Mesoscopic Thermodynamics of Nonequilibrium Open Systems. I. Negentropy Consumption and Residual Entropy

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In order to treat active phenomena of open systems, we present a mesoscopic-level formulation of nonequilibrium thermodynamics, which is adaptable to the intermediate level between microscopic description and macroscopic one. In this formulation, an open system is represented by a mesoscopic model $\mathfrak{M} = (\mathfrak{S}, \mathfrak{T}, s, \sigma, \gamma)$. $\mathfrak{S}$ is a set of mesoscopically coarse-grained states, each of which has the residual entropy $s(a)$ ($a \in \mathfrak{S}$). $\mathfrak{T}$ is a set of transitions τ from $I(\tau) \in \mathfrak{S}$ to $F(\tau) \in \mathfrak{S}$, and each $\tau \in \mathfrak{T}$ occurs at the transition probability rate $\gamma(\tau)$, and with the consumption $\sigma(\tau)$ of the negentropy stored within the environment. The dynamical quantity γ is related to the thermostatic ones s and σ through a postulate, *individual detailed balance*. This scheme is applied to various examples such as chemical reactions, reaction-random walks and lasers. A difference-operator method for lattice systems is also developed.

1. INTRODUCTION

There is a set of approaches to irreversible processes and fluctuations called the "mesoscopic level of description" by van Kampen,[1] who collected under this terminology various semiphenomenological stochastic descriptions by means of the Langevin equation, the Fokker–Planck (FP) equation, the master equation, and their modifications.[2] Such descriptions have two characteristics in common. The first is that the element-states over which the probability distribution is defined are not in general microscopic

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[2] For various examples of the mesoscopic level of description, see Refs. 1–3 and recent contributions to this Journal and others.

quantum states, but are representatives of groups of them, namely, mesoscopically coarse-grained states. The second is that the time-evolution law is closed within the description in a simple form; Markovian evolution or ones simply derived from it are usually assumed. These characteristics, together with the semiphenomenological nature, are the reason for the use of the terminology "mesoscopic level."

The mesoscopic approach has an enormous advantage in that it can fairly easily describe the time evolution of open systems as well as mesoscopic-level fluctuations. However, this advantage cannot be made full use of in discussing thermodynamic propositions about the second law, especially including the effect of the environment, which is usually described on the macroscopic level. The reason for this is the lack of *mesoscopic thermodynamics*, a mesoscopic-level formulation of thermodynamics which has a clear connection with macroscopic thermodynamics or microscopic statistical mechanics. The purpose of this paper is to supply the lack. In particular, it is intended to establish a unified scheme of mesoscopic thermodynamics which is useful in clarifying the thermodynamic aspects of entropy-decreasing processes accompanied with active behaviors seen in relatively small open systems or gatherings of them, such as energy conversion by lasing atoms; biosynthesis; active transport and information transfer by enzymes in a cell; and computation process of electronic machines.[4]

There are three problems to be solved in constructing the mesoscopic thermodynamics. The first is how to express the entropy function of an open system whose state is given by a probability distribution p over the element-states which are mesoscopically coarse grained. Usual definitions[6] for it are $-k\sum p \ln p$ or $-k\sum p \ln p/p_{st}$ with stationary state p_{st}. These are, however, based on a mere analogy with the statistical mechanical definition or a formal correspondence between the second law and the H-theorem of master equation systems. It is necessary to take account of the effect of mesoscopic coarse-graining as well as not to mix the entropy of the system with that of the environment. The second is how to treat the environmental entropy change so as to lead to the proper expression of the second law of open systems. The environment is not in general a single reservoir characterized by a temperature T, but may have more complex structures. For example, it consists of many reservoirs[9,10] with different temperatures or has the potentiality of chemical reactions. Hence, this problem is not so simple as in the case of equilibrium open systems, in which the reservoir effect can be easily taken into account by using the free energy instead of the entropy function. The third, on a settlement of the above two problems, is to know what postulate should be required in order to establish the second law.

In this paper these problems are all settled at one time by introducing a scheme called a mesoscopic model, which plays the same role in the mesoscopic thermodynamics as a microscopic model does in statistical mechanics. The mesoscopic model is supposed to provide a basis from which macroscopic thermodynamics and various types of mesoscopic descriptions are derived through prescribed procedures and, if necessary, with some limiting or approximation processes.

The mesoscopic model contains two basic functions, *residual entropy* (r.e.), $s(a)$, defined to each element state a and *elementary negentropy consumption* (e.n.c.), $\sigma(\tau)$, defined to each elementary process of state transition τ, and a fundamental postulate *individual detailed balance* (i.d.b.). The r.e. $s(a)$ means the thermodynamic entropy attached to the element state a due to the mesoscopic coarse-graining. By using it the first problem is answered; the entropy $S(p)$ is given by the sum of the information entropy $-k\sum p\ln p$ and the average of the r.e. $\sum ps$. The e.n.c. $\sigma(\tau)$ means the environmental entropy production *directly caused* by the elementary transition τ. Being viewed from the side of the system, this quantity should be called negentropy consumption. This terminology is also used in order to distinguish it from the total change of environmental entropy which is caused by various factors other than the transition τ. For the second problem the following form of the second law is proposed:

$$-\frac{d}{dt}S(p_t) \leqslant K(p_t) \tag{1.1}$$

with the negentropy consumption $K(p_t)$ of a state p_t which is defined by the average of e.n.c. $\sigma(\tau)$ multiplied by the transition probability rate $\gamma(\tau)$. Formula (1.1) expresses the statement that the entropy of the system cannot decrease more than the amount of consumed negentropy. The third problem is settled by the i.d.b. postulate [cf. Section 2.1 (vi)] which establishes a relation between s, σ, and γ and guarantees the second law in the form (1.1).

In Section 2, we present a precise definition of the mesoscopic model with its interpretations and explain some notations and conventions used in this paper. In Section 3, we investigate general properties of the mesoscopic model, including definitions of entropy production, equilibrium states, connectedness, and potential functions, and derive the second law in the form (1.1), fundamental formulas of equilibrium thermodynamics, and special expressions of the entropy production.

The remaining five sections are assigned to examples. In these examples we intend to demonstrate how to apply the mesoscopic model scheme, and also to develop a method of difference operators which is useful in treating lattice systems. The first example (Section 4) is a chemical reaction

system, where difference-operator versions of the Fokker–Planck operator are introduced. This example affords a basis for analysis of the other examples. The second one (Section 5) is a random-walk system accompanied by a chemical reaction, where the Einstein formula for the diffusion coefficient is extended. In the third example (Section 6) the random walker of Section 5 is put on a circular lattice and its stationary state is determined. The fourth example (Section 7) is a chemical laser in a simplified style, where the relations between laser gain and chemical potentials are discussed. The last example (Section 8) is the usual three-level laser pumped by a high-temperature beam, where we reveal a heat-engine structure of elementary cyclic processes contained in the stationary state. In the Appendix, some properties of translation and difference operators are listed.

2. MESOSCOPIC MODEL

2.1. Definition of Mesoscopic Model

A mesoscopic model $\mathfrak{M} = (\mathfrak{S}, \mathfrak{T}, s, \sigma, \gamma)$ is defined as follows:

(i) $\mathfrak{S}$ is a denumerable set (where elements are called *points* or *element states*).

(ii) $\mathfrak{T}$ is a denumerable set (*transitions*) with the "transition structure," that is, for every transition $\tau \in \mathfrak{T}$, the *initial point* $I(\tau) \in \mathfrak{S}$, the *final point* $F(\tau) \in \mathfrak{S}$, and the *inverse transition* $\tau^{-1} \in \mathfrak{T}$ are defined with the properties

$$(\tau^{-1})^{-1} = \tau, \qquad F(\tau^{-1}) = I(\tau), \qquad \text{and} \quad I(\tau^{-1}) = F(\tau) \qquad (2.1)$$

The sets $\mathfrak{T}_{a.} \equiv \{\tau \in \mathfrak{T}; I(\tau) = a\}$, $\mathfrak{T}_{.a} \equiv \{\tau \in \mathfrak{T}; F(\tau) = a\}$, and $\mathfrak{T}_{a,b} \equiv \{\tau \in \mathfrak{T}; I(\tau) = a \text{ and } F(\tau) = b\}$ are all finite, and $\mathfrak{T}_{a,a} = \varnothing$ for all $a \in \mathfrak{S}$.

(iii) s is a nonnegative function on $\mathfrak{S}$ (called *residual entropy*).

(iv) σ is a real function on $\mathfrak{T}$ (*elementary negentropy consumption*).

(v) γ is a strictly positive function on $\mathfrak{T}$ (*transition probability rate*).

(vi) Among s, σ, and γ, there is a relationship (called *individual detailed balance*) as follows:

$$\gamma(\tau) = \gamma(\tau^{-1}) \exp \frac{1}{k_B} \left[\sigma(\tau) + \Delta_\tau s \right] \qquad \forall \tau \in \mathfrak{T} \qquad (2.2)$$

where $\Delta_\tau s = s(F(\tau)) - s(I(\tau))$, and k_B is the Boltzmann constant.

(vii) The *state* of $\mathfrak{M}$ is represented by a probability distribution p on $\mathfrak{S}$. The time evolution of the state is given by the master equation

$$\frac{d}{dt} p_t = \Gamma p_t \qquad (2.3)$$

where the evolution operator Γ is defined by

$$\Gamma p(a) = \sum_{\tau \in \mathfrak{T}_{.a}} \left\{ p(I(\tau))\gamma(t) - p(F(\tau))\gamma(\tau^{-1}) \right\} \qquad (2.4)$$

(viii) The *entropy* $S(p)$ of a state p is given by

$$S(p) = -k_B \sum_{a \in S} p(a) \ln p(a) + \sum_{a \in S} p(a) s(a) \qquad (2.5)$$

(ix) The negentropy consumption $K(p)$ of a state p is given by

$$K(p) = \sum_{\tau \in \mathfrak{I}} p(I(\tau)) \gamma(\tau) \sigma(\tau) \qquad (2.6)$$

Remarks. (1) If the pairs $\{\tau, \tau^{-1}\}$ $(\tau \in \mathfrak{I}_{a,b})$ are suitably numbered by $r = 1, 2, \ldots, n$, the transition $\tau \in \mathfrak{I}_{a,b}$ can be represented as $\tau = a \overset{r}{\to} b$ with $I(a \overset{r}{\to} b) = a$, $F(a \overset{r}{\to} b) = b$, $\tau^{-1} = b \overset{r}{\to} a$. This notation, by which the condition (2.1) is naturally fulfilled, is useful in treating concrete examples.

(2) By definition, it is obvious that

$$\mathfrak{I}_{a\cdot} = \{\tau^{-1}; \tau \in \mathfrak{I}_{\cdot a}\} \qquad (2.7)$$

$$\mathfrak{I}_{\cdot a} = \{\tau^{-1}; \tau \in \mathfrak{I}_{a\cdot}\} \qquad (2.8)$$

$$\mathfrak{I}_{a,b} = \mathfrak{I}_{a\cdot} \cap \mathfrak{I}_{\cdot b} \qquad (2.9)$$

From (vi) and (v) it follows that

$$\sigma(\tau) = -\sigma(\tau^{-1}) \qquad (2.10)$$

(3) Henceforth, the mesoscopic model $\mathfrak{M}$ will be written as $\mathfrak{M} = (S, \mathfrak{I}, s, \sigma, \gamma; S, K, \Gamma, \ldots)$ if it is necessary to indicate that the entropy, the negentropy consumption, and the evolution operator are expressed by S, K, and Γ, respectively. The list after the semicolon ";" in the above notation may be supplied when something is defined universally applicable to all mesoscopic models. The fourth position of the list will be occupied by the entropy production P defined in Section 3.1.

2.2. Interpretation of Mesoscopic Model

The mesoscopic model $\mathfrak{M}$ has the following meaning:

(i) Let $\mathcal{K}$ be the Hilbert space representing the quantum states of the system under consideration. The points $a \in S$ are interpreted as states represented by density operators ρ_a on $\mathcal{K}$ which are disjoint and complete in the following sense: $N(\rho_a)^\perp \perp N(\rho_b)^\perp$ if $a \neq b$, and $\oplus_{a \in S} N(\rho_a)^\perp = \mathcal{K}$, where $N(\rho)^\perp$ is the orthogonal complement of the null space $N(\rho) \equiv \{\psi \in \mathcal{K}; \rho\psi = 0\}$.

In this situation, a state p, a probability distribution on S, is identified with the state represented by the density operator

$$\rho \equiv \sum_{a \in S} p(a) \rho_a \qquad (2.11)$$

Following the microscopic definition of entropy, the state p must have the entropy $S(p)$ defined as

$$S(p) = -k_B \operatorname{Tr} \rho \ln \rho = -k_B \operatorname{Tr}\left(\sum p(a)\rho_a\right) \ln\left(\sum p(a)\rho_a\right)$$

$$= -k_B \sum p(a) \ln p(a) + \sum p(a)(-k_B \operatorname{Tr} \rho_a \ln \rho_a) \qquad (2.12)$$

where the last equality is implied by the disjointness of ρ_a's mentioned above. The residual entropy $s(a)$ is, then, interpreted as

$$s(a) = -k_B \operatorname{Tr} \rho_a \ln \rho_a \qquad (2.13)$$

This does not disappear even if the specification of the state is complete on the mesoscopic level. If ρ_a is a projection onto a subspace $A(a)$ of $\mathcal{H}$, then

$$s(a) = k_B \ln \dim A(a) \qquad (2.14)$$

where $\dim A(a)$ is, in other words, the number of the microstates contained in a.

(ii) A transition $\tau \in \mathfrak{T}$ means an elementary reversible process from the initial point $I(\tau)$ to the final point $F(\tau)$ which occurs at the t.p.r. $\gamma(\tau)$ independently of the other transitions. Between two points a and b there may be many kinds of transitions, which form the sets $\mathfrak{T}_{a,b}$ and $\mathfrak{T}_{b,a}$. If an extensive quantity, such as energy, volume, or particle number, is let out from the system to the environment by an amount $f(\tau)$ associated with the transition τ (the influx to the system is expressed by a negative amount), then the reversibility of the transitions involves

$$f(\tau) = -f(\tau^{-1}) \qquad (2.15)$$

The e.n.c. $\sigma(\tau)$ is measured, as mentioned in the Introduction, by the environmental entropy change directly attributed to the transition τ.

Finally, it is expected that within each element state a there are no sublevel processes that cause environmental entropy change or modification of the density operator ρ_a.

In this situation, the time-evolution law is naturally described by (2.3) and (2.4), and the quantity $K(p)$ defined by (2.5) has the meaning of the average negentropy consumption in the state p per unit time.

