Time evolution of fluctuations in the path-probability method. II

Koh Wada
Department of Physics, Hokkaido University, Sapporo 060, Japan

Takuma Ishikawa
Department of Physics, Tokyo Insitute of Technology, Oh-okayama, Meguro-ku, Tokyo 152, Japan

Hiroshi Sato and Ryoichi Kikuchi*
School of Materials Engineering, Purdue University, West Lafayette, Indiana 47907
(Received 19 November 1984; revised manuscript received 9 December 1985)

Comparison of the path-probability method (PPM) with the master-equation method (MEM) is extended to a higher degree of approximation (triangle approximation) for the kinetics of Ising ferromagnetism. The evolution equations of the averages and of the fluctuations around them are derived analytically in this high degree of approximation for the first time for both methods. Contrary to the case of pair approximation presented in Ishikawa *et al.* (the preceding paper), it was not possible to bring the evolution equations derived by the MEM into a complete agreement with those by the PPM even with the use of the most reasonable closure relations.

I. INTRODUCTION

As promised in the preceding paper (hereafter referred to as I),[1] we extend the comparison of the path-probability method (PPM) and the master-equation method (MEM) to a higher degree of approximation (triangle approximation) in deriving the evolution equations for the averages and for the fluctuations based on the Ising model ferromagnetism in the two-dimensional triangular lattice. Never before has the kinetics of Ising ferromagnetism been worked out to such a high degree of approximation analytically both in the PPM and in the MEM.

Although the PPM and the MEM seem to be completely equivalent with respect to the kinetics of Ising model ferromagnetism based on the results of our earlier treatment,[1] the treatment in the triangle approximation shows surprisingly that it is not possible to bring the evolution equations derived by the MEM into a complete agreement with those derived by the PPM even with the most reasonable choice of closure relations. This paper tries to seek possible origins of such discrepancies in order to determine whether they are intrinsic or not. For this purpose, we present the derivation of the evolution equations in detail for both the PPM and the MEM.

The contents of this paper are, therefore, almost parallel to those of I in spirit. The differences from the previous results, however, are emphasized and somewhat detailed explanation of the treatment of the MEM in the triangle approximation is given in Sec. V because this is the first derivation by the MEM in the triangle approximation. Discussions with respect to the possible origin of the discrepancies are given in Sec. VI.

II. THE MOST PROBABLE PATH IN THE PPM

The Hamiltonian for a homogeneous ferromagnetic Ising system is given in I, Eq. (2.1). We apply the PPM in the triangle approximation to this system. The state variables in this approximation are defined as $x_i(t)$ and $y_{ij}(t)$ just as in I together with the triangle variables $z_{ijk}(t)$, where the suffixes i, j, and k designate $+1$ or -1, depending on whether the state of spin is up or down. In a

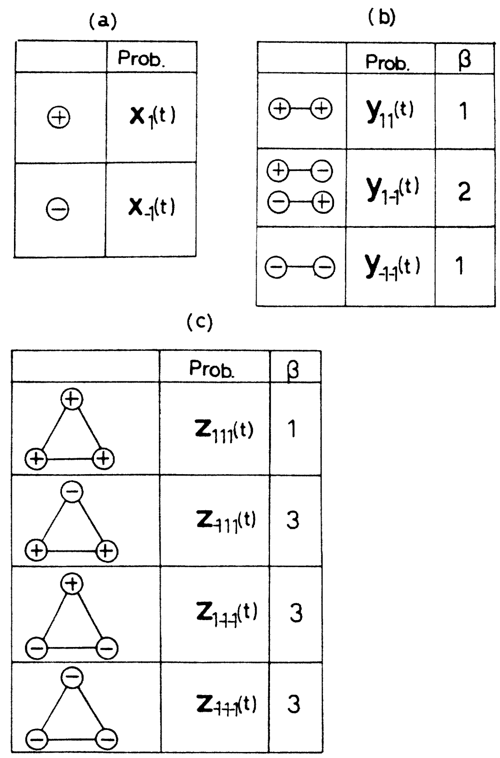

FIG. 1. The state variables $x_i(t)$, $y_{ij}(t)$, and $z_{ijk}(t)$ which specify the probabilities of the configurations at time t for (a) a point, (b) a pair, and (c) a triangle. The value β indicates the weight factor, or the number of different configurations having the same probability.

similar fashion, extra path variables $Z_{ijk,i'j'k'}(t,t+\Delta t)$ are introduced in addition to the path variables $X_{i,i'}(t,t+\Delta t)$ and $Y_{ij,i'j'}(t,t+\Delta t)$ defined in I; $NZ_{ijk,i'j'k'}(t,t+\Delta t)$ (N is the number of lattice points) is the number of triangles which is in the (i,j,k) state at time t and will change to the (i',j',k') state at $t+\Delta t$. The time span, Δt, is chosen short enough so that it is safe to assume that, at most, only one of the second subscripts i', j', and k' is different from the first subscripts i, j, and k. These variables are listed in Figs. 1 and 2, respectively. Because the system is assumed to be homogeneous, abbreviated notations are introduced with the use of the symmetry of the system. These are also shown in Fig. 2.

All path variables are not independent of each other. There are geometrical relations among the state and the path variables. Also, since the path variables are the joint probabilities connecting the state at t and that at $t+\Delta t$, we can write the state variables also as linear combinations of path variables. When the system is specified by the state variables $\{z_{ijk}(t);\ i,j,k=\pm 1\}$ at time t, $\{Z_s(i);\ i=1,-1,\ s=1,2,3\}$ can be chosen as the independent path variables as shown in Fig. 2.

