

## On the Kinetic Equations for Binary Mixtures<sup>\*</sup>

Kazuo KITAHARA and Masatoshi IMADA

*Department of Physics, University of Tokyo, Tokyo 113*

We examined master equations for diffusion processes and propose that the transition probability is proportional to the number of particles of diffusing species, multiplied by the factor  $\exp[-\{E(f) - E(i)\}/2k_B T]$ , which describes the ease of the transition as a function of the energy difference between the final and the initial states. In the case of a binary mixture, the resulting kinetic equation becomes

$$\frac{\partial \rho}{\partial t} = D_0 \nabla \rho (\rho_0 - \rho) \nabla \frac{\delta F}{\delta \rho},$$

where  $\rho$  is the local density of a component,  $\rho_0$  is the total density and  $F$  is the free energy functional. Due to the factor  $\rho (\rho_0 - \rho)$ , there is a situation in which the phase separation rate slows down at later stage of a deep quenching case. On the other hand, in the neighborhood of the critical point, this factor can be replaced by a constant.

### § 1. Introduction

Here in this paper, we want to make a comment on the dynamical description of the concentration profile in a binary mixture. In the theory of spinodal decomposition, a kinetic equation due to Cahn,<sup>1)</sup>

$$\frac{\partial \rho}{\partial t} = D \nabla^2 \frac{\delta F}{\delta \rho} \quad (1.1)$$

has been used. This equation is derived<sup>2)</sup> from a more fundamental master equation for the probability  $P(\{\mathbf{n}\}, t)$  of numbers of particles  $\{\mathbf{n}\} = (n_1, n_2, \dots)$  in cells in the system,

$$\begin{aligned} \frac{\partial}{\partial t} P(\{\mathbf{n}\}, t) = & - \sum_{\mu, \nu, \Delta} W_{\mu\nu}(\{\mathbf{n}\} \rightarrow \{\mathbf{n}\}', n_\mu - \Delta, n_\nu + \Delta) P(\{\mathbf{n}\}, t) \\ & + \sum_{\mu, \nu, \Delta} W_{\mu\nu}(\{\mathbf{n}\}', n_\mu + \Delta, n_\nu - \Delta \rightarrow \{\mathbf{n}\}) \\ & \times P(\{\mathbf{n}\}', n_\mu + \Delta, n_\nu - \Delta, t), \end{aligned} \quad (1.2)$$

where the transition probability is the function of the free energy difference,

<sup>\*</sup> This work is financially supported by the grant from the Ministry of Education and by Sakakoi Foundation.

$$\begin{aligned}
 & W_{\mu\nu}(\{\mathbf{n}\} \rightarrow \{\mathbf{n}'\}, n_\mu - \Delta, n_\nu + \Delta) \\
 &= \frac{1}{\tau} \exp(-\Delta^2/2\Gamma) \exp\left[-\frac{1}{2k_B T} \{F(\{\mathbf{n}'\}, n_\mu - \Delta, n_\nu + \Delta) - F(\{\mathbf{n}\})\}\right].
 \end{aligned}
 \tag{1.3}$$

Equation (1.2) was derived by coarse-graining a more microscopic master equation, which describes each atomic exchange process.<sup>2),3)</sup>

In this paper, we show that another form of coarse-grained master equation is possible and it gives a different kinetic equation

$$\frac{\partial \rho}{\partial t} = D_0 \nabla \rho (\rho_0 - \rho) \nabla \frac{\delta F}{\delta \rho},
 \tag{1.4}$$

where  $\rho$  is the local density of a species and  $\rho_0 - \rho$  is that of the other species. This kinetic equation gives a correct diffusion equation for the dilute limit  $\rho \ll \rho_0$ . In fact, the local chemical potential in such a case is  $\mu = (\delta F / \delta \rho) = k_B T \ln \rho$  and, using  $\rho(\rho_0 - \rho) \simeq \rho_0 \rho$ , we obtain the usual diffusion equation,

$$\frac{\partial \rho}{\partial t} = D_0 \rho_0 \nabla^2 \rho.
 \tag{1.5}$$

In § 2, we will give a derivation of a new coarse-grained master equation. Main idea is borrowed from recent stochastic studies on chemical reaction-diffusion systems.<sup>4)</sup> In those studies, it has usually been assumed that the transition probability for a particle to jump from one cell to another cell in such a system is proportional to the number of particles in the initial cell, because each particle in a cell has the same possibility of jumping from one cell to another. Generalizing this to the case of mutually interacting particles, we may just multiply the transition probability by a factor which depends on the interaction energies of the final and the initial states.

