北海道大学工学部研究報告
第150号（平成2年）

Bulletin of the Faculty of Engineering,
Hokkaido University, No. 150 (1990)

Kinetics of Homogeneous Short Range Ordering in an FCC Spin System Studied by the Path Probability Method

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(Received December 26, 1989)

Abstract

The tetrahedron approximation of the path probability method is formulated and the order relaxation behavior of spin configurations up to the tetrahedron cluster by a flipping mechanism in the fcc disorder phase is investigated.

Free energy functional of a spin system, in which either up or down spin is assigned at each lattice point, can be formally written as

$$F=\sum_{\{\sigma\}}E(\sigma)X(\sigma)+\mathrm{T}k_B\sum_{\{\sigma\}}X(\sigma)\ln X(\sigma) \tag{1}$$

where $E(\sigma)$ and $X(\sigma)$ are, respectively, the internal energy and probability of configuration σ, and the sum runs over 2^N configurations with N lattice points. Given the formidably large value N of a general system, it is, however, a practically intractable task to evaluate the sum in the above expression. The key ingredient devised in Kikuchi's Cluster Variation Method[1] (hereafter abbreviated as CVM) is to approximate the configurational entropy term in eq. (1) by the sum of the entropy-like term in the following manner.

$$k_B\sum_{\{\sigma\}}X(\sigma)\ln X(\sigma)\approx k_B\sum_p\sum_{n,s}\gamma_{n,s}\sum_{J=1}^{2^n}x_{n,s}(J,\ p)\ln x_{n,s}(J,\ p) \tag{2}$$

where p stands for the sublattice, s specifies the geometry of n-points cluster, $x_{n,s}$ the probability of finding a particular spin configuration repesented by $J=\{i_1\ i_2\ i_3\cdots i_n\}$ on the $(n,\ s)$ cluster where i_l takes either 1 (up spin) or $\bar{1}$ (down spin), and the coefficients $\gamma_{n,s}$ depend on both the geometry of the lattice and the type of the cluster. When the configurational energy is assumed to be given by the sum of pair interaction energies, the free energy functional is reduced to

$$F=\frac{1}{2}\sum_p\sum_k \mathrm{J}_k\xi_k(p)+\mathrm{T}k_B\sum_p\sum_{n,s}\gamma_{n,s}\sum_J x_{n,s}(J,\ p)\ln x_{n,s}(J,\ p) \tag{3}$$

where J_k and ξ_k are, respectively, the effective interaction energy (exchange energy) and correlation function[2], of which definition will be given later, for the k-th nearest neighbor pair. Various equilibrium thermodynamic properties can, in principle, be derived by minimiz-

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ing the functional F with respect to independent $x_{n,s}$'s. In general, the larger the maximum cluster involved in the formula is, the higher the accuracy is achieved. This has been amply demonstrated in the various phase diagram calculations[3]. Hence, the maximum cluster explicitly included in the entropy-like term of above eq. (3) characterizes the level of the approximation.

The obtained set of $x_{n,s}$ *(J, p)* at equilibrium state, which have been termed state variable, are regarded as short range order parameters, therefore the CVM has been recognized as a powerful tool to investigate the local spin configurations as well as the bulk thermodynamic properties. The importance of the short range order is particulrally pronounced for a disorder phase, because the apperances of various prorerties owe their origin to the evolution and devolution of local ordering. Since the sublattices are indistinguishable for the disorder phase due to the translational symmetry, the free energy functional (3) is reduced to the following expression in the tetrahedron approximation[4] with first nearest neighbor pair interactions by which the present study is attempted.

$$F=6\sum_{ij}\mathrm{e}_{ij}\mathrm{y}_{ij}+\mathrm{T}k_{\mathrm{B}}\sum_{n=1}^{4}\gamma_n\sum_{J=1}^{2^n}x_n(J)\ln x_n(J) \tag{4}$$

where e_{ij} and y_{ij} are the interaction energy and the concentration for the nearest neighbor pairs i and j, and J_1 in the eq.(3) is related to e_{ij} by $\mathrm{J}_1=(\mathrm{e}_{11}+\mathrm{e}_{\bar{1}\bar{1}})/2-\mathrm{e}_{1\bar{1}}$. The indices $n=1$, 2, 3 and 4 in the entropy term, respectively, correspond to point, pair, triangle and tetrahedron cluster of which concentrations are more explicitly denoted as x_i, y_{ij}, z_{ijk} and w_{ijkl}. In fact, the entropy formula in the CVM is often presented in terms of x_i, y_{ij}.. in the following manner,

