THE CONFIGURATIONAL PARTITION
FUNCTIONS OF SOLID SOLUTIONS

- COMMUNIST CHINA -

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The following is a full translation of an article written by
Chang Tsung-sui, appearing in Wu-
li Maeh-pao (Journal of Physics),

Abstract

This short paper applies a method for studying the
configurational partition function of regular solutions
developed by Wang, Hsu and the author to a number of special
cases. In such concrete calculations it is seen that the
method is applicable to almost every type of solid solutions.
In fact, its applicability is independent of the type of
lattice which atoms of the solution inhabit, of the existence
of the long distance order, of the existence of interactions
between atoms more distant than nearest neighbours, and of
the number of components in the solution. Since the method
is actually an expansion of the configurational free energy
in terms of certain coordination numbers of the lattice,
the results of the calculations after ignoring the higher
coordination numbers become closed expressions in terms of
the Boltzmann factors and thus avoid expansions in kT or in
(kT)^{-1}. Needless to say, expansion of the results obtained
here in (kT)^{-1} gives results identical with those obtained
by Kirkwood's method.

Next we discuss quasi-chemical formulas based on the
above method. We point out that if we neglect all the co-
ordination numbers except the lowest, we obtain the usual
quasi-chemical formula, quite independently of the number of
components in the solution. (A corresponding combinatorial
formula is derived.) On including higher coordination
numbers, we get natural extensions of the quasi-chemical
formula. Thus for a binary solid solution on a face centere
cubic system, the quasi-chemical formula after including the
next higher coordination number becomes

1
\[ X_{AA} = X'_{AA} + 3X''(A_{AA}) + 3X''(A_{AB}). \]
\[ X_{AB} = 2X_{AB} + 6X''(A_{AB}) + 6X''(A_{BB}). \]
\[ X_{BB} = X'_{BB} + 3X''(B_{BB}) + 3X''(B_{BB}). \]

\[
\frac{(X'_{AB})^2}{X'_{AA}X'_{BB}} = \frac{[X''(A_{AB})]^2}{X''(A_{AA})X''(A_{BB})} = \frac{[X''(B_{AB})]^2}{X''(B_{BB})X''(B_{BB})} = \exp(-2\varepsilon_{AA} - 1.4\varepsilon_{BB} - \varepsilon_{AB})kT. \tag{2}
\]

\[
(X'_{AA} + X'_{AB}) = -18N\theta_A.
\]
\[
(X'_{AB} + X'_{BB}) = -18N\theta_B. \tag{3}
\]

\[
X''(A_{AA}) + 2X''(A_{AB}) + X''(A_{BB}) = 8N\theta_A.
\]
\[
X''(B_{BB}) + 2X''(B_{AB}) + X''(B_{BB}) = 8N\theta_B. \tag{4}
\]

In the above, \( N\theta_A, N\theta_B \) denote the numbers of A, B atoms, \( X'_{AA}, X'_{AB} \ldots, X'' \ldots \) are numbers determined by (2), (3), (4), and their substitution into the righthand sides of (1) gives the numbers \( X_{AA}, X_{AB}, X_{BB} \) of AA, AB, BB pairs of nearest neighbours. It may be noted that \( X' \) may be negative and they do not bear any direct physical significance. It is also pointed out that instead of considering the numbers of pairs of nearest neighbours, we may consider directly the numbers of pairs of triplets (ie. 3 atoms forming mutually nearest neighbours) and write down by analogy (to the usual quasi-chemical formula) new quasi-chemical equations for the different numbers of triplets. From this, a combinatory formula is easily derived. It is shown that such a theory differs from (1) - (4) given above.

This short paper consists of two parts. The first part discusses the application of the method of finding the configurational partition functions of solid solutions, which was developed by Wang Te-mao, Hsu Yung-Huan, and the author (1) to different solid solutions. Comparisons have been made of the results obtained to the corresponding ones obtained by the method of Kirkwood. (2, 3, 4, 5) We discuss the following cases:
(1) AB-type crystal lattice; binary solid solution
(2) Face-centered crystal lattice; binary solid solution
(3) AB-type crystal lattice binary solid solution
with interaction between next nearest neighbors.

Essentially, this method takes advantage of the
property that the logarithm of the configurational parti-
tion function, \( F \), is a linear combination of certain co-
ordination numbers of the crystal lattice. After ignoring
the higher coordination numbers of the lattice, we obtain
\( F \) as a closed expression, no longer requiring a series
expansion in \((kT)^{-1}\) or \((kT)\). Therefore, we expect the resul-
thus obtained to be correct for any temperature. And we can
compare the result to that by the Kirkwood method by simply
expanding the result into series in \((kT)^{-1}\). The results
should be the same, and in fact, they are.

In the second part, we use the method of reference 1
to discuss the quasi-chemical approximation. First we point
out that if the lowest coordination number is retained, the
conventional quasi-chemical approximation formulas are
correct no matter how many kinds of atoms there are in the
solid solution. Second, we point out how to improve the con-
ventional quasi-chemical formula by keeping higher coordi-
nation numbers.

PART I

(1) AB-type lattice binary solid solution.

