Journal of Statistical Physics, Vol. 53, Nos. 5/6, 1988

Reformulation of the Path Probability Method and Its Application to Crystal Growth Models

Koh Wada,[1] Makoto Kaburagi,[2] Takashi Uchida,[1] and Ryoichi Kikuchi[3]

Received February 23, 1988; revision received July 26, 1988

The microscopic master equation of a system is derived within the framework of the path probability method (PPM). Then, by extending Morita's method in equilibrium statistical mechanics, the path probability function constructed microscopically can be systematically decomposed to result in the conventional path probability function of cluster approximation when correlations larger than the chosen basic cluster are neglected. In order to critically compare the master equation method with the PPM, the triangle approximation is treated by both methods for crystal growth models. It is found that the PPM gives physically satisfactory kinetic equations, while the master equation (supplemented with a cluster probability in the superposition approximation) does not. The triangle PPM calculation considerably improves the result of the pair approximation for crystal growth velocity in the solid-on-solid model, and compares well with Monte Carlo results.

KEY WORDS: Path probability method; cluster variation method; master equation; crystal growth model; solid-on-solid model.

1. INTRODUCTION

The path probability method (PPM) devised by Kikuchi$^{(1)}$ is a natural extension of the cluster variation method (CVM)$^{(2)}$ in equilibrium statistical mechanics to nonequilibrium kinetics and has been applied successively to various phase transition and transport phenomena.$^{(3)}$ For the nonequilibrium kinetics the master equation has also been used. Starting with the microscopic master equation of the system, Van Baal$^{(4)}$

---

[1] Department of Physics, Faculty of Science, Hokkaido University, Sapporo 060, Japan.

[2] College of Liberal Arts, Kobe University, Tsurukabuto, Nada, Kobe 657, Japan.

[3] Department of Materials Science and Engineering, FB-10, University of Washington, Seattle, Washington 98195.

showed that a coarse-grained master equation of Markovian nature could be derived with the assumption that microscopically different configurations in the same class have the same energy and the same occurrence probability at any time. He applied the coarse-grained master equation in the pair approximation to some problems and found that the results were the same as those obtained from the pair approximation in the PPM. In order to determine the transition rate in the pair approximation he used the cluster probability of superposition approximation in the sense of the CVM. We call Van Baal's treatment, which is supplemented with the cluster probability in the superposition approximation, the master equation method (MEM), to distinguish it from the PPM, although the same fact was also noticed by other authors.(5) Recently we applied both the PPM and the MEM to an Ising ferromagnet in the triangle approximation.(6) To our surprise, the two methods lead to similar but different evolution equations, though they have the identical equilibrium state expected from the CVM as a stationary solution. The problem of why the two (i.e., the MEM and PPM) triangle approximations give different evolution equations (in contrast to the two pair approximations, which lead to an identical equation) and whether this fact is essential or not have been left unsolved.

In this paper we try to make clear the difference between the PPM and the MEM and show that the difference turns out to be significant in the crystal growth kinetics.(7) For that purpose the PPM is reformulated from the microscopic point of view. As a result, the relation between the PPM and the microscopic master equation, which is the starting point for the MEM, is established. Then the decomposed method of the space-time joint probability of the whole system is introduced along the same lines as that of Morita,(8) who decomposed the probability distribution of the whole system into the product of the cluster correlation functions in equilibrium statistical mechanics. It is shown that the neglect of cluster correlation functions larger than the chosen cluster leads to the conventional PPM(1) in the cluster approximation. This decomposition method is a kind of superposition approximation. It will be shown that a similar treatment is involved in the determination of the transition rate in the coarse-grained master equation in the MEM.

We apply both the PPM and the MEM to the monolayer and the solid-on-solid (SOS) model(9) in the triangle approximation. Only the PPM can give physically reasonable evolution equations. In the SOS model the present calculation improves the result of the pair approximation and the present result is in good quantitative agreement with that of the Monte Carlo simulation.

In Section 2 the PPM is reformulated for the comparison with the

MEM. In Section 3 the monolayer crystal growth model is studied in the triangle approximation. The advantage of the PPM over the MEM is discussed. In Section 4 the solid-on-solid model is treated as a direct application of Section 3. Section 5 is devoted to the conclusion and discussion.

2. THE STRUCTURE OF PATH PROBABILITY FUNCTION

First, the statistical mechanical formulation is reviewed from the viewpoint of general cluster approximation. For clarity we consider an Ising system of N spins and write its Hamiltonian $\mathscr{H}(\{\sigma\})$. Here $\{\sigma\}$ stands for one of 2^N configurations $(\sigma_1, \sigma_2,..., \sigma_N)$ with $\sigma_i = \pm 1$ $(i=1\text{–}N)$. Consider an ensemble of L equivalent systems, each system of which has $\mathscr{H}(\{\sigma\})$ in equilibrium with a heat bath of temperature T. Let $LP_1^{(N)}(\{\sigma\})$ be the number of systems having an N-spin configuration $\{\sigma\}$. Since the number of total systems in the ensemble is L, we obtain the relation $\mathrm{Tr}_{\{\sigma\}} P_1^{(N)}(\{\sigma\}) = 1$, where Tr denotes a summation over all spin states. The probability of the ensemble being found in the prescribed states $\{LP_1^{(N)}(\{\sigma\})\}$ is, except for a proportionality constant, given by

$$Z = \frac{L!}{\prod_{\{\sigma\}} (LP_1^{(N)}(\{\sigma\}))!} \prod_{\{\sigma\}} (e^{-\beta\mathscr{H}(\{\sigma\})})^{LP_1^{(N)}(\{\sigma\})} \tag{2.1}$$

Then the free energy per system is given by

$$F = -\frac{k_B T}{L} \ln Z = \sum_{\{\sigma\}} [\mathscr{H}(\{\sigma\}) + k_B T \ln P_1^{(N)}(\{\sigma\})] \, P_1^{(N)}(\{\sigma\}) \tag{2.2}$$

where $E = \sum_{\{\sigma\}} \mathscr{H}(\{\sigma\}) \, P_1^{(N)}(\{\sigma\})$ is the internal energy and

$$S = -k_B \sum_{\{\sigma\}} P_1^{(N)}(\{\sigma\}) \ln P_1^{(N)}(\{\sigma\}) \tag{2.3}$$

is the entropy of the system. The requirement of the maximization of Z or the minimization of F with respect to the $P_1^{(N)}(\{\sigma\})$ leads to the equilibrium distribution

$$P_1^{(N)}(\{\sigma\}) = e^{-\beta\mathscr{H}(\{\sigma\})} / \mathrm{Tr}\, e^{-\beta\mathscr{H}(\{\sigma\})}$$

with $\beta^{-1} = k_B T$. The above procedure can be seen as applying the CVM to the system choosing the system itself as the basic cluster.

Next, let us consider the change of state of the ensemble in a short time interval Δt, that is, from time t to $t + \Delta t$. For this purpose, besides the system number $LP_1^{(N)}(\{\sigma\}, t)$ taking a configuration $\{\sigma\}$ at t, we introduce

$LP_2^{(N)}(\{\sigma\}, t; \{\sigma'\}, t+\Delta t)$, which is defined as the number of systems having a configuration $\{\sigma\}$ at t and $\{\sigma'\}$ at $t+\Delta t$. From above definitions, $P_1^{(N)}(\{\sigma\}, t)$ denotes the one-time point probability function and $P_2^{(N)}(\{\sigma\}, t; \{\sigma'\}, t+\Delta t)$ the two-time point joint probability function, respectively. There are some obvious relations between them:

$$P_1^{(N)}(\{\sigma\}, t) = \operatorname*{Tr}_{\{\sigma'\}} P_2^{(N)}(\{\sigma\}, t; \{\sigma'\}, t+\Delta t) \tag{2.4a}$$

$$P_1^{(N)}(\{\sigma'\}, t+\Delta t) = \operatorname*{Tr}_{\{\sigma\}} P_2^{(N)}(\{\sigma\}, t; \{\sigma'\}, t+\Delta t) \tag{2.4b}$$

$$\operatorname*{Tr}_{\{\sigma\}} \operatorname*{Tr}_{\{\sigma'\}} P_2^{(N)}(\{\sigma\}, t; \{\sigma'\}, t+\Delta t) = 1 \tag{2.4c}$$

