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A Generalization of Thermodynamics of Irreversible Processes on the Basis of Theory of Brownian Movement

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Fluctuations in nature provide a meeting ground between the microscopic and macroscopic levels. In the present state of the theory of irreversibility, a time-space correlation of the fluctuation around an equilibrium state produces an average regression of it giving rise to irreversible processes from a steady state to the equilibrium, in which the dispersion of fluctuations determines a resistance in the process, and vice versa. If we go to a more microscopic level, we ought to encounter more vigorous fluctuations around the steady state. This may be expected from the viewpoint of the theory of Brownian movement in the narrow sense.

ONSAGER and MACHLUP[1] proposed and established a general principle, which is a kinetic analog of BOLTZMANN principle in thermostatics, on a concept of fluctuating paths to develop the theory of thermal fluctuations.

At present we have succeeded in developing the theory of Brownian movement on a dynamical basis[2], so that we should make an effort to seek a clue to the irreversible thermodynamics on the basis of the ONSAGER-MACHLUP principle.

Now, it is very instructive to note the recent improvement in quantum mechanics by FEYNMAN and SCHWINGER along the Lagrangian scheme[3].

As mentioned already by SAITÔ and NAMIKI[4], we may proceed along these lines to deal with the theory of thermal fluctuations consulting with FEYNMAN and SCHWINGER formalism in a corresponding manner. It seems to be a weak point, however, that they have taken an attitude too much corresponding to the quantum mechanical formalism.

In the present article, taking the ONSAGER-MACHLUP principle and the associated dynamical variation principle, we shall develop a generalized thermodynamics including fluctuations around a steady state due to 'micro-Brownian movement'.

Postulate I

In a phase space, a set of initial phase points of $\boldsymbol{E}_0$ is *measureable*, and its *Lebesque measure* is not zero. The set of trajectories drawn by the phase points from $\boldsymbol{E}_0$ must be pursued as a whole. Each of those may be described by the dynamical equation of motion in the true closed system. In a real system, however, the complete closure property does not hold in a strict sense. For this reason, a large number of transitions among the trajectories will take place due to interactions with surroundings during a time interval long enough microscopically to describe the behaviour in terms of macro-variables from macroscopic measurements. Thus the flux of trajectories becomes like a network bundle which is nothing but a path characterized by some sets of macro-variables against a time parameter. In a space of macro-variables versus time, a large number of the paths begin to start from the initial domain $\boldsymbol{E}_0$ in a very irregular manner.

Postulate II

When a 'Lagrangian'[5] of a path is given by $L(\alpha, \dot{\alpha})$ in terms of macro-variables of α and its time derivative $\dot{\alpha}$, a transition probability from a state of $\alpha = \alpha'$ and $t = 0$ to a state of $\alpha = \alpha''$ and $t = \tau$ during the time

[1] L. ONSAGER and S. MACHLUP, Phys. Rev. *91*, 1505 and 1521 (1953).
[2] N. TAKEYAMA, Experientia *22*, 774 (1966).
[3] R. P. FEYNMAN, Phys. Rev. *80*, 440 (1950); Phys. Rev. *84*, 108 (1951). – J. SCHWINGER, Phys. Rev. *82*, 914 (1951).
[4] N. SAITÔ and M. NAMIKI, Prog. theor. Phys., Kyoto *16*, 71 (1956).– N. SAITÔ, J. phys. Soc. Japan *12*, 1321 (1957).
[5] The terminology of 'Lagrangian' can be seen in the article by A. SIEGEL, Phys. Rev. *102*, 953 (1956), in which he called 'Onsager Lagrangian'.

interval of τ is given by the path integral of ONSAGER-MACHLUP as the following:

$$W(\alpha', 0; \alpha'', \tau) = N \int \exp \left\{ -(2k)^{-1} \int_0^\tau L(\alpha, \dot{\alpha})\, dt \right\} d\,(\text{paths}) \quad (1)$$

where N is a normalization constant and k is the BOLTZMANN constant.

