Irreversible Circulation of Flux-Fluctuations

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The concept of the irreversible circulation of fluctuations, proposed by Tomita and Tomita [Prog. Theor. Phys. 51 (1974), 1731] is extended to study irreversible phenomena in a so-called second order systems with inertia. The nature of flux-fluctuations is examined in the master equation approach in the extended space of variables which consists of the $Q$- and the $\alpha$-variables. It is shown that an extended irreversible circulation of flux-fluctuations is related to flux-relaxation times. A simple example is mentioned, the theory grown out of which is the extended irreversible thermodynamics. This paper presents a new and somewhat more general description of transient processes which approach steady states satisfying the detailed balance condition.

§1. Introduction

Many years ago, Tomita and Tomita $^{1,2}$ proposed the interesting notion of irreversible circulation of fluctuations around steady states, which is characteristic of off-equilibrium coupled degrees of freedom. They approached steady state processes by employing the master equation for the Markoffian processes of fluctuating extensive variables. They found that the steady state solution to the original master equation admits a cyclic balance instead of detailed balance. In order to find a non-vanishing irreversible circulation, existence of macroscopic dissipative fluxes through the surface of the system in question is necessary. The processes they considered is a so-called Wiener process, since they tacitly assumed the existence of linear phenomenological laws among the dissipative fluxes and the thermodynamic forces. It has the defect that if one applies it to heat transport, conventional irreversible thermodynamics leads inexorably to Fourier's law and hence to infinite wave-front speeds for the transport of heat. Hence, for some purposes it is desirable to take a broader view of the subject.

There is another type of Markoffian process, the Ornstein-Uhlenbeck process. $^{3}$ From this type of process arises the Wiener process after taking an appropriate time-smoothing. This process is obtained by subjecting particles of a Brownian motion to an elastic force. Since the phenomenological laws for this type of process are written as a set of second-order differential equations, Machlup and Onsager $^{4}$ called this type of process a second-order process with inertia. It is our aim here to try to extend Tomita and Tomita's theory to this type of Markoffian process.

In general, we distinguish between two types of macroscopic variables. The variables of the first type are even functions of the particle velocities and are called the $\alpha$-type, while those of the second type are odd functions of the particle velocities. Casimir $^{5}$ called the latter the $\beta$-variables. The $\alpha$-type variables are even under time reversal, while the $\beta$-variables are odd. It is well known that for irreversible
processes involving both types of variables, microscopic reversibility implies that the reciprocity relations have negative signs for the transport coefficients giving cross phenomena between $\alpha$- and $\beta$-variables. While from the macroscopic point of view the procedure appears to be just as ad hoc as the addition of new variables, recent advances in thermodynamics of irreversible processes have generally substantiated this idea. We see in §2 that this assumption is a central and fundamental condition to write an entropy production in the known bilinear form of the forces and the fluxes.

As demonstrated by Machlup and Onsager, phenomenological laws for irreversible processes in systems with inertia can be written as a set of second-order differential equations in the $\alpha$-variables. However, it is important to remember that we must define two categories of phenomenological coefficients, Onsager coefficients (in the first-order processes) and relaxation times. We know that the irreversible circulation considered by Tomita and Tomita is related to the former category. In this paper, it is demonstrated that an extended irreversible circulation of fluctuations of fluxes can be defined in terms of the latter category. With this in mind, we ask whether this is in fact true, or on the contrary, if the irreversible circulation is related to antisymmetric parts of Onsager's transport coefficients.

The paper is organized in the following way. In §2 the basic elements defining the concept of the irreversible circulation of fluctuations are introduced. Our aim there is to relate the master equation approach to irreversible thermodynamics. We will make some comments on the entropy production. In §3, an extension of Tomita and Tomita's innovation is given in second-order systems out of equilibrium. In order to understand the thermodynamical meanings of the circulation, an expression for the entropy production is derived in §4. Section 5 involves an example of the extended irreversible circulation of fluctuations of dissipative fluxes. In §6 some final remarks and conclusions are presented. Finally, we devote the Appendices to providing an example of irreversible circulation and to discuss the relevance of the present theory to extended irreversible thermodynamics.

§2. Preliminaries

2.1. Hashitsume's theory

In order to have a basis for our subsequent considerations we first recapitulate from the essay (in Japanese) by Hashitsume the main steps involved for convenience. See, Ref. 6) for details.

In most physical situations out of equilibrium, extensive variables, such as particle density and energy density, vary slowly on the scale of typical interparticle distances and the typical time between collisions. However, it is expected that the thermodynamical relations among the extensive and intensive variables are locally expressed by the same laws as for absolute equilibrium. Classical irreversible thermodynamics, in its present form, restricts itself to macroscopic systems that can be treated as continuous media and can be assumed to be in local equilibrium. In order to derive equations describing the time evolution of various extensive variables, it is useful to write an arbitrary extensive variable $\alpha(t)$ as
where $a(r, t)$ represents the density of $a(t)$ per unit mass and $\rho(r, t)$ is the mass density. Here, in Eq. (2.1a), the integration is over the volume $V$ of the system. The most general equation for $a(t)$ is of the form

$$\frac{d}{dt}a(t) = \int_V \sigma_a(r, t)dV - \int_\Sigma J_a(r, t)d\Sigma,$$

(2.1b)

where $\sigma_a(r, t)$ is the source or sink density in the volume and $J_a(r, t)$ is the dissipative flux through the surface $\Sigma$. For conserved quantities, the source terms are set to zero. The surface integral is used to define the so-called $\beta$-variables for discontinuous systems. Note that Onsager considered irreversible processes which take place in a discontinuous system. A typical discontinuous continuous system is a particular experimental set-up, which consists essentially of two large reservoirs connected by a small capillary, hole, porous wall, or the like. The total system is closed (see the standard textbook by de Groot and Mazur).

Let us consider an isolated system, each macroscopic state of which is assumed to be specified by a set of variables $\{\alpha_i; i = 1, \cdots, N\}$, $N$ being the number of the thermodynamical degrees of freedom. At a macroscopic level, these variables are fixed to a strictly thermodynamical concept. At a mesoscopic level, they fluctuate around their equilibrium values. The variables $\alpha_1, \alpha_2, \cdots, \alpha_N$ should be considered as random. Then, Einstein’s principle states that the probability for the macroscopic state characterized by the set of random variables $\{\alpha_1', \alpha_2', \cdots, \alpha_N'\}$ is given by

$$W_{\text{eq}}[\alpha] = \exp \left\{ \frac{S[\alpha]}{k_B} \right\},$$

(2.2)

where $S[\alpha]$ denotes the thermally fluctuating (local) entropy (as referred to by Hashitsume). This is the concept of the thermal motion of entropy. In what follows, for brevity we set the Boltzmann constant $k_B$ to unity.

In order to consider time-dependent phenomena, let us introduce the transition probability from the state $\{\alpha\}$ to the state $\{\alpha'\}$:

$$\Psi(\alpha + \Delta\alpha, t + \Delta t \mid \alpha, t) = W(\alpha + \Delta\alpha, t + \Delta t \mid \alpha, t)/W_{\text{eq}}(\alpha),$$

(2.3)

where $W(\alpha + \Delta\alpha, t + \Delta t \mid \alpha, t)$ denotes the joint probability for the two states $\{\alpha\}$ and $\{\alpha' = \alpha + \Delta\alpha\}$ occurring at $t$ and $t + \Delta t$, respectively. It is assumed that the transition probability satisfies the Chapman-Kolmogorov equation. Hence, it is assumed that the evolution equation for the joint probability is given by the Fokker-Planck equation. It is well known that the transition probability can be written in the form

$$k_B \ln \Psi(\alpha + \Delta\alpha, t + \Delta t \mid \alpha, t) = \frac{1}{2} \left[ \Delta S - \phi(\Delta \alpha; \Delta \alpha) \right] + \text{const},$$

(2.4)
where
\[ \Phi(\Delta \alpha, \Delta \alpha) = \frac{1}{2} \sum R_{ij} \Delta \alpha_i \Delta \alpha_j \] (2·5)
is related to Onsager's dissipation function. Here the \( R_{ij} \) are the transport (Onsager) coefficients. Note that it is only the symmetric part of the matrix \( R (= \{ R_{ij} \}) \) which contributes to the dissipation function. There is freedom to add an antisymmetric part to the matrix \( R \).

