First-Principle Derivation of Entropy Production in Transport Phenomena

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Abstract.

The linear response framework was established by Kubo a half century ago, but no clear explanation of irreversibility namely entropy production has been given in this scheme. This has been now solved. The serious puzzle up to now is the following. Even using the linear response density matrix \( \rho_{lr} = \rho_0 + \rho_1(t) \), it has been difficult to derive the entropy production. Surprisingly, the correct entropy production is given by the second-order term \( \rho_2(t) \) as \( (dS/dt)_{irr} = (1/T) Tr H_0 \rho_{2}^{\prime}(t) > 0 \). It is shown to agree with the ordinary expression \( J \cdot E/T = \sigma E^2/T \) in the case of electric conduction for a static electric field \( E \), where \( \sigma \) denotes the electric conductivity expressed by the famous canonical current-current time correlation functions in equilibrium.

The present article gives a review of the derivation of entropy production (M.S., Physica A 390(2011)1904-1916) based on the first-principle of using the projected density matrix \( \rho_2(t) \) or more generally \( \rho_{even}(t) \), while the previous standard argument is due to the thermodynamic energy balance. This new derivation clarifies conceptually the physics of irreversibility in transport phenomena. In general, the transport phenomena are described by the odd part \( \rho_{odd}(t) \) of the density matrix and the entropy production (namely irreversibility) is described by the even part \( \rho_{even}(t) \). These are related to each other through the coupled equations as

\[
\frac{i\hbar}{\partial t} \rho_{q}(t) = [H_0, \rho_{q}(t)] + [H_1(t), (1-P_{q})\rho(t)] ,
\]

where "even" (symmetric) or "odd" (antisymmetric), \( P_{q} \) is the projection operator to the "q" part of \( \rho(t) \), and \( H_1(t) \) denotes the partial Hamiltonian due to the external force such as \( H_1(t) = -e \sum_j r_j \cdot E \equiv -A \cdot E \) in electric conduction.

The concept of a stationary temperature \( T_{st} \) in steady states with current (say electric current) is also proposed by using the projected and symmetry-separated von Neumann equation introduced by the present author. The entropy production of the relevant steady state depends on this stationary temperature. A mechanical formulation of thermal conduction is given by introducing a thermal field \( E_T \) and its conjugate "heat" operator \( A_H = \sum_j h_j r_j \) for a local internal energy \( h_j \) of the thermal particle \( j \).

1. Introduction

The present paper gives a review of the theory on irreversibility and entropy production in transport phenomena[1]. The problems of transport phenomena and irreversibility have been studied for long years from many viewpoint[1-25]. Boltzmann’s \( H \)-theorem shows the first attempt to explain the broken symmetry of entropy change in time, namely irreversibility. Green[2] formulated transport coefficients using stochastic equations including the time change of microscopic fluctuations[6-9]. Kubo and Tomita[11] succeeded, for the first time, in formulating magnetic linear responses on the basis of the von Neumann equation. Nakano[12, 13] applied
Kubo-Tomita’s method to the problem of electric conduction. Kubo[4] established a general theory of linear responses including the magnetic response and electric conduction.

2. Generalized linear response scheme including thermal conductance

To study transport phenomena, we start with the following von Neumann equation for the density matrix $\rho(t)$:

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

(1)

where the total Hamiltonian is given by

$$\mathcal{H}(t) = \mathcal{H}_0 + \mathcal{H}_1(t); \quad \mathcal{H}_1(t) = -A \cdot F(t).$$

(2)

In Kubo’s original formulation [4], the above Hamiltonian $\mathcal{H}(t)$ is purely mechanical. For example, we have

$$A = e \sum_j r_j \quad \text{and} \quad F(t) = E$$

(3)

in static electric conduction.

Now we interpret the von Neumann equation (1) so that we may treat thermal conductivity as in Kubo’s paper[4]. For this purpose, the Hamiltonian for thermal disturbance should be regarded to be an effective one renormalized in a local but enough large region to catch up the temperature gradient. We assume local equilibrium to define the semi-local temperature $T(r)$.

Then, as has been introduced in Paper II (Ref.[2]), we define a thermal field $E_T = \nabla \beta(r)/\beta_0$ as an external field $F(t)$ in Eq.(2), where $\beta(r) = 1/k_B T(r)$ and $\beta_0$ denotes the characteristic $\beta$.

