Journal of Statistical Physics, Vol. 95, Nos. 5/6, 1999

Continuous Displacement Formulation of Alloys

Ryoichi Kikuchi[1]

Received August 10, 1998

The conventional permutational statistics of cooperative phenomena is extended to include displacement of atoms from their reference lattice points. The formulation is done in the cluster variation method (CVM) framework, by changing summations in energy and entropy to integrals. It is demonstrated for the pair approximation of CVM on phase-separating fcc binary alloys. The treatment can take into account local lattice distortion due to atomic size difference, the elastic effects, and the pressure effects. To compare stability of states under pressure, the grand potential $\Omega(T, V, \{\mu_i\})$ is extended to $Z(T, p, \{\mu_i\})$ by a Legendre transform. Although the new function $Z(T, p, \{\mu_i\})$ vanishes in equilibrium, and is called the ZERO-potential in the paper, it remains nonzero and is used to determine the coexisting phases when the chemical potentials are modified. Numerical calculations are done using the natural iteration technique on model inter-atomic potentials of the Lennard-Jones type. The numerical results of using $\Omega(T, V, \{\mu_i\})$ and $Z(T, p, \{\mu_i\})$ potentials for phase-separating diagrams, for composition and pressure dependence of the lattice constant, and for the bulk modulus are reported and discussed.

KEY WORDS: Statistical mechanics; cluster variation method; ZERO-potential with pressure as the variable; phase-separation diagram calculations; fcc binary alloys; bulk modulus.

1. INTRODUCTION

The work to extend the conventional order-disorder theory to include atomic displacement was started not many years ago,$^{(1-4)}$ and is currently actively studied. A somewhat more extended background is discussed in these references. The present paper is a progress report on fcc binary alloys of phase-separating type using the pairs as the basic cluster. Although a

---

[1] Department of Materials Science and Mineral Engineering, University of California, Berkeley, California 94720; e-mail: klogw@uclink4.berkeley.edu.

tetrahedron is needed to formulate the ordered state in fcc, a pair is acceptable for phase-separating systems. Particular interests of the present paper are the effects of size difference and pressure. Although we follow the general approach of the Cluster Variation Method (CVM),(5) new techniques to be reported in this paper, particularly the ZERO potential, are found useful in the formulation and computation.

In formulating atomic displacement, we consider a reference fcc lattice whose lattice points are fixed in space. We assign an atom at each lattice point to start with, and then let atoms be displaced. The probability of finding an atom at **r** in **dr** from its reference lattice point is written as $f(\mathbf{r})\,\mathbf{dr}$. We use 1 and 2 for A and B atoms. The probability for a nearest-neighbor pair of atoms i and j at displacements $\mathbf{r}_1$ and $\mathbf{r}_2$ is written as $g_{ij}(\mathbf{r}_1, \mathbf{r}_2)$. In the following, a nearest-neighbor lattice pair of the reference lattice is simply called a pair unless otherwise specified.

When the two end points of a pair need to be specified, we use L and R. The reduction relations of f and g functions are

$$f_{iL}(\mathbf{r}_1) = \int d\mathbf{r}_2 \sum_j g_{ij}(\mathbf{r}_1, \mathbf{r}_2) \qquad i = 1, 2 \tag{1.1a}$$

$$f_{iR}(\mathbf{r}_2) = \int d\mathbf{r}_1 \sum_i g_{ij}(\mathbf{r}_1, \mathbf{r}_2) \qquad j = 1, 2 \tag{1.1b}$$

The probability of finding i assigned to the left lattice point of a pair is

$$x_{iL} = \int d\mathbf{r}_1\, f_{iL}(\mathbf{r}_1) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \sum_j g_{ij}(\mathbf{r}, \mathbf{r}_2) \tag{1.2}$$

These functions are normalized with the relations

$$1 = \sum_i x_{iL} = \int d\mathbf{r}_1 \sum_i f_{iL}(\mathbf{r}_1) = \int d\mathbf{r}_2 \sum_j f_{jR}(\mathbf{r}_2) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \sum_{ij} g_{ij}(\mathbf{r}_1, \mathbf{r}_2) \tag{1.3}$$

2. CONSTRAINTS

A point function $f_{iL}(\mathbf{r}_1)$ is reduced from a pair function $g_{ij}(\mathbf{r}_1, \mathbf{r}_2)$ as in (1.1). The point is a subcluster of a pair which is the basic cluster. In fcc, a point belongs to 12 different pairs. When a subcluster belongs to different basic clusters, the reduction relations from different basic clusters must be consistent.

