Ordering in fcc lattices by the Cluster Variation Method 
and Path Probability Method

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A study synthesizing the kinetic and equilibrium aspects of order-disorder phase transitions is attempted for an fcc system at 50 at% using the Cluster Variation Method and the Path Probability Method. The disorder-L12-L10 phase diagram is calculated using the tetrahedron approximation of the CVM. A perturbation expansion of the free energy functional, followed by a Fourier transformation, provides a concentration wave description of the system, from which the ⟨100⟩ instability locus in the phase diagram and the short range order diffuse intensity are obtained. By employing the Path Probability Method, the time evolution of the pair and the tetrahedron correlation functions as well as fluctuations from the most probable path during an isothermal aging process following a quenching operation are calculated for a system at 1:1 stoichiometry. Finally, the most probable path followed by the system during an isothermal aging process is placed in a thermodynamic configuration space.

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I. Introduction

Recently, the Cluster Variation Method (hereafter CVM) has been widely employed for the calculation of various thermodynamic properties. The main advantage of the CVM stems from the fact that a wide range of atomic correlations, which play a significant role in the phase transition, are explicitly incorporated in the free energy formula. The descriptions of local atomic order as well as phase equilibria are, therefore, more accurate than those obtained using the Bragg-Williams approximation.

In addition to the description of the equilibrium state, a stability analysis of the system is carried out by means of a perturbation expansion of the free energy functional. The vanishing condition of the determinant of the stability matrix provides the instability temperature which, in the present case, corresponds to an inherent instability of the system to ⟨100⟩ concentration waves. The instability temperature also corresponds to the limit of metastability for the disordered state in either an equilibrium ordered phase field or a two-phase field.

The Short Range Order (SRO) Diffuse Intensity is directly related to the stability matrix. By inverting the stability matrix in k-space we obtain the SRO intensity distribution, which is directly comparable to experimental measurements. Thus a single free energy formula derived from the CVM provides various information on phase equilibria.

The validity of the perturbation expansion, which is employed for the stability analysis, is guaranteed only when the deviation from the equilibrium state is small enough so that higher order perturbation terms can be neglected. In reality, however, the evolution of the system after a quenching operation, for instance, takes place under far from equilibrium conditions and, therefore, the description based on a perturbation expansion is not applicable. For a far from equilibrium state, a different theoretical framework other than the CVM should be employed.

Most of the kinetic studies carried out to date, such as the Ginzburg-Landau theory, are based on the description of the free energy in a continuous medium. The Path Probability Method (hereafter PPM) devised by Kikuchi, on the other hand, is the natural extension of the CVM to the time domain and, therefore, thermodynamic variables are defined on a discrete lattice. In the PPM, instead of the cluster probabilities of the CVM, the path variables are defined describing the transition probability from one cluster configuration to another during an infinitesimal time interval. The equivalent of the free energy functional in the CVM is the Path Probability Function (PPF) and the most probable path for the time evolution of a system is obtained by maximizing the PPF with respect to the path variables.

In the present report, we use the CVM and the PPM on an fcc lattice to study the time evolution of the system starting from a nonequilibrium state and ending in the equilibrium state predicted by the CVM, thereby we at-
tempted to synthesize thermodynamics and kinetics of the phase transition. The fcc-based phases of interest in this report are disorder, L1₀, and L1₂. The organization of this paper is as follows. The next section is devoted to the theoretical descriptions of the equilibrium state, cluster densities, stability, short range order diffuse intensity and the nonequilibrium time evolution process including fluctuation and kinetic path. The discussions are provided in the last section in which all the results are collected in a single figure to emphasize the synthetic feature of the present calculations.

II. Theoretical Description

1. State of order and transition probability

The state of order is described by the cluster probabilities \( x_{ijk...m}^{\alpha\beta...\delta} \) where the atomic configuration is specified by \( ijk...m \) on sublattices \( \alpha\beta...\delta \), where \( ijk...m \) takes values +1 or −1 for A and B atoms, respectively. Note that, for a disordered phase, all sublattices are equivalent. In order to simplify the notation, the description below is limited to a disordered phase without loss of generality.