$$\ln\frac{(\prod_{ij}(\mathrm{y}_{ij}\mathrm{N})!)^6\cdot\mathrm{N}!}{(\prod_{ijkl}(\mathrm{w}_{ijkl}\mathrm{N})!)^2\ (\prod_{i}(\mathrm{x}_i\mathrm{N})!)^5} \tag{5}$$

A comparison of both equations (4) and (5) fixes the coefficients γ_n, which leads to the equivalent expression derived by Barker[5] and Hijmans et al[6]. Both the free energy and the equilibrium local spin configurations at a given temperature T are obtained by minimizing the functional F with respect to the independent set of state variables subject to

$$\sum_{ijkl}\mathrm{w}_{ijkl}=1 \tag{6}$$

Shown in Fig. 1 is the calculated results of the temperature dependency of the concentration of all types of configurations on a tetrahedron cluster for a fixed spin concentration 50% (equivalently zero chemical potential) with interaction energies $\mathrm{e}_{11}=\mathrm{e}_{\bar{1}\bar{1}}=1.0$ and $\mathrm{e}_{1\bar{1}}(=\mathrm{e}_{\bar{1}1})=-1.0$. Solid and open circles correspond to up and down spin, respectively. Note that the the distinctions of the cluster concentration between $\mathrm{w}_{111\bar{1}}$ and $\mathrm{w}_{1\bar{1}\bar{1}\bar{1}}$ and that between w_{1111} and $\mathrm{w}_{\bar{1}\bar{1}\bar{1}\bar{1}}$ degenerate for the concentration-independent pair interactions at 50%. The horizontal temperature axis in the figure is normalized by J_1 and the negative J_1 in the present study indicates antiferromagnetic interaction. One could observe that the tetrahedron cluster with an equal nember of up and down spins increases its concentration with decreasing temperature, while others decay. It is realized that the growing cluster is the basic constituent of the

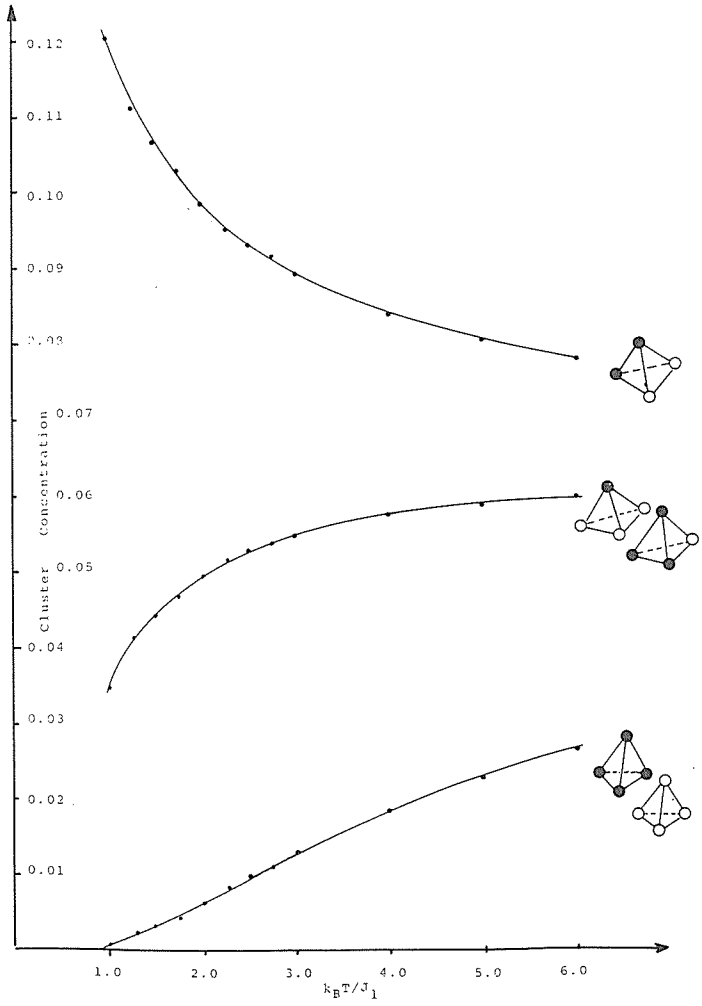

Fig. 1 The equilibrium concentration of spin configurations on a tetrahedron cluster calculated by the tetrahedron approximation of the Cluster Variation Method. The horizontal axis indicates the temperature which is normalized by the effective pair interaction energy J_1. Solid and open circles indicate up and down spins, respectively