From the meaning of σ, we can obtain its explicit form in special cases. For example, let us consider the case in which the environment is characterized by temperature T, pressure π, and chemical potentials μ_i of substances i, and the system lets out to the environment $\epsilon(\tau)$ amount of energy, $v(\tau)$ amount of volume, $n_i(\tau)$ number of i molecules accompanied with each transition τ. Then,

$$\sigma(\tau) = \frac{1}{T}\epsilon(\tau) + \frac{\pi}{T}v(\tau) - \sum_i \frac{\mu_i}{T}n(\tau) \qquad (2.16)$$

and the reversibility (2.15) implies

$$\epsilon(\tau) = -\epsilon(\tau^{-1}) \tag{2.17a}$$

$$v(\tau) = -v(\tau^{-1}) \tag{2.17b}$$

$$n_i(\tau) = -n_i(\tau^{-1}) \tag{2.17c}$$

A mechanical environment is characterized by no capacity for entropy. It has no negentropy to be consumed. In this case,

$$\sigma(\tau) = 0 \tag{2.18}$$

Let us consider a more complicated situation. The environment consists of a mechanical part R_0 and thermal parts R_l ($l = 1, \ldots, n$) with the thermodynamic parameters T^l, π^l, and μ_i^l, and the transition set $\mathfrak{T}$ decomposed into $\mathfrak{T} = \mathfrak{T}_0 \cup \mathfrak{T}_1 \cup \cdots \cup \mathfrak{T}_n$ (disjoint union) such that the transitions $\tau \in \mathfrak{T}_l$ are coupled with R_l in the same way as in the above examples, for $l = 0, 1, \ldots, n$. It should be noted that a transition τ and its inverse τ^{-1} are contained in the same class of the decomposition. In this case, we have

$$\sigma(\tau) = \begin{cases} \dfrac{1}{T^l}\epsilon(\tau) + \dfrac{\pi^l}{T^l}v(\tau) - \displaystyle\sum_i \dfrac{\mu_i^l}{T^l}n_i(\tau) & \text{for} \quad \tau \in \mathfrak{T}_l \ (l \neq 0) \\ 0 & \text{for} \quad \tau \in \mathfrak{T}_0 \end{cases} \tag{2.19}$$

and ϵ, v, and n_i fulfill (2.17). Moreover, the flows of energy, volume, and i molecules from the system to R_l ($l \neq 0$) are defined as follows:

$$J_\epsilon^l(p) = \sum_{\tau \in \mathfrak{T}_l} p(I(\tau))\gamma(\tau)\epsilon(\tau) \tag{2.20a}$$

$$J_v^l(p) = \sum_{\tau \in \mathfrak{T}_l} p(I(\tau))\gamma(\tau)v(\tau) \tag{2.20b}$$

$$J_i^l(p) = \sum_{\tau \in \mathfrak{T}_l} p(I(\tau))\gamma(\tau)n_i(\tau) \tag{2.20c}$$

These flows are also defined likewise for $l = 0$ if the transfers of energy, volume, or molecules occur with $\tau \in \mathfrak{T}_0$. The n.c. $K(p)$ is, then, written in the form

$$K(p) = \sum_{l=1}^{n} K^l(p)$$

$$K^l(p) \equiv \frac{1}{T^l}J_\epsilon^l(p) + \frac{\pi^l}{T^l}J_v(p) - \sum_i \frac{\mu_i^l}{T^l}J_i^l(p) \tag{2.21}$$

(iii) The i.d.b. condition (vi) of Section 2.1 is a postulate which is supposed to hold in the situation where the above interpretations of $\mathfrak{S}$ and $\mathfrak{T}$ are valid. If one pair of transitions $\{\tau, \tau^{-1}\}$ alone is allowed to occur, this

postulate is equivalent to combination of the two requirements for the equilibrium state p_{eq} defined on the pair of points $\{I(\tau), F(\tau)\}$. One is Einstein's fluctuation-entropy relation

$$p_{eq}(F(\tau))/p_{eq}(I(\tau)) = \exp\frac{1}{k_B}\left[\Delta_\tau s + \sigma(\tau)\right] \qquad (2.22)$$

and the other is the detailed balance condition

$$p_{eq}(I(\tau))\gamma(\tau) = p_{eq}(F(\tau))\gamma(\tau^{-1}) \qquad (2.23)$$

These can be required for individual pairs $\{\tau, \tau^{-1}\}$, since all the transitions occur independently of one another. Hence, this postulate will be naturally acceptable.

The significance and the usefulness of the postulate can be seen from the consequences and examples shown in the following sections and in subsequent papers.

2.3. Notations and Conventions

The linear space of all real functions on $\mathbb{S}$ is denoted by $\mathcal{F}(\mathbb{S})$. For a subset $A \subset \mathbb{S}$ and $f, g \in \mathcal{F}(\mathbb{S})$, the following notations are formally defined:

$$\langle f \rangle_A = \sum_{a \in A} f(a) \qquad (2.24)$$

$$\langle f, g \rangle_A = \langle fg \rangle_A \qquad (2.25)$$

Especially, $\langle\ \rangle \equiv \langle\ \rangle_\mathbb{S}$ and $\langle\ ,\ \rangle \equiv \langle\ ,\ \rangle_\mathbb{S}$. Note that the value of $\langle f \rangle_A$ is definable only when $\sum_A |f(a)| < \infty$.

All the operators on $\mathcal{F}(\mathbb{S})$ that appear in this paper are of the finite-matrix type, i.e., for an operator L of this type there exists a $\mathbb{S} \times \mathbb{S}$-indexed matrix $(L_{a,b})$ such that every column and every row have only a finite number of nonzero components and

$$Lf(a) = \sum_b L_{a,b}f(b) \qquad (2.26)$$

The adjoint operator L^* of L is defined by its corresponding matrix $(L^*_{a,b})$ as $L^*_{a,b} = L_{b,a}$. Between L and L^* there is the well-known relationship

$$\langle L^*f, g \rangle = \langle f, Lg \rangle \qquad (2.27)$$

for $f, g \in \mathcal{F}(\mathbb{S})$ such that $\sum_a \sum_b |f(a)L_{a,b}g(b)| < \infty$. For example, the evolution operator Γ defined by (2.5) is of this type since $\mathcal{T}_a.$ and $\mathcal{T}._a$ are finite [cf. (ii) of Section 2.1].

$$\langle f, \Gamma g \rangle = \sum_{a \in \mathbb{S}} f(a) \sum_{\tau \in \mathcal{T}._a} \left\{ g(I(\tau))\gamma(\tau) - g(F(\tau))\gamma(\tau^{-1}) \right\}$$

$$= \sum_{\tau \in \mathcal{T}} (\Delta_\tau f)\gamma(\tau)g(I(\tau)) \qquad (2.28)$$

where

$$\Delta_\tau f = f(F(\tau)) - f(I(\tau)) \tag{2.29}$$

and (2.7) and (2.8) have been used. Formula (2.29) implies

$$\Gamma^* f(a) = \sum_{\tau \in \mathfrak{T}_a} \gamma(\tau) \Delta_\tau f \tag{2.30}$$

The following conventions are adopted:

$$0 \cdot (\pm \infty \text{ for an undefined quantity}) = 0 \tag{2.31}$$

Especially,

$$0 \ln 0 = 0, \qquad 0 \ln \infty / \infty = 0, \qquad 0 \ln 0 / 0 = 0, \dots \tag{2.32}$$

Other than this, the usual conventions regarding the arithmetic of ∞ are adopted, so long as the indefinite forms ∞ / ∞ and $\infty - \infty$ do not appear or are eliminated by the above rules.

Remark. In the case of infinite $\mathfrak{S}$, there is a possibility that the infinite sum in (2.5) or (2.6) does not converge absolutely for some p, and $S(p)$ or $K(p)$ is indefinable. Such a state p should be excluded from consideration by regarding it as physically unrealizable. This standpoint is generally adopted in this paper; we are concerned only with physically realizable states, which are assumed to be well-behaving in the situations that contain limiting procedures, such as the infinite sum by the operation $\langle \, \rangle$ or the exchange of the order of d/dt and $\langle \, \rangle$. By this we can avoid entering the maze of mathematical analysis.

3. GENERAL PROPERTIES OF MESOSCOPIC MODEL

3.1. Definition of Entropy Production and the Second Law

(i) Let $\mathfrak{M} = (\mathfrak{S}, \mathfrak{T}, s, \sigma, \gamma; S, K, \Gamma)$ be a mesoscopic model. We defined the entropy production $P(p)$ of a state p by the sum of the entropy change of the system and that of the environment which is caused by the interaction with the system, i.e.,

$$P(p) = \frac{d}{dt} S(p_t) \bigg|_{t=0} + K(p) \tag{3.1}$$

where p_t is the solution of (2.3) with initial condition $p_0 = p$. Since $\langle \dot{p}_t \rangle = \langle \Gamma p_t \rangle = 0$,

$$\frac{d}{dt} S(p_t) \bigg|_{t=0} = \langle \Gamma p, (-k_B \ln p + s) \rangle \tag{3.2}$$

By applying (2.28) to (3.2) and using (2.6), formula (3.1) is written in the

form

$$P(p) = \sum_{\tau \in \mathscr{T}} p(I(\tau))\gamma(\tau)\left[-k_B \Delta_\tau \ln p + \Delta_\tau s + \sigma(\tau)\right] \qquad (3.3)$$

Moreover, application of the i.d.b. condition yields

$$P(p) = k_B \sum_{\tau \in \mathscr{T}} p(I(\tau))\gamma(\tau) \ln \frac{p(I(\tau))\gamma(\tau)}{p(F(\tau))\gamma(\tau^{-1})} \qquad (3.4)$$

(ii) Since $x \ln(x/y) \geqslant x - y$ ($x \geqslant 0$, $y \geqslant 0$) with equality iff $x = y$, we obtain

$$P(p) \geqslant 0 \qquad (3.5)$$

and

$$P(p) = 0 \qquad \text{iff } p(I(\tau))\gamma(\tau) = p(I(\tau^{-1}))\gamma(\tau^{-1}) \qquad \forall \tau \in \mathscr{T} \quad (3.6)$$

From definition (3.1),

$$P(p_t) = \frac{d}{dt} S(p_t) + K(p_t) \qquad (3.7)$$

where p_t is a solution of (2.3). Therefore inequality (3.5) implies

$$-\frac{d}{dt} S(p_t) \leqslant K(p_t) \qquad (3.8)$$

Thus we have had the second law in the form (1.1).

3.2. Characterization of Equilibrium States

We propose the following characterization of equilibrium states:

$$\text{A state } p \text{ is equilibrium iff } P(p) = 0 \qquad (3.9)$$

This type of characterization of equilibrium states is seen in recent papers,[5-7] which will be referred to in the last section. The characterization (3.9) can be restated in several equivalent forms. From (3.6), we have

$$p \text{ is equilibrium iff } p \text{ fulfills the d.b.} \qquad (3.10)$$

where the d.b. (detailed balance) means the right-hand side of (3.6). By (2.10), $K(p)$ is written as

$$K(p) = \tfrac{1}{2} \sum_{\tau \in \mathscr{T}} \left\{ p(I(\tau))\gamma(\tau) - p(F(\tau))\gamma(\tau^{-1})\right\}\sigma(\tau) \qquad (3.11)$$

Consequently, the d.b. implies $K(p) = 0$ as well as $\Gamma p = 0$ [cf. (2.4)]. Conversely, combination of $K(p) = 0$ and $\Gamma p = 0$ implies $P(p) = 0$. Therefore, we have another characterization of equilibrium states:

$$p \text{ is equilibrium iff } \Gamma \text{ip} = 0 \text{ and } K(p) = 0 \qquad (3.12)$$

Next, let us consider the case in which σ is given by (2.19). The flows $J.(p)$ defined by (2.20) are also written in the same way as (3.11) owing to (2.17). Hence, the d.b. also implies $J.(p) = 0$, and this further implies $K(p) = 0$ [cf. (2.21)]. Thus we have

$$p \text{ is equilibrium iff } \Gamma p = 0 \text{ and } J.(p) = 0 \qquad (3.13)$$

These characterizations are all reasonable for equilibrium states. By any of these we can distinguish the equilibrium states from the stationary states. The equality of (3.8) holds iff p_t is an equilibrium state. If the mesoscopic model $\mathfrak{M}$ has no equilibrium state, the equality is never realized, even though p_t is stationary. The relation between this definition (3.9) and the usual static one is discussed in Section 3.6.

3.3. Definition of Connectedness

Let $\mathfrak{M} = (\mathfrak{S}, \mathfrak{T}, s, \sigma, \gamma; S, K, \Gamma, P)$ be a mesoscopic model. A finite sequence of transitions $(\tau_1, \tau_2, \ldots, \tau_n)$ is called $(n-)$ path, iff $F(\tau_i) = I(\tau_{i+1})$ for $i = 1, \ldots, n-1$. Two points a and $b \in \mathfrak{S}$ are said to be connected and written as $a \sim b$ iff $a = b$ or there exists a path $(\tau_1, \ldots, \tau_n)$ such that $I(\tau_1) = a$ and $F(\tau_n) = b$. By definition, it is obvious that the relation has the reflexivity $a \sim a$, and the transitivity $a \sim b \sim c \Rightarrow a \sim c$. It has also the symmetry $a \sim b \Rightarrow b \sim a$, since the transitions are reversible. Therefore, "$\sim$" is an equivalence relation. A connected class α of $\mathfrak{S}$ is defined as a subset of $\mathfrak{S}$ whose elements are connected to each other and are not to the other points. The set of all the connected classes is written as $\mathfrak{S}/\sim$. The set $\mathfrak{S}/\sim$ makes a partition of $\mathfrak{S}$, that is, $\alpha \cap \beta = \emptyset$ if $\alpha \neq \beta$ for $\alpha, \beta \in \mathfrak{S}/\sim$, and $\mathfrak{S} = \cup \alpha$ $(\alpha \in \mathfrak{S}/\sim)$. The mesoscopic model $\mathfrak{M}$ is said to be connected iff $\mathfrak{S}/\sim = \{\mathfrak{S}\}$, i.e., any two points in $\mathfrak{S}$ are connected.

To each connected class $\alpha \in \mathfrak{S}/\sim$, we define a mesoscopic model $\mathfrak{M}_\alpha = (\alpha, \mathfrak{T}_\alpha, s, \sigma, \gamma; S_\alpha, K_\alpha, \Gamma_\alpha, P_\alpha)$, where $\mathfrak{T}_\alpha = \{\tau \in \mathfrak{T}; F(\tau) \in \alpha \text{ and } I(\tau) \in \alpha\}$, and s, σ, and γ are the same as in $\mathfrak{M}$ except that their domains of definition are restricted to α or $\mathfrak{T}_\alpha$. Evidently, any connected component is a connected mesoscopic model. For a state p of $\mathfrak{M}$ and a connected class α for which $p(\alpha) \equiv \sum_{a \in \alpha} p(a) > 0$, we define a state p_α of $\mathfrak{M}_\alpha$ by $p_\alpha = p/p(\alpha)$. Between $\mathfrak{M}$ and $\mathfrak{M}_\alpha$, there are the following relationships:

$$\Gamma p(a) = p(\alpha) \Gamma_\alpha p_\alpha(a) \qquad \text{if} \quad a \in \alpha \qquad (3.14)$$

$$S(p) = -k_B \sum_\alpha p(\alpha) \ln p(\alpha) + \sum_\alpha p(\alpha) S_\alpha(p_\alpha) \qquad (3.15)$$

$$K(p) = \sum_\alpha p(\alpha) K_\alpha(p_\alpha) \qquad (3.16)$$

$$P(p) = \sum_\alpha p(\alpha) P_\alpha(p_\alpha) \qquad (3.17)$$

From (3.14), it follows that if p_t is a solution of $\dot{p}_t = \Gamma p_t$ then $p_t(\alpha)$ $= p_0(\alpha)$ $\forall t > 0$ for any $\alpha \in \mathbb{S}/\sim$. Moreover, if p is stationary then p_α is also stationary for any $\alpha \in \mathbb{S}/\sim$ for which $p(\alpha) > 0$. Conversely if p^α is a stationary state of $\mathfrak{M}_\alpha$ for $\alpha \in \mathcal{C}$ (where $\mathcal{C}$ is a subset of $\mathbb{S}/\sim$), then the states of $\mathfrak{M}$ defined by

$$p = \sum_{\alpha \in \mathcal{C}} r_\alpha p^\alpha; \qquad \sum r_\alpha = 1, \qquad r_\alpha \geqslant 0 \qquad (3.18)$$

are all stationary, where p^α is regarded as a state of $\mathfrak{M}$ by assigning zero to $a \notin \alpha$.

