

# Statistical-Mechanical Theory of Irreversible Processes. I.

## *General Theory and Simple Applications to Magnetic and Conduction Problems*

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A general type of fluctuation-dissipation theorem is discussed to show that the physical quantities such as complex susceptibility of magnetic or electric polarization and complex conductivity for electric conduction are rigorously expressed in terms of time-fluctuation of dynamical variables associated with such irreversible processes. This is a generalization of statistical mechanics which affords exact formulation as the basis of calculation of such irreversible quantities from atomistic theory. The general formalism of this statistical-mechanical theory is examined in detail. The response, relaxation, and correlation functions are defined in quantummechanical way and their relations are investigated. The formalism is illustrated by simple examples of magnetic and conduction problems. Certain sum rules are discussed for these examples. Finally it is pointed out that this theory may be looked as a generalization of the Einstein relation.

### § 1. Introduction

The principal purpose of the present paper is to develop a general scheme for the calculation of kinetic coefficient, or admittance for external forces such as electric or magnetic susceptibility for alternating field, electric conductivity, heat conductivity and so on. The most common method traditionally employed to calculate such non-equilibrium quantities is to set up the so-called kinetic equation or transport equation for the molecular distribution functions. This will be solved for stationary or periodic conditions. It is however to be reminded that the kinetic equation is itself an approximation and cannot be derived without a certain condition which is rather strict and is not often satisfied.<sup>1)</sup> For weakly interacting particles, it may be justified if the nature of interaction is appropriate. But certainly it is not always true, and we may not be able even to write down any equation of that sort.

On the other hand, the recent development of the thermodynamic of irreversible processes<sup>2)</sup> indicates the possibility of constructing a general statistical-mechanical theory at least for those irreversible processes which are not far apart from thermal equilibrium. In fact, there have been a number of attempts in this direction<sup>3)</sup>. A remarkable pro-

gress has been made by Kirkwood<sup>4)</sup> who showed that the friction constant, for instance, of a Brownian particle is determined by the correlation of forces acting on the particle. This may be looked as a particular case of the so-called dissipation-fluctuation theorem. As was discussed from a general point of view by Callen, Welton,<sup>5)</sup> Takahasi<sup>6)</sup> and others, the general admittance for an external disturbance is related to the expectation of the square of Fourier component of certain physical quantity which fluctuates in time in thermal equilibrium. Thus it is shown that, as far as linear responses are concerned, the admittance is reduced to the calculation of time-fluctuations in equilibrium.

This idea was used by the present author as the basis of the theory of magnetic resonance problem. In a previous paper<sup>7)</sup> the author developed a quantum-mechanical theory of this and has shown a certain method of practical application. A straightforward application of this theory was made by Nakano<sup>8)</sup> for the conduction problem. He showed that the simplest approximation of the fundamental expression of conductivity gives the well-known Grüneisen's formula.

A generalized form of Nyquist's theorem can be easily derived by application of perturbation theory either classical or quantum-

mechanical. The complete conductivity tensor for a given frequency of applied electric field can be rigorously expressed in terms of electric current components fluctuating spontaneously in equilibrium state<sup>9)</sup>. We emphasize here that this expression is quite rigorous though admittedly somewhat abstract. It is however of great value, because the traditional theory of conductivity has not been aware of existence of such rigorous expression (although the Heisenberg-Kramers dispersion formula is an equivalent). The abstract nature of the formula may be compared to that of general theory of statistical mechanics. The statistical mechanics can give a rigorous expression for the equation of state in terms of partition function, but its calculation is not necessarily easy.

This theory of electric conduction has been actively discussed in last two years in Japan since the appearance of our paper on magnetic resonance<sup>7)</sup> and its application to conduction problem by Nakano. Feynman also discussed this when he visited Japan in the summer of 1955. Also it has been discussed by Lax, Luttinger, Kohn and possibly by some others in the United States. Recently Mori<sup>20)</sup> has published a paper on the same problem.

In the present paper, which will be the first part of a series of papers devoted to the development of statistical mechanics of irreversible processes along this line and to its applications, we shall examine in detail the implications of this new method.

In § 2, we shall treat the response of a system to an external force by simple perturbation method. In order to make the idea clearer we first discuss the classical case. Quantum-mechanical formulation is quite in parallel with this classical theory. However, we notice a difficult problem of quantum-mechanical observation which might disturb the natural development of the motion. It will be pointed out that the logical basis of the whole theory is closely related to the ergodic properties of the system and the physical quantities we are concerned with. This is discussed in § 3 in connection with the definition of relaxation functions which describe the relaxation of the system after removal of external disturbance.

In § 4, the correlation functions are introduced which describe the time correlation of

two quantities at different time points. The relation between the correlation function and the relaxation function is derived. This is somewhat complicated in quantum-mechanical case.

§ 5 is devoted to the application of general argument to simple examples of magnetic and conduction phenomena. This is mostly to illustrate the general idea. The symmetry of the relaxation and response functions is discussed in § 6. The Onsager's reciprocity is seen most clearly by this formalism. The complete form of fluctuation-dissipation theorem will be given in § 7 taking the example of conductivity tensor.

As an interesting application of the theory, some general rules for the admittance is discussed in § 8. The most general sum rule is mentioned with regard to the symmetric part of conductivity tensor. The integration of this over the whole range of frequency must be constant irrespective of the presence of interactions or magnetic field and at any temperature. Another type of sum rule is derived for the antisymmetric part of conductivity. An interesting sum rule for the magnetic problem is that the integrated absorption intensity of circular wave by magnetic media is directly related to the gyromagnetic ratio of magnetic particles.

In § 9, it will be pointed out that the theory may be looked as a generalization of Einstein relation which relates the mobility and the diffusion constant. The general nature of Einstein relation is thus most clearly revealed.

In the present paper we confined ourselves to such type of external disturbance which can be expressed definitely as an additional term in the Hamiltonian of the system. Thus the heat flow, or mass flow phenomena under the gradient of temperature or chemical potential is logically out of the frame of this treatment. This problem has been treated recently by Mori.<sup>10)</sup> We shall, however, discuss this in a forthcoming paper from a somewhat different point of view.

We also have applied the present theory to the galvanomagnetic effect at high magnetic field<sup>11)</sup>. This is an example for which the traditional transport equation has to be modified. Our theory will be reported in another paper.

## § 2. Response Function and Admittance of an Isolated System

Let us consider an isolated system, the Hamiltonian of which is denoted by  $\mathcal{H}$ . The dynamical motion of the system determined by  $\mathcal{H}$  is called the “*natural motion*” of the system. We suppose that an external force  $F(t)$  is applied to the system, the effect of which is represented by the perturbation energy,

$$\mathcal{H}'(t) = -AF(t). \quad (2.1)$$

The motion of the system is perturbed by this force, but the perturbation is small if the force is weak. We confine ourselves to weak perturbation and ask for the response of the system in the linear approximation. The response is observed through the change  $\Delta B(t)$  of a physical quantity  $B$ . The problem is now to express  $\Delta B(t)$  in terms of the natural motion of the system.

First, we shall treat this in classical mechanics. We conceive a statistical ensemble which is represented by a distribution function  $f(p, q)$  in the phase space. The *natural motion* is described by the equation of motion,

$$\frac{\partial f}{\partial t} = -\sum \left( \frac{\partial f}{\partial q} \frac{\partial \mathcal{H}}{\partial p} - \frac{\partial f}{\partial p} \frac{\partial \mathcal{H}}{\partial q} \right) = (\mathcal{H}, f), \quad (2.2)$$

where  $p$  and  $q$  mean the set of the canonical moments and coordinates and the bracket means the Poisson bracket,

$$(A, B) = \sum \left( \frac{\partial A}{\partial q} \frac{\partial B}{\partial p} - \frac{\partial A}{\partial p} \frac{\partial B}{\partial q} \right). \quad (2.3)$$

We assume that the distribution function is given by  $f$  at  $t = -\infty$ , that is, at the infinite past. It is assumed to be in equilibrium, that is,  $(\mathcal{H}, f) = 0$ . The perturbation (2.1) is inserted adiabatically at  $t = -\infty$  ( $F(-\infty) = 0$ ). The distribution function  $f'(t)$  obeys the equation

$$\frac{\partial f'(t)}{\partial t} = (\mathcal{H}, f') + (\mathcal{H}'(t), f). \quad (2.4)$$

Since we take the linear approximation, we put

$$f'(t) = f + \Delta f$$

and replace (2.4) by

$$\frac{\partial \Delta f}{\partial t} = (\mathcal{H}, \Delta f) - F(t)(A, f). \quad (2.5)$$

The solution is easily found to be

$$\Delta f(t) = -\int_{-\infty}^t e^{i(t-t')L} (A, f) F(t') dt' \quad (2.6)$$

where the operator  $L$  is defined by the operation<sup>4)</sup>

$$iLg \equiv (\mathcal{H}, g). \quad (2.7)$$

Therefore, the change  $\Delta B(t)$  of a dynamical quantity  $B$  is statistically given by

$$\begin{aligned} \Delta B(t) &= \int \Delta f(t) \cdot B(p, q) d\Gamma \\ &= -\int d\Gamma \int_{-\infty}^t \left\{ e^{i(t-t')L} (A, f) \right\} \cdot F(t') B dt' \\ &= -\int d\Gamma \int_{-\infty}^t (A, f) B(t-t') F(t') dt', \end{aligned} \quad (2.8)$$

$d\Gamma$  being the volume element of the phase space. The last expression is obtained from the second remembering that the transformation  $\exp(iLt)$  is the natural motion which conserves the measure of the phase space and that  $B(t)$  means the dynamical motion of the phase function  $B(p, q)$  which follows the equation

$$\dot{B}(p, q) = (B, \mathcal{H}).$$

This corresponds to the Heisenberg equation of motion in quantum-mechanics. Eq. (2.8) means that the response  $\Delta B(t)$  is a superposition of the effects of pulses  $F(t') dt'$ ,  $-\infty < t' < t$ . The response for an unit pulse will be called the *response function* or the *after-effect function*  $\phi_{AB}(t)$ . From Eq. (2.8) we find at once that it is given by

$$\phi_{BA}(t) = -\int d\Gamma (A, f) B(t) \quad (2.9)$$

which describes the response  $\Delta B$  at the time  $t$  after the pulse. The response  $\Delta B(t)$ , (2.8), is written as

$$\Delta B(t) = \int_{-\infty}^t \phi_{BA}(t-t') F(t') dt'. \quad (2.10)$$

The above consideration applies even when the initial distribution is very sharp, as far the perturbation is weak enough. But our aim is rather to apply this for a macroscopic system, in which case the statistical average itself acquires a realistic meaning. If  $A$  and  $B$  are both macroscopic quantities, we may think the ensemble average  $\Delta B(t)$  is what we actually observe, because a macroscopic system can be conceived to consist of smaller systems so that observed value of  $\Delta B$  is a sum of a number of components and has only

a very small relative fluctuation.