For a binary solid solution with the AB-type lattice,
we assume that the total number of atoms is \( N \), the number of
A atoms is \( N_0 \), and interaction exists only for atoms forming
nearest neighbor pairs. According to reference 1, we can
prove that the logarithm of the configurational partition
function, \( F \), is

\[
\log\left(\frac{N}{N_0}\right) + (\sum_\omega \lambda_\omega) f_1(N, \theta, T) + \\
+ (\sum_\omega \lambda_\omega \lambda_\omega' \lambda_\omega'' \lambda_\omega''') f_2(N, \theta, T) + \cdots,
\]

in which \( \lambda_\omega \) is the neighbor matrix, defined as

\[
\lambda_\omega = \begin{cases} 
1, & \text{if } c, c' \text{ are nearest neighbors} \\
0, & \text{otherwise,}
\end{cases}
\]

and the coefficients of \( f_1, f_2, \ldots, \) etc., are the matrix
elements of the irreducible products of the \( \lambda \)'s summed over
the indices, and are called coordination numbers. The
functions \( f_1, f_2, \ldots \) are certain functions of \( N, \theta, \) and \( T \).
Because these coordination numbers are apparently directly proportional to \( N \), therefore \( f \) does not contain \( N \). Reference 1 indicated that in order to determine \( f_1, f_2, \ldots \), etc., we need consider only the \( F \) of a hypothetical solid solution with the same values of \( N \) and \( \theta \).

Now we are going to consider the following hypothetical lattice: the total number of points \( N \) of the hypothetical lattice are divided into \( N/2 \) groups, each group having two points and forming a nearest-neighbor pair with no nearest neighbor between groups.

Then
\[
F = \frac{1}{2} N \log \left( 1 + 2\lambda + \lambda^2 \xi \right) - N \theta \log \lambda, \tag{2}
\]
in which
\[
\xi = \exp(-V_{AA}kT)
\]
\((V_{AB}, V_{BB} \text{ assumed to be zero}), \) is a function of \( N, \theta \), and \( T \), determined by

\[
\frac{\partial F}{\partial \lambda} = 0 \tag{3}
\]

From (3) we obtain
\[
\frac{1}{\lambda} = \frac{1-\theta}{\theta} + \frac{1}{2\theta} (H-1), \tag{4}
\]
\[
H = \left( 1 + 4(1-\theta)\eta \right)^{1/4},
\]
\[
\eta = \xi - 1.
\]

Substituting into (2), we get
\[
N^{-1} F = -\theta \log \theta - (1-\theta) \log (1-\theta) + \frac{1}{2} \log \left( \frac{1}{2} + \eta \theta + \frac{1}{2} H \right) - \left( 1 - \theta \right) \log \left\{ 1 + \frac{1}{2(1-\theta)} (H-1) \right\}. \tag{5}
\]

Since for this hypothetical lattice
\[
\Sigma \lambda_{ee} = N, \quad \Sigma \lambda_{ee} \lambda_{ee}^{'} \lambda_{ee}^{''} \cdots \lambda_{ee}^{(n)} = 0, \ldots,
\]
we have
\[
f_1(\theta, T) = \frac{1}{2} \log \left( \frac{1}{2} + \eta \theta + \frac{1}{2} H \right) - \left( 1 - \theta \right) \log \left\{ 1 + \frac{1}{2(1-\theta)} (H-1) \right\}. \tag{6}
\]
Expanding with respect to \( \gamma \), we have
\[
\frac{1}{2} \theta \eta + \frac{1}{4} \theta (\theta - 2 \theta) \eta^2 + \frac{1}{6} \{ \theta + \theta (1 - \theta) (1 - 2 \theta + 2 \theta^2) \} \eta^3 + \\
\frac{1}{8} \{ - \theta^2 + \theta (1 - \theta) (1 + 2 \theta + 3 \theta^2 + 5 \theta^3) \} \eta^4 + \ldots. 
\] (7)

To see the symmetry between \( \theta \) and \( (1 - \theta) \), we rewrite the above expression as
\[
\frac{1}{2} \theta \log \xi + \frac{1}{4} \theta (1 - \theta)^2 \eta^2 + \frac{1}{6} \theta^2 (1 - \theta)^2 (1 - \theta)^2 - 2 \eta^3 + \\
\frac{1}{8} \theta (1 - \theta)^2 \left[ \frac{5}{2} \theta + \frac{5}{2} (1 - \theta)^2 - 6 \theta^2 - 6 (1 - \theta)^2 \right] \eta^4 + \ldots. 
\] (8)

To determine \( f_2 \), we consider the following hypothetical lattice: the total points \( N \) of the assumed lattice are divided into \( N/3 \) groups, each group consisting of four points sitting on the four vertices of a cubic lattice, each side of the cubic lattice representing one nearest-neighbor pair; and, as in the former case, no nearest-neighbor pair exists between groups.

Under this condition,
\[
F = \frac{1}{4} N \log (1 + 4 \lambda + 4 \lambda \xi + 2 \lambda^2 + 4 \lambda^2 \xi^2 + \lambda^2 \xi^4) - N \theta \log \lambda, 
\] (9)

where \( \lambda \) satisfies
\[
2F \lambda = 0, 
\] (10)

exactly as in the former case. Equation (10) is of the fourth order in \( \lambda \), and we can solve this equation analytically for \( \lambda \) and then substitute it into expression (9).

