JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN Vol. 12, No. 11, NOVEMBER, 1957

Statistical-Mechanical Theory of Irreversible Processes. II. Response to Thermal Disturbance

By Ryogo KUBO, Mario YOKOTA*

Department of Physics, University of Tokyo

and Sadao NAKAJIMA

Physical Institute, Nagoya University.

(Received August 3, 1957)

The possibility is examined to give rigorous expressions for kinetic coefficients such as heat conductivity, diffusion constant, thermoelectric power and so on which relate the flow of a certain kind to the generalized forces of thermal nature. We take here as the fundamental assumption Onsager's assumption that the average regression of spontaneous fluctuation of macroscopic variables follows the macroscopic physical laws. The kinetic coefficient G_{jl} appearing in the phenomenological equation, $\dot{\alpha}_j=\sum G_{jl}\,(\partial S/\partial\alpha_l)$ is shown then to be expressed as

$$G_{jl}=(k\beta)^{-1}\int_0^\infty d\tau\int_0^\beta <\dot{\alpha}_l(-i\hbar\lambda)\,\dot{\alpha}_j\,(\tau)>d\lambda$$

where k is the Boltzmann constant and $\beta=1/kT$. This is the same type of formula as we have for kinetic coefficients for mechanical disturbances (Kubo, J. Phys. Soc. **12** (1957) 570). The theory is illustrated for the example of electronic transport phenomena.

§ 1. Introduction

In the preceding paper by one of the present authors[1)] a general theory has been developed for the calculation of kinetic coefficients such as electric conductivity and complex susceptibility in periodic field. It was shown that these kinetic coefficients are expressed in terms of time fluctuation of appropriate internal variables of the system. This conclusion was obtained by a perturbational calculation of linear response of the system to the external disturbance which is explicitly involved in the Hamiltonian of the system. We shall call in the following such disturbance as *mechanical*.

The mechanical disturbance is controlled by the observer in a mechanical way and the interaction of the system with the outer body which is directly controlled can be expressed by an additional perturbation energy which perturbs the natural motion of the system. There exists another kind of outer disturbances which will be called *thermal* disturbances. We are dealing with this kind of disturbance when we observe a non-equilibrium system in which temperature, pressure or concentration of particles is changing spacially or temporally. Thermal disturbances can not be expressed by definite perturbation energy in an unambiguous way.

---

* Now at the Research Institute for Fundamental Physics, University of Kyoto, Kyoto.

Now the question arises if it is possible to give similar expressions of the kinetic coefficients for thermal disturbances as those obtained for the mechanical disturbances. The answer should be yes, as we anticipate from the fact that the whole theory developed in I is a sort of generalization of the Einstein relation which means the conductivity is related to the diffusion constant. The aim of the present paper is to give a physical argument to justify this anticipation.[2] We shall do this by following the line of logics used by Onsager[3] in his monumental work on the reciprocity theorem. The general idea will be discussed in the first two sections. This will be further illustrated in the last section by the example of electron transport phenomena. The exact expressions are given for the kinetic coefficients appearing in the linear relations connecting electric and heat currents with the gradient of electrochemical potential and temperature.

§ 2. Application of Onsager's Assumption. Classical Case

In order to derive the generalized reciprocity law, Onsager[3] made the fundamental assumption;

(A) *The average behavior of fluctuation of a physical quantity in an aged system is governed by the macroscopic physical law which governs the macroscopic change of the corresponding macroscopic variable.*

This assumption is easily understood by a simple example. We may have local and temporal fluctuation of the temperature distribution in a system in thermal equilibrium. This fluctuation will decay in time on the average, following the Fourier law of heat conduction. We shall call this *Onsager's assumption.*

This will be expressed mathematically in the following way. Let $\alpha_j (j=1, 2, \cdots n)$ be a set of macroscopic variables of a system which we observe. These variables are considered as stochastic variables. We further introduce the variable,

$$\alpha_j(t+\Delta t|\alpha') \ ,$$

which is defined as the stochastic variable α_j at the time point $t+\Delta t$ when the observed values of $(\alpha_1, \cdots, \alpha_n)$ at the time t are specified to $(\alpha_1', \cdots, \alpha_n')$. Now the assumption asserts that the relation,

$$\overline{\alpha_j(t+\Delta t|\alpha')}-\alpha'_j=\sum_k G_{jk}\frac{\partial S}{\partial \alpha'_k}\Delta t \ , \qquad (2.1)$$

holds for a time interval Δt which is short in macroscopic sense but is sufficiently long on microscopic scale. In Eq. (2.1) $\overline{\alpha_j(t+\Delta t|\alpha')}$ is the average of $\alpha_j(t+\Delta t|\alpha')$ for all possible initial states at the time t, which are compatible with the prescribed values α' at t. On the right hand side of the equation, S is the entropy which is considered as the function of the variables $\alpha_1', \alpha_2', \cdots \alpha_n'$, so that $\partial S/\partial \alpha'_j$ multiplied by the temperature T is the generalized force which drives the variables $\alpha_1', \cdots \alpha_n'$ to change in macroscopic way. The constants G_{jk} are the macroscopic coefficients which correlate the motion of α_j' to the driving forces. As far as we confine ourselves to those cases where the deviation from equilibrium is small enough, we generally expect the existence of linear relations between the average velocity of regression of α_j' and the driving forces.[3][4] In such cases G_{jk}'s are simply constants in which we are now interested.

Onsager obtained his celebrated law of reciprocity from this assumption and the principle of microscopic reversibility by showing that

$$\langle \alpha_j(t+\Delta t)\alpha_l(t)\rangle-\langle \alpha_j(t)\alpha_l(t)\rangle=-kG_{jl}\Delta t \qquad (2.2)$$

where k is the Boltzmann constant and $\langle\ \rangle$ means the average over the equilibrium ensemble.