Hereafter we use the subscript 1 for the one-time point function and 2 for the two-time point function. Referring to Eq. (2.4a), when a state $\{LP_1^{(N)}(\{\sigma\}, t)\}$ the ensemble at t is given, we have the transition probability of the ensemble$^{(1)}$ in the time interval Δt:

$$T(t, t+\Delta t) = \frac{\prod_{\{\sigma\}} (LP_1^{(N)}(\{\sigma\}, t))!}{\prod_{\{\sigma\}} \prod_{\{\sigma'\}} [LP_2^{(N)}(\{\sigma\}, t; \{\sigma'\}, t+\Delta t)]!} \times \prod_{\{\sigma\}} \prod_{\{\sigma'\}} [W^{(N)}(\{\sigma\}, t \mid \{\sigma'\}, t+\Delta t)]^{LP_2^{(N)}(\{\sigma\}, t; \{\sigma'\}, t+\Delta t)} \tag{2.5}$$

where $W^{(N)}(\{\sigma\}, t \mid \{\sigma'\}, t+\Delta t)$ is the transition probability of one system changing from $\{\sigma\}$ at t into $\{\sigma'\}$ at $t+\Delta t$.

The logarithmic form of the above expression is very useful for later purposes:

$$\begin{aligned}
&\ln T(t, t+\Delta t)/L \\
&\quad = \operatorname*{Tr}_{\{\sigma\}} P_1^{(N)}(\{\sigma\}, t) \ln P_1^{(N)}(\{\sigma\}, t) \\
&\qquad + \operatorname*{Tr}_{\{\sigma\}} \operatorname*{Tr}_{\{\sigma'\}} \{\ln W^{(N)}(\{\sigma\}, t \mid \{\sigma'\}, t+\Delta t) \\
&\qquad - \ln P_2^{(N)}(\{\sigma\}, t; \{\sigma'\}, t+\Delta t)\} \, P_2^{(N)}(\{\sigma\}, t; \{\sigma'\}, t+\Delta t)
\end{aligned} \tag{2.6}$$

It is worthwhile to note that Eq. (2.6) is very similar in structure to the free energy expression (2.2). Thus, we may call

$$S_D(\Delta t) = -\operatorname*{Tr}_{\{\sigma\}} \operatorname*{Tr}_{\{\sigma'\}} P_2^{(N)}(\{\sigma\}, t; \{\sigma'\}, t+\Delta t) \ln P_2^{(N)}(\{\sigma\}, t; \{\sigma'\}, t+\Delta t) \tag{2.7}$$

the dynamical entropy, in contrast to (2.3), which may be referred to as the static entropy. When the two-time-point functions $P_2^{(N)}(\{\sigma\}, t; \{\sigma'\}, t+\Delta t)$ are varied starting with the given distribution $P_1^{(N)}(\{\sigma\}, t)$ at t, the maximization requirement of Eq. (2.5) gives the natural relation

$$\begin{aligned} &P_2^{(N)}(\{\sigma\}, t; \{\sigma'\}, t+\Delta t) \\ &\quad = W^{(N)}(\{\sigma\}, t \,|\, \{\sigma'\}, t+\Delta t)\, P_1^{(N)}(\{\sigma\}, t) \end{aligned} \tag{2.8}$$

which expresses the two-time point function in terms of the one-time point function and the transition probability. Since

$$\operatorname*{Tr}_{\{\sigma'\}} W^{(N)}(\{\sigma\}, t \,|\, \{\sigma'\}, t+\Delta t) = 1$$

the transition probability in a short time interval Δt can be written in terms of the transition rate $w^{(N)}(\{\sigma\} \to \{\sigma'\}, t)$ (the transition probability of the system per unit time) as follows:

$$\begin{aligned} &W^{(N)}(\{\sigma\}, t \,|\, \{\sigma'\}, t+\Delta t) \\ &\quad = w^{(N)}(\{\sigma\} \to \{\sigma'\}, t)\, \Delta t (1 - \delta_{\{\sigma\}, \{\sigma'\}}) \\ &\qquad + \left[1 - \sum_{\{\sigma''\}}{}' w^{(N)}(\{\sigma\} \to \{\sigma''\}, t)\, \Delta t \right] \delta_{\{\sigma\}, \{\sigma'\}} \end{aligned} \tag{2.9}$$

where $\delta_{\{\sigma\}, \{\sigma'\}}$ is the usual Kronecker delta symbol and $\sum'$ denotes a summation with $\{\sigma''\} = \{\sigma'\}$ excluded. Substituting Eq. (2.9) into Eq. (2.8) and summing over all the configurations at t, we have an evolution equation of the distribution function of the system in the limit $\Delta t \to 0$:

$$\begin{aligned} \frac{d}{dt} P_1^{(N)}(\{\sigma\}, t) = &- \operatorname*{Tr}_{\{\sigma'\}} w^{(N)}(\{\sigma\} \to \{\sigma'\}, t)\, P_1^{(N)}(\{\sigma\}, t) \\ &+ \operatorname*{Tr}_{\{\sigma'\}} w^{(N)}(\{\sigma'\} \to \{\sigma\}, t)\, P_1^{(N)}(\{\sigma'\}, t) \end{aligned} \tag{2.10}$$

Equation (2.10) is called a microscopic master equation of the system which denotes the conservation of probability of the system. Thus, we could say that Eq. (2.5) represents a variational function for the microscopic master equation. What is done above is to apply the path probability method (PPM) to a system with the system itself chosen as the basic cluster. A function such as Eq. (2.5) is called the path probability function (PPF) since variational parameters $P_2^{(N)}(\{\sigma\}, t; \{\sigma'\}, t+\Delta t)$ determine a path for the time evolution of the ensemble. Up to this point no approximation has been introduced in the free energy treatment or the master equation derivation. Therefore either the CVM or the PPM is not always an approximate method.

However, for practical analytical treatments it is necessary to introduce some approximations. In fact, the CVM and the PPM have been developed for systematic approximations. Generally speaking, the choice of the basic cluster determines the degree of approximation. In each choice, the most important step is how best to formulate approximately the entropy or the dynamical entropy. We can conveniently follow Morita's method, which was developed as an alternative formulation of the CVM.

In order to review his method, we define the one-time point probability for an n cluster of $(i_1, i_2,..., i_n)$ as

$$P_1^{(n)}(\{\sigma_i\}_n) = \operatorname*{Tr}_{\{\sigma\} - \{\sigma_i\}_n} P_1^{(N)}(\{\sigma\}) \qquad (n = 1, 2,..., N) \tag{2.11}$$

where $(i_1, i_2,..., i_n)$ denotes any n set of N lattice points, $\{\sigma_i\}_n$ the set of n spins $(\sigma_{i1}, \sigma_{i2},..., \sigma_{in})$, and $\mathrm{Tr}_{\{\sigma\} - \{\sigma_i\}_n}$ the trace over all N spins except for $\{\sigma_i\}_n$. It is clear that the cluster probability function satisfies an obvious recurrence relation

$$\begin{aligned} &P_1^{(n-1)}(\sigma_{i1},..., \sigma_{in-1}) \\ &\quad = \operatorname*{Tr}_{\sigma_{in}} P_1^{(n)}(\sigma_{i1},..., \sigma_{in}) \qquad (n = 2,..., N) \end{aligned} \tag{2.12}$$