From (3.17), we have $P(p) \geqslant p(\alpha)P_\alpha(p_\alpha)$. Hence, if p is an equilibrium state of $\mathfrak{M}$ and $p(\alpha) \neq 0$, then p_α is also an equilibrium state of $\mathfrak{M}_\alpha$. Conversely, if p^α is an equilibrium state of $\mathfrak{M}_\alpha$ for $\alpha \in \mathcal{C}$, then the states defined by (3.18) are all equilibrium. A connected mesoscopic model has at most one equilibrium state, which is implied by (3.10). Let $\mathcal{C}$ be the set of the connected classes which have equilibrium states, and p_{eq}^α be an equilibrium state of $\mathfrak{M}_\alpha$ ($\alpha \in \mathcal{C}$), which is unique since $\mathfrak{M}_\alpha$ is connected. The set of the equilibrium states of $\mathfrak{M}$ is, then, given by

$$\left\{ \sum_{\alpha \in \mathcal{C}} r_\alpha p_{eq}^a \middle| \sum r_\alpha = 1, r_\alpha \geqslant 0 \right\} \qquad (3.19)$$

The above considerations show that the properties of mesoscopic models can be straightforwardly constructed from those of connected models.

3.4. Definition of Potential Function

Let $\mathfrak{M} = (\mathbb{S}, \mathfrak{T}, s, \sigma, \gamma)$ be a mesoscopic model. A real function ψ on $\mathbb{S}$ is called a *potential function* of $\mathfrak{M}$ iff it satisfies the equation

$$\sigma(\tau) = \Delta_\tau \psi \qquad \forall \tau \in \mathfrak{T} \qquad (3.20)$$

The potential function ψ is said to be normalizable in a connected class α iff

$$\Xi_\alpha(\psi + s) < \infty \qquad (3.21)$$

where $\Xi_A(f)$ is defined for $f \in \mathfrak{F}(\mathbb{S})$ and $A \subset \mathbb{S}$ by

$$\Xi_A(f) = \left\langle \exp \frac{1}{k_B} f \right\rangle_A \qquad (3.22)$$

Note that the potential function does not always exist for every mesoscopic model. $\mathfrak{M}$ is called a (normalizable) potential system iff it has a potential function (normalizable in every connected class).

The general solution of

$$\Delta_\tau g = 0 \qquad \forall \tau \in \mathfrak{T} \qquad (3.23)$$

is given by

$$g(a) = G(\tilde{a}) \tag{3.24}$$

where G is an arbitrary function on $\mathbb{S}/\sim$, and $\tilde{a}$ is the connected class containing the point a. If $\mathfrak{M}$ is connected, g is constant on $\mathbb{S}$. The potential function has arbitrariness of the addition of g. The normalizability of ψ is free from the arbitrariness, because $\Xi_\alpha(f + c) = e^{c/k_B}\Xi_\alpha(f)$ for every constant c.

A path $(\tau_1, \ldots, \tau_n)$ is said to be *cyclic* iff $F(\tau_n) = I(\tau_1)$. In order that equation (3.20) have a solution, it is sufficient and necessary that for every cyclic path $(\tau_1, \ldots, \tau_n)$

$$\sum_{i=1}^{n} \sigma(\tau_i) = 0 \tag{3.25}$$

The necessity is evident. In order to prove the sufficiency, we specify a point a_α for each connected class α. For every $a \in \alpha$ we take a path $(\tau_1, \ldots, \tau_n)$ such that $I(\tau_1) = a_\alpha$ and $F(\tau_n) = a$, and define a function ψ on $\mathbb{S}$ by

$$\psi(a) = \sum_{i=1}^{n} \sigma(\tau_i) \tag{3.26}$$

If (3.25) is fulfilled, the function is well defined, i.e., it is independent of the choice of the paths. If $I(\tau) = a$ and $F(\tau) = b$, then

$$\psi(b) = \sum_{i=1}^{n} \sigma(\tau_i) + \sigma(\tau) = \psi(a) + \sigma(\tau) \tag{3.27}$$

Hence $\Delta_\tau \psi = \sigma(\tau)$, which shows that ψ is a potential function.

3.5. Relationship between Potential Function and Equilibrium States

Let $\mathfrak{M}$ be a connected mesoscopic model with a normalizable potential function ψ. Then it follows that $\mathfrak{M}$ has a unique equilibrium state p_{eq}, which is written as

$$p_{eq} = \Xi(\psi + s)^{-1}\exp\frac{1}{k_B}(s + \psi) \tag{3.28}$$

This is easily checked by (3.10) and (3.20). From (3.28), we have three statements regarding p_{eq}:

(i) $S(p) + \langle p, \psi \rangle = \max \qquad$ iff $\quad p = p_{eq}$ (3.29)

(ii) $p_{eq}(a) = \exp\frac{1}{k_B}\left[s(a) - S_{eq} + \psi(a) - \psi_{eq}\right]$ (3.30)

(iii) $S_{eq} = k_B\ln\Xi(\psi + s) - \psi_{eq}$ (3.31)

where $S_{eq} = S(p_{eq})$ and $\psi_{eq} = \langle \psi, p_{eq} \rangle$. Statements (i), (ii), and (iii) are considered to correspond, respectively, to the entropy-maximal principle for the equilibrium states of open systems, to Einstein's formula for the equilibrium fluctuations,[8] and to the fundamental equation of equilibrium thermodynamics. These correspondences will be more clear, if ψ has the form $\psi = \lambda_1 f_1 + \cdots + \lambda_n f_n$ with environmental parameters $\lambda_1, \ldots, \lambda_n$. In this case, (3.31) leads to

$$dS_{eq} = - \sum_i \lambda_i df_{ieq} \tag{3.32}$$

where $f_{ieq} = \langle f_i, p_{eq} \rangle$ are treated as functions of $\lambda_1, \ldots, \lambda_n$.

Finally, it should be noted that if $\mathfrak{M}$ is connected and has an equilibrium state p_{eq}, then it also has a potential function ψ, which satisfies (3.28) or equivalently,

$$\psi = k_B \ln p_{eq} - s + \text{const} \tag{3.33}$$

3.6. Equilibrium Thermodynamics

Let $\mathfrak{M}$ be a connected mesoscopic model whose e.n.c. σ is given by (2.16). Assume that for every substance i the number N_i of i molecules can be defined as a function on $\mathfrak{S}$ with the relation

$$n_i(\tau) = -\Delta_\tau N_i \qquad \forall \tau \in \mathfrak{T} \tag{3.34}$$

This assumption means that the system contains no chemical reactions and the numbers of molecules are conservative. Since the volume V and the energy E are universally conservative, we have

$$v(\tau) = -\Delta_\tau V \tag{3.35}$$

$$\epsilon(\tau) = -\Delta_\tau E \tag{3.36}$$

In this case, $\mathfrak{M}$ has a potential function ψ defined by

$$\psi = -\frac{1}{T} E - \frac{\pi}{T} V + \sum_i \frac{\mu_i}{T} N_i \tag{3.37}$$

If this ψ is normalizable, the three statements in the previous subsection are translated into

(i) $S(p) - \dfrac{1}{T} \langle E, p \rangle - \dfrac{\pi}{T} \langle V, p \rangle + \sum_i \dfrac{\mu_i}{T} \langle N_i, p \rangle = \max$ iff $p = p_{eq}$

$$\tag{3.38}$$

(ii) $p_{eq}(a) = \exp \dfrac{1}{k_B} \left\{ [s(a) - S_{eq}] - \dfrac{1}{T} [E(a) - E_{eq}] \right.$

$$\left. - \frac{\pi}{T} [V(a) - V_{eq}] + \sum_i \frac{\mu_i}{T} [N_i(a) - N_{ieq}] \right\} \tag{3.39}$$

where $S_{eq} = S(p_{eq})$, $E_{eq} = \langle E, p_{eq} \rangle, \ldots$.

$$(iii) \quad S_{eq} = Y + \frac{1}{T} E_{eq} + \frac{\pi}{T} V_{eq} - \sum_i \frac{\mu_i}{T} N_{ieq} \tag{3.40}$$

where $Y = k_B \ln \Xi(\psi + s)$. Morever, we have

$$dS_{eq} = \frac{1}{T} dE_{eq} + \frac{\pi}{T} dV_{eq} - \sum \frac{\mu_i}{T} dN_{ieq} \tag{3.41}$$

where S_{eq}, E_{eq}, V_{eq}, and N_{ieq} are treated as functions of T, π, μ_i. The thermodynamic interpretations mentioned in the previous section fit this case perfectly. It should be remarked that Einstein's formula for equilibrium fluctuations holds with equality rather than proportionality[8] if the usually adopted entropy difference $\Delta s = s(a) - \max s(a)$ is replaced with $\Delta s = s(a) - S_{eq}$. S_{eq} does not agree with $\max s(a)$ on the mesoscopic level.

3.7. *K* and *P* of Potential Systems

Let $\mathfrak{M}$ be a connected mesoscopic model with a potential function ψ. Then substitution of (3.20) to (2.6) and (3.3) yields

$$K(p) = \sum_{\tau \in \mathfrak{I}} p(I(\tau)) \gamma(\tau) \Delta_\tau \psi \tag{3.42}$$

$$P(p) = \sum_{\tau \in \mathfrak{I}} p(I(\tau)) \gamma(\tau) \Delta_\tau (-k_B \ln p + s + \psi) \tag{3.43}$$

which, by (2.28), lead to

$$K(p) = \langle \Gamma p, \psi \rangle \tag{3.44}$$

$$P(p) = -k_B \langle \Gamma p, \ln p e^{-(s+\psi)/k_B} \rangle \tag{3.45}$$

Moreover, if p_t is a solution of (2.3), then

$$P(p_t) = -k_B \frac{d}{dt} \langle p_t, \ln p_t e^{-(s+\psi)/k_B} \rangle \tag{3.46}$$

In the case of normalizable ψ, we obtain by (3.33)

$$P(p_t) = -k_B \frac{d}{dt} \langle p_t, \ln p_t / p_{eq} \rangle \tag{3.47}$$

It should be remarked that formulas (3.42)–(3.47) are all true for nonconnected potential systems, for which (3.33) holds with respect to each connected component and any equilibrium state in the set (3.19) can be chosen as p_{eq} in (3.47). Formula (3.47) shows that any stationary state p_{st} of a potential system is always in equilibrium, because $P(p_{st}) = 0$. Hence, if a system exhibits some stationary activity with consumption of the negentropy reserved in the environment, it must be a nonpotential system.

3.8. Decomposition of Transition Set

Let $\mathfrak{M} = (\mathbb{S}, \mathfrak{T}, s, \sigma, \gamma; S, K, \Gamma, P)$ be a mesoscopic model. If $\mathfrak{T}$ is decomposed into $\mathfrak{T} = \mathfrak{T}_1 \cup \cdots \cup \mathfrak{T}_n$ (disjoint union) such that

$$\tau^{-1} \in \mathfrak{T}_l \qquad \text{if} \quad \tau \in \mathfrak{T}_l, \quad l = 1, \ldots, n \tag{3.48}$$

then $\mathfrak{M}_l = (\mathbb{S}, \mathfrak{T}_l, s, \sigma, \gamma; S, K, \Gamma, P)$ is also a mesoscopic model for $l = 1, \ldots, n$. Between $\mathfrak{M}$ and $\mathfrak{M}_l$, there are the following relationships:

$$S(p) = S_l(p), \qquad l = 1, \ldots, n \tag{3.49}$$

$$\Gamma = \Gamma_1 + \cdots + \Gamma_n \tag{3.50}$$

$$K(p) = K_1(p) + \cdots + K_n(p) \tag{3.51}$$

$$P(p) = P_1(p) + \cdots + P_n(p) \tag{3.52}$$

These are easily checked.

The case of the compound environment discussed in (ii) of Section 2.2 is an example of this decomposition. In this case, if the system has the function N_i defined by (3.34), then each $\mathfrak{M}_l$ has a potential function ψ^l such as

$$\psi^0 = 0$$

$$\psi^l = -\frac{1}{T^l} E - \frac{\pi^l}{T^l} V + \sum_i \frac{\mu_i^l}{T^l} N_i \qquad \text{if} \quad l \neq 0 \tag{3.53}$$

Therefore, we have from (3.45) and (3.52)

$$P(p) = -k_B \sum_{l=0}^{n} \left\langle \Gamma p, \ln p / e^{(\psi^l + s^l)/k_B} \right\rangle \tag{3.54}$$

This type of expression of entropy production has been adopted in the study of many-reservoir open systems.[9,10] Note that the expression of the type (3.46) or (3.47) is applicable only to potential systems and that (3.54) cannot be reexpressed as (3.46) or (3.47) except for special cases (e.g., $T^l = T$, $\pi^l = \pi$, $\mu_i^l = \mu_i$ for $l = 1, \ldots, n$), because many-reservoir models are, in general, nonpotential systems.

4. EXAMPLE 1: CHEMICAL REACTIONS IN A CELL

4.1. Model, Single-Reaction Case

Let us consider chemical reactions catalytically occurring in a cell which is enclosed with a fixed semipermeable wall and is immersed in a chemical medium with fixed temperature T and chemical potentials μ_i (see Fig. 1). First we are concerned with single-reaction case. The chemical
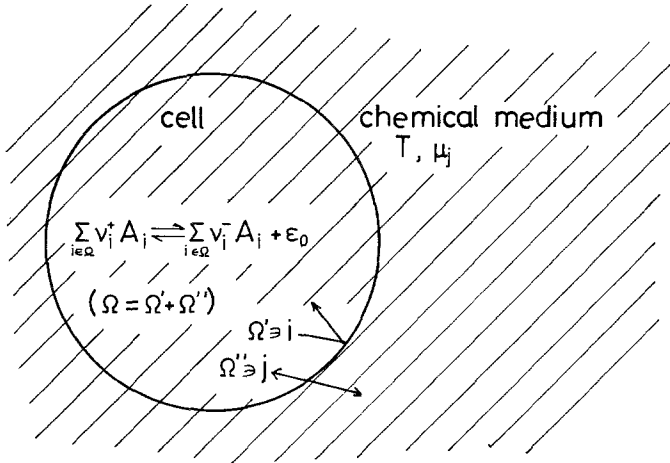
Fig. 1.   Chemical reaction in a cell enclosed with a semipermeable wall.

reaction is expressed by the reaction formula

$$\sum_{i \in \Omega} \nu_i^{+} A_i \rightleftarrows \sum_{i \in \Omega} \nu_i^{-} A_i + \epsilon_0 \tag{4.1}$$

where Ω is the set of the names of substances concerned in the reaction, $\nu_i^{\pm} (\geqslant 0)$ are the stoichiometric coefficients, A_i represent the molecular formula of i, and ϵ_0 is the energy the medium gains in the reaction (not the heat, which is defined by $\epsilon_0 + \sum \mu_i (\nu_i^{+} - \nu_i^{-})$).