Let us construct the path-probability function (PPF), $\mathscr{P}(t+\Delta t)$, which is made of three factors.[2] The first factor is the transition probability of the system in Δt in a unit kinetic process

$$\mathscr{P}_1=\prod_{i=\pm 1}(\theta\,\Delta t)^{NX_{i,-i}}(1-\theta\,\Delta t)^{NX_{i,i}}\ , \tag{2.1}$$

where θ is a spin-flip fractional per unit time. The second factor $\mathscr{P}_2$ is the probability of activating the system through the interaction with the heat reservoir. By using the energy change in Δt of the system

$$\Delta E=N\sum_{i=\pm 1}\{12J[Z_1(i)-Z_3(i)]+2\mu_0 HiX(i)\}\ , \tag{2.2}$$

we can write the second factor as

$$\mathscr{P}_2=\exp(-\Delta E/2k_BT)\ , \tag{2.3}$$

where J and $\mu_0 H$ have the same meanings as in I. The third factor $\mathscr{P}_3$ is the number of possible configurations corresponding to the change given in Eq. (2.1) (this factor corresponds to the entropy in the equilibrium case) in the triangle approximation and is given schematically by

$$\mathscr{P}_3=\frac{P_{\text{pair}}^3}{P_{\text{triangle}}^2 P_{\text{point}}}\ , \tag{2.4}$$

where

$$P_{\text{point}}=\prod_{i,i'}[(NX_{i,i'})!]\ ,$$

$$P_{\text{pair}}=\prod_{(i,j),(i',j')}[(NY_{ij,i'j'})!]\ ,$$

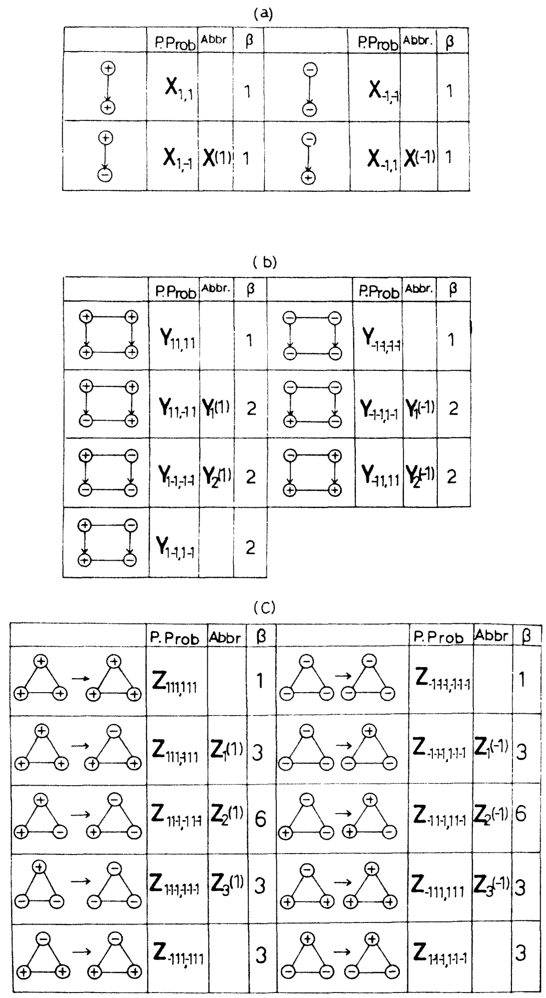

FIG. 2. Definition of the path variables for the Ising model in the triangle approximation. These specify the path fractionals (a) $X_{i,i'}(t,t+\Delta t)$ for a point, (b) $Y_{ij,i'j'}(t,t+\Delta t)$ for a pair, and (c) $Z_{ijk,i'j'k'}(t,t+\Delta t)$ for a triangle. "Abbr." columns show the shortened notations for certain path variables, and the β column indicates the weight factor or the number of equivalent configuration changes for each path variable.

$$P_{\text{triangle}}=\prod_{(i,j,k),(i',j',k')}[(NZ_{ijk,i'j'k'})!]\ .$$

The combinatorial factor, Eq. (2.4), is one of the key relations of the treatment, and has the same expression as that in the triangle approximation of the CVM if the state variables are replaced by the corresponding path variables. By multiplying these factors, we have the PPF in the logarithmic form as

$$\frac{1}{N}\ln\mathscr{P}(t,t+\Delta t)=\sum_{i=\pm 1}[X_{i,-i}\ln(\theta\,\Delta t)+X_{i,i}\ln(1-\theta\,\Delta t)]+3\sum_{(i,j),(i',j')}\mathscr{L}(Y_{ij,i'j'})-2\sum_{(i,j,k),(i',j',k')}\mathscr{L}(Z_{ijk,i'j'k'})$$
$$-\sum_{i,i'}\mathscr{L}(X_{i,i'})-6K\sum_{i=\pm 1}[Z_1(i)-Z_3(i)]-L(X_{1,-1}-X_{-1,1})\ , \tag{2.5}$$

where $\mathscr{L}(x)=x(\ln x-1)$, $K=J/k_BT$, and $L=\mu_0H/k_BT$.

Differentiations of the PPF with respect to the six independent path variables $Z_s(i)$ then give the following relations:

$$\frac{\hat{X}_{i,-i}}{\tilde{x}_i(t)}\left[\frac{\tilde{y}_{ii}(t)}{z_{iii}(t)}\frac{\hat{Z}_1(i)}{\hat{Z}_1(i)+\hat{Z}_2(i)}\right]^6=\theta\,\Delta t\ ,$$

$$\frac{\hat{X}_{i,-1}}{\tilde{x}_i(t)}\left[\frac{\tilde{y}_{i-i}(t)}{z_{i-i-i}(t)}\frac{\hat{Z}_3(i)}{\hat{Z}_2(i)+\hat{Z}_3(i)}\right]^6=\theta\,\Delta t\ , \quad (2.6)$$

$$\frac{\hat{X}_{i,-i}}{\tilde{x}_i(t)}\left[\frac{\tilde{y}_{ii}(t)\tilde{y}_{i-i}(t)}{z_{ii-i}(t)}\times\frac{\hat{Z}_2^2(i)}{[\hat{Z}_1(i)+\hat{Z}_2(i)][\hat{Z}_2(i)+\hat{Z}_3(i)]}\right]^3=\theta\,\Delta t$$

$$(i=\pm1)\ ,$$

where the caret indicates the most probable path variables and the tilde is used for abbreviations as follows:

$$\tilde{x}_i(t)=x_i(t)e^{-ih},\ \ \tilde{y}_{ij}(t)=y_{ij}(t)e^{ijK}\ \ (i,j=\pm1)\ . \quad (2.7)$$