When \( \gamma \) assumes its minimum value, the solution of Equation (10) is
\[
\frac{1}{\lambda} = \frac{1 - \theta}{\theta} + 2(1 - \theta) \eta - \theta(1 - \theta)(1 - 2 \theta) \eta + \\
+ 2 \theta(1 - \theta)^2 (1 - 2 \theta) \eta^3 + \ldots, 
\] (11)

Substituting into expression (9),
\[
N^{-1} F = - \theta \log \theta - (1 - \theta) \log (1 - \theta) + \theta^2 \eta^2 + \frac{1}{2} \theta^2 (\theta - 2 \theta) \eta^3 + \\
+ \frac{1}{3} \{ \theta + \theta (1 - \theta) (1 - 2 \theta + 2 \theta^2) \} \eta^4 + \\
+ \frac{1}{4} \{ - \theta + \theta (1 - \theta)^2 (1 + 2 \theta + 4 \theta^2 - 12 \theta^2 + 6 \theta^3) \} \eta^5 + \ldots. 
\] (12)
Since for this hypothetical lattice
\[ \Sigma \lambda_{\alpha} = 2N, \quad \Sigma \lambda_{\alpha'} \lambda_{\alpha''} \lambda_{\beta} \lambda_{\gamma'} = 2N, \quad \Sigma \lambda_{\ldots} = 0, \ldots, \]
therefore,
\[ N^{-1} F = - \theta \log \theta - (1 - \theta) \log(1 - \theta) + 2 f_1(\theta, T) + 2 f_2(\theta, T). \quad (13) \]

Comparing with (12), and making use of the known \( f \), see expression (7)\(^{1/2} \), we arrive at
\[ f_3 = \frac{1}{8} \theta (1 - \theta) \eta \eta' + \ldots. \quad (14) \]

Substituting \( f_1 \) and \( f_2 \) into expression (1), we obtain the \( F \) for all the other \( f \)'s neglected. If we expand this result as a series in \( (-V_{\text{AA}}/kT)^{-1} \), it appears exactly the same as the result by Kirkwood's method. (3) In making the comparison, we neglected 0 \((kT)^{-6} \).

(2) Face-centered lattice binary solid solution

Here
\[ F = \log \left( \frac{N}{N\theta} \right) + (\Sigma \lambda_{\alpha'}) f_1 + (\Sigma \lambda_{\alpha'} \lambda_{\alpha''} \lambda_{\beta} \lambda_{\gamma'}) f_3 + \]
\[ + (\Sigma \lambda_{\alpha'} \lambda_{\alpha''} \lambda_{\beta} \lambda_{\gamma'}) f_4 + \ldots. \quad (15) \]

Therefore, we should try to evaluate \( f_3 \).

Consider the following hypothetical lattice structure; the \( N \) points of the lattice are divided into \( N/3 \) groups, each group consisting of three points sitting on the vertices of an equilateral triangle. Each side of the triangle represents one nearest-neighbor pair, and there is no interaction among atoms of different groups.

Then the logarithm of the configurational partition function, \( F \), should be
\[ \frac{1}{N} N \log(1 + 3\lambda + 3\lambda^2 \xi + \lambda^3 \xi^2) - N \theta \log \lambda, \quad (16) \]
in which \( \lambda \) is determined by
\[ \frac{\partial F}{\partial \lambda} = 0 \]
When \( \gamma \) assumes small values, it is easy to find
\[
\frac{1}{\lambda} = -\frac{1}{\theta} + 2(1-\theta)\eta - \theta(1-\theta)(1-2\theta)\eta^2 + \ldots
\]
\[
+ \theta(1-\theta)^2(1-2\theta)(1+\theta)\eta^3 + \ldots
\]
\[
N^{-1}F = -\theta \log \theta - (1-\theta) \log (1-\theta) + \theta^2 \eta + \frac{1}{2} \theta^3 (\theta^2 - 2\theta) \eta^3 + \frac{1}{3} [\theta^2 + \theta^2 (1-\theta)^3 (1-\theta + \theta^4)] \eta^4 + \ldots
\]
\[\text{(17)}\]

Since for this lattice system we assumed
\[
\Sigma \lambda_{\alpha \beta} = 2N, \Sigma \lambda_{\alpha \beta} \lambda_{\alpha \beta} = 2N, \Sigma \lambda \lambda \lambda \lambda = 0, \ldots
\]

therefore
\[
N^{-1}F = -\theta \log \theta - (1-\theta) \log (1-\theta) + 2f_1 + 2f_3.
\]
\[\text{(18)}\]

Comparing with expression (17), and making use of the known \( f_1 \), we arrive at
\[
f_3 = \frac{1}{6} \theta^2 (1-\theta)^3 \eta^2 + \theta^4 (1-\theta)^4 \eta^4 + \ldots.
\]
\[\text{(19)}\]

Substituting \( f_1 \), \( f_2 \), and \( f_3 \) into (15), we would obtain immediately the expression of \( F \) with all the other \( f \)'s neglected. If we expand this result into a series in \((kT)^{-1}\), we see that it is identical with that obtained by the Kirkwood method. In making the comparison, \( 0 (kT)^{-5} \) has been neglected.

(3) AB-type crystal lattice solid solution with long-distance order.

In this case, we will describe only the method of calculation. The result apparently should be similar to that obtained before.