Taking the variation of

$$\delta \int_0^\tau L(\alpha, \dot{\alpha})\, dt = \int_0^\tau \delta L\, dt + |L\, \delta t|_{\alpha', t=0}^{\alpha'', t=\tau}$$
$$= \int_0^\tau \left\{ \frac{\partial L}{\partial \alpha} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\alpha}}\right) \right\} \delta\alpha\, dt + \left| \left(\frac{\partial L}{\partial \dot{\alpha}}\right) \Delta\alpha - \left\{ \left(\frac{\partial L}{\partial \dot{\alpha}}\right) \dot{\alpha} - L \right\} \delta t \right|_{\alpha', 0}^{\alpha'', \tau} \quad (2)$$

with the total variation of $\Delta\alpha \equiv \delta\alpha + \dot{\alpha}\, \delta t$, in which the second term in the right-hand side of Eq. (2) comes from the variations in the initial and final boundary regions at $(\alpha', 0)$ and (α'', τ), a dynamical principle which gives a path of most probable course may be expressed by

$$\delta \ln W(\alpha', 0; \alpha'', \tau) = -(2k)^{-1} \delta \int_0^\tau L(\alpha, \dot{\alpha})\, dt. \quad (3)$$

Postulate III

The exponential factor in the integrand of Eq. (1) is a weight-fraction of a path under consideration which is called *Wiener measure* for a quasi-interval of $\{\alpha' < \alpha(t) < \alpha''\}$ for $0 < t < \tau$. Since a path has its own width due to the extent of fluctuation, the *measure* of the path is taken as

Wiener measure of $\alpha(t)$ for $0 < t < \tau$

$$= \exp \left\{ -\left(\frac{1}{2}\right) \left[\int_{-\infty}^{+\infty} \langle F(0)\, F(t') \rangle\, dt' \right]^{-1} \int_0^\tau (F\, F)\, dt \right\}, \quad (4)$$

where F denotes a fluctuating variable, and $\langle\ \rangle$ means the ensemble-averaged quantity. Here F is expressed in terms of α and $\dot{\alpha}$, because F itself is not observable, with help of LANGEVIN's equation of motion in a generalized sense. In comparison with Eq. (1), the 'Lagrangian' becomes

$$L(\alpha, \dot{\alpha}) = k \left[\int_{-\infty}^{+\infty} \langle F(0)\, F(t') \rangle\, dt' \right]^{-1} (F\, F). \quad (5)$$

From Eq. (3), the following equations may be obtained as the special cases of variation mentioned below:

(1) In the case of $\delta\alpha' = \delta\alpha'' = 0$ and $\delta t = 0$, we obtain

$$\frac{\partial L}{\partial \alpha} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\alpha}}\right) = 0, \quad (6)$$

which is an 'Euler-Lagrange' equation.

(2) In the case of $\delta\alpha' = 0$ and $\delta t = 0$, we obtain

$$\left(\frac{\partial \ln W}{\partial \alpha''}\right) \delta\alpha'' = -(2k)^{-1} \left(\frac{\partial L}{\partial \dot{\alpha}''}\right) \delta\alpha'',$$

which defines an operator of 'momentum' as an infinitesimal deformation of α-space by

$$\vec{P}_\alpha\, W \equiv \left(\frac{\partial L}{\partial \dot{\alpha}}\right) W = -2k \frac{\partial}{\partial \alpha} W. \quad (7)$$

(3) In the case of $\Delta\alpha = 0$ and $\delta t \neq 0$ at $t = \tau$, we obtain

$$\frac{\partial W}{\partial t} = (2k)^{-1} H\, W, \quad (8)$$

where H is a 'Hamiltonian' defined by

$$H \equiv \vec{P}_\alpha\, \dot{\alpha} - L. \quad (9)$$

Application to Brownian Movement

According to the LANGEVIN's approach, the fundamental equation is

$$\frac{dp}{dt} = -\frac{p}{\tau_p} + F, \quad (10)$$

where τ_p is the relaxation time of momentum p, and F is the fluctuating force by whose time-correlation the relaxation time is expressed as

$$\frac{1}{\tau_p} = (2\, m\, k\, T)^{-1} \int_{-\infty}^{+\infty} \langle F(0)\, F(t') \rangle\, dt', \quad (11)$$

Here m is the mass of a Brownian particle, and $\langle\ \rangle$ means to take the average with respect to the surroundings of the temperature T.