Such a renormalized particle as moves receiving a force from the field $E_T$ is called "a thermal particle". If we define the heat operator $A_H$ of the form

$$A_H = \sum_j \{h_j r_j\} \equiv \frac{1}{2} \sum_j (h_j r_j + r_j h_j)$$

(4)

when the unperturbed Hamiltonian of the system is given in the form

$$\mathcal{H}_0 = \sum_j h_j; \quad h_j = \epsilon_j + u_j \quad \text{with} \quad \epsilon_j = \frac{1}{2m^*} p_j^2 \quad \text{and} \quad u_j = u(r_j, \{r_k\}),$$

(5)

then, from the relation

$$\dot{A}_H \equiv \frac{1}{i\hbar} [A_H, \mathcal{H}_0] \equiv j_H,$$

(6)

the heat current is given[2] in the form

$$j_H = \sum_j \{h_j v_j\} + \frac{1}{2i\hbar} \sum_{i,j} \{(r_j - r_k)|u_j(r_j, \{r_k\}), \epsilon_k - \epsilon_j\}. $$

(7)

Now we expand $\rho(t)$ in the von Neumann equation (1) as

$$\rho_1(t) = \rho_0 + \rho_1(t); \quad \rho_0 = e^{-\beta \mathcal{H}_0} / Z_0(\beta)$$

(8)

with $Z_0(\beta) = \text{Tr} \exp(-\beta \mathcal{H}_0)$, up to the first order of an external force $F$. Then, the first-order density matrix $\rho_1(t)$ is expressed as

$$\rho_1(t) = \rho_0 \int_{t_0}^t ds \int_0^\beta d\lambda F(s) \cdot \dot{A}(s - t - i\hbar \lambda),$$

(9)
where $\dot{A}$ denotes the current $j$ of $A$, namely $j = \dot{A} = [A, \mathcal{H}_0]/i\hbar$. Thus, we obtain the well-known formula[4, 12]

$$J \equiv \langle j \rangle_t = \text{Tr} \left\{ (\rho_0 + \rho_1(t)) j \right\} = \int_0^\infty ds \int_0^\beta d\lambda e^{-\epsilon s} \langle \dot{jj}(s + i\hbar\lambda) \rangle_0 F(t - s)$$ (10)

by taking the limit $t_0 \to -\infty$ for the initial $t_0$ after the thermodynamic limit. The order of these two limiting procedures and the insertion of the adiabatic factor $e^{-\epsilon s}$ are vital to assure the non-vanishing value of the current, namely to realize the irreversibility in transport phenomena, as was emphasized in [1].

In particular, for the static electric conduction $F(t) = E$(constant), we have

$$J = \sigma E; \quad \sigma = \int_0^\infty dt \int_0^\beta d\lambda e^{-\epsilon t} \langle \dot{jj}(t + i\hbar\lambda) \rangle_0$$ (11)

with the current $j = \dot{A}$ and $A = e \sum_j r_j$. The finiteness ($\sigma > 0$) of this expression is essential to prove the positivity of the entropy production (namely irreversibility) in electric conduction from the first-principle based on the von Neumann equation.

The present formulation of thermal conductivity is similar to Luttinger’s theory[26] based on a gravitational field which causes energy or heat current to flow. However, our formulation of introducing ”thermal field” $E_T$ and its conjugate heat operator $A_H$ through the idea of renormalization of semi-local thermal effects is more transparent for deriving transport coefficients of the Kubo form. (In fact, some approximations among interactions are included in Luttinger’s formulation.)

3. Brief comments on the energy dissipation and entropy production in the linear response scheme

The entropy production is a very subtle problem to study even in the linear response scheme. The ordinary formula $S(t) = -k_B \text{Tr} \rho(t) \log \rho(t)$ is useless for our purpose. There have been proposed many arguments on the entropy production in the linear response scheme.

3.1. Energy-balance argument

The thermodynamic derivation of energy dissipation based on energy balance in a steady state is standard to give the correct energy dissipation $J \cdot E = \sigma E^2$. However, in order to realize this steady-state situation in which the system is stationary, namely the temperature $T$ is constant, we have to modify the von Neumann equation (1) by introducing an appropriate interaction with the heat reservoir and boundary conditions, as will be given later.

3.2. Linear-response approximation

A primitive try to derive entropy production from $S(t) = -k_B \text{Tr} \rho(t) \log \rho(t)$ approximating $\rho(t)$ by the linear density matrix $\rho_L(t)$ is expected to give a correct expression of entropy change from

$$S_L(t) = -k_B \text{Tr} (\rho_0 + \rho_1(t)) \log(\rho_0 + \rho_1(t)),$$ (12)

but the time derivative of this entropy calculated up to the second order of the electric field $E$ is not equal to $\sigma E^2/T$. 