Then Morita's procedure consists in writing $\ln P_1^{(n)}(\{\sigma_i\}_n, t)$ as

$$\begin{aligned} \ln P_1^{(n)}(\{\sigma\}_n) = {} & \sum_{i=1}^{n} \ln P_1^{(1)}(\sigma_i) + \sum_{i<j}^{n} \ln A^{(2)}(\sigma_i, \sigma_j) \\ & + \sum_{i<j<k}^{n} \ln A^{(3)}(\sigma_i, \sigma_j, \sigma_k) + \cdots \\ & + \ln A^{(n)}(\sigma_1,..., \sigma_n) \qquad (n = 2,..., N) \end{aligned} \tag{2.13}$$

where $\{\sigma\}_n \equiv (\sigma_1, \sigma_2,..., \sigma_n)$ of n spins is used instead of $\{\sigma_i\}_n$ without confusion and $A^{(n)}(\{\sigma\}_n)$ represents a correlation function of n spins. Equation (2.13) can be solved successively starting from $n = 2$ to yield

$$\begin{aligned} \ln A^{(2)}(\sigma_i, \sigma_j) &= \ln P_1^{(2)}(\sigma_i, \sigma_j) - \ln P_1^{(1)}(\sigma_i) - \ln P_1^{(1)}(\sigma_j) \\ \ln A^{(3)}(\sigma_i, \sigma_j, \sigma_k) &= \ln P_1^{(3)}(\sigma_i, \sigma_j, \sigma_k) - [\ln P_1^{(2)}(\sigma_i, \sigma_j) \\ &\quad + \ln P_1^{(2)}(\sigma_j, \sigma_k) + \ln P_1^{(2)}(\sigma_k, \sigma_i)] \\ &\quad + \ln P_1^{(1)}(\sigma_i) + \ln P_1^{(1)}(\sigma_j) + \ln P_1^{(1)}(\sigma_k) \\ &\quad \vdots \end{aligned} \tag{2.14}$$

The relations shown here between the P functions and the A functions are sometimes referred to as the cumulant tranform or the Möbius transform.[10] Let us define an n-cluster entropy by

$$S^{(n)}(i_1, i_2,..., i_n) = -\operatorname*{Tr}_{\{\sigma_i\}_n} P_1^{(n)}(\{\sigma_i\}_n) \ln P_1^{(n)}(\{\sigma_i\}_n) \tag{2.15}$$

It is clear from (2.14) that the cluster function

$$\gamma^{(n)}(i_1, i_2,..., i_n) = -\operatorname*{Tr}_{\{\sigma_i\}_n} P_1^{(n)}(\{\sigma_i\}_n) \ln A^{(n)}(\{\sigma_i\}_n) \tag{2.16}$$

is expressed as a linear combination of cluster entropies. From (2.13) and (2.16) the entropy of the whole system is thus written as

$$S/k_B = \sum_j \gamma^{(1)}(j) + \sum_{j<k} \gamma^{(2)}(j, k) + \cdots + \gamma^{(N)}(1, 2,..., N) \tag{2.17}$$

Thus, the entropy of the system can be expressed in terms of cluster entropies owing to (2.14). Morita's interpretation of the CVM is that the n-cluster approximation results when we choose $\gamma^{(m)}(j_1,..., j_m) \equiv 0$ for all m $(>n)$. For example, the point approximation stops at $\gamma^{(1)}(j)$, the pair at $\gamma^{(2)}(j, k)$, and so forth. Here one comment is in order. It is easy to express the internal energy using cluster probabilities.[8]

Up to this point we have discussed the one-time point probability and the statistical mechanical entropy. However, noting the structural similarity of the dynamical entropy in Eq. (2.7) to the static entropy, a completely similar treatment is also possible for the former. The two-time point probability for an n cluster of $(i_1, i_2,..., i_n)$ is defined by

$$\begin{aligned} &P_2^{(n)}(\{\sigma_i\}_n, t; \{\sigma'_i\}_n, t+\Delta t) \\ &\quad = \operatorname*{Tr}_{\{\sigma\}-\{\sigma_i\}_n} \operatorname*{Tr}_{\{\sigma'\}-\{\sigma'_i\}_n} P_2^{(N)}(\{\sigma\}, t; \{\sigma'\}, t+\Delta t) \end{aligned} \tag{2.18}$$

which has the recurrence relation

$$\begin{aligned} &P_2^{(n-1)}(\{\sigma_i\}_{n-1}, t; \{\sigma'_i\}_{n-1}, t+\Delta t) \\ &\quad = \operatorname*{Tr}_{\sigma_{i_n}} \operatorname*{Tr}_{\sigma'_{i_n}} P_2^{(n)}(\{\sigma_i\}_n, t; \{\sigma'_i\}_n, t+\Delta t) \end{aligned} \tag{2.19}$$

We assume a similar form of (2.13) for the two-time-point probability;

$$\begin{aligned} &\ln P_2^{(n)}(\{\sigma\}_n, t; \{\sigma'\}_n, t+\Delta t) \\ &\quad = \sum_{i=1}^{n} \ln P_2^{(1)}(\sigma_i; \sigma'_i) \\ &\qquad + \sum_{i<j}^{n} \ln B^{(2)}(\sigma_i, \sigma_j; \sigma'_i, \sigma'_j) \\ &\qquad + \sum_{i<j<k}^{n} \ln B^{(3)}(\sigma_i, \sigma_j, \sigma_k; \sigma'_i, \sigma'_j, \sigma'_k) + \cdots \\ &\qquad + \ln B^{(n)}(\{\sigma\}_n; \{\sigma'\}_n) \qquad (n = 2,..., N) \end{aligned} \tag{2.20}$$

where $\{\sigma\}_n = \{\sigma_1, \sigma_2,\ldots, \sigma_n\}$ is used for convenience. Making the Möbius transform as in (2.14), we can write $\ln B^{(n)}(\{\sigma\}_n; \{\sigma'\}_n)$ in terms of $\ln P_2^{(l)}(\{\sigma\}_l, t; \{\sigma'\}_l, t+\Delta t)$ $(l=1, 2,\ldots, n)$, successively. Defining an n-cluster dynamical entropy by

$$\begin{aligned} S_D^{(n)}&(i_1, i_2,\ldots, i_n, \Delta t)\\ &= -\operatorname*{Tr}_{\{\sigma_i\}_n} \operatorname*{Tr}_{\{\sigma_i'\}_n} P_2^{(n)}(\{\sigma_i\}_n, t; \{\sigma_i'\}_n, t+\Delta t)\\ &\quad\times \ln P_2^{(n)}(\{\sigma_i\}_n, t; \{\sigma_i'\}_n, t+\Delta t) \end{aligned} \tag{2.21}$$

and a cluster function corresponding to (2.16) by

$$\begin{aligned} \Gamma^{(n)}&(i_1, i_2,\ldots, i_n, \Delta t)\\ &= -\operatorname*{Tr}_{\{\sigma_i\}_n} \operatorname*{Tr}_{\{\sigma_i'\}_n} P_2^{(n)}(\{\sigma_i\}_n, t; \{\sigma_i'\}_n, t+\Delta t)\\ &\quad\times \ln B^{(n)}(\{\sigma\}_n; \{\sigma'\}_n) \end{aligned} \tag{2.22}$$

we can express the dynamical entropy of the system by

$$\begin{aligned} S_D(\Delta t) &= \sum_i \Gamma^{(1)}(i, \Delta t) + \sum_{i<j} \Gamma^{(2)}(i, j, \Delta t)\\ &\quad + \sum_{i<j<k} \Gamma^{(3)}(i, j, k, \Delta t) + \cdots + \Gamma^{(N)}(1, 2,\ldots, N, \Delta t) \end{aligned} \tag{2.23}$$

where some lower-order $\Gamma^{(n)}(\{i\}_n, \Delta t)$ are given explicitly by

$$\begin{aligned} \Gamma^{(1)}(i, \Delta t) &= S_D^{(1)}(i, \Delta t)\\ \Gamma^{(2)}(i, j, \Delta t) &= S_D^{(2)}(i, j, \Delta t) - S_D^{(1)}(i, \Delta t) - S_D^{(1)}(j, \Delta t)\\ \Gamma^{(3)}(i, j, k, \Delta t) &= S_D^{(3)}(i, j, k, \Delta t) - [S_D^{(2)}(i, j, \Delta t)\\ &\quad + S_D^{(2)}(j, k, \Delta t) + S_D^{(2)}(k, i, \Delta t)]\\ &\quad + [S_D^{(1)}(i, \Delta t) + S_D^{(1)}(j, \Delta t) + S_D^{(1)}(k, \Delta t)] \end{aligned} \tag{2.24}$$

In a similar way as before, the n-cluster approximation is obtained when we make $\Gamma^{(m)}(\{i\}_m, \Delta t) \equiv 0$ for all m $(>n)$.