Now we see that Onsager's assumption provides us, besides the general proof of reciprocity, a method of calculating G_{jl} in terms of the time correlation of fluctuating variables α if the correlation can be calculated.

This is essentially the way of our reasoning employed in the present paper. In the preceding paper[1] we pursued the dynamical response of the system to a mechanical outer disturbance to derive the admittance in general, which is expressed as the Fourier component of time fluctuation of corresponding physical quantities (fluctuation-dissipation theorem).[1][5] Onsager's assumption is rather a consequence of that argument. But, now we reverse our standpont, and start from Eq. (2.1), that is the assumption (A).

In order to obtain a concrete expression of the coefficient G_{jl}, we rewrite Eq. (2.2) as follows.

$$G_{jl}=-\frac{1}{k\Delta t}\langle\,\alpha_j(t+\Delta t)\alpha_l(t)-\alpha_j(t)\alpha_l(t)\,\rangle$$
$$=+\frac{1}{k\Delta t}\int_0^{\Delta t}dt'\int_0^{t'}\langle\,\dot{\alpha}_j(t+\tau)\dot{\alpha}_l(t)\,\rangle\,d\tau$$
$$=\frac{1}{k}\int_0^{\Delta t}\left(1-\frac{\tau}{\Delta t}\right)\langle\,\dot{\alpha}_j(t+\tau)\,\dot{\alpha}_l(t)\,\rangle\,d\tau \qquad (2.3)$$

In this transformation we used the relation,

$$\frac{d^2}{d\tau^2}\langle\,\alpha_j(t+\tau)\alpha_l(t)\,\rangle=-\langle\,\dot{\alpha}_j(t+\tau)\dot{\alpha}(t)\,\rangle\,, \qquad (2.4)$$

which follows from the condition of stationary process,

$$\langle\,\alpha_j(t)\alpha_l(t')\,\rangle=\langle\,\alpha_j(t+t_0)\alpha_l(t'+t_0)\,\rangle$$
$$=\langle\,\alpha_j(t-t')\alpha_l(0)\,\rangle$$
$$=\langle\,\alpha_j(0)\alpha_l(t'-t)\,\rangle\,, \qquad (2.5)$$

and the assumption* that

$$\langle\,\dot{\alpha}_j\alpha_l\,\rangle=-\langle\,\alpha_j\dot{\alpha}_l\,\rangle=0\,. \qquad (2.6)$$

Eq. (2.3) can further be written as

$$G_{jl}\simeq\frac{1}{k}\int_0^\infty\langle\,\dot{\alpha}_j(t+\tau)\dot{\alpha}_l(t)\,\rangle\,d\tau$$
$$=\frac{1}{k}\int_0^\infty\langle\,\dot{\alpha}_j(t)\dot{\alpha}_l(0)\,\rangle\,dt\,, \qquad (2.7)^{**}$$

provided that the correlation time of $\dot{\alpha}_j$ and $\dot{\alpha}_l$ is short enough compared with that of α_j and α_l which is governed by the macroscopic law and is measured by

$$\tau_{\text{macro}}=\langle\,\alpha_j\alpha_l\,\rangle\,/\,kG_{jl}\,. \qquad (2.8)$$

As we see from Eq. (2.2), Eq. (2.7) is just the type of expression which we want to discuss in the following.

We shall examine more in detail in later sections the reasoning which leads to Eq. (2.7). We only note here that the argument made here is legitimate only in *classical* mechanics so that a certain revision is required to apply it to quantum-mechanical cases. The revised form is rather easily anticipated from the results of the previous paper. We shall discuss this in the next section.

Before doing that, we shall briefly describe here the classical derivation of (2.2) from (2.1) for the convenience of later reference. We multiply the both sides of Eq. (2.1) by α_l' and average them with the probability distribution density $W(\alpha_1',\ \cdots\ \alpha_n')$, which is the stationary probability for the realization of the values $(\alpha_1',\ \cdots\ \alpha_n')$ in the aged system. The left-hand side becomes evidently the correlation functions which appear in Eq. (2.2). The right-hand side is now transformed as

$$\sum_m G_{jm}\Delta t\int\cdot\cdot\int\alpha_l'\left\{\frac{\partial}{\partial\alpha_m'}S(\alpha_1'\cdots\,\alpha_n')\right\}\cdot W(\alpha_1'\cdots\alpha_n')d\alpha_1'\cdots d\alpha_n'$$
$$=k\sum_m G_{jm}\Delta t\int\cdot\cdot\int\alpha_l'\frac{\partial}{\partial\alpha_m'}W(\alpha_1'\cdots\alpha_n')d\alpha_1'\cdots d\alpha_n'$$
$$=-kG_{jl}\Delta t$$

which coincides with the right-hand side of Eq. (2.2). We made here use of the assumption

$$W(\alpha_1'\cdots\alpha_n')=C\exp\left\{\frac{1}{k}S(\alpha_1\cdots\alpha_n')\right\} \qquad (2.9)$$

where C is the normalization constant.

