

The Pair Approximation of the Cluster Variation Method as Applied to bcc Alloys

A. CADENA-ZARAGOZA, F. MEJÍA-LIRA*) and F. AGUILERA-GRANJA

*Instituto de Física "Manuel Sandoval Vallarta"
Universidad Autónoma de San Luis Potosí
San Luis Potosí, S. L. P. 78000, México*

(Received April 5, 1992)

The phase diagram of the order-disorder transformation in binary alloys A_xB_{1-x} with bcc structure is calculated using the pair approximation of the Cluster Variational Method (CVM). Nearest (NN) and next-nearest neighbor (NNN) interactions are considered. Two types of pairs are taken into account: short pairs for the NN and long pairs for the NNN. The results of our calculation are compared with the CVM tetrahedron approximation and Monte Carlo Simulations (MCS).

§ 1. Introduction

The order-disorder transition in binary A_xB_{1-x} alloys with body center cubic (bcc) structure considering long range interactions has been subject of numerous theoretical and experimental studies.^{1)~4)} From the theoretical point of view the simplest approximation for the study of bcc binary alloys using analytic statistical mechanics is the Bragg-Williams-Gorsky (BWG),^{2),5)} which is equivalent to the point approximation in the hierarchy of the CVM.⁶⁾ From the statistical point of view the point approximation is not satisfactory since it does not take into account the correlation among neighboring points. The following step in the CVM hierarchy is the pair approximation which is equivalent to the Bethe approximation⁷⁾ when only NN are considered. It has been pointed out that this approximation is not sufficient to describe the bcc binary alloys with long range interactions,⁴⁾ however a fact is that many of the main characteristics obtained within this approximation are unknown in the case when long range interactions are considered. We can say without any doubts that the pair approximation with long range interactions is still a closed door. The next improvement in the statistical count is the tetrahedron approximation.^{3),4)} The cluster used in this approximation is an irregular tetrahedron with two short edges (NN pairs) and two long edges (NNN pairs). This is illustrated in Fig. 1(a) with dashed lines that link sites in four different sublattices. This approximation gives excellent results^{3),4)} and compare nicely with the MCS.⁴⁾

In this work, we restrict ourselves to the pair approximation and its limitations when this is applied to described the bcc binary alloys with NN and NNN interactions.

*) Posthumous contribution.

§ 2. The model and the method

For our study we divide the bcc lattice in two interpenetrating simple cubic (sc) sublattices: the sites in the body centers (α) and the sites at cubic edges (β), as illustrated in Fig. 1(a). In our calculation we define three different pairs as the basic clusters. They are shown in Fig. 1(b). The probabilities associated with those pairs are represented by $y_{i,j}^{\alpha,\beta}$ for the pair of sites in the sublattices α and β (short pair), $z_{i,j}^{\alpha,\alpha}$ for the pair of sites located within the sublattice α (long pair) and $z_{i,j}^{\beta,\beta}$ for the pair of sites in the sublattice β (long pair).

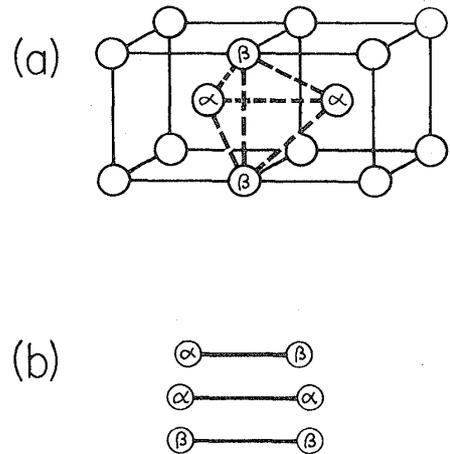


Fig. 1. (a) The irregular cluster used in the tetrahedron approximation of the CVM.^{3),4)} (b) The three different clusters used in the pair approximation. It is worth pointing out that the clusters are drawn in scale and that the size difference between the clusters is very small.

The internal energy

It is assumed that the internal energy is built up with pairwise interactions $W_{i,j}^{(k)}$ between k -th neighbors (with $k=1, 2$). By defining the energy parameters as follows:

$$W_{i,j}^{(k)} = \begin{cases} W_k & \text{for } i \neq j, \\ 0 & \text{when } i = j, \end{cases} \tag{1}$$

the internal energy can be written as

$$E = 4N \sum_{i,j} W_{i,j}^{(1)} y_{i,j}^{\alpha,\beta} + \frac{3N}{2} \sum_{i,j} (W_{i,j}^{(2\alpha)} z_{i,j}^{\alpha,\alpha} + W_{i,j}^{(2\beta)} z_{i,j}^{\beta,\beta}), \tag{2}$$

where N is the total number of lattice points and the super index $\nu=(\alpha, \beta)$ in $W_{i,j}^{(2\nu)}$ indicates the type of second neighbors.