Let us now turn to quantum mechanics. The distribution function in phase space is now replaced by the density matrix  $\rho$ . The initial ensemble which represents statistically the initial state of the system is specified by the density matrix  $\rho$  satisfying  $[\mathcal{H}, \rho] = 0$ , whereas the motion of the ensemble under the perturbation (2.1) is represented by  $\rho'(t)$ , which obeys the equation,

$$\frac{d}{dt} \rho'(t) = \frac{1}{i\hbar} [\mathcal{H} + \mathcal{H}'(t), \rho'(t)]. \quad (2.11)$$

With the initial condition

$$\rho'(-\infty) = \rho,$$

we expand  $\rho'(t)$  as

$$\rho'(t) = \rho + \Delta\rho(t).$$

The same procedure as we used for (2.5) leads us at once to

$$\begin{aligned} \Delta\rho(t) = & -\frac{1}{i\hbar} \int_{-\infty}^t \exp(-i(t-t')\mathcal{H}/\hbar) [A, \rho] \\ & \times \exp(i(t-t')\mathcal{H}/\hbar) F(t') dt'. \end{aligned} \quad (2.12)$$

Incidentally, we note that it is sometimes very convenient to introduce the operator  $a^*$  operating on another operator  $b$  by following definition, i.e.,

$$a^*b = [a, b], \quad (2.13)$$

for which one finds the rule,

$$e^{a^*}b = e^a b e^{-a}. \quad (2.14)$$

With this notation, Eq. (2.11) and (2.12) can be written as

$$\dot{\rho}'(t) = \frac{1}{i\hbar} (\mathcal{H}^* + \mathcal{H}'(t)^*) \rho'(t) \quad (2.15)$$

$$\begin{aligned} \Delta\rho(t) = & -\frac{1}{i\hbar} \int_{-\infty}^t \exp(-i(t-t')\mathcal{H}^*/\hbar) \times \\ & \times [A, \rho] F(t') dt' \end{aligned} \quad (2.16)$$

This will make clear the similarity of Eqs. (2.6) and (2.12).

The response  $\Delta B(t)$  of the quantity  $B$  is statistically

$$\begin{aligned} \Delta B(t) &= \text{Tr } \Delta\rho(t) B \\ &= -\frac{1}{i\hbar} \text{Tr} \int_{-\infty}^t \exp(-i(t-t')\mathcal{H}/\hbar) \\ &\quad \times [A, \rho] \exp(i(t-t')\mathcal{H}/\hbar) B F(t') dt' \\ &= -\frac{1}{i\hbar} \text{Tr} \int_{-\infty}^t [A, \rho] B(t-t') F(t') dt' \end{aligned} \quad (2.17)$$

where  $B(t)$  is the Heisenberg representation of  $B$  following the equation

$$\dot{B}(t) = \frac{1}{i\hbar} [B(t), \mathcal{H}], \quad B(0) = B. \quad (2.18)$$

Eq. (2.17) corresponds to Eq. (2.8)

The response function or the after-effect function is now

$$\phi_{BA}(t) = -\frac{1}{i\hbar} \text{Tr} [A, \rho] B(t) \quad (2.19)$$

corresponding to Eq. (2.9). We naturally have Eq. (2.10) for (2.17) with the use of response function (2.19). If the force is periodic, i.e.,

$$F(t) = F_0 \cos \omega t,$$

the response  $\Delta B(t)$  will be conveniently written as

$$\Delta B(t) = \text{Re } \chi_{BA}(\omega) F_0 e^{i\omega t} \quad (2.20)$$

with the complex admittance  $\chi_{BA}(\omega)$ , for which we have from Eq. (2.10)

$$\chi_{BA}(\omega) = \int_0^\infty \phi_{BA}(t) e^{-i\omega t} dt, \quad (2.21)$$

or more exactly

$$\chi_{BA}(\omega) = \lim_{\varepsilon \rightarrow 0+} \int_0^\infty \phi_{BA}(t) e^{-i\omega t - \varepsilon t} dt.$$

We summarize the above by the theorem:

**Theorem 1.** *The linear response of a physical quantity  $B$  to an external force  $F(t)$  is represented by Eq. (2.10) as the superposition of after-effects. The after-effect function or the response function is given by*

$$\begin{aligned} \phi_{BA}(t) &= \int d\Gamma(f, A) B(t) \quad (\text{classical}) \quad (2.22a) \\ &= \frac{1}{i\hbar} \text{Tr} [\rho, A] B(t) \quad (\text{quantal}). \end{aligned} \quad (2.22b)$$

The admittance  $\chi_{BA}(\omega)$  is given by

$$\begin{aligned} \chi_{BA}(\omega) &= \lim_{\varepsilon \rightarrow 0+} \int_0^\infty e^{-i\omega t - \varepsilon t} dt \int d\Gamma(f, A) B(t) \\ &\quad (\text{classical}) \end{aligned} \quad (2.23a)$$

$$\begin{aligned} &= \lim_{\varepsilon \rightarrow 0+} \int_0^\infty e^{-i\omega t - \varepsilon t} dt \frac{1}{i\hbar} \text{Tr} [\rho, A] B(t). \\ &\quad (\text{quantal}) \end{aligned} \quad (2.23b)$$

Eqs. (2.22) may be written as

$$\phi_{BA}(t) = \int d\Gamma f(A, B(t)) \quad (\text{classical}) \quad (2.24a)$$

$$= \frac{1}{i\hbar} \text{Tr } \rho [A, B(t)] \quad (\text{quantal}) \quad (2.24b)$$

which are sometimes more convenient. One must however be careful about the boundary conditions of  $f$  or  $\rho$ , which may, however,

be replaced by a suitable potential under certain circumstances.

As we mentioned before, there is no difficulty in classical cases to interpret the response thus obtained as the average which approximates closely the actual observation for large systems. In quantum-mechanical cases, however, we must note that there exists a certain difficulty.  $\Delta B$  as given by Eq. (2.17) is the quantum-mechanical expectation of the first order change of  $B$  at the time  $t$ . This means that we prepare at  $t = -\infty$  an ensemble of systems which corresponds to the statistical operator  $\rho$ . At a certain time  $t$ , we pick up a number of systems and observe  $B$ . The average of the observed values will be  $\Delta B(t)$ . We shall not follow these systems after this observation. At a later time point  $t'$ , we choose different systems which have not been observed before. This is the way to follow the time change  $\Delta B(t)$  to avoid the quantum-mechanical disturbance of observation process.

For the most of practical applications, we are rather interested in a continuous observation of a particular system, which is however macroscopic. The use of ensemble average for the actual observation will be justified by the same argument we made for the classical case. But the quantum-mechanical disturbance of observation is another thing. We may, however, expect for most of macroscopic quantities which we observe this disturbance can be neglected. This is a condition for macroscopic observations. Unfortunately, exact conditions for the existence of such quantities are not known.

Thus we shall rather introduce without proof the assumption that the identification of the statistically calculated  $\Delta B(t)$  with the actually observed time variation is legitimate at least for those macroscopic quantities we

shall be concerned with. We should however make reservation that this assumption may not be necessary for the identification of the admittance calculated by Eq. (2.23b) with what will be actually observed, because the observation of admittance, for example, the refractivity and absorption in optical problems, is not the observation of the response function itself. As a matter of fact, Eq. (2.23b) is equivalent to the well known dispersion formula of Heisenberg and Kramers<sup>12)</sup> plus the absorption calculated by time-dependent perturbation method.<sup>7)</sup> The dispersion formula represents the oscillation of expectation value of dipole moments if the formula is applied to optical problems. This is not directly observed. We observe the refraction by measuring the number of photons passed through the material. The logical relation between this and that is not clear enough, but the most common apologize is the use of correspondence principle. Any further analysis of this delicate problem is not our main purpose in this paper so we shall leave it for a future occasion.

Before concluding this section, we remark that the method employed here is also applicable to higher approximations than the linear. For this purpose we note Eq. (2.5) can be used for successive approximation, namely

$$\frac{\partial \Delta_k f}{\partial t} = (\mathcal{H}, \Delta_k f) - F(t')(A, \Delta_{k-1} f), \quad (2.25)$$

where  $\Delta_k f$  means the  $k$ -th term of the expansion

$$f'(t) = f + \Delta_1 f + \Delta_2 f + \dots \quad (2.26)$$

The solution of Eq. (2.25) has the same form as Eq. (2.6),  $f$  being replaced by  $\Delta_{k-1} f(t')$ . Therefore we obtain the complete solution of Eq. (2.4) as

$$\begin{aligned} f'(t) &= f + \sum_{k=1}^{\infty} (-)^k \int_{-\infty}^t \int_{-\infty}^{t_1} \dots \int_{-\infty}^{t_{k-1}} e^{iL(t-t_1)} \left( A, e^{iL(t_1-t_2)} (A, \dots e^{iL(t_{k-1}-t_k)} (A, f)) \dots \right) \\ &\quad \times F(t_1) F(t_2) \dots F(t_k) dt_1 \dots dt_k \\ &= f + \sum_{k=1}^{\infty} (-)^k \int_{-\infty}^t \int_{-\infty}^{t_1} \dots \int_{-\infty}^{t_{k-1}} e^{iLt} \left( A(t_1), (A(t_2), \dots (A(t_k), f) \dots \right) F(t_1) \dots F(t_k) dt_1 \dots dt_k. \end{aligned} \quad (2.27)$$

where  $A(t)$  is defined by

$$A(t) = A(p_t, q_t), \quad p_{t=0} = p, \quad q_{t=0} = q.$$

The same expression is obtained for quantum-mechanical case, namely

$$\rho'(t) = \rho + \sum_{k=1}^{\infty} \left( -\frac{1}{i\hbar} \right)^k \int_{-\infty}^t \int_{-\infty}^{t_1} \int_{-\infty}^{t_{k-1}} \exp(-it\mathcal{H}/\hbar) A(t_1) \times A(t_2) \times \cdots \times A(t_k) \times \rho F(t_1) \cdots F(t_k) dt_1 \cdots dt_k \quad (2.28)$$

where the cross means the commutator operation with the operation on its right hand side (see Eqs. (2.13) and (2.14)). These solutions allow us to write down the expression of responses in higher approximation. For instance, the second order change of  $B$  at the time  $t$  can be written as

$$\Delta_2 B(t) = \left( \frac{1}{i\hbar} \right)^2 \text{Tr} \int_{-\infty}^t \int_{-\infty}^{t_1} [A(t_1 - t_2) [A, \rho]] B(t_1 - t_2) F(t_1) F(t_2) dt_1 dt_2 \quad (2.29)$$

The corresponding classical formula is similar so that it is omitted here.