In § 3, we derive the kinetic equation (1.4) for the average density profile. We make a preliminary numerical comparison on the two kinetic equations (1.1) and (1.4). It turns out that both equations give, even quantitatively, the same evolution of the density profile except at later stage in a deep quenching case.

In § 4, we discuss the nature of fluctuations briefly. We show that the random noise is now a state-dependent quantity.

## § 2. Coarse-grained master equation

We start from a microscopic master equation for a system of particles at lattice sites. Suppose  $n_i$  is the number of particles of a species, say species  $A$ , at the  $i$ -th lattice site;  $n_i = 1$  or  $0$ , according to whether the  $i$ -th site is occupied by an  $A$ -particle or a  $B$ -particle. Thus a configuration of the whole

system is defined by a set of those occupation number  $\{\mathbf{n}\} = (n_1, n_2, \dots)$ . The probability distribution  $P(\{\mathbf{n}\}, t)$  is supposed to be driven by the Markoffian master equation,

$$\begin{aligned} \frac{\partial}{\partial t} P(\{\mathbf{n}\}, t) = & - \sum_{ij} W_{ij}(\{\mathbf{n}\} \rightarrow \{\mathbf{n}\}', n_i-1, n_j+1) P(\{\mathbf{n}\}, t) \\ & + \sum_{ij} W_{ij}(\{\mathbf{n}\}', n_i+1, n_j-1 \rightarrow \{\mathbf{n}\}) \\ & \times P(\{\mathbf{n}\}', n_i+1, n_j-1, t). \end{aligned} \quad (2.1)$$

The transition probability  $W_{ij}(\{\mathbf{n}\} \rightarrow \{\mathbf{n}\}')$  is defined for  $n_i=1$  or  $0$ ,  $n_i'=1$  or  $0$ , otherwise it vanishes by definition. Usually it is assumed that it is a function of the energy difference between the final and the initial states, such as

$$\begin{aligned} W_{ij}(\{\mathbf{n}\} \rightarrow \{\mathbf{n}\}', n_i-1, n_j+1) \\ = \frac{1}{\tau} \exp \left[ - \frac{1}{2k_B T} \{E(\{\mathbf{n}\}', n_i-1, n_j+1) - E(\{\mathbf{n}\})\} \right], \end{aligned} \quad (2.2)$$

which assures the detailed balance at equilibrium.

We now define the coarse-grained probability which is a function of numbers of particles at local cells,

$$P(\{\mathbf{N}\}, t) = \sum_{\{\mathbf{n}\}} \prod_{\mu} \delta(N_{\mu} - \sum_{i \in \mu} n_i) P(\{\mathbf{n}\}, t), \quad (2.3)$$

where we denote by  $N_{\mu}$  the number of particles in the  $\mu$ -th cell and  $\sum_{i \in \mu}$  denotes the summation over lattice sites in the  $\mu$ -th cell. Putting this into Eq.(2.1), we may formally write

$$\begin{aligned} \frac{\partial}{\partial t} P(\{\mathbf{N}\}, t) \\ = - \frac{\sum_{\lambda, \nu} \sum_{i \in \lambda, j \in \nu} \sum_{\{\mathbf{n}\}} \prod_{\mu} \delta(N_{\mu} - \sum_{k \in \mu} n_k) W_{ij}(\{\mathbf{n}\} \rightarrow \{\mathbf{n}\}', n_i-1, n_j+1) P(\{\mathbf{n}\}, t)}{\sum_{\{\mathbf{n}\}} \prod_{\mu} \delta(N_{\mu} - \sum_{k \in \mu} n_k) P(\{\mathbf{n}\}, t)} \\ \times P(\{\mathbf{N}\}, t) \\ + \sum_{\lambda, \nu} \sum_{i \in \lambda, j \in \nu} \\ \times \frac{\sum_{\{\mathbf{n}\}} \prod_{\mu} \delta(N_{\mu} - \sum_{k \in \mu} n_k) W_{ij}(\{\mathbf{n}\}', n_i+1, n_j-1 \rightarrow \{\mathbf{n}\}) P(\{\mathbf{n}\}', n_i+1, n_j-1, t)}{\sum_{\{\mathbf{n}\}} \prod_{\mu} \delta(N_{\mu} - \sum_{k \in \mu} n_k) P(\{\mathbf{n}\}', n_i+1, n_j-1, t)} \\ \times P(\{\mathbf{N}\}', N_{\lambda}+1, N_{\nu}-1, t). \end{aligned} \quad (2.4)$$

