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Irreversibility and entropy production in transport phenomena, III—Principle of minimum integrated entropy production including nonlinear responses

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ABSTRACT

A new variational principle of steady states is found by introducing an integrated type of energy dissipation (or entropy production) instead of instantaneous energy dissipation. This new principle is valid both in linear and nonlinear transport phenomena. Prigogine's dream has now been realized by this new general principle of minimum "integrated" entropy production (or energy dissipation). This new principle does not contradict with the Onsager–Prigogine principle of minimum instantaneous entropy production in the linear regime, but it is conceptually different from the latter which does not hold in the nonlinear regime. Applications of this theory to electric conduction, heat conduction, particle diffusion and chemical reactions are presented.

The irreversibility (or positive entropy production) and long time tail problem in Kubo's formula are also discussed in the Introduction and last section. This constitutes the complementary explanation of our theory of entropy production given in the previous papers (M. Suzuki, Physica A 390 (2011) 1904 and M. Suzuki, Physica A 391 (2012) 1074) and has given the motivation of the present investigation of variational principle.

1. Introduction including the time derivative of entropy production and Gransdorff–Prigogine evolution criterion

In the recent series of papers [1,2] concerning irreversibility and entropy production in transport phenomena, the present author has derived entropy production from the symmetric part (namely the second-order part, in the linear response scheme [3,4]) of the density matrix described by the von Neumann equation [1]. It is crucial that irreversibility has been deduced from the first principles based on the von Neumann equation with time reversal symmetry. This is a big contrast to the derivation of transport coefficients using master equations on stochastic schemes with broken time symmetry (which had been developed before Kubo's theory [3,4]). Even the heat conduction has been shown [2] to be described by introducing in this theory a thermal field $E_{\mathrm{T}} \propto \mathrm{grad}T(\boldsymbol{r})$ for the temperature $T(\boldsymbol{r})$ at the position $\boldsymbol{r}$. A steady state with the current $\boldsymbol{j}$ is maintained by energy supply and heat extraction. This mechanism has been formulated explicitly [2] by extending the von Neumann equation.

Thus, one of long-term puzzles in non-equilibrium statistical mechanics has now been solved [1,2]. However, there remain other difficult problems in this field:

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(i) To derive microscopically the Gransdorff–Prigogine evolution criterion [5–10], which was proposed a long time ago [5] as a first step in the direction of a variational interpretation of nonlinear responses, and
(ii) to find a general principle of minimum entropy production which can be applied even to nonlinear transport phenomena [5]. Prigogine [5] emphasized that to solve this second problem would be of much greater interest.

In order to study the first problem (i), we derive here a rigorous expression of the time derivative $\mathrm{d}\sigma_S(t)/\mathrm{d}t$ of the entropy production which is defined by [1,2]

$$\sigma_S(t) = \left(\frac{\mathrm{d}S}{\mathrm{d}t}\right)_{\mathrm{irr}} = \frac{\mathrm{d}}{\mathrm{d}t}\mathrm{Tr}\mathcal{S}\rho(t) = \frac{1}{T}\frac{\mathrm{d}}{\mathrm{d}t}\mathrm{Tr}\mathcal{H}_0\rho_{\mathrm{sym}}(t) \tag{1}$$

for the symmetric part $\rho_{\mathrm{sym}}(t)$ of the density matrix $\rho(t)$:

$$\rho_{\mathrm{sym}}(t) = \rho_0 + \rho_2(t) + \cdots + \rho_{2n}(t) + \cdots. \tag{2}$$

Here, $\rho_{2n}(t)$ denotes the $2n$-th order term of $\rho(t)$ in the external field $\boldsymbol{F}(t)$ defined by the Hamiltonian

$$\mathcal{H}(t) = \mathcal{H}_0 - \boldsymbol{A}\cdot\boldsymbol{F}(t) \equiv \mathcal{H}_0 + \mathcal{H}_1(t). \tag{3}$$

The density matrix $\rho(t)$ obeys the von Neumann equation

$$\frac{\partial}{\partial t}\rho(t) = \frac{1}{i\hbar}[\mathcal{H}(t), \rho(t)], \tag{4}$$

and the entropy operator $\mathcal{S}$ is defined by [1,2]

$$\mathcal{S} = -k_{\mathrm{B}}\log\rho_{\mathrm{eq}} = (\mathcal{H}_0 - \mathcal{F}_0)/T; \qquad \mathcal{F}_0 = -k_{\mathrm{B}}T\log\mathrm{Tr}\mathrm{e}^{-\beta\mathcal{H}_0} \tag{5}$$

with $\rho_0 = \rho_{\mathrm{eq}}$ at the temperature T. The above expression (1) yields the positive entropy production or irreversibility in transport phenomena under the condition of positivity of the relevant transport coefficients [1,2].