3.3. Negative-sign in Zubarev’s theory
Zubarev extended the linear response scheme to a non-linear regime by introducing a non-equilibrium statistical operator of the form [14]

\[ \rho_{\text{Zub}}(t) = \exp\left( -\Phi(t) - \beta H_0 + \beta \int_{t_0}^{t} ds e^{(s-t)} j(s-t) \cdot E \right) \]

\[ \simeq \rho(t) + \cdots = \rho_0 + \rho_1(t) + \cdots \] (13)
in the case of static electric conduction. Zubarev defined the entropy \( S_{\text{Zub}}(t) \) by

\[ S_{\text{Zub}}(t) = -k_B \text{Tr} \rho_{\text{Zub}}(t) \log \rho_{\text{loc}}, \] (14)

where the local equilibrium density matrix \( \rho_{\text{loc}} \) is given by

\[ \rho_{\text{loc}} = e^{-\beta(H_0+H_1)}/Z(\beta); \quad Z(\beta) = \text{Tr} e^{-\beta(H_0+H_1)} \] (15)
in the present problem with \( H_1 = -A \cdot E \) in static electric conduction. Then, his entropy production is expressed in the form

\[ \frac{d}{dt} S_{\text{Zub}}(t) = \frac{1}{T} \text{Tr}(H_0 + H_1) \rho'_{\text{Zub}}(t). \] (16)

This is reduced to

\[ \frac{d}{dt} S_{\text{Zub}}^{(\text{lr})}(t) = \frac{1}{T} \text{Tr} H_1 \rho'_{\text{Zub}}(t), \] (17)
in the limit of the linear response scheme, which gives the negative value \( -\sigma E^2/T \).

3.4. On the relevance of relative entropy
The relative entropy \( S_{\text{rel}}(t) \) defined by

\[ S_{\text{rel}} = -k_B \text{Tr} \rho(t) \left( \log \rho(t) - \log \rho_{\text{loc}} \right) \] (18)

has been often used to discuss the entropy change. This time-derivative is given by

\[ \frac{d}{dt} S_{\text{rel}}(t) = k_B \frac{d}{dt} \left( \text{Tr} \rho(t) \log \rho_{\text{loc}} \right), \] (19)

and consequently we have

\[ \frac{d}{dt} S_{\text{rel}}^{(\text{lr})}(t) = -\frac{1}{T} \text{Tr} H_1 \rho'_{\text{loc}}(t) \] (20)
in the linear response scheme. This has a correct sign in contrast to Zubarev’s result. However, the usage of the definition (18) is incorrect, because Eq.(19) always vanishes if we include higher-order terms of \( \rho(t) \).

3.5. Variational arguments
Onsagar and Machlup[16] discussed phenomenologically linear transport phenomena, using the variational theory concerning the bilinear form of the energy dissipation with respect to the current. Later, Nakano[12] developed a variational theory of energy dissipation based on his microscopic expression of conductivity. These phenomenological theories are, from the beginning, based on the correct expression of the entropy production.
4. Derivation of entropy production by the symmetry separation of density matrix

In order to clarify the essence of the entropy production in transport phenomena, we concentrate here our arguments on a non-stationary process in static electric conduction[1] described by the Hamiltonian

\[ H = H_0 + H_1; \quad H_1 = -A \cdot E \quad \text{and} \quad A = e \sum_j r_j. \]  

(21)

Here, \( H_0 \) denotes the Hamiltonian of electrons together with impurity potentials to scatter electrons or with electron-phonon interactions. Thus, \( H_0 \) is assumed here to be symmetric with respect to the inversion of space (\( r \rightarrow -r \)), while \( H_1 \) is antisymmetric. Therefore, the average \( \langle H_0 \rangle_t \equiv \text{Tr}H_0 \rho(t) \) can be regarded to be such an internal energy \( U(t) \) as is identified as the heat energy of the relevant system, for the initial state \( \rho_0 \) is given by the equilibrium density matrix using \( H_0 \) without electric field[1].

