigma = -k_B T \int \ln(\mathrm{Tr}\hat{\rho}_\sigma) \prod_{i=1}^{z} \prod_{j=1}^{z'} g_\sigma(l_{\sigma i}) dl_{\sigma i} f_\sigma(k_{\sigma j}) dk_{\sigma j} \;, \tag{5.3}$$

where $\mathrm{Tr}\hat{\rho}_\sigma$ is given by (3.7). Throughout we are using (4.5) and (4.6) to represent the multiple-bond potentials. We note, however, that the potentials (5.1)—(5.3) may also be written in terms of multiple-bond distribution functions. For example, $\phi_{\lambda\kappa}$ may also be written as

$$\begin{aligned}\phi_{\lambda\kappa} = -k_B T \int & \ln(\mathrm{Tr}\hat{\rho}_{\lambda\kappa}) \mathscr{P}(U,\mathscr{U}) dU\, d\mathscr{U} g_\lambda^{(z-1)}(l_\lambda^{(z-1)}) \\ & \times dl_\lambda^{(z-1)} g_\kappa^{(z-1)}(l_\kappa^{(z-1)}) dl_\kappa^{(z-1)} \\ & \times f_\lambda^{(z')}(k_\lambda^{(z')}) dk_\lambda^{(z')} f_\kappa^{(z')}(k_\kappa^{(z')}) dk_\kappa^{(z')} \;, \end{aligned} \tag{5.4}$$

with similar expressions, involving only multiple-bond distribution functions, for $\phi_{\lambda\lambda'}$, $\phi_{\kappa\kappa'}$, ϕ_λ, and ϕ_κ.

The thermodynamic potential per bond for the binary alloy in the pair approximation is given in terms of $\phi_{\sigma\sigma'}$ and ϕ_σ by

$$\begin{aligned}\phi = & \left[\frac{z}{z+z'}\right]\phi_{\lambda\kappa} + \frac{z'}{2(z+z')}(\phi_{\lambda\lambda'}+\phi_{\kappa\kappa'}) \\ & - \left[\frac{z+z'-1}{z+z'}\right](\phi_\lambda+\phi_\kappa) \;. \end{aligned} \tag{5.5}$$

A physical insight into the form of (5.5) may be gained by considering the limit of absolute zero temperature. In this limit the pair potential $\phi_{\lambda\kappa}$ represents the energy of a $\lambda\kappa$ pair of sites, which includes the energy of a $\lambda\kappa$ bond as well as the energies of $(z-1)$ interaction bonds between the λ site of the pair and κ sites outside the pair, $(z-1)$ interaction bonds between the κ sites of the pair and λ sites outside the pair, and z' interaction bonds between both sites of the pair (λ and κ) and, respectively, λ and κ sites outside the pair. Similar interpretations can be given for the pair potentials $\phi_{\lambda\lambda'}$ and $\phi_{\kappa\kappa'}$. The single-site potentials in this limit represent z intersublattice bond energies and z' intrasublattice bond energies (see Table I).

TABLE I. Contributions to pair and site potentials at absolute zero temperature.

		Number of other bonds		
Potential	Pair bond	$\lambda\kappa$	$\lambda\lambda'$	$\kappa\kappa'$
$\phi_{\lambda\kappa}$	$\lambda\kappa$ $(Nz/2)$[a]	$2(z-1)$	z'	z'
$\phi_{\lambda\lambda'}$	$\lambda\lambda'$ $(Nz'/4)$[a]	$2z$	$2(z'-1)$	0
$\phi_{\kappa\kappa'}$	$\kappa\kappa'$ $(Nz'/4)$[a]	$2z$	0	$2(z'-1)$
ϕ_λ		z	z'	0
ϕ_κ		z	0	z'

[a] These numbers are the total number of each type of nearest-neighbor pair bonds over the entire lattice.

From the information in Table I we see that the first three terms in (5.5) are calculating a weighted average of the energies of the three types of bonds, $\lambda\kappa$, $\lambda\lambda'$, and $\kappa\kappa'$, in the alloy. This, however, counts too many bonds and the last term subtracts away all the energies of bonds between the pair sites and the surrounding medium.