In this case, $\alpha = p$, and $F = \dot{p} + p/\tau_p$. The 'Lagrangian' is

$$L(p, \dot{p}) = \left(\frac{\tau_p}{2\, m\, T}\right) \left(\dot{p} + \frac{p}{\tau_p}\right)^2. \quad (12)$$

Using Eq. (6), the 'Euler-Lagrange' equation is obtained:

$$\ddot{p} - \left(\frac{1}{\tau_p}\right)^2 p = 0$$

or

$$\left(\frac{d}{dt} + \frac{1}{\tau_p}\right) \left(\frac{d}{dt} - \frac{1}{\tau_p}\right) p = 0, \quad (13)$$

from which under the initial and final conditions the general solution may be obtained in linear combination of the terms of $\exp(-t/\tau_p)$ and $\exp(+t/\tau_p)$. This fact means that its fundamental dependence on the time is in harmony with the reversibility in dynamical laws. Now the operator of 'momentum' referring to p becomes

$$\vec{P}_p \equiv \frac{\partial L}{\partial \dot{p}} = \left(\frac{\tau_p}{m\, T}\right) \left(\dot{p} + \frac{p}{\tau_p}\right), \quad (14)$$

which operates on the transition probability in p versus t space, W, as a deformation of p-space;

$$\vec{P}_p W = -2k\left(\frac{\partial}{\partial p}\right) W. \tag{15}$$

This shows that the BOLTZMANN constant acts as a sort of 'quantum' in the macroscopic level.

Then the 'Hamiltonian' is

$$\begin{aligned} H(\vec{P}_p, p) &\equiv \vec{P}_p p - L \\ &= \left(\frac{m\,T}{2\tau_p}\right)\vec{P}_p^2 - \vec{P}_p\left(\frac{p}{\tau_p}\right). \end{aligned} \tag{16}$$

Hence, expressing in terms of operators, we obtain the following equation of diffusion in momentum space[6]:

$$\begin{aligned} \frac{\partial W}{\partial t} &= (2k)^{-1} H W \\ &= \left(\frac{m\,k\,T}{\tau_p}\right)\frac{\partial^2 W}{\partial p^2} + \left(\frac{1}{\tau_p}\right)\left(\frac{\partial}{\partial p}\right) p\, W \\ &= -\frac{\partial}{\partial p}\left\{-\left(\frac{m\,k\,T}{\tau_p}\right)\frac{\partial}{\partial p} - \left(\frac{1}{\tau_p}\right)p\right\} W \\ &= -\left(\frac{\partial}{\partial p}\right) J_p W. \end{aligned} \tag{17}$$

Here we have rewritten the momentum flow of J_p as

$$J_p \equiv -\left(\frac{m\,k\,T}{\tau_p}\right)\frac{\partial \ln W}{\partial p} - \frac{p}{\tau_p}, \tag{18}$$

in which the first term in the right-hand side is a diffusion flow in p-space, and the second term is a systematic decaying flow; in other words, in comparison with Eq. (10), the first term is the fluctuating force F itself, and the second term is the phenomenological kinetic relation of decay of p. Of course, in the limit of vanishing the flow in p-space, the W tends to the equilibrium distribution of $W_e = N_e \exp(-p^2/2\,m\,k\,T)$ with N_e the normalization constant.

In this place, it is very interesting to notice that from Eqs. (14) and (15), the fluctuating force has a corresponding relation in the operator form of

$$F = -\left(\frac{2\,m\,k\,T}{\tau_p}\right)\frac{\partial}{\partial p} \tag{19}$$

which means that the fluctuating force under the variation principle in Postulate II acts as an operator to give an infinitesimal deformation to the momentum space 'quantized' by $(2mkT/\tau_p)$.