Physically, the internal energy \( U(t) \) of the system increases owing to the applied electric field, that is, the system heats up in the present non-stationary situation. Thus, the temperature \( T \) of the system depends on time \( t \) as \( T = T(t) \). This is the essence of irreversibility in the electric conduction phenomenon. The entropy change \( dS \) is thermodynamically given by

\[ dS = \frac{dU}{T} \]

and

\[ U(t) = \text{Tr} H(t) P_{\text{sym}} \rho(t) = \text{Tr}(P_{\text{sym}} H(t)) \rho(t) = \text{Tr} H_0 \rho(t), \]

(23)

where \( P_{\text{sym}} \) denotes the projection operator to the symmetric (or even) part of the relevant operator with respect to the inversion of space or the external field \( E \). The definition of \( U(t) \) in terms of Eq.(22) (not defined by the total Hamiltonian) is essential for the following argument. It is also instructive to rewrite Eq.(22) in the form[1]

\[ \left( \frac{dS}{dt} \right)_{\text{irr}} = -k_B \frac{dT}{dt} \text{Tr} \rho \log \rho_{\text{loc}}, \]

(24)

using \( \rho_{\text{loc}} \) given by Eq.(15).

In order to study the time dependence of \( U(t) \) in Eq.(22), we expand the density matrix \( \rho(t) \) as

\[ \rho(t) = \rho_0 + \rho_1(t) + \rho_2(t) + \cdots + \rho_n(t) + \cdots. \]

(25)

From the von Neumann equation (1), we obtain the following hierarchical equations

\[ i\hbar \frac{\partial}{\partial t} \rho_n(t) = [H_0, \rho_n(t)] + [H_1(t), \rho_{n-1}(t)]. \]

(26)

for \( n = 1, 2, \ldots \). A solution of Eq.(26) is given in the form[1]

\[ \rho_n(t) = F(t) (\rho_{n-1}(t)) = F_{t}^{n-1} (\rho_1(t)) = F_{t}^{n} (\rho_0), \]

(27)

where

\[ F(t)(Q(t)) := \frac{1}{i\hbar} \int_{t_0}^{t} \mathcal{U}_0(t-s)[H_1(s), Q(s)] \mathcal{U}_0^\dagger (t-s), \]

(28)
with $U_0(t) = \exp(t\mathcal{H}_0/\hbar)$. In particular, we have
\[
\rho_2(t) = \mathcal{F}_1(\rho_1(t)) = \mathcal{F}_1^2(\rho_0) = \left(\frac{1}{\hbar i}\right)^2 \int_0^t ds \int_0^s ds' U_0(t-s)[\mathcal{H}_1(s),U_0(s-s')][\mathcal{H}_1(s'),\rho_0]\mathcal{U}_0^\dagger(s-s')\mathcal{U}_0^\dagger(t-s).
\] (29)

Now, we calculate the change of the internal energy, $U'(t)$, using Eq.(29). Thus, we obtain
\[
\left(\frac{dS(t)}{dt}\right)_{\text{irr}} = \frac{1}{T} \left(\frac{dU(t)}{dt}\right) = \frac{1}{T} \frac{d\mathcal{H}_0(t)}{dt} = \frac{1}{T} \text{Tr} \mathcal{H}_0 \rho_2'(t) = \frac{\sigma E^2}{T} > 0,
\] (30)

using the expression of $\sigma$ in Eq.(11) or using the relation $\mathbf{J} = \sigma \mathbf{E}$, as far as the second-order of $E$ is concerned.

Now, the time dependence of $T(t)$ is effectively defined[1] by the equation
\[
U(t) = \langle \mathcal{H}_0 \rangle_0(T(t)) \equiv \text{Tr} \mathcal{H}_0 \exp(-\beta(t)\mathcal{H}_0)/Z_0(\beta(t)),
\] (31)

with $\beta(t) = 1/k_B T(t)$, and $Z_0(\beta) = \text{Tr} \exp(-\beta \mathcal{H}_0)$, in a slowly varying state. This ”effective” temperature is a convenient parameter to characterize ”thermodynamically” non-equilibrium systems. Then, $T(t)$ is expanded in the form $T(t) = T + a(t) E^2 + \cdots$. Thus, the entropy production (30) is time-independent in the lowest order.

