

Long Range Order in Binary Alloys with Three Body Potentials

RAZA A. TAHIR-KHELI*

Instituto de Física, Universidade Federal de Pernambuco, Recife, PE

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The problem of long range order (LRO) in two interpenetrating sublattice binary alloys with arbitrary concentration, via pair-wise potentials and pair-wise non-additive three-body potentials, is formulated in terms of an Ising antiferromagnet analog. The relevant Green's functions are decoupled in the first order (RPA) which is equivalent to the Bragg-Williams Approximation (BWA). The results indicate that, similarly to the disordered phase, the effects of the three-body potentials in the ordered phase also are given by a concentration dependent two-body potential.

O problema da ordem de longo alcance (LRO) em ligas de duas sub-redes interpenetrantes com concentrações arbitrárias, via potenciais a dois e a três corpos, é formulado com auxílio de um análogo antiferromagnético de Ising. As funções de Green relevantes são desacopladas em 1.ª ordem em RPA, que é equivalente à aproximação de Bragg-Williams (BWA). Os resultados indicam que, semelhantemente a fase desordenada, os efeitos devidos aos potenciais a três corpos na fase ordenada também são dados por um potencial a dois corpos que depende da concentração.

1. Introduction

Order-disorder phenomena in binary alloys has been the subject of many studies¹⁻². These studies have assumed that the total configurational energy is entirely made up of pair-wise potentials whose strength is dependent both on the interatomic separation as well as the identity of the atomic pairs but is independent of the surroundings of the relevant pairs.

The observed behavior of some Cu-Zn, Co-Fe (Ref. 4), Cu-Au (Refs. 5, 6), Au-Ni, Al-Zn and Al-Ag (Ref. 7) seems, however, to indicate composition dependence of the pair-wise interactions. Clearly, the concept of composition dependent pair-wise potentials is in violation of the premise of two-body central potentials which assumes that for an assembly of n

*Permanent Address: Department of Physics, Temple University, Philadelphia, Pa. 19122.

atoms the total potential energy is made up of $n(n-1)/2$ pair-wise additive terms such that when one of the n atoms is displaced, only its $(n-1)$ pair-wise bonds with the other $(n-1)$ atoms are affected; the rest maintaining their values.

From a more fundamental viewpoint, the pair-wise non-additivity of the interatomic forces has long been realized⁸. Moreover, the ubiquitous violation of the $A \leftrightarrow B$ interchange symmetry (according to which all thermodynamic properties of A , B_{1-n} and $A_{1-n}B$, alloys are the same⁹ if the configurational energy is made up of composition independent pair-wise potentials) suggest a need for examination of the consequences of inclusion of three-body potentials.

In the extreme disordered region, it has been shown that the effects of three and higher-body potentials can be approximated by an appropriate composition renormalization of the two-body potential. However, the effects of the three-body potentials in the ordered region have previously not been investigated.

Our objective here is both to formulate the problem in the ordered region in terms of an Ising antiferromagnet and to present a first order solution which describes the effects of the three-body potentials on the LRO.

2. Formulation

Analogously to the disordered binary alloy¹⁰, we consider only static configurational interactions, $H(\text{config})$. This interaction is dependent upon the particular configuration in which N^A atoms of type A and N^B atoms of type B are distributed over a lattice of $N = N^A + N^B$ sites. We assume that the sites form a regular, rigid lattice.

$$H(\text{config}) = \frac{1}{2!} \sum'_{\lambda, \mu} \sum_{i, j} V^{\lambda\mu}(ij) \sigma_i^\lambda \sigma_j^\mu + \frac{1}{3!} \sum'_{\lambda, \mu, \nu} \sum_{i, j, l} W^{\lambda\mu\nu}(ijl) \sigma_i^\mu \sigma_j^\nu \sigma_l^\lambda \quad (1)$$

The primed sums are over the indices A and B and the unprimed sums range over the entire lattice. The occupation operators, σ_i^λ , etc., have the usual meaning:

$$\sigma_i^\lambda = \begin{cases} +1, & \text{if the } i\text{-th site is occupied by a } \lambda \text{ atom,} \\ = 0, & \text{otherwise.} \end{cases} \quad (2)$$

The two-body interactions have the property

$$\begin{aligned} V^{\lambda\nu}(ij) &= V^{\lambda\nu}(ji) = V^{\nu\lambda}(ij), \\ V^{\lambda\nu}(ii) &= 0. \end{aligned} \quad (3)$$

