

## Transport, Collective Motion, and Brownian Motion<sup>\*)</sup>

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A theory of many-particle systems is developed to formulate transport, collective motion, and Brownian motion from a unified, statistical-mechanical point of view. This is done by, first, rewriting the equation of motion in a generalized form of the Langevin equation in the stochastic theory of Brownian motion and then, either studying the average evolution of a non-equilibrium system or calculating the linear response function to a mechanical perturbation. (1) An expression is obtained for the damping function  $\varphi(t)$ , the real part of whose Laplace transform gives the damping constant of collective motion. (2) A general equation of motion for a set of dynamical variables  $A(t)$  is derived, which takes the form

$$\frac{d}{dt} A(t) - i\hat{\omega} \cdot A(t) + \int_0^t \varphi(t-s) \cdot A(s) ds = f(t),$$

where  $\hat{\omega}$  is a frequency matrix determining the collective oscillation of  $A(t)$ . The quantity  $f(t)$  consists of those terms which are either non-linear in  $A(s)$ ,  $t \geq s \geq 0$ , or dependent on the other degrees-of-freedom explicitly, and its time-correlation function is connected with the damping function  $\varphi(t)$  by  $(f(t_1), f(t_2)^*) = \varphi(t_1 - t_2) \cdot (A, A^*)$ . (3) An expression is obtained for the linear after-effect function to thermal disturbances such as temperature gradient and strain tensor. Both the conjugate fluxes and the time dependence differ from those of the mechanical response function. The conjugate fluxes are *random* parts of the fluxes of the state variables, thus depending on temperature. (4) The difference in the time dependence arises from a special property of the time evolution of  $f(t)$  and ensures that the damping function and the thermal after-effect function are determined by the microscopic processes in strong contrast to the mechanical response function. The difficulty of the plateau value problem in the previous theories of Brownian motion and transport coefficients is thus removed. (5) The theory is illustrated by dealing with the motion of inhomogeneous magnetization in ferromagnets and the Brownian motion of the collective coordinates of fluids. (6) Explicit expressions are derived for the thermal after-effect functions and the transport coefficients of multi-component systems.

### § 1. Introduction

One of the recent developments in the theory of irreversible processes is the derivation of closed formulas for the generalized susceptibilities or admit-

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tances to mechanical perturbations such as magnetic and electric fields and for the kinetic or transport coefficients in non-equilibrium systems in terms of the time correlation of physical quantities. These time-correlation expressions provide us with a basis for the study of irreversible processes in strong-coupling systems for instance, and have been successfully applied to several interesting phenomena.

There are thus two fundamental formulas which relate the dissipative properties to the thermal fluctuations<sup>1)</sup>. The first is the fluctuation-dissipation theorem which connects the generalized susceptibilities with the thermal fluctuations of mechanical quantities<sup>2)-4)</sup>.

The second is the formula which connects the kinetic coefficients with the thermal fluctuations of temperature dependent fluxes. A phenomenological form of this formula has been used in the stochastic theory of Brownian motion<sup>5)</sup>. It assumes that the damping (or generalized friction) constant  $\gamma$  of a dynamical variable  $A(t)$  is related to the time correlation of its *random* force  $f(t)$  by

$$\langle f(t_1) f(t_2)^* \rangle = 2\gamma \langle |A|^2 \rangle \delta(t_1 - t_2), \quad (1.1)$$

where the angular brackets denote an average, and the asterisk the Hermitian conjugate. This formula differs from the first one in two respects. First, the *random* force  $f(t)$  and the corresponding fluxes are not mechanical quantities<sup>6)</sup>. Another difference arises from a special property of the evolution of  $f(t)$ , and will be clarified later.

One of the recent problems is to establish the formula (1.1) or its equivalent from statistical mechanics in order to have a reliable basis for the study of transport phenomena. A number of investigations have been devoted to this problem<sup>7)-15)</sup>. In 1946, Kirkwood attempted to derive a statistical-mechanical theory of a Brownian particle suspended in a liquid, and concluded that the random force  $f(t)$  can be replaced by the force  $F(t)$  acting on the particle in the time-correlation expression for  $\gamma$ <sup>7)</sup>. Here has arisen, however, the difficulty of the plateau value problem. Namely, the time integral vanishes if the integration extends over an interval of the order of magnitude of the relaxation time  $\tau_r$  ( $\equiv 1/\gamma$ ) even in an infinite system. This difficulty will turn out to arise from the neglect of an essential difference between  $f(t)$  and  $F(t)$ . Green has extended Kirkwood's result to general systems in a semi-phenomenological way by assuming a Markoffian random process, and obtained general expressions for the transport coefficients in fluids<sup>8)</sup>. Similar, but different, results have been derived by the present author from a (quantum) statistical-mechanical point of view.<sup>9)</sup> An interesting attempt has been made by Zwanzig to derive a generalized form of the Fokker-Planck equation.<sup>13)</sup> All these approaches have eventually employed an approximation valid only in the limit of  $\tau_r \gg \tau_0$ , where  $\tau_r$  is the macroscopic relaxation time and  $\tau_0$  a microscopic time. Such an approximation, however, is not valid for the study of Brownian motion, since  $\tau_r$  in

this case is essentially finite. Even in the case of the transport coefficients, it is necessary to formulate the problem for finite  $\tau_r$  and then go over, carefully, in the limit of  $\tau_r \rightarrow \infty$ , since the transport processes in a closed system are due to the spatial non-uniformity with a finite relaxation time. Actually, a question has been raised about this limiting process.<sup>14)</sup> This question is related to the plateau value problem, and will be overcome by developing a method outlined elsewhere.<sup>15)</sup>

The stochastic theory of Brownian motion is usually based on the Langevin equation of motion,<sup>1),5)</sup> which takes the form

$$\frac{d}{dt} A(t) - i\Omega A(t) + \gamma A(t) = f(t) \tag{1.2}$$

in the case of a monochromatic sound wave or a spin wave with angular frequency  $\Omega$ , where  $A(t)$  denotes the normal coordinate. The  $f(t)$  represents a *random* part arising from the interaction with the other normal modes and is related to the damping constant  $\gamma$  by (1.1). This equation may be derived, in principle, from the recent theories of many-body systems. In the method of linearizing the equations of motion,<sup>16)</sup> one extracts relevant linear terms with the aid of the random phase approximation. These linear terms will give the systematic part of (1.2) if one goes up to a sufficiently higher approximation. Then the random part  $f(t)$  will represent the remaining terms usually neglected. The problem here is thus the separation of  $A(t)$  from the other degrees-of-freedom between  $t$  and an initial time  $t_0$ . This spirit may be formulated in a general way as follows. Let us suppose that we have separated  $F(t)$  into two parts,

$$\frac{d}{dt} A(t) \equiv F(t) = F_1(A(s), t \geq s \geq t_0) + F_2(t, t_0), \tag{1.3}$$

such that  $F_1$  is a functional of  $A(s)$  depending also on the past history of  $A(t)$  and  $F_2$  represents the terms which depend on the other degrees-of-freedom explicitly. Now let us expand the functional  $F_1$  in terms of  $A(s)$ ,  $t \geq s \geq t_0$ . Then it is easy to see that the linear term thus obtained has a generalized form of the systematic part of the Langevin equation, (refer Eq. (2.1)), and the sum of the non-linear terms and  $F_2$  uniquely defines the quantity  $f(t)$ . The collective description of many-particle systems by much fewer variables than the number of degrees-of-freedom is possible if and only if the fluctuations due to  $f(t)$  are negligible. Thus the study of the general type of Brownian motion would be useful for the investigation, not only, of transport phenomena, but also, of collective motions.

A similar spirit has been developed in the quantum theory of damping phenomena,<sup>17)</sup> and has been employed in recent derivations of kinetic and master equations in order to single out the kinetic stage from the Liouville equation.<sup>18-20)</sup>

Therefore, our problem will also help to bridge the recent theory of irreversibility<sup>21), 22)</sup> and the correlation-function theory of kinetic coefficients from a unified standpoint.

The principal purpose of the present paper is therefore to determine the secular linear term and the non-secular random force explicitly from statistical mechanics. We shall rigorously derive a generalized form of the Langevin equation of motion and establish a generalized form of the second kind of fluctuation-dissipation formula (1.1).

It will turn out that the non-secular force  $f(t)$  has the following properties. First,  $f(t)$  is a *random* part of  $F(t)$ , thus depending upon the thermodynamic state of the system. Secondly, the time evolution of  $f(t)$  differs from that of the mechanical variables, and is governed by the propagator which describes the motion inside the subspace *orthogonal* to the variable  $A$  in a Hilbert space of dynamical variables with a temperature-dependent scalar product. This property will lead to the fact that the secular variation of  $A(t)$  does not appear in the time correlation of  $f(t)$ , thus ensuring a shortlived correlation (a randomness) like (1.1), and will remove the difficulty of the plateau value problem.

An exact expression will be derived for the after-effect function to internal disturbances such as temperature gradient and strain tensor. This expression has a form of the time correlation of certain fluxes *conjugate* to the thermodynamic forces. Its properties, however, differ from the mechanical response function. First, the conjugate fluxes are not simply the fluxes of the conserved variables defined by the conservation equations, but their *random* parts in the same way as  $f(t)$  is a random part of  $F(t)$ . This difference does not vanish even in the limit of  $\tau_r \gg \tau_0$ , and the results agree with those derived by the present author.<sup>6)</sup> Secondly, the time dependence differs from that of the mechanical one. The evolution of the mechanical response function is governed by the usual propagator, whereas that of the thermal one is by the unusual one appearing in the evolution of  $f(t)$ . Thus, whereas the mechanical response function includes macroscopic relaxation processes in accordance with the fact that one can produce a macroscopic non-equilibrium state by disturbing an equilibrium state with a perturbation, the thermal after-effect function does not include a macroscopic process, thus ensuring that the transport coefficients which are given by the Laplace transform of the thermal after-effect functions are determined by the microscopic processes only.

In § 2, we show that extracting the linear term in (1.3) is equivalent to projecting  $A(t)$  into the subspace spanned by  $A$  in a Hilbert space of dynamical variables. With the aid of this geometrical interpretation, we derive, in § 3, an exact equation of motion for  $A(t)$  and establish a generalized form of (1.1). Section 4 is devoted to the study of general properties of the frequency matrix and the kinetic coefficients, and time-reversal properties and other isotropic relations are derived. In § 5, as simple applications, we discuss the spin dynam-

ics of ferromagnets and the collective oscillation of fluids in the isothermal approximation.

In § 6 we derive explicit expressions for the thermal after effect functions, taking the hydrodynamical motion of multicomponent systems, and obtain an exact equation for the time evolution of the conjugate fluxes. The linear relations between fluxes and forces are derived from this equation. In § 7 explicit expressions are given for the conjugate fluxes and the transport coefficients. Section 8 is devoted to a brief summary and a comparison with other theories.

§ 2. The linear term and the  $A$  subspace

Expanding  $F_1$  of (1.3) in terms of  $A(s)$  and separating the linear term, we obtain

$$\frac{d}{dt} A(t) = \int_{t_0}^t \theta(t-s) \cdot A(s) ds + f(t), \tag{2.1}$$

where  $A(s)$  denotes the deviation from its invariant or diagonal part with respect to the Hamiltonian so that

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T A(t) dt = 0, \tag{2.2}$$

and we have assumed that the after-effect function  $\theta$  is a function of time interval only, thus confining ourselves to a closed system without time-dependent external forces. In the present paper, we assume that there is no external field applied other than a uniform magnetic field. Now we shift the time axis so that  $t_0=0$  and introduce the Laplace transform

$$A(z) \equiv \int_0^\infty A(t) e^{-zt} dt. \tag{2.3}$$

Then (2.1) can be integrated easily to give

$$A(t) = \mathcal{E}(t) \cdot A + A'(t), \tag{2.4}$$

$$A'(t) \equiv \int_0^t \mathcal{E}(t-s) \cdot f(s) ds, \tag{2.5}$$

where  $\mathcal{E}(t)$  is defined by its Laplace transform

$$\mathcal{E}(z) \equiv \frac{1}{z - \theta(z)}. \tag{2.6}$$

According to (2.4) the variable  $A(t)$  is split up into two parts; first, a secular part  $\mathcal{E}(t) \cdot A$  whose time evolution is entirely determined by the linear after-

effect function  $\theta(t)$ , and second, a non-secular part  $A'(t)$  which describes non-linear effects, the initial transient process, and fluctuations. This separation leads us to a simple geometrical interpretation of (2.4).