Denote the number of A atoms in the first sublattice by \( 1/2 N \theta \) and the number of A atoms in the second sublattice by \( 1/2 N \theta' \). The points in the first sublattice are represented by \( a \), and the points in the second by \( b \). Then, corresponding to the values \( \theta \) and \( \theta' \), the logarithm of the configurational partition function should be
\[
\log \left( \begin{pmatrix} \frac{1}{2} N \\ \frac{1}{2} N \theta \end{pmatrix} \right) \log \left( \begin{pmatrix} \frac{1}{2} N \\ \frac{1}{2} N \theta' \end{pmatrix} \right) + \Sigma \lambda_{\alpha \beta} f^\alpha_\beta(\theta, \theta', T) + \ldots
\]
\[\text{(20)}\]
Note that since here $f_1$ is defined slightly differently from that in expression (1), we adopt the notation $f_1^*$. To determine $f_1^*$, we will consider again the hypothetical lattice system of expression (1). The logarithm of its configurational partition function, $F$, is

$$\frac{1}{2} N \log (1 + \lambda + \lambda' + \lambda \lambda' \xi) - \frac{1}{2} N \theta \log \lambda - \frac{1}{2} N \theta' \log \lambda',$$  \hspace{1cm} (21)

where $\lambda$ and $\lambda'$ are functions of $\theta, \theta'$ and $T$, determined by

$$\partial F / \partial \lambda = \partial F / \partial \lambda' = 0$$  \hspace{1cm} (22)

From (22), we have

$$\theta = \lambda (1 + \lambda' \xi), (1 + \lambda + \lambda' + \lambda \lambda' \xi),$$  \hspace{1cm} (23)

$$\theta' = \lambda' (1 + \lambda \xi), (1 + \lambda + \lambda' + \lambda \lambda' \xi).$$  \hspace{1cm} (24)

From (23), we have

$$\lambda = \theta (1 + \lambda') (1 - \theta) (1 + \lambda' \xi),$$  \hspace{1cm} (25)

Substituting into (24), we get

$$\xi (1 - \theta') \lambda^2 + \lambda [1 - \theta - \theta' + \xi (\theta - \theta')] - \theta' = 0.$$  \hspace{1cm} (26)

Similarly, solving the equation which satisfied,

$$\xi (1 - \theta) \lambda^2 + \lambda [1 - \theta - \theta' + \xi (\theta' - \theta')] - \theta' = 0,$$

and substituting the values of $\lambda$ and $\lambda'$ into expression (21) and then making use of the property of the hypothetical lattice,

$$\Sigma \lambda \alpha = \frac{1}{2} N, \quad \Sigma \lambda \lambda = \Sigma \lambda \lambda \lambda = \ldots = 0,$$

we could determine $f_1^* (\theta, \theta')$. Because the calculation is very tedious and adds nothing new in the way of results, we omit it.

(4) Binary solid solution of AB-type lattice with next-nearest neighbor interaction:

Apparently, here

$$F = \log \left( \frac{N}{N \theta} \right) + (\Sigma \lambda \alpha \xi) f_1 (\theta, T) + (\Sigma \mu \alpha \xi) f_1 (\theta, T) +$$

$$+ (\Sigma \lambda \alpha \lambda' \xi' \xi) f_1 (\theta, T) + \ldots.$$  \hspace{1cm} (27)
where $\mu''$ represents the "next nearest neighbor" matrix, defined as

$$
\mu''_{c,c'} = \begin{cases} 
1, & \text{if } c', c'' \text{ are next-nearest neighbors} \\
0, & \text{otherwise},
\end{cases}
$$

and $f_\mu$, $f_\mu'$ are functions to be determined. $f_\mu$ in the above expression is the $f_\mu$ used before.

In order to determine $f_\mu$ and $f_\mu'$, we will consider the following hypothetical lattice system: the lattice is divided into $N/3$ groups, each group consisting of three points sitting on the vertices of an isosceles right triangle. The two short sides represent nearest-neighbor pairs, and the diagonal represents the next-nearest-neighbor pair. Then

$$
F = \frac{1}{3} N \log (1 + 3 \lambda + 3 \xi' + 2 \xi^2 + \lambda^3 + \xi^3) - N \theta \log \lambda,
$$

(28)

where $\xi'$ denotes $\exp \left(-\frac{V}{kT}\right)$ constructed from the nearest pair $\kappa \Lambda$ (assuming no interaction between $A\Lambda$ and $B\Lambda$) and is still determined by $\partial F / \partial \lambda = 0$. It can be easily calculated that

$$
\frac{1}{\lambda} = \frac{1-\theta}{\theta} + \frac{2}{3} (1-\theta)(2\eta + \eta') + \ldots, \quad \eta' = \xi' - 1,
$$

(29)

$$
N^{-1} F = -\theta \log \theta - (1-\theta) \log (1-\theta) + \left(\frac{2}{3} \eta + \frac{1}{3} \eta'\right) \theta +
$$

$$
+ \left(\frac{1}{3} \eta^2 + \frac{1}{6} \eta' \right) \theta(\theta - 2 \eta) + \left(\frac{2}{3} \eta^3 + \frac{1}{3} \eta' \right) \theta^2 +
$$

$$
+ \theta(1-\theta)^3 (-1 - 2 \theta + 2 \theta') + \frac{1}{3} \eta^2 \eta' \theta(1-\theta)^2 + \ldots.
$$

(30)

We know that for this hypothetical lattice,

$$
\Sigma \lambda_{\omega} = \frac{4}{3} N, \quad \Sigma \mu_{\omega} = \frac{2}{3} N,
$$

$$
\Sigma \lambda_{\omega} \mu_{\omega''} = \frac{2}{3} N, \quad \Sigma \ldots = 0, \ldots
$$

(31)

and also that $f_\lambda$ is expression (7), and $f_\mu$ is expression (7) in which $\xi$ is replaced by $\xi'$ and is replaced by $\eta'$. Substituting all of them into (27) and then comparing it with (30), we arrive at the result

$$
f_\mu(\theta, T) = \frac{1}{2} \theta'(1-\theta)^2 \eta^2 \eta' + \ldots.
$$

(32)

All the above calculations have shown the applicability of the method of reference 1 to any kind of solid solution. It is much more dependable, because it does not involve series expansion in $(kT)^{-1}$ or $(kT)$. Moreover, from the procedure shown above we can see that this method is much simpler in calculation.
PART II

QUASI-CHEMICAL FORMULAS

A very powerful way to treat quasi-chemical formulas is by the method of reference 1. We will consider two cases:

(1) The quasi-chemical formula of a multiple-component solid solution, neglecting all but one coordination number.