### § 3. Relaxation Function and Other Useful Formulae for Canonical Ensemble

In the following we consider quantum-mechanical problems, because the classical limit is easily obtained from quantum-mechanical formulae by replacing  $[ , ]/i\hbar$  by Poisson bracket or by making  $\hbar \rightarrow 0$ .

First let us observe the behavior of the response function  $\phi_{BA}(t)$  in the limit  $t \rightarrow \infty$ . It may approach to a limiting value or may not approach to any definite value. If it does, we must have

$$\lim_{t \rightarrow \infty} \phi_{BA}(t) = 0 \quad (\text{if the limit exists}). \quad (3.1)$$

This is evident from Abel's theorem

$$\lim_{t \rightarrow \infty} \phi_{BA}(t) = \lim_{\varepsilon \rightarrow 0+} \varepsilon \int_0^{\infty} \phi_{BA}(t) e^{-\varepsilon t} dt \quad (3.2)$$

which holds if the left hand side exists. The right hand side is zero unless  $\phi_{BA}(t)$  has a finite Fourier-amplitude at zero frequency. If  $\phi_{BA}(t)$  has finite Fourier components for a set of discrete frequencies,  $\phi_{BA}(t)$  will oscillate indefinitely and does not have any limit. But, for calculation of admittance we have the convergence factor  $e^{-\varepsilon t}$  so that we may even in this case regard the relation (3.1) to hold. If  $\phi_{BA}(t)$  is expressed by a Fourier integral with continuous Fourier spectrum, Eq. (3.1) is generally true. This corresponds to actual cases of large systems, because the complicated interaction within the system is always enough to split the energy levels into a structure so fine that the observation can not discriminate. The error in the observation of frequency certainly introduces an average which allows us to replace the originally discrete Fourier spectrum by continuous spectrum. Classically this corresponds

to elimination of long Poincaré cycles.

If the perturbation is applied continuously from  $t = -\infty$  up to  $t = 0$  and is cut off at  $t = 0$ , then the response  $\Delta B$  will relax following the formula

$$\begin{aligned} \Delta B(t) &= \int_{-\infty}^0 \phi_{BA}(t-t') dt' F \\ &= F \int_t^{\infty} \phi_{BA}(t') dt', \quad t > 0. \end{aligned} \quad (3.3)$$

Therefore, the function

$$\Phi_{BA}(t) = \lim_{\varepsilon \rightarrow 0+} \int_t^{\infty} \phi_{BA}(t') e^{-\varepsilon t'} dt' \quad (3.4)$$

describes the relaxation of  $\Delta B$  after removal of the outer disturbance. This will be called the relaxation function.

Here, for later reference we note the theorem:

**Theorem 2.** *The admittance  $\chi_{BA}(\omega)$  can be calculated by the following formulae;*

$$\begin{aligned} \chi_{BA}(\omega) &= \lim_{\varepsilon \rightarrow 0+} \int_0^{\infty} \phi_{BA}(t) e^{-i\omega t - \varepsilon t} dt \\ &= \lim_{\varepsilon \rightarrow 0+} \frac{1}{i\omega + \varepsilon} \left\{ \dot{\phi}_{BA}(0) + \int_0^{\infty} \phi_{BA}(t) e^{-i\omega t - \varepsilon t} dt \right\} \\ &= \Phi_{BA}(0) - i\omega \int_0^{\infty} \Phi_{BA}(t) e^{-i\omega t} dt. \end{aligned} \quad (3.5)$$

These transformations are rather evident.

The expression of  $\phi_{BA}(t)$  has already been given by Eq. (2.22). We note here that other functions  $\dot{\phi}_{BA}(t)$  and  $\Phi_{BA}(t)$  have convenient transform if the statistical ensemble is assumed to be *canonical*. For this purpose, we observe the identity

$$\begin{aligned} [A, \exp(-\beta \mathcal{H})] &= \exp(-\beta \mathcal{H}) \int_0^{\beta} \exp(\lambda \mathcal{H}) [\mathcal{H}, A] \\ &\quad \times \exp(-\lambda \mathcal{H}) d\lambda \end{aligned}$$

$$\begin{aligned}
&= \frac{\hbar}{i} \exp(-\beta \mathcal{H}) \int_0^s \exp(\lambda \mathcal{H}) \dot{A} \\
&\quad \times \exp(-\lambda \mathcal{H}) d\lambda \\
&= \frac{\hbar}{i} \exp(-\beta \mathcal{H}) \int_0^\beta \dot{A}(-i\hbar\lambda) d\lambda \quad (3.6)
\end{aligned}$$

or

$$[\rho_\beta, A] = i\hbar \int_0^\beta \rho_\beta \dot{A}(-i\hbar\lambda) d\lambda \quad (3.7)$$

which is easily seen by writing the expression in matrix form in the representation diagonalizing  $\mathcal{H}$ .

Let us now assume that the system we observe is statistically represented by the canonical density matrix,

$$\begin{aligned}
\rho &= \exp(-\beta(\mathcal{H} - \Psi)), \quad \beta = 1/kT, \\
\exp(-\beta\Psi) &= \text{Tr} \exp(-\beta\mathcal{H}). \quad (3.8)
\end{aligned}$$

By Eq. (2.22b) we have

$$\begin{aligned}
\phi_{BA}(t) &= \frac{1}{i\hbar} \text{Tr}[\rho, A] B(t) \\
&= \int_0^\beta \text{Tr} \rho \dot{A}(-i\hbar\lambda) B(t) d\lambda \\
&= - \int_0^\beta \text{Tr} \rho A(-i\hbar\lambda) \dot{B}(t) d\lambda \quad (3.9)
\end{aligned}$$

and also

$$\begin{aligned}
\dot{\phi}_{BA}(t) &= \frac{1}{i\hbar} \text{Tr}[\rho, A] \dot{B}(t) \\
&= \frac{1}{i\hbar} \text{Tr} \rho [A, \dot{B}(t)] = \frac{-1}{i\hbar} \text{Tr} \rho [\dot{A}, B(t)] \\
&= \int_0^\beta \text{Tr} \rho \dot{A}(-i\hbar\lambda) \dot{B}(t) d\lambda \quad (3.10)
\end{aligned}$$

One may use any of these expressions depending on the nature of the quantities  $A$  and  $B$ . This will be illustrated later by examples.

With the aid of Eq. (3.9), the relaxation is transformed into

$$\Phi_{BA}(t) = \frac{i}{\hbar} \int_t^\infty \text{Tr} \rho [B(t'), A] dt' \quad (3.11a)$$

$$= \int_0^\beta \text{Tr} \rho A(-i\hbar\lambda) B(t) d\lambda - \beta \text{Tr} \rho A^0 B^0 \quad (3.11b)$$

where  $A^0$  and  $B^0$  are the diagonal parts of  $A$  and  $B$  with respect to  $\mathcal{H}$ . The second term on the right hand side of Eq. (3.11) is the limit

$$\begin{aligned}
&\lim_{t \rightarrow \infty} \int_0^\beta \text{Tr} \rho A(-i\hbar\lambda) B(t) d\lambda \\
&= \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t dt \int_0^\beta \text{Tr} \rho A(-i\hbar\lambda) B(t) d\lambda \\
&= \beta \text{Tr} \rho A^0 B^0 \quad (3.12)
\end{aligned}$$

because this limit process selects the zero-frequency component of  $B(t)$ . The limit of the first expression, if it exists, must be equal to the last.

We may also define the function

$$\Phi_{BA}^e(t) = \int_0^\beta \text{Tr} \rho A(-i\hbar\lambda) (B - B(t)) \quad (3.13)$$

which we shall call the *excitation* function for convenience, because this describes the increase of  $\Delta B(t)$  when a constant force is applied from  $t=0$ . Thus

$$\lim_{t \rightarrow \infty} \Phi_{BA}^e(t) = \Phi_{BA}(0). \quad (3.14)$$

In particular, for  $t=0$ , we have from Eq. (3.11) and Eq. (3.5)

$$\begin{aligned}
\chi_{BA}(0) &= \Phi_{BA}(0) = \Phi_{BA}^e(\infty) \\
&= \int_0^\beta \text{Tr} \rho A(-i\hbar\lambda) B d\lambda - \beta \text{Tr} \rho A^0 B^0 \\
&= \int_0^\beta \text{Tr} \rho (A(-i\hbar\lambda) - A^0) (B - B^0) d\lambda \quad (3.15)
\end{aligned}$$

where  $\chi_{BA}(0)$  is the static admittance.

Eq. (3.15) is a little embarrassing, since the isothermal admittance,  $\chi_{BA}^T$ , is

$$\chi_{BA}^T = \int_0^\beta \text{Tr} \rho (A(-i\hbar\lambda) - \bar{A})(B - \bar{B}) d\lambda \quad (3.16)$$

where  $\bar{A}$  and  $\bar{B}$  and the equilibrium expectations of  $A$  and  $B$  in thermal equilibrium with  $F=0$ .

Eq. (3.16) is obtained by using the expansion  $\exp\{-\beta(\mathcal{H} - FA)\}$

$$= \exp(-\beta\mathcal{H}) \{1 + \int_0^\beta A(-i\hbar\lambda) d\lambda F + O(F^2)\}$$

for the expression

$$\begin{aligned}
\Delta B &= \frac{\text{Tr} \exp\{-\beta(\mathcal{H} - FA)\} B}{\text{Tr} \exp\{-\beta(\mathcal{H} - FA)\}} - \frac{\text{Tr} \exp(-\beta\mathcal{H}) B}{\text{Tr} \exp(-\beta\mathcal{H})}.
\end{aligned}$$

$\chi_{BA}^T$  is defined by

$$\chi_{BA}^T = \Delta B / F.$$

Expressions (3.15) and (3.16) are different unless

$$\text{Tr} \rho A^0 B^0 = \bar{A} \bar{B} = \text{Tr} \rho A \cdot \text{Tr} \rho B. \quad (3.17)$$

This will not however hold without certain restrictions imposed on  $A$  and  $B$ . In fact,  $\chi_{BA}(0)$  as given by Eq. (3.15) is the static admittance of an isolated system on which the force  $F$  is inserted adiabatically. On the other hand  $\chi_{BA}^T$ , Eq. (3.16), is isothermal,

that gives the response when the system is in thermal contact with the heat reservoir. Thus they need not be equal.