Let us introduce a Hilbert space of dynamical variables whose invariant parts are set to be zero, and denote its scalar product of two variables  $F$  and  $G$  by the parentheses  $(F, G^*)$ . The scalar product will be defined in § 4. In addition to the usual properties

$$(F, G^*) = (G, F^*)^*, \quad (G, G^*) \geq 0, \quad (2.7)$$

$$\left(\sum_j c_j F_j, G^*\right) = \sum_j c_j (F_j, G^*), \quad (2.8)$$

we require that the Liouville operator  $L$  is Hermitian;

$$(L F, G^*) = (F, [L G]^*). \quad (2.9)$$

In the classical case,  $L$  is defined by the differential operator

$$iL \equiv \sum_{j=1}^N \left[ \left( \frac{\partial \mathcal{H}}{\partial \mathbf{p}_j} \right) \cdot \left( \frac{\partial}{\partial \mathbf{r}_j} \right) - \left( \frac{\partial \mathcal{H}}{\partial \mathbf{r}_j} \right) \cdot \left( \frac{\partial}{\partial \mathbf{p}_j} \right) \right], \quad (2.10a)$$

where  $\mathcal{H}$  is the Hamiltonian of the system and  $\mathbf{r}_j$  and  $\mathbf{p}_j$  denote the coordinate and momentum of the  $j$ -th particle, respectively, and, in the quantal case, by the commutator

$$iL F \equiv (i/\hbar) [\mathcal{H}, F]. \quad (2.10b)$$

In terms of this linear operator, the equation of motion can be written

$$\frac{d}{dt} A(t) = iL A(t), \quad (2.11)$$

$$A(t) = \exp[tiL] A. \quad (2.12)$$

The variable  $A$  defines a vector in the Hilbert space, as is shown in Fig. 1. The projection of a vector  $G$  onto this  $A$  axis is given by

$$\mathcal{P}G = (G, A^*) \cdot (A, A^*)^{-1} \cdot A. \quad (2.13)$$

This equation defines a linear Hermitian operator  $\mathcal{P}$  in the Hilbert space, which satisfies  $\mathcal{P}(1 - \mathcal{P}) = 0$ . We shall define the scalar product such that the first term of (2.4) is the projection of  $A(t)$  onto the  $A$  axis and the second term  $A'(t)$  is its vertical component; Namely,

$$\mathcal{E}(t) = (A(t), A^*) \cdot (A, A^*)^{-1}, \quad (2.14)$$

$$A'(t) = (1 - \mathcal{P}) A(t). \quad (2.15)$$

Since (2.5) and (2.15) hold at an arbitrary time  $t$ ,  $f(t)$  should be orthogonal to the  $A$  axis:

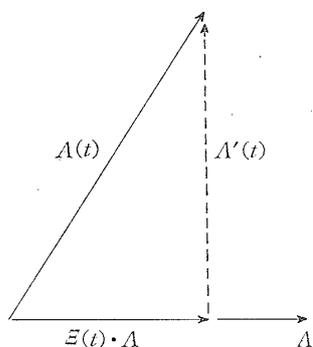


Fig. 1. Projection of  $A(t)$  onto the  $A$  axis

$$(f(t), A^*) = 0. \tag{2.16}$$

Thus  $\mathcal{E}(t)$  describes the time evolution of the projection of  $A(t)$ , and (2.14) determines  $\theta(t)$  uniquely.  $\mathcal{E}(t)$  will be referred to as the evolution function of the secular motion.

Thus extracting the linear term in the equation of motion for  $A(t)$  amounts to projecting  $A(t)$  onto the  $A$  axis. This treatment can be extended to the many-variable case straightforwardly. Let us represent a set of independent variables  $A_1, \dots, A_n$  by an  $n$ -dimensional column matrix  $A$  and denote its Hermitian row matrix by  $A^*$ . The  $n$  variables span an  $n$ -dimensional subspace in the Hilbertspace, and the projection into this subspace is given by (2.13), where  $(A, A^*)^{-1}$  is to be regarded as the inverse of the  $n$  by  $n$  matrix

$$(A, A^*) \equiv [(A_i, A_j^*)], \quad (i, j=1, \dots, n), \tag{2.17}$$

and the dots are to be interpreted as the matrix multiplication. Similarly, (2.1) and its following are regarded as matrix equations, where  $A(t)$  and  $f(t)$  are column matrices, and  $\theta(t)$  and  $(A(t), A^*)$  are square matrices. It should be noted here that the projection (2.13) is invariant under a linear transformation of the  $n$  axis vectors  $A$ .

The most important quantity associated with  $A(t)$  is  $iLA$ . Let us split it into the projection and the vertical component:

$$\dot{A} \equiv iLA = i\hat{\omega} \cdot A + K, \tag{2.18}$$

where

$$i\hat{\omega} \equiv \left[ \frac{d}{dt} \mathcal{E}(t) \right]_{t=0} = (\dot{A}, A^*) \cdot (A, A^*)^{-1}, \tag{2.19}$$

$$K \equiv (1 - \mathcal{P}) \dot{A}. \tag{2.20}$$

The quantities  $\hat{\omega}$  and  $K$  have been introduced in the previous papers with an explicit definition of the scalar product,<sup>(6),23)</sup> and it has been shown that the eigenvalues of the matrix  $\hat{\omega}$  determines the temperature-dependent eigenfrequencies of collective oscillations like sound waves and spin waves. It follows from (2.9) that

$$(A, A^*) \cdot \hat{\omega}^* = \hat{\omega} \cdot (A, A^*), \tag{2.21}$$

$$(A, A^*) \cdot \mathcal{E}^*(t) = \mathcal{E}(-t) \cdot (A, A^*), \tag{2.22}$$

where the asterisks of  $\hat{\omega}^*$  and  $\mathcal{E}^*(t)$  denote the Hermitian conjugate of the square matrices.

### § 3. An exact equation of motion for $A(t)$

Extending a spirit of the equations-of-motion method, we have derived a generalized form of the Langevin equation and given it a simple geometrical mean-

ing. This geometrical interpretation allows us to determine  $\theta(t)$  and  $f(t)$  explicitly.

Operating  $(1 - \mathcal{P})$  on (2.11) and then using (2.15), (2.4) and (2.20) we obtain

$$-\frac{d}{dt} A'(t) - (1 - \mathcal{P})iLA'(t) = \mathcal{E}(t) \cdot K. \quad (3.1)$$

This is integrated to yield

$$A'(t) = \int_0^t \mathcal{E}(s) \cdot f(t-s) ds, \quad (3.2)$$

where

$$f(t) \equiv U(t)K, \quad (3.3)$$

$$U(t) \equiv \exp[t(1 - \mathcal{P})iL]. \quad (3.4)$$

Equation (3.2) has the same form as (2.5), thus ensuring that (3.3) is the desired expression for  $f(t)$ . The propagator (3.4) differs from the usual one (2.12) by the factor  $(1 - \mathcal{P})$ . Propagators of similar kind have been introduced implicitly in the damping theory<sup>17),18)</sup> and explicitly in recent derivations of master equations.<sup>19),20),13)</sup> It will be shown in Appendix A that, if  $f$  and  $g$  are functions orthogonal to the  $A$  subspace,

$$([(1 - \mathcal{P})Lf], g^*) = (f, [(1 - \mathcal{P})Lg]^*), \quad (3.5)$$

$$(U(t)f, g^*) = (f, [U(-t)g]^*). \quad (3.6)$$

Namely,  $(1 - \mathcal{P})L$  is Hermitian in the subspace *orthogonal* to the  $A$  subspace, and  $U(t)$  is unitary inside this subspace. The physical meaning of this will be clarified later.

Differentiating (2.14) and then inserting (2.18),

$$\frac{d}{dt} \mathcal{E}(t) = i\hat{\omega} \cdot \mathcal{E}(t) + (K(t), A^*) \cdot (A, A^*)^{-1}.$$

Since we have  $(K(t), A^*) = (K, A^*(-t))$  from (2.9) and  $K$  is orthogonal to  $A$ , use of (2.4) and (3.2) brings the second term into

$$\int_0^{-t} ds (K, f(-t-s)^*) \cdot \mathcal{E}^*(s) \cdot (A, A^*)^{-1}.$$

Thus using (2.22) and changing the time variable  $s$  to  $s-t$ ,

$$\frac{d}{dt} \mathcal{E}(t) = i\hat{\omega} \cdot \mathcal{E}(t) - \int_0^t \varphi(s) \cdot \mathcal{E}(t-s) ds, \quad (3.7)$$

where

$$\varphi(t) \equiv (f, f(-t)^*) \cdot (A, A^*)^{-1}. \tag{3.8}$$

The Laplace transform of (3.7) leads to

$$\mathcal{E}(z) = \frac{1}{z - i\hat{\omega} + \varphi(z)}, \tag{3.9}$$

which confirms (2.6), thus leading to  $\theta(t) = 2i\hat{\omega}\delta(t) - \varphi(t)$ . This expression for  $\mathcal{E}(z)$  can be applied to the magnetic resonance and neutron scattering problems. The real part of  $\varphi(z)$  then describes the line widths or the damping constants. Therefore,  $\varphi(t)$  will be referred to as the damping function or matrix.

Let us summarize the results. Inserting the expression for  $\theta(t)$  into (2.1), we have

$$\frac{d}{dt} A(t) - i\hat{\omega} \cdot A(t) + \int_0^t \varphi(t-s) \cdot A(s) ds = f(t), \tag{3.10}$$

where

$$(f(t), A^*) = 0, \tag{3.11}$$

$$(f(t_1), f(t_2)^*) = \varphi(t_1 - t_2) \cdot (A, A^*). \tag{3.12}$$

Equation (3.10) is an exact equation of motion for  $A(t)$ . Equation (3.12) leads to a justification and a generalization of the second fluctuation-dissipation formula (1.1).

The random force  $f(t)$  differs from the force  $F(t)$  in two respects. First,  $f(0)$  is the vertical component of  $F(0)$ . This difference arises when  $A(t)$  is capable of a collective oscillation. Secondly, the evolution of  $f(t)$  is governed by the special propagator (3.4), and differs from  $K(t)$ . This difference elucidates an important property of  $\varphi(t)$ . To see this, let us introduce

$$\Phi(t) \equiv (K(t), K^*) \cdot (A, A^*)^{-1}. \tag{3.13}$$

Then, as will be shown in Appendix B,

$$\Phi(z) = \varphi(z) - \varphi(z) \cdot \mathcal{E}(z) \cdot \varphi(z). \tag{3.14}$$

The second term of (3.14) describes the difference between  $\varphi(t)$  and  $\Phi(t)$ .