Denote the number of atoms of each component group by \( N\theta_1, N\theta_2, \ldots \). Here \( \Sigma \theta_i = 1 \). Denote the total number of permutations by \( M \) when we permute them on \( N \) points. Then the logarithm of the configurational partition function is equal to

\[
\log M + (\Sigma \lambda_{ij}) f_1(\theta_1, \theta_2, \ldots, T) + \ldots \quad (33)
\]

By ignoring the unwritten terms in the above expression, we will get the conventional quasi-chemical formula.

In order to determine \( f_1 \), we will discuss again the hypothetical lattice system (1) of Part I. Its \( F \) is

\[
\frac{1}{2} N \log (\Sigma \lambda_i \lambda_j \xi_{ij}) - \Sigma N \theta_i \log \lambda_i \tag{34}
\]

\[
\xi_{ij} = \exp(-V_{ij}/kT),
\]

where the \( \lambda \) are determined by \( \partial F/\partial \lambda_i = 0 \quad i=1, 2, \ldots \) i.e., they are determined by

\[
\theta_i = \frac{\Sigma \lambda_i \lambda_j \xi_{ij}}{\Sigma \lambda_i \lambda_j \xi_{ij}} \tag{35}
\]

Now,

\[
\Sigma \lambda_{ij} = N, \quad \Sigma \lambda \lambda_i \lambda_j = 0, \ldots
\]

Therefore, we have

\[
N f_1(\theta_1, \theta_2, \ldots, T ) = \frac{1}{2} N \log (\Sigma \lambda_i \lambda_j \xi_{ij}) - \Sigma N \theta_i \log \lambda_i - \log M \quad (36)
\]

Substituting into (33), we get

\[
F = (1-N \Sigma \lambda_{ij}) \log M + (\Sigma \lambda_{ij}) \left[ \frac{1}{2} \log (\Sigma \lambda_i \lambda_j \xi_{ij}) - \Sigma \theta_i \log \lambda_i \right] \quad (37)
\]

where the \( \lambda \)'s are functions of \( \theta \) and \( T \), determined by expression (35). The number of pairs of nearest neighbors, \( X_{1j} \), made up of atoms of the \( i \)-th kind and the \( j \)-th kind, is
\[ \xi_u \partial \xi_u \quad F (\xi_{1u}, \xi_{2u}, \ldots, \theta_{1u}, \theta_{2u}) \quad \] 

i.e.,

\[ \xi_u \partial F (\xi_{1u}, \xi_{2u}, \ldots, \lambda_1, \lambda_2, \ldots) \quad \partial \xi_u. \quad (35) \]

Similarly, the number of pairs of nearest neighbors of \( i \)-th kind of atom is

\[ \xi_u \partial F / \partial \xi_u. \]

Therefore,

\[ X_{1u} = (\sum \lambda_w) \lambda_1 \xi_{1u}, \quad \sum \lambda_w \lambda_i \xi_{1u}, \quad \] 

\[ X_{2u} = \frac{1}{2} (\sum \lambda_w) \lambda_1 \lambda_2 \xi_{1u}, \quad \sum \lambda_w \lambda_i \xi_{1u}. \quad (39) \]

Therefore,

\[ X_{1u}^2 / X_{1u} X_{2u} = 4 e^{-3V_{1u} - V_{1u} - V_{2u} / kT}, \quad (40) \]

This is what we want to prove. By a similar procedure, we can obtain the quasi-chemical formulas when the left side of (40) is \( X_{1u} X_{2u} \) or \( X_{1u} X_{1u} \), or \( X_{2u} X_{2u} \).

From expression (40), it is very easy to calculate the total number of permutations obtained by permuting the atoms on the lattice, which produces all the atom pairs of all kinds, \( X_{11}, X_{12}, \ldots, \) etc. First, it can be derived from (40) that

\[ N^{-1} \log g(N, \theta_1, \theta_2, \ldots, X_{1u}, X_{1u}, \ldots) = \phi(N, \theta) - \sum_i X_{1u} \log X_{1u} - \sum_{i > j} X_{ij} \log \frac{1}{2} X_{ij}, \quad (41) \]

where \( \phi(N, \theta) \) is a function to be determined. When

\[ X_{1u} = \frac{1}{2} (\sum \lambda_w) \theta_1; \quad X_{2u} = (\sum \lambda_w) \theta_2 \theta_1, \quad (42) \]

the right side of expression (41) should be equal to \( N \sum \theta_i \log \theta_i \), and therefore \( \phi(N, \theta) \) can be determined. Now denoting the number of nearest neighbors of one point in the lattice, \( N^{-1} \sum \lambda_w \), by \( \Lambda \), we would obtain

\[ \log g(N, \theta_1, \theta_2, \ldots, X_{1u}, X_{1u}, \ldots) = N \sum (\lambda - 1) \theta_i \log \theta_i + \]

\[ + \frac{1}{2} N \sum \lambda w - \sum X_{1u} \log X_{1u} - \sum_{i > j} X_{ij} \log \frac{1}{2} X_{ij}. \quad (43) \]

1) In carrying out this partial differentiation, \( \xi_{ij} \) and \( \xi_{ij} \) are treated as the same quantity, instead of as mutually independent variables.
If there is long-distance order, the quasi-chemical formula can also be derived by following the same procedure. In fact, if we apply the method mentioned here to the AB-type lattice solid solution, we will obtain the conventional quasi-chemical formula immediately (no matter how many kinds of atoms there are).