The approximation we make is that

$$\begin{aligned} \sum_{i \in \lambda, j \in \nu} \prod_{\mu} \delta(N_{\mu} - \sum_{k \in \mu} n_k) W_{ij}(\{\mathbf{n}\} \rightarrow \{\mathbf{n}\}', n_i-1, n_j+1) \\ \simeq \sum_{i \in \lambda, j \in \nu} \prod_{\mu} \delta(N_{\mu} - \sum_{k \in \mu} n_k) W_{\lambda\nu}(\{\mathbf{N}\} \rightarrow \{\mathbf{N}\}', N_{\lambda}-1, N_{\nu}+1), \end{aligned} \quad (2.5)$$

where

$$W_{\lambda\nu}(\{\mathbf{N}\} \rightarrow \{\mathbf{N}'\}, N_\lambda - 1, N_\nu + 1) = \frac{1}{\tau} \exp\left[-\frac{1}{2k_B T} \{E(\{\mathbf{N}'\}, N_\lambda - 1, N_\nu + 1) - E(\{\mathbf{N}\})\}\right], \quad (2.6)$$

that is, the energy difference in the transition probability  $W_{ij}(\{\mathbf{n}\} \rightarrow \{\mathbf{n}'\}, n_i - 1, n_j + 1)$  is not so sensitive to the microscopic configuration  $\{\mathbf{n}\}$ , but rather dependent on the coarse-grained configuration  $\{\mathbf{N}\}$ . The summation on the r.h.s. of Eq. (2.5) is replaced by  $N_\lambda(N - N_\nu)$ , where  $N$  is the total number of particles in a cell. Thus, we obtain the following equation for the coarse-grained probability,

$$\begin{aligned} \frac{\partial}{\partial t} P(\{\mathbf{N}\}, t) = & - \sum_{\lambda\nu} N_\lambda(N - N_\nu) W(\{\mathbf{N}\} \rightarrow \{\mathbf{N}'\}, N_\lambda - 1, N_\nu + 1) P(\{\mathbf{N}\}, t) \\ & + \sum_{\lambda\nu} (N_\lambda + 1)(N - N_\nu + 1) W(\{\mathbf{N}'\}, N_\lambda + 1, N_\nu - 1 \rightarrow \{\mathbf{N}\}) \\ & \times P(\{\mathbf{N}'\}, N_\lambda + 1, N_\nu - 1, t). \end{aligned} \quad (2.7)$$

### § 3. The kinetic equation

From the master equation (2.7), we may derive the kinetic equation for the average density profile on the assumption that the fluctuation is small. Standard procedure<sup>5)</sup> is as follows: We make the Kramers-Moyal expansion of the master equation,