The cluster probabilities are generally not independent but are interrelated by self-consistent relationships of the form:

\[
x_{ijk...m} = \sum_{i_1} \sum_{i_2} \cdots \sum_{i_k} x_{i_1i_2...i_ki_{k+1}...i_m}
\]

and the normalization condition

\[
\sum_i \sum_j \sum_k \cdots \sum_m x_{ijk...m} = 1
\]

It has been shown\(^{33}\) that the set of multisite correlation function \( \{ \xi \} \) form a set of independent variables in the thermodynamic configuration space. The correlation functions are formally defined as the ensemble average of products of the spin operator \( \sigma_p \) at lattice site \( p \), which take values +1 or −1 for A and B atoms, respectively.

\[
\xi_{p_1p_2...p_r} = \langle \sigma_{p_1}\sigma_{p_2}\cdots\sigma_{p_r} \rangle
\]

The correlation functions are related to the cluster probability by

\[
x_{ijk...m} = \frac{1}{2^n} \left[ 1 + \sum_l V(l; ijk...m) \cdot \xi_l \right]
\]

where \( V(l; ijk...m) \) is, in general, a sum of \( l \)-order products involving the indices \( ijk...m \)\(^{33}\) and \( n \) represents the total number of the indices. The detailed form of \( V(l; ijk...m) \) is exemplified in the later section for tetrahedron clusters.

The time evolution of the atomic configuration on a cluster is represented by the following equation:

\[
x_{ijk...m}(t+\Delta t) = x_{npq...}(t) + x_{npq...ijkm}
\]

where \( x_{npq...} \) is a path variable which describes the transition probability from one configuration \( \{ opq... \} \) to another \( \{ ijk... \} \) during an infinitesimal time \( \Delta t \). In the limit of \( t \rightarrow \infty \), each cluster probability \( x_{ijk...} \) should converge to its equilibrium value.

2. Phase equilibria

In the framework of the pair interaction model, the Helmholtz potential is given as

\[
F = \sum_i v_{ij} \xi_j - TS(\{ \xi_l \})
\]

where \( v_{ij} \) and \( \xi_j \) designate the pair interaction energy and pair correlation for the \( i \)-th nearest neighbors, respectively, and \( \{ \xi_l \} \) indicates a set of multisite correlation functions. In general, the incorporation of more correlation functions improves the description of the free energy functional. However, since the correlations decay relatively fast with distance, one can approximate the free energy formula with a limited number of correlation functions. Kikuchi devised an approximate description of the free energy functional, termed Cluster Variation Method\(^{34}\), which is based on the above idea. In the CVM, the level of the approximation is specified by the biggest cluster incorporated in the free energy functional. Although the accuracy is expected to improve with the size of the cluster, severe computational difficulties are introduced at the same time. In the present study, we use the tetrahedron approximation\(^{34}\) in which atomic correlations up to the regular tetrahedron cluster of the fcc lattice are explicitly taken into account. In this approximation, the free energy functional for a disordered phase is given as

\[
F = v_2 \xi_2 - TS(\xi_1, \xi_2, \xi_3, \xi_4)
\]

where \( \xi_i \) is the correlation function for the cluster consisting of \( i \) nearest neighbor lattice point(s), and \( v_2 \) is the nearest neighbor pair interaction energy which was designated as \( v_{ij} \) with \( i = 1 \) in eq. (6). For ordered phases, sub-lattices must be introduced, which increases the number of correlation functions to eight for the L1₀ and seven for the L1₂ structures, respectively. The configurational phase equilibria is, therefore, obtained by minimizing the functional of eq. (7) at constant concentration (or equivalently chemical potential) with respect to the remaining set of correlation functions:

\[
\frac{\partial F}{\partial \langle \xi_l \rangle} = 0
\]

For vanishing next nearest neighbor pair interactions \( (v_{ij}=0) \), the L1₀ and L1₂ structures are degenerate with, respectively, the A₁B₂ and DO₂₃ structures\(^{35}-37\). However, at finite temperatures, it is expected that the L1₀ and L1₂ will be more stable since the entropy lifts the degeneracy in favor of the phases of higher symmetry.