The set Ω is decomposed into the set Ω' of substances nonpermeable through the wall of the cell and the set Ω'' of permeable ones. It is assumed that the permeability of Ω'' substances is so high that their densities are completely controlled by the chemical potentials of the medium. We also assume that the densities of $i \in \Omega$ are sufficiently low both in and outside the cell. In this situation, the mixture of the Ω' molecules in the cell can be treated as that of ideal particle fields each of which is subject to the Boltzmann statistics[11] with an effective energy level ϵ_i and an effective degeneracy $g_i V$ proportional to the cell volume V for $i \in \Omega'$. Here, g_i's and ϵ_i's depend on the physical properties of the medium, especially on the temperature. The medium containing Ω'' molecules acts as an environment for the Ω' mixture in the cell.

Let us construct a mesoscopic model $\mathfrak{M} = (\mathbb{S}, \mathfrak{T}, s, \sigma, \gamma)$ to describe the behavior of the Ω' mixture in the cell:

(1) $\mathbb{S} = \left\{ N = (N_i, i \in \Omega') \in \mathbf{Z}^{\Omega'}; N_i \geqslant 0 \quad \forall i \in \Omega' \right\}$

where $\mathbf{Z}$ is the set of integers and N_i denotes the number of i molecules in the cell for $i \in \Omega'$. $\mathbb{S}$ is, mathematically, a subset of $\mathbf{Z}^{\Omega'}$ in which the operations $x + y$ and mx $(x, y \in \mathbf{Z}^{\Omega'}, m \in \mathbf{Z})$ are defined in the usual vector sense.

$$\mathfrak{T} = \{ N \to N - \nu; N \in \mathbb{S} \cap (\mathbb{S} + \nu)\} \tag{2}$$

$$\cup \{ N \to N + \nu; N \in \mathbb{S} \cap (\mathbb{S} - \nu)\}$$

where $\mathbb{S} + x = \{N + x; N \in \mathbb{S}\}$ for $x \in \mathbf{Z}^{\Omega'}$, and

$$\nu = \nu^+ - \nu^- \qquad \text{with} \quad \nu^\pm = (\nu_i^\pm; i \in \Omega') \tag{4.2}$$

The transition $N \to N - (+)\nu$ is caused by the reaction in the direction $\to (\leftarrow)$ of (4.1).

(3) σ has the form (2.16) without the volume term.

$$n_j(N \to N \mp \nu) = \mp \nu_j \qquad j \in \Omega'' \tag{4.3}$$

$$\epsilon(N \to N \mp \nu) = \pm \epsilon_0 \tag{4.4}$$

$$\sigma(N \to N \mp \nu) = \pm \left(\epsilon_0 + \sum_{j \in \Omega''} \mu_j \nu_j\right)/T \equiv \pm \sigma_0 \tag{4.5}$$

where $\nu_j = \nu_j^+ - \nu_j^-$. By using the effective energy levels ϵ_i, the energy of the system is expressed as

$$E(N) = \sum_{i \in \Omega'} N_i \epsilon_i \equiv N \cdot \epsilon \tag{4.6}$$

Then it follows from the energy conservation that

$$\epsilon_0 = -E(N - \nu) + E(N) = \nu \cdot \epsilon \tag{4.7}$$

(4) As mentioned above, the system is subject to the Boltzmann statistics [cf. (2.14)]

$$s(N) = k_B \sum_{i \in \Omega'} \ln \frac{(g_i V)^{N_i}}{N_i!} \tag{4.8}$$

(5) There is no principle to determine γ a priori in the framework of mesoscopic thermodynamics, except that it must satisfy the i.d.b. condition, i.e., for $N \in \mathbb{S} \cap (\mathbb{S} + \nu)$

$$\gamma_+(N) = \gamma_-(N - \nu)\exp\frac{1}{k_B}\left[\sigma_0 + s(N - \nu) - s(N)\right] \tag{4.9}$$

where $\gamma_\pm \in \mathfrak{F}(\mathbb{S})$ are defined by

$$\gamma_\pm(N) = \begin{cases} \gamma(N \to N \mp \nu) & \text{if} \quad N \mp \nu \in \mathbb{S} \\ 0 & \text{otherwise} \end{cases} \tag{4.10}$$

For the sake of the conciseness of expression, we will use the factorial function[12] $x^{(n)}$ defined by

$$
x^{(n)} = \begin{cases} x(x-1) \cdots (x-n+1) & \text{if } n = 1, 2, 3, \ldots \\ 1 & \text{if } n = 0 \\ \dfrac{1}{(x+1)(x+2) \cdots (x-n)} & \text{if } n = -1, -2, \ldots \end{cases} \tag{4.11}
$$

From the definition, it follows that if m is a positive integer, then

$$
m^{(n)} = \begin{cases} m!/(m-n)! & \text{if } n \leqslant m \\ 0 & \text{if } m < n \end{cases} \tag{4.12}
$$

We also use the following notations for vectors $a = (a_i)$ and $b = (b_i)$:

$$
a^b = \prod_i a_i^{b_i}, \qquad a^{(b)} = \prod_i a_i^{(b_i)}, \qquad \text{and} \quad a! = \prod_i a_i! \tag{4.13}
$$

Using these notations and (4.12), we have, for N and $n \in \mathbb{S}$,

$$
N^{(n)} = 0 \qquad \text{if } N - n \notin \mathbb{S} \tag{4.14}
$$

4.2. Reaction Rate Coefficients

By definition, the functions $\gamma_\pm$ satisfy the conditions

$$
\gamma_\pm(N) \geqslant 0 \tag{4.15}
$$

$$
\gamma_\pm(N) = 0 \qquad \text{if } N \mp \nu \notin \mathbb{S}, \tag{4.16}
$$

$$
\gamma_+(N) = \gamma_-(N - \nu) e^{\sigma_0/k_B} N^{(\nu)} (gV)^{-\nu} \tag{4.17}
$$

where (4.17) follows from (4.8) and (4.9). The set of the above three conditions is fulfilled iff $\gamma_\pm$ can be written in the form

$$
\gamma_\pm(N) = C_\pm(N) N^{(\nu^\pm)} (gV)^{-\nu^\pm} \tag{4.18}
$$

with arbitrary functions $C_\pm$ on $\mathbb{S}$ such that

$$
C_\pm(N) \geqslant 0 \tag{4.19}
$$

and

$$
C_+(N) = C_-(N - \nu) e^{\sigma_0/k_B} \qquad \text{if } N - \nu \in \mathbb{S} \tag{4.20}
$$

This is straightforwardly checked by taking notice of (4.11) and (4.14).

If $C_\pm(N) \to c_\pm(\rho)$ for the thermodynamic limit $V \to \infty$ with $N_i/V \to \rho_i$, expression (4.18) shows that the quantities

$$
k_\pm(\rho) \equiv c_\pm(\rho) g^{-\nu^\pm} \tag{4.21}
$$

provide the reaction rate coefficients. Here, notice the fact that $N^{(\nu^{\pm})}/gV^{\nu^{\pm}} \to \rho^{\nu^{\pm}}/g^{\nu^{\pm}}$ for the thermodynamic limit. From (4.20) we obtain the equilibrium constant K:

$$K \equiv k_+(\rho)/k_-(\rho) = g^{-\nu}e^{\sigma_0/k_B} \qquad (4.22)$$

As for the thermodynamic limit of the mesoscopic model, we will have a thorough discussion in a subsequent paper.

4.3. Discrete Version of FP Operator

The evolution operator Γ is given by

$$\begin{aligned}\Gamma p(N) = {} & p(N + \nu)\gamma_+(N + \nu) - p(N)\gamma_+(N) \\ & + p(N - \nu)\gamma_-(N - \nu) - p(N)\gamma_-(N) \qquad (4.23)\end{aligned}$$

where, if $N \pm \nu \notin \mathbb{S}$, we put $p(N \pm \nu) = 0$ and use the rule (2.31).

Next, let us express Γ with the translation operator U_ν and the difference operators[3] Δ_ν defined on $\mathcal{F}(\mathbf{Z}^{\Omega'})$ by (A.8) and (A.9) in the Appendix. Operator expressions provide interesting information about the structure of Γ as well as convenience of handling. To this end, we identify $f \in \mathcal{F}(\mathbb{S})$ with the function $\bar{f} \in \mathcal{F}(\mathbf{Z}^{\Omega'})$ defined by $\bar{f} = f$ on $\mathbb{S}$, $\bar{f} = 0$ on $\mathbb{S}^c$. By this identification, $\mathcal{F}(\mathbb{S})$ is regarded as a subset of $\mathcal{F}(\mathbf{Z}^{\Omega'})$. Then, Γ and Γ^* are written in the forms

$$\Gamma = \Delta_\nu\gamma_+ \cdot + \Delta_{-\nu}\gamma_- \cdot \qquad (4.24)$$

and

$$\Gamma^* = \gamma_+\Delta_{-\nu} + \gamma_-\Delta_\nu \qquad (4.25)$$

where $\gamma_\pm$ are extended over $\mathbf{Z}^{\Omega'}$ by the above-mentioned identification, and $\gamma_\pm \cdot$ are defined as in (A.6). In the derivation of (4.25), (A.5) and (A.20) have been used. Since Γf and $\Gamma^* f \in \mathcal{F}(\mathbb{S})$ for $f \in \mathcal{F}(\mathbb{S})$, Γ and Γ^* can be regarded as operators on $\mathcal{F}(\mathbb{S})$.

By using the properties of Δ and U listed in the Appendix, Γ and Γ^* are reexpressed in various forms, which have analogy with the continuous Fokker–Planck (FP) operator.

(i) By using (A.15),

$$\Gamma = \Delta_\nu(\gamma_+ \cdot - U_{-\nu}\gamma_- \cdot) \qquad (4.26)$$

$$\Gamma^* = (\gamma_+ - \gamma_- U_{-\nu})\Delta_{-\nu} \qquad (4.27)$$

---

[3] Δ_ν should not be confused with Δ_r defined by (2.29).

Expression (4.26) suggests that the flow of probability j_t (vector) should be defined by

$$j_t = \xi_t \nu \qquad \text{with} \quad \xi_t = (-\gamma_+ + U_{-\nu}\gamma_-) p_t \qquad (4.28)$$

The discrete version of the equation of continuity is, then, as follows:

$$\dot{p}_t + \Delta_\nu \xi_t = 0 \qquad (4.29)$$

In the discrete case, however, another choice of the equation of continuity is possible, i.e.,

$$\dot{p}_t + \Delta_{-\nu}\xi_t' = 0 \qquad \text{with} \quad \xi_t' = (U_\nu\gamma_+ - \gamma_-) p_t \qquad (4.30)$$

In this choice, the flow of probability should be defined as

$$j_t' = -\xi_t' \nu \qquad (4.31)$$

The difference between j and j' is merely due to whether the flow is defined at the initial points or at the final points of transitions, and they have the following relationship:

$$j_t' = U_\nu j_t \qquad (4.32)$$

(ii) On the analogy of the continuous case,[13] we define the drift velocity v (vector) and the diffusion coefficient D (tensor)

$$v = \lim_{h \downarrow 0} \frac{1}{h} E[N_{t+h} - N_t | N_t = N] \qquad (4.33)$$

$$D = \lim_{h \downarrow 0} \frac{1}{2h} E[(N_{t+h} - N_t) \otimes (N_{t+h} - N_t) | N_t = N] \qquad (4.34)$$

where $E[\ |\ ]$ denotes conditional expectation, and N_t is the stochastic process whose transition probability $p(n, t | m)$ (from $N_0 = m$ to $N_t = n$) is subject to the master equation $\dot{p} = \Gamma p$. In order to calculate these quantities, we first notice the fact

$$\lim_{h \downarrow 0} \frac{1}{h} E[f(N_{t+h}) - f(N_t) | N_t = N]$$

$$= \lim_{h \downarrow 0} \frac{1}{h} \sum_n f(n)\{ p(n, h | N) - \delta_N(n) \}$$

$$= \langle f, \Gamma\delta_N \rangle = \langle \Gamma^* f, \delta_N \rangle = \Gamma^* f(N) \qquad (4.35)$$

where δ_N is the δ function concentrated on N [cf. (A.2)]. By this fact, we have

$$v = \Gamma^* N = \gamma_+ \Delta_{-\nu} N + \gamma_- \Delta_\nu N = \alpha\nu \qquad (4.36)$$

$$D = \tfrac{1}{2}\{\Gamma^* N \otimes N - (\Gamma^* N) \otimes N - N \otimes (\Gamma^* N)\}$$

$$= \beta\nu \otimes \nu \qquad (4.37)$$

where we have defined two functions

$$\alpha = \gamma_- - \gamma_+, \qquad \beta = \tfrac{1}{2}(\gamma_+ + \gamma_-) \tag{4.38}$$

Γ and Γ^* are reexpressed with these functions:

$$\Gamma = -\tfrac{1}{2}U_{-\nu}\Delta_{2\nu}\alpha \cdot -\Delta_\nu\Delta_{-\nu}\beta \cdot \tag{4.39a}$$

$$= U_{-\nu}\left(-\tfrac{1}{2}\Delta_{2\nu}\alpha \cdot +\Delta_\nu^2\beta \cdot \right) \tag{4.39b}$$

$$\Gamma^* = \alpha\tfrac{1}{2}U_{-\nu}\Delta_{2\nu} - \beta\Delta_\nu\Delta_{-\nu} \tag{4.40a}$$

$$= \left(\alpha\tfrac{1}{2}\Delta_{2\nu} + \beta\Delta_\nu^2\right)U_{-\nu} \tag{4.40b}$$

where (A.16) and (A.17) have been referred to.

These expressions can be interpreted as discrete versions of the continuous FP operator and its adjoint by making Δ_ν and U_ν correspond to $\nu \cdot \partial/\partial x$ and 1, respectively. This interpretation is consistent with the definitions of drift velocity (4.36) and diffusion coefficient (4.37). In subsequent papers we will discuss a continuum limit in which (4.39) reduces to the FP operator through the correspondence and see how the properties of the discrete case are inherited by the FP operator.