§ 3. Application of Onsager's Assumption

For quantum-mechanical systems, it is not always possible to define a simultaneous distribution of the observed values of α_1, α_2, $\cdots$ and α_n. Or more specifically, we may not be able to prepare a statistical ensemble like that defined classically by (2.9). This is so because such variable are not necessarily commutable with each other or with the Hamiltonian itself. It is true that they are nearly commutable if they are really macroscopic quantities. But still caution is requir-

* If the condition (2.6) is not fulfilled, Eqs. (2.3) and (2.7) must be corrected by the additional term.

$$-\frac{1}{k}\langle\,\dot{\alpha}_j\,\alpha_l\,\rangle=\frac{1}{k}\langle\alpha_j\,\dot{\alpha}_l\,\rangle\,.$$

** The infinite integral here is rather the Cesaro limit as one sees at once from the last form of Eq. (2.3). The Cesaro limit may be replaced by the Abel limit,

$$\lim_{\varepsilon\to+0}\int e^{-\varepsilon t}\langle\,\dot{\alpha}_j(t)\,\dot{\alpha}_l(0)\,\rangle\,dt\,.$$

We omitted here more rigorous mathematical statement because physicists are rather accustomed to use improper integrals which are summarable in some way or another.

ed for the effect which may enter as a consequence of non-commutability.

Considering this circumstance, we propose here to interprete Onsager's assumption in a little less stringent way than what Eq. (2.1) literally implies. Namely, we now regard $\overline{\alpha_j(t+\Delta t|\alpha')}$ as the expectation of the variable α_j at the time $t+\Delta t$ for a statistical ensemble for which the variables $(\alpha_1, \cdots \alpha_n)$ have the expectation values $(\alpha_1', \cdots, \alpha_n')$ at the time t. This ensemble is represented by the statistical operator $\rho(t+\Delta t|\alpha')$ which, by definition, has the properties,

$$\mathrm{Tr}\,\rho(t+0|\alpha')\alpha_j=\alpha_j' , \tag{3.1}$$

$$\mathrm{Tr}\,\rho(t+\Delta t|\alpha')\alpha_j=\overline{\alpha_j(t+\Delta t|\alpha')} . \tag{3.2}$$

According to our new interpretation, Eq. (2.1) is now read as

$$\mathrm{Tr}\,\rho(t+\Delta t|\alpha')\alpha_j-\alpha_j'=\sum_k G_{jk}\frac{\partial S}{\partial \alpha_k'}\Delta t . \tag{3.3}$$

Now the question is what will be this density matrix $\rho(t+0|\alpha')$. This is the most subtle point of the whole argument. It seems to us that the most natural answer for the form of $\rho(t+0|\alpha')$ is

$$\rho(t+\Delta t(\alpha')=\exp[\beta(\Omega-\mathscr{H})-\beta\sum A_j\alpha_j] , \tag{3.4}$$

which is a sort of canonical distribution. Here Ω is a free energy and A_j's $(j=1, 2, \cdots, n)$ are scalar quantities which are defined by the conditions (3.1) and correspond to the forces associated with the coordinates α_j's. The density operator (3.4) is the solution of maximization problem of the entropy

$$S=-k\ \mathrm{Tr}\,\rho\log\rho , \tag{3.5}$$

with the supplementary conditions (3.2) and other well known conditions. The parameters A_j's enter here as the undetermined multipliers. We see at once that

$$\beta\frac{\partial\Omega}{\partial A_j}=\bar{\alpha}_j\equiv\alpha_j' , \tag{3.6}$$

$$S=-k\beta\Omega+k\beta\overline{\mathscr{H}}+\sum_j kA_j\bar{\alpha}_j , \tag{3.7}$$

where $\overline{\mathscr{H}}$ and $\bar{\alpha}_j$ are the everage values for the ensemble represented by (3.4), and

$$\frac{\partial S}{\partial\alpha_j'}=k\beta A_j . \tag{3.8}$$

Therefore Eq. (3.3) now becomes

$$\mathrm{Tr}\exp[\beta(\Omega-\mathscr{H})-\beta\sum_l A_l\alpha_l]\{\alpha_j(\Delta t)-\alpha_j(0)\} =k\beta\sum_l G_{jl}A_l\Delta t . \tag{3.9}$$

where $\alpha_j(\tau)$ means the Heisenberg representation of the variable α_j. Namely they are defined by

$$\dot{\alpha}_j(\tau)=\frac{1}{i\hbar}[\alpha_j(\tau), \mathscr{H}] ,$$
$$\alpha_j(\tau)=\exp(i\mathscr{H}\tau/\hbar)\,d\exp(-i\mathscr{H}\tau/\hbar) . \tag{3.10}$$

We now assume the linear dissipative systems, so that the deviation from the equilibrium is small. This means that the forces A_j's are really small. Thus we expand the left-hand side of Eq. (3.9) and leave only the linear term. Using the formula

$$\exp[-\beta\mathscr{H}-\beta\sum_l A_l\alpha_l] =\exp(-\beta\mathscr{H}) -\int_0^\beta \exp(-\beta\mathscr{H})\sum_l A_l\,\alpha_l(-i\hbar\lambda)d\lambda+o(A) , \tag{3.11}$$

we obtain at once

$$\overline{\alpha_j(t+\Delta t|\alpha')}=\langle\alpha_j\rangle -\sum A_l\int_0^\beta\langle\alpha_l(-i\hbar\lambda)\alpha_j(\Delta t)\rangle d\lambda +o(A) . \tag{3.12}$$

where $\langle\ \rangle$ means the average over the equilibrium distribution $\exp\beta(\Omega^0-\mathscr{H})$ so that $\langle\alpha_j\rangle$ is the equilibrium value of α_j. Eq. (3.12) reduces, in particular for $\Delta t=0$, to

$$\overline{\alpha_j(t|\alpha')}\equiv\alpha_j' =\langle\alpha_j\rangle-\sum_l A_l\int_0^\beta\langle\alpha_l(-i\hbar\lambda)\alpha_j\rangle d\lambda +o(A) , \tag{3.13}$$

which is the condition to determine the forces A in terms of the deviation $\alpha_j'-\langle\alpha_j\rangle$ from the equilibrium. The set of Eq. (3.13) is equivalent to Eq. (3.6).