Application to Irreversible Thermodynamics

In the thermodynamics of irreversible linear processes[7], there is a set of kinetic relations between the thermodynamic forces X_i's and the fluxes $\dot{\alpha}_j$'s connected with the respective kinetic coefficients obeying the ONSAGER's reciprocal relation of $K_{ij} = K_{ji}$:

$$\dot{\alpha}_j = \Sigma_i K_{ji} X_i, \tag{20}$$

or in the form of force equations,

$$X_i = \Sigma_j R_{ij}\dot{\alpha}_j, \tag{21}$$

in which the resistance coefficients are given by $R = K^{-1}$ in a matrix notation. In this case, the entropy of the system of S_s giving rise to the X_i's may be expressed by

$$S_s = S_e - \left(\frac{1}{2}\right)\Sigma_{ij} s_{ij}\alpha_i\alpha_j. \tag{22}$$

Hence,

$$X_i = \frac{\partial S_s}{\partial \alpha_i} = -\Sigma_j s_{ij}\alpha_j. \tag{23}$$

Here S_e denotes the entropy in equilibrium.

In a space of $\alpha(t)$ versus time, each path does not always fulfill the thermodynamic relations. As known from the theory of Brownian movement, the existence of some fluctuating forces F_i's should be taken into account in addition to the X_i's[8]. Thus, the following equations are taken:

$$F_i + X_i = \Sigma_j R_{ij}\dot{\alpha}_j. \tag{24}$$

According to the theorem of fluctuation-dissipation[9], the resistance coefficients are expressed by

$$R_{ij} = (2k)^{-1}\int_{-\infty}^{+\infty} \langle F_i(0)\,F_j(t')\rangle\, dt'. \tag{25}$$

Now we may take the 'Lagrangian' of

$$\begin{aligned} L(\alpha, \dot{\alpha}) &= \left(\frac{1}{2}\right)\Sigma_{ij} K_{ij} F_i F_j \\ &= \left(\frac{1}{2}\right)\Sigma_{ij} K_{ij}\left(\Sigma_g R_{ig}\dot{\alpha}_g - X_i\right) \\ &\times \left(\Sigma_h R_{jh}\dot{\alpha}_h - X_j\right). \end{aligned} \tag{26}$$

Thereby, the 'momentum' referring to α_i becomes

$$\vec{P}_i = \frac{\partial L}{\partial \dot{\alpha}_i} = \Sigma_j(R_{ij}\dot{\alpha}_j - X_i) \tag{27}$$

which acts as an operator to the transition probability of W;

$$\vec{P}_i W = -2k\left(\frac{\partial}{\partial \alpha_i}\right) W. \tag{28}$$

Since the 'Hamiltonian' is

$$\begin{aligned} H &= \Sigma_i \vec{P}_i \alpha_i - L \\ &= \left(\frac{1}{2}\right)\Sigma_{ij}(\vec{P}_i K_{ij}\vec{P}_j + 2\vec{P}_i K_{ij} X_j), \end{aligned} \tag{29}$$

[6] S. CHANDRASEKHAR, Rev. mod. Phys. *15*, 1 (1943).
[7] S. R. DE GROOT, *Thermodynamics of Irreversible Processes* (North-Holland, Amsterdam 1952).
[8] L. TISZA and I. MANNIG, Phys. Rev. *105*, 1695 (1957).
[9] H. B. CALLEN and R. F. GREENE, Phys. Rev. *83*, 1213 (1951).

the equation governing the temporal change of W is given by

$$\begin{aligned}\frac{\partial W}{\partial t} &= (2\,k)^{-1}\,H\,W \\ &= \Sigma_{ij}\left(\frac{\partial}{\partial\alpha_i}\right)\left(k\,K_{ij}\,\frac{\partial}{\partial\alpha_j} - K_{ij}\,X_j\right)W \\ &= -\,\Sigma_i\left(\frac{\partial}{\partial\alpha_i}\right)J_i\,W\,. \end{aligned} \qquad (30)$$

Here we have defined the flow with respect to α_i by

$$J_i = -\,\Sigma_j\,K_{ij}\left(\frac{k\,\partial\ln W}{\partial\alpha_j} - X_j\right), \qquad (31)$$

in which the first term in the right-hand side corresponds to a fluctuating flux term, and the second term to the systematic fluxes given by Eq. (20). In this case, from Eqs. (24), (27) and (28), the fluctuating force F_i corresponds to the operator of $-\,2\,k(\partial/\partial\alpha_i)$ 'quantized' by $2\,k$. Introducing a new entropy term corresponding to the fluctuating fluxes in Eq. (31) by

$$S_f \equiv -\,k\int W\ln W\prod_i d\alpha_i \qquad (32)$$

under the normalization condition of

$$\int W\prod_i d\alpha_i = 1\,,$$

Eq. (31) may be rewritten as

$$J_i = \Sigma_j\,K_{ij}\left(\frac{\partial S_f}{\partial\alpha_j} + \frac{\partial S_s}{\partial\alpha_j}\right). \qquad (33)$$