The non-stationary probability density \( W[\alpha, t] \) is defined as
\[ W[\alpha, t] = \int \Psi(\alpha, t | \alpha^{(a)}; t_a) W[\alpha^{(a)}] d\alpha^{(a)}, \] (2·6)
where \( W[\alpha^{(a)}] \) is a given initial distribution. Hashitsume introduced the entropy for the macroscopic motion which is
\[ S_{\text{macro}}(t) = - \int W[\alpha, t] \ln \left[ \frac{W[\alpha, t]}{W_{\text{eq}}[\alpha]} \right] d\alpha. \] (2·7)

By utilizing Eq. (2·2) into Eq. (2·7), it is readily seen that
\[ S_{\text{macro}}(t) = \langle S[\alpha] \rangle_t + H_{\text{macro}}(t), \] (2·8)
where
\[ \langle S[\alpha] \rangle_t = \int S[\alpha] W[\alpha, t] d\alpha, \] (2·9)
\[ H_{\text{macro}}(t) = - \int W[\alpha, t] \ln W[\alpha, t] d\alpha. \] (2·10)

Consequently, we have three kinds of entropy. Note that \( \langle S[\alpha] \rangle_t \) can be interpreted as the local thermodynamic entropy for which the local equilibrium hypothesis can be adopted. That is, the local thermodynamic entropy is the average of the fluctuating entropy with respect to the non-stationary probability density \( W[\alpha, t] \).

2.2. Irreversible circulation of fluctuations

It is well known that the probability density \( W[\alpha, t] \) obeys the following master equation under the assumption that the transition probability satisfies the Chapman-Kolmogorov equation:
\[ \frac{\partial}{\partial t} W(\alpha; t) = \int d\alpha' \{ W(\alpha'; t) T(\alpha' \rightarrow \alpha) - W(\alpha; t) T(\alpha \rightarrow \alpha') \}, \] (2·11)
where \( T(\alpha \rightarrow \alpha') \) is the transition probability per unit time from \( \{ \alpha \} \) to \( \{ \alpha' \} \). The right-hand side of this equation can be expanded as the Kramers-Moyal expansion,
\[ \frac{\partial}{\partial t} W(\alpha; t) = \sum_{n=1}^{\infty} \frac{1}{n!} \left( -\frac{\partial}{\partial \alpha} \right)^n C_n(\alpha) W(\alpha, t), \] (2·12)
with
\[ C_n(\alpha) = \int d(\Delta \alpha) (\Delta \alpha)^n W(\alpha \rightarrow \alpha + \Delta \alpha). \] (2·13)
in tensor notation.

We shall assume the scaling

\[ W(\alpha \rightarrow \alpha + \Delta \alpha) = \Omega \omega(\alpha; \Delta \alpha), \]

where \( \Omega \) denotes the (local) system size (i.e., a typical cell size) and \( \alpha \) represents

\[ \alpha = \frac{a}{\Omega} = \varepsilon \alpha. \quad (\varepsilon = \Omega^{-1}) \]

Then, defining corresponding changes

\[ c_n(\alpha) = \varepsilon C_n(\alpha), \]

and

\[ \Omega^N W(\alpha, t) = \psi(\alpha, t), \]

Eq. (2.12) becomes

\[ \frac{\partial}{\partial t} \psi(\alpha, t) = \sum_{n=1}^{\infty} \frac{1}{n!} \varepsilon^{n-1} \left( -\frac{\partial}{\partial \alpha} \right)^n c_n(\alpha) \psi(\alpha, t). \]

Kubo, Matsuno and Kitahara \(^{10}\) have argued that the scaled distribution function \( \psi(\alpha, t) \) can be written as

\[ \psi(\alpha, t) \propto \exp[\Omega \phi(\alpha, t)]. \]

This corresponds to the concept of the extensivity of equilibrium statistical thermodynamics.

As demonstrated by Kubo, Matsuno and Kitahara, the postulate (2.19) is equivalent to the assumption that the scaled variables \( \{\alpha\} \) have mean values of order unity and spreads \( \varepsilon^{1/2} \) around them when a Gaussian approximation is valid. Hence, following van Kampen, \(^{11}\) let us set

\[ \alpha = y(t) + \varepsilon^{1/2} \xi, \]

and define a distribution function of the variables \( \{\xi\} \) by

\[ p(\xi, t) = \varepsilon^{N/2} \psi(y(t) + \varepsilon^{1/2} \xi, t). \]

Then, the master equation (2.18) can be written as

\[ \frac{\partial}{\partial t} p(\xi; t) - \Omega^{1/2} \frac{\partial}{\partial \xi} [y(t)p(\xi; t)] \]

\[ = \Omega \int d(\Delta \alpha) \left( \exp \left( -\varepsilon^{1/2} \Delta \alpha \frac{\partial}{\partial \xi} \right) - 1 \right) \omega(y(t) + \varepsilon^{1/2} \xi; \Delta \alpha) p(\xi; t). \]

Modifying Tomita and Tomita's method, we postulate that the evolution equations are given by

\[ \frac{dy(t)}{dt} = c_1(y(t)). \]
This determines the dominant (secular) motion of the system.

If one uses Eq. (2.23) into Eq. (2.22), one obtains, in the lowest order approximation, the master equation

$$\frac{\partial}{\partial t} p(\xi, t) = -\frac{\partial}{\partial \xi} \cdot [K(t) \cdot \xi p(\xi, t)] + \frac{1}{2} \frac{\partial}{\partial \xi} \cdot D(t) \cdot \frac{\partial}{\partial \xi} p(\xi, t), \quad (2.24)$$

where the matrixes $D(t)$ and $K(t)$ are given by

$$D(t) = c_2(y(t)) \quad \text{and} \quad K(t) = \frac{\partial}{\partial y} c_1(y(t)). \quad (2.25)$$

By definition, the diffusion matrix $D(t)$ is symmetric.

Let us introduce the variance matrix $\sigma(t)$, defined by

$$\sigma_{ij}(t) = \int \xi_i \xi_j p(\xi, t) d\xi. \quad (2.26)$$

Then we can write the solution to Eq. (2.24) in the form

$$p(\xi, t) = \frac{\text{Det}(g(t))}{2\pi} \exp \left\{ -\frac{1}{2} \xi \cdot g(t) \cdot \xi \right\}, \quad (2.27)$$

where $g(t)$ is the inverse of the variance $\sigma(t)$. The time derivative of the variance matrix is given by

$$\frac{d}{dt} \sigma_{ij}(t) = D_{ij}(t) + \sum_k (K_{ik}(t) \sigma_{kj}(t) + \sigma_{ik}(t) K_{kj}(t)). \quad (2.28)$$

By taking the averages of $d\alpha/dt$ with respect to the probability density $p(\xi, t)$, we obtain

$$\left\langle \frac{d}{dt} \alpha \right\rangle_{av} = c_1(y(t)) - \epsilon \frac{\partial}{\partial y} \cdot G(t) \quad (2.29)$$

up to order $\epsilon$. Here, in Eq. (2.29),

$$G(t) = K(t) \sigma(t). \quad (2.30)$$

If we define the dissipative fluxes as

$$J(t) = \frac{dy(t)}{dt} = c_1(y(t)), \quad (2.31)$$

it is readily seen that

$$\frac{d}{dt} J(t) = K(t) J(t), \quad (2.32)$$

which represents relaxation equations of the fluxes. Hence, the matrix $K(t)$ is called the regression (or relaxation) matrix.