We now show that ϕ is stationary with respect to variations of the single-bond distribution functions. Consider firstly an arbitrary variation of $g_\lambda(l_\lambda)$ which preserves the normalization of $g_\lambda(l_\lambda)$. Hence,

$$\int \delta g_\lambda(l_\lambda) dl_\lambda = 0 \;. \tag{5.6}$$

The variation of ϕ with respect to $g_\lambda(l_\lambda)$ clearly will only involve terms which depend on $g_\lambda(l_\lambda)$. Therefore, in this case, we need only consider variations of $\phi_{\lambda\kappa}$, $\phi_{\lambda\lambda'}$, and ϕ_λ. The variation of $\phi_{\lambda\kappa}$ gives

$$\begin{aligned}\delta\phi_{\lambda\kappa} = -(z-1)k_B T \int \ln(\mathrm{Tr}\hat{\rho}_{\lambda\kappa}) \mathscr{P}(U,\mathscr{U}) dU\, d\mathscr{U} \prod_{\substack{i=2\\ j=1}}^{z-1} g_\lambda(l_{\lambda i}) dl_{\lambda i} g_\kappa(l_{\kappa j}) dl_{\kappa j} \\ \times \prod_{\substack{m=1\\ n=1}}^{z'} f_\lambda(k_{\lambda m}) dk_{\lambda m} f_\kappa(k_{\kappa n}) dk_{\kappa n} \delta g_\lambda(l_{\lambda 1}) dl_{\lambda 1} \;, \end{aligned} \tag{5.7}$$

and that of $\phi_{\lambda\lambda'}$ gives

$$\begin{aligned}\delta\phi_{\lambda\lambda'} = -2zk_B T \int \ln(\mathrm{Tr}\hat{\rho}_{\lambda\lambda'}) \mathscr{Q}(V,\mathscr{V}) dV\, d\mathscr{V} \prod_{\substack{i=2\\ j=1}}^{z} g_\lambda(l_{\lambda i}) dl_{\lambda i} g_\lambda(l_{\lambda' j}) dl_{\lambda' j} \\ \times \prod_{\substack{m=1\\ n=1}}^{z'-1} f_\lambda(k_{\lambda m}) dk_{\lambda m} f_\lambda(k_{\lambda' n}) dl_{\lambda' n} \delta g_\lambda(l_{\lambda 1}) dl_{\lambda 1} \;, \end{aligned} \tag{5.8}$$

while that of ϕ_λ gives

$$\delta\phi_\lambda = -zk_B T \int \ln(\mathrm{Tr}\hat{\rho}_\lambda) \prod_{i=2}^{z} \prod_{j=1}^{z'} g_\lambda(l_{\lambda i})dl_{\lambda i} f_\lambda(k_{\lambda j})dk_{\lambda j} \delta g_\lambda(l_{\lambda 1})dl_{\lambda 1} \; . \tag{5.9}$$

Substituting for the traces from (3.20), (A8), and (3.7) into (5.7)—(5.9) and combining to give the variation of ϕ, we have

$$\begin{aligned}
\delta\phi = -k_B T \int \delta g_\lambda(l_{\lambda 1})dl_{\lambda 1} \prod_{i=2}^{z-1} \prod_{j=1}^{z'-1} g_\lambda(l_{\lambda i})dl_{\lambda i} f_\lambda(k_{\lambda j})dk_{\lambda j} \\
\times \Bigg[\left[\frac{z}{z'+z} \right] (z-1) \int \ln Z_1 \left[\sum_{m=1}^{z-1} l_{\kappa m} + \mathscr{U} + \sum_{n=1}^{z'} k_{\kappa n} \right] \mathscr{P}(U,\mathscr{U})dU\,d\mathscr{U} \\
\times \prod_{m=1}^{z-1} \prod_{n=1}^{z'} g_\kappa(l_{\kappa m})dl_{\kappa m} f_\kappa(k_{\kappa n})dk_{\kappa n} f_\lambda(k_{\lambda z'})dk_{\lambda z'} \\
+ \left[\frac{z}{z+z'} \right] (z-1) \int \ln Z_1 \left[\sum_{i=1}^{z-1} l_{\lambda i} + \mathscr{U} + L_\lambda + \sum_{j=1}^{z'} k_{\lambda j} \right] \mathscr{P}(U,\mathscr{U})dU\,d\mathscr{U} \\
\times \prod_{m=1}^{z-1} \prod_{n=1}^{z'} g_\kappa(l_{\kappa m})dl_{\kappa m} f_\kappa(k_{\kappa n})dk_{\kappa n} f_\lambda(k_{\lambda z'})dk_{\lambda z'} \\
+ \left[\frac{z'}{z+z'} \right] z \int \ln Z_1 \left[\sum_{m=1}^{z} l_{\lambda' m} + \sum_{n=1}^{z'-1} k_{\lambda' n} + \mathscr{V} \right] \mathscr{Q}(V,\mathscr{V})dV\,d\mathscr{V} \\
\times \prod_{m=1}^{z} \prod_{n=1}^{z'-1} g_\lambda(l_{\lambda' m})dl_{\lambda' m} f_\lambda(k_{\lambda' n})dk_{\lambda' n} g_\lambda(l_{\lambda z})l_{\lambda z} \\
+ \left[\frac{z'}{z+z'} \right] z \int \ln Z_1 \left[\sum_{i=1}^{z} l_{\lambda i} + \sum_{j=1}^{z'-1} k_{\lambda j} + \mathscr{V} + K_\lambda \right] \mathscr{Q}(V,\mathscr{V})dV\,d\mathscr{V} \\
\times \prod_{m=1}^{z} \prod_{n=1}^{z'-1} g_\lambda(l_{\lambda' m})dl_{\lambda' m} f_\lambda(k_{\lambda' n})dk_{\lambda' n} g_\lambda(l_{\lambda z})dl_{\lambda z} \\
- \left[\frac{z+z'-1}{z+z'} \right] z \int \ln Z_1 \left[\sum_{i=1}^{z} l_{\lambda i} + \sum_{j=1}^{z'} k_{\lambda j} \right] g_\lambda(l_{\lambda z})dl_{\lambda z} f_\lambda(k_{\lambda z'})dk_{\lambda z'} \Bigg] \; .
\end{aligned} \tag{5.10}$$