When $\mathcal{H}_1(t)$ is time-independent as in a static electric field, namely $\mathcal{H}_1 = -\boldsymbol{A}\cdot\boldsymbol{F}$, we obtain a general expression of the time derivative of the entropy production $\sigma_S(t)$ as

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\sigma_S(t) &= \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\mathrm{d}S}{\mathrm{d}t}\right)_{\mathrm{irr}} = \frac{1}{T}\mathrm{Tr}\left(\mathcal{H}_0\frac{\mathrm{d}^2}{\mathrm{d}t^2}\rho(t)\right) = \frac{1}{T}\left(\frac{1}{i\hbar}\right)^2\mathrm{Tr}\left([\mathcal{H}_0,\mathcal{H}][\mathcal{H},\rho(t)]\right)\\ &= -\frac{1}{T}\left(\frac{1}{i\hbar}\right)\mathrm{Tr}\dot{\mathcal{H}}_1\left(\mathrm{e}^{\frac{t\mathcal{H}}{i\hbar}}[\mathcal{H},\rho(0)]\mathrm{e}^{\frac{-t\mathcal{H}}{i\hbar}}\right) = \frac{F^2}{T}\int_0^\beta \mathrm{d}\lambda\langle\boldsymbol{j}(-i\hbar\lambda)\boldsymbol{j}(t;\boldsymbol{F})\rangle_0,\end{aligned} \tag{6}$$

where $\dot{\mathcal{H}}_1 = [\mathcal{H}_1, \mathcal{H}_0]/i\hbar, \boldsymbol{j} = \dot{\boldsymbol{A}}$ and

$$\boldsymbol{j}(t;\boldsymbol{F}) = \mathrm{e}^{-\frac{t\mathcal{H}}{i\hbar}}\boldsymbol{j}\mathrm{e}^{\frac{t\mathcal{H}}{i\hbar}}. \tag{7}$$

For more details, see Appendix A.

The above general formula (6) is reduced to Kubo's canonical current–current correlation function

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma_S^{(\mathrm{lr})}(t) = \frac{F^2}{T}\int_0^\beta \mathrm{d}\lambda\langle\boldsymbol{jj}(t+i\hbar\lambda)\rangle_0 \equiv \frac{F^2}{T}C(t) \tag{8}$$

in linear responses. Note that the time integration of Eq. (8) from $t = 0$ up to $t = \infty$ for a finite system vanishes

$$\int_0^\infty C(t)\mathrm{d}t = \int_0^\infty \mathrm{d}t\int_0^\beta \mathrm{d}\lambda\langle\boldsymbol{jj}(t+i\hbar\lambda)\rangle_0 \propto \mathrm{Tr}\boldsymbol{A}[\boldsymbol{A},\rho_0] = 0, \tag{9}$$

as is well known [1,2,11]. Consequently, the expression (8) shows a characteristic behavior as shown in Fig. 1. This is called the "long-time tail problem". For more details, see Section 5 and Appendix B.

This yields that

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma_S^{(\mathrm{lr})}(t) \le 0 \quad \text{(negative long-time tail)} \tag{10}$$

for sufficiently large time t even in the infinite volume limit. This may correspond to Glansdorff–Prigogine's stability condition [5–9] near the steady state in the linear regime. Namely, this is consistent with the Onsager–Prigogine principle of minimum entropy production which holds in the linear response regime.

The above argument does not hold in nonlinear cases. In fact, the ordinary theorem of minimum entropy production is violated in nonlinear cases, as is well known [5–9]. Thus, we try in the present paper to find a new theory on the variational principle of nonlinear transport phenomena. In order to solve this problem (ii), a new concept of "integrated" entropy production is introduced. Some typical variational functions for this new principle are explicitly given by solving the inverse problem of calculus of variations.