Symmetry dictates that the three-body potentials obey the relations

$$\begin{aligned} W^{\lambda\lambda\lambda}(ijl) &= W^{\lambda\lambda\lambda}(jil) = W^{\lambda\lambda\lambda}(lij), \\ W^{\lambda\lambda\lambda}(ijl) &= W^{\lambda\lambda\nu}(jil) = W^{\lambda\nu\lambda}(ilj), \\ W^{\lambda\mu\nu}(ijl) &= W^{\lambda\nu\mu}(ilj) = W^{\nu\mu\lambda}(lji), \text{ etc.} \end{aligned} \quad (4)$$

To insure the irreducibility of the three-body potential we require

$$W^{\lambda\mu\nu}(ijl) = 0, \text{ whenever any two or more of the indices, } i, j, l, \text{ coincide.} \quad (5)$$

Introducing the transformation

$$\sigma_i^A = \frac{1}{2} + S_i^z; \quad \sigma_i^B = \frac{1}{2} - S_i^z \quad (6)$$

and requiring that

$$\sigma_i^\lambda \sigma_i^\mu = \sigma_i^\mu \sigma_i^\lambda; \quad \sigma_i^\lambda \sigma_i^\mu = \sigma_i^\lambda \delta_{\lambda,\mu}, \quad (7)$$

we identify S_i^z to have the character¹¹ of the z-component of spin-1/2, i.e.

$$[S_i^z, S_j^z] = 0; \quad (S_i^z)^2 = 1/4. \quad (8)$$

The grand canonical operator, \mathcal{H} , is now readily found to be

$$\mathcal{H} = \frac{1}{2!} \sum_{i,j} J(ij) S_i^z S_j^z + \frac{1}{3!} \sum_{i,j,l} K(ijl) S_i^z S_j^z S_l^z - \rho \sum_i S_i^z \quad (9)$$

Here we have used the notation

$$\begin{aligned} J(ij) &= J(ji) \\ &= V^{AA}(ij) + V^{BB}(ij) - 2V^{AB}(ij) \\ &+ \frac{1}{2} \sum_l [W^{AAA}(ijl) + W^{BBB}(ijl) + W^{AAB}(ijl) + W^{BBA}(ijl) \\ &\quad - W^{AAB}(ilj) - W^{AAB}(jli) - W^{BBA}(ilj) - W^{BBA}(jli)], \end{aligned} \quad (10)$$

$$\begin{aligned} K(ijl) &= K(ilj) = K(jil) = K(jli) = K(lij) = K(lji) \\ &= W^{AAA}(ijl) - W^{BBB}(ijl) - W^{AAB}(ijl) + W^{BBA}(ijl) \\ &\quad - W^{AAB}(ilj) + W^{BBA}(ilj) - W^{AAB}(jli) + W^{BBA}(jli). \end{aligned} \quad (11)$$

Note that the $A \leftrightarrow B$ interchange is achieved by $S_i^z \leftrightarrow -S_i^z$ and consequently under such an interchange $J \leftrightarrow J$ and $K \leftrightarrow -K$. The chemical potential μ is determined by fixing the concentration, i.e. for $N \rightarrow \infty$

$$p^A = N^A/N = \frac{1}{N} \sum_i \sigma_i^A = \frac{1}{N} \sum_i \langle \sigma_i^A \rangle, \quad (12)$$

where

$$\langle \dots \rangle = \text{Tr}[\exp(-\mathcal{H}/kT) \dots] / \text{Tr}[\exp(-\mathcal{H}/kT)]. \quad (13)$$

Here k is the Boltzmann constant and T is the Kelvin temperature of the system.

3. Two Sub-Lattice Medel and the LRO

We assume that the lattice is described by two inter-penetrating sub-lattices, α and β , such that any atom on the α sub-lattice finds all its nearest neighbors to be on the β sub-lattice and vice versa. Moreover we limit ourselves to considering only short range potentials. In particular, we assume that $J(ij)$ will be non-zero, i.e. $= J$, only if i and j are nearest neighbors. Moreover, because those lattices that admit two, nearest neighbor, inter-penetrating sub-lattices, e.g. simple and body centered cubic lattices, do not contain nearest neighbor triangles, the shortest range three-body potentials will have the character that only two of the three sides of the triangle will be equal to the nearest neighbor separation while the third side will be the length of the second neighbor distance.