Since a set of equations with $i=1$ in Eq. (2.6) is independent of that with $i=-1$, we can treat each set separately. A set of path variables $\{\hat{X}(i),\hat{Z}_s(i),\ s=1,2,3\}$ is associated with a spin flip from an i to a $-i$ state in Δt, and can be transformed as

$$\hat{X}(i)=\theta\,\Delta t\,\tilde{x}_i(t)[\lambda_+(i)]^z \quad (2.8)$$

and

$$\hat{Z}_1(i)=\frac{\theta\,\Delta t}{2}\tilde{x}_i(t)\frac{z_{iii}(t)}{\tilde{y}_{ii}(t)}[\lambda_+(i)]^{z-1}\times\left[1+\left[\frac{z_{iii}(t)}{\tilde{y}_{ii}(t)}-\frac{z_{i-i-i}(t)}{\tilde{y}_{i-i}(t)}\right]\Big/D\lambda(i)\right],$$

$$\hat{Z}_2(i)=\theta\,\Delta t\,\tilde{x}_i(t)\frac{[z_{ii-i}(t)]^2}{\tilde{y}_{ii}(t)\tilde{y}_{i-i}(t)}\frac{[\lambda_+(i)]^{z-1}}{D\lambda(i)}\ , \quad (2.9)$$

$$\hat{Z}_3(i)=\frac{\theta\,\Delta t}{2}\tilde{x}_i(t)\frac{z_{i-i-i}(t)}{\tilde{y}_{i-i}(t)}[\lambda_+(i)]^{z-1}\times\left[1-\left[\frac{z_{iii}(t)}{\tilde{y}_{ii}(t)}-\frac{z_{i-i-i}(t)}{\tilde{y}_{i-i}(t)}\right]\Big/D\lambda(i)\right],$$

where

$$D\lambda(i)=\left[\left[\frac{z_{iii}(t)}{\tilde{y}_{ii}(t)}-\frac{z_{i-i-i}(t)}{\tilde{y}_{i-i}(t)}\right]^2+\frac{4[z_{ii-i}(t)]^2}{\tilde{y}_{ii}(t)\tilde{y}_{i-i}(t)}\right]^{1/2}, \quad (2.10)$$

$$\lambda_+(i)=\frac{1}{2}\left[\frac{z_{iii}(t)}{\tilde{y}_{ii}(t)}+\frac{z_{i-i-i}(t)}{\tilde{y}_{i-i}(t)}+D\lambda(i)\right], \quad (2.11)$$

and z is used for the coordination number ($z=6$ for the triangular lattice). Note that Eq. (2.8) has the same form as Eq. (2.11) in I. We then see that $\lambda_+(i)$ $(i=\pm1)$ represents the environmental effect when a spin at the center of the cluster changes its direction.

In the triangle approximation, the system is characterized by the three-spin correlation $m_3(t)$ in addition to the magnetization $m_1(t)$ and the pair correlation $m_2(t)$ used in I. They are defined with convenient numerical factor as

$$m_1(t)=\sum_{i=\pm1}ix_i(t)\ ,$$
$$m_2(t)=3\sum_{i,j=\pm1}ijy_{ij}(t)\ , \quad (2.12)$$
$$m_3(t)=2\sum_{i,j,k=\pm1}ijkz_{ijk}(t)\ .$$

The changes in Δt can then be written as the linear combination of path variables as

$$\Delta m_1(t)=-2[X(1)-X(-1)]\ ,$$
$$\Delta m_2(t)=-2z\sum_{i=\pm1}[Y_1(i)-Y_2(i)]\ , \quad (2.13)$$
$$\Delta m_3(t)=-2z\sum_{i=\pm1}i[Z_1(i)-2Z_2(i)+Z_3(i)]\ .$$

Substitution of the most probable path variables into Eq. (2.13) leads to the evolution equations for the order parameters in the limit of $\Delta t\to0$ as

$$\frac{d\overline{m}_1(t)}{dt}=-2\theta\sum_{i=\pm1}i\tilde{x}_i(t)[\lambda_+(i)]^z\ ,$$

$$\frac{d\overline{m}_2(t)}{dt}=-2z\theta\sum_{i=\pm1}i\tilde{x}_i(t)\left[\frac{z_{iii}(t)}{\tilde{y}_{ii}(t)}-\frac{z_{i-i-i}(t)}{\tilde{y}_{i-i}(t)}\right]\frac{[\lambda_+(i)]^z}{D\lambda(i)}\ , \quad (2.14)$$

$$\frac{d\overline{m}_3(t)}{dt}=-2z\theta\sum_{i=\pm1}i\tilde{x}_i(t)\left[[\lambda_+(i)]^z-\frac{4[z_{ii-i}(t)]^2}{\tilde{y}_{ii}(t)\tilde{y}_{i-i}(t)}\frac{[\lambda_+(i)]^{z-1}}{D\lambda(i)}\right],$$

where the bar on $m_i(t)$'s indicates the most probable path.

III. THE PROBABILITY DISTRIBUTION OF THE FLUCTUATION PATH

By applying the system size expansion developed by van Kampen[3] to the PPF, we write the path variables as

$$Z_s(i)=\hat{Z}_s(i)+\epsilon^{1/2}\xi_s(i;t,t+\Delta t)\ \ (i=\pm1,\ s=1,2,3)\ , \quad (3.1)$$

where $\epsilon=1/N$ is the smallness parameter of the system and $\xi_s(i;t+\Delta t)$'s represent the deviations from the most probable path. The PPF is expanded up to the second power of the $\xi_s(i)$ as

$$\frac{1}{N}\ln\mathscr{P}(t,t+\Delta t)=2\sum_{i,j,k=\pm1}\mathscr{L}(z_{ijk}(t))-3\sum_{i,j}\mathscr{L}(y_{ij}(t))+\sum_{i}\mathscr{L}(x_i(t))$$
$$+\epsilon\sum_{i=\pm1}\left[-\frac{1}{2}\frac{[\xi_1(i)+2\xi_2(i)+\xi_3(i)]^2}{\hat{X}(i)}-3\left[\frac{[\xi_1(i)+\xi_2(i)]^2}{\hat{Y}_1(i)}+\frac{[\xi_2(i)+\xi_3(i)]^2}{\hat{Y}_2(i)}\right]\right.$$
$$\left.-3\left[\frac{[\xi_1(i)]^2}{\hat{Z}_1(i)}+\frac{2[\xi_2(i)]^2}{\hat{Z}_2(i)}+\frac{[\xi_3(i)]^2}{\hat{Z}_3(i)}\right]\right]+O(\epsilon^2)\ . \tag{3.2}$$