From this it may be known to be taken the total entropy of the system as the following:

$$S = S_s + S_f = \int W(S_s - k\ln W)\prod_i d\alpha_i\,. \qquad (34)$$

We have arrived at the point where the production rate of the total entropy may be discussed;

$$\begin{aligned}\frac{dS}{dt} &= \int\left(\frac{\partial W}{\partial t}\right)(S_s - k\ln W)\prod_i d\alpha_i \\ &= -\int\Sigma_i\left(\frac{\partial}{\partial\alpha_i}\right)(J_i\,W)\,(S_s - k\ln W)\prod_j d\alpha_j \\ &= \int\Sigma_i\,J_i\,W\left(\frac{\partial}{\partial\alpha_i}\right)(S_s - k\ln W)\prod_i d\alpha_j \\ &= \int\Sigma_{ij}\,J_i\,R_{ij}\,J_j\,W\prod_k d\alpha_k\,, \end{aligned} \qquad (35)$$

which is positive definite, therefore, on the path determined by the variation principle, never decreases in course of time.

As well-known, $dS_s/dt = \Sigma_{ij}\,X_i\,K_{ij}\,X_j = \Sigma_{ij}\,\dot\alpha_i\,R_{ij}\,\dot\alpha_j$ is also positive definite, while dS_f/dt may be allowed to take either value positive or negative under the restriction of

$$\frac{dS}{dt} = \frac{dS_s}{dt} + \frac{dS_f}{dt} \geqq 0\,. \qquad (36)$$

Owing to the existence of such a fluctuation, we may observe 2 ways of energy conversion from higher to lower in its grade and also from lower to higher, by which all of the processes are prevented from an eternal ceasing.

Thus it has been shown that by taking account of fluctuating forces as a measure of departure from the phenomenological kinetic behaviours, a unified approach to the theory of irreversibility may be made on the basis of the Onsager-Machlup principle and the associated dynamical principle.

A Molecular-theoretical Foundation of Transition Probability in Postulate III

It is a well-known fact that the concept of the transition probability belongs not to classical mechanics but to quantum mechanics. Therefore, it is very necessary to clarify the physical signification on the classical molecular theory.

A whole system is a molecular system under consideration, which is specified by its Hamiltonian of $H_0(p, q)$, interacting with the surroundings taking the Hamiltonian of $H_s(P, Q)$ through an interaction of V independent of momenta. Here p and q refer to the momentum and position coordinates of the system under consideration, and P and Q are the sets of momenta and positions belonging to the surroundings, respectively.

As a whole, the total ensemble density in phase space $(p, q; P, Q)$ given by $\varrho(p, q; P, Q; t)$ is governed by the Liouville's equation

$$\frac{\partial\varrho}{\partial t} = +\,i\,\mathfrak{L}\,\varrho \equiv \{H, \varrho\}\,, \qquad (37)$$

where $\mathfrak{L}$ is the Liouville's operator defined by the Poisson bracket of $-\,i\{H,\}$, using the total Hamiltonian of $H = H_0 + H_s + V$, by whose respective terms the corresponding Liouville's operators are defined as $\mathfrak{L}_0$, $\mathfrak{L}_s$ and $\mathfrak{L}'$.