(2) The quasi-chemical formula with higher coordination numbers included.

We are going to discuss the quasi-chemical formula when higher coordination numbers are included. For concreteness, we will consider only the case (2) of Part I, and discuss only the $f_1$ and $f_3$ terms (i.e., consider only $\Sigma\Sigma\Sigma$ and $\Sigma\Sigma\Sigma$ terms, and neglect all the other coordination numbers). We can prove that $F$ is equal to

$$\log \left( \frac{N}{N_0} \right) \left( 1 - \frac{\sum \lambda_2}{N} + \frac{\sum \lambda_2 \lambda_3}{2N} \right) +$$

$$+ (\sum \lambda_2 - \sum \lambda_2 \lambda_3 \lambda_5 \lambda_7 \lambda_9 \lambda_{11}) \left\{ \frac{1}{2} \log (\lambda_2 \xi_{AA} + 2 \lambda_2 \lambda_3 \xi_{AB} +$$

$$+ \lambda_3 \xi_{BB}) - \theta_a \log \lambda_a - \theta_b \log \lambda_b \right\} +$$

$$+ \frac{1}{2} \sum \lambda_2 \lambda_3 \lambda_5 \lambda_7 \lambda_9 \lambda_{11} \left\{ \frac{1}{3} \log (K_a \xi_{AA} + 3 K_a K_b \xi_{AB} \xi_{BB} +$$

$$+ 3 K_a K_b \xi_{AA} \xi_{BB} + K_a \xi_{BB} + K_b \xi_{BB}) - \theta_a \log K_a - \theta_b \log K_b \right\},$$

where $\lambda_a, \lambda_b, K_a, K_b$ are functions of $\theta$ and $T$, determined by

$$\frac{\partial}{\partial \lambda_a} = \frac{2}{2} \left\{ \frac{1}{2} \log (\lambda_2 \xi_{AA} + 2 \lambda_2 \lambda_3 \xi_{AB} + \lambda_3 \xi_{BB}) - \theta_a \log \lambda_a - \theta_b \log \lambda_b \right\} = 0,$$

$$\frac{\partial}{\partial \lambda_b} = \frac{2}{2} \left\{ \frac{1}{3} \log (K_a \xi_{AA} + 3 K_a K_b \xi_{AB} \xi_{BB} + \ldots) - \theta_a \log K_a - \theta_b \log K_b \right\} = 0. \quad (45)$$

From (44) and

$$X_{AA} = \xi_{AA}(\theta F, \theta \xi_{AA}), \quad X_{AB} = \xi_{AB}(\theta F, \theta \xi_{AB}), \ldots$$

the numbers $X_{AA}, X_{AB}, X_{BB}$, of AA, AB, BB near-neighbor pairs, can be easily determined. In fact, if we define

$$X'_{AA} = \frac{1}{2} \left( \sum \lambda_2 - \sum \lambda_2 \lambda_3 \lambda_5 \lambda_7 \lambda_9 \lambda_{11} \right) \frac{\lambda_2 \xi_{AA}}{\lambda_2 \xi_{AA} + 2 \lambda_2 \lambda_3 \xi_{AB} + \lambda_3 \xi_{BB}},$$

$$X'_{AB} = \frac{1}{2} \left( \sum \lambda_2 - \sum \lambda_2 \lambda_3 \lambda_5 \lambda_7 \lambda_9 \lambda_{11} \right) \frac{\lambda_2 \lambda_3 \lambda_5 \lambda_7 \lambda_9 \lambda_{11} \xi_{AB}}{\lambda_2 \lambda_3 \lambda_5 \lambda_7 \lambda_9 \lambda_{11} \xi_{AB} + 2 \lambda_2 \lambda_3 \lambda_5 \lambda_7 \lambda_9 \lambda_{11} \xi_{BB} + \lambda_3 \lambda_5 \lambda_7 \lambda_9 \lambda_{11} \xi_{BB}},$$

$$X''(A_{AA}) = \frac{1}{6} \sum \lambda_2 \sum \lambda_3 \sum \lambda_5 \sum \lambda_7 \sum \lambda_9 \sum \lambda_{11} \frac{K_a \xi_{AA}}{K_a \xi_{AA} + 3 K_a K_b \xi_{AB} \xi_{BB} + 3 K_a K_b \xi_{AA} \xi_{BB} + K_b \xi_{BB}},$$