Inserting Eq. (3.11) into (3.9) we get easily

$$\frac{1}{\beta}\int_0^\beta\langle\alpha_l(i\hbar\lambda)\{\alpha_j(\Delta t)-\alpha_j(0)\}\rangle d\lambda =-kG_{jl}\Delta t , \tag{3.14}$$

which corresponds to Eq. (2.2), as we see from the fact that the left-hand side of Eq. (3.14) becomes the correlation function appearing in Eq. (2.2) in the classical limit $\hbar\to 0$.

Like Eq. (2.4) for the classical correlation function, we evidently have the relation

$$\frac{d^2}{d\tau^2}\int_0^\beta\langle\alpha_l(-i\hbar\lambda)\alpha_j\rangle d\lambda =-\int_0^\beta\langle\dot{\alpha}_l(-i\hbar\lambda)\dot{\alpha}_j(\tau)\rangle d\lambda . \tag{3.15}$$

Thus, if the condition

$$\int_0^\beta \langle \dot{\alpha}_l(-i\hbar\lambda)\alpha_j \rangle d\lambda$$
$$=-\int_0^\beta \langle \alpha_l(-i\hbar\lambda)\dot{\alpha}_j \rangle d\lambda=0\ , \tag{3.16}$$

is satisfied, Eq. (3.14) can be transformed into

$$G_{jl}=\frac{1}{k\beta}\int_0^{\Delta t}\left(1-\frac{\tau}{\Delta t}\right)d\tau$$
$$\times\int_0^\beta \langle \dot{\alpha}_l(-i\hbar\lambda)\dot{\alpha}_j(\tau) \rangle d\lambda\ . \tag{3.17}$$

just in the same way as we did in Eq. (2.3). If, furthermore, the characteristic time of decay of the integrand of (3.17) is small enough compared with that which corresponds to (2.8), Eq. (3.17) gives

$$G_{jl}=\frac{1}{k\beta}\int_0^\infty d\tau\int_0^\beta \langle \dot{\alpha}_l(-i\hbar\lambda)\dot{\alpha}_j(\tau) \rangle d\lambda\ . \tag{3.18}$$

as the wanted expression for the kinetic coefficient G_{jl}. The infinite integral may be regarded as the Cesaro limit or the Abel limit. We note finally that the condition (3.16) is satisfied if

$$\frac{1}{i\hbar}\langle [\alpha_l,\ \alpha_j] \rangle=0\ , \tag{3.19}$$

that is, if α_l and α_j are commutable on the average. The equivalence of (3.19) to (3.16) is seen from the identity, Eq. (3.7) of I, i.e.,

$$[\exp(-\beta\mathscr{H}),\ A]$$
$$=i\hbar\int_0^\beta \exp(-\beta\mathscr{H})\dot{A}(-i\hbar\lambda)\,d\lambda\ . \tag{3.20}$$

Therefore we have

$$\int_0^\beta \langle \dot{\alpha}_l(-i\hbar\lambda)\alpha_j \rangle d\lambda$$
$$=(i\hbar)^{-1}\,\mathrm{Tr}\,[\exp\beta(\Omega^0-\mathscr{H}),\alpha_l]\alpha_j$$
$$=(i\hbar)^{-1}\ \mathrm{Tr}\exp\beta(\Omega^0-\mathscr{H})[\alpha_l,\ \alpha_j]\ .$$

It should be remembered that the expression (3.18) becomes rigorous only when the choice of infinitely large Δt is proved to be possible for the particular choice of the variables α. Otherwise, it remains only a certain approximation.

This should be particularly emphasized, because we see in literatures certain confusion about this point.[6)7)] Some of formulae of the type (2.17) or (3.18) given in literatures are by no means rigorous since the above-mentioned choice of $\Delta t\to\infty$ is simply impossible. These approximate formulae, though we should not underestimate their usefulness, must be discriminated from such rigorous formulae as we are concerned with in the present work.

For instance, the expression of conductivity, $S_{\mu\nu}{}^{(1)}$ in Eq. (4.6) of the present paper, which was derived in the preceding paper I, is rigorous. We may write this as

$$\sigma=\int_0^\infty\int_0^\beta \langle J_xJ_x(t+i\hbar\lambda) \rangle d\lambda dt=\frac{ne}{m^*}\tau\ , \tag{3.21}$$

where we defined the effective mass m^* by

$$\frac{ne}{m^*}=\int_0^\beta \langle J_xJ_x(i\hbar\lambda) \rangle d\lambda\ ,$$

(see Eq. (8.12), I) and the average relaxation time τ by

$$\tau=\int_0^\infty \phi(t)dt\ , \tag{3.22}$$

with

$$\phi(t)=\int_0^\beta \langle J_xJ_x(t+i\hbar\lambda) \rangle d\lambda\Big/\int_0^\beta \langle J_xJ_x(i\hbar\lambda) \rangle d\lambda\ . \tag{3.23}$$

Now an approximation for this relaxation time is given by

$$\frac{1}{\tau}\sim-\int_0^{\tau_c}\ddot{\phi}(t)dt$$
$$=\int_0^{\tau_c}dt\int_0^\beta \langle \dot{J}_x\dot{J}_x(t+i\hbar\lambda) \rangle\Big/\int_0^\beta \langle J_xJ_x(i\hbar\lambda) \rangle d\lambda, \tag{3.24}$$

which may be used as good approximation under certain restricted conditions. Namely it may be used when the function $\phi(t)$ behaves like $\exp(-t/\tau)$, or in other words, when the spectrum of relaxation time of $\phi(t)$ is nearly degenerate. It is easy to show that Eq. (3.24) gives the Grüneisen formula when applied to electrons scattered by phonons.[8)] One of the present authors proved many years ago that the Grüneisen formula is derived from the Bloch equation by calculating the average of the relaxation frequencies and equating this to the reciprocal of the average relaxation time τ in Eq. (3.21).[9)]

