Irreversible Circulation of Fluctuation and Entropy Production

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Physical and chemical stochastic processes described by the master equation are investigated. The system-size expansion, called the Ω-expansion, trasnforms the master equation to the corresponding Fokker-Planck equation. In this paper, we examine the entropy production both for the master equation and for the corresponding Fokker-Planck equation. For the master equation, the exact expression of the entropy production was recently derived by Gaspard using the Kolmogorov-Sinai entropy (*J.Stat.Phys.*, **117** (2004), 599; [Errata; **126** (2006), 1109]). Although Gaspard's expression is derived from a stochastic consideration, it should be noted that Gaspard's expression conincides with the thermodynamical expression. For the corresponding Fokker-Planck equation, by using the detailed imbalance relation which appears in the derivation process of the fluctuation theorem through the Onsger-Machlup theory, the entropy production is expressed in terms of the *irreversible circulation of fluctuation*, which was proposed by Tomita and Tomita (*Prog.Theor.Phys.*, **51** (1974), 1731; [Errata; **53** (1975), 1546b]). However, this expression for the corresponding Fokker-Planck equation differs from that of the entropy production for the master equation. This discrepancy is due to the difference between the master equation and the corresponding Fokker-Planck equation, namely the former treats discrete events, but the latter equation is an approximation of the former one. In fact, in the latter equation, the original discrete events are smoothed out. To overcome this difficulty, we propose a hypothetical *path weight principle*. By using this principle, the modified expression of the entropy production for the corresponding Fokker-Planck equation coincides with that of the master equation (i.e., the thermodynamical expression) for a simple chemical reaction system and a diffusion system.

§1. Introduction

Theories on nonequilibrium system near equilibrium are quite successful. In fact, we have the landmarks in nonequilibrium statistical physics, such as the Onsager's reciprocal relation[1),2)] and the Kubo formula.[3)] However, we did not have satisfactory theory on nonequilibrium steady states (NESS) until recent. Recently the discovery of the fluctuation theorem focuses at the NESS.[4)–9)] The study of the NESS is just a little revival. The fluctuation theorem gives us some clue to investigate the NESS. But theorists consider individual problems in their perspective. A unified viewpoint is lacking in the present study of the NESS.

In this paper, as a little attempt to improve the present situation, we aim at constructing a theory of the NESS for certain stochastic process, i.e., the master equation and the Fokker-Planck equation. The entropy production for these equations is examined. For the master equation, there is a pioneering work by Schnaken-

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berg.[10] Schnakenberg derived the exact expression of the entropy production for the master equation. Recently Gaspard rederived this equation starting from the Kolmogorov-Sinai (KS) entropy.[11] His formula is

$$\langle \sigma_e \rangle = \frac{1}{\tau} \Delta S_i = h^R - h, \tag{1·1}$$

where h is the KS-entropy and h^R is the time-reversed KS-entropy. Throughout this paper, we set the Boltzmann constant $k_B = 1$. In this paper, we use the following notations of the entropy production, namely the thermodynamical entropy production, $\sigma_{e,\mathrm{th}}$ and the stochastic averaged entropy production, $\langle \sigma_e \rangle$. The expression, eq. (1·1), coincides with Schnakenberg's result. It should be noted that this expression agrees with the thermodynamical result. Thus, the entropy production defined by the stochastic process coincides with the corresponding thermodynamical entropy production.

In 1970's, there were systematic studies on the master equation.[12),13)] Kubo, Matsuo and Kitahara[12)] applied the system-size expansion, called the Ω-expansion, which was developed by van Kampen,[14)] to the master equation. They derived the corresponding Fokker-Planck equation and analyzed the behavior of the fluctuation. Later Tomita and Tomita followed Kubo *et al* 's work and emphasized importance of circulation of fluctuation in nonequilibrium states.[13)] In particular, in the NESS, they showed that the probability flow circulates. Successively, Tomita, Ohta, and Tomita applied the Onsager-Machlup theory[15),16)] to the result of Ref. 13).[17)] Unfortunately, in Refs. 13) and 17), the entropy production was not investigated.

Recently, Taniguchi and Cohen developed the Onsager-Machlup theory to several Langevin systems[19)–21)] and derived the fluctuation theorem for them. A key relation for the fluctuation theorem is the *detailed imbalance relation* (they call it the nonequilibrium detailed balance relation), i.e., the violation of the detailed balance relation. In this paper, with this key relation, we shall evaluate the entropy production of the Fokker-Planck equation derived from the master equation. However, this entropy production does not coincide with the entropy production for the original master equation. The reason will be examined in detail. The difference of them is due to the fact that our master equation treats discrete events, but the Fokker-Planck equation is an approximation of it. In the Fokker-Planck equation, the original discrete events are smoothed out. In order to overcome this difficulty, we propose the *path weight principle*. With this path weight principle, the modified entropy production for the corresponding Fokker-Planck equation coincides with that of the original master equation, which is just the thermodynamical result.

Organization of this paper is as follows. In Section 2, the master equation is introduced and the expression of its entropy production is given. After that, the master equation is transformed to the corresponding Fokker-Planck equation by the Ω-expansion. In Section 3, the Onsager-Machlup theory is applied to the corresponding Fokker-Planck equation. Calculating the path probability, the detailed imbalance relation is derived. The entropy production term is determined. In Section 4, two example cases are considered. One is a chemical reaction network. The other is one-dimensional diffusion system. For both cases, the entropy production disagrees

with the thermodynamical result. In Section 5, in order to improve the result of the previous section, the *path weight principle* is proposed and is applied to two examples. As a result, the modified entropy production by the path weight principle coincides with the thermodynamical result. In Section 6, we summarize the results.

§2. Master equation, Ω-expansion, and Fokker-Planck equation

In this section, we review Gaspard's result[11] and the results of 1970's.[12)–14),17]

Our starting point is the master equation. The master equation describes physical and chemical processes, such as diffusion system and chemical reaction network. In Section 4, we give such examples. The master equation is given by

$$\frac{\partial}{\partial t}P(\mathbf{X};t) = -\sum_{\mathbf{X}'} W(\mathbf{X}\to\mathbf{X}')P(\mathbf{X};t) + \sum_{\mathbf{X}'} W(\mathbf{X}'\to\mathbf{X})P(\mathbf{X}';t), \tag{2·1}$$

where $\mathbf{X} = (X_1, X_2, \ldots, X_N)^t$ is the variable of the state. $P(\mathbf{X};t)$ is the probability distribution that the system is in the state $\mathbf{X}$ at time t. $W(\mathbf{X}\to\mathbf{X}')$ is the transition probability rate that the system performs a transition from the state $\mathbf{X}$ to the state $\mathbf{X}'$ in a unit time. The entropy production for this master equation was recently calculated by Gaspard using the Kolmogorov-Sinai entropy.[11] Its expression is given by

$$\langle\sigma_e\rangle = \frac{1}{2}\sum_{\mathbf{X},\mathbf{X}'}\left\{P^{\mathrm{st}}(\mathbf{X})W(\mathbf{X}\to\mathbf{X}') - P^{\mathrm{st}}(\mathbf{X}')W(\mathbf{X}'\to\mathbf{X})\right\}\ln\frac{P^{\mathrm{st}}(\mathbf{X})W(\mathbf{X}\to\mathbf{X}')}{P^{\mathrm{st}}(\mathbf{X}')W(\mathbf{X}'\to\mathbf{X})}, \tag{2·2}$$

where $P^{\mathrm{st}}(\mathbf{X})$ is the probability distribution for the NESS. This expression is obtained by rewriting eq. (1·1) and is equivalent to the expression originally obtained by Schnakenberg.[10] Thus, in this paper, we call the expression of eq. (2·2) the Schnakenberg-Gaspard expression. In addition, it should be noted that this expression is nothing but the thermodynamical expression. For chemical reaction systems, eq. (2·2) is rewritten into the form of the sum of the products of the reaction rate and the affinity. Thus, the stochastic consideration gives the thermodynamical result for this problem.