In general, according to the symmetry arguments on $\mathcal{H}_0$ and the current operator $\mathbf{j} = \dot{\mathbf{A}}$, we find that the average of the current, $\mathbf{J}_E(t) = \langle \mathbf{j} \rangle_t = \text{Tr} \mathbf{j} \rho(t)$, is expressed by
\[
\mathbf{J}_E(t) = \text{Tr} \mathbf{j} \rho_\text{sym}(t),
\] (32)

using the antisymmetric part $\rho_\text{sym}(t)$ of $\rho(t)$ given by
\[
\rho_\text{sym}(t) = P_\text{sym} \rho(t) = \rho_1(t) + \rho_3(t) + \cdots,
\] (33)

and that the entropy production is given by $(dS/dt)_{\text{irr}} = \text{Tr} \mathcal{H}_0 \rho_\text{sym}'(t)/T$ using the symmetric part[1]
\[
\rho_\text{sym}(t) = P_\text{sym} \rho(t) = \rho_0 + \rho_2(t) + \cdots.
\] (34)

These symmetry-separated density matrices satisfy the following ”projected von Neumann equations”
\[
i\hbar \frac{\partial}{\partial t} \rho_q(t) = [\mathcal{H}_0, \rho_q(t)] + [\mathcal{H}_1(t), (1-P_q) \rho(t)],
\] (35)

where $q$ denotes ”sym” or ”antisym” and $P_q$ is the projection operator to the ”$q$” part of the density matrix $\rho(t)$; $P_q^2 = P_q$ and $P_\text{sym} + P_\text{antisym} = 1$. This separation of symmetric and antisymmetric parts of $\rho(t)$ plays an essential role in formulating steady states later.

Using these partial (projected) density matrices, the general current $\mathbf{J}_E$, conductivity $\sigma_E$ and entropy production $(dS/dt)_{\text{irr}}(E)$ are expressed[1], respectively, as
\[
\mathbf{J}_E = \text{Tr} \mathbf{j} \rho_\text{sym}(t) = \sigma_E \mathbf{E}; \quad \sigma_E = \sigma_0 + \sigma_2 E^2 + \cdots + \sigma_{2n} E^{2n} + \cdots,
\] (36)

with $\sigma_0 = \sigma$, and
\[
\left(\frac{dS}{dt}\right)_{\text{irr}}(E) = \frac{1}{T(t)} \text{Tr} \mathcal{H}_0 \rho_\text{sym}'(t) = \frac{\mathbf{J}_E \cdot \mathbf{E}}{T(t)} = \frac{\sigma_E E^2}{T(t)} > 0,
\] (37)

for an arbitrary strength of the electric field $\mathbf{E}$.

Thus, the entropy production associated even with the linear transport phenomena is given[1] by the time derivative of the second-order density matrix, $\rho_2'(t)$. That is, the linear response scheme is not closed to the first-order term of the density matrix. As is seen from Eqs.(36) and (37), the current and entropy production have a duality through the conductivity and also through the coupled equations Eq.(35) for $q = \text{sym}$ and $q = \text{antisym}$.
5. Formulation of steady states using relaxation-type symmetry-separated von Neumann equations

In the present section, we study the entropy production in steady states. For this purpose, we have to introduce the interaction of the system with the heat bath, in order to extract generated heat outside of the system[1]. For this purpose, we extend the von Neumann equation (1) as follows:

$$\frac{\partial \rho(t)}{\partial t} = \frac{1}{i\hbar} [\mathcal{H}(t), \rho(t)] - \Gamma(\rho(t)), \quad (38)$$

where the relaxation term $\Gamma(\rho(t))$ may be given generally in the Lindblad form[18]:

$$\Gamma(\rho) = \sum_\alpha \left( V_\alpha \rho V_\alpha^\dagger - \frac{1}{2} \left\{ V_\alpha^\dagger V_\alpha, \rho \right\} \right). \quad (39)$$

As we are here interested only in the conceptual mechanism of the entropy production in steady states, we make use of the simplest form of $\Gamma$. Since the current is related to the conservation of particles or charges, and consequently that it is expressed easily by a kind of non-equilibrium density matrix including current operators[10, 14, 19, 20]. Only the adiabatic factor $e^{-\epsilon t}$ may be necessary for the convergence of the integral of the time-correlation function of the relevant current, which is described by $\rho_a(t)$, as was discussed in [1]. Thus, we assume, for $\Gamma$,

$$\Gamma \rho_a(t) = \epsilon \rho_a(t) \quad (\epsilon \to +0). \quad (40)$$

As the entropy characterizes a qualitative property of the energy in non-equilibrium states, we have to treat the heat change in a way different from treating the current. The generated heat of the system should be extracted outside at a finite speed to construct a steady state and it is expressed by the change of $\rho_s(t)$. Thus, we assume[1]

$$\Gamma \rho_s(t) = \epsilon_r (\rho_s(t) - \rho_0); \quad \epsilon_r = \frac{1}{\tau_r}. \quad (41)$$

The relaxation time $\tau_r$ in Eq.(41) is macroscopic, namely much larger than the collision time $\tau$ of electrons colliding with impurities or phonons (i.e., $\tau \ll \tau_r$).