4.4. Potential Function

(i) The potential function ψ is defined by (3.20), which, in this model, reduces to the difference equation

$$\Delta_\nu\psi = \sigma_0 \tag{4.41}$$

This has a solution, for example,

$$\psi(N) = -\lambda \cdot N\sigma_0 \tag{4.42}$$

where $\lambda = (\lambda_i; \ i \in \Omega')$ is defined by

$$\lambda_i = \begin{cases} (r\nu_i)^{-1} & \text{if } \nu_i \neq 0 \\ 0 & \text{otherwise} \end{cases} \tag{4.43}$$

with the number r of $i \in \Omega'$ such that $\nu_i \neq 0$.

(ii) According to the discussion in Sections 3.4–3.6, the equilibrium state of each connected component of $\mathfrak{M}$ is given by (3.28) with the potential function ψ if it is normalizable. Let A be a connected class containing a point N. Then,

$$A = \{N - n\nu; \ N - n\nu \geqslant 0 \ \text{ and } \ n \in \mathbf{Z}\} \tag{4.44}$$

where $N \geqslant 0$ means $N_i \geqslant 0$ for all $i \in \Omega'$. The condition $N - n\nu \geqslant 0$ implies

$$\max_{i \in \Omega'_-} \frac{N_i}{\nu_i} \leqslant n \leqslant \min_{i \in \Omega'_+} \frac{N_i}{\nu_i} \tag{4.45}$$

if the sets $\Omega'_+ \equiv \{i \in \Omega' : v_i > 0\}$ and $\Omega'_- \equiv \{i \in \Omega' : v_i < 0\}$ are both non empty. In the case $\Omega'_+ = \varnothing$ (or $\Omega'_- = \varnothing$), we have, instead of this,

$$\max_{i \in \Omega'_-} \frac{N_i}{v_i} \leqslant n \qquad \left(\text{or} \quad n \leqslant \min_{i \in \Omega'_+} \frac{N_i}{v_i}\right) \qquad (4.46)$$

Thus, every connected class A is finite if $\Omega'_+ \neq \varnothing$ and $\Omega'_- \neq \varnothing$, and infinite if $\Omega'_+ = \varnothing$ or $\Omega'_- = \varnothing$. In the former case, ψ is, of course, normalizable for every connected class. Even in the latter case, ψ is also normalizable, because

$$\Xi_A(\psi + s) \leqslant \Xi_{\mathbb{S}}(\psi + s) = \sum_{N \in \mathbb{S}} \exp \frac{1}{k_B} \left[\psi(N) + s(N)\right]$$

$$= \sum_i \sum_{N_i = 0}^{\infty} \frac{1}{N_i!} \left(g_i V e^{-\lambda_i \sigma_0 / k_B}\right)^{N_i}$$

$$= \sum_i \exp\left(g_i V e^{-\lambda_i \sigma_0 / k_B}\right) < \infty \qquad (4.47)$$

where we have used (4.8) and (4.42). Thus every connected class A has the equilibrium state

$$P_A(N) = \Xi_A^{-1} e^{-\lambda \cdot N\sigma_0 / k_B} (gV)^N / N! \qquad (4.48)$$

The mesoscopic model $\mathfrak{M}$ is, then, a normalizable potential system. The general expression of equilibrium states of $\mathfrak{M}$ is given by

$$p = \sum_{A \in \mathbb{S}/\sim} a_A p_A; \qquad \sum_A a_A = 1, \qquad a_A \geqslant 0 \qquad (4.49)$$

Especially

$$p_{\text{eq}} \equiv \Xi_{\mathbb{S}}(\psi + s)^{-1} e^{(s + \psi)/k_B} \qquad (4.50)$$

is an equilibrium state with $a_A = \Xi_A / \Xi_{\mathbb{S}}$.

(iii) By the use of ψ, the operators Γ and Γ^* are written in another form. From (4.9) and (4.41),

$$\gamma_+ = (U_{-\nu} \gamma_-) \exp \frac{1}{k_B} \Delta_{-\nu}(s + \psi) \qquad (4.51)$$

Then, by (A.14)

$$\gamma_+ e^{(s + \psi)/k_B} = U_{-\nu} \gamma_- e^{(s + \psi)/k_B} \qquad (4.52)$$

which, upon multiplying $\Xi_{\mathbb{S}}(\psi + s)^{-1}$, leads to

$$\gamma_+ p_{\text{eq}} = U_{-\nu} \gamma_- p_{\text{eq}} \qquad (4.53)$$

where p_{eq} is defined by (4.50). From this it follows that

$$\gamma_+ = B p_{\text{eq}}^{-1} \qquad \text{and} \quad \gamma_- (U_\nu B) p_{\text{eq}}^{-1} \qquad (4.54)$$

with an arbitrary function B on $\mathbf{Z}^{\Omega'}$ such that

$$B \geqslant 0 \tag{4.55}$$

$$B(N) = 0 \quad \text{if} \quad N \notin \mathbb{S} \cap (\mathbb{S} + \nu) \tag{4.56}$$

Here, (4.15) and (4.16) have been taken into consideration. Substitution of (4.54) into (4.26) and (4.27) yields

$$\Gamma = -\Delta_\nu B \Delta_{-\nu} p_{\text{eq}}^{-1} \cdot \tag{4.57}$$

$$\Gamma^* = -p_{\text{eq}}^{-1} \Delta_\nu B \Delta_{-\nu} \tag{4.58}$$

The symmetrization technique[14] of FP equations with detailed balance is also applicable to Γ.

$$L \equiv p_{\text{eq}}^{-1/2} p_{\text{eq}}^{1/2} \cdot = -p_{\text{eq}}^{-1/2} \Delta_\nu B \Delta_{-\nu} p_{\text{eq}}^{-1/2} \cdot \tag{4.59}$$

The symmetry of L is obvious in this form, and the transformed distribution $q_t \equiv p_t p_{\text{eq}}^{1/2}$ is subject to the symmetric evolution equation

$$\dot{q}_t = L q_t \tag{4.60}$$

4.5. Expressions for S, K, and P

By definition, we have

$$S(p) = -k_B \langle p \ln p \rangle + \langle ps \rangle$$

$$= -k_B \langle p \ln p \rangle + \sum_{i \in \Omega'} k_B \left\langle p \ln \frac{(gV)^N}{N!} \right\rangle \tag{4.61}$$

$$K(p) = \langle p, \gamma_+ - \gamma_- \rangle \sigma_0 = \langle p, \Gamma^* \psi \rangle \tag{4.62}$$

The second equality of (4.62) follows from (3.44) or directly from the fact

$$\Gamma^* \psi = (\gamma_+ - \gamma_- U_\nu) \Delta_{-\nu} \psi = (\gamma_+ - \gamma_- U_\nu) \sigma_0 = (\gamma_+ - \gamma_-) \sigma_0 \tag{4.63}$$

In this model, the energy flow J_ϵ and the particle flows J_j ($j \in \Omega'$) are definable:

$$J_\epsilon(p) = \langle p, \gamma_+ - \gamma_- \rangle \epsilon_0 = -\langle p, \Gamma^* E \rangle \tag{4.64}$$

$$J_j(p) = \langle p, \gamma_+ - \gamma_- \rangle (-\nu_j) = -\langle p, \Gamma^* \eta_j \rangle \tag{4.65}$$

where E is defined by (4.6), and $\eta_j = \lambda \cdot N \nu_j$ with λ of (4.43). Although η_j satisfies

$$\Delta_\nu \eta_j = -\nu_j \tag{4.66}$$

it does not have the meaning of the number of j molecules like N_i of (3.34), but it is related to the number of times the reaction (4.1) occurs. Owing to this, expression (4.65) does not hold for the many-reaction case, while (4.64) does hold even for that case (cf. Section 4.6).

Since the model in this section has a normalizable potential function, the discussion in Section 3.7 is applicable to it. Then, we have

$$P(p) = \langle p, \Gamma^*(-k_B \ln p + s + \psi) \rangle \qquad (4.67)$$

$$= -k_B \langle p, \Gamma^* \ln p/p_{eq} \rangle \qquad (4.68)$$

Other than these, $P(p)$ has various expressions corresponding to the various forms of Γ. By using (4.27) for (4.67), we obtain

$$P(p) = \langle (\gamma_+ - U_{-\nu}\gamma_-)p, \Delta_{-\nu}(-k_B \ln p + s + \psi) \rangle \qquad (4.69)$$

which, by (4.51) and (A.14), leads to

$$P(p) = k_B \langle \gamma_+ \, p - U_{-\nu}\gamma_- \, p, \ln \gamma_+ \, p - \ln U_{-\nu}\gamma_- \, p \rangle \qquad (4.70)$$

On the other hand, substitution of (4.58) into (4.68) yields

$$P(p) = k_B \langle \Delta_{-\nu}p/p_{eq}, B\Delta_{-\nu} \ln p/p_{eq} \rangle \qquad (4.71)$$

If $|\Delta_{-\nu}p/p_{eq}| \ll p/p_{eq}$, then

$$\Delta_{-\nu} \ln p/p_{eq} = \ln\{1 + (\Delta_{-\nu}p/p_{eq})/(p/p_{eq})\}$$

$$\approx (\Delta_{-\nu}p/p_{eq})/(p/p_{eq}) \qquad (4.72)$$

Therefore, (4.71) becomes

$$P(p) \approx k_B \langle p, Bp_{eq}^{-1}(\Delta_{-\nu} \ln p/p_{eq})^2 \rangle \qquad (4.73)$$

These expressions will be used in dealing with continuum limit or thermodynamic limit in subsequent papers. Indeed, expression (4.73) is just parallel with that of the continuous case.[10]

4.6. Many-Reaction Case

Let us consider the many-reaction case. The chemical reactions are expressed by the following reaction formulas:

$$\sum_{i \in \Omega} \nu_i^{l+} A_i \underset{\leftarrow}{\rightarrow} \sum_{i \in \Omega} \nu_i^{l-} A_i + \epsilon_0^l, \qquad l = 1, \ldots, n \qquad (4.74)$$

In this expression, the set Ω is taken to be common to every reaction by putting $\nu_i^{l+} = \nu_i^{l-} = 0$ for the substance i which is irrelevant to the reaction l. The mesoscopic model $\mathfrak{M}$ for this case can be constructed similarly to the single-reaction model, except that the transition set $\mathfrak{T}$ is given by the sum $\mathfrak{T} = \bigcup_{l=1}^{n} \mathfrak{T}_l$ of the single-reaction-type transition sets $\mathfrak{T}_l$ associated with individual reactions l, i.e.,

$$\mathfrak{T}_l = \left\{ N \xrightarrow{l} N - \nu^l; N \in \mathfrak{S} \cap (\mathfrak{S} + \nu^l) \right\} \cup \left\{ N \xrightarrow{l} N + \nu^l; N \in \mathfrak{S} \cap (\mathfrak{S} - \nu^l) \right\}$$

where $\nu^l = \nu^{l+} - \nu^{l-}$ with $\nu^{l\pm} = (\nu_i^{l\pm}, i \in \Omega')$. The t.p.r. γ and the e.n.c. σ are defined for each $\mathfrak{T}_l$ in the same way as in the single-reaction case. Since

the family $\{\mathfrak{T}_l\}$ is a partition of $\mathfrak{T}$ with property (3.48), the expressions for S, Γ, K, and P are derived from those of the single-reaction model by using formulas (3.49), . . . , (3.52). The flows $J_.$ are also given by the sum $J_. = J_.^1 + \cdots + J_.^n$ of $J_.^l$ defined for individual $\mathfrak{T}_l$ as (4.64) or (4.65).
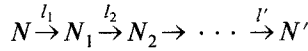
There is an essential difference between the many-reaction model and the single-reaction model; the former does not have a potential function except special cases, while the latter always has it. The potential function ψ is defined as a solution of Eq. (3.20), which is, in this case, reduced to

$$\Delta_{-\nu^l}\psi = \sigma_0^l, \qquad l = 1, \ldots, n \tag{4.75}$$

where σ_0^l is specified for each reaction l in the same way as σ of (4.5). The equation system (4.75) does not always have a solution; for example, if $n = 2$, $\nu^1 = \nu^2$, and $\sigma_0^1 \neq \sigma_0^2$, then obviously it has no solution. As a consequence, P, K, and J_i's can take nonzero stationary values. However, J_ϵ is exceptional owing to the existence of the energy function E:

$$J_\epsilon(p_{\mathrm{st}}) = \sum_l J_\epsilon^l(p_{\mathrm{st}}) = \sum_l \langle \Gamma_l p_{\mathrm{st}}, E \rangle = \langle \Gamma p_{\mathrm{st}}, E \rangle = 0 \tag{4.76}$$

Let

$$N \xrightarrow{l_1} N_1 \xrightarrow{l_2} N_2 \rightarrow \cdots \xrightarrow{l'} N'$$

be a path from N to N'. The final point N' is then expressed as

$$N' = \sum_{l=1}^{n} z_l \nu^l + N \tag{4.77}$$

with integers z_l. The total e.n.c. σ_{tot} along the path is given by

$$\sigma_{\mathrm{tot}} = \sum_{l=1}^{n} z_l \sigma_0^l \tag{4.78}$$

According to the definition of "cyclic" in Section 3.4, the path is cyclic iff $\sum z_l \nu^l = 0$. Therefore, the condition (3.25) is restated as follows:

$$\sum_l z_l \sigma_0^l = 0 \qquad \text{if} \quad \sum_l z_l \nu^l = 0 \qquad \text{and} \quad z_l \in \mathbf{Z} \tag{4.79}$$

As shown in Section 3.4, this is sufficient and necessary for the equation system (4.75) to have a solution. This fact can also be verified directly by using (A.19).

In order to explain the significance of condition (4.79), let us distinguish two cases: (i) the vectors $\nu^1, \ldots, \nu^n$ are linearly independent; and (ii) they are linearly dependent. In the case (i), the equation $\sum z_l \nu^l = 0$ implies $z_l = 0$ ($l = 1, \ldots, n$); hence, condition (4.79) always holds regardless of the environmental parameters T and μ_i on which the σ_0^l's are dependent. The mesoscopic model $\mathfrak{M}$ is, then, a potential system and does not exhibit stationary activities for any T and μ_i.
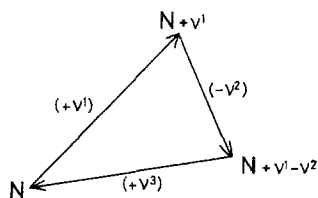
Fig. 2. If $\nu^1 - \nu^2 + \nu^3 = 0$, then the above cyclic path exists. Along this path the negentropy $\sigma_0^1 - \sigma_0^2 + \sigma_0^3$ is consumed, which must vanish if the potential function exists.

In the case (ii), on the other hand, the equation $\sum z_l \nu^l = 0$ holds for certain integers z_l such that $(z_1, \ldots, z_n) \neq (0, \ldots, 0)$. Then the model $\mathfrak{M}$ becomes a potential system only when σ_0^l, or T and μ_i are chosen so as to satisfy (4.79) (see Fig. 2). For example, it is satisfied if the environment is in equilibrium with respect to all the reactions, i.e., $\sigma_0^l = 0$ for $l = 1, \ldots, n$. If the environment is not in chemical equilibrium and reserves negentropy to be used, then the system may exhibit stationary activity by consuming the negentropy. Living cells, in which various cycles of chemical reactions are occurring, are considered typical examples of this case. Lasers are also placed in this category (cf. Sections 7 and 8).