$L1_0$ ordered structure underlying the transition temperature as the most stable phase at the 1 : 1 stoichiometry[4].

Contrary to the equilibrium short range order states described above, less studies have been achieved on the kinetics of short range ordering. In particular, most of the kinetic theories advanced, so far, do not explicitly convey many-body correlation functions beyond a pair. It has been amply demonstrated that the many-body correlation plays a significant role in phase equilibria[3]. Then, in order to deduce the equilibrium properties from a kinetic theory in a consistent manner as the limiting case at infinite time, it is deemed necessary that

a function appearing in the theory carries information of the many-body correlations. For this purpose, Kikuchi's Path Probability Method[7-10] (hereafter abbreviated as PPM) is adopted. In the following, a particular emphasis is placed on the formulation of the spin kinetics based on the PPM, by which our preliminary result[11] is rationalized, as well.

PPM has been known as the soundest approach to the kinetic study. The method is the natural extension of the CVM to the time domain and, therefore, both are compatible with each other. In the PPM, a set of variables $\{X_{ijk\cdots q,rst\cdots v}(t, t+\Delta t)\}$ are defined to represent the transition probability of a local spin configuration specified by $\{ijk\ldots q\}$ at time t to $\{rst\ldots v\}$ at time $t+\Delta t$. These sets of variables, termed path variables, are regarded as the counterpart of the state variables of the CVM, while, as that of the Free energy, the following Path Probability Function P (hereafter PPF) is defined[9].

$$P(t+\Delta t)=P_1\cdot P_2\cdot P_3 \tag{7}$$

where P_1 and P_2 are, respectively, given as

$$P_1=(\theta\Delta t)^{Nx_{1,\uparrow}}\cdot(\theta\Delta t)^{Nx_{\uparrow,\downarrow}}\cdot(1-\theta\Delta t)^{Nx_{1,\downarrow}}\cdot(1-\theta\Delta t)^{Nx_{\downarrow,\uparrow}} \tag{8}$$

and

$$P_2=\exp\left(-\frac{\Delta E}{2k_BT}\right) \tag{9}$$

These P_1 and P_2 terms, respectively, represent the kinetic factor with θ the spin flip probablity and the rate of the absorption of the energy ΔE which is the difference of the internal energy between time t and $t+\Delta t$ from heat reservoir. The key aspect of the PPM is characterized by the final term P_3 which counts numerous equivalent paths from one configuration to another. Hence, the P_3 is constructed in the similar fashion of the configurational entropy in the CVM and, therefore, the expression depends on the level of the approximation employed. The explicit expression adopted for this study will be presented shortly.

The PPM claims that the most probable transition path is obtained by maximizing the PPF with respect to the independent path variables. Despite the potential nature of the PPM, the stumbling block against the wider applicability is the mathematical complicacy inherently involved in the variational method with multi-variables. So far, the PPM studies have been limited to either the fundamental investigations of the interrelation with Master Equation Method[8,9] or applications to a simplified system[10]. In order to study the kinetics of more realistic three dimensional system, it is indispensable to expand the theoretical framework so that bigger cluster can be incorporated. This study has been devoted to a three dimensional fcc lattice, and the time evolution behavior of the cluster configuration of which equilibrium values are demonstrated in Fig. 1 is investigated. Accordingly, the path variables up to the tetrahedron cluster are introduced (tetrahedron approximation) to write the P_3 in the following manner:

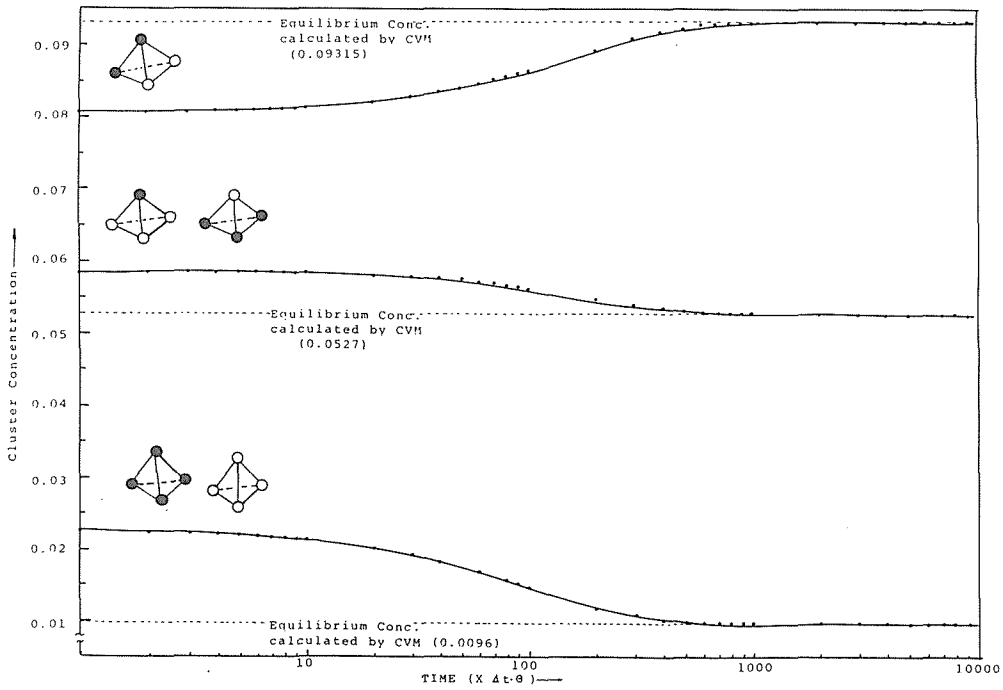

Fig. 2 Time evoltion of the local spin configuration on a tetrahedron cluster which was maintained at $k_BT/J_1=5.0$ then subjected to a quenching operation down to 2.5 at time 0. The horizontal axis indicates the logarithmic time scale normalized by the spin flip probability θ. The dotted lines in the figure indicate the equilibrium concentration at $k_BT/J_1=2.5$ which are independently calculated by the CVM.

$$P_3=\frac{\left[\prod_{ijkl}(y_{ijkl}N)!\right]^6\cdot N!}{\left[\prod_{ijkl,\,mnpq}(w_{ijkl,mnpq}N)!\right]^2\left[\prod_{i,j}(x_{i,j}N)!\right]^5} \tag{10}$$

where $x_{i,j}$, $y_{ij,kl}$ and $w_{ijkl,mnpq}$ are, respectively, the transition probabilities for point, pair and tetrahedron configurations. In the present approximation, one can realize that eight path variables are independent due to the geometrical relationship among the path variables and the interrelation between state variables and path variables. Therefore, the mathematical procedure was reduced to solving the eight simultaneous non-linear equations.

In order to comply with the CVM study presented in Fig. 1, the present PPM calculation was performed at the same spin concentration of 50% under the same effective interaction energy $J_1=-1.0$. Shown in Fig. 2 is the time evolution of the various spin configurations on a tetrahedron cluster in a fcc disorder phase which is maintained at $k_BT/J_1=5.0$ then subjected to a quenching operation down to $k_BT/J_1=2.5$ followed by aging. The initial concentration of each cluster configuration at $k_BT/J_1=5.0$ is assigned by the CVM calcula-