Making use of the transformation of

$$\mathfrak{L}'(t) = \exp\{-\,i(\mathfrak{L}_0 + \mathfrak{L}_s)\,t\}\,\mathfrak{L}'(0)\,, \qquad (38)$$

the solution of Eq. (37) can be found as

$$\begin{aligned}\varrho(t) &= \exp(+\,i\,\mathfrak{L}\,t)\,\varrho(0) \\ &= \exp\{i\,(\mathfrak{L}_0 + \mathfrak{L}_s)\,t\}\,\exp\left\{i\int_0^t \mathfrak{L}'(t')\,dt'\right\}\varrho(0)\,, \end{aligned} \qquad (39)$$

from which, by expanding into a power series of $\mathfrak{L}'$, the following equation may be obtained:

$$\begin{aligned}\varrho(t) = \exp\{i\,(\mathfrak{L}_0 + \mathfrak{L}_s)\,t\}\Bigg[1 &+ i\int_0^t dt'\,\mathfrak{L}'(t') \\ &- \int_0^t dt'\int_0^{t'} dt''\,\mathfrak{L}'(t')\,\mathfrak{L}'(t'') + O(\mathfrak{L}'^3)\Bigg]\varrho(0)\,. \end{aligned} \qquad (40)$$

Since the behaviour of the system is supposed to proceed on an average with respect to the surroundings, the ensemble density referring to the system is defined by

$$\int d\Gamma_s\, \varrho(p, q; P, Q; t) \equiv f(p, q; t), \tag{41}$$

where $d\Gamma_s$ stands for $dQdP$. Thereby, we may take

$$\varrho(p, q; P, Q; t) = f(p, q; t)\, G(P, Q) \tag{41a}$$

under the condition of

$$\int G(P, Q)\, d\Gamma_s = 1. \tag{41b}$$

Taking the average of Eq. (40) with respect to the surroundings, we have

$$\begin{aligned} f(p, q; \tau) = \exp(+ i\, \mathfrak{L}_0 \tau) \Bigg[& f(p, q; 0) + \int_0^\tau dt' \int d\Gamma_s \\ & \times \{V(t'), f(p, q; 0)\}\, G(P, Q) + \int_0^\tau dt' \int_0^{t'} dt'' \\ & \times \int d\Gamma_s \{V(t'), \{V(t''), f(p, q; 0)\}\} \\ & \times G(P, Q) + O(V^3) \Bigg]. \end{aligned} \tag{42}$$

From the definition of Poisson bracket for $V(t)$ independent of momenta,

$$\{V(t), f(p, q; 0)\} = \frac{\partial V(t)}{\partial q} \left(\frac{\partial}{\partial p}\right) f(p, q; 0)$$

follows. Regarding Eq. (42), assuming

$$\int_0^\tau dt' \int d\Gamma_s \{V(t'), f(p, q; 0)\}\, G(P, Q) = 0, \tag{43}$$

which is equivalent to taking the force of

$$F(t) \equiv - \frac{\partial V(t)}{\partial q}$$

as a random variable, and after some rearrangements into an equation of difference quotient, one finds

$$\begin{aligned} \frac{f(p, q; \tau) - f(p, q; 0)}{\tau} & - \{H_0, f(p, q; 0)\} \\ & = \left(\frac{1}{\tau}\right) \int_0^\tau dt' \int_0^{t'} dt'' \int d\Gamma_s\, G(P, Q) \\ & \times \frac{\partial V(t')}{\partial q} \frac{\partial V(t'')}{\partial q} \left(\frac{\partial^2}{\partial p^2}\right) f(p, q; 0) \\ & = \int_0^\tau dt \left(1 - \frac{t}{\tau}\right) \\ & \times \langle F(0)\, F(t)\rangle_s \left(\frac{\partial^2}{\partial p^2}\right) f(p, q; 0) \\ & = \int_0^\infty dt\, \langle F(0)\, F(t)\rangle_s \left(\frac{\partial^2}{\partial p^2}\right) f(p, q; 0), \end{aligned} \tag{44}$$

in which we have written as

$$\int d\Gamma_s\, G(P, Q)\, F(0)\, F(t) = \langle F(0)\, F(t)\rangle_s. \tag{44'}$$

In the last transformation it has been taken into account that τ is shorter macroscopically than the time constant relaxing into an equilibrium, but longer microscopically than the correlation time of forces between the system and the surroundings.