Here the connection between the Schnakenberg-Gaspard expression, i.e., eq. (2·2), and the fluctuation theorem (i.e., the path probability ratio) is shown. The path probability ratio between the forward path and the reversed path is given by

$$\frac{P^{\mathrm{st}}(\mathbf{A})W_{\mathrm{path}}(\mathbf{A}\to\mathbf{B})}{P^{\mathrm{st}}(\mathbf{B})W_{\mathrm{path}}(\mathbf{B}\to\mathbf{A})} = \exp[\Sigma(\mathbf{A}\to\mathbf{B})], \tag{2·3}$$

where $\Sigma(\mathbf{A}\to\mathbf{B})$ is the entropy production for the path $\mathbf{A}\to\mathbf{B}$. This relation is a key relation to show the fluctuation theorem. If the time-reversal symmetry is satisfied, then the right hand side of eq. (2·3) is 1. Now we assume that the forward path is given by

$$\mathbf{A}\to\mathbf{X}^{(1)}\to\mathbf{X}^{(2)}\to\cdots\to\mathbf{X}^{(T-1)}\to\mathbf{B}. \tag{2·4}$$

The path probability is given by the step-by-step transition probabilities as

$$W_{\rm path}(\mathbf{A}\to\mathbf{B}) = W(\mathbf{A}\to\mathbf{X}^{(1)})W(\mathbf{X}^{(1)}\to\mathbf{X}^{(2)})\cdots W(\mathbf{X}^{(T-1)}\to\mathbf{B}), \tag{2·5}$$

namely in a Markov chain. Let the transition probability

$$W^{(t)}(\mathbf{A}\to\mathbf{X}') = \sum_{\mathbf{X}^{(1)}}\sum_{\mathbf{X}^{(2)}}\cdots\sum_{\mathbf{X}^{(t-1)}} W_{\rm path}(\mathbf{A}\to\mathbf{X}'). \tag{2·6}$$

The path probability ratio between the forward and reversed paths is given by

$$\begin{aligned}
&\log\frac{P^{\rm st}(\mathbf{A})W_{\rm path}(\mathbf{A}\to\mathbf{B})}{P^{\rm st}(\mathbf{B})W_{\rm path}(\mathbf{B}\to\mathbf{A})}\\
&=\sum_{t=0}^{T-1}\log\frac{P^{\rm st}(\mathbf{X}^{(t)})W(\mathbf{X}^{(t)}\to\mathbf{X}^{(t+1)})}{P^{\rm st}(\mathbf{X}^{(T-t)})W(\mathbf{X}^{(T-t)}\to\mathbf{X}^{(T-t-1)})}\\
&=\log\frac{P^{\rm st}(\mathbf{A})W(\mathbf{A}\to\mathbf{X}^{(1)})}{P^{\rm st}(\mathbf{X}^{(1)})W(\mathbf{X}^{(1)}\to\mathbf{A})}+\log\frac{P^{\rm st}(\mathbf{X}^{(T-1)})W(\mathbf{X}^{(T-1)}\to\mathbf{B})}{P^{\rm st}(\mathbf{B})W(\mathbf{B}\to\mathbf{X}^{(T-1)})}\\
&\quad+\sum_{t=1}^{T-2}\log\frac{P^{\rm st}(\mathbf{X}^{(t)})W(\mathbf{X}^{(t)}\to\mathbf{X}^{(t+1)})}{P^{\rm st}(\mathbf{X}^{(t+1)})W(\mathbf{X}^{(t+1)}\to\mathbf{X}^{(t)})}.
\end{aligned} \tag{2·7}$$

Before taking the limit $T\to\infty$, the path average is taken. Then we have

$$\begin{aligned}
\langle\Sigma(\mathbf{A}\to\mathbf{B})\rangle &= (\text{both end terms})\\
&\quad+\sum_{t=1}^{T-2}\sum_{\text{all paths}} P^{\rm st}(\mathbf{A})W^{(t)}(\mathbf{A}\to\mathbf{X}^{(t)})W(\mathbf{X}^{(t)}\to\mathbf{X}^{(t+1)})\\
&\quad\times W(\mathbf{X}^{(t+1)}\to\mathbf{B})\log\frac{P^{\rm st}(\mathbf{X}^{(t)})W(\mathbf{X}^{(t)}\to\mathbf{X}^{(t+1)})}{P^{\rm st}(\mathbf{X}^{(t+1)})W(\mathbf{X}^{(t+1)}\to\mathbf{X}^{(t)})}.
\end{aligned} \tag{2·8}$$

For the NESS, we assume that

$$\sum_{\mathbf{A}} P^{\rm st}(\mathbf{A})W^{(t)}(\mathbf{A}\to\mathbf{X}) = P^{\rm st}(\mathbf{X}). \tag{2·9}$$

We use the Bayes relation

$$W(\mathbf{X}^{(t+1)}\to\mathbf{B}) = P^{\rm st}(\mathbf{X}^{(t+1)})^{-1}\overline{W}(\mathbf{X}^{(t+1)}\to\mathbf{B})P^{\rm st}(\mathbf{B}), \tag{2·10}$$

and

$$\sum_{\mathbf{B}}\overline{W}(\mathbf{X}^{(t+1)}\to\mathbf{B})P^{\rm st}(\mathbf{B}) = P^{\rm st}(\mathbf{X}^{(t+1)}). \tag{2·11}$$

where the bar denotes the destined conditional probability. Thus finally the average entropy production is given by

$$\begin{aligned}
\langle\sigma_e\rangle &= \lim_{T\to\infty}\frac{1}{T}\langle\Sigma(\mathbf{A}\to\mathbf{B})\rangle\\
&=\sum_{\mathbf{X},\mathbf{X}'} P^{\rm st}(\mathbf{X})W(\mathbf{X}\to\mathbf{X}')\log\frac{P^{\rm st}(\mathbf{X})W(\mathbf{X}\to\mathbf{X}')}{P^{\rm st}(\mathbf{X}')W(\mathbf{X}'\to\mathbf{X})}.
\end{aligned} \tag{2·12}$$

Equation (2·12) is nothing but the Schnakenberg-Gaspard expression i.e., eq. (2·2). Throughout this paper, we call this relation the *detailed imbalance relation.* The fluctuation theorem mentions the asymptotic behavior of long-time fluctuation. However, note that the entropy production in the NESS is determined by the detailed imbalance of short-time fluctuation in this formula.