Phase equilibria between two phases \( I \) and \( II \) can be conveniently described by the equality of the grand potential which is obtained by means of a Legendre transformation of the Helmholtz potential \( F \):

\[
\Omega = F - \mu \xi_1
\]

where \( \mu \) is the effective chemical potential. It can be prov-
ed that the condition $\Omega^{(1)}(\mu) = \Omega^{(2)}(\mu)$ is equivalent to the conventional common tangent rule between the $F^{(1)}$ and $F^{(2)}$ curves vs. concentration\(^{(2)}\).

3. Stability and short range order diffuse intensity

The free energy functional $F$ is expanded around its equilibrium state $F^*$ with respect to the deviation of cluster probabilities, or equivalently, the correlation functions from their equilibrium values $\langle \xi^* \rangle$. Calling $\xi_i(p)$ the $i$-th correlation function at lattice site $p$, the expansion takes the form:

$$F = F^* + \sum_i \frac{\partial F}{\partial \xi_i(p)} \xi_i(p) + \frac{1}{2!} \sum_i \sum_{p', p''} \frac{\partial^2 F}{\partial \xi_i(p) \partial \xi_i(p')} \xi_i(p) \xi_i(p') + \cdots$$

Since the expansion is carried out around the equilibrium state, the first order term vanishes. Furthermore, assuming that the deviation from the equilibrium state is not significant, the higher order terms can be safely neglected. Thereby, the response of the system to a small deviation from its equilibrium state is governed by the second order derivative matrix:

$$\Delta F = F - F^* = \frac{1}{2!} \sum_i \sum_{p', p''} \frac{\partial^2 F}{\partial \xi_i(p) \partial \xi_i(p')} \xi_i(p) \xi_i(p')$$

The sign of the eigenvalues of the second derivative matrix convey, therefore, all the information with regard to the stability of the system. When all eigenvalues are positive the system is stable, while one or more negative eigenvalues indicate the instability of the system to certain concentration fluctuations. The temperature at which the smallest eigenvalue becomes negative is termed instability temperature ($T_0$)\(^{(2)}\).

The Fourier transform of the correlation functions leads naturally to the concept of concentration wave\(^{(1)}\):

$$\mathbf{d}X_i(k) = \sum_p \mathbf{d}\xi_i(p) e^{i\mathbf{k}\cdot\mathbf{r}_p}$$

where $\mathbf{k}$ stands for a vector in reciprocal space and $\mathbf{r}_p$ is the real space vector corresponding to lattice site $p$. Due to the translational symmetry of the second derivative matrix, eq. (11) takes a simpler form when written in reciprocal space:

$$\Delta F = \frac{1}{2!} \sum_i \sum_{p', p''} \frac{\partial^2 F}{\partial \xi_i(p) \partial \xi_i(p')} \xi_i(p) \xi_i(p') = \sum_k \lambda_i(k) |dZ_i(k)|^2$$

The third equality follows from the diagonalization of the second line: $\lambda_i(k)$ and $Z_i(k)$ are, respectively, eigenvalues and normal concentration waves for reciprocal space vector $k$. Thus, the above equation implies that if an eigenvalue vanishes at a particular wave vector $k^*$ i.e. $\lambda_i(k^*) = 0$, the system becomes unstable with respect to the normal concentration wave $Z_i(k^*)$. Furthermore, if the wave vector $k^*$ is at the Brillouin zone center, the instability is of the clustering type, whereas if it is located at the Brillouin zone boundary the instability is of the ordering type.