For simplicity, let us consider the one variable case and assume that  $\varphi(t)$  decays in a finite time  $\tau_c$ . As far as the time scale of our interest is much larger than  $\tau_c$ , we may put  $\varphi(z)$  to be a constant;

$$\varphi(z) = \Gamma, \text{ i.e. } \varphi(t) = 2\Gamma\delta(t). \tag{3.15}$$

It follows from (3.9) that this is equivalent to

$$\mathcal{E}(t) = \exp[(i\hat{\omega} - \Gamma)t], \quad (t \gg \tau_c). \tag{3.16}$$

If  $\gamma \equiv \text{Re}(\Gamma)$  is much smaller than  $1/\tau_c$ , then (3.15) and (3.16) can be used for describing the slow relaxation. The slow relaxation corresponds to the

pole of  $\Xi(z)$ ,  $z_p = i\hat{\omega} - \Gamma$ . Therefore, the identification of  $\Gamma$  with  $\varphi(z_p)$  leads to the following expression:

$$\Gamma = \lim_{\varepsilon \rightarrow 0^+} \int_0^{\infty} \varphi(t) \cdot \exp[-(i\hat{\omega} + \varepsilon)t] dt. \quad (3.17)$$

Since we allow a non-zero correlation time in (3.17),  $\Gamma$  is complex and (1.1) is to be regarded as expressing the real part of (3.15). Insertion of (3.15) into (3.10) leads to the Langevin equation (1.2) with  $\Omega = \hat{\omega} - \text{Im}(\Gamma)$ . Now let us apply (3.15) and (3.16) to (3.14). Then we obtain

$$\Phi(t) = \varphi(t) - \Gamma^2 \exp[(i\hat{\omega} - \Gamma)t]. \quad (3.18)$$

This satisfies the identity

$$\lim_{\varepsilon \rightarrow 0^+} \int_0^{\infty} \Phi(t) \cdot \exp(-i\hat{\omega}t - \varepsilon t) dt = 0. \quad (3.19)$$

Namely,  $\Phi(t)$  includes the slow process with a long tail, and its time integral vanishes due to the cancellation of the sharply-peaked initial area  $\varphi(t)$  by the negative tail. This is in strong contrast to  $\varphi(t)$  in which the slow process does not appear. The latter is a direct result of the elimination of the secular motion  $\Xi(t)$  from  $f(t)$  and  $\varphi(t)$  by introducing the unusual propagator  $U(t)$ . Thus we may expect, in general, that the damping matrix  $\varphi(t)$  consists of short-lived relaxational modes and are determined by the microscopic processes if the variables  $A$  and the scalar product are properly defined.

In the case of  $\gamma\tau_c \ll 1$ , the fast process  $\varphi(t)$  and the slow process  $\Xi(t)$  are well separated. In such a case, (3.17) may be replaced by

$$\Gamma \doteq \Gamma(\tau) \equiv \int_0^{\tau} \Phi(t) \cdot \exp(-i\hat{\omega}t) dt, \quad (3.20)$$

where  $\tau$  is a time interval satisfying the inequalities  $\tau_r \gg \tau \gg \tau_c$ . Kirkwood's expression for the friction constant of a Brownian particle is a particular case of (3.20),<sup>7)</sup> and this kind of expressions have been successfully applied to several problems.<sup>23), 24), 25)</sup> In the actual calculations, however,  $\Phi(t)$  has been replaced by functions qualitatively similar to  $\varphi(t)$ . The elimination of the not too long and not too short time  $\tau$  is necessary for (3.20) to have a definite meaning. This is possible only when  $\Gamma(\tau)$  has a plateau value in the intermediate region. This condition, however, is not always obvious and prevents a generalization of (3.20). Equation (3.17) has another advantage that the general properties like the dispersion relation can be derived exactly.

Equations (3.16) and (3.17) can be generalized to the many-variable case. Let us assume that the relaxation of  $\Xi(t)$  is distinctly slow compared to that of  $\varphi(t)$ . Then the time integration of (3.7) can be extended to infinity, and the

second term may be written as

$$-\int_0^{\infty} ds \varphi(s) \cdot \exp(-i\hat{\omega}s) \cdot \mathcal{E}(t).$$

Thus we obtain (3.16) and (3.17) with the interpretation of  $F$  as the damping constant matrix and the dot as the matrix multiplication. It may be concluded from this derivation that (3.16) and (3.17) are also valid for high frequency phenomena as far as  $\gamma\tau_c \ll 1$ .

§ 4. The scalar product and the time-reversal symmetry

It will be shown that the following definition of the scalar product is most useful: In the classical case,

$$(F, G^*) \equiv \langle F G^* \rangle, \tag{4.1a}$$

and, in the quantal case,

$$(F, G^*) \equiv \frac{1}{\beta} \int_0^{\beta} \langle \exp(\lambda \mathcal{H}) F \exp(-\lambda \mathcal{H}) G^* \rangle d\lambda, \tag{4.1b}$$

where the angular brackets denote the average over the canonical ensemble

$$\rho \equiv \exp(-\beta \mathcal{H}) / \text{Tr}[\exp(-\beta \mathcal{H})]. \tag{4.2}$$

This scalar product satisfies, in addition to (2.7-9),

$$(F, G^*) = (G^*, F). \tag{4.3}$$

It should be noted that  $\langle F \rangle = \langle G \rangle = 0$  since  $F$  and  $G$  denote the deviations from their invariant parts.

If one neglects  $f(t)$ , then (3.10) will describe a smoothed-out, secular motion. The  $f(t)$  describes the actual deviations from such a secular motion due to non-linear effects, the initial transient process, and fluctuations. We now consider the elimination of such deviations by taking a particular ensemble average. The ensemble average is given by

$$\overline{A(t)} \equiv \text{Tr}[A(t) \rho(0)], \tag{4.4}$$

where  $\rho(0)$  is the phase-space distribution function, in the classical case, and the density matrix, in the quantal case, at the initial time. The average value depends on  $\rho(0)$ . The initial and boundary conditions on the system, however, are very often not enough to fix the initial ensemble  $\rho(0)$  completely. Let us ask what initial ensemble will give the *most probable* value of (4.4) among ensembles subject to the condition that the average values of the extensive constants of motion and the variables  $A$  have prescribed values at the initial time. It is well known that such an ensemble is the equilibrium ensemble

subject to the corresponding constraints and is determined by minimizing the Gibbs  $\mathcal{H}$ -function. The result is

$$\rho_0 = Z^{-1} \exp[-\beta(\mathcal{H} - A^* \cdot B)], \quad (4.5)$$

where  $A$  denote the deviations from their invariant parts and  $B$  the conjugate parameters, and we have omitted the invariant parts and the extensive constants of motion other than  $\mathcal{H}$ . In the linear approximation,

$$\rho_0 = [1 + \int_0^\beta d\lambda A^*(i\hbar\lambda) \cdot B] \rho, \quad (4.6)$$

where  $G^*(i\hbar\lambda) \equiv \exp(-\lambda\mathcal{H}) G^* \exp(\lambda\mathcal{H})$ . The value of the random force along the most probable path is thus given by

$$\bar{f}(t) = \int_0^\beta d\lambda \langle f(t) A^*(i\hbar\lambda) \rangle \cdot B. \quad (4.7)$$

Now we require that this average value be zero. Then the identification of this requirement with the orthogonality condition (3.11) leads to the definition of the scalar product (4.1). In other words, we have defined the scalar product in such a way that, if one neglects  $f(t)$ , then (2.4) and (3.10) describe the *most probable* path of  $A(t)$  in the linear approximation.

Let us assume that  $F$  and  $G$  are linear combinations of the Hermitian functions of particle coordinates  $\mathbf{r}_j$ , momenta  $\mathbf{p}_j$ , and spins  $\mathbf{s}_j$  and are either even or odd with respect to time reversal ( $\mathbf{r}_j \rightarrow \mathbf{r}_j$ ,  $\mathbf{p}_j \rightarrow -\mathbf{p}_j$ ,  $\mathbf{s}_j \rightarrow -\mathbf{s}_j$ ). The mass density and momentum density in fluids are such quantities. The normal coordinate of sound waves does not satisfy this condition. From the time-reversal symmetry  $\mathcal{H}(\mathbf{H}) \rightarrow \mathcal{H}(-\mathbf{H})$  we obtain<sup>4)</sup>

$$(F(t), G^*)_{\mathbf{H}} = \varepsilon_F \varepsilon_G (F(-t), G^*)_{-\mathbf{H}}, \quad (4.8)$$

where  $\varepsilon_F$  or  $\varepsilon_G$  is  $+1$  or  $-1$  according as  $F$  or  $G$  is even or odd and  $-\mathbf{H}$  indicates the reversal of the external magnetic field  $\mathbf{H}$ . Here, (4.3) has been used. In the absence of a magnetic field, therefore, the even and odd variables are orthogonal to each other;

$$(F, G^*) = 0, \text{ if } \varepsilon_F \varepsilon_G = -1. \quad (4.9)$$

Let us assume that each variable of the set  $A$  is either even or odd with respect to time reversal, and denote the sign function of  $A_j$  by  $\varepsilon_j$ . Since the determinant of  $(A, A^*)$  is invariant under time reversal and the cofactor of the  $(i, j)$  element changes its sign by  $\varepsilon_i \varepsilon_j$ , the  $(i, j)$  element of the inverse matrix of  $(A, A^*)$  is transformed similarly to  $(A_i, A_j^*)$ . Therefore, the projection operator (2.13) is invariant under time reversal;

$$[\mathcal{P}G(t)]_{\mathbf{H}} \rightarrow \varepsilon_G [\mathcal{P}G(-t)]_{-\mathbf{H}}. \quad (4.10)$$

For simplicity let us rearrange the set  $A$  in such a way that the first  $m$  variables are even and the rest are odd, and denote the even and odd parts by  $A_e$  and  $A_o$ , respectively. Then the frequency matrix (2.19) has the following property :

$$[\hat{\omega}]_{\mathbf{H}} = \begin{bmatrix} -\hat{\omega}_{ee} & \hat{\omega}_{eo} \\ \hat{\omega}_{oe} & -\hat{\omega}_{oo} \end{bmatrix}_{-\mathbf{H}} \tag{4.11}$$

where  $\hat{\omega}_{ee}$  is the submatrix of  $\hat{\omega}$ , consisting of the elements of the first  $m$  rows and columns, and  $\hat{\omega}_{eo}$  the submatrix of the first  $m$  rows and last  $(n-m)$  columns,  $\hat{\omega}_{oe}$  and  $\hat{\omega}_{oo}$  are defined similarly.

Applying (4.10) to (2.20) and (3.3) we obtain

$$(f_j(t), f_i^*)_{\mathbf{H}} = \varepsilon_j \varepsilon_i (f_j(-t), f_i^*)_{-\mathbf{H}}. \tag{4.12}$$

Separating the real and imaginary parts,

$$\text{Re}(f_j(t), f_i^*)_{\mathbf{H}} = \varepsilon_j \varepsilon_i \text{Re}(f_i(t), f_j^*)_{-\mathbf{H}}, \tag{4.13}$$

$$\text{Im}(f_j(t), f_i^*)_{\mathbf{H}} = -\varepsilon_j \varepsilon_i \text{Im}(f_i(t), f_j^*)_{-\mathbf{H}}. \tag{4.14}$$

These relations determine the symmetry of the kinetic coefficients

$$L_{jl}(\omega) \equiv \frac{1}{k_B} \lim_{\varepsilon \rightarrow 0^+} \int_0^{\infty} (f_j(t), f_i^*) \exp(-i\omega t - \varepsilon t) dt, \tag{4.15}$$

where  $k_B$  is the Boltzmann constant. The damping constants are simply related to  $L_{jl}(\omega)$  by (3.12). From (4.12), we obtain

$$L_{jl}(\omega; \mathbf{H}) = \varepsilon_j \varepsilon_i L_{ij}^*(-\omega; -\mathbf{H}). \tag{4.16}$$

If  $A_j$  are Hermitian, then  $(f_j(t), f_i^*)$  are real and (4.16) reduces to

$$L_{jl}(\omega; \mathbf{H}) = \varepsilon_j \varepsilon_i L_{ij}(\omega; -\mathbf{H}). \tag{4.17}$$

Equations (4.16) and (4.17) prove Onsager's reciprocity theorem<sup>26)</sup> in the general case.