As done in Refs. 14) and 12), the Ω-expansion is used for eq. (2·1). Here Ω is a variable which is related to the system size. For chemical reaction systems, Ω should be the order of the Avogadro number or the volume of the system. We set

$$W(\mathbf{X} \to \mathbf{X} + \mathbf{r}) = \Omega\, w\left(\frac{\mathbf{X}}{\Omega}; \mathbf{r}\right). \tag{2·13}$$

and scale the variable $\mathbf{X}$,

$$\mathbf{x} = \frac{\mathbf{X}}{\Omega}. \tag{2·14}$$

The master equation is rewritten as

$$\frac{\partial}{\partial t} p(\mathbf{x}; t) = -\Omega \sum_{\mathbf{r}} (1 - e^{-\epsilon \mathbf{r} \cdot \frac{\partial}{\partial \mathbf{x}}}) w(\mathbf{x}; \mathbf{r}) p(\mathbf{x}; t), \tag{2·15}$$

where $\epsilon = 1/\Omega$ is used. The probability distribution is now scaled as

$$\Omega^N P(\mathbf{X}; t) = p(\mathbf{x}; t). \tag{2·16}$$

Expanding the right hand side of eq. (2·15) in terms of ϵ, we obtain the following equation.

$$\frac{\partial}{\partial t} p(\mathbf{x}; t) = \sum_{n=1}^{\infty} \frac{\epsilon^{n-1}}{n!} \left(-\frac{\partial}{\partial \mathbf{x}}\right)^n \cdot \mathbf{c}_n(\mathbf{x}) p(\mathbf{x}; t), \tag{2·17}$$

where

$$\mathbf{c}_n(\mathbf{x}) = \sum_{\mathbf{r}} (\mathbf{r})^n w(\mathbf{x}; \mathbf{r}), \tag{2·18}$$

is the nth moments of the transition probability rate. In particular, $\mathbf{c}_1(\mathbf{x})$ and $\mathbf{c}_2(\mathbf{x})$ are given by

$$\mathbf{c}_{1,k}(\mathbf{x}) = \sum_{\mathbf{r}} r_k\, w(\mathbf{x}; \mathbf{r}),\ \mathbf{c}_{2,kl}(\mathbf{x}) = \sum_{\mathbf{r}} r_k r_l\, w(\mathbf{x}; \mathbf{r}). \tag{2·19}$$

Reserving the lowest order of ϵ, we obtain the following equation:

$$\frac{\partial}{\partial t} p(\mathbf{x}; t) = -\frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{c}_1(\mathbf{x}) p(\mathbf{x}; t) + \frac{\epsilon}{2} \frac{\partial}{\partial \mathbf{x}} \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{c}_2(\mathbf{x}) p(\mathbf{x}; t). \tag{2·20}$$

Here the $\mathbf{x}$-dependence of $\mathbf{c}_2(\mathbf{x})$ is explicitly considered. Then we obtain

$$\frac{\partial}{\partial t} p(\mathbf{x}; t) = -\frac{\partial}{\partial \mathbf{x}} \cdot \left[\mathbf{c}_1(\mathbf{x}) - \frac{\epsilon}{2}\mathbf{h}(\mathbf{x}) - \frac{\epsilon}{2}\mathbf{c}_2(\mathbf{x}) \cdot \frac{\partial}{\partial \mathbf{x}}\right] p(\mathbf{x}; t), \tag{2·21}$$

where

$$\mathbf{h}(\mathbf{x}) = \mathbf{c}_2(\mathbf{x}) \cdot \frac{\overleftarrow{\partial}}{\partial \mathbf{x}}. \tag{2·22}$$

Here the term $\epsilon\mathbf{h}(\mathbf{x})/2$ can be neglected, because compared with $\mathbf{c}_1$, it is the order of ϵ. We set for the later use*):

$$\mathbf{D}(\mathbf{x}) = \frac{1}{2}\mathbf{c}_2(\mathbf{x}), \tag{2·23}$$

which is the diffusion constant matrix in the probability space. If the fluctuation is assumed to be normal,[12] i.e.,

$$p(\mathbf{x};t) = A(\mathbf{x};t)e^{-\Omega\phi(\mathbf{x};t)}, \tag{2·24}$$

the probability distribution is well approximated as Gaussian one in the order of ϵ,

$$\phi(\mathbf{x};t) = \frac{1}{2}(\mathbf{x}-\mathbf{y}(t))^t \cdot \boldsymbol{\sigma}^{-1} \cdot (\mathbf{x}-\mathbf{y}(t)). \tag{2·25}$$

Then we obtain the time-evolution of $\mathbf{y}(t)$ and $\boldsymbol{\sigma}(t)$ as follows:

$$\frac{d\mathbf{y}}{dt} = \mathbf{c}_1(\mathbf{y}), \tag{2·26}$$

$$\frac{d\boldsymbol{\sigma}}{dt} = \mathbf{K}\cdot\boldsymbol{\sigma} + \boldsymbol{\sigma}\cdot\widetilde{\mathbf{K}} + \mathbf{c}_2(\mathbf{y}), \tag{2·27}$$

where

$$K_{kl}(\mathbf{y}) = \frac{\partial c_{1,k}(\mathbf{y})}{\partial y_l}. \tag{2·28}$$

The matrix elements of $\boldsymbol{\sigma}$ are given by

$$\sigma_{ij} = \int d\boldsymbol{\xi}\ \xi_i\xi_j\ \tilde{p}(\boldsymbol{\xi};t), \tag{2·29}$$

where

$$\mathbf{x} = \mathbf{y}(t) + \epsilon^{1/2}\boldsymbol{\xi}, \tag{2·30}$$

and $\tilde{p}(\boldsymbol{\xi};t)$ is the probability distribution for $\boldsymbol{\xi}$. Thus, $\boldsymbol{\sigma}$ and $\mathbf{g}$ correspond to the definitions in Ref. 13). Solving eq. (2·26) and inserting its solution into $\mathbf{D}(\mathbf{x})$, we obtain $\mathbf{y}(t)$ and $\mathbf{D}(t)$. Therefore, as a result, we obtain the Fokker-Planck equation:

$$\frac{\partial}{\partial t}p(\mathbf{x};t) = -\frac{\partial}{\partial\mathbf{x}}\cdot\left[\mathbf{c}_1(\mathbf{x}) - \epsilon\mathbf{D}(t)\cdot\frac{\partial}{\partial\mathbf{x}}\right]p(\mathbf{x};t). \tag{2·31}$$

Hereafter we investigate this Fokker-Planck equation in detail.