The short range order diffuse intensity spectrum $I_{SRD}(k)$ resulting from the excitation of the concentration wave is described by the first component of the inverse of the second order derivative matrix $\mathbf{K}^{(0)}$:

$$I_{SRD}(k) = \frac{\partial^2 F}{\partial \mathbf{X}(k) \partial \mathbf{X}(-k)}^{-1} \cdot k_B T$$

In an $k_B T/I_{SRD}(k) - k_B T$ plotting, the instability temperature $T_0$ is given by the vanishing condition of $k_B T/I_{SRD}(k)^{(0)}$. For a disordered phase quenched below the instability temperature, the transformation to the ordered phase takes place by simultaneous excitation and amplification of the ordering wave. Thus, the instability temperature also corresponds to the limit of metastability of the disordered phase.

4. Nonequilibrium evolution process

The stability analysis in the previous section is based on a perturbation expansion which provides the response of a system to an infinitesimal deviation from the equilibrium state. Such an expansion is, therefore, not valid for a far-from-equilibrium state. In order to investigate nonequilibrium evolution processes (relaxation process) the Path Probability Method is employed.

In the PPM, the Path Probability Function (PPF) is defined as the counterpart part of the free energy functional of the CVM. The PPF $P$ is generally given as the product of the following three terms:

$$P_1 = (\theta - \Delta t)^{N_X \cdot 2}(\theta + \Delta t)^{N_X \cdot 2}(1 - \theta - \Delta t)^{N_X \cdot 2}(1 - \theta - \Delta t)^{N_X \cdot 2}$$

$$P_2 = \exp \left( -\frac{\Delta E^*}{2k_B T} \right)$$

and

$$P_3 = \prod_{i,j,k,l} \left( Y_{ijkl} \right)^6 \cdot N! \left( W_{ijkl,mnop} \right)^3 \cdot \prod_{i,j} \left( X_{ij} \right)^5$$

In the equations above, $\theta$ is the spin flip probability from up (down) spin to down (up) spin or atomic exchange probability from A (B) to B (A) atom per unit time, $N$ is the total number of the lattice points, and $\Delta E^*$ is the change of internal energy during an infinitesimal time $\Delta t$. It should be noted that the $\theta$ is generally temperature dependent which can be described by thermal activation process to overcome a saddle point energy of unit flipping (exchange) event. In this study, however, $\theta$ is assumed to be constant for the simplicity. In the pair interaction model, $\Delta E^*$ is given by

$$\Delta E^* = \sum_i e_i \{(y_{ij}(t + \Delta t) - y_{ij}(t))\}$$
where $e_{ij}$ is the nearest neighbor pair interaction energy between $i$ and $j$ species. These interactions are related to the effective pair interaction defined in eq. (7) by $v_2 = (e_{aa} + e_{bb} - 2e_{ab})/2$. Thus, the first term $P_1$ gives the contribution to the PPF by non-correlated atomic jumps whereas the second term $P_2$ describes the thermally activated process. The key feature of the PPM is provided by the last term $P_3$, which represents the number of possible paths from one given configuration to another. The terms $X$, $Y$ and $W$ in $P_1$ are path variables for the point, pair and tetrahedron clusters, respectively, which designate the transition probability from one atomic configuration to another. Note that $X_{opp...jkl...}$ in eq. (5) is intended to express a more general description of the path variable. In these terms, the initial and final configurations are specified by the subscripts before and after the comma sign, respectively. We note the similarity between $P_3$ and the configurational entropy term in the CVM.

The PPM further prescribes that the most probable time evolution process is determined by the maximum of the PPF with respect to the path variables:

$$\frac{\partial P}{\partial X_{ij}} = 0$$

$$\frac{\partial P}{\partial Y_{ijkl}} = 0$$

and

$$\frac{\partial P}{\partial W_{ijkl,menop}} = 0$$

The solutions of the simultaneous set of eqs. (19)–(21) give the optimized path variables. Substitution into the eq. (5) yields the cluster probabilities at time $t + \Delta t$. The successive application of this procedure provides the time evolution process of the cluster probabilities.