In order to complete the path probability function of n-cluster approximation, we have to express $W^{(N)}(\{\sigma\}, t \mid \{\sigma'\}, t+\Delta t)$ in terms of cluster quantities so as to satisfy a detailed balance condition

$$\begin{aligned} P_e^{(N)}&(\{\sigma\})\, W^{(N)}(\{\sigma\}, t \mid \{\sigma'\}, t+\Delta t)\\ &= P_e^{(N)}(\{\sigma'\})\, W^{(N)}(\{\sigma'\}, t \mid \{\sigma\}, t+\Delta t) \end{aligned} \tag{2.25}$$

where $P_e^{(N)}(\{\sigma\})$ is the equilibrium distribution function. However, the detailed balance condition is not enough to determine the transition probability uniquely. The concrete form depends upon individual physical phenomena, as will be seen in Section 3.

At this point we make two comments for the purposes of later use. The first is the relation of this treatment with Kikuchi's original PPM. For the sake of concreteness let us consider a homogeneous Ising system on the two-dimensional hexagonal lattice in the triangle approximation. Then (2.17) and (2.23) give

$$\begin{aligned} S(t)/k_B &= N\gamma^{(1)}(1) + 3N\gamma^{(2)}(1,2) + 2N\gamma^{(3)}(1,2,3) \\ S_D(\Delta t) &= N\Gamma^{(1)}(1) + 3N\Gamma^{(2)}(1,2) + 2N\Gamma^{(3)}(1,2,3) \end{aligned} \tag{2.26}$$

where the point, the nearest neighbor pair, and the smallest triangle cluster are chosen for the formulation. With the use of Eq. (2.24) and definitions of static and dynamical cluster entropies, the path entropy part of (2.5) can be rewritten in this approximation as

$$\begin{aligned} T_s &\approx T_s^{(3)} \\ &= \left[\left(\frac{\{\text{bond}\}_{\Delta t}^3}{\{\text{triangle}\}_{\Delta t}^2, \{\text{point}\}_{\Delta t}} \right) \right. \\ &\quad \times \left. \left(\frac{\{\text{bond}\}_t^3}{\{\text{triangle}\}_t^2 \{\text{point}\}_t} \right)^{-1} \right]^N \end{aligned} \tag{2.27}$$

where

$$\begin{aligned} \{\text{point}\}_{\Delta t} &= \prod_{\sigma,\sigma'} [LP_2^{(1)}(\sigma, t; \sigma', t+\Delta t)]! \\ \{\text{bond}\}_{\Delta t} &= \prod_{\{\sigma\}_2,\{\sigma'\}_2} [LP_2^{(2)}(\{\sigma\}_2, t; \{\sigma'\}_2, t+\Delta t)]! \\ \{\text{triangle}\}_{\Delta t} &= \prod_{\{\sigma\}_3,\{\sigma'\}_3} [LP_2^{(3)}(\{\sigma\}_3, t; \{\sigma'\}_3, t+\Delta t)]! \end{aligned} \tag{2.28}$$

and $\{\cdots\}_t$ is the corresponding one-time-point probability; for instance,

$$\{\text{triangle}\}_t = \prod_{\{\sigma\}_3} [LP_1^{(3)}(\{\sigma\}_3, t)]!$$

The Stirling formula $\ln X! = X(\ln X - 1)$ is used for $X \gg 1$. We now observe that the right hand side of (2.27) is exactly the combinatorial factor derived in the original PPM.$^{(6)}$ Since Morita's method for the static case is known to be equivalent to Kikuchi's CVM, the above example shows that the present procedure for the path probability function gives, as expected, the same result as that of the original PPM.

The second comment we make is that the occurrence probability of a cluster with a center spin surrounded by the nearest neighbor spins can be evaluated by making use of Eqs. (2.13) and (2.14). Let σ_0 be a center spin and $(\sigma_1,..., \sigma_z)$ its nearest neighbors. Rewriting Eq. (2.13) in the form

$$\begin{aligned}\ln P_1^{(N)}(\{\sigma\}_N) = \ln P_1^{(1)}(\sigma_0) &+ \sum_{j=1}^{z} \ln A^{(2)}(\sigma_0, \sigma_j) \\ &+ \sum_{j<k}^{z} \ln A^{(3)}(\sigma_0, \sigma_j, \sigma_k) + \{\text{terms without } \sigma_0 \\ &+ O[\ln A^{(m)}(\{\sigma_i\}_m), m > 3]\}\end{aligned} \tag{2.29}$$

and discarding the last terms in curly brackets, we obtain the cluster probability in the triangle approximation[6,12]

$$P_1^{(z+1)}(\{\sigma\}_{z+1}) = P_1^{(1)}(\sigma_0) \prod_{i=1}^{z} \frac{P_1^{(3)}(\sigma_0, \sigma_i, \sigma_{i+1})}{P_1^{(2)}(\sigma_0, \sigma_i)} \qquad (\sigma_{z+1} = \sigma_1) \tag{2.30}$$

where $P_1^{(z+1)}(\{\sigma\}_{z+1})$ is written for $P_1^{(N)}(\{\sigma\}_N)$. This is interpreted as a superposition relation, and similar relations can be written for any approximation. Relations of this kind are needed in the MEM as the "closure" relation, as will be shown below.

It is worth noting that in the PPM all the ingredients of the approximation are contained in the path probability function at the beginning stage of the formulation. In the MEM, on the other hand, the "closure" relation, which is one of the essential ingredients of the method, comes not at the beginning, but somewhat later in the treatment. As was done by Van Baal and as is shown in (2.30), the needed relations can be supplied conveniently from approximation.

3. MONOLAYER ADSORPTION MODEL

Let us consider a two-dimensional hexagonal lattice on which the concentration of atoms changes through the adsorption of atoms from the vapor and the evaporations of solid atoms into the vapor phase.[7,13] The local concentration of solid atoms on the ith lattice site is defined by C_i, where $C_i = 1$ stands for an occupied site and $C_i = 0$ for a vacancy. The Hamiltonian is given by

$$H = -2J \sum_{\langle ij \rangle} C_i C_j - \Delta\mu_0 \sum_i C_i \tag{3.1}$$

where the first sum runs over nearest neighbor sites, and $\Delta\mu_0$ is the bare chemical potential difference between the solid and the vapor. With the help of the variable transformation $\sigma_i = 2C_i - 1$, the Hamiltonian is rewritten except for a constant $-N(zJ/4 + \Delta\mu_0/2)$ as

$$\mathscr{H}(\{\sigma\}) = -\frac{J}{2} \sum_{\langle ij \rangle} \sigma_i \sigma_j - \frac{1}{2} \Delta\mu \sum_i \sigma_i \tag{3.2}$$

where $z = 6$ is the coordination number and $\Delta\mu = \Delta\mu_0 + zJ$ is the net chemical potential. Now $\sigma_i = 1$ corresponds to an occupied site and $\sigma_i = -1$ to a vacancy. In the crystal growth model the adsorption is assumed to be determined by the net chemical potential difference $\Delta\mu$ and to be independent of the environment of the adsorbing site. On the other hand, the evaporation rate depends on the local configuration explicitly. When a spin σ_0 of the system changes its direction, the energy change is given by $\Delta E(\sigma_0) = J\sigma_0 \sum_{i=1}^{z} \sigma_i + \Delta\mu\sigma_0$, where σ_i $(i = 1\text{–}z)$ is the nearest-neighbor spin of σ_0. In order to meet the crystal growth model, the detailed balance condition requires transition rates for one spin flip:

$$\begin{aligned} w(-1 \to 1) &= \theta \exp H && \text{for adsorption} \\ w(1 \to -1) &= \theta \exp -K \sum_{i=1}^{z} \sigma_i && \text{for evaporation} \end{aligned} \tag{3.3}$$

where $H = \Delta\mu/kT$, $K = J/kT$, and $\tau_R \equiv 1/\theta$ is the microscopic characteristic time. It should be noted that in contrast with the relaxation process of magnetization, the transition rate has asymmetry forms for $\sigma_0 = \pm 1$. We apply the triangle approximation of the PPM to the above crystal growth model. Referring to Eq. (3.3), the kinetic part $T_k(t, t + \Delta t)$ of the path probability function is taken$^{(1)}$ as

$$[T_k(t, t + \Delta t)]^{1/L} = \prod_{\sigma} (\theta\, \Delta t)^{NP_2^{(1)}(\sigma; -\sigma)} [1 - \Theta(\sigma)\, \Delta t]^{NP_2^{(1)}(\sigma;\sigma)}\, e^{-\beta \Delta \bar{E}} \tag{3.4}$$

where

$$\beta\, \Delta \bar{E} = -NHP_2^{(1)}(-1; 1) + zKN[P_2^{(2)}(1, 1; -1, 1) - P_2^{(2)}(-1, 1; -1, -1)] \tag{3.5}$$

is the energy change of the system due to adsorption and evaporation and $1 - \Theta(\sigma)\, \Delta t$ is the residual probability, to be determined self-consistently. The path entropy part T_s was already given by (2.27). Thus, the path probability function is given by $T(t, t + \Delta t) = T_s T_k$ in the present approximation. Under the condition that the one-time point probabilities