But, there are situations in which the difference is quite negligible. For instance, suppose a magnetic system is magnetized by external field. If the magnetic energy is only a very small fraction of the total energy, the magnetization process treated by Eq. (3.15) is practically isothermal. This means that, if the heat capacities associated with  $A$  and  $B$  are only a small fraction of total heat capacity, the equality (3.17) must be practically satisfied.

It is noted here that this is concerned with the ergodic property of the system. Khinchin<sup>13)</sup> has shown that the ergodicity for a quantity  $A$ , namely

$$\langle A \rangle = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t A(t) dt \quad (3.18)$$

must hold if the autocorrelation of  $A$  satisfies the relation

$$\lim_{t \rightarrow \infty} \langle A(0)A(t) \rangle = \langle A \rangle^2. \quad (3.19)$$

Here  $\langle A \rangle$  means the phase average of a phase function  $A(p, q)$  over a microcanonical ensemble. The ergodicity of  $A$ , (3.18), means that the time average of  $A$  starting from any point  $P$  on the ergodic surface approaches to  $\langle A \rangle$  independent of the initial point  $P$ . This will hold on the assumption of (3.19) for almost all of  $P$  except a set of measure zero. This Khinchin's theorem can be reversed. It can be proved that the correlation function  $\langle A(0)A(t) \rangle$  satisfies Eq. (3.19) if (3.18) holds uniformly.

In classical limit, (3.11b) is replaced by

$$\Phi_{BA}(t) = \beta \{ \langle A(0)B(t) \rangle - \langle A^0 B^0 \rangle \}, \quad (3.20)$$

where  $\langle \rangle$  means the phase average, and  $A^0$  means the invariant part of  $A(p_t, q_t)$  with respect to the natural motion. Eq. (3.16) becomes classically

$$\chi_{BA}^T = \beta \langle (A - \langle A \rangle)(B - \langle B \rangle) \rangle. \quad (3.21)$$

In general we must expect

$$\begin{aligned} \Phi_{BA}(0) &= \Phi_{BA}^e(\infty) = \chi_{BA}(0) \\ &= \beta \langle (A - A^0)(B - B^0) \rangle \approx \chi_{BA}^T. \end{aligned} \quad (3.22)$$

The left hand side is the static admittance for an isolated system. This means that

$$\lim_{t \rightarrow \infty} \langle A(0)B(t) \rangle \approx \langle A \rangle \langle B \rangle \quad (3.23)$$

and hence that the ergodicity (3.18) does not

hold. This is quite true as one would easily understand by the example of magnetization process of an ideal magnetic system. The isothermal and adiabatic susceptibilities are different, the later being zero.

However, our aim is to apply the whole theory to realistic systems which contain various interactions. As we have mentioned before, we should expect that

$$\chi_{BA}(0) = \chi_{BA}^T \quad (3.24)$$

will hold if the total system is large enough compared to the degrees of freedom associated with the observed quantities  $A$  and  $B$ .

For a very large system, the canonical distribution is almost equivalent to a microcanonical distribution, the relative fluctuation being very small. The ensemble average in Eqs. (3.20), etc., can be regarded as that over an ergodic surface. Therefore, Eq. (3.24) must hold if the quantities  $A$ ,  $B$ , and  $A(0)B(t)$  are ergodic, namely

$$\begin{aligned} \langle A \rangle &= \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t A(t) dt, \\ \langle B \rangle &= \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t B(t) dt, \\ \langle A(0)B(t) \rangle &= \lim_{t' \rightarrow \infty} \frac{1}{t'} \int_0^{t'} \langle A(t')B(t'+t) \rangle dt' \end{aligned} \quad (3.25)$$

Here the right hand sides of the equations are primarily determined by the location of the initial point of time average, but they do not depend on that. That is the assertion of ergodicity.

If the requirement of ergodicity, (3.25), is fulfilled, we shall have

$$\begin{aligned} \lim_{t \rightarrow \infty} \langle A(0)B(t) \rangle &= \lim_{t \rightarrow \infty} \lim_{t' \rightarrow \infty} \frac{1}{t'} \int_0^{t'} \langle A(t')B(t'+t) \rangle dt' \\ &= \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t \int_0^{t'} \langle A(t')B(t'+t) \rangle dt' dt \\ &= \langle \langle A \rangle \langle B \rangle \rangle = \langle A \rangle \langle B \rangle. \end{aligned} \quad (3.26)$$

Thus Eq. (3.22) holds.

The above arguments apply to quantum-mechanical cases with small modifications that the function  $\int_0^\beta \langle A(-i\hbar\lambda)B(t) \rangle d\lambda$  enters in place of the correlation function.

Let us consider a magnetic system for illustration. The system,  $M$ , of the magnetic units are embedded in another large system,



$R$ , with a certain interaction between  $M$  and  $R$ . The total system  $S$  we consider is  $M+R$ . If the heat capacity of  $R$  is large compared with  $M$ ,  $R$  is a sort of heat bath for  $M$ . If we treat only  $M$ , assuming a canonical distribution and ignore the interaction between  $M$  and  $R$ , the relaxation function calculated by (3.11) describes only the internal process inside the subsystem  $M$ . The magnetic susceptibility, for instance, obtained from this, is adiabatic. For this canonical distribution, the ergodicity such as (3.25) will not hold.

If we consider the interaction and suppose, for instance, that it induces a Markoffian process for the transition of  $M$  among its various states, the ergodicity (3.25) will become true; the Markoffian assumption makes it easy to treat the relaxation process. The Markoffian assumption may be adequate if the interaction is weak and satisfies certain conditions which may be required. If such conditions are not satisfied, we are forced to deal directly with the combined system  $M+R$ . The relaxation function or the response function has to be treated with the complete Hamiltonian for  $M+R$ . In this case, the ergodicity (3.25) may be approximately true if the subsystem  $M$  is small compared to  $R$ . A rigorous formulation of mathematical proof of this is not easy, so that we merely anticipate this.

#### § 4. Correlation Functions

We have seen in the previous section that the relations function  $\Phi_{BA}(t)$  in classical case for canonical ensemble is essentially the correlation function of  $A$  and  $B$ ; namely

$$\Phi_{BA}(t) = \beta \langle A(0)B(t) \rangle - \beta \langle A^0 B^0 \rangle \quad (\text{classical}) \quad (4.1)$$

where the bracket means the phase average over the canonical distribution. Or, the excitation function is

$$\Phi_{BA}^e(t) = \beta \langle A(0)(B - B(t)) \rangle. \quad (4.2)$$

Other functions, for example, the response functions, are also proportional to certain correlation functions; e.g.

$$\phi_{BA}(t) = -\beta \langle A(0)\dot{B}(t) \rangle. \quad (4.3)$$

These are also valid for the microcanonical ensemble provided that the system in question is large.

Now the question arises how the correlation

functions are defined in quantum-mechanics. We may define this by

$$\Psi_{BA}(t) = \text{Tr } \rho \{A(0)B(t)\} = \text{Tr } \rho \{A(t_1)B(t_1+t)\} \quad (4.4)$$

where  $\rho$  is the equilibrium density matrix, either canonical or microcanonical. The bracket means the symmetrized product,

$$\{AB\} = \frac{1}{2}(AB + BA).$$

We may call this the time correlation of  $B$  and  $A$  at the time interval  $t$ , although it is not the correlation of two sets of actually observed values of  $B$  and  $A$  at different time points. The disturbance due to the observation is not taken into account. If the nature of the system and of  $A$  and  $B$  is such that this disturbance is not serious, which will be true for macroscopic systems and macroscopic observations, the function (4.4) describes the actual correlation. Since  $\rho$  is equilibrium density matrix, the time variation of  $A$  and  $B$  makes a stochastic time series which is stationary in time. For the sake of brevity, we rewrite the relaxation function as

$$\Phi_{BA}(t) = \int_0^\beta \text{Tr } \rho(A(-i\hbar\lambda) - A^0)(B - B^0) d\lambda \quad (4.5)$$

and in the following we shall deal with quantities  $A$  and  $B$  which satisfy the condition

$$\text{Tr } \rho A = \text{Tr } \rho B = 0, \quad (4.6)$$

which is achieved merely by subtracting the invariant part from each of the quantities.

We can show easily that the relaxation function and the correlation function are mutually connected by the following theorem:

**Theorem 3.** *Let the Fourier transforms of  $\Phi_{BA}(t)$  and  $\Psi_{BA}(t)$  be*

$$f_{BA}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \Phi_{BA}(t) e^{-i\omega t} dt, \\ g_{BA}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \Psi_{BA}(t) e^{-i\omega t} dt, \quad (4.7)$$

then we have

$$g_{BA}(\omega) = E_\beta(\omega) f_{BA}(\omega) \quad (4.8)$$

where  $E_\beta(\omega)$  is the average energy of the oscillator with the frequency  $\omega$  at temperature  $T = 1/k\beta$ ,

$$E_\beta(\omega) = \frac{\hbar\omega}{2} \coth \frac{\beta\hbar\omega}{2}. \quad (4.9)$$

Eq. (4.8) is equivalent to

$$\Phi_{BA}(t) = \int_{-\infty}^{\infty} \Gamma(t-t') \Psi_{BA}(t') dt' \quad (4.10)$$

where  $\Gamma(t)$  is defined

$$\Gamma(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{e^{i\omega t}}{E_{\beta}(\omega)} d\omega = \frac{2}{\hbar\pi} \log \coth \frac{\pi}{2\beta\hbar} |t|, \quad (4.11)$$

or to

$$\Psi_{BA}(t) = E_{\beta} \left( \frac{d}{idt} \right) \Phi_{BA}(t). \quad (4.12)$$

The easiest way of the proof is to write first the functions  $\Phi_{BA}(t)$  and  $\Psi_{BA}(t)$  as double series over the quantum states of  $\mathcal{H}$  and rearrange the double sum. An alternative method is to assume a function-theoretical conditions, i.e.,

$$\lim_{\text{Ret} \rightarrow \pm\infty} \text{Tr } \rho AB(t) = 0, \quad (4.13)$$

and that  $\text{Tr } \rho AB(t)$  is analytic in the domain

$$0 \leq \text{Im } t \leq \beta\hbar.$$

The condition (4.13) is fulfilled if one extends the meaning of the limit process as was discussed in § 2 and § 3. The second condition is equivalent to the existence  $\text{Tr } \rho AB$  and  $\text{Tr } \rho BA$ .