We note that $P_1$ given by eq. (17) is formulated for a spin flip mechanism in which the concentrations of up and down spins are not conserved quantities. Hence, in a rigorous sense, $P_1$ is not applicable to an alloy system for which atomic migration is driven by either a direct exchange mechanism or a vacancy mechanism and the atomic concentration is a strictly conserved quantity. The present study, however, focuses on 1:1 stoichiometry in which case the spin concentration is conserved without additional constraints. Thus, the formulation given by eqs. (15)–(21) simulates an alloy system to some extent.

In an actual system, fluctuations play a significant role especially during a phase transition. In the context of the PPM, the fluctuation probability around the most probable path is studied in the following manner. The most probable path is first determined by maximizing the PPF, which yields the most probable cluster probabilities $\{x_{ijk...}(t)\}$ at time $t$. In order to study fluctuations, the PPF is maximized under the constraint that the $\{x_{ijk...}(t)\}$ are specified, and the deviation of $\{x_{ijk...}(t)\}$ from the most probable values $\{x_{ijk...}^*(t)\}$ is defined as a fluctuation.

The constraints above requires that an additional term $P_4$ to be multiplied in the PPF $P_4$:

$$P_4 = \exp \left[ \sum_{ijkl} \lambda_{ijkl} \left( x_{ijkl}(t) - x_{ijkl}^*(t - \Delta t) + C_{ijkl} \right) \right]$$

where $\lambda_{ijkl}$ is a Lagrange multiplier and $C_{ijkl}$ designates the fluctuation. In eq. (22), the sum is taken only for an independent set of cluster probabilities.

III. RESULTS AND DISCUSSIONS

The main results obtained by the series of calculations described in the previous section are summarized in Fig. 1. In order to emphasize the synthetic nature of the present calculations, all the results, numbered from Fig. 1-1 to Fig. 1-5, are systematically arranged in a single figure. In particular, the results for phase equilibria obtained by the CVM are collected in the left hand side (Figs. 1-1 and 1-2), while those in the right hand side are for non-equilibria by the PPM (Figs. 1-3, 1-4 and 1-5). In Fig. 1-1, the disorder-L1$_0$-L1$_2$ phase diagram is shown up to 50 at% with the instability temperature and metastable phase boundaries drawn by broken line and dotted lines, respectively. The temperature axis is normalized by the nearest neighbor pair interaction energy $v_2$. The diffuse intensities in the (001) section of a k-space are shown at 1:1 stoichiometry for temperature $k_BT/v_2 = 2.5$ in Fig. 1-2. The magnitude of the isointensity lines increases as we approach the [100] and [010] directions which cross at (1, 1, 0). Shown in Fig. 1-3 is the time evolution of the correlation functions for pair ($\xi_3$) and tetrahedron ($\xi_4$) clusters at a fixed composition of 50 at% when the system is quenched from $k_BT/v_2=5.0$ down to 2.5 and is subjected to isothermal aging. The time axis is normalized by $\theta - \Delta t$, the product of spin flip probability and time step, thereby the dependency on $\Delta t$ of the calculated results is tacitly renormalized in an assigned $\theta$. The fluctuation spectrum from the most probable path is calculated at time $t=100$ and is shown in Fig. 1-4 by a solid line for $k_BT/v_2=2.5$ and by a broken line for 3.5, respectively. The horizontal axis is the deviation of the tetrahedron correlation function from the most probable value $\xi_4^*$ whereas the vertical axis is the PPF i.e., a measure of occurrence. It is noted that the two curves are shifted so that the peak values at $\xi_4^*$ coincide in order to facilitate the comparison. Finally, Fig. 1-5 shows the time evolution of the system during an isothermal aging process at $k_BT/v_2=2.5$ traced in the thermodynamic configuration space spanned by the correlation functions $\xi_2$ and $\xi_4$ starting from $t=100$ up to $t=1000$ at which the equilibrium is attained. Each thin curve indicates the free energy contour of which minimum is designated by Eq in the figure. Note the time correspondences between the points $a$, $b$ and $c$ along the path in the Fig. 1-5 and those $a_1(b_1)$, $b_1(b_2)$ and $c_1(c_2)$ in Fig. 1-3, respectively.