The first and third terms in the square brackets are independent of $l_{\lambda 1}$ and so, by the condition (5.6), give no contribution to the variation of ϕ. The remaining terms in the square brackets must therefore combine to give zero for the potential ϕ to be stationary. Thus, stationarity of the potential imposes the following constraints on the single-bond distribution functions $g_\lambda(l_\lambda)$ and $f_\lambda(k_\lambda)$

$$\begin{aligned}
\int \prod_{i=2}^{z-1} \prod_{j=1}^{z'-1} g_\lambda(l_{\lambda i})dl_{\lambda i} f_\lambda(k_{\lambda j})dk_{\lambda j} \Bigg[\int \ln Z_1 \left[\sum_{i=1}^{z-1} l_{\lambda i} + \mathscr{U} + L_\lambda + \sum_{j=1}^{z'} k_{\lambda j} \right] \mathscr{P}(U,\mathscr{U})dU\,d\mathscr{U} \\
\times \prod_{m=1}^{z-1} \prod_{n=1}^{z'} g_\kappa(l_{\kappa m})dk_{\kappa m} f_\kappa(k_{\kappa n})dk_{\kappa n} f_\lambda(k_{\lambda z'})dk_{\lambda z'} \\
- \int \ln Z_1 \left[\sum_{i=1}^{z} l_{\lambda i} + \sum_{j=1}^{z'} k_{\lambda j} \right] g_\lambda(l_{\lambda z})dl_{\lambda z} f_\lambda(k_{\lambda z'})dk_{\lambda z'} \Bigg] = 0
\end{aligned} \tag{5.11a}$$

and

$$\int \prod_{i=2}^{z-1} \prod_{j=2}^{z'-1} g_\lambda(l_{\lambda i}) dl_{\lambda i} f_\lambda(k_{\lambda j}) dk_{\lambda j} \left[\int \ln Z_1 \left[\sum_{i=1}^{z} l_{\lambda i} + \sum_{j=1}^{z'-1} k_{\lambda j} + \mathscr{V} + K_\lambda \right] \mathscr{Q}(V,\mathscr{V}) dV d\mathscr{V} \right.$$
$$\times \prod_{m=1}^{z} \prod_{n=1}^{z'-1} g_\lambda(l_{\lambda' m}) dl_{\lambda' m} f_\lambda(k_{\lambda' n}) dk_{\lambda' n} g_\lambda(l_{\lambda z}) dl_{\lambda z}$$
$$\left. - \int \ln Z_1 \left[\sum_{i=1}^{z} l_{\lambda i} + \sum_{j=1}^{z'} k_{\lambda j} \right] g_\lambda(l_{\lambda z}) dl_{\lambda z} f_\lambda(k_{\lambda z'}) dk_{\lambda z'} \right] = 0 , \qquad (5.11b)$$

since z and z' are arbitrary.