The PPF, $\mathscr{P}(t,t+\Delta t)$, is then considered as the probability distribution function of the fluctuation path from the most probable path. It is a product of two factors except for an unimportant (for the present purpose) multiplicative factor

$$\mathscr{P}(t,t+\Delta t)\propto\prod_{i=\pm1}F(\xi_1(i),\xi_2(i),\xi_3(i))\ , \tag{3.3}$$

$$F(\xi_1(i),\xi_2(i),\xi_3(i))=C\exp\left[-\tfrac{1}{2}\sum_{s,s'=1,2,3}\xi_s(i)[D(i)]^{-1}_{ss'}\xi_{s'}(i)\right]\ , \tag{3.4}$$

where C is a normalization constant and the matrix $[D(i)]^{-1}$ is given by

$$[D(i)]^{-1}=\begin{bmatrix}\frac{1}{\hat{X}(i)}-\frac{z}{\hat{Y}_1(i)}+\frac{z}{\hat{Z}_1(i)} & \frac{2}{\hat{X}(i)}-\frac{z}{\hat{Y}_1(i)} & \frac{1}{\hat{X}(i)}\\ \frac{2}{\hat{X}(i)}-\frac{z}{\hat{Y}_1(i)} & \frac{4}{\hat{X}(i)}-\frac{z}{\hat{Y}_1(i)}-\frac{z}{\hat{Y}_2(i)}+\frac{2z}{\hat{Z}_2(i)} & \frac{2}{\hat{X}(i)}-\frac{z}{\hat{Y}_2(i)}\\ \frac{1}{\hat{X}(i)} & \frac{2}{\hat{X}(i)}-\frac{z}{\hat{Y}_2(i)} & \frac{1}{\hat{X}(i)}-\frac{z}{\hat{Y}_2(i)}+\frac{z}{\hat{Z}_3(i)}\end{bmatrix}\ . \tag{3.5}$$

The inverse matrix of the above matrix defines the correlation matrix

$$[D(i)]_{ss'}=\langle\xi_s(i)\xi_{s'}(i)\rangle\quad(s,s'=1,2,3)\ , \tag{3.6}$$

where $\langle\ \rangle$ denotes the average over the distribution function, Eq. (3.4). When the fluctuation from the most probable path is taken into account, Eq. (2.13) is rewritten as

$$\Delta m_1(t)-R_1(t)\Delta t=-2\epsilon^{1/2}\sum_{i=\pm1}i[\xi_1(i)+2\xi_2(i)+\xi_3(i)]\ ,$$
$$\Delta m_2(t)-R_2(t)\Delta t=-4\epsilon^{1/2}\sum_{i}[\xi_1(i)-\xi_3(i)]\ , \tag{3.7}$$
$$\Delta m_3(t)-R_3(t)\Delta t=-6\epsilon^{1/2}\sum_{i}i[\xi_1(i)-2\xi_2(i)+\xi_3(i)]\ ,$$

where the average velocities $\{R_s(t),\ s=1,2,3\}$ are defined by

$$\frac{d\overline{m}_s(t)}{dt}=R_s(t)\ . \tag{3.8}$$

Further, when we define the variance matrix $\{R_{ss'}(t)\}$ as

$$\epsilon R_{ss'}(t)\Delta t=\langle[\Delta m_s(t)-R_s(t)\Delta t][\Delta m_{s'}(t)-R_{s'}(t)\Delta t]\rangle$$
$$=\epsilon R_{s's}(t)\Delta t\quad(s,s'=1,2,3)\ , \tag{3.9}$$

we can calculate $R_{ss'}(t)$ with the help of Eqs. (3.3)–(3.7). The explicit results are given in the Appendix.

The following point, however, should be noted here. Let us define a function

$$\overline{G}(t)=\theta\sum_{i=\pm1}\tilde{x}_i(t)\lambda_+^V(i)\ , \tag{3.10}$$

$$\lambda_+^V(i)=\frac{1}{2}\left\{\frac{\tilde{z}_{iii}(t)}{\tilde{y}_{ii}(t)}+\frac{\tilde{z}_{i-i-i}(t)}{\tilde{y}_{i-i}(t)}+\left[\left[\frac{\tilde{z}_{iii}(t)}{\tilde{y}_{ii}(t)}-\frac{\tilde{z}_{i-i-i}(t)}{\tilde{y}_{i-i}(t)}\right]^2+\frac{4[\tilde{z}_{ii-i}(t)]^2}{\tilde{y}_{ii}(t)\tilde{y}_{i-i}(t)}\right]^{1/2}\right\}\ , \tag{3.11}$$

$$\tilde{z}_{ijk}(t)=z_{ijk}(t)e^{-Vijk}\ .$$

Here, $\overline{G}(t)\Delta t$ is identical to $\sum_{i=\pm 1}\hat{X}(i)$ given in Eq. (2.8) if $\tilde{z}_{ijk}(t)$ is replaced by $z_{ijk}(t)$. Then it can be shown, in the limit of $\Delta V \to 0$, that the average velocities $\{R_s(t);\ s=1,2,3\}$ and the variance matrix $\{R_{ss'}(t);\ s,s'=1,2,3\}$ are derived by the differentiation of $\overline{G}(t)$ with respect to the conjugate fields L, K, and V of order parameters as

$$R_1(t)=2\frac{\partial\overline{G}(t)}{\partial L},\quad R_2(t)=2\frac{\partial\overline{G}(t)}{\partial K},\quad R_3(t)=2\frac{\partial\overline{G}(t)}{\partial V} \tag{3.12}$$

and

$$\begin{bmatrix} R_{11}(t) & R_{12}(t) & R_{13}(t) \\ R_{21}(t) & R_{22}(t) & R_{23}(t) \\ R_{31}(t) & R_{32}(t) & R_{33}(t) \end{bmatrix} = 4 \begin{bmatrix} \frac{\partial^2\overline{G}(t)}{\partial L^2} & \frac{\partial^2\overline{G}(t)}{\partial L\partial K} & \frac{\partial^2\overline{G}(t)}{\partial L\partial V} \\ \frac{\partial^2\overline{G}(t)}{\partial K\partial L} & \frac{\partial^2 G(t)}{\partial K^2} & \frac{\partial^2\overline{G}(t)}{\partial K\partial V} \\ \frac{\partial^2\overline{G}(t)}{\partial V\partial L} & \frac{\partial^2\overline{G}(t)}{\partial V\partial K} & \frac{\partial^2\overline{G}(t)}{\partial V^2} \end{bmatrix} \tag{3.13}$$

We obtain the proof of Eqs. (3.12) and (3.13) by first calculating the right-hand sides of Eqs. (3.12) and (3.13), and then by comparing those results with Eqs. (A1) and (A2) in the Appendix.