The above described limitation of the range of the potentials rules out the presence of terms containing $J(\gamma_i\gamma_j)$ and $K(\gamma_i\gamma_j\gamma_l)$, where $\gamma = \alpha$ or β . Therefore, the grand canonical operator becomes:

$$\begin{aligned} \mathcal{H} = & \sum_{\alpha,\beta} J(\alpha\beta) S_\alpha^z S_\beta^z + \frac{1}{2} \sum_{\alpha_1,\alpha_2,\beta} K(\alpha_1\alpha_2\beta) S_{\alpha_1}^z S_{\alpha_2}^z S_\beta^z \\ & + \frac{1}{2} \sum_{\beta_1,\beta_2,\alpha} K(\beta_1\beta_2\alpha) S_{\beta_1}^z S_{\beta_2}^z S_\alpha^z - \rho \left(\sum_\alpha S_\alpha^z + \sum_\beta S_\beta^z \right). \end{aligned} \quad (12)$$

Here a, a, \dots , signify the various atoms in the α sub-lattice. Also the sums over these indices are taken over the entire α sub-lattice consisting of $N/2$ sites. The notation for the β sub-lattice is similar. As such

$$\begin{aligned} J(\alpha\beta) = J(\beta\alpha) = J, & \text{ if } \alpha \text{ and } \beta \text{ are nearest neighbors,} \\ = 0, & \text{ otherwise,} \end{aligned} \quad (13)$$

$$\begin{aligned} K(\gamma_1\gamma_2\delta) = K(\gamma_2\gamma_1\delta) = K, & \text{ if } \delta \text{ is first neighbor of } \gamma_1 \text{ and } \gamma_2, \text{ which are} \\ & \text{ second neighbors of each other (Note that } \gamma \text{ and} \\ & \delta \text{ are on different sub-lattices)} \end{aligned} \quad (14)$$

Within the molecular field approximation (*MFA*) the result for the sublattice magnetization can be obtained by elementary means. Nevertheless, with a view to future improvements on the *MFA*, we give a more powerful formulation below.

Consider the retarded Green's function

$$\langle\langle S_{\alpha}^{+}(t); S_{\alpha}^{-}(t') \rangle\rangle = -2ni \Theta(t-t') \langle [S_{\alpha}^{+}(t), S_{\alpha}^{-}(t')] \rangle. \quad (17)$$

Here $\Theta(t-t')$ is the Heaviside step function and the time dependence is in the Heisenberg representation with respect to \mathcal{H} . The Fourier transform of the equation of motion is

$$\begin{aligned} (E-\rho) \langle\langle S_{\alpha}^{+}; S_{\alpha}^{-} \rangle\rangle_{(E)} &= 2M_{\alpha} - \sum_{\beta} J(\alpha\beta) \langle\langle S_{\beta}^{z} S_{\alpha}^{+}; S_{\alpha}^{-} \rangle\rangle_{(E)} \\ &\quad - \sum_{\alpha_1, \beta} K(\alpha\alpha_1\beta) \langle\langle S_{\beta}^{z} S_{\alpha_1}^{+}; S_{\alpha}^{-} \rangle\rangle_{(E)} \\ &\quad - \frac{1}{2} \sum_{\beta_1, \beta_2} K(\beta_1\beta_2\alpha) \langle\langle S_{\beta_1}^{z} S_{\beta_2}^{z} S_{\alpha}^{+}; S_{\alpha}^{-} \rangle\rangle_{(E)} \end{aligned} \quad (16)$$

where we have used the notation

$$\begin{aligned} \langle\langle A(t); B(t') \rangle\rangle &= \int_{-\infty}^{+\infty} \langle\langle A; B \rangle\rangle_{(E)} e^{-iE(t-t')} dE, \\ \langle\langle S_{\gamma}^{z} \rangle\rangle &= M_{\gamma}; \quad \gamma \equiv \alpha, \beta. \end{aligned} \quad (18)$$

We introduce the first order, *MFA* decouplings,

$$\begin{aligned} \langle\langle S_{\beta}^{z} S_{\alpha_1}^{z} S_{\alpha}^{+}; S_{\alpha}^{-} \rangle\rangle_{(E)} &\sim M_{\alpha} M_{\beta} \langle\langle S_{\alpha}^{+}; S_{\alpha}^{-} \rangle\rangle_{(E)}, \\ \langle\langle S_{\beta_1}^{z} S_{\beta_2}^{z} S_{\alpha}^{+}; S_{\alpha}^{-} \rangle\rangle_{(E)} &\sim (M_{\beta})^2 \langle\langle S_{\alpha}^{+}; S_{\alpha}^{-} \rangle\rangle_{(E)}. \end{aligned} \quad (19)$$

(Note that the sites a , a , and β are distinct. The same is also true of β_1 , β_2 and a).