$\{P_1^{(3)}(\{\sigma\}_3, t)\}$ are given, there are six independent two-time point probabilities. Maximization of the path probability function with respect to these independent probabilities determines two-time point probabilities in terms of the $P_1^{(3)}(\{\sigma\}, t)$ and given parameters in relations similar to Eq. (2.8). For example,

$$P_2^{(1)}(1, t; -1, t+\Delta t) = \theta\, \Delta t\, \lambda_+(1)^z P_1^{(1)}(1, t)$$

$$P_2^{(1)}(-1, t; 1, t+\Delta t) = \theta\, \Delta t\, e^H P_1^{(1)}(-1, t)$$

Here $\lambda_+(1)^z$ represents the environmental effect for evaporation, and the details will be discussed shortly. The probability for a site to remain unchanged is

$$P_2^{(1)}(\sigma, t; \sigma, t+\Delta t) = P_1^{(1)}(\sigma, t)[1 - \Theta(\sigma)\, \Delta t] \qquad \text{for} \quad \sigma = \pm 1$$

Combining these three equations, we obtain $\Theta(-1) = e^H$ and $\Theta(1) = \lambda_+(1)^z$.

Wada *et al.*[11] discussed the relaxation process of magnetization using the triangle approximation of the PPM. In the previous work, however, the Hamiltonian was written as

$$\mathscr{H} = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - \mu_0 H \sum_i \sigma_i - d \sum_{\langle ijk \rangle} \sigma_i \sigma_j \sigma_k \tag{3.6}$$

and the transition rate of a spin flip was chosen symmetrically. Here the three-body interaction of the smallest triangle cluster was used for the introduction of the conjugate field for the three-body correlation. With minor changes the results of ref. 11 can be applied to the present problem. The order parameters of the system are defined by

$$\begin{aligned} m_1(t) &= \operatorname*{Tr}_{\sigma_1} \sigma_1 P_1^{(1)}(\sigma_1, t) \\ m_2(t) &= \frac{z}{2} \operatorname*{Tr}_{\{\sigma\}_2} \sigma_1 \sigma_2 P_1^{(2)}(\{\sigma\}_2, t) \\ m_3(t) &= 2 \operatorname*{Tr}_{\{\sigma\}_3} \sigma_1 \sigma_2 \sigma_3 P_1^{(3)}(\{\sigma\}_3, t) \end{aligned} \tag{3.7}$$

The changes of the order parameters in Δt can be obtained by

$$\begin{aligned} \Delta m_1(t) &= -\operatorname*{Tr}_{\sigma} P_2^{(1)}(\sigma; -\sigma) \\ \Delta m_2(t) &= 2z \operatorname*{Tr}_{\sigma} [P_2^{(2)}(\sigma, \sigma; -\sigma, \sigma) - P_2^{(2)}(-\sigma, \sigma; \sigma, \sigma)] \\ \Delta m_3(t) &= -2z \operatorname*{Tr}_{\sigma} [P_2^{(3)}(\sigma, \sigma, \sigma; \sigma, \sigma, -\sigma) - 2P_2^{(3)}(\sigma, \sigma, -\sigma; \sigma, -\sigma, -\sigma) \\ &\quad + P_2^{(3)}(\sigma, -\sigma, -\sigma; -\sigma, -\sigma, -\sigma)] \end{aligned} \tag{3.8}$$

The most probable path results of the previous paper tell us the following. We define a moment-generating function

$$G(K_1(\sigma), K_2(\sigma), K_3(\sigma)) = \sum_{\sigma} \theta \hat{P}_1^{(1)}(\sigma)\, \lambda_+(\sigma)^z \tag{3.9}$$

where

$$\begin{aligned} \lambda_+(\sigma) &= \frac{1}{2}\left[\frac{\hat{P}_1^{(3)}(\sigma,\sigma,\sigma)}{\hat{P}_1^{(2)}(\sigma,\sigma)} + \frac{\hat{P}_1^{(3)}(\sigma,-\sigma,-\sigma)}{\hat{P}_1^{(2)}(\sigma,-\sigma)} + D(\sigma)\right] \\ D(\sigma)^2 &= \left[\frac{\hat{P}_1^{(3)}(\sigma,\sigma,\sigma)}{\hat{P}_1^{(2)}(\sigma,\sigma)} - \frac{\hat{P}_1^{(3)}(\sigma,-\sigma,-\sigma)}{\hat{P}_1^{(2)}(\sigma,-\sigma)}\right]^2 \\ &\quad + \frac{4\hat{P}_1^{(3)}(\sigma,\sigma,-\sigma)^2}{\hat{P}_1^{(2)}(\sigma,\sigma)\,\hat{P}_1^{(2)}(\sigma,-\sigma)} \end{aligned} \tag{3.10}$$

and

$$\begin{aligned} \hat{P}_1^{(1)}(\sigma) &= P_1^{(1)}(\sigma, t)\, e^{-K_1(\sigma)\sigma} \\ \hat{P}_1^{(2)}(\sigma, \sigma_1) &= P_1^{(2)}(\sigma, \sigma_1, t)\, e^{K_2(\sigma)\sigma\sigma_1} \\ \hat{P}_1^{(3)}(\sigma, \sigma_1, \sigma_2) &= P_1^{(3)}(\sigma, \sigma_1, \sigma_2)\, e^{-K_3(\sigma)\sigma\sigma_1\sigma_2} \end{aligned} \tag{3.11}$$

with $K_1(\pm) = \pm\mu_0 H/kT$, $K_2(\pm) = \pm J/kT$, and $K_3(\pm) = \pm d/kT$. Then we can obtain the evolution equations of order parameters as

$$\frac{dm_i(t)}{dt} = \sum_{\sigma=\pm 1} \frac{\partial}{\partial K_i(\sigma)} G(K_1(\sigma), K_2(\sigma), K_3(\sigma)) \qquad (i = 1, 2, 3) \tag{3.12}$$

Here one comment is in order. These rate equations can be obtained in two ways. First, after substituting $P_2^{(3)}(\{\sigma\}, t; \{\sigma'\}, t + \Delta t)$ obtained from the maximization of the path probability function into Eq. (3.8), we compare them with Eq. (3.12) directly. Another is the way in which we derive the master equation in the triangle approximation by making use of the path probability function.$^{(11)}$ The master equation is given by

$$\varepsilon \frac{\partial Q(\mathbf{m}, t)}{\partial t} = \sum_{\sigma=\pm 1} \left[\exp\left(-2\varepsilon \frac{\partial}{\partial \mathbf{m}} \cdot \frac{\partial}{\partial \mathbf{K}(\sigma)}\right) - 1\right] G(\mathbf{K}(\sigma))\, Q(\mathbf{m}, t) \tag{3.13}$$

where $\mathbf{m} = (m_1, m_2, m_3)$, $\mathbf{K}(\sigma) = (K_1(\sigma), K_2(\sigma), K_3(\sigma))$, $\varepsilon = 1/N$, and $Q(\mathbf{m}, t)$ is the probability density of $\mathbf{m}$ at t. Application of the system size expansion$^{(14)}$ to Eq. (3.13) yields Eq. (3.12).