5. EXAMPLE 2: RANDOM WALK ACCOMPANIED BY A CHEMICAL REACTION

5.1. Model

Let us consider a random-walk system illustrated in Fig. 3. The particle X moves with one step at a time, left or right on the one-
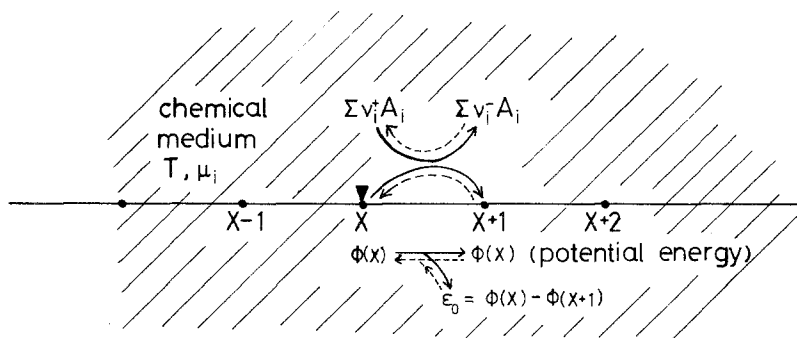

Fig. 3. Reaction-random-walk in a chemical medium.

dimensional lattice **Z**. The lattice is surrounded with a chemical medium with fixed temperature T and chemical potentials μ_i, and is under the influence of a force field which gives the particle the potential energy $\phi(X)$. Each one-step walk is accompanied by a chemical reaction

$$\sum_{i \in \Omega} \nu_i^+ A_i \rightleftarrows \sum_{i \in \Omega} \nu_i^- A_i + \epsilon_0(X) \qquad \text{for} \quad X \rightleftarrows X + 1 \tag{5.1}$$

where ν_i^+ and ν_i^- are independent of X. It is assumed that the intrinsic property of the lattice site is translationally invariant; especially, the coupling energy between the particle and the lattice site is independent of X. Then, by the principle of energy conservation, we have

$$\epsilon(X) = \phi(X) - \phi(X + 1) \tag{5.2}$$

The reaction-random-walk like this really appears in the translation process of genetic information in a living cell. A ribosome moves on a chain of RNA by consuming negentropy through chemical reactions while making protein.[15] Similar structure is also seen in the process of replication or transcription of the DNA–RNA system by enzymes. The model in this section is concerned with an aspect of these processes and does not deal with the process of information transfer explicitly, which will be discussed in a subsequent paper.

The mesoscopic model $\mathfrak{M} = (\mathfrak{S}, \mathfrak{T}, s, \sigma, \gamma)$ describing the reaction-random-walk system is as follows:

(1) $\mathfrak{S} = \mathbf{Z}$. $X \in \mathfrak{S}$ represents the position of the particle in the lattice **Z**.

(2) $\mathfrak{T} = \{X \to X + 1; X \in \mathfrak{S}\} \cup \{X \to X - 1; X \in \mathfrak{S}\}$

(3) $s(X) = s_0$ (const) $\tag{5.3}$

(4) $\sigma(X \to X \pm 1) = (1/T)[\phi(X) - \phi(X \pm 1)] \pm \sigma_0$ $\tag{5.4}$

where

$$\sigma_0 = \sum_{i \in \Omega} \frac{\mu_i}{T} \nu_i \tag{5.5}$$

(5) γ satisfies the relation

$$\gamma_+(X) = \gamma_-(X + 1)\exp\frac{1}{k_B T}\{\phi(X) - \phi(X + 1) + T\sigma_0\} \tag{5.6}$$

where

$$\gamma_\pm(X) = \gamma(X \to X \pm 1) \tag{5.7}$$

Let us define a function ψ by

$$\psi(X) = -\frac{1}{T}\phi(X) + \sigma_0 X \tag{5.8}$$

Then obviously

$$\psi(X \pm 1) - \psi(X) = \sigma(X \to X \pm 1) \tag{5.9}$$

which means that ψ is a potential function of $\mathfrak{M}$. Since $\mathfrak{M}$ is connected, the equilibrium state p_{eq} of $\mathfrak{M}$ is given by

$$p_{eq} = \Xi(\psi)^{-1}\exp\frac{1}{k_B}\psi \tag{5.10}$$

[cf. (3.28)], if ψ is normalizable in the sense of (3.21). Here, note that we can take $\psi - s$ as a potential function, since s is constant.

The expressions of S, K, Γ, and P can be obtained in the same way as in Sections 4.3, 4.4, and 4.5, by replacing $\pm \nu$ with ∓ 1. For example,

$$\Gamma = \Delta_{-1}\gamma_+ + \Delta_1\gamma_- = -\frac{1 + U_{-1}}{2}\Delta_1 v - \Delta_1\Delta_{-1}D \tag{5.11}$$

$$\Gamma^* = \gamma_+\Delta_1 + \gamma_-\Delta_{-1} = v\frac{1 + U_{-1}}{2}\Delta_1 - D\Delta_1\Delta_{-1} \tag{5.12}$$

where $\Delta_{\pm 1}$ are the one-dimensional difference operators (see the Appendix), and

$$v = \gamma_+ - \gamma_-, \qquad D = (\gamma_+ + \gamma_-)/2 \tag{5.13}$$

These are interpreted as the drift velocity and diffusion coefficient, respectively, as discussed in Section 4.3.

5.2. Structure of γ

Since we have assumed that the translational invariance of the lattice, the X dependence of $\gamma_\pm(X)$ is attributed to that of $\phi(X)$. In order to determine more concrete structure of $\gamma_\pm$, we assume the ϕ dependence of $\gamma_\pm$ as follows:

$$\gamma_\pm(X) = f\left(k_B^{-1}\sigma(X \to X \pm 1)\right) \tag{5.14}$$

with a smooth function f. By (5.4), it becomes

$$\gamma_\pm = f(-\Delta_{\pm 1}\phi/k_B T \pm \sigma_0/k_B) \tag{5.15}$$

Roughly speaking, this assumption means that the effect of the potential energy is the same for either direction of the transition. By substituting (5.15) into (5.6), we have

$$f(y) = e^y f(-y) \tag{5.16}$$

This functional equation has the solution

$$f(y) = e^{y/2}A(y) \tag{5.17}$$

with an arbitrary symmetric function $A(y)$. Therefore,

$$\gamma_\pm = A\left(\frac{1}{k_B T}\Delta_{\pm 1}\phi \mp \frac{\sigma_0}{k_B}\right)\exp\frac{1}{2k_B}\left(-\frac{1}{T}\Delta_{\pm 1}\phi \mp \sigma_0\right) \qquad (5.18)$$

where A is a symmetric positive smooth function.

If $\sigma(X \to X \pm 1)$ is sufficiently small, i.e.,

$$|\Delta_{\pm 1}\phi/k_B T - \sigma_0/k_B| \ll 1 \qquad (5.19)$$

then (5.18) can be approximated as

$$\gamma_\pm = A(0)(1 - \Delta_{\pm 1}\phi/2k_B T \pm \sigma_0/2k_B) \qquad (5.20)$$

where we have used the symmetry of A, that is $A'(0) = 0$.

5.5. EINSTEIN'S FORMULA FOR DIFFUSION COEFFICIENT AND ENERGY CONVERSION

The drift velocity v and the diffusion constant D were defined by (5.12). Let $F \equiv -\Delta_1\phi$ be constant. Then v and D are also constant, and by using them the flow j_t of probability is expressed in the form

$$j_t = vp_t - D\Delta_1 p_t \qquad (5.21)$$

Note that two definitions (4.28) and (4.31) of the flow coincide with each other for the constant γ. Expression (5.21) shows that the definitions of drift and diffusion agree, in this case, with the physical ones.[16]

Now let us see whether the Einstein formula[16]

$$D = \mu k_B T \qquad (5.22)$$

holds in the linear region of F, where μ is the mobility coefficient defined by $\mu = \partial v/\partial F|_{F=0}$. First, we consider the case $\sigma_0 = 0$. For sufficiently small F such that $|F/k_B T| \ll 1$, it follows from (5.20) that

$$\gamma_\pm = A(0)(1 \pm F/2k_B T) \qquad (5.23)$$

Then, we have

$$v = \gamma_+ - \gamma_- = A(0)F/k_B T \qquad (5.24)$$

$$D = (\gamma_+ + \gamma_-)/2 = A(0) \qquad (5.25)$$

which implies (5.22).

In the case $\sigma_0 \neq 0$, by replacing F with $F + T\sigma_0$, we have the same result as above. Moreover, we obtain the following drift-diffusion relation:

$$v = D\left(\frac{F}{k_B T} + \frac{\sigma_0}{k_B}\right) \qquad (5.26)$$

in the region of $|(F + T\sigma_0)/k_B T| \ll 1$.

Since $(d/dt)\langle p_t, X \rangle = \langle j_t, \Delta_1 X \rangle = v$, the mean velocity of the particle is also provided by v. Relation (5.26), then, shows the interchangeability between chemical (free) energy and potential energy. Suppose $0 < -F < T\sigma_0$; then $v > 0$. Therefore, the particle moves to the right and gains the potential energy $-F$ per step with the consumption of the chemical energy $T\sigma_0$ (or negentropy σ_0). It is also seen from (5.26) that the loss $T\sigma_0 + F$ in this conversion of energy is proportional to the velocity v.

From another point of view, formula (5.26) provides the condition for design of the movement of the particle. In order to make the particle move in the right direction, it is necessary to set the force F and the chemical potentials μ_i so as to satisfy $F + \sum \mu_i \nu_i > 0$.

In the above consideration, the temperature T has been assumed to be positive. In the case $T < 0$, the particle moves in the direction in which the potential energy increases even if no chemical reaction is accompanying it. This situation is applicable to the laser; the position X of the particle is interpreted as the photon number of a cavity mode with restriction to the positive lattice sites, and the reservoir is interpreted as an assembly of the lasing atoms with population inversion or the negative temperature.[4] By this interpretation, the reaction-random-walk model represents a laser system without cavity loss. The process of cavity loss can be included in the model as a thermal interaction with another reservoir at positive temperature. In Sections 7 and 8 we will discuss laser systems from a different viewpoint by focusing attention on the active atoms.

6. EXAMPLE 3: RANDOM WALK ON A CIRCULAR LATTICE

6.1. Model

This section is concerned with a reaction-random-walk system on a circular lattice (see Fig. 4) as an example of nonpotential systems. The situation of this model is set similarly to that of the model in the previous section except that (a) the circular lattice is not assumed to be rotationally symmetric, and (b) each step $X \rightleftarrows X + 1$ is allowed to be accompanied by a different chemical reaction. The mesoscopic model $\mathfrak{M} = (\mathfrak{S}, \mathfrak{T}, s, \sigma, \gamma)$ is as follows:

(1) $\mathfrak{S} = \{0, 1, 2, \ldots, n - 1\}$

(2) $\mathfrak{T} = \{X \rightarrow X + 1; X \in \mathfrak{S}\} \cup \{X \rightarrow X - 1; X \in \mathfrak{S}\}$ where the conventions $n = 0$ and $-1 = n - 1$ are adopted.

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[4] It should be noted that the concept of negative temperatures can be consistently included in a framework of the heat-engine theory.[17]
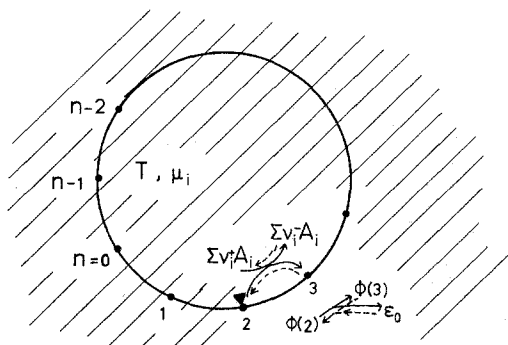
Fig. 4.   Reaction-random-walk on a circular lattice.

(3) Since the rotational symmetry of the lattice is not assumed, the internal state of the particle may vary with the sites of the lattice. Hence, the r.e. s is a function on $\mathcal{S}$ and is not generally constant. Further information is necessary in order to determine the explicit form of s.

(4) $\sigma(X \to X + 1) = \sigma_0(X) + \dfrac{1}{T}\left[\phi(X) - \phi(X + 1)\right]$ \hfill (6.1a)

$\sigma(X \to X - 1) = -\sigma_0(X - 1) + \dfrac{1}{T}\left[\phi(X) - \phi(X - 1)\right]$ \hfill (6.1b)

where ϕ is a potential energy, and $\sigma_0(X)$ is defined as in (5.4) for the chemical reaction accompanying the transition $X \rightleftarrows X + 1$. In this case, ν_i and ϵ_0 in (5.1) may depend on X.

(5) The t.p.r. γ satisfies the i.d.b. condition

$$\gamma_+(X) = \gamma_-(X)\exp\frac{1}{k_B T}\left\{\phi(X) - \phi(X + 1) + T\sigma_0(X)\right\} \qquad (6.2)$$

where

$$\gamma_\pm(X) = \gamma(X \to X \pm 1) \qquad (6.3)$$

This model does not generally have a potential function. The following condition is necessary and sufficient for the existence of a potential function:

$$\langle \sigma_0 \rangle \equiv \sum_{X=0}^{n-1} \sigma_0(X) = 0 \qquad (6.4)$$

If this is fulfilled, then $\psi(X) \equiv \phi(X)/T + \sum_{Y=0}^{X}\sigma(Y)$ is a potential function. It is obviously normalizable since $\mathcal{S}$ is finite. If (6.4) does not hold, ψ is no longer the potential function.

In order to obtain the operator expression of Γ, we identify $f \in \mathcal{F}(\mathsf{S})$ with $\tilde{f} \in \mathcal{F}(\mathbf{Z})$ defined by $\tilde{f}(a) = f(a)$ for $a \in \mathsf{S}$ and $\tilde{f}(a + n) = \tilde{f}(a)$ for any $a \in \mathbf{Z}$. By this identification, $\mathcal{F}(\mathsf{S})$ is regarded as the set of $f \in \mathcal{F}(\mathbf{Z})$ such that $U_n f = f$ (n-periodic functions). In the same way as in the previous two sections, the operator Γ is expressed as

$$\Gamma = \Delta_{-1}\gamma_+ \cdot + \Delta_1\gamma_- \cdot \tag{6.5}$$

where $\gamma_\pm$ are extended to the n-periodic functions on $\mathbf{Z}$ by the above-mentioned identification. Since $\Gamma f \in \mathcal{F}(\mathsf{S})$ for $f \in \mathcal{F}(\mathsf{S})$, Γ can be regarded as an operator on $\mathcal{F}(\mathsf{S})$. We have various expressions for Γ in the same way as in Section 4 except (4.57). This exception is due to the nonexistence of the potential function. Note that the difference equation $\Delta_1\psi = \sigma_0 - \Delta_1\phi/T$ for the potential function ψ does not have a n-periodic solution if (6.4) fails.