As demonstrated by Tomita and Tomita, for steady state variance we have

$$D + K\sigma + \tilde{\sigma}K = 0. \quad (2.33)$$
Here, the symbol \( \sim \) over the matrix denotes the transpose. Then, as a fundamental quantity, they defined the irreversible circulation of fluctuation as

\[
\omega = \frac{1}{2} \{ \sigma \dot{K} - K \sigma \}.
\] (2.34)

They emphasized that the circulation is a measure for a directed flux in a system with more than one degree of freedom and that existence of coupling between modes which results in a direction of flux is necessary.

By solving Eq. (2.33) with respect to \( K \), one obtains the Onsager coefficients \( L \) expressed as

\[
L = \frac{1}{2} (D + 2\omega).
\] (2.35)

For steady states, which do not satisfy detailed balance, the Onsager reciprocity theorem does not hold and there is a possibility of the occurrence of the irreversible circulation of fluctuations.

2.3. Remarks

Before concluding this review section, let us add some remarks on the irreversible production of entropy in the Tomita-Tomita model. 1), 2) Some of the concepts will be clarified by considering the entropy production. Following Hashitsume, 6) we shall define the fluctuating entropy as

\[
s[a, t] = -\ln p(\xi, t). \quad (k_B = 1)
\] (2.36)

Let us calculate the entropy production from Eqs. (2.19) and (2.18). It is readily seen that

\[
- \frac{\partial s}{\partial t} = \sum_{n=1}^{\infty} \frac{1}{n!} \varepsilon^n \left( -\frac{\partial}{\partial a} \right)^n c_n(a) + \sum_{n=1}^{\infty} \frac{1}{n!} \varepsilon^n c_n(a) \left( -\frac{\partial}{\partial a} \right)^n \psi(a, t). \quad (2.37)
\]

By making use of Eq. (2.20) into Eq. (2.37), we obtain the expression for the fluctuating entropy production,

\[
\Omega \frac{\partial s}{\partial t} = - \left( -\frac{\partial}{\partial y(t)} \right) c_1(y(t)) - \sum_{n=1}^{\infty} \frac{1}{n!} \varepsilon^{-1+n/2} \frac{c_n(y(t) + \varepsilon^{1/2} \xi)}{p(\xi, t)} \left( -\frac{\partial}{\partial \xi} \right)^n p(\xi, t)
\]

\[
= \text{Tr} K(t) + J(t) X(t) - \frac{1}{2p(\xi, t)} \left( -\frac{\partial}{\partial \xi} \right) \cdot D(t) \cdot \left( -\frac{\partial}{\partial \xi} \right) p(\xi, t)
\]

\[
- \sum_{n=3}^{\infty} \frac{1}{n!} \varepsilon^{-1+n/2} \frac{c_n(y(t) + \varepsilon^{1/2} \xi)}{p(\xi, t)} \left( -\frac{\partial}{\partial \xi} \right)^n p(\xi, t), \quad (2.38)
\]

where

\[
X(t) = \varepsilon^{-1/2} \frac{\partial}{\partial \xi} \ln p(\xi, t)
\] (2.39)

are the conjugate thermodynamic forces to the dissipative fluxes. Here, in Eq. (2.38), we have set

\[
c_1(y(t)) = J(t), \quad (2.40)
\]
and have discarded terms of order higher than \( \varepsilon \) in the first term on the right-hand side of Eq. (2.38). Note, however, that one must make alternations to the setting (2.40) if one wishes to adapt the procedure to the cases with non-conserved variables. (See Eq. (2.1b) and what follows below Eq. (2.42)). Some source terms should be added to the right-hand side of Eq. (2.40). By making use of Eq. (2.27) into Eq. (2.38), we obtain

\[
\Omega \frac{ds}{dt} = J(t)X(t) + \text{Tr} \left( K(t)\sigma(t) + \frac{1}{2}D(t) \right) g(t) - \frac{1}{2} \text{Tr} \left( (g(t)\xi) \cdot D \cdot (g(t)\xi) \right).
\]

(2.41)

The second term on the right-hand side of Eq. (2.41) can be rewritten as

\[
\frac{1}{2} \text{Tr} \left( K(t)\sigma(t) + \dot{K}(t)\hat{\sigma}(t) + D(t) \right) g(t) - \text{Tr}\omega(t)g(t) = \frac{1}{2} \text{Tr} \hat{\sigma}(t)g(t),
\]

since \( \text{Tr}\omega(t)g(t) \) identically vanishes by the definition of the circulation \( \omega(t) \). Here we have used Eq. (2.28) for the definition of the time evolution of the variance. Accordingly, we can write Eq. (2.41) in the form

\[
\Omega \frac{ds}{dt} = J(t)X(t) + \frac{1}{2} \text{Tr} \hat{\sigma}(t)g(t) - \frac{1}{2} \text{Tr} \left( (g(t)\xi) \cdot D \cdot (g(t)\xi) \right).
\]

(2.41a)

The second term on the right-hand side of Eq. (2.41a) may be interpreted as follows: the “thermodynamic force” conjugate to the “flux”, \( \hat{\sigma}(t)/2 \), is identified with the inverse of the variance, \( g(t) \).

After taking the average of (2.41a) with respect to \( p(\xi, t) \), we obtain

\[
\left\langle \Omega \frac{ds}{dt} \right\rangle_{av} = J(t)X(t) + \text{Tr} K(t).
\]

(2.42)

Here, the symbol \( \langle \ast \rangle_{av} \) denotes the average over the distribution \( p(\xi, t) \), and we have discarded terms of higher order than \( \varepsilon^3 \). The entropy production essentially consists of the two types. The first term of Eq. (2.37), \( J(t)X(t) \), is equal to the entropy production in the classical irreversible thermodynamic sense and the second expresses the effects due to regression. The irreversible circulation does not enter the statement regarding the entropy production in this form. This is in line with the fact that it is only the symmetric part of the matrix \( R \) which contributes to the dissipation function (2.5). Hence, one must find a measure of irreversibility affected by the presence of irreversible circulation of fluctuations.

In order to attack such a problem, it should be noted that if the set of \( \alpha \)-variables involves non-conserved quantities, such as an internal energy density, the expression for the classical entropy production should be modified to take into account the source terms \( \sigma_j \) in their equations of motion. It is known that for continuous systems the thermodynamic forces are the spatial gradients of intensive variables and the additional contributions to the classical entropy production are of the bilinear form \( ^{12a, b} \)

\[
\sum \sigma_j A_j. \quad (A_j; \text{intensive variables})
\]

(2.43)
The source term \( \sigma_j \), in general, is a nonlinear function of the \( \alpha \)-variables. This finding is not irrelevant, since, in the Tomita and Tomita model of circulation, non-conserved variables are used as a typical example of chemical reactions. Indeed, the chemical components, which in general are not conserved separately, are used as the set of the fundamental variables. As demonstrated in a previous paper,\(^{12a} \) Eq. (2·43) then reads\(^{13} \)

\[
\sum \nu_{ra} J_\alpha \left( -\frac{\mu_r}{T} \right) \left( \equiv \sum \alpha J_\alpha A_\alpha \right)_{\text{(2·43a)}}
\]

in this case. Here, \( \nu_{ra} \) stands for the stoichiometric coefficient of component \( r \) in reaction \( \alpha \) and \( J_\alpha \) for the rate of reaction \( \alpha \), \( \mu_r \) is the chemical potential for the \( r \)th component, and \( A_\alpha \) stands for the so-called chemical affinity. De Groot and Mazur\(^{12b} \) treated the entropy production of the form of (2·43a) in a chemical reaction when the detailed balance condition is fulfilled. Tomita and Tomita\(^{2} \) have considered a chemical reaction which is in cyclic balance but not in detailed balance.