There exists a simple relation between the real and imaginary parts of the kinetic coefficients. Let us define

$$g_{jl}(\omega) \equiv \frac{1}{2k_B} \lim_{\varepsilon \rightarrow 0^+} \int_{-\infty}^{\infty} (f_j(t), f_i^*) \exp(-i\omega t - \varepsilon|t|) dt. \tag{4.18}$$

Inserting the inverse Fourier transform into (4.15),

$$L_{jl}(\omega) = g_{jl}(\omega) - \frac{i}{\pi} \int_{-\infty}^{\infty} \frac{g_{jl}(\omega')}{\omega - \omega'} d\omega', \tag{4.19}$$

where the principal part of the integral is to be taken. Since  $g_{ji}^* = g_{ij}$  and,

therefore, its symmetric part  $g_{jl}^s$  is real and its antisymmetric part  $g_{jl}^a$  is imaginary, we obtain

$$\operatorname{Re} L_{jl}^s(\omega) = [g_{jl}(\omega) + g_{lj}(\omega)]/2, \quad (4.20a)$$

$$\operatorname{Im} L_{jl}^a(\omega) = [g_{jl}(\omega) - g_{lj}(\omega)]/2i, \quad (4.20b)$$

$$\operatorname{Im} L_{jl}^s(\omega) = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\operatorname{Re} L_{jl}^s(\omega')}{\omega - \omega'} d\omega', \quad (4.21a)$$

$$\operatorname{Re} L_{jl}^a(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\operatorname{Im} L_{jl}^a(\omega')}{\omega - \omega'} d\omega'. \quad (4.21b)$$

These equations correspond to the Kramers-Kronig relation for the generalized susceptibility.<sup>1),4)</sup>

There are another kind of symmetry relations. Let us denote the Fourier components of the local densities of physical quantities by  $F_{\mathbf{k}}$  and  $G_{\mathbf{k}}$ . Since there is no inhomogeneous field applied, we have, from the translational invariance,

$$(F_{\mathbf{k}}(t), G_{\mathbf{q}}^*) = 0, \text{ if } \mathbf{k} \neq \mathbf{q}. \quad (4.22)$$

Namely, the Fourier components with different wave vectors span disjoint subspaces orthogonal to each other. This is a characteristic of the linear phenomena. If one assumes the inversion symmetry  $(F(\mathbf{r}), G^*(0)) = (F(-\mathbf{r}), G^*(0))$ , then

$$(F_{\mathbf{k}}(t), G_{\mathbf{k}}^*) = (F_{-\mathbf{k}}(t), G_{-\mathbf{k}}^*). \quad (4.23)$$

In most applications, we start from the Fourier components of local Hermitian quantities. Then

$$A_{j,\mathbf{k}}^* = A_{j,-\mathbf{k}}, \quad f_{j,\mathbf{k}}^*(t) = f_{j,-\mathbf{k}}(t), \quad (4.24)$$

and it follows from (4.23) that  $(A_{\mathbf{k}}(t), A_{\mathbf{k}}^*)$  and  $(f_{\mathbf{k}}(t), f_{\mathbf{k}}^*)$  are real matrices. In such cases, the trace of the frequency matrix  $\hat{\omega}_{\mathbf{k}}$  is zero, and the kinetic coefficients satisfy the reciprocity (4.17).

In the case of no magnetic field, the symmetry relations are simplified. It turns out from (4.9) that  $(A, A^*)$  is split into two disjoint submatrices and the projection takes the form

$$\begin{aligned} \mathcal{P}G &= (G, A_e^*) \cdot (A_e, A_e^*)^{-1} \cdot A_e \\ &+ (G, A_0^*) \cdot (A_0, A_0^*)^{-1} \cdot A_0. \end{aligned} \quad (4.25)$$

The diagonal parts of the frequency matrix (4.11) vanish. Therefore, the origin of the collective oscillation and the difference  $\Delta f \equiv f - F$  can be classified into the following two:

- 1) the coupling between the even and odd variables,

2) the broken symmetry due to the magnetic field or other external parameters odd with respect to time reversal.

A typical example of 1) is the sound waves. The spin waves in ferromagnets belong to the second class.

The scalar product (4.1a) agrees with the usual definition of the correlation function.<sup>5)</sup> The function (4.1b) differs from the quantal correlation function

$$\langle \{F, G^*\} \rangle \equiv \frac{1}{2} \langle (FG^* + G^*F) \rangle, \quad (4.26)$$

and has been introduced by Kubo and Tomita in a general theory of magnetic resonance absorption.<sup>3)</sup> The relation between them is given by<sup>4)</sup>

$$\begin{aligned} & \int_{-\infty}^{\infty} \langle \{F(t), G^*\} \rangle \exp(-i\omega t) dt \\ &= \beta E_{\beta}(\omega) \int_{-\infty}^{\infty} (F(t), G^*) \exp(-i\omega t) dt, \end{aligned} \quad (4.27)$$

where

$$E_{\beta}(\omega) \equiv \frac{1}{2} \hbar \omega \coth\left(\frac{1}{2} \beta \hbar \omega\right), \quad (4.28)$$

$$\approx k_B T, \text{ if } \hbar \omega \ll k_B T. \quad (4.29)$$

The correlation function (4.26) also satisfies the conditions for the scalar product (2.7)–(2.9) and the relation (4.3) and, therefore, the foregoing symmetry relations. However, the difference between them is important, in particular, in discussing the quantal collective motions.<sup>9), 23)</sup> Therefore, a question may arise; which one is relevant as the scalar product. We now require that  $f(t)$  should vanish for the average of linear processes. This requirement removes the possibility of taking the quantal correlation function. The scalar product (4.1b) satisfies this requirement if the system have actually started from an equilibrium state described by the ensemble (4.5). It is also quite plausible that the most probable path describes the average evolution for almost all initial ensembles after a short initial period, if the set of variables  $A$  are relevant.

## § 5. Simple examples

A set of variables  $A$  will be called a good set of collective variables if their evolution matrix (2.14) or (3.9) satisfies

$$\mathbf{E}(t+s) = \mathbf{E}(t) \cdot \mathbf{E}(s) \quad (5.1a)$$

in a certain time scale. This translation-operator property states that the evolution along the most probable path is deterministic in that time scale. This is

equivalent to the condition that the relaxation times  $\tau_r$  of  $\Xi(t)$  are distinctly large compared to the decay times  $\tau_c$  of the damping matrix  $\varphi(t)$ ;

$$\tau_r \gg \tau_c. \quad (5.1b)$$

As has been discussed in §3, application of this condition to (3.7) leads to (3.16) and (3.17), which satisfy (5.1a). Inversely, the solution for (5.1a) is an exponential matrix like (3.16), and this form is possible only if (5.1b) is satisfied, as can be seen by inserting it into (3.7).

There are three types of such collective variables. One is the set of the extensive, conserved variables in a nonuniform system. Since the Fourier components with different wave vectors do not couple with each other in the sense of (4.22), the evolution matrix of the Fourier components of the conserved variables with wave vector  $\mathbf{k}$  are characterized by  $k$ , and its relaxation times tend to infinity as  $k \rightarrow 0$ . Any other extensive quantities, coupled with them, change more rapidly with decay constants insensitive to  $k$ , thus ensuring (5.1b) for small  $k$ . The second is the equalization between two weakly interacting systems. Typical examples are the energy transfer between two systems at different temperatures, and the relaxation of the total magnetization in ferro- and antiferromagnets due to small anisotropy. The relaxation of these quantities are very slow, and we can find two time constants satisfying (5.1b). The third is microscopic variables employed in the equations-of-motion method in the theory of many particle systems.<sup>16)</sup> The time scales concerned here are finer than those of the first two types.

For illustration we discuss simple examples. Let us first take an isotropic Heisenberg ferromagnet which consists of a periodic lattice of  $N$  spins in the presence of a uniform magnetic field  $H$  in the negative direction of the  $z$  axis, and consider the time evolution of the Fourier component of the density of transverse spin component with small wave vector  $\mathbf{k}$ <sup>23)</sup>

$$S_{\mathbf{k}}^{\dagger} \equiv \sum_j (S_{jx} - i S_{jy}) \exp(i\mathbf{k} \cdot \mathbf{r}_j). \quad (5.2)$$

In this system, the extensive, conserved quantities are the Fourier components of the spin density and the energy density. Since our Hamiltonian conserves the spin quantum numbers,  $S_{\mathbf{k}}^{\dagger}$  does not couple with any other such conserved quantities. Therefore,  $S_{\mathbf{k}}^{\dagger}$  by itself forms a good set of collective variables. Therefore, from (3.10), (3.16) and (3.17) we obtain

$$\frac{d}{dt} S_{\mathbf{k}}^{\dagger} - (i\omega_{\mathbf{k}}^{\dagger} - \Gamma_{\mathbf{k}}^{\dagger}) S_{\mathbf{k}}^{\dagger} = f_{\mathbf{k}}^{\dagger}, \quad (5.3)$$

where

$$\omega_{\mathbf{k}}^{\dagger} = (\dot{S}_{\mathbf{k}}^{\dagger}, S_{\mathbf{k}}^{\dagger*}) / i(S_{\mathbf{k}}^{\dagger}, S_{\mathbf{k}}^{\dagger*}), \quad (5.4)$$

and putting  $\Gamma_{\mathbf{k}}^{\dagger} = \gamma_{\mathbf{k}}^{\dagger} - i\Delta\omega_{\mathbf{k}}^{\dagger}$ ,

$$\gamma_k^+(\omega_k^+) = \frac{1}{2(S_k^+, S_k^{+*})} \int_{-\infty}^{\infty} (f_k^+(t), f_k^{+*}) \exp(-i\omega_k^+ t) dt, \quad (5.5)$$

$$\Delta\omega_k^+ = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\gamma_k^+(\omega)}{\omega_k^+ - \omega} d\omega, \quad (5.6)$$

where the dispersion relations (4.20a) and (4.21a) have been used. It follows from (4.11) and (4.16) that<sup>\*)</sup>

$$\omega_k^+(\sigma; \mathbf{H}) = -\omega_k^+(-\sigma; -\mathbf{H}), \quad (5.7a)$$

$$\Delta\omega_k^+(\sigma; \mathbf{H}) = -\Delta\omega_k^+(-\sigma; -\mathbf{H}), \quad (5.7b)$$

$$\gamma_k^+(\sigma; \mathbf{H}) = \gamma_k^+(-\sigma; -\mathbf{H}) \geq 0, \quad (5.8)$$

where  $\sigma \rightarrow -\sigma$  indicates the reversal of the spontaneous magnetization below the Curie point. Equation (5.4) gives the frequency spectrum of spin waves. Equations (5.5) and (5.6) give the spin wave damping constant and a shift of frequency. They agree with the previous results<sup>23)</sup> if one uses the same approximation as from (3.17) to (3.20). This approximation is valid as far as one retains the terms of the lowest order in  $k$  only in evaluating the time integral. In the low temperature limit, a straightforward reduction of (5.4) and (5.5) leads to the spin wave frequency and damping equivalent to Dyson's theory of spin wave interactions.

Above the Curie point and in the absence of a magnetic field, the frequency is zero and  $\gamma_k^+$  is identical with the damping constant of the longitudinal component  $S_k^0$ , i.e. the spin diffusion. Below the Curie point, the longitudinal damping has a quite different feature. This has been investigated in a previous paper.<sup>23)</sup>

Let us next consider a collective motion which can be described by a coordinate  $Q$  and its time derivative  $\dot{Q}$ . We assume that the variable  $Q$  is even or odd with respect to time reversal and there is no magnetic field applied. Let us start from an orthogonal set

$$A_1 \equiv \dot{Q} + i\Omega_0 Q, \quad A_2 \equiv \dot{Q} - i\Omega_0 Q, \quad (5.9)$$

where

$$\Omega_0^2 \equiv (\dot{Q}, \dot{Q}^*) / (Q, Q^*). \quad (5.10)$$

Since  $(\dot{Q}, Q^*) = (\ddot{Q}, \dot{Q}^*) = 0$ , we have

$$(A_1, A_2^*) = (\dot{A}_1, A_2^*) = 0, \quad (5.11)$$

$$(A_1, A_1^*) = (A_2, A_2^*) = 2(\dot{Q}, \dot{Q}^*). \quad (5.12)$$

<sup>\*)</sup> In a previous paper,<sup>23)</sup> there is an incorrect statement about the time reversal property. Equations (5.11)-(5.14) of this paper are not correct. The results, however, are correct.