The entropy

The entropy expression using the basic clusters shown in Fig. 1(b) can be evaluated among several different methods. We find that Barker's method^{8),9)} is the most convenient to use in the present case. The entropy is therefore given by

$$\begin{aligned} S = & -k_B N \left(4 \sum_{i,j} \mathcal{L}(y_{i,j}^{\alpha,\beta}) + \frac{3}{2} \sum_{i,j} \mathcal{L}(z_{i,j}^{\alpha,\alpha}) + \frac{3}{2} \sum_{i,j} \mathcal{L}(z_{i,j}^{\beta,\beta}) \right. \\ & - \frac{13}{7} \left[\sum_i \mathcal{L}(x_i^\alpha) + \sum_i \mathcal{L}(x_i^\beta) + \sum_j \mathcal{L}(x_j^\alpha) + \sum_j \mathcal{L}(x_j^\beta) \right] \\ & \left. - \frac{39}{28} \left[\sum_i \mathcal{L}(x_i^\alpha) + \sum_j \mathcal{L}(x_j^\alpha) + \sum_i \mathcal{L}(x_i^\beta) + \sum_j \mathcal{L}(x_j^\beta) \right] - 6 \right), \end{aligned} \tag{3}$$

where k_B is the Boltzmann constant and $\mathcal{L}(x) (= x \ln x - x)$ represent Stirling's func-

tion. In the entropy expression given by Eq. (3) there is the freedom to split in an arbitrary way the coefficient related with the single site probabilities. We did this partition such a way that the final set of equations reduces to the simplest possible form.

Lagrange's multipliers

In addition to the trivial Lagrange multipliers related with the normalization (λ_i with $i=1, 2, 3$), the pair probabilities are constrained by the fact that the single site probabilities can be written in several ways as is indicated by the next set of equations:

$$x_i^\alpha = \sum_j y_{i,j}^{\alpha,\beta} \quad \text{or} \quad x_i^\alpha = \sum_j z_{i,j}^{\alpha,\alpha}, \quad (4a)$$

$$x_i^\beta = \sum_j y_{j,i}^{\alpha,\beta} \quad \text{or} \quad x_i^\beta = \sum_j z_{i,j}^{\beta,\beta}. \quad (4b)$$

Two additional Lagrange multipliers are required in order to satisfy the consistency relationship of the pair probabilities expressed in Eqs. (4) ($x_i^\alpha(y_{i,j}^{\alpha,\beta}) = x_i^\alpha(z_{i,j}^{\alpha,\alpha})$ and $x_i^\beta(y_{j,i}^{\alpha,\beta}) = x_i^\beta(z_{i,j}^{\beta,\beta})$).

Grand potential

Since we fix the chemical potential rather than the composition in the calculation, the thermodynamics function to be minimized is not the Helmholtz free energy ($F = E - TS$) but the grand potential defined as follows:

$$\Omega = F - \sum_i \mu_i N_i, \quad (5)$$

where μ_i and $N_i (= N(x_i^\alpha + x_i^\beta)/2)$ are the chemical potential of the i species and its total number respectively. Finally, the equilibrium conditions are obtained from the minimization of the grand potential

$$\frac{\partial \Omega}{\partial y_{i,j}^{\alpha,\beta}} = 0, \quad \frac{\partial \Omega}{\partial z_{i,j}^{\alpha,\alpha}} = 0, \quad \frac{\partial \Omega}{\partial z_{i,j}^{\beta,\beta}} = 0. \quad (6)$$

The set of equation in (6) is solved using the Natural Iteration Method¹⁰⁾ in a two nested iteration. The external iteration loop is for the normalization process (major iteration)¹¹⁾ and the internal iteration is to satisfy the consistence relationship given by Eqs. (4) (minor iteration).¹¹⁾

§ 3. Results and comparison

In Fig. 2 we present the results obtained by assuming that the interaction energies are: $W_{i,j}^{(1)} < 0.0$ and $W_{i,j}^{(2)} = 0.0$. In this case one obtains only two phases: the A2 or disorder phase and the B2 or order phase. The reader may consult Refs. 1) and 2) for information about the ground states of the bcc binary alloys. The transition from B2 to A2 is a continuous transition (2nd order). When we compare the BWG approximation^{1),2),4)} (not shown in Fig. 2) with the pair approximation, we find that the pair approximation (as well as the tetrahedron approximation) predicts a percolation

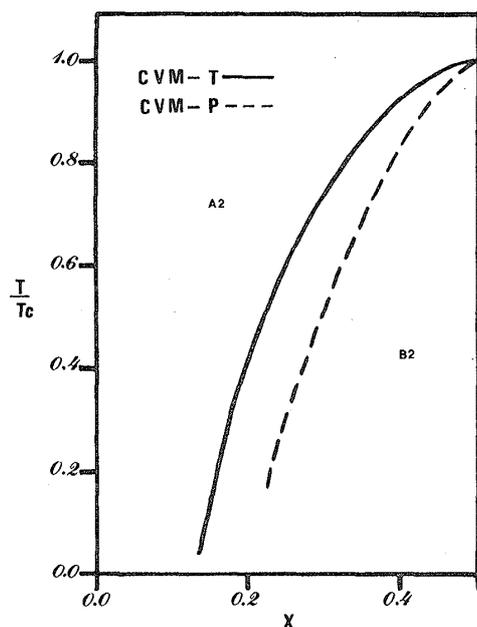


Fig. 2. Calculated phase diagram for $W_{i,j}^{(2\nu)}=0.0$ in the pair (CVM-P) and in the tetrahedron (CVM-T) approximations of the CVM. The phase diagrams are symmetric around $X=0.5$.