$$\begin{aligned} \frac{\partial}{\partial t} P(\{\mathbf{N}\}, t) = & \sum_{\lambda\nu} (e^{(\partial/\partial N_\lambda) - (\partial/\partial N_\nu)} - 1) N_\lambda(N - N_\nu) \\ & \times W_{\lambda\nu}(\{\mathbf{N}\} \rightarrow \{\mathbf{N}'\}, N_\lambda - 1, N_\nu + 1) P(\{\mathbf{N}\}, t) \\ = & - \sum_\lambda \frac{\partial}{\partial N_\lambda} \sum_\nu \{N_\nu(N - N_\lambda) W_{\nu\lambda}(\{\mathbf{N}\} \rightarrow \{\mathbf{N}'\}, N_\lambda - 1, N_\nu + 1) \\ & - N_\lambda(N - N_\nu) W_{\lambda\nu}(\{\mathbf{N}\} \rightarrow \{\mathbf{N}'\}, N_\lambda + 1, N_\nu - 1)\} P(\{\mathbf{N}\}, t) \\ & + \frac{1}{2} \sum_\lambda \left(\frac{\partial}{\partial N_\lambda}\right)^2 \sum_\nu \{N_\nu(N - N_\lambda) \\ & \times W_{\nu\lambda}(\{\mathbf{N}\} \rightarrow \{\mathbf{N}'\}, N_\lambda - 1, N_\nu + 1) + N_\lambda(N - N_\nu) \\ & \times W_{\lambda\nu}(\{\mathbf{N}\} \rightarrow \{\mathbf{N}'\}, N_\lambda + 1, N_\nu - 1)\} P(\{\mathbf{N}\}, t) \\ & - \frac{1}{2} \sum_{\lambda\nu} \frac{\partial^2}{\partial N_\lambda \partial N_\nu} \{N_\nu(N - N_\lambda) \\ & \times W_{\nu\lambda}(\{\mathbf{N}\} \rightarrow \{\mathbf{N}'\}, N_\lambda - 1, N_\nu + 1) + N_\lambda(N - N_\nu) \\ & \times W_{\lambda\nu}(\{\mathbf{N}\} \rightarrow \{\mathbf{N}'\}, N_\lambda + 1, N_\nu - 1)\} P(\{\mathbf{N}\}, t) \\ & + \dots \end{aligned} \quad (3.1)$$

In the small fluctuation limit, the kinetic equation for the most probable density profile is given by the first moment of the transition probability,

$$\begin{aligned} \frac{d}{dt} N_\lambda = \sum_\nu \{ & N_\nu (N - N_\lambda) W_{\nu\lambda}(\{\mathbf{N}\} \rightarrow \{\mathbf{N}\}', N_\nu - 1, N_\lambda + 1) \\ & - N_\lambda (N - N_\nu) W_{\lambda\nu}(\{\mathbf{N}\} \rightarrow \{\mathbf{N}\}', N_\lambda - 1, N_\nu + 1) \}. \end{aligned} \quad (3.2)$$

Assuming that  $E(\{\mathbf{N}\})$  is a slowly varying function of  $\{\mathbf{N}\}$ , we may write

$$\begin{aligned} \frac{d}{dt} N_\lambda \simeq \sum_\nu N (N_\nu - N_\lambda) \\ + \sum_\nu N_\nu (N - N_\lambda) \left( -\frac{\partial E}{\partial N_\lambda} + \frac{\partial E}{\partial N_\nu} \right) \Big|_{2k_B T} \\ - \sum_\nu N_\lambda (N - N_\nu) \left( -\frac{\partial E}{\partial N_\nu} + \frac{\partial E}{\partial N_\lambda} \right) \Big|_{2k_B T}, \end{aligned} \quad (3.3)$$

where the summations are performed over neighboring cells of the  $\lambda$ -th cell. If we take the total entropy to be given by

$$S(\{\mathbf{N}\}) = k_B \ln \prod_\mu \frac{N!}{N_\mu! (N - N_\mu)!} \quad (3.4)$$

and take the continuum limit, we obtain

$$\frac{\partial}{\partial t} N(\mathbf{r}, t) = \frac{1}{k_B T} \frac{a^2}{\tau} \frac{\partial}{\partial \mathbf{r}} N(\mathbf{r}, t) [N - N(\mathbf{r}, t)] \frac{\partial}{\partial \mathbf{r}} \frac{\delta F}{\delta N(\mathbf{r})}, \quad (3.5)$$

where  $a^2$  is the mean free path over which a particle jumps in the time scale  $\tau$ . In terms of the local density  $\rho(\mathbf{r}, t) = N(\mathbf{r}, t)/\Omega$ ,  $\rho_0 = N/\Omega$ , we obtain Eq. (1.4).