A convenient way of writing the consistency requirement in the present case is to observe the symmetry relations which a point function is to satisfy. In fcc, $f(\mathbf{r})$ obeys 4-fold rotations. When we write a 4-fold rotation around the x-axis as $\mathbf{R}_{4x}$, $f(\mathbf{r})$ satisfies

$$f_{iL}(\mathbf{r}_1)=f_{iL}(\mathbf{R}_{4x}\mathbf{r}_1)=f_{iL}(\mathbf{R}_{4y}\mathbf{r}_1)=f_{iL}(\mathbf{R}_{4z}\mathbf{r}_1) \tag{2.1}$$

Since the three rotations in (2.1) are mutually related, we can choose $\mathbf{R}_{4x}$ and $\mathbf{R}_{4z}$ as independent. The 3-fold rotation symmetry around a body-diagonal direction is satisfied when (2.1) holds.

Expecting a minimization process, we introduce Lagrange multipliers $\alpha_{xiL}(\mathbf{r})$ and write the constraint terms as

$$\begin{aligned} C_{\alpha xiL} &\equiv \int d\mathbf{r}_1\, \alpha_{xiL}(\mathbf{r}_1)\{f_{iL}(\mathbf{r}_1)-f_{iL}(\mathbf{R}_{4x}\mathbf{r}_1)\} \\ &= \int d\mathbf{r}_1\{\alpha_{xiL}(\mathbf{r}_1)-\alpha_{xiL}(\mathbf{R}_{4x}\mathbf{r}_1)\}\, f_{iL}(\mathbf{r}_1) \equiv \int d\mathbf{r}_1\, A_{xiL}(\mathbf{r}_1)\, f_{iL}(\mathbf{r}_1) \end{aligned} \tag{2.2}$$

Since $\alpha_{xiL}(\mathbf{r})$ appears always as the difference, we can simplify by introducing

$$A_{xiL}(\mathbf{r}_1)\equiv\alpha_{xiL}(\mathbf{r}_1)-\alpha_{xiL}(\mathbf{R}_{4x}\mathbf{r}_1) \tag{2.3}$$

When we rewrite $f_{iL}(\mathbf{r}_1)$ in (2.2) using the reduction relation (1.1), and further symmetrize L and R, we can write

$$\begin{aligned} C_{\alpha x} &\equiv \sum_i C_{\alpha xiL} + \sum_j C_{\alpha xjR} \\ &= \int d\mathbf{r}_1 \int d\mathbf{r}_2 \sum_{ij} \{A_{xiL}(\mathbf{r}_1)+A_{xjR}(\mathbf{r}_2)\}\; g_{ij}(\mathbf{r}_1,\mathbf{r}_2) \end{aligned} \tag{2.4a}$$

The constraint terms for $\mathbf{R}_{4z}$ is

$$C_{\alpha z} \equiv \int d\mathbf{r}_1 \int d\mathbf{r}_2 \sum_{ij} \{A_{ziL}(\mathbf{r}_1)+A_{zjR}(\mathbf{r}_2)\}\; g_{ij}(\mathbf{r}_1,\mathbf{r}_2) \tag{2.4b}$$

The Lagrange multipliers $A_{xiL}(\mathbf{r}_1)$ and $A_{xiR}(\mathbf{r}_2)$ for the L and R ends of a pair are not the same functions, because the relative geometry of the vector $\mathbf{r}_1$ or $\mathbf{r}_2$ and the bond direction is different for the two end points. However, they are related. Suppose the pair is on the $x-z$ plane. Then $g_{ij}(\mathbf{r}_1,\mathbf{r}_2)$ is invariant under the 180° rotation around the y-axis, $\mathbf{R}_{2y}$. This means that the following relations hold, and we need to formulate only for computing $A_{xiL}(\mathbf{r})$ and $A_{ziL}(\mathbf{r})$.

$$\begin{aligned} A_{xiR}(\mathbf{r}) &= A_{xiL}(\mathbf{R}_{2y}\mathbf{r}) \\ A_{ziR}(\mathbf{r}) &= A_{ziL}(\mathbf{R}_{2y}\mathbf{r}) \end{aligned} \tag{2.5}$$

3. THE Z-POTENTIAL $Z(Z, \mu, p)$

In addition to the previously reported continuous displacement work,[(1–4)] we now take into account the pressure effect explicitly. Previously we minimized the grand potential $\Omega(T, \{\mu_i\}, V)$ which is defined as

$$\Omega(T, \{\mu_i\}, V) \equiv E - TS - \sum_i \mu_i N_i \tag{3.1}$$

The derivative is

$$d\Omega = -S\,dT - p\,dV - \sum_i N_i\,d\mu_i \tag{3.2}$$

We now apply a Legendre transform to Ω and introduce a new function Z^*

$$dZ^* = d\Omega + d(pV) \tag{3.3}$$

to derive

$$dZ^* = -S\,dT + V\,dp - \sum_i N_i\,d\mu_i \tag{3.4}$$

This is the derivative of

$$Z^*(T, \{\mu_i\}, p) = E - TS + pV - \sum_i \mu_i N_i \tag{3.5}$$

which is the thermodynamic potential when T, p and the set of chemical potentials $\{\mu_i\}$ are the given parameters.