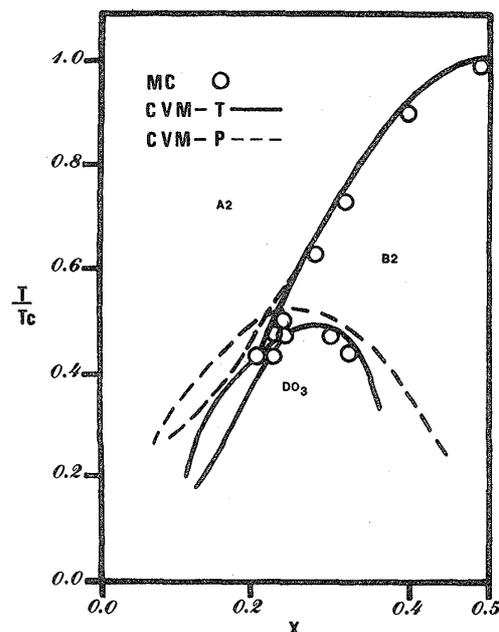


Fig. 3. Calculated phase diagrams for $W_{i,j}^{(2\nu)} \neq 0.0$ in the pair (CVM-P) and in the tetrahedron (CVM-T) approximations of the CVM. The MCS results are represented by circles. The phase diagrams are symmetric around $X=0.5$.

threshold. This means that the system requires of a minimal concentration of the A component in order to present an order phase. This is contrast to the BWG that predict ordered phases in the entire range of A concentration. When the phase diagram obtained with the CVM pair approximation (dashed line) is compared with the phase diagram obtained with the CVM tetrahedron approximation⁴⁾ (continuous line), we find that the pair approximation phase diagram is narrower than the calculated within the tetrahedron approximation.

In Fig. 3 we present the results obtained in the case in which the interaction energies are: $W_{i,j}^{(1)} < 0.0$ and $W_{i,j}^{(2\nu)} \neq 0.0$. In this case the phase diagram presents three phases; the A2 or disorder phase, the B2 or order phase and DO_3 which is a long-range-ordered phase or superstructure.^{1),2)} The transitions from B2 to A2 and from B2 to DO_3 are continuous (2nd order), while the transition from DO_3 to A2 is a first order transition and a coexisting region appears between the two phases. When the phase diagram obtained with the CVM pair approximation (dash line) is compared with the phase diagram obtained with the CVM tetrahedron approximation⁴⁾ (continuous line), we find that the pair approximation gives very good results for the transition between B2 and A2 and not so good for the transitions DO_3 to B2 and DO_3 to A2. There, the pair approximation predicts a wider phase diagram than the tetrahedron approximation and the MCS results, which may be considered as the most reliable calculation. To conclude, we can say that the pair approximation predicts mainly the same topology of the phase diagram as that obtained within the tetrahedron approximation. More details of the calculation and the generalization to the case in which one of the alloy components is magnetic will be given elsewhere.¹²⁾

Acknowledgements

This work was supported by the Consejo Nacional de Ciencia y Tecnología (México) through Grant No. 1774-E9210. One of us (ACZ) likes to acknowledge the partial economical support of CONACyT (México) and to the Fondo de Apoyo a la Investigación (UASLP). We also acknowledge to Professor J. L. Morán-López for a critical reading of the manuscript.

References

- 1) M. C. Cadeville and J. L. Morán-López, *Phys. Rep.* **153** (1987), 331.
- 2) G. Inden, *Acta Metall.* **22** (1974), 945.
- 3) N. S. Golosov and A. M. Tolstik, *J. Phys. Chem. Solids* **36** (1975), 899; **36** (1975), 903; **37** (1976), 273.
- 4) H. Ackermann, G. Inden and R. Kikuchi, *Acta Metall.* **37** (1989), 1.
- 5) W. L. Bragg and E. J. Williams, *Proc. R. Soc. London* **A145** (1934), 699.
- 6) R. Kikuchi, *Phys. Rev.* **81** (1951), 988.
- 7) E. A. Guggenheim, *Proc. R. Soc. London* **A148** (1935), 304.
H. A. Bethe, *Proc. R. Soc. London* **A150** (1935), 552.
R. Peierls, *Proc. R. Soc. London* **A154** (1936), 207.
- 8) R. Kikuchi, *J. Chem. Phys.* **60** (1974), 1071.
- 9) R. Kikuchi, *Computer Modeling of Phase Diagrams*, ed. L. H. Bennett (Metall. Soc. Inc., Warrendale, Pa., 1986), p. 49.
- 10) R. Kikuchi, *Acta Metall.* **25** (1977), 195.
- 11) R. Kikuchi, *J. Chem. Phys.* **65** (1976), 4545.
- 12) A. Cadena-Zaragoza, MSc. Thesis (1994), Facultad de Ciencias de la Universidad Autonoma de San Luis Potosí, San Luis Potosí, México.