For eq. (2·31), several interesting properties for the NESS are known.[13] The probability distribution for the NESS is given by

$$p^{\mathrm{st}}(\mathbf{x}) = \frac{1}{\sqrt{(2\pi\epsilon)^N\det(\boldsymbol{\sigma}^{\mathrm{st}})}}\exp[-\Omega\phi(\mathbf{x})], \tag{2·32}$$

where

$$\phi(\mathbf{x}) = \frac{1}{2}(\mathbf{x}-\langle\mathbf{x}\rangle)^t\cdot\mathbf{g}^{\mathrm{st}}\cdot(\mathbf{x}-\langle\mathbf{x}\rangle), \tag{2·33}$$

*) Here we used the standard definition of $\mathbf{D}$, which is different from that in Ref. 13) by the factor 1/2.

and

$$\mathbf{g}^{\mathrm{st}} = (\boldsymbol{\sigma}^{\mathrm{st}})^{-1}. \tag{2·34}$$

$\boldsymbol{\sigma}^{\mathrm{st}}$ is the variance matrix of the probability distribution of the NESS. In this case, a phenomenological equation is given by

$$\begin{aligned}\mathbf{X} &= -\frac{\partial \phi}{\partial \mathbf{x}} \\ &= -\mathbf{g}^{\mathrm{st}} \cdot (\mathbf{x} - \langle \mathbf{x} \rangle).\end{aligned} \tag{2·35}$$

If $\mathbf{c}_1(\mathbf{x})$ is

$$\mathbf{c}_1(\mathbf{x}) = \mathbf{K}^{\mathrm{st}} \cdot \mathbf{x} + \mathbf{c}, \tag{2·36}$$

(Two examples in Section 4 are the case.), we have

$$\begin{aligned}\dot{\mathbf{x}} &= \mathbf{K}^{\mathrm{st}} \cdot \mathbf{x} + \mathbf{c} \\ &= \mathbf{K}^{\mathrm{st}} \cdot (\mathbf{x} - \langle \mathbf{x} \rangle) \\ &= -\mathbf{L} \cdot \mathbf{X}.\end{aligned} \tag{2·37}$$

Here we have used the fact that $\dot{\mathbf{x}} = 0 \Rightarrow \langle \mathbf{x} \rangle = -(\mathbf{K}^{\mathrm{st}})^{-1} \cdot \mathbf{c}$. $\mathbf{L}$ is the Onsager coefficient. Also we have the following relations.[13)]

$$\mathbf{L} = -\mathbf{K}^{\mathrm{st}}(\mathbf{g}^{\mathrm{st}})^{-1} = \mathbf{D}^{\mathrm{st}} + \boldsymbol{\alpha}, \tag{2·38}$$

$$\begin{aligned}\boldsymbol{\alpha} &= -\mathbf{K}^{\mathrm{st}}\boldsymbol{\sigma}^{\mathrm{st}} - \mathbf{D}^{\mathrm{st}} \\ &= \frac{1}{2}(\boldsymbol{\sigma}^{\mathrm{st}}\widetilde{\mathbf{K}}^{\mathrm{st}} - \mathbf{K}^{\mathrm{st}}\boldsymbol{\sigma}^{\mathrm{st}}).\end{aligned} \tag{2·39}$$

The matrix $\boldsymbol{\alpha}$ vanishes for the case that the detailed balance is satisfied, i.e., in equilibrium. However, for the NESS, $\boldsymbol{\alpha}$ is non-zero, in general. In addition, $\boldsymbol{\alpha}$ is an anti-symmetric matrix. As shown in Ref. 13), $\boldsymbol{\alpha}$ is a measure of the circulation of fluctuation. Therefore, $\boldsymbol{\alpha}$ is called the *irreversible circulation of fluctuation*.

Now we set

$$\mathbf{v}(\mathbf{x}) = \dot{\mathbf{y}}(\mathbf{x}) + \mathbf{D}^{\mathrm{st}} \cdot \nabla\phi(\mathbf{x}). \tag{2·40}$$

We call the vector $\mathbf{v}$ the *irreversible circulation velocity*. If $\dot{\mathbf{y}}(\mathbf{x}) = \mathbf{K}^{\mathrm{st}} \cdot \mathbf{x} + \mathbf{c}$, the irreversible circulation velocity is rewritten into

$$\begin{aligned}\mathbf{v}(\mathbf{x}) &= \mathbf{K}^{\mathrm{st}} \cdot (\mathbf{x} - \langle \mathbf{x} \rangle) + \mathbf{D}^{\mathrm{st}} \cdot \nabla\phi(\mathbf{x}) \\ &= (\mathbf{K}^{\mathrm{st}} + \mathbf{D}^{\mathrm{st}}\mathbf{g}^{\mathrm{st}}) \cdot (\mathbf{x} - \langle \mathbf{x} \rangle) \\ &= -\boldsymbol{\alpha} \cdot \nabla\phi(\mathbf{x}) \\ &= \boldsymbol{\alpha} \cdot \mathbf{X}(\mathbf{x}).\end{aligned} \tag{2·41}$$

Therefore, we have

$$\mathbf{v}(\mathbf{x}) = \mathbf{j}(\mathbf{x})/P^{\mathrm{st}}(\mathbf{x}). \tag{2·42}$$

Here $\mathbf{j}(\mathbf{x})$ is the current of the probability. This relation was also obtained in Ref. 22).

In addition, the irreversible circulation $\boldsymbol{\alpha}$ is related to the breaking of the fluctuation-dissipation theorem. If the fluctuation-dissipation theorem is satisfied, i.e., $\boldsymbol{\alpha} = 0$,

$$-\mathbf{K}^{\mathrm{st}}\boldsymbol{\sigma}^{\mathrm{st}} = \mathbf{D}^{\mathrm{st}}. \tag{2·43}$$

The breaking of the fluctuation-dissipation theorem is recently re-recognized for the corresponding Langevin system.[18)]

§3. Path probability and detailed imbalance relation

Following Tomita, Ohta, and Tomita,[17] we apply the Onsager-Machlup theory[15),16)] to the Fokker-Planck equation, eq. (2·31). The time-evolution of the probability distribution can be written in terms of the transition probability.

$$p(\mathbf{x};t) = \int d\mathbf{x}'\ F\left(\begin{array}{c|c} \mathbf{x} & \mathbf{x}' \\ t & t_0 \end{array}\right) p(\mathbf{x}';t_0) \tag{3·1}$$