We may see the approximation (3.24) roughly by applying the same transformation technique as used for Eqs. (2.3) and (3.17) to the function $\phi(t)$, that is,

$$\phi(t)=1+\int_0^t (t-\tau)\ddot{\phi}(\tau)d\tau\sim1+t\int_0^{\tau_c}\ddot{\phi}(\tau)d\tau\ . \tag{3.25}$$

The last form may be used for t which is much longer than the characteristic time τ_a

of $\ddot{\phi}(\tau)$ and shorter than the relaxation time τ of $\phi(t)$ provided that such a choice of t is possible.* For such t, $\phi(t)$ is decreasing as $1-t/\tau$, τ being that defined by Eq. (3.24). Note that here the assumption is introduced for the existence of a plateau value of the integral, i.e.,

$$\int_0^t \ddot{\phi}(\tau)d\tau \sim \int_0^{\tau_c} \ddot{\phi}(\tau)\, d\tau ,$$

for $\tau_d \ll t \ll \tau$.

It is essential in the expression (3.24) to stop the integration at a finite upper limit, because we ought to have

$$\int_0^\infty dt \int_0^\beta \langle \dot{J}_x \dot{J}_x(t+i\hbar\lambda) \rangle \, d\lambda = 0 , \qquad (3.26)$$

if the integral (3.21) does exist.

It should be also noticed that the Kirkwood formula[6]

$$\zeta = m/\tau = \beta \int_0^{\tau_c} \langle \dot{P}_x \dot{P}_x(t)\, dt , \qquad (3.27)$$

for the friction constant ζ of a Brownian particle is simply a special case of Eq. (3.24).

Thus the Kirkwood formula (3.27) and the similar formula (3.24) rely upon rather restricted assumptions about the nature of $\phi(t)$, which can by no means be proved to be generally valid. On the other hand, Eq. (3.21) itself is rigorous and fundamental as was proved in I and also in § 4 of the present paper. We should discriminate between these two classes of expressions for kinetic coefficients.

§ 4. Electron Transport Phenomena

Let us now consider, as an illuminating example of the argument made in the preceding sections, the electronic transport phenomena in metals or semi-conductors. According to the phenomenological theory,[10] the electric current density $\boldsymbol{j}$ and the heat flow density $\boldsymbol{q}$ are linear functions of the gradients of the electrochemical potential

$$\mu = \zeta - e\varphi , \qquad (4.1)$$

of the electrons and the gradient of temperature. The charge of electron is taken here as $-e$. Namely we have

$$\boldsymbol{j} = \mathfrak{S}^{(1)}\left(\boldsymbol{E} + \frac{T}{e}\nabla\xi\right) + \mathfrak{S}^{(2)}\frac{1}{T}\nabla T$$

$$\boldsymbol{q} = -\mathfrak{S}^{(3)}\left(\boldsymbol{E} + \frac{1}{e}\nabla\xi\right) - \mathfrak{S}^{(4)}\frac{1}{T}\nabla T , \qquad (4.2)$$

where $\boldsymbol{E}$ is the electric field and ξ is defined by

$$\xi = \zeta / T . \qquad (4.3)$$

Eq. (4.2) can be written as

$$\boldsymbol{E} = \rho\, \boldsymbol{j} - \frac{1}{e}\mathfrak{S}\nabla T - \frac{1}{e}\nabla\zeta$$

$$\boldsymbol{q} = \pi \boldsymbol{j} - \kappa\nabla T - \frac{1}{e}\zeta \boldsymbol{j} , \qquad (4.4)$$

where the constants are

$$\rho = \mathfrak{S}^{(1)-1} = \sigma^{-1} ,$$
$$\mathfrak{S} = (e\rho\mathfrak{S}^{(2)} - \zeta) / T ,$$
$$\pi = -\mathfrak{S}^{(3)}\rho - \zeta/T .$$
$$\kappa = (\mathfrak{S}^{(4)} - \mathfrak{S}^{(3)}\rho\mathfrak{S}^{(2)}) / T . \qquad (4.5)$$

Here ρ is the electric resistance, κ the heat conductivity, $-\mathfrak{S}/e$ the absolute thermoelectric power per unit temperature difference, and π is the Peltier constant. All of $\mathfrak{S}^{(r)}$ ($r=1, \cdots 4$) and other coefficients are tensors of the second rank. Our problem is now to find exact expressions for these coefficients in Eqs. (4.2) or (4.4).

The answer is easily anticipated, because we know already the exact expression of $\mathfrak{S}^{(1)}$, that is the conductivity tensor. Thus we want to show that the equations,

$$S^{(1)}_{\mu\nu} = \int_0^\infty \int_0^\beta \langle j_\nu j_\mu(t+i\hbar\lambda) \rangle \, d\lambda dt$$

$$S^{(2)}_{\mu\nu} = \int_0^\infty \int_0^\beta \langle q_\nu j_\mu(t+i\hbar\lambda) \rangle \, d\lambda dt$$

$$S^{(3)}_{\mu\nu} = \int_0^\infty \int_0^\beta \langle j_\nu q_\mu(t+i\hbar\lambda) \rangle \, d\lambda dt$$

$$S^{(4)}_{\mu\nu} = \int_0^\infty \int_0^\beta \langle q_\nu q_\mu(t+i\hbar\lambda) \rangle \, d\lambda dt , \qquad (4.6)$$

hold as rigorous expressions for these kinetic coefficients. Expressions similar to Eqs. (4.6) have been given indepently by Mori[7]. His formulae, however, differ from (4.6) in the upper limit of the time integral which he put as finite. This reflects the difference of the ways of reasoning. We shall show that it can be extended to infinity and that Eqs. (4.6) are rigorous in their nature. We follow

* Physically, the function $\ddot{\phi}(t)$ corresponds to the time correlation of forces acting on the electrons. The characteristic time τ_d of this will be the duration time of collision if the electrons are scattered by phonons or other perturbers only with rare chances and short duration of collision.

the line of reasoning described in the foregoing sections in order to arrive at these results.