Now, taking an initial condition of

$$f(p, q; 0) = \delta(q - q_0)\, \delta(p - p_0), \tag{45}$$

it may be shown that the 'transition probability' during a time interval Δt is given in an operator form by

$$\begin{aligned} W(p_0, q_0; p, q; \Delta t) = & D_p(\Delta t) \\ & \times \left(\frac{\partial^2}{\partial p^2}\right) \delta(q - q_0)\, \delta(p - p_0) \end{aligned} \tag{46}$$

with the introduction of 'diffusion constant in p-space' of

$$\begin{aligned} D_p & = \int_0^\infty dt\, \langle F(0)\, F(t)\rangle_s \\ & = \left(\frac{1}{2}\right) \int_{-\infty}^{+\infty} dt\, \langle F(0)\, F(t)\rangle_s, \end{aligned} \tag{46a}$$

or alternatively as the solution of Eq. (44) under Eq. (45) by

$$\begin{aligned} W(p_0, q_0; p, q; \Delta t) = & (4\pi\, D_p\, \Delta t)^{-3/2} \exp\left[- \frac{(p - p_0)^2}{4\, D_p \Delta t}\right] \\ & \times \exp(+ i\, \mathfrak{L}_0\, \Delta t)\, \delta(q - q_0). \end{aligned} \tag{46b}$$

From Eq. (46b), the diffusion constant in p-space is given by

$$D_p = \frac{\overline{(p - p_0)^2}}{2\, \Delta t}, \tag{46c}$$

where the mean square of $(p - p_0)$ is averaged by Eq. (46b).

Introducing the root mean square values of p and $\dot{p}$ by

$$\langle \delta p \rangle \equiv \{\overline{(p - p_0)^2}\}^{1/2} = (2\, D_p\, \Delta t)^{1/2} \tag{47a}$$

and

$$\langle \delta F \rangle \equiv \{\overline{(\delta \dot{p})^2}\}^{1/2} = \frac{\langle \delta p \rangle}{\Delta t} = (2\, D_p)^{1/2}\, (\Delta t)^{-1/2}, \tag{47b}$$

we find a relationship of uncertainty between p and F given by

$$\langle \delta p \rangle\, \langle \delta F \rangle = 2\, D_p \tag{47c}$$

which is analogous to the Heisenberg's uncertainty relation in quantum mechanics, and also a physical meaning of Eq. (19), because of

$$D_p = \frac{m\, k\, T}{\tau_p}. \tag{47d}$$

Of course, both definitions of Eq. (46a) and Eq. (46c) for D_p must be coincident; thus

$$\frac{\overline{(p - p_0)^2}}{\Delta t} = \int_{-\infty}^{+\infty} dt\, \langle F(0)\, F(t)\rangle_s = 2\, D_p. \tag{47e}$$

Making use of a new variable defined by

$$\Delta p \equiv p - p_0, \tag{48a}$$

we may ascertain that Eq. (46b) can be transformed into a partial differential equation of

$$\frac{\partial W}{\partial(\Delta p)} = -(2\,D_p)^{-1}\,\frac{\Delta p}{\Delta t}\,W, \tag{48b}$$

from which the following operator relation may be obtained:

$$-\frac{2\,D_p\,\partial}{\partial(\Delta p)} = \frac{\Delta p}{\Delta t} \equiv F, \tag{48c}$$

where F is defined by $(\Delta p/\Delta t)$. This is nothing but Eq. (19).

By means of Eq. (48c), Eq. (46b) may be rewritten as

$$W(p_0, q_0; p, q; \Delta t) = (4\,\pi\,D_p\,\Delta t)^{-3/2}$$

$$\times \exp\left[-\left(\frac{1}{2}\right)\left\{\int_{-\infty}^{+\infty}\langle F(0)\,F(t)\rangle_s\,dt\right\}^{-1} \times \int_0^{\Delta t}(F\,F)\,dt\right]\delta(\Delta q - \dot{q}\,\Delta t) \tag{49}$$

with $\dot{q} = -\,i\mathfrak{L}_0 q = -\{H_0, q\}$, which agrees with Eq. (4) in Postulate III except a term of Dirac's delta function regarding the dynamical motion of q. In an operator form, Eq. (46b) may be expressed alternatively as the following:

$$W(p_0, q_0; p, q; \Delta t) = (4\,\pi\,D_p\,\Delta t)^{-3/2}$$

$$\times \exp\left\{-(\Delta t)\,D_p\,\frac{\partial^2}{\partial p^2}\right\}$$

$$\times \exp(+\,i\,\mathfrak{L}_0\,\Delta t)\,\delta(q - q_0), \tag{50}$$

which is equivalent to Eq. (46) in playing a role of transition probability with respect to p-space.