Now Eq. (4.8) is derived as follows. By definition we can write

$$\begin{aligned} f_{BA}(\omega) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} \int_0^{\beta} \text{Tr } \rho AB(t+i\hbar\lambda) \exp(-i\omega t) d\lambda dt \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} \int_0^{\beta} \text{Tr } \rho AB(t+i\hbar\lambda) \\ &\quad \times \exp\{-i\omega(t+i\hbar\lambda) - \lambda\hbar\omega\} d\lambda dt \\ &= \frac{1}{2\pi} \int_0^{\beta} d\lambda \exp(-\lambda\hbar\omega) \\ &\quad \times \int_{-\infty+i\hbar\lambda}^{\infty+i\hbar\lambda} \text{Tr } \rho AB(t) \exp(-i\omega t) dt. \end{aligned}$$

Thus interchanging the order of integration and shifting the path of integration, we obtain by the above-mentioned assumptions

$$\begin{aligned} f_{BA}(\omega) &= \frac{1 - \exp(-\beta\hbar\omega)}{\hbar\omega} \\ &\quad \times \frac{1}{2\pi} \int_{-\infty}^{\infty} \text{Tr } \rho AB(t) \exp(i\omega t) dt. \end{aligned} \quad (4.14)$$

Similarly we can show that

$$\begin{aligned} &\int_{-\infty}^{\infty} \text{Tr } \rho AB(t) e^{-i\omega t} dt \\ &= \exp(\beta\hbar\omega) \int_{-\infty}^{\infty} \text{Tr } \rho B(t) A \exp(-i\omega t) dt \end{aligned} \quad (4.15)$$

by shifting the integration path to  $-i\hbar\beta - \infty$

to  $-i\hbar\beta + \infty$ . In the above transformations, we took  $\rho$  as canonical given by Eq. (3.8).

Eqs. (4.15) gives

$$\int_{-\infty}^{\infty} \text{Tr } \rho AB(t) e^{-i\omega t} dt = \frac{2}{1 + \exp(-\beta\hbar\omega)} g_{BA}(\omega),$$

so that Eq. (4.14) leads Eq. (4.8).

Eq. (4.10) is easily obtained from (4.8). The kernel  $\Gamma(t)$ , (4.11) is calculated using the partial fraction expansion of  $\tanh z/z$ . We note further that it has the property

$$\lim_{\hbar \rightarrow 0} \Gamma(t) = \beta \delta(t), \quad (4.16)$$

which is naturally to be expected.

## § 5. Simple Examples

It will be adequate to insert here simple examples to illustrate the general idea developed in the previous sections. The author has applied this in a previous paper<sup>7)</sup> to the problem of magnetic resonance absorption. An uniform magnetic field  $\mathbf{H}(t)$  is applied to a magnetic system, the total magnetic moment of which is denoted by  $\mathbf{M}$ . The perturbation energy due to  $\mathbf{H}(t)$  is now

$$\mathcal{H}'(t) = -\mathbf{M}\mathbf{H}(t). \quad (5.1)$$

The natural motion of the magnetic moment in the absence of the external field is represented by  $\mathbf{M}(t)$ . Then, the response function  $\phi_{\mu\nu}(t)$  for the magnetization in  $\mu$ -direction when the external field  $\mathbf{H}(t)$  lies in  $\nu$ -direction, is by Eq. (2.22).

$$\begin{aligned} \phi_{\mu\nu}(t) &= \frac{i}{\hbar} \langle [M_{\mu}(t), M_{\nu}] \rangle \\ &= \int_0^{\beta} \langle \dot{M}_{\nu}(-i\hbar\lambda) M_{\mu}(t) \rangle d\lambda, \end{aligned} \quad (5.2)$$

and the relaxation function is, by Eq. (3.11),

$$\Phi_{\mu\nu}(t) = \int_0^{\beta} \langle (M_{\nu}(-i\hbar\lambda) - M_{\nu}^0) (M_{\mu}(t) - M_{\mu}^0) \rangle d\lambda \quad (5.3)$$

where  $M_{\nu}^0$  and  $M_{\mu}^0$  mean the diagonal parts of  $M_{\nu}$  and  $M_{\mu}$  with respect to the unperturbed Hamiltonian  $\mathcal{H}$ .

If we consider a system with unit volume, the admittance becomes the magnetic susceptibility. Thus the complex magnetic susceptibility tensor can be expressed either by  $\phi_{\mu\nu}(t)$  or  $\Phi_{\mu\nu}(t)$ . The convenient expression is, by Eq. (3.5)

$$\chi_{\mu\nu}(\omega) = \Phi_{\mu\nu}(0) - i\omega \int_0^{\infty} \Phi_{\mu\nu}(t) e^{-i\omega t} dt. \quad (5.4)$$

The static susceptibility is, in particular,

$$\chi_{\mu\nu}(0) = \int_0^\beta \langle (M_\nu(-i\hbar\lambda) - M_\nu^0)(M_\mu - M_\mu^0) \rangle d\lambda \quad (5.5)$$

which is the susceptibility for the isolated system and is not necessarily equal to the isothermal susceptibility,

$$\chi_{\mu\nu}^T = \int_0^\beta \langle M_\nu(-i\hbar\lambda) M_\mu \rangle d\lambda - \beta \langle M_\nu \rangle \langle M_\mu \rangle. \quad (5.6)$$

In the expression for  $\chi_{\mu\nu}(0)$ , the diagonal parts of  $M_\nu$  and  $M_\mu$  are subtracted. This corresponds to the fact the magnetization in an isolated system proceeds adiabatically, the occupation probabilities of the levels remaining unchanged. On the other hand they are changed in isothermal process for  $\chi_{\mu\nu}^T$ . The difference becomes smaller if the environment is taken into account in greater extent.

In the classical limit, Eq. (5.5) becomes

$$\chi_{\mu\nu}(0) = \frac{1}{kT} \langle (M_\nu - \langle M_\nu \rangle)(M_\mu - \langle M_\mu \rangle) \rangle. \quad (5.7)$$

while Eq. (5.6) becomes

$$\chi_{\mu\nu}^T = \frac{1}{kT} \langle (M_\nu - \langle M_\nu \rangle)(M_\mu - \langle M_\mu \rangle) \rangle. \quad (5.8)$$

The last expression is first noticed by Kirkwood<sup>14)</sup> for the classical theory of dielectric polarization. Eq. (5.7) is its extension to adiabatic susceptibility, and Eq. (5.4) to general complex susceptibility for non-equilibrium states. It is evident that the similar formulae are obtained for dielectric polarizations.

As a second example we shall consider the electric conductivity. For an electric  $\mathbf{E}(t)$ , the perturbation energy is

$$\mathcal{H}'(t) = - \sum_i e_i \mathbf{r}_i \mathbf{E}(t) \quad (5.7)$$

where  $e_i$  is the charge of the  $i$ -th particle in the system and  $\mathbf{r}_i$  its position vector. The response of current in  $\mu$ -direction when a pulse of electric field is applied in  $\nu$ -direction at  $t=0$  is, by Eq. (2.22) or Eq. (3.9)

$$\begin{aligned} \phi_{\mu\nu}(t) &= -\frac{1}{i\hbar} \text{Tr} [\rho, \sum_i e_i x_{i\nu}] \sum_i e_i \dot{x}_{i\mu}(t) \\ &= \int_0^\beta \langle J_\nu(-i\hbar\lambda) J_\mu(t) \rangle d\lambda \end{aligned} \quad (5.10)$$

where

$$J_\mu = \sum_i e_i \dot{x}_{i\mu}$$

is the total current in the system.

If we take the volume of the system as unity, the conductivity tensor  $\sigma_{\mu\nu}(\omega)$  for periodic field is given by

$$\sigma_{\mu\nu}(\omega) = \int_0^\infty e^{-i\omega t} dt \int_0^\beta d\lambda \langle J_\nu(-i\hbar\lambda) J_\mu(t) \rangle. \quad (5.11)$$

This is an exact expression for the conductivity. In particular, for the static conductivity we have

$$\sigma_{\mu\nu} = \int_0^\infty \int_0^\beta d\lambda \langle J_\nu(-i\hbar\lambda) J_\mu(t) \rangle. \quad (5.12)$$

This may be expressed in another form,

$$\sigma_{\mu\nu} = \lim_{s \rightarrow 0+} \frac{1}{s} \left\{ \phi_{\mu\nu}(0) + \int_0^\infty \dot{\phi}_{\mu\nu}(t) e^{-st} dt \right\} \quad (5.13)$$

where

$$\dot{\phi}_{\mu\nu}(t) = -\frac{1}{i\hbar} \text{Tr} \rho [J_\nu, J_\mu(t)]. \quad (5.14)$$

The above expressions of conductivity tensor are, as a matter of fact, what one would obtain by simple application of dispersion formula of Heisenberg and Kramers. But they are more convenient and much clearer for physical interpretation. Nakano<sup>8)</sup> has shown that the Grüneisen formula is obtained from (5.11) as the first approximation. We emphasize again that the formulae given in the above are exact although they are admittedly rather abstract and have to be approximated in some way to deduce useful answers for assumed physical models. We can show that the usual method of employing Boltzmann-Bloch type transport equations makes a certain approximation to calculate these exact expressions. But the transport equation can not always be justified since the Markoffian assumption involved is only valid under rather strict conditions for the scattering processes.<sup>15)</sup> The exact theory will certainly give a starting point of actual calculations when the traditional methods are not justified. A good example of this is provided by the problem of electronic conduction in strong magnetic field.<sup>11)</sup> This will be treated in a forthcoming paper.

## § 6. Symmetry Relations

We note here some symmetry properties of the response and relaxation functions and those of the admittance. Let us consider for convenience the relaxation function defined by Eq. (3.11), for which we have the theorem:

**Theorem 4.** *The relaxation function  $\Phi_{BA}(t)$  has the following properties;*

$$1) \quad \Phi_{BA}(t) \text{ is real} \quad (6.1)$$

$$2) \quad \Phi_{BA}(-t) = \Phi_{AB}(t) \quad (6.2)$$

3) *reciprocity law: if a static magnetic field  $\mathbf{H}$  is present, the reversal of the direction of  $\mathbf{H}$  results in*

$$\begin{aligned} \Phi_{BA}(t, \mathbf{H}) &= \varepsilon_A \varepsilon_B \Phi_{BA}(-t, -\mathbf{H}) \\ &= \varepsilon_A \varepsilon_B \Phi_{AB}(t, -\mathbf{H}) \end{aligned} \quad (6.3)$$

where  $\varepsilon_A$  or  $\varepsilon_B$  is  $+1$  or  $-1$  according to the quantity  $A$  or  $B$  is even or odd with respect to the reversal of time.