Of course, as long as  $\rho$  does not change so much, the factor  $\rho(\rho_0 - \rho)$  can be replaced by a constant, thus Eq. (1.1) results. On the other hand, when one of the factors  $\rho$ , or  $(\rho_0 - \rho)$  becomes small, as in the case of deep quenching of binary systems, it may slow down the transport process. We made numerical comparison on the evolution of the density profile for those two kinetic equations. It turns out that up to fairly deep quenching, both equations give almost, even quantitatively, the same evolution of the density profile. In the numerical calculation, we put

$$\frac{\delta F}{\delta \rho} = f'(\rho) - K \nabla^2 \rho \quad (3.6)$$

and

$$f'(\rho) - \mu = Q(\rho - \rho_1)(\rho - \rho_2)(\rho - \rho_3), \quad (3.7)$$

where  $\rho_1 > \rho_2 > \rho_3$  and  $\mu$  is the chemical potential at equilibrium.  $\rho_2$  corre-

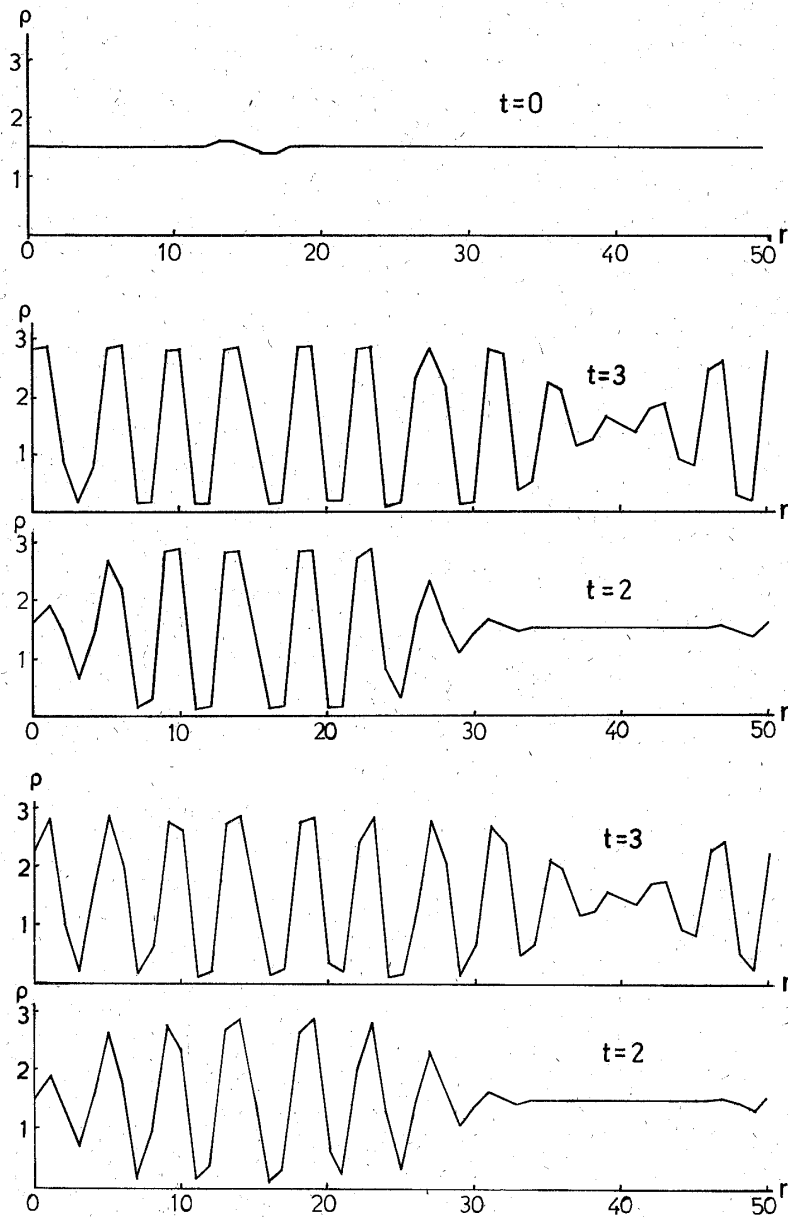


Fig. 1. Evolution of the density profile for the two equations, (1.1) and (1.4). The parameters are chosen as  $D_0=1$ ,  $\rho_0=3$  [see Eq. (1.4)],  $Q=1$ ,  $K=0.1$ ,  $\rho_1=2.9$ ,  $\rho_2=1.5$ ,  $\rho_3=0.1$  [see Eqs. (3.6) and (3.7)], and  $D$  [see Eq. (1.1)]= $D_0\rho_2$  ( $\rho_0-\rho_2$ )=2.25. We approximate the partial differential equations by difference equations. We consider the system to be one-dimensional and divide it into 50 cells.