$$X''(A_{AB}) = \frac{1}{6} \sum \lambda_2 \sum \lambda_3 \sum \lambda_5 \sum \lambda_7 \sum \lambda_9 \sum \lambda_{11} \frac{K_a \lambda_2 \lambda_3 \lambda_5 \lambda_7 \lambda_9 \lambda_{11} \xi_{AB}}{K_a \lambda_2 \lambda_3 \lambda_5 \lambda_7 \lambda_9 \lambda_{11} \xi_{AB} + 3 K_a \lambda_2 \lambda_3 \lambda_5 \lambda_7 \lambda_9 \lambda_{11} \xi_{BB} + K_b \lambda_2 \lambda_3 \lambda_5 \lambda_7 \lambda_9 \lambda_{11} \xi_{BB}}. \quad (46)$$
then we will have

\[ X_{AA} = X'' + 3X''(A) + 3X''(B) , \]
\[ X_{AB} = 2X'' + 6X''(A) + 6X''(B) , \]
\[ X_{BB} = X'' + 3X''(B) + 3X''(A) , \] (47)

and

\[ \frac{(X''_{AA})^2}{X''_{AA}X_{BB}} = \frac{[X''(A)]^2}{X''(A)} - \frac{[X''(B)]^2}{X''(B)} \]
\[ = \exp\left(-\frac{2V_{AA} - V_{AB} - V_{BB}}{kT}\right) , \]
\[ = \exp\left(-\frac{1}{2}(\Sigma\lambda - \Sigma\lambda\lambda\lambda)\theta_4 \right) , \]
\[ = \exp\left(-\frac{1}{2}(\Sigma\lambda - \Sigma\lambda\lambda\lambda)\theta_6 \right) . \] (48)

\[ 3X''(A) + 6X''(B) + 3X''(A) = \frac{1}{2}(\Sigma\lambda\lambda\lambda)\theta_4 \]
\[ 3X''(B) + 6X''(A) + 3X''(B) = \frac{1}{2}(\Sigma\lambda\lambda\lambda)\theta_6 . \] (49)

Expressions (47), (48), (49) and (50) are the extended quasi-chemical formulas. We want to point out that \( X' \) can be found from (48) and (49), \( X'' \) can be found from (48) and (50), and then we can calculate \( X \). The influence of introducing more coordination numbers is exactly the same so we will not bother to show the development.

The number of permutations corresponding to \( X' \) and \( X'' \) can easily be calculated from expressions (48) -- (50), but since the physical significances of \( X' \) and \( X'' \) are ambiguous we do not make that calculation. For face-centered cubic system,

\[ \Sigma\lambda = 12N, \quad \Sigma\lambda\lambda\lambda = 48N, \]

so that \( X'_{AA}, X'_{AB}, X'_{BB} \) and \( X''_{AB} \) may assume negative values. Therefore they do not bear any direct physical significance.

We can see that, if we do not use the above-mentioned method but introduce \( X'_{AA} \) directly to represent the number of atom groups containing three \( A \) atoms which form mutually nearest neighbors, and introduce also \( X'_{AB} \) to represent the number of groups containing two \( A \) atoms and one \( B \) atom which form mutually nearest neighbors, etc., then we can extend the conventional quasi-chemical formula of the face-centered binary solid solution as follows:
\[ \frac{[X(A_B)]^a}{X(A_A)X(A_{BB})} - \frac{[X(A_B)]^a}{X(A_{BB})X(B_{BB})} = 3\exp[-(2V_{AB} - V_{AA} - V_{BB})kT], \quad (51) \]

\[ 3X(A_A) + 2X(A_{AB}) + X(A_{BB}) = 24N\theta_A, \quad (52) \]

\[ 3X(B_{BB}) + 2X(B_{BA}) + X(A_{AB}) = 24N\theta_B. \]

(In the above expression, 24N is equal to \(1/2 \sum N \lambda \)). In this theory, the numbers \(X_{AA}, X_{AB}\) and \(X_{BB}\) of AA, AB, and BB pairs of nearest neighbors are determined by the following expressions:

\[ X_{AA} = \frac{1}{4}\left[3X(A_A) + X(A_{AB})\right], \]

\[ X_{AB} = \frac{1}{4}\left[2X(A_A) + 2X(A_{BB})\right], \]

\[ X_{BB} = \frac{1}{4}\left[3X(B_{BB}) + X(B_{BA})\right]. \quad (53) \]

On comparing this theory with expressions (47)-(50), we must note that the expressions here

\[ X(A_B), X(A_{BB}) \]

correspond to

\[ 3X'(A_{AB}), 3X'(B_{BB}). \]

Therefore, in both theories, the parts involving

\[ X(A_A), X(A_{AB}), X(A_{BB}), X(B_{BB}) \]

are identical. But expression (53), for determining \(X_{AA}\),

etc., is essentially different from (47). Expression (53)

has a factor of 1/4 on its right side, arising from the

fact that one pair of nearest neighbors exists for every
four atom groups, each group containing three atoms forming mutually nearest neighbors. In expression (47), we do not have a factor corresponding to this. Finally, we will derive the number of combination $g$, of

$$X(A_A), X(A_B), X(A_B), X(B_B)$$

corresponding to $N, \Theta_A, \Theta_B$.

Suppose log $g$ takes the following form:

$$-c_1(X_{ABB} \log X_{ABB} + X_{ABB} \log X_{ABB}) - c_1(X_{ABB} \log X_{ABB} +$$
$$+X_{BBB} \log X_{BBB} + c_1(X_{ABB} + X_{ABB}) + c_1(X_{ABB} + X_{BBB}) + \phi(N, \theta),$$

where $X_{AAA}$, $X_{ABB}$, ..., i.e., $X_{AA}$, $X_{AB}$, ..., $c_1$, $c_2$, $c_3$, $c_4$, are constants to be determined and $\phi(N, \theta)$ is a function to be determined.