It is most convenient to consider the electron number density $n(\boldsymbol{r})$ and the energy density $\mathcal{E}(\boldsymbol{r})$. We regard an electron gas system with the volume V as an isolated system and define the total entropy as the sum of entropy density under the assumption of local equilibrium. The local entropy density is a function of $n(\boldsymbol{r})$ and $\mathcal{E}(\boldsymbol{r})$. Thus the entropy S can be expanded in terms of fluctuations $\Delta n(\boldsymbol{r})$ and $\Delta\mathcal{E}(\boldsymbol{r})$ of $n(\boldsymbol{r})$ and $\mathcal{E}(\boldsymbol{r})$ as

$$\begin{aligned} S&=\int s(\boldsymbol{r})d\boldsymbol{r} \\ &=\int\left[s_0+\frac{\partial s}{\partial\mathcal{E}}\Delta\mathcal{E}+\frac{\partial s}{\partial n}\Delta n+\frac{1}{2}\left\{\frac{\partial^2 s}{\partial\mathcal{E}^2}(\Delta\mathcal{E})^2+2\frac{\partial^2 s}{\partial\mathcal{E}\partial n}(\Delta\mathcal{E}\,\Delta n)+\frac{\partial^2 s}{\partial n^2}(\Delta n)^2\right\}\right]d\boldsymbol{r}+\cdots \\ &=S_0+\frac{1}{2}\left(\frac{\partial}{\partial\mathcal{E}}\frac{1}{T}\right)\int(\Delta\mathcal{E})^2 d\boldsymbol{r}+\left(\frac{\partial}{\partial n}\frac{1}{T}\right)\int\Delta\mathcal{E}\Delta n d\boldsymbol{r}-\frac{1}{2}\left(\frac{\partial}{\partial n}\right)\int(\Delta n)^2 d\boldsymbol{r}+\cdots, \end{aligned} \tag{4.7}$$

where S_0 is the equilibrium entropy of whole system so that the linear terms in $\Delta\mathcal{E}$ and Δn must vanish. We made in Eq. (4.7) use of the relations,

$$\frac{\partial s}{\partial\mathcal{E}}=\frac{1}{T}, \quad \text{and} \quad \frac{\partial s}{\partial n}=-\frac{\zeta}{T}.$$

Now the fluctuations $\Delta\mathcal{E}(\boldsymbol{r})$ and $\Delta n(\boldsymbol{r})$ are developed in the Fourier components. Eq. (4.7) is rewritten as

$$S=S-\frac{1}{2}\frac{1}{T^2}\left(\frac{\partial T}{\partial\mathcal{E}}\right)_n V\sum_k \mathcal{E}_k\mathcal{E}_{-k}-\frac{1}{T^2}\left(\frac{\partial T}{\partial n}\right)_\varepsilon V\sum_k \mathcal{E}_k n_{-k}-\frac{1}{2}\left(\frac{\partial\xi}{\partial n}\right)_\varepsilon V\sum_k n_k n_{-k}+\cdots, \tag{4.8}$$

where n_k and $\mathcal{E}_k$ are the Fourier components of $n(\boldsymbol{r})$ and $\mathcal{E}(\boldsymbol{r})$ respectively.

The general thermodynamics of irreversible processes here asserts that the flows $\dot{\mathcal{E}}_k$ and $\dot{n}_k$, when they are present as macroscopic observables and hence their fluctuation is neglected, are linearly related to the driving forces, $\partial S/\partial n_k$ and $\partial S/\partial\mathcal{E}_k$. Namely the phenomenological equations are

$$\dot{n}_k=\sum_{k'}G^{(1)}_{kk'}\frac{\partial S}{\partial n_{k'}}+\sum_{k'}G^{(2)}_{kk'}\frac{\partial S}{\partial\mathcal{E}_{k'}}, \qquad \dot{\mathcal{E}}_k=\sum_{k'}G^{(3)}_{kk'}\frac{\partial S}{\partial n_{k'}}+\sum_{k'}G^{(4)}_{kk'}\frac{\partial S}{\partial\mathcal{E}_{k'}}, \tag{4.9}$$

which, with the aid of Eq. (4.8), are written as

$$\begin{aligned} \dot{n}_k=&-V\sum_{k'}G^{(1)}_{kk'}\left\{\left(\frac{\partial\xi}{\partial n}\right)_\varepsilon n_{-k'}+\frac{1}{T^2}\left(\frac{\partial T}{\partial n}\right)_\varepsilon\mathcal{E}_{-k'}\right\} \\ &-V\sum_{k'}G^{(2)}_{kk'}\left\{\frac{1}{T^2}\left(\frac{\partial T}{\partial n}\right)_\varepsilon n_{-k'}+\frac{1}{T^2}\left(\frac{\partial T}{\partial\mathcal{E}}\right)_n\mathcal{E}_{-k'}\right\} \\ \dot{\mathcal{E}}_k=&-V\sum_{k'}G^{(3)}_{kk'}\left\{\left(\frac{\partial\xi}{\partial n}\right)_\varepsilon n_{-k'}+\frac{1}{T^2}\left(\frac{\partial T}{\partial n}\right)_\varepsilon\mathcal{E}_{-k'}\right\} \\ &-V\sum_{k'}G^{(4)}_{kk'}\left\{\frac{1}{T^2}\left(\frac{\partial T}{\partial n}\right)_\varepsilon n_{-k'}+\frac{1}{T^2}\left(\frac{\partial T}{\partial\mathcal{E}}\right)_n\mathcal{E}_{-k'}\right\}. \end{aligned} \tag{4.10}$$