More explicitly we present Eq.(38) in the following coupled equations

$$\frac{1}{\epsilon_r} \frac{d}{dt} \rho_a(t) = -A \rho_a(t) + B \rho_s(t) + \rho_0, \quad (42)$$

and

$$\frac{1}{\epsilon} \frac{d}{dt} \rho_a(t) = -C \rho_a(t) + D \rho_s(t). \quad (43)$$

Here, the hyper-operators $A, B, C$ and $D$ are defined by

$$A = 1 - \omega_r \delta_{\mathcal{H}_0}, \quad B = \omega_r \delta_{\mathcal{H}_1}, \quad C = 1 - \omega_c \delta_{\mathcal{H}_0}, \quad \text{and} \quad D = \omega_c \delta_{\mathcal{H}_1}, \quad (44)$$

where $\omega_c = 1/(i\hbar \epsilon_c)$, $\omega_r = 1/(i\hbar \epsilon_r) = \tau_r/(i\hbar)$ and the inner derivation $\delta_Q$ is defined by[17]

$$\delta_Q R = [Q, R] = QR - RQ. \quad (45)$$

In a unified way, we have Eq.(38) with $\Gamma \rho(t) = \Gamma(\rho_a(t)) + \Gamma(\rho_s(t))$. Thus, we obtain the differential equation of the internal energy $U(t)$ for $\mathcal{H}_1 = -A \cdot E$ as

$$\frac{d}{dt} U(t) = J_E(t) \cdot E - \epsilon_r (U(t) - U(t_0)), \quad (46)$$

where $J_E(t)$ is the current.
using the relation[1]
\[
\frac{1}{\hbar} \text{Tr} \mathcal{H}_0 [\mathcal{H}_1, \rho_a(t)] = -\text{Tr} \dot{\mathcal{H}}_1 \rho_a(t) = \text{Tr}(\mathbf{j} \cdot \mathbf{E}) \rho_a(t) = \mathbf{J}_E(t) \cdot \mathbf{E}.
\] (47)

The solution of Eq.(46) is given by[1]
\[
U(t) = \int_{t_0}^{t} e^{-t_s (t-s)} \mathbf{J}_E(s) \cdot \mathbf{E} \, ds + U(t_0).
\] (48)

From Eqs.(42) and (43) in the limit \( t \to \infty \), we obtain the stationary density matrices \( \rho_a^{(st)} \) and \( \rho_a^{(st)} \):
\[
\rho_a^{(st)} = (1 - A^{-1}BC^{-1}D)^{-1} \rho_0, \quad \text{and} \quad \rho_a^{(st)} = C^{-1}D(1 - A^{-1}BC^{-1}D)^{-1} \rho_0.
\] (49)

and thereby we can evaluate the stationary values \( \mathbf{J}_E^{(st)} \) and \( U^{(st)} \). It may be also interesting to note that \( \rho_a^{(st)} \) can be expanded in a power series of \( E^2 \) in the form
\[
\rho_a^{(st)} = (1 - E^2 \mathcal{G})^{-1} \rho_0 = \sum_{n=0}^{\infty} (\mathcal{G}^n \rho_0) E^{2n}; \quad \mathcal{G} = A^{-1}BC^{-1}D/E^2 = E\text{-independent}.
\] (50)

A similar expansion formula holds also for \( \rho_a^{(st)} \):
\[
\rho_a^{(st)} = EC^{-1}(D/E)(1 - E^2 \mathcal{G})^{-1} \rho_0 = \sum_{n=0}^{\infty} (C^{-1}(D/E)\mathcal{G}^n \rho_0) E^{2n+1},
\] (51)

where \( D/E \) is independent of \( E \). More explicitly, \( \rho_1^{(st)} \) and \( \rho_2^{(st)} \) are given by
\[
\rho_1^{(st)} = \frac{1}{1 - \omega_i \delta \mathcal{H}_0} \omega_i \delta \mathcal{H}_0 \rho_0 = \int_0^{\infty} dt \exp \left( \frac{t}{\hbar} \delta \mathcal{H}_0 \right) \left( \frac{1}{\hbar} \delta \mathcal{H}_1, \rho_0 \right) e^{-\epsilon t}
\]
\[
= \rho_0 \int_0^{\infty} dt \int_0^{\beta} d\lambda (-t - i\hbar \lambda) \cdot \mathbf{E} e^{-\epsilon t},
\] (52)

and
\[
\rho_2^{(st)} = \int_0^{\infty} dt \exp \left( -\left( \epsilon - \frac{1}{\hbar} \delta \mathcal{H}_0 \right) t \right) \left( \frac{1}{\hbar} \delta \mathcal{H}_1, \rho_1^{(st)} \right),
\] (53)

respectively.