IV. THE FOKKER-PLANCK EQUATION FOR FLUCTUATION OF ORDER PARAMETERS

The derivation here can be made in a completely similar fashion to that in I. By making use of the velocities $R_i(t)$ and the variance matrix $\{R_{ij}(t)\}$, we can represent the transition probability $\psi(\Delta\mathbf{m};\mathbf{m},t)$ that the state $\mathbf{m}$ at time t changes into $\mathbf{m}+\Delta\mathbf{m}$ at $t+\Delta t$ as

$$\Psi(\Delta\mathbf{m};\mathbf{m},t)=C'\exp\left\{-\frac{1}{2\epsilon\Delta t}[\Delta\mathbf{m}-\Delta\overline{\mathbf{m}}(t)] \times[\mathbf{R}(t)]^{-1}[\Delta\mathbf{m}-\Delta\overline{\mathbf{m}}(t)]^T\right\}, \tag{4.1}$$

where C' is a normalization constant, the vector notation for m_s is introduced as $\mathbf{m}=(m_1,m_2,m_3)$, and the superscript T denotes the transpose of the vector concerned.

Because the Markovian process is assumed, the probability function $W(\mathbf{m},t+\Delta t)$ of finding $\mathbf{m}$ at $t+\Delta t$ is connected with $W(\mathbf{m}',t)$ at t through the transition probability, Eq. (4.1), by[4]

$$W(\mathbf{m},t+\Delta t) = \int\int\int W(\mathbf{m}-\Delta\mathbf{m},t)\Psi(\Delta\mathbf{m};\mathbf{m}-\Delta\mathbf{m},t)d(\Delta\mathbf{m}) . \tag{4.2}$$

By expanding both sides of Eq. (4.2) with respect to Δt and $\Delta\mathbf{m}$, and by noting the following relations

$$\begin{aligned} &\int \Delta m_s\psi(\Delta\mathbf{m};\mathbf{m},t)d(\Delta\mathbf{m})=R_s(t)\Delta t , \\ &\int \Delta m_s\Delta m_{s'}\psi(\Delta\mathbf{m};\mathbf{m},t)d(\Delta\mathbf{m})=\epsilon R_{ss'}(t)\Delta t + R_s(t)R_{s'}(t)(\Delta t)^2 , \\ &\int \Delta m_s\Delta m_{s'}\Delta m_{s''}\psi(\Delta\mathbf{m};\mathbf{m},t)d(\Delta\mathbf{m})=O((\Delta t)^2) \quad (s,s',s''=1,2,3) , \end{aligned} \tag{4.3}$$

we obtain in the limit of $\Delta t\to 0$

$$\frac{\partial W(\mathbf{m},t)}{\partial t}=-\sum_{s=1}^{3}\frac{\partial}{\partial m_s}[R_s(t)W(\mathbf{m},t)] +\frac{1}{2}\epsilon\sum_{s,s'=1}^{3}\frac{\partial^2}{\partial m_s\partial m_{s'}}[R_{ss'}(t)W(\mathbf{m},t)] . \tag{4.4}$$

This is the master equation for order parameters which is correct up to the order $O(\epsilon)$. Note that Eq. (4.4) is essentially the same as Eq. (4.3) in I except that s in the triangle approximation runs up to 3 instead of 2 in the pair approximation. Therefore, when the probability distribution function for the fluctuation from the average path is defined by

$$Q(\eta,t)=W(\overline{\mathbf{m}}(t)+\epsilon^{1/2}\boldsymbol{\eta},t) , \tag{4.5}$$

we have the Fokker-Planck equation for the fluctuation:

$$\frac{\partial Q(\eta,t)}{\partial t}=-\sum_{s=1}^{3}\frac{\partial}{\partial\eta_s}\left[\sum_{s'=1}^{3}\frac{\partial R_s(\overline{\mathbf{m}}(t))}{\partial\overline{m}_{s'}(t)}\eta_{s'}Q(\boldsymbol{\eta},t)\right] +\frac{1}{2}\sum_{s,s'=1}^{3}\frac{\partial^2}{\partial\eta_s\partial\eta_{s'}}[R_{ss'}(\overline{\mathbf{m}}(t))Q(\boldsymbol{\eta},t)] , \tag{4.6}$$

where the dependence of $\overline{m}(t)$ on $R_s(t)$ and $R_{ss'}(t)$ is denoted explicitly. From Eq. (4.6), the evolution equations for the fluctuation such as $\langle\langle\eta_s(t)\rangle\rangle$ and $\langle\langle\eta_s(t)\eta_{s'}(t)\rangle\rangle$ can be readily derived, where $\langle\langle\ \rangle\rangle$ denotes the average with respect to $Q(\boldsymbol{\eta},t)$. Thus, the evolution equations for both the average and for the fluctuation of order parameters can be derived directly by the PPM in the triangle approximation.

V. THE MEM IN THE TRIANGLE APPROXIMATION

The basic equation of the MEM is the evolution equation of the probability function $P(\mathbf{M},t)$ with $\mathbf{M}=N\mathbf{m}$. The function $P(\mathbf{M},t)$ gives the probability that, at time t, the system has the configuration $\mathbf{M}$, where $\mathbf{m}$ is defined in Eq. (2.12). Then the master equation for a homogeneous system is written in the triangle approximation as

$$\frac{\partial P(\mathbf{M},t)}{\partial t} = -\int W(\mathbf{M}\to\mathbf{M}';t)P(\mathbf{M},t)d\mathbf{M}' + \int W(\mathbf{M}'\to\mathbf{M};t)P(\mathbf{M}',t)d\mathbf{M}' , \quad (5.1)$$

where $W(\mathbf{M}\to\mathbf{M}';t)$ is the transition probability from the state $\mathbf{M}$ to $\mathbf{M}'$ per unit time at t. When a spin of the system with spin state i changes its direction, the order parameter $\mathbf{M}$ of the system changes by the amounts

$$\Delta M_1(i) = -2i ,$$
$$\Delta M_2(i,\{j_s\}) = -2i(j_1+j_2+\cdots+j_z) , \quad (5.2)$$
$$\Delta M_3(i,\{j_s\}) = -2i(j_1j_2+j_2j_3+\cdots+j_zj_1) ,$$

where ($j_s=\pm 1$, $s=1,2,\ldots,z$) is a configuration of the nearest-neighboring spins around the center spin with i. Because spin flips are assumed to occur independently at each lattice point, the transition rate of the system can be given as

$$W(\mathbf{M}\to\mathbf{M}+\Delta\mathbf{M};t) = Nw(\mathbf{m};\Delta\mathbf{M}(i,\{j_s\}),t) . \quad (5.3)$$