The Z^* function defined in (3.5) has a noteworthy property that it vanishes at equilibrium. This is because both the first three terms $E - TS + pV$ and the last term $\sum_i \mu_i N_i$ are the Gibbs free energy when T and p are fixed. For this reason, it is appropriate to name Z^* the ZERO-potential or the Z-potential. Because of this special property, Z^* cannot be used in comparing stability of two states.

However, we can modify $Z^*(T, \{\mu_i\}, p)$ in (3.5) and derive a function useful for comparing stability. We introduce μ^* and μ and write μ_1 and μ_2 as

$$\mu_1 = \mu^* - \mu; \qquad \mu_2 = \mu^* + \mu \tag{3.6}$$

Our choice of μ is that it increases as B increases. We rewrite (3.4) and (3.5):

$$dZ^* = -S\,dT + V\,dp - N\,d\mu^* - (N_2 - N_1)\,d\mu \tag{3.7}$$

$$Z^*(T, \mu^*, \mu, p) = E - TS + pV - N\mu^* - (N_2 - N_1)\mu \tag{3.8}$$

In (3.7) we can regard μ^* and μ as Lagrange multipliers to control N and $(N_2 - N_1)$. Since $N = N_1 + N_2$ is fixed, we do not need to control it, and hence we can redefine a new function Z from (3.8) as

$$Z(T, \mu, p) \equiv Z^* + N\mu^* = E - TS + pV - (N_2 - N_1)\mu \tag{3.9}$$

In equilibrium, Z^* becomes zero, but Z does not. Since no confusion is expected, we call $Z(T, \mu, p)$ also the Z-potential. The derivative of (3.9) is

$$dZ = -S\,dT + V\,dp - (N_2 - N_1)\,d\mu \tag{3.10}$$

C. G. Schön showed [6] that corresponding to Z^*, the grand potential Ω^* in its original form vanishes in equilibrium, and what we have been using in the multicomponent CVM treatments were $\Omega = \Omega^* + N\mu^*$ corresponding to Z in (3.9).

4. FORMULATION OF $Z(T, \mu, p)$

For a system of N lattice points, we write the Z-potential in (3.9) as

$$\beta\zeta \equiv \frac{Z}{NkT} = \beta\frac{E}{N} - \frac{S}{kN} + \beta\frac{C_p}{N} - \beta\frac{C_\mu}{N} - 6\{C_{ax} + C_{ay}\} + C_\lambda \tag{4.1}$$

where $\beta \equiv 1/kT$, $\zeta \equiv Z/N$ and C_λ is the normalization term. We now derive each term of (4.1) in terms of the pair variables and the lattice constant.

For the inter-atomic energies $e_{ij}(r)$ we use the Lennard–Jones potential of the form

$$\frac{e_{ij}(r)}{e_{ij0}} = \left(\frac{r_{ij0}}{r}\right)^{12} - 2\left(\frac{r_{ij0}}{r}\right)^{6} \tag{4.2}$$

where quantities with 0 are the parameters and r is the inter-atomic distance. Energy minima are at r_{ij0} and the values are

$$e_{ij}(r_{ij0}) = -e_{ij0} \tag{4.3}$$

For a phase-separating system, we may choose

$$e_{110} + e_{220} - 2e_{120} > 0 \tag{4.4}$$

although this is not the absolute guarantee for phase separation.

The basic requirement of the continuous displacement formulation is that the inter-atomic potentials are given as the input of the computation in terms of relative positions of atoms in the basic cluster. Hopefully the potential functions are to be given by quantum mechanics without using experimental data, as are done in the first-principle formulation of phase diagrams,$^{(7, 8)}$ and hence they are fixed functions throughout the phase diagram independent of density and temperature.