$F(\dots)$ is the transition probability. As a short time propagation, the transition probability is evaluated as

$$\begin{aligned} & F\left(\begin{array}{c|c} \mathbf{x}+\Delta\mathbf{x} & \mathbf{x} \\ t+\Delta t & t \end{array}\right) \\ &= \frac{1}{\sqrt{(2\pi)^N \det(\mathbf{D}(t))(\epsilon\Delta t)^N}} \\ &\quad \times \exp\left[-\frac{\Delta t\Omega}{4}\left(\frac{\Delta\mathbf{x}}{\Delta t} - \dot{\mathbf{y}}(\mathbf{x})\right)^t \cdot \mathbf{R} \cdot \left(\frac{\Delta\mathbf{x}}{\Delta t} - \dot{\mathbf{y}}(\mathbf{x})\right)\right] + \mathcal{O}((\Delta t)^2), \end{aligned} \tag{3·2}$$

where $\mathbf{R} = \mathbf{D}^{-1}$. From eq. (3·2), the Lagrangian for the path integral (i.e., the Onsager-Machlup function) is given by

$$\mathcal{L}(\dot{\mathbf{x}},\mathbf{x}) = -\frac{\Omega}{4}\left(\dot{\mathbf{x}} - \dot{\mathbf{y}}(\mathbf{x})\right)^t \cdot \mathbf{R} \cdot \left(\dot{\mathbf{x}} - \dot{\mathbf{y}}(\mathbf{x})\right). \tag{3·3}$$

The path probability is given by

$$W_{\rm path}(\{\mathbf{x}\}; A \to B) = \exp\left[\int_{t_0}^{t} ds\ \mathcal{L}(\dot{\mathbf{x}}^*(s), \mathbf{x}^*(s))\right], \tag{3·4}$$

where $\mathbf{x}^*(s)$ is to be taken along a given path $A \to B$. We set $A = \mathbf{x}(t_0)$ and $B = \mathbf{x}(t)$. In order to calculate the path probability ratio, we evaluate the difference of the Langrangians.

$$\mathcal{L}(\dot{\mathbf{x}},\mathbf{x}) - \mathcal{L}(-\dot{\mathbf{x}},\mathbf{x}) = \Omega\dot{\mathbf{x}} \cdot \mathbf{R} \cdot \dot{\mathbf{y}}(\mathbf{x}) \tag{3·5}$$

Here we assume that the probability distribution in the NESS is given by

$$p^{\rm st}(\mathbf{x}) \propto \exp[-\Omega\phi(\mathbf{x})]. \tag{3·6}$$

Thus we have

$$\mathcal{L}(\dot{\mathbf{x}},\mathbf{x}) - \mathcal{L}(-\dot{\mathbf{x}},\mathbf{x}) = -\Omega\dot{\phi}(\mathbf{x}) + \Omega\dot{\mathbf{x}} \cdot \mathbf{R}^{\rm st} \cdot \left[\dot{\mathbf{y}}(\mathbf{x}) + \mathbf{D}^{\rm st} \cdot \nabla\phi(\mathbf{x})\right]. \tag{3·7}$$

We have used the following relation $\dot{\phi}(\mathbf{x}) = \nabla\phi \cdot \dot{\mathbf{x}}$. Then for the NESS, we obtain

$$\frac{P^{\rm st}(A)W_{\rm path}(\{\mathbf{x}\}; A \to B)}{P^{\rm st}(B)W_{\rm path}(\{\mathbf{x}\}; B \to A)} = \exp\left[\Omega\int_A^B dt\ \dot{\mathbf{x}}^t \cdot \mathbf{R}^{\rm st} \cdot \mathbf{v}\right]. \tag{3·8}$$

Similar relations were also obtained for the Langevin systems by Taniguchi and Cohen[19)–21)*)], Seifert,[22)] and Chernyak *et al.*[23)] If the detailed balance relation is satisfied, the right hand side of eq. (3·8) is equal to 1, i.e., it is in equilibrium and the entropy production is zero, because $\boldsymbol{\alpha} = 0$. It is known that compared with the Onsager-Machlup theory, the argument of the exponential function is related to the entropy production. Therefore, the argument of the exponential function in the right hand side is the entropy production rate for the path $A \to B$. Thus, finally we obtain a stochastic form of the entropy production rate,

$$\sigma_e(\dot{\mathbf{x}}, \mathbf{x}) = \Omega\, \dot{\mathbf{x}}^t \cdot \mathbf{R}^{\mathrm{st}} \cdot \mathbf{v}(\mathbf{x}). \tag{3·9}$$

Next consider the average value of the entropy production term. As in the Onsger-Machlup theory, the most probable paths are categorized into two types, i.e., the forward evolution and the reversed evolution. For the forward evolution, the most probable path is given by

$$\dot{\mathbf{x}} = \mathbf{K}^{\mathrm{st}} \cdot \mathbf{x} + \mathbf{c} = \mathbf{K}^{\mathrm{st}} \cdot (\mathbf{x} - \langle \mathbf{x} \rangle). \tag{3·10}$$

Inserting eq. (3·10) into eq. (3·9), we have

$$\sigma_e(\mathbf{x}) = \Omega\, \{\mathbf{K}^{\mathrm{st}} \cdot (\mathbf{x} - \langle \mathbf{x} \rangle)\}^t \cdot \mathbf{R}^{\mathrm{st}} \boldsymbol{\alpha} \cdot \mathbf{X}(\mathbf{x}). \tag{3·11}$$

Now taking an average over the NESS, we finally obtain

$$\begin{aligned} \langle \sigma_e \rangle &= \int d\mathbf{x}\, P^{\mathrm{st}}(\mathbf{x})\, \sigma_e(\mathbf{x}) \\ &= -\mathrm{Tr}(\boldsymbol{\alpha} \mathbf{R}^{\mathrm{st}} \boldsymbol{\alpha} \mathbf{g}^{\mathrm{st}}). \end{aligned} \tag{3·12}$$

This is the central result of this section, i.e., another form of the detailed imbalance relation. Note that the entropy production is expressed in terms of the irreversible circulation $\boldsymbol{\alpha}$. If in equilibrium, i.e., the detailed balance is satisfied, $\boldsymbol{\alpha}$ is zero. Then, the entropy production vanishes. This is consistent with physical requirement. It is important that the entropy production is expressed in a quadratic form of $\boldsymbol{\alpha}$.

§4. Examples

In this section, we check whether the derived expression of the entropy production coincides with the thermodynamical expression or not. Two examples are considered. One is a chemical reaction network. The other is a one-dimensional diffusion system.

4.1. *Chemical reaction network*

Let us consider the following simple case:

$$\mathrm{A} \underset{\kappa}{\overset{\kappa}{\rightleftharpoons}} \mathrm{X} \underset{\kappa}{\overset{\kappa}{\rightleftharpoons}} \mathrm{Y} \underset{\kappa}{\overset{\kappa}{\rightleftharpoons}} \mathrm{B}. \tag{4·1}$$

*) They call this relation the nonequilibrium detailed balance relation.