§3. The master equation approach of second-order systems

In this section we generalize the method of Tomita and Tomita to second order processes. Again, let us assume that \{\( \alpha, \dot{\alpha} \}\} is a set of stochastic variables following a Markoffian process, which is described by the master equation of the form

\[
\frac{\partial}{\partial t} W(\alpha, \dot{\alpha}; t) = \int d\alpha' d\dot{\alpha}' \left\{ W(\alpha', \dot{\alpha}'; t) T(\alpha' \rightarrow \alpha; \dot{\alpha}' \rightarrow \dot{\alpha}) - W(\alpha; \dot{\alpha}; t) T(\alpha \rightarrow \alpha'; \dot{\alpha} \rightarrow \dot{\alpha}') \right\},
\]

where \( W(\alpha, \dot{\alpha}; t) \) denotes the probability density and \( T(\alpha \rightarrow \alpha', \dot{\alpha} \rightarrow \dot{\alpha}') \) is the transition probability per unit time from \{\( \alpha, \dot{\alpha} \)\} to \{\( \alpha', \dot{\alpha}' \)\}. We apply the Kramers-Moyal expansion to the right-hand side of Eq. (3·1), yielding

\[
\frac{\partial}{\partial t} W(\alpha, \dot{\alpha}; t) = -\int d(\Delta \alpha) d(\Delta \dot{\alpha}) \left\{ 1 - \exp \left( -\Delta \alpha \frac{\partial}{\partial \alpha} - \Delta \dot{\alpha} \frac{\partial}{\partial \dot{\alpha}} \right) \right\} T(\alpha, \dot{\alpha}; \Delta \alpha, \Delta \dot{\alpha}) W(\alpha, \dot{\alpha}; t),
\]

where \( T(\alpha, \dot{\alpha}; \Delta \alpha, \Delta \dot{\alpha}) \) is the transition probability per unit time from \{\( \alpha, \dot{\alpha} \)\} to \{\( \alpha + \Delta \alpha, \dot{\alpha} + \Delta \dot{\alpha} \)\}.

When the transitions are considered as local events, i.e.,

\[
T(\alpha, \dot{\alpha}; \Delta \alpha, \Delta \dot{\alpha}) = \Omega \omega(\underline{x}, j; \Delta \alpha, \Delta \dot{\alpha}),
\]

the system size expansion plays an important role. Here, in Eq. (3·3), \( \Omega \) is the system size and

\[
\underline{x} = \frac{\alpha}{\Omega} = \varepsilon \alpha, \quad \text{and} \quad j = \varepsilon \dot{\alpha} \quad (\varepsilon = 1/\Omega)
\]
denote the densities of the extensive variables and of the fluxes. The corresponding
scale change is
\[ \Omega^{2N} W(\alpha, \dot{\alpha}, t) = \phi(x, j, t). \]  
(3.5)
To proceed, we introduce the entities
\[ c_{n,m}[x, j] = -\int d(\Delta \alpha) d(\Delta \dot{\alpha}) (\Delta \alpha)^n (\Delta \dot{\alpha})^m \omega(x, j; \Delta \alpha, \Delta \dot{\alpha}). \]  
(3.6)
By the definition given by Eq. (3.6) and by noting the fact that \( \Delta \alpha \) is the step per unit time, the dissipative fluxes are identified by
\[ j = c_{1,0}[x, j]. \]  
(3.7a)
Note here that Eq. (3.7a) is not an equation like Eq. (2.23) determining \( j \) as a function of \( x \) but an identity.
By assuming that the fluctuations are of order \( \varepsilon^{1/2} \), let us introduce the mean values \( x(t) \) and \( j(t) \) and set
\[ x = x(t) + \varepsilon^{1/2} \xi \quad \text{and} \quad j = j(t) + \varepsilon^{1/2} \zeta. \]  
(3.8)
Then, let us introduce a distribution function \( p(\xi, \zeta; t) \) for the fluctuations;
\[ p(\xi, \zeta; t) = \Omega^N \phi(x(t) + \varepsilon^{1/2} \xi, j(t) + \varepsilon^{1/2} \zeta; t). \]  
(3.9)
It is readily seen that the master equation (3.2) reads
\[ \frac{\partial}{\partial t} p(\xi, \zeta; t) - \Omega^{1/2} \left[ \frac{\partial}{\partial \xi} \cdot \dot{x}(t) + \frac{\partial}{\partial \zeta} \cdot \dot{j}(t) \right] p(\xi, \zeta; t) \]
\[ = \Omega \int d(\Delta \alpha) d(\Delta \dot{\alpha}) \left( \exp \left( -\varepsilon^{1/2} \Delta \alpha \frac{\partial}{\partial \xi} \Delta \alpha \frac{\partial}{\partial \zeta} - \varepsilon^{1/2} \Delta \dot{\alpha} \frac{\partial}{\partial \zeta} \right) - 1 \right) \]
\[ \times \omega \left( x(t) + \varepsilon^{1/2} \xi, j(t) + \varepsilon^{1/2} \zeta; \Delta \alpha, \Delta \dot{\alpha} \right) p(\xi, \zeta; t). \]  
(3.10)
By expanding the exponential factor involved in Eq. (3.10), we postulate that
\[ \frac{d}{dt} x(t) = j(t), \]  
(3.7b)
and
\[ \frac{d}{dt} j(t) = c_{0,1}[x(t), j(t)]. \]  
(3.11)
These equations determine the dominant motion of the system. Equation (3.7b) corresponds to Eq. (3.7a).
By using Eqs. (3.7b) and (3.11) into Eq. (3.10), we obtain
\[ \frac{\partial}{\partial t} p(\xi, \zeta; t) + \frac{\partial}{\partial \xi} (\xi p) + \frac{\partial}{\partial \zeta} \left\{ \xi \cdot \frac{\partial}{\partial x} c_{0,1}[x(t), j(t)] + \zeta \cdot \frac{\partial}{\partial j} c_{0,1}[x(t), j(t)] \right\} \]
\[ = \Omega \int d(\Delta \alpha) d(\Delta \dot{\alpha}) \sum_{n=2}^{\infty} \frac{1}{n!} \varepsilon^{n/2} \left( -\Delta \alpha \frac{\partial}{\partial \xi} - \Delta \dot{\alpha} \frac{\partial}{\partial \zeta} \right)^n \omega(x, j; \Delta \alpha, \Delta \dot{\alpha}) p(\xi, \zeta; t). \]  
(3.12)
Accordingly, we see that the distribution function satisfies

$$\frac{\partial}{\partial t} p(\xi, \zeta; t) = \frac{\partial}{\partial \xi} (\zeta p) + \frac{\partial}{\partial \zeta} \left\{ \xi \cdot \frac{\partial}{\partial x} c_{0,1}[x(t), j(t)] + \zeta \cdot \frac{\partial}{\partial j} c_{0,1}[x(t), j(t)] \right\} + \frac{\partial^2}{\partial \xi \partial \zeta} [C(t)p(\xi, \zeta; t)]$$

$$+ \frac{1}{2} \frac{\partial^2}{\partial \xi^2} [B(t)p(\xi, \zeta; t)] + \frac{1}{2} \frac{\partial^2}{\partial \zeta^2} [D(t)p(\xi, \zeta; t)],$$

(3-13)

in the limit $\varepsilon \to 0$. Here, in Eq. (3-13), the quantities are defined as

$$D(t) = c_{2,0}[x(t), j(t)],$$

(3-14)

$$B(t) = c_{0,2}[x(t), j(t)],$$

(3-15)

and

$$C(t) = c_{1,1}[x(t), j(t)].$$

(3-16)

It is noted here that these quantities are defined along the dominant but stochastic motion of the system defined by Eq. (3-7b). If one assumes that, for near equilibrium systems, the steps $\Delta \alpha$ and $\Delta \dot{\alpha}$ are statistically independent, $C(t)$ goes to zero. Furthermore, it is normally assumed that $B(t)$ vanishes for the second-order processes considered. Since we wish to consider a more general non-equilibrium case, we do not make such assumptions.