When a pair of atoms are displaced at $\mathbf{r}_1$ and $\mathbf{r}_2$, and the inter-atomic distance is r, we may interchangeably write without confusion

$$\varepsilon_{ij}(\mathbf{r}_1, \mathbf{r}_2) \equiv e_{ij}(r) \tag{4.5}$$

The energy term in (4.1) is then written as

$$\frac{E}{N} = 6 \int d\mathbf{r}_1 \int d\mathbf{r}_2 \sum_{ij} \varepsilon_{ij}(\mathbf{r}_1, \mathbf{r}_2)\, g_{ij}(\mathbf{r}_1, \mathbf{r}_2) \tag{4.6}$$

The entropy expression is derived by changing summations in the conventional permutation formulation to integrals as refs. 1, 3, 4

$$\begin{aligned}\frac{S}{kN} = \frac{S^*}{kN} + \frac{11}{2}\left(\int d\mathbf{r}_1 \sum_{i=1}^{2} L[f_{iL}(\mathbf{r}_1)] + \int d\mathbf{r}_2 \sum_{j=1}^{2} L[f_{jR}(\mathbf{r}_2)]\right) \\ -6 \int d\mathbf{r}_1 \int d\mathbf{r}_2 \sum_{i=1}^{2} \sum_{j=1}^{2} L[g_{ij}(\mathbf{r}_1, \mathbf{r}_2)]\end{aligned} \tag{4.7}$$

where S^* is an unknown additional constant which originates in the transformation of summations into integrals, and can be disregarded when stability of phases at the same temperature is of question. The $L[f(\mathbf{r})]$ expression is a functional defined as

$$L[f(\mathbf{r})] \equiv f(\mathbf{r}) \ln(f(\mathbf{r})) - f(\mathbf{r}) \tag{4.8}$$

The volume of the system V in (3.9) is written using the lattice constant a of the reference lattice, which is defined as the distance between the nearest-neighbor lattice points. The edge of an fcc cube is $\sqrt{2}\, a$, and the volume V of the fcc with N lattice points is $V = Na^3/\sqrt{2}$. The corresponding pressure term in Z is

$$\frac{C_p}{N} = p \frac{a^3}{\sqrt{2}} \tag{4.9}$$

The chemical potential term is the last term in (3.9). It is convenient to written it as

$$\frac{C_\mu}{N} = \sum_i x_i \mu_i \tag{4.10}$$

where x_i is the fraction of species i as defined in (1.2), and we redefine $\mu_1 \equiv -\mu$ and $\mu_2 \equiv \mu$ without μ^* in (3.6). Using (1.2), we rewrite (4.10) in terms of $g(\mathbf{r}_1, \mathbf{r}_2)$ in a symmetrized form as

$$\frac{C_\mu}{N} = \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \sum_{ij} \{\mu_i + \mu_j\}\ g_{ij}(\mathbf{r}_1, \mathbf{r}_2) \tag{4.11}$$

The last term C_λ in (4.1) is for the normalization of the basic function:

$$C_\lambda = \beta\lambda \left(1 - \int d\mathbf{r}_1 \int d\mathbf{r}_2 \sum_{ij} g_{ij}(\mathbf{r}_1, \mathbf{r}_2)\right) \tag{4.12}$$

where $\beta\lambda$ is the Lagrange multiplier.

In finding the equilibrium state, we fix T, μ and p, and minimize Z. It is done in two steps. First we fix a and differentiate $\beta\zeta$ with respect to $g_{ij}(\mathbf{r}_1, \mathbf{r}_2)$ to find $Z(T, \mu, p; a)$, and then vary a to find the minimum $Z(T, \mu, p)$. The first minimization process leads to

$$\begin{aligned} g_{ij}(\mathbf{r}_1, \mathbf{r}_2) = \exp\left(\frac{\beta\lambda}{6} - \beta\varepsilon_{ij}(\mathbf{r}_1, \mathbf{r}_2) + \frac{\beta}{12}\{\mu_i + \mu_j\}\right) \{f_{iL}(\mathbf{r}_1)\, f_{jR}(\mathbf{r}_2)\}^{11/12} \\ \times \exp\{A_{xiL}(\mathbf{r}_1) + A_{xjR}(\mathbf{r}_2) + A_{ziL}(\mathbf{r}_1) + A_{zjR}(\mathbf{r}_2)\} \qquad i, j = 1, 2 \end{aligned} \tag{4.13}$$

This set of equations is to be combined with the reduction equations in (1.1) and the normalization equations (1.3) to be solved for the basic probability function $g_{ij}(\mathbf{r}_1, \mathbf{r}_2)$.

When the minimization has been done, we can evaluate the Z-function using the normalization parameter λ. Subtracting zero terms from ζ and neglecting S^*, we reduce

$$\zeta = \zeta - \int \frac{\partial\zeta}{\partial g_{ij}(\mathbf{r}_1, \mathbf{r}_2)}\, dg_{ij}(\mathbf{r}_1, \mathbf{r}_2) = \lambda + p\frac{a^3}{\sqrt{2}} \tag{4.14}$$

Differing from previous treatments, λ itself is not equal to ζ.