Here all rate constants are equal to κ. In order to maintain the steady state, the concentrations of the chemical species A and B are kept constant by reservoirs. This chemical reaction system is linear. Using eqs. (2·28) and (2·36), the matrix $\mathbf{K}^{\mathrm{st}}$ and the vector $\mathbf{c}$ are given by

$$\mathbf{K}^{\mathrm{st}} = \kappa \begin{pmatrix} -2 & 1 \\ 1 & -2 \end{pmatrix}, \ \mathbf{c} = \kappa \begin{pmatrix} \langle a \rangle \\ \langle b \rangle \end{pmatrix}, \tag{4·2}$$

where $\langle a \rangle = \langle A \rangle / \Omega$ and $\langle b \rangle = \langle B \rangle / \Omega$. Using eq. (2·23) for $\mathbf{D}^{\mathrm{st}}$, eq. (2·28) for $\mathbf{K}^{\mathrm{st}}$, and making zero the right hand side of eq. (2·27) for $\boldsymbol{\sigma}^{\mathrm{st}}$, we obtain the matrix $\boldsymbol{\sigma}^{\mathrm{st}}$.

$$\boldsymbol{\sigma}^{\mathrm{st}} = \frac{1}{3} \begin{pmatrix} 2\langle a \rangle + \langle b \rangle & 0 \\ 0 & \langle a \rangle + 2\langle b \rangle \end{pmatrix}. \tag{4·3}$$

Using eq. (2·39), the matrix $\boldsymbol{\alpha}$ is given by

$$\boldsymbol{\alpha} = \frac{\kappa(\langle a \rangle - \langle b \rangle)}{6} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}. \tag{4·4}$$

The entropy production derived from the Fokker-Planck equation becomes

$$\begin{aligned} \langle \sigma_e \rangle &= -\mathrm{Tr}(\boldsymbol{\alpha} \mathbf{R}^{\mathrm{st}} \boldsymbol{\alpha} \mathbf{g}^{\mathrm{st}}) \\ &= \kappa \frac{4(\langle a \rangle - \langle b \rangle)^2}{23\langle a \rangle^2 + 62\langle a \rangle \langle b \rangle + 23\langle b \rangle^2} \\ &\approx \frac{4\kappa(\langle a \rangle - \langle b \rangle)^2}{27(\langle a \rangle + \langle b \rangle)^2}. \end{aligned} \tag{4·5}$$

The last line is the approximation near equilibrium, i.e., $\langle a \rangle \sim \langle b \rangle$. We have employed an expansion in a symmetric form.

In the thermodynamical consideration, the entropy production is given by

$$\sigma_{e,\mathrm{th}} = \sum_{i=1}^{3} \mathcal{J}_i \frac{\mathcal{A}_i}{T}, \tag{4·6}$$

where

$$\mathcal{J}_1 = \kappa(\langle A \rangle - \langle X \rangle), \qquad \mathcal{A}_1 = T \log \frac{\langle A \rangle}{\langle X \rangle}, \tag{4·7}$$

$$\mathcal{J}_2 = \kappa(\langle X \rangle - \langle Y \rangle), \qquad \mathcal{A}_2 = T \log \frac{\langle X \rangle}{\langle Y \rangle}, \tag{4·8}$$

$$\mathcal{J}_3 = \kappa(\langle Y \rangle - \langle B \rangle), \qquad \mathcal{A}_3 = T \log \frac{\langle Y \rangle}{\langle B \rangle}. \tag{4·9}$$

$\mathcal{J}_i$ is the reaction rate of the reaction i. $\mathcal{A}_i$ is the affinity of the reaction i. This expression is equivalent to eq. (2·2). Near equilibrium case, the entropy production is

$$\sigma_{e,\mathrm{th}} \approx \frac{2\kappa\Omega(\langle a \rangle - \langle b \rangle)^2}{3(\langle a \rangle + \langle b \rangle)}. \tag{4·10}$$

The result of eq. (4·5) disagrees with the thermodynamical result of eq. (4·10).

4.2. *One-dimensional diffusion system*

In this subsection, one-dimensional diffusion system is considered. The system is a pipe with the cross section Σ. This pipe is divided into L cells of the length λ. Thus the volume of each cell is $\Omega = \lambda\Sigma$. Particles exhibit random walk between cells. All rate constants are given by κ. The reaction is represented as

$$\mathrm{A} \underset{\kappa}{\overset{\kappa}{\rightleftharpoons}} \mathrm{N}_1 \underset{\kappa}{\overset{\kappa}{\rightleftharpoons}} \mathrm{N}_2 \underset{\kappa}{\overset{\kappa}{\rightleftharpoons}} \dots \underset{\kappa}{\overset{\kappa}{\rightleftharpoons}} \mathrm{N}_{L-1} \underset{\kappa}{\overset{\kappa}{\rightleftharpoons}} \mathrm{B}. \tag{4·11}$$

The time evolution of the population N_i is determined by the following rate equation:

$$\dot{N}_i = \kappa(N_{i+1} - 2N_i + N_{i-1}), \tag{4·12}$$

and at both edges,

$$N_0 = A,\ N_L = B. \tag{4·13}$$

At the edges, the number of the particles is supplied to be constant by the reservoirs. We denote the density of the particle in the ith cell by n_i, i.e., $n_i = N_i/\Omega$.

$$\begin{aligned} \dot{n}_i &= \kappa(n_{i+1} - 2n_i + n_{i-1}), \\ &\approx \kappa\lambda^2\nabla^2 n. \end{aligned} \tag{4·14}$$

Thus the spatial diffusion coefficient is given by

$$\mathcal{D} = \kappa\lambda^2. \tag{4·15}$$

Now let us consider the master equation for this system. The transition probabilities are given by

$$W(\dots, N_i, N_{i+1}, \cdots \to \dots, N_i - 1, N_{i+1} + 1, \dots) = \kappa N_i \tag{4·16}$$

$$W(\dots, N_i, N_{i+1}, \cdots \to \dots, N_i + 1, N_{i+1} - 1, \dots) = \kappa N_{i+1} \tag{4·17}$$

This problem was analyzed in the context of the fluctuation theorem.[24] The steady solution of the master equation is multi-Poissonian.

$$P^{\mathrm{st}}(N_1, N_2, \dots, N_{L-1}) = \prod_{i=1}^{L-1} e^{-\langle N_i \rangle} \frac{\langle N_i \rangle^{N_i}}{N_i!}. \tag{4·18}$$

The thermodynamical entropy production is given by

$$\sigma_{e,\mathrm{th}} = \frac{\kappa(\langle A \rangle - \langle B \rangle)}{L} \log \frac{\langle A \rangle}{\langle B \rangle}. \tag{4·19}$$

This equation is equivalent to the Schnakenberg-Gaspard expression, eq. (2·2). One can confirm that inserting eq. (4·18) into eq. (2·2), eq. (4·19) is satisfied. In the continuous limit, we have

$$\sigma_{e,\mathrm{th}} = \Sigma\mathcal{D} \int_0^{L\lambda} dx \frac{|\nabla n(x)|^2}{n(x)} \tag{4·20}$$

where $\Sigma\ dx$ is the volume element here. In the last line, we employed the linear approximation near equilibrium.