- (a) The initial density profile.
- (b) The evolution of the density profile for Eq. (1.1).
- (c) The evolution of the density profile for Eq. (1.4).

sponds to the density of the unstable equilibrium. Initially we set  $\rho(\mathbf{r}, t_0) = \rho_2$  almost everywhere except that at some points we put small deviation from the

unstable equilibrium value. In Fig. 1 we show the evolution of the density profile for a deep quenching. The slowing down of the process in the later stage is seen in the Figure. In the numerical calculation, we approximated the partial differential equations by difference equations. Therefore, there is some ambiguity in this approximation.

#### § 4. Discussion

The discussion in the previous section is not sufficient for the description of the binary system; we have to include fluctuations. We may write the Langevin equation as

$$\begin{aligned} \frac{d}{dt} N_\mu = & \sum_\nu N_\nu (N - N_\mu) W_{\nu\mu}(\{\mathbf{N}\} \rightarrow \{\mathbf{N}\}', N_\nu - 1, N_\mu + 1) \\ & - \sum_\nu N_\mu (N - N_\nu) W_{\mu\nu}(\{\mathbf{N}\} \rightarrow \{\mathbf{N}\}', N_\mu - 1, N_\nu + 1) \\ & + R_\mu(t) \end{aligned} \quad (4.1)$$

by adding to Eq. (3.2) an extra term  $R_\mu(t)$ . Then, following the standard procedure,<sup>6)</sup> which relates the Langevin equation to the master equation, we may write

$$\langle R_\mu(t) R_\nu(t') \rangle = D_{\mu\nu} \delta(t - t'), \quad (4.2)$$

where

$$\begin{aligned} D_{\mu\nu} = & \delta_{\mu\nu} \sum_\lambda \{ N_\lambda (N - N_\mu) W_{\lambda\mu}(\{\mathbf{N}\} \rightarrow \{\mathbf{N}\}', N_\mu + 1, N_\lambda - 1) \\ & + N_\mu (N - N_\lambda) W_{\mu\lambda}(\{\mathbf{N}\} \rightarrow \{\mathbf{N}\}', N_\mu - 1, N_\lambda + 1) \} \\ & - (1 - \delta_{\mu\nu}) \{ N_\nu (N - N_\mu) W_{\nu\mu}(\{\mathbf{N}\} \rightarrow \{\mathbf{N}\}', N_\mu + 1, N_\nu - 1) \\ & + N_\mu (N - N_\nu) W_{\mu\nu}(\{\mathbf{N}\} \rightarrow \{\mathbf{N}\}', N_\mu - 1, N_\nu + 1) \}. \end{aligned} \quad (4.3)$$

Further, assuming that  $E(\{\mathbf{N}\})$  is a slowly varying function of  $\{\mathbf{N}\}$ , we obtain,

$$\begin{aligned} D_{\mu\nu} \simeq & \delta_{\mu\nu} \frac{1}{\tau} \sum_\lambda \{ N_\lambda (N - N_\mu) + N_\mu (N - N_\lambda) \} \\ & - (1 - \delta_{\mu\nu}) \frac{1}{\tau} \{ N_\nu (N - N_\mu) + N_\mu (N - N_\nu) \}. \end{aligned} \quad (4.4)$$

In the continuum limit, it is

$$\begin{aligned} \langle R(\mathbf{r}, t) R(\mathbf{r}', t') \rangle \\ = - \frac{2a^2}{\tau} \frac{\partial}{\partial \mathbf{r}} N(\mathbf{r}, t) [N - N(\mathbf{r}, t)] \frac{\partial}{\partial \mathbf{r}} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \end{aligned} \quad (4.5)$$

or, writing in terms of a current  $\mathbf{j}(\mathbf{r}, t)$ ,

$$R(\mathbf{r}, t) = -\nabla \mathbf{j}(\mathbf{r}, t), \quad (4.6)$$

$$\begin{aligned} \langle \mathbf{j}(\mathbf{r}, t) \mathbf{j}(\mathbf{r}', t') \rangle &= 2(a^2/\tau) N(\mathbf{r}, t) [N - N(\mathbf{r}, t)] \\ &\times \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'). \end{aligned} \quad (4.7)$$

Thus the current fluctuation is now state-dependent and it is proportional to the number of particles of the two species in a cell.