It follows from (5.11) that the frequency matrix  $\hat{\omega}$  is diagonal and the random forces are given by

$$f_1(0) = f_2(0) = f(0) \equiv \ddot{Q} + \Omega_0^2 Q. \quad (5.13)$$

For times sufficiently larger than the correlation time  $\tau_c$  of  $f(t)$ , therefore, the equations of motion take the form

$$\frac{d}{dt} A_j + \sum_l A_{jl} A_l = f, \quad (5.14)$$

where

$$A_{jl} \equiv -i\Omega_j \delta_{j,l} + \gamma, \quad (5.15)$$

where

$$\Omega_1 = -\Omega_2 = \Omega_0, \quad (5.16)$$

$$\gamma \equiv \frac{1}{2} (\dot{Q}, \dot{Q}^*) \frac{1}{2} \int_{-\infty}^{\infty} (f(t), f^*) \exp(-i\Omega_0 t) dt, \quad (5.17)$$

and we have neglected the imaginary part of the damping constant matrix  $\Gamma$ . The matrix  $A$  can be easily diagonalized, and its eigenvalues turn out to be

$$\lambda_1 = -i\Omega + \gamma, \quad \lambda_2 = i\Omega + \gamma, \quad (5.18)$$

where

$$\Omega^2 \equiv \Omega_0^2 - \gamma^2. \quad (5.19)$$

The corresponding eigenvectors are

$$I_1 = A_1 + (i\gamma/\Omega_0 + \Omega) A_2, \quad (5.20a)$$

$$I_2 = (-i\gamma/\Omega_0 + \Omega) A_1 + A_2. \quad (5.20b)$$

Since  $Q$  and  $\dot{Q}$  can be written as linear combinations of the normal modes  $I_1$  and  $I_2$ , their relaxation functions can be easily obtained;

$$(Q(t), Q^*) = \frac{(\dot{Q}, \dot{Q}^*)}{\Omega_0^2} e^{-\gamma t} \left[ \cos(\Omega t) + \frac{\gamma}{\Omega} \sin(\Omega t) \right], \quad (5.21a)$$

$$(\dot{Q}(t), \dot{Q}^*) = (\dot{Q}, \dot{Q}^*) e^{-\gamma t} \left[ \cos(\Omega t) - \frac{\gamma}{\Omega} \sin(\Omega t) \right]. \quad (5.21b)$$

Equations (5.21) have the same form as the correlation matrix in the stochastic theory of the Brownian motion of a simple harmonic oscillator.<sup>5)</sup> It should be noted here that these equations have been derived without any stochastic assumption.

The above model can be used for the study of the sound waves and the plasma oscillations in the isothermal approximation by taking as  $Q$  the Fourier

component of the mass density of the fluid

$$\rho_k \equiv \int_V \rho(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) \, d\mathbf{r} = m \sum_j \exp(i\mathbf{k} \cdot \mathbf{r}_j), \quad (5.22)$$

which yields

$$(\dot{Q}, \dot{Q}^*) = V k^2 \rho k_B T, \quad (5.23)$$

where  $\rho$  denotes the mass per unit volume. Then (5.17) gives the sound attenuation constant and the plasma damping. If one uses the same approximation as from (3.17) to (3.20), then (5.17) agrees with the previous result<sup>6)</sup> which has been applied to the first sound attenuation in liquid helium at low temperatures.<sup>25)</sup> In a normal fluid of one component, the extensive, conserved quantities are the Fourier components of the mass density  $\rho_k$ , the momentum density  $\mathbf{j}_k$  and the energy density  $H_k$ . Since  $\rho_k$  couples with  $H_k$  as well as  $\dot{\rho}_k = i\mathbf{k} \cdot \mathbf{j}_k$ , we have to take  $(\rho_k, \dot{\rho}_k, H_k)$  as  $A$  in order to obtain a better approximation.\*) This is particularly important in studying the neutron scattering by liquids. To determine the frequencies, the line widths and the intensities of the three resonance lines of the neutron scattering, we can proceed similarly to the above treatment.<sup>6)</sup>

It would be worth while to discuss what happens if one does not take a good set of variables. If one takes  $S_k^+$  and  $\dot{S}_k^+$  in the first example, then the relaxation time  $\tau_r$  of the corresponding evolution matrix becomes insensitive to  $k$  and (5.1b) is not ensured. Actually it can be seen easily above the Curie point that, as  $k$  goes to zero,  $\tau_r$  tends to a finite time of the same order of magnitude as  $\tau_c$ . If one takes  $\rho_k$  only in the sound wave case, then  $\tau_c$  is of the same order of magnitude as  $\tau_r$ , and tends to infinity as  $k \rightarrow 0$ . If one takes  $\rho_k$  and  $\dot{\rho}_k$ , then  $\varphi_k(t)$  includes a slow relaxation arising from the coupling with  $H_k$ . Only by neglecting this slow relaxation, one can have (5.1b) and obtain the isothermal sound waves. In this way, the condition (5.1) rules out not-good sets of collective variables.

### § 6. Thermal after-effect functions

Transport coefficients can be obtained by calculating the damping constants of relevant collective motions in the same manner as in the preceding section. It is customary, however, to define them with the use of the linear relations between fluxes  $\bar{J}_\mu$  and forces  $\bar{X}_\nu$ ;

$$\bar{J}_\mu(\mathbf{r}, t) = \sum_\nu L_{\mu\nu} \bar{X}_\nu(\mathbf{r}, t). \quad (6.1)$$

\*) In liquid helium at very low temperatures, the isothermal approximation gives a better agreement with experiments on attenuation.<sup>25)</sup> This seems to be due to the special situation that  $H_k$  and  $\dot{H}_k$  form the second sound waves whose coupling with the first sound waves may be neglected at very low temperatures.

The typical forces, giving rise to thermal disturbances, are the gradients of local temperature  $T(\mathbf{r})$  and local velocity  $\mathbf{u}(\mathbf{r})$  in non-uniform fluids;

$$\bar{X}_T = -\nabla T(\mathbf{r})/T^2, \quad (6.2)$$

$$(\bar{X}_v)_{xy} = -\left(\frac{\partial u_y}{\partial x} + \frac{\partial u_x}{\partial y}\right)/2T. \quad (6.3)$$

In order to determine the linear coefficients  $L_{\mu\nu}$ , therefore, it is necessary to introduce the state parameters, such as  $T(\mathbf{r})$  and  $\mathbf{u}(\mathbf{r})$ , which specify the macroscopic, statistical state of the system. These parameters which we denote by  $B(t)$  are associated with conserved quantities  $A$  and are defined with the aid of the constrained equilibrium ensemble (4.5), built up at time  $t$ , which is identical with the local equilibrium ensemble. Let us consider a non-uniform fluid of  $g$  components. The Fourier components of  $A$  and  $B(t)$  with non-zero wave vector  $\mathbf{k}$  are given by<sup>9),30)</sup>

$$A_{\mathbf{k}} \equiv \begin{bmatrix} \rho_{\mathbf{k}}^\alpha \\ H_{\mathbf{k}} - \sum_{\alpha=1}^g \dot{h}^\alpha \rho_{\mathbf{k}}^\alpha \\ \mathbf{j}_{\mathbf{k}} \end{bmatrix}, \quad B_{\mathbf{k}}(t) \equiv \begin{bmatrix} \mu_{\mathbf{k}}^\alpha + s^\alpha T_{\mathbf{k}} \\ T_{\mathbf{k}}/T \\ \mathbf{u}_{\mathbf{k}} \end{bmatrix}, \quad (6.4)$$

where  $\rho_{\mathbf{k}}^\alpha$ ,  $H_{\mathbf{k}}$  and  $\mathbf{j}_{\mathbf{k}}$  are the Fourier components of the mass density of component  $\alpha$ , the energy density, and the momentum density defined in the same manner as (5.22);  $\mu_{\mathbf{k}}^\alpha$  the local chemical potential per unit mass of component  $\alpha$ ;  $s^\alpha$  and  $\dot{h}^\alpha$  are the equilibrium entropy and enthalpy per unit mass of component  $\alpha$ . In (6.4),  $\rho_{\mathbf{k}}^\alpha$ ,  $\mu_{\mathbf{k}}^\alpha$  and  $s^\alpha$  are to be regarded as  $g$ -dimensional column matrices. One may choose, as  $A$  and  $B(t)$ , any other linear combinations which leave  $A^* \cdot B(t)$  invariant; for instance,  $(\rho_{\mathbf{k}}^\alpha, H_{\mathbf{k}}, \mathbf{j}_{\mathbf{k}})$  and  $(\mu_{\mathbf{k}}^\alpha - \mu^\alpha(T_{\mathbf{k}}/T), T_{\mathbf{k}}/T, \mathbf{u}_{\mathbf{k}})$  where  $\mu^\alpha = \dot{h}^\alpha - Ts^\alpha$ . The choice (6.4), however, will turn out to be more convenient for practical applications. Now our problem is to know the non-equilibrium density matrix  $\rho(t)$  in terms of the state parameters in some detail.

Let us denote the deviation of  $\rho(t)$  from the local equilibrium ensemble  $\rho_t$  by  $\rho'(t)$ ,

$$\rho(t) = \rho_t + \rho'(t), \quad (6.5)$$

and put

$$\begin{bmatrix} \rho(t) \\ \rho_t \\ \rho'(t) \end{bmatrix} = \frac{1}{\beta} \int_0^\beta d\lambda \exp(-\lambda \mathcal{H}) \begin{bmatrix} 1 + \phi(t) \\ 1 + \phi_t \\ \phi'(t) \end{bmatrix} \exp(\lambda \mathcal{H}) \rho, \quad (6.6)$$

introducing new quantities  $\phi(t)$ ,  $\phi_t$  and  $\phi'(t)$ . Then we have

$$\phi(t) = \phi_t + \phi'(t), \quad (6.7)$$

$$\phi_t = \beta A^* \cdot B(t), \tag{6.8}$$

where (6.8) has been obtained by comparing with (4.6). In terms of  $\psi(t)$  the average value of a dynamical variable  $G$  can be written

$$\bar{G}(t) \equiv \text{Tr}[G\rho(t)] = (G, \psi(t)), \tag{6.9}$$

where  $G$  denotes the deviation from its invariant part, and the parentheses denote the scalar product (4.1). The parameters  $B(t)$  are defined in such a way that the average of  $A$  over  $\rho(t)$  is equal to that over  $\rho_t$ . This leads to

$$\bar{A}(t) = \text{Tr}[A\rho_t] = \beta(A, A^*) \cdot B(t), \tag{6.10}$$

which allows us to write (6.8) in the form

$$\phi_t = A^* \cdot (A, A^*)^{-1} \cdot (A, \psi(t)). \tag{6.11}$$

According to (2.13), (6.11) is equal to the Hermitian conjugate of  $\mathcal{P}\psi^*(t)$ . Thus denoting the complex conjugate of  $\mathcal{P}$  by  $\tilde{\mathcal{P}}$ ,

$$\phi_t = \tilde{\mathcal{P}}\psi(t), \tag{6.12}$$

$$\psi'(t) = (1 - \tilde{\mathcal{P}})\psi(t). \tag{6.13}$$

If one extends the set of variables  $A$  so as to include  $A_{-k}$ , then  $\tilde{\mathcal{P}} = \mathcal{P}$  and the Hermitian property of  $\phi_t$  is ensured. Equations (6.12) and (6.13) enable us to solve the Liouville equation in a similar manner as from (2.11) to (3.2). The Liouville equation for  $\rho(t)$  is brought into

$$\frac{\partial}{\partial t} \psi(t) = -iL\psi(t). \tag{6.14}$$

Operating  $(1 - \tilde{\mathcal{P}})$  on this, and then using (6.8) and (2.20),

$$\frac{\partial}{\partial t} \psi'(t) + (1 - \tilde{\mathcal{P}})iL\psi'(t) = -\beta K^* \cdot B(t). \tag{6.15}$$

This is integrated to yield

$$\psi'(t) = -\beta \int_{t_0}^t [U(-t+s)K]^* \cdot B(s) ds + \tilde{U}(-t+t_0)\psi'(t_0) \tag{6.16}$$

where  $U(t)$  is defined by (3.4). Equations (6.7), (6.8) and (6.16) provide us with an exact expression for the density matrix  $\psi(t)$  or  $\rho(t)$  in terms of  $B(s)$ ,  $t \geq s \geq t_0$ , and the initial deviation ensemble  $\psi'(t_0)$ . The non-linear effects and the initial transient process are included in the second term of (6.16).