The flows $\boldsymbol{j}(\boldsymbol{r})$ and $\boldsymbol{q}(\boldsymbol{r})$ are related to the densities $n(\boldsymbol{r})$ and $\mathcal{E}(\boldsymbol{r})$ by the phenomenological equations,*

* These equations leave an ambiguity for the current components which are derived from the antisymmetric part of the tensors $\mathfrak{S}^{(r)}$, which vanish automatically in the divergence.[4] Thus the following argument is, strictly speaking, incompetent as the proof of the antisymmetric parts of Eqs. (4.6). This point will be considered in a forthcoming paper.

$$\dot{n}(\boldsymbol{r})=\frac{1}{e}\operatorname{div}\boldsymbol{j}(\boldsymbol{r}) ,$$

$$\dot{\varepsilon}(\boldsymbol{r})=-\operatorname{div}\boldsymbol{q}(\boldsymbol{r}) , \tag{4.11}$$

so that we have

$$\dot{n}_{\boldsymbol{k}}=\frac{1}{e}i(\boldsymbol{k}\boldsymbol{j}_k) ,$$

$$\dot{\varepsilon}_{\boldsymbol{k}}=-i(\boldsymbol{k}\boldsymbol{q}_k) , \tag{4.12}$$

where $\boldsymbol{j}_k$ and $\boldsymbol{q}_k$ are the Fourier components of the flow densities. Inserting the Fourier components of Eq. (4.2) into Eq. (4.12) and making use of the equations,

$$\nabla T=\frac{\partial T}{\partial \varepsilon}\nabla\varepsilon+\frac{\partial T}{\partial n}\nabla n ,$$

$$\nabla\xi=\frac{\partial \xi}{\partial \varepsilon}\nabla\varepsilon+\frac{\partial \xi}{\partial n}\nabla n .$$

we obtain

$$e\dot{n}_{\boldsymbol{k}}=-\left(\frac{T}{e}\frac{\partial\xi}{\partial\varepsilon}\boldsymbol{k}\mathfrak{S}^{(1)}\boldsymbol{k}+\frac{1}{T}\frac{\partial T}{\partial\varepsilon}\boldsymbol{k}\mathfrak{S}^{(2)}\boldsymbol{k}\right)\varepsilon_k -\left(\frac{T}{e}\frac{\partial\xi}{\partial n}\boldsymbol{k}\mathfrak{S}^{(1)}\boldsymbol{k}+\frac{1}{T}\frac{\partial T}{\partial n}\boldsymbol{k}\mathfrak{S}^{(2)}\boldsymbol{k}\right)n_k$$

$$\dot{\varepsilon}_{\boldsymbol{k}}=-\left(\frac{T}{e}\frac{\partial\xi}{\partial\varepsilon}\boldsymbol{k}\mathfrak{S}^{(3)}\boldsymbol{k}+\frac{1}{T}\frac{\partial T}{\partial\varepsilon}\boldsymbol{k}\mathfrak{S}^{(4)}\boldsymbol{k}\right)\varepsilon_k -\left(\frac{T}{e}\frac{\partial\xi}{\partial n}\boldsymbol{k}\mathfrak{S}^{(3)}\boldsymbol{k}+\frac{1}{T}\frac{\partial T}{\partial n}\boldsymbol{k}\mathfrak{S}^{(4)}\boldsymbol{k}\right)n_k . \tag{4.13}$$

Comparing Eq. (4.10) with Eq. (4.13) we find that

$$eVG^{(r)}_{\boldsymbol{k},-\boldsymbol{k}}=\frac{T}{e}\boldsymbol{k}\mathfrak{S}^{(r)}\boldsymbol{k} , \qquad r=1, \cdots 4, \tag{4.14}$$

and that

$$G^{(r)}_{\boldsymbol{k},\boldsymbol{k}'}=0 , \qquad \text{if} \quad \boldsymbol{k}+\boldsymbol{k}'\neq 0 .$$

These relations must hold in order that the "thermodynamic" relations, (4.9), are consistent with the phenomenological equations (4.2).

Now we are in position to apply our logics of previous section to obtain rigorous expressions for $G^{(r)}_{\boldsymbol{k},-\boldsymbol{k}}$. Eq. (3.14) is now read as

$$\frac{1}{\beta}\int_0^\beta\langle n_{-\boldsymbol{k}}(t-i\hbar\lambda)\{n_{\boldsymbol{k}}(t+\Delta t)-n_{\boldsymbol{k}}(t)\}\rangle d\lambda=-kG^{(1)}_{\boldsymbol{k},-\boldsymbol{k}}\Delta t ,$$

$$\frac{1}{\beta}\int_0^\beta\langle \varepsilon_{-\boldsymbol{k}}(t-i\hbar\lambda)\{n_{\boldsymbol{k}}(t+\Delta t)-n_{\boldsymbol{k}}(t)\}\rangle d\lambda=-kG^{(2)}_{\boldsymbol{k},-\boldsymbol{k}}\Delta t .$$

$$\frac{1}{\beta}\int_0^\beta\langle n_{-\boldsymbol{k}}(t-i\hbar\lambda)\{n_{\boldsymbol{k}}(t+\Delta t)-\varepsilon_{\boldsymbol{k}}(t)\}\rangle d\lambda=-kG^{(3)}_{\boldsymbol{k},-\boldsymbol{k}}\Delta t ,$$

$$\frac{1}{\beta}\int_0^\beta\langle \varepsilon^{-}_{\boldsymbol{k}}(t-i\hbar\lambda)\{\varepsilon_{\boldsymbol{k}}(t+\Delta t)-\varepsilon_{\boldsymbol{k}}(t)\}\rangle d\lambda=-kG^{(4)}_{\boldsymbol{k},-\boldsymbol{k}}\Delta t . \tag{4.15}$$