Two kinds of metastable equilibria are indicated in the
Fig. 1 Systematic view of CVM-PPM based analysis for Phase Equilibria and Nonequilibria.

Fig. 1-1 Disorder-L1₀-L₁₂ phase diagram calculated by the tetrahedron approximation of the CVM. ⟨100⟩ indicates the instability locus. The temperature axis (vertical axis) is normalized by the nearest neighbor pair interaction energy E₁, while the horizontal axis indicates atomic composition up to 50 at%.

Fig. 1-2 Short range order diffuse intensity distribution on (001) section of the k-space. The magnitude of the iso-intensity lines increases towards (1, 1, 0) as is indicated by an arrow.

Fig. 1-3 Time evolution of pair (ξ₂) and tetrahedron (ξ₄) correlation functions. Time axis is normalized by spin flip probability (θ Δ). The dotted lines indicate the equilibrium values.

Fig. 1-4 Fluctuation spectrums for tetrahedron correlation function at kF T/E₁ = 2.5 (solid line) and 3.5 (broken line). ξ₄ is the most probable value at time t = 100. The vertical axis is the path probability function in arbitrary unit.

Fig. 1-5 Kinetic path of the system at kF T/E₁ = 2.5 traced in the thermodynamic configuration space spanned by the pair and tetrahedron correlation functions. In this figure, the path between t = 100 and 1000 is shown, and at time t = 1000, the equilibrium (designated as Eq.) is attained.

phase diagram (Fig. 1-1): one for the metastable phase boundary between disorder and L₁₀ in the L₁₂ phase field (dotted lines), and the other for the ⟨100⟩ ⟨1 1/2 0⟩ instability locus (broken line). The former is not a simple extension of the equilibrium phase boundary but a calculated result by CVM. The latter is obtained by the stability analysis described in Section II. 3.

Among the various concentration waves, kF T/Iₘₕₐₜₐ₅ vanishes at the highest temperature for k = ⟨100⟩ and ⟨1 1/2 0⟩. In fact, from symmetry considerations it may be shown that there are four special point vectors in fcc systems that give rise to four different type of instabilities. The ⟨100⟩ and ⟨1 1/2 0⟩ are two of these special point waves for which the ground state energy is degenerate in the case of vanishing 2nd nearest neighbor pair interactions. As mentioned in the Introduction section, the degeneracy is expected to be lifted at finite temperature by the entropy term, although as shown in the Fig. 1-1 this is not the case for the instability temperatures. This is also reflected in the calculated Iₘₐₕₐ₅ along the directions (1h0) in the Fig. 1-2. As pointed out previously this is a shortcoming of the tetrahedron approximation. The correct Fourier spectrum is obtained, however, in higher approximations such as tetrahedron-octahedron approximation. Nevertheless, the tetrahedron approximation correctly yields two important features of the phase diagram: one is the correct topology of the phase boundary and the other is the correct order of the transition at 1:1 and 1:3 stoichiometries.

In fact, the separation between the transition temperature and the instability temperature is a measure of the order of the transition. For a second order transition, both temperatures coincide, indicating that the ordering transition takes place continuously without an activation barrier. The more the two temperatures are separated the stronger the nature of the first order transition becomes.
The obtained results clearly indicate that the transition at both stoichiometries are strongly first order, which is in agreement with the symmetry analysis based on the Landau-Lifshitz rules. The Bragg-Williams approximation, on the other hand, predicts an isolated critical point (i.e., second order transition) for 1:1 stoichiometry.

The physical significance of the instability temperature can be described in the following way. When a sample is quenched from high temperatures to a temperature between the transition and the instability temperatures, the ordering reaction takes place by the classical nucleation and growth mechanism. However, if the quenching is carried out below the instability temperature, the transition to the ordering phase takes place by the continuous excitation and amplification of \( \langle 100 \rangle \) concentration waves. This process is similar to the spinodal decomposition mechanism proposed by Cahn and has been termed ordering spinodal by de Fontaine.