Using eq. (2·19), the moments are calculated as

$$\mathbf{c}_{1,i} = \kappa(n_{i+1} - 2n_i + n_{i-1}), \tag{4·21}$$

$$\mathbf{c}_{2,i,i} = \kappa(n_{i+1} + 2n_i + n_{i-1}), \tag{4·22}$$

$$\mathbf{c}_{2,i,i+1} = \mathbf{c}_{2,i+1,i} = \kappa(n_i + n_{i+1}). \tag{4·23}$$

For $\mathbf{c}_2$, other entries are zero. The matrices $\mathbf{K}^{\mathrm{st}}$ and $\mathbf{D}^{\mathrm{st}}$ are given by

$$\mathbf{K}^{\mathrm{st}} = \kappa \begin{pmatrix} -2 & 1 & 0 & \cdots & \dots & 0 \\ 1 & -2 & 1 & \cdots & \cdots & 0 \\ 0 & 1 & -2 & \ddots & \cdots & 0 \\ \vdots & \dots & \ddots & \ddots & \ddots & \vdots \\ 0 & \cdots & \cdots & 1 & -2 & 1 \\ 0 & \cdots & \cdots & 0 & 1 & -2 \end{pmatrix}. \tag{4·24}$$

and

$$D^{\mathrm{st}}_{i,i} = \frac{\kappa}{2}(n^{\mathrm{st}}_{i-1} + 2n^{\mathrm{st}}_i + n^{\mathrm{st}}_{i+1}) = 2\kappa n^{\mathrm{st}}_i, \tag{4·25}$$

$$D^{\mathrm{st}}_{i,i+1} = D^{\mathrm{st}}_{i+1,i} = -\frac{\kappa}{2}(n^{\mathrm{st}}_i + n^{\mathrm{st}}_{i+1}). \tag{4·26}$$

For $\mathbf{D}^{\mathrm{st}}$, other entries are zero. We used the fact that the steady solution is given by

$$n^{\mathrm{st}}_i = n_0 - i\lambda|\nabla n|. \tag{4·27}$$

The variance matrix $\boldsymbol{\sigma}^{\mathrm{st}}$ and the circulation matrix $\boldsymbol{\alpha}$ are given by

$$\boldsymbol{\sigma}^{\mathrm{st}} = \begin{pmatrix} n^{\mathrm{st}}_1 & 0 & 0 & \dots & 0 \\ 0 & n^{\mathrm{st}}_2 & 0 & \dots & 0 \\ \vdots & & \ddots & & \vdots \\ 0 & \dots & & n^{\mathrm{st}}_{L-2} & 0 \\ 0 & \dots & & 0 & n^{\mathrm{st}}_{L-1} \end{pmatrix}, \tag{4·28}$$

and

$$\begin{aligned} \boldsymbol{\alpha} &= \frac{1}{2}(\boldsymbol{\sigma}^{\mathrm{st}}\widetilde{\mathbf{K}}^{\mathrm{st}} - \mathbf{K}^{\mathrm{st}}\boldsymbol{\sigma}^{\mathrm{st}}) \\ &= \frac{\kappa\lambda\nabla n}{2} \begin{pmatrix} 0 & 1 & 0 & \cdots & \dots & 0 \\ -1 & 0 & 1 & \cdots & \cdots & 0 \\ 0 & -1 & 0 & \ddots & \cdots & 0 \\ \vdots & \dots & \ddots & \ddots & \ddots & \vdots \\ 0 & \cdots & \cdots & -1 & 0 & 1 \\ 0 & \cdots & \cdots & 0 & -1 & 0 \end{pmatrix}. \end{aligned} \tag{4·29}$$

The entropy production for the corresponding Fokker-Planck equation is given by eq. (3·12). Then we have

$$\begin{aligned}\langle\sigma_e\rangle &= -\mathrm{Tr}(\boldsymbol{\alpha}\mathbf{R}^{\mathrm{st}}\boldsymbol{\alpha}\mathbf{g}^{\mathrm{st}})\\ &\approx \frac{\kappa\lambda^2|\nabla n|^2}{4\overline{n}^2}\frac{2(L-2)(L-1)}{L}\\ &= \frac{\mathcal{D}}{2\lambda\overline{n}}\int_0^{L\lambda} dx\,\frac{|\nabla n(x)|^2}{n(x)} \qquad (L\to\infty).\end{aligned} \tag{4·30}$$

This result does not agree with the thermodynamical result of eq. (4·20). In particular, the order of eq. (4·30) is different by the factor of $1/\Omega$ compared with that of eq. (4·20) and the concentration dependence disagrees.

§5. Path weight principle

As shown in the previous section, the entropy production derived directly from our Fokker-Planck equation disagrees with that of the original master equation and thermodynamical one. This discrepancy should be examined.

First, let us consider the reason of this discrepancy. Our original master equation describes the phenomena of the discrete jump events such as the occasional collisions in the chemical reaction system. On the other hand, the corresponding Fokker-Planck equation treats the averaged continuous evolution of the original physical random process. This relation is just similar to that between a random walk and a Brownian motion which corresponds to the former. Note that the different random walks, say, (i) random jump $\pm\Delta$ at each mean interval τ_0, and (ii) random jump $\pm 2\Delta$ at each mean interval $4\tau_0$, are described by the same Brownian motion with the diffusion coefficient $D = \Delta^2/2\tau_0$. However, the entropy production differs from each other evidently, i.e., that of the case (i) is four times larger than that of (ii). This fact tells us that the Fokker-Planck equation and the Brownian motion are not used for the purpose to calculate the correct entropy production, at least, when the original master equation describes a discrete stochastic process. However they well describe the long time evolution of the probability itself due to the central limit theorem. The entropy production is due to the short time behavior of fluctuations, i.e., the detailed imbalance relation. Entropy is created at each discrete jump process such as reactive collisions among atoms or molecules in the chemical reaction. Let us call it the elementary process of entropy production.

Secondly, let us introduce the *path weight principle*, which is a kind of correspondence rule for recovering this difficulty. The above consideration suggests us that in order to calculate a correct entropy production in the present Fokker-Planck scheme, we should take account of the information how many elementary processes are included in a given continuous stochastic path.

For example, let us consider a chemical reaction network,

$$\rho\text{th reaction:} \qquad \sum_i \nu_{\rho i}\mathrm{X}_i \underset{\overline{\kappa}_\rho}{\overset{\kappa_\rho}{\rightleftharpoons}} \sum_i \overline{\nu}_{\rho i}\mathrm{X}_i. \tag{5·1}$$

The elementary random walk is each reactive collision which causes $\Delta Y_\rho = \pm 1$ in a mean interval $\kappa_\rho^{-1}(\overline{\kappa}_\rho^{-1})$, where Y_ρ is a reaction coordinate of the ρth reaction defined by

$$\delta X_i = \sum_\rho (\overline{\nu}_{\rho i} - \nu_{\rho i})\delta Y_\rho. \tag{5·2}$$

With use of the reaction coordinates as the set of stochastic variables, the frequency of the plus and minus reactions in the ρth-direction per unit time is related to the second moment of the transition probability,

$$2\Omega D'^{\mathrm{st}}_\rho = W(\Delta Y_\rho = +1)(+1)^2 + W(\Delta Y_\rho = -1)(-1)^2, \tag{5·3}$$

when the reaction flow can be neglected in near equilibrium situations. This condition will be satisfied in the linearized, local equilibrium estimation below.