Substituting the integral equations (4.13) for $g_\lambda(l_{\lambda z})$ and (4.14) for $f(k_{\lambda z'})$ into (5.11a) and (5.11b) ensures that both equations are satisfied. Following a similar procedure for arbitrary variations of $g_\kappa(l_\kappa)$, $f_\lambda(k_\lambda)$, and $f_\kappa(k_\kappa)$ leads to the conclusion that the integral equations (4.13) and (4.14) are a sufficient condition to ensure the stationarity of ϕ.

Finally, the thermodynamic potential per site for the RBA is given by $\Phi=(z+z')\phi/2$ since there are $z+z'$ bonds emerging from each site and each bond contributes to the energy of two sites. This may be rewritten using (5.5) as

$$\Phi = (z/2)\phi_{\lambda\kappa} + (z'/4)(\phi_{\lambda\lambda'} + \phi_{\kappa\kappa'}) - (z+z'-1)(\phi_\lambda + \phi_\kappa) . \qquad (5.12)$$

VI. DISCUSSION AND CONCLUSION

In this paper we have presented a formalism which enables us to find the thermodynamic potential for a binary alloy system with pair interactions randomly distributed over the entire lattice. In a following paper,[26] we will use the formalism and introduce specific forms for the probability distributions $\mathscr{P}(U,\mathscr{U})$ and $\mathscr{Q}(V,\mathscr{V})$. We will then present a detailed analysis of the behavior of the alloy in certain cases of special interest.

We have shown in Sec. II that the alloy must be treated differently from the Ising antiferromagnet, despite the obvious similarities between the two models used to describe them. We showed that with the RBA, random pairwise interactions necessarily produce random site-dependent potentials, while in the antiferromagnet, random magnetic fields and randomness in the pairwise interactions can occur independently.

The problems caused by introducing sublattices and by considering both nearest- and next-nearest-neighbor interactions simultaneously were overcome in Secs. III and IV by defining effective potentials (and corresponding distributions for each effective potential) at each type of site (i.e., from sublattice λ or κ) and for each type of bond (i.e., intersublattice or intrasublattice). We have derived a closed set of integral equations for the single-bond distribution functions. Although our treatment of the second-neighbor interactions is simple, we note that an analogous treatment was applied to a magnetic mixture and gave reasonable results for magnetic phase boundaries.[29]

The derivation of the thermodynamic potential in Sec. V is relatively straightforward. We have shown that our theory is consistent by showing that the thermodynamic potential is stationary with respect to variations in the single-bond distribution functions.

Clearly, it would be possible to extend the method of distribution function to include the effects of a subdivision of the lattice into more sublattices and hence to formulate the method for face-centered-cubic lattices. Similarly, the inclusion of magnetic interactions would also be possible and may in fact be interesting since spin glasses are indeed dilute alloys of a magnetic atom in a nonmagnetic medium. However, both of these extensions of the method involve a considerable increase in the complexity of the notation.

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APPENDIX A

In this Appendix we present the results obtained by the requirement of self-consistency placed on the pair density matrices. The consistency condition is

$$\mathrm{Tr}_{\sigma'} \rho_{\sigma\sigma'} \propto \hat{\rho}_\sigma , \qquad (3.10)$$

and there are three choices for the values of σ and σ' different from that given in the text (case 1: $\sigma=\lambda$, $\sigma'=\kappa$). The important results are the following for cases 2–4.

Case 2: $\sigma=\kappa$, $\sigma'=\lambda$; $\mathrm{Tr}_\lambda \hat{\rho}_{\lambda\kappa} \propto \hat{\rho}_\kappa$. We have

$$\hat{\rho}_\kappa = \exp[\beta(\mu + l_\kappa^{(z-1)} + l_{\kappa 1} + k_\kappa^{(z')}) t_\kappa] , \qquad (A1)$$

where

$$l_{\kappa 1} = L_\kappa(U, \mathscr{U}, l_\lambda^{(z-1)}, k_\lambda^{(z')}) + \mathscr{U} \qquad (A2)$$

and

$$L_\kappa(U,\mathscr{U},l_\lambda,k_\lambda) = \frac{1}{\beta} \ln \left[\frac{Z_1(l_\lambda + \mathscr{U} + U + k_\lambda)}{Z_1(l_\lambda + \mathscr{U} + k_\lambda)} \right] , \qquad (A3)$$

$$\mathrm{Tr}\hat{\rho}_{\lambda\kappa} = Z_1(l_\lambda^{(z-1)} + \mathscr{U} + k_\lambda^{(z')}) Z_1(l_\kappa^{(z-1)} + \mathscr{U} + L_\kappa + k_\kappa^{(z')}) . \qquad (A4)$$