As was done in the Appendix of I, we can write w as a product of two factors.[5] The first factor, the energy factor, is the same as Eq. (A4) in I and is given as

$$\exp\left[-\frac{\Delta E(i,\{j_s\})}{2k_BT}\right] = \exp\left[-i\left[K\sum_{j=1}^{z} j_s + L\right]\right] . \quad (5.4)$$

The second factor, the probability factor, p_{z+1}, of Eq. (A3) in I was written as a product of the pair probabilities $y_{ij}(t)$. In the present treatment, we have to use the triangle probabilities $z_{ijk}(t)$ instead. However, there is no prescribed rule for writing $p_{z+1}(i,\{j_s\},t)$ in terms of $z_{ijk}(t)$ in the MEM, and this is where the arbitrariness of the MEM exists. On the other hand, in the PPM, each step in the formulation is strictly prescribed once the basic cluster is specified. Therefore, we tentatively write the following relation for the $p_{z+1}(i,\{j_s\},t)$ in the MEM on the basis of the superposition concept[6] as

$$p_{z+1}(i,j_1,j_2,\ldots,j_z,t) = \mathcal{N}x_i(t)\prod_{s=1}^{z}\left[\frac{z_{ij_sj_{s+1}}(t)}{y_{ij_s}(t)}\right] , \quad (5.5)$$

where $\mathcal{N}$ is a normalization constant and $j_{z+1}=j_1$. By combining Eqs. (5.4) and (5.5), we obtain the transition rate

$$w(\mathbf{m};\Delta\mathbf{M}(i,\{j_s\}),t) = \lim_{V\to 0}\mathcal{N}\theta x_i \exp(-Li)\prod_{s=1}^{z} A^i(j_s,j_{s+1}) ,$$

$$A^i(j_s,j_{s+1}) = \frac{z_{ij_sj_{s+1}}\exp\left[-\frac{K}{2}i(j_s+j_{s+1})\right]\exp(-Vij_sj_{s+1})}{y_{ij_s}y_{ij_{s+1}}} , \quad (5.6)$$

where the conjugate field V for the combination of three spins is introduced for the convenience in later arguments. Since the state variables are expressed in terms of order parameters as

$$x_i = \tfrac{1}{2}(1+im_1),\quad y_{ij} = \frac{1}{4}\left[1+(i+j)m_1+\frac{2}{z}ijm_2\right] ,$$
$$z_{ijk} = \frac{1}{8}\left[1+(i+j+k)m_1+\frac{2}{z}(ij+jk+ki)m_2 + \frac{1}{2}ijkm_3\right] , \quad (5.7)$$

the transition probability depends on order parameters $\mathbf{m}$ at t. By substituting Eq. (5.6) into (5.1) along with the replacement of $P(\mathbf{M},t)$ by $P(\mathbf{m},t)$, we obtain the master equation in the triangle approximation

$$\epsilon\frac{dP(\mathbf{m},t)}{dt} = -\mathrm{tr}[w(\mathbf{m};\Delta\mathbf{M}(i,\{j_s\}))P(\mathbf{m},t)] + \mathrm{tr}[w(\mathbf{m}-\epsilon\,\Delta\mathbf{M}(i,\{j_s\});\Delta\mathbf{M}(i,\{j_s\}))P(\mathbf{m}-\Delta\mathbf{M}(i,\{j_s\}),t)] , \quad (5.8)$$

where $\mathrm{tr} = \sum_{i=\pm 1}\sum_{j_1,j_2,\ldots,j_z=\pm 1}$. When we define the moments with respect to the transition probability as

$$C_{l_1l_2l_3}(\mathbf{m},t) = \mathrm{tr}[[\Delta M_1(i)]^{l_1}[\Delta M_2(i,\{j_s\})]^{l_2}[\Delta M_3(i,\{j_s\})]^{l_3}w(\mathbf{m};\Delta\mathbf{M}(i,\{j_s\}))] , \quad (5.9)$$

we have the Kramers-Moyal expansion of the master equation

$$\frac{\partial P(\mathbf{m},t)}{\partial t} = -\sum_{\substack{l_1=0\\ l_1+l_2+l_3\neq 0}}^{\infty}\sum_{l_2=0}^{\infty}\sum_{l_3=0}^{\infty}\frac{(-\epsilon)^{l_1+l_2+l_3-1}}{l_1!l_2!l_3!} \times\frac{\partial^{l_1}}{\partial m_1{}^{l_1}}\frac{\partial^{l_2}}{\partial m_2{}^{l_2}}\frac{\partial^{l_3}}{\partial m_3{}^{l_3}} \times C_{l_1l_2l_3}(\mathbf{m},t)P(\mathbf{m},t) , \quad (5.10)$$

where the moment function is further transformed as

$$C_{l_1l_2l_3}(\mathbf{m},t) = \left[2\frac{\partial}{\partial L}\right]^{l_1}\left[2\frac{\partial}{\partial K}\right]^{l_2}\left[2\frac{\partial}{\partial V}\right]^{l_3}G(t) , \quad (5.11)$$

$$G(t) = \mathrm{tr}[w(\mathbf{m};\Delta\mathbf{M}(i,\{j_s\}),t)] . \quad (5.12)$$