Let us return to the monolayer model. Since there are only two parameters H and K in the present system, in order to use the above result it is taken that after differentiation in Eq. (3.12) the parameters $\{K_i(\sigma)\}$ are always taken to be

$$K_1(-1)=H, \qquad K_2(1)=K, \qquad K_1(1)=K_2(-1)=K_3(\pm 1)=0 \tag{3.13a}$$

The final kinetic equations are written explicitly as

$$\begin{aligned}
\frac{dm_1(t)}{dt} &= 2\theta[P_1^{(1)}(-1,t)\,e^H - P_1^{(1)}(1,t)\,\lambda_+(1)^z] \\
\frac{dm_2(t)}{dt} &= 2z\theta\Bigg[P_1^{(1)}(-1)\,e^H\,\frac{P_1^{(2)}(-1,1)-P_1^{(2)}(-1,-1)}{P_1^{(1)}(-1)} \\
&\quad - P_1^{(1)}(1)\,\lambda_+(1)^z \\
&\quad \times \frac{P_1^{(3)}(1,1,1)/\hat{P}^{(2)}(1,1)-P_1^{(3)}(1,-1,-1)/\hat{P}^{(2)}(1,-1)}{D(1)}\Bigg] \\
\frac{dm_3(t)}{dt} &= 2z\theta\Bigg[P_1^{(1)}(-1)\,e^H\left(1-\frac{4P_1^{(3)}(-1,-1,1)}{P_1^{(1)}(-1)}\right) \\
&\quad - P_1^{(1)}(1)\,\lambda_+(1)^z\left(1-4\,\frac{P_1^{(3)}(-1,1,1)^2}{P_1^{(2)}(1,1)\,P_1^{(2)}(1,-1)\,D(1)\,\lambda_+(1)}\right)\Bigg]
\end{aligned} \tag{3.14}$$

Let us examine the dm_1/dt equation. Since the concentration of atoms $P_1^{(1)}(1,t)$ is expressed by $P_1^{(1)}(1,t)=\frac{1}{2}[1+m_1(t)]$, the first term of the right-hand side shows the adsorption of atoms and the second term represents that the evaporation occurs with the environmental effect $\lambda_+(1)^z$ if the site is occupied. The important result is that the environmental effect for adsorption gives exactly $\lambda_+(-1)^z=1$, as is expected physically.

At this point we compare the above results obtained from the PPM with those from the coarse-grained master equation derived by Van Baal.(4,5) The coarse-grained master equation can be written as(6)

$$\begin{aligned}
\varepsilon\frac{d\bar{Q}(\mathbf{m},t)}{dt} &= -\mathrm{tr}[\bar{w}(\mathbf{m};\Delta\mathbf{M}(\sigma_0))\,\bar{Q}(\mathbf{m},t)] \\
&\quad + \mathrm{tr}[\bar{w}(\mathbf{m}-\varepsilon\,\Delta\mathbf{M}(\sigma_0);\Delta\mathbf{M}(\sigma_0))\,\bar{Q}(\mathbf{m},t)]
\end{aligned} \tag{3.15}$$

where $\bar{Q}(\mathbf{m},t)$ is the probability density of $\mathbf{m}$ at t and $\Delta\mathbf{M}(\sigma_0)$ denotes changes of $N\mathbf{m}$ when a spin σ_0 flips. The key question is how to determine the transition rate $\bar{w}(\mathbf{m};\Delta M(\sigma_0))$ in the triangle approximation. The most natural procedure is to take into account the probability of a center spin σ_0

surrounded by its nearest neighbors $(\sigma_1,\ldots,\sigma_z)$ and the transition rates (3.3). Thus, combining Eq. (2.30) and (3.3), we write $\bar{w}(\mathbf{m};\Delta\mathbf{M}(\sigma_0))$ as

$$\bar{w}(\mathbf{m};\Delta\mathbf{M}(\sigma_0))=\theta P_1^{(1)}(\sigma_0,t)\,e^{-K_1(\sigma_0)\,\sigma_0}$$
$$\times\prod_{i=1}^{z}\frac{P_1^{(3)}(\sigma_0,\sigma_i,\sigma_{i+1},t)\,e^{-K_3(\sigma_0)\,\sigma_0\sigma_i\sigma_{i+1}}}{P_1^{(2)}(\sigma_0,\sigma_i,t)\,e^{K_2(\sigma_0)\,\sigma_0\sigma_i}} \qquad (3.16)$$

where the same convention as stated in (3.13a) is used for the $K_i(\sigma_0)$. By using the ε expansion$^{(14)}$ to Eq. (3.15), one can derive the kinetic equations for the order parameters by

$$\frac{d\mathbf{m}(t)}{dt}=\operatorname{Tr}\Delta\mathbf{M}(\sigma_0)\,\bar{w}(\mathbf{m};\Delta\mathbf{M}(\sigma_0)) \qquad (3.17)$$

This equation can be rewritten as

$$\frac{dm_i(t)}{dt}=\sum_{\sigma_0}\frac{\partial}{\partial K_i(\sigma_0)}\,\bar{G}(K(\sigma_0)) \qquad (3.18)$$

where a moment-generating function $\bar{G}(K(\sigma_0))$ is defined by

$$\bar{G}(\mathbf{K}(\sigma_0))=\operatorname*{Tr}_{\sigma_1\sim\sigma_z}\ \bar{w}(\mathbf{m};\Delta M(\sigma_0)) \qquad (3.19)$$

By making use of the fact that $\bar{w}(\mathbf{m};\Delta\mathbf{M}(\sigma_0))$ is transformed as

$$w(\mathbf{m};\Delta\mathbf{M}(\sigma_0))=\theta\hat{P}_1^{(1)}(\sigma_0)\operatorname*{Tr}_{\sigma_1\sim\sigma_z}\ \hat{A}^{\sigma_0}(\sigma_1,\sigma_2)\,\hat{A}^{\sigma_0}(\sigma_2,\sigma_3)\cdots\hat{A}^{\sigma_0}(\sigma_z,\sigma_1) \qquad (3.20)$$

with

$$\hat{A}^{\sigma_0}(\sigma_i,\sigma_{i+1})=\hat{P}_1^{(3)}(\sigma_0,\sigma_i,\sigma_{i+1})/[\hat{P}_1^{(2)}(\sigma_0,\sigma_i)\,\hat{P}_1^{(2)}(\sigma_0,\sigma_{i+1})]^{1/2}$$

we can write $\bar{G}(\mathbf{K}(\sigma_0))$ in terms of two eigenvalues of $\{\hat{A}^{\sigma_0}(\sigma_i,\sigma_{i+1})\}$ as

$$\bar{G}(\mathbf{K}(\sigma_0))=\sum_{\sigma_0}\theta\hat{P}_1^{(1)}(\sigma_0)[\lambda_+(\sigma_0)^z+\lambda_-(\sigma_0)^z] \qquad (3.21)$$

where $\lambda_-(\sigma)=\lambda_+(\sigma)-D(\sigma)$ is the conjugate root of $\lambda_+(\sigma)$ appearing in (3.10). In comparison with (3.9), in addition to $\lambda_+(\sigma_0)^z$ there appears another term $\lambda_-(\sigma_0)^z$. While $\lambda_+(-1)=1$, $\lambda_-(-1)$ depends on the $P_1^{(3)}(\{\sigma\},t)$ explicitly. This fact means that in this treatment not only the evaporation of solid atoms, but also the adsorption process depends upon the environment in spite of the requirements that the adsorption is assumed to be determined only by the chemical potential difference. Thus, for the crystal growth kinetics only the PPM yields the correct kinetic equations. The reason for the failure of the MEM is judged to originate in the superposition approximation in (3.16) which is needed for the purpose of closure. The trouble is that there is no guiding principle for writing the closure relation.