When we include the pressure effect, we can calculate the bulk modulus B defines as

$$B = -V\frac{\Delta p}{\Delta V} = -\frac{a}{3}\frac{\Delta p}{\Delta a} \tag{4.15}$$

5. MINOR ITERATION

We solve $g_{ij}(\mathbf{r}_1, \mathbf{r}_2)$ from the basic set of equations using the Natural Iteration Method (NIM).$^{(5)}$ We start with guess values of the point functions

$f_i(\mathbf{r})$, use them on the right-hand side of (4.13) to derive $g_{ij}(\mathbf{r}_1, \mathbf{r}_2)$, use the latter in (1.1) to obtain the next input of $f_i(\mathbf{r})$, and repeat the process. It was proved for the pair approximation of the conventional substitutional CVM that the NIM always converges.(5) Since in other cases also where no proof was done yet, NIM never failed to converge, we can safely use the method in the present case. A shortcoming of the method is that it is slow compared with the Newton Rathson method, if the latter is available, and the advantage is that NIM converges from whatever initial guess values we may start.

When Lagrange multipliers are used, we have to supplement the major iteration steps with the minor ones. The latter solve the Lagrange multipliers $A_{xiL}(\mathbf{r})$ and $A_{ziL}(\mathbf{r})$ to satisfy the constraint relations among $f_i(\mathbf{r})$ before computing $g_{ij}(\mathbf{r}_1, \mathbf{r}_2)$ from (4.13). We determine $A_{xiL}(\mathbf{r})$ from the first equation of (2.1). When we use (1.1a) for $f_{iL}(\mathbf{r}_1)$, the exponential factor for $A_{xiL}(\mathbf{r}_1)$ can be brought out of the $\mathbf{r}_2$ integral, and we make this factor the output factor $A_{xiL}(\mathbf{r}_1)^{[\mathrm{out}]}$. The corresponding factor needed in $g_{ij}(\mathbf{r}_1, \mathbf{r}_2)$ inside the integral is the input factor $A_{xiL}(\mathbf{r}_1)^{[\mathrm{in}]}$. Then we obtain

$$\begin{aligned}&\exp\{A_{xiL}(\mathbf{r}_1)^{[\mathrm{out}]} - A_{xiL}(\mathbf{r}_1)^{[\mathrm{in}]}\} \int d\mathbf{r}_2 \sum_j g^*_{ij}(\mathbf{r}_1, \mathbf{r}_2)\\ &\quad = \exp\{A_{xiL}(\mathbf{R}_{4x}\mathbf{r}_1)^{[\mathrm{out}]} - A_{xiL(}\mathbf{R}_{4x}\mathbf{r}_1)^{[\mathrm{in}]}\} \int d\mathbf{r}_2 \sum_j g^*_{ij}(\mathbf{R}_{4x}\mathbf{r}_1, \mathbf{r}_2)\end{aligned} \tag{5.1}$$

where an asterisk indicates that the normalization factor is omitted. We define

$$\Delta A_{xiL}(\mathbf{r}_1) \equiv A_{xiL}(\mathbf{r}_1)^{[\mathrm{out}]} - A_{xiL}(\mathbf{r}_1)^{[\mathrm{in}]} \tag{5.2}$$

and derive from (5.1)

$$\Delta A_{xiL}(\mathbf{r}_1) - \Delta A_{xiL}(\mathbf{R}_{4x}\mathbf{r}_1) = \varphi \ln\left(\frac{f^*_{iL}(\mathbf{R}_{4x}\mathbf{r}_1)}{f^*_{iL}(\mathbf{r}_1)}\right) \equiv H_{iL}(\mathbf{R}_{4x}\mathbf{r}_1) \tag{5.3}$$

where (1.1) is used to write the integrals in f^*, and the function H is introduced. The damping factor φ has a value less than unity and is often needed to reduce the size of increment $\Delta A_{xiL}(\mathbf{r}_1)$ to avoid the iteration to diverge.