Then, the averages of the current \( \mathbf{J}_E^{(st)} \) and the internal energy \( U^{(st)} \) are given, respectively, by
\[
\mathbf{J}_E^{(st)} = \text{Tr} \mathbf{j} \rho_a^{(st)} \quad \text{and} \quad U^{(st)} = \text{Tr} \mathcal{H}_0 \rho_a^{(st)}.
\] (54)

Correspondingly, the stationary temperature \( T_{st} \) is expressed using the relation[1]
\[
\langle \mathcal{H}_0 \rangle_0(T_{st}) = U^{(st)},
\] (55)
as a function of the relaxation time \( \tau_r \). More explicitly, from Eq.(44), we obtain the relation
\[
\langle \mathcal{H}_0 \rangle_0(T_{st}) - \langle \mathcal{H}_0 \rangle_0(T) = U^{(st)} - U(t_0) = \tau_r \mathbf{J}_E^{(st)} \cdot \mathbf{E}.
\] (56)

This gives the expression of \( T_{st} \) as
\[
T_{st} = T + \tau_r \sigma E^2/C(T) + O(E^4)
\] (57)
with the specific heat \( C(T) \) of the system described by \( \mathcal{H}_0 \). The stationary temperature \( T_{\text{st}} \) is generally expanded in a power series of \( E^2 \), whose expansion coefficients are expressed in terms of the specific heat \( C(T) \) and its temperature derivations \( \{C^{(n)}(T)\} \) as well as \( \sigma \) and \( \tau_r \). Note that \( T_{\text{st}} = T \) only when \( \tau_r = 0 \). This condition \( (\tau_r = 0) \) corresponds to the instantaneous extraction of generated heat outside of the system. Practically we have \( T_{\text{st}} > T \) (i.e., \( \tau_r > 0 \)), as was discussed in [1].

Next, we study the entropy change \( \langle dS/dt \rangle_{\text{irr}} \) in the stationary state. We study the right-hand side of Eq.(46) from a physical point of view. The first term \( J_E(t) \cdot E \) of it is expressed in the form
\[
J_E(t) \cdot E = \text{Tr}\mathcal{H}_0 D_d(\rho(t)) = \text{Tr}(\tilde{D}_d(\mathcal{H}_0))\rho(t),
\]
where
\[
\tilde{D}_d(\mathcal{H}_0) \equiv \frac{1}{i\hbar}[\mathcal{H}_0, \mathcal{H}(t)], \quad \text{and} \quad D_d(\rho(t)) \equiv \frac{1}{i\hbar}[\mathcal{H}(t), \rho(t)] = \frac{\partial \rho(t)}{\partial t} + \Gamma(\rho(t)).
\]
That is, the hyper-operators \( D_d \) and \( \tilde{D}_d \) denote the time derivatives of the density matrix and an operator, respectively. These are called[1] as "dynamical-derivative representations". Note that the hyper-operator \( \tilde{D}_d \) defined by \((i/\hbar)\delta\mathcal{H}(t)\) satisfies the Leibniz rule \( \tilde{D}_d(AB) = (\tilde{D}_d(A))B + A(\tilde{D}_d(B)) \).