4. SOLID-ON-SOLID MODEL

The previous results of the monolayer-adsorption model can be easily extended to the solid-on-solid (SOS) model,(9) which has been used as a multilayer model for crystal growth from the vapor. The present SOS model is defined as a hexagonal lattice which can be filled with atoms, but in such a way that in the upward direction from solid to vapor, normal to the hexagonal layer {001}, a solid atom can occupy only a site above and adjacent to an existing solid atom. This so-called SOS condition excludes vacant sites inside the solid part and overhangs at the solid–vapor interface. Let us divide the crystal into monatomic layers with N sites each, parallel to the hexagonal face, and assign a number l $(-\infty < l < \infty)$. The Hamiltonian is given by

$$H_{\mathrm{SOS}} = \sum_l \left(-2J \sum_{\langle ij \rangle} C_i^{(l)} C_j^{(l)} - \Delta\mu_0 \sum_i C_i^{(l)} \right) \tag{4.1}$$

where $C_i^{(l)} = 1$ $(=0)$ stands for the ith site on the lth layer being occupied (vacant). With $\sigma_i^{(l)} = 2C_i^{(l)} - 1$ and $z = 6$, the Hamiltonian is rewritten, except for a constant, as

$$\mathscr{H}_{\mathrm{SOS}}(\{\sigma^{(l)}\}) = \sum_l \left(-\frac{J}{2} \sum_{\langle ij \rangle} \sigma_i^{(l)} \sigma_j^{(l)} - \frac{1}{2} \Delta\mu \sum_i \sigma_i^{(l)} \right) \tag{4.2}$$

We apply the PPM to the SOS model in the triangle approximation. We could repeat the PPM calculation of Section 3 in each layer, attaching an additional superscript of the layer number to all the one- and two-time probabilities such as $P_1^{(1l)}(\sigma^{(l)}, t)$ and $P_2^{(1l)}(\sigma^{(l)}, t; \sigma^{(l)}, t+\Delta t)$ $(l = -\infty$ to $\infty)$. With the definition that $N\rho_l(t) = NP_1^{(1l)}(1, t) - NP_1^{(1l+1)}(1, t)$ is the number of surface atoms finding themselves in the lth layer, the SOS condition is taken into account in the path entropy as

$$\begin{aligned}
[T_c(t, t+\Delta t)]^{1/L} = \prod_{l=-\infty}^{\infty} & \frac{[N\rho^{(l)}(t)]!}{[NP_2^{(1l)}(1; -1)]!\,[NP_2^{(1l+1)}(-1; 1)]!} \\
& \times \frac{1}{[N\rho^{(l)}(t) - NP_2^{(1l)}(1; -1) - NP_2^{(1l+1)}(-1; 1)]!} \\
& \times \left[\prod_\sigma \frac{[NP_1^{(1l)}(\sigma)]!}{[NP_2^{(1l)}(\sigma; \sigma)]!\,[NP_2^{(1l)}(\sigma; -\sigma)]!} \right]^{-1}
\end{aligned} \tag{4.3}$$

where the time parameter t is suppressed since no confusion is expected. The path entropy correction T_c represents the fact that only surface atoms out of lth layer atoms can take part in evaporation and adsorption processes. Then the path probability function of the present system is given by the products of those of all the layers given in Section 3 times $T_c(t, t+\Delta t)$. The maximization with respect to independent two-time point functions yields the evolution equation of the system. The moment-generating function in the lth layer is then given by

$$\begin{aligned} G^{(l)}(K^{(l)}(\sigma)) = {} & \theta_R \rho_{l-1}(t)\{\exp[K_1^{(l)}(-1)]\}\, \lambda_+^{(l)}(-1)^z \\ & + \theta_R \rho_l(t)\{\exp[-K_1^{(l)}(1)]\}\, \lambda_+^{(l)}(+1)^z \end{aligned} \tag{4.4}$$

where the convention concerning the $K_i^{(l)}(\sigma)$ is also used. This function should be compared with the monolayer generating function (3.9). That is, the lth layer superscript is attached to all the quantities and $P_1^{(1l)}(-1, t)$ and $P_1^{(1l)}(1, t)$ are replaced by the fraction of surface atoms $\rho_{l-1}(t)$ and $\rho_l(t)$, respectively. With the use of this generating function, we have the following set of equations for crystal growth:

$$\begin{aligned} \frac{dm_1^{(l)}(t)}{dt_R} = {} & 2\theta_R[\rho_{l-1}(t)\, e^H - \rho_l(t)\, \lambda_+^{(l)}(1)^z] \\ \frac{dm_2^{(l)}(t)}{dt_R} = {} & z\theta_R\left[\rho_{l-1}(t)\, e^H\, \frac{P_1^{(2l)}(-1, 1) - P_1^{(2l)}(-1, -1)}{P_1^{(1l)}(-1)}\right. \\ & - \rho_l(t)\, \lambda_+^{(l)}(1)^z \left(\frac{P_1^{(3l)}(1, 1, 1)\, e^{-K}}{P_1^{(2l)}(1, 1)} - \frac{P_1^{(3l)}(1, 1, -1)\, e^{K}}{P_1^{(2l)}(1, -1)}\right) \\ & \left.\times\; [D^{(l)}(1)]^{-1}\right] \\ \frac{dm_3^{(l)}(t)}{dt_R} = {} & 2z\theta_R\left[\rho_{l-1}(t)\, e^H\left(1 - \frac{4P_1^{(3l)}(-1, -1, 1)}{P_1^{(1l)}(-1)}\right)\right. \\ & - \rho_l(t)\, \lambda_+^{(l)}(1)^z \\ & \left.\times\left(1 - 4\, \frac{P_1^{(3l)}(1, 1, -1)^2}{P_1^{(2l)}(1, 1)\, P_1^{(2l)}(1, -1)\, D^{(l)}(1)\, \lambda_+^{(l)}(1)}\right)\right], \qquad -\infty < l < \infty \end{aligned} \tag{4.5}$$

where the subscript R for time t is introduced for a relaxation process. With the help of the CVM we have the following free energy F corresponding to these rate equations:

$$\begin{aligned} F/NkT = {} & \sum_l \,[zKP_1^{(2l)}(1, -1) - HP_1^{(1l)}(1) + \mathscr{L}(\rho_l) \\ & - 3 \operatorname*{Tr}_{\{\sigma\}} \mathscr{L}(P_1^{(2l)}(\{\sigma\})) + 2 \operatorname*{Tr}_{\{\sigma\}} \mathscr{L}(P_1^{(3l)}(\{\sigma\}))] \end{aligned} \tag{4.6}$$

where $\mathscr{L}(x) = x(\ln x - 1)$. It can be confirmed that the configuration of the minimum free energy satisfies the steady-state condition of Eq. (4.5). Further, it is possible to take care of inter- and intralayer diffusion processes if the adsorption force e^H due to the chemical potential difference is replaced just by

$$e^{H_0} = \sum_{l=-\infty}^{\infty} \rho_l(t)[\lambda_+^{(l)}(1)]^z \tag{4.7}$$

and θ_R by θ_D in the kinetic equations (4.5).(15) This means that atoms evaporated from different layers can contribute to the adsorption. It should be noticed that though this exchange process does not change the total concentration $\sum_l P_1^{(1l)}(1, t)$, it increases the growth velocity of the crystal.

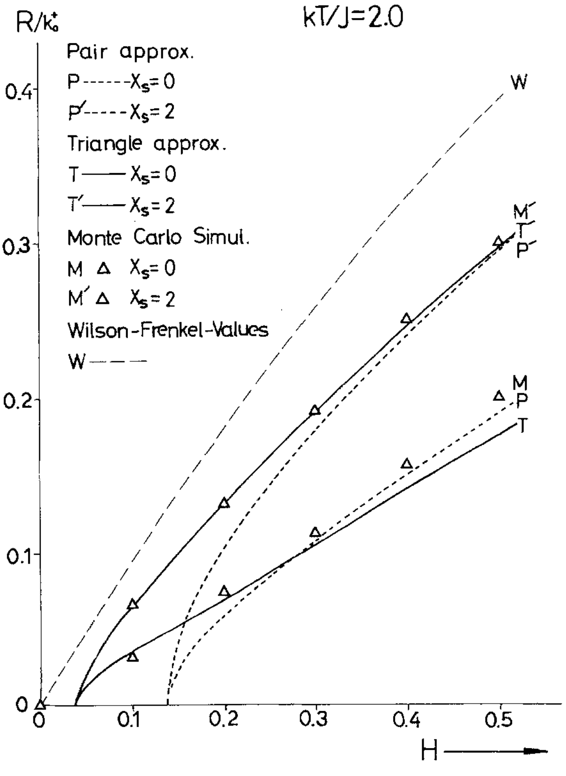

Fig. 1. The average growth rate R versus driving force H at temperature $kT/J = 2.0$ for the SOS model. The results of the triangle approximation (T) with and without diffusion are shown along with those of the pair approximation (P) and Monte Carlo simulation (M).