Solution of $\Delta A_{xiL}(\mathbf{r}_1)$ needs several steps. We write the set of equations in (5.3) explicitly:

$$\begin{aligned}
\Delta A_{xiL}(\mathbf{r}_1)-\Delta A_{xiL}(\mathbf{R}_{4x}\mathbf{r}_1)&=H_{iL}(\mathbf{R}_{4x}\mathbf{r}_1)\\
\Delta A_{xiL}(\mathbf{R}_{4x}\mathbf{r}_1)-\Delta A_{xiL}((\mathbf{R}_{4x})^2\,\mathbf{r}_1)&=H_{iL}(\mathbf{R}_{4x})^2\,\mathbf{r}_1)\\
\Delta A_{xiL}((\mathbf{R}_{4x})^2\,\mathbf{r}_1)-\Delta A_{xiL}((\mathbf{R}_{4x})^3\,\mathbf{r}_1)&=H_{iL}((\mathbf{R}_{4x})^3\,\mathbf{r}_1)\\
\Delta A_{xiL}((\mathbf{R}_{4x})^3\,\mathbf{r}_1)-\Delta A_{xiL}(\mathbf{r}_1)&=H_{iL}(\mathbf{r}_1)
\end{aligned}\tag{5.4}$$

We form a sum and make use of the definition in (2.3) to derive

$$\sum_{m=0}^{3}\Delta A_{xiL}((\mathbf{R}_{4x})^m\,\mathbf{r}_1)=\sum_{m=0}^{3}\{\alpha_{xiL}((\mathbf{R}_{4x})^m\,\mathbf{r}_1)-\alpha_{xiL}((\mathbf{R}_{4x})^{m+1}\,\mathbf{r}_1)\}=0\tag{5.5}$$

When we use the relations in (5.4), we can solve from (5.5) as

$$\Delta A_{xiL}(\mathbf{r}_1)=\tfrac{1}{4}\{3H_{iL}(\mathbf{R}_{4x}\mathbf{r}_1)+2H_{iL}((\mathbf{R}_{4x})^2\,\mathbf{r}_1)+H_{iL}((\mathbf{R}_{4x})^3\,\mathbf{r}_1)\}\tag{5.6}$$

This expression is not unique, because of the following identity derived from (5.4):

$$\sum_{m=0}^{3}H_{iL}((\mathbf{R}_{4x})^m\,\mathbf{r}_1)=0\tag{5.7}$$

When $\Delta A_{xiL}(\mathbf{r}_1)$ is solved as in (5.6), $A_{xiL}(\mathbf{r}_1)^{[\mathrm{out}]}$ is obtained from (5.2) as

$$A_{xiL}(\mathbf{r}_1)^{[\mathrm{out}]}=A_{xiL}(\mathbf{r}_1)^{[\mathrm{in}]}+\Delta A_{xiL}(\mathbf{r}_1)\tag{5.8}$$

When we change the subscript x to z in the formulation, we can derive $A_{ziL}(\mathbf{r}_1)^{[\mathrm{out}]}$ similarly. When we have solved $A_{xiL}(\mathbf{r}_1)$ for the L point as in (5.8), the solution $A_{xjR}(\mathbf{r}_2)$ for the R point is derived from the symmetry requirement in (2.5) without doing further iterations. Note (2.5) uses 2-fold rotation $\mathbf{R}_{2y}$ rather than $\mathbf{R}_{4y}$.

6. NUMERICAL RESULTS

As a numerical example of the method, we show results for the interatomic energy (d) in our previous paper.[4] This case is chosen because it takes into account both the atomic size difference and the difference in the energy depths, and also because the iteration in numerical computation is relatively fast. Previously[4] we used the 2-fold rotation symmetry for each point function $f(\mathbf{r})$ in order to make every other tetrahedron to be consistent, but this time we make it 4-fold which is required when all tetrahedra

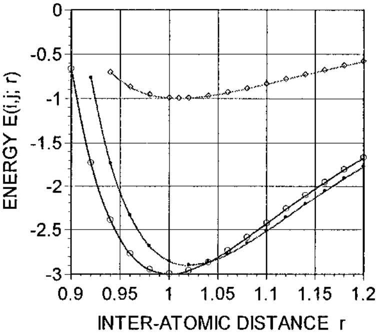

Fig. 1. The 6-12 Lennard–Jones potentials (6.1). Circles are for $A-A$, small dots are for $B-B$ and diamonds are for $A-B$.

are equivalent. The parameters we use for the Lennard-Jones potentials in (4.2) are

$$e_{110}=3.0,\quad e_{120}=1.0,\quad e_{220}=2.9,\quad r_{110}=1.00,\quad r_{120}=1.01,\quad r_{220}=1.02 \tag{6.1}$$

The unit of the energy is written as ε. Written in this unit, the key quantity to discriminate the phase separating system shown on the left-hand side of (4.4) is 3.9ε. The three Lennard–Jones curves are drawn in Fig. 1. The interaction for the mixed pair is chosen much higher than the pure pairs, over-guaranteeing that the system is phase-separating.