The proof is simple. The complex conjugate of  $\Phi_{BA}(t)$  is calculated as follows.

$$\begin{aligned} \overline{\Phi_{BA}(t)} &= \int_0^\beta \text{Tr } \rho B(t) A(i\hbar\lambda) d\lambda \\ &= \int_0^\beta \text{Tr } \rho B(t - i\hbar\lambda) A d\lambda \\ &= \int_0^\beta \text{Tr } \rho B(t - i\hbar(\beta - \lambda)) A d\lambda \\ &= \int_0^\beta \text{Tr } \rho AB(t + i\hbar\lambda) d\lambda = \Phi_{BA}(t). \end{aligned}$$

The transformation from the second to the third line is simply the change of integration variable from  $\lambda$  to  $\beta - \lambda$ .

Similarly, we may proceed as

$$\begin{aligned} \Phi_{BA}(-t) &= \int_0^\beta \text{Tr } \rho AB(-t + i\hbar\lambda) d\lambda \\ &= \int_0^\beta \text{Tr } \rho A(t - i\hbar\lambda) B d\lambda \\ &= \int_0^\beta \text{Tr } \rho BA(t + i\hbar\lambda) d\lambda = \Phi_{BA}(t). \end{aligned}$$

Eq. (6.3) follows from the fact that the simultaneous reversal of  $t$  and  $\mathbf{H}$  changes the  $q$ -representation of the Hamiltonian and the wave function to their complex conjugates. A corollary of the theorem is the symmetry of other functions such as  $\phi_{BA}(t) = -\dot{\Phi}_{BA}(t)$ . This is clear and so is omitted here.

The second corollary is the symmetry of admittance. We write down here the symmetry of the quantity defined by

$$\sigma_{BA}(\omega) = \int_0^\infty \Phi_{BA}(t) e^{-i\omega t} dt \quad (6.4)$$

for which we have

$$\text{Re } \sigma_{BA}(\omega) = \text{Re } \sigma_{BA}(-\omega), \quad (6.5)$$

$$\text{Im } \sigma_{BA}(\omega) = -\text{Im } \sigma_{BA}(-\omega), \quad (6.6)$$

$$\sigma_{BA}(\omega, -\mathbf{H}) = \varepsilon_A \varepsilon_B \sigma_{AB}(\omega, \mathbf{H}). \quad (6.7)$$

Eq. (6.7) is the well-known Onsager's relation.<sup>15)</sup> The derivation here made is very simple.

As examples, we note the symmetry of magnetic susceptibility tensor and that of the conductivity tensor. The susceptibility tensor has the symmetry

$$\begin{aligned} \text{Re } \chi_{\mu\nu}(\omega, \mathbf{H}) &= \text{Re } \chi_{\mu\nu}(-\omega, \mathbf{H}) \\ &= \text{Re } \chi_{\nu\mu}(\omega, -\mathbf{H}), \\ \text{Im } \chi_{\mu\nu}(\omega, \mathbf{H}) &= -\text{Im } \chi_{\mu\nu}(-\omega, \mathbf{H}) \\ &= \text{Im } \chi_{\nu\mu}(\omega, -\mathbf{H}). \end{aligned} \quad (6.8)$$

For the conductivity tensor we have the same relations

$$\begin{aligned} \text{Re } \sigma_{\mu\nu}(\omega, \mathbf{H}) &= \text{Re } \sigma_{\mu\nu}(-\omega, \mathbf{H}) \\ &= \text{Re } \sigma_{\nu\mu}(\omega, -\mathbf{H}), \\ \text{Im } \sigma_{\mu\nu}(\omega, \mathbf{H}) &= -\text{Im } \sigma_{\mu\nu}(-\omega, \mathbf{H}) \\ &= \text{Im } \sigma_{\nu\mu}(\omega, -\mathbf{H}). \end{aligned} \quad (6.9)$$

Thus, for the change  $\omega$  to  $-\omega$ , the real part is even while the imaginary part is odd. For the reversal of  $\mathbf{H}$ , the symmetric part is even and the antisymmetric part is odd.

## § 7. Fluctuation-Dissipation Theorems

We have shown in § 4 that the response and relaxation functions can be expressed by correlation functions. Thus the admittance can also be expressed in terms of correlation functions. This is rather trivial for classical cases, but in quantum mechanics it becomes rather complicated. The relation between the admittance and the Fourier components correlation functions is usually called the fluctuation-dissipation theorem. Thus our aim here is to give this theorem in its complete form.

We treat as a typical example the case of electric conduction. Let us rewrite Eq. (5.11) in terms of the Fourier component of response function  $\phi_{\mu\nu}(t)$ , i.e.,

$$f_{\mu\nu}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \phi_{\mu\nu}(t) e^{-i\omega t} dt. \quad (7.1)$$

Eq. (5.11) is transformed as

$$\begin{aligned} \sigma_{\mu\nu}(\omega) &= \int_0^\infty \phi_{\mu\nu}(t) e^{-i\omega t} dt \\ &= \int_0^\infty dt \int_{-\infty}^\infty d\omega' f_{\mu\nu}(\omega') e^{i\omega' t - i\omega t} \\ &= \pi f_{\mu\nu}(\omega) + i \int_{-\infty}^\infty \frac{f_{\mu\nu}(\omega')}{\omega' - \omega} d\omega'. \end{aligned} \quad (7.2)$$

Thus we obtain at once

$$\text{Re } \sigma_{\mu\nu}(\omega) = \pi f_{\mu\nu}^s(\omega) \equiv \frac{\pi}{2} \{ f_{\mu\nu}(\omega) + f_{\nu\mu}(\omega) \}$$

$$\text{Im } \sigma_{\mu\nu}^a(\omega) = \frac{\pi}{2} f_{\mu\nu}^a(\omega) \equiv \frac{\pi}{2i} \left\{ f_{\mu\nu}(\omega) - f_{\nu\mu}(\omega) \right\} \quad (7.3)$$

$$\begin{aligned} \text{Im } \sigma_{\mu\nu}^s(\omega) &= \int_{-\infty}^{\infty} \frac{f_{\mu\nu}^s(\omega')}{\omega' - \omega} d\omega' \\ \text{Re } \sigma_{\mu\nu}^a(\omega) &= i \int_{-\infty}^{\infty} \frac{f_{\mu\nu}^a(\omega')}{\omega' - \omega} d\omega', \end{aligned} \quad (7.4)$$

where the superscript  $s$  or  $a$  means the symmetric or the anti-symmetric part of the tensor. By the theorem 4 one has the symmetry

$$\bar{f}_{\mu\nu}(\omega) = f_{\nu\mu}(\omega), \quad (7.5)$$

which shows  $f_{\mu\nu}^s(\omega)$  is real while  $f_{\mu\nu}^a(\omega)$  is purely imaginary. Eqs. (7.3) and (7.4) give the well-known Kramers-Kronig relation. Note that it holds for each of the symmetric and antisymmetric parts separately.

Now let us introduce the correlation function of current components,

$$\Psi_{\mu\nu}(t) = \text{Tr } \rho \{ j_{\mu}(0) j_{\nu}(t) \}, \quad (7.6)$$

which describes the correlation of spontaneous current fluctuating in equilibrium. We can show the following theorem:

**Theorem 5.** *The conductivity tensor  $\sigma_{\mu\nu}(\omega)$  is connected with correlation function of current components, (7.6), by the following relations:*

$$\begin{aligned} E_{\beta}(\omega) \text{Re } \sigma_{\mu\nu}^s(\omega) &= \pi g_{\mu\nu}^s(\omega) \\ &= \int_0^{\infty} \Psi_{\mu\nu}^s(t) \cos \omega t dt \end{aligned} \quad (7.7a)$$

$$\begin{aligned} E_{\beta}(\omega) \text{Im } \sigma_{\mu\nu}^a(\omega) &= \frac{\pi}{i} g_{\mu\nu}^a(\omega) \\ &= - \int_0^{\infty} \Psi_{\mu\nu}^a(t) \sin \omega t dt \end{aligned} \quad (7.7b)$$

$$\Psi_{\mu\nu}^s(t) = \frac{2}{\pi} \int_0^{\infty} E_{\beta}(\omega) \text{Re } \sigma_{\mu\nu}^s(\omega) \cos \omega t d\omega \quad (7.8a)$$

$$\Psi_{\mu\nu}^a(t) = - \frac{2}{\pi} \int_0^{\infty} E_{\beta}(\omega) \text{Im } \sigma_{\mu\nu}^a(\omega) \sin \omega t d\omega, \quad (7.8b)$$

and

$$\begin{aligned} \text{Im } \sigma_{\mu\nu}^s(\omega) &= \int_{-\infty}^{\infty} \frac{1}{E_{\beta}(\omega')} \cdot \frac{g_{\mu\nu}^s(\omega')}{\omega' - \omega} d\omega' \\ &= -2 \int_0^{\infty} \Gamma(\tau) \cos \omega \tau d\tau \int_{\tau}^{\infty} \Psi_{\mu\nu}^s(t) \sin \omega t dt \\ &\quad - 2 \int_0^{\infty} \Gamma(\tau) \sin \omega \tau d\tau \int_0^{\tau} \Psi_{\mu\nu}^s(t) \cos \omega t dt \end{aligned} \quad (7.9a)$$

$$\begin{aligned} \text{Re } \sigma_{\mu\nu}^a(\omega) &= - \frac{1}{i} \int_{-\infty}^{\infty} \frac{1}{E_{\beta}(\omega')} \frac{g_{\mu\nu}^a(\omega')}{\omega' - \omega} d\omega' \\ &= 2 \int_0^{\infty} \Gamma(\tau) \cos \omega \tau d\tau \int_{\tau}^{\infty} \Psi_{\mu\nu}^a(t) \cos \omega t dt \\ &\quad - 2 \int_0^{\infty} \Gamma(\tau) \sin \omega \tau d\tau \int_0^{\tau} \Psi_{\mu\nu}^a(t) \sin \omega t dt \end{aligned} \quad (7.9b)$$

$$\Psi_{\mu\nu}^s(t) = \frac{2}{\pi} \int_0^{\infty} \text{Im } \sigma_{\mu\nu}^s(\omega) \text{Re } \Delta(\omega, t) d\omega \quad (7.10a)$$

$$\Psi_{\mu\nu}^a(t) = \frac{2}{\pi} \int_0^{\infty} \text{Re } \sigma_{\mu\nu}^a(\omega) \text{Im } \Delta(\omega, t) d\omega, \quad (7.10b)$$

where the kernel  $\Delta(\omega, t)$  is defined by

$$\Delta(\omega, t) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{du}{u - \omega} E_{\beta}(u) e^{iut}. \quad (7.11)$$