The growth rate of the crystal is defined as the combined processes of relaxation and diffusion:

$$R = \frac{d}{dt} \sum_{l=-\infty}^{\infty} P_1^{(1l)}(1, t) \tag{4.8}$$

where $d/dt = d/dt_R + d/dt_D$ and d/dt_D denotes the contribution from the diffusion process. The Wilson–Frenkel growth rate representing the maximum growth rate is defined by

$$R_{\mathrm{WF}} = k_0^+(1 - e^{-H}) \qquad (k_0^+ = \theta_R e^H) \tag{4.9}$$

The diffusion length X_S is defined as $X_S^2 \equiv z\theta_D/\theta_R$ since an isolated atom diffuses a distance X_S in its lifetime $1/\theta_R$. The results in the present approximation are shown for two typical temperatures together with those of the pair approximation and the Monte Carlo simulation in Fig. 1 and 2.[15] The Monte Carlo simulation on the present model is carried out

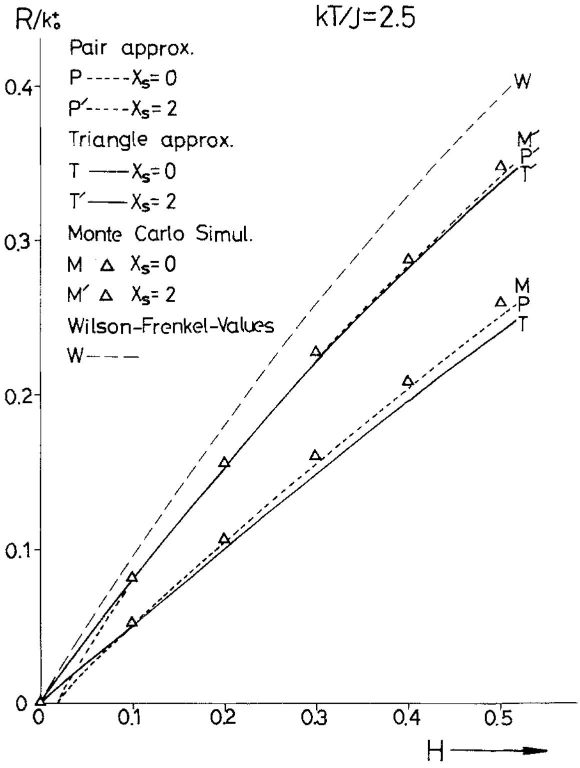

Fig. 2. The average growth rate R versus driving force H for temperature $kT/J = 2.5$ for the SOS model. Only the temperature is changed from the $kT/J = 2.0$ in Fig. 1 to the value of 2.5 here.

by using the method of Gilmer and Bennema.(16) For low temperatures and weak driving forces the growth rate in the present calculation is improved considerably compared with that of the pair approximation.

5. CONCLUSIONS AND DISCUSSION

We have shown that when we apply the PPM to the model system choosing the whole system itself as the basic cluster, we can obtain the microscopic master equation of the system as a result of the extremum principle. Thus, the PPM also gives a variational principle for the microscopic master equation. Since the microscopic master equation is the starting point of the coarse-grained master equation derived by Van Baal, the common basis for his approach and ours is thus established. In order to compare the PPM and the coarse-grained master equation method (MEM), we follow the technique which Morita developed when he decomposed the distribution function of the whole system in his reformulation of the CVM. In the decomposition scheme, to neglect correlations of clusters larger than a chosen basic cluster exactly corresponds to the coarse graining of information in the MEM and leads to the path probability function usually obtained by the conventional combinatorial arguments. In other words, the path probability function thus obtained is the one derived by the PPM using the chosen basic cluster. The above decomposition scheme seems to be a kind of superposition approximation. Since in the MEM there is no systematic guiding principle to determine the transition rate for any degree of approximation, a similar superposition approximation is adopted by Van Baal and by us for the occurrence probability of clusters. However, in the MEM the superposition approximation is used in a local sense, while in the PPM that approximation is used for the whole system and the variational principle should also be supplemented. This difference reveals itself in the triangle approximation. This is related to the following fact. Consider the cluster occurrence probability of a center spin σ_0 surrounded by its z nearest neighbor spins. With the use of the local superposition approximation the trace procedure over the nearest neighbor spins gives the correct center spin probability $P_1^{(1)}(\sigma_0)$ in the point and the pair approximation but not in the higher-order cluster approximations such as triangle approximation. On the other hand, the PPM seems to guarantee this correct center spin probability in any degree of approximation. This explains the fact that the PPM and the MEM lead to identical results only in the point and the pair approximations. We applied both methods in the triangle approximations to the crystal growth from the vapor phase on the monolayer model, where the adsorption is assumed to be determined only by the chemical potential difference $\Delta\mu$ but the evaporation rate depends on the local configuration explicitly. For the reason discussed above, in the triangle approximation only the PPM can give the evolution equations consistent with the physical situation. The same problem appears on the solid-on-solid crystal growth model, in which only the surface atoms of the solid part could take part in the growth kinetics. Thus, we conclude that the PPM is a justifiable method to give evolution equations of the system in the cluster approximation, while the MEM supplemented with a cluster probability of superposition approximation leads to an unphysical consequence in the triangle approximation unless the closure relation can be improved in the future.

Finally, in the SOS crystal model our treatment in the pair approximation reduces to that of the MEM by Saito and Müller-Krumbhaar.(7) Compared with their results, the present calculation in the triangle approximation considerably improved the unphysical metastable region at low temperatures for small driving force $\Delta\mu/kT$ and the present result is in good quantitative agreement with that of the Monte Carlo simulation.

ACKNOWLEDGMENTS

We thank Profs. H. Sato and T. Ishikawa for continual discussions. One of the authors (K. W.) thanks H. Tsuchinaga for cooperative work on the SOS calculation and also Prof. T. Asahi and his laboratory members for encouraging discussions.

REFERENCES

1. R. Kikuchi, *Ann. Phys.* **10**:127 (1960); *Phys. Rev.* **124**:1682, 1691 (1961); *Prog. Theor. Phys.* (Kyoto) *Suppl.* **35**:1 (1966).
2. R. Kikuchi, *Phys. Rev.* **81**:988 (1951).
3. A. Suzuki, H. Sato, and R. Kikuchi, *Phys. Rev. B* **29**:3550 (1984); Y. Ozeki and T. Ishikawa, *J. Phys. Soc. Japan* **55**:3931 (1986); T. Ishii, H. Sato, and R. Kikuchi, *Phys. Rev. B* **34**:8335 (1986).
4. C. M. Van Baal, *Physica* **111A**:591 (1982); **129A**:601 (1985).
5. Y. Saito and R. Kubo, *J. Stat. Phys.* **15**:233 (1976).
6. T. Ishikawa, K. Wada, H. Sato, and R. Kikuchi, *Phys. Rev. A* **33**:4164 (1986); K. Wada, T. Ishikawa, H. Sato, and R. Kikuchi, *Phys. Rev. A* **33**:4171 (1986).
7. Y. Saito and H. Müller-Krumbhaar, *J. Chem. Phys.* **70**:1079 (1979).
8. T. Morita, *J. Phys. Soc. Japan* **12**:753; *J. Math. Phys.* **13**:115 (1972).
9. D. E. Temkin, *Sov. Phys. Crystallogr.* **14**:344 (1969).
10. A. J. Schlijper, *Phys. Rev. B* **27**:6841 (1983); G. An, private communication (1988).
11. K. Wada, T. Ishikawa, and H. Tsuchinaga, *Physica* **142A**:38 (1987).
12. R. Kikuchi, *Phys. Rev. B* **22**:3784 (1980).
13. R. Kikuchi, *J. Chem. Phys.* **41**:1653 (1967).
14. N. G. van Kampen, *Can. J. Phys.* **39**:551 (1961).
15. K. Wada, H. Tsuchinaga, and T. Uchida, in *Proceedings of "Dynamics of Ordering Processes in Condensed Matter,"* Kyoto, Japan (1987), to be published.
16. G. H. Gilmer and P. Bennema, *J. Appl. Phys.* **43**:1347 (1972).