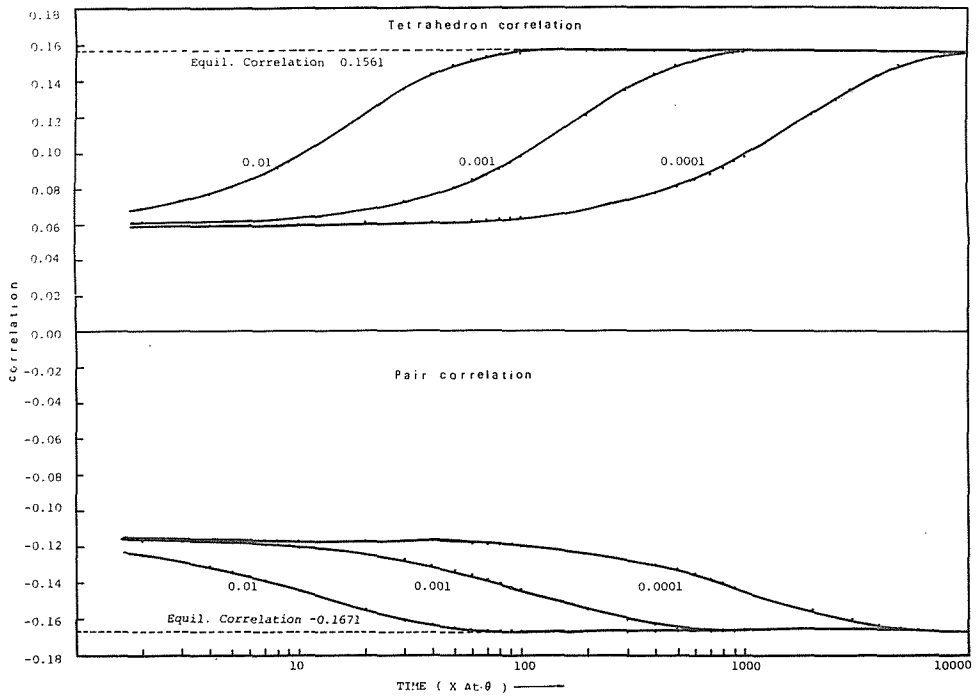

Fig. 3 Time evolution of the tetrahedron correlation function ξ_4 and pair correlation function ξ_2 for the three kinds of spin flip probability $\theta\Delta t$, 0.01, 0.001 and 0.0001. The initial and quenching conditions are the same ones described in the Fig. 2. The dotted lines again, indicate the equilibrium correlations independently calculated by the CVM for $k_B T/J_1 = 2.5$.

tion, and the time evolution process at $k_B T/J_1 = 2.5$ is calculated by repeatedly employing the interrelation between the state variables and path variables. The horizontal axis is a logarithmic time scale normalized by spin flip probability θ which is 0.01 for this calculation. One could realize that the particular cluster which has 50% of concentration and represents most the underlying $L1_0$ order phase grows rapidly with time, while others decay. The limiting values asymptotically approached by each cluster, which are indicated by dotted lines in the figure, are exactly the equilibrium ones independently calculated by the CVM for $k_B T/J_1 = 2.5$. This guarantees the accuracy of the present calculation which has passed through a intolerable numerical process.

Fig. 3 demonstrates the time evolution of tetrahedron ξ_4 and pair correlation functions ξ_2 for three kinds of spin flip probability θ. The correlation function for a nearest neighbor i-points cluster is defined by

$$\xi_i = \langle i_1 i_2 \ldots i_k \ldots i_i \rangle \tag{11}$$

where i_k takes 1 for an up spin and -1 for a down spin, respectively, at k-th lattice point in

the i-points cluster and $\langle\rangle$ indicates ensemble average. The initial and quenching conditions are the same as those assumed in the Fig. 2. Since the horizontal axis is normalized by spin flip probability the three curves are isomorphic. Both correlations are confirmed to approach toward equilibrium values which are independently calculated by the CVM. It should be noted that the point correlation is equivalent to the concentration which should not vary ($\xi_1 = 0$) because of being of a conservative quantity, while triangle correlation should be also kept constant ($\xi_3 = 0$) for the 50% in the disordered phase. These are exactly realized in the present study.

As an initial attempt to apply the PPM to realistic three dimensional system, the present letter is limited to the introduction of the theoretical frameworks and calculated results for a spin system. Together with a more detailed discussion of relaxation behavior, an applicability to an alloy system is demonstrated in a separate issue.

Acknowledgement

The author greatly appreciates the stimulating discussion with Professor K. Wada of Hokkaido University. He also expresses sincere thanks to Mr. Okubo for his assistance in preparing this manuscript. This work was supported in part by a Grant-in-Aid for Cooperative Research from the Japanese Ministry of Education, Science and Culture and by a research funding from Production Engineering Research Laboratory, Hitachi Ltd.

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