Consequently, the Green's function is given by

$$\begin{aligned} \langle\langle S_{\alpha}^{+}; S_{\alpha}^{-} \rangle\rangle_{(E)} &= 2M_{\alpha} [E - E(\alpha)]^{-1}, \\ E(\alpha) &= \rho - M_{\beta} J \xi - M_{\alpha} M_{\beta} K \xi - (M_{\beta})^2 K \eta. \end{aligned} \quad (20) \quad (21)$$

Here ξ is the number of nearest neighbors and η the number of distinct equilateral triangles that can be formed with a given atom as the vertex between the two **short** sides, which are equal to the nearest neighbor distance, and the long **side** equal to the second neighbor separation. For the simple and the body centered cubic lattices, $\xi = 6$ and 8 and $\eta = 1\%$ for both the lattices. Here,

$$K\xi = \sum_{\alpha_1, \beta} K(\alpha\alpha_1\beta). \quad (22)$$

Using the relation

$$\langle BA \rangle = -\frac{1}{\pi} \int_{-\infty}^{+\infty} [\text{Im} \ll A; i \mathfrak{z} \mathfrak{z} (\omega + i0)] d\omega / (e^{\omega/kT} - 1) \quad (23)$$

and re -arranging the result slightly, we get

$$\rho - M_\beta J\xi - M_\alpha M_\beta K\xi - M_\beta^2 K\eta = kT \ln \left(\frac{1 + 2M_\alpha}{1 - 2M_\alpha} \right). \quad (24)$$

The chemical potential ρ is fixed by the requirement

$$\frac{N}{2} M_\alpha + \frac{N}{2} M_\beta = N \langle S_i^z \rangle = \frac{1}{2} (N^A - N^B). \quad (25)$$

The LRO parameter, L , is quite naturally described by the difference

$$M_\alpha - M_\beta = L. \quad (26)$$

The sub-lattice magnetization M_α and M_β therefore have the description

$$2M_\alpha = p^A - p^B + L, \quad (27a)$$

$$2M_\beta = p^A - p^B - L. \quad (27b)$$

(Eqs.(27a, b) follow from the sum and the difference of Eqs.(25) and 26)). Here p^A and p^B are the atomic concentrations of the A and the B atoms in the alloy, i.e.

$$p^A = N^A/N; \quad p^A + p^B = 1. \quad (28)$$

Equation (24) is now readily solved. Subtracting (24) from the corresponding equation obtained from it by interchanging indices a and β , and re-arranging the result slightly, we get

$$\frac{2L}{L^2 + 4p^A p^B} = \tanh \left(\frac{\tilde{J}L\xi}{2kT} \right), \quad (30)$$

where

$$\tilde{J} = J + (p^A - p^B) K\eta/\xi. \quad (31)$$

Except for the re-normalization of the pair-potential J to \tilde{J} , this result is identical to the well known BWA result'. The renormalization is con-

centration dependent and is directly proportional to the three-body potential K .

4. Interpretation of the LRO

The introduction of the LRO through the relation (26) seems quite natural. It is interesting to examine how this LRO relates to the usual LRO parameter, S , which is introduced through the relation¹

$$p_\alpha^A = p^A(1 + S); \quad p_\beta^A = p^A(1 - S), \text{ etc.} \quad (32)$$

Here p_α^A is the probability of finding an A atom on the sub-lattice α .

In terms of the occupation operators, p_γ^λ can be represented as follows

$$p_\gamma^\lambda \equiv \langle \sigma_\gamma^\lambda \rangle; \quad \lambda = A, B; \quad \gamma = \alpha, \beta. \quad (33)$$

Therefore, Eqs. (6), (18) and (27a, b) give

$$\begin{aligned} p_\alpha^A &= \frac{1}{2} + M_\alpha = p^A + \frac{L}{2}; & p_\beta^A &= \frac{1}{2} + M_\beta = p^A - \frac{L}{2}; \\ p_\alpha^B &= \frac{1}{2} - M_\alpha = p^B - \frac{L}{2}; & p_\beta^B &= \frac{1}{2} - M_\beta = p^B + \frac{L}{2}. \end{aligned} \quad (34)$$

In view of the above, the identification of L with S is immediate:

$$L = 2p^A S. \quad (35)$$

5. Concluding Remarks

We have presented here a formulation for the study of LRO in a binary alloy with pair-wise non-additive potentials. Within the molecular field approximation we have shown that the presence of three-body potentials only renormalizes the two-body potential with concentration. This result is entirely analogous to the result obtained for the disordered phase in the high temperature limit. Consequently, as for the disordered phase, we expect the presence of even higher n -body potentials to also contribute to the renormalization of the effective two-body potential.

It is clear from the structure of the renormalization given in Eq. (31) that within the MFA, the renormalization caused by irreducible n -body potentials will be proportional to $(p^A - p^B)^{n-2}$.

More refined solution of the Green's functions¹² than given in Eq. (19)

will in all probability introduce some LRO driven renormalization of the effective potential. Moreover, we expect such an analysis to show the existence of additional details, resulting from the presence of many body irreducible potentials, that cannot be described by any simple renormalization of the two-body potential.

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