In order to solve Eq. (3-13), it is convenient to introduce the notation $\eta = (\xi, \zeta)$. Then, Eq. (3-13) can be rewritten in the form

$$\frac{\partial}{\partial t} p(\xi, \zeta; t) = - \frac{\partial}{\partial \eta} (F(t) \eta p) + \frac{1}{2} \frac{\partial^2}{\partial \eta^2} [\Gamma(t)p(\xi, \zeta; t)],$$

(3-13a)

where

$$(\Gamma_{ij}(t)) = \begin{pmatrix} D(t) & C(t) \\ C(t) & B(t) \end{pmatrix},$$

(3-17)

and

$$F(t) = \begin{pmatrix} 0 & 1 \\ K_1 & K_2 \end{pmatrix},$$

(3-18)

where

$$K_1(t) = \frac{\partial}{\partial x} c_{0,1}[x(t), j(t)],$$

(3-18a)

$$K_2(t) = \frac{\partial}{\partial j} c_{0,1}[x(t), j(t)].$$

(3-18b)

It is well known that Eq. (3-13a) is satisfied by a Gaussian distribution function of the form

$$p(\eta, t) = [\det(m(t)/2\pi)]^{1/2} \exp \left\{ -\frac{1}{2} \eta \cdot m(t) \cdot \eta \right\}, \quad (\eta = (\xi, \zeta))$$

(3-19)
where \( m(t) \) is the inverse of the variance \( \Sigma(t) \) whose matrix elements are defined by

\[
\Sigma_{ij}(t) = \int d\eta p(\eta, t) \eta_i \eta_j.
\] (3.20)

Note that the matrix \( \Sigma(t) \), in general, is not block-diagonalized. The evolution equation of \( \Sigma(t) \) is

\[
\frac{d}{dt} \Sigma_{ij}(t) = \Gamma_{ij}(t) + \sum_k [F_{ik} \Sigma_{kj} + \Sigma_{ik} F_{kj}].
\] (3.21)

\((i, j = 1, 2, \cdots, 2N)\)

Since we have Eq. (3.11) for the temporal change of the fluxes, \( F(t) \) defined above describes the regression processes. Accordingly, we have the stationarity conditions in matrix form,

\[
\Gamma + F \Sigma + \tilde{\Sigma} \tilde{F} = 0.
\] (3.22)

This is a generalization of the condition (2.33) to second order systems.

(A) The first case, \( C(t) = 0 \)

Let us consider first the case in which \( C(t) \) and \( D(t) \) vanish. In this case, it is easy to verify that the evolution equation for the variance \( \Sigma(t) \) is block-diagonalized:

\[
\Sigma(t) = \begin{pmatrix}
\sigma(t) & 0 \\
0 & \sigma_j(t)
\end{pmatrix}.
\] (3.23)

where \( \sigma(t) \) is the symmetric matrix defined by Eq. (2.26), whose evolution equation now is given by

\[
\frac{d}{dt} \sigma_{ij}(t) = 0. \quad (i, j = 1, 2, \cdots, N)
\] (3.21a)

The variance of the slow variables is stationary. Hence, it is convenient to write Eq. (3.21) in the form

\[
\frac{d}{dt} \Sigma_{ij}(t) = B_{ij}(t) + \sum_k [F_{ik} \Sigma_{kj} + \Sigma_{ik} F_{kj}]. \quad (i, j = N + 1, \cdots, 2N)
\] (3.24)

Equation (3.24) corresponds to the evolution equation (2.28) in this case. The stationarity condition (3.22) involves the following relation between the two kinds of variance:

\[
\tilde{\sigma}(t) + \sigma(t) K_1(t) = 0.
\] (3.25)

As we will see in § 5, these conditions are fulfilled by some known models.

(B) The second case, \( C(t) \neq 0 \)

Following Wang and Uhlenbeck, the condition (3.24) can be proved in a general way. Since, by definition, the variance matrix \( \Sigma(t) \) is symmetric, we shall write it as

\[
\Sigma(t) = \begin{pmatrix}
\Sigma_1(t) & \Sigma_2(t) \\
\Sigma_2(t) & \Sigma_3(t)
\end{pmatrix}
\] (3.26)
where the matrices $\Sigma_i(t)$ $(i = 1, 2, 3)$ are symmetric. Hence, from Eq. (3·22), we obtain

$$\Sigma_2(t) = -D(t)/2, \quad (3·27a)$$

$$\Sigma_3(t) + \Sigma_1(t)K_1(t) + \Sigma_2K_2(t) = -C(t)/2, \quad (3·27b)$$

$$\Sigma_2(t)K_1(t) + \Sigma_3(t)K_2(t) + (\Sigma_2(t)K_1(t) + \Sigma_3(t)K_2(t))^\text{trans} = -B(t)/2, \quad (3·27c)$$

where $A^\text{trans}$ represents the transpose. Equation (3·27c) is the counterpart to the steady-state condition (2·33).

Finally, modifying Tomita and Tomita’s argument, let us define a generalized irreversible circulation of fluctuation in second-order systems. We shall postulate that the quantity defined in the flux subspace

$$\Omega = -\frac{1}{2} \left\{ (\Sigma_2(t)K_1(t) + \Sigma_3(t)K_2(t)) - (\Sigma_2(t)K_1(t) + \Sigma_3(t)K_2(t))^\text{trans} \right\} \quad (3·28)$$

is the concept analogous to the irreversible circulation, Eq. (2·34).

§4. The entropy production

We are interested in a generalization of entropy. First of all, we postulate to extend Eq. (2·19) in the following way:

$$W(\alpha, \dot{\alpha}, t) \propto \exp[\Omega s(\alpha, \dot{\alpha}, t)]. \quad (4·1)$$

Here, $\Omega s(\alpha, \dot{\alpha}, t)$ denotes a generalized entropy which is a function of $\alpha$ as well as $\dot{\alpha}$. Then, the formula for the time-derivative of $s(\alpha, \dot{\alpha}, t)$ can be obtained by utilizing Eq. (3·2):

$$\Omega \frac{\partial}{\partial t} s(\alpha, \dot{\alpha}, t) = \frac{1}{W(\alpha, \dot{\alpha}, t)} \times \int d(\Delta\alpha)d(\Delta\dot{\alpha}) \left\{ \exp \left( -\Delta\alpha \frac{\partial}{\partial \alpha} - \Delta\dot{\alpha} \frac{\partial}{\partial \dot{\alpha}} \right) - 1 \right\} T(\alpha, \dot{\alpha}; \Delta\alpha, \Delta\dot{\alpha})W(\alpha, \dot{\alpha}; t)$$

$$= \int d(\Delta\alpha)d(\Delta\dot{\alpha}) \left\{ \exp \left( -\Delta\alpha \frac{\partial}{\partial \alpha} - \Delta\dot{\alpha} \frac{\partial}{\partial \dot{\alpha}} \right) - 1 \right\} T(\alpha, \dot{\alpha}; \Delta\alpha, \Delta\dot{\alpha})$$

$$+ \frac{1}{W(\alpha, \dot{\alpha}, t)} \int d(\Delta\alpha)d(\Delta\dot{\alpha})T(\bullet) \left\{ \exp \left( -\Delta\alpha \frac{\partial}{\partial \alpha} - \Delta\dot{\alpha} \frac{\partial}{\partial \dot{\alpha}} \right) - 1 \right\} W(\alpha, \dot{\alpha}; t). \quad (4·2)$$

By employing the same method developed in the previous section, and by making use of Eqs. (3·5), (3·6) and (3·9) together with Eq. (3·7), we can write Eq. (4·2) as

$$\Omega \frac{\partial}{\partial t} s(\alpha, \dot{\alpha}, t) = \Omega \int d(\Delta\alpha)d(\Delta\dot{\alpha}) \left\{ \exp \left( -\epsilon \Delta\alpha \frac{\partial}{\partial x} - \epsilon \Delta\dot{\alpha} \frac{\partial}{\partial j} \right) - 1 \right\} \omega(x, j; \Delta\alpha, \dot{\alpha})$$
Accordingly, we see that the first term on the right-hand side of Eq. (4.3) is equal to the entropy production in extended irreversible thermodynamics (EIT).15) (See the Appendix for the contraction of EIT). To explain concisely how this "transient thermodynamics" differs from classical irreversible thermodynamics, we will add a typical example in § 5.