As we have seen in the previous section, the two kinetic equations give the same evolution of the density profile except at the later stage in a deeply quenched system. Therefore, in the theory of spinodal decomposition near the critical temperature, the choice of the transition probability does not matter so much.

### References

- 1) J. W. Cahn, *Acta Metal.* **9** (1961), 795; *Trans. Met. Soc. AIME* **242** (1968), 166.
- 2) J. S. Langer, *Ann. of Phys.* **54** (1969), 258; **65** (1971), 53.  
H. Metiu, K. Kitahara and J. Ross, *J. Chem. Phys.* **65** (1976), 393.
- 3) Y. Saito, *J. Phys. Soc. Japan* **41** (1976), 1129.
- 4) See, for example, G. Nicolis and I. Prigogine, *Self-Organization in Non Equilibrium Systems* (John-Wiley, New York, 1977).
- 5) See, for example, N. G. van Kampen, *Stochastic Processes in Physics* (Lecture Note, University of Utrecht, 1970); *Adv. Chem. Phys.* **34** (1976), 245.
- 6) M. Lax, *Rev. Mod. Phys.* **32** (1960), 25; **38** (1966), 359, 541.  
D. Bedeaux, *Phys. Letters* **62A** (1977), 10.

### Discussion

**N. G. van Kampen:** In the expression for the jump probability you took  $1/2kT$  times the energy difference, but that is not the only way in which detailed balance can be satisfied. I could arrange that one must take  $1/k_B T$  times the energy increase, if that is positive; and unity if the energy jumps down. Why did you make this particular choice? Let me add that I think that after you have made the Fokker-Planck approximation the result is the same.

**K. Kitahara:** As you said, there are many choices for the transition probability, which satisfy the condition of the detailed balance at equilibrium. In general, we may write the transition probability as

$$\begin{aligned} W_{\lambda\nu}(\{\mathbf{N}\} \rightarrow \{\mathbf{N}\}', N_\lambda - 1, N_\nu + 1) &= w_{\lambda\nu}(\{\mathbf{N}\}; \{\mathbf{N}\}', N_\lambda - 1, N_\nu + 1) \\ &\times \exp\left[-\frac{1}{2k_B T} \{F(\{\mathbf{N}\}', N_\lambda - 1, N_\nu + 1) - F(\{\mathbf{N}\})\}\right] \end{aligned}$$

as Prof. Langer showed some years ago. Here, the preexponential factor  $w_{\lambda\nu}(\{\mathbf{N}\}; \{\mathbf{N}\}', N_\lambda - 1, N_\nu + 1)$  is positive and symmetric,



$$w_{\lambda\nu}(\{N\}:\{N\}', N_\lambda-1, N_\nu+1) = w_{\nu\lambda}(\{N\}', N_\lambda-1, N_\nu+1:\{N\}) > 0.$$

The Fokker-Planck approximation results in the following equation for the probability,

$$\begin{aligned} \frac{\partial}{\partial t} P(\{N\}, t) = & \frac{1}{2k_B T} \sum_{\lambda\nu} \left( \frac{\partial}{\partial N_\lambda} - \frac{\partial}{\partial N_\nu} \right) \Omega_{\lambda\nu}(\{N\}) \\ & \times \left[ \left( \frac{\partial F}{\partial N_\lambda} - \frac{\partial F}{\partial N_\nu} \right) + k_B T \left( \frac{\partial}{\partial N_\lambda} - \frac{\partial}{\partial N_\nu} \right) \right] P(\{N\}, t), \end{aligned}$$

where

$$\Omega_{\lambda\nu}(\{N\}) \equiv w_{\lambda\nu}(\{N\}:\{N\}).$$

Thus as far as the steady solution of the master equation is concerned, we have the same result for different choices of  $w_{\lambda\nu}$ , but we have different kinetic equations.

**H. Nakano:** I think that the ground of the assumption on the expression for the transition rate satisfying the detailed balance was most clearly discussed by R. Kikuchi. He showed that it comes from the energy conservation of the system and the surroundings as a whole at the transition. A more realistic derivation was made by Kirkwood.