6.2. Stationary State

Let p_{st} be the stationary state, i.e.,

$$\Gamma p_{st} = \Delta_{-1}(\gamma_+ - U_1\gamma_{-1})p_{st} = 0 \tag{6.6}$$

Then

$$(\gamma_+ - U_1\gamma_{-1})p_{st} = c \tag{6.7}$$

where c is a constant, which is determined by the normalization condition of p_{st}. Equation (6.7) is equivalent to

$$p_{st}(i + j)\gamma(i + j - n) - p_{st}(i + j + 1)\gamma(i + j + 1) = c \qquad \forall i, j \in \mathbf{Z} \tag{6.8}$$

where

$$\gamma_\pm(i + n) = \gamma_\pm(i) \qquad \forall i \in \mathbf{Z} \tag{6.9}$$

$$p_{st}(i + n) = p_{st}(i) \qquad \forall i \in \mathbf{Z} \tag{6.10}$$

Define

$$U(i, j) = \begin{cases} \displaystyle\prod_{k=1}^{j-1} \gamma_+(k) & \text{if } i < j \\ 1 & \text{if } i = j \\ \displaystyle\prod_{k=j-1}^{i} \gamma_-(k) & \text{if } i > j \end{cases}$$

This quantity can be illustrated by a sequence of arrows on the circular lattice as shown in Fig. 5. Multiplying both sides of (6.8) by

$$j(j + i, j)u(j + i + 1 - n, j) \qquad (0 \leqslant i \leqslant n - 1) \tag{6.11}$$
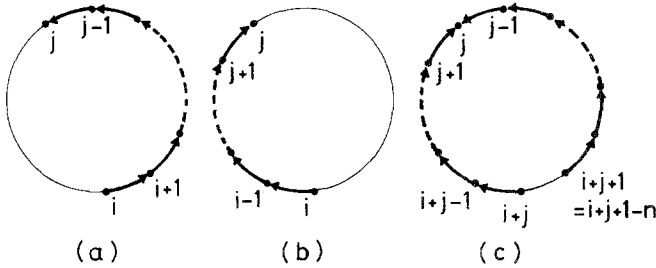
Fig. 5.   The clockwise arrow and the counterclockwise one which are starting from a site i correspond to $\gamma_-(i)$ and to $\gamma_+(i)$ respectively. Diagrams (a), (b), and (c) represent, respectively, $u(i, j)$ $(i < j)$, $j(i, j)$ $(i > j)$, and $u(i + j, j)u(j + i + 1 - n, j)$ by taking the product of quantities corresponding to the arrows.

we have

$$u(j + i, j)u(j + i - n, j)p_{st}(i + j)$$
$$- u(j + i + 1, j)u(j + i + 1 - n, j)p_{st}(i + j + 1)$$
$$= cu(j + i, j)u(j + i + 1 - n, j) \qquad (6.12)$$

Upon taking the summation over $i = 0, 1, \ldots, n - 1$, this leads to

$$u(i, j)u(j - n, j)p_{st}(j) - u(j + n, j)u(i, j)p_{st}(j + n)$$
$$= c \sum_{i=0}^{n-1} u(j + i, j)u(j + i + 1 - n, j) \qquad (6.13)$$

Then

$$p_{st}(j)\left[\prod_{i \in \mathbb{S}} \gamma_+(i) - \prod_{i \in \mathbb{S}} \gamma_-(i) \right] = c \sum_{i=0}^{n-1} u(j + i, j)u(j + i + 1 - n, j) \quad (6.14)$$

where we have used these facts: $p_{st}(i) = p_{st}(i + n)$, $u(j, j) = 1$, $u(j - n, j)$ $= \prod_{i \in \mathbb{S}} \gamma_+(i)$, and $u(j + n, j) = \prod_{i \in \mathbb{S}} \gamma_-(i)$. By the normalization of p_{st}, we obtain

$$c = Z^{-1}\left[\prod_{i \in \mathbb{S}} \gamma_+(i) - \prod_{i \in \mathbb{S}} \gamma_-(i) \right] \qquad (6.15)$$

where

$$Z = \sum_{j=0}^{n-1} \sum_{i=0}^{n-1} u(j + i, j)u(j + i + 1 - n, j) \qquad (6.16)$$

From (6.14) and (6.15), one can obtain an expression for p_{st}.

Now let us calculate $P(p_{st})$ [or $K(p_{st})$].

$$
\begin{aligned}
P(p_{st}) &= K(p_{st}) \\
&= \langle P_{st}\gamma_+, -\Delta_1\phi/T + \sigma_0 \rangle + \langle p_{st}\gamma_-, -\Delta_{-1}\phi/T - \sigma_0 \rangle \\
&= \langle (\gamma_+ - U_1\gamma_-)p_{st}, -\Delta_1\phi/T + \sigma_0 \rangle \\
&= \langle c, -\Delta_1\phi/T + \sigma_0 \rangle \\
&= \langle \Delta_{-1}c, -\phi/T \rangle + \langle c, \sigma_0 \rangle \\
&= c\langle \sigma_0 \rangle \qquad (\because \Delta_{-1}c = 0) \\
&= Z^{-1}(\textstyle\prod\gamma_+ \langle \sigma_0 \rangle + \prod\gamma_- \langle -\sigma_0 \rangle)
\end{aligned}
\tag{6.17}
$$

This formula shows that $P(p_{st})$ $[= K(p_{st})]$ is given by an average of the contributions from the two cyclic paths: $0 \to 1 \to \cdots \to n-1 \to 0$ and its inverse $0 \to n-1 \to \cdots \to 1 \to 0$; the former occurs with the probability $w_+ \equiv Z^{-1}\prod\gamma_+$ per unit time and consumes the negentropy $\langle \sigma_0 \rangle$ per cycle, and the latter occurs with the probability $w_- \equiv Z^{-1}\prod\gamma_-$ per unit time and consumes the negentropy $\langle -\sigma_0 \rangle$ per cycle. This interpretation of the entropy production or negentropy consumption in the stationary state is applicable to general mesoscopic models. The generalization will be discussed in a subsequent paper through graph-theoretical methods.

By the i.d.b. condition (6.2), w_+ and w_- are connected as follows:

$$
w_+ = w_- \exp\frac{1}{k_B}\langle \sigma_0 \rangle
\tag{6.18}
$$

Then,

$$
P(p_{st}) = w_- \langle \sigma_0 \rangle \left(1 - \exp\frac{1}{k_B}\langle \sigma_0 \rangle\right) \geqslant 0
\tag{6.19}
$$

The equality of (6.19) holds iff (6.4) is fulfilled. This fact is, of course, consistent with the before-mentioned one that $\mathfrak{M}$ is a potential system iff (6.4) holds.

The flows $J_i(p_{st})$ and $J_\epsilon(p_{st})$ are also written in a form similar to (6.17):

$$
J_i(p_{st}) = w_+ \langle \nu_i \rangle + w_- \langle -\nu_i \rangle
\tag{6.20}
$$

$$
J_\epsilon(p_{st}) = w_+ \langle \epsilon \rangle + w_- \langle -\epsilon \rangle = 0
\tag{6.21}
$$

where the last equality follows from $\langle \epsilon \rangle = \langle \phi \rangle - \langle \phi \rangle = 0$ [cf. (5.2)].

7. EXAMPLE 4: CHEMICAL LASER

7.1. Model

In this section we consider a coupling between chemical reaction and lasing in a two-level atom.[18] Figure 6 illustrates the model. An atom with
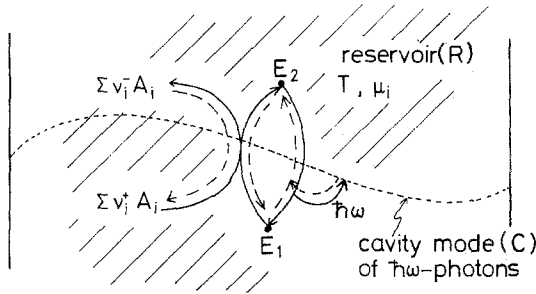
Fig. 6. Two-level laser pumped by a chemical reaction.

two levels labeled 1 and 2 is put in an environment which consists of a reservoir R (T, μ_i's) and a cavity mode C of $\hbar\omega$ photons. The cavity mode is assumed to have no (or negligibly small) thermal noise in it and to be treated as a mechanical environment. The transitions $1 \rightleftarrows 2$ are accompanied by the chemical reaction

$$\sum_i \nu_i A_i \rightleftarrows \epsilon_0 \quad \text{with respect to R} \tag{7.1}$$

and the lasing

$$0 \rightleftarrows -\hbar\omega \quad \text{with respect to C} \tag{7.2}$$

where (7.1) is an abridged form of (4.1) with $\nu_i = \nu_i^+ - \nu_i^-$, and the lasing is expressed as a special case of chemical reactions.

The mesoscopic model $\mathfrak{M} = (\mathbb{S}, \mathfrak{T}, s, \sigma, \gamma)$ for this system is as follows:

$$\mathbb{S} = \{1, 2\}$$

$$\mathfrak{T} = \left\{ 1 \overset{R}{\rightarrow} 2, 2 \overset{R}{\rightarrow} 1, 1 \overset{C}{\rightarrow} 2, 2 \overset{C}{\rightarrow} 1 \right\}$$

$$s(i) = k_B \ln g(i): \qquad i = 1, 2 \tag{7.3}$$

where $g(i)$ is the degeneracy of the level i.

$$\sigma\left(1 \overset{R}{\rightleftarrows} 2\right) = \pm\left(\epsilon_0 + \sum \mu_i \nu_i\right) / T \equiv \pm \sigma_0 \tag{7.4}$$

$$\sigma\left(\overset{C}{\rightleftarrows} 2\right) = 0 \qquad [\text{cf. (2.18)}] \tag{7.5}$$

$$\gamma_+^R = \gamma_-^R \exp\frac{1}{k_B}\left[\sigma_0 + s(2) - s(1)\right] \tag{7.6}$$

$$\gamma_+^C = \gamma_-^C \exp\frac{1}{k_B}\left[s(2) - s(1)\right] \tag{7.7}$$

where

$$\gamma_\pm^R = \gamma\left(1 \overset{R}{\rightleftarrows} 2\right) \quad \text{and} \quad \gamma_\pm^C = \gamma\left(1 \overset{C}{\rightleftarrows} 2\right)$$

Let $E(i)$ be the energy of the level $i(=1,2)$. Then, by the principle of energy conservation [cf. (3.36)], we have

$$\epsilon_0 = E(1) - E(2) = -\hbar\omega \tag{7.8}$$

7.2. Energy Conversion from R to C

Let us discuss the condition for the cavity mode C gains energy from the reservoir R through the atom in its stationary state. The flow of energy from the atom into C is given by

$$J_C(p) = \hbar\omega\left[\gamma_-^C p(2) - \gamma_+^C p(1)\right] \tag{7.9}$$

In the stationary state p_{st}, this quantity is also regarded as a flow from R to C. The condition for $J_C(p_{st}) > 0$ is, then, desired. P_{st} is defined by

$$p_{st}(1)\left(\gamma_+^R + \gamma_+^C\right) = p_{st}(2)\left(\gamma_-^R + \gamma_+^C\right). \tag{7.10}$$

Then

$$p_{st}\binom{1}{2} = \left(\gamma_\mp^R + \gamma_\mp^C\right)/\left(\gamma_+^R + \gamma_+^C + \gamma_-^R + \gamma_-^C\right) \tag{7.11}$$

By substituting this into (7.9), we obtain

$$J_C(p_{st}) = \frac{\hbar\omega\left(\gamma_+^R \gamma_-^C - \gamma_-^R \gamma_+^C\right)}{\gamma_+^R + \gamma_+^C + \gamma_-^R + \gamma_-^C} \tag{7.12}$$

From (7.6) and (7.7) we have

$$\gamma_+^R \gamma_-^C = \gamma_-^R \gamma_+^C e^{\sigma_0/k_B} \tag{7.13}$$

Hence, we obtain

$$J_C(p_{st}) = A\left(e^{\sigma_0/k_B} - 1\right) \tag{7.14}$$

where

$$A = \hbar\omega\gamma_-^R \gamma_+^C \left(\gamma_+^R + \gamma_+^C + \gamma_-^R + \gamma_-^C\right) > 0 \tag{7.15}$$

Thus, the desired condition is given by

$$\sigma_0 > 0 \tag{7.16}$$

which leads, by (7.4) and (7.8), to

$$\frac{1}{T}\sum_i \mu_i \nu_i > \frac{1}{T}\hbar\omega \tag{7.17}$$

In the case of normal temperature ($T > 0$), this condition is reduced to

$$\sum_i \mu_i \nu_i > \hbar\omega \qquad (7.18)$$

In order to convert the chemical energy to the mode energy it is necessary to set the chemical potentials so as to satisfy (7.18). On the other hand, if $T < 0$, then (7.17) becomes

$$\sum_i \mu_i \nu_i < \hbar\omega \qquad (7.19)$$

which shows that we can obtain the energy flow from R to C without a chemical reaction (i.e., $\nu_i = 0$). These results are quite parallel with those obtained at the end of Section 5.

According to the way of explanation in the previous section, inequality (7.16) is interpreted as a condition that must be fulfilled in order that the probability of the cyclic path $1 \overset{R}{\to} 2 \overset{C}{\to} 1$ be larger than that of its inverse $1 \overset{C}{\to} 2 \overset{R}{\to} 1$.