Treating the configurational free energy as a function of $N, \theta, \theta_A, X_{AAA}, X_{ABB}, X_{BBB}, (so that we can put $c_4 = 0$), and setting its derivatives with respect to $X_{ABB}, X_{ABB}$ equal to zero, we obtain

$$-c_1 \log X_{ABB} - c_1 + \frac{2}{3} c_2 \log X_{ABB} + \frac{2}{3} c_1 \log X_{BBB}$$
$$+ \frac{1}{3} c_4 + c_5 + (-2V_{AB} + V_{AA} + V_{BB})/kT = 0,$n

$$-c_1 \log X_{ABB} - c_1 + \frac{2}{3} c_2 \log X_{BBB} + 0,$$

But from (51), we have

$$(-2V_{AB} + V_{AA} + V_{BB})/kT = -\log \frac{1}{X_{AAA} X_{ABB}} = \log \frac{3 X_{BBB}^2}{X_{BBB} X_{AAA}^3},$$

i.e.,

$$(-2V_{AB} + V_{AA} + V_{BB})/kT = \frac{1}{3} \log \frac{27 X_{AAA}^2}{X_{AAA} X_{BBB}^3},$$

Substituting into the first expression of (55), we get

$$c_1 = 1, \quad c_2 = 1, \quad c_3 = \log 3.$$  

And by the same time, the second equation of (55) is also satisfied. Therefore, expression (54) is proved to be the exact expression of log $g$, and it is also equal to

$$\log g = \phi(N, \theta) - X_{ABB} \log \frac{1}{3} X_{ABB} - X_{ABB} \log \frac{1}{3} X_{ABB}$$
$$- X_{ABB} \log X_{AAA} - X_{BBB} \log X_{BBB},$$

(58)
an expression very similar to (41).

When

\[ X_{\text{AAA}} = \frac{1}{3} N 24 \theta_1, \quad X_{\text{ABB}} = N 24 \theta_2 \theta_1, \]
\[ X_{\text{BBB}} = N \theta_3 \theta_1, \quad X_{\text{BBB}} = \frac{1}{3} N 24 \theta_3 \]

\( \log g \) should be equal to \( N \theta_1 \log \theta_1 - N \theta_2 \log \theta_2 \), and then we have

\[ \phi(N, \theta) = -N \theta_1 \log \theta_1 - N \theta_2 \log \theta_2 + \frac{1}{3} \theta_1 \theta_2 \theta_3 N 24 \log \theta_1 + \frac{1}{3} \theta_1 \theta_2 \theta_3 N 24 \log \theta_2 + \frac{1}{3} \theta_1 \theta_2 \theta_3 N 24 \log \theta_3, \]

where the summation is taken over \( \theta_1, \theta_2, \) and \( \theta_3 \), and each of \( \theta_1, \theta_2, \theta_3 \) can assume two values, \( \theta_1, \theta_3 \). Therefore

\[ \phi(N, \theta) = -N \theta_1 \log \theta_1 - N \theta_2 \log \theta_2 + 8 N \log 8 N + \frac{1}{3} \theta_1 \theta_2 \theta_3 N 24 \log \theta_1 \]
\[ = -N \theta_1 \log \theta_1 - N \theta_2 \log \theta_2 + 8 N \log 8 N + N 24 (\theta_3 \log \theta_1 + \theta_2 \log \theta_2). \]

Substituting into (58), we obtain the desired result:

\[ \log g = 8 N \log 8 N + 23 N (\theta_1 \log \theta_1 + \theta_2 \log \theta_2) - \]
\[ -X_{\text{AAA}} \log X_{\text{AAA}} - X_{\text{BBB}} \log X_{\text{BBB}} - X_{\text{BBB}} \log \frac{1}{3} X_{\text{ABB}} - X_{\text{ABB}} \log \frac{1}{3} X_{\text{ABB}}. \]  (60)

Undoubtedly, this treatment can be extended to the face-centered lattice solid solution of multiple components. The result corresponding to (60) is

\[ \log g = 8 N \log 8 N + 23 N \sum \theta_i \log \theta_i \]
\[ -\sum X_{ij} \log X_{ij} \sum_{i<j} \left[ X_{ij} \log \frac{1}{3} X_{ij} + X_{ij} \log \frac{1}{3} X_{ij} \right] - \sum_{i>j>k} X_{ijk} \log \frac{1}{3} X_{ijk}. \]  (61)

All the notations in this expression follow the usual convention, and \( X_{iij}, X_{iij}, X_{iijk}, X_{ii}, X_{iij} \), have the following relations:

\[ 3 X_{ij} + \sum_{j \neq k} (X_{ij} + 2 X_{ij}) + \sum_{j > k} X_{ijk} = 24 N \theta_i, \]

\[ X_{ij} = \frac{1}{4} \left( 3 X_{ij} + \sum_{j} X_{ij} \right), \]

\[ X_{ij} = \frac{1}{4} \left( 2 X_{ij} + 2 X_{ij} + \sum_{k} X_{ijk} \right). \]  (62)

The author wishes to express his thanks to Ting Hou-chiang, Chi-ao Teng-chiang, Wang Te-mao, Hsu Yung-huan, with whom he worked on this problem. From them, the author received many suggestions and hints, which made him interested again in this problem.
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