These expressions reduce, in classical limit, to

$$\text{Re } \sigma_{\mu\nu}(\omega) = \int_0^{\infty} \Psi_{\mu\nu}(t) \cos \omega t dt$$

$$\text{Im } \sigma_{\mu\nu}(\omega) = - \int_0^{\infty} \Psi_{\mu\nu}(t) \sin \omega t dt \quad (7.12)$$

First we note that the symmetry of  $\Psi_{\mu\nu}(t)$  is the same as that we have for  $\phi_{\mu\nu}(t)$  (Theorem 4). Eqs. (7.7) and the first parts of (7.9a) and (7.9b) are obvious from Eq. (4.8). Eq. (7.8a, b) is simply the inverse of Eq. (7.7a, b). We need some calculation to derive (7.9) and (7.10) but the details are omitted here. Only we note for the convenience of reference that the function (7.11) can be transformed to

$$\begin{aligned} \text{Re } \Delta(\omega, t) &= -E_{\beta}(\omega) \sin \omega t \cdot \text{sign } t \\ &\quad + \frac{1}{\pi\beta} \sum_{n=1}^{\infty} \frac{(n\pi)^2 \exp(-2n\pi|t|/\beta\hbar)}{(n\pi)^2 + (\beta\hbar\omega)^2/4} \end{aligned} \quad (7.13a)$$

$$\begin{aligned} \text{Im } \Delta(\omega, t) &= E_{\beta}(\omega) \cos \omega t \cdot \text{sign } t \\ &\quad - \frac{1}{\pi\beta} \sum_{n=1}^{\infty} \frac{(n\pi/2)\beta\hbar\omega \exp(-2n\pi|t|/\beta\hbar)}{(n\pi)^2 + (\beta\hbar\omega)^2/4} \text{sign } t. \end{aligned} \quad (7.13b)$$

An useful corollary of the theorem is the expression of static conductivity  $\sigma_{\mu\nu}(0)$ . We have the formulae;

$$\sigma_{\mu\nu}^s(0) = \beta \int_0^{\infty} \Psi_{\mu\nu}^s(t) dt \equiv \frac{\beta}{2} \int_{-\infty}^{\infty} \Psi_{\mu\nu}^s(t) dt \quad (7.14)$$

$$\begin{aligned} \sigma_{\mu\nu}^a(0) &= 2 \int_0^{\infty} \Gamma(\tau) d\tau \int_{\tau}^{\infty} \Psi_{\mu\nu}^a(t) dt \\ &= 2 \int_0^{\infty} \Psi_{\mu\nu}^a(t) \int_0^t \Gamma(\tau) d\tau. \end{aligned} \quad (7.15)$$

Thus the symmetric part of the static conductivity is calculated either as the integration of the response function or as that of the correlation function. The situation is more complicated for the antisymmetric part. If one wishes to use the correlation function instead of the response function, one has to be careful about a quantum effect which appears as  $\Gamma(\tau)$  in Eq. (7.15).

Another remark is that, even at finite frequencies, the symmetric part is easily obtained if the correlation function is known. This is, of particular interest, for instance, in the case of magnetic problem<sup>7)</sup>. For a linearly polarized radiation, the absorption is determined by the imaginary part of susceptibility tensor, for which we have from Eq. (5.4)

$$\begin{aligned}\chi''_{xx}(\omega) &= -\text{Im } \chi_{xx} \\ &= \frac{\omega}{2E_\beta(\omega)} \int_{-\infty}^{\infty} \langle \{M_x(0)M_x(t)\} \rangle \cos \omega t dt.\end{aligned}\quad (7.16)$$

The corresponding expression for conduction is (7.7a) itself, i.e.,

$$\sigma_{xx}(\omega) = \frac{1}{2E_\beta(\omega)} \int_{-\infty}^{\infty} \langle \{J_x(0)J_x(t)\} \rangle \cos \omega t dt \quad (7.17)$$

The last equation is the well-known Niquist's theorem<sup>16)</sup>. If the fluctuating current is expanded into the Fourier components, Eq. (7.17) reduces to

$$\sigma_{xx}(\omega) = \frac{\pi}{E_\beta(\omega)} \langle |J_x(\omega)|^2 \rangle. \quad (7.18)$$

## § 8. Sum Rules

It is interesting that the exact expressions of admittance derived in the above give proof of certain general laws. The simplest example of this is the well-known sum-rule of oscillator strength. This is generalized in the following way.

We consider the expression (6.4), from which we obtain

$$\frac{1}{\pi} \int_{-\infty}^{\infty} \sigma_{BA}(\omega) d\omega = 2 \int_0^{\infty} \Phi_{BA}(t) \delta(t) dt = \Phi_{BA}(0). \quad (8.1)$$

and

$$\lim_{\omega \rightarrow \infty} i\omega \sigma_{BA}(\omega) = \Phi_{BA}(0) \quad (8.2)$$

by Abel's theorem if the left hand side does exist.

Let us now apply this for electric conduction. By Eq. (5.10) one can write

$$\phi_{\mu\nu}(t) = \frac{1}{i\hbar} \text{Tr } \rho \left[ \sum e_i x_{i\nu}, \sum e_j \dot{x}_{j\mu}(t) \right] \quad (8.3)$$

If the Hamiltonian  $\mathcal{H}$  has the general form

$$\mathcal{H} = \sum_i \left[ p_{i\nu} - \frac{e_i}{c} A_\nu(\mathbf{r}_i) \right]^2 / 2m_i + V(\mathbf{r}_1, \dots, \mathbf{r}_N),$$

$A$  being the vector potential we have the commutation rule

$$[x_{i\nu}, \dot{x}_{j\mu}] = \frac{i\hbar}{m_i} \delta_{ij} \delta_{\mu\nu} \quad (8.4)$$

which gives

$$\phi_{\mu\nu}(0) = \sum_{i=1}^N \frac{e_i^2}{m_i} \delta_{\mu\nu} = \sum_r \frac{n_r e_r^2}{m_r} \quad (8.5)$$

where  $r$  means the species of charge carriers,  $n_r$  being the number of carriers of  $r$ -th kind.

Eq. (8.3) is derived from Eq. (5.10) by changing the order in the trace operation. One might doubt whether this is justified or not, pointing out that the operators  $x_{i\nu}$  may be singular if one uses the Born-Karman boundary conditions. As a matter of fact this will not affect the validity of the proof, because the commutators are actually regular operators. It might be worth while to see what one has in classical case. Classically we may proceed as (see Eq. (2.22a))

$$\begin{aligned}\phi_{\mu\nu}(t) &= \int d\Gamma (f, \sum e_i x_{i\nu}) \sum e_j \dot{x}_{j\mu}(t) \\ &= - \int d\Gamma \sum_i e_i \frac{\partial f}{\partial p_{i\nu}} \cdot \sum e_j \dot{x}_{j\mu}(t) \\ &= \int d\Gamma f \sum_i \sum_j e_i e_j^* \frac{\partial}{\partial p_{i\nu}} \dot{x}_{j\mu}(t).\end{aligned}\quad (8.6)$$

Thus we have

$$\begin{aligned}\phi_{\mu\nu}(0) &= \int d\Gamma f \sum_i \sum_j e_i e_j^* \frac{\partial}{\partial p_{i\nu}} \cdot \frac{1}{m_j} \left\{ p_{j\mu} - \frac{e_j}{c} A_\mu(\mathbf{r}_j) \right\} \\ &= \int d\Gamma f \sum_i e_i^2 / m_i \delta_{\mu\nu}\end{aligned}\quad (8.7)$$

This is exactly the same as Eq. (8.5). This does not prove directly the validity of (8.3), but will be enough to make it convincing. As as proof one may introduce a suitable potential to avoid the difficulty of singular operators  $x_{i\nu}$ , and make it vanish if one wants.

Thus we have proved the sum rule

$$\frac{2}{\pi} \int_0^{\infty} \text{Re } \sigma_{\mu\nu}^s(\omega) d\omega = \sum_r \frac{e_r^2 n_r}{m_r} \delta_{\mu\nu} \quad (8.8)$$

and

$$\lim_{\omega \rightarrow \infty} \omega \operatorname{Im} \sigma_{\mu\nu}^s = - \sum_r \frac{e^2 n_r}{m_r} \delta_{\mu\nu} \quad (8.9)$$

which hold for any system irrespective of the interaction of particles, the temperature, the statistics and even in the presence of magnetic field. This is the most general form of the sum rule.

For a system of electrons, Eqs. (8.8) and (8.9) are written as

$$\frac{2}{\pi} \int_0^\infty \operatorname{Re} \sigma_{\mu\nu}^s(\omega) d\omega = \frac{ne^2}{m} \delta_{\mu\nu} \quad (8.10)$$

$$\operatorname{Im} \sigma_{\mu\nu}^s(\omega) \rightarrow - \frac{e^2 n}{m\omega} \delta_{\mu\nu} \quad (\omega \rightarrow \infty). \quad (8.11)$$

Here we should remember that  $m$  is the true mass of electrons. The integration of  $\sigma(\omega)$  has to be carried over all range of frequencies.

If one considers electrons in a crystal and confines himself to the electrons in a particular band neglecting interband transitions, the sum rule has to be modified to

$$\begin{aligned} \frac{2}{\pi} \int_0^\infty \operatorname{Re} \sigma_{\mu\nu}^s(\omega) d\omega \\ = - \lim_{\omega \rightarrow \infty} \omega \operatorname{Im} \sigma_{\mu\nu}^s(\omega) \\ = e^2 \operatorname{Tr} \{ \rho \cdot \partial^2 E(\mathbf{p}) / \partial p_\nu \partial p_\mu \}. \end{aligned} \quad (8.12)$$

This holds if the electron system is described by the Hamiltonian

$$\mathcal{H} = \sum_i E(\mathbf{p}_i) + V(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (8.13)$$

where  $E(\mathbf{p})$  is the energy of an electron with the crystal moments  $\mathbf{p}$ . Also one has to omit the interband elements of the potential  $V$ . The theorem (8.12) is wider than that usually given in text books only for the oscillator strength connecting one-electron states.