8. EXAMPLE 5: LASER PUMPED BY HIGH-TEMPERATURE BEAM

8.1. Model

The last example in this paper is a three-level atom[18] placed in the situation illustrated in Fig. 7. The atom has three levels $i = 1, 2, 3$ participat-
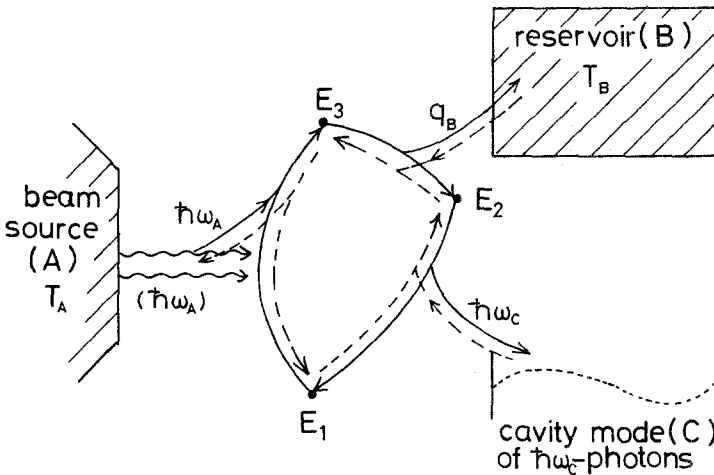

Fig. 7. Three-level laser pumped by a high-temperature beam.

ing in the laser action, whose level energies $E(i)$ are set as $E(1) < E(2)$ $< E(3)$. It interacts with the reservoir B of temperature T_B, the cavity mode C of $\hbar\omega_C$ photons, and the beam of $\hbar\omega_A$–photons from the source A with temperature T_A $(> T_B)$. The following reactions are assumed to accompany the transitions between the levels of the atom:

$$0 \rightleftarrows -\hbar\omega_A \qquad \text{for } 1 \rightleftarrows 3 \text{ interaction with A} \qquad (8.1)$$

$$0 \rightleftarrows q_B \qquad \text{for } 3 \rightleftarrows 2 \text{ interaction with B} \qquad (8.2)$$

$$0 \rightleftarrows \hbar\omega_C \qquad \text{for } 2 \rightleftarrows 1 \text{ interaction with C} \qquad (8.3)$$

From the principle of energy conservation,

$$\hbar\omega_A = E(3) - E(1) \qquad (8.4a)$$

$$q_B = E(3) - E(2) \qquad (8.4b)$$

$$\hbar\omega_C = E(2) - E(1) \qquad (8.4c)$$

The mesoscopic model $\mathfrak{M} = (\mathfrak{S}, \mathfrak{T}, s, \sigma, \gamma)$ for this system is as follows:

$$\mathfrak{S} = \{1, 2, 3\}$$

$$\mathfrak{T} = \left\{ 1 \overset{A}{\to} 3, 3 \overset{A}{\to} 1, 3 \overset{B}{\to} 2, 2 \overset{B}{\to} 3, 2 \overset{C}{\to} 1, 1 \overset{C}{\to} 2 \right\}$$

$$s(i) = k_B \ln g(i) \qquad (8.5)$$

where $g(i)$ is the degeneracy of the level i.

$$\sigma\left(1 \overset{A}{\rightleftarrows} 3\right) = \mp\hbar\omega_A / T_A \qquad (8.6a)$$

$$\sigma\left(3 \overset{B}{\rightleftarrows} 2\right) = \pm q_B / T_B \qquad (8.6b)$$

$$\sigma\left(2 \overset{C}{\rightleftarrows} 1\right) = 0 \qquad (8.6c)$$

$$\gamma_+^A = \gamma_-^A \exp \frac{1}{k_B} \left[s(3) - s(1) - \frac{\hbar\omega_A}{T_A} \right] \qquad (8.7a)$$

$$\gamma_+^B = \gamma_-^B \exp \frac{1}{k_B} \left[s(2) - s(3) + \frac{q_B}{T_B} \right] \qquad (8.7b)$$

$$\gamma_+^C = \gamma_-^C \exp \frac{1}{k_B} \left[s(1) - s(2) \right] \qquad (8.7c)$$

where $\gamma_\pm^A = \gamma(1 \overset{A}{\rightleftarrows} 3)$, $\gamma_\pm^B = \gamma(3 \overset{B}{\rightleftarrows} 2)$, and $\gamma_\pm^C = \gamma(2 \overset{C}{\rightleftarrows} 1)$.

8.2. Heat-Engine Structure of Cyclic Paths in Stationary State

In order to obtain the stationary state p_{st}, we can use the method formulated in Section 6.2. The result is

$$p_{st}(1) = Z^{-1}(\gamma_-^B \gamma_-^A + \gamma_-^A \gamma_+^C + \gamma_+^C \gamma_+^B)$$

$$p_{st}(2) = Z^{-1}(\gamma_-^A \gamma_-^C + \gamma_-^C \gamma_+^B + \gamma_+^B \gamma_+^A) \qquad (8.8)$$

$$p_{st}(3) = Z^{-1}(\gamma_-^C \gamma_-^B + \gamma_-^B \gamma_+^A + \gamma_+^A \gamma_+^C)$$

where Z is the normalization constant. Let J_A, J_B, and J_C be the energy flows from the atom into A, B, and C, respectively. In the state p_{st}, they are calculated as

$$J_A(p_{st}) = -\hbar\omega_A(w_+ - w_-) \qquad (8.9a)$$

$$J_B(p_{st}) = q_B(w_+ - w_-) \qquad (8.9b)$$

$$J_C(p_{st}) = \hbar\omega_C(w_+ - w_-) \qquad (8.9c)$$

where

$$w_\pm = Z^{-1}\gamma_\pm^A \gamma_\pm^B \gamma_\pm^C \qquad (8.10)$$

By (8.7), w_+ and w_- are related to each other as follows:

$$\frac{w_+}{w_-} = \exp\frac{1}{k_B}\left(\frac{q_B}{T_B} - \frac{\hbar\omega_A}{T_A}\right) = \exp\frac{\hbar\omega_C}{k_B T_B}(\eta_{ideal} - \eta) \qquad (8.11)$$

where

$$\eta_{ideal} = 1 - \frac{T_B}{T_A} \quad \text{and} \quad \eta = \frac{\hbar\omega_C}{\hbar\omega_A} = \frac{\omega_C}{\omega_A} \qquad (8.12)$$

Therefore, the condition for $J_C(p_{st}) > 0$ is given by

$$\eta_{ideal} > \eta \qquad (8.13)$$

The meaning of η_{ideal} is the efficiency of the ideal Carnot cycle operating between two temperatures T_A and T_B, while η is regarded as the real efficiency of the energy conversion from A to C in the cyclic path $1 \to 3 \to 2 \to 1$ (gain cycle). Hence, condition (8.13) is equivalent to saying that the second law in the Carnot sense must be fulfilled in the gain cycle. Note that the macroscopic second law $P(p_{st}) \geqslant 0$ is always true, whether (8.13) holds or not. This is explained as follows: In comparing the gain cycle and the loss cycle $1 \to 2 \to 3 \to 1$, the dominant one is the cycle which satisfies the second law, and as a result we have the macroscopic second law, which represents the mean effect of these two cycles. Summing up, the

following three statements are equivalent: (a) The second law in the Carnot sense holds in the gain cycle, (b) the gain cycle is the dominant one, and (c) $J_C(p_{st}) > 0$.

In order to investigate the relation between the efficiency and the speed of the conversion of energy (represented by $w_+ - w_-$, the net number of revolutions along the cyclic path per unit time), it is necessary to have further information about the structure of γ. However, in the small $|\eta_{ideal} - \eta|$ region, we can say that the speed $w_+ - w_-$ is proportional to $\eta_{ideal} - \eta$, as we did in Section 5.3.

A similar discussion of the heat-engine structure of the laser has been given by Konyukhov and Prokhorov[18] in the context of macroscopic cycles. As for the heat-engine theory of the second law, there is a quite abstract formulation[17] without the use of such concepts as states and quasistatic processes, which will be useful in discussing the heat-engine structure of elementary cycles in the space $\mathbb{S}$ of element states.

9. CONCLUDING REMARKS

The value of the mesoscopic thermodynamics consists in its adaptability to intermediate levels between macroscopic and microscopic descriptions, and also in its ability to associate the irreversible dynamics of open systems with thermostatic quantities. The adaptability is due to the r.e. s, which serves as a measure for the degree of coarse-graining. At the coarsest extreme, s coincides with the usual thermodynamic entropy, and at the finest extreme it vanishes. The t.p.r. γ is connected with the r.e. s and the e.n.c. σ through the i.d.b. condition (2.2). σ is expressed as Eq. (2.16) or (2.19) with thermostatic parameters of the environment, and s is also usually given from equilibrium statistical considerations as shown in the examples. By the introduction of σ, it has become possible to discuss the system–environment interaction from the entropy–negentropy viewpoint even on a quantitative basis. So it will bring interesting results if applied to concrete problems in various fields; for example, Schrödinger's description[20] of the living cell by the use of the negentropy concept will be more definitely established in the mesoscopic thermodynamics.

Schnakenberg's work[5] is similar to ours in the point that both are concerned with the thermodynamics of master-equation systems. However, the two are essentially different: The aim of the former is to establish a *formal* thermodynamiclike structure on the basis of master equations without *real* linkage to existing thermodynamics and statistical mechanics, and hence his formalism does not contain such quantities as our σ and s which realize this linkage. As a result, his definitions of entropy production and

equilibrium state are different from ours, although there are some similarities in appearance, except a special case that the set $\mathcal{T}_{a,b}$ contains at most one element for any two points a and b.

Alexandrowicz[6] has introduced a quantity called "detailed imbalance," which is equivalent to Schnakenberg's entropy production. He has attempted to relate the quantity to real entropy change by taking into account the environmental effect, though restricted to an equilibrium reservoir.

A more complex environment that consists of many reservoirs with different temperatures has been treated by Lebowitz *et al.*,[9] who give a sensible definition of entropy production for such many-reservoir open systems. The treatment has suggested the i.d.b. condition and our definition of P. Various expressions of P are connected with each other through the i.d.b. condition, as shown in Section 3.

The plan of subsequent papers is as follows: (a) As a generalization of example 3 (Section 6), graph-theoretical expressions are given to the entropy production and the flows in the steady state. We will there propose a statistical mechanics of steady states on the basis of statistics over the elementary heat engines or cycles (cf. Sections 7 and 8). (b) Continuum limit of the mesoscopic model is discussed to know how the i.d.b. postulate is inherited in a continuous case (cf. Section 4), where the thermodynamic limit is also treated in the same framework. (c) The role of the projection operator method in the mesoscopic model is clarified. (d) The mesoscopic model is applied to the case of variable or finite-size environment, where synergetic phenomena will be investigated including nonlinear response to the change of environment. (e) By improving the reaction-random-walk model (Section 5), we present a mesoscopic model which describes the information transfer in the DNA $\rightarrow$ RNA $\rightarrow$ protein process, the so-called central dogma, where the relation between information and negentropy consumption will be qualitatively calculated. (f) And, concrete examples will be taken in physics, chemistry, biology, economics, and technology.

ACKNOWLEDGMENT

APPENDIX: TRANSLATION AND DIFFERENCE OPERATORS ON A LATTICE

(i) Let $\mathcal{F}(\mathbf{Z}^d)$ be the set of all real functions defined on d-dimensional lattice $\mathbf{Z}^d$. The linear combinations $nx + my$ and $\alpha f + \beta g$ and the product

fg are defined in the usual sense for $x, y \in \mathbf{Z}^d$; $m, n \in \mathbf{Z}$; $f, g \in \mathscr{F}(\mathbf{Z}^d)$; and $\alpha, \beta \in \mathbf{R}$. The notation $\langle \ , \ \rangle$ is used in the same way as (2.25) with $A = \mathbf{Z}^d$.

Let $\mathscr{L}$ be the set of finite-matrix-type operators (cf. Section 2.3) defined on $\mathscr{F}(\mathbf{Z}^d)$. For $L_1, L_2 \in \mathscr{L}$ and $f, g \in \mathscr{F}(\mathbf{Z}^d)$, the product $L_1 L_2 \in \mathscr{L}$ and the linear combination $fL_1 + gL_2$ are defined by $L_1 L_2 h = L_1(L_2 h)$ and $(fL_1 + gL_2)h = f(L_1 h) + g(L_2 h)$ for any $h \in \mathscr{F}(\mathbf{Z}^d)$.

The adjoint operator $L^* \in \mathscr{L}$ of $L \in \mathscr{L}$ is defined in Section 2.3 and is characterized by

$$\langle \delta_n, L^* \delta_m \rangle = \langle \delta_m, L\delta_n \rangle, \qquad n, m \in \mathbf{Z}^d \tag{A.1}$$

where $\delta_n \in \mathscr{F}(\mathbf{Z}^d)$ is the δ function concentrated on n, i.e.,

$$\delta_n(n') = \begin{cases} 1 & \text{if} \quad n = n' \\ 0 & \text{if} \quad n \neq n' \end{cases} \tag{A.2}$$

By definition, it is obvious that for $L, L_1, L_2 \in \mathcal{S}$ and $f, g \in \mathscr{F}(\mathbf{Z}^d)$:

$$L^{**} = L \tag{A.3}$$

$$(L_1 L_2)^* = L_2^* L_1^* \tag{A.4}$$

$$(fL_1 + gL_2)^* = L_1^* f \cdot + L_2^* g \cdot \tag{A.5}$$

where $f \cdot \in \mathscr{L}$ is defined by

$$f \cdot h = fh \qquad \forall h \in \mathscr{F}(\mathbf{Z}^d) \tag{A.6}$$

Note that the identity

$$f \cdot L = fL \qquad \forall f \in \mathscr{F}(\mathbf{Z}^d) \qquad \text{and} \qquad \forall L \in \mathscr{L} \tag{A.7}$$

(ii) For every $\nu \in \mathbf{Z}^d$, the translation operator $U_\nu \in \mathscr{L}$ and the difference operator $\Delta_\nu \in \mathscr{L}$ are defined by

$$U_\nu f(n) = f(n + \nu) \qquad \forall f \in \mathscr{F}(\mathbf{Z}^d) \tag{A.8}$$

$$\Delta_\nu = U_\nu - I \tag{A.9}$$

where I is the identity operator. The family $\{U_\nu : \nu \in \mathbf{Z}^d\}$ makes a $\mathbf{Z}^d$-parameter group, that is,

$$U_{\nu + \nu'} = U_\nu U_{\nu'} \qquad \text{and} \qquad U_0 = I \tag{A.10}$$

The following properties are easily checked from definition, where f is an arbitrary one in $\mathscr{F}(\mathbf{Z}^d)$:

(a) Any two out of U_ν, $U_{\nu'}$, Δ_ν, and $\Delta_{\nu'}$ are commutable.

(b) $$U_\nu f \cdot = (U_\nu f) U_\nu \tag{A.11}$$

(c) $$\Delta_\nu f \cdot = (\Delta_\nu f) U_\nu + f\Delta_\nu \tag{A.12}$$

$$\Delta_\nu f \cdot = (\Delta_\nu f) \cdot + (U_\nu f)\Delta_\nu \tag{A.13}$$

(d) $$U_\nu g(f) = g(U_\nu f) \tag{A.14}$$

where g is a real function on **R**, and the composition function $g(f) \in \mathcal{F}(\mathbf{Z}^d)$ is defined by $g(f)(x) = g(f(x))$.

$$\text{(e)} \qquad\qquad \Delta_\nu = -U_\nu \Delta_{-\nu} \qquad\qquad (A.15)$$

$$\text{(f)} \qquad \Delta_\nu - \Delta_{-\nu} = (I + U_{-\nu})\Delta_\nu = U_{-\nu}\Delta_{2\nu} \qquad (A.16)$$

$$\text{(g)} \qquad \Delta_\nu + \Delta_{-\nu} = -\Delta_\nu\Delta_{-\nu} = U_{-\nu}\Delta_\nu^2 \qquad (A.17)$$

$$\text{(h)} \qquad \Delta_{n\nu} = U_\nu^n - I = (\Delta_\nu - I)^n - I$$

$$= \sum_{k=1}^{n} \binom{n}{k}\Delta_\nu^k \qquad (A.18)$$

$$\text{(i)} \qquad \Delta_{\nu_1 + \cdots + \nu_n} = \sum_{k=1}^{n} U_{\nu_1 + \cdots + \nu_{k-1}}\Delta_{\nu_k} \qquad (A.19)$$

$$\text{(j)} \qquad U_\nu^* = U_{-\nu}, \qquad \Delta_\nu^* = \Delta_{-\nu}, \qquad (f\cdot)^* = f\cdot \qquad (A.20)$$

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