The state parameters  $B(t)$ , multiplied by  $K^*$ , are brought into the thermodynamic forces  $\bar{X}_\nu$  by the relation

$$\frac{1}{T} K^* \cdot B(t) = -\sum_\nu J_\nu^* \bar{X}_\nu(t), \tag{6.17}$$

where  $J_\nu$  denote the vertical components of the fluxes of the state variables  $A$ . This relation can be obtained in the following manner. Let us consider (6.4). From (2.20) we have

$$K_k \equiv (1 - \mathcal{P}) \dot{A}_k = \begin{bmatrix} i\mathbf{k} \cdot \mathbf{J}_{dk}^\alpha \\ i\mathbf{k} \cdot \mathbf{J}_{Tk} \\ i\mathbf{k} \cdot \mathbf{J}_{vk} \end{bmatrix} \quad (6.18)$$

where

$$\mathbf{J}_{dk}^\alpha \equiv (1 - \mathcal{P}) \mathbf{j}_k^\alpha, \quad (6.19)$$

$$\mathbf{J}_{Tk} \equiv (1 - \mathcal{P}) \mathbf{j}_{Hk} - \sum_\alpha h^\alpha \mathbf{J}_{dk}^\alpha, \quad (6.20)$$

$$\mathbf{J}_{vk} \equiv (1 - \mathcal{P}) \Pi_k, \quad (6.21)$$

where  $\mathbf{j}_k^\alpha$ ,  $\mathbf{j}_{Hk}$  and  $\Pi_k$  denote the mass flux of component  $\alpha$ , the energy flux, and the momentum flux, respectively. Since  $\mathbf{j}_k \equiv \sum_\alpha \mathbf{j}_k^\alpha$  is one of the vectors spanning the  $A$  subspace in the Hilbert space,

$$\sum_\alpha \mathbf{J}_{dk}^\alpha = 0. \quad (6.22)$$

Therefore,  $\mathbf{J}_{dk}^\alpha = 0$  in the one-component system. Now use of (6.18) leads to

$$\frac{1}{T} K_k^* \cdot B_k(t) = - \sum_\alpha \mathbf{J}_{dk}^{\alpha*} \cdot \bar{\mathbf{X}}_{dk}^\alpha - \mathbf{J}_{Tk}^* \cdot \bar{\mathbf{X}}_{Tk} - \mathbf{J}_{vk}^* \cdot \bar{\mathbf{X}}_{vk} \quad (6.23)$$

where

$$\bar{\mathbf{X}}_{dk}^\alpha \equiv i\mathbf{k} (\mu_k^\alpha + s^\alpha T_k) / T, \quad (6.24)$$

and  $\bar{\mathbf{X}}_k = i\mathbf{k} B_k / T$ .  $\bar{\mathbf{X}}_{Tk}$  and  $\bar{\mathbf{X}}_{vk}$  are the Fourier components of (6.2) and (6.3), and  $\bar{\mathbf{X}}_{dk}$  are the thermodynamic forces responsible for the diffusion of particles. Equation (6.23) can be written in the form of the relation (6.17). Since  $J_\nu$  are orthogonal to the  $A$  subspace,

$$\text{Tr}[J_\nu \rho_\nu] = (J_\nu, \psi_\nu) = 0. \quad (6.25)$$

The quantities  $J_\nu$  differ from the fluxes of the state variables by the projective components of the latter, and will be referred to as the *conjugate fluxes* to the thermodynamic forces.

From (6.16) and (6.17), we thus obtain

$$\bar{J}_\mu(t) = \sum_\nu \int_0^{t-t_0} L_{\mu\nu}(s) \bar{X}_\nu(t-s) ds + R_\mu(t, t_0) \quad (6.26)$$

where

$$L_{\mu\nu}(t) \equiv k_B^{-1} (\mathcal{J}_\mu(t), \mathcal{J}_\nu^*), \quad (6.27)$$

$$R_\mu(t, t_0) \equiv (\mathcal{J}_\mu(t-t_0), \psi'(t_0)) = \text{Tr}[\mathcal{J}_\mu(t-t_0) \rho(t_0)] \quad (6.28)$$

where

$$\mathcal{J}_\mu(t) \equiv U(t) J_\mu. \tag{6.29}$$

$R_\mu(t, t_0)$  represents the memory of the fine details of the initial ensemble.

The thermodynamic forces  $\bar{X}_\nu(t)$  can be expressed as linear functions of  $\bar{A}(t)$  with the aid of (6.10). Therefore, we can introduce linear functions of  $A(t)$  whose ensemble averages are equal to  $\bar{X}_\nu(t)$ ; denoting the  $j$ -th component of  $A_k$  by  $A_{jk}$ ,

$$\mathbf{X}_{jk}(t) = ikk_B \sum_l [(A_k, A_k^*)^{-1}]_{jl} A_{lk}(t). \tag{6.30}$$

Since (6.26) is valid for any initial ensemble  $\rho(t_0)$ , we can take off the averaging and obtain

$$J_\mu(t) = \sum_\nu \int_0^t L_{\mu\nu}(s) X_\nu(t-s) ds + \mathcal{J}_\mu(t), \tag{6.31}$$

where

$$(\mathcal{J}_\mu(t_1), \mathcal{J}_\nu(t_2)^*) = k_B L_{\mu\nu}(t_1 - t_2). \tag{6.32}$$

Application of (4.24) and (4.13) leads to

$$L_{\mu\nu}(t; \mathbf{H}) = \varepsilon_\mu \varepsilon_\nu L_{\mu\nu}(-t; -\mathbf{H}) = \varepsilon_\mu \varepsilon_\nu L_{\nu\mu}(t; -\mathbf{H}) \tag{6.33}$$

where  $\varepsilon_\mu$  and  $\varepsilon_\nu$  denote the sign functions of  $J_\mu$  and  $J_\nu$  with respect to time reversal.  $L_{\mu\nu}(t)$  describes the after effect of the thermodynamic force  $X_\nu(t)$  on the flux  $J_\mu(t)$ , and therefore will be referred to as the thermal after-effect function. The transport coefficients are given by the Laplace transform of these functions. Equation (6.31) is thus the most general form of the linear relations between fluxes and forces, and gives not only the molecular expressions for the transport coefficients, but also a justification and a generalization of the phenomenological theory of fluctuations in fluid dynamics.<sup>27)</sup> It is worth noting that (6.31) can be derived also from (3.10) by using (6.18) and (6.30).

Let us assume that  $L_{\mu\nu}(t)$  decays in a finite time  $\tau_c$ , and shift the initial time  $t_0$  to  $-\infty$  in (6.26). This corresponds to extending the time integration in (6.31) to  $\infty$ . Thus, taking the Fourier transform with respect to time, we obtain

$$J_{\mu\omega} = \sum_\nu L_{\mu\nu}(\omega) X_{\nu\omega} + \mathcal{J}_{\mu\omega}, \tag{6.34}$$

where

$$L_{\mu\nu}(\omega) \equiv \lim_{\varepsilon \rightarrow 0^+} \int_0^\infty L_{\mu\nu}(t) \exp(-i\omega t - \varepsilon t) dt. \tag{6.35}$$

Equation (6.34) describes the fluctuations of the fluxes from the most probable path after an initial period of the order of  $\tau_c$ . From (6.33), we have

$$L_{\mu\nu}(\omega; \mathbf{H}) = \varepsilon_\mu \varepsilon_\nu L_{\nu\mu}(\omega; -\mathbf{H}). \quad (6 \cdot 36)$$

There are thus two ways of arriving at the linear relations (6.1);

- 1) from (6.26) by observing a non-equilibrium system,
- 2) from (6.34) by looking at a large fluctuation in an aged system.

Equation (6.34) is exact for an aged system. Therefore if one admits Onsager's postulate<sup>26)</sup> that the average regression of spontaneous fluctuations in aged systems obeys the same laws as the corresponding irreversible processes, then one can get (6.1) from (6.34) by a) neglecting the fluctuation term  $\mathcal{J}_{\mu\omega}$  and then b) assuming that  $\tau_c$  is much shorter than any typical values of  $1/\omega$  so that (6.35) can be replaced by

$$VL_{\mu\nu} \equiv L_{\mu\nu}(\omega = 0).$$

The first way is more directly related to the recent attempt to reconcile macroscopic irreversibility with microscopic reversibility.<sup>21), 22)</sup> It is well known that in order to derive an irreversible process, it is necessary to introduce a relevant contraction of the description of the system.<sup>28)</sup> The projection into the  $A$  subspace in the Hilbert space of extensive quantities will provide us with such a contraction. Namely, it will be thus possible to set up an appropriate initial ensemble and to remove improbable motions for a large system. Such an initial ensemble will be provided by the constrained equilibrium ensemble (4.5), since starting from any initial condition consistent with the prescribed values for the macroscopic state variables one will almost always get the same physical process after a finite time  $\tau_0$ . Thus we may take the local equilibrium ensemble at  $t_0$ ,

$$\psi'(t_0) = 0, \text{ i.e., } R_\mu(t, t_0) = 0, \quad (6 \cdot 37)$$

in order to determine the average behavior after an initial transient period  $\tau_0$ . For a stable system,  $\tau_0$  will be at most of the order of the decay times of the thermal after-effect functions  $L_{\mu\nu}(t)$ . Since (1)  $A_k$ 's consist of and exhaust the extensive conserved variables, (2) there is no coupling between the Fourier components with different wave vectors in the sense of (4.22), (3) the time evolution of  $L_{\mu\nu}(t)$  does not include the secular motion of  $A_k(t)$ , we may expect that the relaxation of  $\bar{A}_k(t)$  with small  $k$  is distinctly slow compared to the decay of  $L_{\mu\nu}(t)$ . Thus we obtain (6.1) for describing the average behavior of the system in the final stage of evolution.

The linear response to a mechanical disturbance can be expressed in terms of the relaxation function of the corresponding flux.<sup>4), 11)</sup>  $L_{\mu\nu}(t)$  has a similar form. However, there are two differences which exactly correspond to those between  $f(t)$  and  $F(t)$ . First,  $J_\nu$  are not mechanical quantities, but the vertical components of the fluxes of the state variables. Some examples are found in (7.18) in § 7. The second difference is the difference in time evolution. A simple transformation of (3.14) leads to

$$(K(z), K^*) = \frac{1}{1 + \varphi(z) \cdot (z - i\dot{\omega})^{-1}} \cdot (f(z), f^*). \quad (6 \cdot 38)$$

Denoting the non-secular force and flux of  $A_{jk}$  by  $f_{jk}$  and  $\mathcal{J}_{jk}$ , we have, in the isotropic case,

$$(f_{jk}(t), f_{ik}^*) = k^2 (\mathcal{J}_{jk}^x(t), \mathcal{J}_{ik}^{x*}), \tag{6.39}$$

where  $\mathcal{J}_j^x$  denotes the  $x$  component of the vector  $\mathcal{J}_j$  in the coordinate space. The right-hand side of (6.39) gives the thermal after-effect functions. Denoting this by  $k^2 L_{jlk}(t)$  and defining the corresponding mechanical response function

$$\phi_{jlk}(t) \equiv (J_{jk}^x(t), J_{ik}^{x*}), \tag{6.40}$$

we obtain<sup>\*</sup>

$$\phi_k(z) = \frac{1}{1 + k^2 L_k(z) \cdot (A_k, A_k^*)^{-1} \cdot (z - i\hat{\omega}_k)^{-1}} \cdot L_k(z). \tag{6.41}$$

This equation shows the second difference clearly. This difference, however, vanishes in the limit of  $k \rightarrow 0$  in the case of the normal system. Let  $k$  tend to zero after making the volume  $V$  of the system infinity with the fixed values of the intensive quantities. Then we have

$$\lim_{k \rightarrow 0} \lim_{V \rightarrow \infty} \frac{1}{V} [\phi_k(z) - L_k(z)] = 0, \tag{6.42}$$

where  $z \neq i\hat{\omega}_k$ . Here, however, we have assumed that  $L_k/V$  is finite and the second term of the denominator vanishes in this limit. Plasmas and several quantum systems like phonons in liquid Helium II and magnons in ferromagnets, however, do not always satisfy this assumption.