Here, it should be noted that the limiting operation $\lim_{V\to 0}$ is always taken after the differentiation with respect to V is made. The function $G(t)$ in Eq. (5.12) is thus the moment generating function. It is seen that the evaluation of $G(t)$ is reduced to an eigenvalue problem if $A^i(j_s,j_{s+1})$ is identified as the (j_s,j_{s+1}) element of a matrix A^i, and is transformed as

$$G(t) = \mathcal{N}\theta\sum_{i=\pm 1} x_i e^{-hi}\mathrm{tr}[(A^i)^z]$$
$$= \mathcal{N}\theta\sum_{i=\pm 1} x_i e^{-hi}\{[\lambda_+^V(i)]^z + [\lambda_-^V(i)]^z\} , \quad (5.13)$$

where $\lambda_+^V(i)$ and $\lambda_-^V(i)$ are eigenvalues of the matrix A^i, i.e.,

$$\lambda_s^V(i)=\frac{1}{2}\left\{\frac{\tilde{z}_{iii}}{\tilde{y}_{ii}}+\frac{\tilde{z}_{i-i-i}}{\tilde{y}_{i-i}}+s\left[\left(\frac{\tilde{z}_{iii}}{\tilde{y}_{ii}}-\frac{\tilde{z}_{i-i-i}}{\tilde{y}_{i-i}}\right)^2+\frac{4\tilde{z}_{ii-i}\tilde{z}_{i-ii}}{\tilde{y}_{ii}\tilde{y}_{i-i}}\right]^{1/2}\right\} \quad (s=\pm 1)\ . \tag{5.14}$$

Note that only $\lambda_+^V(i)$ appears in the equivalent expression in the PPM, Eq. (3.11). In the limit of $V\rightarrow 0$, $\lambda_+^V(i)$ naturally becomes $\lambda_+(i)$ in Eq. (2.11). It is also noteworthy that $\lambda_-(i=\pm 1)$ appears in Eq. (5.13), but not in corresponding expressions, Eqs. (2.8) and (2.9) in the PPM. This indicates the difference between the PPM and the present version of the MEM.

Up to $O(\epsilon)$ in Eq. (5.10), the master equation is written as

$$\frac{\partial P(\mathbf{m},t)}{\partial t}=-\sum_{s=1}^{3}\frac{\partial}{\partial m_s}[C_s(t)P(\mathbf{m},t)]+\frac{\epsilon}{2}\sum_{s,s'=1}^{3}\frac{\partial^2}{\partial m_s\partial m_{s'}}[C_{ss'}(t)P(\mathbf{m},t)]\ , \tag{5.15}$$

where

$$C_1(t)=C_{100}(\mathbf{m},t),\quad C_2(t)=C_{010}(\mathbf{m},t),\quad C_3(t)=C_{001}(\mathbf{m},t) \tag{5.16}$$

and

$$\begin{bmatrix} C_{11}(t) & C_{12}(t) & C_{13}(t)\\ C_{21}(t) & C_{22}(t) & C_{23}(t)\\ C_{31}(t) & C_{32}(t) & C_{33}(t)\end{bmatrix}=\begin{bmatrix} C_{200}(t) & C_{110}(t) & C_{101}(t)\\ C_{110}(t) & C_{020}(t) & C_{011}(t)\\ C_{101}(t) & C_{011}(t) & C_{002}(t)\end{bmatrix} \tag{5.17}$$

are introduced. By applying the system size expansion to Eq. (5.15) or (5.10) with the transformation

$$\overline{Q}(\zeta,t)=P[\hat{\mathbf{m}}(t)+\epsilon^{1/2}\zeta,t]\ , \tag{5.18}$$

we obtain the Fokker-Planck equation for fluctuation of order parameters in the MEM

$$\frac{\partial\overline{Q}(\zeta,t)}{\partial t}=-\sum_{s=1}^{3}\frac{\partial}{\partial\zeta_s}\left[\sum_{s'=1}^{3}\frac{\partial C_s(\hat{\mathbf{m}}(t))}{\partial m_{s'}(t)}\zeta_{s'}\overline{Q}(\zeta,t)\right]+\frac{1}{2}\sum_{s,s'=1}^{3}\frac{\partial^2}{\partial\zeta_s\partial\zeta_{s'}}[C_{ss'}(\hat{\mathbf{m}}(t))\overline{Q}(\zeta,t)]\ , \tag{5.19}$$

where the evolution equations of order parameters are chosen as

$$\frac{d\hat{m}_s(t)}{dt}=C_s(\hat{\mathbf{m}}(t))\ . \tag{5.20}$$

Equations (5.19) and (5.20) are to be compared with Eq. (4.6) and (3.8), respectively. It is seen that, because the kernel functions such as R_s, $R_{ss'}$, C_s, and $C_{ss'}$ can be derived from the moment generating functions, the difference in the evolution equations derived by the PPM and those by the MEM is derived from the difference of $\overline{G}(t)$ in the PPM and $G(t)$ in the MEM.

VI. DISCUSSION

In the present paper, we have extended the treatment of kinetics of Ising ferromagnetism both by the PPM and by the MEM to the triangle approximation[7] for the first time. Our special interest is to compare the treatment of the PPM and the MEM in such a high degree of approximation. Our major aim was to clarify the features of the PPM as a kinetic method so that its applicability to a variety of irreversible phenomena could be correctly understood and ways to broaden the applicability can be found as stated in the preceding paper (I).[1] For this reason, in the PPM we have derived the evolution equations not only for the order parameters but also for the fluctuation from the most probable path with such a high degree of approximation. In dealing with the MEM in the triangle approximation, we derive the evolution equations for corresponding quantities by making use of the superposition approximation, Eq. (5.5), familiar in the CVM.[5] The superposition approximation was also used in the treatment in the pair approximation.[1]

In the point and the pair approximations, the PPM and the MEM give identical results.[1] On the other hand, in the triangle approximation the results thus derived by the two methods are not exactly identical. In the MEM, all moments with respect to the transition probability, which specifies the evolution of the system, are obtained simply by the differentiation of a generating function even in the triangle approximation, if an additional conjugate field to the three-spin correlation is introduced. The generating function $G(t)$ thus far derived is characterized by two kinds of characteristic values $\lambda_\pm(i)$ [see Eqs. (5.13) and (5.14)]. Thus, $\lambda_+(i)$ and $\lambda_-(i)$ appear on the same footing in the MEM, while in the PPM, $\lambda_-(i)$ is always missing [Eqs. (2.8) and (2.9)]. In the PPM, the meaning of $\lambda_+(i)$ is clear in that it represents the effect of the environment on the center i spin when it flips its direction. Therefore, it can be said that the PPM and MEM in the present treatment give different environmental effects. Because of the relation, $\lambda_+(i)>\lambda_-(i)$, this difference is expected to vanish in the limit of high coordination number. Also, it can be shown that both results lead to the same equilibrium expected from the triangle approximation of the CVM.[8] Thus the difference between them is related only to the kinetics. On the other hand, even if the equilibrium state is unique, there can, in general, be many kinetic paths converging to the same final equilibrium state. As is shown in Sec. V, if we drop the $\lambda_-^V(i)$ term in Eq. (5.13) for $G(t)$ and choose $\overline{G}(t)$ in Eq. (3.10) as the generating function of transition moments, the MEM leads to exactly the same evolution equations of the average and the fluctuation as those by the PPM. However, the physical origin of the modified $\overline{G}(t)$ in such a case cannot be justified from the viewpoint of the MEM.