The mechanism of heat generation should be the same as in the absence of the relaxation term \( \Gamma(\rho) \). Thus, the entropy production in our new situation described by Eq.(46) is expressed in the form
\[
\frac{dS}{dt} = \text{Tr}SD_d(\rho(t)) = \frac{1}{T(t)}\text{Tr}(\tilde{D}_d(\mathcal{H}_0))\rho(t) = (J_E(t) \cdot E) / T(t),
\]
with the time-dependent temperature \( T(t) \) defined by
\[
\langle \mathcal{H}_0 \rangle_0(T(t)) = U(t) \equiv \langle \mathcal{H}_0 \rangle_t \equiv \text{Tr}\mathcal{H}_0 \rho(t),
\]
and \( \mathcal{H}_0 \) together with Eq.(48). The stationary entropy production is expressed in the form
\[
\left( \frac{dS}{dt} \right)_{\text{irr}}^{(\text{st})} = \frac{U^{(\text{at})} - U(t_0)}{T_{\text{st}} \tau_r}.
\]
In order to explain the logic of our theory, we rewrite Eq.(46) in the following form[1]
\[
\frac{dU(t)}{dt} = \left( \text{Tr}(\tilde{D}_d(\mathcal{H}_0))\rho(t) \right)_{\text{generated heat}} - \left( \frac{U(t) - U(t_0)}{\tau_r} \right)_{\text{extracted heat}}
\]
which vanishes in the steady state, owing to the balance of the two terms in the right-hand side of Eq.(63). The first term of the right-hand side in Eq.(63) contributes to the entropy production.

6. Entropy production for thermal disturbance
According to the general formula (2), the entropy production for the thermal disturbance is given by
\[
\frac{dS_{\text{irr}}}{dt} = \frac{\sigma H E_T^2}{T}.
\]
The validity of the above result is easily confirmed[1] thermodynamically by computing the entropy changes at the two sides of the system of the temperatures \( T \) and \( (T + \Delta T) \) for the heat current \( J_H = \sigma H E_T \).

Thus, the entropy production for electric conduction and thermal conduction is presented in a unified way using the second-order term \( \rho_2(t) \) or more generally the symmetric part \( \rho_{\text{sym}}(t) \) of the density matrix.
7. Discussion
In the present review article, two typical examples of static electric conduction and thermal conduction have been discussed in order to elucidate the mechanism of entropy production (and consequently irreversibility) in transport phenomena. However, the present idea and schemes will be easily extended to other more general cases of transport phenomena, which will be reported elsewhere in the near future[29].

It will be instructive for realizing intuitively the role of ${\mathcal{H}}_0$ in the first-principle approach to apply the present symmetry-separated treatment to relaxation-type Boltzmann equation of the form

\[ \frac{\partial f(t)}{\partial t} + eE : \frac{\partial f(t)}{\partial E} = \frac{1}{\tau} (f(t) - f_0) \] (65)

in the uniform case [1]. We separate $f(t)$, by symmetry, as follows:

\[ f(t) = f_{\text{sym}}(t) + f_{\text{antisym}}(t), \] (66)

where $f_{\text{sym}}(t) = f_0 + f_2(t) + \cdots$, and $f_{\text{antisym}}(t) = f_1(t) + f_3(t) + \cdots$. As was shown in [1], we can derive easily that

\[ J = \int f_{\text{antisym}}(t)e\mathbf{v}D(\epsilon)d\epsilon = \sigma E = (\sigma + \sigma_2 E^2 + \cdots)E = \frac{ne^2\tau}{m}E + \cdots, \] (67)

and

\[ \left( \frac{dS}{dt} \right)_{\text{irr}} = \frac{1}{T} \int \frac{\epsilon}{\tau} (f_{\text{sym}}(t) - f_0) D(\epsilon)d\epsilon \simeq \frac{\sigma E^2}{T}, \] (68)

for large $t$, where $D(\epsilon)$ denotes the density of states and $\epsilon = p^2/2m$ (namely the kinetic energy of an electron with the momentum $p$ and mass $m$). We find again that the second-order term $f_2(t)$ gives the lowest-order contribution to the entropy production.

If we assume that the time correlation of current $\langle \mathbf{j}(t)\mathbf{j} \rangle_0$ decays in the form $\langle \mathbf{j}(t)\mathbf{j} \rangle_0 = \langle \mathbf{j}^2 \rangle_0 \exp(-t/\tau)$ owing to the effect of $\mathcal{H}_0$, then using the formula (11) for $h = 0$ we obtain $\sigma = (ne^2\tau)/m$, which agrees with Eq.(67). This can be also derived phenomenologically by Einstein’s theory of Brownian motion of electrons[1].

The symmetry-separated treatment of the von Neumann equation in deriving entropy production as well as electric current through the conductivity may be regarded to be a typical example of the strategy of separation and unification of procedures in theoretical sciences[30].

It should be also remarked that the present treatment of entropy production based on the (symmetry-separated) von Neumann equation yields the unification of Prigogine’s nonequilibrium thermodynamical research trend and Kubo’s rigorous work based on quantum statistical mechanics.

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