### § 7. Transport coefficients

We now proceed to determine the vertical components of the fluxes,  $J_\nu$ , explicitly and find expressions for the transport coefficients. We assume that no external field is applied. From (4.25) we obtain

$$\mathcal{P}j_k^\alpha = (\mathbf{j}_k^\alpha, \mathbf{j}_k^*) \cdot (\mathbf{j}_k, \mathbf{j}_k^*)^{-1} \cdot \mathbf{j}_k, \tag{7.1}$$

$$\mathcal{P}j_{Hk} = (\mathbf{j}_{Hk}, \mathbf{j}_k^*) \cdot (\mathbf{j}_k, \mathbf{j}_k^*)^{-1} \cdot \mathbf{j}_k, \tag{7.2}$$

$$\mathcal{P}\Pi_k = (\Pi_k, A_{ek}^*) \cdot (A_{ek}, A_{ek}^*)^{-1} \cdot A_{ek}. \tag{7.3}$$

Since the system is isotropic, we have

$$(\mathbf{j}_k^\alpha, \mathbf{j}_k^*) = \mathbf{1} (\dot{\rho}_k^\alpha, \dot{\rho}_k^*) / k^2 = \mathbf{1} (\rho_k^\alpha, \Pi_k^{xx*}), \tag{7.4}$$

$$(\mathbf{j}_{Hk}, \mathbf{j}_k^*) = \mathbf{1} (\dot{H}_k, \dot{\rho}_k^*) / k^2 = \mathbf{1} (H_k, \Pi_k^{xx*}), \tag{7.5}$$

where  $\mathbf{1}$  is the three-dimensional unit tensor and  $\Pi_k^{xx}$  denotes the  $x-x$  com-

<sup>\*</sup>) A similar equation to (6.41) has been obtained by P. Martin and discussed at the International Conference on Statistical Mechanics in Aachen, June 15-20, 1964.

ponent of the momentum flux tensor.

Let us introduce the average of a quantity  $G$  over the local equilibrium ensemble;

$$\langle G \rangle_t \equiv \text{Tr}[G\rho_t] = \beta(G, A^*) \cdot B(t), \quad (7.6)$$

$$= (G, A^*) \cdot (A, A^*)^{-1} \cdot \bar{A}(t), \quad (7.7)$$

where (6.8) and (6.10) have been inserted. Differentiating this with respect to  $B(t)$  and  $\bar{A}(t)$ ,

$$\beta(G, A_j^*) = [\partial \langle G \rangle_t / \partial B_j], \quad (7.8)$$

$$\mathcal{L}G = \sum_j A_j [\partial \langle G \rangle_t / \partial \bar{A}_j]. \quad (7.9)$$

These identities can be employed to calculate (7.4), (7.5) and (7.3) by taking as  $G$  the momentum flux tensor<sup>9)</sup>

$$\begin{aligned} \Pi_k = & \sum_j \{ \mathbf{p}_j \mathbf{p}_j \exp(\mathbf{i}\mathbf{k} \cdot \mathbf{r}_j) + \mathbf{p}_j \exp(\mathbf{i}\mathbf{k} \cdot \mathbf{r}_j) \mathbf{p}_j \\ & + [\mathbf{p}_j \exp(\mathbf{i}\mathbf{k} \cdot \mathbf{r}_j) \mathbf{p}_j]^\dagger + \exp(\mathbf{i}\mathbf{k} \cdot \mathbf{r}_j) \mathbf{p}_j \mathbf{p}_j \} / 4m_j \\ & + \frac{1}{4} \sum_{j,l} \mathbf{r}_{jl} \mathbf{F}_{jl} [\exp(\mathbf{i}\mathbf{k} \cdot \mathbf{r}_j) + \exp(\mathbf{i}\mathbf{k} \cdot \mathbf{r}_l)], \end{aligned} \quad (7.10)$$

where  $\mathbf{r}_{jl} \equiv \mathbf{r}_j - \mathbf{r}_l$ , and  $\mathbf{F}_{jl}$  denotes the intermolecular force between  $j$  and  $l$  and  $\dagger$  means the transpose of the tensor. Equation (7.10) is valid for a short-range force when  $ak \ll 1$ ,  $a$  being the mean linear force range. According to the virial theorem, the equilibrium pressure  $p$  is given by

$$p = \langle [\Pi_k^{xx}]_{k=0} \rangle / V. \quad (7.11)$$

This may be generalized to the case of local equilibrium state. Denoting the local pressure by  $p(\mathbf{r})$  and taking the Fourier transform of its deviation from the equilibrium value, we have

$$p_k = \frac{1}{V} \left( \frac{\partial p}{\partial E} \right) \bar{H}_k + \sum_\alpha \frac{1}{V} \left( \frac{\partial p}{\partial \rho^\alpha} \right) \bar{\rho}_k^\alpha, \quad (7.12)$$

where  $E$  is the equilibrium energy density. Let us now take the combination  $A_k = [\rho_k^\alpha, H_k]$  and  $B_k = [T\delta(\mu^\alpha/T), -T\delta(1/T)]$ . It follows from (7.3) and (7.7) that  $\langle \Pi_k^{xx} \rangle_t$  is the linear combination of the same form as (7.12). Therefore, we may identify  $p_k$  with  $\langle \Pi_k^{xx} \rangle_t / V$  as a generalization of (7.11). From (7.9) and (7.8) we thus obtain

$$\mathcal{L}\Pi_k^{xx} = \left( \frac{\partial p}{\partial E} \right) H_k + \sum_\alpha \left( \frac{\partial p}{\partial \rho^\alpha} \right) \rho_k^\alpha, \quad (7.13)$$

$$\beta(\Pi_k^{xx}, \rho_k^{\alpha*}) / V = (\partial p / \partial \mu^\alpha)_{T, V} = \rho^\alpha, \quad (7.14)$$

$$\beta(\Pi_k^{xx}, H_k^*) / V = -\beta(\partial p / \partial \beta)_{\xi^{\alpha, V}} = \sum_\alpha \rho^\alpha h^\alpha, \quad (7.15)$$

where  $\rho^\alpha$  is the mass of component  $\alpha$  per unit volume, and  $\zeta^\alpha \equiv \beta\mu^\alpha$ . Therefore, use of (7.4) and (7.5) leads to

$$\mathcal{P}\mathbf{j}_k^\alpha = (\rho^\alpha/\rho)\mathbf{j}_k, \quad \rho = \sum_\alpha \rho^\alpha, \quad (7.16)$$

$$\mathcal{P}\mathbf{j}_{Hk} = h\mathbf{j}_k, \quad \rho h = \sum_\alpha \rho^\alpha h^\alpha. \quad (7.17)$$

Equations (7.13), (7.16) and (7.17) provide us with the explicit expressions for the projections of the fluxes. Inserting these results into (6.19)–(6.21) we obtain the following expressions for the conjugate fluxes  $J_\nu$ :

$$\mathbf{J}_{dk}^\alpha = \mathbf{j}_k^\alpha - (\rho^\alpha/\rho)\mathbf{j}_k, \quad (7.18a)$$

$$\mathbf{J}_{Tk} = \mathbf{j}_{Hk} - \sum_\alpha h^\alpha \mathbf{j}_k^\alpha, \quad (7.18b)$$

$$J_{vk} = H_k - \mathbf{1} \left[ \left( \frac{\partial p}{\partial E} \right) H_k + \sum_\alpha \left( \frac{\partial p}{\partial \rho^\alpha} \right) \rho_k^\alpha \right]. \quad (7.18c)$$

Denoting the fluxes of the state variables  $A_{jk}$  defined by (6.4) by  $G_\mu(\mathbf{r})$  in the coordinate space,

$$\mathbf{G}_\mu(\mathbf{r}, t) = \mathcal{P}\mathbf{G}_\mu(\mathbf{r}, t) + \mathbf{J}_\mu(\mathbf{r}, t). \quad (7.19)$$

The first term is determined from (7.13), (7.16) and (7.17). The second term is given by the linear relations (6.1) with the following expressions for the linear coefficients:

$$L_{\mu\nu} = \lim_{\varepsilon \rightarrow 0^+} \left[ \lim_{k \rightarrow 0} \lim_{V \rightarrow \infty} \frac{1}{k_B V} \int_0^\infty (J_{\mu k}(t), J_{\nu k}^*) \exp(-\varepsilon t) dt \right], \quad (7.20)$$

where  $J_{\mu k}$  are the conjugate fluxes given by (7.18). Since the system is isotropic, the linear coefficients are characterized by a few parameters, i.e. the familiar transport coefficients.<sup>29)</sup> Denoting the integral (7.20) by  $L(J_\mu, J_\nu^*)$ , the thermal conductivity  $\kappa$ , the thermal diffusion constant  $D_\alpha$  and the constants  $D'_{\alpha\beta}$  related to the diffusion constants<sup>9)</sup> are expressed by

$$\kappa = L(J_T^x, J_T^{x*})/T^2, \quad (7.21)$$

$$D_\alpha = L(J_d^{\alpha x}, J_T^{x*})/T, \quad (7.22)$$

$$D'_{\alpha\beta} = L(J_d^{\alpha x}, J_d^{\beta x*})/T = D'_{\beta\alpha}, \quad (7.23)$$

where  $x$  indicate the  $x$  components of the conjugate fluxes. Similarly, the shear viscosity  $\eta$  and the bulk viscosity  $\varphi$  are given by  $L(F, F^*)/T$  with the following expressions for  $F$ :

$$F_\eta = J_v^{xy} \text{ or } [J_v^{xx} - J_v^{yy}]/2, \quad (7.24)$$

$$F_\varphi = [J_v^{xx} + J_v^{yy} + J_v^{zz}]/3. \quad (7.25)$$

Thus, for instance, the average value of the energy flux is written, in the linear approximation, as

$$\mathbf{j}_H(\mathbf{r}, t) = h\mathbf{j}(\mathbf{r}, t) + \bar{\mathbf{J}}_T(\mathbf{r}, t) + \sum_{\alpha} h^{\alpha} \bar{\mathbf{J}}_d^{\alpha}(\mathbf{r}, t), \quad (7.26)$$

where

$$\frac{1}{T} \bar{\mathbf{J}}_T = \kappa T \bar{\mathbf{X}}_T + \sum_{\alpha} D_{\alpha} \bar{\mathbf{X}}_d^{\alpha}, \quad (7.27)$$

$$\frac{1}{T} \bar{\mathbf{J}}_d^{\alpha} = D_{\alpha} \bar{\mathbf{X}}_T + \sum_{\beta} D_{\alpha\beta} \bar{\mathbf{X}}_d^{\beta}. \quad (7.28)$$

If there is no flow of the total mass element, then the first term of (7.26) vanishes.

Inserting (7.19) into the conservation equations, one gets the hydrodynamical equations in the linear approximation. The non-linear terms with respect to the local velocity  $\mathbf{u}(\mathbf{r})$  can be obtained by starting from the local equilibrium ensemble without the linearization and then rewriting the local fluxes in terms of the thermal momentum  $\mathbf{p}_i - m_i \mathbf{u}$  with the aid of a Galilean transformation  $\mathbf{p}_i \rightarrow \mathbf{p}_i - m_i \mathbf{u}$ .<sup>30)</sup> The average of the Galilei transformed fluxes over the deviation ensemble  $\rho'(t)$  can be calculated in the linear approximation to yield the same results for the linear relations as the foregoing.