From the computational point of view, the main difference of the continuous displacement scheme from the conventional permutation case is the integration over displaced coordinates **r** around a reference lattice point instead of summation over species. Integration over **r** is done by dividing the **r** space into cells and summing the integrand over the cells. In the present work, around each lattice point we have 33 cells spread over two-layers of spherical shells. A larger number of cells are more desirable, but we used the smallest acceptable number 33 to satisfy the time limitation of computation.

The coexistence points at a given temperature T are calculated from the intersection of the Z-curves against μ for the left and the right phases as shown in Fig. 2. The upper curve in Fig. 2 is for $p=0.1$ and the lower ones for $p=0.0$. The Z-potential for the $p=0$ case in Fig. 2 is identical with the grand potential Ω. Figure 2 shows that the Z treatment is a natural extension of the Ω treatment.

These curves do show that Z is non-zero, although we know that Z^* in (3.8) vanishes in equilibrium. If we were to plot Z^* in (3.8), the two

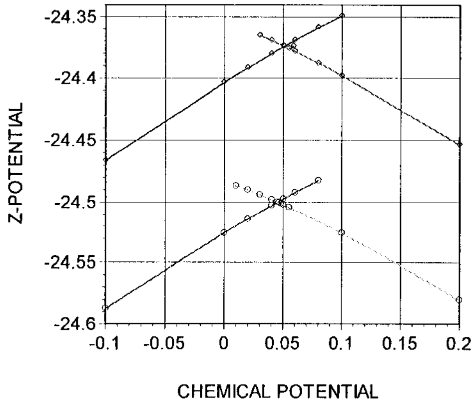

Fig. 2. The Z-potentials vs. chemical potential μ for $p = 1.0$ (upper curves) and $p = 0.0$ (lower curve). The intersection determines the coexisting phases.

curves in Fig. 2 would be both plat at zero, since each point on the curve represents a local equilibrium state.

The phase-separation diagrams are shown in Fig. 3. The upper curve is for $p = 1.0$ and the lower one is for $p = 0$. When the pressure is applied, the lattice constant decreases, and it becomes more difficult for foreign atoms to mix in. Therefore, the coexistence curve becomes wider and higher. With regard to Fig. 3, it is to be remembered that without the continuous displacement the congruent point of the phase diagram for the pair approximation is at $kT/\varepsilon = 10.7$. The curves in Fig. 3 are lower to about a half.

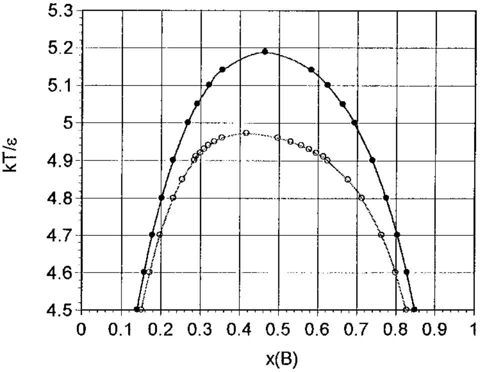

Fig. 3. Results of the phase-separation diagrams for $p = 1.0$ (upper curve) and for $p = 0.0$ (lower curve).

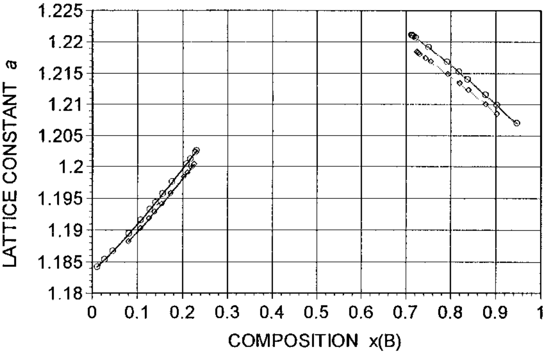

Fig. 4. Results of the lattice constant a against the composition, in the A-rich phase (left) and the B-rich one (right). The upper curves are for $p = 0.0$, and the lower ones for $p = 0.1$. The end points near the center are for the coexisting phases.

Figure 4 shows how the lattice constant varies in the A-rich and B-rich phases at a constant temperature. As impurities mix in, the average atomic volume increases, making the space wider for an atom to move around so that the entropy becomes larger. The upper curves are for $p = 0$ and the lower ones for $p = 0.1$.