The second term on the right-hand side of Eq. (4.3) is related to the occurrence of the irreversible circulation. We expand

\[ \omega(x(t) + \varepsilon^{1/2} \xi, j(t) + \varepsilon^{1/2} \zeta; \Delta \alpha, \Delta \dot{\alpha}) \]

\[ = \omega(x(t), j(t); \Delta \alpha, \Delta \dot{\alpha}) + \varepsilon^{1/2} \left[ \xi \cdot \frac{\partial}{\partial x} + \zeta \cdot \frac{\partial}{\partial j} \right] \omega(x(t), j(t); \Delta \alpha, \Delta \dot{\alpha}). \]

(4.4)

Then, by making use of Eq. (4.4) into Eq. (4.3), we make the approximations

\[ \Omega \int d(\Delta \alpha) d(\Delta \dot{\alpha}) \left\{ \exp \left( -\varepsilon \Delta \alpha \frac{\partial}{\partial \xi} - \varepsilon \Delta \dot{\alpha} \frac{\partial}{\partial \zeta} \right) - 1 \right\} \omega(x, j; \Delta \alpha, \Delta \dot{\alpha}) \approx - \int d(\Delta \alpha) d(\Delta \dot{\alpha}) \left( \Delta \alpha \frac{\partial}{\partial x} + \Delta \dot{\alpha} \frac{\partial}{\partial j} \right) \omega(x, j; \Delta \alpha, \Delta \dot{\alpha}) \]

\[ = -F(t), \quad (4.5) \]

where \( F(t) \) is defined by Eq. (3.18), and

\[ \frac{\Omega}{p(\xi, \zeta; t)} \int d(\Delta \alpha) d(\Delta \dot{\alpha}) \left\{ \exp \left( -\varepsilon^{1/2} \Delta \alpha \frac{\partial}{\partial \xi} - \varepsilon^{1/2} \Delta \dot{\alpha} \frac{\partial}{\partial \zeta} \right) - 1 \right\} \omega(\bullet) p(\xi, \zeta; t) \approx - \frac{\Omega \varepsilon^{1/2}}{p(\xi, \zeta; t)} \int d(\Delta \alpha) d(\Delta \dot{\alpha}) \left( \Delta \alpha \frac{\partial}{\partial \xi} + \Delta \dot{\alpha} \frac{\partial}{\partial \zeta} \right) \omega(x, j; \Delta \alpha, \Delta \dot{\alpha}) \]

\[ + \frac{1}{2p(\xi, \zeta; t)} \int d(\Delta \alpha) d(\Delta \dot{\alpha}) \left( \Delta \alpha \frac{\partial}{\partial \xi} + \Delta \dot{\alpha} \frac{\partial}{\partial \zeta} \right)^2 \omega(x, j; \Delta \alpha, \Delta \dot{\alpha}) \]

\[ = j(t) X(t) + j(t) Y(t), \quad (4.6) \]

Thus, the right-hand side of Eq. (4.6) can be interpreted as the regression matrix, analogous to Eq. (2.30). Here, in Eq. (4.6) we have used the fact that \( -\frac{\partial}{\partial x} c_1, o(x, j) \) is zero, since we have set the variables \( x \) and \( j \) to be independent. By definition, if \( F(t) \) is positive, the orbits described by \( x(t) \) and \( j(t) \) might be unstable against the fluctuations considered.

By making use of Eqs. (3.11) and (3.7a), we can rewrite the first term on the right-hand side of Eq. (4.6) in the form

\[ - \frac{\Omega \varepsilon^{1/2}}{p(\xi, \zeta; t)} \int d(\Delta \alpha) d(\Delta \dot{\alpha}) \left( \Delta \alpha \frac{\partial}{\partial \xi} + \Delta \dot{\alpha} \frac{\partial}{\partial \zeta} \right) \omega(x, j; \Delta \alpha, \Delta \dot{\alpha}) \]

\[ = j(t) X(t) + j(t) Y(t), \quad (4.7) \]
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where

\[ j(t) = c_1 \circ \circ (x(t), j(t)), \quad \text{and} \quad \dot{j}(t) = c_0, \circ (x(t), j(t)), \]

\[ X(t) = -\varepsilon^{-1/2} \frac{\partial}{\partial \xi} \ln p(\xi, \zeta; t), \quad \text{and} \quad Y(t) = -\varepsilon^{-1/2} \frac{\partial}{\partial \xi} \ln p(\xi, \zeta; t). \tag{4.9} \]

Equation (4.7) is nothing but the entropy production in the thermodynamic sense. Then, we obtain the extended version of Eq. (2.41),

\[ \Omega \frac{\partial S}{\partial t} = j(t)X(t) + \dot{j}(t)Y(t) + \frac{1}{2} \text{Tr} \Sigma(t) g^{ext}(t) - \frac{1}{2} \text{Tr} (g^{ext}(t)\zeta) \cdot \Gamma(t) \cdot (g^{ext}(t)\zeta), \tag{4.10} \]

where \( g^{ext}(t) \) is the inverse matrix of \( \Sigma(t) \). By substituting Eqs. (3.21) and (3.22) into Eq. (4.10) it is a simple matter of calculation to verify that

\[ \left\langle \Omega \frac{\partial S}{\partial t} \right\rangle_{\text{av}} = j(t)X(t) + \dot{j}(t)Y(t) + \text{Tr} F(t). \tag{4.11} \]

Equation (4.11) is the generalization of Eq. (2.42) to second-order systems. Again, extended irreversible circulation does not contribute to the entropy production. Only the symmetric Onsager coefficients enter the statement.

Before concluding, it should be commented that since the \( \beta \)-variables are not conserved, as noted in §2, the source terms must be added to the second term on the right-hand side of Eq. (4.11).

§5. An irreversible circulation in a modified Onsager model

At the end of §2.2, we noted that the existence of dissipative fluxes is necessary to find a non-vanishing circulation. The occurrence of flux-relaxation will offer an interesting possibility of generalizing irreversible circulation. The existence of irreversible circulation would not be the outcome of an absence of the reciprocal relations for transport coefficients. In order to see this point in detail, we study irreversible processes of second order in open (discontinuous) systems, i.e., in systems with inertia, which were considered by Machlup and Onsager. \(^4\) It is assumed that the entropy is a function of the \( 2N \) variables \( \alpha_i \) and \( \alpha'_i \). Here, it is assumed that the variables \( \alpha_i \) are even functions of time. We shall call this space of the variables the extended Gibbs (or Machlup-Onsager) space. We can think of the fluctuating entropy consisting of a potential and a kinetic part as

\[ S[\alpha_i; \alpha'_i] = S_0 - \frac{1}{2} \sum g_{ij} \alpha_i \alpha_j - \frac{1}{2} \sum m_{ij} \alpha_i \alpha'_j, \tag{5.1} \]

where \( S_0 \) is the entropy for an absolute equilibrium state. It is usually assumed that the matrix \( g(= g_{ij}) \) is symmetric with respect to the suffixes \( i \) and \( j \). The matrix \( m(= m_{ij}) \) is not necessarily symmetric. We shall call \( S[\alpha_i; \alpha'_i] \) the generalized entropy. The purpose of this generalization is to write the linear phenomenological laws as

\[ \sum R_{j\alpha_i} \dot{\alpha}_i = \frac{\partial S}{\partial \alpha_j} + \frac{d}{dt} \left( \frac{\partial S}{\partial \dot{\alpha}_j} \right) (\equiv \phi_j). \tag{5.2} \]
Here, $R_{ij}$ denotes the transport coefficient introduced. Then, the entropy production takes the form

$$\frac{d}{dt}S[\alpha, \dot{\alpha}] = \sum_{i, k=1}^{N} \dot{\alpha}_i R_{ik} \dot{\alpha}_k.$$  \hfill (5·3)

It is at this point that the classical irreversible thermodynamics and EIT part company. In general, the second term on the right-hand side of Eq. (5·2) is small compared to the other term. The matrix $R$ might be symmetric by the Onsager reciprocity theorem. However, as was demonstrated by Tomita and Tomita, in contrast to the case of aged system, the matrix $R$ has a non-vanishing antisymmetric part in the general off-equilibrium case.