Thus the transport coefficients can be expressed in terms of the time correlation of the conjugate fluxes. The conjugate fluxes (7.18) are algebraic sums of the molecular quantities of one or two molecules. For small  $k$  satisfying  $ak \ll 1$ , they all take the same form as (7.10). Thus in the classical case, their explicit expressions are given by

$$J_{\mu k} = \frac{1}{2} \sum_{j=1}^N \sum_{l=1}^N [J_{1\mu}(j) \delta_{j,l} + J_{2\mu}(j, l)] [\exp(i\mathbf{k} \cdot \mathbf{r}_j) + \exp(i\mathbf{k} \cdot \mathbf{r}_l)], \quad (7.29)$$

where

$$\mathbf{J}_{1d}^{\alpha}(j) = [\delta(j, \alpha) - (\rho^{\alpha}/\rho)] \mathbf{p}_j, \quad \mathbf{J}_{2d}^{\alpha} = 0, \quad (7.30)$$

$$\mathbf{J}_{1T}(j) = \left[ \frac{p_j^2}{2m_j} - m_j \sum_{\alpha} h^{\alpha} \delta(j, \alpha) \right] \frac{\mathbf{p}_j}{m_j}, \quad (7.31a)$$

$$\mathbf{J}_{2T}(j, l) = \frac{1}{4} [u_{jl} \mathbf{1} + \mathbf{r}_{jl} \mathbf{F}_{jl}] \cdot \left[ \frac{\mathbf{p}_j}{m_j} + \frac{\mathbf{p}_l}{m_l} \right], \quad (7.31b)$$

$$J_{1v}(j) = \frac{\mathbf{p}_j \mathbf{p}_j}{m_j} - \mathbf{1} \left[ \left( \frac{\partial p}{\partial E} \right) \frac{p_j^2}{2m_j} + m_j \sum_{\alpha} \left( \frac{\partial p}{\partial \rho^{\alpha}} \right) \delta(j, \alpha) \right], \quad (7.32a)$$

$$J_{2v}(j, l) = \frac{1}{2} \left[ \mathbf{r}_{jl} \mathbf{F}_{jl} - \mathbf{1} \left( \frac{\partial p}{\partial E} \right) u_{jl} \right], \quad (7.32b)$$

where  $\delta_{j,l}$  is the Kronecker delta;  $\delta(j, \alpha)$  is unity when the molecule  $j$  belongs to the  $\alpha$  component and zero otherwise;  $u_{jl}$  is the intermolecular potential between  $j$  and  $l$ . Inserting (7.29) into (7.20), we obtain

$$\begin{aligned}
 L_{\mu\nu} = & \sum_{\alpha} \frac{n^{\alpha}}{k_B} \int_0^{\infty} dt \int d\mathbf{p}_j f(p_j) [J_{1\nu}(j_{\alpha}) \xi_{1\mu}(j_{\alpha}; t) \\
 & + \sum_{\beta} n^{\beta} \iint J_{2\nu}(j_{\alpha}, l_{\beta}) \xi_{2\mu}(j_{\alpha}, l_{\beta}; t) f(p_l) g(r_{lj}) d\mathbf{p}_l d\mathbf{r}_{lj}], \quad (7.33)
 \end{aligned}$$

where  $n^{\alpha}$  is the molecular density of component  $\alpha$ ;  $j_{\alpha}$  represents an  $\alpha$  molecule whose momentum and coordinate are denoted by  $\mathbf{p}_j$  and  $\mathbf{r}_j$ ;  $f(p)$  and  $g(r)$  are the momentum distribution and the pair correlation functions, respectively. The quantities  $\xi_{\mu}$  are defined by

$$\xi_{1\mu}(j; t) \equiv \lim_{\varepsilon \rightarrow 0+} \lim_{V \rightarrow \infty} \sum_{j', l'} \langle \exp[(iL - \varepsilon)t] [J_{1\mu}(j') \delta_{j', l'} + J_{2\mu}(j', l')] \rangle_{(j)}, \quad (7.34a)$$

$$\xi_{2\mu}(j, l; t) \equiv \lim_{\varepsilon \rightarrow 0+} \lim_{V \rightarrow \infty} \sum \langle \exp[(iL - \varepsilon)t] [J_{1\mu}(j') \delta_{j', l'} + J_{2\mu}(j', l')] \rangle_{(j, l)}, \quad (7.34b)$$

where  $\langle \dots \rangle_{(j)}$  or  $\langle \dots \rangle_{(j, l)}$  denotes the conditional average with the given values of the coordinates and momenta of molecule  $j$  or pair  $(j, l)$ . The summands in (7.34) are non-zero only when the space-time correlation between  $(j)$  or  $(j, l)$  and  $(j', l')$  exists.

In order to see the relation with the kinetic theory, let us consider a dilute gas of one component. Since  $m\hbar = 5k_B T/2$ ,  $(\partial p/\partial E) = 2/3$  and  $(\partial p/\partial \rho) = 0$ , the kinetic parts  $J_{1\mu}$  agree with the conjugate fluxes of the linearized Boltzmann equation.<sup>29)</sup> The intermolecular parts  $J_{2\mu}$  and, therefore, the second term of (7.33) can be neglected. We can calculate  $\xi_{1\mu}$  and its time integral (7.33) in the same manner as in the previous paper.<sup>30)</sup> An analysis of molecular motion in terms of binary collisions leads to

$$\xi_{1\mu}(j; t) = \exp(-tD) J_{1\mu}(j), \quad (7.35)$$

where  $D$  is the same collision operator as in the linearized Boltzmann equation<sup>28)</sup>

$$Dh(\mathbf{p}) \equiv - \int d\mathbf{p}_1 f_B(p_1) \int d\Omega g \sigma(g, \theta) [h' + h_1' - h - h_1], \quad (7.36)$$

where  $f_B(p) = nf(p)$  is the Boltzmann distribution,  $g$  the relative speed, and  $\sigma(g, \theta)$  the differential scattering cross section. Inserting (7.35) into (7.33) and then evaluating the time integral with the aid of a variational principle, we can obtain Enskog and Chapman's equations for the viscosity and thermal conductivity.

### § 8. Short summary and some remarks

Our particular intention was to establish some fundamental equations for describing time-dependent phenomena. Separating the linear term in the equation of motion, we derived an exact equation of motion (3.10)–(3.12). This has a generalized form of the Langevin equation. Rewriting this equation for the conjugate fluxes with the aid of (6.30), we obtained a generalized form of

the linear relations (6·31)–(6·36). These equations describe the evolution of the collective variables  $A_j(t)$  and the conjugate fluxes  $J_\nu(t)$ , including their fluctuations from the most probable path. These equations give us not only the molecular expressions for the *random* forces and the kinetic coefficients, but also serve to investigate the limit of validity of stochastic assumptions and approximations involved in various theories of many-particle systems.

On the basis of these equations, we discussed the Brownian motion, the collective motion and the transport coefficients by taking simple examples. In particular, explicit expressions were derived for the thermal after-effect functions and the transport coefficients of multi-component fluids.

The transport coefficients were expressed in terms of the conjugate fluxes. Since the projective components of the fluxes are non-zero as can be seen from (7·13), (7·16) and (7·17), the conjugate fluxes, in general, differ from the fluxes themselves. The significance of this difference was discussed in §§ 3 and 6. This difference is particularly important for the thermal conductivity and the bulk viscosity. Let us consider a dilute gas of one component. Due to the existence of the difference,  $J_{1\mu}$ 's are *orthogonal* to the collisional invariants which have the zero eigenvalue of the collision operator  $D$ . This orthogonality ensures that the time integral of (7·35) have definite values.\*)

The expressions for the transport coefficients should be independent of the total ensemble used, as can be seen most clearly from (7·33). Therefore it turns out that Green's comment<sup>31)</sup> on the difference is not relevant.

This difference vanishes for the shear viscosity flux. It has been shown by Montroll<sup>11)</sup> that the same expression for the shear viscosity can be obtained by treating the shear flow as the linear response to a mechanical perturbation. Even in this case, however, if one considers the non-uniform processes with non-zero  $k$ , then another difference comes up as discussed in §§ 3 and 6. These two differences between the thermal after-effect function and the mechanical response function originate from the fact that the mechanical external forces can be controlled by outer bodies irrespectively of the state of the system, whereas the thermodynamic forces are the state functions, thus evolving together with the system.

Recently Zwanzig<sup>13)</sup> has derived a generalized form of the Fokker-Planck equation for the probability distribution of the state variables by assuming a particular initial ensemble which corresponds to (4·5). His projection into the  $A$  subspace differs from ours, thus leading to results different from ours. The

\*) If one of real variables  $A(\mathbf{r})$  and  $B(\mathbf{r})$  is conserved, then

$$\lim_{k \rightarrow 0} \lim_{V \rightarrow \infty} \frac{1}{V} \int_0^{\infty} (A_{\mathbf{k}}(t), B_{\mathbf{k}}^*) e^{-\varepsilon t} dt = \frac{C}{\varepsilon}$$

where  $C$  is a real number. Therefore, if one uses the both-sided Fourier integral representation,<sup>12)</sup> then the projective components can be omitted in the limit of  $k \rightarrow 0$ .

linearized version of his final, approximate equation of motion for  $\bar{A}$ , Eq. (40) of reference 13), differs from our corresponding equation (3.7) in two respects. Namely, his equation has an additional term, the derivative of kinetic coefficients with respect to  $\bar{A}$ , and his thermal after-effect function has a difficulty of the plateau value problem. A further investigation is needed to clarify the relation between his exact master equation and our exact equation of motion.

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**Appendix A**

*Derivation of (3.5) and (3.6)*

Since the projection operator (2.13) is Hermitian,

$$([\!(1-\mathcal{P})Lf], g^*) = (Lf, [\!(1-\mathcal{P})g]^*).$$

Since  $g$  is orthogonal to the  $A$  subspace, this is equal to

$$= (Lf, g^*) = (f, [Lg]^*),$$

where (2.9) has been used. Since  $f$  is orthogonal to the  $A$  subspace, this can be brought into

$$= (f, [\!(1-\mathcal{P})Lg]^*).$$

Thus we obtain (3.5). Equation (3.6) can be obtained by expanding  $U(t)$  in powers of  $t$  and then using that every term is orthogonal to the  $A$  subspace.

**Appendix B**

*Derivation of (3.14) and its generalization*

From (3.10) and (2.18) we obtain

$$f(t) = K(t) + \int_0^t ds \varphi(t-s) \cdot A(s). \tag{B.1}$$

Inserting (2.4) and (2.5) and multiplying by  $K^* \cdot (A, A^*)^{-1}$  from the right, we obtain

$$\varphi(t) = \Phi(t) + \int_0^t ds \int_0^s \varphi(t-s) \cdot \Xi(s-s') \cdot \varphi(s') ds'. \tag{B.2}$$

Since the second term has a convolution form, the Laplace transform readily leads to (3·14).

Equation (B·2) can be generalized. Namely, if  $f$  and  $g$  are functions orthogonal to the  $A$  subspace, then

$$(f(z), g^*) = (U(z)f, g^*) - (U(z)f, K^*) \cdot (A, A^*)^{-1} \cdot \mathcal{E}(z) \cdot (U(z)K, g^*). \quad (\text{B} \cdot 3)$$

This is useful in discussing the relation between the mechanical and thermal after effect functions in the anisotropic case.

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**Note added in proof:** Recently Luttinger [Phys. Rev. **135** (1964), A1505] derived the same expressions as ours for the transport coefficients  $L_{\mu\nu}(\omega=0)$  without the explicit use of the local equilibrium ensemble. We wish to discuss here the role of the local equilibrium ensemble by reversing the reasoning of § 6.

As noted in the text, the generalized linear relations (6·31) are equivalent to the exact equations of motion (3·10), and in fact can be derived from the latter directly. Namely, taking  $A_k$  defined by (6·4) as  $A$  and comparing with (2·18), we obtain

$$K_k(t) = - \int_0^t \varphi_k(s) \cdot A_k(t-s) ds + f_k(t).$$

To rewrite this for the conjugate fluxes  $J_\mu$ , we substitute (3·12) for  $\varphi_k(s)$  and then apply  $f_k(t) = U(t)K_k$  and insert (6·18). Then separating  $i\mathbf{k}$  and using (6·30) we arrive at (6·31).

Now we introduce the local equilibrium ensemble (6·8) supplemented by (6·10) in order to define the macroscopic state parameters  $B_k(t)$  and relate the average values  $\bar{X}_\mu$  to them. Then it is easy to show that  $\bar{X}_\mu$ 's are equal to the usual thermodynamic forces (6·2), (6·3) and (6·24). Therefore, on the basis of (6·31), we can identify the quantity  $L_{\mu\nu}(\omega)$  with the transport coefficients, since the second term of (6·31) does not contain any linear term of  $X_\mu$ 's.