In order to clarify the physical meaning of the transition probability given by Eq. (46), we shall derive the KRAMERS-CHANDRASEKHAR equation of diffusion in phase space[10] by applying that to an integro-differential equation describing irreversible behaviours in a thermally open system, proposed by BERGMANN and LEBOWITZ[11], that is,

$$\frac{\partial f(x;t)}{\partial t} - i\,\mathfrak{L}_0\,f(x;t) = \int dx'\,\{W(x';x)\,f(x';t) - W(x;x')\,f(x;t)\} \tag{51}$$

with

$$\frac{W(x';x)}{W(x;x')} = \exp\left[\frac{\{E(x') - E(x)\}}{k\,T}\right], \tag{51'}$$

where $x = (p, q)$ denotes a phase point, and $w(x; x')$ is the transition probability per unit time from $x = (p, q)$ to $x' = (p', q')$. Here $E(x)$ means the energy of the system under consideration at $x = (p, q)$; e.g.,

$$E(x) = \frac{p^2}{2\,m} + U(q), \tag{52}$$

where $U(q)$ is the potential energy at q.

By Eq. (51'), Eq. (51) becomes

$$\frac{\partial f(x;t)}{\partial t} - i\,\mathfrak{L}_0\,f(x;t) = \int dx'\,W(x';x)\left[f(x';t) - \exp\left[\frac{\{E(x) - E(x')\}}{k\,T}\right]f(x;t)\right]. \tag{53}$$

Applying the transition probability given by Eq. (46) to $W(x'; x)$,

$$W(x';x) = D_p\left(\frac{\partial^2}{\partial p^2}\right)\delta(p - p')\,\delta(q - q'), \tag{54}$$

we obtain

$$\frac{\partial f(x;t)}{\partial t} - i\,\mathfrak{L}_0\,f(x;t) = \int dx'\,D_p\left[f(x';t) - \exp\left[\frac{\{E(x) - E(x')\}}{k\,T}\right]f(x;t)\right]\left(\frac{\partial^2}{\partial p^2}\right)\delta(x - x')$$

$$= D_p\left(\frac{\partial^2}{\partial p^2}\right)f(x;t) + \left(\frac{D_p}{m\,k\,T}\right)\left(\frac{\partial}{\partial p}\right) \times \{p\,f(x;t)\} \tag{55}$$

which is the equation of diffusion in phase space required to be derived.

Here we have used Eq. (52) in $\partial E(x)/\partial p = p/m$.

In conclusion, we have succeeded in formulating irreversible thermodynamics generalized to include 'fluctuating flows' in addition to the ordinary term of systematic flows on the basis of the theory of Brownian movement. Such a fluctuating flow may offer an additional insight into factors influencing an activation and deactivation around a systematic kinetic behaviour. The present formulation based on ONSAGER-MACHLUP 'Lagrangian' scheme has been shown to be very powerful and useful by making use of Postulates II and III. For the Postulate III, a molecular theoretical foundation has been given from the view-point of the statistical mechanical theory of Brownian movement[12].

Zusammenfassung. Die Thermodynamik der irreversiblen Prozesse wird im Sinne der Theorie der Brownschen Bewegung erweitert, um die Beschreibung der Schwankungen um einen stationären Zustand zu ermöglichen. Die Formulierung basiert auf den Postulaten I bis III, welche das Prinzip der kleinsten Wirkung von ONSAGER und MACHLUP ausdrücken. Letzteres wird durch eine Lagrange-Funktion beschrieben, welche von der fluktuierenden Kraft F abhängt, Gl. (5). F selbst ist als Funktion der makroskopischen Variablen α und $d\alpha/dt$ dargestellt.

Zum Schluss wird eine molekular-theoretische Begründung von Gl. (5) in Postulat III vom Gesichtspunkt der statistisch mechanischen Theorie der Brownschen Bewegung aus diskutiert.

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