If there exists a time interval which is so short that the change of the $\beta$-variables during the time interval can be considered to be small, the Fokker-Planck equation for this model reads

$$\frac{\partial p}{\partial t} = - \sum_{i=1}^{2N} \frac{\partial}{\partial \eta_i} \left( \sum_{k=1}^{2N} \bar{K}_{ik} \eta_k p \right) + \frac{1}{2} \sum_{i, k=1}^{2N} \frac{\partial^2}{\partial \eta_i \partial \eta_k} (\bar{D}_{ik} p),$$  \hfill (5·4)

where the $2N$ by $2N$ matrices $\bar{K}$ and $\bar{D}$ are given by

$$\bar{K} = \begin{pmatrix} 0 & I \\ -M^{-1}G & -M^{-1}R \end{pmatrix},$$  \hfill (5·5)

and

$$\bar{D} = \begin{pmatrix} 0 & 0 \\ 0 & 2M^{-1}RM^{-1} \end{pmatrix},$$  \hfill (5·6)

respectively. Here, the matrices $G$ and $M$ are defined as

$$G = \Omega(g_{ik}) \quad \text{and} \quad M = \Omega(m_{ik}).$$  \hfill (5·7)

It is noted that the conditions (3·22) are not fulfilled by the specific forms of $\bar{K}$ and $\bar{D}$.

Next, let us adopt the method described in § 3 to the system considered. First of all, let us introduce Eqs. (3·8), together with Eq. (3·4), into Eq. (5·1) to model the expression for the fluctuating entropy,

$$s[x(t) + \varepsilon^{1/2} \xi, j(t) + \varepsilon^{1/2} \zeta]$$

$$= s_0 - \frac{1}{2} \sum G_{ik} x_i(t)x_k(t) - \frac{1}{2} \sum M_{ik} j_i(t)j_k(t) - \varepsilon^{1/2} \sum G_{ik} x_i(t)\xi_k$$

$$- \sum M_{ik} j_i(t)\xi_k - \frac{1}{2} \sum g_{ik}(t)\xi_i\xi_k - \frac{1}{2} \sum m_{ik}(t)\zeta_i\zeta_k.$$  \hfill (5·8)

(The symbol $\xi$ should not be confused with the generalized forces $\xi$ which Machlup and Onsager used as the right-hand side of Eq. (5·2). In this paper, $\phi_j$ (defined by Eq. (5·2)) represents the generalized force). Here, we have assumed the matrix $m(t)$
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to be time-dependent. That is, the coefficients appeared in the Fokker-Planck equation are different from the coefficients that determine the macroscopic laws. This assumption is plausible, since the characteristic time of the α-variables, in general, is much longer than that of the β-variables. Note here that, as elucidated by van Kampen,\textsuperscript{16} the fluctuation-dissipation theorem implies that the coefficients appearing in the Fokker-Planck equation are the same Onsager coefficients that determine the fluctuations. In this regard, the present example assumes that the classical fluctuation-dissipation theorem (to be interpreted in accordance in van Kampen’s sense) cannot be adopted to flux-relaxation phenomena. That is, the relaxation times for flux-relaxations are not the same $F_{ij}$ that determine the phenomenological laws, (5·2).

We are interested in the part of the fluctuating-entropy production, $-\frac{1}{2} \sum \dot{m}_{ik} \zeta_i \zeta_k$, whose averages with respect to the probability distribution function $p(\xi, \zeta, t)$ go to

$$-\frac{1}{2} \sum \dot{m}_{ik} \langle \zeta_i \zeta_k \rangle_{av}(t) = \frac{1}{2} \sum m_{ik} \frac{d}{dt} \langle \zeta_i \zeta_k \rangle_{av}(t).$$

(5·9a)

This is the non-classical entropy production, which corresponds to the second term on the right-hand side of Eq. (2·40). However, by utilizing Eq. (5·3), together with Eqs. (5·5) and (5·6), into Eq. (5·9a), it is readily seen that

$$\frac{1}{2} \sum m_{ik} \frac{d}{dt} \langle \zeta_i \zeta_k \rangle_{av}(t) = 0.$$  

(5·9b)

Hence, there is no generalized circulation of fluctuations in this model.

In order to rescue the model from this shortcoming, it is sufficient to modify the matrix $\tilde{D}$ in the following form:

$$\tilde{D} = \begin{pmatrix} 0 & 0 \\ 0 & 2M^{-1}RM^{-1} + D' \end{pmatrix}. \quad (D' \neq 0) 

(5·10)

This is a counterpart to set up antisymmetric Onsager coefficients. It is not difficult to realize that the postulate (5·10) is equivalent to giving up the fluctuation-dissipation theorem (see, Eq. (57) of the second paper of Ref. 3)). It is then easy to see that the extended circulation $\Omega$, defined by Eq. (3·30), is written as

$$\Omega_{ij} = \frac{1}{2} \sum \langle \zeta_i \zeta_k \rangle_{av}(t) F_{j,k}(t) - F_{i,k}(t) \langle \zeta_k \zeta_j \rangle_{av}(t),$$

(5·11)

where the elements of the matrix $F$ are given by

$$F_{ij} = (M^{-1}R)_{ij}. 

(5·12a)

These values define the inverse of the relaxation-times. Hence, we have

$$T = F^{-1} = LM.$$ 

(5·12b)

The extended irreversible circulation is directly related to the transport coefficients as well as the flux-flux correlations. For near equilibrium cases, the matrix $R$ might
be symmetric by the reciprocity theorem. Hence, when the matrix $M(t)$ is symmetric, there is no extended irreversible circulation in such cases. It is noted that Machlup and Onsager $^4$ only treated the case in which the matrix $M(t)$ is symmetric and stationary. Accordingly, we conclude that the sufficient condition for the existence of generalized irreversible circulation is that the matrix $R$ is not symmetric as long as $M(t)$ is symmetric. The relaxation-time matrix $F$ has a non-vanishing antisymmetric part if this condition is fulfilled.