Another interesting result is obtained from the second expression of (3.5) when applied to conduction problem. This give

$$\begin{aligned} \frac{1}{\pi} \int_{-\infty}^\infty \{ i \sigma_{\mu\nu}(\omega) \omega - \phi_{\mu\nu}(0) \} d\omega \\ = - \lim_{\omega \rightarrow \infty} \omega^2 \left\{ \sigma_{\mu\nu}(\omega) - \frac{\phi_{\mu\nu}(0)}{i\omega} \right\} = \dot{\phi}_{\mu\nu}(0) \end{aligned} \quad (8.14)$$

The tensor

$$\dot{\phi}_{\mu\nu}(0) = - \frac{i}{\hbar} \operatorname{Tr} \rho [J_\mu, J_\nu] \quad (8.15)$$

is antisymmetric. Therefore Eq. (8.14) is rewritten as

$$\begin{aligned} - \frac{1}{\pi} \int_{-\infty}^\infty \operatorname{Im} \sigma_{xy}^a(\omega) \omega d\omega \\ = \lim_{\omega \rightarrow \infty} \omega^2 \sigma_{xy}^a(\omega) = - \sum_r \frac{n_r e_r^3 H_z}{m_r^2 c}. \end{aligned} \quad (8.16)$$

Both sides of this equation are identically zero unless the system is in a magnetic field (or rotating, in which case  $e_r H_z / m_r c$  must be replaced by the angular frequency of the rotation). This is seen from the fact that the velocity of charged particles in magnetic field is

$$\mathbf{v} = \frac{1}{m} \left( \mathbf{p} - \frac{e}{c} \mathbf{A} \right)$$

and the commutation rule is now

$$[v_x, v_y] = - \frac{e H_z}{m^2 c} \frac{\hbar}{i}. \quad (8.17)$$

This gives

$$\frac{i}{\hbar} \operatorname{Tr} \rho [J_x, J_y] = \sum n_r e_r^3 H_z / m_r^2 c, \quad (8.18)$$

which is the last expression in Eq. (8.16).

In particular, for electrons we have

$$\begin{aligned} \frac{2}{\pi} \int_0^\infty \operatorname{Im} \sigma_{\mu\nu}^a(\omega) \omega d\omega = - \lim_{\omega \rightarrow \infty} \omega^2 \sigma_{\mu\nu}^a(\omega) \\ = \frac{ne^3}{m^2 c} H_z. \end{aligned} \quad (8.19)$$

This is another type of sum-rule which holds quite generally, but is not usually remarked. Eq. (8.19) may also be written as

$$\sum_i \operatorname{Im} \langle k | J_x | I \rangle \langle I | J_y | k \rangle = - \frac{ne^3}{2m^2 c} H_z \quad (8.20)$$

for a system of  $n$  electrons.

Similar arguments can also be made for tensors of other kinds. For instance, the magnetic susceptibility tensor satisfies the rules,

$$- \frac{1}{\pi} \int_{-\infty}^\infty \operatorname{Im} \chi_{\mu\nu}^s(\omega) \frac{d\omega}{\omega} = \chi_{\mu\nu}^s(0), \quad (8.21)$$

$$\lim_{\omega \rightarrow \infty} \operatorname{Re} \chi_{\mu\nu}^s(\omega) = 0, \quad (8.22)$$

$$\begin{aligned} \frac{1}{\pi} \int_{-\infty}^\infty \operatorname{Re} \chi_{\mu\nu}^a(\omega) d\omega \\ = - \lim_{\omega \rightarrow \infty} \omega \operatorname{Im} \chi_{\mu\nu}^a(\omega) = \frac{i}{\hbar} \operatorname{Tr} \rho [M_\mu, M_\nu]. \end{aligned} \quad (8.23)$$

The relation (8.21) is well-known. This states that the properly weighted integration of absorption intensity for linearly polarized radiation is equal to the static susceptibility. The third relation, (8.23), requires more at-

tention.

If  $M_\mu$  is written as

$$M_\mu = \sum_i \gamma_i I_{i\mu},$$

where  $I_i$  is the angular momentum associated with the magnetic moment, we have

$$-\frac{i}{\hbar} [M_x, M_y] = -\sum \gamma_i^2 I_{iz}.$$

Therefore Eq. (8.23) can be written as

$$\begin{aligned} & \frac{1}{2} \int_0^\infty \text{Re } \chi_{xy}^a(\omega) d\omega \\ &= -\lim_{\omega \rightarrow \infty} \omega \text{Im } \chi_{xy}^a(\omega) = -\sum \gamma_i^2 \bar{I}_{iz} = -\sum \gamma_i \bar{M}_{rz} \end{aligned} \quad (8.24)$$

where  $\bar{M}_{rz}$  means the magnetization due to  $r$ -th component in the system.

For circularly polarized radiation, the rate of energy absorption per unit volume is

$$Q = \frac{\omega}{2} H_1^2 \{ \chi'_{xy} - \chi'_{yx} + \chi''_{xx} + \chi''_{yy} \}$$

$H_1$  being the amplitude of the magnetic field of radiation. Thus,  $\text{Re } \chi_{xy}^a(\omega)$  is related to the absorption intensity of circular waves. The total integration of the absorption intensity is directly connected with the gyro-magnetic ratio  $\gamma$ . This may not be of much value if  $\gamma$  can be measured accurately by sharp resonance. But one has to remember that (8.24) is generally valid even in the presence of strong interaction between magnetic moments. Thus the effects related to the absorption of circular wave may be used for the determination of  $\gamma$ , for instance, for electronic magnetic moments in ferromagnets or paramagnets. This sort of experiments may be considered to corresponds in a sense to those of gyromagnetic effects.

## § 9. Einstein Relations

We note here that the expression of conductivity given by Eq. (5.12) or (7.14) is the most general form of Einstein relation, which connects the conductivity or the mobility with the diffusion constant.

To see this, let us take the simplest example of charged particles which are moving independently. By Eq. (7.14), the conductivity is

$$\sigma_{\mu\nu}^s = -\frac{ne^2}{kT} \int_0^\infty \langle v_\nu(0) v_\mu(t) \rangle dt, \quad (9.1)$$

if we regard the system to be classical. If

we admit

$$\lim_{t \rightarrow \infty} \langle v_\nu(0) v_\mu(t) \rangle = \langle v_\nu \rangle \langle v_\mu \rangle = 0$$

we can transform the right hand side of Eq. (9.1) as

$$\begin{aligned} & \int_0^\infty \langle v_\nu(0) v_\mu(t) \rangle dt \\ &= \lim_{T \rightarrow \infty} -\frac{1}{2T} \int_0^T \int_0^T \langle v_\nu(t') v_\mu(t) \rangle dt dt' \\ &= \lim_{T \rightarrow \infty} -\frac{1}{2T} \langle (x_\nu(T) - x_\nu(0)) (x_\mu(T) - x_\mu(0)) \rangle \\ &= D_{\mu\nu}. \end{aligned} \quad (9.2)$$

where  $D_{\mu\nu}$  is the diffusion constant defined by the third expression of Eq. (9.2). Eqs. (9.2) and (9.1) give at once

$$\sigma_{\mu\nu}^s = e^2 n D_{\mu\nu} / kT \quad (9.3)$$

which is the well known Einstein relation.

For a system of interacting particles, the exact form of Einstein relation is

$$\sigma_{\mu\nu}^s = e^2 \bar{D}_{\mu\nu} / kT \quad (9.4a)$$

$$= e^2 D_{\mu\nu} / \left( \frac{\partial \mu}{\partial n} \right)_T \quad (9.4b)$$

where  $D_{\mu\nu}$  is the diffusion constant in isothermal conditions,  $\bar{D}_{\mu\nu}$  the average fluctuation of particle density, and  $\mu$  the chemical potential of the particle. This relation gives, for the diffusion constant,

$$\begin{aligned} D_{\mu\nu}^s &= \left( \frac{\partial \mu}{\partial n} \right)_T \int_0^\infty dt \int_0^\beta \text{Tr } \rho I_\nu(-i\hbar) I_\mu(t) d\lambda \\ &= \left( \frac{\partial \mu}{\partial n} \right)_T \frac{1}{2} \int_{-\infty}^\infty dt \text{Tr } \rho \{ I_\nu I_\mu(t) \} \end{aligned} \quad (9.5)$$

where

$$I_\nu = \sum_i v_{i\nu}$$

is the total particle flow per unit volume. Eq. (9.5) can be used for the calculation of diffusion constant in gases and also condensed phases. This will be discussed further in a forthcoming paper.

It might be worth while to note that Eq. (9.4) indicates at once how the factor  $1/kT$  appearing in the expression of electric conductivity, Eq. (7.14) cancels out for degenerate Fermi particles. In this case,  $\bar{D}_{\mu\nu}$  is proportional to  $T$ , or in other words  $(\partial \mu / \partial n)_T$  is a constant of the order of  $\mu_0/n$ ,  $\mu_0$  being the Fermi-level at the absolute zero.

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### References

- 1) I. Prigogine: Proceedings of the International Conference on Electron Transport in Metals and Solids, Canadian J. Physics, **34**, No12A (1956) 1236; L. Van Hove: Physica **21** (1955) 517, **22** (1956) 343.
- 2) See for instance, S. R. de Groot, Thermodynamics of Irreversible Processes, North Holland Pub. Co. 1952.
- 3) See for instance, R. T. Cox, Statistical Mechanisc of Irreversible Change.
- 4) J. G. Kirkwood: J. Chem. Phys. **14** (1946) 180.
- 5) H. B. Callen and T. A. Welton: Phys. Rev. **83** (1951) 34.
- 6) H. Takahasi: J. Phys. Soc. Japan **7** (1952) 439.
- 7) R. Kubo and K. Tomita: J. Phys. Soc. Japan **9** (1954) 888.
- 8) H. Nakano: Prog. Theor. Phys. **15** (1956) 77, Busseiron-Kenkyu (in Japanese) **84** (1955) 25, **88** (1955) 53.
- 9) The preliminary reports by the author; R. Kubo: Proceedings of the International Conf. on Electron Transport in Metals and Solids. Canadian J. Phys. **34** No12A (1956) 1274, Kagaku (in Japanese) **27** (1957) 58, Busseiron-Kenkyu (in Japanese) **89** (1955) 79, R. Kubo and M. Yokota: ibid. **89** (1955), 99, R. Kubo, N. Hashitsume and M. Yokota: ibid. **91** (1955) 32.
- 10) H. Mori: J. Phys. Soc. Japan **11** (1956) 1029.
- 11) Reported by R. Kubo at the Conference on Physics of Magnetic Phenomena, Moskow, 1956 May.
- 12) See for instance, G. Placzek: Handbuch der Radiologie, Bd VI, Teil ii, p. 211.
- 13) A. I. Khintchin: Mathematical Foundations of Statistical Mechanics.
- 14) J. Kirkwood: J. Chem. Phys. **7** (1939) 911, H. Frohlich: Theory of Dielectrics, 1949.
- 15) L. Onsager: Phys. Rev. **37** (1931) 405, **38** (1931) 2265.  
H. B. G. Casimir: Rev. Mod. Phys. **17** (1945) 343.
- 16) H. Nyquist: Phys. Rev. **32** (1928) 110.