While the MEM is a differential type of formulation, the PPM is of integral type. The latter can thus be directly connected to the path-integral formulation. We expect that this viewpoint would make the relation between the two methods clearer. It is, therefore, necessary to clarify why the PPM and the MEM should lead to similar but different results in the triangle approximation. In other words, it is necessary to answer if there is a reasonable MEM formulation which gives the same results as those of the PPM in the triangle approximation before we can conclude that both the PPM and the MEM are equivalent. At the same time, the clarification of this problem would be very useful to critically review the features of the PPM as a kinetic method.

ACKNOWLEDGMENTS

Fruitful discussions with Dr. M. Kaburagi and Dr. A. Suzuki of Purdue University are gratefully acknowledged. This work was supported in part by the National Science Foundation under Grant No. DMR-82-04104.

APPENDIX

In order to calculate the variance matrix, we first note that the determinant of $D(i)^{-1}$ is given by

$$|[D(i)]^{-1}| = \frac{36\hat{X}(i)}{\hat{Y}_1(i)\hat{Y}_2(i)\hat{Z}_1(i)\hat{Z}_3(i)} \quad (i=1,-1)\,. \tag{A1}$$

Since the inverse matrix of $D(i)^{-1}$ gives the correlation matrix

$$[D(i)]_{ss'} = \langle \xi_s(i)\xi_{s'}(i)\rangle \quad (s,s'=1,2,3)\,, \tag{A2}$$

we reach after some calculations by using Eq. (3.7),

$$\begin{aligned}
R_{11}(t)\Delta t &= 4\sum_{i=\pm1}\langle[\xi_1(i)+2\xi_2(i)+\xi_3(i)]^2\rangle \\
&= 4\sum_{i=\pm1}\hat{X}(i)\,, \\
R_{12}(t)\Delta t &= 8\sum_{i=\pm1}\langle i[\xi_1(i)+2\xi_2(i)+\xi_3(i)][\xi_1(i)-\xi_3(i)]\rangle \\
&= 8\sum_{i=\pm1} i[\hat{Z}_1(i)-\hat{Z}_3(i)] = R_{21}(t)\Delta t\,, \\
R_{13}(t)\Delta t &= 12\sum_{i=\pm1}\langle[\xi_1(i)+2\xi_2(i)+\xi_3(i)][\xi_1(i)-2\xi_2(i)+\xi_3(i)]\rangle \\
&= 12\sum_{i=\pm1}[\hat{Z}_1(i)-2\hat{Z}_2(i)+\hat{Z}_3(i)] = R_{31}(t)\Delta t\,, \\
R_{22}(t)\Delta t &= 16\sum_{i=\pm1}\langle[\xi_1(i)-\xi_3(i)]^2\rangle \\
&= 16\sum_{i=\pm1}\left[\frac{[\hat{Z}_1(i)-\hat{Z}_3(i)]^2}{\hat{X}(i)} + \frac{2\hat{Y}_1(i)\hat{Y}_2(i)[\hat{Z}_1(i)\hat{Y}_2(i)+\hat{Z}_3(i)\hat{Y}_1(i)]}{3\hat{Z}_2(i)\hat{X}(i)}\right], \\
R_{23}(t)\Delta t &= 24\sum_{i=\pm1}\langle i[\xi_1(i)-\xi_3(i)][\xi_1(i)-2\xi_2(i)+\xi_3(i)]\rangle \\
&= 24\sum_{i=\pm1} i\{[\hat{Z}_1(i)-\hat{Z}_3(i)-4\hat{Z}_2(i)][\hat{Z}_1(i)-\hat{Z}_3(i)]/\hat{X}(i)+\tfrac{4}{3}[\hat{Z}_1(i)-\hat{Z}_3(i)]\hat{Y}_1(i)\hat{Y}_2(i)/\hat{X}(i)^2\} \\
&= R_{32}(t)\Delta t\,, \\
R_{33}(t)\Delta t &= 36\sum_{i=\pm1}\langle[\xi_1(i)-2\xi_2(i)+\xi_3(i)]^2\rangle \\
&= 36\sum_{i=\pm1}([\hat{Z}_1(i)-2\hat{Z}_2(i)+\hat{Z}_3(i)]^2/\hat{X}(i)-\tfrac{8}{3}\{\hat{Z}_1(i)\hat{Z}_2(i)/\hat{X}(i)-[\hat{Z}_1(i)+\hat{Z}_3(i)]\hat{Y}_1(i)\hat{Y}_2(i)/\hat{X}(i)^2\})\,.
\end{aligned} \tag{A3}$$

In the calculation, the relation

$$\langle \xi_s(i)\xi_{s'}(i')\rangle = 0 \quad \text{for } i\neq i' \tag{A4}$$

is used.

*Permanent address: Department of Materials Science and Engineering, Roberts Hall (FB-10), University of Washington, Seattle, WA 98195.

[1]T. Ishikawa, K. Wada, H. Sato, and R. Kikuchi, preceding paper, Phys. Rev. A 33, 4164 (1986).
[2]R. Kikuchi, Prog. Theor. Phys. (Kyoto) Suppl. 35, 1 (1966).
[3]N. G. van Kampen, Can. J. Phys. 39, 551 (1961).
[4]S. Chandrasekhar, Rev. Mod. Phys. 15, 1 (1943).
[5]C. M. Van Baal, Physica 111A, 233 (1982).
[6]R. Kikuchi, Phys. Rev. B 22, 3784 (1980).
[7]J. K. McCoy, R, Kikuchi, K. Gschwend, and H. Sato, Phys. Rev. B 25, 1734 (1982).
[8]K. Wada and T. Ishikawa (unpublished).