Case 3: $\sigma=\lambda$, $\sigma'=\lambda'$; $\mathrm{Tr}_{\lambda'} \hat{\rho}_{\lambda\lambda'} \propto \hat{\rho}_\lambda$. We have

$$\hat{\rho}_\lambda = \exp[\beta(\mu + l_\lambda^{(z)} + k_\lambda^{(z'-1)} + k_{\lambda 1}) t_\lambda] , \qquad (A5)$$

where

$$k_{\lambda 1} = K_\lambda(V, \mathscr{V}, l_{\lambda'}^{(z)}, k_{\lambda'}^{(z'-1)}) + \mathscr{V} \qquad (A6)$$

and

$$K_\lambda(V,\mathscr{V},l_{\lambda'},k_{\lambda'})=\frac{1}{\beta}\ln\left[\frac{Z_1(l_{\lambda'}+k_{\lambda'}+V+\mathscr{V})}{Z_1(l_{\lambda'}+k_{\lambda'}+\mathscr{V})}\right], \tag{A7}$$

$$\begin{aligned}\mathrm{Tr}\hat{\rho}_{\lambda\lambda'}=&\,Z_1(l_{\lambda'}^{(z)}+k_{\lambda'}^{(z'-1)}+\mathscr{V})\\&\times Z_1(l_{\lambda}^{(z)}+k_{\lambda}^{(z'-1)}+\mathscr{V}+K_\lambda)\,.\end{aligned} \tag{A8}$$

Case 4: $\sigma=\kappa$, $\sigma'=\kappa'$; $\mathrm{Tr}_{\kappa'}\hat{\rho}_{\kappa\kappa'}\propto\hat{\rho}_{\kappa}$. We have

$$\hat{\rho}_\kappa=\exp[\beta(\mu+l_\kappa^{(z)}+k_\kappa^{(z'-1)}+k_{\kappa 1})t_\kappa]\,, \tag{A9}$$

where

$$k_{\kappa 1}=K_\kappa(V,\mathscr{V},l_{\kappa'}^{(z)},k_{\kappa'}^{(z'-1)})+\mathscr{V} \tag{A10}$$

and

$$K_\kappa(V,\mathscr{V},l_{\kappa'},k_{\kappa'})=\frac{1}{\beta}\ln\left[\frac{Z_1(l_{\kappa'}+k_{\kappa'}+\mathscr{V}+V)}{Z_1(l_{\kappa'}+k_{\kappa'}+\mathscr{V})}\right], \tag{A11}$$

$$\begin{aligned}\mathrm{Tr}\hat{\rho}_{\kappa\kappa'}=&\,Z_1(l_{\kappa'}^{(z)}+k_{\kappa'}^{(z'-1)}+\mathscr{V})\\&\times Z_1(l_{\kappa}^{(z)}+k_{\kappa}^{(z'-1)}+\mathscr{V}+K_\kappa)\,.\end{aligned} \tag{A12}$$

APPENDIX B

In this Appendix we show that the two alternative ways of evaluating the average of a function of the operators t_σ and $t_{\sigma'}$ both give the same result. Consider Eq. (4.18) for $\sigma=\lambda$ and $\sigma'=\kappa$

$$\begin{aligned}\langle\langle A(t_\lambda)\rangle_{\lambda\kappa}\rangle_R=\int&\left[\frac{\mathrm{Tr}[A(t_\lambda)\hat{\rho}_{\lambda\kappa}]}{\mathrm{Tr}\hat{\rho}_{\lambda\kappa}}\right]\mathscr{P}(U,\mathscr{U})dU\,d\mathscr{U}\\&\times g_\lambda^{(z-1)}(l_\lambda^{(z-1)})dl_\lambda^{(z-1)}g_\kappa^{(z-1)}(l_\kappa^{(z-1)})\\&\times dl_\kappa^{(z-1)}f_\lambda^{(z')}(k_\lambda^{(z')})dk_\lambda^{(z')}\\&\times f_\kappa^{(z')}(k_\kappa^{(z')})dk_\kappa^{(z')}\,.\end{aligned} \tag{B1}$$