§6. Concluding remarks

In summary, the concept of irreversible circulation of fluctuations, which was originally developed for first-order systems by Tomita and Tomita, $^1,2$ has been extended to the second-order systems with inertia. The present analysis of the irreversible circulation of fluctuations elucidates their thermodynamical meaning. We have demonstrated that there are additional contributions from such circulation to the entropy production, which are due to the presence of the source terms in the balance equation for the fundamental thermodynamic variables. In the cases of first-order systems, the importance of such terms has been pointed out by de Groot and Mazur.$^{12b}$

In the case of the second-order systems defined by Onsager, $^4$ we have obtained the irreversible circulation of flux-fluctuations which is related to the properties of the relaxation processes, as seen from Eq. (3·21). It is worth noting the fact that the extended irreversible circulation for the second-order systems is defined in a manner almost parallel with the first-order systems considered by Tomita and Tomita. $^2$ The mathematical structures of the two cases are quite similar. However, the present consideration should not be considered to be involved in Tomita and Tomita’s theory. As seen from the definition (2·35), when the transport-coefficient matrix $L$ ($= \text{the inverse of } R$) is symmetric, there is no circulation in Tomita and Tomita’s form. The corresponding concept to $L$ is $Rm^{-1}$ in the new theory. The latter is the relaxation-time matrix. The extended irreversible circulation, therefore, is not directly related to the absence of detailed balance. The extended irreversible circulation of flux-fluctuations is not necessarily vanishing, even if the matrix $R$ is symmetric, since there is freedom to add an antisymmetric matrix to $M$ (or $m$) without changing the expression for the generalized entropy, (5·1).

Appendix A  

--- A Simple Example ---

Let us consider a simple example. First of all, we shall write Eq. (5·2) in the following form for the case $n = 2$:

\[
\frac{d}{dt} J_1 = -\frac{1}{\tau_1} (J_1 - L_{11}\alpha_1 - L_{12}\alpha_2) + a(J_2 - L_{21}\alpha_1 - L_{22}\alpha_2), \quad (A·1)
\]

\[
\frac{d}{dt} J_2 = -\frac{1}{\tau_2} (J_2 - L_{21}\alpha_1 - L_{22}\alpha_2) + b(J_1 - L_{11}\alpha_1 - L_{12}\alpha_2). \quad (A·2)
\]
Here, \( a (\geq 0) \) and \( b \) are constants.

1. The case with the detailed balance condition

In the special case of steady states in which detailed balance (hence, the reciprocity relation) is maintained, the set of equations above can be written as

\[
\frac{d}{dt} \Delta J_1 = -\frac{1}{\tau_1} \Delta J_1 + a \Delta J_2, \quad (A\cdot3)
\]

\[
\frac{d}{dt} \Delta J_2 = -\frac{1}{\tau_2} \Delta J_2 + b \Delta J_1, \quad (A\cdot4)
\]

where

\[
\Delta J_i = \mathbf{J}_i - \mathbf{J}_i^{st}, \quad (i = 1, 2) \quad (A\cdot5)
\]

When it is assumed that \( b = -a \), (say, anti-symmetric), from Eqs. (A\cdot3) and (A\cdot4) we obtain

\[
\left( \frac{d}{dt} + \tau_1 \right) \left( \frac{d}{dt} + \tau_2 \right) \Delta J_i = -a^2 \Delta J_i. \quad (A\cdot6)
\]

Then, it is a simple matter of calculation to see that if the condition

\[
2a \geq \left| \frac{1}{\tau_1} - \frac{1}{\tau_2} \right| \quad (A\cdot7)
\]

is fulfilled, the solution of (A\cdot6) exhibits oscillations with damping. This is a prototype of extended irreversible circulation.

2. A general case

When the Onsager coefficient, \( L_{12} \), has a sufficiently small antisymmetric part, \( L_{12}^a \), Eqs. (A\cdot1) and (A\cdot2) yield

\[
\left[ \left( \frac{d}{dt} + \frac{1}{\tau_1} \right) \left( \frac{d}{dt} + \frac{1}{\tau_2} \right) + a^2 - 2aL_{12}^a \right] \Delta \mathbf{J}_1
\]

\[
= L_{12}^a \left( a \mathbf{J}_1^{st} - \frac{1}{\tau_2} \mathbf{J}_2^{st} \right) + (L_{12}^a)^2 \left( a \alpha_2 - \frac{1}{\tau_2} \alpha_1 \right) \quad (A\cdot8)
\]

with

\[
\Delta \mathbf{J}_1 = \mathbf{J}_1 - \mathbf{J}_1^c, \quad \text{with} \quad \mathbf{J}_1^c = \mathbf{J}_1^{st} + L_{12}^a \alpha_2, \quad (A\cdot9)
\]

and a similar equation for \( \Delta \mathbf{J}_2 \). The last term on the right-hand side of Eq. (A\cdot8) can be discarded by assumption. Accordingly, the condition (A\cdot7) is modified to the form

\[
2(a - L_{12}^a) \geq \left| \frac{1}{\tau_1} - \frac{1}{\tau_2} \right| \quad (A\cdot10)
\]

If the effect of flux-fluctuations can be neglected as small, we infer Tomita and Tomita's circulation.
A new formulation of irreversible thermodynamics, currently known as extended irreversible thermodynamics, has fueled attention only recently. A tentative introduction will be made. There exists an enormous gap between microscopic and the macroscopic descriptions that is bridged by statistical mechanics. The main problem is how can we reconcile the reversible microscopic laws with the macroscopic laws of thermodynamics? It is impossible to obtain irreversible equations without additional hypothesis proceeding from reversible microscopic equations. For instance, a presumption of local equilibrium is made, although containing several physical ideas, amounts to the assertion that the microscopic equations are also valid as a macroscopic laws. On the other hand, a new formulation has been sought for some intermediate, or mesoscopic, approach in which an off-equilibrium system is described not only by classical extensive (conserved) variables but also by some other variables. From the standpoint of physics, we must first examine the meaning of such mesoscopic descriptions. The present author feels confident that the second law of thermodynamics belongs to a class of physical laws which does not refer to what laws govern the world at the molecular level.

Since several versions of the extended theory have been proposed, we shall settle here on a simplified formal structure for EIT. It is well known that, in dealing with systems out of equilibrium, one has more variables than equations for the extensive variables used, because the fluxes of the variables remain unspecified. In the case of heat conduction, the heat flux appearing in the energy balance equation is indeed unspecified. To complete the theory one has to resort to experiment and write the constitutive equations relating the fluxes and the functionals of the extensive variables, the thermodynamic forces, in a particular system. To set up such phenomenological laws, we linearize the dependence of the fluxes upon the forces. Classical irreversible thermodynamics, for instance, leads inexorably to Fourier's law. It was recognized that conventional irreversible thermodynamics has a deficiency when applied to the description of transient effects. For instance, Fourier's law leads to a parabolic equation and an infinite wave-front speed. Müller traced the origin of the difficulty to the neglect of terms of second order in the heat flux in the conventional expression for entropy. The analogous paradox in classical kinetic theory was solved by Grad by employing a method of moments.

In EIT, the independent variables include both the extensive variables $\alpha$ and the fluxes $\phi$. By setting up an extended Gibbs space of fundamental variables, the physical nature of the fluxes is found to be completely different from that of the conserved extensive variables. The fluxes are non-conserved and fast. However, the fluxes are associated with well-defined microscopic operators, and they allow for a more direct comparison with statistical mechanics. EIT aims to go beyond the hypothesis of local equilibrium. In developing the theory, one assumes that the entropy differential is exact in the extended Gibbs space of independent variables. Then, EIT derives the evolution equations for the fluxes from the assumed form of the (extended) Gibbs relation for the generalized entropy. The balance and the
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constitutive equations are obtained in the forms

\[ \frac{d}{dt} \alpha = \dot{\alpha} \quad \text{and} \quad \frac{d}{dt} \dot{\alpha} = \tau^{-1}(LX - \alpha), \]

(B.1)

respectively, where \( \tau \) is the relaxation-time matrix and \( X \) the thermodynamic force vector. The second equation describes a relaxation of the fluxes to the form given in the Onsager theory and is called the Maxwell-Cattaneo equation. The rationale for this is that if a thermodynamic force were suddenly switched off, the ordered microscopic (or mesoscopic) motion which constitutes the fluxes would require a mean "collision" time to be dissipated.

We know by now that the Onsager theory is a thermodynamic approach to the transport coefficients \( L \) involved in (B.1). EIT is necessary for a thermodynamics description of the relaxation times and is an alternative to the Fokker-Planck theory for second-order systems.

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References

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