In general, the diffuse intensity spectrum becomes sharper as the temperature decreases due to the fact that the correlation range in a real space increases at lower temperatures, which has been confirmed by the diffuse intensity calculation at a lower temperature although not shown in the figure. Furthermore, the increase of the SRO intensity peak at the special point vector is due to the fact that the integrated diffuse intensity is conserved.

It is easily understood, from the evolution of the correlation functions at 1:1 stoichiometry (Fig. 1-3), that the probability of the tetrahedron cluster which has equal number of A and B atoms, which is characteristic of the Li phase equilibrium phase, increases while the probability of all other tetrahedron clusters decays. This is because of the following reason. Among the five atomic configurations on a tetrahedron cluster, only three of them are independent at 1:1 stoichiometry due to symmetry. The atomic configuration on these clusters are AAAA(BBBB), AAAB(ABBB) and AABB for which probabilities are written as

\[
W_{\text{AAAA}} = \frac{1}{2} \left( 1 + 6\xi_2 + \xi_4 \right)
\]

(23)

\[
W_{\text{AAAB}} = \frac{1}{2} \left( 1 - \xi_4 \right)
\]

(24)

and

\[
W_{\text{AABB}} = \frac{1}{2} \left( 1 - 2\xi_2 + \xi_4 \right).
\]

(25)

respectively, through eq. (4). Since \( \xi_2 \) and \( \xi_4 \) are monotonically decreasing and increasing functions, respectively, as it is shown in Fig. 1-3, only \( W_{\text{AAAB}} \) for the cluster AABB increases while others decay monotonically.

It is important to note that the correlation functions at infinite time converge exactly to those values calculated independently by the CVM for \( k_B T / \nu_2 = 2.5 \) which are indicated by broken lines in the Fig. 1-3. The monotonic behavior of each correlation function implies that for the present case a single relaxation process is involved. Since the time axis is normalized by the spin flip probability (more precisely \( \theta \cdot \Delta t \)), assigning a different value to the flip probability will shift the entire curve along the time axis isomorphically.

In the Fig. 1-4, the fluctuation spectra of the tetrahedron correlation function are indicated at \( t = 100 \) for the two temperatures. The peak value of the PPF for each temperature is confirmed to coincide with the one calculated using the conventional PPM, although the two spectra in the figure are shifted to facilitate comparison. One can see that the spectra are symmetrical with respect to the most probable value, and the half width is sharper for the lower temperature. Because of numerical difficulties, the spectra for large values of fluctuations were not calculated. However, we believe that the entire curve will approach a Gaussian distribution.

At the fixed stoichiometry of 50 at\%, both point \( (\xi_2) \) and triangle \( (\xi_3) \) correlations are equal to zero at all times. Hence, \( \xi_2 \) and \( \xi_4 \) are the only independent thermodynamic variables by which the thermodynamic configuration space is spanned as is shown in Fig. 1-5. It can be confirmed that the free energy of the system decreases monotonically towards the equilibrium value. Furthermore, the most probable path deviates from the steepest decent direction, indicating the effect of the kinetic factors.

IV. Concluding Remarks

Based on the CVM and the PPM, we attempt to synthesize the thermodynamics and kinetics of the ordering behavior in fcc lattices at 50 at\%. From a single free energy formula one obtains all the information pertaining to phase equilibria as well as the stability of the system for small perturbations. The PPM, on the other hand, is employed to study the evolution of non-equilibrium relaxation processes. Among the salient features of the PPM based approach is that the calculated results at infinite time converge naturally to the equilibrium values independently obtained by the CVM.

The present PPM calculation was limited to the disordered phase with a spin flip mechanism. The extension to ordered phases as well as the introduction of a more realistic vacancy mechanism remains the subject of future investigations.

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