We write the trace term as

$$\frac{\mathrm{Tr}[A(t_\lambda)\hat{\rho}_{\lambda\kappa}]}{\mathrm{Tr}\hat{\rho}_{\lambda\kappa}}=\frac{\mathrm{Tr}_\lambda(A(t_\lambda)\mathrm{Tr}_\kappa\hat{\rho}_{\lambda\kappa})}{\mathrm{Tr}_\lambda(\mathrm{Tr}_\kappa\hat{\rho}_{\lambda\kappa})}=\frac{\mathrm{Tr}_\lambda[A(t_\lambda)\hat{\rho}_\lambda]}{\mathrm{Tr}_\lambda\hat{\rho}_\lambda}, \tag{B2}$$

using (3.15) and (3.18). Hence, we have

$$\begin{aligned}\langle\langle A(t_\lambda)\rangle_{\lambda\kappa}\rangle_R=\int&\left[\frac{\mathrm{Tr}[A(t_\lambda)\hat{\rho}_{\lambda}]}{\mathrm{Tr}\hat{\rho}_{\lambda}}\right]\mathscr{P}(U,\mathscr{U})dU\,d\mathscr{U}\\&\times g_\lambda^{(z-1)}(l_\lambda^{(z-1)})dl_\lambda^{(z-1)}g_\kappa^{(z-1)}(l_\kappa^{(z-1)})\\&\times dl_\kappa^{(z-1)}f_\lambda^{(z')}(k_\lambda^{(z')})dk_\lambda^{(z')}\\&\times f_\kappa(k_\kappa^{(z')})dk_\kappa^{(z')}\,.\end{aligned} \tag{B3}$$

Now,

$$\begin{aligned}\langle\langle A(t_\lambda)\rangle_{\lambda}\rangle_R=\int&\left[\frac{\mathrm{Tr}[A(t_\lambda)\hat{\rho}_{\lambda}]}{\mathrm{Tr}\hat{\rho}_{\lambda}}\right]g_\lambda^{(z)}(l_\lambda^{(z)})dl_\lambda^{(z)}\\&\times f_\lambda^{(z')}(k_\lambda^{(z')})dk_\lambda^{(z')}\,,\end{aligned} \tag{B4}$$

but using (3.18) and (3.19), we can write $\hat{\rho}_\lambda$ and $l_\lambda^{(z)}$ as

$$\hat{\rho}_\lambda=\exp[\beta(\mu+l_\lambda^{(z-1)}+l_{\lambda 1}+k_\lambda^{(z')})]$$

and

$$l_\lambda^{(z)}=l_\lambda^{(z-1)}+l_{\lambda 1}\,. \tag{B5}$$

Therefore, (B4) can be rewritten in the form

$$\begin{aligned}\langle\langle A(t_\lambda)\rangle_{\lambda}\rangle_R=\int&\left[\frac{\mathrm{Tr}[A(t_\lambda)\hat{\rho}_{\lambda}]}{\mathrm{Tr}\hat{\rho}_{\lambda}}\right]g_\lambda^{(z-1)}(l_\lambda^{(z-1)})\\&\times dl_\lambda^{(z-1)}g_\lambda(l_{\lambda 1})dl_{\lambda 1}\\&\times f_\lambda^{(z')}(k_\lambda^{(z')})dk_\lambda^{(z')}\,,\end{aligned} \tag{B6}$$

and substituting for $g_\lambda(l_{\lambda 1})$ from (4.2) and integrating over $l_{\lambda 1}$ gives

$$\begin{aligned}\langle\langle A(t_\lambda)\rangle_{\lambda}\rangle_R=\int&\left[\frac{\mathrm{Tr}[A(t_\lambda)\hat{\rho}_{\lambda}]}{\mathrm{Tr}\hat{\rho}_{\lambda}}\right]g_\lambda^{(z-1)}(l_\lambda^{(z-1)})\\&\times dl_\lambda^{(z-1)}\mathscr{P}(U,\mathscr{U})dU\,d\mathscr{U}g_\kappa^{(z-1)}\\&\times(l_\kappa^{(z-1)})dl_\kappa^{(z-1)}f_\kappa^{(z')}(k_\kappa^{(z')})\\&\times dk_\kappa^{(z')}f_\lambda^{(z')}(k_\lambda^{(z')})dk_\lambda^{(z')}\end{aligned} \tag{B7}$$

which is identical to (B3). Hence,

$$\langle\langle A(t_\lambda)\rangle_{\lambda}\rangle_R\equiv\langle\langle A(t_\lambda)\rangle_{\lambda\kappa}\rangle_R\,,$$

and our theory is consistent in evaluating simultaneous averages of operators over the thermal distribution and the randomness in the system.

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