By the remark made at the end of § 3, it is evident that we have

$$\int_0^\beta\langle n_{-\boldsymbol{k}}(t-i\hbar\lambda)\,\dot{n}_{\boldsymbol{k}}(t)\rangle d\lambda=0 ,$$

and

$$\int_0^\beta\langle \varepsilon_{-\boldsymbol{k}}(t-i\hbar\lambda)\,\dot{\varepsilon}_{\boldsymbol{k}}(t)\rangle d\lambda=0 .$$

Corresponding expressions containing $n_{\boldsymbol{k}}$ and $\varepsilon_{\boldsymbol{k}}$ are also zero, because we have by virtue of Eq. (3.20)

$$\int_0^\beta\langle \dot{n}_{-\boldsymbol{k}}(t-i\hbar\lambda)\,\varepsilon_{\boldsymbol{k}}(t)\rangle d\lambda=\frac{1}{i\hbar}\langle[n_{-\boldsymbol{k}}, \varepsilon_{\boldsymbol{k}}]\rangle=-i(\boldsymbol{k}\boldsymbol{j})/e .$$

The last expression is obtained by explicit calculation of the commutator $[n_{-\boldsymbol{k}}, \varepsilon_{\boldsymbol{k}}]$ in terms of quantized wave functions. The average of current in equilibrium is equal to zero, so that we may put

$$\int_0^\beta\langle n_{-\boldsymbol{k}}(t-i\hbar\lambda)\,\dot{\varepsilon}_{\boldsymbol{k}}(t)\rangle d\lambda=\int_0^\beta\langle \varepsilon_{-\boldsymbol{k}}(t-i\hbar\lambda)\dot{n}_{\boldsymbol{k}}(t)\rangle d\lambda=0 .$$

Therefore we can safely rewrite Eqs. (4.14) in the form of Eq. (3.17).

Furthermore, Eq. (4.14) shows that the decay of the functions on the left-hand sides of Eq. (4.15) becomes infinitely slow if the wave number k approaches to zero. Speaking in classical language, the time of the decay of the fluctuation of n and ε becomes infinitely slow as the wave length of the spacial fluctuation becomes infinitely large. This is physically evident. This provides a sound basis for the transformation of Eq. (4.15) into the expressions of the type Eq. (3.18) in the limit of $k\to 0$. Thus we arrive at the equations

$$\lim_{k\to 0} G^{(1)}_{k,-k} = \lim \frac{1}{k}\int_0^\infty\int_0^\beta \langle \dot{n}_{-k}(-i\hbar\lambda)\,\dot{n}_k(t)\rangle\, d\lambda dt\,,$$
$$\lim_{k\to 0} G^{(2)}_{k,-k} = \lim \frac{1}{k}\int_0^\infty\int_0^\beta \langle \dot{\varepsilon}_{-k}(-i\hbar\lambda)\,\dot{n}_k(t)\rangle\, d\lambda dt\,,$$
$$\lim_{k\to 0} G^{(3)}_{k,-k} = \lim \frac{1}{k}\int_0^\infty\int_0^\beta \langle \dot{n}_{-k}(-i\hbar\lambda)\,\dot{\varepsilon}_k(t)\rangle\, d\lambda dt\,,$$
$$\lim_{k\to 0} G^{(4)}_{k,-k} = \lim \frac{1}{k}\int_0^\infty\int_0^\beta \langle \dot{\varepsilon}_{-k}(-i\hbar\lambda)\,\dot{\varepsilon}_k(t)\rangle\, d\lambda dt\,. \tag{4.16}$$

Now Eq. (4.12) is used to rewrite the expressions on the right-hand sides of these equations and the resulting expressions are compared with Eq. (4.14). Thus we find that Eq. (4.6) are obtained rigorously from Onsager's assumption.

Acknowledgements

The authors wish to express their thank to our colleagues at the Department of Physics, University of Tokyo, and the Physical Institute, Nagoya University, for illuminating discussions. The present study was partially financed by the Scientitic Research Fund of the Ministry of Education.

References

1) R. Kubo: J. Phys. Soc. Japan **12** (1957) 570.
2) The material of this paper was preliminarily reported in; R. Kubo and M. Yokota: Busseiron-Kenkyu, **89** (1955) 99 and S. kakajima: ibid **102** (1956) 24, **104** (1957) 6.
3) L. Onsager: Phys. Rev. **37** (1931) 405; **38** (1931) 2265.
4) See for instance, S. R. de Groot: Thermodynamics of Irreversible Processes.
5) H. B. Callen and T. A. Welton: Phys. Rev. **83** (1951) 34. H. Takahasi: J. Phys. Soc. Japan **7** (1952) 439.
6) J. G. Kirkwood: J. Chem. Phys. **14** (1946) 180.
7) H. Mori: J. Phys. Soc. Japan **11** (1956) 1029.
8) H. Nakano: Prog. Theor. Phys. **15** (1956) 77; Busseiron-Kenku **84** (1955) 25. S. Nakajima: Busseiron-Kenkyu **88** (1955) 45.
9) R. Kubo: Nippon Sugaku-Butsuri-Gakkaishi **16** (1942) 243; Busseiron-Kenkyu **89** (1955) 72.
10) M. Kohler: Ann. Phys. (5) **40** (1941) 601.
A. H. Wilson: Theory of Metals, 2nd ed. p. 194.