The pressure in Fig. 4 is $p = 0.1$ rather than 1.0 in Fig. 3. We use the results of the two pressures in Fig. 4 and calculate the bulk modulus B in (4.15). Since each marked point on the curves in Fig. 4 is computed for a fixed μ, we numerically interpolate the results to derive a for chosen $x(B)$. The results are shown in Fig. 5. As we see in (4.15), the dimension and hence the unit of B are those of the pressure. Since we use ε and r_0 as the units of the energy and the length in the formulation, the unit of the

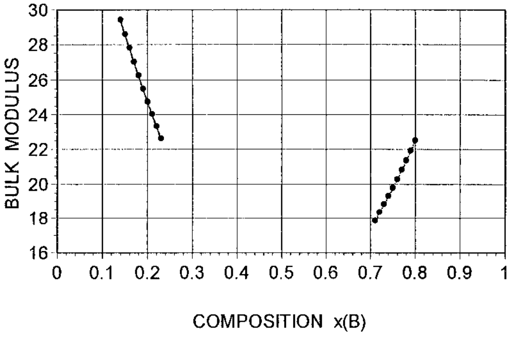

Fig. 5. Bulk modulus calculated based on the $p = 0.0$ and $p = 0.1$ curved in Fig. 4.

pressure and of B is $\varepsilon/(r_0)^3$. In order to see the rough estimate of the computation, we may use $\varepsilon = 800°$ K and $r_0 = 2.5$ Å for an example. Then the conversion, $1°$ K/Å$^3 = 13.806 \times 10^6$ Pascal, brings $B = 25$ in Fig. 5 to $B = 0.18 \times 10^{11}$ Pascal. This value is about the factor 5 smaller than $\mathrm{B} \approx 10^{11}$ Pascal for Cu. Considering the arbitrary nature of the energy parameters assumed in (6.1), this factor 5 shows that the present formulation and computation are qualitatively acceptable.

SUMMARY AND COMMENTS

The present paper extends the continuous displacement formulation by including the pressure effect explicitly. The grand potential which was used previously in deriving the equilibrium state is replaced by the ZERO potential, also called the Z-potential, in (3.9). The reason why the ZERO potential used in the computation of the treatment does not become zero is discussed. As far as the author is aware of, this is the first time the ZERO potential is presented explicitly in English publication,(9) although no doubt the concept was implicit in thermodynamics literature.

A numerical example is shown using a set of model energy parameters listed in (6.1). We did integration over displacements of an atom by summing over 33 points. Figure 2 shows that our Z-potential did lead to the coexisting phases as the intersection of two branches. The phase-separation diagrams are shown in Fig. 3 for $p = 0.0$ and 1.0, the $p = 1.0$ curve being at higher temperatures. The lattice constant in the A-rich and B-rich phases are shown in Fig. 4 for $p = 0.0$ and 0.1. Results of two pressure calculations of Fig. 4 lead to the bulk modulus B, which is shown in Fig. 5. The numerical values of B indicate that the present computation is acceptable.

As the next extension of the pressure effect, we plan to calculate Young's modulus and the shear modulus by making the pressure and hence the lattice anisotropic. Future plans include bcc alloys, the tetrahedron treatment, ordered states, more accurate computation of integrals, realistic systems, and demonstration of local distortion.

ACKNOWLEDGMENTS

Thanks are due to Drs. T. Mohri, K. Masuda-Jindo and C. Schön for their helpful discussions concerning this work.

It was a very good fortune for the present author to have overlapped with John Cahn for one year in 1953-4 at Institute for the Study of Metals at the University of Chicago. In 1956 he suggested to me the application of my CVM approach to compute the structure of an APB. It was the beginning of our long cooperation, and of his tutoring for my CVM

applications to materials science. Since my background was physics and my knowledge of materials science was not strong, his advice has been invaluable in the development of my entire research activities. The present work is on an extension of our joint studies of alloy structures. It is my great pleasure to dedicate this work of my recent study at John's 70th birthday celebration.

REFERENCES

1. R. Kikuchi and A. Beldjenna, *Physica A* **182**:617 (1992).
2. A. Finel, *Prog. Th. Phys. Suppl.* **115**:59 (1994).
3. R. Kikuchi and K. Masuda-Jindo, *Computational Materials Science* **8**:1 (1997).
4. R. Kikuchi, "Space is Continuous," *J. Phase Equilibria* **19**:412 (1998).
5. R. Kikuchi, *J. Chem. Phys.* **60**:1071 (1974).
6. C. G. Schön, Thermodynamics of Multicomponent System with Chemical and Magnetic Interactions, Fachbereich Chemietechnik der Universität Dortmund, Germany, Jan. 1998.
7. K. Terakura, T. Mohri, and T. Oguchi, *Mat. Sci. Forum* **37**:39(1989).
8. J. M. Sanchez, J. P. Stark, and V. L. Moruzzi, *Phys. Rev. B* **44**:5411 (1991).
9. R. Kikuchi and T. Mohri, *Cluster Variation Method* (MORIKITA Publishing Co., Tokyo, Japan) in Japanese (1997).