Thus the diffusion constants directly give the number of elementary random walks in a unit time, if the reaction rates satisfy $\kappa_\rho = \overline{\kappa}_\rho$. However, it is difficult to find a general correspondence rule for the population coordinate $\{X_i\}$ except for the following special cases.

5.1. *One-dimensional diffusion system*

In the diffusion model used in Section 4, the rate constants κ_ρ's are assumed to be a constant, κ, i.e.,

$$i\text{th reaction:} \qquad \mathrm{N}_i \underset{\kappa}{\overset{\kappa}{\rightleftharpoons}} \mathrm{N}_{i+1}, \qquad (i = 0, 1, 2, \ldots, L-1), \tag{5·4}$$

where $\mathrm{N}_0 = \mathrm{A}$ and $\mathrm{N}_L = \mathrm{B}$. The diffusion matrix in the reaction coordinates is given by a diagonal matrix $\{D'^{\mathrm{st}}_i \delta_{ij}\}$, where

$$D'^{\mathrm{st}}_i = \frac{\kappa}{2}(n^{\mathrm{st}}_i + n^{\mathrm{st}}_{i+1}), \tag{5·5}$$

with $n_i = N_i/\Omega$. The elementary process in this case is a jump of one particle in a given cell to the left or the right cells in the mean interval time, κ^{-1}, that is, the uniform random walk in the one-dimensional real space. Therefore, at least in this special case, the number of the elementary jump processes included in a continuous unit-time path of the ith-direction is given by the ratio, $2\Omega D'^{\mathrm{st}}_i/\kappa$. Then the correspondence rule in this case is given by

$$\dot{\eta}_i \longrightarrow 2\kappa^{-1}\Omega D'^{\mathrm{st}}_i \dot{\eta}_i, \tag{5·6}$$

where $\eta_\rho = Y_\rho/\Omega$. Thus, the diffusion constant can be used for the path weight.

In the concentration space $\{n_i\}$, let us assume that the same correspondence rule can be applied in the principal-axis space where the diffusion matrix $\{D^{\mathrm{st}}_{ij}\}$ is diagonalized, though we have no definite principle to determine the coefficient κ^{-1} itself in the present case. Note that this space is not necessarily equivalent to the reaction coordinate space $\{\eta_i\}$. We have linear relations,

$$\dot{n}_i = \sum_\rho (\delta_{\rho,i-1} - \delta_{\rho,i})\dot{\eta}_\rho, \tag{5·7}$$

and

$$D_{ij}^{\rm st} = \sum_{\rho} (\delta_{\rho,i-1} - \delta_{\rho,i})(\delta_{\rho,j-1} - \delta_{\rho,j}) D'^{\rm st}_{\rho}, \tag{5·8}$$

where $\delta_{\rho,i}$ is the usual Kronecker's symbol. However, this transformation is not represetned as a square matrix, i.e., not invertible and not an orthogonal transformation, Thus we get a *hypothetical* correspondence rule in the concentration space

$$\dot{n}_i \longrightarrow 2\kappa^{-1}\Omega D_{ij}^{\rm st} \dot{n}_j. \tag{5·9}$$

Let us call it the *path weight principle.*

As a conclusion, we have a corrected expression for the entropy production rate,

$$\langle \sigma_e \rangle' = -2\kappa^{-1}\Omega \ {\rm Tr}(\boldsymbol{\alpha} \mathbf{g}^{\rm st} \boldsymbol{\alpha}). \tag{5·10}$$

Here the prime means that the entropy production is modified by the path weight principle. Using the explicit forms of $\boldsymbol{\alpha}$ and $\mathbf{g}^{\rm st}$ in Section 4, we find a final result,

$$\langle \sigma_e \rangle' = \Sigma \int_0^{L\lambda} \frac{\mathcal{D}|\nabla n(x)|^2}{n(x)} dx, \tag{5·11}$$

in the continuum limit $L \to \infty$, where $\mathcal{D} = \kappa\lambda^2$ is the spatial diffusion constant again. This coincides just with the thermodynamic result, i.e., eq. (4·20).

5.2. *Chemical reaction network*

The path weight principle may be applied to the simple chemical reaction ($L = 3$) in Section 4.1 also. An easy result is given by

$$\langle \sigma_e \rangle' = \frac{2\kappa\Omega(\langle a \rangle - \langle b \rangle)^2}{9(\langle a \rangle + \langle b \rangle)}, \tag{5·12}$$

in a symetrized form near equilibrium. Compared with eq. (4·10), there is a difference of the factor 1/3.

The reason is very evident. We should treat the boundary effect more carefully for finite L. In the present case there are three different random walks in xy-plane, i.e. two boundary modes $\dot{Y}_0$ along x-axis and $\dot{Y}_2$ along y-axis in addition to the diagonal mode $\dot{Y}_1$ in the direction $(1, -1)$. Therefore, the elementary processes are not isotropic in xy-plane.

Instead of performing this ambiguous transformation, the reason of the factor 1/3 may be interpreted as that the irreversible circulations corresponding to both end reactions have not been taken into account in the present scheme. It can be easily shown that this factor 1/3 is removed exactly when the variables A and B are added in the set of stochastic variables as

$$\dot{A} = \kappa(X - A) - c, \tag{5·13}$$

$$\dot{X} = \kappa(A - 2X + Y), \tag{5·14}$$

$$\dot{Y} = \kappa(X - 2Y + B), \tag{5·15}$$

$$\dot{B} = \kappa(Y - B) - c', \tag{5·16}$$

where c and c' are parameters controlled by external equilibrium reservoirs to keep A and B constant. Here $c = \kappa(\langle X \rangle - A)$ and $c' = \kappa(\langle Y \rangle - B)$. Except for the matrix $\mathbf{K}^{\mathrm{st}}$ is modified slightly as

$$\mathbf{K}^{\mathrm{st}} = \kappa \begin{pmatrix} -1 & 1 & 0 & 0 \\ 1 & -2 & 1 & 0 \\ 0 & 1 & -2 & 1 \\ 0 & 0 & 1 & -1 \end{pmatrix}, \tag{5·17}$$

other quantities are just the same as those given in Section 4.2 for $L - 1 = 4$.

§6. Concluding remarks

We have shown that the entropy production of the Fokker-Planck equation derived from the master equation differs from that for the original master equation. The reason of this is clearly due to the fact that the master equation treats discrete events, but the Fokker-Planck equation is an approximation of the master equation. In the Fokker-Planck equation, the original discrete events are smoothed out. To evaluate the entropy production, one have to recover the discreteness of the events in the treatment of the corresponding Fokker-Planck equation. In order to overcome this problem, we have proposed the *path weight principle*. The entropy production from the corresponding Fokker-Planck equation is modified by multiplying the diffusion coefficient. For two simple examples, it has been demonstrated that the path weight principle yields the entropy production for the original master equation.

At present, we do not know whether the path weight principle can be applied for any kinds of master equations or not. But we believe that the path weight principle can be applied, at least, to the cases that jumps in the transitions are small compared with Ω, namely $|\Delta| \sim 1$.

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